**Electronic Supplementary Information (ESI)**

# "$I_2$-catalyzed regioselective oxo- and hydroxy-acyloxylation of alkenes and enol ethers: a facile access to α-acyloxyketones, esters and diol derivatives"

**Rambabu N. Reddi, Pragati K. Prasad and Arumugam Sudalai***

Chemical Engineering and Process Development Division, National Chemical Laboratory, Pashan Road, Pune 411008, INDIA.

***Corresponding author. Tel: +91-20-25902174; Fax: +91-20-25902676; e-mail: a.sudalai@ncl.res.in**

## Table of Contents

| Sr.No. | Description | Page No. |
|---|---|---|
| 1 | General information | 2 |
| 2 | Experimental section | 2-16 |
| 3 | Spectra | 17-57 |

## 1. General Information

Solvents were purified and dried by standard procedures before use. IR spectra were recorded on a Perkin-Elmer model 683 B and absorption is expressed in $cm^{-1}$. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on Brucker AC-200 spectrometer unless mentioned otherwise. Purification was done using column chromatography (100-200 mesh). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. All chemicals are purchased from Sigma-Aldrich and used without further purification.

## 2. Experimental section

**2.1.** General experimental procedure for preparation of compounds **2a-z:**

To a stirred solution of alkene (1 mmol) in dry DMSO (8 mL), $I_2$ (10 mol %), $Et_3N$ (1.2 mmol), TBHP (1 mmol) and carboxylic acid (1.1 mmol) was added and the reaction mixture was then stirred at 25 °C under an $N_2$ atmosphere. After completion of the reaction (as monitored by TLC), it was quenched with $H_2O$ (20 mL) at 0 °C. It was then extracted with EtOAc (3 x 20 mL) followed by washing with brine (3x20 mL) and the combined organic layers were dried over anhydrous $Na_2SO_4$. Concentration of solvent under reduced pressure gave the crude product, which was then purified by column chromatography over silica gel using Pet. ether/EtOAc (9:1) as eluent to obtain α-acyloxy carbonyl compounds **2a-z** and **4a-e** in high purity.

**2.1.** General experimental procedure for preparation of compounds **3a-n**

To a stirred solution of alkene (1 mmol) in dry DMSO (8 mL), $I_2$ (10 mol %), TBHP (1 mmol), $Et_3N$ (1.2 mmol) and benzoic acid (1 mmol) were added and the resulting reaction mixture was

then stirred at 25 °C under $N_2$ atmosphere. Once α-benzyloxy ketone (**2a-n**) was formed (monitored by TLC), $Na_2SO_4$ (10 mmol) and $BH_3.SMe_2$ (0.5 mmol) were added to the reaction mixture at 0° C. After completion of the reaction (monitored by TLC), it was quenched with ice and then $H_2O$ at 0 °C. It was then extracted with EtOAc (3 x 20 mL) followed by washing with brine (3x20 mL) and the combined organic layers were dried over anhydrous $Na_2SO_4$. The organic layer was concentrated under reduced pressure to give the crude product, which was then purified by column chromatography over silica gel using pet ether/EtOAc (8:2) as eluent to obtain diol derivative **3a-n** in high purity.

2.2 General experimental procedure for the preparation methyl vinyl ethers **1o-s:**

To a stirred solution of (methoxymethyl)triphenylphosphonium chloride (10.0 mmol) in THF (25 mL) was added *n*-BuLi (9.0 mmol) at 0 °C. The resulting mixture was stirred at the same temperature for 0.25 h. A solution of corresponding aldehydes (8.0 mmol) in THF (10 mL) was added to the reaction mixture, and the resulting mixture stirred at room temperature. After completion of reaction (as monitored by TLC) it was quenched with water, and diluted with EtOAc. The organic layer was separated and aqueous layer extracted with ethyl acetate (3 x 20 ml); the combined organic layers were washed with brine (2 x 20 mL), dried over anhyd. $Na_2SO_4$ and concentrated under reduced pressure to give the crude product. Chromatographic purification using flash silica gel (230-400 mesh) and petroleum ether: ethyl acetate = 9:1 yielded products **1o-s.**

**2-oxo-2-phenylethyl benzoate (2a): Yield:** 88% (210 mg), colorless solid, mp: 119-120 °C; **IR** (Nujol, $cm^{-1}$): 705, 1015, 1374, 1459, 1596, 1714, 1750, 2851, 2923; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 5.58 (s, 2H), 7.48 - 7.61 (m, 6H), 7.97 - 8.13 (m, 2H), 8.14 - 8.17 (m, 2H); **$^{13}$C NMR**

(50 MHz, $CDCl_3$): δ 66.2, 127.7, 128.2, 128.73, 129.9, 130.1, 133.1, 133.7, 134.2, 165.7, 191.7; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{12}O_3$+Na: 263.0683; found: 263.0692.

**2-oxo-2-(p-tolyl)ethyl benzoate** (**2b**) **: Yield:** 85% (216 mg), colorless solid, mp: 105-106 °C ; **IR** (Nujol, $cm^{-1}$): 713, 1135, 1231, 1289, 1459, 1604, 1698, 1732, 2840, 2923; **$^1$H NMR** (500 MHz, $CDCl_3$): δ 2.47 (s, 3H), 5.57 (s, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.61 - 7.63 (m, 1H), 7.90 (d, *J* = 7.9 Hz, 2H), 8.17 (d, *J* = 7.3 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$): *δ* 21.8, 66.9, 123.5, 127.8, 129.6, 131.1, 131.5, 134.8, 145.1, 150.7, 164.1, 190.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{14}O_3$+Na: 277.0840; found: 277.0848.

**2-(4-bromophenyl)-2-oxoethyl benzoate** (**2c**): **Yield**: 88% (280 mg), colorless solid, mp. 78-79°C; **IR** ($CHCl_3$, $cm^{-1}$): 719, 967, 1115, 1124, 1701, 1723, 2848, 2930; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 5.52 (s, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 8.09 - 8.18 (m, 2H); **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 66.2, 128.4, 128.6, 129.3, 129.9, 130.3, 132.2, 133.3, 165.7, 191.0: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{11}BrO_3$+Na: 340.9789; found: 340.9799.

**2-(4-cyanophenyl)-2-oxoethyl benzoate** (**2d**): **Yield:** 82% (217 mg), colorless solid, mp: 89-91 °C ; **IR** ($CHCl_3$, $cm^{-1}$): 717, 871, 1131, 1155, 1231, 1595, 1698, 1722, 1746, 2250, 2940, ; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.53 (s, 2H), 7.48 (s, 2H), 7.60 - 7.61 (m, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 8.06 (s, 2H), 8.12 (br. s., 2H): **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 66.3, 117.4, 117.4, 128.3, 128.6, 129.1, 130.0, 132.7, 133.6, 137.3, 165.7, 190.9; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{11}NO_3$+Na: 288.0637; found: 288.0646.

**2-(4-acetoxyphenyl)-2-oxoethyl benzoate (2e)**: **Yield:** 84% (250 mg), colorless solid, mp: 106-107 °C ; **IR** (Nujol, $cm^{-1}$): 716, 1166, 1212, 1294, 1460, 1593, 1690, 1717, 1753, 2846, 2917;

**$^1$H NMR** (200 MHz, $CDCl_3$) δ 2.34 (s, 3H), 5.55 (s, 2H), 7.23 (s, 2H), 7.48 - 7.51 (m, 2 H), 7.61 - 7.66 (m, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 8.12 - 8.16 (m, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 20.9, 66.1, 121.9, 128.3, 129.2, 129.8, 131.6, 133.1, 154.7, 165.6, 168.2, 190.6: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{14}O_5$+Na: 321.0739; found: 321.0748.

**2-(3,4-dimethoxyphenyl)-2-oxoethyl benzoate** (**2f**): **Yield:** 83% (249 mg), colorless solid, mp: 121-123 °C**; IR** (Nujol, $cm^{-1}$): 720, 1031, 1161, 1255, 1460, 1685, 1725, 2857, 2925; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.91 (s, 3H), 3.94 (s, 3H), 5.51 (s, 2H), 6.87 (d, *J* = 7.9 Hz, 1H) 7.28 - 7.61 (m, 6H), 8.12 (d, *J* = 7.2 Hz, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 55.8, 56.0, 66.0, 109.9, 110.0, 122.1, 127.3, 128.2, 129.4, 129.8, 133.0, 149.1, 153.7, 165.7, 190.2; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{16}O_5$+Na: 323.0895; found: 323.0884.

**3-((4-methoxybenzyl)oxy)-2-oxopropyl benzoate (2g): Yield:** 83% (260 mg), oily liquid; **IR** (Nujol, $cm^{-1}$): 718, 1063, 1263, 1375, 1457, 1567, 1725, 1749, 2861, 2893; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.83 (s, 3H), 4.19 (s, 2H), 4.57 (s, 2H), 5.13 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.31 (s, 2H), 7.43 - 7.50 (m, 2H), 7.56 - 7.60 (m, 1H), 8.09 (d, *J* = 8.6 Hz, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$); 55.2, 67.3, 73.4, 73.5, 114.0, 128.4, 129.7, 129.9, 133.3, 159.7, 165.7, 201.8; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{18}H_{18}O_5$+Na: 337.1052; found: 337.1074.

**3-acetoxy-2-oxopropyl benzoate (2h): Yield:** 91% (214 mg), Colorless liquid ; **IR** (Nujol, $cm^{-1}$) 715, 1030, 1347, 1426, 1509, 1749, 1761, 2886, 2941: **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.19 (s, 3H), 4.84 (s, 2H), 4.98 (s, 2H), 7.46 - 7.50 (m, 2H), 7.61 (t, *J* = 6.9 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 20.2, 66.2, 66.7, 128.5, 128.9, 129.9, 133.5, 165.5, 169.8, 197.6. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{12}H_{12}O_5$+Na: 259.0582; found: 259.0576.

**2-oxohexyl benzoate (2i): Yield:** 88% (193 mg), Colorless liquid; **IR** (Nujol, $cm^{-1}$): 719, 1151, 1236, 1323, 1344, 1453, 1576, 1578, 1733, 1744, 2894, 2943; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.89 - 0.96 (t, 3H), 1.36 (dd, *J* = 15.0, 7.3 Hz, 2H), 1.60 - 1.67 (m, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 4.87 (s, 2H), 7.48 (d, *J* = 6.1 Hz, 2H), 7.55 - 7.62 (m, 1H), 8.09 (d, *J* = 7.0 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 13.7, 22.1, 25.2, 38.4, 68.2, 128.3, 129.2, 129.7, 133.2, 165.6, 198.1, 203.6. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3$+Na: 243.0997; found: 243.0965.

**2-oxooctyl benzoate (2j): Yield:** 92% (228 mg), Colorless liquid, **IR** (Nujol, $cm^{-1}$): 714, 1125, 1279, 1357, 1376, 1443, 1566, 1523, 1742, 1753, 2754, 2983: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.86 - 0.93 (t, 3H), 1.30 (br. s., 7H), 1.62 - 1.69 (m, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 4.88 (s, 2H), 7.47 - 7.51 (m, 2H), 7.60 - 7.62 (m, 1 H), 8.08 - 8.13 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 22.4, 23.2, 28.8, 31.5, 38.8, 68.3, 128.4, 129.8, 130.1, 133.3, 165.8, 203.9. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{20}O_3$+Na: 271.1310; found: 271.1321.

**2-oxodecyl benzoate (2k): Yield:** 89% (245 mg), Colorless liquid; **IR** (Nujol, $cm^{-1}$): 745, 1179, 1250, 1314, 1469, 1571, 1650, 1725, 1747, 2856, 2928; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.85 - 0.92 (m, 3H), 1.22 - 1.36 (m, 9H), 1.57 - 1.64 (m, 3H), 2.49 (t, *J* = 7.3 Hz, 2H), 4.86 (s, 1H), 7.40 - 7.52 (m, 2H), 7.53 - 7.65 (m, 1H), 8.03 - 8.14 (m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.5, 29.1, 29.4, 31.8, 35.0, 40.5, 71.0, 128.4, 129.2, 129.8, 133.3, 165.8, 198.5. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{24}O_3$+Na: 299.1623; found: 299.1623.

**2-oxotridecyl benzoate (2l): Yield:** 86 % (273 mg), Colorless liquid; **IR** (Nujol, $cm^{-1}$) 742, 1065, 1314, 1469, 1506, 1724, 1740, 2812, 2943; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.86 - 0.92 (t, 3H), 1.17 - 1.35 (m, 17H), 1.51 - 1.68 (m, 2H), 2.31 (s, 1H), 2.49 (t, *J* = 7.3 Hz, 1H), 4.86 (s, 1H), 7.41 - 7.49 (m, 2 H), 8.07 – 8.08 (m, 1 H), 8.11 - 8.12 (m, 2H); **$^{13}$C NMR** (100 MHz,

$CDCl_3$) δ 14.0, 22.6, 25.5, 29.1, 31.8, 35.0, 38.8, 40.5, 71.0, 128.4, 129.2, 129.8, 133.3, 165.8, 198.5; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{20}H_{30}O_3$+Na: 341.2093; found: 341.2086.

**2-oxocyclohexyl benzoate (2m): Yield:** 82% (178 mg), Colorless liquid; **IR** (Nujol, $cm^{-1}$) 785, 1115, 1394, 1419, 1556, 1734, 1760, 2891, 2933; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.71 – 1.97 (m, 6H), 2.43 - 2.54 (m, 3H), 5.35 - 5.43 (m, 1H), 7.40 - 7.47 (m, 2H), 7.52 - 7.56 (m, 1H), 8.06 - 8.10 (m, 2H); **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 23.6, 27.0 , 33.0, 40.5, 76.7, 128.1, 129.7, 132.9, 165.1, 203.6. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{13}H_{14}O_3$+Na: 241.0841; found: 241.0847.

**1-oxo-2,3-dihydro-1H-inden-2-yl benzoate (2n)**: **Yield:** 76% (191 mg), colorless solid, mp: 141-143 °C; **IR** (Nujol, $cm^{-1}$): 714, 1126, 1275, 1379, 1373, 1582, 1634, 1749, 1822, 2896, 2943; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.20 (dd, *J* = 17.0, 4.8 Hz, 1H), 3.79 (dd, *J* = 17.0, 8.0 Hz, 1H), 5.64 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.42 - 7.49 (m, 5H), 7.59 - 7.71 (m, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 8.08 - 8.12 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 33.7, 74.5, 124.6, 126.7, 128.2, 128.5, 129.4, 130.1, 133.4, 134.8, 135.9, 150.4, 166.0, 200.2; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{12}O_3$+Na: 275.0684; found: 275.0672.

**2-Oxo-1,2-diphenylethyl 4-nitrobenzoate (2o): Yield**: 78% (281 mg), colorless solid, Mp: 114-115 °C; **IR** (Nujol, $cm^{-1}$): 762, 1097, 1288, 1341, 1374, 1462, 1522, 1692, 1720, 2851, 2923; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 7.13 (s, 1H), 7.41 - 7.58 (m, 8H), 7.99 (d, *J* = 7.2 Hz, 2H), 8.28 (s, 4H); **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 78.7, 123.5, 128.7, 128.8, 129.3, 129.7, 131.1, 133.2, 133.6, 134.4, 134.8, 150.7, 164.0, 192.6: **HRMS (ESI)**: $[M+Na]^+$ calcd for: $C_{21}H_{15}NO_5$+Na: 384.0848; found: 384.0853.

**1-Oxo-1-phenylpropan-2-yl 4-nitrobenzoate (2p)**: **Yield**: 81% (242 mg), colorless solid, Mp: 119-120°C; **IR** (Nujol, $cm^{-1}$): 721, 965, 1122, 1270, 1374, 1462, 1522, 1599, 1692, 1725, 2851,

2923; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 1.72 (d, *J* = 6.9 Hz, 3H), 6.23 (q, *J* = 6.9 Hz, 1H), 7.52 - 7.63 (m, 3H), 7.97 - 8.01 (m, 2H), 8.29 - 8.30(m, 4H) ; **$^{13}$C NMR** (100 MHz, $CDCl_3$); δ 17.2, 72.6, 123.4, 128.4, 128.8, 130.9, 133.7, 134.8, 150.6, 163.9, 195.5; **HRMS (ESI)**: $[M+H]^+$ calcd for: $C_{16}H_{13}NO_5$+H :300.0872; found: 300.0877.

**3-((Tert-butyldimethylsilyl)oxy)-1-oxo-1-phenylpropan-2-yl 4-nitro benzoate (2q)**: **Yield**: 84% (360 mg) Mp: 77-78 °C; **IR** (Nujol, $cm^{-1}$): 718, 839, 1270, 1371, 1459, 1530, 1695, 1733, 2851, 2917; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 0.00 (s, 3H), 0.02 (s, 3H), 0.82 (s, 9H), 4.18 (d, *J* = 5.1 Hz, 2H), 6.25 (t, *J* = 5.1 Hz, 1H), 7.47 - 7.62 (m, 3H), 8.00 - 8.04 (m, 2H), 8.29 - 8.30 (m, 4H); **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ -5.4, 18.1, 25.6, 29.7, 62.9, 77.3, 123.5, 128.5, 128.7, 131.0, 133.7, 134.8, 135.2, 150.7, 163.9, 194.4; **HRMS (ESI)**: $[M+H]^+$ calcd for: $C_{22}H_{27}NO_6Si$+H: 430.1686; found: 430.1689.

**1-(4-bromophenyl)-2-methoxy-2-oxoethyl benzoate (2s): Yield:** 78% (273 mg), Colorless liquid: **IR** (Nujol, $cm^{-1}$): 724, 1089, 1277, 1462, 1523, 1600, 1718, 1732, 2855, 2926: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.11 (s, 1H), 7.46 - 7.48 (m, 5H), 7.56 - 7.58 (m, 2H), 8.11 - 8.13 (m, 2H); **$^{13}$C NMR** (100 MHz,$CDCl_3$) δ 52.7, 74.2, 128.4, 129.2, 129.3, 129.9, 132.0, 132.2, 133.3, 133.5, 165.7 168.7; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{13}BrO_4$+Na: 370.9895; found: 370.9885.

**1-(4-cyanophenyl)-2-methoxy-2-oxoethyl benzoate (2t): Yield:** 81% (238 mg), Colorless liquid; **IR** ($CHCl_3$, $cm^{-1}$): 718, 1101, 1167, 1269, 1348, 1508, 1606, 1731, 1760, 2210, 2856, 2953 : **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.21 (s, 1H), 7.57 - 7.73 (m, 7H), 8.12 (d, *J* = 7.2 Hz, 2H) $^{13}$C NMR (50 MHz, $CDCl_3$) δ 53.0, 73.9, 100.2, 127.0, 128.2, 128.6, 130.0, 132.1,

132.6, 133.8, 148.2, 165.3, 168.1; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{13}NO_4$+Na: 318.0742; found: 318.0742.

**1-(4-nitrophenyl)-2-methoxy-2-oxoethyl benzoate (2u): Yield:** 82% (258 mg), Colorless liquid; **IR** ($CHCl_3$, $cm^{-1}$): 718, 1101, 1169, 1269, 1346, 1366, 1508, 1527, 1696, 1731, 1760; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.28 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 8.13 (m, *J* = 8.5 Hz, 2H), 8.31 (m, *J* = 8.8 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 53.1, 73.7, 124.1, 128.4, 128.6, 130.0, 133.8, 140.8, 165.3, 168.1. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_6$+Na: 338.0641; found: 338.0661.

**1-(furan-2-yl)-2-methoxy-2-oxoethyl benzoate (2v): Yield:** 78% (203 mg), white solid, mp: 100-102 °C; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.31 (s, 1H), 6.42 (dd, 1H), 6.55 (d, 1H), 7.38 - 7.51 (m, 3H), 7.55 (d, 1H), 8.02 - 8.15 (m, 2H): **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 52.7, 67.8, 110.7, 111.1, 128.3, 128.9, 130.0, 133.4, 143.8, 146.8, 165.3, 166.9; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{14}H_{12}O_5$+Na: 283.0582; found: 283.0577.

**1-((1-(4-methoxyphenyl)pentyl)oxy)-1-oxopropan-2-yl benzoate (2w): Yield:** 74% (275 mg), Colorless liquid; **IR** ($CHCl_3$, $cm^{-1}$): 728, 1131, 1269, 1349, 1376, 1558, , 1696, 1745, 1760, 2845, 2905; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.26 - 1.41 (m, 4H), 1.53 - 1.57 (m, 3H), 1.70 - 1.82 (m, 2H), 3.81 (s, 3H), 4.56 - 4.68 (m, 1H), 5.25 - 5.35 (m, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.58 - 7.65 (m, 1H), 8.08 - 8.13 (m, 2H); **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 14.1, 22.6, 28.1, 38.7, 55.1, 74.2, 75.1, 77.4, 113.7, 127.1, 128.2, 128.5, 129.7, 129.9, 132.9, 133.5, 137.2, 158.9, 159.1, 165.8. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{22}H_{26}O_5$+Na: 393.1678; found: 393.1634.

**dimethyl 2-(benzoyloxy)malonate (2x): Yield**: 83% (210 mg), colorless liquid,**: IR** ($CHCl_3$, $cm^{-1}$): 1176, , 1591, 1695, 1726, 1766, 2854, 2870, 2923; **1H NMR** ( 400 MHz $CDCl_3$) δ 3.87 (s, 6H), 5.83 (s, 1H), 7.49–7.54(m, 2H), 7.59–7.65 (m, 1H), 8.15–8.18 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 52.6, 53.3, 85.2, 128.4, 128.6, 130.4, 134.0, 159.4, 164.1. **HRMS (ESI)**: $[M+H]^+$ calcd for $C_{12}H_{13}O_6$+H: 253.0712; found: 253.0746.

**2-ethoxy-2-oxoethyl benzoate (2y): Yield:** 89% (185 mg), Colorless liquid; **IR** (neat, $cm^{-1}$): 1121 1285, 1738, 1759, , 1732, 2983, 2926 ; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.2 Hz, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.84 (s, 2H), 7.40 - 7.52 (m, 2H), 7.54 - 7.67 (m, 1H), 7.92 - 8.19 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 13.9, 60.9, 128.2, 129.7, 133.1, 165.5, 167.4. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{11}H_{12}O_4$+Na: 231.0633; found: 231.0653.

**2-oxotetrahydro-2H-pyran-3-yl benzoate (2z): Yield:** 84% (185 mg), Colorless liquid; **IR** (Nujol, $cm^{-1}$): 858, 1124, 1273, 1377, 1456, 1511, 1602, 1725, 1753, 2857, 2912: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.61 - 1.75 (m, 1H), 1.77 – 1.88 (m, 2H), 1.90 - 2.15 (m, 1H), 3.57 - 3.64 (m, 1H), 4.01 - 4.06 (m, 1H), 4.90 - 4.94 (m, 1H), 7.39 - 7.56 (m, 3H), 8.06 (d, *J* = 8.7 Hz, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 22.3, 25.2, 62.3, 71.1, 128.4, 129.9, 130.2, 133.1, 166.1, 166.1. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{12}H_{12}O_4$+Na: 243.0663; found: 243.0665.

**2-oxo-2-phenylethyl acetate** (**4a**): Yield: 64% (114 mg), colorless liquid; **$^1$H NMR** (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 5.30 (s, 2H), 7.46 (t, *J*=7.58 Hz, 2H), 7.58 (t, *J*=7.34 Hz, 1H), 7.89 (d, *J*=8.31 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 20.4, 65.9, 127.7, 128.8, 133.7, 134.3, 170.1, 191.8; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{10}H_{10}O_3$+Na: 201.0527; found: 201.0516.

**2-Oxo-2-phenylethyl 4-nitrobenzoate (4b): Yield**: 72% (204 mg), colorless solid, Mp: 123-124 °C ; **IR** (Nujol, $cm^{-1}$): 719, 1104, 1229, 1294, 1376, 1462, 1524, 1598, 1696, 1727, 275, 2840, 2923; **$^1$H NMR** (200 MHz, $CDCl_3$): $\delta$ 5.64 (s, 2H), 7.51 - 7.55 (m, 2H), 7.63 - 7.65 (m, 1H), 7.97 (d, $J$ = 8.5 Hz, 2H), 8.33 (s, 4H); **$^{13}$C NMR** (50 MHz, $CDCl_3$) : δ 66.9, 123.4, 127.7, 128.9, 130.9, 133.8, 134.0, 134.7, 150.6, 164.0, 191.0: **HRMS (ESI)**: $[M+H]^+$ calcd for $C_{15}H_{11}NO_5$+H: 286.0715; found: 286.0726. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{11}NO_5$+Na: 308.0535; found: 308.0547.

**2-Oxo-2-phenylethyl 4-chlorobenzoate (4c)**: **Yield**: 76% (208 mg), colorless solid, Mp: 127-128 °C ; **IR** (Nujol, $cm^{-1}$): 753, 1091, 1226, 1273, 1376, 1456, 1595, 1697, 1726, 2724, 2857, 2926; **$^1$H NMR** (500 MHz, $CDCl_3$): δ 5.58 (s, 2H) 7.44- 7.56 (m, 5H), 7.97(d, $J$ = 7.3 Hz, 2H) 8.07 – 8.11 (d, $J$ = 7.3 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$): δ 66.5, 77.0, 127.8, 128.6, 128.8, 128.9, 131.3, 133.9, 134.2, 139.8, 165.0, 191.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{11}ClO_3$+Na: 297.0294; found: 297.0292.

**2-Oxo-2-phenylethyl nicotinate (4d): Yield**: 74% (180 mg) **$^1$H NMR** (400 MHz, $CDCl_3$); δ 5.61 (s, 2H), 7.44 (dd, $J$ = 7.6, 4.9 Hz, 1H) 7.50 - 7.54 (m, 2H), 7.62 - 7.64 (m, 1H), 7.97 (d, $J$ = 7.5 Hz, 2H), 8.40 (d, $J$ = 7.7 Hz, 1H), 8.82 (br. s, 1H), 9.33 (br. s, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 66.6, 123.3, 125.6, 127.8, 128.9, 134.0, 134.1, 137.4, 151.2, 153.7, 164.6, 191.1; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{14}H_{11}NO_3$+Na: 264.0637; found: 264.0648.

**2-oxo-2-phenylethyl (E)-but-2-enoate (4e): Yield**: 79% (160 mg), colorless liquid; **$^1$H NMR** (400 MHz,$CDCl_3$): δ 1.95 (dd, $J$ = 6.9, 1.8 Hz, 3H), 5.38 (s, 2H), 5.99 - 6.03 (m, 1H), 7.07 - 7.16 (m, 1 H), 7.50 (d, $J$ = 8.2 Hz, 2H), 7.58 - 7.62 (m, 1H), 7.93 (d, $J$ = 6.9 Hz, 2H); **$^{13}$C NMR** (50

MHz, $CDCl_3$) δ 17.9, 65.5, 121.7, 127.6, 128.6, 133.5, 145.8, 165.2, 191.8; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{12}H_{12}O_3$+Na: 227.0684; found: 227.0675.

**2-iodo-1-phenylethyl benzoate**: **Yield**: 70%, colorless liquid: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 3.63 (dd, *J* = 6.4, 2.1 Hz, 2H), 6.10 (dd, *J* = 7.2, 5.6 Hz, 1H), 7.29 - 7.67 (m, 9H), 8.11 - 8.16 (m, 2H); **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 8.1, 75.2, 126.1, 128.3, 128.5, 129.7, 133.0, 138.4, 164.9; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3$+Na: 243.0997; found: 243.0965.

**2-hydroxy-2-phenylethyl benzoate (3a): Yield:** 86% (208 mg), colorless solid, mp: 65-67 °C; $^1$H NMR (400 MHz, $CDCl_3$); δ 2.67 (s, 1H), 4.42 - 4.51 (m, 1H), 4.52 - 4.55 (m, 1H), 4.69 (s, 1H), 5.09-5.12 (dd, *J* = 8.2, 3.2 Hz, 1H), 7.35 - 7.47 (m, 7H), 7.53 - 7.56 (m, 1H), 8.06 (d, *J* = 9.6 Hz, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 69.7, 72.4, 126.2, 126.9, 128.1, 128.3, 128.5, 129.7, 133.1 , 140.0, 166.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{14}O_3$+Na: 265.0835; found: 265.0839.

**2-hydroxy-2-(p-tolyl)ethyl benzoate (3b) Yield:** 84% (215 mg), colorless solid, mp: 79-80 °C; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.66 (br. s., 1H), 4.35 - 4.49 (m, 2H), 5.07 (dd, *J* = 8.0, 3.5 Hz, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.41 - 7.49 (m, 2H), 7.55 - 7.58 (m, 1H), 8.06 (d, *J* = 7.2 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 21.2, 69.8, 72.4, 126.1, 128.4, 129.3, 129.8, 133.1, 137.1, 137.8, 166.6: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{16}O_3$+Na: 256.1099; found: 256.1094.

**2-(4-bromophenyl)-2-hydroxyethyl benzoate (3c) Yield:** 86% (275 mg), colorless solid, mp: 115-117 °C; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 2.77 (br. s., 1H) 4.32 - 4.53 (m, 2H), 5.07 (dd, *J* = 7.89, 3.22 Hz, 1H), 7.31 - 7.36 (m, 2H), 7.42 - 7.50 (m, 4H), 7.59 - 7.63 (m, 1H), 8.03 (d, *J* = 8.59 Hz, 2H); **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 69.5, 71.8, 122.0, 127.9, 128.4, 129.6, 131.6,

133.2, 139.0, 166.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{13}BrO_3$+Na: 320.0048; found: 320.0056.

**2-(4-cyanophenyl)-2-hydroxyethyl benzoate (3d): Yield:** 79% (210 mg), colorless solid, mp: 94-96 °C: **$^1$H NMR** (400 MHz, $CDCl_3$): δ 3.51 - 3.55 (m, 1H), 3.63 - 3.68 (m, 1H), 3.98 (d, *J*=7.3 Hz, 1H), 4.91 - 5.01 (m, 1H), 7.32 - 7.39 (m, 2H), 7.50 - 7.57 (m, 3H), 7.63-7.65 (m, 1H), 7.71- 7.79 (m, 2H), 7.96-8.16 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 56.6, 73.3, 126.4, 126.4, 128.0, 130.7, 130.8, 134.2, 139.0, 139.7, 143.8, 157.9; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_3$+Na: 290.0793; found: 290.0782.

**2-(4-acetoxyphenyl)-2-hydroxyethyl benzoate (3e) Yield:** 83% (250 mg), colorless solid, mp: 105-117 °C ; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.68 (br. s., 1H), 4.39 - 4.55 (m, 2 H), 5.11 (dd, *J* = 8.0, 3.3 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.46 - 7.63 (m, 5H), 8.03 - 8.07 (m, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 21.1, 69.7, 72.0, 121.7, 127.3, 128.4, 129.8, 133.2, 137.6, 150.4, 166.6, 169.2: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{16}O_5$+Na: 300.0998; found: 300.0992

**2-(3,4-dimethoxyphenyl)-2-hydroxyethyl benzoate (3f) Yield:** 81% (245 mg), colorless solid, mp: 129-130 °C; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 2.65 - 2.67 (m, 1H), 3.89 (s, 6H), 4.41 - 4.52 (m, 2H), 5.03 - 5.07 (m, 1H), 6.83 - 6.87 (m, 1H), 6.95- 6.99 (m, 2H), 7.41 - 7.54 (m, 3H), 8.05 (d, *J* = 7.20 Hz, 2 H): **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 55.6, 55.7, 69.7, 71.8, 109.4, 111.1, 118.5, 128.3, 129.8, 133.0, 133.1, 148.6, 148.9, 166.5; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{18}O_5$+Na: 271.0970; found: 271.0984.

**3-((4-methoxybenzyl)oxy)propane-1,2-diol (3g): Yield:** 82% (173 mg), colourless liquid, **$^1$H NMR** (400 MHz,$CDCl_3$) δ 3.43 - 3.51 (m, 1H), 3.56 (d, *J* = 5.1 Hz, 1H), 3.76 (d, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 3.88 (t, *J* = 4.8 Hz, 2H), 4.16 (quin, *J* = 5.7 Hz, 1H), 4.49 - 4.51 (m, 2H), 6.89

(d, *J* = 8.6 Hz, 2H), 7.25 (s, 2H); **$^{13}$C NMR** (100 MHz,$CDCl_3$) δ 52.4, 55.0, 64.4, 70.9, 72.9, 113.7, 128.2, 129.2, 159.2. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{11}H_{16}O_4$+Na: 235.0946; found: 235.0985.

**3-acetoxy-2-hydroxypropyl benzoate** (**3h**): Yield: 89% (212 mg), colorless liquid: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.80-3.82 (m, 2H), 4.41-4.52 (m, 3H), 5.19-5.22 (t, 1H), 7.39 - 7.59 (m, 3H), 8.02 (d, *J*= 6.9, 2H); **$^{13}$C NMR** ($CDCl_3$) δ 20.2, 66.3, 66.7, 67.7, 128.5, 128.9, 129.9, 133.5, 165.5, 169.8; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{12}H_{14}O_5$+Na: 261.0738; found: 261.0741.

**2-hydroxyhexyl benzoate (3i): Yield:** 88% (195 mg), colorless liquid ; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.94 (t, *J* = 6.95 Hz, 3H), 1.35 - 1.56 (m, 6H), 2.25 (br. s., 1H), 3.96 (m, 1H), 4.17 - 4.43 (m, 2H), 7.27 - 7.57 (m, 3H), 8.03 - 8.12 (m, 2 H); **$^{13}$C NMR** (50 MHz, $CDCl_3$): δ 14.1, 22.7, 27.6, 33.2, 69.2, 70.1, 128.4, 129.7, 130.0, 133.1, 166.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{13}H_{18}O_3$+Na: 245.1148; found: 245.1149.

**2-hydroxyoctyl benzoate (3j): Yield:** 90% (225 mg), colorless liquid: $^1$H NMR (200 MHz, $CDCl_3$) δ 0.86 - 0.91 (t, *J* = 7.3 Hz, 3H), 1.30 (br. s., 8H), 1.55 (br. s., 2 H) 2.09 (br. s., 1H), 3.97 (t, *J* = 9.03 Hz, 1H), 4.21 (dd, *J* = 11.4, 7.0 Hz, 1H), 4.39 (dd, *J* = 11.4, 3.2 Hz, 1H), 7.41 - 7.48 (m, 2H), 7.54 - 7.57 (m, 1H), 8.05 (dd, *J* = 8.3, 1.3 Hz, 2H): **$^{13}$C NMR** (50 MHz, $CDCl_3$) δ 14.0, 22.5, 25.3, 29.2, 31.7, 33.4, 69.2, 70.0, 128.3, 129.6, 129.9, 133.1, 166.7: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{15}H_{22}O_3$+Na: 273.1461; found: 273.1438.

**2-hydroxydecyl benzoate (3k): Yield:** 87% (240 mg), colorless liquid; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.86 - 0.92 (t, *J* = 7.3, 3H), 1.28 (br. s., 13H), 2.09 (br. s., 1H), 3.99 (br. s., 1H), 4.23 (dd, *J* = 11.4, 7.1 Hz, 1 H), 4.41 (dd, *J* = 11.4, 3.2 Hz, 1H), 7.27 - 7.62 (m, 3H), 8.06 (d, *J* = 8.5

Hz, 2H) **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.1, 22.7, 25.5, 29.3, 29.5, 29.6, 31.9, 33.5, 69.3, 70.2, 128.4, 129.7, 130.0, 133.1, 166.7: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{26}O_3$+Na: 301.1774; found:301.1778.

**2-hydroxytridecyl benzoate (3l): Yield:** 84% (268 mg), colorless liquid; **$^1$H NMR** (200 MHz, $CDCl_3$): δ 0.85 - 0.91 (m, 3H), 1.26 (s, 20H), 1.45 - 1.60 (m, 3H), 2.14 (br. s., 1H), 3.98 (br. s., 1H), 4.17 - 4.43 (m, 2H), 7.41 - 7.61 (m, 3H), 8.05 (d, *J* = 6.9 Hz, 2H): **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ: 14.2, 22.7, 25.5, 29.4, 29.6, 29.7, 31.9, 33.5, 69.3, 70.2, 128.4, 129.7, 130.0, 133.1, 166.6: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{20}H_{32}O_3$+Na: 343.2244; found: 343.2239.

**2-hydroxycyclohexyl benzoate (3m): Yield:** 83% (183 mg), colorless liquid; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.39 - 1.47 (m, 3H), 1.67 - 1.76 (m, 4H), 1.96 (br. s., 1 H), 2.14 (d, *J* = 11.7 Hz, 2H), 3.67 - 3.98 (m, 1H), 4.83 - 5.23 (m, 1H), 7.40 - 7.56 (m, 3H), 8.05 (d, *J* = 7.2 Hz, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 23.6, 23.8, 29.9, 32.9, 72.5, 78.5, 128.2, 129.6, 132.9, 166.6: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{13}H_{16}O_3$+Na: 243.0992; found: 243.0998.

**1-hydroxy-2,3-dihydro-1H-inden-2-yl benzoate (3n): Yield:** 72% (182 mg), colorless solid, mp: 169-170 °C ; **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.63 (bs., 1H), 3.12 - 3.26 (m, 1H), 3.55 (dd, *J* = 16.3, 8.0 Hz, 1H), 5.30 - 5.43 (m, 2H), 7.25 - 7.30 (m, 3H), 7.44 - 7.46 (m, 3H), 7.49 – 8.04 (m, 1H), 8.05 - 8.09 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 36.0, 76.8, 77.1, 77.4, 80.5, 84.8, 96.2, 124.7, 124.8, 127.6, 128.4, 128.5, 128.9, 129.8, 129.8, 129.9, 133.4, 138.5 , 141.3, 167.7; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{16}H_{14}O_3$+Na: 277.0835; found: 277.0840.

**11-hydroxyoxacyclododecan-2-one (3r): Yield:** 82% (165 mg), colorless liquid: **$^1$H NMR** (200 MHz, $CDCl_3$) δ 1.32 (br. s., 10H), 1.53 - 1.56 (m, 4H), 1.72 - 1.84 (m, 1H), 2.06 - 2.21 (m, 1H), 3.59 - 3.66 (m, 2H), 3.81 - 3.88 (m, 1H), 4.09 - 4.20 (m, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$): δ

25.6, 26.7, 28.7, 29.2, 29.4, 32.6, 35.9, 36.3, 53.1, 63.0, 153.7. **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{11}H_{20}O_3$+Na: 223.1310; found: 223.1398.

**2-allyl-2-hydroxytridecyl benzoate (5):**

To a solution of (R)-BINOL (0.233 g, 0.817 mmol) and $Ti(OiPr)_4$ (0.230 g, 0.817 mmol) in $CH_2Cl_2$ (60 mL) in the presence of 4 Å molecular sieves (MS) (4 g) was stirred at reflux. After 1 h, the reaction mixture was cooled to room temperature and to it was added ketone **2l** (2.6 g, 8.176 mmol) in dry $CH_2Cl_2$ and the resulting mixture was stirred for 10 min. The reaction mixture was then cooled to -78 °C and allyl tributylstannane (3.82 g, 10.220 mmol) was added to the reaction mixture and the stirring was continued at -20 °C for 36 h. After completion of the reaction as noticed by TLC, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and the reaction mixture was stirred for an additional 30 min and extracted into $CH_2Cl_2$ (40 mL). The organic phase was washed with brine (30 mL), dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced pressure to give crude residue, which was purified over silica gel column chromatography using EtOAc–hexane (2:8) to afford homoallylic alcohol **5** (2.61 g, 81%) as a clear liquid with 81% ee. **Yield:** 81% (2.61 g), colorless liquid; **$^1$H NMR** (400 MHz,) δ, 0.87 - 0.91 (t, *J* = 7.3, 3H), 1.25 - 1.59 (m, 19H), 1.67 - 1.86 (m, 1H), 2.37 - 2.38 (m, 2H), 4.23 (s, 1H), 5.11 - 5.18 (m, 2H), 5.84 - 5.89 (m, 1H), 7.43 - 7.44 (m, 2H), 7.54 - 7.58 (m, 1H), 8.04 - 8.06 (m, 2H): **$^{13}$C NMR** (100 MHz, $CDCl_3$): δ 14.2, 22.7, 23.1, 25.5, 29.4, 29.6, 29.7, 30.2, 31.9, 37.1, 37.3, 41.6, 69.5, 72.1, 118.3, 119.1, 128.4, 129.7, 133.0, 134.4, 166.3: **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{23}H_{36}O_3$+Na: 383.2557; found: 383.2552.

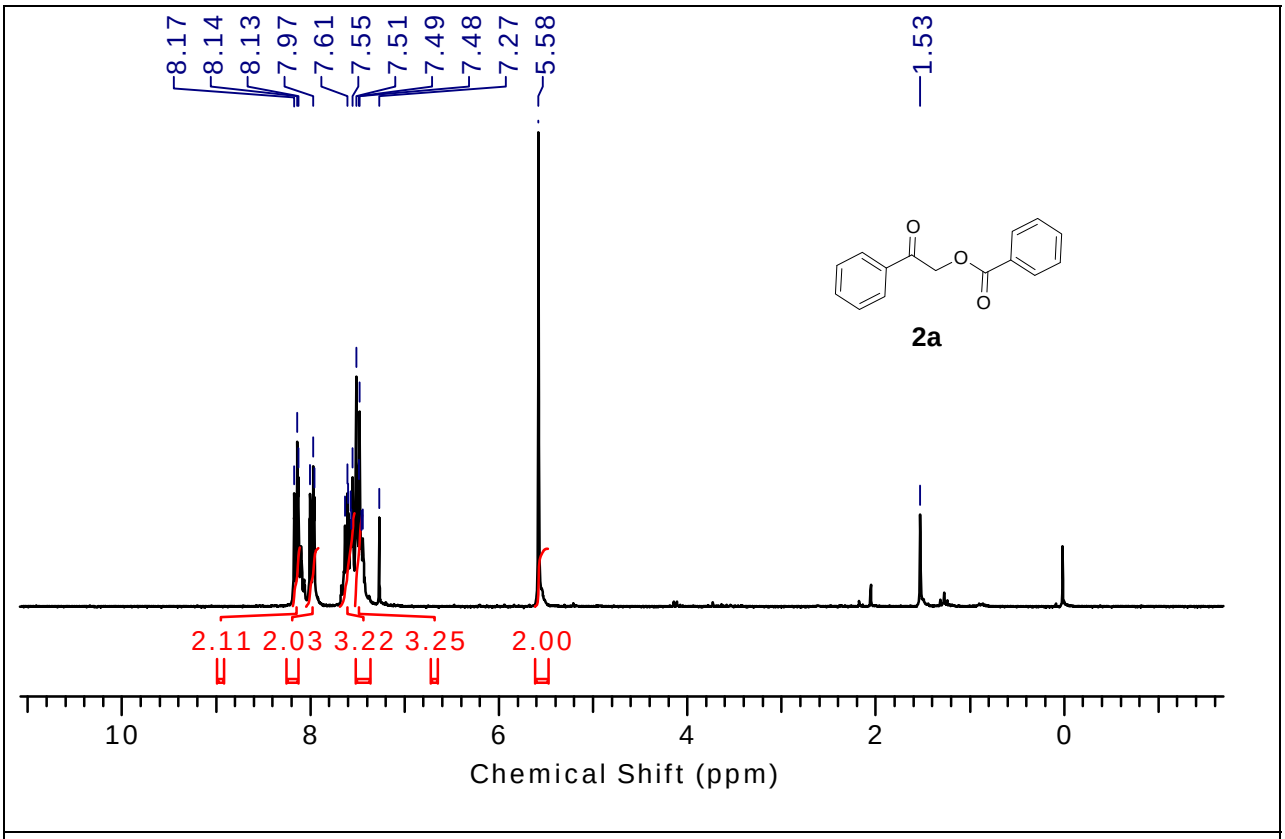
**(E)-2-hydroxy-2-(4-methoxy-4-oxobut-2-en-1-yl)tridecyl benzoate (6):** To a solution of homoallylic alcohol **5** (1.5g, 4.167 mmol) in degassed $CH_2Cl_2$ (20.0 mL) were added methyl

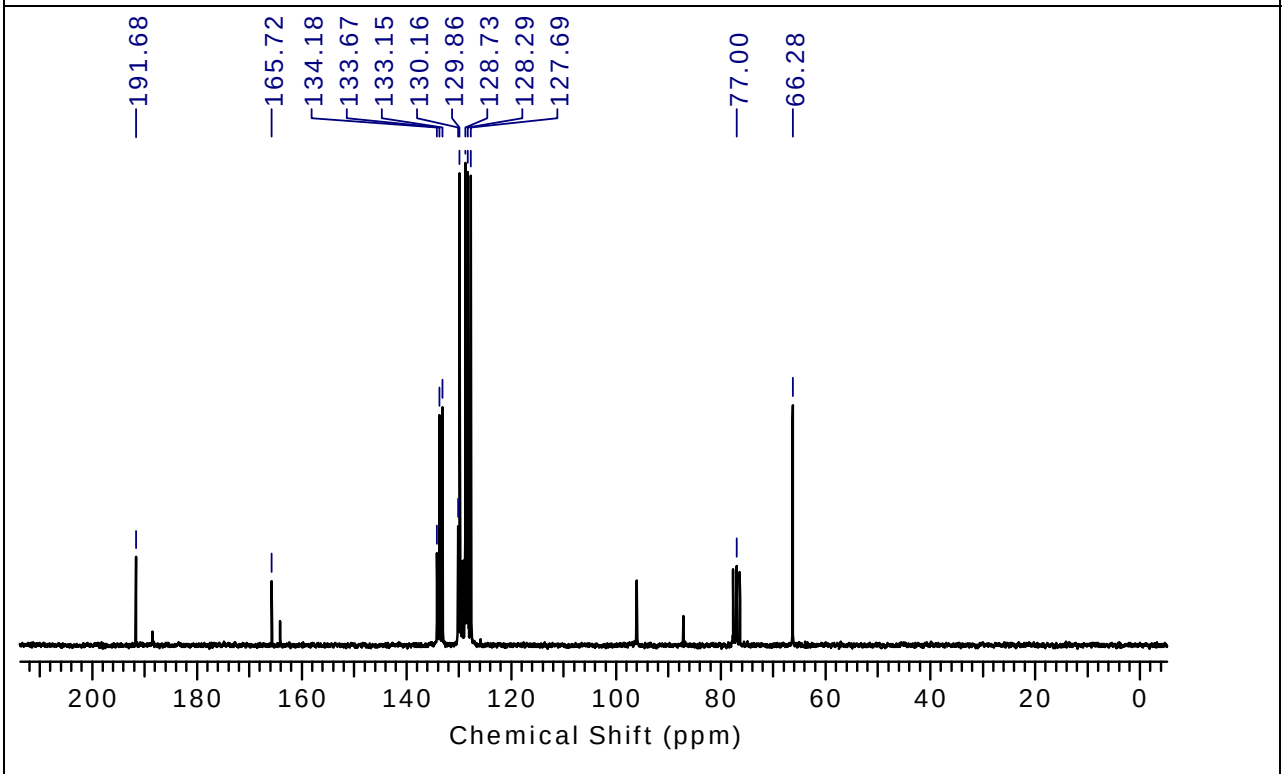
acrylate (3.58g, 41.670 mmol) and a solution of Grubbs-II$^{nd}$ generation catalyst (160 mg, 0.208 mmol) in degassed $CH_2Cl_2$ (2.0 mL) dropwise, and the resultant solution was stirred at room temperature for 3 h. The reaction mixture was then stirred at room temperature under air to destroy the ruthenium catalyst. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (20 to 30% EtOAc/hexanes) to give α,β-unsaturated ester **6** (1.53 g) in pure form.

**Yield**: 88% (1.53 g) colourless oil. **$^1$H NMR** (200 MHz, $CDCl_3$) δ 0.86 - 0.91 (m, 3H), 1.26 (s, 16H), 1.56 - 1.64 (m, 2 H), 2.21 (s, 1H), 2.52 (dd, *J* = 7.7, 1.0 Hz, 2H), 3.72 (s, 3H), 4.19 - 4.33 (m, 2H), 5.88 – 5.96 (m, 1H), 6.96 - 7.12 (m, 1H), 7.42 - 7.50 (m, 2H), 7.55 - 7.64 (m, 1H), 8.01 - 8.06 (m, 2H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 14.2, 22.7, 23.2, 29.4, 29.5, 29.6, 29.6, 29.7, 30.1, 32.0, 37.5, 40.3, 51.5, 69.7, 73.6, 124.4, 128.5, 129.8, 133.3, 143.6, 166.3, 166.4

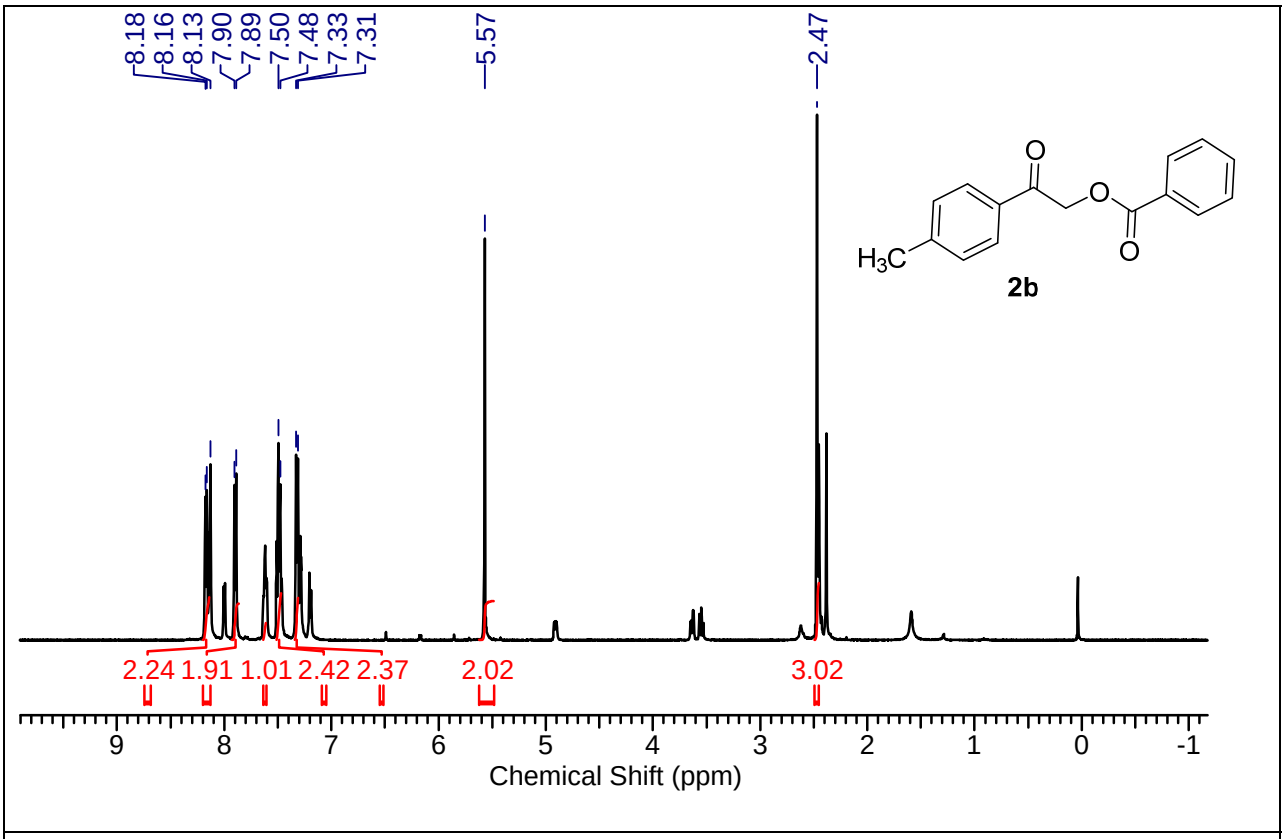
**(+)-Tanikolide (7):** To a solution of α,β-unsaturated ester **6** (1.0g, 2.386 mmol) in methanol was added 10% Pd/C (20 mg), and the resultant suspension was stirred at room temperature under an atmosphere of $H_2$ (1 atm.) overnight. The catalyst was filtered off, to the filtrate $K_2CO_3$ (0.692g, 5.016 mmol) was added. The reaction mixture was stirred at room temperature for 3 h. After completion (as monitored by TLC), the reaction mixture was concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (40 to 50% EtOAc/pet ether) gave (+)-Tanikolide (7) (0.576g, 85%) as a colorless oil. The spectroscopic data of this material were in full accordance with the literature reports. **Yield:** 85% (0.576 g), colourless oil. $[\alpha]_D^{25}$ = +1.91 (*c* = 0.72, $CHCl_3$) {lit.ref $[\alpha]_D^{20}$ = +2.3 (*c* = 0.65, $CHCl_3$)}. **$^1$H NMR** (200 MHz,$CDCl_3$): δ 0.86 - 0.91 (m, 3H), 1.26 (br. s., 18H), 1.56 - 1.62 (m, 3H), 1.72-1.79 (br. s., 2 H), 2.00 (br. s., 1 H), 2.36 (t, *J* = 7.0 Hz, 2H), 3.67 (s, 2 H); **$^{13}$C NMR** (100 MHz,$CDCl_3$) 14.2,

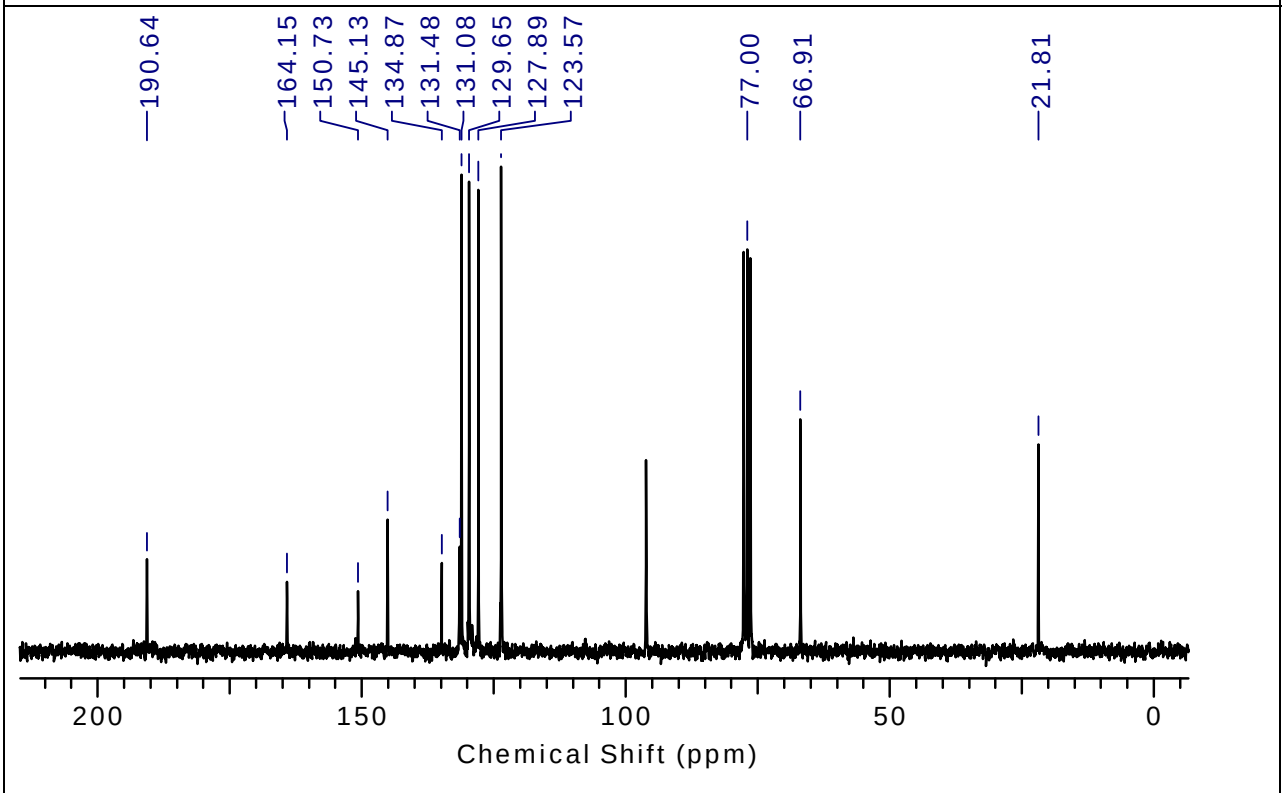
18.8, 22.8, 23.4, 29.4, 29.6, 29.7, 29.7, 29.7, 30.3, 32.0, 34.3, 36.1, 36.9, 69.8, 73.5, 173.6; **HRMS (ESI)**: $[M+Na]^+$ calcd for $C_{17}H_{32}O_3$+Na: 307.2249; found: 307.2213.



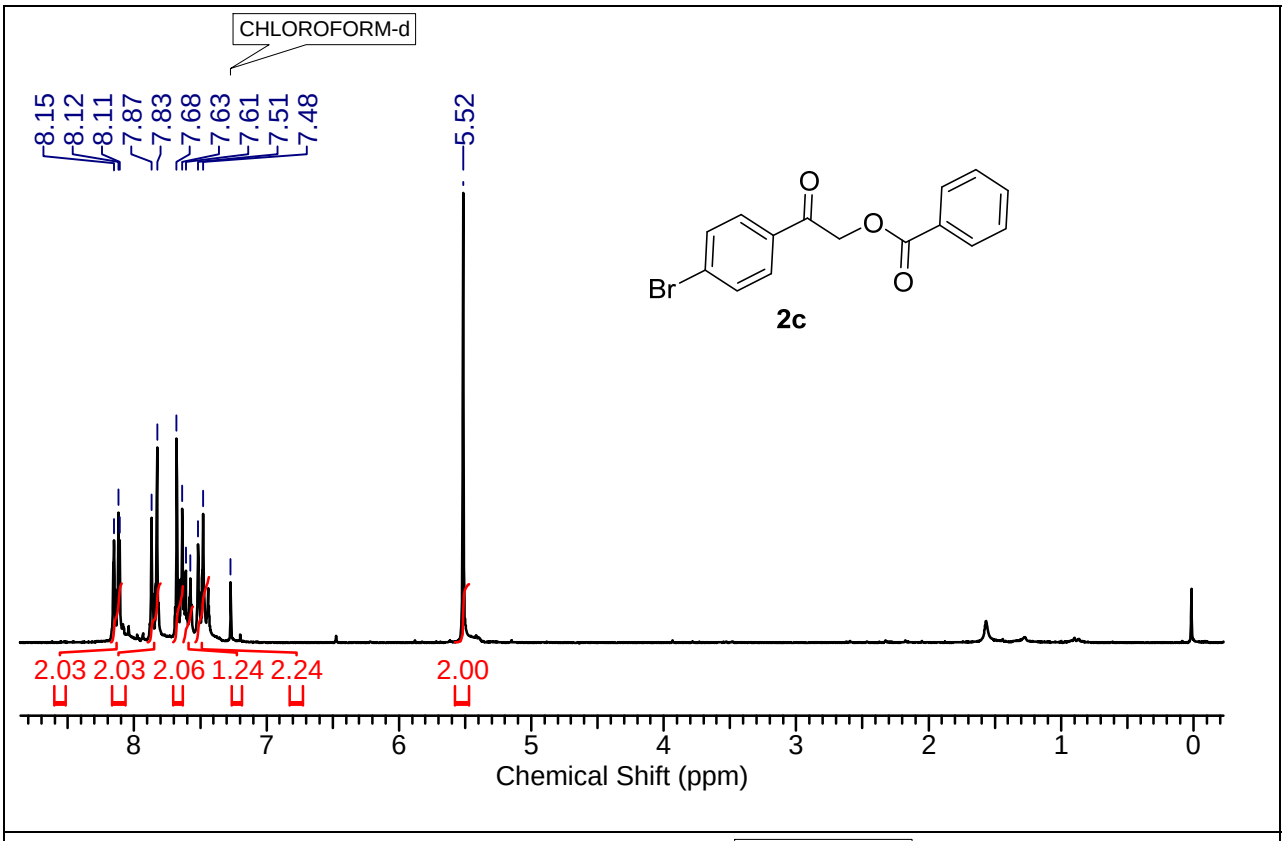



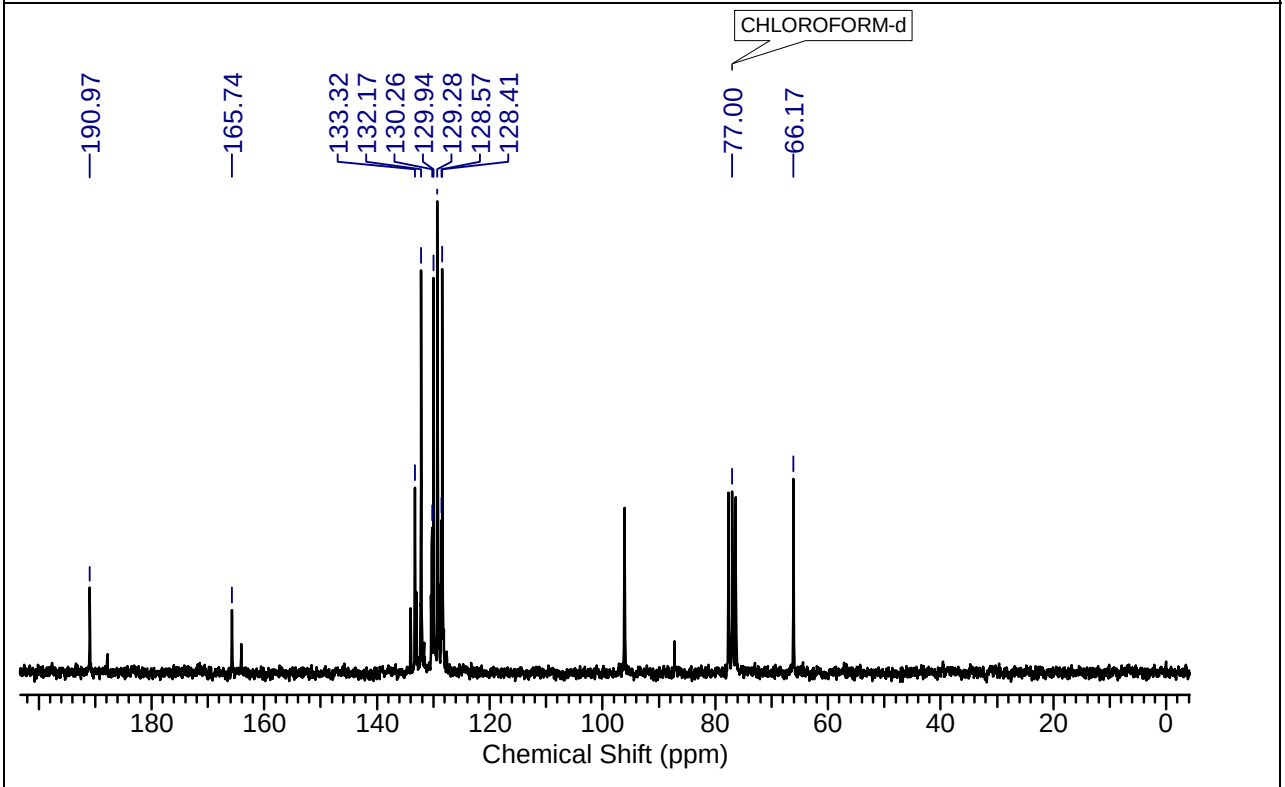

**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-phenylethyl benzoate (2a)**



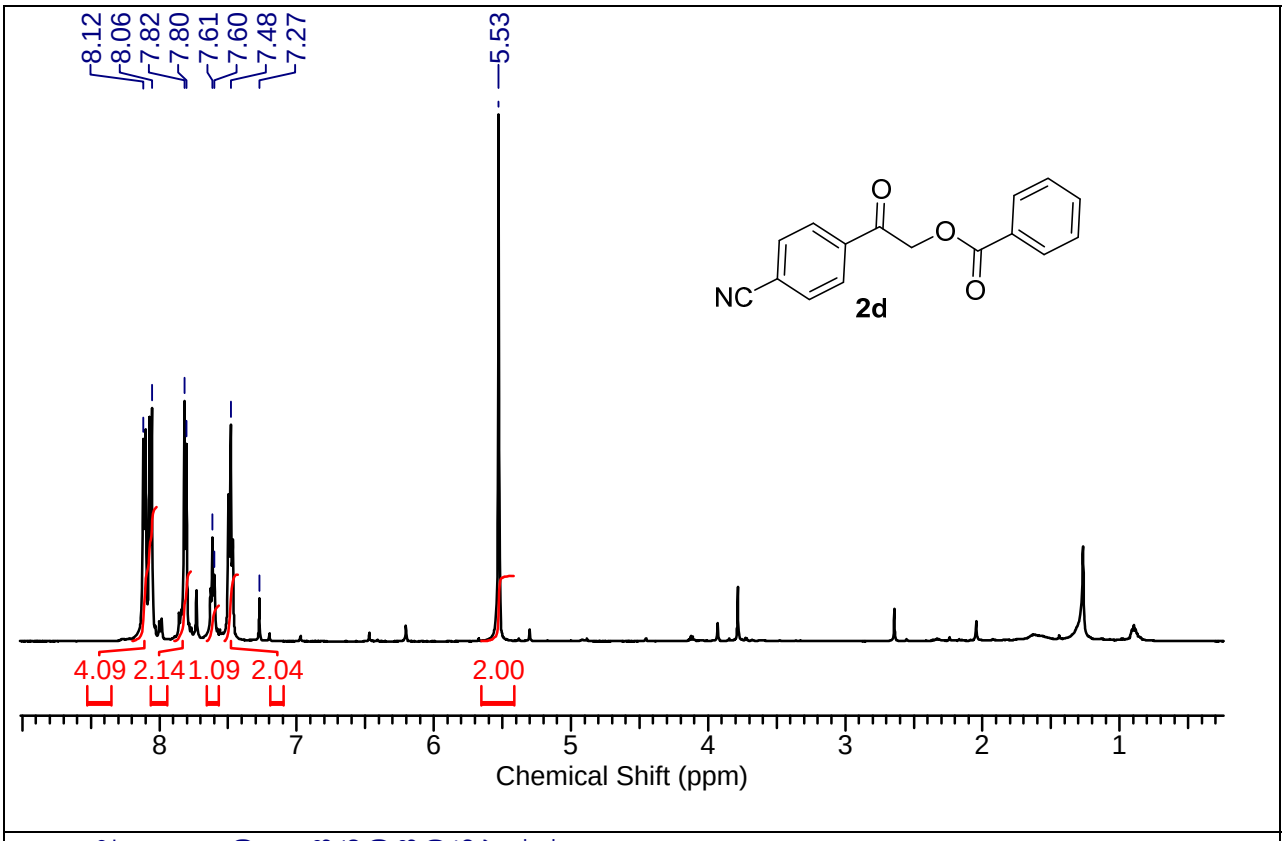



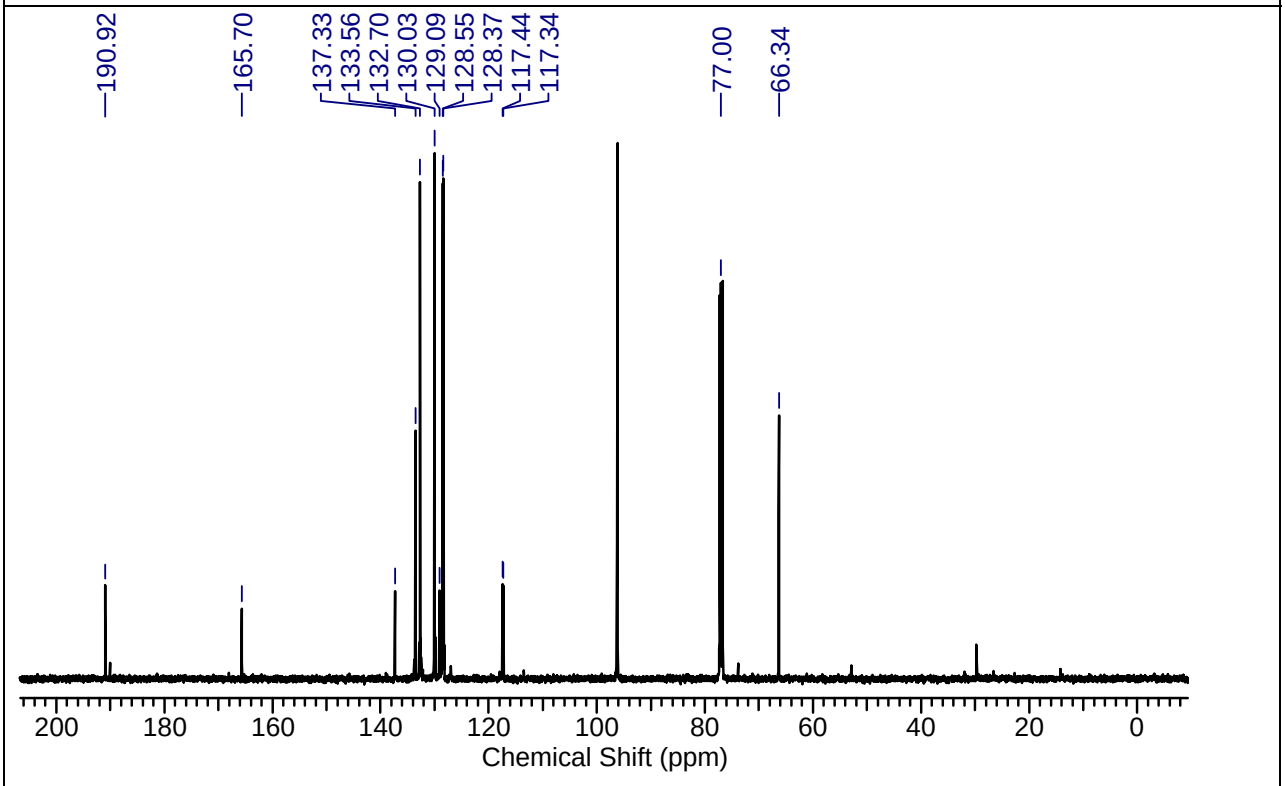

**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-(p-tolyl)ethyl benzoate (2b)**



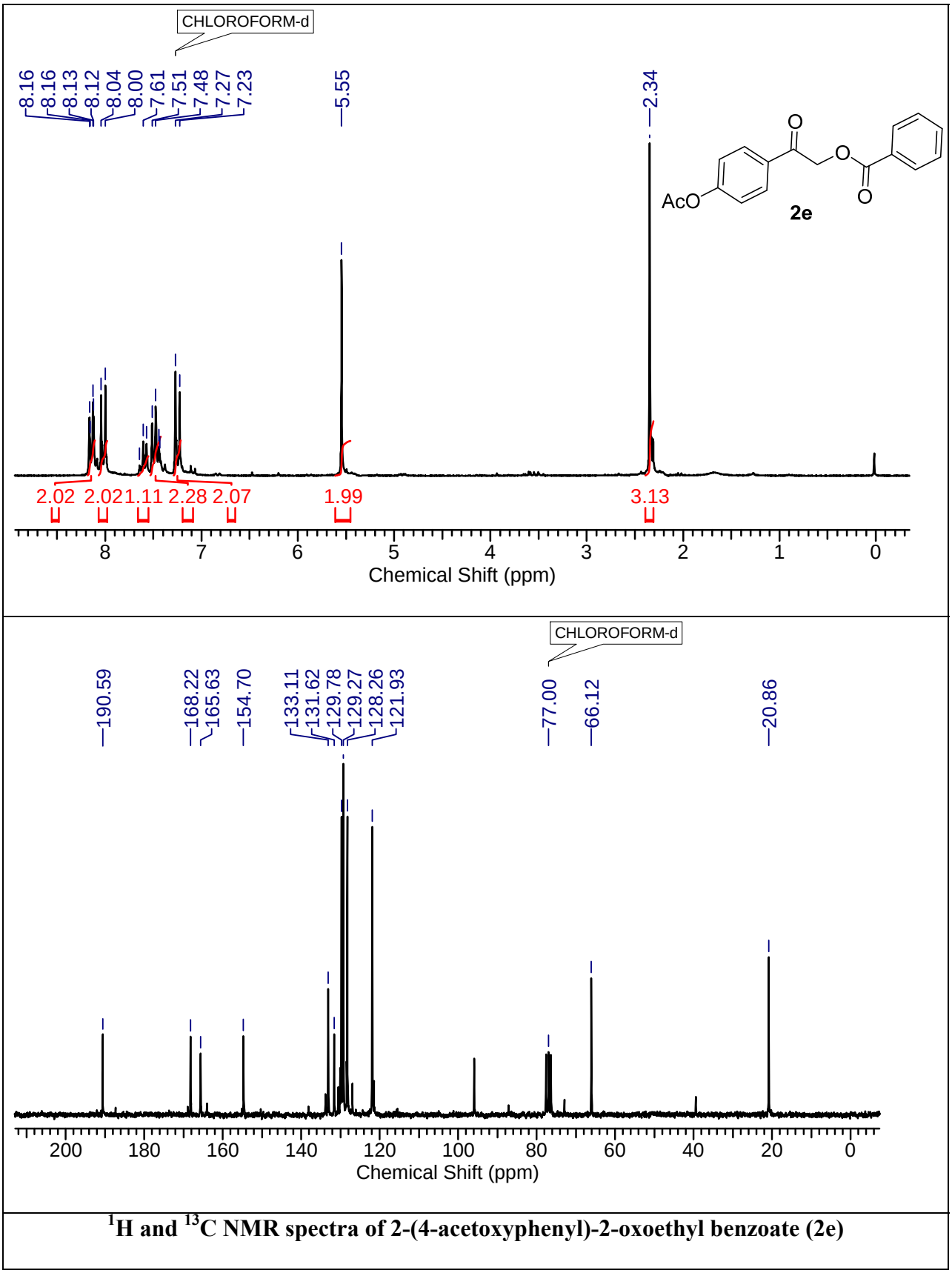




**$^{1}$H and $^{13}$C NMR spectra of 2-(4-bromophenyl)-2-oxoethyl benzoate (2c)**

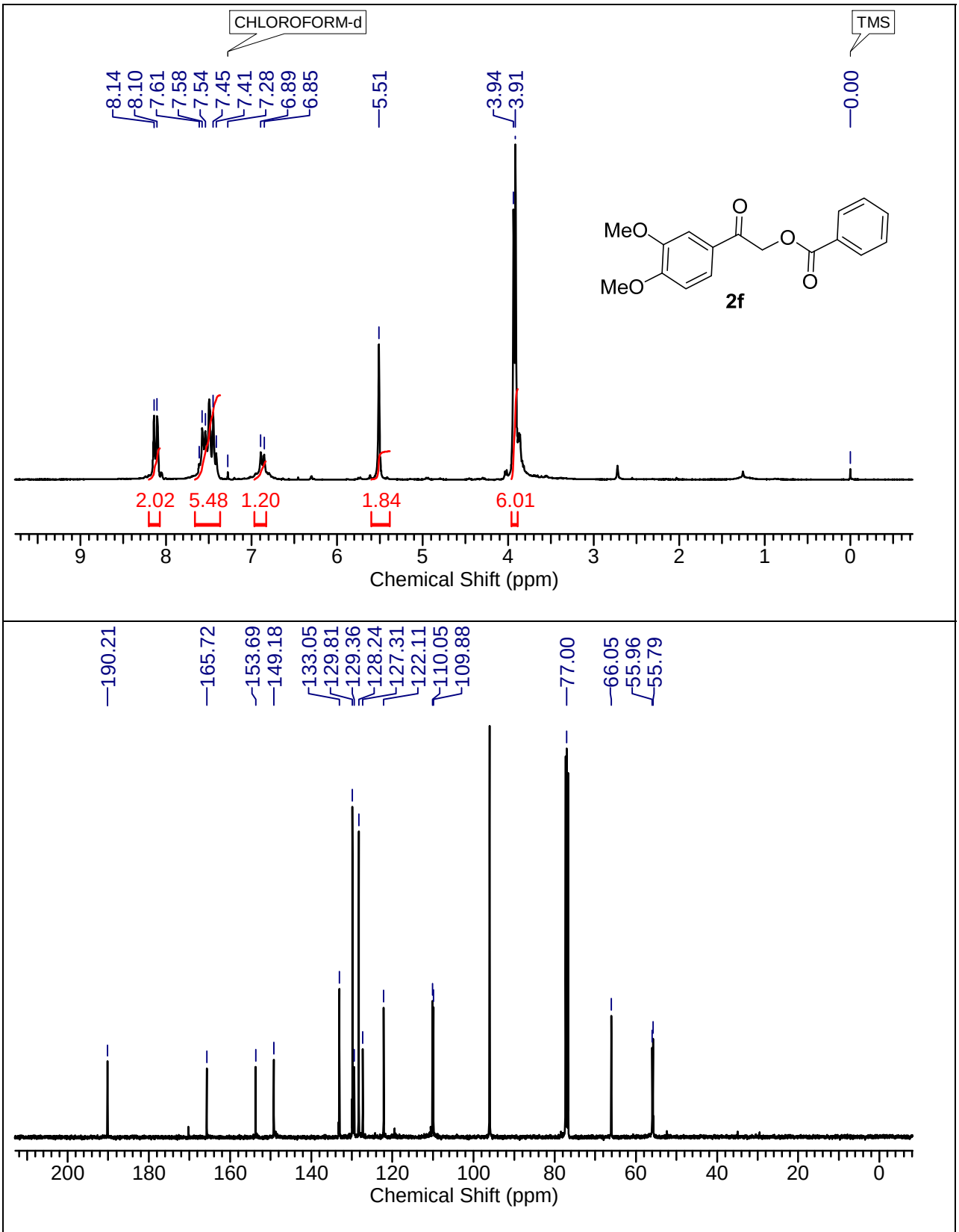


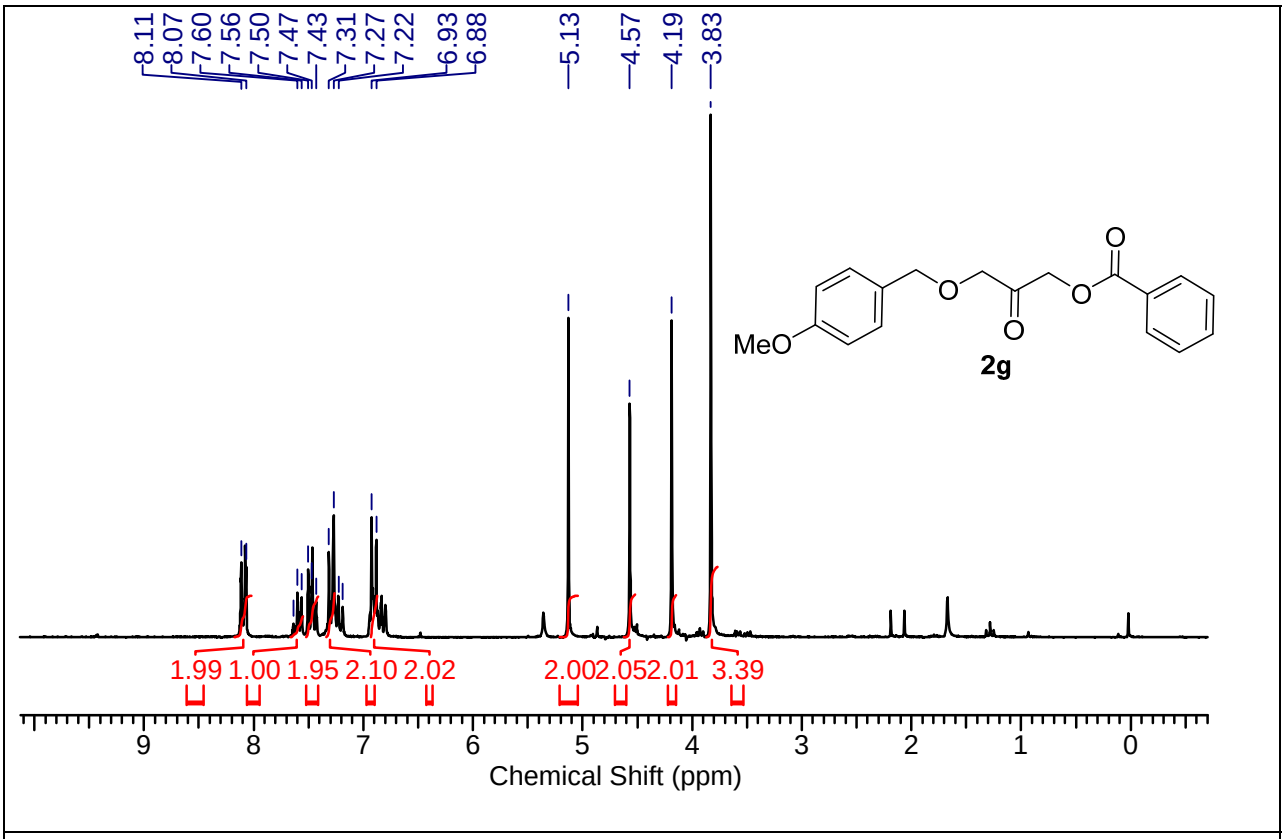

**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-(p-cyano)ethyl benzoate (2d)**

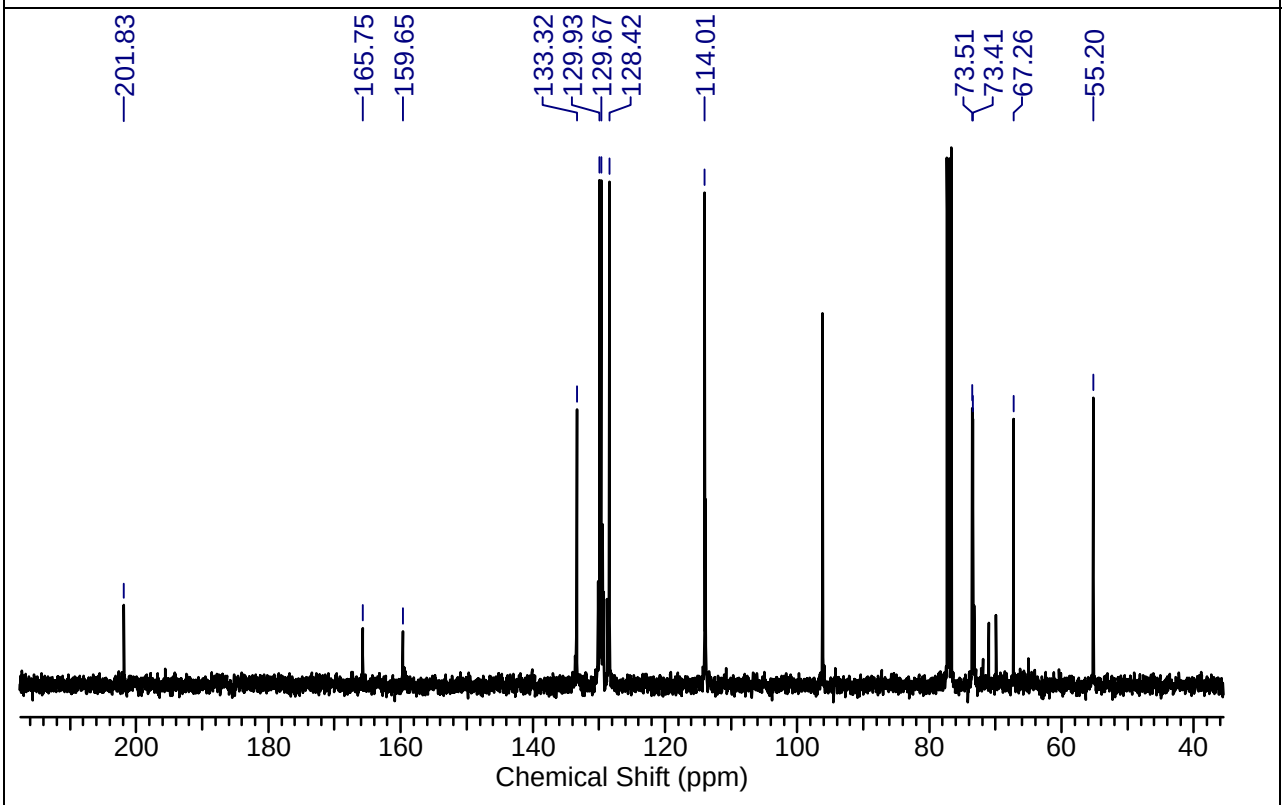



**$^{1}$H and $^{13}$C NMR spectra of 2-(4-acetoxyphenyl)-2-oxoethyl benzoate (2e)**

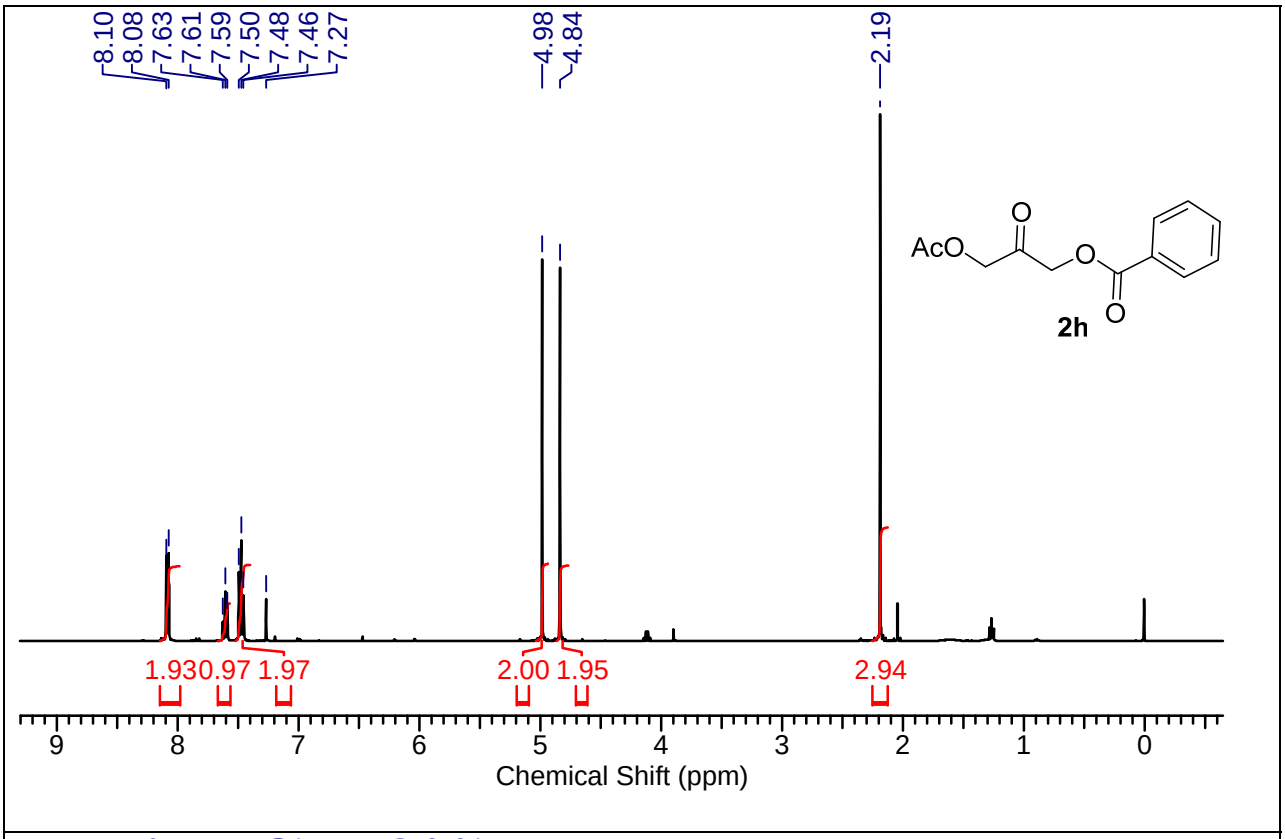


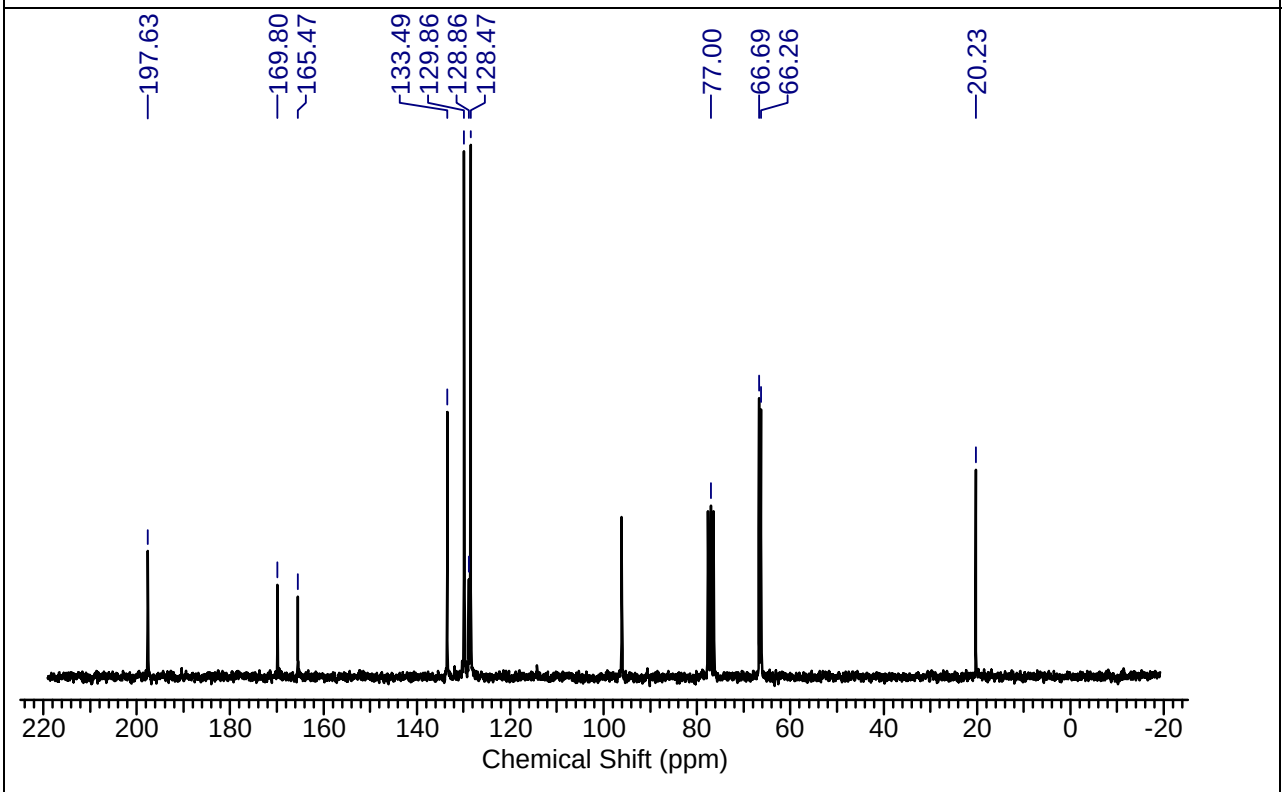

**$^{1}$H and $^{13}$C NMR spectra of 2-(3,4-dimethoxyphenyl)-2-oxoethyl benzoate (2f)**



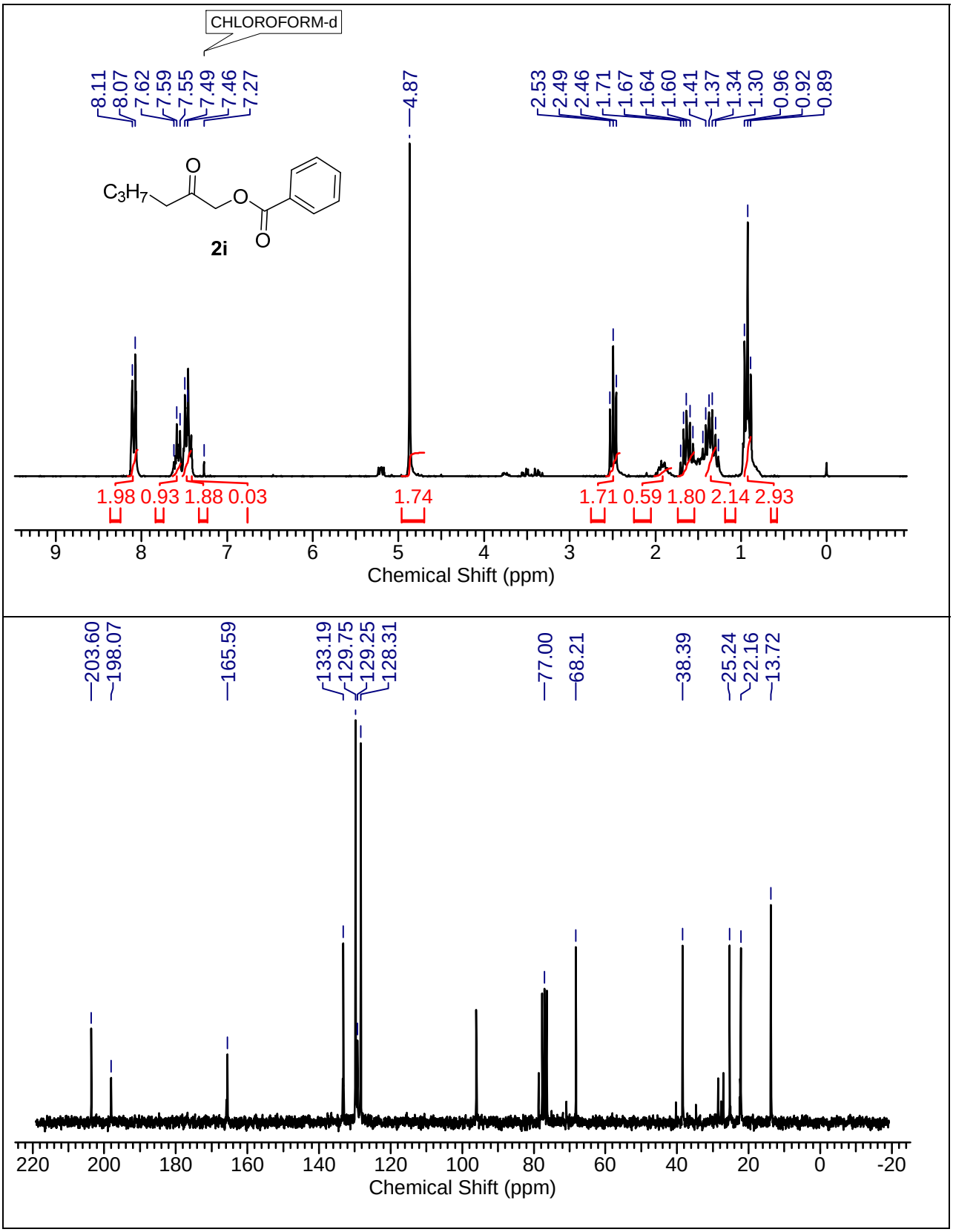




**$^{1}$H and $^{13}$C NMR spectra of 3-((4-methoxybenzyl)oxy)-2-oxopropyl benzoate (2g)**

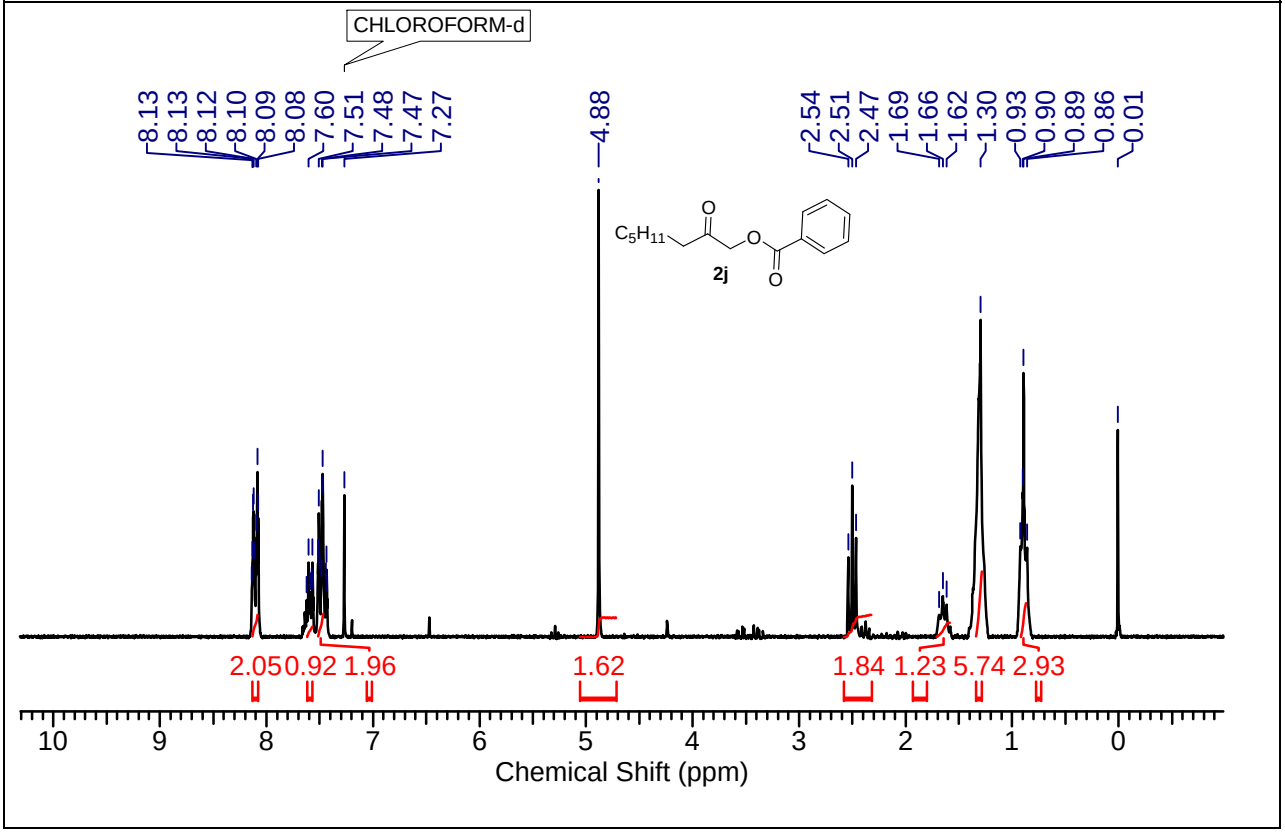


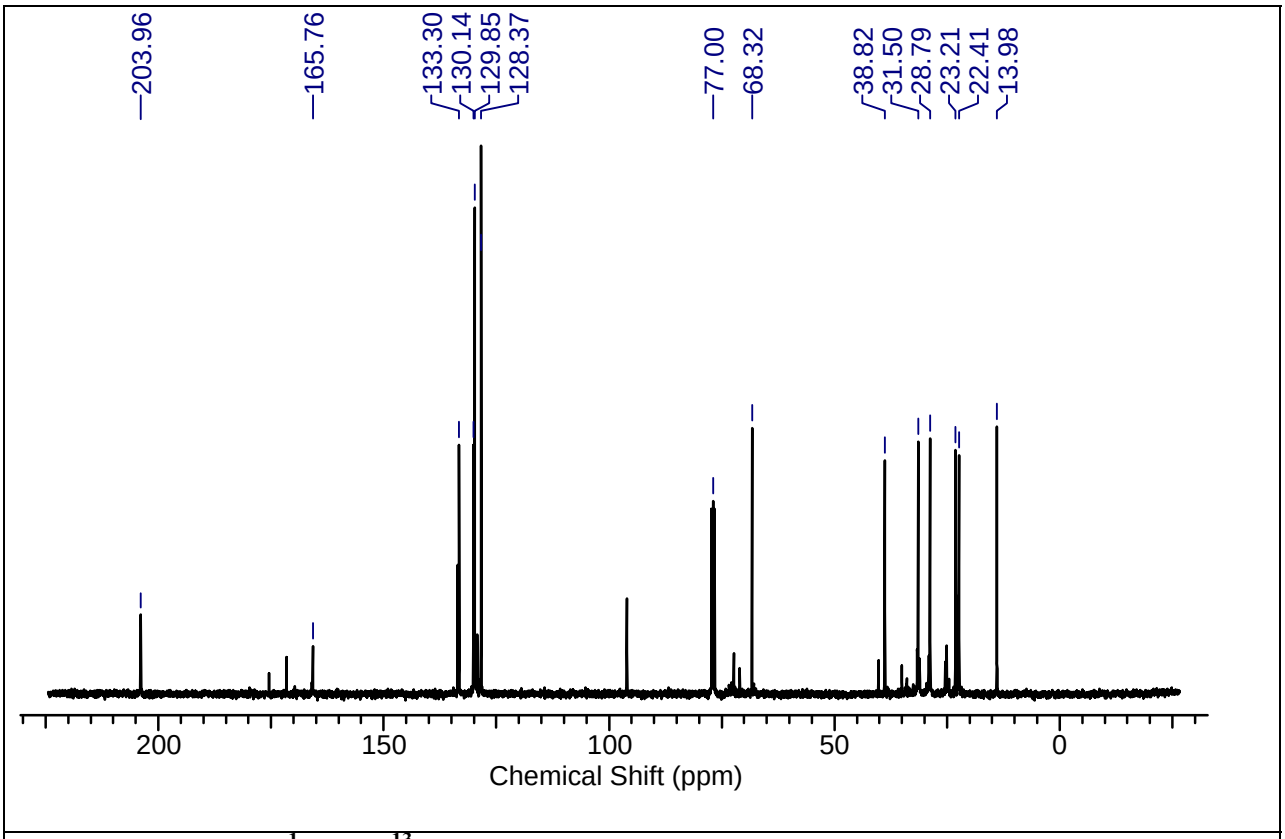




**$^{1}$H and $^{13}$C NMR spectra of 3-acetoxy-2-oxopropyl benzoate (2h)**

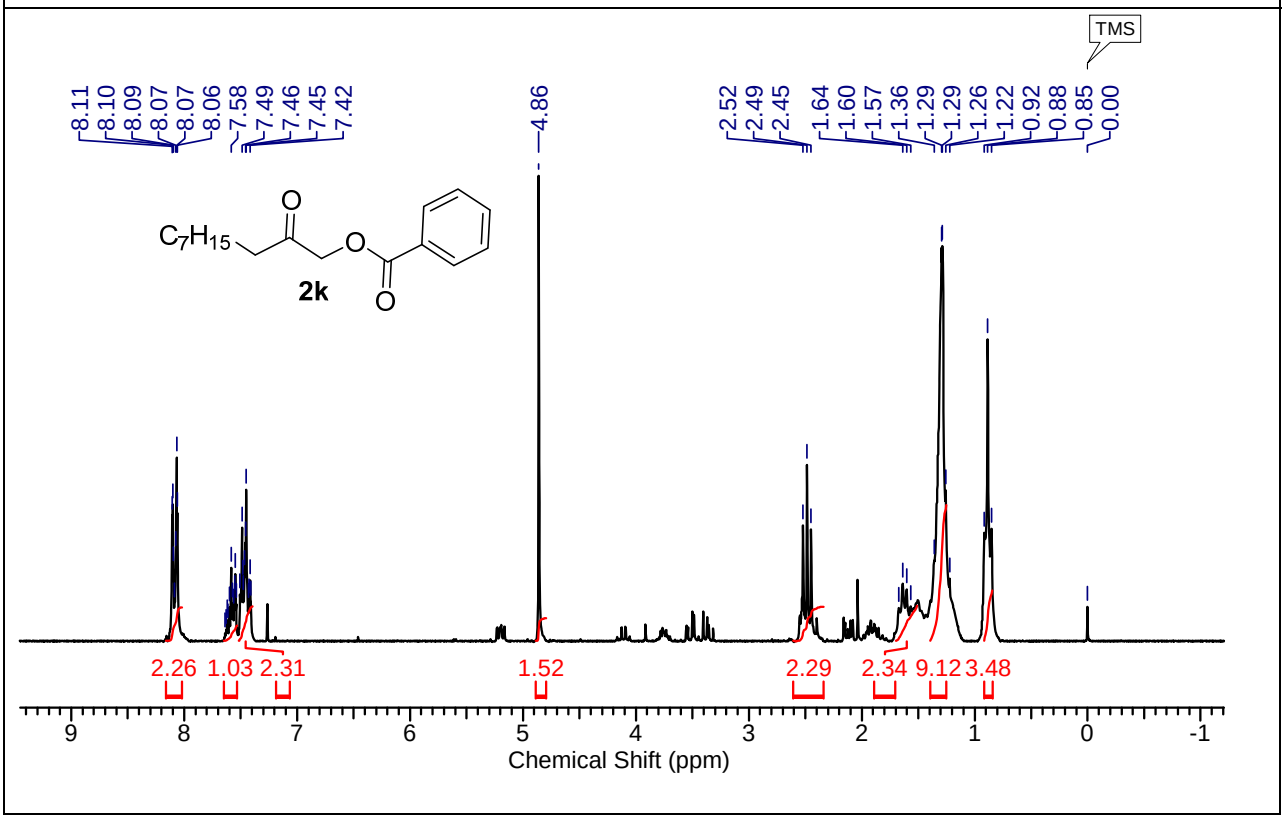

CHLOROFORM-d
8.11
8.07
7.62
7.59
7.55
7.49
7.46
7.27
4.87
2.53
2.49
2.46
1.71
1.67
1.64
1.60
1.41
1.37
1.34
1.30
0.96
0.92
0.89
C3H7
O
O
O
2i
1.98 0.93 1.88 0.03
1.74
1.71 0.59 1.80 2.14 2.93
Chemical Shift (ppm)
203.60
198.07
165.59
133.19
129.75
129.25
128.31
77.00
68.21
38.39
25.24
22.16
13.72
Chemical Shift (ppm)

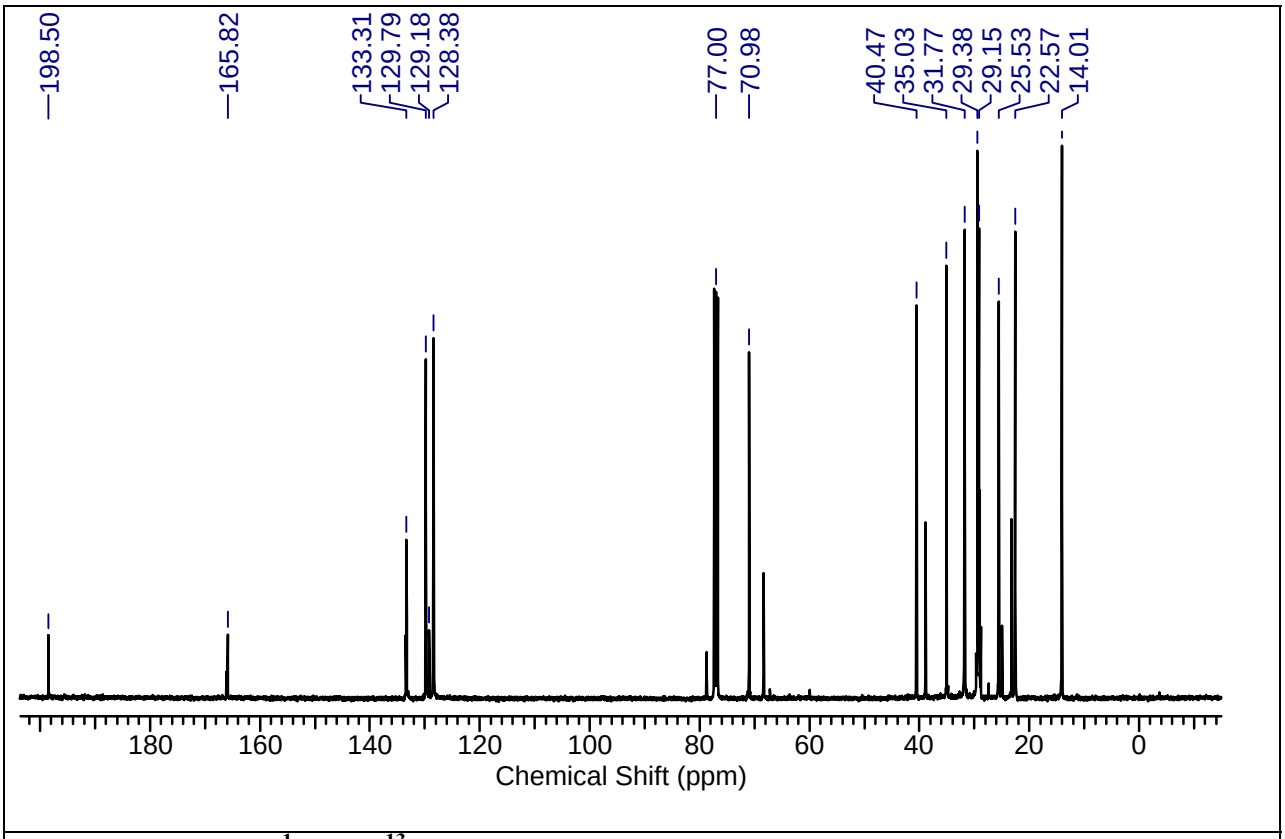
**$^{1}H$ and $^{13}C$ NMR spectra of 2-oxohexyl benzoate (2i)**



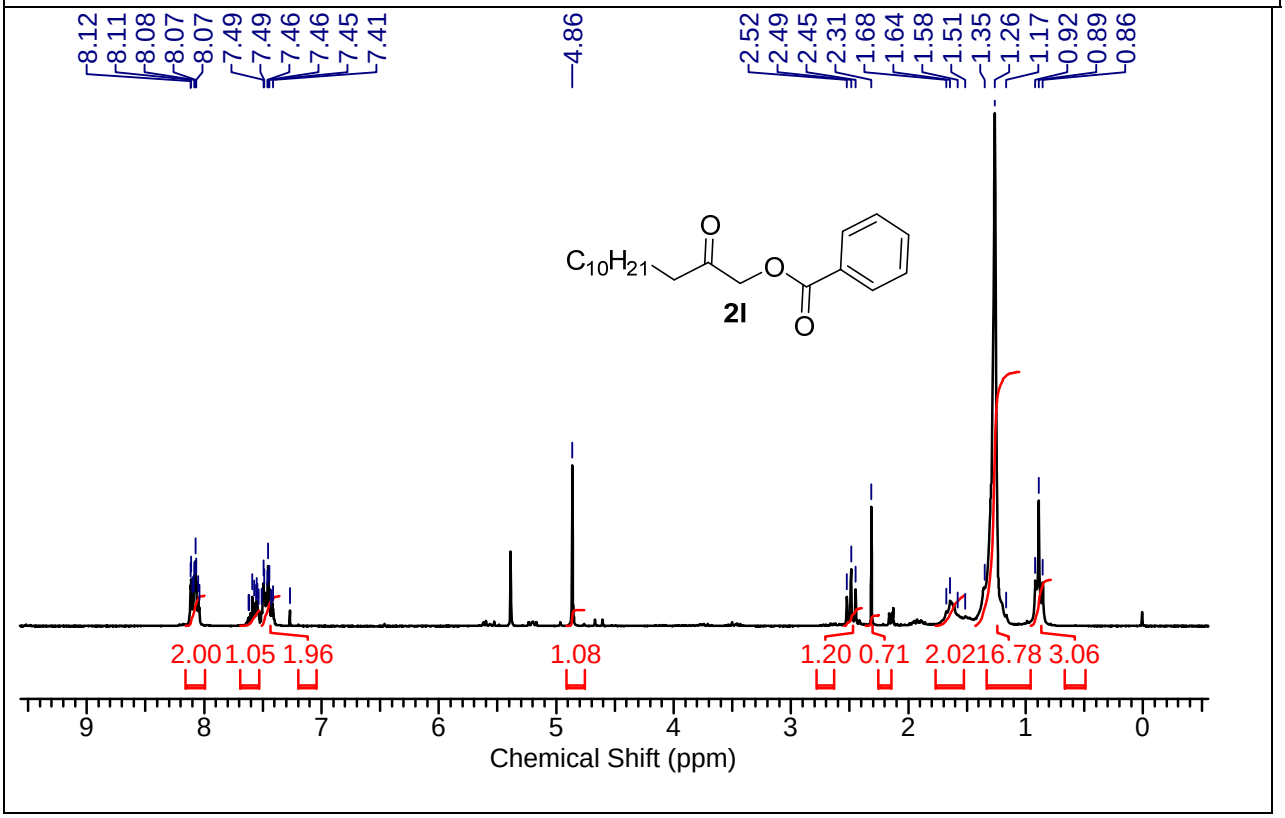


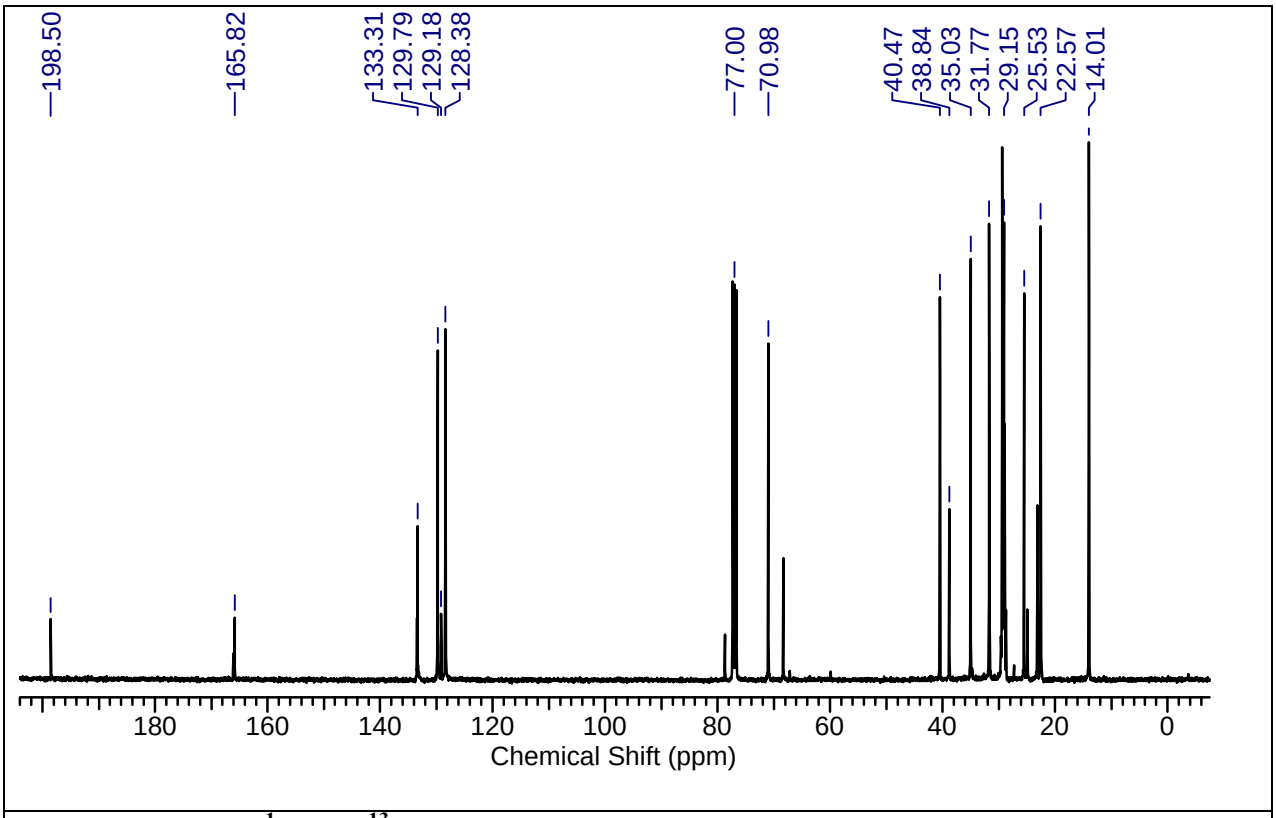

**$^{1}$H and $^{13}$C NMR spectra of 2-oxooctyl benzoate (2j)**



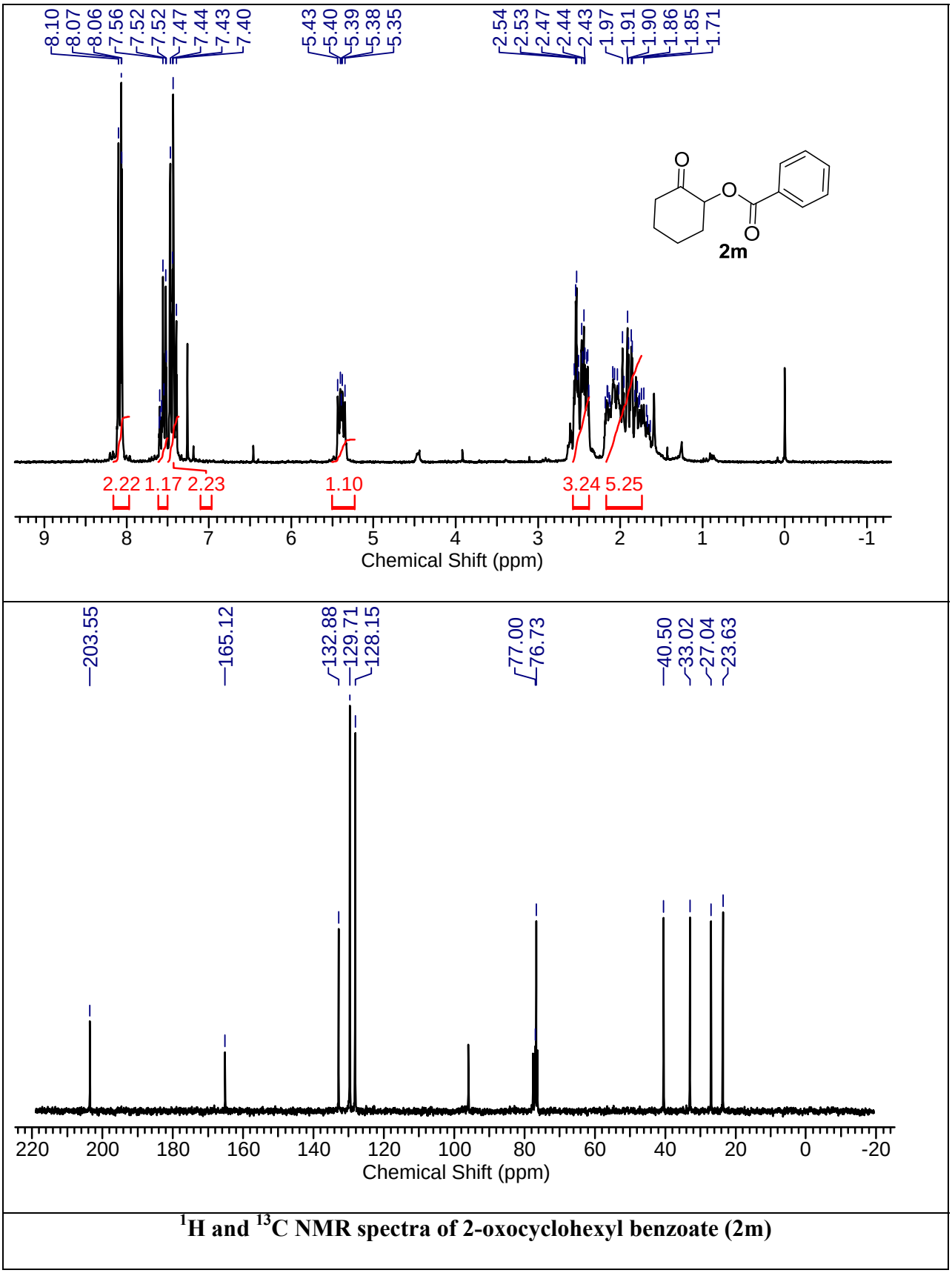



**$^{1}$H and $^{13}$C NMR spectra of 2-oxodecyl benzoate (2k)**

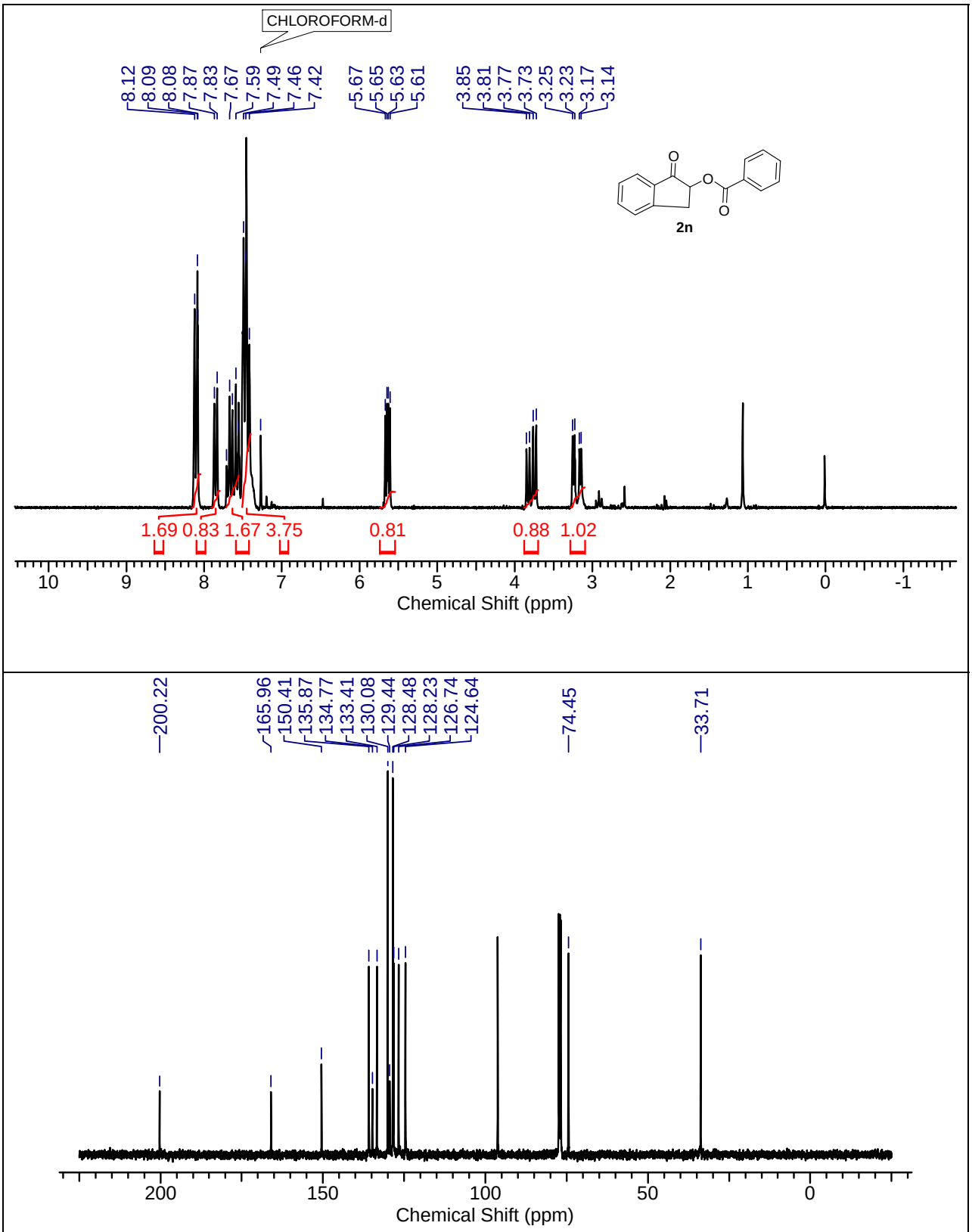




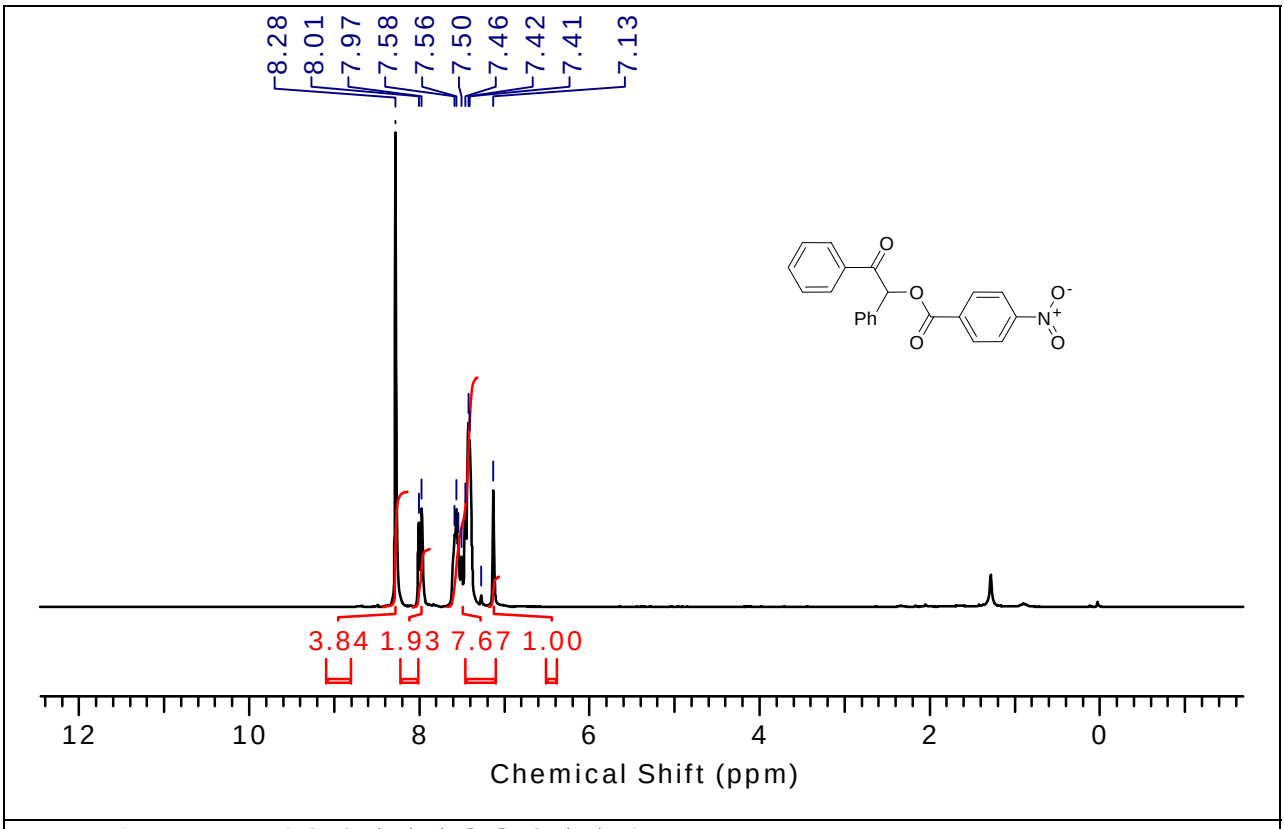

**$^{1}$H and $^{13}$C NMR spectra of 2-oxotridecyl benzoate (2l)**

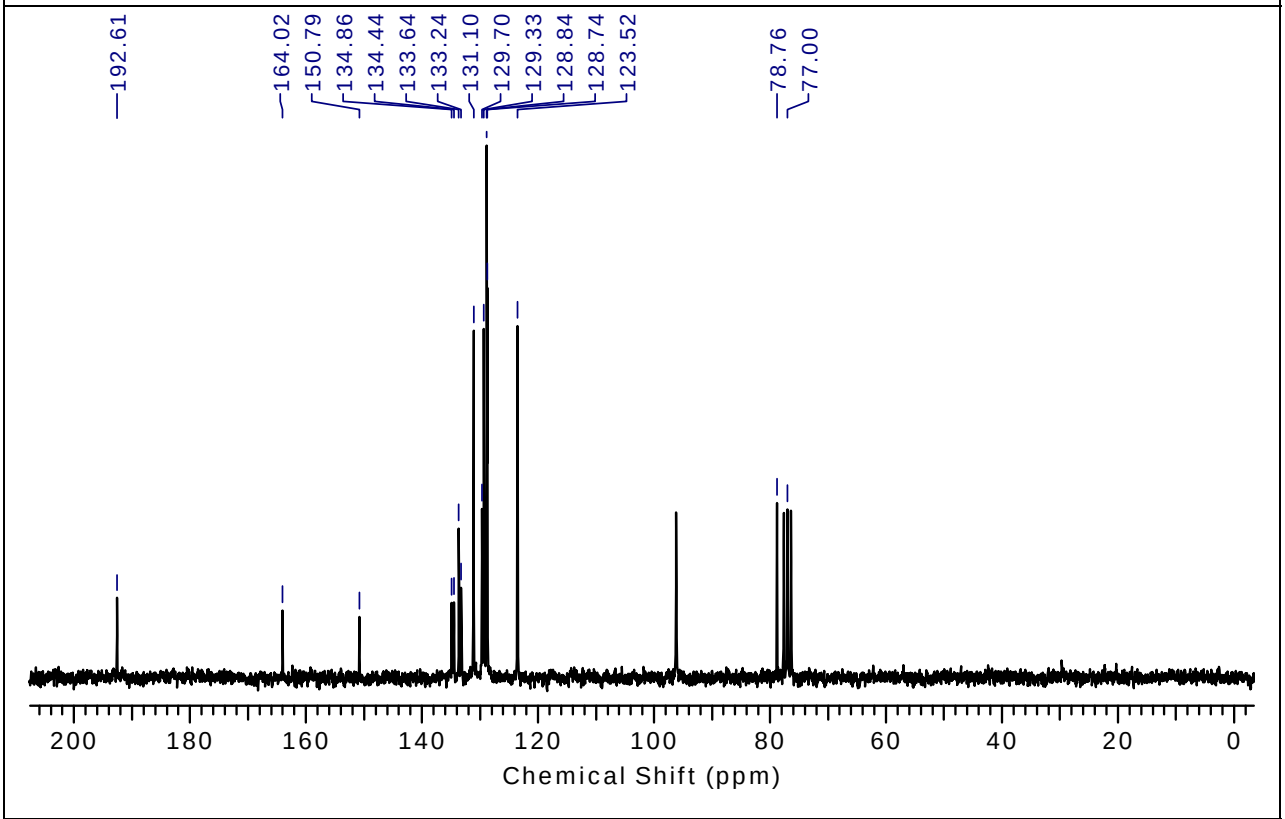



**$^{1}$H and $^{13}$C NMR spectra of 2-oxocyclohexyl benzoate (2m)**

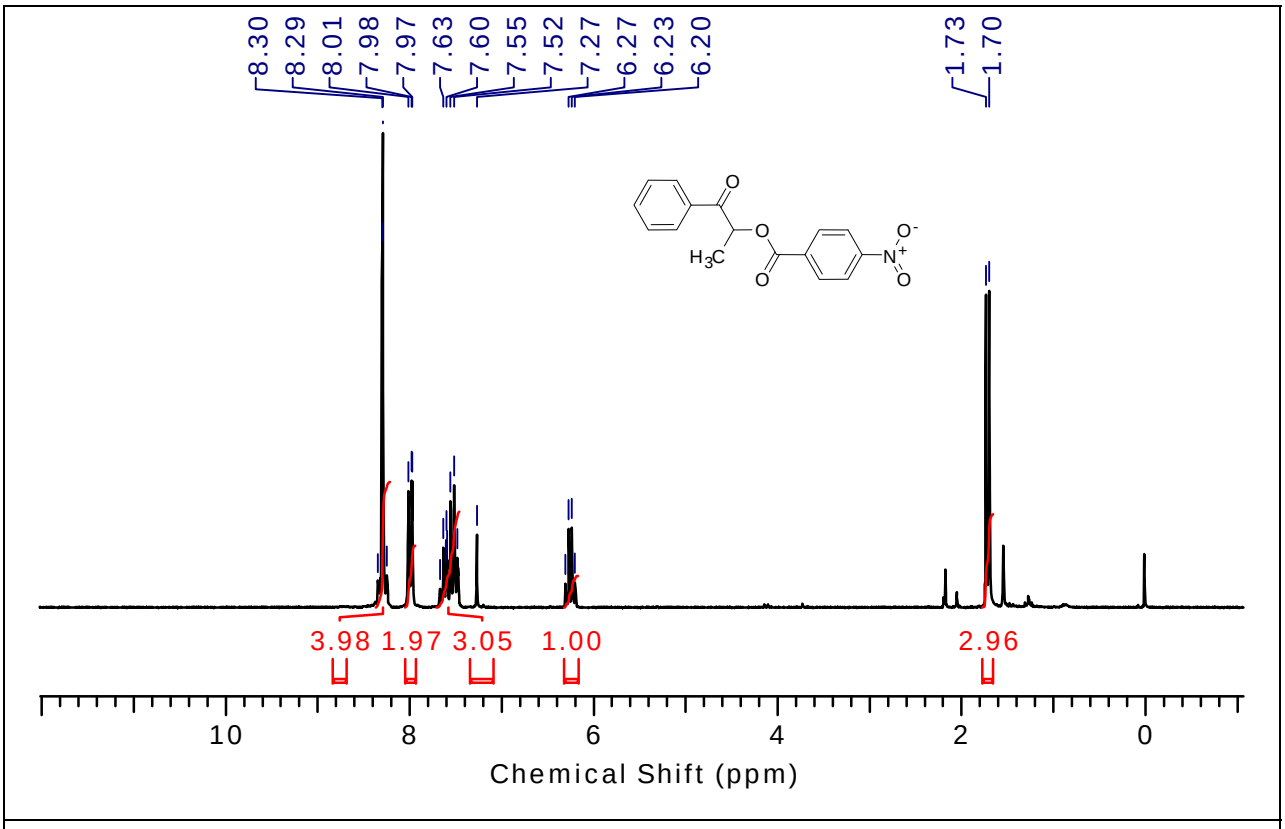


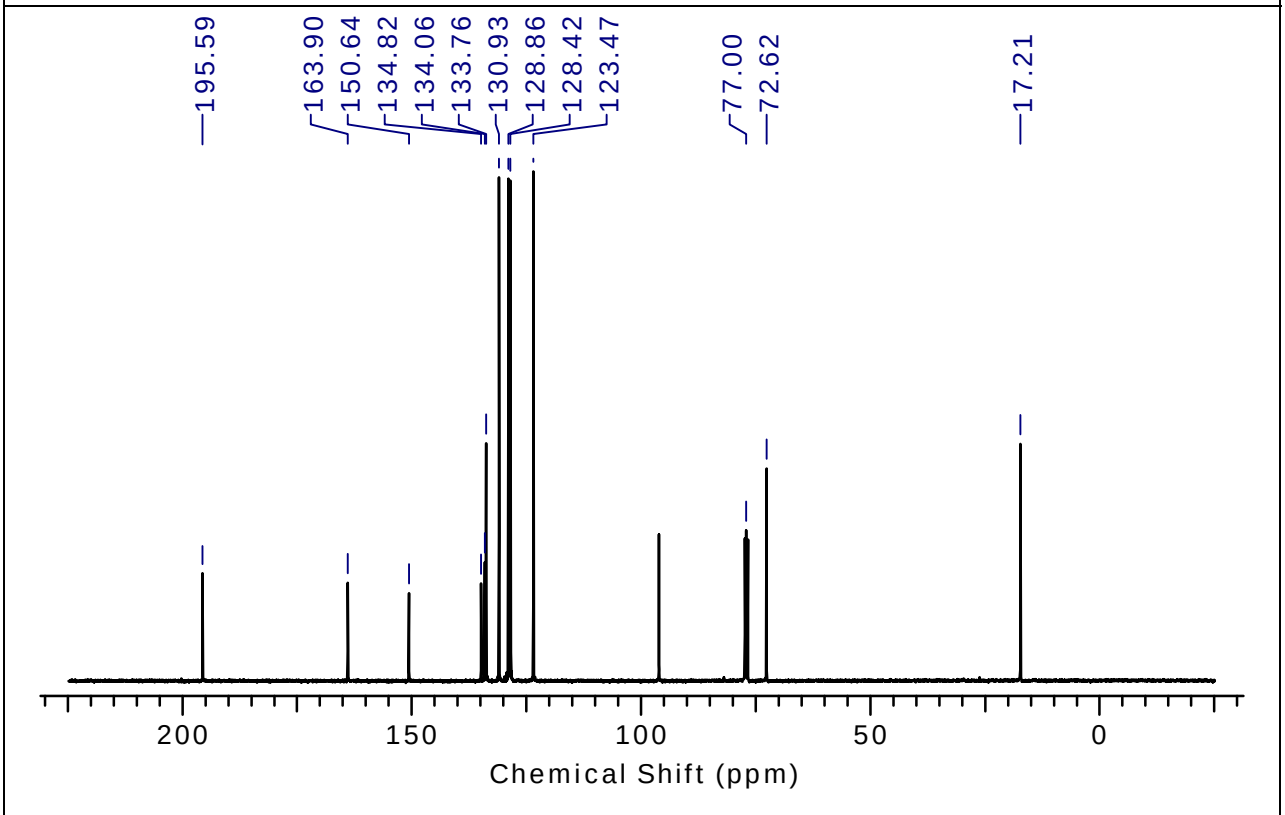

**$^{1}$H and $^{13}$C NMR spectra of 1-oxo-2,3-dihydro-1H-inden-2-yl benzoate (2n)**



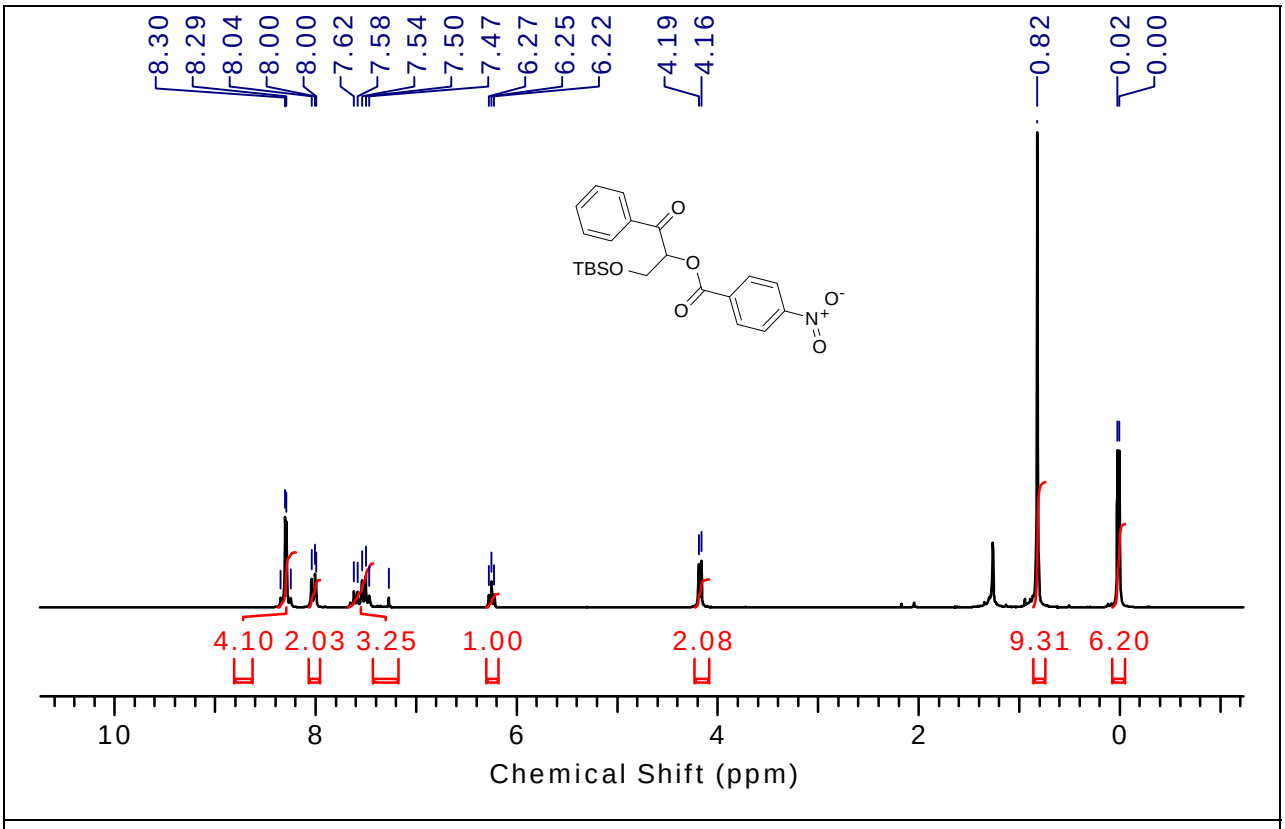



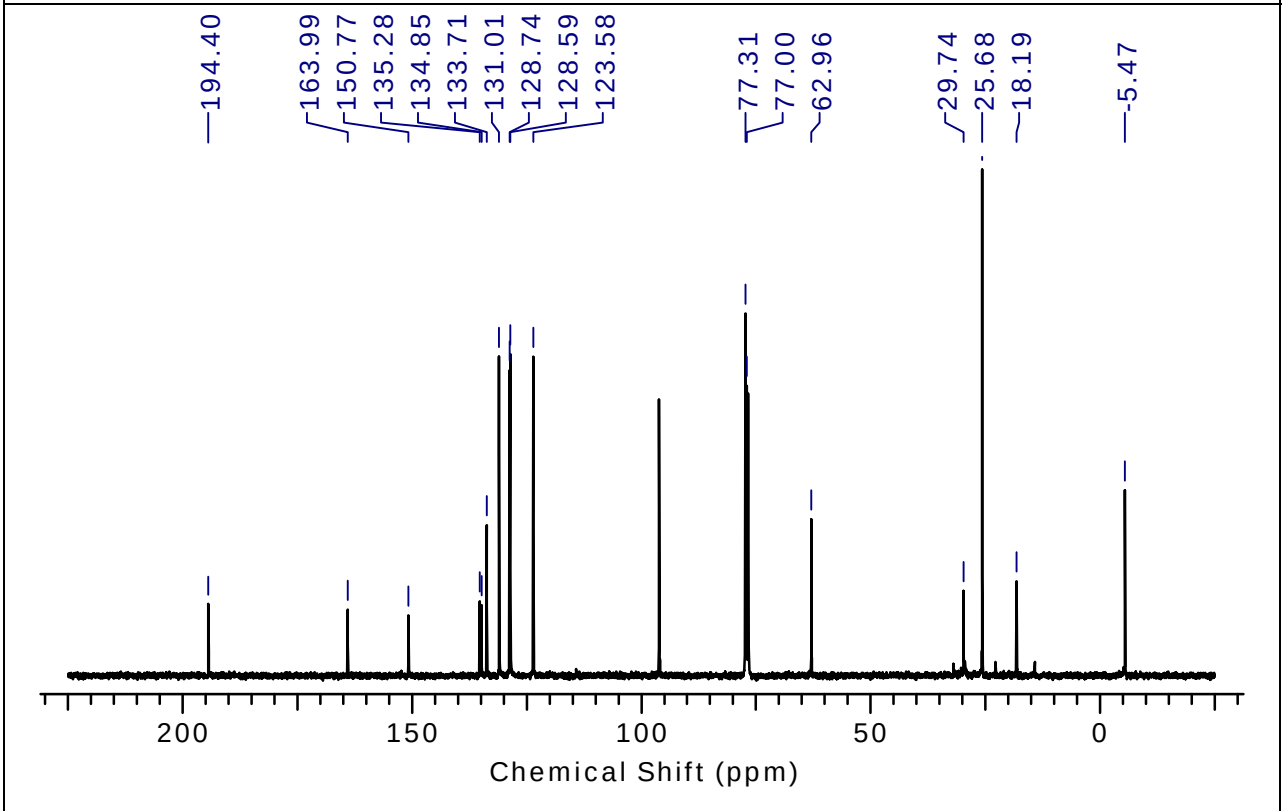

**$^{1}$H and $^{13}$C NMR spectra of 2-Oxo-1, 2-diphenylethyl 4-nitrobenzoate (2o)**



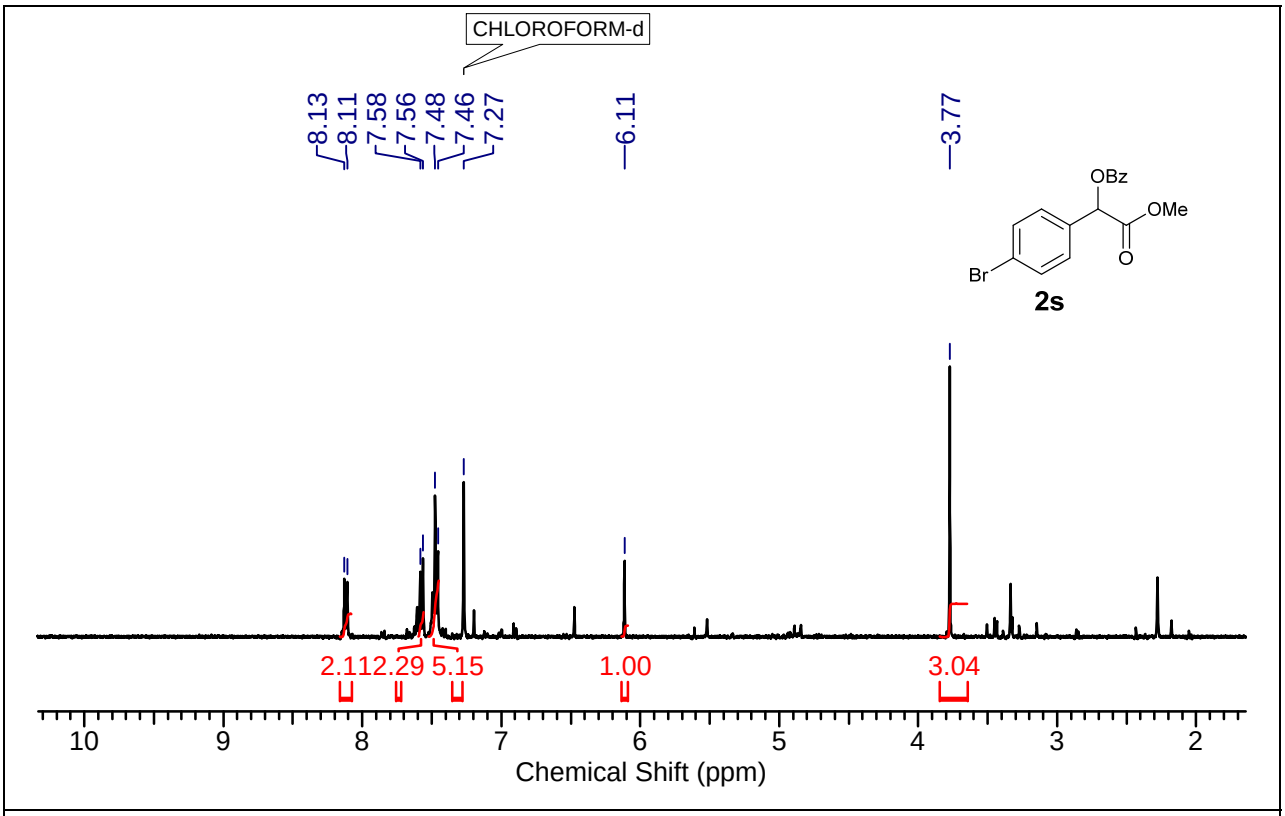



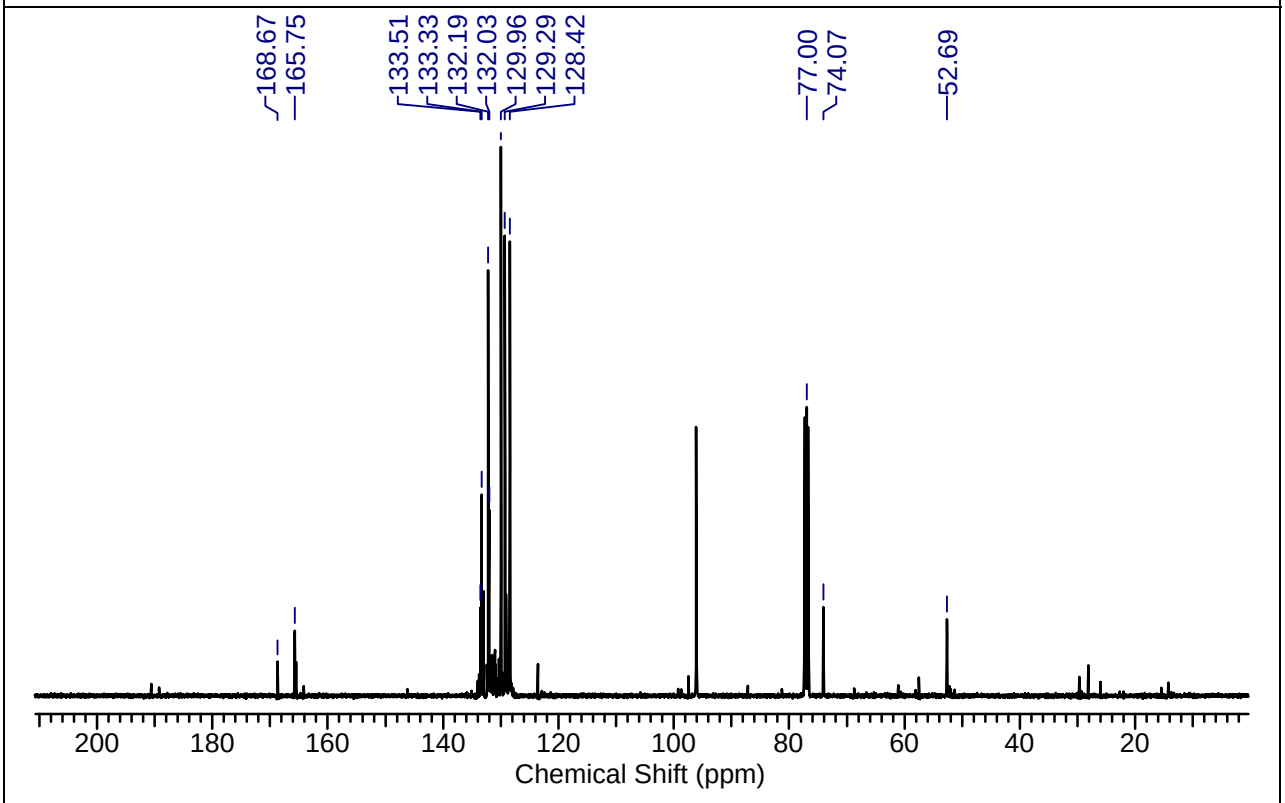

**$^{1}$H and $^{13}$C NMR spectra of 1-Oxo-1-phenylpropan-2-yl 4-nitrobenzoate (2p)**



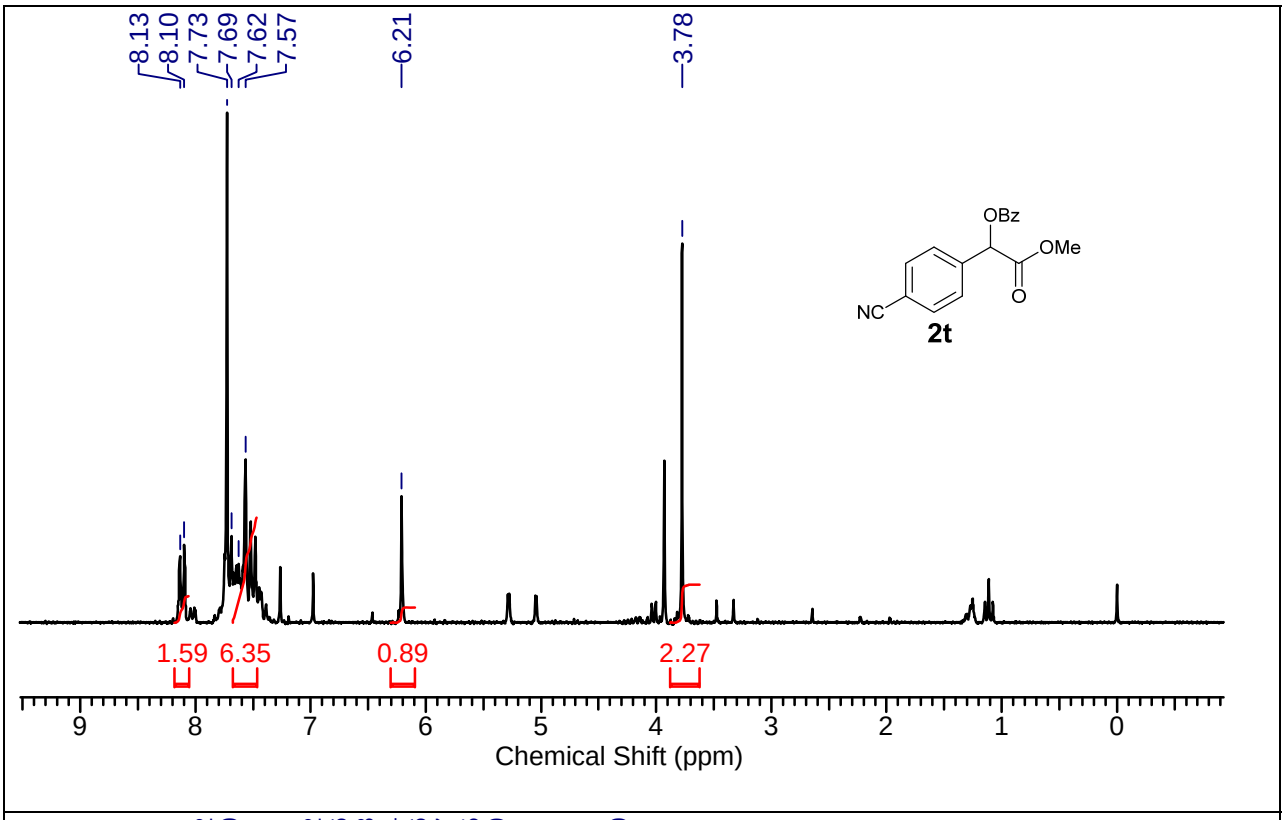



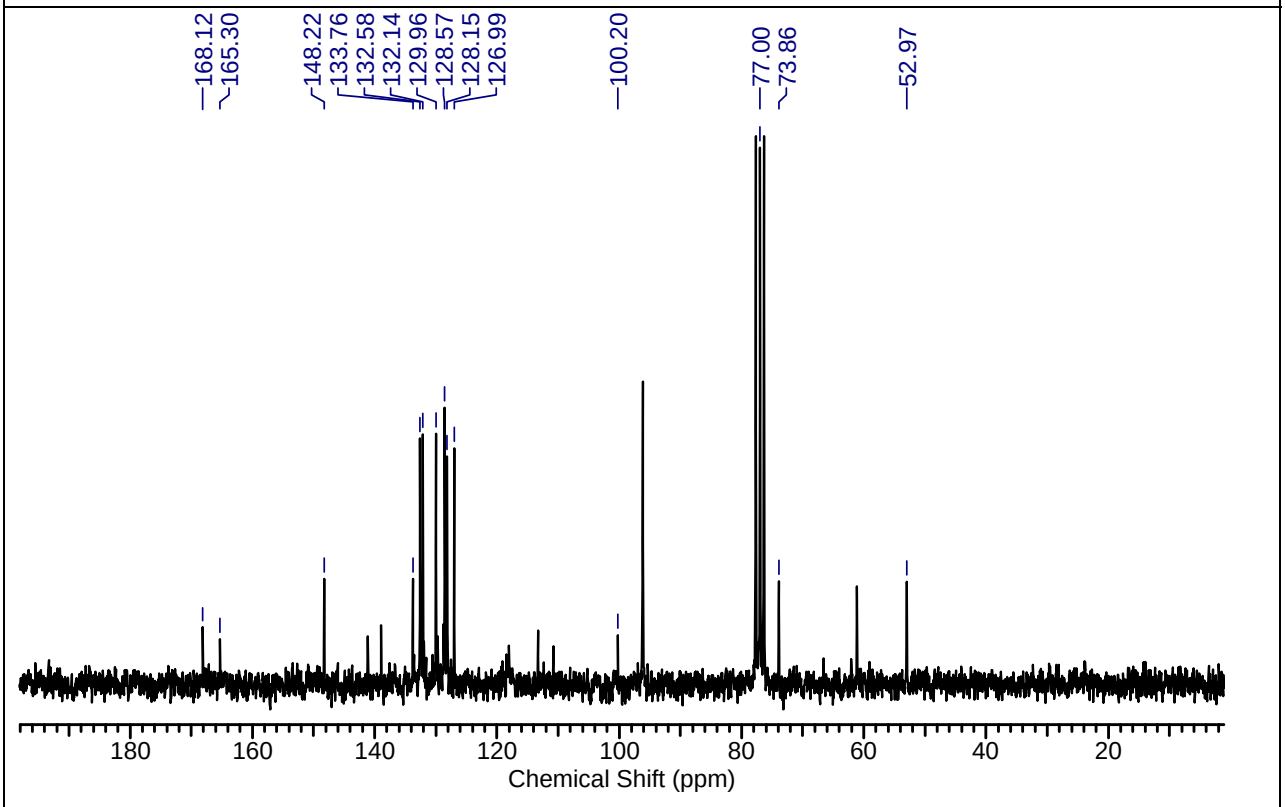

**$^{1}$H and $^{13}$C NMR spectra of 3-((Tert-butyldimethylsilyl)oxy)-1-oxo-1-phenylpropan-2-yl 4-nitro benzoate (2q)**



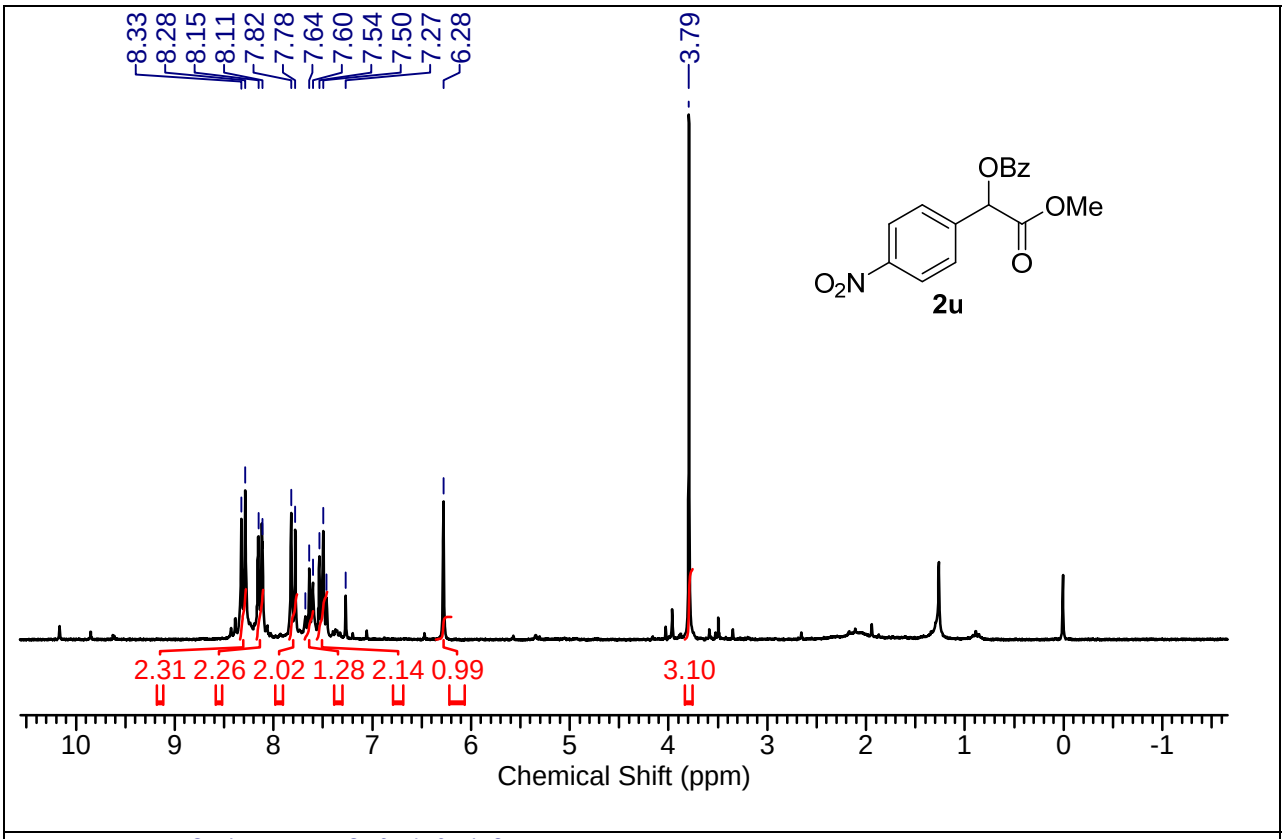



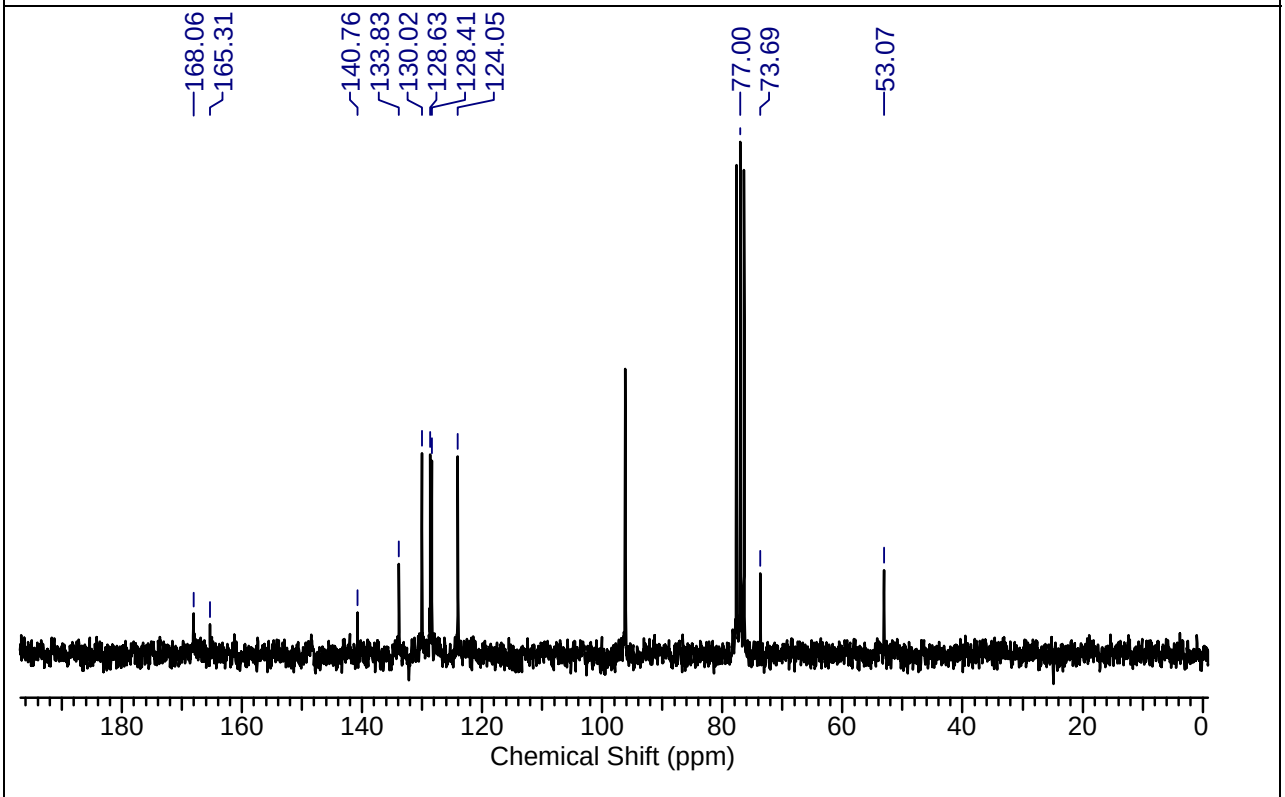

**$^{1}$H and $^{13}$C NMR spectra of 1-(4-bromophenyl)-2-methoxy-2-oxoethyl benzoate (2s)**



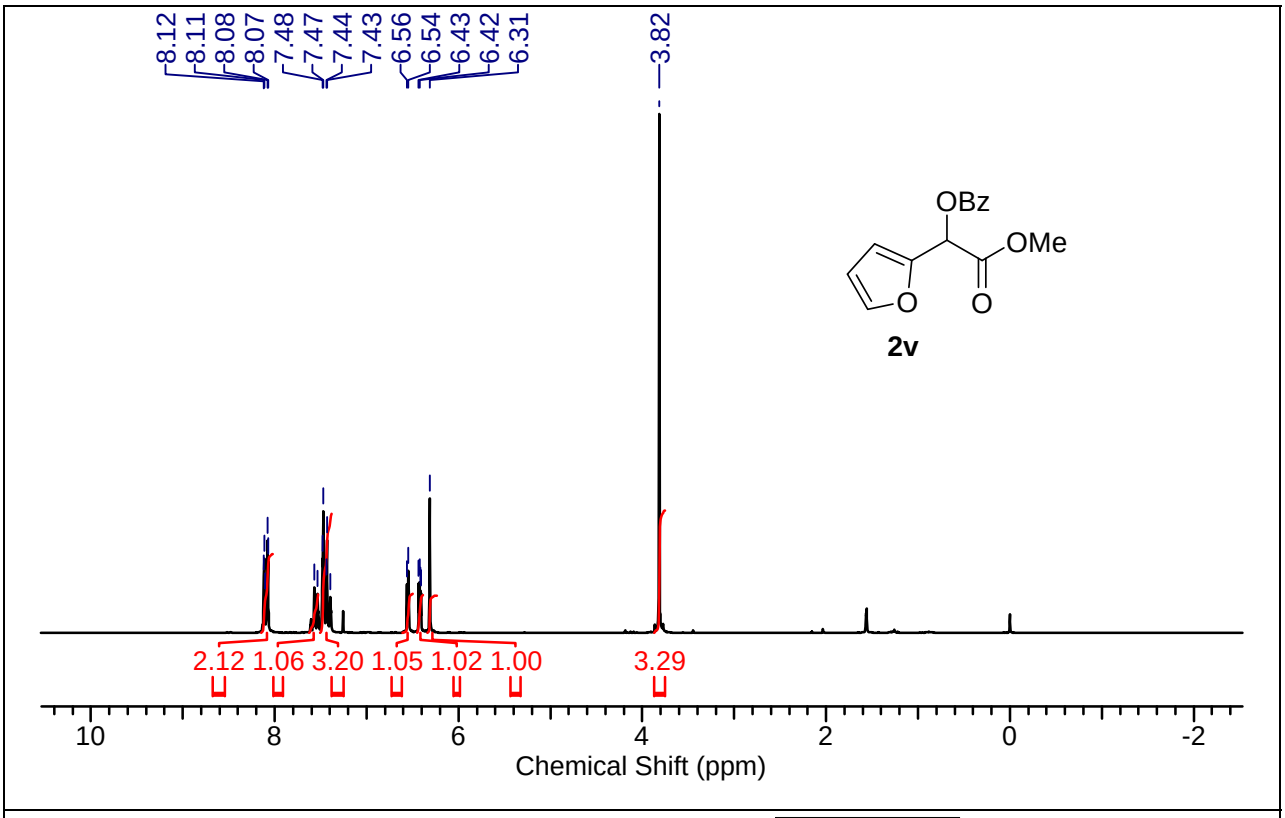



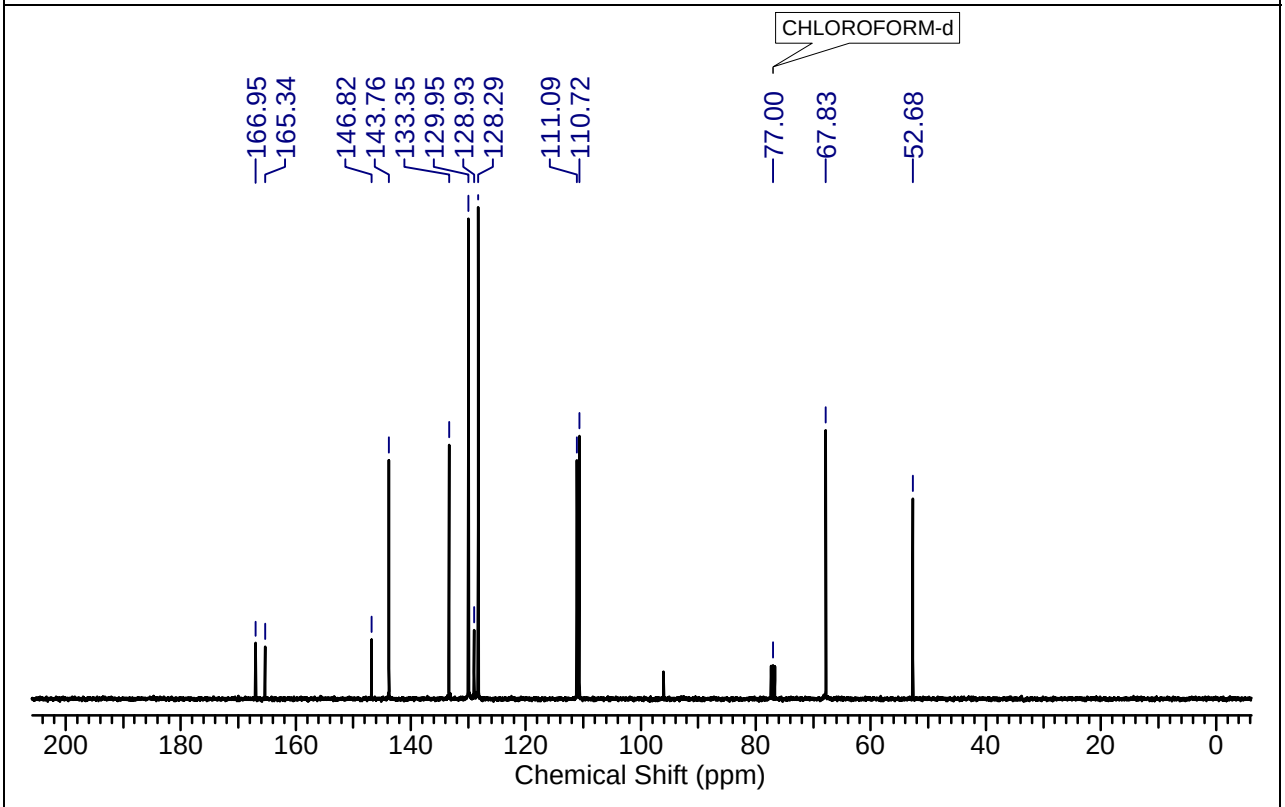

**$^{1}$H and $^{13}$C NMR spectra of 1-(4-cyanophenyl)-2-methoxy-2-oxoethyl benzoate (2t)**



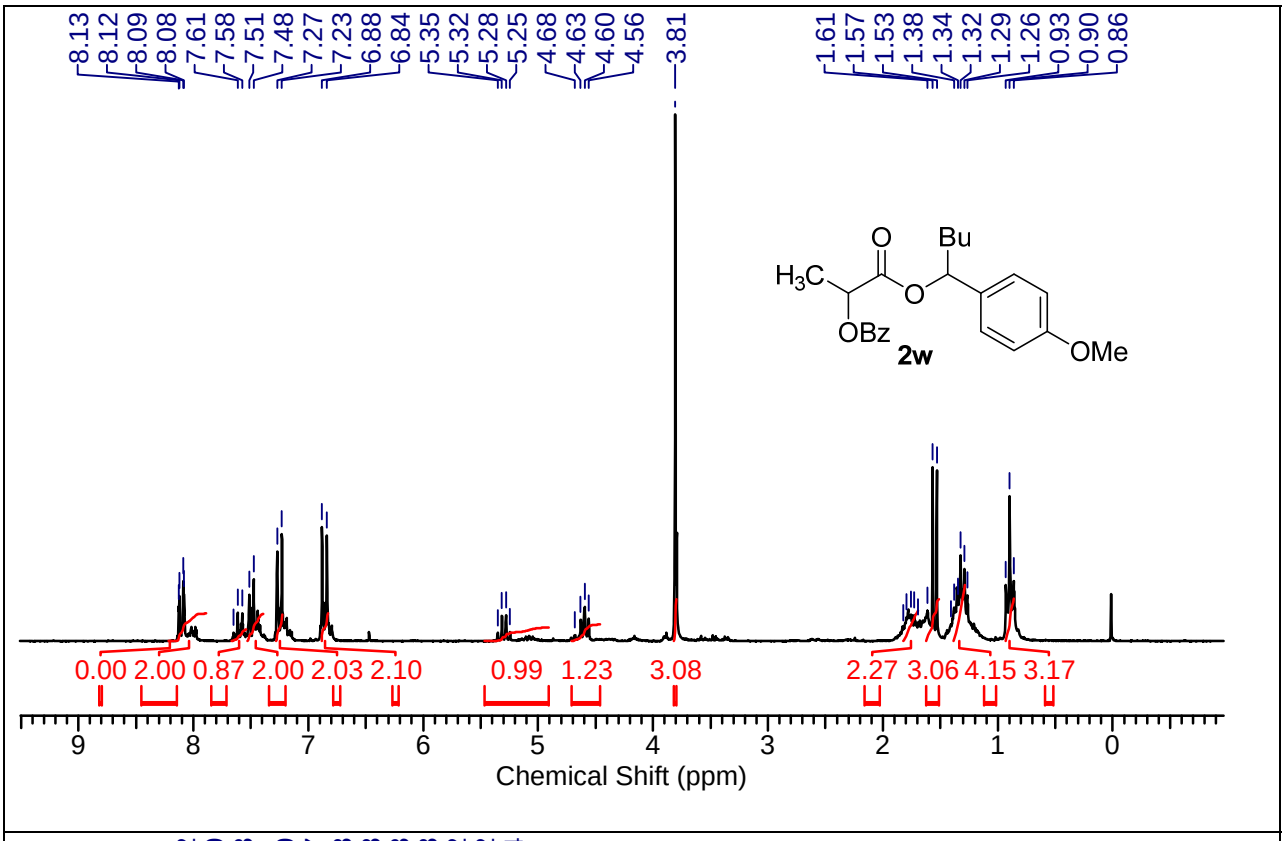



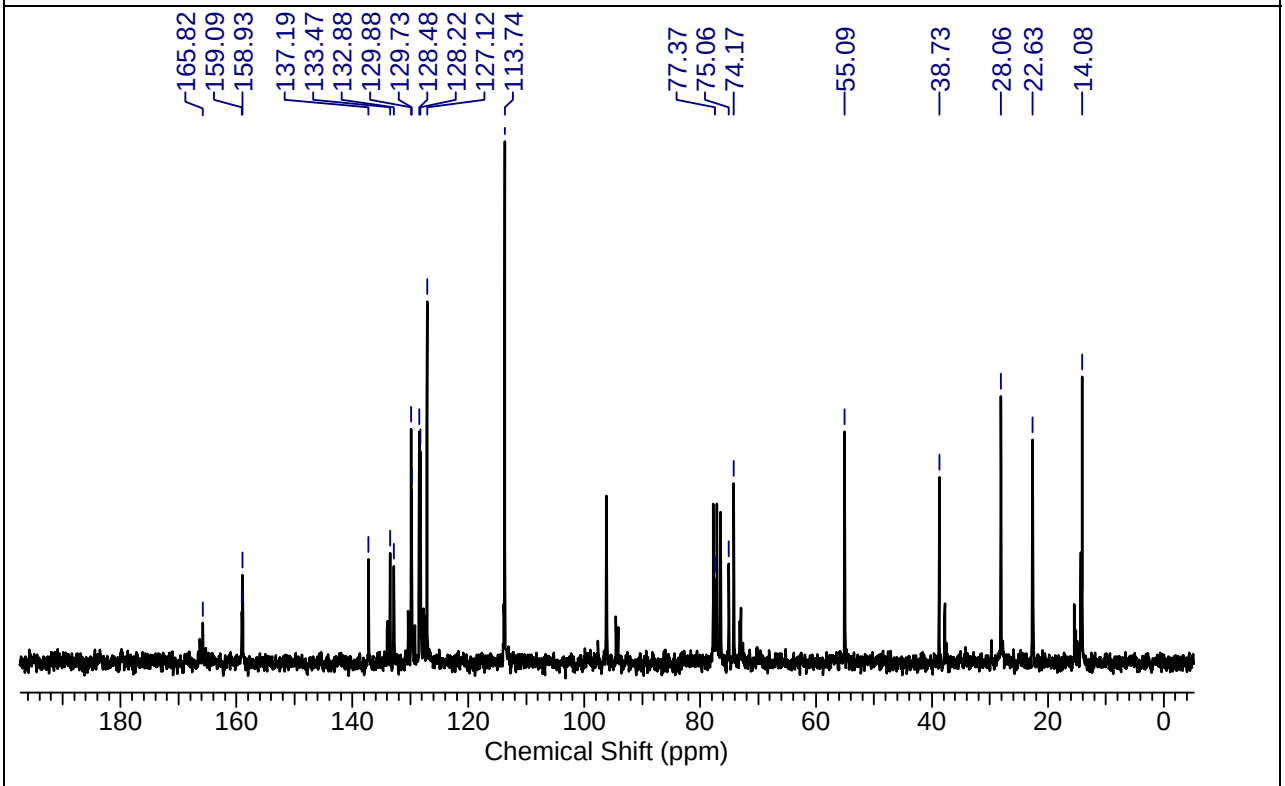

**$^{1}$H and $^{13}$C NMR spectra of 1-(4-nitrophenyl)-2-methoxy-2-oxoethyl benzoate (2u)**



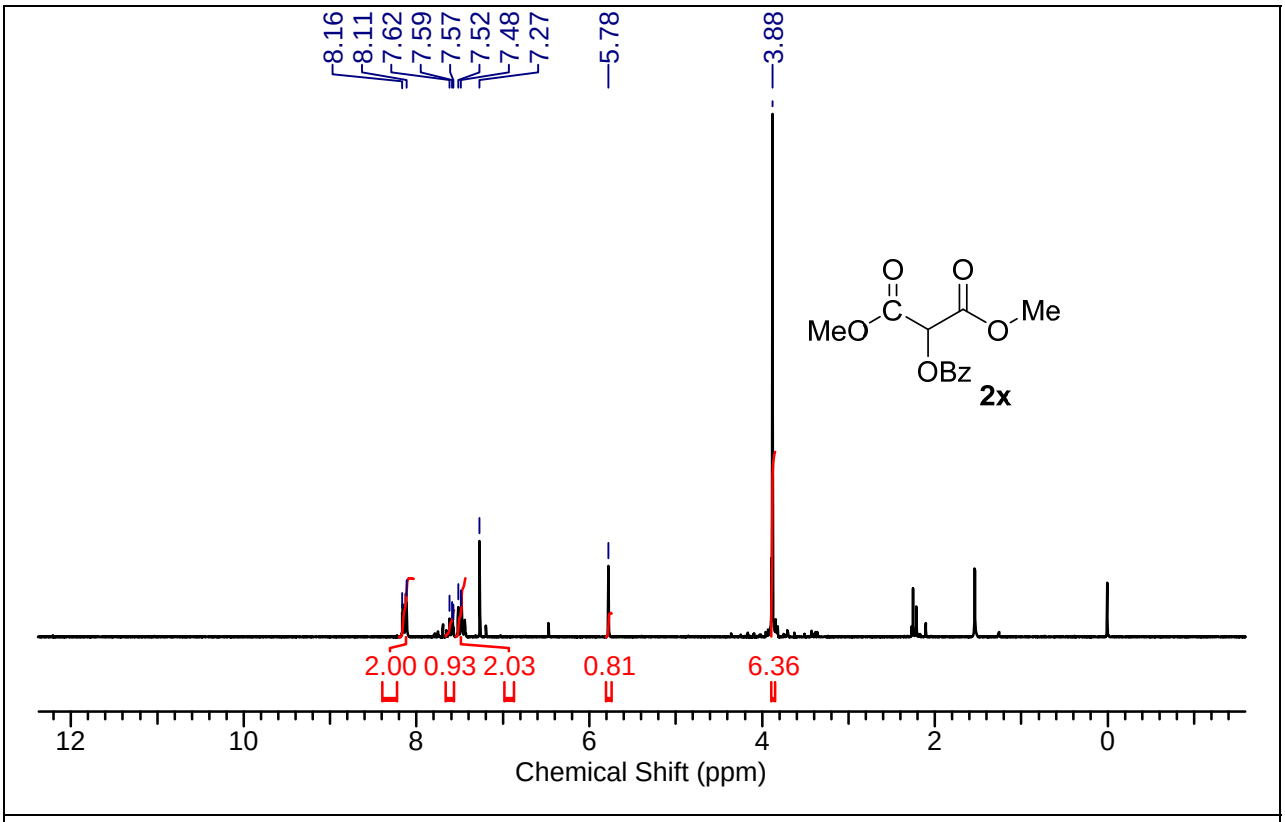



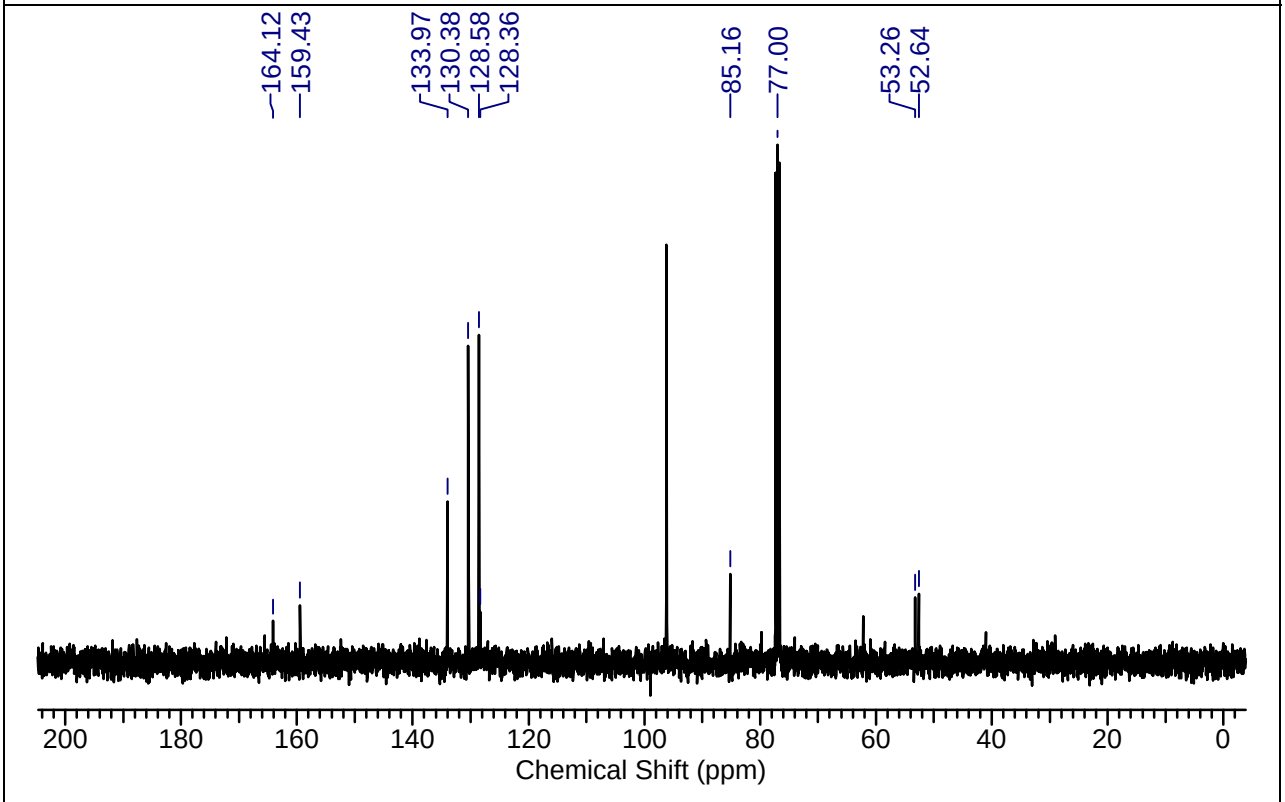

**$^{1}$H and $^{13}$C NMR spectra of 1-(furan-2-yl)-2-methoxy-2-oxoethyl benzoate (2v)**



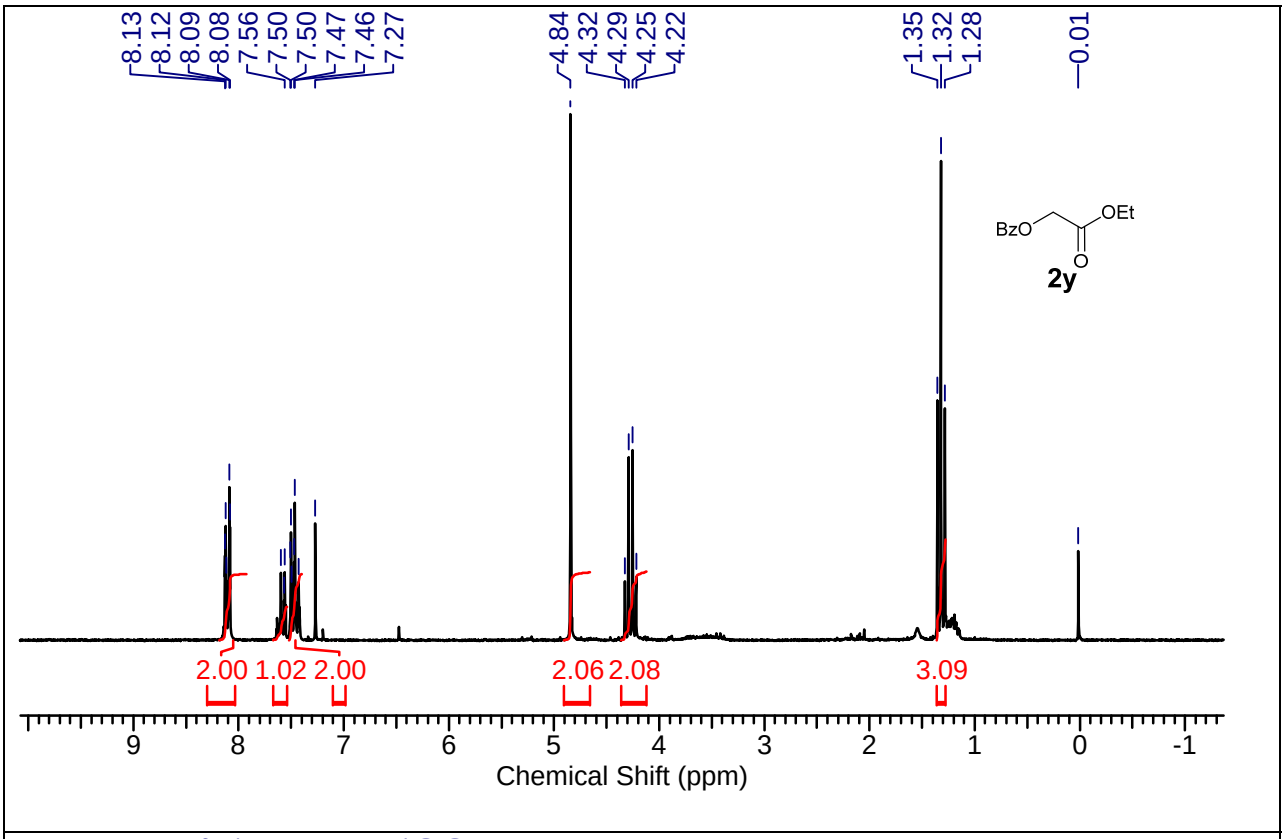



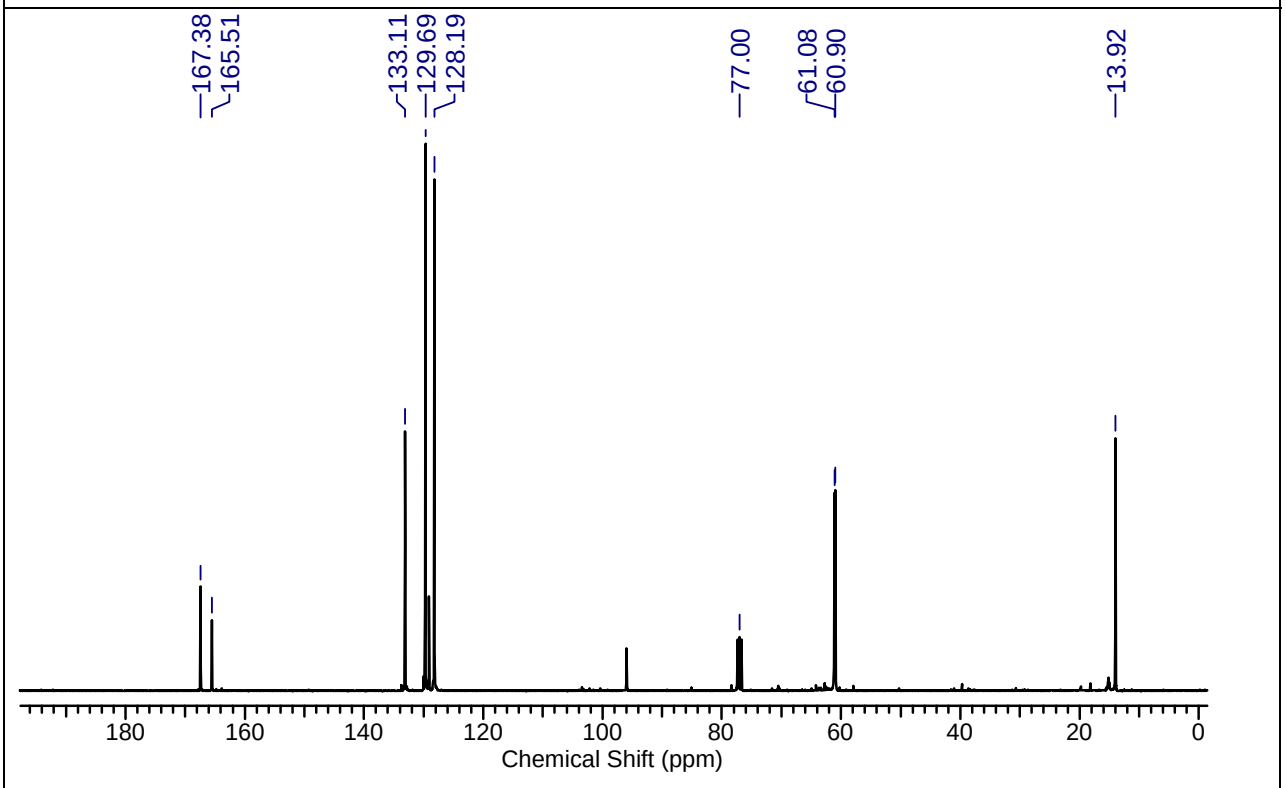

**$^{1}$H and $^{13}$C NMR spectra of 2-methoxy-2-oxoethyl benzoate (2w)**



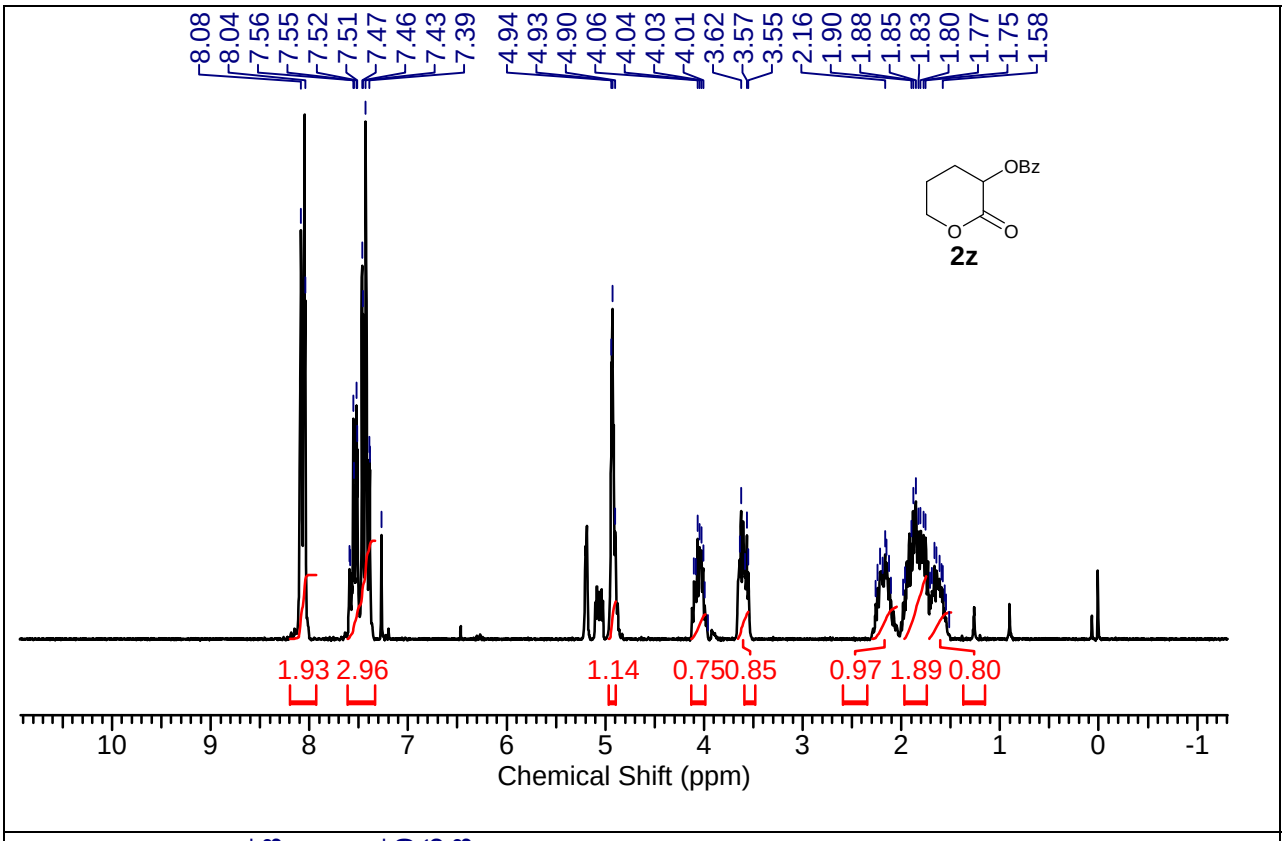



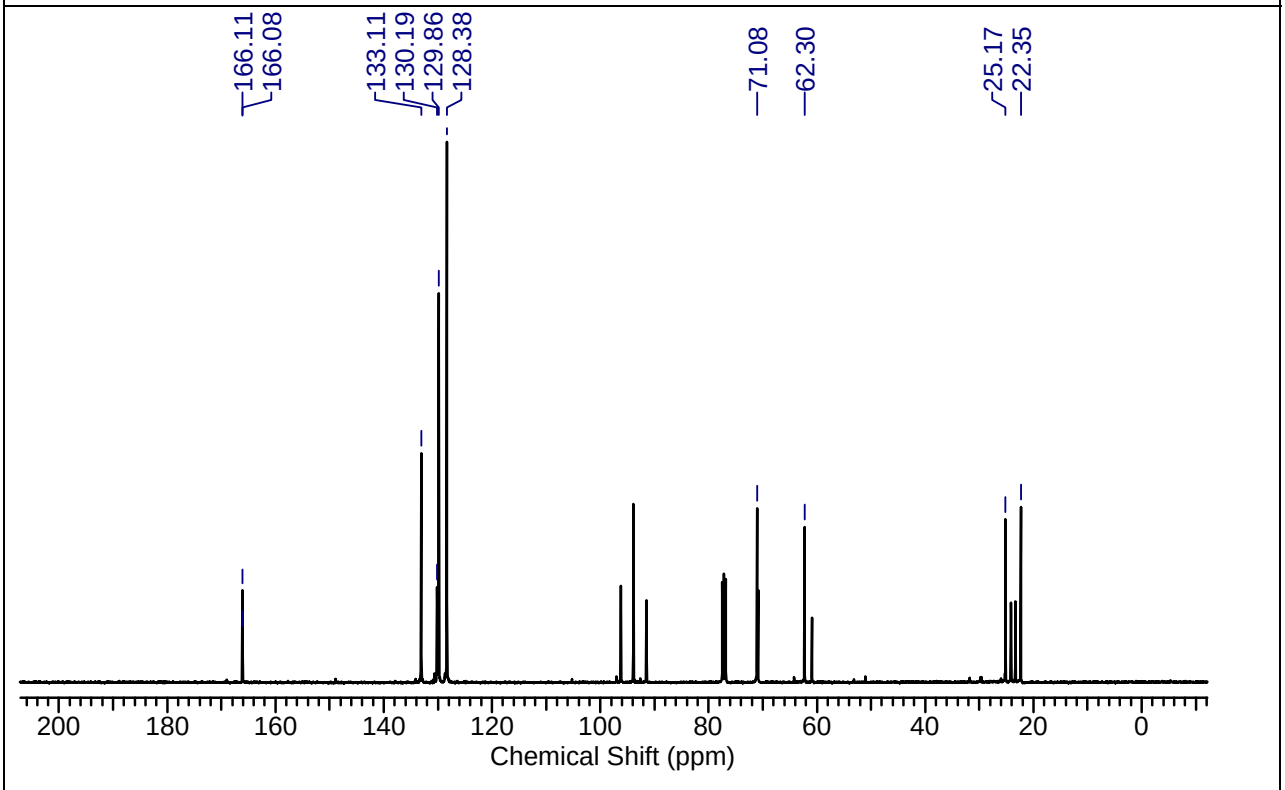

**$^{1}$H and $^{13}$C NMR spectra of dimethyl 2-(benzoyloxy)malonate (2x)**



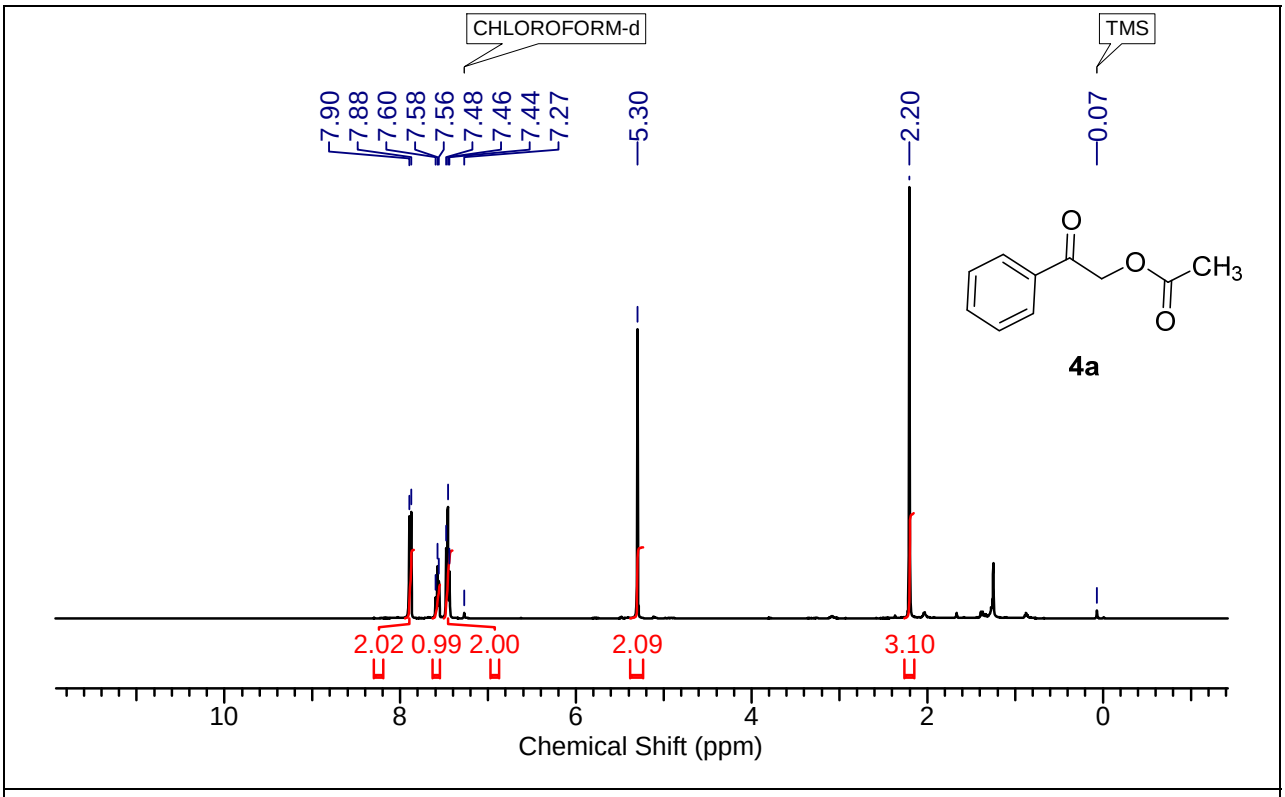



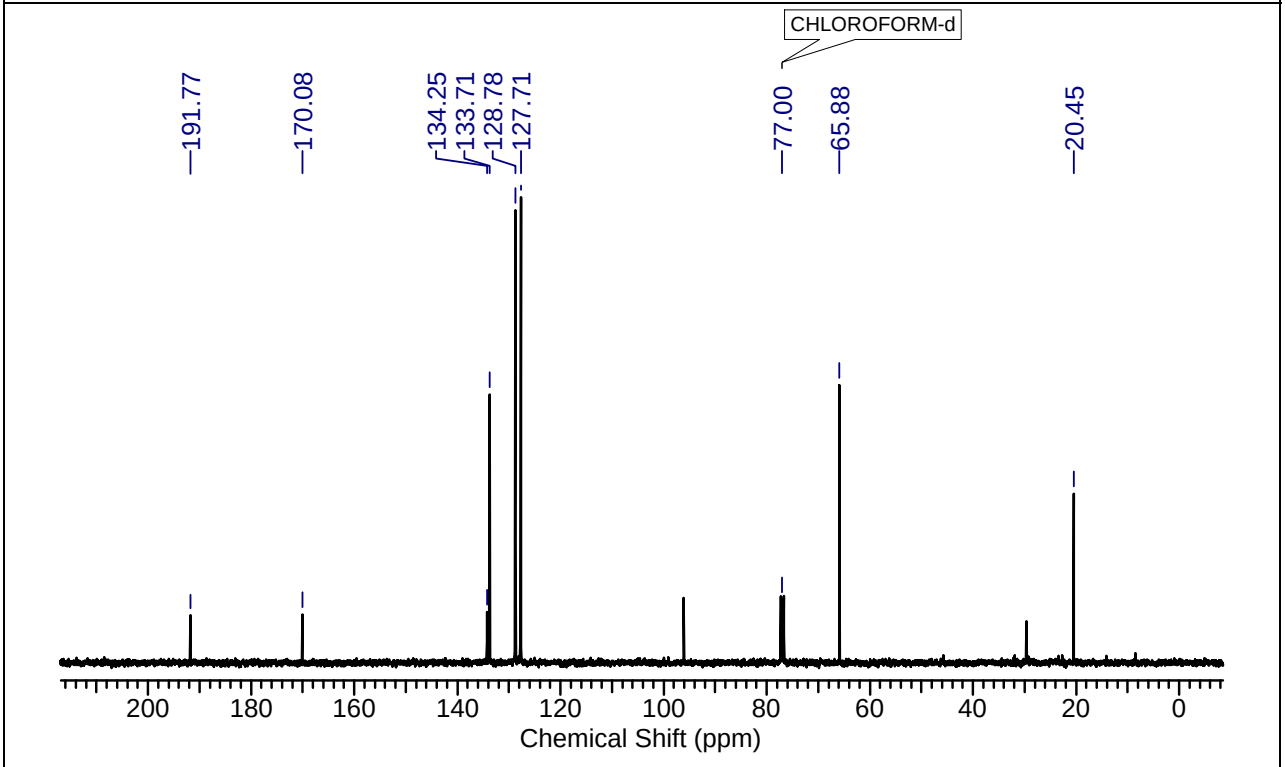

**$^{1}$H and $^{13}$C NMR spectra of 2-methoxy-2-oxoethyl benzoate (2y)**



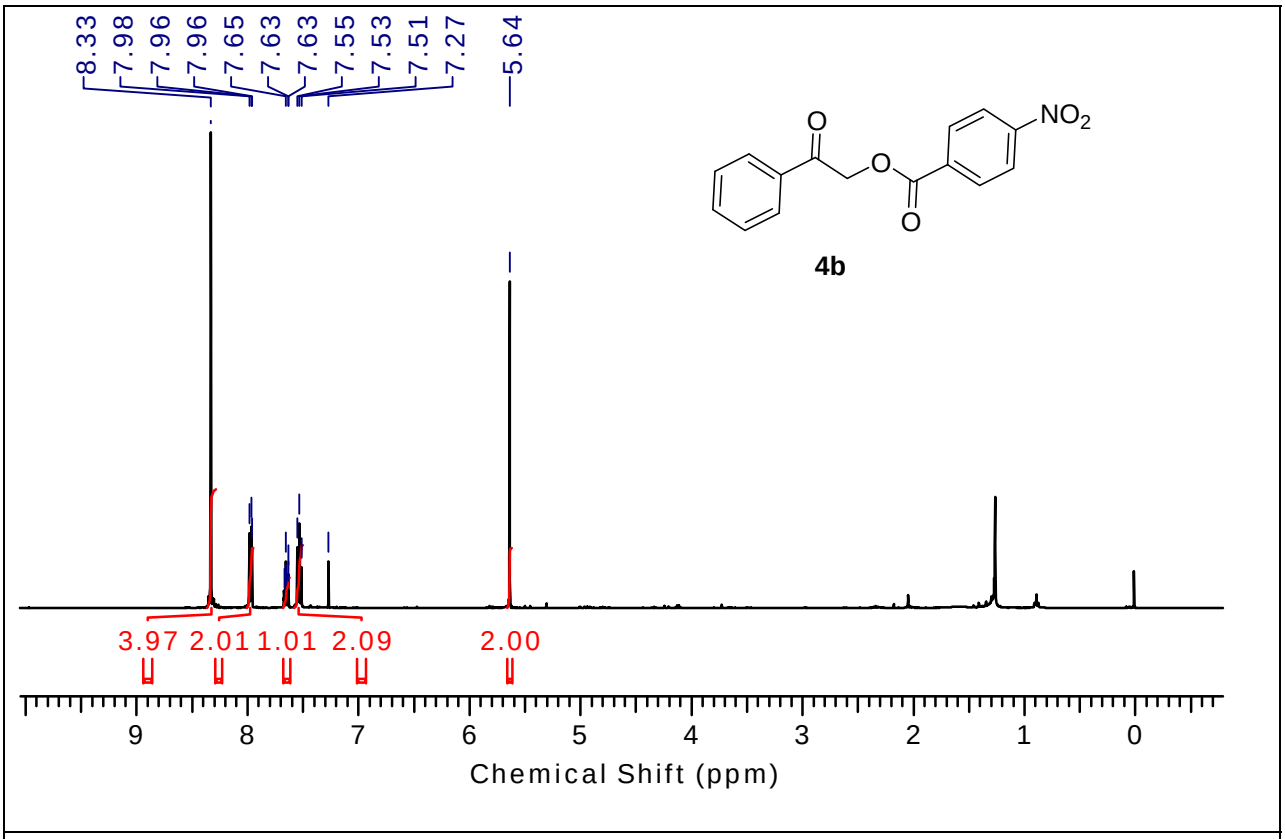



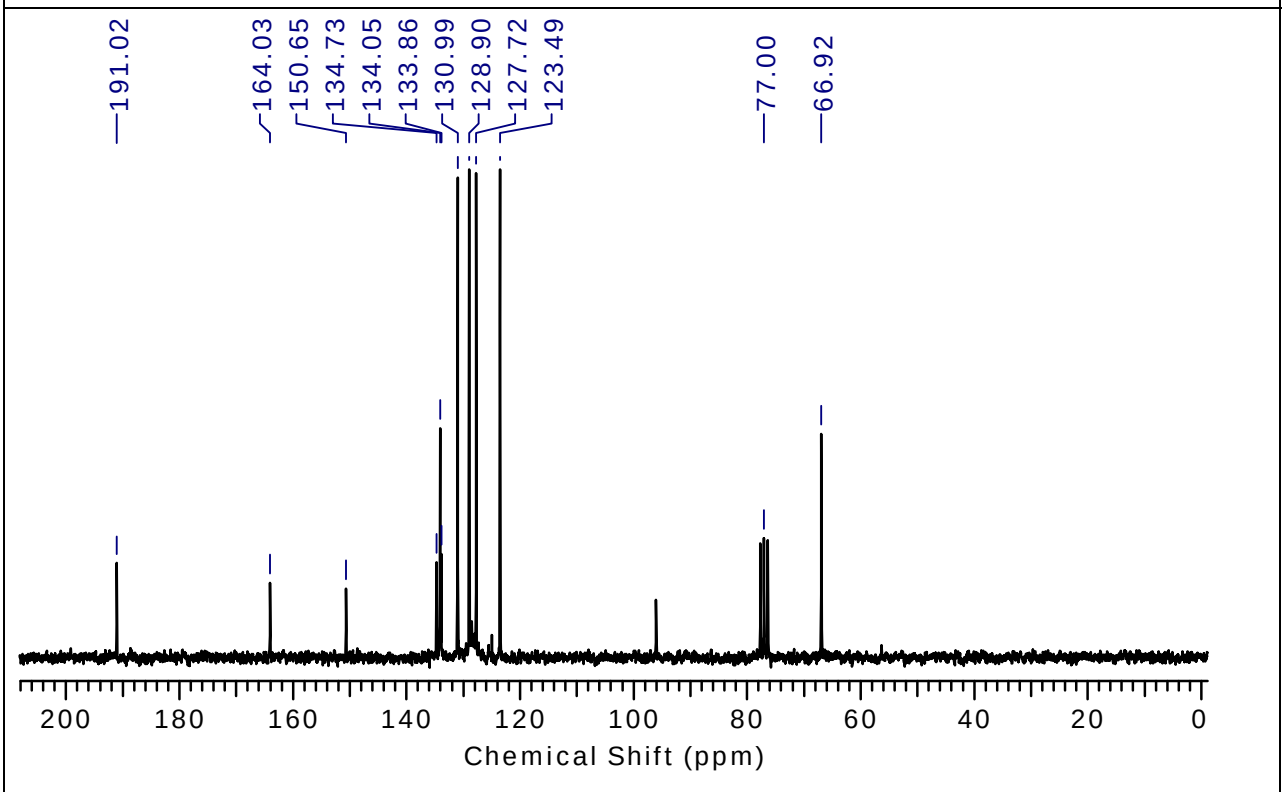

**$^{1}$H and $^{13}$C NMR spectra of 2-oxotetrahydro-2H-pyran-3-yl benzoate (2z)**



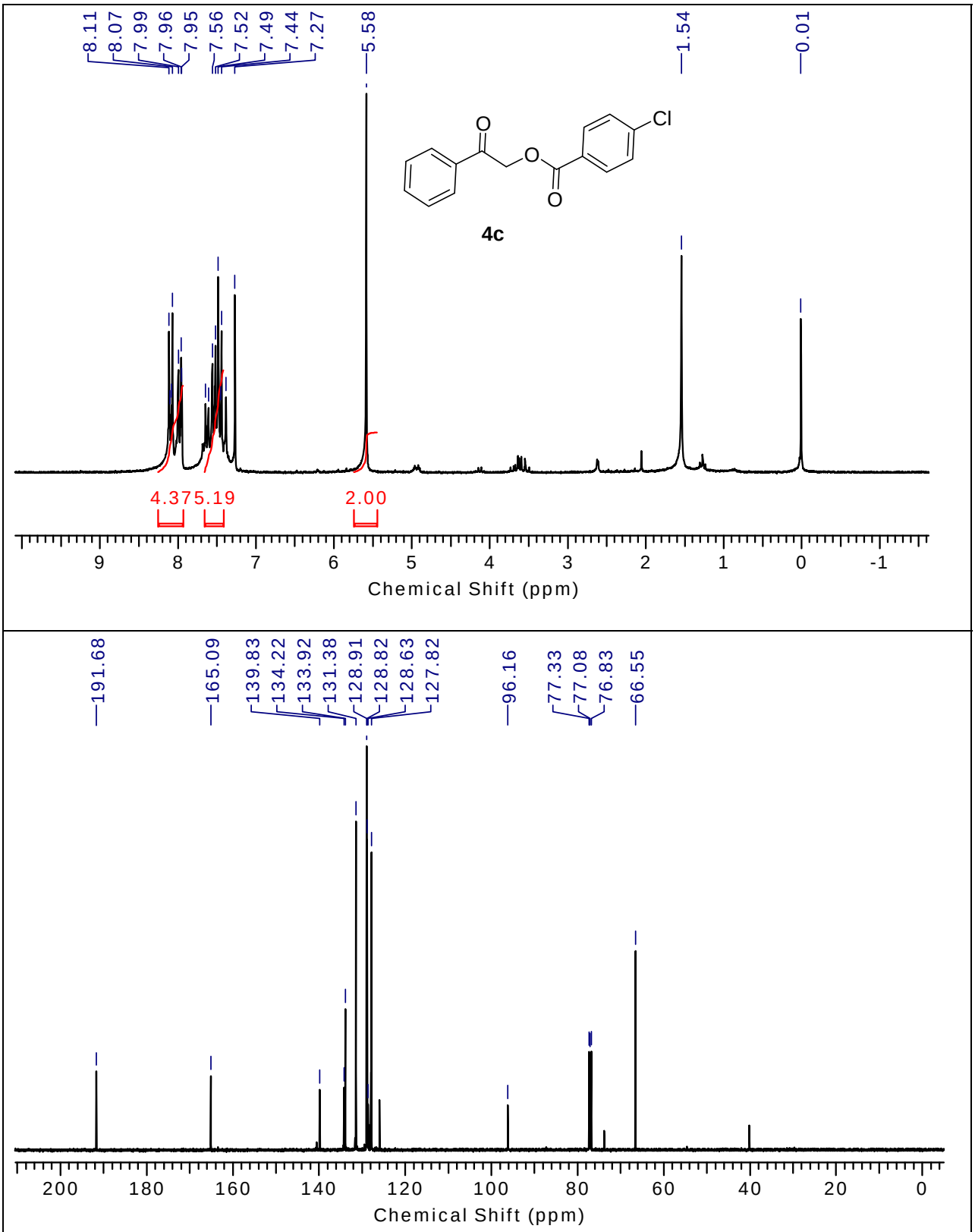




**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-phenylethyl acetate (4a)**

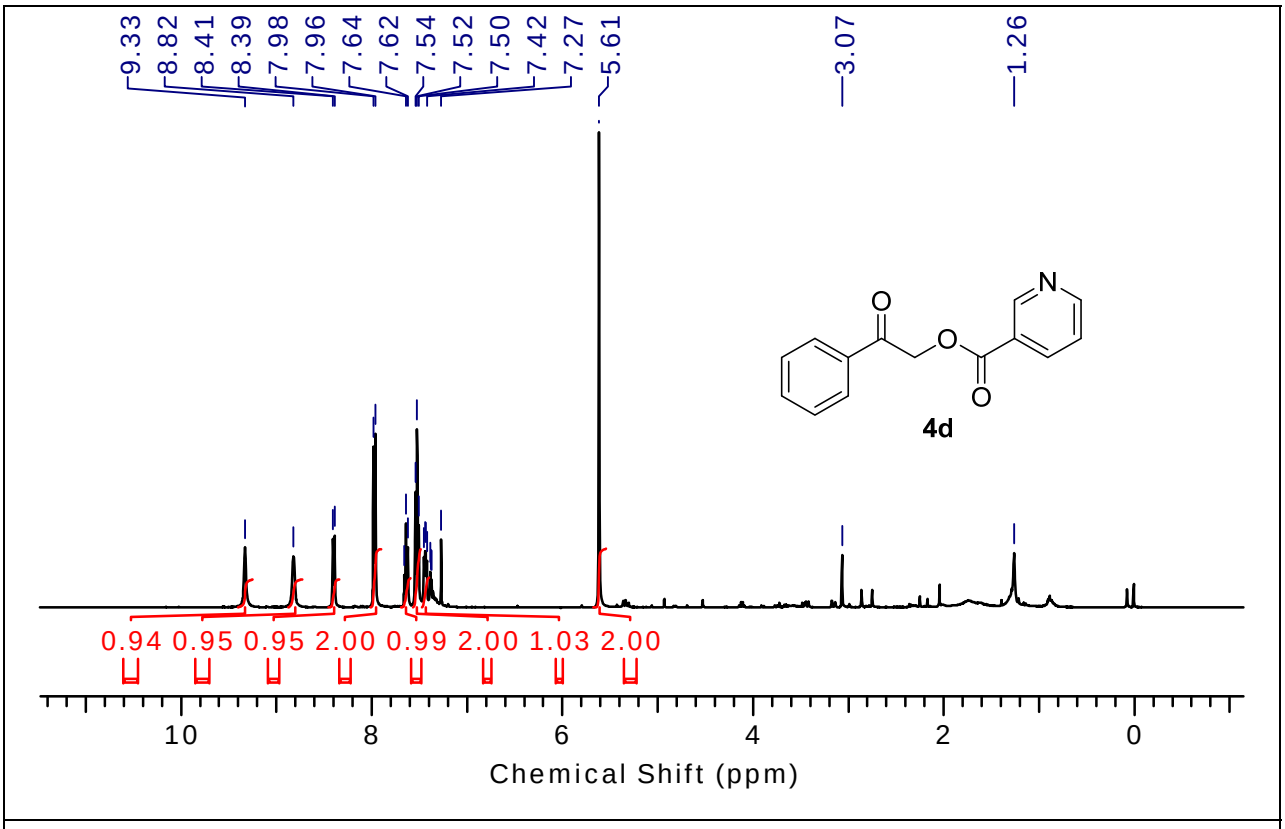


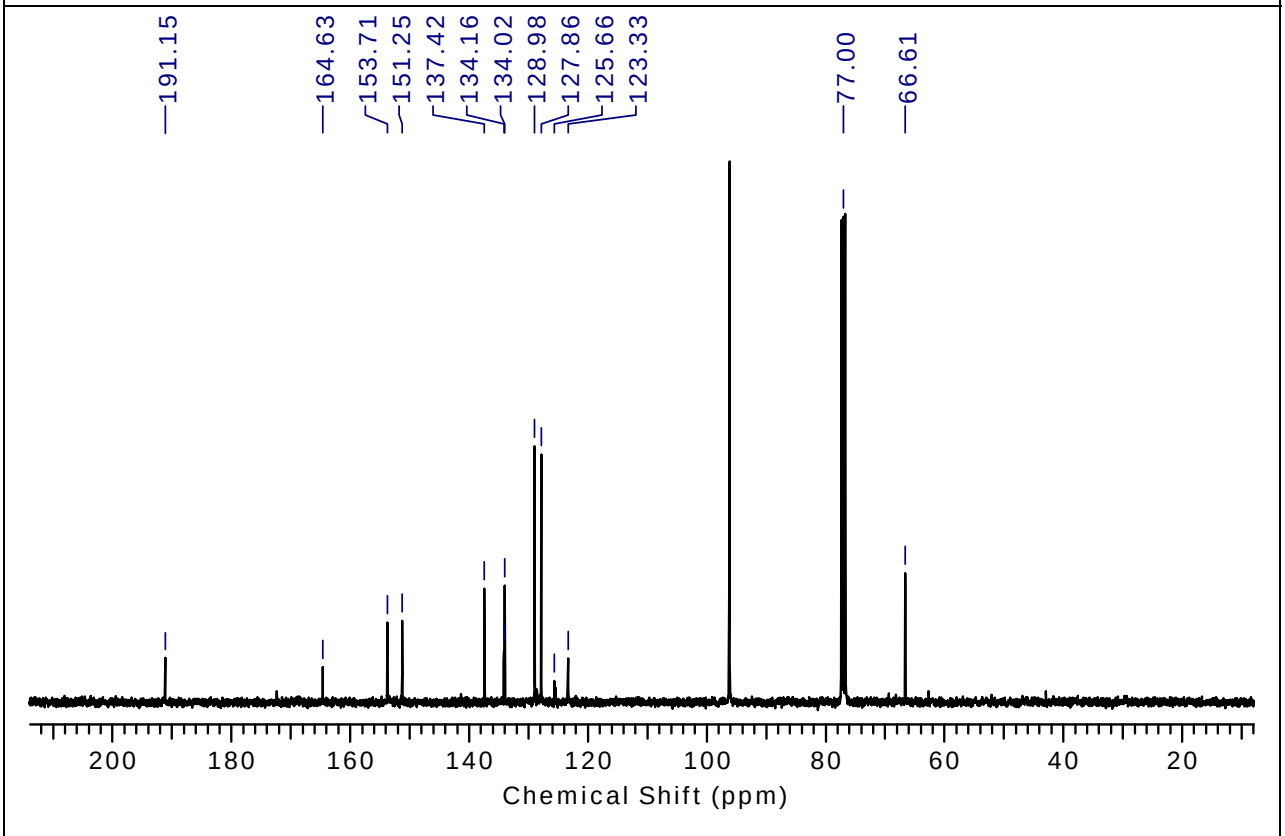




**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-phenylethyl 4-nitrobenzoate (4b)**

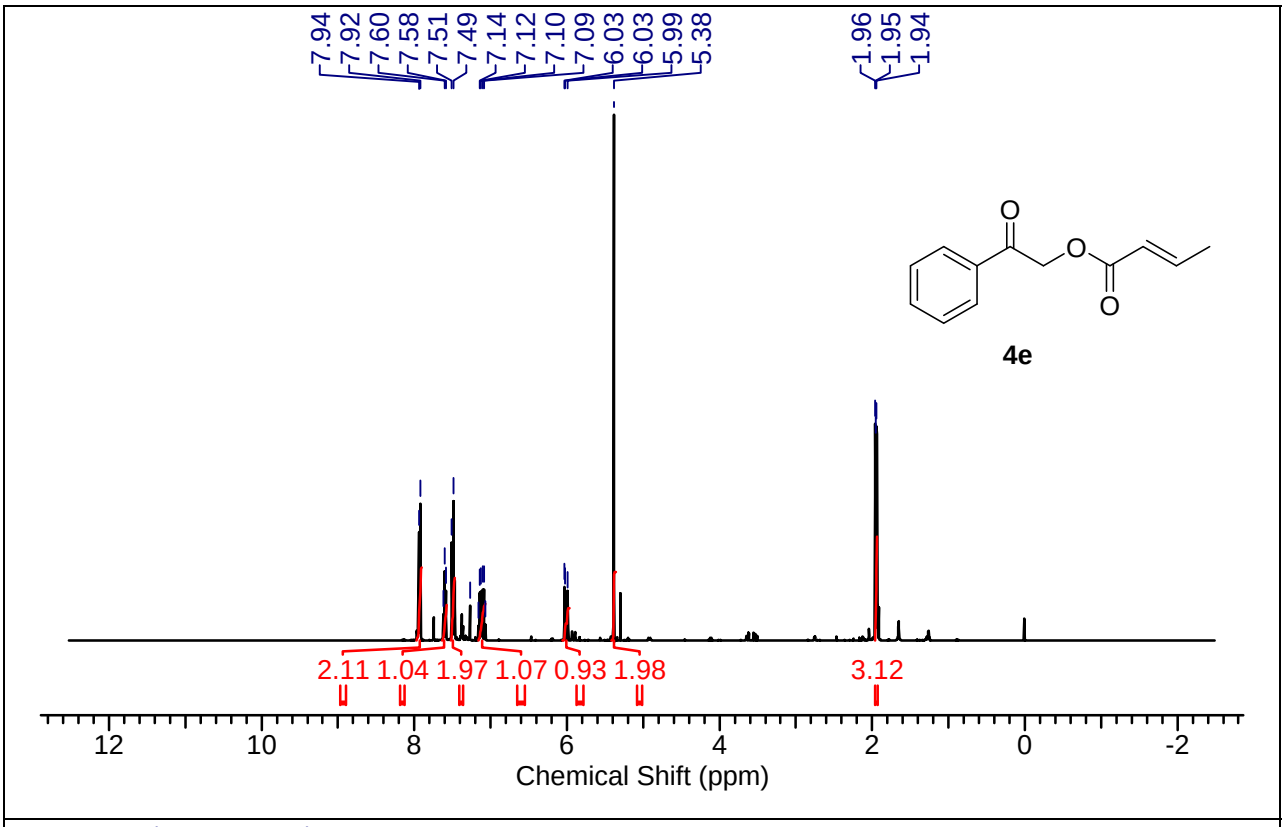


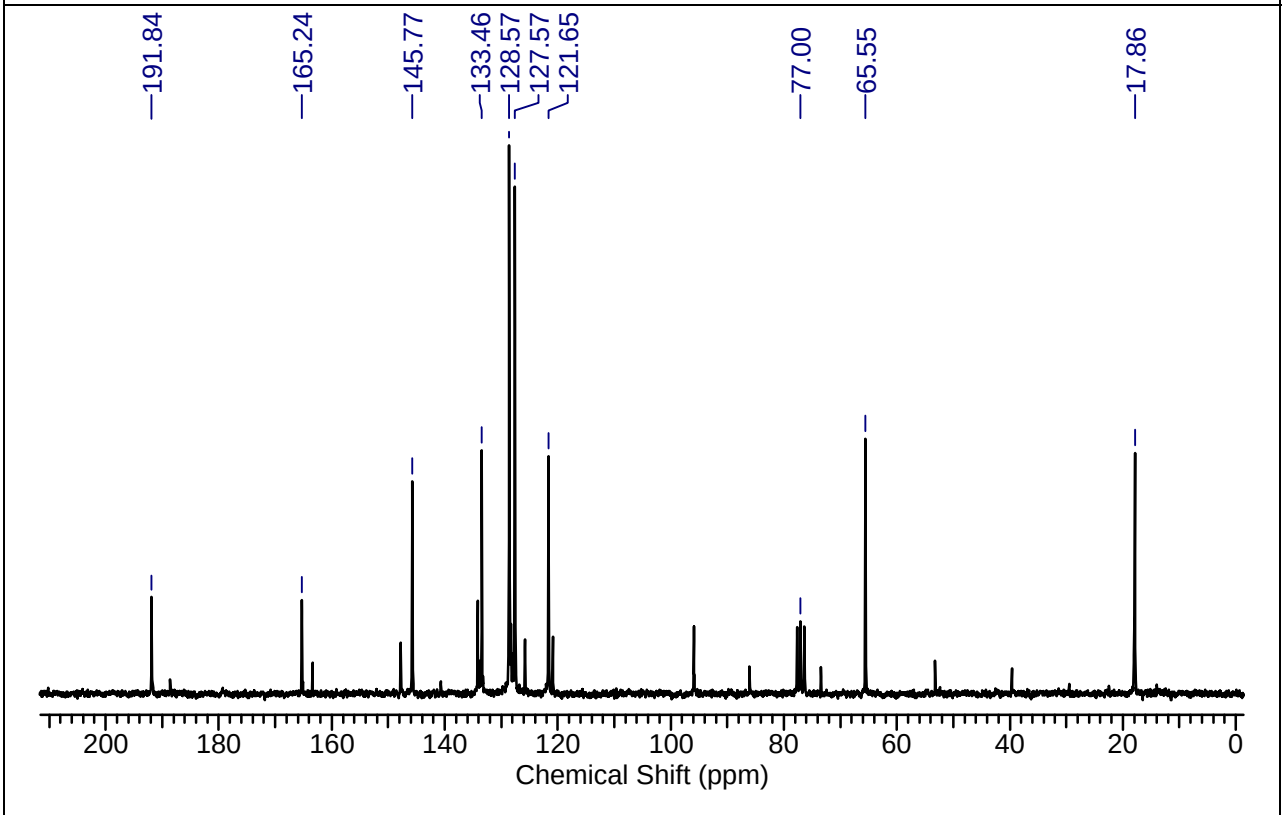

**$^{1}$H and $^{13}$C NMR spectra of 2-Oxo-2-phenylethyl 4-chloro benzoate (4c)**



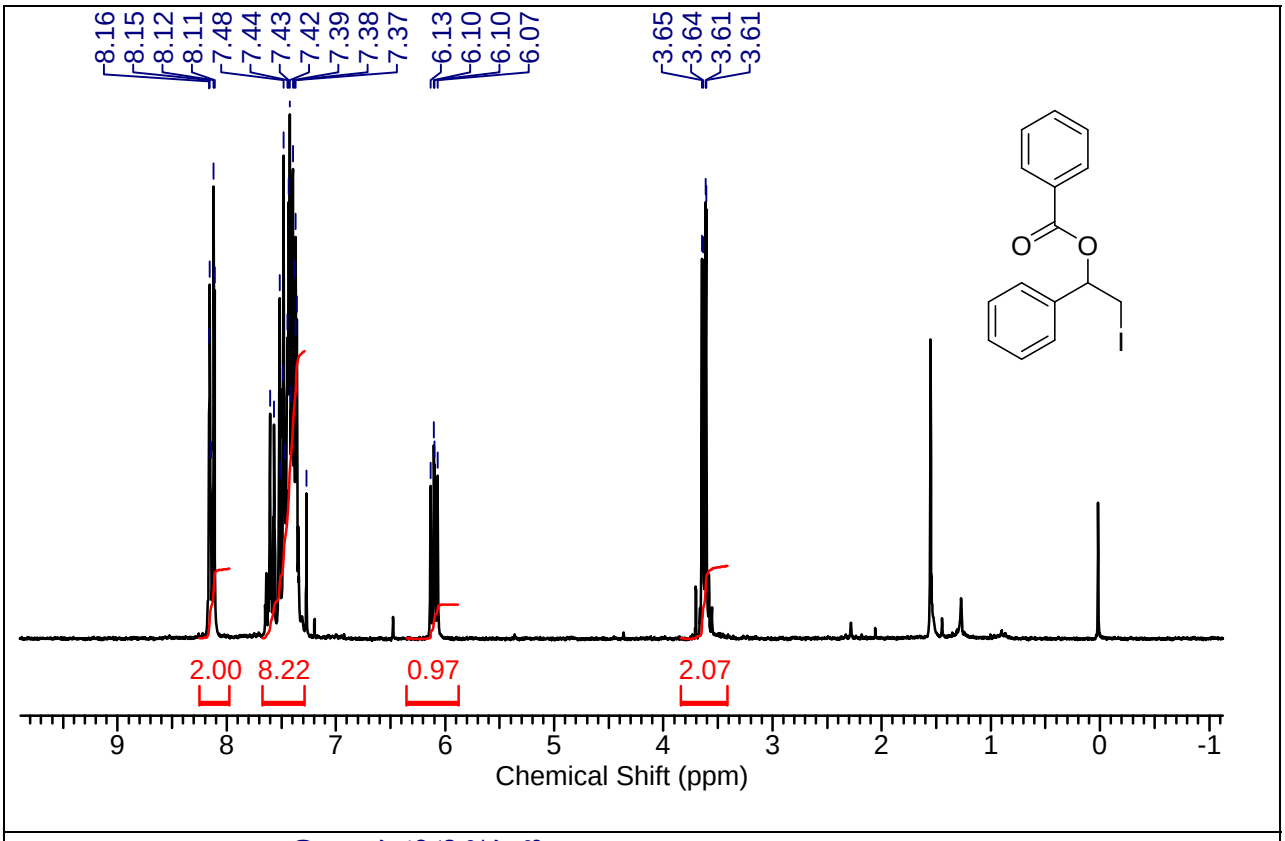



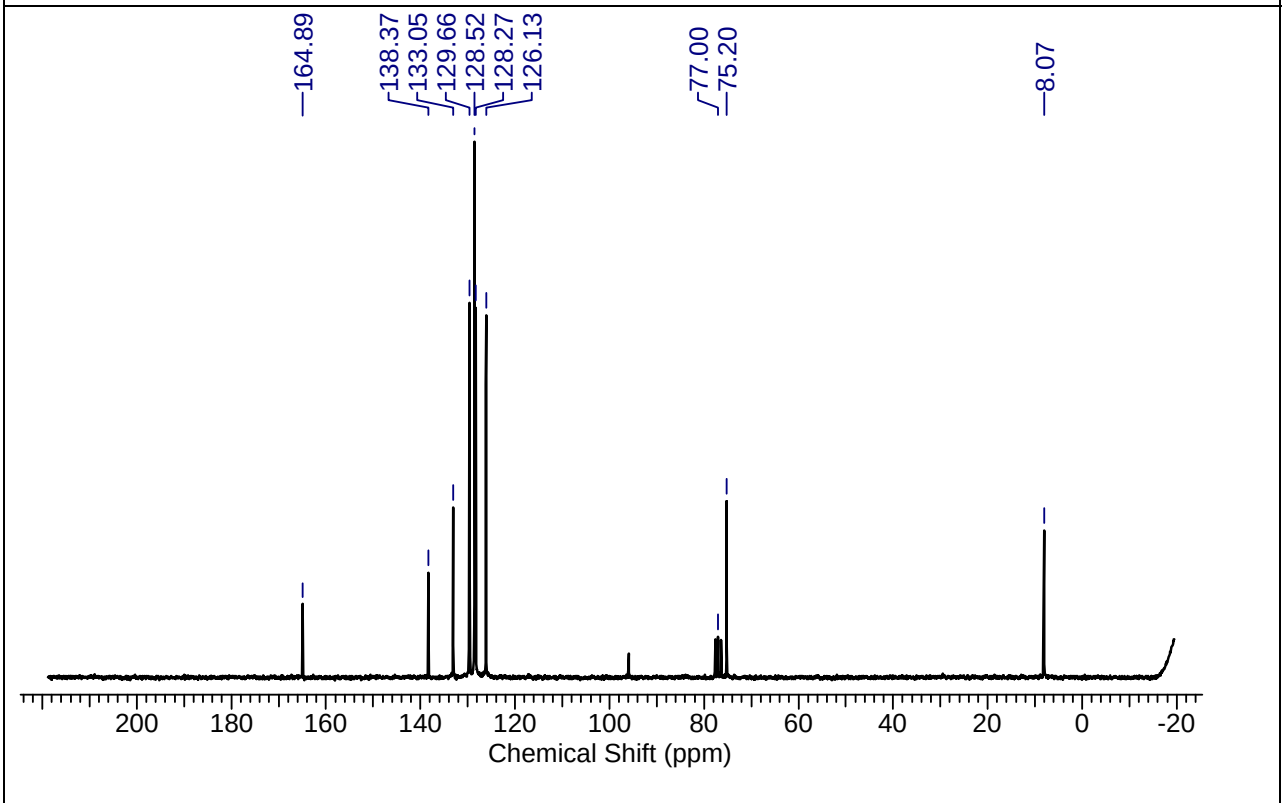

**$^{1}$H and $^{13}$C NMR spectra of 2-Oxo-2-phenylethyl nicotinate (4d)**



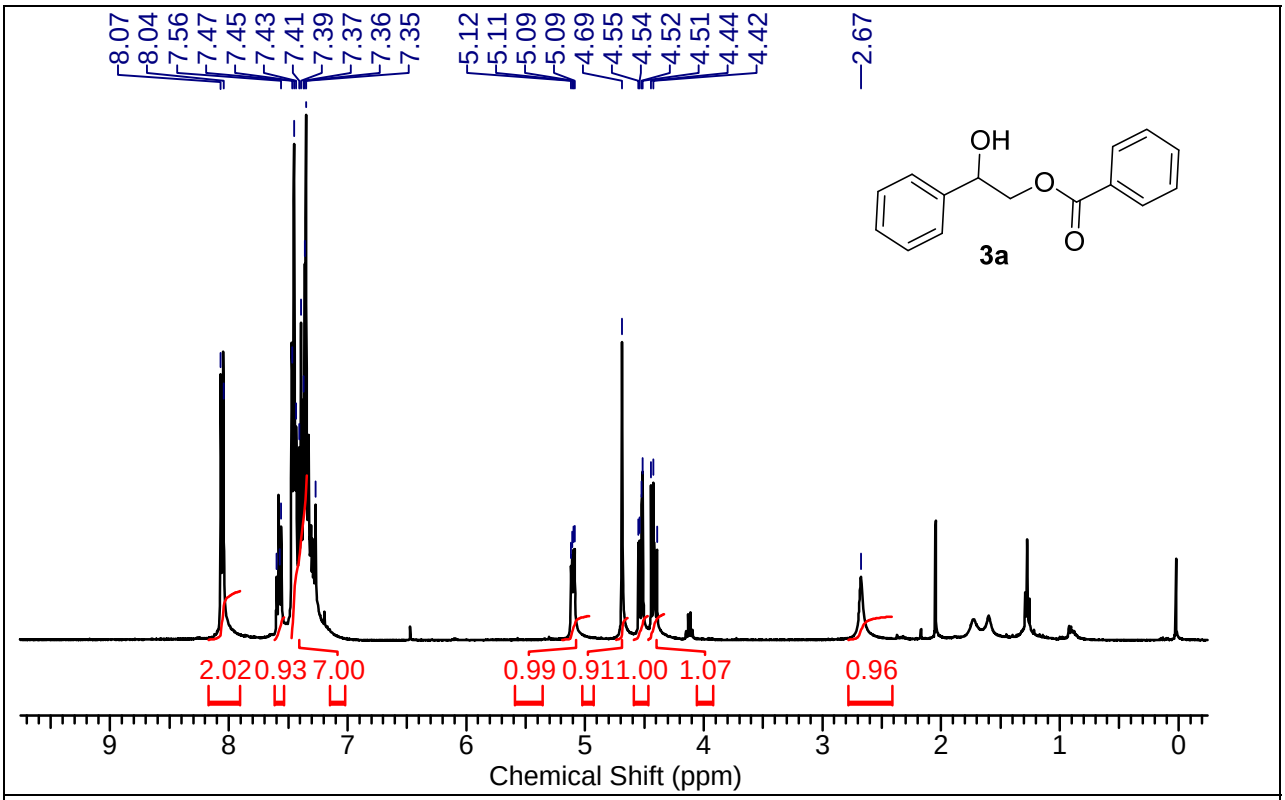



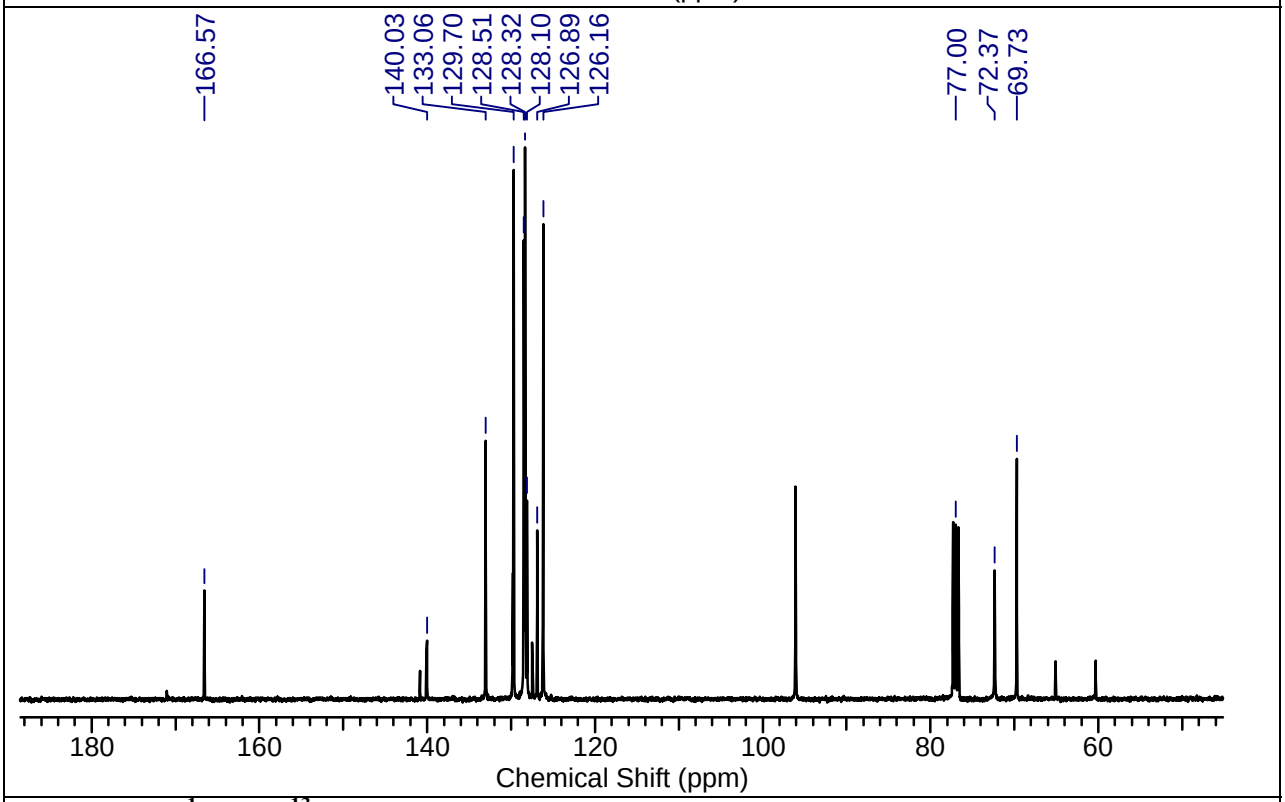

**$^{1}$H and $^{13}$C NMR spectra of 2-oxo-2-phenylethyl (E)-but-2-enoate (4e)**



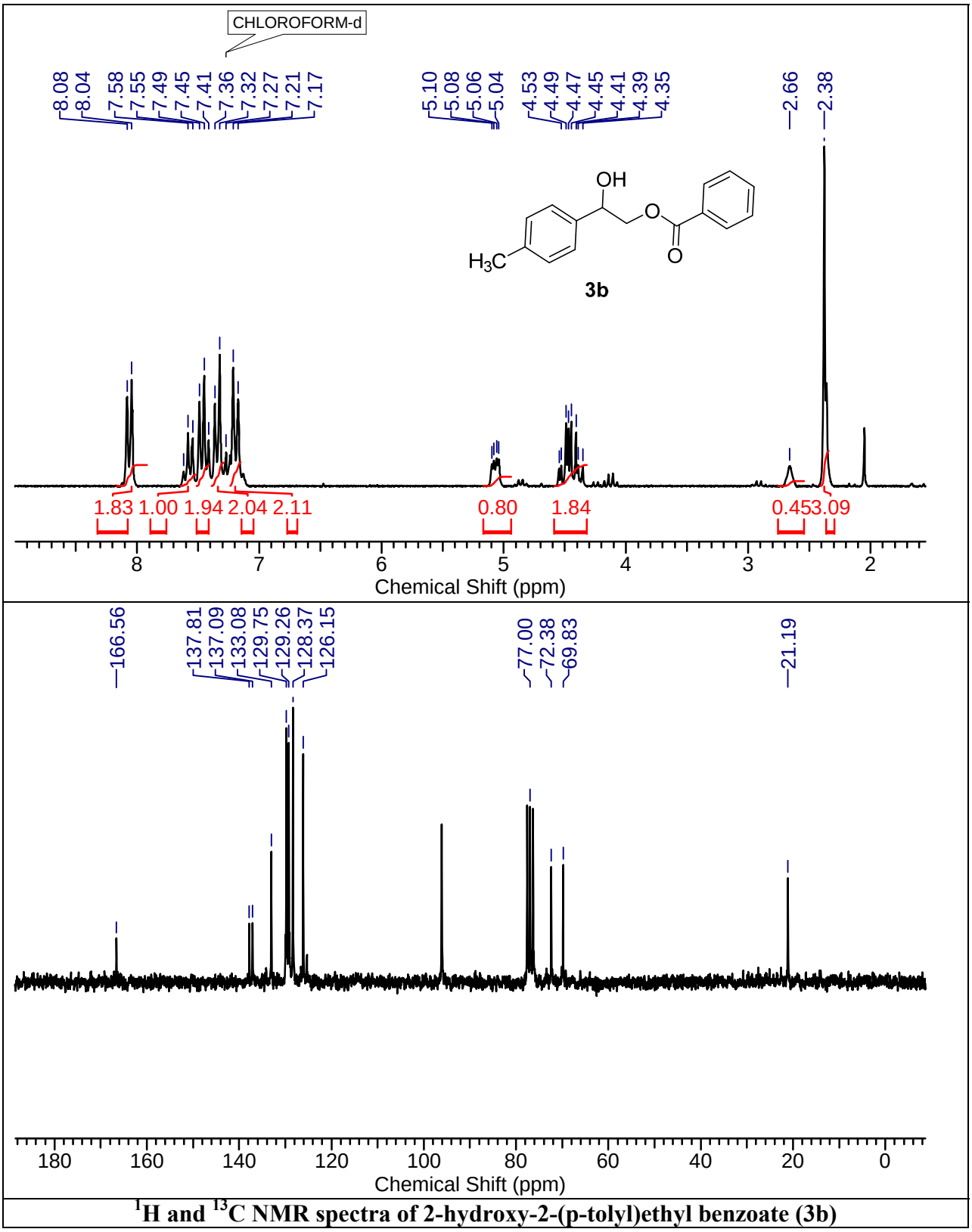




**$^{1}$H and $^{13}$C NMR spectra of 2-iodo-1-phenylethyl benzoate (II)**

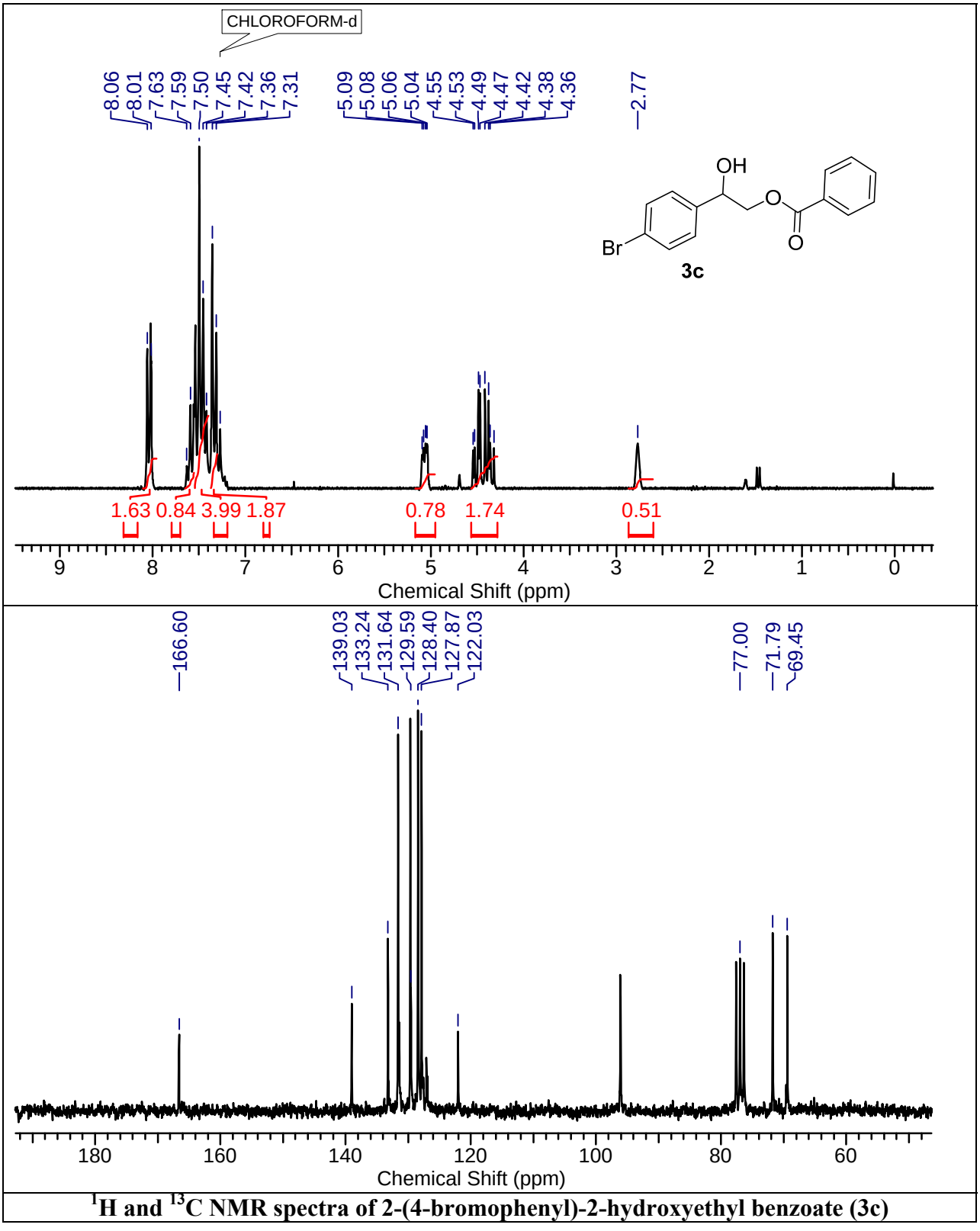


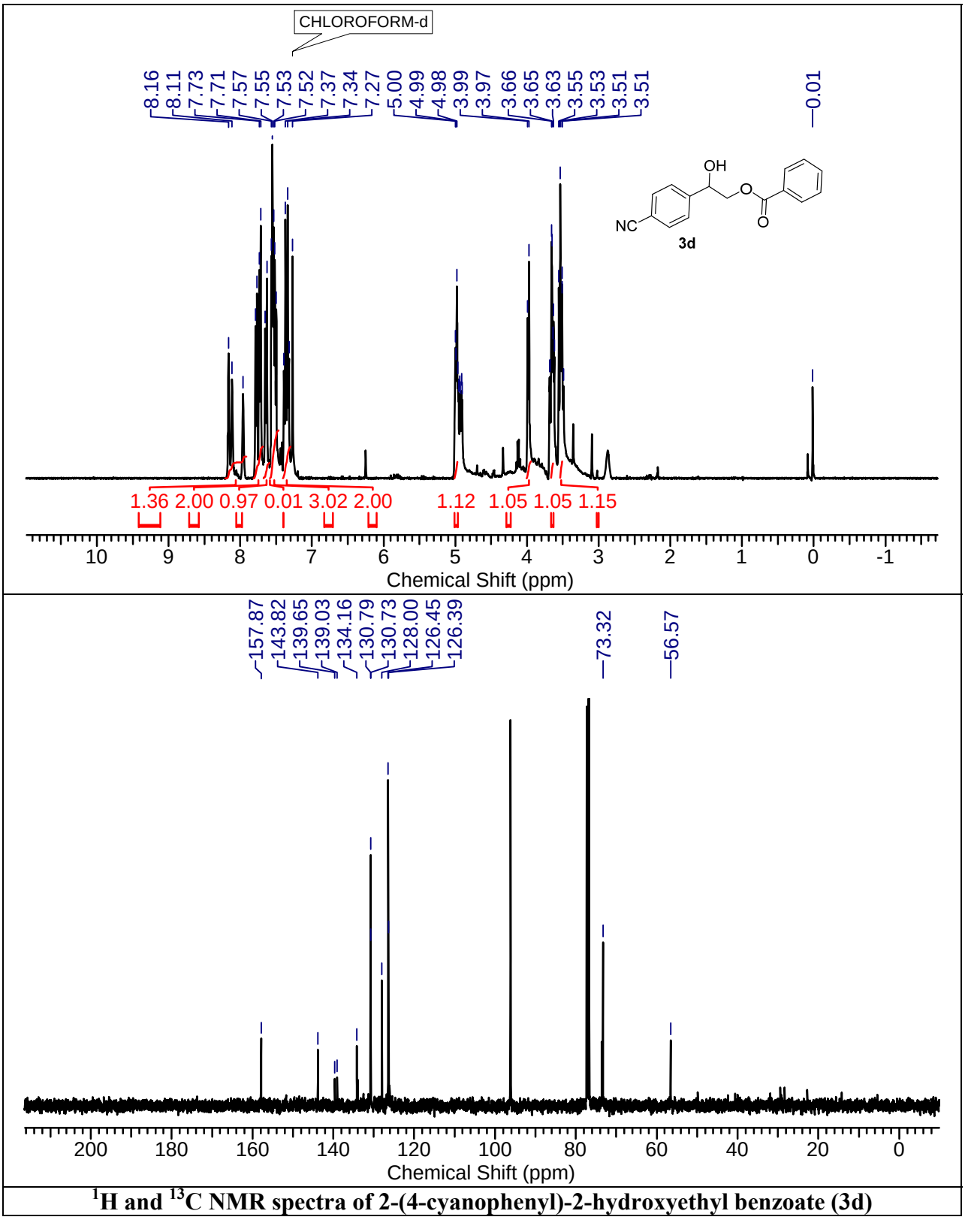

**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxy-2-phenylethyl benzoate (3a)**



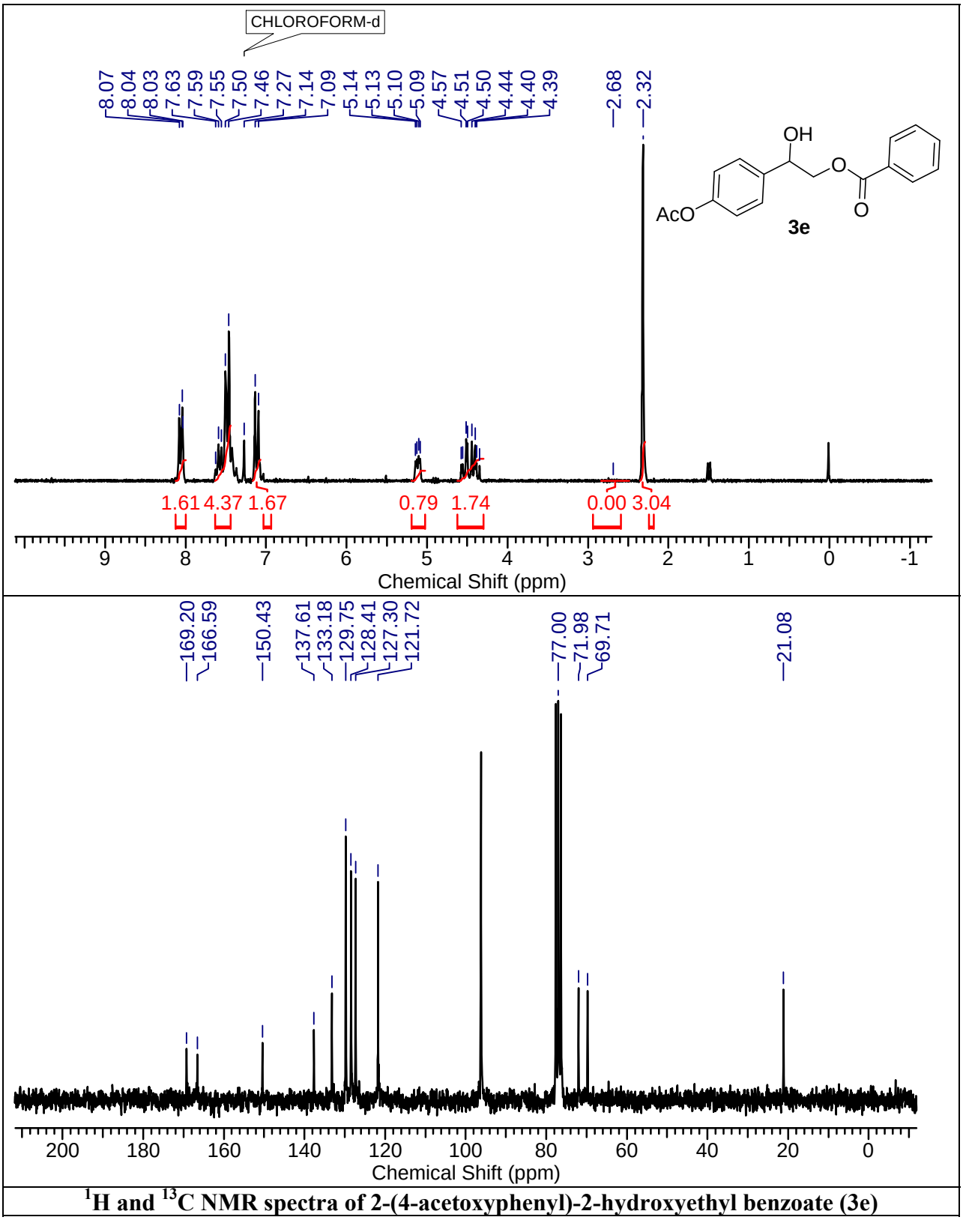

**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxy-2-(p-tolyl)ethyl benzoate (3b)**



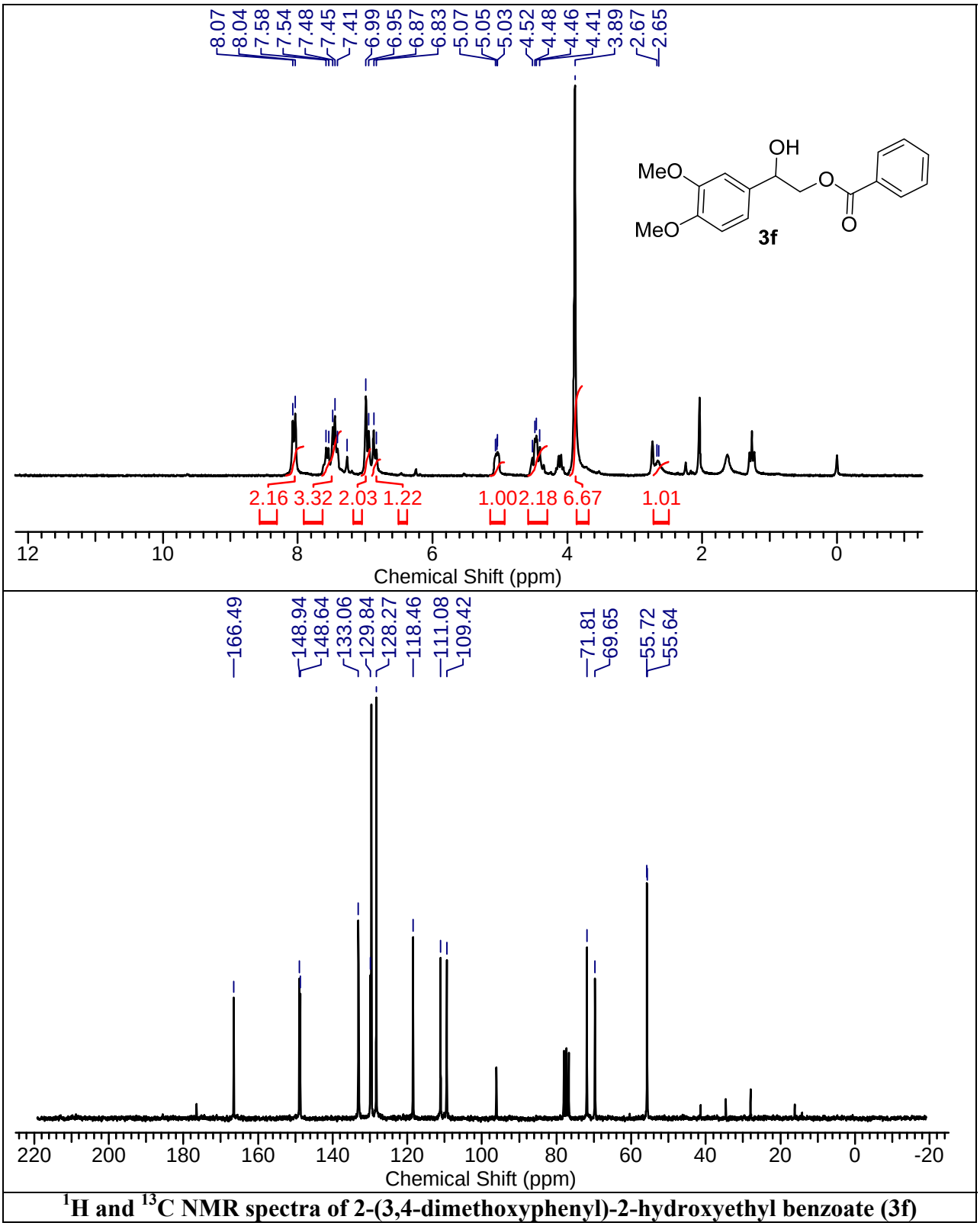

**$^{1}$H and $^{13}$C NMR spectra of 2-(4-bromophenyl)-2-hydroxyethyl benzoate (3c)**



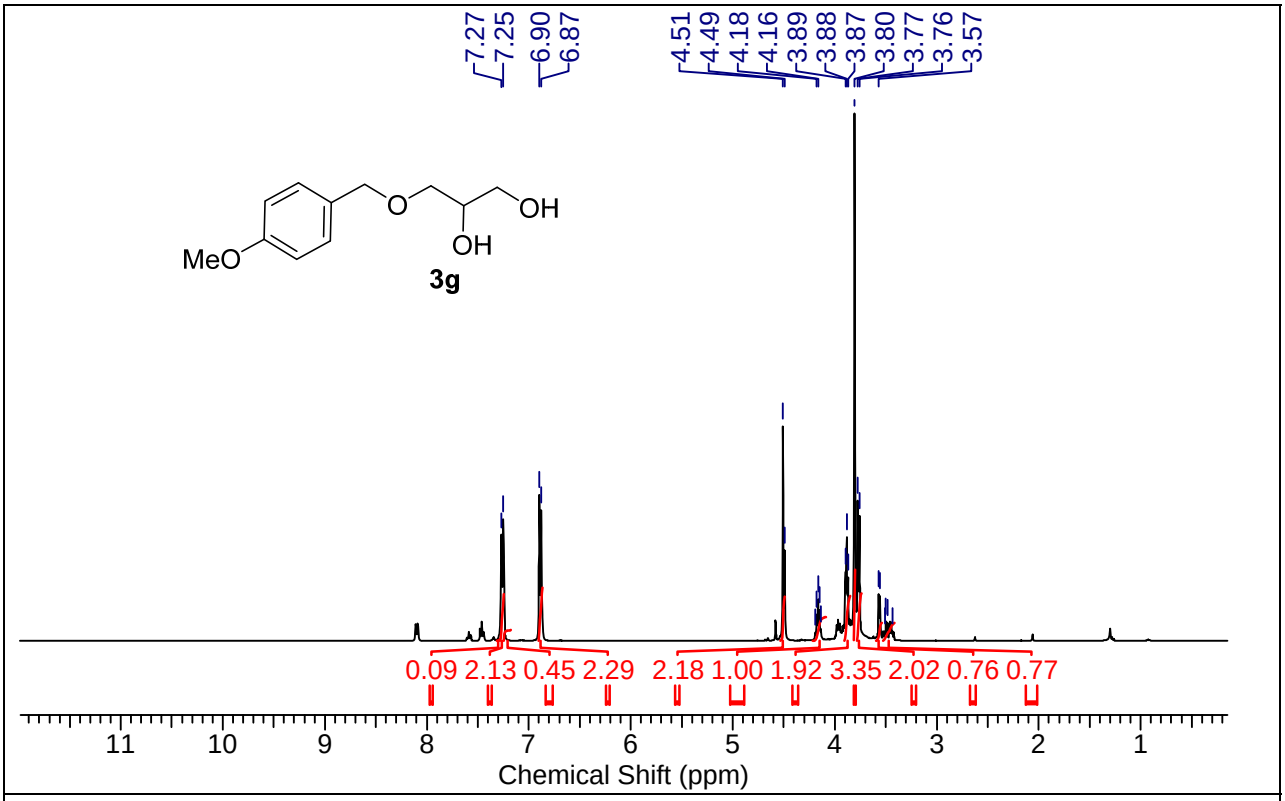

**$^{1}$H and $^{13}$C NMR spectra of 2-(4-cyanophenyl)-2-hydroxyethyl benzoate (3d)**

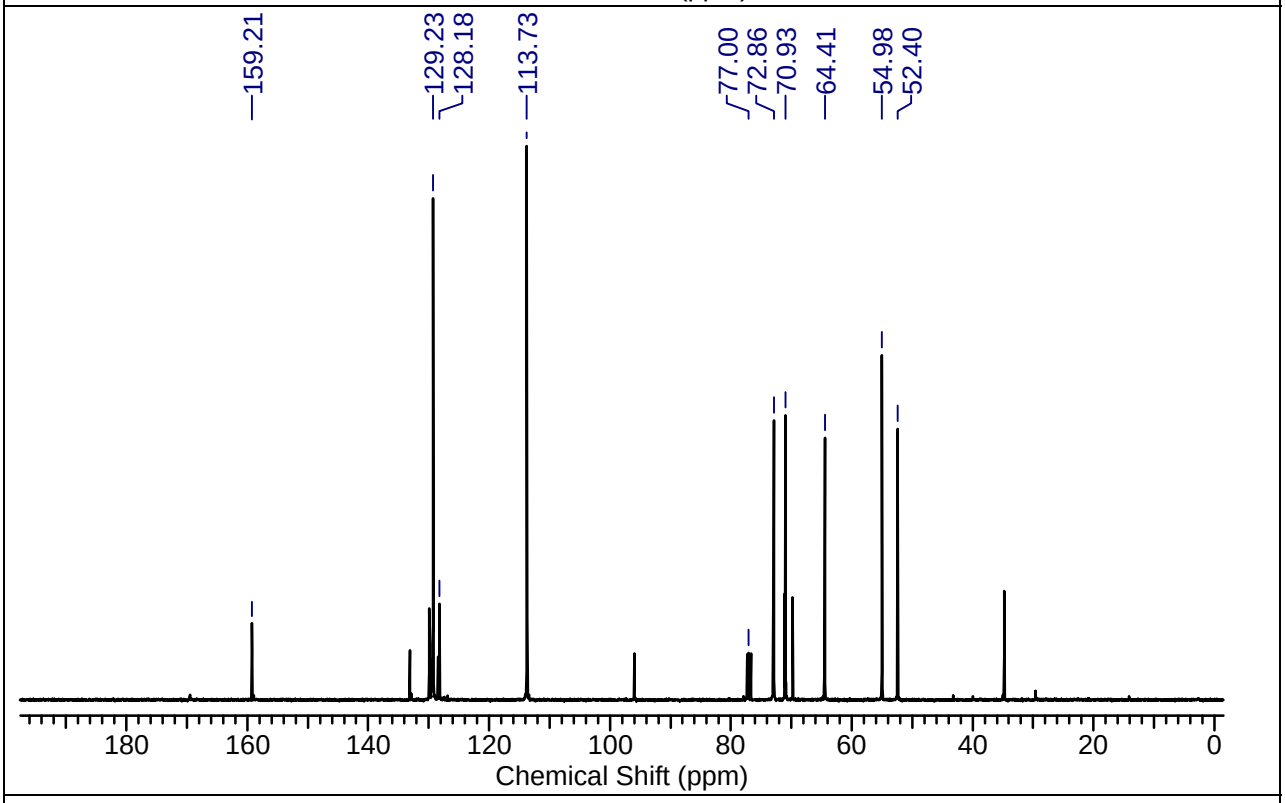



**$^{1}$H and $^{13}$C NMR spectra of 2-(4-acetoxyphenyl)-2-hydroxyethyl benzoate (3e)**

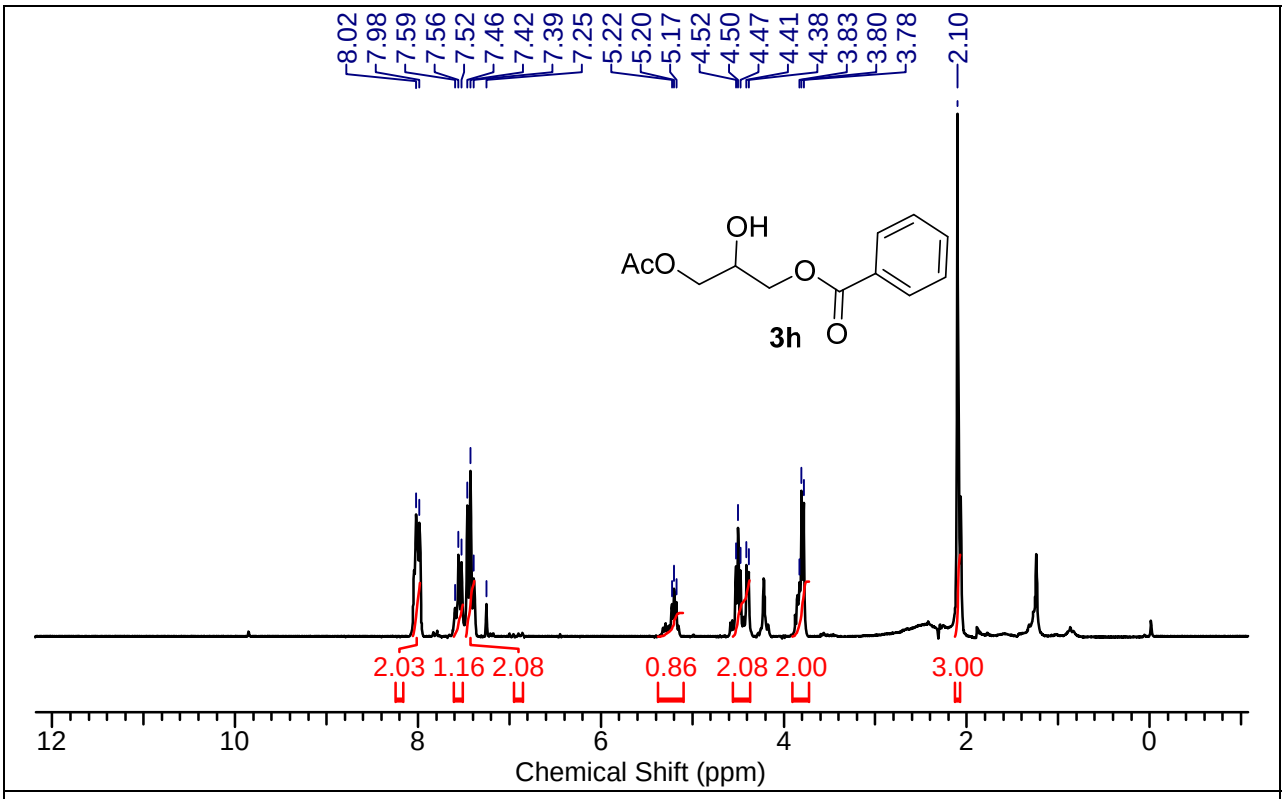


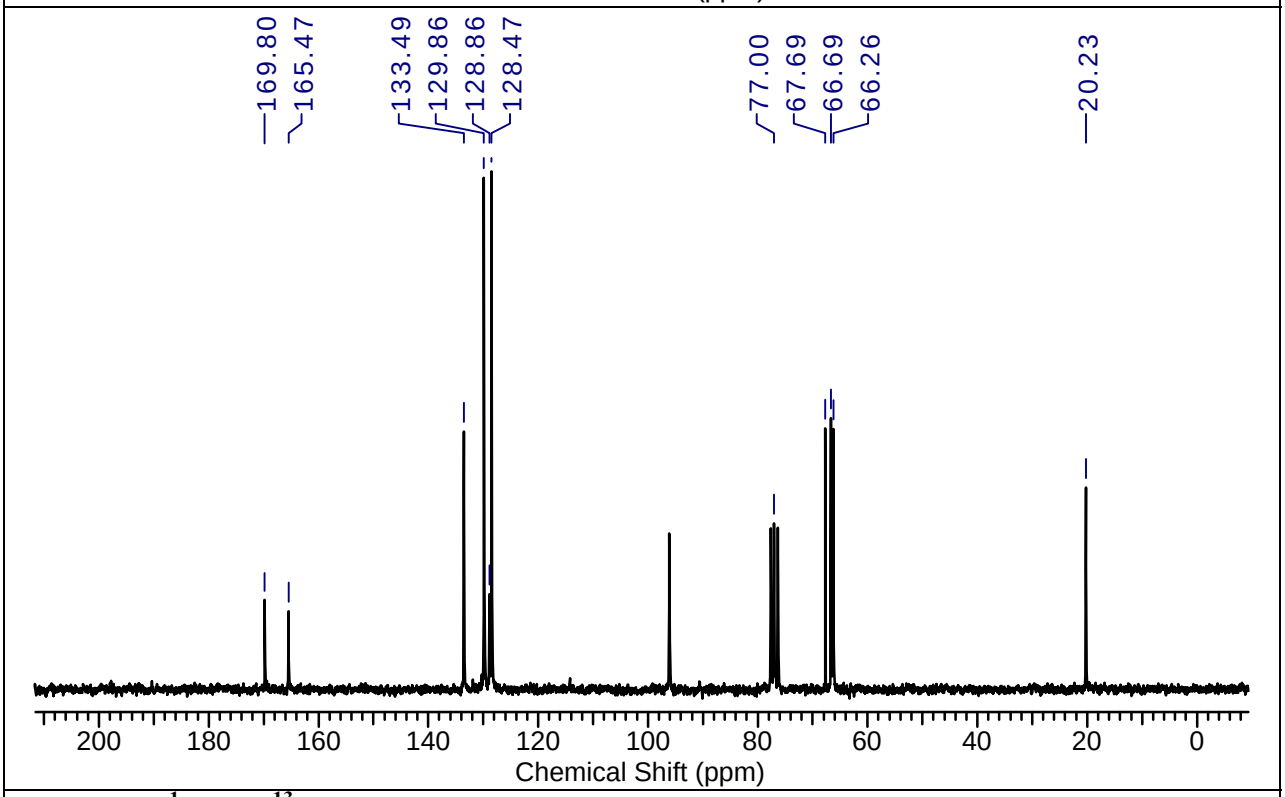

**$^{1}$H and $^{13}$C NMR spectra of 2-(3,4-dimethoxyphenyl)-2-hydroxyethyl benzoate (3f)**



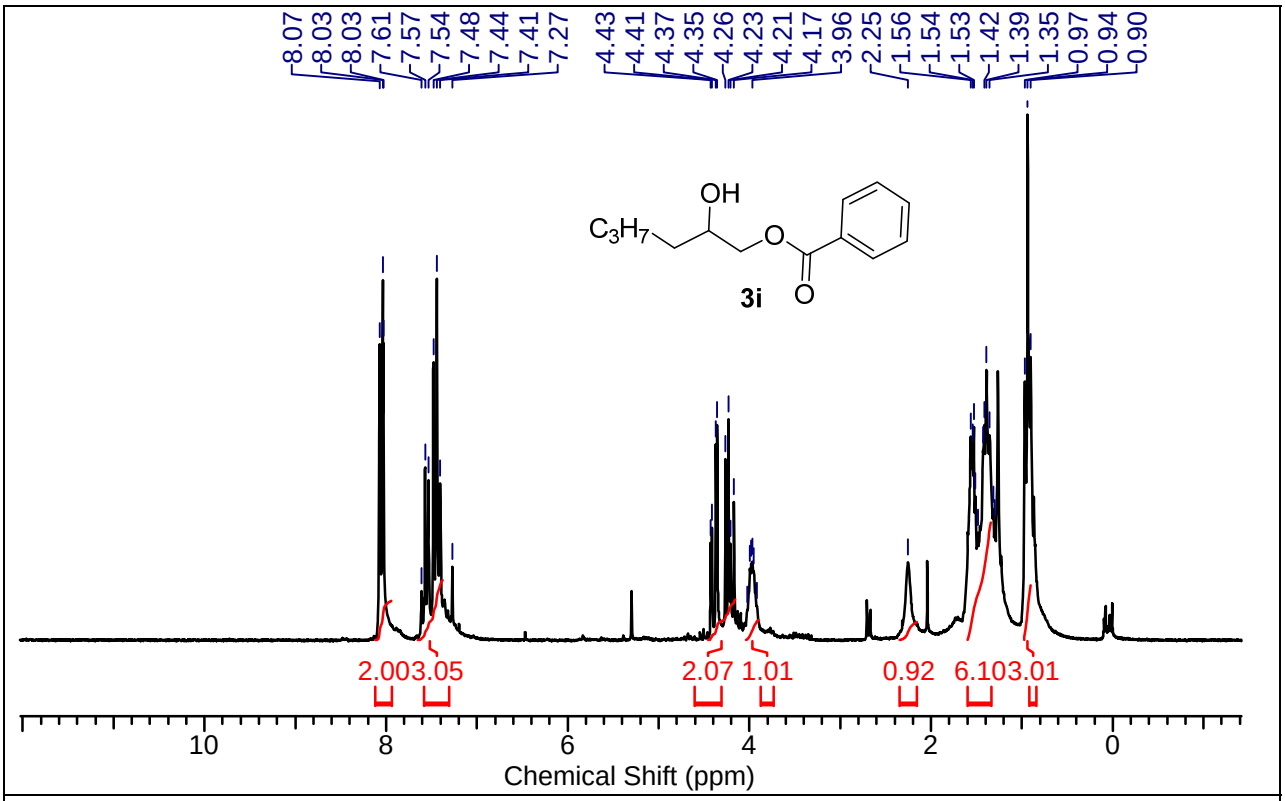



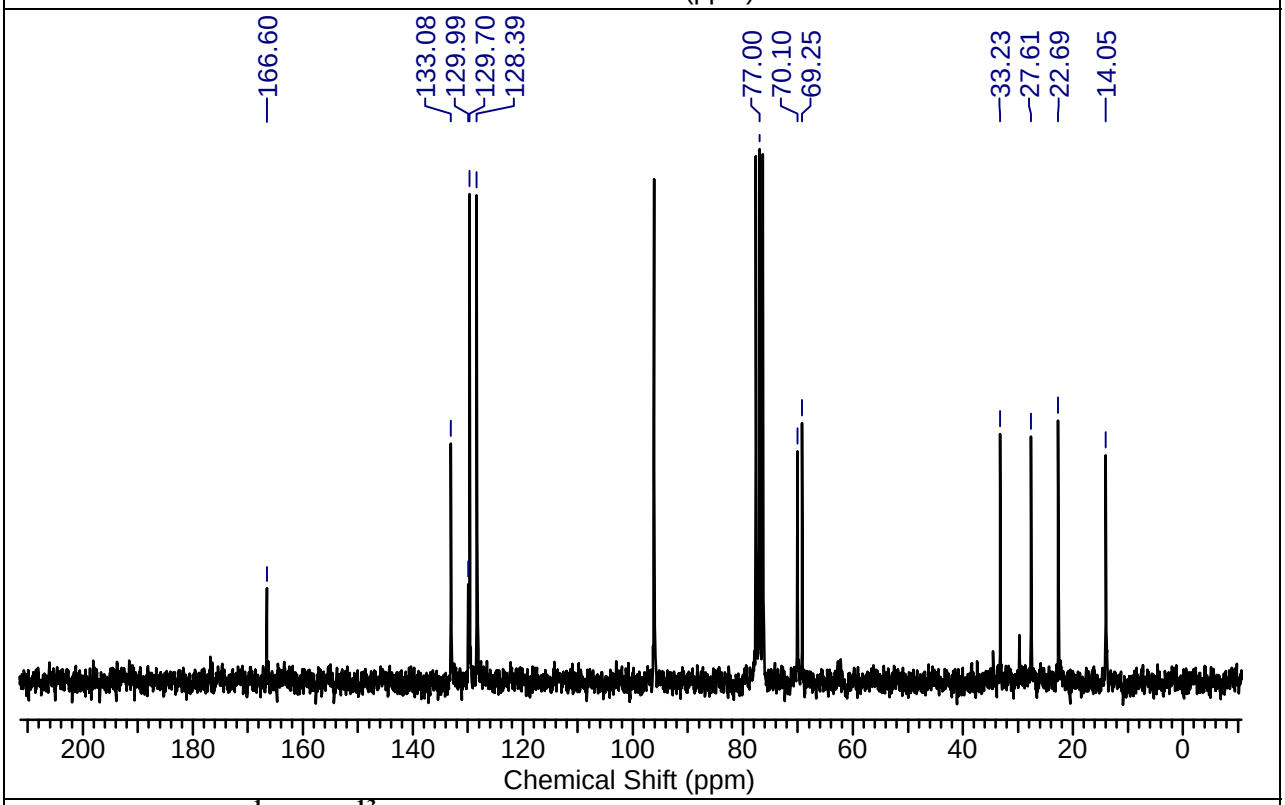

**1H and 13C NMR spectra of 3-((4-methoxybenzyl)oxy)propane-1,2-diol (3g)**



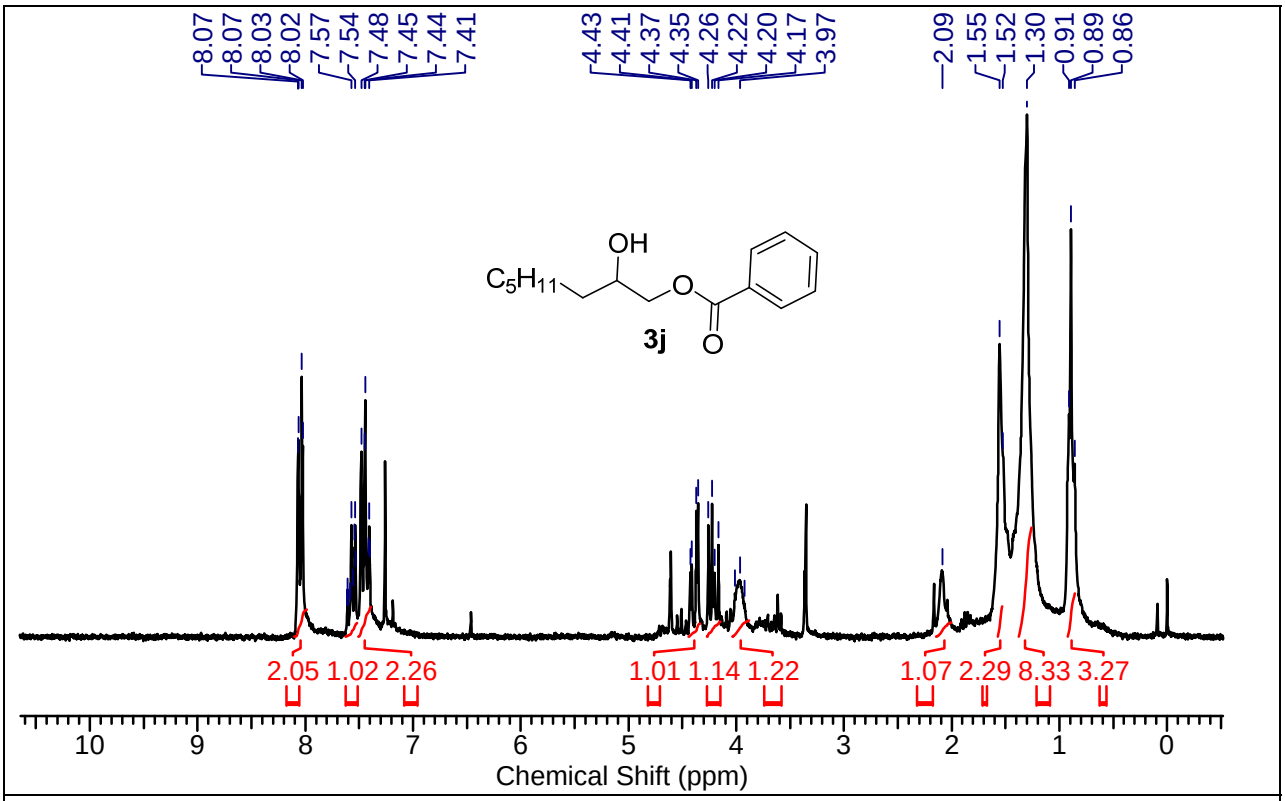



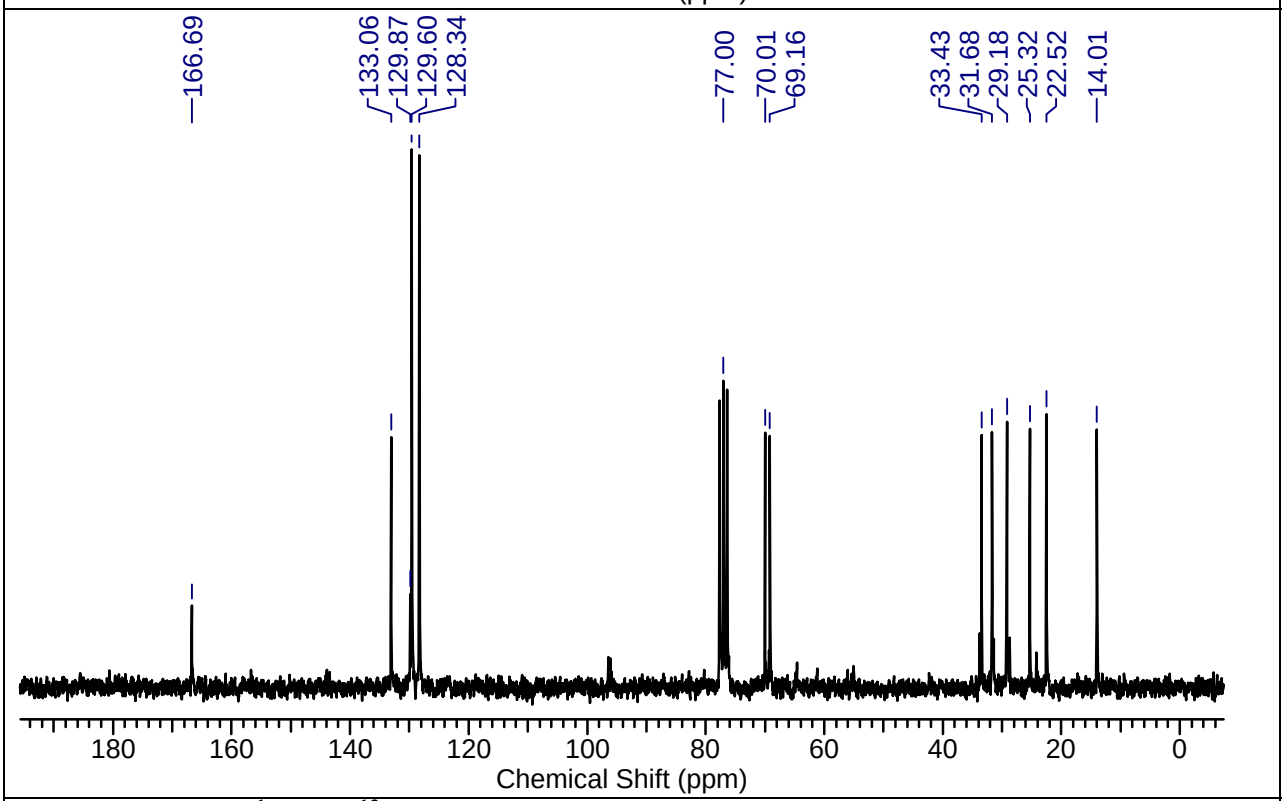

**$^{1}$H and $^{13}$C NMR spectra of 3-acetoxy-2-hydroxypropyl benzoate (3h)**



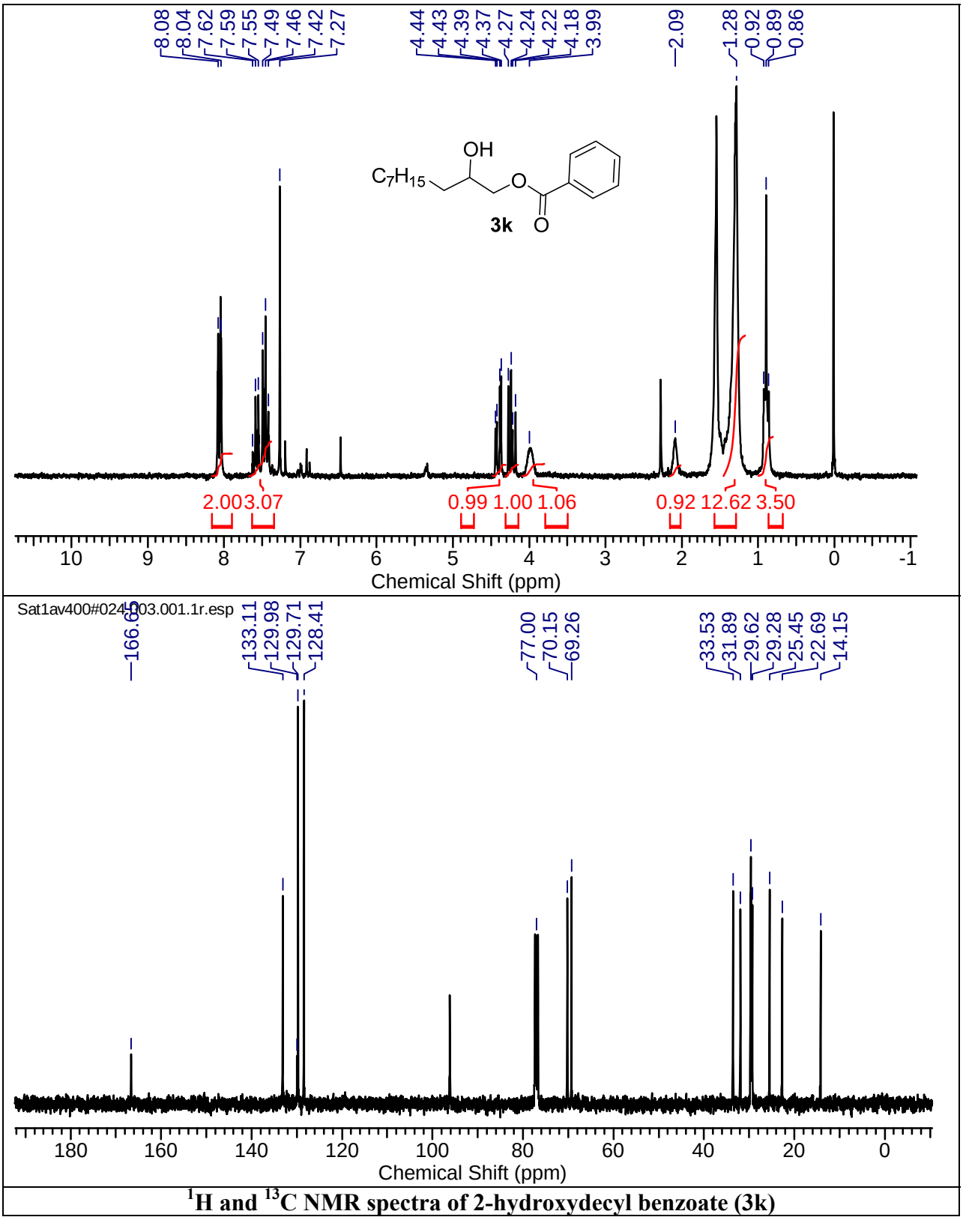




**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxyhexyl benzoate (3i)**

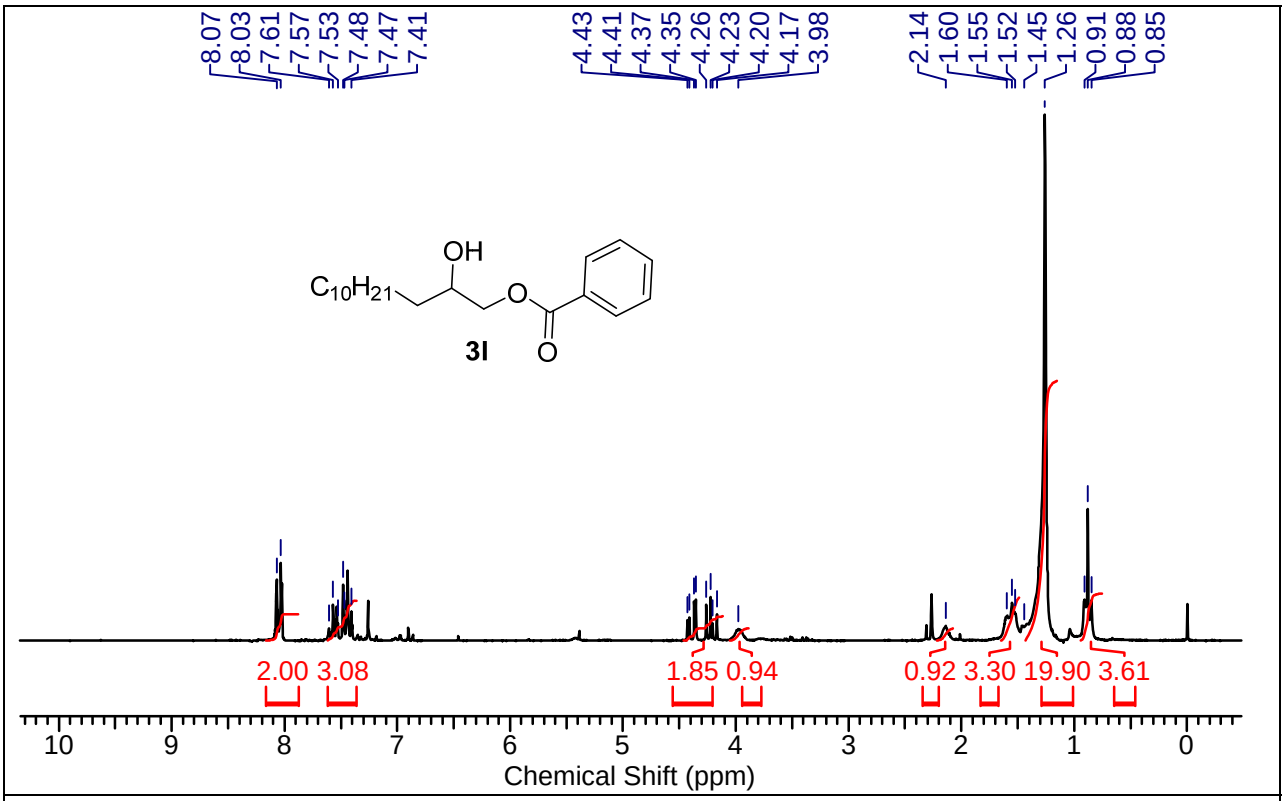


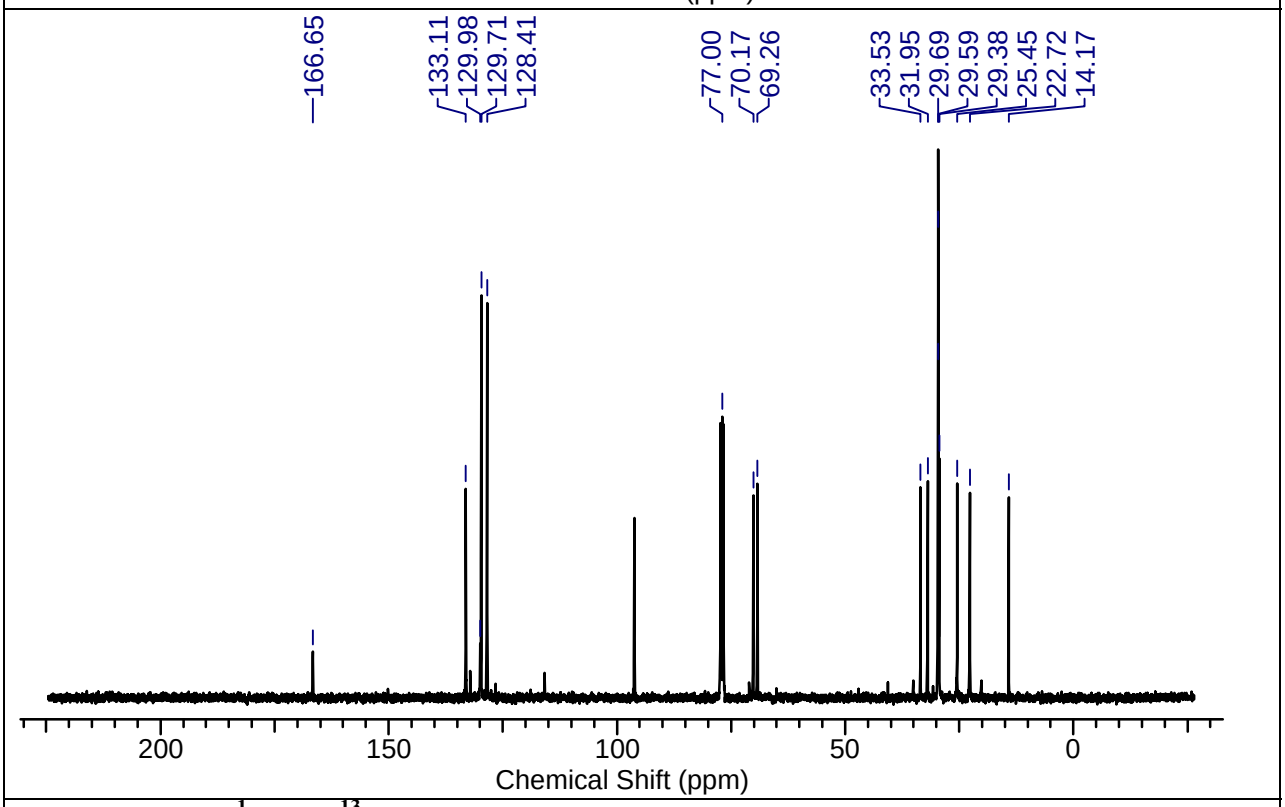




**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxyoctyl benzoate (3j)**

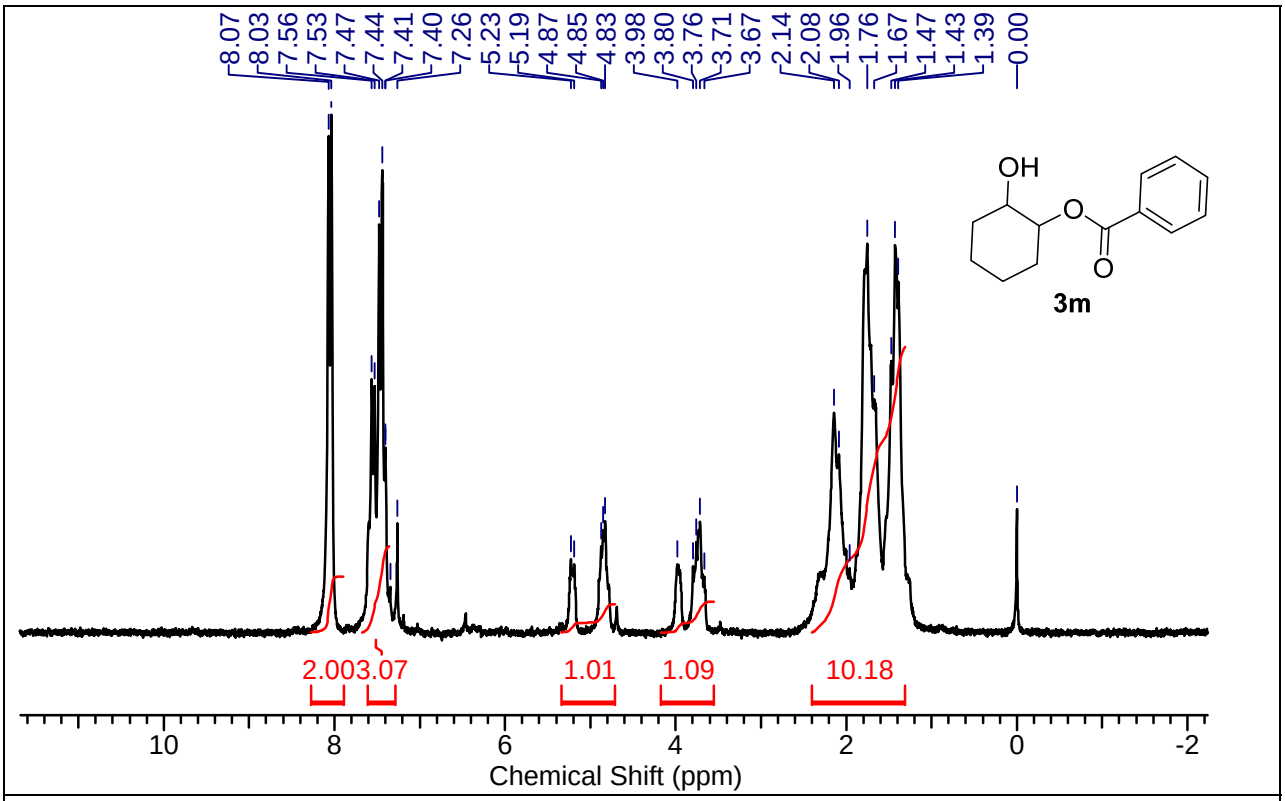


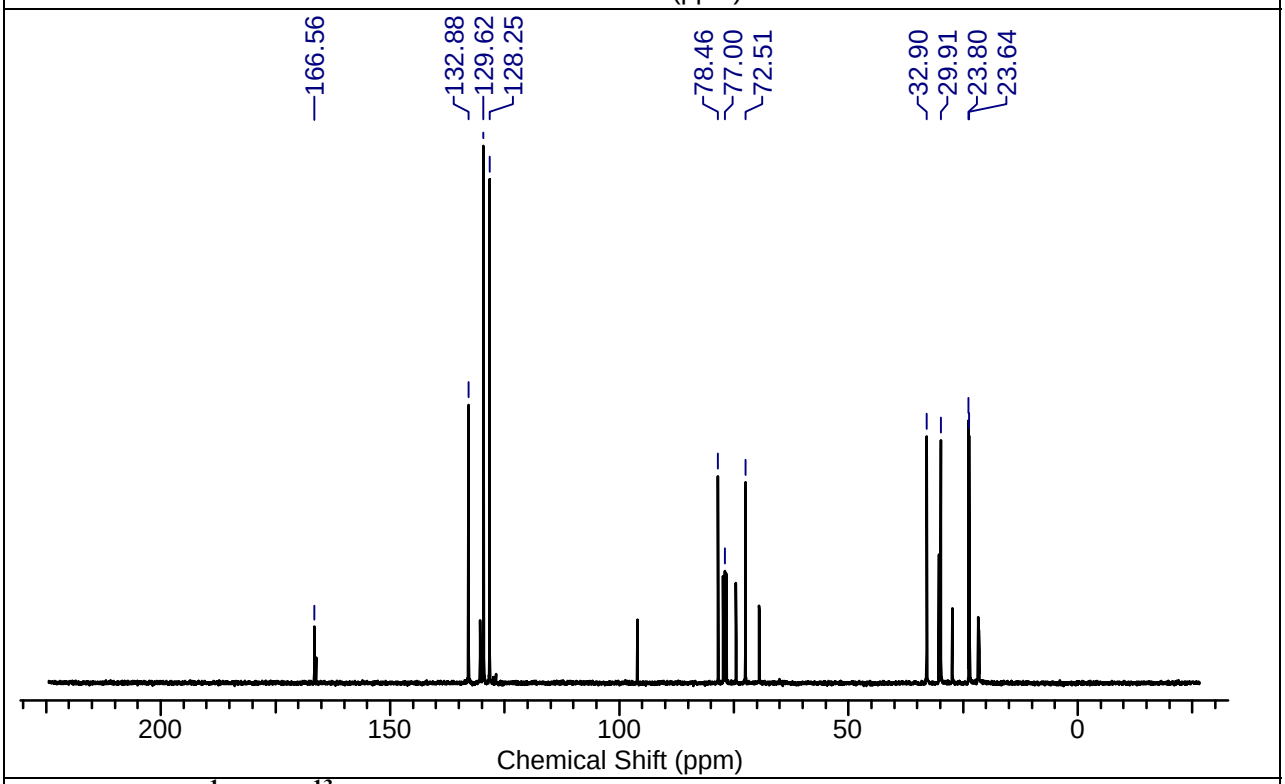

**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxydecyl benzoate (3k)**



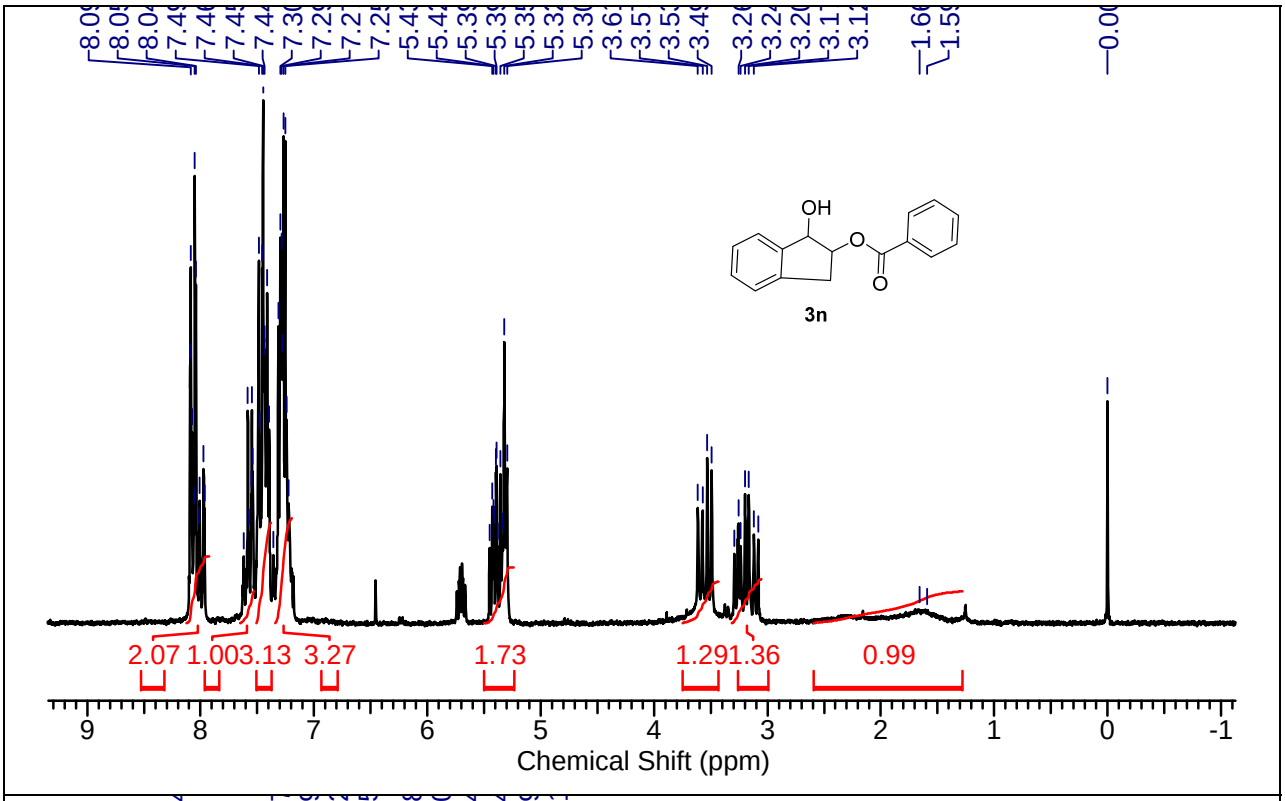



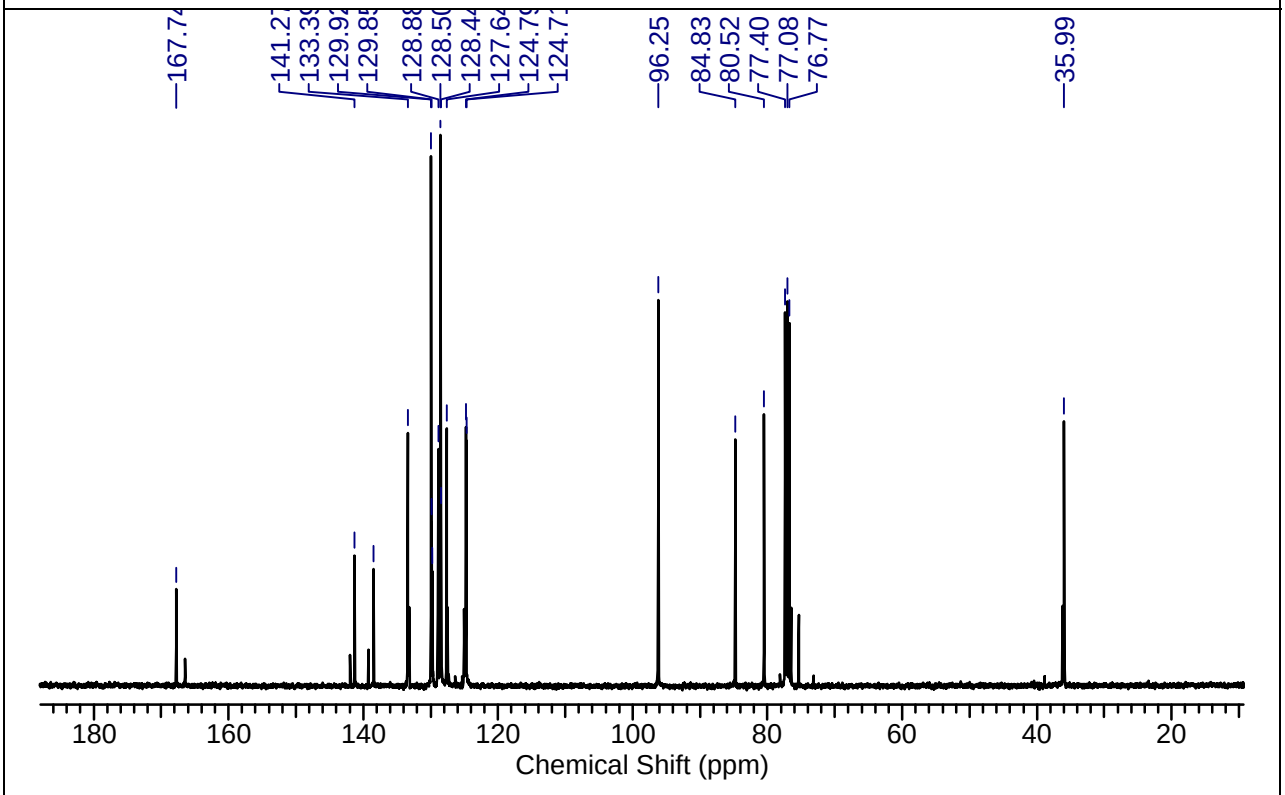

**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxytridecyl benzoate (3l)**



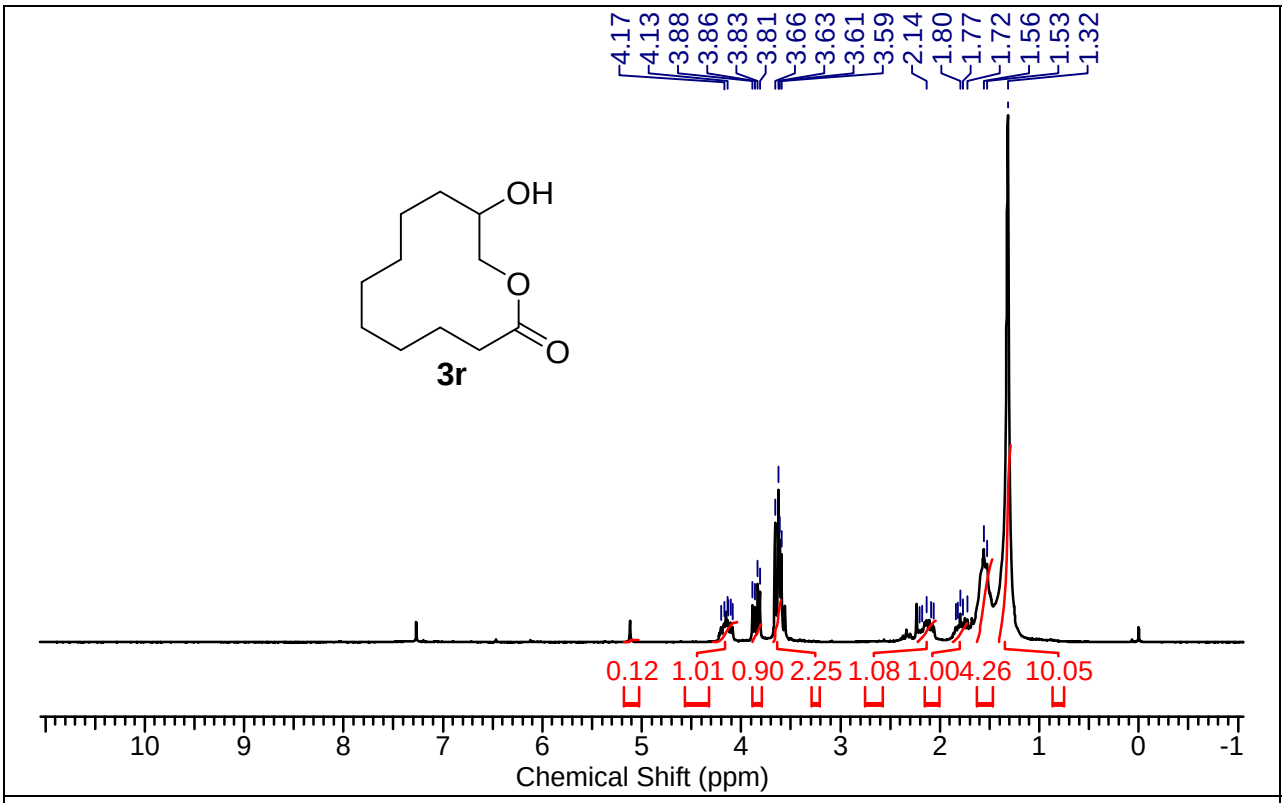



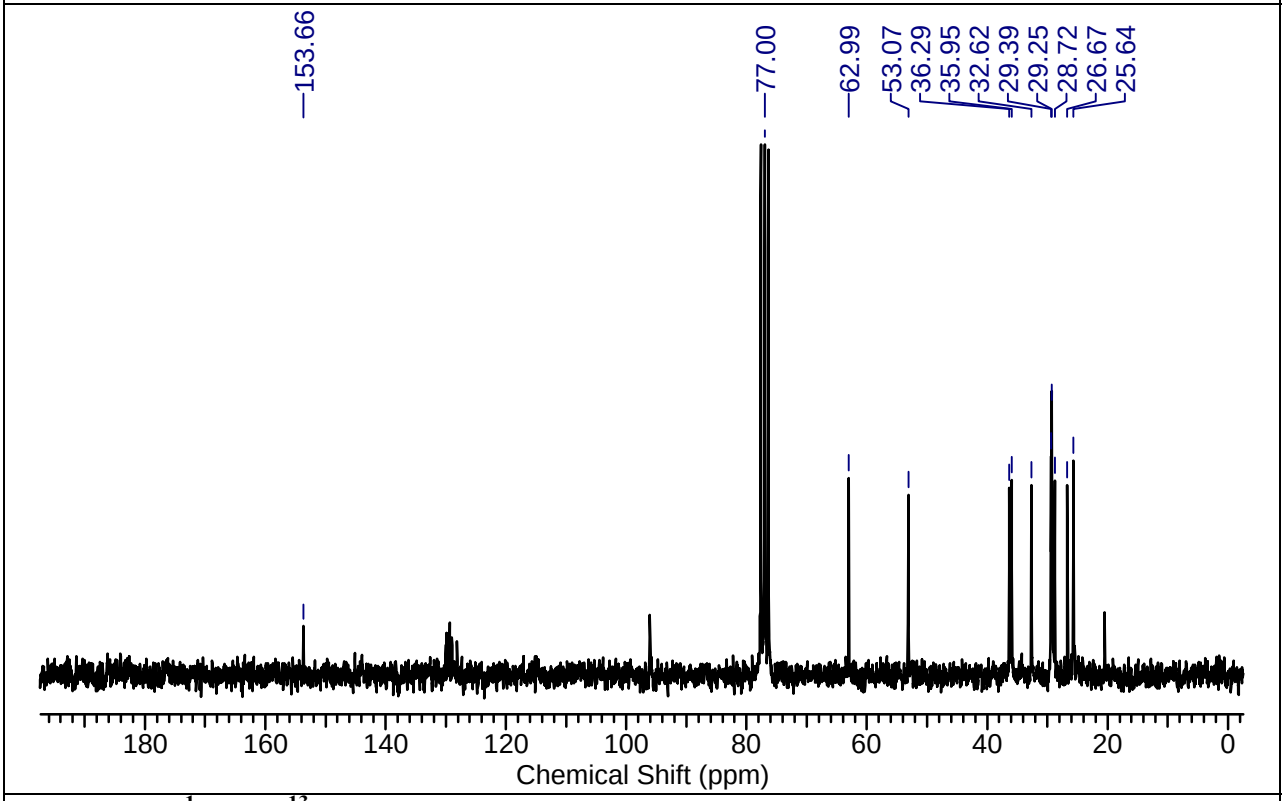

**$^{1}$H and $^{13}$C NMR spectra of 2-hydroxycyclohexyl benzoate (3m)**



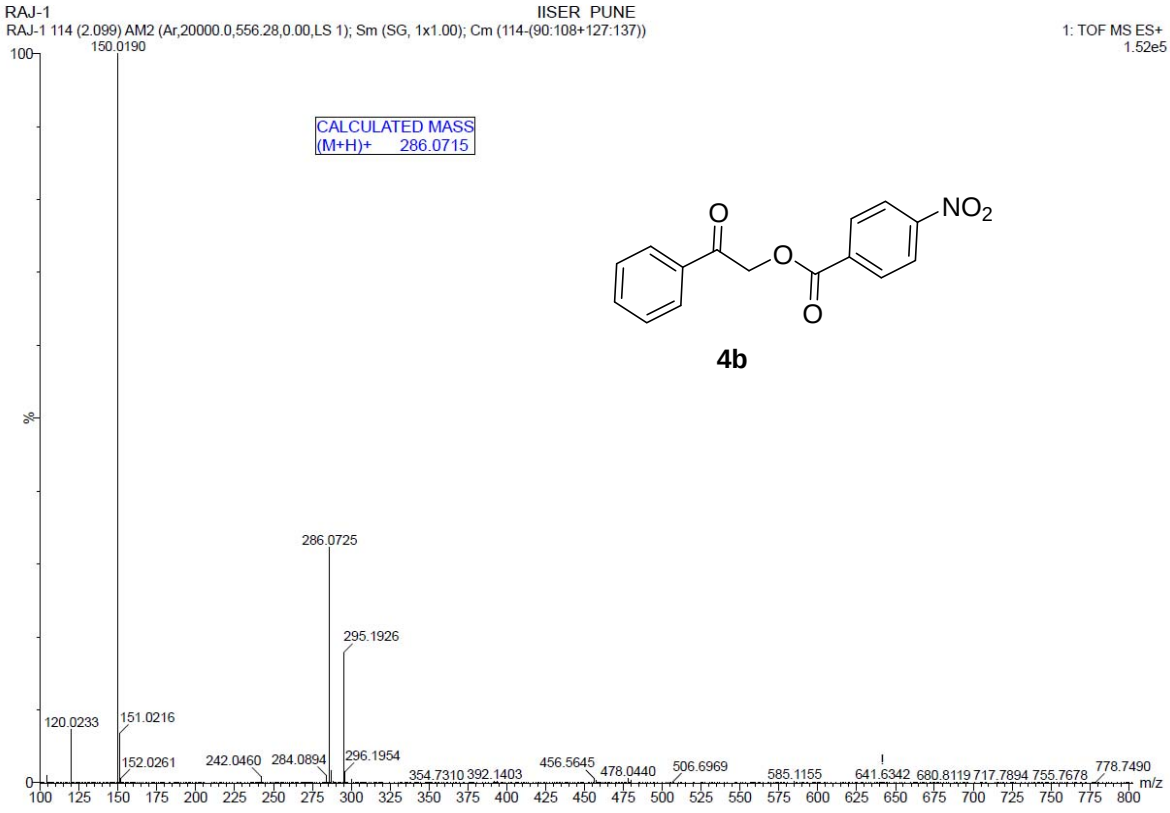




**1H and 13C NMR spectra of 1-hydroxy-2,3-dihydro-1H-inden-2-yl benzoate (3n)**

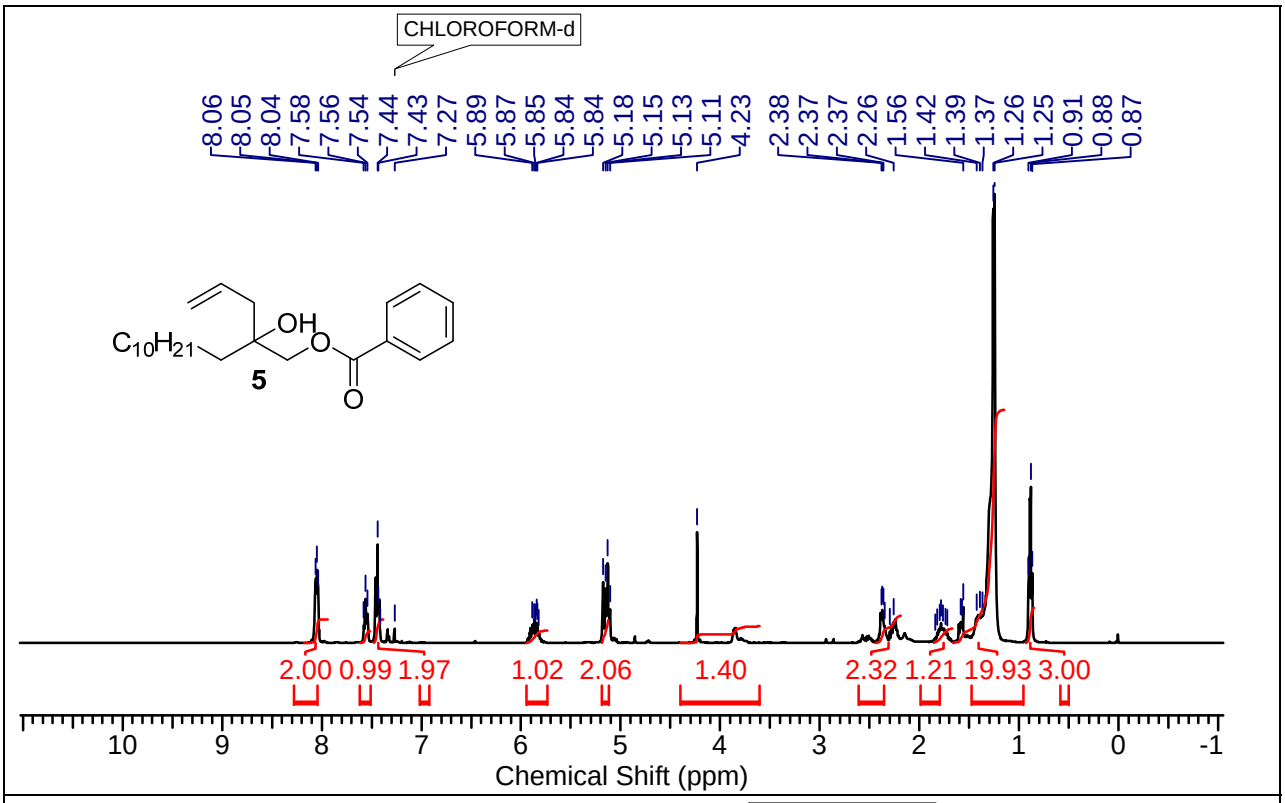


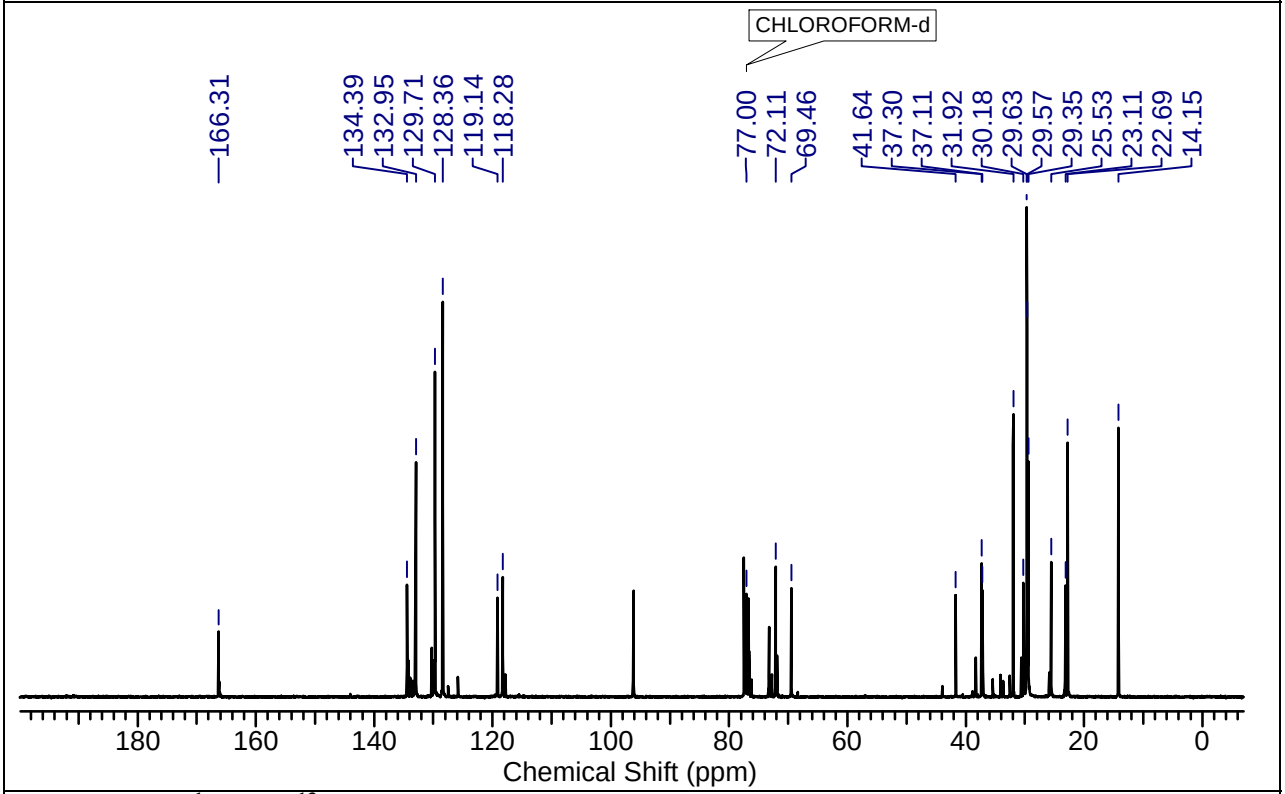




**$^{1}$H and $^{13}$C NMR spectra of 11-hydroxyoxacyclododecan-2-one (3r)**

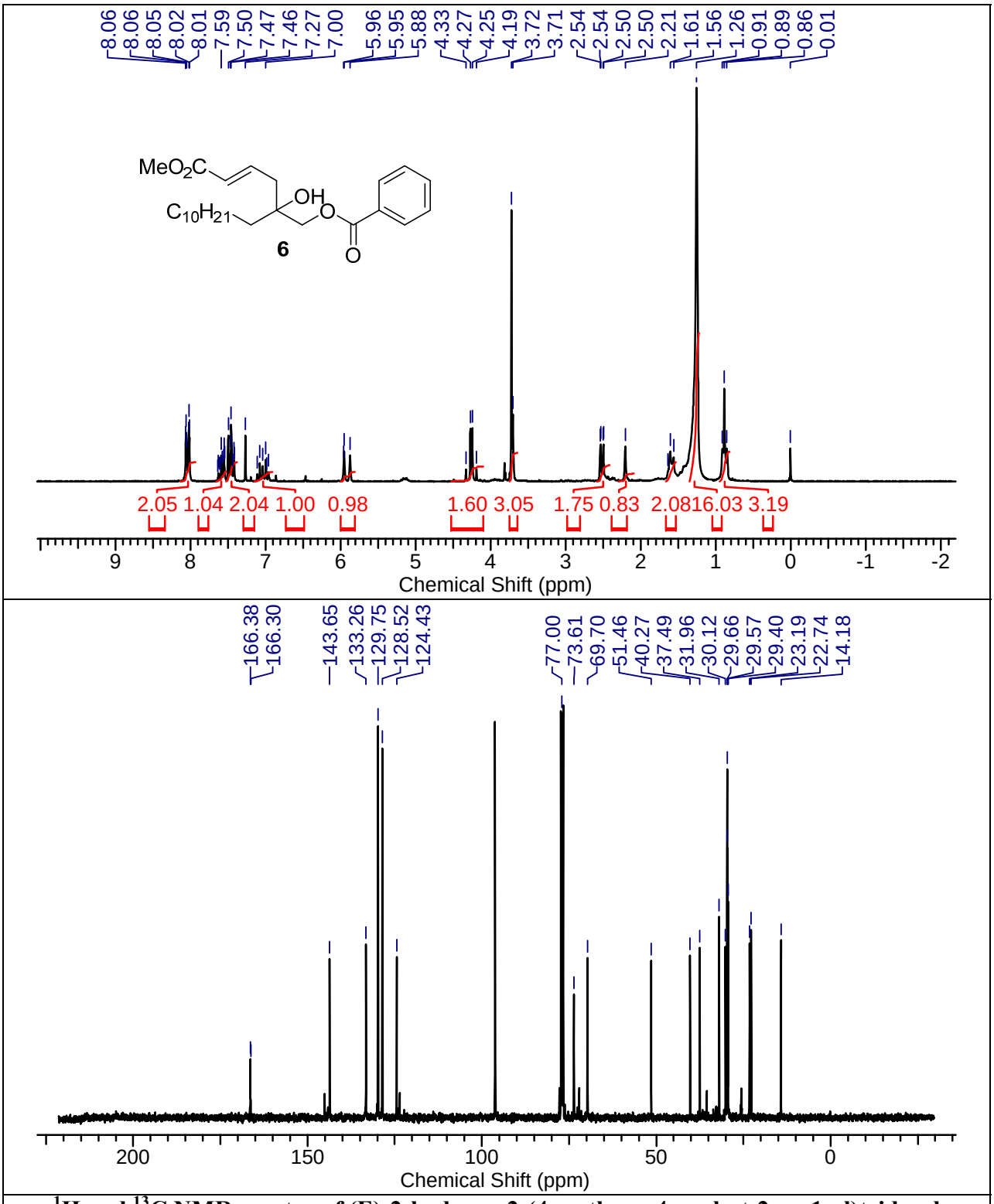



**HRMS of 2-oxo-2-phenylethyl 4-nitrobenzoate (4b)**

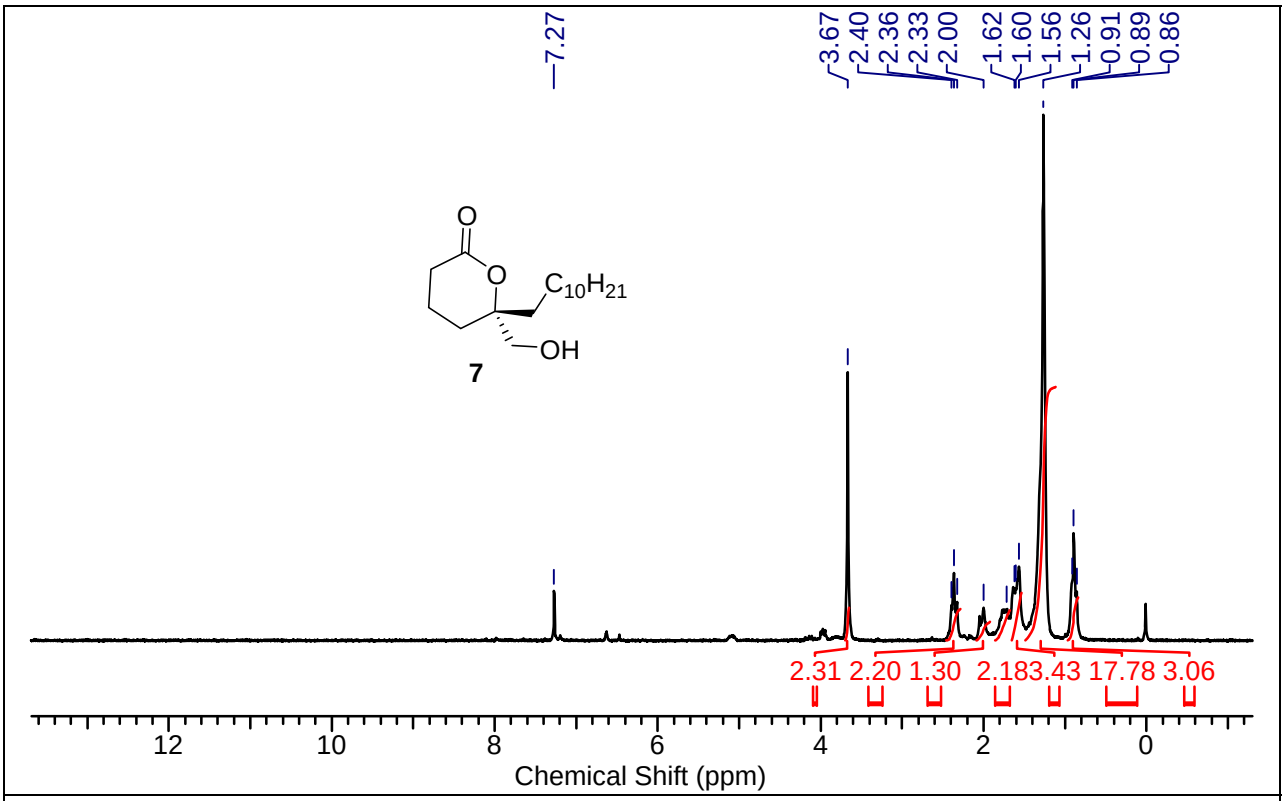


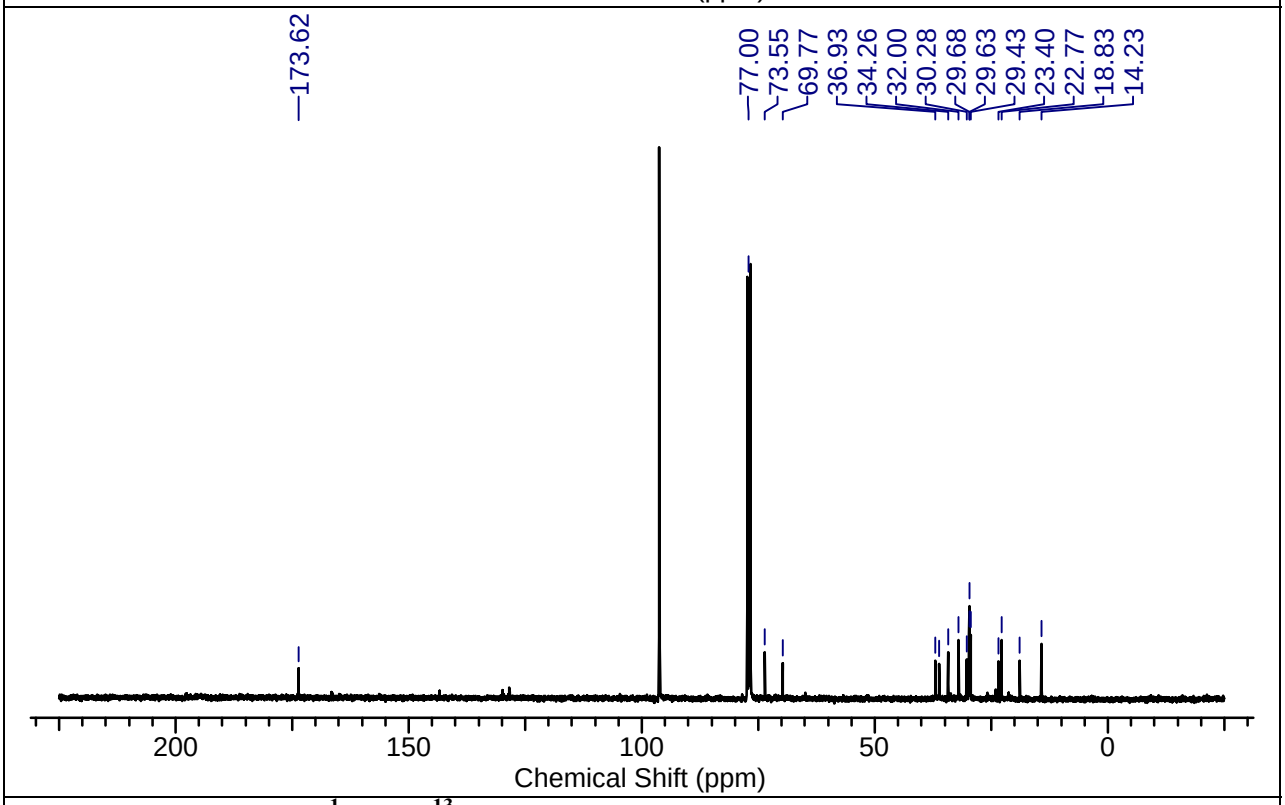




**$^{1}$H and $^{13}$C NMR spectra of 2-allyl-2-hydroxytridecyl benzoate (5)**




**$^{1}$H and $^{13}$C NMR spectra of (E)-2-hydroxy-2-(4-methoxy-4-oxobut-2-en-1-yl)tridecyl benzoate (6)**




**$^{1}$H and $^{13}$C NMR spectra of (+)-Tanikolide (7)**