

From Plant to Plastic: Synthesis of Renewable Polyamide-15 Building Block

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Introduction

A valuable route to obtain nitrogen-containing molecules is via the cross-metathesis of acrylonitrile with olefins.¹ Recently, the cross-metathesis of fatty acid derivatives with acrylonitrile – which has become a sustainable raw material² – has been demonstrated.³ This cross-metathesis is a key reaction for the synthesis of linear amino acid derivatives, synthesized via hydrogenation of the intermediate α,ω -unsaturated cyano-acids or -esters. These linear amino acid derivatives can be used as renewable building blocks for the synthesis of polyamides.

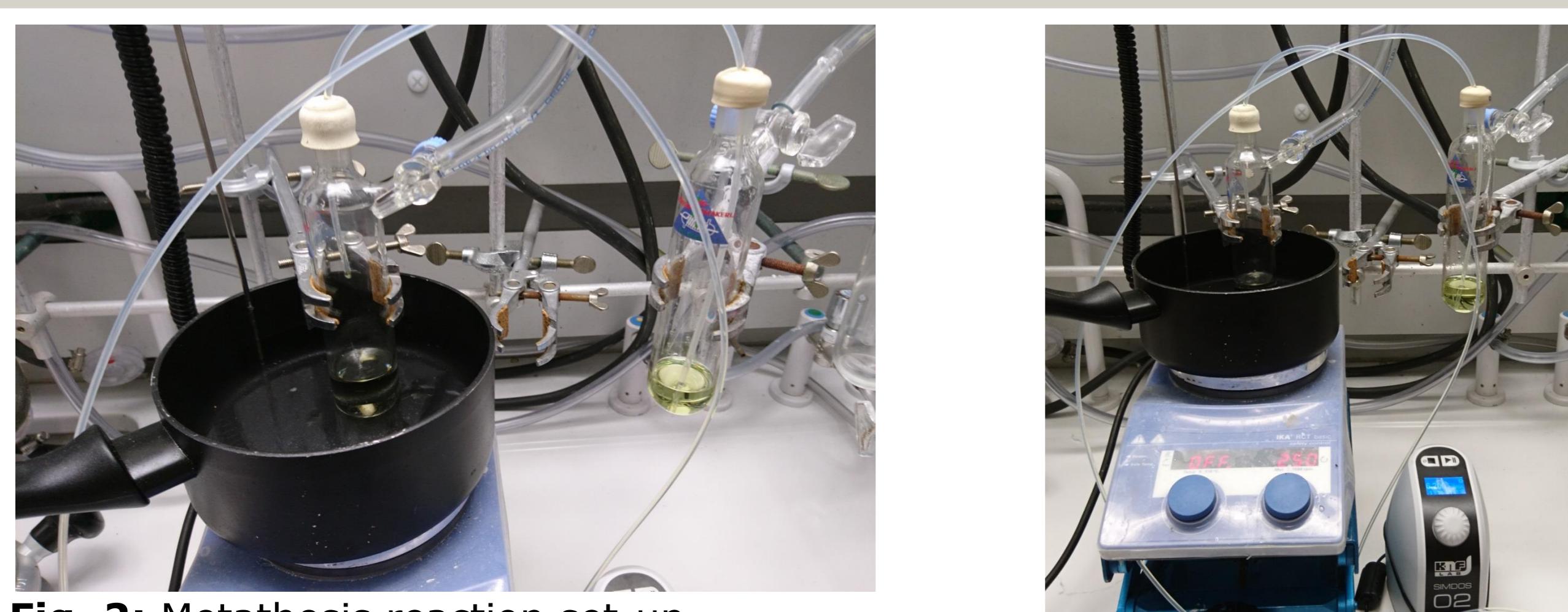


Fig. 2: Metathesis reaction set-up

Goal

The cross-metathesis of technical erucic acid, a fatty acid found in the *Crambe abyssinica*, and acrylonitrile was studied. Via this route, the C_{15} ω -amino acid methyl 15-aminopentadecanoate is accessible (fig. 1), which is a sustainable building block for polyamide-15.⁴

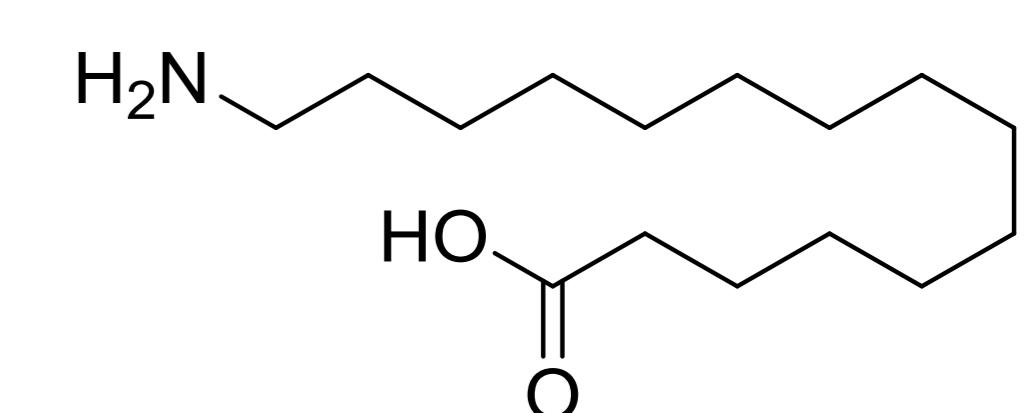
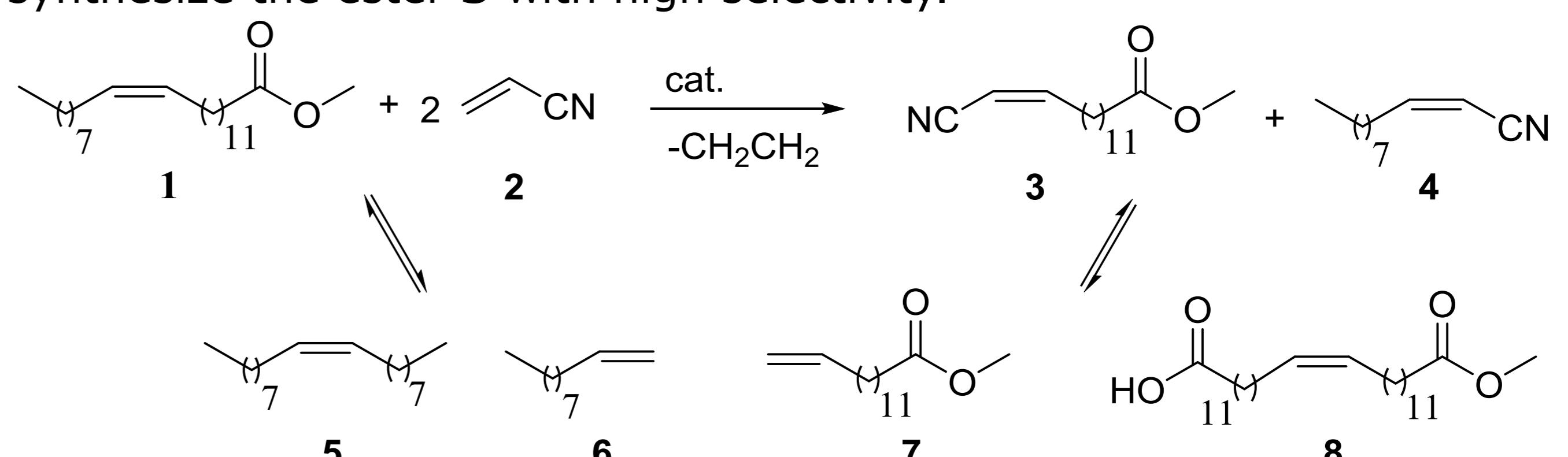


Fig. 1: 15-aminopentadecanoic acid

Different reaction conditions for the cross-metathesis of methyl erucate and acrylonitrile (Scheme 1) were explored. The main objective was to synthesize the ester **3** with high selectivity.



Scheme 1: Cross-metathesis of methyl erucate with acrylonitrile

Cross-metathesis

Table 1: Cross-metathesis of methyl erucate with acrylonitrile

Entry	1 (mmol)	ACN (eq.)	Catalyst (mol%)	Dosing time (min)	Conversion (%)	Yield ^a 3/7
1	0.8	2.1	1.0	30	>99	97.3/2.6
2	7.8	2.4 ^b	1.0	60	>99	94.1/5.5
3	15.9	2.5^b	1.0	90	>99	89.8 (83.3)/9.5
4	15.8	2.5 ^b	0.5	90	99.0	87.2/11.8
5	15.8	2	0.5	90	>99	84.0/15.1
6	15.8	2.1	0.5	30	>99	86.1/13.1

Reaction conditions: Toluene (0.05 M solution of substrate), Grubbs-Hoveyda 2nd generation catalyst, 100°C, 30 min additional stirring after catalyst addition; a) Calculated according to GC analysis; isolated yield in parentheses. b) Reaction started with 1 equivalent of acrylonitrile present, the remaining acrylonitrile was dosed by hand in 30 min.

Hydrogenation

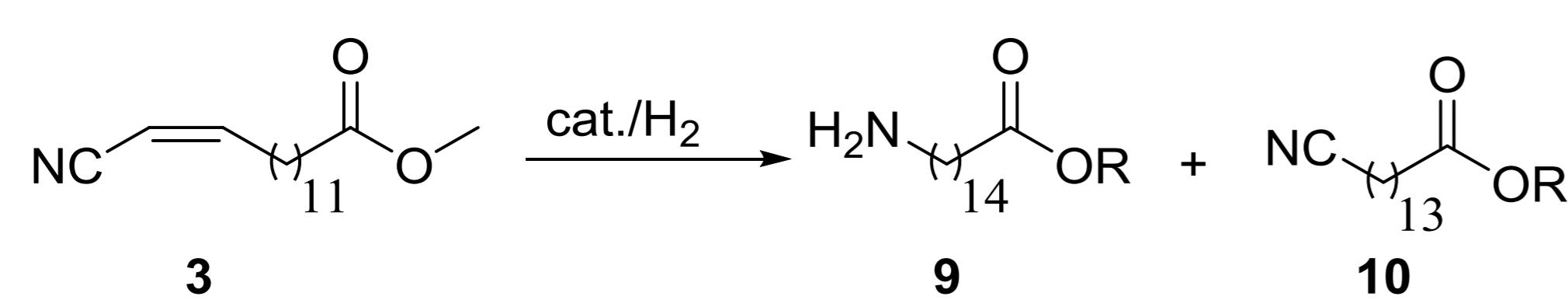


Fig. 4: Hydrogenation of α,ω -unsaturated cyano ester

Table 2: Hydrogenation of α,ω -unsaturated cyano ester

Entry	Catalyst (mol%)	H ₂ (bar)	Temperature (°C)	Time	Ratio 9/10 (%) ^a
1	Grubbs 2 nd (1)	20	80	24	39.0/61.0
2	Grubbs 2 nd (3)	20	80	24	97.9/2.1
3	Grubbs 2nd (1)	20	140	24	98.5/1.5
4	[RuCl ₂ (PPh ₃) ₃] (1)	50	80	24	4/96
5	[RuCl ₂ (PPh ₃) ₃] (3)	50	140	24	58.5/27.8
6 ^b	[Ru(cod)methylallyl] ₂ /DPPF (1.0)	50	140	24	38.8/61.2

Reaction conditions: toluene (20 mL), tBuOK (10-30 mol%), catalyst, H₂; a) Calculated according to GC analysis with the peak areas of **9** and **10**; b) 10 mol % NH₄Cl was added

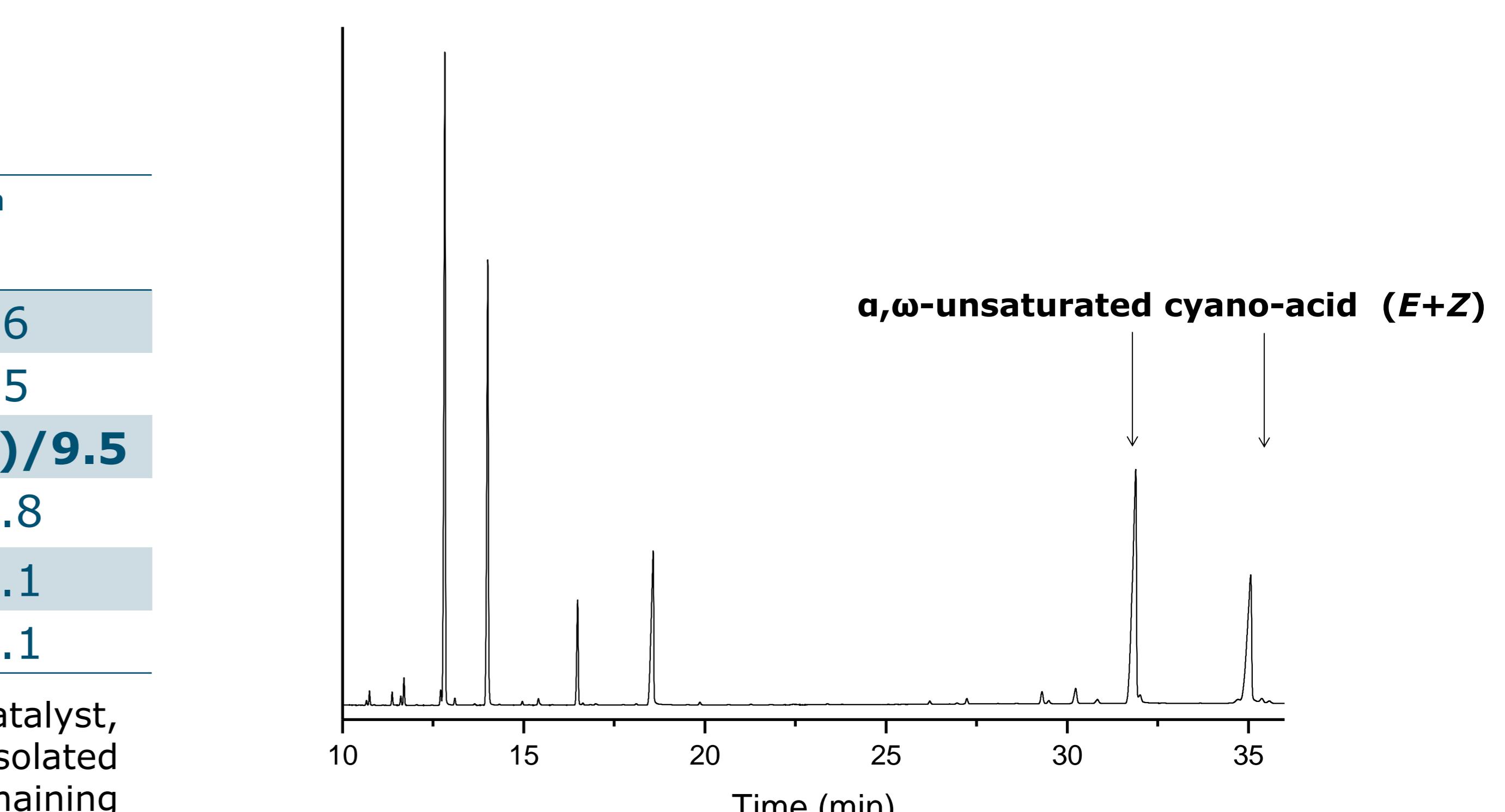


Fig. 3: Crude GC after cross-metathesis (table 1, entry 3)

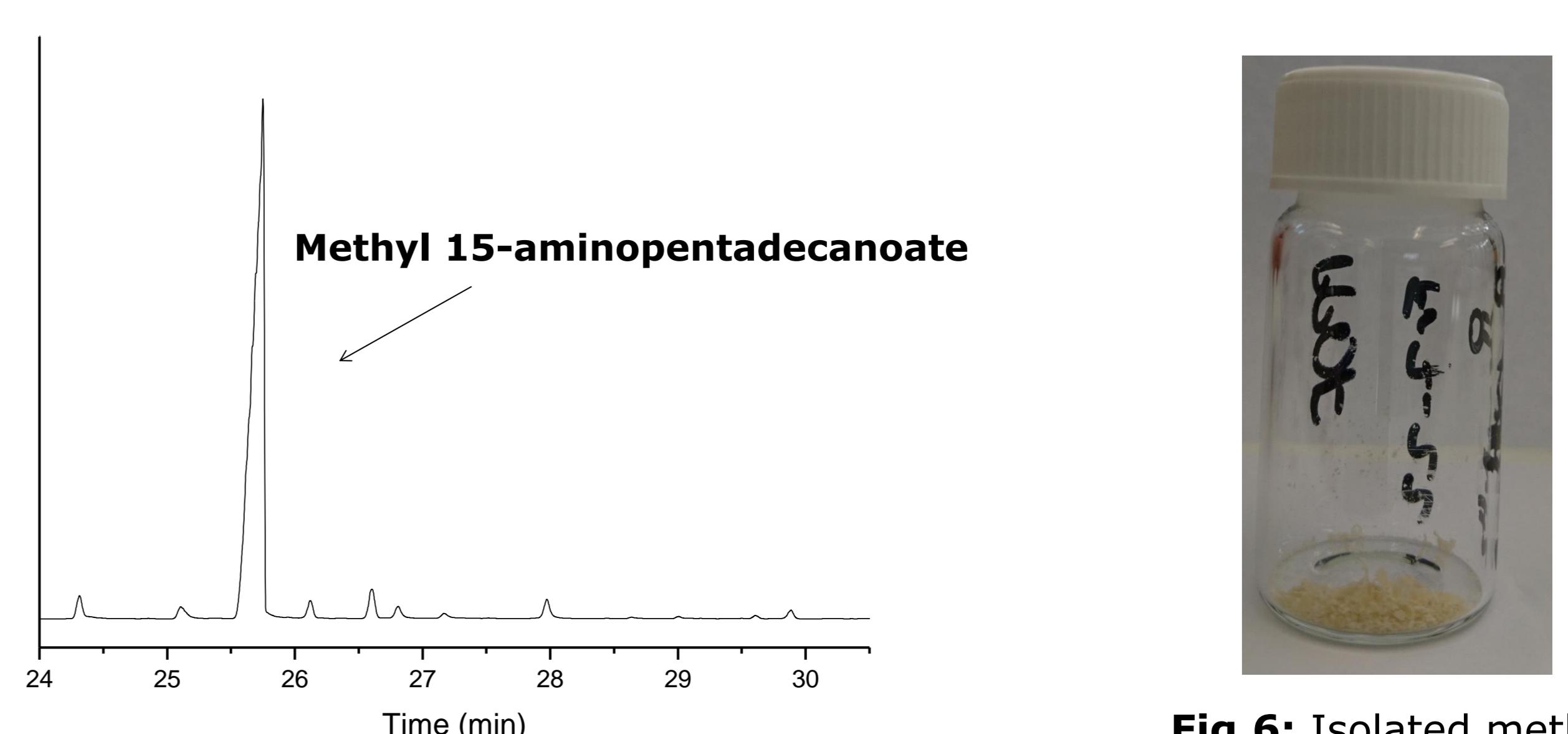


Fig. 5: Crude GC after hydrogenation (table 2, entry 3)

Conclusion

- Optimal conditions for metathesis reaction are in agreement with reported literature procedures
- Selectivity becomes lower upon upscaling
- Hydrogenation of α,ω -unsaturated cyano-acid can be performed using the Grubbs 2nd generation catalyst (1 mol%, 140°C, 24h)
- Methyl 15-aminopentadecanoate was successfully isolated

