JOC The Journal of Organic Chemistry

Article

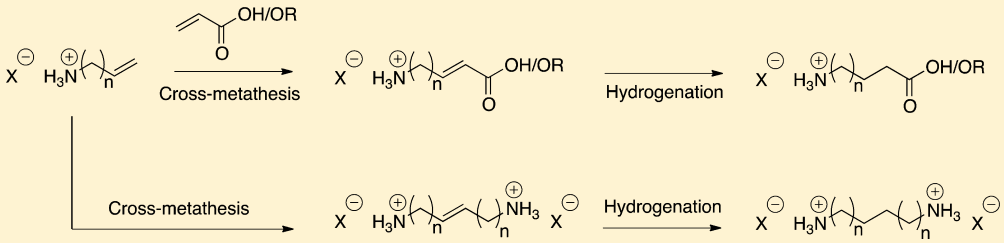
pubs.acs.org/joc

Cross-Metathesis of Brønsted Acid Masked Alkenylamines with Acrylates for the Synthesis of Polyamide Monomers

Nicolas Daniel Spiccia, Szabolcs Solyom, Clint Peter Woodward, William Roy Jackson, and Andrea Jane Robinson*

School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

Supporting Information



ABSTRACT: Ruthenium−alkylidene-catalyzed cross-metathesis of a range of homologous alkenylamine salts provides expedient and high-yielding routes to commercially valuable polyamide monomers using a single catalyst, telescopic workup, and mild experimental conditions.

INTRODUCTION

Since the early 20th century, polyamides have been used in the production of synthetic resins and fibers for a variety of applications such as clothing, home wares, electronics, and automotive parts.[1,2] Copolymer polyamides are synthesized by the condensation step-growth polymerization of diamines with dicarboxylic acids (e.g., PA-6,6, Kevlar, Nomex, and Stanyl).[3] Homopolymer polyamides are synthesized by the condensation step-growth polymerization of amino acids or their derivatives, PA-6 and Rilsan (PA-11).[4] The traditional production of these monomers relies on the use of chemicals such as acrylonitrile, carbon monoxide, hydrogen cyanide, and high-pressurized hydrogen, which pose handling risks to manufacturers and the surrounding environment.[3−6]

In a previous communication, we outlined a catalytic synthesis for the production of acyclic unsaturated diamines **1** using olefin metathesis (Scheme 1).[7] In this paper, we describe an extension of this work and show how unsaturated amine salts **2** can be diversionally transformed by cross-metathesis with either methyl acrylate **3** or acrylic acid **4** into unsaturated aminoesters or acids **5**. These, or the previously described diamine salts **1**, can be hydrogenated in tandem using the residual ruthenium as catalyst to give saturated amino esters/acids **6** or diamines **7** for commercial polymer production.

Numerous examples of accessing PA monomers via olefin metathesis have been reported.[8] Omega-unsaturated fatty acids (and their esters) have been used as starting materials whereupon (i) CM with alkenylnitriles and hydrogenation;[9a,b] (ii) conversion to cyanoalkenes[10a−c] or carbamates,[11] CM with methyl acrylate and hydrogenation; (iii) CM with allyl chloride and amination;[12] (iv) ethenolysis, reductive ozonolysis, and reductive amination;[13] (v) isomerization−methoxycarbonylation−transesterification[14] and (vi) amidation with alkenylamines and RCM/hydrogenation[15] yield PA monomers; and (vii) CM with methyl acrylate[16] yields dicarboxylic acid esters.

RESULTS AND DISCUSSION

Our previous work showed that self-metathesis of alkenylamine salts **2** with ruthenium(I) benzylidene precatalyst (**8**) proceeded in good yield to provide unsaturated diamine salts **1**, as illustrated by the reaction of allylamine triflate (Scheme 1).[7,17] The choice of counterion and solvent was found to be of paramount importance since they jointly control starting material and product solubility and hence reaction yield. Toward this end, the most suitable counterions for metathesis reactions with allylammonium salts were the tetrafluoroborate and triflate anions, which also exhibited good solubility in ethyl acetate. The conjugate acids of each of these anions possess pK_a values <3 in acetonitrile.[18a,b] However, longer chain alkenylamines gave excellent conversions when using their cheaper and easier to handle tosylate salts.

The optimized reaction conditions used for tandem self-metathesis have now been applied to the cross-metathesis of alkenylammonium salts with methyl acrylate **3** and acrylic acid **4** (Scheme 1). Initial studies were carried out using salts of allylamine, leading to the formation of unsaturated Nylon-4 precursors. A large excess of the acrylate (20 equiv) was used to give a high equilibrium yield of the cross-product. The yields were found to be dependent on the anion as per the homodimerization experiments.[7] Nearly complete conversion of allylammonium salts **2** was obtained for the triflate (TfO^-,

Received: October 28, 2015
Published: January 22, 2016

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

Scheme 1. Polyamide Monomers

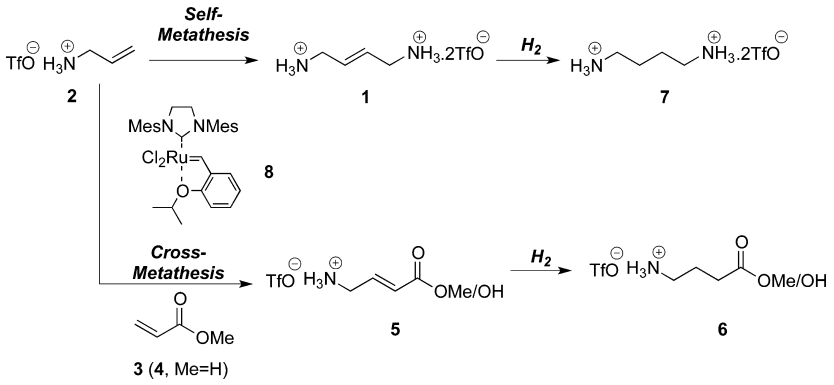
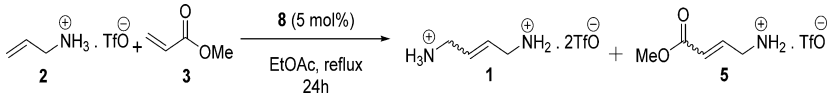


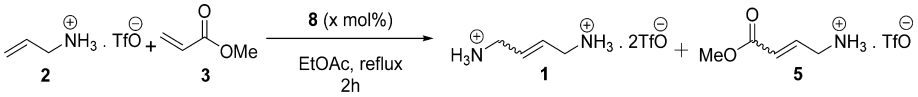
Table 1. Reactions of Allylamine Triflate 2 with Differing Equivalents of Methyl Acrylate 3



entry	equiv of **3**	homodimer **1** (%)	cross-product **5** (%)	E/Z[a]
1	1	70	30	9:2
2	2	60	40	9:2
3	5	40	60	9:2
4	10	18	82	9:2
5	20	<5	>95	9:2

[a]As determined by NMR spectroscopy on crude reaction mixtures.

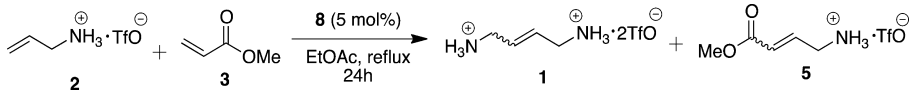
Table 2. Effect of Catalyst Loading on Conversion of 2[a,b]



mol % of catalyst **8**	conversion (%)	homodimer **1** (%)	cross-product **5** (%)
0.1	81	20	61
0.5	89	20	69
1	93	9	83
2.5	98	7	91
5	97	2	95

[a]Reactions with methyl acrylate **3**/ammonium salt **2** (20:1). [b]Conversion of **2** and product ratios (**1** and **5**) determined by NMR spectroscopy on crude reaction mixtures.

Table 3. Reactions Using Recovered Methyl Acrylate 3 and Solvent[a]



cycle no.	conversion (%)	homodimer **1** (%)	cross-product **5** (%)
1	93	13	78
2	87	8	79
3	88	17	72
4	94	15	79

[a]Reactions with methyl acrylate **3**/ammonium salt **2** (20:1).

>99%) using optimized conditions; slightly lower yields were obtained using tetrafluoroborate salts (BF_4^-, 81%), and a lower yield still (26%) was obtained with the tosylate salt (TsO^-). As expected, the yields of cross-metathesis products were highly dependent on the molar equivalents of acrylate, as shown in Table 1, for reaction of methyl acrylate **3** with allylamine triflate **2**.

The results show that homodimerization of the unsaturated ammonium salt **2** competes with cross-metathesis with **3** to yield **5**, and that molar ratios of less than 10:1 (entries 1−3) gave significant amounts of homodimer **1**. Only very small amounts of homodimer were obtained when a 20:1 ratio of methyl acrylate to amine salt **2** was used (entry 5). Conveniently, it was found that the minor homodimer salt

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

could be precipitated from the reaction mixture by the addition of a small volume of ethyl acetate. This allowed pure target molecule **5** to be isolated after filtration in all cases.

The reaction time required for complete conversion of **2** to **5** using the 20:1 ratio of reactants was also investigated, and it was found that reaction for 2 h was sufficient to give complete conversion. This reaction time was therefore used in most of the subsequent reactions. Catalyst loading was also investigated, and the result is summarized in Table 2. Nearly complete conversion was obtained with 1 mol % of catalyst **8**, but the yield decreased when lower catalyst loading, 0.5 and 0.1 mol %, was used. The ratio of homodimer **1** to cross-product **5** also increased as the catalyst loading was reduced.

Recovery and reuse of excess methyl acrylate was investigated using 1 mol % of catalyst. The result in Table 3 shows that high and consistent conversion to the required cross-product **5** can be achieved using recycled methyl acrylate.

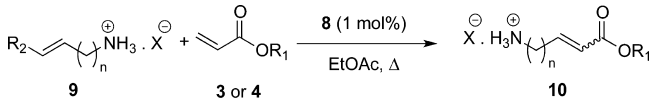
The formation of large amounts of the amine homodimer when low ratios of methyl acrylate to ammonium salts were used was disappointing. Homodimerization of methyl acrylate **3**, an electron-poor alkene, is expected to be slow,[19] and only a small amount of dimethylfumarate or maleate was detected. The formation of cross-product **5** can arise either by direct reaction of the methyl acrylate **3** with the ammonium salt **2** or by indirect reaction with the homodimer salt **1**. Reaction of the cross-product **5** with the other alkenes present in the reaction mixture (i.e., itself **5**, methyl acrylate **3**, or the homodimer **1**) would be expected to be slow, and the equilibrium constants for these reactions would be expected to favor the cross-product **5**. Reactions were carried out with a 1:1 molar ratio of ammonium salt **2** and cross-partner **3** for 1, 2, and 3 days. However, the ratio of homodimer salt **1** to cross-product **5** was found to increase only slightly with increasing time.[20]

Further attempts to overcome the need for a large excess of acrylate involved the slow addition of the allylamine triflate salt **2** to a solution of the catalyst (**8**, 5 mol %) and methyl acrylate **3**. Significantly, this approach reduced the ratio of **2**/**3** to 1:2. Addition of **2** over 1 h resulted in improved conversion to the target cross-product **5**: two reactions gave 93 and 89% conversion with homodimer/cross-product ratios of ∼1:2. Unfortunately, further experiments with slower addition times of 2 and 4 h, or reactions with only 1 mol % of catalyst, gave less favorable ratios of homodimer **1** and cross-product **5**. In contrast, a longer chain analogue, an undecenylammonium tosylate salt, reacted well under slow addition conditions; with 2 equiv of methyl acrylate **3** and 1 mol % of catalyst **8**, the target cross-product was obtained in 70% isolated yield.

Cross-metathesis of the above-described C3 allylamine substrate proved to be the most challenging unsaturated amine we investigated. To expand the scope toward other potentially useful polyamide monomers, previously described cross-metathesis conditions were applied to the reaction of higher-order alkenylammonium salts **9** with both methyl acrylate and acrylic acid (Table 4).

All of the reactions gave >95% conversion to **10**. ^{1}H NMR spectroscopy of the total reaction products is shown in the Experimental Section, and only a trace of homodimer or unreacted unsaturated amine salts can be seen. Reactions of methyl acrylate with butenylamine (entries 1 and 2) and pentenylamine salts (entries 3−5) all gave clean conversion to the desired cross-products **10** (n = 2 and 3), respectively; reaction at gram scale under identical conditions also gave quantitative yield of the target cross-product. Increase in chain

Table 4. Generation of Nylon-4, -5, and -6 Precursors[a]



9 **3 or 4** **10**

entry	n	X	R_1	R_2	CM product (conv %)[b]	E/Z
1	2	TfO	Me	H	>99[c]	6:1
2	2	BF_4	Me	H	>99	7:1
3	3	TfO	Me	H	>95	7:1
4	3	BF_4	Me	H	>99	10:1
5	3	TsO	Me	H	>99	10:1
6	8	BF_4	Me	Me	>99[d]	10:1
7	8	TsO	Me	Me	>99[d]	20:1
8	1	TfO	H	H	>95	>3:1
9	2	BF_4	H	H	>99	7:1
10	3	BF_4	H	H	>99 (70)[e]	>20:1
11	3	TfO	H	H	>99 (95)[e]	>20:1
12	3	TsO	H	H	>99	>20:1
13	8	TsO	H	Me	>99	>20:1

[a]Reactions with methyl acrylate **3** or acrylic acid **4**/ammonium salt **9** (20:1), catalyst (**8**, 1 mol %), EtOAc, Δ, 1 h. [b]As determined by NMR spectroscopy on crude reaction mixtures. [c]Reaction performed as for (a) using 5 mol % of catalyst **8**. [d]Isomerization products (minor) detected by ESI$^+$ mass spectrometry. [e]Isolated yield (%) by precipitation (in parentheses).

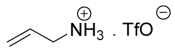
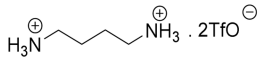
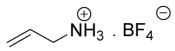
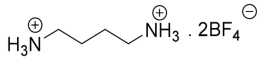
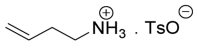
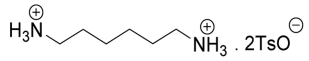
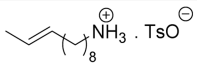
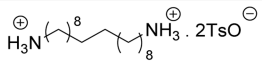
length (n = 8) led to even smaller traces of homodimeric product, probably due to steric reasons (entries 6 and 7). Once again, excellent ratios of E/Z were observed with increasing chain length. Reaction of the undec-2-enylamine tetrafluoroboric acid salt (entry 6) gave complete conversion, but ESI mass spectrometry showed evidence of shorter chain analogues arising from double-bond isomerization prior to cross-metathesis. Reaction of the unsaturated amine salts with acrylic acid (entries 8−13) also gave excellent results. Recovery and reuse of the acrylic acid involved distillation of the unreacted acid at 60 °C/40 mmHg. The recovered acid from a reaction of 4-pentenylammonium triflate under the same conditions as described in Table 4 (entry 13) again gave >99% conversion to the cross-product, with only a trace of homodimer. Reaction of the tosylate salt of undec-2-enylamine with acrylic acid using 5 mol % of catalyst also gave the cross-product in excellent conversion, without byproducts arising from isomerization. Slow addition of 4-pentenylammonium triflate (over 1 h) to a solution of acrylic acid and HG second catalyst **8** was also investigated. Using a 2:1 ratio of amine salt to acrylic acid gave complete conversion to almost pure cross-product (<5% homodimer) when the tosylate salt was used. A similar result was obtained for a reaction of the undecenylamine tosylate even when using only 1% catalyst loading.

In order to produce monomers suitable for established commercial condensation polyamides, such as PA-6,6, the introduced C═C bond needs to be reduced. The tandem metathesis/hydrogenation of both the homodimers (e.g., **1**) and the cross-metathesis products (e.g., **5**) was therefore investigated (Tables 5 and 6). It has previously been shown that residual ruthenium from the metathesis reaction can be used as the catalyst for subsequent hydrogenation reactions under mild experimental conditions.[21a,b,22a−i]

Self-metathesis of allylammonium triflate and tetrafluoroborate salts followed by tandem hydrogenation gave the desired saturated diammonium salts in excellent yield (91 and >99%, respectively) after precipitation (Table 5, entries 1 and 2).

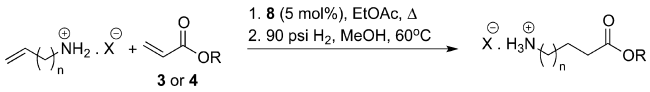
DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

Table 5. Tandem Cross-Metathesis/Hydrogenation Route to Diamine Salts 1[a]

Entry	Substrate	Product	Isolated Yield
1			91%
2			>99%
3			90%
4			>99%

[a]Reaction conditions: (i) metathesis: amine, catalyst (**8**, 5 mol %), EtOAc, Δ, 16 h, followed by (ii) hydrogenation: reaction mixture from (i), MeOH, H_2 (60 psi), room temperature, 16 h.

Table 6. Metathesis/Hydrogenation Route to Nylon-4, -5, and -6 Monomers[a]



entry	*n*	X	R	CM/H_2 product (conv %)[b]
1	1	TfO	Me	>99
2	2	BF_4	Me	>99
3	3	BF_4	Me	95[c]
4	3	BF_4	H	97[d]

[a]Reactions with methyl acrylate **3** or acrylic acid **4**/ammonium salt **9** (20:1), catalyst (**8**, 5 mol %), EtOAc, Δ, 16–24 h, followed by solvent exchange to MeOH, H_2 (90 psi), 60 °C, 16 h. [b]As determined by NMR spectroscopy on reaction mixtures. [c]Dimethyl succinate present in crude reaction product. [d]Cross-metathesis reaction (1 h); transesterification (10%) to the methyl ester was also observed in the crude reaction product. Product characterized via esterification.

Tandem self-metathesis/hydrogenation of 3-butenylammonium tosylate gave the saturated diammonium salt, which is a protonated form of the useful PA-6,6 monomer hexamethylene diamine, in excellent isolated yield 90% (entry 3). No homologues were detected by mass spectrometry, indicating that the mild conditions prevent concomitant isomerization during the metathesis step. The long-chain undec-9-enylamine tosylate also gave the saturated long-chained diammonium salt in excellent yield (>99%) (entry 4).

Tandem hydrogenation was then attempted with the intention of generating saturated amino ester salts suitable for synthesis of saturated Nylon precursors (Table 6). Unsurprisingly, the amino acrylate products were more difficult to hydrogenate than the unsaturated diamines, where previously established conditions (60 psi H_2, room temperature) failed to yield any of the desired saturated amino esters. Fortunately, quantitative conversion to the saturated amino ester salts was obtained when a higher pressure of hydrogen (90 psi) and elevated temperature (60 °C) were employed in the presence of the residual Ru residue from the metathesis reaction. Using this two step-tandem approach, C4, C5, and C6 amino ester salts (Table 6, entries 1–3) and Nylon-6 amino acid monomer (entry 4), all suitable for homopolymer polyamide synthesis, were prepared in excellent conversion.

■ CONCLUSION

Ruthenium-catalyzed cross-metathesis of alkenylamine salts with an excess of methyl acrylate or acrylic acid gives excellent yields of unsaturated amino acids or aminoesters. The excess methyl acrylate or acrylic acid can be recovered and reused. Slow addition of the amine salt to a solution of the catalyst and methyl acrylate or acrylic acid gives excellent yields of cross-products for the longer chain alkenes, even when using only 1% catalyst and especially when tosylate salts are used. The ruthenium residues from the metathesis catalyst can be used as catalysts for the hydrogenation of both homodimeric unsaturated diamine salts and the unsaturated cross-metathesis amino acid salts to give Nylon precursors of different chain lengths.

■ EXPERIMENTAL SECTION

Procedure for Cross-Metathesis of Unsaturated Ammonium Salts with Acrylates. The following is an example of a conventional cross-metathesis of alkenylammonium salts with methyl acrylate (e.g., Table 1, entry 5): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with allylammonium triflate (**2**, 35 mg, 0.17 mmol), 20 equiv of methyl acrylate **3**, Hoveyda–Grubbs second-generation catalyst (5 mg, 5 mol %), and a small magnetic stir bar. The EtOAc (2.5 mL) was added through a rubber septum, and the tube was sealed and heated at reflux under nitrogen for 24 h. The crude reaction mixture was then diluted with water (4 mL), and the phases were separated. The organic phase was further extracted with water (3 × 4 mL). The combined aqueous phase was washed with EtOAc (4 mL) and then concentrated in vacuo to give a hygroscopic yellow oil (51 mg). ^{1}H NMR spectroscopy showed >95% conversion to the desired cross-product **5**.

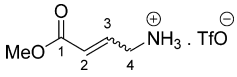
Reaction optimization studies were performed with allylammonium triflate **2** and methyl acrylate **3** as follows:

- In Table 1, molar equivalents of methyl acrylate **3** were varied from 1:20 relative to the substrate **2**.

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798–1805

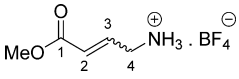
- In Table 2, the loading of Hoveyda−Grubbs second-generation catalyst **8** was varied from 0.1 to 5 mol %.
- In Table 3, methyl acrylate **3** was recovered and recycled in subsequent reactions. At cycle completion, the reaction was cooled to room temperature and connected to a vacuum line (0.1 mmHg). The reaction solvent and **3** were distilled from the reaction into a new vessel. Catalyst (1 mol %) and substrate were then added maintaining the substrate/**3** ratio at 1:20.

Methyl 4-Ammonium But-2-enoate Triflate.



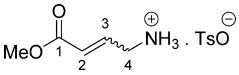
Allylammonium triflate (35 mg) gave the title ester (51 mg, 98%) as an oil (Table 1, entry 5): IR ν_{max} 3163m, 2977m, 1716s, 1507s, 1224s, 1165s, 1027s, 988s, 875s, 762s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.92 (dt, *J* = 15.9, 5.8 Hz, 1H), 6.24−6.12 (m, 1H), 3.83−3.70 (m, 5H); ^{13}C NMR (100 MHz, MeOD) δ 167.1, 139.7, 126.0, 121.8 (q, *J* = 318 Hz), 52.4, 40.0; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.33 (dt, *J* = 12.1, 6.1 Hz, 1H), 6.20−6.09 (m, 1H), 4.14 (dd, *J* = 6.1, 1.8 Hz, 2H), 3.83−3.70 (m, 3H); ^{13}C NMR (100 MHz, MeOD) δ 167.3, 140.2, 125.1, 121.8 (q, *J* = 318 Hz), 52.2, 38.7; HRMS (ESI/FTMS) *m*/*z* $[M - TfOH + H]^+$ calcd for $C_5H_{10}NO_2$ 116.0706; found 116.0710.

Methyl 4-Ammonium but-2-enoate Tetrafluoroborate.



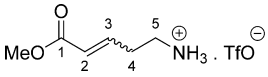
Product did not crystallize, with 81% conversion by ^1H NMR spectroscopy: IR ν_{max} 3266m, 2963m, 1712s, 1502s, 1001s, 975s, 866s, 732s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.92 (dt, *J* = 15.9, 6.0 Hz, 1H), 6.17 (dt, *J* = 15.9, 1.7 Hz, 1H), 3.79−3.77 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, MeOD) δ 167.1, 139.9, 126.1, 52.5, 41.0; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.33 (dt, *J* = 11.5, 6.2 Hz, 1H), 6.12 (dt, *J* = 11.5, 1.9 Hz, 1H), 4.18−4.07 (m, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, MeOD) δ 167.3, 140.5, 125.1, 52.3, 38.9; HRMS (ESI/FTMS) *m*/*z* $[M - HBF_4 + H]^+$ calcd for $C_5H_{10}NO_2$ 116.0706; found 116.0703.

Methyl 4-Ammonium But-2-enoate Tosylate.



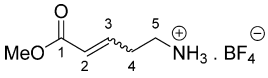
Product did not crystallize, with 26% conversion by ^1H NMR spectroscopy: ^1H NMR (400 MHz, MeOD) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.90 (dt, *J* = 15.9, 5.9 Hz, 1H), 6.15 (dt, *J* = 15.9, 1.6 Hz, 1H), 3.74 (s, 3H), 3.63−3.46 (m, 2H), 2.73 (s, 3H); HRMS (ESI/FTMS) *m*/*z* $[M - TsOH + H]^+$ calcd for $C_5H_{10}NO_2$ 116.0706; found 116.0705.

Methyl 5-Ammonium Pent-2-enoate Triflate.



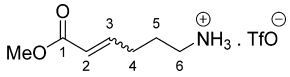
3-Butenylammonium triflate (50 mg) gave the title ester (68 mg, 99%) as an oil (Table 4, entry 1): IR ν_{max} 3105m, 1702s, 1222s, 1165s, 1024s, 982s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.91 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.02 (dt, *J* = 15.8, 1.5 Hz, 1H), 3.73 (s, 3H), 3.16−3.04 (m, 2H), 2.59 (qd, *J* = 7.2, 1.5 Hz, 2H) (*Z*)-isomer δ 6.29 (dt, *J* = 11.4, 7.5 Hz, 1H), 6.02 (m, 1H), 3.73 (s, 3H), 3.16−3.04 (m, 2H), 2.59 (qd, *J* = 7.2, 1.5 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 167.9, 144.3, 125.2, 52.1, 39.2, 30.9; HRMS (ESI/FTMS) *m*/*z* $[M - TfOH + H]^+$ calcd for $C_6H_{12}NO_2$ 130.0863; found 130.0859.

Methyl 5-Ammonium Pent-2-enoate Tetrafluoroborate.



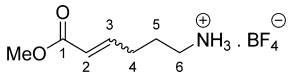
3-Butenylammonium tetrafluoroborate (37 mg) gave the title ester (57 mg, 99%) as an oil (Table 4, entry 2): ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.96−6.85 (dt, *J* = 15.7, 7.1 Hz, 1H), 6.02 (d, *J* = 15.7 Hz, 1H), 3.73 (s, 3H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.59 (q, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.0, 144.3, 125.1, 52.1, 39.2, 30.8; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.29 (dt, *J* = 11.4, 7.5 Hz, 1H), 6.17 (d, *J* = 15.9 Hz, 1H), 3.76 (s, 3H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.59 (q, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.0, 144.4, 123.8, 51.8, 39.8, 30.8; HRMS (ESI/FTMS) *m*/*z* $[M - HBF_4 + H]^+$ calcd for $C_6H_{12}NO_2$ 130.0863; found 130.0869.

Methyl 6-Ammonium Hex-2-enoate Triflate.



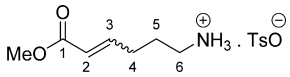
4-Pentenylammonium triflate (50 mg) gave the title ester (60 mg, 97%) as an oil (Table 4, entry 3): IR ν_{max} 3089m, 2958m, 1708s, 1639m, 1223s, 1160s, 1026s, 760s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.95 (dt, *J* = 15.6 Hz, 6.5 Hz, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 3.71 (s, 3H), 3.03−2.87 (m, 2H), 2.39−2.28 (m, 2H), 1.89−1.76 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.5, 148.7, 123.0, 52.1, 40.2, 29.7, 26.9; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.38−6.26 (m, 1H), 5.99−5.85 (m, 1H), 3.74 (s, 1H), 3.03−2.87 (m, 2H), 2.39−2.28 (m, 2H), 1.89−1.76 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 169.7, 148.5, 123.8, 51.9, 40.2, 29.7, 27.0; HRMS (ESI/FTMS) *m*/*z* $[M - TfOH + H]^+$ calcd for $C_7H_{14}NO_2$ 144.1019; found 144.1029.

Methyl 6-Ammonium Hex-2-enoate Tetrafluoroborate.



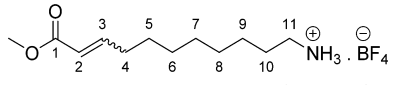
4-Pentenylammonium tetrafluoroborate (50 mg) gave the title ester (76 mg, 99%) as an oil (Table 4, entry 4): IR ν_{max} 3256m, 3207m, 2955m, 1702s, 1507s, 1439s, 1287s, 1012m, 956m, 720s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.95 (dt, *J* = 15.6 Hz, 6.5 Hz, 1H), 5.93 (d, *J* = 15.5 Hz, 1H), 3.71 (s, 3H), 3.03−2.87 (m, 2H), 2.39−2.28 (m, 2H), 1.89−1.76 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.5, 148.7, 123.0, 52.1, 40.2, 29.7, 26.9; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.38−6.26 (m, 1H), 5.99−5.85 (m, 1H), 3.74 (s, 1H), 3.03−2.87 (m, 2H), 2.39−2.28 (m, 2H), 1.89−1.76 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.4, 149.0, 121.8, 51.9, 40.2, 29.5, 26.9; HRMS (ESI/FTMS) *m*/*z* $[M - HBF_4 + H]^+$ calcd for $C_7H_{14}NO_2$ 144.1019; found 144.1024.

Methyl 6-Ammonium Hex-2-enoate Tosylate.



4-Pentenylammonium tosylate (50 mg) gave the title ester (76 mg, 99%) as an oil (Table 4, entry 5): IR ν_{max} 3061m, 2950m, 2087m, 1717s, 1649s, 1493s, 1438s, 1313s, 1277s, 1178s, 1037s, 816s, 684s cm^{-1}; ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 6.92 (dt, *J* = 15.6 Hz, 6.5 Hz, 1H), 5.89 (d, *J* = 15.5 Hz, 1H), 3.71 (s, 3H), 2.92−2.90 (m, 2H), 2.37 (s, 3H), 2.29−2.27 (m, 2H), 1.79−1.78 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.3, 148.6, 143.3, 141.7, 129.8, 126.8, 122.8, 52.0, 40.5, 29.6, 26.8, 21.2; ^1H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.27 (dt, 1H), 5.86 (d, 1H), 3.73 (s, 3H), 2.88−2.86 (m, 2H), 2.37 (s, 3H), 2.22−2.20 (m, 2H), 1.70−1.68 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.3, 148.6, 143.3, 141.7, 129.8, 126.8, 122.8, 52.0, 40.5, 29.6, 26.8, 21.2; HRMS (ESI/FTMS) *m*/*z* $[M - TsOH + H]^+$ calcd for $C_7H_{14}NO_2$ 144.1019; found 144.1021. The reaction was also performed on larger scale. 4-Pentenylammonium tosylate (1.10 g) gave the title ester (1.30 g, 99%) as an oil.

Methyl 11-Ammonium Undec-2-enoate Tetrafluoroborate.

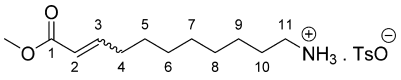


9-Undecenylammonium tetrafluoroborate (100 mg) gave the title ester (78 mg, 99%) as an oil (Table 4, entry 6). Isomerization was observed by LRMS: ^1H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.96 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.84 (dt, *J* = 15.6, 1.6 Hz, 1H), 3.70 (s, 3H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.28−2.17 (m, 2H), 1.76−1.28 (m, 12H); ^{13}C NMR (100 MHz, MeOD) δ 168.9, 151.3, 121.8, 51.9, 40.8, 33.1, 30.1,

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

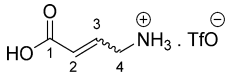
30.1, 30.0, 29.1, 28.5, 27.3; HRMS (ESI/FTMS) m/z [M ± $(CH_2)_n$ − HBF_4 + H]$^+$ calcd for $C_{12}H_{24}NO_2$ 214.1802; found 214.1802 ± 14n.

Methyl 11-Ammonium Undec-2-enoate Tosylate.



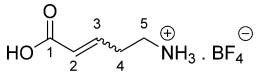
9-Undecenylammonium tosylate (100 mg) gave the title ester (78 mg, 99%) as an oil (Table 4, entry 7): IR ν_{max} 3134m, 3050m, 2923m, 2854s, 2059m, 1719s, 1656s, 1492s, 1436s, 1176s, 1124s, 1036s, 1012s, 815s, 683s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 7.70 (d, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.96 (dt, J = 15.6, 7.0 Hz, 1H), 5.84 (dt, J = 15.6, 1.6 Hz, 1H), 3.70 (s, 3H), 2.91 (t, J = 7.6 Hz, 2H), 2.28−2.17 (m, 2H), 1.76−1.28 (m, 12H); ^{13}C NMR (100 MHz, MeOD) δ 168.6, 151.1, 121.6, 143.3, 141.5, 129.6, 126.7, 51.7, 40.6, 32.8, 30.0, 29.9, 28.9, 28.8, 28.3, 27.2, 21.2; HRMS (ESI/FTMS) m/z [M ± $(CH_2)_n$ − TsOH + H]$^+$ calcd for $C_{12}H_{24}NO_2$ 214.1802; found 214.1804 ± 14n.

4-Ammonium But-2-enoic Acid Triflate.



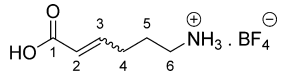
Allylammonium triflate (50 mg) gave the title acid (59 mg, 98%) as an oil (Table 4, entry 8): IR ν_{max} 3239m, 2873m, 1690s, 1226s, 1167m, 1028m, 868s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.89 (dt, J = 15.9, 5.8 Hz, 1H), 6.14−6.10 (m, 1H), 3.75 (dd, J = 6.0, 1.6 Hz, 2H); ^{1}H NMR (400 MHz, MeOD) (*Z*)-isomer δ 6.31 (dt, J = 12.1, 6.1 Hz, 1H), 6.14−6.10 (m, 1H), 4.12 (dd, J = 6.2, 1.8 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 168.2, 139.4, 126.8, 40.8; HRMS (ESI/FTMS) m/z [M − TfOH + H]$^+$ calcd for $C_4H_8NO_2$ 102.0550; found 102.0554.

5-Ammonium Pentenoic Acid Tetrafluoroborate.



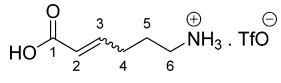
Butenylammonium tetrafluoroborate (37 mg) gave the title acid (72 mg, 99%) as an oil (Table 4, entry 9): IR ν_{max} 3410m, 3158m, 1708m, 1508m, 1224m, 1005s, 944m cm^{-1}; ^{1}H NMR (300 MHz, MeOD) (*E*)-isomer δ 6.89 (dt, J = 15.6, 7.0 Hz, 1H), 5.98 (d, J = 15.7 Hz, 1H), 3.09 (t, J = 7.3 Hz, 2H), 2.58 (qd, J = 7.2, 1.4 Hz, 2H); ^{13}C NMR (75 MHz, MeOD) δ 169.1, 144.2, 126.2, 39.2, 30.0; ^{1}H NMR (300 MHz, MeOD) (*Z*)-isomer δ 6.26 (dt, J = 11.3 Hz, 7.5 Hz, 1H), 6.07−5.89 (m, 1H), 3.03−2.94 (m, 2H), 2.46−2.35 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 169.1, 144.2, 126.2, 39.8, 27.9; HRMS (ESI/FTMS) m/z [M − HBF_4 + H]$^+$ calcd for $C_5H_{10}NO_2$ 116.0706; found 116.0700.

6-Ammonium Hex-2-enoic Acid Tetrafluoroborate.



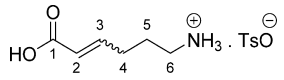
4-Pentenylammonium tetrafluoroborate (50 mg) gave the title acid (76 mg, 99%) (Table 4, entry 10). Product (*E*)-isomer (44 mg) precipitated from EtOAc, 70% yield: colorless solid, mp 191 °C; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.93 (dt, J = 15.5, 6.8 Hz, 1H), 5.89 (d, J = 15.6 Hz, 1H), 2.99−2.92 (m, 2H), 2.37−2.29 (m, 2H), 1.82 (p, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 169.7, 148.4, 123.9, 40.2, 29.7, 27.0; HRMS (ESI/FTMS) m/z [M − HBF_4 + H]$^+$ calcd for $C_6H_{12}NO_2$ 130.0863; found 130.0865.

6-Ammonium Hex-2-enoic Acid Triflate.



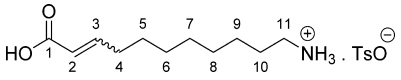
4-Pentenylammonium triflate (100 mg) gave the title acid (140 mg, 99%) (Table 4, entry 11). Product (*E*)-isomer (135 mg) precipitated from EtOAc, 95% yield: IR ν_{max} 3098m, 2977m, 1703m, 1647m, 1499s, 1223s, 1069s, 1027s, 980s, 816s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 6.93 (dt, J = 15.6, 6.8 Hz, 1H), 5.88 (d, J = 15.6 Hz, 1H), 2.97−2.93 (m, 2H), 2.34−2.32 (m, 2H), 1.84−1.80 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 169.7, 148.5, 123.8, 40.2, 29.7, 27.0; HRMS (ESI/FTMS) m/z [M − TfOH + H]$^+$ calcd for $C_6H_{12}NO_2$ 130.0863; found 130.0863.

6-Ammonium Hex-2-enoic Acid Tosylate.



4-Pentenylammonium tosylate (50 mg) gave the title acid (72 mg, 99%) (Table 4, entry 12): IR ν_{max} 3050m, 2917m, 2085m, 1690m, 1633s, 1492s, 1421s, 1177s, 1125s, 1012s, 974s, 819s, 682s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 7.71 (d, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.01 (dt, J = 15.6, 6.8 Hz, 1H), 5.95 (d, J = 15.6 Hz, 1H), 2.42 (s, 3H), 3.05−3.01 (m, 2H), 2.36−2.33 (m, 2H), 1.88−1.85 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 170.5, 149.6, 142.5, 139.5, 129.4, 125.4, 121.4, 38.8, 28.3, 25.0, 20.5; HRMS (ESI/FTMS) m/z [M − TsOH + H]$^+$ calcd for $C_6H_{12}NO_2$ 130.0863; found 130.0864.

11-Ammonium Undec-2-enoic Acid Tosylate.



9-Undecenylammonium tosylate (100 mg) gave the title acid (78 mg, 99%) as an oil (Table 4, entry 13): IR ν_{max} 3437m, 3055m, 2953m, 2082m, 1678s, 1492s, 1280s, 1176m, 1122s, 1009s, 816s, 680s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) (*E*)-isomer δ 7.70 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.95 (dt, J = 15.6, 7.0 Hz, 1H), 5.81 (dt, J = 15.6, 1.6 Hz, 1H), 2.89 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 2.23−2.21 (m, 2H), 1.63−1.34 (m, 12H); ^{13}C NMR (100 MHz, MeOD) δ 169.9, 151.1, 143.3, 141.6, 129.7, 126.8, 122.3, 40.6, 32.9, 30.0, 29.9, 28.9, 28.3, 27.2, 21.2; HRMS (ESI/FTMS) m/z [M ± $(CH_2)_n$ − TsOH + H]$^+$ calcd for $C_{11}H_{22}NO_2$ 200.1645; found 200.1648 ± 14n.

Procedure for Slow Addition of Unsaturated Ammonium Salts to Mixtures of Acrylates and Catalyst. The following is an example of a conventional slow addition of alkenylammonium salts to mixtures of acrylates and catalyst: Under an inert atmosphere of nitrogen, a Schlenk tube was charged with Hoveyda−Grubbs second-generation catalyst (1 or 5 mol %) and 2 equiv of methyl acrylate in EtOAc (1 mL) and a small magnetic stir bar. The unsaturated ammonium salts (50−100 mg) in EtOAc (2 mL) were injected through a rubber septum with the aid of a syringe pump (flow rate 0.3 mL/min), and after complete addition, the tube was sealed and heated at reflux under nitrogen for 30 min. The reaction mixture was then diluted with water (4 mL), and the phases were separated. The organic phase was further extracted with water (3 × 4 mL). The combined aqueous phase was washed with EtOAc (4 mL) and then concentrated in vacuo to give the crude reaction product. ^{1}H NMR spectroscopy showed conversion to the desired cross-product in all cases.

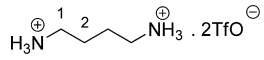
A tosylate reaction involved addition of undecenylammonium tosylate salt (100 mg, 0.29 mmol) in EtOAc (2 mL) to a mixture of methyl acrylate (0.05 mL, 0.58 mmol) and Hoveyda−Grubbs second-generation catalyst (2 mg, 1 mol %) over 1 h. The reaction was heated at reflux for 0.5 h. The product was isolated as described above to give the target product **10** (n = 8, 78 mg, 70% yield).

Procedure for Tandem Self-Metathesis−Hydrogenation of Unsaturated Ammonium Salts to Diamine Salts 1. The following is an example of a conventional tandem metathesis/hydrogenation procedure for the metathesis of alkenylammonium salts (e.g., Table 5, entry 1): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with 3-butenylammonium triflate (33 mg, 0.16 mmol), Hoveyda−Grubbs second-generation catalyst (5 mg, 5 mol %), and a small magnetic stir bar. The EtOAc (4 mL) was added through a rubber septum, and the tube was sealed and heated at reflux under nitrogen for 16 h. The crude reaction mixture was then exposed to air and concentrated in vacuo, redissolved in methanol (2 mL), and transferred to a Fischer−Porter pressure tube. The tube was evacuated three times with hydrogen, charged to a final pressure of 60 psi, and left to stir at ambient temperature for 16 h. The vessel was then vented to air, and the solvent was removed by rotary evaporation. The resultant mixture was dissolved in a minimum volume of acetone, triturated with excess diethyl ether (approx 1:10), and filtered (or

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

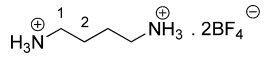
centrifuged) to give 1,4-diammonium-2-butane triflate (28 mg, 91%) as an off-white solid.

Butane-1,4-diammonium Ditriflate.



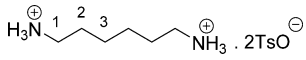
Allylammonium triflate (33 mg) gave the title diamine salt (28 mg, 91% yield) (Table 5, entry 1). It precipitated from acetone with ether (approx 1:10) to give an off-white solid: mp 208 °C (dec); ^{1}H NMR (400 MHz, MeOD) δ 3.03−2.93 (m, 2H), 1.80−1.68 (m, 2H); ^{13}C NMR (150 MHz, MeOD) δ 121.7 (q, J = 317 Hz), 40.1, 25.6; HRMS (ESI/FTMS) m/z [M − 2TfOH + H]$^+$ calcd for $C_4H_{13}N_2$ 89.1073; found 89.1080.

Butane-1,4-Diammonium Ditetrafluoroborate.



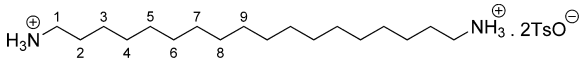
Allylammonium tetrafluoroborate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, entry 2). It precipitated from acetone with ether (approx 1:10) to give an off-white solid: mp 199 °C (dec); ^{1}H NMR (400 MHz, MeOD) δ 3.06−2.84 (m, 2H), 1.82−1.64 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 40.1, 25.5; HRMS (ESI/FTMS) m/z [M − 2HBF$_4$ + H]$^+$ calcd for $C_4H_{13}N_2$ 89.1073; found 89.1073.

Hexane-1,6-diammonium Ditosylate.



3-Butenylammonium tosylate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, entry 3). It precipitated from acetone as an off-white solid: mp 172 °C; ^{1}H NMR (400 MHz, MeOD) δ 7.71 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.02−2.84 (t, J = 7.8 Hz, 2H), 1.76−1.58 (m, 2H), 1.51−1.32 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 143.5, 141.8, 129.9, 126.9, 40.6, 28.3, 26.8, 21.3; HRMS (ESI/FTMS) m/z [M − 2TsOH + H]$^+$ calcd for $C_6H_{17}N_2$ 117.1386; found 117.1391.

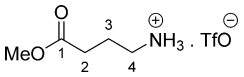
Octadecane-1,18-diammonium Ditosylate.



9-Undecenylammonium tosylate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, entry 4). It precipitated from acetone as a colorless solid: ^{1}H NMR (400 MHz, MeOD) δ 7.71 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.03−2.72 (m, 2H), 2.37 (s, 3H), 1.64 (p, 7.4 Hz, 2H), 1.53−1.20 (m, 14H); ^{13}C NMR (100 MHz, MeOD) δ 141.7, 129.8, 127.0, 40.8, 30.9, 30.8, 30.8, 30.7, 30.6, 30.3, 28.6, 27.5, 21.3, quaternary Ar-C-SO$_3$H not observed; LRMS (ESI/FTMS) m/z [M − 2TsOH + H]$^+$ calcd for $C_{18}H_{41}N_2$ 143.1; found 143.1. HRMS conditions failed to yield a molecular ion for this compound.

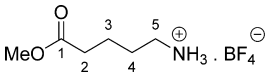
Procedure for Tandem Cross-Metathesis/Hydrogenation of Unsaturated Ammonium Salts to Nylon-4, -5, and -6 Monomers. The following is an example of a conventional tandem metathesis/hydrogenation procedure for the metathesis of alkenylammonium salts (e.g., Table 6, entry 1): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with allylammonium triflate (35 mg, 0.17 mmol), 20% methyl acrylate in EtOAc (1.53 mL, 3.4 mmol), Hoveyda−Grubbs second-generation catalyst (5 mg, 5 mol %), and a small magnetic stir bar. The EtOAc (4 mL) was added through a rubber septum, and the tube was sealed and heated at reflux under nitrogen for 24 h (unless specified otherwise). The crude reaction mixture was then exposed to air and concentrated in vacuo, redissolved in methanol (4 mL), and transferred to a Fischer−Porter pressure tube. The tube was evacuated three times with hydrogen, charged to a final pressure of 90 psi, and left to stir at 60 °C for 16 h. The vessel was then vented to air, and the solvent was removed by rotary evaporation. The mixture was redissolved in EtOAc (4 mL) and diluted with water (4 mL), and the phases were separated. The organic phase was further extracted with water (3 × 4 mL), and the combined aqueous extract was washed with EtOAc (4 mL) and concentrated in vacuo to give a hygroscopic yellow oil (67 mg). ^{1}H NMR spectroscopy showed >95% conversion to the desired hydrogenated cross-product.

Methyl 4-Ammonium Butanoate Triflate.



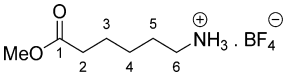
Allylammonium triflate (35 mg) gave the title ester (67 mg, 99%) (Table 6, entry 1). Product did not crystallize, with almost quantitative conversion by ^{1}H NMR spectroscopy: ^{1}H NMR (400 MHz, MeOD) δ 3.69 (s, 3H), 2.99 (t, J = 7.6 Hz, 2H), 2.48 (t, J = 7.2 Hz, 2H), 1.95 (p, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, MeOD) δ 174.6, 52.3, 40.1, 31.4, 23.7; HRMS (ESI/FTMS) m/z [M − TfOH + H]$^+$ calcd for $C_5H_{12}NO_2$ 118.0863; found 118.0864.

Methyl 5-Ammonium Pentanoate Tetrafluoroborate.



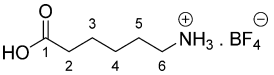
3-Butenylammonium tetrafluoroborate (37 mg) gave the title ester (39 mg, 99%) (Table 6, entry 2). Product did not crystallize, with almost quantitative conversion by ^{1}H NMR spectroscopy: ^{1}H NMR (400 MHz, MeOD) δ 3.67 (s, 3H), 3.03−2.88 (m, 2H), 2.47−2.36 (m, 2H), 1.77−1.62 (m, 4H); ^{13}C NMR (100 MHz, MeOD) δ 175.4, 52.1, 40.5, 34.0, 27.9, 22.7; HRMS (ESI/FTMS) m/z [M − HBF$_4$ + H]$^+$ calcd for $C_6H_{14}NO_2$ 132.1019; found 132.1021.

Methyl 6-Ammonium Hexanoate Tetrafluoroborate.



4-Pentenylammonium tetrafluoroborate (97 mg) gave the title ester (124 mg, 95%) (Table 6, entry 3). Product did not crystallize: IR ν_{max} 3275m, 2942m, 1716s, 1509s, 1219s, 1004m, 946m, 824s, 771s, 746s, 680s cm^{-1}; ^{1}H NMR (400 MHz, MeOD) δ 3.66 (s, 3H), 2.93 (t, J = 7.5 Hz, 2H), 2.36 (t, J = 7.3 Hz, 2H), 1.72−1.61 (m, 2H), 1.47−1.36 (m, 4H); ^{13}C NMR (100 MHz, MeOD) δ 175.8, 52.1, 40.7, 34.4, 28.2, 26.8, 25.4; HRMS (ESI/FTMS) m/z [M − HBF$_4$ + H]$^+$ calcd for $C_7H_{16}NO_2$ 146.1176; found 146.1175.

6-Ammonium Hexanoic Acid Tetrafluoroborate.



4-Pentenylammonium tetrafluoroborate (50 mg) gave the crude title acid (102 mg, 97%) (Table 6, entry 4). Product did not crystallize. ^{1}H NMR spectroscopy revealed a mixture of the title compound, methyl 6-ammonium hexanoate tetrafluoroborate and succinic acid (^{1}H NMR (400 MHz, MeOD) δ 2.57 (s, 4H)), which was not removed by aqueous extraction: ^{1}H NMR (400 MHz, MeOD) δ 2.93 (t, J = 7.5 Hz, 2H), 2.33 (t, J = 7.3 Hz, 2H), 1.76−1.57 (m, 4H), 1.53−1.32 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 40.6, 34.3, 28.2, 26.8, 25.4, C1 not observed; LRMS (ESI/FTMS) m/z [M − HBF$_4$ + H]$^+$ calcd for $C_6H_{14}NO_2$ 132.1; found 132.1.

The crude amino acid mixture was added to methanol (20 mL) containing three drops of 40% aqueous HBF$_4$. The mixture was stirred at 70 °C for 72 h. The mixture was then concentrated in vacuo and partitioned between EtOAc (15 mL) and water (15 mL), and the phases were separated. The organic phase was further extracted with water (3 × 15 mL), and the combined aqueous extract was washed with EtOAc (15 mL) and concentrated in vacuo to give methyl 6-ammonium hexanoate tetrafluoroborate as an oil (90 mg, >95% conversion by ^{1}H NMR spectroscopy). Spectral data were consistent with those reported previously.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02484.

Spectral data for new compounds (PDF)

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805

AUTHOR INFORMATION

Corresponding Author

*E-mail: andrea.robinson@monash.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the Australian Research Council (ARC) for financial assistance (Discovery Grant DP120104169) and an Australian Postgraduate Award (to N.D.S.).

REFERENCES

(1) Biermann, U.; Friedt, W.; Lang, S.; Lühs, W.; Machmüller, G.; Metzger, J. O.; Klaas, M. R. g.; Schäfer, H. J.; Schneider, M. *Angew. Chem.* **2000**, *112*, 2292−2310.

(2) Kohan, M. I. *Nylon Plastics*; Wiley Interscience, 1973; pp 13−82.

(3) *Stanyl(R) Introduction*; DSM Engineering Plastics, 2004.

(4) (a) Rulkens, R.; Koning, C. Chemistry and technology of polyamides. In *Polymer science: a comprehensive reference*; Matyjaszewski, K., Möller, M., Eds.; Elsevier: Amsterdam, 2012; pp 431−467. (b) *http://www.arkema.com/*.

(5) Bonner, R. M.; Kohan, M. I.; Lacey, E. M.; Richardson, P. N.; Roder, T. M.; Sherwood, J. L. T. In *Nylon Plastics*; Kohan, M. I., Ed.; Wiley Interscience, 1973; pp 327−408.

(6) Audi, J.; Belson, M.; Patel, M.; Schier, J.; Osterloh, J. *J. Am. Med. Assoc.* **2005**, *294*, 2342−2351.

(7) Woodward, C. P.; Spiccia, N. D.; Jackson, W. R.; Robinson, A. J. *Chem. Commun.* **2011**, *47*, 779−781.

(8) Nickel, A.; Pederson, R. L. Commercial Potential of Olefin Metathesis of Renewable Feedstocks. In *Olefin Metathesis: Theory and Practice*; Grela, K., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2014; DOI: 10.1002/9781118711613.ch11.

(9) (a) Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H.; Dubois, J.-L.; Couturier, J.-L. *ChemSusChem* **2012**, *5* (8), 1410−1414. (b) Ameh Abel, G.; Oliver Nguyen, K.; Viamajala, S.; Varanasi, S.; Yamamoto, K. *RSC Adv.* **2014**, *4* (98), 55622−55628.

(10) (a) Miao, X.; Fischmeister, C.; Dixneuf, P. H.; Bruneau, C.; Dubois, J.-L.; Couturier, J.-L. *Green Chem.* **2012**, *14* (8), 2179−2183. (b) Rajendran, G.; Zheng, C.; Gaffney, A. PCT Int. Appl. WO 2013136111 A2 20130919, 2013. (c) Couturier, J.-L.; Dubois, J.-L. PCT Int. Appl. WO 2013030481 A1 20130307, 2013.

(11) Winkler, M.; Meier, M. A. R. *Green Chem.* **2014**, *16* (6), 3335−3340.

(12) Jacobs, T.; Rybak, A.; Meier, M. A. R. *Appl. Catal., A* **2009**, *353* (1), 32−35.

(13) Dubois, J.-L. PCT Int. Appl. WO 2010004220 A2 20100114, 2010.

(14) Zhu, Y.; Patel, J.; Mujcinovic, S.; Jackson, W. R.; Robinson, A. J. *Green Chem.* **2006**, *8*, 746−749.

(15) Yapa Mudiyanselage, A.; Viamajala, S.; Varanasi, S.; Yamamoto, K. *ACS Sustainable Chem. Eng.* **2014**, *2* (12), 2831−2836.

(16) Rybak, A.; Meier, M. A. R. *Green Chem.* **2007**, *9* (12), 1356−1361.

(17) Spiccia, N. D.; Woodward, C. P.; Jackson, W. R.; Robinson, A. J. Processes for producing amine compounds. WO/2014/005196, PCT/AU2013/000745, July 2013.

(18) (a) Eckert, F.; Leito, I.; Kaljurand, I.; Kütt, A.; Klamt, A.; Diedenhofen, M. *J. Comput. Chem.* **2009**, *30*, 799−810. (b) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391−395.

(19) Teoh, E.; Campi, E. M.; Jackson, W. R.; Robinson, A. J. *Chem. Commun.* **2002**, *53*, 978−979.

(20) Interestingly, under extended reaction conditions (24 h) and higher catalyst loading (5 mol% of **8**), higher order, preformed ditosylate homodimers synthesised from **9** (n = 3 and 8) also failed to quantiatively react with 20 equiv of methyl acrylate. In the n = 3 case, only 15% of the target CM product **10** (n = 3, X = OTs) was obtained; 54% conversion to **10** (n = 8, X = OTs) was observed for the longer chain substrate.

(21) (a) Wang, Z. J.; Spiccia, N. D.; Jackson, W. R.; Robinson, A. J. *J. Pept. Sci.* **2013**, *19*, 470. (b) Wang, Z. J.; Spiccia, N. D.; Jackson, W. R.; Robinson, A. J. Amino acid analogues and methods for their synthesis.WO/2014/005197, PCT/AU2013/000747, July 2013.

(22) (i) Tandem metathesis−hydrogenation at elevated H_2 pressure/temperature: (a) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 3196−3201 (GI, 120 psi H_2, 90 °C). (b) Louie, J.; Bielawski, C. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312−11313 (GI/GII, 800 psi H_2, 80 °C). (c) Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *ChemSusChem* **2009**, *2*, 542−545 (HGII, 145 psi H_2, 50 °C). (d) Ramharter, J.; Weinstabl, H.; Mulzer, J. *J. Am. Chem. Soc.* **2010**, *132*, 14338−14339 (GII, 140 psi H_2, 70 °C). (e) Clark, J. S.; Labre, F.; Thomas, L. H. *Org. Biomol. Chem.* **2011**, *9*, 4823−4830 (HGII, 100 psi H_2, 70 °C). (ii) Tandem metathesis−hydrogenation in the presence of added base: (f) Schmidt, B.; Pohler, M. *Org. Biomol. Chem.* **2003**, *1*, 2512−2517 (GII, NaH). (g) Camm, K. D.; Martinez Castro, N.; Liu, Y.; Czechura, P.; Snelgrove, J. L.; Fogg, D. E. *J. Am. Chem. Soc.* **2007**, *129*, 4168−4169 (GI/GII, NEt_3). (h) Miao, X.; Fischmeister, C.; Dixneuf, P. H.; Bruneau, C.; Dubois, J. L.; Couturier, J. L. *Green Chem.* **2012**, *14*, 2179−2183 (HGII, ^{t}BuOK). (i) Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H.; Dubois, J. L.; Couturier, J. L. *ChemSusChem* **2012**, *5*, 1410−1414 (GII/HGII, LDA, ^{t}BuOK).

DOI: 10.1021/acs.joc.5b02484
J. Org. Chem. 2016, 81, 1798−1805