*Electronic Supplementary Information (ESI) for*

# A Thermoregulated Phase-Separable Chiral Pt Nanocatalyst for Recyclable Asymmetric Hydrogenation of α-Ketoesters

Xiuru Xue,[a] Yanhua Wang*,[a] and Fu-She Han*,[b]

[a] State Key Laboratory of Fine Chemical, Dalian University of Technology, Dalian 116024, China.
[b] Key Lab of Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun 130022, China.

* Corresponding author. *E-mail: yhuawang@dlut.edu.cn; fshan@ciac.ac.cn.

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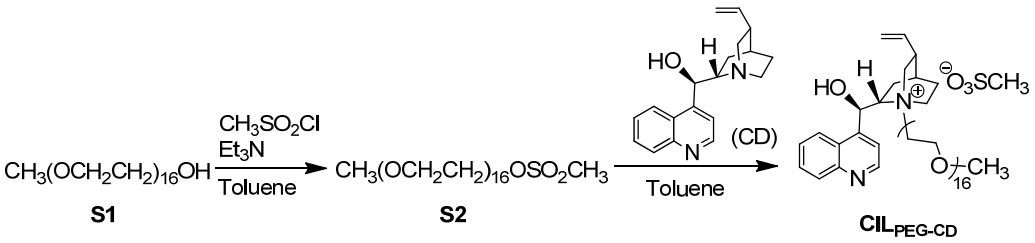
# 1. General Information

Unless otherwise noted, all chemicals were purchased from commercial sources without further purification. $PtCl_4$ (57.6% Pt) was purchased from Japan. Cinchonidine (CD, 99%), polyethylene glycol monoethylether ($CH_3(OCH_2CH_2)_{16}OH$), ethyl pyruvate (98%), methyl pyruvate (98%), ethyl benzoylformate (98%) and ethyl 3-methyl-2-oxobutanoate (97%) were from Alfa Aesar. Ethyl 2-oxobutanoate (95%), ethyl 2-oxopentanoate (95%), ethyl 4-methyl-2-oxopentanoate (95%), ethyl 2-oxohexanoate (96%) were purchased from Ark. Methyl 4-methyl-2-oxopentanoate (95%) was from Accela. Pyruvic acid (*Z*)-3-hexenyl ester (95%) and pyruvic acid were from TCI. Ethyl 2-oxo-4-phenylbutyrate (92%) and cinchonidine dihydrochloride (98%) were from Aladdin. Isoamyl pyruvate (97%), methyl 2-oxobutanoate (98%), ethyl 4-methylbenzoylformate (96%), ethyl 3-chlorobenzoylformate (96%), methyl 3-methyl-2-oxobutanoate (96%), methyl benzoylformate (99%) and ethyl 3-methoxybenzoylformate (97%) were purchased from J&K Chemical. Dihydro-4,4-dimethyl-2,3-furandione (97%) was from Sigma-Aldrich. Methylsulfonyl chloride and allyl alcohol were supplied from Sinopharm Chemical Reagent Co.Ltd. Other solvents, such as toluene, triethylamine, glacial acetic acid, *n*-heptane, cyclohexane and anhydrous diethyl ether were analytical reagents and purchased from Kermel. Pyruvic acid allyl ester was synthesized as reported.[1] NMR were recorded on a Varian (400 MHz and 100 MHz). Chemical shifts (δ) are denoted in ppm using residual solvent peaks as internal standard ($CDCl_3$: 7.26 ppm for $^1H$ NMR; 77.16 ppm for $^{13}C$ NMR); coupling constants (*J*) are reported in Hz. Chiral GC analyses were carried out on Fuli 9790 GC instrument equipped with an Agilent CP-Chirasil-Dex (25 m × 0.25 mm × 0.25 μm) and an FID detector ($N_2$ as a carrier gas). Transmission electron microscopic analyses (TEM) were carried out by using a Tecnai $G^2$ 20 S-TWIN (200 kV) instrument. Inductively coupled plasma atomic emission spectrometer (ICP-AES) was performed on Optima 2000 DV (detection limit is 5 ppm).

# 2. Experiment Procedures

### 2.1 Synthesis of $CIL_{PEG\text{-}CD}$




**S1** **S2** $\mathbf{CIL_{PEG\text{-}CD}}$

To a toluene (50 mL) solution of polyethylene glycol monomethylether **S1** (n = 16, 0.01 mol) and triethylamine (0.01 mol) was added dropwise the methylsulfonyl chloride (0.01 mol) under the cooling of an ice-water bath. The reaction mixture was stirred overnight at room temperature. The resulting mixture was filtered to remove the triethylamine hydrochloride precipitate, and the filtrate was concentrated under reduced pressure. The residue was dried under vacuum to remove the volatile materials to give a white waxy solid **S2** which was used directly without purification. To a toluene solution (60 mL) of crude **S2** was added cinchonidine (CD, 0.012 mol). The mixture was refluxed for 30 h. After being cooled to 10 °C, the excess CD was removed by filtration. The organic filtrate was extracted with anhydrous diethyl ether (60 mL × 3) to remove possible byproducts. The claret slurry was then dried under vacuum to afford the chiral ionic liquid $CIL_{PEG\text{-}CD}$ as viscous liquid in 89% yield.

### 2.2 Preparation of chiral Pt nanoparticles

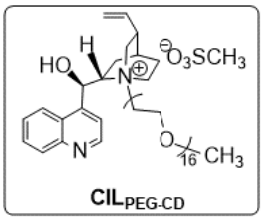
As a typical example, a mixture of $PtCl_4$ (0.6 mg, 1.78 × $10^{-3}$ mmol) and $CIL_{PEG\text{-}CD}$ (10 mg, 8.90 × $10^{-3}$ mmol) was added to a 75 mL stainless-steel autoclave. The autoclave was flushed for three times with 2.0 MPa $H_2$ and then inflated to 4.0 MPa with $H_2$. After being stirred at 80 ºC for 8 h, the reactor was cooled to room temperature and depressurized. The color of the mixture changed from claret to black, indicative of the formation of chiral Pt nanoparticles. The preparation of other Pt nanocatalyst with different ratios of $CIL_{PEG\text{-}CD}$ to Pt was carried out according to the same procedure.

**2.3 Asymmetric hydrogenation of α-ketoesters:**

**The asymmetric hydrogenation of ethyl pyruvate was used as a representative**: To a 75 ml stainless-steel autoclave charged with chiral Pt nanoparticles as prepared above (10 mg, containing 1.78 × $10^{-3}$ mmol Pt) was added $CIL_{PEG\text{-}CD}$ (20 mg), toluene (1.0 g), *n*-heptane (0.3 g), and glacial acetic acid (1.3 g), cyclohexane (50 mg, internal standard). The mixture was stirred for 30 min at room temperature, and then ethyl pyruvate (52 mg, substrate/Pt = 250:1) was added. The autoclave was flushed three times with 2.0 MPa $H_2$, and then was pressurized with $H_2$ up to an appointed pressure at a scheduled temperature under stirring. After the completion of reaction, the autoclave was depressurized and cooled in an ice-water bath to ensure a complete phase separation. The lower phase containing the chiral nanoparticles was separated simply by phase separation and reused in the next cycle. The upper phase was directly analyzed by chiral GC, and the optical yield was expressed as the enantiomeric excess (ee) of R-(+)-enantiomer:

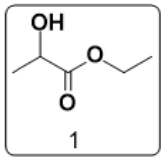
ee (%) = ([R] - [S]) / ([R] + [S]) × 100.

## 3. Characterization Data of products



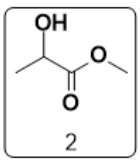

$CIL_{PEG\text{-}CD}$

**$CIL_{PEG\text{-}CD}$:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 8.56 (1H, d, *J* = 8.8 Hz), 8.17 (1H, dd, *J* = 8.7, 3.2 Hz), 7.95 (1H, dd, *J* = 8.7, 3.2 Hz), 7.76 (1H, m), 7.59 (1H, m), 7.38 (1H, d, *J* = 8.8 Hz), 5.70 (1H, m), 5.12 (1H, s), 5.07-5.02 (2H, m), 4.05 (1H, m), 3.83 (2H, q, *J* = 7.0 Hz), 3.68 (1H, s), 3.54-3.12 (72H, m), 2.78 (1H, m), 1.80 (2H, m), 1.50 (3H, m); $^{13}$C NMR (100 MHz, $CDCl_3$) δ = 149.8, 148.5, 138.3, 130.3, 128.5, 126.9, 121.7, 119.2, 118.5, 80.4, 71.6, 70.4, 68.5, 65.8, 63.8, 62.7, 58.8, 53.2, 38.9, 28.3, 26.4, 23.9.



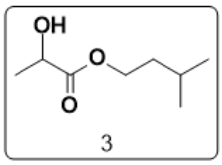

1

**Ethyl pyruvate 1:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.24 (1H, q, *J* = 7.1 Hz), 4.18 (2H, q, *J* = 7.1 Hz), 3.09 (1H, brs), 1.35 (3H, d, *J* = 7.1 Hz), 1.23 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[2]



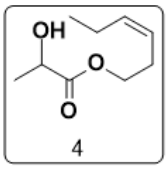

2

**Methyl pyruvate 2:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.26 (1H, q, *J* = 7.1 Hz), 3.76 (3H, s), 3.23 (1H, s), 1.39 (3H, d, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[3]



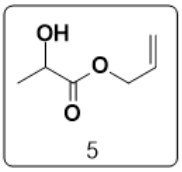

3

**Isoamyl pyruvate 3:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.20 (2H, t, *J* = 7.1 Hz), 4.18 (1H, q, *J* = 7.1 Hz), 2.96 (1H, s), 1.67 (1H, m), 1.55 (2H, m), 1.39 (3H, d, *J* = 7.1 Hz), 0.92 (6H, d, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[4]



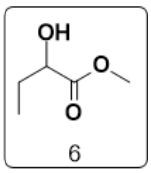
4

**Pyruvic acid (*Z*)-3-hexenyl ester 4:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 5.53 (1H, m), 5.32 (1H, m), 4.26 (1H, q, *J* = 7.1 Hz), 4.18 (2H, t, *J* = 7.1 Hz), 2.91 (1H, s), 2.43 (2H, m), 2.06 (2H, m), 1.39 (3H, d, *J* = 7.1 Hz), 0.93 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[4]



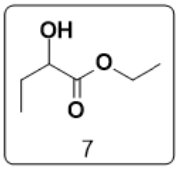
5

**Pyruvate allyl ester 5:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 6.05 (1H, m), 5.42 (1H, dd, *J* = 17.2, 2.4 Hz), 5.27 (1H, dd, *J* = 10.4, 2.4 Hz), 4.75 (2H, d, *J* = 7.1 Hz), 4.29 (1H, q, *J* = 7.1 Hz), 1.36 (3H, d, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[5]



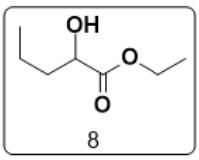
6

**Methyl 2-oxobutanoate 6:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.17 (1H, t, *J* = 6.0 Hz), 3.75 (3H, s), 2.84 (1H, s), 1.90 (2H, m), 0.93 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[3]



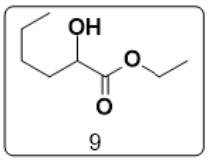
7

**Ethyl 2-oxobutanoate 7:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.36 (2H, q, *J* = 7.1 Hz), 4.17(1H, t, *J* = 6.0 Hz), 2.84 (1H, s), 1.90 (2H, m), 1.32 (3H, t, *J* = 7.1 Hz), 0.93 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[2]



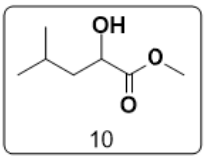
8

**Ethyl 2-oxopentanoate 8:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.36 (2H, q, *J* = 7.1 Hz), 4.17 (1H, t, *J* = 6.0 Hz), 2.84 (1H, s), 1.90 (2H, m), 1.38 (5H, m), 0.93 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[6]



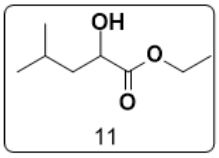
9

**Ethyl 2-oxohexanoate 9:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.26 (2H, q, *J* = 7.1 Hz), 4.06 (1H, t, *J* = 6.0 Hz), 2.84 (1H, s), 1.83 (2H, m), 1.24-1.35 (7H, m), 0.93 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[7]



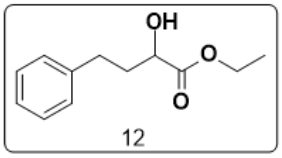
10

**Methyl 4-methyl-2-oxopentanoate 10:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.06 (1H, t, *J* = 6.0 Hz), 3.68 (3H, s), 2.86 (1H, s), 1.80 (2H, dd, *J* = 6.0, 3.5 Hz), 1.63 (1H, m), 0.93 (6H, d, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[3]



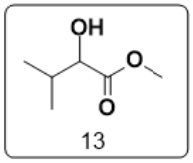
11

**Ethyl 4-methyl-2-oxopentanoate 11:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.32 (2H, q, *J* = 7.1 Hz), 4.06 (1H, t, *J* = 6.0 Hz), 3.06 (1H, s), 1.79 (2H, dd, *J* = 6.0, 3.5 Hz), 1.63 (1H, m), 1.32 (3H, t, *J* = 7.1 Hz), 0.93 (6H, d, *J* = 6.0 Hz). The $^1$H NMR data were consistent with those reported.[8]



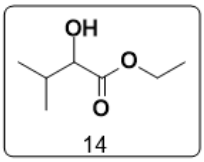
12

**Ethyl 2-oxo-4-phenylbutyrate 12:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.32 (2H, m), 7.24 (3H, m), 4.24 (2H, q, *J* = 7.1 Hz), 4.23 (1H, t, *J* = 6.0 Hz), 2.94 (1H, s), 2.82 (2H, m), 2.16 (1H, m),1.99 (1H, m), 1.32 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[9]



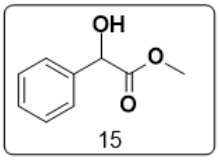
13

**Methyl 3-methyl-2-oxobutanoate 13:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.06 (1H, d, *J* = 3.6 Hz), 3.68 (3H, s), 2.83 (1H, s), 2.56 (1H, m), 0.93 (6H, d, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[3]



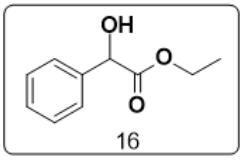
14

**Ethyl 3-methyl-2-oxobutanoate 14:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.26 (2H, q, *J* = 7.1 Hz), 4.03 (1H, d, *J* = 3.6 Hz), 2.83 (1H, s), 2.54 (1H, m), 1.23 (3H, t, *J* = 7.1 Hz), 0.93 (6H, d, *J* = 7.0 Hz). The $^1$H NMR data were consistent with those reported.[7]



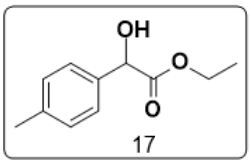
15

**Methyl benzoylformate 15:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.45 (2H, m), 7.36 (3H, m), 5.18 (1H, d, *J* = 6.0 Hz), 3.77 (3H, s), 3.42 (1H, d, *J* = 6.0 Hz). The $^1$H NMR data were consistent with those reported.[3]



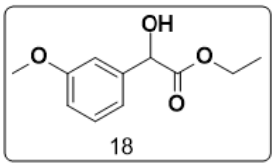
16

**Ethyl benzoylformate 16:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.43 (2H, m), 7.32 (3H, m), 5.18 (1H, s), 4.25 (2H, q, *J* = 7.1 Hz) , 3.70 (1H, s), 1.29 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[7]



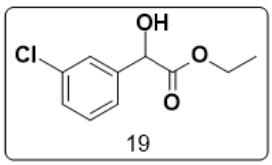
17

**Ethyl 4-methylbenzoylformate 17:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.25 (2H, d, *J* = 8.0 Hz), 7.19 (2H, d, *J* = 8.0 Hz), 5.24 (1H, s), 4.24 (2H, q, *J* = 7.1 Hz), 3.65 (1H, s), 2.36 (3H, s), 1.29 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[7]



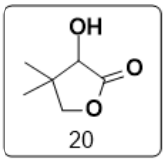
18

**Ethyl 3-methoxybenzoylformate 18:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.25 (1H, t, *J* = 8.0 Hz), 7.14 (1H, t, *J* = 3.2 Hz), 6.93 (2H, dd, *J* = 8.0, 3.2 Hz), 5.34 (1H, s), 4.23 (2H, q, *J* = 7.1 Hz), 3.84 (3H, s), 3.66 (1H, br, *J* = 5.7 Hz), 1.31 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[9]



19

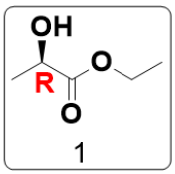
**Ethyl 3-chlorobenzoylformate 19:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.56 (1H, t, *J* = 3.1 Hz), 7.45 (1H, dt, *J* = 8.0, 3.1 Hz), 7.37 (1H, t, *J* = 8.0 Hz), 7.24 (1H, dt, *J* = 8.0, 3.1 Hz), 5.35 (1H, s), 4.23 (2H, q, *J* = 7.1 Hz), 3.65 (1H, s), 1.31 (3H, t, *J* = 7.1 Hz). The $^1$H NMR data were consistent with those reported.[7]

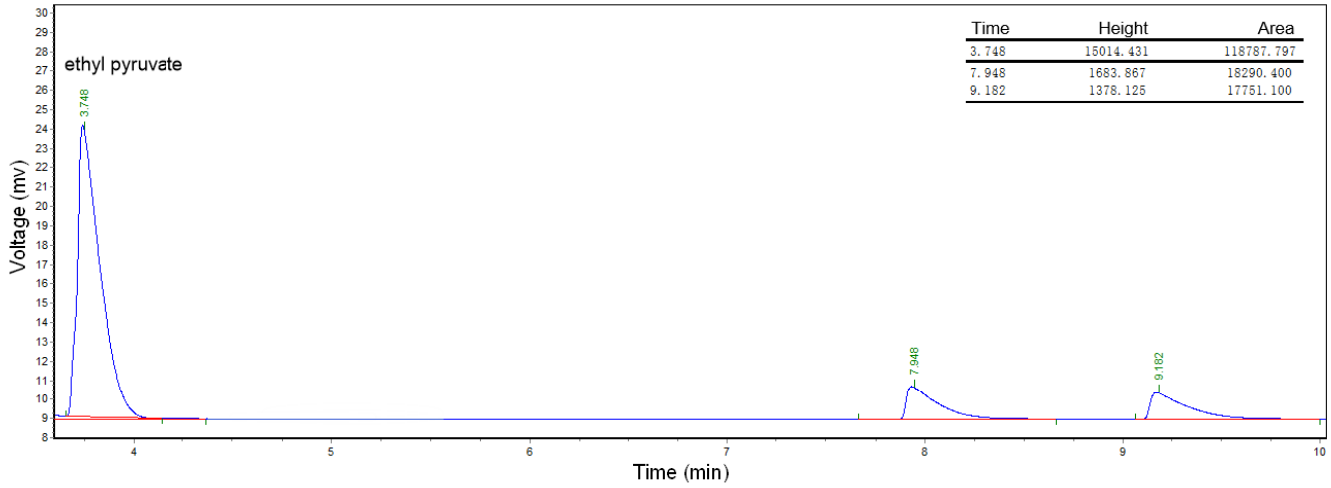


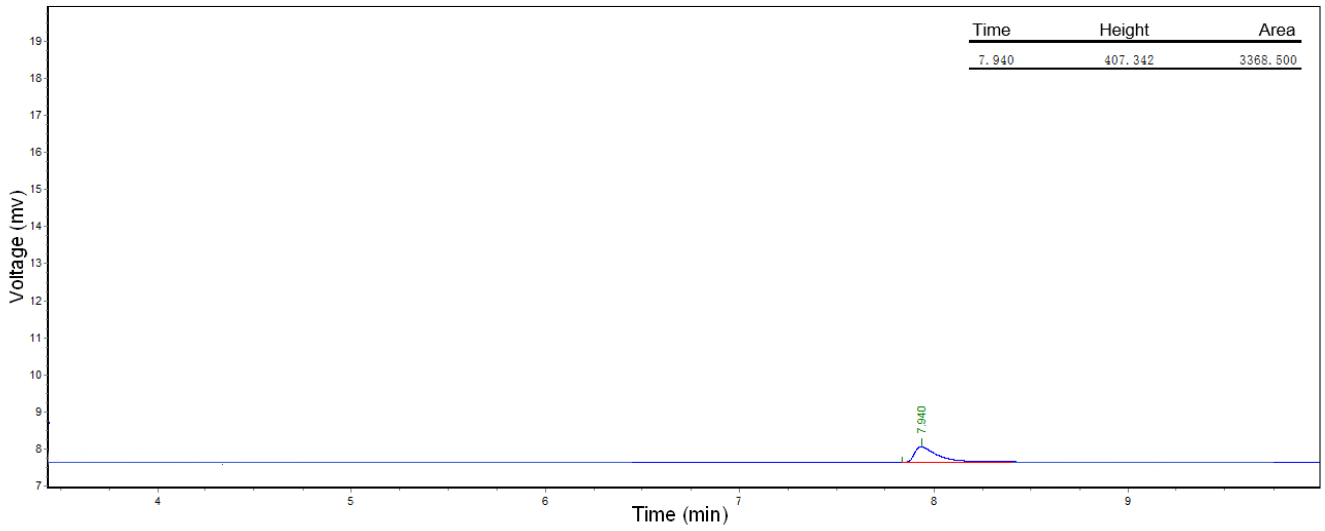
20

**Dihydro-4,4-dimethyl-2,3-furandione 20:** $^1$H NMR (400 MHz, $CDCl_3$) δ = 4.11 (1H, s), 4.03 (1H, d, *J* = 9.0 Hz), 3.94 (1H, d, *J* = 9.0 Hz), 2.67 (1H, s), 1.24 (3H, s), 1.03 (3H, s). The $^1$H NMR data were consistent with those reported.[7]

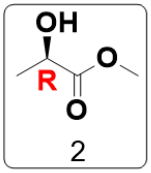
## 4. GC Charts




GC analytical conditions for **1**: The temperature of gasify room, column, and detector were 200 °C, 70 °C, and 200 °C respectively.

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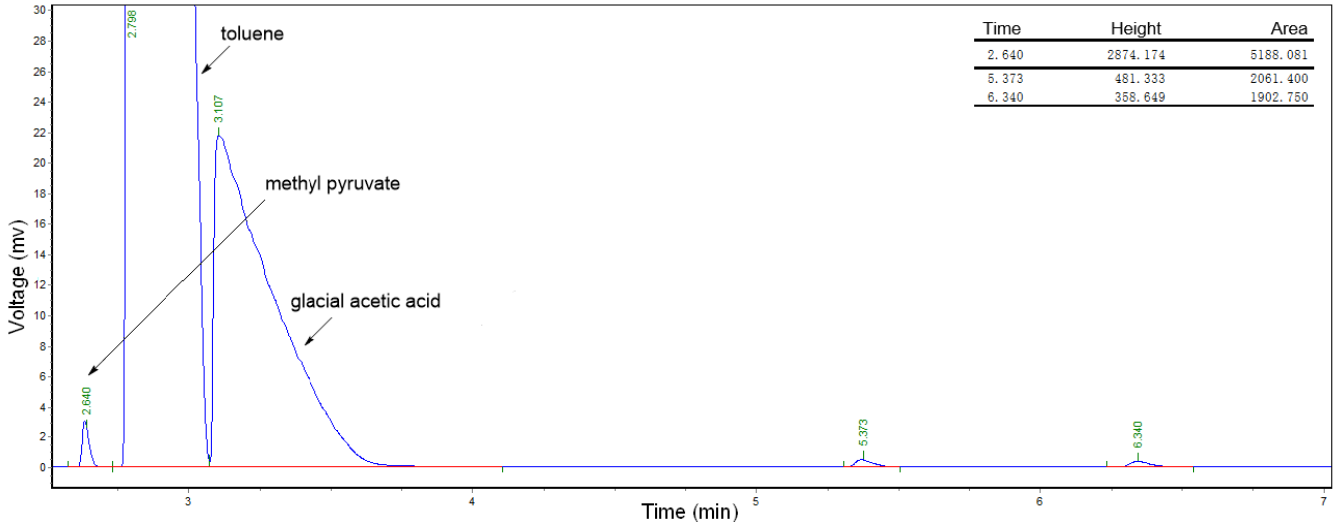
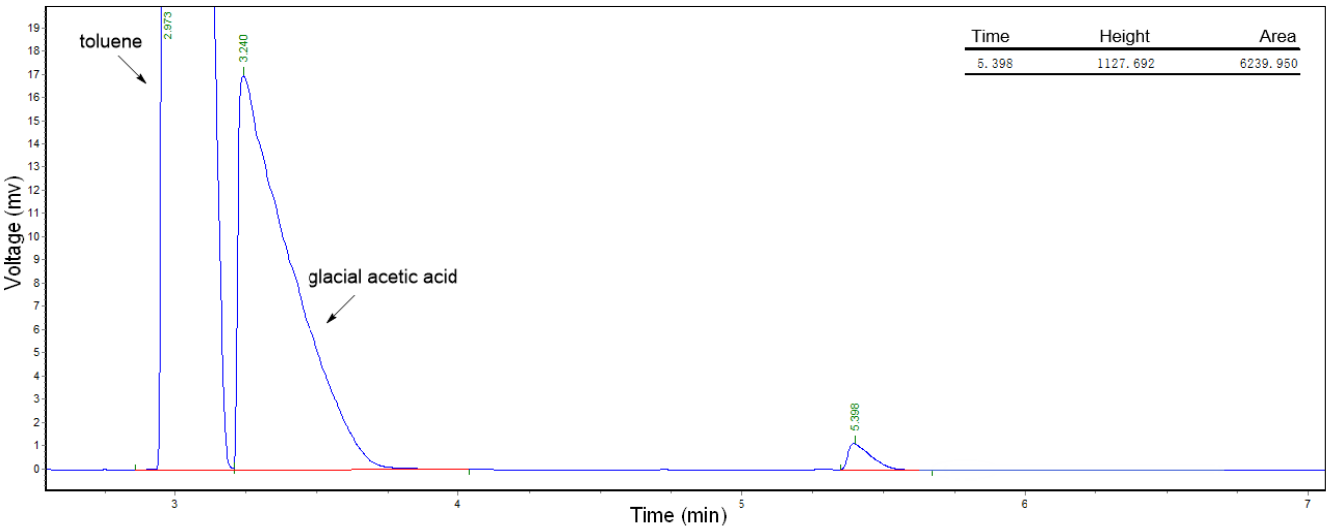
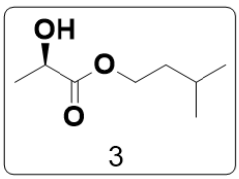



GC GC analytical conditions for **2**: The temperature of gasify room, column, and detector were 200 °C, 70 °C, and 200 °C respectively.

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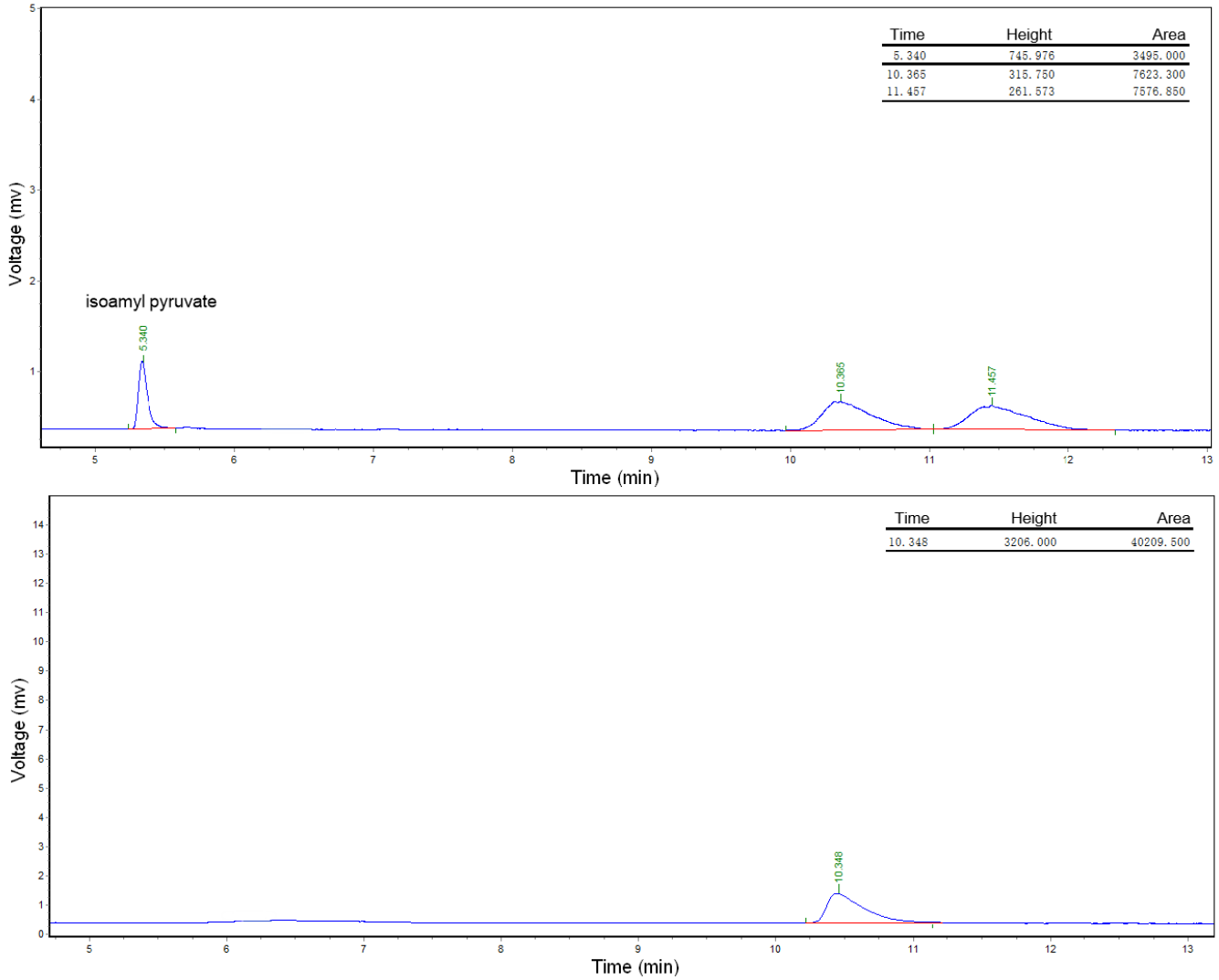
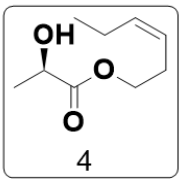



GC analytical conditions for **3**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 80 $^{o}$C, and 200 $^{o}$C respectively.

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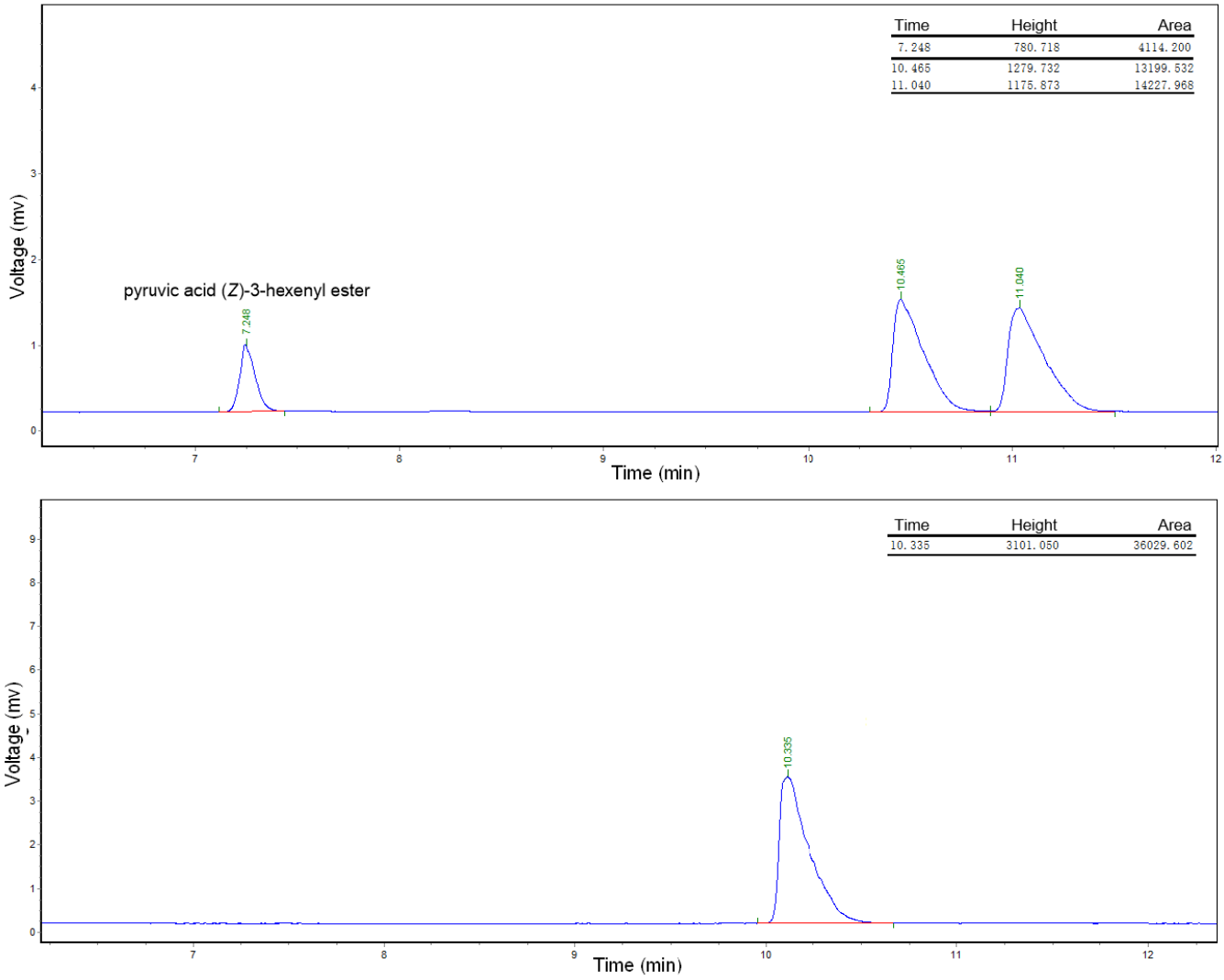
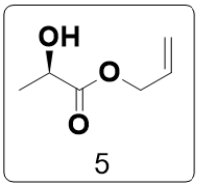



GC analytical conditions for **4**: The temperature of gasify room, column, and detector were 200 °C, 120 °C, and 200 °C respectively.

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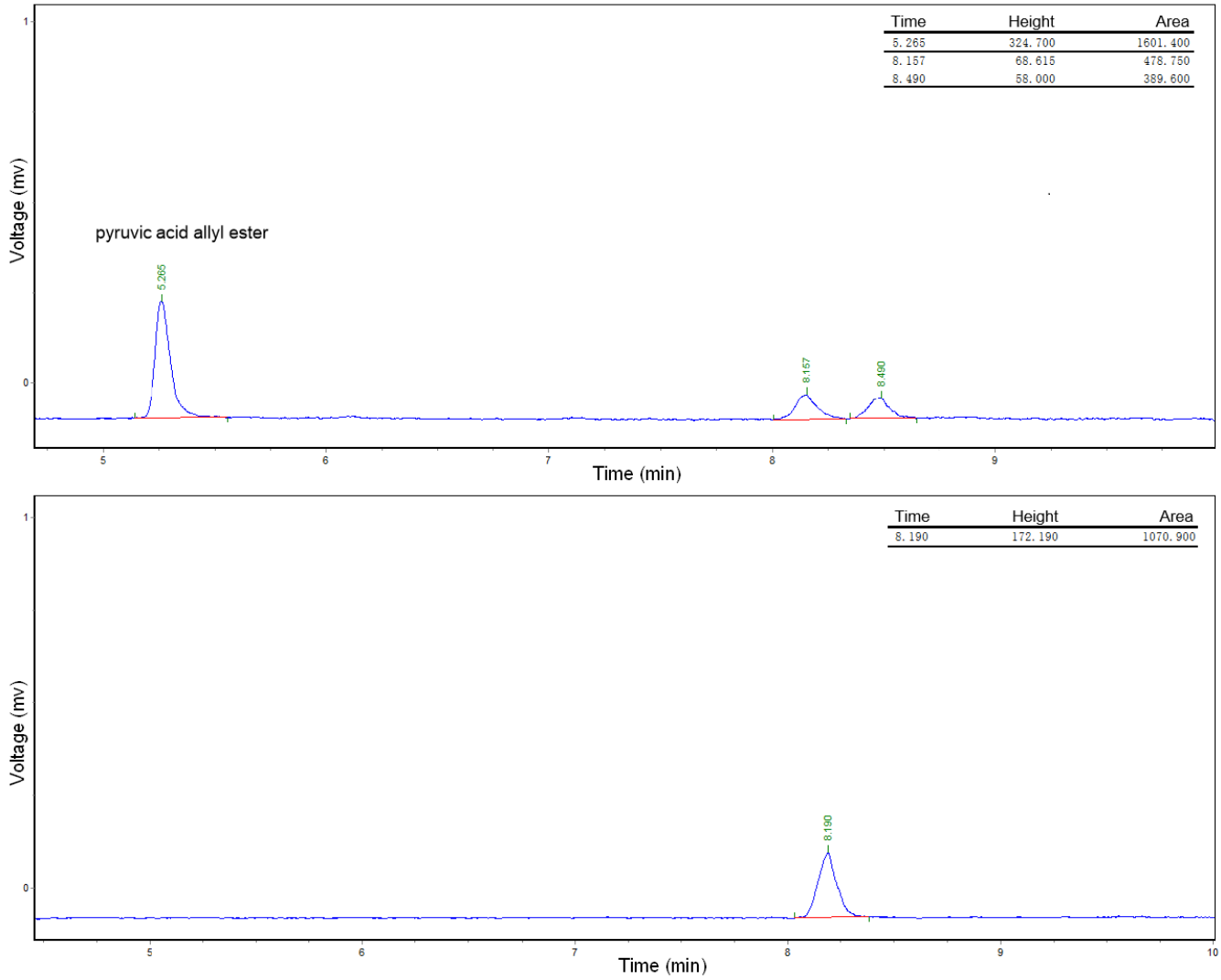
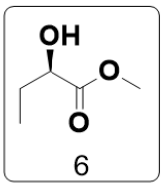



GC analytical conditions for **5**: The temperature of gasify room, column, and detector were 200 °C, 100 °C, and 200 °C respectively.

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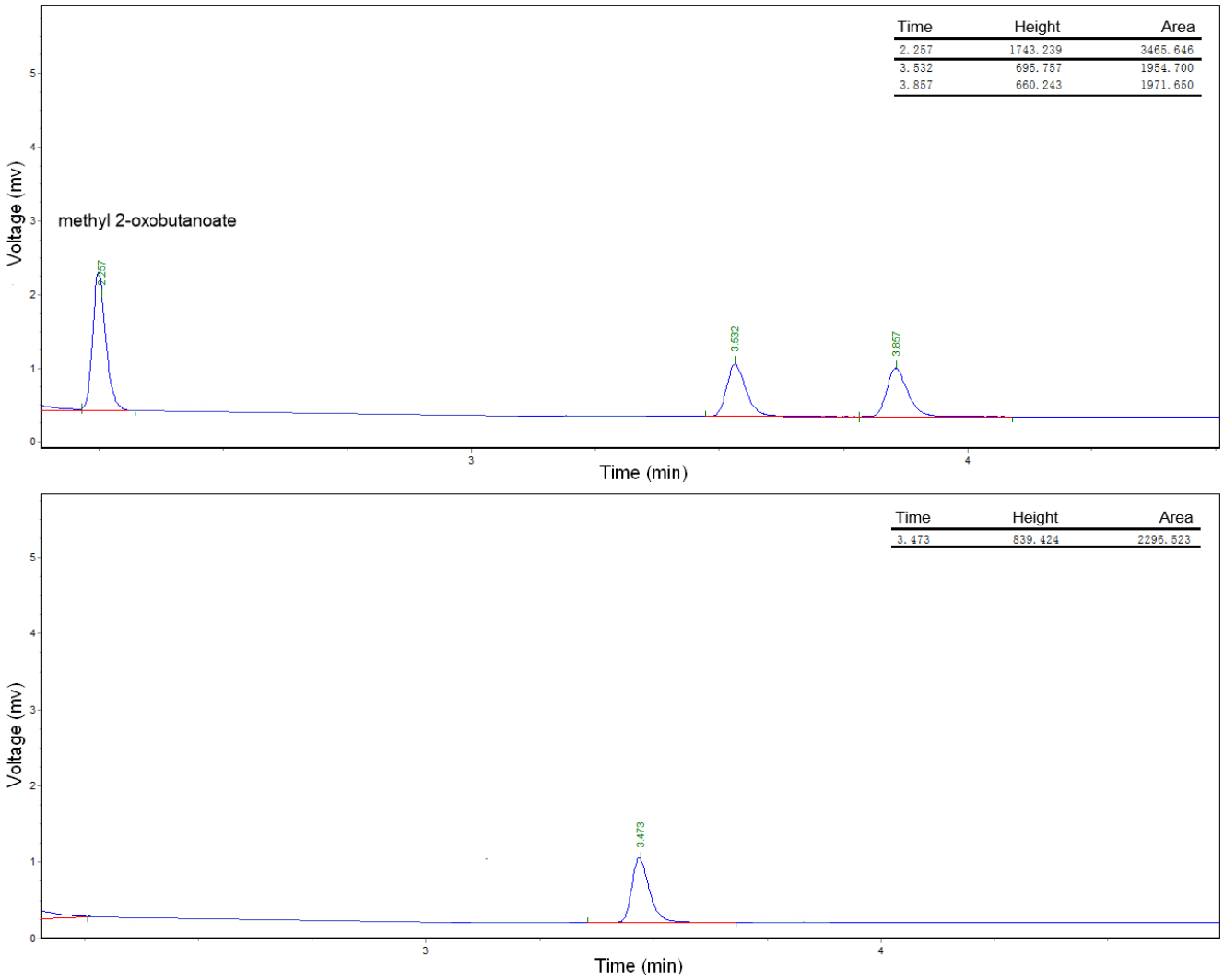
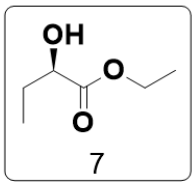



GC analytical conditions for **6**: The temperature of gasify room, column, and detector were 200 °C, 100 °C, and 200 °C respectively.

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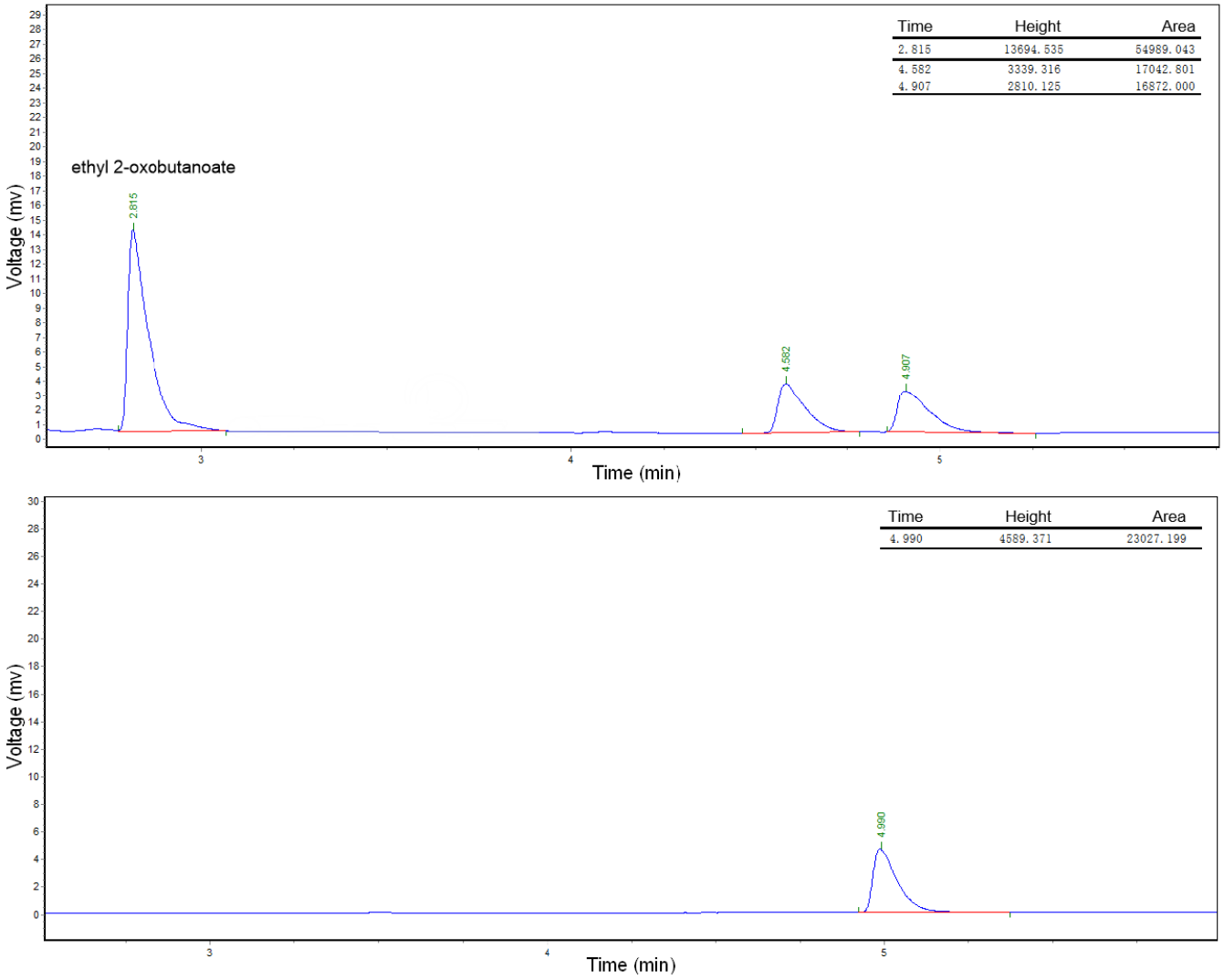
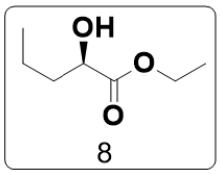



GC analytical conditions for **7**: The temperature of gasify room, column, and detector were 200 °C, 100 °C, and 200 °C respectively.

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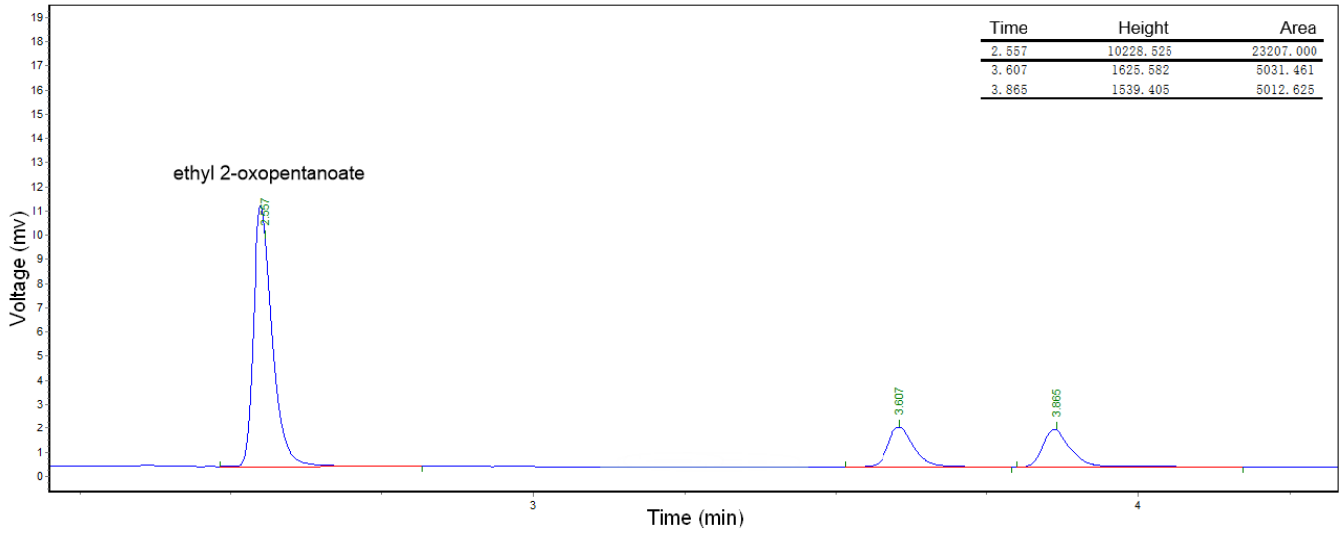
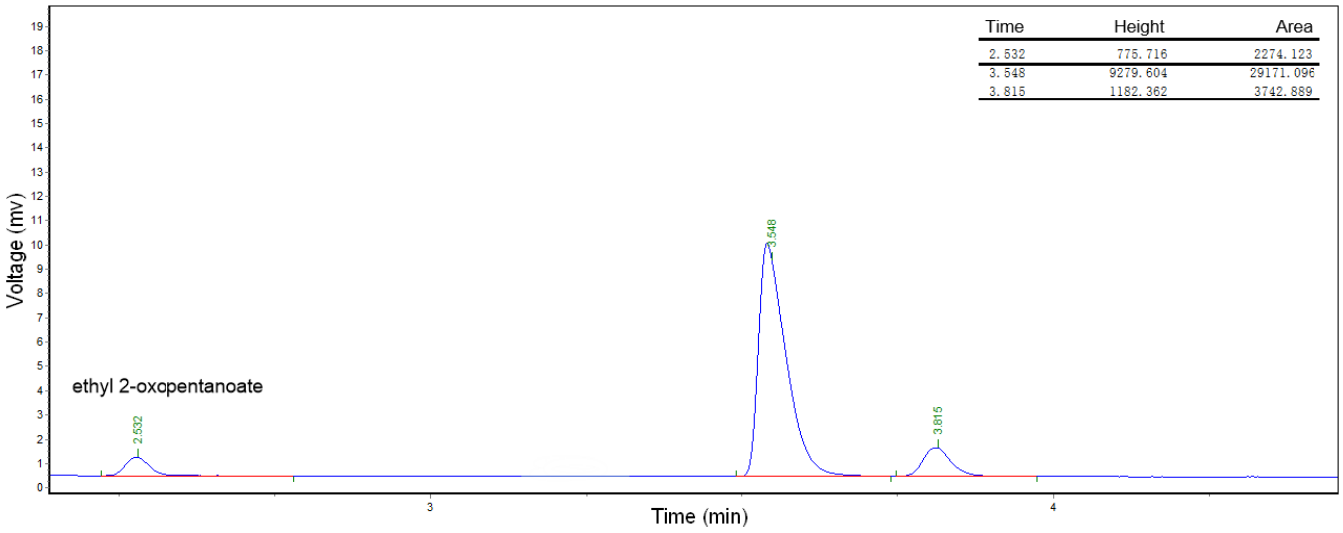
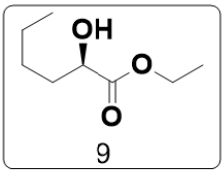



GC analytical conditions for **8**: The temperature of gasify room, column, and detector were 200 °C, 120 °C, and 200 °C respectively.

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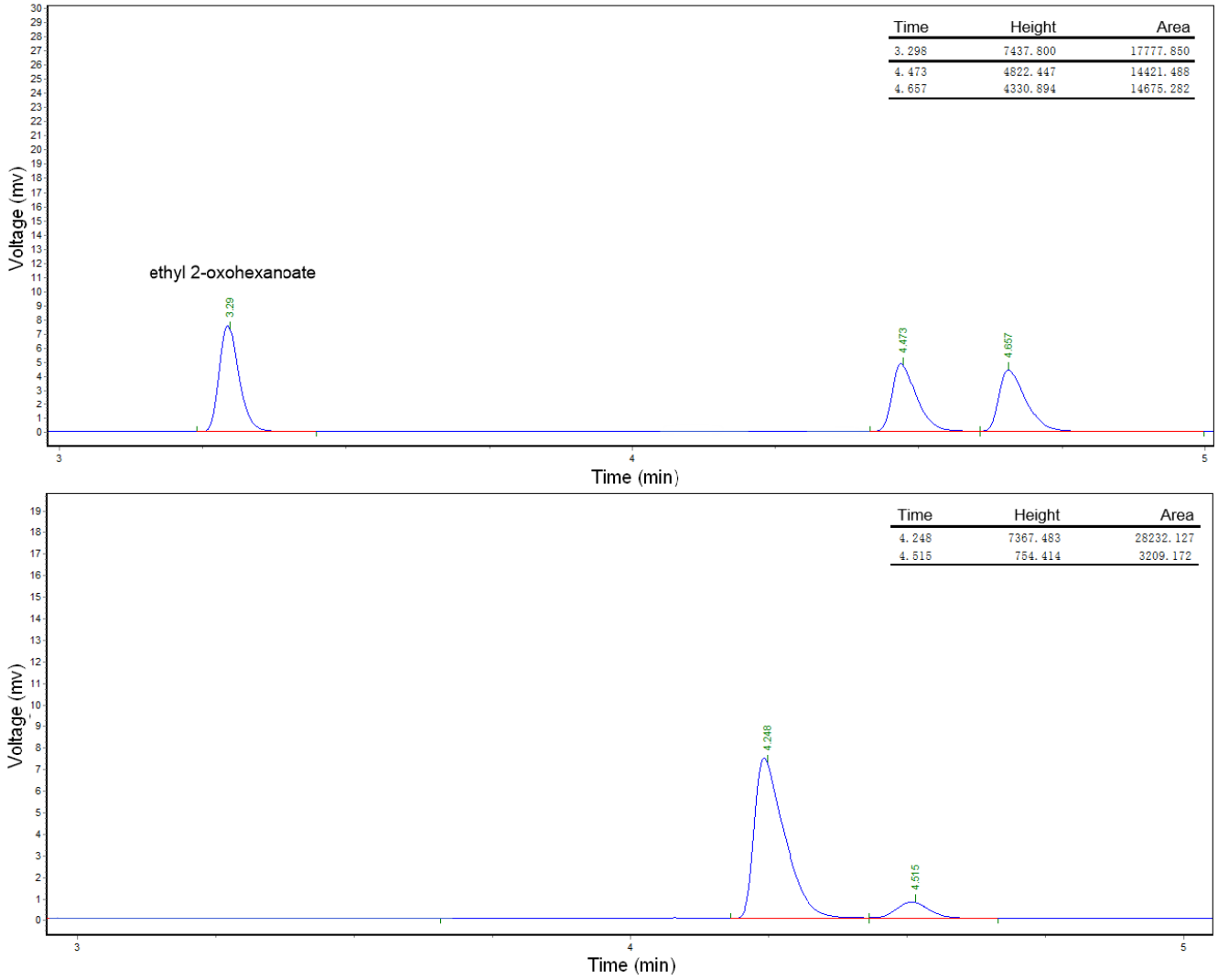
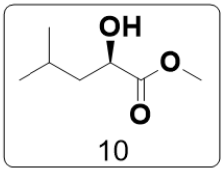



GC analytical conditions for **9**: The temperature of gasify room, column, and detector were 200 °C, 120 °C, and 200 °C respectively.

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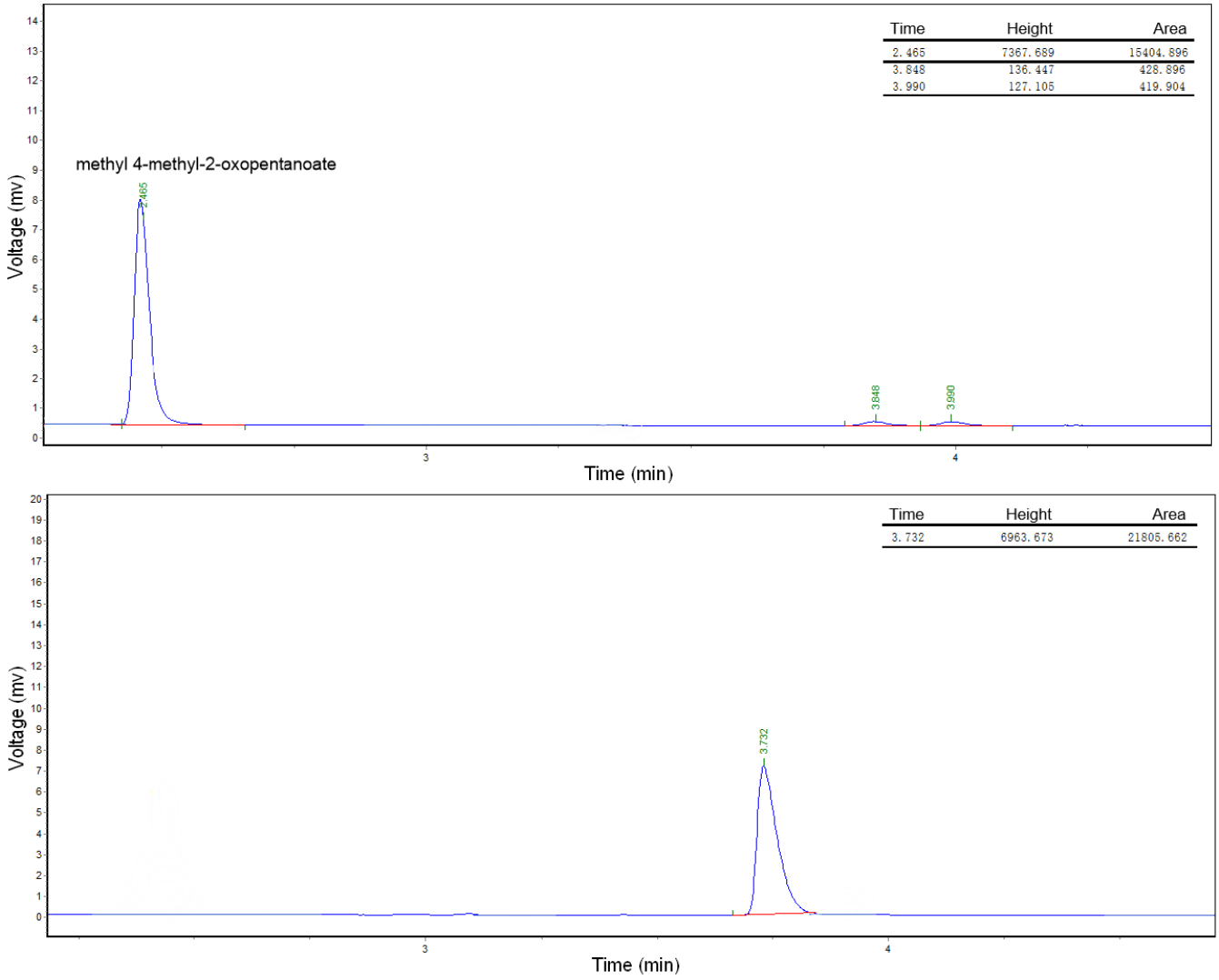
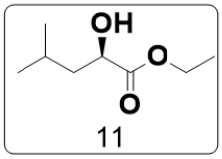



GC analytical conditions for **10**: The temperature of gasify room, column, and detector were 200 °C, 120 °C, and 200 °C respectively.

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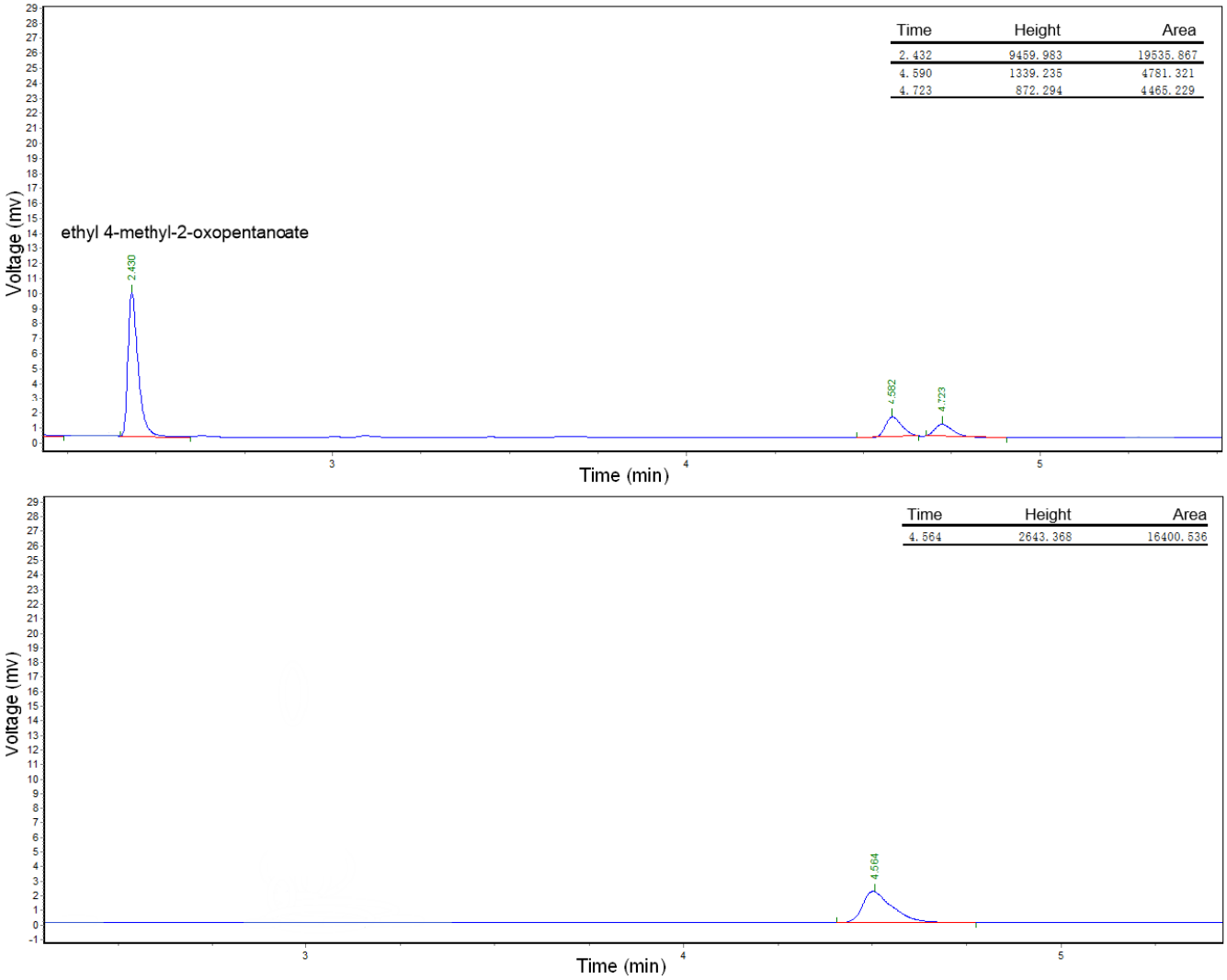
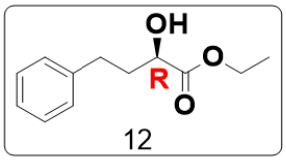






GC analytical conditions for **11**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 120 $^{o}$C, and 200 $^{o}$C respectively.

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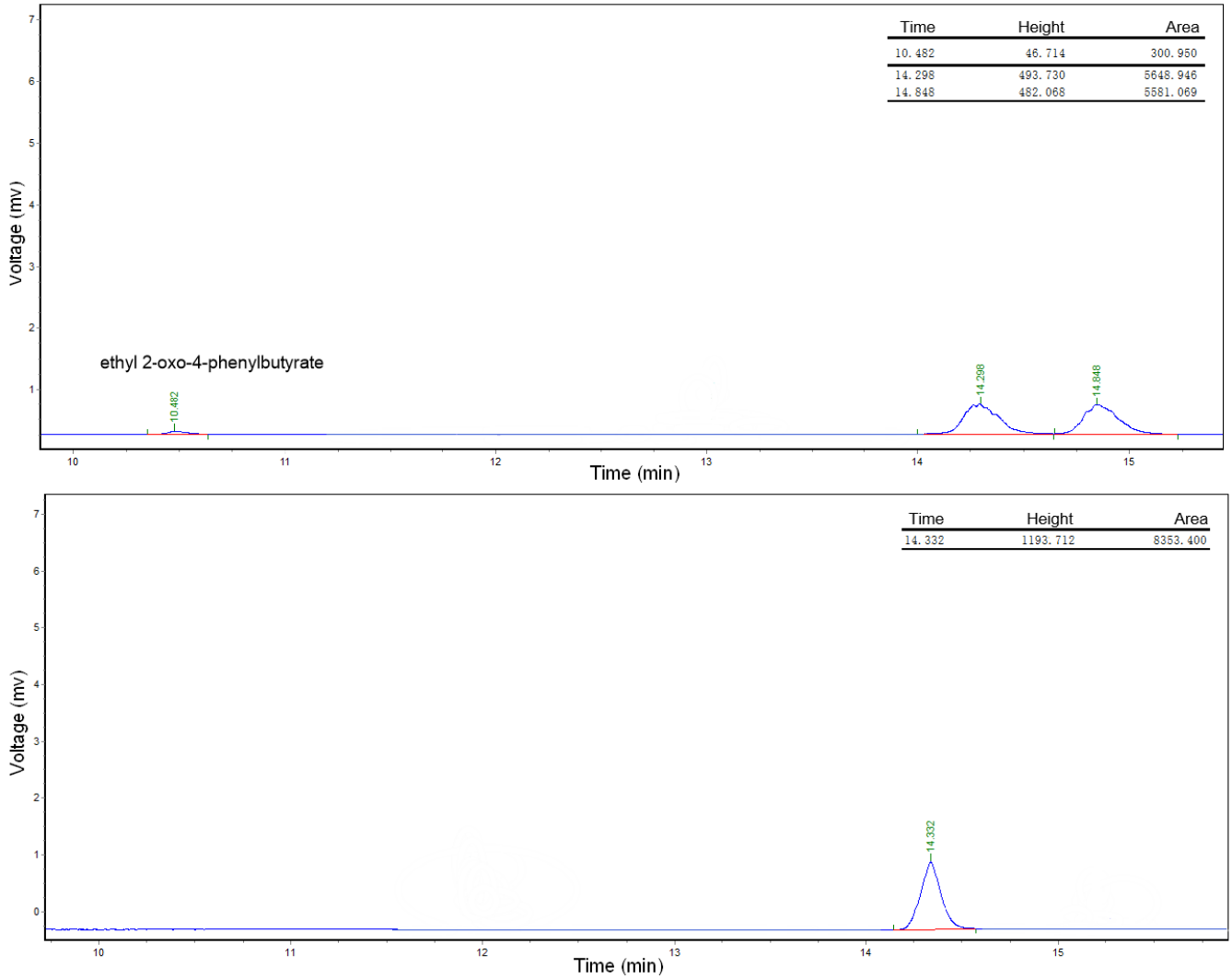
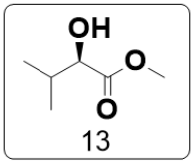



GC analytical conditions for **12**: The temperature of gasify room, column, and detector were 200 °C, 140–160 °C (heating rate 5 °C/ min), and 200 °C respectively.

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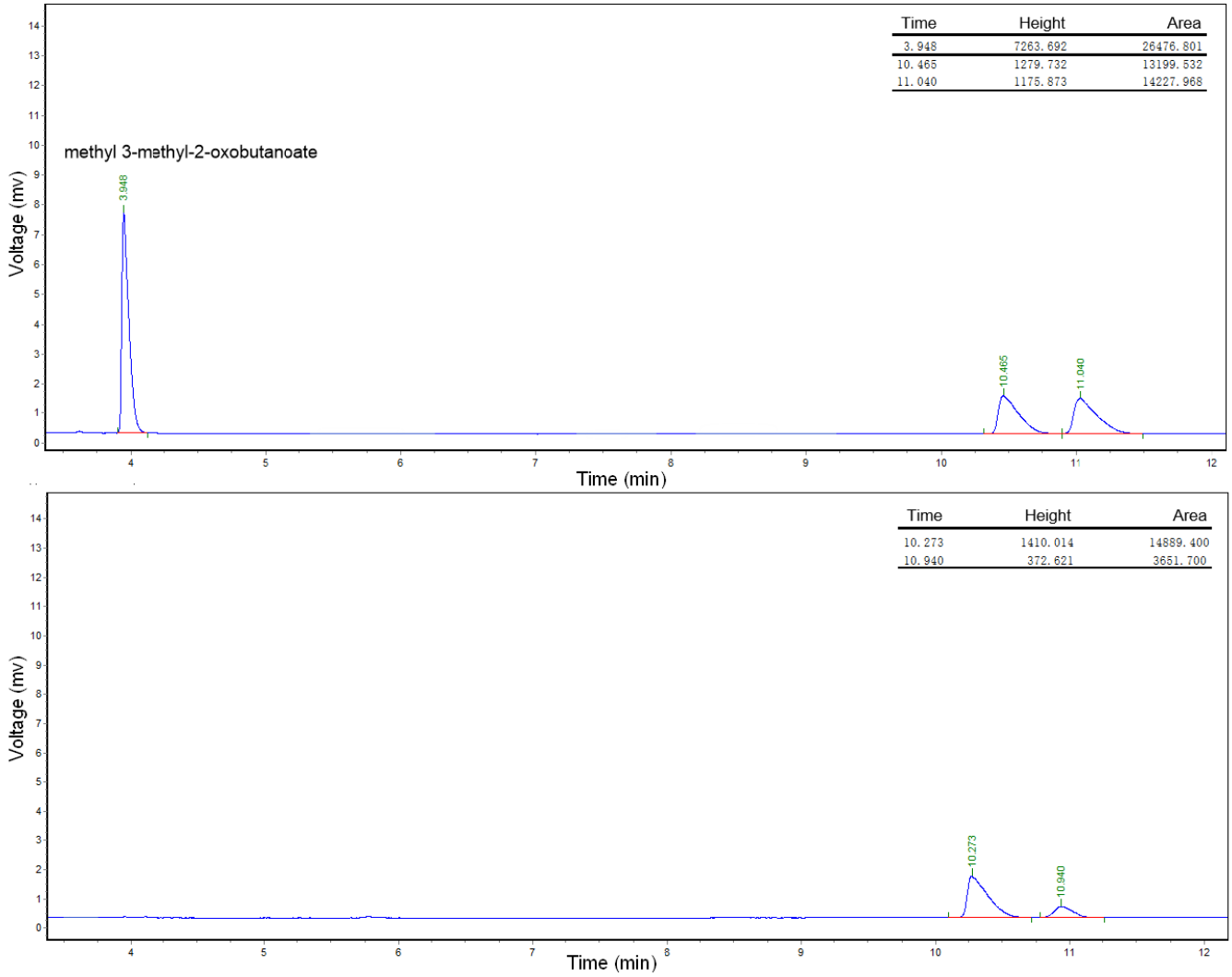
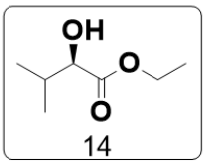



GC analytical conditions for **13**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 100 $^{o}$C, and 200 $^{o}$C respectively.

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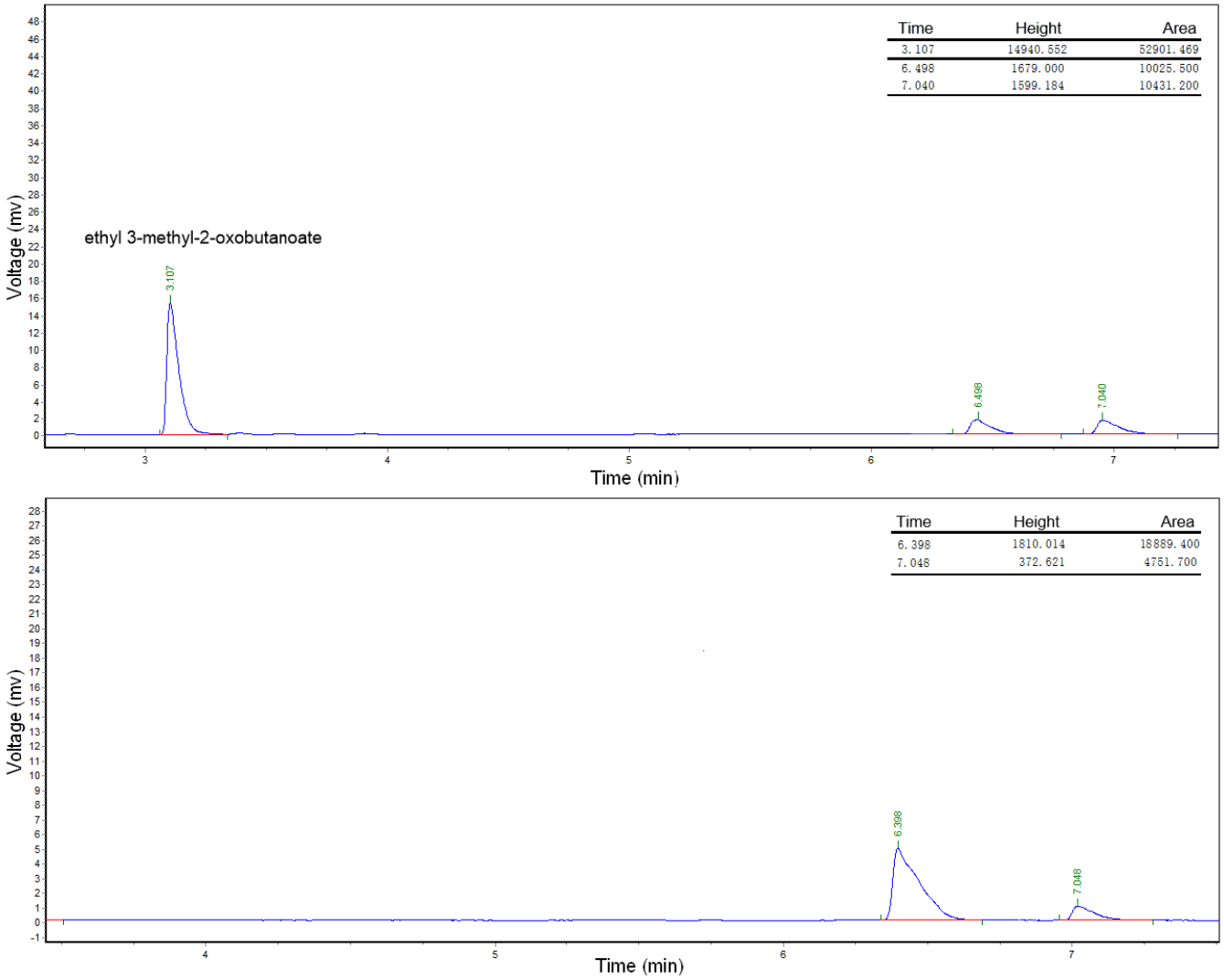
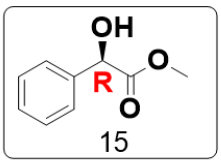



GC analytical conditions for **14**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 100 $^{o}$C, and 200 $^{o}$C respectively.

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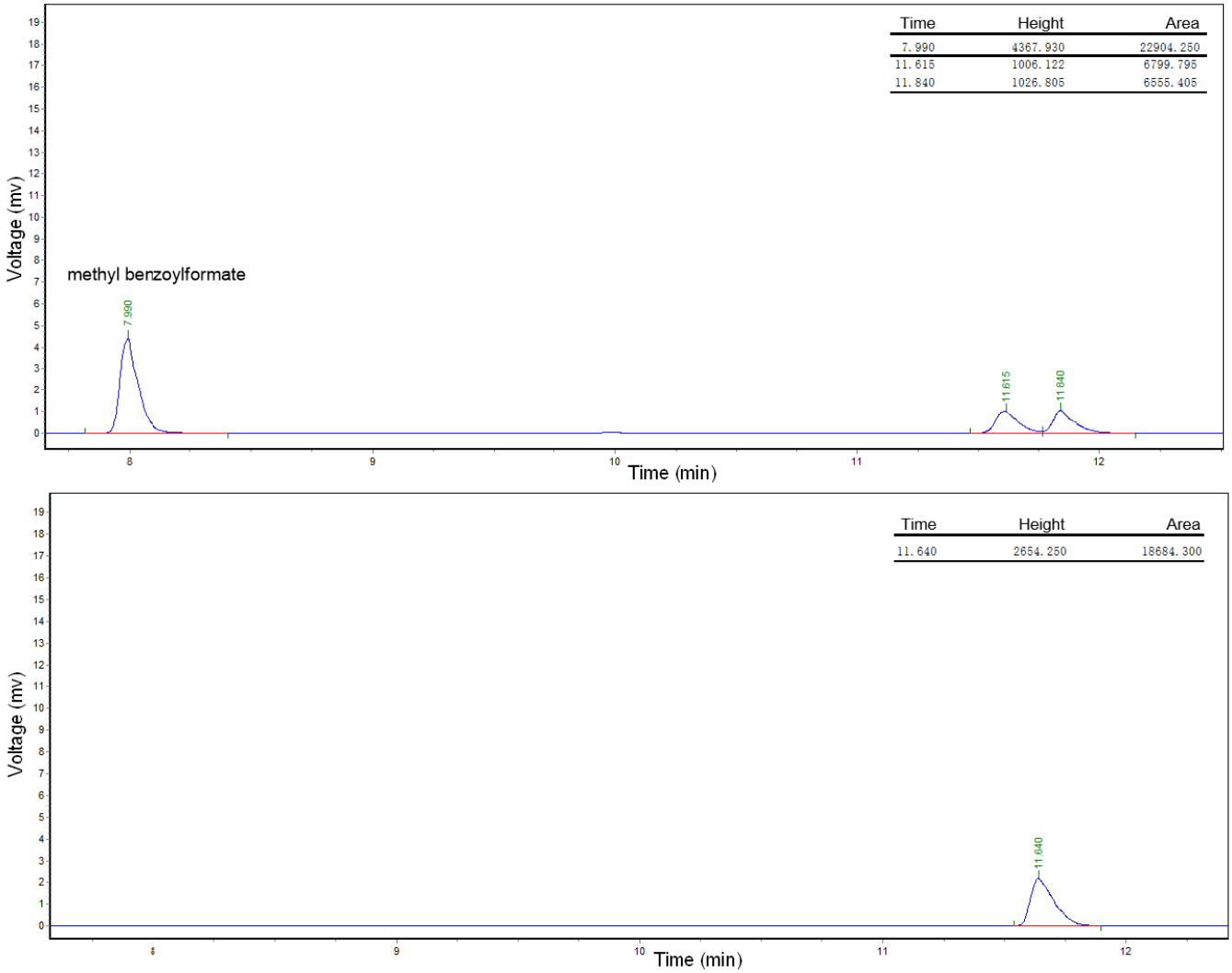
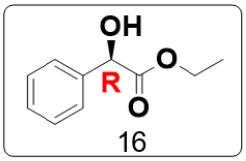
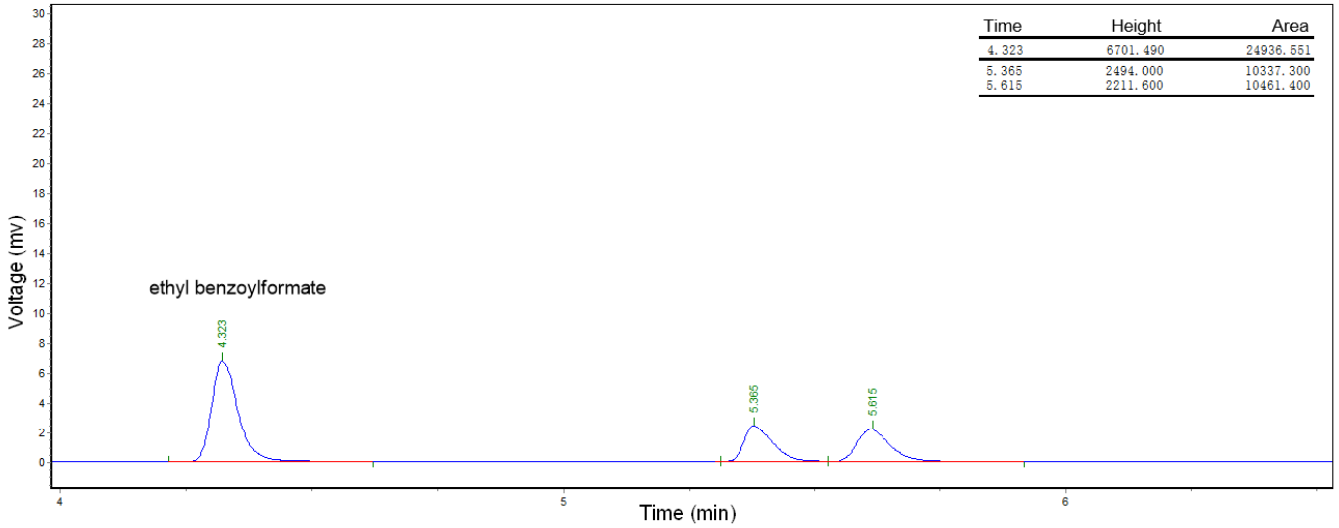
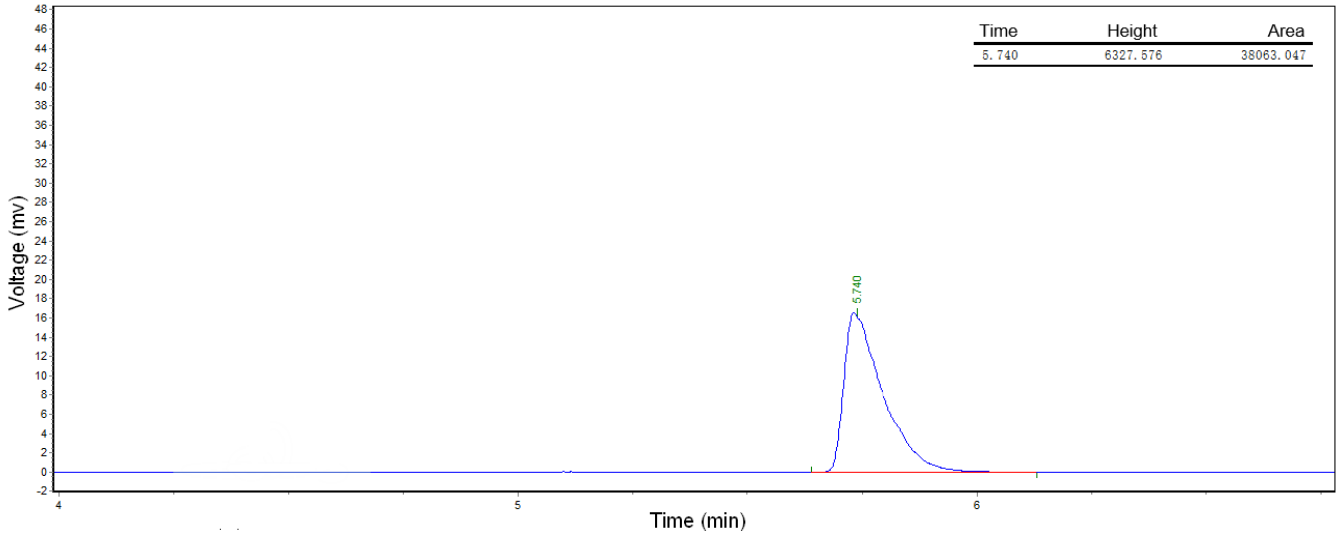



GC analytical conditions for **15**: The temperature of gasify room, column, and detector were 200 °C, 120–150 °C (heating rate 3 °C/ min), and 200 °C respectively.

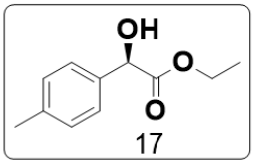


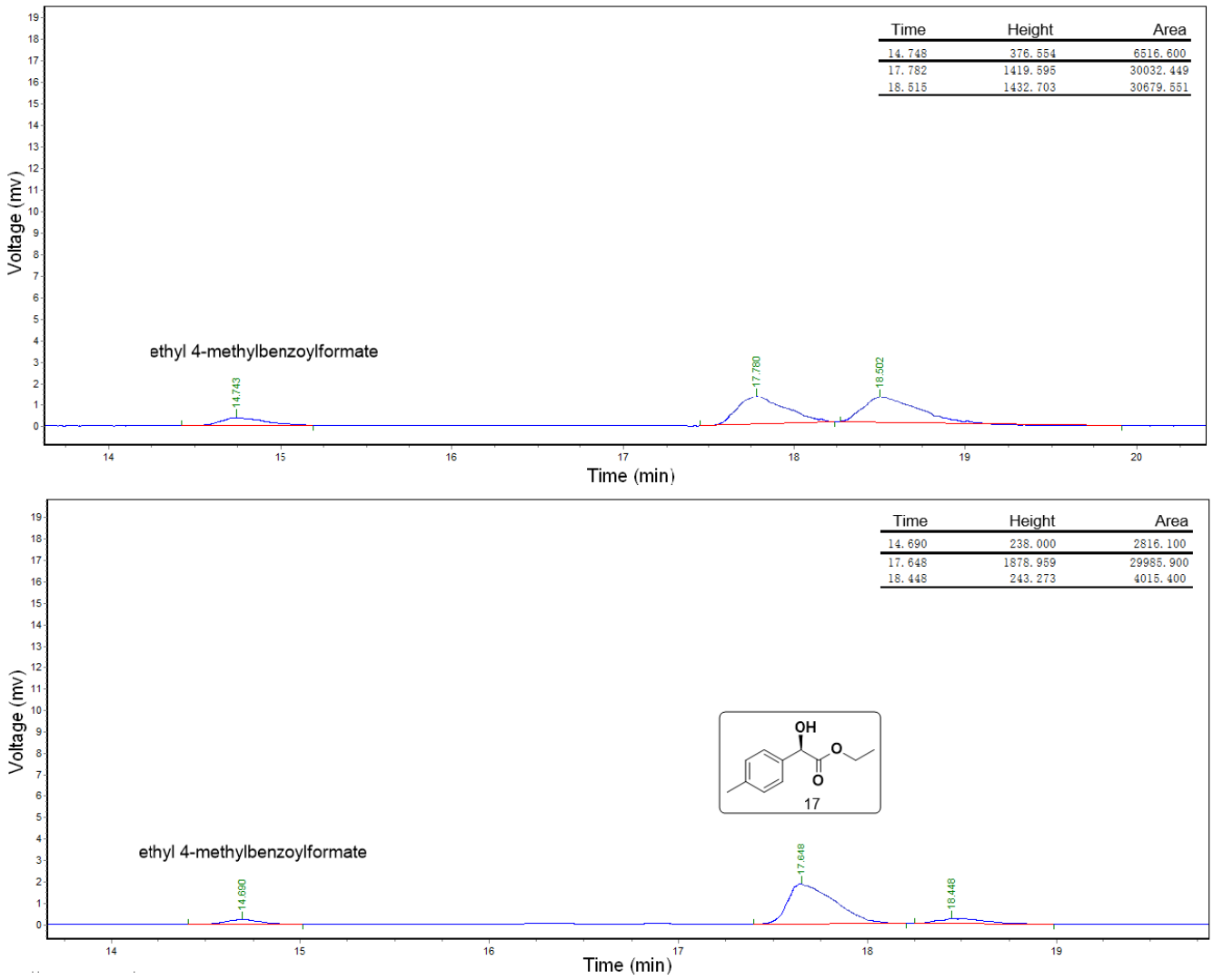

16



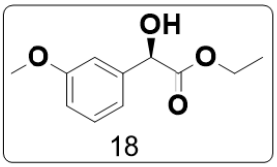




GC analytical conditions for **16**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 160 $^{o}$C, and 200 $^{o}$C respectively.

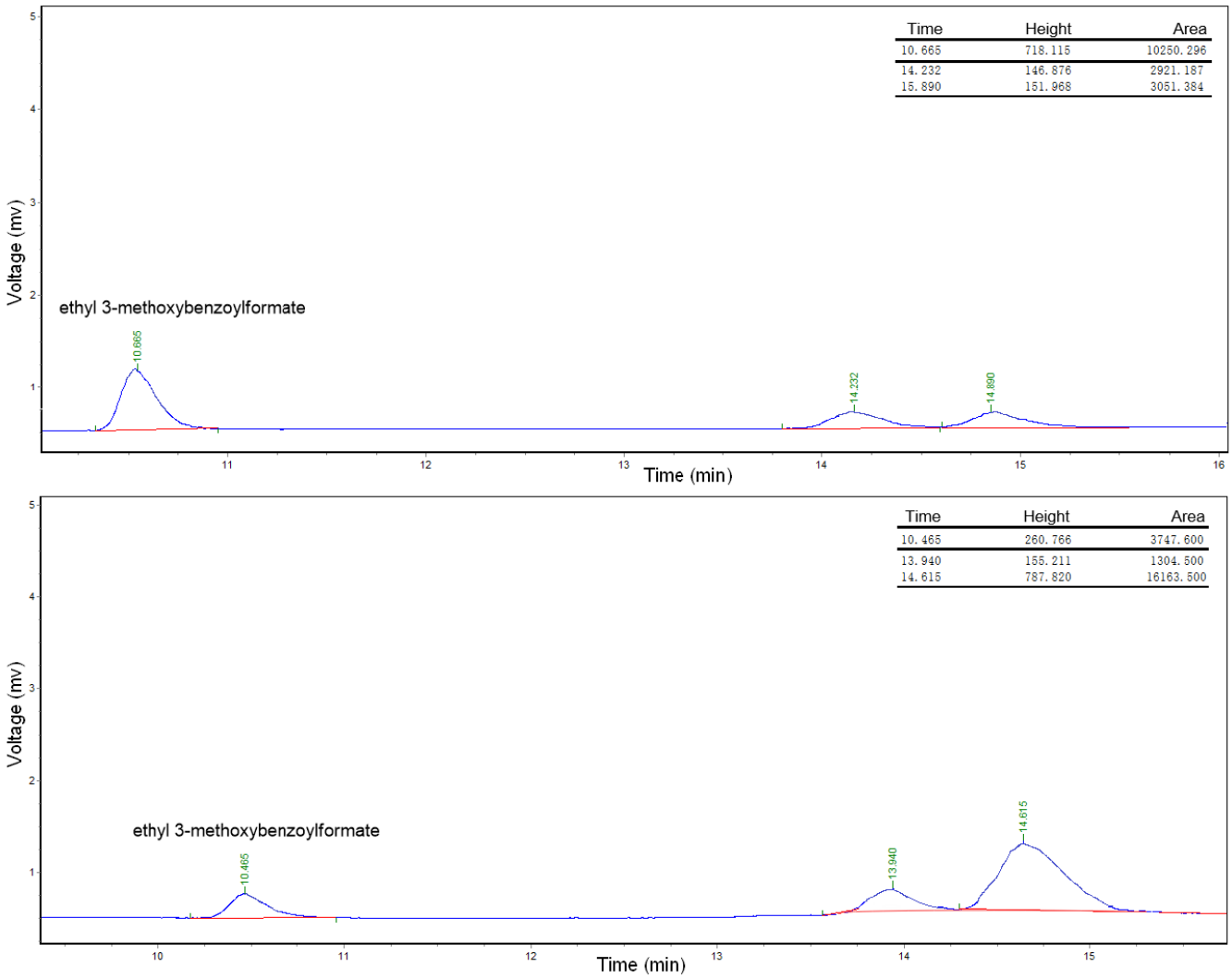


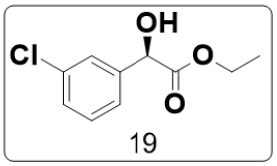

GC analytical conditions for **17**: The temperature of gasify room, column, and detector were 200 °C, 140 °C, and 200 °C respectively.




18




GC analytical conditions for **18**: The temperature of gasify room, column, and detector were 200 °C, 160 °C, and 200 °C respectively.

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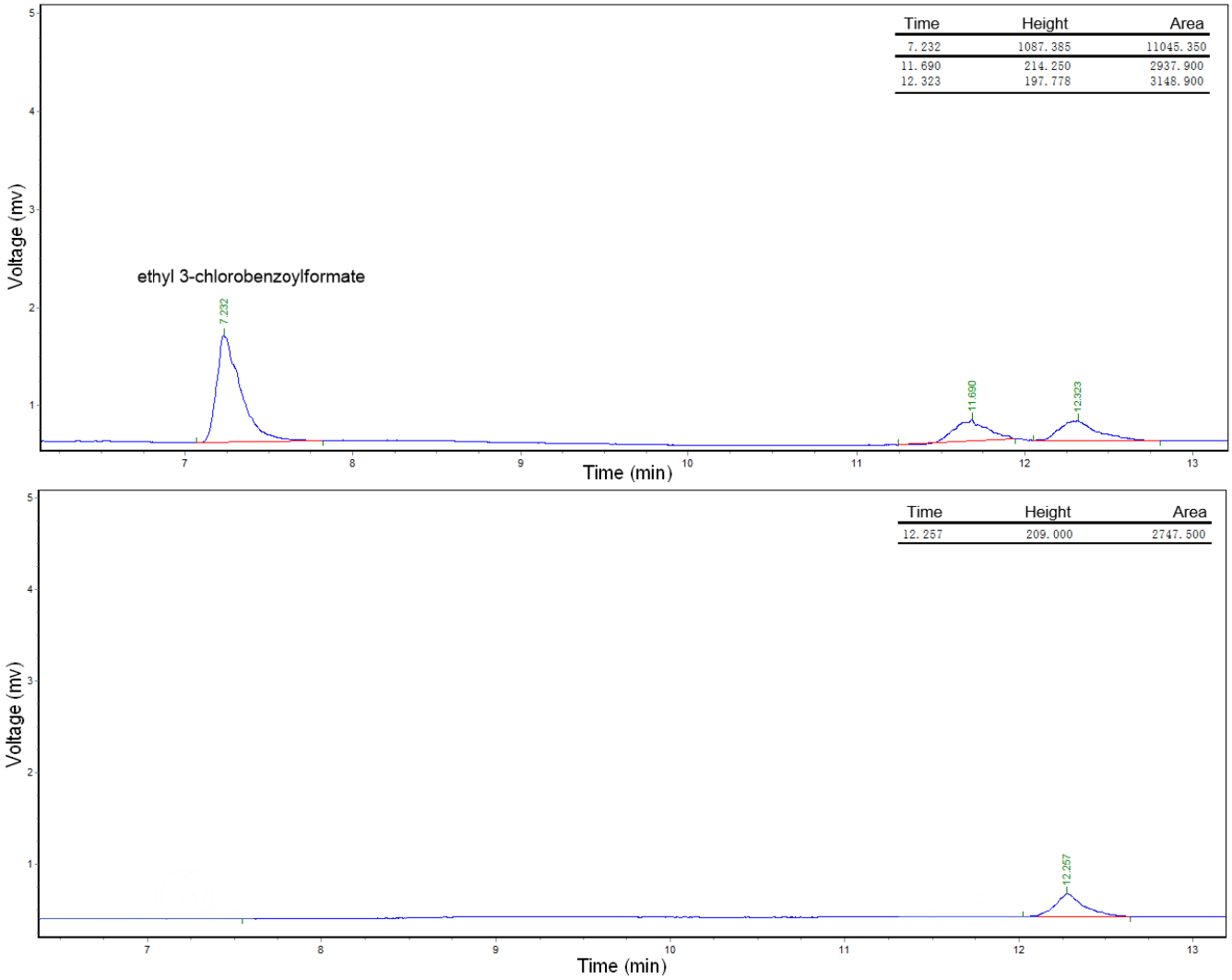
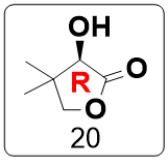
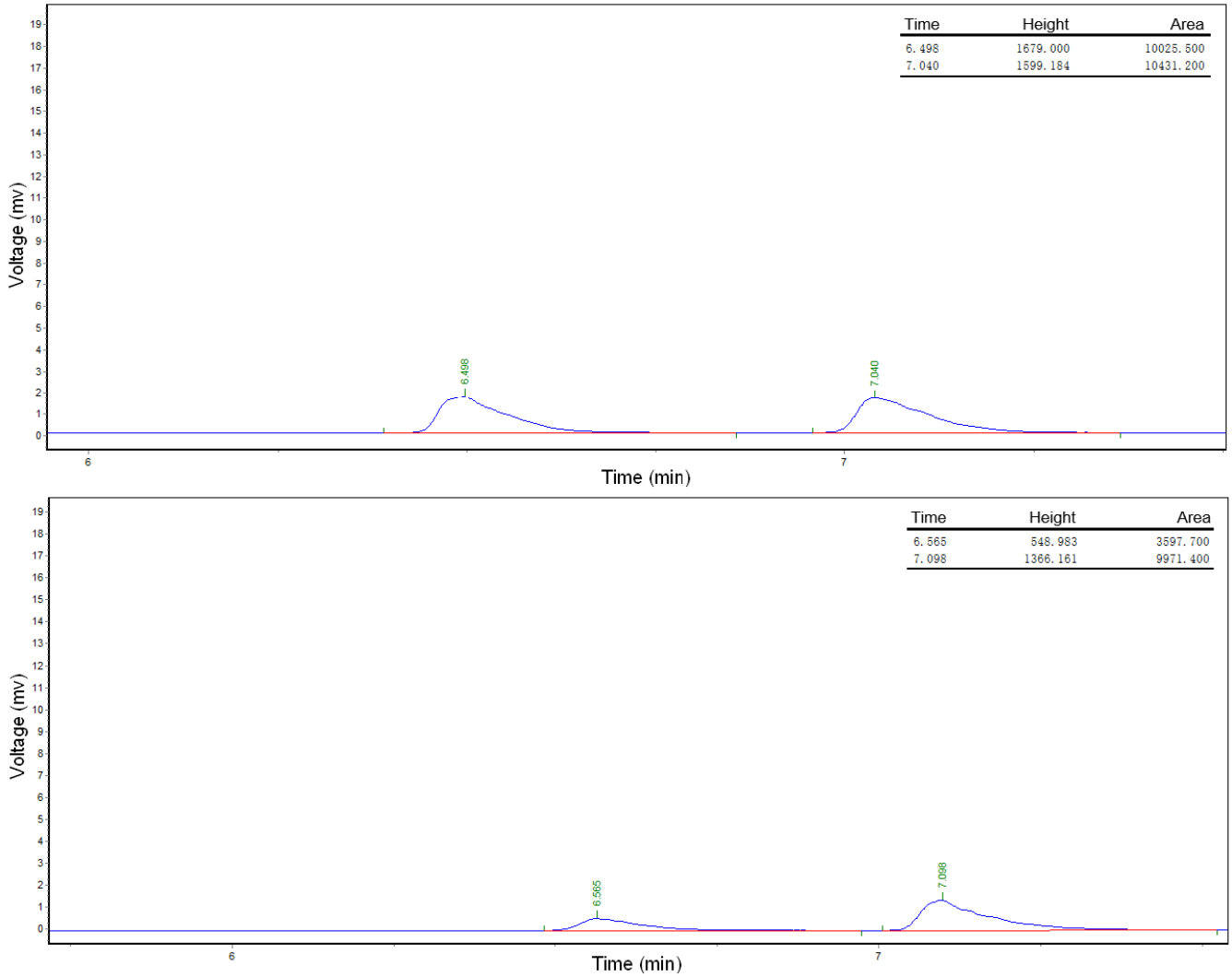



GC analytical conditions for **19**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 160 $^{o}$C, and 200 $^{o}$C respectively.

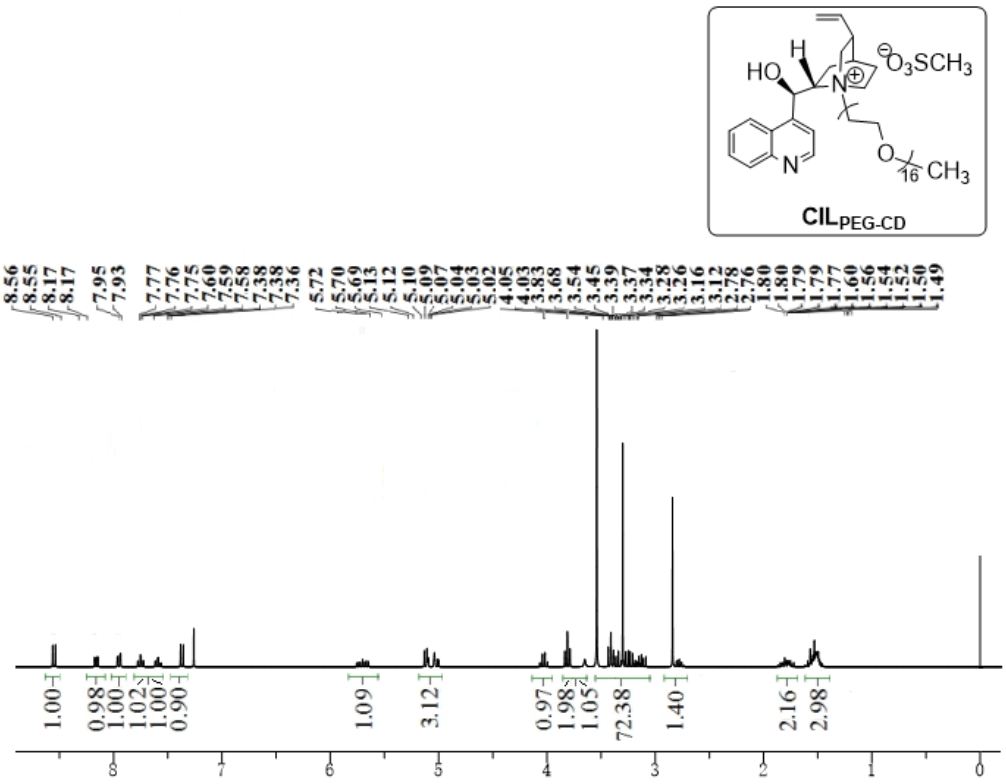


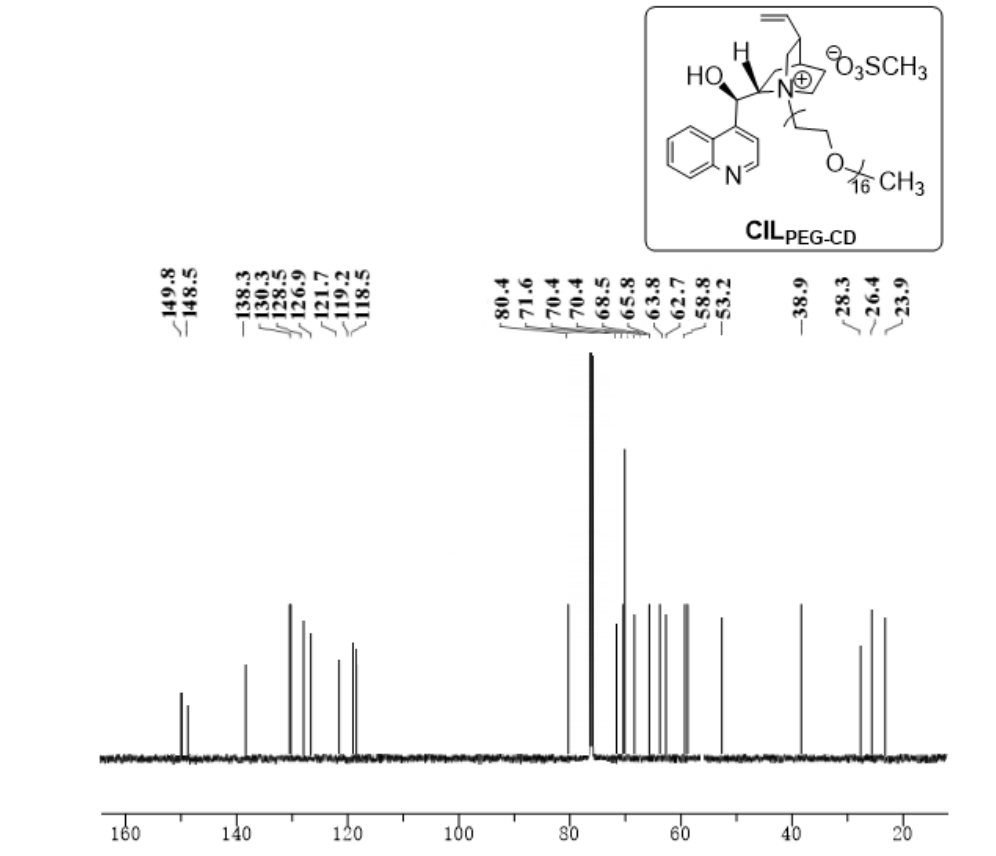

20

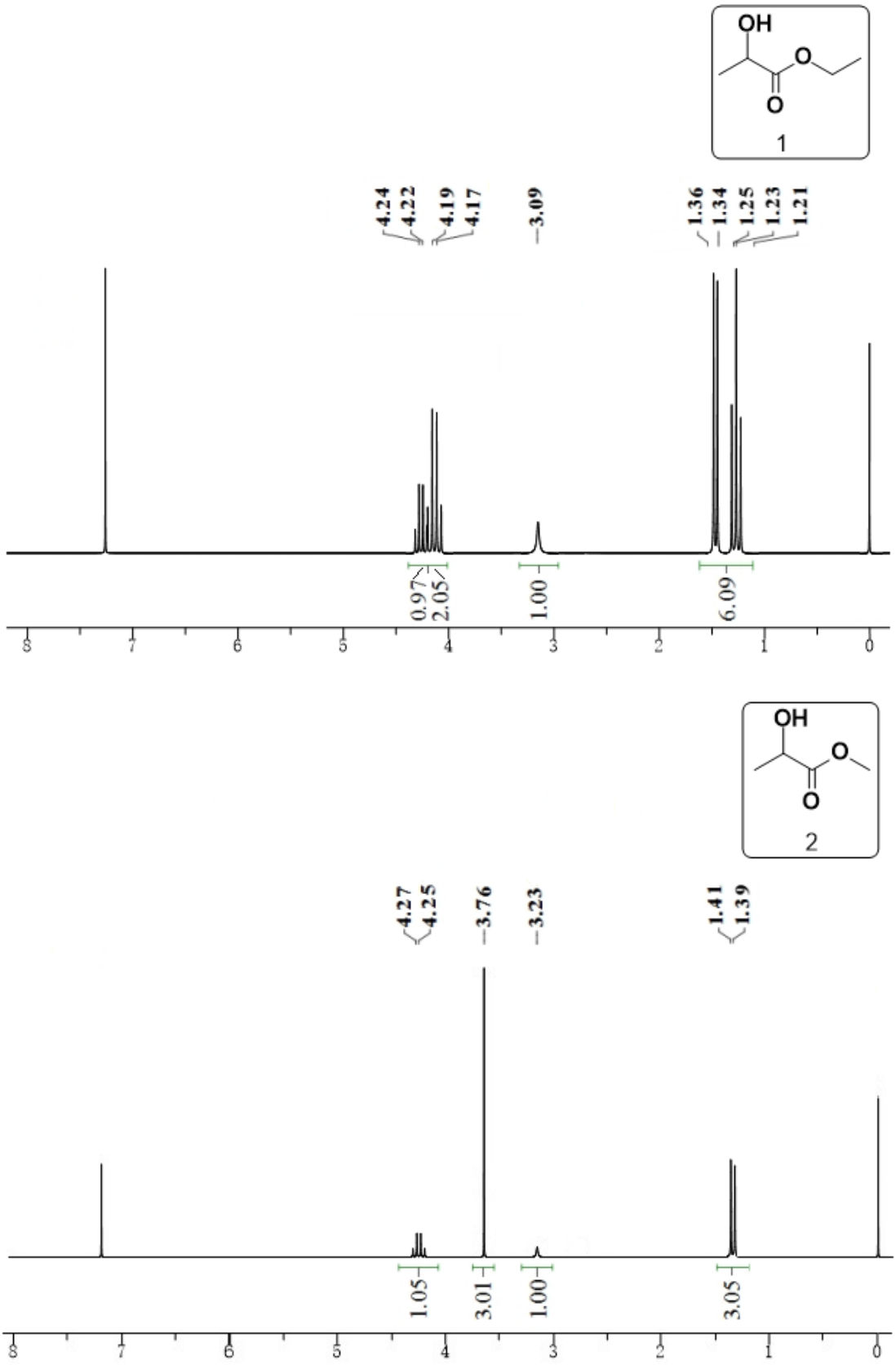



GC analytical conditions for **20**: The temperature of gasify room, column, and detector were 200 $^{o}$C, 140 $^{o}$C, and 200 $^{o}$C respectively.

## 5. Copies of NMR Spectra

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O
O
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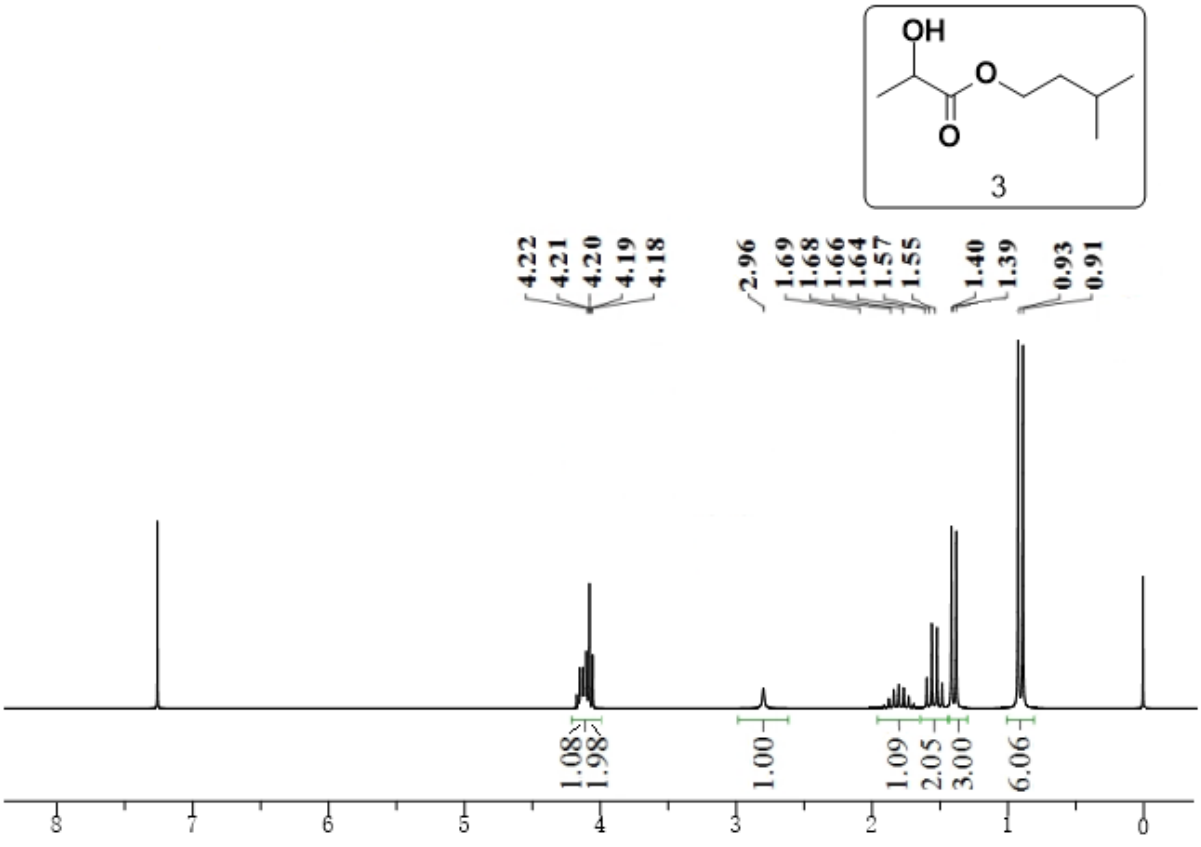
4.19
4.17
3.09
1.36
1.34
1.25
1.23
1.21
0.97
2.05
1.00
6.09
8
7
6
5
4
3
2
1
0
OH
O
O
2
4.27
4.25
3.76
3.23
1.41
1.39
1.05
3.01
1.00
3.05
8
7
6
5
4
3
2
1
0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O
O
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4.19
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2.96
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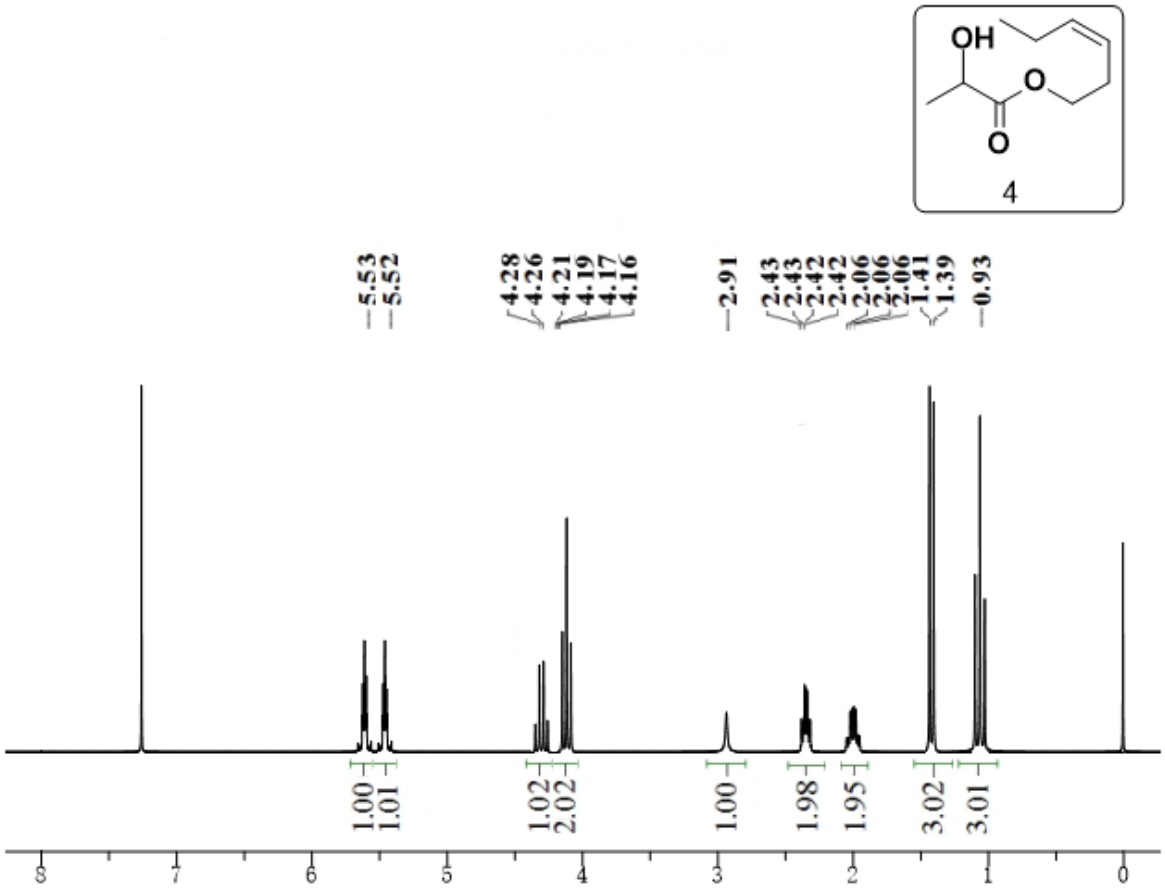
1.64
1.57
1.55
1.40
1.39
0.93
0.91
1.08
1.98
1.00
1.09
2.05
3.00
6.06
8
7
6
5
4
3
2
1
0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2.43
2.43
2.42
2.42
2.06
2.06
2.06
1.41
1.39
0.93
1.00
1.01
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1.98
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3.01
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7
6
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3
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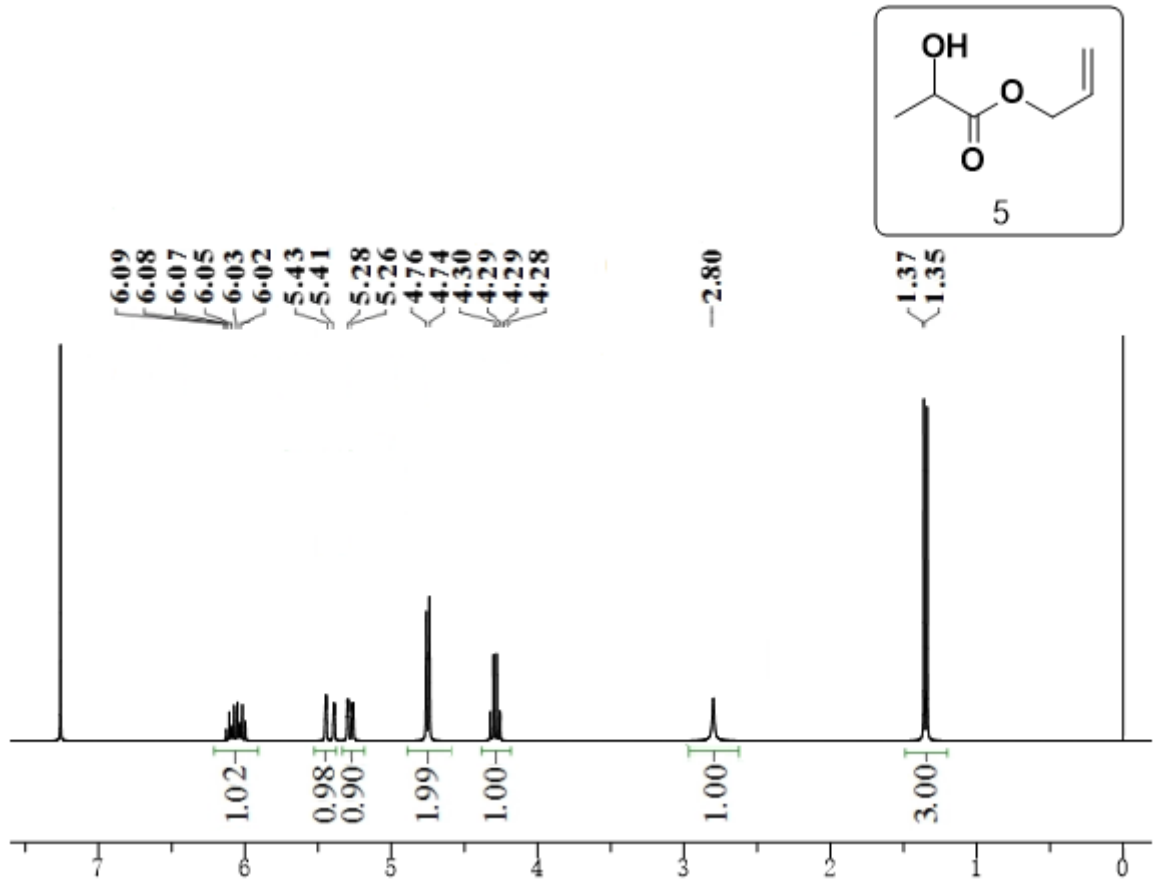
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6.05
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6.02
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5.26
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4.74
4.30
4.29
4.29
4.28
2.80
1.37
1.35
1.02
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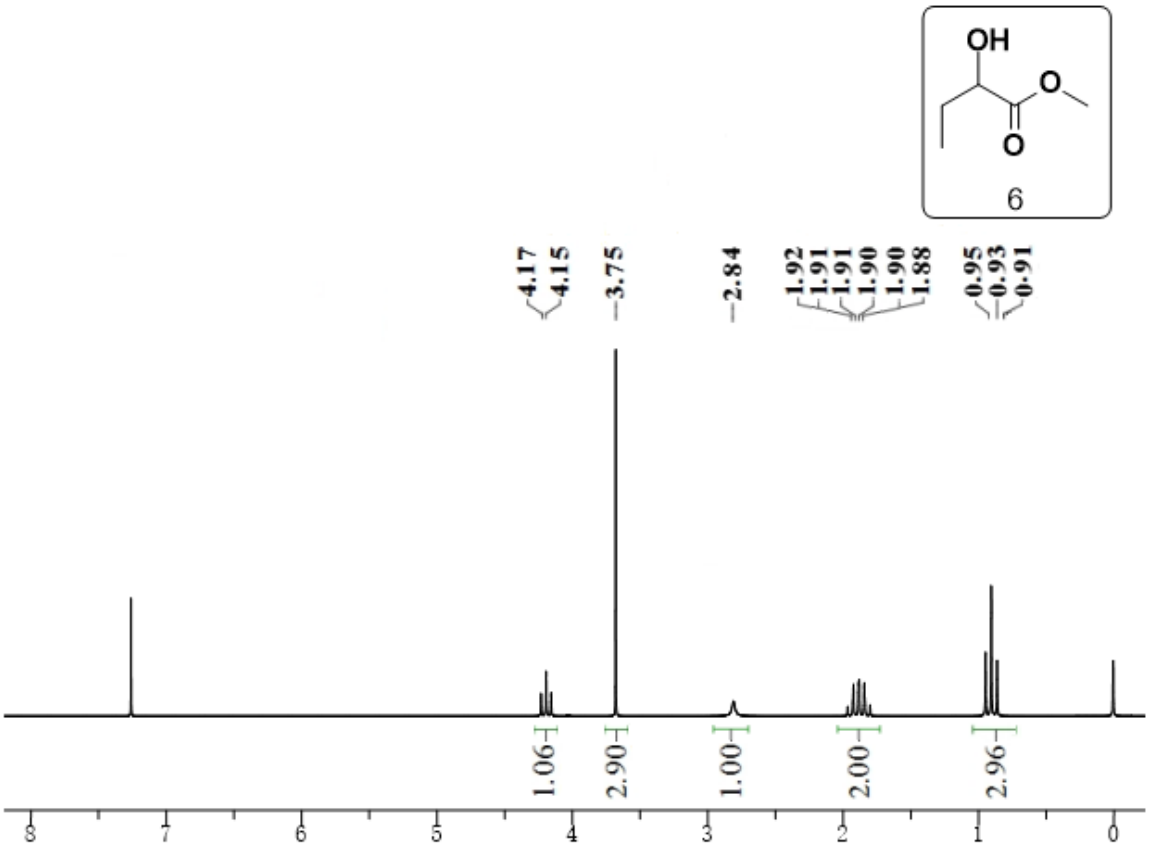
0.90
1.99
1.00
1.00
3.00
7
6
5
4
3
2
1
0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O
O
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1.91
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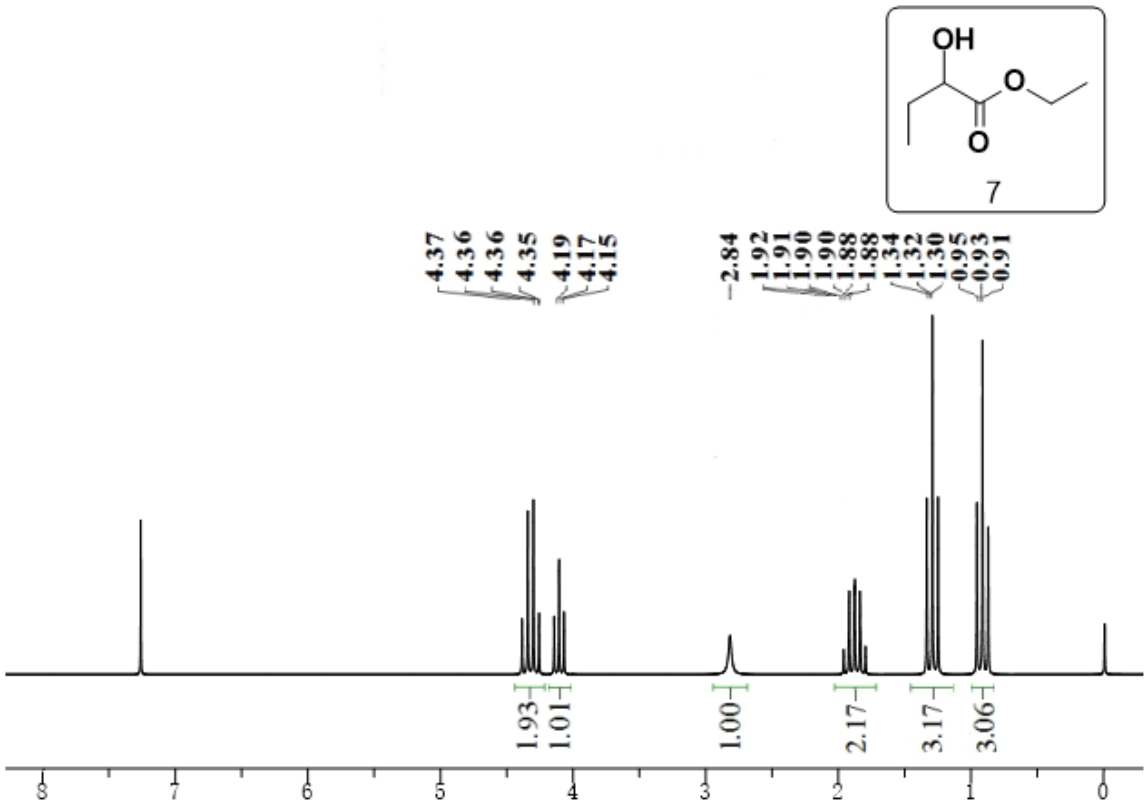
1.90
1.90
1.88
0.95
0.93
0.91
1.06
2.90
1.00
2.00
2.96
8
7
6
5
4
3
2
1
0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4.17
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1.90
1.90
1.88
1.88
1.34
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1.30
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0.93
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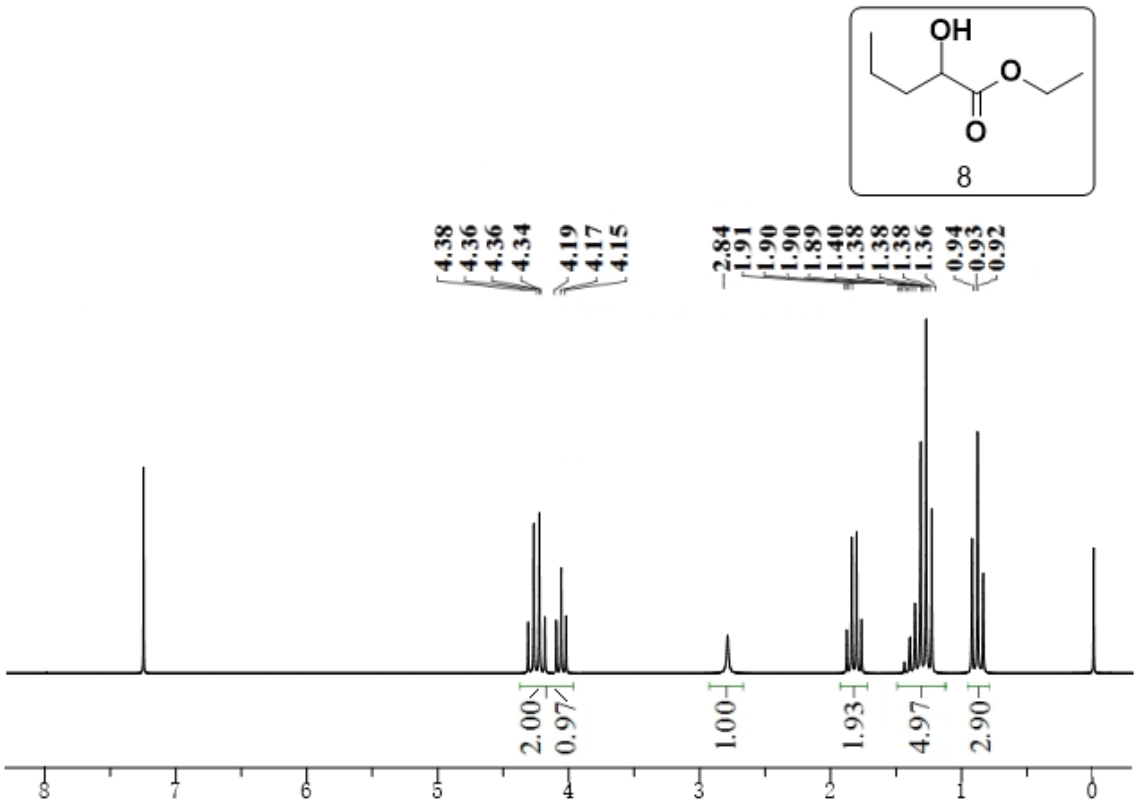
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1.90
1.89
1.40
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1.38
1.38
1.36
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0.93
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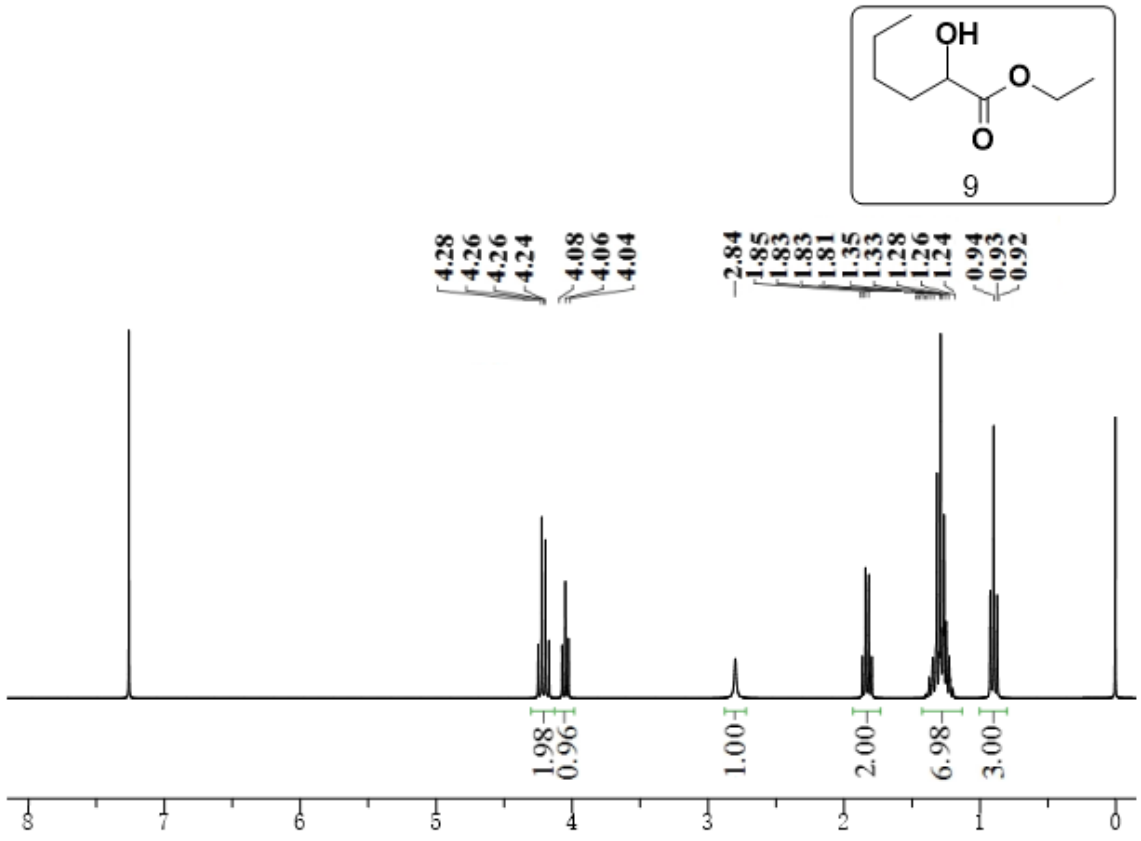
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1.81
1.35
1.33
1.28
1.26
1.24
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0.93
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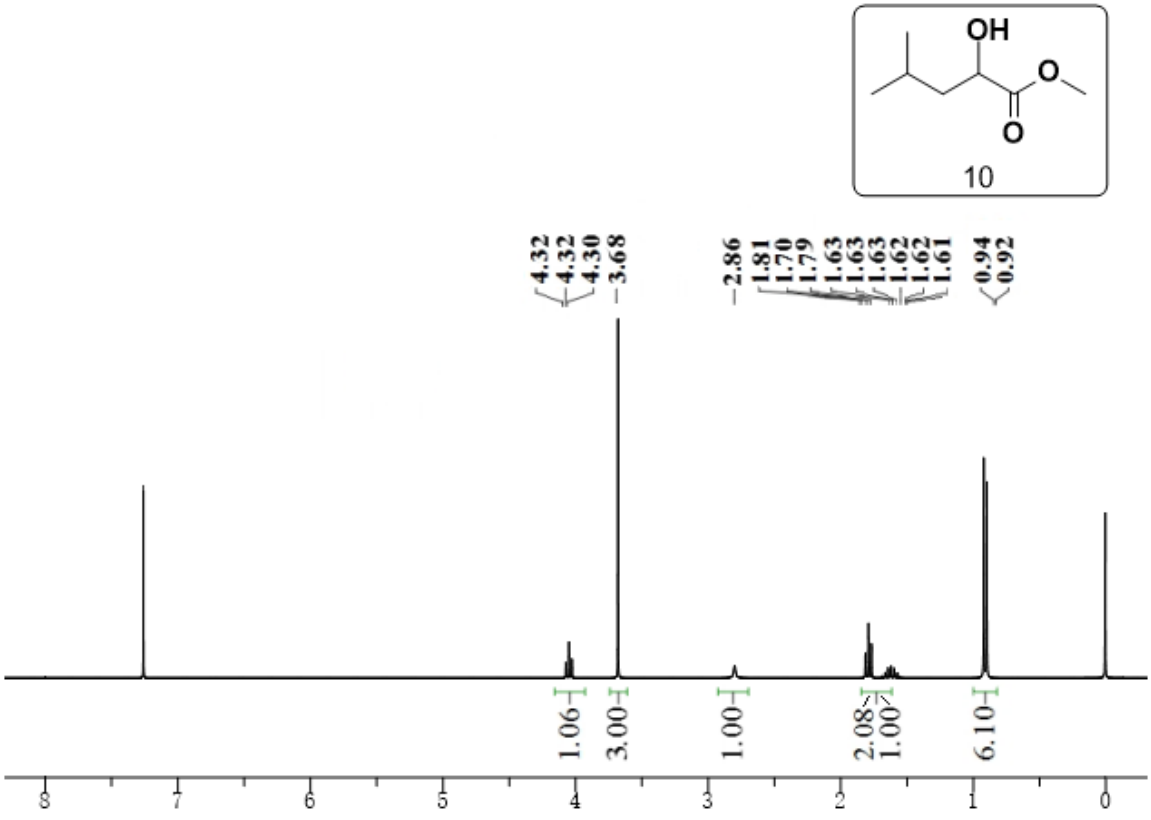
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1.63
1.62
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1.61
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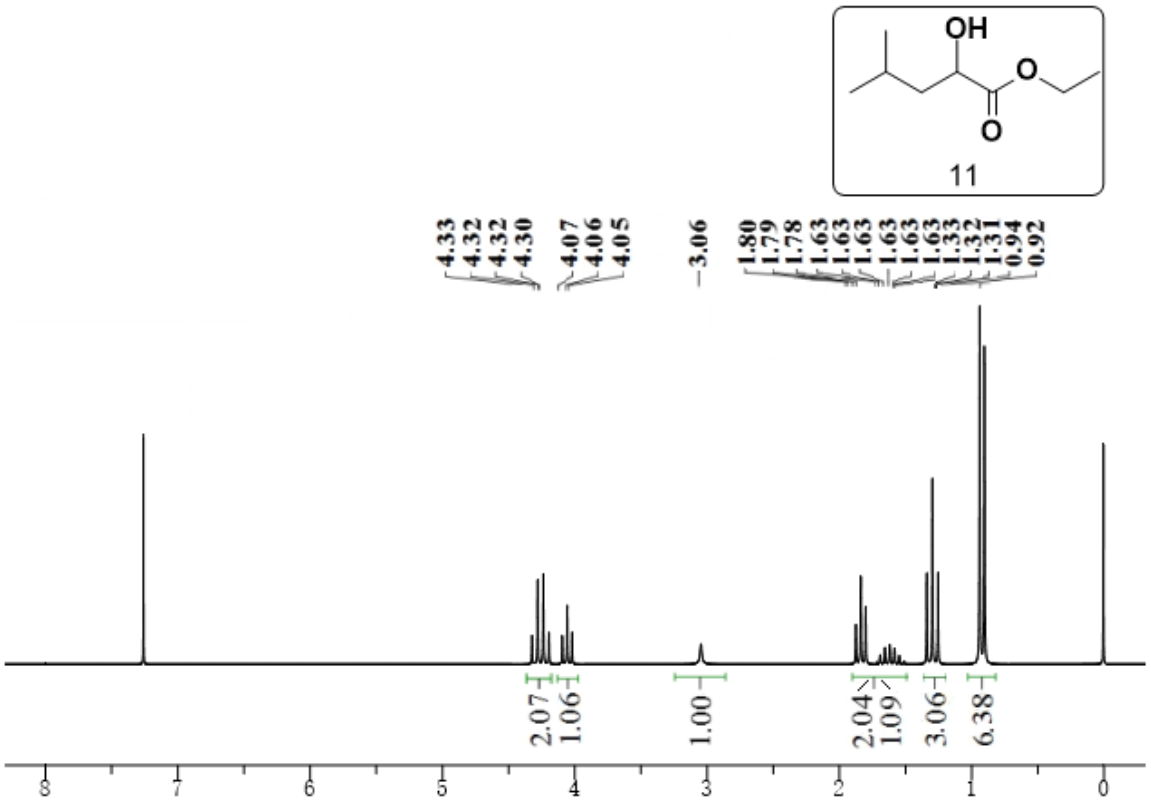
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0.92
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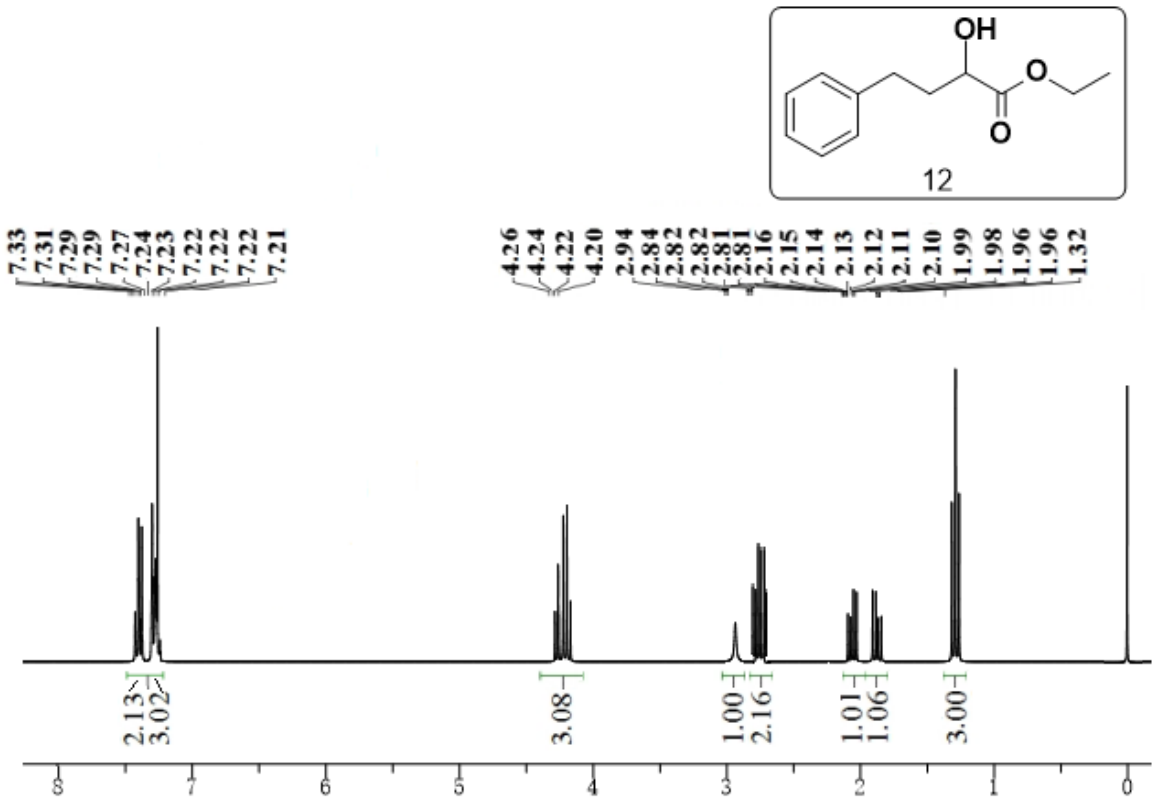
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2.82
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2.15
2.14
2.13
2.12
2.11
2.10
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1.98
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1.96
1.32
2.13
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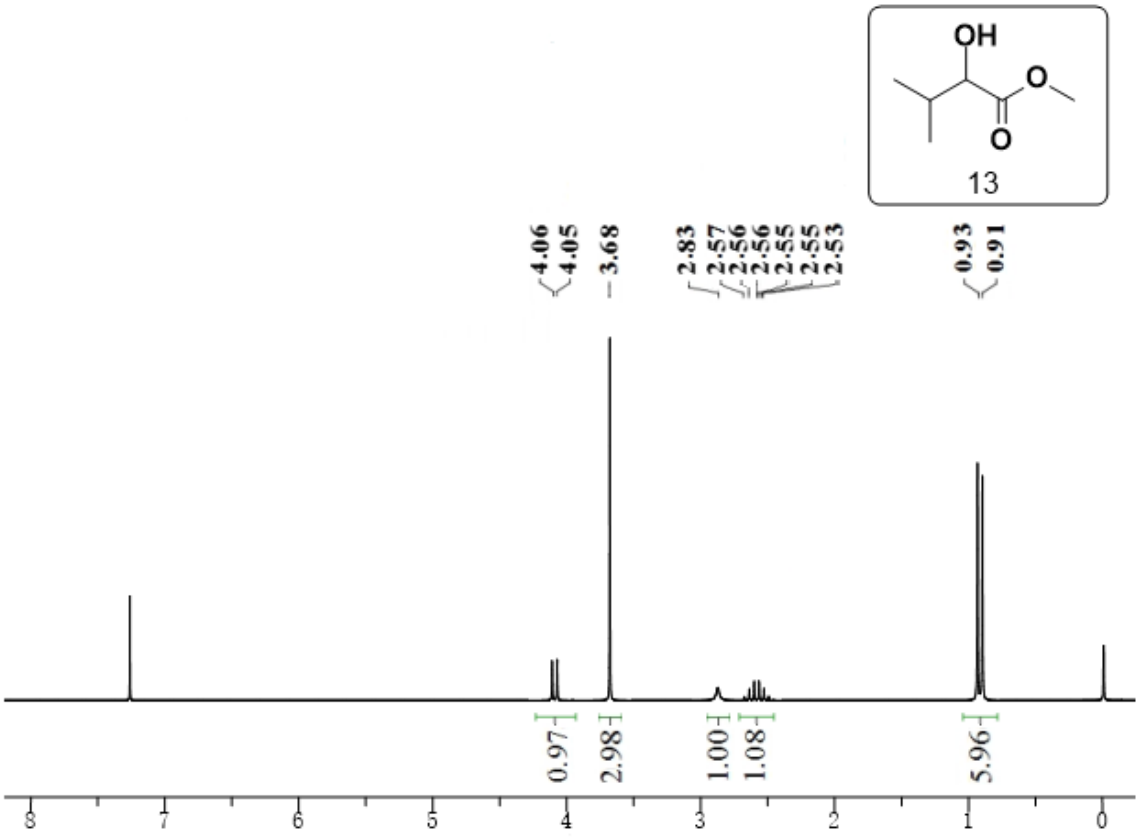
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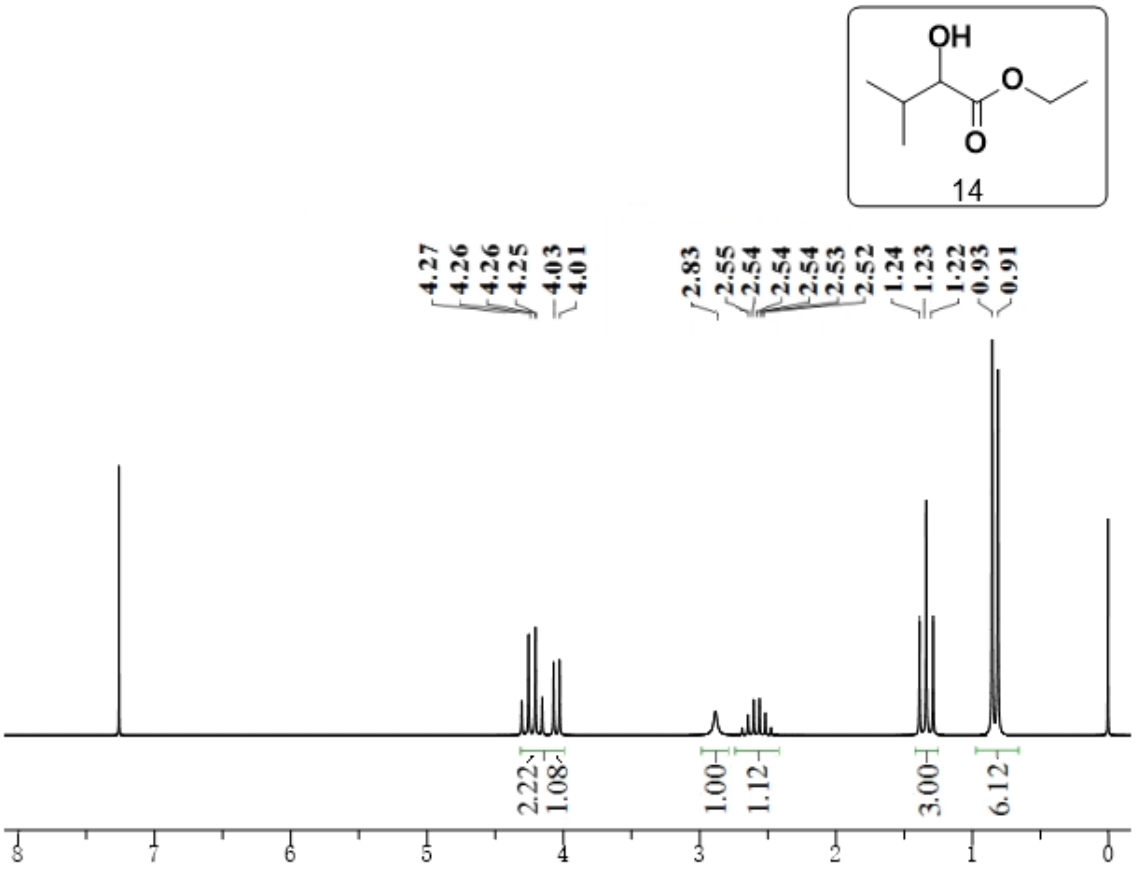
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1.22
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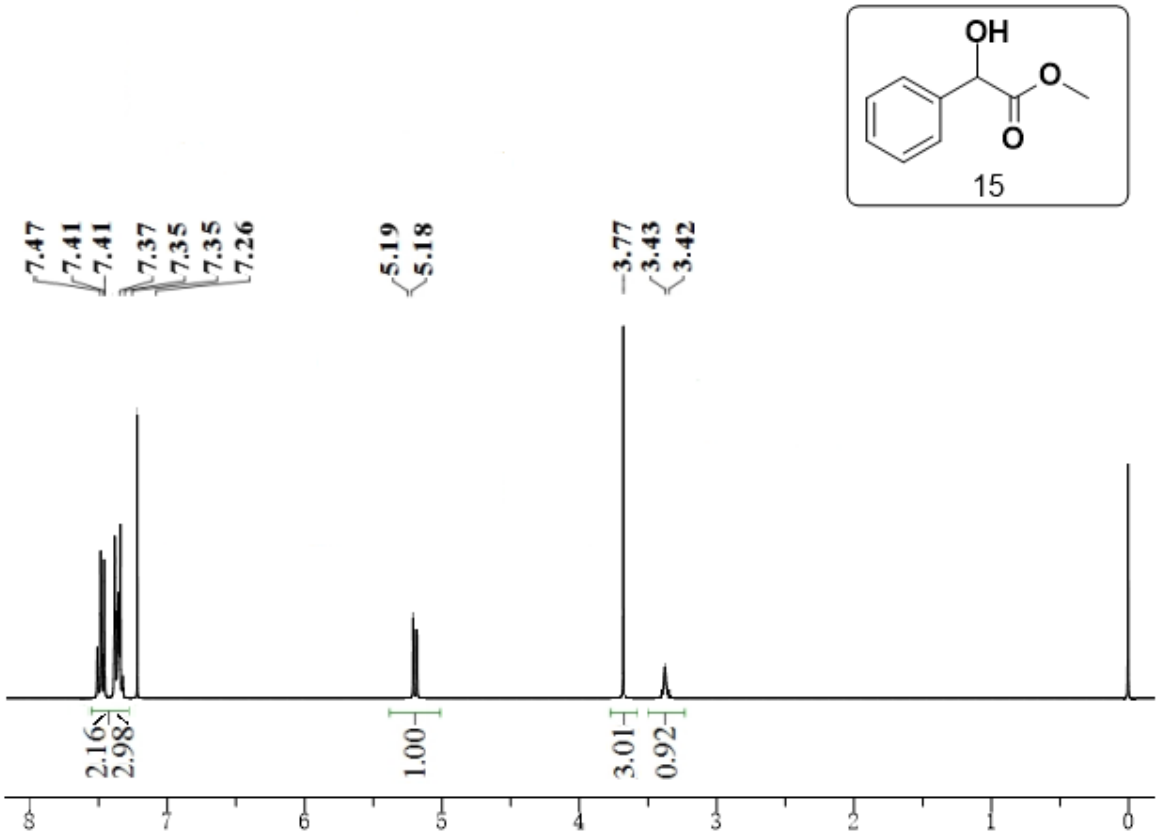
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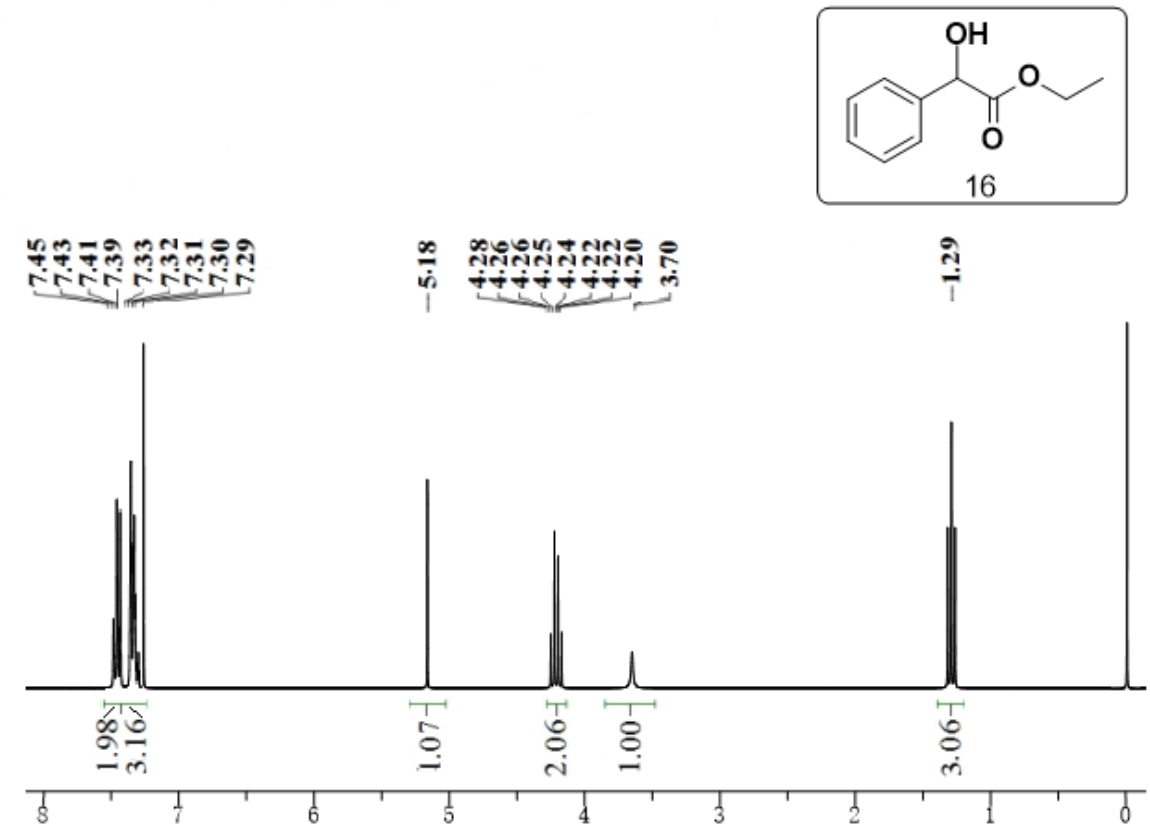
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4.25
4.24
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4.22
4.20
3.70
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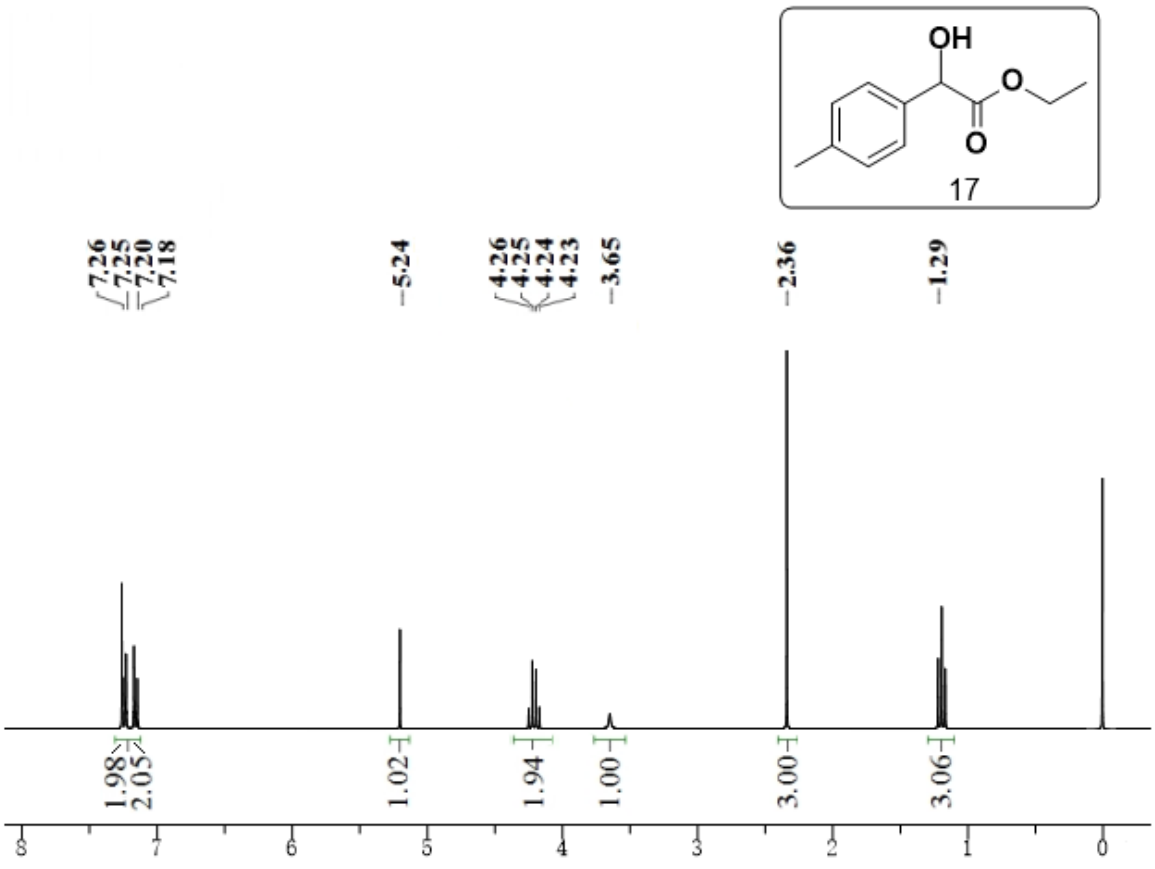
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1.29
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3.00
3.06
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7
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1
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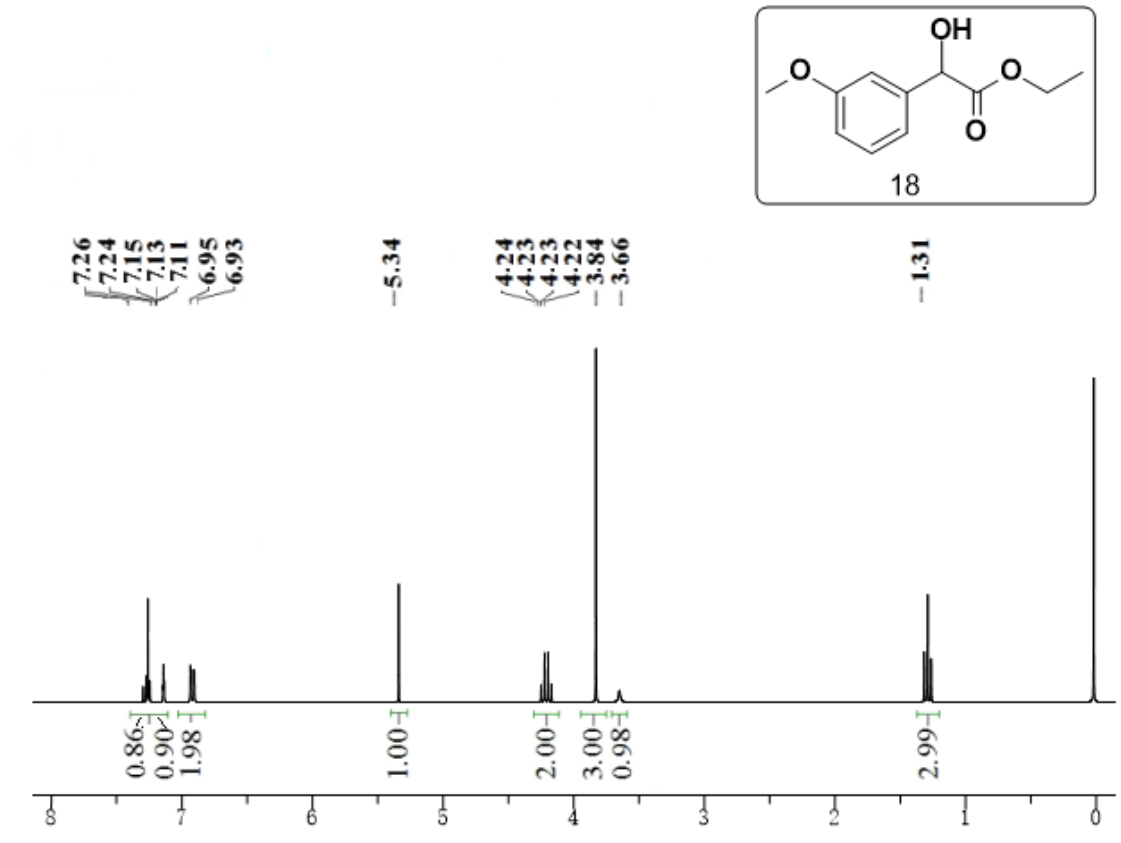
OH
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O
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7.11
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5.34
4.24
4.23
4.23
4.22
3.84
3.66
1.31
0.86
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6
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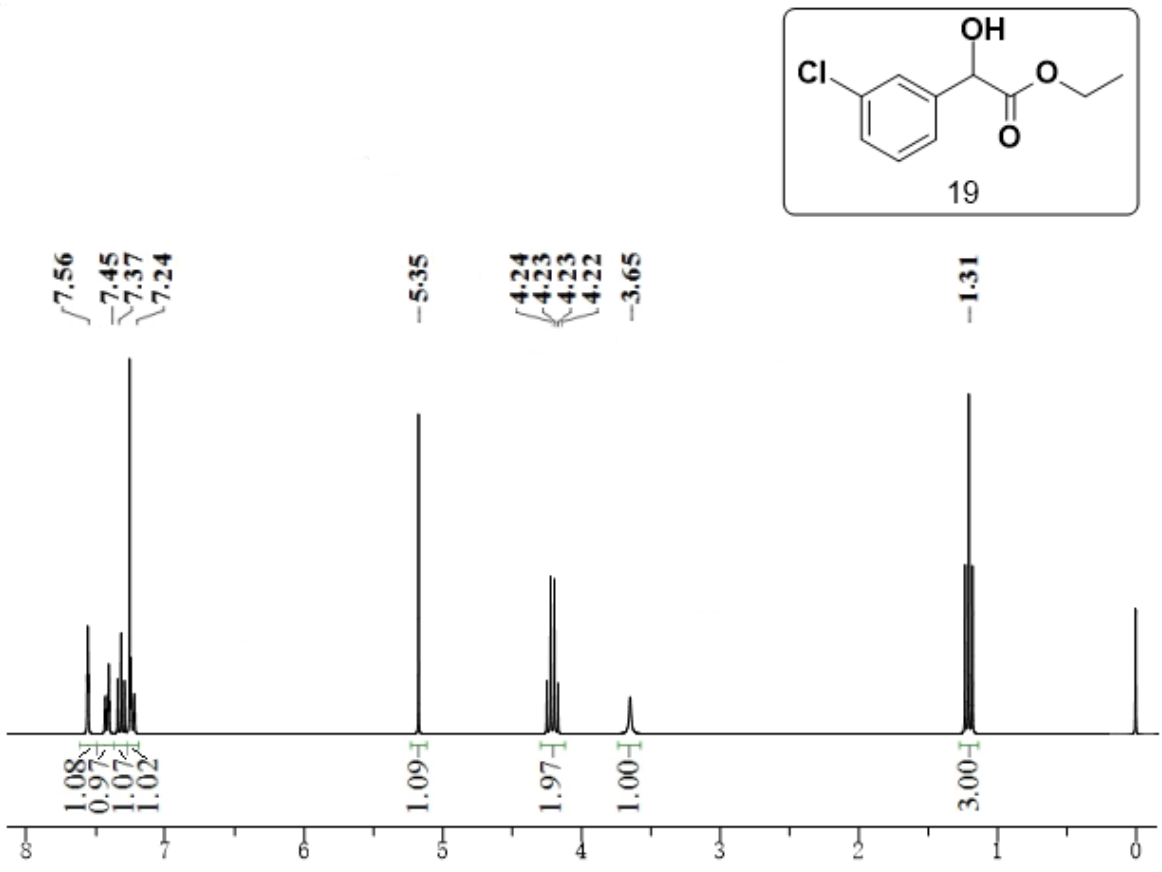
3
2
1
0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1.08
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1.00
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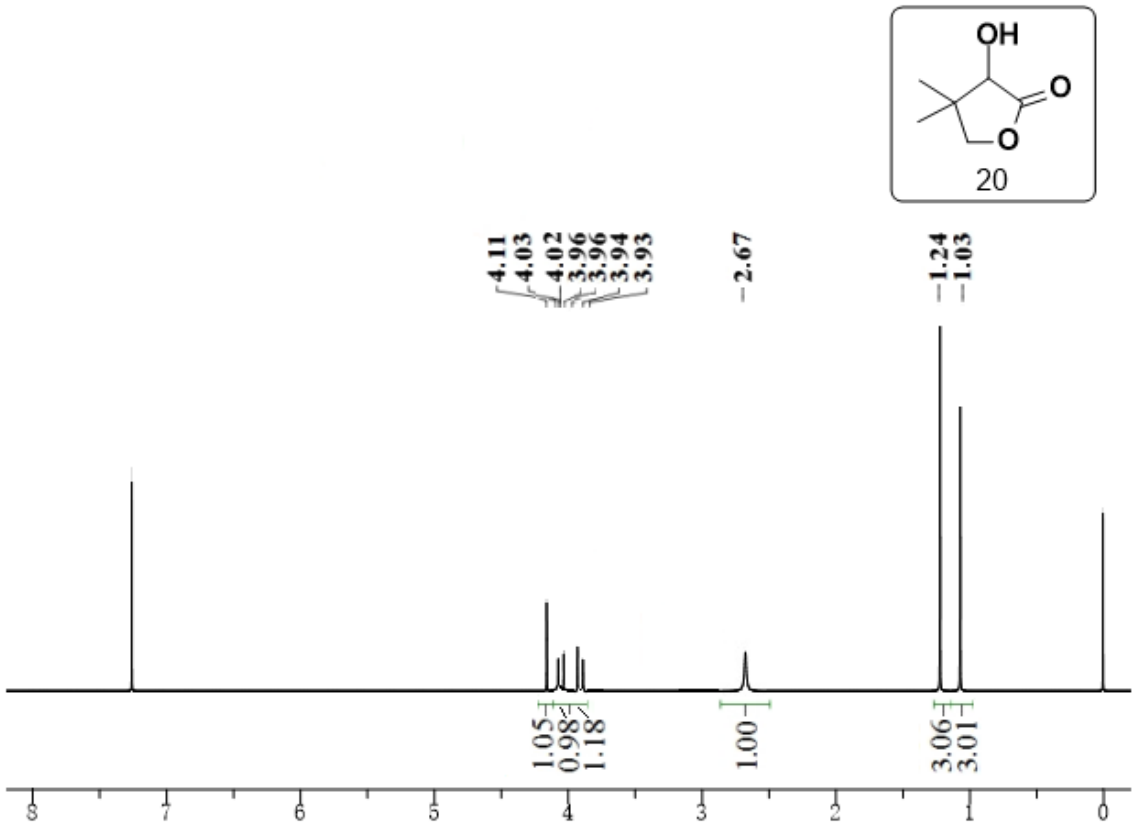
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1.05
0.98
1.18
1.00
3.06
3.01
8
7
6
5
4
3
2
1
0

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