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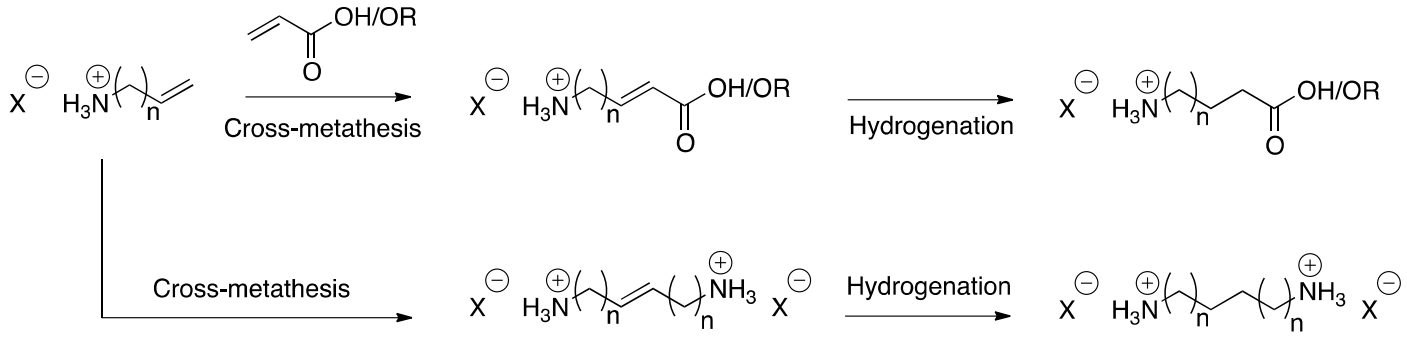
Cross-metathesis of Brønsted acid-masked alkenyl amines with acrylates for the synthesis of polyamide monomers

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

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

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

Graphical Abstract



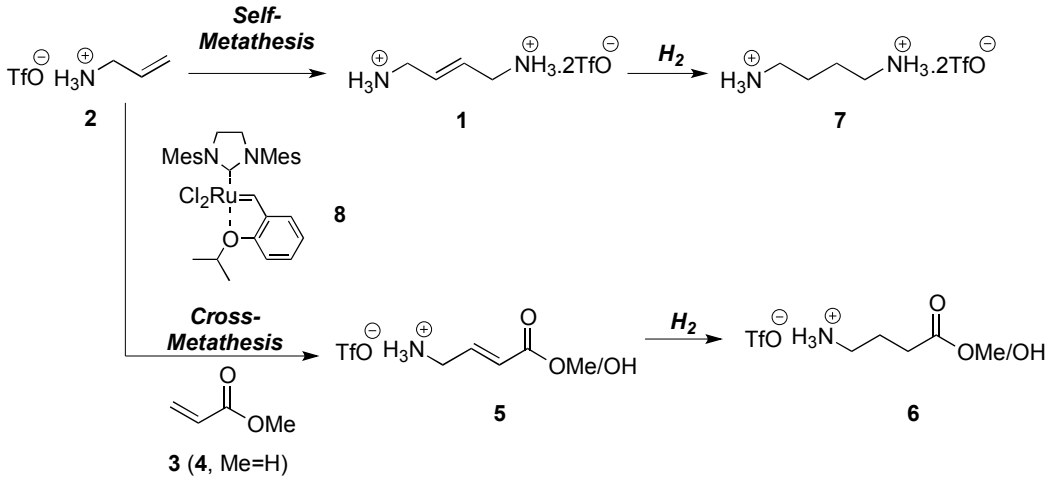
Ruthenium-alkylidene catalyzed cross metathesis of a range of homologous alkenylamine salts provides expedient and high yielding routes to commercially valuable polyamide monomers using a single catalyst, telescopic workup and mild experimental conditions.

Introduction

Since the early 20th century, polyamides have been used in the production of synthetic resins and fibres for a variety of applications such as clothing, home wares, electronics and automotive parts.[1, 2] Copolymer polyamides are synthesised by the condensation step-growth polymerisation of diamines with dicarboxylic acids, e.g. PA-6,6, Kevlar®, Nomex® and Stanyl®.[3] Homopolymer polyamides are synthesised by the

condensation step-growth polymerisation of amino acids or their derivatives, e.g 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 pressurised 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.



Scheme 1. Polyamide monomers

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]

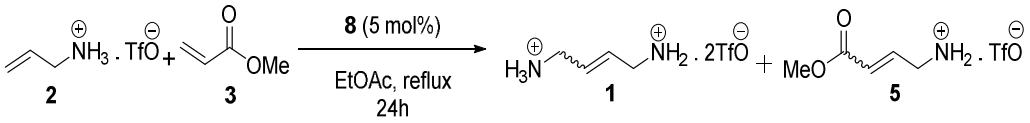
and vi) amidation with alkenylamines and RCM/hydrogenation[15] yields PA monomers, and vii) CM with methyl acrylate[16] yields dicarboxylic acid esters.

Results and Discussion

Our previous work showed that self-metathesis of alkenyl amine salts **2** with ruthenium(I) benzylidene pre-catalyst (**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. Towards this end, the most suitable counterions for metathesis reactions with allyl ammonium salts were the tetrafluoroborate and triflate anions, which also exhibited good solubility in ethyl acetate. The conjugate acids of each of these anions possess pKa values < 3 in acetonitrile.[18a-b] However, longer chain alkenyl amines gave excellent conversions when using their cheaper and easier to handle tosylate salts.

The optimised reaction conditions used for tandem self-metathesis have now been applied to the cross-metathesis of alkenyl ammonium 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 eq.) 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] Near complete conversion of allylammonium salts **2** was obtained for the triflate (TfO^-, >99%) using optimised conditions; slightly lower yields were obtained using tetrafluoroborate salts (BF_4^-, 81%) and a lower yield still (26%) with the tosylate salt (TsO^-). As expected the yields of cross metathesis products were highly dependant on the molar equivalents of acrylate as shown in Table 1 for reaction of methyl acrylate (**3**) with allylamine triflate (**2**).

Table 1. Reactions of allylamine triflate (2) with differing equivalents of methyl acrylate (3)



2 **3** **1** **5**

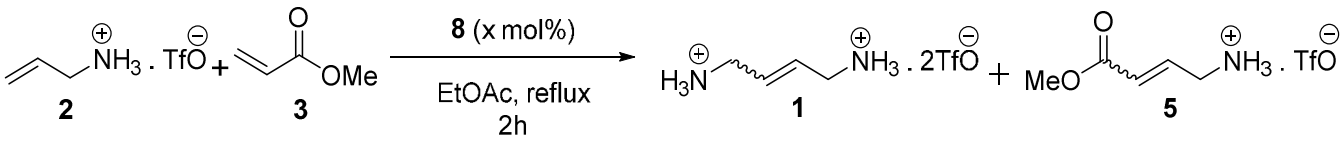
Entry	Eq. of **3**	Homodimer **1**	Cross product **5**	(*E*:*Z*)[a]
1	1	70%	30%	9:2
2	2	60%	40%	9:2
3	5	40%	60%	9:2
4	10	18%	82%	9:2
5	20	<5%	>95%	9:2

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

The results show that homodimerisation 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 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 two hours 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. Near complete conversion was obtained with 1 mol% of catalyst (**8**) but the yield decreased when lower catalyst loading, 0.5 mol% and 0.1 mol%, was used. The ratio of homodimer **1** to cross product **5** also increased as the catalyst loading was reduced.

Table 2. Effect of catalyst loading on conversion of (2)[a,b]



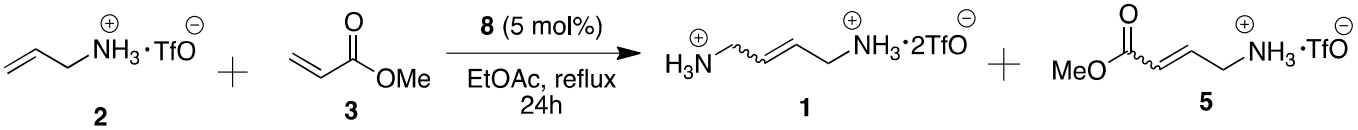
2 **3** **1** **5**

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.

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.

Table 3. Reactions using recovered methyl acrylate (3) and solvent[a]



2 **3** **1** **5**

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).

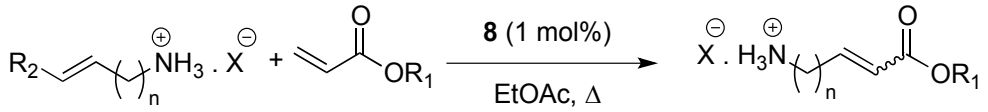
The formation of large amounts of the amine homodimer when low ratios of methyl acrylate to ammonium salts were used was disappointing. Homodimerisation of methyl acrylate (**3**), an electron poor alkene is expected to be slow[19] and only a small amount of dimethylfumarate or maleate was detected. The formation of cross-product **5** can arise either by direct reaction of the methyl acrylate (**3**) with the ammonium salt **2** or indirectly by 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 favour 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 only slightly increase 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 one hour 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 two and four hours, or reactions with only 1 mol% catalyst, gave less favourable ratios of homodimer **1** and cross product **5**. In contrast, a longer chain analogue, an undecenyl ammonium tosylate salt, reacted well under slow addition conditions: with two equivalents 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 towards other potentially useful polyamide

monomers, previously described cross-metathesis conditions were applied to the reaction of higher order alkenyl ammonium salts **9** with both methyl acrylate and acrylic acid (Table 4).

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[f]
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[f]	>20:1

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

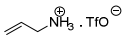
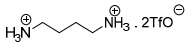
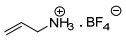
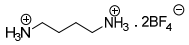
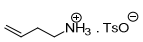
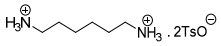
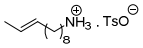
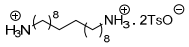
All of the reactions gave >95% conversion to **10**. ^{1}H-NMR spectroscopy of the total reaction products are

shown in the appendix 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 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 isomerisation 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 ^{o}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% catalyst also gave the cross product in excellent conversion without byproducts arising from isomerisation. Slow addition of 4-pentenylammonium triflate (over 1 hour) to a solution of acrylic acid and HG 2nd 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, e.g. 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 residual ruthenium from the metathesis reaction can be used as the catalyst for

subsequent hydrogenation reactions under mild experimental conditions.[21a-b, 22a-22i]

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%

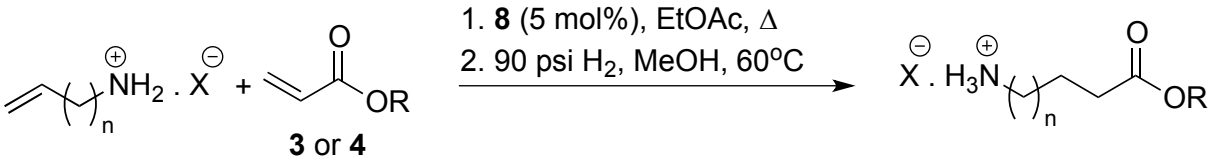
[a]Reaction conditions: i) Metathesis: Amine, catalyst (**8**, 5 mol%), EtOAc, Δ, 16 hrs, followed by ii) Hydrogenation: Reaction mixture from i), MeOH, H_2 (60 psi), room temperature, 16 hrs.

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). 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 isomerisation 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.

Table 6. Metathesis/hydrogenation route to Nylon 4, 5 and 6 monomers[a]



3 or **4**

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 hrs, followed by solvent exchange to MeOH, H_2 (90 psi), 60 °C, 16 hrs. [b]As determined by NMR spectroscopy on reaction mixtures. [c]Dimethyl succinate present in crude reaction product. [d]Cross metathesis reaction (1 hr); Transesterification (10%) to the methyl ester was also observed in the crude reaction product. Product characterised *via* esterification.

Conclusion

Ruthenium catalysed cross metathesis of alkenylamine salts with an excess of methyl acrylate or acrylic acid gives excellent yields of unsaturated aminoacids 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 aminoacid salts to give Nylon precursors of different chain lengths.

Experimental

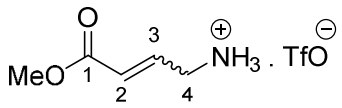
Procedure for cross-metathesis of unsaturated ammonium salts with acrylates

The following is an example of a conventional cross-metathesis of alkenyl ammonium salts with methyl acrylate (e.g. Table 1, Entry 5): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with allyl ammonium triflate (**2**, 35 mg, 0.17 mmol), 20 equivalents 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 hours. 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 n.m.r. spectroscopy showed >95% conversion to the desired cross product **5**.

Reaction optimisation 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**).
- In Table 2, the loading of Hoveyda-Grubbs second generation catalyst (**8**) was varied from 0.1 – 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.

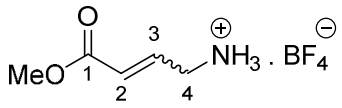
Methyl 4-ammonium but-2-enoate triflate



Allyl ammonium triflate (35 mg) gave 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}. ^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 167.1, 139.7, 126.0, 121.8 (q, *J* = 318 Hz), 52.4, 40.0. ^{1}H n.m.r. (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 n.m.r. (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* $[M\text{-}TfOH+H]^+$ Calcd for $C_5H_{10}NO_2$ 116.0706; Found 116.0710.

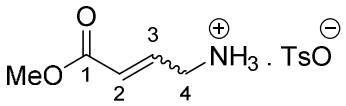
Methyl 4-ammonium but-2-enoate tetrafluoroborate



Product did not crystallise, 81% conversion by ^{1}H n.m.r. spectroscopy.

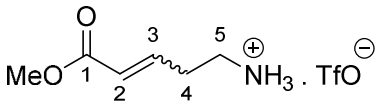
IR: ν_{max} 3266m, 2963m, 1712s, 1502s, 1001s, 975s, 866s, 732s cm^{-1}. ^{1}H n.m.r. (400 MHz, MeOD), (*E*)-Isomer: δ 6.92 (dt, *J* = 15.9, 6.0 Hz, 1H), 6.17 (dt, *J* = 15.9, 1.7 Hz, 1H), 3.79 – 3.77 (m, 2H), 3.76 (s, 3H). ^{13}C n.m.r. (100 MHz, MeOD) δ 167.1, 139.9, 126.1, 52.5, 41.0. ^{1}H n.m.r. (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 n.m.r. (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 crystallise, 26% conversion by ^{1}H n.m.r. spectroscopy. ^{1}H n.m.r. (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

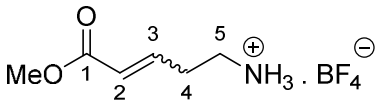


3-Butenyl ammonium triflate (50 mg) gave the title ester (68 mg, 99%) as an oil (Table 4, Entry 1).

IR: ν_{max} 3105m, 1702s, 1222s, 1165s, 1024s, 982s cm^{-1}. ^{1}H n.m.r. (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

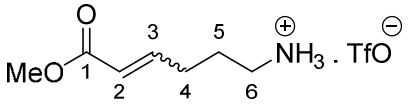
(qd, *J* = 7.2, 1.5 Hz, 2H). ^{13}C n.m.r. (100 MHz, MeOD) δ 167.9, 144.3, 125.2, 52.1, 39.2, 30.9. HRMS (ESI/FTMS): *m/z* $[M\text{-}TfOH+H]^+$ Calcd for $C_6H_{12}NO_2$ 130.0863; Found 130.0859.

Methyl 5-ammonium pent-2-enoate tetrafluoroborate



3-Butenyl ammonium tetrafluoroborate (37 mg) gave title ester (57 mg, 99%) as an oil (Table 4, Entry 2). ^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.0, 144.3, 125.1, 52.1, 39.2, 30.8. ^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.0, 144.4, 123.8, 51.8, 39.8, 30.8. HRMS (ESI/FTMS): *m/z* $[M\text{-}HBF_4+H]^+$ Calcd for $C_6H_{12}NO_2$ 130.0863; Found 130.0869.

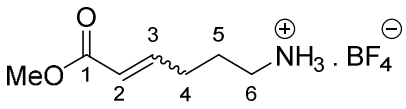
Methyl 6-ammonium hex-2-enoate triflate



4-Pentenyl ammonium 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}. ^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.5, 148.7, 123.0, 52.1, 40.2, 29.7, 26.9. ^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 169.7,

148.5, 123.8, 51.9, 40.2, 29.7, 27.0. HRMS (ESI/FTMS): *m/z* $[M\text{-}TfOH+H]^+$ Calcd for $C_7H_{14}NO_2$ 144.1019; Found 144.1029.

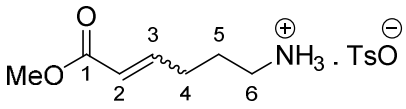
Methyl 6-ammonium hex-2-enoate tetrafluoroborate



4-Pentenyl ammonium 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 n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.5, 148.7, 123.0, 52.1 , 40.2, 29.7, 26.9. ^1H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.4, 149.0, 121.8, 51.9, 40.2, 29.5, 26.9. HRMS (ESI/FTMS): *m/z* $[M\text{-}HBF_4+H]^+$ Calcd for $C_7H_{14}NO_2$ 144.1019; Found 144.1024.

Methyl 6-ammonium hex-2-enoate tosylate



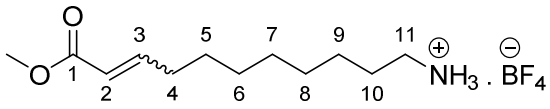
4-Pentenyl ammonium tosylate (50 mg) gave the title ester (76 mg, 99%) as an oil (Table 4, Entry 5).

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 n.m.r. (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. ^{1}H 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 n.m.r. (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* $[M\text{-}TsOH+H]^+$ Calcd for $C_7H_{14}NO_2$ 144.1019; Found 144.1021.

The reaction was also performed on larger scale. 4-Pentenyl ammonium tosylate (1.10 g) gave the title ester (1.30 g, 99%) as an oil.

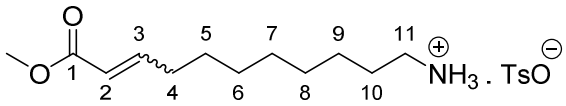
Methyl 11-ammonium undec-2-enoate tetrafluoroborate



9-Undecenyl ammonium tetrafluoroborate (100 mg) gave the title ester (78 mg, 99%) as an oil (Table 4, Entry 6). Isomerisation observed by LRMS.

^{1}H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.9, 151.3, 121.8, 51.9, 40.8, 33.1, 30.1, 30.1, 30.0, 29.1, 28.5, 27.3. HRMS (ESI/FTMS): *m/z* $[M\pm(CH_2)_n\text{-}HBF_4+H]^+$ Calcd for $C_{12}H_{24}NO_2$ 214.1802; Found 214.1802 ± 14n.

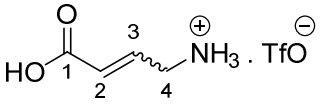
Methyl 11-ammonium undec-2-enoate tosylate



9-Undecenyl ammonium 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}. ^1H 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* $[M\pm(CH_2)_n\text{-TsOH+H}]^+$ Calcd for $C_{12}H_{24}NO_2$ 214.1802; Found 214.1804 ± 14n.

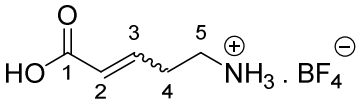
4-Ammonium but-2-enoic acid triflate



Allyl ammonium 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}. ^1H n.m.r. (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). ^1H n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 168.2, 139.4, 126.8, 40.8. HRMS (ESI/FTMS): *m/z* $[M\text{-TfOH+H}]^+$ Calcd for $C_4H_8NO_2$ 102.0550; Found 102.0554.

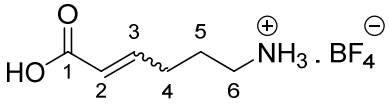
5-Ammonium pentenoic acid tetrafluoroborate



Butenyl ammonium 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 n.m.r. (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 n.m.r. (75 MHz, MeOD) δ 169.1, 144.2, 126.2, 39.2, 30.0. ^{1}H n.m.r. (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 n.m.r. (75 MHz, MeOD) δ 169.1, 144.2, 126.2, 39.8, 27.9. HRMS (ESI/FTMS): *m/z* $[M\text{-}HBF_4+H]^+$ Calcd for $C_5H_{10}NO_2$ 116.0706; Found 116.0700.

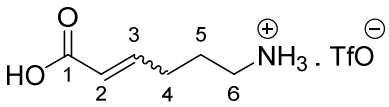
6-Ammonium hex-2-enoic acid tetrafluoroborate



4-Pentenyl ammonium tetrafluoroborate (50 mg) gave the title acid (76 mg, 99%) (Table 4, Entry 10). Product (*E*)-Isomer (44 mg) precipitated from EtOAc, 70% yield.

Colourless solid, m.p. 191 °C. ^{1}H N.M.R. (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 N.M.R. (100 MHz, MeOD) δ 169.7, 148.4, 123.9, 40.2, 29.7, 27.0. HRMS (ESI/FTMS): *m/z* $[M\text{-}HBF_4+H]^+$ Calcd for $C_6H_{12}NO_2$ 130.0863; Found 130.0865.

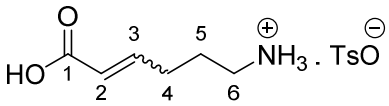
6-Ammonium hex-2-enoic acid triflate



4-Pentenyl ammonium 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 n.m.r. (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 n.m.r. (100 MHz, MeOD) δ 169.7, 148.5, 123.8, 40.2, 29.7, 27.0. HRMS (ESI/FTMS): *m/z* $[M\text{-}TfOH+H]^+$ Calcd for $C_6H_{12}NO_2$ 130.0863; Found 130.0863.

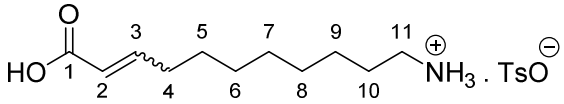
6-Ammonium hex-2-enoic acid tosylate



4-Pentenyl ammonium 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 n.m.r. (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* $[M\text{-}TsOH+H]^+$ Calcd for $C_6H_{12}NO_2$ 130.0863; Found 130.0864.

11-Ammonium undec-2-enoic acid tosylate



9-Undecenyl ammonium 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* $[M\pm(CH_2)_n\text{-TsOH+H}]^+$ 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

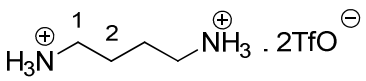
The following is an example of a conventional slow addition of alkenyl ammonium salts to mixtures of acrylates and catalyst: Under an inert atmosphere of nitrogen, a Schlenk tube was charged with Hoveyda-Grubbs second generation catalyst (1 or 5 mol%) and 2 equivalents of methyl acrylate in EtOAc (1 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 half an hour. The reaction mixture was then diluted with water (4 mL) and the phases 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 n.m.r. spectroscopy showed conversion to the desired cross product in all cases.

A tosylate reaction involved addition of undecenyl ammonium tosylate salt (100 mg, 0.29 mmol) in EtOAc (2mL) to a mixture of methyl acrylate (0.05 mL, 0.58 mmol) and Hoveyda-Grubbs second generation catalyst (2 mg, 1 mol%) over one hour. The reaction was heated at reflux for 0.5 hours. 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 → diamine salts (1)

The following is an example of a conventional tandem metathesis / hydrogenation procedure for the metathesis of alkenyl ammonium salts (e.g. Table 5, Entry 1): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with 3-butenyl ammonium triflate (33 mg, 0.16 mmol), Hoveyda-Grubbs second generation catalyst (5 mg, 5 mol%) and a small magnetic stir bar. The EtOAc (4mL) was added through a rubber septum and the tube was sealed and heated at reflux under nitrogen for 16 hours. The crude reaction mixture was then exposed to air and concentrated *in vacuo*, re-dissolved in methanol (2mL) and transferred to a Fischer-Porter pressure tube. The tube was evacuated thrice with hydrogen, charged to a final pressure of 60 psi and left to stir at ambient temperature for 16 hours. 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 centrifuged) to give 1,4-diammonium-2-butane triflate (28 mg, 91%) as an off-white solid.

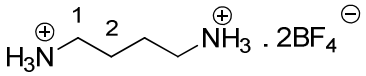
Butane-1,4-diammonium ditriflate



Allyl ammonium triflate (33 mg) gave the title diamine salt (28 mg, 91% yield) (Table 5, Entry 1).

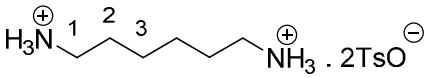
Precipitated from acetone with ether (approx 1: 10) to give an off-white solid, m.p. 208°C (dec). ^{1}H n.m.r. (400 MHz, MeOD): δ 3.03-2.93 (m, 2H), 1.80-1.68 (m, 2H). ^{13}C n.m.r. (150 MHz, MeOD): 121.7 (q, J = 317 Hz), 40.1, 25.6. HRMS (ESI/FTMS): *m/z* $[M\text{-}2TfOH+H]^+$ Calcd for $C_4H_{13}N_2$ 89.1073; Found 89.1080.

Butane-1,4-diammonium ditetrafluoroborate



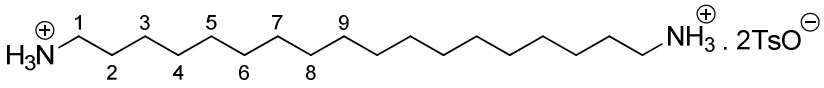
Allyl ammonium tetrafluoroborate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, Entry 2). Precipitated from acetone with ether (approx 1: 10) to give an off-white solid, m.p. 199°C (dec). ^{1}H n.m.r. (400 MHz, MeOD): δ 3.06 – 2.84 (m, 2H), 1.82 – 1.64 (m, 2H). ^{13}C n.m.r. (100 MHz, 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-Butenyl ammonium tosylate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, Entry 3). Precipitated from acetone as an off-white solid, m.p. 172°C. ^{1}H n.m.r. (400 MHz, MeOD): δ7.71 (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 n.m.r. (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



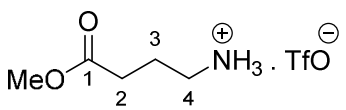
9-Undecenyl ammonium tosylate (50 mg) gave the title diamine salt (89 mg, 99% yield) (Table 5, Entry 4). Precipitated from acetone as a colourless solid. ^{1}H n.m.r. (400 MHz, MeOD): δ 7.71 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.03 – 2.72 (m, 2H), 2.37 (s, 3H), 1.64 (p, 7.4 Hz, 2H), 1.53-1.20 (m, 14H). ^{13}C n.m.r. (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_3H not observed. LRMS (ESI/FTMS): *m/z* $[M\text{-}2TsOH+H]^+$ 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 → Nylon 4, 5 and 6 monomers

The following is an example of a conventional tandem metathesis / hydrogenation procedure for the metathesis of alkenyl ammonium salts (e.g. Table 6, Entry 1): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with allyl ammonium 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 (4mL) was added through a rubber septum and the tube was sealed and heated at reflux under nitrogen for 24 hours (unless specified otherwise). The crude reaction mixture was then exposed to air and concentrated *in vacuo*, re-dissolved in methanol (4 mL) and transferred to a Fischer-Porter pressure tube. The tube was evacuated thrice with hydrogen, charged to a final pressure of 90 psi and left to stir at 60 °C for 16 hours. The vessel was then vented to air and the solvent was removed by rotary evaporation. The mixture was re-dissolved in EtOAc (4 mL), 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 n.m.r. spectroscopy showed >95% conversion to the desired hydrogenated cross product.

Methyl 4-ammonium butanoate triflate

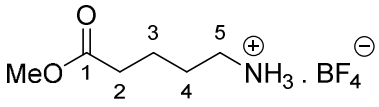


Allyl ammonium triflate (35 mg) gave the title ester (67 mg, 99%) (Table 6, Entry 1).

Product did not crystallise, ~ quantitative conversion by ^{1}H n.m.r. spectroscopy.

^{1}H n.m.r. (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 n.m.r. (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.

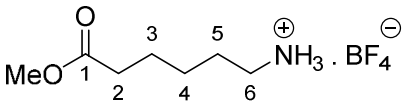
Methyl 5-ammonium pentanoate tetrafluoroborate



3-Butenyl ammonium tetrafluoroborate (37 mg) gave the title ester (39 mg, 99%) (Table 6, Entry 2). Product did not crystallise, ~ quantitative conversion by ^{1}H n.m.r. spectroscopy.

^{1}H n.m.r. (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 n.m.r. (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

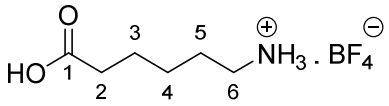


4-Pentenyl ammonium tetrafluoroborate (97 mg) gave title ester (124 mg, 95%) (Table 6, Entry 3).

Product did not crystallise.

IR: ν_{max} 3275m, 2942m, 1716s, 1509s, 1219s, 1004m, 946m, 824s, 771s, 746s, 680s cm^{-1}. ^{1}H n.m.r. (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 n.m.r. (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-Pentenyl ammonium tetrafluoroborate (50 mg) gave the crude title acid (102 mg, 97%) (Table 6, Entry 4). Product did not crystallise. ^{1}H n.m.r. spectroscopy revealed a mixture of the title compound, methyl 6-ammonium hexanoate tetrafluoroborate and succinic acid (^{1}H n.m.r. (400 MHz, MeOD): δ 2.57 (s, 4H)), which was not removed by aqueous extraction.

^{1}H n.m.r. (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 n.m.r. (75 MHz, MeOD) δ 40.6, 34.3, 28.2, 26.8, 25.4, C1 not observed. LRMS (ESI/FTMS): *m/z* $[M\text{-}HBF_4+H]^+$ Calcd for $C_6H_{14}NO_2$ 132.1; Found 132.1.

The crude amino acid mixture was added to methanol (20 mL) containing 3 drops of 40% aqueous HBF_4. The mixture was stirred at 70 °C for 72 hours. 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 n.m.r. spectroscopy). Spectral data were consistent with those reported previously.

Acknowledgements

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Supplementary information

Electronic Supplementary Information is available: Spectral data for new compounds.

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