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## ARTICLE

## Cross-metathesis approach to produce precursors of nylon 12 and nylon 13 from methyl oleate

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A two-step synthesis for producing methyl 12-aminododecanoate and 13-aminotridecanoate, the precursors of nylon 12 and nylon 13, from methyl oleate is described. First, methyl 11-cyano-9-undecenoate or 12-cyano-9-dodecenoate were prepared by cross metathesis of methyl oleate with either allyl cyanide or homoallyl cyanide, respectively. Subsequently, all the unsaturation of the two intermediates was hydrogenated to deliver the final products. This method represents the first synthesis of nylon 12 and 13 precursors from methyl oleate, an ester of an abundant and renewable natural fatty acid present in vegetable oil or microalgae. It also represents the shortest synthesis of nylon precursors from fatty acids.

### Introduction

Nylons are synthetic polyamides with extensive applications in modern society. In particular, nylon 11 and 12 possess excellent chemical properties and are widely used in automotive, medical, and electronic industries as well as for sport equipment, back panel for solar cells, and lenses for glasses. Nylon 13 is reported to have similar properties to nylon 12. These nylons are produced from amino acids or their derivatives with a corresponding number (11, 12 or 13) of carbon-chain backbone.<sup>1</sup>

Currently, the precursor of nylon 12 is manufactured from petroleum-derived butadiene in a six-step process.<sup>2</sup> However, there is an increasing interest in use of renewable sources for production of these amino acid precursors, because of concerns over environmental sustainability of petrochemical products.<sup>3</sup> As such, synthetic approaches that use natural fatty acids and esters from plant- or algae-derived feedstocks are especially attractive.<sup>4-6</sup> Among the natural fatty acids, oleic acid is the predominant component of lipids in a large variety of vegetable oils (e.g. soy or canola) as well as oleaginous microorganisms such as algae.<sup>7</sup>

The precursor of nylon 11 is manufactured from ricinoleic acid, a natural fatty acid available only in castor beans.<sup>2</sup> In this method, the acid is first converted to its methyl ester and then subjected to pyrolysis to produce 10-undecyleate, which is then converted to the nylon 11 precursor in two additional steps. Several other multi-step (>4 steps) approaches to produce nylon 11 precursors from either ricinoleic acid or oleic acid derivatives are reported in patents<sup>8-14</sup> and journals,<sup>15-22</sup> but have likely not been utilized for industrial process.

While there is one study on a concise three-step metathesis-based approach for producing nylon 11 from oleic acid,<sup>17</sup> the method has previously not been applied for producing nylons 12 or 13, likely due to challenges associated with selectivities (discussed in more detail in the Results section). The other reported methods to produce nylons 12 and 13 from non-petrochemical sources are lengthy, and also employ exotic fatty acids as starting materials. For example, there are several reported nylon 12 precursor syntheses that use

ricinoleic acid from castor beans as the feedstock and require 4–6 steps.<sup>15-16, 20-21, 23</sup> Synthesis of nylon 13 has not been fully studied except for one reported approach that involved several steps from either erucic or lesquerolic acid, another atypical acid available from rapeseed oil.<sup>24</sup>

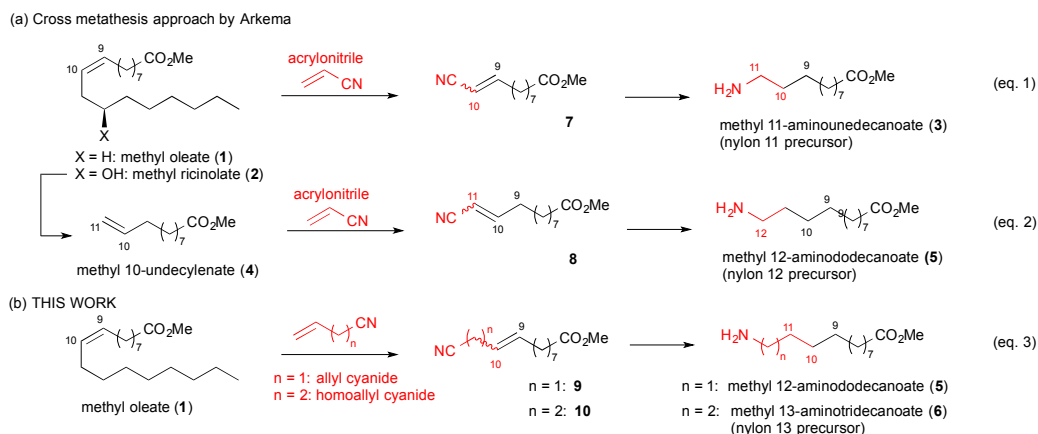
Herein, we report the successful application of cross metathesis to synthesize nylon 12 and 13 precursors from oleic acid. Our method provides a shorter and simpler route for production of both nylon 12 and nylon 13 from an abundant and inexpensive, and thus preferred starting material.

### Results and discussion

The previously reported cross metathesis approach to produce the nylon 11 precursor (Figure 1, (a)) involved reacting methyl oleate (**1**) or ricinoleate (**2**) with acrylonitrile.<sup>15, 17, 20</sup> The resulting 10-cyano-9-decenoate (**7**) was subjected to high-pressure hydrogenation to remove all unsaturation and deliver the nylon 11 precursor (**3**) (Figure 1, eq. 1). Nylon 12 precursor was also prepared in analogous fashion by cross metathesis with acrylonitrile and methyl 10-undecylenate (**4**) prepared from pyrolysis of **2** (Figure 1, eq. 2). In related approaches, methyl oleate (**1**) or ricinoleate (**2**) was first converted to their derivatives such as dimers or terminal alkenes before subjecting to metathesis – these routes showed improved throughput to the original approach, although lengthened the overall synthetic steps.<sup>15-16, 20-21</sup>

Since our intention was to find a direct pathway toward nylon 12 and 13 precursors from oleic acid, we attempted cross metathesis of methyl oleate with alkenylcyanides with longer chain length (Figure 1, eq. 3). In the first step, we subjected methyl oleate to cross metathesis with allyl or homoallyl cyanides with the intent of generating the corresponding cyano ester intermediates **9** and **10**. Subsequently, the double and triple bonds of these intermediates could be hydrogenated to deliver the nylon 12 and 13 precursors **5** and **6**, respectively. Our approach, although related to the reported nylon 11 synthesis,<sup>17</sup> behaved completely differently when their

reaction conditions were used.<sup>25</sup> In this report, we disclose our studies to overcome the issue, as well as eventual success in delivering the desired nylon precursors.



**Figure 1.** (a) Previously reported cross metathesis approach. (b) Our approach to nylon precursors from methyl oleate.

We began our investigation of the cross metathesis step using allyl cyanide and methyl 9-decenoate (**11**), a model substrate for methyl oleate (Table 1). Under the reported reaction conditions (entries 1–3), while the reaction conversion is good (>92%) at the temperature >95 °C, only 25–30% (by GC area) of the desired product was seen. The complex mixture of other products comprises unsaturated cyano esters with various alkyl chain lengths, with molecular weight varying by 14, which led us to speculate that they arose from olefin isomerization. Other major side-products of the reaction were series of dimers with structures yet to be determined.

In order to suppress the undesired isomerization, the reaction was examined with several additives.<sup>22, 26</sup> We found that addition of 1,4-benzoquinone nearly completely suppressed the side reaction in our system (Table 1, entries 4). In order to fully suppress the isomerization, 50 mol% of the additive was required (entries 12 vs 14).

Subsequently, the other reaction parameters were screened to suppress dimerization and to further improve the reaction conversion. The reaction conversion was good at temperature >95 °C; however, the best product profile was observed at 110 °C (entries 5 vs 7). The conversion was further improved by a continuous injection of the ruthenium catalyst over 1–2 h period (entries 5 vs 8). The reactant concentration ~0.033 M was found to provide the best selectivity for the desired reaction (entries 11, 13 and 14). The preferred molar ratio of allyl cyanide was found to be five equivalents (entries 2 vs 3, 10 vs 12). Use of cross metathesis for oleochemical production from fatty acids has been a subject of several reviews.<sup>19, 22, 27</sup> Consistent with other reports, Hoveyda-Grubbs second generation catalyst showed better conversion than Grubbs catalyst (entries 5 and 9) for our system. At least 2 mol% of this catalyst was required to achieve full conversion under the reaction conditions shown (entries 4 vs 5).

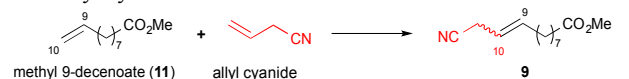
**Table 1 :** Cross-metathesis of Methyl 9-decenoate with allyl cyanide<sup>[a]</sup>

Entry	Additive <sup>[h]</sup> (mol%)	Catalyst (mol%)	Temperature (°C)	Time (h)	Conversion (%)	GC area%	
						9	dimers
1	/	1	80	17	6.9	6.1	0
2 <sup>[b]</sup>	/	1	95	21	94.7	25.5	35.8
3	/	1	95	8	92.2*	28.2	21.7
4	BQ (10)	1	95	5	78.7*	52.0	7.8
5	BQ (10)	2	95	4	92.2	49.2	17.0
6	AA (10)	2	95	6	48.1	20.7	4.5
7	BQ (10)	2	110	6	84.4	56.4	9.0
8 <sup>[c]</sup>	BQ (10)	2	95	6	42.7	23.5	7.8
9 <sup>[e]</sup>	BQ (10)	2	95	6	49.1	27.8	3.3
10 <sup>[b]</sup>	BQ (10)	2	110	4	93.8	44.2	11.1
11 <sup>[d]</sup>	BQ (10)	2	95	6	64.6	39.2	11.0
12 <sup>[e]</sup>	BQ (10)	2	110	6	37.7	16.9	4.0
13 <sup>[f]</sup>	BQ (50)	2	110	4	84.7	42.2	3.0
14	BQ (50)	2	110	4	78.8	58.3	5.5

[a] Reaction conditions: To a flask containing methyl 9-decenoate (0.1 mmol), allyl cyanide (0.5 mmol), and toluene (2 mL) was added Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (1–2 mol%) in toluene (1 mL) dropwise over 1h. [b] 2 equiv. of allyl cyanide was used. [c] The catalyst added in one portion. [d] 0.5mL of solvent was used for catalyst delivery; no other solvent was used. [e] 10 equiv. of allyl cyanide was used. [f] 12 mL (11mL + 1mL) of solvent for the whole reaction was used instead of 3 mL (2 mL + 1 mL). [g] Grubbs 2<sup>nd</sup> generation catalyst was used. [h] BB: Benzoquinone; AA: Acetic acid. \* Approximate values.

It is known that solvent selection significantly influences conversion and selectivity in metathesis reactions. In particular, halogenated solvents are considered to be superior.<sup>28</sup> In our system, solvents with lower boiling point were not suitable (Table 2, entry 2) and fluorinated solvents increased the dimer formation (entries 3 and 5). However, use of chlorobenzene provided good reaction conversion and better selectivity than other solvents (entries 4 and 6).

**Table 2 :** Solvent screening on cross metathesis of 9-decenoate with allyl cyanide<sup>[a]</sup>



Entry	Solvent	Time (h)	Conv. (%)	GC area%	
				9	dimers
1	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	4	78.8	58.3	5.5
2 <sup>[b]</sup>	(CH <sub>2</sub> Cl) <sub>2</sub>	8	41.2	17.8	11.6
3	C <sub>6</sub> F <sub>5</sub> Cl	2	95.3	60.1	20.6
4	C <sub>6</sub> H <sub>5</sub> Cl	2	90.3	62.6	13.8
5	C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub>	5	77.2	18.6	46.0
6 <sup>[c]</sup>	C <sub>6</sub> H <sub>5</sub> Cl	3	93.5	71.2 (58) <sup>[d]</sup>	4.1

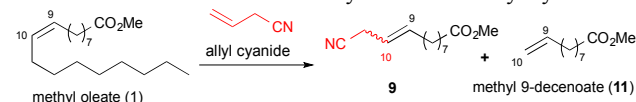
[a] Reaction condition: To the flask containing methyl oleate (0.1 mmol), allyl cyanide (0.5 mmol), 1,4-benzoquinone (0.05 mmol), in chlorobenzene (2 mL) was added Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (2 mol%) in chlorobenzene (1 mL) was added drop wise at 110 °C. [b] Reaction temperature: 80 °C. [c] 4.5 mol% of the catalyst was used. [d] Isolated yield.

Subsequently, these optimized cross metathesis conditions for methyl 9-decenoate (**11**) were applied to methyl oleate (**1**) (Table 3). It was observed that dimerization was suppressed with this substrate likely due to its lower reactivity. Use of **1** instead of **11** made the product analysis more complex, because of formation of non-volatile by-products, including methyl 9-decenoate (**11**).

We have examined several reaction parameters in the attempt to optimize the reaction. We first examined use of lower temperature (95 °C) with hope to lower the catalyst deactivation and increase the selectivity. However, the lower temperature reactions resulted in increased formation of **11** and dimers (entry 2). To suppress the catalyst decomposition, the catalyst addition time was further extended. This attempt was partially successful and extending the time to 3h improved the conversion as well as the selectivity for **9** (entries 3–4). Attempt to drive **11** to desired **9** with use of excess of cyanide led to low reaction conversion, possibly due to catalyst

poisoning (entry 5). Increasing the catalyst loading up to 4.5 mol% only provided similar reaction profiles (entry 6–7). To date, we concluded that the current best reaction conditions for this conversion to be the one used in entry 3 or 4. This procedure reliably provides the desired **8** in ~55% yield while suppressing olefin isomerization and dimer formation (<10 %).

**Table 3:** Cross-metathesis of methyl oleate with allyl cyanide<sup>[a]</sup>

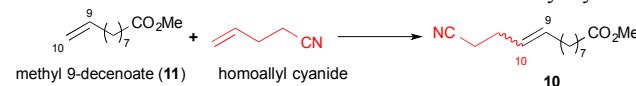


Entry	Time (h)	Time (h) <sup>[b]</sup>	Conv. (%)	GC area%		
				9	dimers	11
1	3	1	78.5	46.5	3.9	14.5
2 <sup>[c]</sup>	3	1	70.2	34.4	4.0	14.9
3	4	2	85.3	49.0	5.6	9.3
4	4	3	87.0	55.3 (55) <sup>[h]</sup>	7.5	9.2
5 <sup>[d]</sup>	4	2	38.5	16.0	0.0	9.8
6 <sup>[e]</sup>	3	2	86.3	37.5 (56) <sup>[g]</sup>	7.1	7.0
7 <sup>[f]</sup>	4	2	96.3	47.1	4.1	11.7

[a] Reaction conditions: To the flask containing methyl oleate (0.1 mmol), allyl cyanide (0.5 mmol), 1,4-benzoquinone (0.05 mmol), in chlorobenzene (2 mL) was added Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (2 mol%) in chlorobenzene (1 mL) added dropwise at 110 °C. [b] Catalyst addition time. [c] Reaction temperature: 95 °C. [d] 10 equiv. of allyl cyanide was used. [e] 4.5 mol% of catalyst was used. [f] 3 mol% of catalyst was used. [g] GC yield (quantified). [h] Isolated yield.

Cross-coupling with homoallyl cyanide was also investigated using both 9-decenoic acid (Table 4) and methyl oleate (Table 5). Some reaction tuning was required in order to achieve a good conversion with this coupling partner. In particular, we found that the reaction conversion was sensitive to equivalency of homoallyl cyanide. Under the optimal conditions used for allyl cyanide metathesis, the reaction conversion was as low as 4–5 % (Table 4, entries 5–6) or 23% if using methyl oleate (**1**) (Table 5, entry 6). We suspected that this behaviour may relate to the faster dimerization of homoallyl cyanide. In any event, lowering the homoallyl cyanide equivalency to 1–2 equiv. resulted in good reaction conversion and selectivity with both substrates (Table 4, entry 2; table 5, entry 4). Thus, both methyl 9-decenoate (**11**) and methyl oleate (**1**) effectively underwent cross-metathesis reaction with non-conjugated nitriles. We were able to obtain the desired product at a comparable isolated yield of 43% from this reaction.

**Table 4:** Cross-metathesis of 9-decenoate with homoallyl cyanide

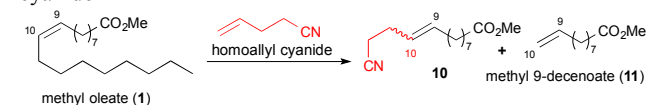


Entry	Time	cyanide	Conv.	GC area %
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	(h)	(mmol)	(%)	<b>10</b>	dimers
1	6	0.1	82.2	43.8	31.8
2	6	0.15	83.5	51.2	27.6
3	4	0.15	78.0	48.1	25.0
4	6	0.25	78.9	48.9	24.1
5	6	0.25	56.3	38.5	15.9
6	4	0.5	4.7	4.0	0.0
7	6	0.5	4.2	4.2	0.6

[a] Reaction condition: 0.1 mmol of methyl oleate, 50 mol% 1,4-Benzoquinone, 2 mol% of Hoveyda-Grubbs 2<sup>nd</sup> generation in chlorobenzene (1 mL) added dropwise into 1.5mL of chlorobenzene at 110 °C.

**Table 5:** Cross-metathesis of methyl oleate with homoallyl cyanide<sup>[a]</sup>



Entry	Time (h)	cyanide (mmol)	Conv. (%)	GC area %		
				<b>10</b>	Dimer	<b>11</b>
1	6	0.15	68.6	31.5	15.3	7.8
2	6	0.25	78.8	42.9	10.9	10.1
3	8	0.25	74.4	34.5	12.6	9.9
4	4	0.25	88.7	52.3 (42.9) <sup>[b]</sup>	8.7	16.2
5	6	0.3	77.6	38.0	7.5	16.8
6	6	0.5	23.3	0.4	6.6	11.7

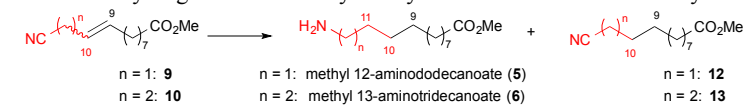
[a] Reaction condition: 0.1 mmol of methyl oleate, 50 mol% 1,4-Benzoquinone, 2 mol% of Hoveyda-Grubbs 2<sup>nd</sup> generation in chlorobenzene (1 mL) added dropwise into 1.5mL of chlorobenzene at 110 °C. [b] Isolated yield.

In the second step, although hydrogenation of olefins is an established reaction that many catalysts are available, the reduction of nitriles to amines conventionally uses stoichiometric

strong hydride reducing agents such as lithium aluminium hydride or borane, or hydrosilylation with Lewis acids such as titanium isopropoxide. Alternately, strong heterogeneous catalysts such as Raney nickel or cobalt can be used to catalyze addition of molecular hydrogen, but reaction conditions are harsh and only moderate selectivity is afforded. Studies on hydrogenation of nitriles with homogenous catalysts have been limited although catalysts based on rhodium, iridium, rhenium, and ruthenium have recently been investigated.<sup>29</sup> Most recent studies used ruthenium complexes, which by far gave the best selectivity under mild reaction conditions. Many studied catalytic systems use phosphine ligands as well as potassium *tert*-butoxide additive. Typical reactions conditions are 80–140 °C at H<sub>2</sub> pressure of 14–75 bars. It was also shown that milder reaction conditions could be used when the phosphine ligands of the metal complex are replaced with carbene ligands. Finally, the metathesis catalyst has also been shown to facilitate the hydrogenation reaction, and that it is possible to use residual catalyst from metathesis for hydrogenation.<sup>20-21</sup>

The previous studies for hydrogenation of fatty acid derivatives indicated that either the Grubbs or Hoveyda-Grubbs second generation catalyst would be effective.<sup>20-21</sup> However, only Grubbs second generation catalyst provided the desired product in our experiments. Using this catalyst, we found that toluene, benzene, or chlorobenzene solvents were all suitable and the reaction temperature of 80 °C provided the best overall conversion. Thus these reaction conditions were adopted for the subsequent studies (Table 6). The base additive is essential in this catalyst system, and 30 mol% of potassium *tert*-butoxide was sufficient to ensure the full reaction conversion (entries 1–2 vs 3–11). The catalyst loading of >2 mol% was found essential for good conversion (entries 3–5; 8–10). The reaction mixture was kept for 17–44 h under hydrogen pressure in between 20–25 bar. These reaction conditions consistently provided >50% (by GC area) of the desired methyl 12-aminododecanoate (**5**) (entries 4, 6). The same reaction conditions, when used to hydrogenate C13 cyano ester (**10**), resulted in comparable yields (entry 6,7 vs 9,10). These products were readily isolated and purified by column chromatography to yield 62% and 53% of the nylon 12 and nylon 13 precursors.

**Table 6 :** Hydrogenation of methyl 11-cyanoundec-9-enoate and 12-cyanododec-9-enoate<sup>[a]</sup>



Entry	n	Cat. (mol %)	<i>t</i> -BuOK (mol %)	Pressure (Bar)	Time (h)	GC area (%)		
						<b>5 or 6</b>	<b>12 or 13</b>	By products
1	1	1	15	20	20	1.4	71.6	15.4
2	1	3	15	25	20 <sup>[b]</sup>	6.8	55.6	29.6
3	1	1	30	20	17	10.4	83.0	1.6
4	1	2	30	20	17	78.3	10.6	6.2
5	1	3	30	20	17	68.5	2.3	17.4
6	1	3	30	25	20 <sup>[b]</sup>	56.8	4.1	27.0
7	1	3	30	24	44	68.6 (62) <sup>[c]</sup>	2.6	16.2
8	2	1	30	20	19	41.0 (53) <sup>[c]</sup>	30.3	16.9
9	2	2	30	20	19	58.2	2.9	30.0



10	2	3	30	20	19 <sup>[d]</sup>	43.3	2.1	42.2
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[a] Reaction condition: 20 mg of methyl 11-cyano-9-undecenoate, 30 mol% of t-BuOK, 3 mol% of Grubbs 2<sup>nd</sup> generation catalyst, 3mL of chlorobenzene at 80 °C, 30 bars during 20 h with stirring. [b] Isolated yield. [c] Extending the reaction period for additional 45 h under otherwise same conditions did not improve the product profile.

## Conclusion

We have demonstrated synthesis of nylon 12 and nylon 13 precursors from methyl oleate via cross metathesis reactions with allyl and homoallyl cyanides, respectively. Our work represents the shortest synthetic route to these precursors from the abundantly available oleic acid. The key feature of our approach includes use of 1,4-benzoquinone as additive, which completely suppressed the undesired isomerization side reaction during the metathesis step. Our approach not only enables preparation of nylon 12 and 13 precursors directly from methyl oleate, but also offers new pathways to access precursors of other nylons of different chain-length, economically and sustainably.

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## Notes and references

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## Cross-metathesis approach to produce precursors of nylon 12 and nylon 13 from methyl oleate

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A two-step synthesis for producing nylon 12 and 13 precursors from methyl oleate is described. This method represents the first and shortest synthesis to directly access these precursors from methyl oleate, an ester of an abundant and renewable natural fatty acid present in vegetable oil or microalgae.

