Electronic Supplementary Information

Effects of the Ether Oxygen Atom in Alkyl Side Chains on the Physical Properties of Piperidinium Ionic Liquids

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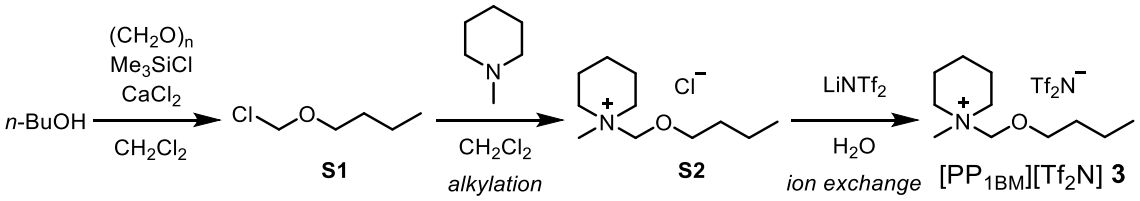
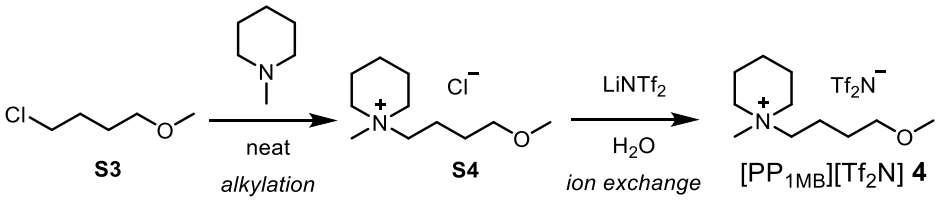


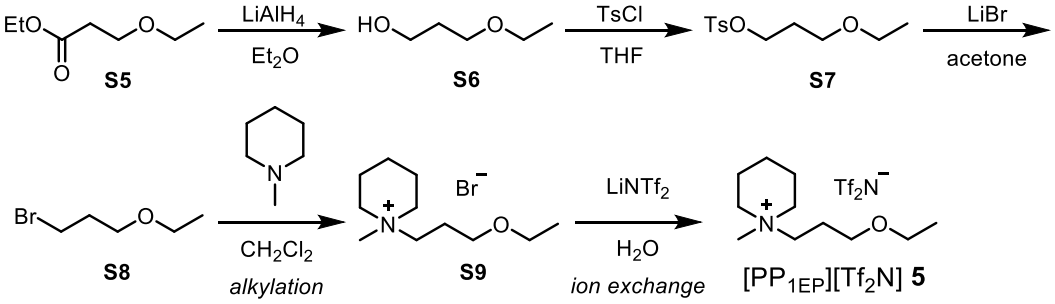
Scheme S1.[1]

$CaCl_2$ (22.5 mmol, 2.50 g), paraformaldehyde (140 mmol, 4.21 g), and butan-1-ol (101 mmol, 7.45 g) were added to anhydrous CH_2Cl_2 (dried, 100 mL) at 0 ^oC and stirred for 15 min. Then trimethylsilyl chloride (Me_3SiCl) (200 mmol, 21.7 g) was added dropwise to the mixture with a syringe pump (0.2 mL/min). After addtition of Me_3SiCl, the reaction mixture was filterated with a paper filter and solvent was removed under vacuum. Distillation of the crude product afforded 1-(chloromethoxy)butane (**S1**) in 49% yield as colorless liquid (52.0 mmol, 8.77 g). 1-(Chloromethoxy)butane (**S1**) was dissolved in CH_2Cl_2 and stirred at 0 ^oC. 1-Methylpiperidine (58.3 mmol, 5.78 g) was added dropwise to the solution with a syringe pump (0.2 mL/min). Then the reaction mixture was stirred at room temperature for 1 h and solvent was removed under reduced pressure. The crude product was washed with Et_2O and then dissolved in MeOH (100 mL) and activated carbon (ca 10 g) was added. After futhrer stirring for 1 day at room temperature the activated carbon was removed by paper filteration. Removal of solvent *in vacuo* afforded 1-(butoxymethyl)-1-methylpiperidin-1-ium chloride (**S2**) as a white solid in 82% yield (42.4 mmol, 9.40 g). Lithium bis((trifluoromethane)sulfonyl)amide ($LiNTf_2$) (43.2 mmol, 12.4 g) was added to the aqueous solution of **S2** and stirred for 1 h. The reaction mixture was extracted with CH_2Cl_2 (100 mL) and the thus-obtained organic layer was washed with deionized water to remove LiCl. Removal of solvent under reduced pressure afforded $[PP_{1BM}][Tf_2N]$ **3** in 77% yield as a colorless liquid. **1-(butoxymethyl)-1-methylpiperidin-1-ium bis((trifluoromethyl)sulfonyl)amide ($[PP_{1BM}][Tf_2N]$) (3)** ^1H NMR (600 MHz, $CDCl_3$) δ 0.94 (t, J = 7.2 Hz, 3 H), 1.35 - 1.41 (m, 2 H), 1.60 - 1.67 (m, 3 H), 1.80 - 1.84 (m, 1 H), 1.90 (quin, J = 9.6, 4.2 Hz, 4 H), 3.03 (s, 3 H), 3.31 (quin, J = 9.6, 4.2 Hz, 2 H), 3.39 (quin, J = 6.6 Hz, 2 H), 3.79 (t, J = 6.6 Hz, 2 H), 4.61 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6, 18.8, 19.5, 20.8, 31.4, 45.0, 57.6, 73.4, 90.7, 119.7 (q, J = 319.2 Hz); IR (neat, cm^{-1}) 2963, 1352, 1193, 1138, 1057. HRMS (ESI) *m/z* calcd for $[C_{11}H_{24}NO]^+$, 186.1852; found 186.1853. calcd for $[C_2F_6NO_4S_2]^-$, 279.9178; found 279.9175.



Scheme S2.

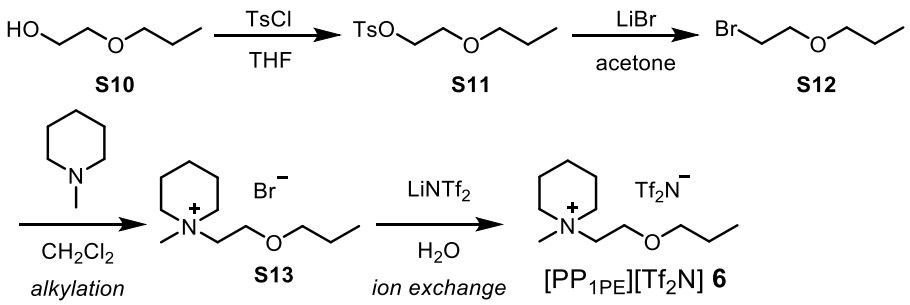
1-Chloro-4-methoxybutane **(S3)** (132 mmol, 16.2 g) and 1-methyl piperidine (141 mmol, 14.0 g) were stirred at 120℃ for 22 h to obtain piperidinium salt **S4** as a white solid in 53% yield (50.0 mmol, 15.1 g). Ion exchange of **S4** (23.6 mmol, 5.22 g) with $LiNTf_2$ (24.1 mmol, 6.90 g) afforded $[PP_{1MB}][Tf_2N]$ **4** as a colorless liquid in 62% yield (14.5 mmol, 6.78 g). **1-(4-methoxybutyl)-1-methylpiperidin-1-ium bis((trifluoromethyl)sulfonyl)amide ($[PP_{1MB}][Tf_2N]$) (4)** ^{1}H NMR (600 MHz, Acetone-d_6) δ 1.63 – 1.85 (m, 6 H), 1.89 - 1.90 (m, 4 H), 3.04 (s, 3 H), 3.33 (s, 3 H), 3.35 (t, *J* = 6.0 Hz, 6 H), 3.43 (t, *J* = 6.0 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.0, 1.98, 20.6, 26.0, 47.8, 58.5, 61.3, 71.3, 119.7 (q, *J* = 319.5 Hz); IR (neat, cm^{-1}) 2951, 1352, 1192, 1137, 1057; HRMS (ESI) *m/z* calcd for $[C_{24}H_{48}N_3O_6S_2]^+$: $[2M^+ + Tf_2N^-]^+$, 652.2883; found, 652.2868.



Scheme S3.[2]

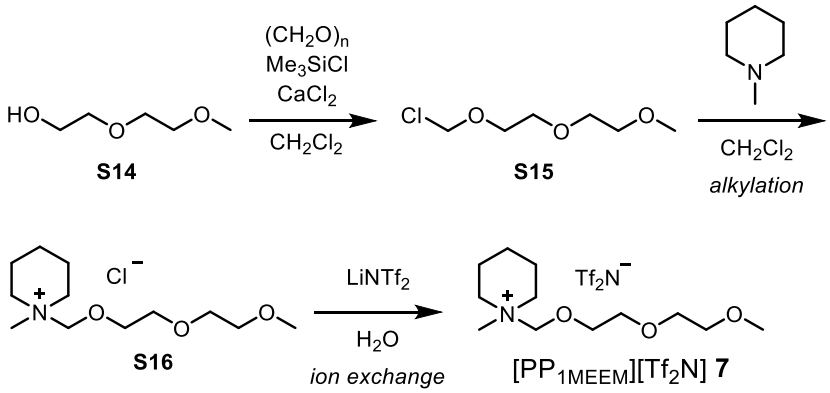
Lithium aluminum hydride ($LiAlH_4$) (8.84 g, 233 mmol) was place in a dry flask under argon atomosphere and dry Et_2O (350 mL) was added and stirred at room temperature. Et_2O solution of ethyl 3-ethoxypropanoate (**S5**) (51.5 g, 352 mmol) was added dropwise to the mixture and stirred for 2 h. After completion of the reaction confirmed by gas chromatography tetrahydrofuran (THF) containing water was added slowly at 0 ^{o}C. Then $NaSO_4$ was added to remove water and the reaction mixture was filtered. Removal of solvent at reduced pressure afforded 3-ethoxypropan-1-ol (**S6**) as a colorless liquid in 76% yield (266 mmol, 27.7 g). THF solution of **S6** was place in flask and then NaOH (12 g, 300 mmol) was added with water (75 mL). After stirring at 0 ^{o}C, THF solution of *para*-toluenesulfonyl chloride (TsCl) (45.9 g, 240 mmol) was added at 0 ^{o}C. The reation was quenched with 6 M HCl aqueous solution after further stirring at room temperature for overnight. The reaction mixture was extraceted with CH_2Cl_2 and the organic layer was concentrated *in vacuo* to obtain 3-ethoxypropyl 4-methylbenzenesulfonate (**S7**) in 74% yield (38.58 g, 148 mmol). **S7** was dissolved in acetone and lithium bromide (LiBr) (15.4 g, 178 mmol) was added in one portion. The reaction mixture was heated at 65 ^{o}C and stirred for 15 h. LiBr was removed by paper filteration and solvent was removed under reduced pressure. The crude product was diluted with CH_2Cl_2 and washed with water. Removal of solvent in vacuo afforded 1-bromo-3-ethoxypropane (**S8**) as a colorless liquid in quantitative yield (28.2 g, 169 mmol). Bromide **S8** (4.98 g, 29.8 mmol) was dissolved in CH_3CN and 1-methyl piperidine (3.57 g, 36 mmol) was added to the solution. After stirring of the reaction mixture at 60 ^{o}C for 3 days, solvent was removed under reduced pressure and dried *in vacuo*. The crude product was recrystallized with mix-solvent of 2-propanol and Et_2O to afford 1-(3-ethoxypropyl)-1-methylpiperidin-1-ium bromide (**S9**) in 86% (6.79 g, 25.5 mmol). Ion exchange of **S9** (10.3 mmol, 2.75 g) with $LiNTf_2$ (10.5 mmol, 3.02 g) afforded $[PP_{1EP}][Tf_2N]$ **5** as a colorless liquid in 95% yield (9.8 mmol, 4.58 g). **1-(3-ethoxypropyl)-1-methylpiperidin-**

1-ium bis((trifluoromethyl)sulfonyl)amide ([PP_{1EP}][Tf_2N]) (5) ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.18 (t, *J* = 6.6 Hz, 3 H), 1.57 (s, 3 H), 1.71 – 1.81 (m, 2 H), 1.92 (pseudo-t, *J* = 5.4 Hz, 4 H), 1.97 – 2.02 (m, 2 H), 3.07 (s, 3 H), 3.38 (pseudo-t, *J* = 6.0 Hz, 4 H), 3.45 – 3.48 (m, 2 H), 3.48 (q, *J* = 7.2 Hz 2 H), 3.52 (pseudo-t, *J* = 6.0 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.9, 19.8, 20.5, 22.5, 48.1, 61.5, 61.6, 66.1, 66.4, 119.8 (q, *J* = 319.4 Hz); IR (neat, cm^{-1}) 2977, 2875, 1352, 1193, 1137, 1057; HRMS (ESI) *m/z* calcd for $[C_{11}H_{24}NO]^+$, 186.1852; found 186.1846. calcd for $[C_2F_6NO_4S_2]^-$, 279.9178; found 279.9180.



Scheme S4.

THF solution of 2-propoxyethan-1-ol (**S10**) (20.4 g, 200 mmol) was place in flask and then NaOH (12 g, 300 mmol) was added with water (75 mL). After stirring at 0 ^oC, THF solution of *para*-toluenesulfonyl chloride (TsCl) (45.9 g, 240 mmol) was added at 0 ^oC. The reation was quenched with 6 M HCl aqueous solution after further stirring at room temperature for overnight. The reaction mixture was extraceted with CH_2Cl_2 and the organic layer was concentrated *in vacuo* to obtain 2-propoxyethyl 4-methylbenzenesulfonate (**S11**) in 93% yield (48.0 g, 185.7 mmol). Tosylate **S11** (48.0 g, 185.7 mmol) was dissolved in acetone and LiBr (19.4 g, 223 mmol) was added in one portion. The reaction mixture was heated at 65 ^oC and stirred for 15 h. LiBr was removed by paper filteration and solvent was removed under reduced pressure. The crude product was diluted with CH_2Cl_2 and washed with water. Removal of solvent in vacuo and distillation afforded 1-(2-bromoethoxy)propane (**S12**) as a colorless liquid in 58% yield (18.1 g, 108 mmol). Bromide **S12** (17.5 g, 105 mmol) was dissolved in CH_3CN and 1-methyl piperidine (12.5 g, 126 mmol) was added to the solution. After stirring of the reaction mixture at 55 ^oC for 4 days, solvent was removed under reduced pressure and dried *in vacuo*. The crude product was treated with activated carbon to afford 1-methyl-1-(2-propoxyethyl)piperidin-1-ium bromide (**S13**) in 68% (18.9 g, 70.9 mmol). Ion exchange of **S13** (68.2 mmol, 18.2 g) with $LiNTf_2$ (69.7 mmol, 20.0 g) afforded [PP_{1PE}][Tf_2N] **6** as a colorless liquid in 92% yield (62.9 mmol, 29.3 g). **1-methyl-1-(2-propoxyethyl)piperidin-1-ium bis((trifluoromethyl)sulfonyl)amide ([PP_{1PE}][Tf_2N]) (6)** ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz, 3 H), 1.57 (s, 3 H), 1.59 (sext, *J* = 7.8 Hz, 2 H), 1.71 – 1.76 (m, 2 H), 1.88 - 1.98 (m, 4 H), 3.16 (s, 3 H), 3.39 (ddd, *J* = 13.2, 7.2, 4.2 Hz, 2 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 3.53 (ddd, *J* = 12.6, 8.4, 4.2 Hz, 2 H), 3.61 (pseudo-t, *J* = 4.8 Hz, 2 H), 3.84 – 3.87 (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 10.4, 19.9, 20.5, 22.5, 49.5, 62.5, 63.7, 73.2, 119.8 (q, *J* = 319.4 Hz); IR (neat, cm^{-1}) 2967, 2880, 1352, 1193, 1137, 1057; HRMS (ESI) *m/z* calcd for $[C_{11}H_{24}NO]^+$, 186.1852; found 186.1845. calcd for $[C_2F_6NO_4S_2]^-$, 279.9178; found 279.9181.



Scheme S5.

$CaCl_2$ (22.8 mmol, 2.50 g), paraformaldehyde (141 mmol, 4.24 g), and diethylene glycohol monomethylether (**S14**) (101 mmol, 12.1g) were added to anhydrous CH_2Cl_2 (dried, 100 mL) at 0 ^oC and stirred for 15 min. Then Me_3SiCl (200 mmol, 21.7 g) was added dropwise. After addtition of Me_3SiCl, the reaction mixture was filterated and solvent was removed under vacuum. Distillation of the crude product afforded 1-(chloromethoxy)-2-(2-methoxyethoxy)ethane (**S15**) in 52% yield as colorless liquid (52.0 mmol, 8.77 g). Chloride **S15** was dissolved in CH_2Cl_2 and stirred at 0 ^oC. 1-Methylpiperidine (62.4 mmol, 6.19 g) was added dropwise to the solution. Then the reaction mixture was stirred at room temperature for 1 h and solvent was removed under reduced pressure. The crude product was washed with Et_2O and then dissolved in MeOH (130 mL) and activated carbon (ca 13 g) was added. After futhrer stirring for 1 day at room temperature the activated carbon was removed by paper filteration. Removal of solvent *in vacuo* afforded 1-((2-(2-methoxy-ethoxy)ethoxy)methyl)-1-methylpiperidin-1-ium chloride (**S16**) as a white solid in 72% yield (37.2 mmol, 9.94 g). **S16** was dissolved in water and $LiTf_2N$ (40.6 mmol, 11.7 g) was added. After stirring for 1 h at room temperature, the aqueous solution was extracted with CH_2Cl_2 (60 mL). The organic layer was washed with water to remove LiCl and evaporated to remove solvent. Further vacuum drying afforded $[PP_{1MEEM}][Tf_2N]$ **7** as colorless liquid in 95% yield (35.2 mmol, 18.0 g). **1-((2-(2-methoxy-ethoxy)ethoxy)methyl)-1-methylpiperidin-1-ium bis((trifluoromethyl)sulfonyl)-amide ($[PP_{1MEEM}][Tf_2N]$) (7)** ^1H NMR (600 MHz, $CDCl_3$) δ 1.62 - 1.69 (m, 1 H), 1.78 - 1.84 (m, 1 H), 1.91 (quin, J = 12.0, 6.6 Hz, 4 H), 3.04 (s, 3 H), 3.30 - 3.34 (m, 2 H), 3.52 - 3.54 (m, 2 H), 3.62 - 3.64 (m, 2 H), 3.68 - 3.69 (m, 2 H), 3.97 - 3.99 (m, 2 H), 4.71 (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.5, 20.8, 45.1, 57.5, 58.5, 70.1, 70.3, 71.7, 72.5, 90.8, 119.7 (q, J = 319.4 Hz); IR (neat, cm^{-1}) 2948, 1353, 1193, 1137, 1057; HRMS (ESI) *m/z* calcd for $[C_{12}H_{26}NO_3]^+$, 232.1907; found 232.1909 calcd for $[C_2F_6NO_4S_2]^-$, 279.9178; found, 279.9175.

2. Liner Sweep Voltammetry of Ionic Liquids 2-7

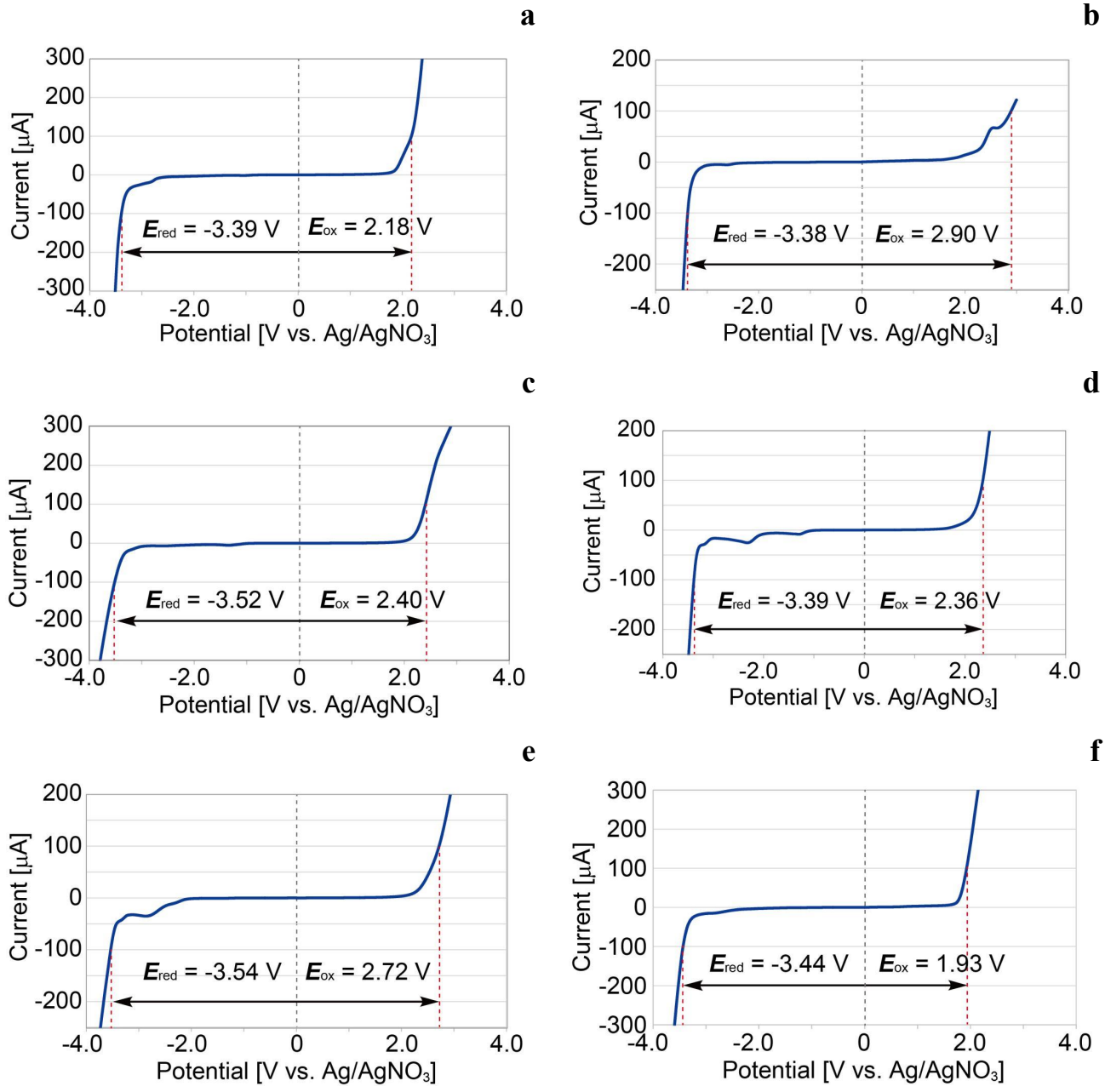
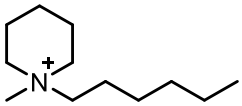
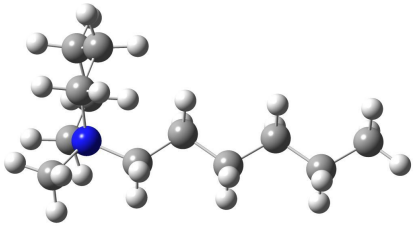


Figure S1. Linear Sweep Voltammtery of Ionic Liquids **2-7**. (a) $[PP_{1MEM}][Tf_2N]$ **2** (b) $[PP_{1BM}][Tf_2N]$ **3** (c) $[PP_{1MB}][Tf_2N]$ **4** (d) $[PP_{1EP}][Tf_2N]$ **5** (e) $[PP_{1PE}][Tf_2N]$ **6** (f) $[PP_{1MEEM}][Tf_2N]$ **7**

3. DFT calculations of the Piperidinium Cations

Calculations of the cation parts of ionic liquids **1-7** were carried out with the three-parameter functional of Becke,[3] the correlation functional of Lee, Yang, and Parr (B3LYP),[4] and the 6-31G* basis set.[5] Geometries were optimized and vibrational analyses were performed at the B3LYP/6-31G* level of theory. The vibrational analyses were used to confirm energetic stability of the optimized structures. All of the calculations were carried out with the Gaussian 09 suite of programs.[6] Cartesian coordinates and energies of computationally characterized species are as follows:

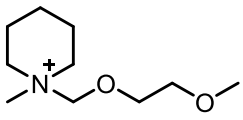


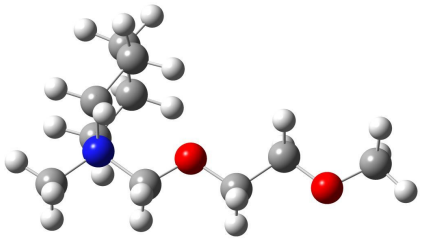


Piperidinium cation of $[PP_{16}][Tf_2N]$ **1** (white: H, gray: C, blue: N)

Atom	X	Y	Z
C	-6.72903	-1.34919	-1.80049
N	-8.16336	-0.93941	-1.54985
C	-8.13795	-0.20113	-0.1951
C	-9.4421	0.158184	0.512775
C	-9.12136	0.928745	1.809319
C	-10.3841	1.299513	2.599676
C	-8.57683	-0.03251	-2.71904
C	-10.0804	0.143986	-2.91864
C	-10.7927	-1.20899	-3.01161
C	-10.5054	-2.03593	-1.75437
C	-9.00513	-2.22297	-1.52208
C	-10.0798	2.070409	3.891379
C	-11.3427	2.440445	4.675296
H	-6.65918	-1.84203	-2.77047
H	-6.09852	-0.45849	-1.79182
H	-6.41225	-2.036	-1.01428
H	-7.54771	-0.84892	0.459221
H	-7.54912	0.701114	-0.38468
H	-10.0876	0.777212	-0.11664
H	-10.0014	-0.7467	0.771888

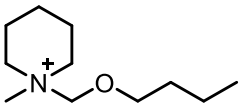
Atom	X	Y	Z
H	-8.45957	0.321493	2.442861
H	-8.5629	1.842682	1.563159
H	-11.0475	1.903195	1.963561
H	-10.9419	0.384153	2.844861
H	-8.154	-0.50518	-3.61009
H	-8.06018	0.91782	-2.56282
H	-10.5183	0.755712	-2.12468
H	-10.2012	0.713458	-3.84736
H	-11.8707	-1.06235	-3.12574
H	-10.4504	-1.7495	-3.90478
H	-10.9857	-1.57736	-0.88639
H	-10.9274	-3.0434	-1.84545
H	-8.78877	-2.70639	-0.56557
H	-8.59363	-2.85038	-2.31803
H	-9.41669	1.46588	4.52561
H	-9.51972	2.983057	3.644587
H	-11.092	2.988655	5.58911
H	-12.0093	3.074789	4.079
H	-11.9061	1.546346	4.967652

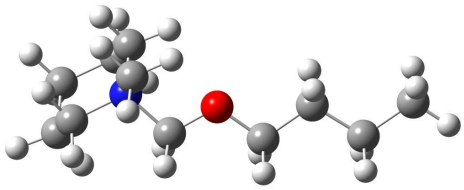




Piperidinium cation of $[PP_{1MEM}][Tf_2N]$ **2** (white: H, gray: C, blue: N, red: O)

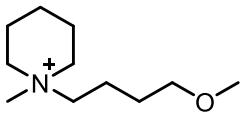
Atom	X	Y	Z
N	-1.22855	1.171807	0.416251
C	-0.8225	0.34538	-0.79309
O	-1.13278	-0.97075	-0.51776
C	-0.80766	-1.87503	-1.59343
C	-1.21421	-3.27697	-1.16098
O	-0.8878	-4.11689	-2.23686
C	-1.20216	-5.48109	-1.99781
C	-0.89981	2.633622	0.114402
C	-1.43185	3.59752	1.174466
C	-2.94197	3.427901	1.386174
C	-3.284	1.965726	1.701649
C	-2.73793	1.014409	0.639224
C	-0.45197	0.678898	1.611783
H	-1.37885	0.744248	-1.65348
H	0.254374	0.511379	-0.94647
H	0.26953	-1.83897	-1.80058
H	-1.35178	-1.58713	-2.50213
H	-2.29342	-3.30024	-0.93413
H	-0.67321	-3.55767	-0.24171
H	-0.90866	-6.03282	-2.89263
H	-2.27951	-5.61946	-1.82408
H	-0.64885	-5.87405	-1.13213
H	0.186327	2.695306	0.006961
H	-1.35708	2.846303	-0.85699
H	-1.19778	4.609912	0.827446
H	-0.88971	3.467724	2.118523
H	-3.28301	4.079646	2.196013
H	-3.47755	3.743616	0.480784
H	-4.36929	1.817864	1.728697
H	-2.91776	1.687084	2.696971
H	-2.90452	-0.0358	0.87786
H	-3.19648	1.222691	-0.33275
H	-0.75149	1.233365	2.497489
H	0.611358	0.834584	1.420186
H	-0.65664	-0.38269	1.735909



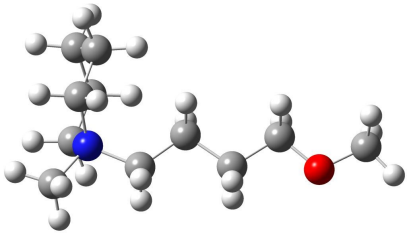


Piperidinium cation of $[PP_{1BM}][Tf_2N]$ **3** (white: H, gray: C, blue: N, red: O)

Atom	X	Y	Z
C	-7.61425	-2.46294	-0.91747
N	-8.80572	-1.57567	-0.65602
C	-8.51789	-0.74791	0.587551
O	-7.41284	0.030547	0.308774
C	-7.02679	0.907432	1.396077
C	-5.82233	1.720924	0.952761
C	-9.02703	-0.67336	-1.87507
C	-10.3182	0.135835	-1.78895
C	-11.541	-0.76619	-1.57725
C	-11.346	-1.66583	-0.34908
C	-10.0363	-2.45181	-0.42491
C	-5.34145	2.685224	2.048041
C	-4.12585	3.508341	1.610227
H	-7.80072	-3.03976	-1.82387
H	-6.73293	-1.83482	-1.03314
H	-7.48687	-3.13653	-0.06781
H	-9.40977	-0.15271	0.812323
H	-8.34802	-1.46681	1.403272
H	-7.87742	1.55805	1.646042
H	-6.79204	0.295168	2.27848
H	-5.01257	1.033636	0.676492
H	-6.08781	2.283523	0.048525
H	-9.0539	-1.35278	-2.73206
H	-8.14167	-0.04219	-1.94804
H	-10.2457	0.889546	-0.99536
H	-10.4054	0.694195	-2.72751
H	-12.4439	-0.16005	-1.45781
H	-11.6952	-1.38952	-2.46817
H	-11.3932	-1.07599	0.573872
H	-12.1521	-2.40428	-0.27523
H	-9.84315	-3.0282	0.484268
H	-10.0557	-3.14651	-1.26967
H	-6.16176	3.361196	2.325807
H	-5.09148	2.11468	2.952926
H	-3.8054	4.186138	2.407546
H	-3.27694	2.861297	1.360826
H	-4.35431	4.116366	0.727107



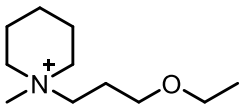
Piperidinium cation of $[PP_{1MB}][Tf_2N]$ **4**



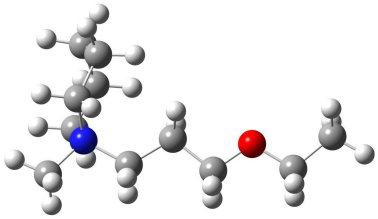
(white: H, gray: C, blue: N, red: O)

Atom	X	Y	Z
C	-6.90971	-1.26314	-1.56352
N	-8.34138	-0.83345	-1.32909
C	-8.32057	-0.09826	0.026259
C	-9.62813	0.267843	0.725236
C	-9.29699	1.030907	2.020493
C	-10.5475	1.406223	2.814488
C	-8.72788	0.080998	-2.50182
C	-10.2264	0.282054	-2.71533
C	-10.9586	-1.05942	-2.81936
C	-10.6968	-1.89478	-1.56205
C	-9.202	-2.1049	-1.31422
O	-10.1189	2.096436	3.961378
C	-11.1874	2.50578	4.799009
H	-6.83524	-1.75349	-2.53435
H	-6.26664	-0.38164	-1.54373
H	-6.61286	-1.95724	-0.77597
H	-7.74057	-0.7506	0.68489
H	-7.72479	0.800778	-0.15582
H	-10.2647	0.89214	0.091761

Atom	X	Y	Z
H	-10.194	-0.63506	0.977469
H	-8.64951	0.425186	2.666701
H	-8.74617	1.951367	1.791083
H	-11.2181	2.035205	2.201257
H	-11.1158	0.498662	3.087736
H	-8.30421	-0.39857	-3.38878
H	-8.1969	1.022432	-2.34
H	-10.6621	0.898679	-1.92383
H	-10.3293	0.856124	-3.64332
H	-12.0331	-0.89601	-2.9439
H	-10.6157	-1.60239	-3.71074
H	-11.1794	-1.432	-0.69762
H	-11.1328	-2.8955	-1.66089
H	-9.00269	-2.59472	-0.35723
H	-8.7912	-2.73557	-2.10791
H	-10.7418	3.024997	5.649789
H	-11.8704	3.192034	4.275461
H	-11.7659	1.643968	5.165305



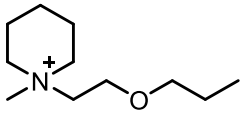
Piperidinium cation of $[PP_{1EP}][Tf_2N]$ **5**



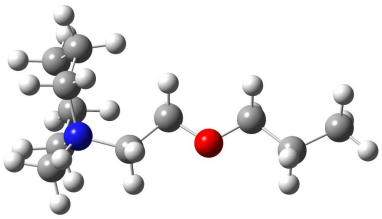
(white: H, gray: C, blue: N, red: O)

Atom	X	Y	Z
C	-6.5836	-1.23936	-1.67866
N	-8.01095	-0.84251	-1.37114
C	-7.94552	-0.15052	0.001366
C	-9.23723	0.25881	0.698146
C	-8.91722	0.981349	2.0149
O	-10.1518	1.30329	2.597436
C	-8.46438	0.10156	-2.49816
C	-9.97452	0.257958	-2.67003
C	-10.6712	-1.10136	-2.78268
C	-10.3529	-1.95163	-1.54907
C	-8.84671	-2.13255	-1.35536
C	-10.0327	1.991356	3.846183
C	-11.4289	2.287611	4.362648
H	-6.54635	-1.7147	-2.65897
H	-5.95786	-0.34536	-1.67727
H	-6.23566	-1.9382	-0.91645
H	-7.3934	-0.84856	0.637544
H	-7.30827	0.724161	-0.16037
H	-9.83936	0.937704	0.090729

Atom	X	Y	Z
H	-9.85382	-0.60909	0.94511
H	-8.31792	0.331428	2.677615
H	-8.31713	1.888449	1.821065
H	-8.04642	-0.32844	-3.41257
H	-7.96305	1.055066	-2.31329
H	-10.4103	0.844789	-1.85691
H	-10.1164	0.846377	-3.58389
H	-11.7525	-0.96437	-2.87547
H	-10.3379	-1.6185	-3.69295
H	-10.8186	-1.51648	-0.66121
H	-10.7683	-2.96064	-1.65285
H	-8.60485	-2.63764	-0.41635
H	-8.44983	-2.73692	-2.17593
H	-9.47302	1.365614	4.559395
H	-9.4607	2.921515	3.700684
H	-11.3712	2.815248	5.320104
H	-11.978	2.915762	3.654382
H	-11.9908	1.360501	4.512316



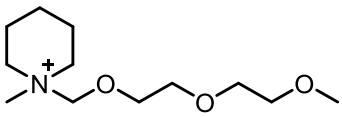
Piperidinium cation of $[PP_{1PE}][Tf_2N]$ **6**



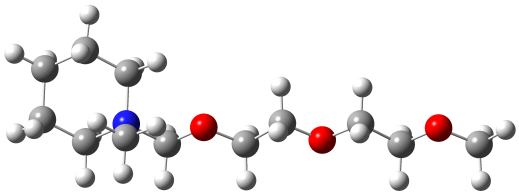
(white: H, gray: C, blue: N, red: O)

Atom	X	Y	Z
C	-7.30684	-1.36732	-1.57821
N	-8.74201	-0.92025	-1.39812
C	-8.75137	-0.1385	-0.0815
C	-10.0722	0.213808	0.614084
O	-9.6379	0.961272	1.71797
C	-10.6955	1.351544	2.606543
C	-9.09342	-0.05055	-2.6153
C	-10.5847	0.185123	-2.83645
C	-11.3534	-1.13916	-2.896
C	-11.1061	-1.94947	-1.61875
C	-9.61575	-2.18214	-1.36456
C	-10.0941	2.155053	3.749598
C	-11.1559	2.602914	4.759813
H	-7.20895	-1.88425	-2.53289
H	-6.65896	-0.48942	-1.56203
H	-7.04074	-2.04093	-0.76262
H	-8.16502	-0.73018	0.62461
H	-8.20538	0.78773	-0.27434
H	-10.7489	0.799815	-0.02451

Atom	X	Y	Z
H	-10.6086	-0.69239	0.935481
H	-11.4366	1.949708	2.052868
H	-11.2055	0.450989	2.984253
H	-8.68304	-0.58684	-3.47574
H	-8.53361	0.880157	-2.49541
H	-10.9999	0.841407	-2.06537
H	-10.6738	0.730703	-3.7828
H	-12.4241	-0.95105	-3.01846
H	-11.0313	-1.7154	-3.77397
H	-11.5797	-1.45956	-0.76385
H	-11.5621	-2.94331	-1.69306
H	-9.42574	-2.65917	-0.39933
H	-9.21044	-2.82925	-2.1478
H	-9.33276	1.540881	4.245586
H	-9.5761	3.026267	3.330819
H	-10.6973	3.178736	5.569143
H	-11.9158	3.238703	4.290555
H	-11.6678	1.74547	5.212124



Piperidinium cation of $[PP_{1MEEM}][Tf_2N]$ **7**



(white: H, gray: C, blue: N, red: O)

Atom	X	Y	Z
C	-4.72991	3.285659	-3.02578
C	-4.63851	1.973426	-2.25011
N	-3.37872	1.882615	-1.37907
C	-2.13922	2.141611	-2.23476
C	-2.21145	3.456856	-3.00975
C	-3.47619	3.53434	-3.87484
C	-3.26834	0.473936	-0.81876
C	-3.45034	2.850244	-0.22417
O	-4.39448	0.242531	-0.05588
C	-4.41673	-1.06286	0.55729
C	-5.70317	-1.1717	1.36402
O	-5.69248	-2.45376	1.935358
C	-6.83549	-2.72057	2.74335
C	-6.70148	-4.134	3.290988
O	-7.83994	-4.3689	4.086185
C	-7.85033	-5.65841	4.670026
H	-5.62058	3.214921	-3.65992
H	-4.91144	4.12631	-2.34545
H	-5.48489	1.810245	-1.5832
H	-4.57479	1.124663	-2.9384
H	-1.27943	2.105687	-1.56057

Atom	X	Y	Z
H	-2.07362	1.295557	-2.92603
H	-1.31036	3.508299	-3.63065
H	-2.15625	4.310356	-2.32381
H	-3.5377	4.511325	-4.36329
H	-3.41977	2.784563	-4.6754
H	-3.18769	-0.20596	-1.67915
H	-2.33683	0.434955	-0.23428
H	-3.56869	3.862659	-0.60166
H	-2.52332	2.773959	0.347144
H	-4.29709	2.571956	0.400193
H	-3.54476	-1.18335	1.212998
H	-4.38705	-1.84079	-0.21643
H	-6.57274	-1.02547	0.702146
H	-5.73092	-0.38151	2.13242
H	-6.89809	-2.00228	3.57428
H	-7.75769	-2.63568	2.149513
H	-6.63485	-4.85284	2.457394
H	-5.77246	-4.22	3.878822
H	-8.76698	-5.73441	5.25911
H	-6.98355	-5.80962	5.331877
H	-7.84812	-6.44922	3.903973

4. References

(1) Protocol of chloromethylation: Vo, C.-V. T.; Mitchell, T. A.; Bode, J. W. *J. Am. Chem. Soc.* **2011**, *134*, 14082-14089.

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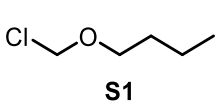
5. ^{1}H NMR spectra of Alkyl Halide Intermediates S1, S8, S12, and S15

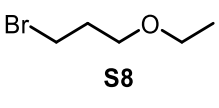
These alkyl halides and their precursors in this article are all known compounds. We added ^{1}H NMR spectra of alkyl halides to show their purity.



S1


```
NAME            TAY-58-syuryu
EXPNO                      10
PROCNO                      1
Date_                20151102
Time                    13.53
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                12335.526 Hz
FIDRES              0.188225 Hz
AQ                  2.6564426 sec
RG                       114
DW                    40.533 usec
DE                     6.50 usec
TE                    295.8 K
D1                 1.00000000 sec
TD0                        1

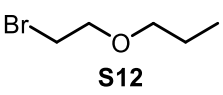
======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                    -2.00 dB
PL1W            18.91009140 W
SFO1            600.1337060 MHz
SI                     32768
SF              600.1300142 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



S8


```
NAME            TAY-134 syuryu
EXPNO                      10
PROCNO                      1
Date_                20160708
Time                    15.02
INSTRUM                 spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                12335.526 Hz
FIDRES              0.188225 Hz
AQ                  2.6564426 sec
RG                       161
DW                    40.533 usec
DE                     6.50 usec
TE                    297.8 K
D1                 1.00000000 sec
TD0                        1

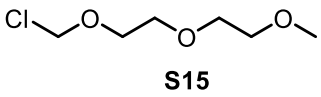
======== CHANNEL f1 ========
NUC1                      1H
P1                     13.00 usec
PL1                    -2.00 dB
PL1W            18.91009140 W
SFO1            600.1337060 MHz
SI                     32768
SF              600.1300146 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



S12


```
NAME          TAY-131 syuryu
EXPNO                     10
PROCNO                     1
Date_               20160706
Time                   15.43
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               12335.526 Hz
FIDRES             0.188225 Hz
AQ                2.6564426 sec
RG                      128
DW                 40.533 usec
DE                   6.50 usec
TE                  298.1 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    13.00 usec
PL1                   -2.00 dB
PL1W             18.91009140 W
SFO1            600.1337060 MHz
SI                      32768
SF               600.1300138 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```

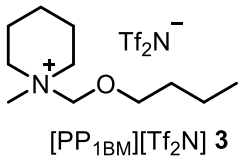


S15


```
NAME          TAY-78-syuryu
EXPNO                     10
PROCNO                     1
Date_               20151210
Time                   13.48
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               12335.526 Hz
FIDRES             0.188225 Hz
AQ                2.6564426 sec
RG                      114
DW                 40.533 usec
DE                   6.50 usec
TE                  296.3 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    13.00 usec
PL1                   -2.00 dB
PL1W             18.91009140 W
SFO1            600.1337060 MHz
SI                      32768
SF               600.1300116 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```

6. ^{1}H and ^{13}C NMR spectra of Ionic Liquids 3-7



[PP_{1BM}][Tf_2N] **3**

```
NAME              TAY-88
EXPNO                 10
PROCNO                 1
Date_           20160119
Time               21.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH            12335.526 Hz
FIDRES         0.188225 Hz
AQ             2.6564426 sec
RG                   114
DW              40.533 usec
DE                6.50 usec
TE                295.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.00 usec
PL1               -2.00 dB
PL1W        18.91009140 W
SFO1        600.1337060 MHz
SI                 32768
SF          600.1300112 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
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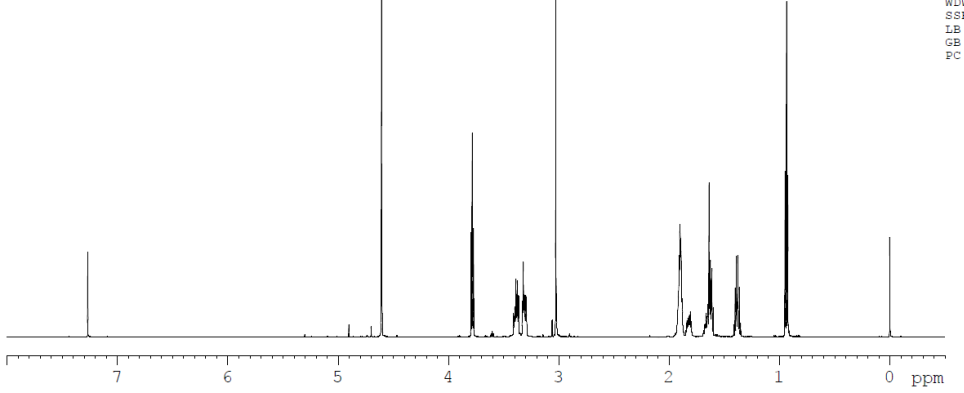
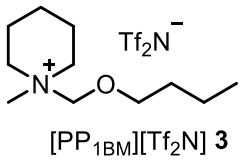


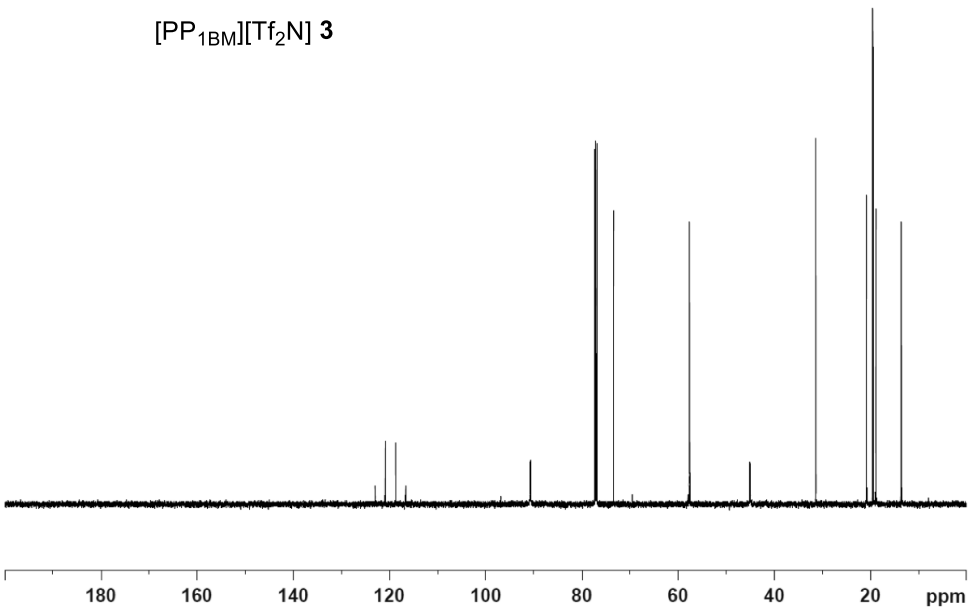


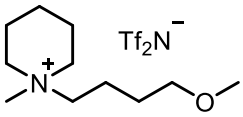
[PP_{1BM}][Tf_2N] **3**

```
NAME          TAY-88 13C
EXPNO                 10
PROCNO                 1
Date_           20160119
Time               21.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   150
DS                     2
SWH            36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9088159 sec
RG                   203
DW              13.867 usec
DE                6.50 usec
TE                296.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

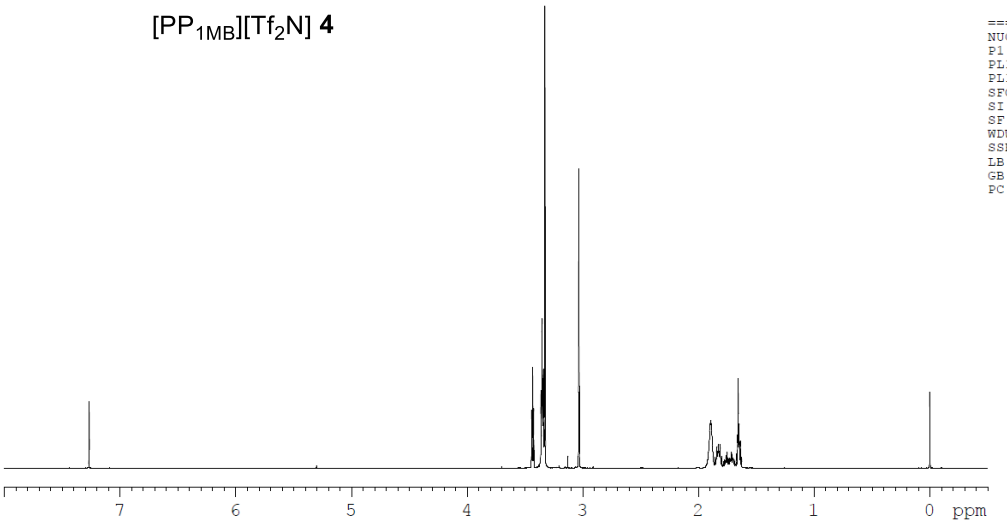
======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1               -1.00 dB
PL1W       125.22619629 W
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              13.78 dB
PL13              14.00 dB
PL2W        18.91009140 W
PL12W        0.49968192 W
PL13W        0.47499999 W
SFO2        600.1324005 MHz
SI                 32768
SF          150.9028090 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```



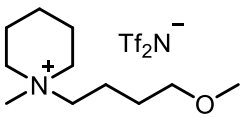


[PP_{1MB}][Tf_2N] **4**

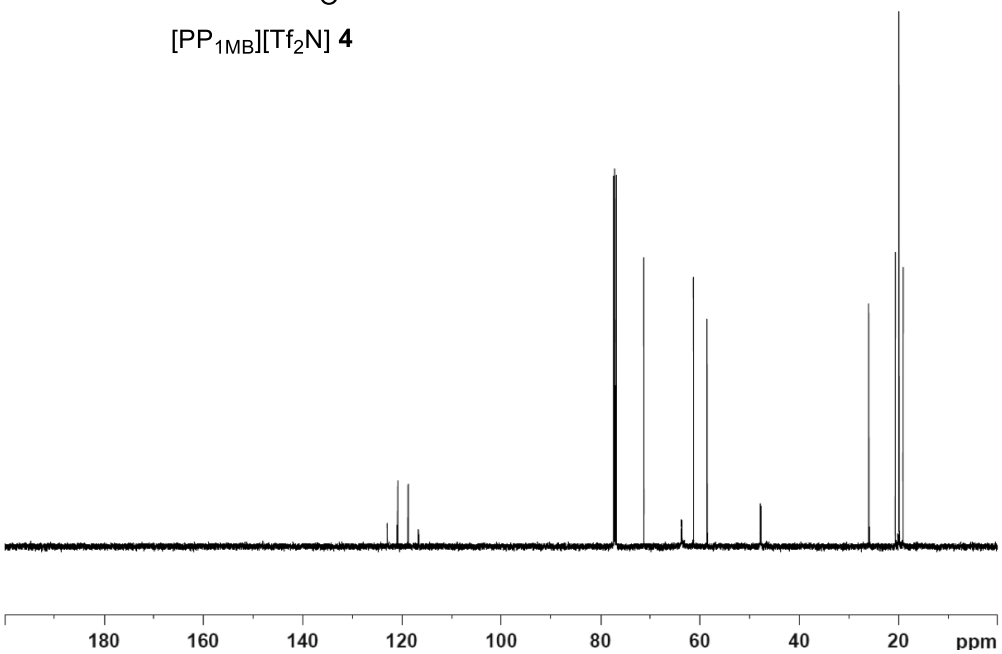



```
NAME                TAY-97
EXPNO                   10
PROCNO                   1
Date_             20160209
Time                 14.06
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                       8
DS                       2
SWH              12335.526 Hz
FIDRES           0.188225 Hz
AQ               2.6564426 sec
RG                     114
DW                40.533 usec
DE                 6.50 usec
TE                295.0 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                -2.00 dB
PL1W         18.91009140 W
SFO1         600.1337060 MHz
SI                   32768
SF           600.1300115 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



[PP_{1MB}][Tf_2N] **4**

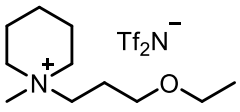


BRUKER

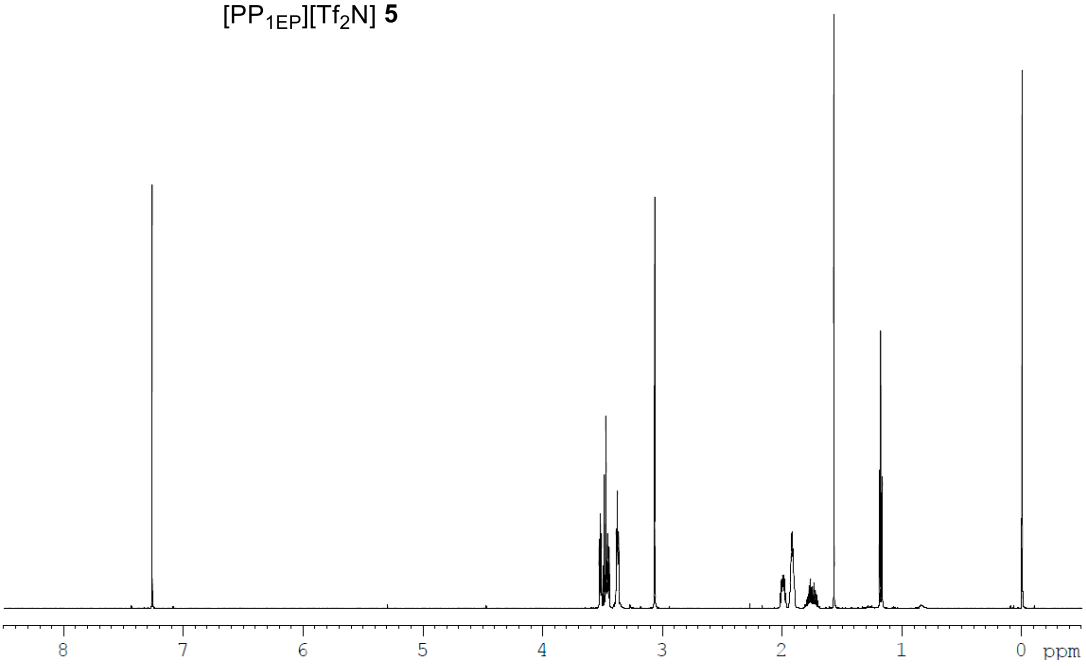
```
NAME            TAY-97 13C
EXPNO                   10
PROCNO                   1
Date_             20160209
Time                 14.20
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     150
DS                       2
SWH              36057.691 Hz
FIDRES           0.550197 Hz
AQ               0.9088159 sec
RG                     203
DW                13.867 usec
DE                 6.50 usec
TE                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -1.00 dB
PL1W        125.22619629 W
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.78 dB
PL13               14.00 dB
PL2W         18.91009140 W
PL12W         0.49968192 W
PL13W         0.47499999 W
SFO2         600.1324005 MHz
SI                   32768
SF           150.9028090 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

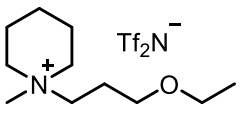


[PP$_{1EP}$][Tf$_2$N] **5**




```
NAME              TAY-142
EXPNO                  10
PROCNO                  1
Date_            20160804
Time                19.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             12335.526 Hz
FIDRES          0.188225 Hz
AQ              2.6564426 sec
RG                    203
DW                 40.533 usec
DE                  6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
PL1                 -2.00 dB
PL1W         18.91009140 W
SFO1        600.1337060 MHz
SI                  32768
SF          600.1300152 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



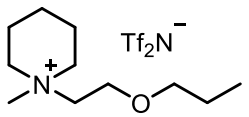
[PP$_{1EP}$][Tf$_2$N] **5**

BRUKER

```
NAME          TAY-142 13C
EXPNO                 10
PROCNO                 1
Date_           20160927
Time               16.01
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   150
DS                     2
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ              0.9088159 sec
RG                   203
DW                13.867 usec
DE                 6.50 usec
TE                299.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -1.00 dB
PL1W        125.22619629 W
SFO1         150.9178988 MHz

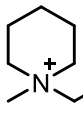
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.78 dB
PL13               14.00 dB
PL2W         18.91009140 W
PL12W         0.49968192 W
PL13W         0.47499999 W
SFO2        600.1324005 MHz
SI                 32768
SF          150.9028090 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



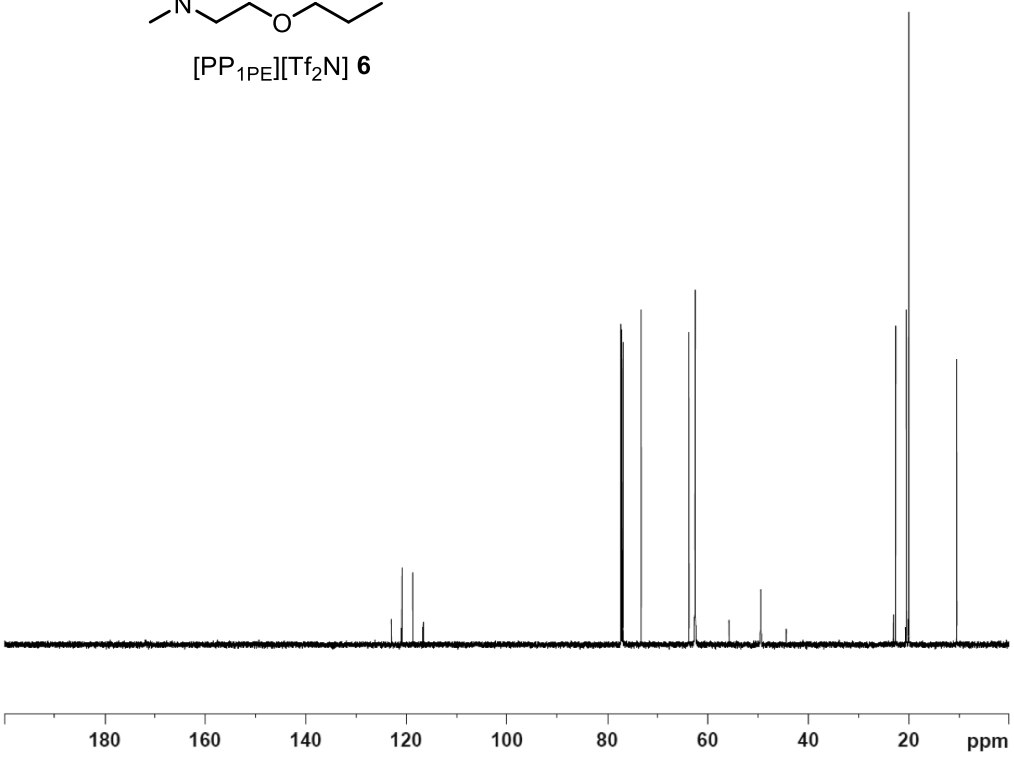
[PP_{1PE}][Tf_2N] **6**


```
NAME                TAY-143
EXPNO                    10
PROCNO                    1
Date_              20160829
Time                  20.33
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ                2.6564426 sec
RG                      203
DW                   40.533 usec
DE                    6.50 usec
TE                   297.8 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   13.00 usec
PL1                  -2.00 dB
PL1W          18.91009140 W
SFO1         600.1337060 MHz
SI                    32768
SF           600.1300151 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



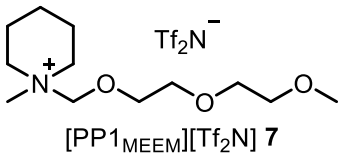
[PP_{1PE}][Tf_2N] **6**



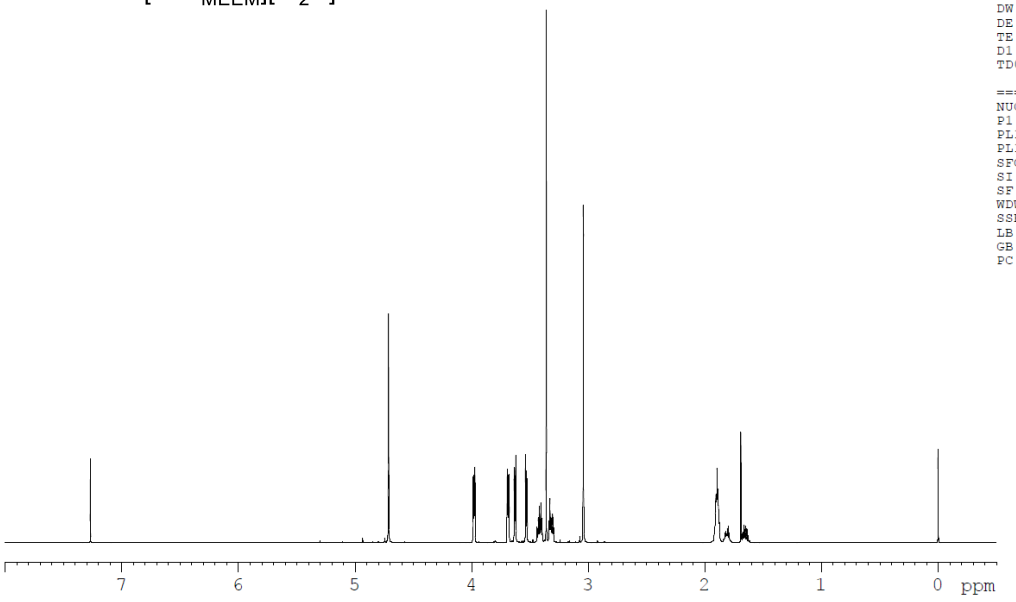

```
NAME          TAY-143 13C
EXPNO                 10
PROCNO                 1
Date_           20160927
Time               16.12
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  150
DS                    2
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9088159 sec
RG                  203
DW                13.867 usec
DE                 6.50 usec
TE                299.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PL1                -1.00 dB
PL1W       125.22619629 W
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.00 dB
PL12               13.78 dB
PL13               14.00 dB
PL2W       18.91009140 W
PL12W       0.49968192 W
PL13W       0.47499999 W
SFO2       600.1324005 MHz
SI               32768
SF         150.9028090 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

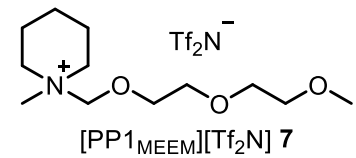


[PP1$_{MEEM}$][Tf$_2$N] **7**




```
NAME                TAY-80
EXPNO                   10
PROCNO                   1
Date_             20151227
Time                 14.06
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              12335.526 Hz
FIDRES           0.188225 Hz
AQ               2.6564426 sec
RG                    114
DW                40.533 usec
DE                   6.50 usec
TE                 295.8 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  13.00 usec
PL1                 -2.00 dB
PL1W           18.91009140 W
SFO1          600.1337060 MHz
SI                   32768
SF            600.1300109 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



[PP1$_{MEEM}$][Tf$_2$N] **7**


```
NAME              TAY-80 C
EXPNO                   10
PROCNO                   1
Date_             20160129
Time                 19.30
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    150
DS                      2
SWH              36057.691 Hz
FIDRES           0.550197 Hz
AQ               0.9088159 sec
RG                    203
DW                13.867 usec
DE                   6.50 usec
TE                 296.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                 -1.00 dB
PL1W          125.22619629 W
SFO1           150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -2.00 dB
PL12                13.78 dB
PL13                14.00 dB
PL2W           18.91009140 W
PL12W           0.49968192 W
PL13W           0.47499999 W
SFO2          600.1324005 MHz
SI                   32768
SF            150.9028090 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```