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Cross metathesis of bio-sourced fatty nitriles with acrylonitrile

Johan Bidange • Cédric Fischmeister • Christian Bruneau • Jean-Luc Dubois • Jean-Luc Couturier

Dedication

Dedicated to Franz Stelzer for his important contribution to polymer science.

Abstract We report the cross metathesis of two olefinic partners containing different types of nitrile functionality. Thus, cross metathesis of fatty nitriles with acrylonitrile have been achieved with olefin metathesis ruthenium catalysts. 10-Undecenitrile provides 2-dodecenedinitrile with a high turnover number of 13280 in the green solvent diethyl carbonate. Cross metathesis with the internal carbon-carbon double bond of oleonitrile gave the expected products and the cleavage of the internal double bond proved to be more difficult probably owing to faster catalyst decomposition.

Keywords Homogeneous catalysis • Ruthenium catalysis • α,ω -dinitriles • Renewables • Green chemistry

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Introduction

In the context of sustainable chemistry, the use of renewable and bio-sourced carbon feedstocks has a strong potential to complement and replace petrochemical resources [1-3]. Among natural resources, fats and oils derived from triglycerides have found a place of choice for the access to biofuels [4, 5], polymers, [6-9] and fine chemicals [10-12]. Taking advantage of the reactivity of carbon-carbon double bonds, olefin cross metathesis is especially appropriate to shorten carbon chains by cleavage of unsaturations by ethenolysis [13-18], and to introduce functional groups at the terminal or internal position of unsaturated of fatty acid derivatives. Introduction of ester groups to produce diesters, precursors of polyesters, has been achieved by cross metathesis with acrylates [19-21]. Acrolein has also been used as cross metathesis partner to introduce a reactive aldehyde that can be easily transformed into a fatty alcohol or an amine derivative [22-24]. Functional allylic partners such as allylic halide [25-26] or acetate [27-28] have also been used to introduce a reactive allylic functionality at the end of

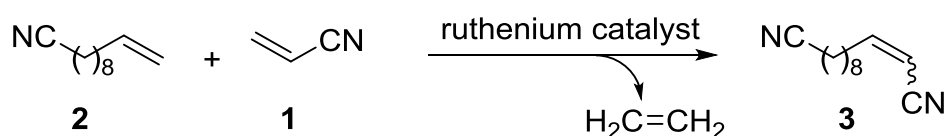
a fatty carbon chain. Another important cross metathesis partner that allows further transformation into amines is acrylonitrile [29]. It has been considered for a long time as a reluctant substrate for cross metathesis and has been applied for fats and oils transformations only when ruthenium catalysts bearing a chelating benzylidene carbene ligand appeared [30, 31]. Thus undec-10-enoic acid and methyl ester [32], undecyl-10-enic aldehyde [22] bearing a terminal double bond, and methyl oleate [32, 33] octadec-9-enoic diacid and diester [32] as internal olefins reacted efficiently with acrylonitrile in the presence of the second generation Hoveyda catalyst giving access to α,ω -bifunctional products. To our knowledge, cross metathesis of 10-undecenitrile with methyl acrylate represents a scarce example of metathesis involving an unsaturated bio-sourced fatty nitrile with an electron deficient olefin [34]. We now show that cross metathesis of 10-undecenitrile and oleonitrile with acrylonitrile can be achieved with Hoveyda type catalysts to give α,ω -dinitriles, precursors of diamine monomers for polyamide preparation, and mononitriles that can be hydrogenated into fatty amines.

Results and Discussion

Cross metathesis of 10-undecenitrile with acrylonitrile

10-Undecenitrile is a bio-sourced product arising from castor oil. Thermal cleavage of methyl ricinoleate produces methyl 10-undecenoate [35]. Hydrolysis into the corresponding acid followed by ammoxidation provides 10-undecenitrile [36].

The cross metathesis of the terminal olefin 10-undecenitrile **2** with acrylonitrile **1** was first investigated (Scheme 1). This reaction produced the unsaturated 2-dodecenedinitrile **3** together with ethylene.



Scheme 1 Cross metathesis of undecenitrile with acrylonitrile

Based on our knowledge on cross metathesis of fatty acid derivatives with acrylonitrile, the second generation Hoveyda catalyst **I** was selected to investigate the possibility of achieving this transformation. (Table 1). In toluene as solvent, using 0.5-1 mol% of catalyst and 2 equivalents of acrylonitrile, the cross metathesis reaction took place efficiently in short reaction time when the temperature was higher than 80 °C. The reaction was selective as the expected stereoisomers of **3** were formed as major products with only trace amounts of undesired products, which were probably

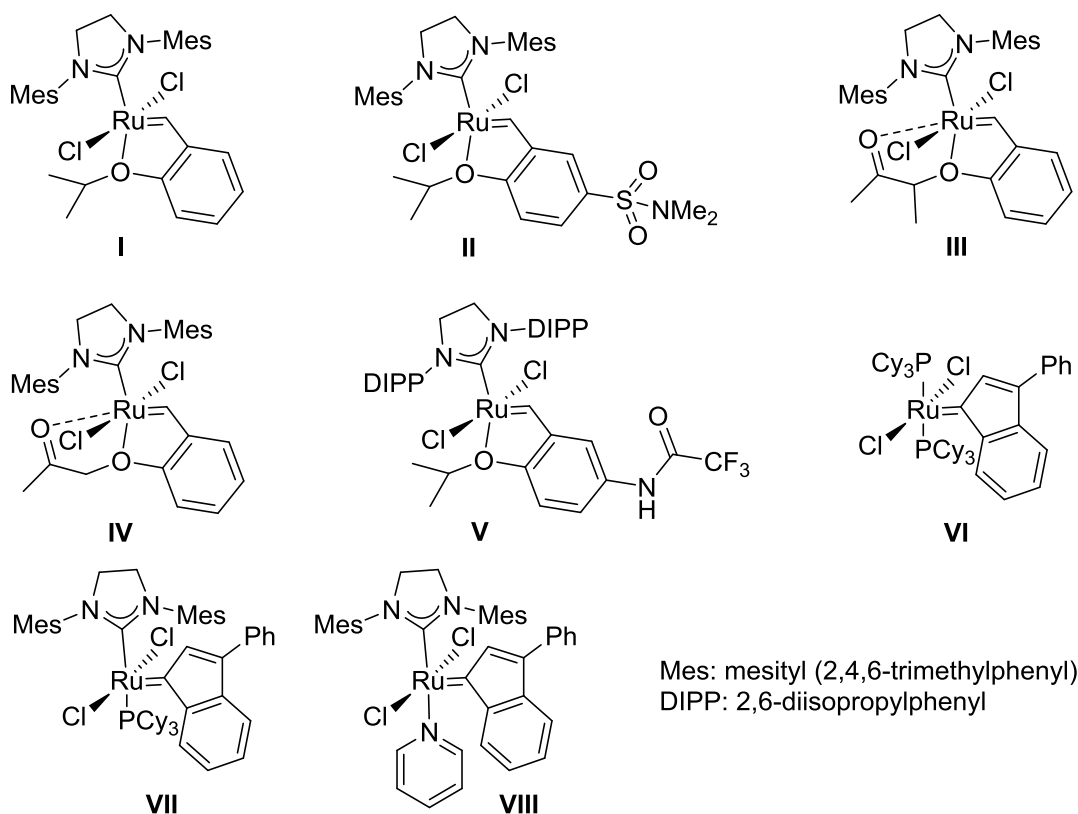
resulting from cross metathesis of acrylonitrile with 9-undecenenitrile resulting from double bond migration. In particular, no C20 unsaturated dinitrile (9-eicosenedinitrile) resulting from self-metathesis of **2** was detected, and self-metathesis of acrylonitrile is not expected to occur as it has been shown to be a difficult reaction [37] and only a low reactivity producing but-2-enedinitrile at high catalyst loading (2-10 mol%) was reported with a third generation ruthenium(NHC)(benzylidene)(bis-(pyridine)) catalyst (NHC= (bis-(2,6-xylyl)imidazolidinylidene) [38]. As always observed with acrylonitrile as cross metathesis partner, the (*Z*)-dinitrile **3** was obtained as the major stereoisomer in variable ratios (from 4.2 to 7.2), and the efficiency of the reaction was improved in diluted conditions (Table 1, entries 2 and 3). The negative effect of high concentration of nitrile substrates has already been pointed out with ruthenium catalysts and also very early with rhenium catalysts [39] and was attributed to catalyst poisoning by the nitrile functionality. Increasing the reaction temperature from 80 to 120 °C allowed achieving higher conversions from 88 to 97% (entries 3, 4, 5).

Table 1 Cross-metathesis of 10-undecenitrile and acrylonitrile with catalyst **I**^a

entry	catalyst loading (mol%)	[2] (mol/L)	temp. (°C)	reaction time (h)	conv. (%)	yield of 3 (mol%) (Z/E) ratio
1	1	0.1	80	3	78	75 (4.8)
2	0.5	0.1	80	3	66	65 (7.2)
3	0.5	0.05	80	3	88	87 (4.2)
4	0.5	0.05	100	4	89	88 (5.1)
5	0.5	0.05	120	5	97	96 (5.5)

^aReaction conditions: 10-undecenitrile **2** (0.5 mmol), acrylonitrile **1** (1 mmol), toluene (5 cm³ or 10 cm³), catalyst **I** (0.005 or 0.0025 mmol), conversion of **2** and yield of **3** determined by GC using dodecane as internal standard.

Then other ruthenium catalysts were tested with the objective of reaching high turnover numbers (TON) (Scheme 2).

**Scheme 2** Selected ruthenium catalysts

Hoveyda type catalysts, which have shown their efficiency in cross metathesis with acrylonitrile, and ruthenium indenylidene complexes that are known for their robustness and efficiency in cross metathesis were selected. The best conditions obtained with **I** in the initial screening, e. g. 0.5 mol% of catalyst in toluene at 120 °C for 5 h with a substrate **2** concentration of 0.05 M, were applied. As depicted in Table 2, the first generation ruthenium indenylidene catalyst **VI** was not reactive and the corresponding second generation catalyst **VII** exhibited poor reactivity. Complex **VIII** showed interesting catalytic activity (entry 7) but the best catalysts were obviously in the series of chelating benzylidene ruthenium complexes (entries 1, 2, 3, 4) leading to TONs of about 180-190. We have already shown that organic dialkyl carbonates were green solvents of choice for olefin metathesis, and again it appeared that the use of diethyl carbonate as solvent with high boiling point (126-128 °C) led to very similar results (entries 1 and 8). Under these conditions of high catalyst loading, it was difficult to select a more active catalyst among **I**, **II**, **III** and **IV**.

Table 2 Cross-metathesis of 10-undecenenitrile **2** and acrylonitrile **1**: screening of ruthenium catalysts^a

entry	catalyst	conversion (%)	yield (%)	(Z:E) ratio	TON
1	I	97	84	3.0	188
2	II	93	82	2.3	186
3	III	91	80	2.5	182
4	IV	91	81	2.5	182
5	VI	0	-	-	-
6	VII	13	-	3.5	26
7	VIII	83	73	2.4	166
8 ^b	I	91	-	2.8	182

^aReaction conditions: 10-undecenenitrile **2** (0.5 mmol), acrylonitrile **1** (1 mmol), toluene (10 cm³), catalyst **I** (0.0025 mmol, 0.5 mol%), 120 °C, 5 h, conversion of **2** determined with dodecane as internal standard. Isolated yields. TON: conversion/catalyst loading.

^bsolvent : DEC

In previous works on cross metathesis of acrylonitrile with fatty acid esters, we have shown a very positive effect on the TONs of the slow addition of the catalyst. This effect was attributed to short lifetime of the catalyst due to fast decomposition at high catalyst concentration. Therefore, the slow addition of a catalyst solution to the reaction mixture was explored by syringe-pump addition over a period of 2.7 h followed by 2.3 h reaction time (Table 3). In order to significantly increase the TONs of the reaction, catalysts **I**, **II**, **III**, **IV** and **VIII** were chosen to perform the cross metathesis of **1** and **2** under these conditions with decreasing catalyst loadings at 100 and 120 °C. First, only the catalyst was added dropwise with a syringe pump (entries 1-5), and then the catalyst and 1 equivalent excess of acrylonitrile were added simultaneously *via* two syringes pumps in order to decrease the duration of their detrimental interaction at high temperature in the reaction mixture.

Table 3 Cross-metathesis of 10-undecenenitrile **2** and acrylonitrile **1**: slow addition of catalyst and acrylonitrile^a

entry	catalyst (mol%)	solvent	temp. (°C)	conv. (%)	yield (%)	(Z:E) ratio	TON
1	I (0.05)	toluene	100	89	80	2.7	1780
2	II (0.05)	toluene	100	92	83	3.6	1840
3	III (0.05)	toluene	100	92	75	3.4	1840
4	IV (0.05)	toluene	100	85	76	3.2	1700
5	VIII (0.05)	toluene	100	87	82	3.8	1740
6	I (0.0125) ^b	toluene	100	67	59	2.0	5360
7	II (0.0125) ^b	toluene	100	76	66	2.0	6080
8	III (0.0125) ^b	toluene	100	74	63	2.2	5920
9	IV (0.0125) ^b	toluene	100	62	53	2.6	4960
10	VIII (0.0125) ^b	toluene	100	51	43	3.0	4080
11	I (0.0125) ^b	DEC	120	84	80	3.4	6720
12	II (0.0125) ^b	DEC	120	93	90	2.9	7440
13	III (0.0125) ^b	DEC	120	91	87	3.1	7280
14	IV (0.0125) ^b	DEC	120	87	84	3.2	6960
15	VIII (0.0125) ^b	DEC	120	60	53	3.5	4800
16	I (0.00625) ^b	DEC	120	76	70	3.4	12160
17	II (0.00625) ^b	DEC	120	80	76	3.4	12800
18	III (0.00625) ^b	DEC	120	76	73	3.4	12160
19	IV (0.00625) ^b	DEC	120	68	64	3.5	10880
20	V (0.00625) ^b	DEC	120	83	78	3.2	13280
21	I (0.00625) ^b	<i>p</i> -xylene	120	59	52	3.1	8320

^a Reaction conditions: 10-undecenenitrile **2** (0.5 mmol), acrylonitrile **1** (1 mmol), solvent (8 cm³), conversion of **2** determined with dodecane as internal standard. Isolated yields. Injection of a catalyst solution (2 cm³ added within 2.7 h) then 2.3 h prolonged heating. TON: conversion/catalyst loading

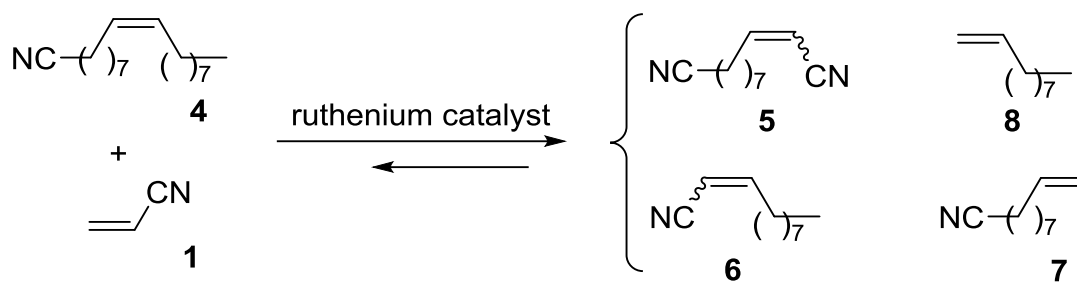
^b Initial introduction of 1 equiv. of acrylonitrile **1** (0.5 mmol) and injection of the catalyst + 1 equiv. of acrylonitrile (2 cm³ added within 2.7 h) then 2.3 h prolonged heating.

With this technique, at 100 °C in toluene, the conversions were satisfactory and TONs could be increased to 6000 with catalysts **II** and **III** (entries 7, 8). However, it became apparent that when the catalyst loading decreased the activities of catalysts **I**, **IV** and **VIII** were lower than those of **II** and **III**. The decrease of conversion induced by lower catalyst loading could be compensated by increasing the reaction temperature. Owing to its higher

boiling point, diethyl carbonate was preferable to toluene for using the slow addition of catalyst procedure. The higher catalytic efficiency of **II** was confirmed under low catalyst loading (0.00625 mol%) and a TON of 12800 was reached (entry 17). Catalyst **V** featuring a DIPP-NHC ligand and an isopropoxybenzylidene ligand, was also very efficient (entry 20). It can be noted that the most efficient catalysts **II** and **V** are equipped with isopropoxybenzylidene ligands, which are known to favour fast initiation of the metathesis process. The smaller differences between conversions and isolated yields observed in DEC (entries 11-20) as compared to toluene (entries 1-19) showed that the reaction was cleaner in diethyl carbonate. In addition the beneficial impact of this solvent is also illustrated by the much lower conversion observed in *p*-xylene at 0.00625 mol% catalyst loading with catalyst **I**, which gave only 59% conversion of **2** (entries 16 and 21).

Cross metathesis of oleonitrile with acrylonitrile

Oleonitrile is a fatty nitrile that is prepared by ammoniation of oleic acid. Ethenolysis of oleonitrile has been recently reported and the difficulty to reach high turnover numbers with the crude material has been pointed out [40]. Cross metathesis of oleonitrile **4** with acrylonitrile **1** can potentially produce the four main products **5-8** depending on the relative efficiencies of the primary and secondary metathesis transformations (Scheme 3).



Scheme 3 Cross metathesis of oleonitrile with acrylonitrile

Each pure nitrile-containing product was isolated for quantitative determinations by gas chromatography. Compounds **5** and **6** were isolated by silica gel chromatography from oleonitrile/acrylonitrile cross metathesis, and **7** from ethenolysis of **4** [40], 1-decene **8** being a commercially available product. To ensure maximum formation of nitrile products, an excess of acrylonitrile was necessary.

We first explored the reaction in diluted solution of toluene ($[4] = 0.05 \text{ M}$) at $100 \text{ }^\circ\text{C}$ with high catalyst loading (0.5 mol%) and 4 equivalents of acrylonitrile using directly the slow addition of catalyst technique. Catalysts **I**, **II**, **III** and **IV** were active and led to 98% conversion after 4 h, which corresponds to a TON of 196. (Table 4, entries 1-4). No self-metathesis products were detected with this high catalyst loading, but the 4 expected products were formed in various proportions. However, probably due to higher reactivity of terminal olefins with acrylonitrile in secondary cross metathesis processes, the dinitrile **5** and mononitrile **6** were the major

products. Similar results were obtained when the catalyst loading was decreased to 0.025 mol% and a TON of 3760 with 94% conversion was obtained with catalyst **V**. However, products resulting from self-metathesis were produced when the catalyst loading decreased. It was possible to decrease the catalyst loading to 0.0125 mol% but the conversion dropped to 56%, which gave a slightly higher TON of 4480. Attempts to decrease the catalyst loading in diethyl carbonate did not improve the results with these substrates.

Table 4 Cross-metathesis of oleonitrile **4** and acrylonitrile **1**^a

entry	catalyst (mol%)	conversion (%)	TON	selectivity SM/5/6/7/8
1	I (0.5)	98	196	
2	II (0.5)	98	196	
3	III (0.5)	98	196	
4	IV (0.5)	97	194	
5	I (0.25)	97	388	
6	II (0.25)	98	392	
7	III (0.25)	96	384	
8	IV (0.25)	96	384	
9	I (0.025)	86	3440	16/39/35/6/4
10	II (0.025)	92	3680	16/44/34/3/3
11	III (0.025)	83	3320	13/36/38/8/5
12	V (0.025)	94	3760	15/41/35/5/4
13	V (0.0125)	56	4480	22/33/29/7/9

^aReaction conditions: oleonitrile **4** (0.5 mmol), acrylonitrile **1** (2 mmol), toluene (8 cm³), conversion of **4** and selectivity were determined by GC using dodecane as internal standard. Injection of a catalyst solution (2 cm³ added within 1 h) then 3 h prolonged heating. TON: conversion/catalyst loading. SM: self-metathesis product.

Conclusion

We have shown that cross metathesis of 10-undecenitrile with acrylonitrile takes place efficiently with Hoveyda type catalysts at 120 °C in diethyl

carbonate as solvent with continuous addition of the catalyst and the excess of acrylonitrile. Under the best conditions, a high turnover number of 13280 at 83% conversion was obtained with catalyst **V**. Cross metathesis of acrylonitrile with oleonitrile led to the formation of four main products together with self-metathesis products that appeared at low catalyst loading. Turnover numbers close to 4000 could be obtained with high conversions, but a drop of conversion rapidly occurred when the catalyst loading was decreased below 0.0125 mol%.

Experimental

All reactions were carried out using Schlenk tube techniques. Toluene was dried using a MBraun Solvent Purification System. 10-Undecenenitrile and oleonitrile were supplied by Arkema, distilled under vacuum and stored under argon. Acrylonitrile was purchased from Acros Organics and stored under Argon over 4 Å MS followed by distillation over P₂O₅ prior to use. ¹H NMR spectra were recorded at 300 MHz and ¹³C NMR spectra were recorded at 75.5 MHz on a Bruker 300 WB spectrometer. Reactions were monitored using a Shimadzu 2014 gas chromatograph equipped with Equity TM – 1 Fused Silica capillary column. Pure products were obtained by

column chromatography on silica gel (Merck Silica Gel 60) using mixtures of petroleum ether and diethyl ether as the eluent.

General procedure for the cross metathesis of 10-undecenenitrile with acrylonitrile in diethylcarbonate (slow addition of catalyst)

82 mg of **2** (0.5 mmol, 1 equiv.) and 26.5 mg of acrylonitrile **1** (0.5 mmol, 1 equiv.) were dissolved in 8 cm³ of DEC with dodecane as internal standard. The desired amount of catalyst and 1 equiv. of acrylonitrile (0.5 mmol, 26.5 mg) were dissolved in 2 cm³ of DEC and added dropwise over a period of 2 h 40 min into the reaction mixture heated at 120 °C. After completion of the addition, the reaction was stirred for 2 h 20 min. After a total reaction time of 5 h, ethyl vinyl ether was added and a sample was collected for GC analysis. After solvent evaporation, the product was purified by column chromatography over silica gel using a mixture of petroleum ether/diethyl ether (9/1) as eluent to furnish **3** as a mixture of *E* and *Z* isomers.

2-dodecenedinitrile (**3**, C₁₂H₁₈N₂, *Z*:*E*= 4): ¹H NMR (300 MHz, CDCl₃) δ= 1.34-1.72 (m, 12H, 6 CH₂), 2.18-2.47 (m, 4H, NCCH₂ + CH₂CH=CHCN), 5.30-5.37 (m, 1H, CH=CHCN, *Z* + *E*), 6.49 (dt, 0.8H, ³*J*= 10.9, 7.7 Hz, CH=CHCN, *Z*), 6.72 (dt, 0.2H, ³*J*= 16.3, 7.0 Hz, CH=CHCN, *E*). ¹³C NMR (75 MHz, CDCl₃) δ= 17.1, 25.3, 27.6, 28.1, 28.6, 28.8, 28.9, 29.0, 31.8, 33.3, 99.6, 99.8, 116.1, 119.8, 155.1, 156.0. Elemental analysis: calcd: C: 75.74,

H: 9.53, N: 14.72; Found: C: 75.51, H: 9.46, N: 14.58. HRMS: $[M+Na]^+$
calcd: 213.13677; found 213.1366

General procedure for the cross metathesis of oleonitrile with acrylonitrile in toluene (slow addition of catalyst)

132 mg of **4** (0.5 mmol, 1 equiv.) and 106 mg of acrylonitrile **1** (2 mmol, 4 equiv.) were dissolved in 8 cm³ of toluene with dodecane as internal standard. The desired amount of catalyst was dissolved in 2 cm³ of toluene and added dropwise over a period of 1 h into the reaction mixture heated at 100 °C. After completion of the addition, the reaction was stirred for 3 h. After a total reaction time of 4 h, ethyl vinyl ether was added and a sample was collected for GC analysis. After solvent evaporation, the product was purified by column chromatography over silica gel using a mixture of petroleum ether/diethyl ether (9/1) as eluent to furnish a mixture of products, from which **5** and **6** could be isolated in pure form.

2-undecenedinitrile (5, C₁₁H₁₆N₂, Z:E= 4): ¹H NMR (300 MHz, CDCl₃) δ= 1.34-1.73 (m, 10H, 5 CH₂), 2.18-2.45 (m, 4H, NCCH₂ + CH₂CH=CHCN), 5.31 (d, 1H, ³J= 11.0 Hz, CH=CHCN, Z + E), 6.47 (m, 0.76H, CH=CHCN, Z), 6.70 (m, 0.24H, CH=CHCN, E). ¹³C NMR (75 MHz, CDCl₃) δ= 17.1, 25.2, 27.4, 28.0, 28.4, 28.6, 31.7, 33.2, 99.6, 99.8, 116.0, 119.8, 155.0, 155.9
Elemental analysis: calcd: C: 74.96, H: 9.15, N: 15.89; Found: C: 75.61, H: 8.94, N: 15.35. HRMS: $[M+Na]^+$ calcd: 199.12112; found 199.1210

2-undecenenitrile 6 [41]: ^1H NMR (300 MHz, CDCl_3) δ = 0.89 (t, 3H, CH_3), 1.29-1.50 (m, 12H, 6 CH_2), 2.19-2.27 (m, 0.64H, $\text{CH}_2\text{CH}=\text{CHCN}$, *E*), 2.40-2.47 (m, 1.36H, $\text{CH}_2\text{CH}=\text{CHCN}$, *Z*), 5.30-5.36 (m, 1H, $\text{CH}=\text{CHCN}$, *Z + E*), 6.50 (dt, 0.68H, $^3J= 10.8, 7.8$ Hz, $\text{CH}=\text{CHCN}$, *Z*), 6.73 (dt, 0.32H, $^3J= 16.3, 7.0$ Hz, $\text{CH}=\text{CHCN}$, *E*). ^{13}C NMR (75 MHz, CDCl_3) δ = 14.1, 22.6, 27.6, 28.2, 29.0, 29.1, 29.2, 31.8, 31.9, 33.3, 99.4, 99.6, 116.1, 155.3, 156.2

9-Decenenitrile 7 [40, 42]: ^1H NMR (300 MHz, CDCl_3) δ = 1.29-1.65 (m, 10H, 5 CH_2); 2.17-2.41 (m, 4H, $\text{NCCH}_2 + \text{CH}_2\text{CH}=\text{CHCN}$); 4.83-5.07 (m, 2H, $\text{CH}=\text{CH}_2$); 5.70–5.84 (m, 1H, $\text{CH}=\text{CH}_2$). ^{13}C NMR (75 MHz, CDCl_3) δ = 17.1, 25.2, 27.5, 28.1, 28.3, 28.3, 114.1, 115.3, 139.2

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