Novel L-Tartaric Acid Derived Pyrrolidinium Cations for the Synthesis of Chiral Ionic Liquids

Marco Bonanni, Gianluca Soldaini, Cristina Faggi, Andrea Goti, Francesca Cardona*

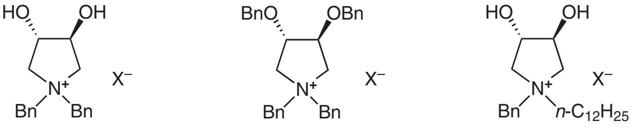
Dipartimento di Chimica Organica 'Ugo Schiff', HeteroBioLab, Università di Firenze, Associated with INSTM and ICCOM-C.N.R., Via della Lastruccia 13, 50019 Sesto Fiorentino (FI), Italy
Fax +39(055)4573531; E-mail: francesca.cardona@unifi.it

Received 27 November 2008

Abstract: Novel pyrrolidinium salts based on L-(+)-tartaric acid were designed and synthesized in very good yields with a simple and practical strategy. Twelve new chiral ionic potential task-specific catalysts, two of which are room-temperature chiral ionic liquids (RTCIL), were obtained, and their properties are discussed.

Key words: chiral pool, green solvents, ionic liquid, microwaves, chiral molecular recognition

The interest in using room-temperature ionic liquids (RTIL) as alternative solvents for organic synthesis, extractions, electrochemistry, and material science has increased tremendously in recent years.[1] Among them, chiral ionic liquids (CIL) are of special interest, and their use as reaction media for asymmetric organic reactions, chiral discrimination, analytical chemistry, as well as optical resolution of racemic mixtures has increased dramatically.[2] However, to date, there are only few chiral ionic liquids that have been designed, synthesized, and used as solvents[3] or organocatalysts[4] for asymmetric reactions achieving high ee. Therefore, the search for new CIL is still demanding, the main target being the synthesis of functionalized CIL which may work as task-specific catalysts or mediators. Considering that ionic liquids are regarded as green solvents, particularly promising are those obtained from renewable sources rather than from chemicals derived from petroleum.[5] In this context, compounds from the chiral pool constitute a low cost source for new CIL.



1: X = Br
2: X = BF_4
3: X = PF_6
4: X = NTf_2

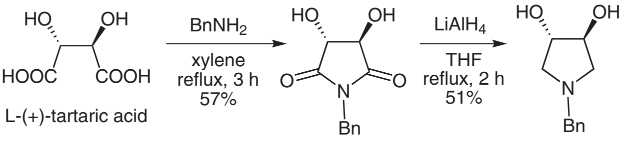
5: X = Br
6: X = BF_4
7: X = PF_6
8: X = NTf_2

9: X = Br
10: X = BF_4
11: X = PF_6
12: X = NTf_2

Figure 1

In this Letter we report the synthesis of compounds **1**–**12** (Figure 1), constituting a novel class of enantiopure pyrrolidinium chiral ionic materials based on L-(+)-tartaric acid as starting material. A few examples of ionic liquids based on L-tartaric acid have been previously reported, but in all cases an imidazolium moiety was always introduced.[6] Recently, syntheses of some ionic liquids embodying the tartaric acid skeleton in the anion were also reported.[7]

Our synthetic strategy started from low-cost L-tartaric acid, which was reacted with benzylamine in refluxing xylene to afford pyrrolidindione **13**[8] (Scheme 1) in 57% yield. Upon reduction with $LiAlH_4$ in dry THF the benzylpyrrolidine **14**[9] was obtained in 51% yield on a multigram scale.[10,11]



13 **14**

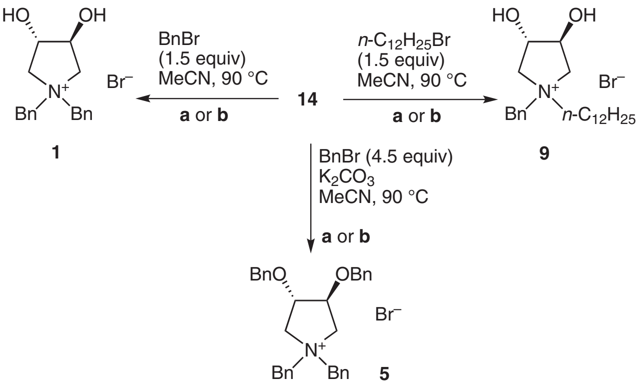
Scheme 1

Quaternization of pyrrolidine **14** was achieved using a slight excess of benzyl or *n*-dodecyl bromide in acetonitrile at 90 °C (Scheme 2). The reaction was performed either with traditional and microwave (MW) heating. Traditional heating gave the best results in most cases; however, excellent yields under MW heating were obtained for bromide salt **1** with reduced reaction times (10 min).[12] When using MW, prolonging the reaction times did not further increase the isolated yields.

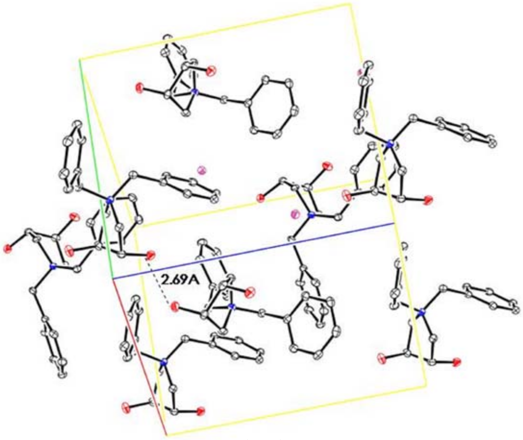
Good yields of the tetrabenzyl pyrrolidinium bromide **5** were obtained by slow addition (10 h, syringe pump) of 4.5 equivalents of BnBr in the presence of an excess of potassium carbonate (Scheme 2). This reaction is quite peculiar, considering that O-benzylations of tartaric acid derivatives generally proceed with low yields, and require the use of silver salts[13] or a phase-transfer catalyst.[14] Likely the success of the reported mild procedure can be ascribed to the early formation of the quaternary ammonium salt **5** (or its mono-O-benzylated parent), which autocatalyzes the reaction, being soluble in the reaction mixture and acting as a phase-transfer catalyst.

Bromides **1**, **5**, and **9** readily crystallized from the reaction mixture or by addition of diethyl ether and were recovered by simple filtration. Protection of the hydroxy groups pro-

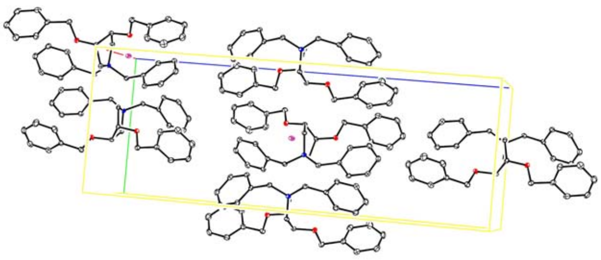
SYNLETT 2009, No. 5, pp 0747–0750
Advanced online publication: 24.02.2009
DOI: 10.1055/s-0028-1087950; Art ID: G38508ST



Scheme 2 *Reagents and conditions*: (a) oil bath: **1** (30 min, 93%); **9** (72 h, 70%); **5** (10 h, 87%); (b) microwaves: **1** (10 min, 150 W, 94%); **9** (10 min, 150 W, 25%); **5** (10 min, 150 W, 35%).



a) cell of **1**



b) cell of **5**

Figure 2

vided a means for lowering the melting point of the salt. Indeed, on passing from [dibenpyr]Br (**1**) to the tetrabenzylated [tetrabenpyr]Br (**5**), the melting point dropped considerably (205–206 °C vs. 169–172 °C, entries 1 and 5, Table 1), despite the sharp increase of molecular weight, presumably due to the lack of hydrogen-bonding interactions between cations. Indeed, this was also observed in the X-ray structures of compounds **1** and **5** (Figure 2), collected after crystallization from a solution in MeCN by slow addition of diethyl ether. Crystals of **1**[15] showed hydrogen bonding between one oxygen atom with an oxygen atom of another molecule (distance O1–O2 = 2.69 Å, Figure 2, a). The distance N–Br was found to be 4.105 Å. No π-stacking between the aromatic rings was observed. In crystals of **5**,[16] no interactions (hydrogen bonding or π-stacking) were observed between two cations (Figure 2, b). The distance N–Br was found to be 4.017 Å.

Alternatively, disrupting the C_2-symmetry of the molecule resulted a more effective way for obtaining low-melting-point salts. Indeed, for [dodebenpyr]Br (**9**), a melting point of 111–112 °C was observed (entry 9, Table 1), approaching the conventional limit (100 °C)[1c] for a salt to be regarded as a ionic liquid.

Anion exchange was straightforward, occurring simply by suspending the solid material at the interphase of a biphasic mixture of water and ethyl acetate. Upon addition of one equivalent of the appropriate potassium or lithium salt (KBF_4, KPF_6, or $LiNTf_2$), the two phases became transparent within five minutes and evaporation of the organic phase afforded the corresponding ionic compounds **2–4** and **6–8** (Table 1), always in quantitative yields.[17] Titration of the collected aqueous phases with a standard solution of $AgNO_3$ (using K_2CrO_4 as indicator) proved that substitution of the bromide ions was quantitative.[18] These ionic compounds were easily prepared in multigram scale. Anion exchange to give products **10–12** was better performed in water.[19]

Among the twelve novel chiral ionic materials obtained, only the bis(triflyl)amide salts were truly ionic liquids: two of them (**8**[20] and **12**[21]) were liquid at room temperature and [dibenpyr]NTf_2 (**4**[22]) showed a very low melting point. They all showed an excellent thermal stability, showing no sign of decomposition upon heating at 120 °C for 15 hours.

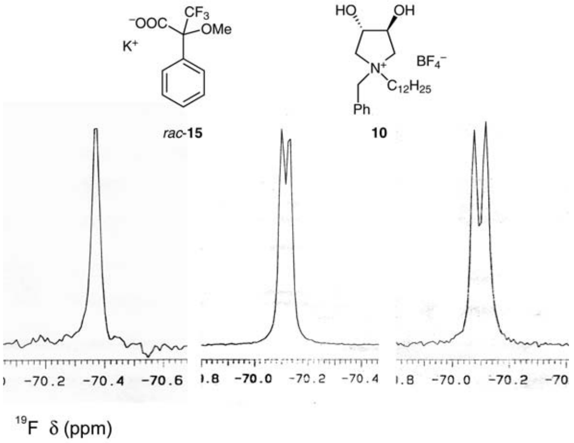
Table 1 Melting Points or Glass-Transisition Temperatures of Compounds **1–12**

Entry	Name	Compd	Mp or *Tg* (°C)
1	[dibenpyr]Br	**1**	205–206
2	[dibenpyr]BF_4	**2**	140–142
3	[dibenpyr]PF_6	**3**	107–108
4	[dibenpyr]NTf_2	**4**	50–53
5	[tetrabenpyr]Br	**5**	169–172
6	[tetrabenpyr]BF_4	**6**	126–127
7	[tetrabenpyr]PF_6	**7**	154–156
8	[tetrabenpyr]NTf_2	**8**	+1[a]
9	[dodebenpyr]Br	**9**	111–112
10	[dodebenpyr]BF_4	**10**	99–100
11	[dodebenpyr]PF_6	**11**	waxy solid
12	[dodebenpyr]NTf_2	**12**	–31[a]

[a] Glass-transition temperature (*Tg*).

A preliminary evaluation of the chiral recognition ability of these novel pyrrolidinium salts was carried out in attempting to detect diastereomeric interactions between the enantiopure cations **1–12** and the racemic Mosher acid anion.[23]

We used the potassium salt **15** and recorded the NMR spectra in $CDCl_3$ with the addition of 18-crown-6 to facilitate solubilization and dissociation. Interaction between salt **10** and Mosher acid salt **15** induced a shift of the fluorine atom signals in the ^{19}F NMR spectrum recorded at 188 MHz (Figure 3). The CF_3 groups of the two enantiomers of carboxylate **15** (Figure 3, a) split into two signals with a slight difference in the chemical shift that depended on the **10:15** ratio as previously observed.[23f] Varying the **10:15** ratio from 1 to 3 the shift passed from 6.1 Hz (Figure 3, b) to 7.6 Hz (Figure 3, c). Splitting of the signals for the *R*- and *S*-configured anions indicates the formation of diastereomeric salts and the ability of the chiral cation to influence the anion response.



a) no **10** b) 1 equiv of **10** c) 3 equiv of **10**

Figure 3

In conclusion, we have reported a straightforward strategy for the synthesis of a series of novel pyrrolidinium ionic liquids and ionic materials based on tartaric acid. Their potential in asymmetric synthesis as solvents, catalysts, or ligands is currently under investigation in our laboratories.

Acknowledgment

We thank INSTM (Progetto PRISMA 2004) for financial support. We are grateful to Ente Cassa di Risparmio di Firenze (CRF), Italy for granting a 400 MHz NMR spectrometer. We thank INSTM and CRF for a grant to M.B. We thank Brunella Innocenti and Maurizio Passaponti for technical assistance.

References and Notes

(1) For reviews on ionic liquids (IL), see: (a) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351. (b) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (c) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772. (d) Sheldon, R. *Chem. Commun.* **2001**, 2399. (e) Rogers, R. D.; Seddon, K. R.; Volkov, S. *Green Industrial Applications of Ionic Liquids*; Kluwer Academic: Drodrecht, **2002**. (f) Wasserscheid, P. *Ionic Liquids in Synthesis*; Wiley-Interscience: New York, **2003**. (g) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. *Tetrahedron* **2005**, *61*, 1015. (h) Muzart, J. *Adv. Synth. Catal.* **2006**, *348*, 275.

(2) For reviews on the synthesis and applications of chiral ionic liquids (CIL), see: (a) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A.-C.; Plaquevent, J.-C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081. (b) Baudequin, C.; Brégeon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *Tetrahedron: Asymmetry* **2005**, *16*, 3921. (c) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281. (d) Winkel, A.; Reddy, P. V. G.; Wilhelm, R. *Synthesis* **2008**, 999. (e) Bica, K.; Gaertner, P. *Eur. J. Org. Chem.* **2008**, 3235. (f) Plaquevent, J.-C.; Levillain, J.; Guillen, F.; Malhiac, C.; Gaumont, A.-C. *Chem. Rev.* **2008**, *108*, 5035.

(3) See, for example: (a) Gausepohl, R.; Buskens, P.; Kleinen, J.; Bruckmann, A.; Lehmann, C. W.; Klankermayer, J.; Leitner, W. *Angew. Chem. Int. Ed.* **2006**, *45*, 3689. (b) Malhotra, S. V.; Wang, Y. *Tetrahedron: Asymmetry* **2006**, *17*, 1032. (c) Schmitkamp, M.; Chen, D.; Leitner, W.; Klankermayer, J.; Franciò, G. *Chem. Commun.* **2007**, 4012. (d) Chen, D.; Schmitkamp, M.; Franciò, G.; Klankermayer, J.; Leitner, W. *Angew. Chem. Int. Ed.* **2008**, *47*, 7339.

(4) See, for example: (a) Luo, S.; Mi, Z.; Liu, S.; Xu, H.; Cheng, J.-P. *Angew. Chem. Int. Ed.* **2006**, *45*, 3093. (b) Miao, W.; Chan, T. H. *Adv. Synth. Catal.* **2006**, *348*, 1711. (c) Ni, B.; Zhang, Q.; Headley, A. D. *Green Chem.* **2007**, *9*, 737.

(5) (a) Imperato, G.; König, B.; Chiappe, C. *Eur. J. Org. Chem.* **2007**, 1049. (b) Chen, X.; Li, X.; Hu, A.; Wang, F. *Tetrahedron: Asymmetry* **2008**, *19*, 1.

(6) (a) Wang, Z.; Wang, Q.; Zhang, Y.; Bao, W. *Tetrahedron Lett.* **2005**, *46*, 4657. (b) Machado, M. Y.; Dorta, R. *Synthesis* **2005**, 2473.

(7) Allen, C. R.; Richard, P. L.; Ward, A. J.; van de Water, L. G. A.; Masters, A. F.; Maschmeyer, T. *Tetrahedron Lett.* **2006**, *47*, 7367.

(8) (a) Nagel, U.; Kinzel, E.; Andrade, J.; Prescher, G. *Chem. Ber.* **1986**, *119*, 3326. (b) Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *J. Org. Chem.* **1996**, *61*, 8099.

(9) Bridgeman, E.; Cavill, J. L.; Schofield, D. J.; Wilkins, D. S.; Tomkinson, N. C. O. *Tetrahedron Lett.* **2005**, *46*, 8521.

(10) **(3*R*,4*R*)-1-Benzyl-3,4-dihydroxy-2,5-pyrrolidinedione (13)**
Benzylamine (11 mL, 100 mmol) were added to a 250 mL round-bottom flask containing a suspension of L-(+)-tartaric acid (15.0 g, 100 mmol) in xylene (80 mL). The mixture was refluxed in a Dean–Stark apparatus for 4 h, and H_2O (3.6 mL, 200 mmol) was collected. Then the solid was filtered off, washed with acetone, and recrystallized from EtOH (12.5 g, 57 mmol, 57%).
(3*S*,4*S*)-1-Benzyl-3,4-pyrrolidinediol (14)
To a cooled (0 °C) suspension of $LiAlH_4$ (2.28 g, 60 mmol) in dry THF (100 mL) in a 500 mL round-bottom flask the pyrrolidinedione **13** (4.42 g, 20 mmol) was added portionwise, and the mixture was heated at reflux for 12 h. The mixture was then cooled to 0 °C, and a sat. solution of Na_2SO_4 was added until no gas evolution was observed, then additional anhyd Na_2SO_4 was added, and the mixture was filtered through Celite washing with EtOAc. Evaporation of the solvent yielded a white solid (1.97 g, 10.2 mmol, 51%). Spectral data were identical to those reported in the literature, see ref. 9.

(11) This two-step procedure has been reported to give higher yields. However, in our hands, these yields were not reproducible, and we introduced some slight modifications

to render the synthesis reliable when extended to a multigram scale.

(12) **General Procedure for Quaternization under Conventional Heating**

In a round-bottom flask the pyrrolidinediol **14** and alkyl or benzyl bromide (1.5 equiv) were suspended in MeCN. The mixture was heated at 90 °C until disappearance of the starting material (TLC control). The reaction mixture was cooled at 0 °C, and Et_2O was added to crystallize the pure product as a white solid.

General Procedure for Quaternization under Microwave Heating

In a microwave reactor, the pyrrolidinediol **14** and alkyl or benzyl bromide (1.5 equiv) were suspended in MeCN. The reaction was carried out at 90 °C, 150 W for 10 min (TLC control), then the reaction mixture was cooled to 0 °C, and the pure product crystallizes as a white solid.

(13) Fowler, P. A.; Haines, A. H.; Taylor, R. J. K.; Chrystal, E. J. T.; Gravestock, M. B. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1003.

(14) (a) Dubreil, D.; Cleopax, J.; Loupy, A. *Carbohydr. Res.* **1994**, *252*, 149. (b) Ikemoto, N.; Schreiber, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 2524.

(15) **Crystal Data for 1**

MW = 364.3, trigonal, space group $P31$, $Z = 3$, $D_c = 1.46$, $a = b = 10.686$ (1) Å, $c = 12.580$ (1) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 1244.1$ (2) Å^3. The X-ray CIF file for this structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition number 710820.

(16) **Crystal Data for 5**

MW = 544.5, orthorhombic, space group $P212121$, $Z = 4$, $D_c = 1.37$, $a = 9.767$ (1) Å, $b = 9.805$ (1) Å, $c = 27.605$ (1) Å, $\alpha = \beta = \gamma = 90°$, $V = 2643.6$ (4) Å^3. The X-ray CIF file for this structure has been deposited at the CCDC, deposition number 710821.

(17) **Anion Exchange (Procedure A)**

In a round-bottom flask the pyrrolidinium bromide **1** or **5** (1–5 mmol) were suspended in H_2O–EtOAc (1:1), then the appropriate potassium or lithium salt was added. After 5 min the two phases became limpid, and the reaction was finished. The organic phase was separated and dried with anhyd Na_2SO_4. Solvent evaporation gave the pure product.

(18) Upon addition of a slight excess of $AgNO_3$ the solution became yellow due to formation of Ag_2CrO_4.

(19) **Anion Exchange (Procedure B)**

In a round-bottom flask the pyrrolidinium bromide **9** was suspended in H_2O, then the appropriate potassium or lithium salt was added. The mixture was left to react overnight at r.t., and the formation of a pale yellow oil, insoluble in H_2O, was observed. Ethyl acetate was then added. The organic phase was separated and dried with anhyd Na_2SO_4. Solvent evaporation gave the pure product.

(20) **Data for Ionic Liquid 8**

Pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 10 H), 7.35–7.32 (m, 6 H), 7.22–7.19 (m, 4 H), 4.73 (A part of an AB system, *J* = 13.1 Hz, 2 H), 4.63 (B part of an AB system, *J* = 13.1 Hz, 2 H), 4.46 (A part of an AB system, *J* = 11.9 Hz, 2 H), 4.42 (B part of an AB system, *J* = 11.9 Hz, 2 H), 4.24 (br s, 2 H), 3.85 (dd, *J* = 13.5, 5.6 Hz, 2 H), 3.71 (dd, *J* = 13.5, 2.6 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 135.9 (s, 2 C), 133.3 (d, 4 C), 131.0 (d, 2 C), 129.4 (d, 4 C), 128.5 (d, 4 C), 128.3 (d, 2 C), 127.9 (d, 4 C), 126.6 (s, 2 C), 119.9 (q, 2 C, CF_3, *J* = 319.9 Hz), 80.2 (d, 2 C), 72.3 (t, 2 C), 66.9 (t, 2 C), 60.8 (t, 2 C). ^{19}F NMR (188 MHz, acetone-d_6,): δ = –79.9 (s). IR ($CDCl_3$): 3090 (w), 3068 (m), 3034 (m), 2923 (w), 2872 (w), 2260 (m), 1497 (m), 1456 (s), 1350 (s), 1199 (s), 1134 (s), 1059 (s) cm^{-1}. MS: *m/z* (%) = 464 (0.4), 160 (9), 120 (19), 91 (100), 69 (46), 41 (52). Anal. Calcd for $C_{34}H_{34}F_6N_2O_6S_2$: C, 54.83; H, 4.60; N, 3.76. Found: C, 54.82; H, 4.86; N, 3.86. $[\alpha]_D^{23}$ +0.9 (*c* 1.00, CH_2Cl_2).

(21) **Data for Ionic Liquid 12**

Pale yellow viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.41 (m, 5 H), 4.66–4.53 (m, 4 H), 4.17 (br s, 1 H), 4.09 (dd, *J* = 13.1, 4.0 Hz, 1 H), 3.98 (br s, 1 H), 3.79 (d, *J* = 12.8 Hz, 1 H), 3.73 (dd, *J* = 12.8, 4.0 Hz, 1 H), 3.37 (d, *J* = 13.1 Hz, 1 H), 3.30–3.15 (m, 2 H), 1.95–1.84 (m, 2 H), 1.32–1.25 (m, 18 H), 0.87 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.1 (d, 2 C), 130.9 (d, 1 C), 129.4 (d, 2 C), 127.4 (s, 1 C), 119.5 (q, 2 C, CF_3, *J* = 318.7 Hz), 75.8 (d, 1 C), 75.5 (d, 1 C), 68.6 (t, 1 C), 67.7 (t, 1 C), 66.9 (t, 1 C), 63.8 (t, 1 C), 31.9 (t, 1 C), 29.6 (t, 2 C), 29.5 (t, 1 C), 29.4 (t, 1 C), 29.3 (t, 1 C), 29.0 (t, 1 C), 26.2 (t, 1 C), 23.7 (t, 1 C), 22.8 (t, 1 C), 14.2 (q, 1 C). ^{19}F NMR (188 MHz, acetone-d_6): δ = –79.8 (s, 6 F). IR ($CHCl_3$): 3507 (m), 3033 (w), 2927 (m), 2855 (w), 1457 (w), 1349 (s), 1192 (s), 1133 (m), 1059 (m) cm^{-1}. MS: *m/z* (%) = 362 (35), 288 (12), 270 (11), 206 (6), 193 (7), 134 (5), 116 (100), 91 (45), 69 (11), 55 (15). Anal. Calcd for $C_{25}H_{40}F_6N_2O_6S_2$: C, 46.72; H, 6.27; N, 4.36. Found: C, 46.70; H, 6.55; N, 4.35. $[\alpha]_D^{22}$ –5.1 (*c* 0.985, MeOH).

(22) **Data for Ionic Liquid 4**

Pale yellow solid; mp 50–53 °C. ^{1}H NMR (200 MHz, CD_3OD): δ = 7.63–7.50 (m, 10 H), 4.89 (br s, 2 H), 4.71 (br s, 2 H), 4.32–4.24 (m, 2 H), 3.87 (dd, *J* = 12.5, 5.1 Hz, 2 H), 3.60 (dd, *J* = 13.2, 1.5 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 133.2 (d, 4 C), 131.1 (d, 2 C), 129.5 (d, 4 C), 127.1 (s, 2 C), 119.6 (q, 2 C, CF_3, *J* = 320.5 Hz), 76.1 (d, 2 C), 67.4 (t, 2 C), 63.3 (t, 2 C). ^{19}F NMR (188 MHz, acetone-d_6): δ = –79.9 (s). IR (CH_2Cl_2): 3593 (w), 3502 (m), 3059 (w), 3032 (w), 2923 (w), 1494 (w), 1457 (w), 1351 (s), 1199 (s), 1134 (m), 1060 (m) cm^{-1}. MS: *m/z* (%) = 284 (22), 210 (7), 193 (6), 133 (11), 120 (11), 91 (100), 65 (25), 51 (7). Anal. Calcd for $C_{20}H_{22}F_6N_2O_6S_2$: C, 42.55; H, 3.93; N, 4.96. Found: C, 42.36; H, 4.12; N, 4.95. $[\alpha]_D^{23}$ –24.5 (*c* 1.01, CH_2Cl_2).

(23) (a) Wasserscheid, P.; Bösmann, A.; Bolm, C. *Chem. Commun.* **2002**, 200. (b) Levillain, J.; Dubant, G.; Abrunhosa, I.; Gulea, M.; Gaumont, A.-C. *Chem. Commun.* **2003**, 2914. (c) Clavier, H.; Boulanger, L.; Audic, N.; Toupet, L.; Mauduit, M.; Guillemin, J.-C. *Chem. Commun.* **2004**, 1224. (d) Patil, M. L.; Rao, C. V. L.; Yonezawa, K.; Takizawa, S.; Onitsuka, K.; Sasai, H. *Org. Lett.* **2006**, *8*, 227. (e) Jurčík, V.; Gilani, M.; Wilhem, R. *Eur. J. Org. Chem.* **2006**, 5103. (f) Kumer, V.; Olsen, C. E.; Schäffer, S. J. C.; Parmar, V. S.; Malhotra, S. V. *Org. Lett.* **2007**, *9*, 3905.