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Exceptional efficiency of palladium nanoparticle catalyzed Heck cross-coupling in binary task specific ionic liquids

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ABSTRACT

The utilization of the task specific onium salt supported substrates in ionic liquids as solvents (i.e., binary task specific ionic liquids) for palladium nanoparticle catalyzed Heck cross-coupling reactions is presented. Adequate substrates have been prepared and used leading to expected products in very high yields. Exceptionally high turnover (TON = 940,000, TOF = 208,000) can be achieved taking advantages of this combination. Additional advantages of this technology reside in the monitoring of the reaction and purification of products after degrafting which are simplified to the extreme.

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1. Introduction

Since the 1960s, solid phase supported organic synthesis has proven to be one of the best systems for synthesis of libraries of compounds in a short period of time [1]. Phase discrepancy is allowing drastic simplification in purification and, despite the addition of large excesses of reagents usually used to drive reactions to completion, only filtration and washes are often necessary to obtain products with good purities. However, some limitations remain to this appealing technology, including low loading capacity and poor kinetics. Indeed, the heterogeneous nature of mixture is slowing down reactions due to poor diffusion of reagents and/or difficulties in accessing the reaction site on the resin. Moreover, monitoring reactions is somehow tricky and can require special analysis techniques such as HR MAS NMR. As an answer to this drawback, some systems have been developed in solution phase. If perfluorous systems are efficient in multiphasic reactions [2–4], other approaches using dendrimeric alcohols [5], soluble polystyrene [6–8], or polyethylene glycols were successful as well. The last, for example have been used for synthesizing peptides [9], oligosaccharides

[10], or oligonucleotides [11]. Despite their success, multimeric soluble systems still have drawbacks limiting their applicability. Indeed, low loading capacity (PEG 5000 has a 0.2 mmol.g^{-1} loading capacity, for example) along with high water solubility prevent large scale use of PEG as support in synthesis. Furthermore, reagents and side products often co-precipitate during the purification step leading to impure products after cleavage.

An alternative to these systems has arisen recently from the field of ionic liquids. Liquid below 100 °C, ionic liquids consist only of ions conferring them a unique structure and characteristics otherwise unattainable [12]. Besides their extremely low vapor pressure, inflammability and thermal stability, their physical and chemical properties can be finely tuned by adjusting a volo the nature of the cation and the anion. Indeed, by grafting a functional group to an ionic core, one can administrate special chemical properties to an onium salt which can then serve as a reagent or reactant. These so-called Task Specific Ionic Liquids (TSILs) [13] possess all ionic liquid advantages and can be used as templates for supported organic synthesis on onium salts in solution [14,15]. Besides offering a nice alternative to solid phase supported synthesis, advantages of these soluble supports are numerous: reactions are carried out under homogeneous phase, recovering liquid phase kinetics; a classical work-up would consist only in filtration and washing several times to remove excess

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reagent and side products; solubility properties of reagent can be adjusted by changing the counterion; reactions are easily monitored by simple ^{1}H NMR experiments; these supports have high loading capacity (4.87 mmol.g^{-1} for [HO(CH$_2$)$_3$NMe$_3$][BF$_4$] for example). Moreover, if they are not liquid at room temperature or slightly above, due, for example, to functionalization which increases their melting point, they can be used as solutions in molecular solvents or ionic liquids. These binary task specific ionic liquids have already been successfully used for the synthesis of numerous species [13,16]. Some representative examples include peptides synthesis [17], radical reactions [18], multicomponent reactions [19–21], biochemical transformations [22–27] and transition metal catalyzed reactions [28–30]. The last are particularly interesting in the sense that ionic liquids have already been shown to be good solvents for Heck reactions [31–34] for multiple reasons [35–41]. Indeed, the ionic nature of the solvent naturally favors dissolution and capture of catalyst in the ionic liquid phase which can be recycled with or without supporting a ligand [42,43]. It also accelerates considerably kinetic rates by in situ formation of NHC-carbene ligands when using imidazolium salts [44].

In this article, we would like to report the use of task specific onium salts as soluble supports in Heck reactions. Supporting either olefins or aryl halides has been envisioned and used with a comparable success. Moreover, by investigating low catalyst loading, we discovered how [Pd(OAc)$_2$] by reaction with [tmba][PF$_6$] is forming palladium nanoparticles leading to TON up to 10^6 and TOF up to 2×10^5 h^{-1}.

2. Results and discussion

2.1. Supports synthesis

First, onium salt supported acrylates were obtained via coupling between acryloyl chloride **2** and ω-hydroxylated onium salts **1**. Interestingly, triethylamine, classically used in this type of reaction was efficient but led to purification difficulties of salts **3–6** which were bypassed by using potassium carbonate instead followed by a simple filtration of mineral salts after reaction. Following this procedure, 10 different supported acrylates **3** were obtained in good yields (Table 1) with various cations such as imidazolium (Entry 1, **6a$_1$**), pyridinium (Entry 2, **4a$_1$**), tributylphosphonium (Entry 3, **5a$_1$**) or trimethylammonium (Entry 4, **3a$_1$**). Chain spacing length can also be modified from two to six carbons without notably affecting yields (Entry 4–7). Similarly to triflimide, other anions can be used in this reaction, such as bromide (Entry 8, **3b$_1$**), tetrafluoroborate (Entry 9, **3c$_1$**) or hexaflurophosphate (Entry 10, **3d$_1$**). In all cases, acrylates were obtained under pure form with no remaining starting alcohol.

Eventually, one could envisage supporting the Heck reaction via the iodoarenes instead of the acrylates. Therefore, we decided to synthesize supported iodobenzene with the same sort of strategy. Benzoylation of N,N-dimethyl-1-aminobutan-4-ol **7** with 4-iodo benzoyl chloride under the same reaction conditions as previously
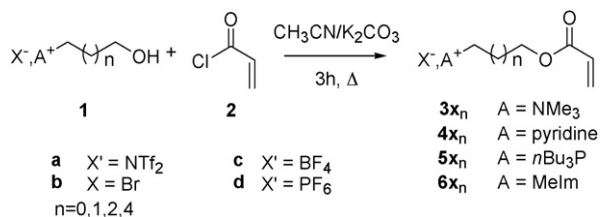
described afforded N,N-dimethyl-1-aminobutan-4-yl-4'-iodobenzoate **9** in 88% yield. Quaternisation of tertiary amine **9** led to supported iodobenzene **10x$_n$** bearing a counteranion depending on the reagent used for methylation (triflate, iodide, methylsulfate). More diversity could be introduced by a simple ion metathesis in water leading to triflimide, hexafluorophosphate and tetrafluoroborate analogs (Method A). After anion metathesis, halide content turned out to be negligible as the silver nitrate test was negative (Schemes 1 and 2, Table 2).
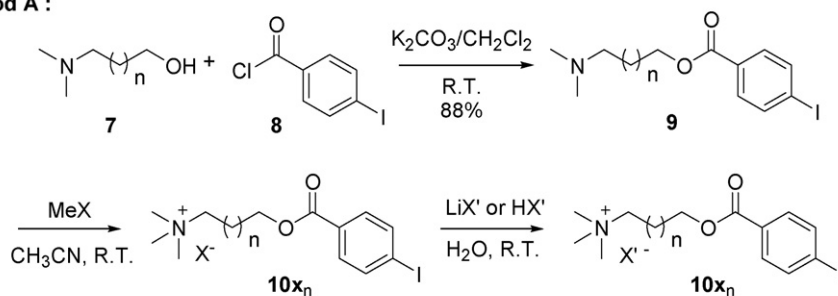
2.2. Conditions optimization

Indeed, the Heck reaction has already been largely studied in ionic liquids. This coupling reaction is particularly well suited to ionic liquids physicochemical properties as it is favored by using polar solvents or in the presence of ammonium salts [45] which stabilize Pd complexes [46]. Preliminary experiments were conducted in both ionic liquid and molecular solvents. In the presence of 1% of [Pd(OAc)$_2$] as a catalyst and potassium carbonate as a base, supported olefin **3a$_1$** reacts efficiently at 80 °C with iodobenzene to afford cinnamate **Ph-14a$_1$**. Quantitative conversions were achieved in [tmba][NTf$_2$] and [emim][NTf$_2$] after 2 h at 110 °C, but only 70% were observed in acetonitrile. Furthermore E/Z selectivity was highly superior in ionic liquids as only the (E)-isomer is observed where 12% of the (Z)-compound was obtained in CH$_3$CN. Notably, supported acrylate is much more reactive than the corresponding methyl ester as unsupported acrylate underwent reaction with a poor 26% conversion under the same conditions in acetonitrile (Scheme 3).

Like traditionally observed in the case of the Heck reaction, increasing temperature is improving kinetics, and either organic or mineral bases can alternatively be

Table 1
Supported acrylates prepared following Scheme 1 synthesis.

Entry	A$^+$	n	X−	Product	Yield^a (%)
1	Imidazolium	1	NTf$_2^-$	**6a$_1$**	85
2	Pyridinium	1	NTf$_2^-$	**4a$_1$**	80
3	Tri(n-butyl)phosphonium	1	NTf$_2$	**5a$_1$**	77
4	Trimethylammonium	1	NTf$_2^-$	**3a$_1$**	98
5	Trimethylammonium	0	NTf$_2^-$	**3a$_0$**	90
6	Trimethylammonium	2	NTf$_2^-$	**3a$_2$**	77
7	Trimethylammonium	4	NTf$_2^-$	**3a$_4$**	78
8	Trimethylammonium	1	Br$^-$	**3b$_1$**	98
9	Trimethylammonium	1	BF$_4^-$	**3c$_1$**	93
10	Trimethylammonium	1	PF$_6^-$	**3d$_1$**	90

^{a} Isolated yield after purification.

Scheme 1. Preparation of onium salt supported acrylates.

Method A :

Method B :

a X' = NTf$_2$ e X = I
b X = Br   f X = SO$_4$Me
c X' = BF$_4$ g X = Cl
d X' = PF$_6$ h X = OTf

10x$_n$ A = NMe$_3$
13x$_n$ A = MeIm
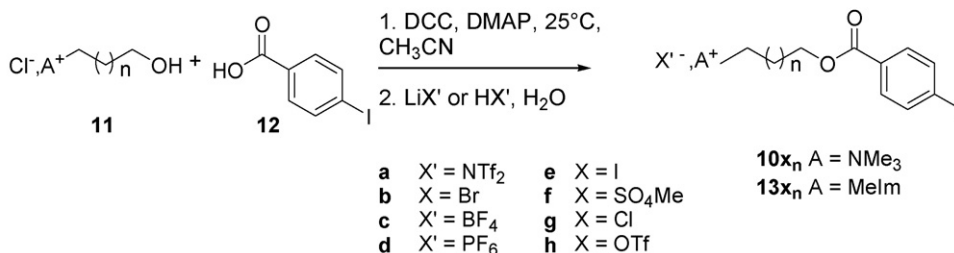
Scheme 2. Preparation of onium salt supported aryl iodides.

used although Et$_3$N was found to accelerate reactions. An attempt to diminish palladium concentration turned out to be particularly interesting. Indeed, for practical reasons, when using less than 100 ppm of Pd, simply weighting palladium acetate on a precision scale is not sufficiently satisfactory enough for loading accuracy. We decided to dilute palladium acetate in an ionic matrix whose melting point is above room temperature [tmba][PF$_6$] (m.p. = 156 °C). By simply heating above this temperature a mixture of 0.1% [Pd(OAc)$_2$] in [tmba][PF$_6$] under inert atmosphere, a grey powder **Pd-CAT** was obtained after cooling which can be used directly to catalyze Heck reactions. This powder **Pd-CAT** is composed of palladium nanoparticles (4 nm) probably responsible for activity and larger aggregates (~10 μm) (Fig. 1).

Our best result was obtained using [tmba][PF$_6$] (m.p. = 156 °C) as a solvent: at 110 °C, using only 1 ppm of **Pd-CAT**, 94% conversion was obtained after 270 min

corresponding to a TON of 9.4×10^5 and a TOF of $2 \times 10^5 \, h^{-1}$. These results are particularly significant for ligandless palladium catalysis as only few examples [47] are available in the literature with catalytic loading reaching below 10 ppm, even using a specially designed ligand (Scheme 4).

Similarly, supported iodobenzene was tested in Heck reaction with acrylates. To our delight, the reaction is equally efficient and cinnamic esters are isolated in good yields after only 10 min at 110 °C using 0.1% **Pd-CAT**. Catalyst loading diminution was also investigated in this case, and using 10 ppm of **Pd-CAT** in the same conditions as previously described, quantitative conversion was achieved after a short 90-min period. However, attempts to use only 1 ppm of palladium turned out to be less successful as only 35% conversion was reached after 12 h where 99% were attained using **3a$_1$** under the very same conditions. Transesterification of the crude cinnamic ester **Ph-14a$_1$** in boiling methanol in the presence of traces of HCl gave quantitatively the methyl trans cinnamic ester after removal of excess of MeOH under vacuum and extraction with ether in an excellent state of purity > 99%, as indicated by GC/MS analysis. By using a two-carbon chain onium salt support, the hydrolysis of cinamate esters occurred during work-up. For linkers bearing more than four carbons, the final transesterification was too slow for practical applications. Three carbons turned out to be the best compromise between reactivity and stability.

Table 2
Supported aryl iodides prepared following Scheme 2 procedure.

Entry	Product	Method	Reagent	Yield[a] (%)
1	**10e$_2$**	A	MeI	99
2	**10h$_2$**	A	MeOTf	96
3	**10f$_2$**	A	Me$_2$SO$_4$	94
4	**10a$_1$**	B	LiNTf$_2$	95
5	**10d$_2$**	A	MeI then LiNTf$_2$	90
6	**10c$_0$**	B	HBF$_4$	90
7	**10c$_1$**	A	MeI then HBF$_4$	86
8	**10c$_2$**	B	HBF$_4$	83
9	**10c$_4$**	A	MeI then HBF$_4$	87
10	**10d$_2$**	A	MeI then HPF$_6$	96
11	**10g$_0$**	B	–	93
12	**10g$_1$**	B	–	95
13	**13b$_0$**	B	–[b]	92
14	**13c$_0$**	B	HBF$_4$	85

[a] Isolated yield from **7** or **11**.
[b] Bromide was used instead of **11**.
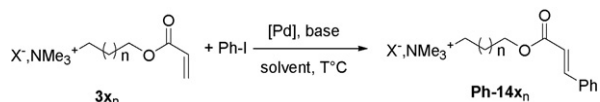
Scheme 3. Mizoroki-Heck cross-coupling with supported acrylates.
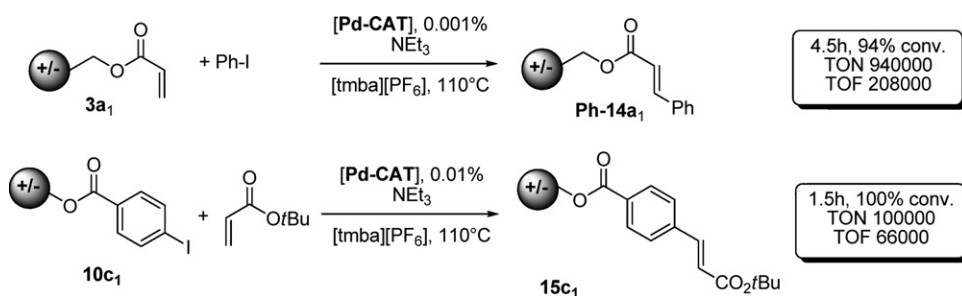
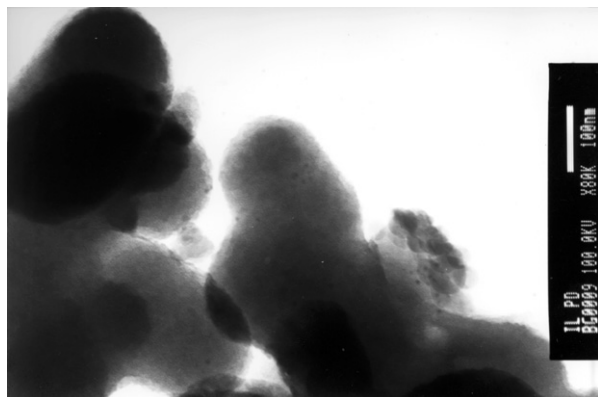**Scheme 4.** Mizoroki-Heck cross-coupling using **Pd-CAT**.

Fig. 1. TEM picture of **Pd-CAT**.

Concerning use of supported iodobenzene, the reaction was found to be much more efficient in ammonium salt than in imidazolium based ionic liquids, probably due to inhibition of the catalyst by formation of Pd-NHC complexes [48]. However, this effect was only detectable using less than 100 ppm of palladium, slowing down the reaction enough to accurately perform kinetic experiments. Interestingly, support counter anion showed great influence on kinetics. Using 100 ppm of $[Pd(OAc)_2]$ in [tmba][NTf$_2$], the reaction was quantitative after 1 h with **10c$_2$** (BF$_4$) where lower conversion was observed for the same time with another anion (PF$_6$, **10d$_2$**, 93%; NTf$_2$, **10a$_2$**, 93%; OTf, **10h$_2$**, 82%; MeSO$_4$, **10f$_2$**, 41%; I, **10e$_2$**, 28%). Ester **15c$_1$** could be transesterified under the conditions described above to the corresponding methyl cinnamic diester in very good yield. After transesterification, the remaining Binary Task Specific Ionic Liquids could be recycled several times without loss of matter beside other than mechanical loss during solid transfer. Interestingly, if the ppm level of palladium could not be reused, no side reactions were observed even after several cycles.

2.3. Synthesis of a library of cinnamic esters

In order to validate our methodology for parallel synthesis, we used this method to prepare a small library of substituted acrylates. Hence, a mixture of nine substituted iodobenzenes has been coupled with the supported acrylate **3a$_1$**. Noteworthy, all conversions were quantitative after 3 h in [tmba][NTf$_2$]. Supported cinnamates were obtained with good purity as no (Z)-isomer could be detected by ^{1}H NMR (< 1%) (Table 3).

Table 3
Synthesis of a library of cinnamic esters.

Entry	Ar	Conv.[a] (%)	E/Z ratio[a]
1	Ph	100	99/1
2	2-MePh	100	99/1
3	3-MePh	100	99/1
4	4-MePh	100	99/1
5	1-Napth	100	99/1
6	2-NO$_2$Ph	100	99/1
7	4-MeOPh	100	99/1
8	4-FPh	100	99/1
9	3-BrPh	100	99/1

[a] Determined by ^{1}H NMR.

3. Conclusion

We showed here that the onium salt supported organic synthesis (OSSOS) strategy is highly versatile and can also be used in combination with palladium catalyzed reaction. Noteworthy, we found that a simple catalyst, prepared from a mixture of a high melting point onium salt and palladium acetate displays exceptional activity as a ligandless catalyst [49]. Moreover, this material, mostly composed of nanoparticles is a non-hygroscopic, grey powder, *stable at room temperature under inert atmosphere*.

4. Experimental

4.1. General methods

All glassware was oven-dried prior to use and reactions were run under an inert atmosphere of argon using standard Schlenk techniques. Yields reported were from isolated products and determined to be pure by GC (DB-5 column) or TLC (pre-coated plates of silica gel 60 F_{254}, stained with a potassium permanganate solution), and NMR spectroscopy. Solvents were carefully dried and purified following known procedures prior to use [50]. All other standard chemicals were purchased from Fisher, Alfa Aesar or Aldrich Chemical Co. and used without further purification. Reactions were monitored by gas chromatography (GC-MS) (GC system: HP 6890 series, Mass selective detector HP 5973) using a capillary column DB-5MS. Column chromatography purifications were performed on silica gel Si 60 (40–63 μm, 230–400 mesh, Merck). Melting points were determined on an electro-thermal IA9300 digital melting point instrument. NMR spectra were recorded on a Bruker ARX 200 (1H: 200.13 MHz, 13C: 50.32 MHz) or AC 300 P (1H: 300.13 MHz), ^{1}H chemical shifts (δ) are given with apparent multiplicities in ppm relative to TMS as external standard, J values in Hz, ^{13}C chemical shifts are given relative to the central signal of CDCl$_3$ at 77.0 ppm. IR spectra were obtained on a Bio-Rad FTS 175C FT-IR spectrophotometer. High resolution mass spectra measurements were performed at the Centre regional de mesures physiques de l'Ouest (CRMPO, University of Rennes 1) using a Varian MAT 311 with BE geometry (reversed Nier-Johnson) and EI athod or Micromass ZABSpec TOF with EBE OA TOF geometry with LSIMS ionization (liquid secondary ion mass spectrometry) at 8 kV with Cs+ gun in *m*-nitrobenzyl alcohol (*m*NBA).

4.2. General procedure for supported acrylate synthesis (Procedure I)

To a solution of hydroxyl derivatized onium salt and K$_2$CO$_3$ (5 eq) in acetonitrile (0.1 M) was added 3 eq. of acylating agent. After 2 h at 80 °C, solvents and unreacted acyl chloride were removed under vacuum. Product was extracted with 3 × 10 mL.mmol^{-1} CH$_2$Cl$_2$. Organic layers were combined and concentrated under reduced pressure to afford analytically pure onium salt supported acrylate.

4.3. General procedure for anion metathesis with HPF$_6$ (Procedure II)

To a solution of onium halide (0.1 mmol) in 15 mL of water was added 0.15 mmol of an aqueous HPF$_6$ solution (60%). After 2 h at r.t., a solid has formed. Filtration and washes (3 × 10 mL Et$_2$O) afforded analytically pure onium hexafluorophosphate.

4.4. General procedure for anion metathesis with LiNTf$_2$ (Procedure III)

To a solution of onium halide (0.1 mmol) in 10 mL of water was added 0.11 mmol of an aqueous LiNTf$_2$ solution (10 mL). After 2 h at r.t., the aqueous phase was extracted with 3 × 15 mL of CH$_2$Cl$_2$. Organic fractions were combined and concentrated under reduced pressure. To remove remaining traces of water, the oil was dried under vacuum (0.5 mmHg) at 60 °C for 2 h.

4.5. General procedure for anion metathesis with HBF$_4$ (Procedure IV)

To a solution of onium halide (0.1 mmol) in 15 mL of water was added 0.15 mmol of an aqueous HBF$_4$ solution (50%). After 12 h at r.t., water was removed under reduced pressure affording a white solid. The residue was filtered and washed with 2 × 15 mL Et$_2$O affording analytically pure onium tetrafluoroborate.

4.6. General procedure for Heck coupling with supported acrylate (Procedure V)

A mixture of **3a$_1$** (1.5 mmol), iodobenzene (839 μL, 7.5 mmol, 5 eq), [Pd(OAc)$_2$] (2.43 mg, 0.015 mmol, 1%), and K$_2$CO$_3$ (331 mg, 2.25 mmol, 1.5 eq) in 2 mL of [tmba][NTf$_2$] or (DMF) was heated at 80 °C. Reaction was monitored by ^{1}H NMR. After completion of the reaction, remaining reactants were eliminated with washes using alternatively water and Et$_2$O.

4.7. General procedure for Heck coupling with supported iodobenzoic acids (Procedure VI)

A mixture of **10a$_2$** (1.5 mmol), olefin (7.5 mmol, 5 eq), [Pd(OAc)$_2$] (2.43 mg, 0.015 mmol, 1%), and K$_2$CO$_3$ (331 mg, 2.25 mmol, 1.5 eq) in 2 mL of [tmba][NTf$_2$] (or DMF) was heated at 80 °C. Reaction was monitored by ^{1}H NMR; at the end of the reaction, remaining reactants were eliminated with washes using alternatively water and Et$_2$O.

4.8. Onium salt supported products

4.8.1. [AcrEtTMA][NTf$_2$] **3a$_0$** (2-acryolyloxyethyl) trimethylammonium bistrifluoromethanesulfonamide

Following general procedure I using (2-hydroxyethyl)-trimethylammonium bistrifluoromethanesulfonamide [HOEtTMA][NTf$_2$] and acryloyl chloride, [AcrEtTMA][NTf$_2$] was obtained in 90% yield as a pink oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 3.50(s, 9H), 4.03–4.40 (m, 2H), 4.73–4.85 (m, 2H), 6.05 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.5 Hz), 6.25 (dd, 1H,

J_1 = 10.5 Hz, J_2 = 17.3 Hz), 6.45 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.3 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 54.0 (t, J = 4.2 Hz), 58.2, 65.2, 121.0 (q, J_{CF} = 374 Hz), 128.8, 132.2, 165.5. LRMS(APCI): [C$^+$] (C$_8$H$_{16}$NO$_2$) 158.3.

4.8.2. [AcrPrTMA][Br] 3b$_1$ (3-acryolyloxypropyl) trimethylammonium bromide

Following general procedure **I** using (3-hydropropyl)-trimethylammonium bromide [HOPrTMA][Br] and acryloyl chloride, [AcrPrTMA][Br] was obtained in 98% yield as a colorless oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.15–2.20 (m, 2H), 3.15 (s, 9H), 3.48–3.52 (m, 2H), 4.18 (t, 2H, J = 6.0 Hz), 5.75 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.5 Hz), 6.15 (dd, 1H, J_1 = 10.5 Hz, J_2 = 17.3 Hz), 6.15 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.3 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 21.7, 52.2 (t, J = 4.2 Hz), 60.4 (t, J = 3.0 Hz), 62.6, 127.4, 130.6, 165.0. HRMS(FAB): [C$^+$] (C$_9$H$_{18}$NO$_2$). Calcd: 172.1338, found: 172.1356.

4.8.3. [AcrPrTMA][BF$_4$] 3c$_1$ (3-acryolyloxypropyl) trimethylammonium tetrafluoroborate

Following general procedure **I** using (3-hydropropyl)-trimethylammonium tetrafluoroborate [HOPrTMA][BF$_4$] and acryloyl chloride, [AcrPrTMA][BF$_4$] was obtained in 93% yield as a white solid. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.28–3.31 (m, 2H), 3.32 (s, 9H), 3.06–3.15 (m, 2H), 4.52 (t, 2H, J = 6.6 Hz), 5.80 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.0 Hz), 6.05 (dd, 1H, J_1 = 18.3 Hz, J_2 = 10.0 Hz), 6.15 (dd, 1H, J_1 = 1.9 Hz, J_2 = 18.3 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 22.8; 53.3, 61.5, 63.8, 128.5, 131.7, 167.3. LRMS(APCI): [2C$^+$, BF$_4$] 431.

4.8.4. [AcrPrTMA][NTf$_2$] 3a$_1$ (3-acryolyloxypropyl) trimethylammonium bistrifluoromethanesulfonamide

Following general procedure **I** using (3-hydropropyl)-trimethylammonium bistrifluoromethanesulfonamide [HOPrTMA][NTf$_2$] and acryloyl chloride, [AcrPrTMA][NTf$_2$] was obtained in 90% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.22–2.25 (m, 2H), 3.25 (s, 9H), 3.60–3.75 (m, 2H), 4.15 (t, 2H, J = 6.0 Hz), 5.80 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.7 Hz), 6.05 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.7 Hz), 6.15 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.2 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 29.2, 54.2 (t, J_{C-N} = 4.0 Hz), 65.2, 65.2, 121.0 (q, J_{CF} = 374 Hz), 129.4, 132.1, 165.6. ^{19}F (282 MHz, acetone-d_6): −79.8. HRMS(FAB): [C$^+$] (C$_9$H$_{18}$NO$_2$). Calcd: 172.1338, found: 172.1346.

4.8.5. [AcrPrTMA][PF$_6$] 3d$_1$ (3-acryolyloxypropyl) trimethylammonium hexafluorophosphate

Following general procedure **I** using (3-hydropropyl)-trimethylammonium hexafluorophosphate [HOPrTMA][PF$_6$] and acryloyl chloride, [AcrPrTMA][PF$_6$] was obtained in 90% yield as a white solid. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.28–3.31 (m, 2H), 3.32 (s, 9H), 3.06–3.15 (m, 2H), 4.52 (t, 2H, J = 6.0 Hz), 5.80 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.2 Hz), 6.05 (dd, 1H, J_1 = 17.1 Hz, J_2 = 10.2 Hz), 6.15 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.2 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 22.4, 52.7 (t, J = 3.9 Hz), 61.0, 63.8 (t, J = 3.2 Hz), 128.1, 131.2, 165.7. HRMS(FAB): [2C$^+$, PF$_6$] (C$_{18}$H$_{36}$N$_2$O$_4$PF$_6$). Calcd: 489.2317, found: 489.2319.

4.8.6. [AcrBuTMA][NTf$_2$] 3a$_2$ (6-acryolyloxybutyl) trimethylammonium bistrifluoromethanesulfonamide

Following general procedure **I** using (4-hydroxybutyl)-trimethylammonium bistrifluoromethanesulfonamide [HOBuTMA][NTf$_2$] and acryloyl chloride, [AcrBuTMA][NTf$_2$] 3a$_2$ was obtained in 77% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.70–1.90 (m, 2H), 2.00–2.20 (m, 2H), 3.40 (s, 9H), 3.58–3.72 (m, 2H), 4.25 (t, 2H, J = 6.0 Hz), 5.80 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.7 Hz), 6.05 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.7 Hz), 6.15 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.2 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 20.9, 26.4, 54.0, 64.5, 67.4, 122.2 (q, J_{CF} = 374 Hz), 129.7, 131.8, 167.0. HRMS (FAB): [C$^+$] (C$_{10}$H$_{20}$NO$_2$). Calcd: 186.1494, found: 186.1506.

4.8.7. [AcrHexTMA][NTf$_2$] 3a$_4$ (6-acryolyloxyhexyl) trimethylammonium bistrifluoromethanesulfonamide

Following general procedure **I** using (6-hydrohexyl)-trimethylammonium bistrifluoromethanesulfonamide [HOHexTMA][NTf$_2$] and acryloyl chloride, [AcrHexT-MA][NTf$_2$] 3a$_4$ was obtained in 78% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.40–1.60 (m, 4H), 1.65–1.85 (m, 2H), 1.90–2.10 (m, 2H), 3.32 (s, 9H), 3.06–3.15 (m, 2H), 4.52 (t, 2H, J = 6.4 Hz), 5.80 (dd, 1H, J_1 = 2.1 Hz, J_2 = 10.1 Hz), 6.05 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.1 Hz), 6.15 (dd, 1H, J_1 = 2.1 Hz, J_2 = 17.2 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 23.4, 26.1, 26.5, 26.5, 53.6, 64.8, 67.4, 121.0, 129.6, 131.1, 166.6.

4.8.8. [AcrPrTBP][NTf$_2$] 5a$_1$ (3-acryolyloxypropyl) tributylphosphonium bistrifluoromethanesulfonamide

Following general procedure **I** using (3-hydropropyl)-tributylphosphonium bistrifluoromethanesulfonamide [HOPrTBP][NTf$_2$] and acryloyl chloride, [AcrPrTBP][NTf$_2$] was obtained in 77% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.00 (t, 9H, J = 7.2 Hz), 1.45–1.85 (m, 12H), 2.10–2.28 (m, 2H), 2.48–2.70 (m, 8H), 4.30 (t, 2H, J = 6.3 Hz), 5.58 (dd, 1H, J_1 = 10.2 Hz, J_2 = 1.9 Hz), 6.18 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.2 Hz), 6.40 (dd, 1H, J_1 = 17.2 Hz, J_2 = 1.9 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 13.1, 17.8, 18.8, 21.1, 23.4, 23.5, 23.9, 63.8, 121.1 (q, J_{CF} = 374 Hz), 128.6, 131.1, 165.7.

4.8.9. [AcrPrPyr][NTf$_2$] 4a$_1$ (3-acryolyloxypropyl)pyridinium bistrifluoromethanesulfonamide

Following general procedure **I** using (3-hydropropyl)-pyridinium bistrifluoromethanesulfonamide [HOPr-Pyr][NTf$_2$] and acryloyl chloride, [AcrPrPyr][NTf$_2$] was obtained in 80% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.43–2.72 (m, 2H), 4.15 (t, 2H, J = 5.8 Hz), 5.08 (t, 2H, J = 6.8 Hz), 5.90 (dd, 1H, J_1 = 10.3 Hz, J_2 = 2.0 Hz), 6.18 (dd, 1H, J_1 = 17.0 Hz, J_2 = 10.3 Hz), 6.40 (dd, 1H, J_1 = 17.0 Hz, J_2 = 2.0 Hz), 8.10 (t, 2H, J = 7.0 Hz), 8.52 (m, 1H), 8.98 (m, 2H). ^{13}C (50 MHz, acetone-d_6): δ = 30.4, 60.0, 61.4, 121.0 (q, J_{CF} = 374 Hz), 128.7, 129.0, 131.4, 145.5, 146.5, 165.8. HRMS(FAB): [C$^+$] (C$_{11}$H$_{14}$NO$_2$). Calcd: 192.1025, found: 192.1026.

4.8.10. [AcrPrMIm][NTf$_2$] 6a$_1$ (3-acryolyloxypropyl) methylimidazolium bistrifluoromethanesulfonamide

Following general procedure **I** using (3-hydropropyl) methylimidazolium bistrifluoromethanesulfonamide

[HOPrMIm][NTf$_2$] and acryloyl chloride, [AcrPrMIm][NTf$_2$] was obtained in 85% yield as a pale yellow oil. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.30–2.50 (m, 2H), 4.15 (s, 3H), 4.28 (t, 2H, J = 6.0 Hz), 4.63 (t, 2H, J = 6.9 Hz), 5.95 (dd, 1H, J_1 = 1.9 Hz, J_2 = 10.7 Hz), 6.18 (dd, 1H, J_1 = 17.2 Hz, J_2 = 10.7 Hz), 6.40 (dd, 1H, J_1 = 1.9 Hz, J_2 = 17.2 Hz), 7.80 (t, 1H, J = 1.7 Hz), 7.95 (t, 1H, J = 1.7 Hz), 9.2 (s, 1H). ^{13}C (50 MHz, acetone-d_6): δ = 29.3, 36.2, 47.4, 61.4, 121.0 (q, J_{CF} = 374 Hz), 123.0, 124.3, 128.4, 131.3, 136.9, 166.1. HRMS(FAB): [C$^+$] (C$_{10}$H$_{15}$N$_2$O$_2$). Calcd: 195.1134, found: 192.1132.

4.8.11. 4-Dimethylaminobutyl 4-iodobenzoate 9$_2$

To a solution of 4-hydroxybutyldimethylamine (2.8 g, 23.9 mmol) and K$_2$CO$_3$ (6.6 g) in 10 mL of CH$_2$Cl$_2$ were added at 0 °C 4-iodobenzoyl chloride (7.0 g, 26.3 mmol). The reaction mixture was allowed to warm up to room temperature. After 3 h at r.t., the mixture was filtered and concentrated under reduced pressure to afford 7.3 g of a colorless oil in analytically pure form (88% yield). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.78–1.90 (m, 4H), 2.50 (s, 6H), 2.65 (t, 2H, J = 5.3 Hz), 4.35 (t, 2H, J = 6.0 Hz), 7.70–7.85 (m, 4H). ^{13}C (50 MHz, CDCl$_3$): δ = 20.2, 24.9, 43.5, 57.3, 63.5, 99.0, 128.4, 129.4, 136.2, 164.3.

4.8.12. [IBzBuTMA][OTf] 10h$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium trifluoromethanesulfonate

To a solution of 9$_2$ (4.0 g, 11 mmol) in acetonitrile (10 mL) was added at 0 °C methyltriflate (1.1 mL, 13.5 mmol). After 15 min at 0 °C, the white solid is filtered and washed with 3 × 10 mL of Et$_2$O to afford 4.83 g of a white solid (96% yield). m.p. 176–178 °C. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 1.80–2.10 (m, 4H), 3.06 (s, 9H), 3.35–3.45 (m, 2H), 4.40 (t, 2H, J = 6.1 Hz), 7.85 (d, 2H, J = 8.6 Hz), 8 (d, 2H, J_1 = 8.6 Hz). ^{13}C (50 MHz, CD$_3$CN): δ = 19.2, 24.7, 52.5 (t, J = 4.0 Hz), 63.7, 65.6 (t, J = 3.2 Hz), 99.9, 121.3 (q, J_{C-F} = 321 Hz), 129.6, 130.6, 137.6, 165.4. LRMS(FAB): (2C$^+$, OTf$^-$)$^+$ (C$_{29}$H$_{42}$N$_2$O$_7$F$_3$I$_2$S) 873.1.

4.8.13. [IBzBuTMA][MeSO$_4$] 10f$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium trifluoromethanesulfate

To a solution of 9$_2$ (4.0 g, 11 mmol) in acetonitrile (10 mL) was added at 0 °C dimethylsulfate (1.24 mL, 13.2 mmol). After 15 min at 0 °C, the white solid was filtered and washed with 3 × 10 mL of Et$_2$O to afford 4.99 g of a white solid (96% yield). m.p. 190–192 °C. ^{1}H NMR (200 MHz, MeOD): δ = 1.80–2.10 (m, 4H), 3.20 (s, 9H), 3.38–3.50 (m, 2H), 3.70 (s, 3H), 4.40 (t, 2H, J = 6.0 Hz), 7.78 (dd, 2H, J_1 = 2.0 Hz, J_2 = 6.8 Hz), 7.90 (dd, 2H, J_1 = 2.0 Hz, J_2 = 6.8 Hz). ^{13}C (50 MHz, MeOD): δ = 21.3, 27.0, 54.3 (t, J = 3.9 Hz), 56.0, 66.1, 67.8, 102.4, 131.1, 132.5, 139.7, 168.5. HRMS(FAB): (C$^+$) (C$_{14}$H$_{21}$NO$_2$I). Calcd: 362.0617, found: 362.0618.

4.8.14. [IBzBuTMA][I] 10f$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium iodide

To a solution of 9$_2$ (4.0 g, 11 mmol) in acetonitrile (10 mL) was added at 0 °C iodomethane (820 μL mL, 13.2 mmol). After 15 min at 0 °C, the white solid was filtered and washed with 3 × 10 mL of Et$_2$O to afford 5.32 g of a white solid (99% yield). m.p. 248–250 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.90–2.05 (m, 4H), 3.20 (s, 9H), 3.42–3.55 (m, 2H), 4.45 (t, 2H, J = 6.1 Hz), 7.80 (d, 2H, J = 8.7 Hz), 7.95 (d, 2H, J_1 = 8.7 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 19.9, 25.5, 53.4 (t, J_{C-N} = 4.1 Hz), 65.1, 66.4, 101.6, 131.2, 131.4, 138.4, 166.8. HRMS(FAB): (2C$^+$, I$^-$) (C$_{14}$H$_{21}$NO$_2$I$_2$) 851.1.

4.8.15. [IBzBuTMA][PF$_6$] 10d$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium hexafluorophosphate

Following procedure II using 10f$_2$, [IBzBuTMA][PF$_6$] was obtained as a white solid in 96% yield. m.p. 204–206 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.05–2.20 (m, 2H), 2.28–2.47 (m, 2H), 3.6 (s, 9H), 3.80–3.97 (m, 2H), 4.6 (t, 2H, J = 6.3 Hz), 8 (d, 2H, J = 8.6 Hz), 8.15 (d, 2H, J = 8.6 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 21.0, 26.6, 54.1 (t, J = 4.0 Hz), 65.3, 67.4 (t, J = 3.2 Hz), 101.6, 131.2, 132.3, 139.2, 166.7. HRMS(FAB): (2C$^+$, PF$_6^-$)$^+$ (C$_{28}$H$_{42}$N$_2$O$_4$F$_6$I$_2$P). Calcd: 869.0876, found: 869.0879.

4.8.16. [IBzBuTMA][NTf$_2$] 10a$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium bistrifluoromethylsulfonamide

Following procedure III using 10f$_2$, [IBzBuTMA][NTf$_2$] was obtained as a white solid in 90% yield. m.p. 48–50 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.82–2.00 (m, 2H), 2.10–2.22 (m, 2H), 3.38 (s, 9H), 3.60–3.72 (m, 2H), 4.40 (t, 2H, J = 6.2 Hz), 7.80 (d, 2H, J = 8.5 Hz), 7.95 (d, 2H, J = 8.5 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 26.7, 29.1, 54.1 (t, J_{C-N} = 4.1 Hz), 65.3, 67.4, 101.6, 121.2 (q, J_{C-F} = 321 Hz), 131.2, 132.3, 139.2, 166.7. HRMS(FAB): (2C$^+$, NTf$_2^-$)$^+$ (C$_{30}$H$_{42}$N$_3$O$_8$F$_6$I$_2$S$_2$). Calcd: 1004.0407, found: 1004.0427.

4.8.17. [IBzBuTMA][Cl] 10g$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium chloride

A solution of [HOBuTMA][Cl], DCC (1.5 eq), 4-iodobenzoic acid (1.5 eq) and DMAP (0.2 eq) in acetonitrile (0.1 M) was allowed to react 4 h at room temperature. After concentration under reduced pressure, 4-iodobenzoic acid crushed out upon water addition (10 mL). After filtration and concentration under vacuum, product was recrystallized in acetone, and used directly in anion metathesis reactions without further purification.

4.8.18. [IBzBuTMA][BF$_4$] 10c$_2$ {4-(4-iodobenzoyloxy) butyl}trimethylammonium tetrafluoroborate

Following procedure IV using 10g$_2$, [IBzBuTMA][BF$_4$] was obtained as a white solid in 86% yield. m.p. 184–186 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 1.90–2.00 (m, 2H), 2.15–2.28 (m, 2H), 3.40 (s, 9H), 3.65–3.80 (m, 2H), 4.42 (t, 2H, J = 6.3 Hz), 7.85 (d, 2H, J = 8.6 Hz), 8.15 (d, 2H, J = 8.6 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 21.0, 26.6, 54.0 (t, J = 4.0 Hz), 65.3, 67.4, 101.5, 131.2, 132.3, 139.2, 166.7. HRMS(FAB): (2C$^+$, BF$_4^-$)$^+$ (C$_{28}$H$_{42}$N$_2$O$_4$F$_4$I$_2$B). Calcd: 811.1263, found: 811.1259.

4.8.19. [IBzPrTMA][Cl] 10g$_1$ {3-(4-iodobenzoyloxy) propyl}trimethylammonium chloride

A solution of [HOPrTMA][Cl], DCC (1.5 eq), 4-iodobenzoic acid (1.5 eq) and DMAP (0.2 eq) in acetonitrile (0.1 M) was allowed to react 4 h at room temperature. After concentration under reduced pressure, 4-iodobenzoic acid crushed out upon water addition (10 mL). After filtration

and concentration under vacuum, product was recrystallized in acetone, and used directly in anion metathesis reactions without further purification. (95% yield) m.p. 218–220 °C. ^{1}H NMR (200 MHz, D$_2$O): δ = 2.12–2.35 (m, 2H), 3.12 (s, 9H), 3.38–3.52 (m, 2H), 4.32 (t, 2H, J = 5.9 Hz), 7.65 (dd, 2H, J_1 = 1.8 Hz, J_2 = 6.6 Hz), 7.83 (dd, 2H, J_1 = 1.8 Hz, J_2 = 6.7 Hz). ^{13}C (50 MHz, D$_2$O): δ = 22.6, 53.4 (t, J_{C-N} = 3.9 Hz), 62.8, 64.2, 102.0, 128.8, 131.2, 138.2, 167.8. LRMS(APCI): (C$^+$) (C$_{13}$H$_{19}$INO$_2$) 348.3.

4.8.20. [IBzPrTMA][NTf$_2$] 10a$_1$ {3-(4-iodobenzoyloxy) propyl}trimethylammonium bistrilfuoromethylsulfonamide

Following procedure **III** using **10g$_1$**, [IBzBuTMA][NTf$_2$] was obtained as a white solid in 95% yield. m.p. 48–50 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.40–2.60 (m, 2H), 3.47 (s, 9H), 3.80–4.00 (m, 2H), 4.53 (t, 2H, J = 5.9 Hz), 7.83 (d, 2H, J = 8.3 Hz), 7.97 (d, 2H, J = 8.3 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 23.1, 53.4 (t, J = 3.8 Hz), 62.2, 64.5, 100.9, 120.5 (q, J_{CF} = 321 Hz), 130.0, 131.5, 138.3, 165.7. LRMS(APCI): (C$^+$) (C$_{13}$H$_{19}$INO$_2$) 348.3.

4.8.21. [IBzPrTMA][BF$_4$] 10c$_1$ {3-(4-iodobenzoyloxy) propyl}trimethylammonium tetrafluoroborate

Following procedure **IV** using **10g$_1$**, [IBzBuTMA][BF$_4$] was obtained as a white solid in 83% yield. m.p. 190–192 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ = 2.38–2.63 (m, 2H), 3.45 (s, 9H), 3.75–3.93 (m, 2H), 4.52 (t, 2H, J = 5.9 Hz), 7.85 (dd, 2H, J_1 = 1.9 Hz, J_2 = 6.6 Hz), 7.98 (dd, 2H, J_1 = 1.9 Hz, J_2 = 6.7 Hz). ^{13}C (50 MHz, acetone-d_6): δ = 23.0, 53.2 (t, J = 4.0 Hz), 62.3, 64.2, 100.8, 130.0, 131.6, 138.3, 165.8. LRMS(APCI): (C$^+$) (C$_{13}$H$_{19}$INO$_2$) 348.3.

4.8.22. [IBzEtTMA][Cl] 10g$_0$ {2-(4-iodobenzoyloxy)ethyl} trimethylammonium chloride

A solution of [HOEtTMA][Cl], DCC (1.5 eq), 4-iodobenzoic acid (1.5 eq) and DMAP (0.2 eq) in acetonitrile (0.1 M) was allowed to react 4 h at room temperature. After concentration under reduced pressure, 4-iodobenzoic acid crushed out upon water addition (10 mL). After filtration and concentration under vacuum, product was recrystallized in acetone, and used directly in anion metathesis reactions without further purification (93% yield).

4.8.23. [IBzEtTMA][BF$_4$] 10c$_0$ {2-(4-iodobenzoyloxy)ethyl} trimethylammonium tetrafluoroborate

Following procedure **IV** using **10g$_0$**, [IBzEtTMA][BF$_4$] was obtained as a white solid in 90% yield. m.p. 200–202 °C. ^{1}H NMR (300 MHz, CD$_3$CN): δ = 3.18 (s, 9H), 3.68–3.80 (m, 2H), 4.50–4.73 (m, 2H), 7.78 (dd, 2H, J_1 = 1.9 Hz, J_2 = 6.7 Hz), 7.90 (dd, 2H, J_1 = 1.8 Hz, J_2 = 6.6 Hz). ^{13}C (75 MHz, CD$_3$CN): δ = 53.4 (t, J = 3.8 Hz), 58.3, 64.4 (t, J = 3.8 Hz), 100.6, 128.6, 130.7, 137.8, 164.7. LRMS(APCI): (C$^+$) (C$_{12}$H$_{17}$INO$_2$) 334.0.

4.8.24. [IBzHexTMA][Cl] 10g$_4$ {6-(4-iodobenzoyloxy)hexyl} trimethylammonium chloride

A solution of [HOEtTMA][Cl], DCC (1.5 eq), 4-iodobenzoic acid (1.5 eq) and DMAP (0.2 eq) in acetonitrile (0.1 M) was allowed to react 4 h at room temperature. After concentration under reduced pressure, 4-iodobenzoic acid crushed out upon water addition (10 mL). After filtration

and concentration under vacuum, product was recrystallized in acetone, and used directly in anion metathesis reactions without further purification.

4.8.25. [IBzHexTMA][BF$_4$] 10c$_4$ {6-(4-iodobenzoyloxy) hexyl}trimethylammonium tetrafluoroborate

Following procedure **IV** using **10g$_4$**, [IBzHexTMA][BF$_4$] was obtained as a white solid in 87% yield. m.p. 170–172 °C. ^{1}H NMR (300 MHz, CD$_3$CN): δ = 1.30–1.62 (m, 4H), 1.70–2.02 (m, 4H), 3.30 (s, 9H), 3.45–3.60 (m, 2H), 4.30 (t, 2H, J = 6.5 Hz), 7.80 (dd, 2H, J_1 = 1.7 Hz, J_2 = 6.7 Hz), 7.90 (dd, 2H, J_1 = 1.7 Hz, J_2 = 6.7 Hz). ^{13}C (75 MHz, CD$_3$CN): δ = 23.4, 26.2, 26.5, 53.5 (t, J = 3.8 Hz), 65.6, 67.3, 101.0, 128.6, 131.0, 131.8, 138.8, 166.4. LRMS(APCI): (C$^+$) (C$_{16}$H$_{25}$INO$_2$) 390.0.

4.8.26. [IBzEtMIm][Br] 13b$_0$ {3-(4-iodobenzoyloxy)ethyl} methylimidazolium bromide

A solution of [HOEtMIm][Br], DCC (1.5 eq), 4-iodobenzoic acid (1.5 eq) and DMAP (0.2 eq) in acetonitrile (0.1 M) was allowed to react 4 h at room temperature. After concentration under reduced pressure, 4-iodobenzoic acid crushed out upon water addition (10 mL). After filtration and concentration under vacuum, product was recrystallized in acetone, and used directly in anion metathesis reactions without further purification. (92% yield).

4.8.27. [IBzEtMIm][BF$_4$] 13c$_0$ {3-(4-iodobenzoyloxy)ethyl} methylimidazolium tetrafluoroborate

Following procedure **IV** using **10b$_0$**, [IBzEtMIm][BF$_4$] was obtained as a white solid in 90% yield. m.p. 146–148 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ = 4.10 (s, 3H), 4.73–4.82 (m, 2H), 4.85–4.92 (m, 2H), 7.75–7.85 (m, 3H), 7.92–8.00 (m, 3H), 9.27 (s, 1H). ^{13}C (75 MHz, acetone-d_6): δ = 36.7, 49.5, 64.2, 101.6, 124.0, 124.9, 130.0, 132.1, 138.2, 138.9, 166.0. LRMS(APCI): (C$^+$) (C$_{13}$H$_{14}$IN$_2$O$_2$) 357.0.

4.8.28. [CinPrTMA][NTf$_2$] Ph-14a1 {3-(3-phenylprop-2-enoylox)propyl}trimethylammonium bistrifluoromethanesulfonamide

Following general procedure **V** using **3a$_1$** and iodobenzene in DMF, [CinPrTMA][NTf$_2$] was obtained in 86% yield as a purple solid. m.p. 172–174 °C ^{1}H NMR (300 MHz, CD$_3$CN): δ = 2.18–2.35 (m, 2H), 3.15 (s, 9H), 3.43–3.58 (m, 2H), 4.34 (t, 2H, J = 5.9 Hz), 6.55 (d, 1H, J = 16.1 Hz), 7.41–7.53 (m, 3H), 7.65–7.88 (m, 3H). ^{13}C (75 MHz, CD$_3$CN): δ = 22.9, 53.6, 61.3, 64.2, 118.1, 128.7, 129.4, 131.0, 134.7, 145.4, 167.0. LRMS(APCI): [C$^+$] (C$_{15}$H$_{22}$NO$_2$) 248.2.

4.8.29. [tBuOCOCHCHBzPrTMA][NTf$_2$] 15c$_1$ {3-(2-tert-butoxycarbonylvinyl)benzoyloxypropyl}trimethylammonium bistrifluoromethanesulfonamide

Following general procedure **VI** using **10c$_1$** and tertbutylacrylate in DMF, [tBuOCOCHCHBzPrTMA][NTf$_2$] was obtained in 86% yield as a brown solid. m.p. 170–172 °C ^{1}H NMR (300 MHz, CD$_3$CN): δ = 1.53 (s, 9H), 2.18–2.35 (m, 2H), 3.15 (s, 9H), 3.43–3.58 (m, 2H), 4.44 (t, 2H, J = 5.8 Hz), 6.55 (d, 1H, J = 16.1 Hz), 7.58–7.78 (m, 3H), 8.09 (d, 2H, J = 8.4 Hz). ^{13}C (75 MHz, CD$_3$CN): δ = 22.0, 26.9, 52.6 (t, J = 4.0 Hz), 61.4, 63.4 (t, J = 3.3 Hz), 80.6, 122.3, 127.8, 129.6, 130.4, 138.8, 141.7, 165.6, 165.6. LRMS(APCI): [C$^+$] (C$_{20}$H$_{30}$NO$_4$) 348.3.

4.8.30. Methyl cinamate [103-26-4]

A 1 M HCl solution of supported cinnamate (0.1 M) was heated to reflux under argon atmosphere. After 3 h, methanol was removed under reduced pressure. The product was extracted from the remaining oil by adding five times 4 mL/mmol of Et$_2$O. After concentration of the ether fraction under reduced pressure, methyl cinnamate was obtained in 97% yield with > 99% purity (GC/MS).

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