Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt(III)-catalyzed ketone-directed C–H vinylation using vinyl acetate

Md Raja Sk and Modhu Sudan Maji*

Department of Chemistry, Indian Institute of Technology Kharagpur
Kharagpur 721302, W. B., India.

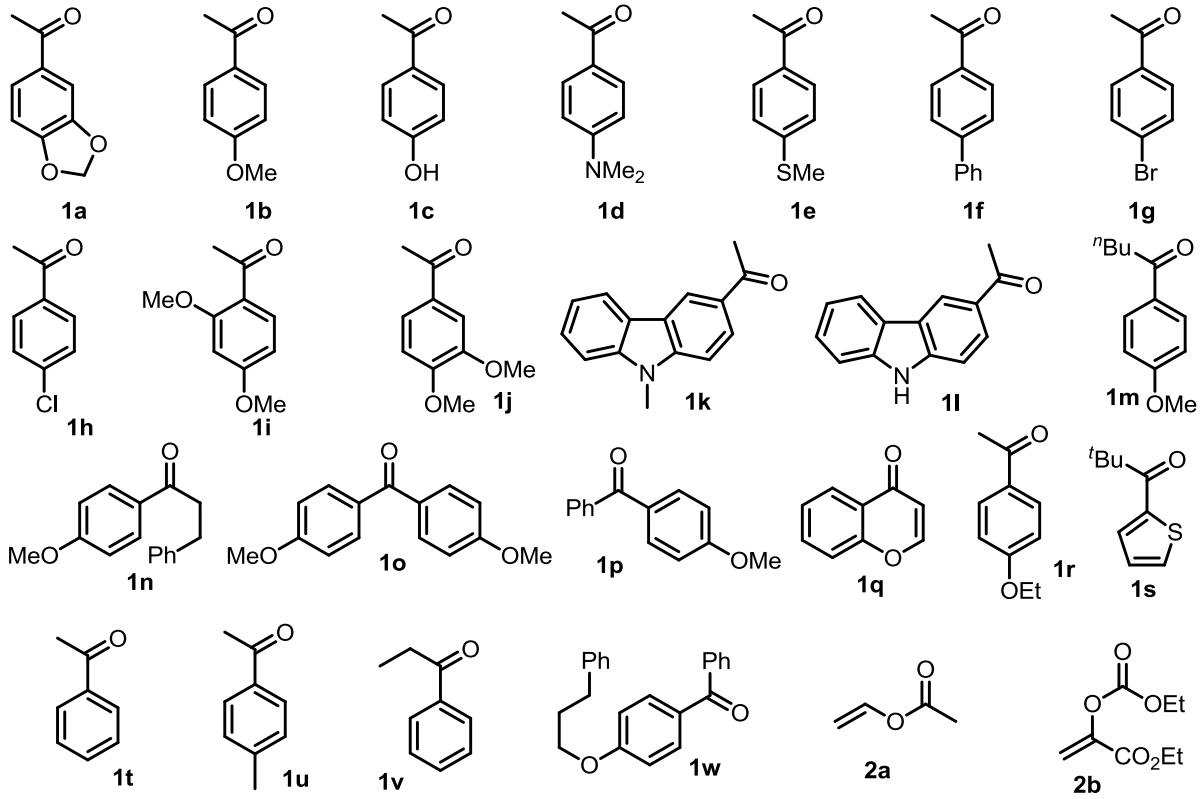
E-mail: msm@chem.iitkgp.ac.in

Table of Contents	Page No.

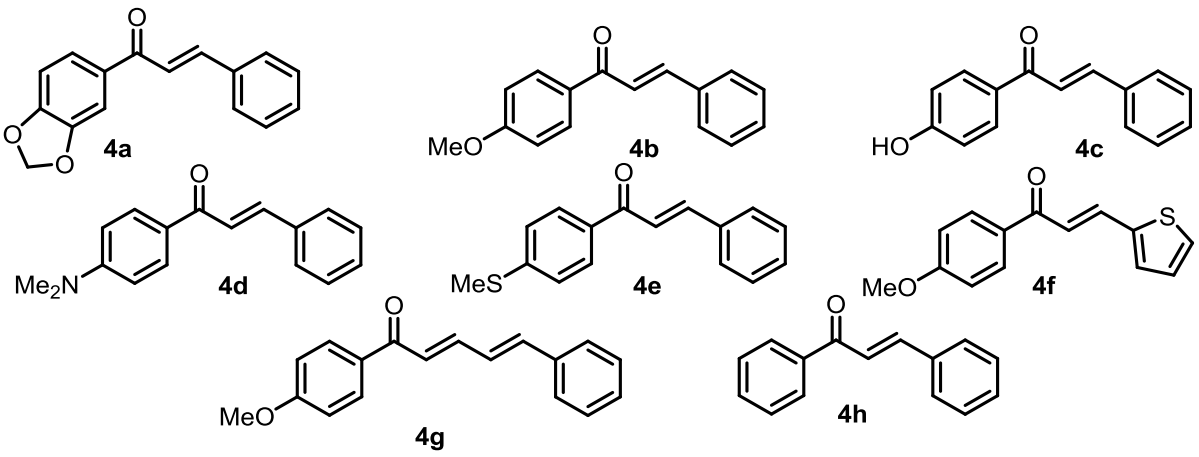
Experimental Section

General: All reactions were carried out in an oven dried sealed tube. Unless otherwise stated, all solvents were dried by standard procedure: 1,2-dichloroethane was distilled over calcium hydride and 2,2,2-trifluro ethanol was directly used as received from commercial sources. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 plates. Visualization on TLC was achieved under UV light (254 nm), exposure to iodine vapour or treatment with $KMnO_4$ solution followed by heating. Column chromatography was performed through silica gel (100-200 mesh) using a proper solvent system. Infrared (IR) spectra were recorded by FTIR spectrometer and reported in terms of wave number (cm^{-1}). The ^1H NMR spectroscopic data were recorded with a Bruker 400, 500 or 600 MHz NMR instruments. ^{13}C NMR spectra were similarly recorded by using 101, 126 or 151 MHz NMR instruments applying a broadband decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in $CDCl_3$ (δ = 7.26, 77.16) and DMSO-d_6 (δ = 2.50, 39.52). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, dd: doublet of doublets, dt: doublet of triplets, ddd: doublet of doublet of doublets, tt: triplet of triplets, td: triplet of doublets, m: multiplet, br: broad. High resolution mass spectra (HRMS) were recorded in ESI (+ Ve) method using a time-of-flight (TOF) mass analyzer. Other chemicals were obtained from commercial sources and used without further purification. Starting materials [**1b**–**j**], [**1t**–1**v**] and **2a** are commercially available. **1a**,[1a] [**1k**–**l**],[1b] **1m**,[1c] **1n**,[1d] [**1o**–**p**],[1e] **1q**,[1f] **1w**[1g] and **2b**[1h] were synthesized following literature procedure. Chalcones **4a**,[2a] **4b**,[1d] **4c**,[2b] **4d**,[2c] **4e**,[2d] **4f**,[2e] **4g**[2f] and **4h**[2g] were synthesized using corresponding acetophenone and aldehyde according to the literature reports.

Starting Materials: Ketones



Starting Materials: Chalcones



General Procedure for the Ketone-Directed Vinylation: (GP I)

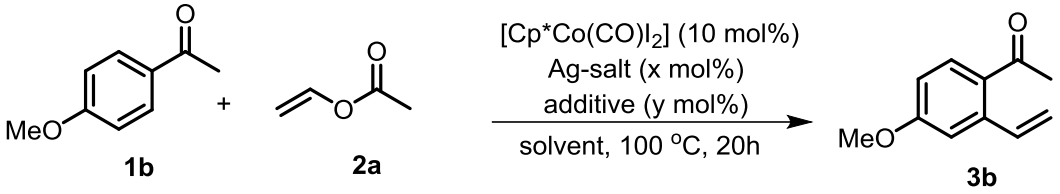
The aryl/heteroaryl ketone **1** (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube and 1.8 mL of 2,2,2-trifluro ethanol was added. Then catalyst $[Cp^*CoI_2]_2$ (5–10 mol %) or $Cp^*Co(CO)I_2$ (10–20 mol %), $AgSbF_6$ (20–40 mol %) and $Cu(OAc)_2$ (20–40 mol %) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, vinyl acetate **2a** (90.4 mg, 1.05 mmol, 3.5 equiv) was added to the reaction mixture

and the resultant reaction mixture was allowed to stir at 100 °C for 20 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography by using petroleum ether/ethylacetate eluent.

General Procedure for the Ketone-Directed Alkenylation with ethyl 2-((ethoxycarbonyl)oxy)acrylate 2b: (GP II)

The aryl/heteroaryl ketone **1** (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube and 1.8 mL of 2,2,2-trifluro ethanol was added. Then catalyst Cp*Co(CO)I_2 (20 mol %), $AgSbF_6$ (40 mol %) and $Cu(OAc)_2$ (40 mol %) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, ethyl 2-((ethoxycarbonyl)oxy)acrylate **2b** (84.7 mg, 0.45 mmol, 1.5 equiv) was added to the reaction mixture and the resultant reaction mixture was allowed to stir at 100 °C for 20 h. After completion of the reaction as indicated by TLC, the crude product was directly purified by silica gel column chromatography using petroleum ether/ethylacetate eluent.

Optimization of the Reaction Conditions for Ketone 1b:[a,b]

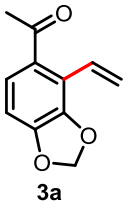


entry	Ag-salt (x mol%)	additive (y mol%)	solvent	**3b** yield (%)
1	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	DCE	30
2	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	48
3	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	EtOH	0
4	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	$PhCF_3$	12
5[c]	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	none	26
6	$AgBF_4$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	43
7	$AgPF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	9
8	AgOTf (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	29
9	$AgNTf_2$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	36
10	$AgSbF_6$ (30 mol%)	NaOAc (30 mol%)	TFE	19
11	$AgSbF_6$ (30 mol%)	$Cu(OTf)_2$ (30 mol%)	TFE	0
12	$AgSbF_6$ (30 mol%)	KOAc (30 mol%)	TFE	23
13	$AgSbF_6$ (30 mol%)	AcOH (30 mol%)	TFE	0

14	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2 \cdot H_2O$ (30 mol%)	TFE	46
15[d]	$AgSbF_6$ (30 mol%)	$Cu(OAc)_2$ (30 mol%)	TFE	62
16[e]	$AgSbF_6$ (40 mol%)	$Cu(OAc)_2$ (40 mol%)	TFE	69
17[f]	**$AgSbF_6$ (40 mol%)**	**$Cu(OAc)_2$ (40 mol%)**	**TFE**	**71**

[a] Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2a** (1.05 mmol, 3.5 equiv) and 1.8 mL solvent were used; [b]- Isolated yield of **3b**; [c] With 0.5 mL **2a**; [d] With 15 mol % catalyst; [e] With 20 mol % catalyst; [f] With 10 mol % $[Cp^*CoI_2]_2$ catalyst.

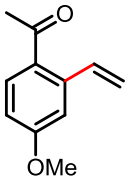
1-(4-Vinylbenzo[*d*][1,3]dioxol-5-yl)ethan-1-one (3a):



3a

The title compound **3a** was synthesized according to the **GP I** and isolated as light yellow solid (44.5 mg, 78%). **IR**: 2903, 1670, 1587, 1444, 1250 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.30 (d, *J* = 8.2 Hz, 1H), 7.05 (dd, *J* = 17.8, 11.7 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.07 (s, 2H), 5.95 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.56 (dd, *J* = 11.6, 1.5 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.2, 150.4, 146.5, 132.1, 130.2, 125.2, 120.6, 120.5, 106.4, 101.8, 29.7. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_{11}O_3$, 191.0703; found 191.0703.

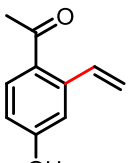
1-(4-Methoxy-2-vinylphenyl)ethan-1-one (3b):



3b

The title compound **3b** was synthesized according to the **GP I** and isolated as colorless oil (37.5 mg, 71%). **IR**: 2941, 1671, 1596, 1560, 1231 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 8.7 Hz, 1H), 7.34 (dd, *J* = 17.4, 10.9 Hz, 1H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.59 (dd, *J* = 17.4, 1.0 Hz, 1H), 5.33 (dd, *J* = 10.9, 1.0 Hz, 1H), 3.86 (s, 3H), 2.55 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 199.8, 162.3, 141.4, 137.0, 132.1, 129.6, 116.5, 113.2, 112.6, 55.5, 29.3. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_{13}O_2$, 177.0910; found 177.0909.

1-(4-Hydroxy-2-vinylphenyl)ethan-1-one (3c):

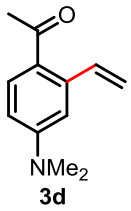


3c

The title compound **3c** was synthesized according to the **GP I** and isolated as white solid (32.9 mg, 68%). **IR**: 3208, 2924, 1646, 1610, 1556, 1306 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.5 Hz, 1H), 7.31 (dd, *J* = 17.3, 10.9 Hz, 1H), 7.05 (s, 1H), 7.01 (d, *J* = 2.3 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.55 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm)

201.1, 159.7, 142.0, 136.7, 132.7, 129.1, 116.8, 114.9, 114.5, 29.3. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{10}H_{11}O_2$,163.0754; found 163.0750.

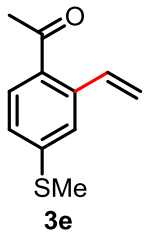
1-(4-(Dimethylamino)-2-vinylphenyl)ethan-1-one (3d):



3d

The title compound **3d** was synthesized according to the **GP I** and isolated as light yellow gummy solid (37.3 mg, 66%). **IR**: 2922, 1656, 1590, 1544, 1364, 1261 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.71 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.47 (dd, *J* = 17.3, 10.8 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.58 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 3.06 (s, 6H), 2.52 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 198.6, 152.7, 141.8, 139.0, 132.7, 124.2, 115.2, 110.8, 109.8, 40.1, 28.7. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{12}H_{16}NO$, 190.1226; found 190.1231.

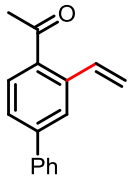
1-(4-(Methylthio)-2-vinylphenyl)ethan-1-one (3e):



3e

The title compound **3e** was synthesized according to the **GP I** and isolated as colorless oil (33.3 mg, 58%). **IR**: 3086, 2923, 1672, 1583, 1541, 1354 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.63 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 1H), 7.27 (dd, *J* = 17.4, 10.9 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 5.60 (d, *J* = 17.4 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 2.56 (s, 3H), 2.53 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.5, 144.3, 139.1, 136.5, 133.2, 130.0, 124.6, 124.1, 117.0, 29.5, 15.0. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{11}H_{13}OS$, 193.0682; found 193.0685.

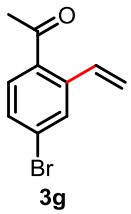
1-(3-Vinyl-[1,1'-biphenyl]-4-yl)ethan-1-one (3f):



3f

The title compound **3f** was synthesized according to the **GP I** and isolated as white solid (31.2 mg, 47%). **IR**: 2926, 1677, 1599, 1501, 1355, 1246 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.77–7.74 (m, 2H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.56 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.31 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.70 (d, *J* = 17.4 Hz, 1H), 5.40 (d, *J* = 11.0 Hz, 1H), 2.62 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 201.5, 144.7, 140.1, 138.8, 136.4, 136.0, 129.8, 129.1, 128.3, 127.4, 126.6, 126.2, 117.0, 29.9. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{16}H_{15}O$, 223.1117; found 223.1111.

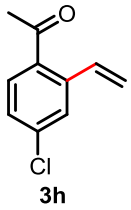
1-(4-Bromo-2-vinylphenyl)ethan-1-one (3g):



3g

The title compound **3g** was synthesized according to the **GP I** and isolated as colorless oil (26.3 mg, 39%). **IR**: 2926, 1686, 1583, 1548, 1356 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.70 (s, 1H), 7.52–7.46 (m, 2H), 7.15 (dd, *J* = 17.0, 11.1 Hz, 1H), 5.65 (d, *J* = 17.3 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 201.0, 140.0, 136.0, 134.9, 130.8, 130.6, 130.4, 126.5, 118.1, 29.9. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{10}H_{10}BrO$, 224.9910; found 224.9900.

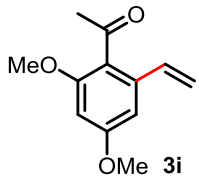
1-(4-Chloro-2-vinylphenyl)ethan-1-one (3h):



3h

The title compound **3h** was synthesized according to the **GP I** and isolated as colorless oil (18.9 mg, 35%). **IR**: 2963, 1683, 1588, 1551, 1355, 1240 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.31 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.17 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.65 (d, *J* = 17.4 Hz, 1H), 5.39 (d, *J* = 10.9 Hz, 1H), 2.56 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 200.8, 139.9, 138.0, 135.6, 135.1, 130.4, 127.8, 127.6, 118.0, 29.9. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{10}H_{10}ClO$, 181.0415; found 181.0423.

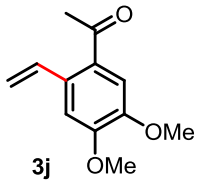
1-(2,4-Dimethoxy-6-vinylphenyl)ethan-1-one (3i):



3i

The title compound **3i** was synthesized according to the **GP I** and isolated as colorless oil (23.5 mg, 38%). **IR**: 2940, 1690, 1595, 1571, 1456, 1316 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 6.72 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.65 (s, 1H), 6.39 (s, 1H), 5.66 (d, *J* = 17.3 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 204.4, 161.5, 158.3, 137.7, 134.4, 123.9, 117.0, 102.2, 98.1, 55.8, 55.6, 32.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{12}H_{15}O_3$, 207.1016; found 207.1021.

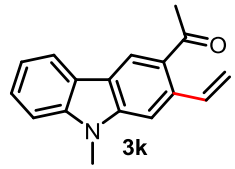
1-(4,5-Dimethoxy-2-vinylphenyl)ethan-1-one (3j):



3j

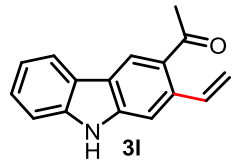
The title compound **3j** was synthesized according to the **GP I** and isolated as colorless oil (22.8 mg, 37%). **IR**: 2928, 1672, 1599, 1560, 1512 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.24 (dd, *J* = 17.4, 10.9 Hz, 1H), 7.17 (s, 1H), 7.00 (s, 1H), 5.55 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.56 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.3, 151.9, 148.2, 136.4, 132.9, 130.1, 115.6, 112.3, 110.2, 56.3, 56.1, 30.0. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{12}H_{15}O_3$, 207.1016; found 207.1023.

1-(9-Methyl-2-vinyl-9*H*-carbazol-3-yl)ethan-1-one (3k):



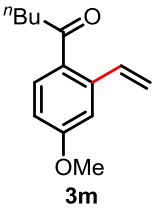
The title compound **3k** was synthesized according to the **GP I** and isolated as white solid (35.8 mg, 48%). **IR**: 2922, 1656, 1591, 1474, 1357, 1242 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.46 (s, 1H), 8.09 (d, *J* = 7.7 Hz, 1H), 7.56–7.50 (m, 2H), 7.46 (s, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 5.69 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.37 (dd, *J* = 10.8, 1.2 Hz, 1H), 3.86 (s, 3H), 2.73 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.6, 142.9, 142.2, 138.5, 137.7, 128.9, 126.6, 122.92, 122.87, 121.7, 120.5, 120.1, 115.2, 109.1, 107.6, 29.6, 29.4. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{17}H_{16}NO$, 250.1226; found 250.1235.

1-(2-Vinyl-9*H*-carbazol-3-yl)ethan-1-one (3l):



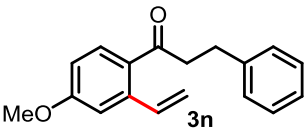
The title compound **3l** was synthesized according to the **GP I** and isolated as white solid (28.8 mg, 41%). **IR**: 3230, 2923, 1647, 1600, 1338, 1244 cm^{-1}. **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) 11.60 (s, 1H), 8.76 (s, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.62 (s, 1H), 7.55–7.53 (m, 1H), 7.46–7.37 (m, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.67 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 10.9 Hz, 1H), 2.70 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ (ppm) 200.2, 141.6, 140.8, 137.8, 136.1, 128.3, 126.4, 123.5, 122.5, 121.4, 120.7, 119.6, 114.6, 111.4, 109.1, 29.5. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{16}H_{14}NO$, 236.1070; found 236.1076.

1-(4-Methoxy-2-vinylphenyl)pentan-1-one (3m):



The title compound **3m** was synthesized according to the **GP I** and isolated as colorless oil (41.8 mg, 64%). **IR**: 2958, 2872, 1674, 1597, 1561, 1464 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.65 (d, *J* = 8.6 Hz, 1H), 7.24 (dd, *J* = 17.3, 10.9 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.60 (d, *J* = 17.4 Hz, 1H), 5.32 (d, *J* = 10.9 Hz, 1H), 3.87 (s, 3H), 2.86 (t, *J* = 7.4 Hz, 2H), 1.69–1.65 (m, 2H), 1.40–1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 203.1, 162.0, 141.0, 136.8, 131.0, 130.3, 116.4, 113.0, 112.7, 55.5, 41.1, 27.0, 22.6, 14.1. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{14}H_{19}O_2$, 219.1380; found 219.1387.

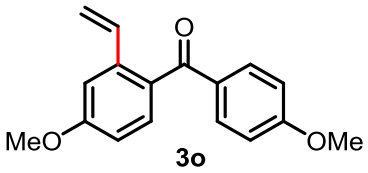
1-(4-Methoxy-2-vinylphenyl)-3-phenylpropan-1-one (3n):



The title compound **3n** was synthesized according to the **GP I** and isolated as colorless oil (50.2 mg, 63%). **IR**: 2918, 1673, 1597, 1560, 1232 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.64 (d, *J* = 8.7 Hz, 1H), 7.30–7.27 (m, 2H), 7.25–7.18 (m, 4H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.3

Hz, 1H), 5.59 (d, *J* = 17.3 Hz, 1H), 5.33 (d, *J* = 10.9 Hz, 1H), 3.87 (s, 3H), 3.22–3.19 (m, 2H), 3.03 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 201.5, 162.2, 141.4, 141.2, 136.8, 131.1, 129.8, 128.64, 128.58, 126.2, 116.6, 113.2, 112.7, 55.6, 43.0, 30.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{18}H_{19}O_2$, 267.1380; found 267.1380.

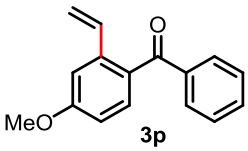
(4-Methoxy-2-vinylphenyl)(4-methoxyphenyl)methanone (3o):



3o

The title compound **3o** was synthesized according to the **GP I** and isolated as light yellow gummy solid (36.8 mg, 46%). **IR**: 2932, 1648, 1596, 1561, 1461, 1254 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.84 (dd, *J* = 17.4, 10.8 Hz, 2H), 5.69 (d, *J* = 17.4 Hz, 1H), 5.24 (d, *J* = 10.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 196.3, 163.6, 161.2, 139.3, 134.9, 132.8, 131.3, 131.2, 131.1, 116.5, 113.7, 112.7, 111.3, 55.64, 55.55. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{17}H_{17}O_3$, 269.1172; found 269.1178.

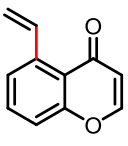
(4-Methoxy-2-vinylphenyl)(phenyl)methanone (3p):



3p

The title compound **3p** was synthesized according to the **GP I** and isolated as light yellow gummy solid (30.7 mg, 43%). **IR**: 2932, 1653, 1596, 1561, 1268 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45–7.43 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.17 (s, 1H), 6.92 (dd, *J* = 17.3, 10.9 Hz, 1H), 6.84 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.69 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 197.5, 161.6, 140.1, 138.6, 135.0, 132.9, 132.0, 130.41, 130.38, 128.5, 116.7, 112.6, 111.6, 55.6. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{16}H_{15}O_2$, 239.1067; found 239.1061.

5-Vinyl-4*H*-chromen-4-one (3q):

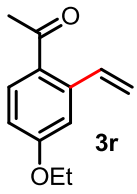


3q

The title compound **3q** was synthesized according to the **GP I** and isolated as light yellow gummy solid (19.1 mg, 37%). **IR**: 3084, 2926, 1638, 1594, 1471, 1345 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.04 (dd, *J* = 17.4, 10.9 Hz, 1H), 7.75 (d, *J* = 5.9 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 6.28 (d, *J* = 5.9 Hz, 1H), 5.60 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.40 (dd, *J* = 10.9, 1.3 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 179.5, 157.7, 153.9, 140.9, 137.1, 133.1, 124.2,

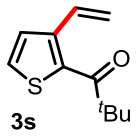
121.9, 117.9, 117.1, 114.4. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_9O_2$, 173.0597; found 173.0603.

1-(4-Ethoxy-2-vinylphenyl)ethan-1-one (3r):



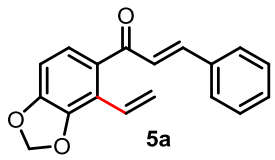
The title compound **3r** was synthesized according to the **GP I** and isolated as colorless oil (38.7 mg, 68%). **IR**: 2982, 1671, 1596, 1559, 1229 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.6 Hz, 1H), 7.34 (dd, *J* = 17.3, 10.9 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.57 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H), 4.09 (q, *J* = 6.9 Hz, 2H), 2.54 (s, 3H), 1.43 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 199.8, 161.7, 141.3, 137.0, 132.0, 129.5, 116.3, 113.8, 113.0, 63.8, 29.3, 14.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{12}H_{15}O_2$, 191.1067; found 191.1068.

2,2-Dimethyl-1-(3-vinylthiophen-2-yl)propan-1-one (3s):



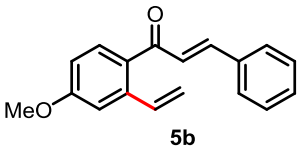
The title compound **3s** was synthesized according to the **GP I** and isolated as colorless oil (30 mg, 51%). **IR**: 2972, 1654, 1505, 1475, 1365 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.34 (d, *J* = 5.2 Hz, 1H), 7.30 (d, *J* = 5.2 Hz, 1H), 7.21 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.68 (dd, *J* = 17.7, 1.3 Hz, 1H), 5.36 (dd, *J* = 11.0, 1.3 Hz, 1H), 1.36 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 201.9, 145.7, 132.5, 131.4, 127.6, 126.2, 117.2, 45.0, 27.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_{14}NaOS$, 217.0658; found 217.0664.

(*E*)-3-Phenyl-1-(4-vinylbenzo[*d*][1,3]dioxol-5-yl)prop-2-en-1-one (5a):



The title compound **5a** was synthesized according to the **GP I** and isolated as gummy solid (56.6 mg, 68%). **IR**: 2903, 1659, 1595, 1445, 1228 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.56–7.51 (m, 3H), 7.46–7.35 (m, 3H), 7.16–7.11 (m, 2H), 6.85 (dd, *J* = 17.7, 11.6 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.11 (s, 2H), 6.05 (d, *J* = 17.7 Hz, 1H), 5.55 (d, *J* = 11.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 194.3, 149.9, 146.3, 145.4, 134.8, 133.4, 130.7, 129.7, 129.1, 128.6, 126.9, 124.0, 120.9, 119.9, 106.8, 101.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{18}H_{15}O_3$, 279.1016; found 279.1027.

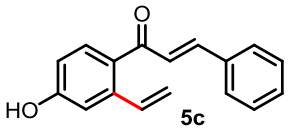
(*E*)-1-(4-Methoxy-2-vinylphenyl)-3-phenylprop-2-en-1-one (5b):



5b

The title compound **5b** was synthesized according to the **GP I** and isolated as yellow gummy solid (37.9 mg, 48%). **IR**: 3011, 2963, 1697, 1596, 1492, 1449 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.61–7.52 (m, 4H), 7.41–7.39 (m, 3H), 7.20 (d, *J* = 15.9 Hz, 1H), 7.15–7.08 (m, 2H), 6.88 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.71 (d, *J* = 17.3 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 3.90 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 194.1, 161.8, 144.9, 140.0, 135.6, 134.9, 131.3, 131.1, 130.6, 129.1, 128.5, 126.6, 116.8, 112.9, 112.2, 55.6. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{18}H_{17}O_2$, 265.1223; found 265.1225.

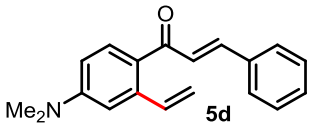
(*E*)-1-(4-Hydroxy-2-vinylphenyl)-3-phenylprop-2-en-1-one (5c):



5c

The title compound **5c** was synthesized according to the **GP I** and isolated as white solid (45.6 mg, 61%). **IR**: 3243, 2920, 1592, 1559, 1448, 1332 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.58–7.53 (m, 4H), 7.40–7.39 (m, 3H), 7.20 (d, *J* = 15.9 Hz, 1H), 7.09–7.04 (m, 3H), 6.84 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.63 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 195.3, 159.0, 145.8, 140.4, 135.3, 134.7, 131.5, 130.9, 130.7, 129.1, 128.6, 126.5, 117.0, 114.8, 113.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{17}H_{15}O_2$, 251.1067; found 251.1062.

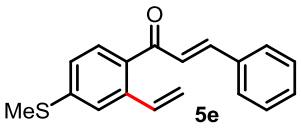
(*E*)-1-(4-(Dimethylamino)-2-vinylphenyl)-3-phenylprop-2-en-1-one (5d):



5d

The title compound **5d** was synthesized according to the **GP I** and isolated as yellow gummy solid (46.5 mg, 56%). **IR**: 2916, 1586, 1542, 1364, 1330 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J* = 8.7 Hz, 1H), 7.62–7.58 (m, 3H), 7.41–7.36 (m, 3H), 7.35–7.29 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 1H), 6.63 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.65 (d, *J* = 17.3 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H), 3.08 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 192.1, 152.5, 143.0, 141.0, 137.8, 135.5, 131.8, 130.1, 129.0, 128.3, 126.3, 125.9, 115.6, 110.21, 110.17, 40.2. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{19}H_{20}NO$, 278.1539; found 278.1539.

(*E*)-1-(4-(Methylthio)-2-vinylphenyl)-3-phenylprop-2-en-1-one (5e):

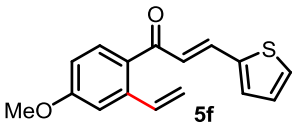


5e

The title compound **5e** was synthesized according to the **GP I** and isolated as yellow gummy solid (36.8 mg, 44%). **IR**: 2919, 1658, 1583, 1539, 1329 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.57–7.55 (m, 2H), 7.53–7.50 (m, 2H), 7.45 (s, 1H), 7.41–7.40 (m, 3H), 7.20 (dd, *J* = 8.1, 1.3 Hz,

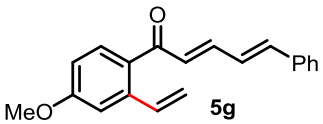
1H), 7.15 (d, *J* = 16.0 Hz, 1H), 7.03 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.71 (d, *J* = 17.4 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 2.55 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 194.9, 145.7, 143.0, 138.0, 135.1, 134.9, 134.8, 130.8, 129.3, 129.1, 128.6, 126.7, 124.5, 123.8, 117.2, 15.3. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{18}H_{17}OS$, 281.0995; found 281.0992.

(*E*)-1-(4-Methoxy-2-vinylphenyl)-3-(thiophen-2-yl)prop-2-en-1-one (5f):



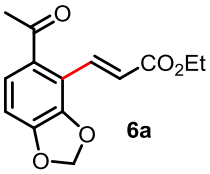
The title compound **5f** was synthesized according to the **GP I** and isolated as yellow oil (39.7 mg, 49%). **IR**: 2938, 1652, 1582, 1559, 1230 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.67 (d, *J* = 15.5 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 4.7 Hz, 1H), 7.29 (d, *J* = 3.5 Hz, 1H), 7.14–7.06 (m, 3H), 7.00 (d, *J* = 15.6 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.70 (d, *J* = 17.4 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 193.5, 161.8, 140.3, 140.0, 137.3, 135.6, 132.0, 131.1, 131.0, 129.1, 128.5, 125.4, 116.8, 112.9, 112.1, 55.6. **HRMS (ESI) m/z**: $[M + Na]^+$ calcd for $C_{16}H_{14}NaO_2S$, 293.0607; found 293.0612.

(2*E*,4*E*)-1-(4-Methoxy-2-vinylphenyl)-5-phenylpenta-2,4-dien-1-one (5g):



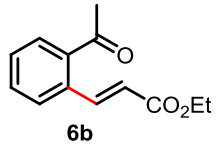
The title compound **5g** was synthesized according to the **GP I** and isolated as yellow gummy solid (38.2 mg, 44%). **IR**: 2936, 1652, 1596, 1489, 1449 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.38–7.29 (m, 4H), 7.13–7.06 (m, 2H), 6.97–6.91 (m, 2H), 6.87 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.74 (d, *J* = 15.1 Hz, 1H), 5.69 (d, *J* = 17.3 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 194.3, 161.7, 145.1, 141.7, 139.9, 136.2, 135.6, 131.4, 131.0, 130.0, 129.3, 129.0, 127.4, 127.0, 116.6, 112.9, 112.1, 55.6. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{20}H_{19}O_2$, 291.1380; found 291.1377.

Ethyl (*E*)-3-(5-Acetylbenzo[*d*][1,3]dioxol-4-yl)acrylate (6a):[3a]



The title compound **6a** was synthesized according to the **GP II** and isolated as white solid (52.8 mg, 67%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.02 (d, *J* = 16.2 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 16.2 Hz, 1H), 6.10 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.56 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 199.3, 167.20, 150.7, 147.7, 137.7, 132.8, 125.5, 124.1, 117.3, 108.0, 102.2, 60.6, 29.4, 14.4.

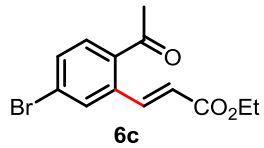
Ethyl (*E*)-3-(2-Acetylphenyl)acrylate (6b):[3b]



6b

The title compound **6b** was synthesized according to the **GP II** and isolated as colorless oil (28.1 mg, 43%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.14 (d, *J* = 15.9 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 201.0, 166.7, 144.0, 138.4, 135.0, 132.1, 129.5, 129.4, 128.6, 121.2, 60.7, 29.4, 14.5.

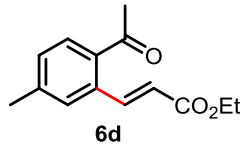
Ethyl (*E*)-3-(2-Acetyl-5-bromophenyl)acrylate (6c):[3c]



6c

The title compound **6c** was synthesized according to the **GP II** and isolated as white solid (35.4 mg, 40%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.08 (d, *J* = 15.9 Hz, 1H), 7.72 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.27 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 199.8, 166.3, 142.7, 137.2, 136.7, 132.4, 131.6, 130.9, 126.9, 122.3, 60.9, 29.3, 14.4.

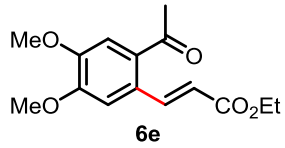
Ethyl (*E*)-3-(2-Acetyl-5-methylphenyl)acrylate (6d):[3b]



6d

The title compound **6d** was synthesized according to the **GP II** and isolated as yellow oil (32.0 mg, 46%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.17 (d, *J* = 15.8 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.36 (s, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 4.26–4.23 (m, 2H), 2.58 (s, 3H), 2.40 (s, 3H), 1.32 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 200.4, 166.7, 144.6, 142.8, 135.41, 135.40, 130.1, 129.8, 129.3, 120.8, 60.6, 29.1, 21.6, 14.4.

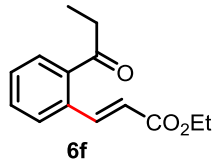
Ethyl (*E*)-3-(2-Acetyl-4,5-dimethoxyphenyl)acrylate (6e):[3d]



6e

The title compound **6e** was synthesized according to the **GP II** and isolated as yellow solid (28.2 mg, 34%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.17 (d, *J* = 15.8 Hz, 1H), 7.21 (s, 1H), 7.03 (s, 1H), 6.23 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 6H), 2.60 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 199.5, 166.9, 151.8, 149.6, 144.0, 131.6, 129.2, 119.9, 112.2, 110.4, 60.7, 56.32, 56.26, 29.6, 14.5.

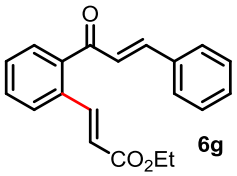
Ethyl (*E*)-3-(2-Propionylphenyl)acrylate (6f):[3e]



6f

The title compound **6f** was synthesized according to the **GP II** and isolated as colorless oil (28.9 mg, 42%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 8.05 (d, *J* = 15.8 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 4.26–4.24 (m, 2H), 2.94–2.92 (m, 2H), 1.33 (t, *J* = 6.4 Hz, 3H), 1.21 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 204.4, 166.7, 143.9, 138.9, 134.7, 131.7, 129.5, 128.5, 128.4, 121.1, 60.7, 34.9, 14.4, 8.5.

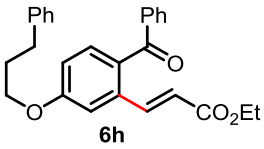
Ethyl (*E*)-3-(2-Cinnamoylphenyl)acrylate (6g):[2g]



6g

The title compound **6g** was synthesized according to the **GP II** and isolated as gummy solid (35.6 mg, 39%). **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 15.9 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.57–7.55 (m, 2H), 7.53–7.46 (m, 3H), 7.41–7.38 (m, 3H), 7.16 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 195.2, 166.6, 147.0, 142.4, 140.0, 134.6, 134.1, 131.12, 131.06, 129.6, 129.2, 128.74, 128.70, 127.7, 126.5, 121.2, 60.7, 14.4.

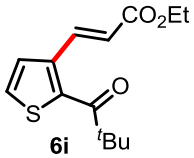
Ethyl (*E*)-3-(2-Benzoyl-5-(3-phenylpropoxy)phenyl)acrylate (6h):[3a]



6h

The title compound **6h** was synthesized according to the **GP II** and isolated as light yellow oil (63.1 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 15.9 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48–7.42 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24–7.19 (s, 3H), 6.91 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.34 (d, *J* = 15.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.05 (t, *J* = 6.2 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.19–2.13 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 196.5, 166.5, 161.2, 142.7, 141.3, 138.3, 137.3, 133.1, 132.6, 131.5, 130.4, 128.6, 128.5, 126.2, 121.1, 114.9, 113.3, 67.3, 60.7, 32.1, 30.7, 14.4.

Ethyl (*E*)-3-(2-pivaloylthiophen-3-yl)acrylate (6i):

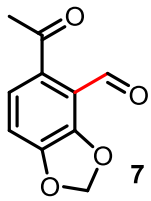


6i

The title compound **6i** was synthesized according to the **GP II** and isolated as colorless oil (23 mg, 43%). **IR**: 2977, 1709, 1657, 1630, 1404, 1244 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 8.03 (d, *J* = 16.1 Hz, 1H), 7.39 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 5.2 Hz, 1H), 6.31 (d, *J* = 16.1 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.36 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 201.5,

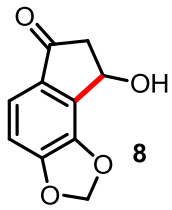
167.0, 142.0, 138.1, 136.8, 128.0, 126.4, 121.6, 60.7, 45.1, 27.7, 14.5. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{14}H_{19}O_3S$, 267.1049; found 267.1048.

5-Acetylbenzo[*d*][1,3]dioxole-4-carbaldehyde (7):



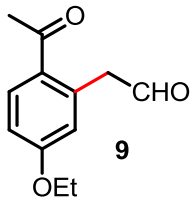
The title compound **7** was synthesized in one-pot from **3a** using OsO_4-catalyzed dihydroxylation followed by diol-cleavage with $NaIO_4$. The vinylated product **3a** (19.0 mg, 0.1 mmol) was dissolved in 1.0 mL THF/H_2O (1:1) and then 5 mol % OsO_4 (0.1 ml, 0.05 M in toluene) was added followed by the addition of 4-methylmorpholine *N*-oxide (29.3 mg, 2.5 equiv) at room temperature. The reaction mixture was then stirred at 50 ^oC for 20 min. After complete consumption of the **3a**, $NaIO_4$ (21.4 mg, 0.2 mmol) was added and stirred at the same temperature for 15 min. Then the crude reaction mixture was diluted with ethyl acetate, extracted, the organic layers were dried over Na_2SO_4 and concentrated under *vacuo*. The pure product **7** was isolated as a white solid in 54% overall yield (10.4 mg). **IR**: 2923, 1688, 1669, 1591, 1446 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 10.22 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.17 (s, 2H), 2.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 198.5, 189.6, 152.2, 148.5, 133.3, 125.2, 119.9, 110.3, 103.4, 28.1. **HRMS (ESI) m/z**: [M + H]$^+$ calcd for $C_{10}H_9O_4$, 193.0495; found 193.0497.

8-Hydroxy-7,8-dihydro-6*H*-indeno[4,5-*d*][1,3]dioxol-6-one (8):[4]



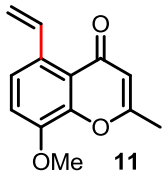
In an oven-dried reaction tube compound **7** (10.4 mg, 0.054), 1.0 mL ethanol and 20 mol % LiOH were taken and the reaction mixture was stirred at the room temperature for 15 min. After evaporating the solvent, crude residue was diluted with ethyl acetate and water, extracted with ethyl acetate and dried over Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified on a silica gel column to afford product **8** as white solid in 56% yield (5.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.39 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 6.15 (s, 1H), 5.58–5.53 (m, 1H), 3.11 (dd, *J* = 18.8, 7.0 Hz, 1H), 2.65 (dd, *J* = 18.8, 2.8 Hz, 1H), 2.31 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 201.0, 153.5, 144.2, 134.4, 132.3, 119.0, 110.6, 102.9, 65.9, 47.1.

2-(2-Acetyl-5-ethoxyphenyl)acetaldehyde (9):[5]



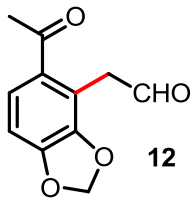
The title compound **9** was synthesized according to the modified literature procedure.[6] An oven-dried Schlenk tube was charged with $PdCl_2$ (26.5 mg, 1.0 equiv), 1.5 mL DMF/water (10:1) and compound **3r** (28.5 mg, 0.15 mmol). The mixture was then stirred at 30 to 35 ^oC for 1 h under nitrogen atmosphere. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The collected organic layers were dried over sodium sulfate and concentrated under *vacuo*. The crude residue was then purified on a silica-gel column to obtain **9** as sticky solid in 43% yield (based on recovered starting material). **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 9.75 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.71 (d, *J* = 2.3 Hz, 1H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.97 (s, 2H), 2.56 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 199.0, 198.9, 162.2, 137.0, 133.5, 128.9, 119.6, 112.8, 64.0, 50.0, 28.4, 14.8.

8-Methoxy-2-methyl-5-vinyl-4*H*-chromen-4-one (11):



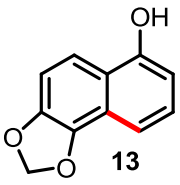
The title compound **11** was synthesized according to the **GP I** and isolated as yellow gummy solid (27.2 mg, 42%). **IR**: 2926, 1650, 1575, 1489, 1390 cm^{-1}. **^{1}H NMR** (600 MHz, $CDCl_3$): δ (ppm) 7.98 (dd, *J* = 17.4, 10.8 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.14 (s, 1H), 5.49 (d, *J* = 17.4 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 3.98 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ (ppm) 180.2, 164.6, 148.2, 147.7, 136.9, 131.7, 123.3, 121.5, 115.0, 113.9, 112.2, 56.5, 20.3. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{13}H_{13}O_3$, 217.0859; found 217.0856.

2-(5-Acetylbenzo[*d*][1,3]dioxol-4-yl)acetaldehyde (12):



The title compound **12** was synthesized according to the procedure used for the synthesis of compound **9** in 0.4 mmol scale and isolated as white solid in 45% yield (based on recovered starting material). **IR**: 2919, 1667, 1453, 1259, 1057 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$): δ (ppm) 9.76 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.04 (s, 2H), 4.01 (s, 2H), 2.54 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ (ppm) 198.8, 198.1, 150.7, 148.5, 130.7, 127.1, 115.6, 106.7, 102.0, 41.5, 28.5. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_{11}O_4$, 207.0652; found 207.0657.

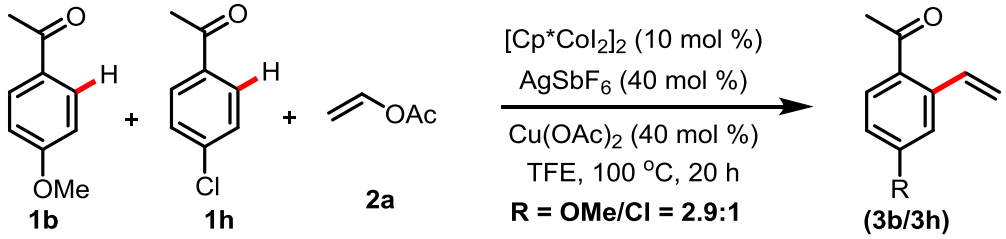
Naphtho[1,2-*d*][1,3]dioxol-6-ol (13):



In an oven-dried reaction tube compound **12** (20.6 mg, 0.1 mmol), 1.0 mL ethanol and 10 mol % LiOH were added and the reaction mixture was stirred at the room temperature for 1 h. The solvent was then evaporated under vacuo and refilled with ethyl acetate and water. The crude residue was extracted with ethyl acetate, dried over Na_2SO_4, organic solvent was removed under reduced pressure, and purified on a silica gel column to afford white solid product **13** in 72% yield (13.5 mg). **IR**: 2901, 1655, 1603, 1572, 1471, 1420 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.29–7.25 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.65 (d, *J* = 7.3 Hz, 1H), 6.16 (s, 2H), 5.34 (brs, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ (ppm) 152.1, 144.0, 141.3, 126.7, 121.4, 121.2, 116.0, 112.6, 109.7, 106.8, 101.8. **HRMS (ESI) m/z**: $[M + H]^+$ calcd for $C_{11}H_9O_3$, 189.0546; found 189.0556.

Control Experiments:

Intermolecular Competition Experiments between Different Acetophenones with 2a:



The 4-methoxyacetophenone **1b** (0.3 mmol, 1.0 equiv) and 4-chloroacetophenone **1h** (0.3 mmol, 1.0 equiv) were taken in a 15.0 mL screw capped sealed tube and 1.8 mL of 2,2,2-trifluro ethanol was added. Then catalyst $[Cp^*CoI_2]_2$ (26.9 mg, 0.06 mmol, 10.0 mol %), $AgSbF_6$ (41.2 mg, 0.12 mmol, 40.0 mol %) and $Cu(OAc)_2$ (21.8 mg, 0.12 mmol, 40.0 mol %) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, vinyl acetate **2a** (90.4 mg, 1.05 mmol, 3.5 equiv) was added to the reaction mixture and the resultant reaction mixture was allowed to stir at 100 °C for 20 h. Then the crude product was directly filtered through a silica gel column using 30% ethylacetate in pet ether as eluent. The ratio **3b**:**3h** = 2.9:1 is being calculated by ^{1}H NMR analysis (Figure S1).

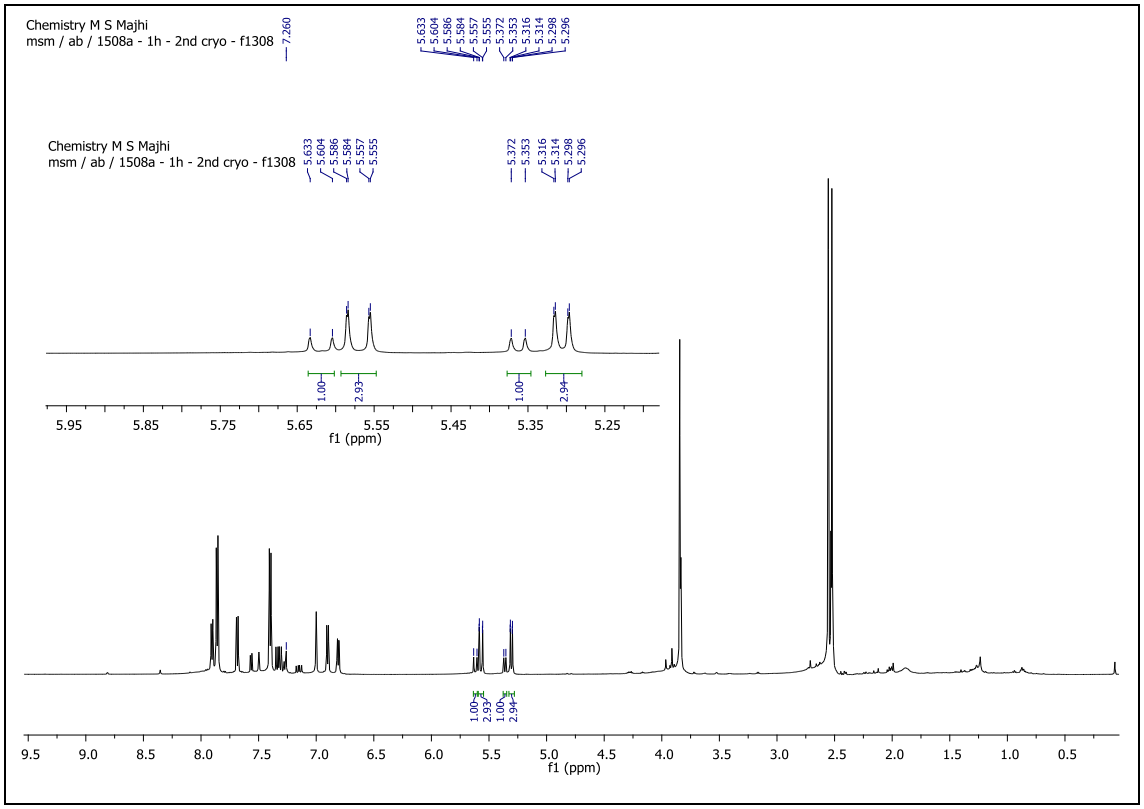
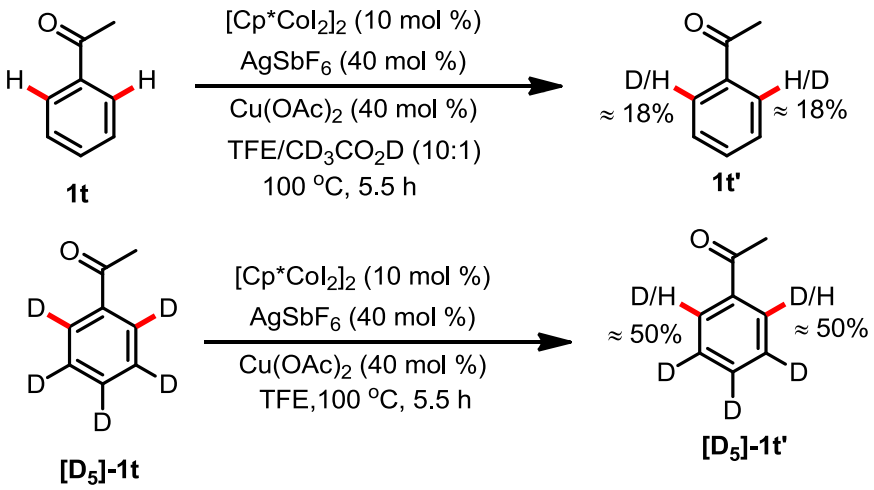


Figure S1: ^{1}H NMR spectra of competition experiment between acetophenones **1b** and **1h**.

Deuterium Labelling Experiments Using Deuterated Solvent as a co-Solvent:



General Method of Deuterium Labelling Experiments with 1t:

Acetophenone **1t** (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube. 2,2,2-Trifluro ethanol and the deuterated solvent were added (total volume 1.8 mL) to it maintaining the ratio of 10:1. Then catalyst $[Cp^*CoI_2]_2$ (26.9 mg, 0.06 mmol, 10.0 mol %), $AgSbF_6$ (41.2 mg, 0.12 mmol, 40.0 mol %) and $Cu(OAc)_2$ (21.8 mg, 0.12 mmol, 40.0 mol %)

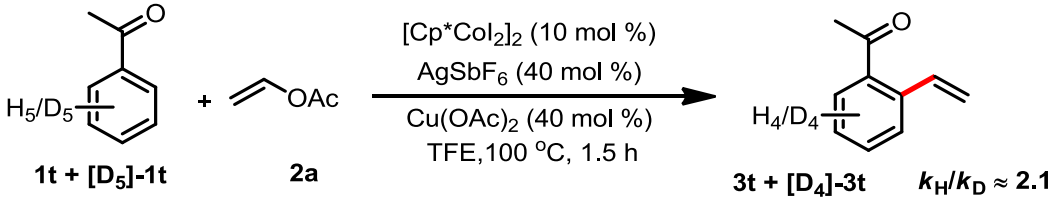
were added successively to the reaction mixture and was stirred for 5.5 h at 100 °C. Purification by silica gel column chromatography using 20% ethylacetate in pet ether as eluent provided mixture of **1t** and **1t′**. ^{1}H NMR analysis revealed ~18% deuterium incorporation at the *ortho*-position in acetophenone.

Representative Method of Proton Incorporation to [D$_5$]-1t:

Acetophenone **[D$_5$]-1t** (0.3 mmol, 1.0 equiv) was taken in a 15.0 mL screw capped sealed tube and 1.8 mL of 2,2,2-trifluro ethanol was added. Then catalyst [Cp*CoI$_2$]$_2$ (26.9 mg, 0.06 mmol, 10.0 mol %), AgSbF$_6$ (41.2 mg, 0.12 mmol, 40.0 mol %) and Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 40.0 mol %) were added successively to the reaction mixture and was stirred for 5.5 h at 100 °C. Purification by silica gel column chromatography using 20% ethylacetate in pet ether as eluent provided mixture of **[D$_5$]-1t** and **[D$_5$]-1t′**. ^{1}H NMR analysis revealed ~50% of ^{1}H incorporation at *ortho*-position in compound **[D$_5$]-1t**.

Note: During reaction no special care was taken to exclude moisture present in the air which may also play a role as a source of ^{1}H along with TFE.

Determination of KIE from Intermolecular Competition Experiments:



Acetophenone **1t** (36.0 mg, 0.3 mmol) and pentadeuterio acetophenone [**D$_5$**]**-1t** (37.5 mg, 0.3 mmol) were taken in a 15.0 mL screw capped sealed tube and 1.8 mL of 2,2,2-trifluro ethanol was added. Then catalyst [Cp*CoI$_2$]$_2$ (26.9 mg, 0.06 mmol, 10.0 mol %), AgSbF$_6$ (41.2 mg, 0.12 mmol, 40.0 mol %) and Cu(OAc)$_2$ (21.8 mg, 0.12 mmol, 40.0 mol %) were added successively to the reaction mixture and was stirred for 5 min at the room temperature. After that, vinyl acetate **2a** (90.4 mg, 1.05 mmol, 3.5 equiv) was added to the reaction mixture and the resultant reaction mixture was allowed to stir at 100 °C for 1.5 h. After the passing the crude mixture through a silica gel column by eluting with 30% ethylacetate in pet ether, the mixture was isolated together. The ratio of **3t:**[**D$_4$**]**-3t** was determined by ^{1}H NMR analysis to obtain a KIE value of approximately 2.1 (Figure S2).

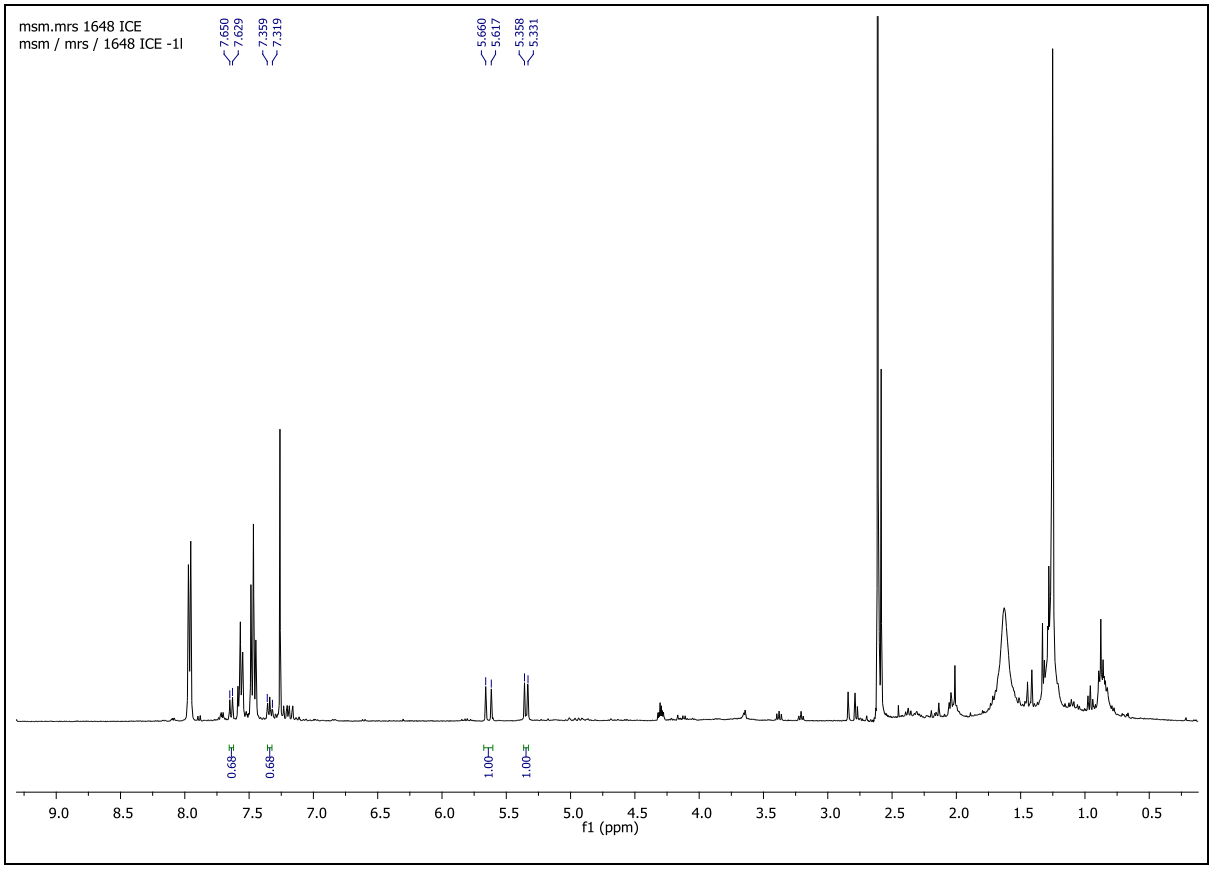
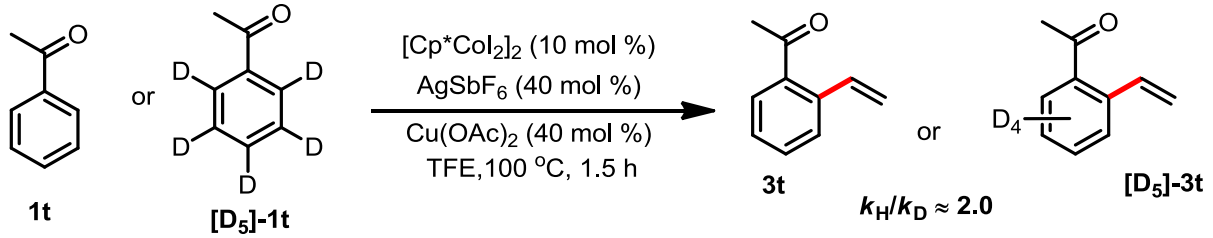


Figure S2: ^{1}H NMR Spectra for determination of KIE value by intermolecular competition experiment.

Determination of k_H/k_D from Parallel Experiments:



Acetophenone **1t** (36.0 mg, 0.3 mmol) and pentadeuterio acetophenone [**D**$_5$]-**1t** (37.5 mg, 0.3 mmol) were separately taken in 15.0 mL screw capped sealed tubes and 1.8 mL of 2,2,2-trifluro ethanol was added to each tube. Then catalyst $[Cp^*CoI_2]_2$ (26.9 mg, 0.06 mmol, 10.0 mol %), $AgSbF_6$ (41.2 mg, 0.12 mmol, 40.0 mol %) and $Cu(OAc)_2$ (21.8 mg, 0.12 mmol, 40.0 mol %) were added successively to each reaction mixture and was stirred for 5 min at the room temperature. After that, vinyl acetate **2a** (90.4 mg, 1.05 mmol, 3.5 equiv) was added to each reaction mixture and two resultant reaction mixtures were allowed to stir at 100 °C for1.5 h. Then both the reaction mixture was mixed together. After the passing the crude mixture through a silica gel column by eluting with 30% ethylacetate in pet ether, the mixture was isolated

together. The ratio of **3t:**[**D**$_4$]**-3t** was determined by ^{1}H NMR analysis to obtain a k_H/k_D value of approximately 2.0 (Figure S3).

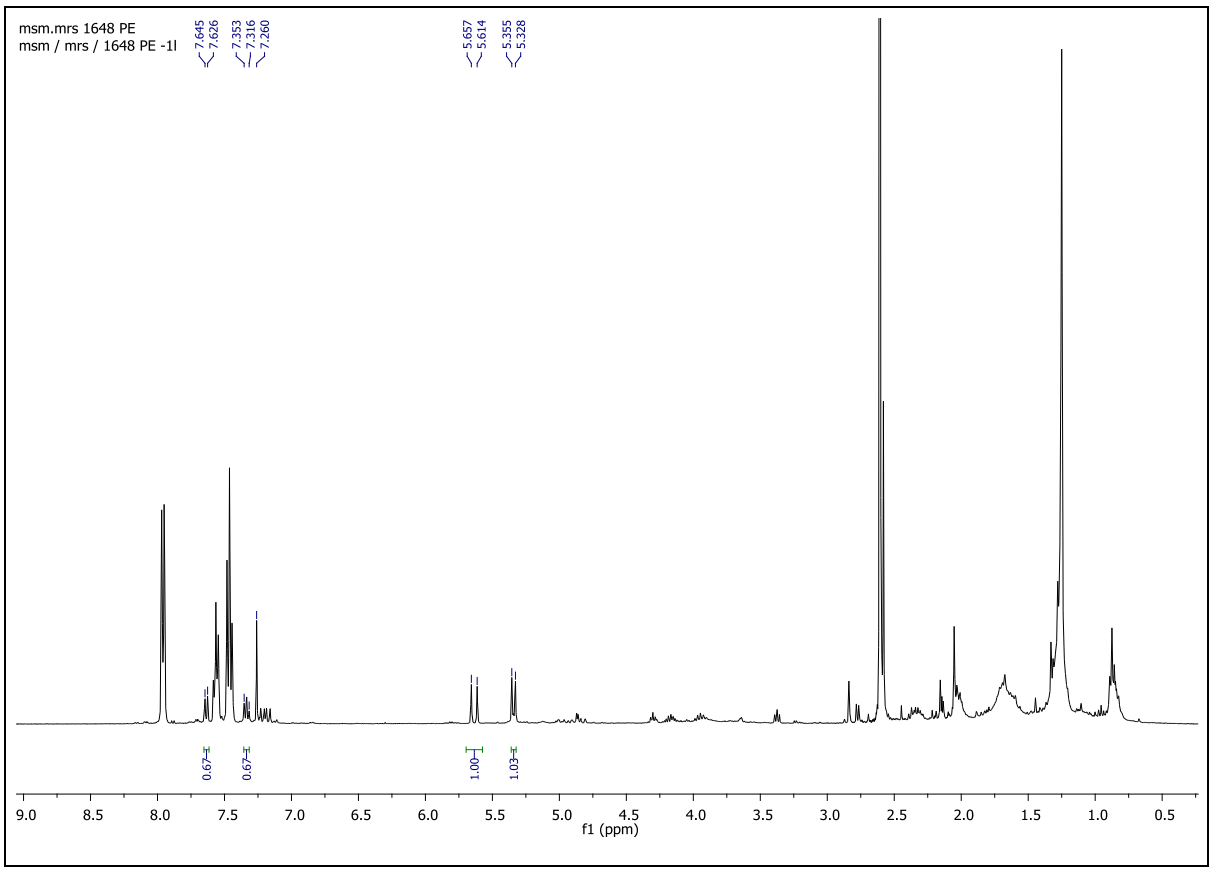
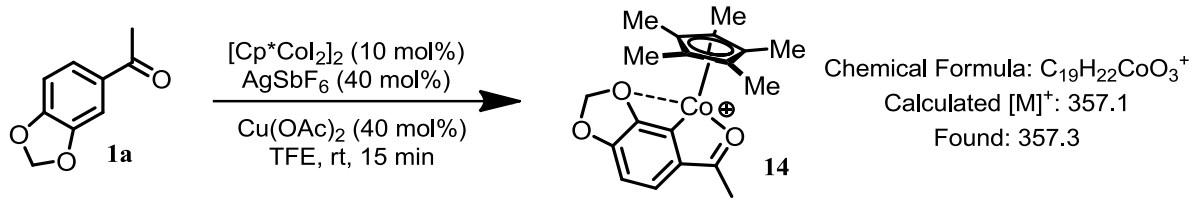


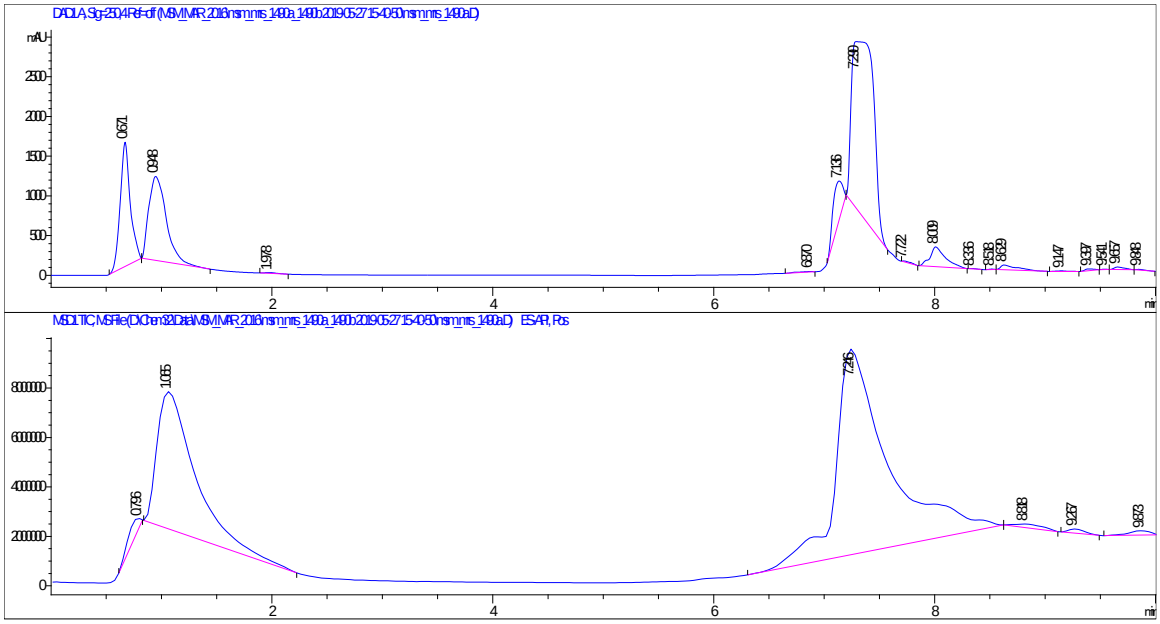
Figure S3: ^{1}H NMR Spectra for the determination of k_H/k_D value from parallel experiments.

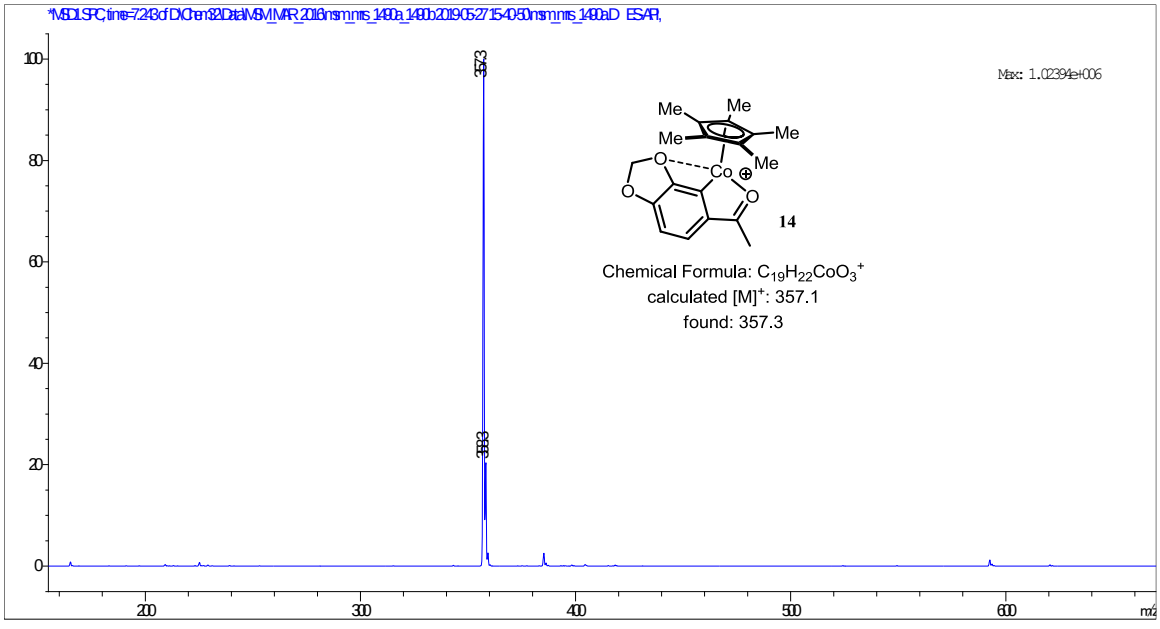
Experiments Conducted to Detect the Reaction Intermediates Proposed in the Catalytic Cycle:

We conducted several control experiments by LC-MS analysis using the crude reaction mixture to get further information regarding the reaction mechanism or the intermediates formed during the course of the reaction. The presence of several peaks under the analysis indicated the involvement of important intermediates or the fragment of the intermediates proposed in the catalytic cycle. Thus, studies with ketone **1a** under different reaction conditions indicated the presence of the cyclometallated species **14** and on addition of the vinyl acetate **2a** the LC-MS analysis indicated the presence of the cobaltacycle **15**. Although the similar intermediate **17** will have the same mass as **15**, previous studies related to Cp*Rh(III)-catalysis indicated the presence of the intermediate similar to **15** through crystal structure analysis.[7]

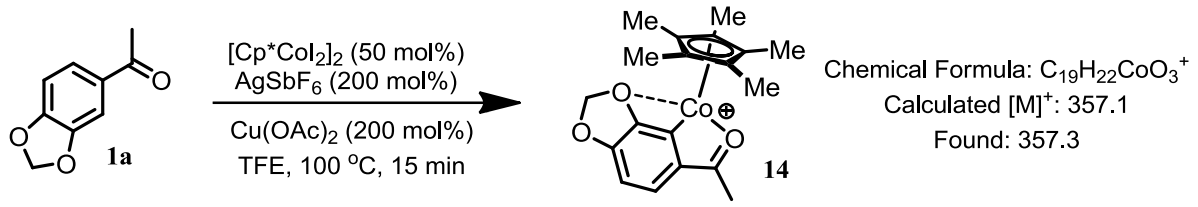
Experiment 1: Cyclometallation of **1a** using 10 mol% $[Cp^*CoI_2]_2$

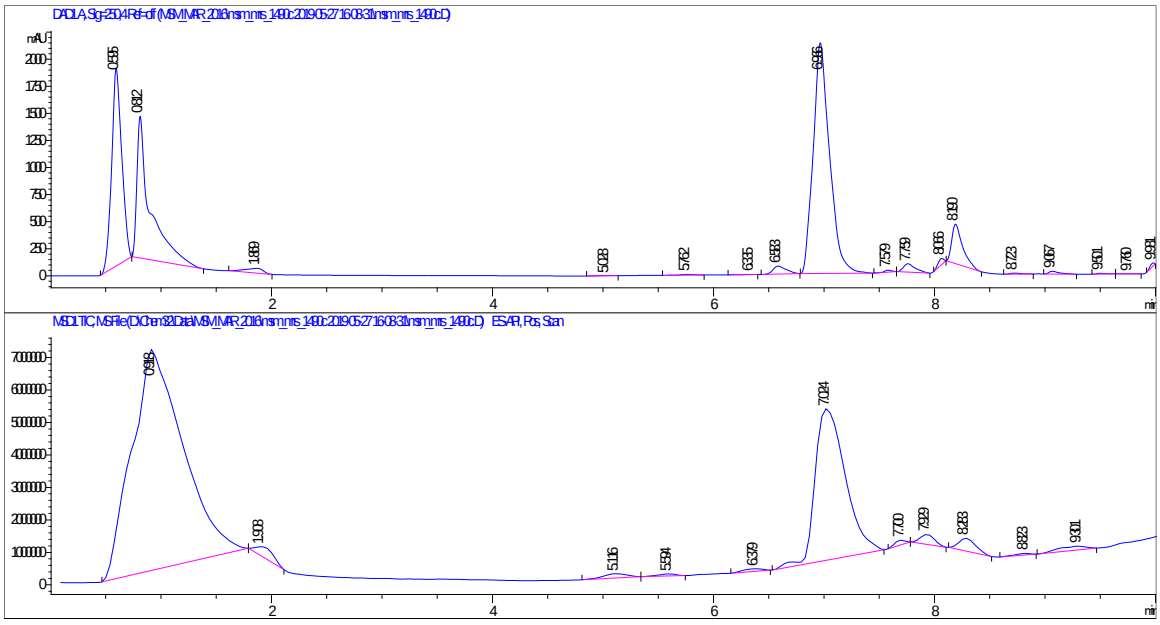


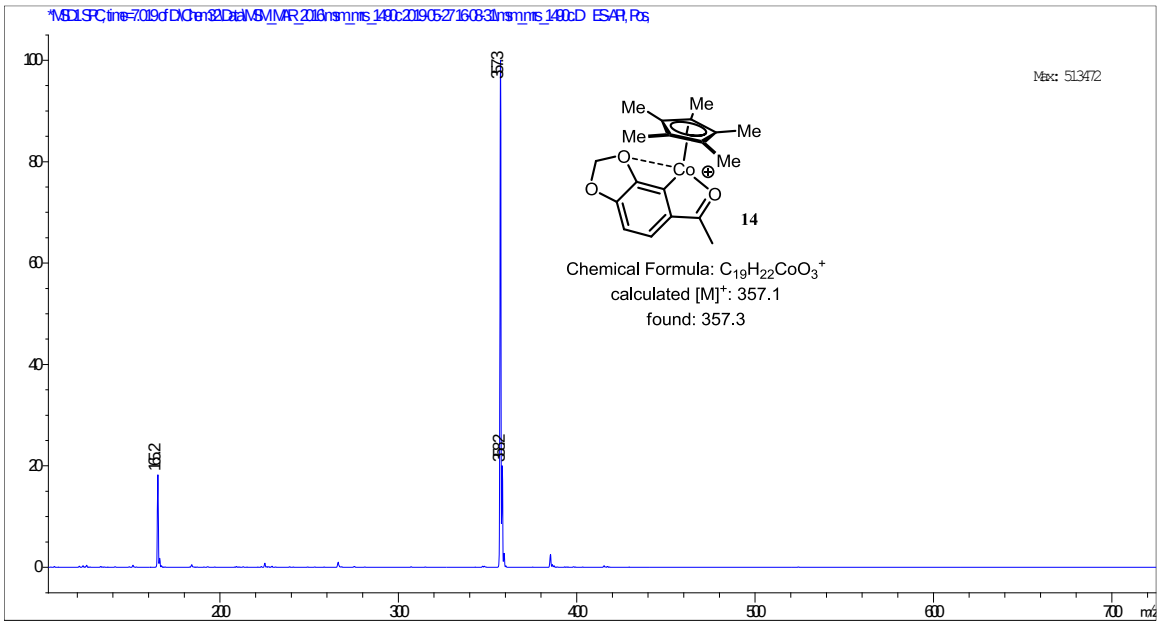




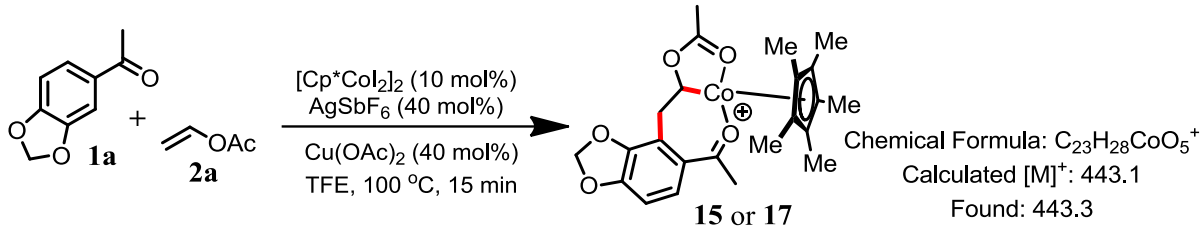
Experiment 2: Cyclometallation of **1a** using 50 mol% $[Cp^*CoI_2]_2$.

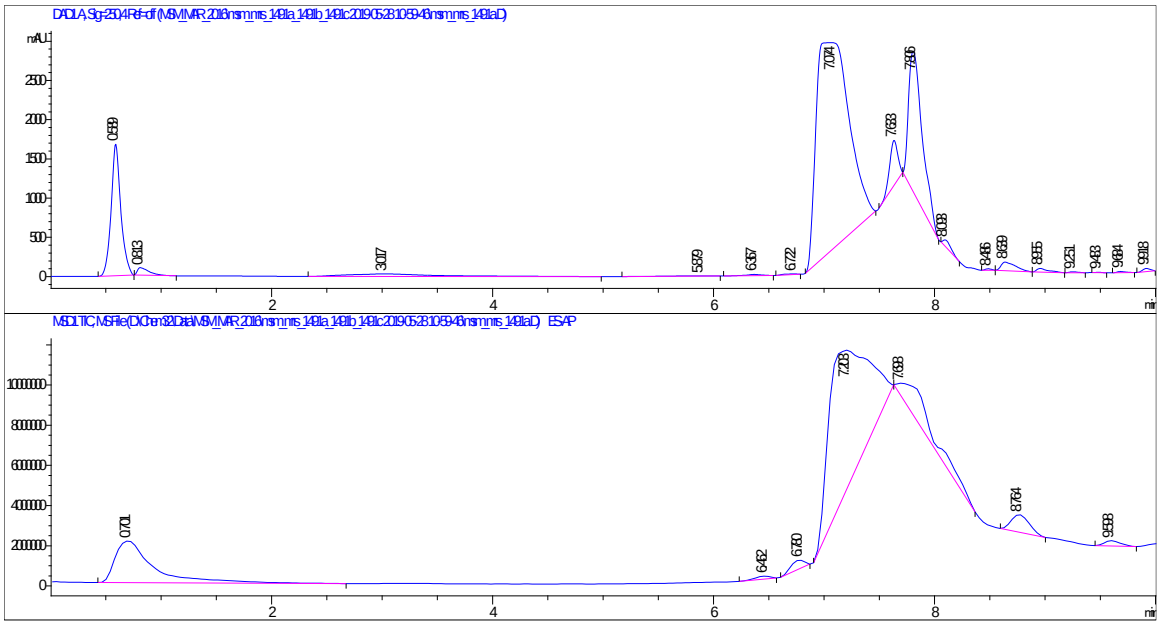


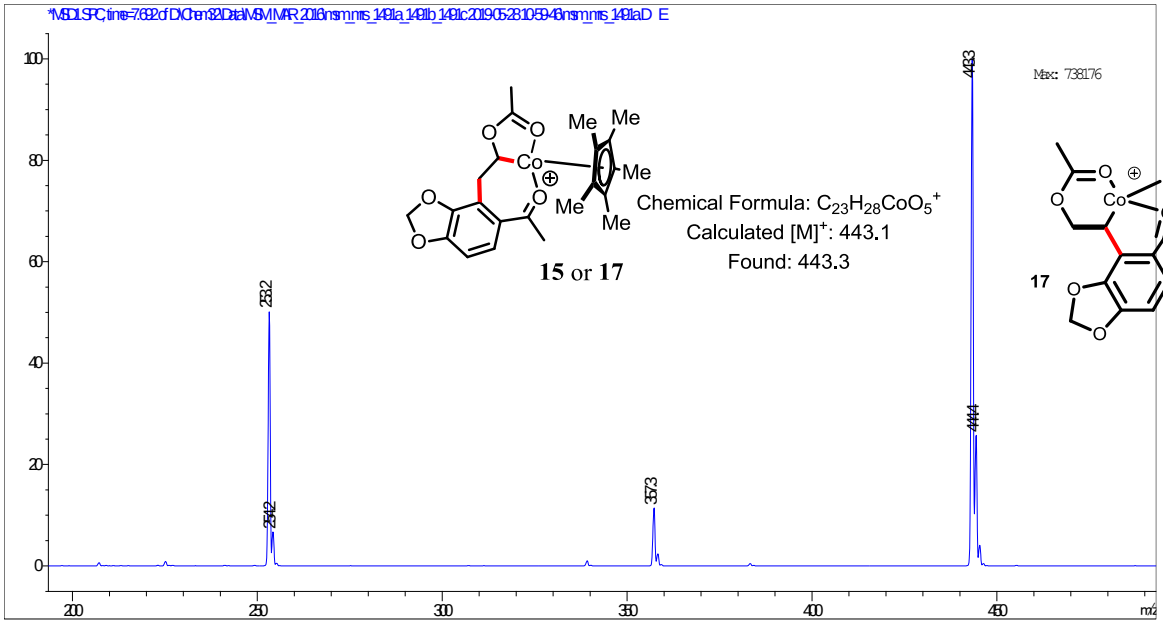




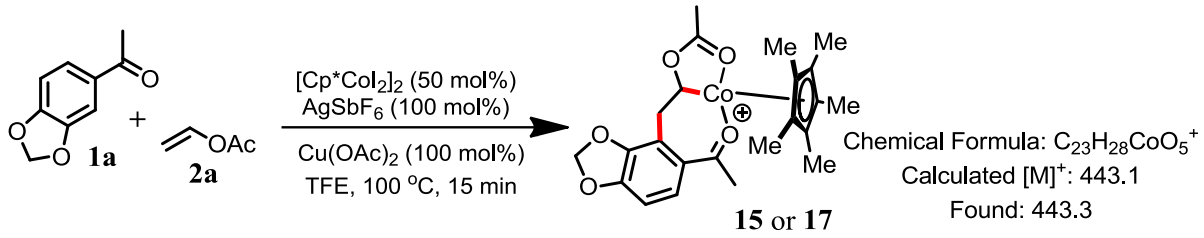
Experiment 3: Cyclometallation of **1a** in the presence of **2a** using 10 mol% $[Cp^*CoI_2]_2$.

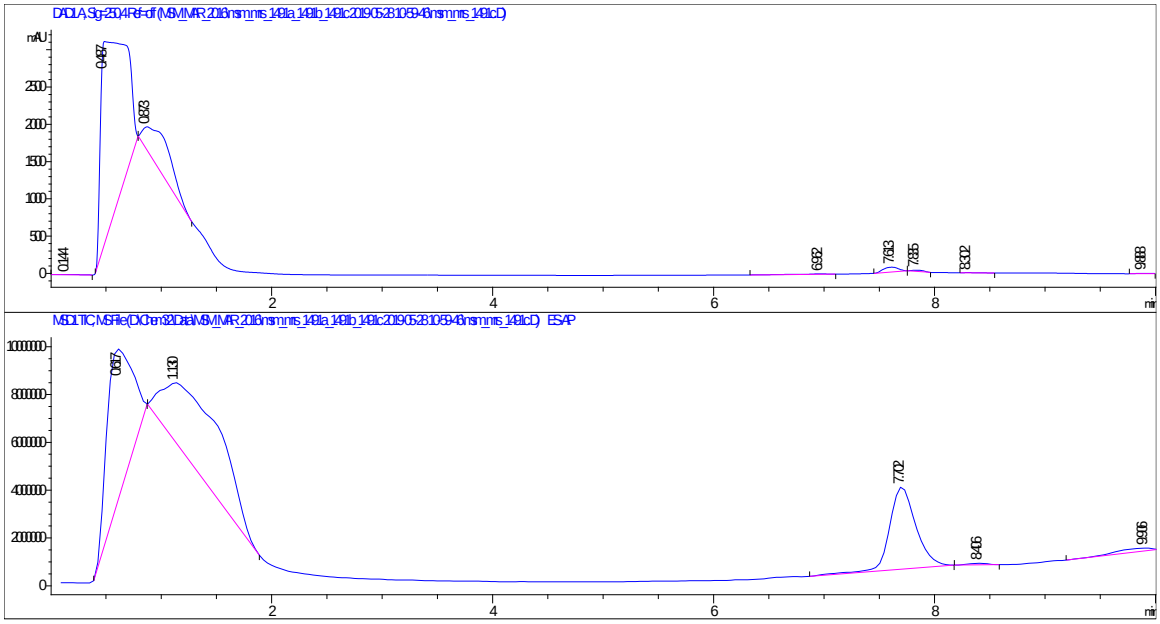


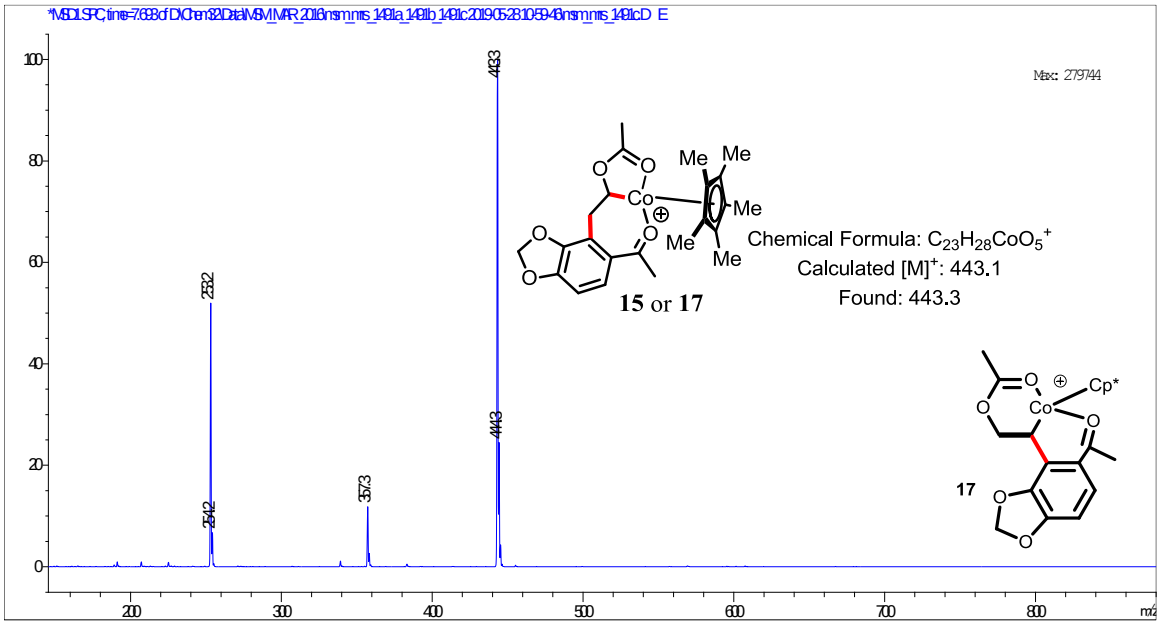




Experiment 4: Cyclometallation of **1a** in the presence of **2a** using 50 mol% $[Cp^*CoI_2]_2$.







References:

(1) (a) Sum, T. H.; Sum, T. J.; Stokes, J. E.; Galloway, W. R.J.D.; Spring, D. R. *Tetrahedron* **2015**, *71*, 4557. (b) Bzeih, T.; Naret, T.; Hachem, A.; Jaber, N.; Khalaf, A.; Bignon, J.; Brion, J.-D.; Alami, M.; Hamze, A. *Chem. Commun.* **2016**, *52*, 13027. (c) Ma, Y.; Lv, J.; Liu, C.; Yao, X.; Yan, G.; Yu, W.; Ye, J. *Angew. Chem., Int. Ed.* **2019**, *58*, 6756. (d) Xu, Z.; Ba , M.; Zhou, H.; Cao, Y.; Tang, C.; Yang, Y.; He, R.; Liang, Y.; Zhang, X.; Li, Z.; Zhu, L.; Guo, Y.; Guo, C. *Eur. J. Med. Chem.* **2014**, *85*, 27. (e) Huang, H.-L.; Yan, H.; Gao, G.-L.; Yang, C.; Xia, W. *Asian J. Org. Chem.* **2015**, *4*, 674. (f) Rodríguez-Ramos, F.; Navarrete, A.; González-Andrade, M.; Alarcón, C.; Aguilera-Cruz, A.; Reyes-Ramírez, A. *Bioorg. Chem.* **2013**, *50*, 17. (g) Guyaux, M.; Dinesh, C. U.; Mioskowski, C.; Quere, L.; Starck, J.-P.; Talaga, P.; Wagner, A.; Zanda, M. *PCT Int. Appl.* **2003**, 2003033495. (h) Fujihara, T.; Kukita, S.; Kirihara, M.; Nogi, K.; Tsuji, Y. *Asian J. Org. Chem.* **2018**, *7*, 2456.

(2) (a) Singh, J.; Saini, V.; Kumar, A.; Bansal, R. *Bioorg. Chem.* **2017**, *71*, 201. (b) Luan, S.; Zhong, H.; Zhao, X.; Yang, J.; Jing, Y.; Liu, D.; Zhao, L. *Eur. J. Med Chem.* **2017**, *141*, 584. (c) Ovais, S.; Pushpalatha, H.; Reddy, G. B.; Rathore, P.; Bashir, R.; Yaseen, S.; Dheyaa, A.; Yaseen, R.; Tanwar, O.; Akthar, M.; Samim, M.; Javed, K. *Eur. J. Med. Chem*. **2014**, *80*, 209. (d) Wang, S.-K.; You, X.; Zhao, D.-Y.; Mou, N.-J.; Luo, Q.-L. *Chem. -Eur. J.* **2017**, *23*, 11757. (e) Gezegen, H.; Ceylan, M.; Karaman, İ.; Şahin, E. *Synth. Commun.* **2014**, *44*, 1084. (f) Sharma, V.; Sharma, K. V. *E-J. Chem.* **2010**, *7*, 203. (g) Bakthadoss, M.; Kumar, P. V. *Adv. Synth. Catal.* **2018**, *360*, 2650.

(3) (a) Sk, M. R.; Bera, S. S.; Maji, M. S. *Adv. Synth. Catal.* **2019**, *361*, 585. (b) Fustero, S.; Elsa Rodríguez, E.; Herrera, L.; Asensio, A.; Maestro, M. A.; Barrio, P. *Org. Lett.* **2011**, *13*, 6564. (c) Padala, K.; Jeganmohan, M. *Org. Lett*. **2011**, *13*, 6144. (d) Madhurima, H.; Krishna, J.; Satyanarayana, G. *Synthesis* **2015**, *47*, 1245. (e) Wang, P.; Verma, P.; Xia, G.; Shi, J.; Qiao, J. X.; Tao, S.; Cheng, P. T. W.; Poss, M. A.; Farmer, M. E.; Yeung, K.-S.; Yu, J.-Q. *Nature* **2017**, *551*, 489.

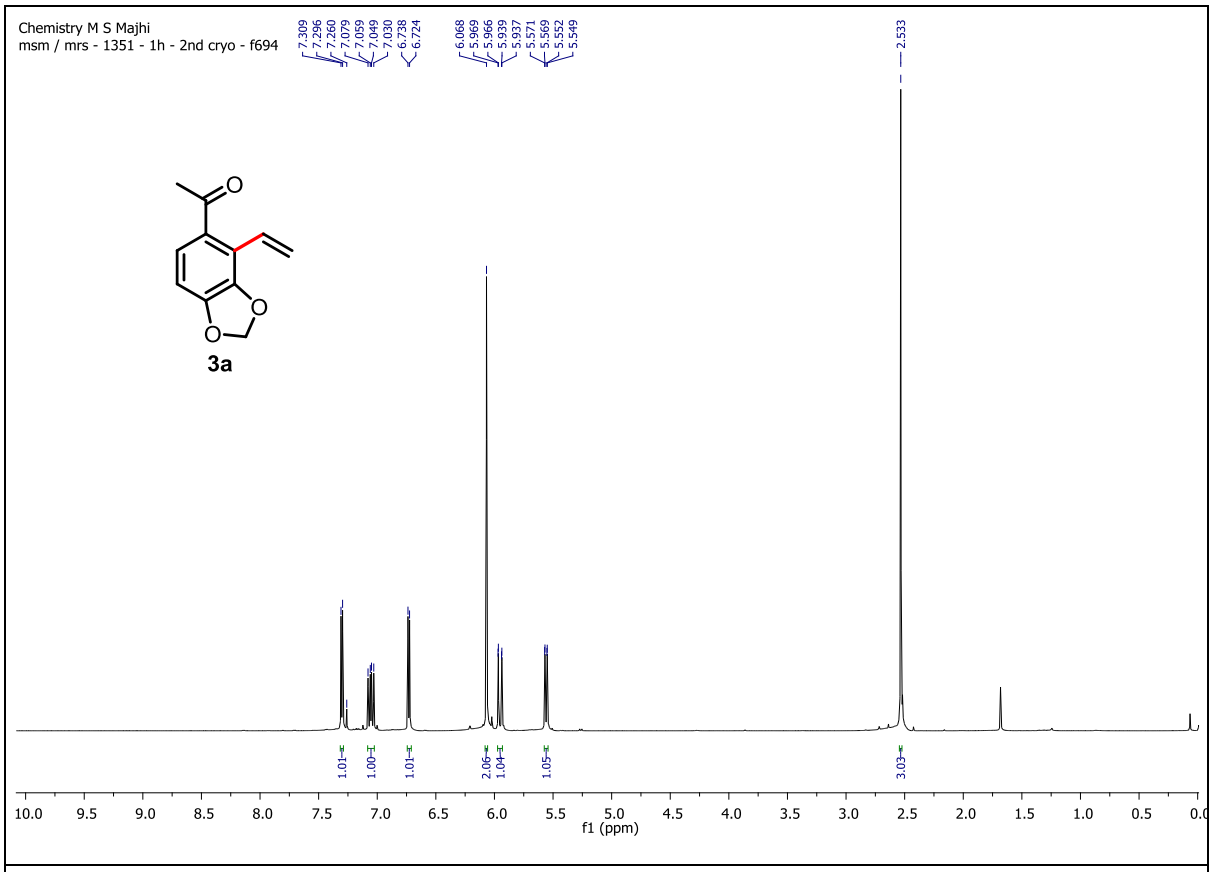
(4) Ruan, J.; Iggo, J. A.; Xiao, J. *Org. Lett.* **2011**, *13*, 268.

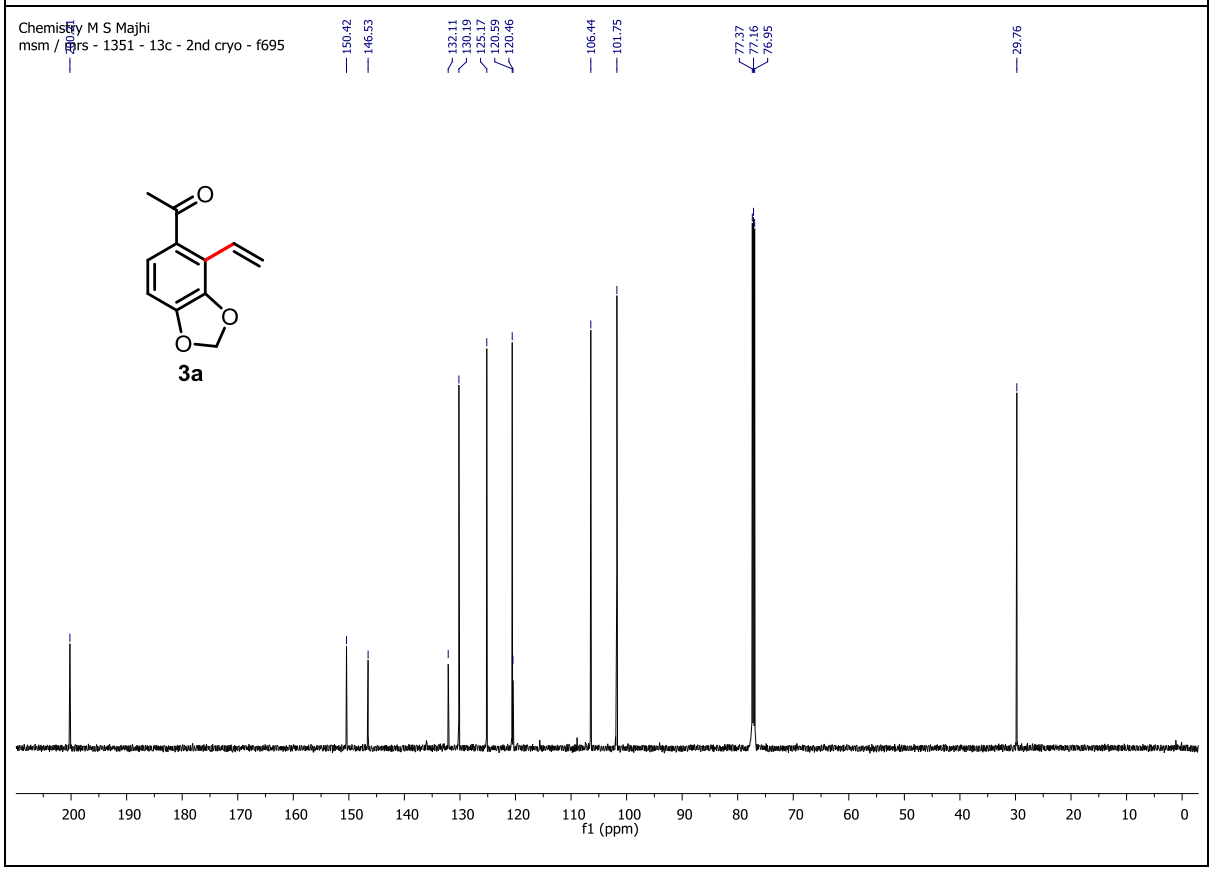
(5) Sarkar, D.; Venkateswaran, R. V. *Tetrahedron Lett.* **2011**, *52*, 3232.

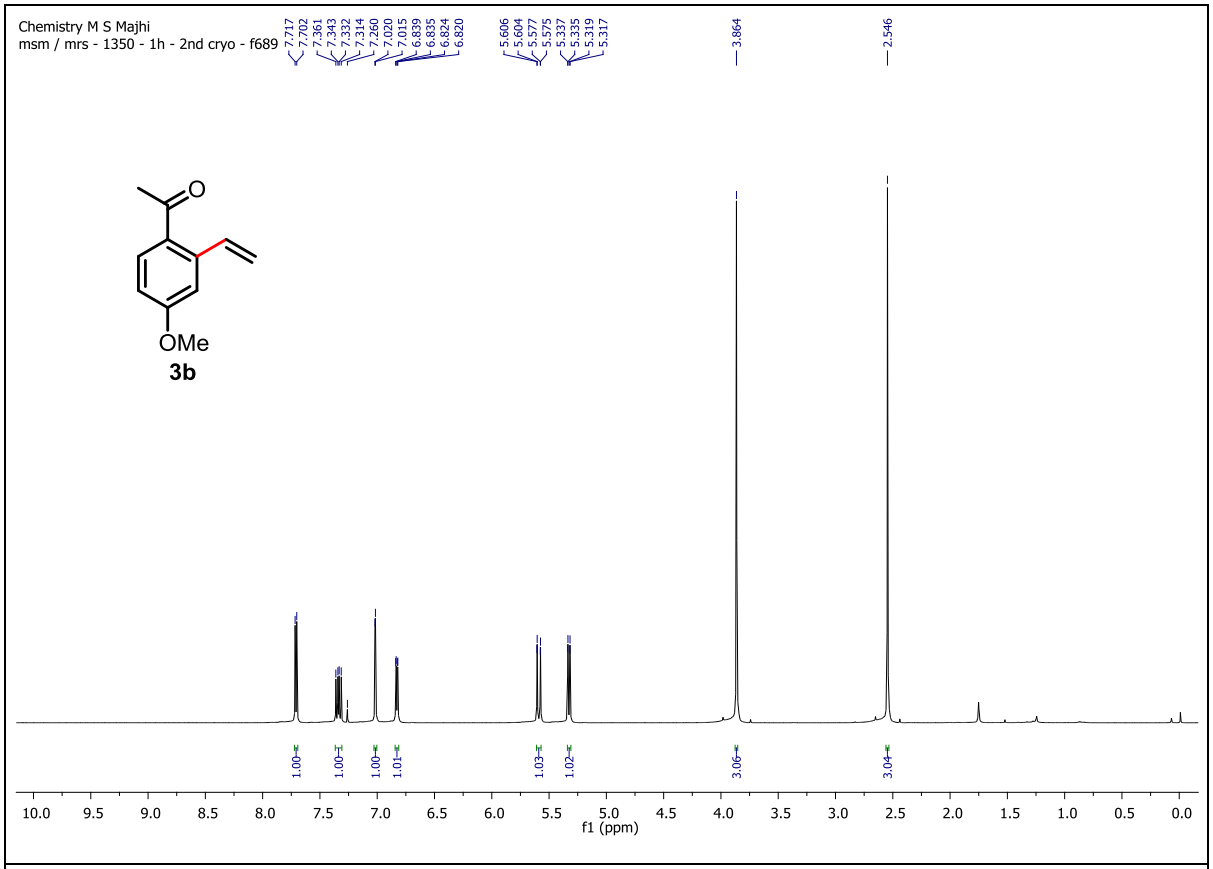
(6) Wright, J. A.; Gaunt, M. J.; Spencer, J. B. *Chem. - Eur. J.* **2006**, *12*, 949.

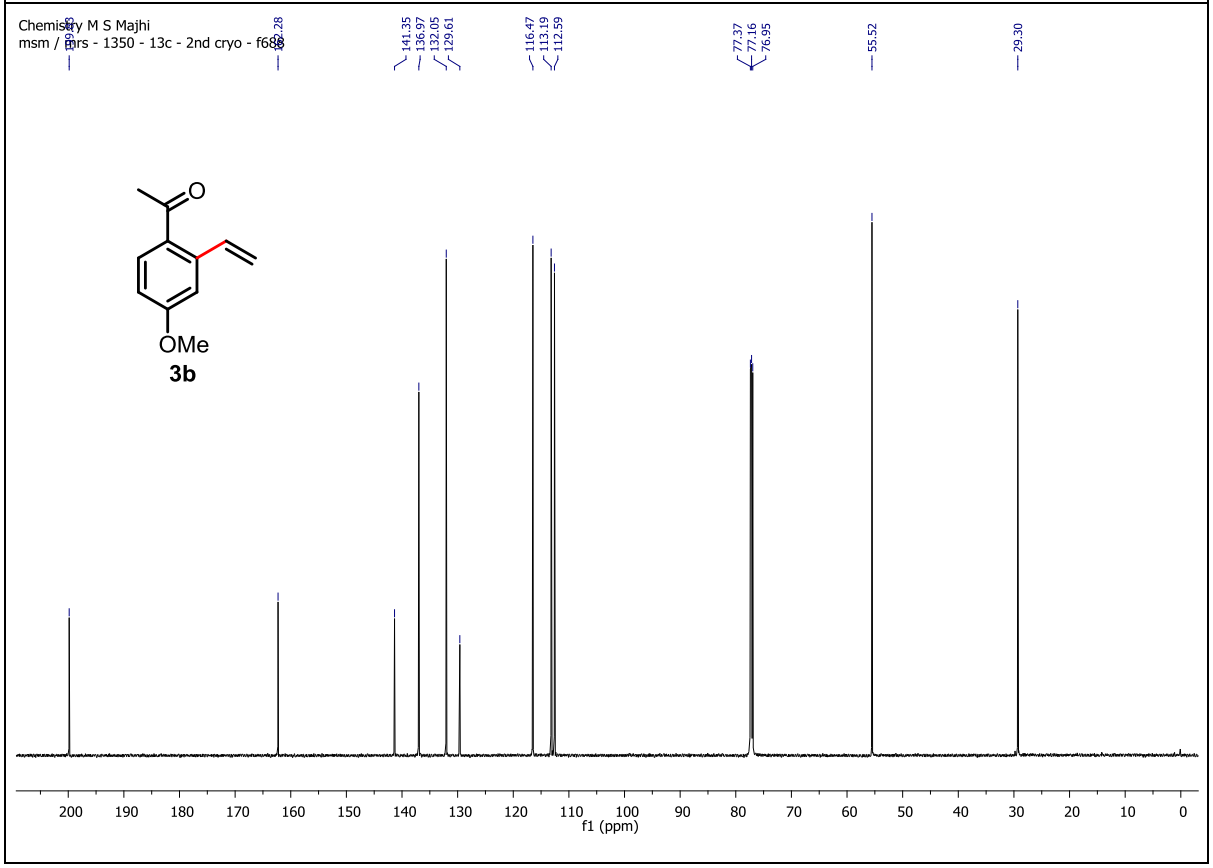
7. (a) Otley, K. D.; Ellman, J. A. *Org. Lett.* **2015**, *17*, 1332. (b) Lin, W.; Li, W.; Lu, D.; Su, F.; Wen, T.-B.; Zhang, H.-J. *ACS Catal.* **2018**, *8*, 8070.

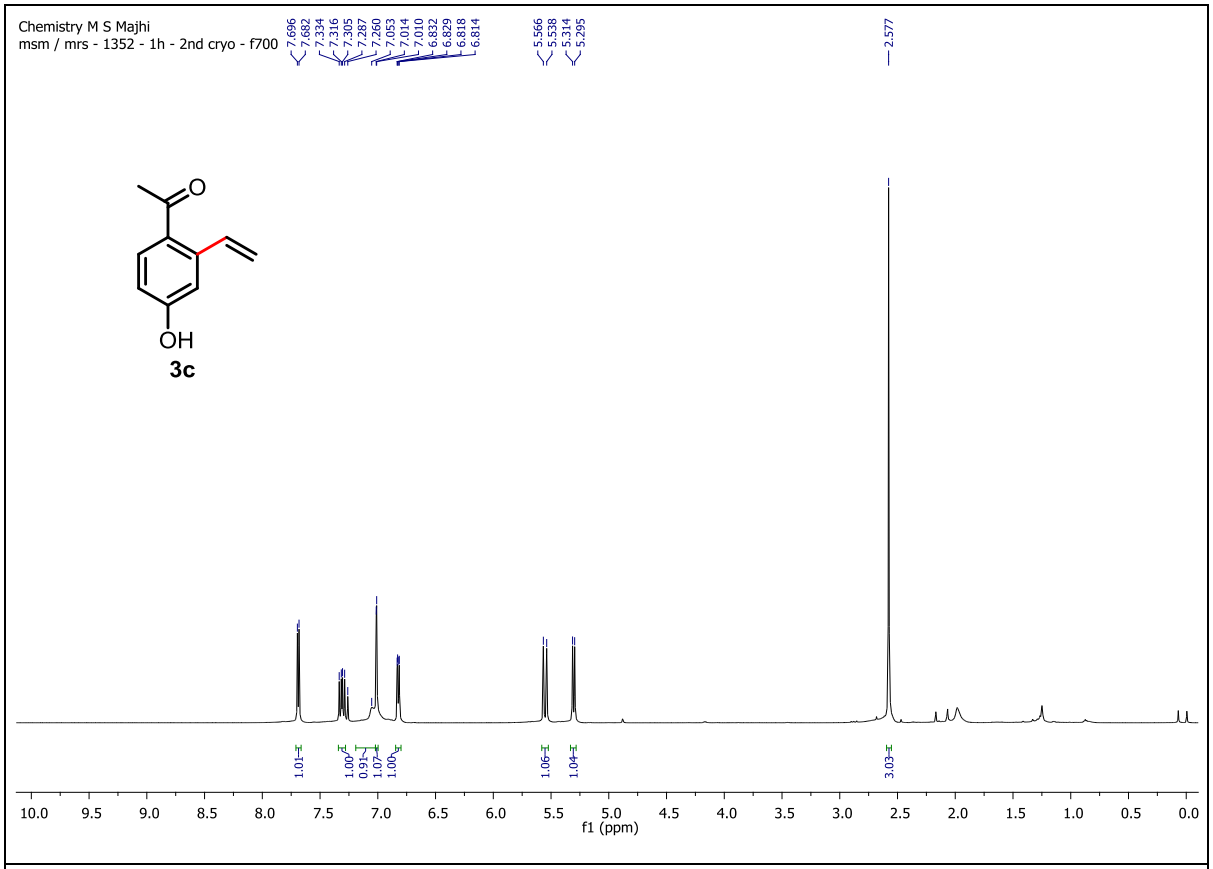
^{1}H NMR and ^{13}C NMR Spectra:

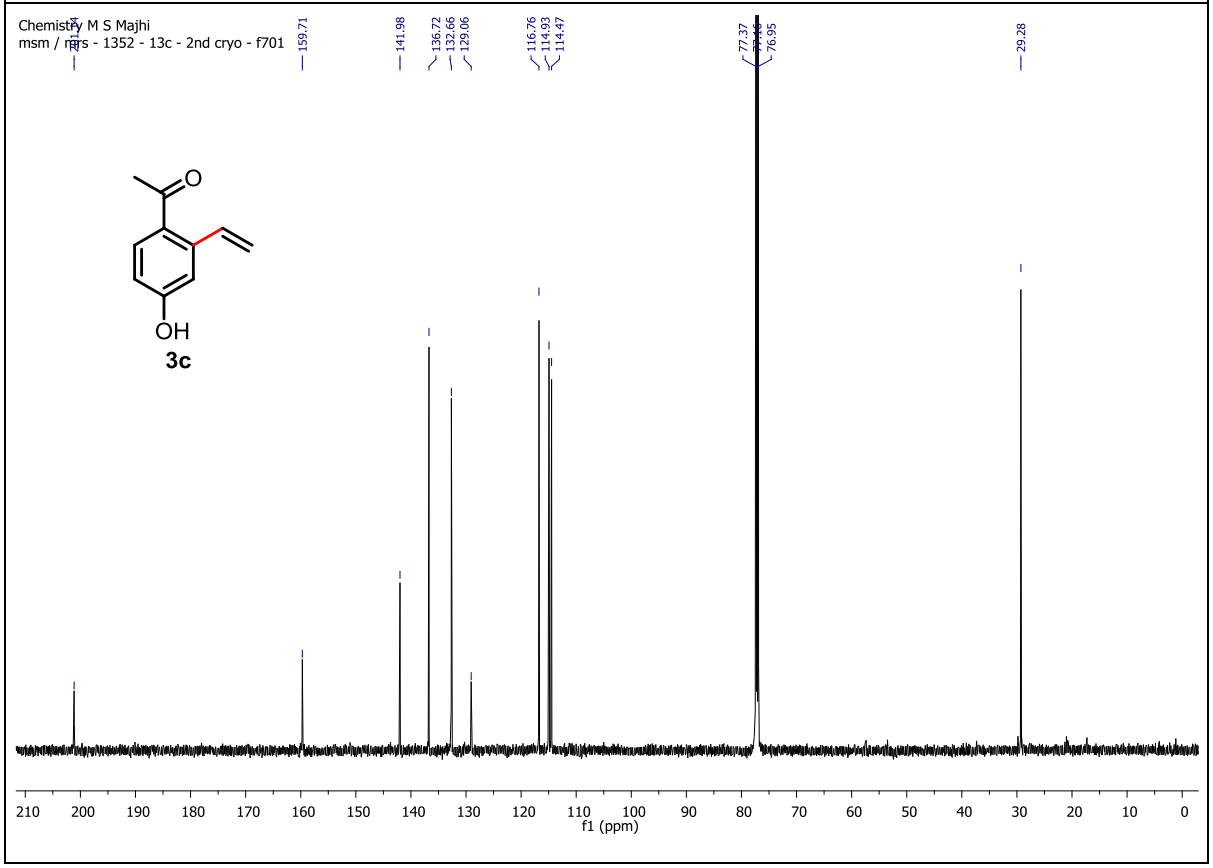


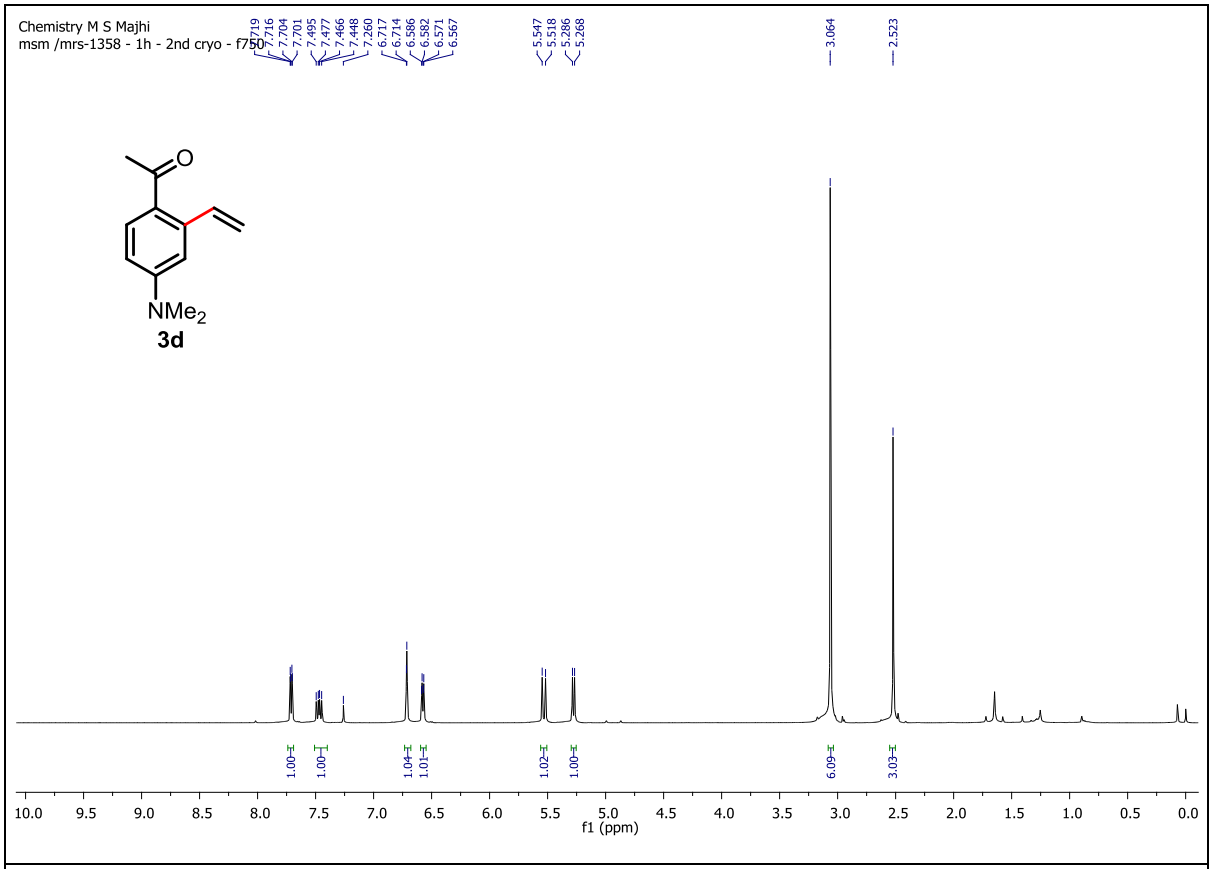


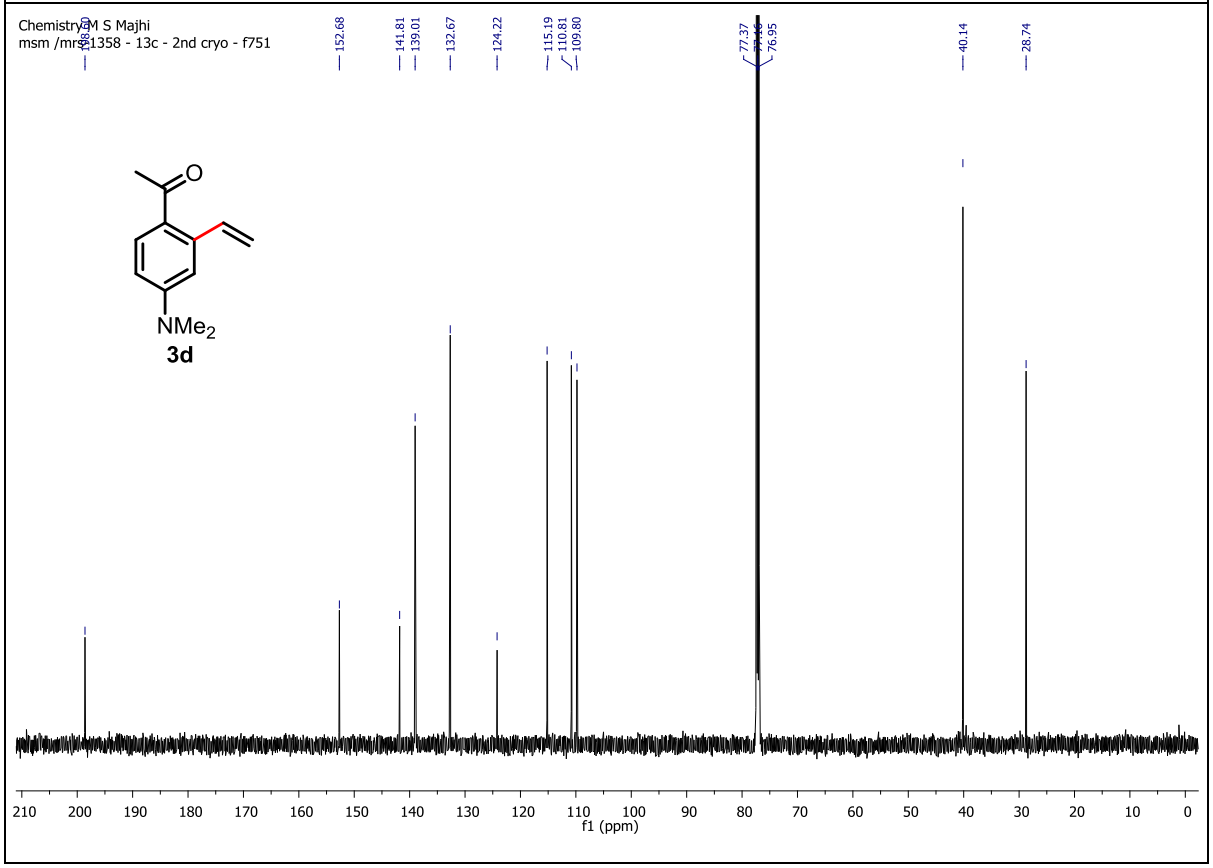

Chemistry M S Majhi
msm / mrs - 1350 - 1h - 2nd cryo - f689
7.717
7.702
7.361
7.343
7.332
7.314
7.260
7.020
7.015
6.839
6.835
6.824
6.820
5.606
5.604
5.577
5.575
5.337
5.335
5.319
5.317
3.864
2.546
O
OMe
3b
1.00
1.00
1.00
1.01
1.03
1.02
3.06
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

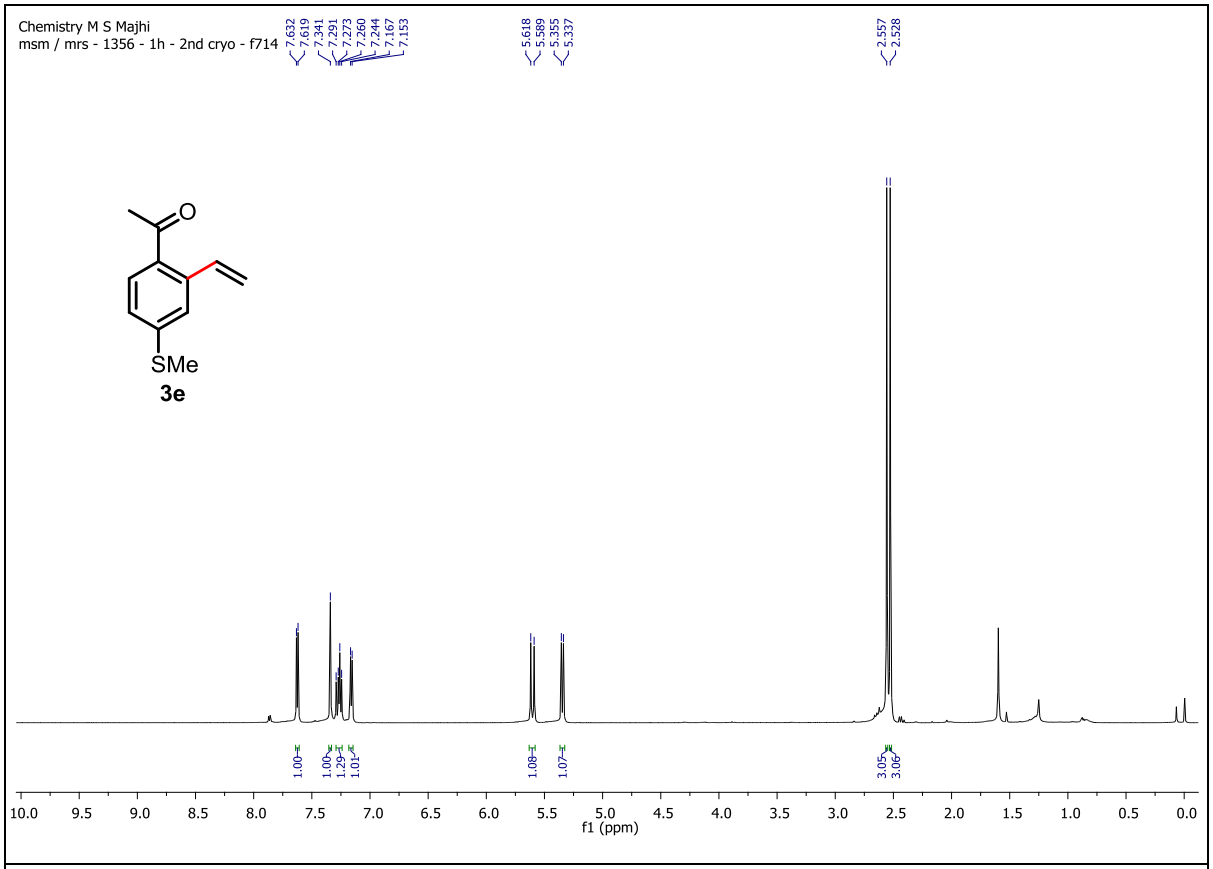

Chemistry M S Majhi
msm / mrs - 1350 - 13c - 2nd cryo - f689
199.92
157.28
141.35
136.97
132.05
129.61
116.47
113.19
112.59
77.37
77.16
76.95
55.52
29.30
O
OMe
3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

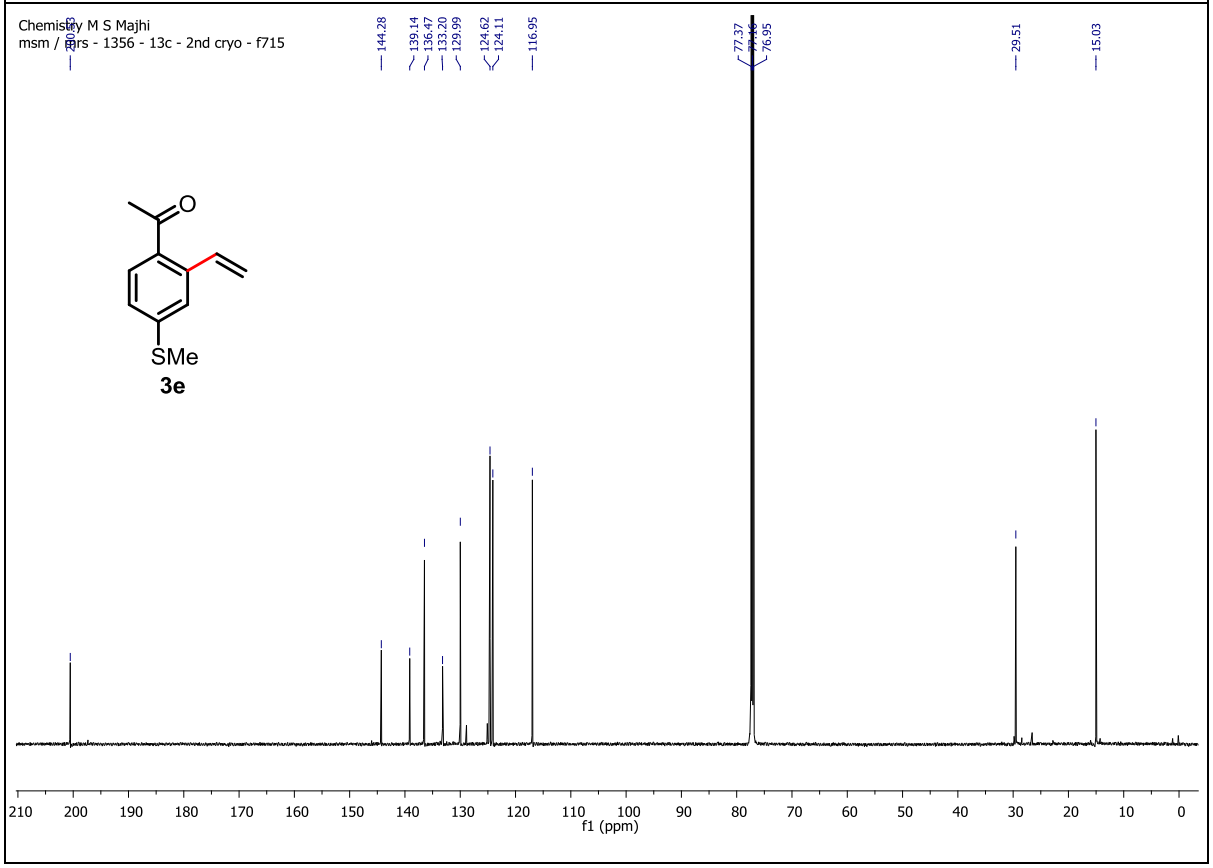

Chemistry M S Majhi
msm / mrs - 1352 - 1h - 2nd cryo - f700
7.696
7.682
7.334
7.316
7.305
7.287
7.260
7.053
7.014
7.010
6.832
6.829
6.818
6.814
5.566
5.538
5.314
5.295
2.577
O
OH
3c
1.01
1.00
0.91
1.07
1.00
1.06
1.04
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

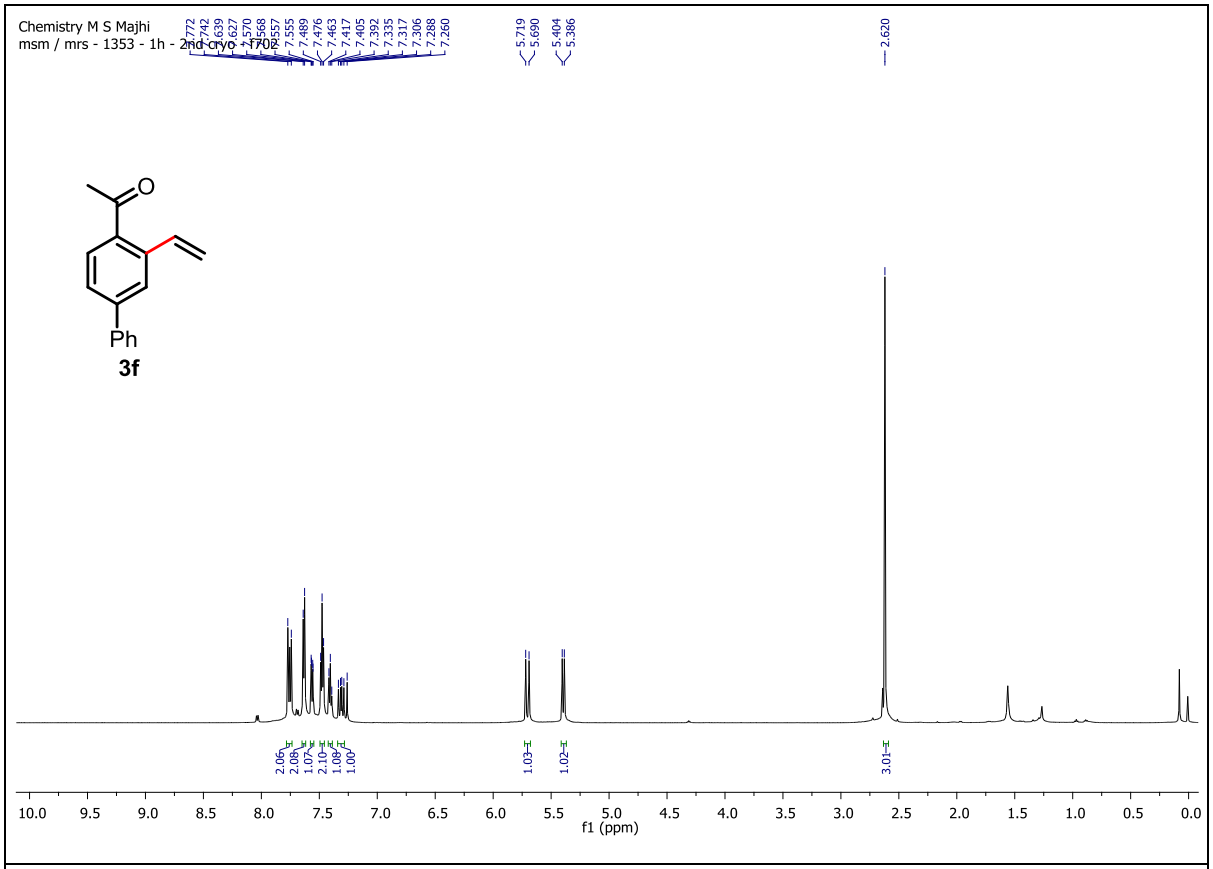

Chemistry M S Majhi
msm / mrs - 1352 - 13c - 2nd cryo - f701
159.71
141.98
136.72
132.66
129.06
116.76
114.93
114.47
77.37
77.16
76.95
29.28
O
OH
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

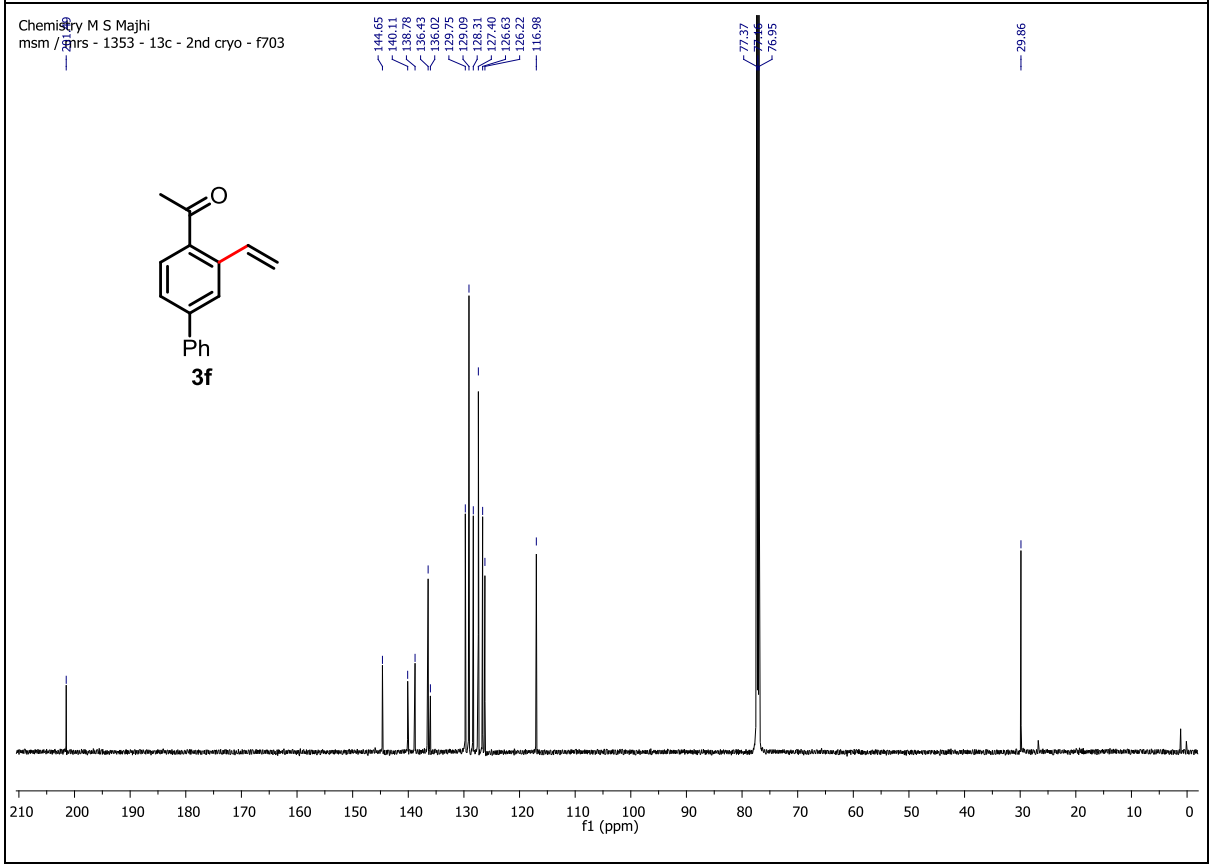

Chemistry M S Majhi
msm /mrs-1358 - 1h - 2nd cryo - f750
7.719
7.716
7.704
7.701
7.495
7.477
7.466
7.448
7.260
6.717
6.714
6.586
6.582
6.571
6.567
5.547
5.518
5.286
5.268
3.064
2.523
O
NMe2
3d
1.00
1.00
1.04
1.01
1.02
1.00
6.09
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

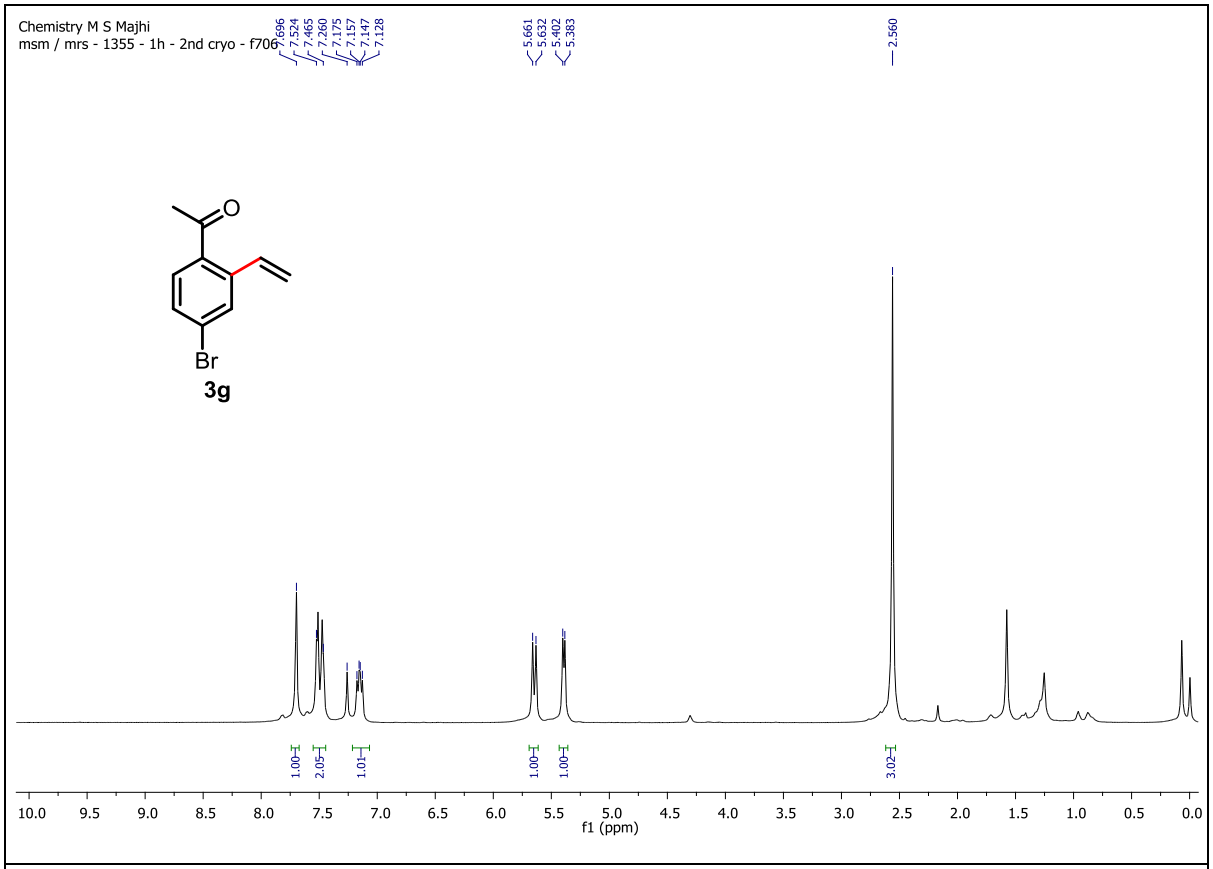

Chemistry M S Majhi
msm /mrs-1358 - 13c - 2nd cryo - f751
198.50
152.68
141.81
139.01
132.67
124.22
115.19
110.81
109.80
77.37
77.16
76.95
40.14
28.74
O
NMe2
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

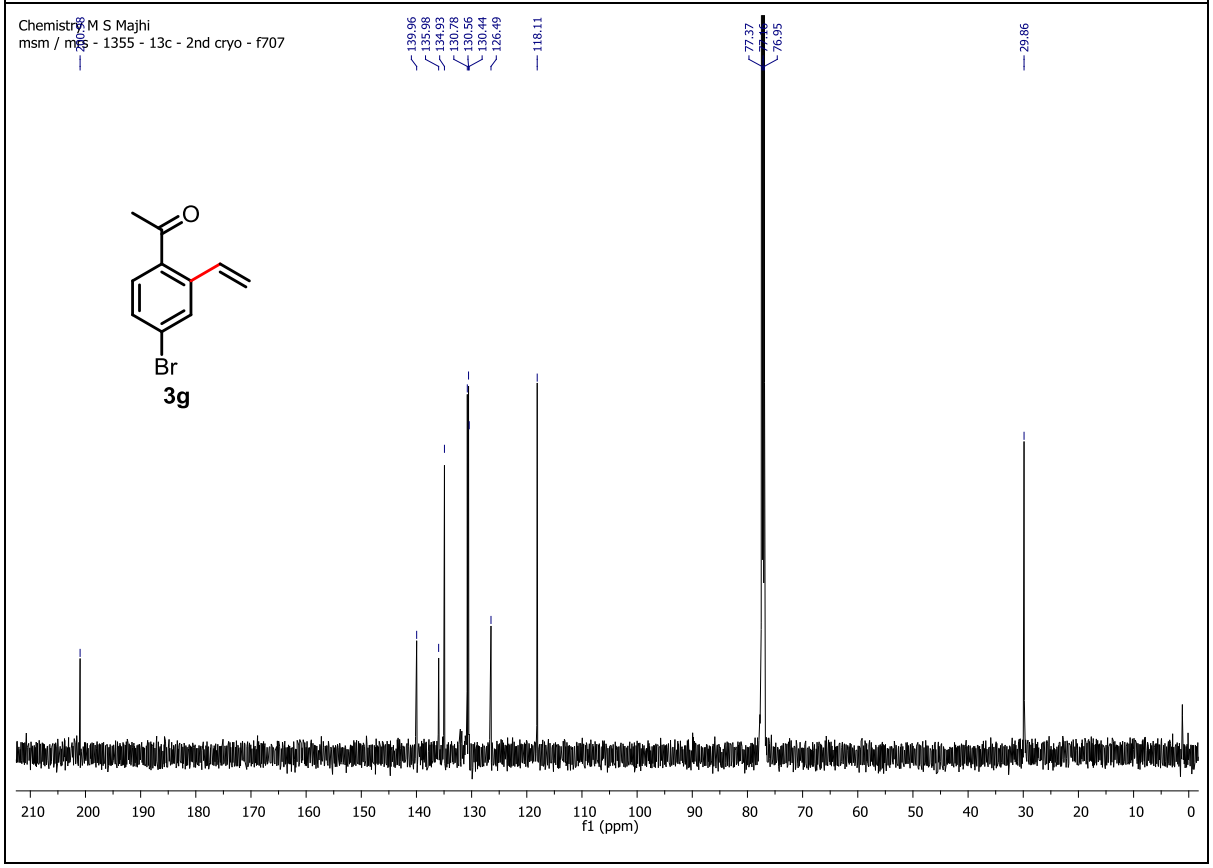

Chemistry M S Majhi
msm / mrs - 1356 - 1h - 2nd cryo - f714
7.632
7.619
7.341
7.291
7.273
7.260
7.244
7.167
7.153
5.618
5.589
5.355
5.337
2.557
2.528
O
SMe
3e
1.00
1.00
1.29
1.01
1.08
1.07
3.05
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

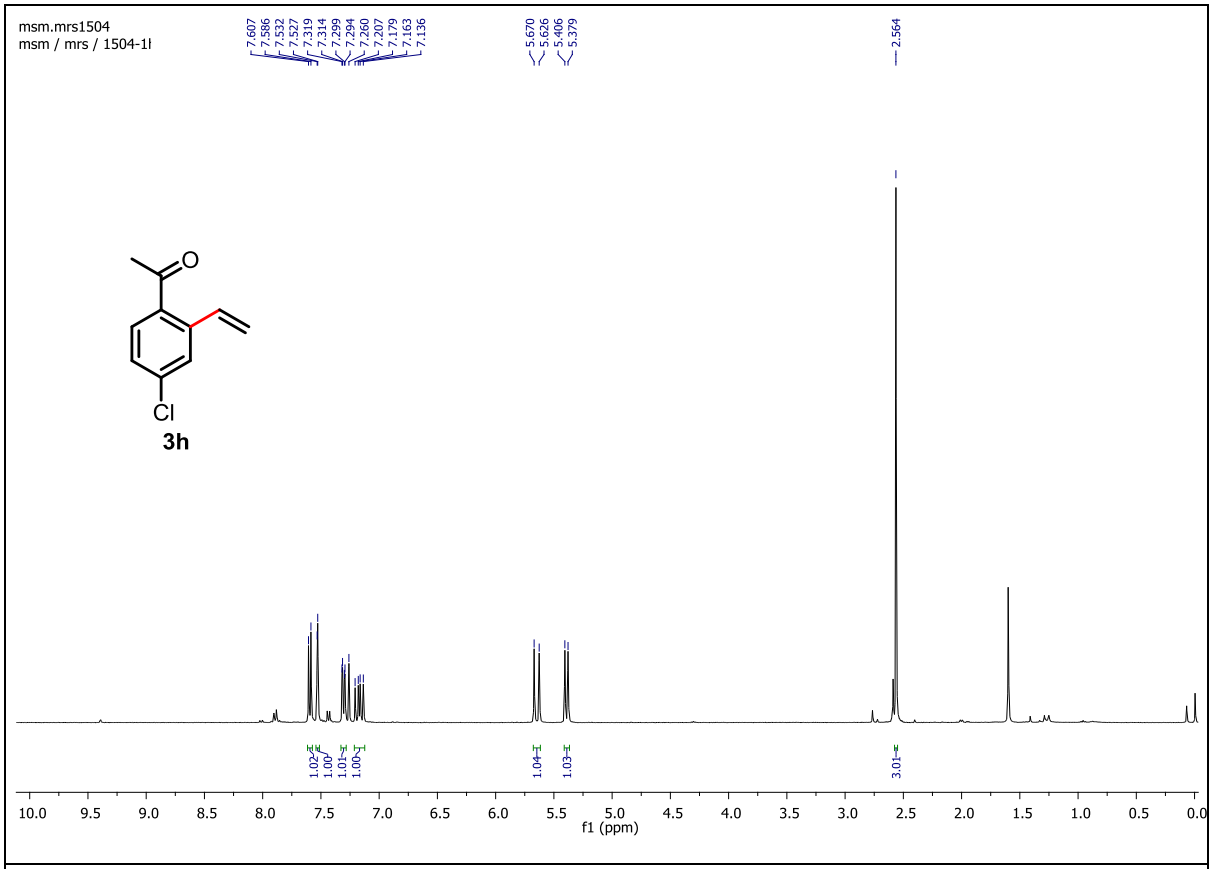

Chemistry M S Majhi
msm / mrs - 1356 - 13c - 2nd cryo - f715
144.28
139.14
136.47
133.20
129.99
124.62
124.11
116.95
77.37
76.95
29.51
15.03
O
SMe
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

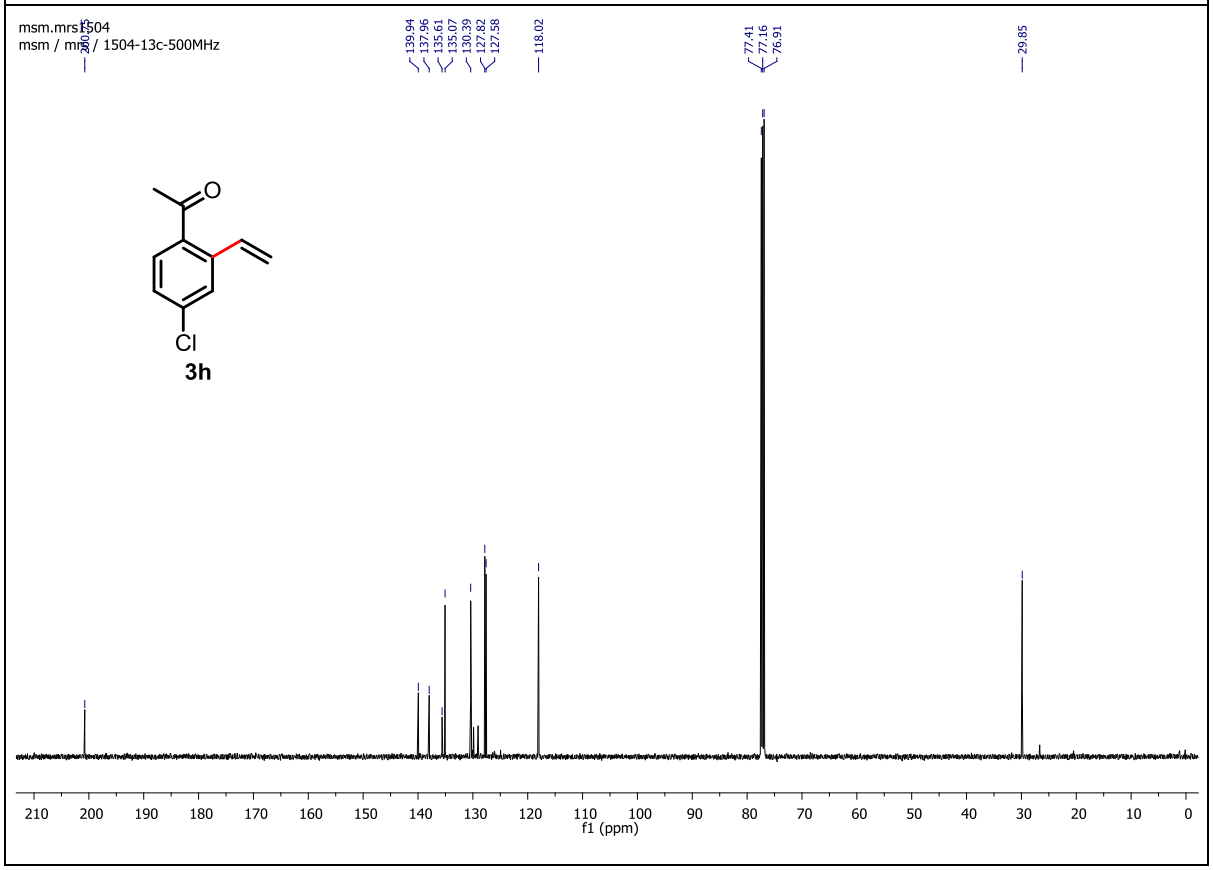

Chemistry M S Majhi
msm / mrs - 1353 - 1h - 2nd cryo - f702
7.772
7.742
7.639
7.627
7.570
7.568
7.557
7.555
7.489
7.476
7.463
7.417
7.405
7.392
7.335
7.317
7.306
7.288
7.260
5.719
5.690
5.404
5.386
2.620
O
Ph
3f
2.06
2.08
1.07
2.10
1.08
1.00
1.03
1.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

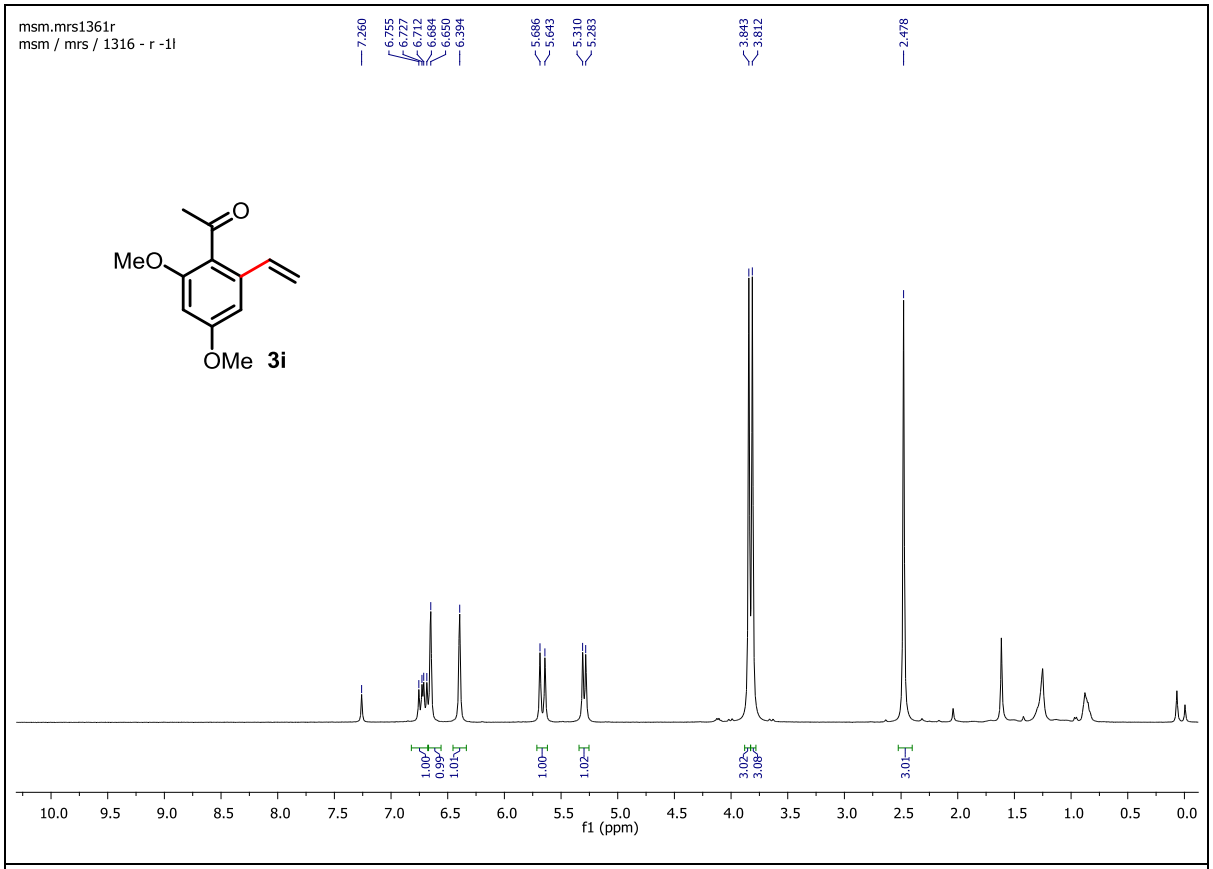

Chemistry M S Majhi
msm / mrs - 1353 - 13c - 2nd cryo - f703
144.65
140.11
138.78
136.43
136.02
129.75
129.09
128.31
127.40
126.63
126.22
116.98
77.37
77.16
76.95
29.86
O
Ph
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

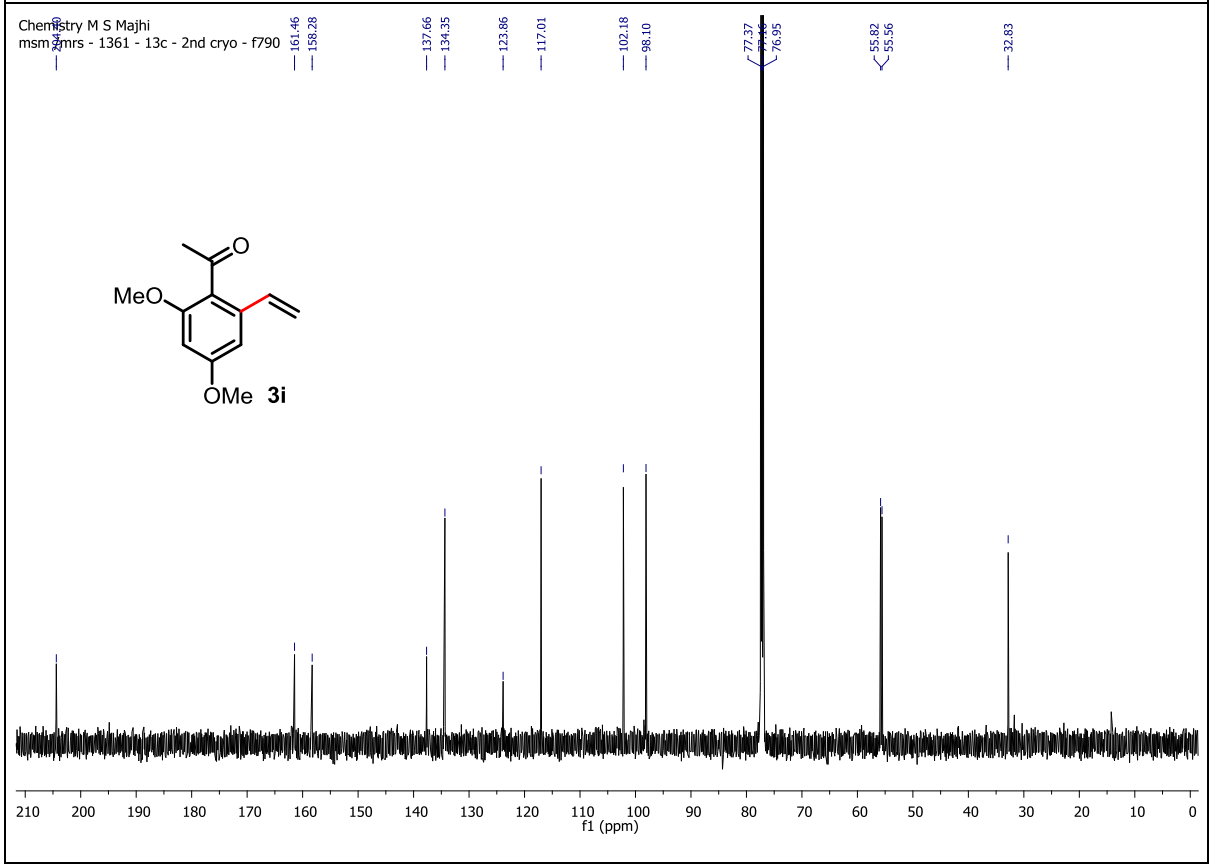

Chemistry M S Majhi
msm / mrs - 1355 - 1h - 2nd cryo - f706
7.696
7.524
7.465
7.260
7.175
7.157
7.147
7.128
5.661
5.632
5.402
5.383
2.560
O
Br
3g
1.00
2.05
1.01
1.00
1.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

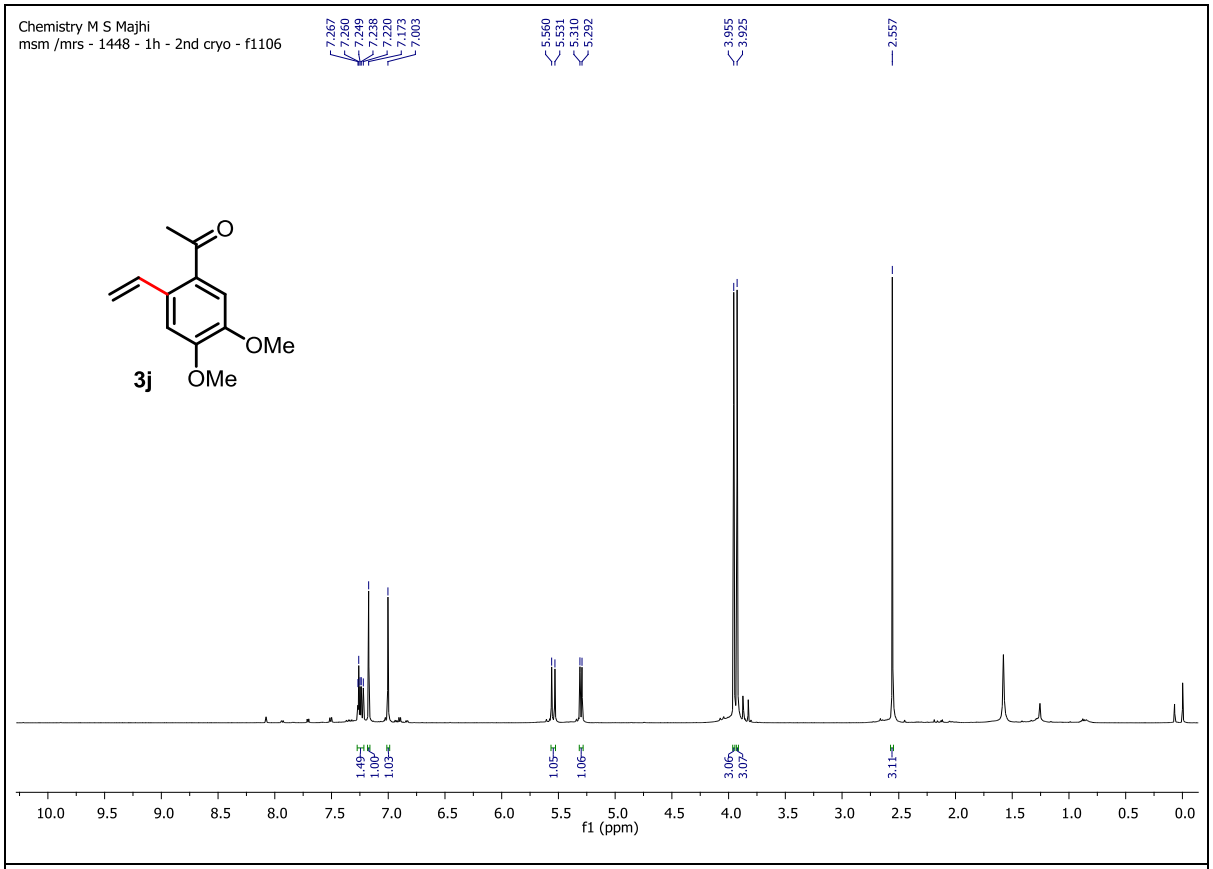

Chemistry M S Majhi
msm / mrs - 1355 - 13c - 2nd cryo - f707
139.96
135.98
134.93
130.78
130.56
130.44
126.49
118.11
77.37
77.06
76.95
29.86
O
Br
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

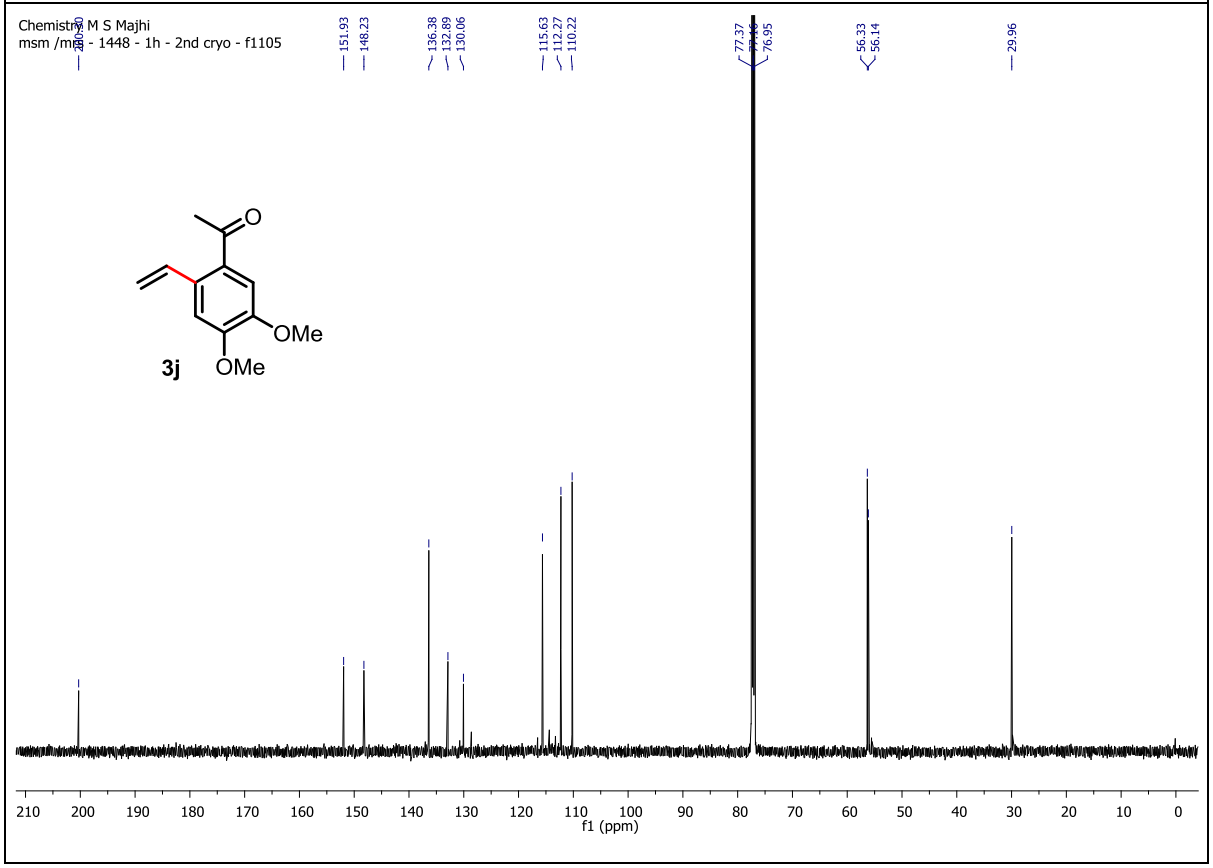

msm.mrs1504
msm / mrs / 1504-1l
7.607
7.586
7.532
7.527
7.319
7.314
7.299
7.294
7.260
7.207
7.179
7.163
7.136
5.670
5.626
5.406
5.379
2.564
O
Cl
3h
1.02
1.00
1.01
1.00
1.04
1.03
3.01
f1 (ppm)

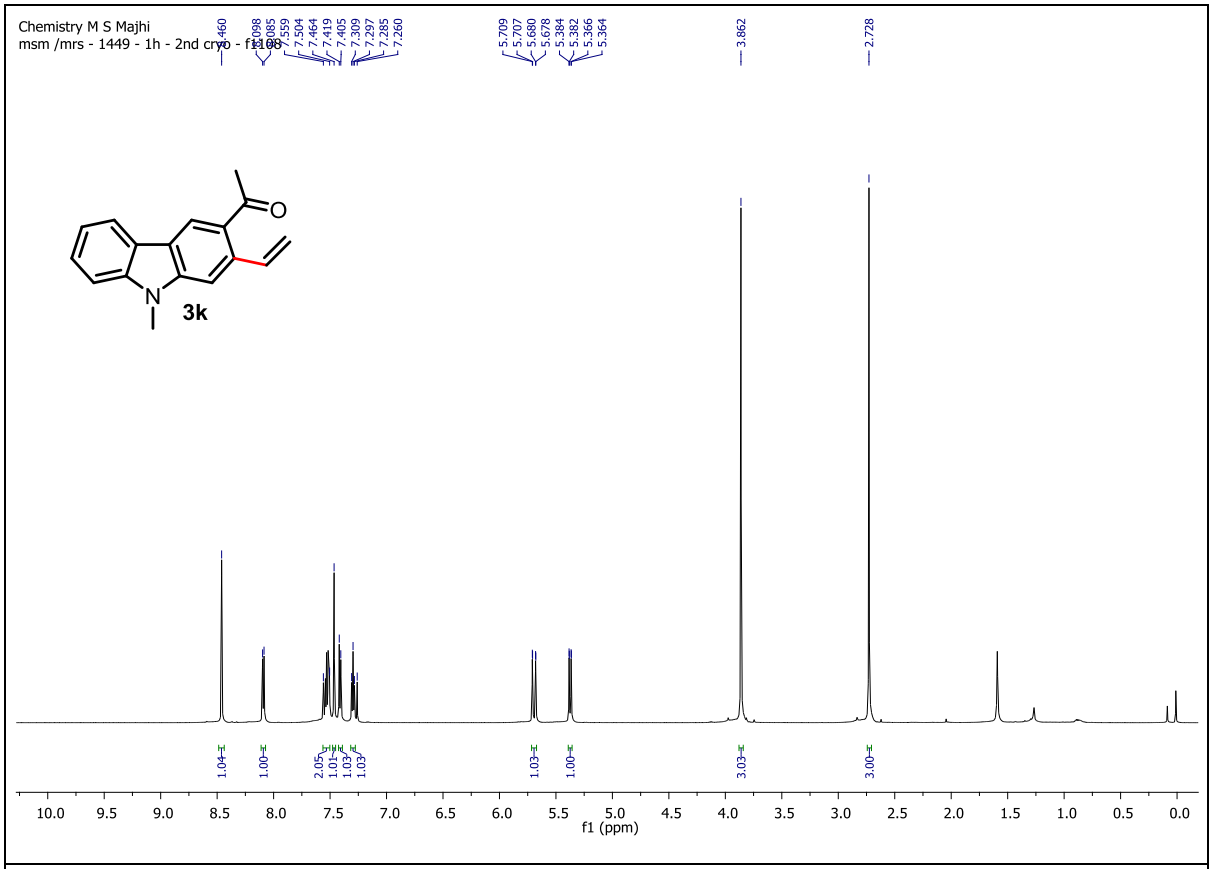

msm.mrs1504
msm / mrs / 1504-13c-500MHz
200.75
139.94
137.96
135.61
135.07
130.39
127.82
127.58
118.02
77.41
77.16
76.91
29.85
O
Cl
3h
f1 (ppm)

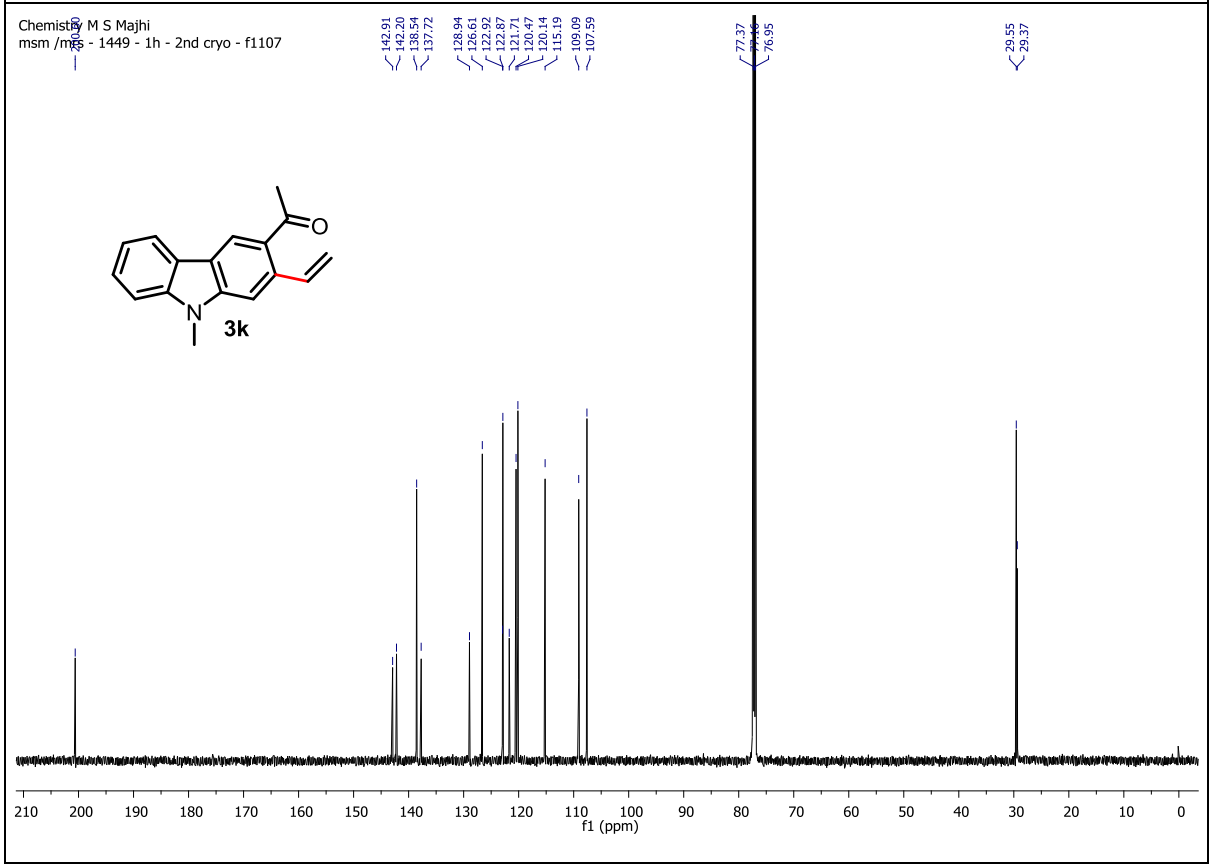

msm.mrs1361r
msm / mrs / 1316 - r -1l
7.260
6.755
6.727
6.712
6.684
6.650
6.394
5.686
5.643
5.310
5.283
3.843
3.812
2.478
MeO
OMe
3i
1.00
0.99
1.01
1.00
1.02
3.02
3.08
3.01
f1 (ppm)

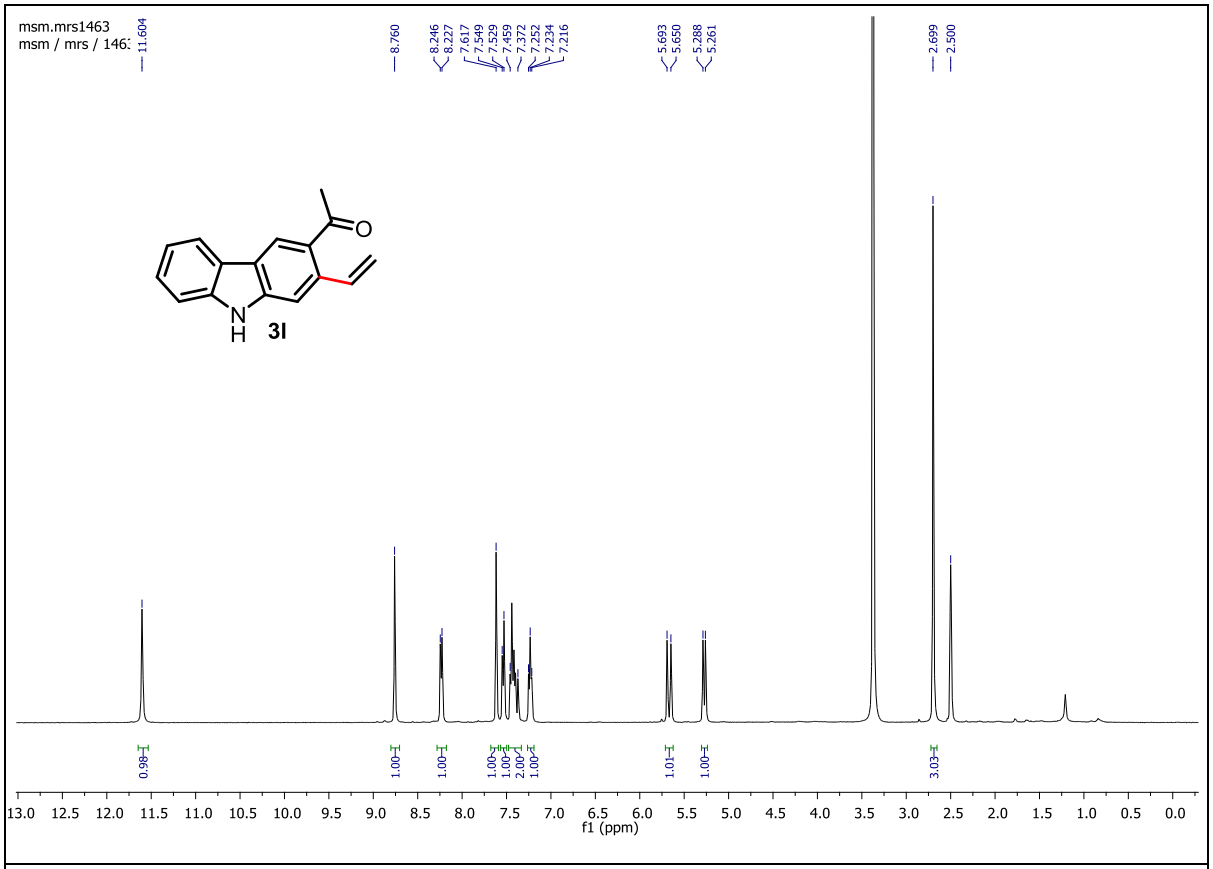

Chemistry M S Majhi
msm.mrs - 1361 - 13c - 2nd cryo - f790
161.46
158.28
137.66
134.35
123.86
117.01
102.18
98.10
77.37
76.95
55.82
55.56
32.83
MeO
OMe
3i
f1 (ppm)

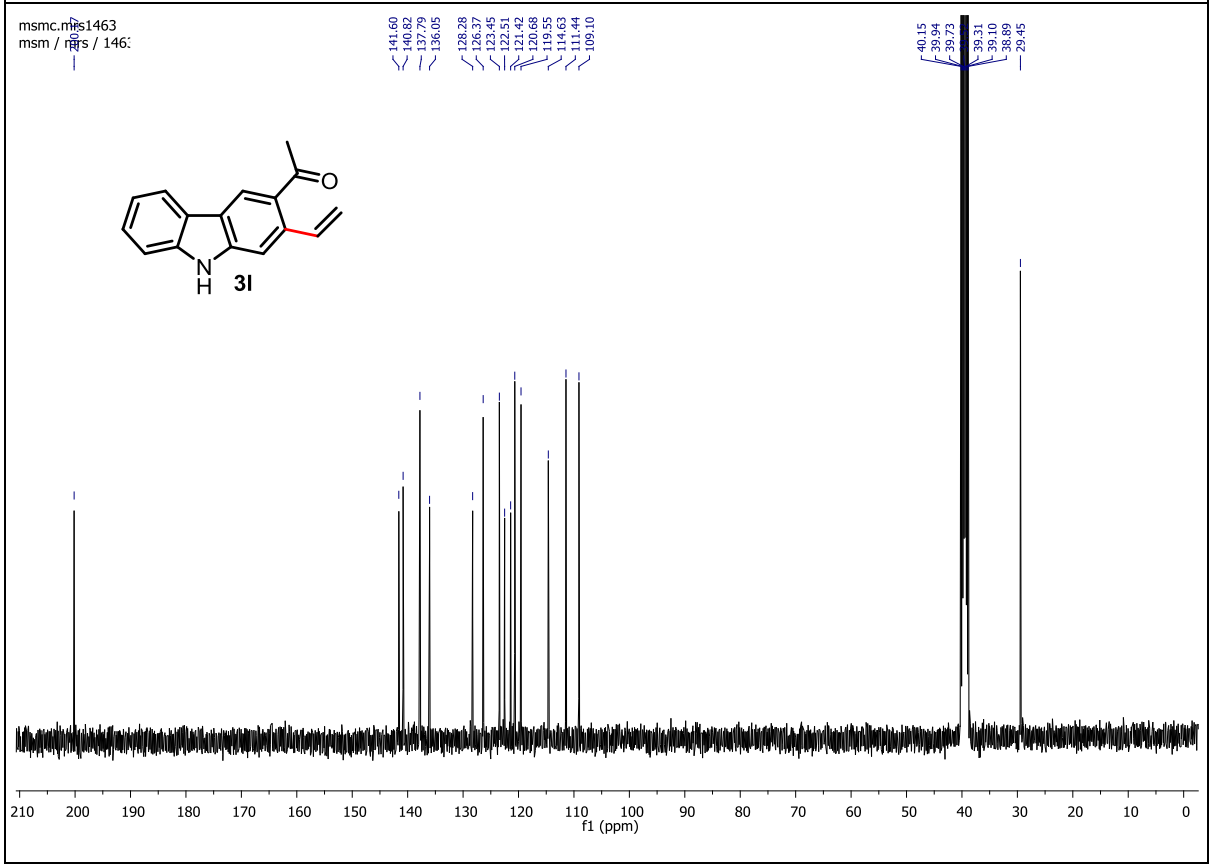

Chemistry M S Majhi
msm /mrs - 1448 - 1h - 2nd cryo - f1106
7.267
7.260
7.249
7.238
7.220
7.173
7.003
5.560
5.531
5.310
5.292
3.955
3.925
2.557
O
OMe
OMe
3j
1.49
1.00
1.03
1.05
1.06
3.06
3.07
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

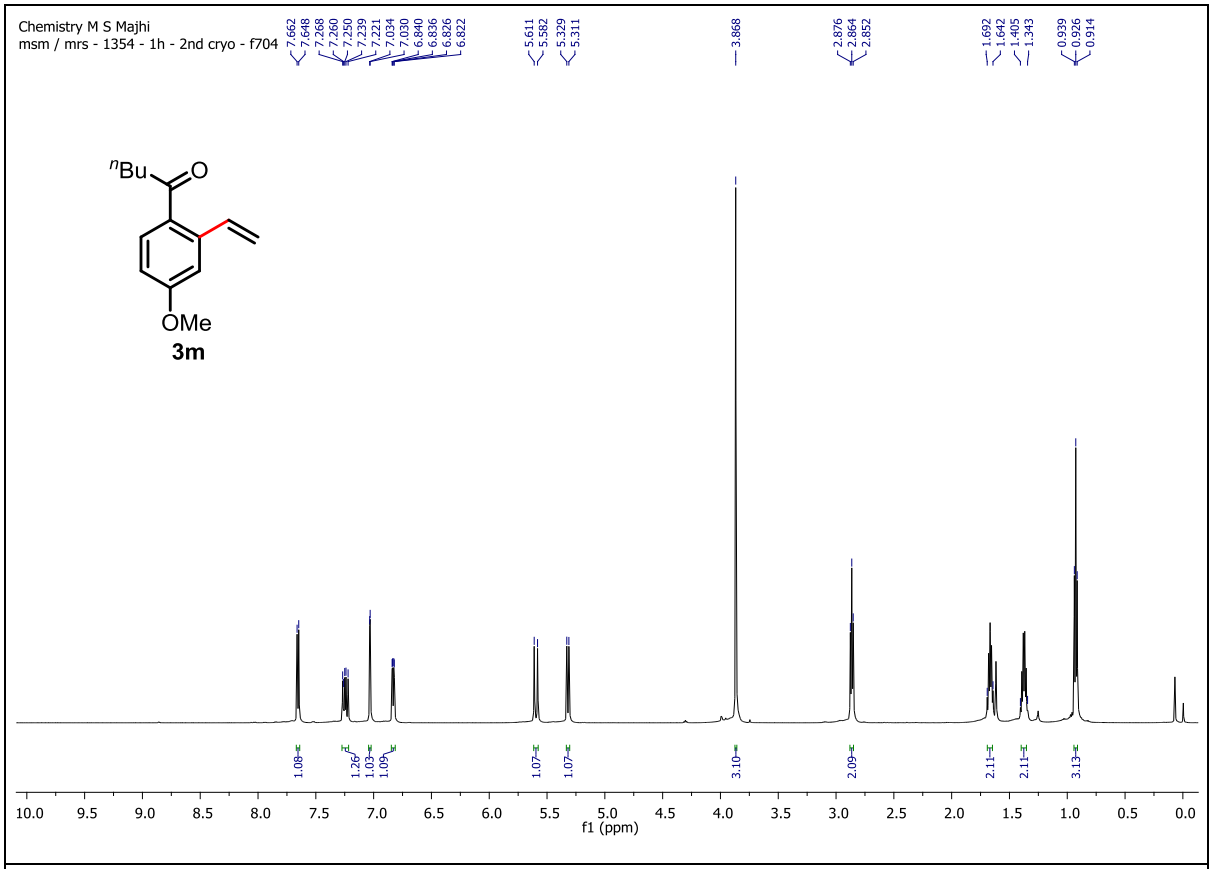

Chemistry M S Majhi
msm /mrs - 1448 - 1h - 2nd cryo - f1105
200.30
151.93
148.23
136.38
132.89
130.06
115.63
112.27
110.22
77.37
77.16
76.95
56.33
56.14
29.96
O
OMe
OMe
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

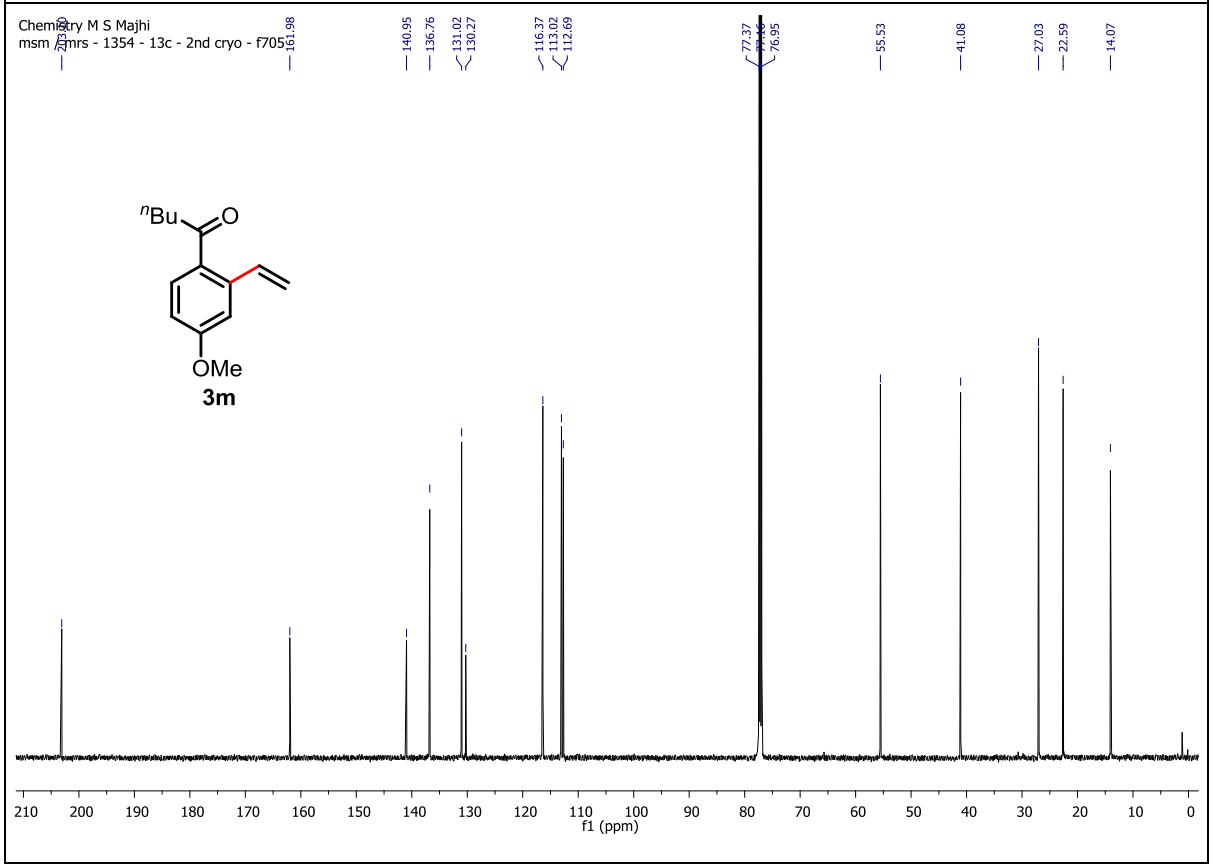

Chemistry M S Majhi
msm /mrs - 1449 - 1h - 2nd cryo - f1108
8.460
8.098
8.085
7.559
7.504
7.464
7.419
7.405
7.309
7.297
7.285
7.260
5.709
5.707
5.680
5.678
5.384
5.382
5.366
5.364
3.862
2.728
O
N
3k
1.04
1.00
2.05
1.01
1.03
1.03
1.03
1.00
3.03
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

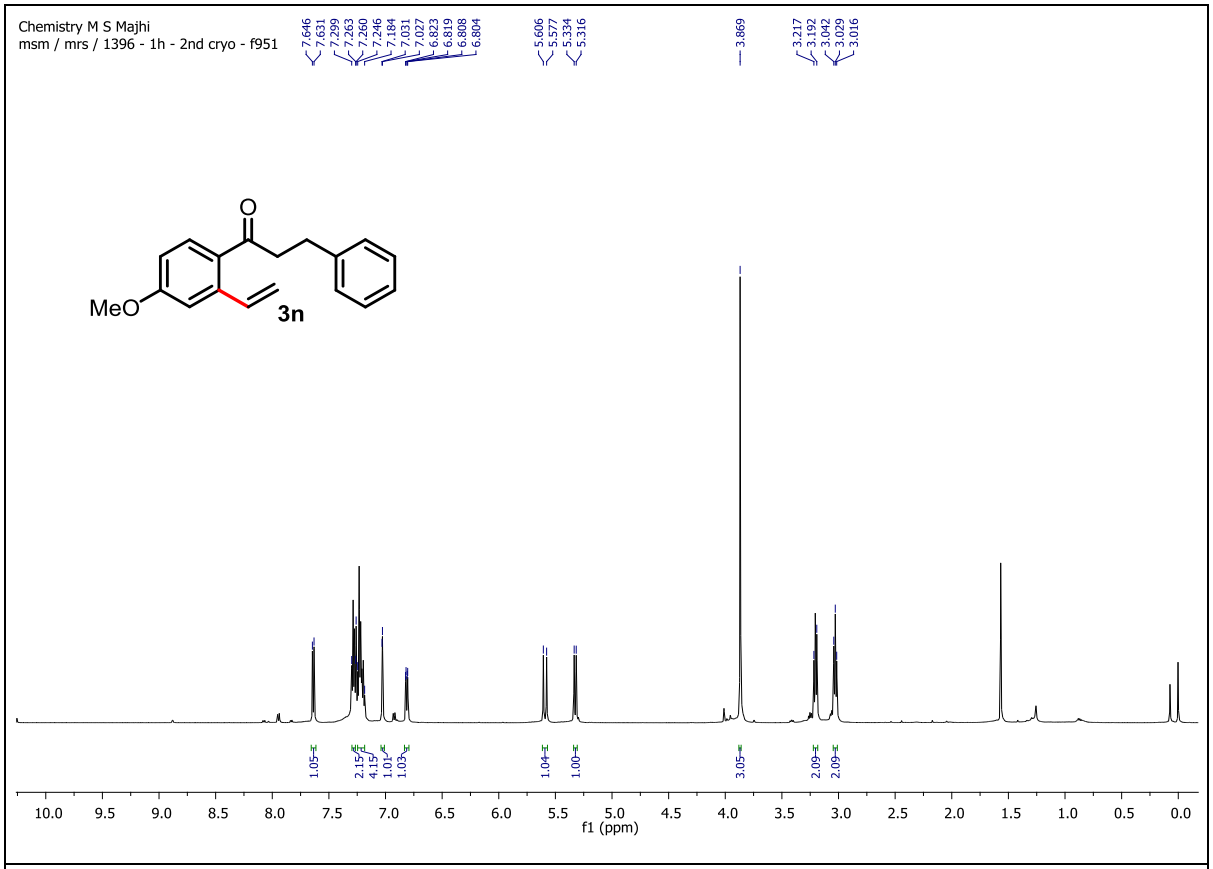

Chemistry M S Majhi
msm /mrs - 1449 - 1h - 2nd cryo - f1107
142.91
142.20
138.54
137.72
128.94
126.61
122.92
122.87
121.71
120.47
120.14
115.19
109.09
107.59
77.37
77.16
76.95
29.55
29.37
O
N
3k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

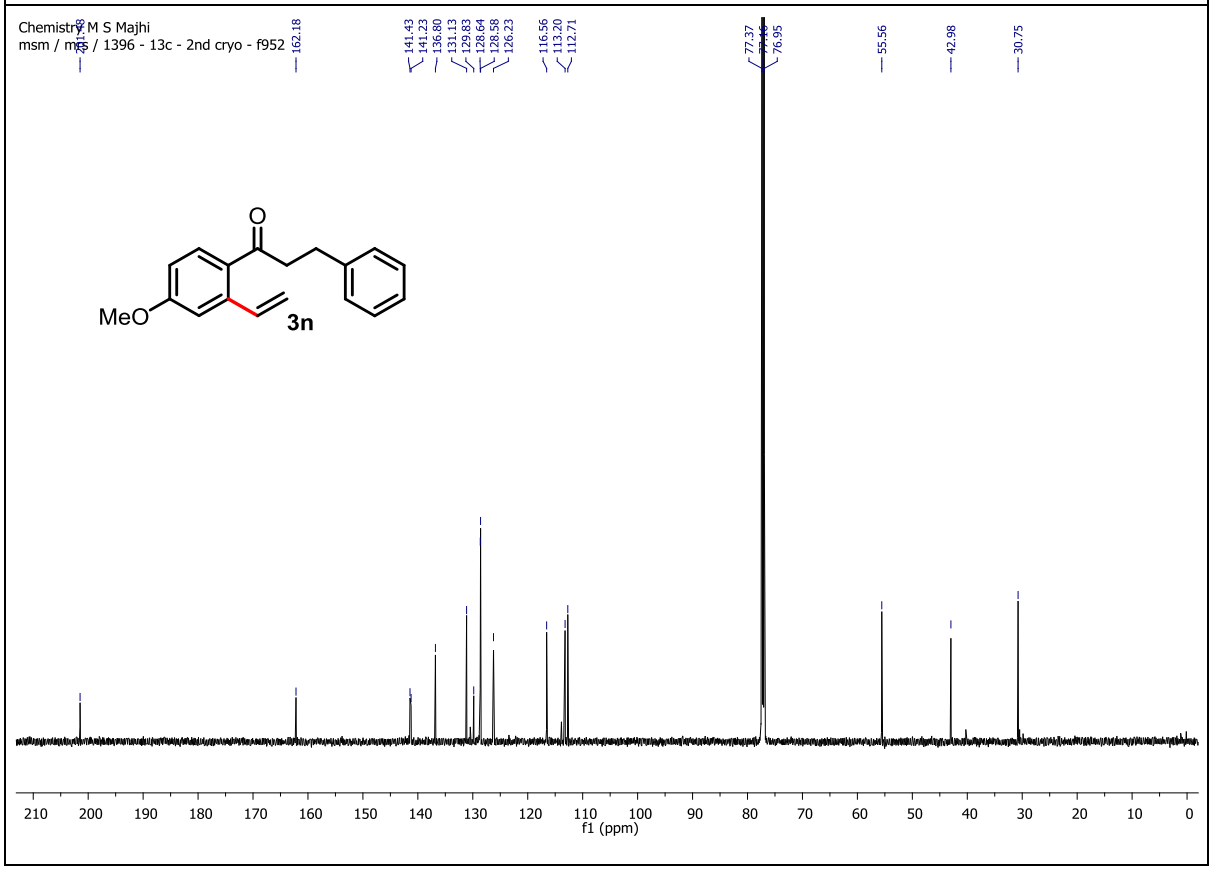

msm.mrs1463
msm / mrs / 1463
11.604
8.760
8.246
8.227
7.617
7.549
7.529
7.459
7.372
7.252
7.234
7.216
5.693
5.650
5.288
5.261
2.699
2.500
O
N
H
3l
0.98
1.00
1.00
1.00
1.00
2.00
1.00
1.01
1.00
3.03
f1 (ppm)

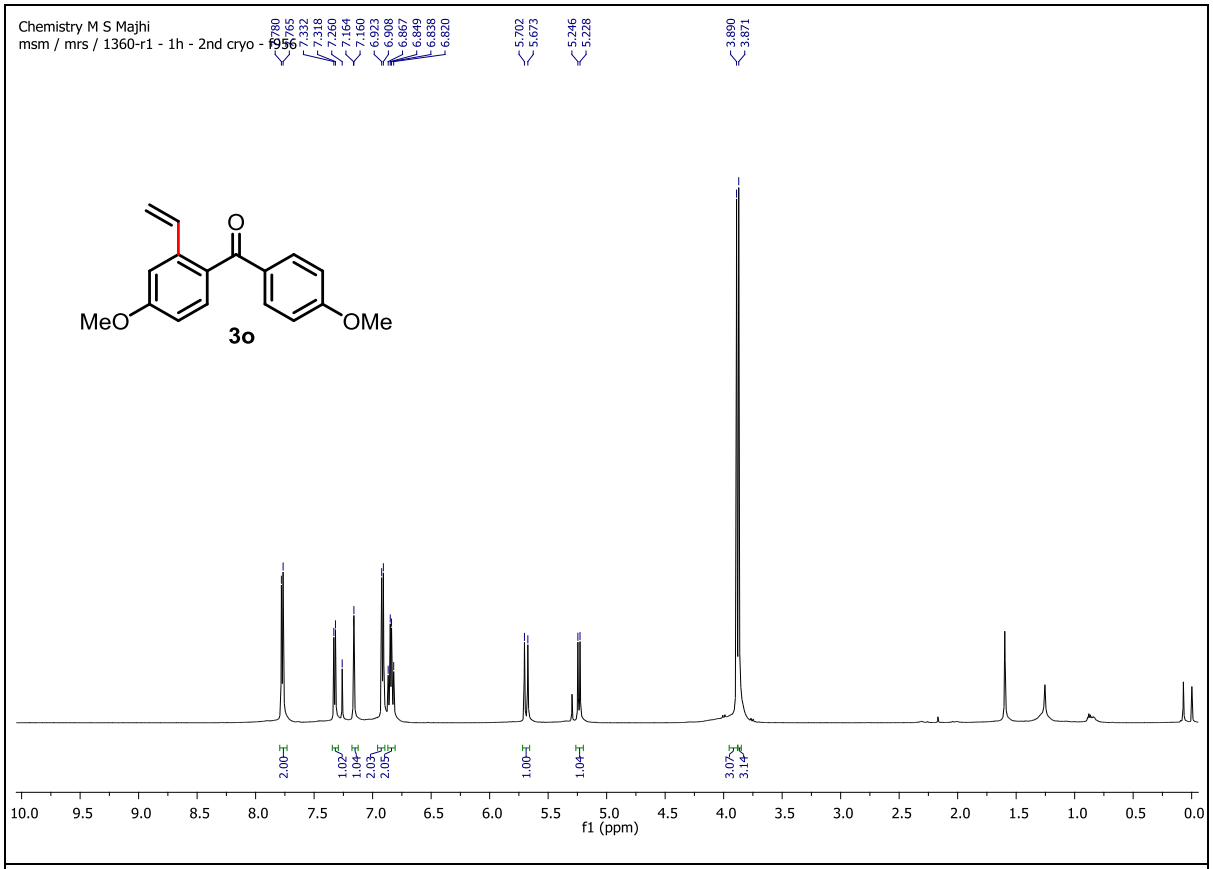

msmc.mrs1463
msm / mrs / 1463
200.52
141.60
140.82
137.79
136.05
128.28
126.37
123.45
122.51
121.42
120.68
119.55
114.63
111.44
109.10
40.15
39.94
39.73
39.31
39.10
38.89
29.45
O
N
H
3l
f1 (ppm)

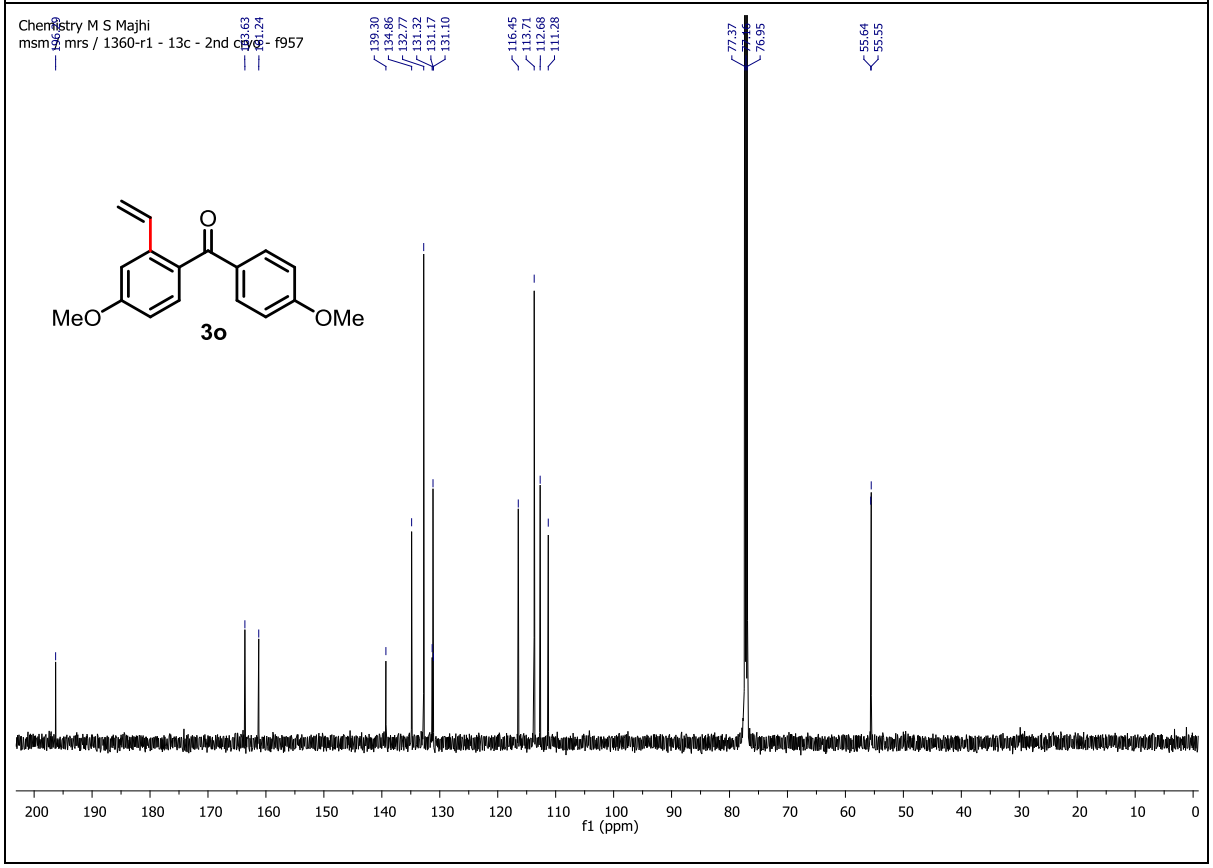

Chemistry M S Majhi
msm / mrs - 1354 - 1h - 2nd cryo - f704
7.662
7.648
7.268
7.260
7.250
7.239
7.221
7.034
7.030
6.840
6.836
6.826
6.822
5.611
5.582
5.329
5.311
3.868
2.876
2.864
2.852
1.692
1.642
1.405
1.343
0.939
0.926
0.914
nBu
O
OMe
3m
1.08
1.26
1.03
1.09
1.07
1.07
3.10
2.09
2.11
2.11
3.13
10.0
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)

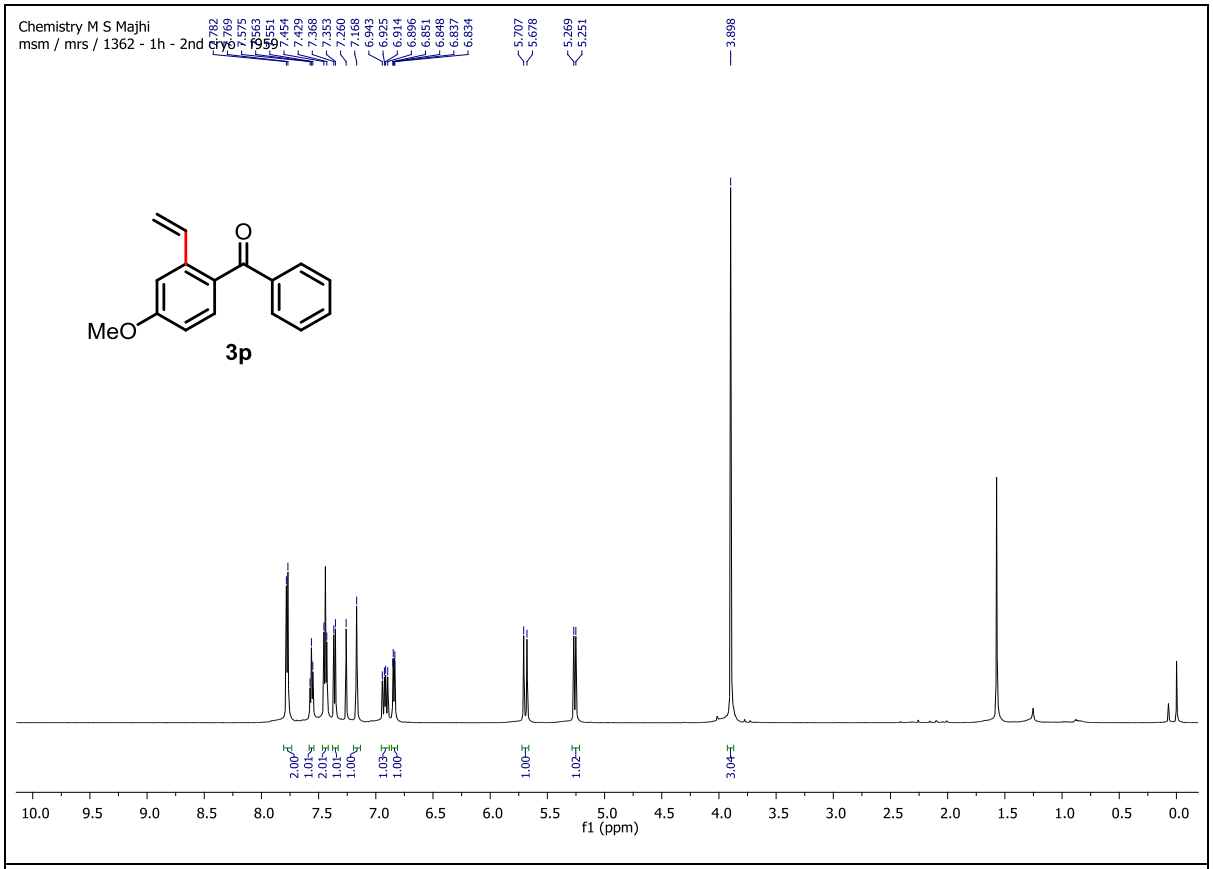

Chemistry M S Majhi
msm 2mrs - 1354 - 13c - 2nd cryo - f705
161.98
140.95
136.76
131.02
130.27
116.37
113.02
112.69
77.37
77.16
76.95
55.53
41.08
27.03
22.59
14.07
nBu
O
OMe
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

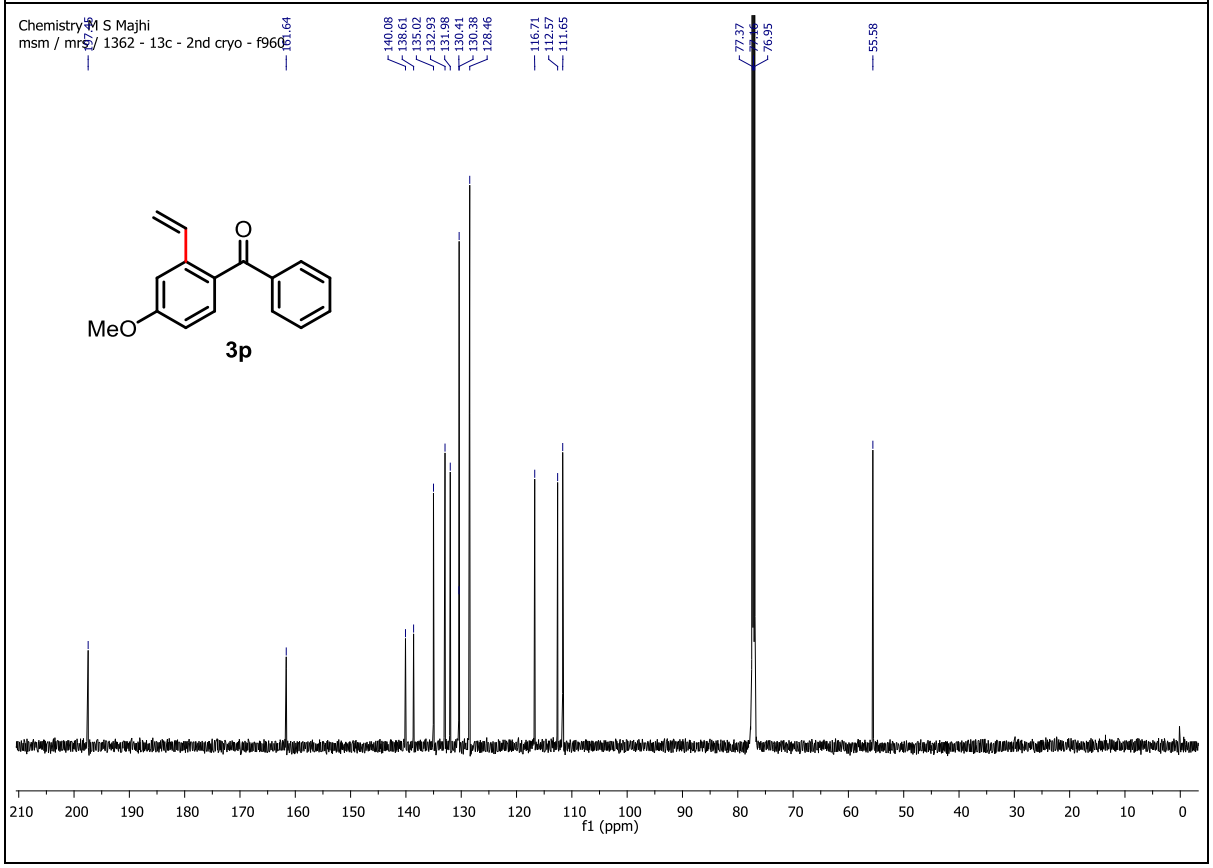

Chemistry M S Majhi
msm / mrs / 1396 - 1h - 2nd cryo - f951
7.646
7.631
7.299
7.263
7.260
7.246
7.184
7.031
7.027
6.823
6.819
6.808
6.804
5.606
5.577
5.334
5.316
3.869
3.217
3.192
3.042
3.029
3.016
MeO
3n
1.05
2.15
4.15
1.01
1.03
1.04
1.00
3.05
2.09
2.09
f1 (ppm)

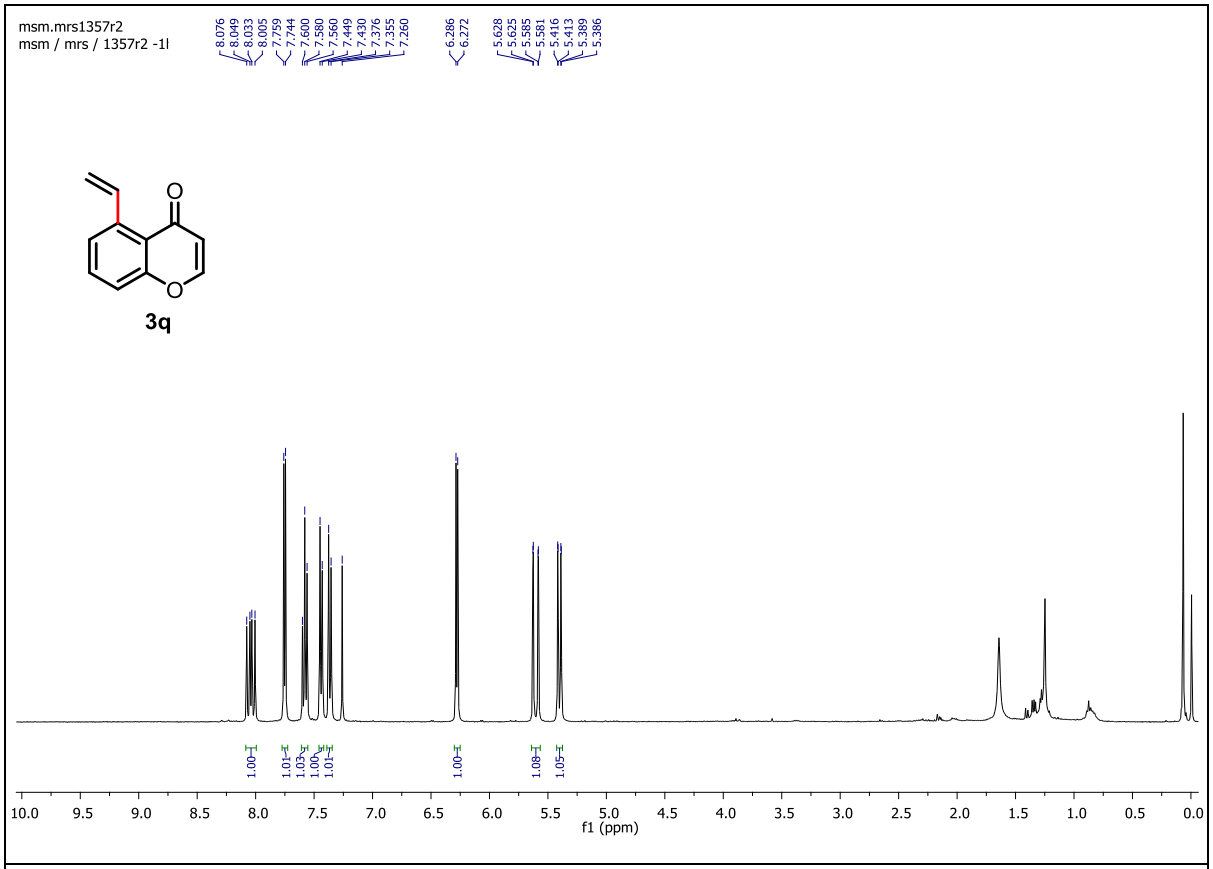

Chemistry M S Majhi
msm / mrs / 1396 - 13c - 2nd cryo - f952
162.18
141.43
141.23
136.80
131.13
129.83
128.64
128.58
126.23
116.56
113.20
112.71
77.37
77.06
76.95
55.56
42.98
30.75
MeO
3n
f1 (ppm)

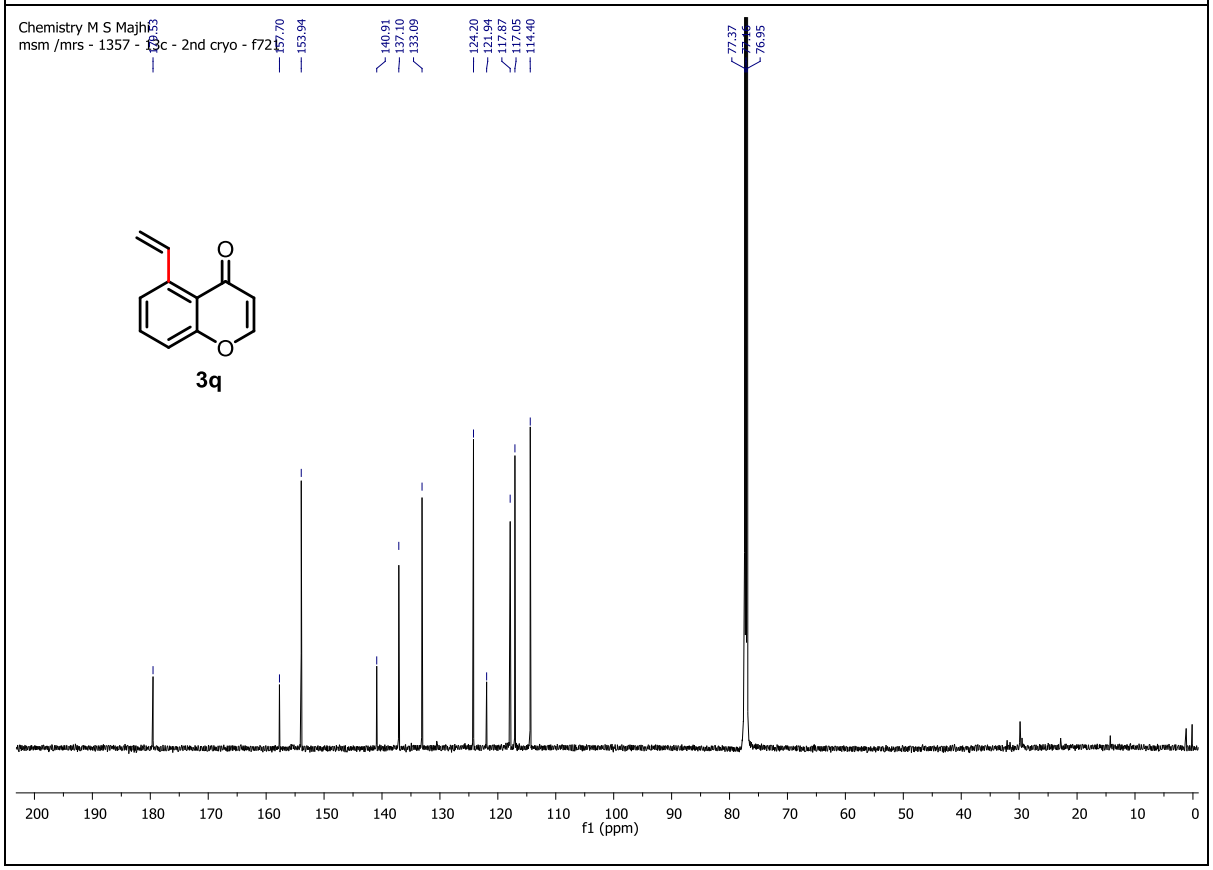

Chemistry M S Majhi
msm / mrs / 1360-r1 - 1h - 2nd cryo - f956
7.780
7.765
7.332
7.318
7.260
7.164
7.160
6.923
6.908
6.867
6.849
6.838
6.820
5.702
5.673
5.246
5.228
3.890
3.871
O
MeO
OMe
3o
2.00
1.02
1.04
2.03
2.05
1.00
1.04
3.07
3.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

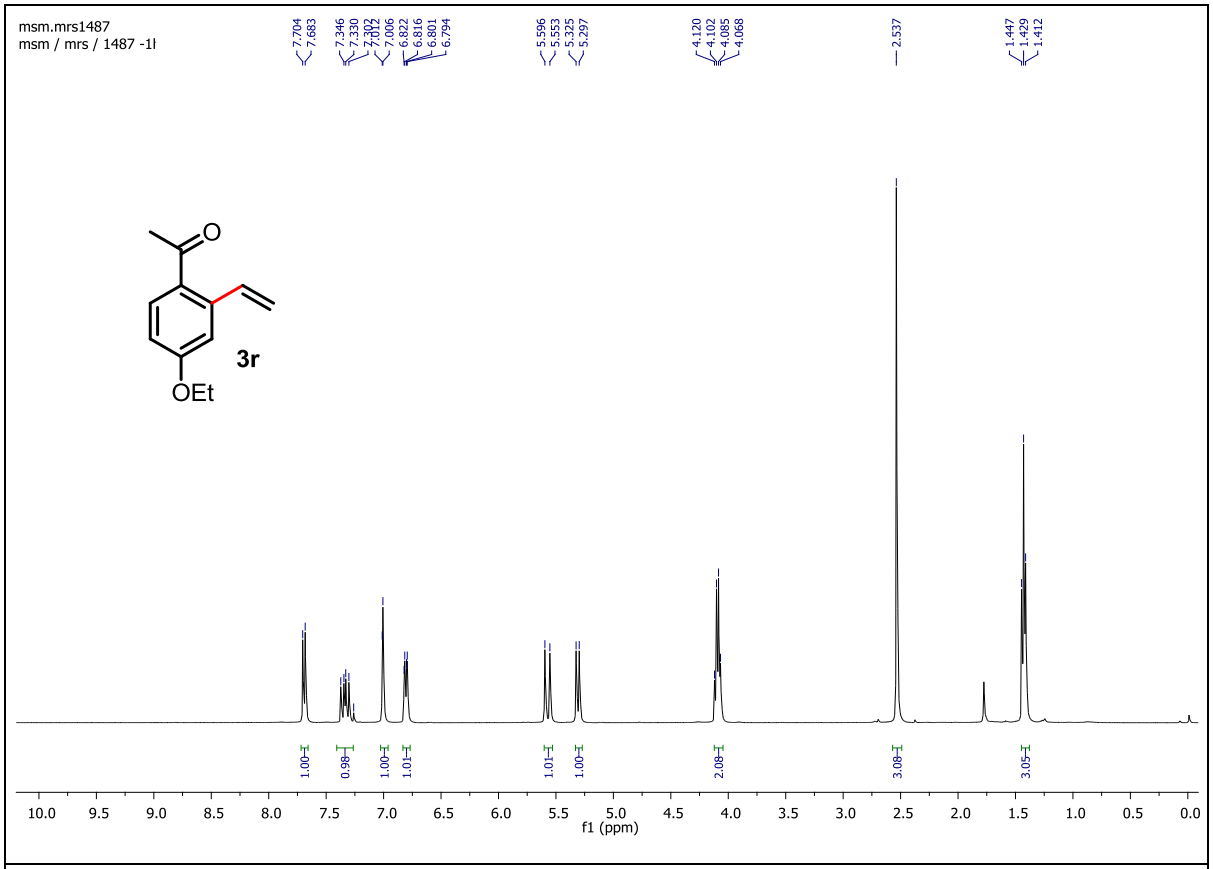

Chemistry M S Majhi
msm / mrs / 1360-r1 - 13c - 2nd cryo - f957
196.83
163.63
161.24
139.30
134.86
132.77
131.32
131.17
131.10
116.45
113.71
112.68
111.28
77.37
77.16
76.95
55.64
55.55
O
MeO
OMe
3o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

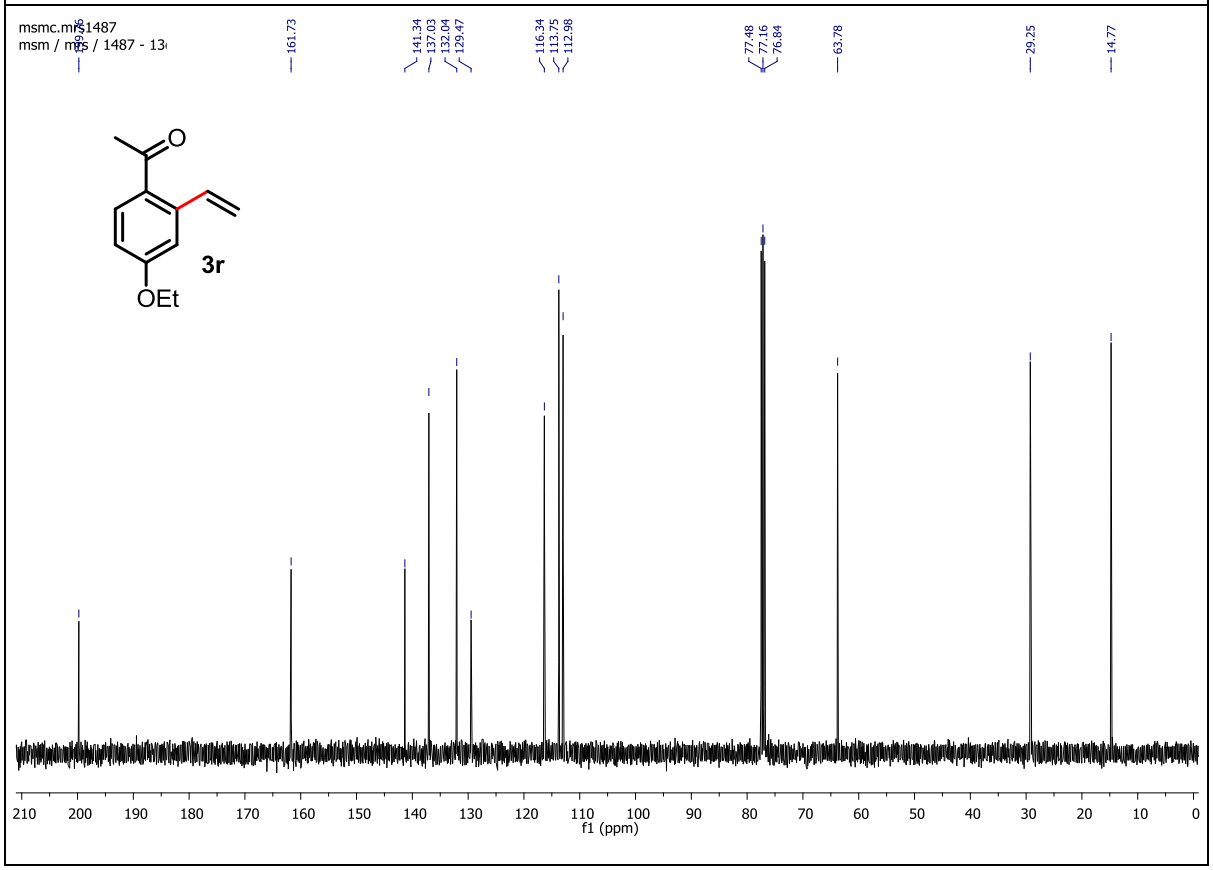

Chemistry M S Majhi
msm / mrs / 1362 - 1h - 2nd cryo - f959
7.782
7.769
7.575
7.563
7.551
7.454
7.429
7.368
7.353
7.260
7.168
6.943
6.925
6.914
6.896
6.851
6.848
6.837
6.834
5.707
5.678
5.269
5.251
3.898
MeO
O
3p
2.00
1.01
2.01
1.01
1.00
1.03
1.00
1.00
1.02
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

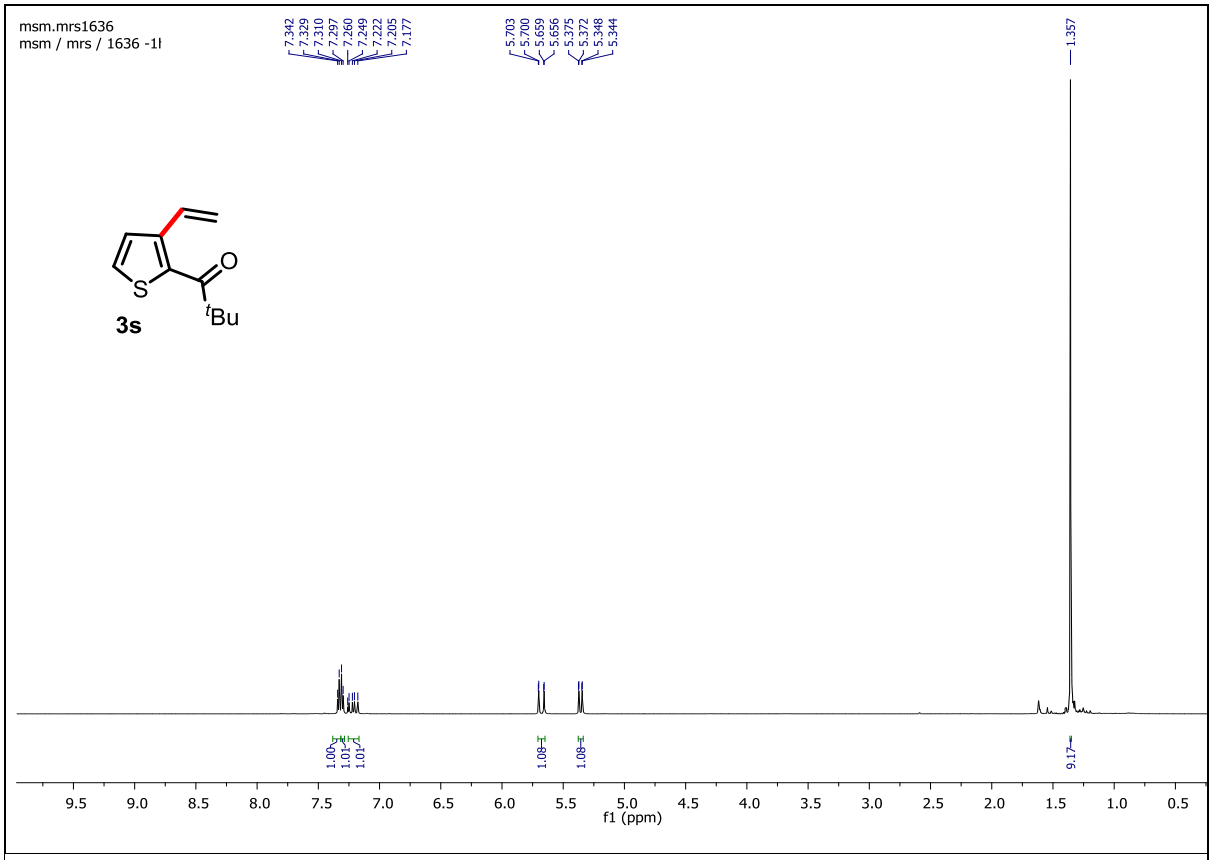

Chemistry M S Majhi
msm / mrs / 1362 - 13c - 2nd cryo - f960
197.46
161.64
140.08
138.61
135.02
132.93
131.98
130.41
130.38
128.46
116.71
112.57
111.65
77.37
77.16
76.95
55.58
MeO
O
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

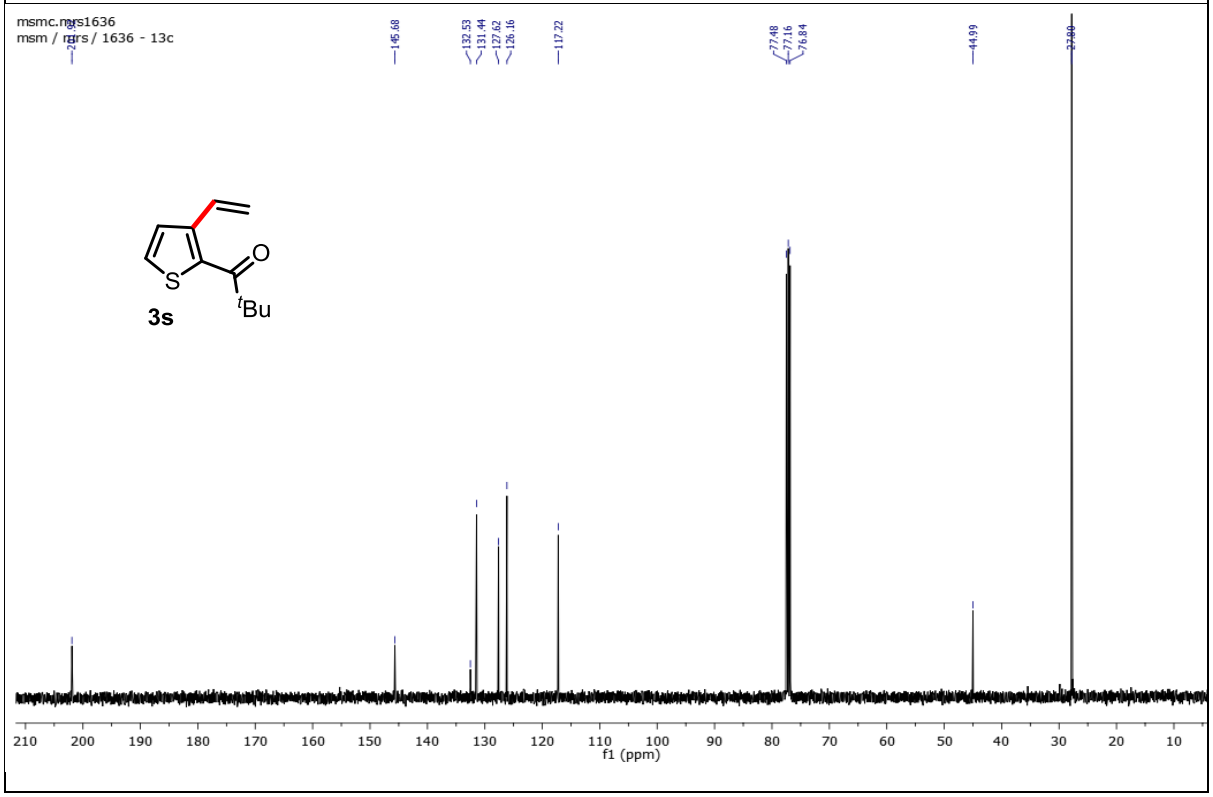

msm.mrs1357r2
msm / mrs / 1357r2 -1l
8.076
8.049
8.033
8.005
7.759
7.744
7.600
7.580
7.560
7.449
7.430
7.376
7.355
7.260
6.286
6.272
5.628
5.625
5.585
5.581
5.416
5.413
5.389
5.386
3q
1.00
1.01
1.03
1.00
1.01
1.00
1.08
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

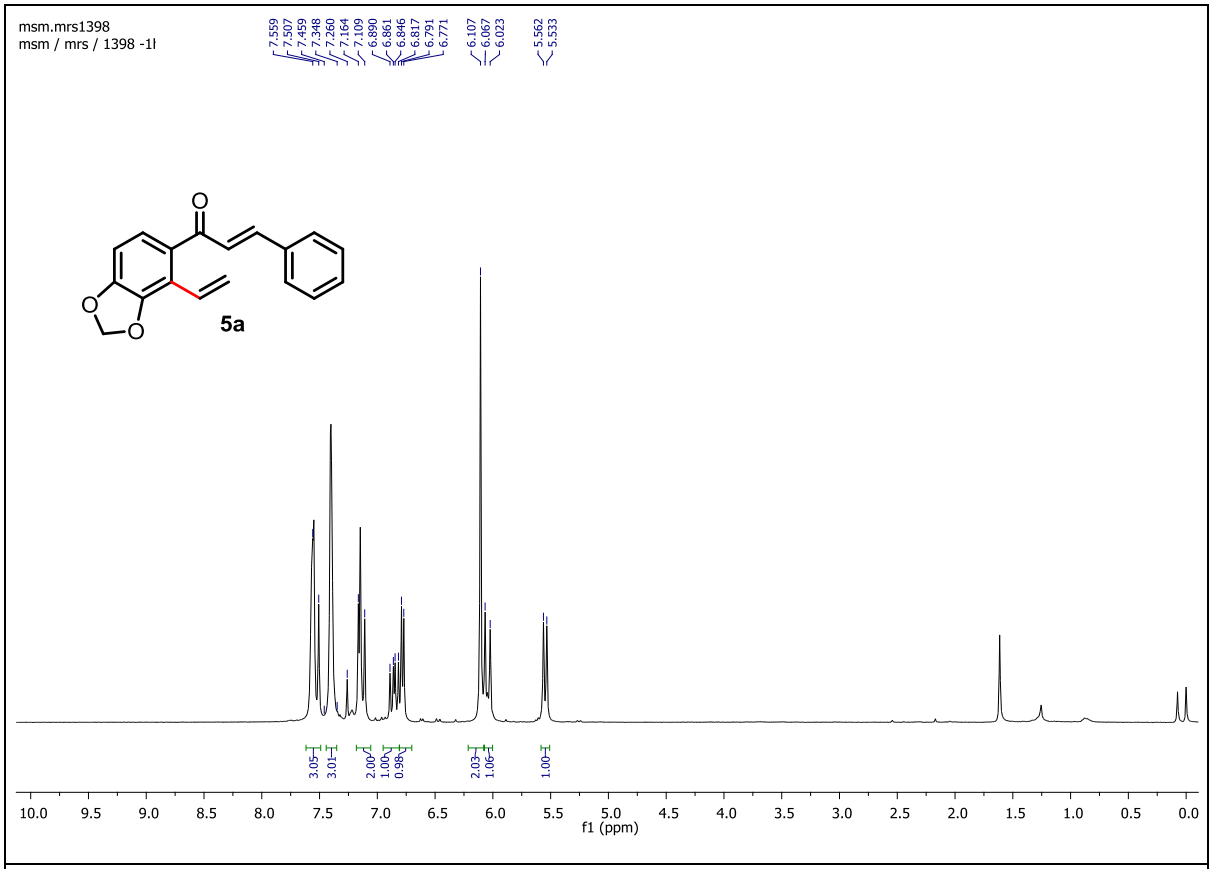

Chemistry M S Majhi
msm /mrs - 1357 - 13c - 2nd cryo - f72
179.53
157.70
153.94
140.91
137.10
133.09
124.20
121.94
117.87
117.05
114.40
77.37
77.16
76.95
3q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

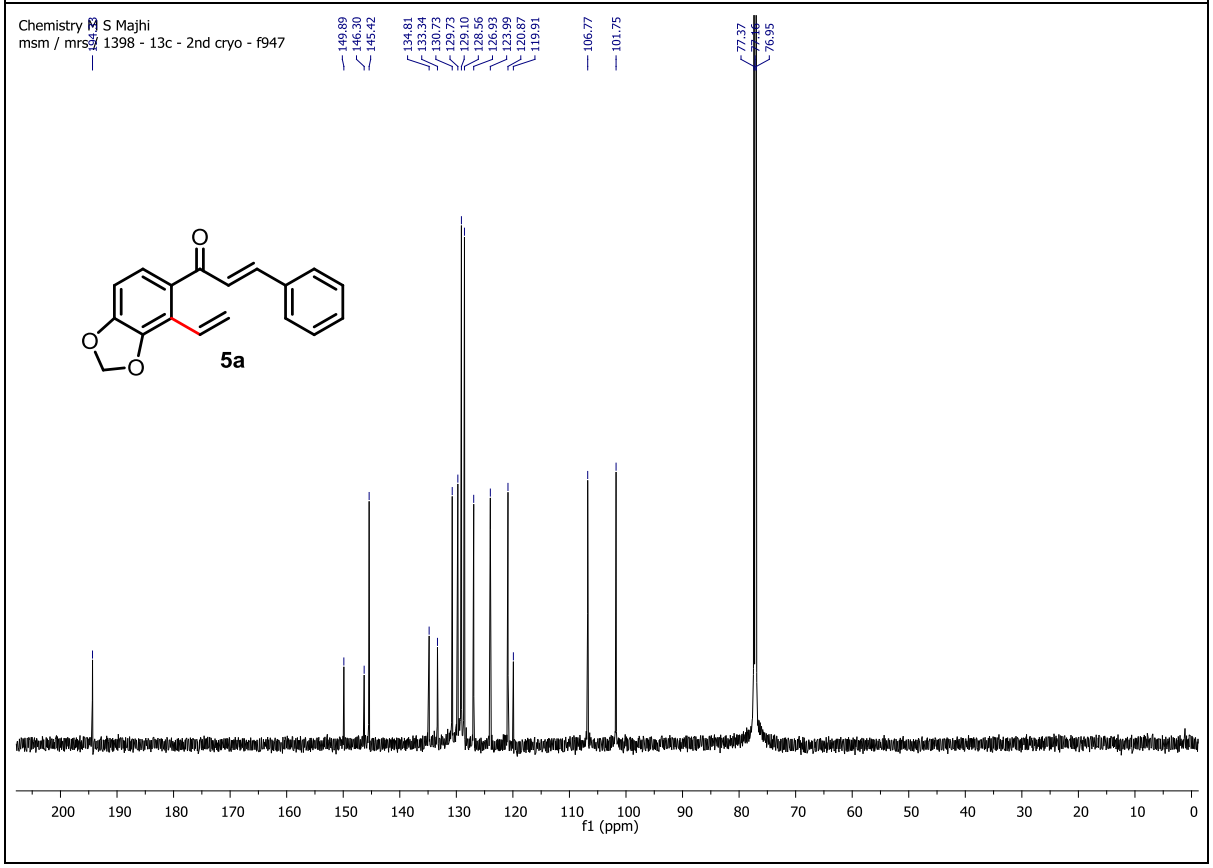

msm.mrs1487
msm / mrs / 1487 -1
7.704
7.683
7.346
7.330
7.302
7.012
7.006
6.822
6.816
6.801
6.794
5.596
5.553
5.325
5.297
4.120
4.102
4.085
4.068
2.537
1.447
1.429
1.412
O
3r
OEt
1.00
0.98
1.00
1.01
1.01
1.00
2.08
3.08
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

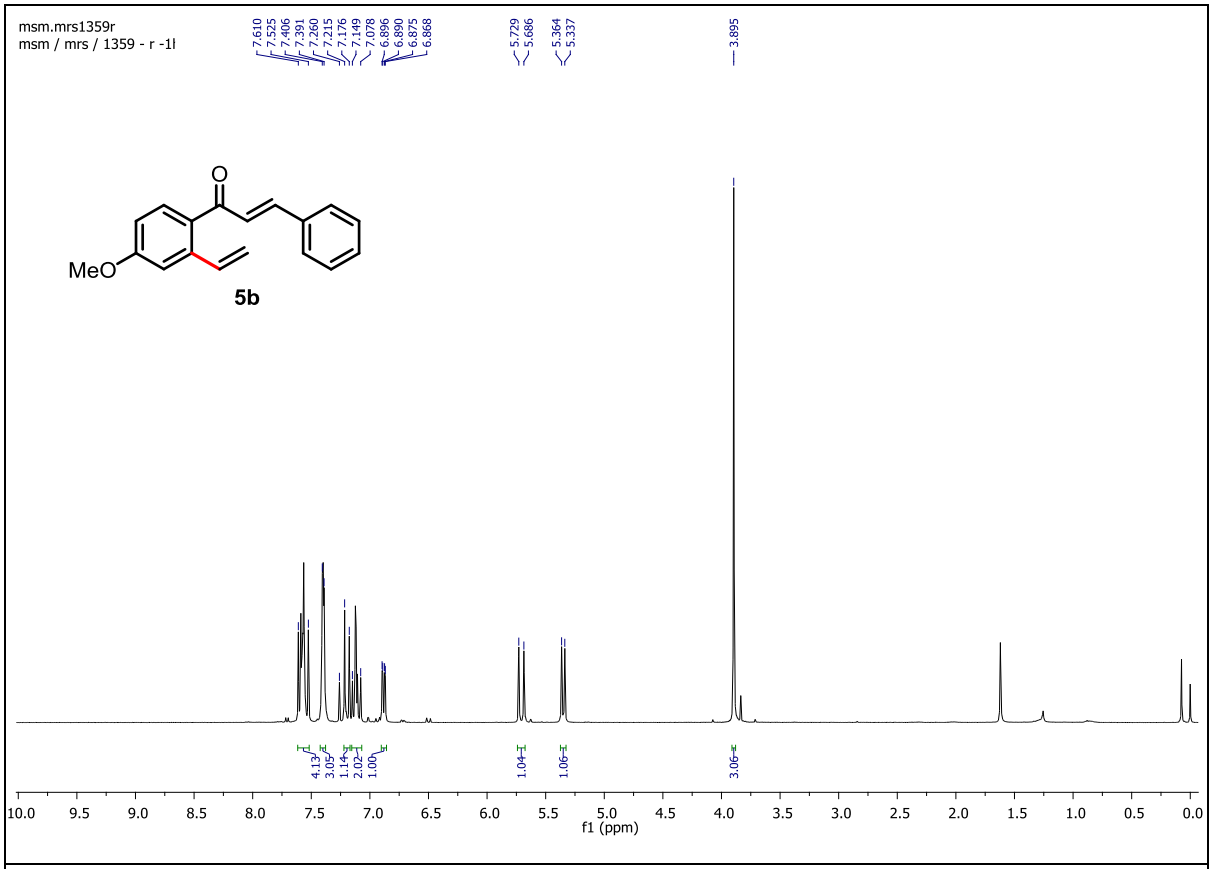

msmc.mrs1487
msm / mrs / 1487 - 13
161.73
141.34
137.03
132.04
129.47
116.34
113.75
112.98
77.48
77.16
76.84
63.78
29.25
14.77
O
3r
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

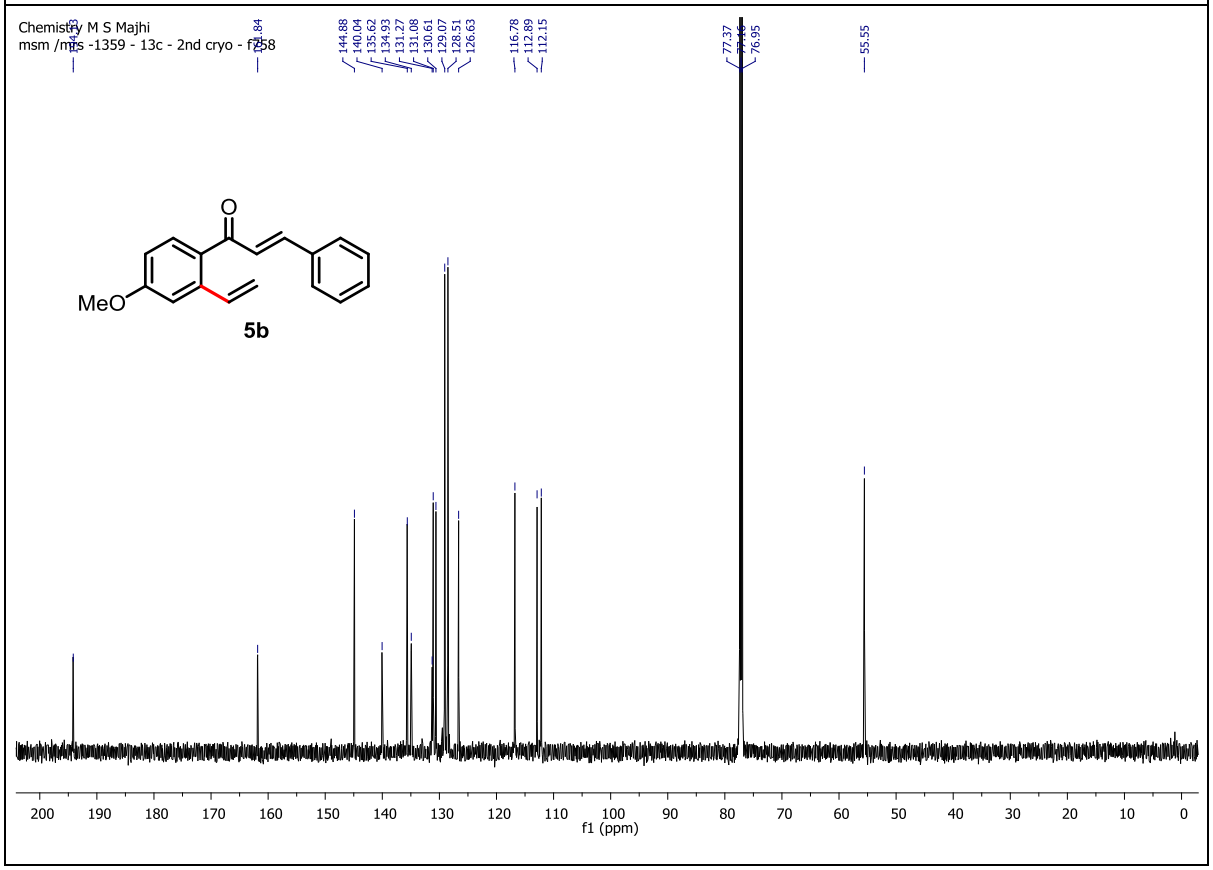

msm.mrs1636
msm / mrs / 1636 -1l
7.342
7.329
7.310
7.297
7.260
7.249
7.222
7.205
7.177
5.703
5.700
5.659
5.656
5.375
5.372
5.348
5.344
1.357
3s
tBu
1.00
1.01
1.01
1.08
1.08
9.17
f1 (ppm)

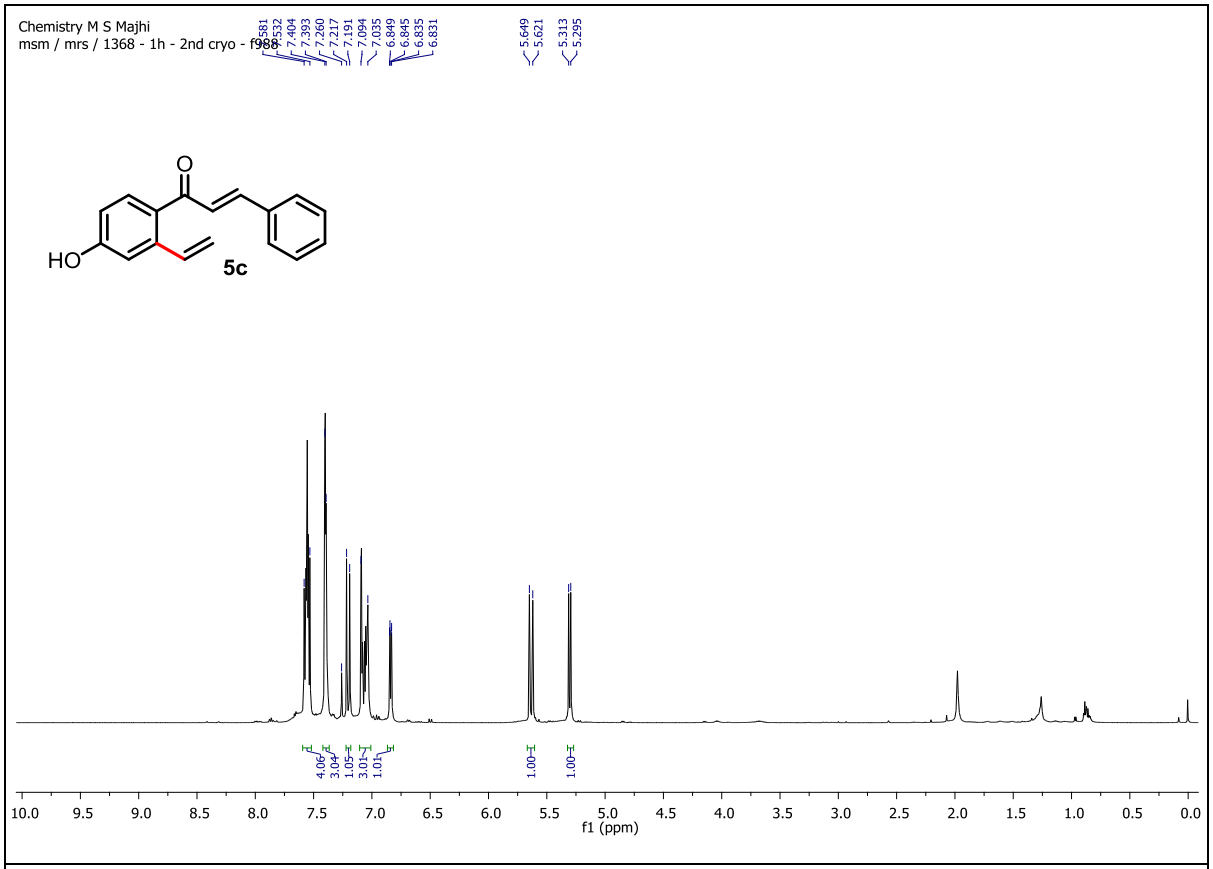

msmc.mrs1636
msm / mrs / 1636 - 13c
145.68
132.53
131.44
127.62
126.16
117.22
77.48
77.16
76.84
44.99
27.80
3s
tBu
f1 (ppm)

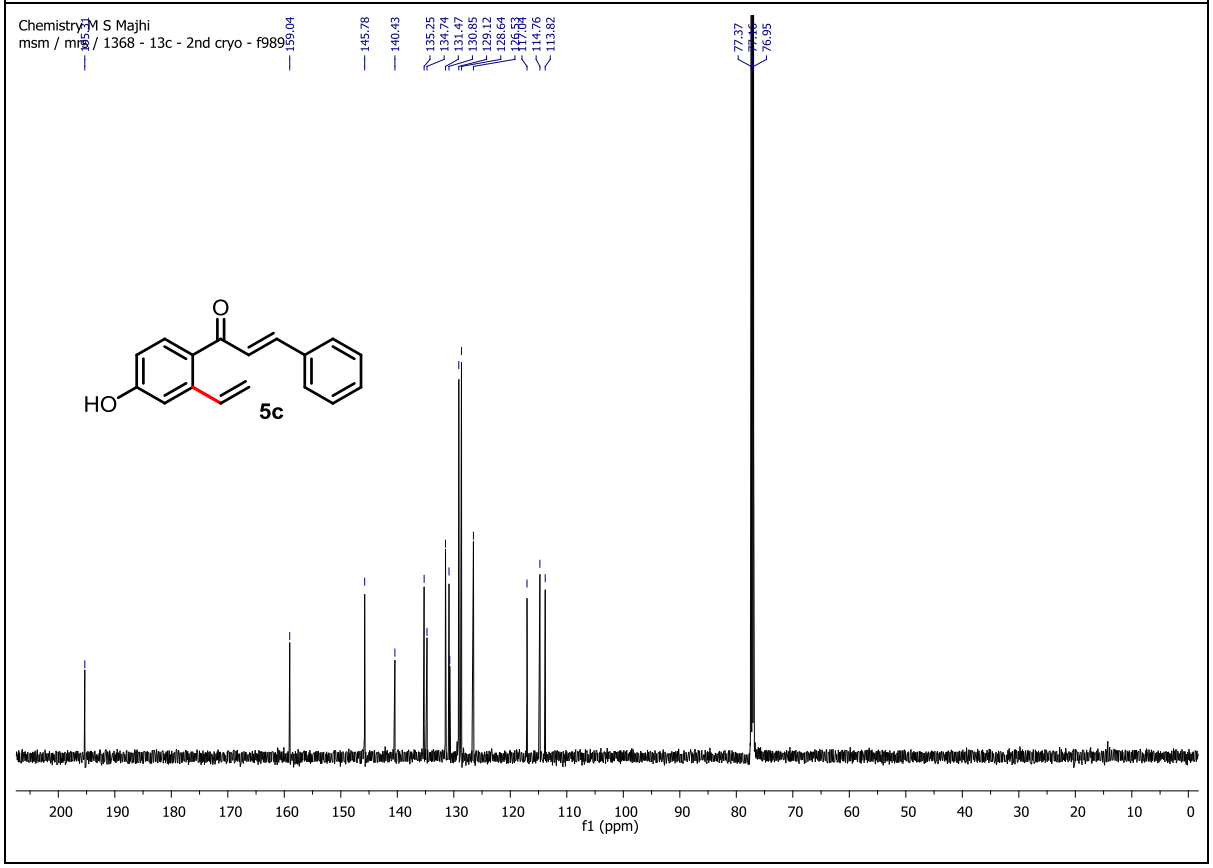

msm.mrs1398
msm / mrs / 1398 -1l
7.559
7.507
7.499
7.348
7.260
7.164
7.109
6.890
6.861
6.846
6.817
6.791
6.771
6.107
6.067
6.023
5.562
5.533
5a
3.05
3.01
2.00
1.00
0.98
2.03
1.06
1.00
f1 (ppm)

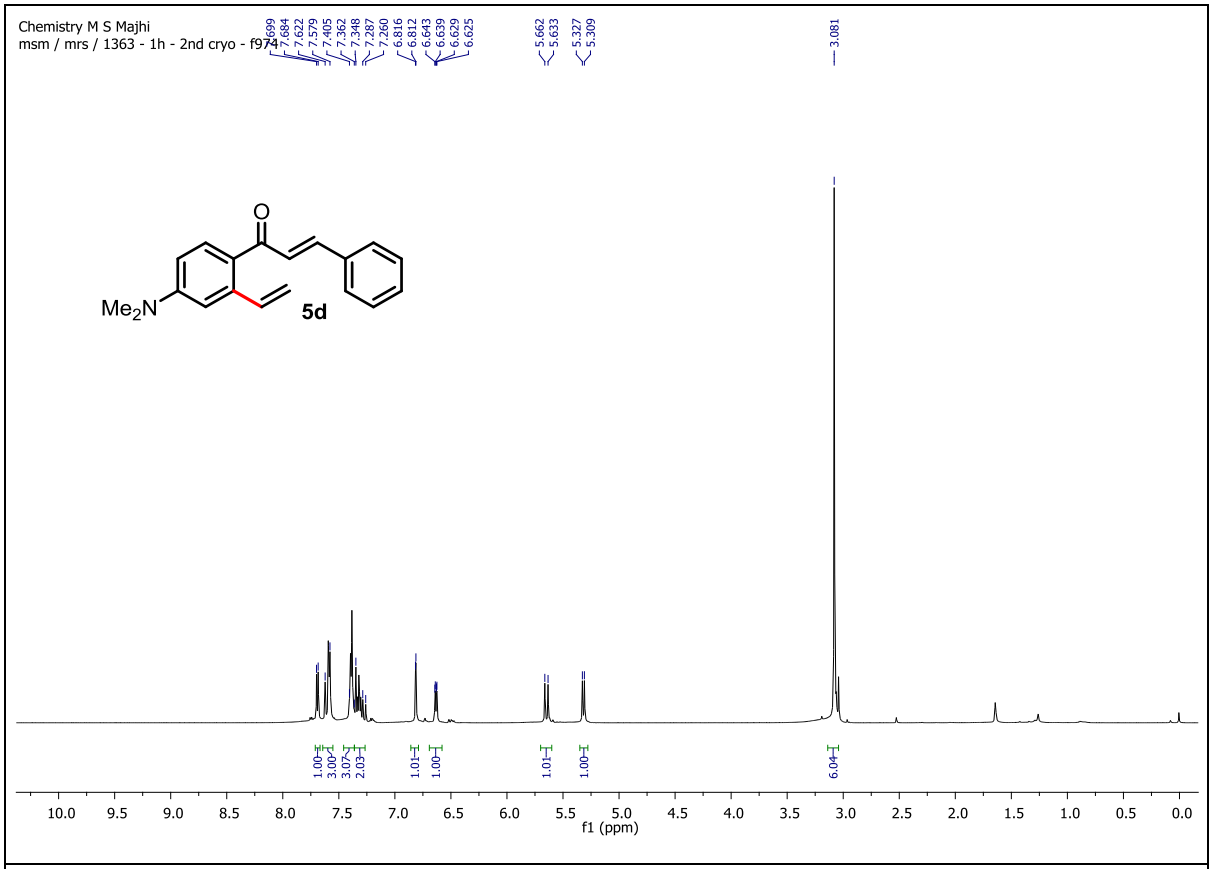

Chemistry M S Majhi
msm / mrs / 1398 - 13c - 2nd cryo - f947
149.89
146.30
145.42
134.81
133.34
130.73
129.73
129.10
128.56
126.93
123.99
120.87
119.91
106.77
101.75
77.37
77.16
76.95
5a
f1 (ppm)

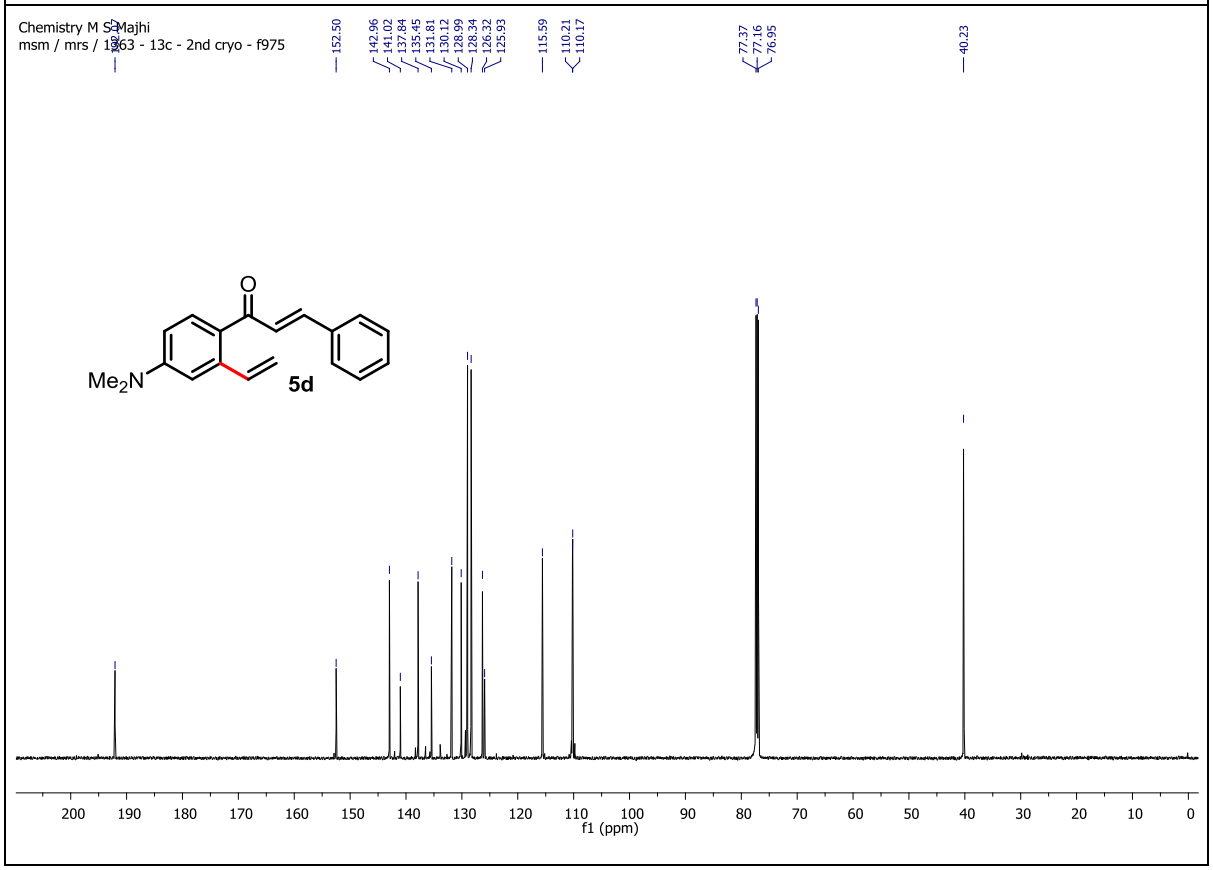

msm.mrs1359r
msm / mrs / 1359 - r -1l
7.610
7.525
7.406
7.391
7.260
7.215
7.176
7.149
7.078
6.896
6.890
6.875
6.868
5.729
5.686
5.364
5.337
3.895
MeO
5b
4.13
3.02
1.14
2.02
1.00
1.04
1.06
3.06
f1 (ppm)

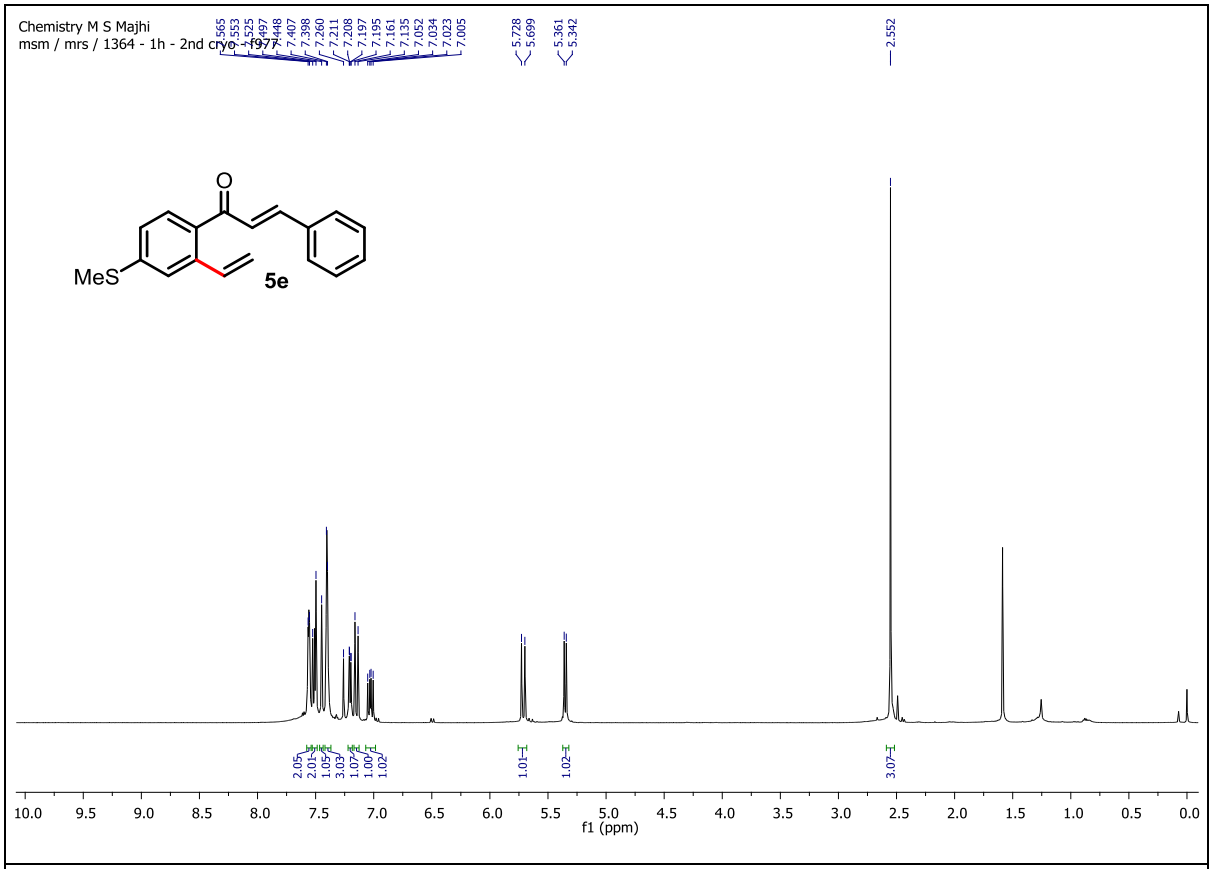

Chemistry M S Majhi
msm /mrs -1359 - 13c - 2nd cryo - f2 58
197.84
144.88
140.04
135.62
134.93
134.27
131.27
131.08
130.61
129.07
128.51
126.63
116.78
112.89
112.15
77.37
77.16
76.95
55.55
MeO
5b
f1 (ppm)

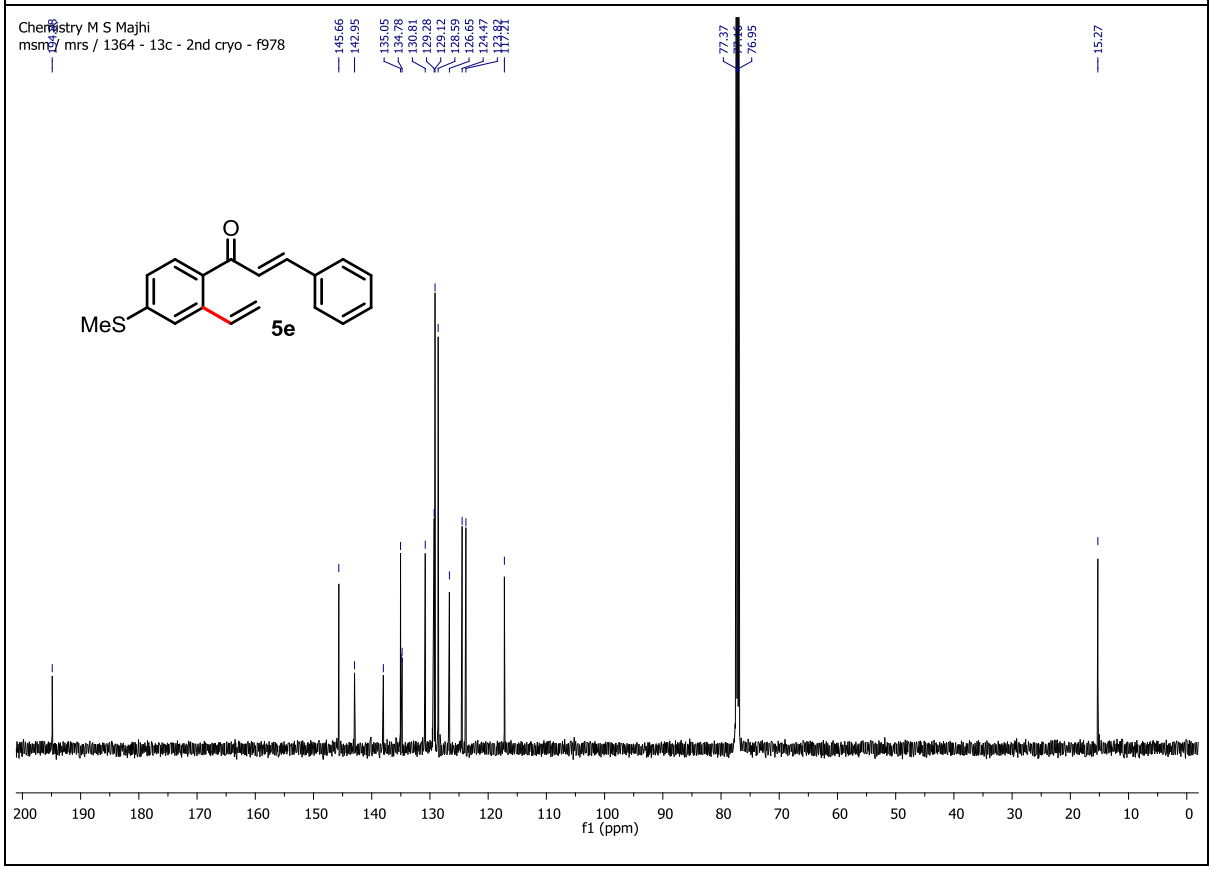

Chemistry M S Majhi
msm / mrs / 1368 - 1h - 2nd cryo - f989
7.581
7.532
7.404
7.393
7.260
7.217
7.191
7.094
7.035
6.849
6.845
6.835
6.831
5.649
5.621
5.313
5.295
O
HO
5c
4.06
3.04
1.05
3.01
1.01
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

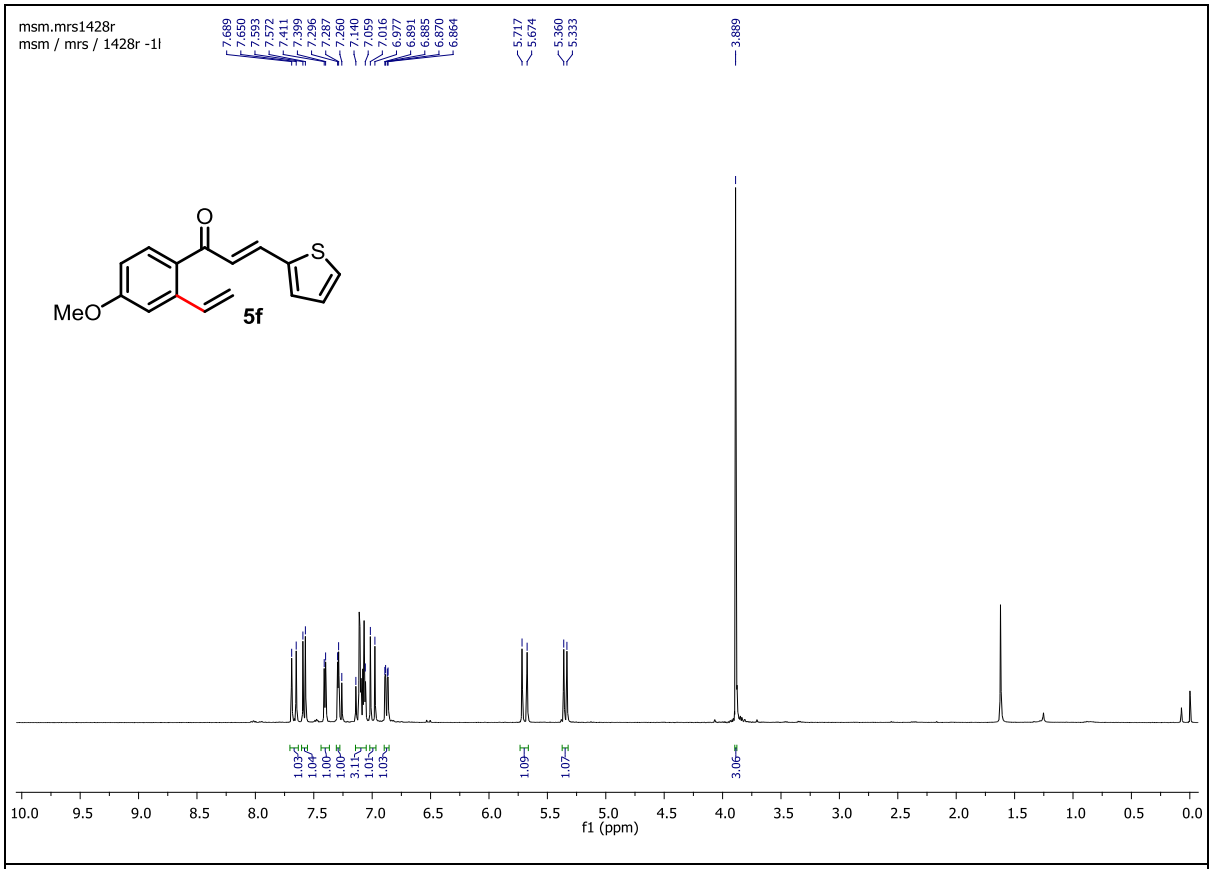

Chemistry M S Majhi
msm / mrs / 1368 - 13c - 2nd cryo - f989
195.73
159.04
145.78
140.43
135.25
134.74
131.47
130.85
129.12
128.64
117.53
114.76
113.82
77.37
77.16
76.95
O
HO
5c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

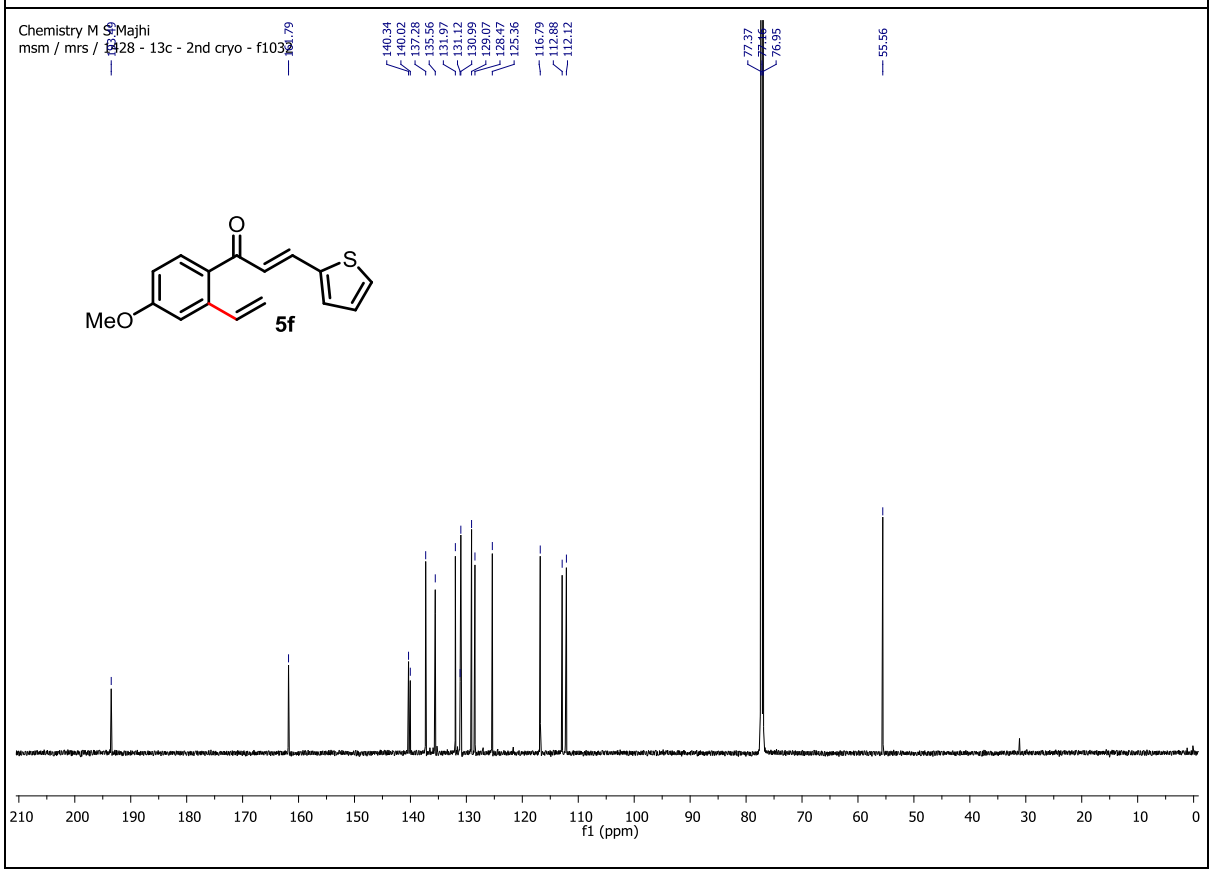

Chemistry M S Majhi
msm / mrs / 1363 - 1h - 2nd cryo - f974
7.699
7.684
7.622
7.579
7.405
7.362
7.348
7.287
7.260
6.816
6.812
6.643
6.639
6.629
6.625
5.662
5.633
5.327
5.309
3.081
O
Me2N
5d
1.00
3.00
3.07
2.03
1.01
1.00
1.01
1.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

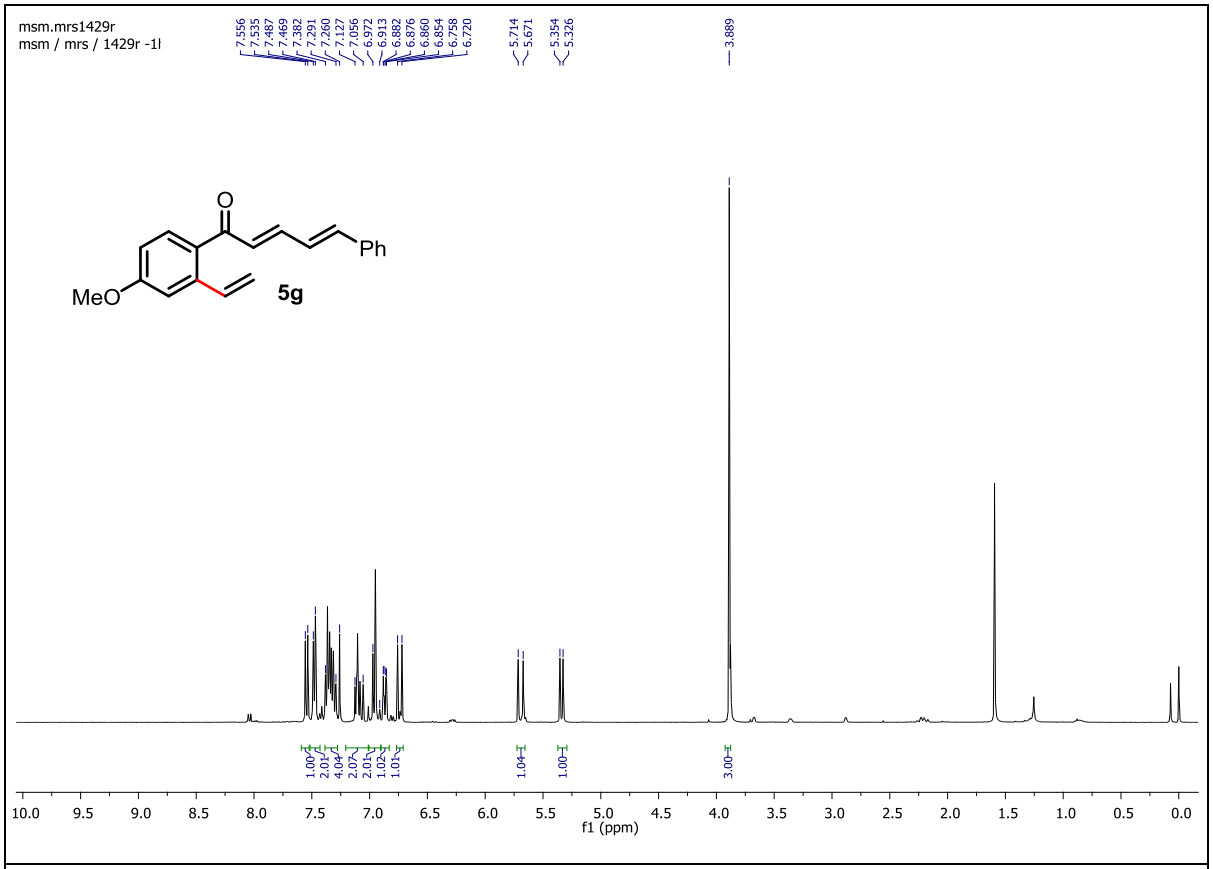

Chemistry M S Majhi
msm / mrs / 1363 - 13c - 2nd cryo - f975
192.52
152.50
142.96
141.02
137.84
135.45
131.81
130.12
128.99
128.34
126.32
125.93
115.59
110.21
110.17
77.37
77.16
76.95
40.23
O
Me2N
5d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

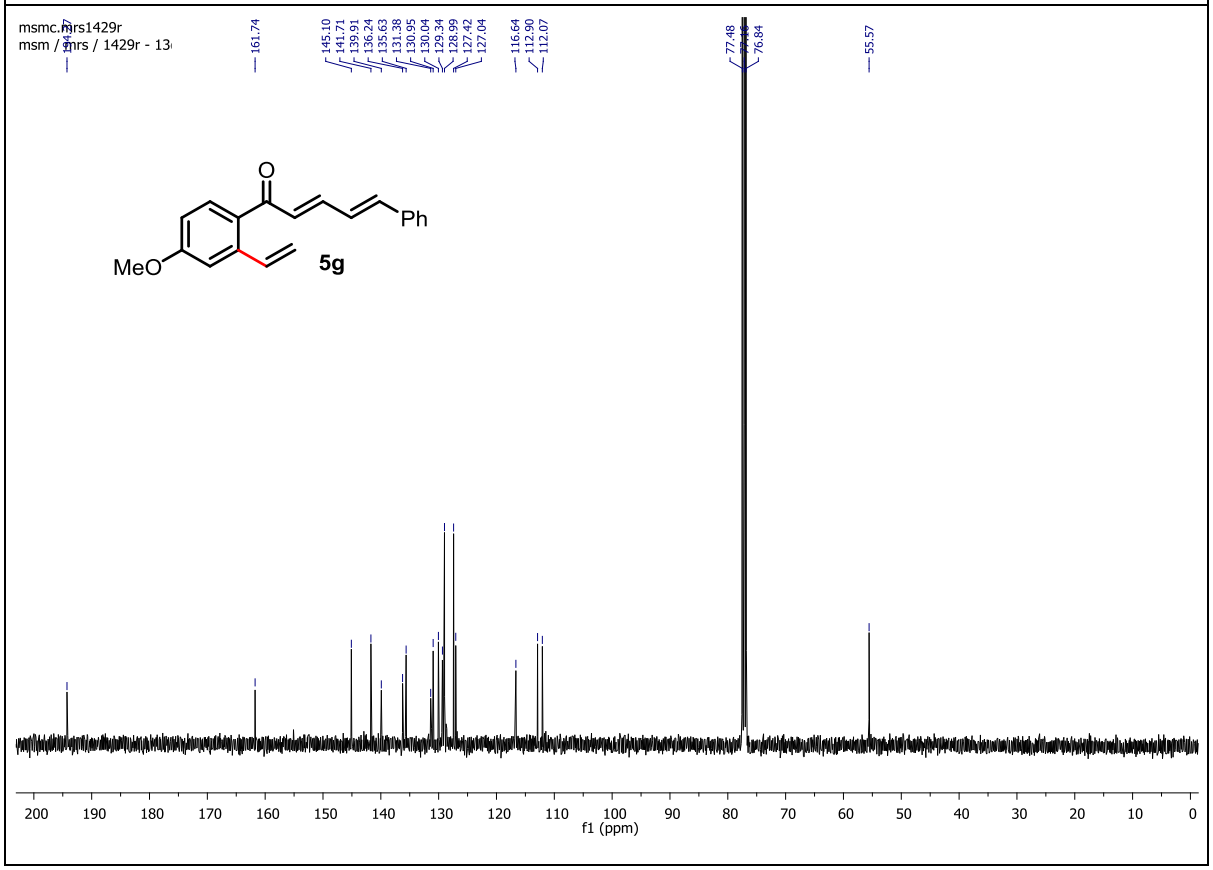

Chemistry M S Majhi
msm / mrs / 1364 - 1h - 2nd cryo - f977
7.565
7.553
7.525
7.497
7.448
7.407
7.398
7.260
7.211
7.208
7.197
7.195
7.161
7.135
7.052
7.034
7.023
7.005
5.728
5.699
5.361
5.342
2.552
MeS
5e
2.05
2.01
1.05
3.03
1.07
1.00
1.02
1.01
1.02
3.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

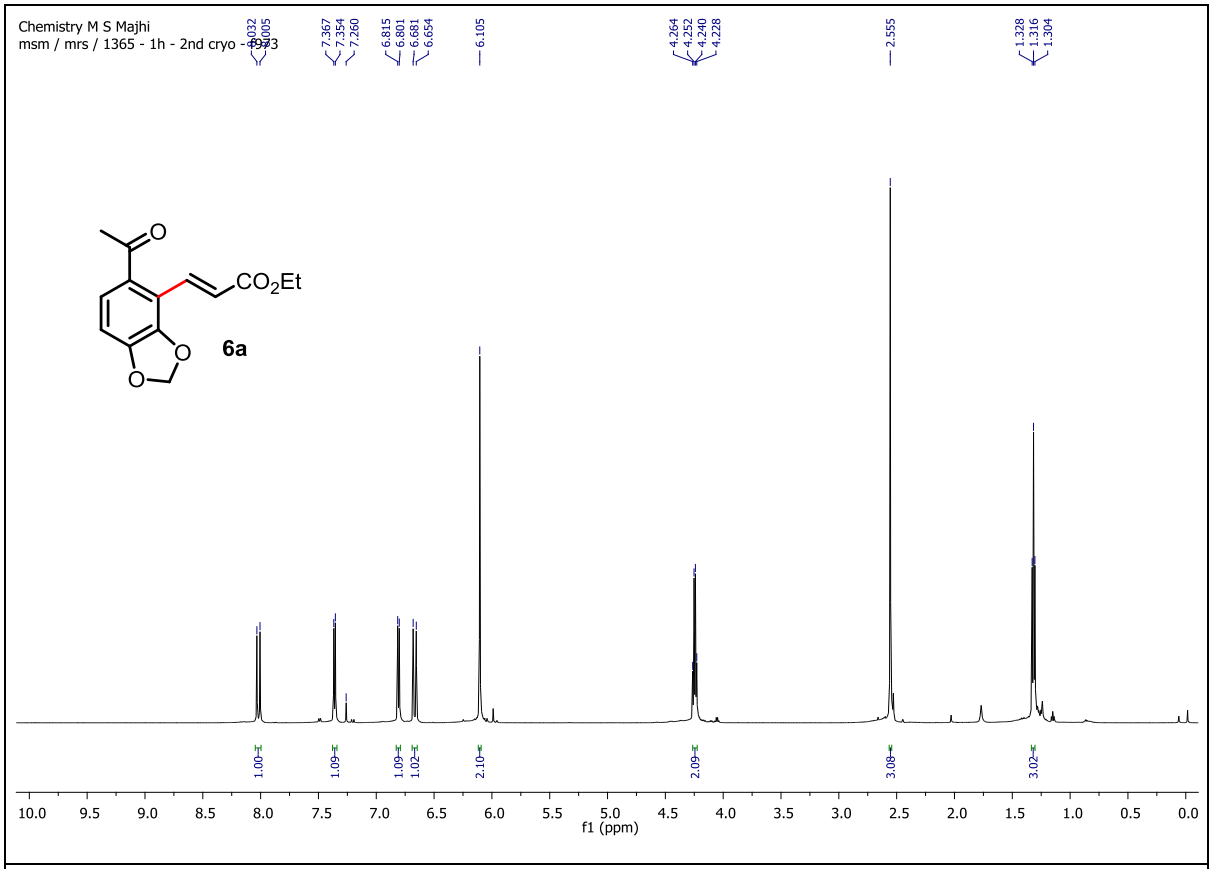

Chemistry M S Majhi
msm / mrs / 1364 - 13c - 2nd cryo - f978
145.66
142.95
135.05
134.78
130.81
129.28
129.12
128.59
126.65
124.47
123.82
77.37
76.95
15.27
MeS
5e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

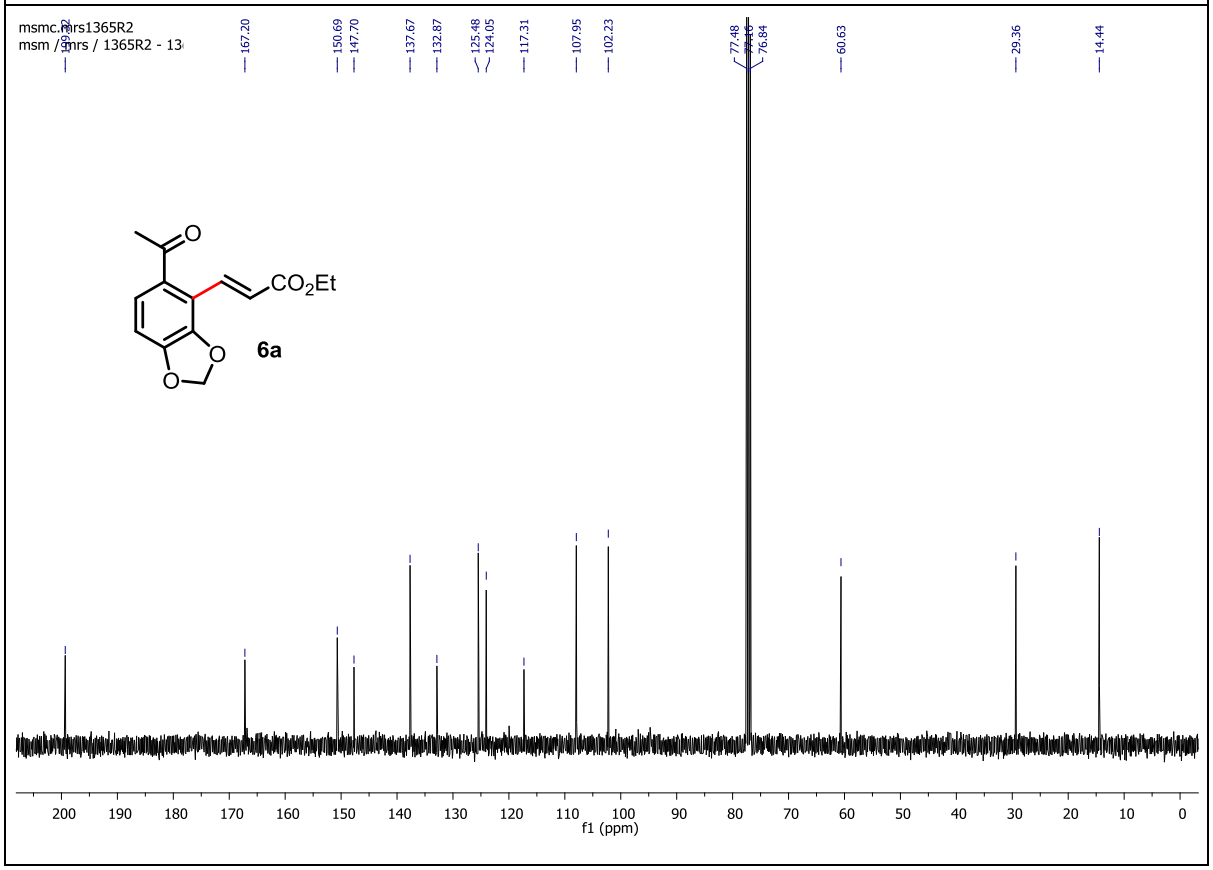

msm.mrs1428r
msm / mrs / 1428r -1l
7.689
7.650
7.593
7.572
7.411
7.399
7.296
7.287
7.260
7.140
7.059
7.016
6.977
6.891
6.885
6.870
6.864
5.717
5.674
5.360
5.333
3.889
O
S
MeO
5f
1.03
1.04
1.00
1.00
3.11
1.01
1.03
1.09
1.07
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

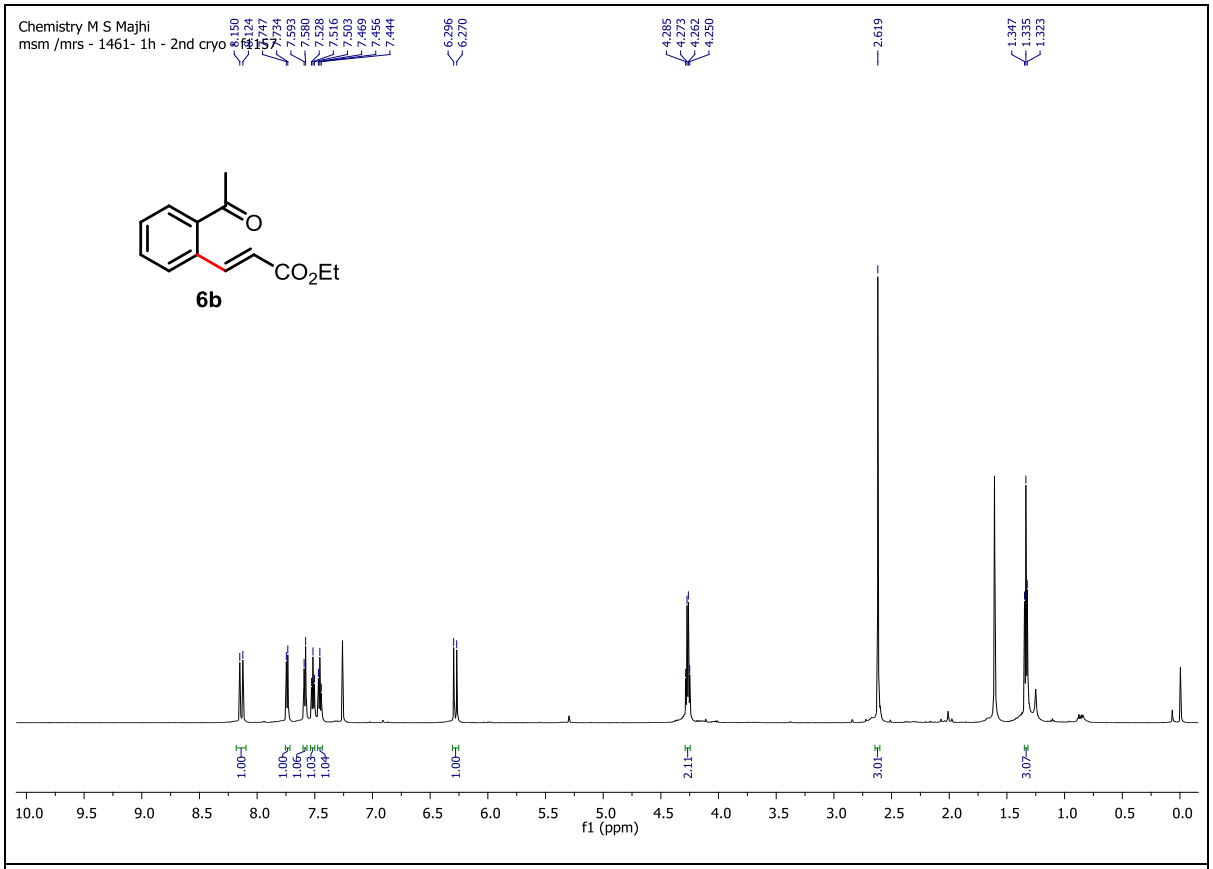

Chemistry M S Majhi
msm / mrs / 1428 - 13c - 2nd cryo - f103
194.79
140.34
140.02
137.28
135.56
131.97
131.12
130.99
129.07
128.47
125.36
116.79
112.88
112.12
77.37
77.16
76.95
55.56
O
S
MeO
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

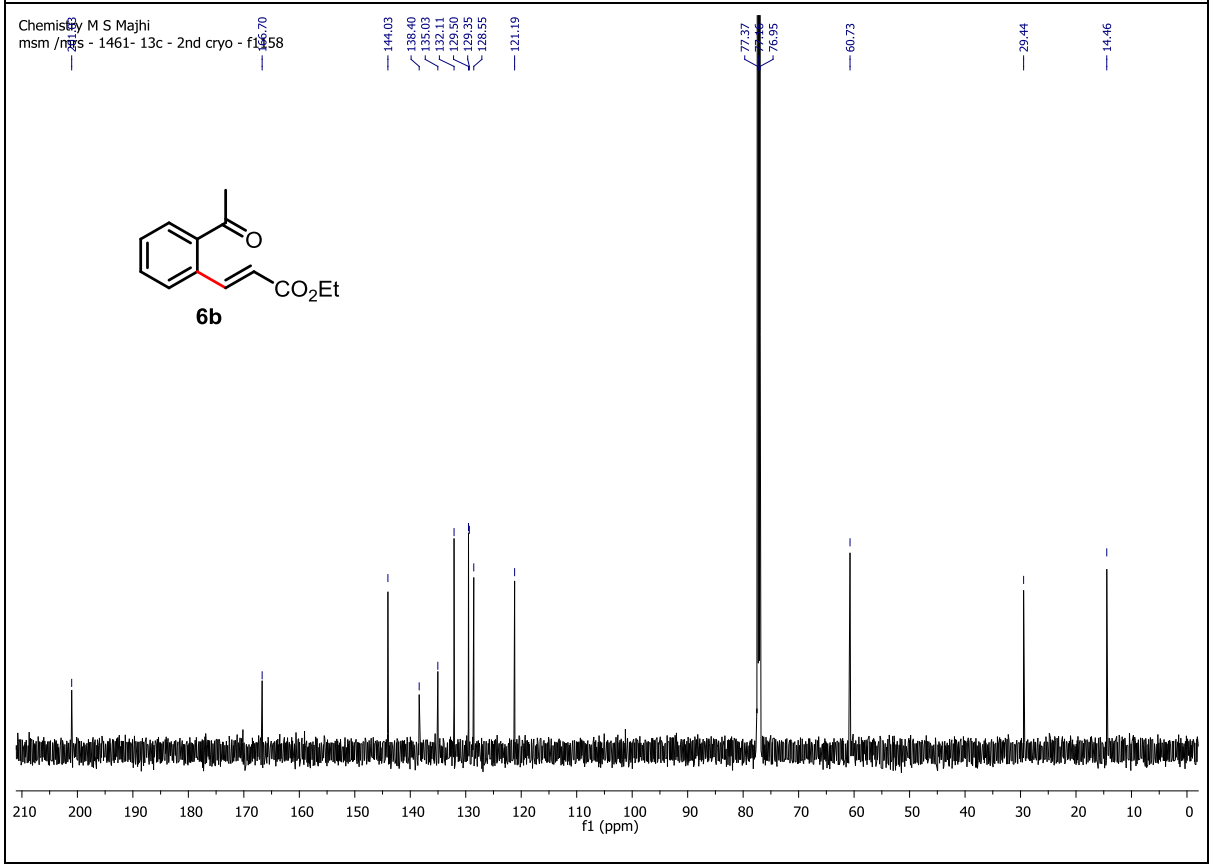

msm.mrs1429r
msm / mrs / 1429r -1l
7.556
7.535
7.487
7.469
7.382
7.291
7.260
7.127
7.056
6.972
6.913
6.882
6.876
6.860
6.854
6.758
6.720
5.714
5.671
5.354
5.326
3.889
O
Ph
MeO
5g
1.00
2.01
4.04
2.07
2.01
1.02
1.01
1.04
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

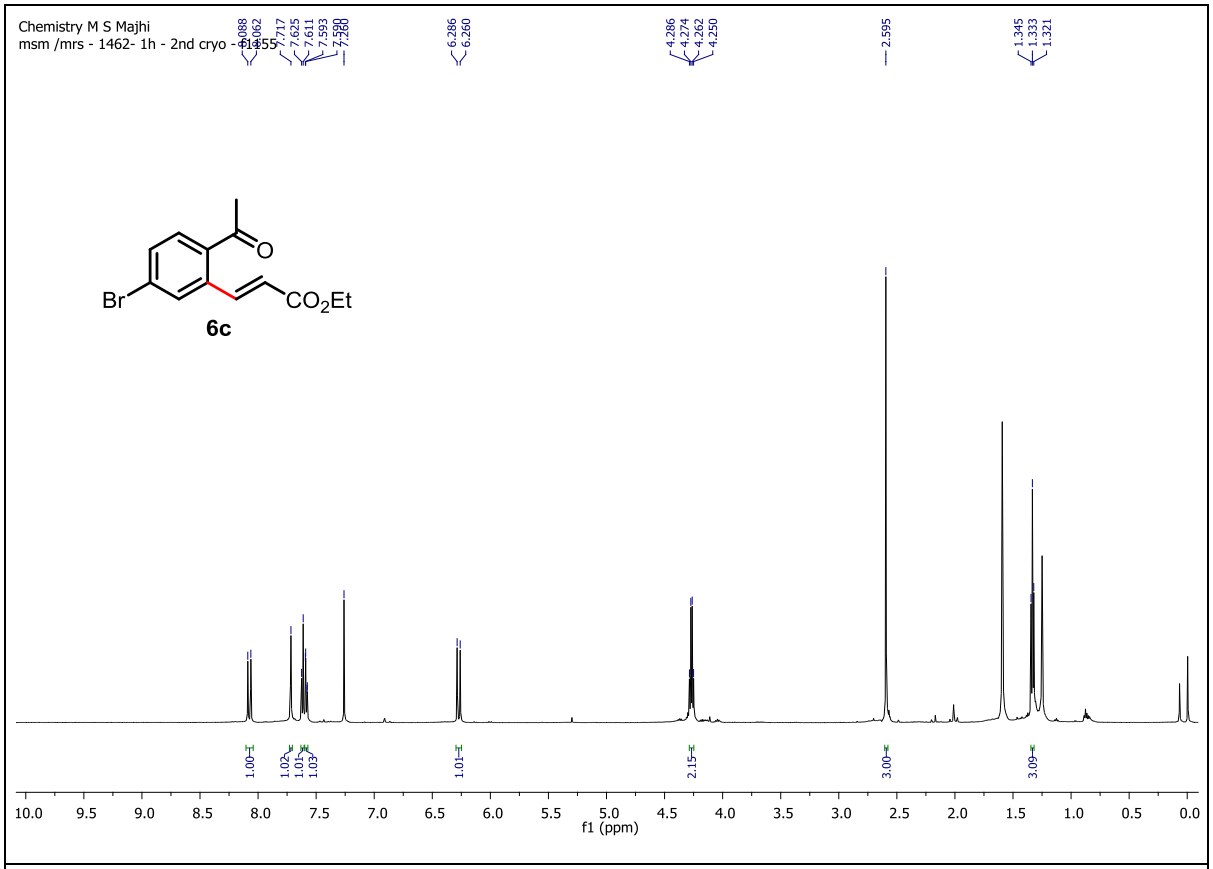

msmc.mrs1429r
msm / mrs / 1429r - 13
161.74
145.10
141.71
139.91
136.24
135.63
131.38
130.95
130.04
129.34
128.99
127.42
127.04
116.64
112.90
112.07
77.48
76.84
55.57
O
Ph
MeO
5g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

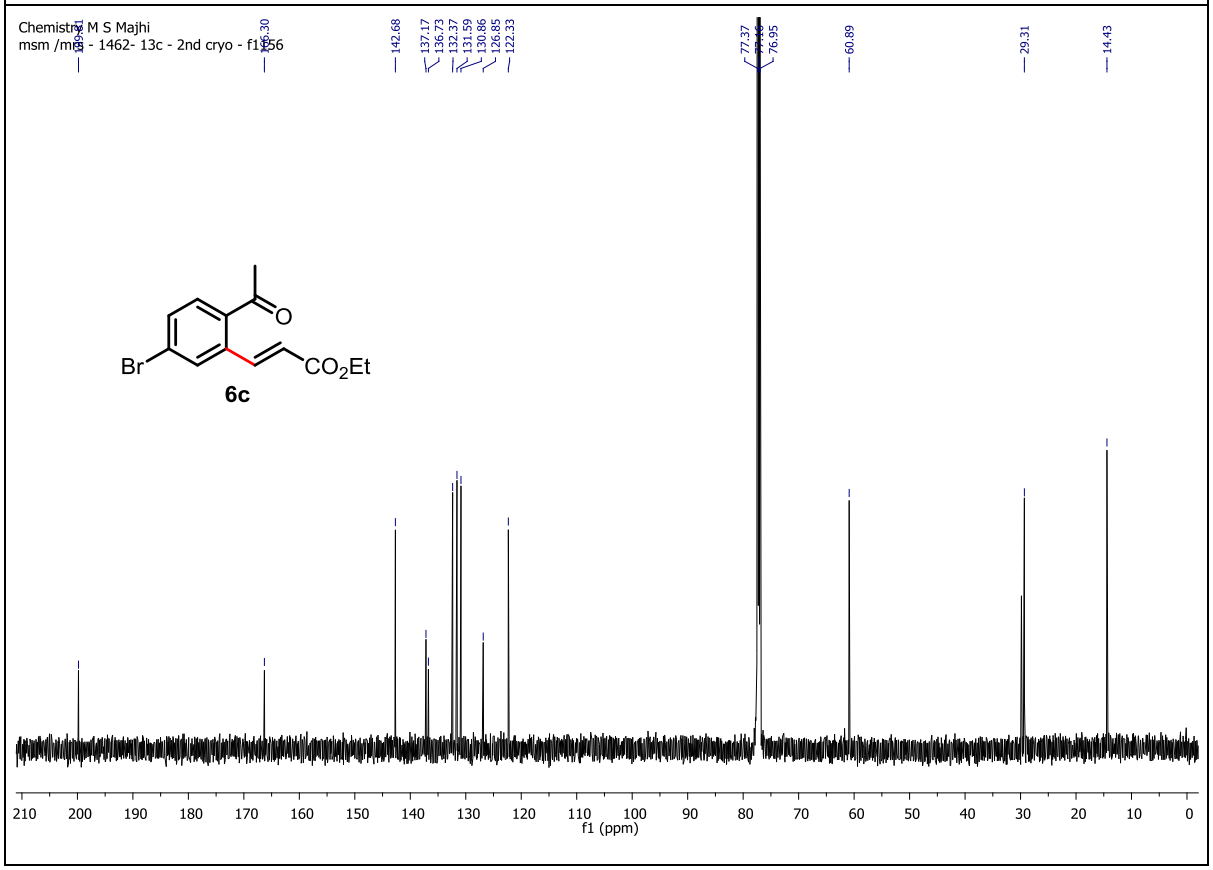

Chemistry M S Majhi
msm / mrs / 1365 - 1h - 2nd cryo - 9973
7.367
7.354
7.260
6.815
6.801
6.681
6.654
6.105
4.264
4.252
4.240
4.228
2.555
1.328
1.316
1.304
1.00
1.09
1.09
1.02
2.10
2.09
3.08
3.02
CO2Et
O
O
O
6a
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

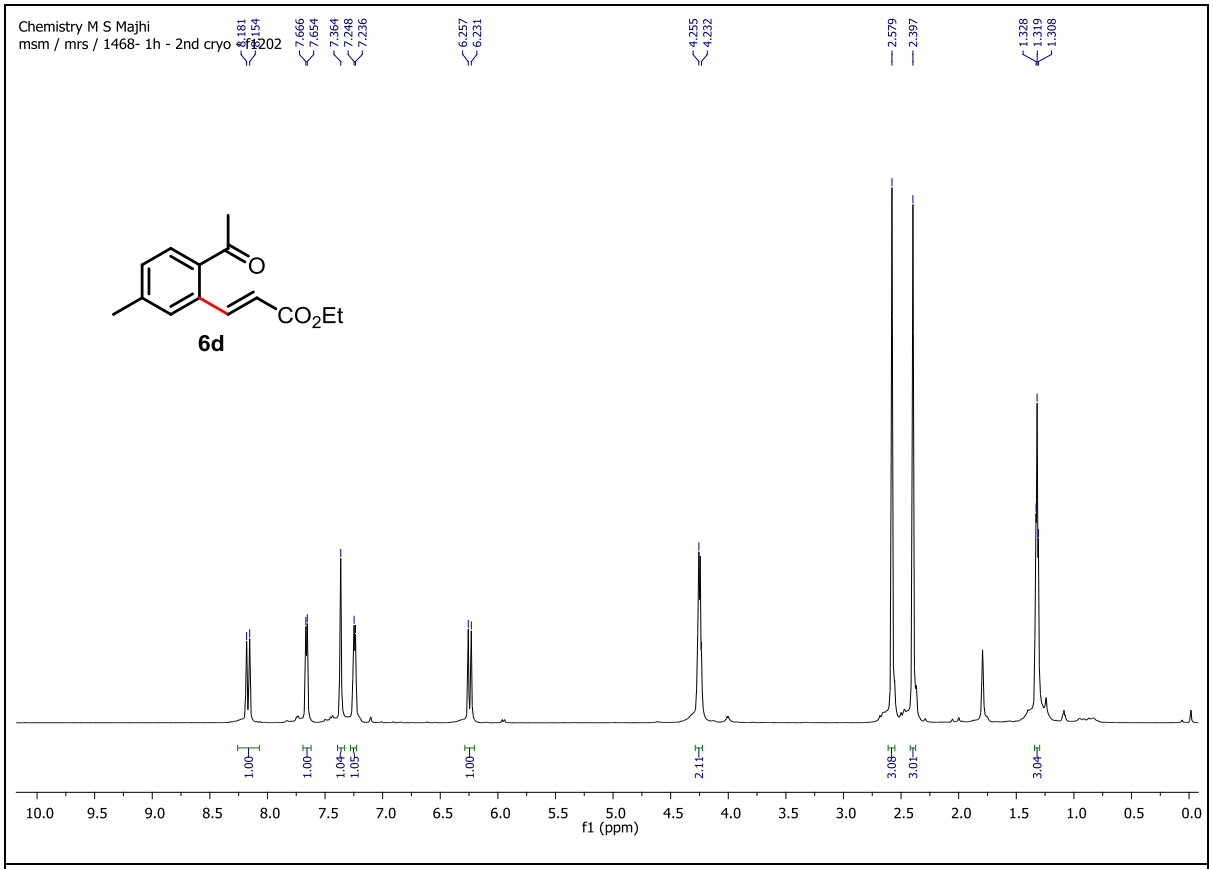

msmc.mrs1365R2
msm / mrs / 1365R2 - 13
167.20
150.69
147.70
137.67
132.87
125.48
124.05
117.31
107.95
102.23
77.48
76.84
60.63
29.36
14.44
CO2Et
O
O
O
6a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

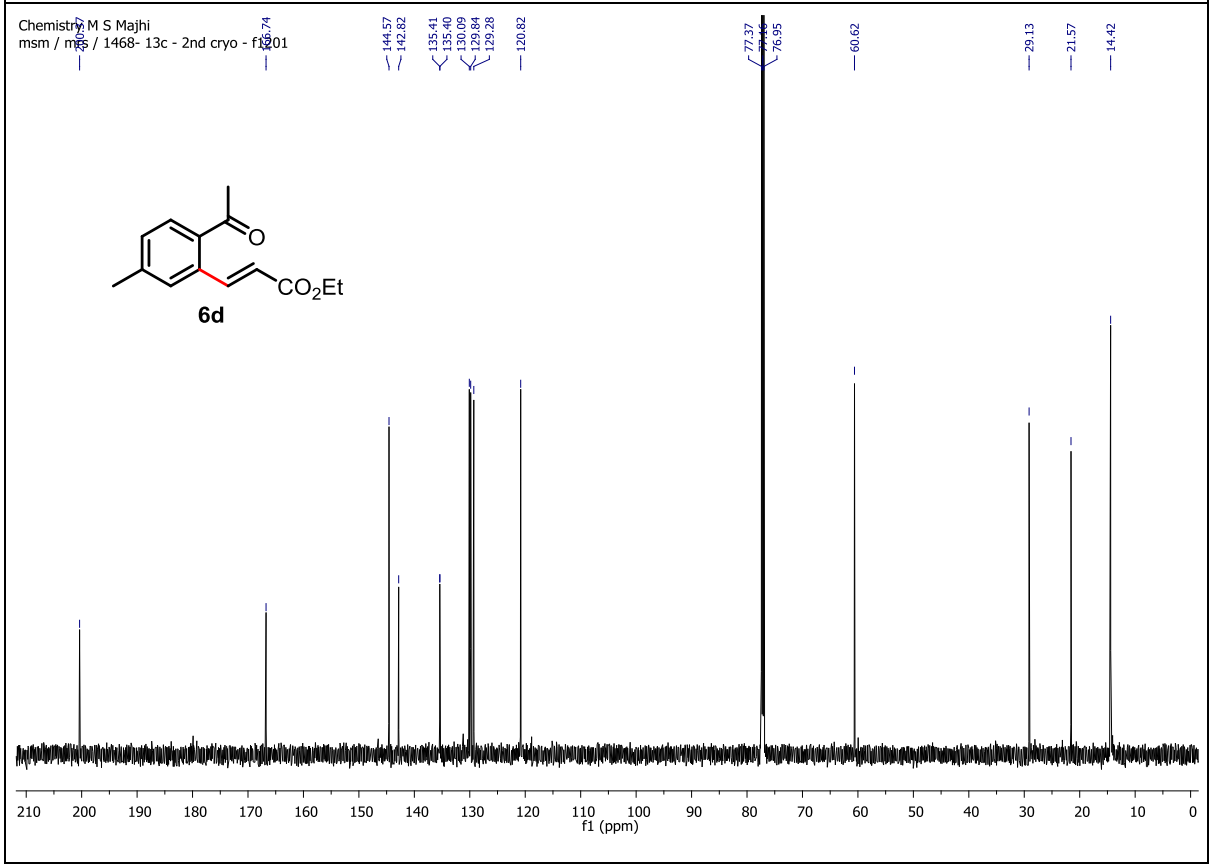

Chemistry M S Majhi
msm /mrs - 1461- 1h - 2nd cryo - f1157
7.747
7.734
7.593
7.580
7.528
7.516
7.503
7.469
7.456
7.444
6.296
6.270
4.285
4.273
4.262
4.250
2.619
1.347
1.335
1.323
O
CO2Et
6b
1.00
1.00
1.06
1.03
1.04
1.00
2.11
3.01
3.07
f1 (ppm)

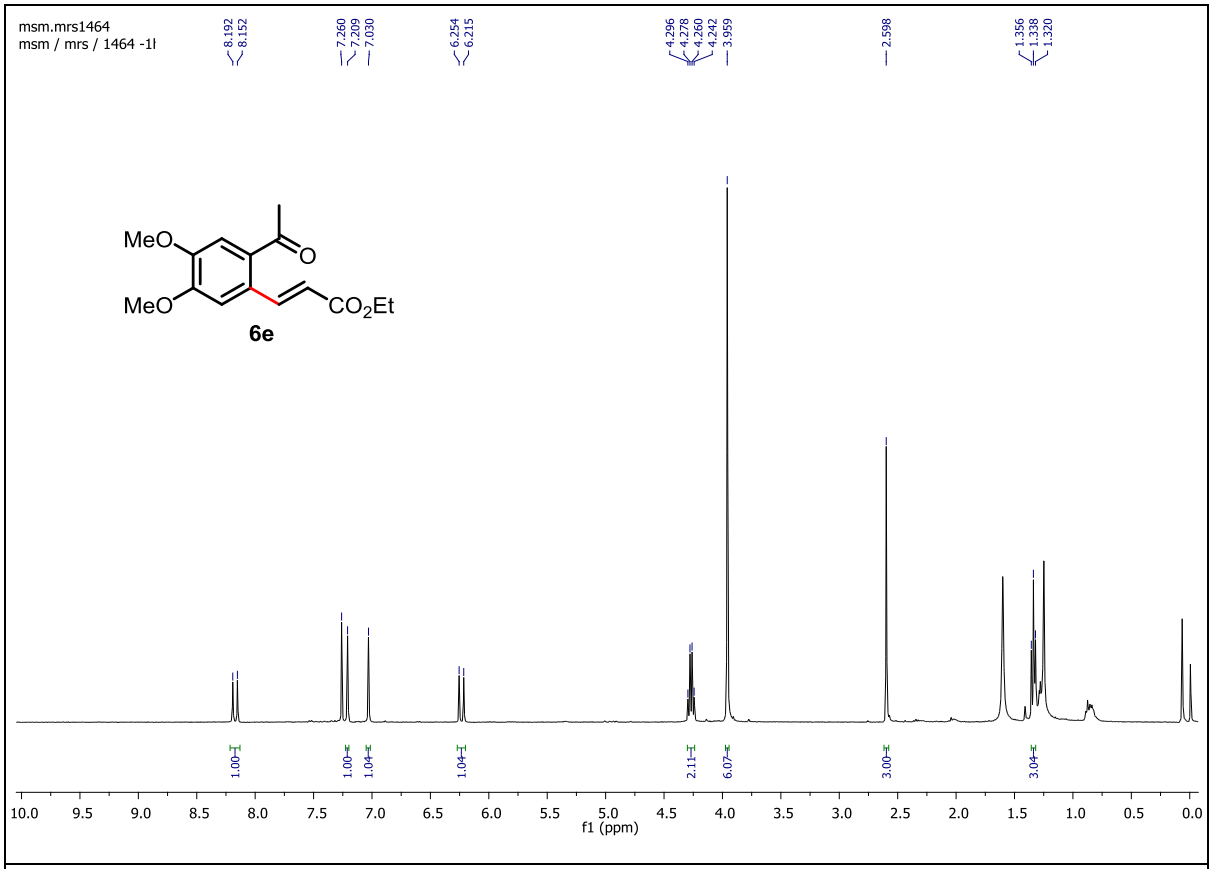

Chemistry M S Majhi
msm /mrs - 1461- 13c - 2nd cryo - f1158
144.03
138.40
135.03
132.11
129.50
129.35
128.55
121.19
77.37
76.95
60.73
29.44
14.46
O
CO2Et
6b
f1 (ppm)

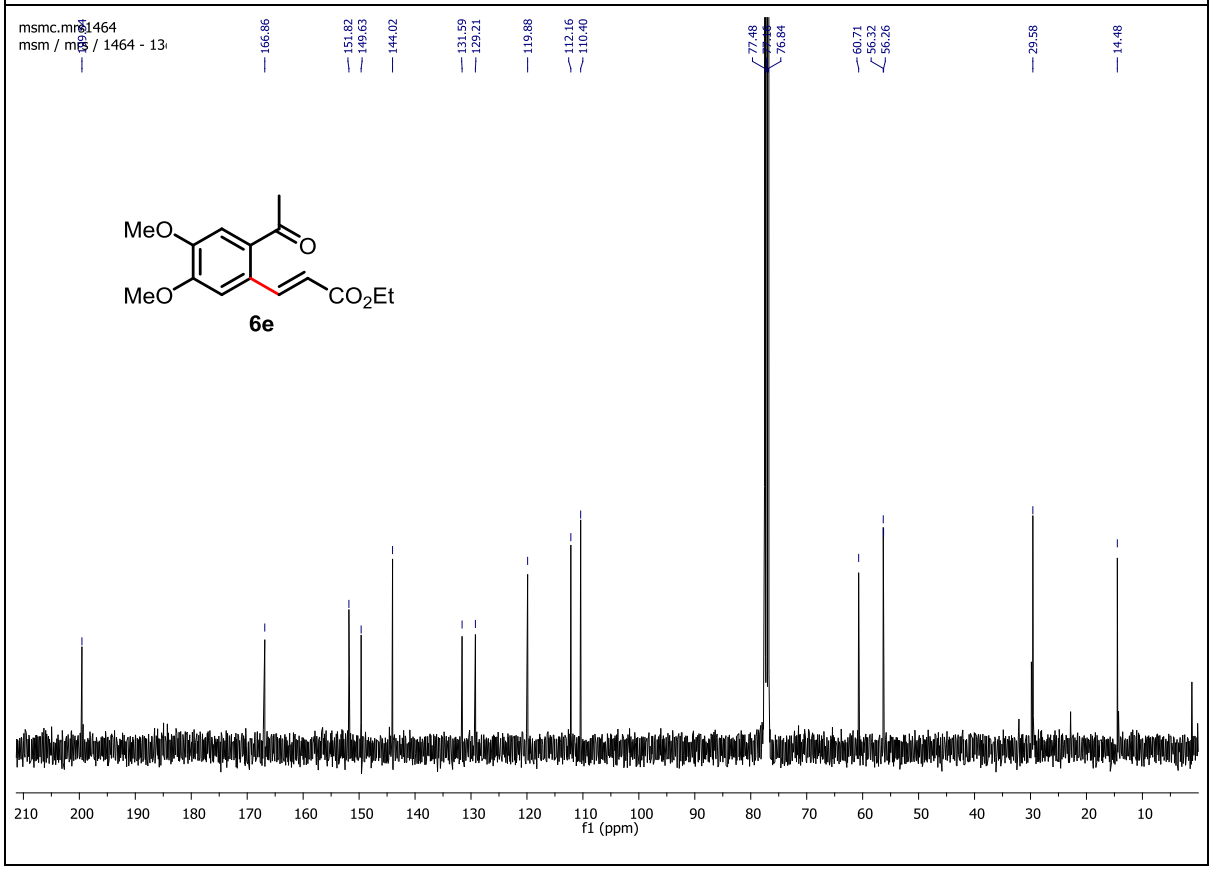

Chemistry M S Majhi
msm /mrs - 1462- 1h - 2nd cryo - f1455
8.088
8.062
7.717
7.625
7.611
7.593
7.590
7.280
6.286
6.260
4.286
4.274
4.262
4.250
2.595
1.345
1.333
1.321
Br
O
CO2Et
6c
1.00
1.02
1.01
1.03
1.01
2.15
3.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

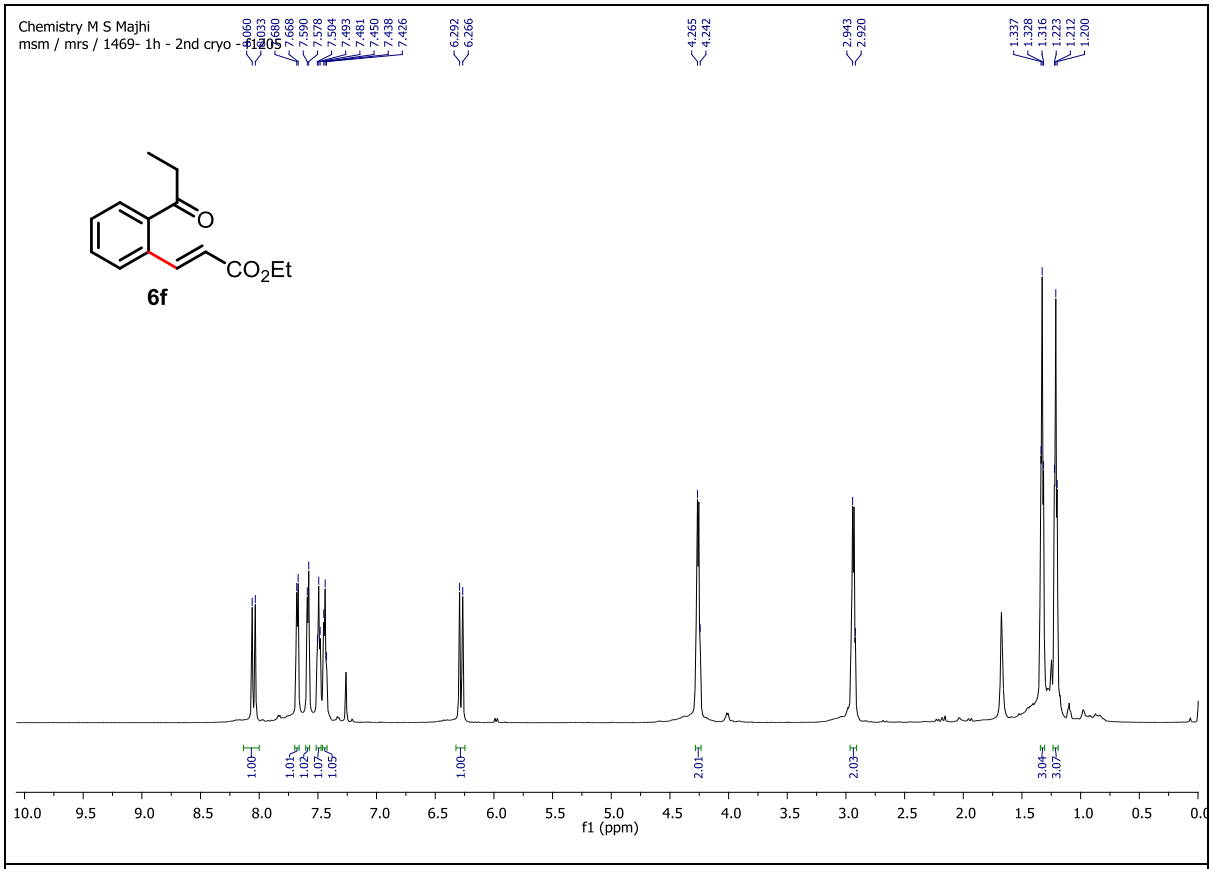

Chemistry M S Majhi
msm /mrs - 1462- 13c - 2nd cryo - f1456
169.41
166.30
142.68
137.17
136.73
132.37
131.59
130.86
126.85
122.33
77.37
77.16
76.95
60.89
29.31
14.43
Br
O
CO2Et
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

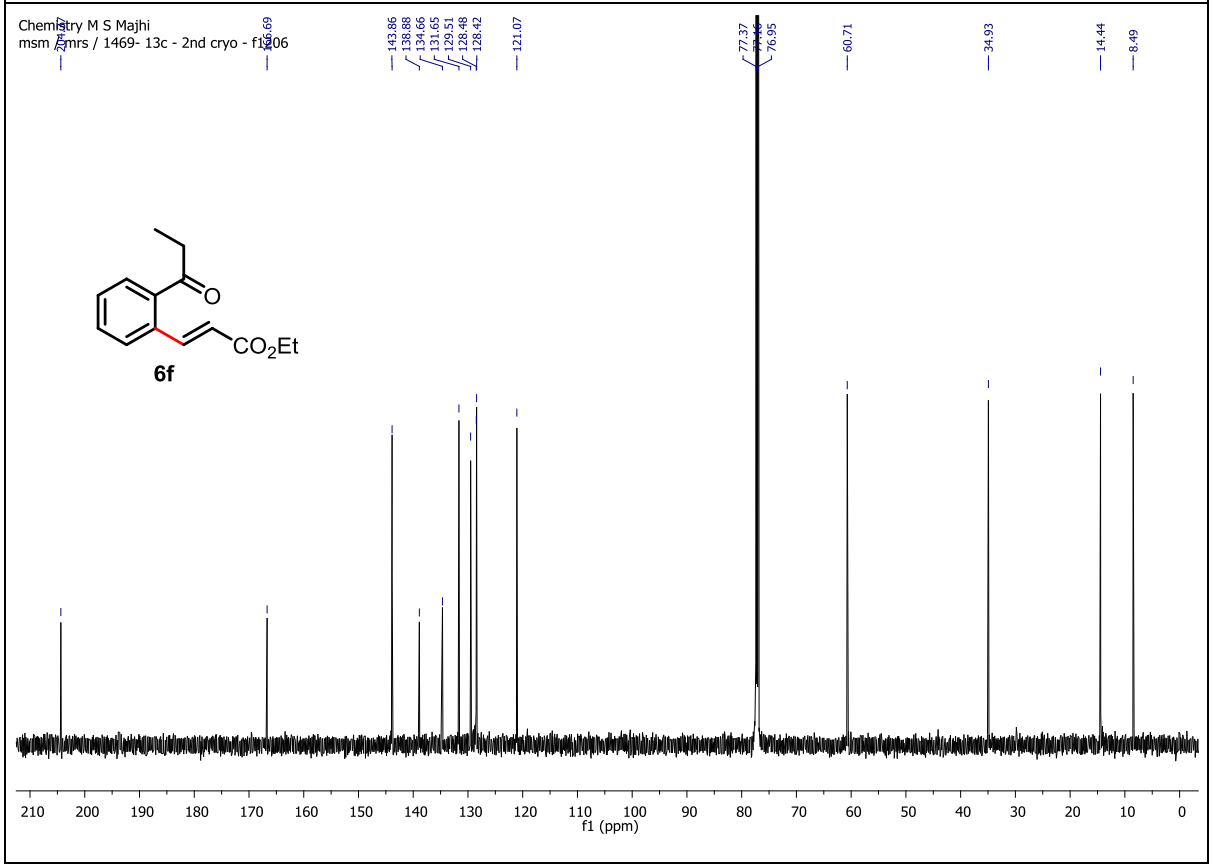

Chemistry M S Majhi
msm / mrs / 1468- 1h - 2nd cryo - f1202
7.666
7.654
7.364
7.248
7.236
6.257
6.231
4.255
4.232
2.579
2.397
1.328
1.319
1.308
O
CO2Et
6d
1.00
1.00
1.04
1.05
1.00
2.11
3.08
3.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

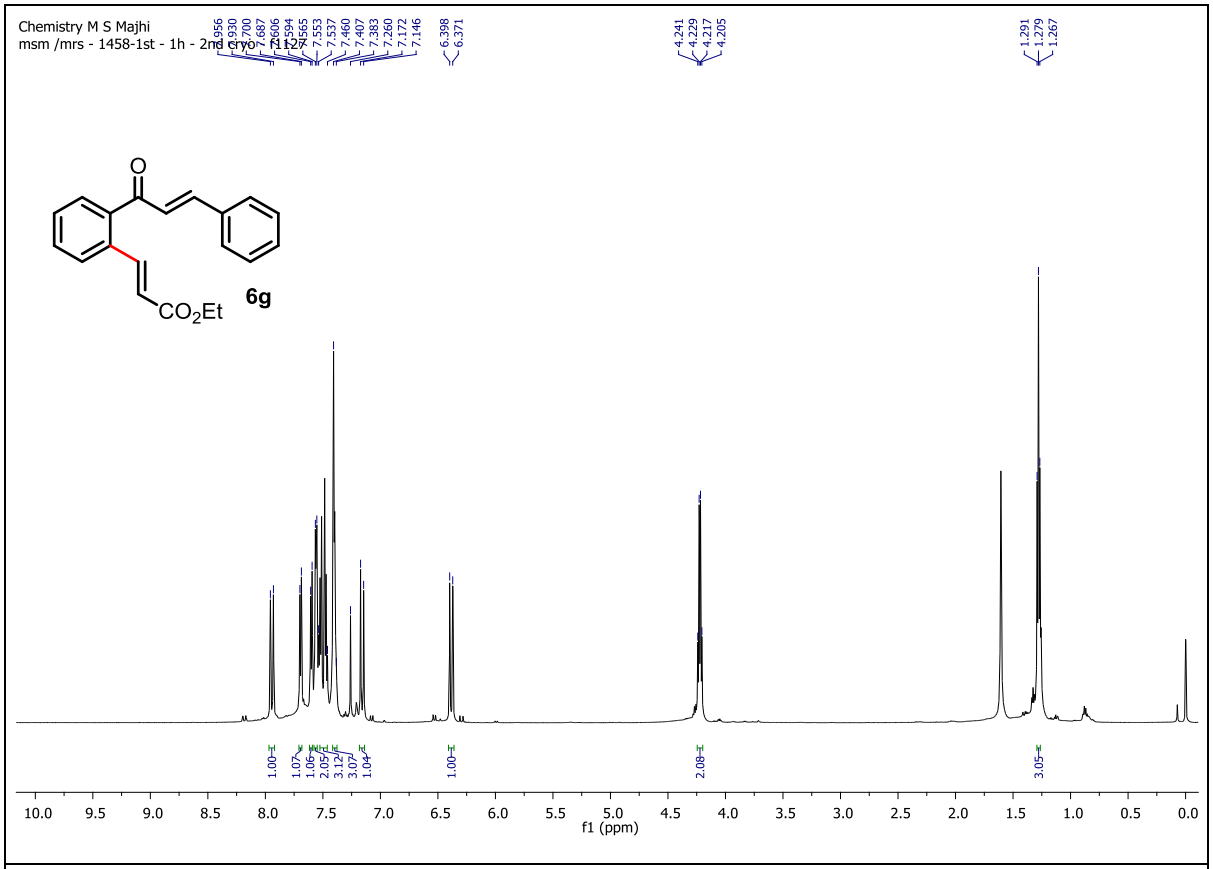

Chemistry M S Majhi
msm / mrs / 1468- 13c - 2nd cryo - f1201
166.74
144.57
142.82
135.41
135.40
130.09
129.84
129.28
120.82
77.37
76.95
60.62
29.13
21.57
14.42
O
CO2Et
6d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

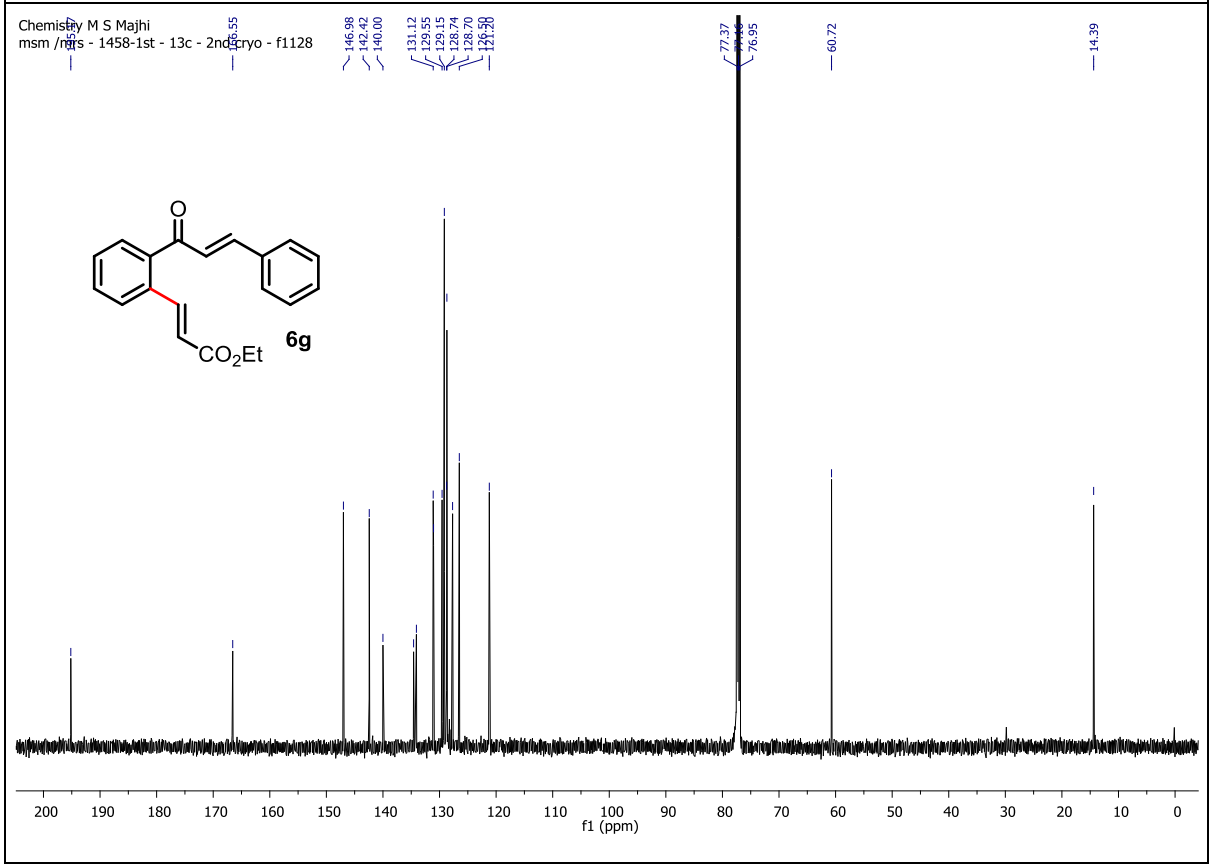

msm.mrs1464
8.192
8.152
7.260
7.209
7.030
6.254
6.215
4.296
4.278
4.260
4.242
3.959
2.598
1.356
1.338
1.320
MeO
MeO
O
CO2Et
6e
1.00
1.00
1.04
1.04
2.11
6.07
3.00
3.04
f1 (ppm)

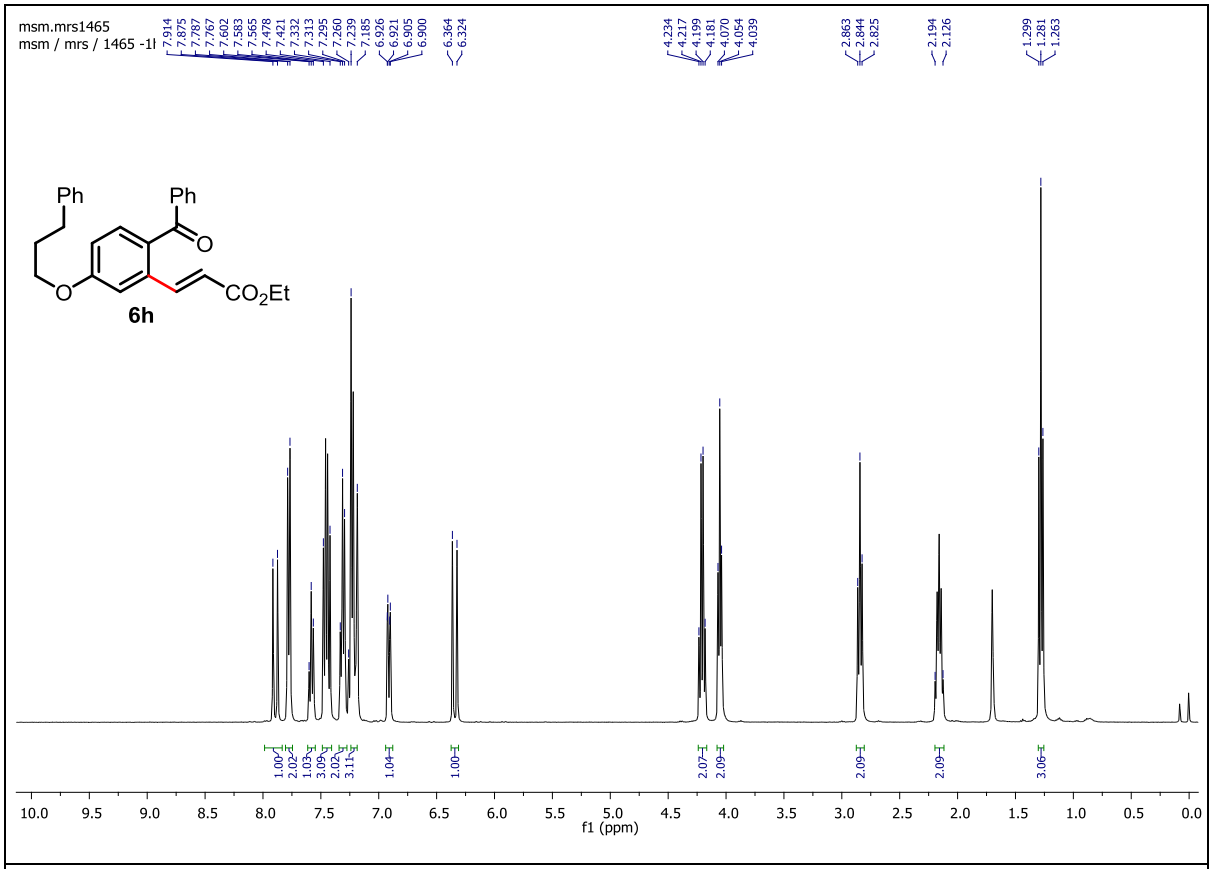

msmc.mrs1464
166.86
151.82
149.63
144.02
131.59
129.21
119.88
112.16
110.40
77.48
76.84
60.71
56.32
56.26
29.58
14.48
MeO
MeO
O
CO2Et
6e
f1 (ppm)

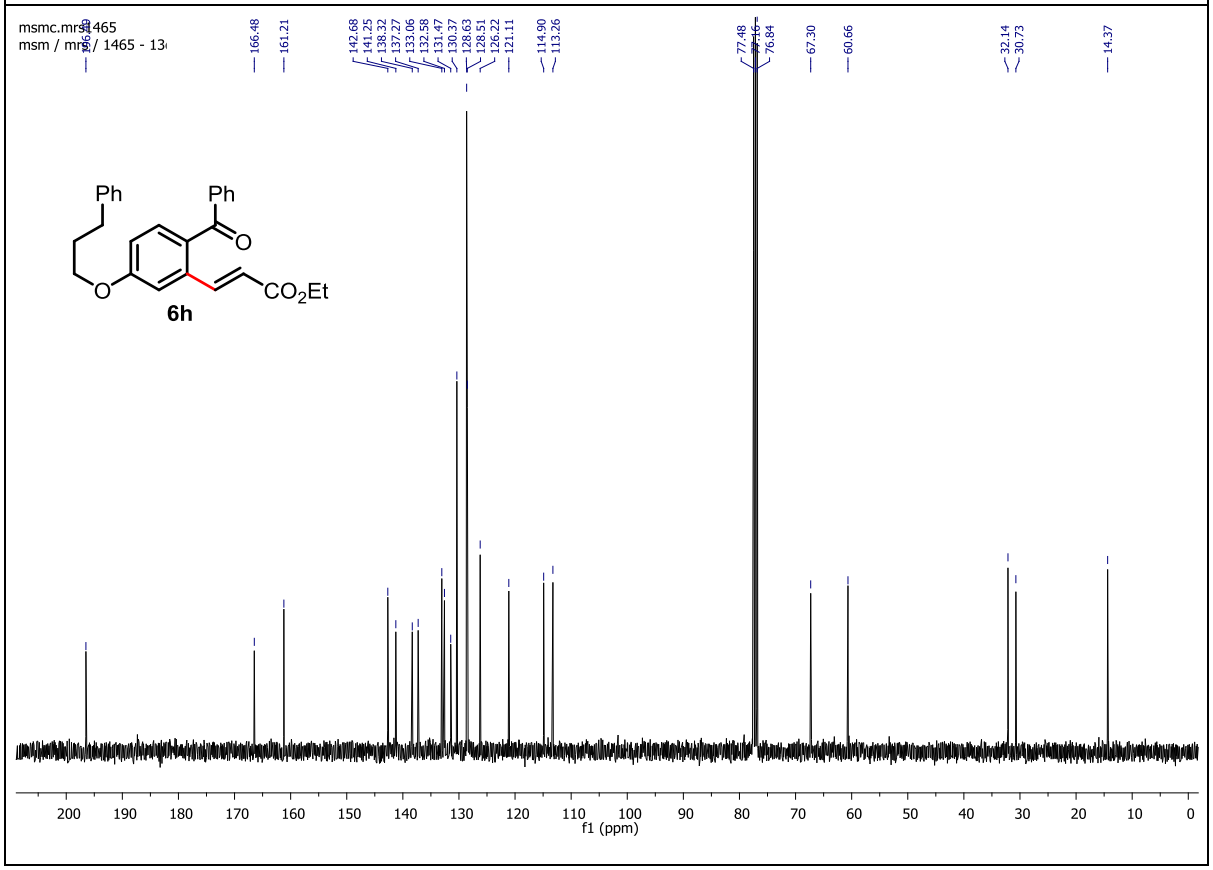

Chemistry M S Majhi
msm / mrs / 1469- 1h - 2nd cryo - 41205
8.060
8.033
7.680
7.668
7.590
7.578
7.504
7.493
7.481
7.450
7.438
7.426
6.292
6.266
4.265
4.242
2.943
2.920
1.337
1.328
1.316
1.223
1.212
1.200
O
CO2Et
6f
1.00
1.01
1.02
1.07
1.05
1.00
2.01
2.03
3.04
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 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)

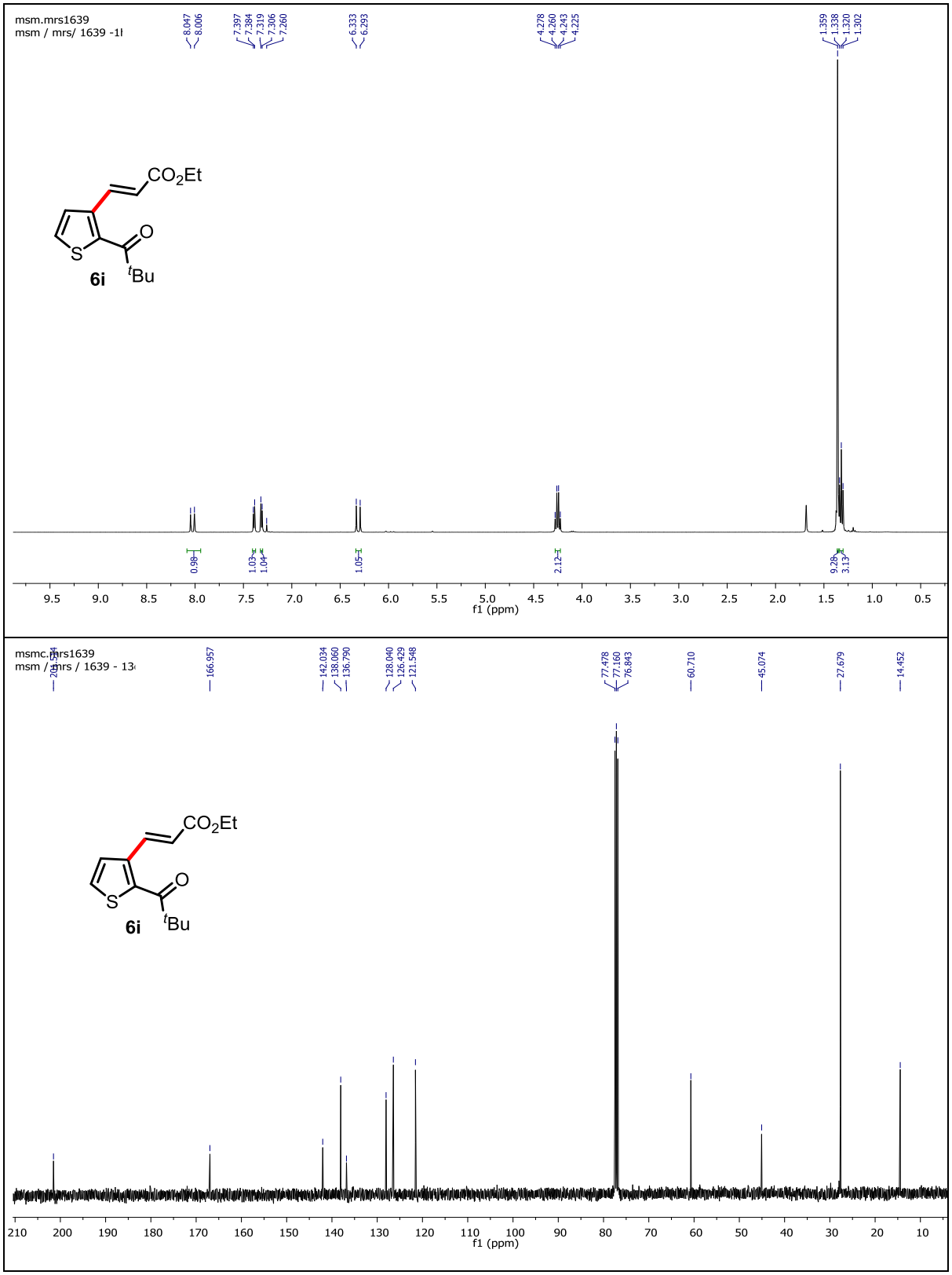

Chemistry M S Majhi
msm / mrs / 1469- 13c - 2nd cryo - f1206
174.69
166.69
143.86
138.88
134.66
131.65
129.51
128.48
128.42
121.07
77.37
77.16
76.95
60.71
34.93
14.44
8.49
O
CO2Et
6f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

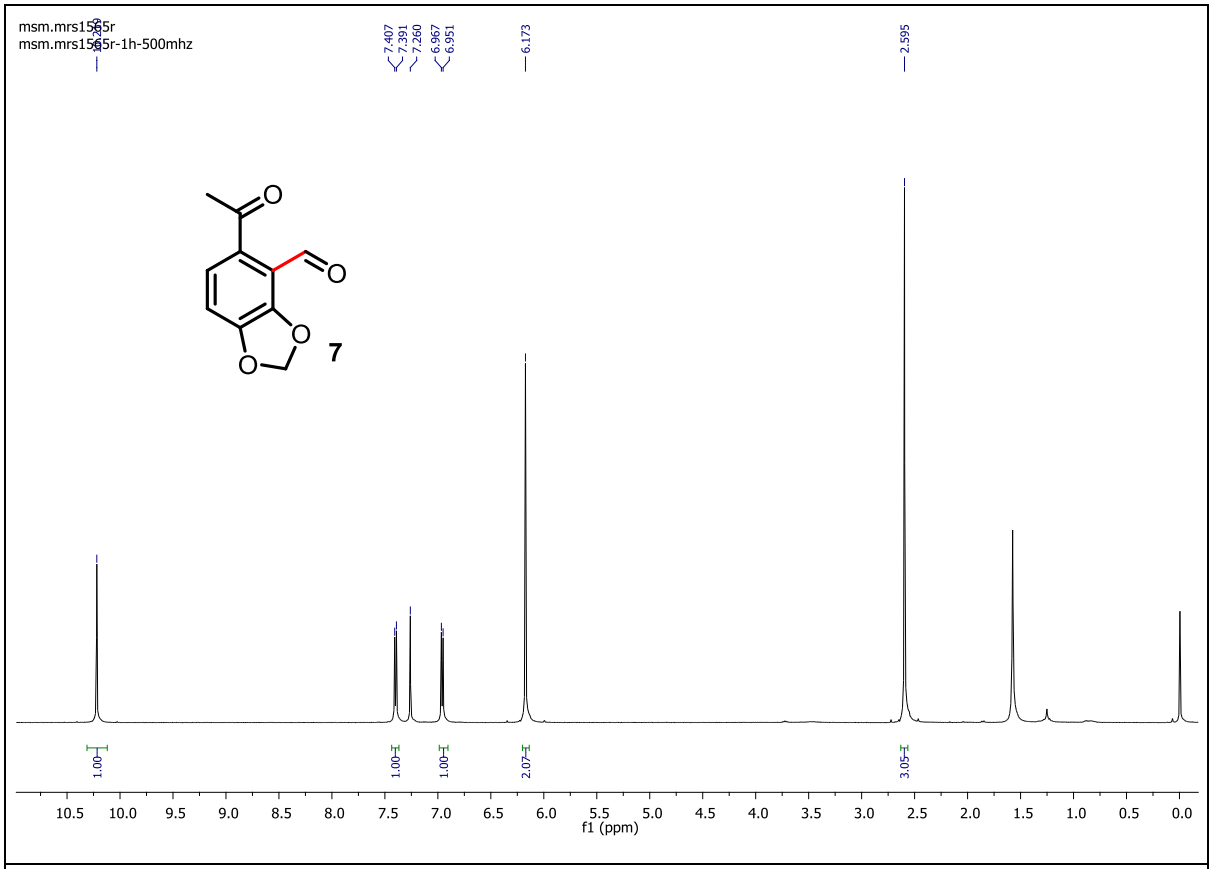

Chemistry M S Majhi
msm /mrs - 1458-1st - 1h - 2nd cryo - f1127
7.956
7.930
7.700
7.687
7.606
7.594
7.565
7.553
7.537
7.460
7.407
7.383
7.260
7.172
7.146
6.398
6.371
4.241
4.229
4.217
4.205
1.291
1.279
1.267
O
CO2Et
6g
1.00
1.07
1.06
2.05
3.12
3.07
1.04
1.00
2.08
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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)

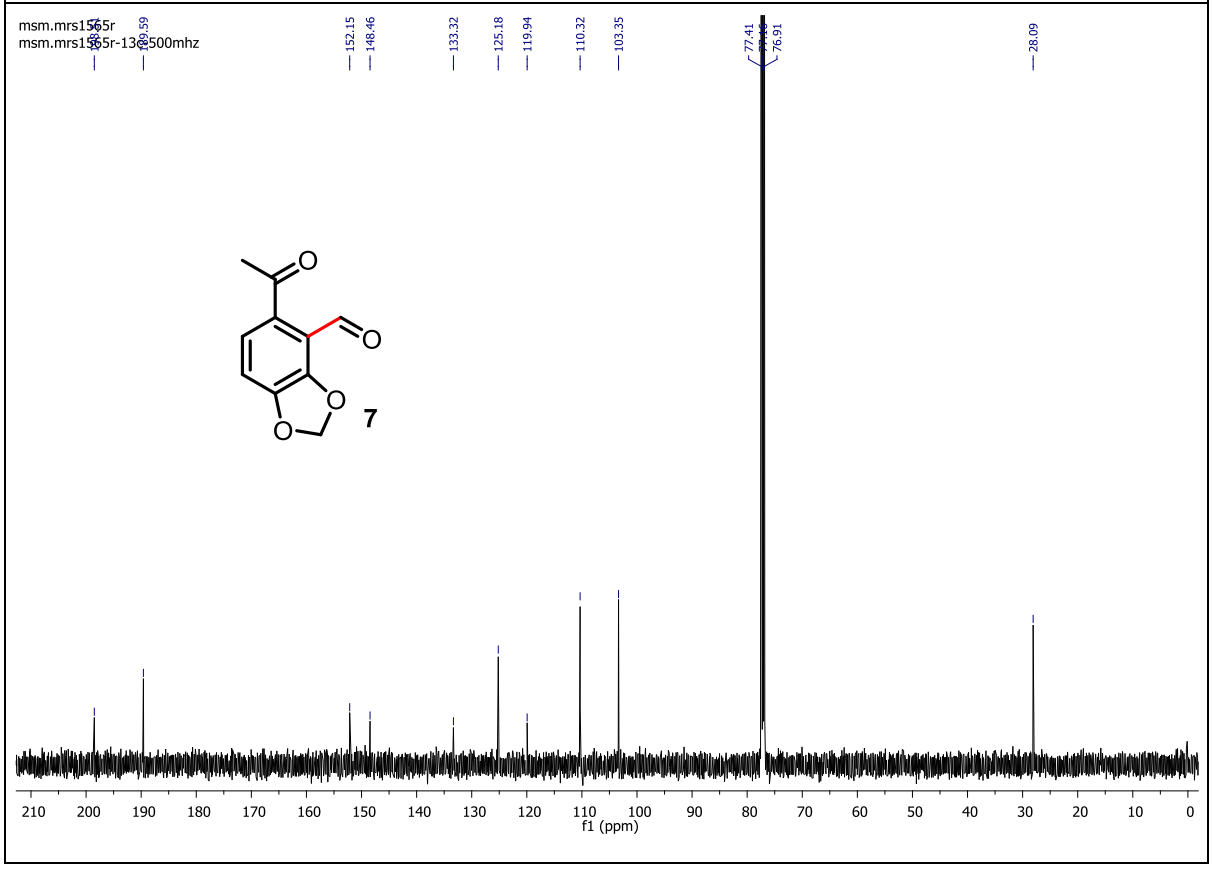

Chemistry M S Majhi
msm /mrs - 1458-1st - 13c - 2nd cryo - f1128
195.57
168.55
146.98
142.42
140.00
131.12
129.55
129.15
128.74
128.70
126.50
121.20
77.37
76.95
60.72
14.39
O
CO2Et
6g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

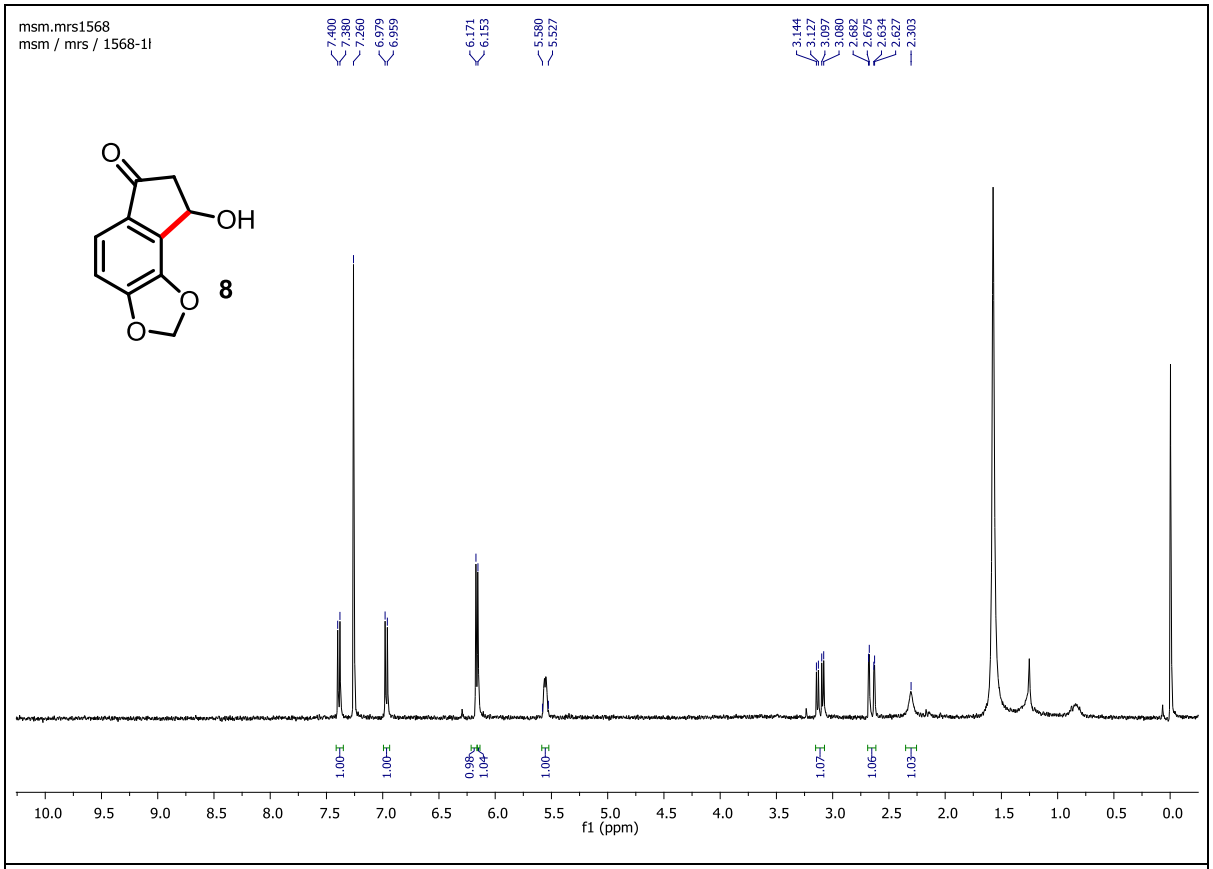

msm.mrs1465
msm / mrs / 1465 -1l
7.914
7.875
7.787
7.767
7.602
7.583
7.565
7.478
7.421
7.332
7.313
7.295
7.260
7.239
7.185
6.926
6.921
6.905
6.900
6.364
6.324
4.234
4.217
4.199
4.181
4.070
4.054
4.039
2.863
2.844
2.825
2.194
2.126
1.299
1.281
1.263
Ph
Ph
O
O
CO2Et
6h
1.00
2.02
1.03
3.09
2.02
3.11
1.04
1.00
2.07
2.09
2.09
2.09
3.06
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)

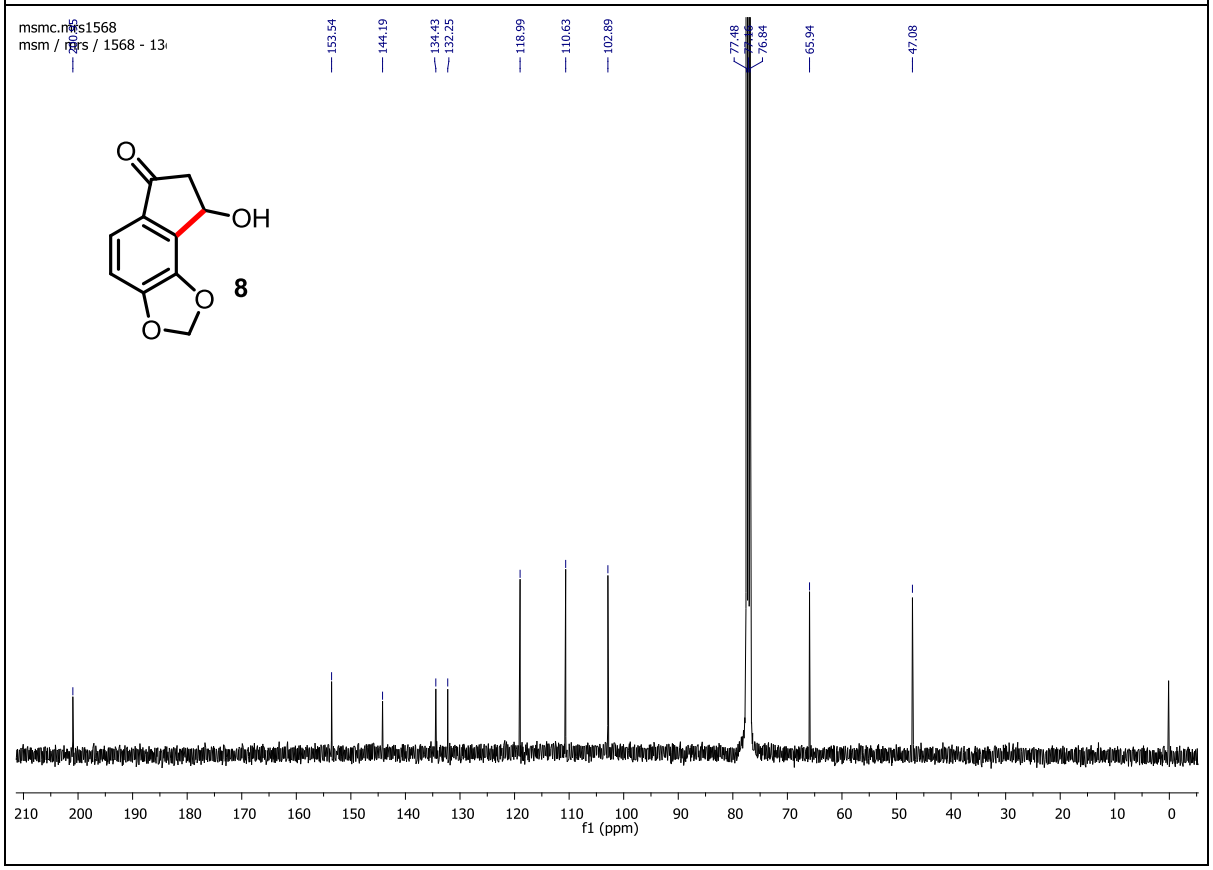

msmc.mrs1465
msm / mrs / 1465 - 13
166.48
161.21
142.68
141.25
138.32
137.27
133.06
132.58
131.47
130.37
128.63
128.51
126.22
121.11
114.90
113.26
77.48
77.16
76.84
67.30
60.66
32.14
30.73
14.37
Ph
Ph
O
O
CO2Et
6h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

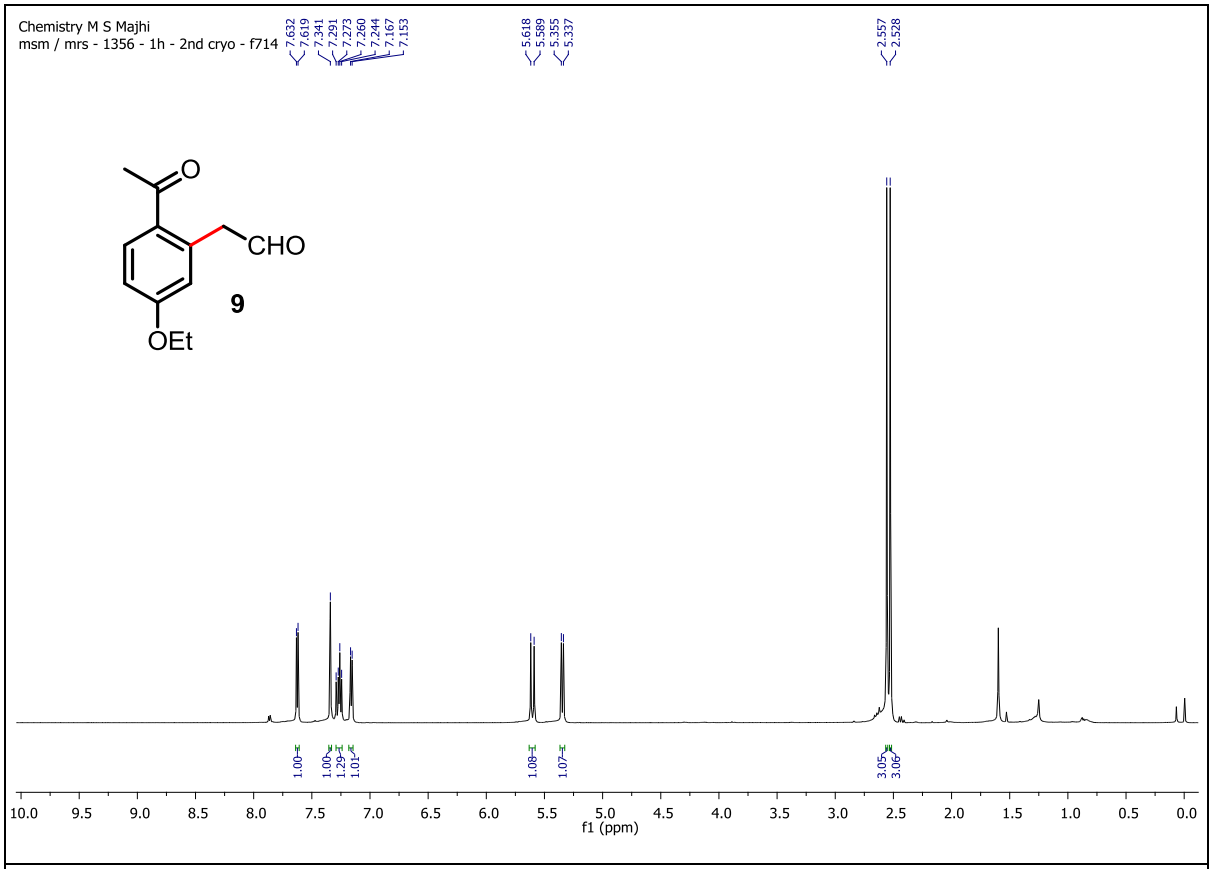

msm.mrs1639
msm / mrs/ 1639 -1
8.047
8.006
7.397
7.384
7.319
7.306
7.260
6.333
6.293
4.278
4.260
4.243
4.225
1.359
1.338
1.320
1.302
CO2Et
O
S
6i
tBu
0.98
1.03
1.04
1.05
2.12
9.28
3.13
f1 (ppm)
msmc.mrs1639
msm / mrs / 1639 - 13
166.957
142.034
138.060
136.790
128.040
126.429
121.548
77.478
77.160
76.843
60.710
45.074
27.679
14.452
CO2Et
O
S
6i
tBu
f1 (ppm)

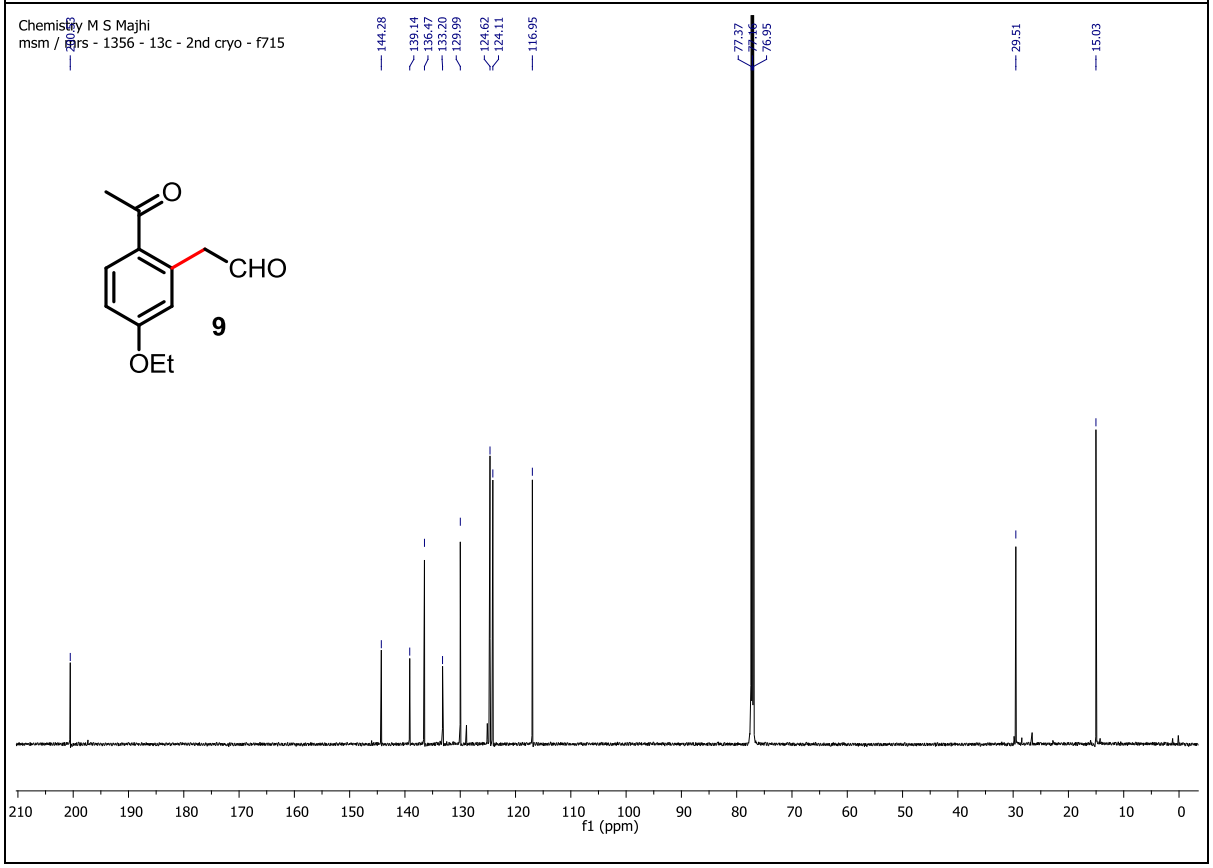

msm.mrs1565r
msm.mrs1565r-1h-500mhz
7.407
7.391
7.260
6.967
6.951
6.173
2.595
7
1.00
1.00
1.00
2.07
3.05
f1 (ppm)

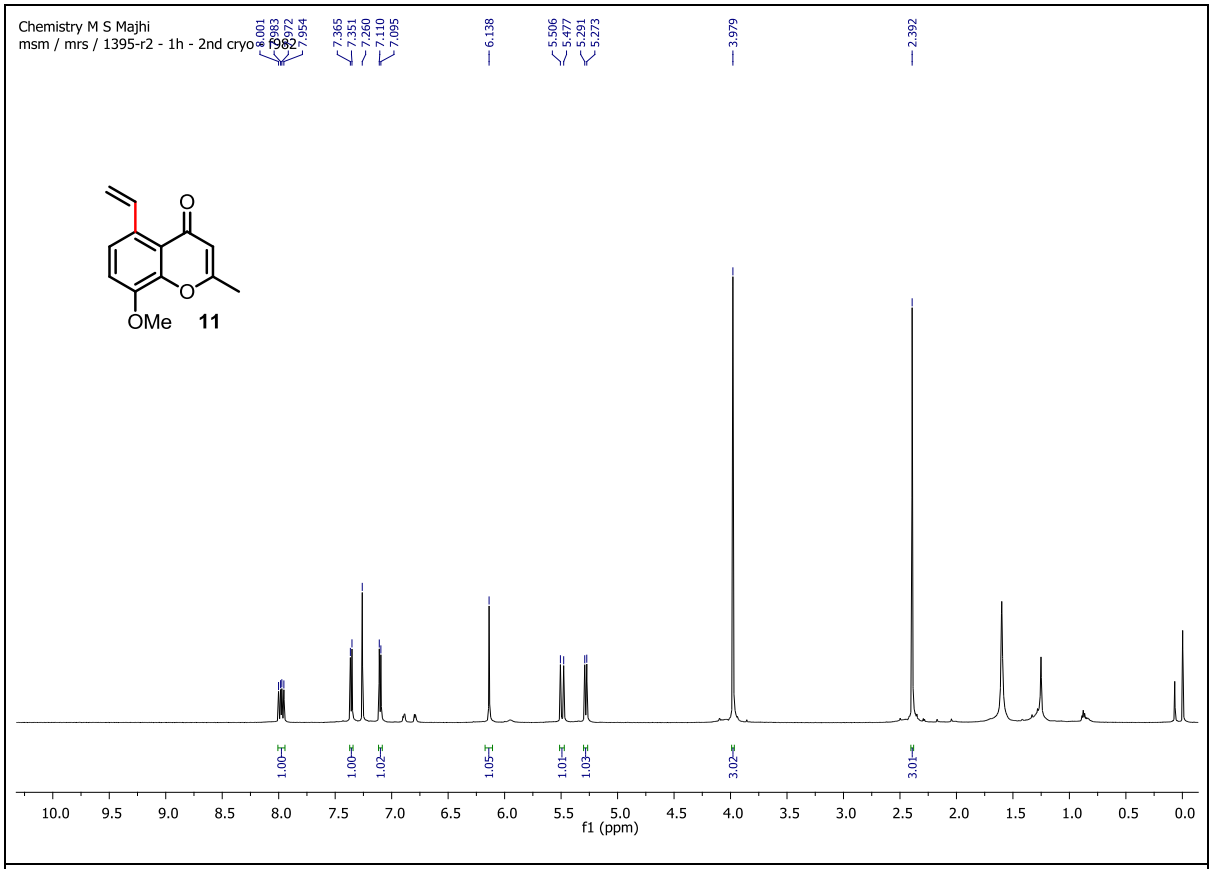

msm.mrs1565r
msm.mrs1565r-13c-500mhz
152.15
148.46
133.32
125.18
119.94
110.32
103.35
77.41
76.91
28.09
7
f1 (ppm)

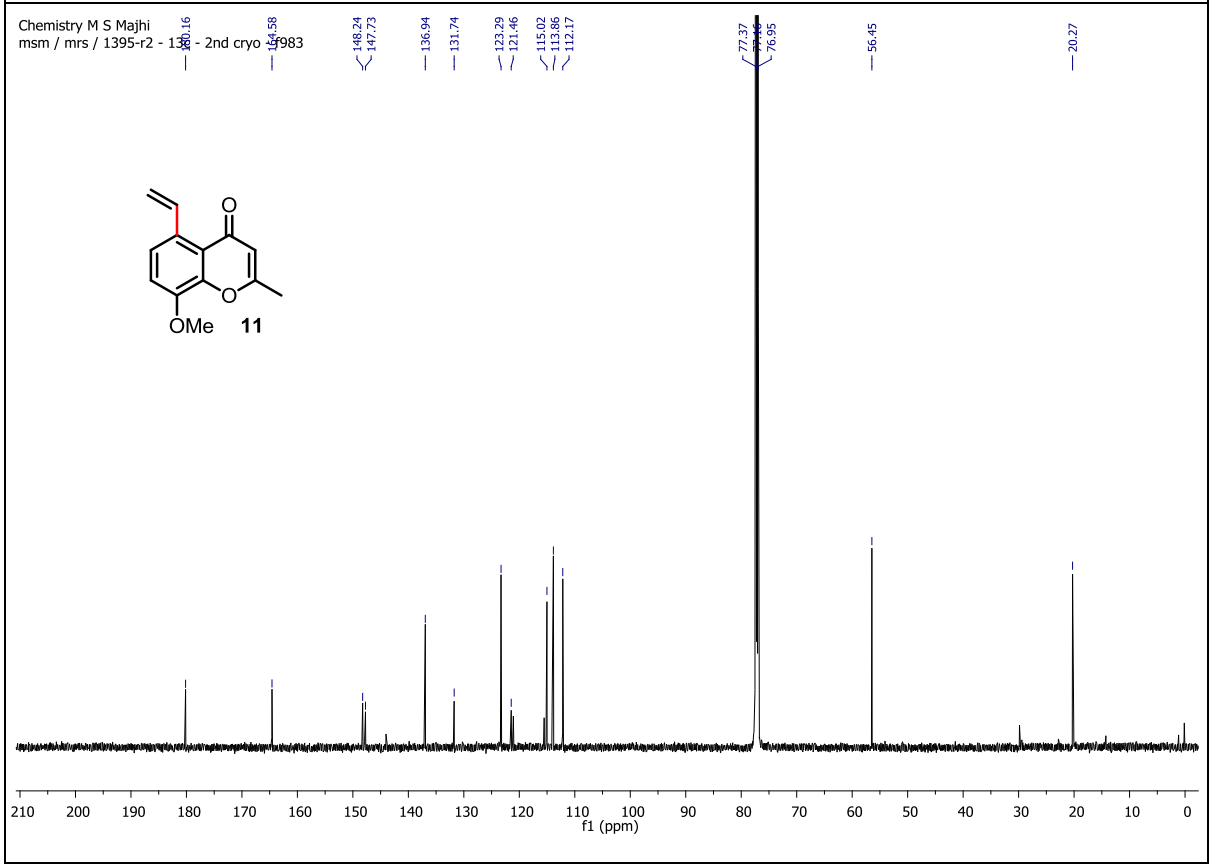

msm.mrs1568
msm / mrs / 1568-1l
7.400
7.380
7.260
6.979
6.959
6.171
6.153
5.580
5.527
3.144
3.127
3.097
3.080
2.682
2.675
2.634
2.627
2.303
OH
O
O
O
8
1.00
1.00
0.98
1.04
1.00
1.07
1.06
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

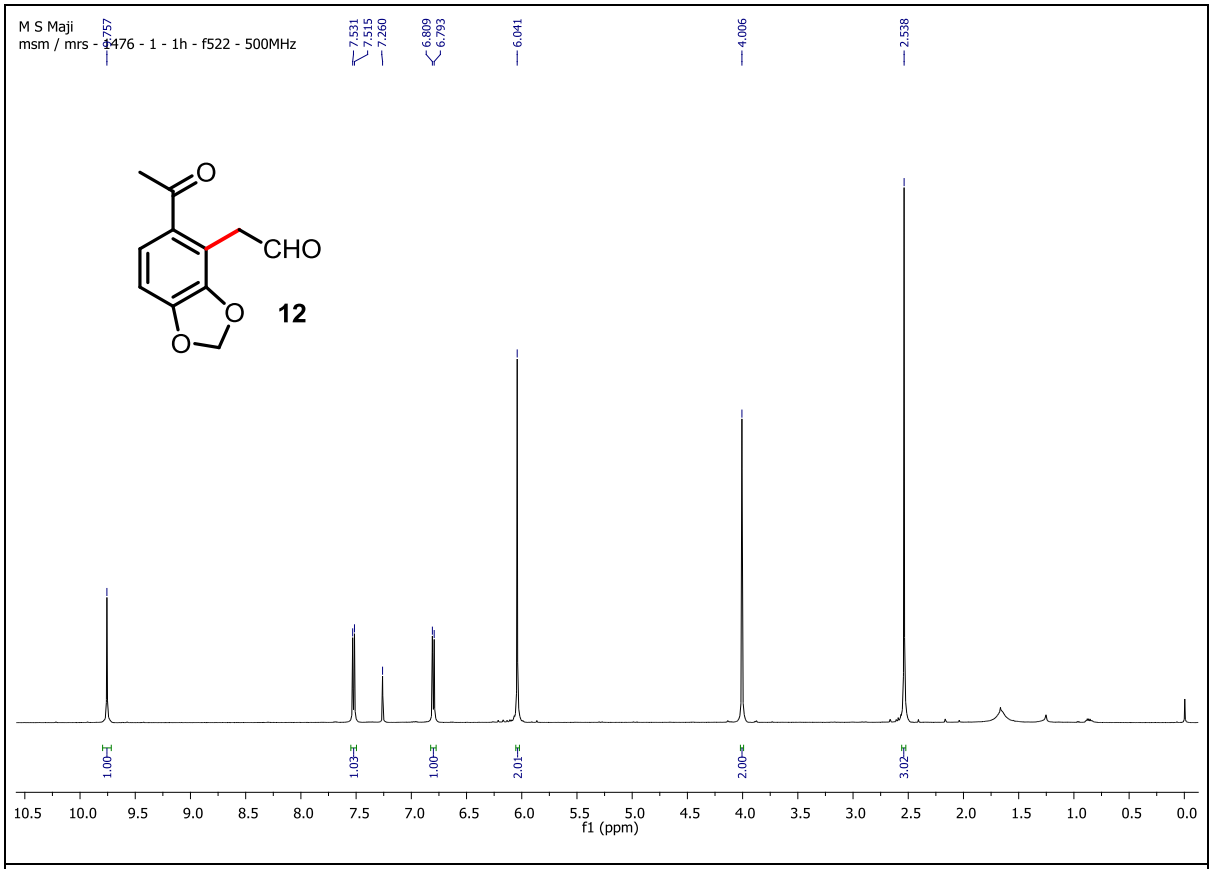

msmc.mrs1568
msm / mrs / 1568 - 13
153.54
144.19
134.43
132.25
118.99
110.63
102.89
77.48
76.84
65.94
47.08
OH
O
O
O
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

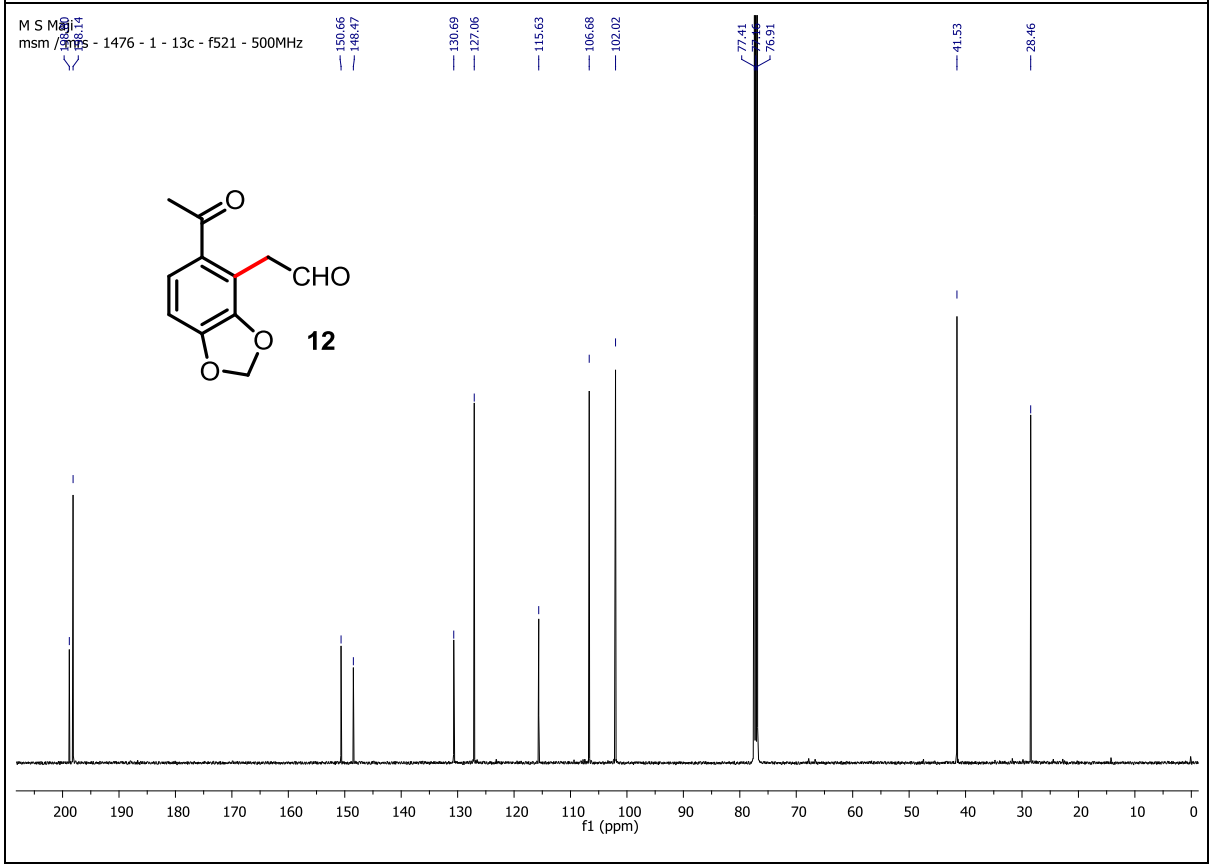

Chemistry M S Majhi
msm / mrs - 1356 - 1h - 2nd cryo - f714
7.632
7.619
7.341
7.291
7.273
7.260
7.244
7.167
7.153
5.618
5.589
5.355
5.337
2.557
2.528
O
CHO
9
OEt
1.00
1.00
1.29
1.01
1.08
1.07
3.05
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

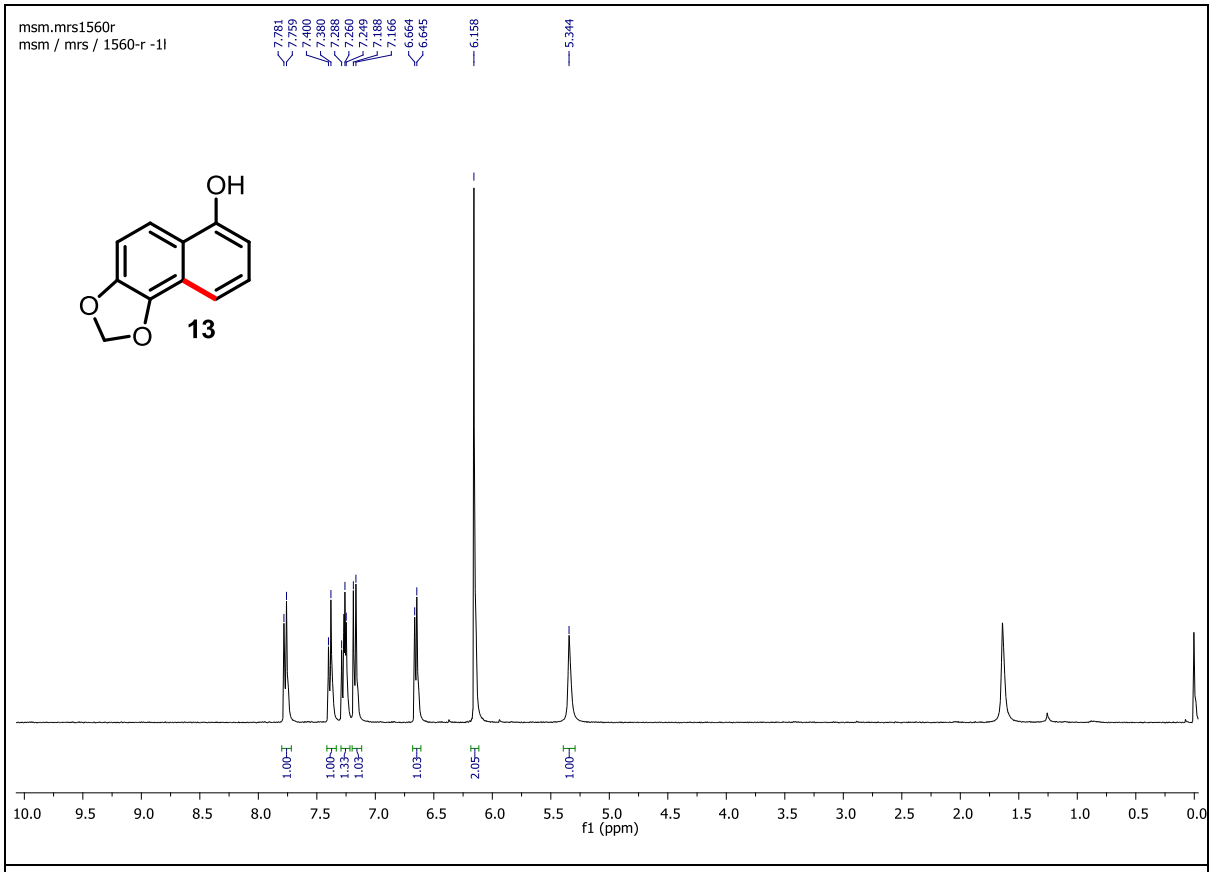

Chemistry M S Majhi
msm / mrs - 1356 - 13c - 2nd cryo - f715
144.28
139.14
136.47
133.20
129.99
124.62
124.11
116.95
77.37
76.95
29.51
15.03
O
CHO
9
OEt
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

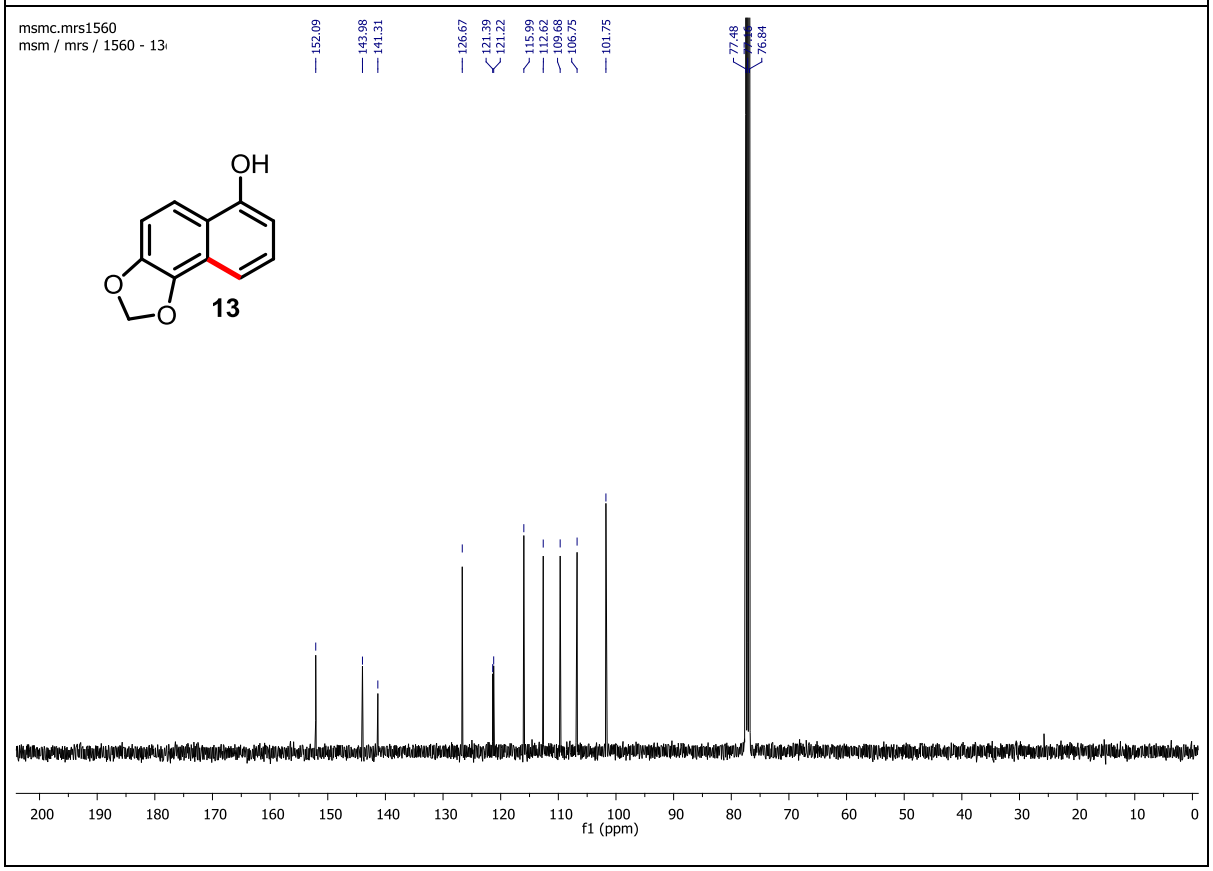

Chemistry M S Majhi
msm / mrs / 1395-r2 - 1h - 2nd cryo - f982
8.001
7.983
7.972
7.954
7.365
7.351
7.260
7.110
7.095
6.138
5.506
5.477
5.291
5.273
3.979
2.392
O
O
OMe
11
1.00
1.00
1.02
1.05
1.01
1.03
3.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Chemistry M S Majhi
msm / mrs / 1395-r2 - 13c - 2nd cryo - f983
180.16
154.58
148.24
147.73
136.94
131.74
123.29
121.46
115.02
113.86
112.17
77.37
77.16
76.95
56.45
20.27
O
O
OMe
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


M S Maji
msm / mrs - 1476 - 1 - 1h - f522 - 500MHz
9.757
7.531
7.515
7.260
6.809
6.793
6.041
4.006
2.538
CHO
12
1.00
1.03
1.00
2.01
2.00
3.02
f1 (ppm)


M S Maji
msm / mrs - 1476 - 1 - 13c - f521 - 500MHz
198.14
150.66
148.47
130.69
127.06
115.63
106.68
102.02
77.41
76.91
41.53
28.46
CHO
12
f1 (ppm)


msm.mrs1560r
msm / mrs / 1560-r -1l
7.781
7.759
7.400
7.380
7.288
7.260
7.249
7.188
7.166
6.664
6.645
6.158
5.344
OH
O
O
13
1.00
1.00
1.33
1.03
1.03
2.05
1.00
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)


msmc.mrs1560
msm / mrs / 1560 - 13
152.09
143.98
141.31
126.67
121.39
121.22
115.99
112.62
109.68
106.75
101.75
77.48
76.84
OH
O
O
13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)