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SUPPORTING INFORMATION

Title: Oxidative Desulfurization of Azole-2-thiones with Benzoyl Peroxide: Syntheses of Ionic Liquids and Other Azolium Salts
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Ref. No.: O200700114

Contents

EXPERIMENTAL

General. Methyl isothiocyanate (97%) was purchased from Aldrich and distilled prior to use. All other reagents were purchased at p.a. grade or higher from commercial sources and used as received. NMR spectra of compounds in the [C_4mim] series were recorded on a Varian Mercury 400 MHz instrument; compounds in the [C_1mim] series were analyzed on a Bruker AV400WB. Infrared spectra were collected in ATR mode on a BioRad Excalibur Series FTS 4000 (Harrick Split Pea accessory) or Bruker Optics IFS 48 (Specac Golden Gate Diamond device). HRMS analyses were performed on a Finnigan MAT 95. Melting points were recorded on a MelTemp apparatus or a Büchi SMP-20 and are uncorrected. All chromatographic purifications were performed with 230–400 mesh silica gel. The process of calibration, anion exchange in 2:1 EtOH/water, and chromatographic purification following $(BzO)_2$ oxidation is presented in detail in the text for the isolation of [C_4mim][OBz]. The process of benzoate acidification and IL purification is described in detail in the text for the preparation of [C_4mim][BF_4]. The same methods were used for the IL syntheses described below using the amounts of silica gel, eluents, and volumes specified.

1-Butyl-3-methyl-2-thiohydantoin (4). Methyl isothiocyanate (44.15 g, 604 mmol) was dissolved in 50 mL dry Et_2O and added dropwise to freshly distilled **2** (96.15 g, 604 mmol) cooled with an ice bath. The reaction was continued at 0 ^oC for 10 min after complete addition, then fitted with a simple distillation aperture for the removal of Et_2O. The thick orange residue was heated 3 d at 140–150 ^oC. The product at this stage was used for the synthesis of **5** described below, but can be distilled ($bp_{0.55}$ = 126 ^oC) to 79% yield. After one distillation each, compound **4** was the same red hue as **5** made from it. The distillates had similar boiling points, which probably reflect a common codistilling impurity. Their appearance and bps were resolved by further purification. In this case, an analytical sample (4.63 g distilled **4**) was chromatographed (100 g silica gel, eluent: 2:1 Et_2O/pet. ether, $R_f = 0.6$) and redistilled ($bp_{0.15}$ = 86 ^oC) to deliver 3.25 g **4** as a dull yellow oil (70% recovery, 55% yield from **2**). ^1H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 2H), 3.81 (t, 2H, J = 8 Hz), 3.24 (s, 3H), 1.65 (quintet, 2H, J = 7.4 Hz), 1.40 (sextet, 2H, J = 7.4), 0.97 (t, 3H, J = 7.4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.7, 28.1, 29.0, 46.5, 51.7, 170.6, 183.0; IR (film) 3597, 3480, 2958, 2932, 2872, 1744, 1496, 1334 cm^{-1}; HRMS (EI) calcd for $C_8H_{14}N_2OS$: 186.0827, found 186.0822.

1-Butyl-3-methylimidazole-2-thione (5). With DIBALH: Using glassware dried at 180 °C overnight, assembled while hot, and cooled under argon, freshly distilled **2** (2.44 g, 15.3 mmol) was treated with 1.12 g (15.3 mmol) methyl isothiocyanate as described in the preparation of **4**. After addition was complete, the reaction achieved rt over the course of 30 min, then was cooled to -78 °C for the addition of 32 mL (27.5 g) 20 wt. % DIBALH in PhMe (5.50 g DIBALH, 38.7 mmol, 2.5 eq.). The mixture was stirred for 30 min, the cold bath was removed, and the reaction was quenched and worked up as described by Markwalder and coworkers[2] to yield 2.68 g crude product that was chromatographed (70 g silica gel, eluent: 2:1 Et_2O/pet. ether, $R_f = 0.4$) to 1.91 g (11.2 mmol, 73%) **5**. From **4**: Crude **4** prepared as described above was diluted with 200 mL EtOH and cautiously treated with 22.84 g (604 mmol) $NaBH_4$ in 600 mL EtOH. Any $NaBH_4$ residue was washed in with EtOH (2 × 100 mL portions). The mixture turned from the deep red color of crude **4** to a bright purple over the course of 7 h, and was then slowly treated with 200 mL concd aq HCl, turning an intense yellow while stirring 30 min. The slurry was poured into 750 mL water, 100 g NaCl, 500 mL DCM and shaken. The mixture slowly separated into two layers. The aq layer was extracted with more DCM (3 × 100 mL), the combined organic layers were washed with water (1 × 100 mL) and repetitively with 100 mL brine until the volume recovered was approximately equal to the volume invested (requiring at least 3 ×), then dried ($MgSO_4$), filtered and concentrated to 98.97 g oil that distills ($bp_{0.4} = 132$ °C) to 81.15 g **5** (477 mmol, 79% yield from **2**, 99% from **4**). After one distillation each, compound **5** was the same red hue as **4** used to make it. The distillates had similar boiling points, which probably reflect a common codistilling impurity. Their appearance and bps were resolved by further purification. In this case, an analytical sample was prepared by chromatographing 4.38 g distilled **5** (105 g silica gel, eluent: 2:1 Et_2O/pet. ether, $R_f = 0.4$) and redistilling the isolate ($bp_{0.15} = 77$ °C) to deliver 1.68 g (38% recovery, 30% from **2**) yellow oil.

1-Butyl-3-methylimidazole-2-thione methyl iodide (6). A solution of 9.56 g **5** (56.1 mmol) in 100 mL DME in an Erlenmeyer flask was treated with 5.5 mL (12.54 g, 88.3 mmol, 1.6 eq.). A precipitate formed while stirring at rt 30 min, and was dissolved by bringing the mixture to a gentle reflux by direct contact with a hot plate and adding 125 mL *t*-BuOH. The solution was cooled back to rt, frozen at -30 °C overnight, thawed, and filtered to yield 15.70 g **6** (50.3 mmol, 90%), mp 110–115 °C. ^{1}H NMR (400 MHz, D_2O) δ 7.61 (s, 1H), 7.57 (s, 1H), 4.31 (t, 2H, *J* = 6.3 Hz), 3.94 (s, 3H), 2.48 (s, 3H), 1.83 (quintet, 2H, *J* = 6.6 Hz), 1.34 (sextet, 2H, *J* = 6.5 Hz), 0.91 (t, 3H, *J* = 6.6 Hz); ^{13}C NMR (100 MHz, D_2O) δ 12.8, 17.2, 18.9, 31.5, 35.8, 49.3, 123.2, 124.8, 140.8.

Anion exchange to [C_4mim][ClO_3].[1] A 33.35 g portion of the calibrated solution (6.0 mmol, 8.2% of the stock solution, representing 9.6 mmol **5**) was treated with 0.64 g $NaClO_3$ (6.0 mmol), stirred 2.5 h, filtered, concentrated, and purified like [C_4mim][OBz] using 5 g silica gel, 1:1 Et_2O/EtOH as eluent, and 10 mL ea. loading, rinsing, and washing volumes. A second chromatographic step followed by drying in vacuo returned 1.24 g [C_4mim][ClO_3] (58% yield from **5**). ^{1}H NMR (400 MHz, D_2O) δ 8.81 (s, 1H), 7.57 (s, 1H), 7.52 (s, 1H), 4.26 (t, 2H, *J* = 7.2), 3.97 (s, 3H), 1.89 (quintet, 2H, *J* = 7.4), 1.38 (sextet, 2H, *J* = 7.4), 0.99 (t, 3H, *J* = 7.4); ^{13}C NMR (100 M = Hz, D_2O) δ 17.4, 23.5, 36.0, 43.6, 53.9, 126.9, 128.2, 140.5.

Acidification of [C_4mim][OBz] to [C_4mim][CF_3CO_2]. Once-chromatographed [C_4mim][OBz] (2.0 g, 7.7 mmol) was treated with 1.2 mL (1.75 g, 15.3 mmol, 2 eq.) neat TFA. Before cooling it was loaded on 5 g silica gel packed in Et_2O and washed with Et_2O until the collected wash did not respond to UV light when spotted on a TLC plate and was not acidic, requiring ca. 30 mL. [C_4mim][CF_3CO_2] (0.82 g, 3.3 mmol, 42%) was washed off with 50 mL 1:1 Et_2O-ethanol. ^{1}H NMR (400 MHz, D_2O) δ 8.75 (s, 1H), 7.48 (s, 1H), 7.44 (s, 1H), 4.17 (t, 2H, *J* = 7.2 Hz), 3.89 (s, 3H), 1.81 (quintet, 2H, *J* = 7.4 Hz), 1.29 (sextet, 2H, *J* = 7.4 Hz), 0.89 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, D_2O) δ 17.4, 23.5, 36.0, 43.6, 54.0, 119.8 (q, $^1J(^{13}C–^{19}F)$ = 290.9 Hz), 127.0, 128.3, 140.4, 166.8 (q, $^2J(^{13}C–^{19}F)$ = 34.7); IR (film) 3157, 3092, 2966, 2865, 1683, 1197, 1164, 1110 cm^{-1}.

1,3-Dimethyl-2-thiohydantoin (8). Fresh NaOMe/MeOH was prepared with 4.12 g Na (179.3 mmol, 1.0 eq.) in 50 mL MeOH. Solid methyl sarcosinate hydrochloride (25.00 g, 179.1 mmol) was added to the solution and stirred 30 min, cooled to 0 ^{o}C, treated with methyl isothiocyanate (13.10 g, 179.2 mmol, 1.0 eq.) in 100 mL xylenes, stirred 10 min, and stirred 30 more min after removal of the ice bath. A simple distillation aperture was installed, MeOH was removed, then a condenser was attached and the reaction was refluxed 3 d. After a hot gravity filtration, the filtrate was cooled to rt, then to -30 ^{o}C overnight. The precipitate was recovered by filtration and crystallized thrice from 20:20:1 PhMe/*n*-C_7H_{14}/EtOH to deliver 5.17 g **8** (35.8 mmol, 20%), mp 91.5–93 ^{o}C (lit.[3] 92–92.5 ^{o}C). ^{1}H (400 MHz, $CDCl_3$) δ 4.06 (s, 2H), 3.33 (s, 3H), 3.21 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 28.3, 33.9, 53.86, 170.3, 183.4.

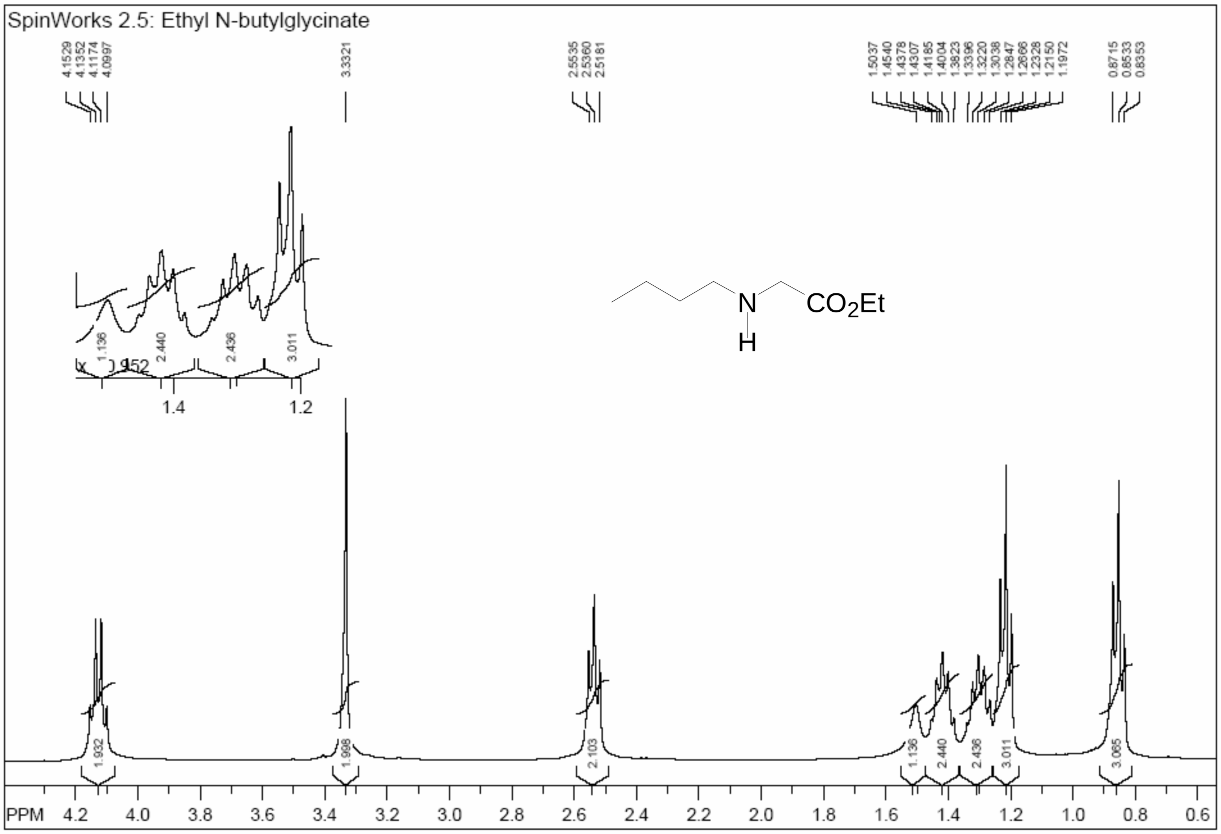
Anion exchange to [C$_1$mim][OBz]. A 614.57 g portion of the calibrated solution (166.4 mmol, 76.5% of the stock solution, representing 195.2 mmol **7**) was treated with 23.98 g NaOBz (166.4 mmol, 1.0 eq.), stirred 2.5 h, filtered, and concentrated. The residue was purified on 65 g silica gel by the same technique described for the purification of [C$_4$mim][OBz], using loading and rinsing volumes of 200 mL 1:1 Et_2O/EtOH, and 250 mL fresh eluent to wash the column. Concentration and drying in vacuo left 31.80 g [C$_1$mim][OBz] (145.7 mmol, 75%) of which 2 g was rechromatographed over 5 g silica gel using loading, rinsing, and washing volumes of 25 mL ea. Concentration and drying left 1.35 g (68% recovery, 51% from **7**). ^{1}H NMR (400 MHz, D_2O) δ 8.46 (s, 1H), 7.82 (d, 2H, *J* = 5.2 Hz), 7.50 (t, 1H, *J* = 7.0 Hz), 7.42 (t, 2H, *J* = 7.0 Hz), 7.27 (s, 2H), 3.76 (s, 6H); ^{13}C (100 MHz, D_2O) δ 37.1, 125.0, 129.9, 130.4, 132.9, 137.5, 137.9, 176.4; IR (film) 3381, 3147, 3062, 2960, 2935, 2873, 1596, 1553, 1368 cm^{-1}.

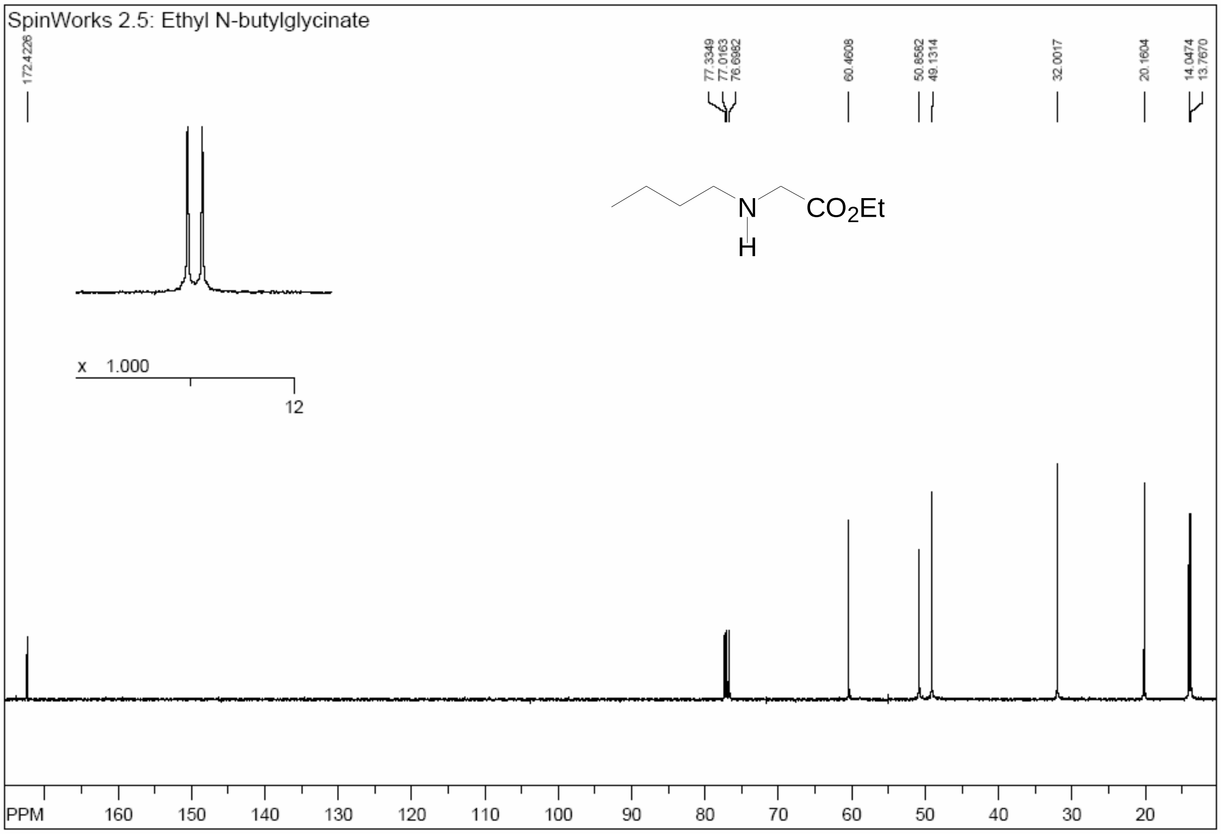
Anion exchange to [C$_1$mim][ClO$_3$].[1] A 182.73 g portion of the calibrated solution (49.5 mmol, 22.7% of the stock solution, representing 58.0 mmol **7**) was treated with 5.27 g $NaClO_3$ (49.5 mmol), stirred 2.5 h, filtered, and concentrated. The residue was purified on 20 g silica gel by the same technique described for the purification of [C$_4$mim][OBz], using loading and rinsing volumes of 100 mL, and 150 mL fresh eluent to wash the column. Concentration and drying in vacuo left 7.32 g [C_1mim][ClO_3] (40.5 mmol, 70% from **7**), of which 2.042 g was rechromatographed over 5 g silica gel using loading, rinsing, and washing volumes of 20 mL ea. Concentration and drying in vacuo left 1.38 g (68% recovery, 47% from **7**). ^{1}H NMR (400 MHz, D_2O) δ 8.68 (s, 1H), 7.45 (s, 2H), 3.92 (s, 6H); ^{13}C (100 MHz, D_2O): δ 37.2, 125.0, 138.1.

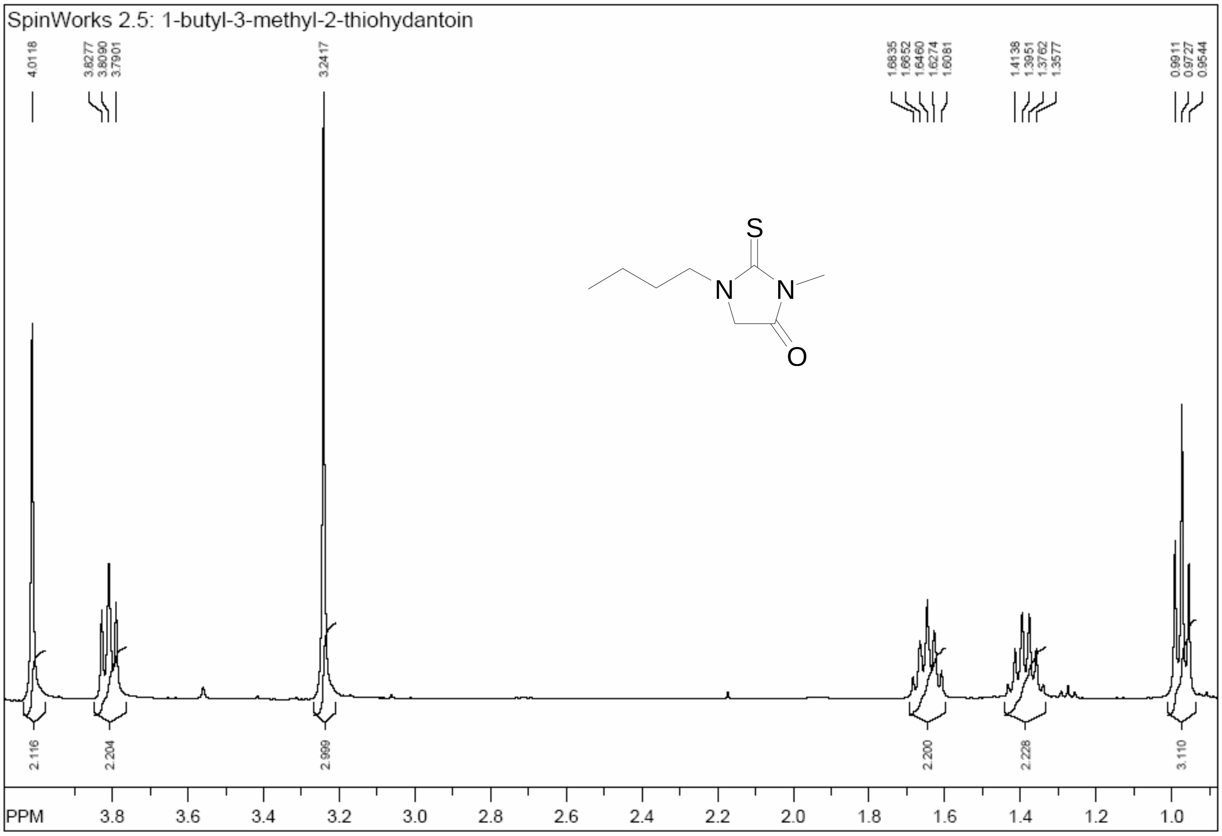
Acidification of [C_1mim][OBz] to [C_1mim][CF_3CO_2]. One-pass [C_1mim][OBz] (2 g, 9.2 mmol) was treated with 2.3 g neat TFA (20.2 mmol, 2.2 eq.), loaded on 5 g silica gel packed in Et_2O before cooling, and required 130 mL Et_2O to wash off BzOH and excess TFA. The product was washed off with 60 mL 1:1 Et_2O/EtOH. Concentration and drying in vacuo left 1.31 g [C_1mim][CF_3CO_2] (6.2 mmol, 68%). ^{1}H NMR (400 MHz, D_2O) δ 8.64 (s, 1H), 7.41 (s, 2H), 3.89 (s, 6H); ^{13}C (100 MHz, D_2O) δ 37.2, 119.5, (q, $^1J(^{13}C{-}^{19}F)$ = 290.4 Hz), 125.0, 163.8 (q, $^1J(^{13}C{-}^{19}F)$ = 35.0 Hz); IR (film) 3424, 3150, 3095, 2965, 2939, 2878, 1683, 1198, 1166, 1119 cm^{-1}.

Synthesis of [C_4mim][BF_4] from 1-methylimidazole. Distilled 1-methylimidazole (230 mL, 236.9 g, 2.88 mol) was treated with 360 mL distilled *n*-BuCl (316.8 g, 3.42 mol, 1.2 eq.) and refluxed for 40 h, then excess *n*-BuCl was removed by distillation. Unable to secure crystals of [C_4mim][Cl],[4] we diluted the mixture with 160 mL water and added 50% aq HBF_4 (365 mL, 514.7 g, 2.93 mol, 1.0 eq.). The solution was stirred 24 h, then aq HCl was removed by distillation. The residue was taken up in 2.2 L DCM, the ca. 2.8 L solution was split in half, and each half was repeatedly washed with 15 mL water. The separatory funnel was rinsed with fresh water between each wash. After ca. 20 washes per half, the water wash had the same pH as the water invested, and no precipitate formed when $AgNO_3$ was added. Each cloudy and yellow half was washed twice more with water,[5] then dried and decolorized by the addition of 20 g Celite-521. Celite was removed by gravity filtration, the halves were recombined, DCM was removed, and the product was dried in vacuo 8 h at 100 °C to leave 494.05 g [C_4mim][BF_4] (2.19 mol, 76%). The concentrated product was slightly yellow en masse, but samples up to ca. 20 mL were colorless.

^{1}H AND ^{13}C NMR SPECTRA



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3.8277
3.8090
3.7901
3.2417
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1.6652
1.6460
1.6274
1.6081
1.4138
1.3951
1.3762
1.3577
0.9911
0.9727
0.9544
S
N
N
O
2.116
2.204
2.999
2.200
2.228
3.110
PPM
3.8
3.6
3.4
3.2
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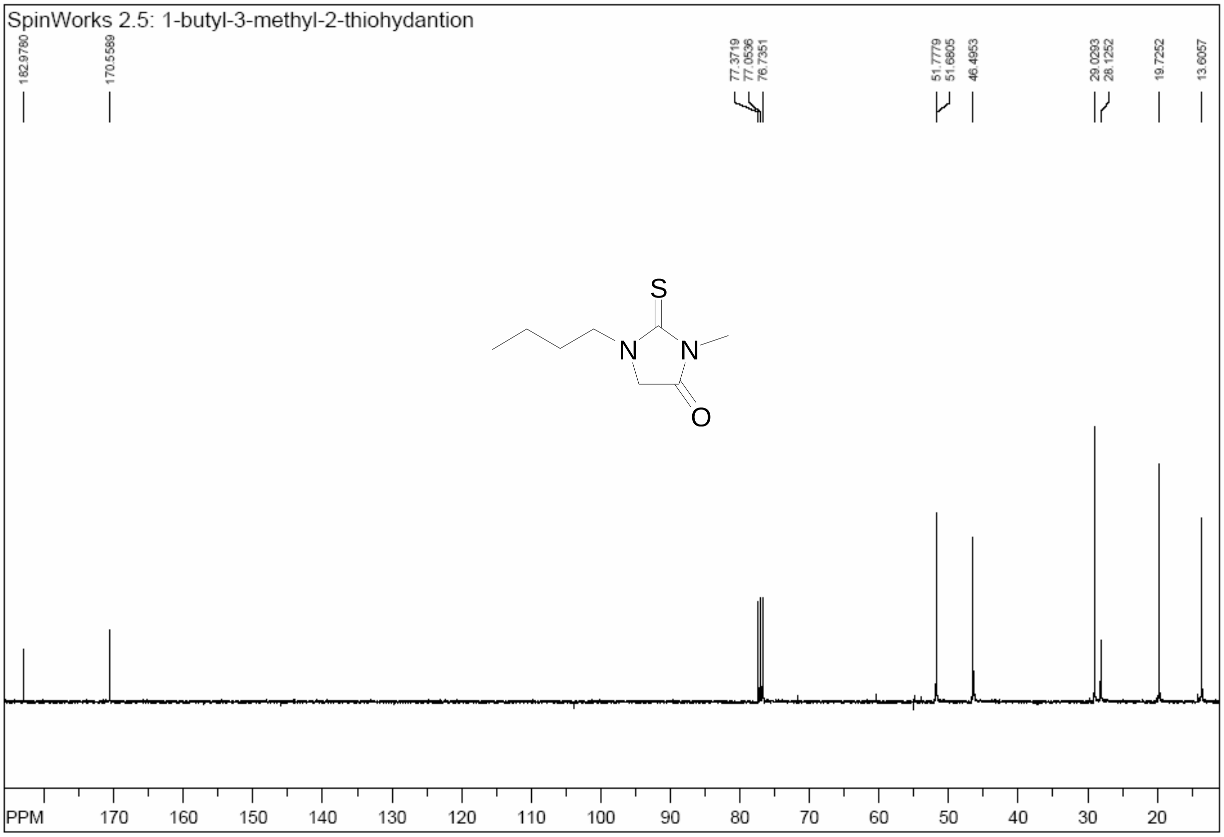
1.2
1.0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170.5589
77.3719
77.0536
76.7351
51.7779
51.6805
46.4953
29.0293
28.1252
19.7252
13.6057
S
N
N
O
PPM
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160
150
140
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100
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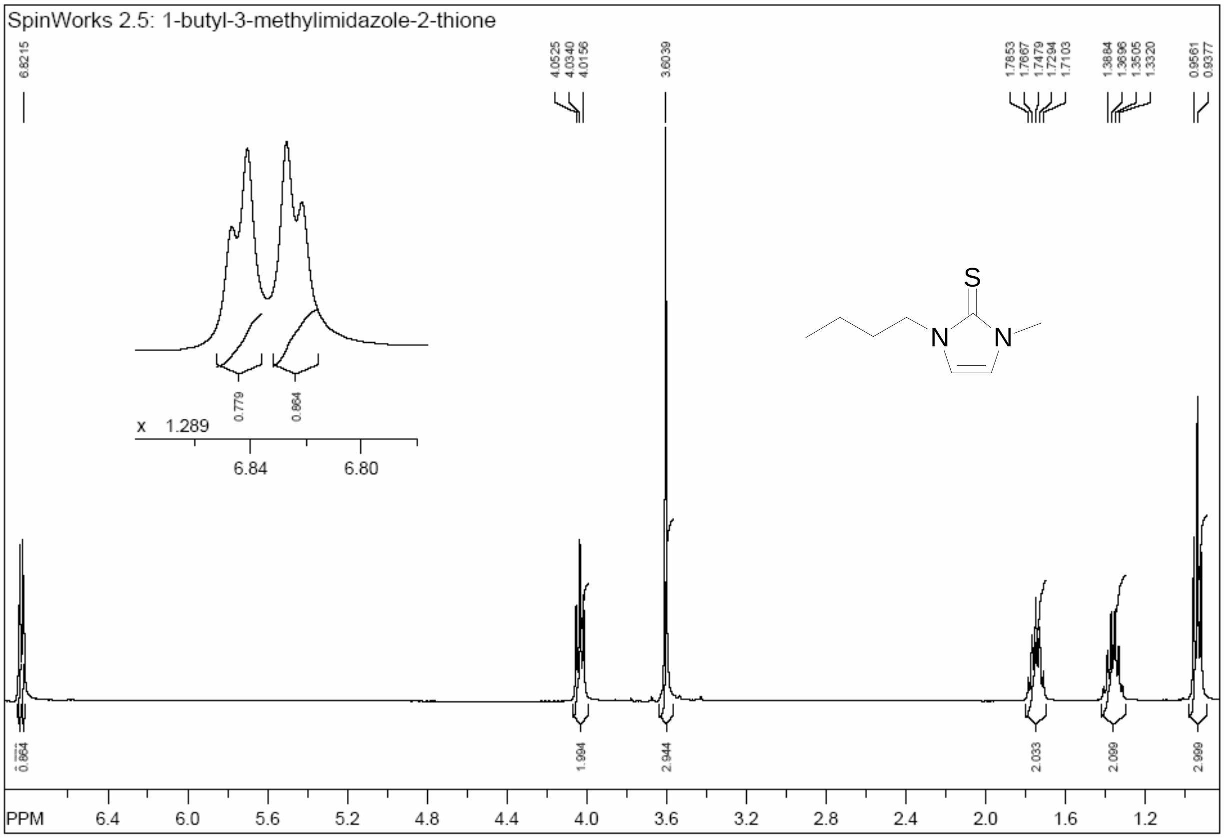
80
70
60
50
40
30
20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4.0340
4.0156
3.6039
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1.7667
1.7479
1.7294
1.7103
1.3884
1.3696
1.3505
1.3320
0.9561
0.9377
S
N
N
0.779
0.864
x 1.289
6.84
6.80
0.864
1.994
2.944
2.033
2.099
2.999
PPM
6.4
6.0
5.6
5.2
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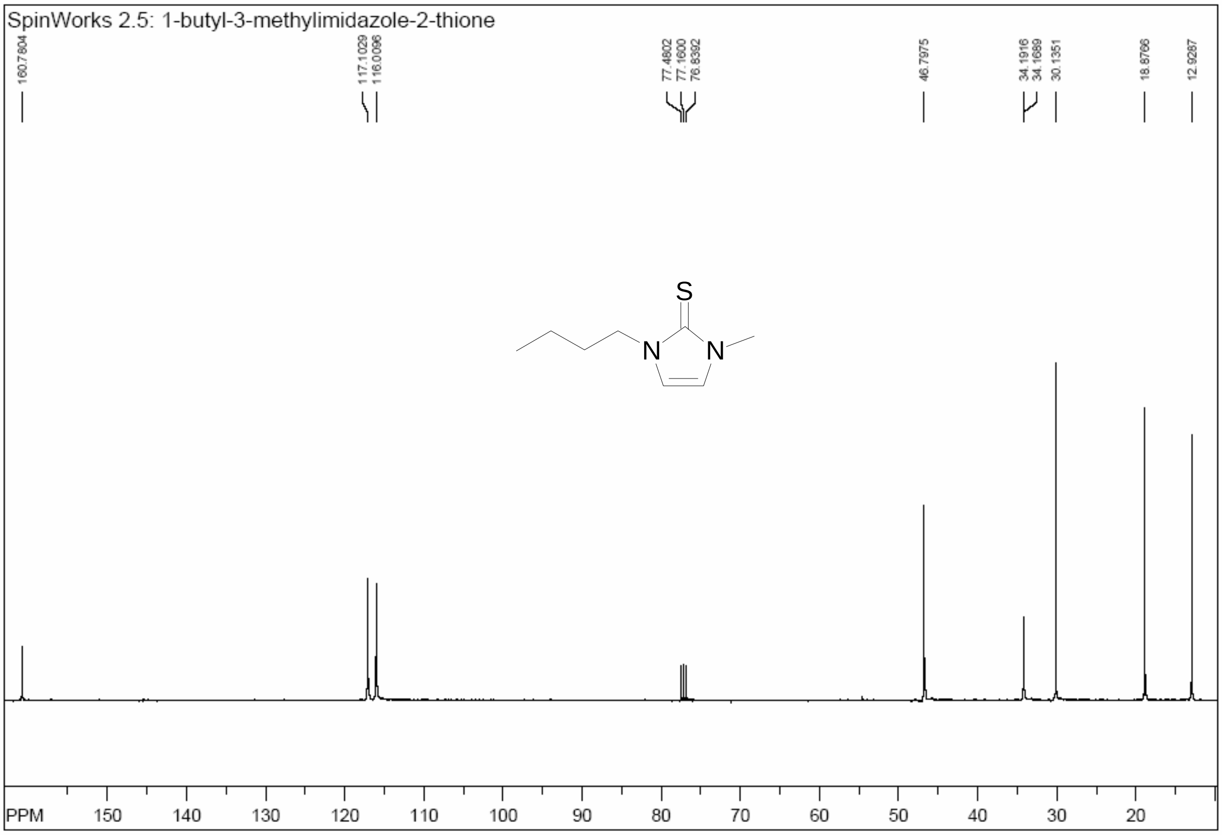
1.2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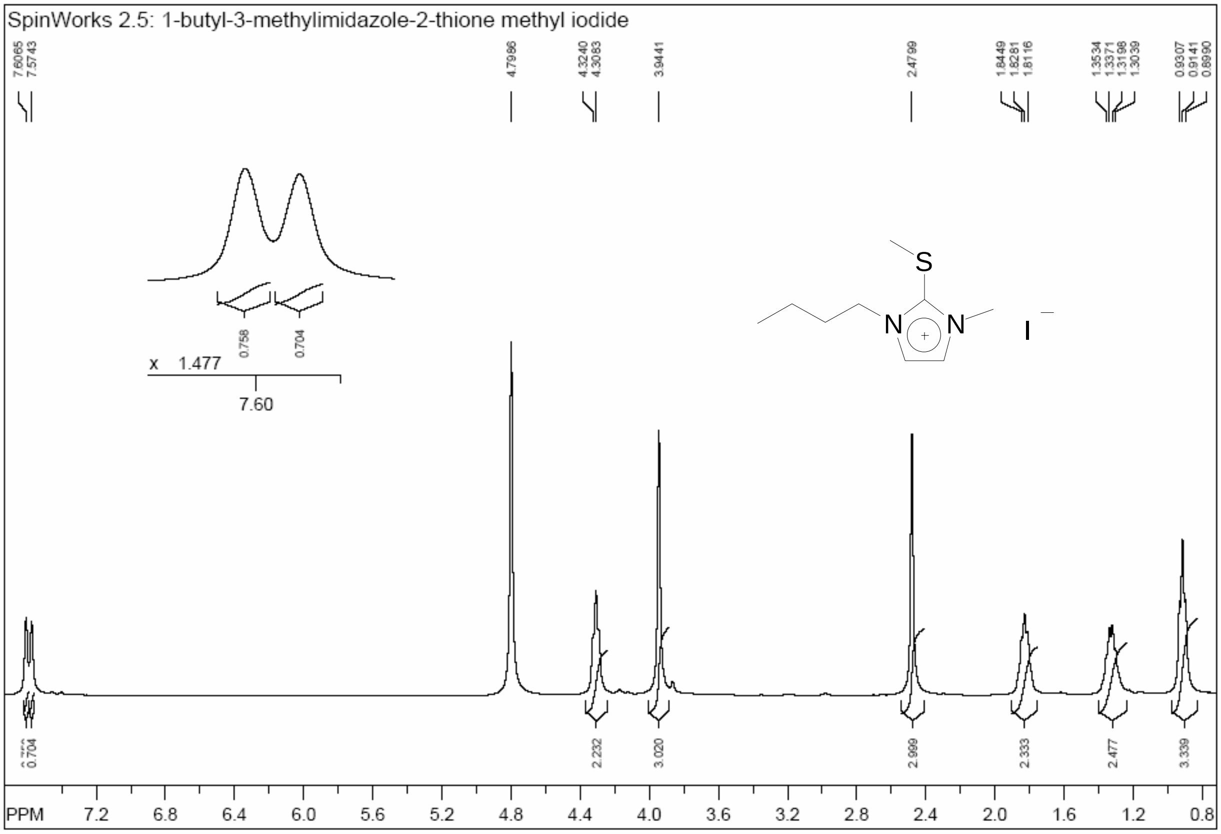
117.1029
116.0096
77.4802
77.1600
76.8392
46.7975
34.1916
34.1689
30.1351
18.8766
12.9267
S
N
N
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20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7.5743
4.7986
4.3240
4.3083
3.9441
2.4799
1.8449
1.8281
1.8116
1.3534
1.3371
1.3198
1.3039
0.9307
0.9141
0.8990
S
N
N
I −
0.758
0.704
x 1.477
7.60
0.704
2.232
3.020
2.999
2.333
2.477
3.339
PPM
7.2
6.8
6.4
6.0
5.6
5.2
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3.6
3.2
2.8
2.4
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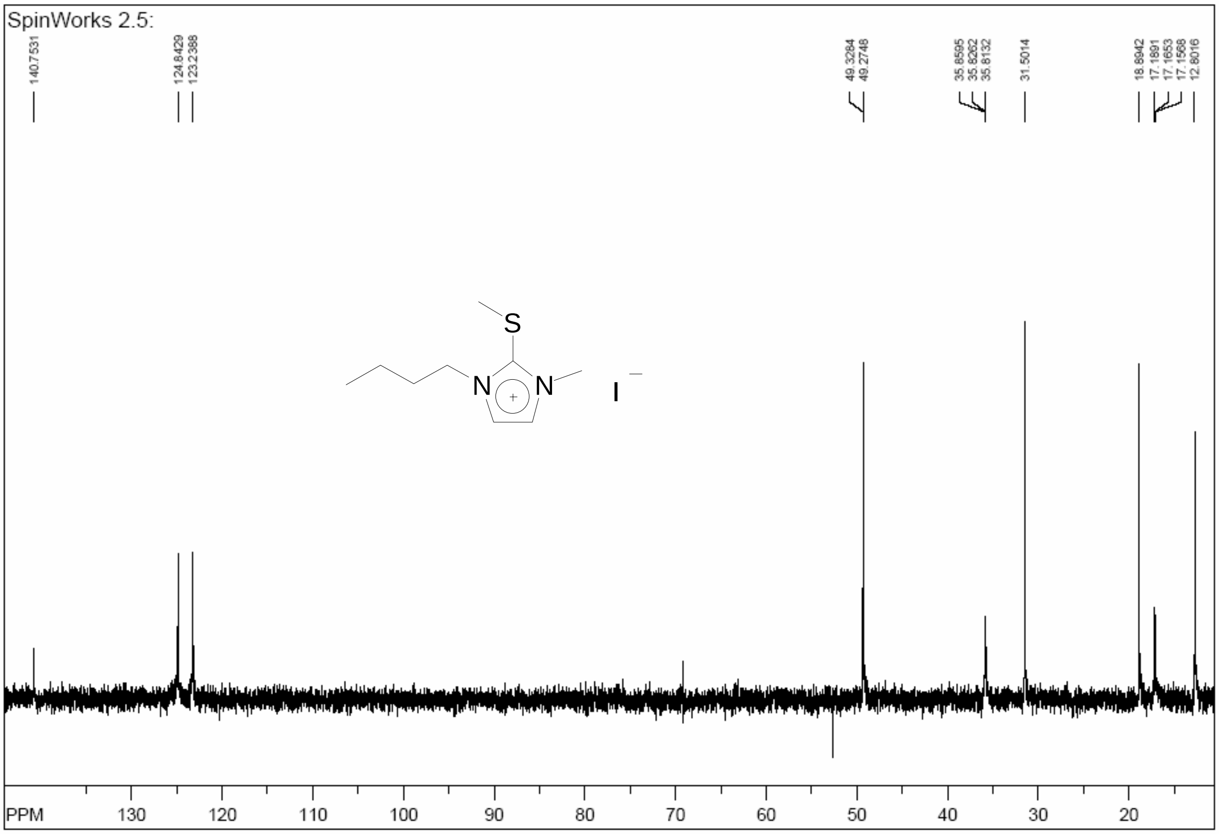
1.6
1.2
0.8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124.8429
123.2388
49.3284
49.2748
35.8595
35.8262
35.8132
31.5014
18.8942
17.1891
17.1653
17.1568
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S
N
N
I −
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130
120
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60
50
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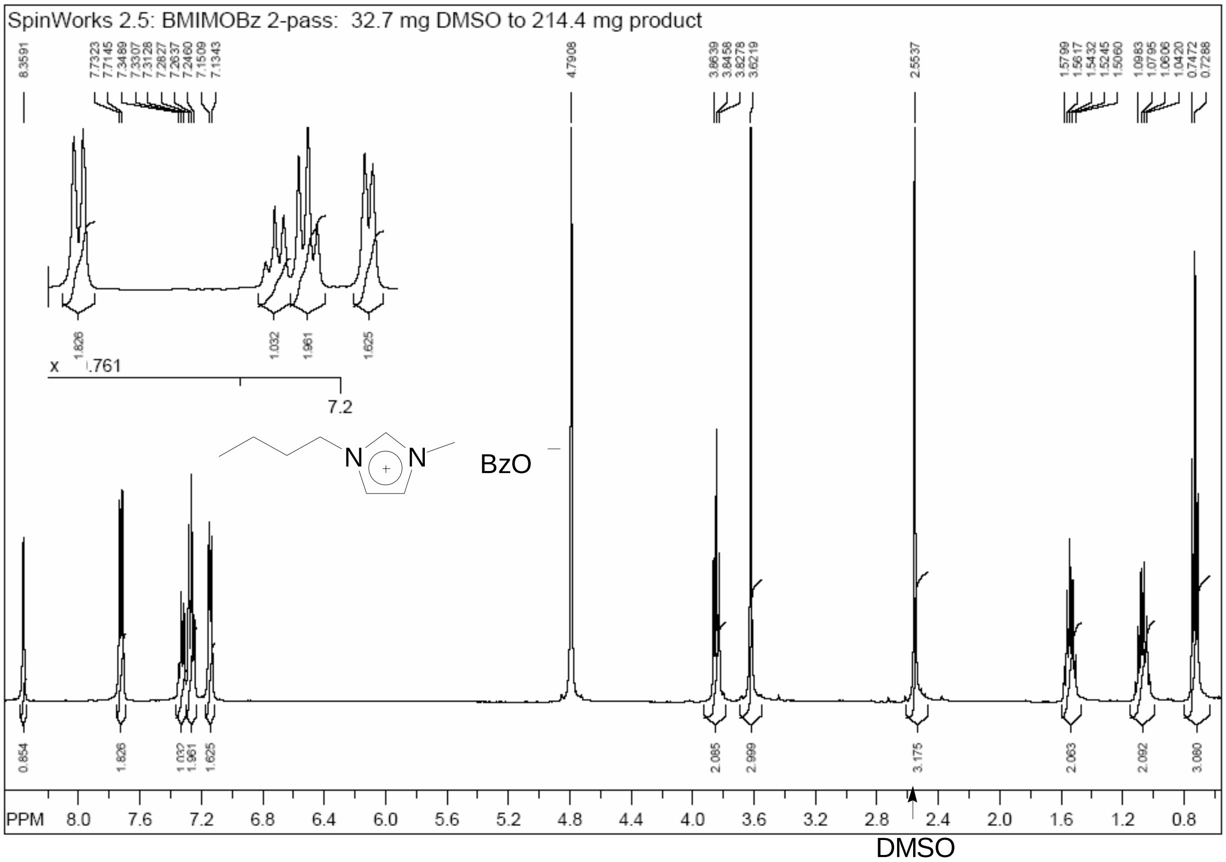
30
20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7.7145
7.3489
7.3307
7.3128
7.2827
7.2637
7.2460
7.1509
7.1343
4.7908
3.8639
3.8458
3.8278
3.6219
2.5537
1.5799
1.5617
1.5432
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1.5060
1.0983
1.0795
1.0606
1.0420
0.7472
0.7288
1.826
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1.961
1.625
x .761
7.2
N
N
+
BzO −
0.854
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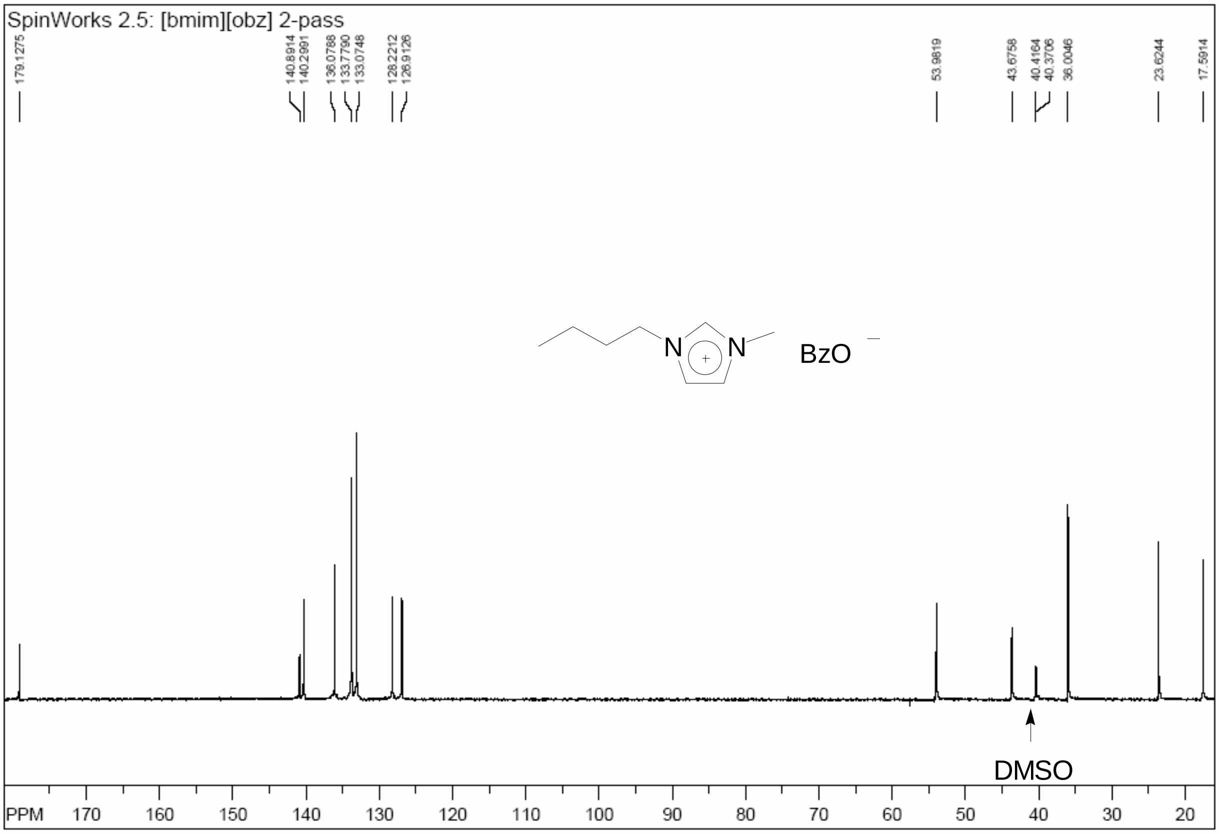
1.032
1.961
1.625
2.085
2.999
3.175
2.063
2.092
3.080
PPM 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8
DMSO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179.1275
140.8914
140.2991
136.0788
133.7790
133.0748
128.2212
126.9126
53.9819
43.6758
40.4164
40.3706
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N
N
+
BzO −
DMSO
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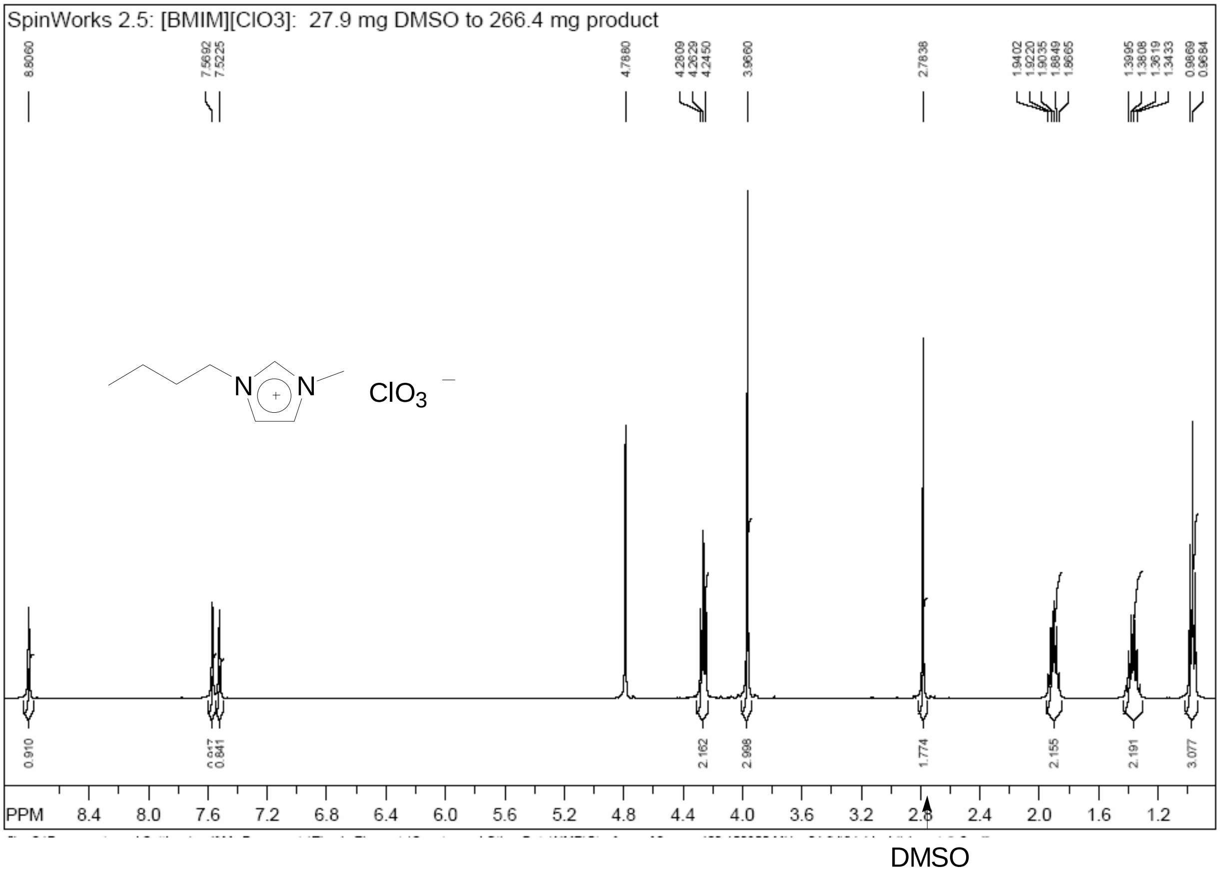
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7.5692
7.5225
4.7880
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4.2450
3.9660
2.7838
1.9402
1.9220
1.9035
1.8849
1.8665
1.3995
1.3808
1.3619
1.3433
0.9869
0.9684
N
N
+
ClO3 −
0.910
0.917
0.841
2.162
2.998
1.774
2.155
2.191
3.077
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
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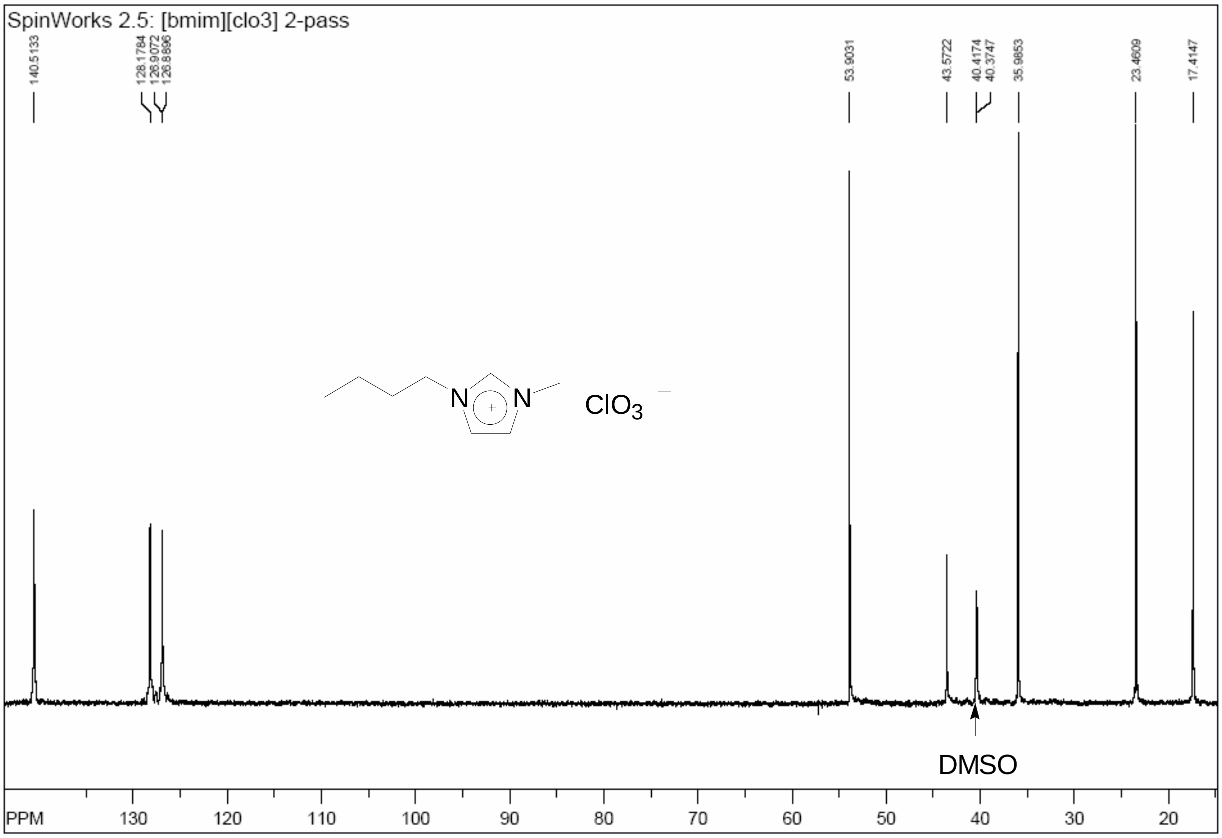
2.0
1.6
1.2
DMSO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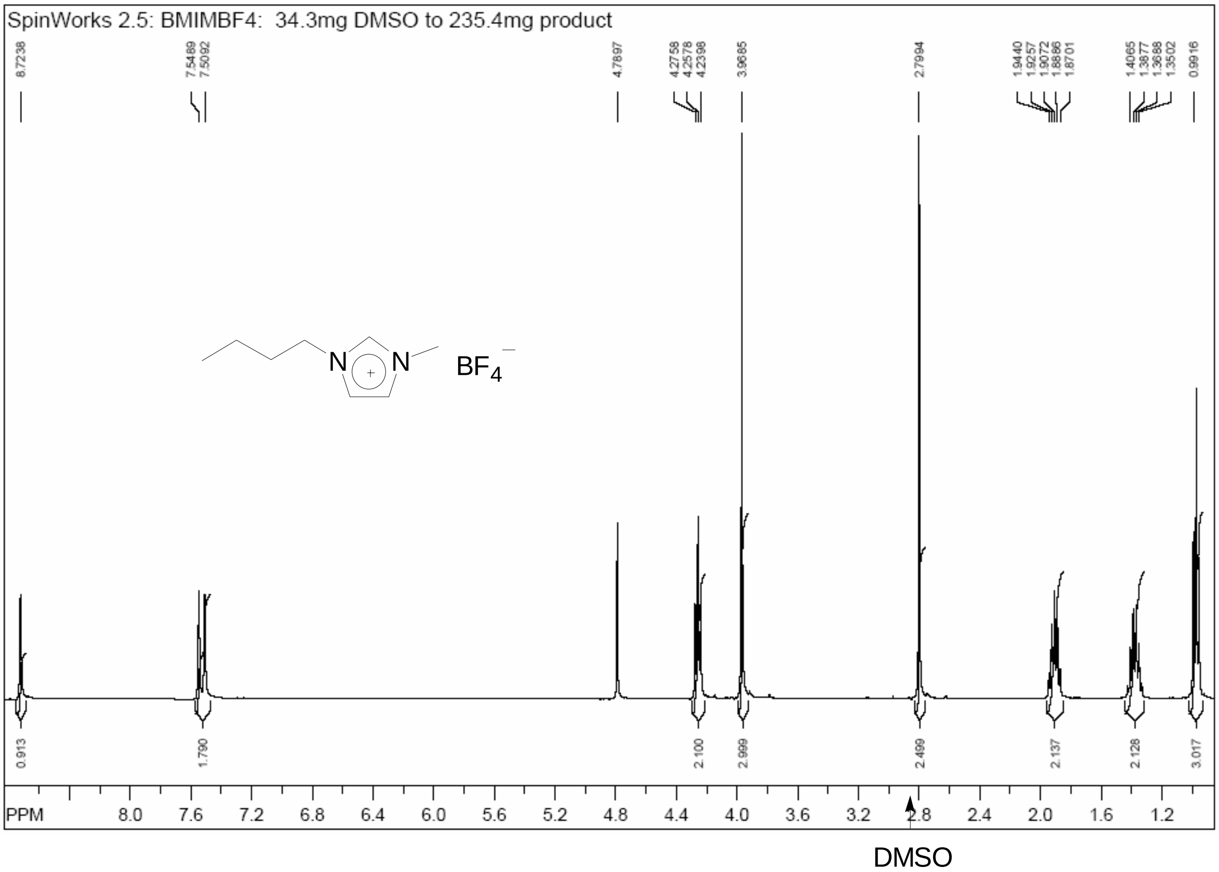
128.1784
126.9072
126.8896
53.9031
43.5722
40.4174
40.3747
35.9853
23.4609
17.4147
N
N
+
ClO3 −
DMSO
PPM
130
120
110
100
90
80
70
60
50
40
30
20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7.5489
7.5092
4.7897
4.2758
4.2578
4.2398
3.9685
2.7994
1.9440
1.9257
1.9072
1.8886
1.8701
1.4065
1.3877
1.3688
1.3502
0.9916
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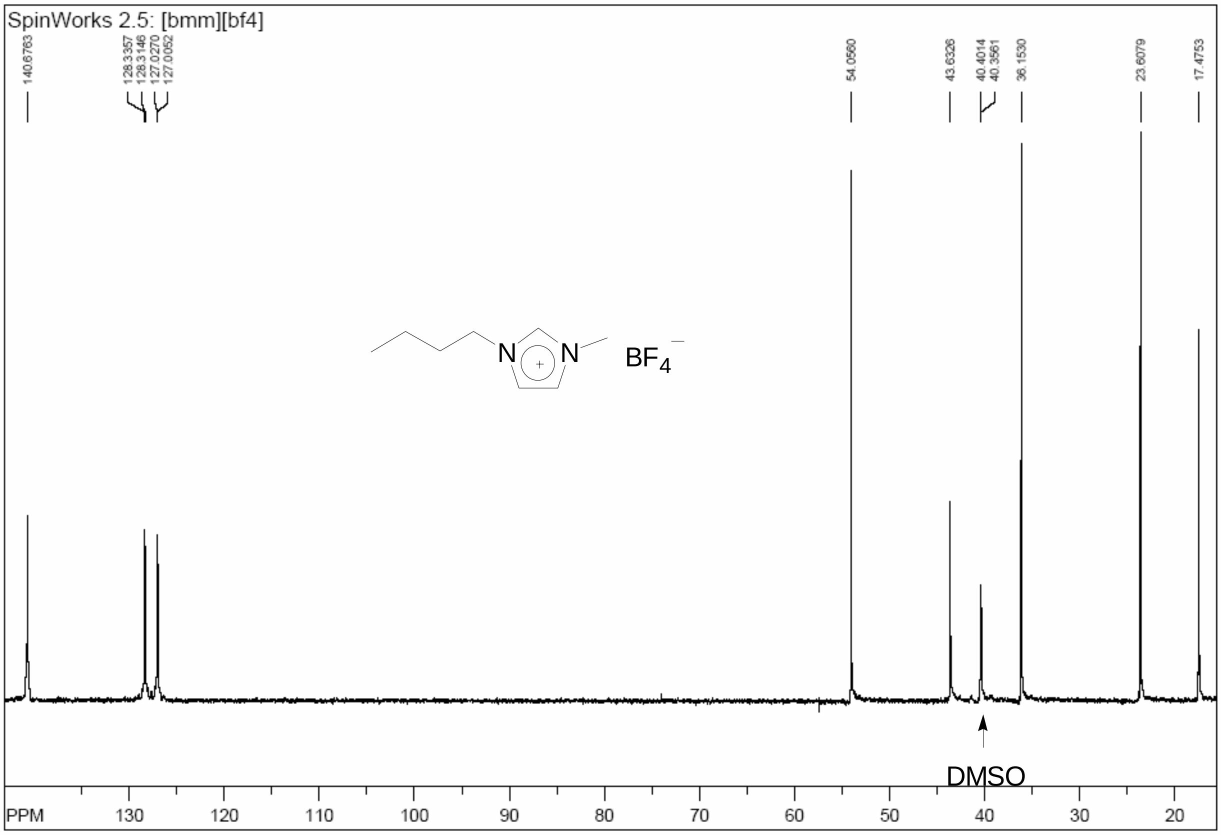
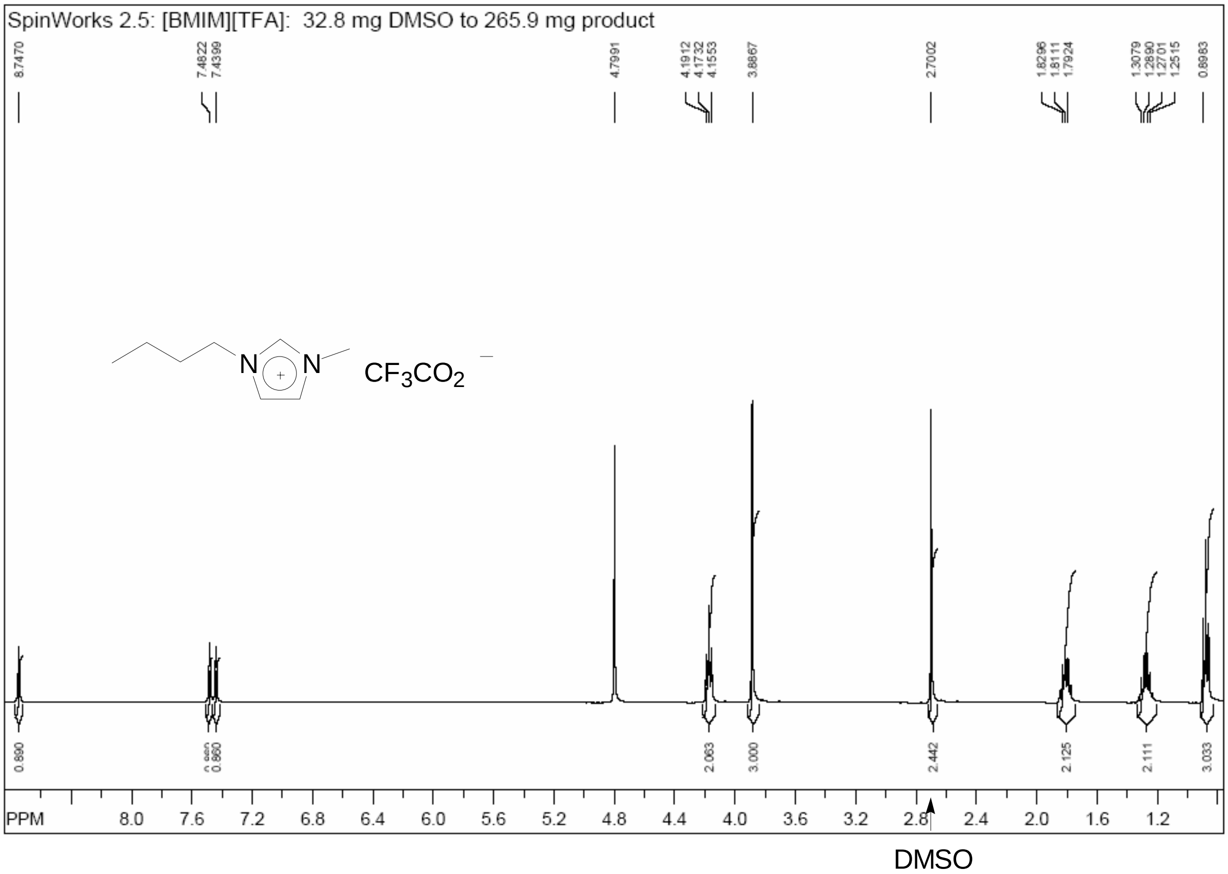
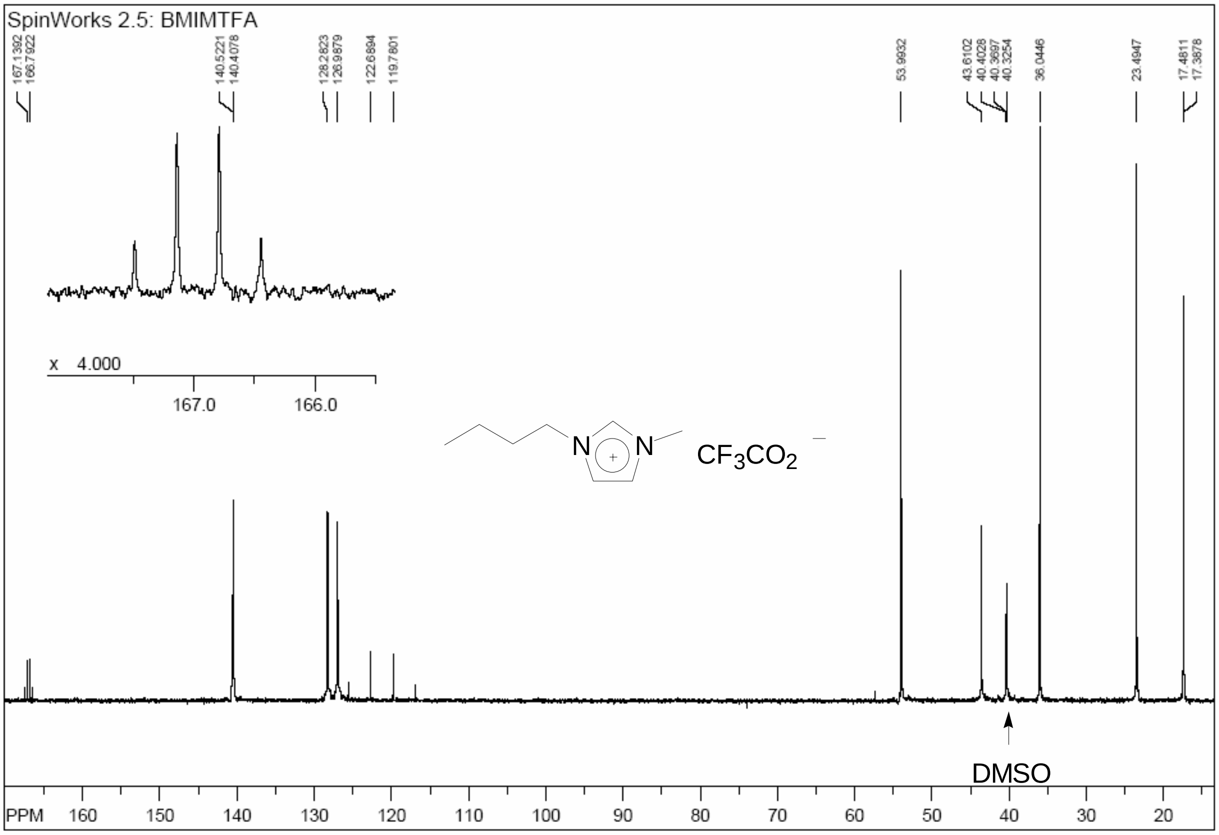
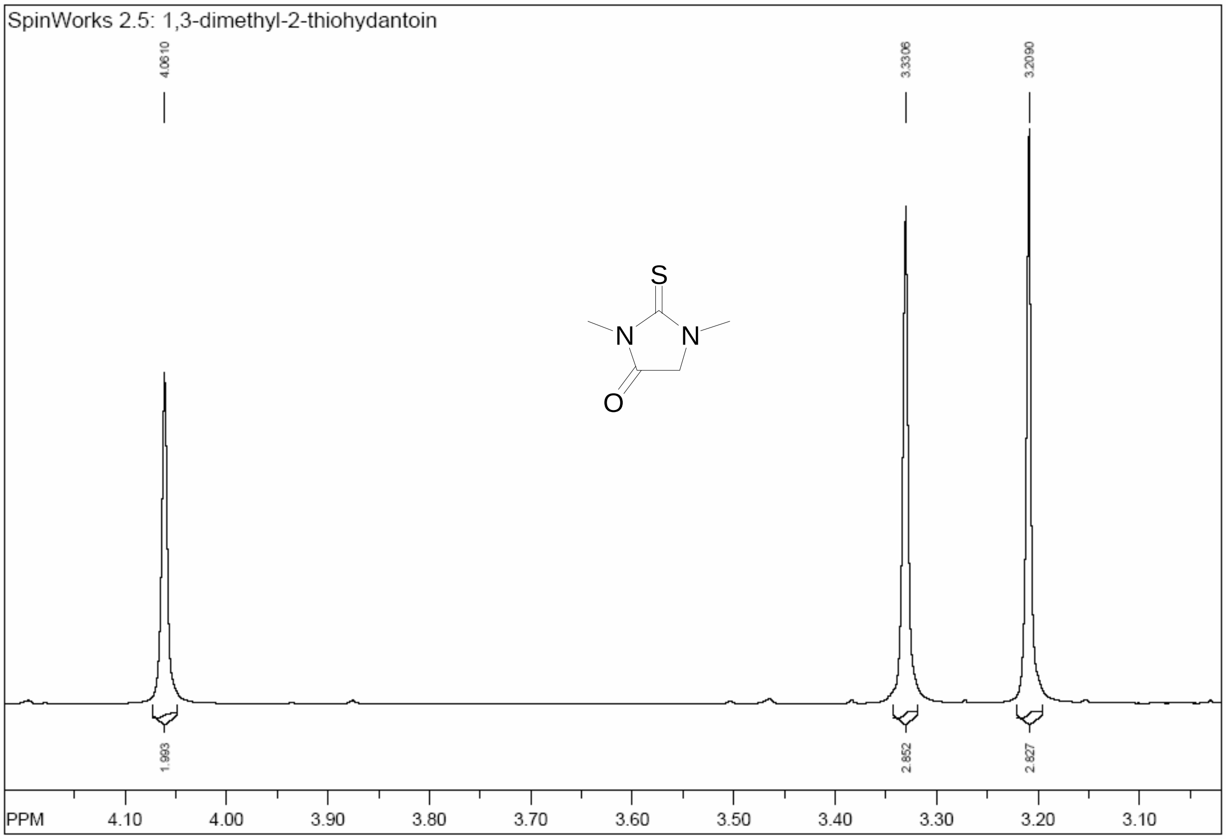
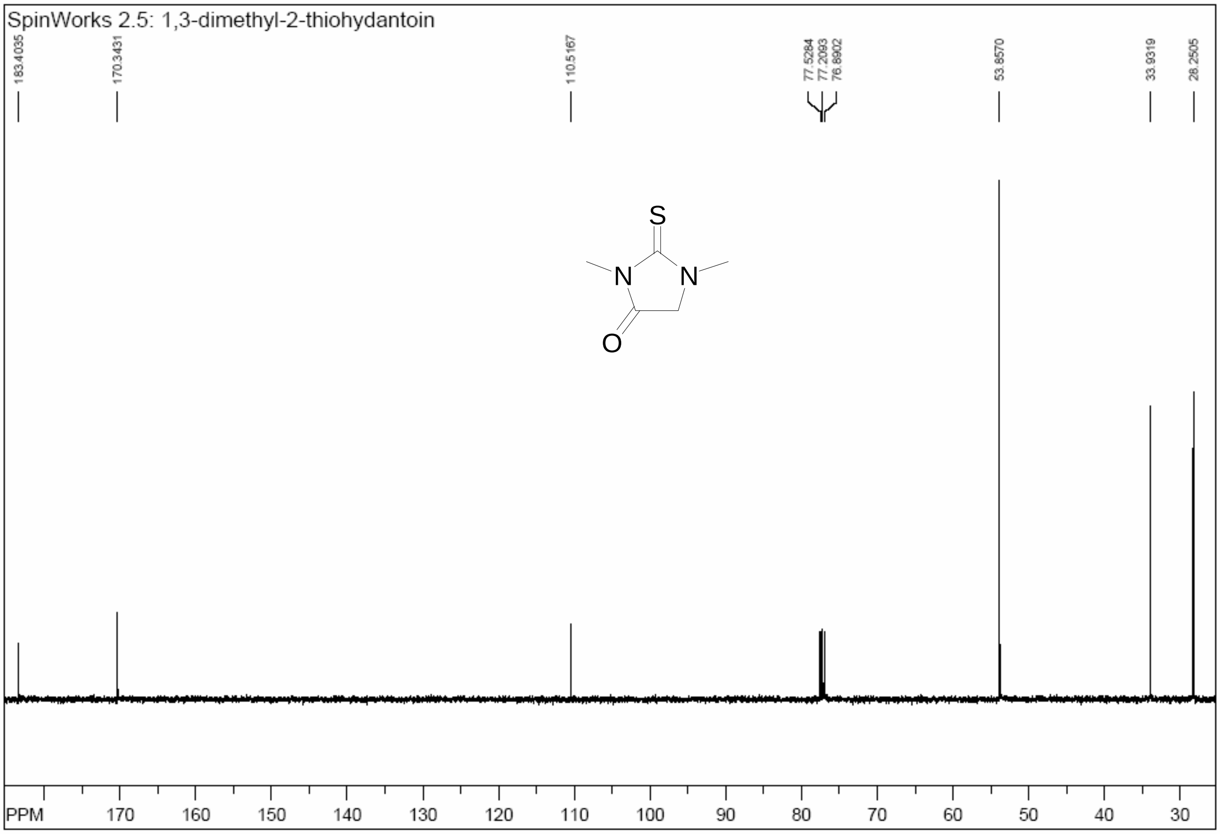
+
N
BF_4^-
0.913
1.790
2.100
2.999
2.499
2.137
2.128
3.017
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
DMSO


SpinWorks 2.5: [bmm][bf4]
140.6763
128.3357
128.3146
127.0270
127.0052
54.0560
43.6326
40.4014
40.3561
36.1530
23.6079
17.4753
N
+
N
BF_4^-
DMSO
PPM
130
120
110
100
90
80
70
60
50
40
30
20

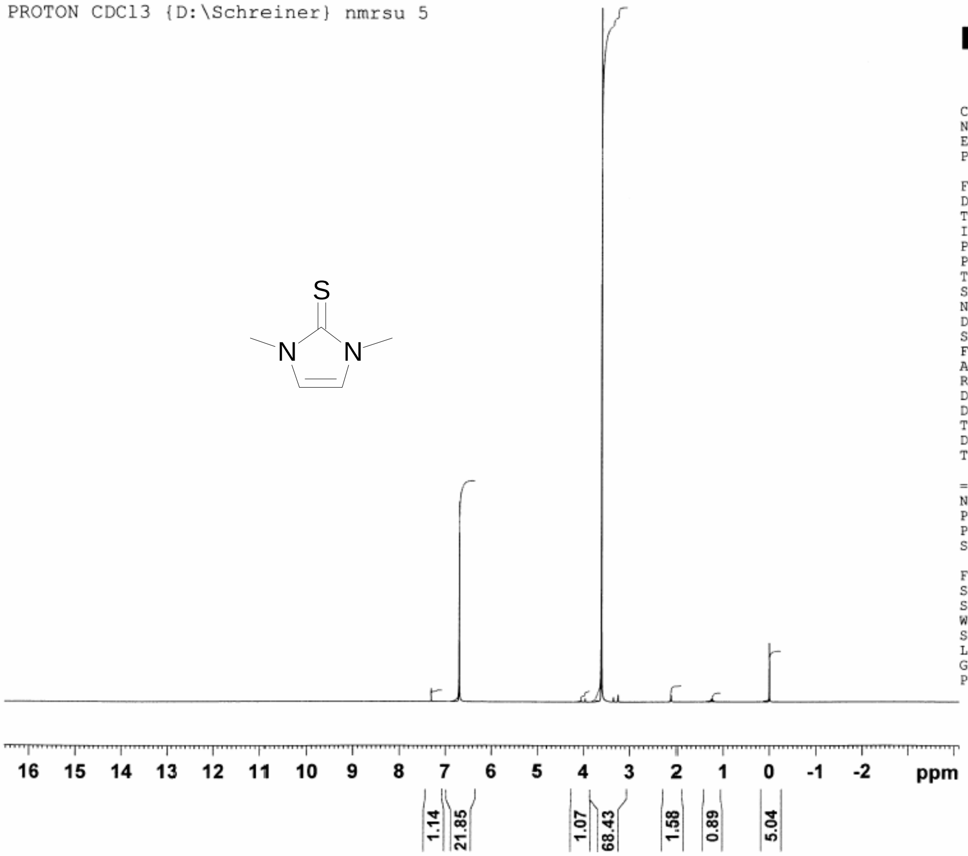

SpinWorks 2.5: [BMIM][TFA]: 32.8 mg DMSO to 265.9 mg product
8.7470
7.4822
7.4399
4.7991
4.1912
4.1732
4.1553
3.8867
2.7002
1.8296
1.8111
1.7924
1.3079
1.2890
1.2701
1.2515
0.8983
N
N
CF$_3$CO$_2$ −
0.890
0.860
0.860
2.063
3.000
2.442
2.125
2.111
3.033
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
DMSO


SpinWorks 2.5: BMIMTFA
167.1392
166.7922
140.5221
140.4078
128.2823
126.9879
122.6894
119.7801
53.9932
43.6102
40.4028
40.3697
40.3254
36.0446
23.4947
17.4811
17.3878
x 4.000
167.0
166.0
N
N
CF$_3$CO$_2$ −
DMSO
PPM
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


SpinWorks 2.5: 1,3-dimethyl-2-thiohydantoin
4.0610
3.3306
3.2090
S
N
N
O
1.993
2.852
2.827
PPM
4.10
4.00
3.90
3.80
3.70
3.60
3.50
3.40
3.30
3.20
3.10

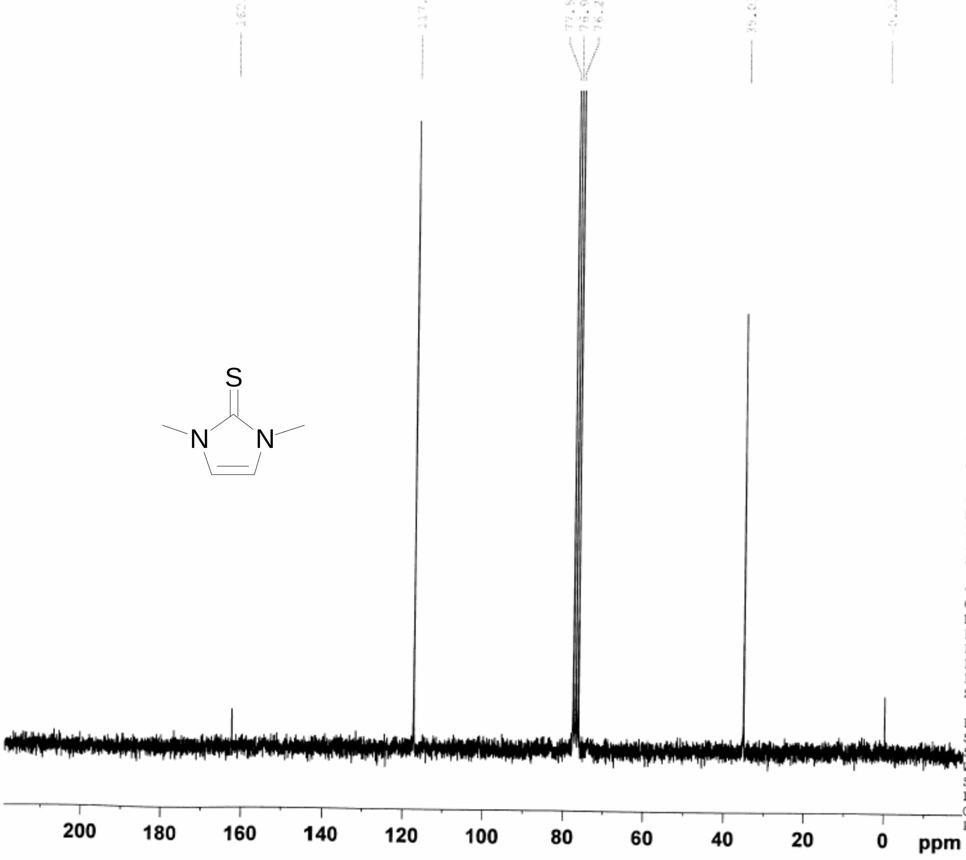

SpinWorks 2.5: 1,3-dimethyl-2-thiohydantoin
183.4035
170.3431
110.5167
77.5284
77.2093
76.8902
53.8570
33.9319
28.2505
S
N
N
O
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30

Wolfe NewMMI2T
PROTON CDCl3 {D:\Schreiner} nmrsu 5

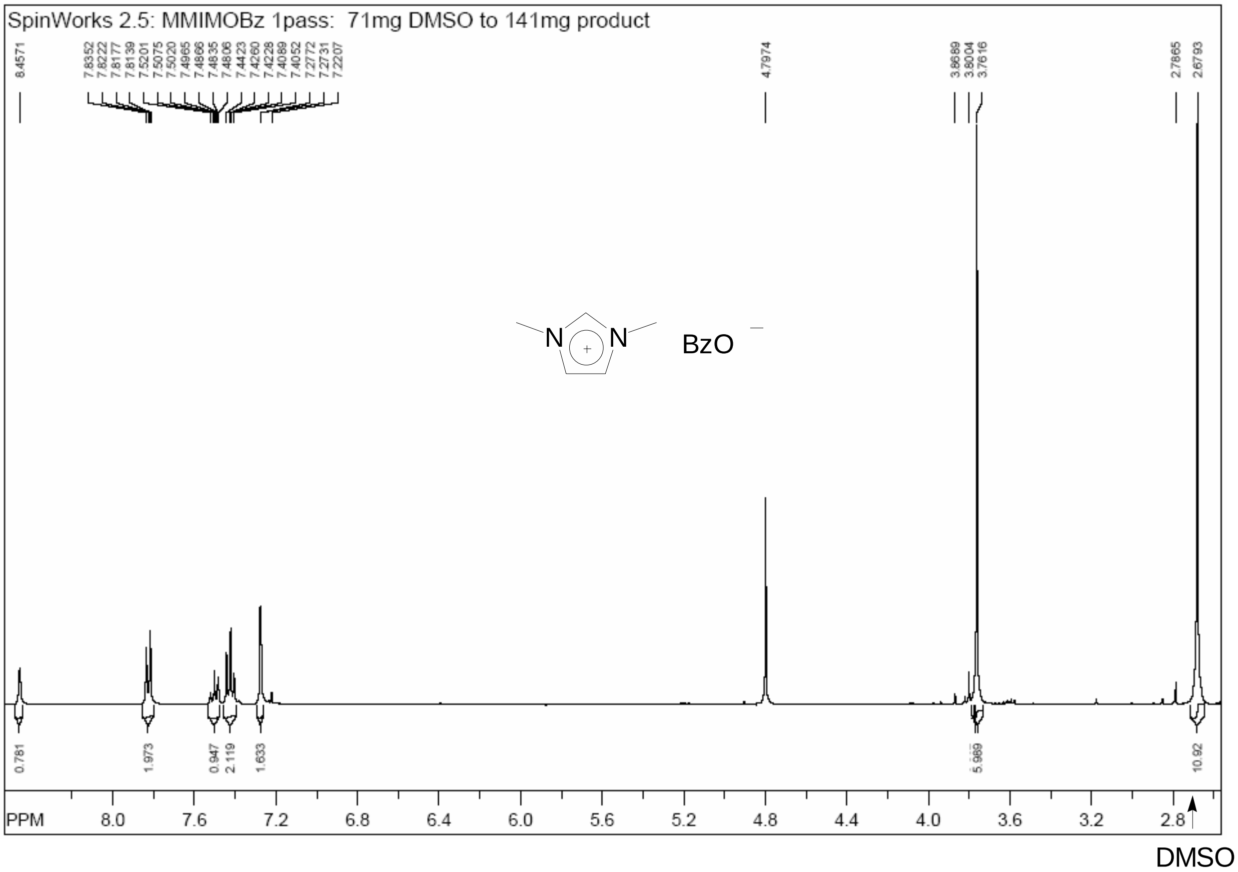


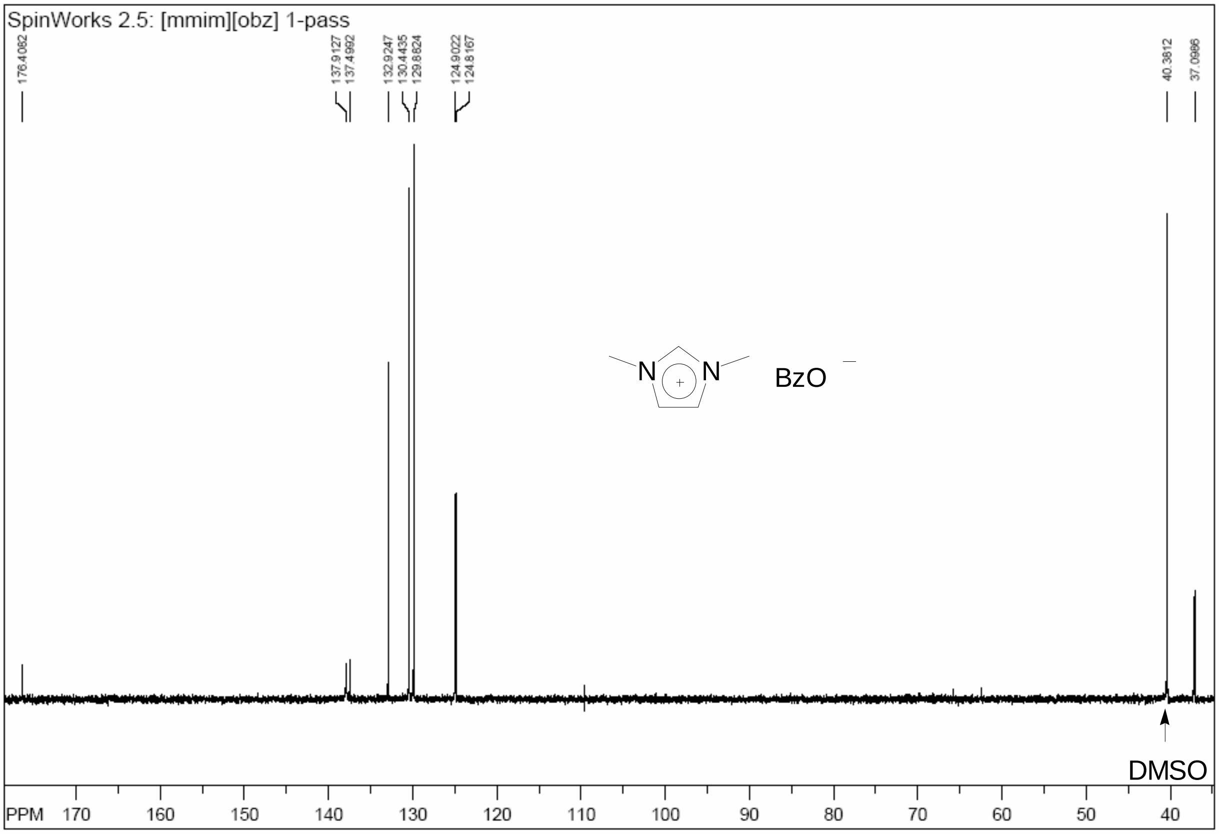
```
Current Data Parameters
NAME          Nov04-2005
EXPNO                 50
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051104
Time               15.28
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             4132.231 Hz
FIDRES          0.063053 Hz
AQ             7.9299059 sec
RG                   645
DW               121.000 usec
DE                  6.00 usec
TE                 673.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.50 usec
PL1                -3.00 dB
SFO1         200.1312359 MHz

F2 - Processing parameters
SI                 32768
SF           200.1299927 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

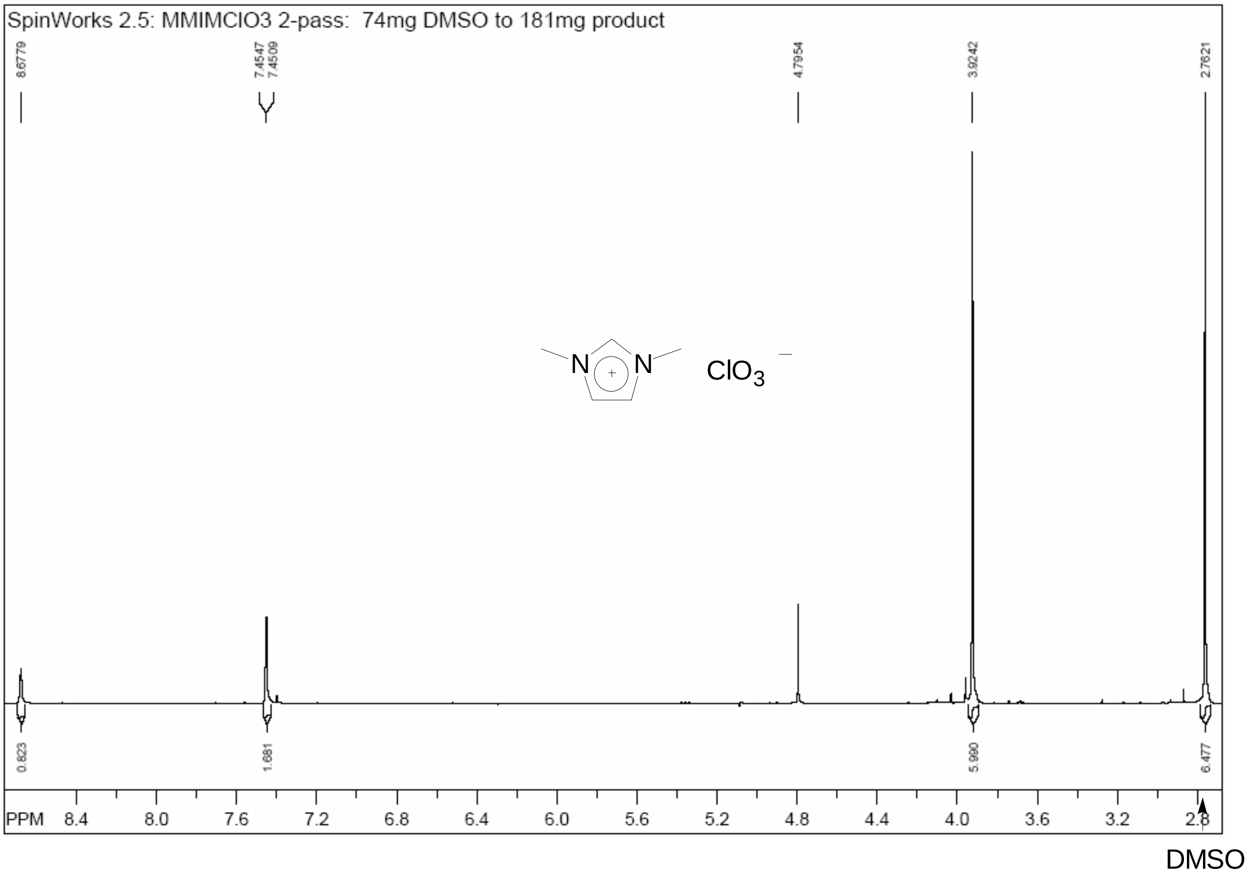
Wolfe NewMMI2T
C13CPD CDCl3 {D:\Schreiner} nmrsu 5

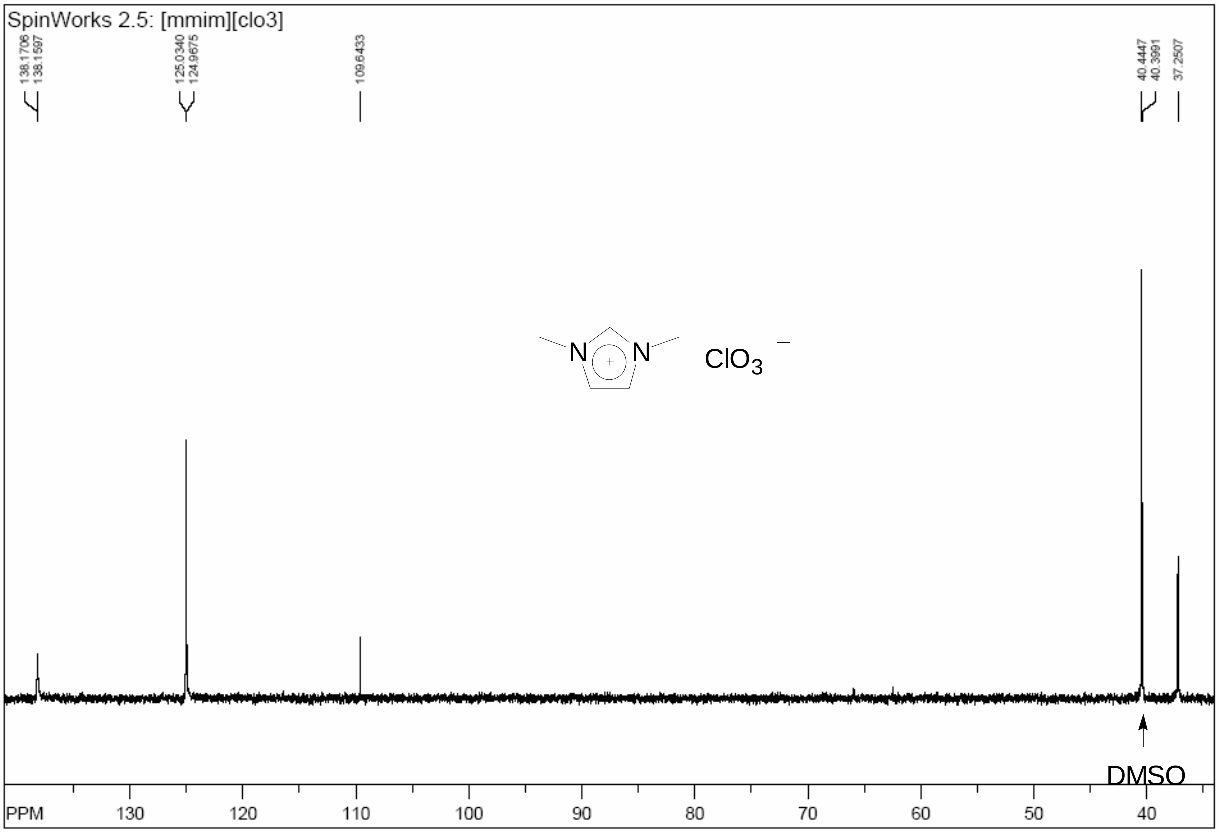


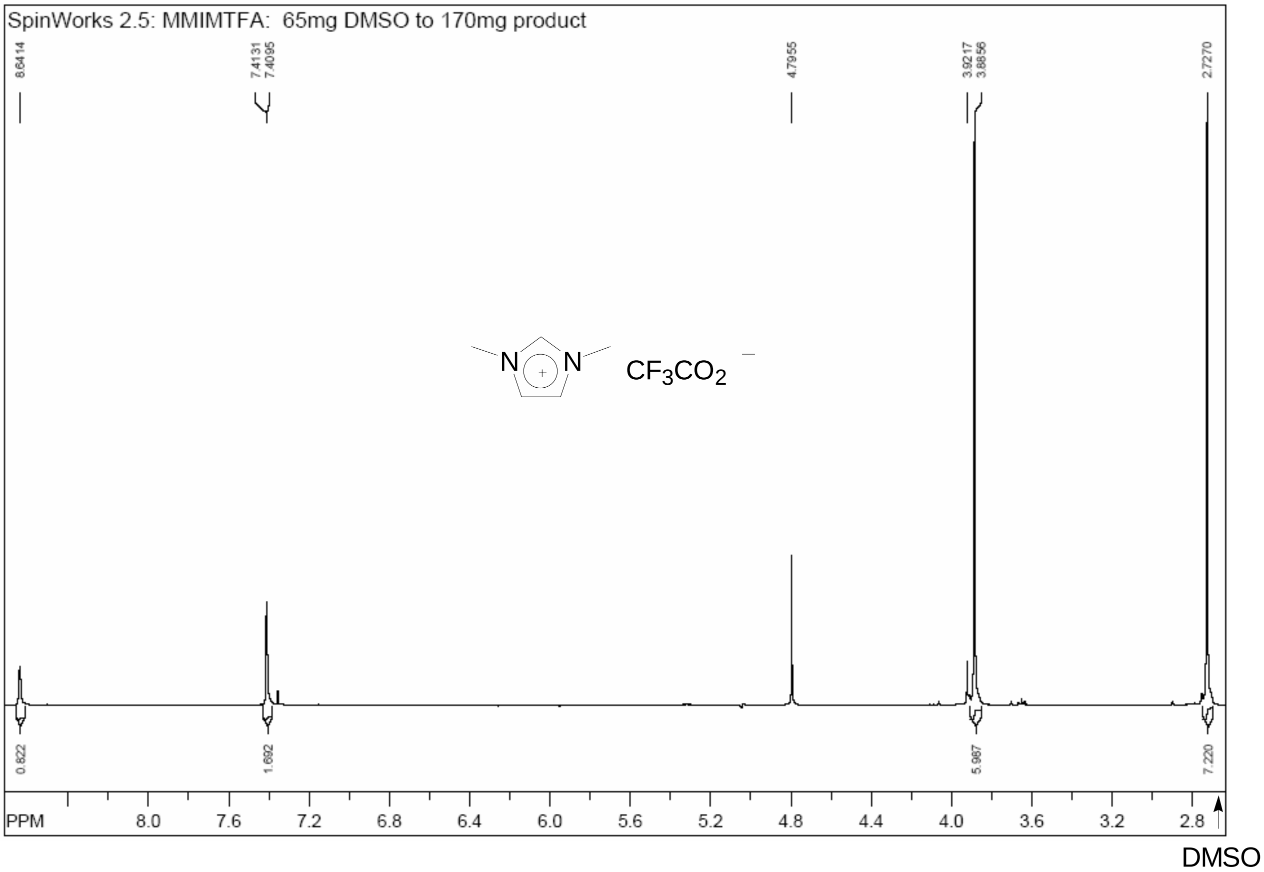
```
Current Data Parameters
NAME          Nov04-2005
EXPNO                 51
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051104
Time               16.04
INSTRUM            spect
PROBHD   5 mm Dual 13C/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            12019.230 Hz
FIDRES          0.183399 Hz
AQ             2.7263477 sec
RG                   5.6
DW                41.600 usec
DE                  6.00 usec
TE                 673.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 2.00 dB
SFO1          50.3277608 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               16.47 dB
PL13               62.00 dB
SFO2         200.1308005 MHz

F2 - Processing parameters
SI                 32768
SF            50.3227382 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

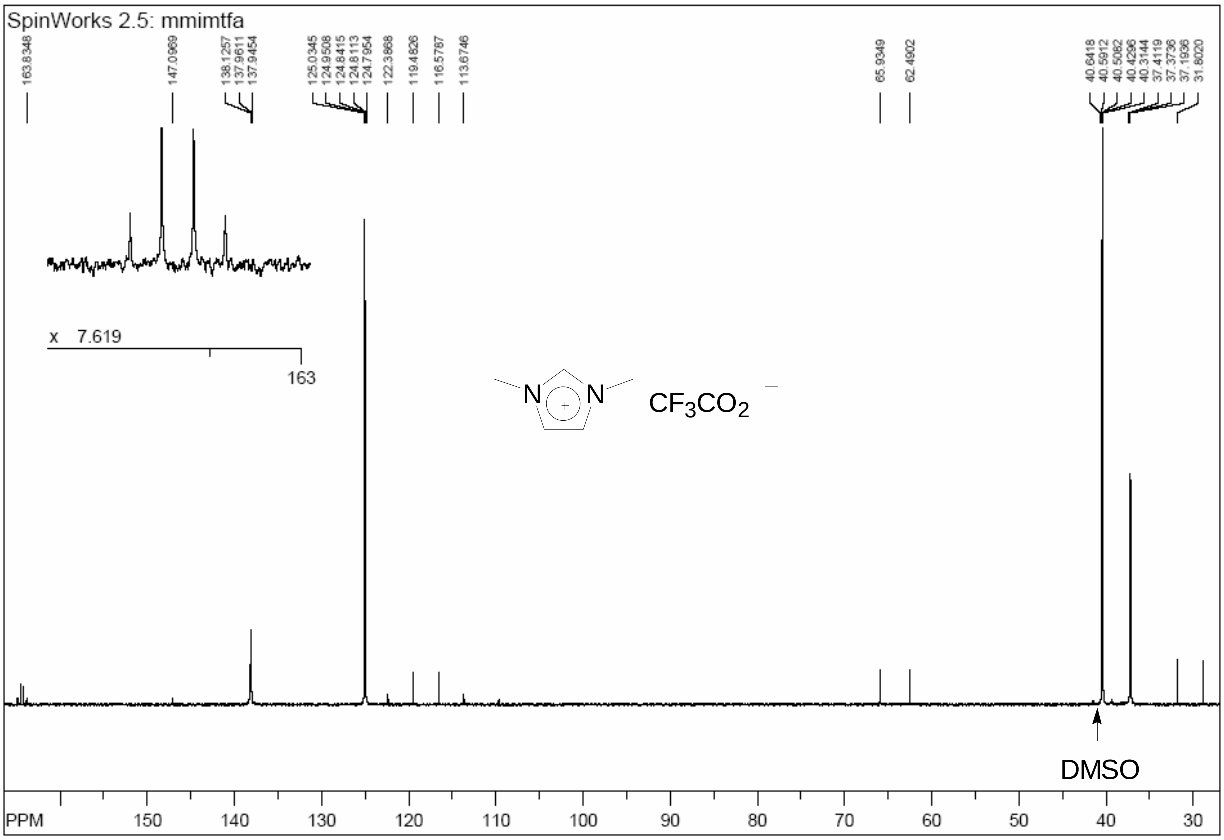

SpinWorks 2.5: MMIMOBz 1pass: 71mg DMSO to 141mg product
8.4571
7.8352
7.8222
7.8177
7.8139
7.5201
7.5075
7.5020
7.4965
7.4866
7.4835
7.4806
7.4423
7.4260
7.4228
7.4089
7.4052
7.2772
7.2731
7.2207
4.7974
3.8689
3.8004
3.7616
2.7865
2.6793
N
N
+
BzO
−
0.781
1.973
0.947
2.119
1.633
5.989
10.92
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
DMSO


SpinWorks 2.5: [mmim][obz] 1-pass
176.4082
137.9127
137.4992
132.9247
130.4435
129.8624
124.9022
124.8167
40.3812
37.0986
N
N
+
BzO
−
DMSO
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40

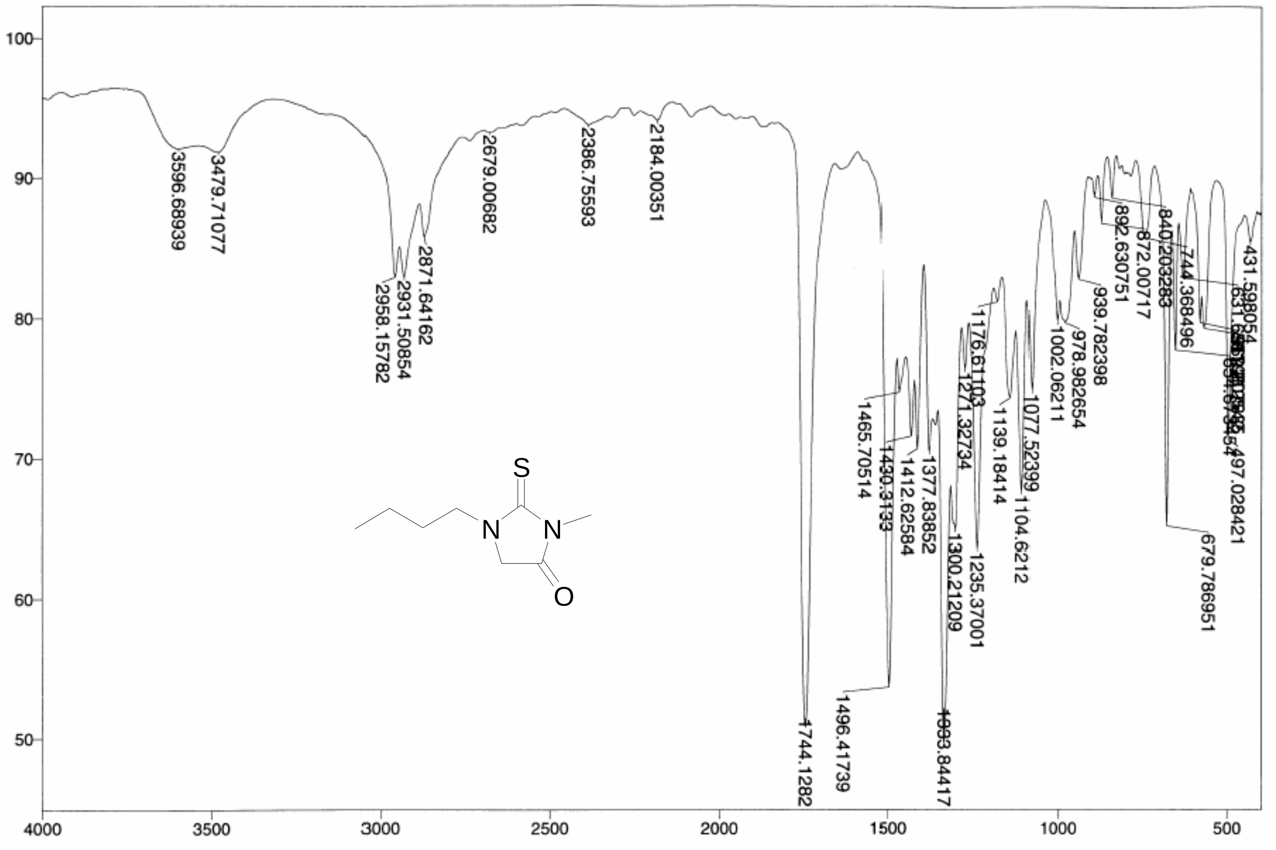

SpinWorks 2.5: MMIMClO3 2-pass: 74mg DMSO to 181mg product
8.6779
7.4547
7.4509
4.7954
3.9242
2.7621
N
N
+
ClO_3^-
0.823
1.681
5.990
6.477
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
DMSO


SpinWorks 2.5: [mmim][clo3]
138.1706
138.1597
125.0340
124.9675
109.6433
40.4447
40.3991
37.2507
N
N
+
ClO_3^-
DMSO
PPM
130
120
110
100
90
80
70
60
50
40


SpinWorks 2.5: MMIMTFA: 65mg DMSO to 170mg product
8.6414
7.4131
7.4095
4.7955
3.9217
3.8856
2.7270
N
+
N
CF3CO2 −
0.822
1.692
5.987
7.220
PPM
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
DMSO


SpinWorks 2.5: mmimtfa
163.8348
147.0969
138.1257
137.9611
137.9454
125.0345
124.9508
124.8415
124.8113
124.7954
122.3868
119.4826
116.5787
113.6746
65.9349
62.4902
40.6418
40.5912
40.5082
40.4296
40.3144
37.4119
37.3736
37.1936
31.8020
x 7.619
163
N
+
N
CF3CO2 −
DMSO
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30

IR SPECTRA


100
90
80
70
60
50
4000
3500
3000
2500
2000
1500
1000
500
3596.68939
3479.71077
2958.15782
2931.50854
2871.64162
2679.00682
2386.75593
2184.00351
1744.1282
1496.41739
1465.70514
1430.3133
1412.62584
1377.83852
1333.84417
1300.21209
1271.32734
1235.37001
1176.61103
1139.18414
1104.6212
1077.52399
1002.06211
978.982654
939.782398
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744.368496
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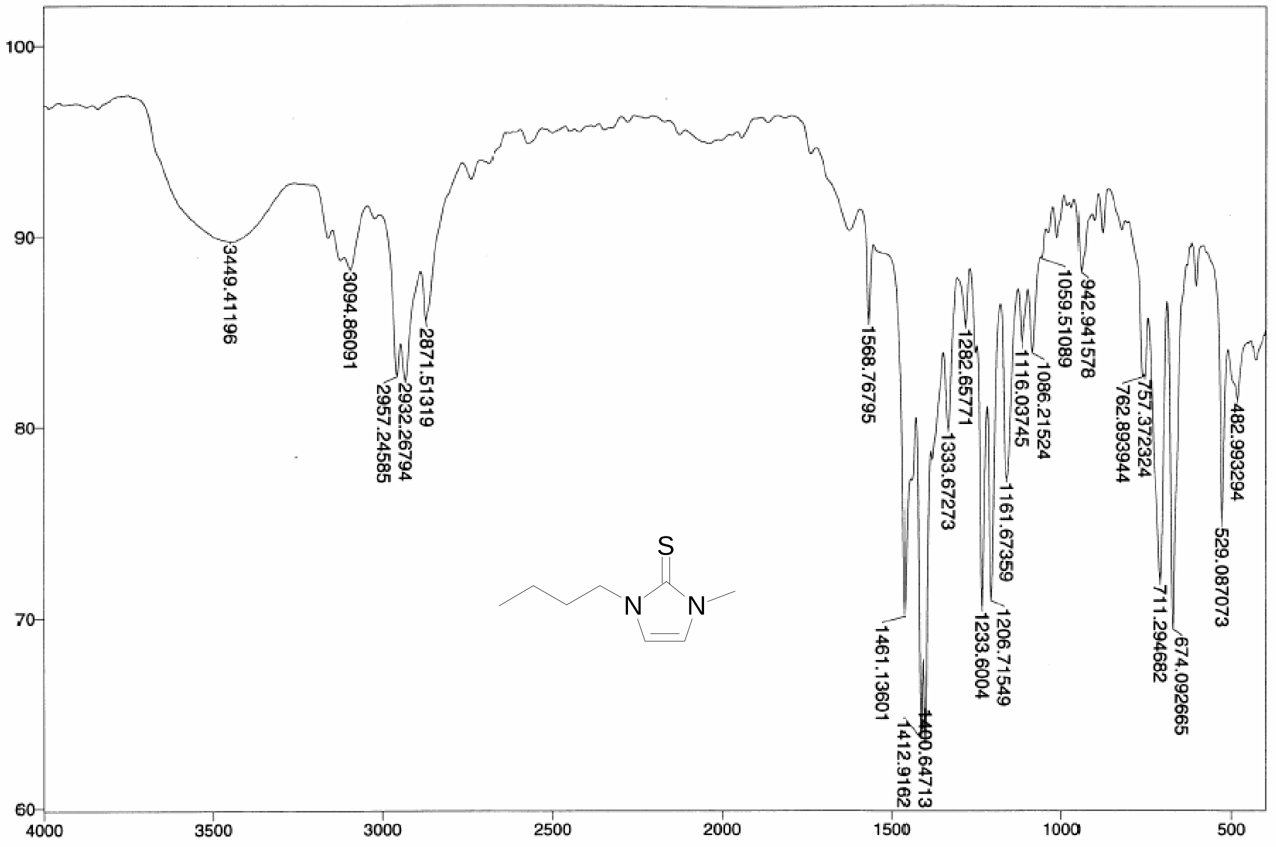
497.028421
431.598054
S
N
N
O


100
90
80
70
60
4000
3500
3000
2500
2000
1500
1000
500
3449.41196
3094.86091
2957.24585
2932.26794
2871.51319
1568.76795
1461.13601
1412.9162
1400.64713
1333.67273
1282.65771
1233.6004
1206.71549
1161.67359
1116.03745
1086.21524
1059.51089
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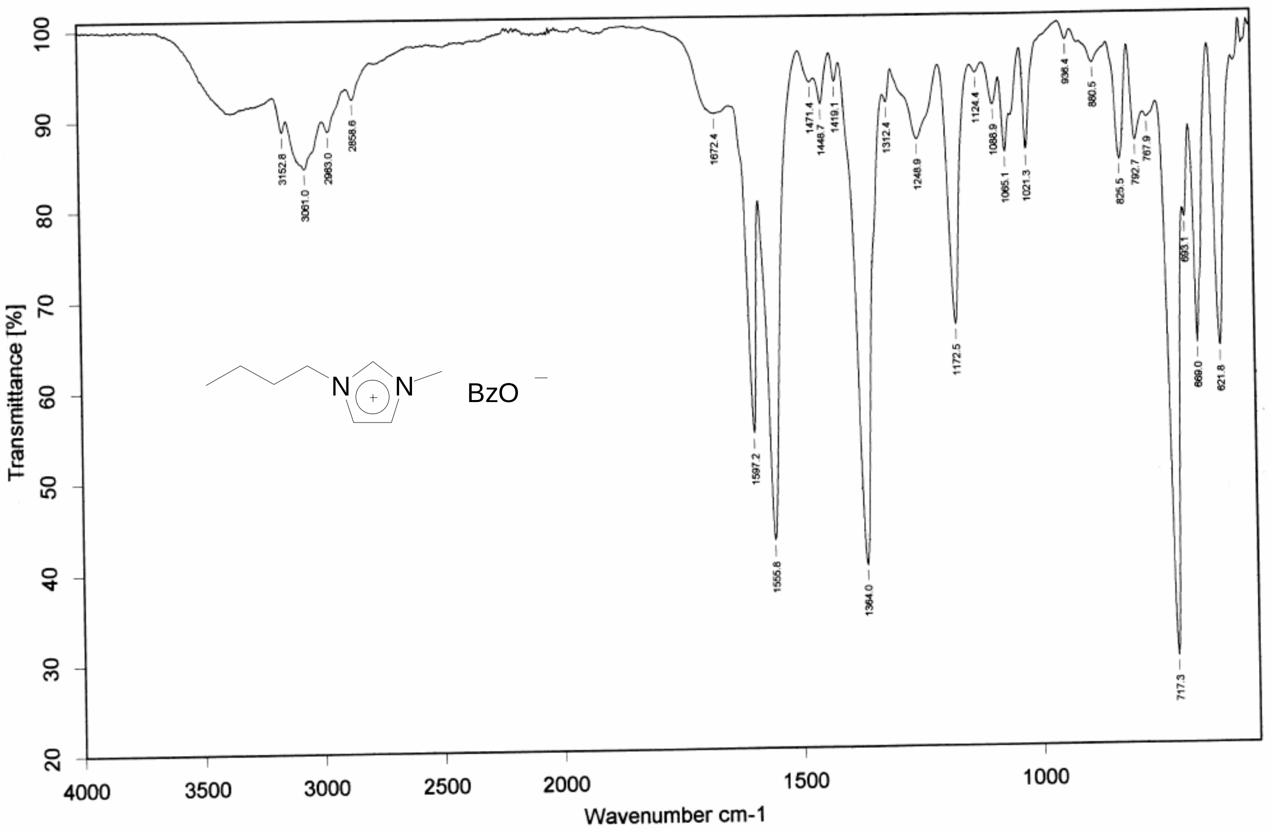
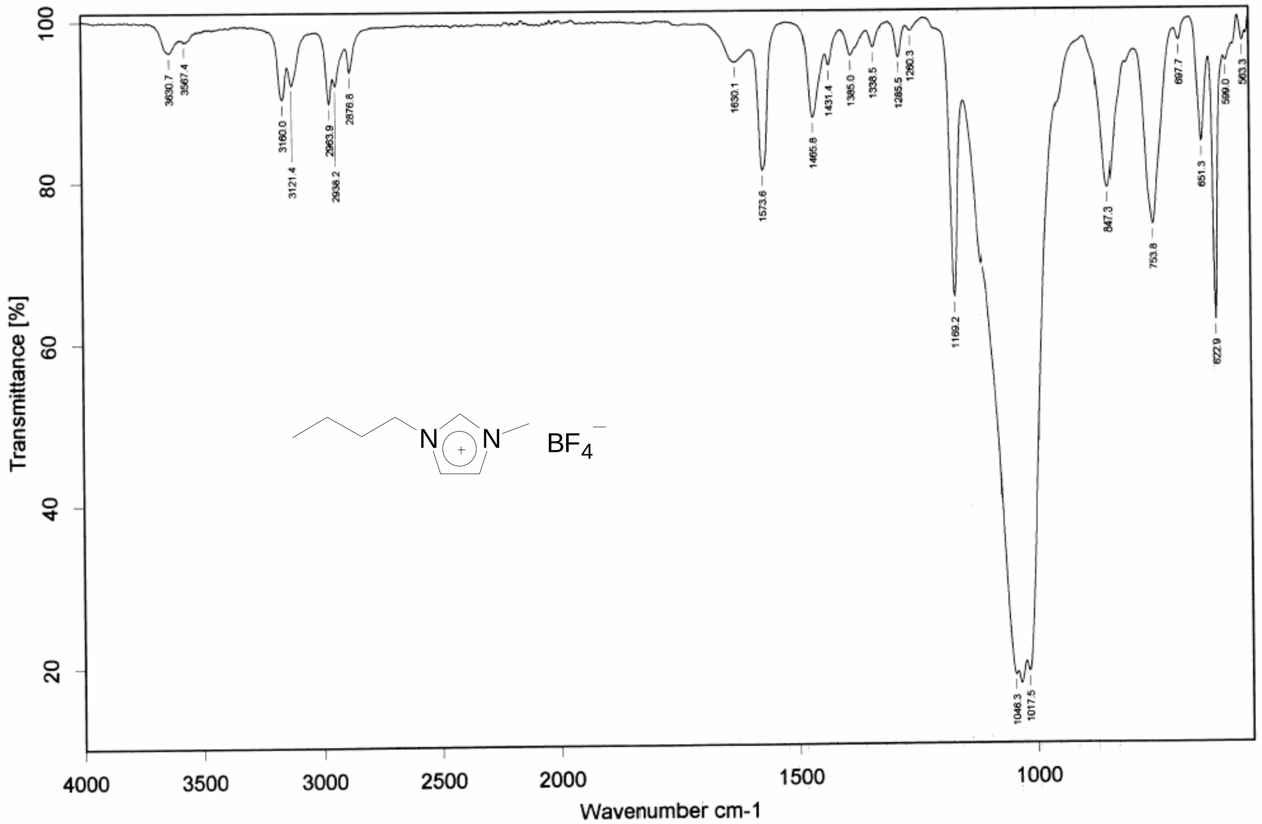
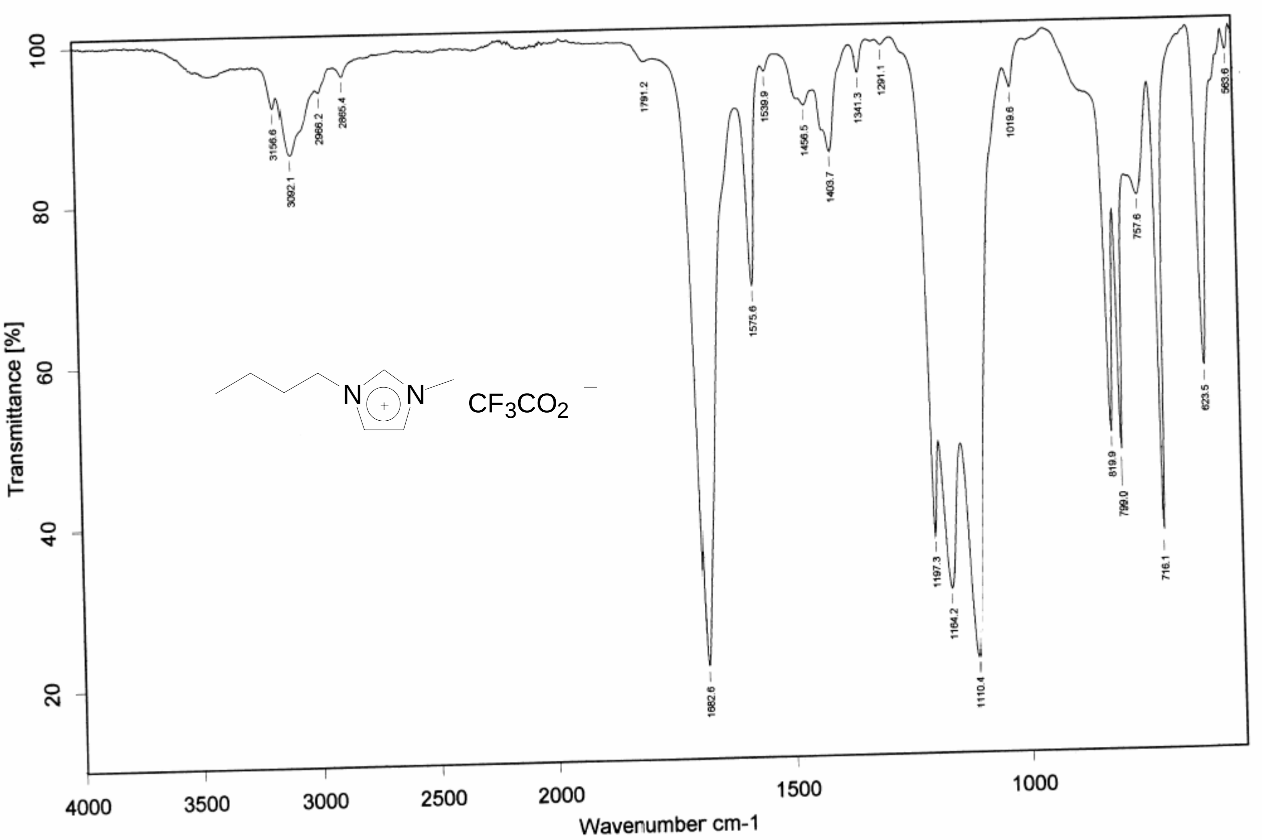
762.893944
757.372324
711.294682
674.092665
529.087073
482.993294
S
N
N

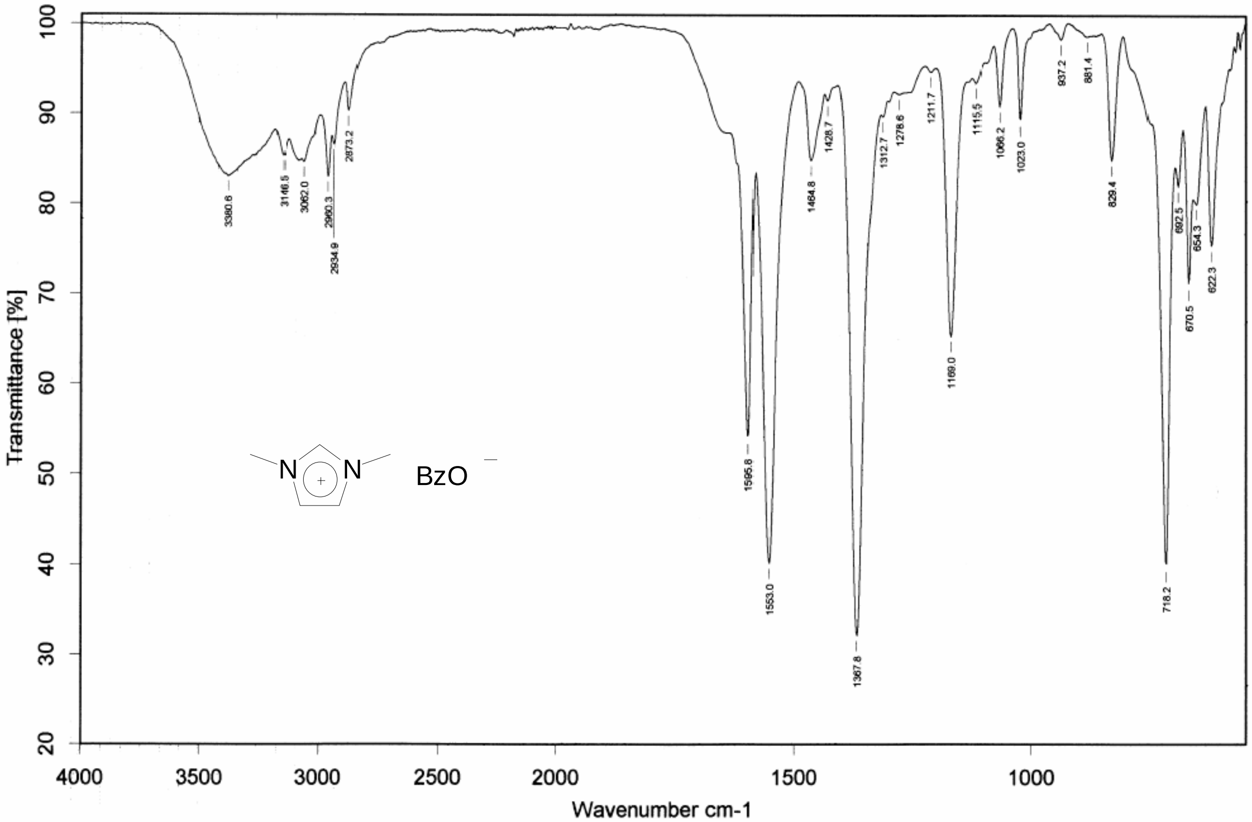


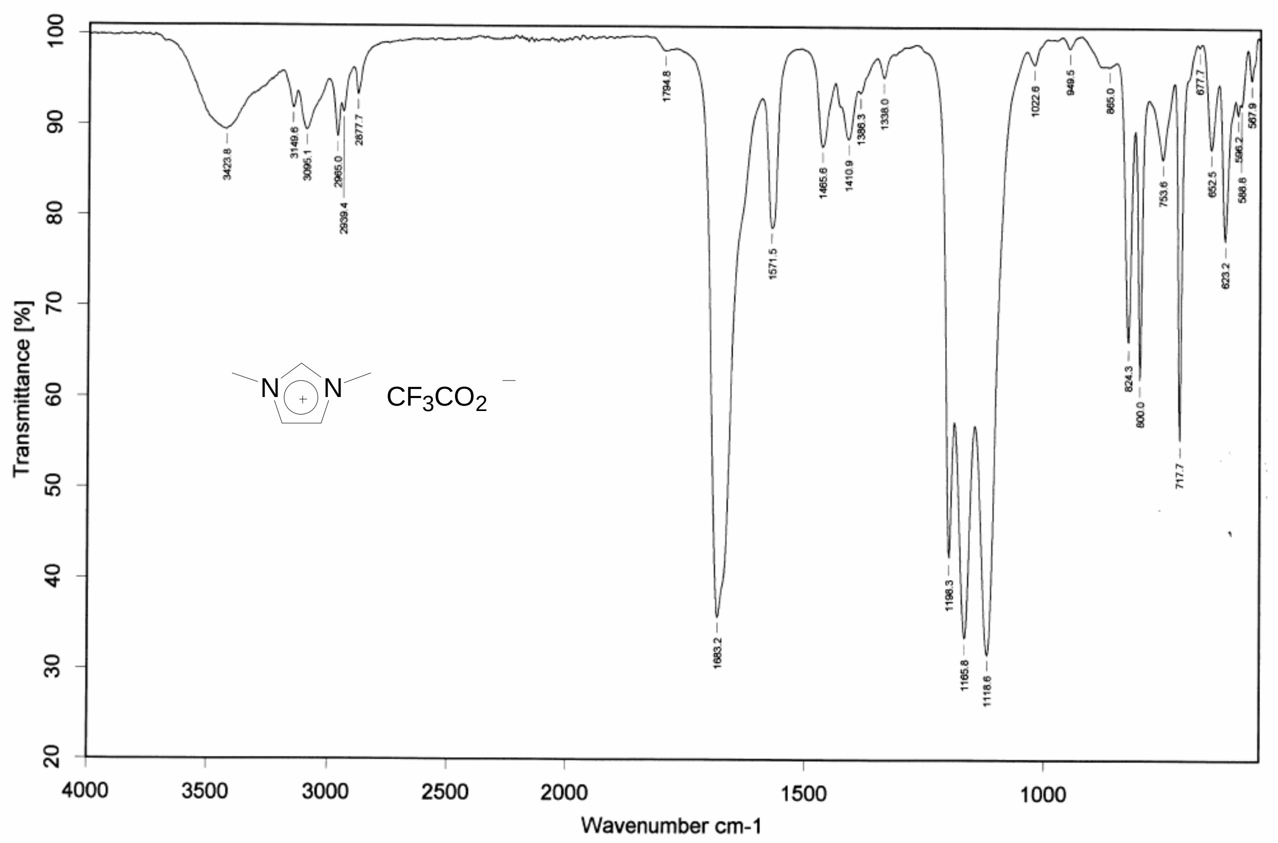
Transmittance [%]
Wavenumber cm-1
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
N
N
+
BzO −
3152.8
3081.0
2963.0
2858.6
1672.4
1597.2
1555.8
1471.4
1448.7
1419.1
1364.0
1312.4
1248.9
1172.5
1124.4
1088.9
1065.1
1021.3
936.4
880.5
825.5
792.7
767.9
717.3
693.1
669.0
621.8



Transmittance [%]
Wavenumber cm-1
100
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
N
N
+
BF_4^-
3630.7
3567.4
3160.0
3121.4
2963.9
2938.2
2876.8
1630.1
1573.6
1465.8
1431.4
1385.0
1338.5
1285.5
1260.3
1169.2
1046.3
1017.5
847.3
753.8
697.7
651.3
622.9
599.0
563.3


Transmittance [%]
100
80
60
40
20
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
3156.6
3092.1
2966.2
2865.4
1791.2
1682.6
1575.6
1539.9
1456.5
1403.7
1341.3
1291.1
1197.3
1164.2
1110.4
1019.6
819.9
799.0
757.6
716.1
623.5
563.6
N
+
N
$CF_3CO_2^-$


Transmittance [%]
100
90
80
70
60
50
40
30
20
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
3380.6
3146.5
3062.0
2960.3
2934.9
2873.2
1595.8
1553.0
1464.8
1428.7
1367.8
1312.7
1278.6
1211.7
1169.0
1115.5
1066.2
1023.0
937.2
881.4
829.4
718.2
692.5
670.5
654.3
622.3
N
+
N
BzO −


100
90
80
70
60
50
40
30
20
Transmittance [%]
4000
3500
3000
2500
2000
1500
1000
Wavenumber cm-1
3423.8
3149.6
3095.1
2965.0
2939.4
2877.7
1794.8
1683.2
1571.5
1465.6
1410.9
1386.3
1338.0
1198.3
1165.8
1118.6
1022.6
949.5
865.0
824.3
800.0
753.6
717.7
677.7
652.5
623.2
596.2
588.6
567.9
N
N
+
$CF_3CO_2^-$

REFERENCES

(1) **CAUTION**: Although $[C_1mim][ClO_3]$ was formed, concentrated at 60 ^oC, chromatographed, concentrated again at 60 ^oC, and seemingly unremarkable, there was an explosion in an unococupied lab several weeks later which we have every reason to believe was caused by a 5 g sample of the once chromatographed chlorate. A 1 g sample from the same batch of offending chlorate and a 1 g sample of twice chromatographed material were unchanged, and a 1 g sample of $[C_4mim][ClO_3]$ was stable for several months, but we must insist no one else attempt the synthesis of these (or any other) imidazolium chlorates by this (or any other) method.

(2) Markwalder, J. A.; Pottorf, R. S.; Seitz, S. P. *Synlett* **1997**, 521-522.

(3) Scott, J. E.; Henderson, G. *Biochem. J.* **1968**, *109*, 209-15.

(4) Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; De Souza, R. F. *Org. Synth.* **2003**, *79*, 236-243.

(5) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192-5200.