DOI: 10.1002/ejoc.201000801

New Chiral Ionic Liquids Based on Enantiopure Sulfate and Sulfonate Anions for Chiral Recognition

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Keywords: Ionic liquids / Chirality / Anions / Green chemistry / Chiral recognition

The synthesis of new chiral ionic liquids with chiral anions is described. Chiral sulfate anions were prepared from alcohols of the "chiral pool" in good yields. Subsequent ion metathesis resulted in new salts with tetrabutylphosphonium and 1-butyl-3-methylimidazolium (BMIM) cations. In addition, the synthesis of chiral sulfonate anions from (*R*)-phenylethylamine and formaldehyde–sodium hydrogen sulfate, or sodium vinyl sulfonate is shown, giving new Brønsted basic chiral ionic liquids. The potential of the new ionic liquids as chiral shift reagents was explored. It was possible to use, in addition to Mosher's acid and the Brønsted basic ionic liquids, also 2,2,2-trifluoro-1-phenylethanol with the chiral salts. The neutral alcohol was found to interact with the chiral anions by hydrogen bonding.

Introduction

Ionic liquids have been the focus of increased attention over the last two decades. These salts have, by definition, a melting point below 100 °C and often contain organic ions. Several of these salts constitute a promising class of organic material due to their potential as novel solvents for reactions and electrochemical processes.[1] In addition, a number of these liquids could be regarded as potential "green solvents" due to their negligible vapor pressure and efficient recovery.[2]

When the ionic liquids are chiral, they can become interesting for further applications, such as chiral solvents, chiral chromatography, shift reagents, and catalysts.[3] Chiral ionic liquids (CILs) are, in general, either based on chiral cations[3,4] or on chiral anions.[3,5]

Due to our efforts in the field of chiral ionic liquids[4k,4l,4t,4w] and because of our interest in exploring their potential as chiral shift reagents, we have recently reported a salt with a chiral anion that was able to interact and provide stereodiscrimination in NMR experiments with 2,2,2-trifluoro-1-phenylethanol.[4w] This was the first time that a chiral ionic liquid was used as a shift reagent with a neutral compound. Normally, salts of racemic Mosher's carboxylates are used with chiral ionic liquids based on chiral cations. Due to the formation of diastereomeric salt pairs, a differentiation of the enantiomers of Mosher's carboxylates in the NMR spectra was possible.[4b–4e,4g,4k,4l,4r,4w,4y] The application of a neutral alcohol now allows a better exploration of salts with chiral anions and, in addition, broadens the scope of chiral ionic liquids that can be used in chiral shift experiments.

Here, we show the synthesis of a series of new chiral ionic liquids based on chiral sulfonates and sulfates and describe their use as chiral shift reagents with 2,2,2-trifluoro-1-phenylethanol.

Results and Discussion

First, the desired sulfate and sulfonate based ionic liquids were prepared. Synthesis of the organic sulfates from alcohols as starting material is straightforward, and is most often conducted by the use of an excess of readily available pyridine sulfur trioxide complex in the presence of acetic anhydride and an amine.[6] When the reaction is complete, a mixture of the pyridinium sulfate and the remaining pyridine sulfur trioxide complex is obtained, which is treated with aqueous potassium hydroxide to gain the desired potassium sulfate. The potassium hydroxide also destroys the remaining pyridine sulfur trioxide complex. This method was first applied to prepare potassium bornyl sulfate. We planned to exchange the potassium cation with a more lipophilic cation in the next step through cation metathesis. However, after the addition of potassium hydroxide to the reaction mixture, the desired potassium bornyl sulfate could not be obtained in either pure form or high yield, because of its high water-solubility and its tendency to wash out during workup.

Besides inorganic cations, such as sodium and potassium, similar sized organic cations such as pyridinium could also be employed in cation metathesis. Therefore, the prepa-

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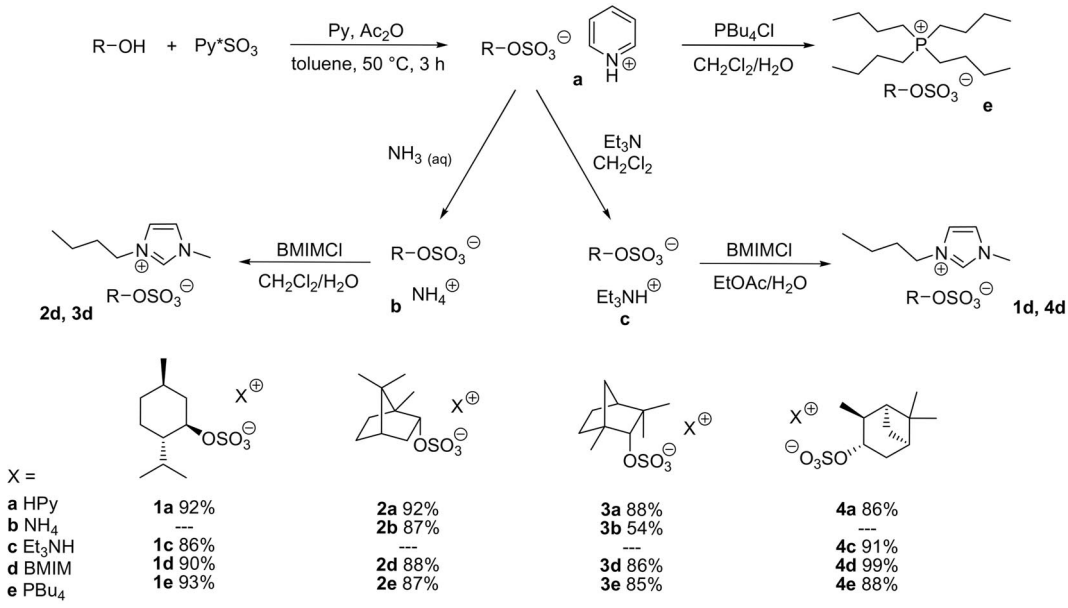


Scheme 1. Preparation of CIL sulfates.

ration of pure pyridinium sulfate seemed beneficial. The previously used method was slightly changed and an excess of enantiopure alcohol (1.0 equiv.) and pyridinium sulfur trioxide complex (0.9 equiv.) were used (Scheme 1). The desired pyridinium bornyl sulfate **2a** could be obtained in up to 92% yield. In addition, the salts could be successfully applied in the ion metathesis with tetrabutylphosphonium chloride.

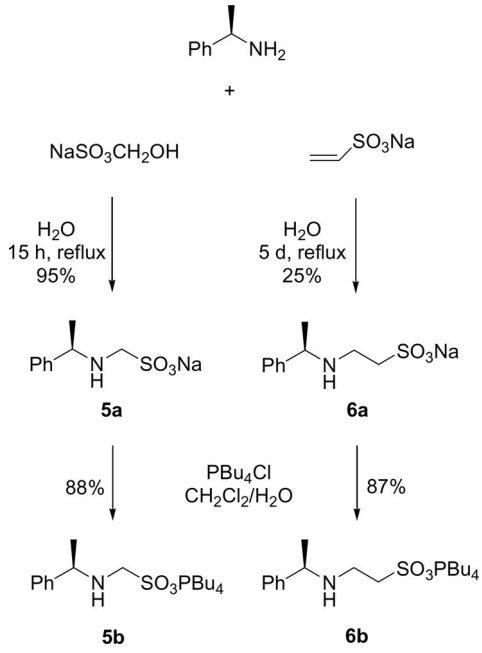
When an aqueous solution of the phosphonium chloride and the pyridinium bornyl sulfate were mixed, the phosphonium sulfate precipitated and could be filtered off. However, because further addition of water redissolved the desired product, the application of a dichloromethane/water mixture was found to be more beneficial for the isolation of the desired phosphonium sulfate **2e** in good yield.

In addition, sulfates were also prepared from the enantiopure alcohols menthol, fenchol, and α-isopinocampheol. Along with the phosphonium chloride, 1-butyl-3-methylimidazolium (BMIM) chloride was also applied for the cation metathesis.

Unfortunately, when the ion metathesis was conducted with BMIM chloride, the obtained solids proved to be mixtures of BMIM and pyridinium salts, as shown by NMR analysis. Further washing with water caused a reduction in the yield and led, in only a few cases, to pure products. Because BMIM and pyridinium cations seem to exhibit comparable hydrophilicities, a cation exchange was necessary. To this end, the pyridinium salts were dissolved in a minimum amount of water and excess aqueous ammonia was added. After evaporating the water, ammonia and pyridine, the pure ammonium fenchoyl- and bornyl sulfates **3b** and **2b** could be obtained. This method unfortunately failed with pyridinium menthyl- and α-isopinocampheoyl sulfates **1a** and **4a**. These two salts were therfore dissolved in dichloromethane and an excess of triethylamine was added. After removal of all liquids by distillation under high vacuum, a solid was obtained that was successively washed with diethyl ether. NMR analysis indicated that the pure triethylammonium sulfates **1c** and **4c** were obtained. The salts were subsequently used in the metathesis with BMIM chloride in a water/ethyl acetate mixture.

Salts **1d** and **4d** were thereafter successfully obtained in 90 and 99% yield, respectively, by using a water/ethyl acetate mixture for the metathesis reaction.

Next, two salts with chiral sulfonate anions were prepared. Amines can be transformed into sulfonates by means



Scheme 2. Preparation of CIL sulfonates.

of nucleophilic attack, and two readily available reaction partners for amines are sodium formaldehyde bisulfite and sodium vinyl sulfonate (Scheme 2). The reaction of (*R*)-phenylethylamine with these sodium salts in water yielded the corresponding sodium sulfonates **5a** and **6a** in 95 and 25%, respectively.

The basic sulfonates thus obtained were used in a subsequent cation metathesis with tetrabutylphosphonium chloride, which gave the resulting room temperature ionic liquids **5b** and **6b** in 88 and 87% yield, respectively. The cation metathesis with BMIM chloride failed to give any of the desired salts. Differential scanning calorimetry (DSC) measurements documented the therml stability of the phosphonium salts up to 220 °C (**5b**) and 345 °C (**6b**).

To explore the potential of the new chiral ionic liquids for chiral recognition, the prepared ionic liquids were tested as chiral shift reagents with 2,2,2-trifluoro-1-phenylethanol (**7**). In addition, the basic ionic liquids **5b** and **6b** were also explored with Mosher's carboxylic acid **8** (Scheme 3).

7 **8**

Scheme 3. Alcohol **7** and Mosher's acid **8**.

Because it was expected that the racemic alcohol **7** would interact with the enantiopure anions of the ionic liquids through hydrogen bonding, the polarity of the solvent should have a strong influence on the formation of a diastereomeric adduct. Hence, it was decided to perform the ^{19}F NMR experiments in deuterated chloroform and in toluene. However, because the solubility of salts incorporating BMIM as the cation was often very low in toluene, not all salts could be investigated in both solvents.

In most cases, when chloroform was used, no splitting of the ^{19}F NMR doublet signal for alcohol **7** was observed. The fenchol-based salts **3e** and **3d**, however, showed a splitting of the doublet in $CDCl_3$ by around 3.4 and 1.9 Hz, respectively. Better results were obtained in [D_8]toluene, probably due to enhanced hydrogen bonding because of the decreased polarity of the solvent and, thus, salt **1e** showed a splitting of 3.5 Hz, whereas the ^{19}F NMR spectra in $CDCl_3$ showed no splitting. Furthermore, in the case of salt **3e**, changing the solvent to [D_8]toluene caused an increased splitting of the ^{19}F NMR signal of the alcohol (7.0 Hz in [D_8]toluene compared to 3.4 Hz in $CDCl_3$). Table 1 summarizes the results; Figure 1 shows the ^{19}F NMR signals observed for 2,2,2-trifluoro-1-phenylethanol in the presence of salt **3e** in the two solvents.

Furthermore, when the basic phosphonium salts **5b** and **6b** were submitted to ^{19}F NMR analysis with alcohol **7** (Table 2), **5b** caused no splitting of the CF_3-group of the alcohol in $CDCl_3$, whereas use of [D_8]toluene as solvent resulted in a splitting of 6.7 Hz. Regardless of the solvent, salt **6b** caused a splitting of the ^{19}F NMR signal of alcohol **7**; in $CDCl_3$ a splitting of J = 6.3 Hz was observed wheras in [D_8]toluene a splitting of J = 6.8 Hz was found.

In addition, racemic Mosher's acid **8** was also applied as a substrate with the basic salts **5b** and **6b**; the results are shown in Table 2. In this case, the splitting of the ^{19}F NMR signal varied from J = 19.2 Hz in deuterated chloroform to J = 40.6 Hz in deuterated toluene for salt **5b**; salt **6b** gave comparable results (J = 18.8 Hz and 40.6 Hz, respectively).

For comparison, salt **3e** was also used under the same conditions with racemic Mosher's acid (**8**), because it gave the best results with alcohol **7**. However, Mosher's acid showed no splitting in the presence of **3e** in deuterated chloroform..

Conclusions

The synthesis of new chiral ionic liquids with chiral anions has been developed. The chiral sulfate and sulfonate anions were prepared from compounds derived from the chiral pool in a straightforward manner in good yields. During the preparation of the desired ionic liquids it was also possible to circumvent problems associated with ion metathesis with pyridinium salts. Whereas salts **1c**, **4c**, **1d**, and **4d** had melting points below 100 °C, salts **5b** and **6b**

Table 1. ^{19}F NMR (375 MHz) chemical shifts of 2,2,2-trifluoro-1-phenylethanol (**7**) with sulfate salts.

Entry	Salt	Solvent	^{19}F NMR δ [ppm]	^{19}F NMR $\Delta\delta$ [Hz][a]
1	–	[D_8]toluene	–78.27 (d, J = 6.9 Hz)	–
2	**1e**	[D_8]toluene	–77.41 (d, J = 7.2 Hz) –77.42 (d, J = 7.3 Hz)	3.5
3	**2e**	[D_8]toluene	–77.40 (d, J = 7.3 Hz)	–
4	**3e**	[D_8]toluene	–77.37 (d, J = 7.0 Hz) –77.39 (d, J = 6.9 Hz)[b]	7.0
5	**4e**	[D_8]toluene	–77.41 (d, J = 7.4 Hz)	–
6	–	$CDCl_3$	–78.84 (d, J = 6.6 Hz)	–
7	**1e**	$CDCl_3$	–78.34 (d, J = 6.9 Hz)	–
8	**1d**	$CDCl_3$	–78.45 (d, J = 7.1 Hz)	–
9	**2e**	$CDCl_3$	–78.34 (d, J = 7.2 Hz)	–
10	**2d**	$CDCl_3$	–78.48 (d, J = 7.2 Hz)	–
11	**3e**	$CDCl_3$	–78.28 (d, J = 7.2 Hz) –78.29 (d, J = 7.1 Hz)	3.4
12	**3d**	$CDCl_3$	–78.41 (d, J = 7.1 Hz) –78.42 (d, J = 7.0 Hz)	1.9
13	**4e**	$CDCl_3$	–78.32 (d, J = 7.1 Hz)	–
14	**4d**	$CDCl_3$	–78.47 (d, J = 7.1 Hz)	–

[a] Distance between the two doublets. [b] The two doublets actually appear as a triplet at δ = –77.38 ppm with J = 7.0 Hz. This signal is divided into its two overlaying doublets for better comparison.

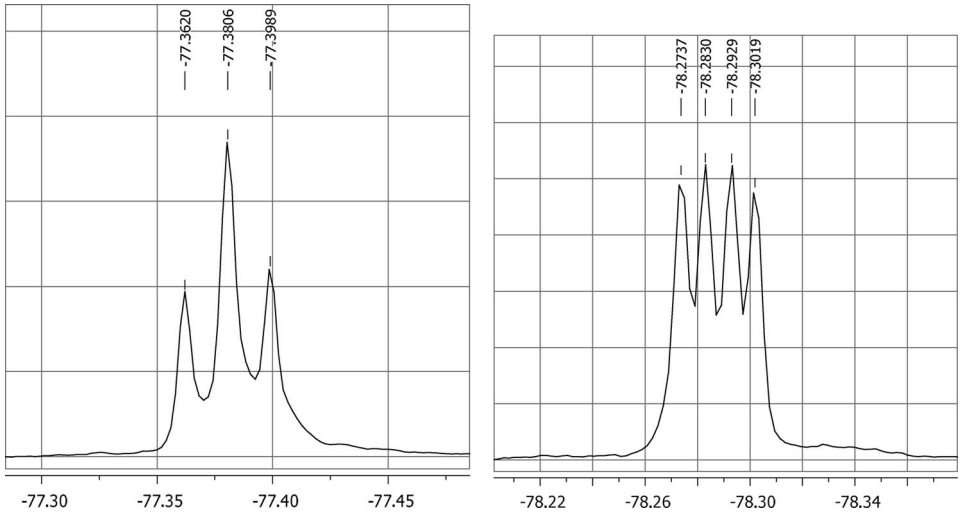


Figure 1. ^{19}F NMR spectra of alcohol **7** with salt **3e** in [D_8]toluene (left) and in $CDCl_3$ (right).

Table 2. ^{19}F NMR (375 MHz) chemical shifts of 2,2,2-trifluoro-1-phenylethanol (**7**) and Mosher's acid (**8**).

Entry	Salt	Solvent	^{19}F NMR δ [ppm]	^{19}F NMR $\Delta\delta$ [Hz][a]
	7 or **8**			
1	**5b/7**	[D_8]toluene	–82.25 (d, J = 6.7 Hz) –82.27 (d, J = 6.7 Hz)[b]	6.7
2	**6b/7**	[D_8]toluene	–82.22 (d, J = 6.8 Hz) –82.24 (d, J = 6.8 Hz)[c]	6.8
4	**5b/7**	$CDCl_3$	–78.25 (d, J = 7.1 Hz)	–
5	**6b/7**	$CDCl_3$	–78.20 (d, J = 6.3 Hz) –78.22 (d, J = 6.3 Hz)[d]	6.3
6	**–/8**	[D_8]toluene	–71.67	–
7	**5b/8**	[D_8]toluene	–75.03 –75.14	40.6
8	**–/8**	$CDCl_3$	–71.78	–
9	**5b/8**	$CDCl_3$	–70.84 –70.89	19.2
10	**6b/8**	$CDCl_3$	–70.65 –70.70	18.8
11	**3e/8**	$CDCl_3$	–72.22	–

[a] Distance between the two doublets or singlets. [b] The two doublets appear as a triplet at δ = –82.26 ppm (J = 6.7 Hz). This signal is divided into its two overlaying doublets for better comparison. [c] The two doublets appear as a triplet at δ = –82.23 ppm (J = 6.8 Hz). This signal is divided into its two overlaying doublets for better comparison. [d] The two doublets appear as a triplet at δ = –78.21 ppm (J = 6.3 Hz). This signal is divided into its two overlaying doublets for better comparison.

were room-temperature ionic liquids. The potential of these new ionic liquids as chiral shift reagents was explored and it was possible to use 2,2,2-trifluoro-1-phenylethanol with some of the chiral salts in NMR experiments. The neutral alcohol interacts with the chiral anions through hydrogen bonding. In addition, Mosher's acid could also be used with the Brønsted basic ionic liquids **5b** and **6b**. This work should enable an expansion of the applications of chiral ionic liquids in chiral recognition. Currently, further analogues of the presented chiral anions are being prepared and will be investigated for the chiral recognition of a broader set of alcohols.

Experimental Section

Pyridinium (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl Sulfate (1a): The preparation of pyridinium sulfates was based on a modified method described by Natelson:[6] (–)-Menthol (5.47 g, 35 mmol) was dissolved in toluene (50 mL) and a mixture of pyridine (5 mL) and acetic anhydride (5 mL) was added. Pyridine-sulfur trioxide complex (5 g, 31.4 mmol) was added and the mixture was heated to 50 °C for 30 min. After cooling, petroleum ether (50 mL) was added and the precipitated solid was filtered off, washed with petroleum ether and dried in vacuo to give a white solid (9.41 g, 92%); m.p. 169.8 °C. $[\alpha]_D^{25}$ = –48.8 (c = 1.23, $CHCl_3$). MS (ES, 0 V, neg. scan): m/z (%) = 234.9 (32) [M_{anion}], 471.1 (71) [$2M_{anion} + H^+$], 751.0 (7) [$3M_{anion} + 2Na^+$]. IR (KBr): $\tilde{\nu}$ = 2958, 1491, 1247, 1193, 1053, 973, 800 cm^{-1}. ^1H NMR (400 MHz): δ = 14.06 (br. s, 1 H, N*H*), 9.01 (dd, J = 6.6, 1.5 Hz, 2 H, ArH), 8.57 (tt, J = 7.9, 1.5 Hz, 1 H, ArH), 8.10 (dd, J = 7.8, 6.7 Hz, 2 H, ArH), 4.27 (td, J = 10.8, 4.4 Hz, 1 H, *H*$COSO_3$), 2.49 (ddd, J = 9.4, 7.4, 4.8 Hz, 1 H, *H*CH), 2.22 (dtd, J = 13.9, 7.0, 2.4 Hz, 1 H, CH), 1.73–1.57 (m, 2 H, 2 × *H*CH), 1.52–1.35 (m, 1 H, CH), 1.35–1.24 (m, 1 H, CH), 1.10 (dd, J = 23.3, 12.1 Hz, 1 H, *H*CH), 1.06–0.97 (m, 1 H, *H*CH), 0.89 (d, J = 6.5 Hz, 3 H, CH_3), 0.85 (d, J = 7.1 Hz, 3 H, CH_3), 0.84–0.78 (m, 4 H, *H*CH, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 146.3, 142.2, 127.5, 79.6, 48.0, 42.0, 34.3, 31.6, 25.6, 23.2, 22.2, 21.1, 16.1 ppm. HRMS (ESI): calcd. for $C_{10}H_{19}O_4S$ [M_{anion}] 235.1004; found 235.0995.

The other pyridinium salts were prepared in the same manner as described for (–)-menthol.

Pyridinium (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (2a): White solid (9.05 g, 92%); m.p. 182.2–184.1 °C. $[\alpha]_D^{25}$ = –15.7 (c = 1.08, $CHCl_3$). MS (ES, 0 V, neg. scan): m/z (%) = 233.1 (16) [M_{anion}], 467.0 (100) [$2M_{anion} + H^+$]. IR (KBr): $\tilde{\nu}$ = 2952, 1629, 1548, 1484, 1280, 1208, 1008 cm^{-1}. ^1H NMR (400 MHz): δ = 12.40 (s, 1 H, N*H*), 9.04 (dd, J = 5.1, 1.5 Hz, 2 H, ArH), 8.57 (tt, J = 7.9, 1.5 Hz, 1 H, ArH), 8.21–8.03 (m, 2 H, ArH), 4.73–4.54 (m, 1 H, *H*$COSO_3$), 2.37–2.25 (m, 1 H, *H*CH), 1.97–1.86 (m, 1 H, *H*CH), 1.77–1.61 (m, 2 H, C*H*, *H*CH), 1.39 (dd, J = 13.8, 3.3 Hz, 1 H, *H*CH), 1.28–1.16 (m, 2 H, 2 × *H*CH), 0.90 (d, J = 1.8 Hz, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 146.2, 142.3, 127.5, 84.2, 49.3, 47.5, 44.9, 36.7, 28.1, 26.7, 19.8, 18.9, 13.5 ppm. HRMS (ESI): calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0840.

Pyridinium (1*S*,2*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (3a): White solid (8.66 g, 88%); m.p. 200.1 °C. $[\alpha]_D^{25}$ = +11.3 (*c* = 1.06, $CHCl_3$). MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.1 (14) [M_{anion}], 467.0 (100) [$2M_{anion}$ + H^+]. IR (KBr): $\tilde{\nu}$ = 2962, 1634, 1486, 1258, 1187, 1025, 992 cm^{-1}. ^1H NMR (400 MHz): δ = 12.58 (br. s, 1 H, N*H*), 9.03 (dd, *J* = 6.6, 1.5 Hz, 2 H, ArH), 8.55 (tt, *J* = 7.9, 1.5 Hz, 1 H, ArH), 8.09 (dd, *J* = 7.8, 6.7 Hz, 2 H, ArH), 4.03 (d, *J* = 1.8 Hz, 1 H, *H*$COSO_3$), 1.76–1.62 (m, 3 H, CH, CH_2), 1.51 (dd, *J* = 10.3, 1.6 Hz, 1 H, *H*CH), 1.40 (ddt, *J* = 11.1, 8.6, 4.2 Hz, 1 H, *H*CH), 1.20–1.11 (m, 4 H, Me, *H*CH), 1.09 (s, 3 H, CH_3), 1.07–0.98 (m, 1 H, *H*CH), 0.96 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 146.2, 142.3, 127.5, 90.6, 49.0, 48.2, 41.3, 39.2, 30.1, 26.1, 26.0, 20.8, 19.5 ppm. HRMS (ESI): calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0849.

Pyridinium (1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl Sulfate (4a): White solid (8.46 g, 86%); m.p. 114.3 °C. $[\alpha]_D^{25}$ = +25.7 (*c* = 1.00, $CHCl_3$). MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.1 (12) [M_{anion}], 467.0 (100) [$2M_{anion}$ + H^+]. IR (KBr): $\tilde{\nu}$ = 2871, 1629, 1547, 1485, 1276, 1208, 1185 cm^{-1}. ^1H NMR (400 MHz): δ = 11.54 (br. s, 1 H, NH), 9.02 (dd, *J* = 6.7, 1.5 Hz, 2 H, ArH), 8.53 (tt, *J* = 7.8, 1.5 Hz, 1 H, ArH), 8.07 (dd, *J* = 7.8, 6.7 Hz, 2 H, ArH), 4.75 (ddd, *J* = 9.7, 5.2, 4.5 Hz, 1 H, *H*$COSO_3$), 2.63–2.55 (m, 1 H, *H*CH), 2.34–2.26 (m, 1 H, *H*CH), 2.20–2.13 (m, 1 H, CH), 2.05 (ddd, *J* = 14.5, 4.5, 2.8 Hz, 1 H, *H*CH), 1.88 (tt, *J* = 5.9, 3.1 Hz, 1 H, CH), 1.76 (td, *J* = 5.9, 2.1 Hz, 1 H, CH), 1.17 (s, 3 H, CH_3), 1.13 (d, *J* = 7.4 Hz, 3 H, CH_3), 1.02 (d, *J* = 9.8 Hz, 1 H, *H*CH), 0.89 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 146.3, 142.3, 127.5, 79.1, 47.6, 44.7, 41.6, 38.4, 36.5, 33.8, 27.5, 23.9, 20.4 ppm. HRMS (ESI): calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0842.

Ammonium Sulfates 2b and 3b: Pyridinium sulfates **2a** or **3a** were dissolved in a minimum amount of water. Ammonia (10 equiv. in water) was added and the solution was stirred for 15 min. Excess water, ammonia and pyridine were distilled off and the remaining solid was further dried in vacuo, washed with diethyl ether to remove traces of pyridine and dried in vacuo.

Ammonium (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (2b): White solid (6.32 g, 87%); m.p. 216.2 °C. $[\alpha]_D^{25}$ = –20.3 (*c* = 1.08, MeOH). MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.0587 (100) [M_{anion}], 467.1701 (18) [$2M_{anion}$ + H^+]. IR (KBr): $\tilde{\nu}$ = 2956, 1456, 1264, 1200, 1065, 1009, 864 cm^{-1}. ^1H NMR (400 MHz): δ = 4.67–4.55 (m, 1 H, *H*$COSO_3$), 2.47–2.32 (m, 1 H, *H*CH), 1.97–1.73 (m, 3 H, CH, 2 × *H*CH), 1.45–1.29 (m, 3 H, 3 × *H*CH), 1.05–0.90 (m, 9 H, 3 × CH_3) ppm. ^{13}C NMR (100 MHz): δ = 85.8, 48.9, 47.2, 44.6, 36.1, 27.7, 26.3, 19.5, 18.4, 12.8 ppm. HRMS (ESI): calcd. for $C_{10}H_{21}O_4S$ [M_{anion}] 233.0848; found 233.0858.

Ammonium (1*S*,2*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (3b): White solid (3.75 g, 54%); m.p. 218.3 °C. $[\alpha]_D^{25}$ = +14.8 (*c* = 1.08, MeOH). MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.0587 (100) [M_{anion}], 467.1781 (10) [$2M_{anion}$ + H^+]. IR (KBr): $\tilde{\nu}$ = 2963, 1472, 1243, 1174, 1067, 975, 873 cm^{-1}. ^1H NMR (400 MHz): δ = 3.97 (d, *J* = 1.8 Hz, 1 H, *H*$COSO_3$), 1.82–1.72 (m, 2 H, CH, *H*CH), 1.70–1.59 (m, 2 H, 2 × *H*CH), 1.56–1.45 (m, 1 H, *H*CH), 1.26 (dd, *J* = 10.4, 1.4 Hz, 1 H, *H*CH), 1.16 (s, 3 H, CH_3), 1.16–1.08 (m, 4 H, CH_3, *H*CH), 0.98 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 92.2, 48.5, 47.9, 40.7, 38.8, 29.4, 25.6, 25.5, 20.2, 18.7 ppm. HRMS (ESI): calcd. for $C_{10}H_{21}O_4S$ [M_{anion}] 233.0848; found 233.0847.

Triethylammonium Sulfates 1c and 4c: Pyridinium sulfates **1a** and **4a** were dissolved in a minimum amount of dichloromethane. Triethylamine (10 equiv.) was added and the solution was stirred for 15 min. Excess CH_2Cl_2, triethylamine and pyridine were distilled off and the remaining solid was washed with diethyl ether to remove traces of pyridine and dried in vacuo.

Triethylammonium (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl Sulfate (1c): White solid (8.39 g, 86%); m.p. 78.2 °C. $[\alpha]_D^{25}$ = –54.2 (*c* = 1.00, $CHCl_3$). MS (ES, 0 V, pos. scan): *m*/*z* (%) = 102.1169 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m*/*z* (%) = 235.0800 (100) [M_{anion}]. IR (KBr): $\tilde{\nu}$ = 2958, 2935, 1476, 1251, 1209, 972, 791 cm^{-1}. ^1H NMR (400 MHz): δ = 9.77 (s, 1 H, NH), 4.19 (td, *J* = 10.8, 4.4 Hz, 1 H, $HCOSO_3$), 3.18 (qd, *J* = 7.3, 4.7 Hz, 6 H, 3 × NCH_2), 2.54–2.44 (m, 1 H, *H*CH), 2.28 (dtd, *J* = 13.9, 7.0, 2.4 Hz, 1 H, CH), 1.71–1.59 (m, 2 H, 2 × *H*CH), 1.49–1.34 (m, 10 H, 3 × CH_3, CH), 1.33–1.23 (m, 1 H, CH), 1.07 (dd, *J* = 23.3, 12.3 Hz, 2 H, 2 × *H*CH), 0.89 (q, *J* = 6.8, 5.5 Hz, 6 H, 2 × CH_3), 0.84 (d, *J* = 6.9 Hz, 4 H, CH_3, *H*CH) ppm. ^{13}C NMR (100 MHz): δ = 79.0, 48.0, 46.6, 42.0, 34.4, 31.6, 25.4, 23.2, 22.2, 21.2, 16.0, 8.8 ppm. HRMS (ESI): calcd. for $C_6H_{16}N$ [M_{cation}] 102.1283; found 102.1284; calcd. for $C_{10}H_{19}O_4S$ [M_{anion}] 235.1004; found 235.1002.

Triethylammonium (1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptan-3-yl Sulfate (4c): White solid (8.25 g, 91%); m.p. 72.7 °C. $[\alpha]_D^{25}$ = +26.7 (*c* = 1.03, $CHCl_3$). MS (ES, 0 V, pos. scan): *m*/*z* (%) = 102.1169 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.0531 (100) [M_{anion}], 467.1701 (12) [$2M_{anion}$ + H^+]. IR (KBr): $\tilde{\nu}$ = 2941, 1478, 1248, 1211, 978, 779, 615 cm^{-1}. ^1H NMR (400 MHz): δ = 9.76 (s, 1 H, NH), 4.72 (dt, *J* = 9.7, 4.9 Hz, 1 H, $HCOSO_3$), 3.29–3.11 (m, 6 H, 3 × NCH_2), 2.68–2.56 (m, 1 H, *H*CH), 2.41–2.28 (m, 1 H, *H*CH), 2.27–2.14 (m, 1 H, CH), 2.08 (ddd, *J* = 14.5, 4.2, 2.7 Hz, 1 H, *H*CH), 1.92 (ddd, *J* = 8.6, 5.7, 3.1 Hz, 1 H, CH), 1.80 (td, *J* = 5.8, 1.8 Hz, 1 H, CH), 1.39 (t, *J* = 7.3 Hz, 9 H, 3 × CH_3), 1.21 (s, 3 H, CH_3), 1.18 (d, *J* = 7.4 Hz, 3 H, CH_3), 1.07 (d, *J* = 9.7 Hz, 1 H, *H*CH), 0.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 78.4, 47.7, 46.6, 44.7, 41.6, 38.4, 36.5, 33.8, 27.6, 23.8, 20.3, 8.8 ppm. HRMS (ESI): calcd. for $C_6H_{16}N$ [M_{cation}] 102.1283; found 102.1284; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0856.

3-Butyl-1-methyl-1*H*-imidazol-3-ium Sulfates 1d, 2d, 3d, and 4d: Prepared using standard cation metathesis in a CH_2Cl_2/water or ethyl acetate/water mixture from BMIM chloride and ammonium or triethylammonium sulfates.

1-Butyl-3-methyl-1*H*-imidazolium (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl Sulfate (1d): Slightly yellow solid (8.37 g, 90%); m.p. 88.4 °C. $[\alpha]_D^{25}$ = –45.1 (*c* = 1.02, $CHCl_3$). MS (ES, 0 V, pos. scan): *m*/*z* (%) = 139.1022 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m*/*z* (%) = 235.0800 (100) [M_{anion}], 493.1810 (5) [$2M_{anion}$ + Na^+]. IR (KBr): $\tilde{\nu}$ = 2960, 1577, 1463, 1166, 977, 798, 605 cm^{-1}. ^1H NMR (400 MHz): δ = 9.68 (s, 1 H, N=CHN), 7.53 (s, 1 H, CH), 7.40 (s, 1 H, CH), 4.26 (t, *J* = 7.3 Hz, 2 H, NCH_2), 4.24–4.16 (m, 1 H, $HCOSO_3$), 4.03 (s, 3 H, NCH_3), 2.53 (br. d, *J* = 12.2 Hz, 1 H, *H*CH), 2.32 (dtd, *J* = 13.9, 6.9, 2.2 Hz, 1 H, CH), 1.95–1.81 (m, 2 H, CH_2), 1.72–1.61 (m, 2 H, 2 × *H*CH), 1.52–1.42 (m, 1 H, CH), 1.43–1.33 (m, 2 H, CH_2), 1.32–1.23 (m, 1 H, CH), 1.13–0.99 (m, 2 H, 2 × *H*CH), 0.96 (t, *J* = 7.4 Hz, 3 H, CH_3), 0.93–0.81 (m, 10 H, 3 × CH_3, *H*CH) ppm. ^{13}C NMR (100 MHz): δ = 138.0, 123.8, 122.1, 78.3, 49.8, 48.2, 42.3, 36.5, 34.5, 32.2, 31.7, 25.5, 23.3, 22.3, 21.3, 19.5, 16.2, 13.5 ppm. HRMS (ESI): calcd. for $C_8H_{15}N_2$ [M_{cation}] 139.1235; found 139.1232; calcd. for $C_{10}H_{19}O_4S$ [M_{anion}] 235.1004; found 235.1002.

1-Butyl-3-methyl-1*H*-imidazolium (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (2d): Slightly yellow solid (8.24 g, 88%); m.p. 107.3 °C. $[\alpha]_D^{25}$ = –14.1 (*c* = 1.09, $CHCl_3$). MS (ES, 0 V, pos. scan): *m*/*z* (%) = 139.1022 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m*/*z* (%) = 233.0591 (100) [M_{anion}], 489.1416 (5) [$2M_{anion}$ + Na^+]. IR (KBr): $\tilde{\nu}$ = 3101, 2957, 1639, 1260, 1212, 1010, 854 cm^{-1}.

^{1}H NMR (400 MHz): δ = 9.59 (s, 1 H, N=CHN), 7.60 (t, J = 1.7 Hz, 1 H, CH), 7.47 (t, J = 1.7 Hz, 1 H, CH), 4.58 (ddd, J = 9.8, 3.3, 1.9 Hz, 1 H, $HCOSO_3$), 4.26 (t, J = 7.3 Hz, 2 H, NCH_2), 4.03 (s, 3 H, NCH_3), 2.36–2.22 (m, 1 H, *H*CH), 2.00–1.91 (m, 1 H, *H*CH), 1.91–1.82 (m, 2 H, CH_2), 1.75–1.65 (m, 1 H, *H*CH), 1.63 (t, J = 4.5 Hz, 1 H, *H*CH), 1.42–1.31 (m, 3 H, 3 *H*CH), 1.27–1.15 (m, 2 H, CH_2), 0.95 (t, J = 7.4 Hz, 3 H, CH_3), 0.89 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.85 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 137.5, 124.0, 122.2, 82.8, 49.7, 49.1, 47.4, 44.9, 36.9, 36.4, 32.1, 28.1, 26.7, 19.8, 19.4, 18.9, 13.4 ppm. HRMS (ESI): calcd. for $C_8H_{15}N_2$ [M_{cation}] 139.1235; found 139.1232; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0839.

1-Butyl-3-methyl-1*H*-imidazolium (1*S*,2*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl Sulfate (3d): Slightly yellow solid (4.78 g, 86%); m.p. 104.7 °C. $[\alpha]_D^{25}$ = +11.1 (c = 1.06, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 139.1022 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): m/z (%) = 233.0648 (100) [M_{anion}], 489.1497 (5) [$2M_{anion}$ + Na^+]. IR (KBr): $\tilde{\nu}$ = 2960, 1574, 1468, 1244, 992, 849, 619 cm^{-1}. ^{1}H NMR (600 MHz): δ = 9.58 (s, 1 H, N=CHN), 7.54 (t, J = 1.8 Hz, 1 H, CH), 7.40 (t, J = 1.8 Hz, 1 H, CH), 4.21 (t, J = 7.4 Hz, 2 H, NCH_2), 3.99 (s, 3 H, NCH_3), 3.94 (d, J = 1.8 Hz, 1 H, $HCOSO_3$), 1.88–1.79 (m, 2 H, CH_2), 1.72–1.60 (m, 3 H, CH, CH_2), 1.51–1.44 (m, 1 H, *H*CH), 1.41–1.35 (m, 1 H, *H*CH), 1.35–1.29 (m, 2 H, CH_2), 1.14–1.07 (m, 4 H, CH_3, *H*CH), 1.05 (s, 3 H, CH_3), 0.96–0.93 (m, 4 H, CH_3, *H*CH), 0.91 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (150 MHz): δ = 137.7, 123.9, 122.2, 89.4, 49.8, 48.9, 48.2, 41.3, 39.1, 36.4, 32.2, 30.1, 26.2, 26.1, 20.8, 19.52, 19.49, 13.5 ppm. HRMS (ESI): calcd. for $C_8H_{15}N_2$ [M_{cation}] 139.1235; found 139.1230; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0841.

1-Butyl-3-methyl-1*H*-imidazolium (1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]-heptan-3-yl Sulfate (4d): White solid (9.06 g, 99%); m.p. 51.9 °C. $[\alpha]_D^{25}$ = +19.0 (c = 1.74, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 139.1032 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): m/z (%) = 233.0587 (100) [M_{anion}], 467.1781 (10), [M_{anion} + H]. IR (KBr): $\tilde{\nu}$ = 2961, 1573, 1469, 1222, 1057, 976, 928 cm^{-1}. ^{1}H NMR (400 MHz): δ = 9.63 (s, 1 H, N=CHN), 7.55 (t, J = 1.6 Hz, 1 H, CH), 7.43 (t, J = 1.7 Hz, 1 H, CH), 4.72 (ddd, J = 9.7, 5.1, 4.6 Hz, 1 H, $HCOSO_3$), 4.26 (t, J = 7.4 Hz, 2 H, NCH_2), 4.04 (s, 3 H, NCH_3), 2.67–2.56 (m, 1 H, *H*CH), 2.37–2.27 (m, 1 H, *H*CH), 2.23–2.12 (m, 1 H, C*H*), 2.07 (ddd, J = 14.6, 4.5, 2.6 Hz, 1 H, *H*CH), 1.94–1.82 (m, 3 H, CH, CH_2), 1.79 (td, J = 5.9, 2.0 Hz, 1 H, CH), 1.43–1.30 (m, 2 H, CH_2), 1.20 (s, 3 H, CH_3), 1.17 (d, J = 7.4 Hz, 3 H, CH_3), 1.05 (d, J = 9.7 Hz, 1 H, *H*CH), 0.98–0.91 (m, 6 H, 2 × CH_3) ppm. ^{13}C NMR (100 MHz): δ = 137.7, 123.9, 122.2, 77.8, 49.8, 47.7, 44.8, 41.7, 38.4, 36.8, 36.5, 33.8, 32.2, 27.6, 23.9, 20.4, 19.5, 13.5 ppm. HRMS (ESI): calcd. for $C_8H_{15}N_2$ [M_{cation}] 139.1235; found 139.1240; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0852.

Tetrabutylphosphonium Sulfates 1e, 2e, 3e, and 4e: Prepared by standard ion metathesis in a CH_2Cl_2/water mixture from tetrabutylphosphonium chloride and pyridinium sulfates.

Tetrabutylphosphonium (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl Sulfate (1e): White solid (11.43 g, 93%); m.p. 127.7 °C. $[\alpha]_D^{25}$ = –36.7 (c = 1.02, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 259.2060 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): m/z (%) = 235.0800 (100) [M_{anion}], 493.1810 (5) [$2M_{anion}$ + Na]. IR (KBr): $\tilde{\nu}$ = 2958, 2932, 1466, 1249, 1222, 981, 783 cm^{-1}. ^{1}H NMR (400 MHz): δ = 4.15 (td, J = 10.7, 4.4 Hz, 1 H, $HCOSO_3$), 2.60–2.50 (m, 1 H, *H*CH), 2.42–2.20 (m, 9 H, 4 × PCH_2, CH), 1.66–1.58 (m, 2 H, 2 × *H*CH), 1.58–1.46 (m, 16 H, 8 × CH_2), 1.46–1.34 (m, 1 H, CH), 1.30–1.19 (m, 1 H, CH), 1.10–0.91 (m, 15 H, 4 × CH_3, *H*CH, CH_2), 0.91–0.76 (m, 10 H, 3 × CH_3, *H*CH) ppm. ^{13}C NMR (100 MHz): δ = 77.5, 48.2, 42.3, 34.6, 31.6, 25.3, 24.0 (d, J_{PC} = 15 Hz), 23.8 (d, J_{PC} = 5 Hz), 23.2, 22.2, 21.3, 18.7 (d, J_{PC} = 47 Hz), 16.13, 13.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2550; calcd. for $C_{10}H_{19}O_4S$ [M_{anion}] 235.1004; found 235.0996.

Tetrabutylphosphonium (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]-heptan-2-yl Sulfate (2e): White solid (10.77 g, 87%); m.p. 148.2–150.4 °C. $[\alpha]_D^{25}$ = –12.4 (c = 1.05, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 259.2119 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): m/z (%) = 233.0535 (100) [M_{anion}], 489.1416 (5) [$2M_{anion}$ + Na]. IR (KBr): $\tilde{\nu}$ = 2958, 2875, 1467, 1248, 1221, 1011, 784 cm^{-1}. ^{1}H NMR (400 MHz): δ = 4.56 (ddd, J = 9.9, 3.3, 2.0 Hz, 1 H, $HCOSO_3$), 2.40–2.21 (m, 9 H, 4 × PCH_2, *H*CH), 2.11–1.99 (m, 1 H, *H*CH), 1.73–1.58 (m, 2 H, CH, *H*CH), 1.58–1.46 (m, 16 H, 8 × CH_2), 1.39 (dd, J = 13.7, 3.4 Hz, 1 H, *H*CH), 1.31–1.14 (m, 2 H, 2 × *H*CH), 0.97 (t , J = 7.0 Hz, 12 H, 4 × CH_3), 0.92 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.84 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 82.1, 49.1, 47.3, 45.0, 36.9, 28.1, 26.8, 24.0 (d, J_{PC} = 15 Hz), 23.8 (d, J_{PC} = 5 Hz), 19.9, 19.0, 18.7 (d, J_{PC} = 47 Hz), 13.5, 13.4 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2547; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0840.

Tetrabutylphosphonium (1*S*,2*R*,4*S*)-1,3,3-Trimethylbicyclo[2.2.1]-heptan-2-yl Sulfate (3e): White solid (6.25 g, 85%); m.p. 161.6–163.5 °C. $[\alpha]_D^{25}$ = +7.0 (c = 0.58, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 259.2119 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): m/z (%) = 233.0591 (100) [M_{anion}], 489.1416 (5) [$2M_{anion}$ + Na]. IR (KBr): $\tilde{\nu}$ = 2962, 2934, 2873, 1468, 1247, 1220, 1005 cm^{-1}. ^{1}H NMR (400 MHz): δ = 3.95 (d, J = 1.8 Hz, 1 H, $HCOSO_3$), 2.41–2.23 (m, 8 H, 4 × PCH_2), 1.85–1.74 (m, 1 H, *H*CH), 1.70 (dt, J = 12.1, 2.7 Hz, 1 H, *H*CH), 1.67–1.60 (m, 1 H, CH), 1.60–1.46 (m, 17 H, 8 × CH_2, *H*CH), 1.43–1.32 (m, 1 H, *H*CH), 1.16 (s, 3 H, CH_3), 1.14–1.06 (m, 4 H, CH_3, *H*CH), 1.04–0.88 (m, 16 H, 5 × CH_3, *H*CH) ppm. ^{13}C NMR (100 MHz): δ = 88.6, 48.9, 48.3, 41.4, 39.1, 30.1, 26.2, 26.1, 24.0 (d, J_{PC} = 15 Hz), 23.8 (d, J_{PC} = 5 Hz), 20.8, 19.5, 18.7 (d, J_{PC} = 47 Hz), 13.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2547; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0838.

Tetrabutylphosphonium (1*S*,2*S*,3*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]-heptan-3-yl Sulfate (4e): White solid (10.66 g, 88%); m.p. 116.3 °C. $[\alpha]_D^{25}$ = +17.7 (c = 1.16, $CHCl_3$). MS (ES, 0 V, pos. scan): m/z (%) = 259.3 (35) [M_{cation}], 751.5 (100) [$2M_{cation}$ + M_{anion}]. MS (ES, 0 V, neg. scan): m/z (%) = 725.3 (100) [$2M_{anion}$ + M_{cation}]. IR (KBr): $\tilde{\nu}$ = 2961, 2934, 1467, 1246, 1219, 978, 616 cm^{-1}. ^{1}H NMR (400 MHz): δ = 4.69 (ddd, J = 9.7, 5.3, 4.6 Hz, 1 H, $HCOSO_3$), 2.68–2.56 (m, 1 H, *H*CH), 2.39–2.24 (m, 9 H, 4 × PCH_2, *H*CH), 2.24–2.14 (m, 1 H, CH), 2.09 (ddd, J = 14.5, 4.4, 2.7 Hz, 1 H, *H*CH), 1.89 (tt, J = 5.9, 3.1 Hz, 1 H, CH), 1.77 (td, J = 5.9, 2.0 Hz, 1 H, CH), 1.63–1.45 (m, 16 H, 8 × CH_2), 1.20 (s, 3 H, CH_3), 1.18 (d, J = 7.4 Hz, 3 H, CH_3), 1.10 (d, J = 9.6 Hz, 1 H, *H*CH), 0.97 (t, J = 7.0 Hz, 12 H, 4 × CH_3), 0.94 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 77.0, 47.7, 44.8, 41.7, 38.4, 36.7, 33.7, 27.6, 24.0 (d, J_{PC} = 15 Hz), 23.8 (d, J_{PC} = 5 Hz), 23.8, 20.4, 18.7 (d, J_{PC} = 47 Hz), 13.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2549; calcd. for $C_{10}H_{17}O_4S$ [M_{anion}] 233.0848; found 233.0841.

Sodium (*R*)-(1-Phenylethylamino)methanesulfonate (5a): Sodium hydroxymethanesulfonate (10 g, 74.6 mmol) was dissolved in water (100 mL) and (*R*)-1-phenylethylamine (14.3 mL, 111.9 mmol) was added. The mixture was refluxed for 15 h then the solvent was distilled off and the remaining white solid was successively washed with diethyl ether to remove traces of amine. The solid obtained was dried in vacuo to give the product as a white solid (16.81 g,

95%); m.p. 211.8 °C. $[\alpha]_D^{25}$ = +63.7 (*c* = 1.48, H_2O). MS (ES, 0 V, neg. scan): *m/z* (%) = 214.0417 (100) [M_{anion}], 429.1015 (30) [$2M_{anion}$ + H], 644.1714 (7) [$3M_{anion}$ + 2H], 859.2197 (15) [$4M_{anion}$ + 3H]. IR (KBr): ṽ = 3509, 2965, 1454, 1211, 1052, 762, 700 cm^{-1}. ^1H NMR (400 MHz): δ = 7.38–7.30 (m, 4 H, ArH), 7.31–7.24 (m, 1 H, ArH), 4.22 (q, *J* = 6.6 Hz, 1 H, CH), 3.62 (d, *J* = 14.0 Hz, 1 H, *H*CH), 3.50 (d, *J* = 14.0 Hz, 1 H, *H*CH), 1.29 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz): δ = 143.5, 128.8, 127.6, 127.1, 62.8, 55.3, 22.2 ppm. HRMS (ESI): calcd. for $C_9H_{12}NO_3S$ [M_{anion}] 214.0538; found 214.0535.

Sodium (*R*)-2-(1-Phenylethylamino)ethanesulfonate (6a): An aqueous solution (25%) of sodium vinylsulfonate (77 mmol) and (*R*)-phenylethylamine (15 mL, 111.5 mmol) was mixed and heated at reflux temperature for 5 d. The mixture was filtered and the solvent was removed from the filtrate by distillation under vacuum. The remaining solid was washed with THF and dried in vacuo to give the product as a white solid (4.84 g, 25%); m.p. 345.0 °C. $[\alpha]_D^{25}$ = +33.0 (*c* = 1.22, MeOH). MS (ES, 0 V, neg. scan): *m/z* (%) = 228.0558 (100) [M_{anion}], 457.1284 (55) [$2M_{anion}$ + H], 686.2181 (12) [$3M_{anion}$ + 2H], 915.2859 (8) [$4M_{anion}$ + 3H]. IR (KBr): ṽ = 2967, 1416, 1219, 1205, 1056, 761, 700 cm^{-1}. ^1H NMR (200 MHz): δ = 7.49–7.31 (m, 5 H, ArH), 3.91–3.81 (m, 1 H, CH), 3.09–3.01 (m, 2 H, CH_2SO_3), 2.87–2.79 (m, 2 H, NCH_2), 1.37 (d, *J* = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (50 MHz): δ = 146.4, 131.3, 130.0, 129.4, 59.5, 52.4, 44.1, 24.5 ppm. HRMS (ESI): calcd. for $C_{10}H_{14}NO_3S$ [M_{anion}] 228.0694; found 228.0701.

Preparation of Tetrabutylphosphonium (*R*)-(1-Phenylethylamino) Alkanesulfonates: Tetrabutylphosphonium chloride (500 mg, 1.7 mmol) was dissolved in CH_2Cl_2 (10 mL) and a solution of **5a** or **6a** (4 equiv., 6.8 mmol) in a minimum amount of water was added. The mixture was stirred vigorously for 3 h, then the phases were separated and the organic phase was washed with a minimum amount of water. The organic phase was dried with sodium sulfate and the solvent was removed under vacuum.

Tetrabutylphosphonium (*R*)-(1-Phenylethylamino)methanesulfonate (5b): Yellow liquid (709 mg, 88%). $[\alpha]_D^{25}$ = +28.7 (*c* = 1.16, $CHCl_3$). MS (ES, 0 V, pos. scan): *m/z* (%) = 259.6197 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m/z* (%) = 214.0471 (100) [M_{anion}], 429.1167 (24) [$2M_{anion}$ + H], 644.1807 (4) [$3M_{anion}$ + 2H], 859.2413 (10) [$4M_{anion}$ + 3H]. IR (NaCl): ṽ = 2960, 2933, 2873, 1493, 1194, 1031, 441 cm^{-1}. ^1H NMR (400 MHz): δ = 7.43–7.38 (m, 2 H, ArH), 7.32–7.24 (m, 2 H, ArH), 7.19 (tt, *J* = 7.2, 1.4 Hz, 1 H, ArH), 4.52 (q, *J* = 6.5 Hz, 1 H, $HCOSO_3$), 3.65 (d, *J* = 13.3 Hz, 1 H, *H*CH), 3.53 (d, *J* = 13.3 Hz, 1 H, *H*CH), 2.48 (br. s, 1 H, NH), 2.40–2.25 (m, 8 H, 4 × PCH_2), 1.61–1.44 (m, 16 H, 8 × CH_2), 1.35 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.96 (t, *J* = 7.0 Hz, 12 H, 4 × CH_3) ppm. ^{13}C NMR (100 MHz): δ = 145.7, 128.1, 127.3, 126.6, 64.0, 55.3, 24.11, 24.0 (d, *J* = 15 Hz), 23.8 (d, *J* = 5 Hz), 18.76 (d, *J* = 47 Hz), 13.5 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2568; calcd. for $C_9H_{12}NO_3S$ [M_{anion}] 214.0538; found 214.0548.

Tetrabutylphosphonium (*R*)-2-(1-Phenylethylamino)ethanesulfonate (6b): Yellow liquid (721 mg, 87%). $[\alpha]_D^{25}$ = +20.2 (*c* = 1.10, $CHCl_3$). MS (ES, 0 V, pos. scan): *m/z* (%) = 259.6197 (100) [M_{cation}]. MS (ES, 0 V, neg. scan): *m/z* (%) = 228.0558 (100) [M_{anion}], 457.1364 (50) [$2M_{anion}$ + H], 686.2181 (10) [$3M_{anion}$ + 2H], 915.3082 (6) [$4M_{anion}$ + 3H]. IR (NaCl): ṽ = 2961, 2933, 2873, 1493, 1205, 1035, 414 cm^{-1}. ^1H NMR (400 MHz): δ = 7.38–7.32 (m, 2 H, ArH), 7.32–7.25 (m, 2 H, ArH), 7.19 (tt, *J* = 7.2, 1.4 Hz, 1 H, ArH), 3.82 (q, *J* = 6.6 Hz, 1 H, CH), 3.04–2.84 (m, 4 H, 2 × CH_2), 2.72 (br. s, 1 H, NH), 2.40–2.18 (m, 8 H, 4 × PCH_2), 1.63–1.41 (m, 16 H, 8 × CH_2), 1.33 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.0 Hz, 12 H, 4 × CH_3) ppm. ^{13}C NMR (100 MHz): δ = 145.7, 128.1, 126.7, 126.5, 57.9, 51.1, 43.9, 24.3, 23.8 (d, *J* = 15 Hz), 23.6 (d, *J* = 5 Hz), 18.5 (d, *J* = 47 Hz), 13.4 ppm. HRMS (ESI): calcd. for $C_{16}H_{36}P$ [M_{cation}] 259.2555; found 259.2563; calcd. for $C_{10}H_{14}NO_3S$ [M_{anion}] 228.0694; found 228.0699.

Acknowledgments

The authors would like to thank Dr. Namyslo for performing the ^{19}F NMR measurements and Dr. G. Dräger from the University of Hannover, Germany for HRMS measurements.

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Received: June 4, 2010
Published Online: September 1, 2010

