Supporting Information

Catalytic Nucleophilic Glyoxylation of Aldehydes

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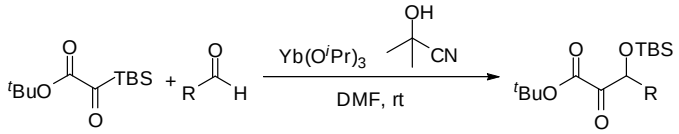
Experimental Section

Methods: General. Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 (^{1}H NMR at 400 MHz and ^{13}C NMR at 100 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, br t = broad triplet, q = quartet, sept = septuplet, oct = octuplet, m = multiplet), coupling constants (Hz), and integration. Analytical thin layer chromatography (TLC) was performed on Whatman 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light and/or aqueous ceric ammonium molybdate solution followed by heating. Purification of the reaction products was carried out by using Siliaflash-P60 silica gel (40-63μm) purchased from Silicycle. Mass spectra were obtained using a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization (Note: All samples prepared in methanol). All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Yield refers to isolated yield of analytically pure material unless otherwise noted. Yields and diastereomeric ratios (dr) are reported for a specific experiment and as a result may differ slightly from those found in the tables, which are averages of at least two experiments. Enantiomeric excesses were obtained using a Supercritical Fluid Chromatograph equipped with a UV-Vis detector using a Chiralcel Chiralpak AD HPLC column. Samples were eluted with SFC grade CO_2 at the indicated percentage of MeOH.

Materials: General. *N*,*N*-Dimethylformamide was distilled from P_2O_5 and stored under N_2 over 3Å molecular sieves. Benzaldehyde, *p*-anisaldehyde, 4-methylbenzaldehyde, and 2-methylbenzaldehyde were purified by the following procedure: The neat aldehydes were washed sequentially with a 1 M sodium hydroxide solution and a saturated aqueous sodium bicarbonate solution, dried with magnesium sulfate, and distilled under reduced pressure. 4-Chlorobenzaldehyde was sublimed under reduced pressure. Isobutyraldehyde and propionaldehyde were dried over $CaSO_4$ and distilled under N_2 prior to use. Silyl glyoxylate **1** was prepared according to the published procedure.[1] All other reagents were obtained from commercial sources and used without further purification unless otherwise noted.

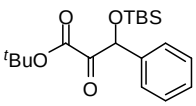
[1] Nicewicz, D. A.; Brétéché, G.; Johnson, J. S. *Org. Synth.* **2008**, *85*, 278.

General Procedure A for the Yb(O^{i}Pr)$_3$ catalyzed nucleophilic glyoxylation of aryl aldehydes to afford β-siloxy-α-ketoesters 4a-j:



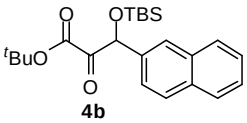
1 **4a-j**

In an inert atmosphere glovebox, a 10-mL round-bottomed flask containing a magnetic stir bar was charged with Yb(O^{i}Pr)$_3$ (0.05 equiv). The flask was sealed with a rubber septum and removed from the glovebox. To this flask was added DMF (1 mL), and this solution was allowed to stir until complete dissolution of the Yb(O^{i}Pr)$_3$ occurred. A shell vial containing silyl glyoxylate (1.0 equiv), aldehyde (2.0 equiv) and acetone cyanohydrin (0.20 equiv) in DMF ([**1**]$_0$ = 0.20 M) was transferred to the round-bottomed flask *via* cannula. Upon the disappearance of the silyl glyoxylate (as indicated by TLC analysis: 10% EtOAc/hexanes), the reaction was quenched with 2 M aqueous silver nitrate (1 mL).[2] The resultant silver salts were removed via filtration through a pad of silica gel with EtOAc (20 mL). The organic layer was washed with water (3x), brine, dried over Na_2SO_4 and concentrated *in vacuo*. The resulting α-ketoesters were obtained in analytically pure form after the removal of the excess aldehyde as described below.



4a

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxo-3-phenylpropanoate (4a).** The title compound was prepared according to General Procedure A using **1** (1.00 g, 4.09 mmol, 1.0 equiv), benzaldehyde (0.868 g, 8.18 mmol, 2.0 equiv), acetone cyanohydrin (0.070 g, 0.818 mmol, 0.20 equiv), Yb(O^{i}Pr)$_3$ (0.072 g, 0.205 mmol, 0.05 equiv) and DMF (10 mL). The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4a** (1.20 g, 3.57 mmol, 87% yield) was obtained as a clear yellow oil. Analytical data for **4a**: **IR** (thin film, cm^{-1}) 2956, 2931, 2857, 1748, 1725, 1472, 1257, 1132, 872, 838, 426; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.42 (m, 5H), 5.56 (s, 1H), 1.43 (s, 9H), 0.90 (s, 9H), 0.10 (s, 3H), -0.010 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 162.2, 137.0, 128.5, 127.3, 84.2, 78.3, 27.9, 25.7, 18.3, -5.0; **TLC** (10% EtOAc/hexanes) R_f 0.46; **LRMS** (ESI) Calcd. For $C_{19}H_{30}O_4SiNa$ + CH_3OH): 405.21. Found: 405.20.

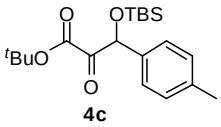


4b

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-3-(naphthalen-2-yl)-2-oxopropanoate (4b)**. The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), 2-napthaldehyde (0.064 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), Yb(O^{i}Pr)$_3$ (0.0035 g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and purification by flash chromatography (10% EtOAC/hexanes), **4b** (0.076 g, 0.188 mmol, 92% yield) was obtained as a clear colorless oil. Analytical data for **4b**: **IR** (thin film, cm^{-1}) 2955, 2931, 2886, 2857, 1747, 1724, 1370, 1255, 1164, 1127, 839, 782; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.87 (m, 4H), 7.48-7.55 (m, 3H), 5.74 (s, 1H), 1.42 (s, 9H), 0.92 (s, 9H), 0.14 (s, 3H), 0.007 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 162.3, 134.5, 133.4, 133.2, 128.4, 128.1, 127.8,

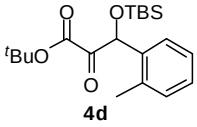
[2] This was necessary to remove all trace amounts of the cyanohydrin product **3**.

126.8, 126.4, 126.3, 124.7, 84.3, 78.4, 27.9, 25.7, 18.4, -4.9; **TLC** (10% EtOAc/hexanes) R_f 0.42; **LRMS** (ESI) Calcd. For $C_{23}H_{32}O_4SiNa + CH_3OH$: 455.22. Found: 455.21.



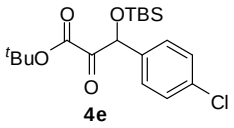
4c

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxo-3-*p*-tolylpropanoate (4c).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), *p*-tolualdehyde (0.049 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), $Yb(O^iPr)_3$ (0.0035g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4c** (0.060 g, 0.164 mmol, 80% yield) was obtained as a clear colorless oil. Analytical data for **4c**: **IR** (thin film, cm^{-1}) 2957, 2930, 2858, 1721, 1462, 1369, 1254, 1151, 1103, 838, 779; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 5.52 (s, 1H), 2.34 (s, 3H), 1.44 (s, 9H), 0.90 (s, 9H), 0.095 (s, 3H), -0.018 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 162.3, 138.3, 134.0, 129.2, 127.3, 84.1, 78.2, 27.9, 25.7, 21.1, 18.3, -4.99; **TLC** (10% EtOAc/hexanes) R_f 0.49; **LRMS** (ESI) Calcd. For $C_{20}H_{32}O_4SiNa + CH_3OH$: 419.22 Found: 419.22.



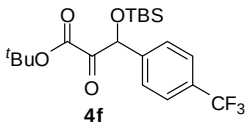
4d

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxo-3-*o*-tolylpropanoate (4d).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), *o*-tolualdehyde (0.049 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), $Yb(O^iPr)_3$ (0.0035g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4c** (0.064 g, 0.176 mmol, 86% yield) was obtained as a clear colorless oil. Analytical data for **4d**: **IR** (thin film, cm^{-1})2955, 2931, 2858, 1747, 1725, 1462, 1370, 1257, 1132, 838, 780, 746; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.37 (m, 1H), 7.14-7.22 (m, 3H), 5.69 (s, 1H), 2.36 (s, 3H), 1.39 (s 9H), 0.89 (s, 9H), 0.11 (s, 3H), -0.048 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 162.7, 136.7, 135.1, 130.8, 129.1, 128.6, 126.0, 84.1, 77.3, 27.8, 25.7, 19.2, 18.2, -4.99, -5.03; **TLC** (10% EtOAc/hexanes) R_f 0.49; **LRMS** (ESI) Calcd. For $C_{20}H_{32}O_4SiNa + CH_3OH$: 419.22 Found: 419.22.



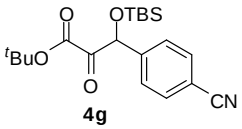
4e

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-3-(4-chlorophenyl)-2-oxopropanoate (4e).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), 4-chlorobenzaldehyde (0.058 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), $Yb(O^iPr)_3$ (0.0035g, 0.0102 mmol, 0.05 equiv)and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4e** (0.070 g, 0.182 mmol, 89% yield) was obtained as a clear colorless oil. Analytical data for **4e**: **IR** (thin film, cm^{-1}) 2955, 2931, 2887, 2859, 1749, 1725, 1490, 1371, 1257, 1132, 1089, 869, 839; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.51 (s, 1H), 1.46 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), -0.009 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.3, 162.0, 135.7, 134.5, 128.7, 128.5, 84.5, 77.6, 27.9, 25.7, 18.3, -5.02; **TLC** (10% EtOAc/hexanes) R_f 0.41; **LRMS** (ESI) Calcd. For $C_{19}H_{29}ClO_4SiNa + CH_3OH$: 439.17. Found: 439.15.



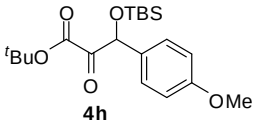
4f

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxo-3-(4-(trifluoromethyl)phenyl)propanoate (4f).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), 4-(trifluoromethyl)benzaldehyde (0.071 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), Yb(O^iPr)$_3$ (0.0035g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4f** (0.077g, 0.185 mmol, 90% yield) was obtained as a clear colorless oil. Analytical data for **4b**: **IR** (thin film, cm^{-1}) 2956, 2933, 2889, 2860, 1750, 1726, 1326, 1258, 1167, 1131, 1067, 870, 839, 782; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8 Hz, 2H), 7.56 (d, *J* = 8 Hz, 2H), 5.58 (s, 1H), 1.46 (s, 9H), 0.91 (s, 9H), 0.12 (s, 3H), 0.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1, 161.9, 141.2, 127.4, 125.5, 84.7, 77.8, 27.9, 25.7, 18.3, -5.00, -5.03; **TLC** (10% EtOAc/hexanes) R_f 0.43; **LRMS** (ESI) Calcd. For $C_{20}H_{29}F_3O_4SiNa$ + CH_3OH: 473.19. Found: 473.17



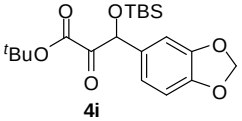
4g

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-3-(4-cyanophenyl)-2-oxopropanoate (4g).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), 4-cyanobenzaldehyde (0.054 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), Yb(O^iPr)$_3$ (0.0035g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and purification by flash chromatography (10% EtOAC/hexanes), **4g** (0.071 g, 0.189 mmol, 92% yield) was obtained as a clear colorless oil. Analytical data for **4g**: **IR** (thin film, cm^{-1}) 2955, 2931, 2859, 2230, 1750, 1730, 1502, 1394, 1257, 1133, 868, 840, 783; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8 Hz, 2H), 7.56 (d *J* = 8 Hz, 2H), 5.55 (s, 1H), 1.46 (s, 9H), 0.91 (s, 9H), 0.12 (s, 3H), 0.010 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 192.7, 161.7, 142.5, 132.3, 127.6, 118.4, 112.5, 84.9, 77.7, 27.9, 25.6, 18.3, -5.01, -5.06; **TLC** (10% EtOAc/hexanes) R_f 0.25; **LRMS** (ESI) Calcd. For $C_{20}H_{29}NO_4SiNa$ + CH_3OH: 430.20. Found: 430.18



4h

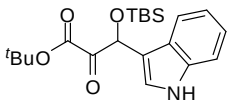
***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-oxopropanoate (4h)**. The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), *p*-anisaldehyde (0.056 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), Yb(O^iPr)$_3$ (0.0035g, 0.0102 mmol, 0.05 equiv), 2,6-lutidine (0.022 g, 0.205 mmol, 1.0 equiv) and DMF (2 mL). After stirring 20 min, the reaction was complete as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4h** (0.066 g, 0.174 mmol, 85% yield) was obtained as a clear colorless oil. Analytical data for **4h**: **IR** (thin film, cm^{-1}) 2955, 2932, 2856, 1748, 1723, 1611, 1512, 1464, 1303, 1254, 1171, 1130, 1033, 870, 838, 781; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* =8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz), 5.52 (s, 1H), 3.80 (s, 3H), 1.45 (s, 9H), 0.89 (s, 9H), 0.094 (s, 3H), -0.024 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 162.4, 159.9, 129.1, 128.8, 114.0, 84.1, 77.9, 55.3, 27.9, 25.7, 18.3, -4.95; **TLC** (10% EtOAc/hexanes) R_f 0.35; **LRMS** (ESI) Calcd. For $C_{20}H_{32}O_5SiCs$ + CH_3OH: 545.13. Found: 545.11



4i

***tert*-Butyl 3-(benzo[d][1,3]dioxol-5-yl)-3-(*tert*-butyldimethylsilyloxy)-2-oxopropanoate(4i).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), piperonal (0.062 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), Yb(O^iPr)$_3$ (0.0035g,

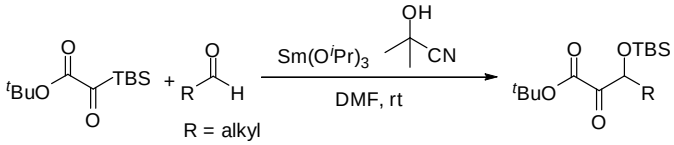
0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde *in vacuo* (<1 mm Hg), **4i** (0.069 g, 0.176 mmol, 86% yield) was obtained as a clear colorless oil. Analytical data for **4i**: **IR** (thin film, cm^{-1}) 2955, 2931, 2895, 2856, 1747, 1725, 1489, 1445, 1371, 1252, 1143, 1040, 873, 839, 782; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.86 (s, *J* = 8 Hz, 2H), 6.77 (d, *J* = 8 Hz, 2H), 5.96 (s, 2H), 5.47 (s, 1H), 1.47 (s, 9H), 0.90 (s, 1H), 0.098 (s, 3H), -0.005 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.5, 162.3, 147.9, 131.0, 121.2, 108.2, 107.7, 101.2, 84.3, 77.9, 27.9, 25.7, 18.3, -4.96, -4.99; **TLC** (10% EtOAc/hexanes) R_f 0.36; **LRMS** (ESI) Calcd. For $C_{20}H_{30}O_6SiNa$ + CH_3OH: 449.20. Found: 449.15.



4j

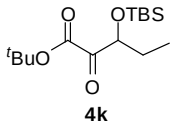
***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-3-(1H-indol-3-yl)-2-oxopropanoate (4j).** The title compound was prepared according to General procedure A using **1** (0.050 g, 0.205 mmol, 1.0 equiv), indole-3-carboxaldehyde (0.060 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g, 0.041 mmol, 0.20 equiv), $Yb(O^iPr)_3$ (0.0035g, 0.0102 mmol, 0.05 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup and removal of the excess aldehyde by treatment with hexanes and filtration, **4j** (0.070 g, 0.180 mmol, 88% yield) was obtained as a light brown oil. Analytical data for **4b**: **IR** (thin film, cm^{-1}) 2955, 2931, 2857, 1755, 1668, 1537, 1461, 1395, 1370, 1255, 1149, 839, 783; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 8.30-8.33 (m, 1H), 7.96 (s, 1H), 7.47-7.49 (m, 1H), 7.31-7.33 (m, 2H), 6.02 (s, 1H), 1.38 (s, 9H), 0.91 (s, 9H), 0.18 (s, 3H), -0.004 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.0, 166.2, 136.2, 136.1, 125.5, 124.2, 123.3, 122.3, 119.4, 110.8, 83.6, 79.2, 27.8, 25.4, 18.1, -5.26, -5.31; **TLC** (10% EtOAc/hexanes) R_f 0.14; **LRMS** (ESI) Calcd. For $C_{21}H_{31}NO_4SiNa$: 412.19. Found: 412.18.

General Procedure B for the $Sm(O^iPr)_3$ catalyzed nucleophilic glyoxylation of aliphatic aldehydes to afford β-siloxy-α-ketoesters 4k-l:



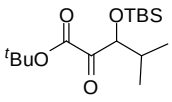
1 **4k-l**

These substrates were prepared in the same manner described in General Procedure A except 10 mol % $Sm(O^iPr)_3$ was substituted for $Yb(O^iPr)_3$.



4k

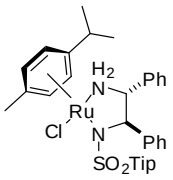
***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxopentanoate (4k).** The title compound was prepared according to General procedure B using **1** (0.050 g, 0.205 mmol, 1.0 equiv), propionaldehyde (0.024 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035, g 0.041 mmol, 0.20 equiv), $Sm(O^iPr)_3$ (0.0067 g, 0.0205 mmol, 0.10 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup, **4k** (0.060 g, 0.197 mmol, 96% yield) was obtained as a clear colorless oil. Analytical data for **4k**: **IR** (thin film, cm^{-1}) 2958, 2932, 2885, 2859, 1746, 1722, 1472, 1463, 1371, 1256, 1147, 1111, 862, 839, 780; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.47 (t, *J* = 6.4 Hz, 1H), 1.71-1.86 (m, 2H), 1.70 (s, 9H), 0.962 (t, *J* = 7.6 Hz, 3H), 0.91 (s, 9H), 0.081 (s, 3H), 0.066 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 162.8, 84.2, 77.32, 28.0, 27.3, 25.7, 18.3, 9.3, -4.81, -5.14; **TLC** (10% EtOAc/hexanes) R_f 0.48; **LRMS** (ESI) Calcd. For $C_{15}H_{30}O_4SiNa$ + CH_3OH: 357.21. Found: 357.20.



4l

***tert*-Butyl 3-(*tert*-butyldimethylsilyloxy)-4-methyl-2-oxopentanoate (4l).** The title compound was prepared according to General procedure B using **1** (0.050 g, 0.205 mmol, 1.0 equiv), isobutyraldehyde (0.030 g, 0.410 mmol, 2.0 equiv), acetone cyanohydrin (0.0035 g 0.041 mmol, 0.20 equiv), $Sm(O^iPr)_3$ (0.0067 g, 0.0205 mmol, 0.10 equiv) and DMF (2 mL).The reaction was complete immediately upon the addition of all reagents as determined by TLC analysis. After workup, **4l** (0.055 g, 0.174 mmol, 85% yield) was obtained as a clear colorless oil. Analytical data for **4l**: **IR** (thin film, cm^{-1}) 2960, 2932, 2859, 1745, 1722, 1472, 1371, 1255, 1147, 1073, 863, 839, 780; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.33 (d, *J* = 5.2 Hz, 1H), 2.11-2.17 (m, 1H), 1.54 (s, 9H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.049 (s, 3H), 0.038 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 162.6, 84.1, 80.6, 31.8, 27.9, 25.8, 19.0, 18.3, 17.0, -4.74, -5.31; **TLC** (10% EtOAc/hexanes) R_f 0.50; **LRMS** (ESI) Calcd. For $C_{16}H_{32}O_4SiNa + CH_3OH$: 371.22. Found: 371.24.

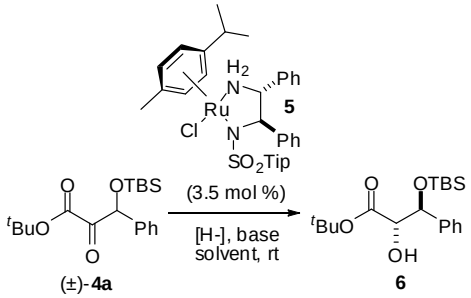
Preparation of Ruthenium Catalyst 5



5

A solution of $[Ru(p\text{-cymene})Cl_2]_2$ (4 mg/mL) and (*R*, *R*)-2,4,6-$^iPr_3C_6H_2SO_2$DPEN[3] (8 mg/mL) in DMF were prepared. In an inert atmosphere glovebox, a 1-dram vial containing a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (0.383 mL, 0.005 mmol, 0.035 equiv) and (*R*, *R*)-2,4,6-$^iPr_3C_6H_2SO_2$DPEN (0.375 mL, 0.006 mmol, 0.042 equiv). The vial was sealed with a PTFE-lined screw cap, removed from the glovebox, and allowed to stir at 80 °C for 30 min. After cooling to room temperature, the remaining reagents were added as described below.

General Procedures for the Asymmetric Hydrogenation of 4a



(±)-**4a** **6**

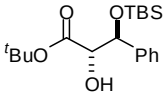
Method A (Table 2, entries 1-3, 7): Formic acid (0.021 g, 0.458 mmol, 3.2 equiv) was added to the amine base (1.43 mmol, 10.0 equiv) at 0 °C. The resultant mixture was then added to the 1-dram vial followed by a 1 mL solution of **4a** (0.050 g, 0.143 mmol, 1.0 equiv) in DMF. The reaction was allowed to stir at the specified temperature overnight and then diluted with EtOAc. The organic layer was washed with water (3x) then brine, dried over Na_2SO_4, and concentrated *in vacuo*.

[3] Yin, L.; Shan, W.; Jia, X.; Li, X., Chan, A. S. C. *J. Organomet. Chem.* **2009**, *694*, 2092.

Method B (Table 2, entries4-6, 12): A 1 mL solution of **4a** (0.050 g, 0.143 mmol, 1.0 equiv)in DMF was added to the 1-dram vial followed by sodium or cesium formate (0.715 mmol. 5.0 equiv) in 0.50 mL of water. The reaction was allowed to stir at the specified temperature overnight and then diluted with EtOAc. The organic layer was washed with water (3x) then brine, dried over Na_2SO_4, and concentrated *in vacuo*.

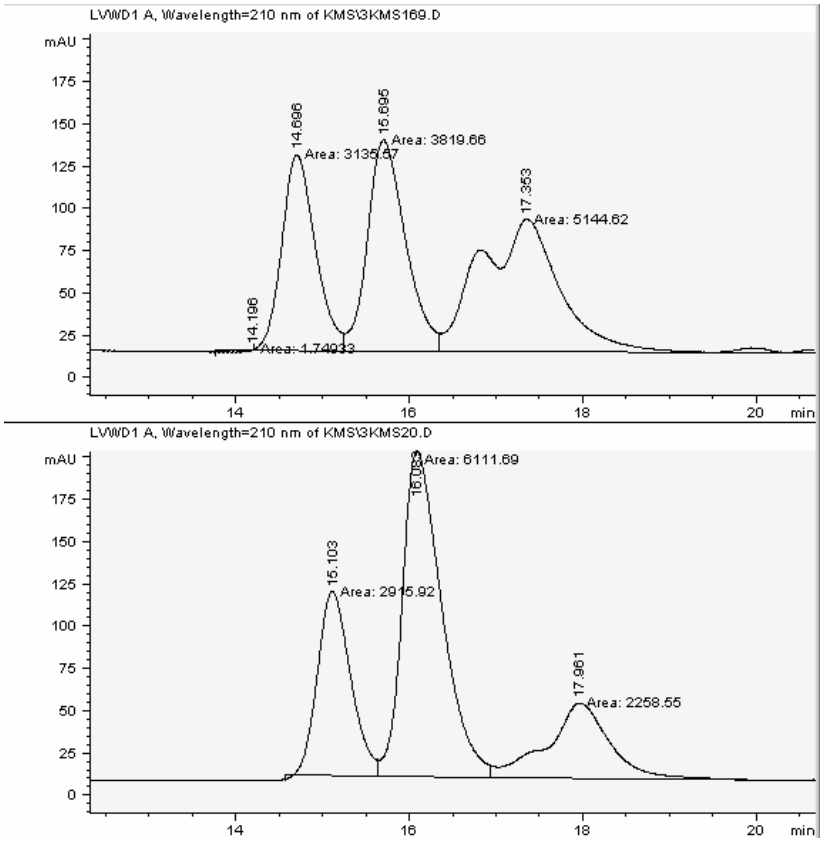
Method C (Table 2, entries 8-11): The procedure described in Method B was followed. After the addition of the formate, the base (0.143 mmol, 10.0 equiv) was added to the reaction mixture.

(Note: After catalyst preparation in the vial, no precautions were taken to exclude air from the vessel.)

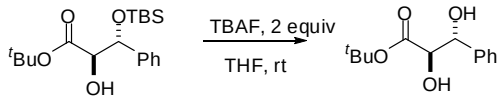


6

(*2S,3S*)-*tert*-butyl 3-(*tert*-butyldimethylsilyloxy)-2-hydroxy-3-phenylpropanoate (6). The title compound was prepared following Method B using **4a** (0.050 g, 0.143 mmol, 1.0 equiv) and sodium formate (0.049 g, 0.715 mmol, 5.0 equiv). After workup and purification by flash chromatography (10% EtOAc/hexanes), **6** (0.044 g, 0.124 mmol, 87% yield) was obtained as a clear colorless oil in a 3:1 dr and a 68: 32 er(for the *anti*-diastereomer) as determined by chiral SFC analysis (Chiralpack AD 3% MeOH, 1.5 mL/min, 40 °C, 210 nm, t_r-major 15.1 min, t_r-minor 16.0 min). Analytical data for **6**: **IR** (thin film, cm^{-1}) 2958, 2930, 2857, 1726, 1368, 1252, 1161, 1119, 935, 837, 778, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) major: δ 7.24-7.36 (m, 5H), 5.05 (d, *J* = 2.4 Hz), 4.24 (dd, *J* = 2.8 Hz, 8 Hz), 3.18 (d, *J* = 7.2 Hz), 1.46 (s, 9H), 0.93 (s, 9H), 0.11 (s, 3H), -0.045 (s, 3H) minor: δ 7.24-7.36 (m, 5H), 4.95 (d, *J* = 2.4 Hz), 4.03 (dd, *J* = 2.8 Hz, 8 Hz), 2.99 (d, *J* = 8.8 Hz), 1.58 (s, 9H), 0.89 (s, 9H), 0.043 (s, 3H), -0.22 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) major: δ 171.0, 140.4, 127.8, 127.2, 126.4, 77.3, 27.9, 25.9, 18.3, -4.8, -5.0 minor: 171.5, 141.0, 128.0, 127.0, 82.3, 76.3, 28.1, 25.8, 18.1, -4.5, -5.1; **TLC** (10% EtOAc/hexanes) R_f major: 0.43, minor: 0.38; **LRMS** (ESI) Calcd. For $C_{19}H_{32}O_4SiNa$: 375.20. Found: 375.18.



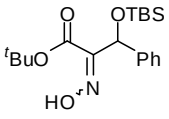
Determination of Diastereomer Identity



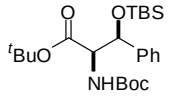
6

***tert*-Butyl 2,3-dihydroxy-3-phenylpropanoate.** The title compound was prepared by dissolving **6** (0.040 g, 0.113 mmol, 1.0 equiv) in THF (2 mL) followed by addition of TBAF trihydrate (0.071 g, 0.226 mmol, 2.0 equiv). After stirring five minutes, TLC analysis (10% EtOAc/hexanes) showed that deprotection was complete (R_f(diol) ≈ 0). The reaction mixture was passed through a plug of silica gel with EtOAc (30 mL) and filtrate was concentrated. The spectroscopic data matched that in the literature.[4]

Preparation of β-silyoxy-α-aminoester 7



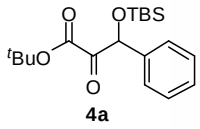
***tert*-butyl 3-(*tert*-butyldimethylsilyloxy)-2-(hydroxyimino)-3-phenylpropanoate.** Hydroxylamine hydrochloride (0.396 g, 5.70 mmol, 10.0 equiv) and sodium acetate (0.468 g, 5.70 mmol, 10.0 equiv) were dissolved separately in the minimum amount of water (~ 0.5 mL) and added sequentially to a solution of **4a** (0.200 g, 0.570 mmol, 1.0 equiv) in ethanol (5 mL). The reaction was allowed to stir overnight and diluted with EtOAc. The layers were separated and the organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was passed through a plug of silica gel using 20% EtOAc/hexanes to afford the oxime (0.194 g, 0.531 mmol, 93% yield) as a clear colorless oil (d.r. 5:1). Analytical data: **IR** (thin film, cm^{-1}) 2955, 2930, 2887, 2858, 1736, 1369, 1256, 1148, 869, 838, 780, 700; **^{1}H NMR** (400 MHz, $CDCl_3$) major: δ 11.0 (bs, 1H), 7.24-7.50 (m, 5H), 5.54 (s, 1H), 1.33(s, 9H), 0.95 (s, 9H), 0.11 (s, 3H), 0.07 (s, 3H) minor δ 7.24-7.50 (m, 5H), 6.30 (s, 1H), 1.42 (s, 9H), 0.94 (s, 9H), 0.109 (s, 3H), 0.07 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) major: δ 161.6, 152.2, 140.4, 127.9, 127.2, 126.0, 84.0, 74.0, 66.7, 27.9, 25.8, 18.21, -4.8, -5.2; minor: δ 160.9, 154.7, 140.2, 127.4, 125.8, 82.6, 66.7, 29.7, 27.9, 25.7, 18.2, -4.8, -5.2; **TLC** (10% EtOAc/hexanes) R_f major: 0.45, minor: 0.34; **LRMS** (ESI) Calcd. For $C_{19}H_{31}NO_4SiNa$: 388.19. Found: 388.18.



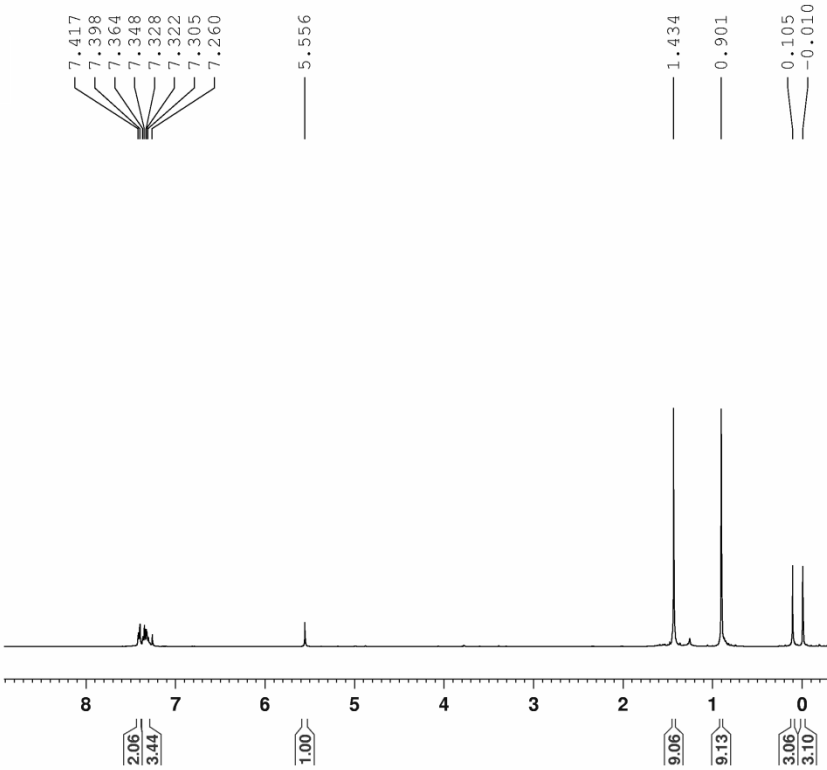
(±)-**7**

***tert*-Butyl 2-(*tert*-butoxycarbonylamino)-3-(*tert*-butyldimethylsilyloxy)-3-phenylpropanoate (7).** To a 10-mL round-bottomed flask was added zinc dust (0.173 g, 2.65 mmol, 5.0 equiv) and ammonium formate (0.167 g, 2.65 mmol, 5.0 equiv). A solution of the oxime (0.194 g, 0.530 mmol, 1.0 equiv) in MeOH (5 mL) was added and the reaction was heated at reflux overnight. After cooling to room temperature, the reaction was filtered through a pad of celite. The pad was washed with MeOH (20 mL) and the filtrate was concentrated. The crude material was dissolved in EtOAc, washed with saturated $NaHCO_3$, water, brine, dried over Na_2SO_4, and concentrated. The crude material was dissolved in THF (3 mL) and (^{t}BuOC)$_2$O (0.231 g, 1.06 mmol, 2.0 equiv) was added. Sodium hydroxide (0.042 g, 1.06 mmol, 2.0 equiv) in water (2 mL) was added and the reaction was allowed to stir overnight. The reaction was diluted with water and the aqueous layer was extracted with EtOAc (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Purification by flash chromatography (eluting with 5% EtOAc/hexanes) afforded **7** (0.155 g, 0.410 mmol, 72% yield over three steps) as a clear colorless oil. The spectroscopic data matched that in the literature.[5]

[4] Gawas, D.; Kazmaier, U. *J. Org. Chem.* **2009**, *74*, 1788.
[5] Hasegawa, K.; Arai, S.; Nishida, A. *Tetrahedron*, **2006**, *62*, 1390.



4a

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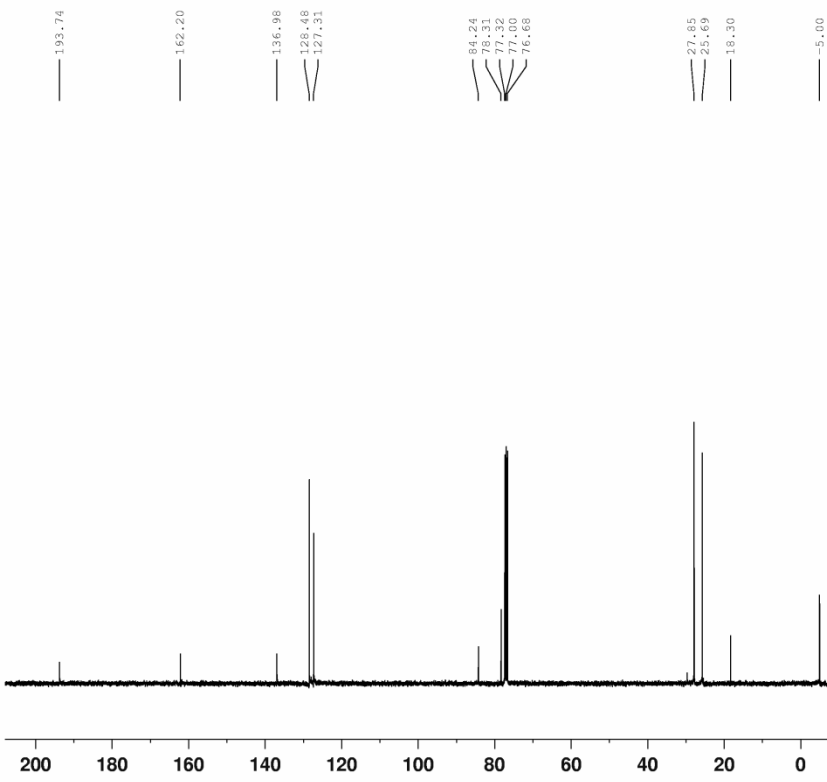


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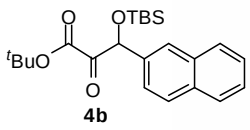

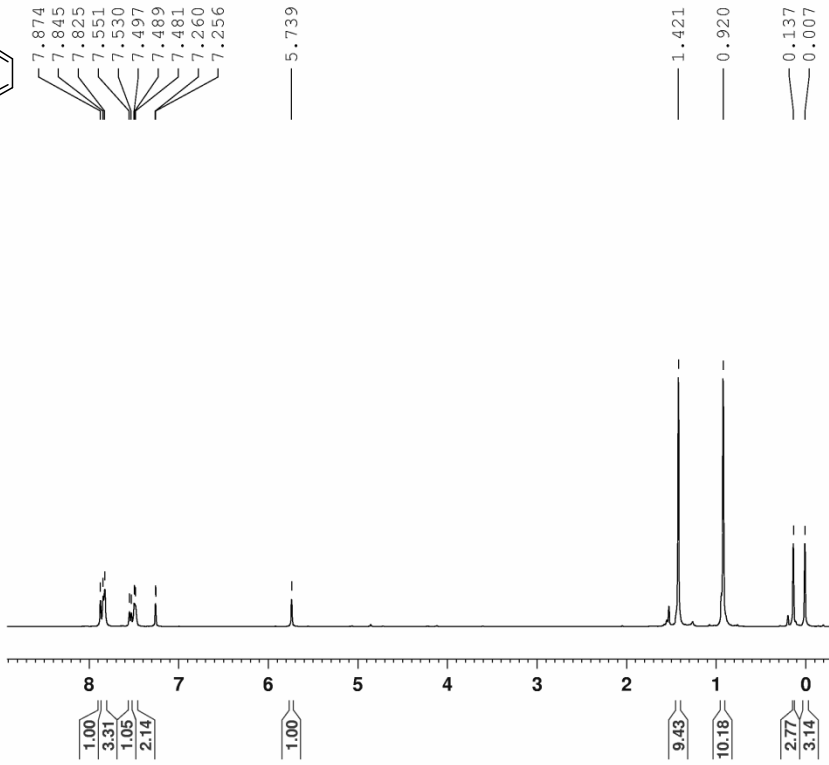


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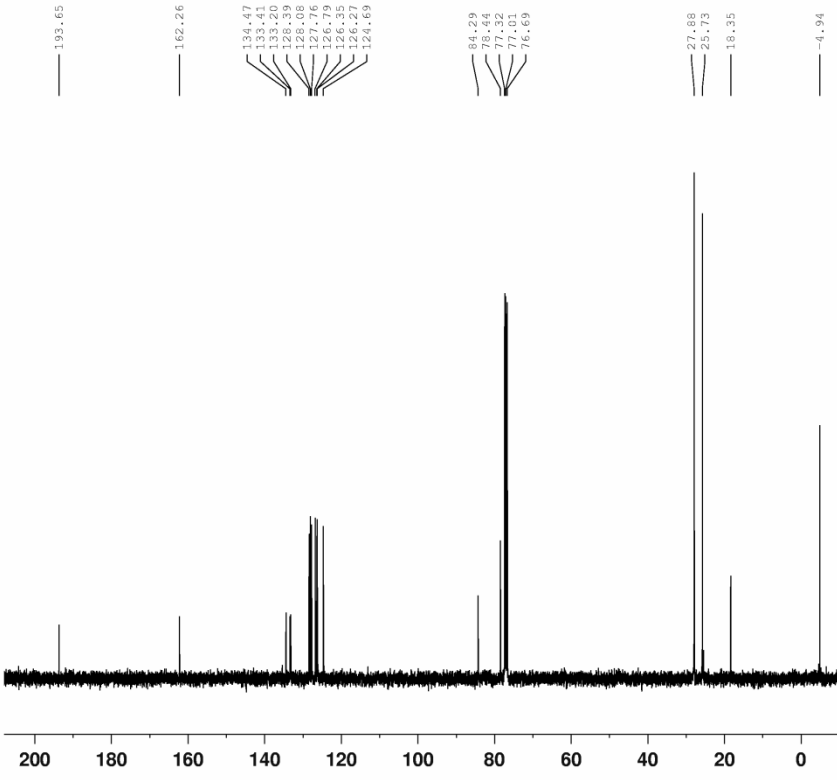


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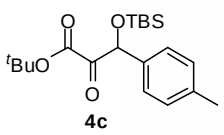

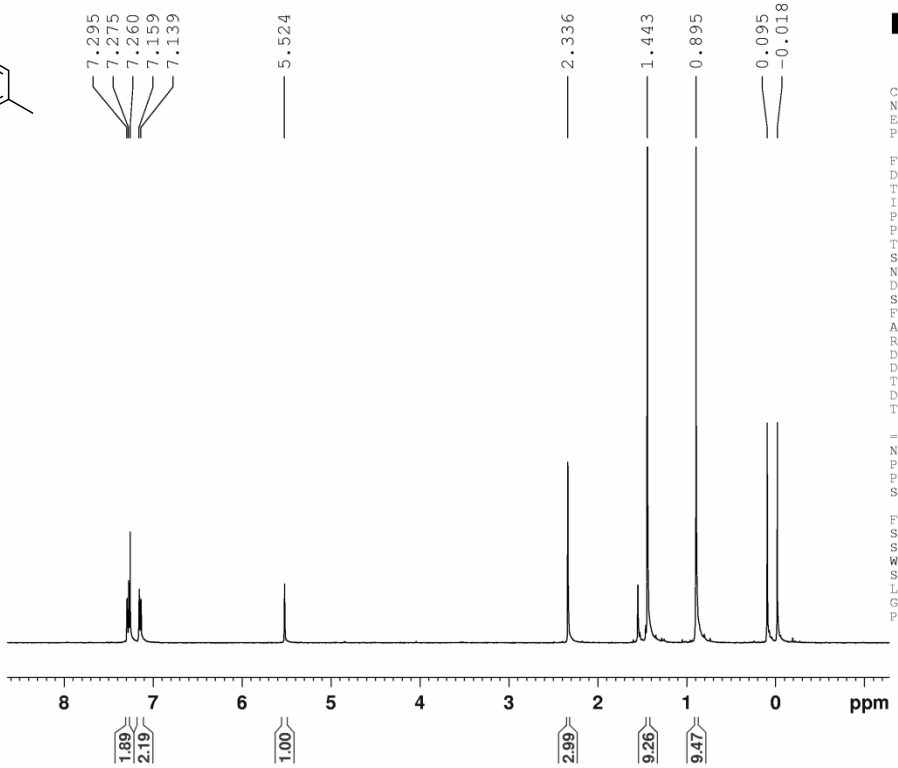


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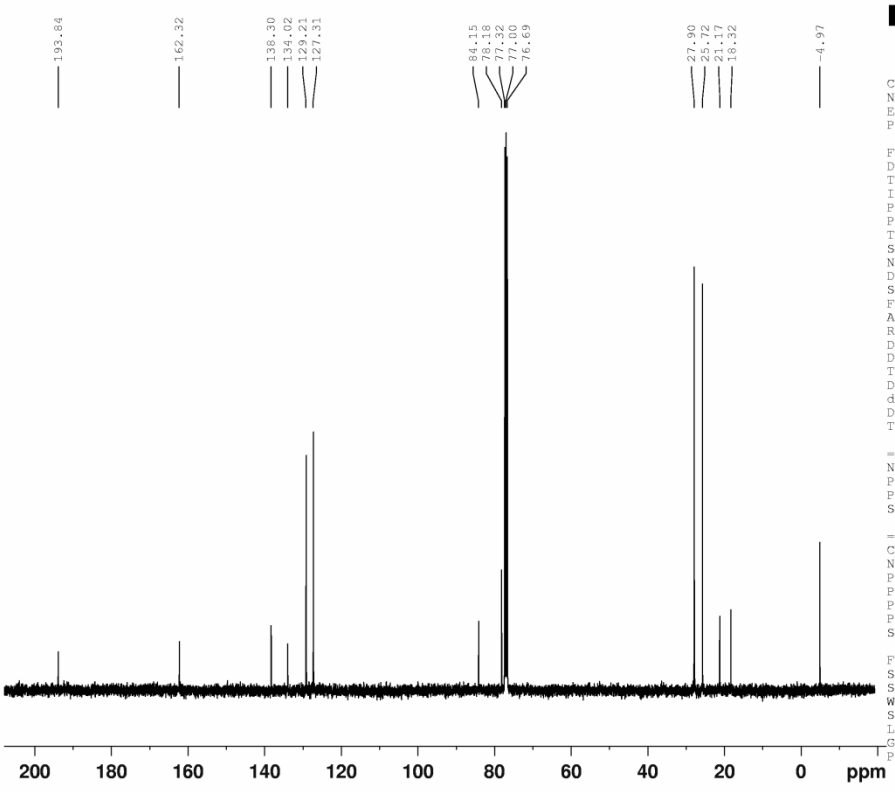


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PC                    1.40
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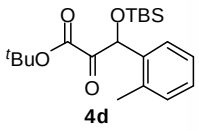
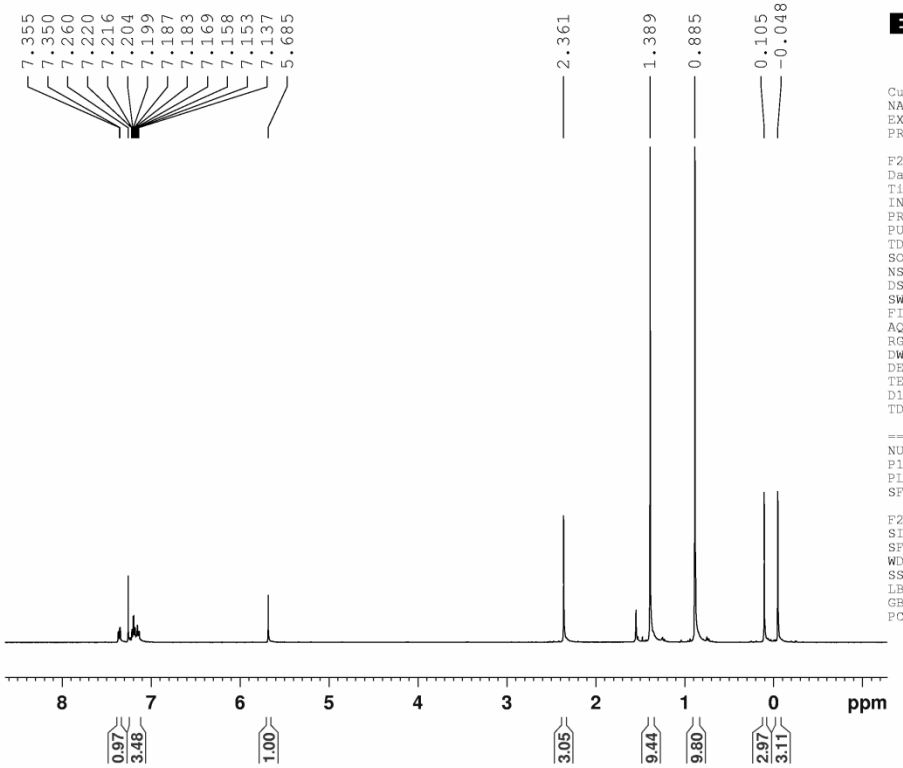
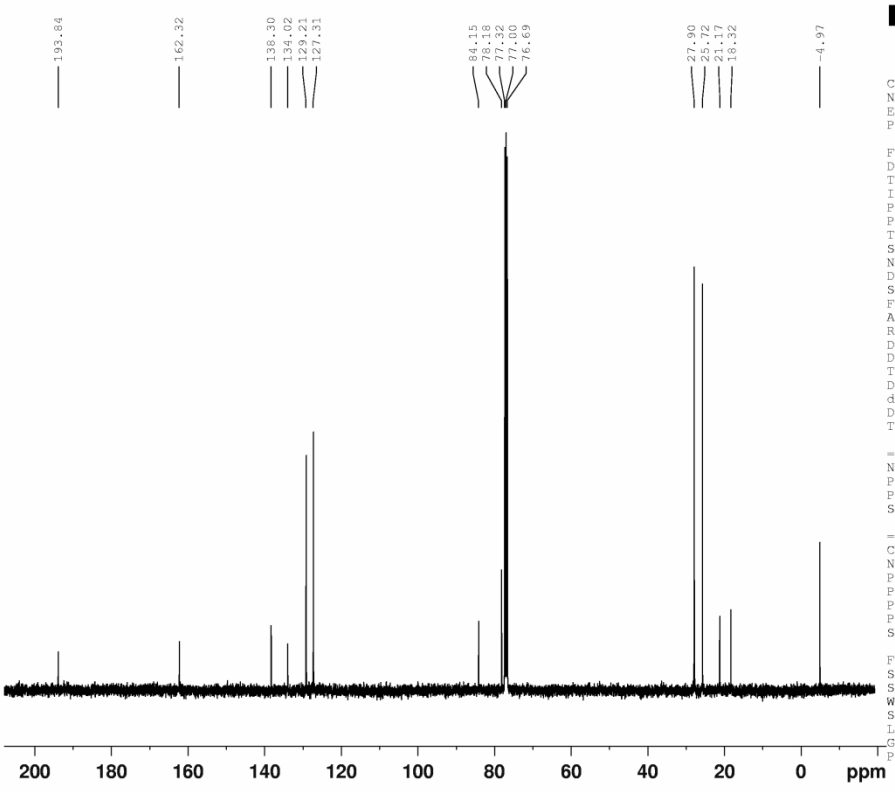
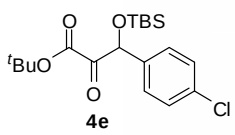


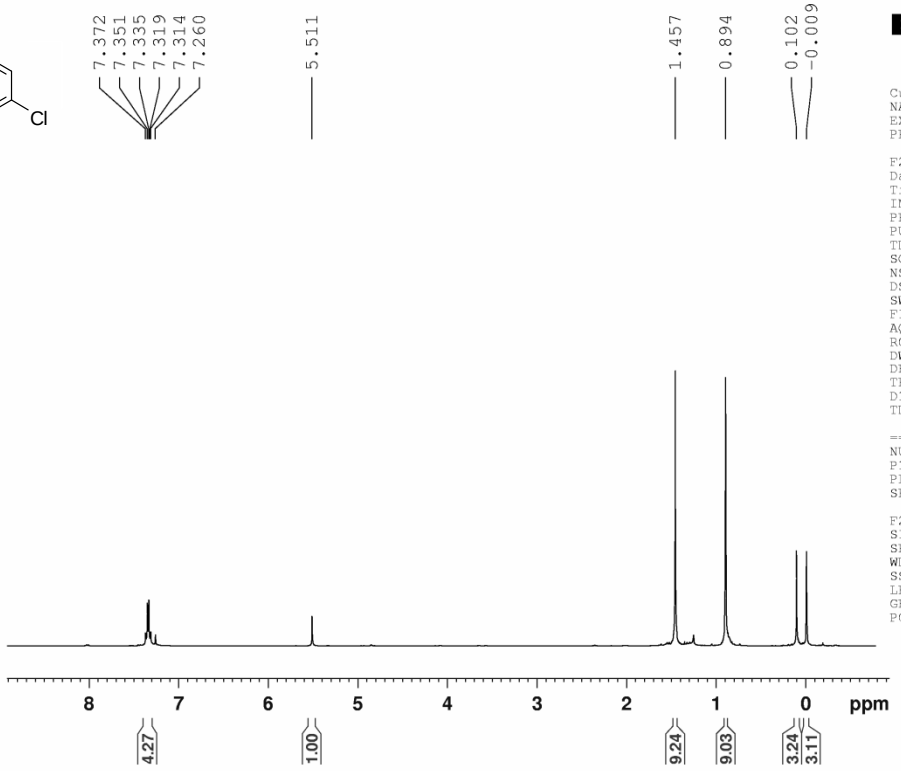



```
Current Data Parameters
NAME                  2MePh
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20100209
Time                 18.12
INSTRUM              spect
PROBHD   5 mm QNP  1H/1
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6218.905 Hz
FIDRES           0.189786 Hz
AQ               2.6345973 sec
RG                     256
DW                80.400 usec
DE                 6.00 usec
TE                 300.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.30 usec
PL1                 -3.00 dB
SFO1          399.7824920 MHz

F2 - Processing parameters
SI                   32768
SF            399.7800103 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

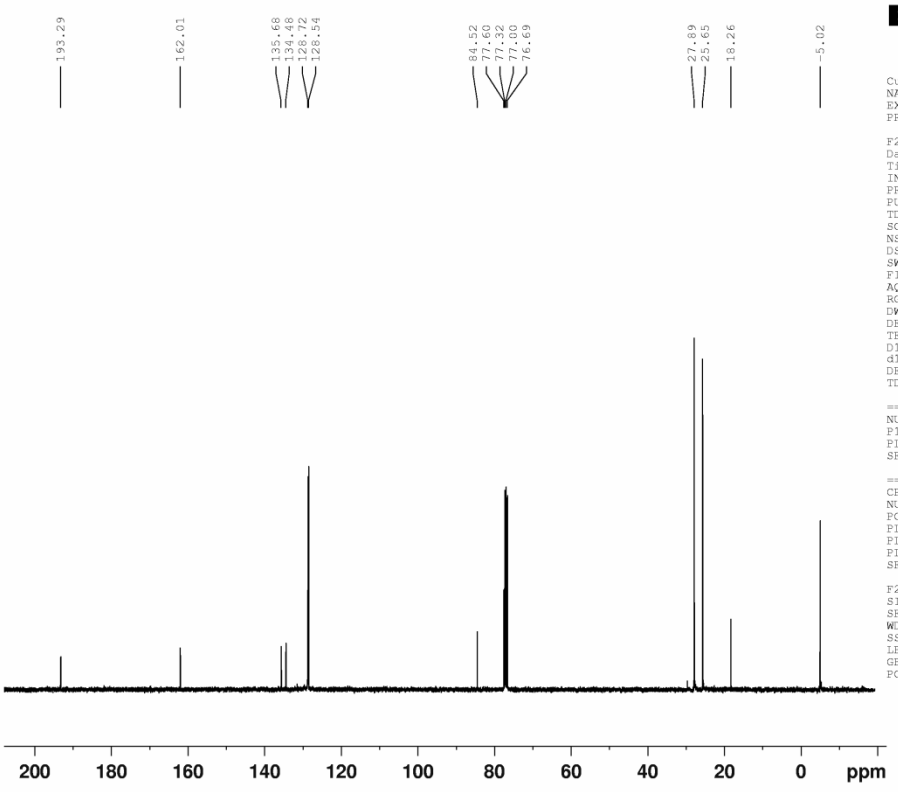



```
Current Data Parameters
NAME          4MePhcarbonb
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20100213
Time                 11.31
INSTRUM              spect
PROBHD   5 mm QNP  1H/1
PULPROG            zgpg30
TD                  32768
SOLVENT              CDCl3
NS                    1986
DS                       2
SWH              23980.814 Hz
FIDRES           0.731836 Hz
AQ               0.6832628 sec
RG                   203.2
DW                20.850 usec
DE                 6.00 usec
TE                 300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   7.25 usec
PL1                  0.00 dB
SFO1          100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                16.72 dB
PL13                20.00 dB
SFO2          399.7815991 MHz

F2 - Processing parameters
SI                   32768
SF            100.5247586 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

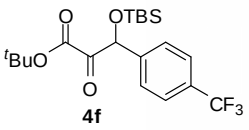




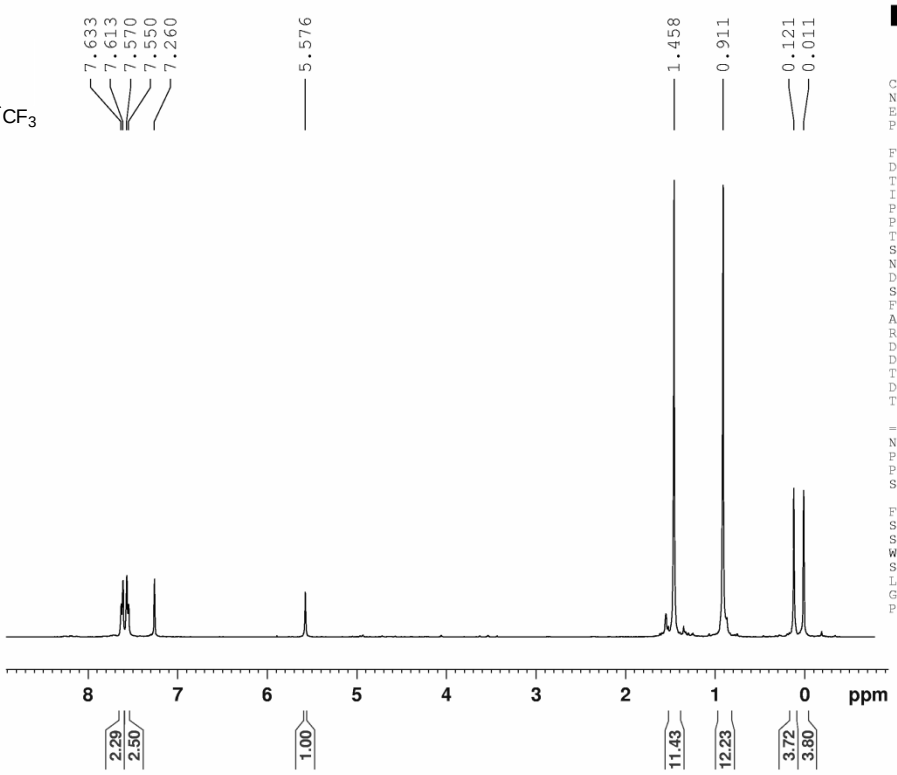

```
Current Data Parameters
NAME            Clhighvac
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090605
Time                9.12
INSTRUM            spect
PROBHD   5 mm TXI 13C Z
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5341.880 Hz
FIDRES          0.163021 Hz
AQ              3.0672283 sec
RG                    64
DW                93.600 usec
DE                 6.00 usec
TE                295.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.95 usec
PL1                0.00 dB
SFO1         400.0923618 MHz

F2 - Processing parameters
SI                 32768
SF          400.0900043 MHz
WDW                   EM
SSB                    0
LB                 0.25 Hz
GB                     0
PC                 1.00
```



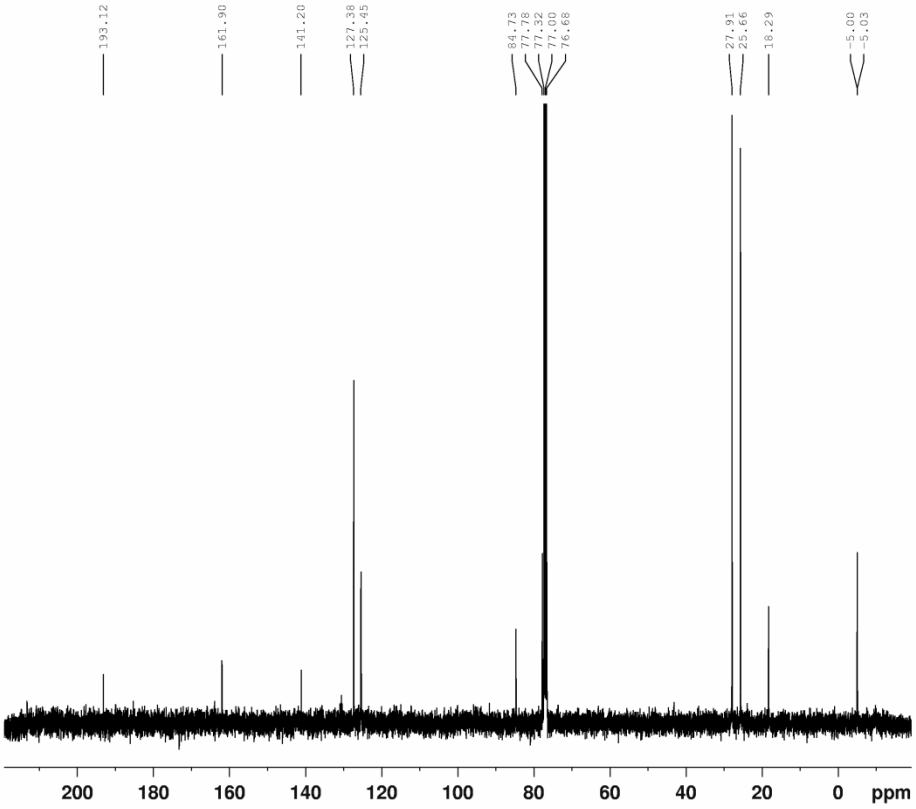

```
Current Data Parameters
NAME      4-Clbenzaldehyde carbon
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090711
Time                9.53
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  1024
DS                     2
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ              0.6832628 sec
RG                 16384
DW                20.850 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.8999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.25 usec
PL1                0.00 dB
SFO1         100.5499020 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2               -3.00 dB
PL12              16.72 dB
PL13              20.00 dB
SFO2         399.8415994 MHz

F2 - Processing parameters
SI                 32768
SF          100.5398467 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```



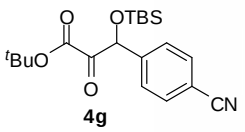
4f



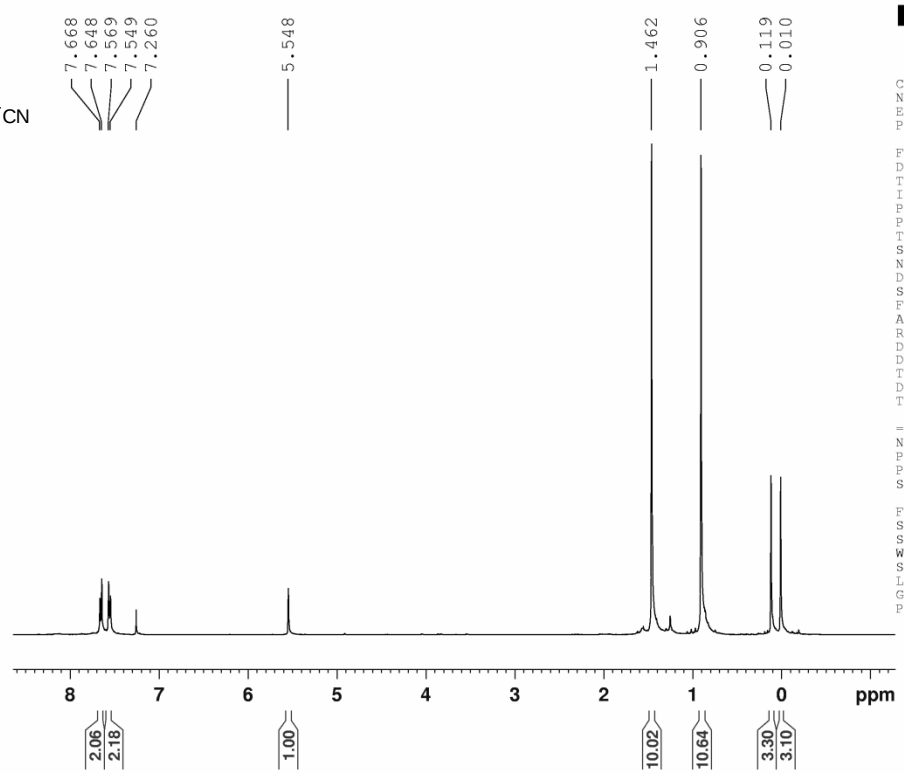

```
Current Data Parameters
NAME                 3KMS239
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20100220
Time                   14.37
INSTRUM                spect
PROBHD    5 mm TXI 13C Z
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                5341.880 Hz
FIDRES            0.163021 Hz
AQ                3.0672283 sec
RG                    161.3
DW                 93.600 usec
DE                  6.00 usec
TE                  294.7 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.95 usec
PL1                    0.00 dB
SFO1           400.0923618 MHz

F2 - Processing parameters
SI                        32768
SF               400.0900040 MHz
WDW                          EM
SSB                           0
LB                         0.25 Hz
GB                            0
PC                         1.00
```



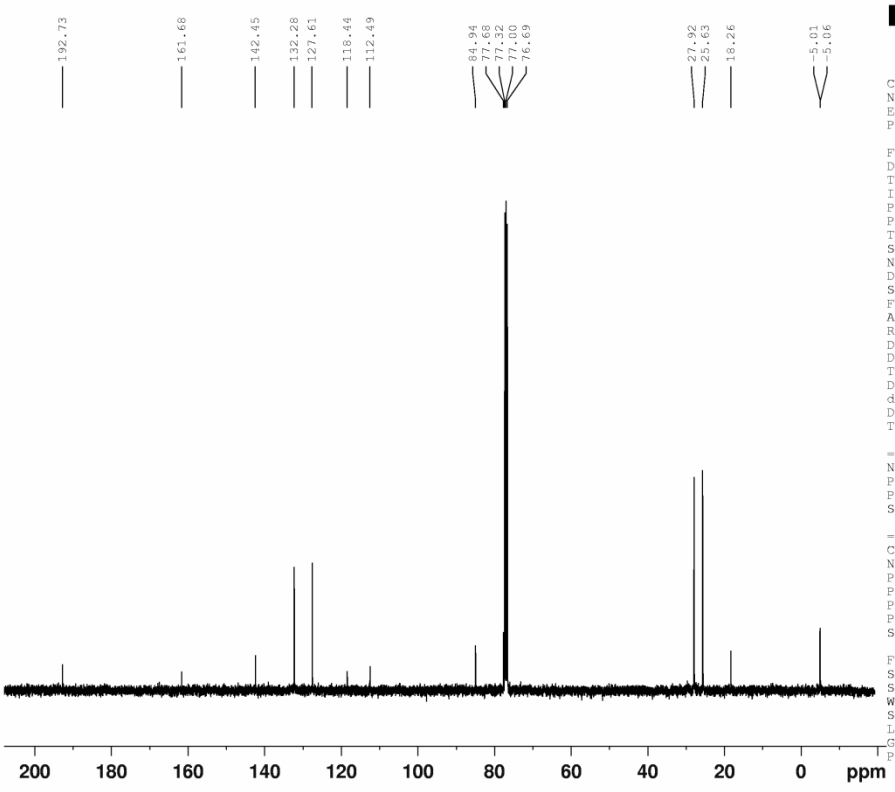

```
Current Data Parameters
NAME            3KMS239carbon
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20100327
Time                   10.06
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG            zgpg30
TD                    32768
SOLVENT               CDCl3
NS                     3111
DS                        2
SWH               23980.814 Hz
FIDRES            0.731836 Hz
AQ                0.6832628 sec
RG                    143.7
DW                 20.850 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     7.25 usec
PL1                    0.00 dB
SFO1           100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -3.00 dB
PL12                  16.72 dB
PL13                  20.00 dB
SFO2           399.7815991 MHz

F2 - Processing parameters
SI                        32768
SF               100.5247571 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



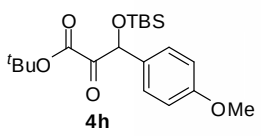
4g



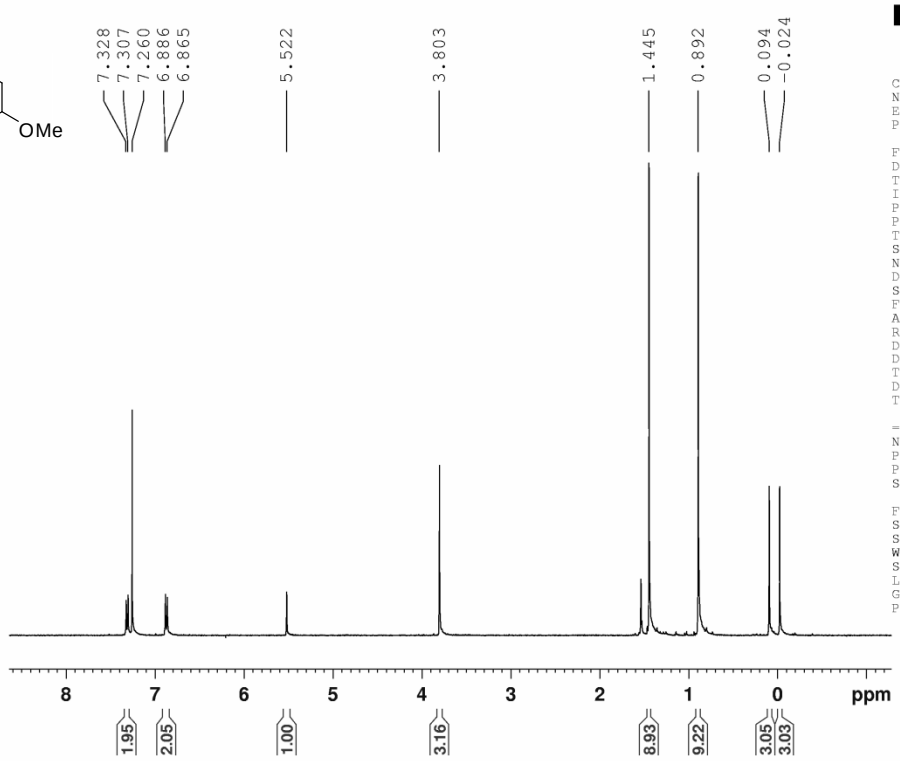

```
Current Data Parameters
NAME                 3KMS278
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20100420
Time                   9.20
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6218.905 Hz
FIDRES            0.189786 Hz
AQ                2.6345973 sec
RG                    161.3
DW                 80.400 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.30 usec
PL1                   -3.00 dB
SFO1           399.7824920 MHz

F2 - Processing parameters
SI                    32768
SF             399.7800105 MHz
WDW                      EM
SSB                       0
LB                   0.30 Hz
GB                        0
PC                     1.00
```



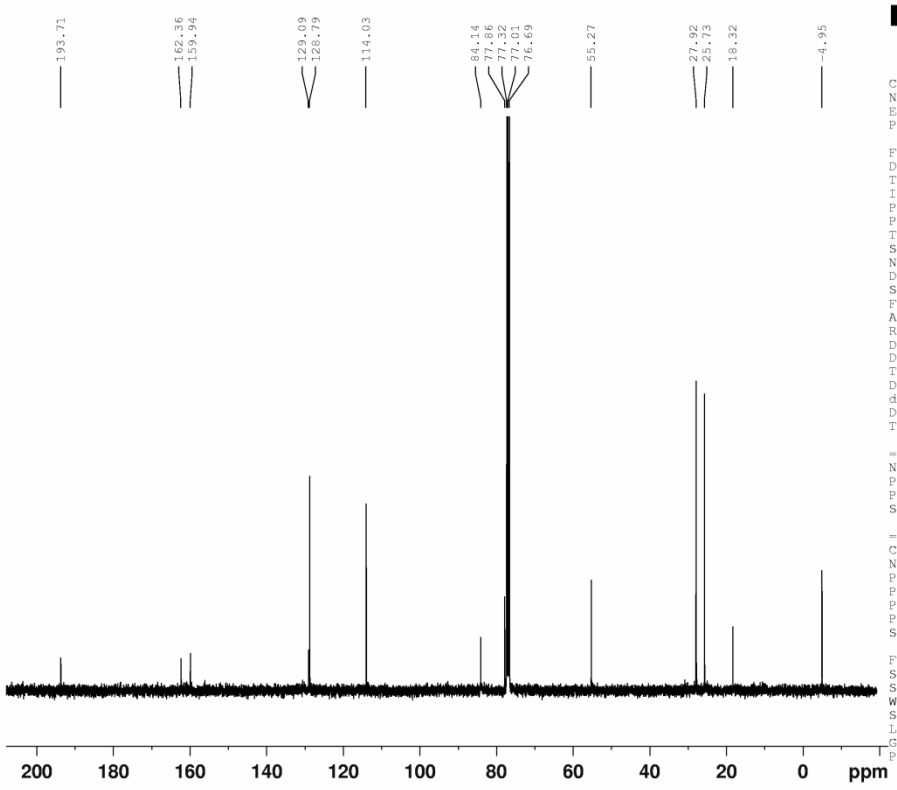

```
Current Data Parameters
NAME           3KMS278carbon
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20100420
Time                   9.27
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG            zgpg30
TD                    32768
SOLVENT               CDCl3
NS                     1528
DS                        2
SWH               23980.814 Hz
FIDRES            0.731836 Hz
AQ                0.6832628 sec
RG                    203.2
DW                 20.850 usec
DE                  6.00 usec
TE                  300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     7.25 usec
PL1                    0.00 dB
SFO1           100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                   -3.00 dB
PL12                  16.72 dB
PL13                  20.00 dB
SFO2           399.7815991 MHz

F2 - Processing parameters
SI                    32768
SF             100.5247593 MHz
WDW                      EM
SSB                       0
LB                   1.00 Hz
GB                        0
PC                     1.40
```



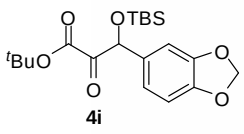
4h

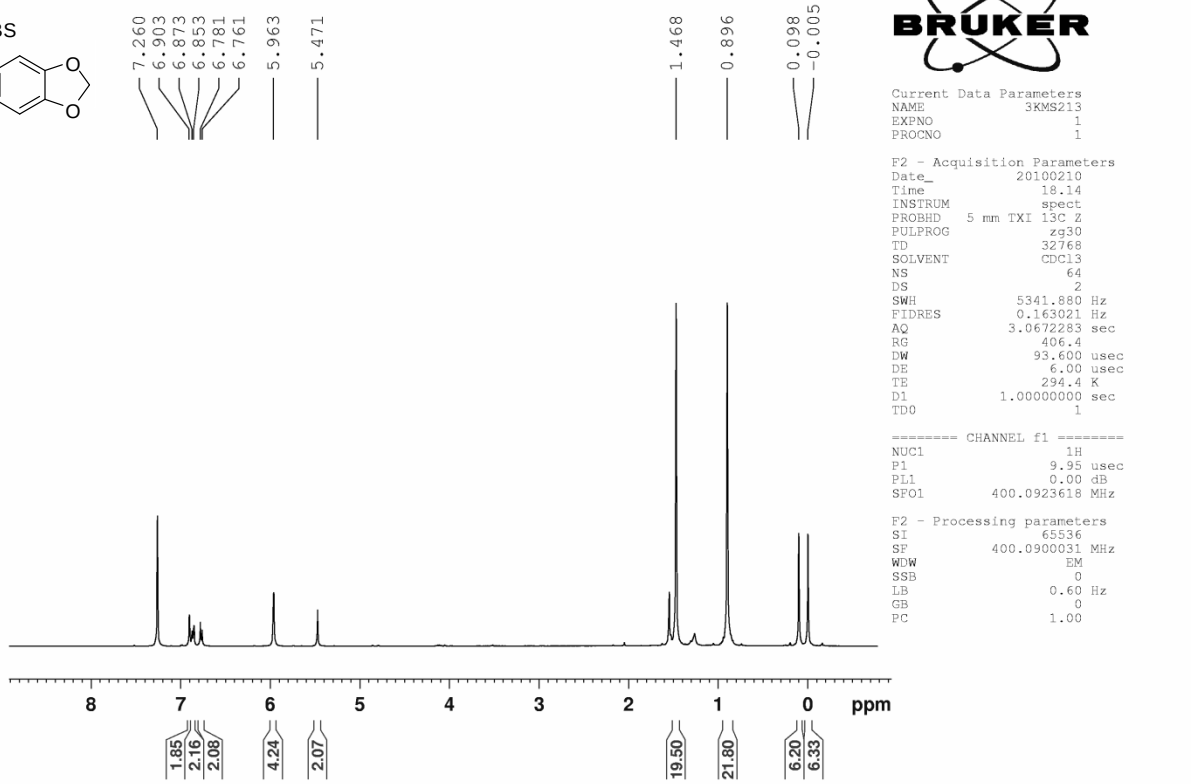



```
Current Data Parameters
NAME       4OMePhprotonb
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100220
Time               14.04
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           6218.905 Hz
FIDRES        0.189786 Hz
AQ           2.6345973 sec
RG               287.4
DW              80.400 usec
DE               6.00 usec
TE              300.0 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1               -3.00 dB
SFO1       399.7824920 MHz

F2 - Processing parameters
SI                32768
SF         399.7800101 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



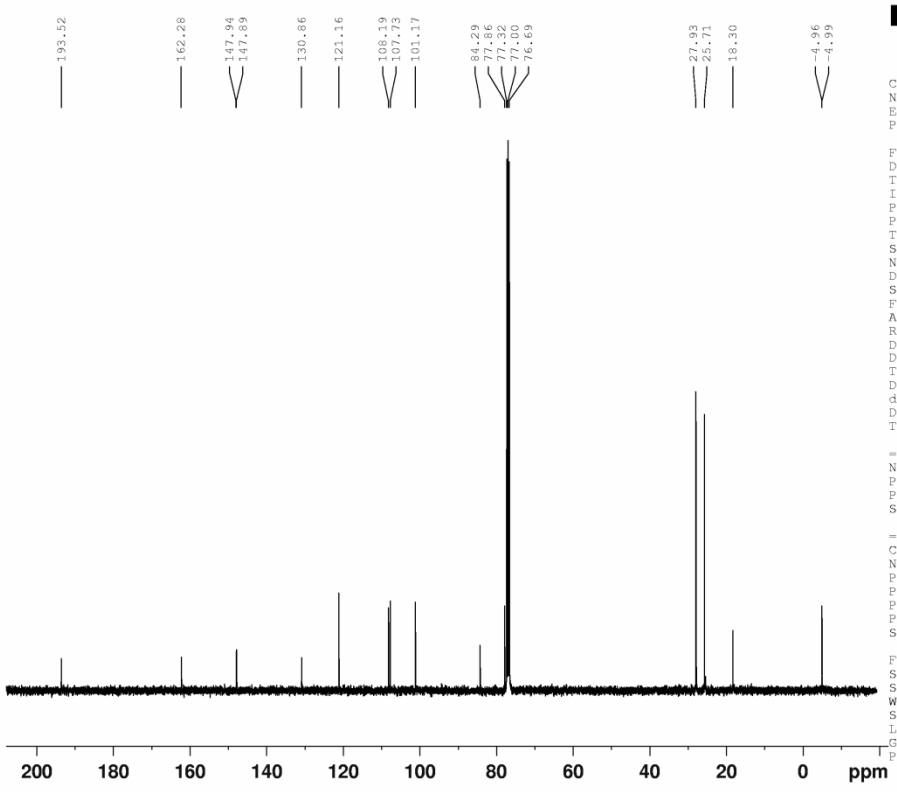

```
Current Data Parameters
NAME       4OMePhprotoncarbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100220
Time               14.14
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                 3250
DS                    2
SWH          23980.814 Hz
FIDRES        0.731836 Hz
AQ           0.6832628 sec
RG               143.7
DW              20.850 usec
DE               6.00 usec
TE              300.0 K
D1          1.00000000 sec
d11         0.03000000 sec
DELTA       0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.25 usec
PL1                0.00 dB
SFO1       100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.72 dB
PL13              20.00 dB
SFO2       399.7815991 MHz

F2 - Processing parameters
SI                32768
SF         100.5247572 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```





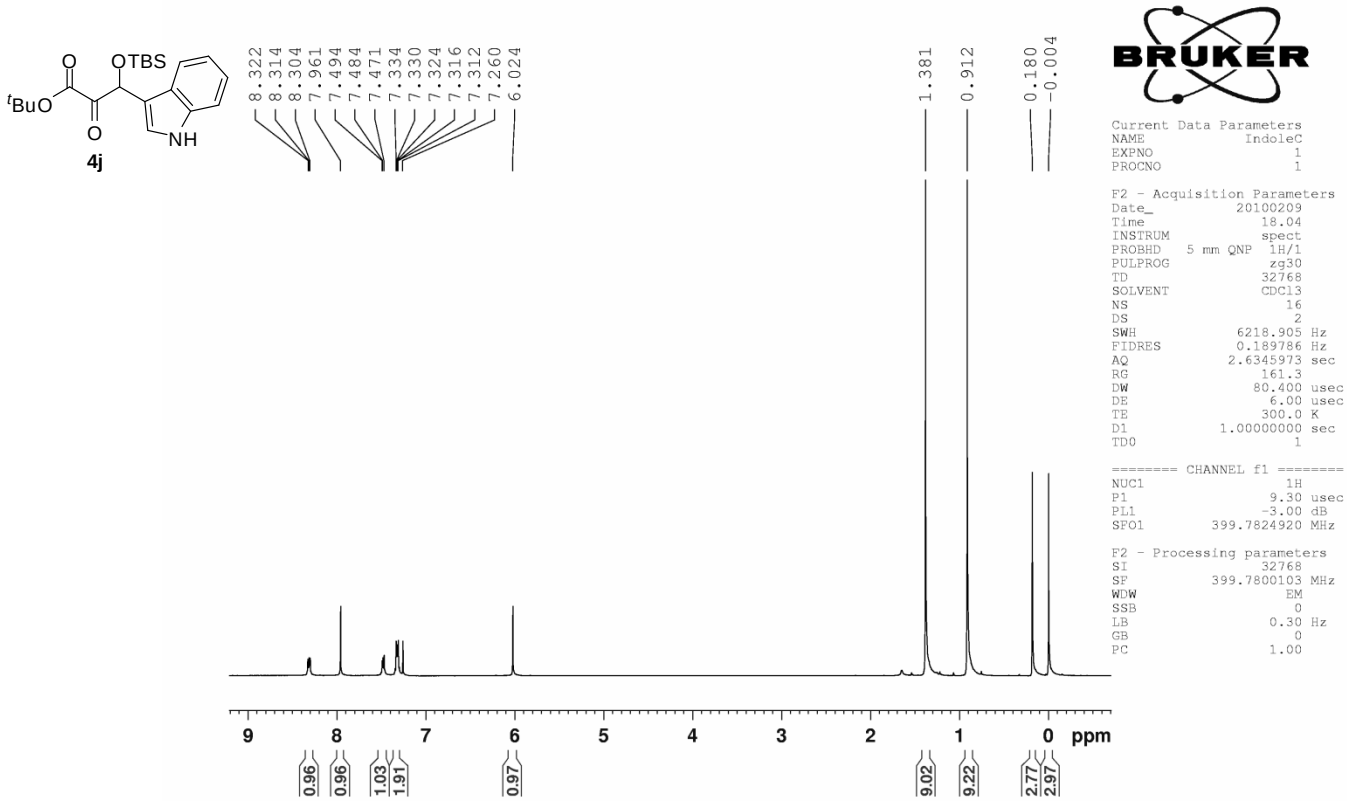
BRUKER

```
Current Data Parameters
NAME                  3KMS213
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100210
Time                  18.14
INSTRUM               spect
PROBHD    5 mm TXI 13C Z
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      64
DS                       2
SWH               5341.880 Hz
FIDRES               0.163021 Hz
AQ                3.0672283 sec
RG                    406.4
DW                   93.600 usec
DE                    6.00 usec
TE                   294.4 K
D1               1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.95 usec
PL1                    0.00 dB
SFO1           400.0923618 MHz

F2 - Processing parameters
SI                      65536
SF             400.0900031 MHz
WDW                        EM
SSB                         0
LB                     0.60 Hz
GB                          0
PC                     1.00
```

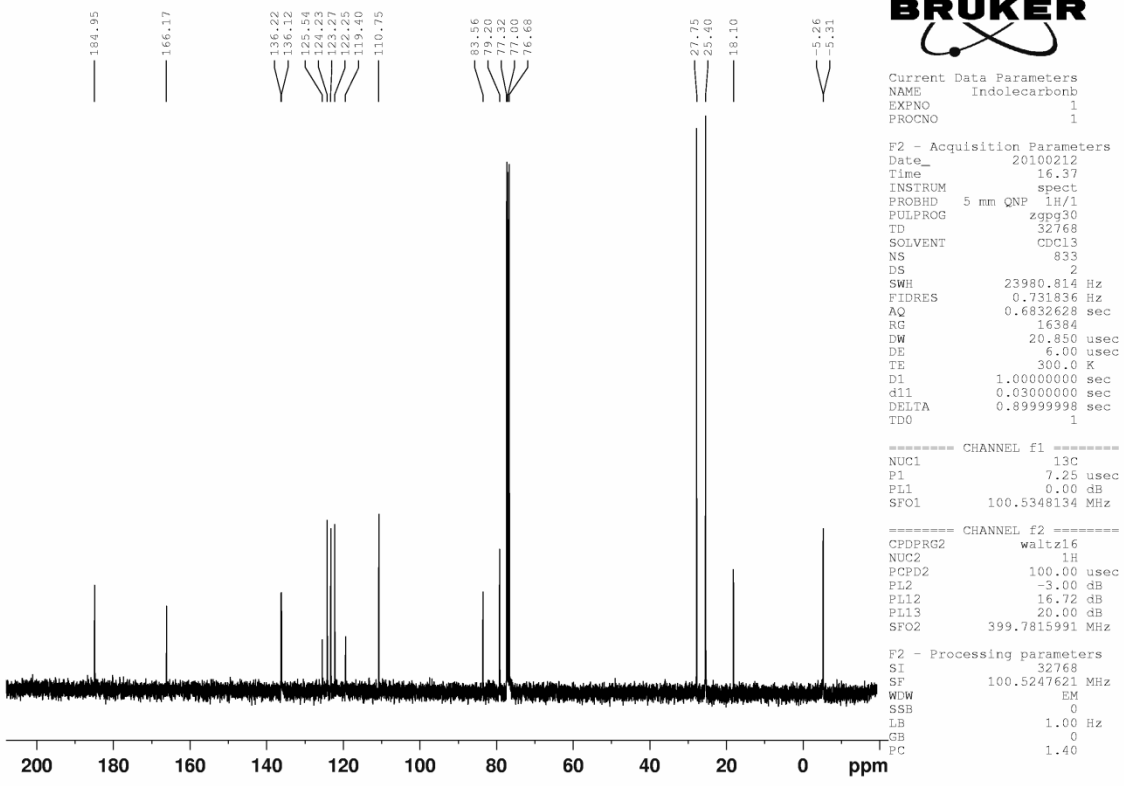


BRUKER

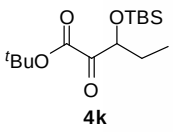
```
Current Data Parameters
NAME                  3KMS239
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20100403
Time                  10.30
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG             zgpg30
TD                   32768
SOLVENT              CDCl3
NS                    3066
DS                       2
SWH              23980.814 Hz
FIDRES               0.731836 Hz
AQ                0.6832628 sec
RG                    1024
DW                   20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1               1.00000000 sec
d11              0.03000000 sec
DELTA            0.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                     13C
P1                     7.25 usec
PL1                    0.00 dB
SFO1           100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -3.00 dB
PL12                  16.72 dB
PL13                  20.00 dB
SFO2           399.7815991 MHz

F2 - Processing parameters
SI                      32768
SF             100.5247586 MHz
WDW                        EM
SSB                         0
LB                     1.00 Hz
GB                          0
PC                     1.40
```



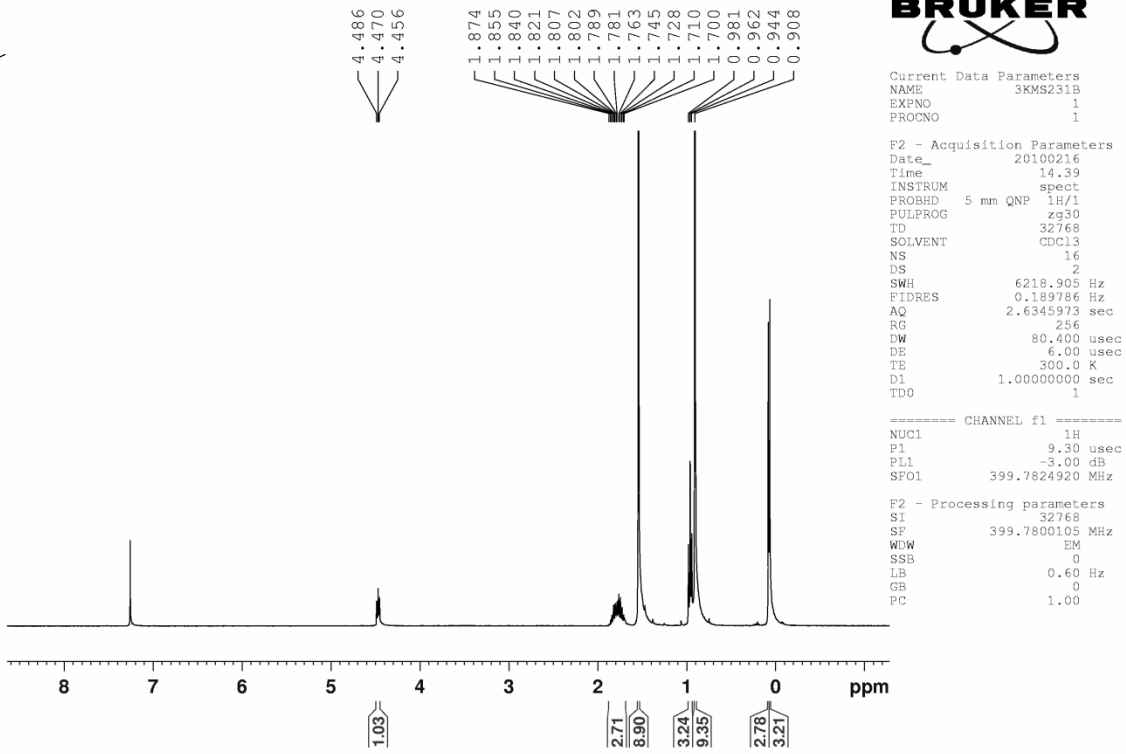

```
Current Data Parameters
NAME                  IndoleC
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20100209
Time                   18.04
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6218.905 Hz
FIDRES             0.189786 Hz
AQ                 2.6345973 sec
RG                     161.3
DW                    80.400 usec
DE                     6.00 usec
TE                     300.0 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.30 usec
PL1                     -3.00 dB
SFO1            399.7824920 MHz

F2 - Processing parameters
SI                         32768
SF              399.7800103 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```



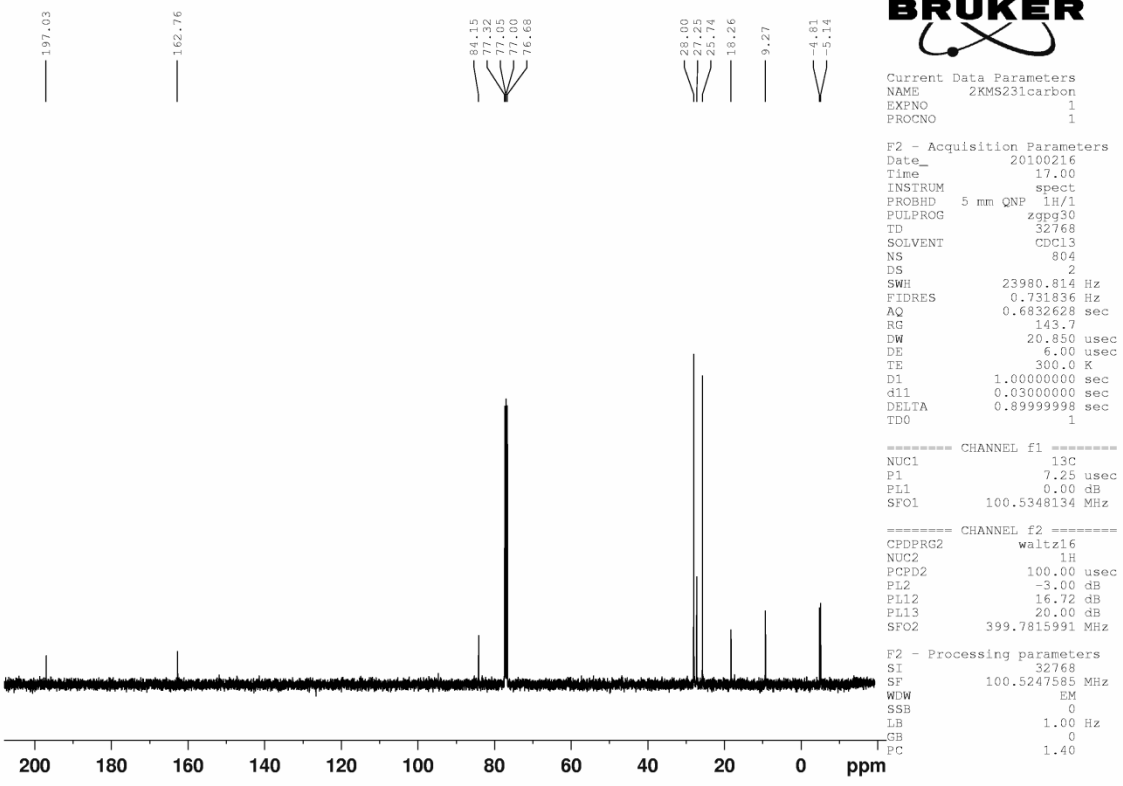

```
Current Data Parameters
NAME          Indolecarbonb
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20100212
Time                   16.37
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG             zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      833
DS                        2
SWH               23980.814 Hz
FIDRES             0.731836 Hz
AQ                 0.6832628 sec
RG                     16384
DW                   20.850 usec
DE                     6.00 usec
TE                     300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       7.25 usec
PL1                      0.00 dB
SFO1            100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                 100.00 usec
PL2                     -3.00 dB
PL12                    16.72 dB
PL13                    20.00 dB
SFO2            399.7815991 MHz

F2 - Processing parameters
SI                         32768
SF              100.5247621 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```



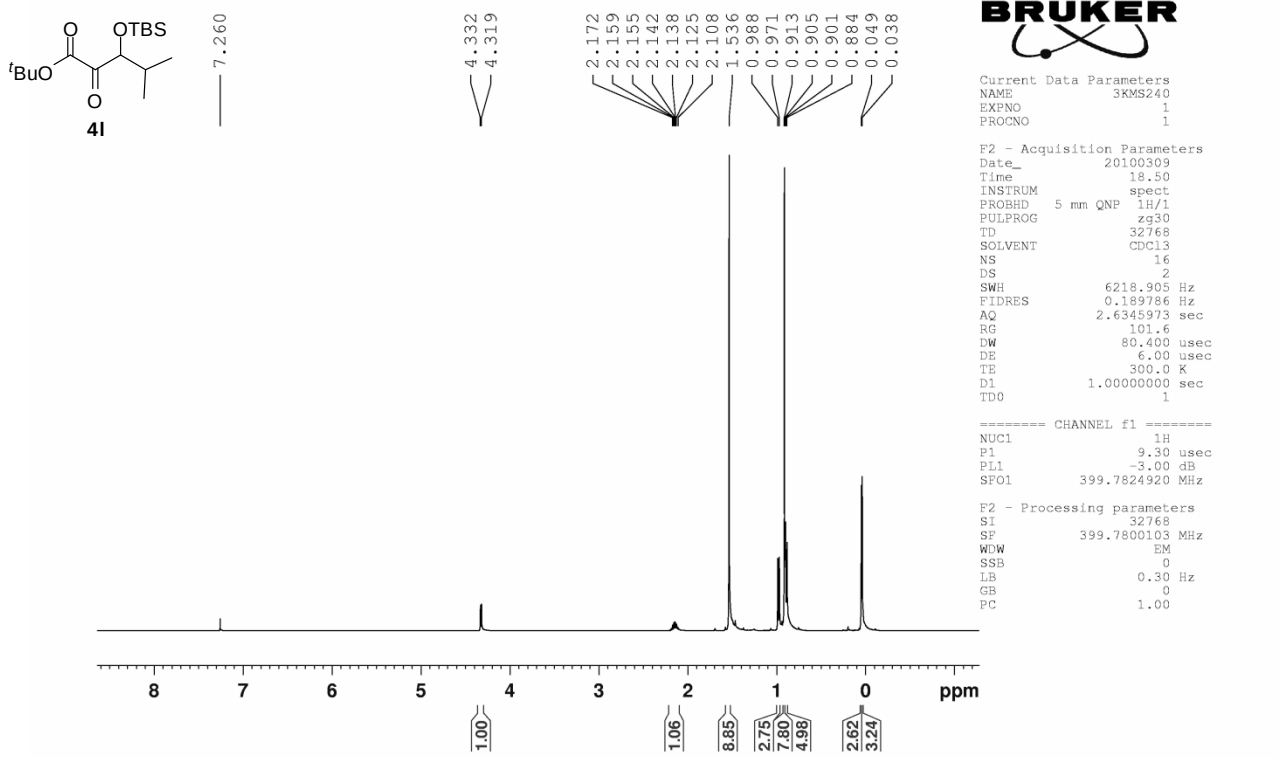
4k




```
Current Data Parameters
NAME                 3KMS231B
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20100216
Time                   14.39
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6218.905 Hz
FIDRES            0.189786 Hz
AQ                2.6345973 sec
RG                      256
DW                   80.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       9.30 usec
PL1                     -3.00 dB
SFO1           399.7824920 MHz

F2 - Processing parameters
SI                        32768
SF             399.7800105 MHz
WDW                          EM
SSB                           0
LB                         0.60 Hz
GB                            0
PC                         1.00
```




```
Current Data Parameters
NAME          2KMS231carbon
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_               20100216
Time                   17.00
INSTRUM                spect
PROBHD    5 mm QNP  1H/1
PULPROG             zgpg30
TD                    32768
SOLVENT               CDCl3
NS                      804
DS                        2
SWH               23980.814 Hz
FIDRES            0.731836 Hz
AQ                0.6832628 sec
RG                    143.7
DW                   20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1              1.00000000 sec
d11             0.03000000 sec
DELTA           0.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       7.25 usec
PL1                      0.00 dB
SFO1           100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                       1H
PCPD2                100.00 usec
PL2                     -3.00 dB
PL12                    16.72 dB
PL13                    20.00 dB
SFO2           399.7815991 MHz

F2 - Processing parameters
SI                        32768
SF             100.5247585 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```



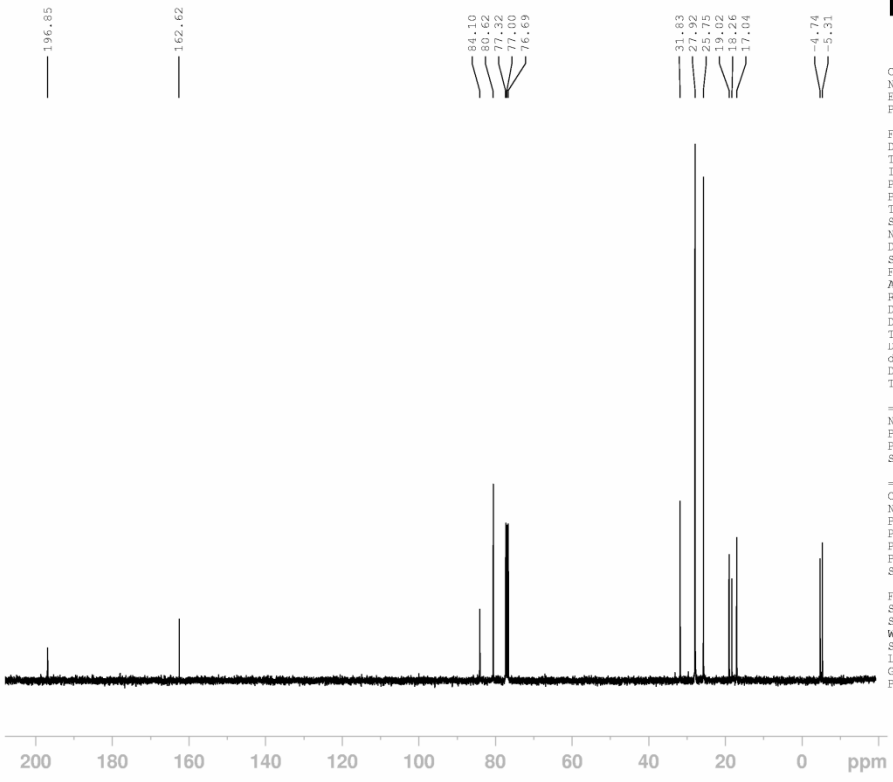
BRUKER

Current Data Parameters
NAME 3KMS240
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100309
Time 18.50
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6218.905 Hz
FIDRES 0.189786 Hz
AQ 2.6345973 sec
RG 101.6
DW 80.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.30 usec
PL1 -3.00 dB
SFO1 399.7824920 MHz

F2 - Processing parameters
SI 32768
SF 399.7800103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



BRUKER

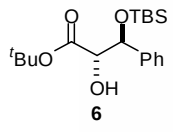
Current Data Parameters
NAME isobutyraldehydecarbon
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100203
Time 13.51
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 464
DS 2
SWH 23980.814 Hz
FIDRES 0.731836 Hz
AQ 0.6832628 sec
RG 128
DW 20.850 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

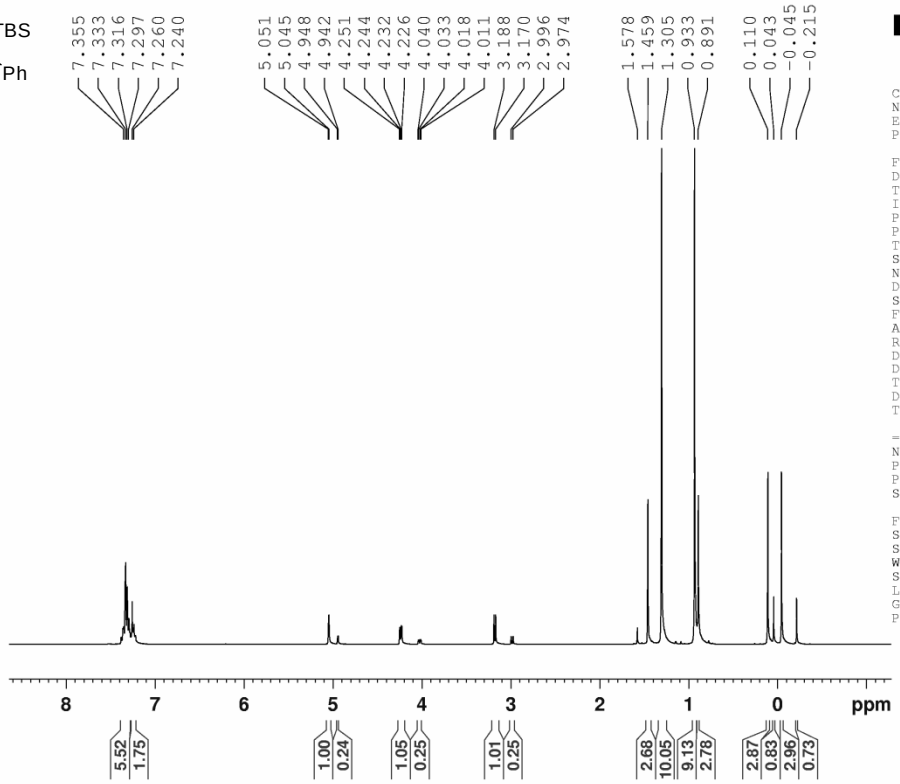
======== CHANNEL f1 ========
NUC1 13C
P1 7.25 usec
PL1 0.00 dB
SFO1 100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 16.72 dB
PL13 20.00 dB
SFO2 399.7815991 MHz

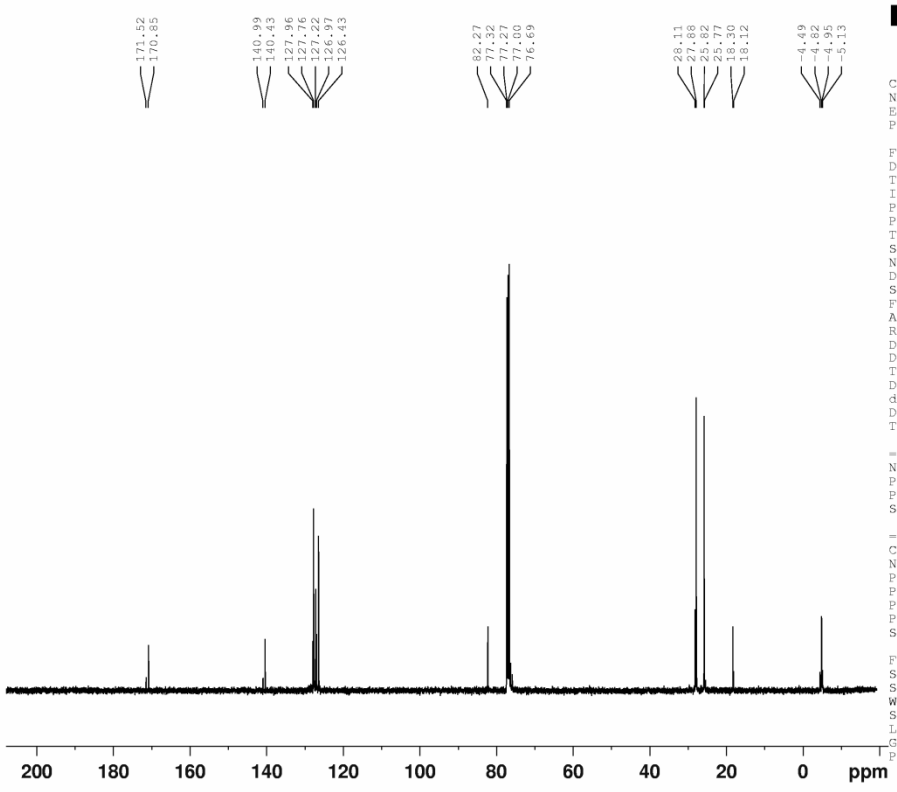
F2 - Processing parameters
SI 32768
SF 100.5247595 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



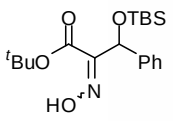
6

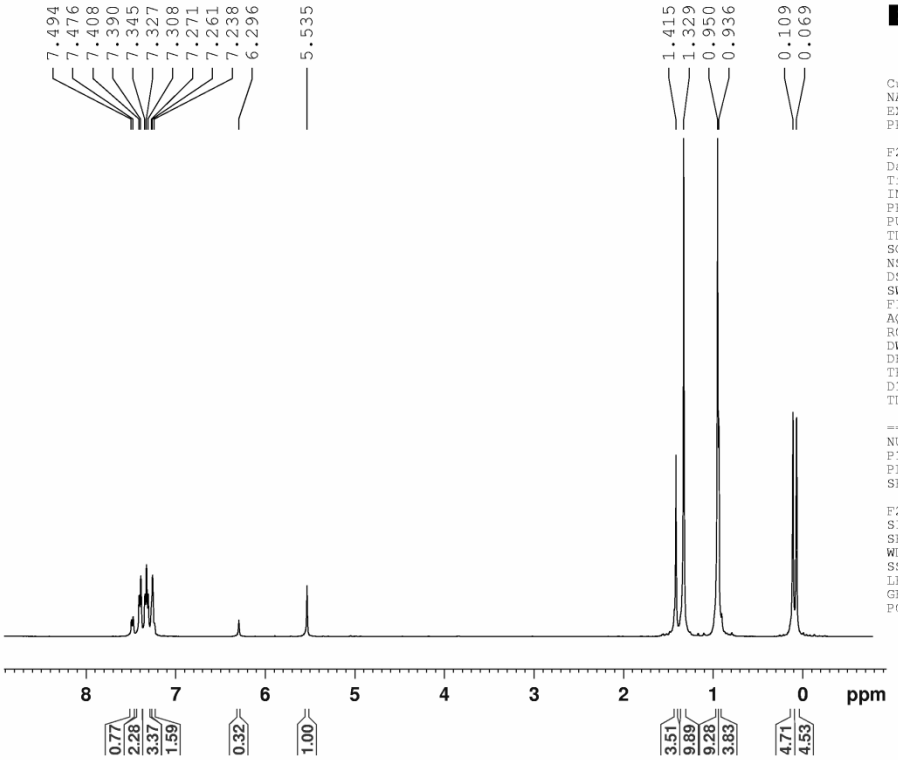


```
Current Data Parameters
NAME                 3KMS209
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20100319
Time                  11.33
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG               zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6218.905 Hz
FIDRES            0.189786 Hz
AQ                2.6345973 sec
RG                    143.7
DW                   80.400 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.30 usec
PL1                    -3.00 dB
SFO1           399.7824920 MHz

F2 - Processing parameters
SI                        32768
SF             399.7800101 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

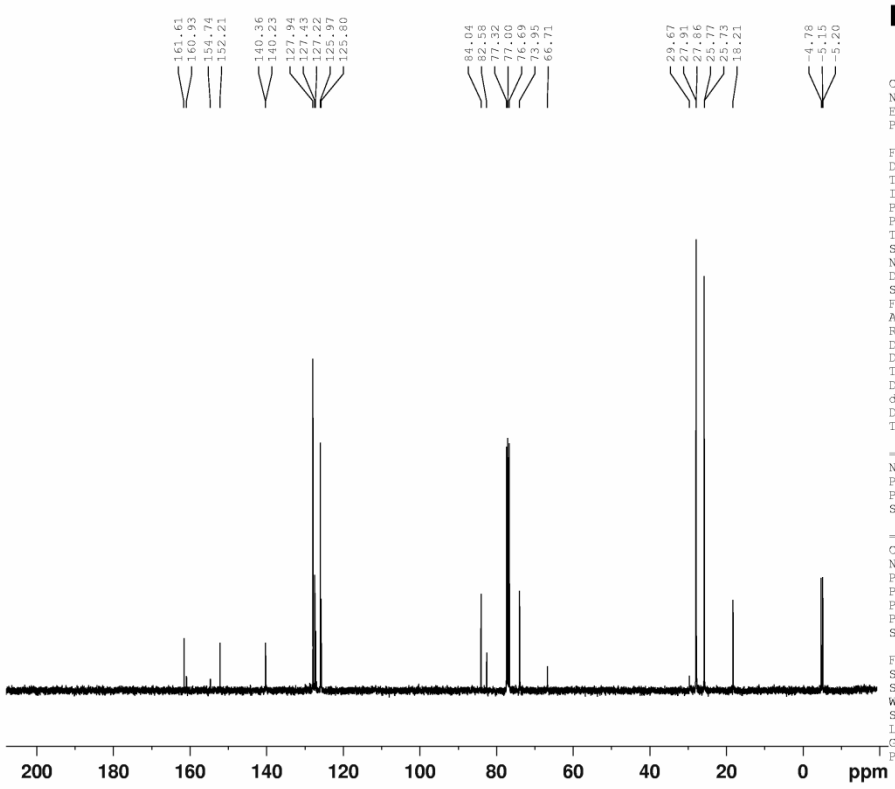


```
Current Data Parameters
NAME            Phdiolcarbon
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20100206
Time                   9.20
INSTRUM               spect
PROBHD    5 mm QNP  1H/1
PULPROG            zgpg30
TD                    32768
SOLVENT               CDCl3
NS                     2749
DS                        2
SWH               23980.814 Hz
FIDRES            0.731836 Hz
AQ                0.6832628 sec
RG                    161.3
DW                   20.850 usec
DE                    6.00 usec
TE                   300.0 K
D1                1.00000000 sec
d11               0.03000000 sec
DELTA             0.89999998 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      7.25 usec
PL1                     0.00 dB
SFO1           100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                100.00 usec
PL2                   -3.00 dB
PL12                  16.72 dB
PL13                  20.00 dB
SFO2           399.7815991 MHz

F2 - Processing parameters
SI                        32768
SF             100.5247601 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```






```
Current Data Parameters
NAME       3KMS232column
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100217
Time               13.59
INSTRUM            spect
PROBHD   5 mm TXI 13C Z
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5341.880 Hz
FIDRES          0.163021 Hz
AQ              3.0672283 sec
RG                   114
DW                93.600 usec
DE                 6.00 usec
TE                294.7 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.95 usec
PL1                0.00 dB
SFO1         400.0923618 MHz

F2 - Processing parameters
SI                 32768
SF           400.0900042 MHz
WDW                   EM
SSB                    0
LB                  0.25 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME       3KMS265carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100311
Time               16.11
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  1024
DS                     2
SWH            23980.814 Hz
FIDRES          0.731836 Hz
AQ              0.6832628 sec
RG                 161.3
DW                20.850 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
d11            0.03000000 sec
DELTA          0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 7.25 usec
PL1                0.00 dB
SFO1         100.5348134 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -3.00 dB
PL12               16.72 dB
PL13               20.00 dB
SFO2         399.7815991 MHz

F2 - Processing parameters
SI                 32768
SF           100.5247622 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```