

Supporting Information

Simultaneous production of bio-based styrene and acrylates using ethenolysis

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Experimental

All experiments carried out at elevated pressures were performed in 6 individual 75-mL Parr pressure reactors (Parr multiple reactor system series 5000). Reaction mixtures were prepared in Schlenk tubes glassware under a positive pressure of nitrogen and transferred to the reactors *via* syringe. Ethylene 3.5 (purity \geq 99.95%) was supplied by Linde Gas Benelux and used as received. Dichloromethane was dried over CaCl₂ and distilled under nitrogen before use. Other anhydrous solvents (purchased from Sigma-Aldrich) and Milli-Q water were degassed with nitrogen before use. Cinnamic acid (**2**) was supplied by Sigma-Aldrich and use without additional purification. Methyl (**5**) and ethyl (**6**) cinnamate (Sigma-Aldrich) and butyl cinnamate (**7**) (prepared following a standard esterification procedure) were filtered through a plug of neutral alumina and degassed with nitrogen before use. All ruthenium catalysts were obtained from Sigma-Aldrich. Concentration of solutions was carried out by using a rotary evaporator. Purification by filtration over a silica plug was undertaken on silica gel (400-630 mesh). Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Bruker AM-400 (400 MHz). GC-MS analyses were performed on a CE Instrument GC 8000 Top (capillary column SGE-Forte, 30 m x 0.25 mm, 0.25 μ m) chromatograph linked to an Automass II Finnigan MAT (70 eV) apparatus. The temperature profile was held at 50 °C for 2 minutes, then increased to 300 °C (10 °C per minute), and held at 300 °C for 2 minutes.

Esterification with H₂SO₄

0.74 g (5.0 mmol) of cinnamic acid (**2**) was dissolved in 25 mL alcohol. 0.2 mL H₂SO₄ was added to the mixture. For the reactions with MgSO₄, *ca.* 1.5 g of MgSO₄ was added. The mixture was refluxed and stirred during the reaction time. The alcohol was removed under reduced pressure. Work up proceeded through basification to *ca.* pH 8-10 with a saturated NaHCO₃ solution and extraction with diethyl ether. The ether was removed under reduced pressure. The product was purified by column chromatography (1/10 diethyl ether/hexane) and analysed by ¹H NMR spectroscopy. Isolated yields and catalysts used are reported in table S11.

Esterification with FeCl₃

0.74 g (5.0 mmol) of cinnamic acid (**2**) was dissolved into 25 mL of alcohol. FeCl₃ (0.068g, 5 mol%) was added. The reaction was refluxed for 24 hours and allowed to cool down to room temperature. The alcohol was removed under reduced pressure and the FeCl₃ was removed by adding ethyl acetate and extracting the solution with H₂O. After drying with MgSO₄ and removing the solvent under reduced pressure, the conversion was measured by ¹H NMR spectroscopy. Isolated yields and catalysts used are reported in table S11.

Esterification with heterogeneous catalysts

0.74 g (5.0 mmol) of cinnamic acid (**2**) was dissolved in 25 mL alcohol. 150 mg of heterogeneous catalyst was added to the mixture. The catalyst was washed with the alcohol and dried before use. The mixture refluxed and stirred during the reaction time. The enzymatic reaction was heated to only 50 °C. The heterogeneous catalyst was filtered off and the alcohol was removed under reduced pressure. The crude was analyzed by ¹H NMR spectroscopy. Isolated yields and catalysts used are reported in table S11.

Self-metathesis tests

0.34 mL (2 mmol) ethyl cinnamate (**6**) was added to 10 mL dichloromethane (DCM) in a Schlenk tube under a nitrogen atmosphere. 5 mol% catalyst was added and the reaction was heated to 40 °C and stirred for 24 hours. The DCM was evaporated under atmospheric pressure and the crude was analysed by ¹H NMR spectroscopy.

Ethenolysis

A stock solution was prepared in a Schlenk tube containing DCM with the substrate (0.02-0.50M) and the catalyst (**I**) to (**V**) (5–12.5 mol%). The solution was divided over the reactors using a syringe (10 mL per reactor) and the reactors were purged three times with N₂. The reactors were placed in the control system and purged three times with ethylene. The pressure of ethylene was applied and the reactions were heated and stirred during the reaction time. (For reaction pressure depicted as

being less than 1 bar of ethylene, mixtures of ethylene and nitrogen were prepared and reactions were performed under 1 bar of the gas mixture atmosphere. For instance, a reaction performed with 0.5 bar of ethylene was performed with 1 bar of a 50/50 ethylene/nitrogen gas mixture). After the reaction, the reactors were opened and an aliquot was filtered over a plug of silica, washed with the used solvent once and injected into the GC-MS. The crude was concentrated by heating it to 50 °C for a couple of minutes under atmospheric pressure. The conversion of the cinnamic acid (**2**) or its esters (**5-7**) was measured by ¹H NMR.

For the catalyst screening the stock solution consisted of solvent and substrate. The catalyst was introduced in the reactor immediately followed by the stock solution. The rest of the procedure was followed as described above.

For the solvent and substrate screening, no stock solution was used. The catalyst, substrate and solvent were directly added into the reactor, which was directly purged with N₂. The rest of the procedure was followed as described above.

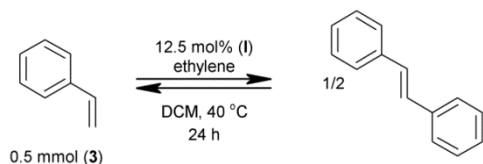
Table S11 Esterification of cinnamic acid (**2**).

| Entry | Catalyst | Loading | Alcohol | Time (h) | Yield (%) |
|-----------------|--------------------------------|---------|-----------|----------|-----------|
| 1 | H ₂ SO ₄ | 0.2 ml | n-butanol | 4 | 64 |
| 2 | H ₂ SO ₄ | 0.2 ml | ethanol | 2.5 | 79 |
| 3 ^a | H ₂ SO ₄ | 0.2 ml | ethanol | 2.5 | 91 |
| 4 | H ₂ SO ₄ | 0.2 ml | methanol | 4 | 82 |
| 5 | FeCl ₃ | 68 mg | ethanol | 24 | 74 |
| 6 | ZnCl ₂ | 68 mg | ethanol | 24 | 4 |
| 7 | LaCl ₃ | 93 mg | ethanol | 24 | 55 |
| 8 | Zeolite-β | 148 mg | n-butanol | 24 | 7 |
| 9 | Amberlyst 15 | 151 mg | ethanol | 24 | 38 |
| 10 | Amberlyst 36 | 257 mg | ethanol | 24 | 36 |
| 11 ^b | CAL-B | 50 mg | n-butanol | 312 | 16 |

^aMgSO₄ added to the reaction as drying agent. ^bT = 50 °C

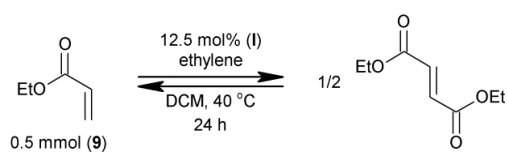
Control experiments

Control ethenolysis experiments performed on the products styrene (**3**) and ethyl acrylate (**9**) to study the influence of the ethylene pressure on the formation of side products via self-metathesis.



| Entry | P _{ethylene} (bar) | Ratio ^a styrene/stilbene |
|-------|-----------------------------|-------------------------------------|
| 1 | 1 | 57/43 |
| 2 | 20 | 83/17 |

^aDetermined by ¹H NMR.



| Entry | P _{ethylene} (bar) | Conversion ^a (%) |
|-------|-----------------------------|-----------------------------|
| 1 | 1 | 0 |
| 2 | 20 | 0 |

^aDetermined by ¹H NMR.

Data points for figure 1

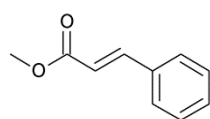
Table S12 Data points for figure 1.^a

| Entry | P _{ethylene} (bar) | Conversion of cinnamic acid (2) (%) | Conversion of ethyl cinnamate (6) (%) |
|-------|-----------------------------|-------------------------------------|---------------------------------------|
| 1 | 0.01 | 8 | |
| 2 | 0.05 | 11 | |
| 3 | 0.10 | 12 | |
| 4 | 0.50 | 19 | |
| 5 | 0.75 | 20 | |
| 6 | 1.0 | 13 | 15 |
| 7 | 2.0 | 7 | 4 |
| 8 | 3.5 | 6 | 3 |
| 9 | 13.2 | 4 | 1 |

^aReaction conditions: 0.02 M substrate, 24 h, 40 °C, 5 mol% (I). (Pressures of ethylene below one bar represent a pressure of one bar of nitrogen and ethylene, where the partial pressure of ethylene is shown)

NMR – spectra

Methyl Cinnamate (5)



Product from the esterification of cinnamic acid with methanol, catalysed by H₂SO₄. ¹H NMR-spectrum is in accordance to the literature.¹

Yellow liquid, ¹H NMR (400 MHz, CDCl₃): δ 3.80 (3H, s, OCH₃), 6.44 (1H, d, J = 16.0 Hz, MeOCC=), 7.37-7.39 (3H, m, Ar-H), 7.51-7.52 (2H, m, Ar-H), 7.70 (1H, d, J = 16.0 Hz, ArCH=).

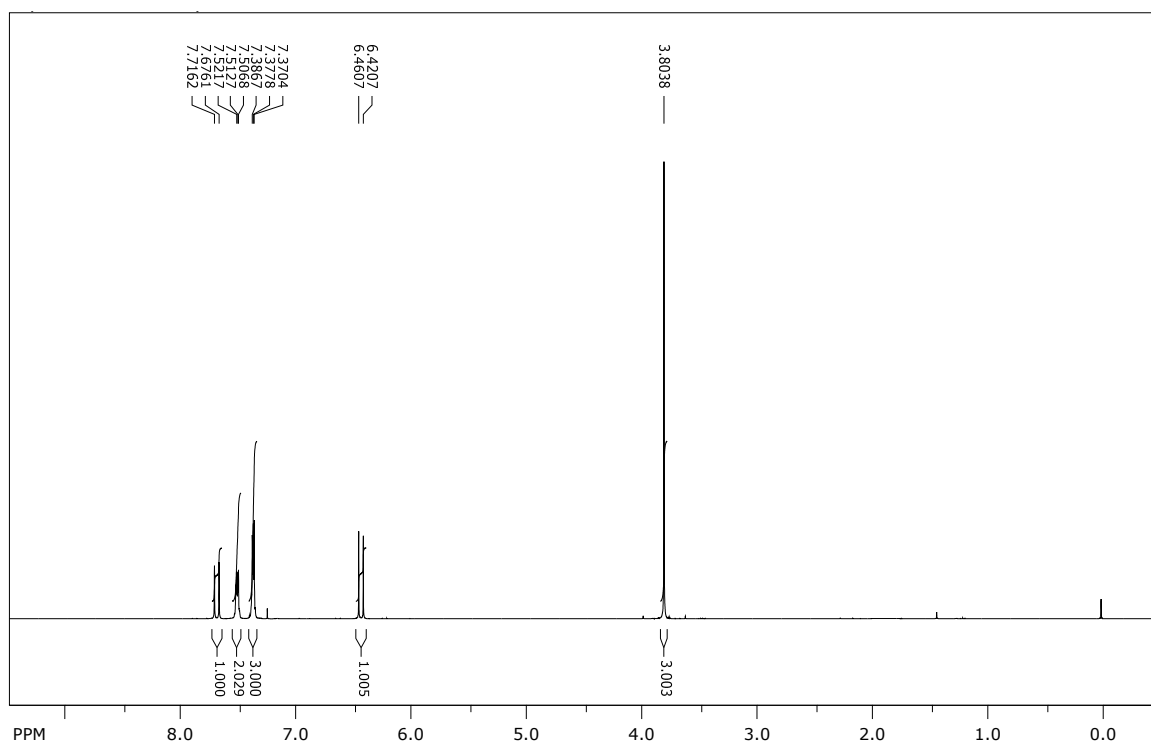
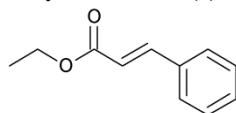


Fig. S11 ¹H NMR of Methyl Cinnamate (5) in CDCl₃

Ethyl Cinnamate (6)



Product from the esterification of cinnamic acid with ethanol, catalysed by H₂SO₄. ¹H NMR-spectrum is in accordance to the literature.²

Yellow liquid, ¹H NMR (400 MHz, CDCl₃): δ 1.34 (3H, t, J = 7.1 Hz, CH₃), 4.27 (2H, q, J = 7.1

Hz, OCH₂), 6.44 (1H, d, J = 16.0, EtOCCH=), 7.37-7.39 (3H, m, Ar-H), 7.51-7.52 (2H, m, Ar-H), 7.69 (1H, d, J = 16.0, ArCH=).

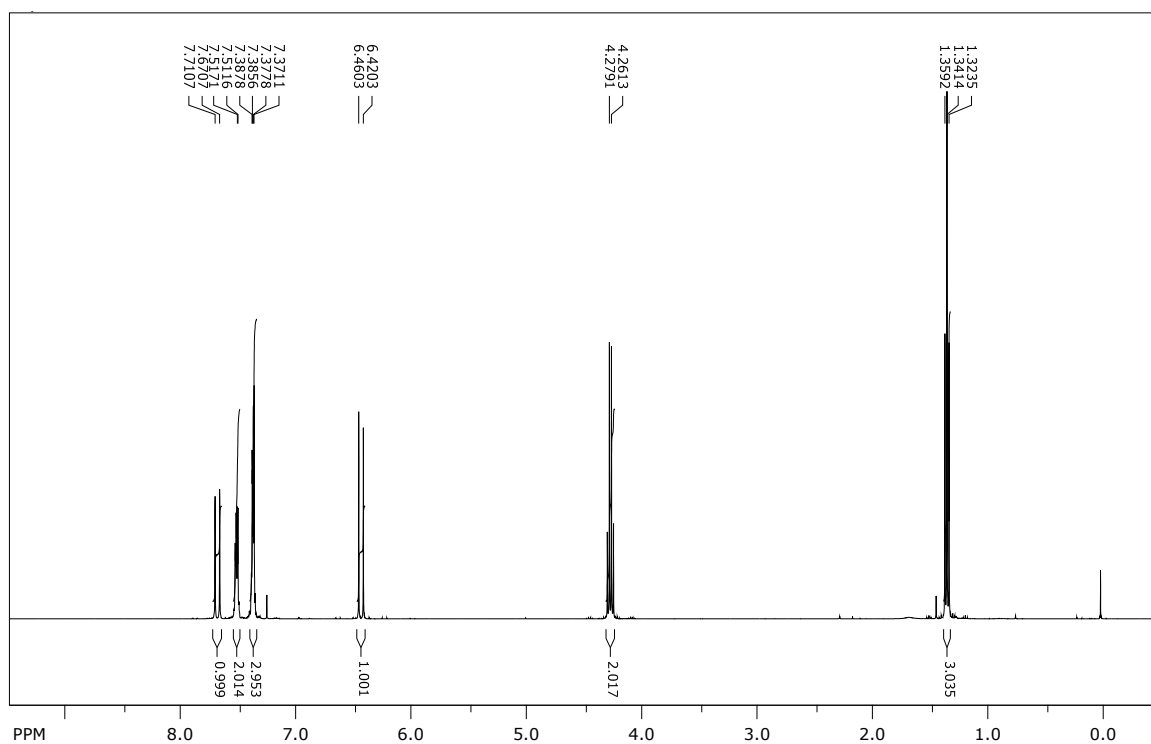
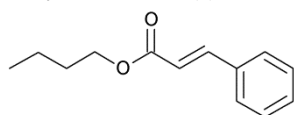


Fig. S12 ¹H NMR of Ethyl Cinnamate (6) in CDCl₃

Butyl Cinnamate (7)



Product from the esterification of cinnamic acid with *n*-butanol, catalysed by H₂SO₄. ¹H NMR-spectrum is in accordance to the literature.¹

Yellow liquid, ¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.97 (3H, t, J = 7.4 Hz, CH₃), 1.40-1.49 (2H, m, CH₂-Me), 1.66-1.73 (2H, m, CH₂-Et), 4.21 (2H, t, J = 6.7 Hz, OCH₂), 6.44 (1H, d, J = 16.0 Hz, BuOCCH=), 7.37-7.39 (3H, m, Ar-H), 7.51-7.53 (2H, m, Ar-H), 7.68 (1H, d, J = 16.0, ArCH=).

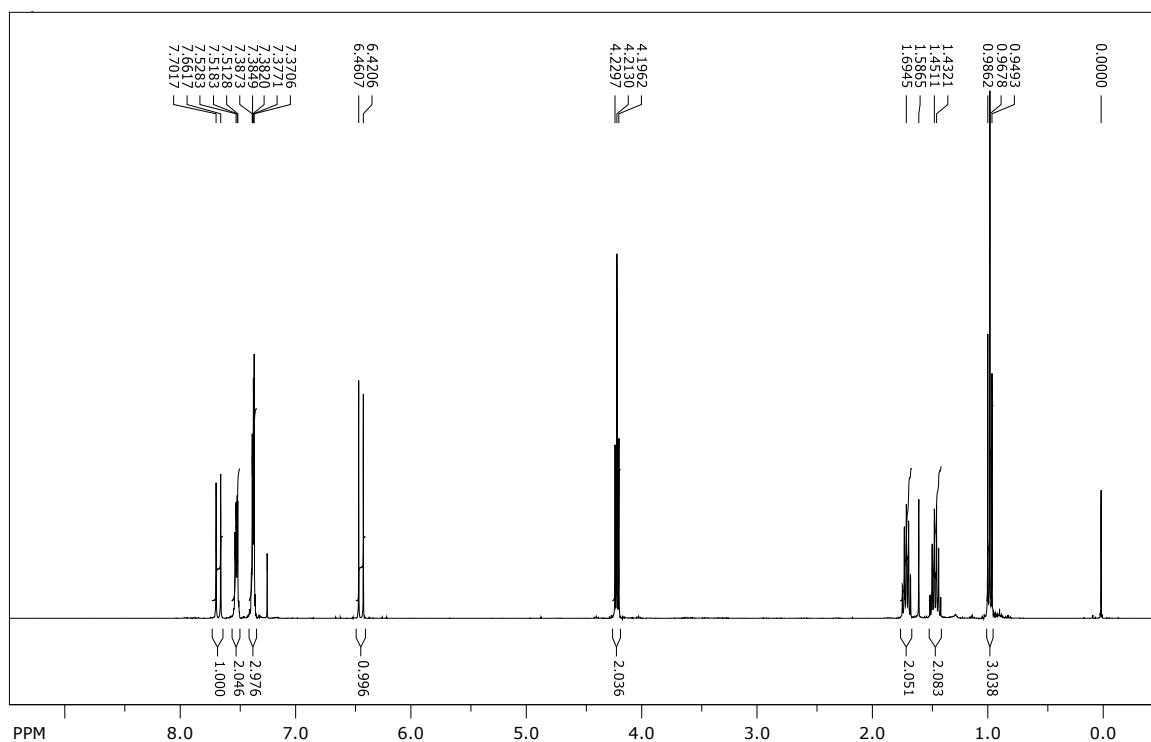


Fig. S13 ^1H NMR of Butyl Cinnamate (7) in CDCl_3

Ethenolysis

For the ethenolysis reactions the conversion was determined by unique peaks of ethyl cinnamate (6) at $\delta = 7.68$ ppm, styrene (3) at $\delta = 6.72$ ppm and 5.74 ppm and ethyl acrylate (9) at $\delta = 5.81$ ppm and 6.11 ppm.

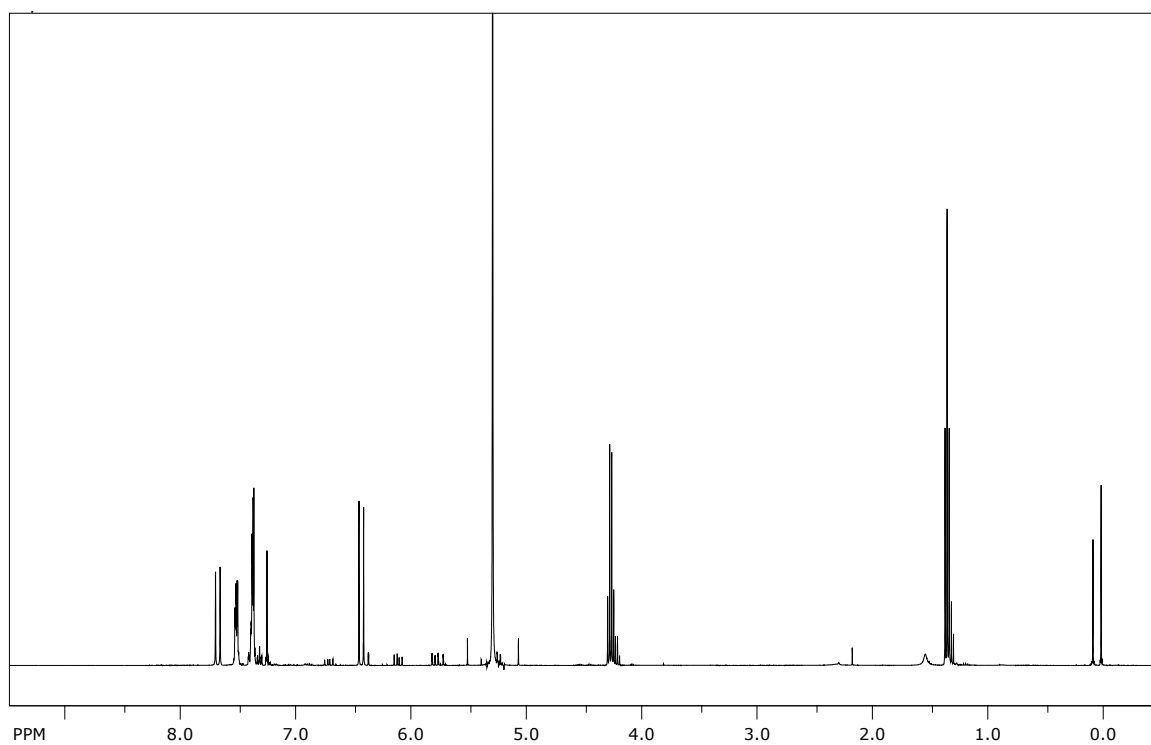


Fig. S14 Example of crude ^1H NMR spectrum of the ethyl cinnamate (6) ethenolysis into styrene (3) and ethyl acrylate (9).

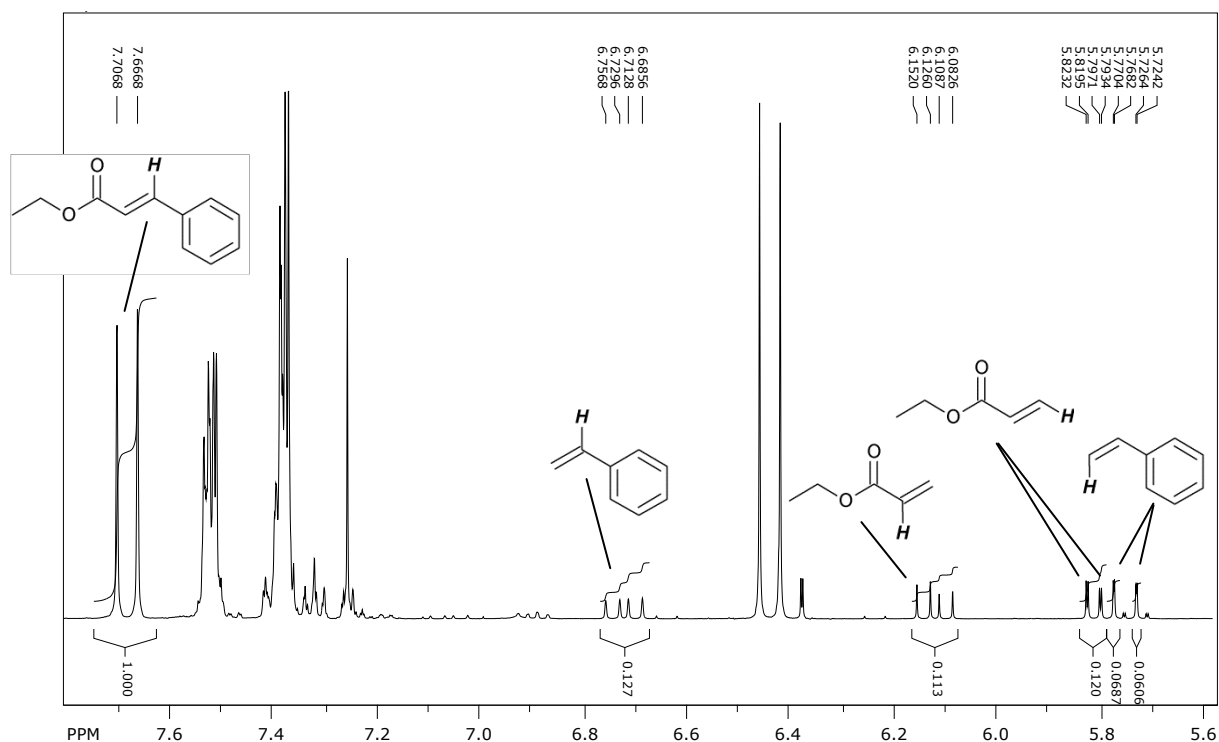


Fig. S15 Zoom of figure S14, showing unique peaks of ethyl cinnamate (**6**), styrene (**3**) and ethyl acrylate (**9**) used to determine conversions. In this example the conversion is 11%.

GCMS

The reaction mixture resulting from the ethenolysis has also been analysed by GCMS to prove formation of the products. However, ethyl acrylate (**9**) could not be separated from DCM on the GCMS column and could therefore not be observed by GCMS.

Styrene (**3**), GC (DCM): RT = 4.96 min; MS: m/z (%) = 105 ([M]⁺, 12), 104 (100), 103 (50), 102 (10), 78 (61), 77 (30), 63 (12), 52 (15), 51 (48), 50 (29)

References

1. T. Chen, J. Gao and M. Shi, *Tetrahedron*, 2006, **62**, 6289-6294.
2. S. Chandrasekhar, G. P. K. Reddy, Ch. Nagesh and Ch. R. Reddy, *Tetrahedron Lett.*, 2007, **48**, 1269-1271.