Electronic Supplementary Information (ESI) for

A miraculous chiral Ir-Rh bimetallic nanocatalyst for asymmetric hydrogenation of activated ketones

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1. General Information

Unless otherwise noted, all chemicals were purchased from commercial sources without further purification. $IrCl_3$ (99.99%), $RhCl_3 \bullet xH_2O$ (99.99%) and 1,1-dimethoxyacetone **1a** (97%) were purchased from Alfa Aesar. 1-(1,3-Dioxan-2-yl)ethanone **1b**, 1,1-diethoxy-2-propanone **1c**, 1,1-dipropoxy-2-propanone **1d**, 1,1-dibutoxy-2-propanone **1e**, 1,1-diisopropoxy-2-propanone **1f** and 1,1-ditertbutoxy-2-propanone **1g** were synthesized as described in the literatures.[1-2] 2,2-Diethoxyacetophenone **1h** (96%) was purchased from Acros. 3,3-Dimethoxybutan-2-one **1i** (97%) and 3-hydroxy-2-butanone **1k** (97%) were from Adamas.1-Hydroxybutan-2-one **1j** (98%), 2-hydroxy-1-phenylethanone **1l** (97%) and (1-hydroxycyclohexyl)(phenyl)methanone **1m** (98%) were from Ark. Pyruvic aldehyde (30 wt.% in H_2O) was from Accela. 1,3-Propanediol (98%) was from Innochem. Chiral ionic liquid $CIL_{PEG\text{-}CD750}$ ($[CH_3(OCH_2CH_2)_{16}CD]^+[CH_3SO_3]^-$ (CD = cinchonidine)) was synthesized as reported[3]. Ethyl alcohol, propanol, isopropanol, *n*-butanol, *t*-butyl alcohol, toluene, glacial acetic acid, *n*-heptane and cyclohexane were all analytical reagents and purchased from Kermel. ^1H NMR was recorded on a Varian (400 MHz). Chemical shifts (δ) were denoted in ppm using residual solvent peaks as internal standard ($CDCl_3$, δ = 7.26 ppm). 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). HRTEM (Transmission electron microscopic) images were carried out by using a Tecnai F 30 (300 kV) instrument. ICP-AES (Inductively coupled plasma atomic emission spectrometer) analyses were performed on Optima 2000 DV (detection limit is 10 ppm).

2. Experiment Procedures

2.1 Preparation of chiral Ir-Rh bimetallic nanocatalyst

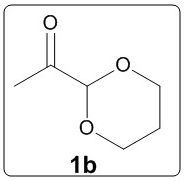
The chiral Ir-Rh bimetallic nanocatalyst was prepared as a typical example: a mixture of $IrCl_3$ (2.13 mg, 7.13×10^{-3} mmol), $RhCl_3 \bullet xH_2O$ (0.47 mg, 1.78×10^{-3} mmol) and $CIL_{PEG\text{-}CD750}$ (30 mg, 26.7×10^{-3} mmol) was added to a 75 mL stainless-steel autoclave. Then the autoclave was flushed for three times with 2.0 MPa H_2 and inflated to 4.0 MPa (H_2). After being stirred at 70 °C for 7 h, the reactor was cooled to room temperature and depressurized. At

this time, the color of the mixture changed from claret to black, which indicated that the chiral Ir-Rh bimetallic nanocatalyst formed. The preparation of other chiral Ir-Rh bimetallic nanocatalysts was carried out according to the same procedure.

2.2 Asymmetric hydrogenation of activated ketones

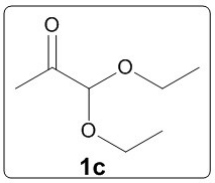
1,1-Dimethoxyacetone **1a** was used as a model reaction substrate: the autoclave was charged with the above-prepared chiral Ir-Rh bimetallic nanocatalyst , $CIL_{PEG\text{-}CD750}$ (12 mg), glacial acetic acid (0.85 g), toluene (0.3 g), *n*-heptane (0.15 g) and cyclohexane (50 mg, internal standard) and 1,1-dimethoxyacetone (53 mg, **1a**/Ir-Rh = 50, mol/mol). Then the reactor was flushed three times with 2.0 MPa H_2 and pressurized to the required hydrogen pressure at an appointed temperature for a designated time. After reaction, the autoclave was cooled in an ice-water bath and then depressurized. The lower chiral Ir-Rh bimetallic nanocatalyst phase was easily separated from the upper product phase by simple phase separation and directly reused in next catalytic cycle. The upper phase was directly analyzed by chiral GC.

3. ^{1}H NMR Data



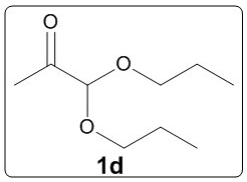
1b

1-(1,3-Dioxane-2-yl)ethanone **1b:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.75 (1H, s, OC*H*O), 3.96-3.78 (4H, m, OCH_2CH_2CH_2O), 2.24 (3H, s, COCH_3), 2.15 (2H, m, OCH$_2$CH_2CH$_2$O). The ^{1}H NMR data were consistent with those reported.[4]



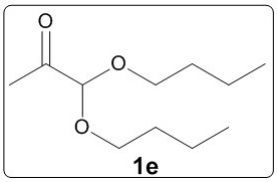
1c

1,1-Diethoxy-2-propanone **1c:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.34 (1H, s, OC*H*O), 3.43-3.36 (4H, q, OCH_2CH$_3$), 2.24 (3H, s, COCH_3), 1.27 (6H, t, CH$_2$CH_3). The ^{1}H NMR data were consistent with those reported.[5]



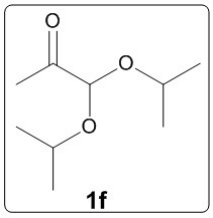
1d

1,1-Dipropoxy-2-propanone **1d:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.26 (1H, s, OC*H*O), 3.43-3.36 (4H, t, OCH_2CH$_2$), 2.05 (3H, s, COCH_3), 1.53 (4H, m, CH_2CH$_3$), 0.90 (6H, t, CH$_2$CH_3). The ^{1}H NMR data were consistent with those reported.[6]



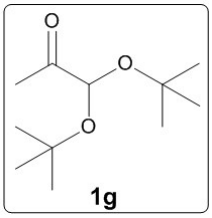
1e

1,1-Dibutoxy-2-propanone **1e:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.26 (1H, s, OC*H*O), 3.45 (4H, t, OC*H*$_2$CH$_2$), 2.05 (3H, s, COC*H*$_3$), 1.53-1.40 (8H, m, *CH*$_2$*CH*$_2$CH$_3$), 0.90 (6H, t, CH$_2$CH$_2$*CH*$_3$). The ^{1}H NMR data were consistent with those reported.[4]



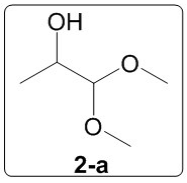
1f

1,1-Diisopropoxy-2-propanone **1f:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.39 (1H, s, OC*H*O), 3.83-3.75 (2H, m, OC*H*(CH$_3$)$_2$), 2.07 (3H, s, COC*H*$_3$), 1.27 (12H, d, OCH(C*H*$_3$)$_2$). The ^{1}H NMR data were consistent with those reported.[6]



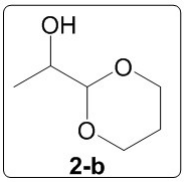
1g

1,1-Ditertbutoxy-2-propanone **1g:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.70 (1H, s, OC*H*O), 2.24 (3H, s, COC*H*$_3$), 1.26 (18H, s, C(C*H*$_3$)$_3$). The ^{1}H NMR data were consistent with those reported.[6]



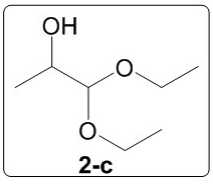
2-a

1,1-Dimethoxy-2-propanol **2-a:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.08 (1H, d, OC*H*O), 3.75 (1H, m, CH$_3$C*H*OH), 3.45 (6H, s, OC*H*$_3$), 2.17 (1H, br s, O*H*), 1.15 (3H, d, CHC*H*$_3$). The ^{1}H NMR data were consistent with those reported.[7]



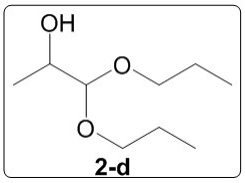
2-b

1-(1,3-Dioxane-2-yl)ethanol **2-b:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.27 (1H, d, OC*H*O), 4.15-3.92 (4H, m, OC*H*$_2$), 3.83 (1H, m, CH$_3$C*H*OH), 2.17 (1H, br s, O*H*), 1.90 (2H, m, CH$_2$C*H*$_2$CH$_2$), 1.15 (3H, d, CHC*H*$_3$). The ^{1}H NMR data were consistent with those reported.[4]



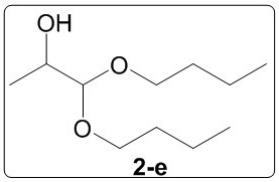
2-c

1,1-Diethoxy-2-propanol **2-c:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.10 (1H, d, OC*H*O), 3.75 (1H, m, CH_3C*H*OH), 3.53 (4H, q, OC*H*$_2$$CH_3$), 2.16 (1H, br s, O*H*), 1.21 (6H, t, CH_2*CH*$_3$), 1.15 (3H, d, CHC*H*$_3$). The ^{1}H NMR data were consistent with those reported.[8]



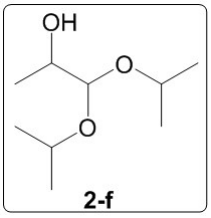
2-d

1,1-Dipropoxy-2-propanol **2-d:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.12 (1H, d, OC*H*O), 3.75 (1H, m, CH_3C*H*OH), 3.57 (4H, t, OC*H*$_2$$CH_2CH_3$), 2.16 (1H, br s, O*H*), 1.50 (4H, m, OCH_2C*H*$_2$$CH_3$), 1.15 (3H, d, CHC*H*$_3$), 0.99 (6H, t, OCH_2CH_2*CH*$_3$). The ^{1}H NMR data were consistent with those reported.[6]



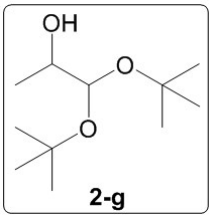
2-e

1,1-Dibutoxy-2-propanol **2-e:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.29 (1H, d, OC*H*O), 3.83 (1H, m, CH_3C*H*OH), 3.47 (4H, t, OC*H*$_2$$CH_2CH_2CH_3$), 2.17 (1H, br s, O*H*), 1.41-1.27 (8H, m, OCH_2C*H*$_2$*CH*$_2$$CH_3$), 1.15 (3H, d, CHC*H*$_3$), 0.96 (6H, t, $OCH_2CH_2CH_2$C*H*$_3$). The ^{1}H NMR data were consistent with those reported.[4]



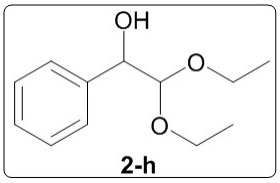
2-f

1,1-Diisopropoxy-2-propanol **2-f:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.12 (1H, d, OC*H*O), 3.75 (1H, m, CH_3C*H*OH), 3.63 (2H, m, OC*H*$(CH_3)_2$), 2.17 (1H, br s, O*H*), 1.15 (3H, d, CHC*H*$_3$), 0.91 (12H, d, CH(*CH*$_3$)$_2$). The ^{1}H NMR data were consistent with those reported.[6]



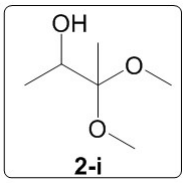
2-g

1,1-Ditertbutoxy-2-propanol **2-g:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.12 (1H, d, OC*H*O), 3.75 (1H, m, CH_3C*H*OH), 2.17 (1H, br s, O*H*), 1.15 (3H, d, CHC*H*$_3$), 0.89 (18H, s, C(*CH*$_3$)$_3$). The ^{1}H NMR data were consistent with those reported.[6]



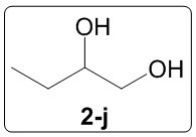
2-h

α-(Diethoxymethyl)benzenemethanol **2-h:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.42 (2H, m, C*H*CC*H*), 7.24 (3H, m, C*H*C*H*C*H*), 4.60 (1H, d, OC*H*O), 4.39 (1H, d, C*H*OH), 3.76 (4H, q, O$CH_2$$CH_3$), 2.77 (1H, br s, O*H*), 1.27 (6H, t, OCH_2CH_3). The ^{1}H NMR data were consistent with those reported.[9]



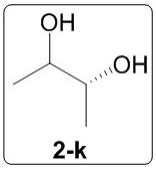
2-i

3,3-Dimethoxy-2-butanol **2-i:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 3.85 (1H, q, CH_3C*H*OH), 3.28 (6H, s, OCH_3), 2.17 (1H, br s, O*H*), 1.27 (3H, s, CCH_3), 1.15 (3H, d, CHCH_3). ^{1}H NMR data were consistent with those reported.[6]



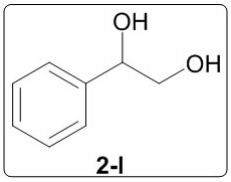
2-j

1,2-Butanediol **2-j:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 4.15 (1H, br s, CHO*H*), 4.05 (1H, br s, CH_2O*H*), 3.57 (2H, d, CH_2OH), 3.38 (1H, m, C*H*OH), 1.41(2H, m, C$H_2$$CH_3$), 0.93 (3H, t, CH_2CH_3). ^{1}H NMR data were consistent with those reported.[10]



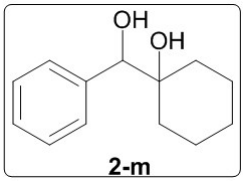
2-k

2,3-Butanediol **2-k:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 3.89 (2H, m, C*H*OH), 3.53 (2H, br s, O*H*), 1.17 (6H, d, CH_3). ^{1}H NMR data were consistent with those reported.[11]



2-l

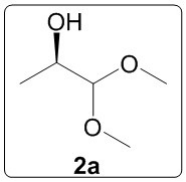
1-Phenyl-1,2-ethanediol **2-l:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.32 (2H, m, C*H*CC*H*), 7.24 (3H, m, C*H*C*H*C*H*), 4.76 (1 H, t, C*H*OH), 3.69-3.60 (2H, dd, CH_2OH), 3.07 (1 H, br s, CHO*H*), 2.83 (1 H, br s, CH_2O*H*),. ^{1}H NMR data were consistent with those reported.[12]



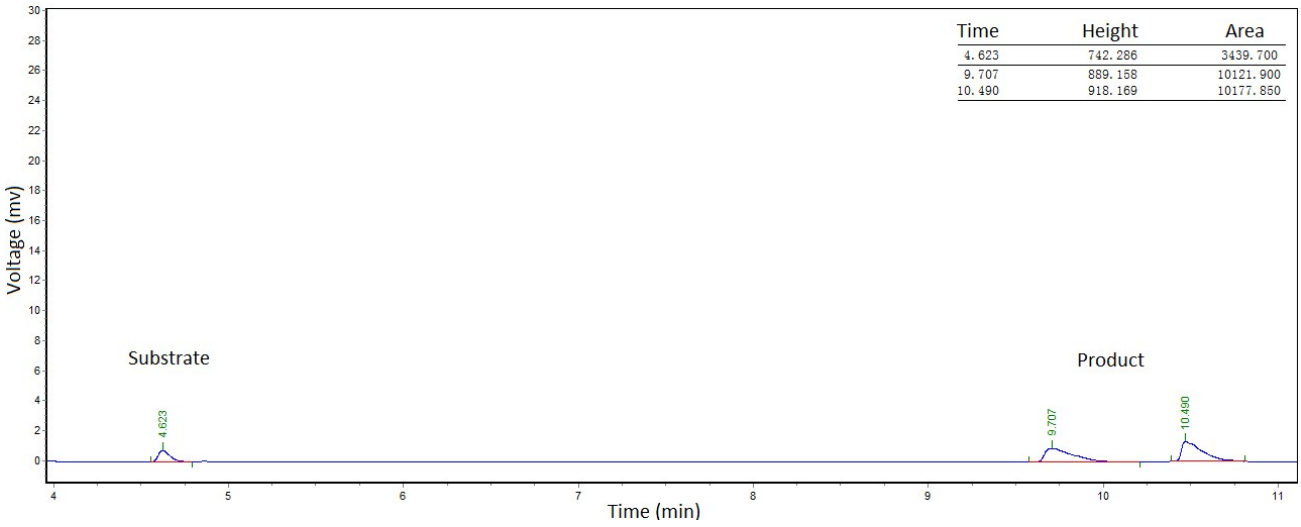
2-m

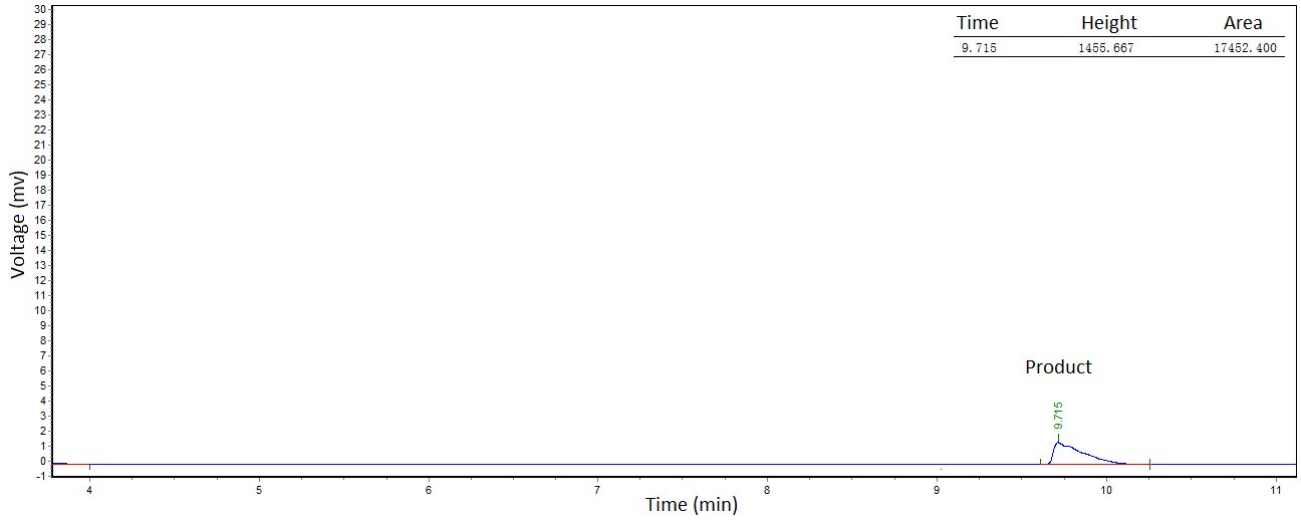
α-(1-Hydroxycyclohexyl)benzenemethanol **2-m:** ^{1}H NMR (400 MHz, $CDCl_3$), δ = 7.36 (2H, m, C*H*CC*H*), 7.25 (3H, m, C*H*C*H*C*H*), 4.47 (1H, s, C*H*OH), 2.48 (1H, br s, CHO*H*), 1.79 (1H, br s, O*H*), 1.63-1.21 (10H, m, CH_2CH_2CH_2CH_2CH_2). ^{1}H NMR data were consistent with those reported.[13]

4. GC Charts

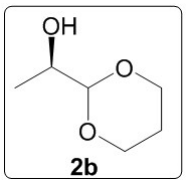


2a

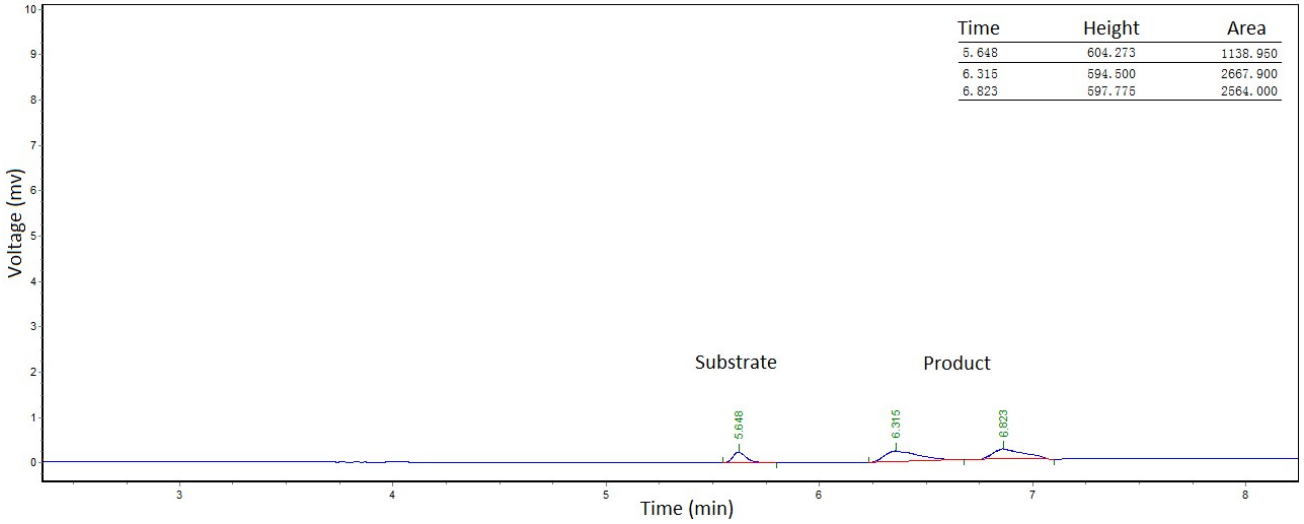


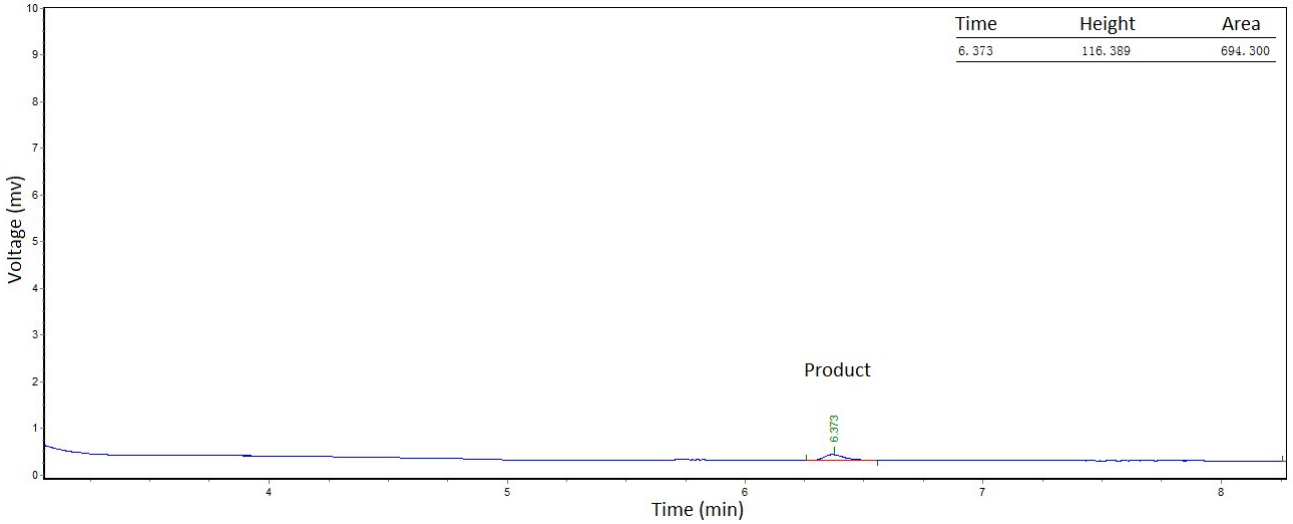


GC analytical conditions for **2a**: the temperature of gasify room, column, and detector were 200 ºC, 70 ºC and 200 ºC, respectively.

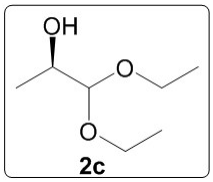


2b

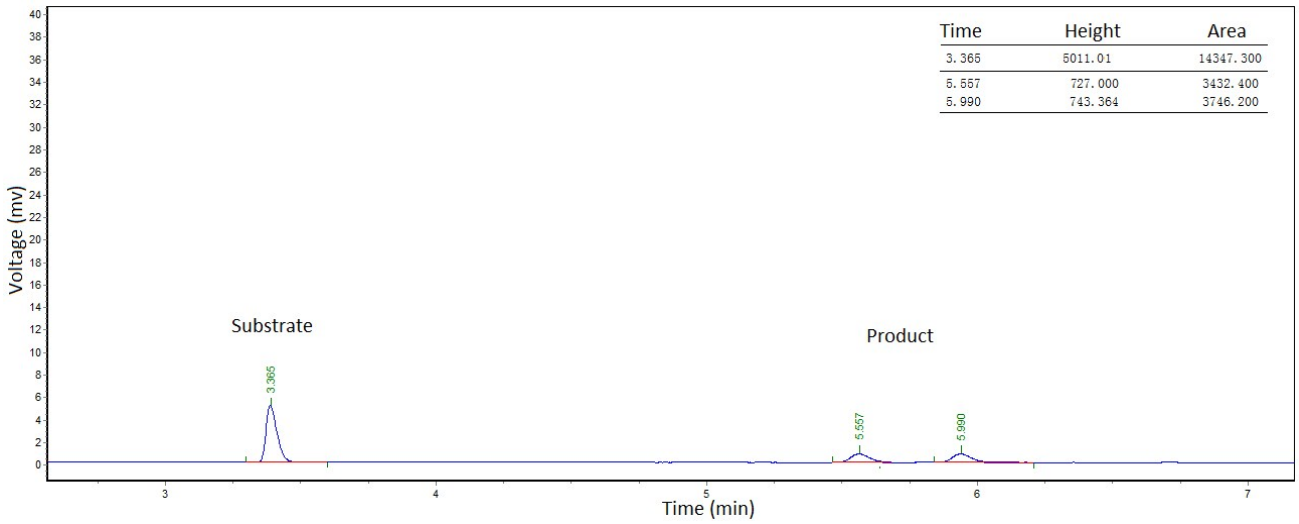


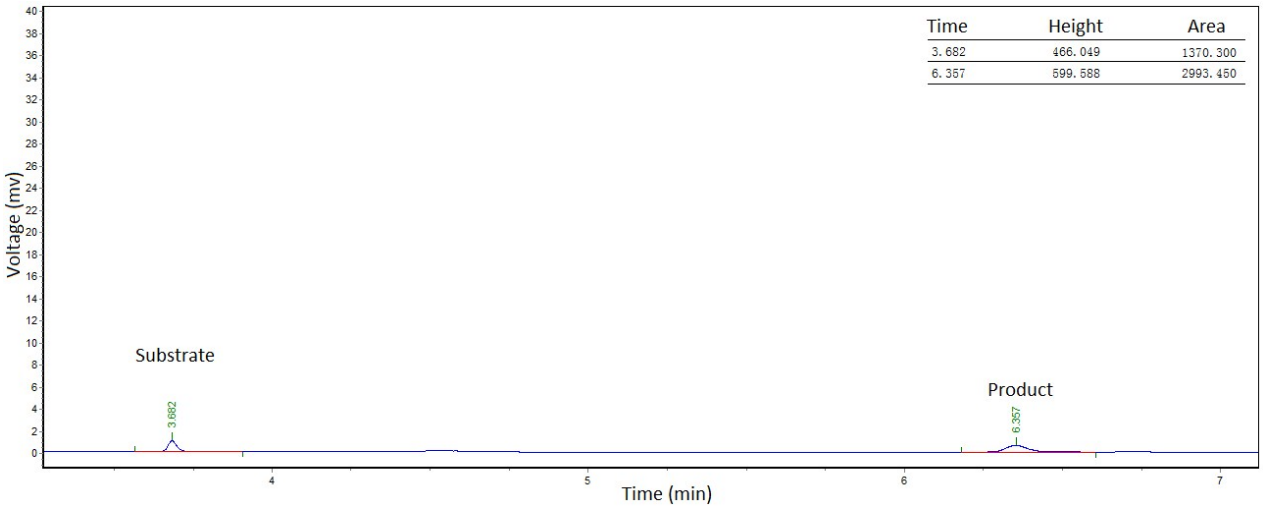


GC analytical conditions for **2b**: the temperature of gasify room, column, and detector were 200 ºC, 90 ºC and 200 ºC, respectively.

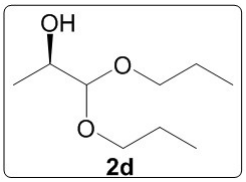


2c

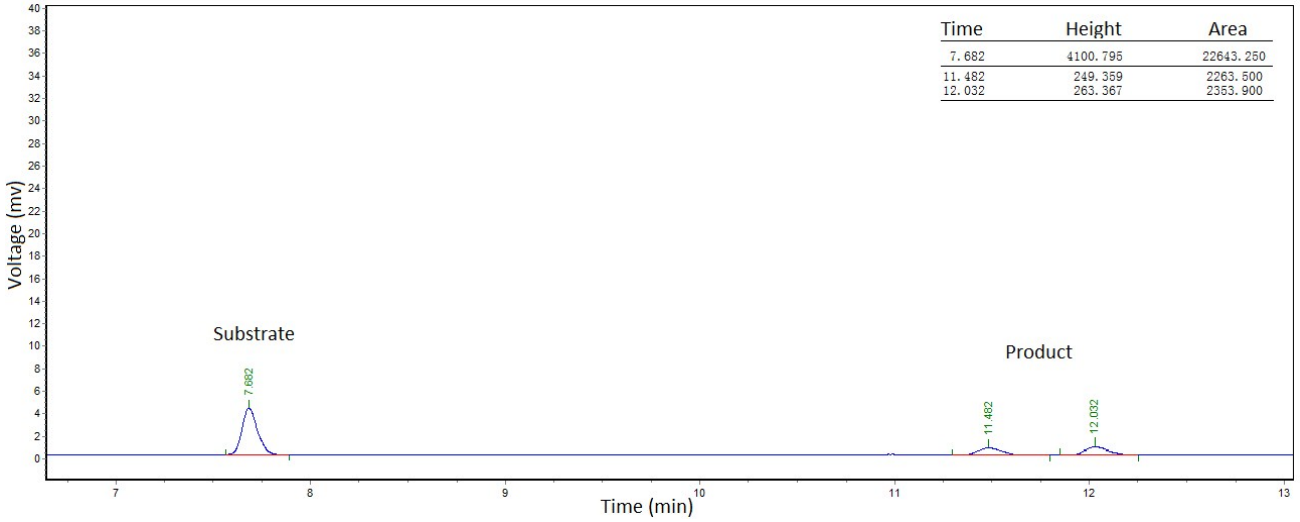


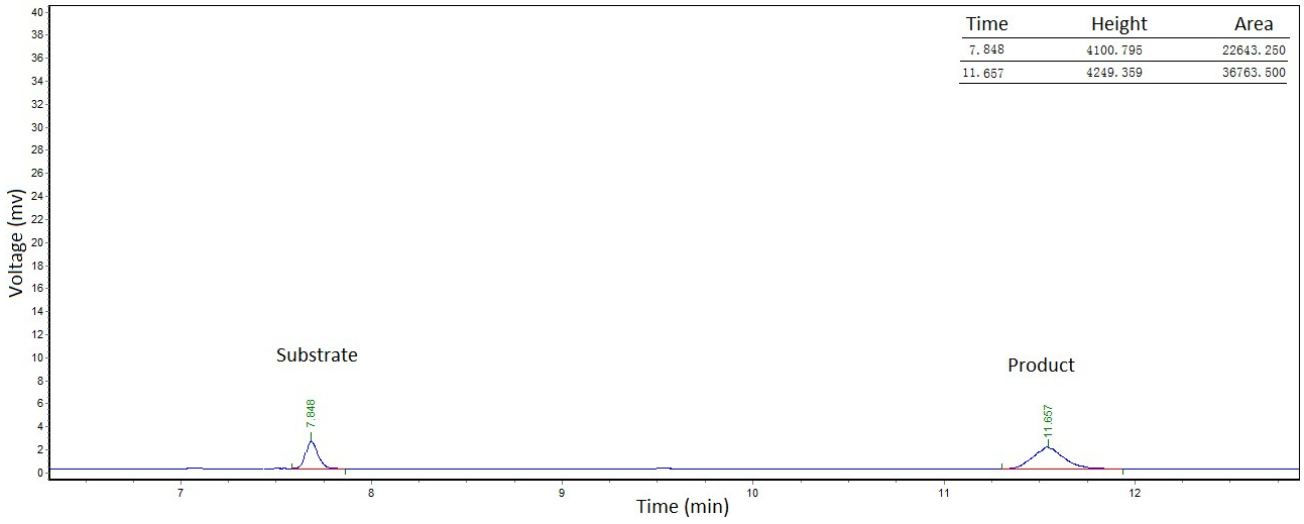


GC analytical conditions for **2c**: the temperature of gasify room, column, and detector were 200 ºC, 90 ºC and 200 ºC, respectively.

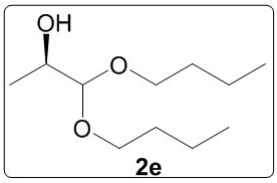


2d

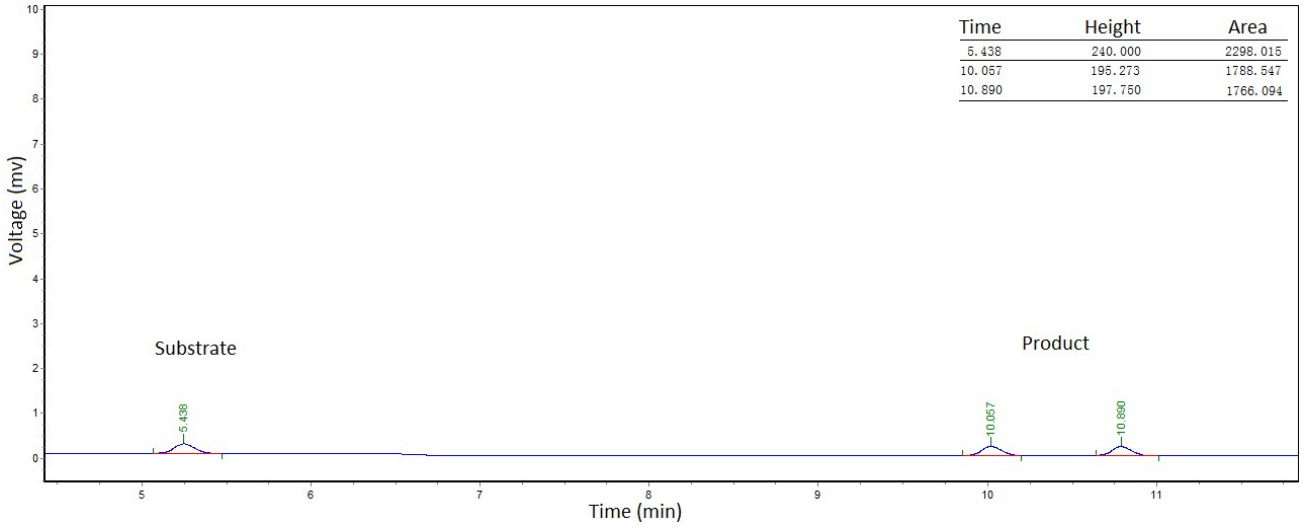


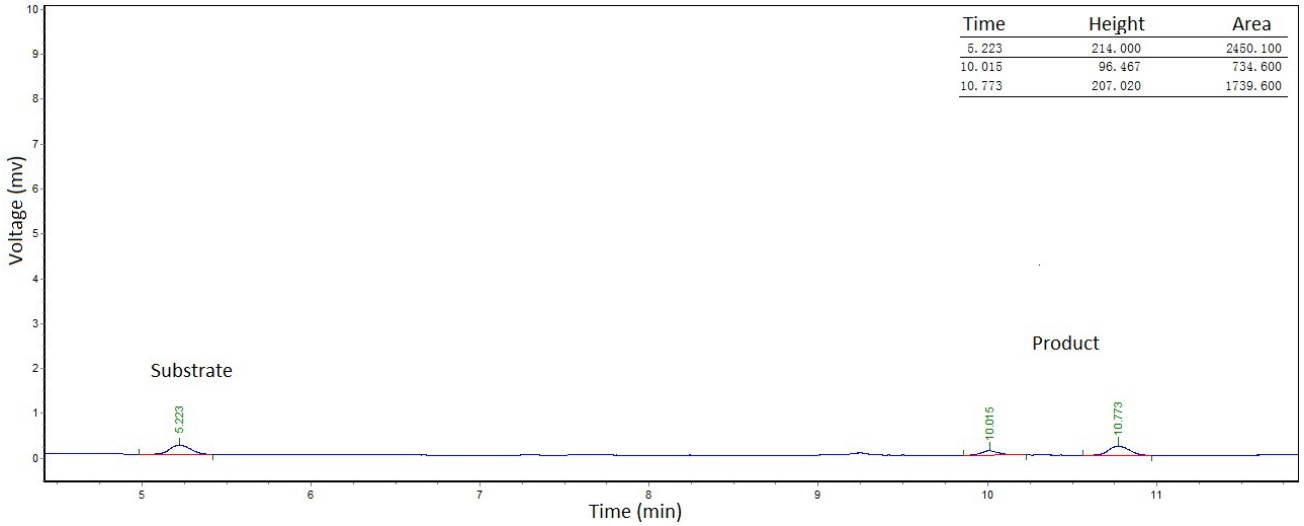


GC analytical conditions for **2d**: the temperature of gasify room, column, and detector were 200 ºC, 90 ºC and 200 ºC, respectively.

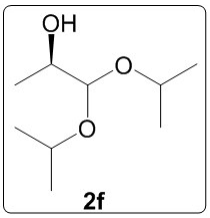


2e

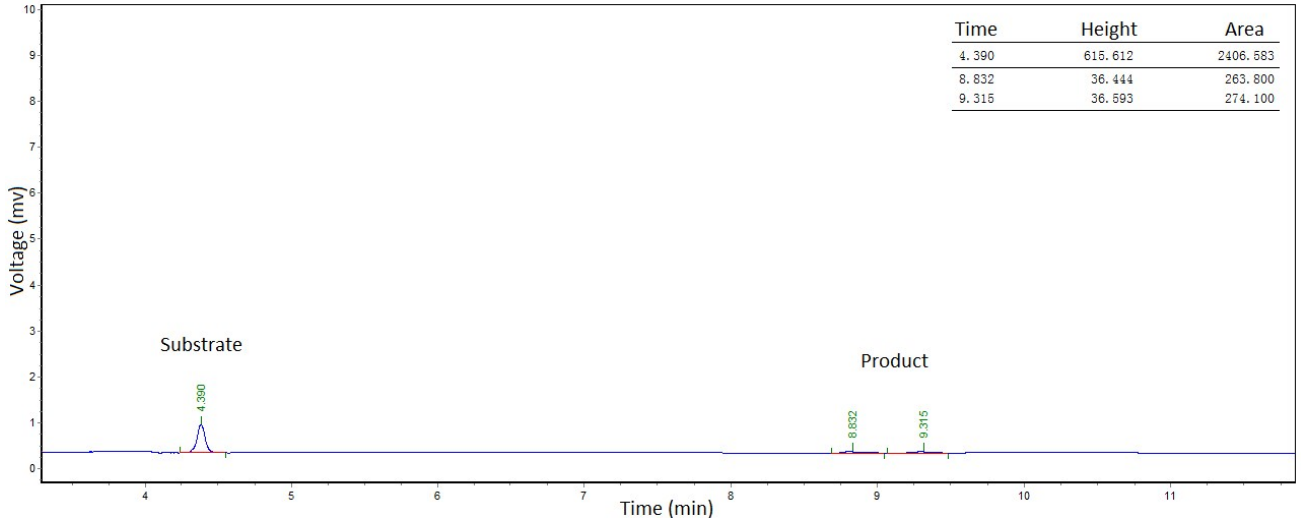


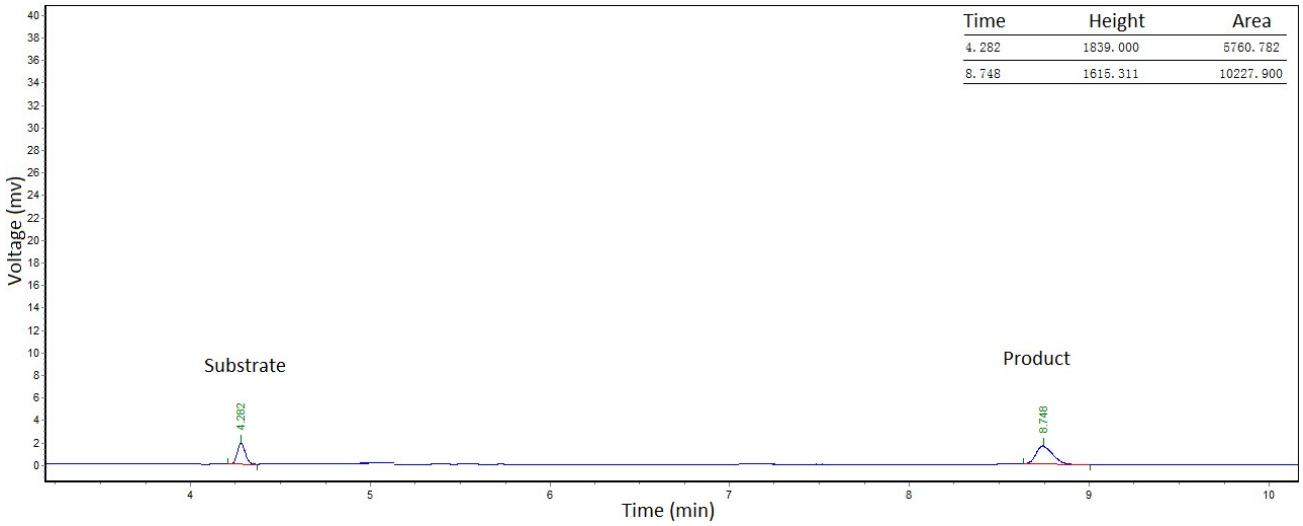


GC analytical conditions for **2e**: the temperature of gasify room, column, and detector were 200 ºC, 100 ºC and 200 ºC, respectively.

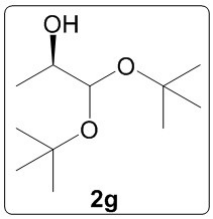


2f

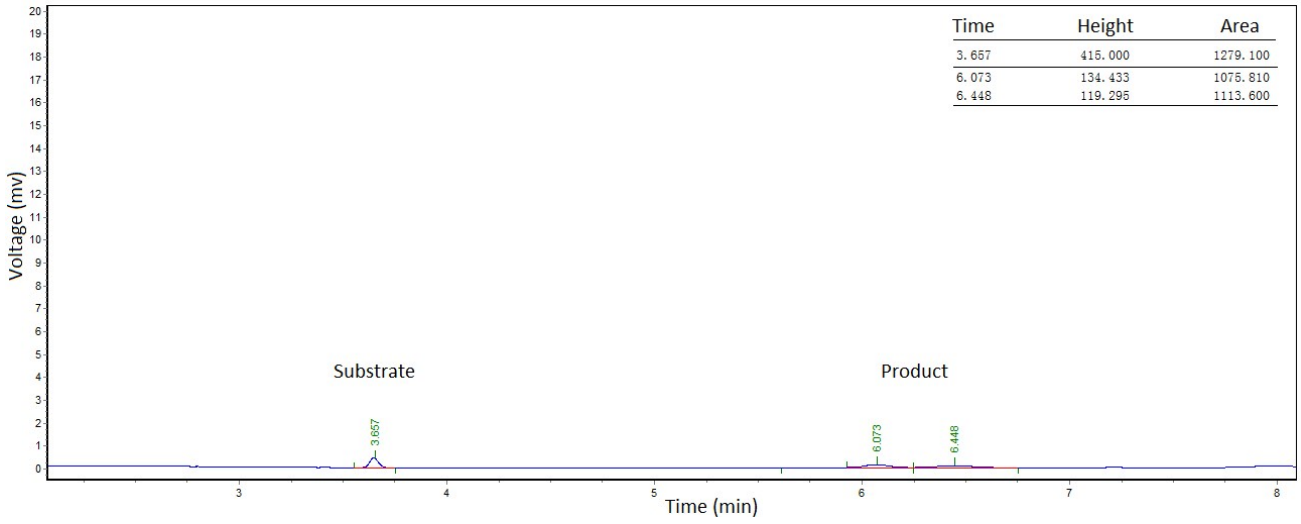


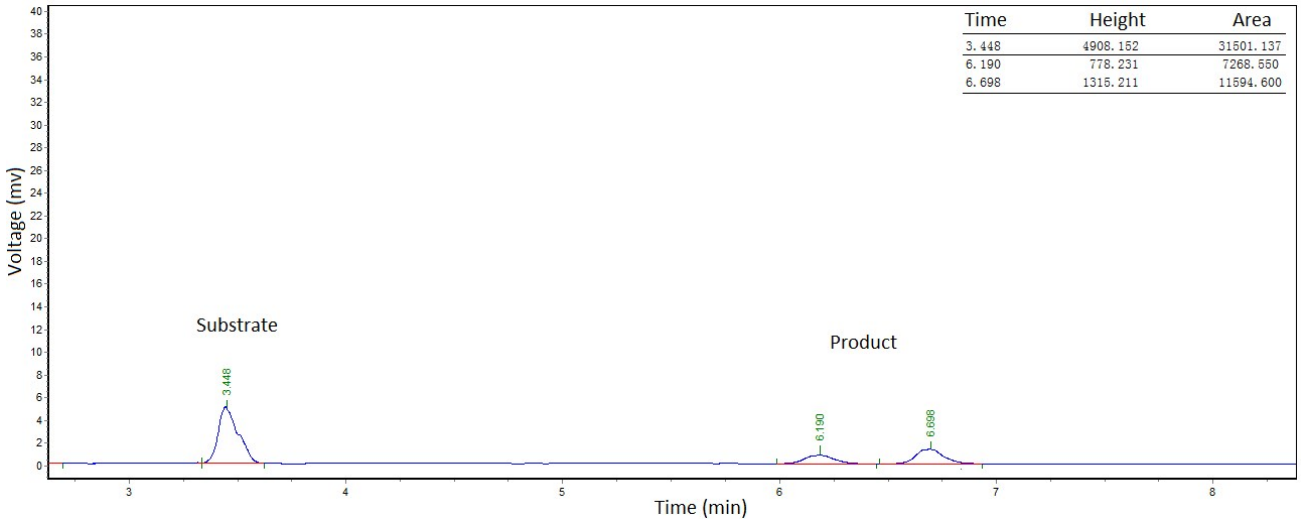


GC analytical conditions for **2f**: the temperature of gasify room, column, and detector were 200 ºC, 90 ºC and 200 ºC, respectively.

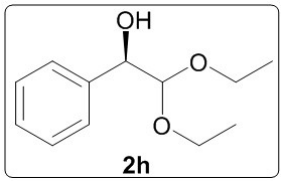


2g

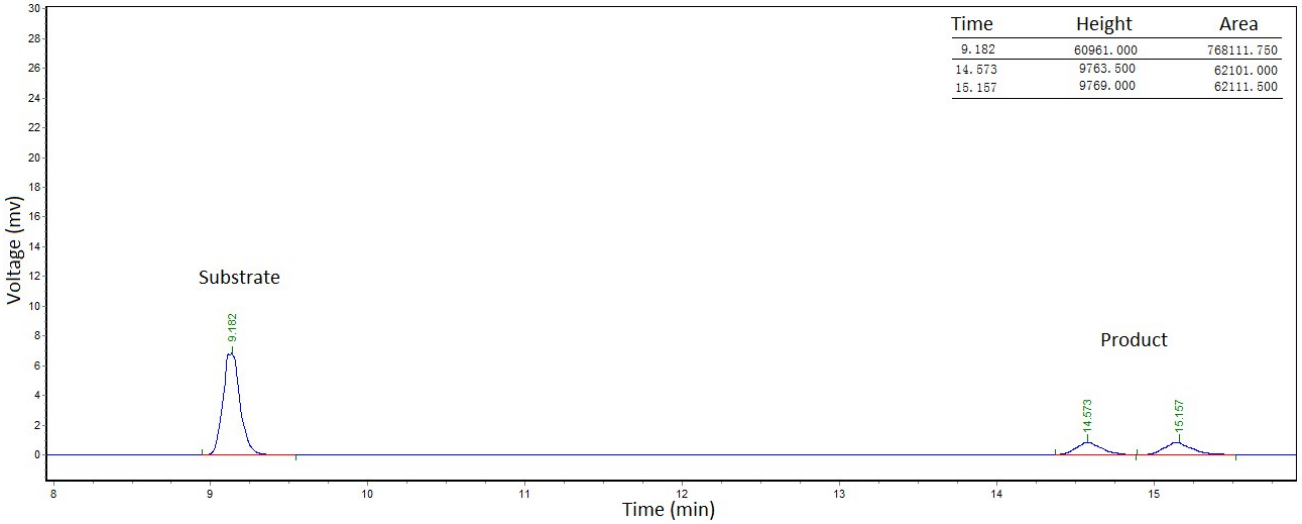


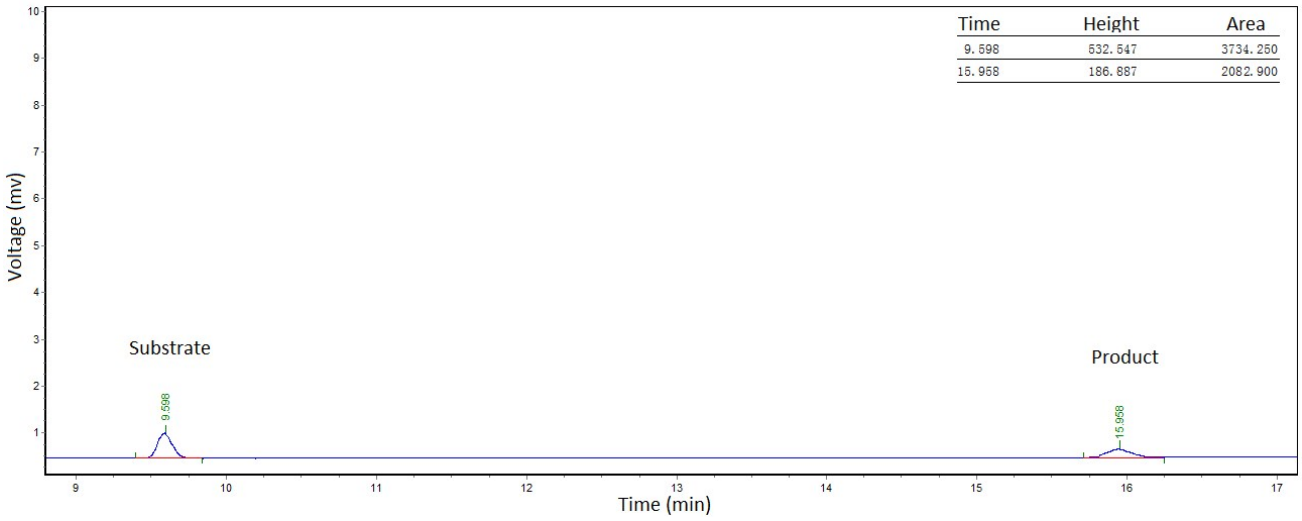


GC analytical conditions for **2g**: the temperature of gasify room, column, and detector were 200 ºC, 120 ºC and 200 ºC, respectively.

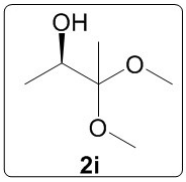


2h

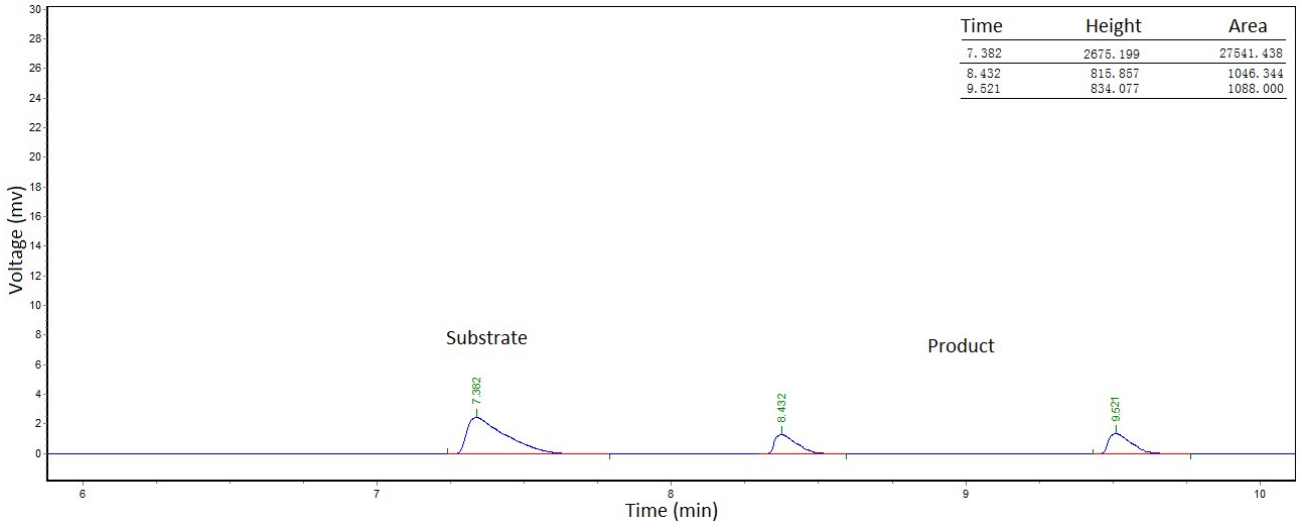


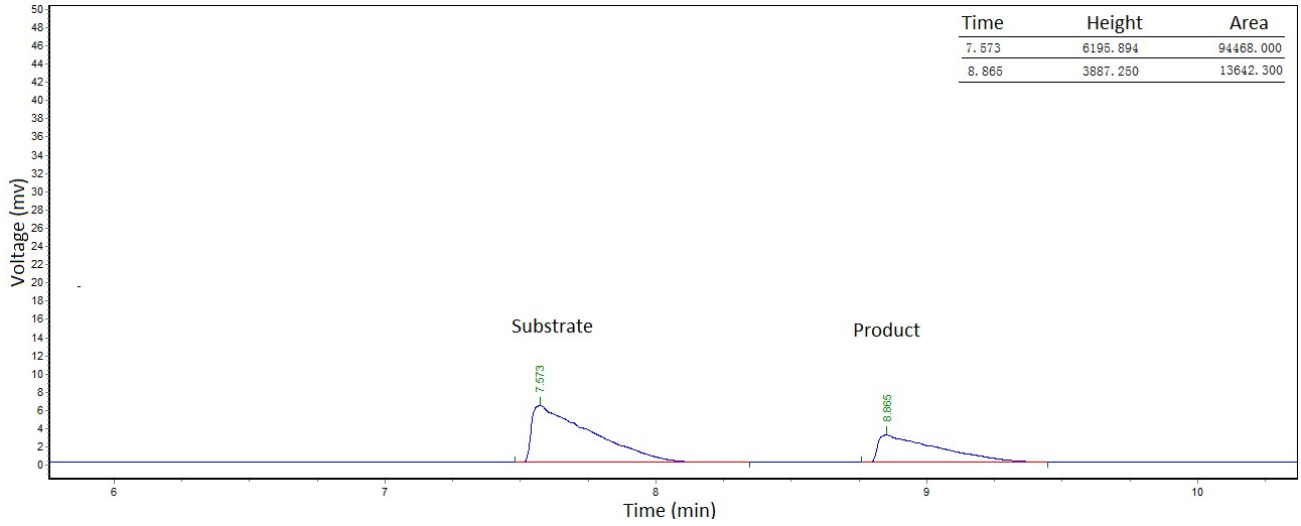


GC analytical conditions for **2h**: the temperature of gasify room, column, and detector were 200 ºC, 140 ºC and 200 ºC, respectively.

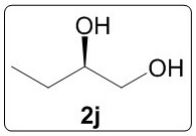


2i

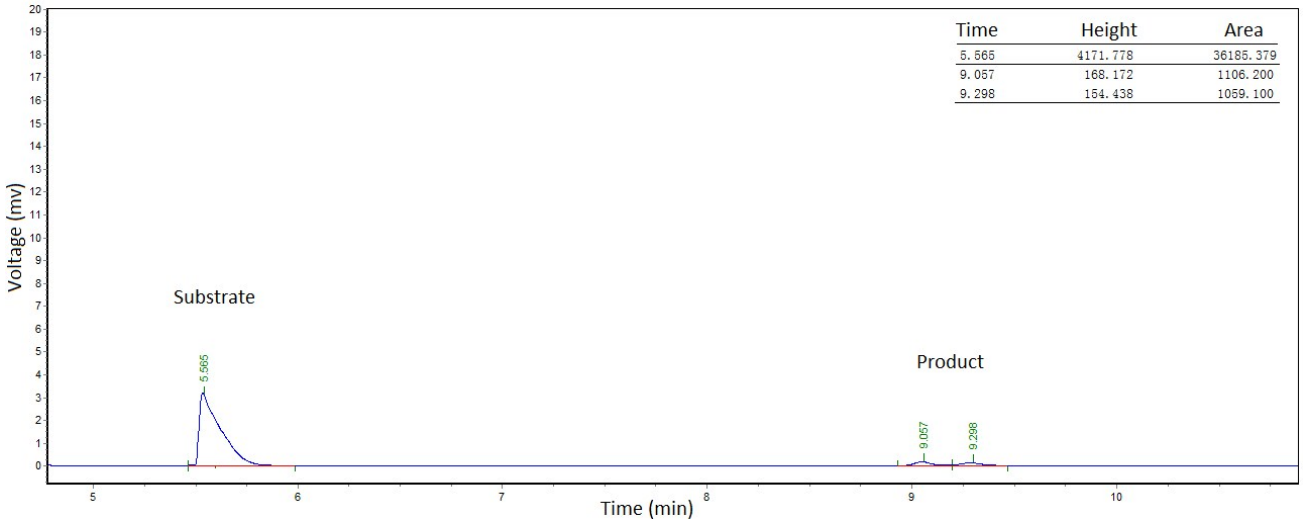


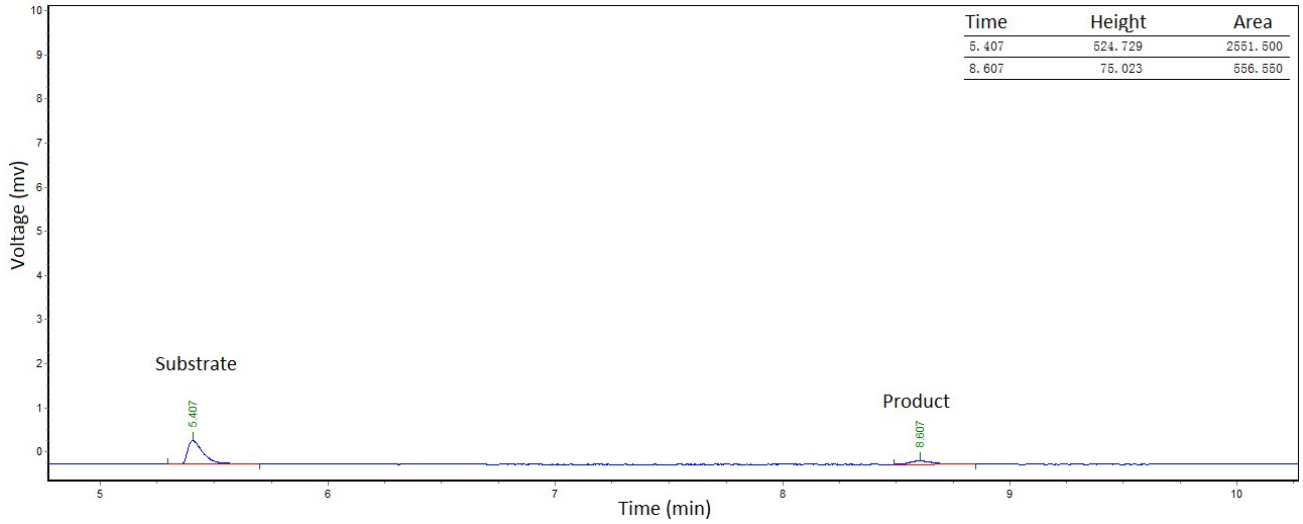


GC analytical conditions for **2i**: the temperature of gasify room, column, and detector were 200 ºC, 70 ºC and 200 ºC, respectively.

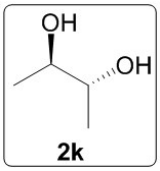


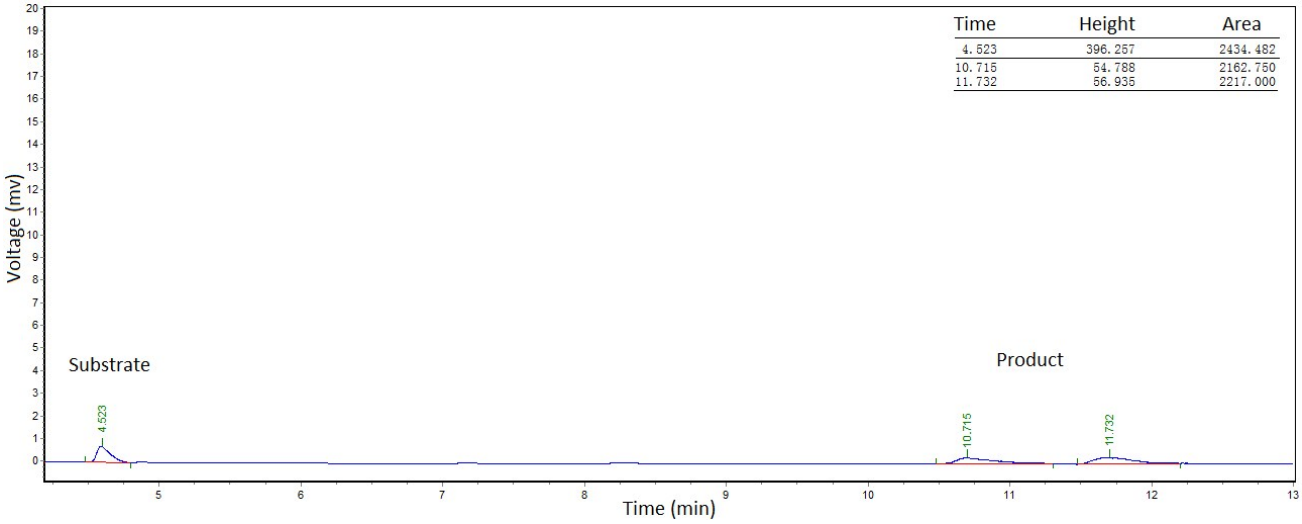
2j

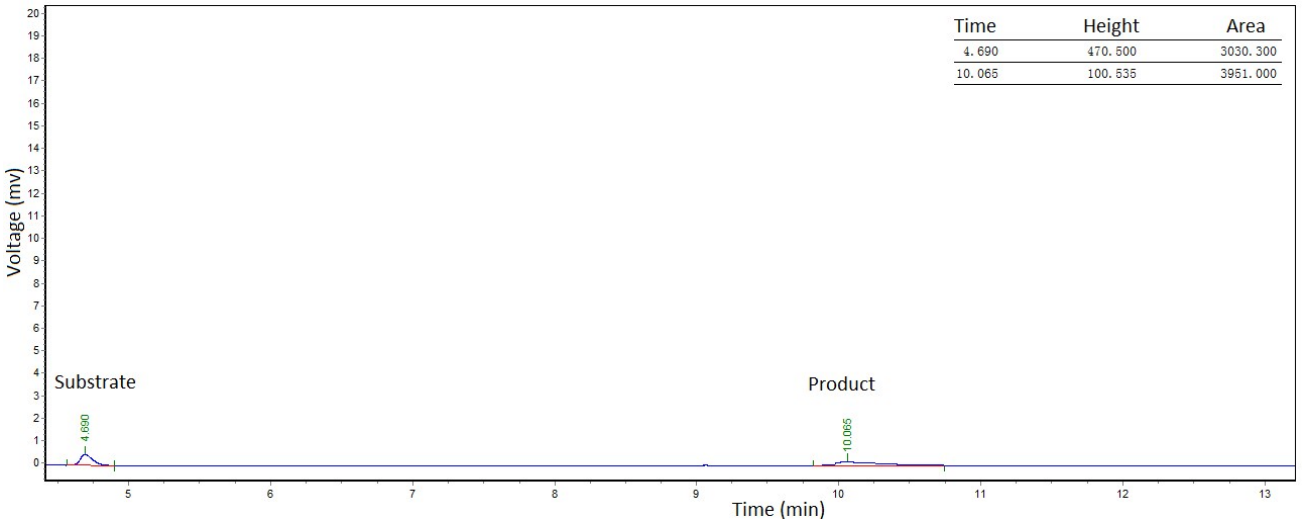




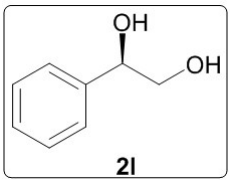
GC analytical conditions for **2j**: the temperature of gasify room, column, and detector were 200 ºC, 70 ºC and 200 ºC, respectively.



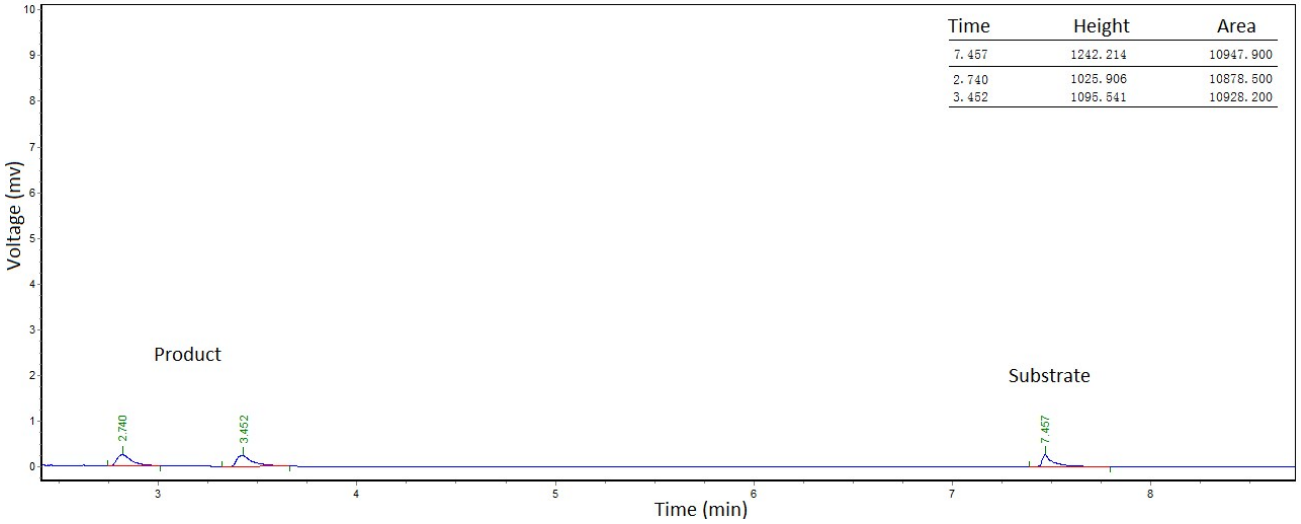


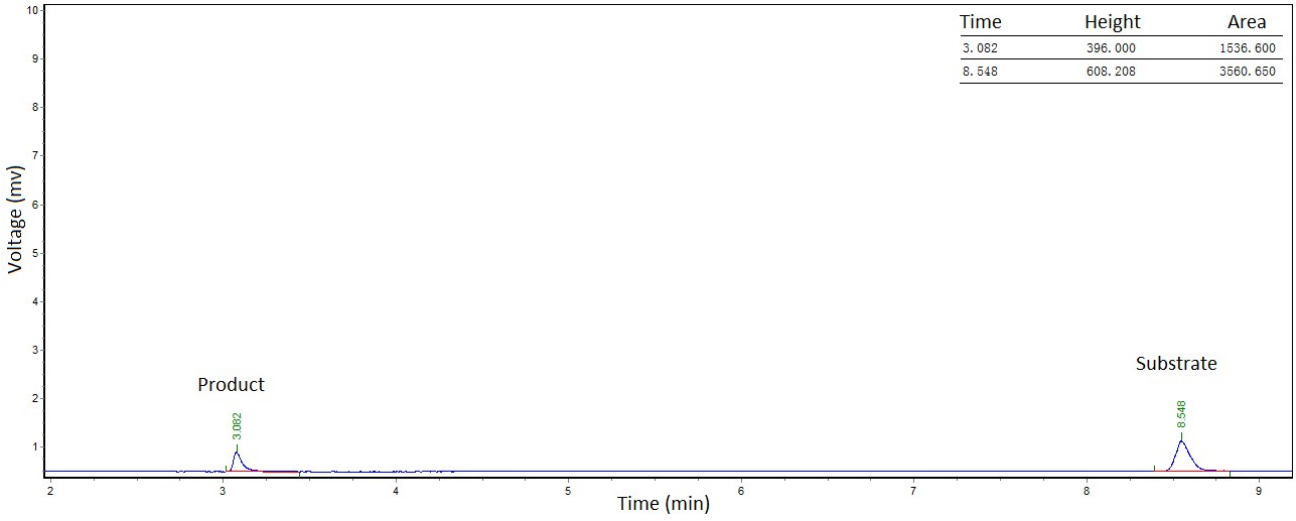


GC analytical conditions for **2k**: the temperature of gasify room, column, and detector were 200 ºC, 70 ºC and 200 ºC, respectively.

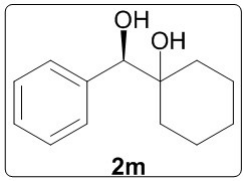


2l

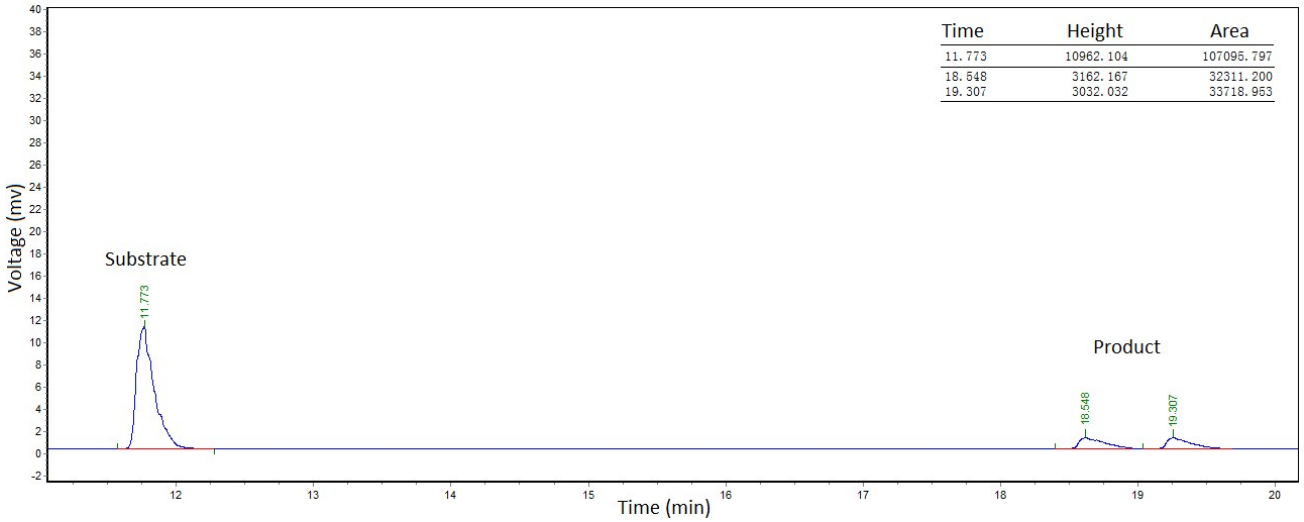


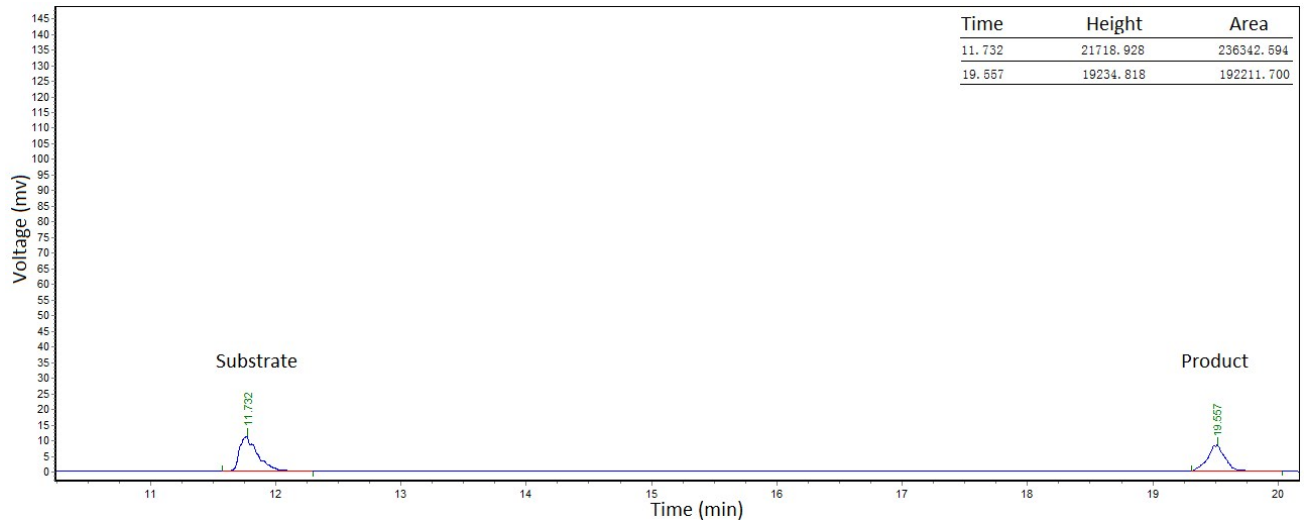


GC analytical conditions for **2l**: the temperature of gasify room, column, and detector were 200 ºC, 140 ºC and 200 ºC, respectively.



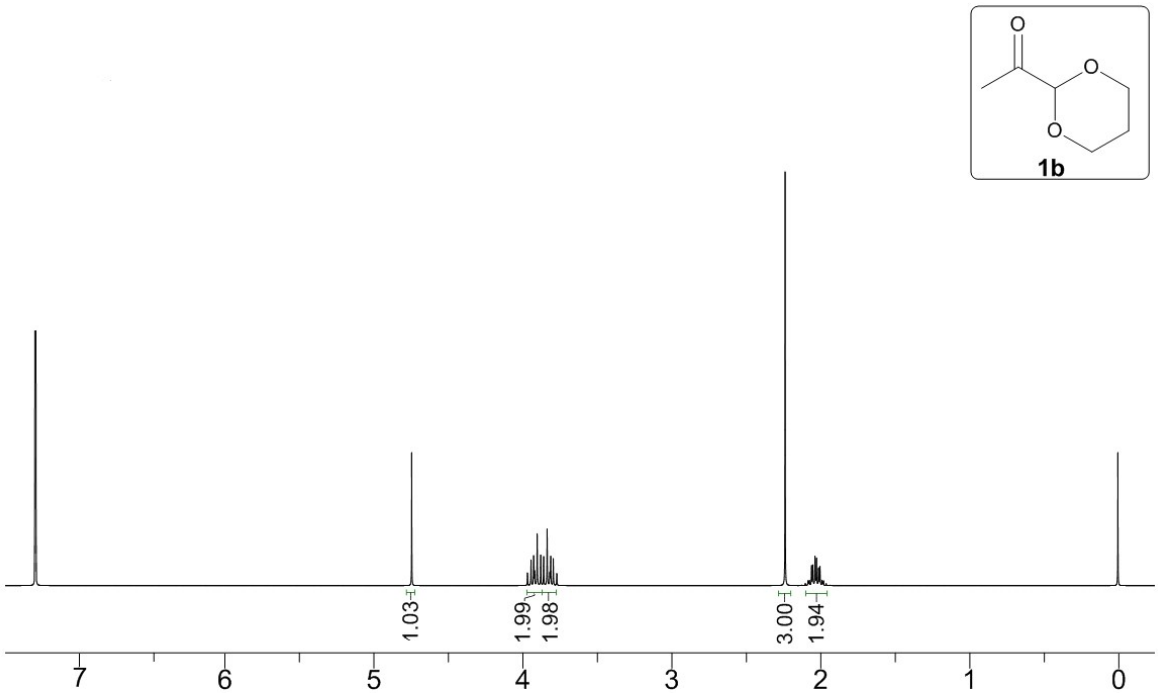
2m

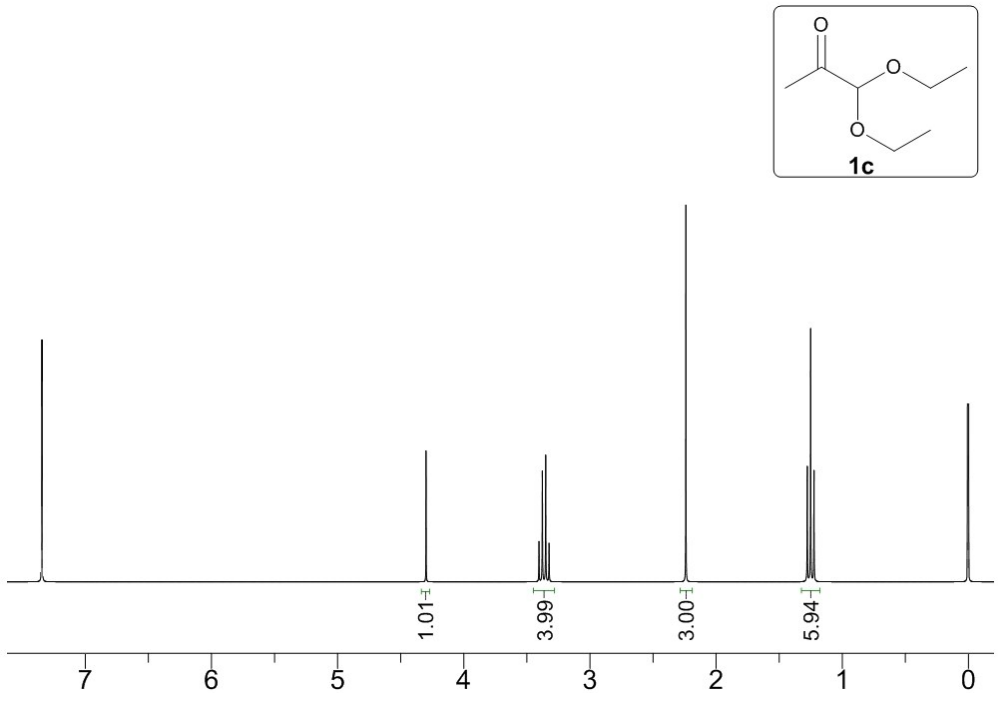


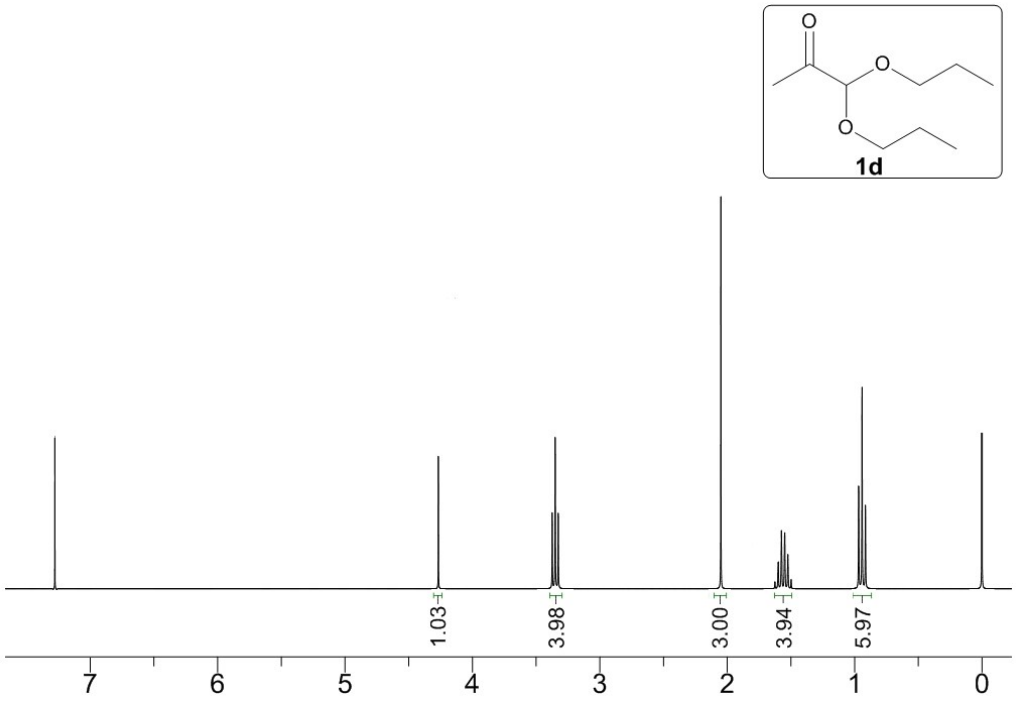


GC analytical conditions for **2m**: the temperature of gasify room, column, and detector were 200 ºC, 180 ºC and 200 ºC, respectively.

5. Copies of ^{1}H NMR Spectra



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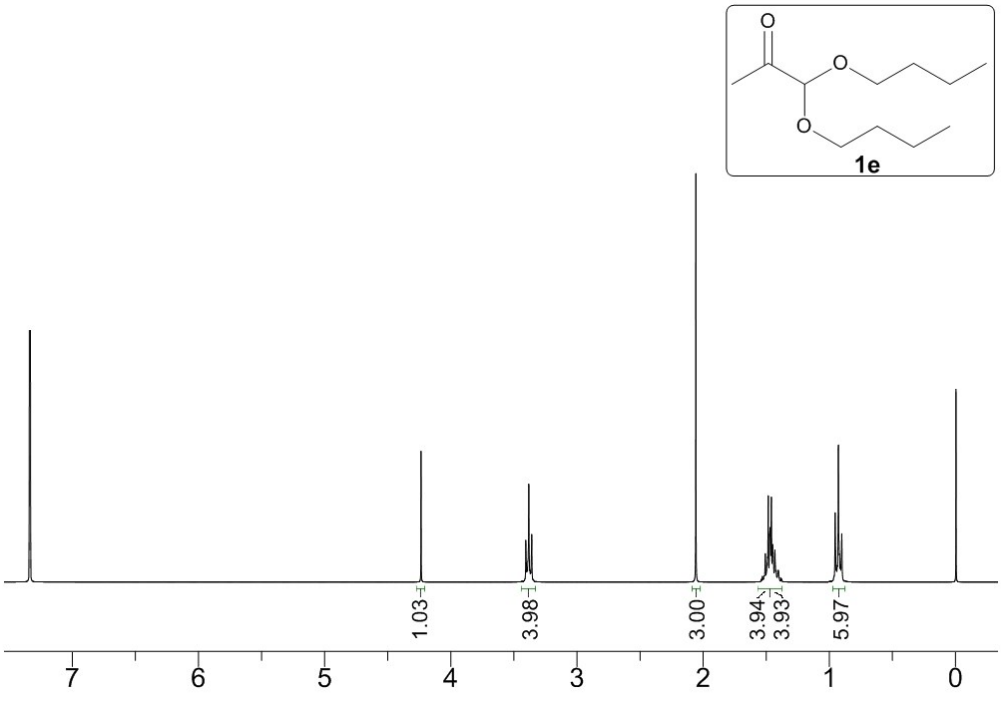
3.94
5.97
7
6
5
4
3
2
1
0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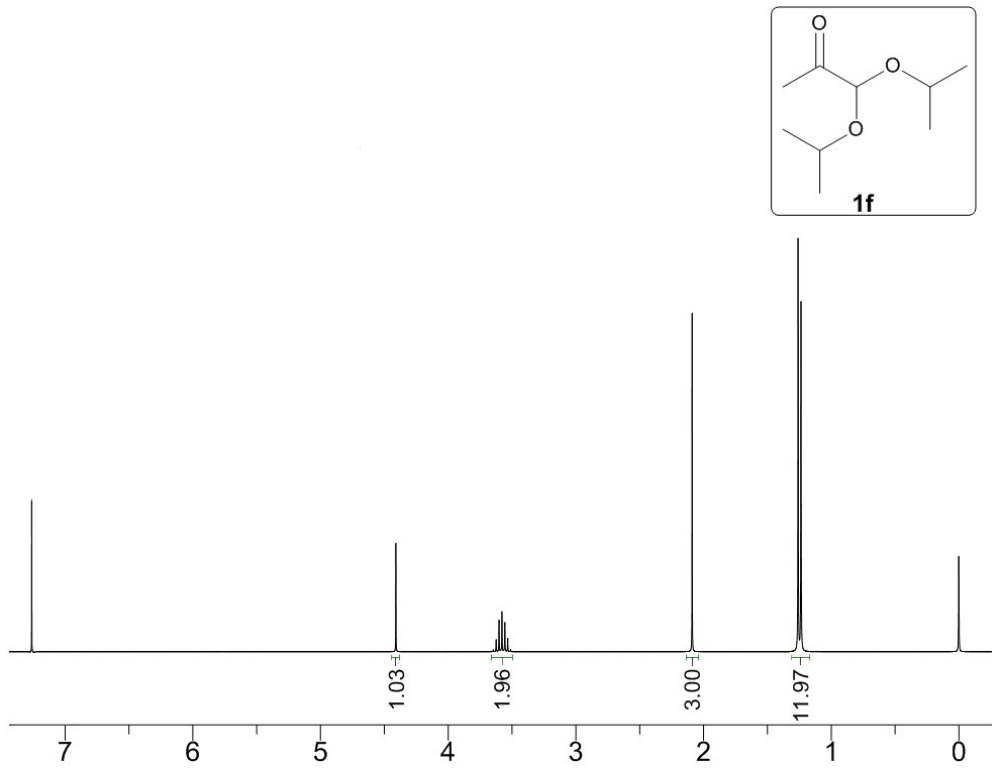
3.00
3.94
3.93
5.97
7
6
5
4
3
2
1
0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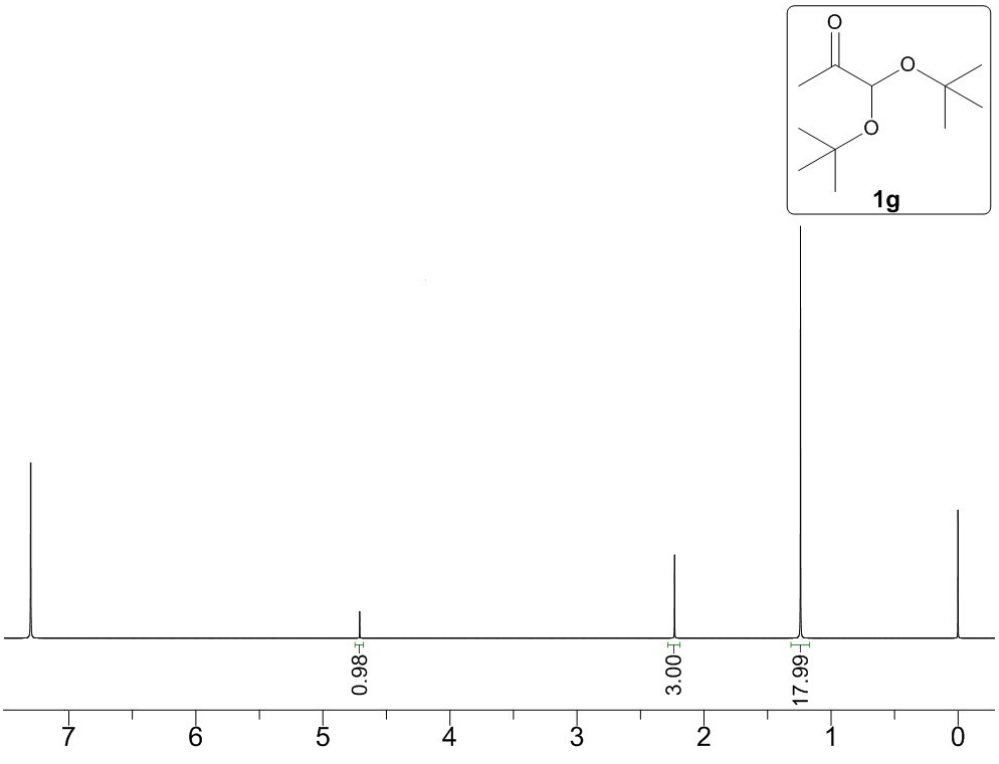
3.00
11.97
7
6
5
4
3
2
1
0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5
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3
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1
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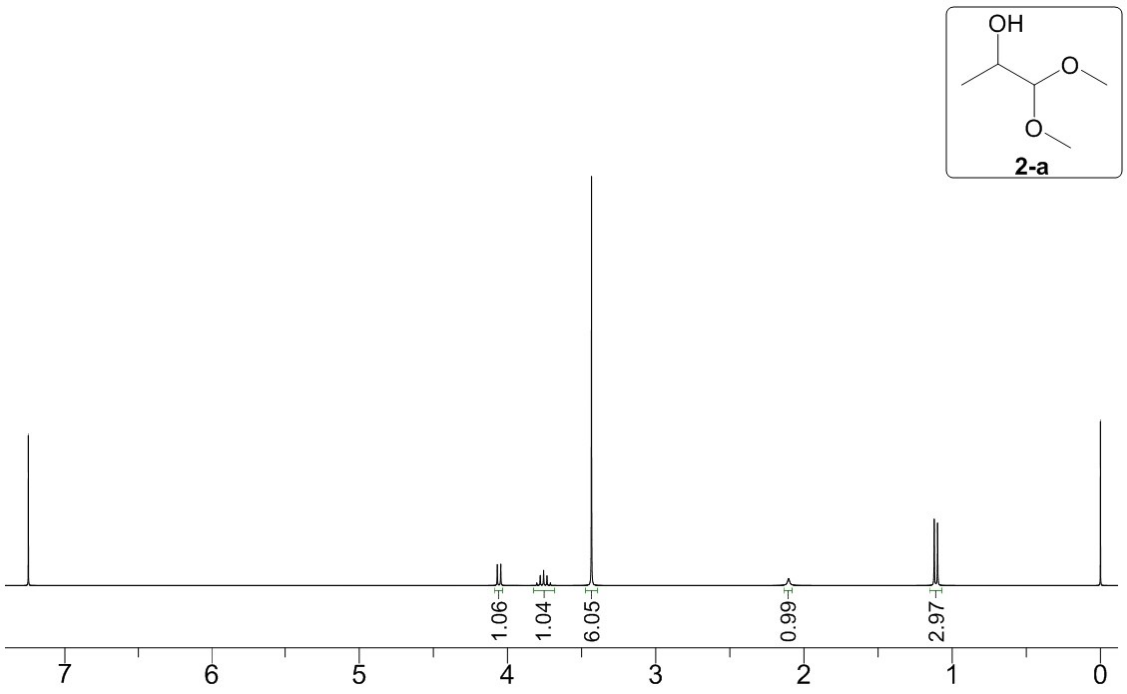
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2.97
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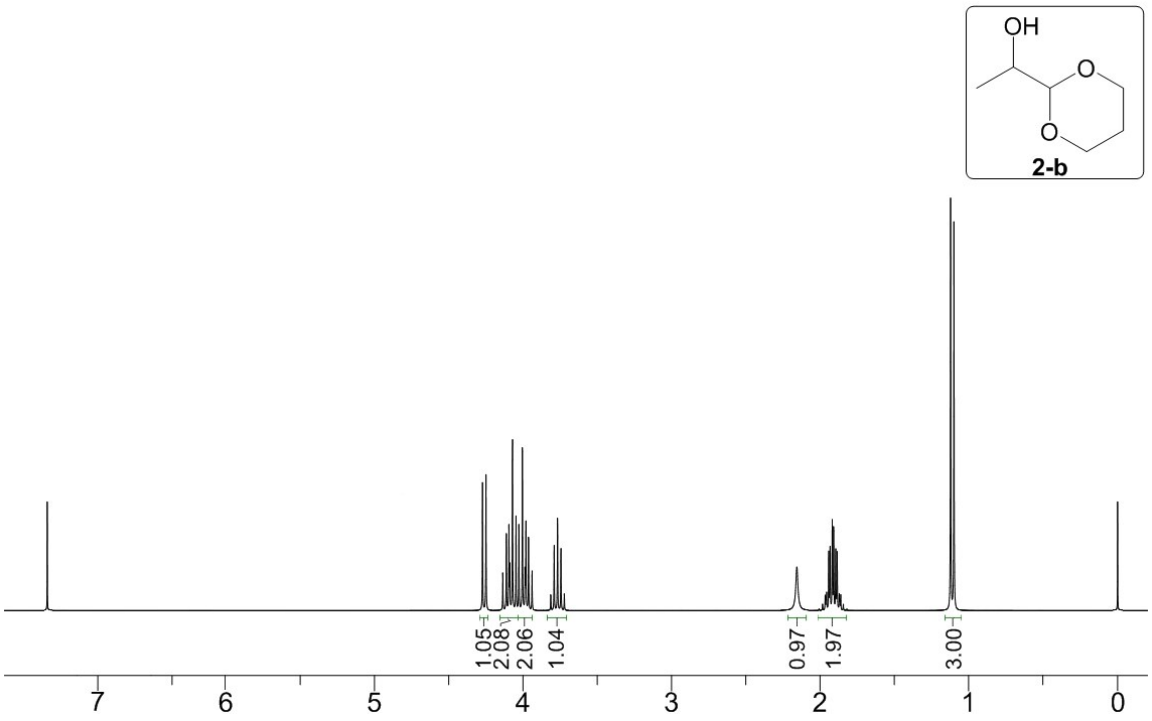
3
2
1
0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2.06
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7
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3
2
1
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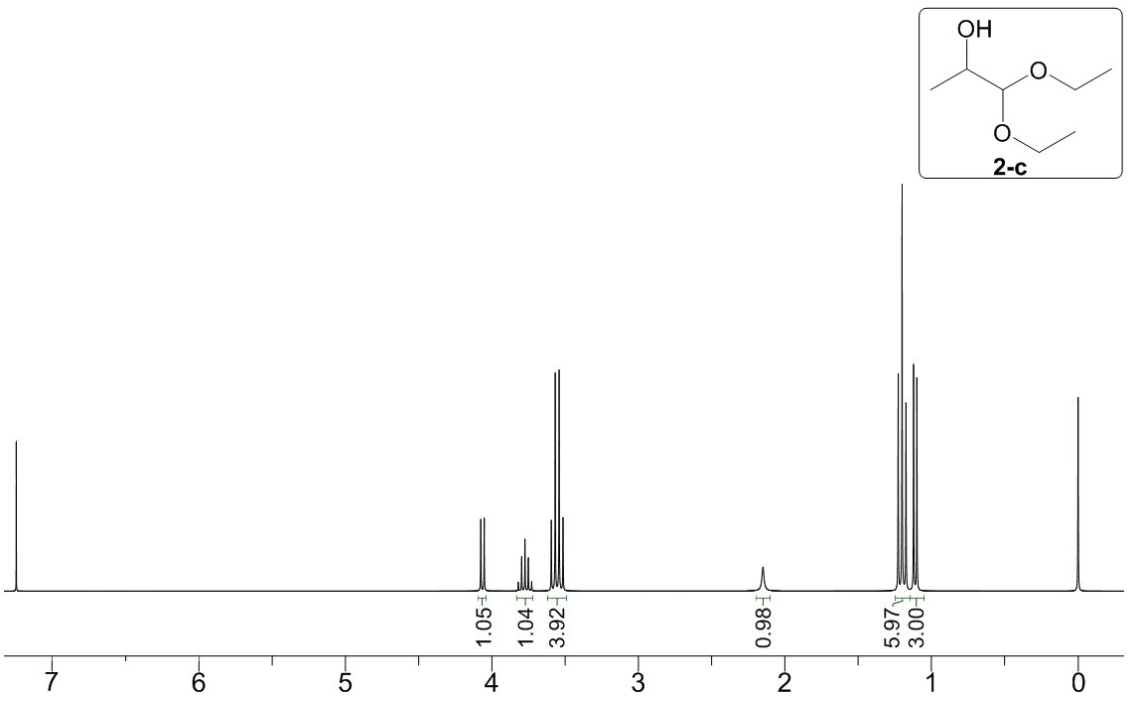
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O
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7
6
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3
2
1
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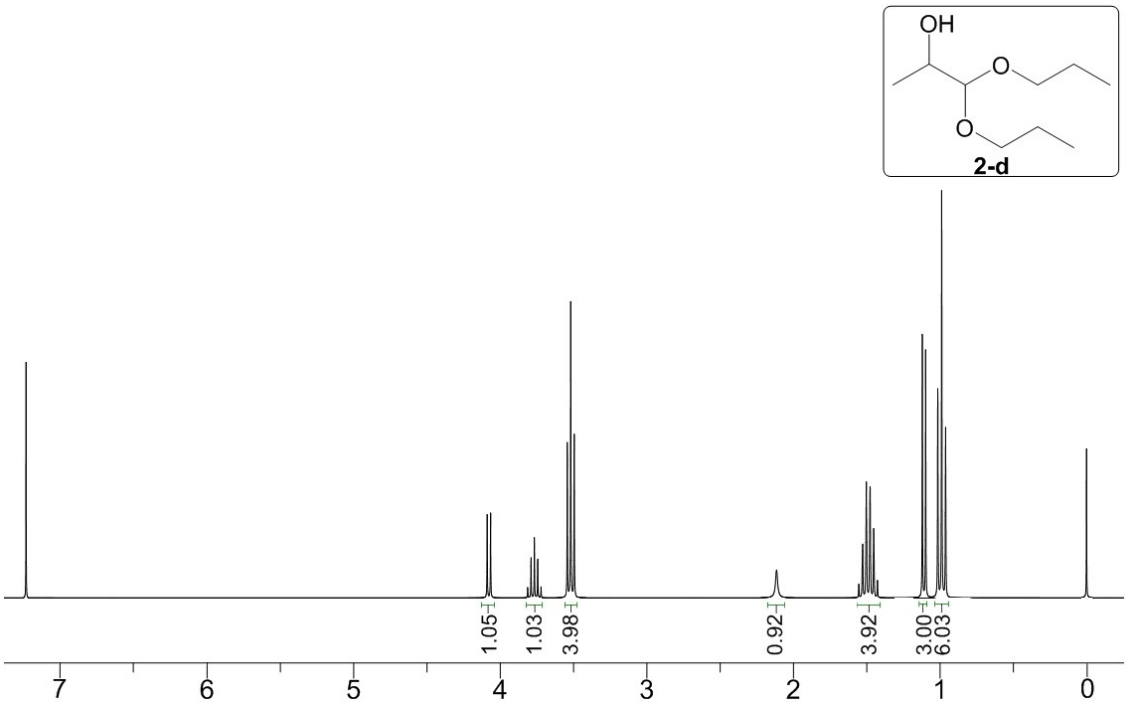
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O
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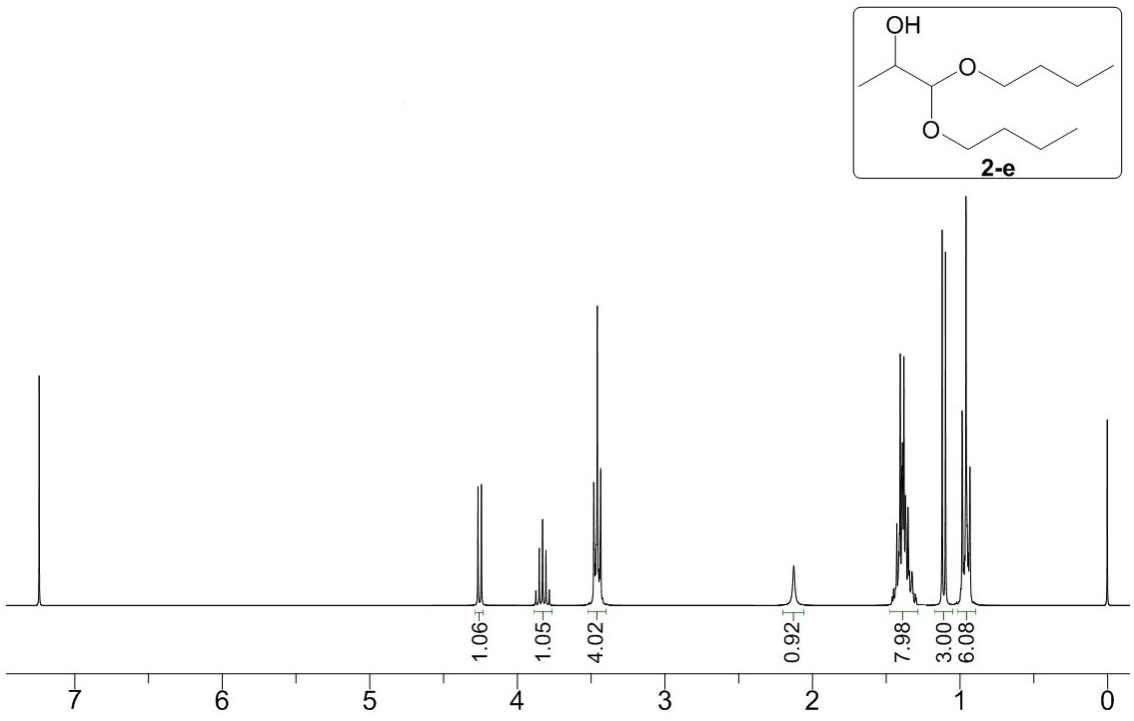
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7
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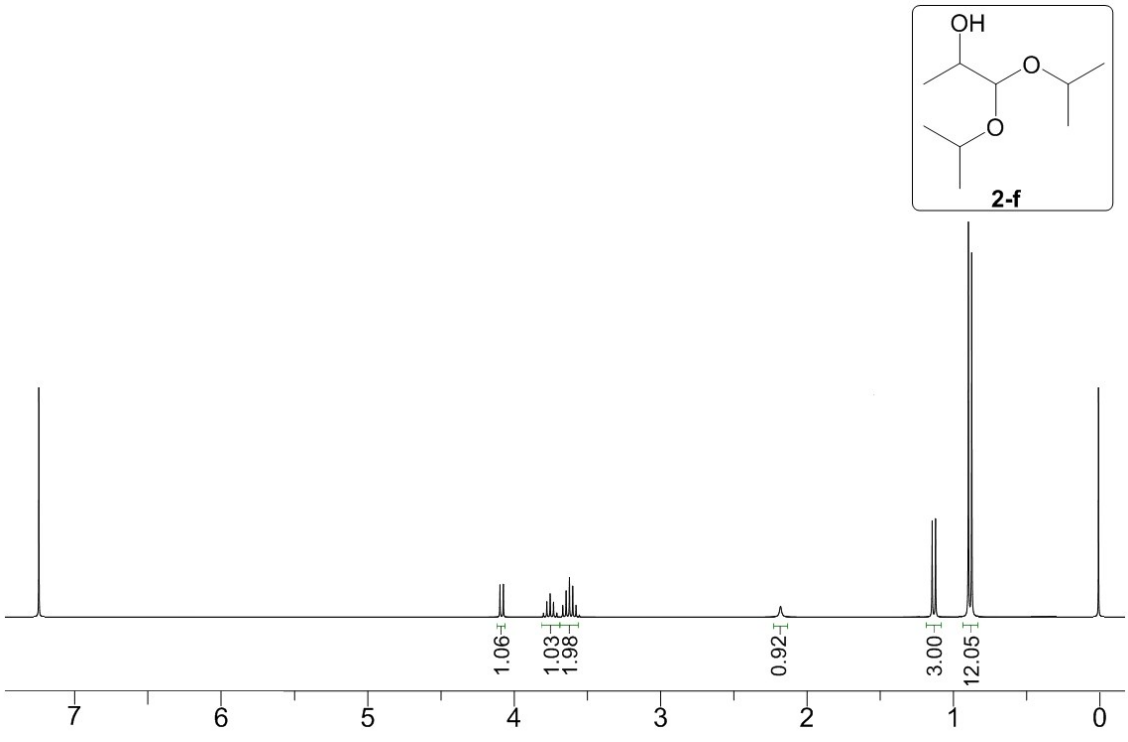
3
2
1
0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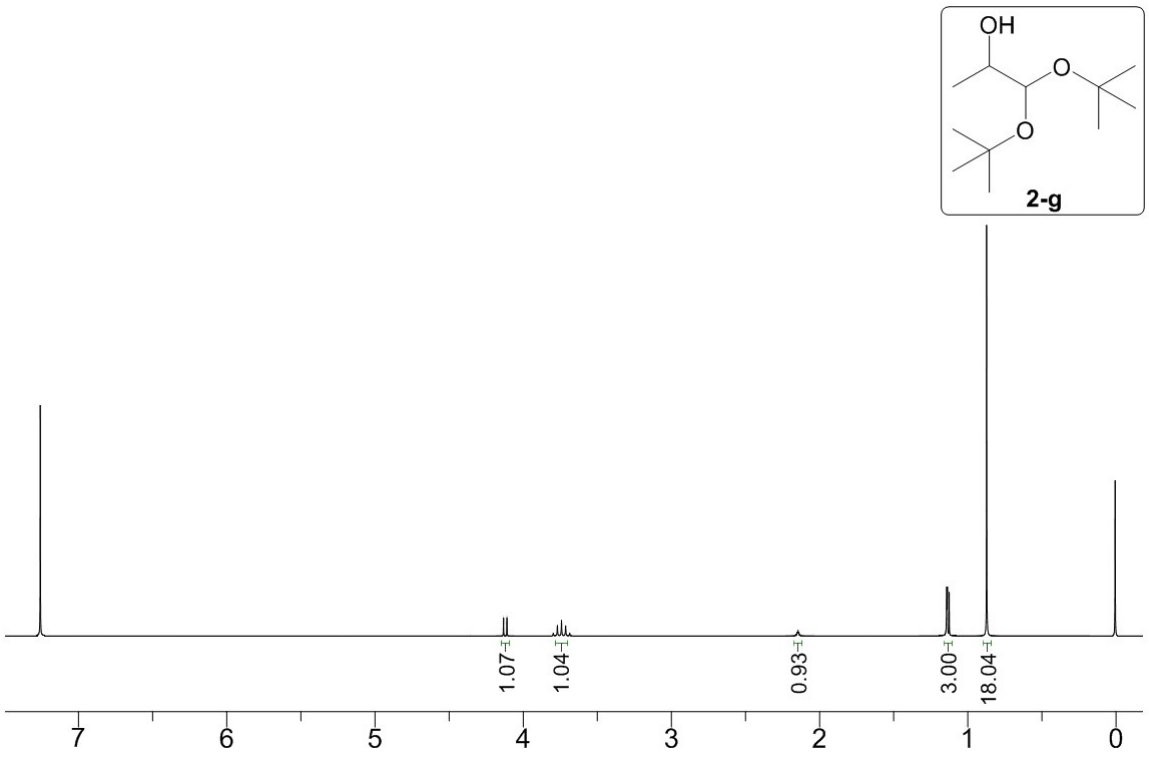
1
0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7
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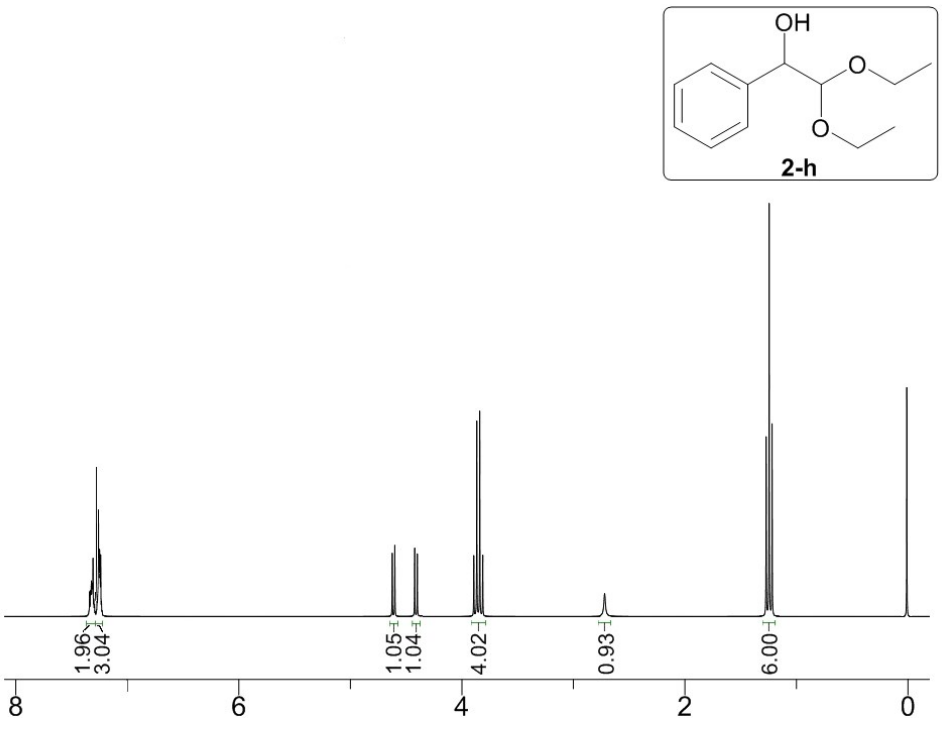
2
1
0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4.02
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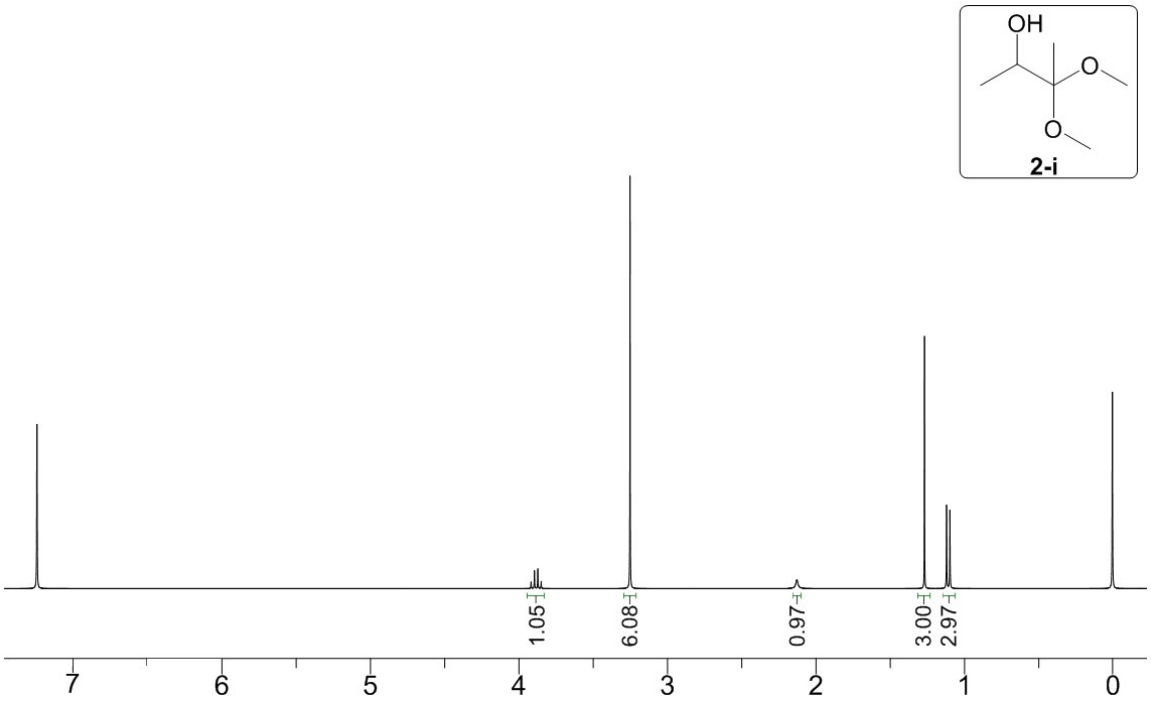
6.00
8
6
4
2
0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2.97
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3
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1
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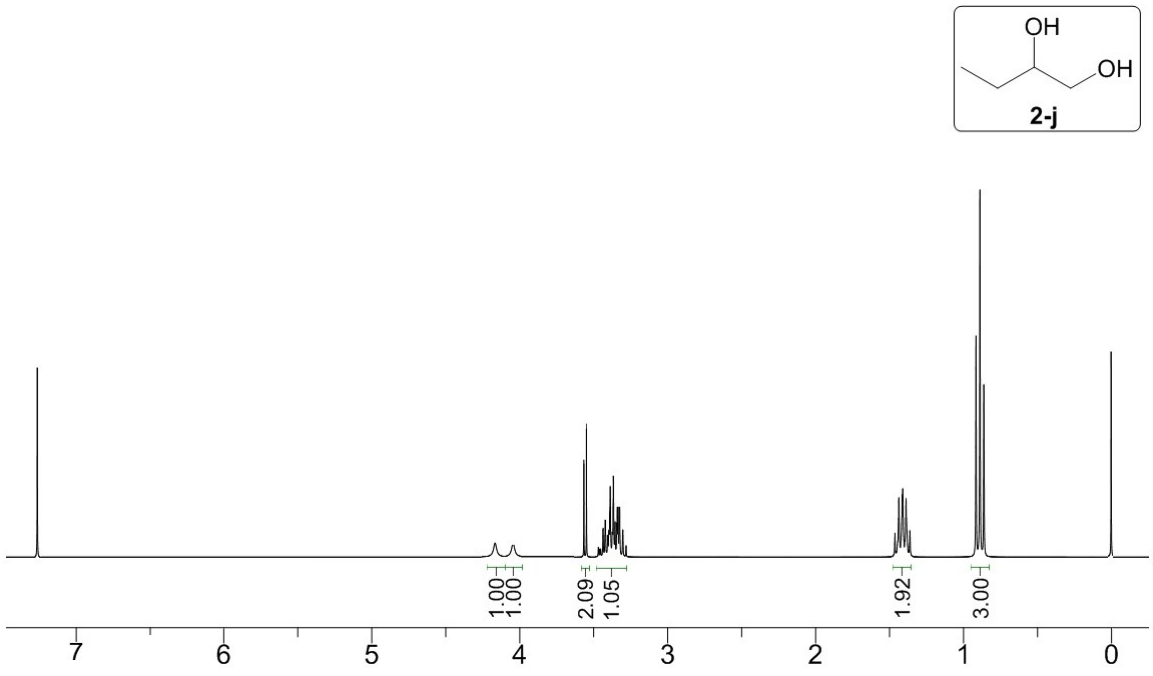
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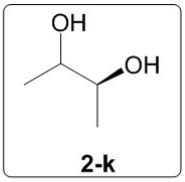
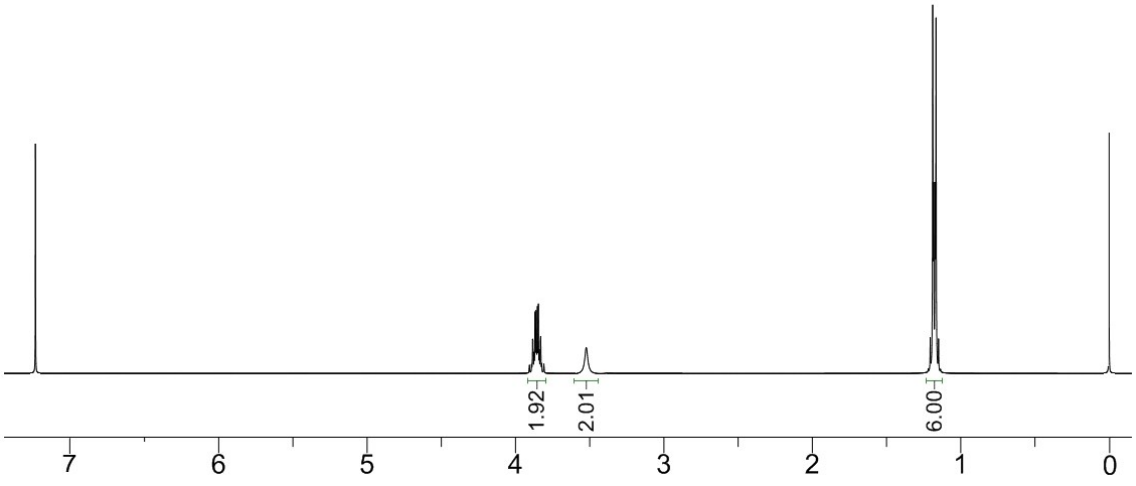

OH
OH

2-k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4
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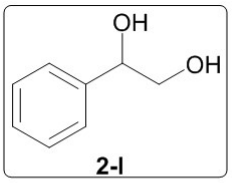
2
1
0

F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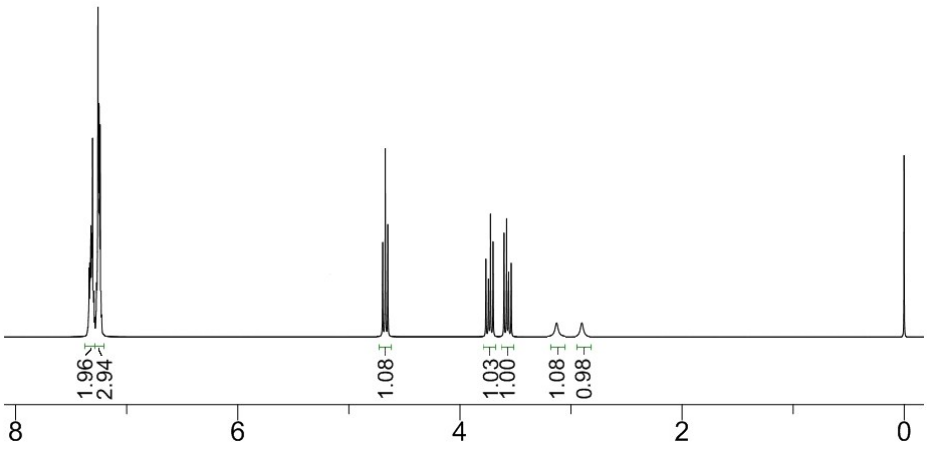
OH

2-l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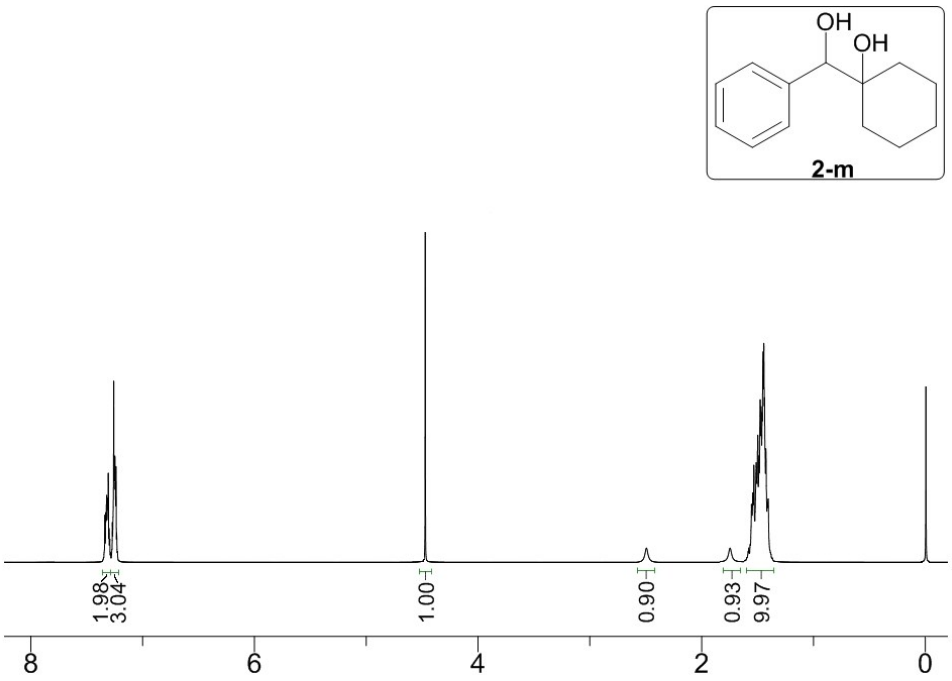
2
0



6. References

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(2) N. Pichon, A. Harrison-Marchand, L. Toupet and J. Maddaluno, *J. Org. Chem.*, 2006, **71**, 1892.

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