

Supporting Information

Metalloradical Activation of α -Formyldiazoacetates for Catalytic Asymmetric Radical Cyclopropanation of Alkenes

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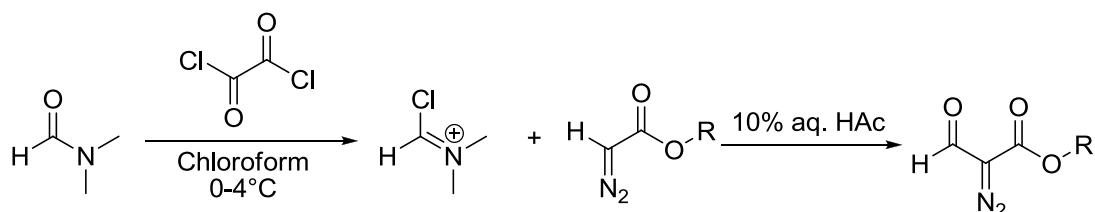
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Table of Contents

I. General Considerations-----	S2
II. General Procedure for α -Formyldiazoacetates Synthesis-----	S2
III. General Procedure for the Reduction of Cyclopropane Carbaldehydes-----	S3
IV. General Procedure for Asymmetric Cyclopropanation-----	S3
V. Further Transformations of Chiral 1,1-Cyclopropaneformylesters-----	S10
VI. X-ray Crystallography-----	S13
VII. References-----	S15
X. Spectra-----	S16

I. General Considerations. All cyclopropanation reactions were carried out under a nitrogen atmosphere in oven-dried glassware following standard Schlenk techniques. Toluene was distilled under nitrogen from sodium benzophenone ketyl. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with ICN silica gel (60 Å, 230-400 mesh, 32-63 µm). Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Bruker250 (250 MHz) or Varian Inova400 (400 MHz) or UnityInova 600 (600 MHz) instrument with chemical shifts reported relative to residual solvent. HPLC measurements were carried out on a Shimadzu HPLC system with Whelk-O1,Chiralcel OD-H, OJ-H, and AD-H columns. GC measurements were carried out on a Shimadzu GCMS system with Chiral GTA and Dex-CB column. HRMS data was obtained on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization.

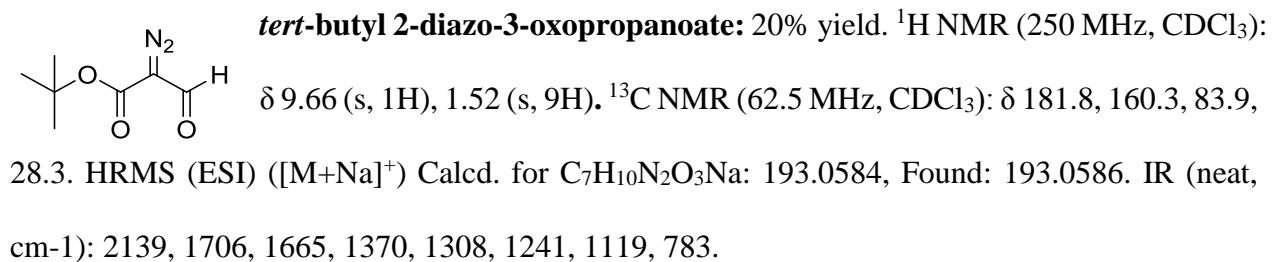
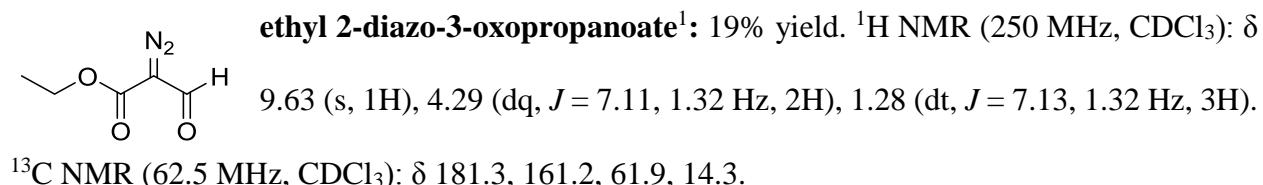
II. General Procedure for α -Formyldiazoacetates Synthesis:¹



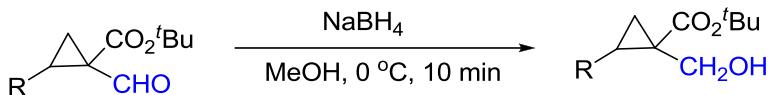
(*Diazo reagents are a class of potentially explosive compounds. Protections must be applied for the operation. Handling of diazo compounds must be done within a fume hood with a safety shield around the reaction. All the diazo reagents used in this work were stored in a freezer at -20 °C*)

In a dried three-necked flask is placed a CHCl₃ solution of DMF (1.1 g, 15 mmol/30 ml). While stirring in a freezing mixture, 2.2 g of oxalyl chloride (18 mmol) was added dropwise. After the vigorous evolution of CO and CO₂ has ceased, the mixture was heated to 40 °C for 10 min. The mixture was then cooled to -10 °C and diazoacetate (30 mmol) was added dropwise, maintaining the temperature no higher than 0 °C. After the brisk evolution of N₂ has subsided, the mixture was stirred at r.t. for 1 h. The solution was concentrated, and 100 ml of cold dry Et₂O were added. The formed crystals were filtered immediately, washed successively with dry Et₂O and then dissolved in 10% aq. AcOH. After stirring for 2 h, the mixture was extracted with Et₂O, washed with brine,

dried with Na_2SO_4 , filtered, and concentrated, followed by flash silica gel chromatography (pentane/diethyl ether) to afford desired product with around 20% overall yield.



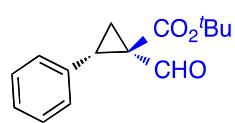
III. General Procedure for the Reduction of Cyclopropane Carbaldehydes (*In some cases, a further reduction step is needed for the determination of ee*)



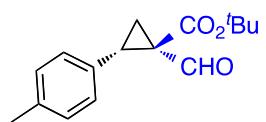
To a stirred at 0 °C solution of cyclopropyl aldehydes (0.1 mmol) in methanol (5 ml) was added dropwise a solution of sodium borohydride (1.2-1.5 equiv.) in methanol (1 ml). The mixture was stirred for 10 min at 0 °C, and then quenched by 3N aqueous NaOH (3 ml), the mixture was then extracted by ethyl acetate (3 x 5 ml), and the combined organic phases were washed with brine, dried with Na_2SO_4 , filtered, and concentrated. Purification of the crude residue by flash silica gel chromatography afforded the corresponding alcohol.

IV. General Procedure for Asymmetric Cyclopropanation: $[\text{Co}(\textbf{P2})]$ (5 mol %) was placed in an oven-dried, resealable Schlenk tube. The tube was capped with a Teflon screwcap, evacuated, and backfilled with nitrogen. The screwcap was replaced with a rubber septum. 1.0 Equivalent of

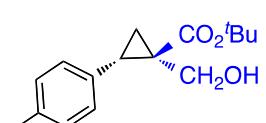
alkene (0.10 mmol), 1.2 equivalents of diazo compound (0.12 mmol) in 0.5 ml toluene was added once via syringe. Schlenk tube was capped by teflon screwcap instead of rubber septum and stirred at room temperature. Following completion of the reaction, the reaction mixture was purified by flash chromatography. The fractions containing product were collected and concentrated by rotary evaporation to afford the compound. In most cases, the product was visualized on TLC using the cerium ammonium molybdate (CAM) stain.



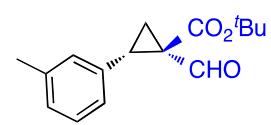
tert-butyl 1-formyl-2-phenylcyclopropanecarboxylate (1a): $[\alpha]^{20}_D = -79.04$ ($c = 1.01$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.85 (s, 1H), 7.25-7.08 (m, 5H), 3.29 (t, $J = 8.91$ Hz, 1H), 2.26 (dd, $J = 8.70, 4.35$ Hz, 1H), 1.90 (dd, $J = 9.11, 4.34$ Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.4, 169.6, 133.1, 129.7, 128.1, 127.7, 82.5, 42.0, 41.3, 28.2, 19.9. IR (neat, cm^{-1}): 1704, 1369, 1293, 1259, 1144, 763, 697. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{19}\text{O}_3$: 247.1329, Found: 247.1330. HPLC analysis: $ee = 96\%$. OJ-H (97% hexanes: 3% isopropanol, 0.8 ml/min) $t_{\text{major}} = 20.43$ min, $t_{\text{minor}} = 16.50$ min.



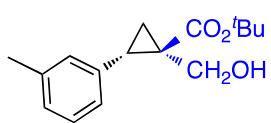
tert-butyl 1-formyl-2-p-tolylcyclopropanecarboxylate (1b): $[\alpha]^{20}_D = -80.60$ ($c = 0.34$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 9.84 (s, 1H), 7.09 (m, 4H), 3.26 (t, $J = 8.90$ Hz, 1H), 1.88 (dd, $J = 9.09, 4.30$ Hz, 1H), 2.26-2.20 (m, 4H), 1.48 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.5, 169.7, 137.4, 130.0, 129.5, 128.8, 82.5, 42.2, 41.4, 28.4, 28.2, 21.2, 19.9. IR (neat, cm^{-1}): 1702, 1369, 1275, 1154, 1127, 1098, 763, 700. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3\text{Na}$: 283.1305, Found: 283.1306.



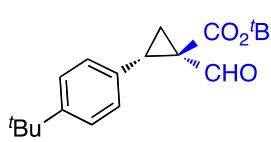
tert-butyl 1-(hydroxymethyl)-2-p-tolylcyclopropanecarboxylate (1ba): ^1H NMR (250 MHz, CDCl_3): δ 7.05 (m, 4H), 3.40 (ddd, $J = 12.33, 2.91, 0.92$ Hz, 1H), 3.26 (dd, $J = 12.32, 5.27$ Hz, 1H), 2.82 (br, 1H), 2.25 (s, 3H), 1.51 (dd, $J = 8.69, 4.58$ Hz, 1H), 1.44 (s, 9H), 1.28 (dd, $J = 7.14, 4.75$ Hz, 1H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 173.8, 136.6, 132.9, 129.0, 129.0, 81.4, 62.3, 32.3, 30.5, 28.2, 21.1, 17.4. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}$: 285.1461, Found: 285.1457. HPLC analysis: $ee = 97\%$. Whelk (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 24.24$ min, $t_{\text{minor}} = 28.18$ min.



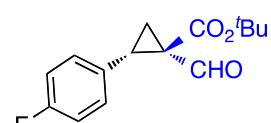
tert-butyl 1-formyl-2-m-tolylcyclopropanecarboxylate (1c): $[\alpha]^{20}_D = -90.03$ ($c = 0.12$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.84 (s, 1H), 7.15-6.86 (m, 4H), 1.88 (dd, $J = 9.09, 4.36$ Hz, 1H), 2.25 (dd, $J = 14.24, 5.67$ Hz, 1H), 2.25 (s, 3H) 3.26 (t, $J = 8.93$ Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.5, 169.7, 137.7, 133.0, 130.4, 128.4, 128.0, 126.6, 82.5, 42.0, 41.3, 28.2, 21.4, 19.8. IR (neat, cm^{-1}): 1702, 1369, 1275, 1127, 1098, 763. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_3$: 261.1485, Found: 261.1480.



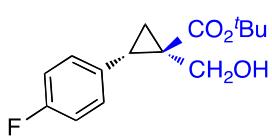
tert-butyl 1-(hydroxymethyl)-2-m-tolylcyclopropanecarboxylate (1ca): ^1H NMR (250 MHz, CDCl_3): δ 7.17-6.91 (m, 4H), 3.46 (d, $J = 12.32$ Hz, 1H), 3.29-3.13 (m, 1H), 2.83 (t, $J = 8.33$ Hz, 1H), 2.45-2.33 (m, 1H), 2.26 (s, 3H), 1.56-1.50 (m, 1H), 1.31 (dd, $J = 7.18, 4.78$ Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 173.7, 137.9, 135.9, 129.9, 128.2, 127.8, 126.1, 81.5, 62.3, 32.3, 30.7, 28.1, 21.4, 17.4. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{16}\text{H}_{23}\text{O}_3$: 285.1461, Found: 285.1461. HPLC analysis: $ee = 99\%$. AD-H (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 33.50$ min, $t_{\text{minor}} = 21.76$ min.



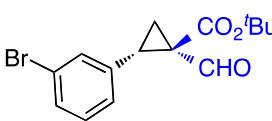
tert-butyl 2-(4-tert-butylphenyl)-1-formylcyclopropanecarboxylate (1d): $[\alpha]^{20}_D = -117.53$ ($c = 0.98$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.84 (s, 1H), 7.26-7.19 (m, 2H), 7.07 (d, $J = 8.24$ Hz, 2H), 3.25 (t, $J = 8.97$ Hz, 1H), 2.25 (dd, $J = 8.74, 4.36$ Hz, 1H), 1.89 (dd, $J = 9.10, 4.32$ Hz, 1H), 1.48 (s, 9H), 1.23 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.5, 169.7, 150.6, 130.0, 129.3, 125.067, 82.5, 42.3, 41.3, 34.5, 31.3, 28.2, 19.8. IR (neat, cm^{-1}): 1721, 1369, 1294, 1259, 1146, 1098, 841, 753. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Na}$: 325.1774, Found: 325.1773. HPLC analysis: $ee = 97\%$. Whelk (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 11.56$ min, $t_{\text{minor}} = 33.36$ min.



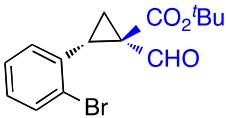
tert-butyl 2-(4-fluorophenyl)-1-formylcyclopropanecarboxylate (1e): $[\alpha]^{20}_D = -193.32$ ($c = 0.67$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.87 (s, 1H), 7.08-7.14 (m, 2H), 6.95-6.84 (m, 2H), 3.26 (t, $J = 8.91$ Hz, 1H), 2.21 (dd, $J = 8.68, 4.38$ Hz, 1H), 1.91 (dd, $J = 9.13, 4.34$ Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.5, 169.5, 164.1, 160.2, 131.3, 131.2, 128.8, 128.8, 115.2, 114.9, 82.7, 42.0, 40.6, 28.2, 20.3. IR (neat, cm^{-1}): 1702, 1514, 1369, 1295, 1146, 1109, 841, 756. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{17}\text{FO}_3\text{Na}$: 287.1054, Found: 287.1055.



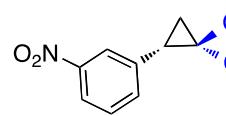
tert-butyl 2-(4-fluorophenyl)-1-(hydroxymethyl)cyclopropanecarboxylate (1ea): ^1H NMR (250 MHz, CDCl_3): δ 7.16 (dd, $J = 8.55, 5.76$ Hz, 2H), 6.92 (t, $J = 8.68$ Hz, 2H), 3.31 (s, 2H), 2.81 (m, 1H), 2.57-2.40 (br, 1H), 1.53 (dd, $J = 8.97, 4.79$ Hz, 1H), 1.44 (s, 9H), 1.21 (m, 1H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 173.6, 163.8, 159.9, 131.8, 130.9, 130.8, 129.2, 128.3, 115.4, 115.0, 81.7, 62.2, 32.2, 30.1, 28.1, 17.6. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{19}\text{FO}_3\text{Na}$: 289.1210, Found: 289.1211. HPLC analysis: $ee = 97\%$. AD-H (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 25.90$ min, $t_{\text{minor}} = 23.42$ min.



tert-butyl 2-(3-bromophenyl)-1-formylcyclopropanecarboxylate (1f): $[\alpha]^{20}_D = -67.81$ ($c = 1.00$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.87 (s, 1H), 7.29 (m, 2H), 7.07 (m, 2H), 3.23 (t, $J = 8.85$ Hz, 1H), 2.20 (dd, $J = 8.60, 4.38$ Hz, 1H), 1.89 (dd, $J = 9.13, 4.37$ Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.2, 169.3, 135.5, 132.8, 130.8, 129.6, 128.2, 122.2, 82.8, 41.8, 40.1, 28.2, 20.1. IR (neat, cm^{-1}): 1702, 1370, 1326, 1296, 1146, 846, 752. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{18}\text{BrO}_3$: 325.0434, Found: 325.0442. HPLC analysis: $ee = 99\%$. Whelk (98% hexanes: 2% isopropanol, 0.8 ml/min) $t_{\text{major}} = 12.65$ min, $t_{\text{minor}} = 27.37$ min.

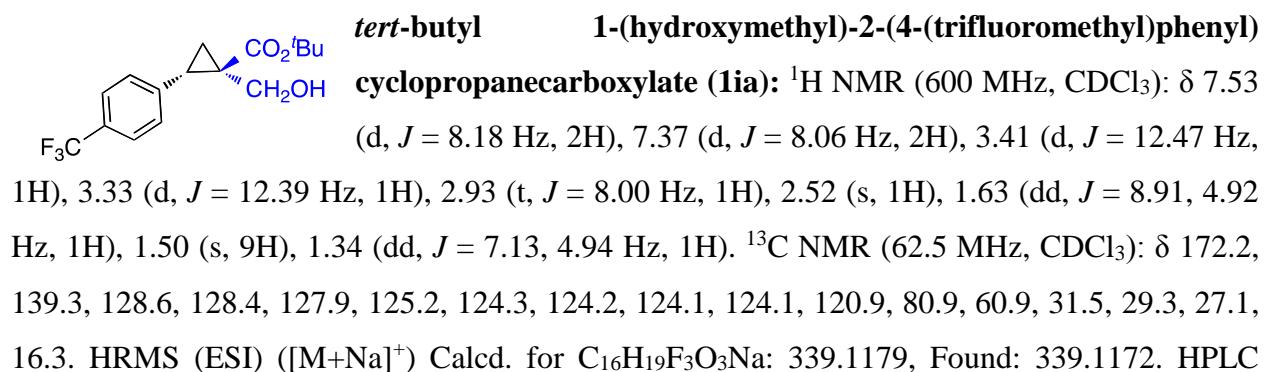
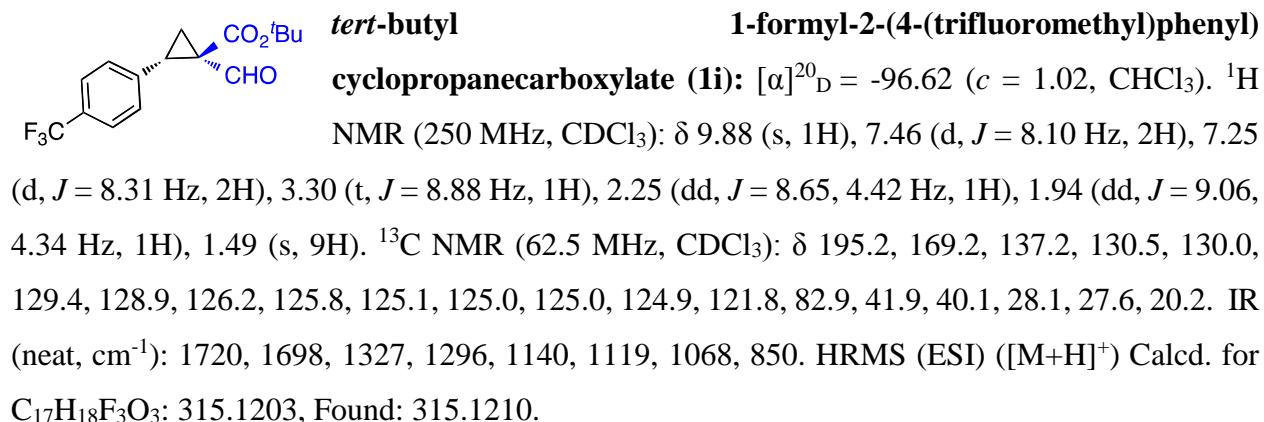
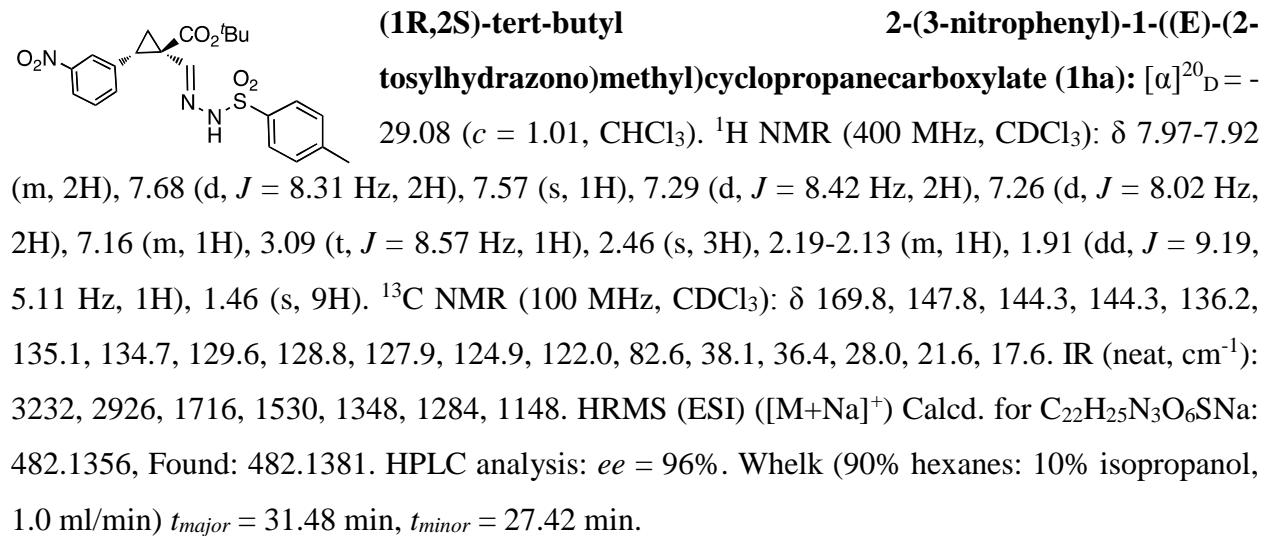


tert-butyl 2-(2-bromophenyl)-1-formylcyclopropanecarboxylate (1g): $[\alpha]^{20}_D = 26.94$ ($c = 0.88$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 10.01 (s, 1H), 7.43 (d, $J = 7.87$ Hz, 1H), 7.21 (m, 2H), 7.11-7.02 (m, 1H), 3.12 (t, $J = 8.79$ Hz, 1H), 2.20 (dd, $J = 8.71, 4.20$ Hz, 1H), 1.97 (dd, $J = 8.89, 4.24$ Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 194.9, 169.5, 134.0, 132.1, 131.4, 129.3, 127.1, 126.5, 82.5, 42.2, 40.7, 28.2, 20.9. IR (neat, cm^{-1}): 1702, 1368, 1315, 1297, 1146, 845, 759. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{17}\text{BrO}_3\text{Na}$: 347.0253, Found: 347.0252. HPLC analysis: $ee = 98\%$. Whelk (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 15.50$ min, $t_{\text{minor}} = 57.33$ min.

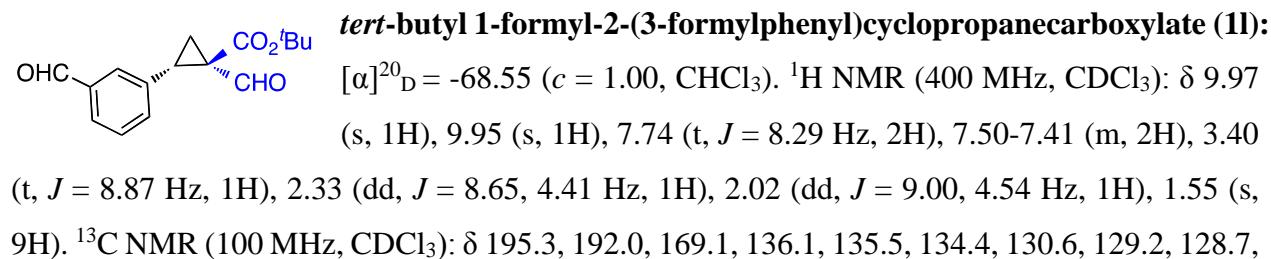
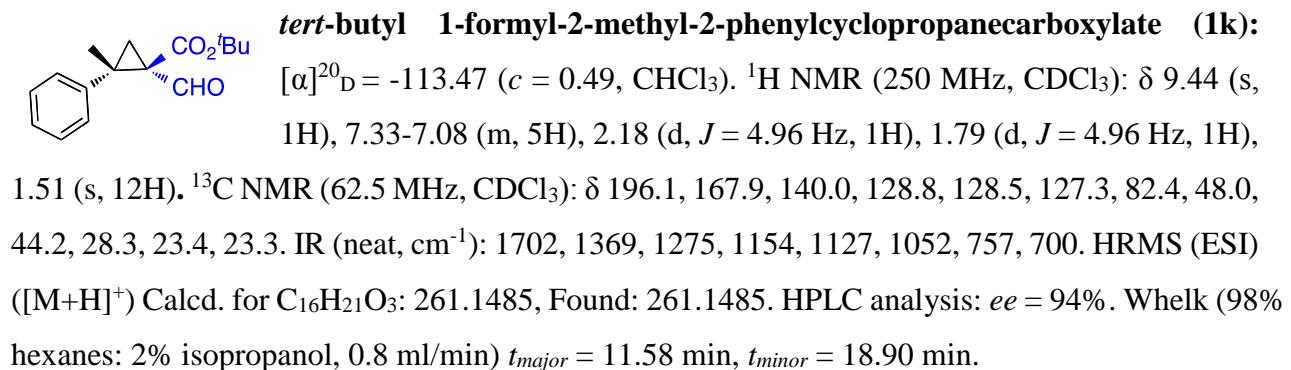
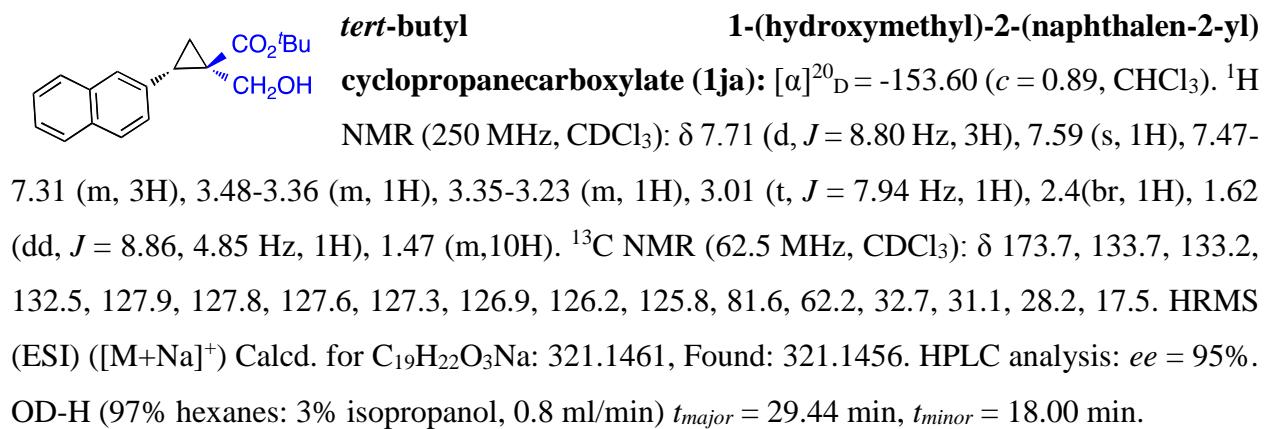
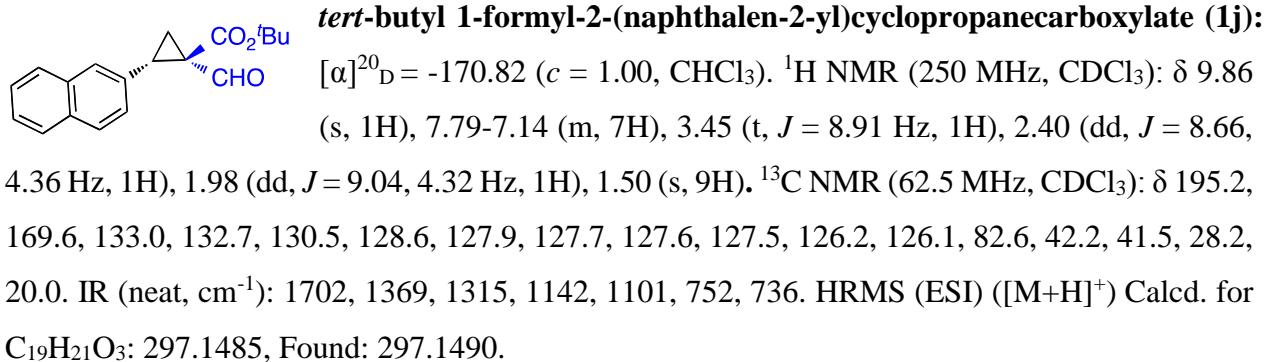


tert-butyl 1-formyl-2-(3-nitrophenyl)cyclopropanecarboxylate (1h): $[\alpha]^{20}_D = -73.59$ ($c = 1.04$, CHCl_3). ^1H NMR (250 MHz, CDCl_3): δ 9.93 (s, 1H), 8.08-7.98 (m, 2H), 7.54-7.32 (m, 2H), 3.35 (t, $J = 8.89$ Hz, 1H), 2.27 (dd, $J = 8.61, 4.45$ Hz, 1H), 2.00 (dd, $J = 9.13, 4.43$ Hz, 1H), 1.51 (s, 9H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 194.3, 167.9, 146.9, 134.6, 127.9, 123.8, 121.6, 82.1, 40.5, 38.5, 27.1, 19.8. IR

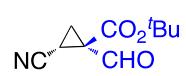
(neat, cm^{-1}): 1702, 1530, 1349, 1296, 1146, 752. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{15}\text{H}_{18}\text{NO}_5$: 292.1179, Found: 292.1180. HPLC analysis: $ee = 97\%$. Whelk (98% hexanes: 2% isopropanol, 0.8 ml/min) $t_{\text{major}} = 29.74$ min, $t_{\text{minor}} = 50.48$ min.

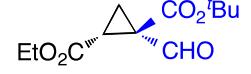


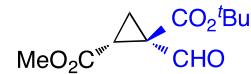
analysis: *ee* = 96%. AD-H (99% hexanes: 1% isopropanol, 0.8 ml/min) *t_{major}* = 21.08 min, *t_{minor}* = 46.67 min.



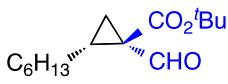
82.8, 41.7, 40.1, 28.1, 20.4. IR (neat, cm^{-1}): 1700, 1369, 1295, 1144, 751. HPLC analysis: $ee = 95\%$. OJ-H (95% hexanes: 5% isopropanol, 1.0 ml/min) $t_{major} = 11.54$ min, $t_{minor} = 10.17$ min.

 **(1R,2R)-tert-butyl 2-cyano-1-formylcyclopropanecarboxylate (1m): Major isomer:** ^1H NMR (500 MHz, CDCl_3): δ 10.25 (s, 1H), 2.37 (dd, $J = 9.52, 7.54$ Hz, 1H), 2.11-2.04 (m, 1H), 1.81 (dd, $J = 9.55, 4.28$ Hz, 1H), 1.58 (s, 9H). **Minor isomer:** ^1H NMR (500 MHz, CDCl_3): δ 10.26 (s, 1H), 2.49 (dd, $J = 9.46, 7.65$ Hz, 1H), 2.11-2.04 (m, 1H), 1.89 (dd, $J = 9.48, 4.26$ Hz, 1H), 1.54 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3): δ 195.3, 193.2, 166.3, 165.3, 115.9, 115.2, 84.9, 84.6, 37.4, 37.3, 27.9, 22.9, 21.7, 16.9, 16.3. IR (neat, cm^{-1}): 2250, 1712, 1325, 1144, 840. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{10}\text{H}_{14}\text{NO}_3$: 178.0974, Found: 178.0974. HPLC analysis: ee (major) = 77 %. AD-H (99% hexanes: 1% isopropanol, 1.0 ml/min) $t_{major} = 25.28$ min, $t_{minor} = 11.49$ min.

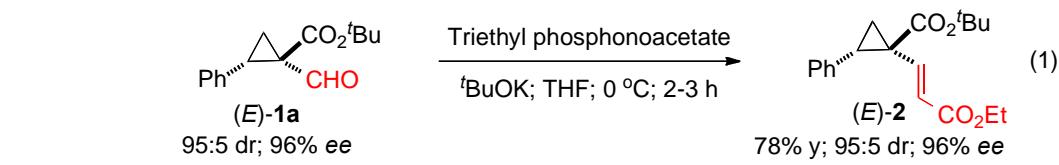
 **tert-butyl 2-ethyl 1-formylcyclopropane-1,2-dicarboxylate (1n):** $[\alpha]^{20}_D = -16.37$ ($c = 0.98$, CHCl_3). **Major isomer:** ^1H NMR (250 MHz, CDCl_3): δ 9.93 (s, 1H), 4.08 (m, 2H), 2.63 (t, $J = 8.22$ Hz, 1H), 2.07-1.91 (m, 1H), 1.72-1.54 (m, 1H), 1.43 (s, 9H), 1.26-1.11 (m, 3H). **Minor isomer:** ^1H NMR (250 MHz, CDCl_3): δ 9.94 (s, 1H), 4.08 (m, 7H), 2.50 (t, $J = 8.44$ Hz, 1H), 2.07-1.91 (m, 1H), 1.72-1.54 (m, 1H), 1.43 (s, 9H), 1.26-1.11 (m, 3H). ^{13}C NMR (62.5 MHz, CDCl_3): δ 195.3, 193.3, 166.7, 166.6, 166.5, 165.3, 82.3, 82.0, 60.6, 60.5, 39.8, 38.1, 31.9, 31.5, 27.0, 26.9, 20.1, 19.2, 13.1, 13.0. IR (neat, cm^{-1}): 1724, 1370, 1290, 1143, 752. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{12}\text{H}_{19}\text{O}_5$: 243.1227, Found: 243.1229. GC analysis: ee (major) = 96 %. CP-Chirasil-Dex CB (Temp program: initial temp = 50° C, hold time = 5 min, Rate: 5.00° C/min, max temp = 200° C, hold time = 5 min): $t_{minor} = 25.80$ min, $t_{major} = 25.74$ min.

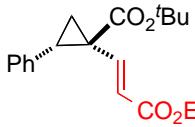
 **1-tert-butyl 2-methyl 1-formylcyclopropane-1,2-dicarboxylate(1o):** $[\alpha]^{20}_D = -15.19$ ($c = 1.01$, CHCl_3). **Major isomer:** ^1H NMR (250 MHz, CDCl_3): δ 9.94 (s, 1H), 3.64 (s, 3H), 2.64 (dd, $J = 8.94, 7.82$ Hz, 1H), 2.06-1.93 (m, 1H), 1.72-1.60 (m, 1H), 1.43 (s, 9H). **Minor isomer:** ^1H NMR (250 MHz, CDCl_3): δ 1H NMR (250 MHz, Solvent) d ppm 9.96 (s, 1H), 3.65 (s, 3H), 2.51 (m, 1H), 2.06-1.93 (m, 1H), 1.72-1.60 (m, 1H), 1.44 (s, 9H), ^{13}C NMR (62.5 MHz, CDCl_3): δ 196.3, 194.4, 168.1, 168.0, 167.7, 166.4, 83.4, 83.1, 52.5, 52.4, 40.7, 39.1, 32.7, 32.3, 28.0, 27.9, 21.2, 20.4. IR (neat, cm^{-1}): 1712, 1370, 1290, 1249, 1142, 843, 753. HRMS (ESI) ($[\text{M}+\text{H}]^+$) Calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_5$: 229.1071, Found: 229.1071. GC analysis: ee

(major) = 97 %. CP-Chirasil-Dex CB (Temp program: initial temp = 50° C, hold time = 5 min, Rate: 5.00° C/min, max temp = 200° C, hold time= 5 min) $t_{\text{minor}} = 24.68$ min, $t_{\text{major}} = 24.63$ min.

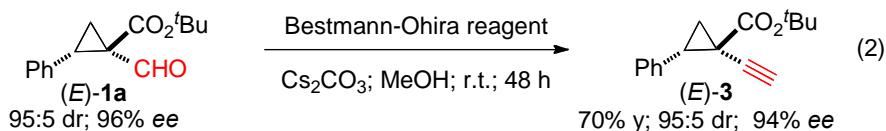
 **tert-butyl 1-formyl-2-hexylcyclopropanecarboxylate (1p):** $[\alpha]^{20}_{\text{D}} = -7.13$ ($c = 1.01$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 10.28 (s, 1H), 2.07-1.96 (m, 1H), 1.63 (ddd, $J = 18.88, 8.68, 3.59$ Hz, 2H), 1.46 (m, 11H), 1.28-1.19 (m, 8H), 0.85 (t, $J = 6.90$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 197.9, 170.4, 81.8, 39.3, 31.6, 29.6, 28.6, 28.1, 28.0, 25.8, 23.5, 22.5, 13.9. IR (neat, cm^{-1}): 1702, 1369, 1296, 1144, 751. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{27}\text{O}_3$: 277.1774, Found: 277.1781. GC analysis: ee = 80 %. CP-Chirasil-Dex CB (Temp program: initial temp = 50° C, hold time = 5 min; Rate: 3.00° C/min, max temp = 200° C, hold time= 5 min) $t_{\text{minor}} = 37.68$ min, $t_{\text{major}} = 37.53$ min.

V. Further Transformations of Chiral 1,1-Cyclopropaneformylesters

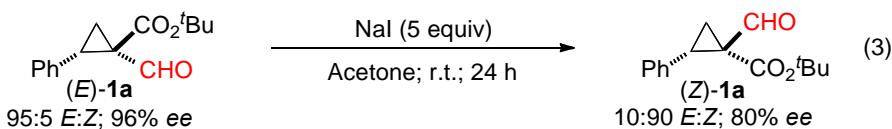


 **(E)-tert-butyl cyclopropanecarboxylate (2):** To an RBF containing potassium tert-butoxide (40.0 mg, 0.36 mmol) in THF (5 ml) at 0 °C, triethyl phosphonoacetate (81 mg, 0.36 mmol) in THF (2 ml) was added slowly via syringe. The mixture was allowed to stir for 30 min and then cyclopropane aldehyde **1a** (74 mg, 0.3 mmol) in THF (3 ml) was added dropwise via syringe. The reaction was allowed to stir at 0 °C for 2 h at which time TLC indicated all starting material was consumed. The reaction was then quenched by the addition of water. This mixture is extracted with ether (3 x 5 ml) and the combined organics are dried over Na_2SO_4 . After concentration the crude mixture was purified by silica gel column chromatography to give pure product **2** in 78% yield. $[\alpha]^{20}_{\text{D}} = -36.11$ ($c = 0.97$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.29-7.06 (m, 6H), 6.87 (d, $J = 15.95$ Hz, 1H), 5.60 (d, $J = 15.95$ Hz, 1H), 4.04 (q, $J = 7.11$ Hz, 2H), 3.12 (t, $J = 8.42$ Hz, 1H), 2.01 (dd, $J = 9.15, 5.04$ Hz, 1H), 1.68 (dd, $J = 7.65, 5.04$ Hz, 1H), 1.50 (s, 9H), 1.17 (t, $J = 7.11$ Hz, 3H), ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 166.1, 142.9, 134.6, 129.4, 128.2, 127.1, 121.3, 81.6, 60.0, 37.0, 33.1, 28.0, 19.8, 14.1. IR (neat, cm^{-1}): 1709, 1369, 1270, 1185, 1145, 750. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{Na}$: 339.1567, Found:

339.1575. HPLC analysis: *ee* = 96%. Whelk (99% hexanes: 9% isopropanol, 1.0 ml/min) *t_{major}* = 16.79 min, *t_{minor}* = 22.21 min.

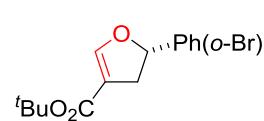
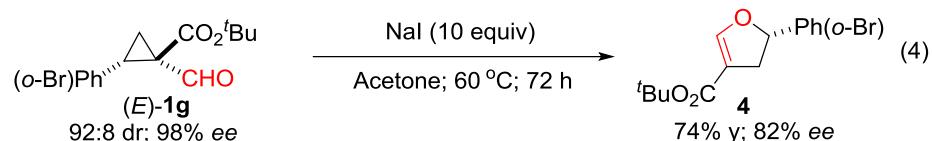


tert-butyl 1-ethynyl-2-phenylcyclopropanecarboxylate (3): In a flame-dried flask under an atmosphere of nitrogen, the cyclopropane aldehyde **1a** (74 mg, 0.3 mmol) was dissolved in methanol (10 ml), and Cs_2CO_3 (815 mg, 2.5 mmol) was added. Then, the Bestmann-Ohira reagent³ (192 mg, 1.0 mmol) was added, and the reaction mixture was stirred at room temperature for 48 h. After complete conversion, water was added, and the aqueous layer was extracted with ether (3 x 5 ml) and the combined organics are dried over Na_2SO_4 , and filtered. The solvent was removed under reduced pressure, and the product was purified by flash column chromatography to give pure product **3** in 70% yield. $[\alpha]^{20}_{\text{D}} = -46.23$ (*c* = 0.98, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.30 (m, 5H), 2.93 (t, *J* = 8.66 Hz, 1H), 1.99 (s, 1H), 1.96 (dd, *J* = 9.20, 4.62 Hz, 1H), 1.69 (dd, *J* = 7.92, 4.62 Hz, 1H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 135.4, 128.7, 127.9, 127.1, 82.0, 80.1, 71.3, 34.7, 27.9, 25.5, 23.6. IR (neat, cm^{-1}): 1714, 1369, 1302, 1267, 1149, 755, 695. HRMS (ESI) ([M+Na]⁺) Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Na}$: 265.1199, Found: 265.1231. HPLC analysis: *ee* = 94%. OD-H (100% hexanes: 0% isopropanol, 1.0 ml/min) *t_{major}* = 19.61 min, *t_{minor}* = 18.22 min.



tert-butyl 1-formyl-2-phenylcyclopropanecarboxylate ((Z)-1a): To a solution of (*E*)-cyclopropane **1a** (0.1 mmol) in acetone (1 ml) was added NaI (0.5 mmol). The mixture was stirred at room temperature for 24 h. The resulting mixture was concentrated and the residue was dissolved in ethyl acetate, and then washed with water. The organic layer was concentrated, according to crude NMR, (*Z*)-**1a** was formed in 90% yield. $[\alpha]^{20}_{\text{D}} = -131.42$ (*c* = 0.63, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 10.32 (s, 1H), 7.27 (m, 5H), 3.13 (t, *J* = 8.86 Hz, 1H), 2.29 (dd, *J* = 8.54, 4.27 Hz, 1H), 1.98 (dd, *J* = 9.18, 4.27 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 198.6, 167.1, 134.2, 129.5, 128.0, 127.6, 81.9, 43.0, 40.8, 27.5,

21.3. IR (neat, cm^{-1}): 1707, 1326, 1144, 696. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{18}\text{O}_3$: 269.1148, Found: 269.1150. GC analysis: $ee = 79\%$. CP-Chirasil-Dex CB (Temp program: initial temp = 50° C , hold time = 5 min; Rate: $5.00^\circ \text{ C}/\text{min}$, max temp = 200° C , hold time = 5 min) $t_{\text{minor}} = 28.30 \text{ min}$, $t_{\text{major}} = 28.60 \text{ min}$.



tert-butyl 5-(2-bromophenyl)-4,5-dihydrofuran-3-carboxylate (4): To a solution of (E)-cyclopropane aldehyde **1g** (0.1 mmol) in acetone (1 ml) was added NaI (1.0 mmol). The mixture was stirred at 60° C for 72 h. The resulting mixture was concentrated and the residue was dissolved in ethyl acetate, and then washed with water. The organic layer was concentrated, followed by flash silica gel chromatography to give dihydrofuran **4** in 74% yield. $[\alpha]^{20}_{\text{D}} = -57.76$ ($c = 0.49$, CHCl_3). ^1H NMR (400 MHz, CDCl_3): δ 7.19–7.14 (m, 1H), 7.56 (dd, $J = 7.97, 1.13 \text{ Hz}$, 1H), 7.38 (dd, $J = 7.80, 1.74 \text{ Hz}$, 1H), 7.33 (dd, $J = 7.36, 0.97 \text{ Hz}$, 1H), 7.31 (t, $J = 1.88 \text{ Hz}$, 1H), 5.97 (dd, $J = 11.05, 8.04 \text{ Hz}$, 1H), 3.43 (ddd, $J = 15.10, 11.06, 1.96 \text{ Hz}$, 1H), 2.61 (ddd, $J = 15.10, 8.04, 1.84 \text{ Hz}$, 1H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 164.3, 155.2, 140.9, 132.7, 129.2, 127.6, 126.2, 120.7, 110.2, 84.7, 80.0, 35.9, 28.2. IR (neat, cm^{-1}): 1698, 1630, 1123, 1099, 752. HRMS (ESI) ($[\text{M}+\text{Na}]^+$) Calcd. for $\text{C}_{15}\text{H}_{17}\text{BrO}_3\text{Na}$: 347.0253, Found: 347.0263. HPLC analysis: $ee = 82\%$. Whelk (99% hexanes: 1% isopropanol, 0.8 ml/min) $t_{\text{major}} = 11.82 \text{ min}$, $t_{\text{minor}} = 13.94 \text{ min}$.

VI. X-ray Crystallography

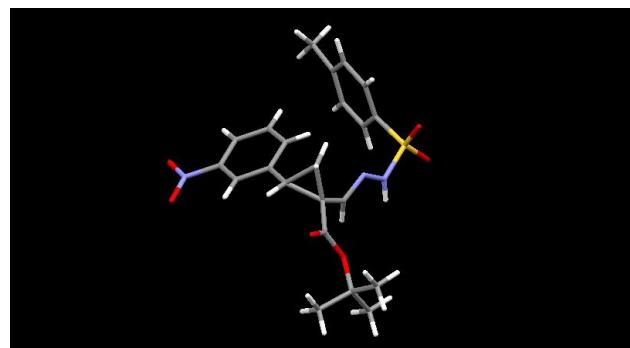
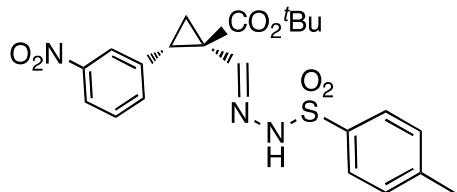


Table S1. Crystal data and structure refinement for 1ha

Identification code	1ha
Empirical formula	C ₂₂ H ₂₅ N ₃ O ₆ S
Formula weight	459.51
Temperature/K	100.0
Crystal system	monoclinic
Space group	P21
a/Å	13.2053(5)
b/Å	5.3447(2)
c/Å	15.9599(7)
α/°	90
β/°	93.6740(10)
γ/°	90
Volume/Å ³	1124.11(8)
Z	2
ρ _{calc} mg/mm ³	1.358
m/mm ⁻¹	1.656

F(000)	484.0
Crystal size/mm ³	0.16 × 0.14 × 0.11
Radiation	CuK α (λ = 1.54178)
2 Θ range for data collection	8.43 to 132.63°
Index ranges	-15 ≤ h ≤ 15, -6 ≤ k ≤ 6, -18 ≤ l ≤ 18
Reflections collected	13901
Independent reflections	3462 [R _{int} = 0.0437, R _{sigma} = 0.0392]
Data/restraints/parameters	3462/1/301
Goodness-of-fit on F ²	1.070
Final R indexes [I>=2σ (I)]	R ₁ = 0.0258, wR ₂ = 0.0595
Final R indexes [all data]	R ₁ = 0.0267, wR ₂ = 0.0604
Largest diff. peak/hole / e Å ⁻³	0.26/-0.17
Flack parameter	0.092(8)

The X-ray diffraction data for compound **1ha** were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K α INCOATEC Imus micro-focus source (λ = 1.54178 Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F²) contained in APEX2 [1] and WinGX v1.70.01 [4,5,6,7] programs packages. All non-hydrogen atoms were refined anisotropically. H9 hydrogen atom of -NH group and H15 of -CH group have been found from difference Fourier

map and were freely refined. The remaining hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(-\text{CH}, -\text{CH}_2)$, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(-\text{CH}_3)$. Crystal data and refinement conditions are shown in Table S1.

[1] Bruker (2008). *APEX2* (Version 2008.1-0). Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2001b). SAINT-V6.28A. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany.

[4] Farrugia L.J. *Appl. Cryst.* (1999). **32**, 837±838

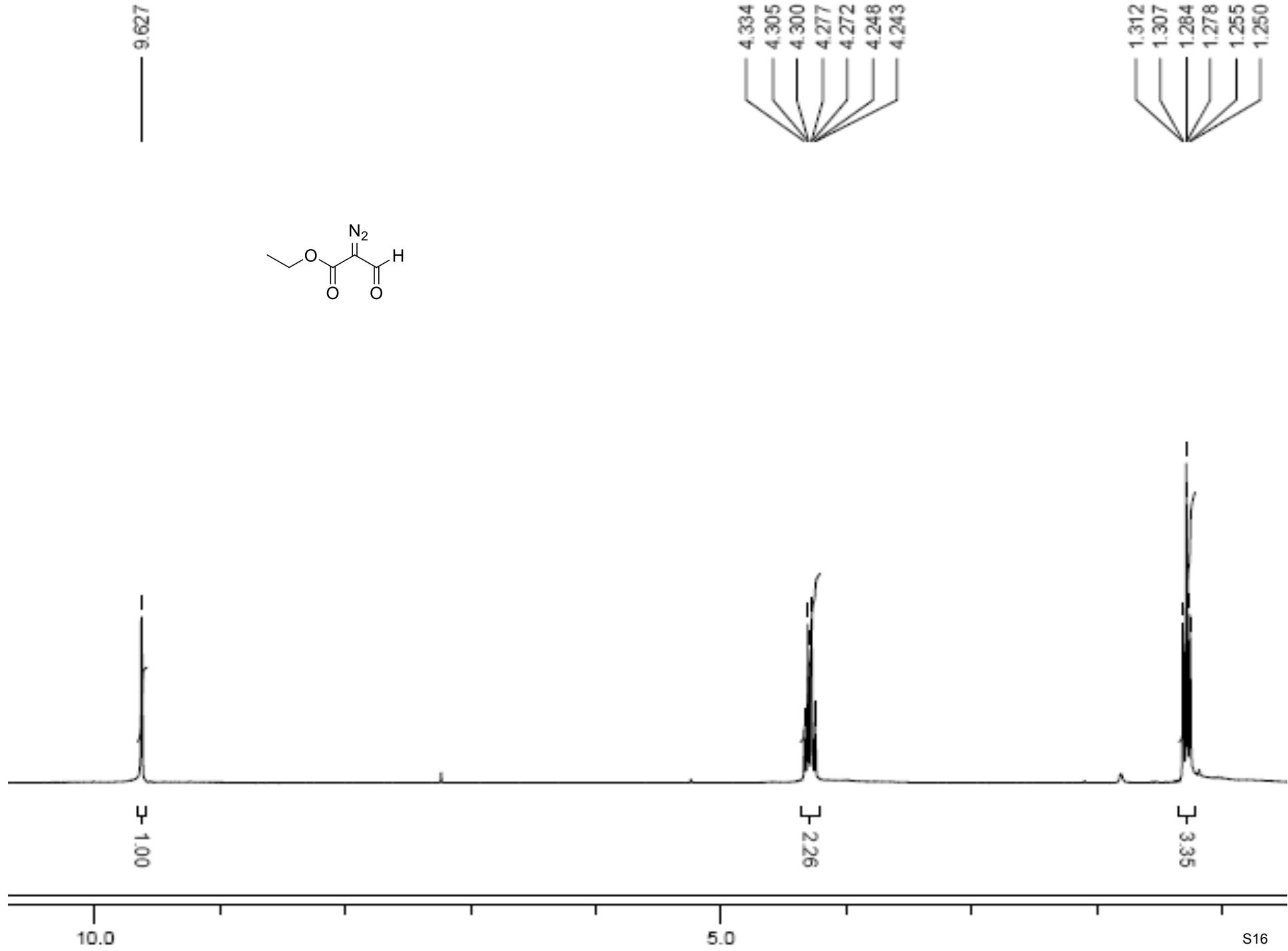
[5] Sheldrick, G.M. (1997) *SHELXL-97. Program for the Refinement of Crystal*

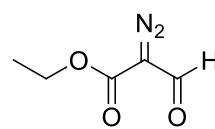
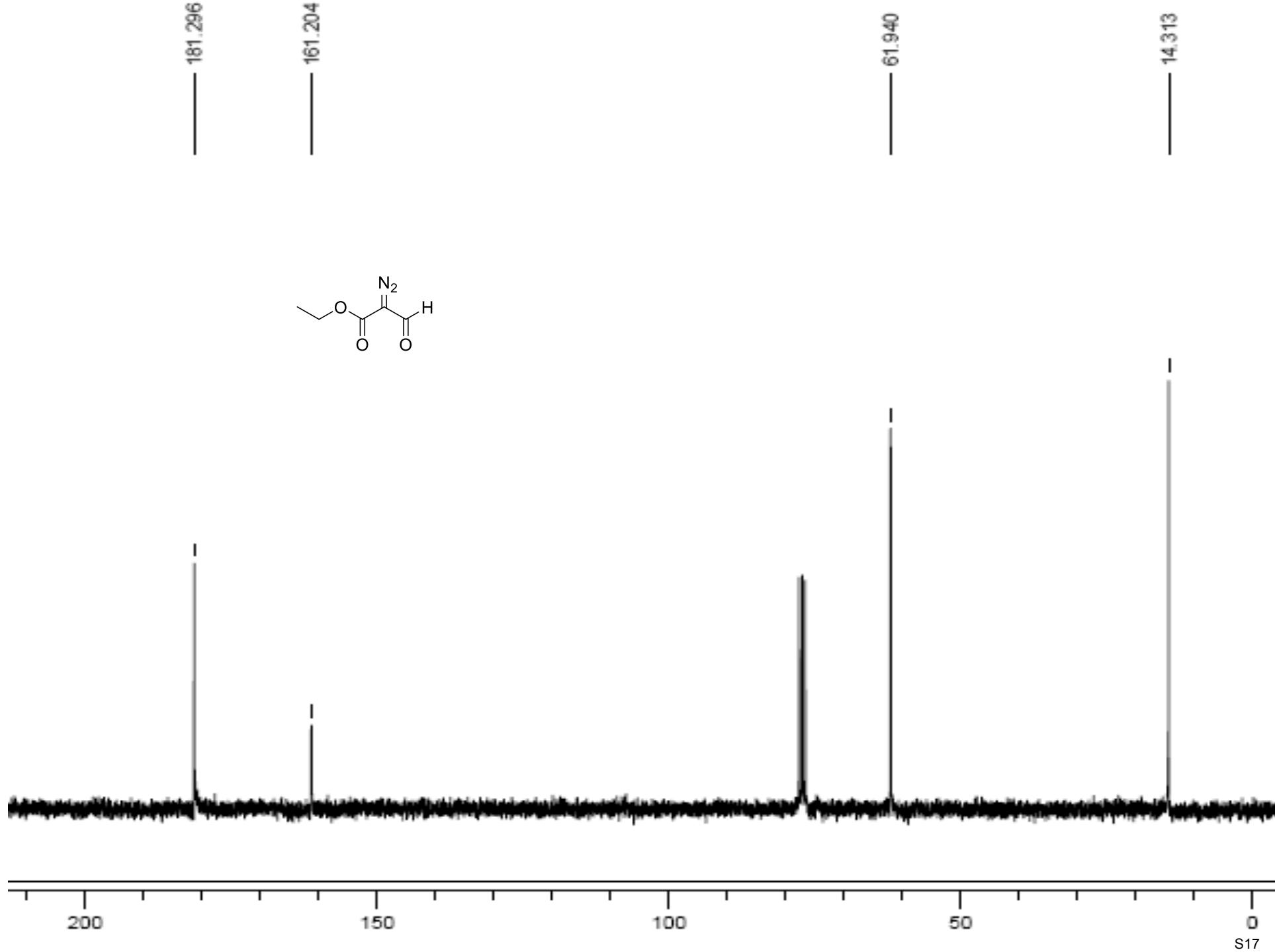
[6] Sheldrick, G.M. (1990) *Acta Cryst. A* **46**, 467-473

[7] Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112-122.

VII. References

- (1) Stojanov.Fm; Arnold, Z. *Collect. Czech. Chem. C.* **1967**, *32*, 2155.
- (2) Gao, L. Z.; Hwang, G. S.; Ryu, D. H. *J. Am. Chem. Soc.* **2011**, *133*, 20708.
- (3) Ohira, S. *Syn. Comm.* **1989**, *19*, 561.





200

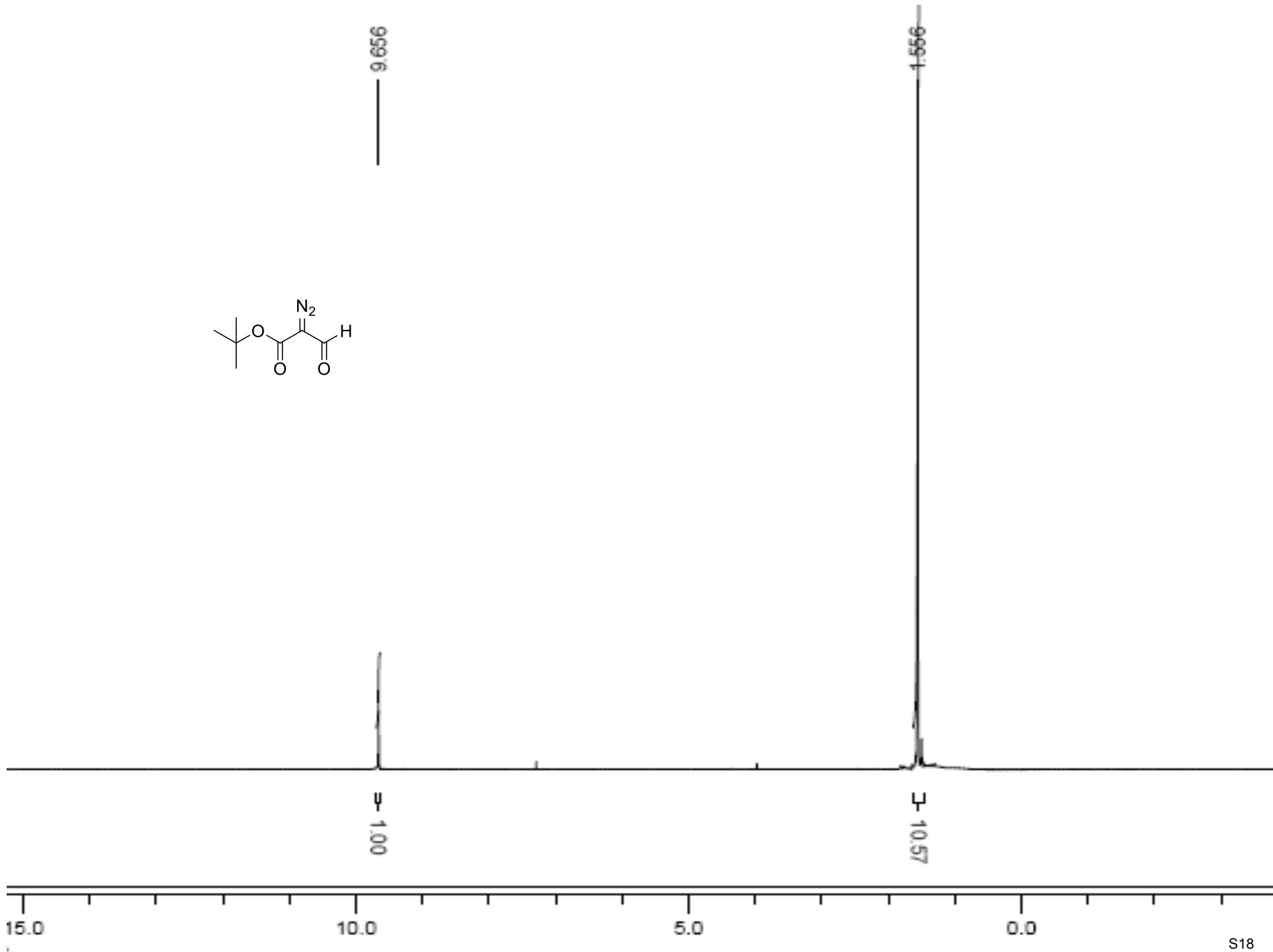
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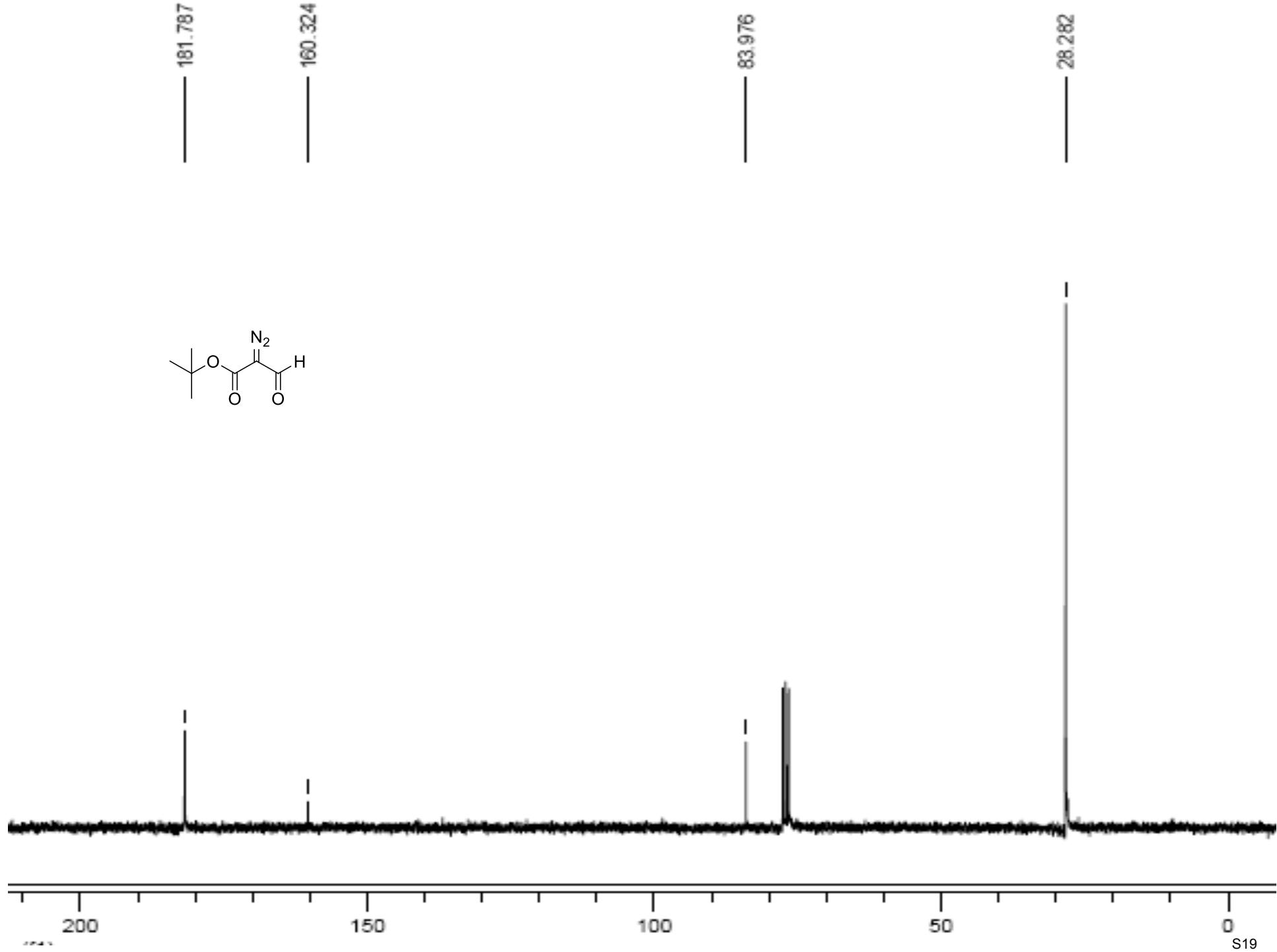
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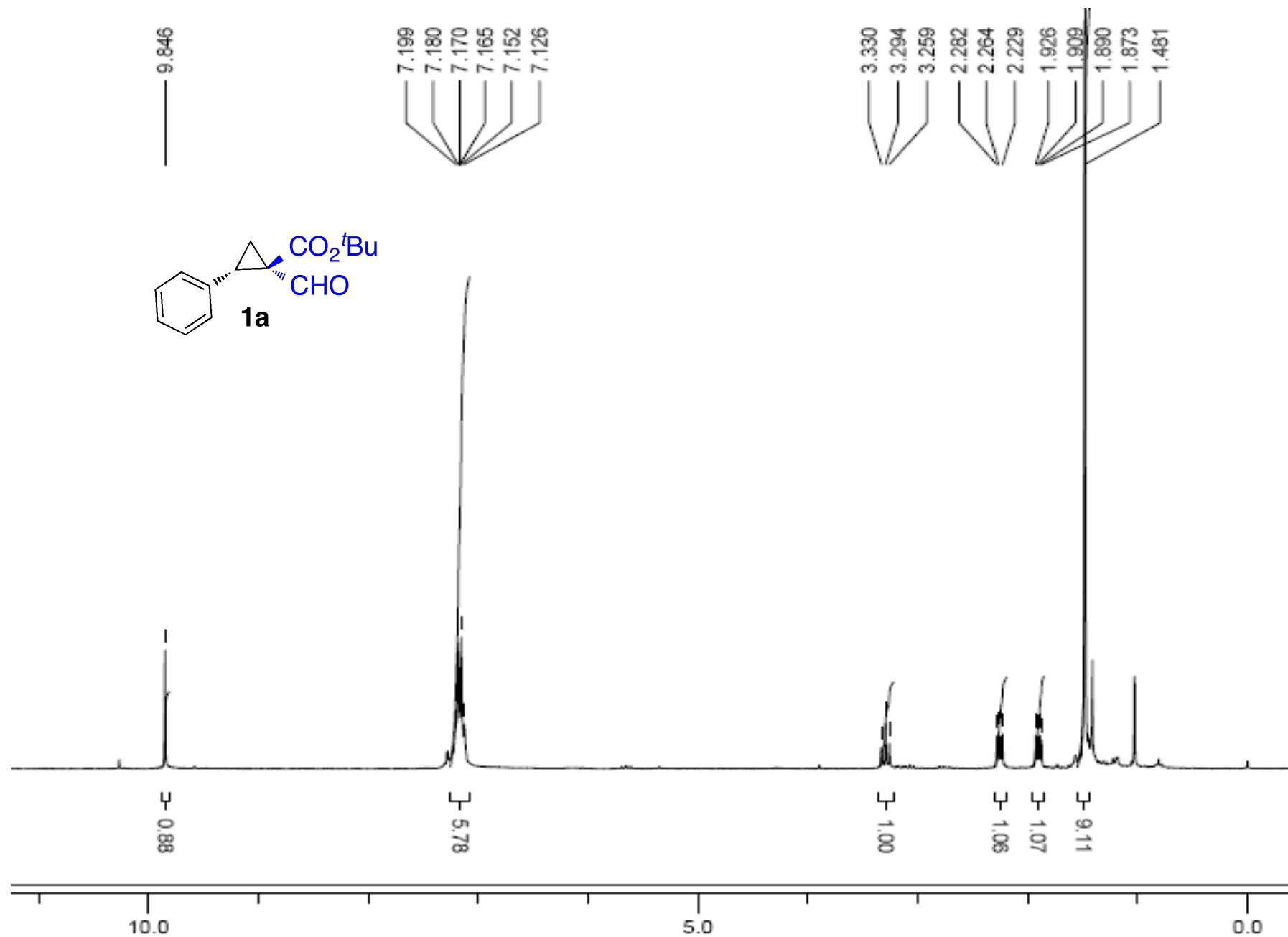
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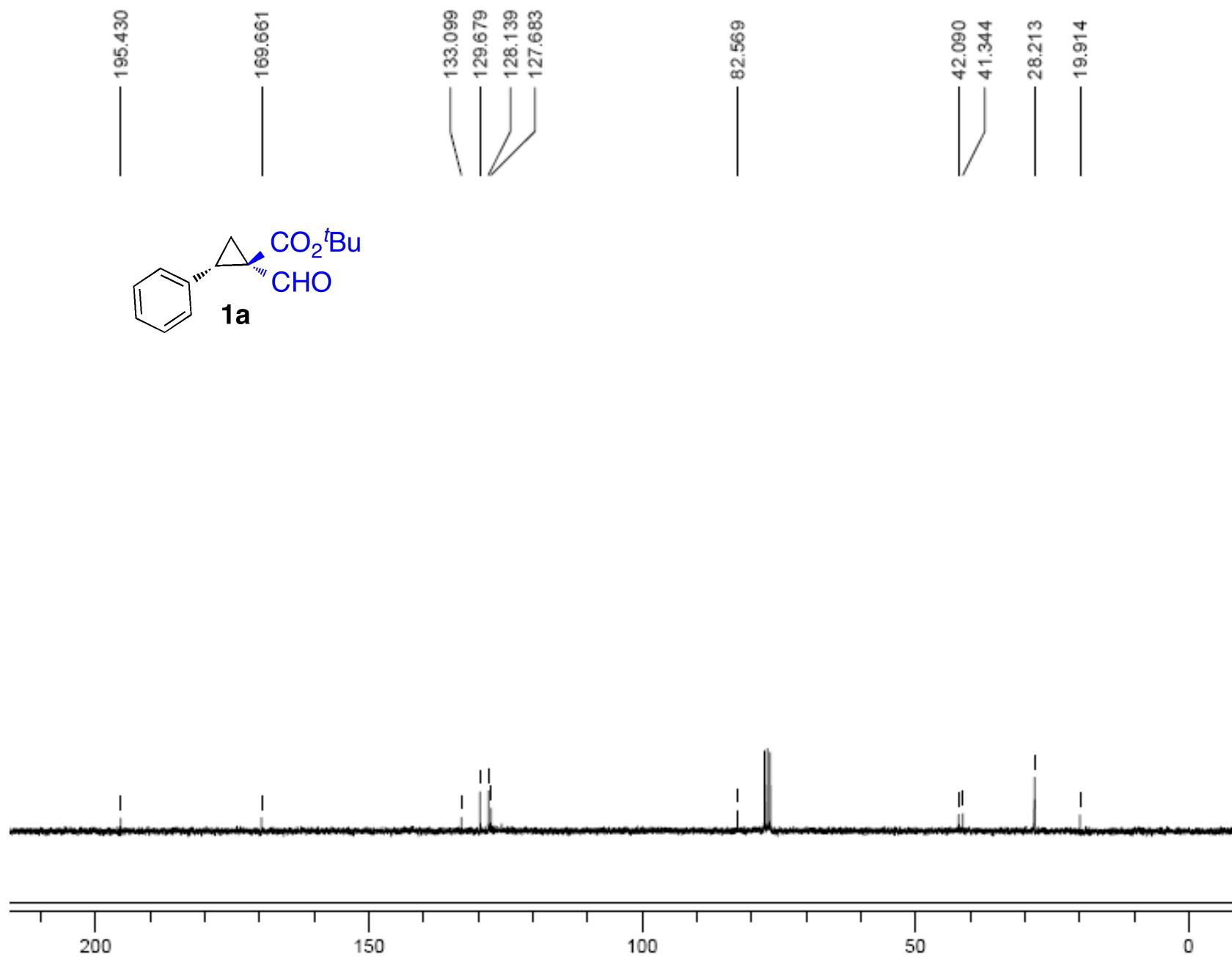
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S17





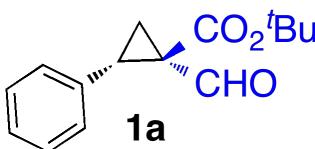
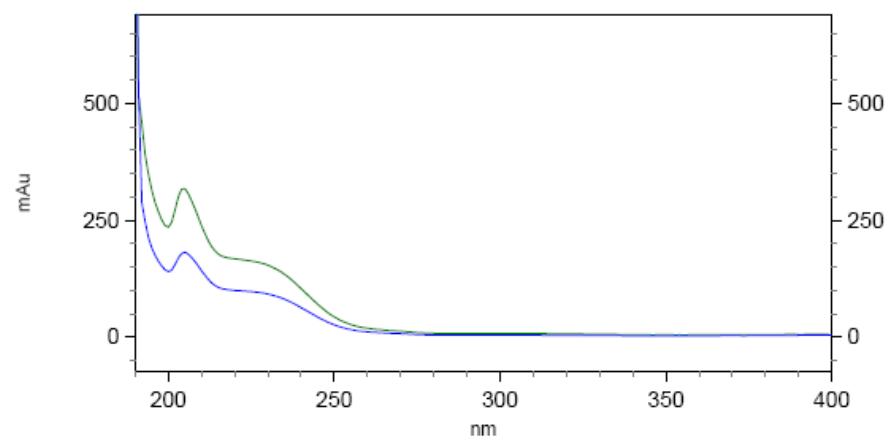
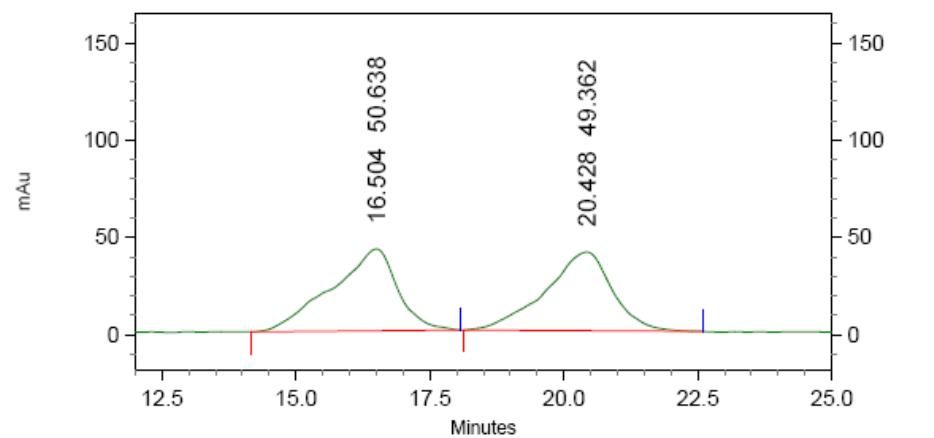




xx-vi-7 OJH 3%@0.8 ml

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4: 231 nm, 4 nm

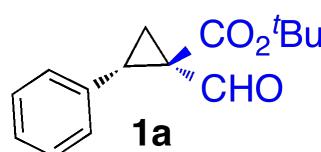
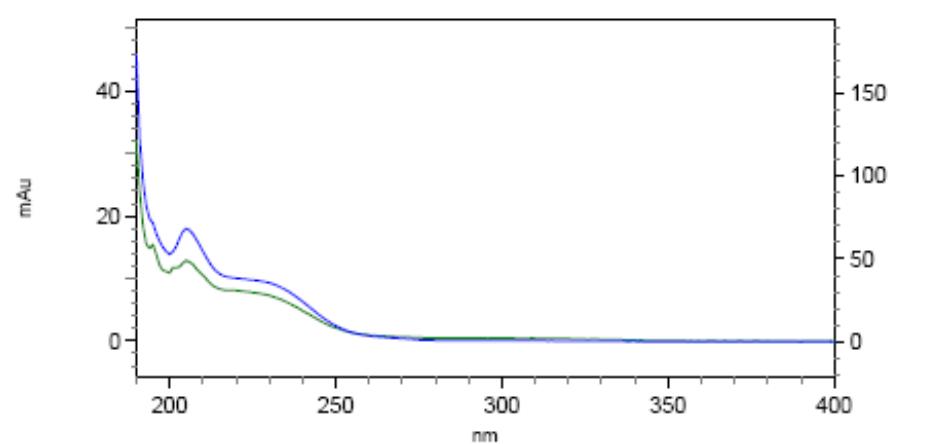
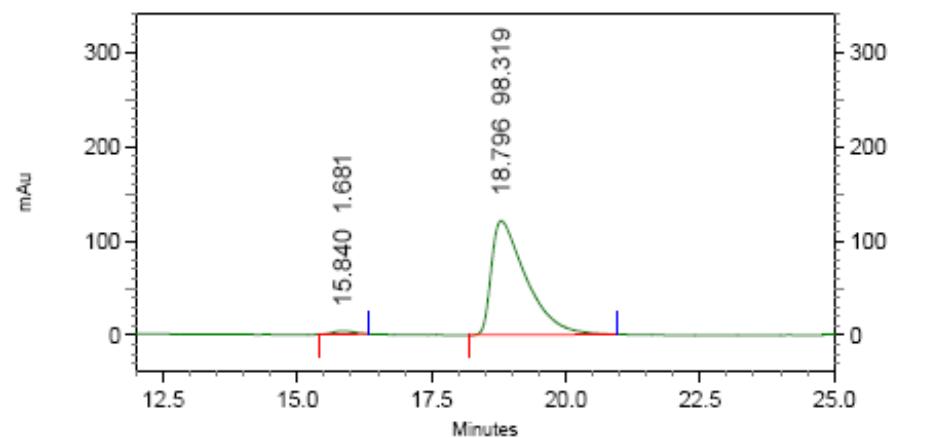
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2		20.428	49.362
Totals			100.000

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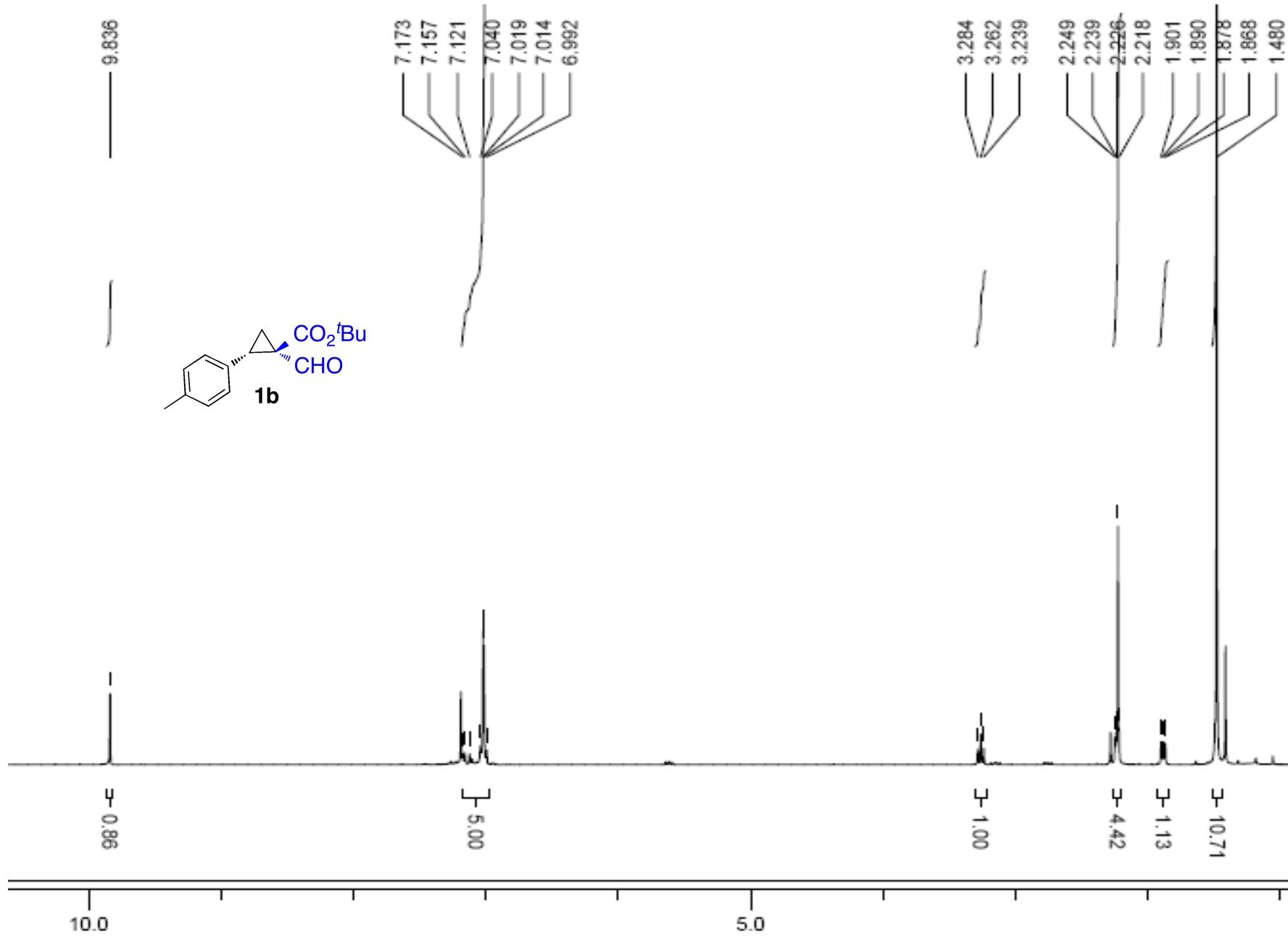
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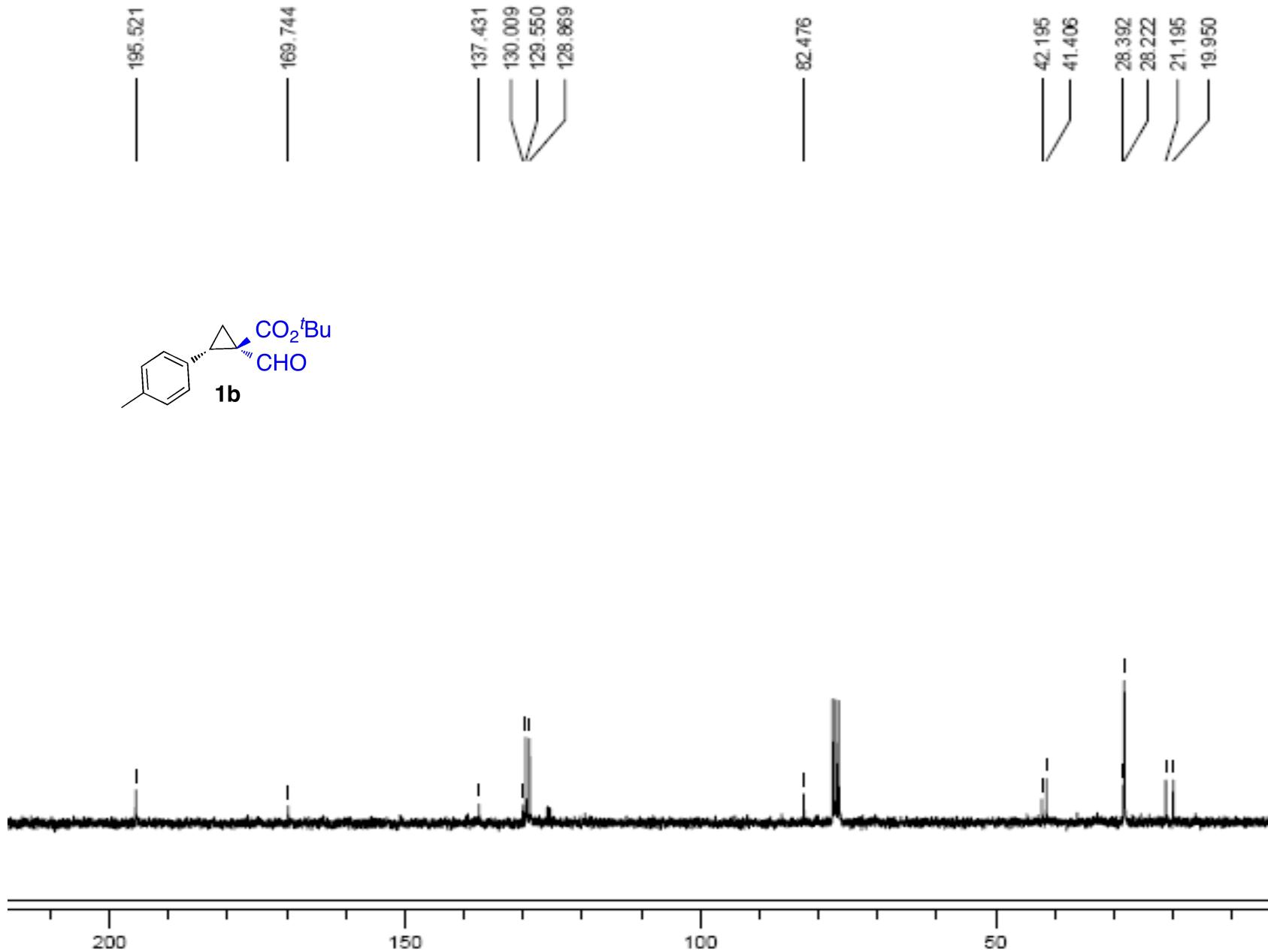


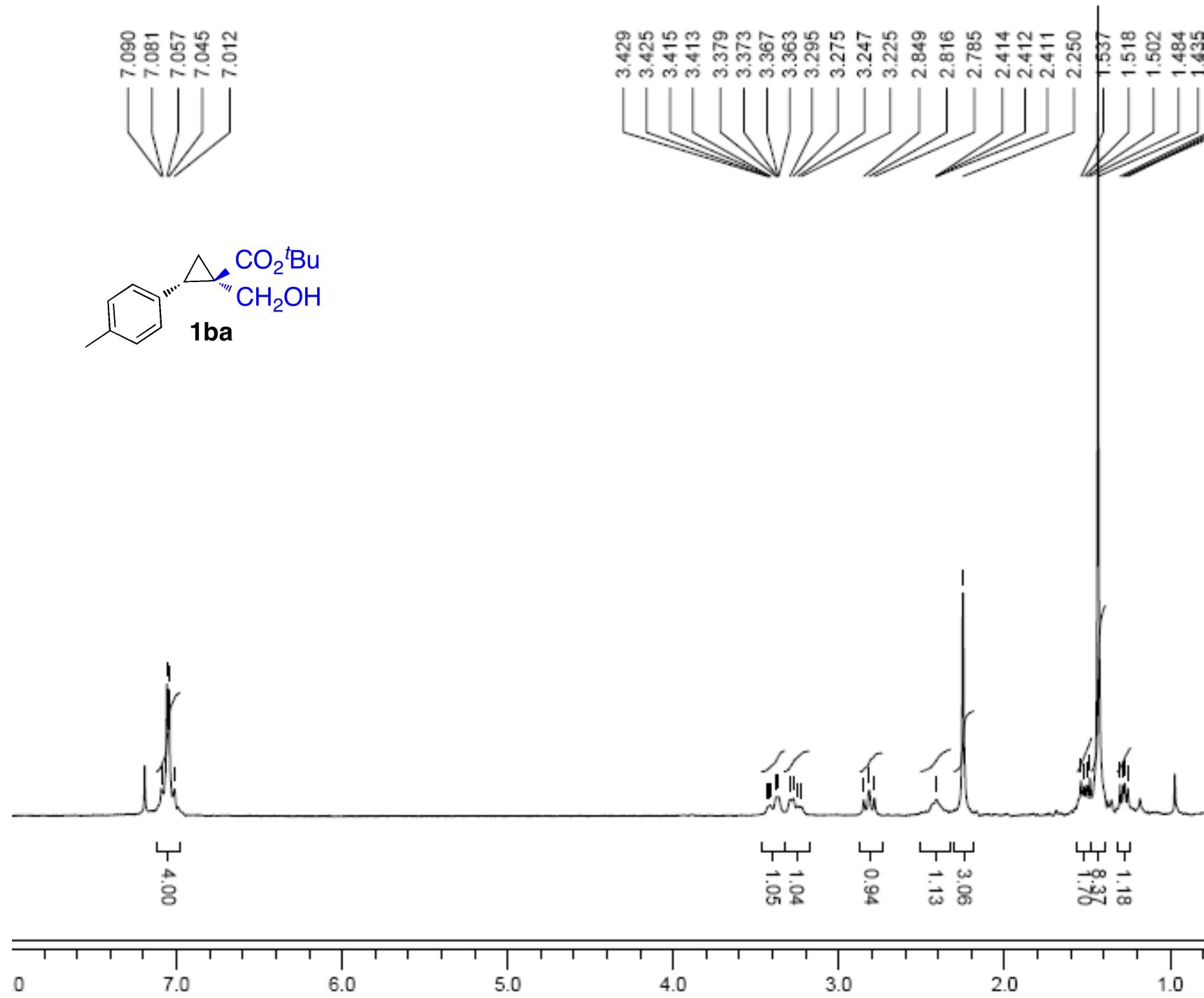
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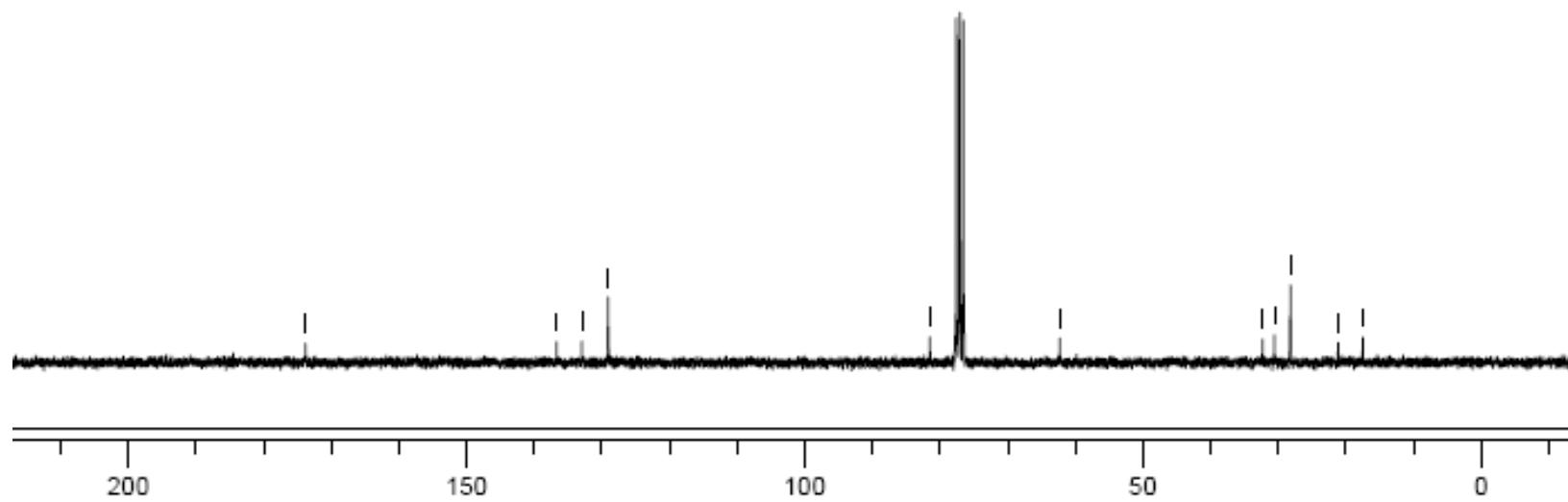
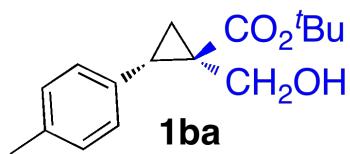
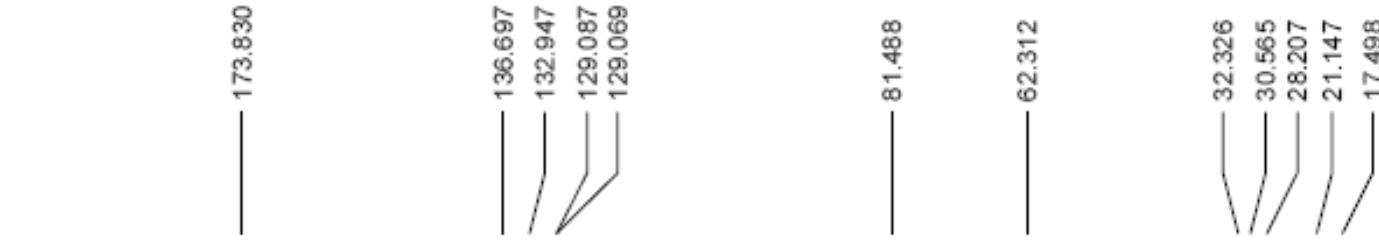
Results

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Totals			100.000





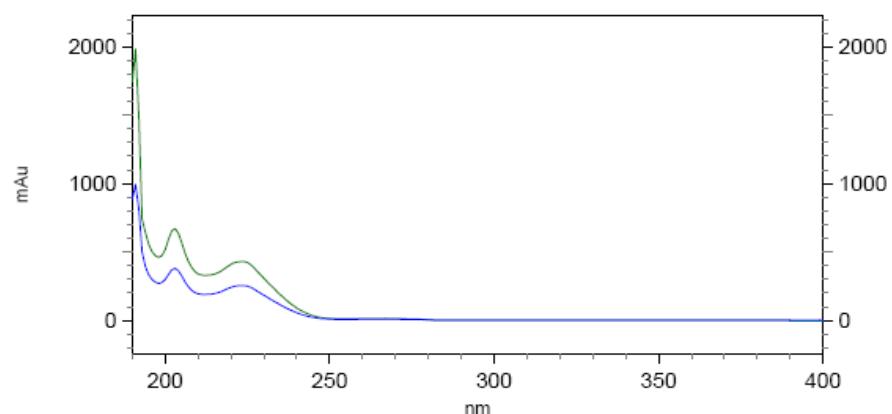
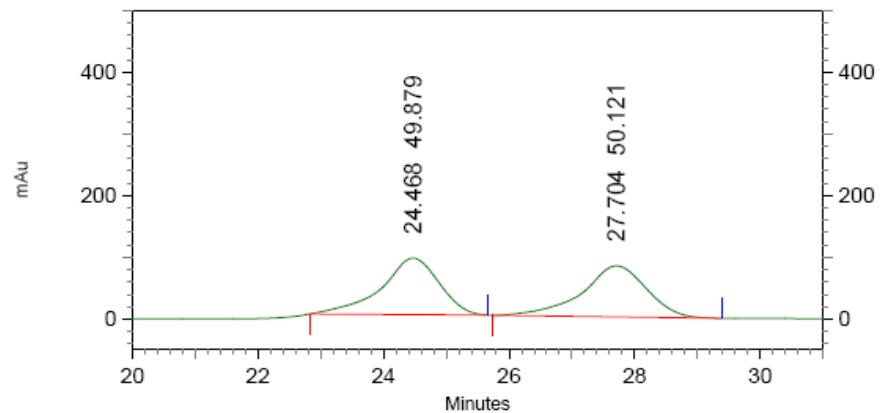




xx-vi-112 whelk 1%@0.8 ml

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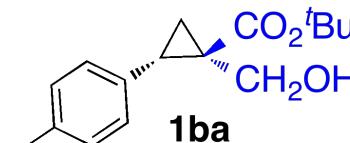
C:\EZStart\Projects\Default\Data\xx-vi-112 whelk 1%@0.8 ml



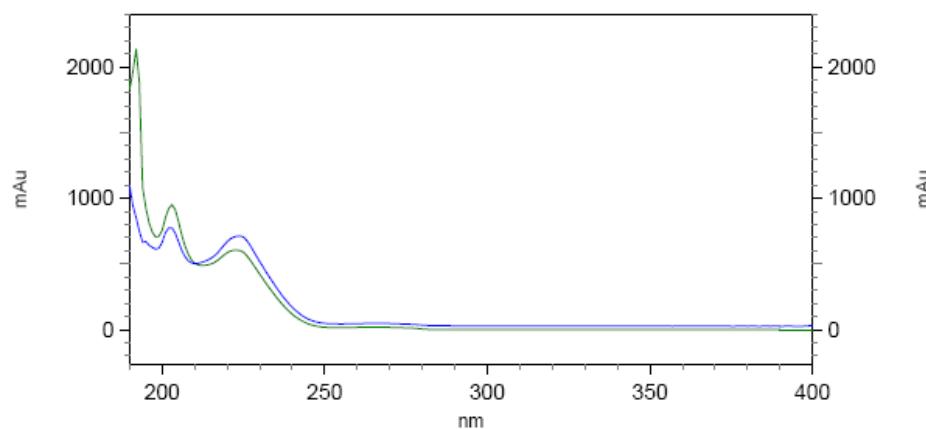
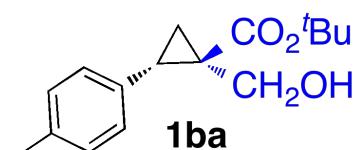
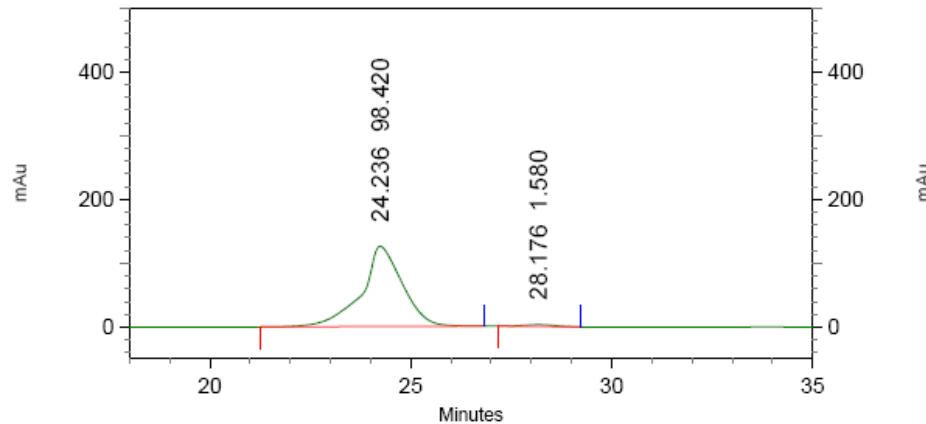
8: 242 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		24.468	49.879
2		27.704	50.121
Totals			100.000



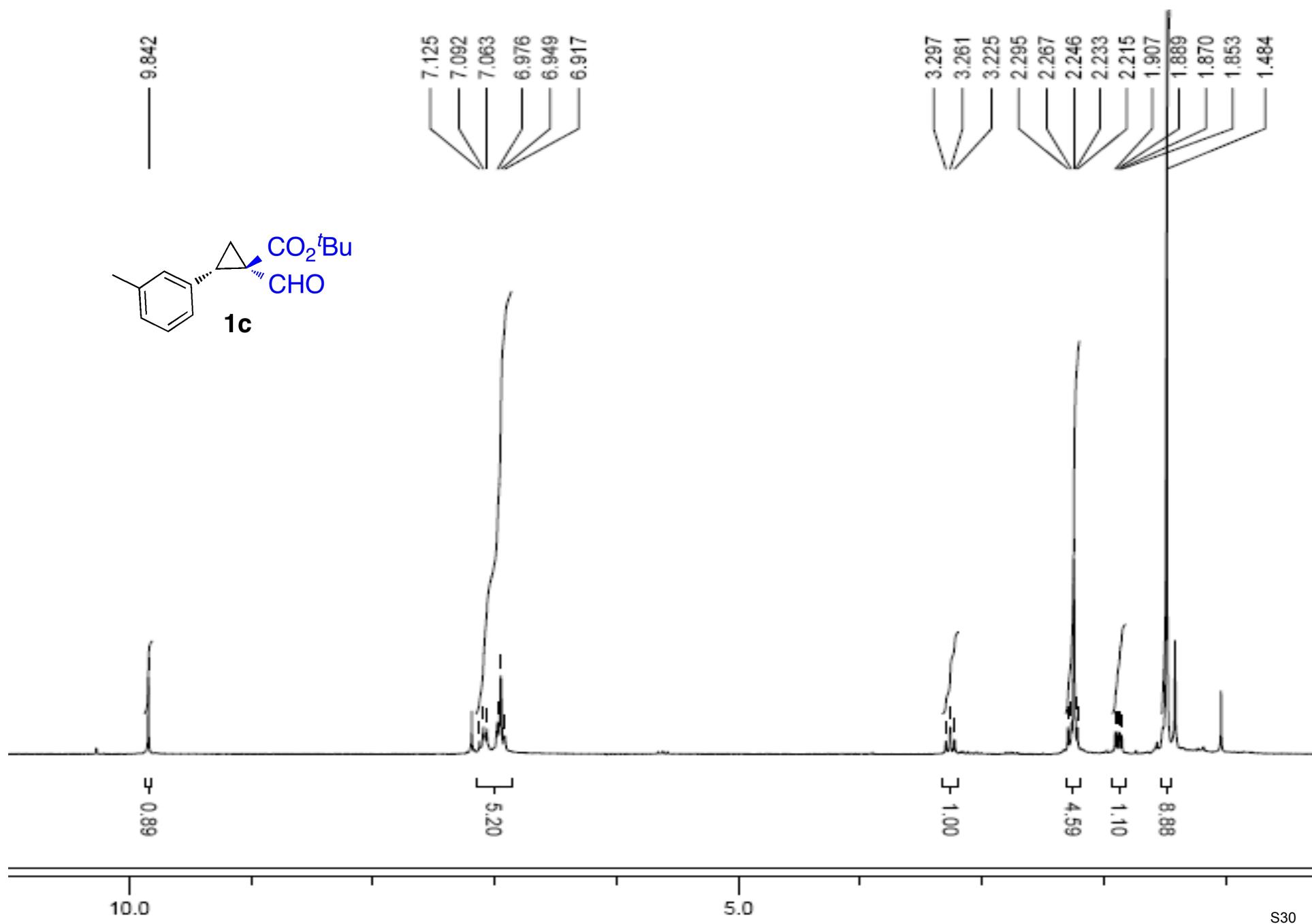
xx-vi-113 whelk 1%@0.8 ml
C:\EZStart\Projects\Default\Method\lmj-adh1&.met
C:\EZStart\Projects\Default\Data\xx-vi-113 whelk 1%@0.8 ml

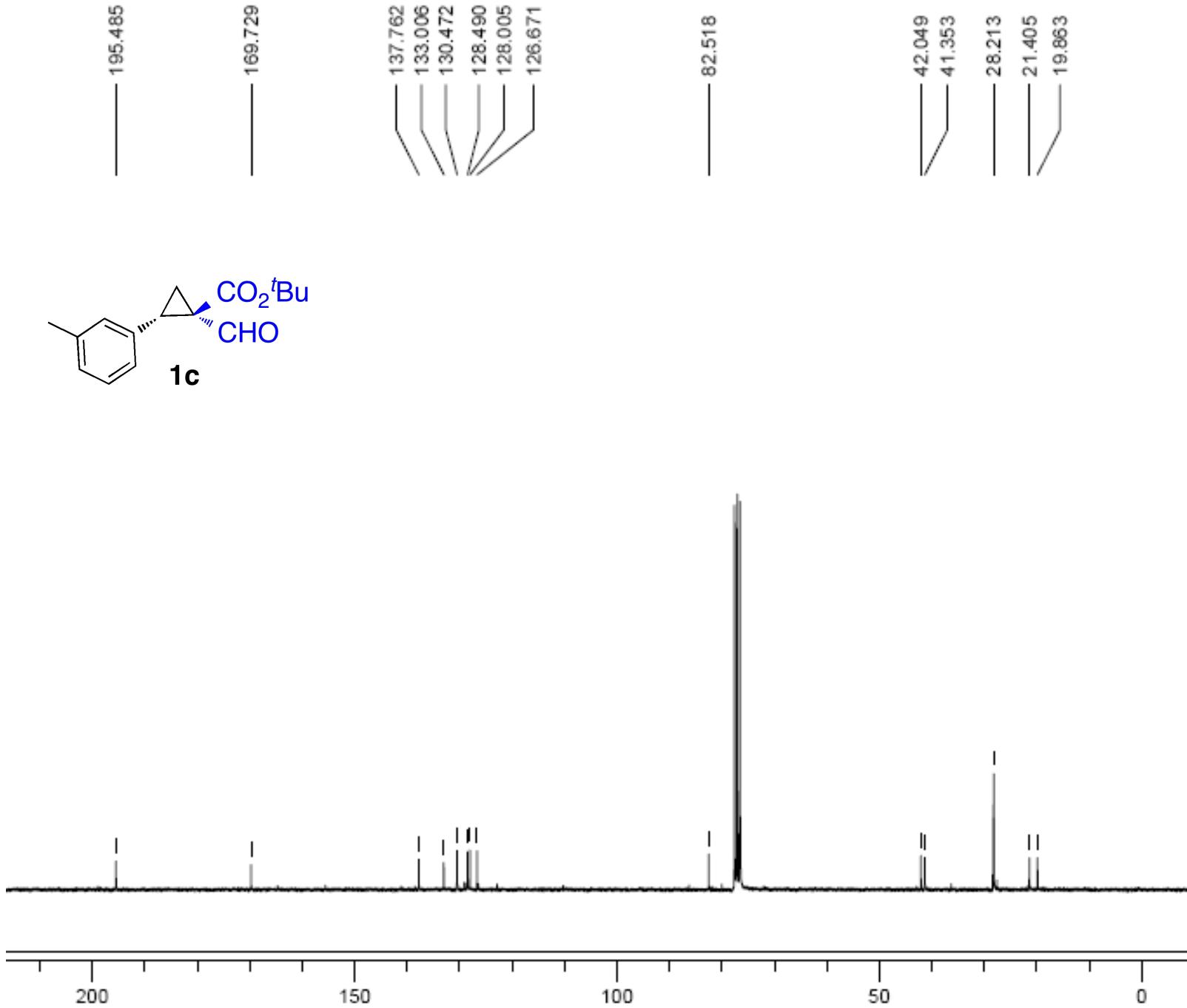


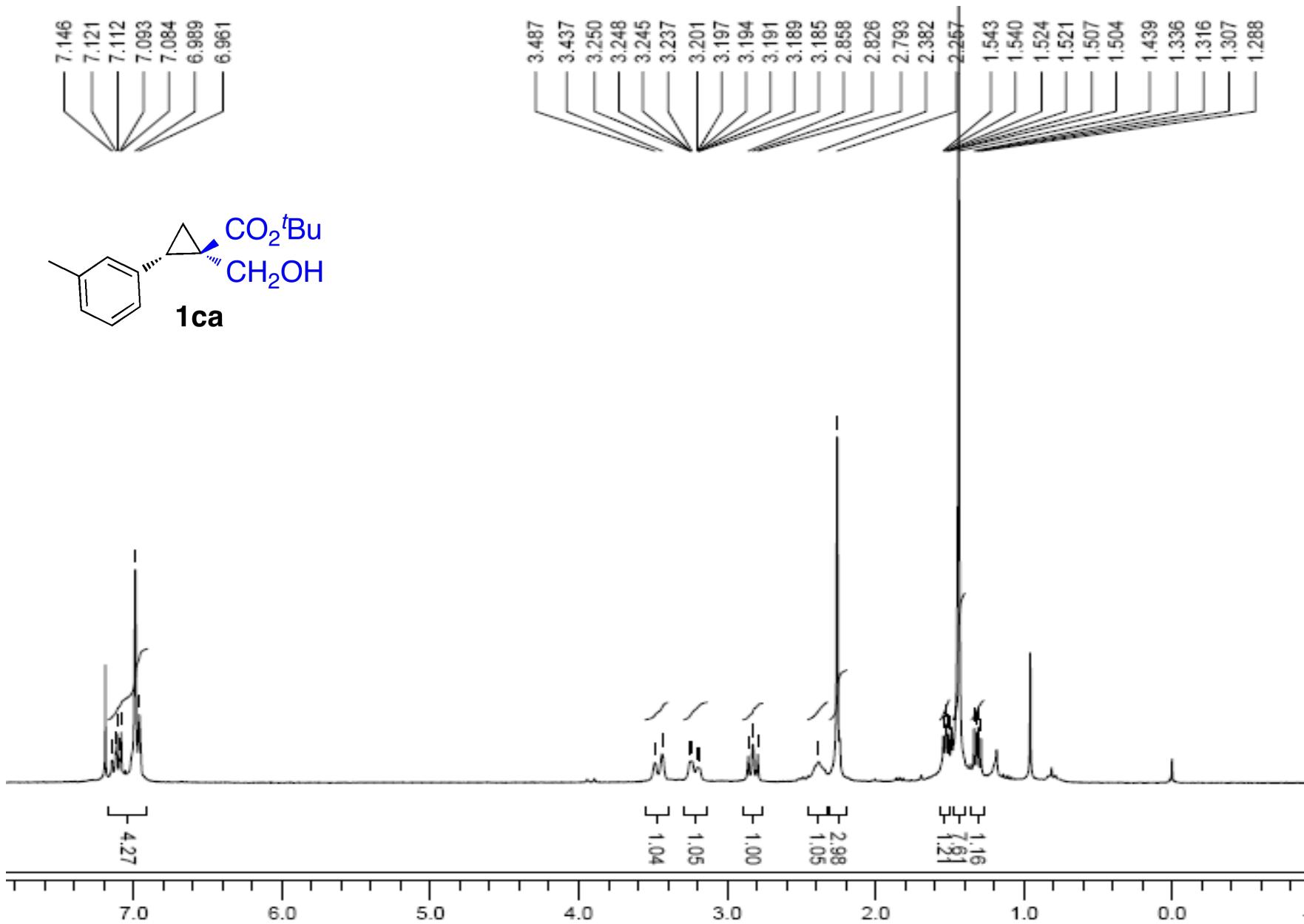
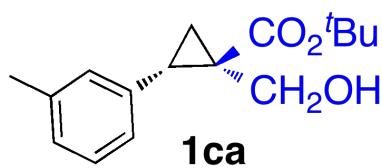
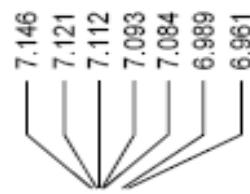
8: 232 nm, 4 nm

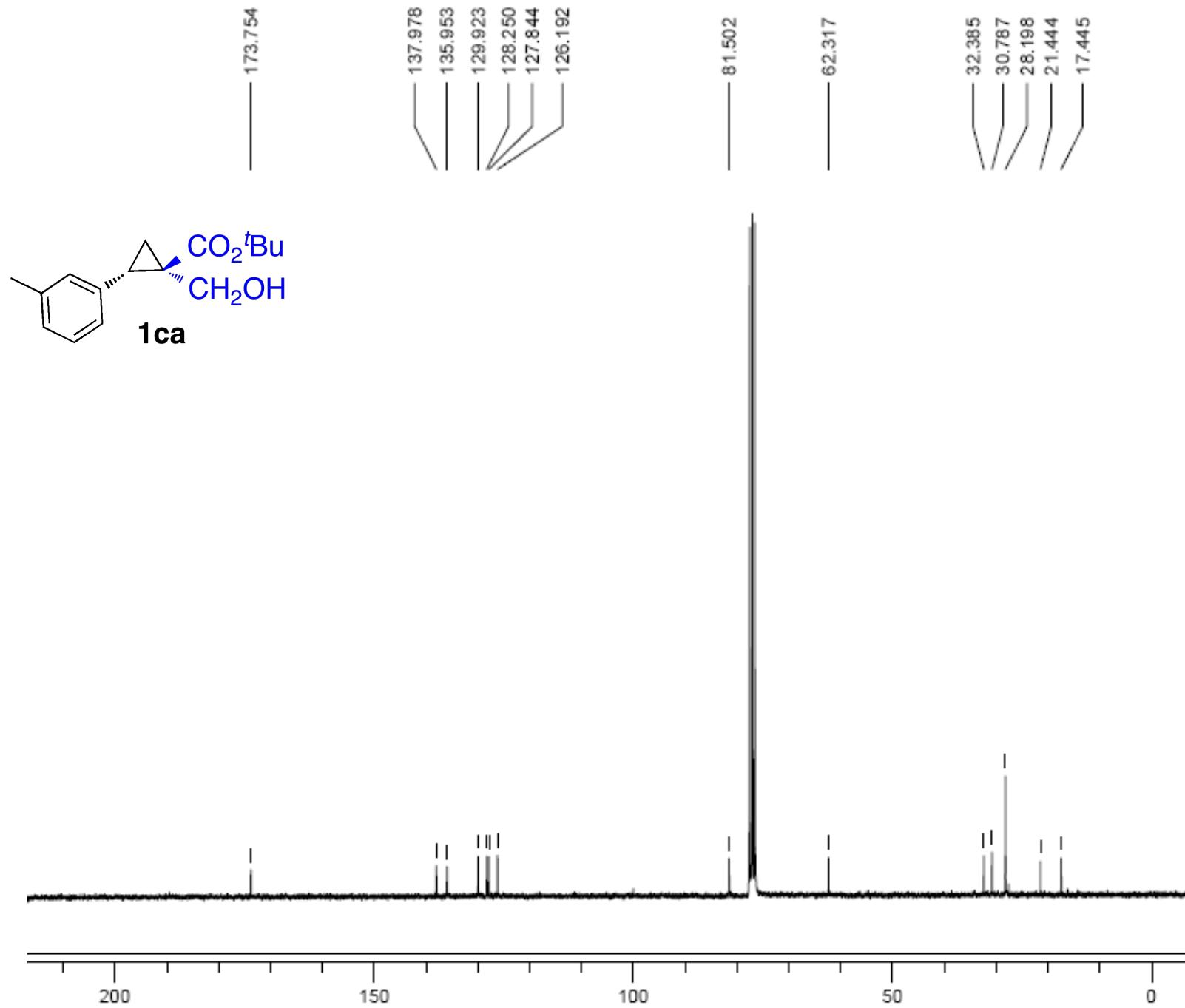
Results

Pk # Name	Retention Time	Area Percent
1	24.236	98.420
2	28.176	1.580
Totals		100.000





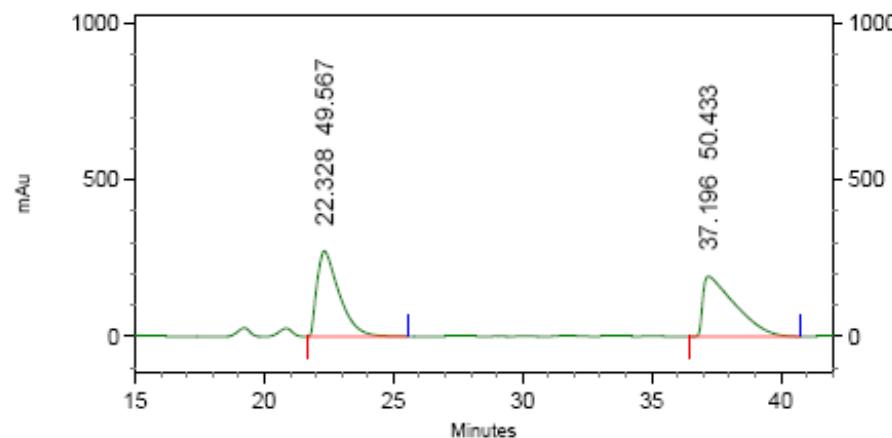




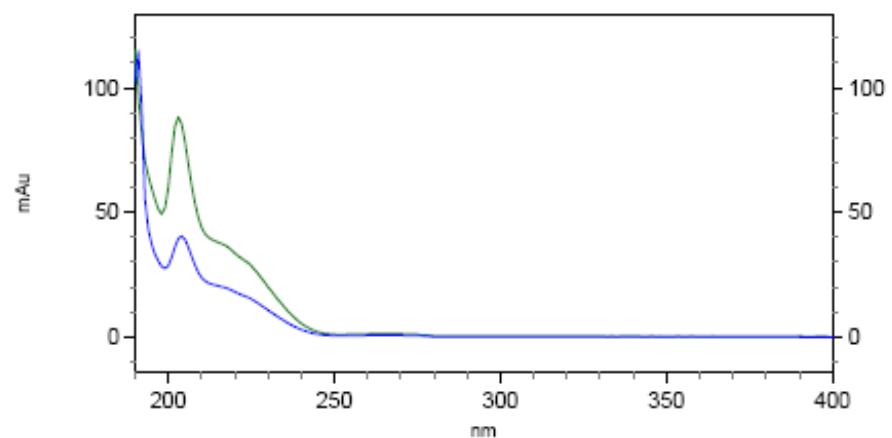
xx-vii-293 ADH 1%@0.8 ml

C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 1%Whelk.met

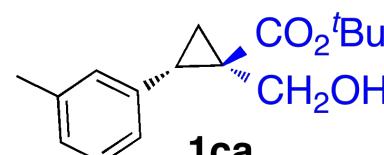
C:\EZStart\Projects\Default\Data\xx-vii-293 ADH 1%@0.8 ml



mAU



mAU



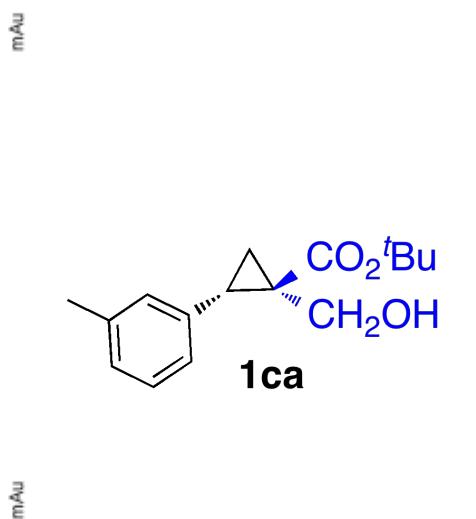
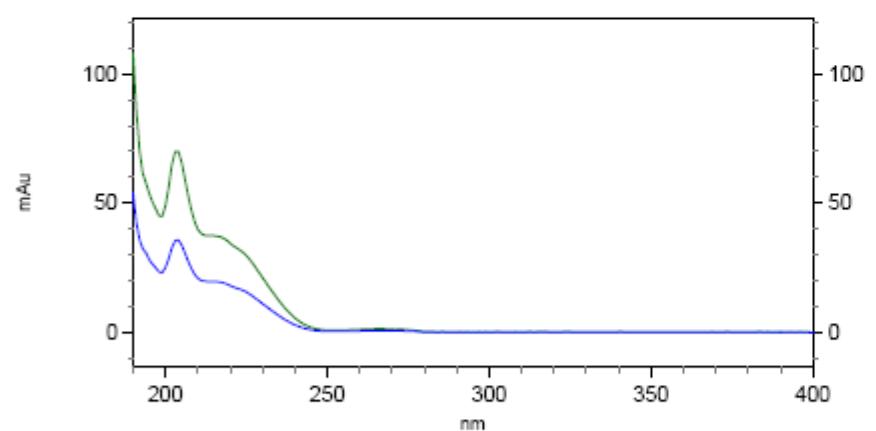
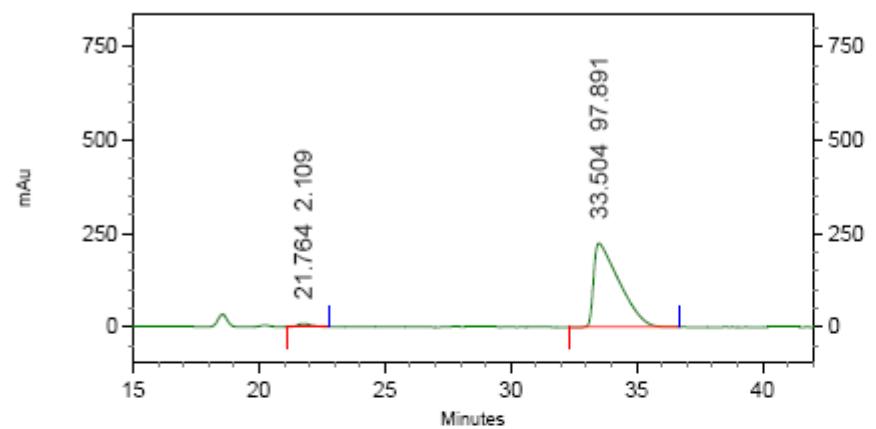
1ca

2: 225 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		22.328	49.567
2		37.196	50.433
Totals			100.000

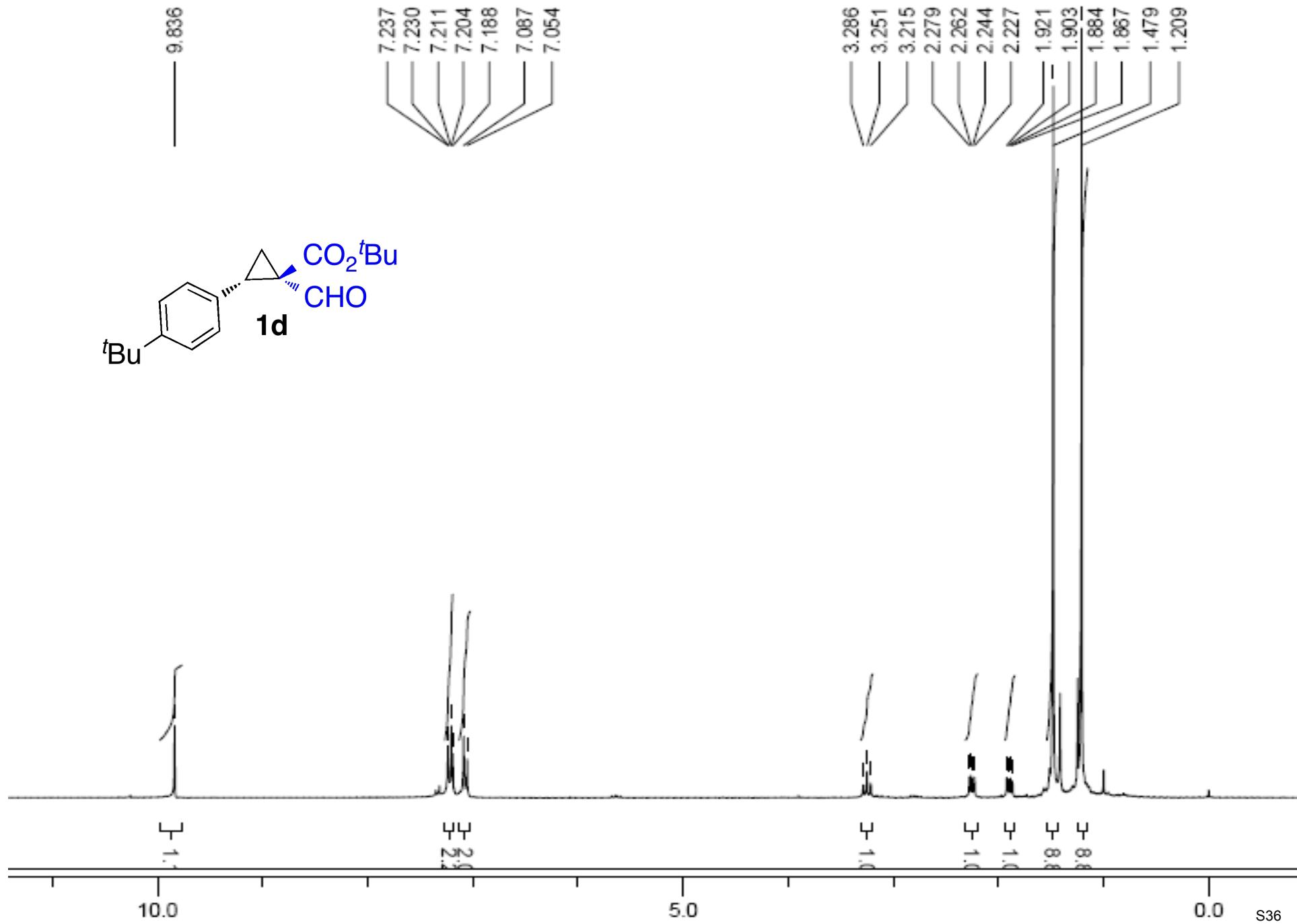
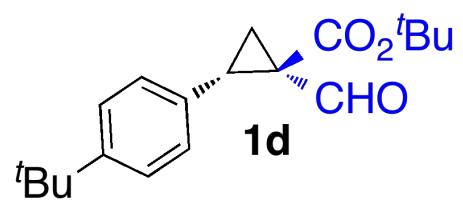
xx-vi-121 ADH 1%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 1%Whelk.met
C:\EZStart\Projects\Default\Data\xx-vi-122 ADH 1%@0.8 ml

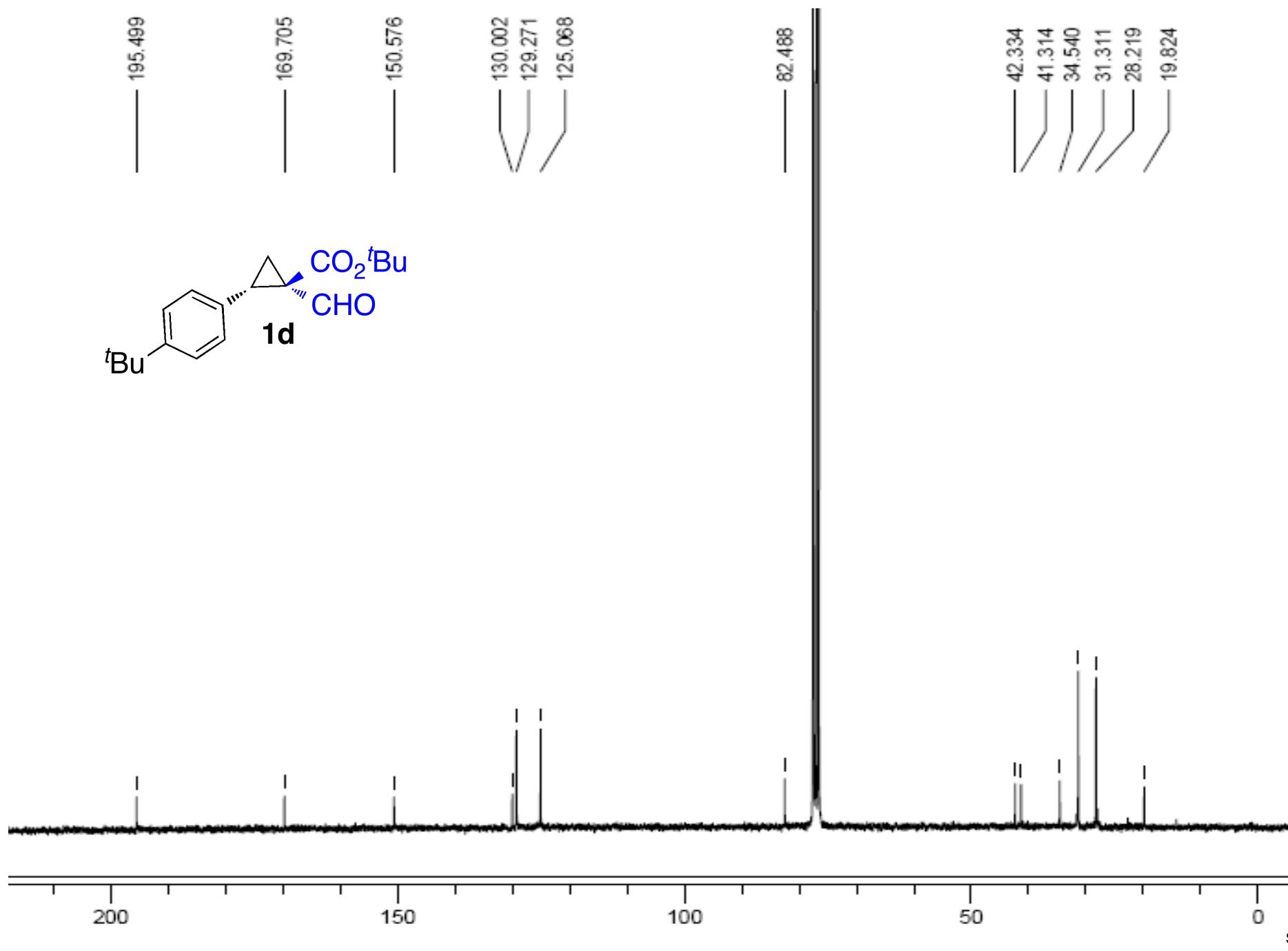


2: 225 nm, 4 nm

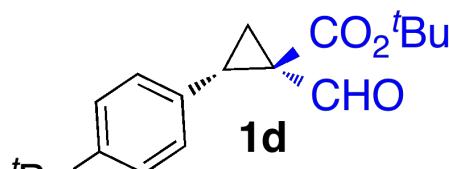
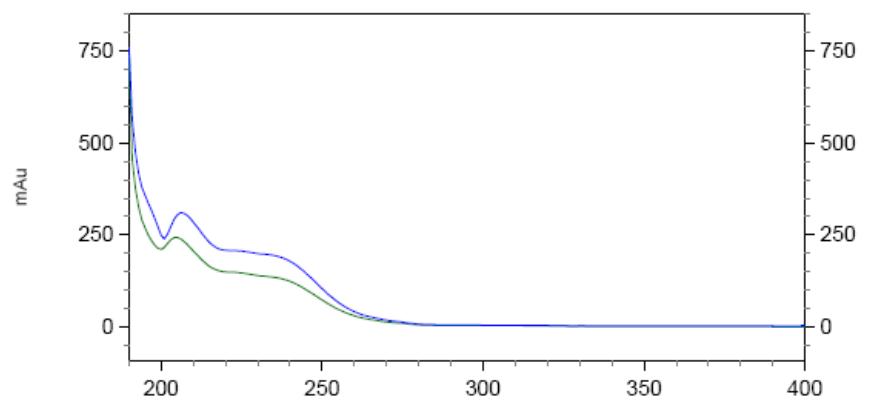
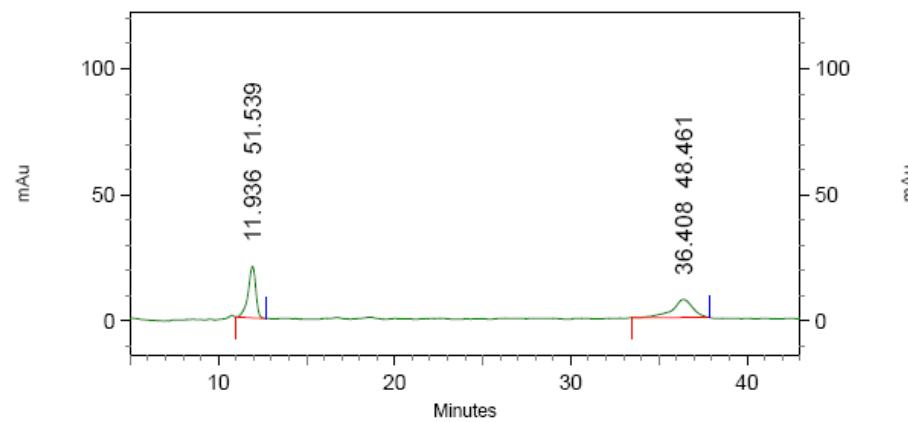
Results

Pk #	Name	Retention Time	Area Percent
1		21.764	2.109
2		33.504	97.891
Totals			100.000





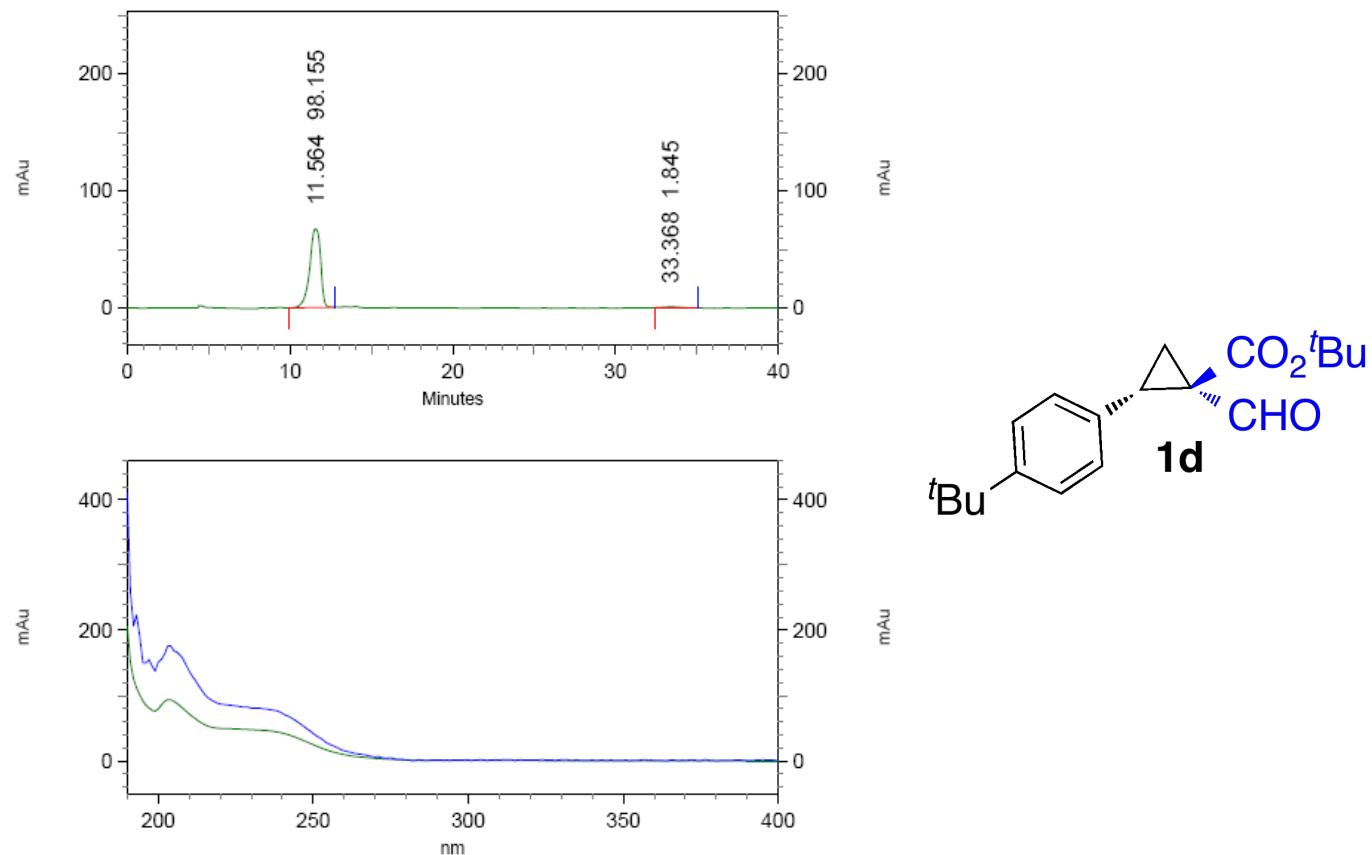
xx-vi-121SD whelk 1%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
E:\HPLC\xx-vi-121SD whelk 1%@0.8 ml



1: 224 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		11.936	51.539
2		36.408	48.461
Totals			100.000

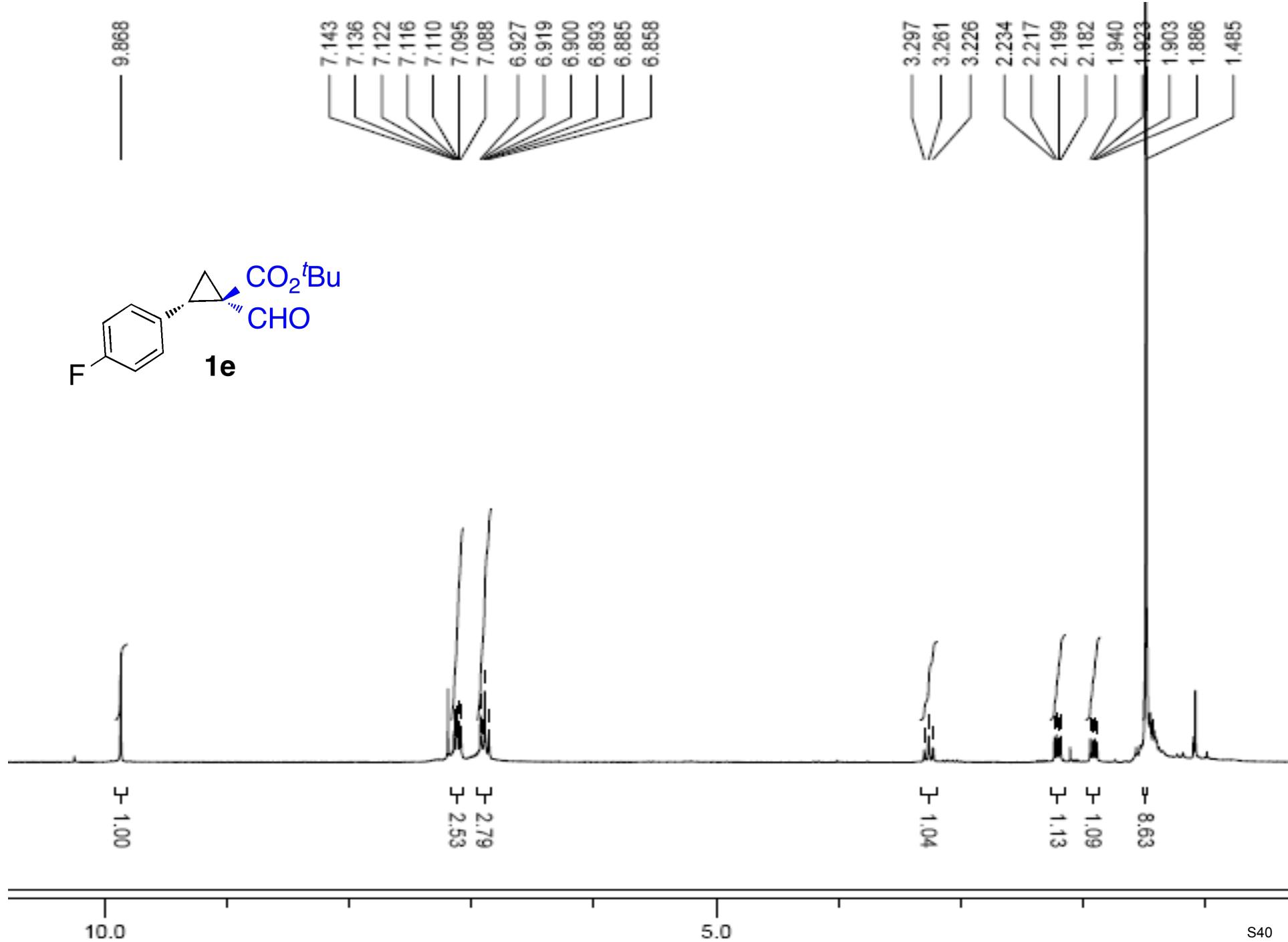
xx-vi-120SD whelk 1%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
C:\EZStart\Projects\Default\Data\xx-vi-120SD whelk 1%@0.8 ml

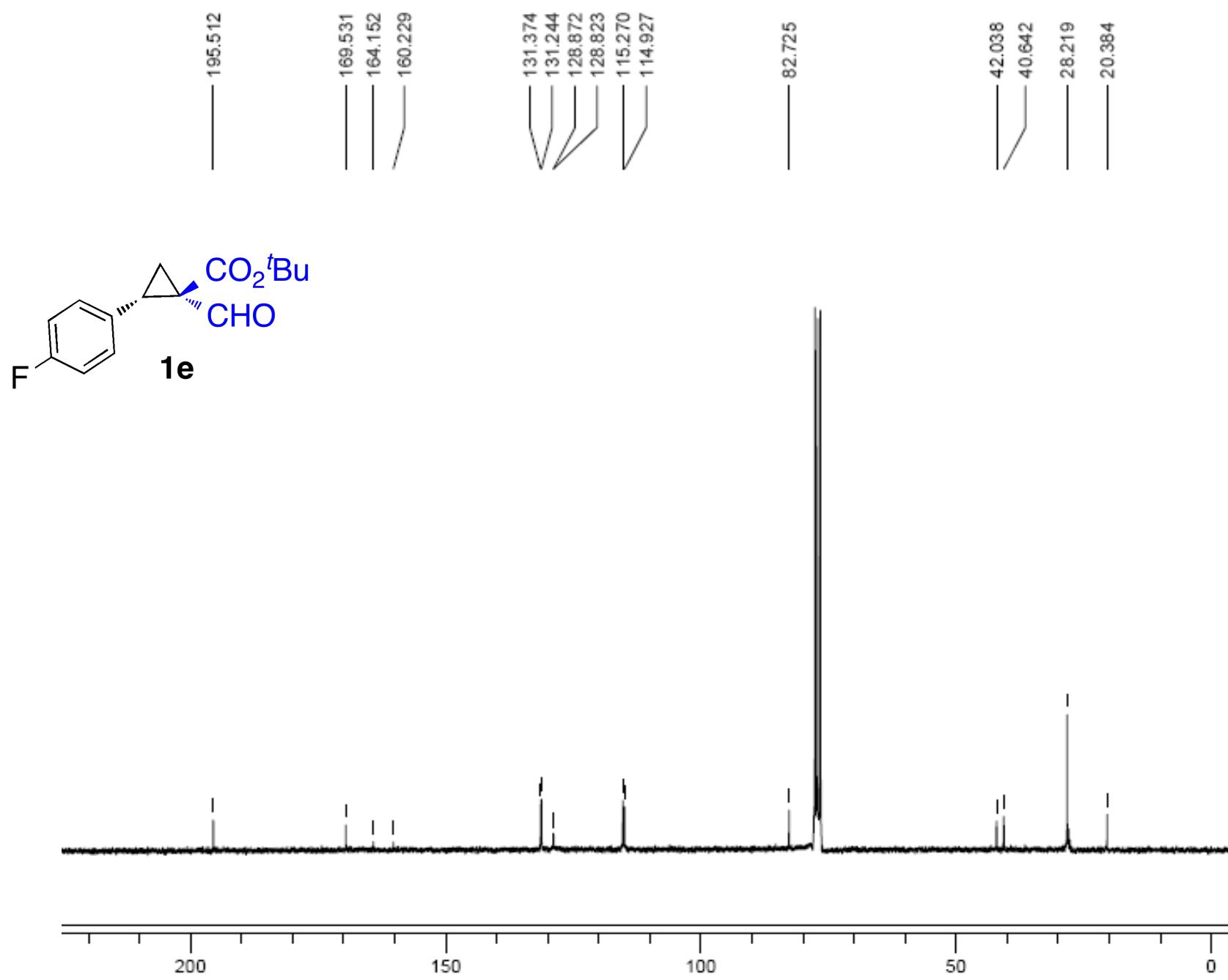


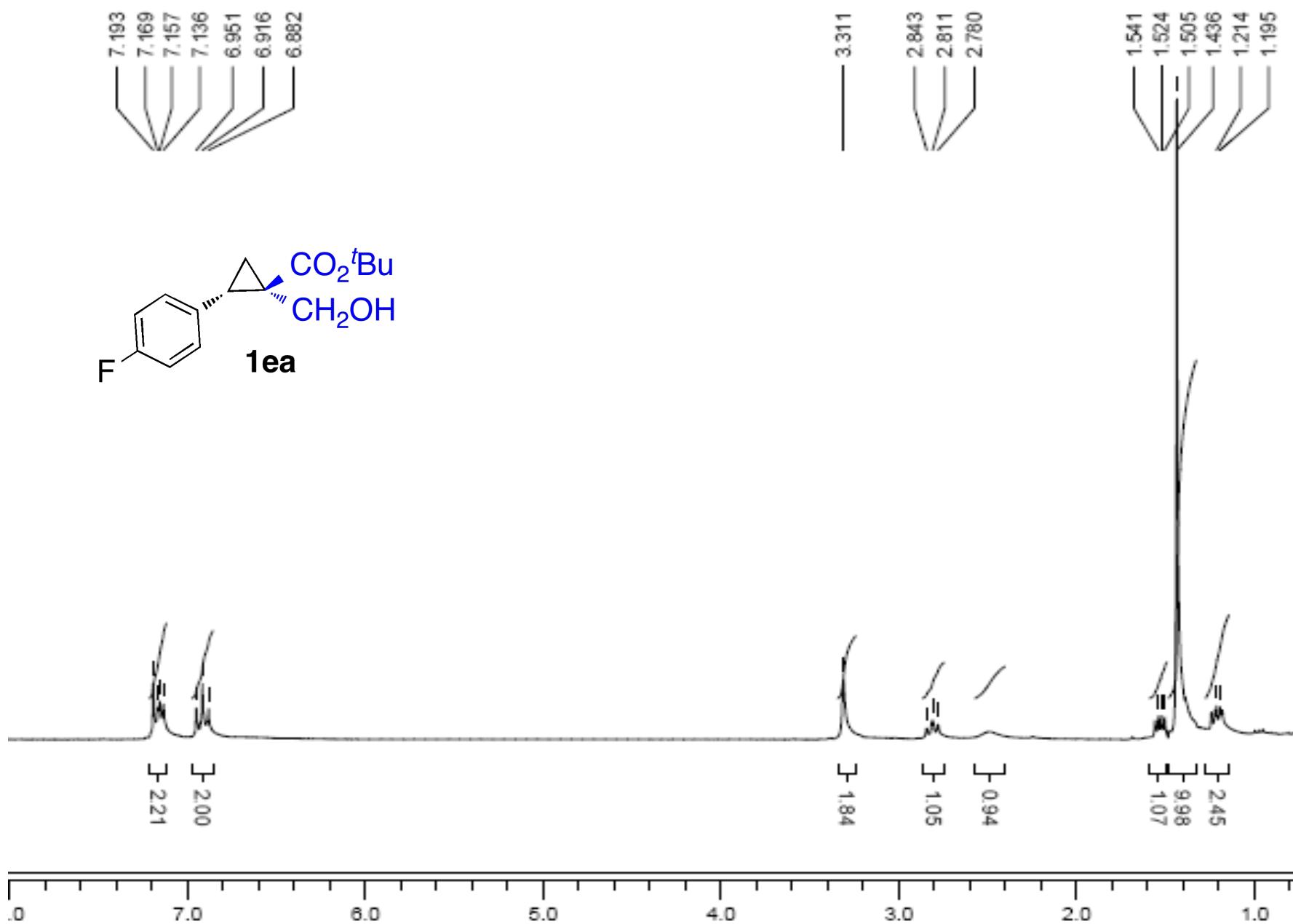
2: 250 nm, 4 nm

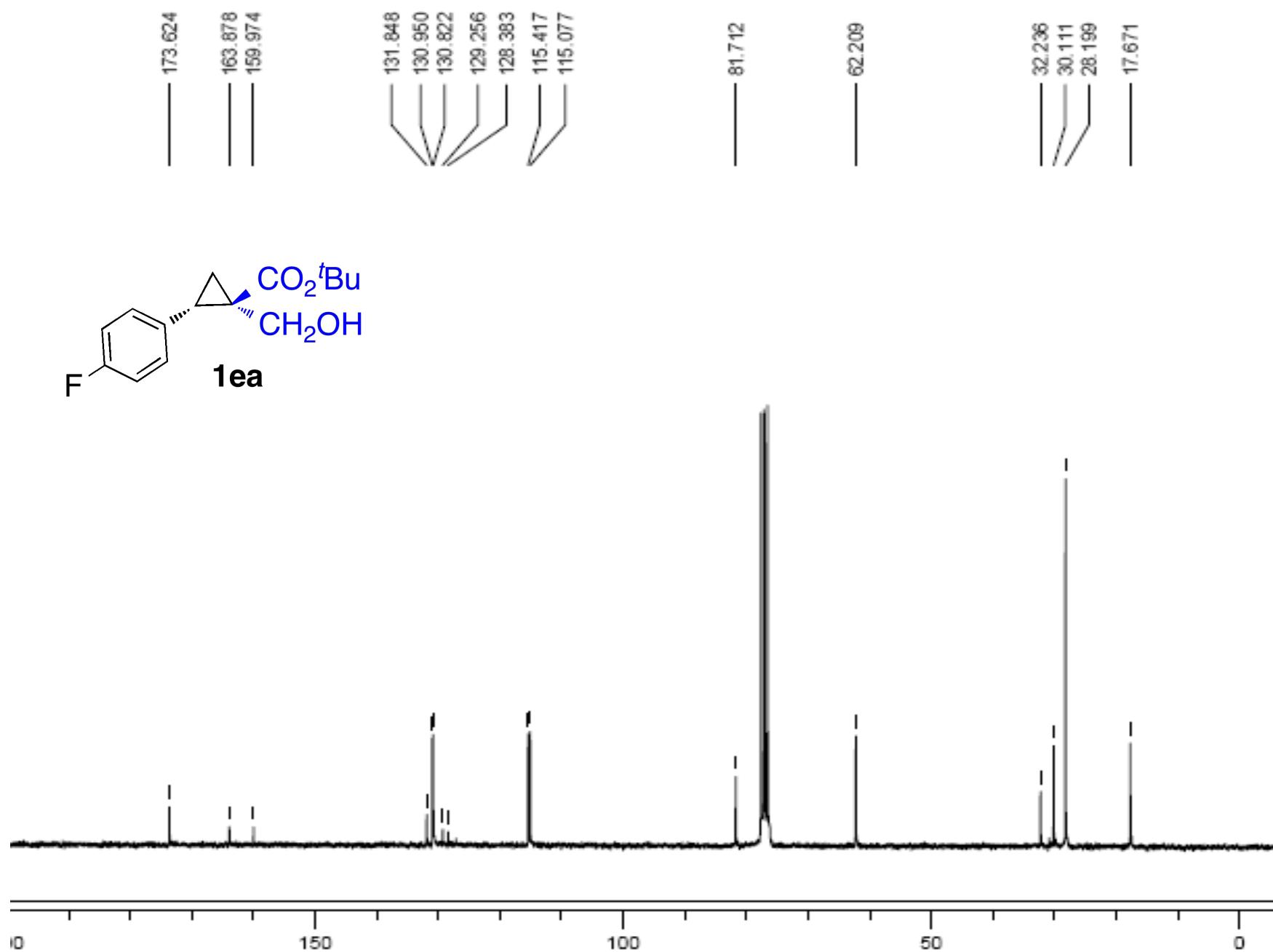
Results

Pk #	Name	Retention Time	Area Percent
1		11.564	98.155
2		33.368	1.845
Totals			100.000

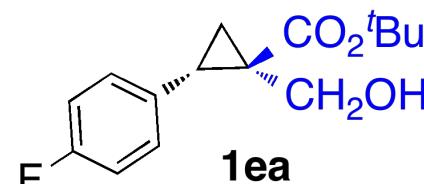
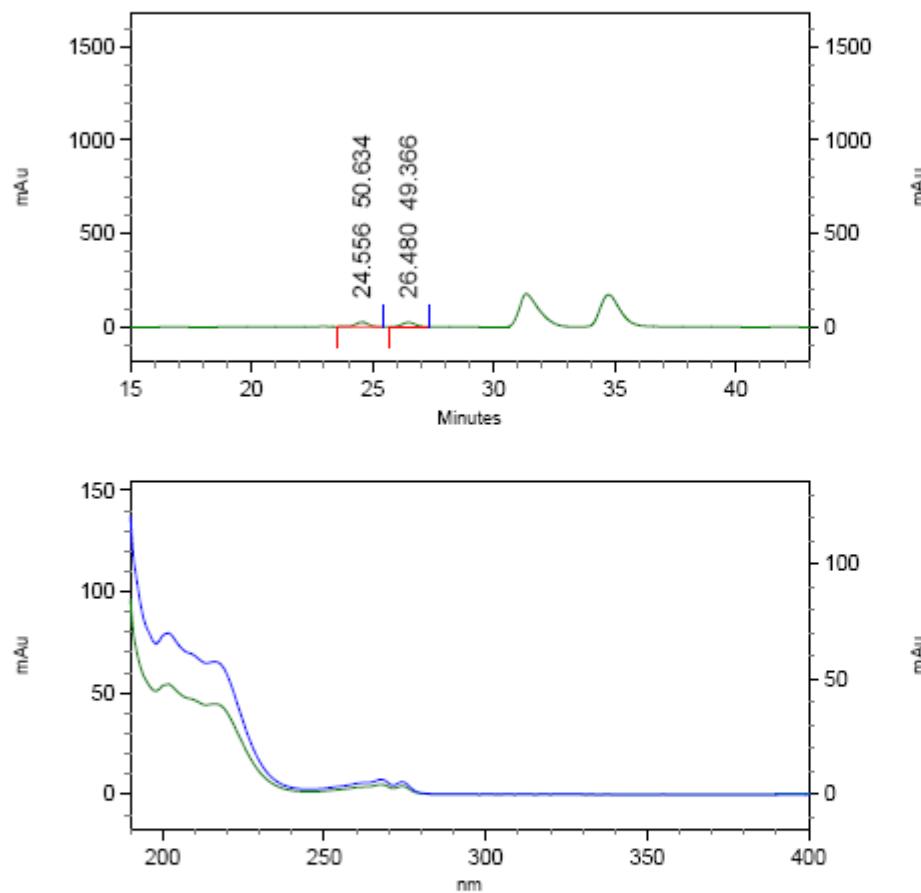








xx-vii-295 ADH 1%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa 4-t-Butylbenzene (OD-H 10-90).met
C:\EZStart\Projects\Default\Data\xx-vii-295 ADH 1%@0.8 ml

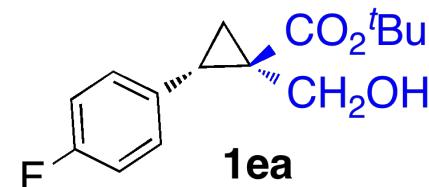
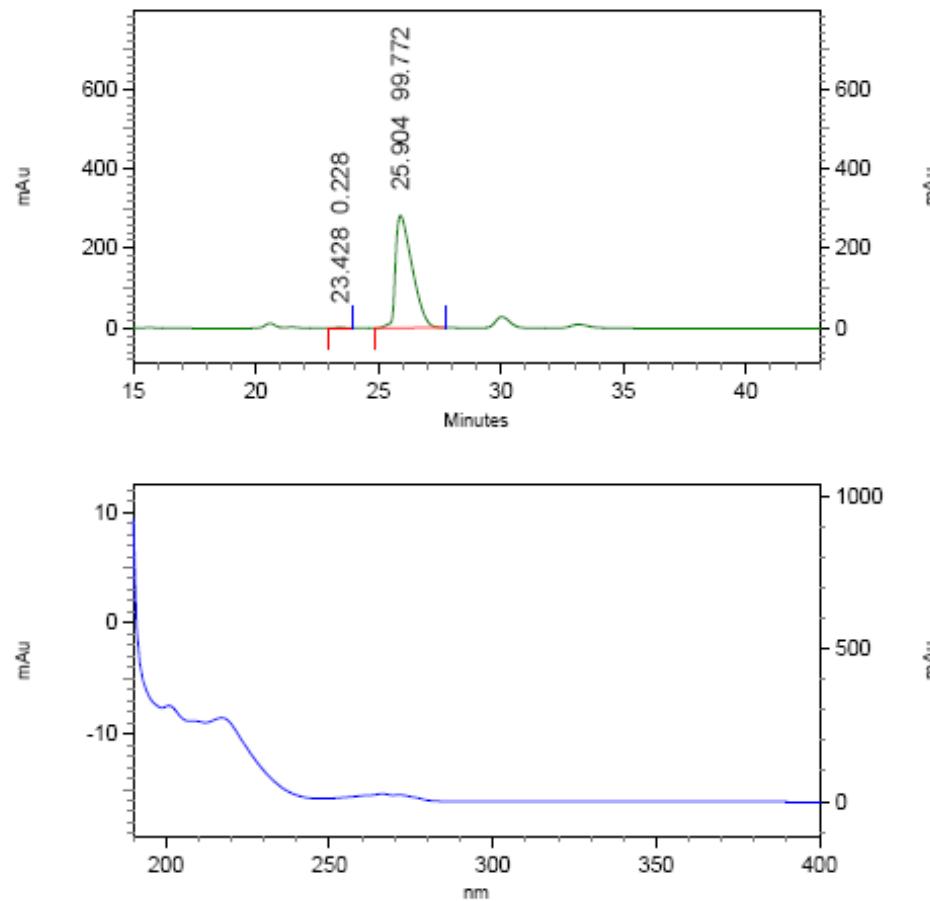


3: 216 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		24.556	50.634
2		26.480	49.366
Totals			100.000

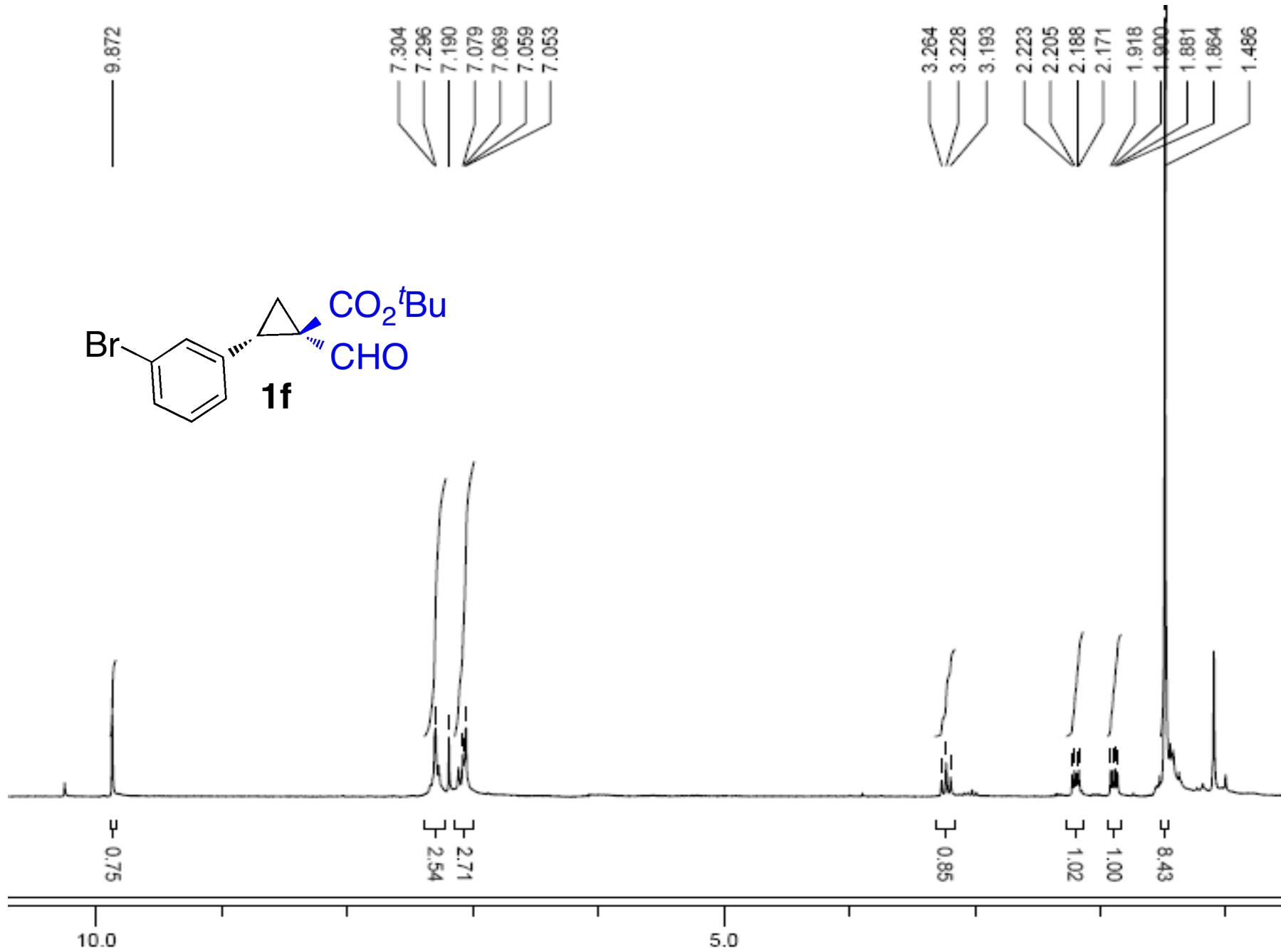
xx-vii-299 ADH 1%@0.8 ml again
C:\EZStart\Projects\Default\Method\Shifa 4-t-Butylbenzene (OD-H 10-90).met
C:\EZStart\Projects\Default\Data\xx-vii-299 ADH 1%@0.8 ml again

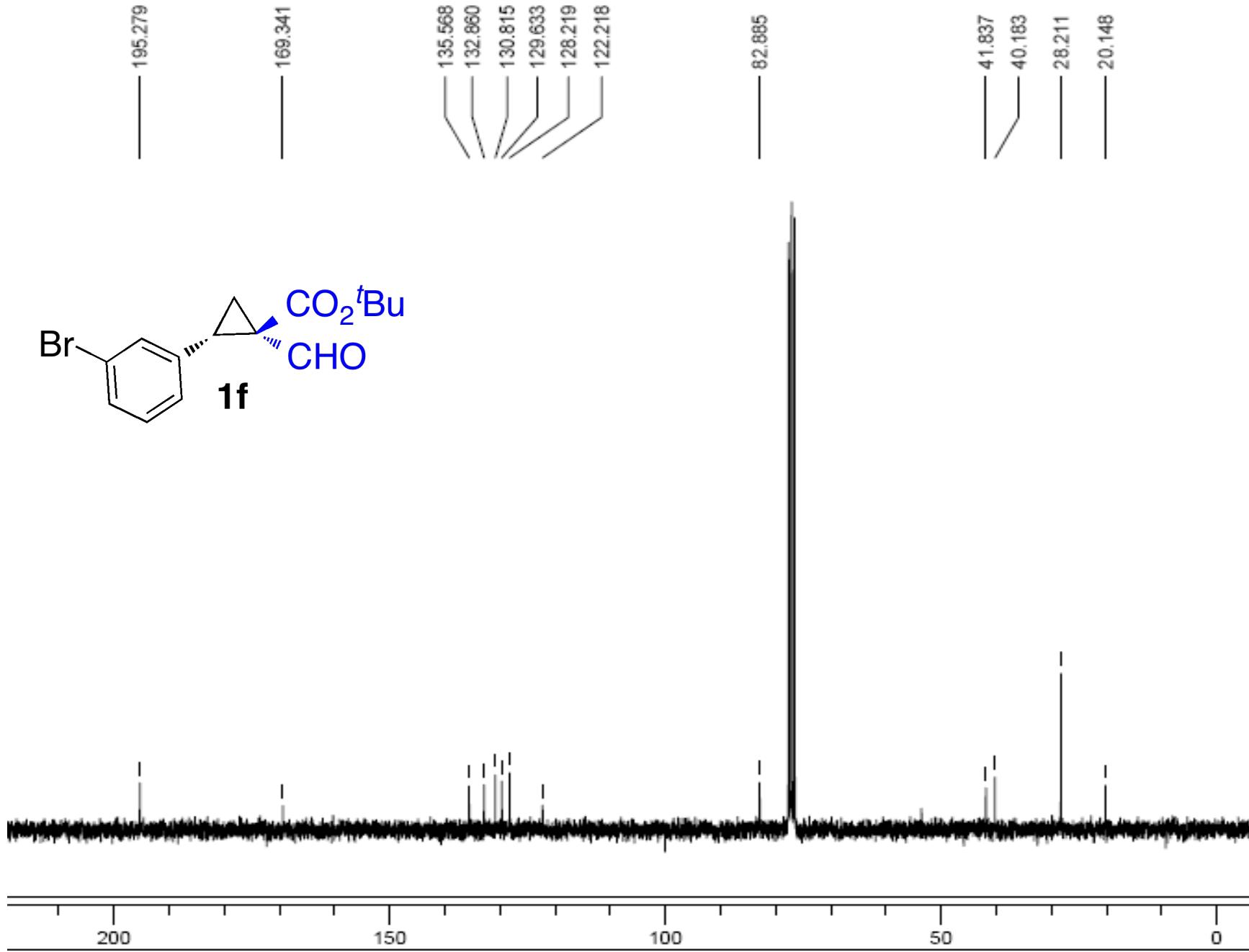


3: 229 nm, 4 nm

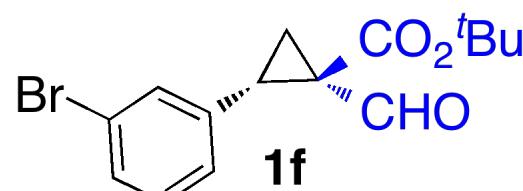
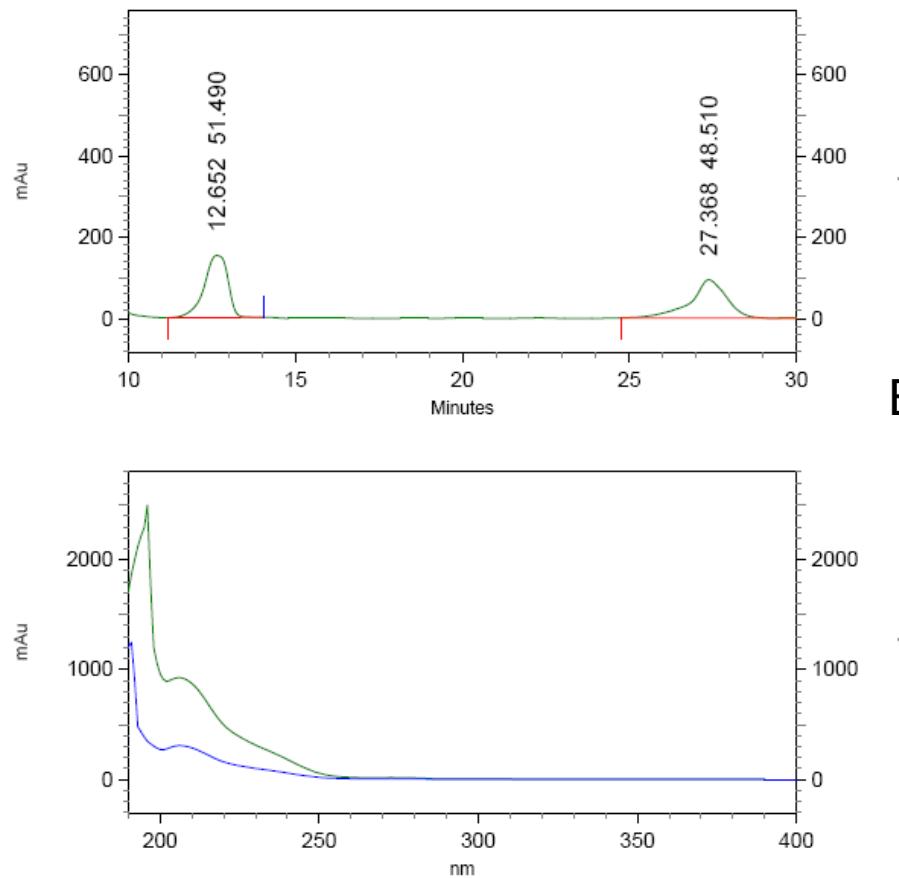
Results

Pk #	Name	Retention Time	Area Percent
1		23.428	0.228
2		25.904	99.772
Totals			100.000





xx-vi-67-2 SDwhelk 2%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-Nitro-Cyclopropane-1%.met
C:\EZStart\Projects\Default\Data\xx-vi-67-2 SDwhelk 2%@0.8 ml



4: 231 nm, 4 nm

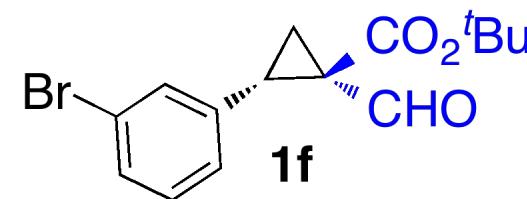
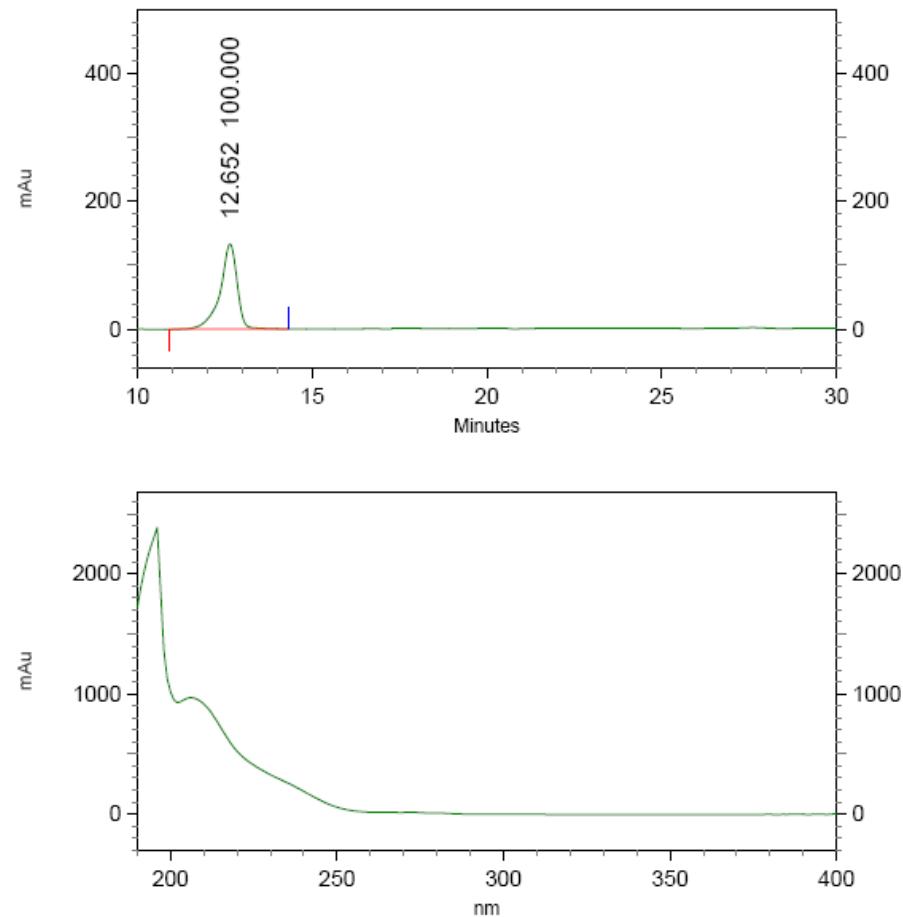
Results

Pk #	Name	Retention Time	Area Percent
1		12.652	51.490
2		27.368	48.510
Totals			100.000

xx-vi-82 SDwhelk 2%@0.8 ml

C:\EZStart\Projects\Default\Method\Shifa-Nitro-Cyclopropane-1%.met

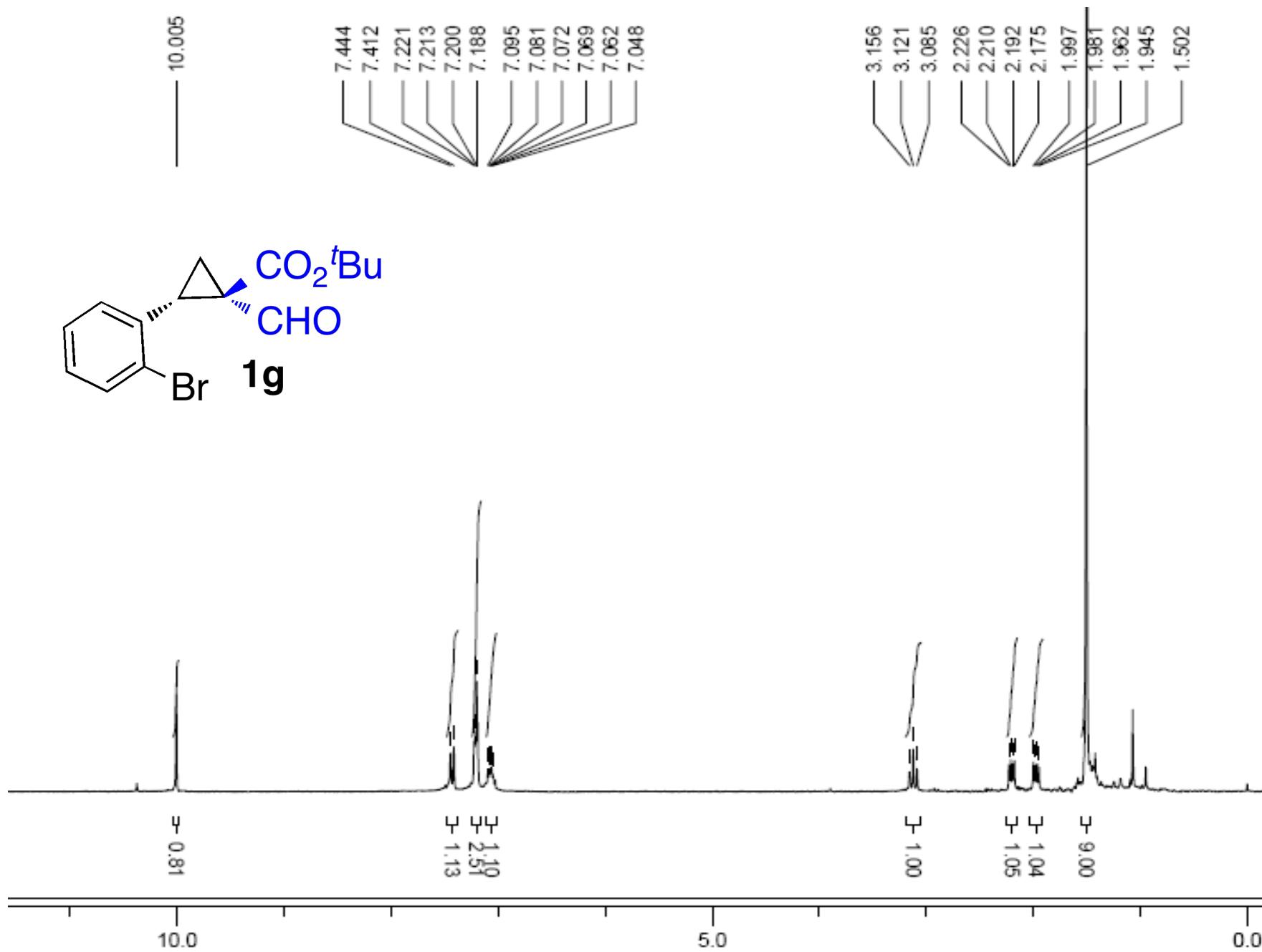
C:\EZStart\Projects\Default\Data\xx-vi-82 SDwhelk 2%@0.8 ml

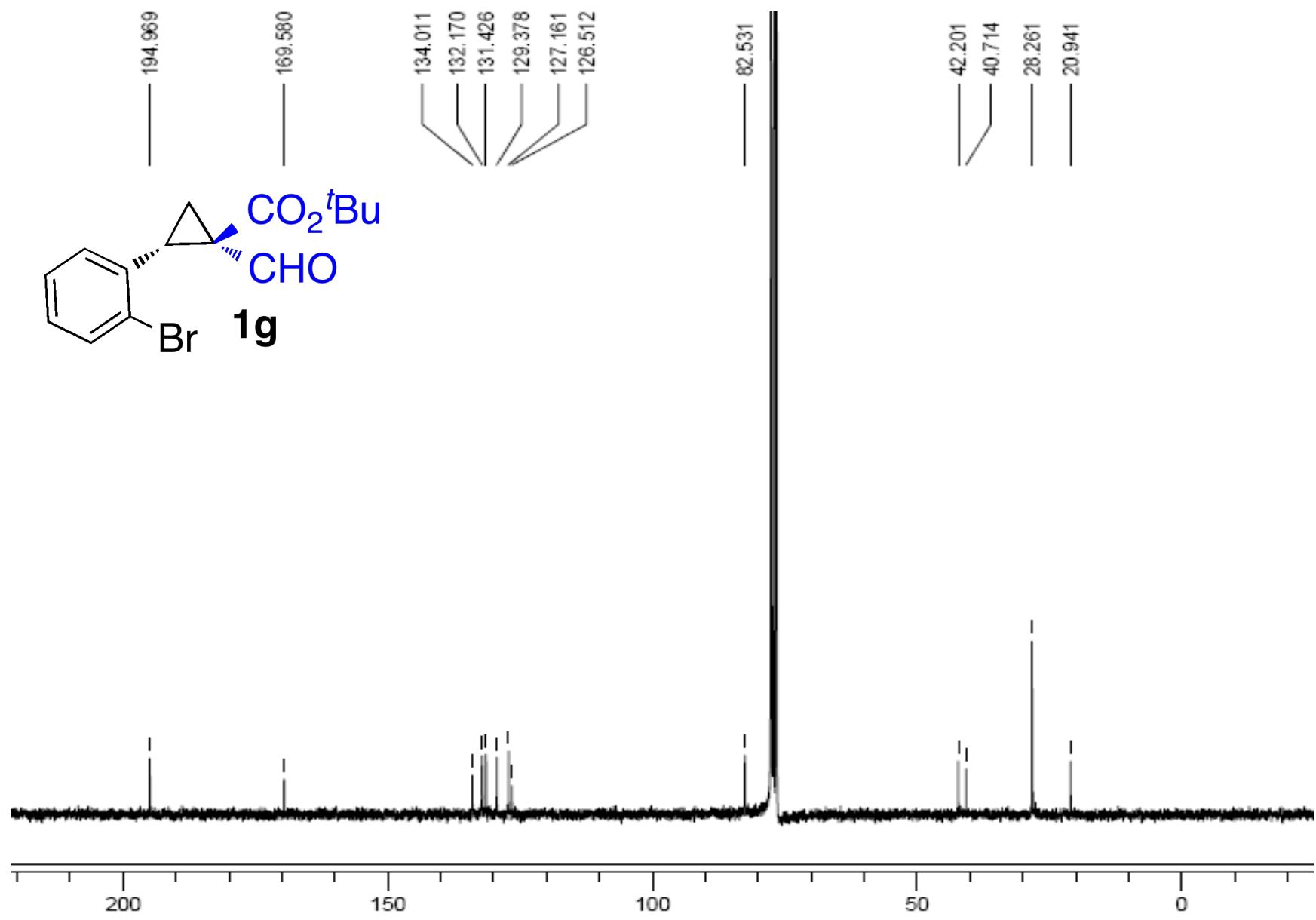


4: 230 nm, 4 nm

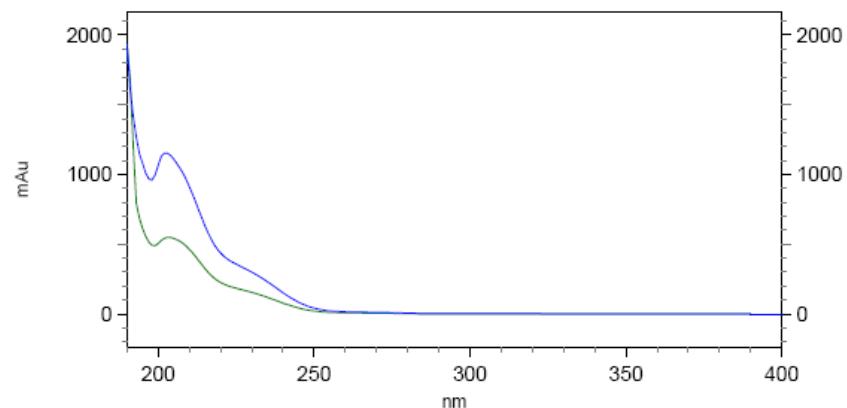
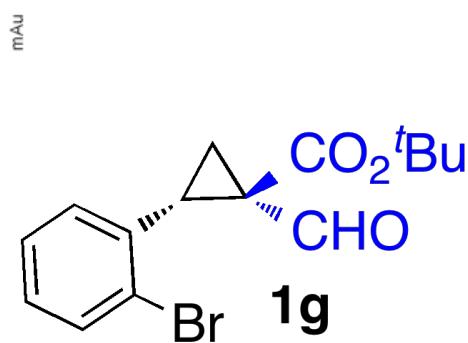
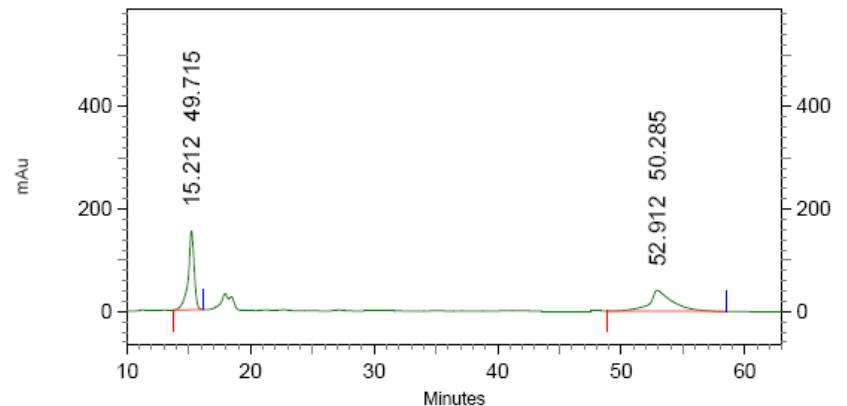
Results

Pk #	Name	Retention Time	Area Percent
1		12.652	100.000
Totals			100.000





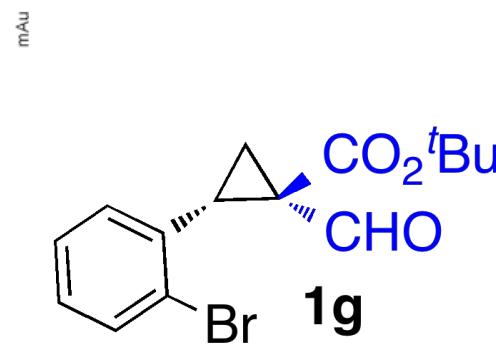
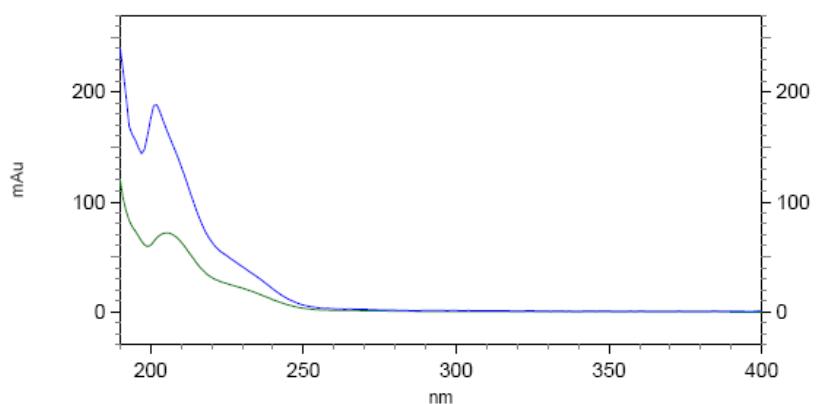
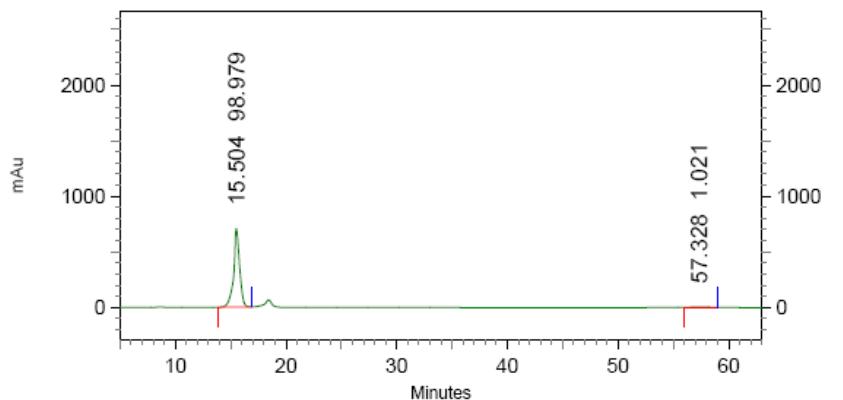
xx-vi-67-3 whelk 1%@0.8 ml AGAIN
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
E:\HPLC\xx-vi-67-3 whelk 1%@0.8 ml AGAIN



2: 226 nm, 4 nm
Results

Pk #	Name	Retention Time	Area Percent
1		15.212	49.715
2		52.912	50.285
Totals			100.000

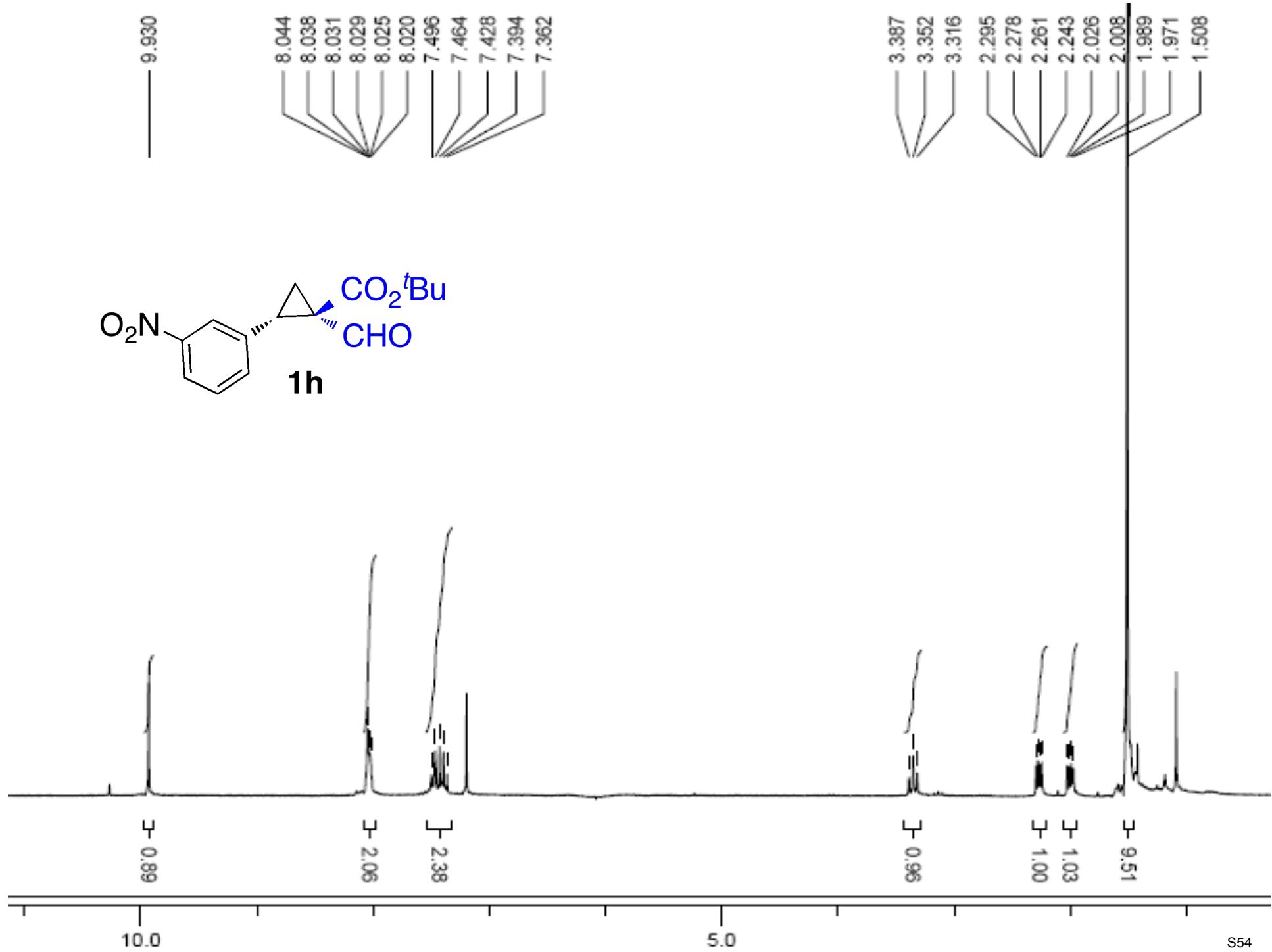
xx-vi-83 whelk 1%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
E:\HPLC\xx-vi-83 whelk 1%@0.8 ml

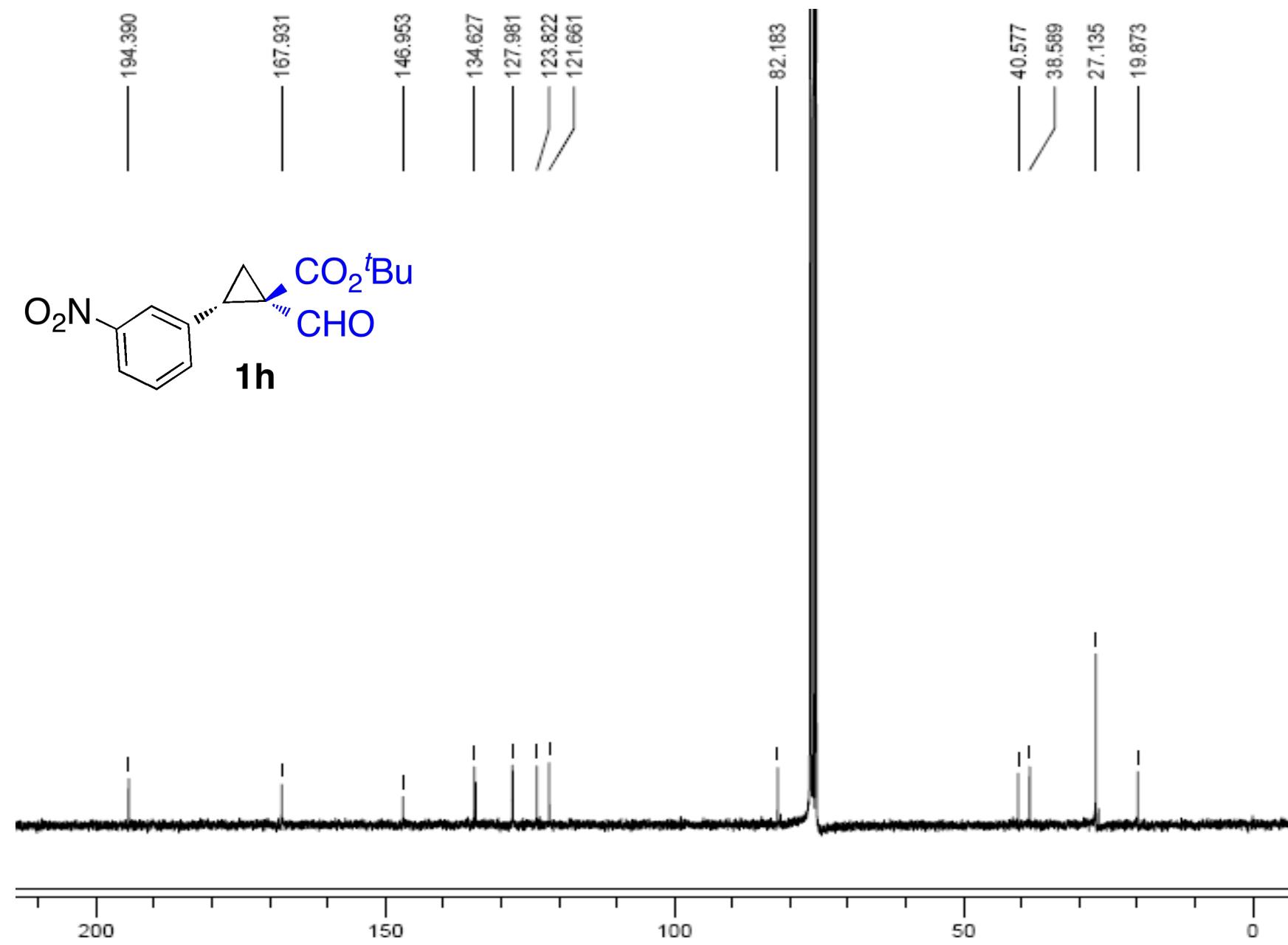


2: 226 nm, 4 nm

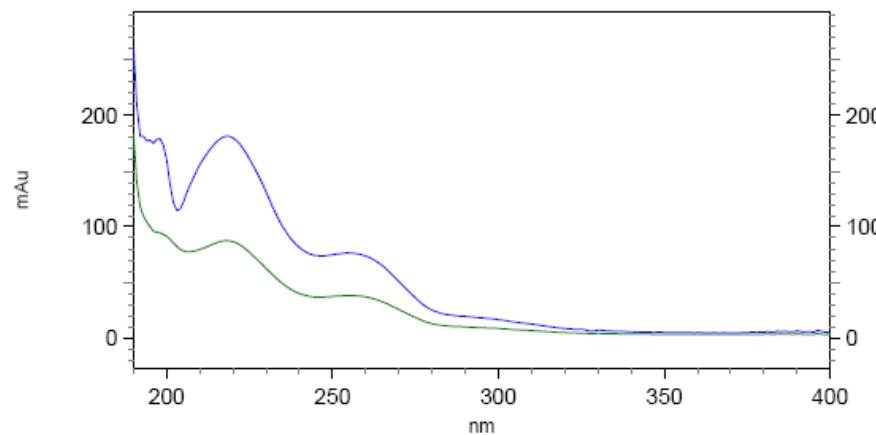
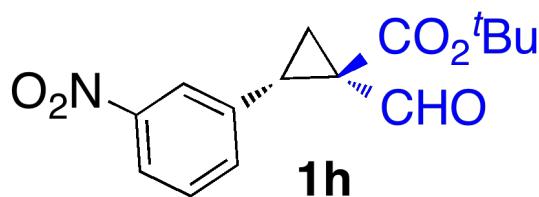
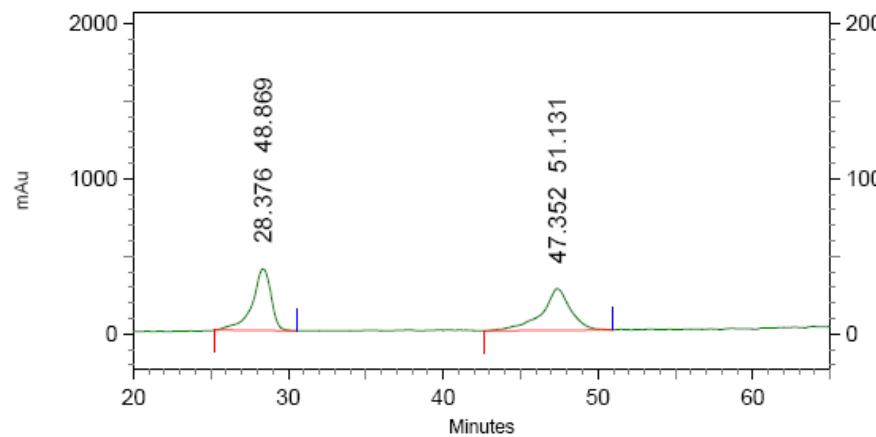
Results

Pk #	Name	Retention Time	Area Percent
1		15.504	98.979
2		57.328	1.021
Totals			100.000





xx-vi-67-1SDwhelk 2%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-Nitro-Cyclopropane-1%.met
C:\EZStart\Projects\Default\Data\xx-vi-67-1SDwhelk 2%@0.8 ml



4: 221 nm, 4 nm

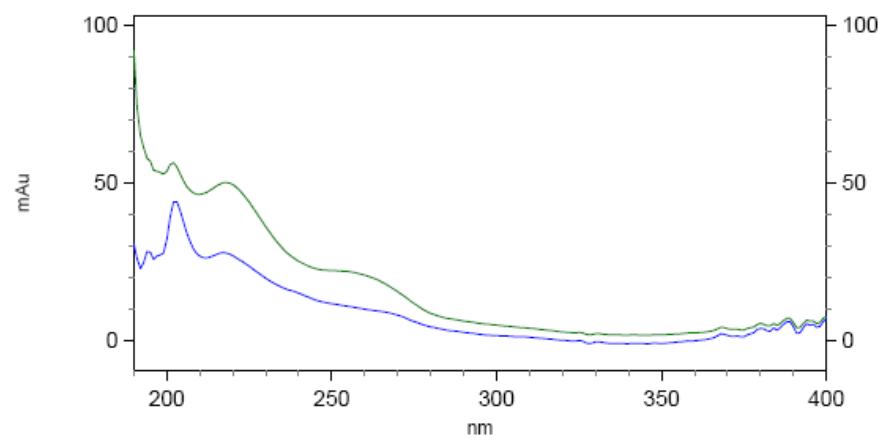
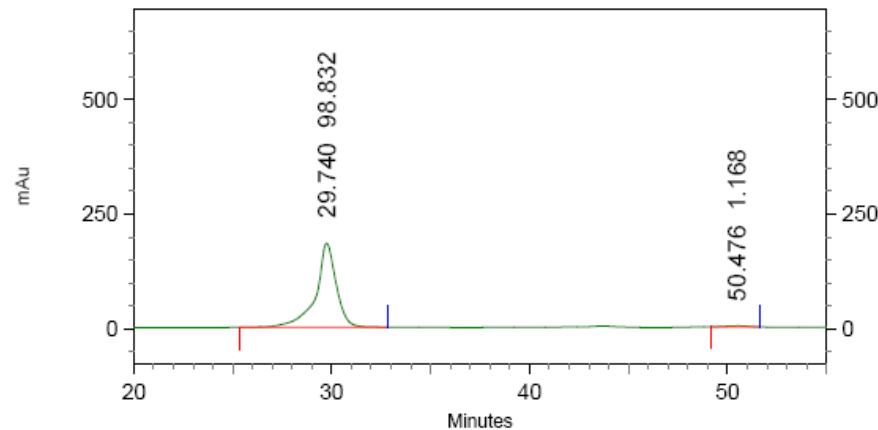
Results

Pk #	Name	Retention Time	Area Percent
1		28.376	48.869
2		47.352	51.131
Totals			100.000

xx-vi-81 SDwhelk 2%@0.8 ml

C:\EZStart\Projects\Default\Method\Shifa-Nitro-Cyclopropane-1%.met

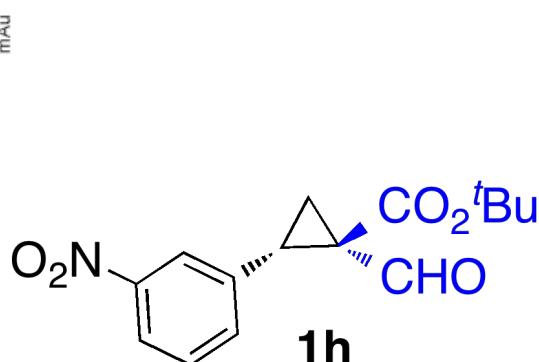
C:\EZStart\Projects\Default\Data\xx-vi-81 SDwhelk 2%@0.8 ml

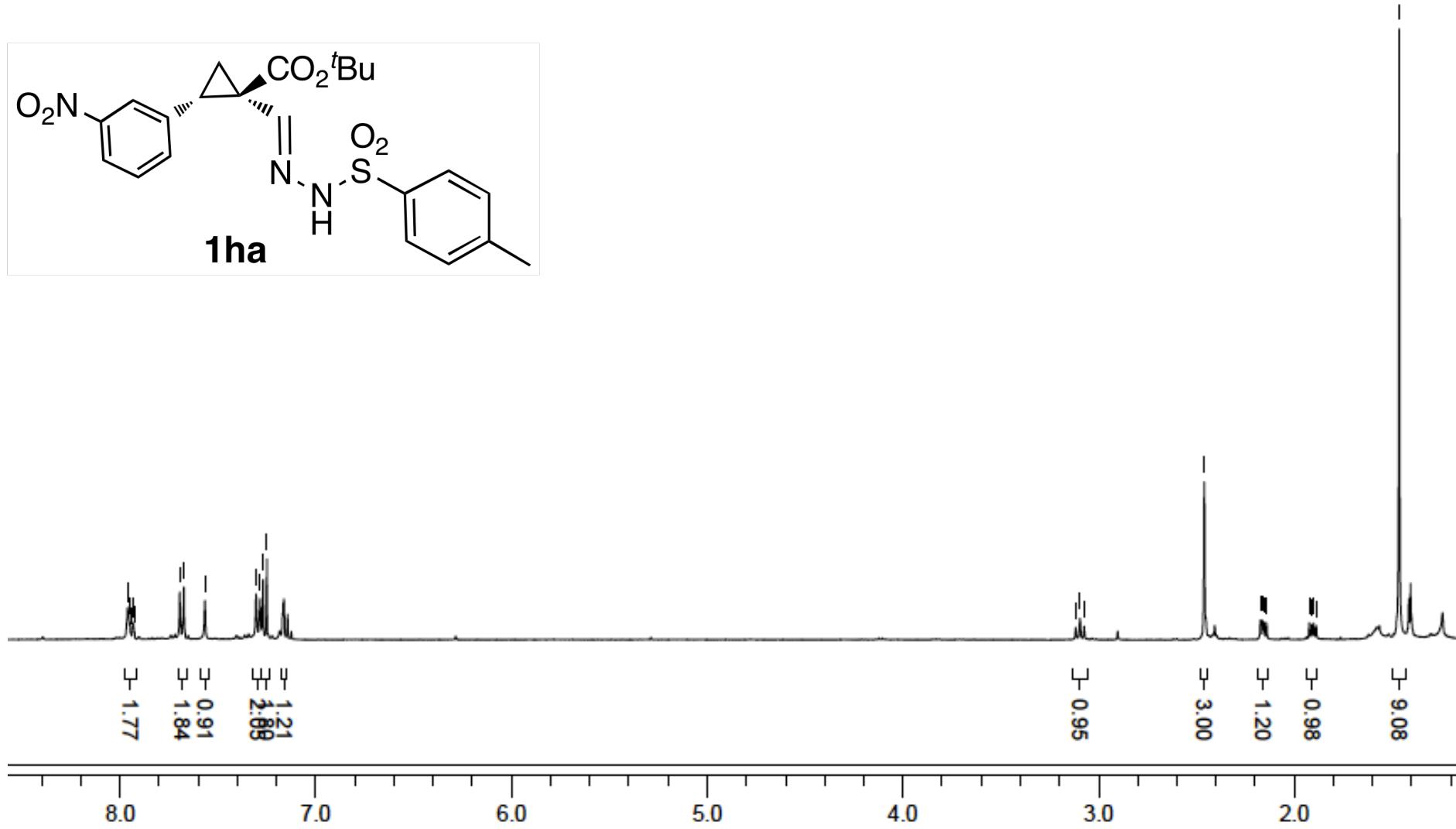
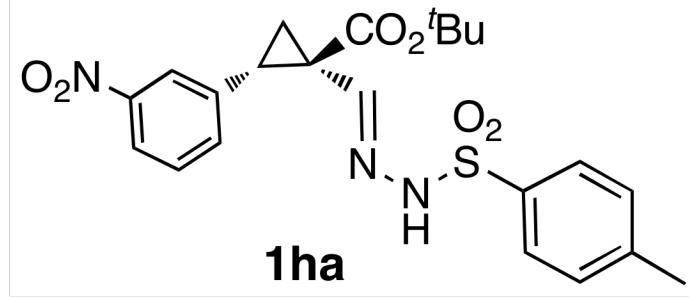
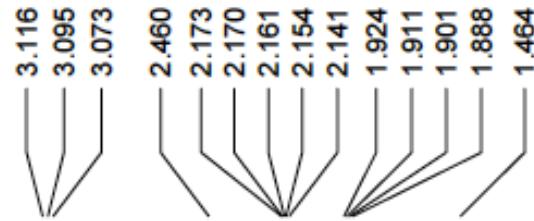
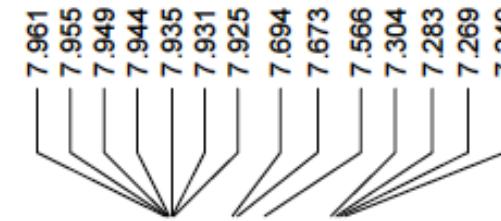


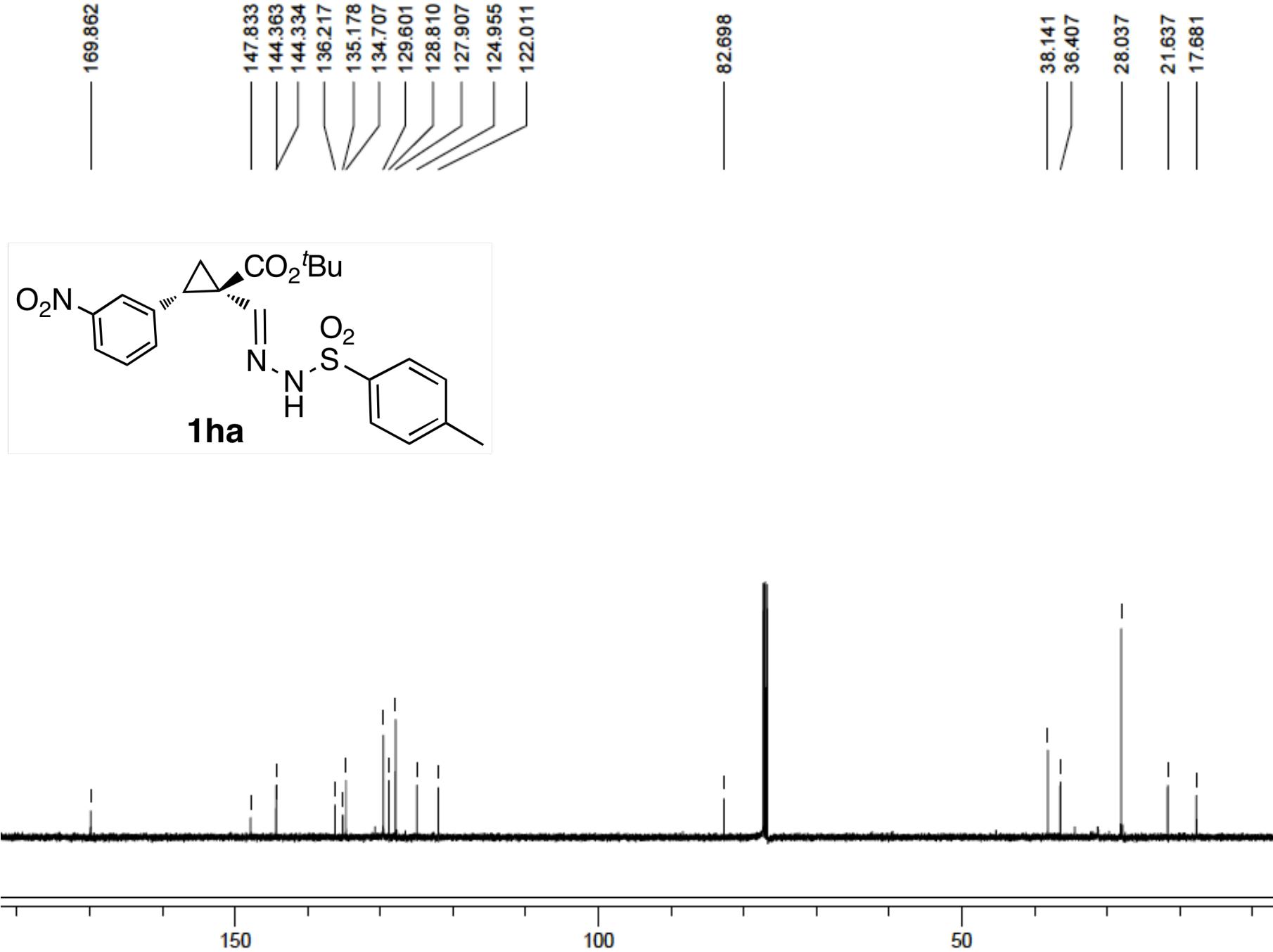
4: 231 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		29.740	98.832
2		50.476	1.168
Totals			100.000



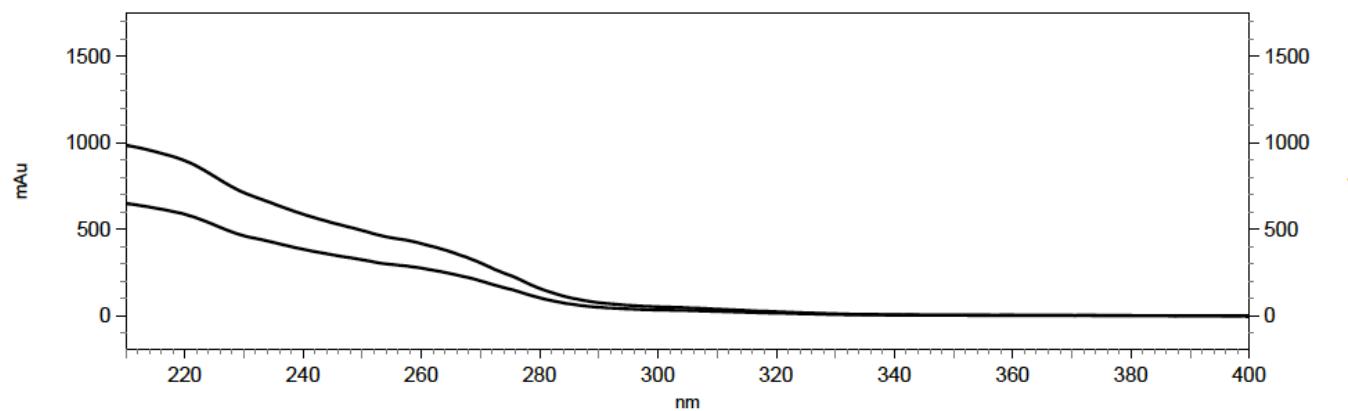
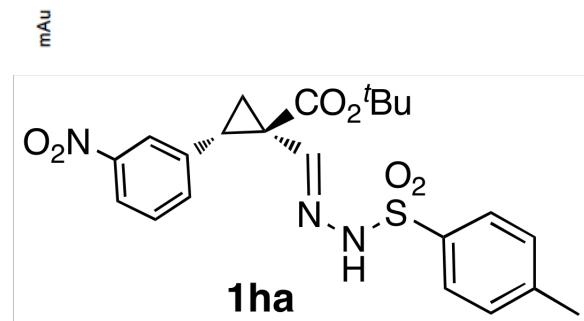
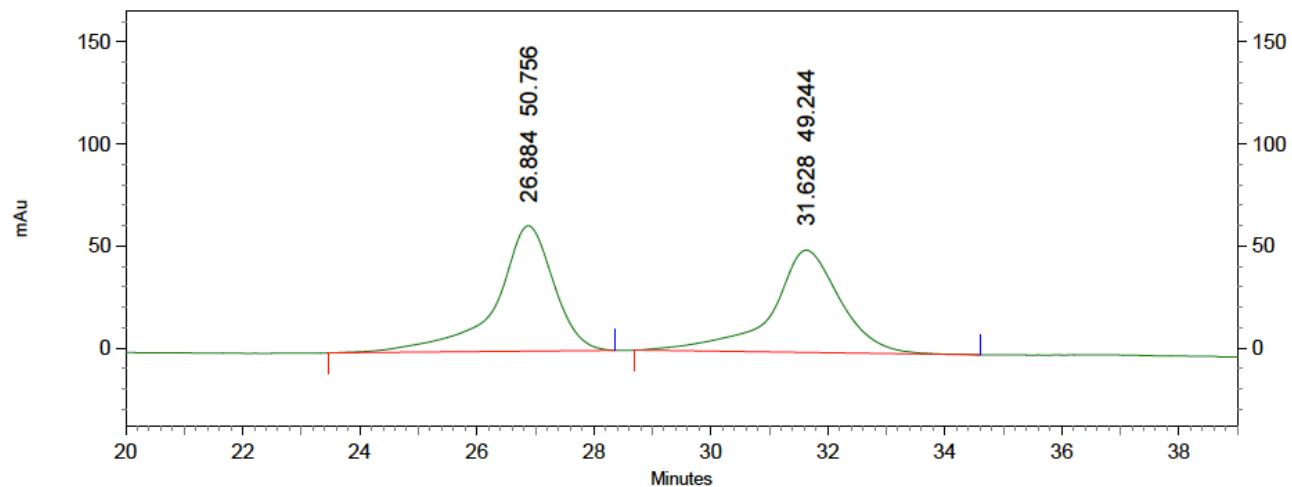




XC-IX-84-10%-WHELK1ml

C:\EZStart\Projects\Default\Data\XC-IX-84-10%-WHELK1ml

C:\EZStart\Projects\Default\Method\XC-Whelk10%1ml.met



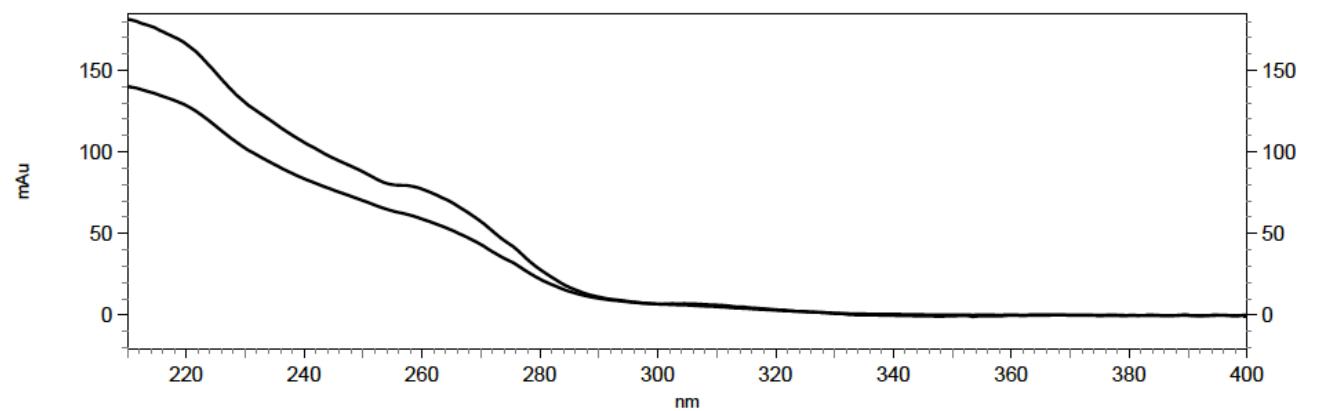
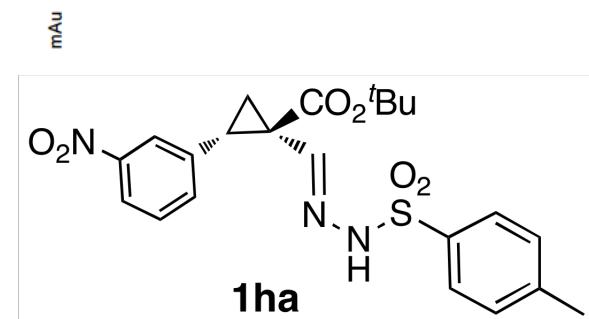
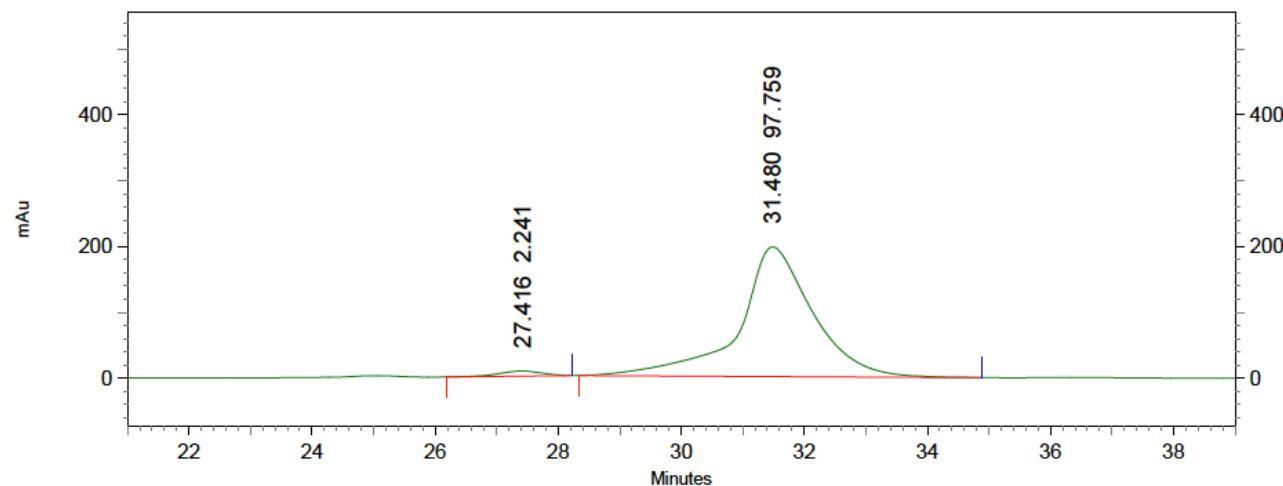
8 : 230 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	26.884	50.756
2	31.628	49.244
Totals		100.000

XC-IX-69-10%-WHELK1ml

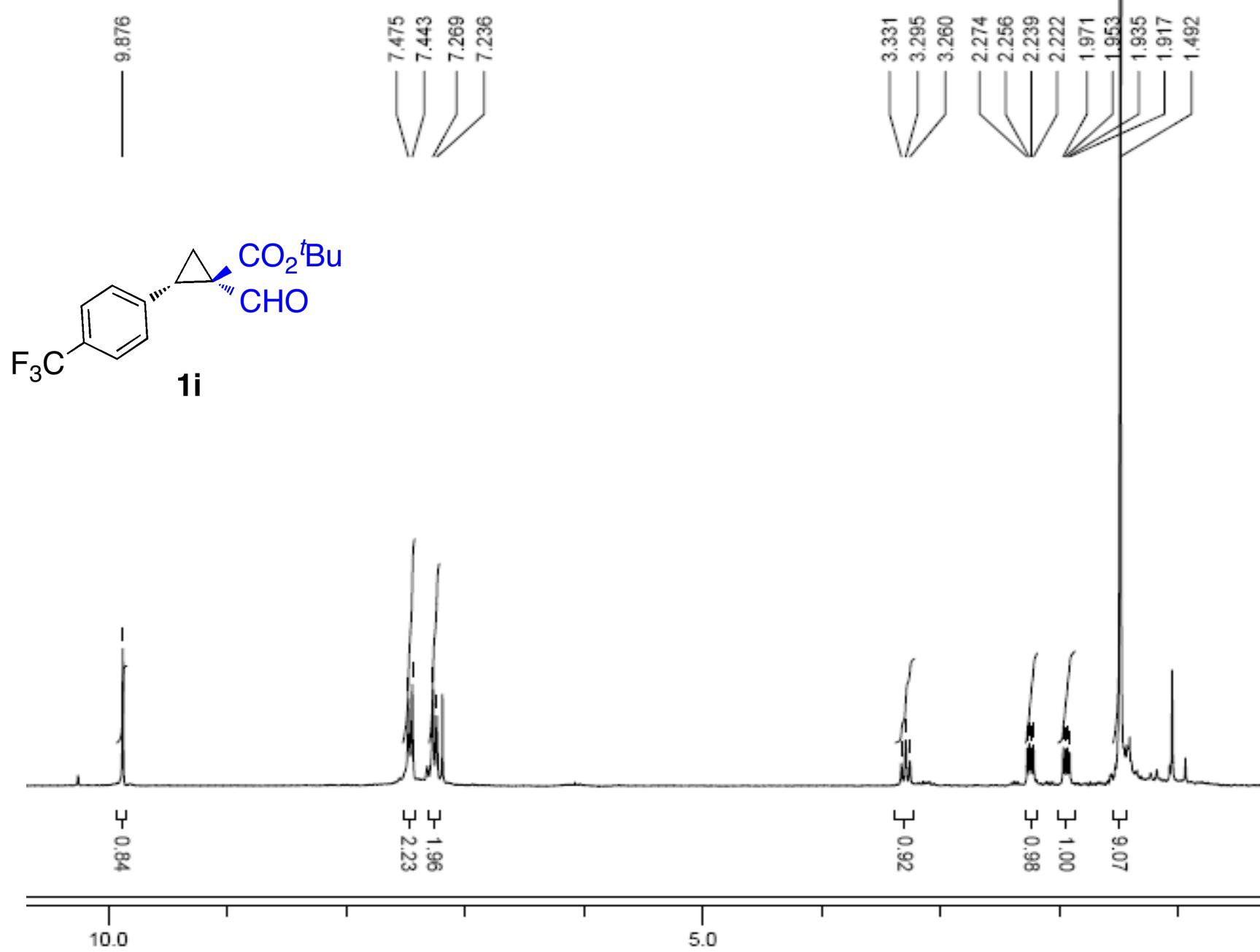
C:\EZStart\Projects\Default\Data\XC-IX-69-10%-WHELK1ml

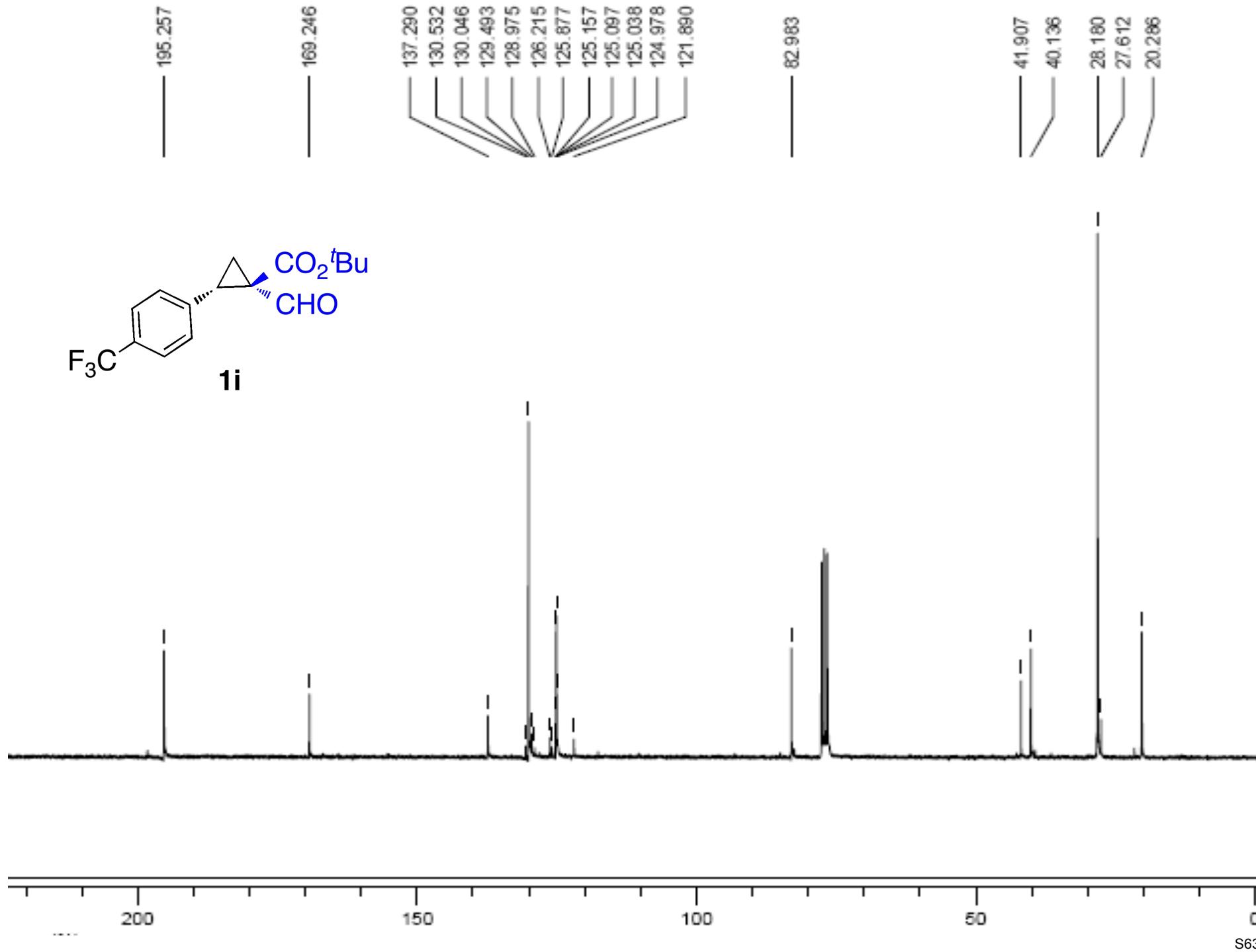
C:\EZStart\Projects\Default\Method\XC-Whelk10%1ml.met

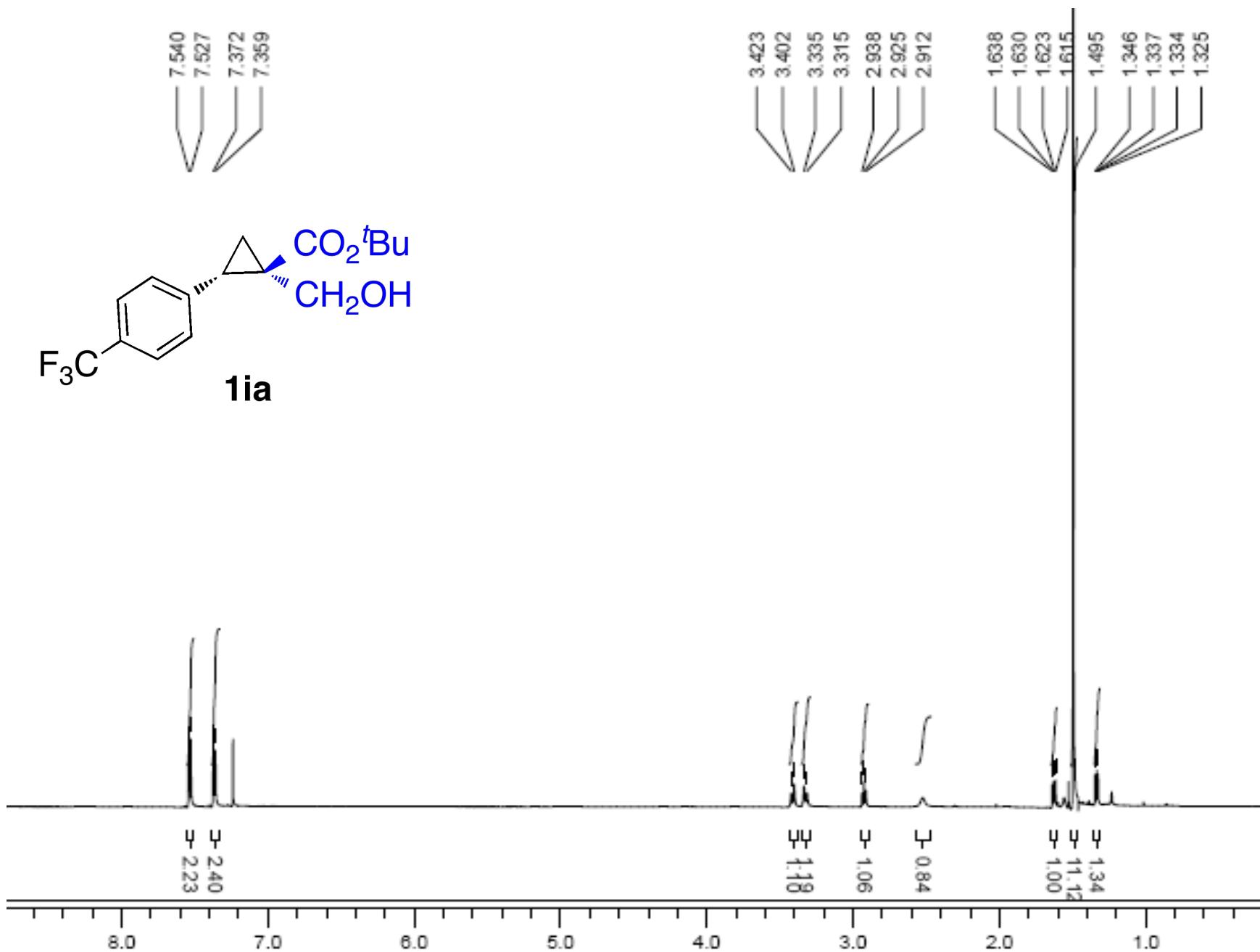


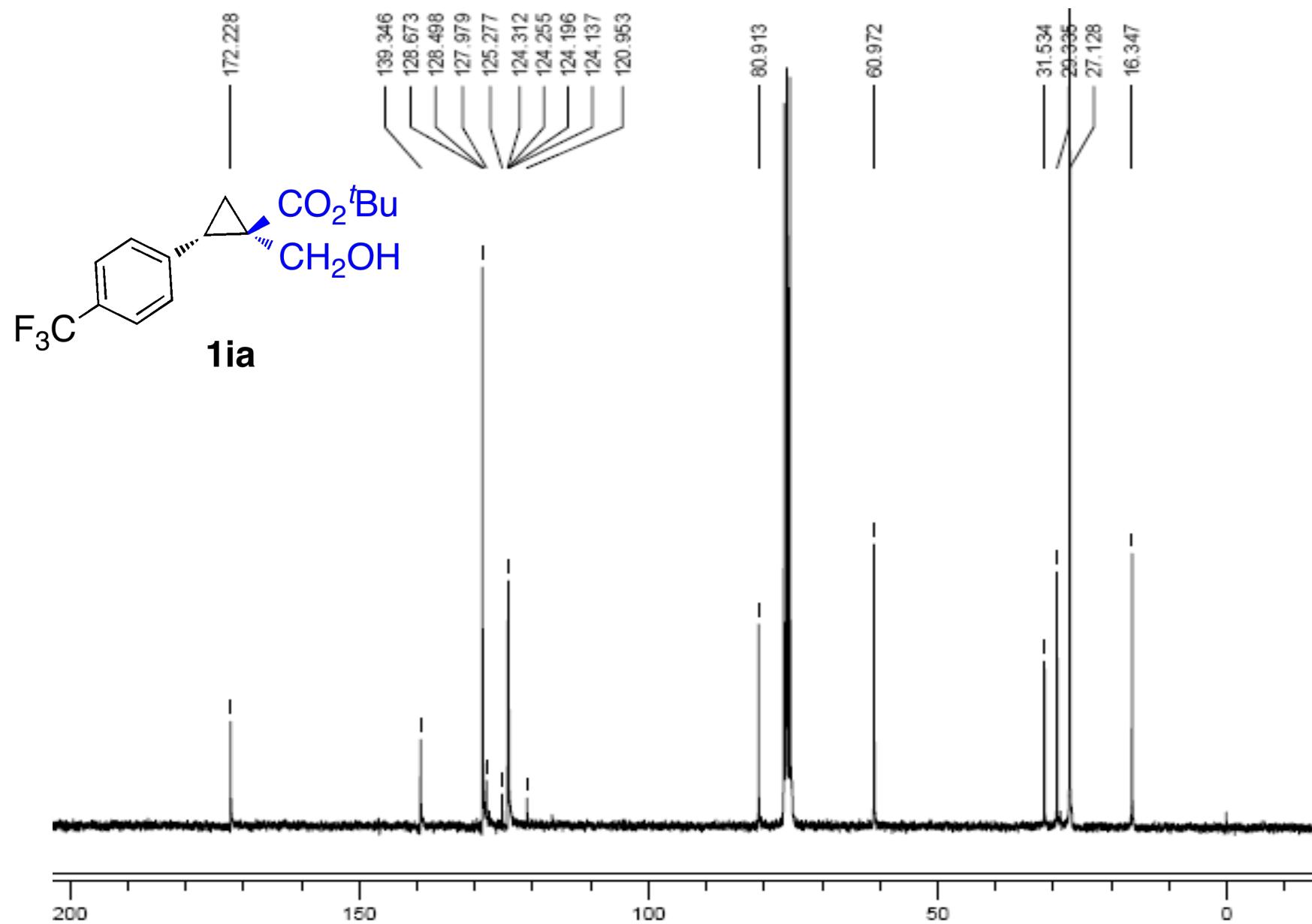
8 : 239 nm, 4 nm Results

Pk #	Retention Time	Area Percent
1	27.416	2.241
2	31.480	97.759
Totals		100.000

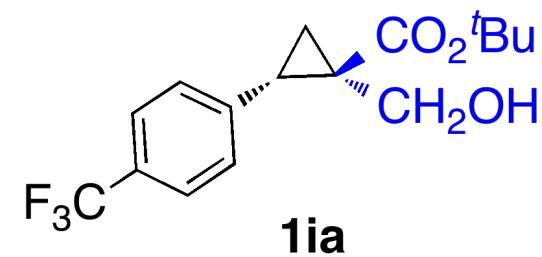
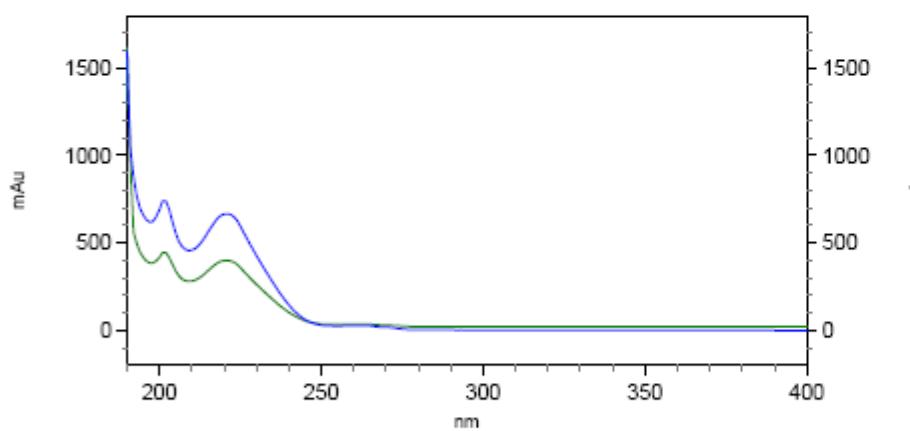
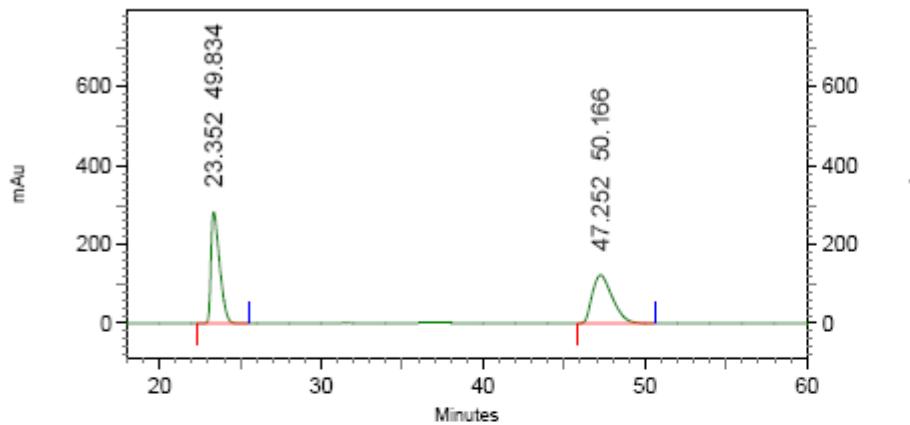








xx-vii-294 ADH 1%@0.8 ml
C:\EZStart\Projects\Default\Method\JRT-WK-1%1ML90MIN.met
C:\EZStart\Projects\Default\Data\xx-vii-294 ADH 1%@0.8 ml

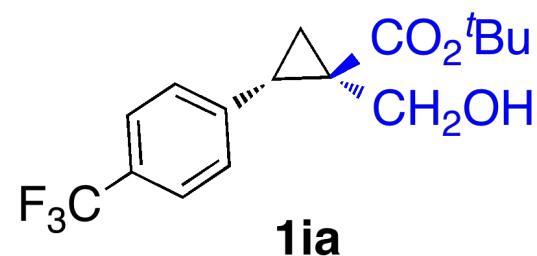
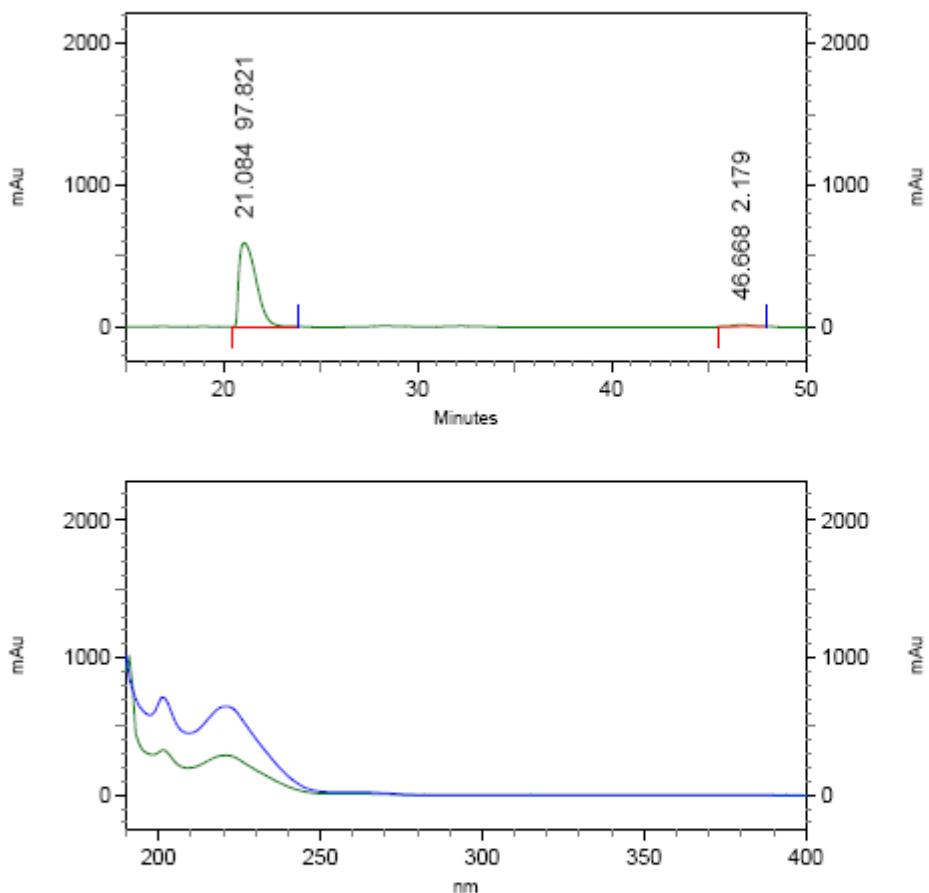


Pk #	Name	Retention Time	Area Percent
1		23.352	49.834
2		47.252	50.166
Totals			100.000

xx-vii-300 ADH 1%@0.8 ml

C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 1%Whelk.met

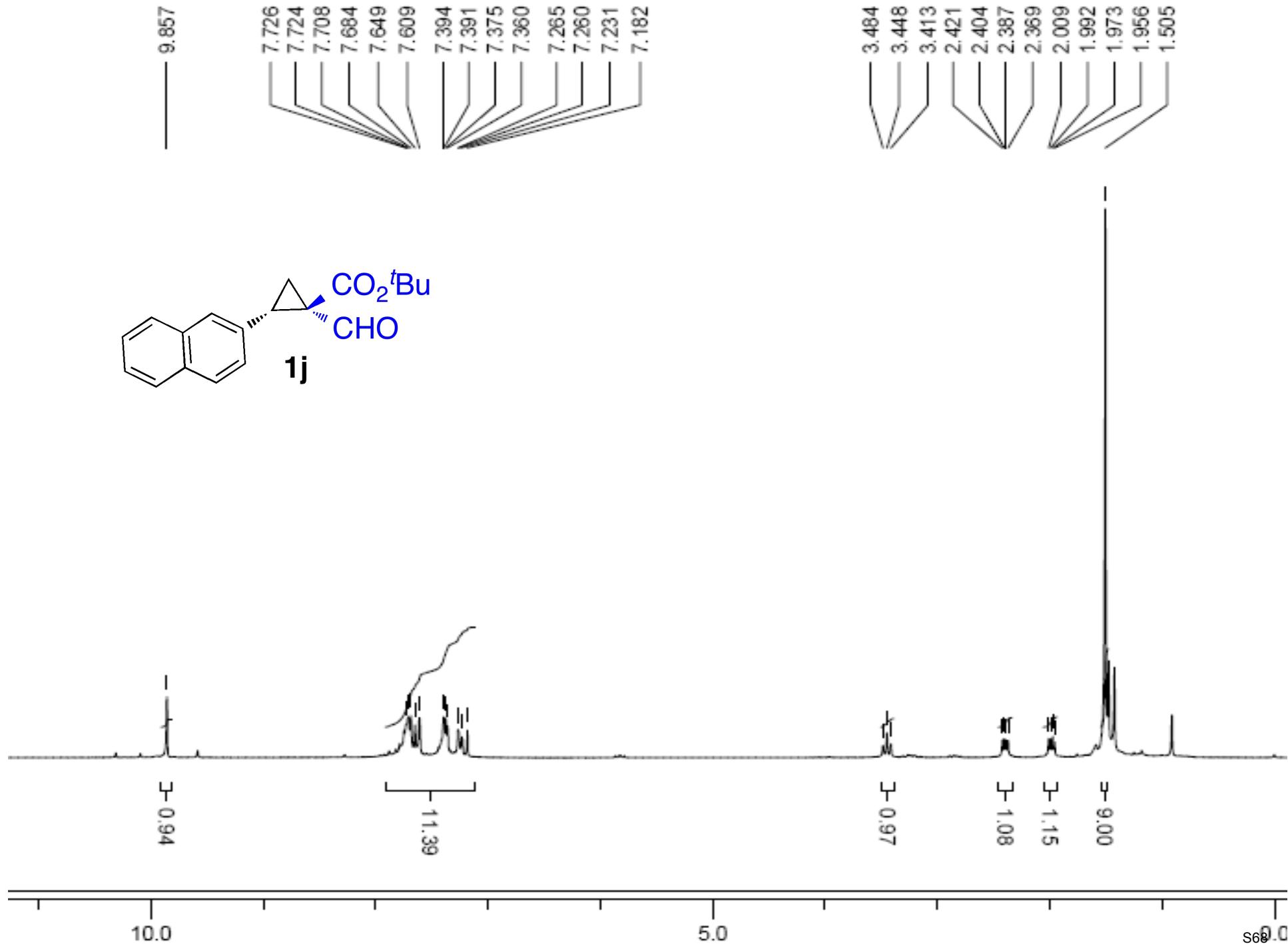
C:\EZStart\Projects\Default\Data\xx-vii-300 ADH 1%@0.8 ml

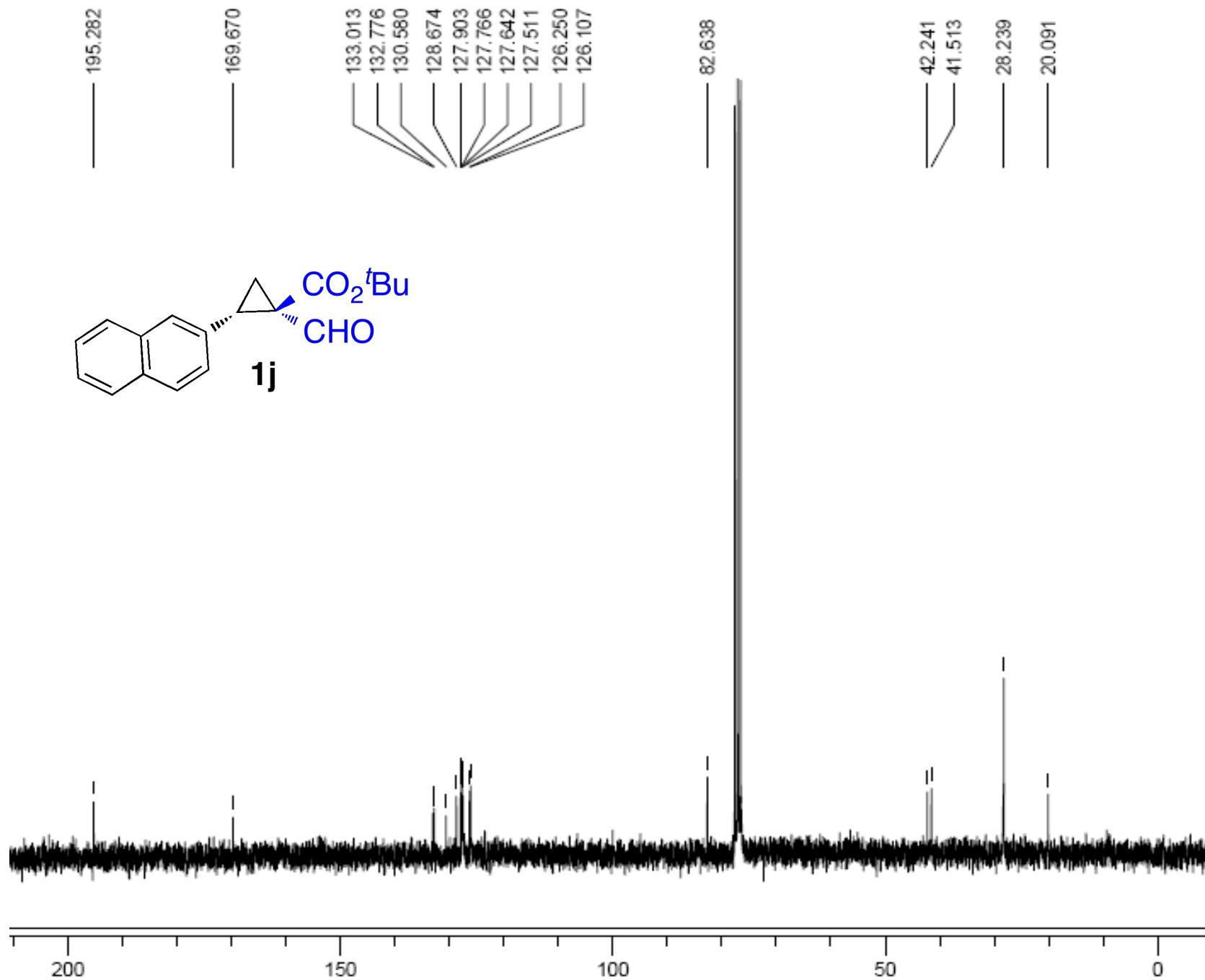


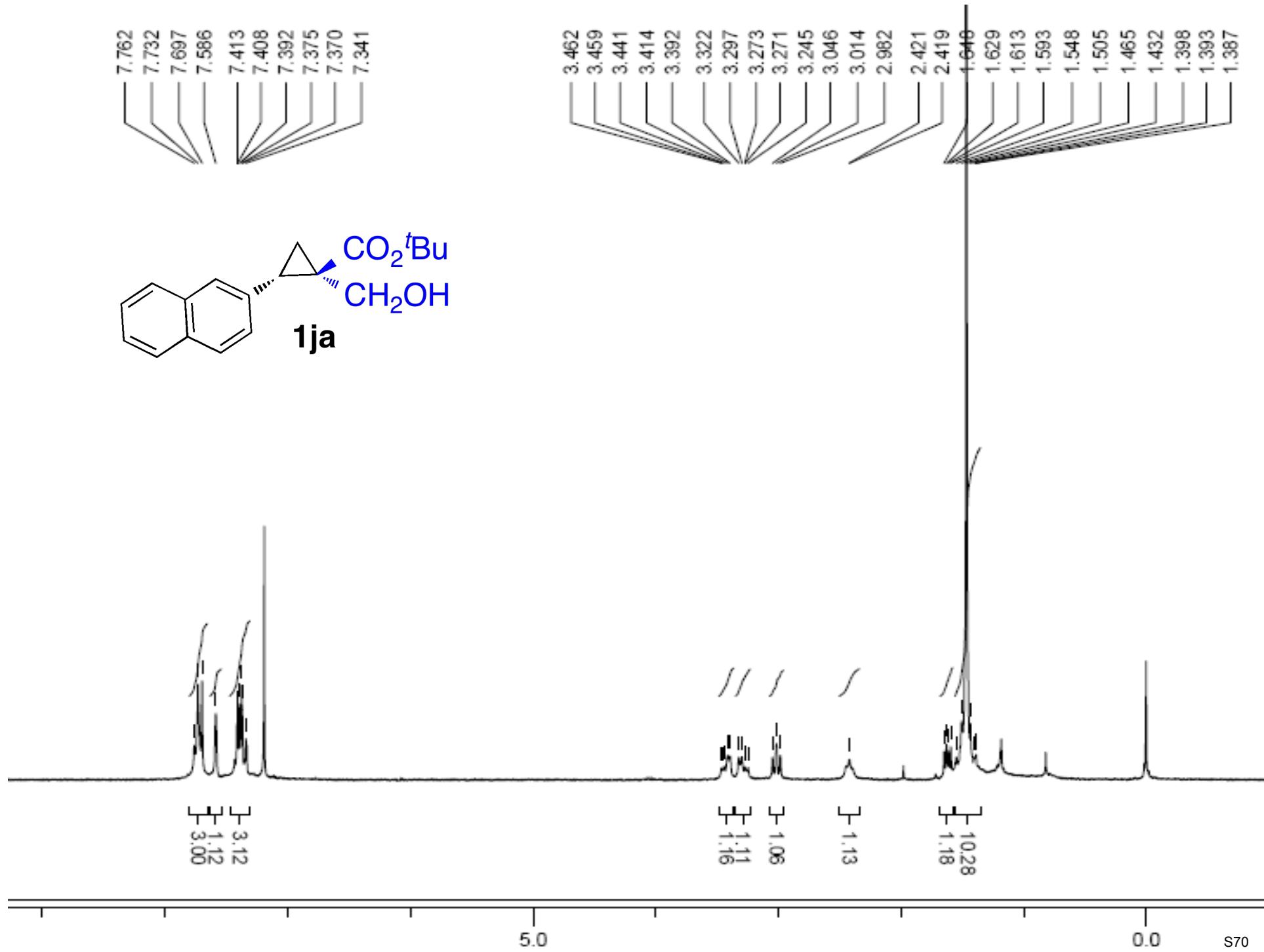
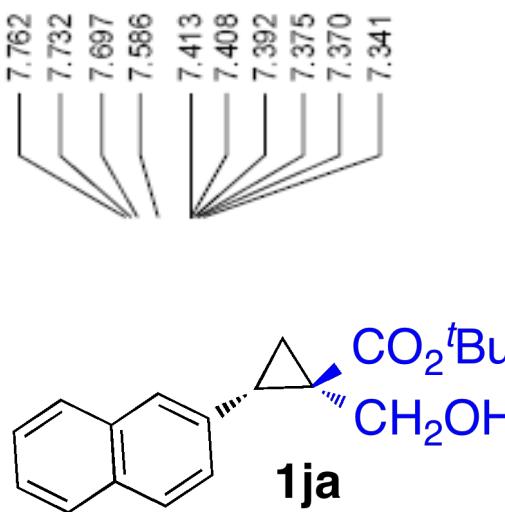
2: 225 nm, 4 nm

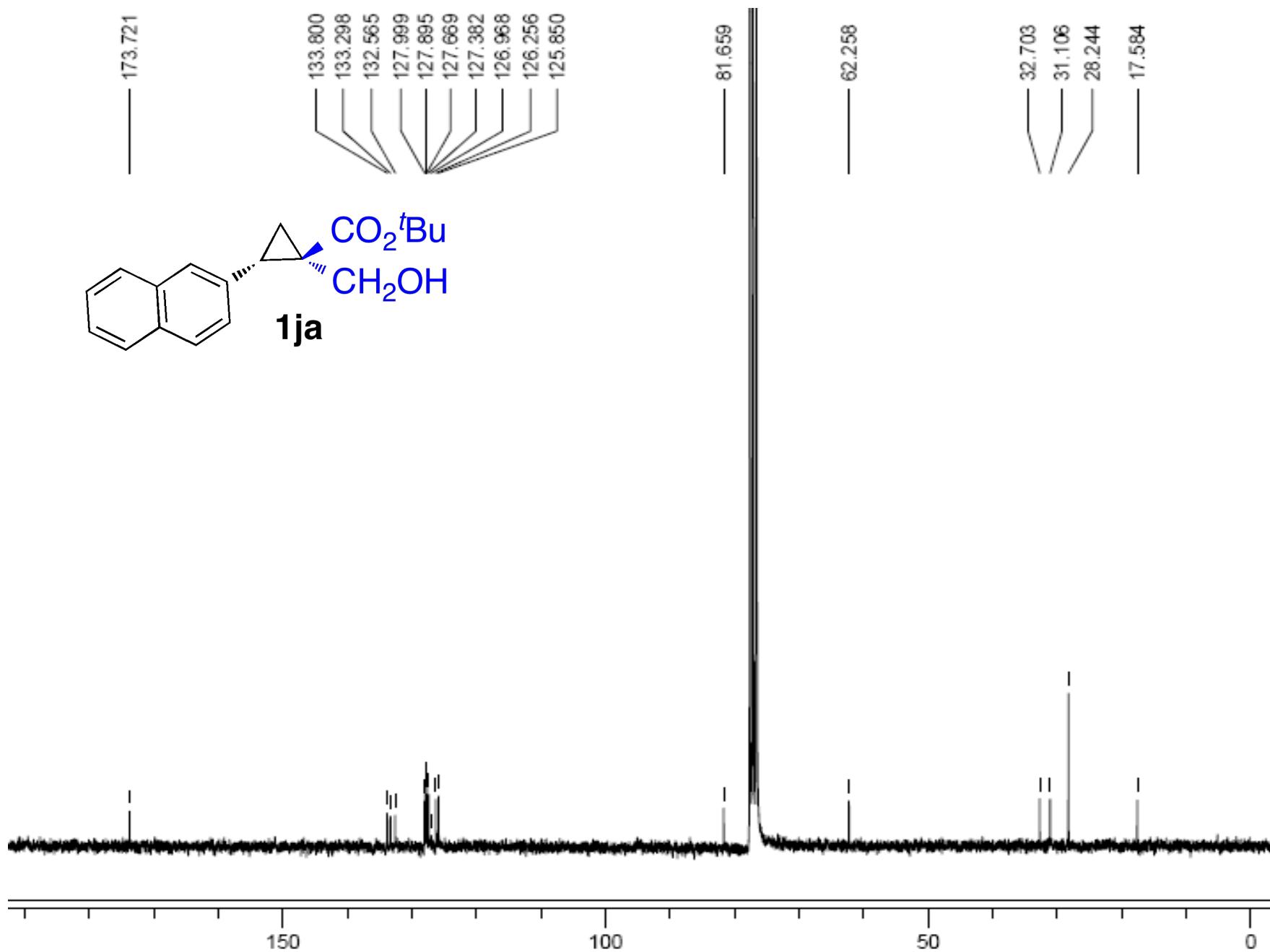
Results

Pk #	Name	Retention Time	Area Percent
1		21.084	97.821
2		46.668	2.179
Totals			100.000

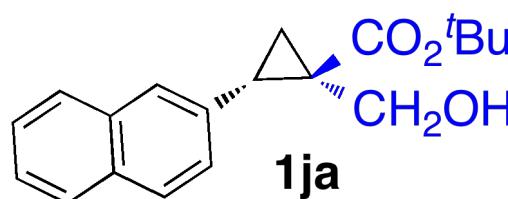
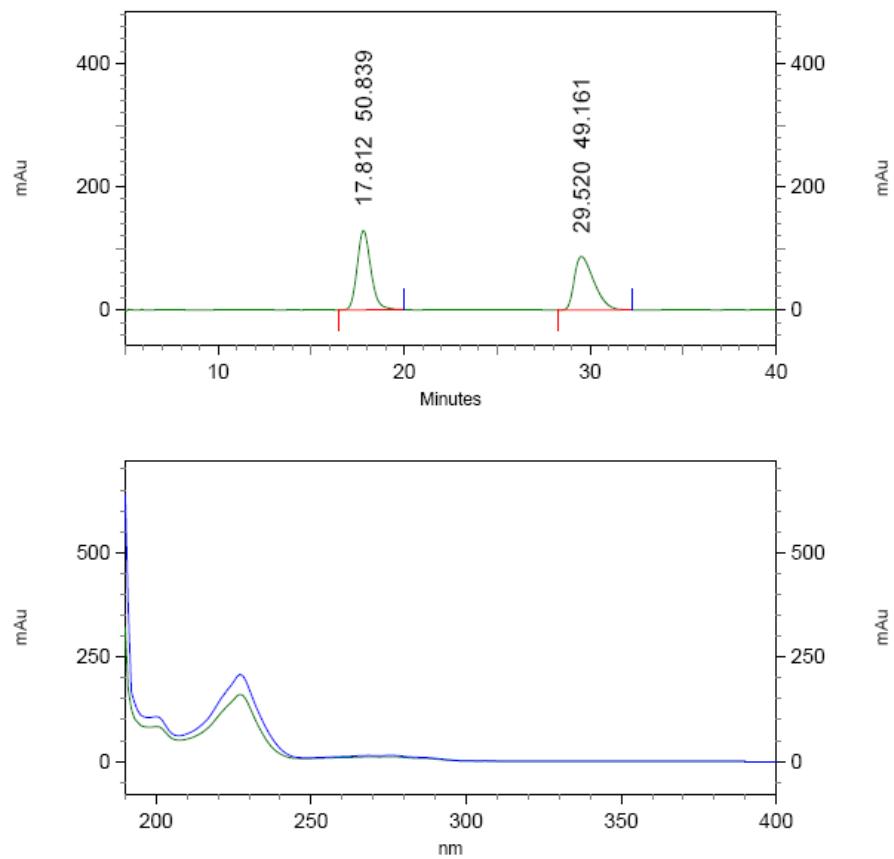








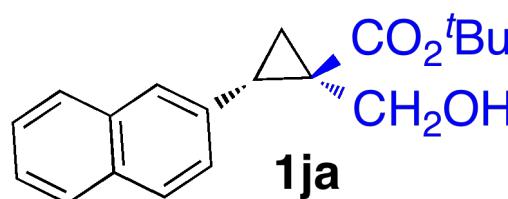
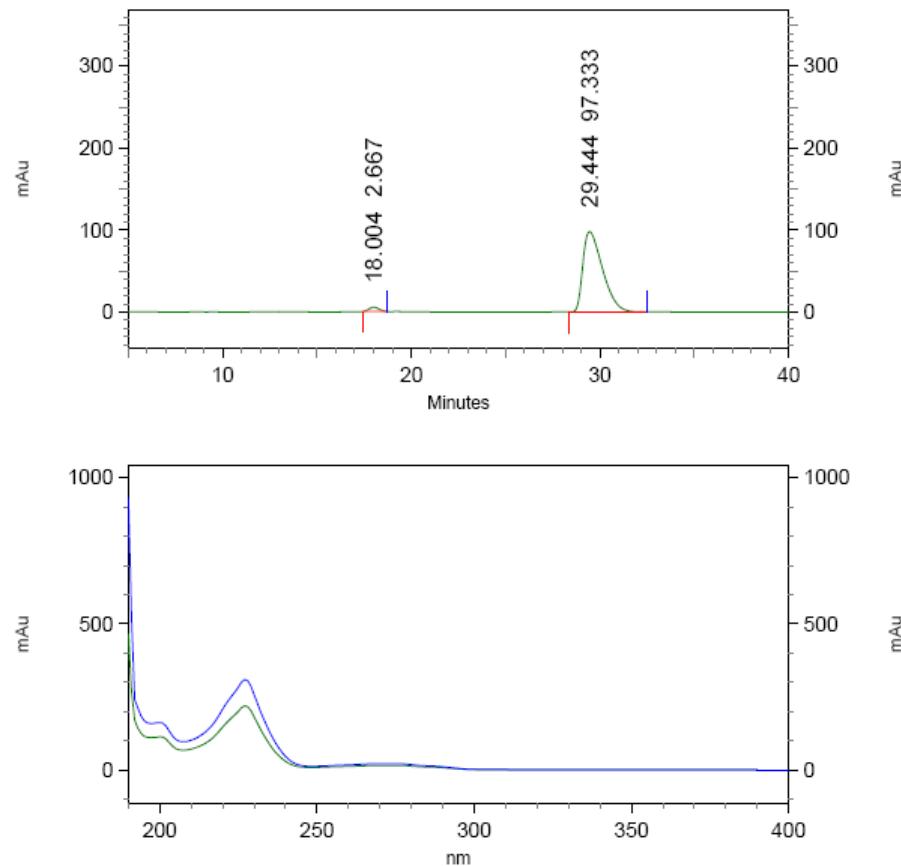
xx-vi-137 ODH 3%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
C:\EZStart\Projects\Default\Data\xx-vi-137 ODH 3%@0.8 ml



2: 254 nm, 4 nm
Results

Pk # Name	Retention Time	Area Percent
1	17.812	50.839
2	29.520	49.161
Totals		100.000

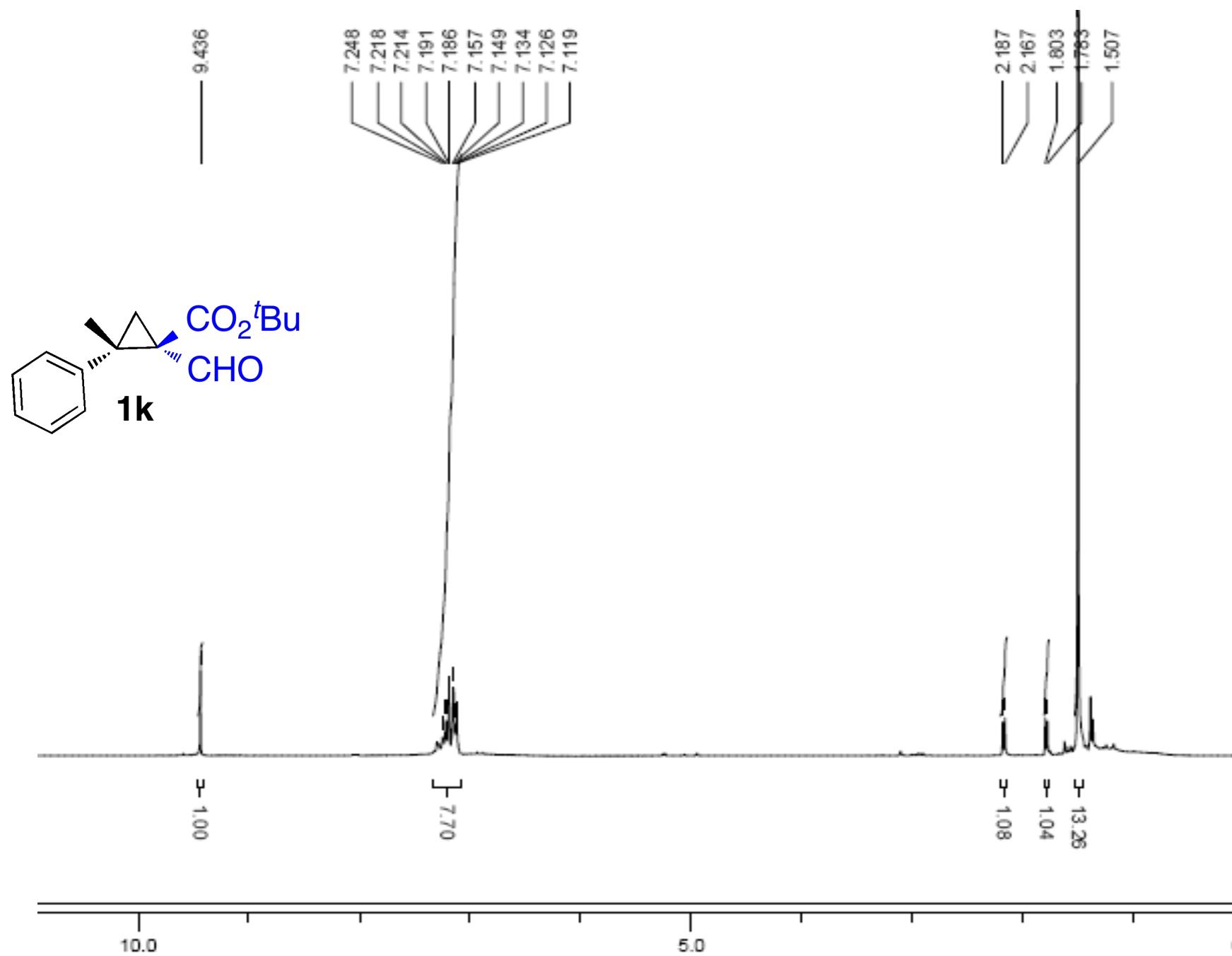
xx-vi-139 ODH 3%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa-EDA.met
C:\EZStart\Projects\Default\Data\xx-vi-139 ODH 3%@0.8 ml

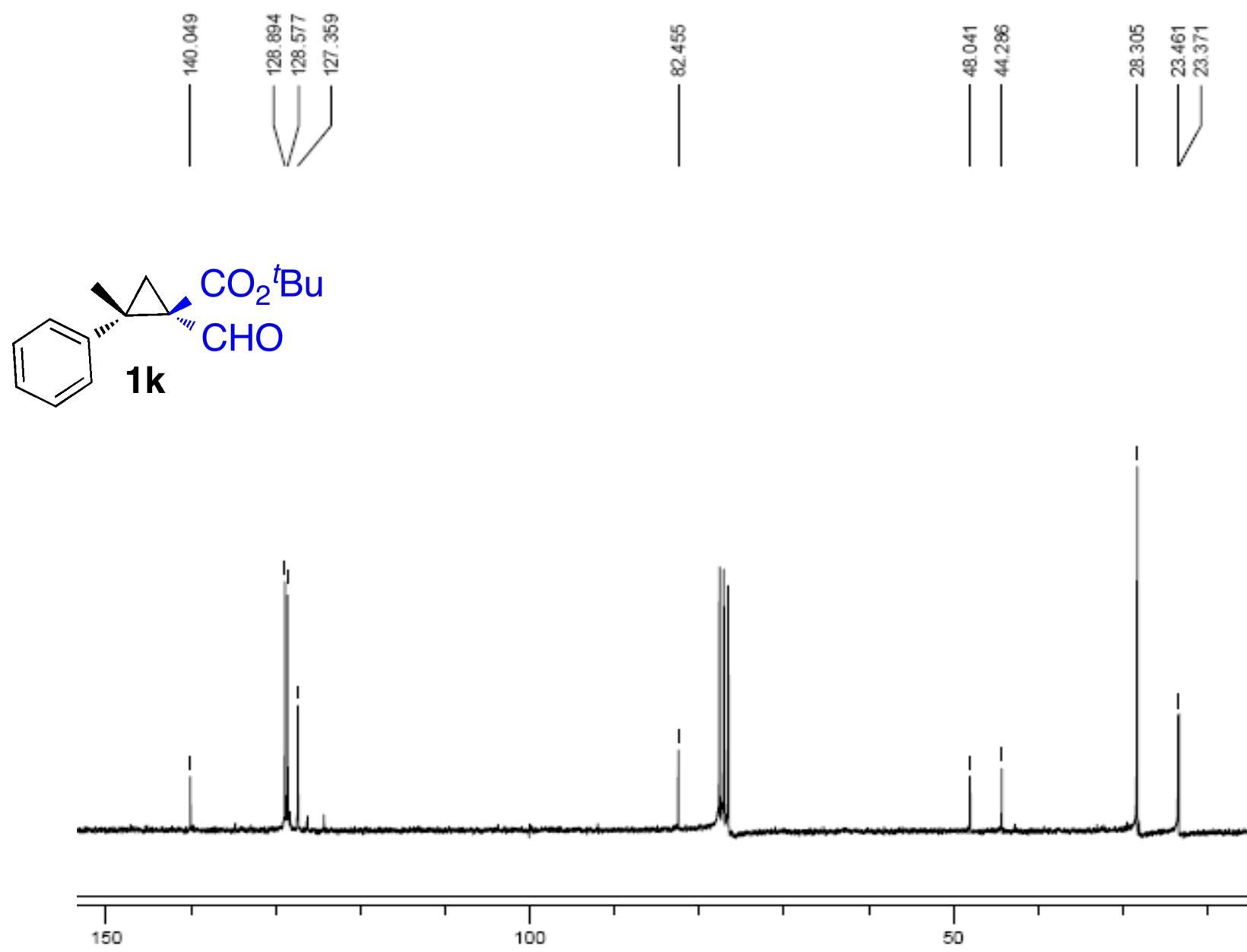


2: 254 nm, 4 nm

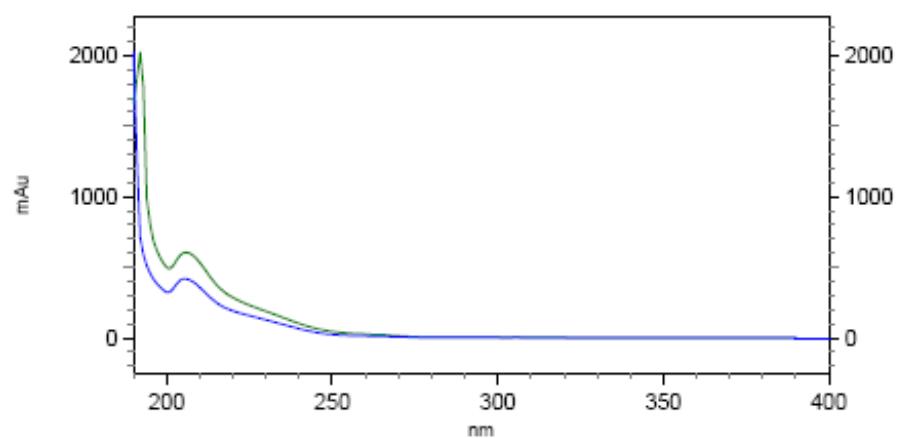
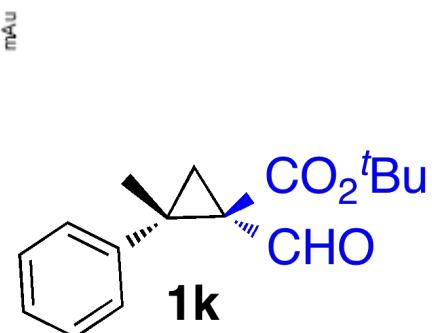
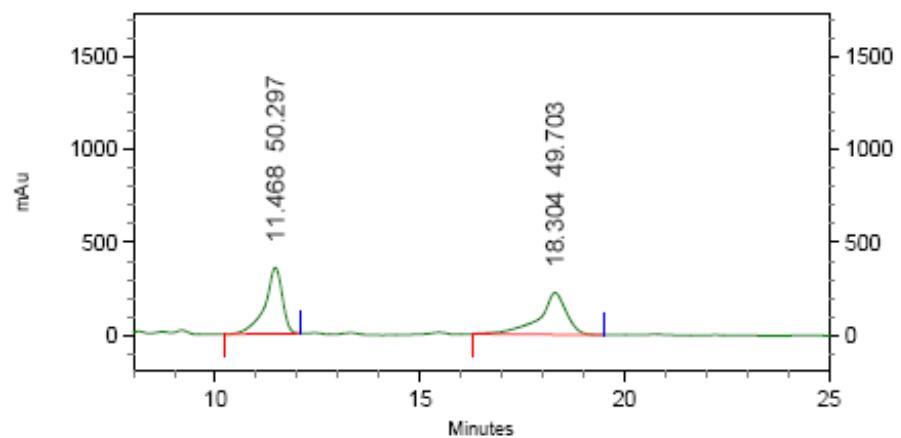
Results

Pk #	Name	Retention Time	Area Percent
1		18.004	2.667
2		29.444	97.333
Totals			100.000





xx-vii-298 whelk 2%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa 4-t-Butylbenzene (OD-H 10-90).met
C:\EZStart\Projects\Default\Data\xx-vii-298 whelk 2%@0.8 ml

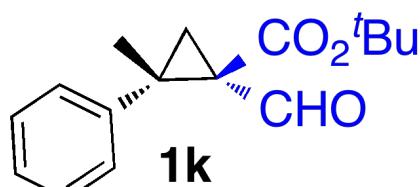
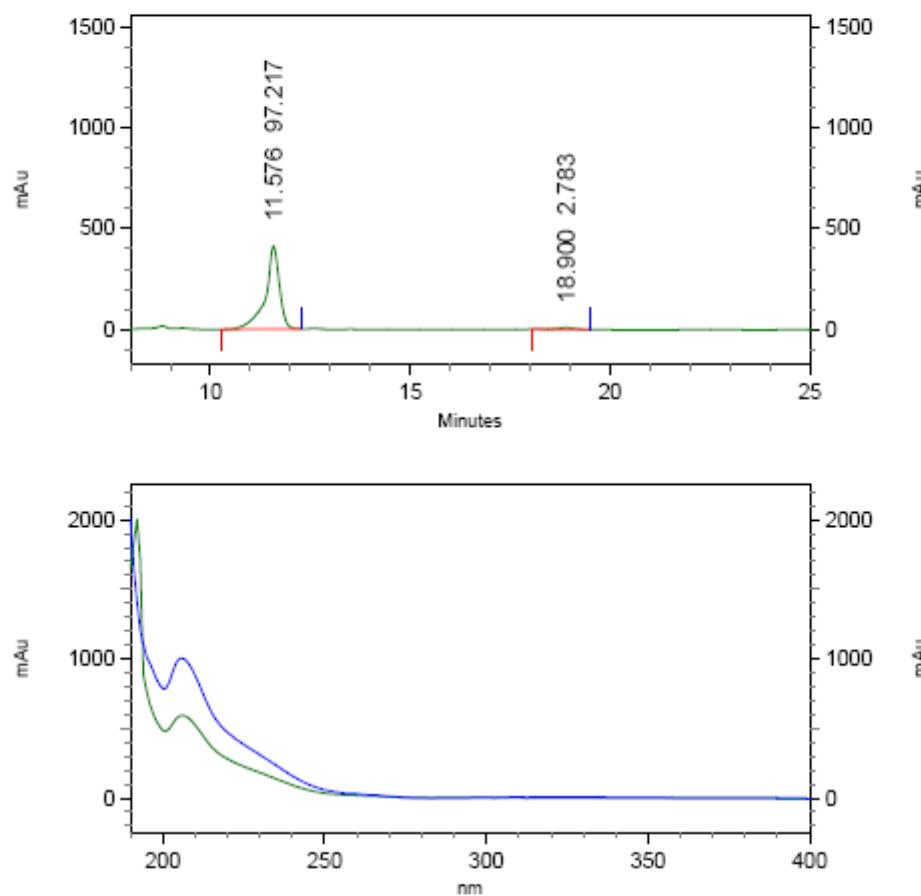


4: 219 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		11.468	50.297
2		18.304	49.703
Totals			100.000

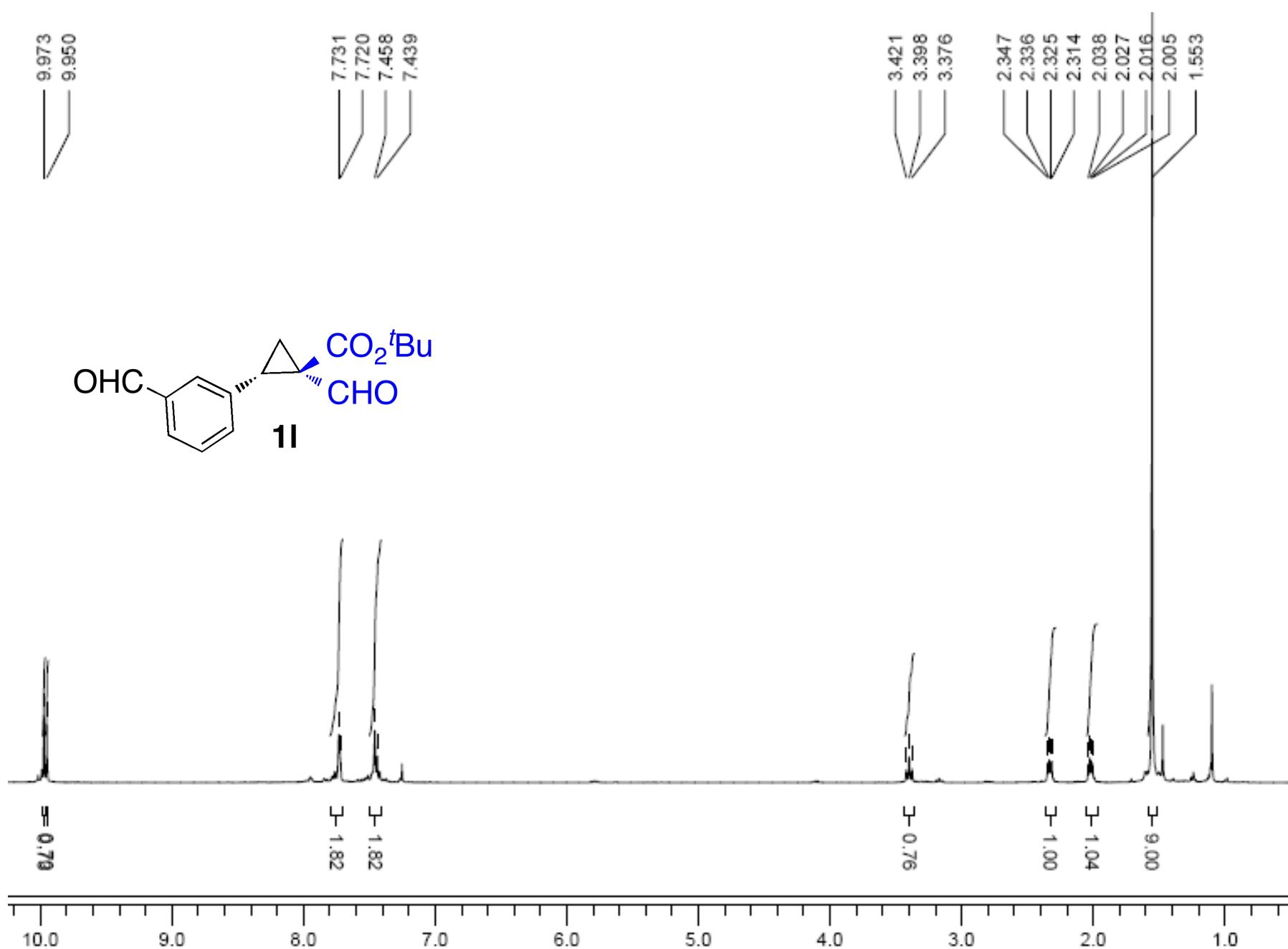
xx-vii-297 whelk 2%@0.8 ml
C:\EZStart\Projects\Default\Method\Shifa 4-t-Butylbenzene (OD-H 10-90).met
C:\EZStart\Projects\Default\Data\xx-vii-297 whelk 2%@0.8 ml

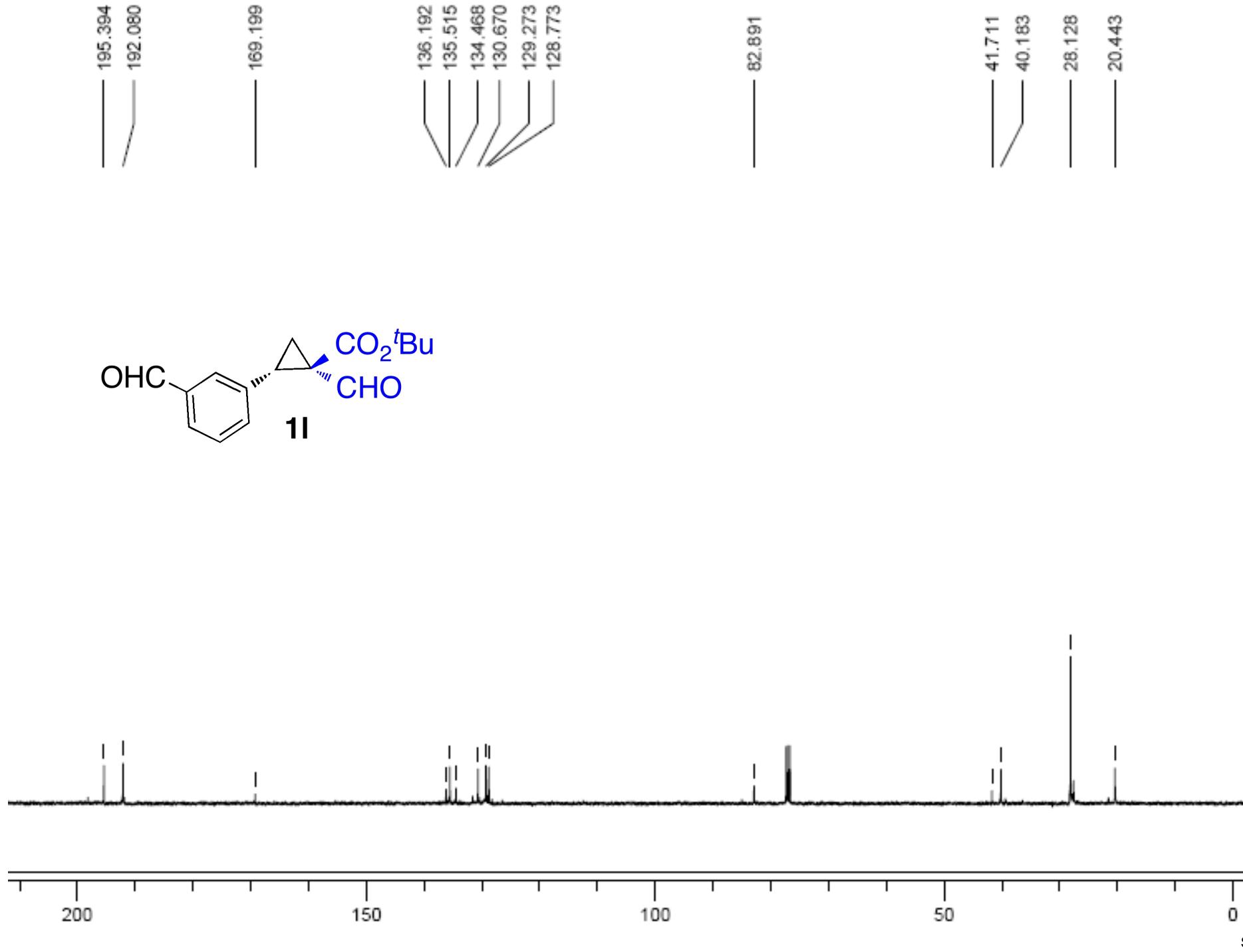


4: 219 nm, 4 nm

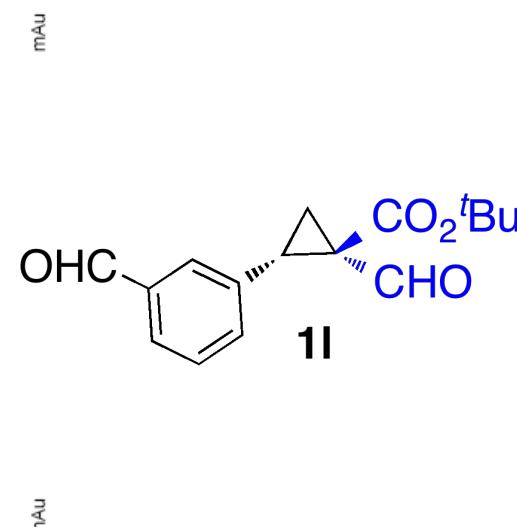
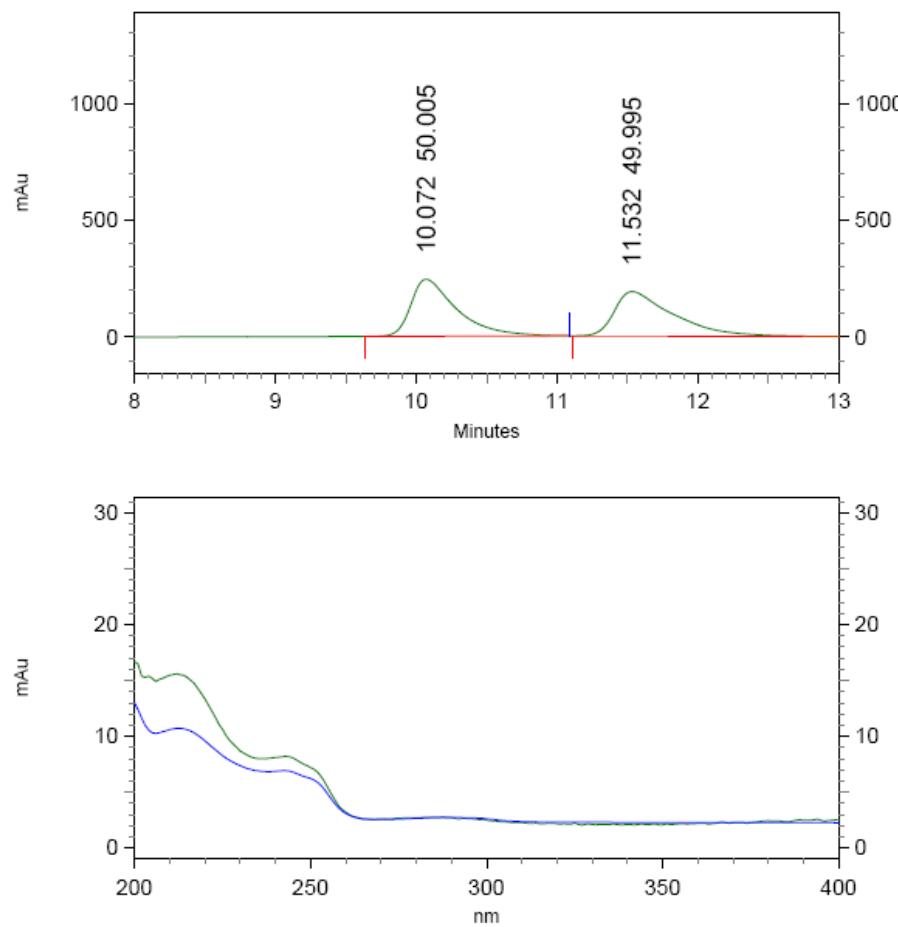
Results

Pk #	Name	Retention Time	Area Percent
1		11.576	97.217
2		18.900	2.783
Totals			100.000





xx-viii-122-1 OJH 5%@1.0 ml
C:\EZStart\Projects\Default\Method\snowtemp short.met
C:\EZStart\Projects\Default\Data\xx-viii-122-1 OJH 5%@1.0 ml



8: 223 nm, 4 nm

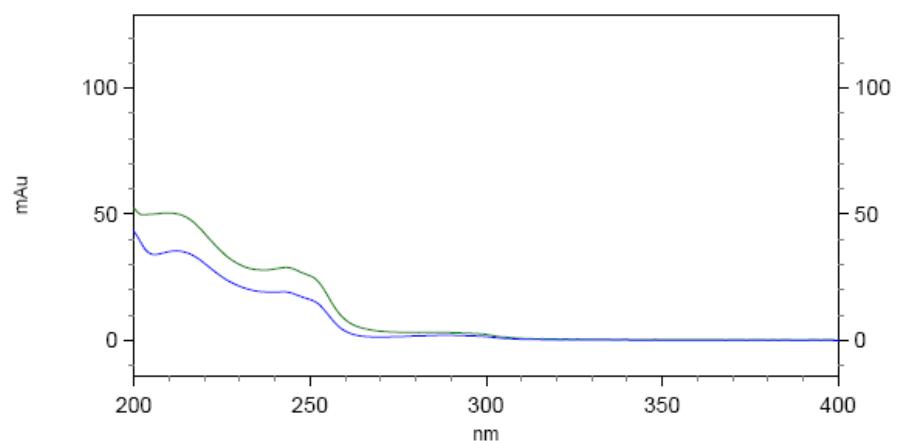
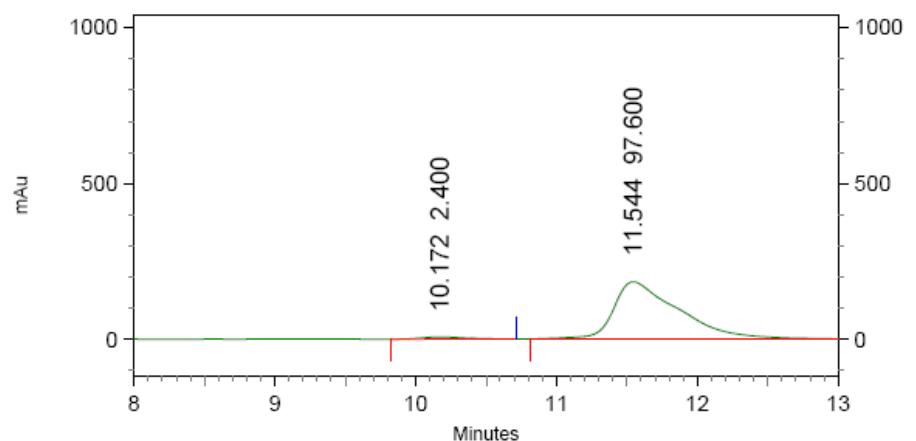
Results

Pk #	Name	Retention Time	Area Percent
1		10.072	50.005
2		11.532	49.995
Totals			100.000

xx-viii-122-2 OJH 5%@1.0 ml

C:\EZStart\Projects\Default\Method\snowtemp short.met

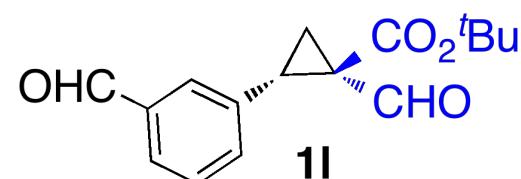
C:\EZStart\Projects\Default\Data\xx-viii-122-2 OJH 5%@1.0 ml

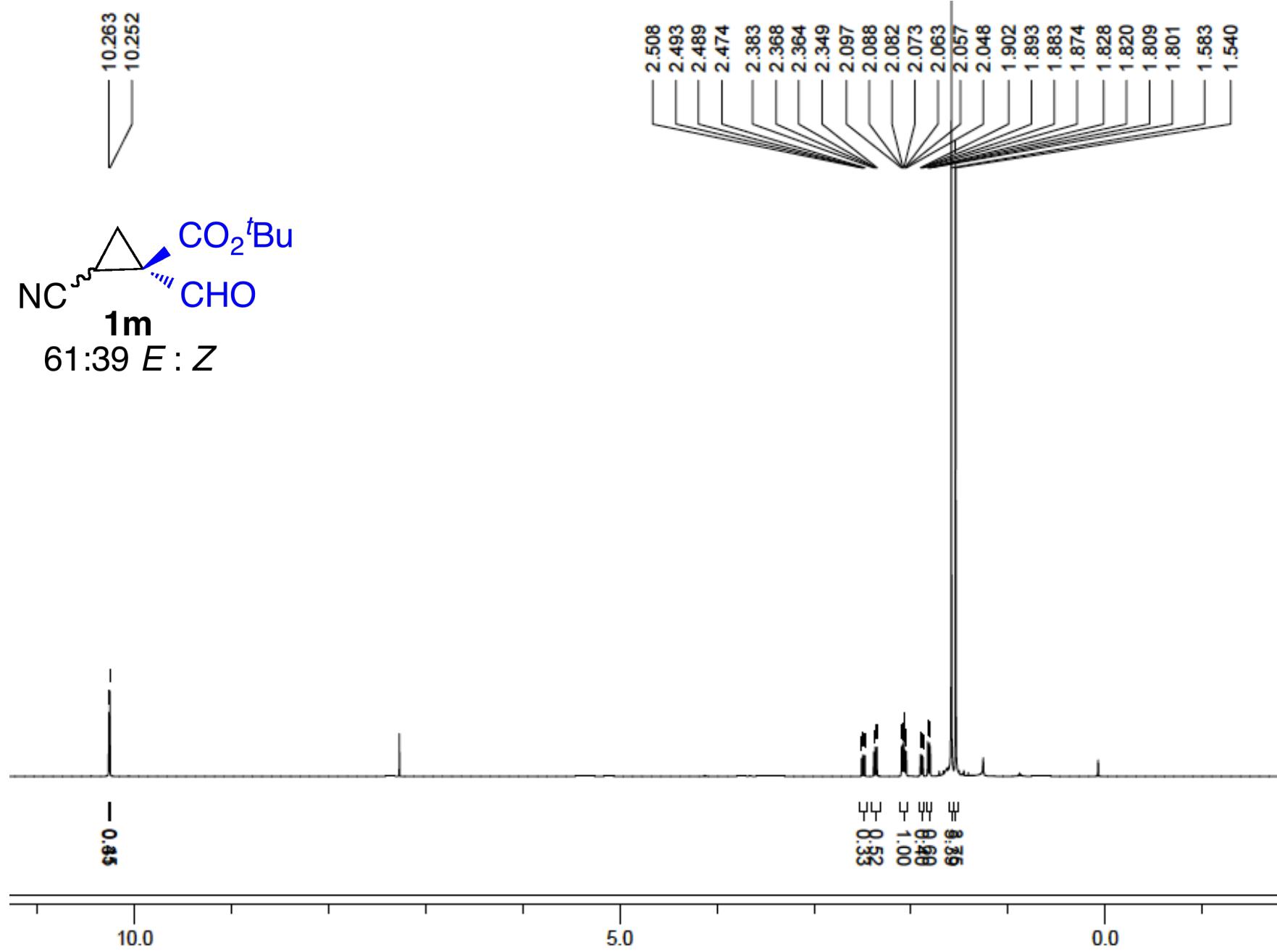


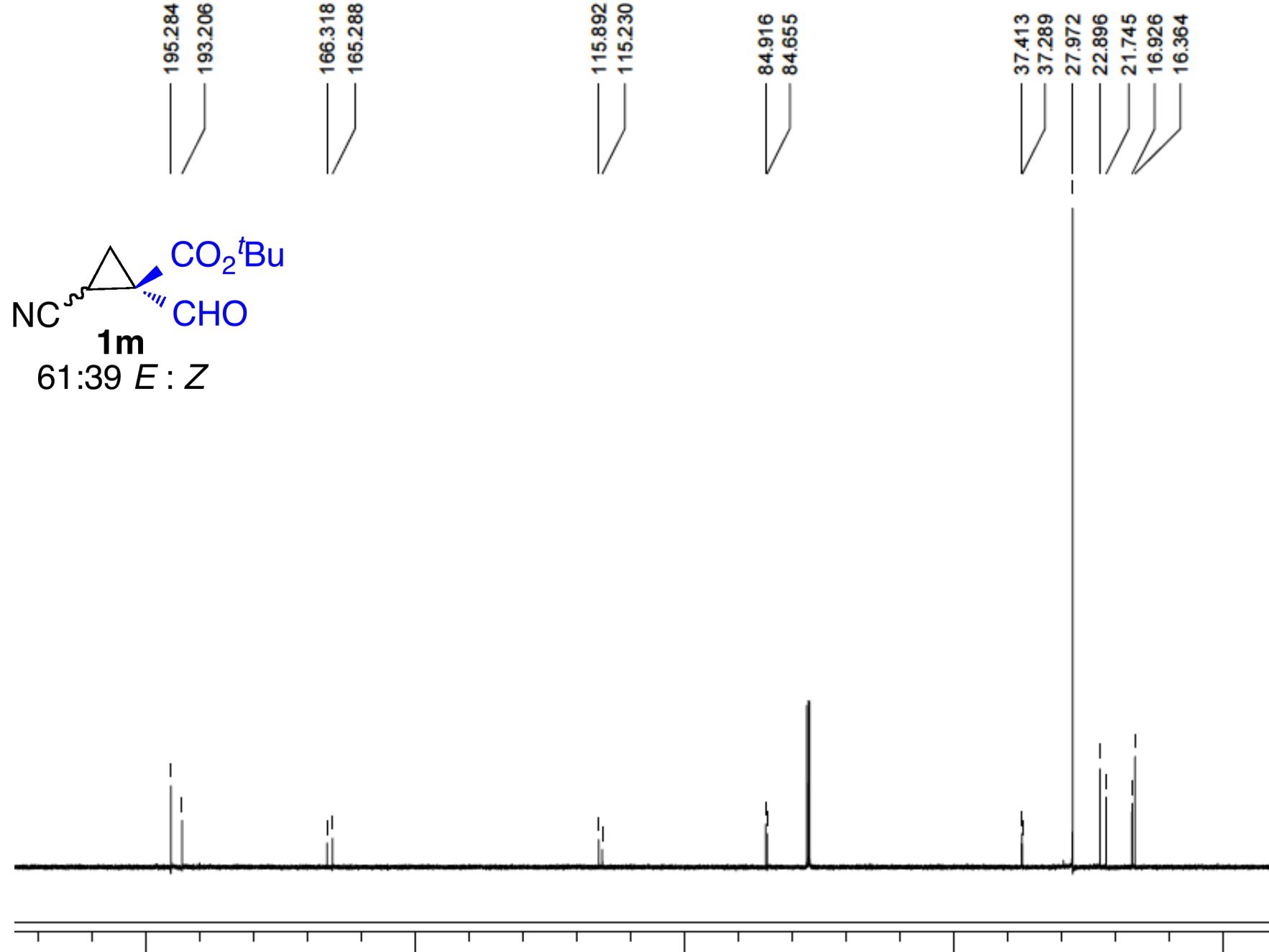
8: 223 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		10.172	2.400
2		11.544	97.600
Totals			100.000



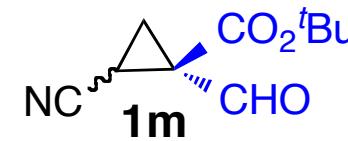
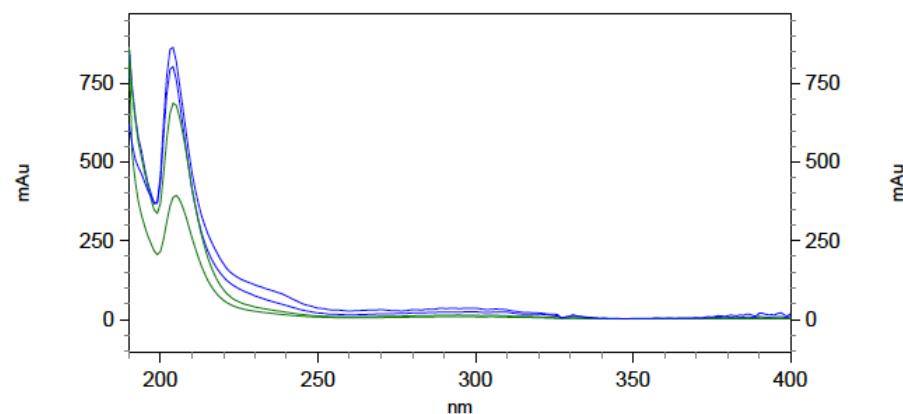
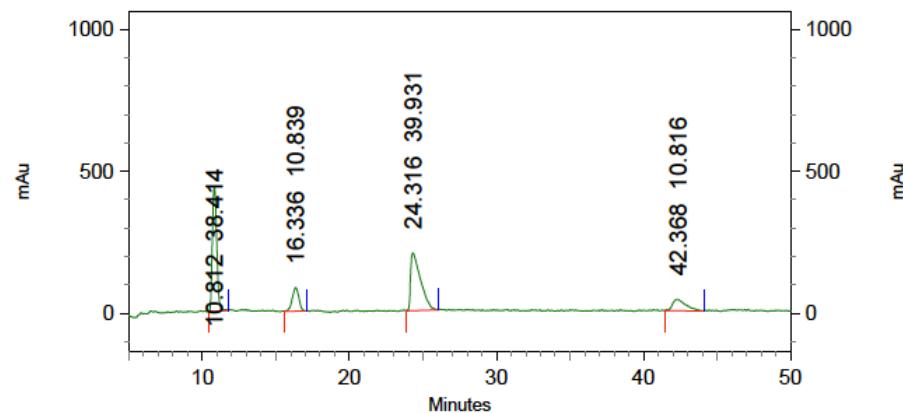




XC-IX-216RE-ADH1%1ml

C:\EZStart\Projects\Default\Method\XC-1%-ADH1ml.met

C:\EZStart\Projects\Default\Data\XC-IX-216RE-ADH1%1ml



3: 206 nm, 4 nm

Results

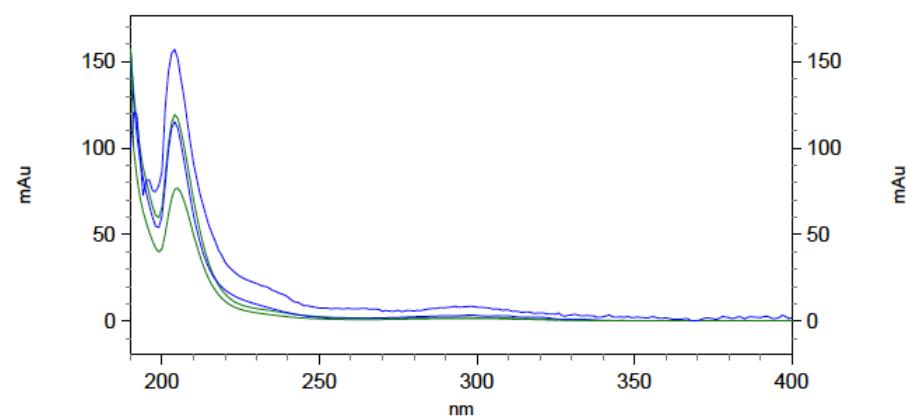
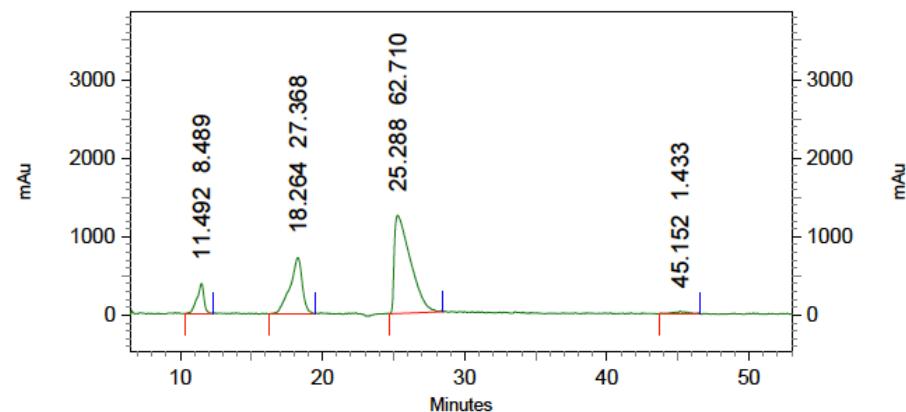
Name	Retention Time	Area Percent	Pk #
	10.812	38.414	1
	16.336	10.839	2
	24.316	39.931	3
	42.368	10.816	4

Totals	100.000
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XC-IX-220-ADH1%1ml

C:\EZStart\Projects\Default\Method\XC-1%-ADH1ml.met

C:\EZStart\Projects\Default\Data\XC-IX-220-ADH1%1ml

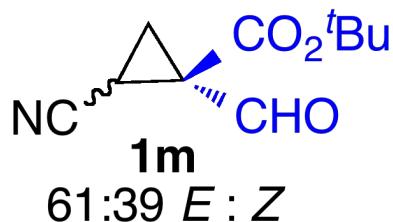


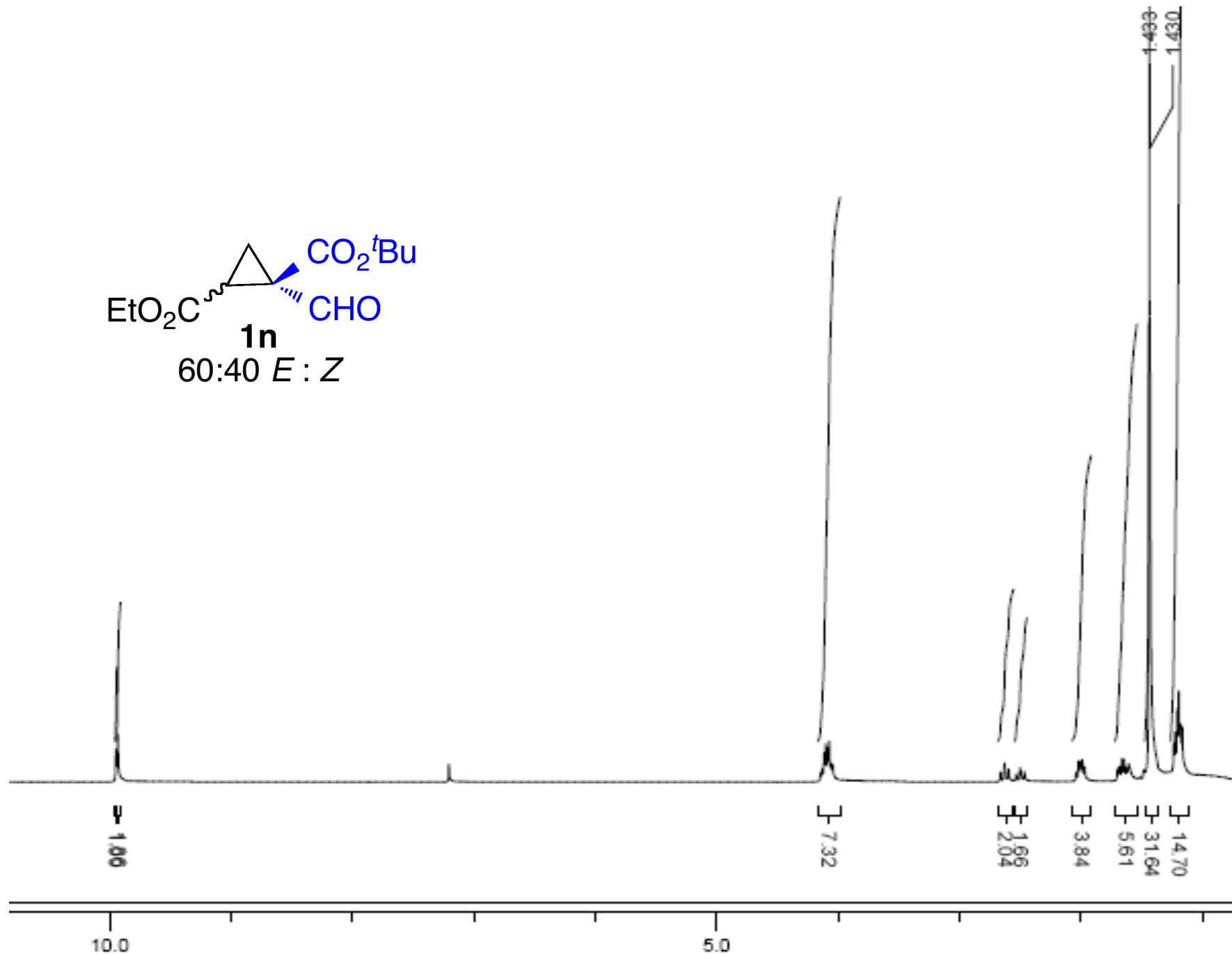
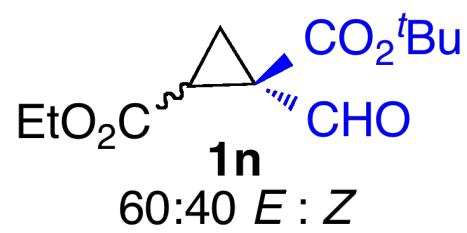
3: 207 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	11.492	8.489	1
	18.264	27.368	2
	25.288	62.710	3
	45.152	1.433	4

Totals	100.000
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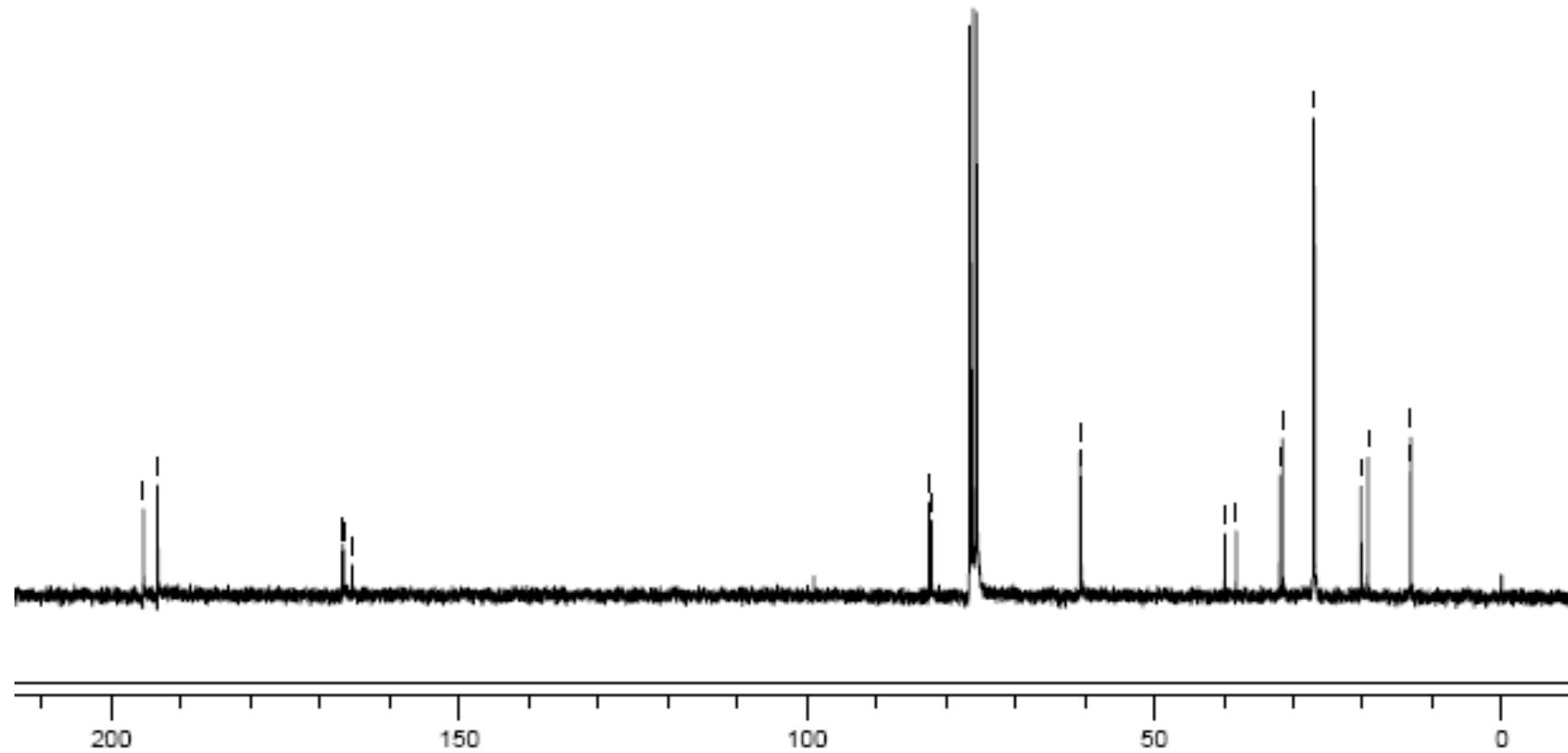
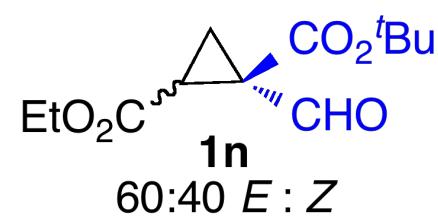
195.387
193.354

166.794
166.671
166.553
165.370

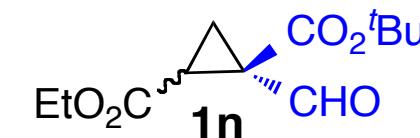
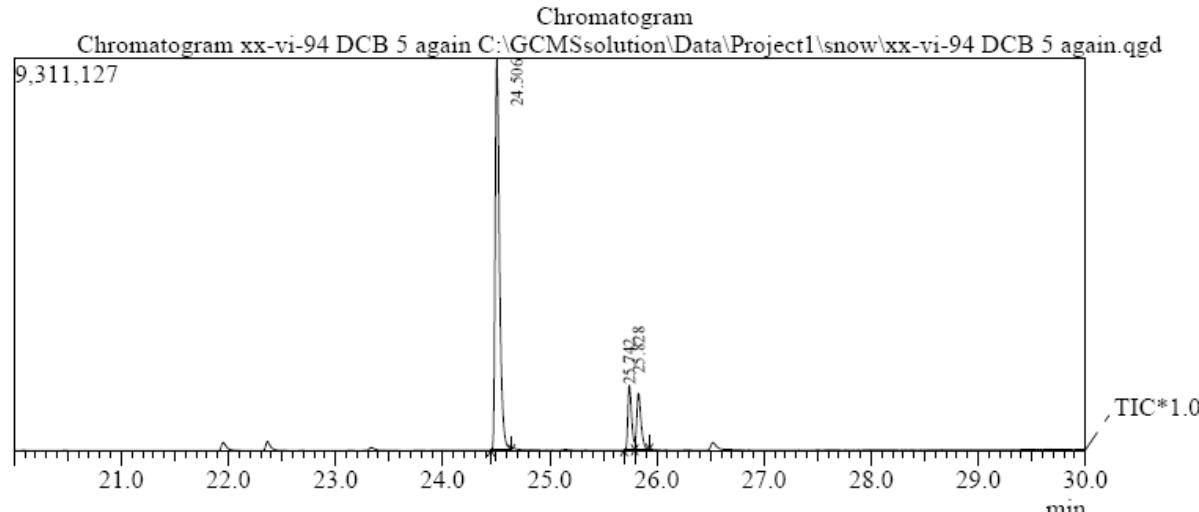
82.360
82.051

60.611
60.527

39.817
38.178
31.913
31.505
27.005
26.932
20.193
19.233
13.119
13.068



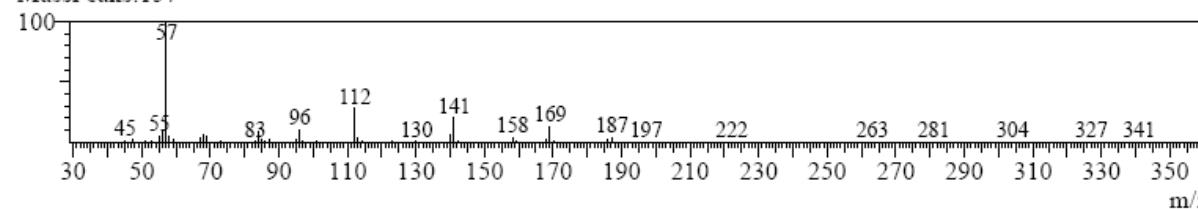
Sample Name : xx-vi-94 DCB 5 again
 Sample ID : xx-vi-94 DCB 5 again



Spectrum

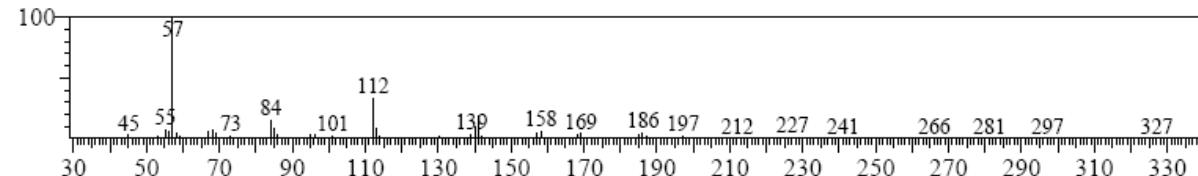
Peak#:1 R.Time:24.5(Scan#:5853)

MassPeaks:157

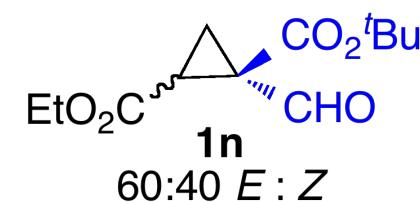
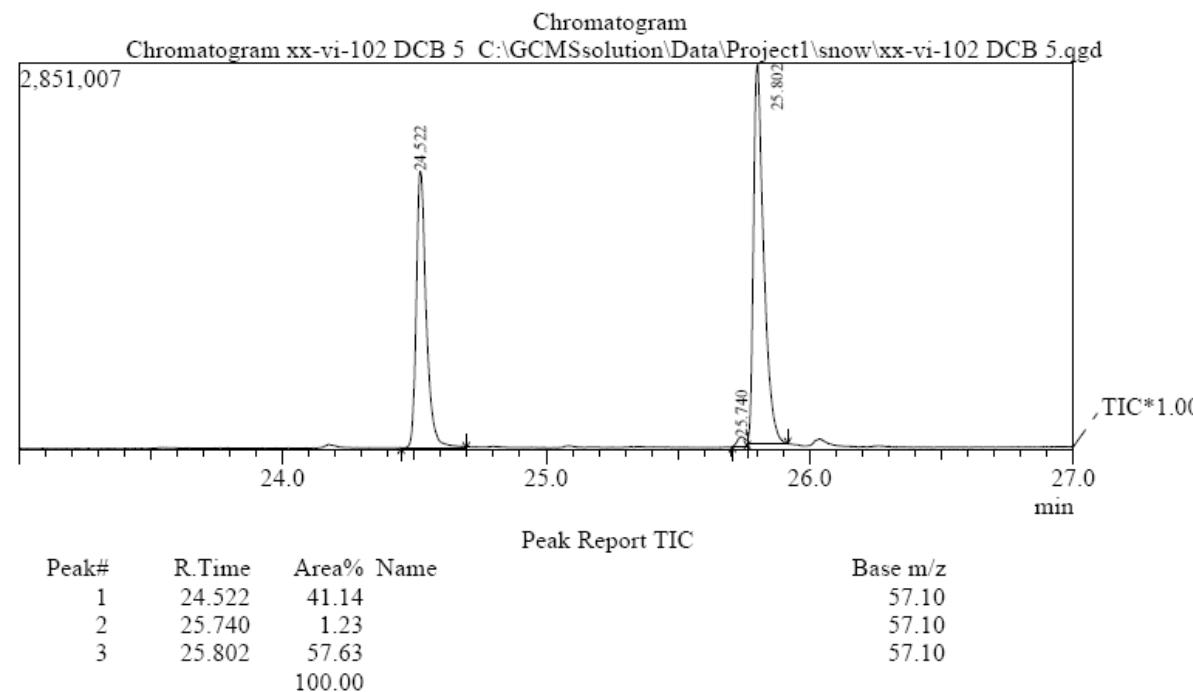


Peak#:2 R.Time:25.7(Scan#:6224)

MassPeaks:140



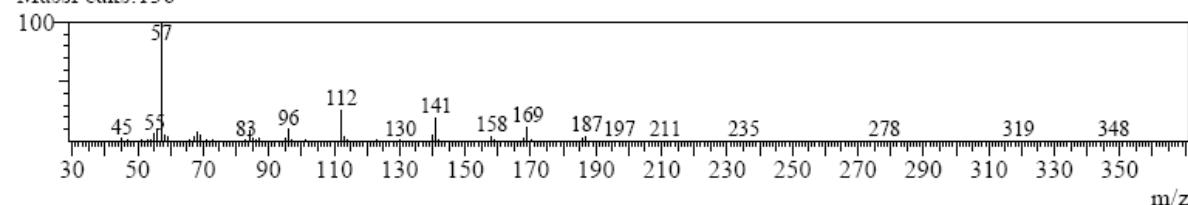
Sample Name : xx-vi-102 DCB 5
 Sample ID : xx-vi-102 DCB 5



Spectrum

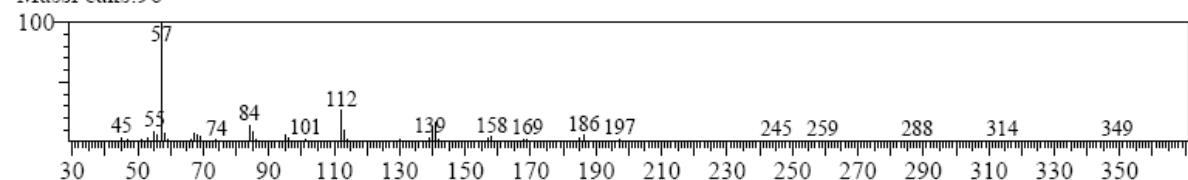
Peak#:1 R.Time:24.5(Scan#:5858)

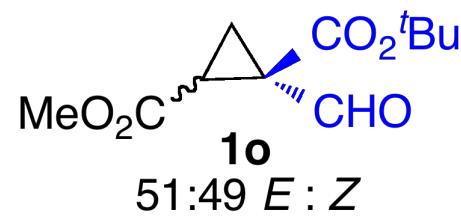
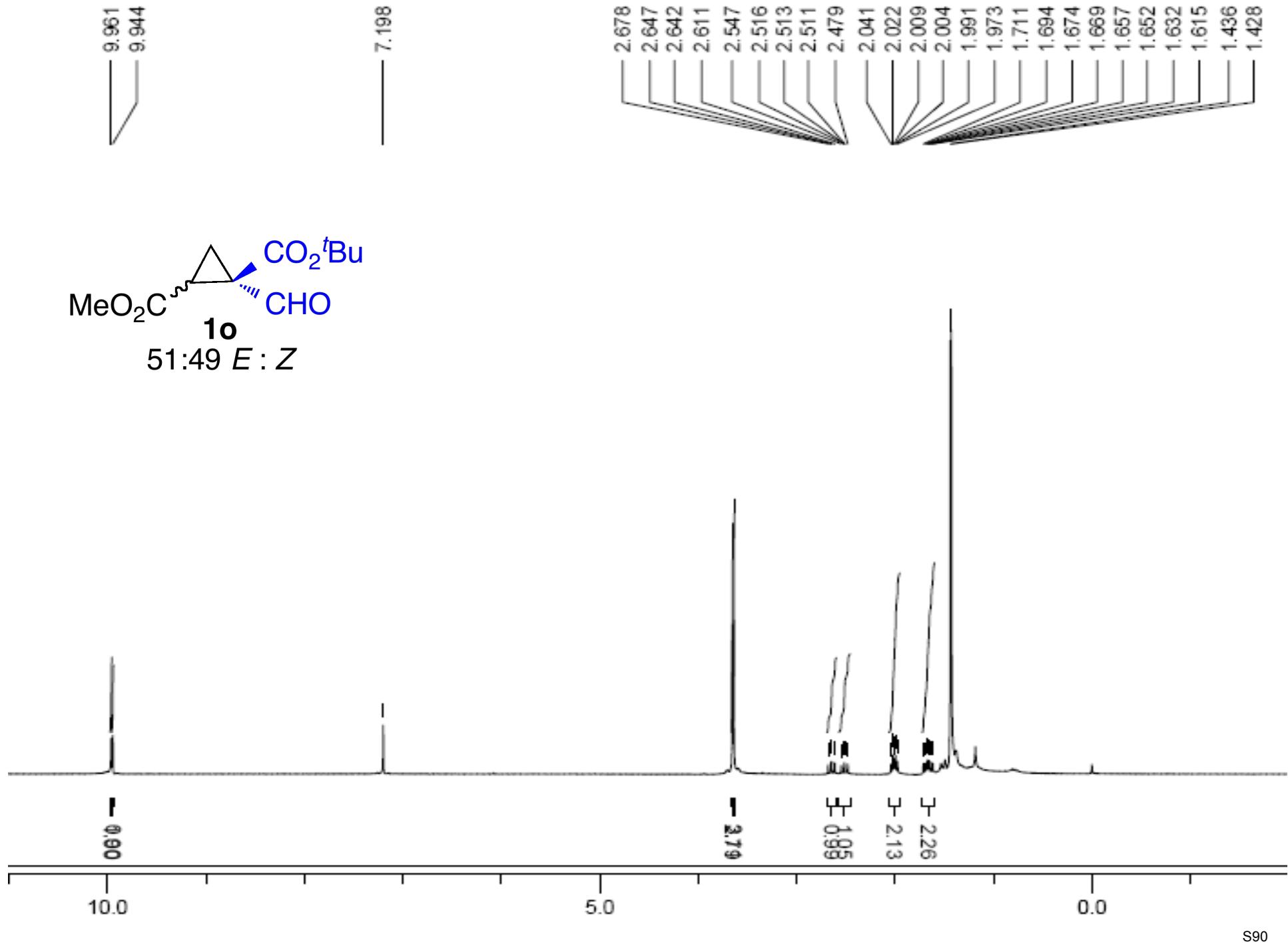
MassPeaks:136

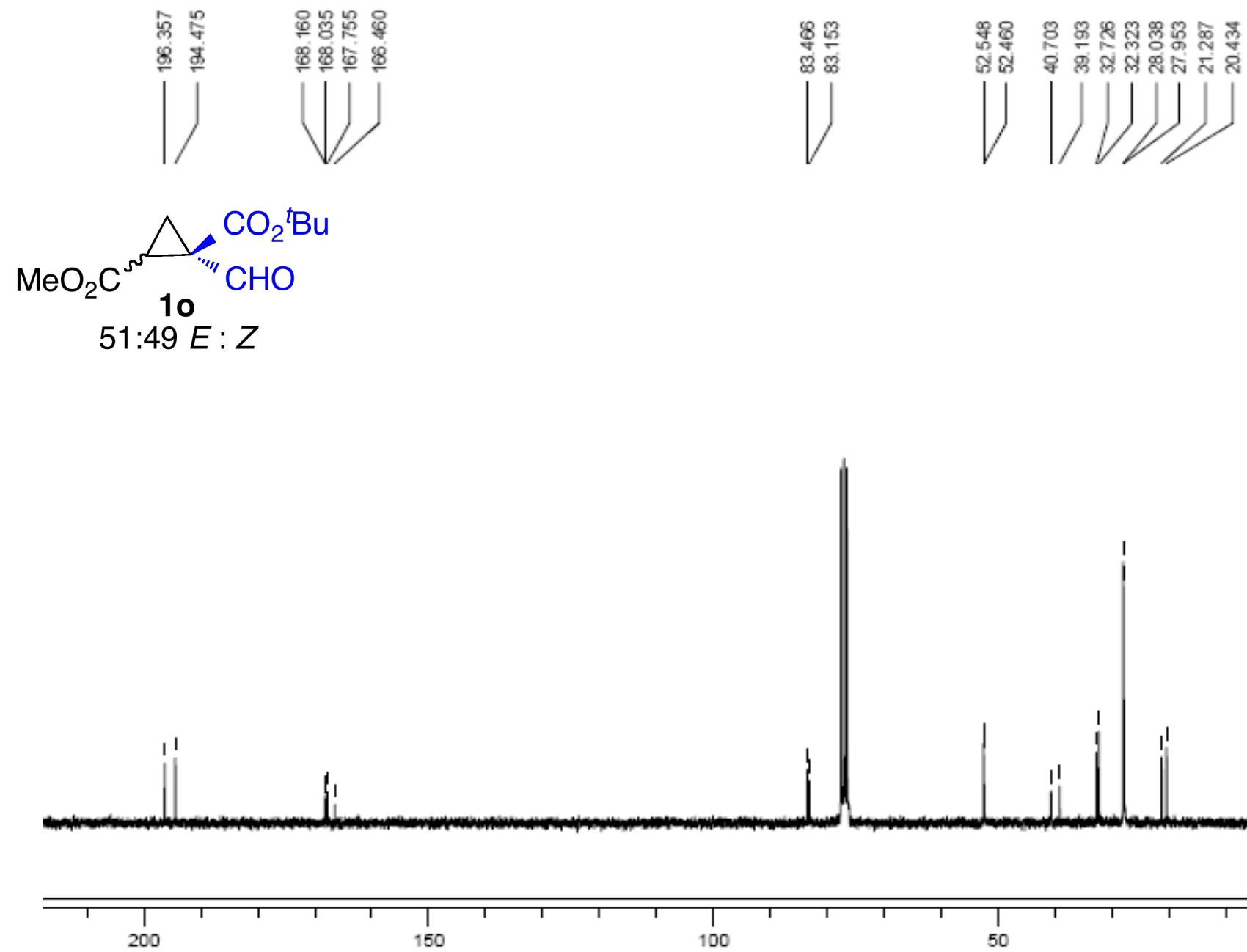


Peak#:2 R.Time:25.7(Scan#:6223)

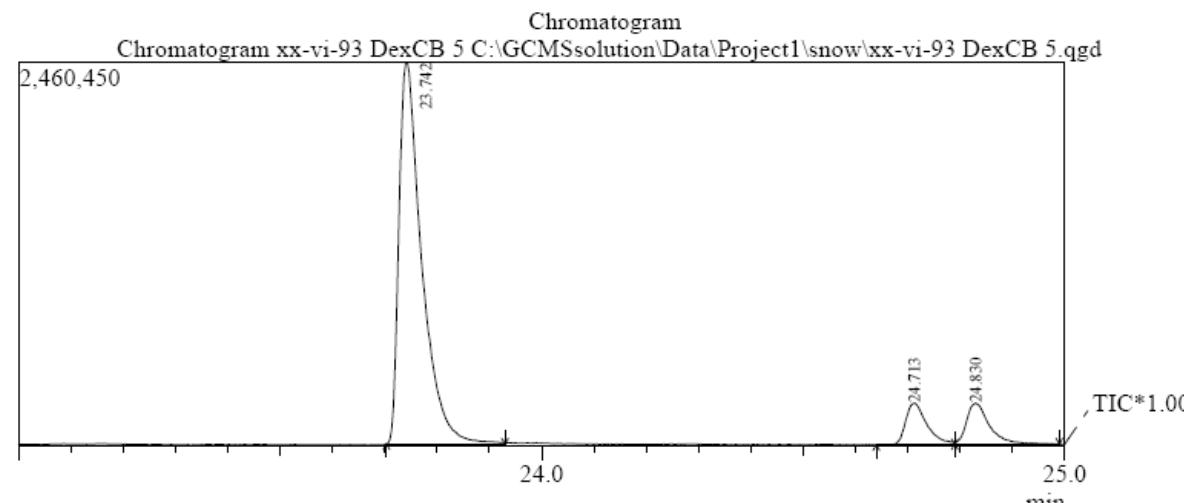
MassPeaks:96



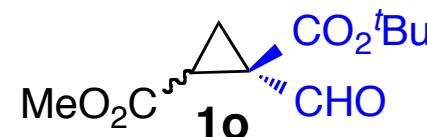




Sample Name : xx-vi-93 DexCB 5
 Sample ID : xx-vi-93 DexCB 5



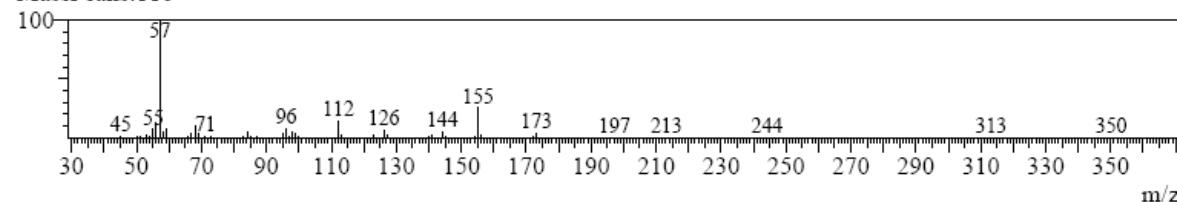
Peak#	R.Time	Area%	Name	Base m/z
1	23.742	82.78		57.10
2	24.713	8.44		57.10
3	24.830	8.78		57.10
		100.00		



Spectrum

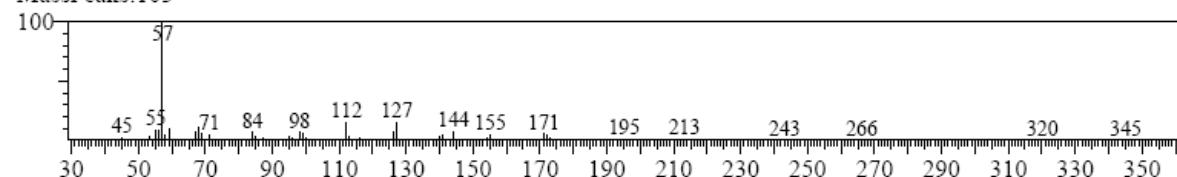
Peak#:1 R.Time:23.7(Scan#:5624)

MassPeaks:116

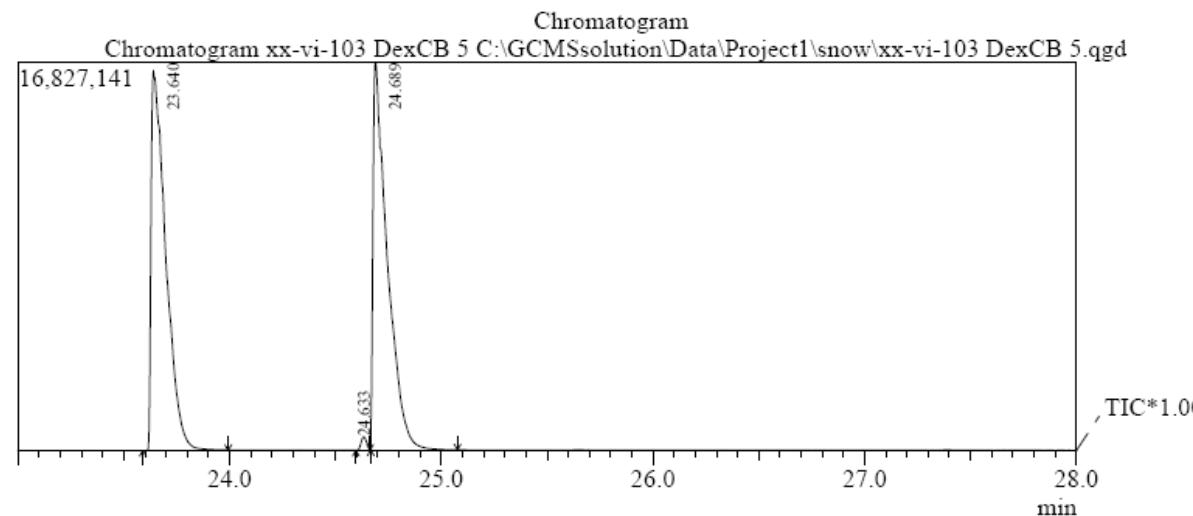


Peak#:2 R.Time:24.7(Scan#:5915)

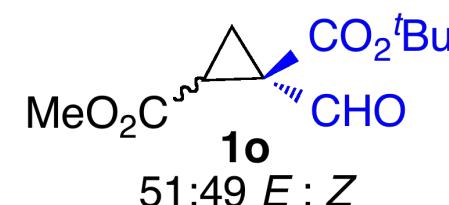
MassPeaks:103



Sample Name : xx-vi-103 DexCB 5
Sample ID : xx-vi-103 DexCB 5



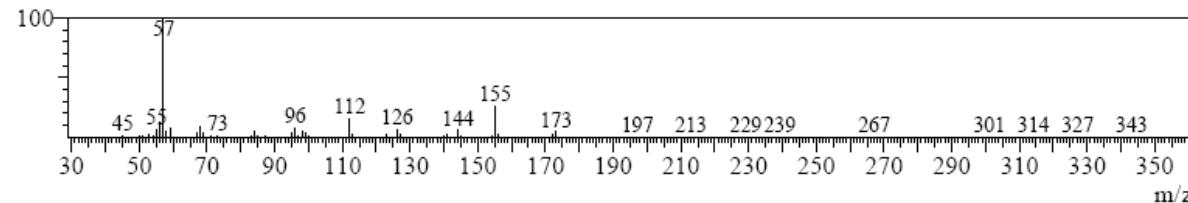
Peak#	R.Time	Area%	Name	Base m/z
1	23.640	49.71		57.10
2	24.633	0.74		57.10
3	24.689	49.55		57.10
		100.00		



Spectrum

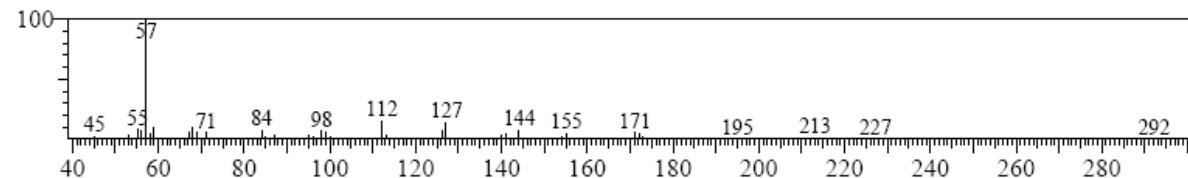
Peak#:1 R.Time:23.6(Scan#:5593)

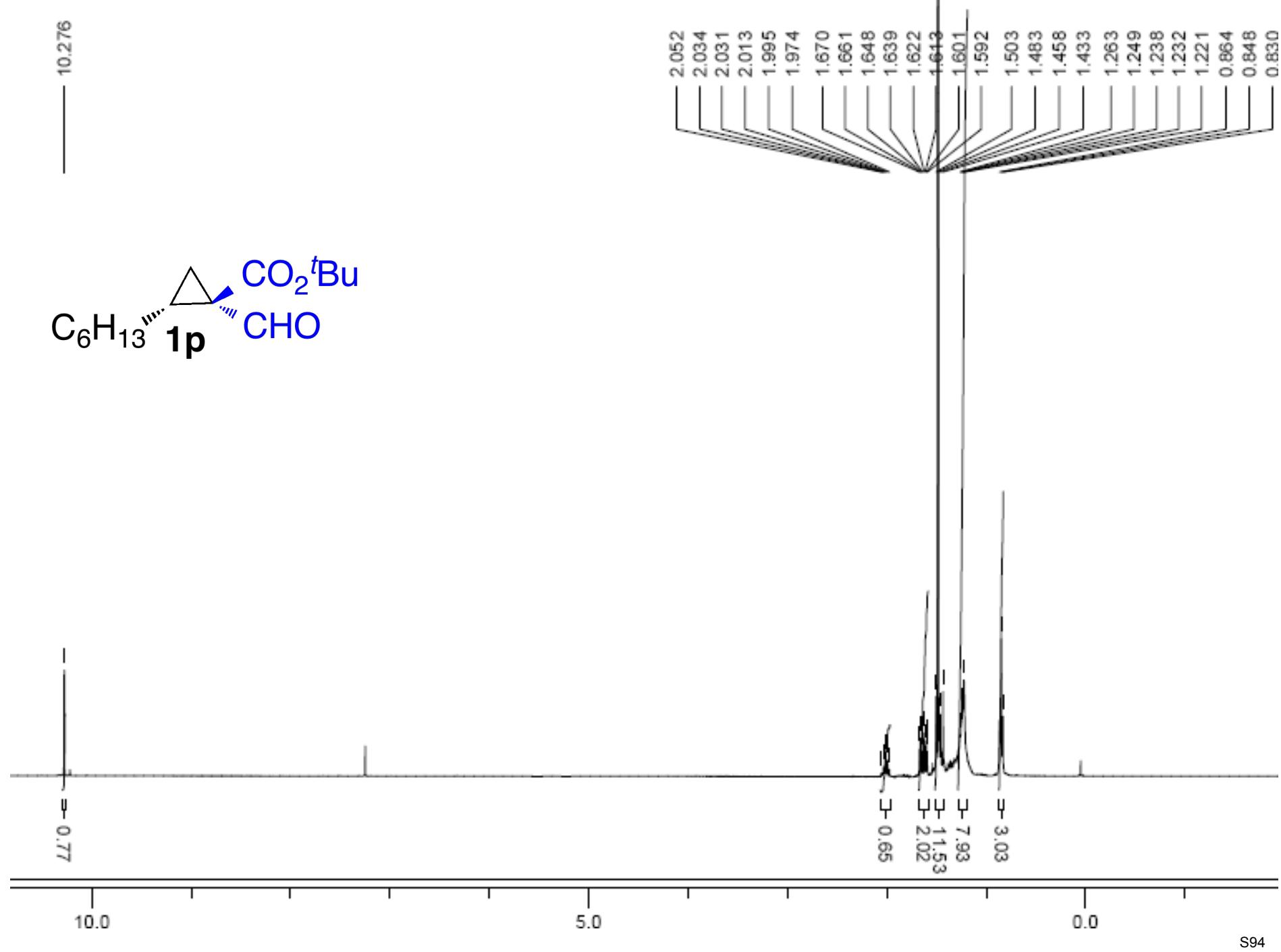
MassPeaks:150

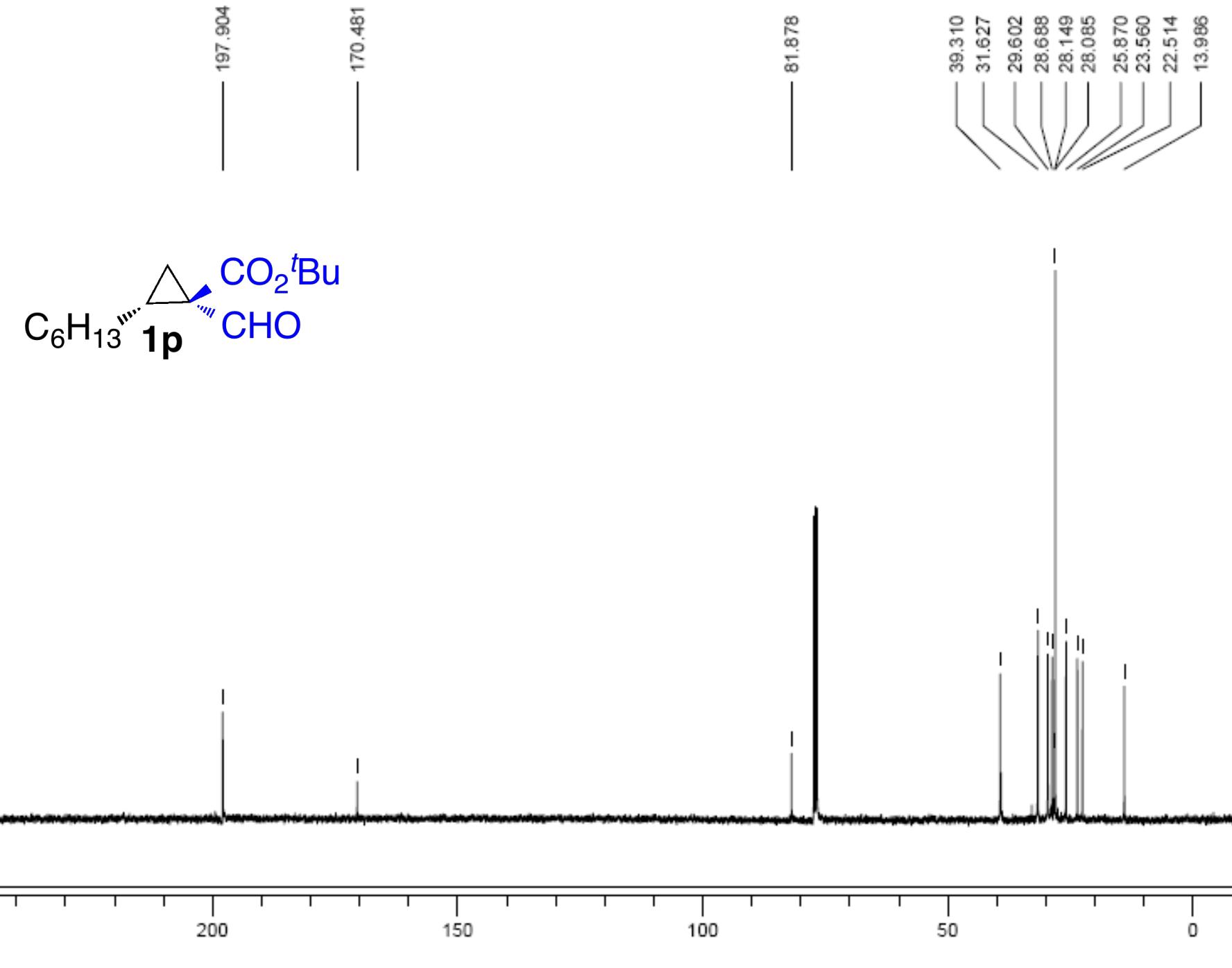


Peak#:2 R.Time:24.6(Scan#:5891)

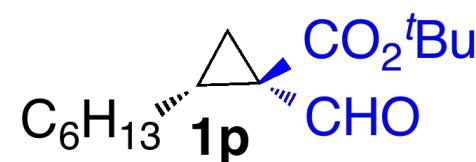
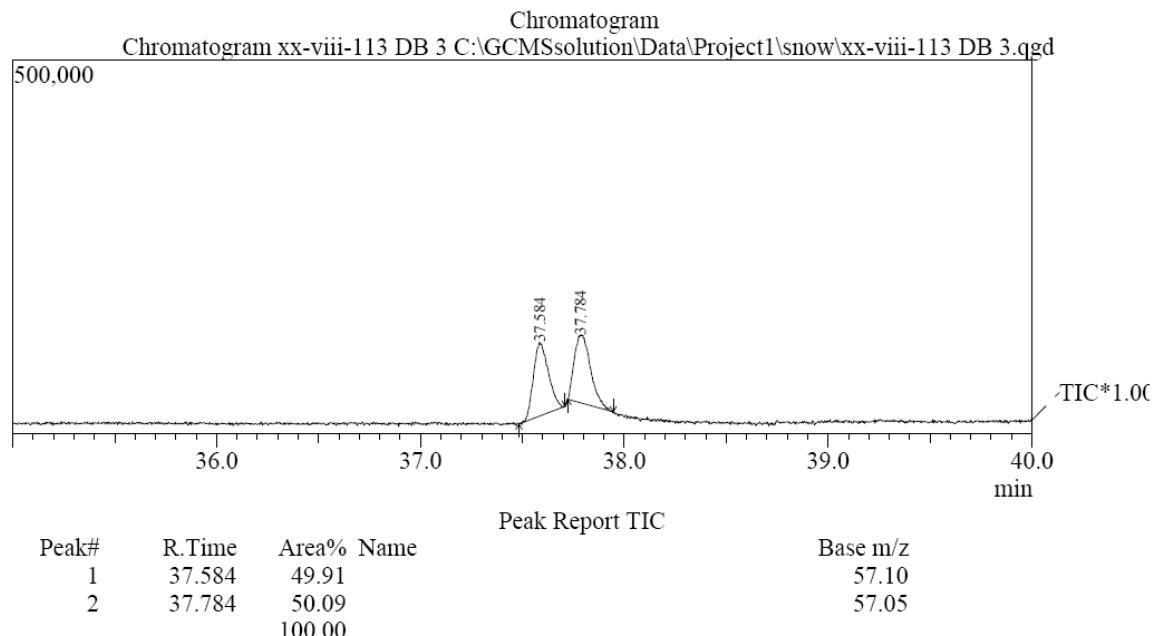
MassPeaks:104







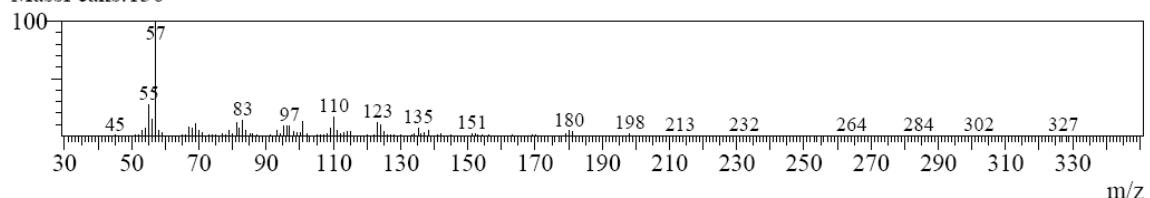
Sample Name : xx-viii-113 DB 3
 Sample ID : xx-viii-113 DB 3



Spectrum

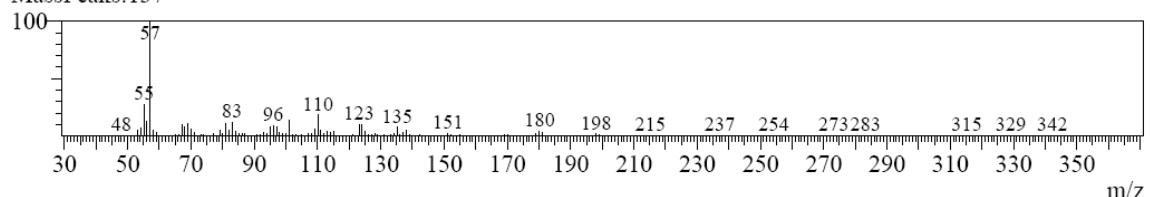
Peak#:1 R.Time:37.6(Scan#:9776)

MassPeaks:136

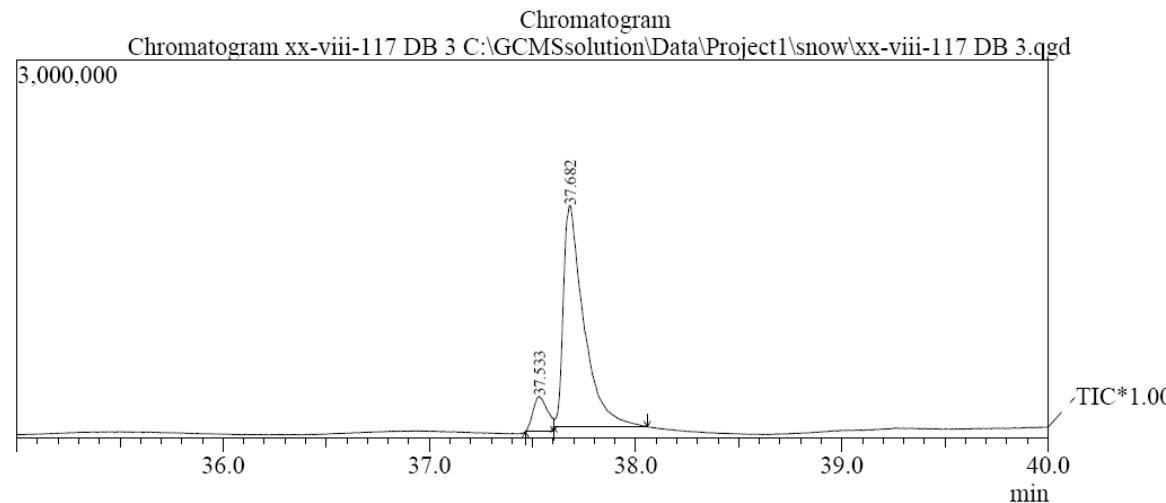


Peak#:2 R.Time:37.8(Scan#:9836)

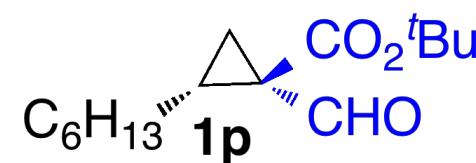
MassPeaks:137



Sample Name : xx-viii-117 DB 3
Sample ID : xx-viii-117 DB 3



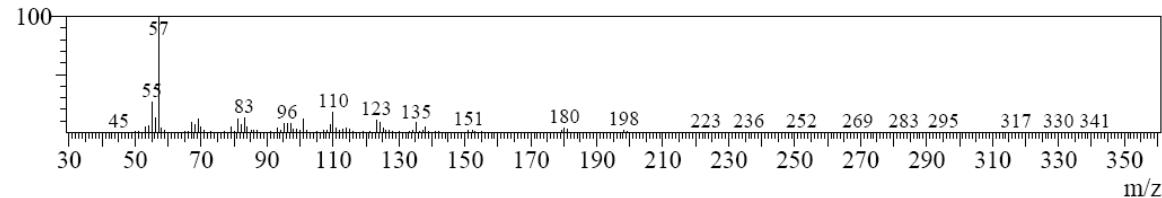
Peak Report TIC			
Peak#	R.Time	Area%	Name
1	37.533	10.12	
2	37.682	89.88	
		100.00	



Spectrum

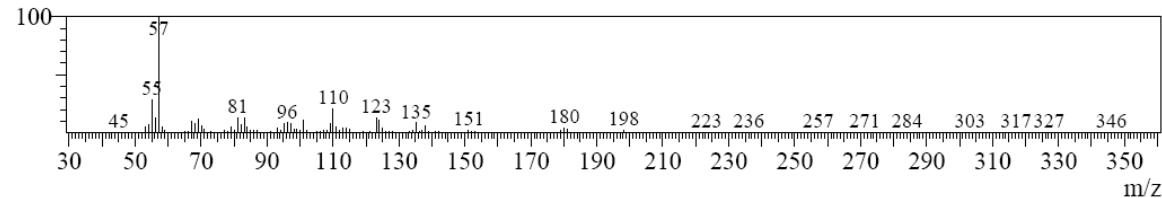
Peak#:1 R.Time:37.5(Scan#:9761)

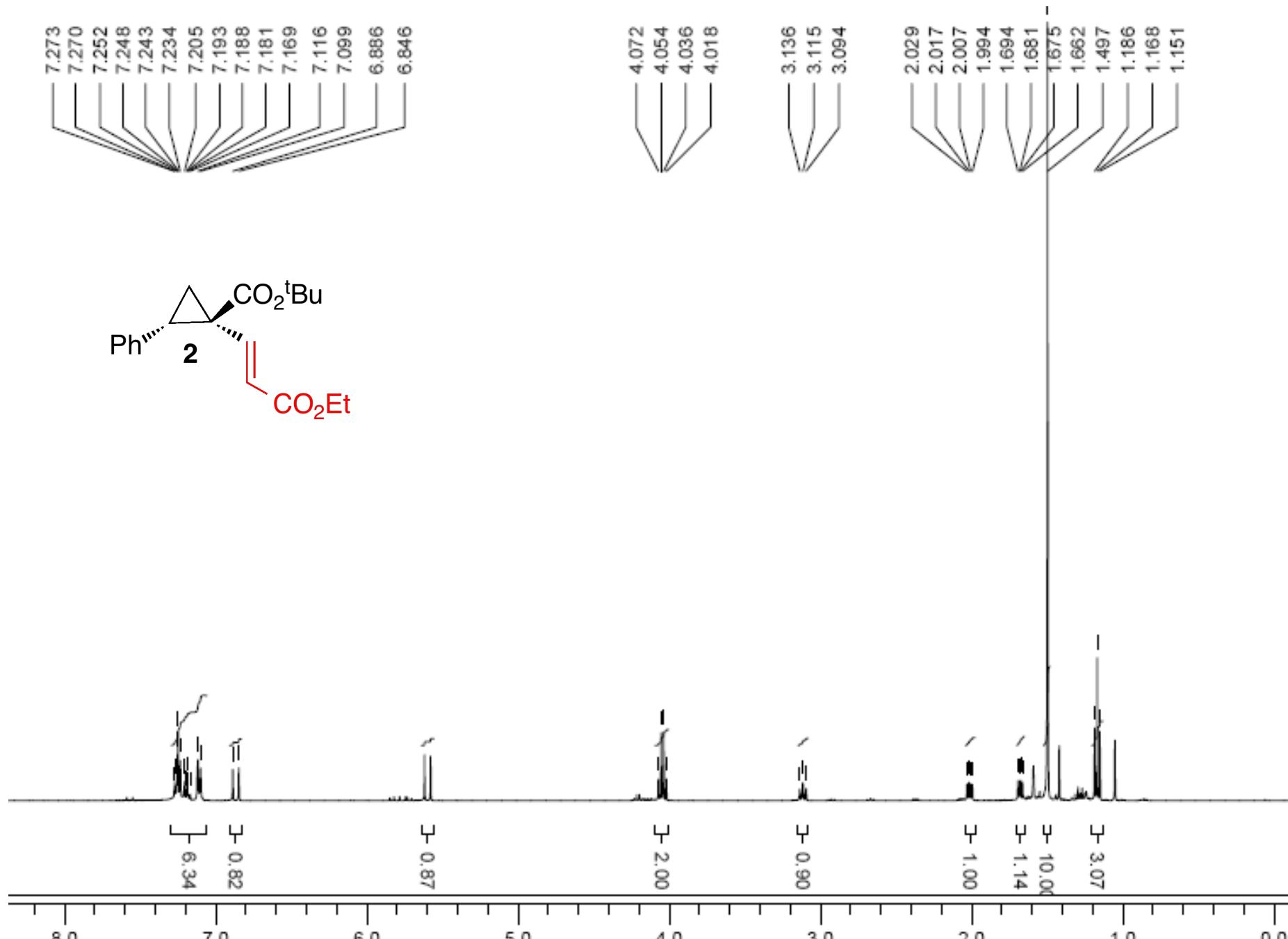
MassPeaks:165

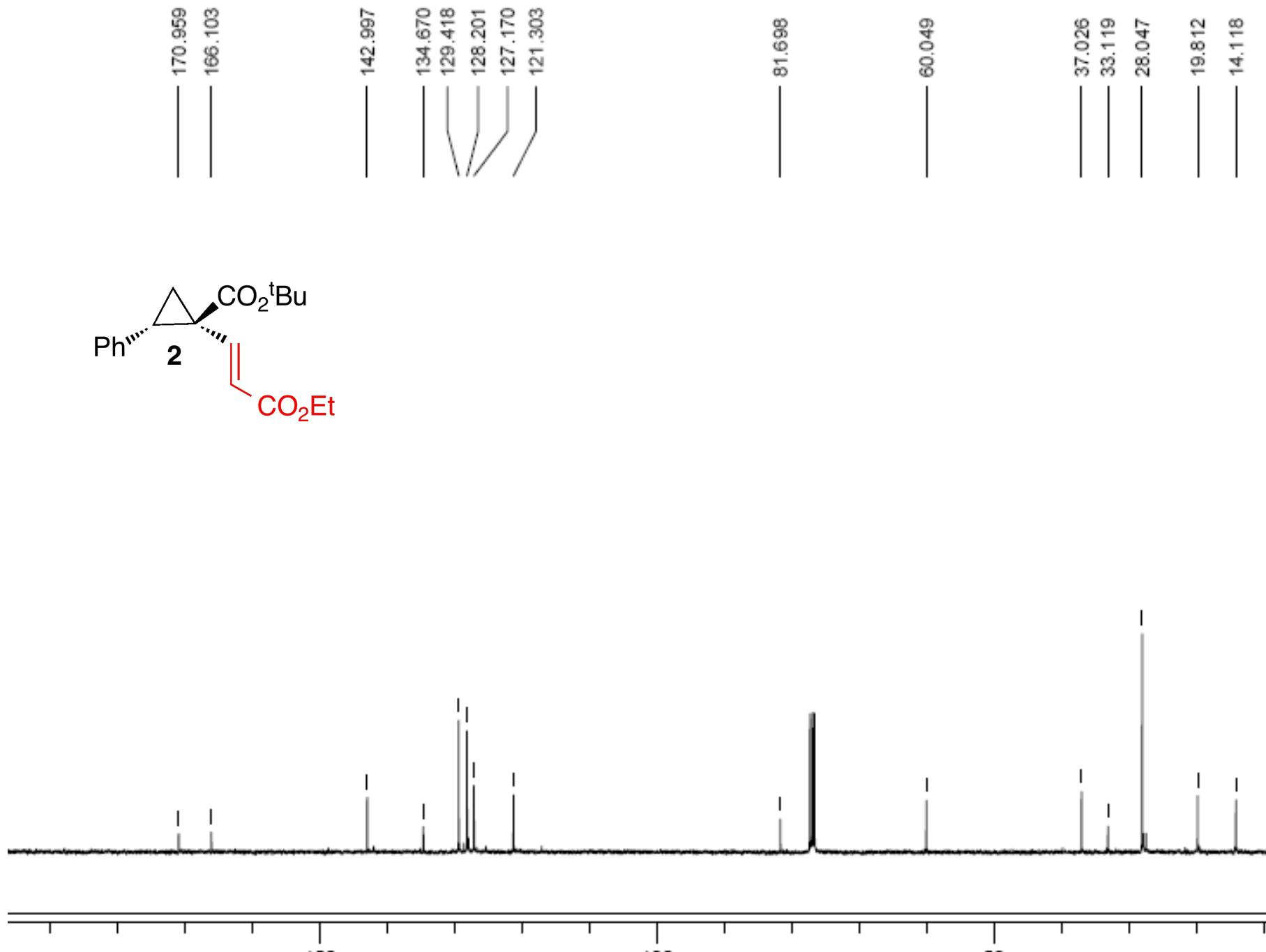


Peak#:2 R.Time:37.7(Scan#:9806)

MassPeaks:169



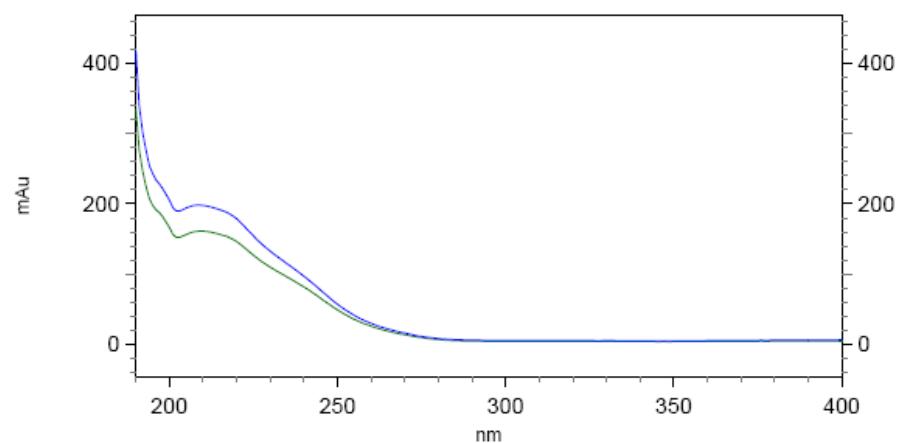
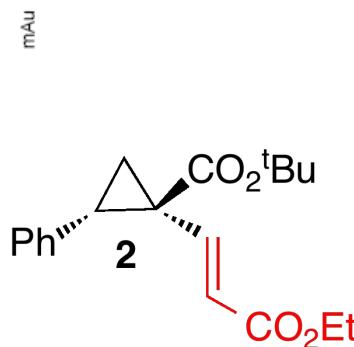
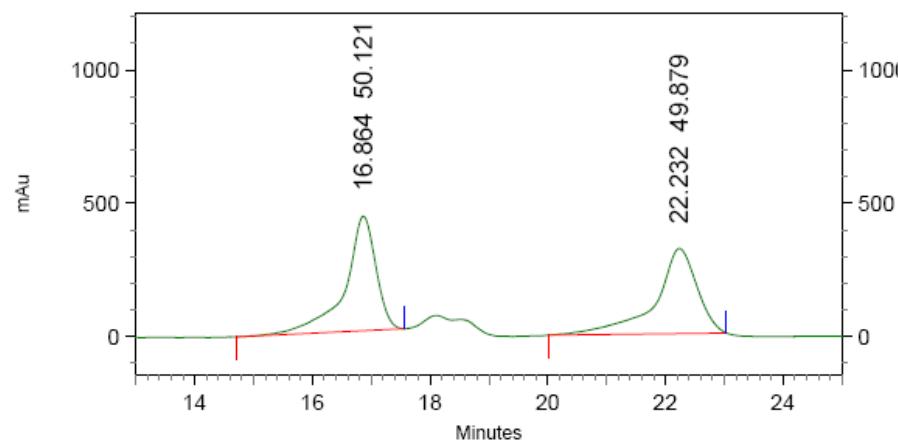




xx-viii-110 whelk 1%@1.0 ml

C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 5%Whelk.met

C:\EZStart\Projects\Default\Data\xx-viii-110 whelk 1%@1.0 ml



2: 209 nm, 4 nm

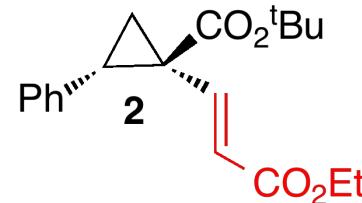
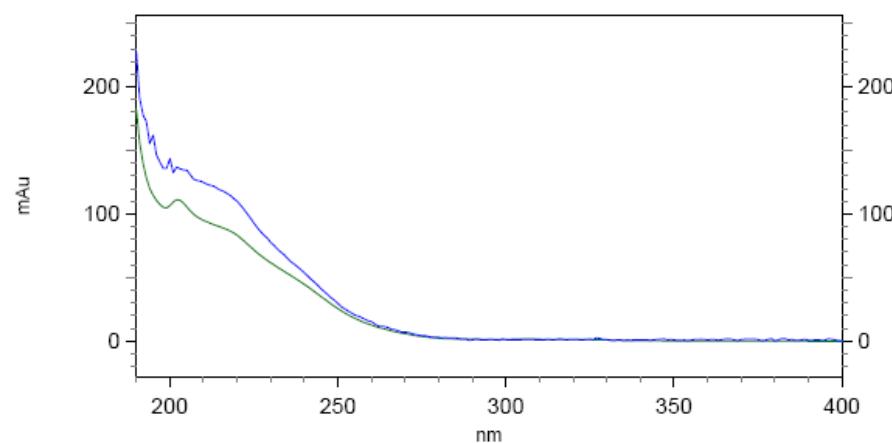
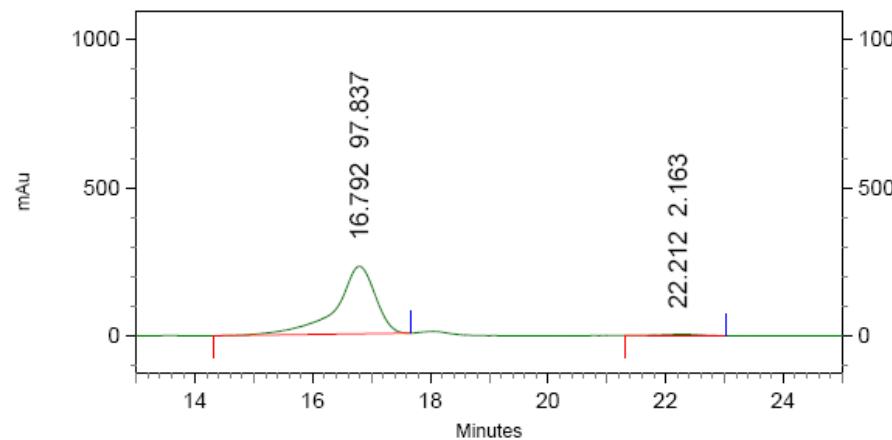
Results

Pk # Name	Retention Time	Area Percent
1	16.864	50.121
2	22.232	49.879
Totals		100.000

xx-viii-114 whelk 1%@1.0 ml again

C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 5%Whelk.met

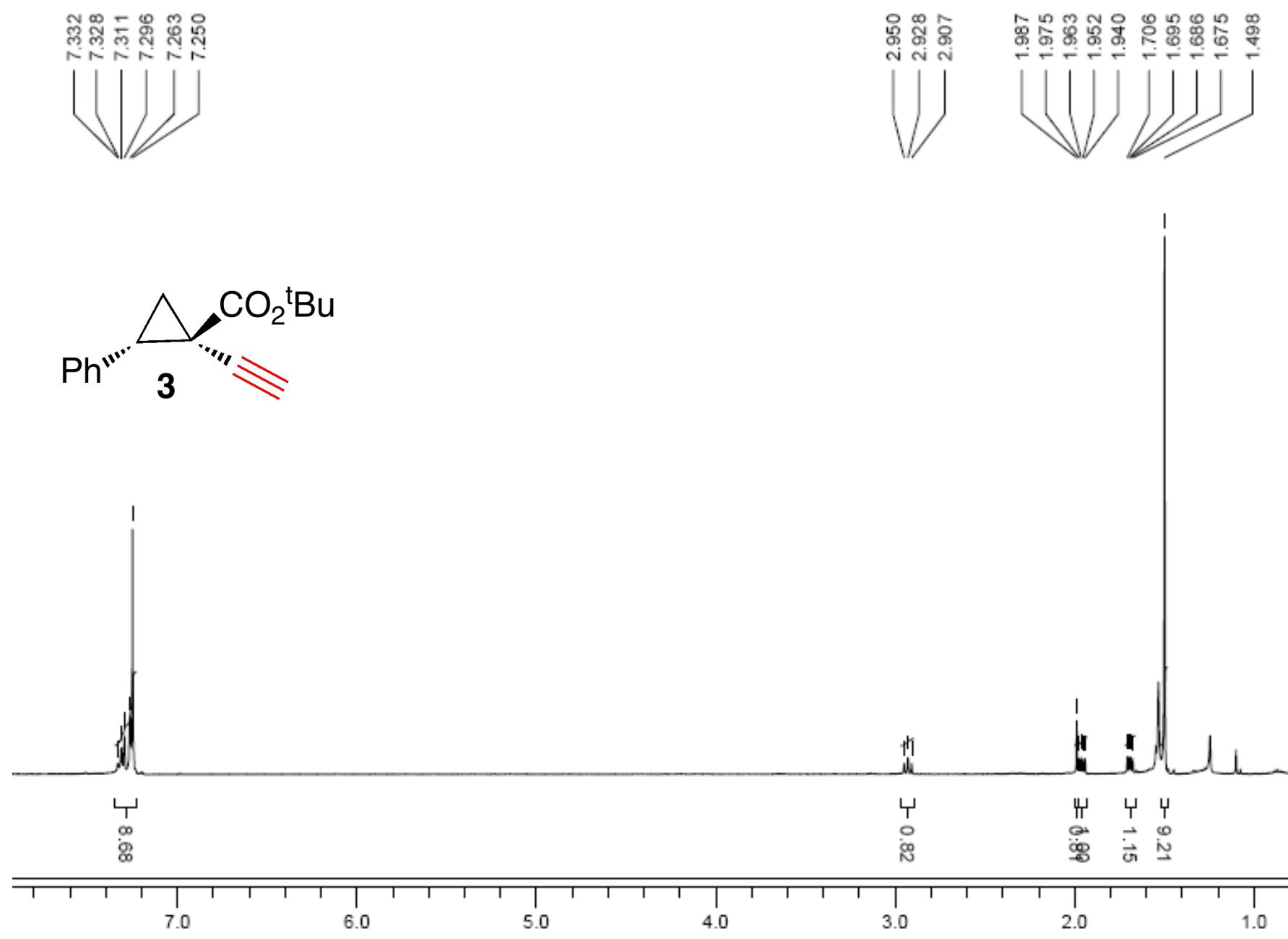
C:\EZStart\Projects\Default\Data\xx-viii-114 whelk 1%@1.0 ml again

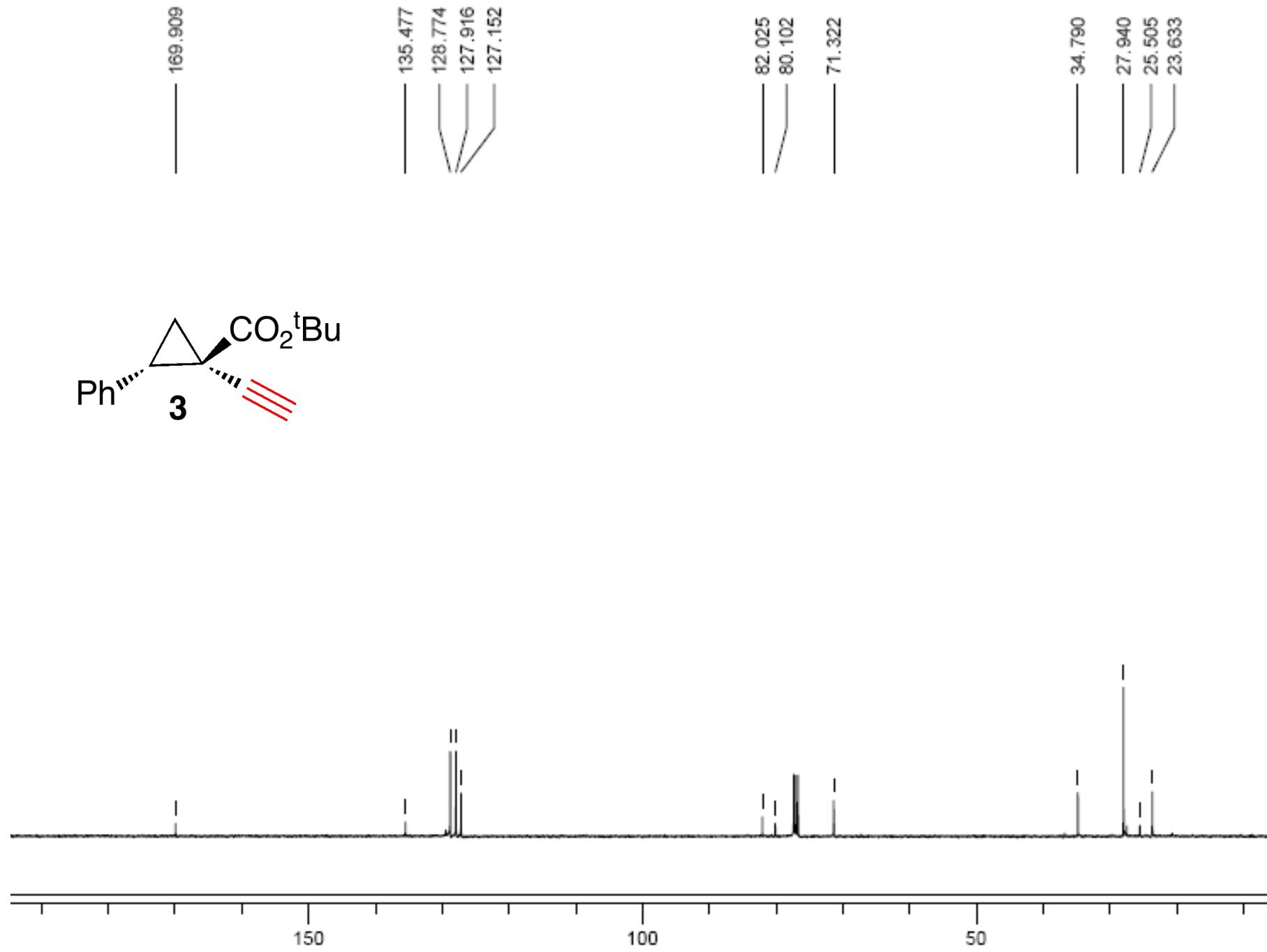


2: 209 nm, 4 nm

Results

Pk #	Name	Retention Time	Area Percent
1		16.792	97.837
2		22.212	2.163
Totals			100.000

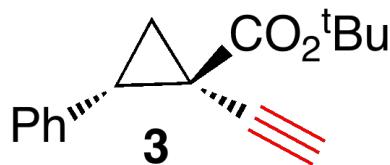
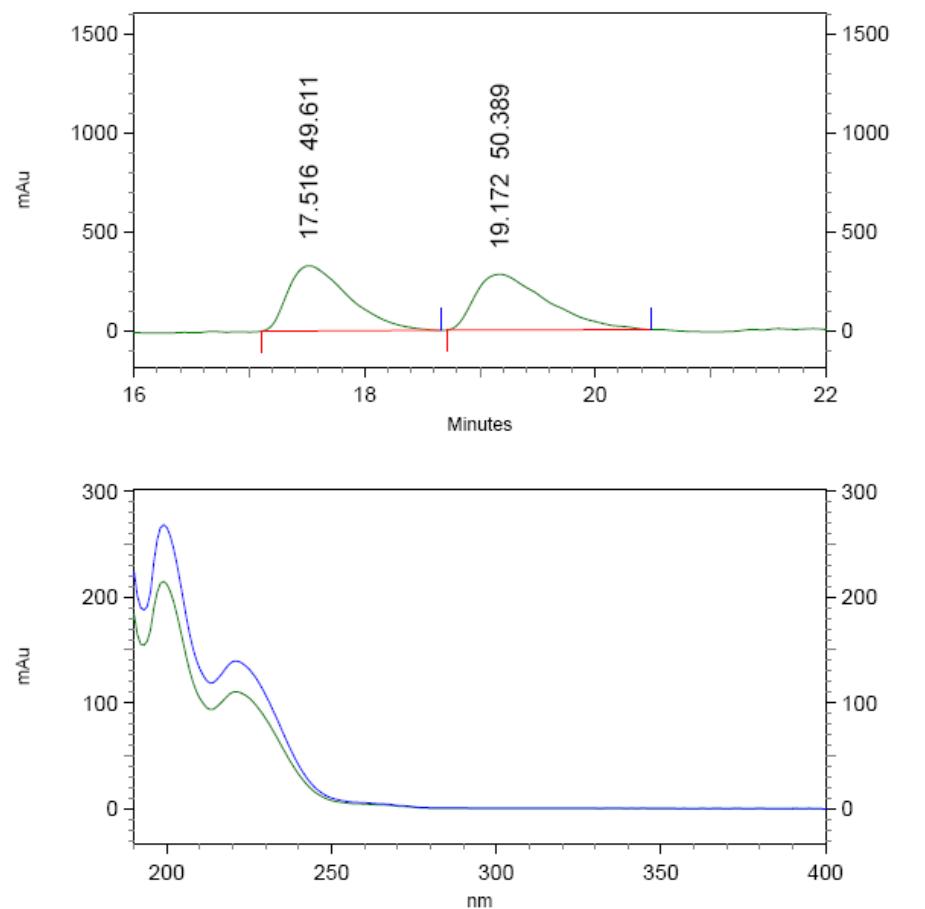




xx-viii-112 ODH 0%@1.0 ml

C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 5%Whelk.met

C:\EZStart\Projects\Default\Data\xx-viii-112pure ODH 0%@1.0 ml again

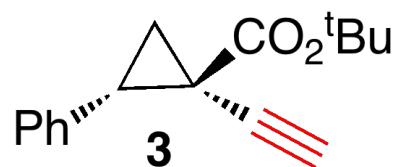
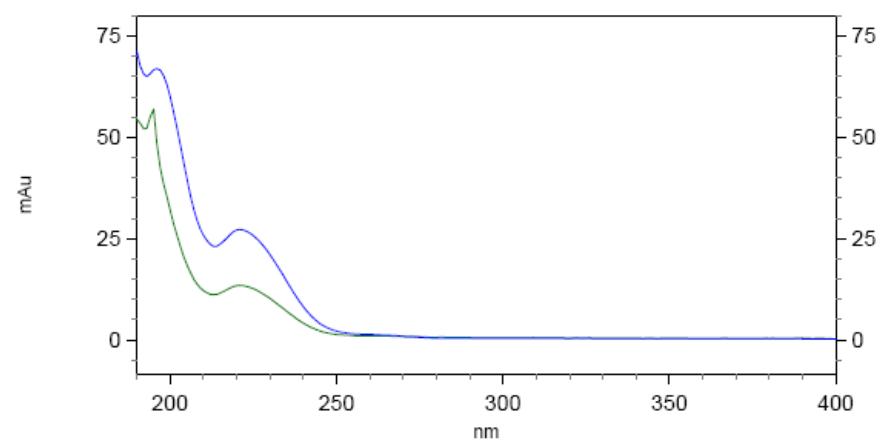
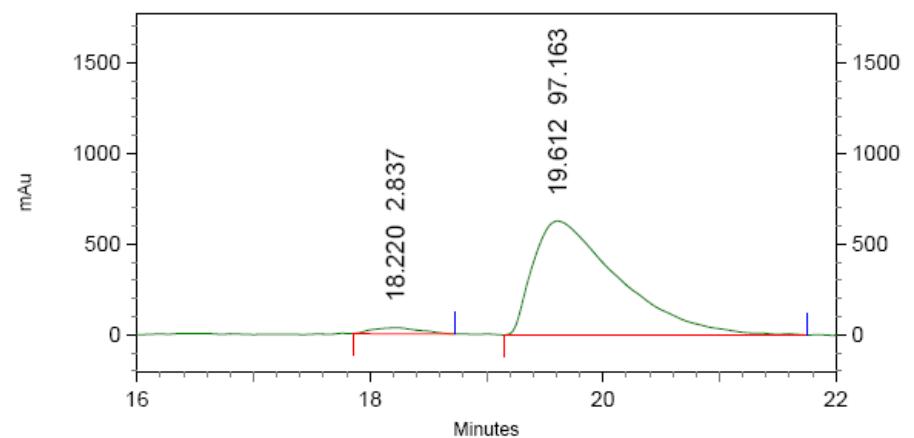


6: 207 nm, 4 nm

Results

Pk # Name	Retention Time	Area Percent
1	17.516	49.611
2	19.172	50.389
Totals		100.000

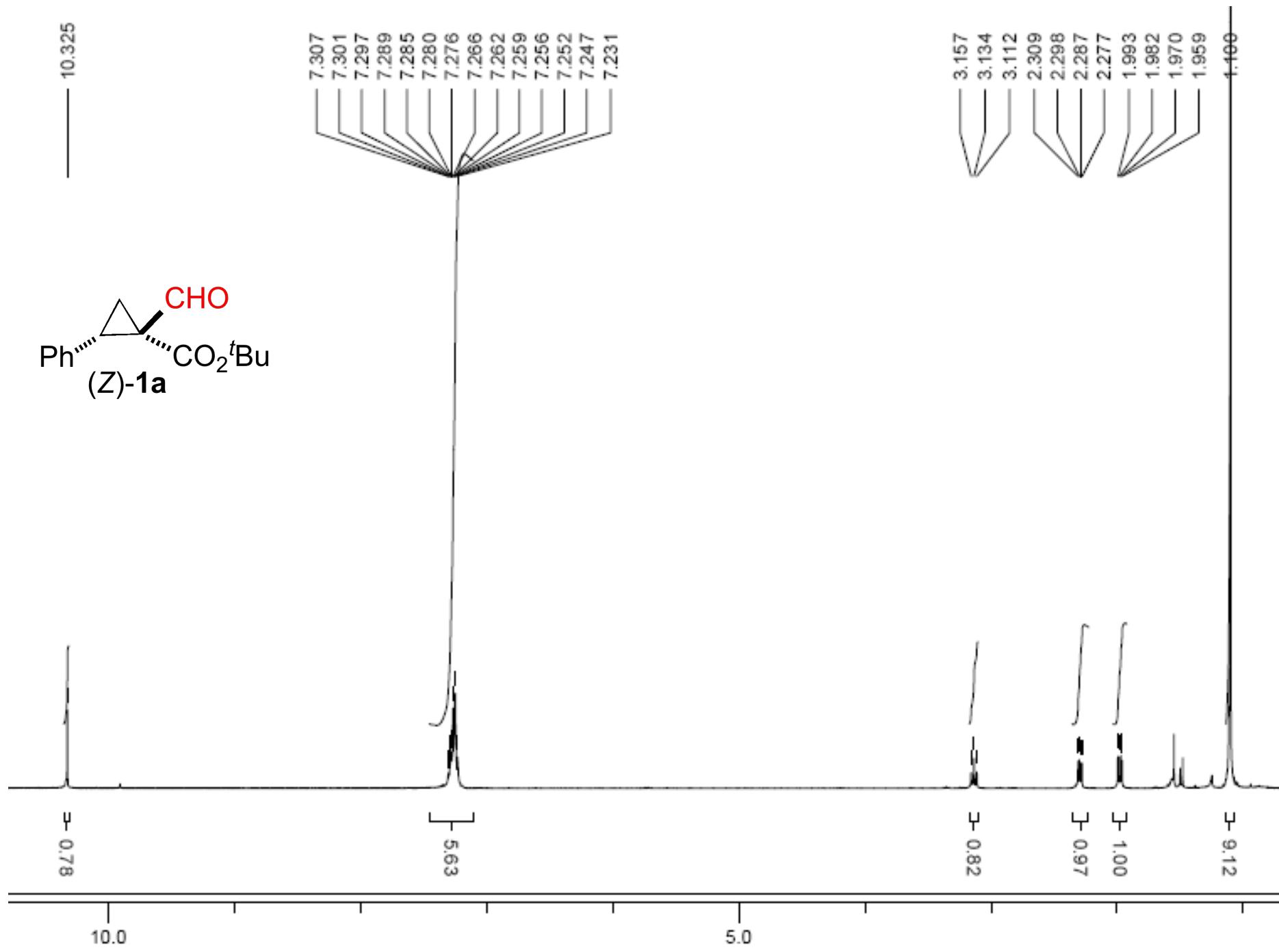
xx-viii-116pure ODH 0%@1.0 ml again
C:\EZStart\Projects\Default\Method\Shifa-P-Cyclopropane 5%Whelk.met
C:\EZStart\Projects\Default\Data\xx-viii-116pure ODH 0%@1.0 ml again

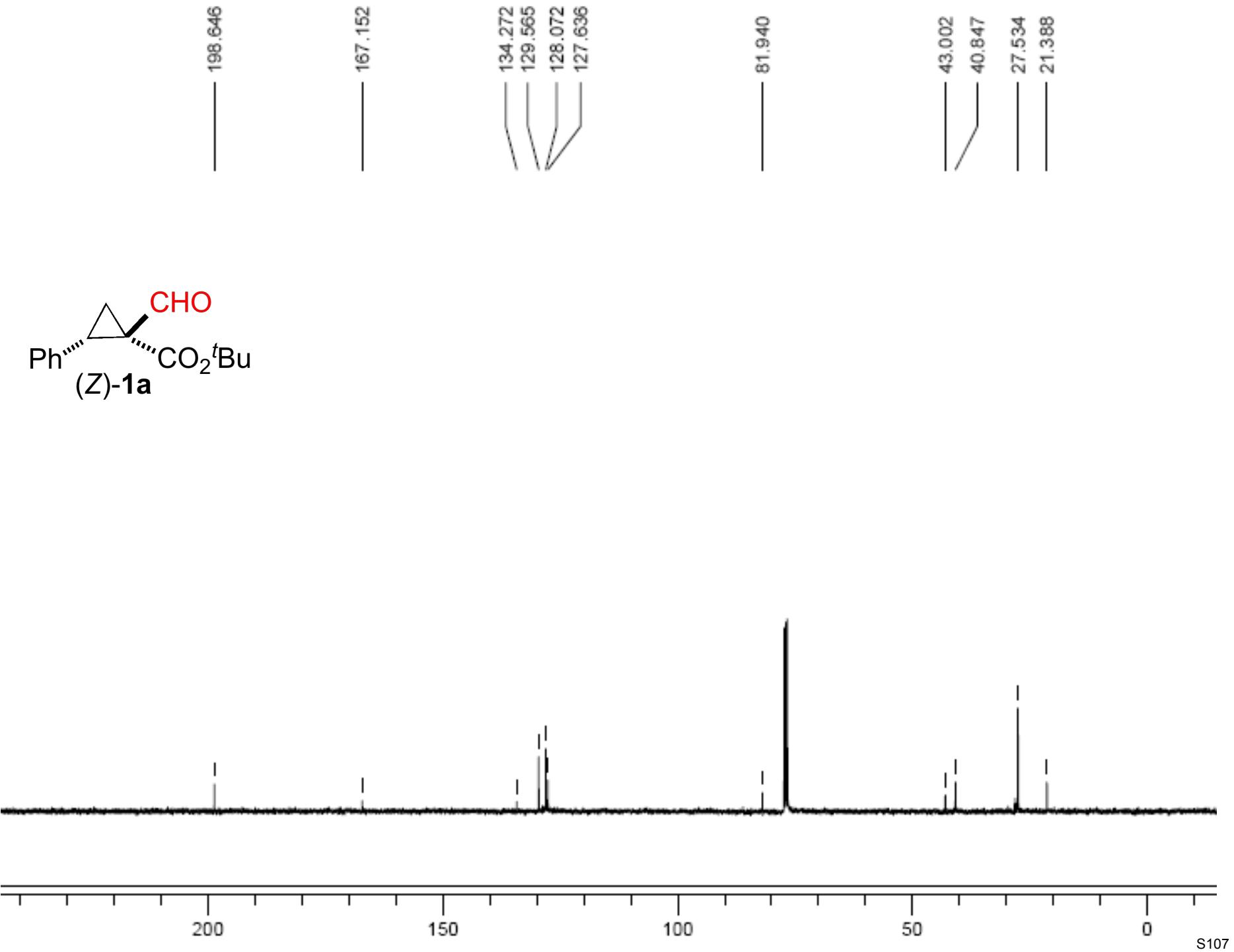


6: 207 nm, 4 nm

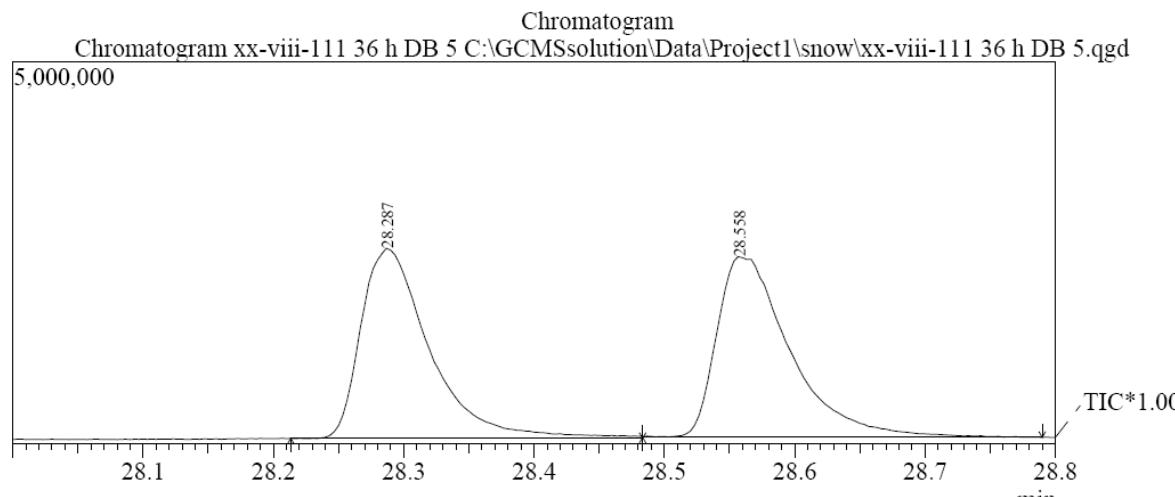
Results

Pk #	Name	Retention Time	Area Percent
1		18.220	2.837
2		19.612	97.163
Totals			100.000

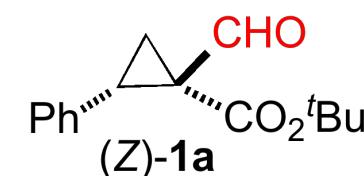




Sample Name : xx-viii-111 36 h DB 5
 Sample ID : xx-viii-111 36 h DB 5

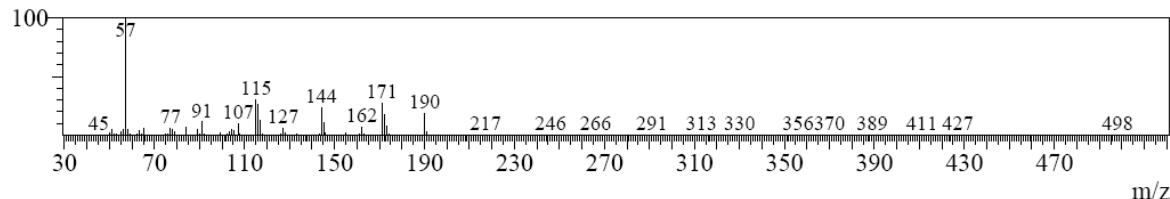


Peak Report TIC			
Peak#	R.Time	Area%	Name
1	28.287	49.60	
2	28.558	50.40	
		100.00	

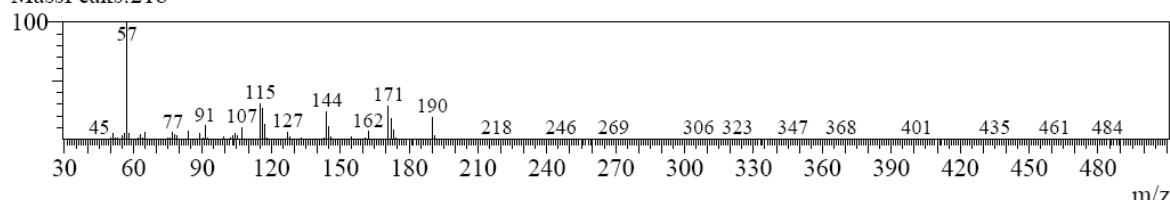


Spectrum

Peak#:1 R.Time:28.3(Scan#:6987)
 MassPeaks:199

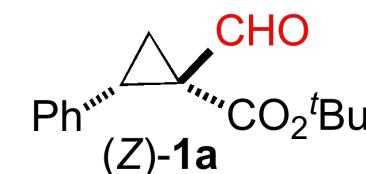
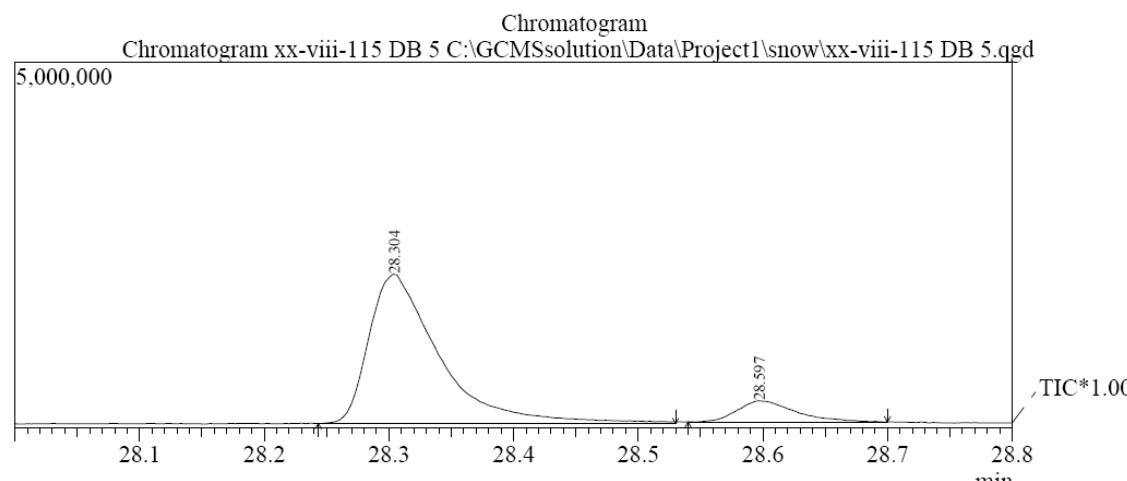


Peak#:2 R.Time:28.6(Scan#:7068)
 MassPeaks:218



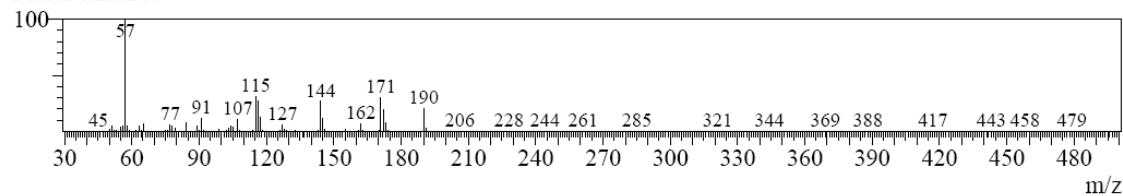
Sample Information

Sample Name : xx-viii-115 DB 5
 Sample ID : xx-viii-115 DB 5

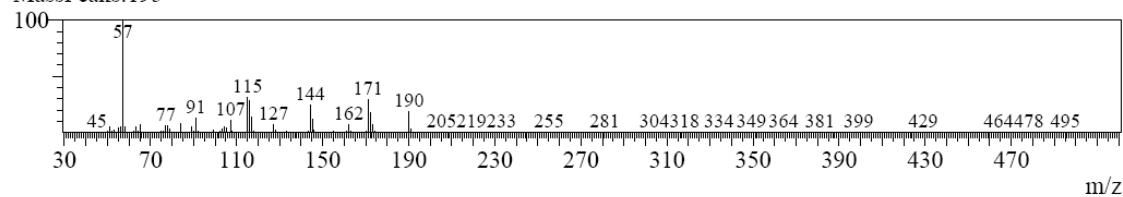


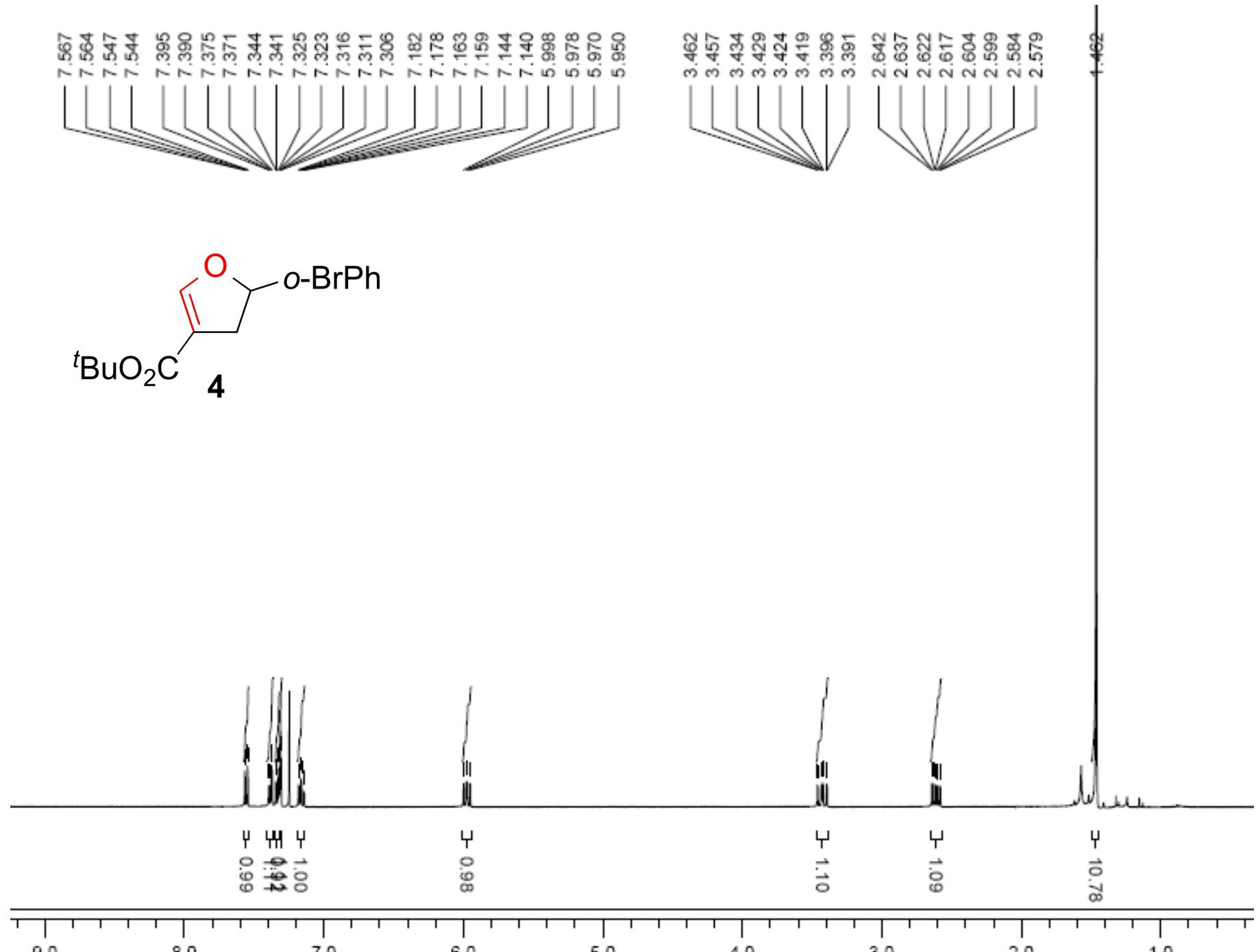
Spectrum

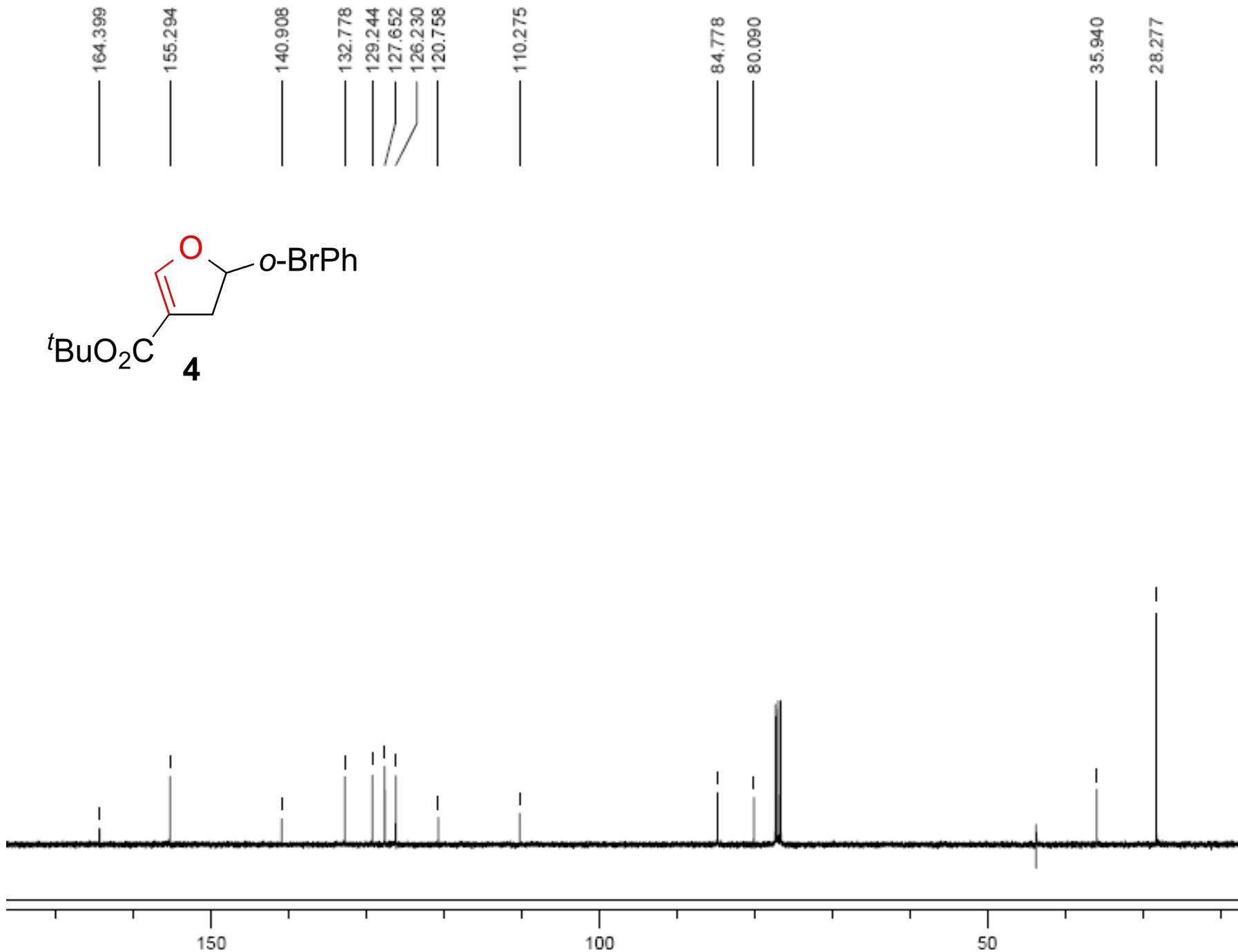
Peak#:1 R.Time:28.3(Scan#:6992)
 MassPeaks:206



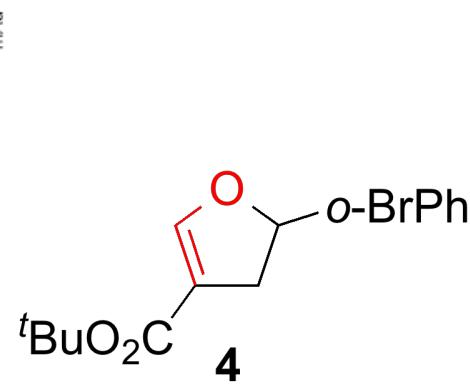
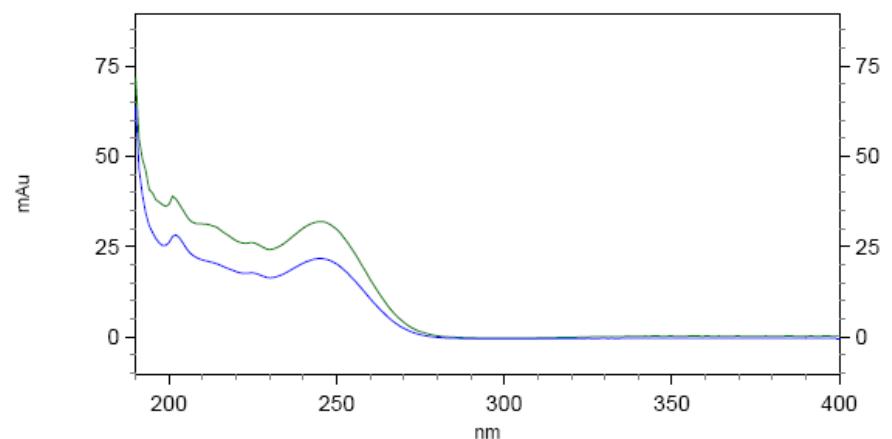
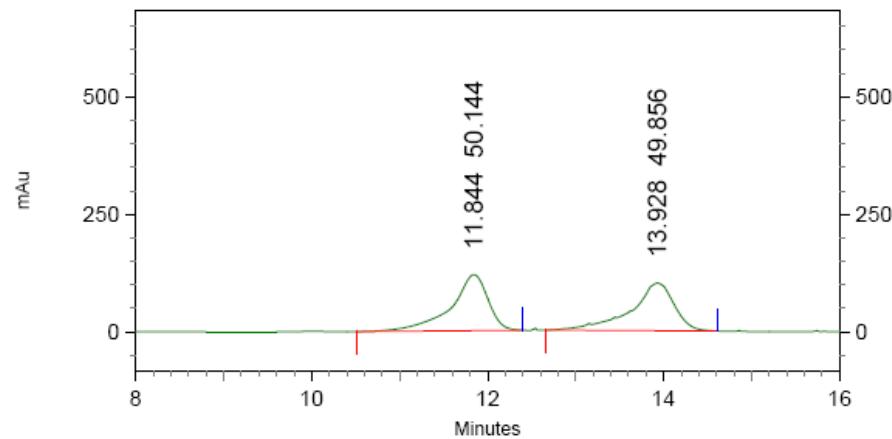
Peak#:2 R.Time:28.6(Scan#:7080)
 MassPeaks:195







xx-viii-31-1 Whelk 1%@0.8 ml
C:\EZStart\Projects\Default\Method\snowtemp 2 .met
C:\EZStart\Projects\Default\Data\xx-viii-31-1 Whelk 1%@0.8 ml



1: 247 nm, 4 nm

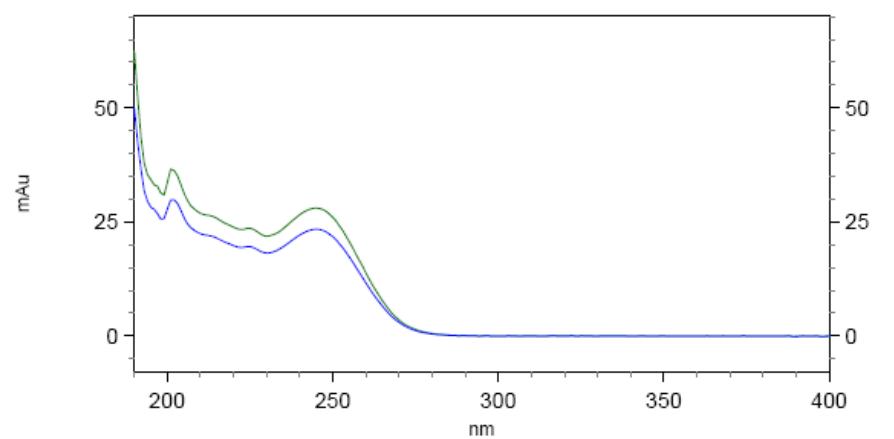
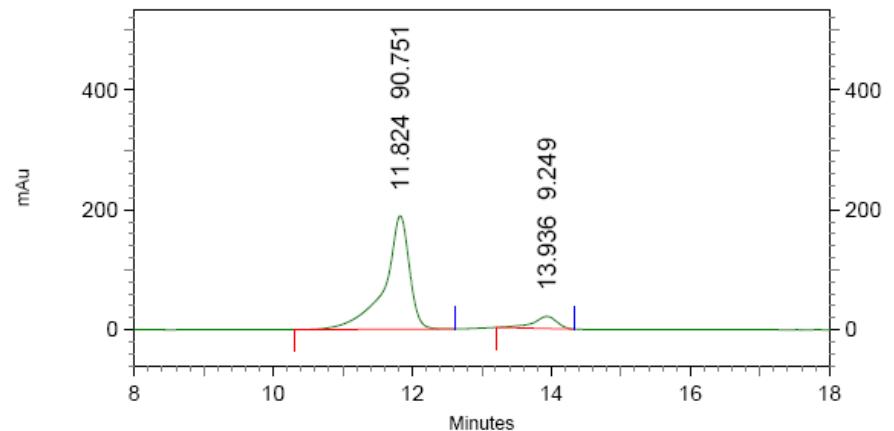
Results

Pk #	Name	Retention Time	Area Percent
1		11.844	50.144
2		13.928	49.856
Totals			100.000

xx-viii-51-3 whelk 1%@0.8 ml

C:\EZStart\Projects\Default\Method\JTL-3%-ODH1ml.met

E:\xx-viii-51-3 whelk 1%@0.8 ml



5: 228 nm, 4 nm

Results

Name	Retention Time	Area Percent	Pk #
	11.824	90.751	1
	13.936	9.249	2

Totals	100.000	
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