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Ruthenium-Catalyzed Alkoxycarbonylation of Alkenes Using Carbon Monoxide

Contents

1. Analytical Methods

Analytical data of literature known compounds were in accord with reported data. NMR spectra were recorded on Bruker Avance 300 (300 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210 Time-of-Flight LC/MS (Agilent) with electrospray ionization (ESI). The data are given as mass units per charge (m/z) and intensities of signals are given in brackets. For GC analyses, HP 6890 chromatograph with a 29 m HP5 column was used.

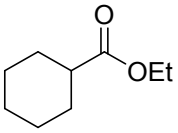
2. Materials

All commercial reagents were ordered from Alfa Aesar, Aldrich or Strem. Unless otherwise statement, commercial reagents were used without purification. Air- and moisture-sensitive syntheses were performed under argon atmosphere in heating gun vacuum dried glassware. Dry solvents and alkenes were prepared according to standard procedures.

3. General Procedure

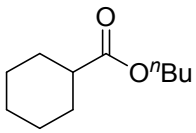
The alkoxycarbonylation reactions were run in 600 mL autoclave. Typically, a 4 mL vial was charged with $Ru_3(CO)_{12}$ 8 mg, [Bmim]Cl 0.44g, then alkenes (1.25 mmol) and alcohols (2 mL) was added. The alcohols added were reactant as well as solvents. Then the autoclave were pressurized with CO (2 bar) and nitrogen (40 bar) and the reaction was carried out at 130 °C for 48 hours. Then the autoclave was cooled to room temperature and depressurized. The contents in vials were analyzed by gas chromatography using isooctane as internal standard.

4. Characterization of Esters.



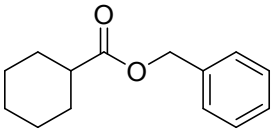
ethyl cyclohexanecarboxylate 4a

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 – 4.05 (m, 2H), 2.39 – 2.16 (m, 1H), 1.94 – 1.80 (m, 2H), 1.79 – 1.68 (m, 2H), 1.62 (dt, *J* = 2.1, 0.9 Hz, 1H), 1.51 – 1.31 (m, 2H), 1.24 – 1.19 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 60.0, 43.2, 29.0, 25.7, 25.4, 14.2. **MS (EI):** m/z = 156 $[M]^+$, 141, 128, 111, 101, 88, 83, 73, 55, 41, 29. **HRMS:** calcd. for $[C_9H_{16}O_2+H]^+$: 157:12231, found 157.12211.



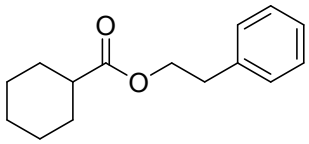
butyl cyclohexanecarboxylate 4b

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.02 (t, *J* = 6.6 Hz, 2H), 2.30 – 2.20 (m, 1H), 1.99 – 1.81 (m, 2H), 1.72 – 1.68 (m, 2H), 1.59 – 1.54 (m, 3H), 1.46 – 1.15 (m, 7H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 63.9, 43.2, 30.7, 29.0, 25.7, 25.4, 19.1, 13.6. **MS (EI):** m/z = 184 $[M]^+$, 143, 129, 111, 83, 73, 55, 41, 29. **HRMS:** calcd. for $[C_{11}H_{20}O_2+Na]^+$: 207.13555, found 207.13532.



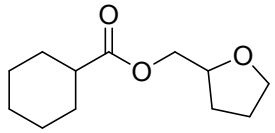
benzyl cyclohexanecarboxylate 4d

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 3.5 Hz, 5H), 5.12 (s, 2H), 2.41 – 2.31 (m, 1H), 2.08 – 1.86 (m, 2H), 1.83 – 1.71 (m, 2H), 1.71 – 1.57 (m, 1H), 1.57 – 1.38 (m, 2H), 1.36 – 1.19 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.9, 136.28, 128.47, 128.01, 127.91, 65.84, 43.17, 28.98, 25.71, 25.40. **MS (EI):** m/z = 218 $[M]^+$, 200, 127, 111, 91, 83, 77, 65, 55, 41, 29. **HRMS:** calcd. for $[C_{14}H_{18}O_2+Na]^+$: 241.1199, found 241.11993.



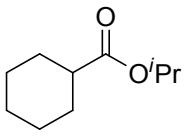
phenethyl cyclohexanecarboxylate 4e

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.00 (m, 5H), 4.21 (t, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 7.0 Hz, 2H), 2.20 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.87 – 1.74 (m, 2H), 1.74 – 1.61 (m, 2H), 1.58 – 1.56 (m, 1H), 1.42 – 1.24 (m, 2H), 1.24 – 1.05 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 137.9, 128.9, 128.4, 126.5, 64.6, 43.2, 35.2, 29.0, 25.7, 25.4. **MS (EI):** m/z = 111, 104, 91, 83, 77, 65, 55, 41, 29. **HRMS:** calcd. for $[C_{15}H_{20}O_2+Na]^+$: 233.15361, found 233.15317.



(tetrahydrofuran-2-yl)methyl cyclohexanecarboxylate 4f

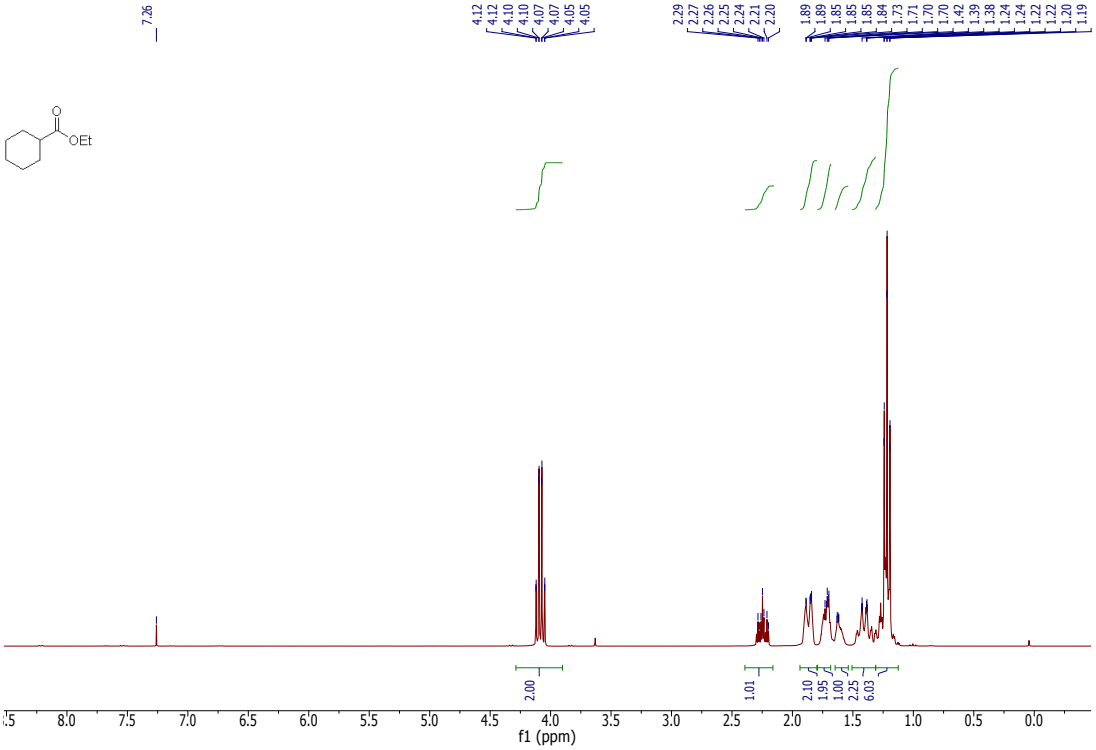
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 – 4.05 (m, 2H), 4.03 – 3.93 (m, 1H), 3.92 – 3.72 (m, 2H), 2.45 – 2.24 (m, 1H), 2.07 – 1.81 (m, 5H), 1.81 – 1.54 (m, 4H), 1.54 – 1.35 (m, 2H), 1.35 – 1.10 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 68.4, 66.1, 43.1, 29.0, 29.0, 27.9, 25.7, 25.7, 25.4. **MS (EI):** m/z = 212 $[M]^+$, 157, 143, 129, 111, 84, 71, 55, 43, 29.

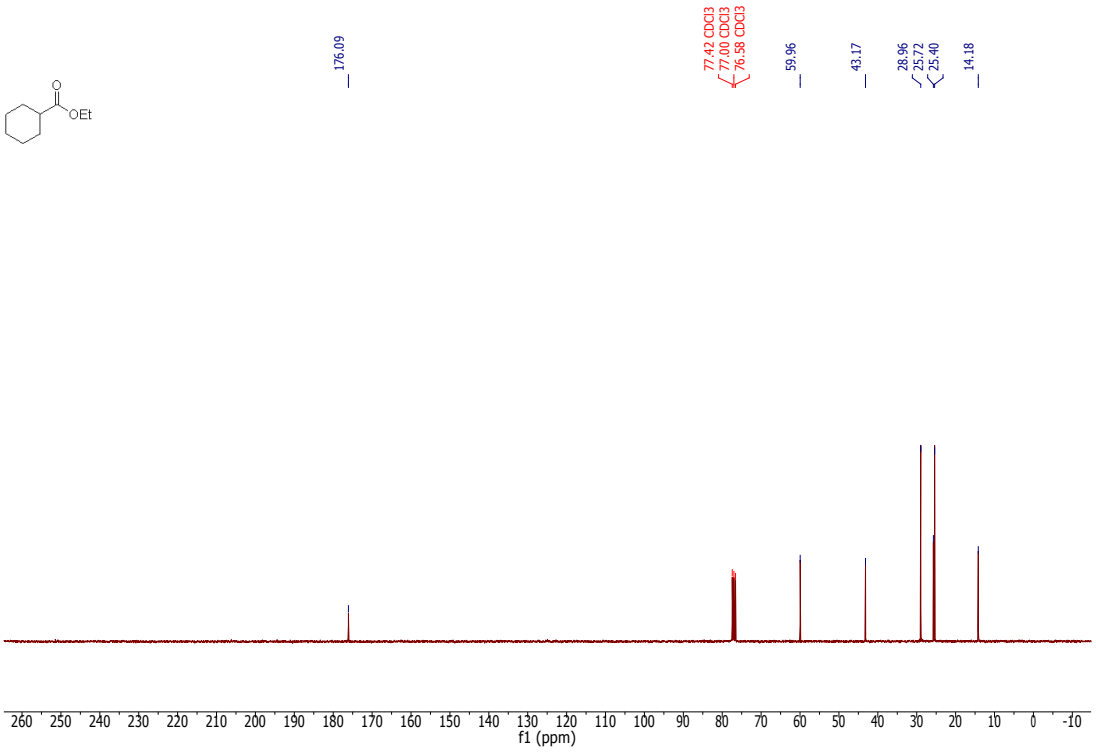


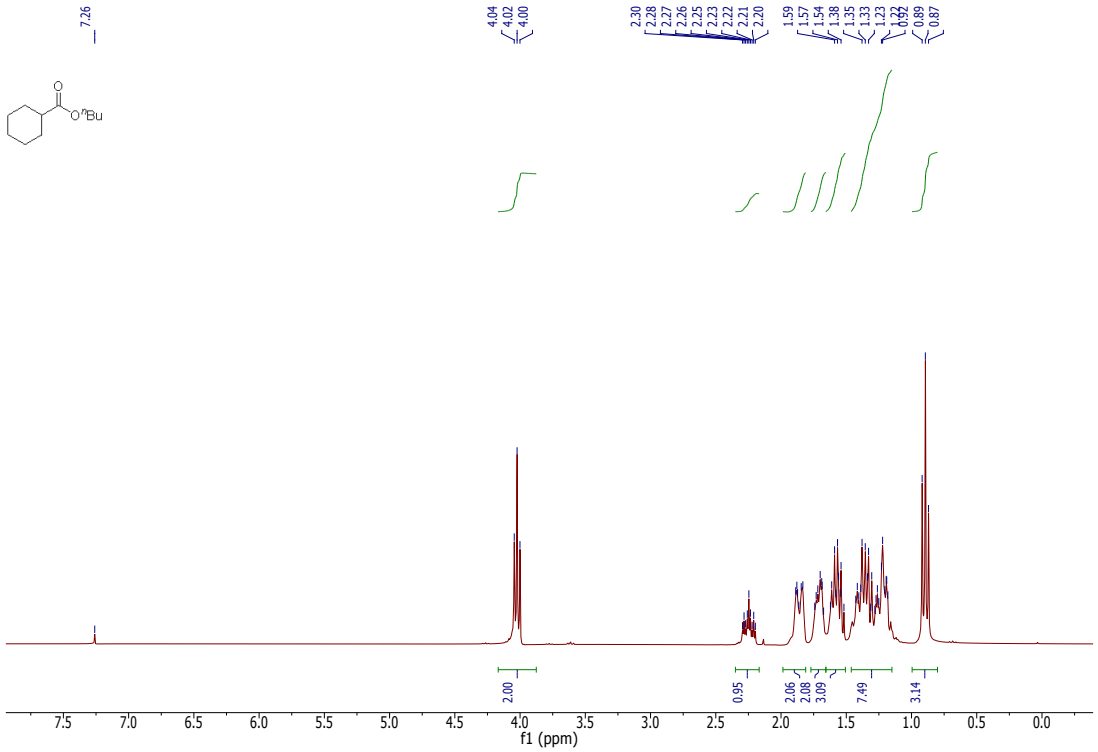
isopropyl cyclohexanecarboxylate 4g

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 – 4.95 (m, 1H), 2.23 (tt, *J* = 11.3, 3.7 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.75 – 1.70 (m, 2H), 1.63 (d, *J* = 6.8 Hz, 1H), 1.46 – 1.34 (m, 2H), 1.33 – 1.24 (m, 3H), 1.21 (s, 3H), 1.20 – 1.19 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.7, 67.0, 43.4, 29.0, 25.8, 25.4, 21.8. **MS (EI):** m/z = 170 $[M]^+$, 155, 129, 111, 83, 55, 43, 29.

5. NMR Spectra



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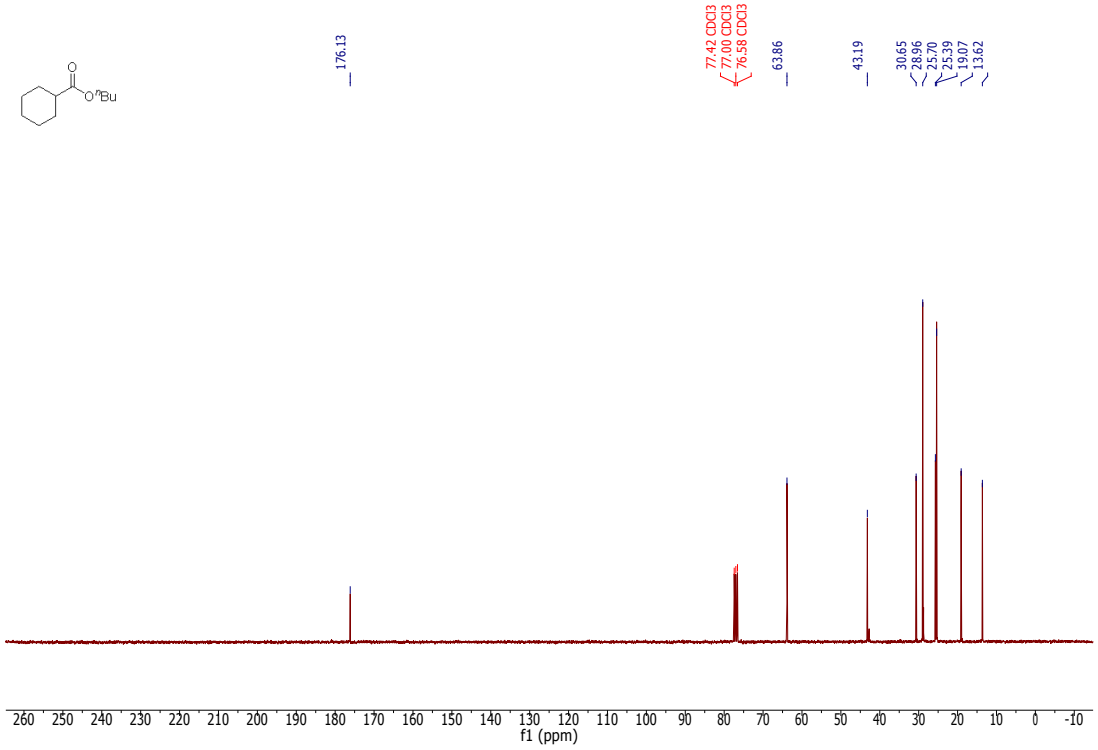
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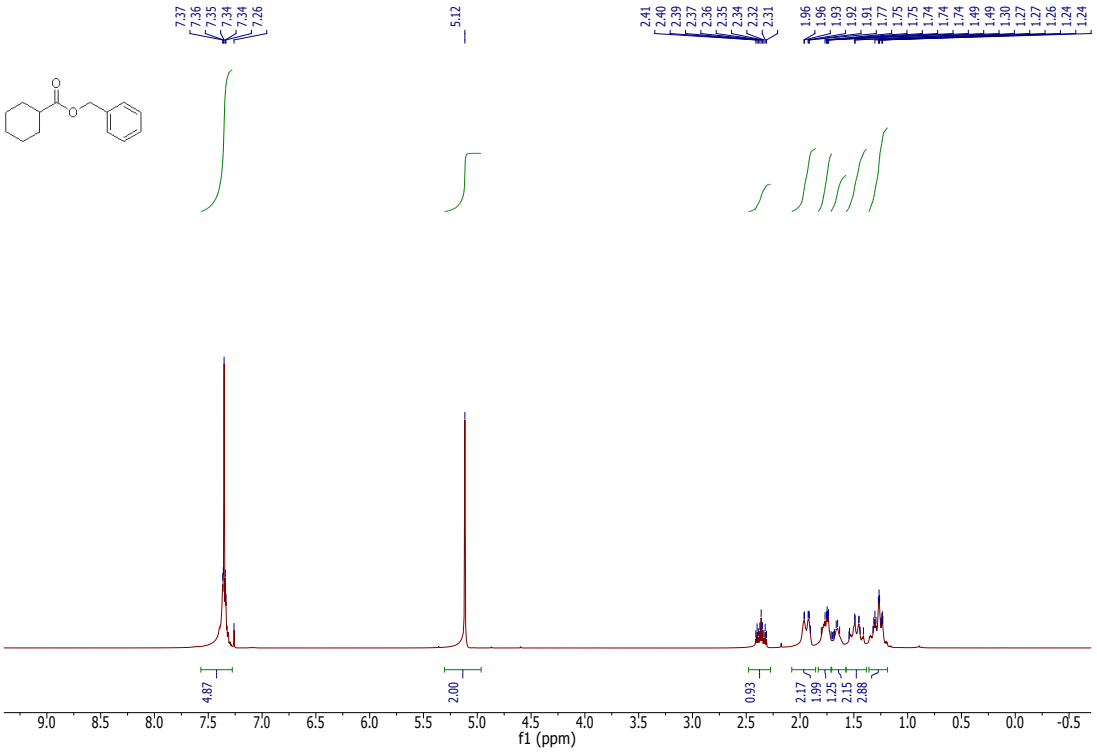
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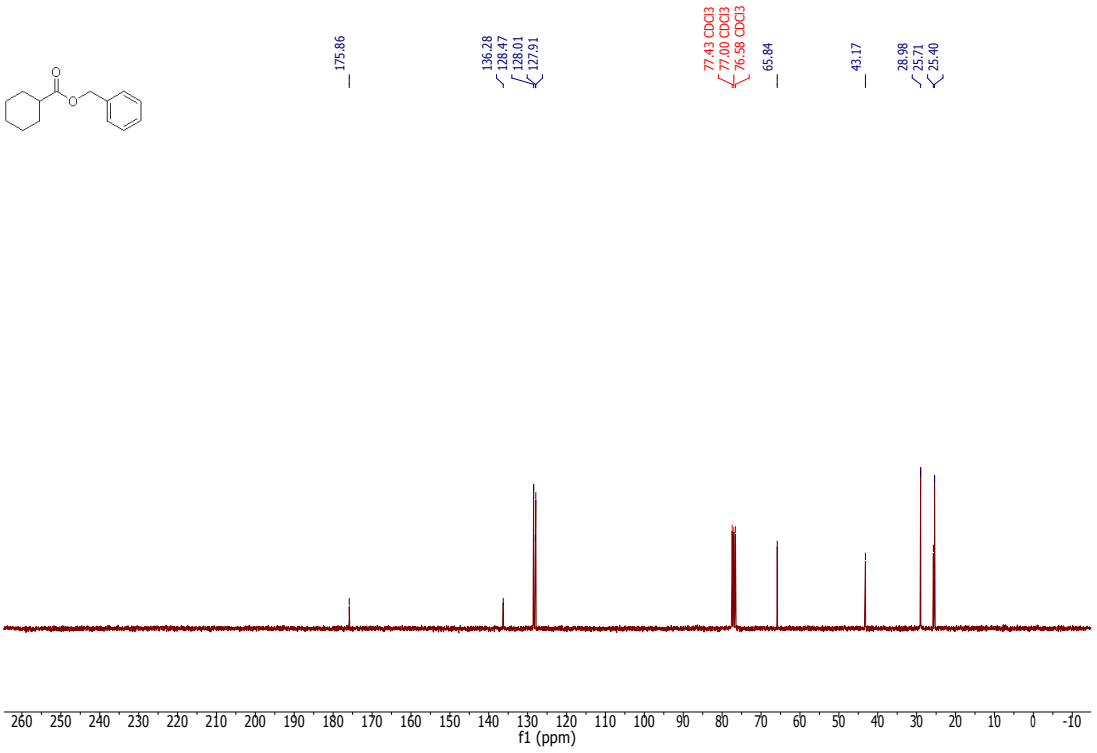
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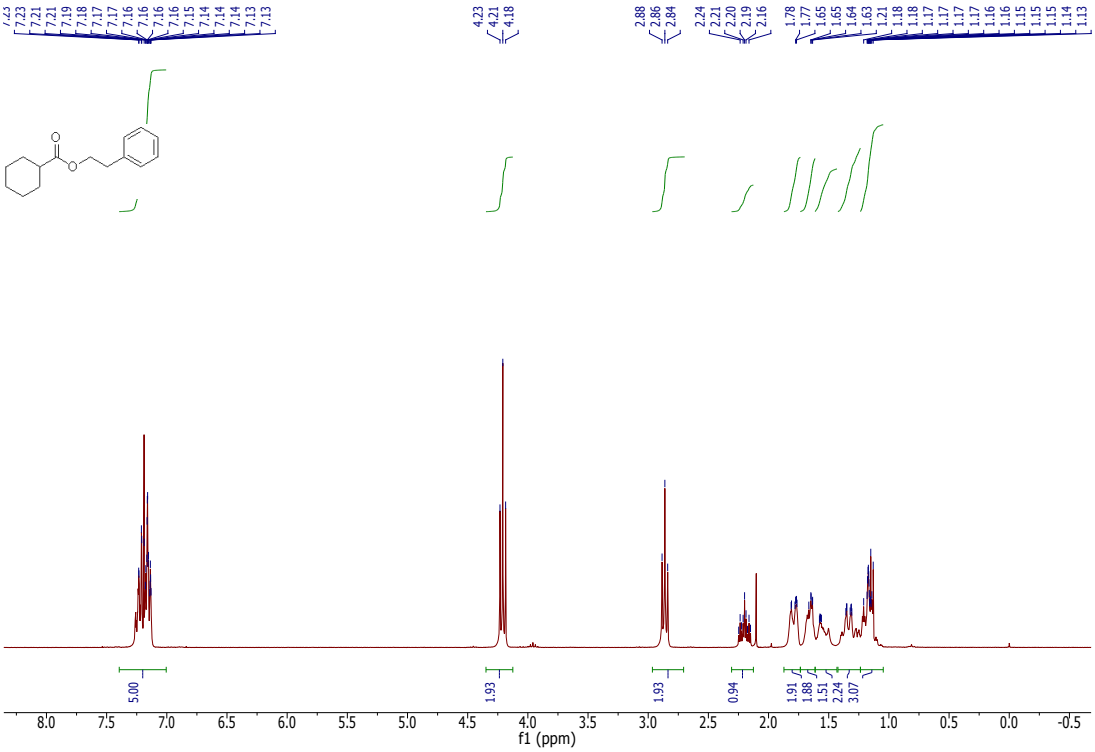
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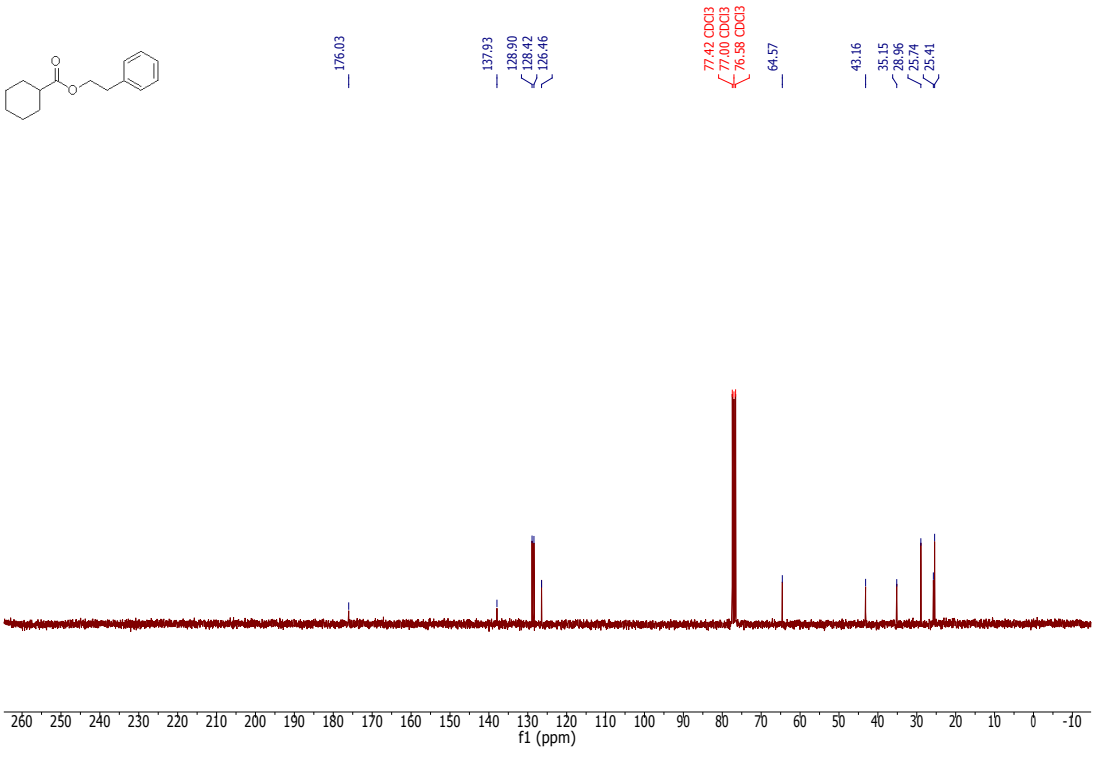
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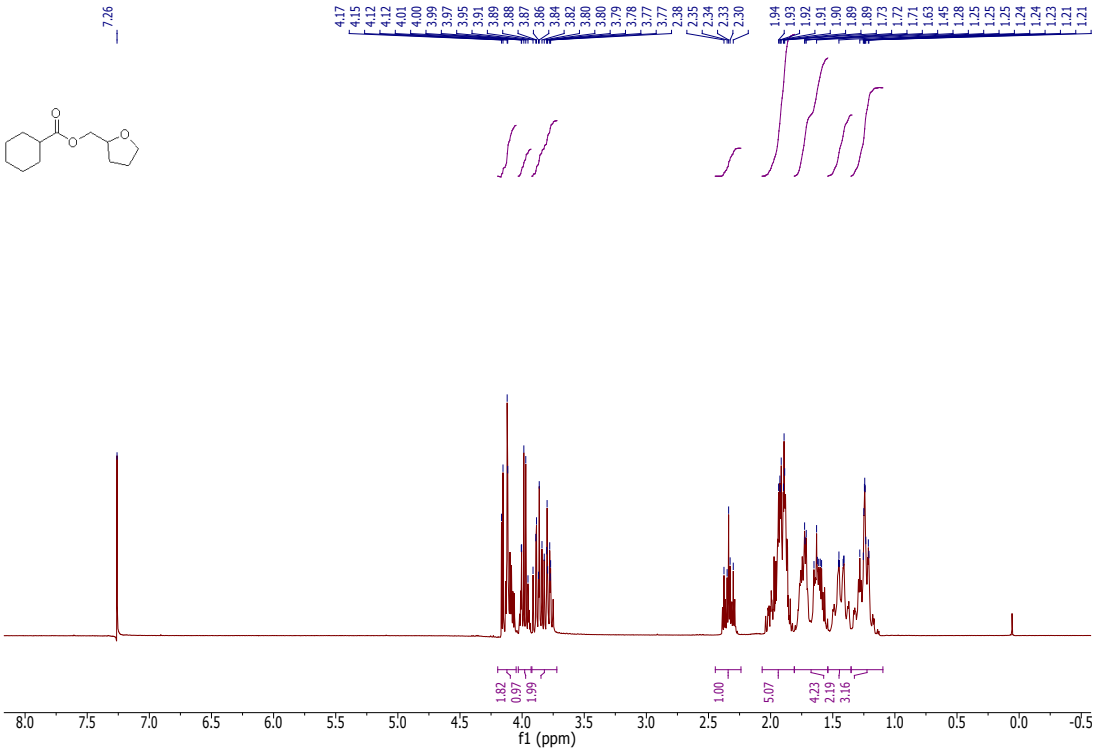
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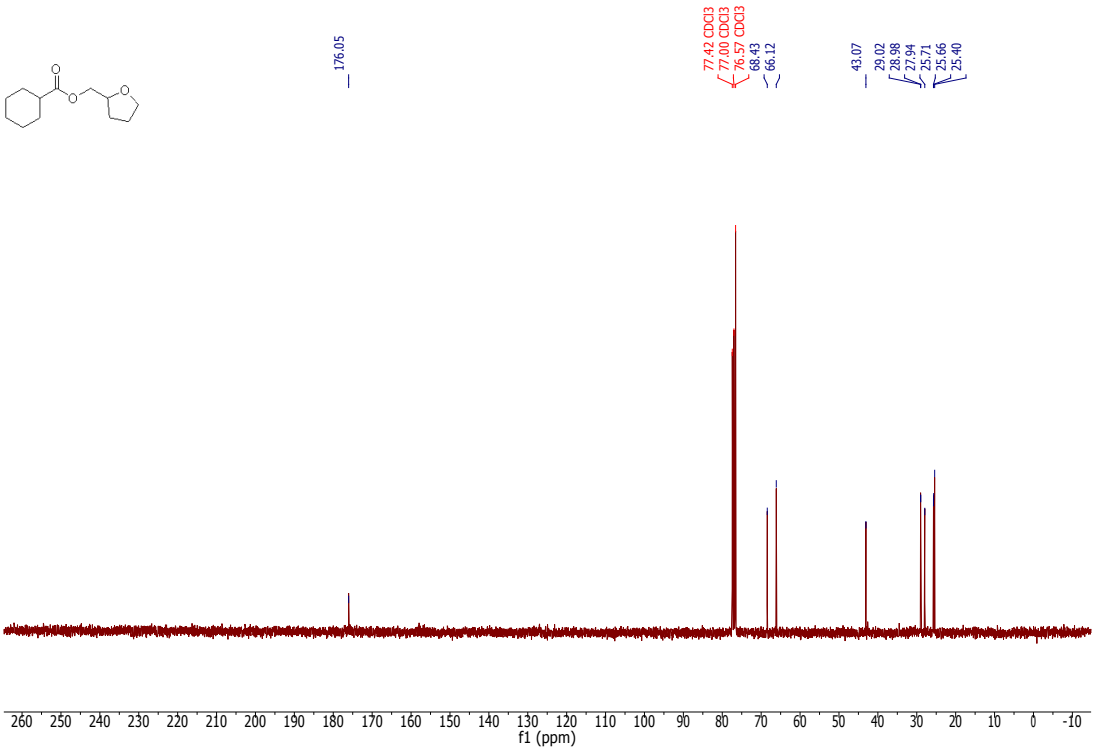
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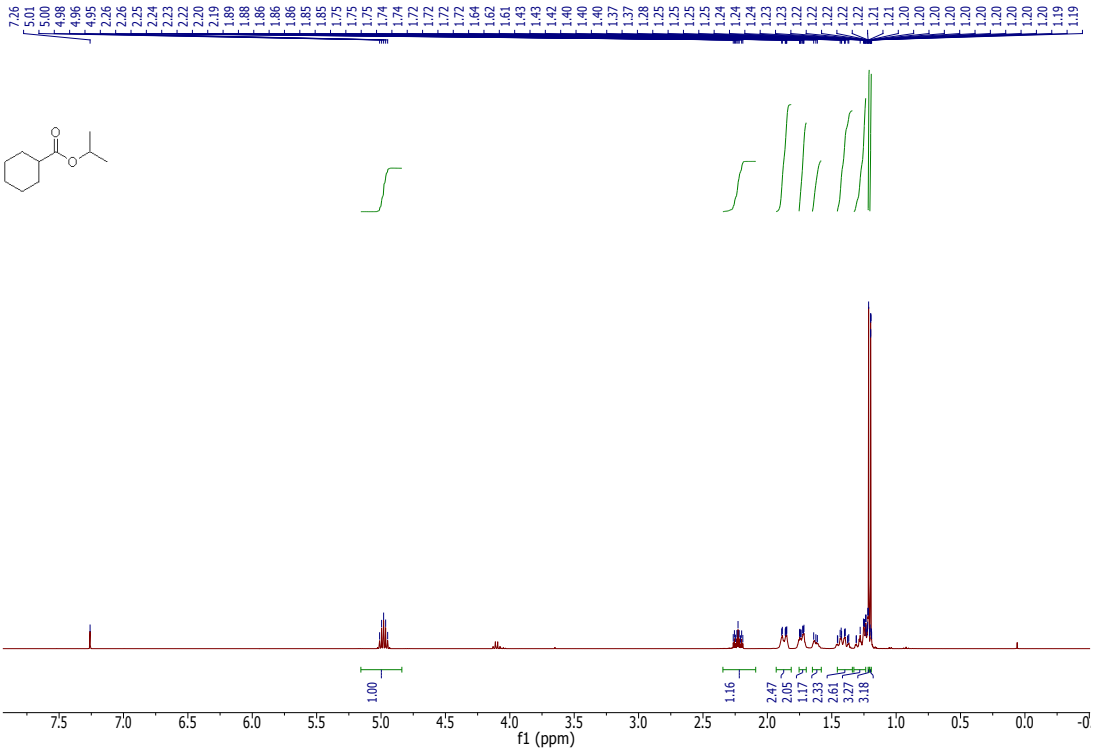
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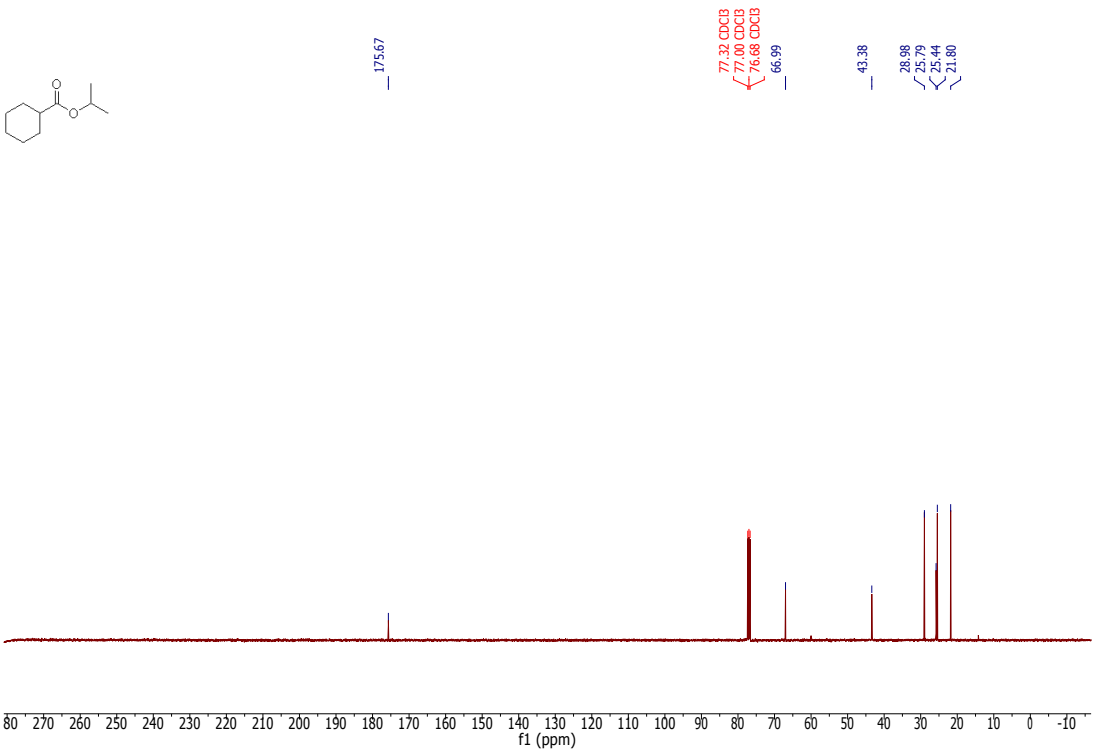
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