

## Supporting information

### Chiral *N,N'*-Dioxide/ $\text{In}(\text{OTf})_3$ -Catalyzed Asymmetric Vinylogous Mukaiyama Aldol Reactions

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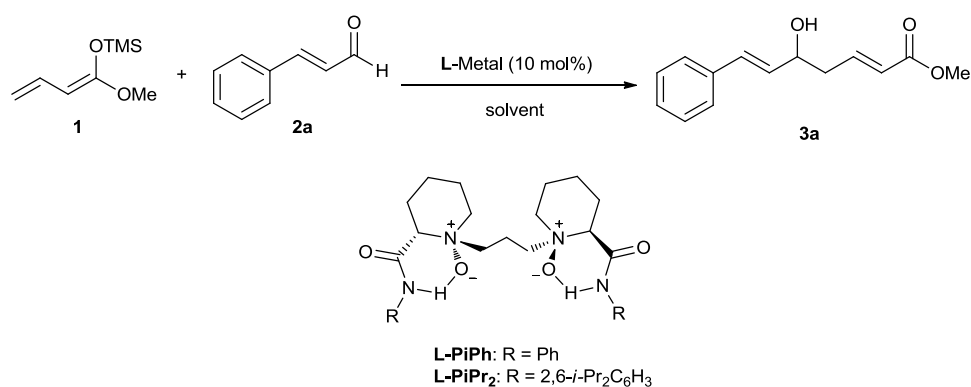
## 1. General remarks

<sup>1</sup>H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ = 7.26). Spectra are reported as follows: chemical shift (δ = ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration and assignment. <sup>13</sup>C NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl<sub>3</sub>, δ = 77.0). Enantiomeric excesses (ee) were determined by chiral HPLC on corresponding commercial chiral column. Optical rotations were reported as follows: [α]<sub>D</sub><sup>T</sup> (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). Reactions were carried out using commercial available reagents in oven dried apparatus. Acyclic silyl dienolate **1**, were prepared from methyl crotonate according to a literature procedure.<sup>1</sup> The *N,N'*-dioxide ligands were synthesized by the same procedure in the literature.<sup>2</sup>

## 2. General procedure for the catalytic asymmetric VMAR

*N,N'*-dioxide **L-PiPr**<sub>2</sub> (0.02 mmol), In(OTf)<sub>3</sub> (0.01 mmol), and 5-methylsalicylic acid (0.02 mmol) were stirred in 0.5 mL ethyl caproate solvent at 35 °C for 0.5 h under an N<sub>2</sub> atmosphere. Subsequently, acyclic silyl dienol ester **1** (0.15 mmol) and aldehydes **2** (0.1 mmol) were added under -20 °C. The mixture was stirred for further 48 h, and then was purified directly by column chromatography on silica gel (ethyl acetate/petroleum ether 1/7–1/4).

## 3. Other conditions of VMAR

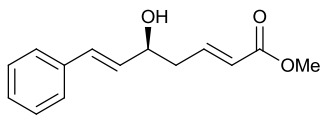
**Table 1** Other conditions of VMAR

| Entry <sup>a</sup> | Ligand                    | Metal                | L:Metal | Solvent        | Additive                        | Temp. [°C] | T [h] | Yield <sup>b</sup> (%) | ee <sup>c</sup> (%) |
|--------------------|---------------------------|----------------------|---------|----------------|---------------------------------|------------|-------|------------------------|---------------------|
| 1                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 1:0.8   | ethyl caproate | —                               | −20        | 48    | 45                     | 26                  |
| 2                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 1:1     | ethyl caproate | —                               | −20        | 48    | 60                     | 45                  |
| 3                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 1.2:1   | ethyl caproate | —                               | −20        | 48    | 63                     | 86                  |
| 4                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 1.5:1   | ethyl caproate | —                               | −20        | 48    | 73                     | 89                  |
| 5                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | —                               | −20        | 48    | 89                     | 89                  |
| 6                  | <b>L-PiPr<sub>2</sub></b> | Y(OTf) <sub>3</sub>  | 2:1     | THF            | —                               | 35         | 24    | 23                     | 50                  |
| 7                  | <b>L-PiPh</b>             | In(OTf) <sub>3</sub> | 2:1     | THF            | —                               | 35         | 24    | 56                     | 43                  |
| 8                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | DCM            | —                               | 35         | 24    | Trace                  | 42                  |
| 9                  | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | —                               | 0          | 48    | 86                     | 81                  |
| 10                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | —                               | −30        | 48    | 62                     | 89                  |
| 11                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | DABCO                           | −20        | 48    | N.R.                   |                     |
| 12                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | Na <sub>2</sub> SO <sub>4</sub> | −20        | 48    | 74                     | 89                  |
| 13                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | Salicylic acid                  | −20        | 48    | 75                     | 91                  |
| 14                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | benzoic acid                    | −20        | 48    | 94                     | 87                  |
| 15                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | 4-tert-butylbenzoic acid        | −20        | 48    | 98                     | 89                  |
| 16                 | <b>L-PiPr<sub>2</sub></b> | In(OTf) <sub>3</sub> | 2:1     | ethyl caproate | 3-hydroxybenzoic acid           | −20        | 48    | 70                     | 90                  |

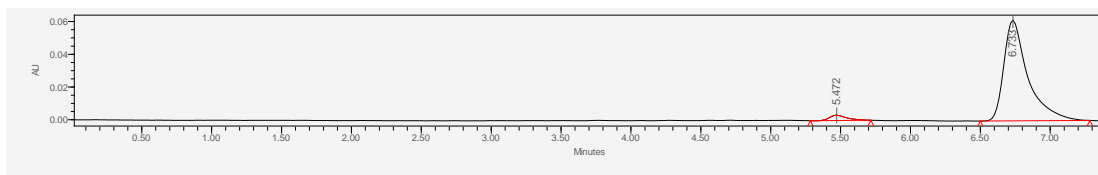
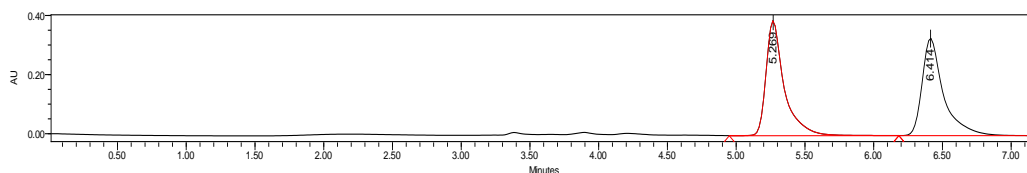
<sup>a</sup> Unless specified, all reactions were performed with L-metal (10 mol%, 2:1), **1** (0.15 mmol), **2a** (0.10 mmol) in THF (0.5 mL). <sup>b</sup> Isolated yield. <sup>c</sup> Determined by HPLC analysis.

#### 4. The analytical and spectral characterization data of the VMAR products

(*S,2E,6E*)-methyl 5-hydroxy-7-phenylhepta-2,6-dienoate **3a**

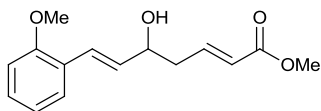


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 5.57$  min,  $t_{r2} = 6.79$  min, ee = 92%.  $[\alpha]_D^{23.7} = -3.57$  (c = 0.42 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 – 7.24 (m, 5H), 7.01 (dt,  $J = 15.5, 7.3$  Hz, 1H), 6.61 (d,  $J = 15.9$  Hz, 1H), 6.22 (dd,  $J = 15.9, 6.6$  Hz, 1H), 5.95 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.44 (q,  $J = 6.2$  Hz, 1H), 3.72 (s, 3H), 2.56 – 2.52 (m, 2H), 2.04 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.84, 144.83, 136.30, 131.09, 130.91, 128.65, 127.93, 126.58, 123.68, 71.37, 51.59, 40.11. HRMS (SEI-TOF) calcd for C<sub>14</sub>H<sub>16</sub>NaO<sub>3</sub><sup>+</sup> ( $[M+Na^+]$ ) = 255.0992, Found 255.0998.

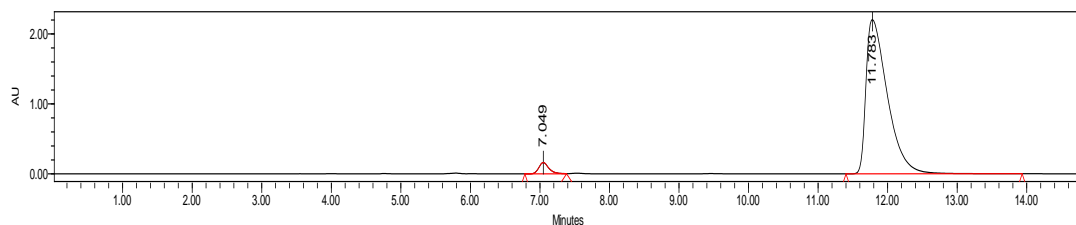
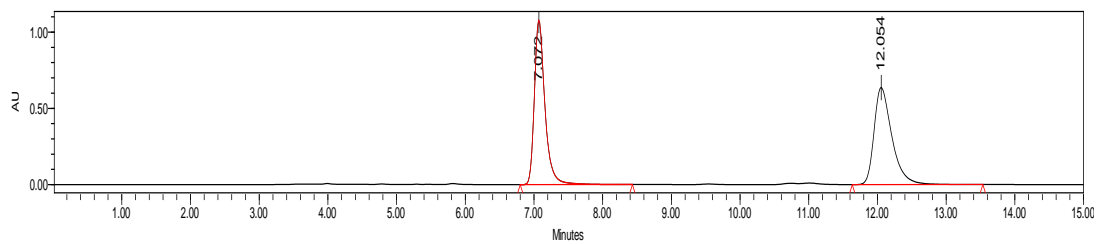


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 5.472          | 3.65   |
| 2 | 6.733          | 96.35  |

(*2E,6E*)-methyl 5-hydroxy-7-(2-methoxyphenyl)hepta-2,6-dienoate **3b**

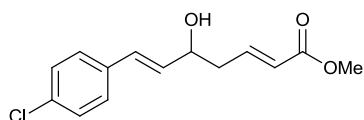


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 70/30, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 7.05$  min,  $t_{r2} = 11.78$  min, ee = 93%.  $[\alpha]_D^{26.5} = -2.67$  (c = 0.60 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.26 – 7.21 (m, 1H), 7.06 – 6.97 (m, 1H), 6.96 – 6.84 (m, 3H), 6.24 (dd,  $J = 16.0, 6.8$  Hz, 1H), 6.02 – 5.89 (m, 1H), 4.44 (q,  $J = 6.3$  Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.62 – 2.46 (m, 2H), 1.98 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.77, 156.84, 144.96, 131.62, 129.00, 127.02, 126.12, 125.30, 123.57, 120.67, 110.91, 72.01, 55.43, 51.48, 40.16. HRMS (SEI-TOF) calcd for C<sub>15</sub>H<sub>18</sub>NaO<sub>4</sub><sup>+</sup> ( $[M+Na^+]$ ) = 285.1097, Found 285.1107.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 7.049          | 3.38   |
| 2 | 11.783         | 96.62  |

(2*E*,6*E*)-methyl 7-(4-chlorophenyl)-5-hydroxyhepta-2,6-dienoate **3c**



A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 90/10, flow

rate = 1.0 ml/min,  $\lambda$  = 254 nm), retention time:  $t_{r1}$  = 10.78 min,  $t_{r2}$  = 11.91 min, ee = 90%.  $[\alpha]_D^{22.6}$  =

-7.62 (c = 0.30 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.23 (m, 4H), 7.09 – 6.90 (m, 1H),

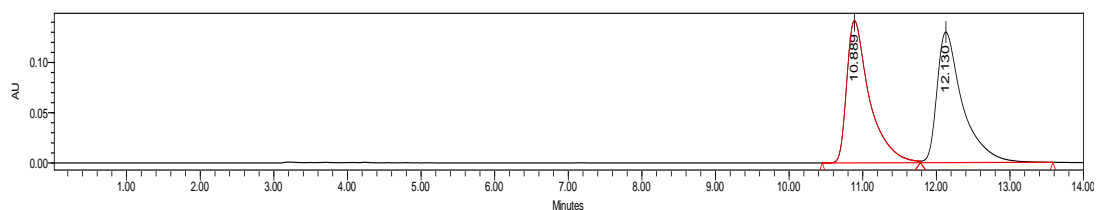
6.58 (dd,  $J$  = 15.9, 0.8 Hz, 1H), 6.20 (dd,  $J$  = 15.9, 6.4 Hz, 1H), 5.99 – 5.91 (m, 1H), 4.45 (q,  $J$  = 6.1

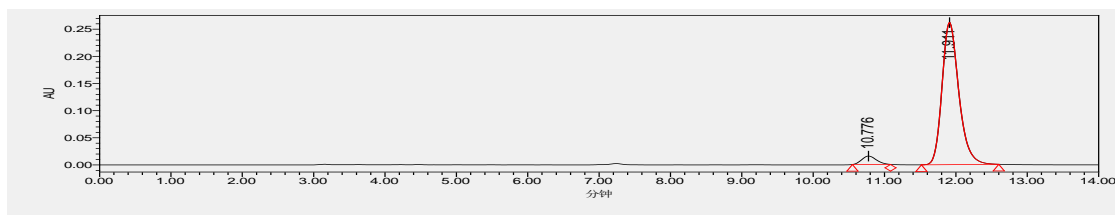
Hz, 1H), 3.73 (s, 3H), 2.58 – 2.48 (m, 2H), 1.97 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.71, 144.45,

134.80, 133.57, 131.52, 129.85, 128.80, 127.77, 123.88, 71.32, 51.58, 40.11. HRMS (SEI-TOF) calcd

for C<sub>14</sub>H<sub>15</sub><sup>34.9689</sup>ClNaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 289.0602, Found 289.0604; HRMS (SEI-TOF) calcd for

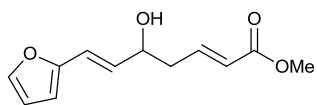
C<sub>14</sub>H<sub>15</sub><sup>36.9659</sup>ClNaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 291.0572, Found 291.0583.



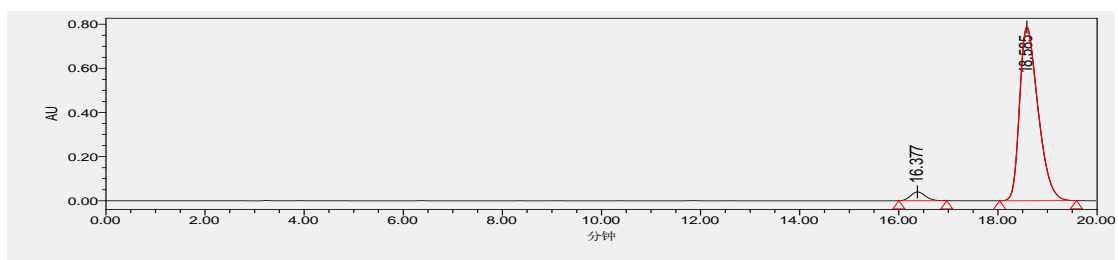
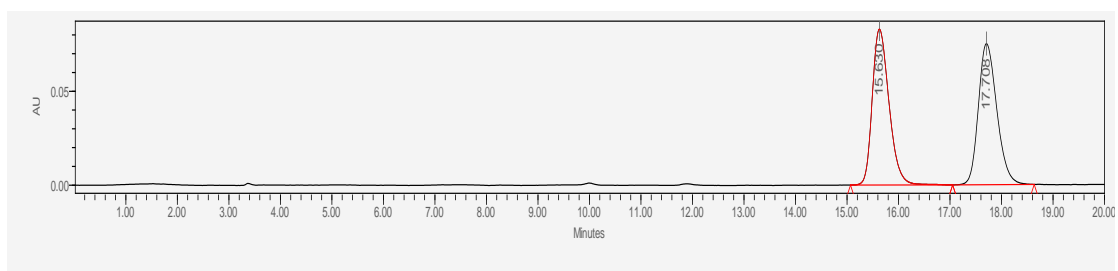


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 10.776         | 4.97   |
| 2 | 11.911         | 95.03  |

(2*E*,6*E*)-methyl 7-(furan-2-yl)-5-hydroxyhepta-2,6-dienoate **3d**



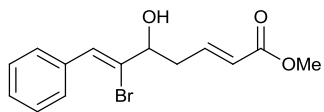
A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 16.38$  min,  $t_{r2} = 18.59$  min, ee = 92%.  $[\alpha]_D^{27.3} = -14.38$  (c = 0.15 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (d,  $J = 1.5$  Hz, 1H), 6.99 (dt,  $J = 15.5, 7.3$  Hz, 1H), 6.49 – 6.41 (m, 1H), 6.38 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.26 (d,  $J = 3.3$  Hz, 1H), 6.17 (dd,  $J = 15.8, 6.3$  Hz, 1H), 5.95 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.46 – 4.37 (m, 1H), 3.73 (s, 3H), 2.63 – 2.42 (m, 2H), 1.82 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.70, 151.96, 144.51, 142.22, 129.38, 123.84, 119.31, 111.37, 108.66, 77.34, 77.03, 76.71, 71.08, 51.54, 40.14. HRMS (SEI-TOF) calcd for C<sub>12</sub>H<sub>14</sub>NaO<sub>4</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 245.0784, Found 245.0788.



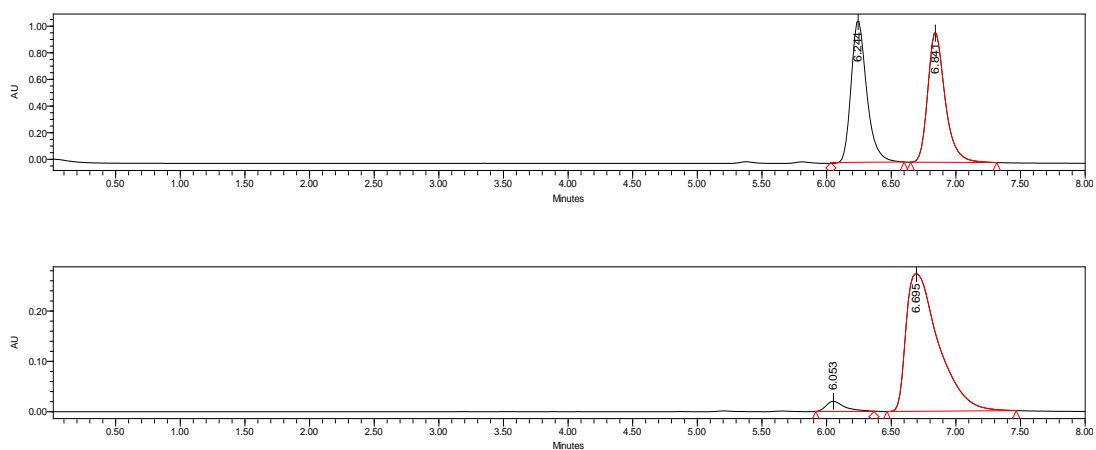
|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 16.377         | 3.91   |

|   |        |       |
|---|--------|-------|
| 2 | 18.585 | 96.09 |
|---|--------|-------|

(2*E*,6*Z*)-methyl 6-bromo-5-hydroxy-7-phenylhepta-2,6-dienoate **3e**

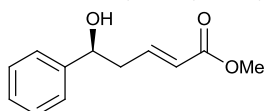


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 6.05$  min,  $t_{r2} = 6.70$  min, ee = 92%.  $[\alpha]_D^{28.1} = -13.30$  (c = 1.20 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 – 7.53 (m, 2H), 7.42 – 7.28 (m, 3H), 7.10 (s, 1H), 6.98 (dt,  $J = 15.6, 7.3$  Hz, 1H), 5.98 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.46 – 4.38 (m, 1H), 3.72 (s, 3H), 2.79 – 2.61 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.75, 143.96, 134.80, 129.14, 128.69, 128.53, 128.34, 128.22, 123.89, 76.15, 51.60, 38.60. HRMS (SEI-TOF) calcd for C<sub>14</sub>H<sub>15</sub><sup>78,9183</sup>BrNaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 333.0097, Found 333.0100; HRMS (SEI-TOF) calcd for C<sub>14</sub>H<sub>15</sub><sup>80,9163</sup>BrNaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 335.0077, Found 335.0111.



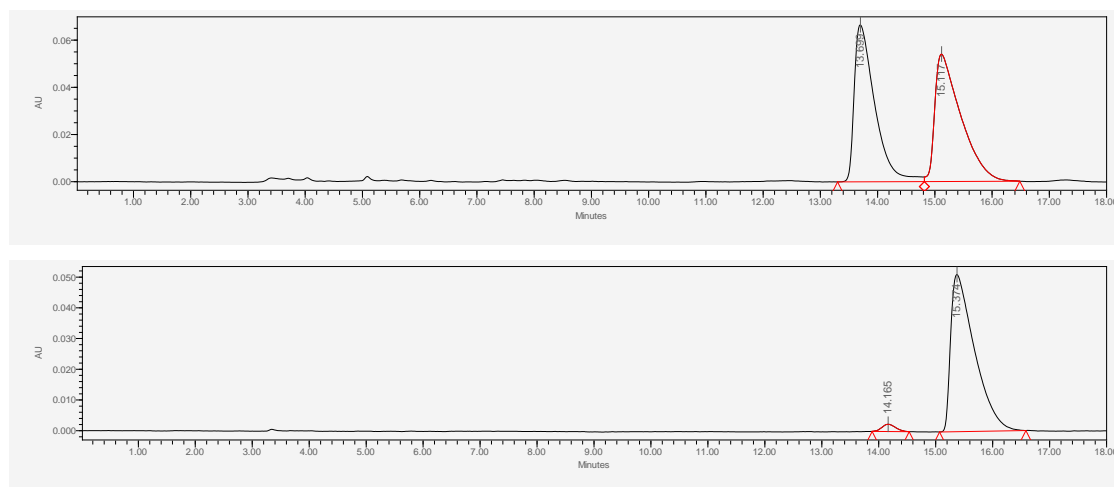
|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 6.053          | 4.12   |
| 2 | 6.695          | 95.88  |

(*S,E*)-methyl 5-hydroxy-5-phenylpent-2-enoate **3f**



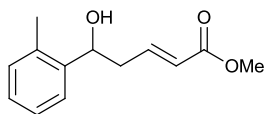
A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 14.17$  min,  $t_{r2} = 15.37$  min, ee = 95%.  $[\alpha]_D^{21.6} = -41.32$  (c = 0.48 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.25 (m, 5H), 6.96 (dt,  $J = 15.5, 7.3$  Hz, 1H), 5.89 (dt,  $J = 15.7, 1.3$  Hz, 1H), 4.81 (dd,  $J = 7.6, 5.3$  Hz, 1H), 3.70 (s, 3H), 2.72 – 2.54 (m, 2H), 2.30 (s,

1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.79, 145.08, 143.45, 128.63, 127.94, 125.74, 123.56, 73.07, 51.53, 41.84. HRMS (SEI-TOF) calcd for C<sub>12</sub>H<sub>14</sub>NaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 229.0835, Found 229.0843.

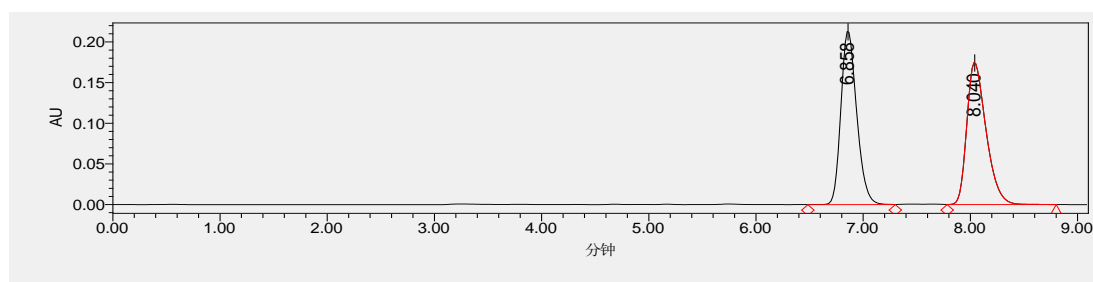


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 14.165         | 2.57   |
| 2 | 15.374         | 97.43  |

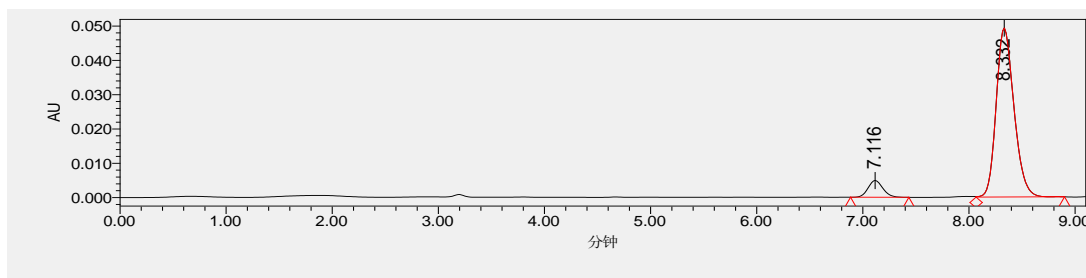
(*E*)-methyl 5-hydroxy-5-(*o*-tolyl)pent-2-enoate **3g**



A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda$  = 254 nm), retention time:  $t_{r1}$  = 7.12 min,  $t_{r2}$  = 20.64 min, ee = 86%.  $[\alpha]_D^{22.1}$  = -60.62 (c = 0.39 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51 – 7.42 (m, 1H), 7.26 – 7.11 (m, 3H), 7.01 (dt,  $J$  = 15.6, 7.3 Hz, 1H), 5.92 (dt,  $J$  = 15.7, 1.4 Hz, 1H), 5.10 – 4.98 (m, 1H), 3.72 (s, 3H), 2.65 – 2.55 (m, 2H), 2.32 (s, 3H), 2.10 (d,  $J$  = 3.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.78, 145.35, 141.55, 134.27, 130.54, 127.61, 126.47, 125.06, 123.47, 69.42, 51.51, 40.73, 18.99. HRMS (SEI-TOF) calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 243.0992, Found 243.0999.

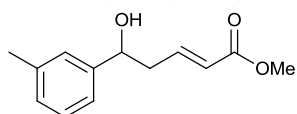




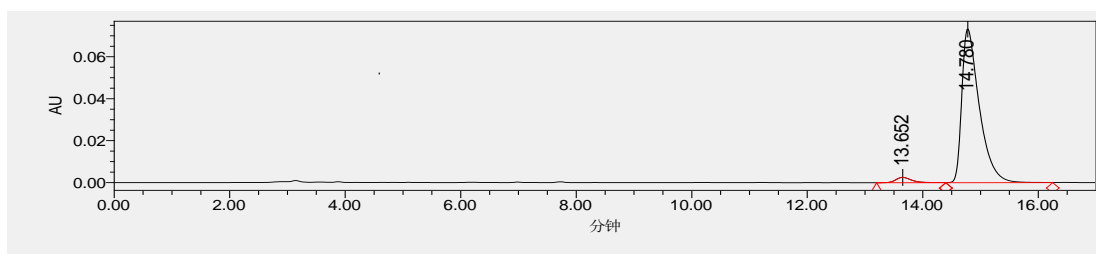
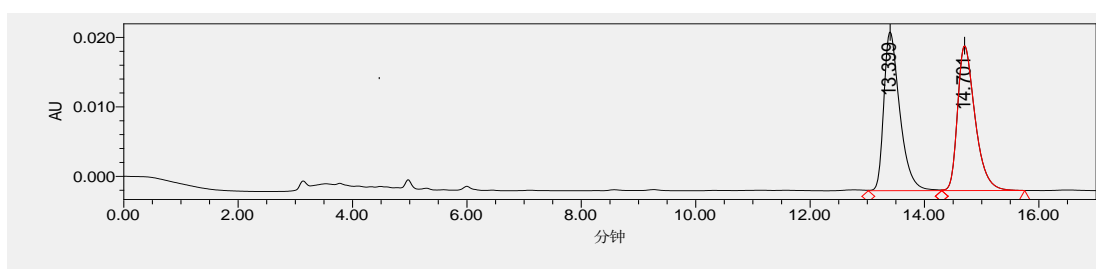


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 7.116          | 7.65   |
| 2 | 8.332          | 92.35  |

(*E*)-methyl 5-hydroxy-5-(*m*-tolyl)pent-2-enoate **3h**

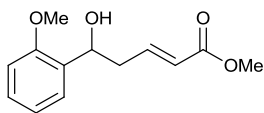


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 95/05, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 13.65$  min,  $t_{r2} = 14.78$  min, ee = 94%.  $[\alpha]_D^{28.9} = -29.62$  (c = 0.26 in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 – 7.21 (m, 1H), 7.19 – 7.08 (m, 3H), 7.02 – 6.92 (m, 1H), 5.91 (d,  $J = 15.7$  Hz, 1H), 4.78 (t,  $J = 5.8$  Hz, 1H), 3.72 (s, 3H), 2.72 – 2.55 (m, 2H), 2.36 (s, 3H), 2.08 (s, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) 166.76, 145.13, 143.39, 138.36, 128.71, 128.55, 126.40, 123.54, 122.79, 73.14, 51.50, 41.81, 21.45. HRMS (SEI-TOF) calcd for  $\text{C}_{13}\text{H}_{16}\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 243.0992, Found 243.1000.

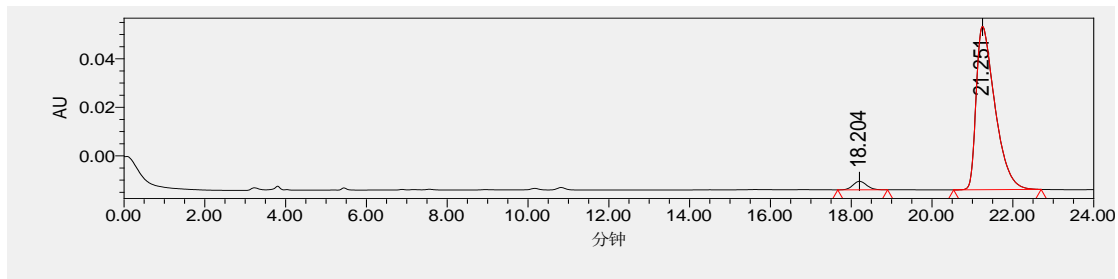
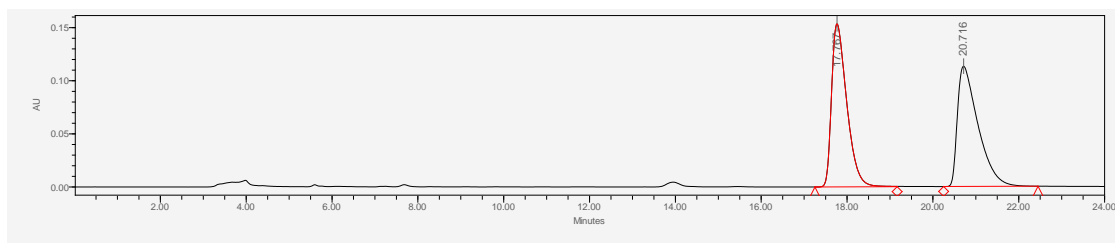


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 13.652         | 3.04   |
| 2 | 14.780         | 96.96  |

(*E*)-methyl 5-hydroxy-5-(2-methoxyphenyl)pent-2-enoate **3i**

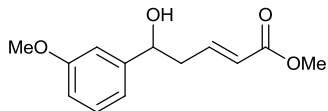


A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 18.20$  min,  $t_{r2} = 21.25$  min, ee = 92%.  $[\alpha]_D^{26.5} = -25.25$  (c = 0.80 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (dd,  $J = 7.5, 1.6$  Hz, 1H), 7.28 – 7.23 (m, 1H), 7.05 – 6.94 (m, 2H), 6.88 (d,  $J = 8.2$  Hz, 1H), 5.88 (dt,  $J = 15.7, 1.4$  Hz, 1H), 5.03 (dd,  $J = 12.4, 5.8$  Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 2.76 (dd,  $J = 5.5, 2.1$  Hz, 1H), 2.70 – 2.63 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.87, 156.30, 145.97, 131.26, 128.66, 126.67, 122.98, 120.86, 110.52, 69.38, 55.27, 51.40, 40.12. HRMS (SEI-TOF) calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>4</sub><sup>+</sup> ( $[M+Na^+]$ ) = 259.0941, Found 259.0946.



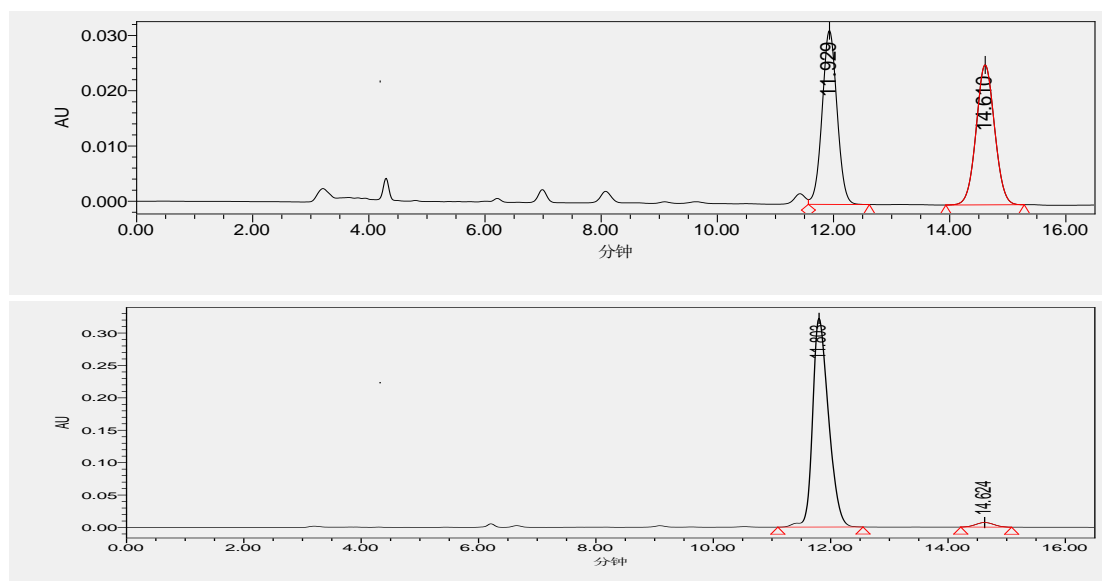
|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 18.204         | 3.68   |
| 2 | 21.251         | 96.32  |

(*E*)-methyl 5-hydroxy-5-(3-methoxyphenyl)pent-2-enoate **3j**



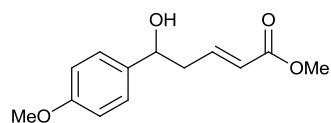
A colorless oil; HPLC (Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 11.80$  min,  $t_{r2} = 14.62$  min, ee = 95%.  $[\alpha]_D^{28.7} = -33.33$  (c = 0.30 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.24 (m, 1H), 7.03 – 6.86 (m, 3H), 6.87 – 6.79 (m, 1H), 5.95 – 5.86 (m, 1H), 4.80 (t,  $J = 5.2$  Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 2.72 – 2.55 (m, 2H), 2.22 (d,  $J = 8.8$  Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.76, 159.85, 145.15, 145.00, 129.69, 123.58, 118.00, 113.38, 111.23, 73.01, 55.26, 51.53, 41.80. HRMS (SEI-TOF) calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>4</sub><sup>+</sup>

$([M+Na^+]) = 259.0941$ , Found 259.0946.

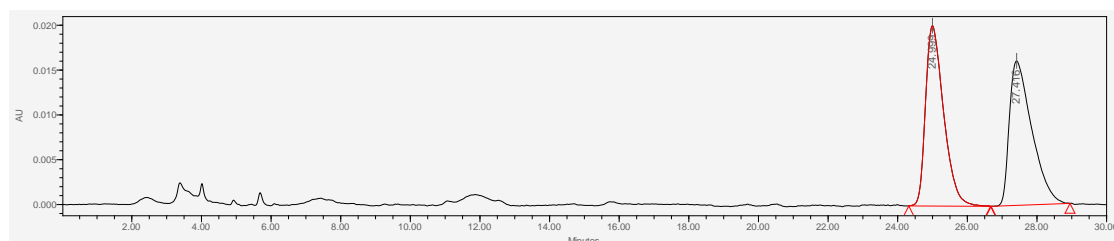


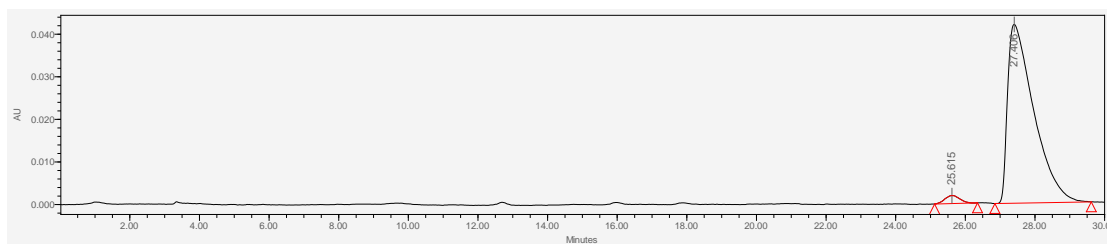
|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 11.803         | 97.57  |
| 2 | 14.624         | 2.43   |

(*E*)-methyl 5-hydroxy-5-(4-methoxyphenyl)pent-2-enoate **3k**



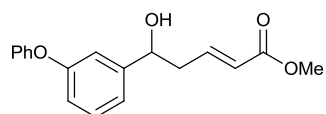
A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 25.62$  min,  $t_{r2} = 27.41$  min, ee = 95%.  $[\alpha]_D^{28.7} = -7.84$  (c = 0.10 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 – 7.23 (m, 2H), 7.02 – 6.83 (m, 3H), 5.89 (dt, J = 15.7, 1.3 Hz, 1H), 4.82 – 4.71 (m, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 2.74 – 2.50 (m, 2H), 2.08 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.75, 159.31, 145.11, 135.58, 127.03, 123.49, 114.01, 72.74, 55.30, 51.48, 41.77. HRMS (SEI-TOF) calcd for C<sub>13</sub>H<sub>16</sub>NaO<sub>4</sub><sup>+</sup> ( $[M+Na^+]$ ) = 259.0941, Found 259.0942.



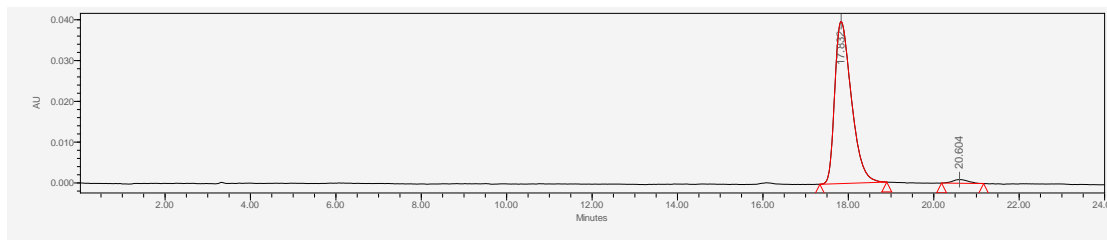
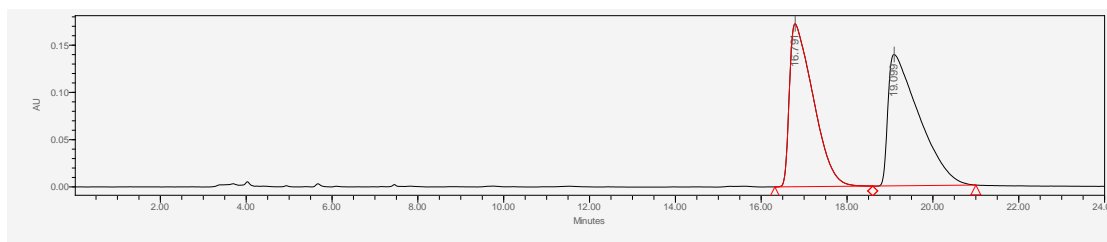


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 25.615         | 2.49   |
| 2 | 27.406         | 97.51  |

*(E)*-methyl 5-hydroxy-5-(3-phenoxyphenyl)pent-2-enoate **3l**

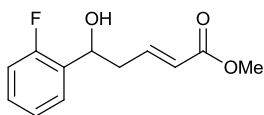


A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda$  = 254 nm), retention time:  $t_{r1}$  = 17.82 min,  $t_{r2}$  = 20.64 min, ee = 96%.  $[\alpha]_D^{25.1} = -19.69$  (c = 0.66 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.25 (m, 3H), 7.14 – 7.05 (m, 2H), 7.04 – 6.87 (m, 5H), 5.88 (dt,  $J$  = 15.7, 1.3 Hz, 1H), 4.84 – 4.70 (m, 1H), 3.70 (s, 3H), 2.68 – 2.54 (m, 2H), 2.33 (d,  $J$  = 3.4 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 166.71, 157.57, 157.00, 145.60, 144.77, 129.98, 129.82, 123.71, 123.42, 120.47, 118.96, 118.14, 116.12, 72.70, 51.53, 41.79. HRMS (SEI-TOF) calcd for  $\text{C}_{18}\text{H}_{18}\text{NaO}_4^+$  ( $[\text{M}+\text{Na}^+]$ ) = 321.1097, Found 321.1100.

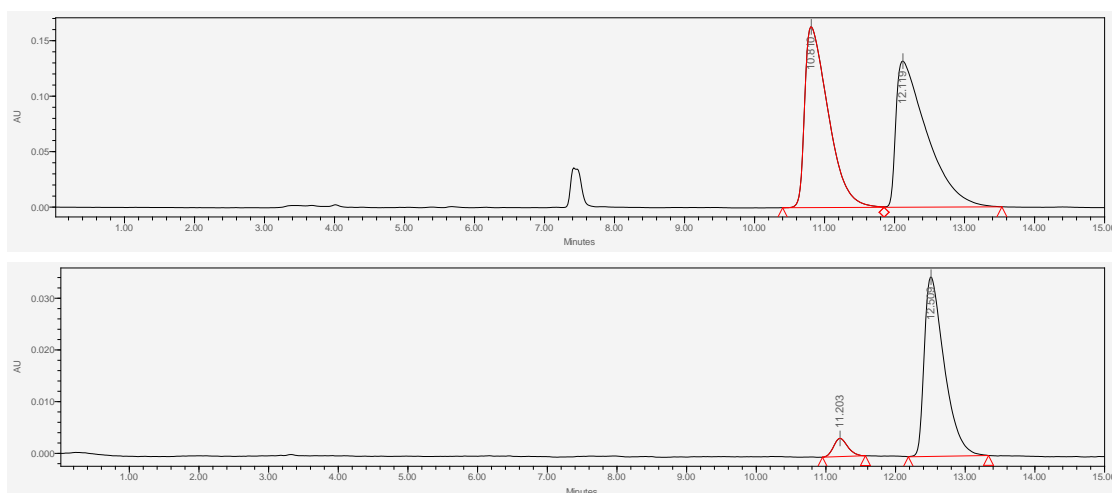


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 17.832         | 97.94  |
| 2 | 20.604         | 2.06   |

*(E)*-methyl 5-(4-fluorophenyl)-5-hydroxypent-2-enoate **3m**

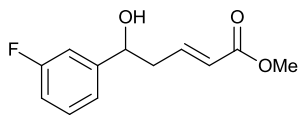


A colorless oil; HPLC (Chiralcel IE, hexane/i-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 11.20$  min,  $t_{r2} = 12.51$  min, ee = 87%.  $[\alpha]_D^{27.8} = -40.00$  (c = 0.40 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (td,  $J = 7.5, 1.7$  Hz, 1H), 7.30 – 7.23 (m, 1H), 7.16 (td,  $J = 7.5, 1.0$  Hz, 1H), 7.08 – 6.91 (m, 2H), 5.91 (dt,  $J = 15.7, 1.4$  Hz, 1H), 5.15 (t,  $J = 5.9$  Hz, 1H), 3.71 (s, 3H), 2.76 – 2.59 (m, 2H), 2.30 (s, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 166.71, 160.80, 158.36, 144.62, 130.45, 130.32, 129.28, 129.20, 127.13, 127.09, 124.44, 124.41, 123.79, 115.49, 115.28, 67.03, 67.01, 51.52, 40.60. HRMS (SEI-TOF) calcd for  $\text{C}_{12}\text{H}_{13}\text{FNaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 247.0741, Found 247.0746.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 11.203         | 6.71   |
| 2 | 12.509         | 93.29  |

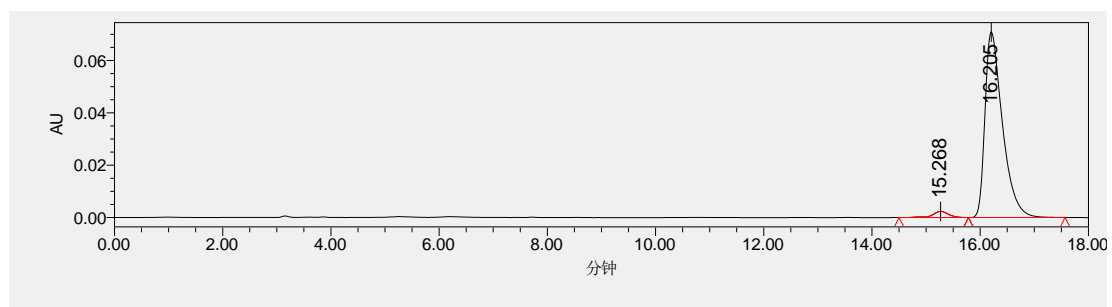
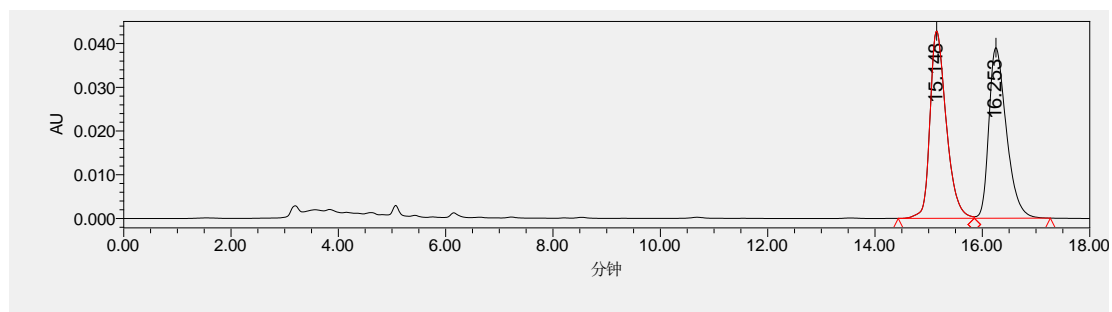
**(E)-methyl 5-(3-fluorophenyl)-5-hydroxypent-2-enoate **3n****



A colorless oil; HPLC (Chiralcel IB, hexane/i-PrOH = 95/05, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 15.27$  min,  $t_{r2} = 16.21$  min, ee = 94%.  $[\alpha]_D^{28.4} = -20.83$  (c = 0.36 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.28 (m, 1H), 7.14 – 7.06 (m, 2H), 7.01 – 6.90 (m, 2H), 5.95 – 5.86 (m, 1H), 4.87 – 4.80 (m, 1H), 3.72 (s, 3H), 2.67 – 2.59 (m, 2H), 2.29 (d,  $J = 3.2$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 166.67, 164.23, 161.78, 146.12, 146.05, 144.42, 130.20, 130.12,

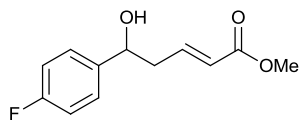
123.91, 121.31, 121.28, 114.86, 114.64, 112.79, 112.57, 72.41, 72.40, 51.57, 41.80. HRMS (SEI-TOF)

calcd for  $C_{12}H_{13}FNaO_3^+$  ( $[M+Na^+]$ ) = 247.0741, Found 247.0746.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 15.268         | 2.96   |
| 2 | 16.205         | 97.04  |

(*E*)-methyl 5-(4-fluorophenyl)-5-hydroxypent-2-enoate **3o**



A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate =

1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 10.85$  min,  $t_{r2} = 11.85$  min, ee = 95%.  $[\alpha]_D^{22.4} = -35.11$  (c

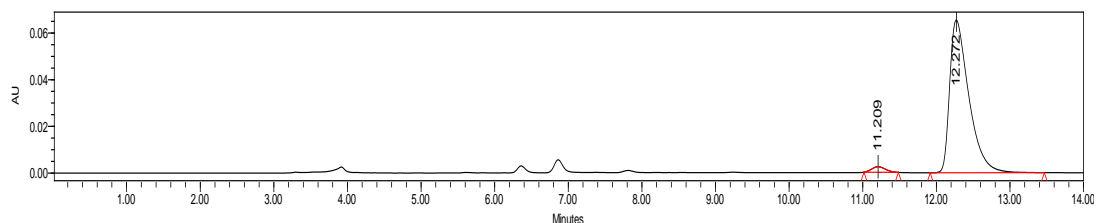
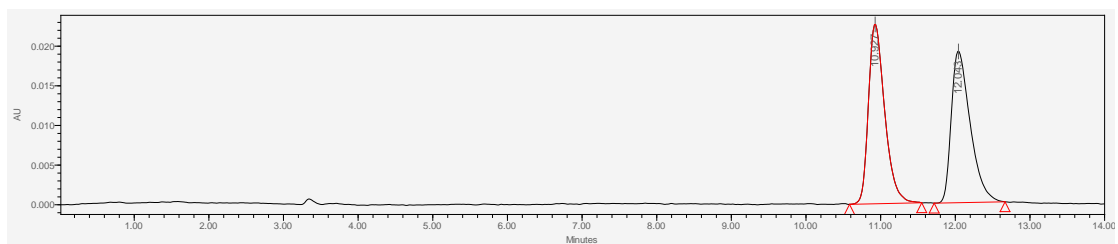
= 0.54 in  $CHCl_3$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.35 – 7.26 (m, 2H), 7.09 – 6.99 (m, 2H), 6.98 – 6.87

(m, 1H), 5.88 (dt,  $J = 15.7, 1.3$  Hz, 1H), 4.80 (dd,  $J = 7.5, 5.4$  Hz, 1H), 3.70 (s, 3H), 2.69 – 2.56 (m,

2H), 2.56 – 2.27 (m, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ) 166.77, 163.53, 161.08, 144.76, 139.23, 139.20,

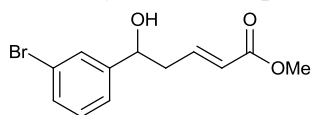
127.47, 127.39, 123.69, 115.54, 115.33, 72.38, 51.56, 41.92. HRMS (SEI-TOF) calcd for

$C_{12}H_{13}FNaO_3^+$  ( $[M+Na^+]$ ) = 247.0741, Found 247.0744.

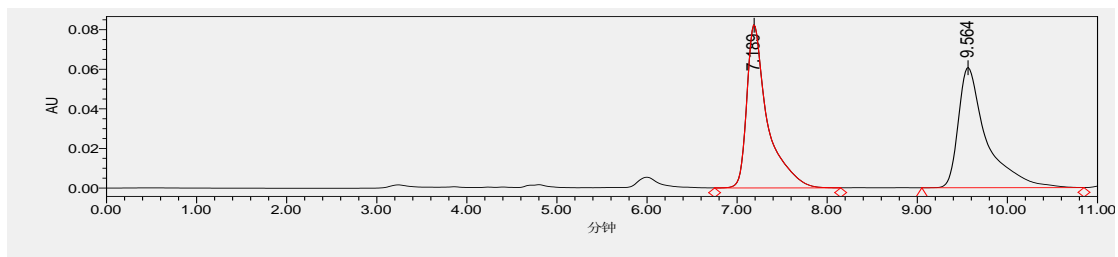


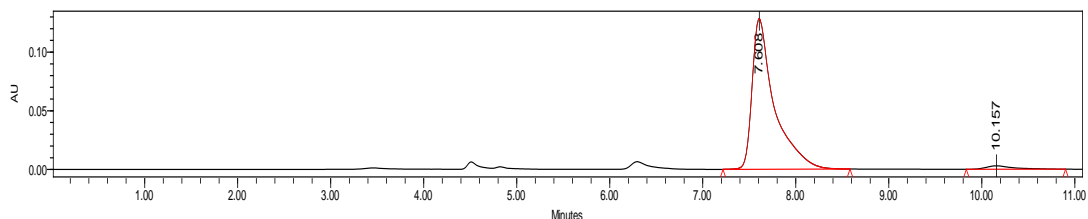
|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 11.209         | 2.52   |
| 2 | 12.272         | 97.48  |

(*E*)-methyl 5-(3-bromophenyl)-5-hydroxypent-2-enoate **3p**



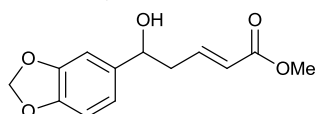
A colorless oil; HPLC (Chiralcel IC, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 7.61$  min,  $t_{r2} = 10.16$  min, ee = 96%.  $[\alpha]_D^{28.6} = -29.69$  ( $c = 0.32$  in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (s, 1H), 7.44 – 7.39 (m, 1H), 7.28 – 7.19 (m, 2H), 7.02 – 6.85 (m, 1H), 5.90 (d,  $J = 15.7$  Hz, 1H), 4.83 – 4.75 (m, 1H), 3.71 (s, 3H), 2.69 – 2.55 (m, 2H), 2.41 (d,  $J = 3.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) 166.70, 145.78, 144.45, 130.95, 130.19, 128.86, 124.38, 123.92, 122.75, 72.33, 51.59, 41.82. HRMS (SEI-TOF) calcd for  $\text{C}_{12}\text{H}_{13}^{78,9183}\text{BrNaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 306.9940, Found 306.9941; HRMS (SEI-TOF) calcd for  $\text{C}_{12}\text{H}_{13}^{80,9163}\text{BrNaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 308.9920, Found 308.9948.



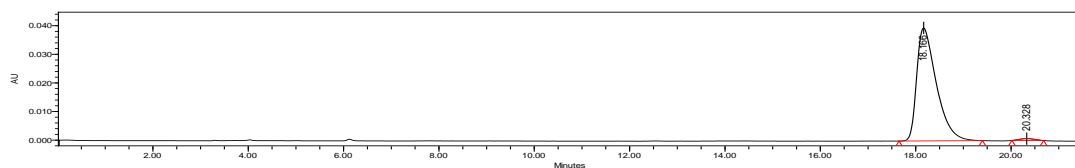
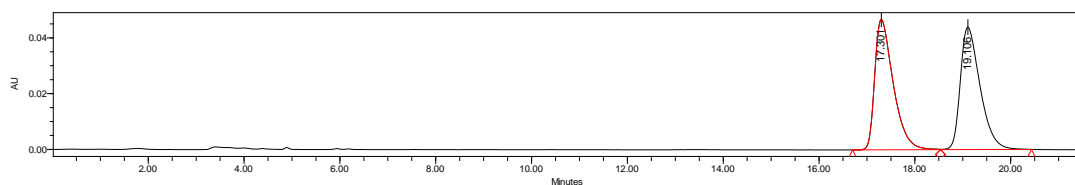


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 7.608          | 97.28  |
| 2 | 10.157         | 2.72   |

(*E*)-methyl 5-(benzo[d][1,3]dioxol-5-yl)-5-hydroxypent-2-enoate **3q**

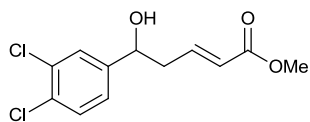


A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 80/20, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 18.17$  min,  $t_{r2} = 20.33$  min, ee = 98%.  $[\alpha]_D^{22.3} = -16.84$  (c = 0.37 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.93 (dt,  $J = 15.5, 7.3$  Hz, 1H), 6.86 (s, 1H), 6.82 – 6.73 (m, 2H), 5.95 (s, 2H), 5.89 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.73 (dd,  $J = 7.6, 5.4$  Hz, 1H), 3.71 (s, 3H), 2.71 – 2.52 (m, 2H), 2.20 (s, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.76, 147.92, 147.22, 144.93, 137.50, 123.54, 119.23, 108.20, 106.23, 101.10, 72.95, 51.53, 41.82. HRMS (SEI-TOF) calcd for C<sub>13</sub>H<sub>14</sub>NaO<sub>5</sub><sup>+</sup> ( $[M+Na^+]$ ) = 273.0733, Found 273.0735.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 18.166         | 98.71  |
| 2 | 20.328         | 1.29   |

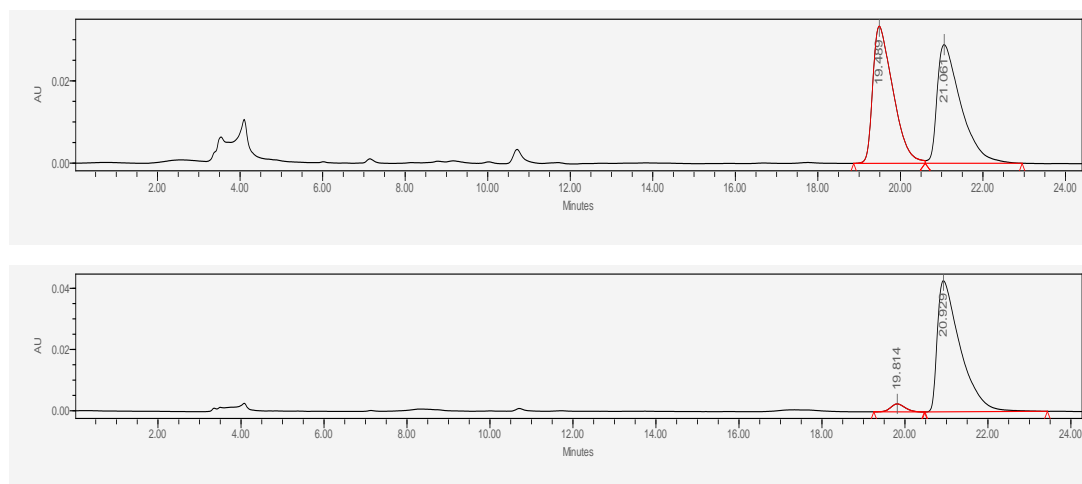
(*E*)-methyl 5-(3,4-dichlorophenyl)-5-hydroxypent-2-enoate **3r**



A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 95/05, flow rate =

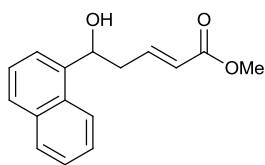


1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 19.81$  min,  $t_{r2} = 20.93$  min, ee = 93%.  $[\alpha]_D^{27.9} = -26.45$  (c = 0.76 in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 18.1, 5.1$  Hz, 2H), 7.17 (dd,  $J = 8.3, 2.0$  Hz, 1H), 6.92 (dt,  $J = 15.6, 7.3$  Hz, 1H), 5.89 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.79 (dd,  $J = 8.0, 6.6$  Hz, 1H), 3.71 (s, 3H), 2.67 – 2.53 (m, 3H), 1.82 (s, 0H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) 166.69, 144.11, 143.71, 132.71, 131.68, 130.54, 127.79, 125.10, 124.08, 71.77, 51.62, 41.75. HRMS (SEI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}^{34.9689}\text{Cl}_2\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 297.0056, Found 297.0063; HRMS (SEI-TOF) calcd for  $\text{C}_{12}\text{H}_{12}^{36.9659}\text{Cl}_2\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 300.9996, Found 301.0003.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 19.814         | 3.69   |
| 2 | 20.929         | 96.31  |

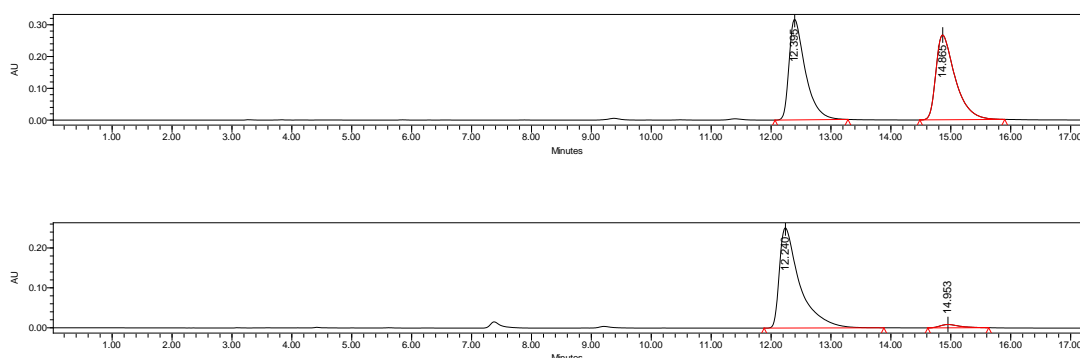
(*E*)-methyl 5-hydroxy-5-(naphthalen-1-yl)pent-2-enoate **3s**



A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 12.24$  min,  $t_{r2} = 14.95$  min, ee = 94%.  $[\alpha]_D^{27.5} = -70.45$  (c = 0.22 in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.1$  Hz, 1H), 7.92 – 7.86 (m, 1H), 7.80 (d,  $J = 8.2$  Hz, 1H), 7.67 (d,  $J = 7.1$  Hz, 1H), 7.57 – 7.45 (m, 3H), 7.16 – 7.06 (m, 1H), 6.00 – 5.90 (m, 1H), 5.61 (dd,  $J = 8.0, 3.8$  Hz, 1H), 3.73 (s, 3H), 2.90 – 2.72 (m, 2H), 2.19 (s, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) 166.77, 145.38, 138.94, 133.85, 130.05, 129.09, 128.40, 126.32, 125.71, 125.48, 123.53,

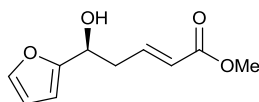
122.87, 122.70, 69.87, 51.55, 40.89. HRMS (SEI-TOF) calcd for  $C_{16}H_{16}NaO_3^+$  ( $[M+Na^+]$ ) = 279.0992,

Found 279.0996.

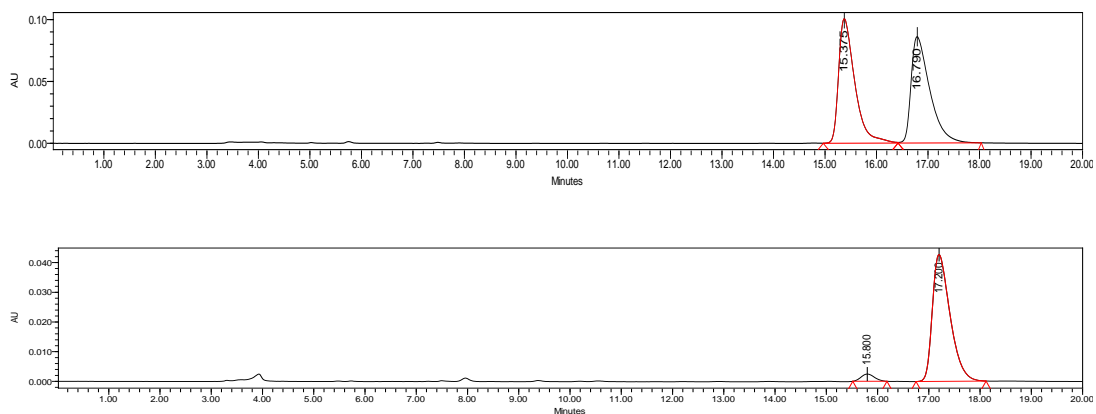


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 12.240         | 96.89  |
| 2 | 14.953         | 3.11   |

(*S,E*)-methyl 5-(furan-2-yl)-5-hydroxypent-2-enoate **3t**

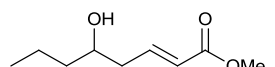


A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 15.80$  min,  $t_{r2} = 17.20$  min, ee = 92%.  $[\alpha]_D^{22.9} = -22.73$  (c = 0.09 in  $CHCl_3$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43 – 7.36 (m, 1H), 7.01 – 6.91 (m, 1H), 6.34 (dd,  $J = 3.2, 1.9$  Hz, 1H), 6.27 (d,  $J = 3.2$  Hz, 1H), 5.94 (dt,  $J = 15.7, 1.4$  Hz, 1H), 4.84 (dd,  $J = 11.1, 6.4$  Hz, 1H), 3.71 (s, 3H), 2.84 – 2.69 (m, 2H), 2.14 (d,  $J = 4.7$  Hz, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ) 169.04, 166.66, 155.32, 144.12, 142.30, 123.85, 110.30, 106.50, 66.46, 51.55, 38.26. HRMS (SEI-TOF) calcd for  $C_{10}H_{12}NaO_4^+$  ( $[M+Na^+]$ ) = 219.0628, Found 219.0637.

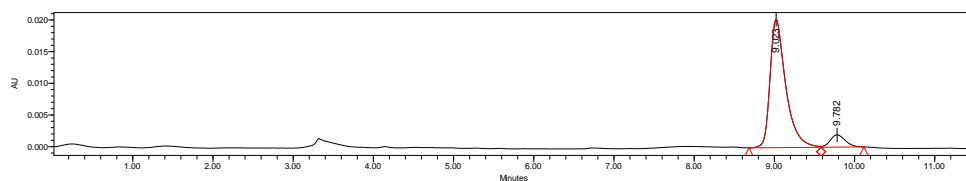
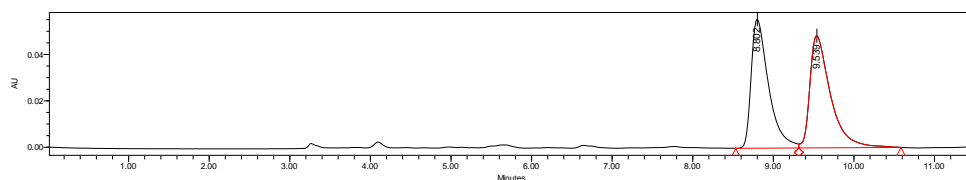


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 15.800         | 4.13   |
| 2 | 17.200         | 95.87  |

*(E)*-methyl 5-hydroxyoct-2-enoate **3u**

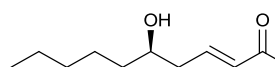


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 95/05, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 9.02$  min,  $t_{r2} = 9.78$  min, ee = 83%.  $[\alpha]_D^{23.5} = -8.89$  (c = 0.18 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.08 – 6.92 (m, 1H), 5.91 (d,  $J = 15.7$  Hz, 1H), 3.78 (s, 1H), 3.74 (s, 3H), 2.46 – 2.28 (m, 2H), 1.62 (s, 1H), 1.51 – 1.32 (m, 4H), 0.99 – 0.88 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 170.61, 166.79, 145.59, 123.43, 70.30, 51.51, 40.19, 39.26, 18.78, 13.97. HRMS (SEI-TOF) calcd for C<sub>9</sub>H<sub>16</sub>NaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 195.0992, Found 195.0999.

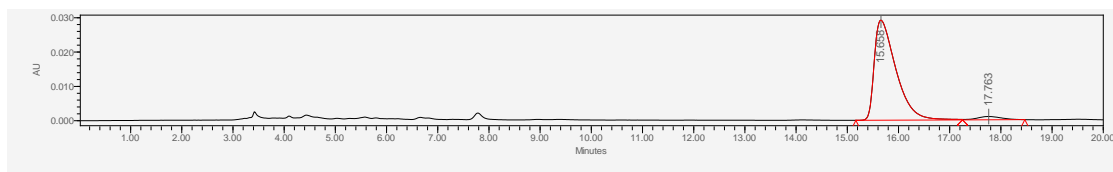
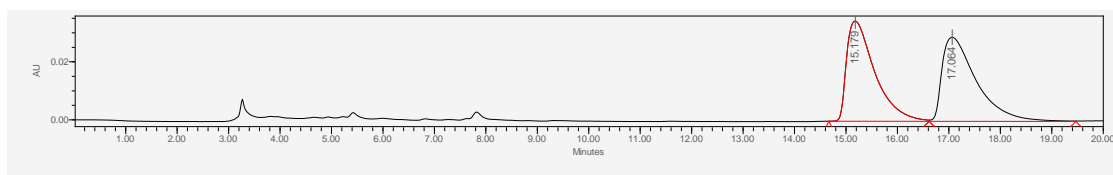


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 9.023          | 91.63  |
| 2 | 9.782          | 8.37   |

*(R,E)*-methyl 5-hydroxydec-2-enoate **3v**

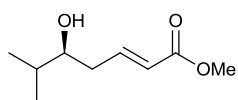


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/02, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 15.66$  min,  $t_{r2} = 17.76$  min, ee = 93%.  $[\alpha]_D^{25.1} = -6.25$  (c = 0.40 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.06 – 6.93 (m, 1H), 5.91 (dt,  $J = 15.7, 1.3$  Hz, 1H), 3.81 – 3.72 (m, 4H), 2.45 – 2.24 (m, 2H), 1.68 (s, 1H), 1.51 – 1.26 (m, 8H), 0.89 (t,  $J = 6.8$  Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 166.81, 145.64, 123.40, 70.57, 51.50, 40.17, 37.11, 31.73, 25.26, 22.59, 14.01. HRMS (SEI-TOF) calcd for C<sub>16</sub>H<sub>16</sub>NaO<sub>3</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 223.1305, Found 223.1309.

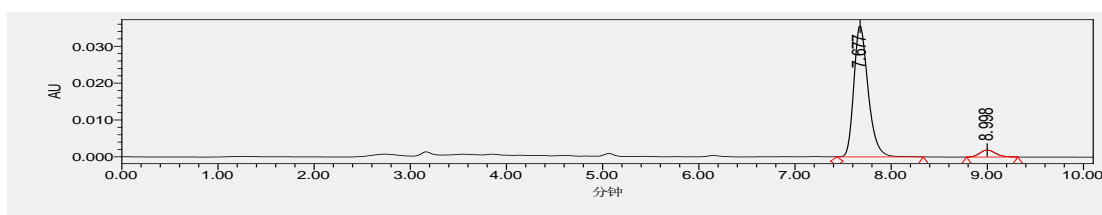
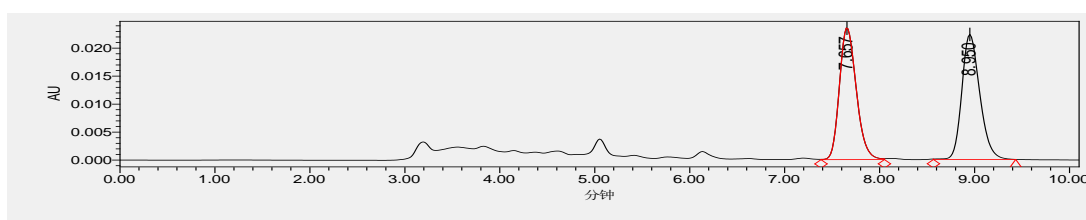


|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 15.658         | 96.45  |
| 2 | 17.763         | 3.55   |

(*S,E*)-methyl 5-hydroxy-6-methylhept-2-enoate **3w**

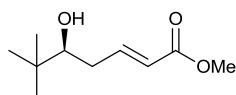


A colorless oil; HPLC (Chiralcel IB, hexane/*i*-PrOH = 95/05, flow rate = 1.0 ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 7.68$  min,  $t_{r2} = 9.00$  min, ee = 89%.  $[\alpha]_D^{29.1} = -13.89$  ( $c = 0.18$  in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.09 – 6.95 (m, 1H), 5.92 (dt,  $J = 15.7, 1.4$  Hz, 1H), 3.73 (s, 3H), 3.57 – 3.45 (m, 1H), 2.51 – 2.21 (m, 2H), 1.76 – 1.68 (m, 1H), 1.66 (d,  $J = 3.5$  Hz, 1H), 0.95 (d,  $J = 1.1$  Hz, 3H), 0.94 (d,  $J = 1.2$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) 166.79, 146.20, 123.24, 75.34, 51.47, 37.17, 33.40, 18.69, 17.22. HRMS (SEI-TOF) calcd for  $\text{C}_9\text{H}_{16}\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 195.0992, Found 195.1000.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 7.677          | 94.42  |
| 2 | 8.998          | 5.58   |

(*S,E*)-methyl 5-hydroxy-6,6-dimethylhept-2-enoate **3x**



A colorless oil; HPLC (Chiralcel IE, hexane/*i*-PrOH = 90/10, flow rate = 1.0

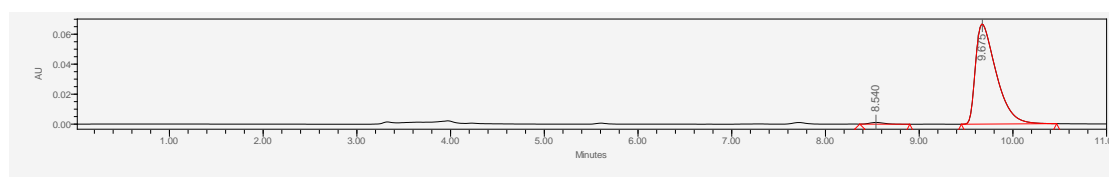
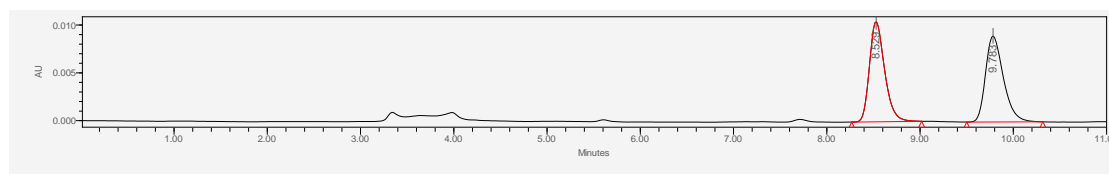
ml/min,  $\lambda = 254$  nm), retention time:  $t_{r1} = 8.54$  min,  $t_{r2} = 9.68$  min, ee = 98%.  $[\alpha]_D^{23.9} = -10.00$  ( $c = 0.08$

in  $\text{CHCl}_3$ ).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12 – 6.97 (m, 1H), 5.93 (d,  $J = 15.7$  Hz, 1H), 3.73 (s, 3H),

3.37 (d,  $J = 10.1$  Hz, 1H), 2.52 – 2.35 (m, 1H), 2.25 – 2.10 (m, 1H), 1.56 (d,  $J = 2.7$  Hz, 1H), 0.93 (s,

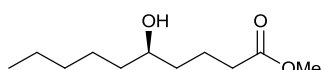
9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ) 166.83, 147.49, 122.97, 78.38, 51.47, 35.01, 34.85, 25.60. HRMS

(SEI-TOF) calcd for  $\text{C}_{10}\text{H}_{18}\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 209.1148, Found 209.1153.



|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 8.540          | 1.20   |
| 2 | 9.675          | 98.80  |

methyl 5-hydroxydecanoate **5v**



To a solution of **3v** (3.7 mmol, 741.3 mg) in  $\text{CH}_3\text{OH}$  (12 mL), 5% Pd/C (100 mg) was added. The mixture was stirred under  $\text{H}_2$  atmosphere (5 MPa) at 25 °C until the reaction

was finished (12 h). Then, Pd/C was removed by filtration and washed with  $\text{CH}_2\text{Cl}_2$ . The filtrate was concentrated and isolated via column chromatography (1/7, ethyl acetate/petroleum ether). A colorless

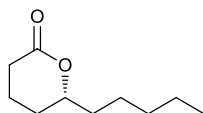
oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.67 (s, 3H), 3.63 – 3.54 (m, 1H), 2.35 (t,  $J = 7.4$  Hz, 2H), 1.84 –

1.61 (m, 3H), 1.54 – 1.38 (m, 5H), 1.34 – 1.22 (m, 5H), 0.89 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,

$\text{CDCl}_3$ ) 174.26, 71.36, 51.53, 37.43, 36.68, 33.89, 31.86, 25.29, 22.61, 20.98, 14.02. HRMS (SEI-TOF)

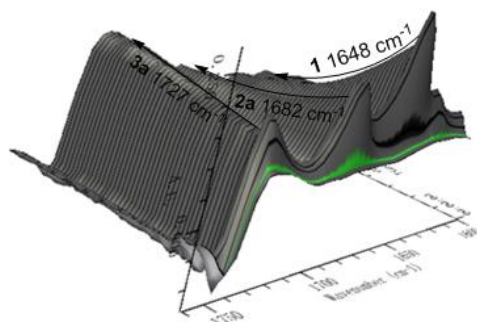
calcd for  $\text{C}_{11}\text{H}_{22}\text{NaO}_3^+$  ( $[\text{M}+\text{Na}^+]$ ) = 225.1461, Found 225.1465.

(*R*)-6-pentyltetrahydro-2H-pyran-2-one **6v**

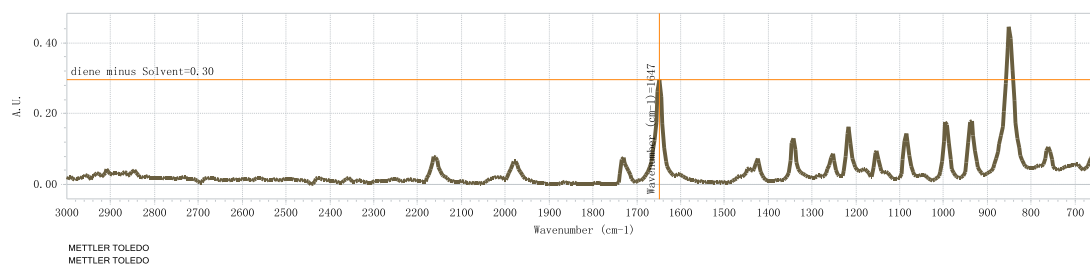


The product of **5v** (0.665g) was dissolved in 12 mL DCM, 16.5 mg of *p*-TSA was added, and the mixture was stirred for 12 h. the mixture was subjected to chromatography using ethyl acetate/petroleum ether = 1/7. A colorless oil; ee = 94%.  $[\alpha]_D^{20.0} = 39.00$  (c = 0.50 in CHCl<sub>3</sub>), lit.<sup>3</sup>  $[\alpha]_D^{25.0} = 52.20$  (c = 1.00 in CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.33 – 4.24 (m, 1H), 2.64 – 2.53 (m, 1H), 2.51 – 2.38 (m 1H), 1.98 – 1.83 (m, 3H), 1.75 – 1.65 (m, 1H), 1.62 – 1.44 (m, 3H), 1.42 – 1.25 (m, 5H), 0.89 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 179.55, 80.57, 35.76, 31.55, 29.42, 27.75, 24.56, 22.47, 18.45, 13.94. HRMS (SEI-TOF) calcd for C<sub>10</sub>H<sub>18</sub>NaO<sub>2</sub><sup>+</sup> ([M+Na<sup>+</sup>]) = 193.1199, Found 193.1209.

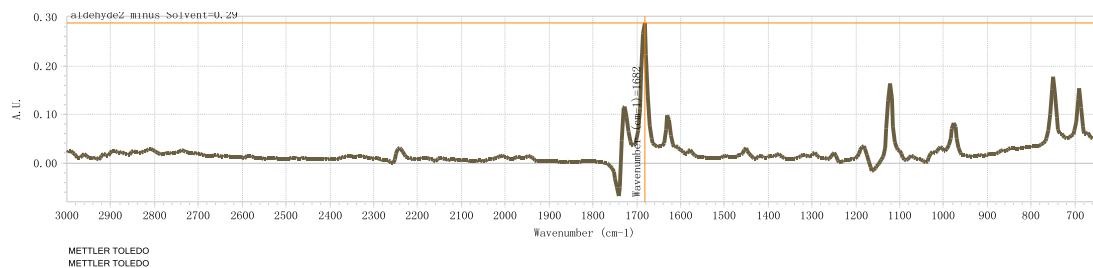
## 5. The operando IR experiments of the reaction



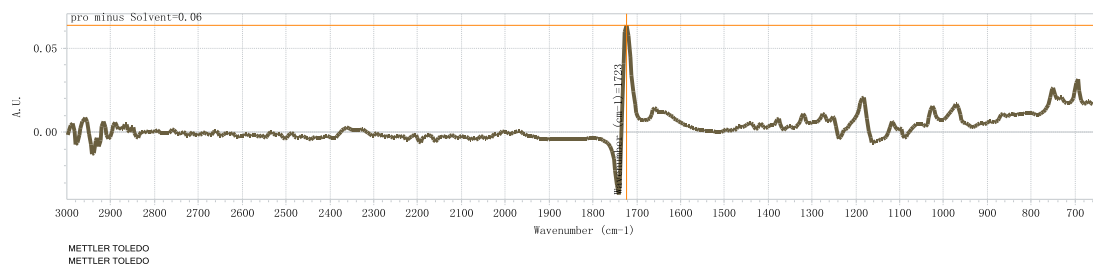
The 3D ATR-FTIR profile of the reaction



The IR spectrum of diene **1**



The IR spectrum of aldehyde **2a**



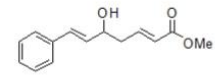
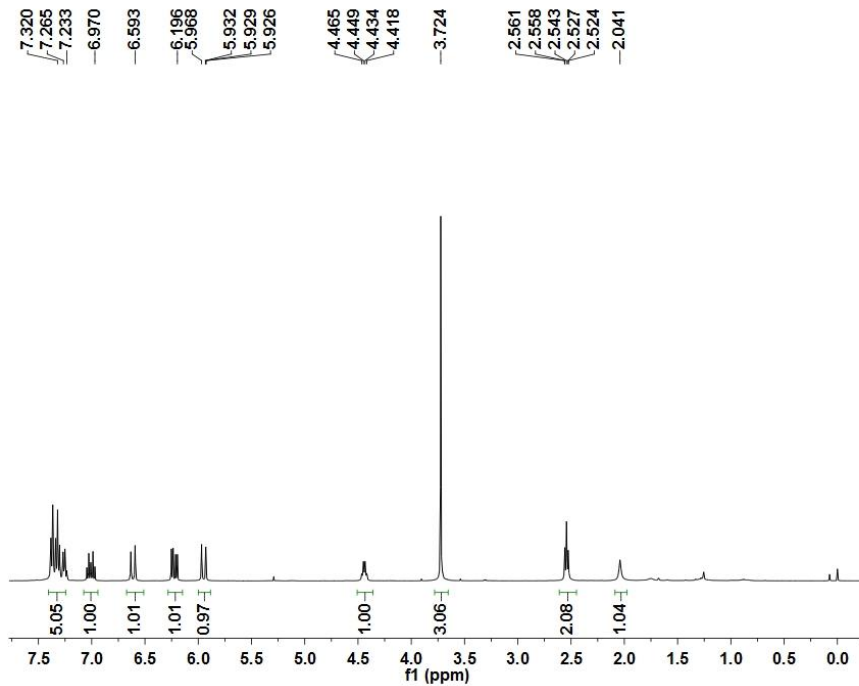
The IR spectrum of product **3a**

## 6. References

- 1 (a) S. E. Denmark, J. R. Heemstra, Jr., *J. Org. Chem.* 2007, **72**, 5668; (b) S. E. Denmark, G. L. Beutner, *J. Am. Chem. Soc.* 2003, **125**, 7800.
- 2 (a) D. J. Shang, J. G. Xin, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *J. Org. Chem.* 2008, **73**, 630; (b) Y. L. Zhang, X. H. Liu, X. H. Zhao, J. L. Zhang, L. Zhou, L. L. Lin, X. M. Xiao, *Chem. Commun.* 2013, **49**, 11311.
- 3 G. Sabitha, V. Bhaskar, J. S. Yadav, *Tetrahedron Lett.* 2006, **47**, 8179.

## 7. Copies of NMR spectra for VMAR products

(*S*,*2E*,*6E*)-methyl 5-hydroxy-7-phenylhepta-2,6-dienoate **3a**

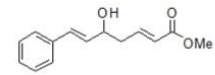
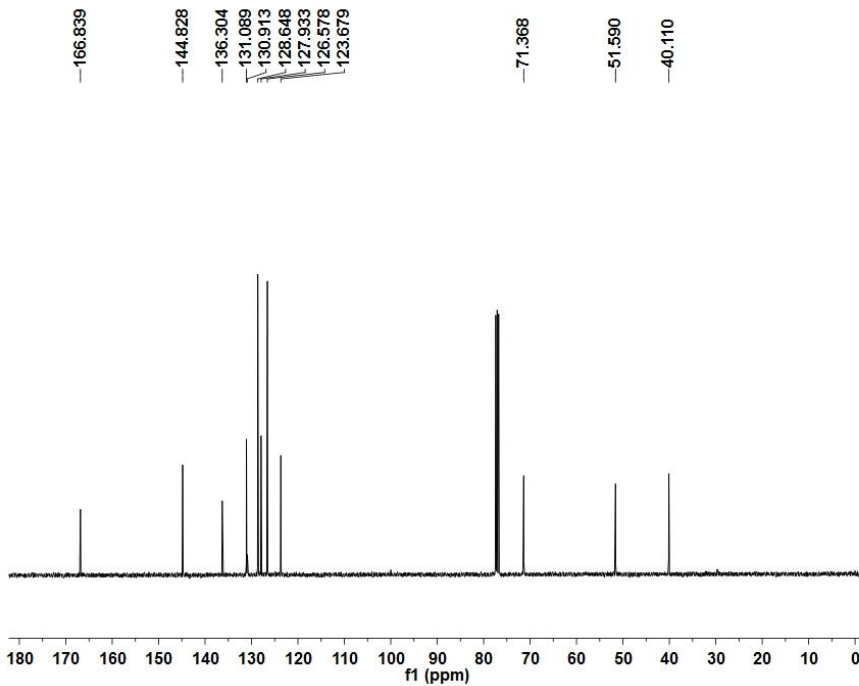


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 AQ: undefined  
 TE: 295.3 C

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 SFO1: undefined MHz

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 Ph1: 4.70



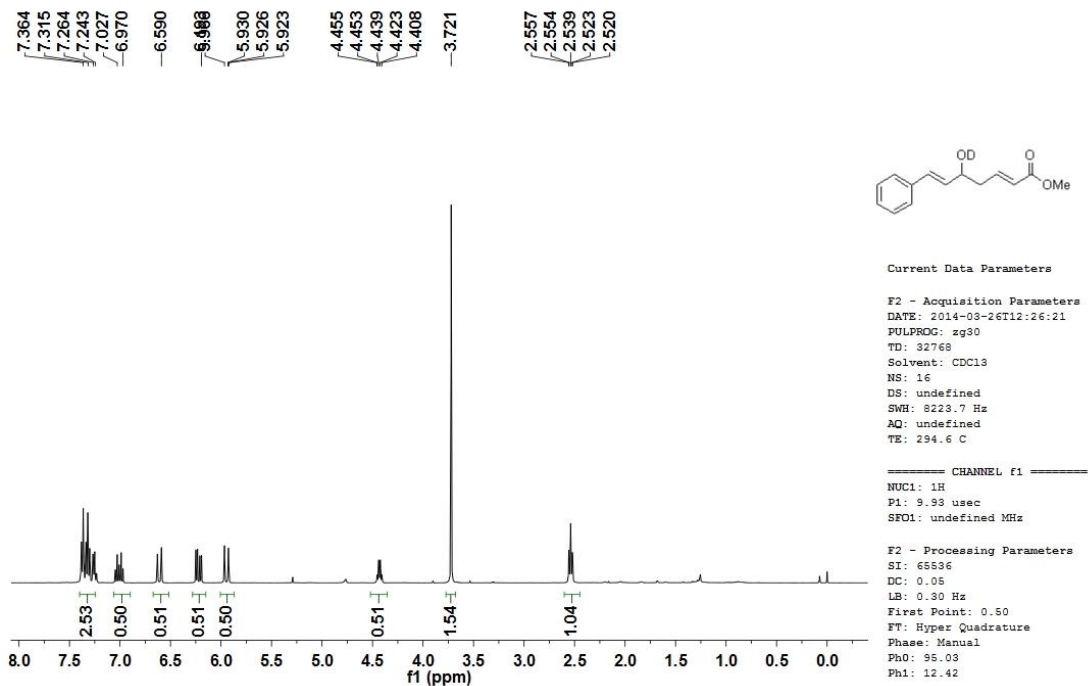
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 TE: 294.8 C

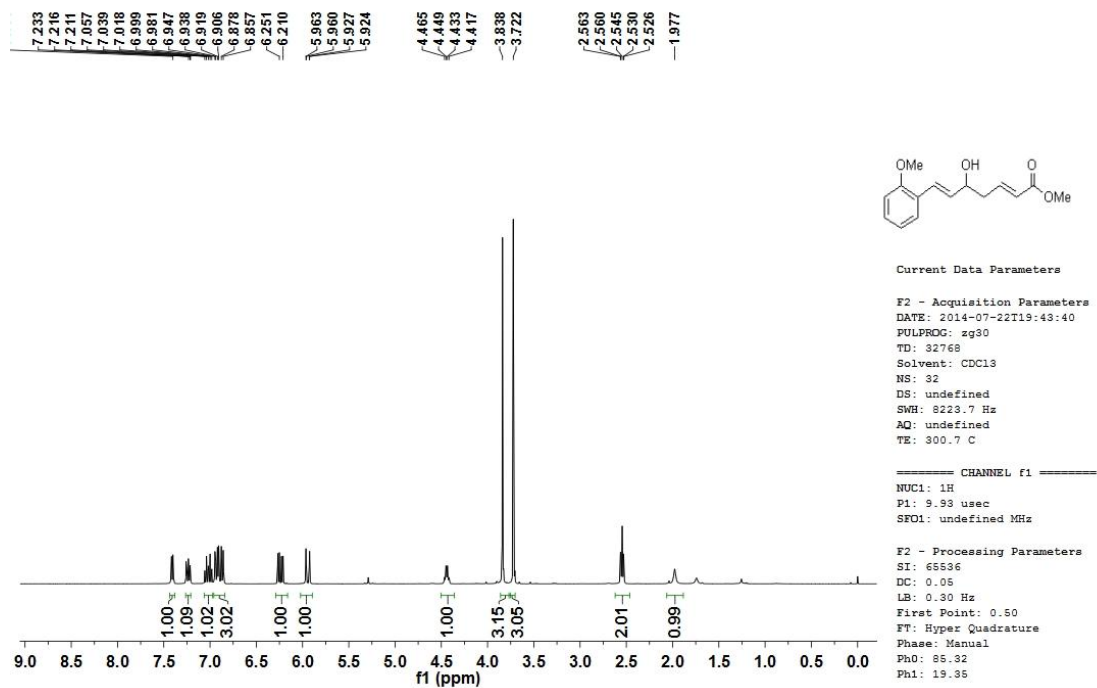
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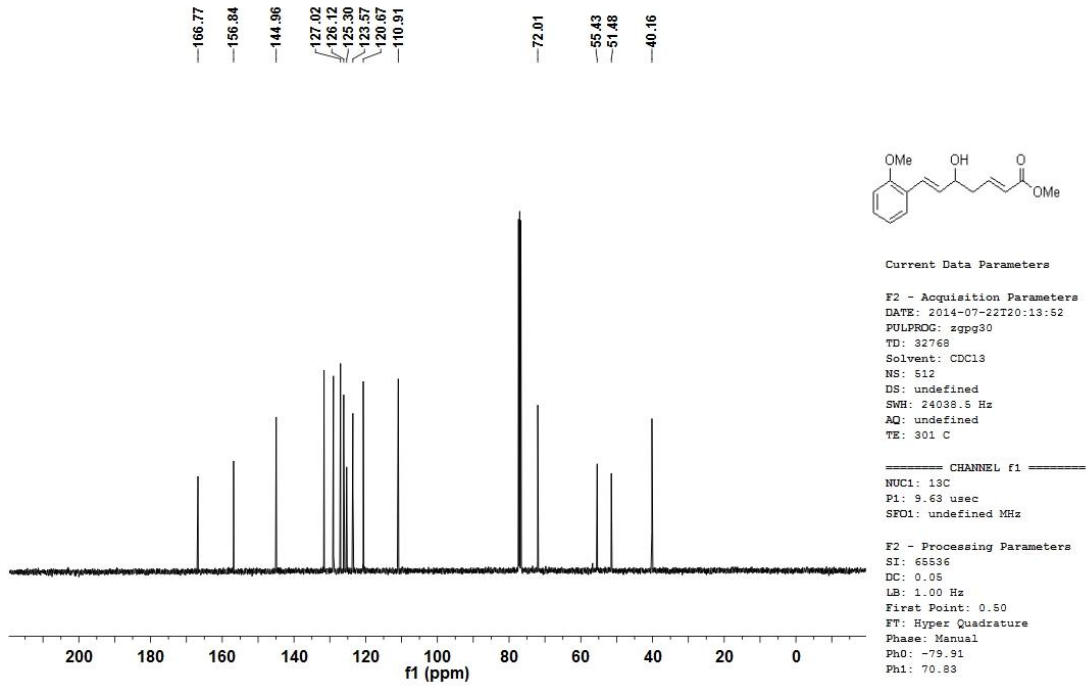
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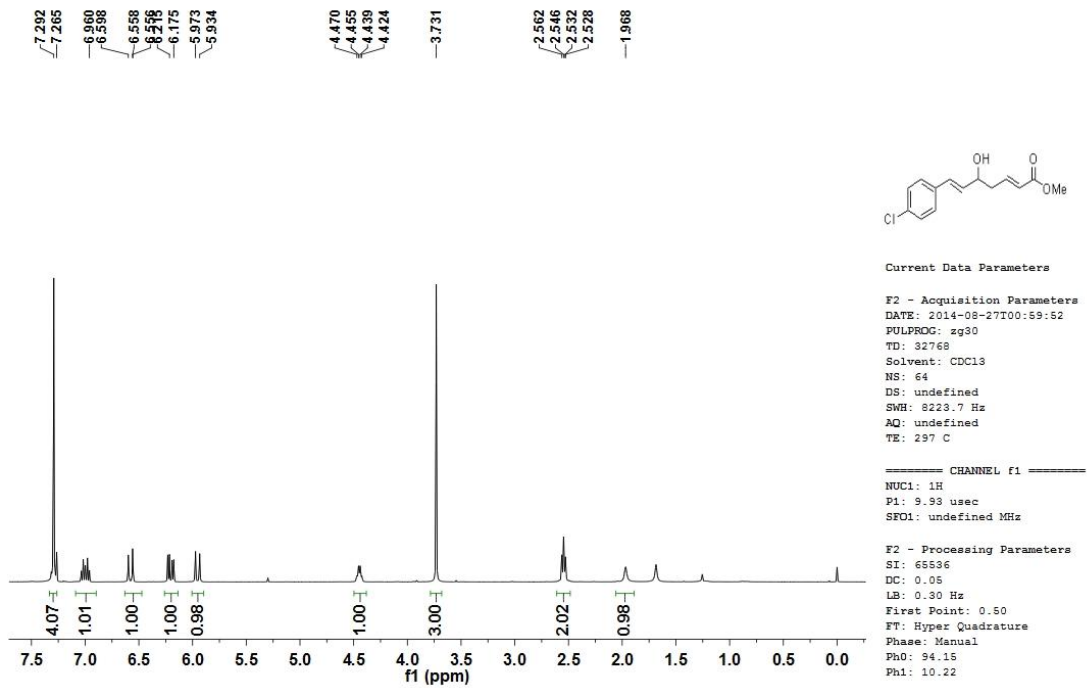


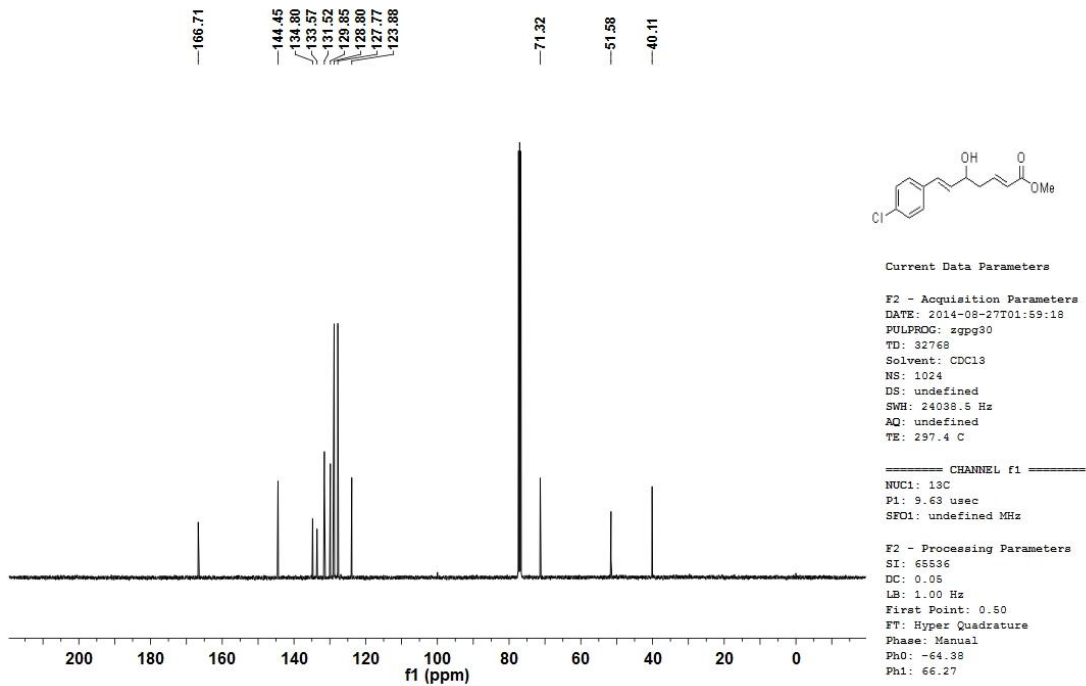
(2E,6E)-methyl 5-hydroxy-7-(2-methoxyphenyl)hepta-2,6-dienoate **3b**



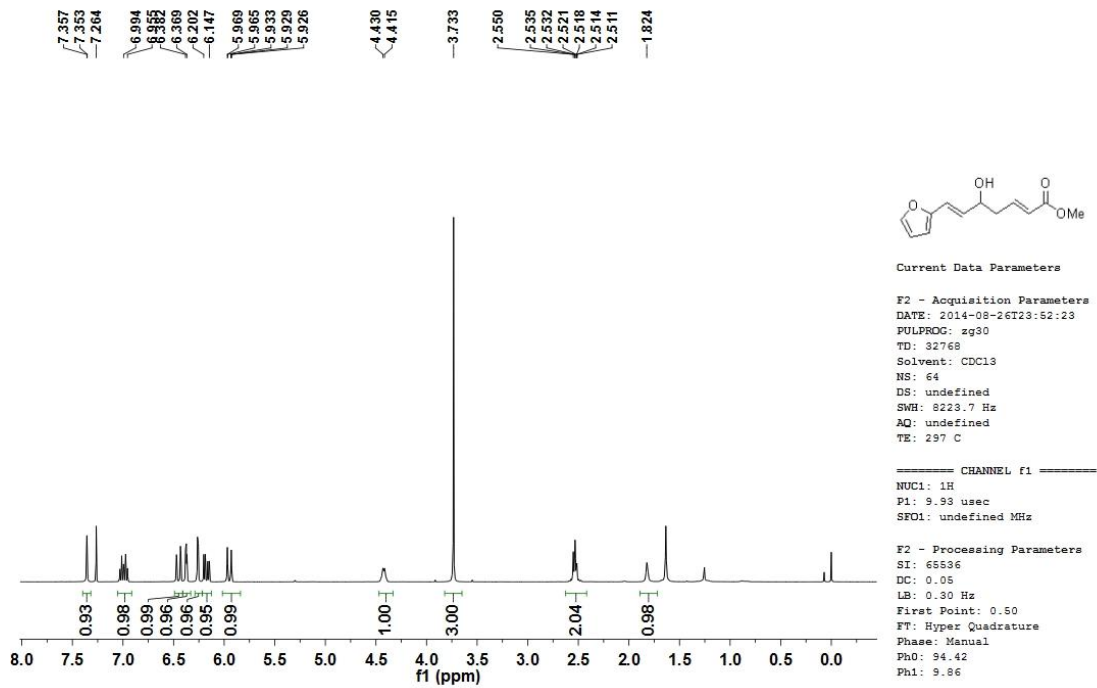


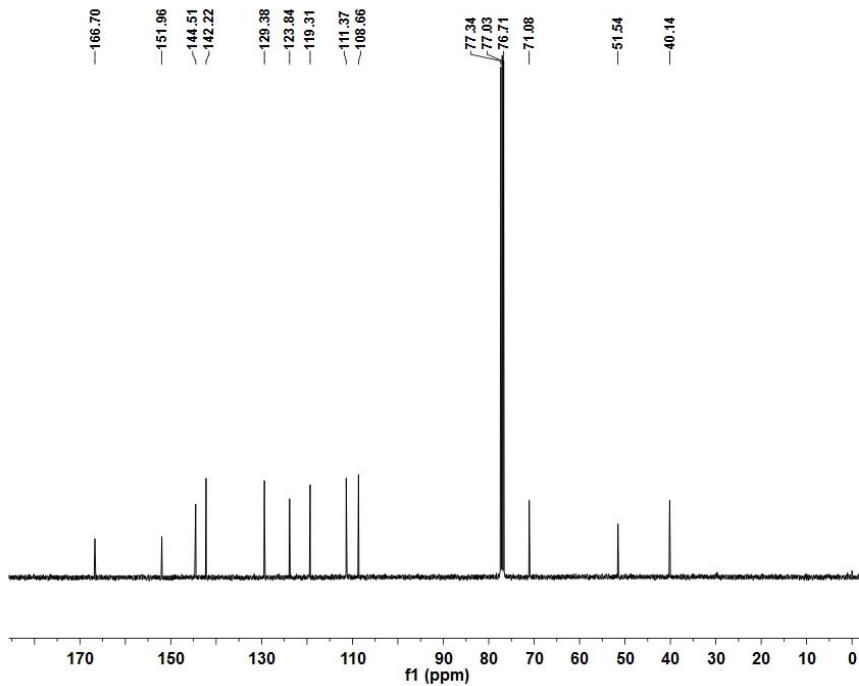
(2E,6E)-methyl 7-(4-chlorophenyl)-5-hydroxyhepta-2,6-dienoate **3c**



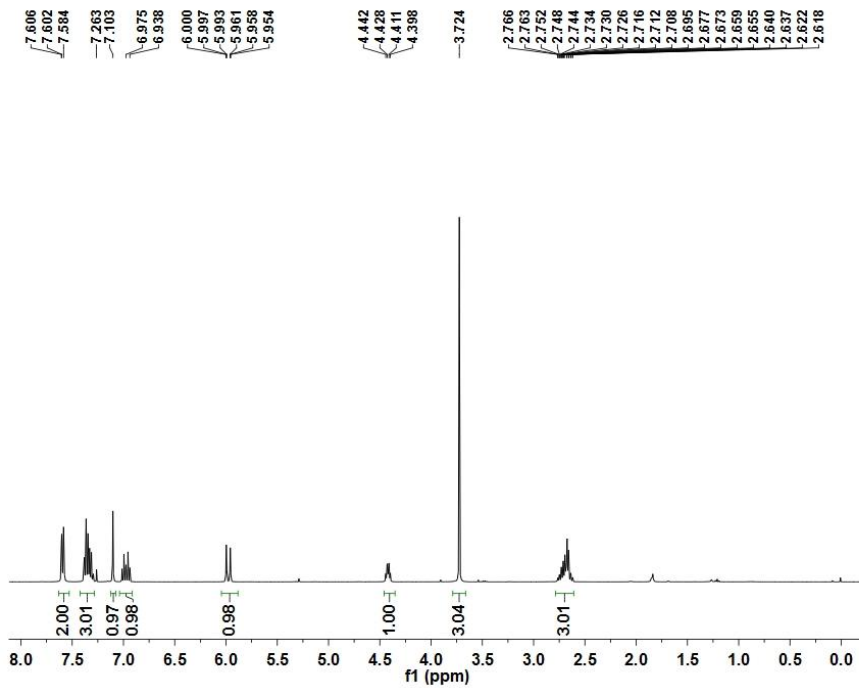


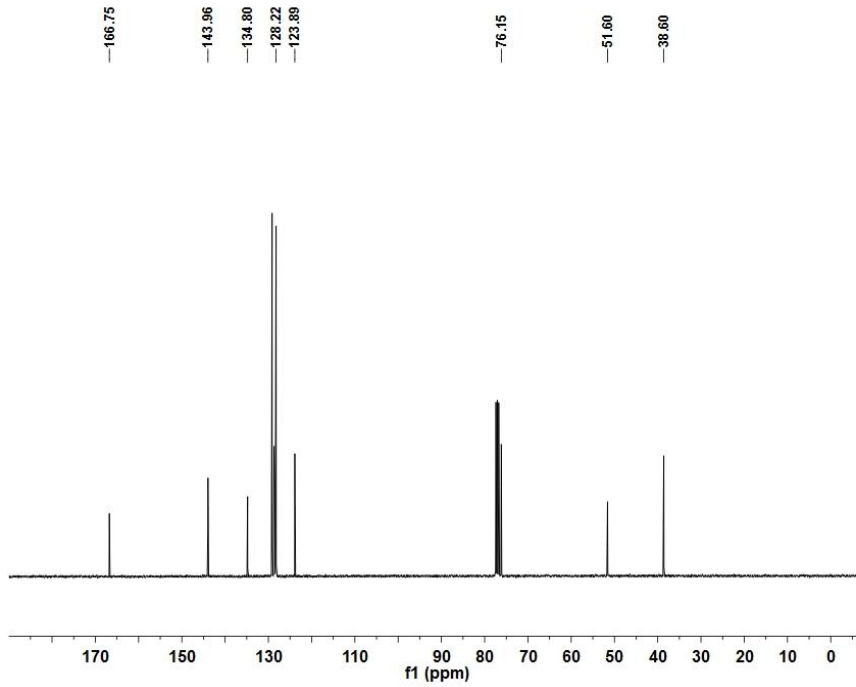
(2E,6E)-methyl 7-(furan-2-yl)-5-hydroxyhepta-2,6-dienoate **3d**



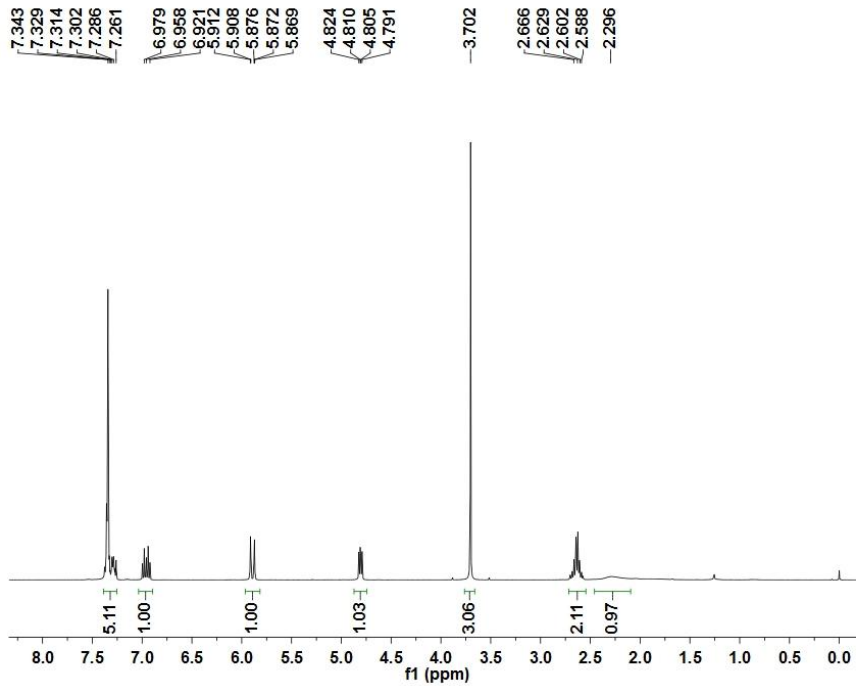


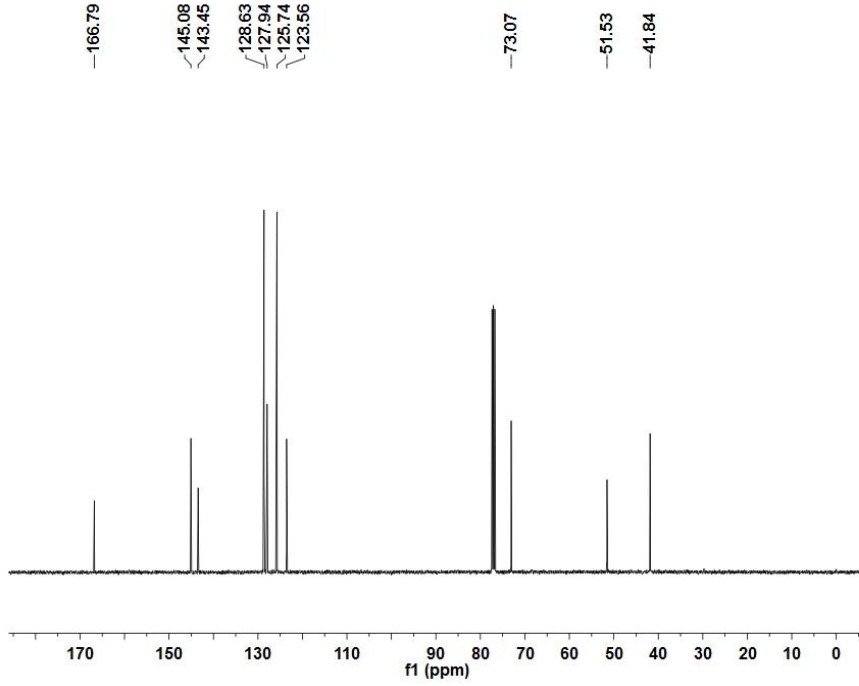
(2E,6Z)-methyl 6-bromo-5-hydroxy-7-phenylhepta-2,6-dienoate 3e



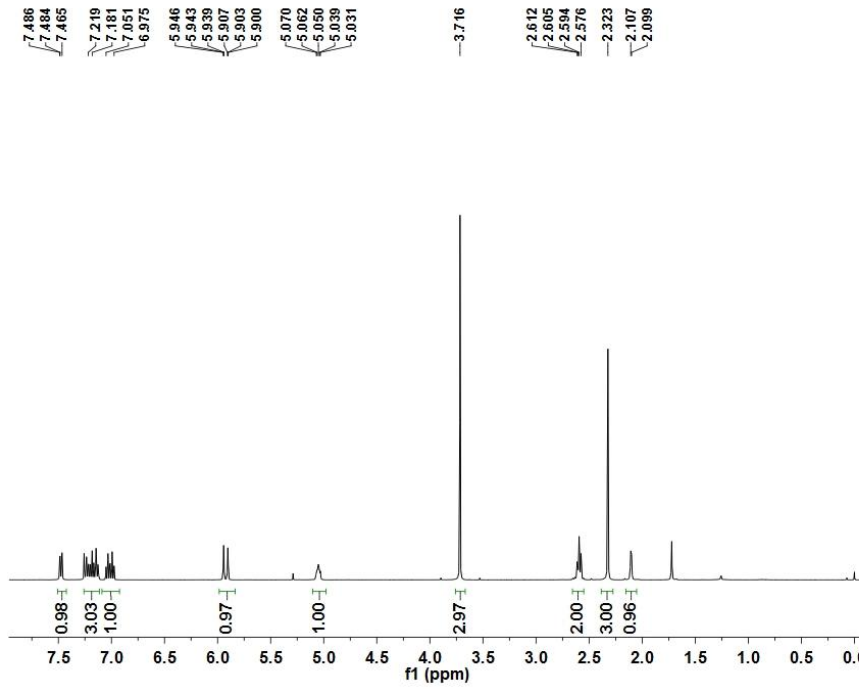


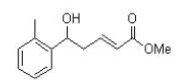
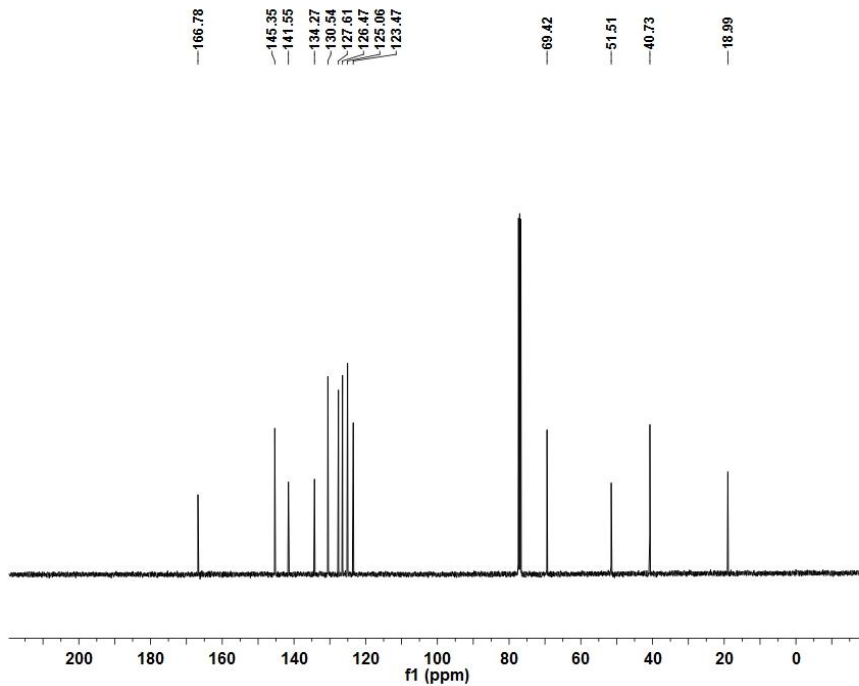
(S,E)-methyl 5-hydroxy-5-phenylpent-2-enoate **3f**





(E)-methyl 5-hydroxy-5-(o-tolyl)pent-2-enoate **3g**





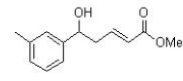
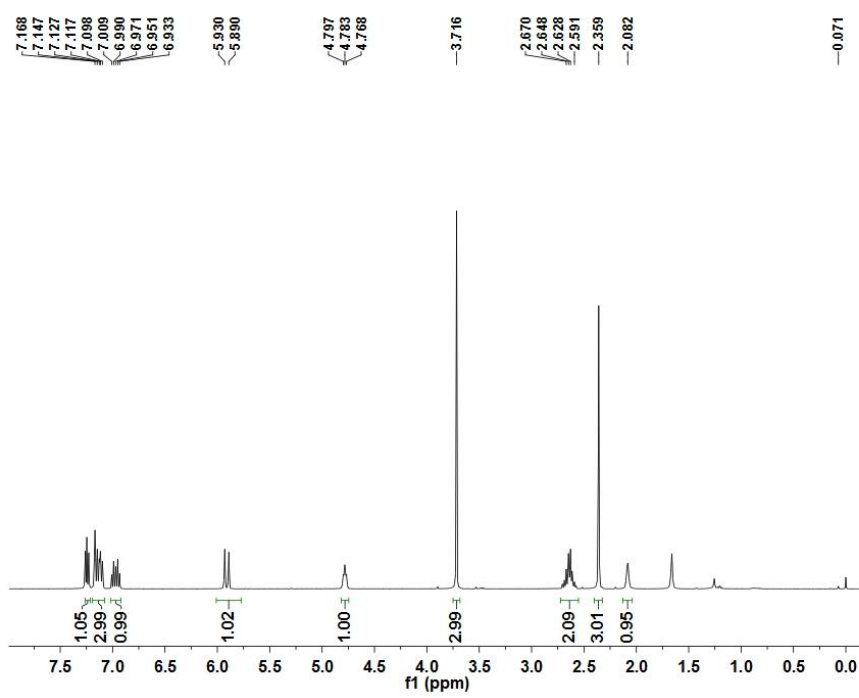
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 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 300.4 C

CHANNEL f1  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -82.97  
 Ph1: 82.78

(E)-methyl 5-hydroxy-5-(m-tolyl)pent-2-enoate **3h**

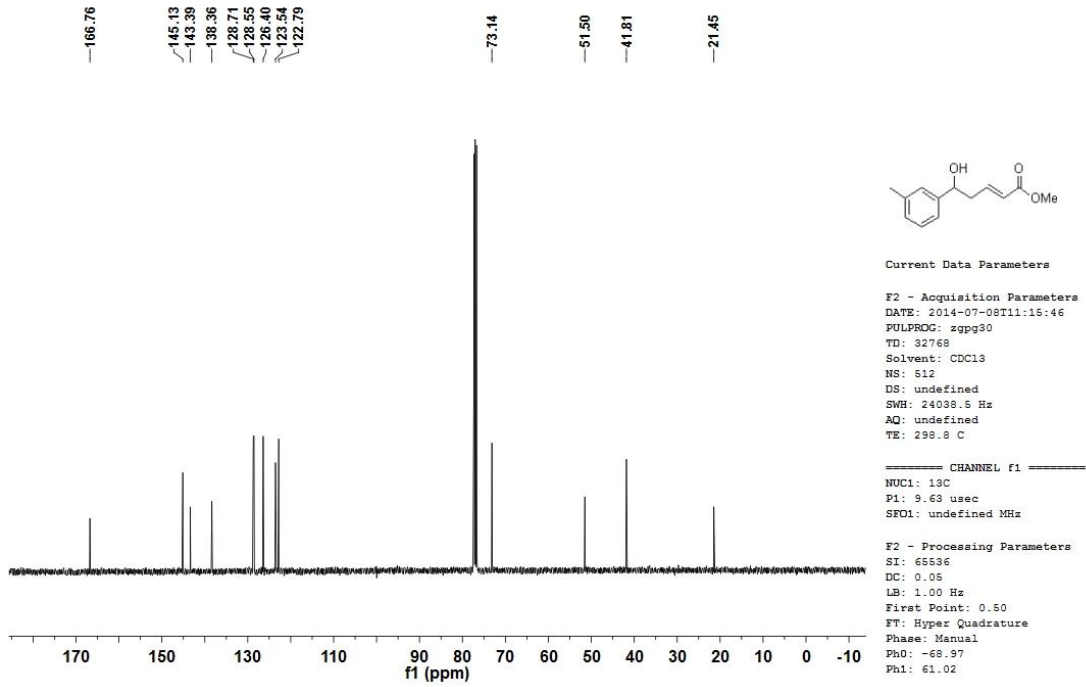


Current Data Parameters

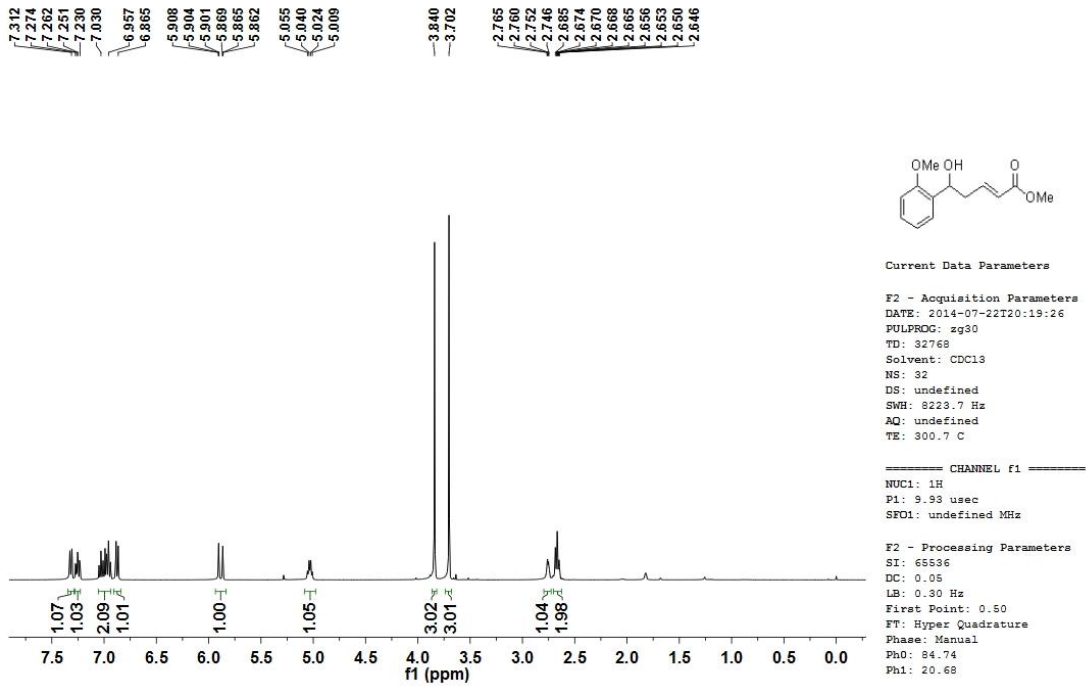
F2 - Acquisition Parameters  
 DATE: 2014-07-08T10:45:35  
 PULPROG: zg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 32  
 DS: undefined  
 SWH: 8223.7 Hz  
 AQ: undefined  
 TE: 298.5 C

CHANNEL f1  
 NUC1: 1H  
 P1: 9.93 usec  
 SFO1: undefined MHz

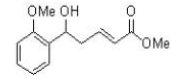
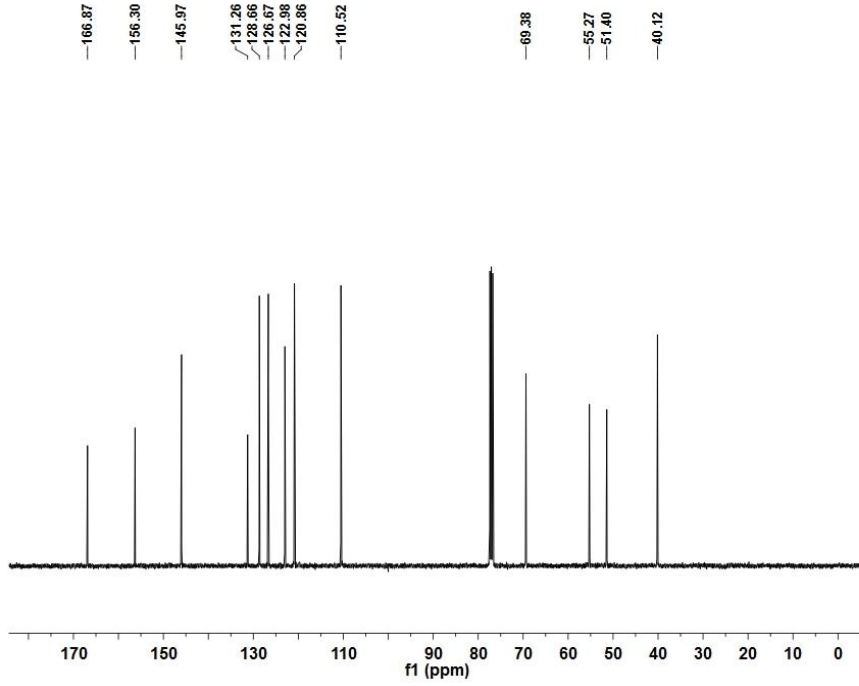
F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 0.30 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: 85.55  
 Ph1: 23.64



(E)-methyl 5-hydroxy-5-(2-methoxyphenyl)pent-2-enoate **3i**







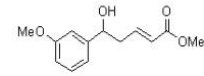
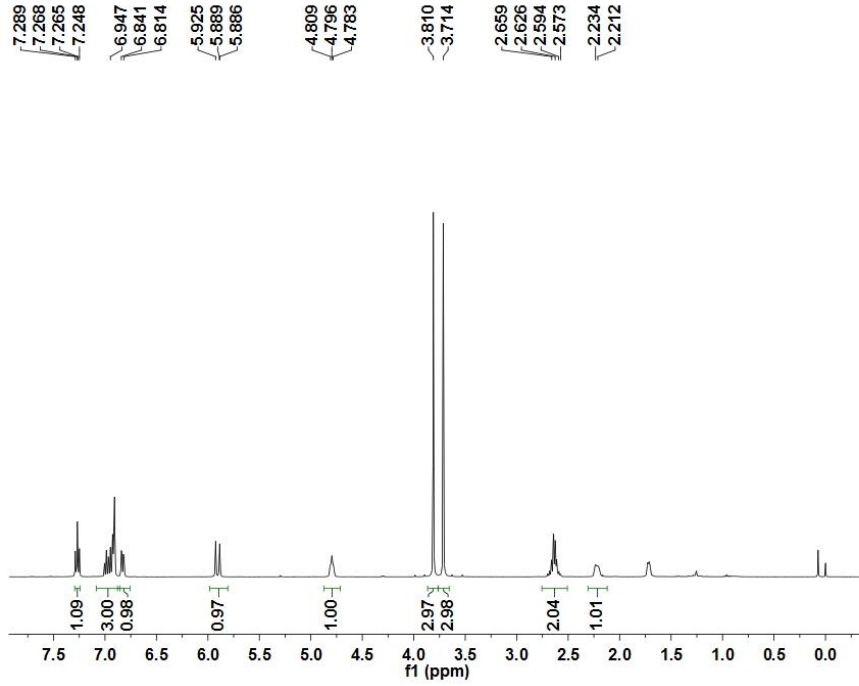
Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-07-22T20:49:37  
 PULPROG: zgpg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 512  
 DS: undefined  
 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 301 C

CHANNEL f1  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -66.06  
 Ph1: 62.21

(E)-methyl 5-hydroxy-5-(3-methoxyphenyl)pent-2-enoate **3j**

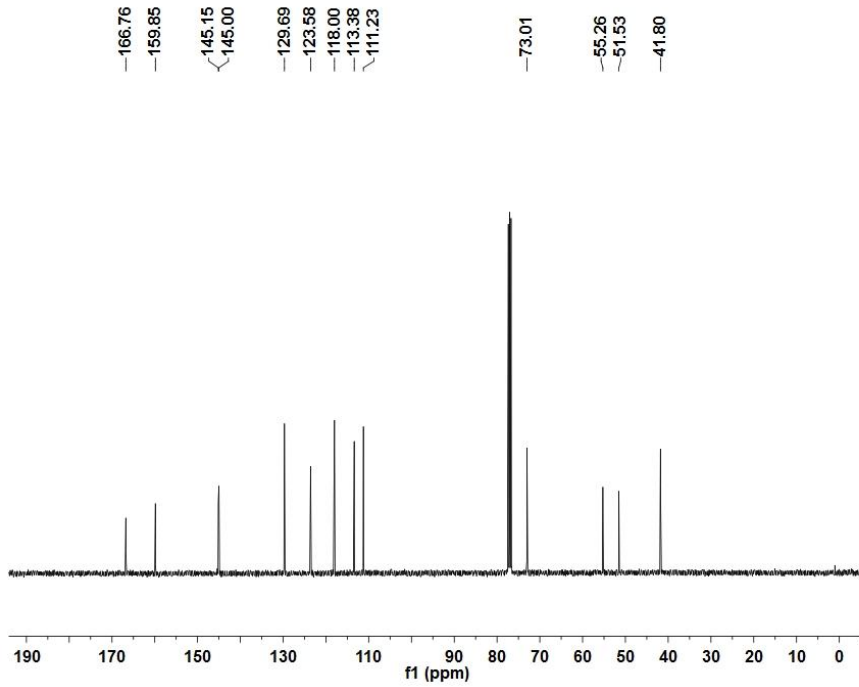


Current Data Parameters

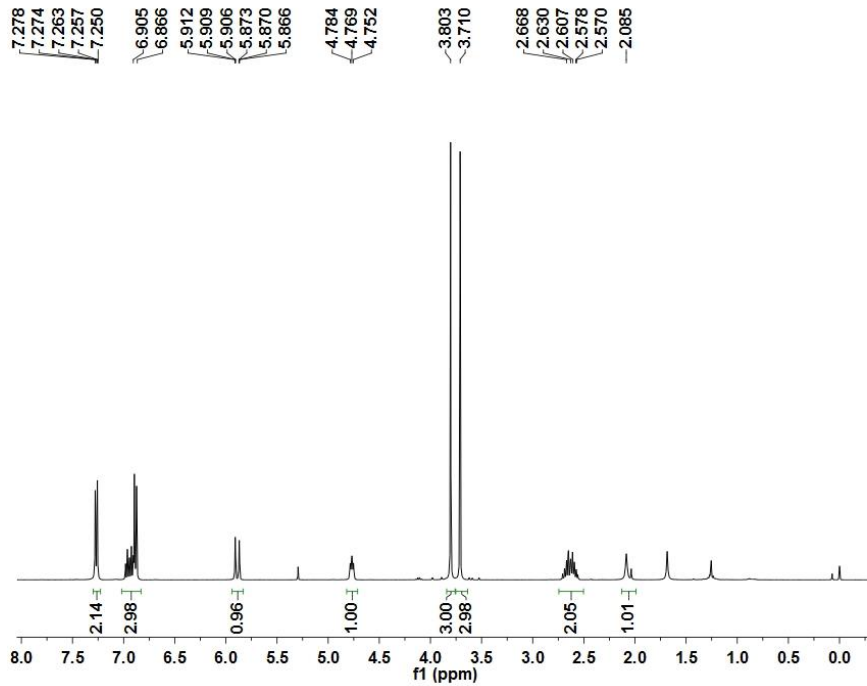
F2 - Acquisition Parameters  
 DATE: 2014-05-24T05:02:36  
 PULPROG: zg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 16  
 DS: undefined  
 SWH: 8223.7 Hz  
 AQ: undefined  
 TE: 296.7 C

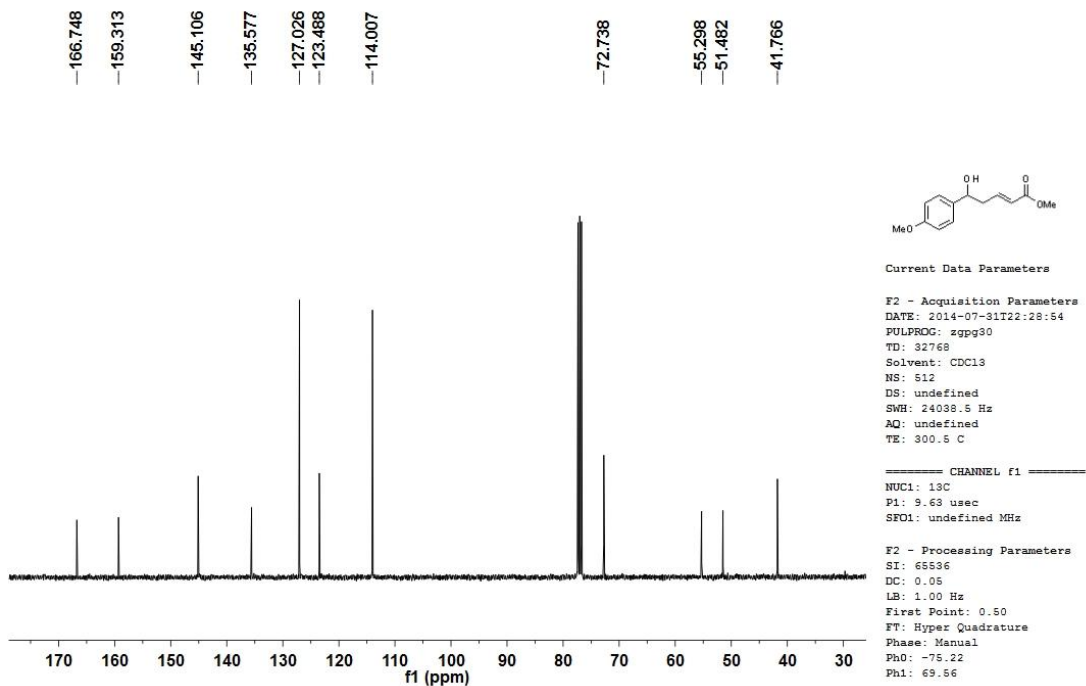
CHANNEL f1  
 NUC1: 1H  
 P1: 9.93 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 0.30 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: 88.15  
 Ph1: 13.82

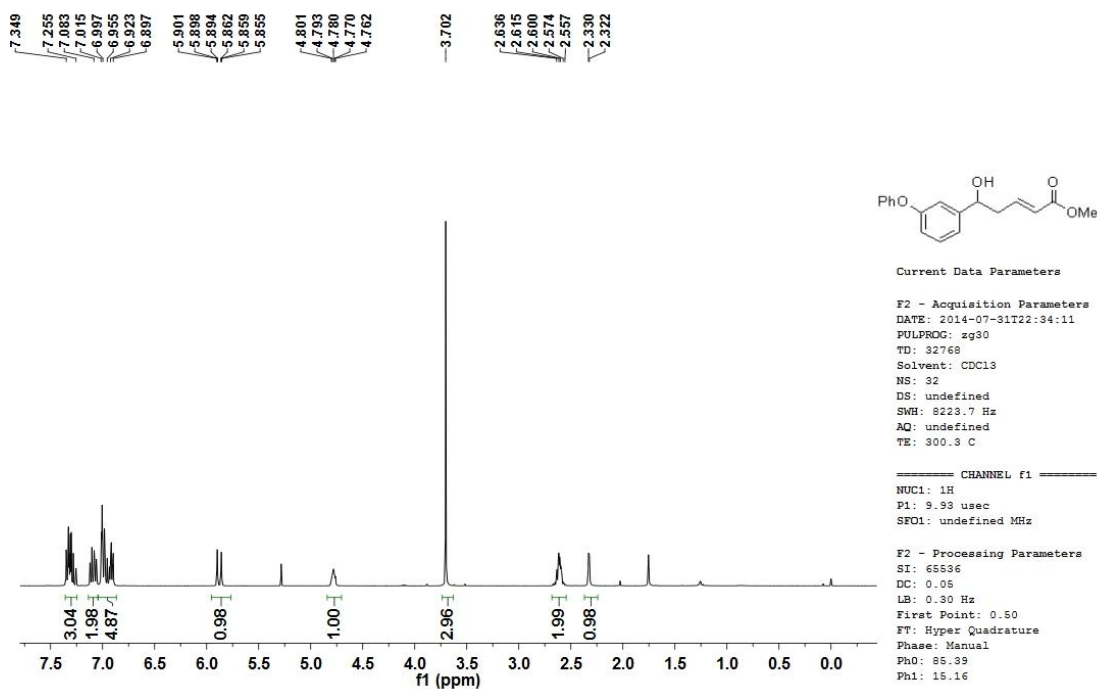


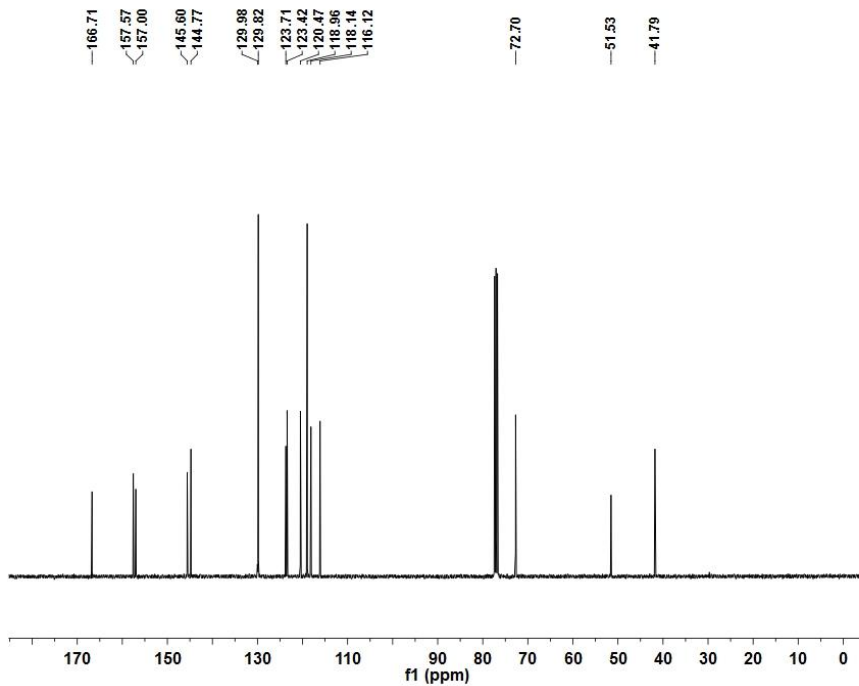
(E)-methyl 5-hydroxy-5-(4-methoxyphenyl)pent-2-enoate **3k**



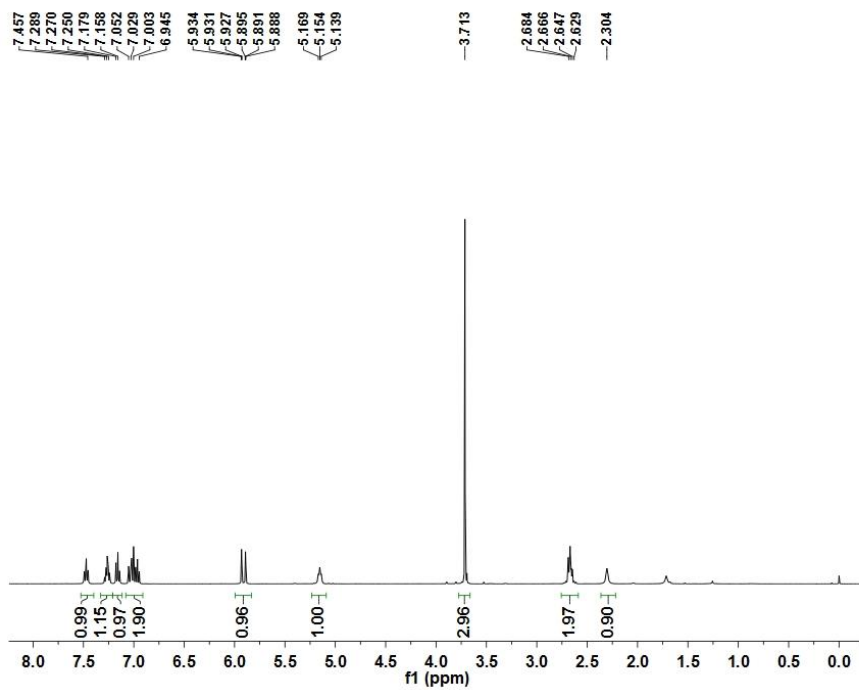


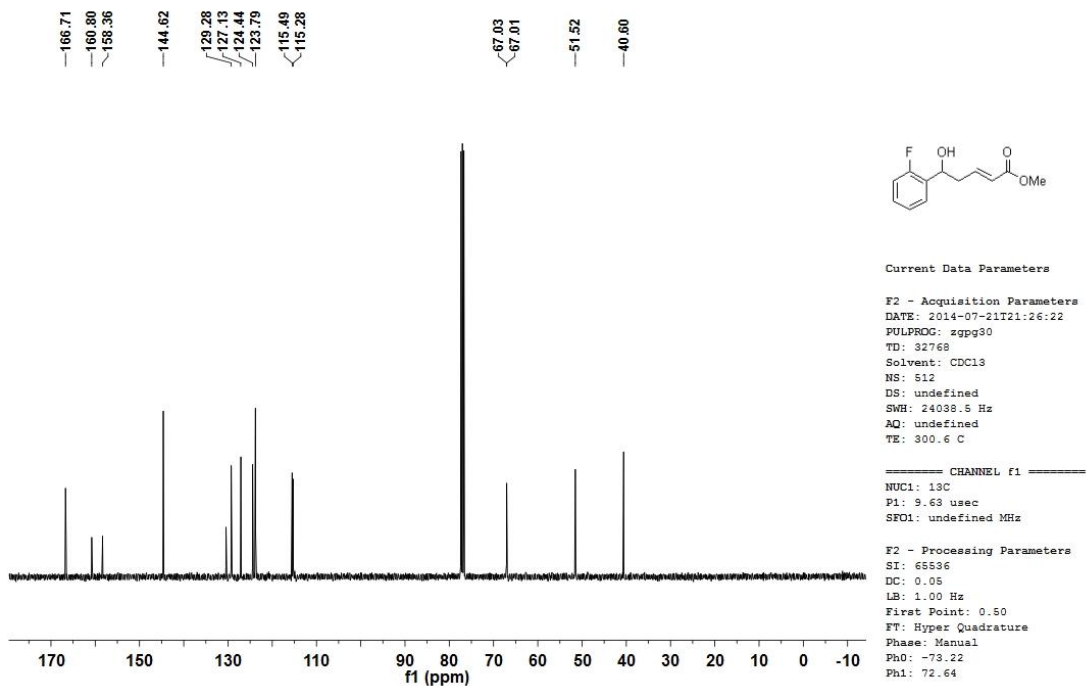
(*E*)-methyl 5-hydroxy-5-(3-phenoxyphenyl)pent-2-enoate **3I**



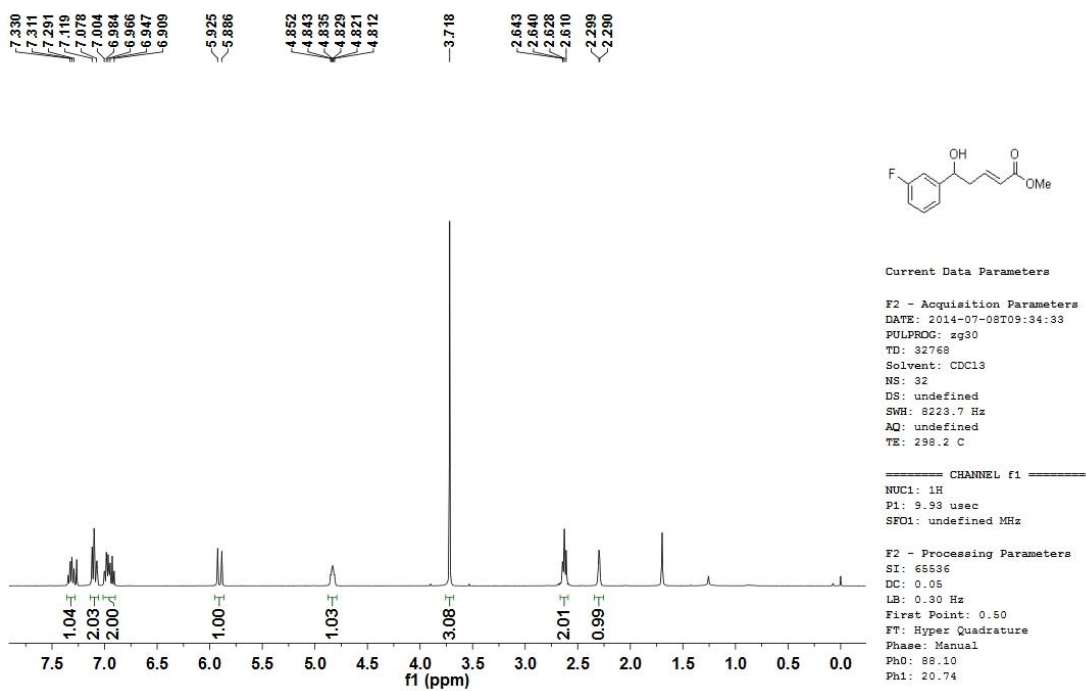


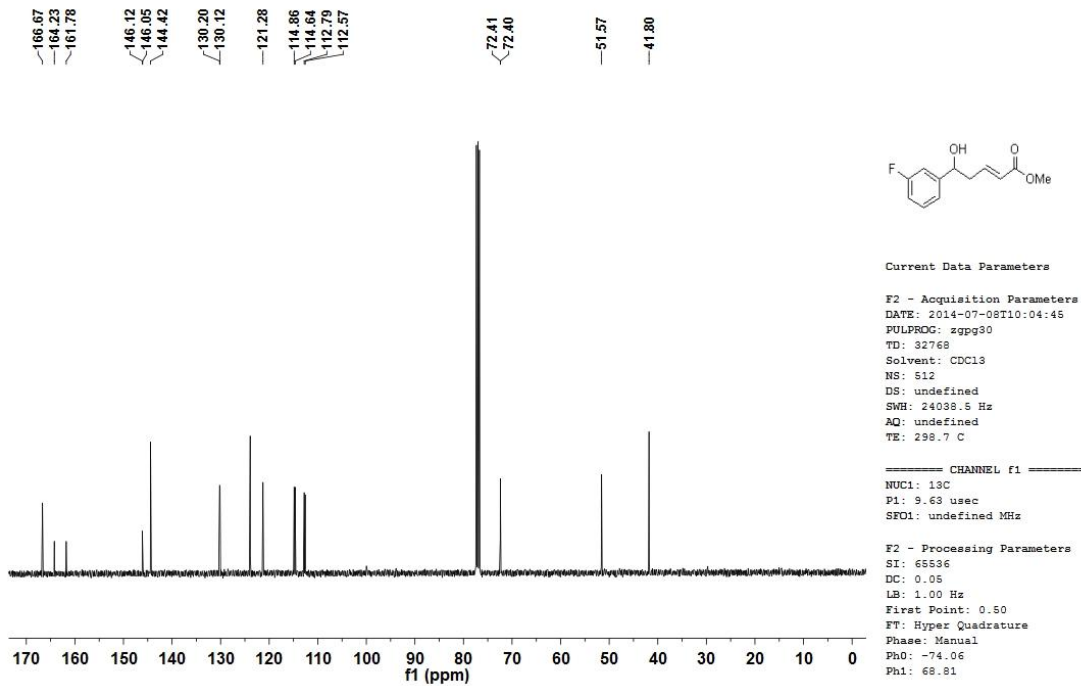
(E)-methyl 5-(4-fluorophenyl)-5-hydroxypent-2-enoate **3m**



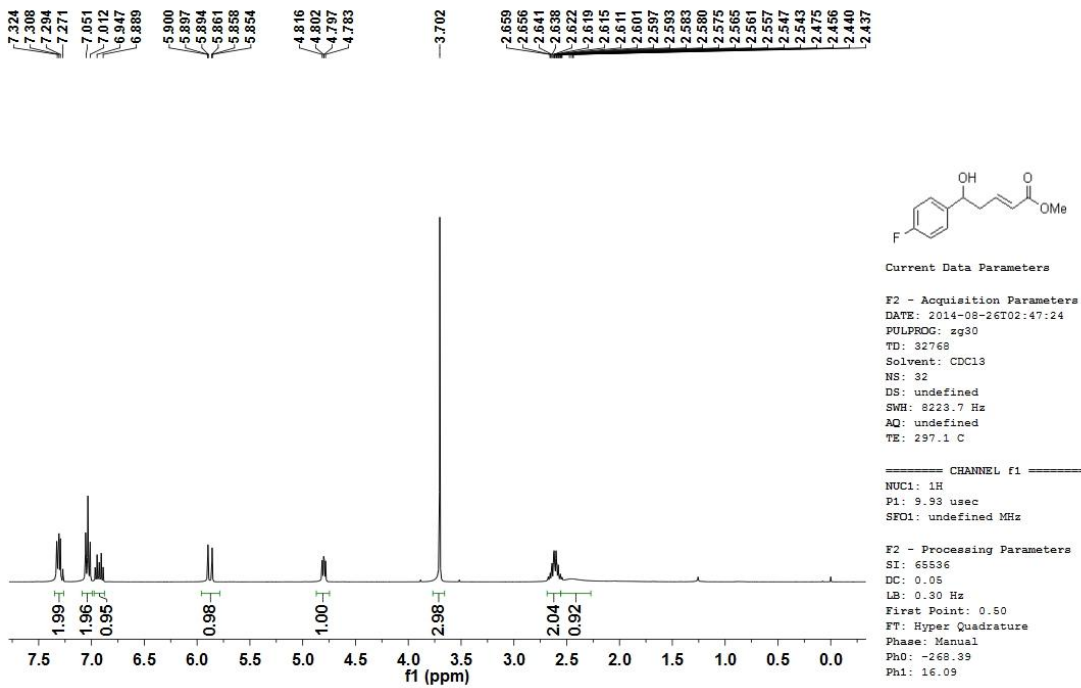


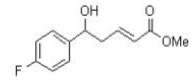
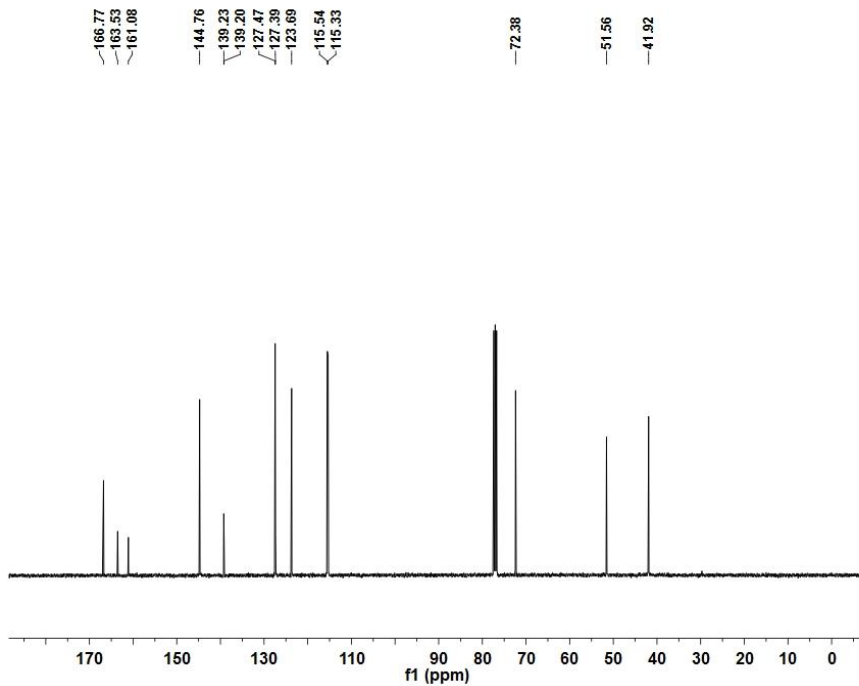
(*E*)-methyl 5-(3-fluorophenyl)-5-hydroxy-2-enoate **3n**





(E)-methyl 5-(4-fluorophenyl)-5-hydroxypent-2-enoate **3o**





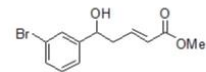
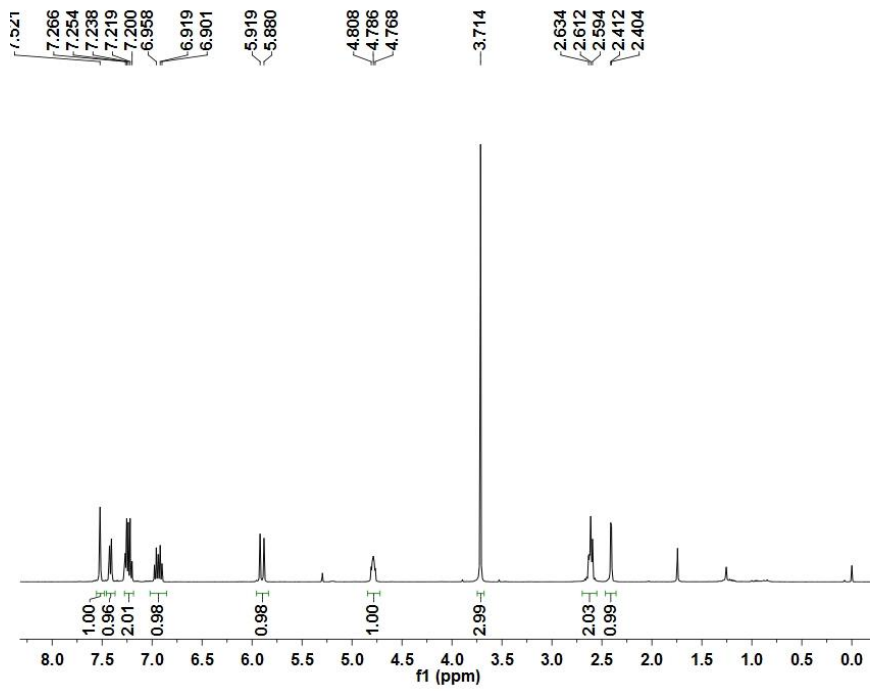
Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-08-26T03:17:36  
 PULPROG: zgpg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 512  
 DS: undefined  
 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 297.4 C

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -75.74  
 Ph1: 71.11

(E)-methyl 5-(3-bromophenyl)-5-hydroxypent-2-enoate **3p**

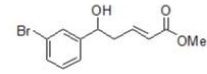
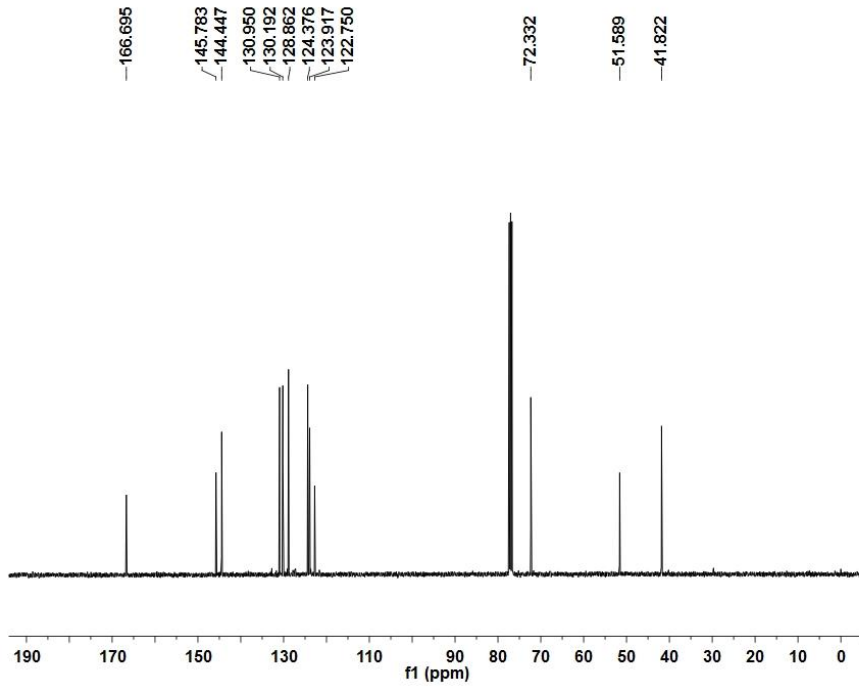


Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-10-05T19:12:19  
 PULPROG: zg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 32  
 DS: undefined  
 SWH: 8223.7 Hz  
 AQ: undefined  
 TE: 298.9 C

===== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 9.93 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 0.30 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: 87.40  
 Ph1: 20.11



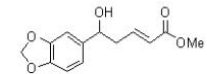
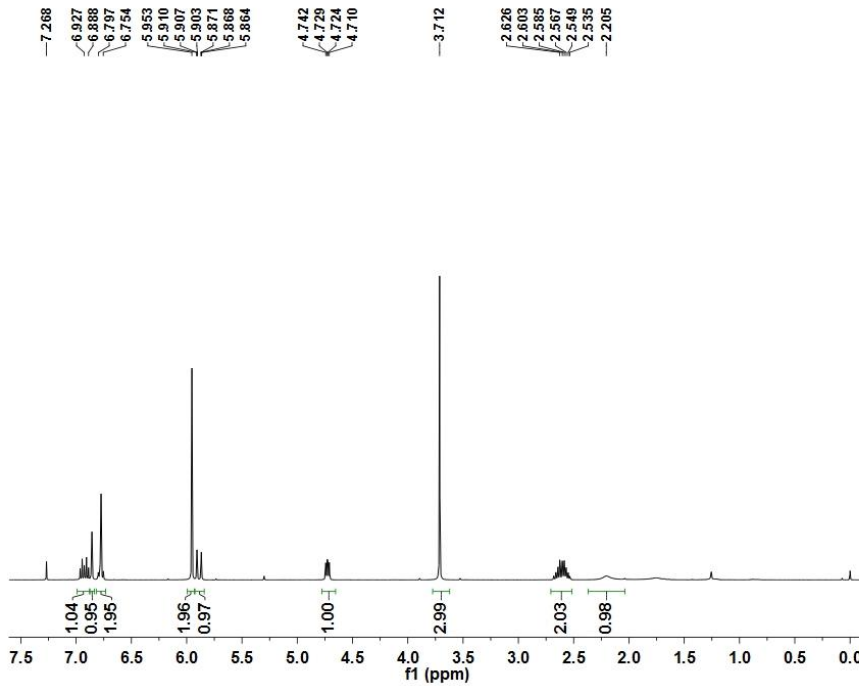
Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-10-05T19:42:31  
 PULPROG: zgpg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 512  
 DS: undefined  
 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 299.1 C

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -79.91  
 Ph1: 76.77

(E)-methyl 5-(benzo[d][1,3]dioxol-5-yl)-5-hydroxypent-2-enoate **3q**



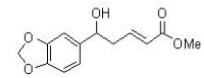
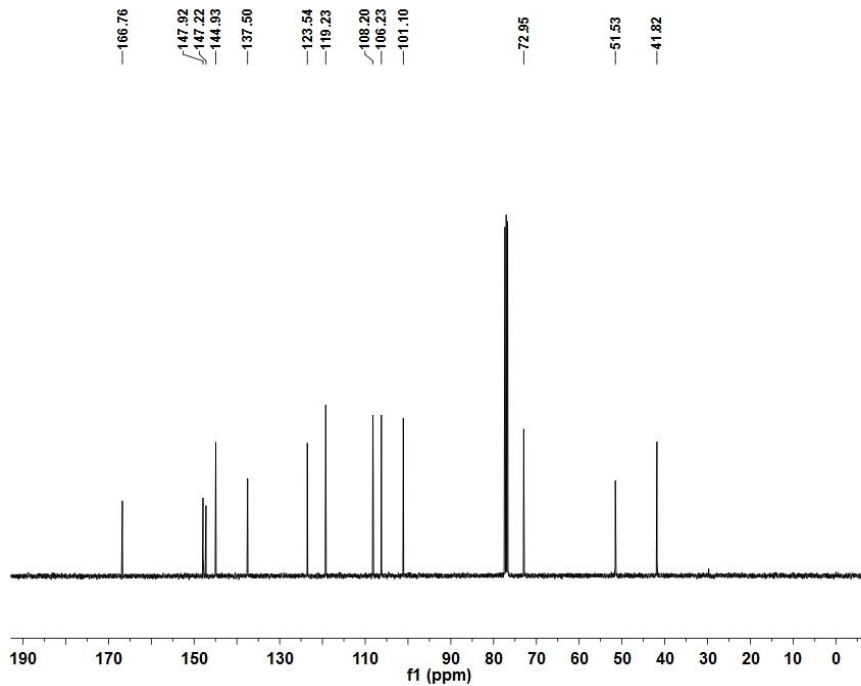
Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-08-26T03:58:11  
 PULPROG: zg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 32  
 DS: undefined  
 SWH: 8223.7 Hz  
 AQ: undefined  
 TE: 297.1 C

===== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 9.93 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 0.30 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -267.83  
 Ph1: 14.82





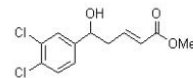
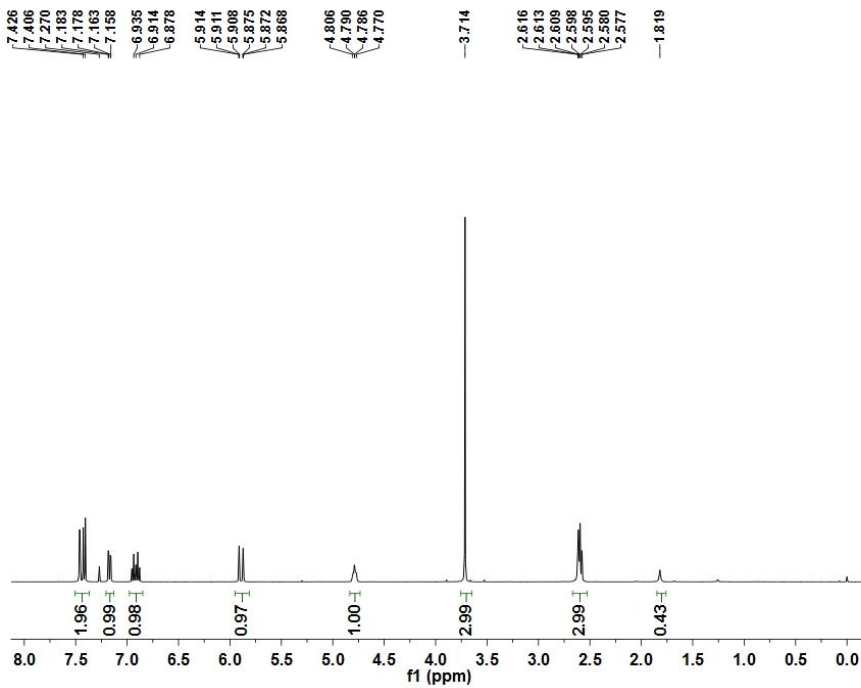
Current Data Parameters

F2 - Acquisition Parameters  
DATE: 2014-08-26T04:28:23  
PULPROG: zgpg30  
TD: 32768  
Solvent: CDCl3  
NS: 512  
DS: undefined  
SWH: 24038.5 Hz  
AQ: undefined  
TE: 297.4 C

CHANNEL f1  
NUC1: 13C  
P1: 9.63 usec  
SFO1: undefined MHz

F2 - Processing Parameters  
SI: 65536  
DC: 0.05  
LB: 1.00 Hz  
First Point: 0.50  
FT: Hyper Quadrature  
Phase: Manual  
Ph0: -75.70  
Ph1: 65.66

(E)-methyl 5-(3,4-dichlorophenyl)-5-hydroxypent-2-enoate **3r**

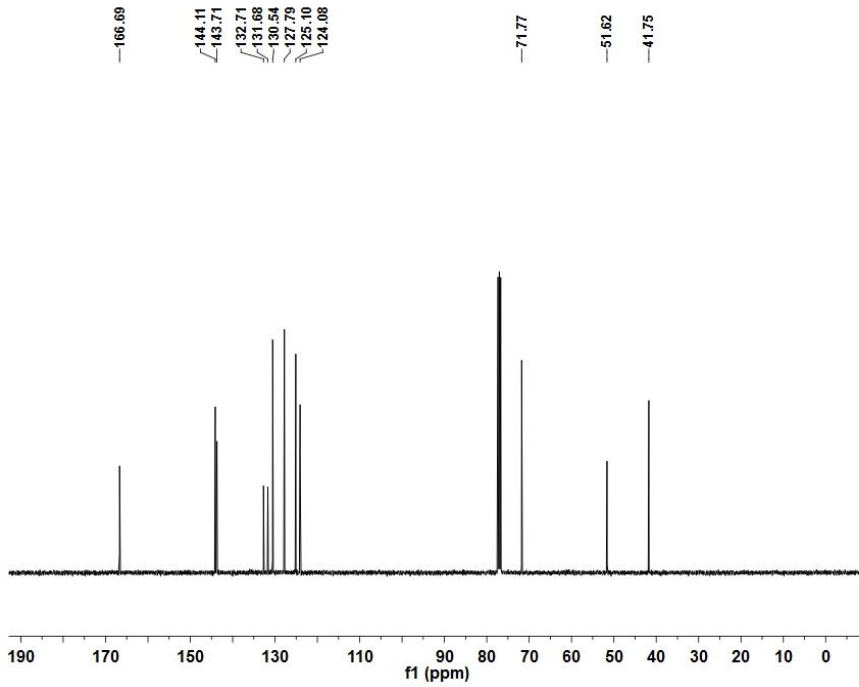


Current Data Parameters

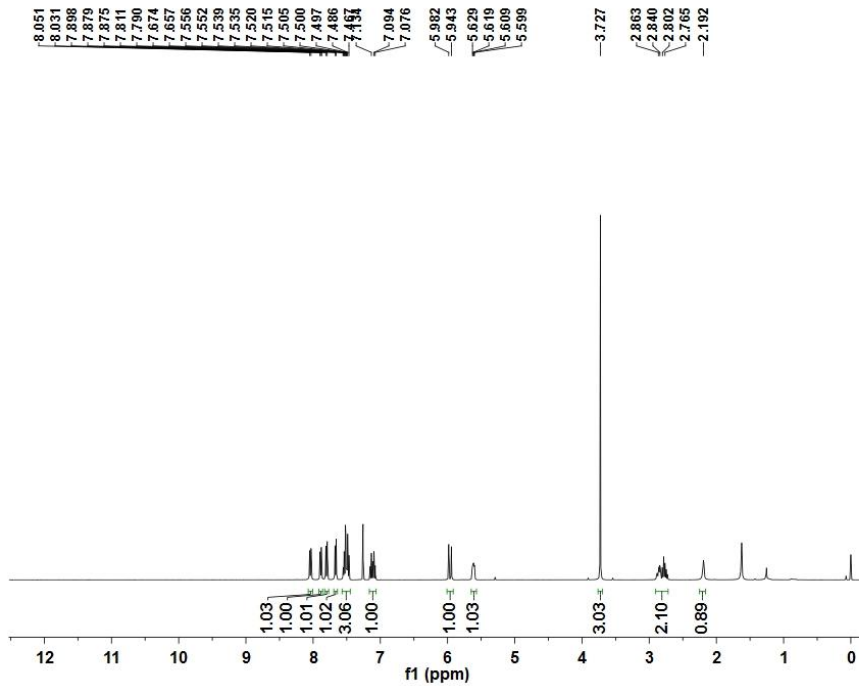
F2 - Acquisition Parameters  
DATE: 2014-07-21T22:43:37  
PULPROG: zg30  
TD: 32768  
Solvent: CDCl3  
NS: 32  
DS: undefined  
SWH: 8223.7 Hz  
AQ: undefined  
TE: 300.4 C

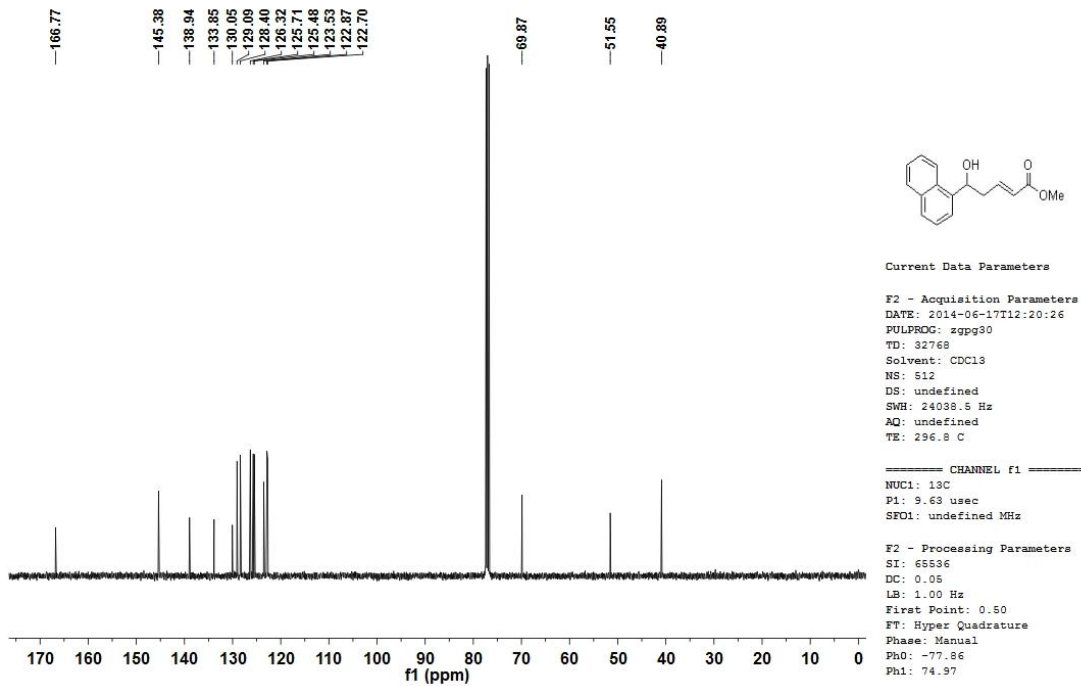
CHANNEL f1  
NUC1: 1H  
P1: 9.93 usec  
SFO1: undefined MHz

F2 - Processing Parameters  
SI: 65536  
DC: 0.05  
LB: 0.30 Hz  
First Point: 0.50  
FT: Hyper Quadrature  
Phase: Manual  
Ph0: 81.86  
Ph1: 23.46

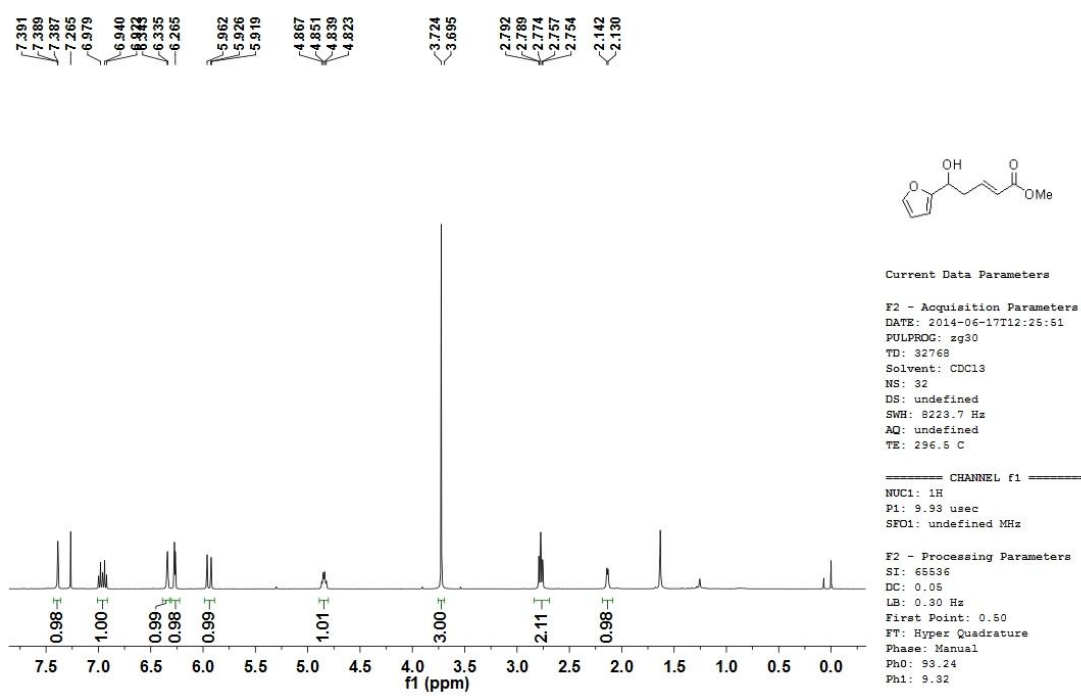


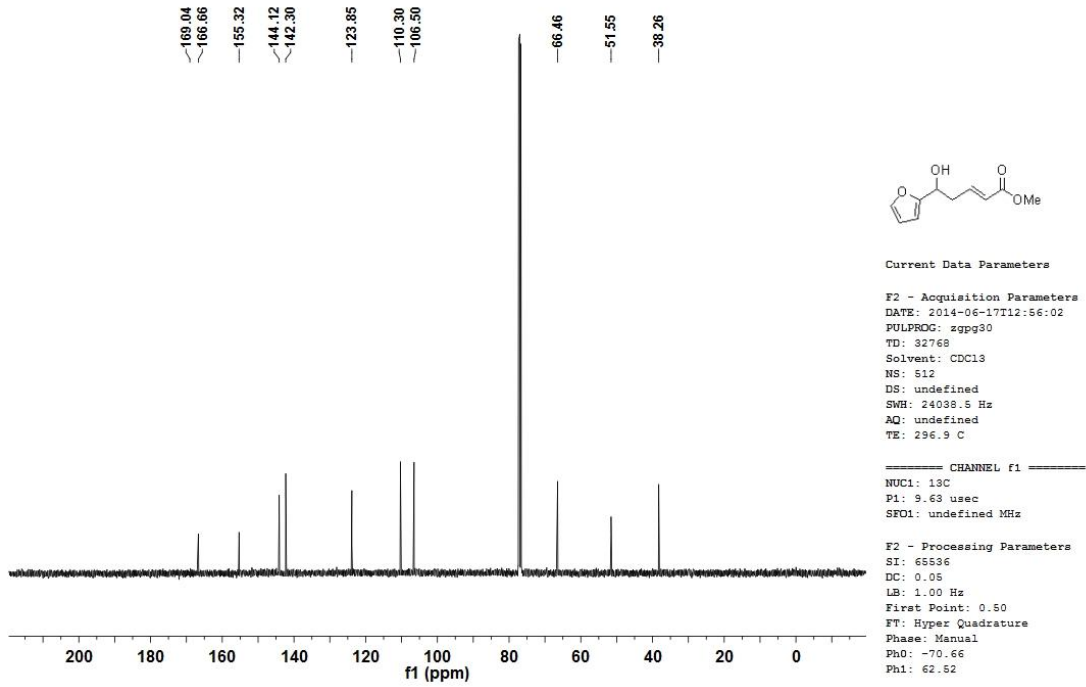
(E)-methyl 5-hydroxy-5-(naphthalen-1-yl)pent-2-enoate 3s



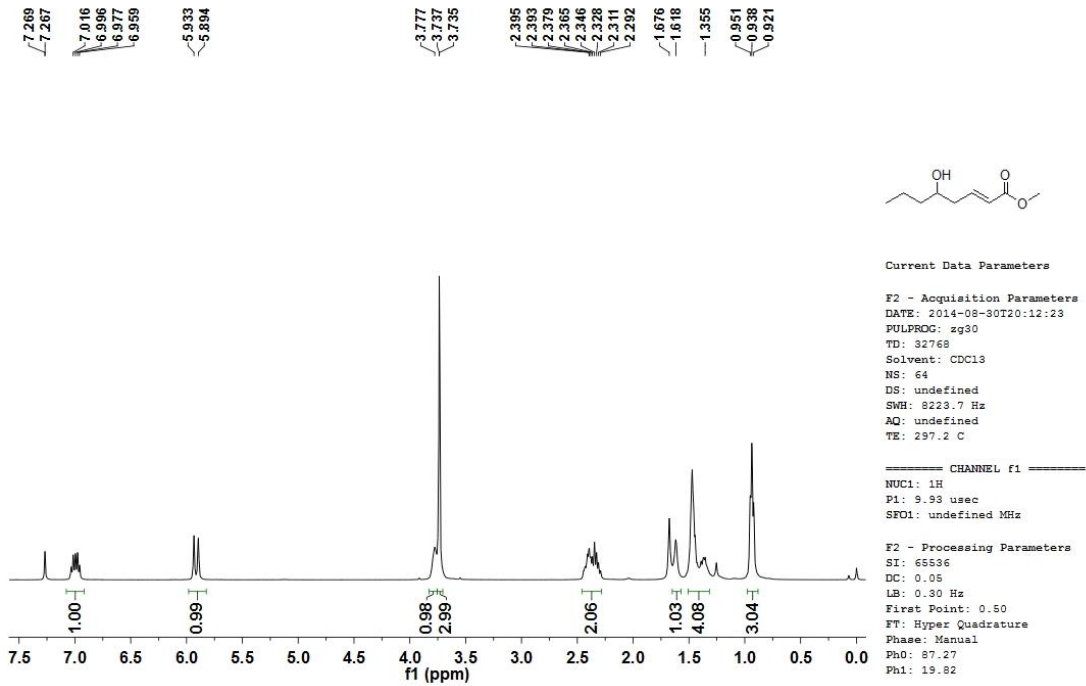


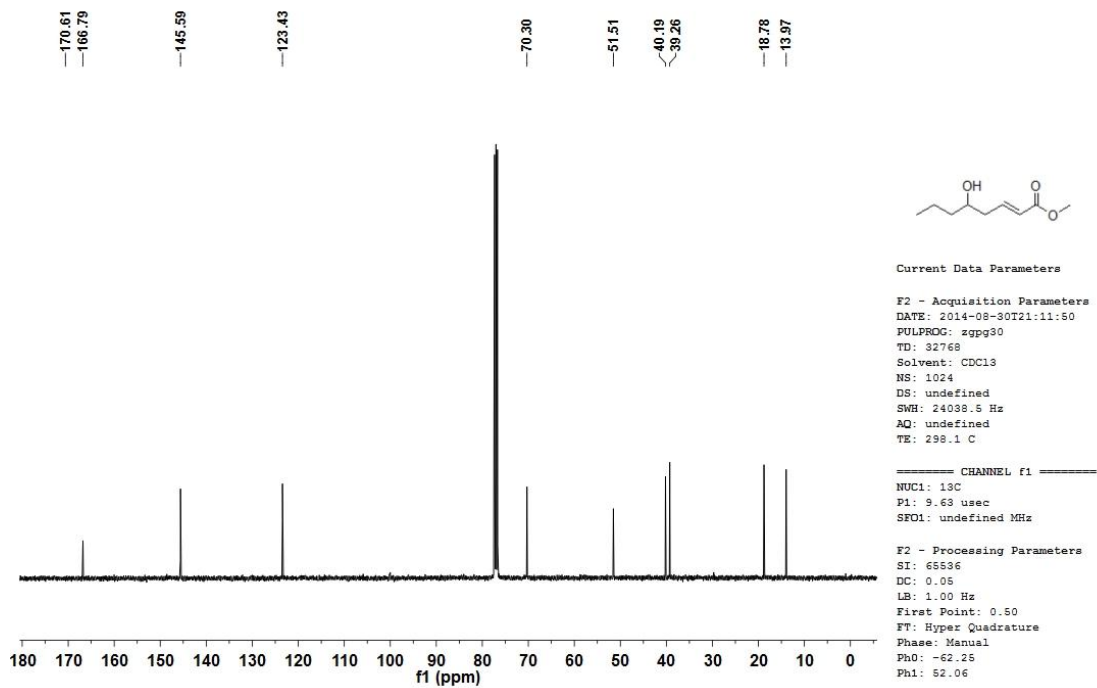
(S,E)-methyl 5-(furan-2-yl)-5-hydroxypent-2-enoate **3t**



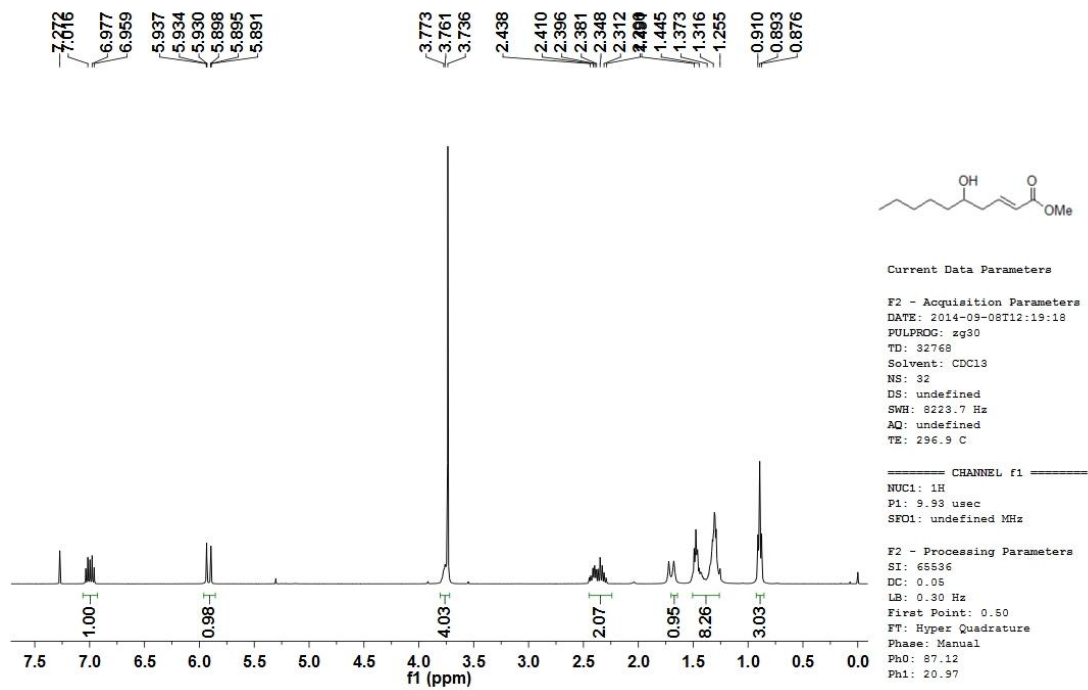


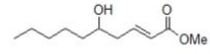
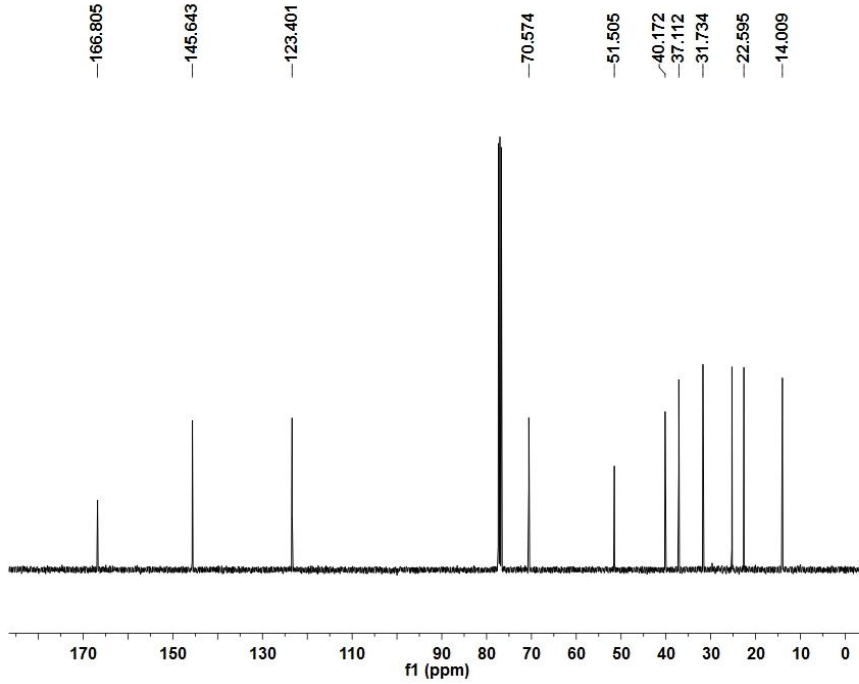
(E)-methyl 5-hydroxyoct-2-enoate **3u**





(*S,E*)-methyl 5-hydroxydec-2-enoate **3v**





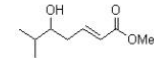
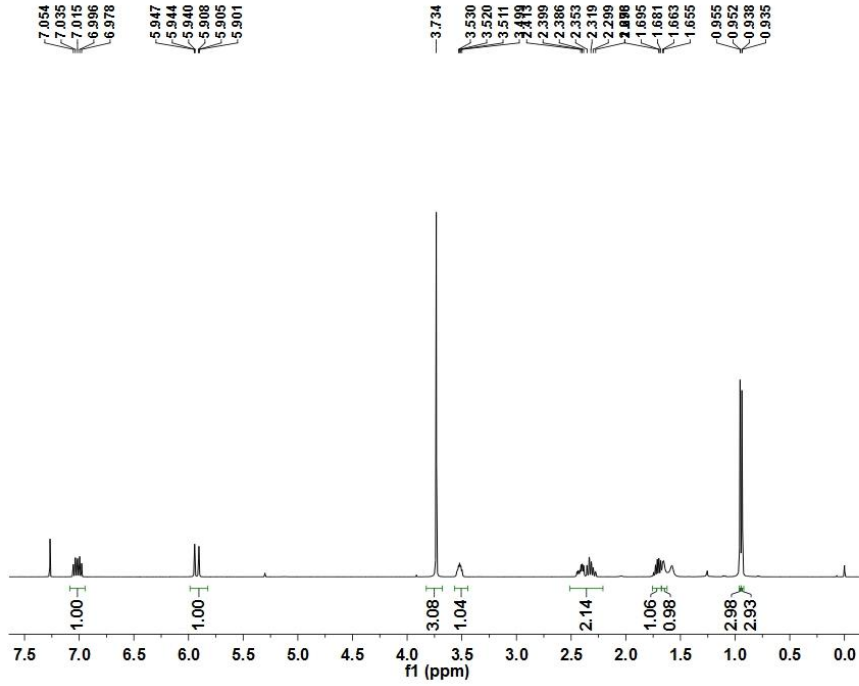
Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-09-08T12:49:30  
 PULPROG: zgpg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 512  
 DS: undefined  
 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 297.3 C

==== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -64.67  
 Ph1: 55.31

(*S,E*)-methyl 5-hydroxy-6-methylhept-2-enoate **3w**

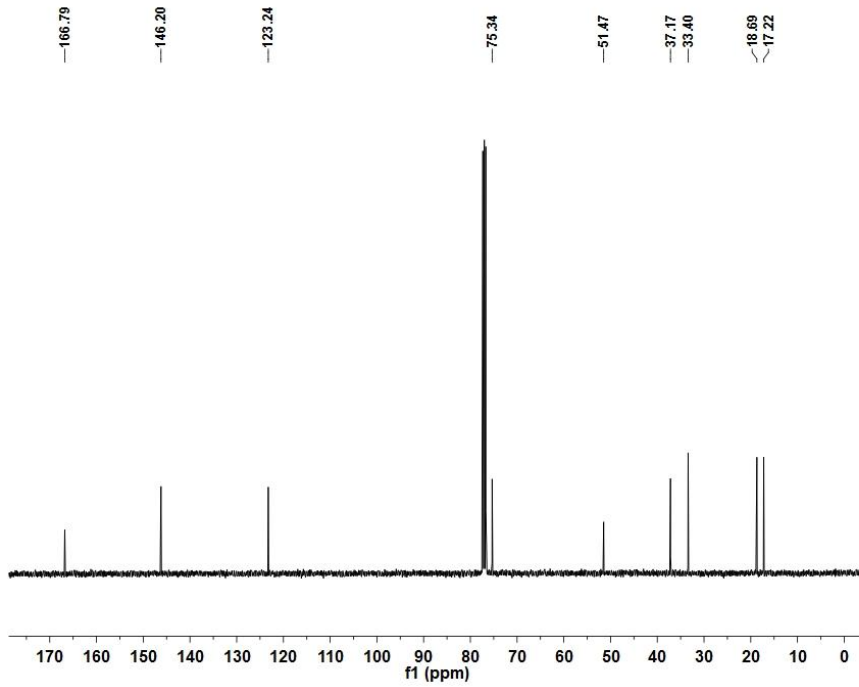


Current Data Parameters

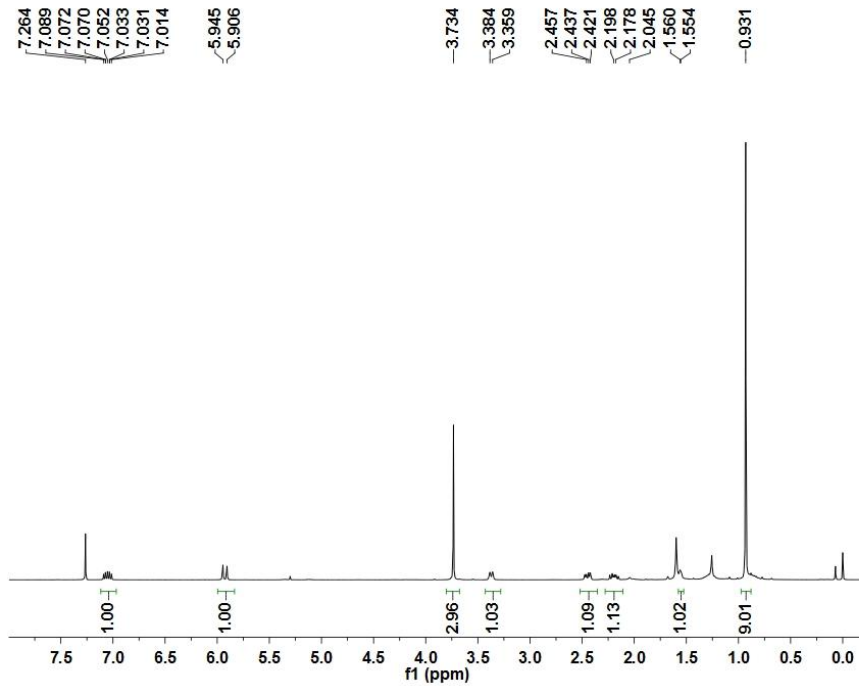
F2 - Acquisition Parameters  
 DATE: 2014-07-21T23:19:50  
 PULPROG: zg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 32  
 DS: undefined  
 SWH: 8223.7 Hz  
 AQ: undefined  
 TE: 300.3 C

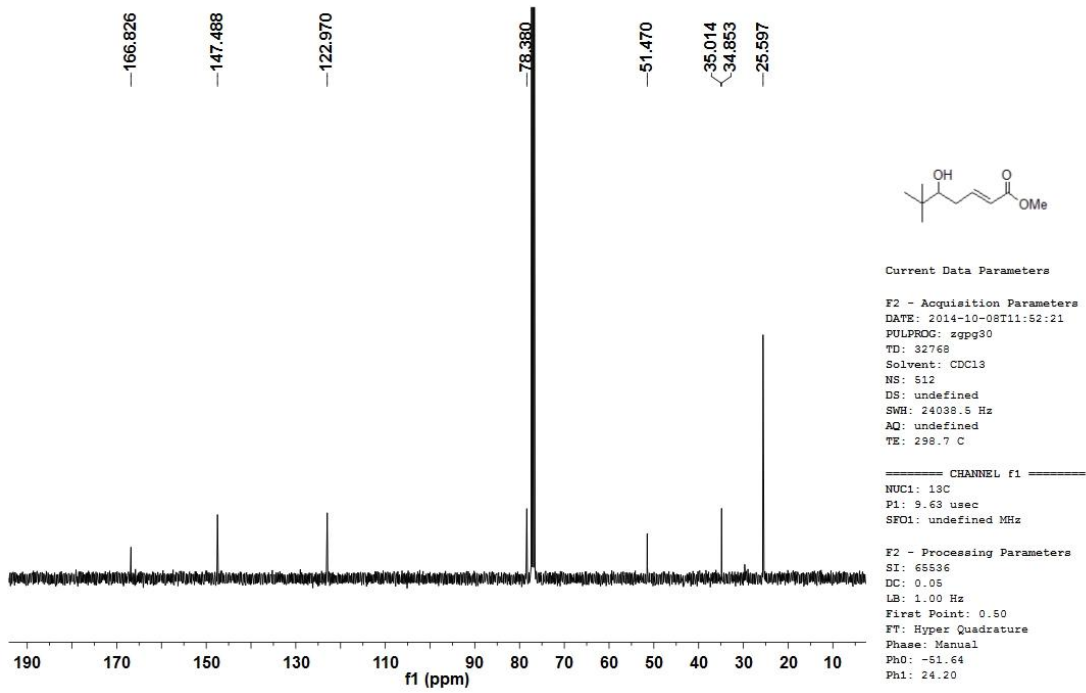
==== CHANNEL f1 =====  
 NUC1: 1H  
 P1: 9.93 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 0.30 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: 81.89  
 Ph1: 20.48

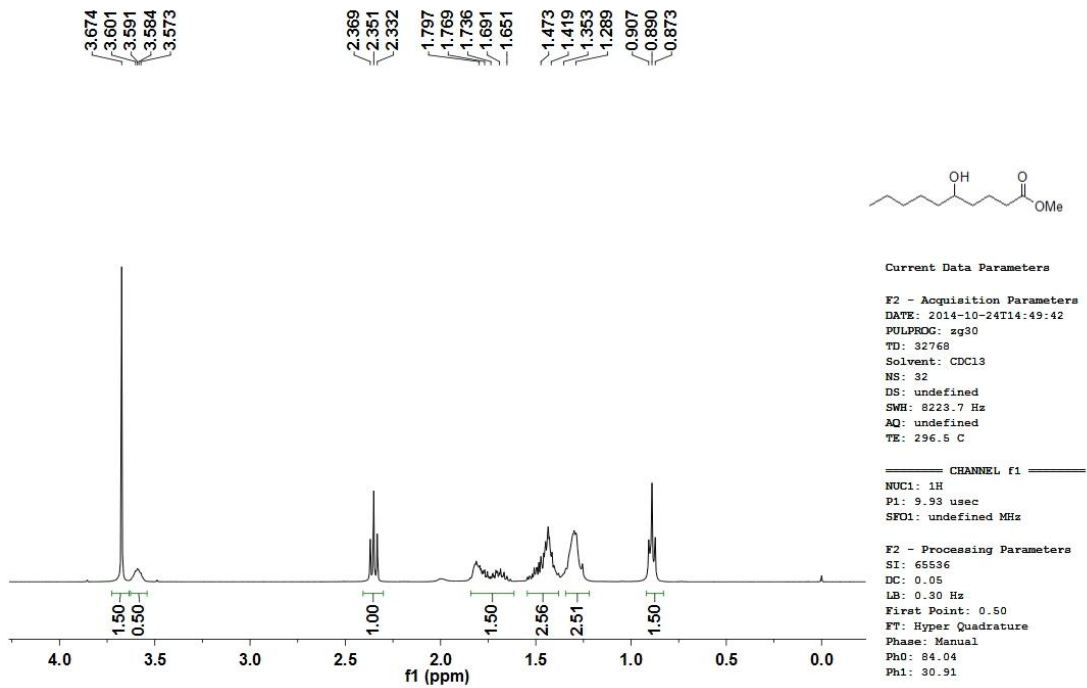


(*S,E*)-methyl 5-hydroxy-6,6-dimethylhept-2-enoate **3x**

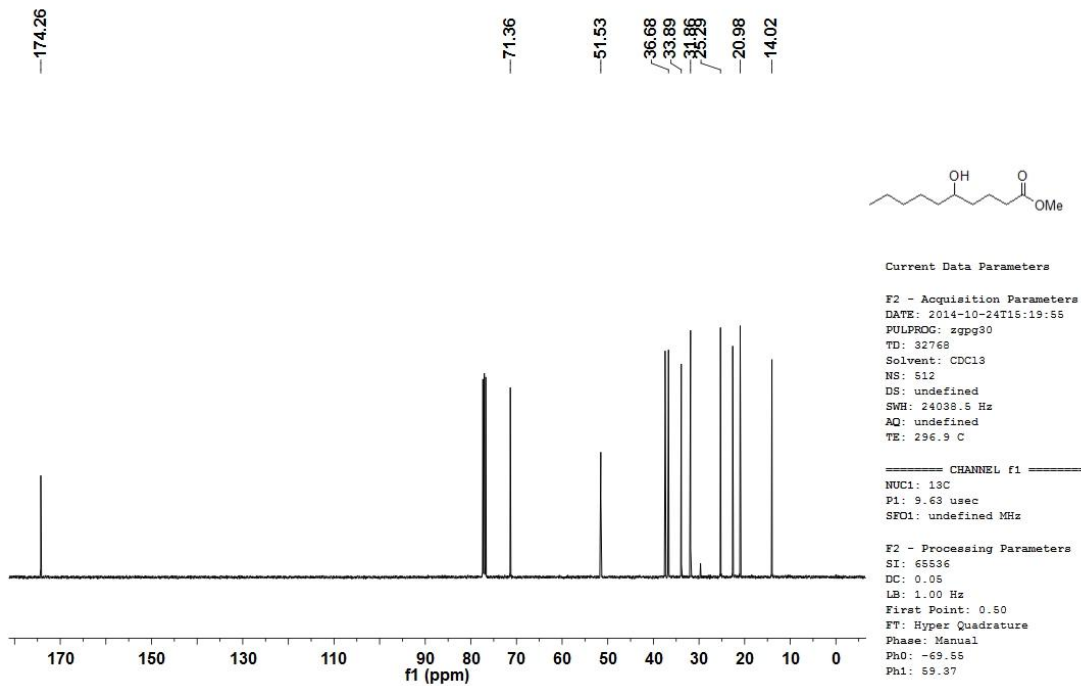




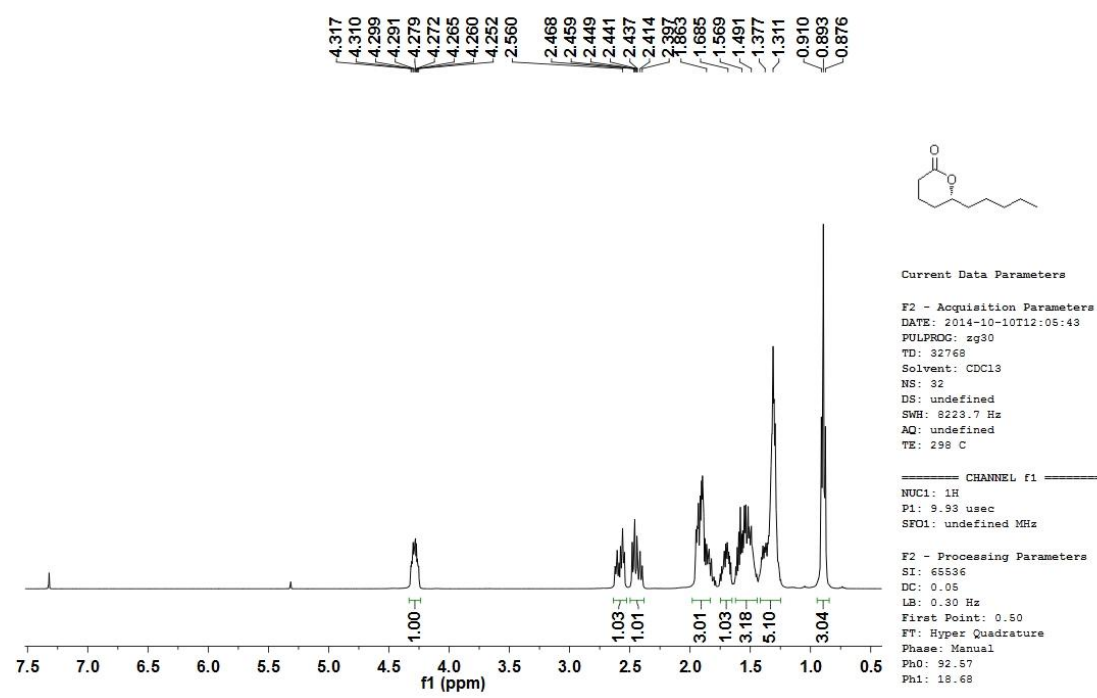
methyl 5-hydroxydecanoate **5v**

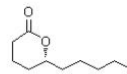
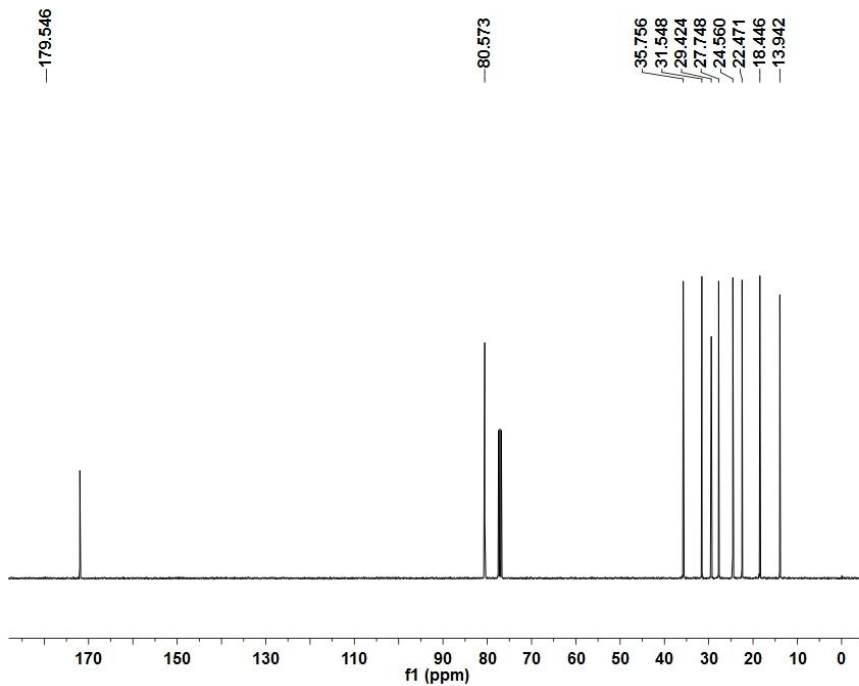






(R)-6-pentyltetrahydro-2H-pyran-2-one **6v**





Current Data Parameters

F2 - Acquisition Parameters  
 DATE: 2014-10-10T12:36:08  
 PULPROG: zgpg30  
 TD: 32768  
 Solvent: CDCl3  
 NS: 512  
 DS: undefined  
 SWH: 24038.5 Hz  
 AQ: undefined  
 TE: 298.3 C

===== CHANNEL f1 =====  
 NUC1: 13C  
 P1: 9.63 usec  
 SFO1: undefined MHz

F2 - Processing Parameters  
 SI: 65536  
 DC: 0.05  
 LB: 1.00 Hz  
 First Point: 0.50  
 FT: Hyper Quadrature  
 Phase: Manual  
 Ph0: -61.61  
 Ph1: 58.46