Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Oxidation of Allylic and Benzylic Alcohols to Aldehydes and Carboxylic Acids

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GENERAL CONSIDERATIONS

Dry solvents were provided by a solvent purification system M-BRAUN Glovebox Technology SPS-800 working with solvents of HPLC grade purchased from Fisher Scientific or VWR (Prolabo). *Solvent removal* after reaction workup was achieved using rotational evaporator systems BÜCHI Rotavapor R-210 or R-200 with a bath temperature of 50 °C. Unless otherwise noted all *starting material and reagents* used were supplied by Aldrich, Acros, AlfaAesar, CarboSynth UK, Carbolution Chemicals or TCI Europe and used without further purification or their synthesis is reported in the literature. Purities of the commercially available reagents were as follows: Copper(I) bromide: 98%, 2,2'-bipyridine: 99%, 2,2,6,6-tetramethylpiperidine-1-oxyl: 98%, 4-(dimethylamino)pyridine: 99%, 9-azajulolidine: 97%, sodium dihydrogenphosphate: 95%, hydrogen peroxide: 35% aqueous solution, sodium chlorite: 80%.

Thin layer chromatographical analyses were performed using silica gel on aluminum plates (MERCK silica gel 60 F_{254}, 40 x 40 mm). *NMR spectroscopic analyses* were performed with a BRUKER Avance DRX-400 NMR spectrometer at rt. *NMR spectra* were referenced to the internal solvent [$CHCl_3$: δ 7.27 ppm (^{1}H NMR) and 77.00 ppm (^{13}C NMR); DMSO: δ 2.50 ppm (^{1}H NMR) and 39.50 ppm (^{13}C NMR)] and chemical shifts reported in ppm relative to tetramethylsilane as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sxt = sextet, m = multiplet, br = broad), integration and coupling constant. The carboxylic acids NMR spectra reported represent the crude substances as they were achieved as mentioned in the general procedure below. There was no further purification. The concentrations of all NMR samples were chosen between 80 and 130 mg/mL to visualize impurities occurring in very small amounts.

EXPERIMENTAL PROCEDURES

General Procedure for the One-Pot Alcohol Oxidation-/Isomerization Reaction (table 1)

In a 100 mL Schlenk flask the alcohol **4a-j** (10.0 mmol, 1.00 equiv) was dissolved in dry MeCN (5.34 mL) and stirred at rt. The following solutions were subsequently added: CuBr (10.98 mg, 0.075 mmol, 0.75 mol %) in MeCN (2.00 mL), 2,2'-bipyridine (11.83 mg, 0.075 mmol, 0.75 mol %) in MeCN (2.00 mL), 2,2,6,6-tetramethylpiperidine-1-oxyl (11.96 mg, 0.075 mmol, 0.75 mol %) in MeCN (2.00 mL) and the appropriate base/isomerization reagent [4-(dimethylamino)pyridine (DMAP, 18.51 mg, 0.15 mmol, 1.5 mol %) or 9-azajulolidine (26.94 mg, 0.15 mmol, 1.5 mol %)] in MeCN (2.00 mL). An O_2-balloon was fit to the flask, the reaction mixture degassed under vacuum and the flask backfilled with oxygen. The degassing/refilling-procedure was repeated three times and the red/brown solution stirred at rt for the time indicated in table 1. Upon complete oxidation (and isomerization, checked by TLC or GC) water (50 mL) was added to the reaction mixture followed by extraction with Et_2O (4x). The combined organic phases were dried ($MgSO_4$), filtered and the solvent was evaporated. Column chromatography of the crude product on silica gel or distillation afforded the α,β-unsaturated aldehydes **5a-j**.

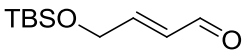
General Procedure for the One-Pot Alcohol Oxidation-(Isomerisation-)Aldehyde Oxidation Sequence (table 2)

In a 100 mL Schlenk flask equipped with a cross stir bar the alcohol **4a-j** (10.0 mmol, 1.00 equiv) was dissolved in dry MeCN (9.34 mL) and stirred at rt. The following solutions were subsequently added: CuBr (10.98 mg, 0.075 mmol, 0.75 mol %) in MeCN (1.00 mL), 2,2'-bipyridine (11.83 mg, 0.075 mmol, 0.75 mol %) in MeCN (1.00 mL), 2,2,6,6-tetramethylpiperidine-1-oxyl (11.96 mg, 0.075 mmol, 0.75 mol %) in MeCN (1.00 mL) and the appropriate base/isomerization reagent [4-(dimethylamino)pyridine (DMAP, 18.51 mg, 0.15 mmol, 1.5 mol %) or 9-azajulolidine (26.94 mg, 0.15 mmol, 1.5 mol %)] in MeCN (1.00 mL). An O_2-balloon was fit to the flask, the reaction mixture degassed under vacuum and the flask backfilled with oxygen. The degassing/refilling-procedure was repeated three times and the red/brown solution stirred at rt for the time t_1 indicated in table 2. Upon complete oxidation (and isomerization; checked by TLC or GC) the reaction mixture was cooled to 0 °C followed by addition of NaH_2PO_4 (568 mg, 4.50 mmol,

0.45 equiv) in water (5.20 mL) and hydrogen peroxide (35% in water, 1.09 mL, 1.21 g, 12.5 mmol, 1.25 equiv). A solution of $NaClO_2$ (2.26 g, 20.0 mmol, 2.00 equiv) in water (15.6 mL) was added dropwise at 0 °C over 15 min. Stirring at 0 °C was continued for 15 min before removing the ice bath and stirring at rt for the time t_2 indicated in table 2. After complete consumption of the aldehyde (checked by TLC) solid Na_2SO_3 (322 mg, 2.50 mmol, 0.25 equiv) was added and the solution stirred for 5 min at rt. The mixture was diluted with water and EtOAc, the phases were separated, the aqueous phase extracted with EtOAc (3x), the combined organic phases washed with 1 M HCl (aq., 2x), water (2x) and brine (1x), dried over $MgSO_4$, filtered and the solvent was removed in vacuum. The residual carboxylic acids **6a-j** were dried in fine vacuum for several hours to completely remove the solvents. A further purification of the acids was not necessary in most cases.

Aldehydes 5a-j:

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)but-2-en-1-al (5a) (table 1, entry 1)



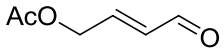
5a

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)but-2-en-1-ol (**4a**) was oxidized with 0.75 mol % catalyst loading using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 2.5 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 8:1) to give **5a** as a colorless oil (1.98 g, 9.88 mmol, 99%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

R_f = 0.52 (pentane:Et_2O = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.60 (d, 1H, *J* = 8.1 Hz), 6.89 (dt, 1H, *J* = 15.4, 3.3 Hz), 6.40 (ddt, 1H, *J* = 15.5, 8.1, 2.1 Hz), 4.45 (dd, 2H, *J* = 3.3, 2.2 Hz), 0.92 (s, 9H), 0.09 ppm (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 193.3, 156.4, 130.5, 62.2, 25.8, 18.3, -5.50 ppm.

[1] Könning, D.; Hiller, W.; Christmann, M.; *Org. Lett.* **2012**, *14*(20), 5258-5261.

(*E*)-4-Acetoxybut-2-en-1-al (5b) (table 1, entry 2)

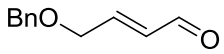


5b

(*Z*)-4-Acetoxybut-2-en-1-ol (**4b**) was oxidized with 0.75 mol % catalyst loading using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 1.75 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 3:1 → 2:1) to give **5b** as a colorless oil (1.18 g, 9.21 mmol, 92%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

R_f = 0.58 (pentane:Et_2O = 1:2); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.59 (dd, 1H, *J* = 7.8, 0.4 Hz), 6.84 (dt, 1H, *J* = 15.8, 4.3 Hz(2x)), 6.30 (m, 1H), 4.87 (dd, 1H, *J* = 4.3, 1.9 Hz), 2.15 ppm (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 192.7, 170.2, 149.5, 132.1, 62.3, 20.6 ppm.

(*E*)-4-(Benzyloxy)but-2-en-1-al (5c) (table 1, entry 3)

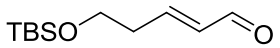


5c

(*Z*)-4-(Benzyloxy)but-2-en-1-ol (**4c**) was oxidized with 0.75 mol % catalyst loading using DMAP as the isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 4 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 5:1 → 3:1) to give **5c** as a colorless oil (1.72 g, 9.76 mmol, 98%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

R_f = 0.33 (pentane:Et_2O = 5:1, run 2x); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.60 (d, 1H, *J* = 7.9 Hz), 7.40-7.31 (m, 5H), 6.86 (dt, 1H, *J* = 15.8, 4.1 Hz), 6.42 (ddt, 1H, *J* = 15.8, 7.9, 1.9 Hz), 4.61 (s, 2H), 4.30 ppm (dd, 2H, *J* = 4.1, 1.9 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 193.3, 153.0, 137.3, 131.7, 128.5, 127.6, 73.0, 68.5 ppm.

(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-al (5d) (table 1, entry 4)

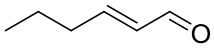


5d

(*Z*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-ol (**4d**) was oxidized with 1.00 mol % catalyst loading using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 25 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 8:1 → 4:1) to give **5d** as a colorless oil (1.91 g, 8.93 mmol, 89%, *E*:*Z* = 99:1).

R_f = 0.47 (pentane:Et_2O = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.51 (d, 1H, *J* = 7.9 Hz), 6.89 (dt, 1H, *J* = 15.8, 7.0 Hz,), 6.13 -6.21 (m, 1H), 3.78 (t, 2H, *J* = 6.2 Hz), 2.51 – 2.58 (m, 2H), 0.89 (s, 9H), 0.06 ppm (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 194.0, 155.6, 134.3, 61.1, 36.1, 25.8, 18.2, 5.4 ppm; **IR** (neat film) (cm^{-1}): 2949, 2923, 2844, 1701, 1648, 1471, 1385, 1254, 1103, 1004, 972, 926, 834, 781; **HPLC-ESI-HRMS** *m/z* calc. for $C_{11}H_{23}O_2Si$ ($[M+H]^+$) 215.14618, found 215.14617.

(*E*)-Hex-2-en-1-al (5e) (table 1, entry 5)

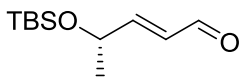


5e

(*Z*)-2-Hexen-1-ol (**4e**) was oxidized with 1.00 mol % catalyst loading using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 18 h. Extraction of the crude product was achieved by pentane (3x) instead of Et_2O for more efficient separation of solvent and product upon distillation. Purification of the crude product was achieved by distillation through a Vigreux-column (atmospheric pressure, bath temp.: 190 °C, head temp.: 147 °C) to give **5e** as a colorless oil (618 mg, 6.18 mmol, 62%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

R_f = 0.66 (pentane:Et_2O = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.51 (d, 1H, *J* = 7.9 Hz), 6.85 (dt, 1H, *J* = 15.6, 6.8 Hz), 6.12 (m, 1H), 2.32 (m, 2H), 1.55 (pseudo sxt, 2H, *J* = 7.4 Hz), 0.97 ppm (t, 3H, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 194.1, 158.8, 133.1, 34.7, 21.1, 13.6 ppm.

(*S*,*E*)-4-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-al (5f) (table 1, entry 6)

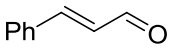


5f

(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-ol (**4f**) was oxidized with 1.00 mol % catalyst loading using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 17 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 10:1) to give **5f** as a slightly yellow oil (2.09 g, 9.74 mmol, 97%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

(*Z*)-5f: $\mathbf{R_f}$ = 0.67 (pentane:Et_2O = 3:1); **(*E*)-5f**: $\mathbf{R_f}$ = 0.55 (pentane:Et_2O = 3:1; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.58 (d, 1H, *J* = 8.0 Hz), 6.81 (dd, 1H, *J* = 15.4, 4.0 Hz), 6.28 (ddd, 1H, *J* = 15.4, 8.0, 1.7 Hz), 4.58 (m, 1H), 1.32 (d, 3H, *J* = 6.6 Hz), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 ppm (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 193.7, 160.9, 129.8, 67.7, 25.7, 23.3, 18.1, -4.9, -5.0 ppm.

(*E*)-3-Phenylprop-2-en-1-al (*trans*-cinnamaldehyde) (5g) (table 1, entry 7)

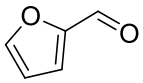


5g

(*Z*)-3-Phenylprop-2-en-1-ol (**4g**) was oxidized with 0.75 mol % catalyst loading using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time for the oxidation and isomerization was 16.5 h. The isomerization was monitored by GC. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 10:1) to give **5g** as a slightly yellow liquid (1.30 g, 9.84 mmol, 98%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[1]

$\mathbf{R_f}$ = 0.48 (pentane:Et_2O = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.72 (d, 1H, *J* = 7.7 Hz), 7.58 (m, 2H), 7.49 (d, 1H, *J* = 15.9 Hz), 7.45 (m, 3H), 6.73 ppm (dd, 1H, *J* = 15.9, 7.7 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 193.5, 152.6, 133.7, 131.1, 128.9, 128.3, 128.3 ppm.

Furan-2-carbaldehyde (5h) (table 1, entry 8)

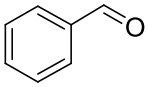


5h

2-Furylmethanol (**4h**) was oxidized with 0.75 mol % catalyst loading using DMAP as the base of choice according to the general procedure mentioned above. The reaction time for the oxidation was 6 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 5:1) to give **5h** as a slightly yellow liquid (530 mg, 5.52 mmol, 55%). The analytical data fit to those reported in the literature.[2]

R_f = 0.52 (pentane:Et_2O = 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 7.67 – 7.70 (m, 1H), 7.23 – 7.26 (m, 1H), 6.73 ppm (dd, 1H, *J* = 3.5, 1.5 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 177.8, 152.8, 148.0, 121.1, 112.5 ppm.

Benzaldehyde (5i) (table 1, entry 9)



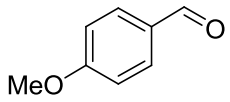
5i

Benzyl alcohol (**4i**) was oxidized with 0.75 mol % catalyst loading using DMAP as the base of choice according to the general procedure mentioned above. The reaction time for the oxidation was 1 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 10:1) to give **5i** as a yellow liquid (894 mg, 8.42 mmol, 84%). The analytical data fit to those reported in the literature.[2]

R_f = 0.58 (pentane:Et_2O = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.89 (dd, *J* = 7.9, 0.9 Hz, 2H), 7.61 – 7.68 (m, 1H), 7.51 – 7.58 (m, 1H), 7.51 – 7.58 ppm (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 192.3, 136.2, 134.3, 129.8, 128.9 ppm.

[2] Di, L.; Hua, Z.; *Adv. Synth. Catal.* **2011**, *353*(8), 1253-1259.

4-Methoxybenzaldehyde (5j) (table 1, entry 10)



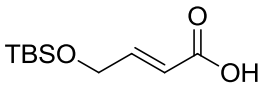
5j

4-Methoxybenzyl alcohol (**4j**) was oxidized with 0.75 mol % catalyst loading using DMAP as the base of choice according to the general procedure mentioned above. The reaction time for the oxidation was 1 h. Purification of the crude product was achieved by column chromatography (SiO_2, pentane:Et_2O = 10:1) to give **5j** as a colorless liquid (1.31 g, 9.64 mmol, 96%). The analytical data fit to those reported in the literature.[2]

R_f = 0.31 (pentane:Et_2O = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.88 – 9.90 (m, 1H), 7.84 - 7.86 (m, 1H), 7.82 – 7.84 (m, 1H), 7.01 – 7.03 (m, 1H), 6.99 – 7.01 (m, 1H), 3.88 – 3.90 ppm (m, 3 H) ; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 190.8, 164.5, 131.9, 129.8, 114.2, 55.5 ppm.

<u>Carboxylic Acids 6a-j:</u>

(*E*)-4-((*tert*-Butyldimethylsilyl)oxy)but-2-enoic acid (6a) (table 2, entry 1)



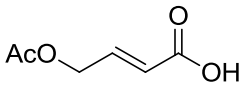
6a

(*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)-but-2-ene-1-ol (**4a**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 3 h, the reaction time t_2 for the aldehyde oxidation was 6.25 h. The carboxylic acid **6a** was achieved as a white solid after extraction as mentioned in the general procedure (2.02 g, 9.35 mmol, 94%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.11 (br. s, 1H), 7.16-7.10 (dt, 1H, *J* = 15.4, 3.2 Hz), 6.15-6.10 (dt, 1H, *J* = 15.4, 2.3 Hz), 4.38-4.37 (dd, 2H, *J* = 3.1, 2.4 Hz), 0.93 (s, 9H), 0.09 ppm (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.3, 150.3, 118.9, 62.1, 25.8, 18.3, -5.5 ppm.

[3] Tilley, S. D.; Reber, K. P.; Sorensen, E. J.; *Org. Lett.* **2009**, *11*(3), 701-703.

(*E*)-4-Acetoxybut-2-enoic acid (6b) (table 2, entry 2)

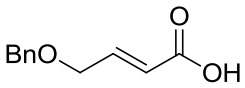


6b

(*Z*)-4-Acetoxybut-2-ene-1-ol (**4b**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 3 h, the reaction time t_2 for the aldehyde oxidation was 6.75 h. The carboxylic acid **6b** was achieved as a white solid after extracting five times with EtOAc due to the products high polarity (1.24 g, 8.58 mmol, 86%, *E*:*Z* = 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.86 (br. s, 1H), 7.07-7.01 (dt, 1H, *J* = 15.8, 4.4 Hz), 6.05-6.00 (dt, 1H, *J* = 15.8, 2.0 Hz), 4.77-4.75 (dd, 2H, *J* = 4.4, 2.0 Hz), 2.12 ppm (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 171.1, 170.3, 143.9, 121.1, 62.3, 20.6 ppm; **ATR-IR** (neat film) (cm^{-1}): 3052, 2922, 2678, 2548, 1737, 1729, 1678, 1658, 1640, 1441, 1381, 1366, 1310, 1291, 1236, 1211, 1079, 1049, 1019, 952, 926, 840, 706, 604, 555, 537; **HPLC-ESI-HRMS** *m/z* calc. for $C_6H_9O_4$ ($[M+H]^+$) 145.04954, found 145.04923.

(*E*)-4-(Benzyloxy)but-2-enoic acid (6c) (table 2, entry 3)



6c

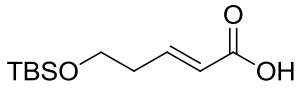
(*Z*)-4-(Benzyloxy)but-2-ene-1-ol (**4c**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 5 h, the reaction time t_2 for the aldehyde oxidation was 6 h. The carboxylic acid **6c** was achieved as a slightly yellow solid after extraction as mentioned in the general procedure (1.86 g, 9.66 mmol, 97%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.96 (br. s, 1H), 7.42-7.32 (m, 5H), 7.16-7.10 (dt, 1H, *J* = 15.8, 4.0 Hz), 6.22-6.18 (dt, 1H, *J* = 15.7, 2.1 Hz), 4.61 (s, 2H), 4.24-4.23 ppm (dd, 2H,

[4] Ito, M.; Clark, C. W.; Mortimore, M.; Goh, J. B.; Martin, S. F.; *J. Am. Chem. Soc.* **2001**, *123*(33), 8003-8010.

J = 4.1, 2.1 Hz); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 171.8, 147.1, 137.5, 128.4, 127.8, 127.6, 120.4, 72.8, 68.4 ppm.

(*E*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-enoic acid (6d) (table 2, entry 4)

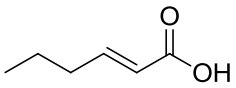


6d

(*Z*)-5-((*tert*-Butyldimethylsilyl)oxy)pent-2-ene-1-ol (**4d**) was oxidized with 1.00 mol % catalyst loading in the alcohol oxidation step using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 15 h, the reaction time t_2 for the aldehyde oxidation was 19 h. The carboxylic acid **6d** was achieved as a colorless oil after extraction as mentioned in the general procedure which solidifies on standing to give a white solid (2.23 g, 9.39 mmol, 94%, *E*:*Z* = 99:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.48 (br. s, 1H), 7.13-7.05 (dt, 1H, *J* = 15.6, 7.1 Hz), 5.91-5.87 (m, 1H), 3.76-3.73 (t, 2H, *J* = 6.4 Hz), 2.48-2.42 (m, 2H), 0.89 (s, 9H), 0.06 ppm (s, 6H); **$^{13}C\{^{1}H\}$ NMR** (101 MHz, $CDCl_3$): δ 171.9, 148.9, 122.3, 61.3, 35.7, 25.8, 18.3, -5.4 ppm; **ATR-IR** (neat film) (cm^{-1}): 2953, 2929, 2885, 2857, 1697, 1653, 1471, 1419, 1307, 1283, 1254, 1095, 980, 938, 833, 808, 774, 662; **HPLC-ESI-HRMS** *m/z* calc. for $C_{11}H_{23}O_3Si$ ($[M+H]^+$) 231.14110, found 231.14138.

(*E*)-Hex-2-enoic acid (6e) (table 2, entry 5)



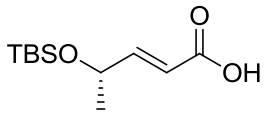
6e

(*Z*)-Hex-2-ene-1-ol (**4e**) was oxidized with 1.00 mol % catalyst loading in the alcohol oxidation step using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 16 h, the reaction time t_2 for the aldehyde oxidation was 11.75 h. The carboxylic acid **6e** was achieved as a colorless oil after extraction as mentioned in the general

procedure which solidifies on standing to give an off-white solid (930 mg, 8.15 mmol, 82%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.21 (br. s, 1H), 7.13-7.05 (dt, 1H, *J* = 15.6, 7.0 Hz), 5.85-5.81 (dt, 1H, *J* = 15.6, 1.6 Hz), 2.24-2.18 (qd, 2H, *J* = 7.2, 1.5 Hz), 1.55-1.46 (pseudo-sxt, 2H, *J* = 7.4 Hz), 0.96-0.92 ppm (t, 3H, *J* = 7.4 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.4, 152.2, 120.8, 34.3, 21.1, 13.6 ppm.

(*S*,*E*)-4-((*tert*-Butyldimethylsilyl)oxy)pent-2-enoic acid (6f) (table 2, entry 6)



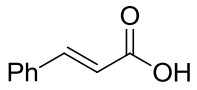
6f

(*S*,*Z*)-4-((*tert*-Butyldimethylsilyl)oxy)pent-2-en-1-ol (**4f**) was oxidized with 1.00 mol % catalyst loading in the alcohol oxidation step using DMAP as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 15 h, the reaction time t_2 for the aldehyde oxidation was 12 h. The carboxylic acid **6f** was achieved as a colorless oil after extraction as mentioned in the general procedure (2.19 g, 9.52 mmol, 95%, *E*:*Z* = 99:1).

$[\alpha]_D^{20}$ +3.7° (*c* 1.04, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 12.07 (br. s, 1H), 7.09-7.04 (dd, 1H, *J* = 15.4, 3.9 Hz), 6.04-6.00 (dd, 1H, *J* = 15.4, 1.8 Hz), 4.52-4.46 (m, 1H), 1.29-1.27 (d, 3H, *J* = 6.7 Hz), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 ppm (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.5, 154.7, 118.3, 67.6, 25.8, 23.3, 18.2, -4.9 ppm; **ATR-IR** (neat film) (cm^{-1}): 2955, 2929, 2886, 2857, 1696, 1656, 1416, 1297, 1252, 1151, 1091, 1054, 977, 917, 826, 808, 775, 694, 663; **HPLC-ESI-HRMS** *m/z* calc. for $C_{11}H_{21}O_2Si$ ($[(M-H_2O)+H]^+$) 213.13053, found 213.13072, *m/z* calc. for $C_{11}H_{23}O_3Si$ ($[M+H]^+$) 231.14110, found 231.14137.

[5] Kon, Y.; Imao, D.; Nakashima, T.; Sato, K.; *Chem. Lett.* **2009**, *38*, 430-431.

(*E*)-3-Phenylprop-2-enoic acid (*trans*-cinnamic acid) (6g) (table 2, entry 7)

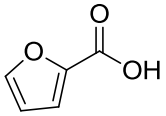


6g

(*Z*)-3-Phenylprop-2-en-1-ol (**4g**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using 9-azajulolidine as the base/isomerization reagent of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation and isomerization was 13 h, the reaction time t_2 for the aldehyde oxidation was 9 h. The carboxylic acid **6g** was achieved as a white solid after extraction as mentioned in the general procedure (1.40 g, 9.46 mmol, 95%, *E*:*Z* = 99:1). The analytical data fit to those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.56 (br. s, 1H), 7.85-7.81 (d, 1H, *J* = 15.9 Hz), 7.59-7.56 (dd, 2H, *J* = 6.8, 2.9 Hz), 7.45-7.41 (m, 3H), 6.51-6.47 ppm (d, 1H, *J* = 15.9 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.8, 147.1, 133.9, 130.7, 128.9, 128.3, 117.3 ppm.

Furan-2-carboxylic acid (6h) (table 2, entry 8)



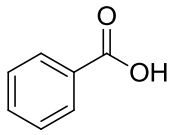
6h

2-Furylmethanol (**4h**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation was 5 h, the reaction time t_2 for the aldehyde oxidation was 8.5 h. The carboxylic acid **6h** was achieved as a light brown solid after extraction as mentioned in the general procedure (594 mg, 5.30 mmol, 53%). The analytical data fit to those reported in the literature.[6] The NMR spectra of this substance show significant amounts of impurities so that purification is necessary in this case.

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.08 (br. s, 1H), 7.90 (dd, 1H, *J* = 1.7, 0.8 Hz), 7.21-7.20 (dd, 1H, *J* = 3.5, 0.8 Hz), 6.64-6.63 ppm (dd, 1H, *J* = 3.5, 1.8 Hz); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 159.4, 147.1, 145.0, 117.8, 112.2 ppm.

[6] Zhang, X.; Zhang, W.-Z.; Shi, L.-L.; Guo, C.-X.; Zhang, L.-L.; Lu, X.-B.; *Chem. Commun.* **2012**, *48*, 6292-6294.

Benzoic acid (6i) (table 2, entry 9)

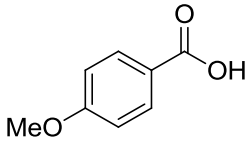


6i

Benzyl alcohol (**4i**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation was 1 h, the reaction time t_2 for the aldehyde oxidation was 1.25 h. The carboxylic acid **6i** was achieved as a white solid after extraction as mentioned in the general procedure (1.16 g, 9.50 mmol, 95%). The analytical data fit to those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 12.99 (br. s, 1H), 8.18-8.15 (m, 2H), 7.66-7.62 (m, 1H), 7.52-7.48 ppm (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ 172.7, 133.8, 130.2, 129.3, 128.4 ppm.

4-Methoxybenzoic acid (6j) (table 2, entry 10)

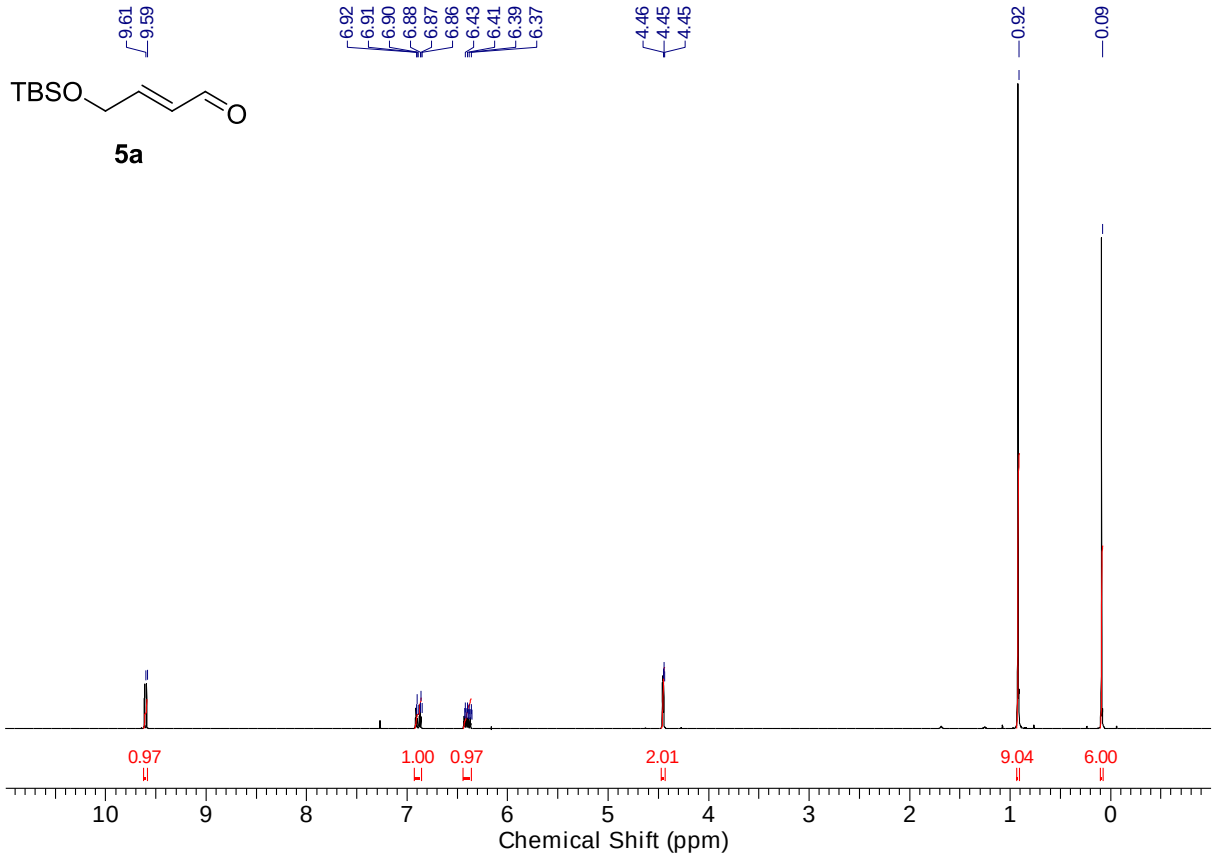


6j

4-Methoxybenzyl alcohol (**4j**) was oxidized with 0.75 mol % catalyst loading in the alcohol oxidation step using DMAP as the base of choice according to the general procedure mentioned above. The reaction time t_1 for the alcohol oxidation was 1 h, the reaction time t_2 for the aldehyde oxidation was 9 h. The carboxylic acid **6j** was achieved as a white solid after extraction as mentioned in the general procedure (1.46 g, 9.58 mmol, 96%). The analytical data fit to those reported in the literature.[6]

^{1}H NMR (400 MHz, DMSO-d_6): δ 12.64 (br. s, 1H), 7.91-7.88 (m, 2H), 7.02-6.98 (m, 2H), 3.81 ppm (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6): δ 167.1, 162.9, 131.4, 123.0, 113.9, 55.5 ppm.

SPECTRA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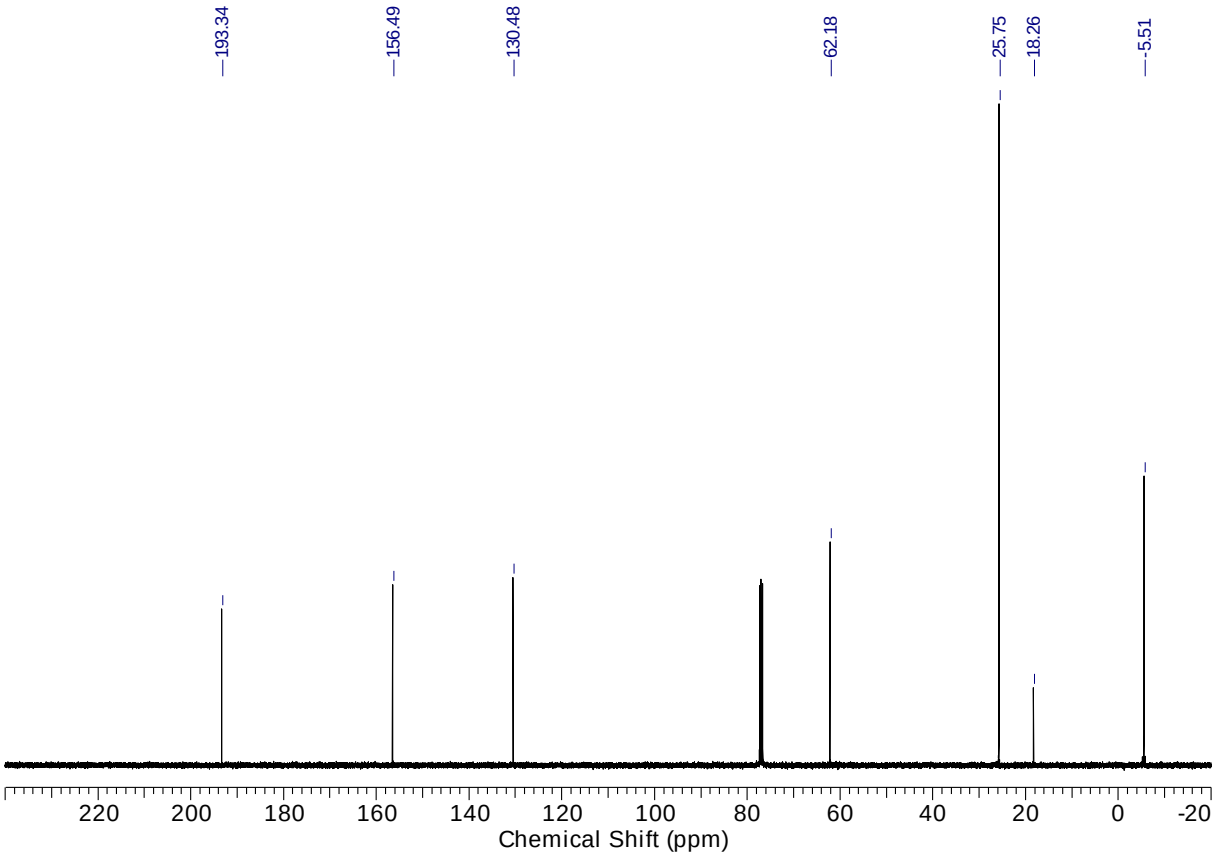
9.59
6.92
6.91
6.90
6.88
6.87
6.86
6.43
6.41
6.39
6.37
4.46
4.45
4.45
0.92
0.09
TBSO
O
5a
0.97
1.00
0.97
2.01
9.04
6.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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62.18
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18.26
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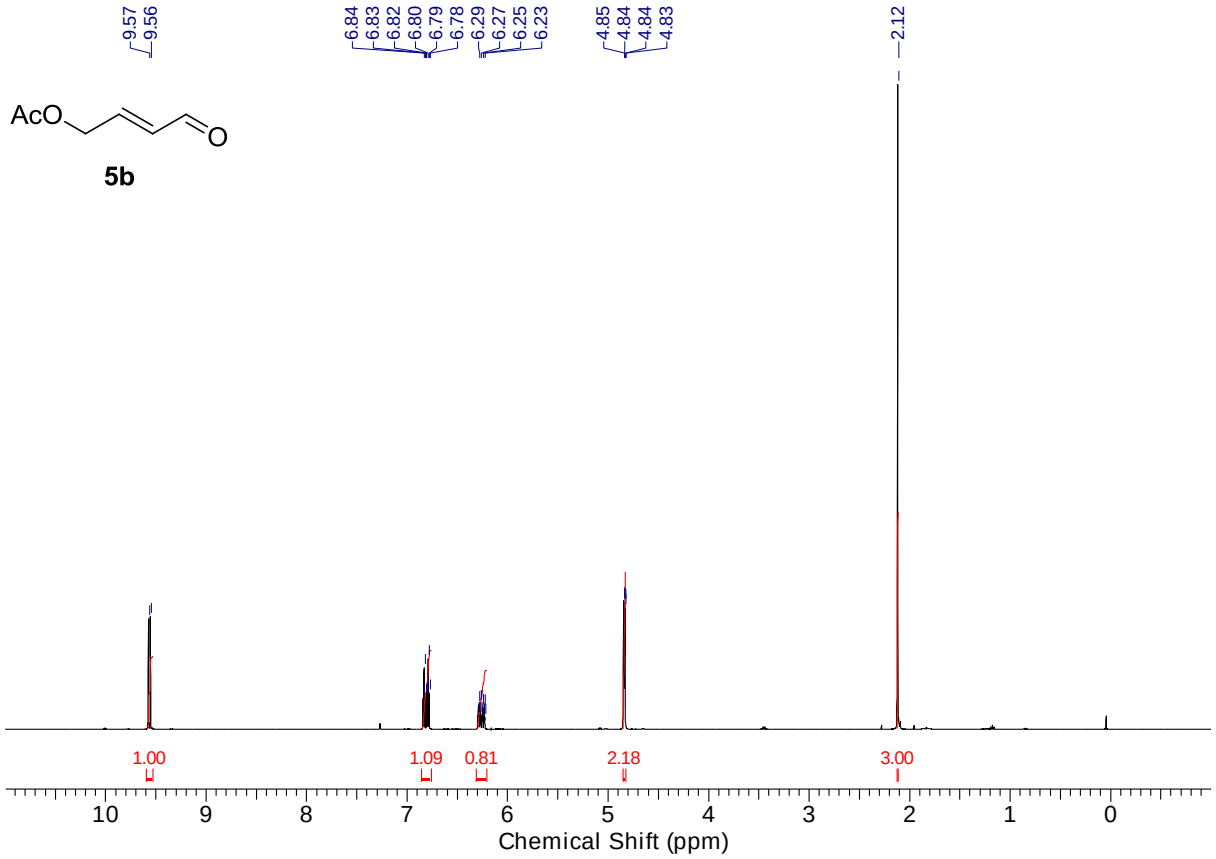
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)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6.83
6.82
6.80
6.79
6.78
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6.27
6.25
6.23
4.85
4.84
4.84
4.83
2.12
AcO
O
5b
1.00
1.09
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3.00
10
9
8
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5
4
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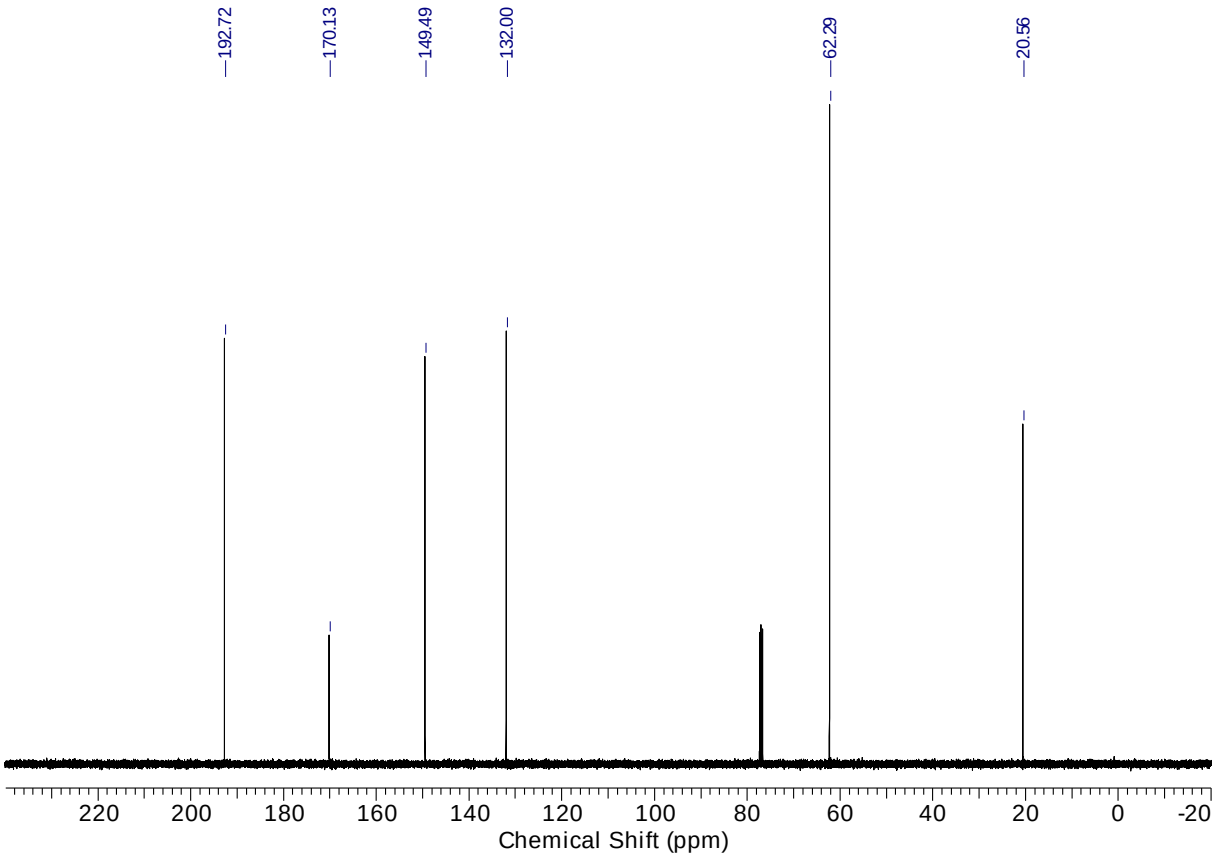
0
Chemical Shift (ppm)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120
100
80
60
40
20
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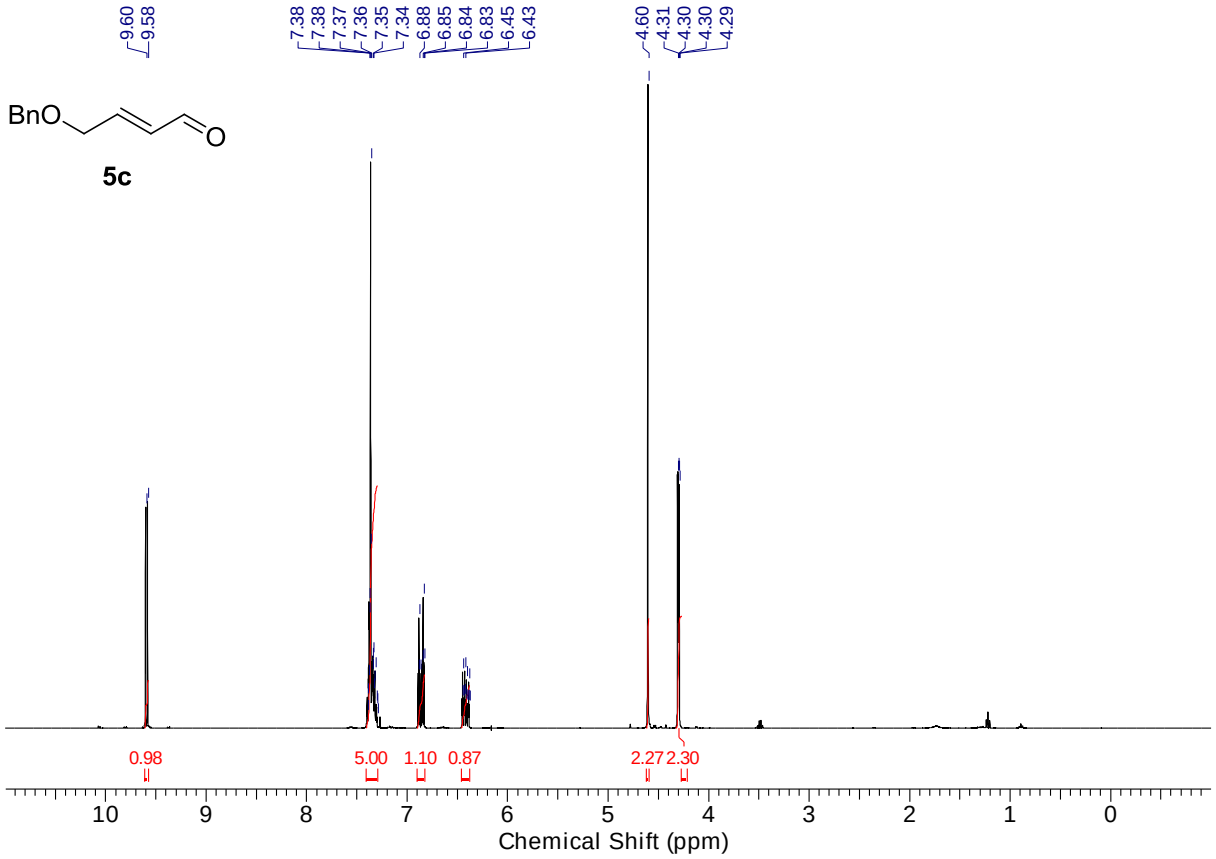
-20
Chemical Shift (ppm)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7.38
7.37
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7.34
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6.85
6.84
6.83
6.45
6.43
4.60
4.31
4.30
4.30
4.29
BnO
O
5c
0.98
5.00
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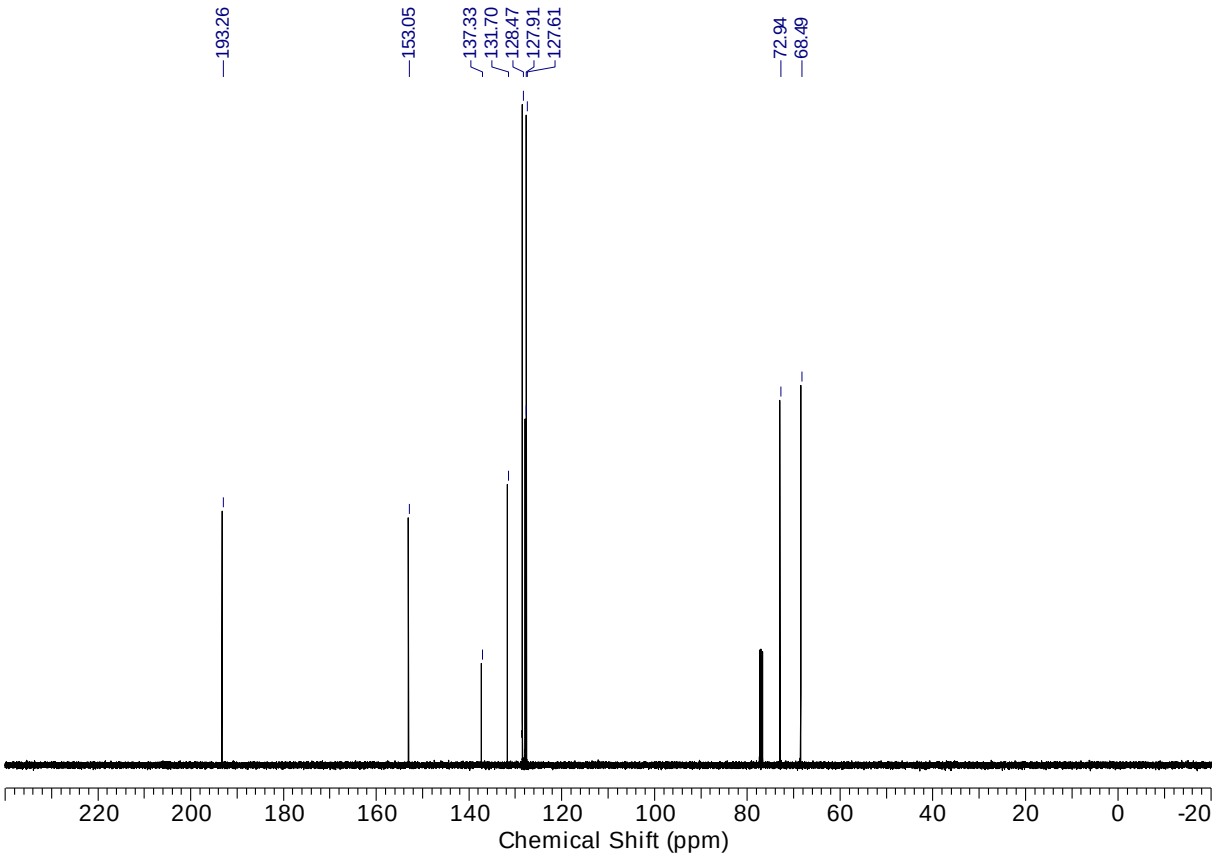
2.27
2.30
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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200
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120
100
80
60
40
20
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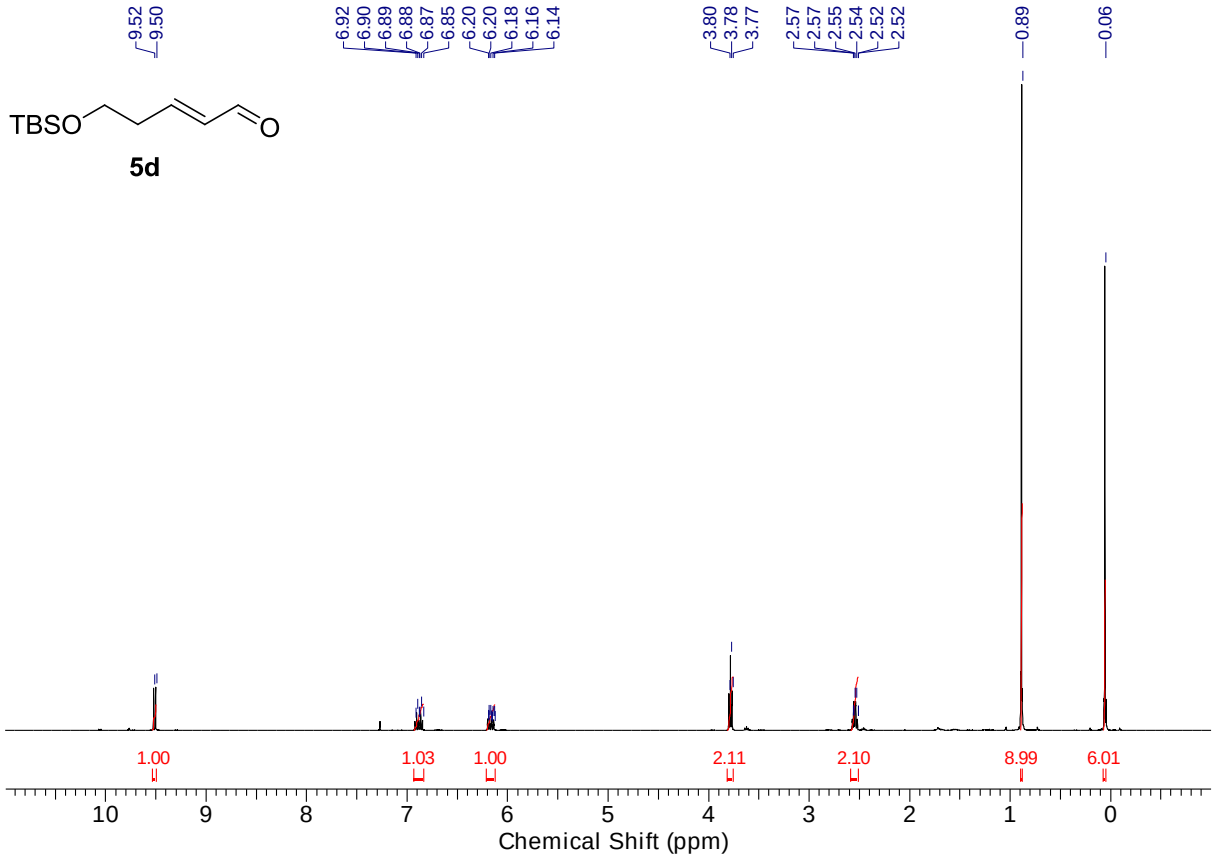
-20
Chemical Shift (ppm)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6.16
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3.77
2.57
2.57
2.55
2.54
2.52
2.52
0.89
0.06
TBSO
O
5d
1.00
1.03
1.00
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6.01
10
9
8
7
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5
4
3
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1
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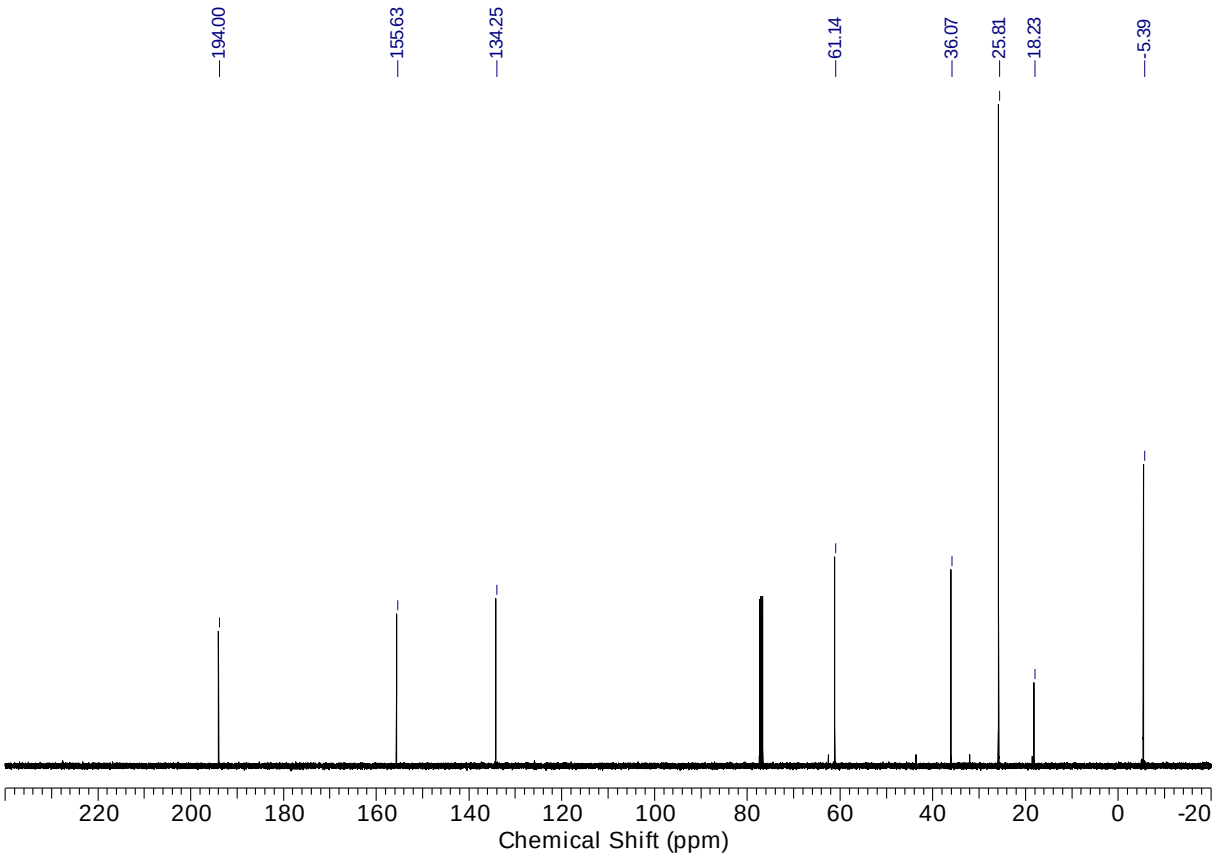
Chemical Shift (ppm)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80
60
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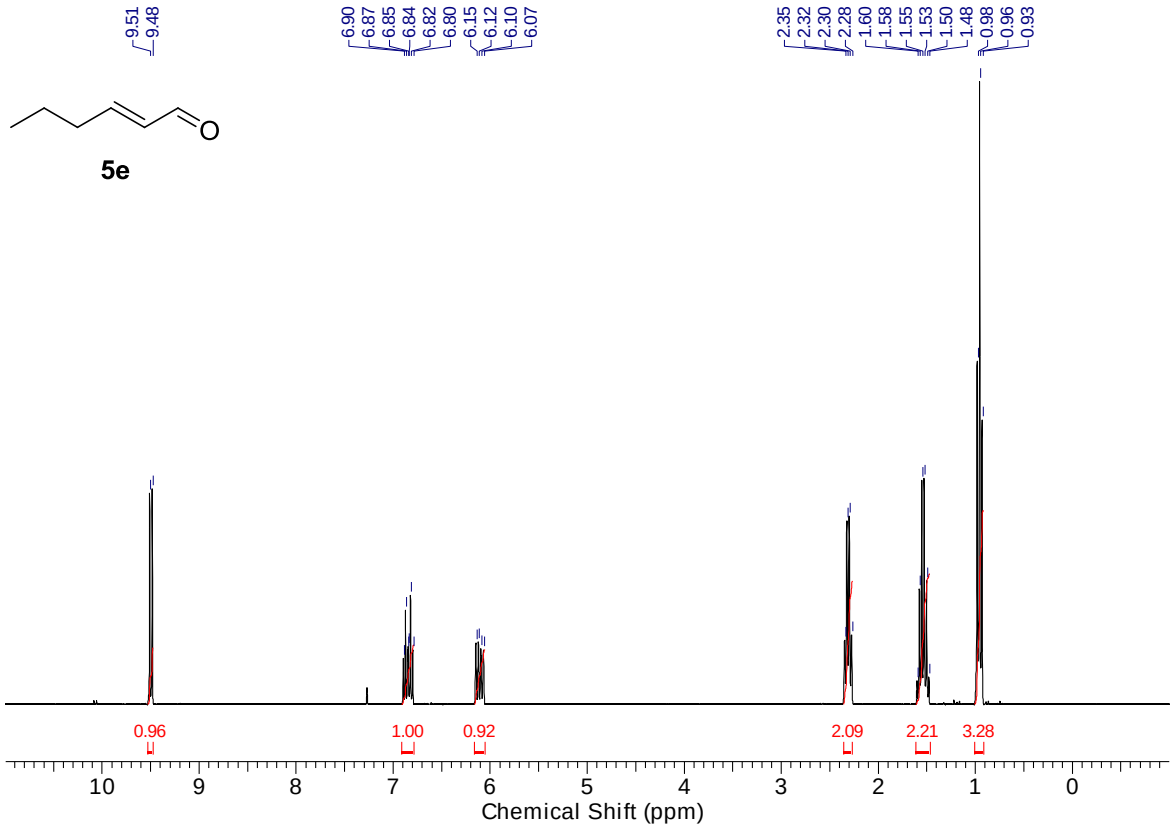
0
-20
Chemical Shift (ppm)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9.48
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6.84
6.82
6.80
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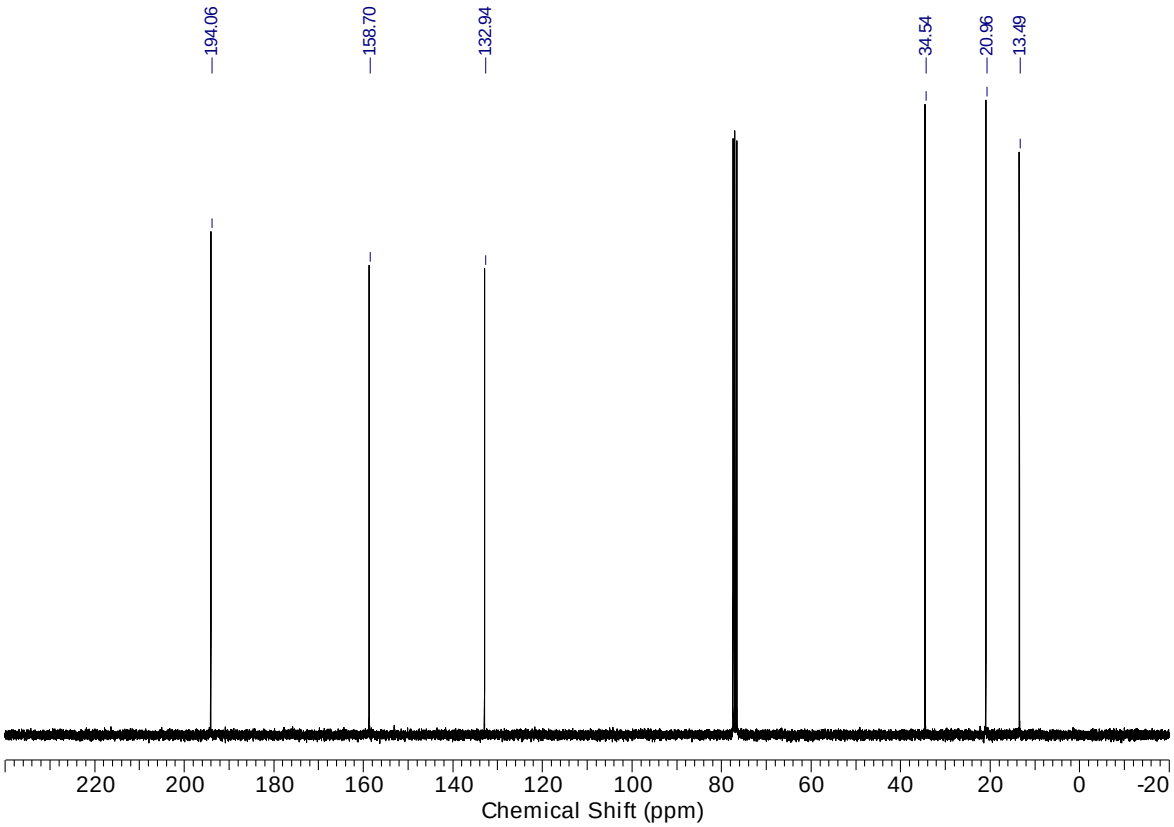
6.12
6.10
6.07
2.35
2.32
2.30
2.28
1.60
1.58
1.55
1.53
1.50
1.48
0.98
0.96
0.93
O
5e
0.96
1.00
0.92
2.09
2.21
3.28
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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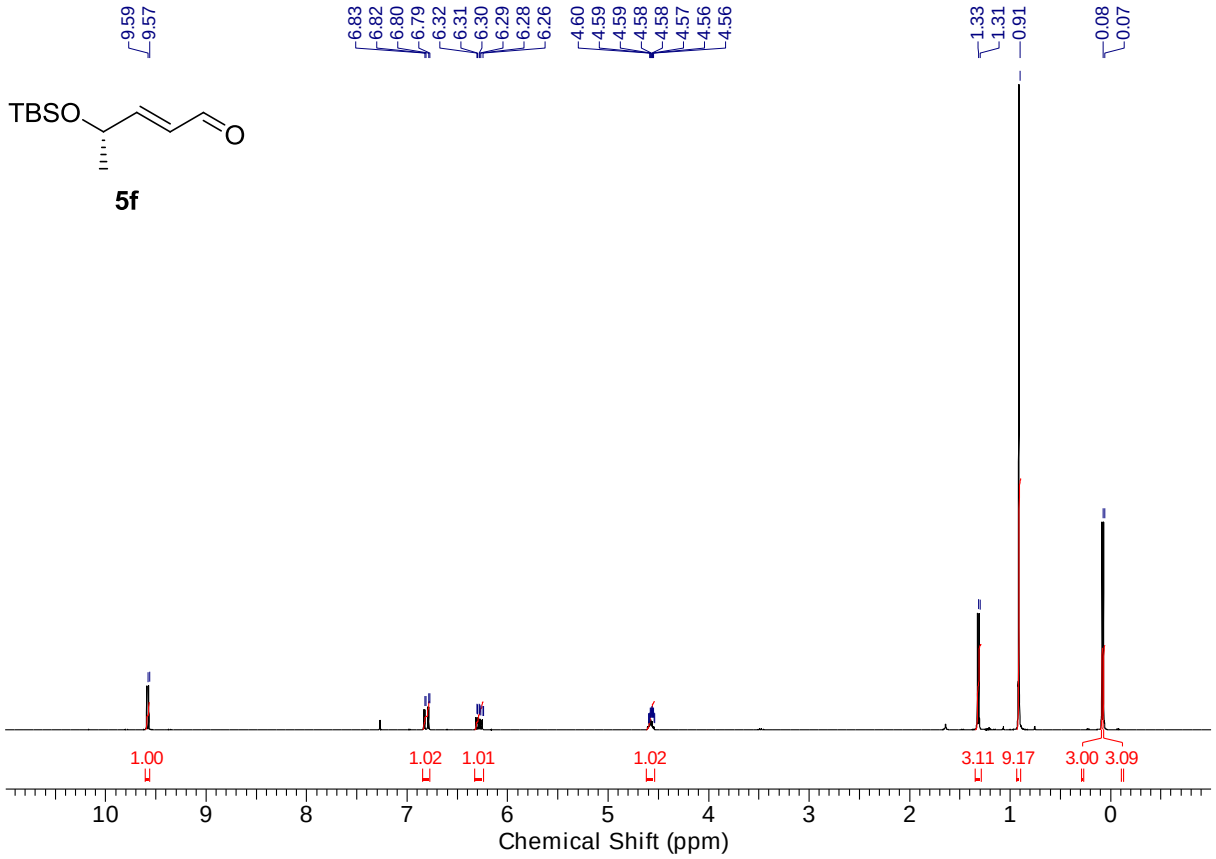
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)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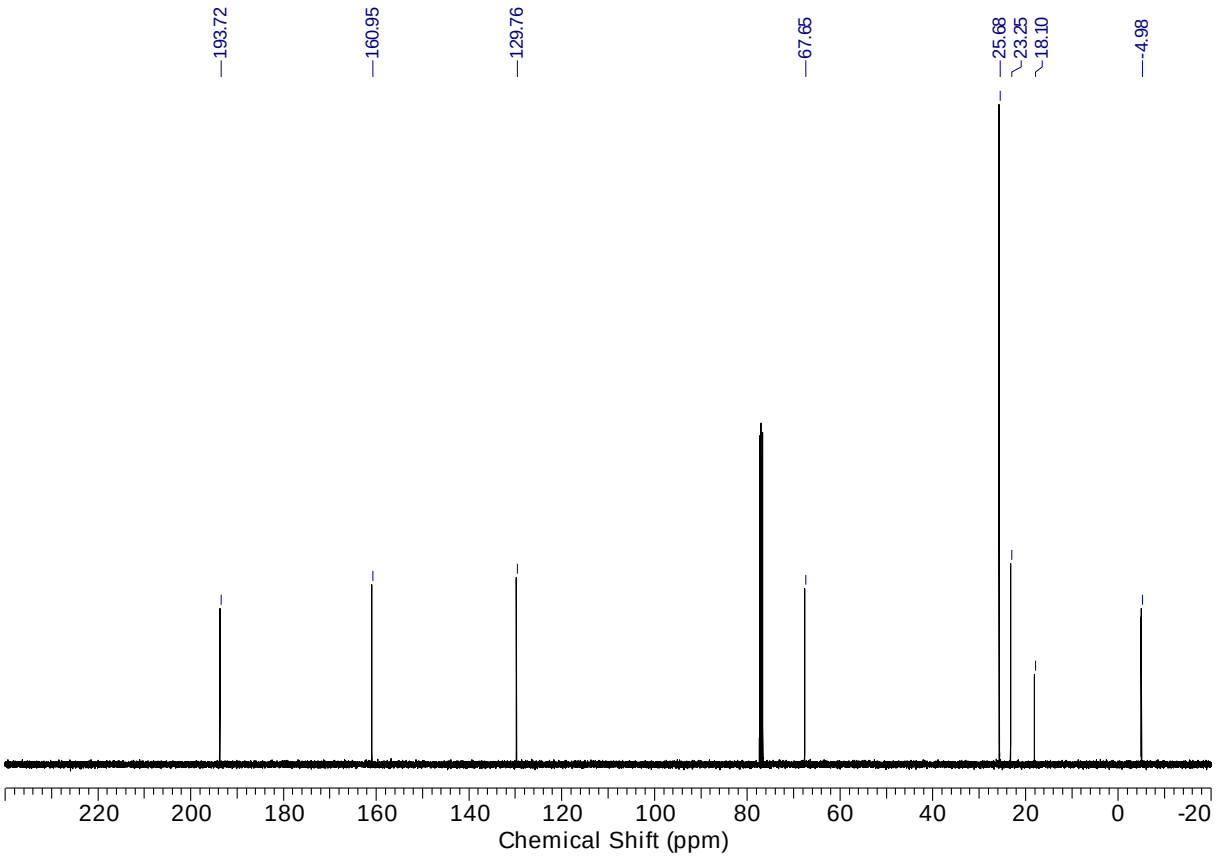
6.29
6.28
6.26
4.60
4.59
4.59
4.58
4.58
4.57
4.56
4.56
1.33
1.31
0.91
0.08
0.07
TBSO
O
5f
1.00
1.02
1.01
1.02
3.11
9.17
3.00
3.09
Chemical Shift (ppm)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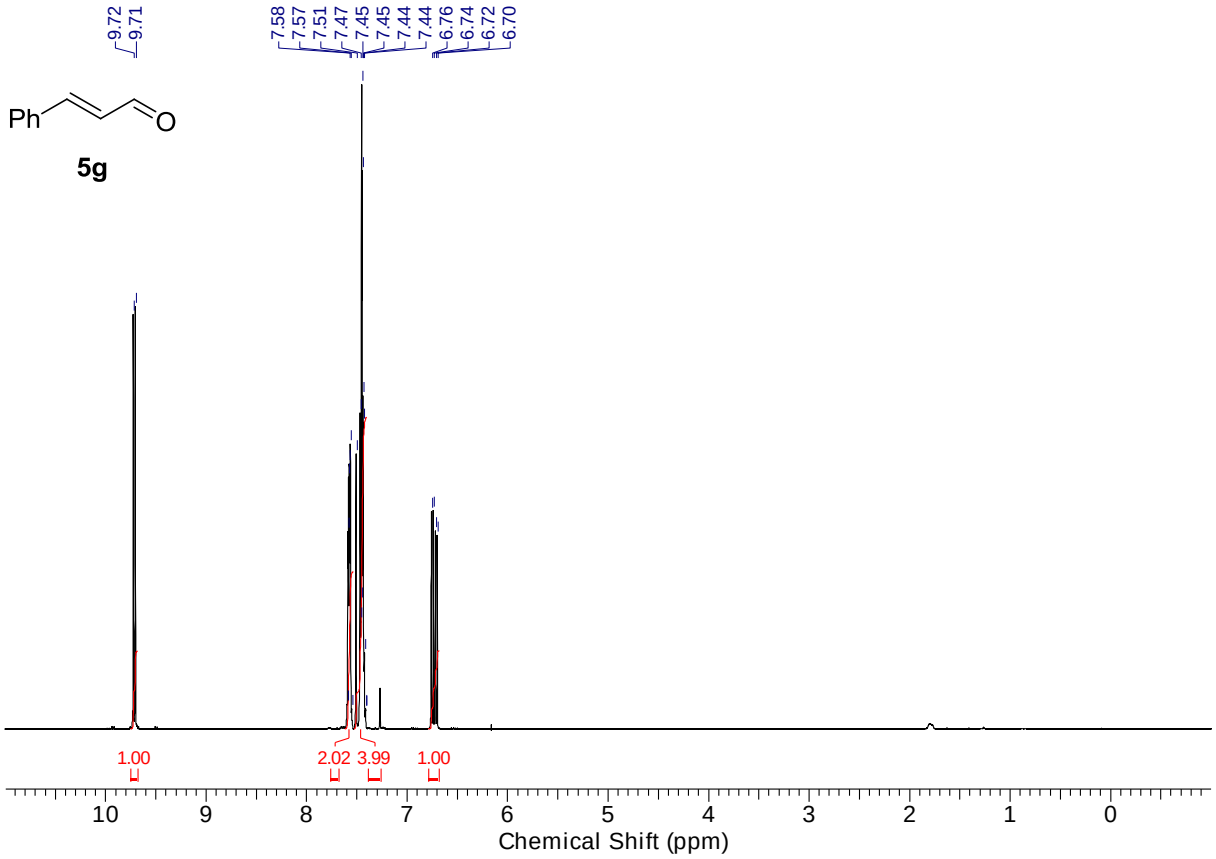
Chemical Shift (ppm)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7.45
7.44
7.44
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6.74
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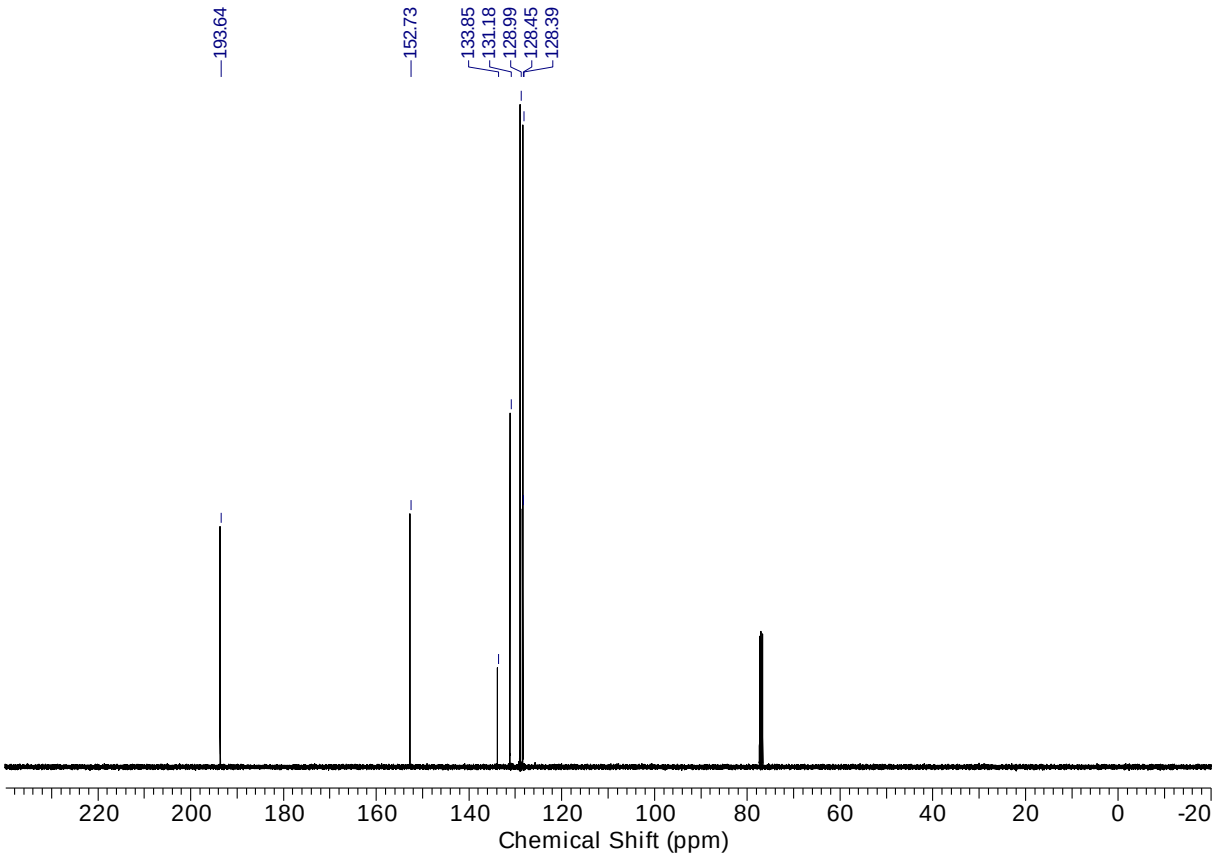
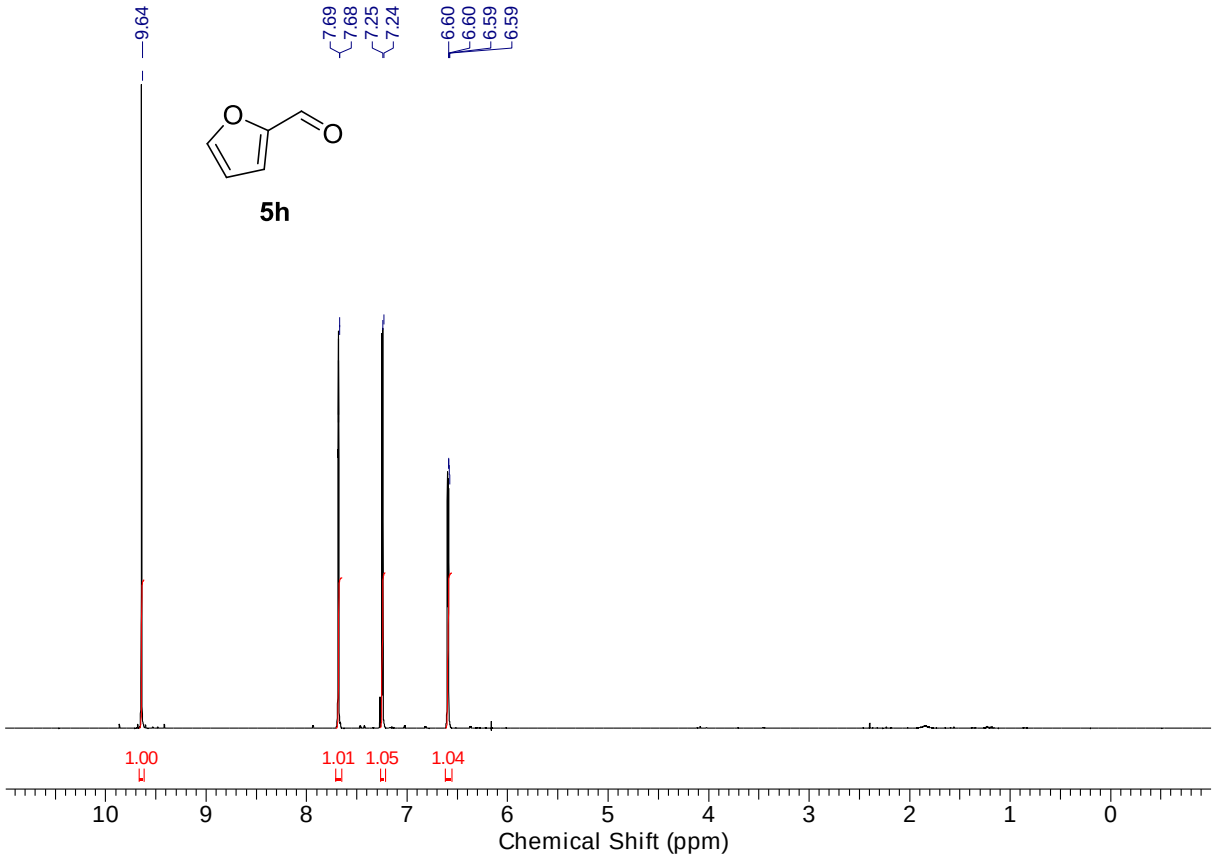
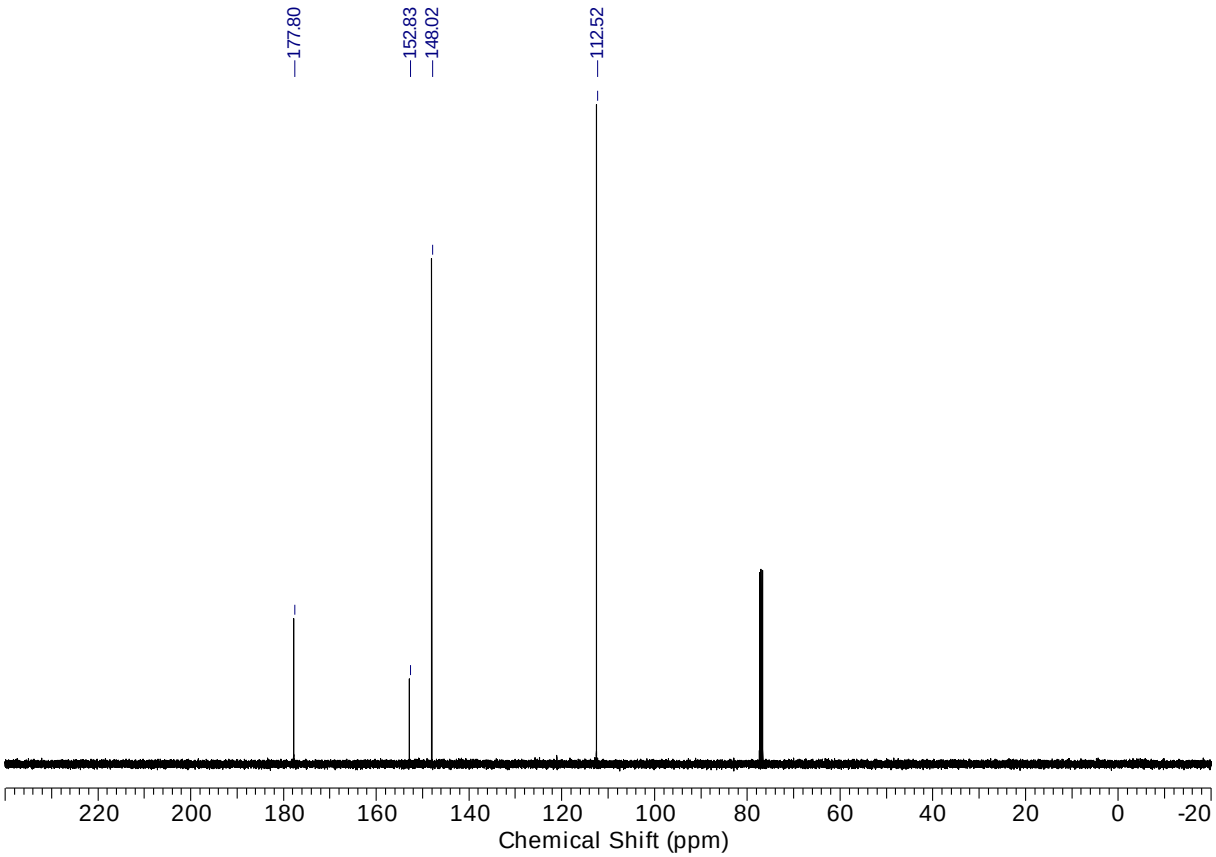
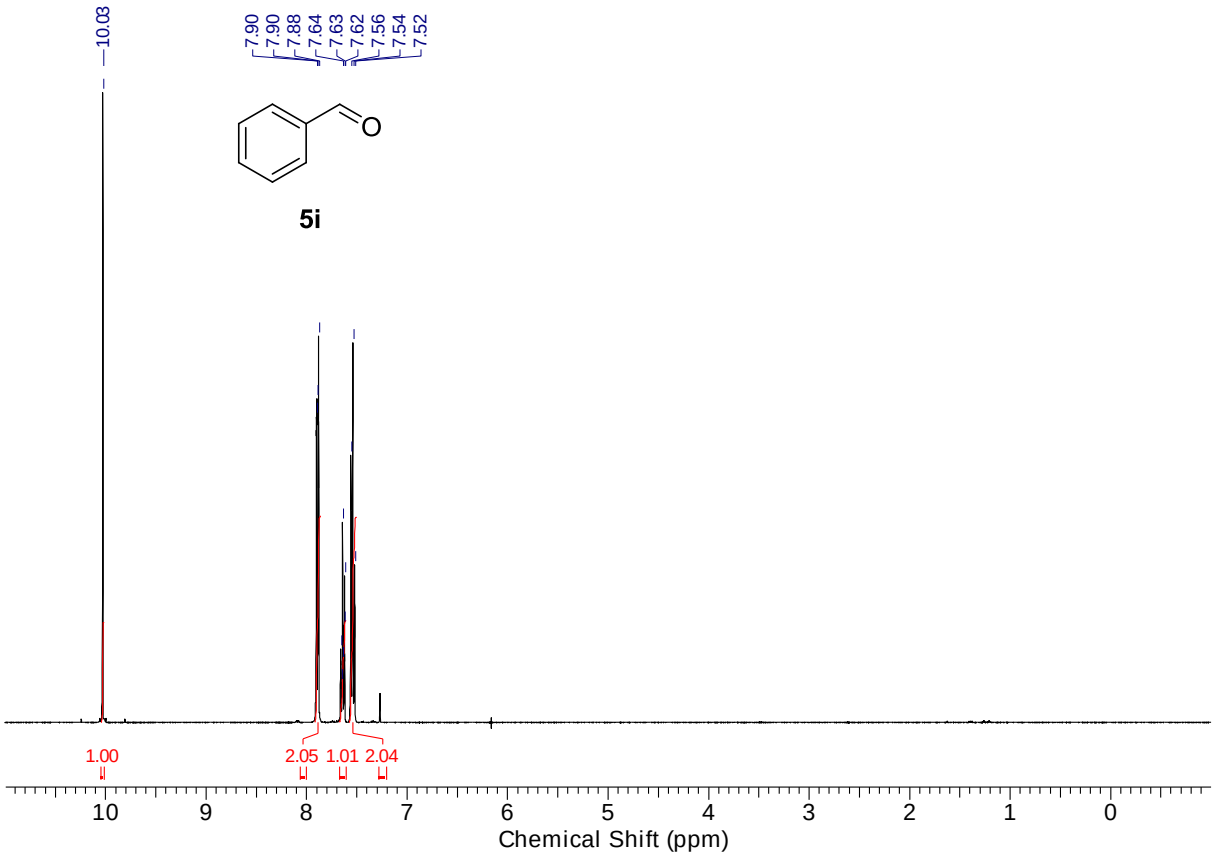
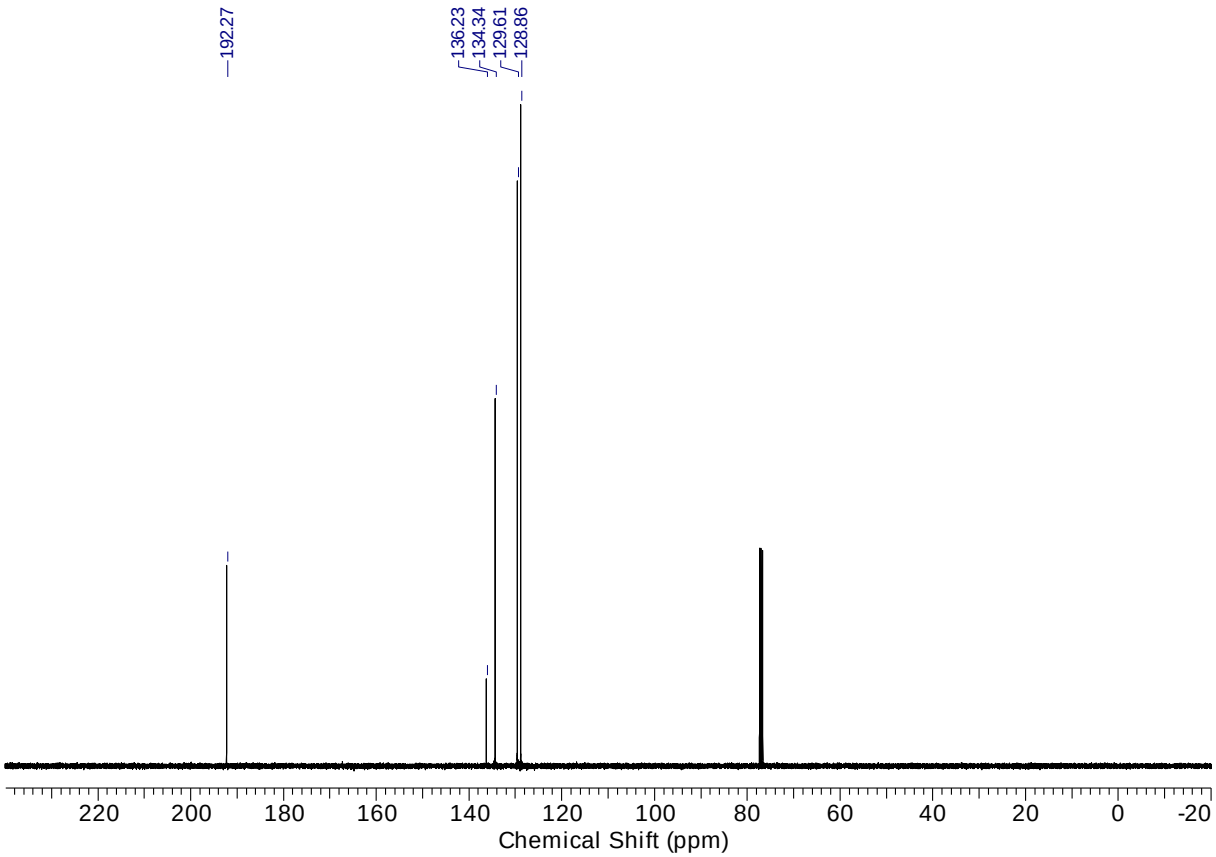
6.70
Ph
O
5g
1.00
2.02
3.99
1.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

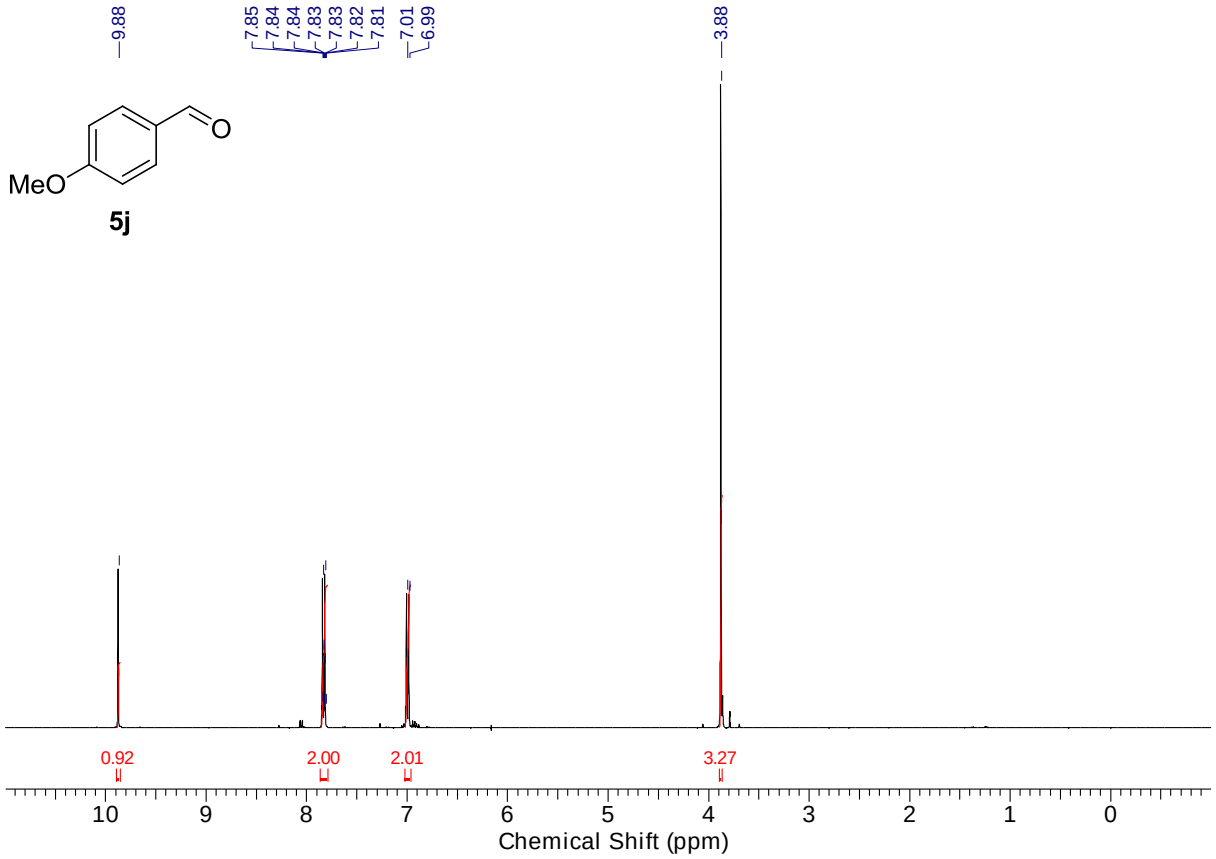

193.64
152.73
133.85
131.18
128.99
128.45
128.39
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

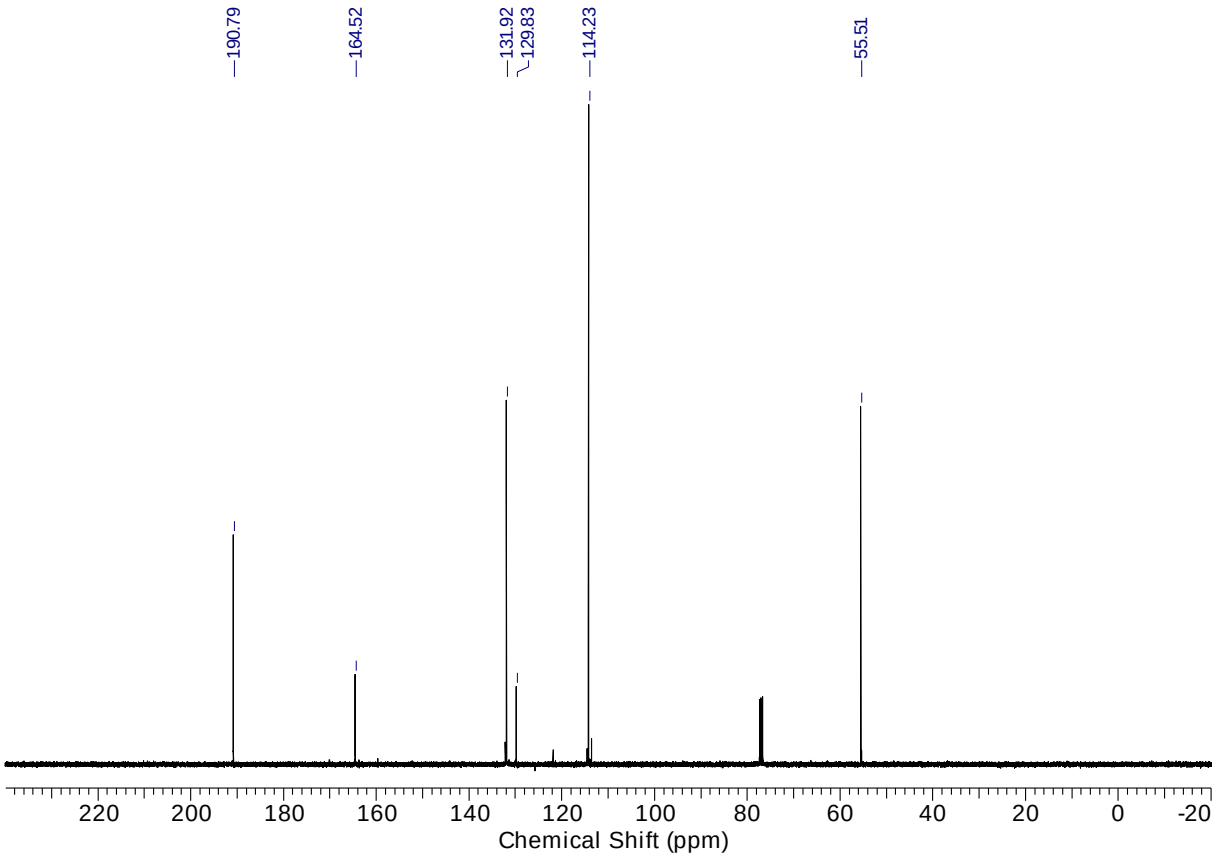

9.64
7.69
7.68
7.25
7.24
6.60
6.60
6.59
6.59
O
O
5h
1.00
1.01
1.05
1.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

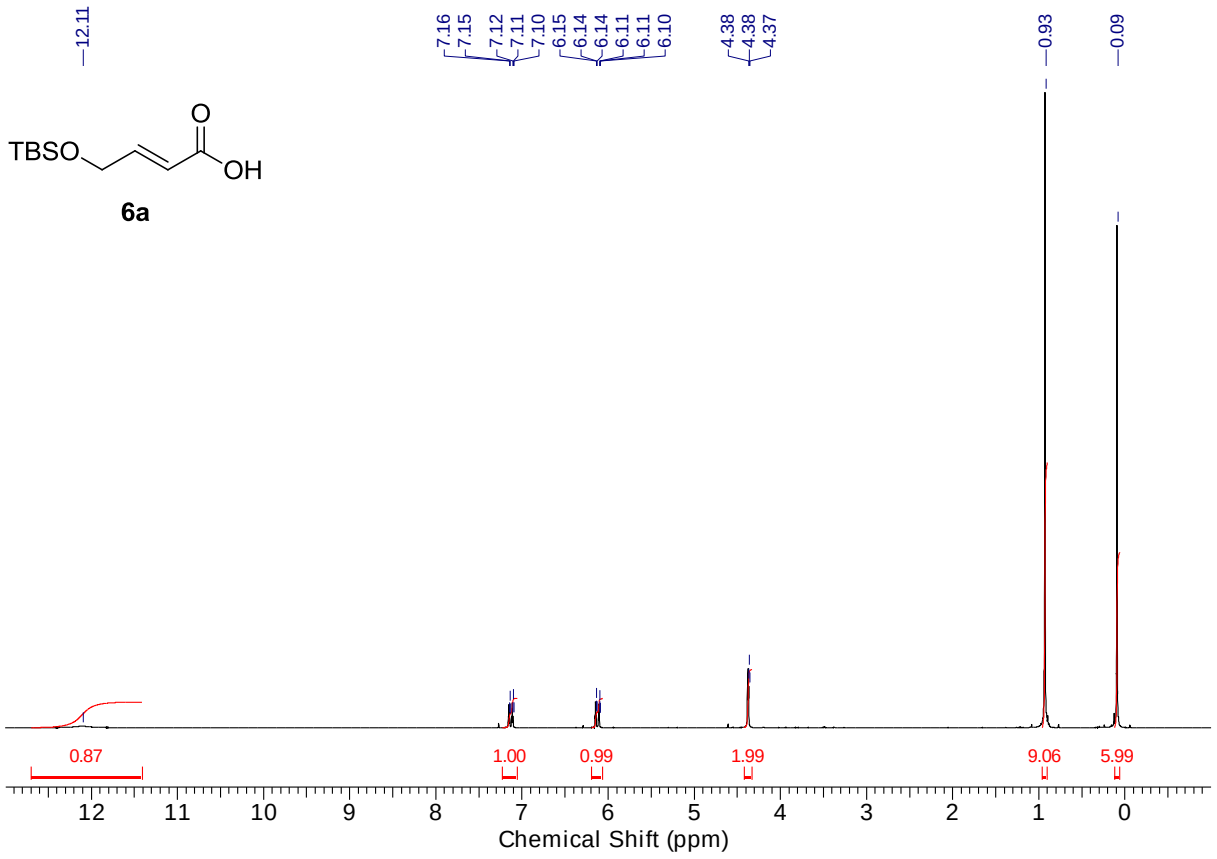

177.80
152.83
148.02
112.52
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

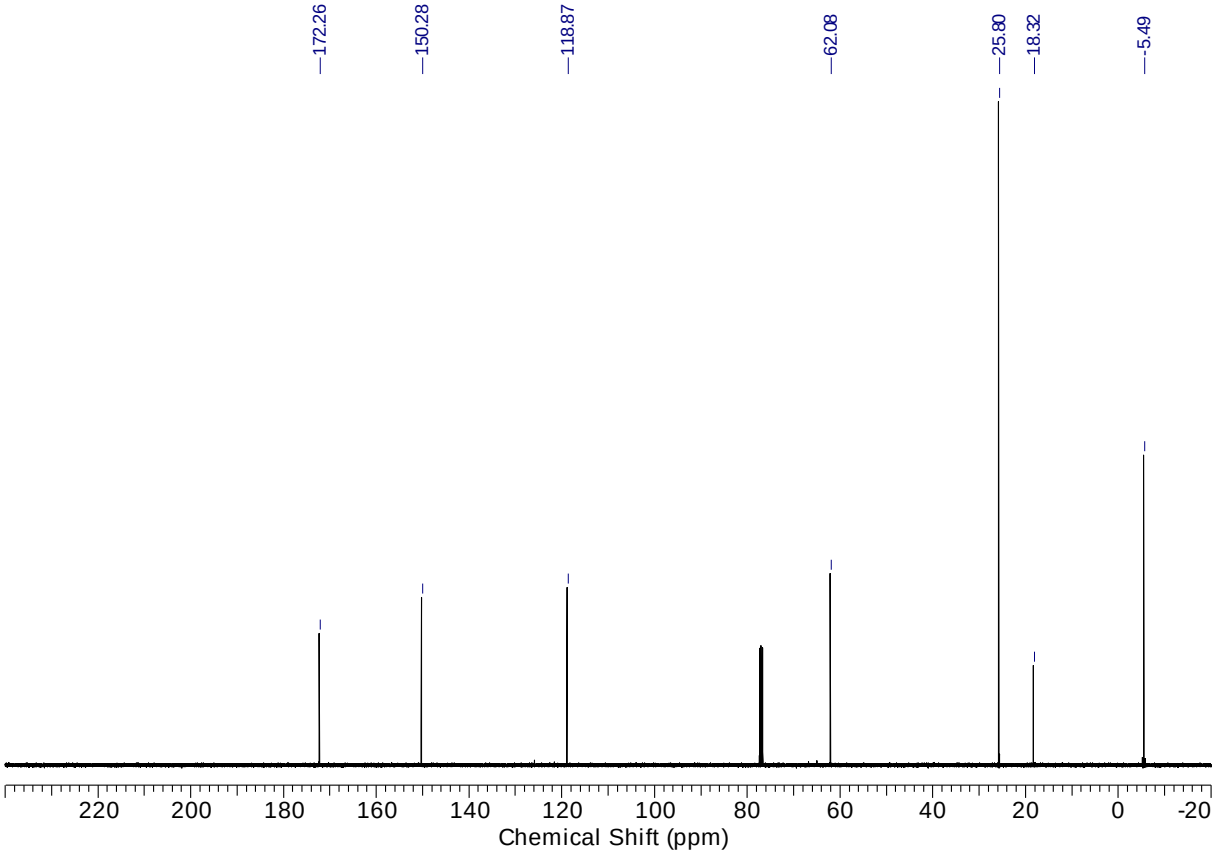

10.03
7.90
7.90
7.88
7.64
7.63
7.62
7.56
7.54
7.52
O
5i
1.00
2.05
1.01
2.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

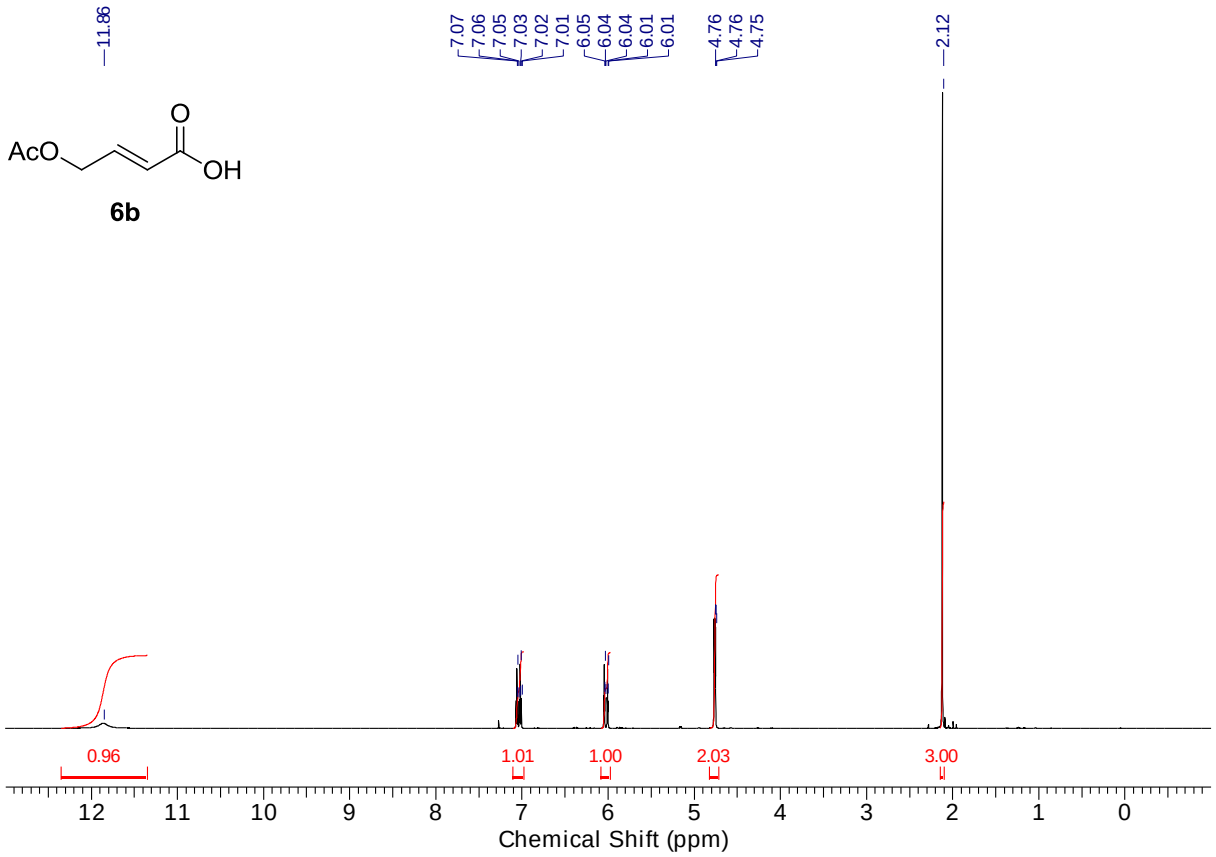

192.27
136.23
134.34
129.61
128.86
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

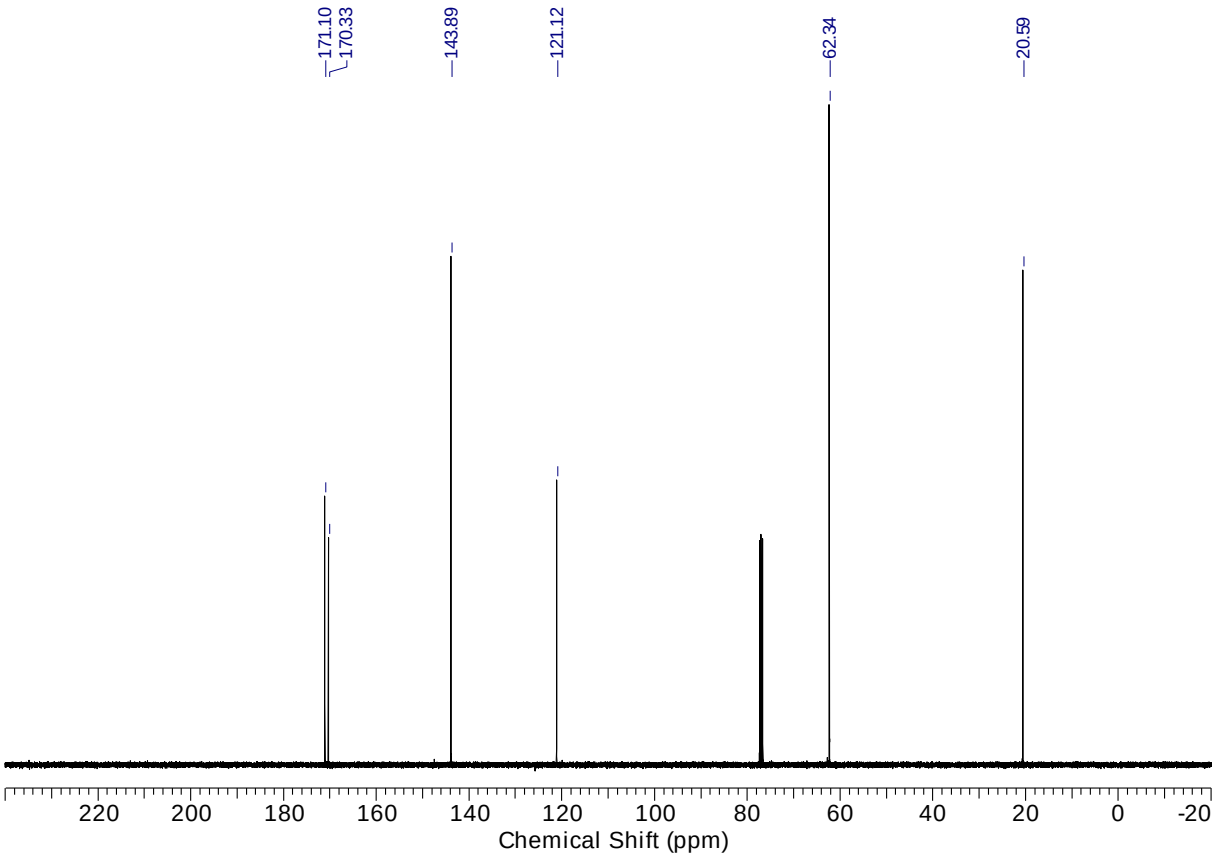

9.88
7.85
7.84
7.84
7.83
7.83
7.82
7.81
7.01
6.99
3.88
O
MeO
5j
0.92
2.00
2.01
3.27
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

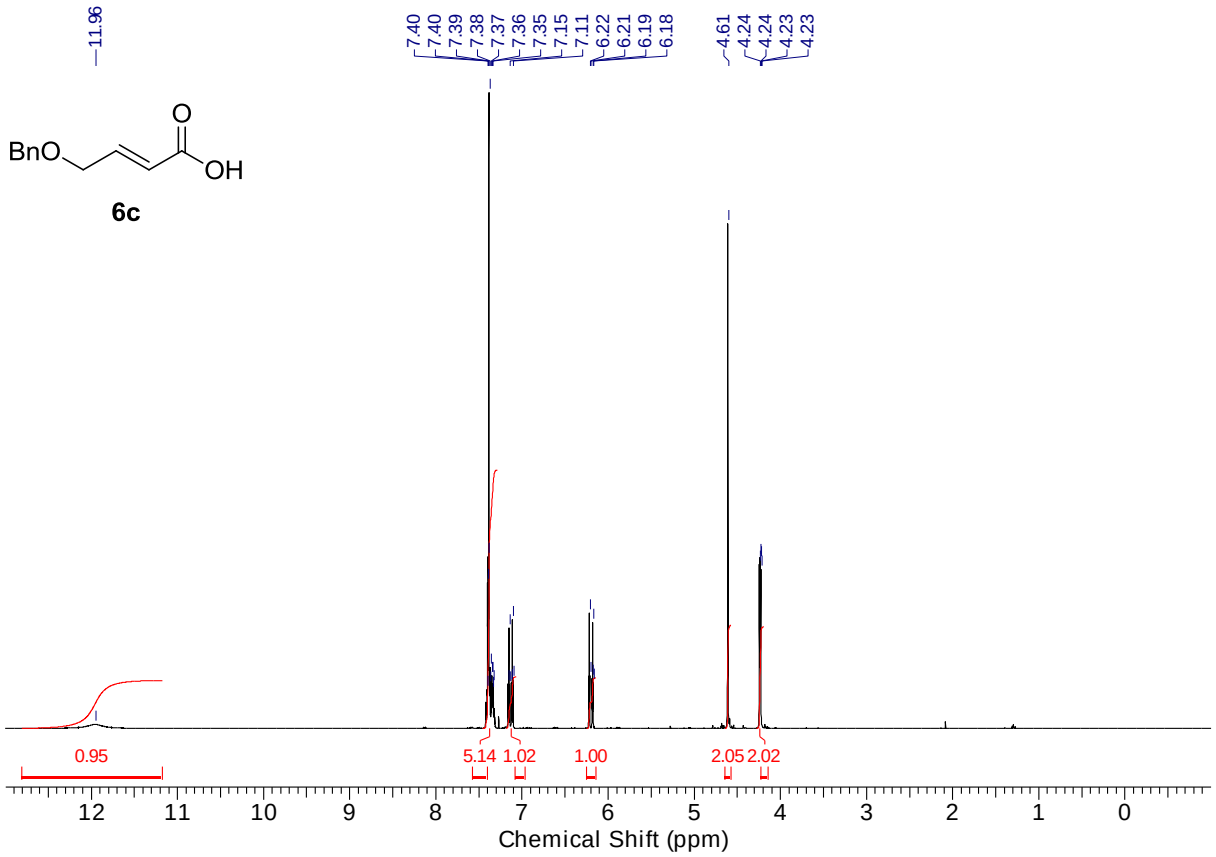

190.79
164.52
131.92
129.83
114.23
55.51
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

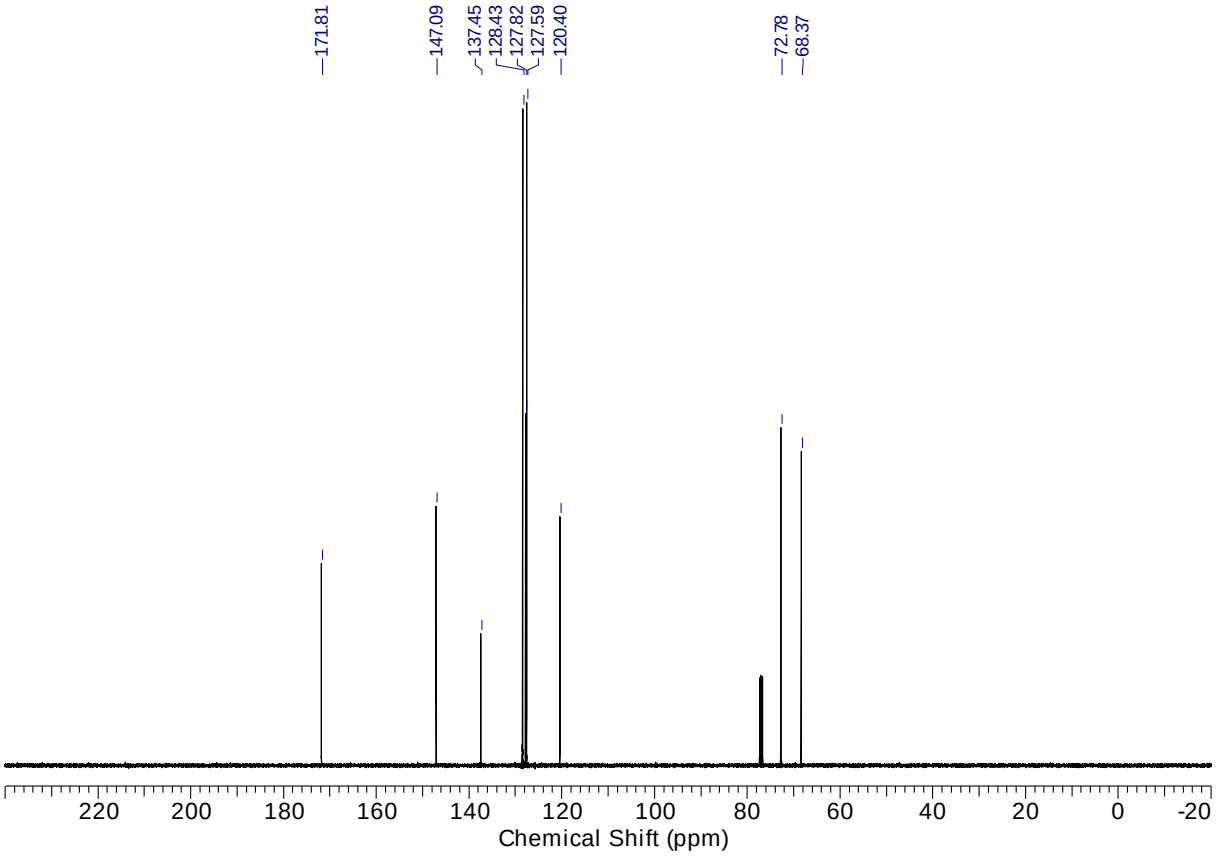

12.11
7.16
7.15
7.12
7.11
7.10
6.15
6.14
6.14
6.11
6.11
6.10
4.38
4.38
4.37
0.93
0.09
TBSO
O
OH
6a
0.87
1.00
0.99
1.99
9.06
5.99
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

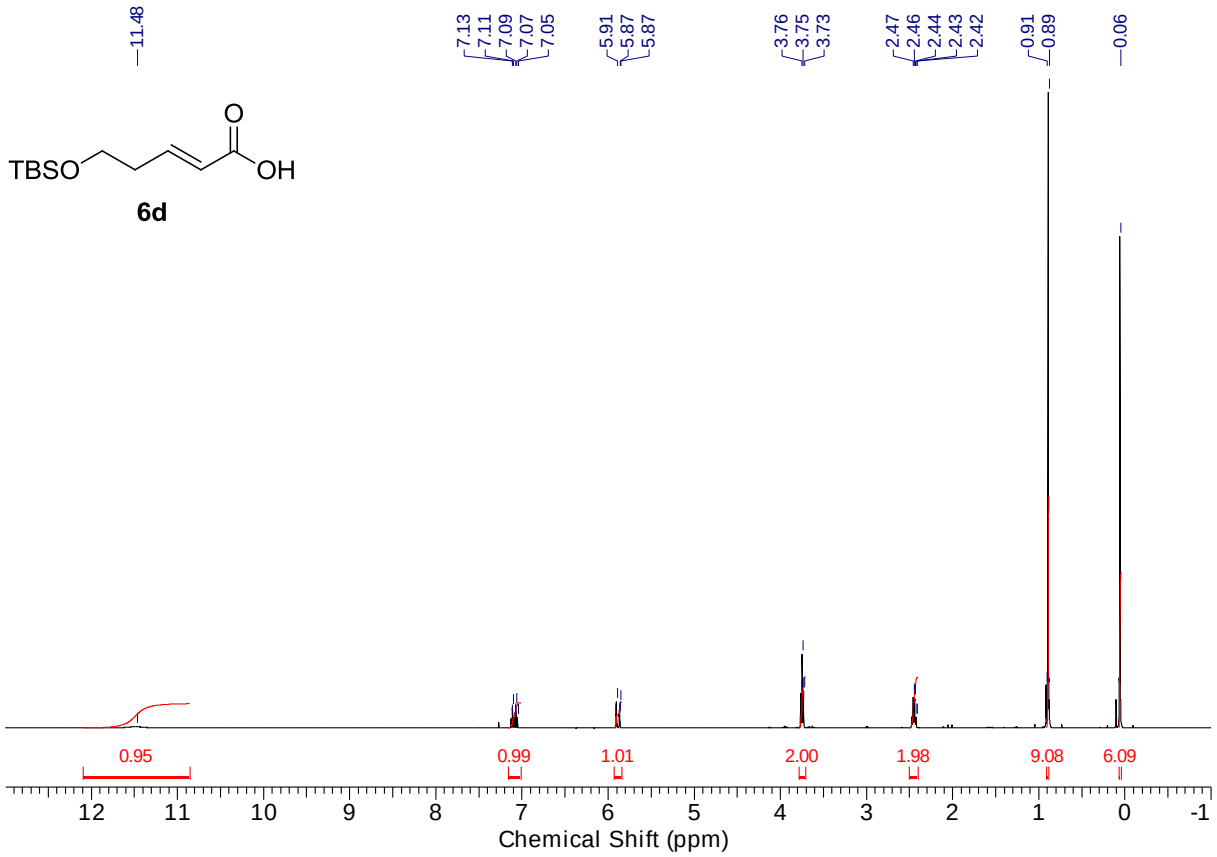

172.26
150.28
118.87
62.08
25.80
18.32
-5.49
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

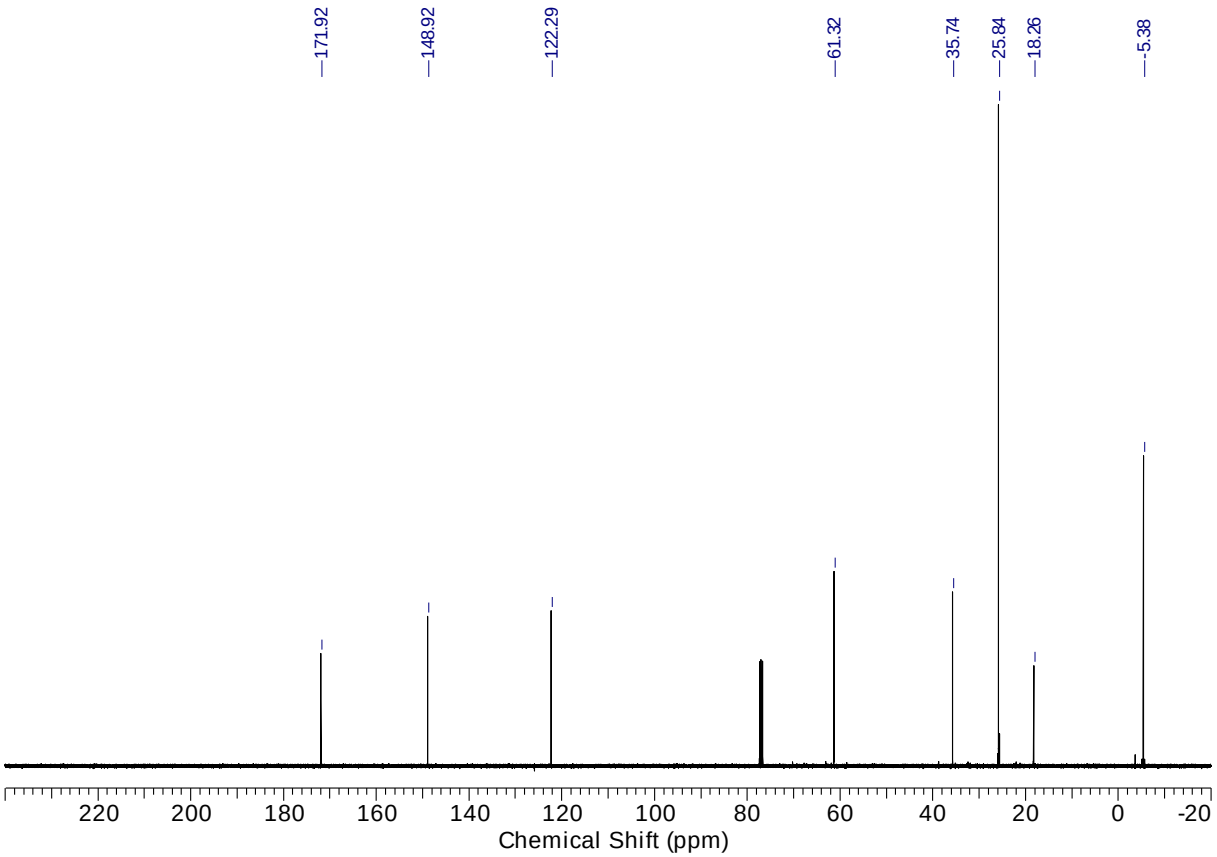

11.86
7.07
7.06
7.05
7.03
7.02
7.01
6.05
6.04
6.04
6.01
6.01
4.76
4.76
4.75
2.12
AcO
O
OH
6b
0.96
1.01
1.00
2.03
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

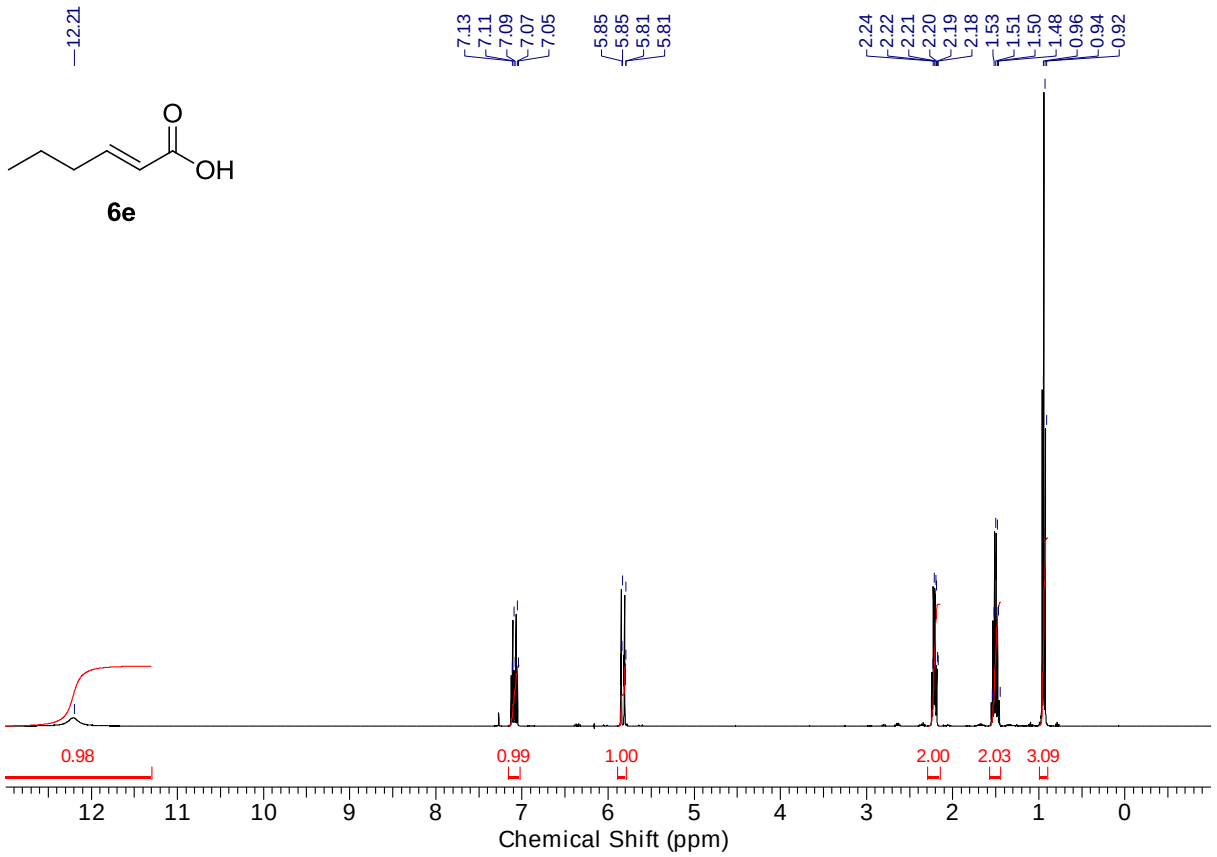

171.10
170.33
143.89
121.12
62.34
20.59
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

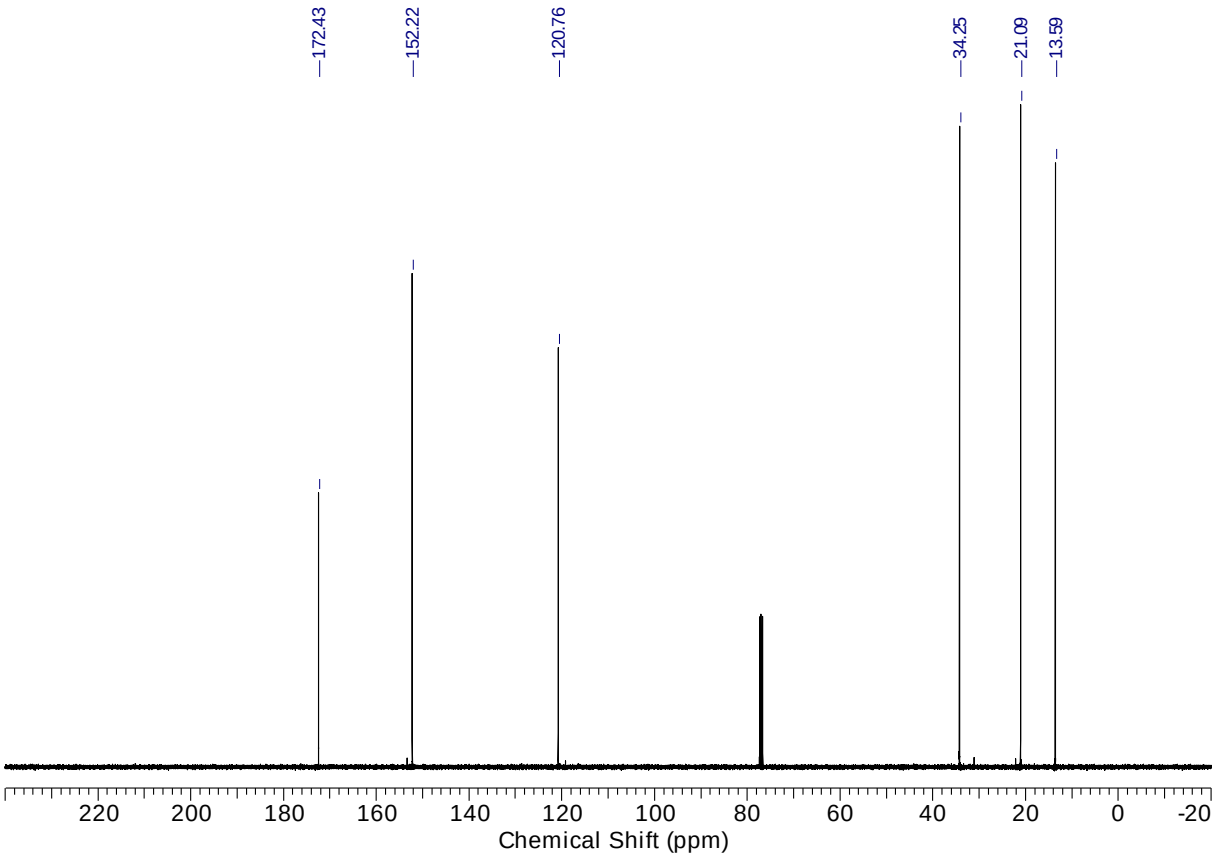

11.96
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.15
7.11
6.22
6.21
6.19
6.18
4.61
4.24
4.24
4.23
4.23
BnO
O
OH
6c
0.95
5.14
1.02
1.00
2.05
2.02
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

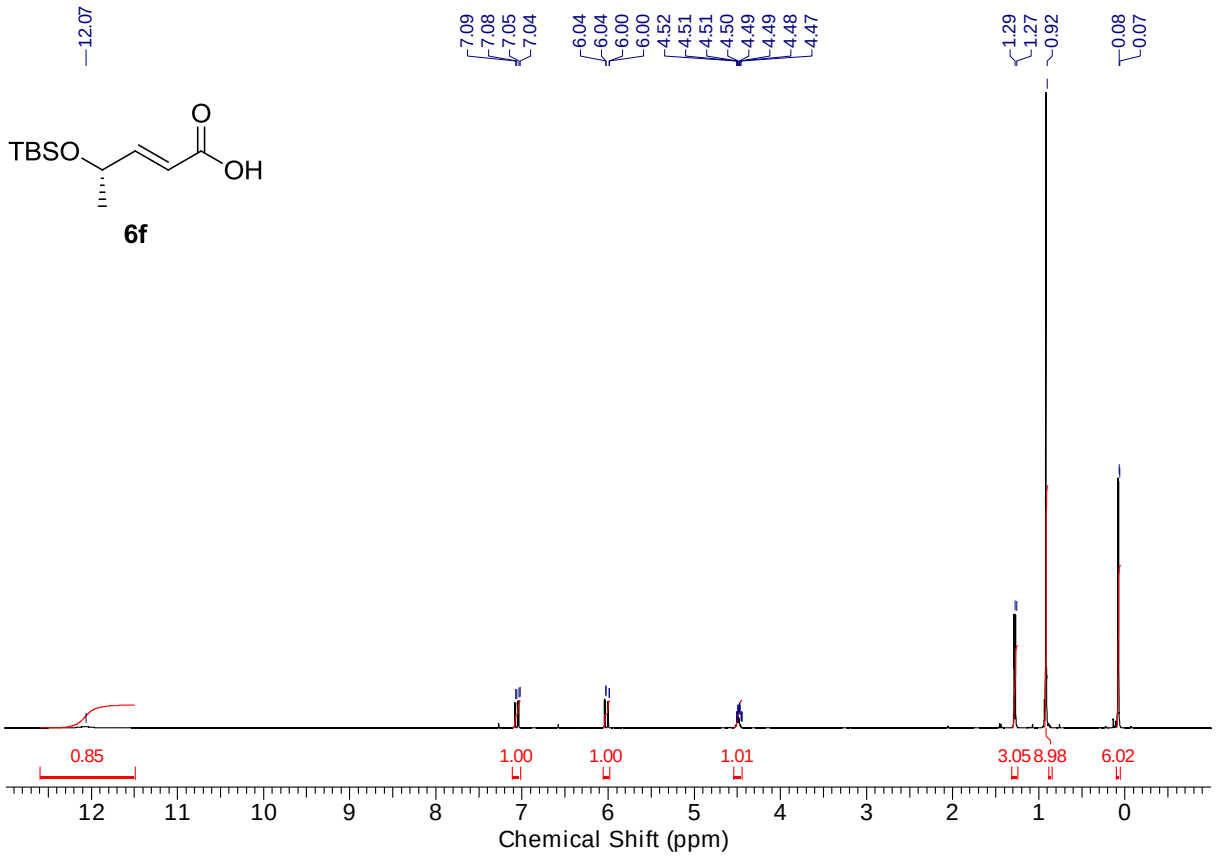

171.81
147.09
137.45
128.43
127.82
127.59
120.40
72.78
68.37
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

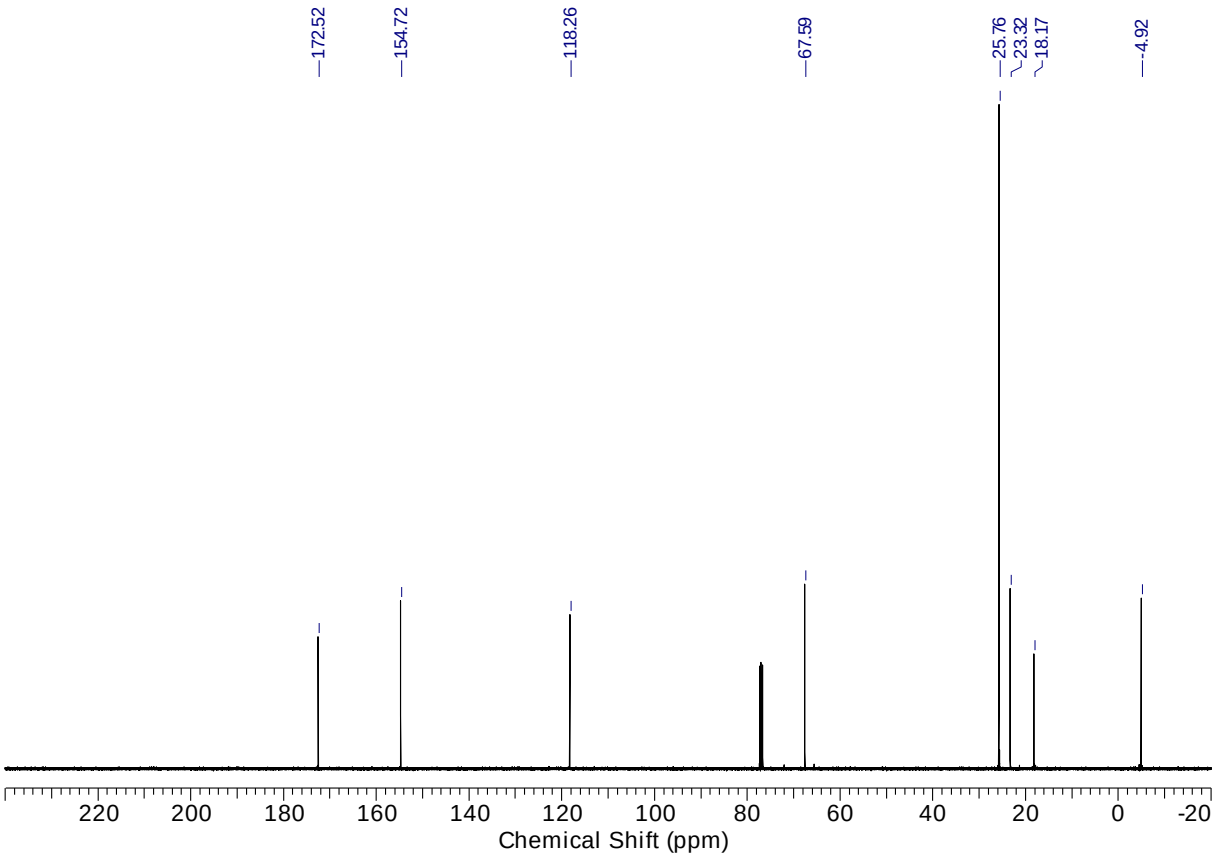

11.48
7.13
7.11
7.09
7.07
7.05
5.91
5.87
5.87
3.76
3.75
3.73
2.47
2.46
2.44
2.43
2.42
0.91
0.89
0.06
TBSO
O
OH
6d
0.95
0.99
1.01
2.00
1.98
9.08
6.09
Chemical Shift (ppm)

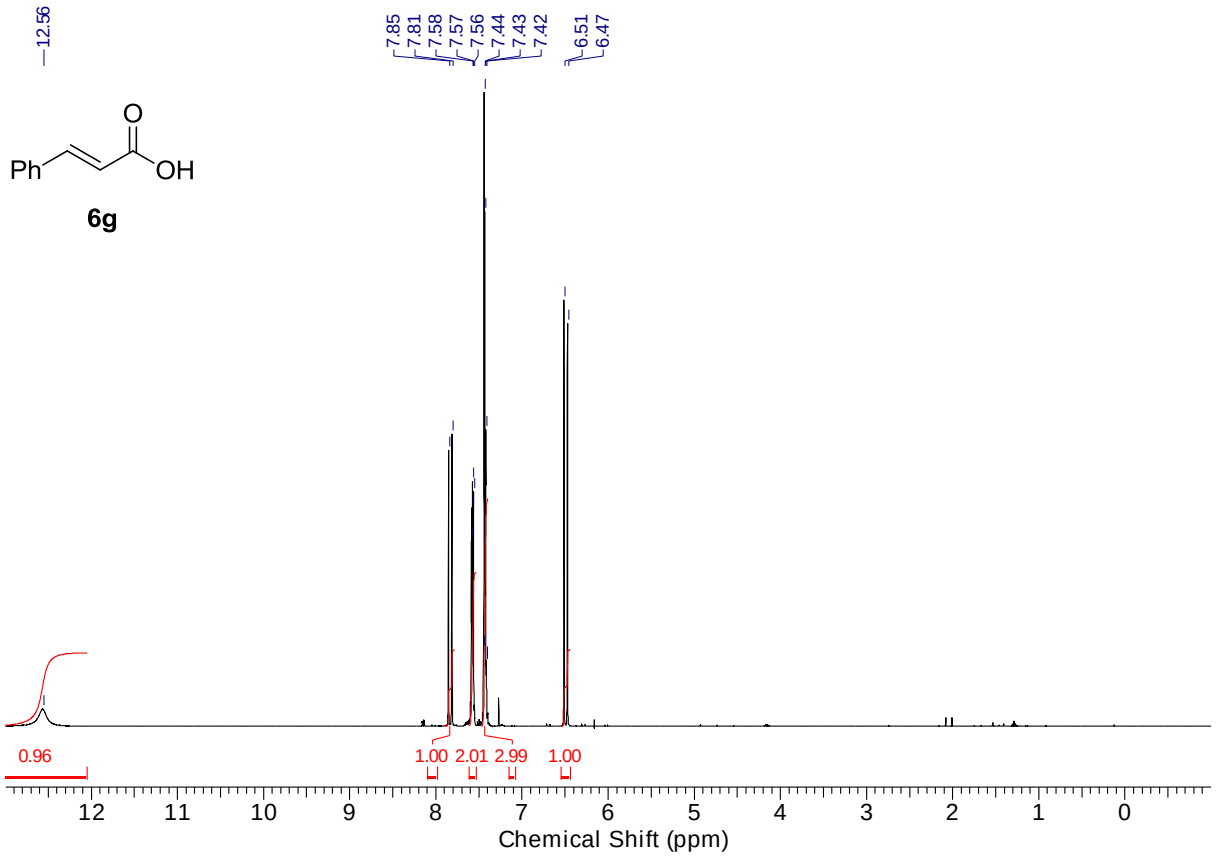

171.92
148.92
122.29
61.32
35.74
25.84
18.26
5.38
Chemical Shift (ppm)

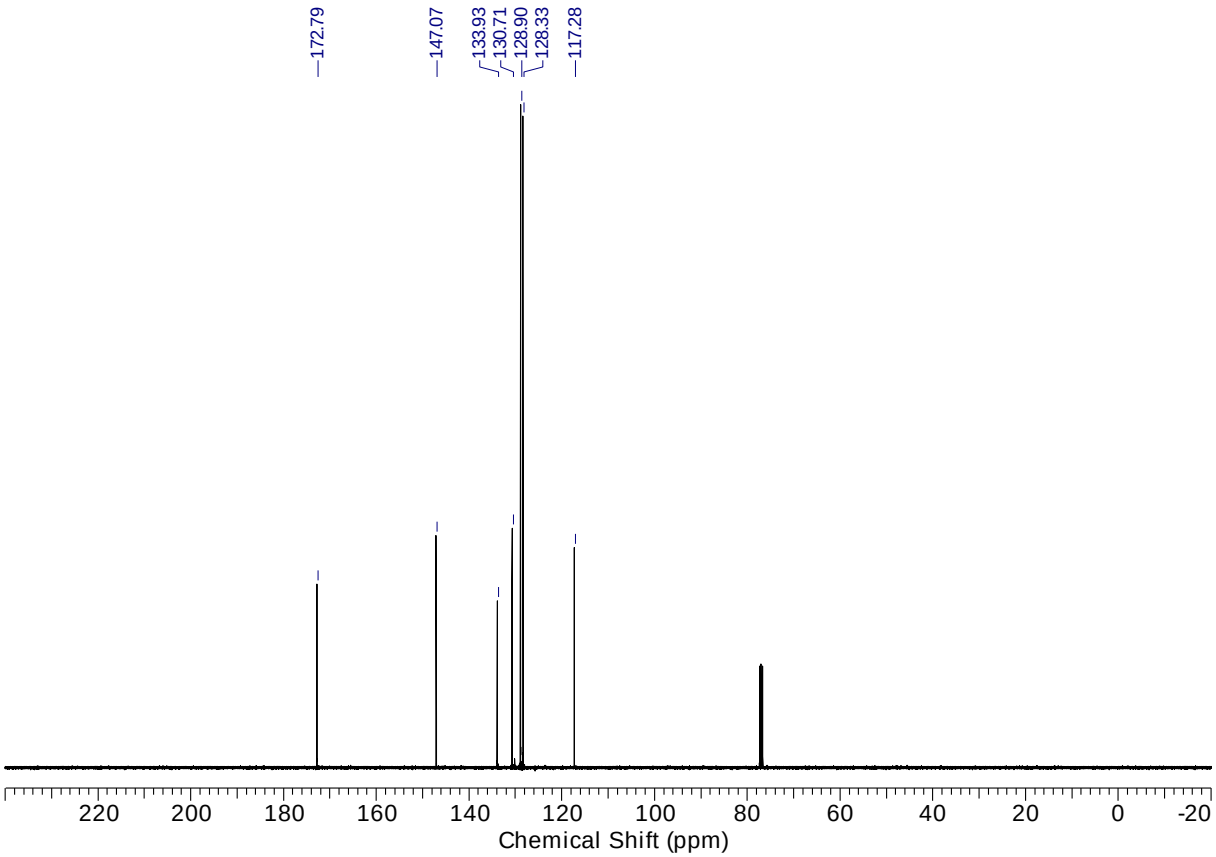

12.21
7.13
7.11
7.09
7.07
7.05
5.85
5.85
5.81
5.81
2.24
2.22
2.21
2.20
2.19
2.18
1.53
1.51
1.50
1.48
0.96
0.94
0.92
O
OH
6e
0.98
0.99
1.00
2.00
2.03
3.09
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

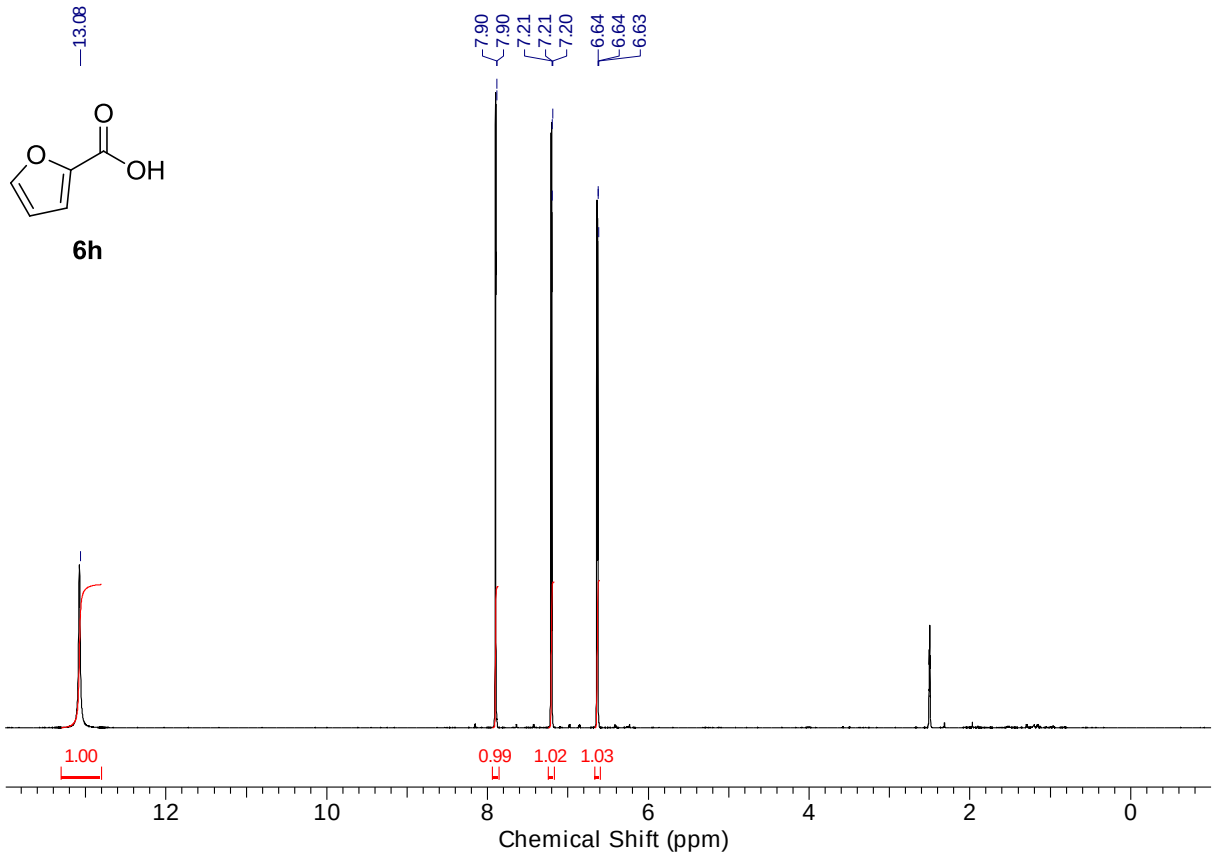

172.43
152.22
120.76
34.25
21.09
13.59
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

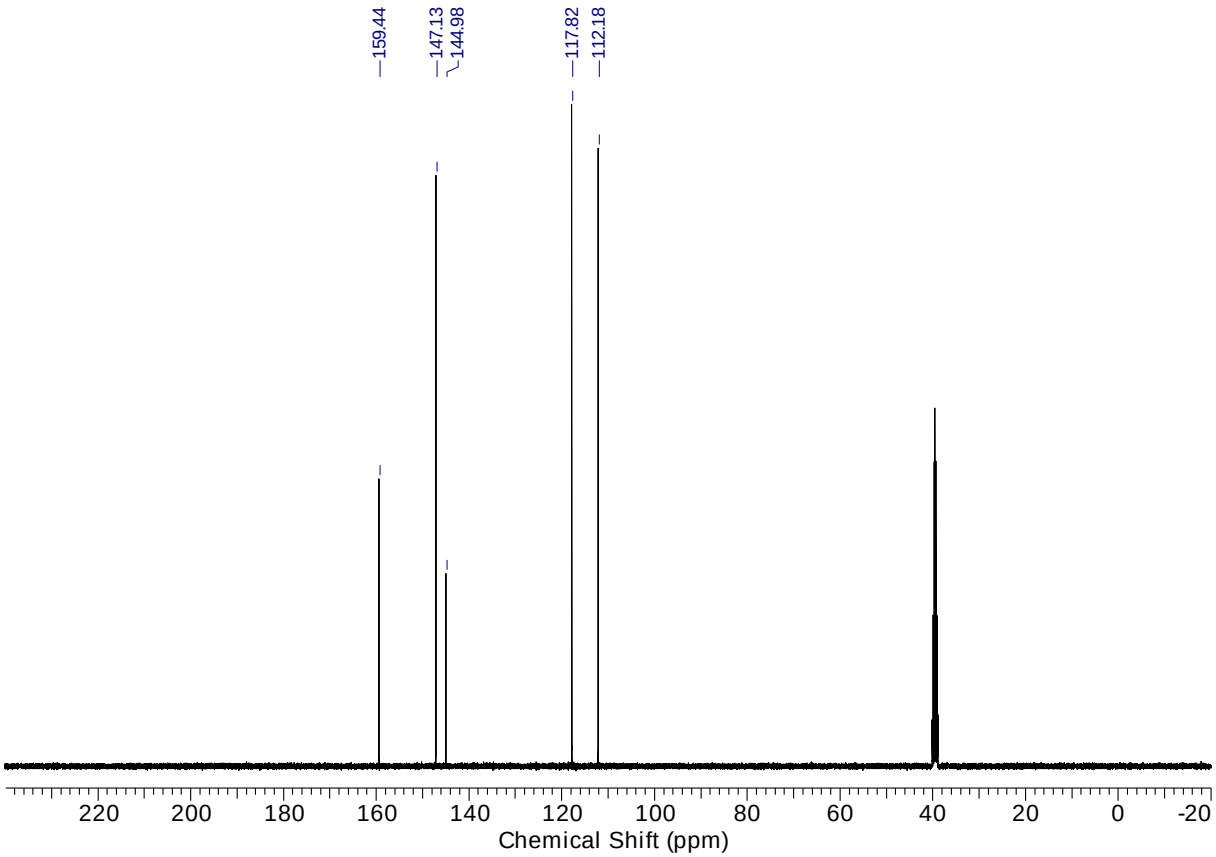

12.07
7.09
7.08
7.05
7.04
6.04
6.04
6.00
6.00
4.52
4.51
4.51
4.50
4.49
4.49
4.48
4.47
1.29
1.27
0.92
0.08
0.07
TBSO
O
OH
6f
0.85
1.00
1.00
1.01
3.05
8.98
6.02
Chemical Shift (ppm)

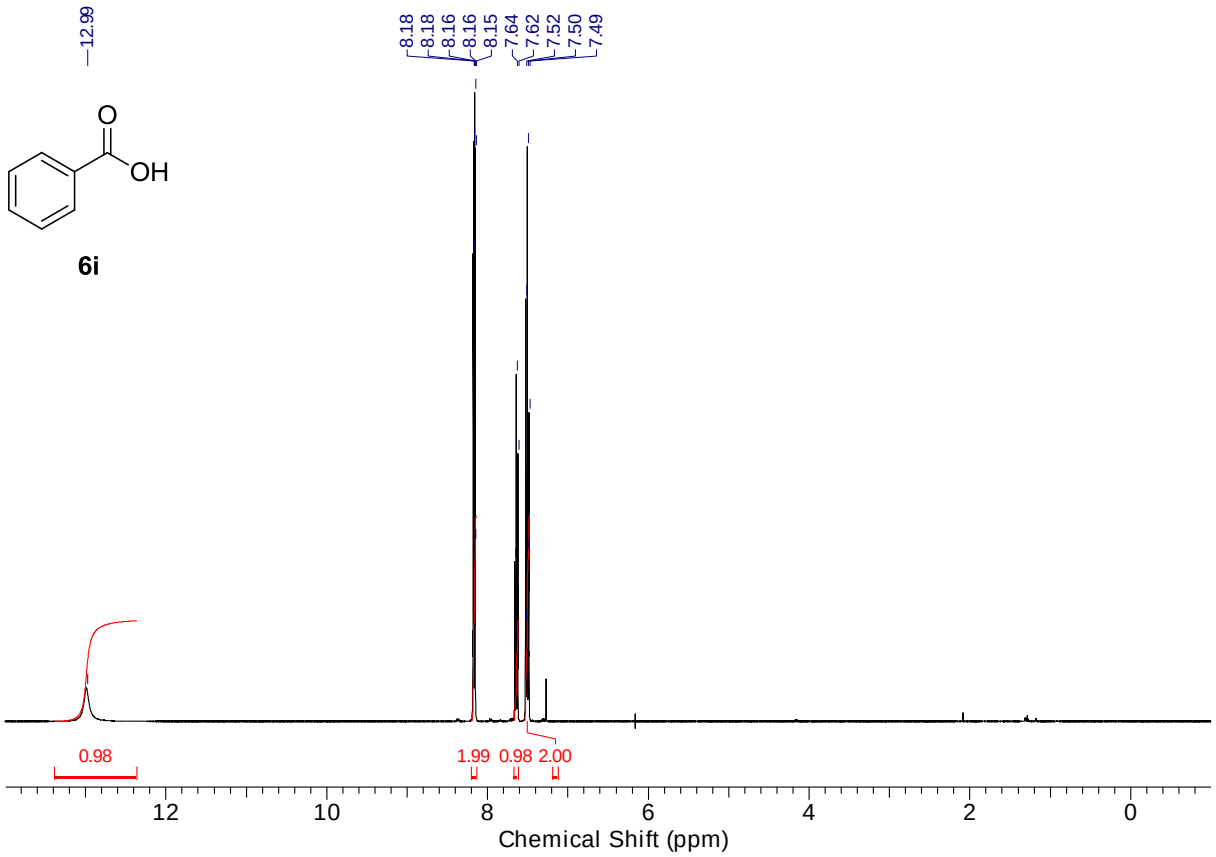

172.52
154.72
118.26
67.59
25.76
23.32
18.17
-4.92
Chemical Shift (ppm)

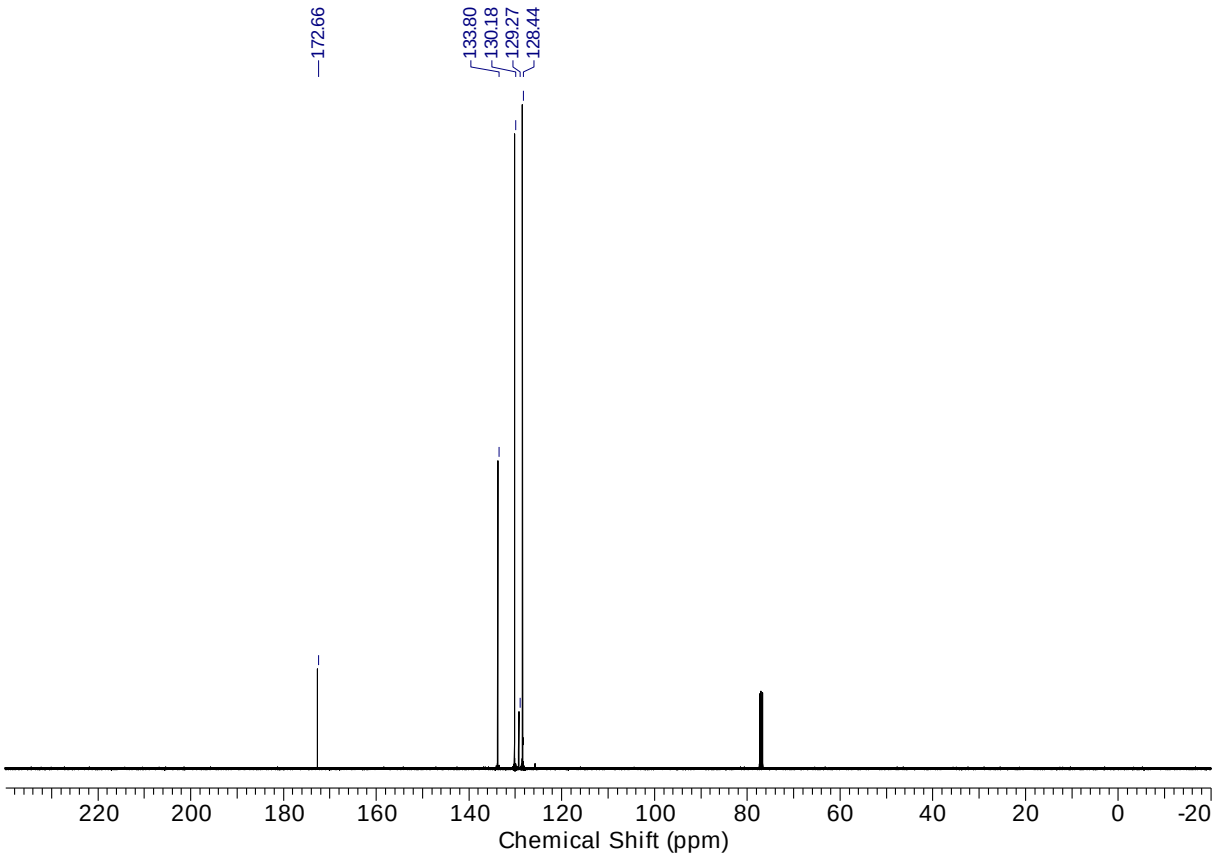

12.56
7.85
7.81
7.58
7.57
7.56
7.44
7.43
7.42
6.51
6.47
O
Ph
OH
6g
0.96
1.00
2.01
2.99
1.00
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

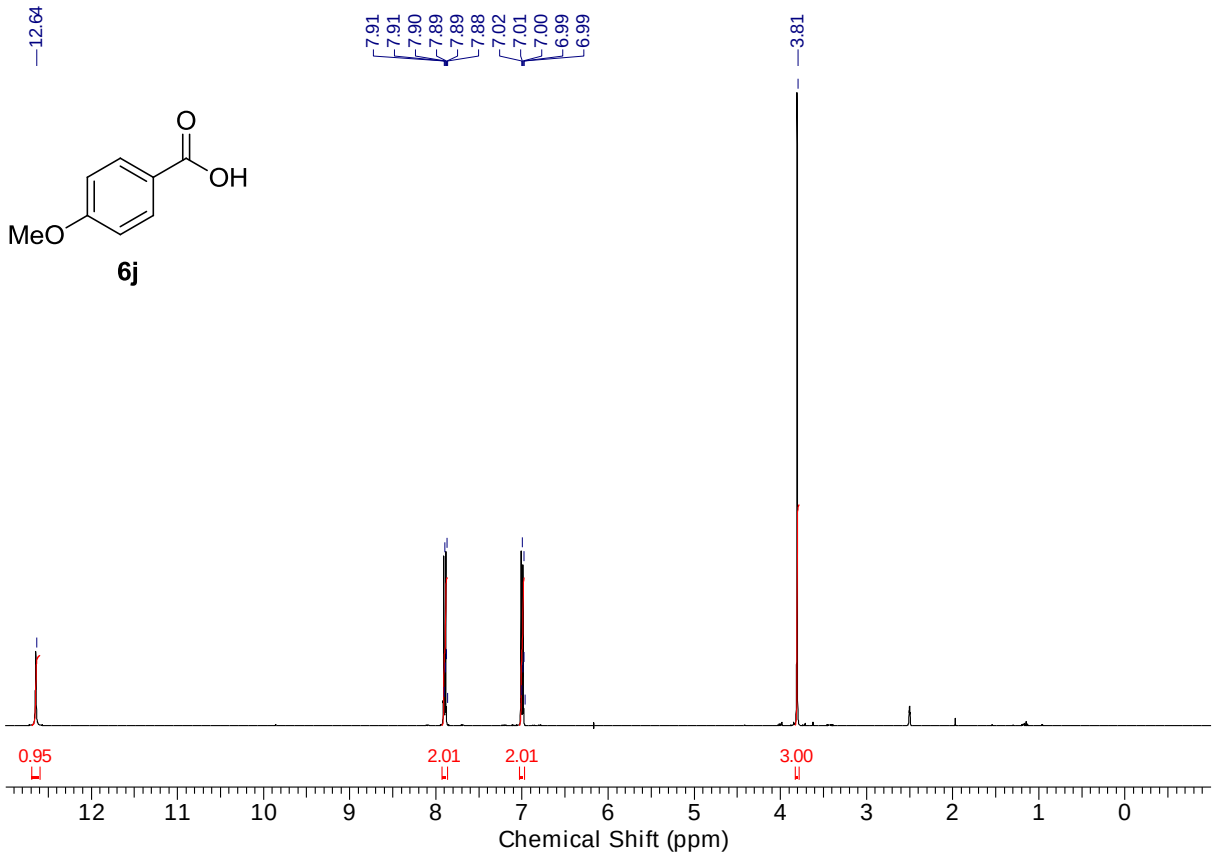

172.79
147.07
133.93
130.71
128.90
128.33
117.28
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


13.08
7.90
7.90
7.21
7.21
7.20
6.64
6.64
6.63
O
O
OH
6h
1.00
0.99
1.02
1.03
12
10
8
6
4
2
0
Chemical Shift (ppm)

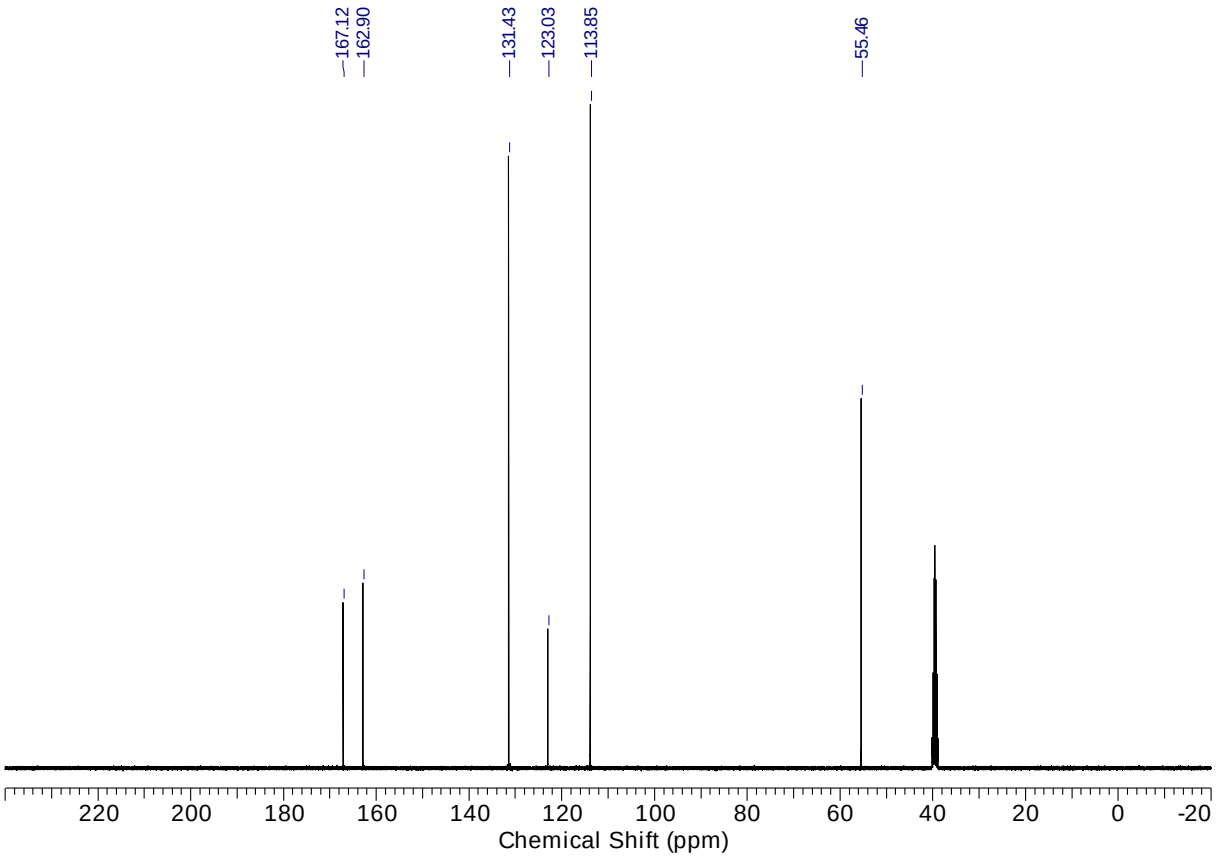

159.44
147.13
144.98
117.82
112.18
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


12.99
8.18
8.18
8.16
8.16
8.15
7.64
7.62
7.52
7.50
7.49
O
OH
6i
0.98
1.99
0.98
2.00
12
10
8
6
4
2
0
Chemical Shift (ppm)


172.66
133.80
130.18
129.27
128.44
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


12.64
7.91
7.91
7.90
7.89
7.89
7.88
7.02
7.01
7.00
6.99
6.99
3.81
O
OH
MeO
0.95
2.01
2.01
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

6j


167.12
162.90
131.43
123.03
113.85
55.46
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)