

Lewis Acid / CpRu Dual-Catalysis in the Enantioselective Decarboxylative Allylation of Ketone Enolates

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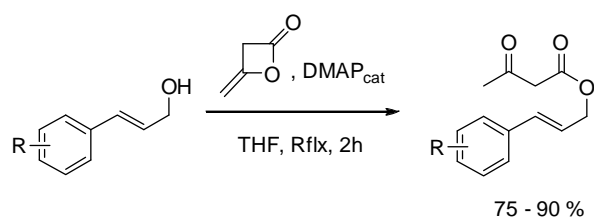
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Quai Ernest Ansermet 30, 1211 Genève 4, Switzerland.

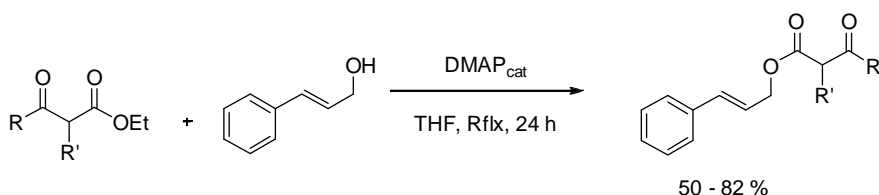
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Supporting Information

General procedure for the synthesis of cinnamyl acetoacetates of type **3** and **7**.

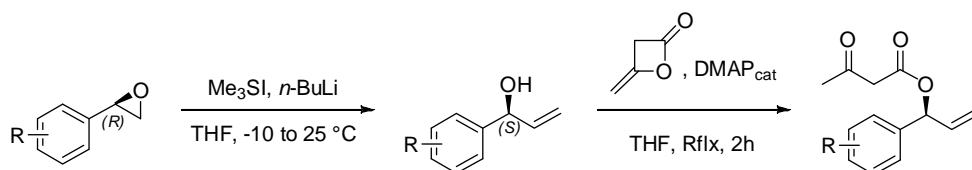


β -ketoesters **3a**, **3c**, **3d**, **3f** and **3g** were prepared by DMAP-catalyzed addition of the corresponding allylic alcohols to diketene.¹



β -ketoesters **3b**, **3e** and **3h** were prepared by DMAP catalyzed transesterification of the corresponding ethylketoesters. Compounds **3a** to **3h** have spectral characteristics corresponding to those described already in the literature.²

Branched β -ketoester **7** was synthesized as follows:



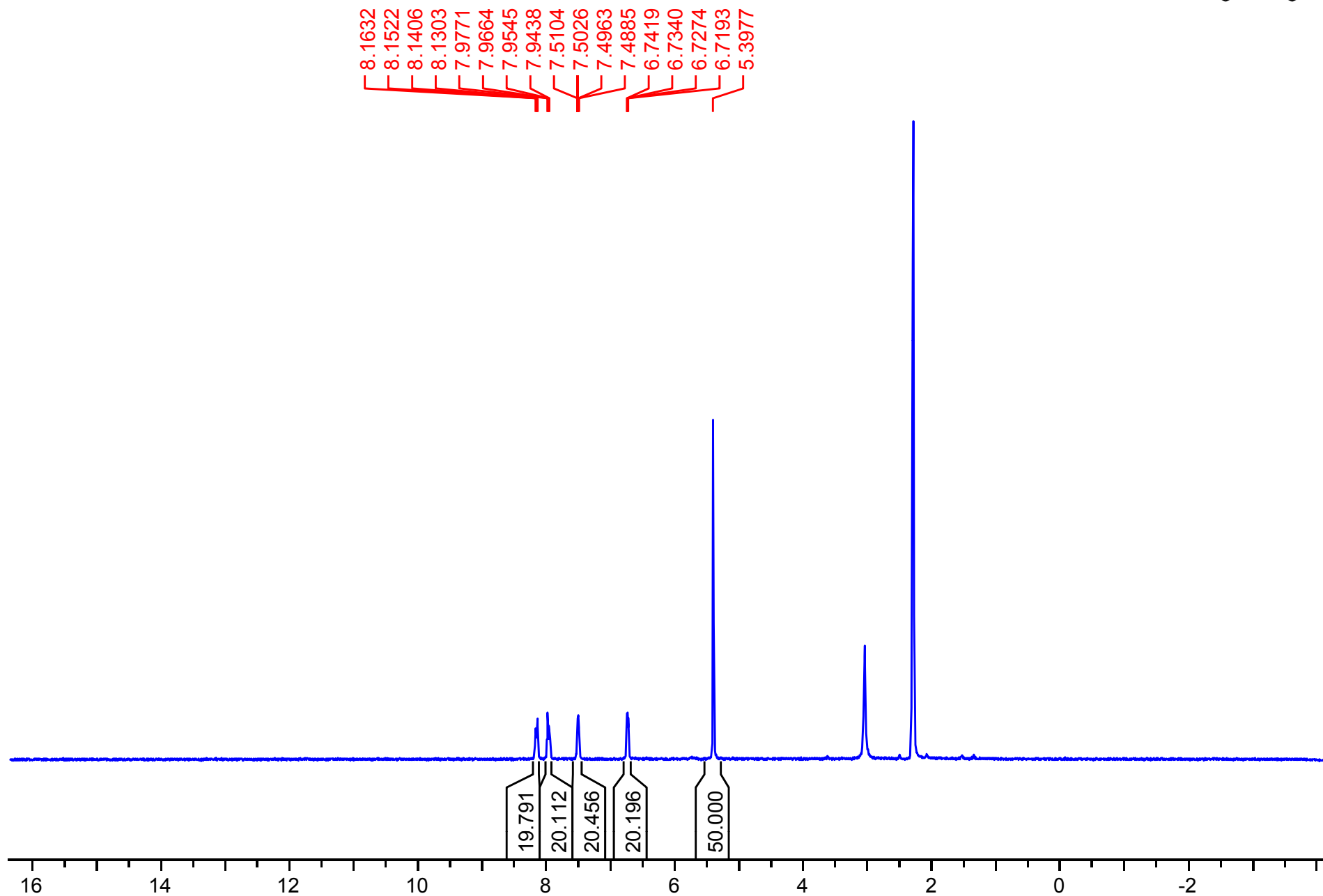
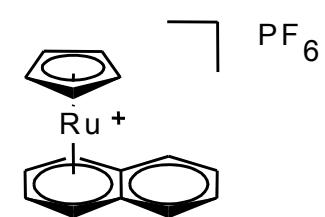
CpRu-catalyzed Carroll rearrangement – dual-catalysis procedure.

Typical procedure. In a 2 mL screw-cap vial equipped with a magnetic stirring bar, [CpRu(η^6 -naphthalene)][PF₆] **1** (5.3 mg, 0.012 mmol, 2 mol%) and ligand **2** (8.1 mg, 0.033 mmol, 4.4 mol%) were dissolved in 0.6 mL dry THF. The vial was flushed with argon and capped. After a 1h heating at 60 °C, the vial was cooled to room temperature (~ 25 °C) and allyl β -ketoester **3a** (150 mg, 0.6 mmol) was added in one portion followed by [Mg(OTf)₂] (2.0 mg, 0.006 mmol, 1 mol%) and the vial was flushed again with argon and stirred at room temperature for 24 h. The cooled reaction mixture was diluted with 1.5 mL of a mixture of ether and pentane (60 : 40). After precipitation, the metal salts were filtered off on a short SiO₂ column (0.5 cm x 4 cm, elution ether : pentane, 60 : 40); the solvents being then evaporated under reduced pressure to afford the crude reaction mixture (**4a** + **5a**) as a pale yellow oil which was analysed without further purification. The sign of the optical rotation was measured from a solution of crude product (~10 mg) in 1 mL CDCl₃.

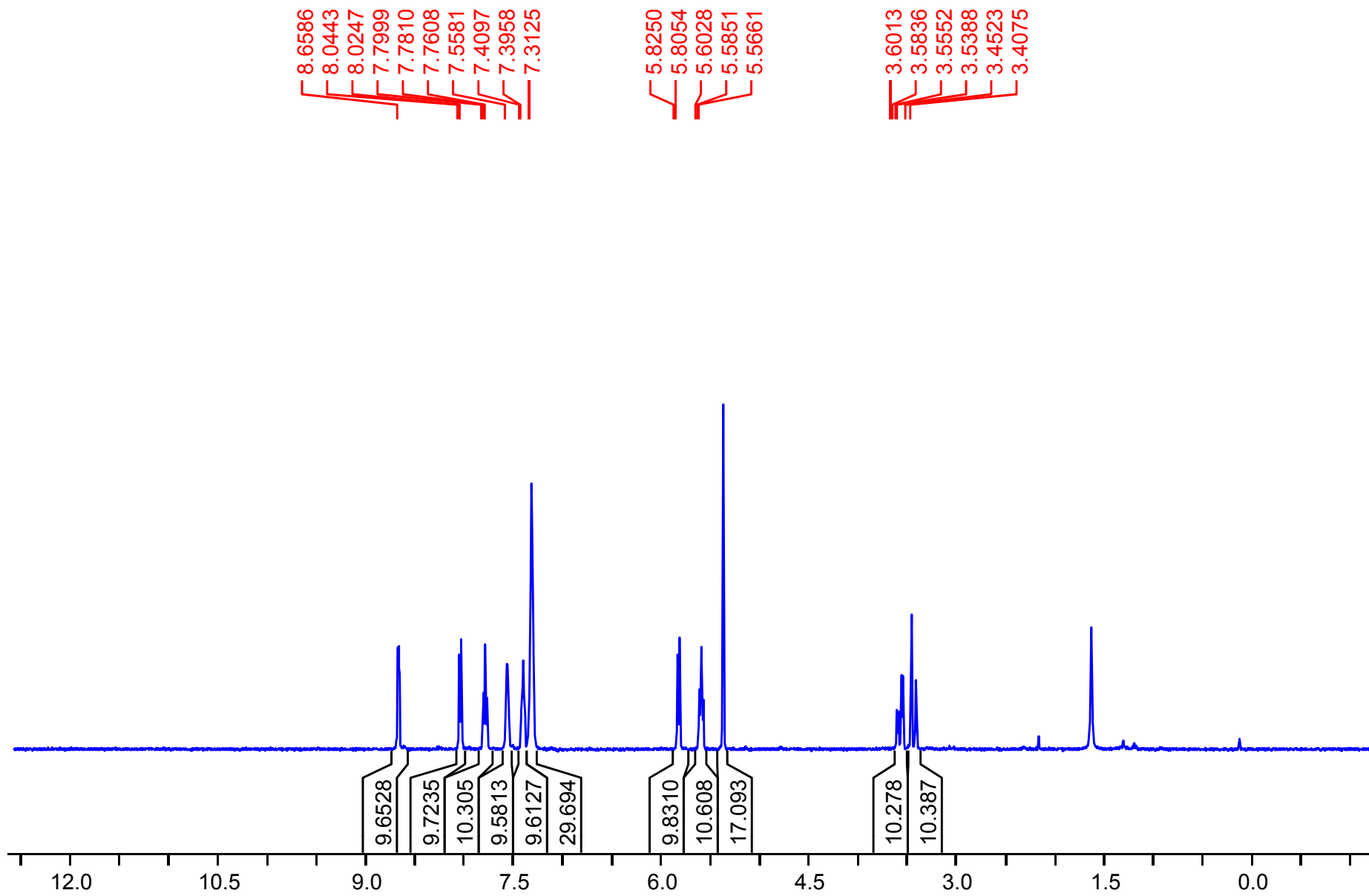
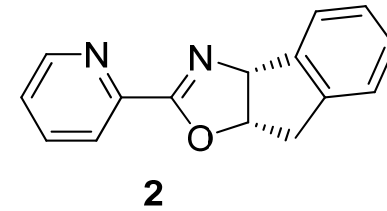
Reference

- 1 I. Collado, C. Pedregal, A. Mazon, J. F. Espinosa, J. Blanco-Urgoiti, D. D. Schoepp, R. A. Wright, B. G. Johnson and A. E. Kingston, *J. Med. Chem.*, 2002, **45**, 3619.
- 2 E. C. Burger and J. A. Tunge, *Org. Lett.*, 2004, **6**, 2603.

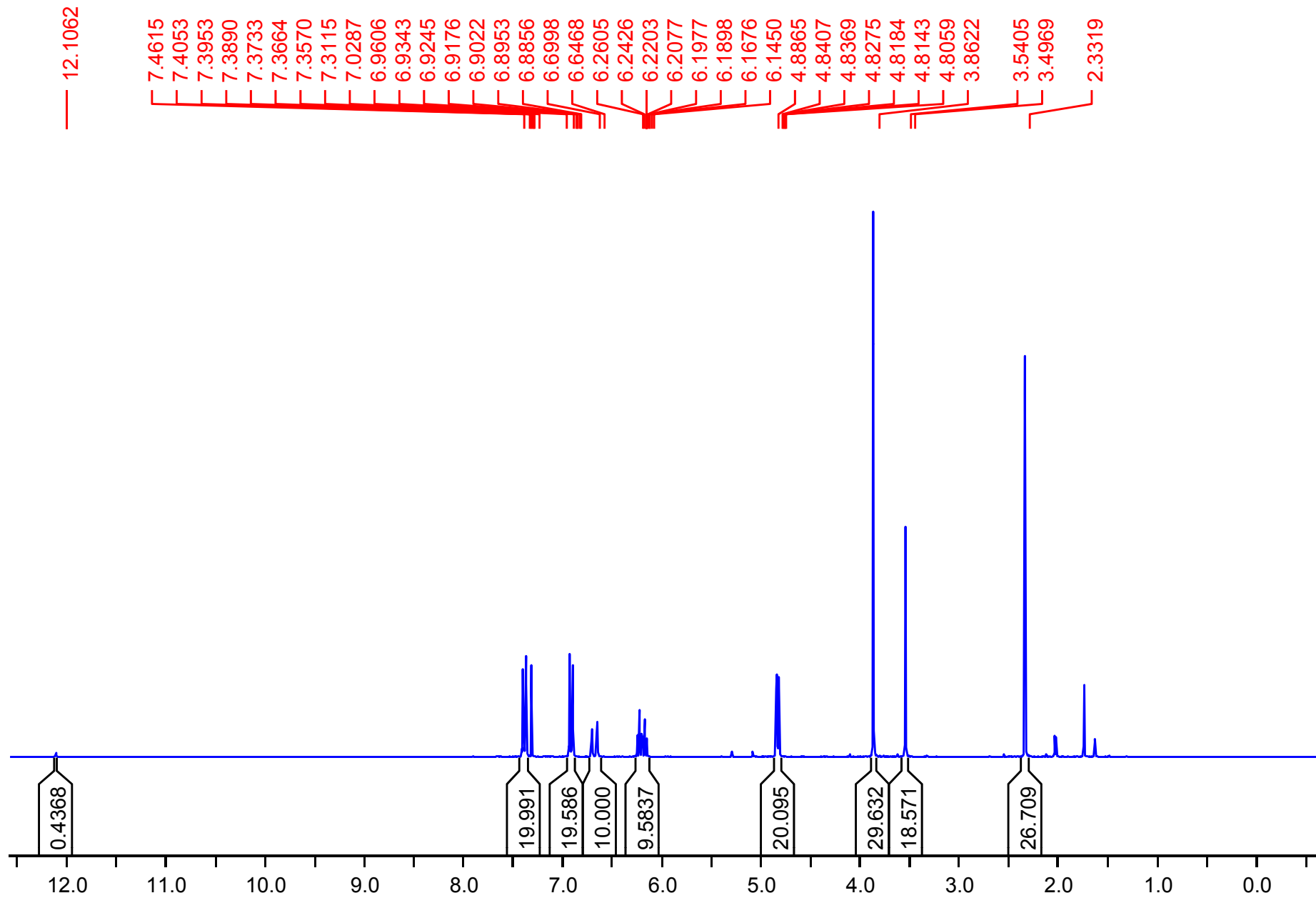
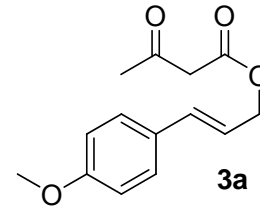
¹H NMR spectrum of **1** (300 MHz, Acetone-d₆)



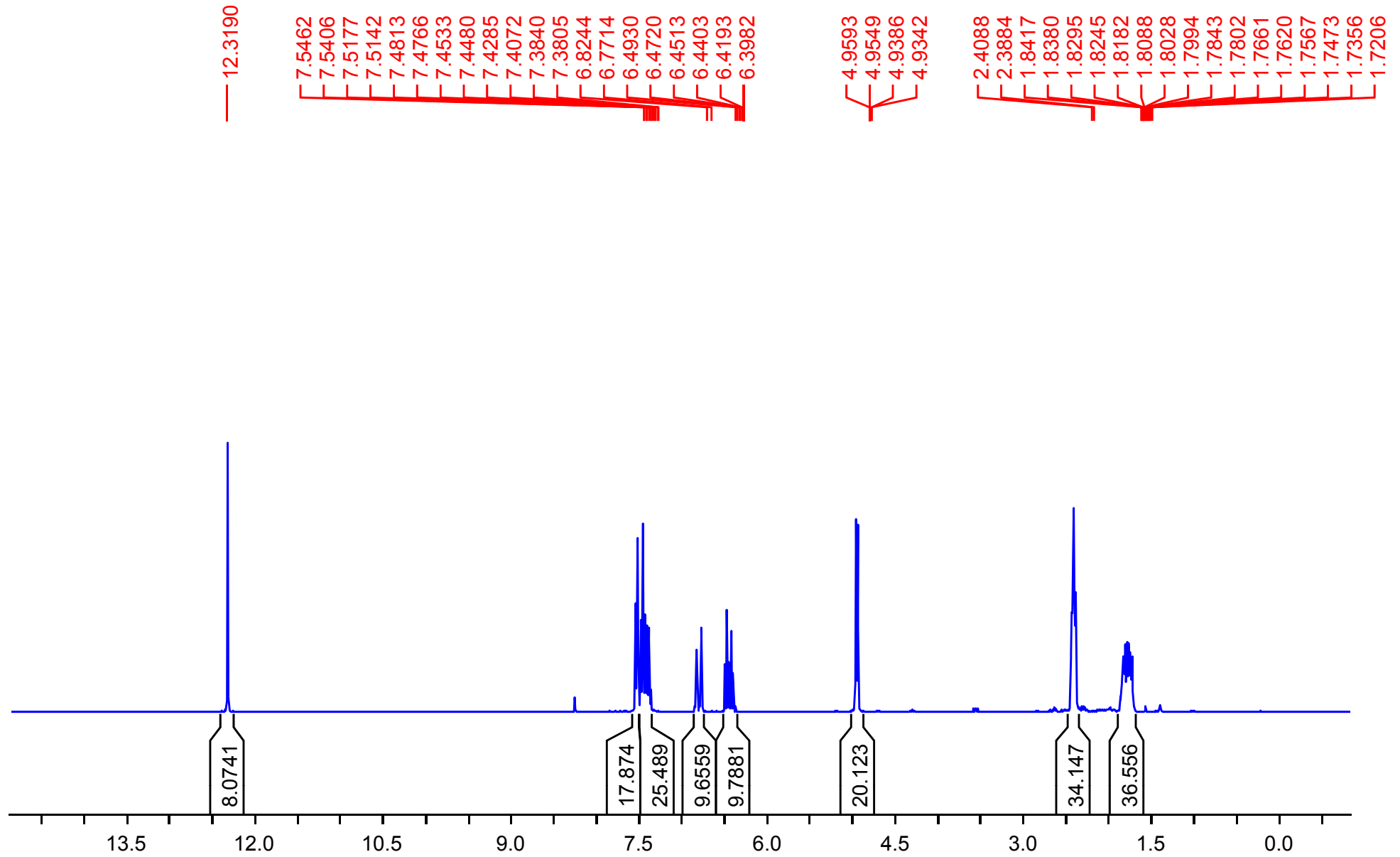
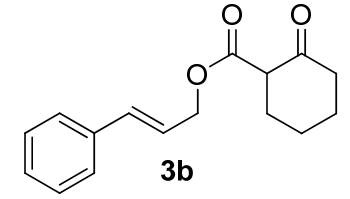
¹H NMR spectrum of **2** (300 MHz, CD₂Cl₂)



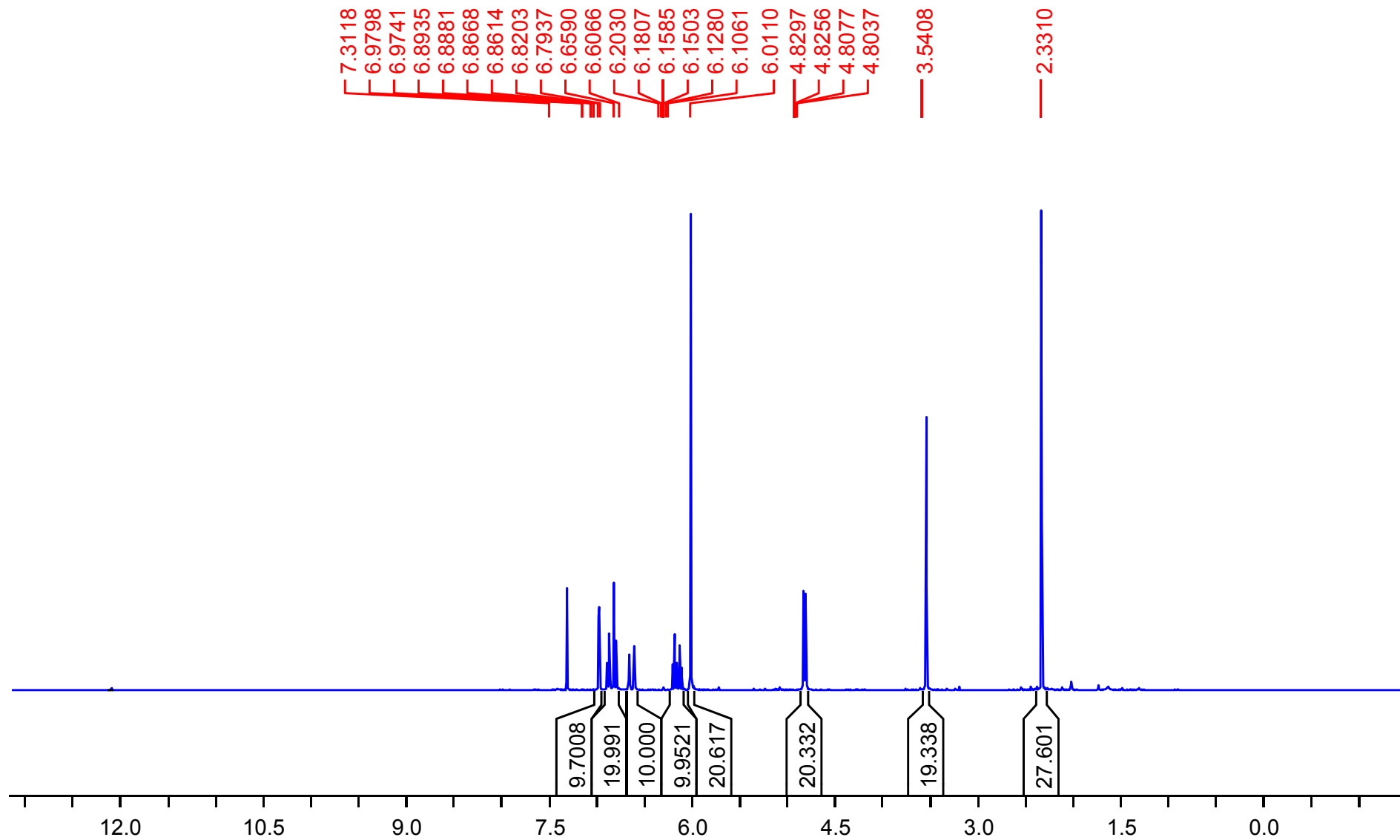
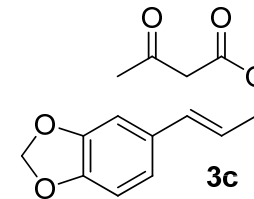
^1H NMR spectrum of **3a** (300 MHz, CDCl_3)



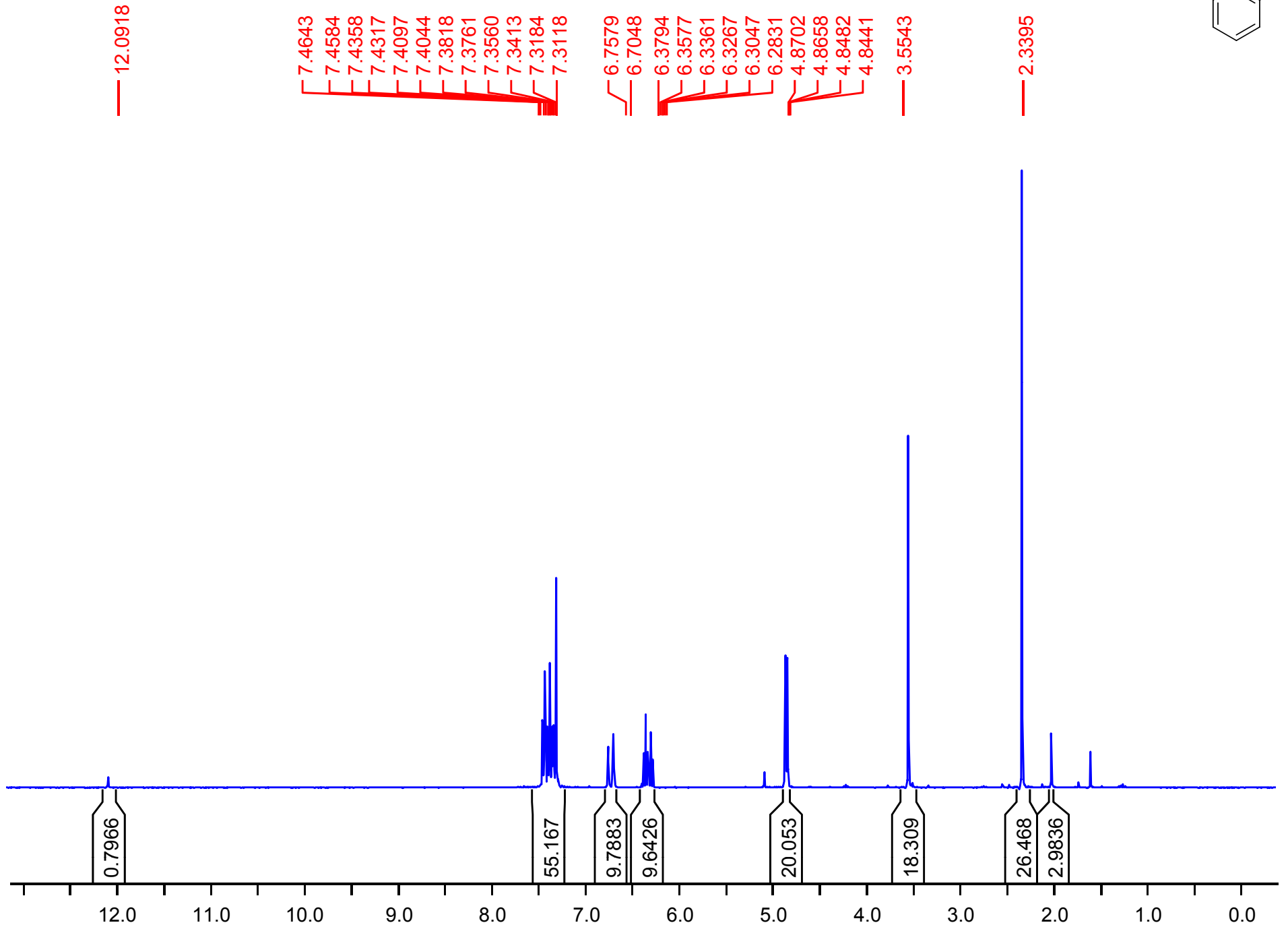
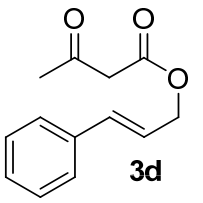
¹H NMR spectrum of **3b** (400 MHz, CDCl₃)



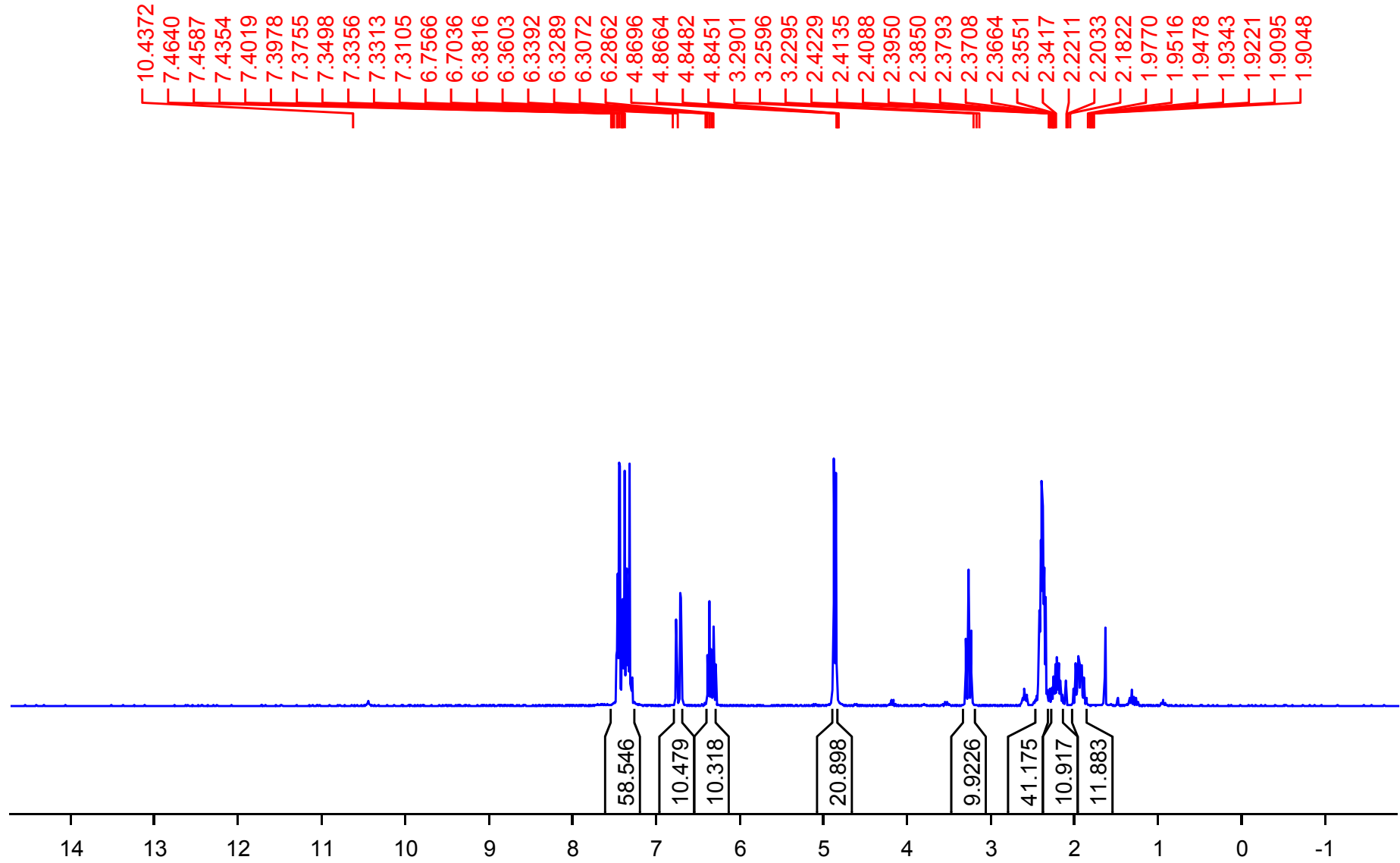
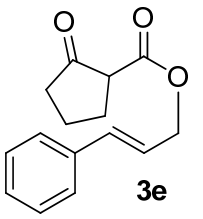
¹H NMR spectrum of **3c** (400 MHz, CDCl₃)



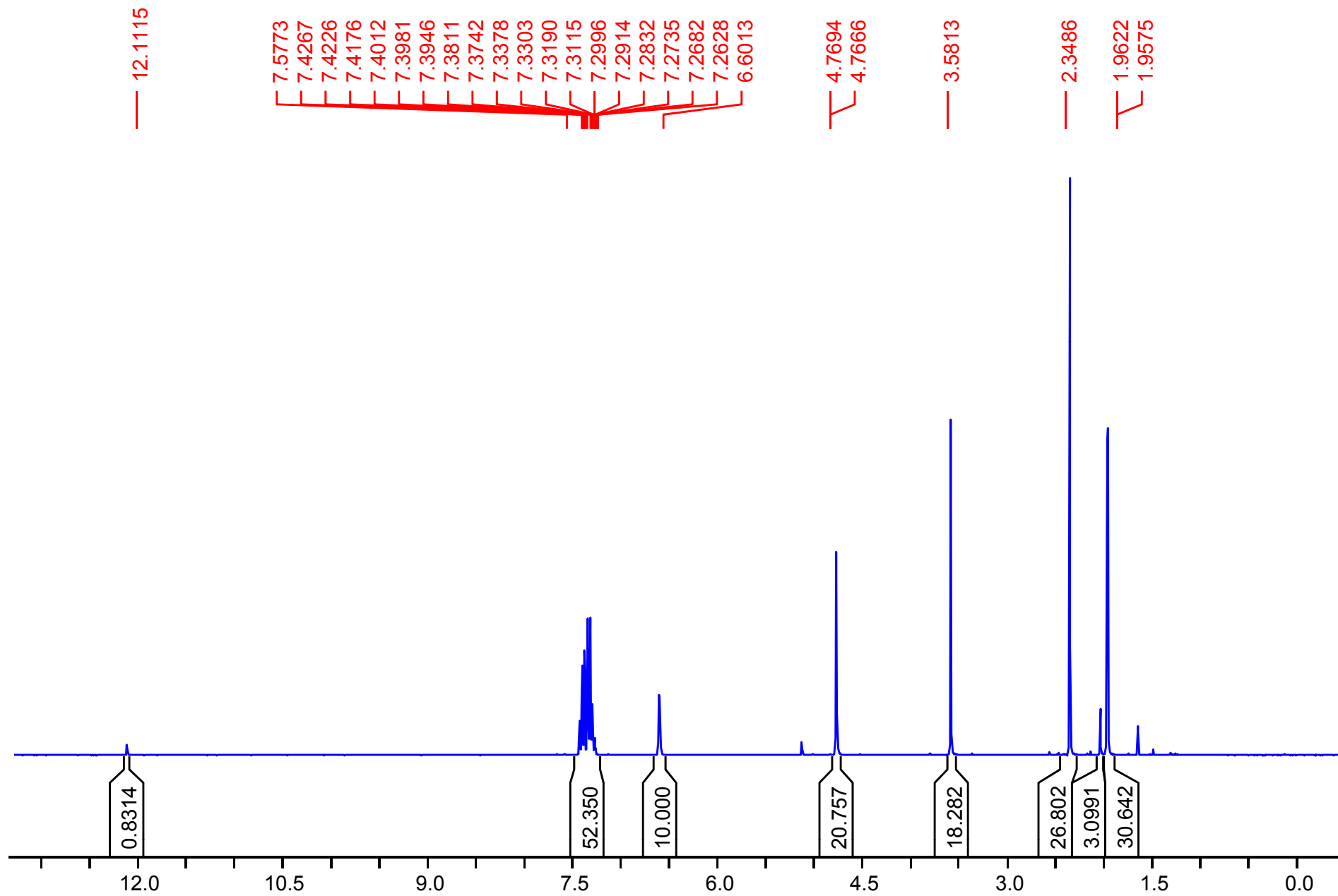
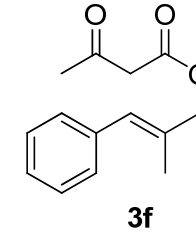
¹H NMR spectrum of **3d** (400 MHz, CDCl₃)



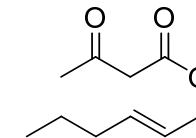
¹H NMR spectrum of **3e** (400 MHz, CDCl₃)



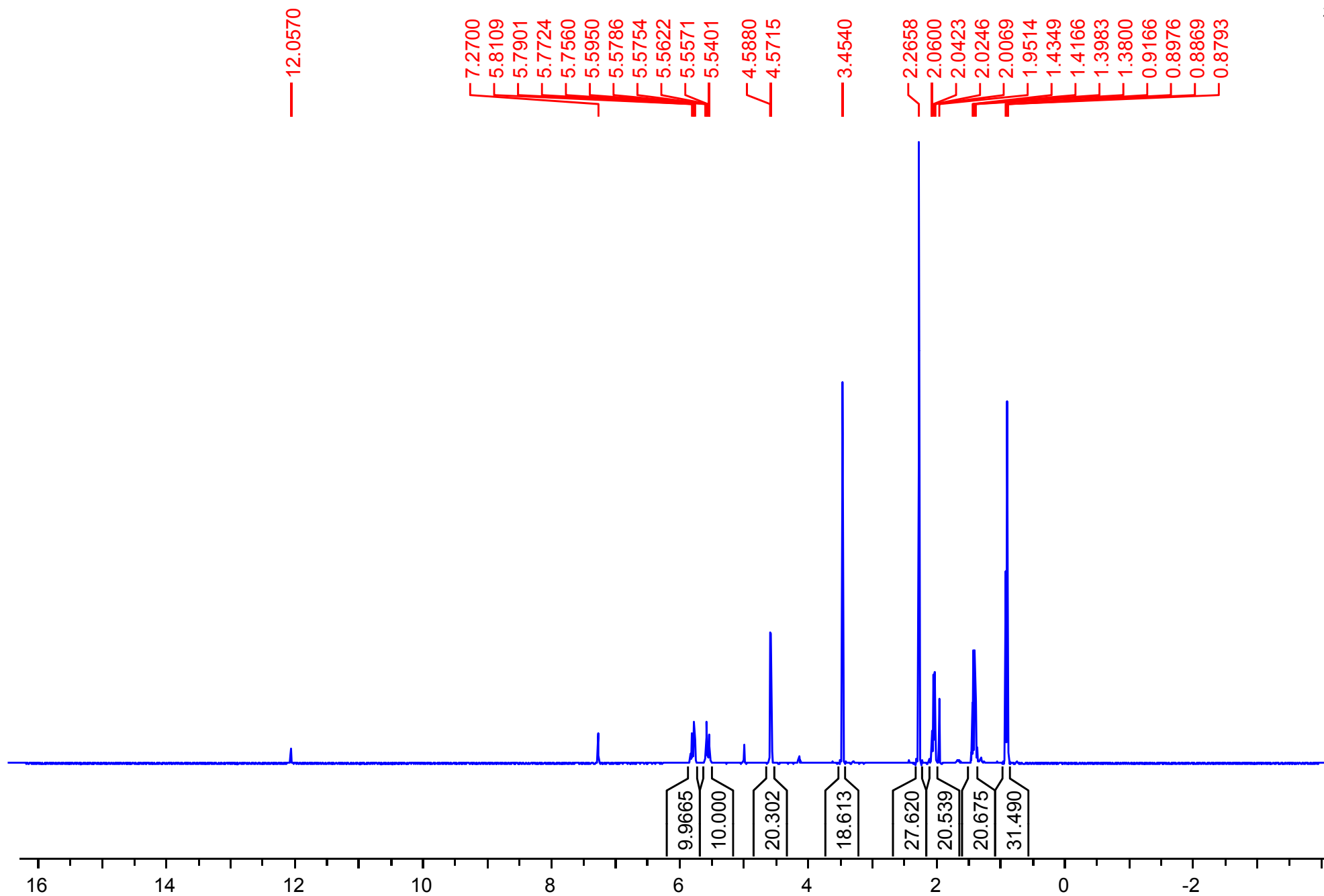
¹H NMR spectrum of **3f** (400 MHz, CDCl₃)



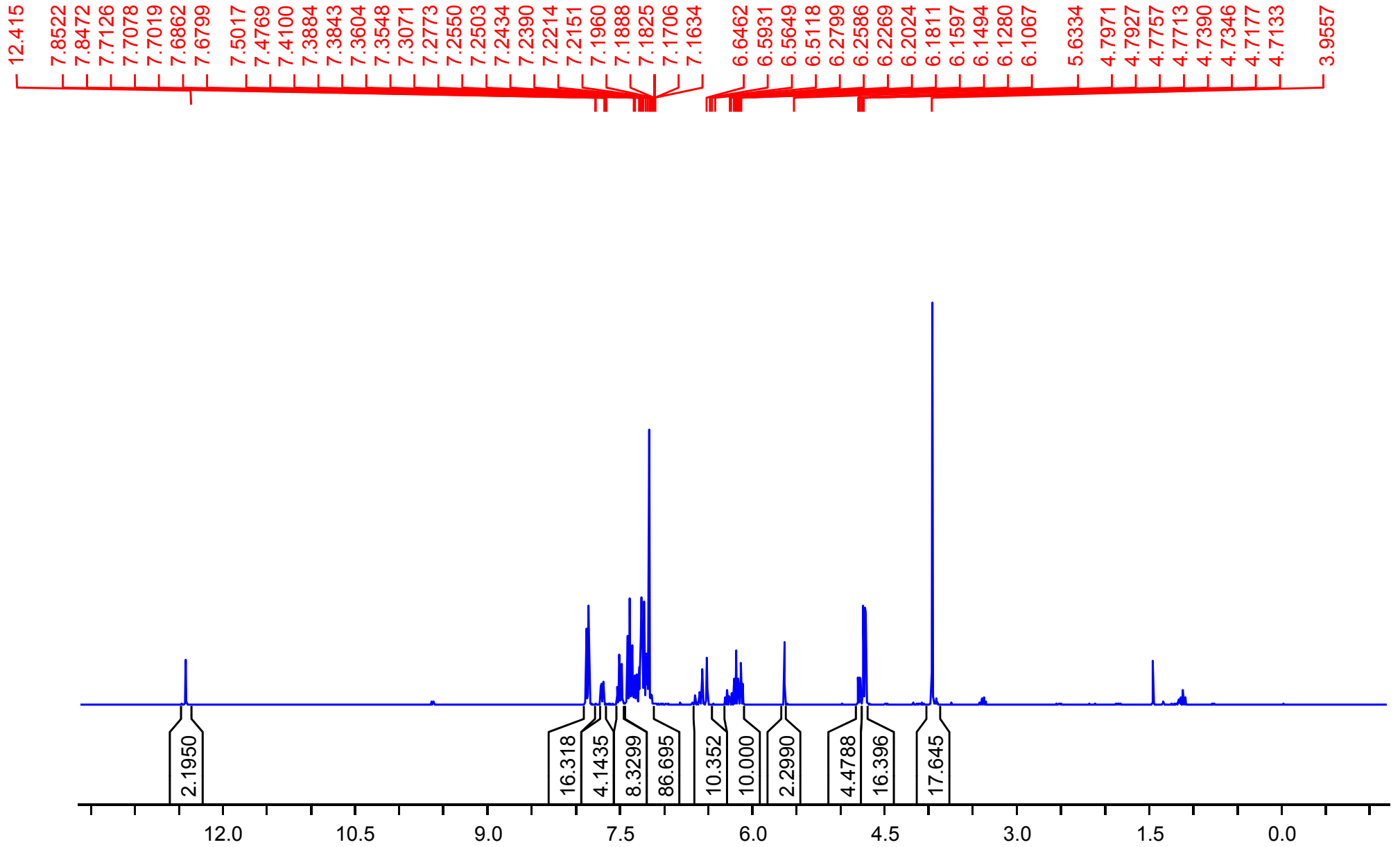
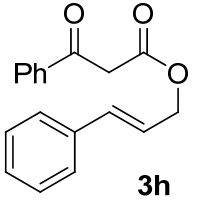
¹H NMR spectrum of **3g** (300 MHz, CDCl₃)



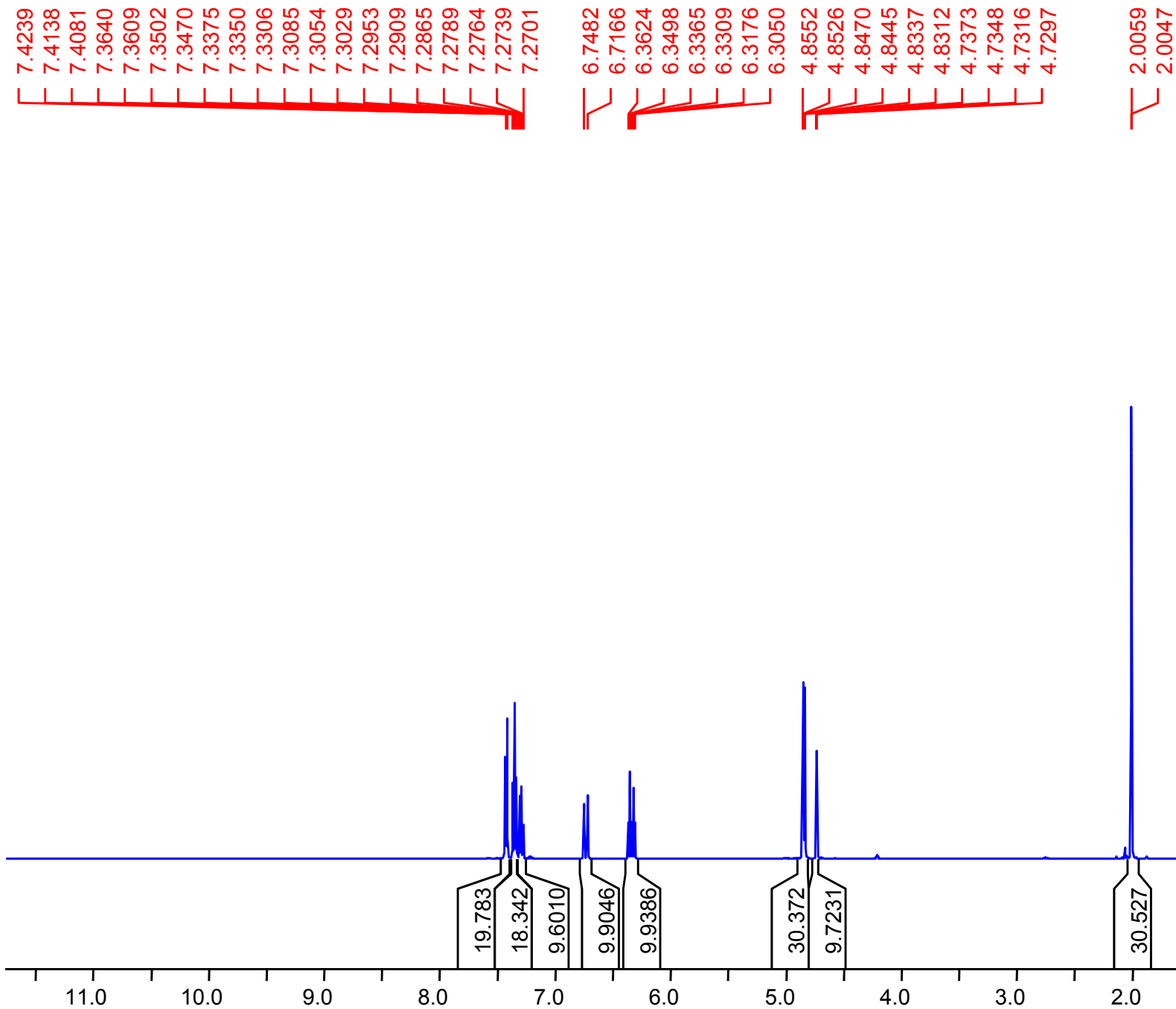
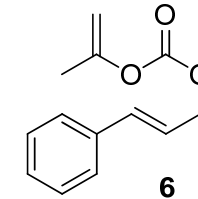
3g



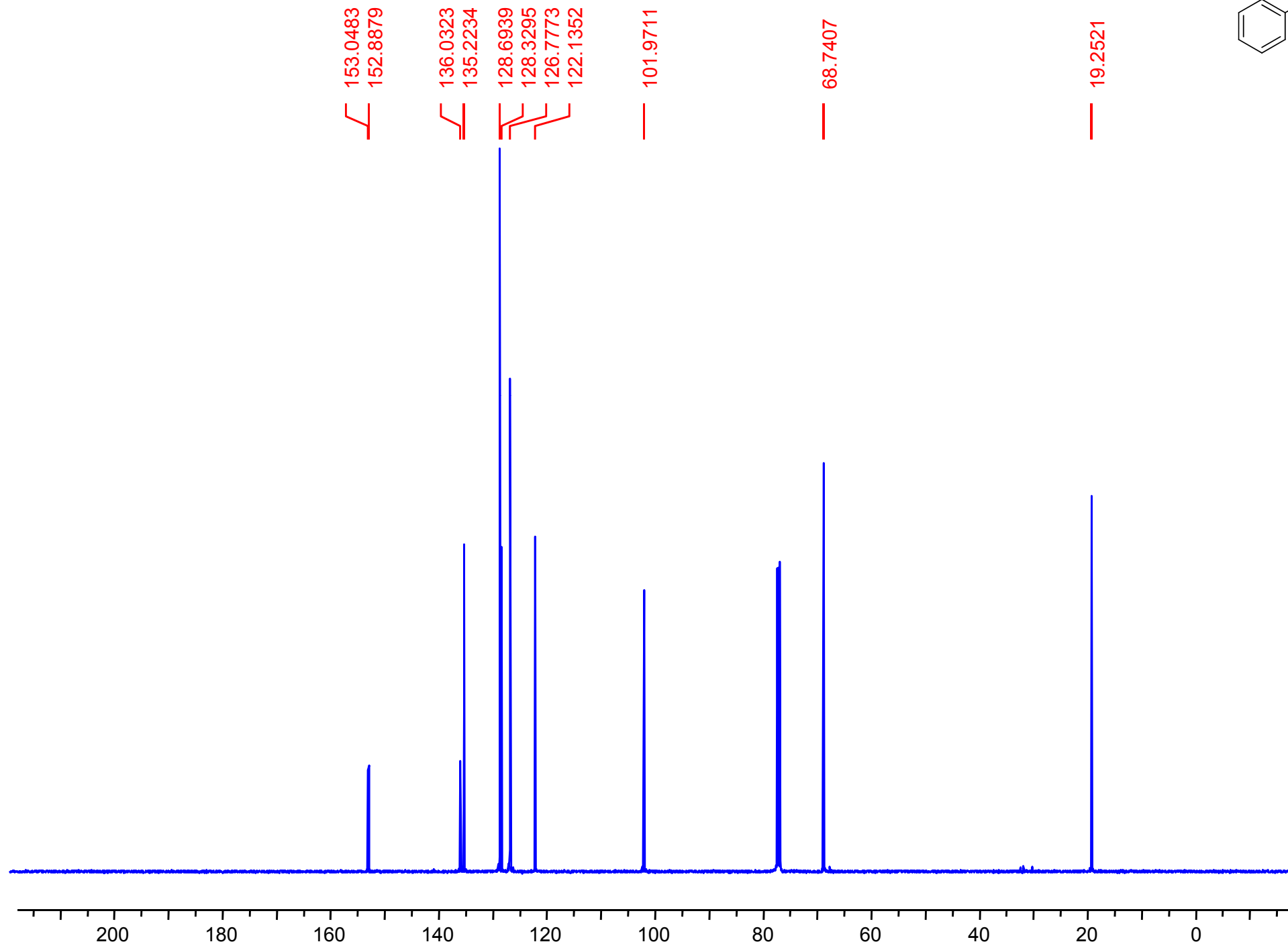
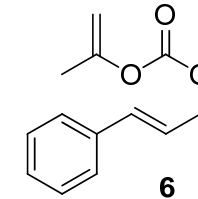
¹H NMR spectrum of **3h** (400 MHz, CDCl₃)



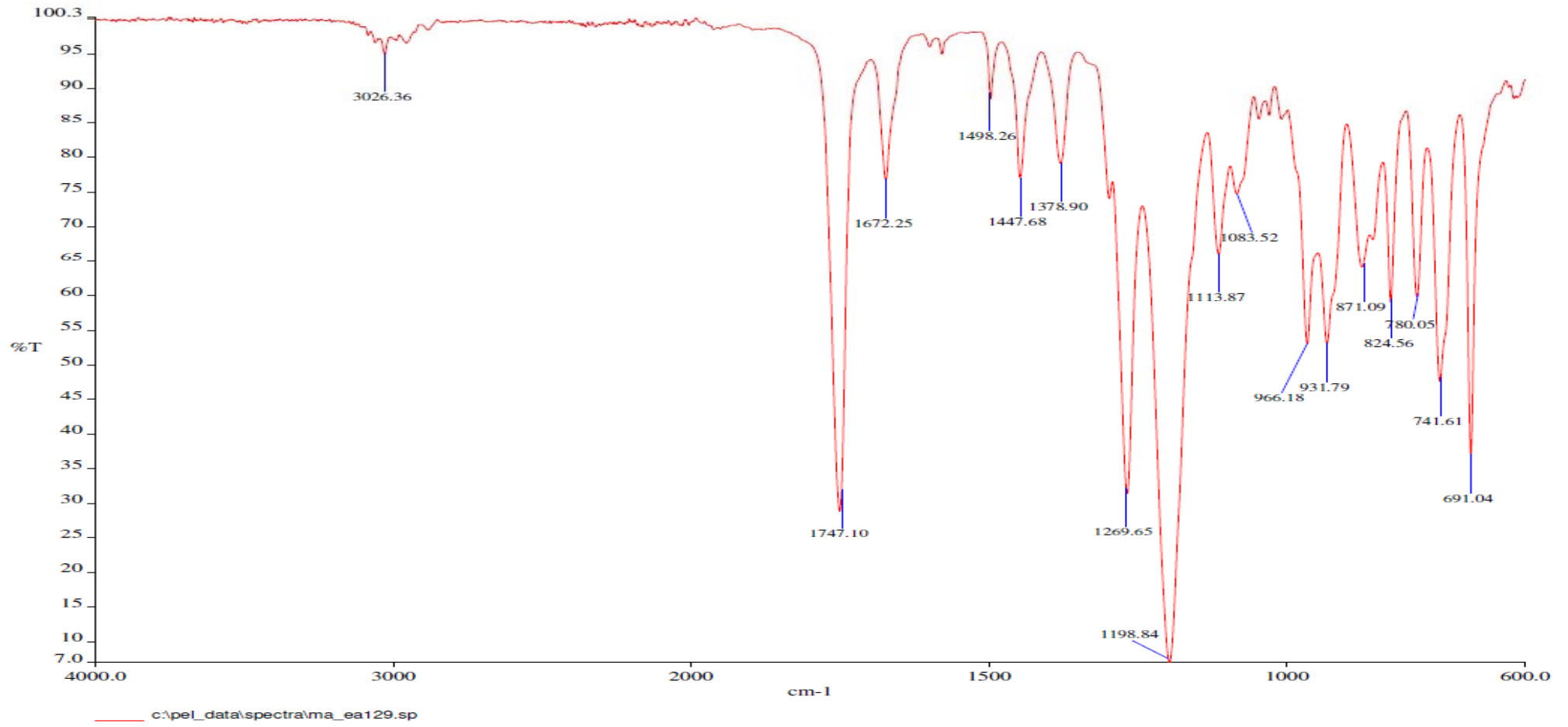
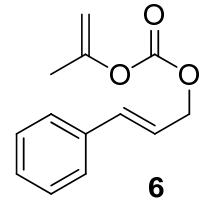
¹H NMR spectrum of **6** (500 MHz, CDCl₃)

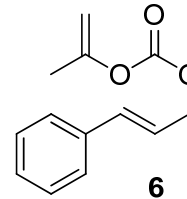


¹³C NMR spectrum of **6** (125 MHz, CDCl₃)



IR spectrum of **6** (Neat)





UNIVERSITY OF GENEVA

Faculty of Sciences

Sciences Mass Spectrometry



Sample name: EA129

Sample number: 0354

Operator: Eliane Sandmeier

Principal investigator: Prof. G. Hopfgartner

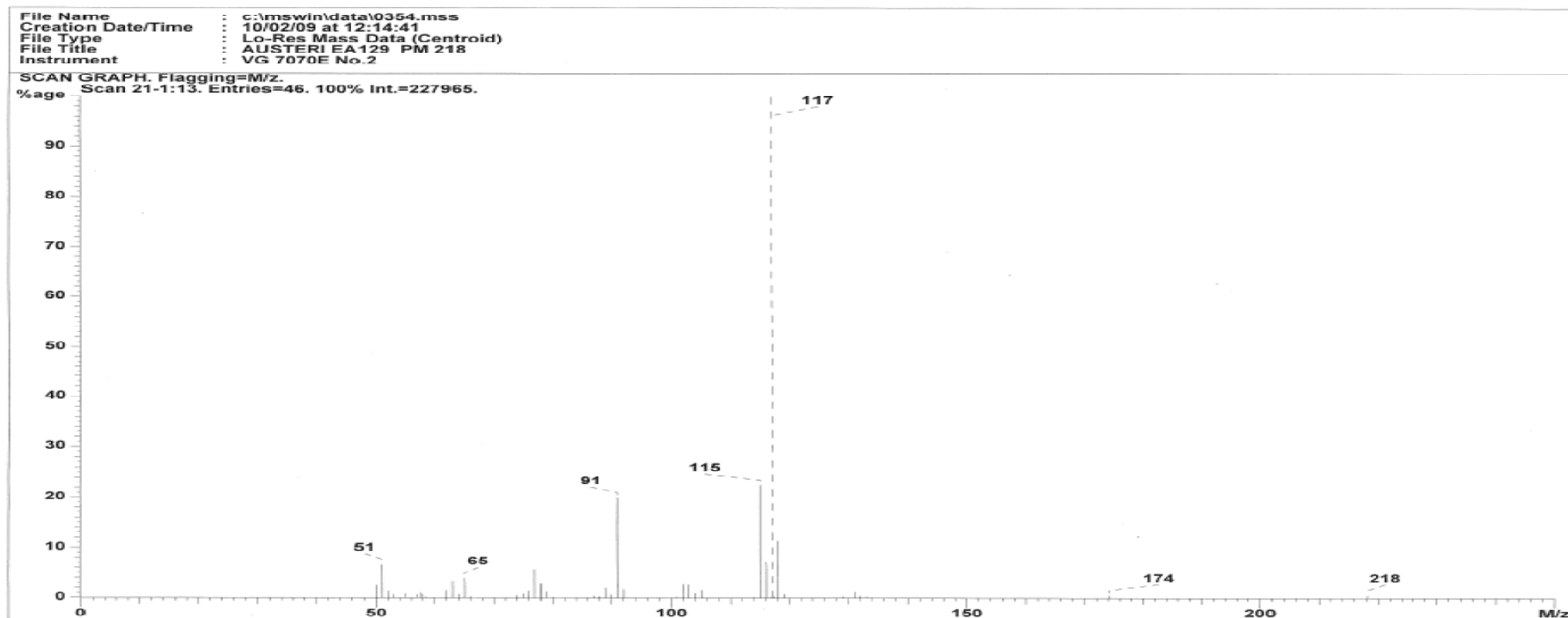
Date of reception: 10/02/09

Date of analysis: 10/02/09

Instrument: VG 7070E

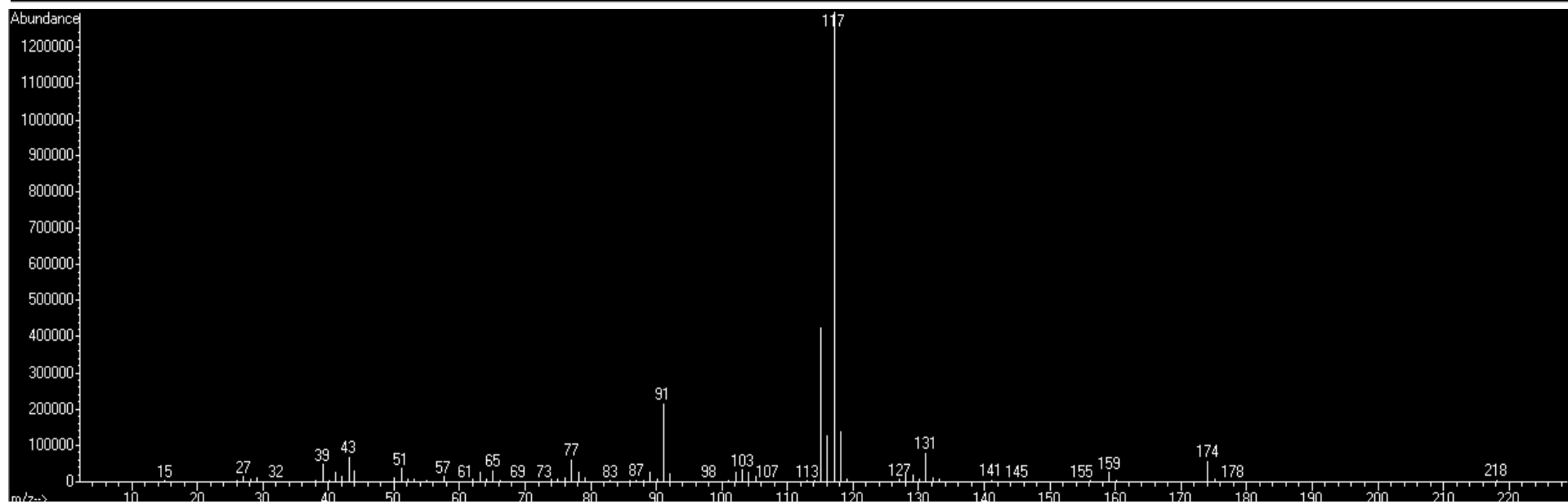
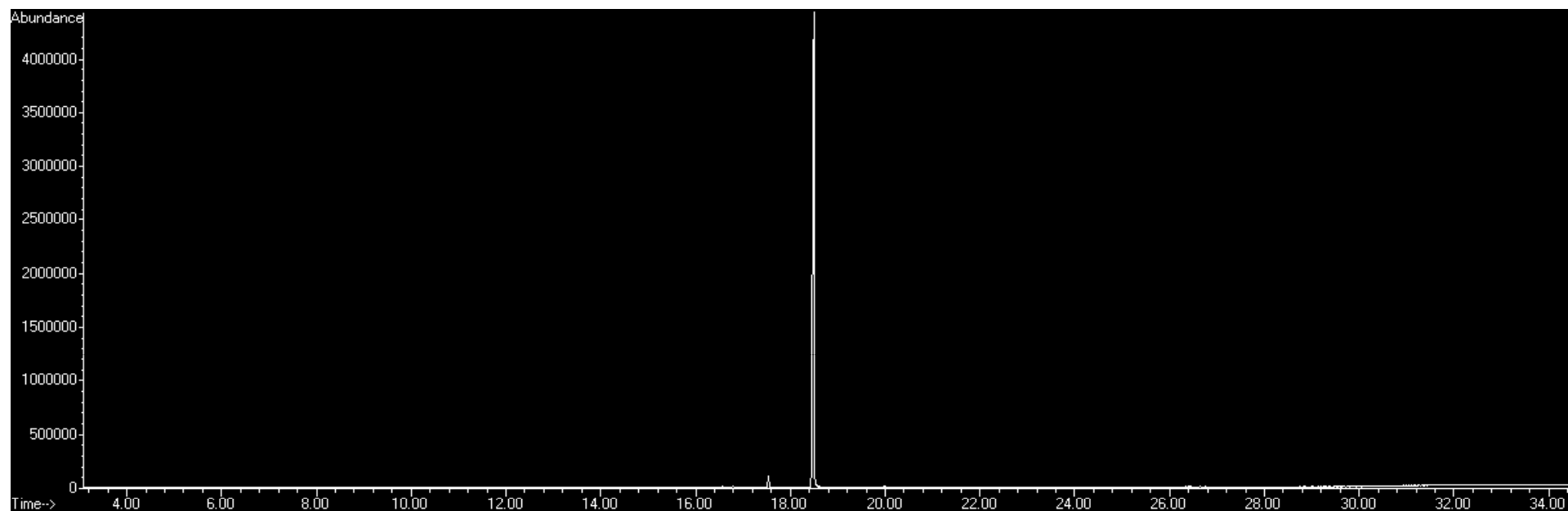
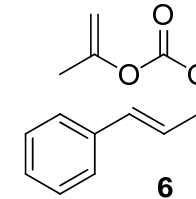
Ionisation mode: EI - LR

Mass spectrum of the sample:

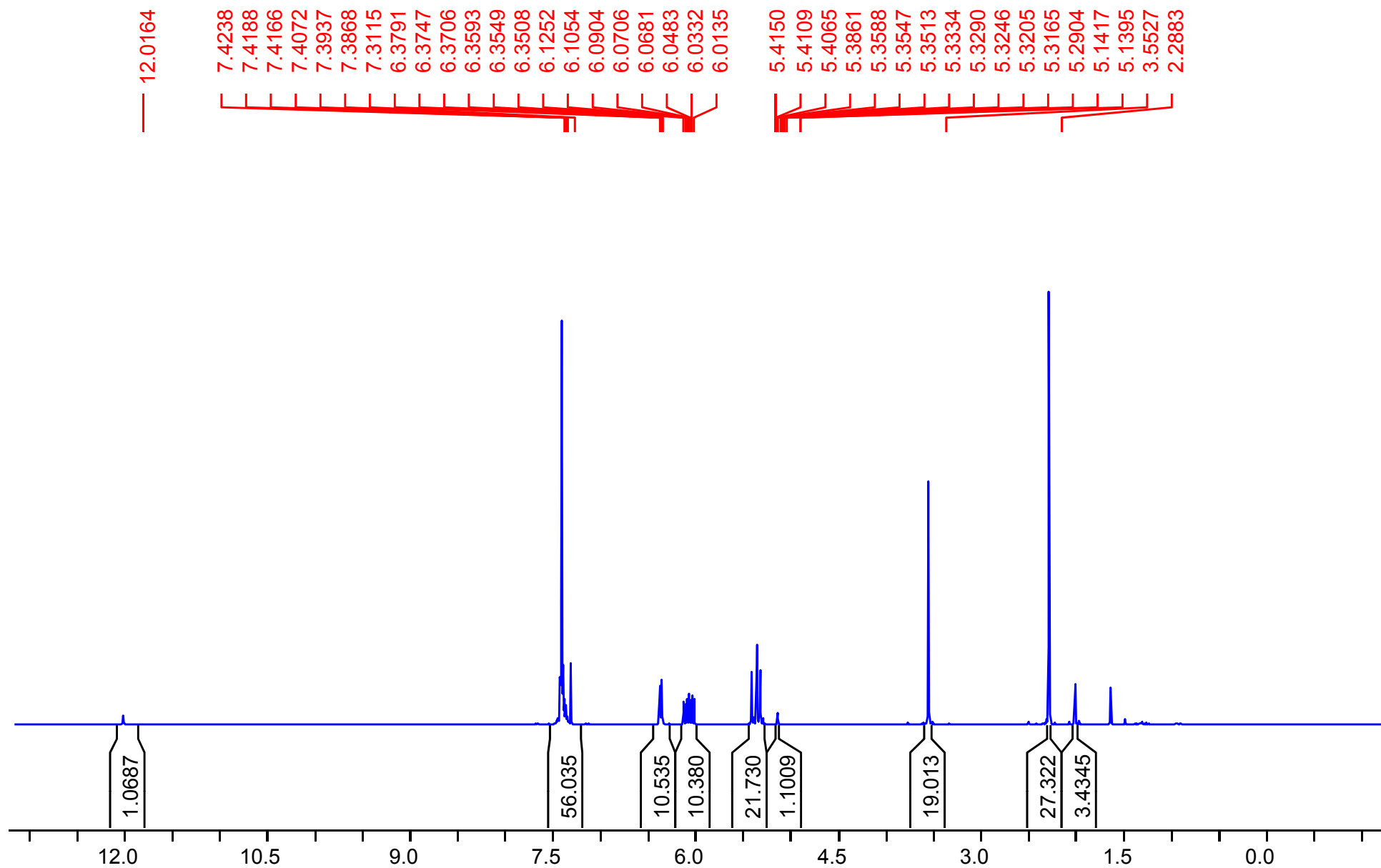
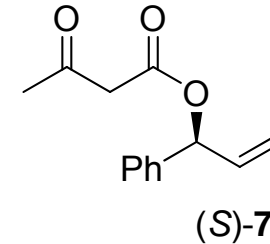


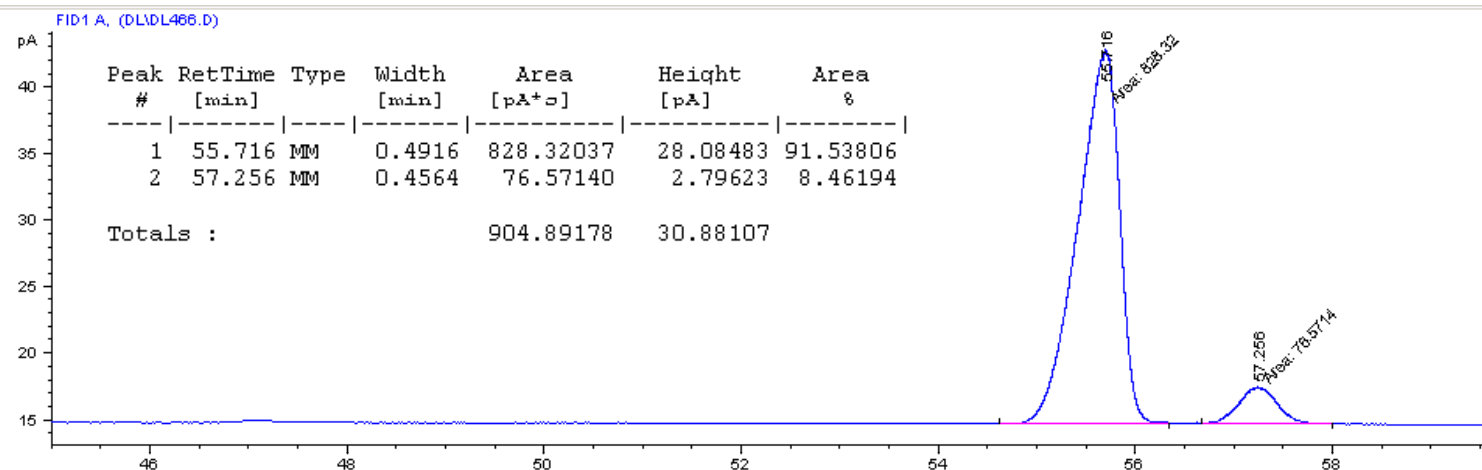
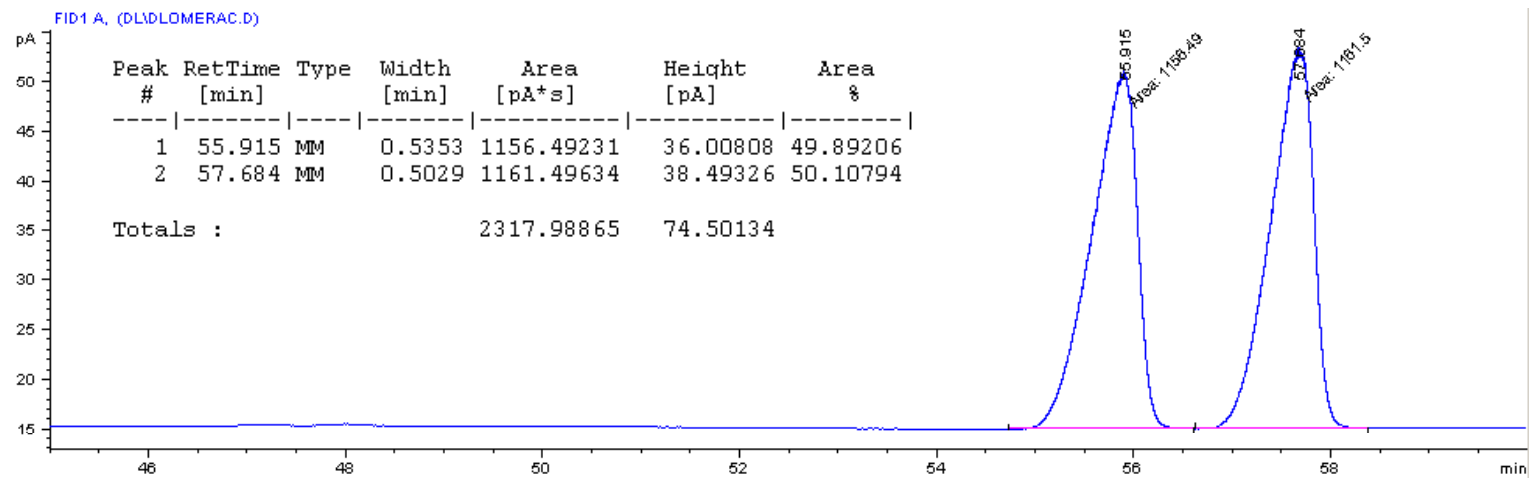
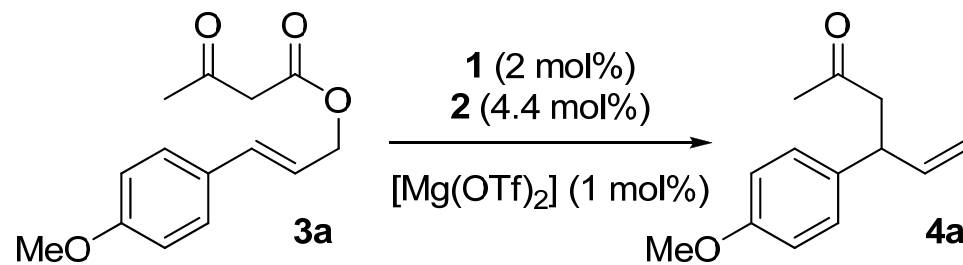
GCMS trace and mass spectrum of **6**

(HP 5 MS: T_{inj} 250 °C, P = 0.48 bar; 60 °C, isotherm 5 min then temperature gradient 10 °C.min⁻¹ until 320 °C, isotherm 5 min)

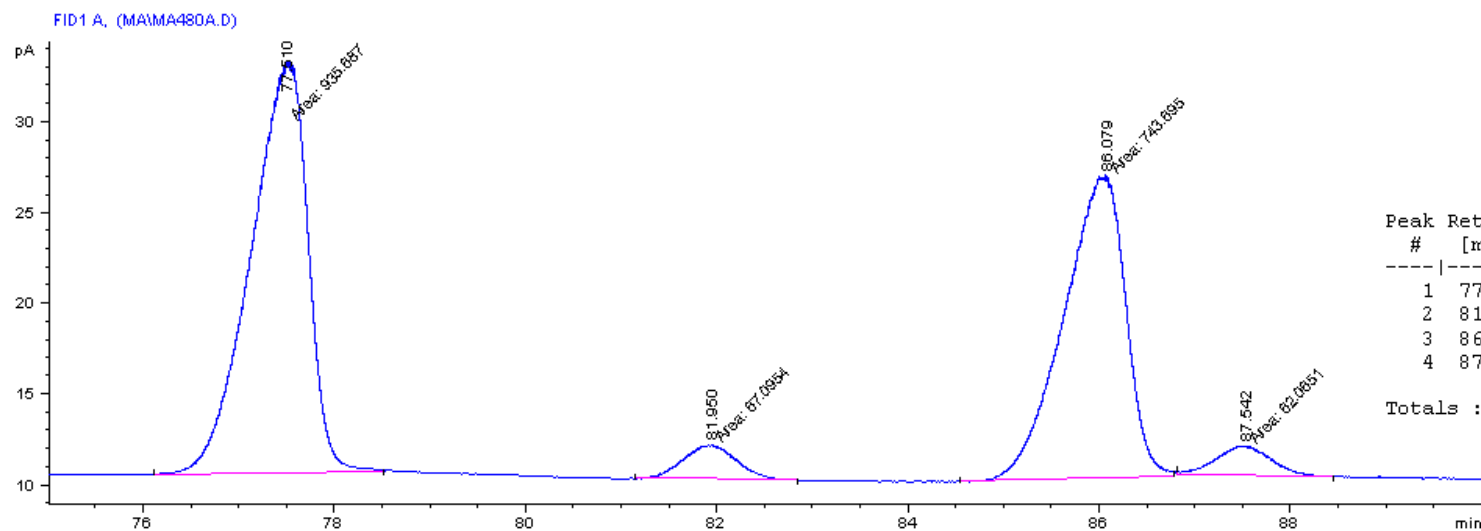
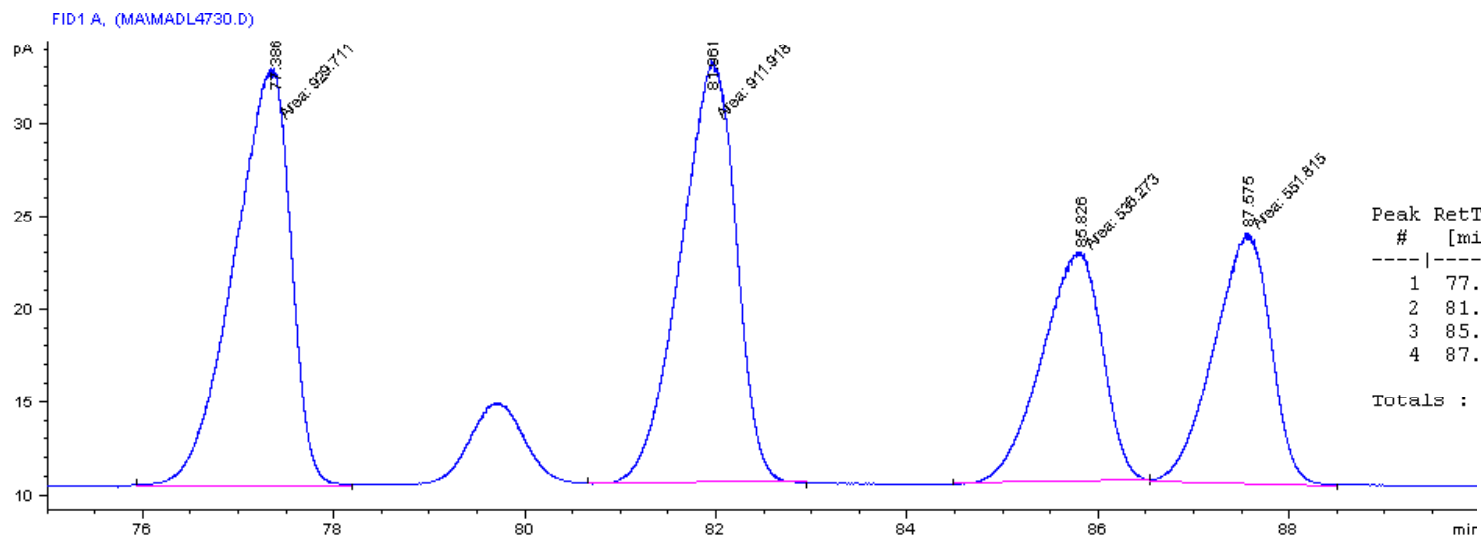
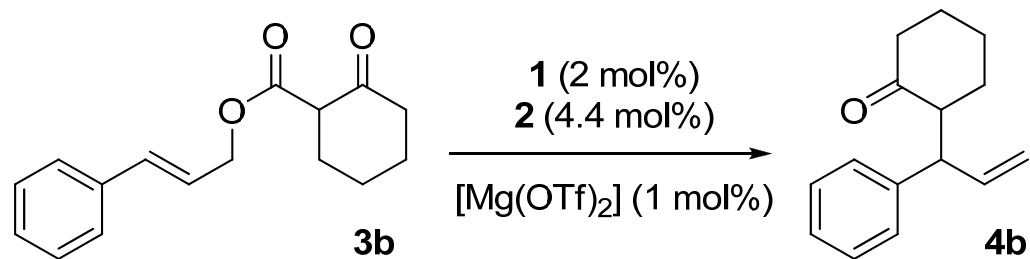


¹H NMR spectrum of **7** (400 MHz, CDCl₃)

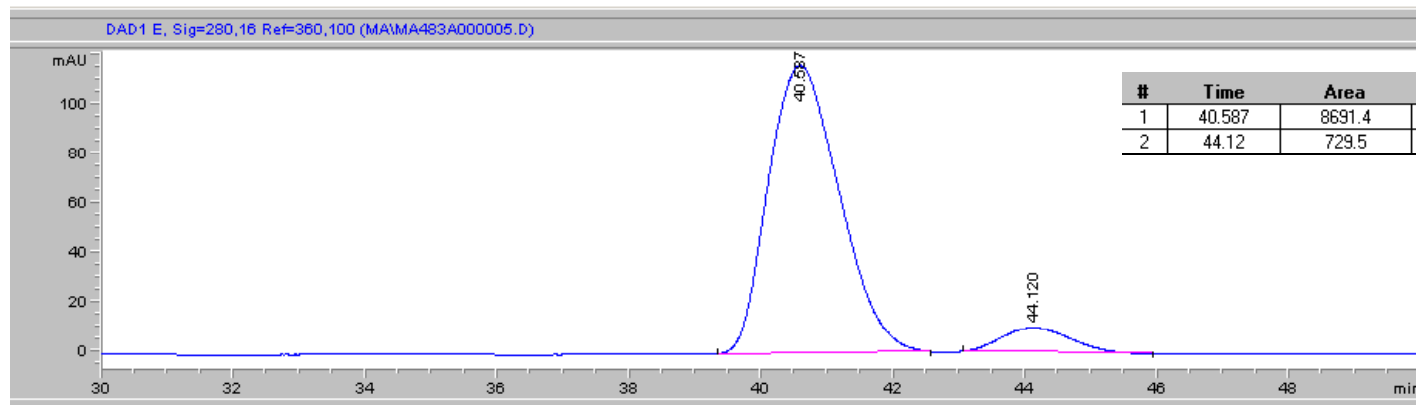
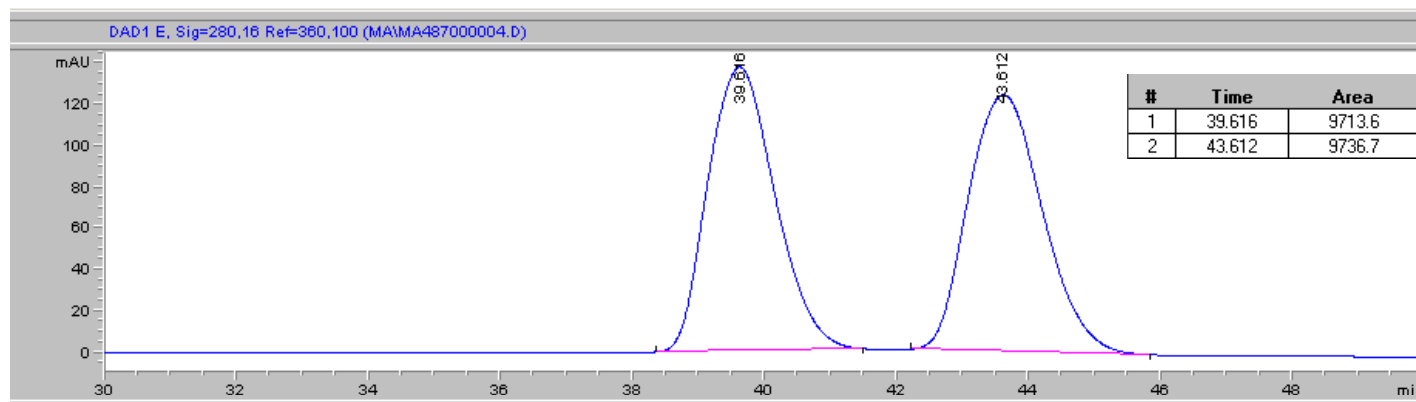
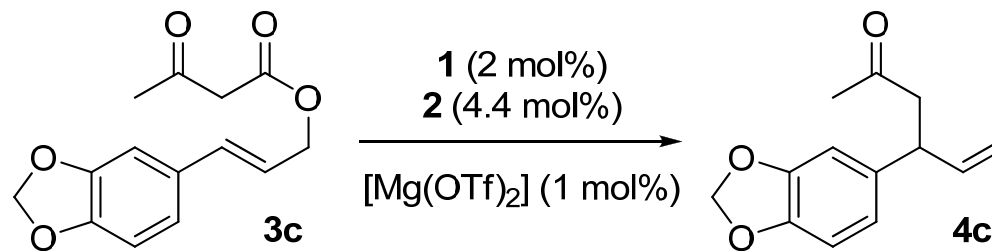




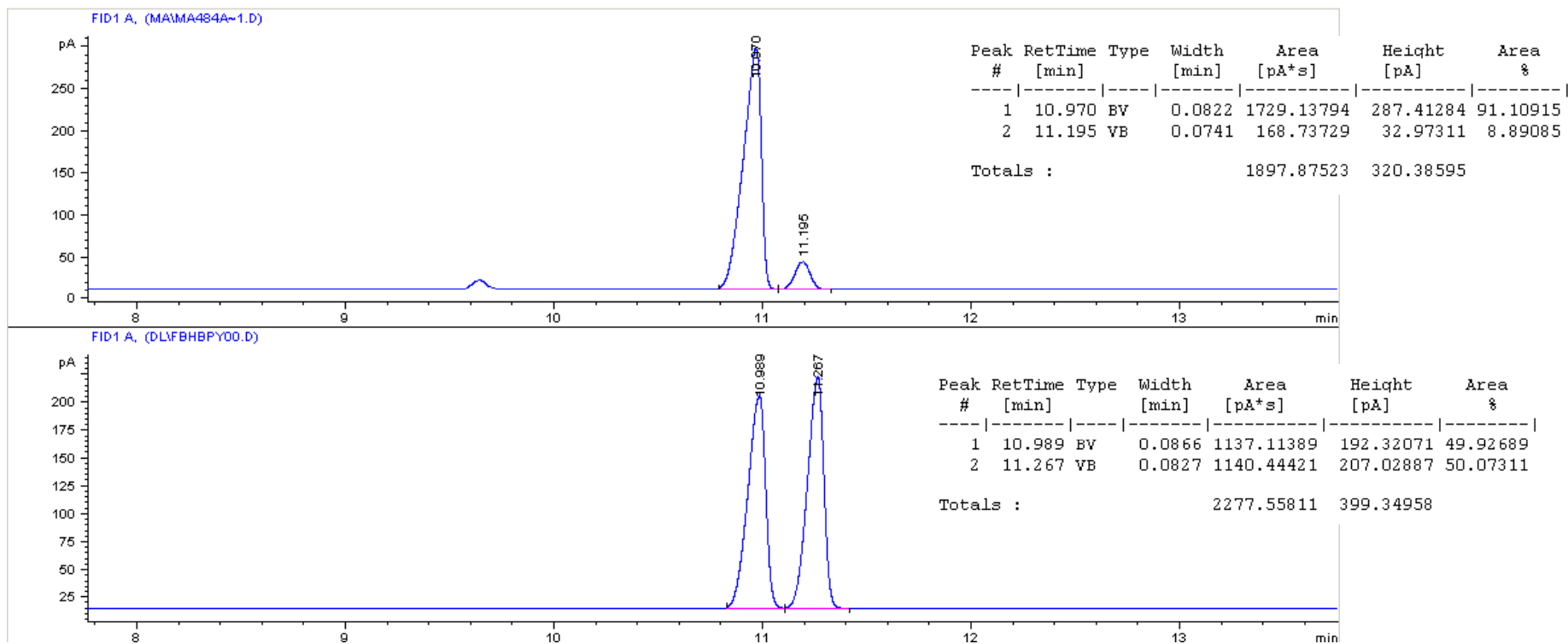
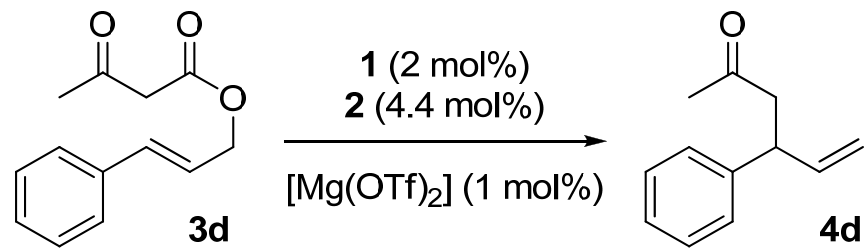
Determined by CSP-GC (Chiraldex Hydrodex β -3P), T_{inj} 250 °C, P = 0.596 bar; 130 °C, isotherm.



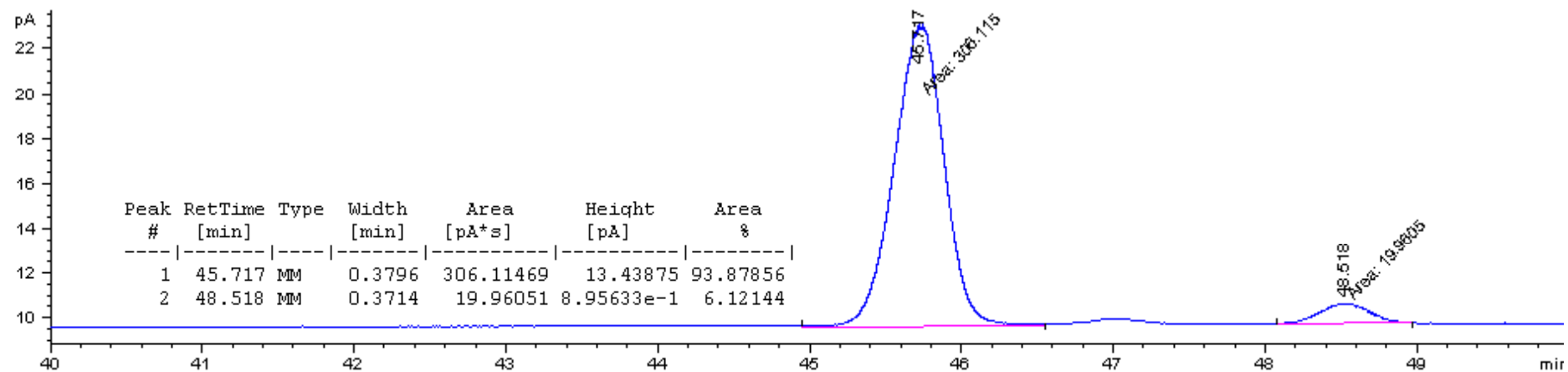
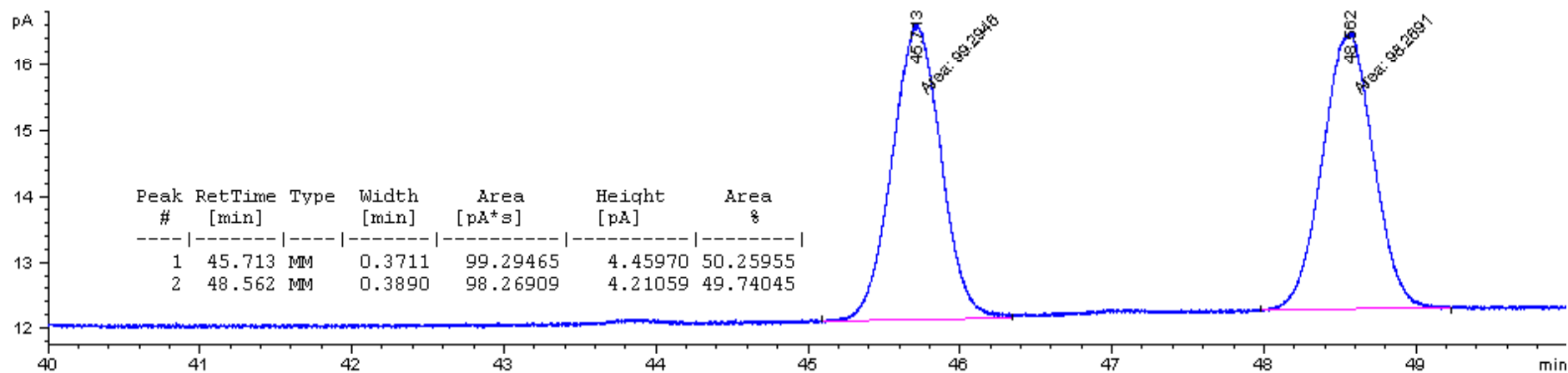
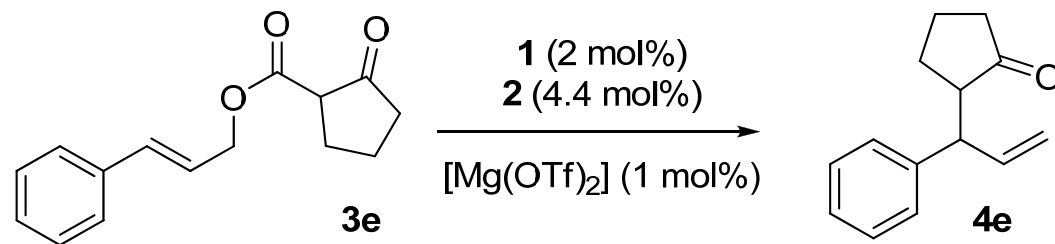
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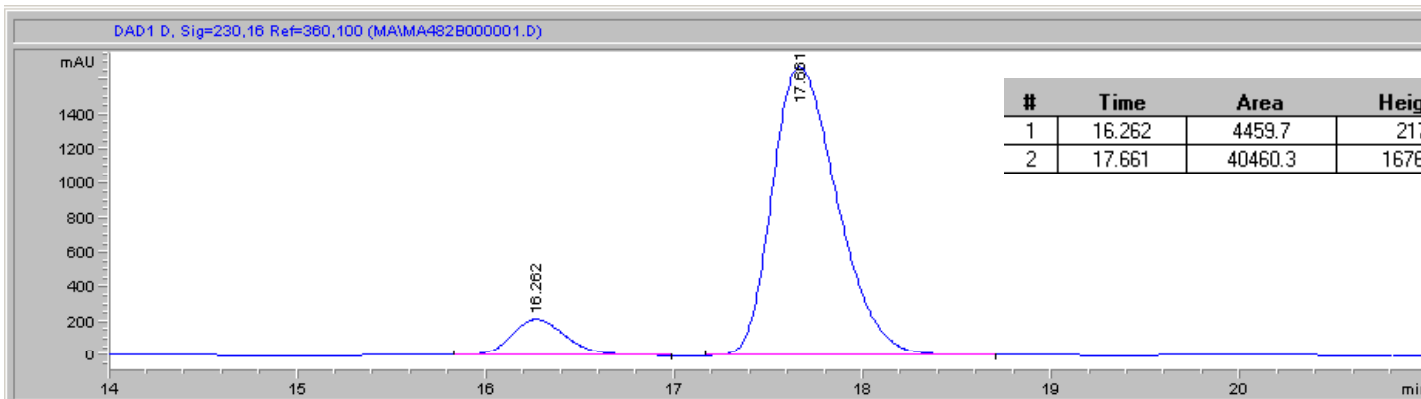
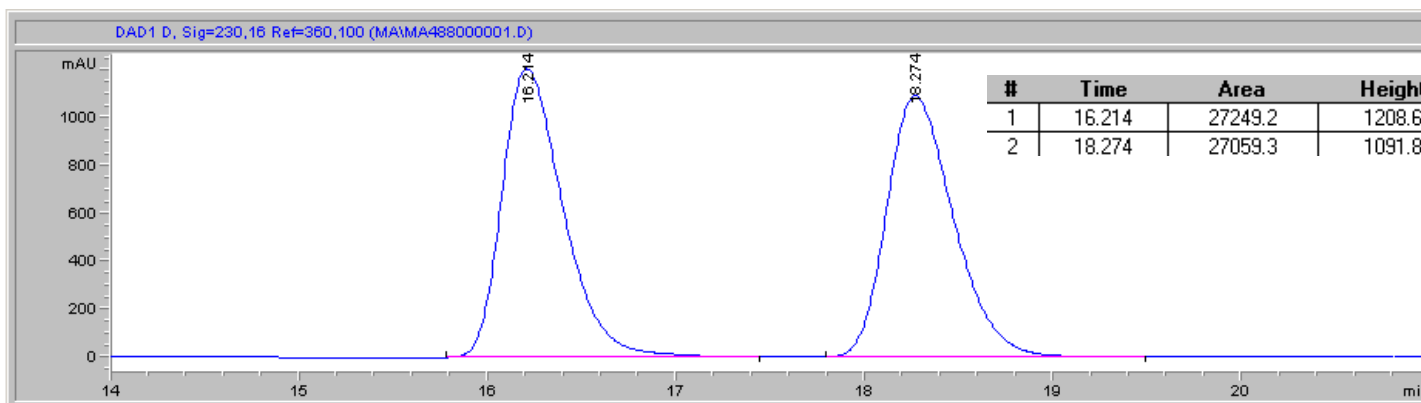
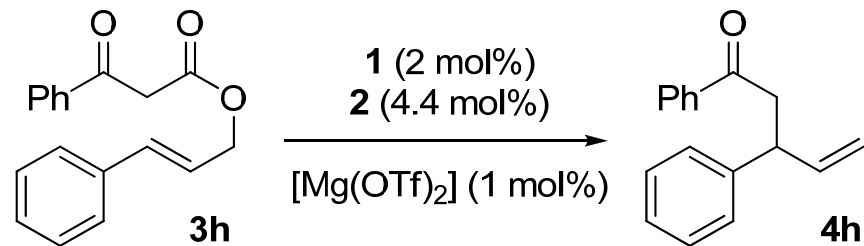
Determined by CSP-HPLC Column OD-H Hex/i-PrOH 99.5/0.5 flow 0.5 mL/min, 23 °C



Determined by CSP-GC (Chiraldex Hydrodex β -3P), T_{inj} 250 °C, P = 0.596 bar; 130 °C, isotherm.

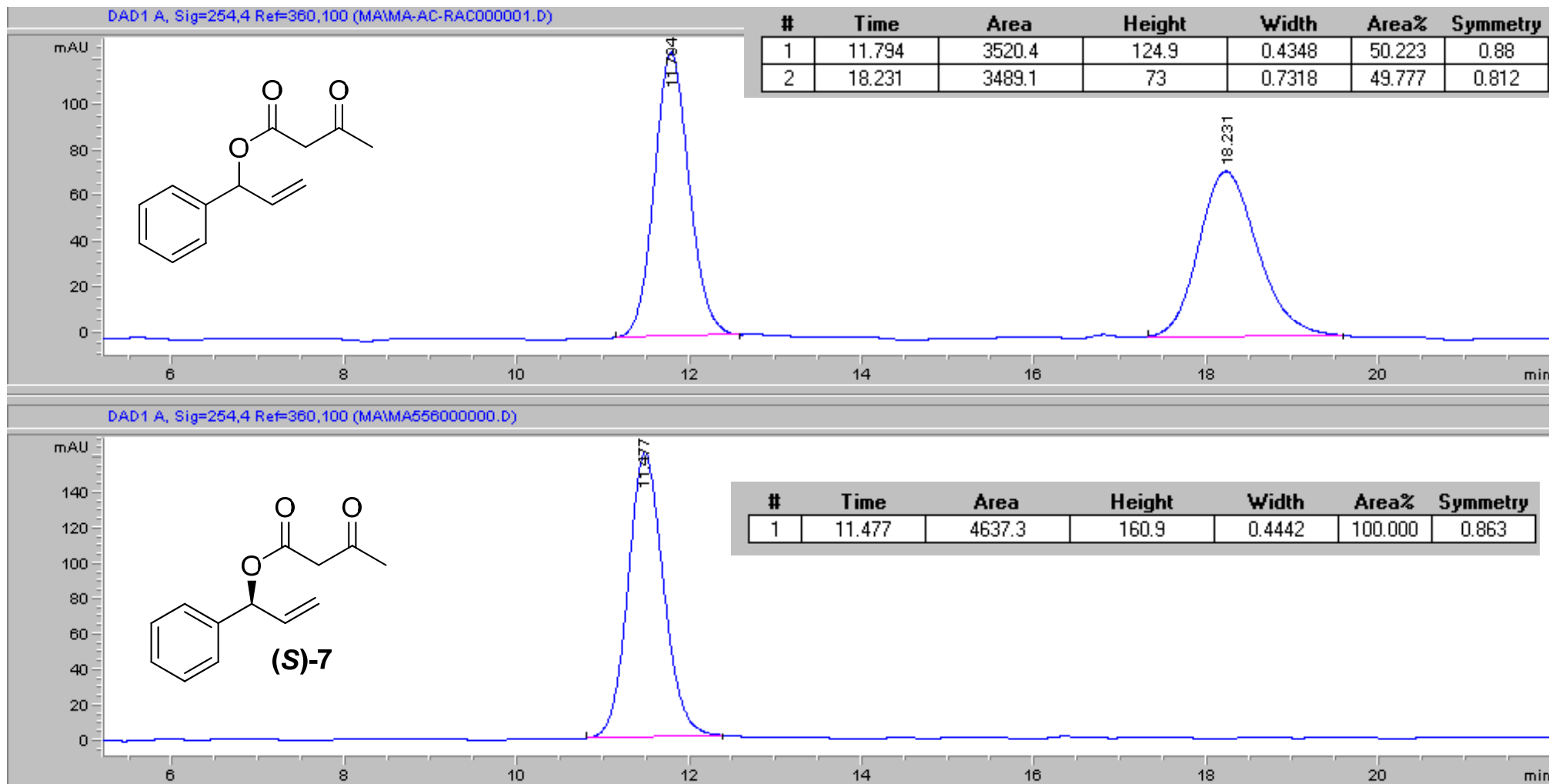


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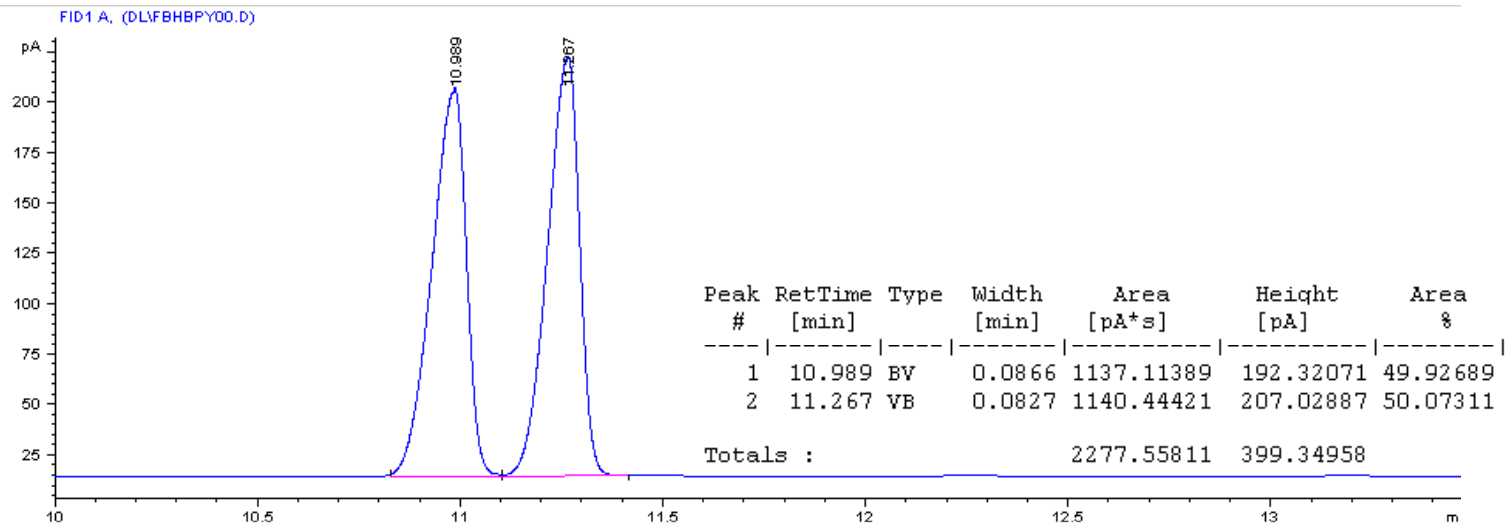
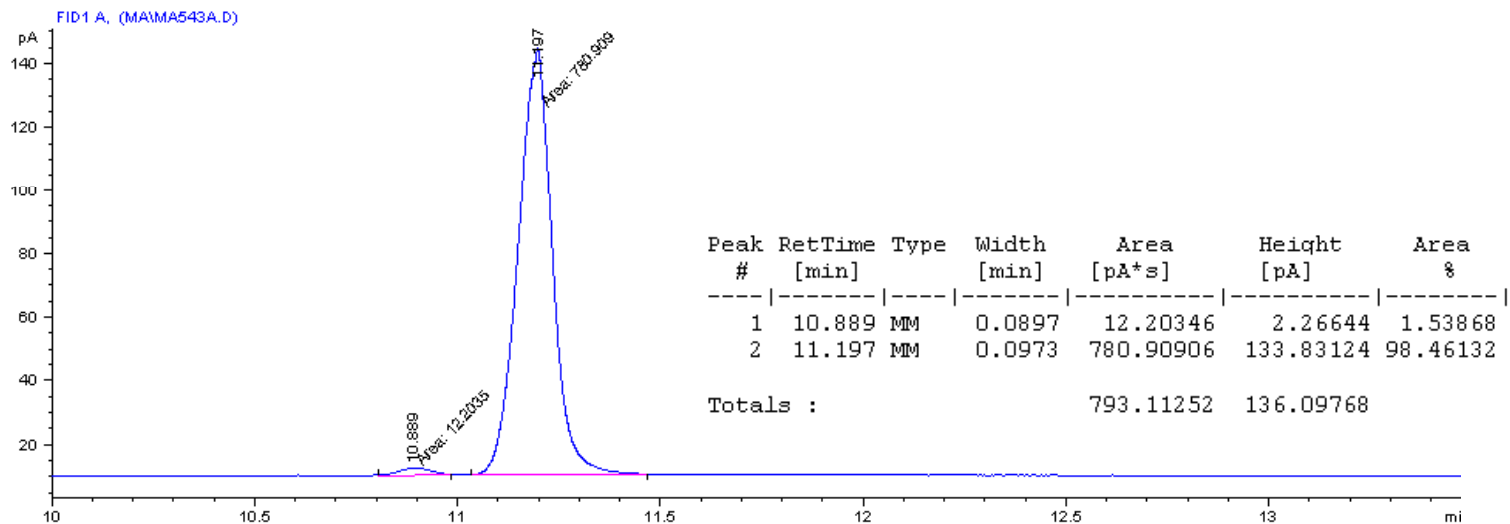
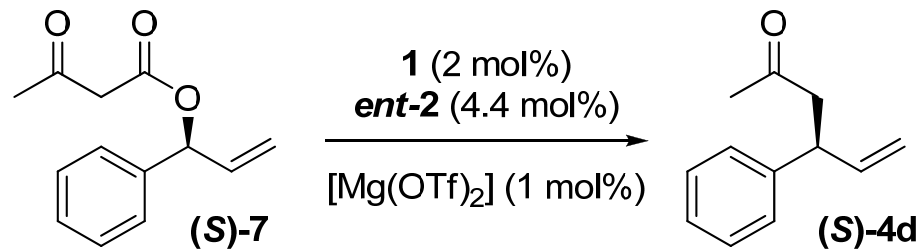


Determined by CSP-HPLC Column OD-H Hex/i-PrOH 98/2 flow 0.5 mL/min, 23 °C

Racemic and enantiopure secondary ester 7



Determined by CSP-HPLC Column Whelk-O1 Hex/i-PrOH 99/1 flow 1 mL/min, 23 °C



Determined by CSP-GC (Chiraldex Hydrodex β-3P), T_{inj} 250 °C, P = 0.596 bar; 130 °C, isotherm.