Supporting Information

2-BROMO-1,3-DIMETHOXYIMIDAZOLIUM TRIBROMIDE AS STARTING SALT FOR 2-ARYL- AND 2-HETEROARYLMERCAPTO DERIVATIVES

Lukas Fliri,[1] Sandro Neuner,[1] Martin Lampl,[1] Gabriel Partl,[1] Holger Kopacka,[1] Klaus Wurst,[1] Thomas Gelbrich,[1] Volker Kahlenberg,[2] Sven Nerdinger [3*] and Herwig Schottenberger [1*]

[1]University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 80-82, [2]University of Innsbruck, Institute of Mineralogy and Petrography, Innrain 52, 6020 Innsbruck, Austria; [3]Sandoz GmbH, Biochemiestrasse 10, 6250 Kundl, Austria..

E-mail: sven.nerdinger@sandoz.com; herwig.schottenberger@uibk.ac.at; lukas.fliri@uibk.ac.at

Table of Contents

PXRD Data and TGA Analysis

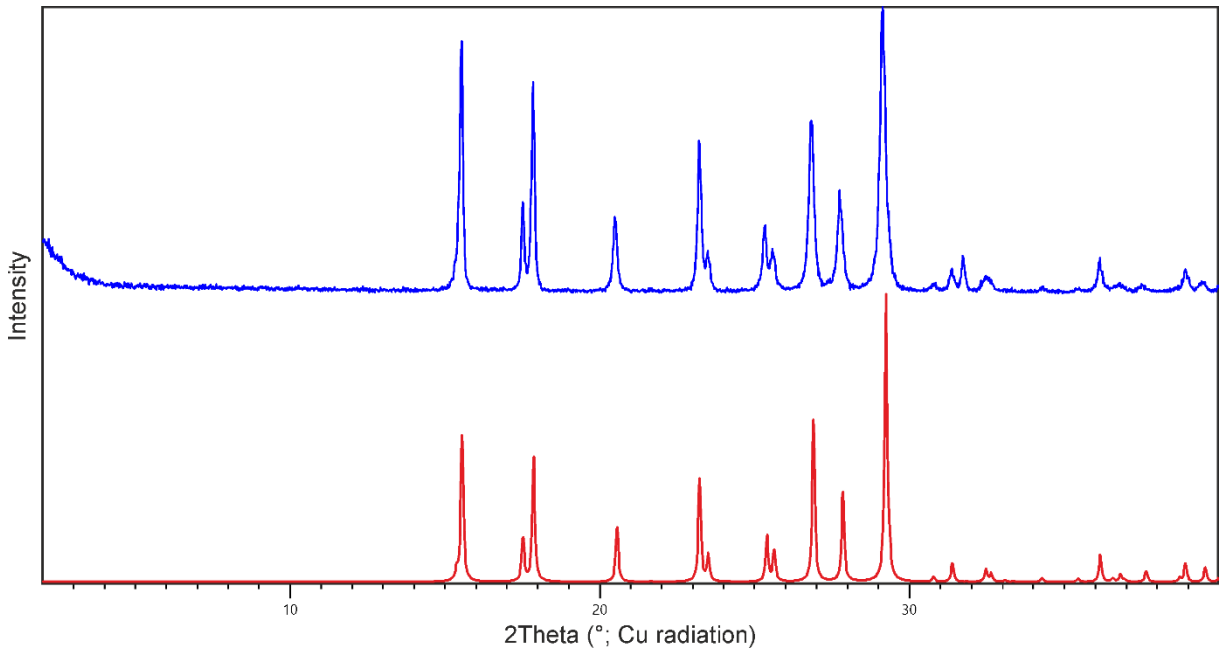

Figure S1. Top: Experimental PXRD pattern of 1-hydroxyimidazole 3-oxide [35321-46-1] at 20 °C. **Bottom:** Simulated PXRD pattern for the structure model of 1-hydroxyimidazole 3-oxide [35321-46-1] (Laus *et al.*, *Z. Naturforsch. B*, 2008, **63**, 447; CSD refcode DOJKUJ).

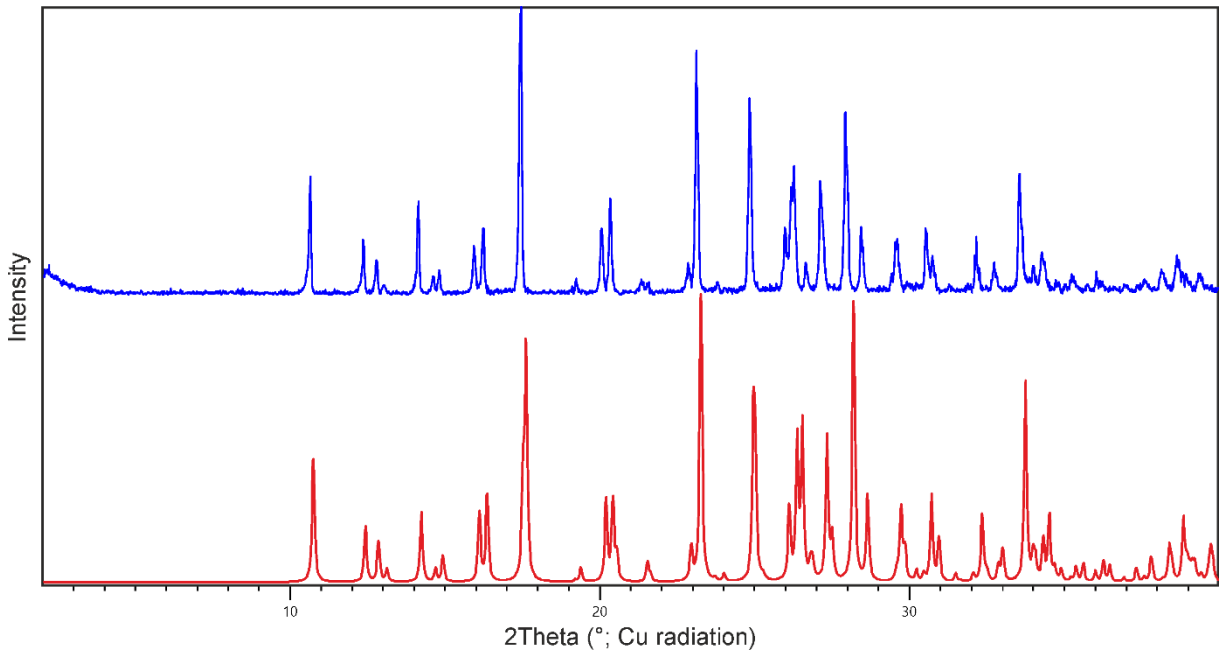

Figure S2. Top: Experimental PXRD pattern of **1** recorded at 20 °C. **Bottom:** Simulated PXRD pattern for the structure model established for **1** on the basis of single crystal data recorded at -100 °C (CCDC no. 1969810).

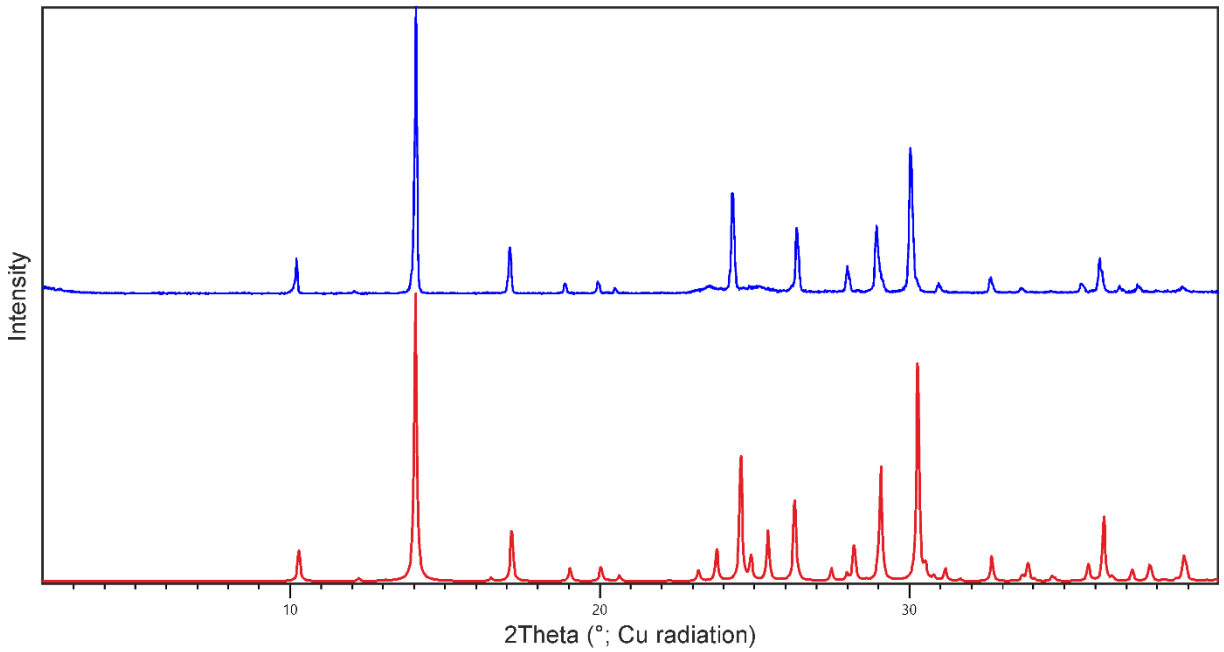

Figure S3. Top: Experimental PXRD pattern of **2** recorded at 20 °C. **Bottom:** Simulated PXRD pattern for the structure model established for **2** on the basis of single crystal data recorded at -80 °C (CCDC no. 1969807).

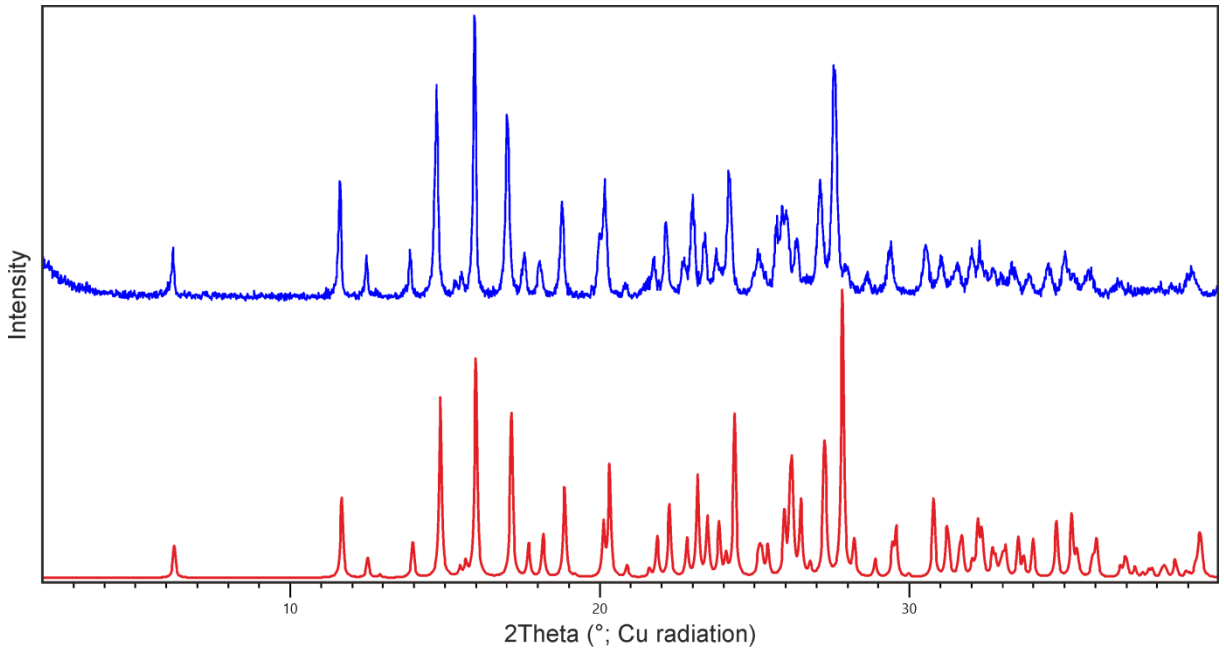

Figure S4. Top: Experimental PXRD pattern of **8 · 0.5(H_2O)** recorded at 20 °C. **Bottom:** Simulated PXRD pattern for the structure model established for **8 · 0.5(H_2O)** on the basis of single crystal data recorded at -100 °C (CCDC no. 1969808).

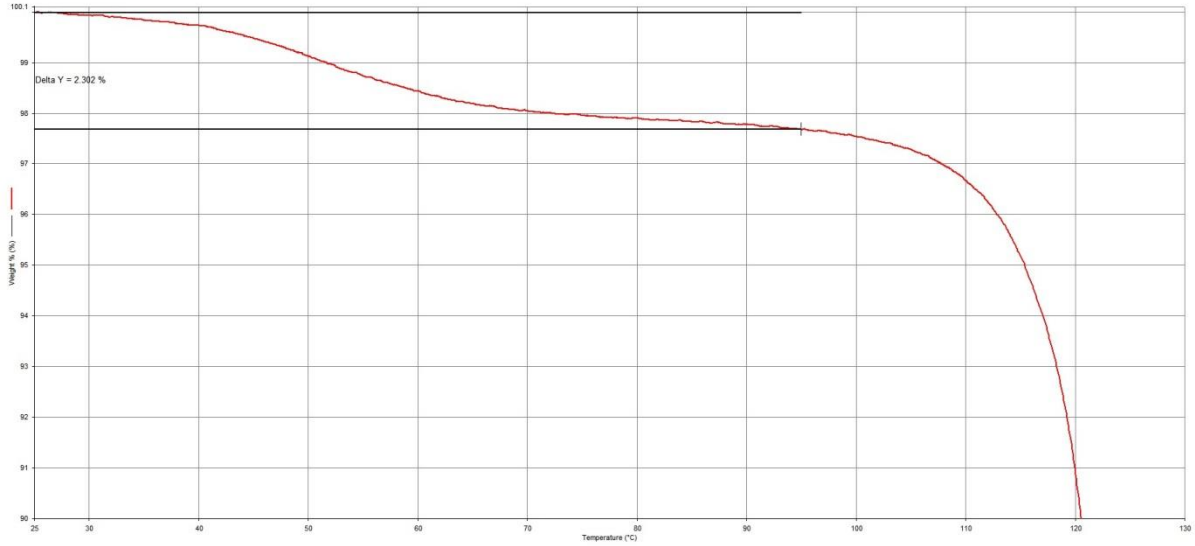

Figure S5. TGA curve for **8 · 0.5(H_2O)** (heating rate 5 K/min), showing a mass loss of 2.3% between 25 °C and 95 °C, which is consistent with the loss of 0.5 mol H_2O (theoretical value: 2.35%), followed by decomposition. [thermogravimetric system TGA-7 and Pyris software (Perkin-Elmer, Norwalk, Ct., USA), Pt sample holder (50 µl), purge gas N2 (sample purge: 20 ml/min, balance purge: 40 ml/min)]

^{1}H-NMR, ^{13}C-NMR and IR-absorption spectra

1-Hydroxyimidazole 3-oxide [35321-46-1]

^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.64 (t, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.0 Hz, 2H) ppm.

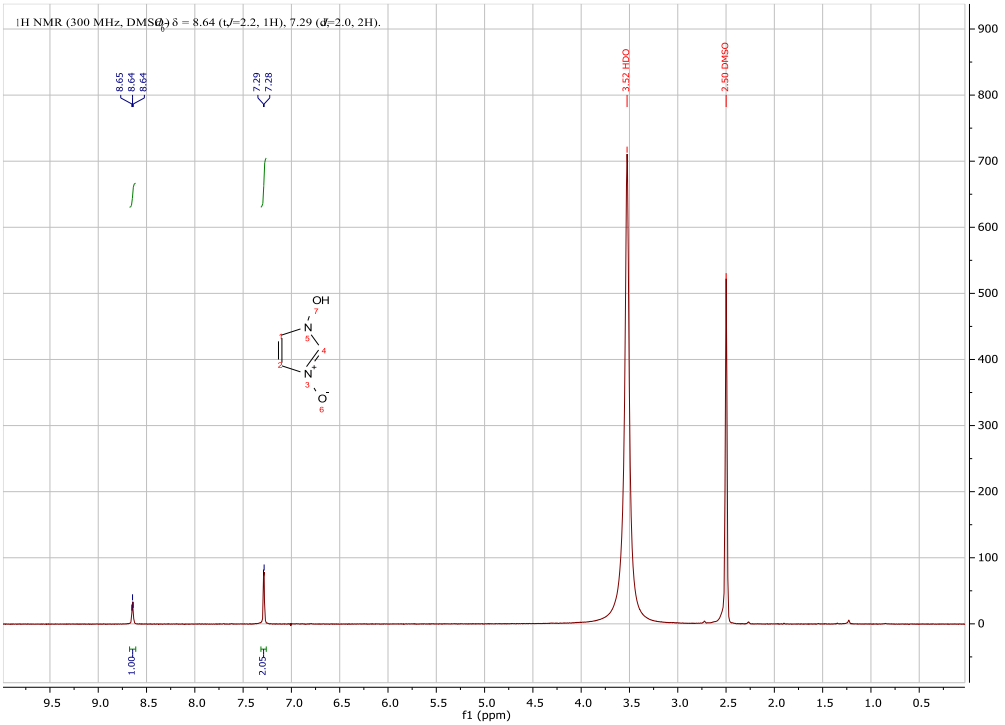

Figure S6. ^{1}H-NMR (DMSO-d_6) of 1-Hydroxyimidazole 3-oxide [35321-46-1]

^{13}C NMR (75 MHz, DMSO-d_6) δ = 124.49, 116.53 (2C) ppm.

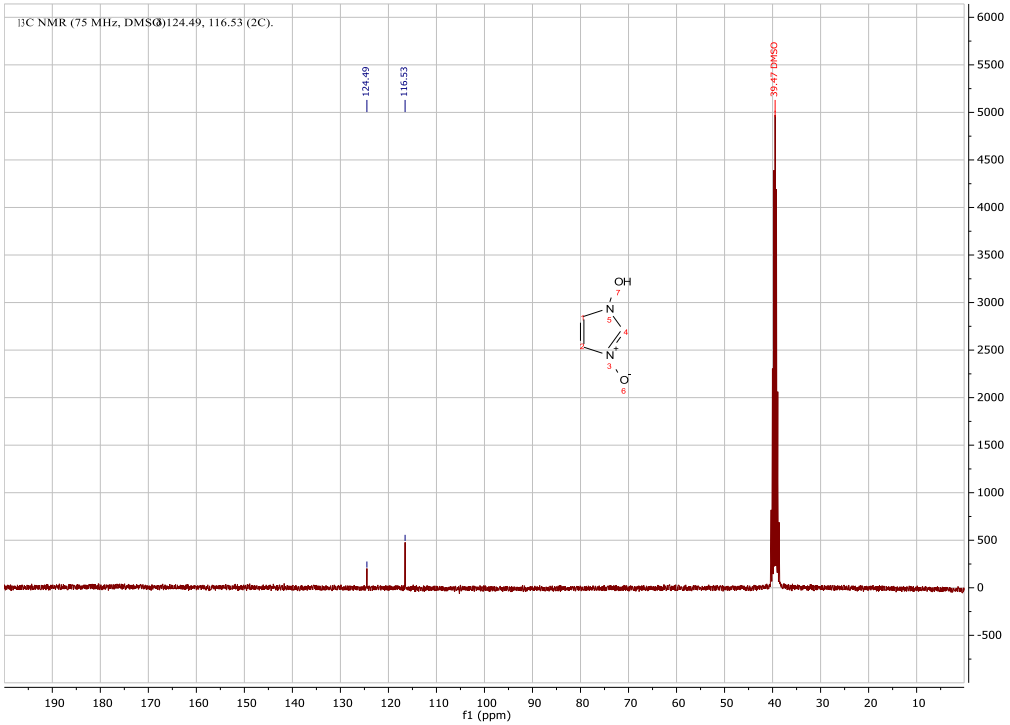

Figure S7. ^{13}C-NMR (DMSO-d_6) of 1-Hydroxyimidazole 3-oxide [35321-46-1]

IR(neat): ν = 3165 (w), 3137 (m), 3104 (m), 1508 (w), 1363 (m), 1247 (m), 1185 (s), 1109 (m), 1058 (m), 1020 (m), 965 (s), 914 (s), 886 (s), 778 (vs), 748 (s), 725 (vs), 659 (m), 616 (s), 594 (vs), 492 (s), 435 (m) cm^{-1}.

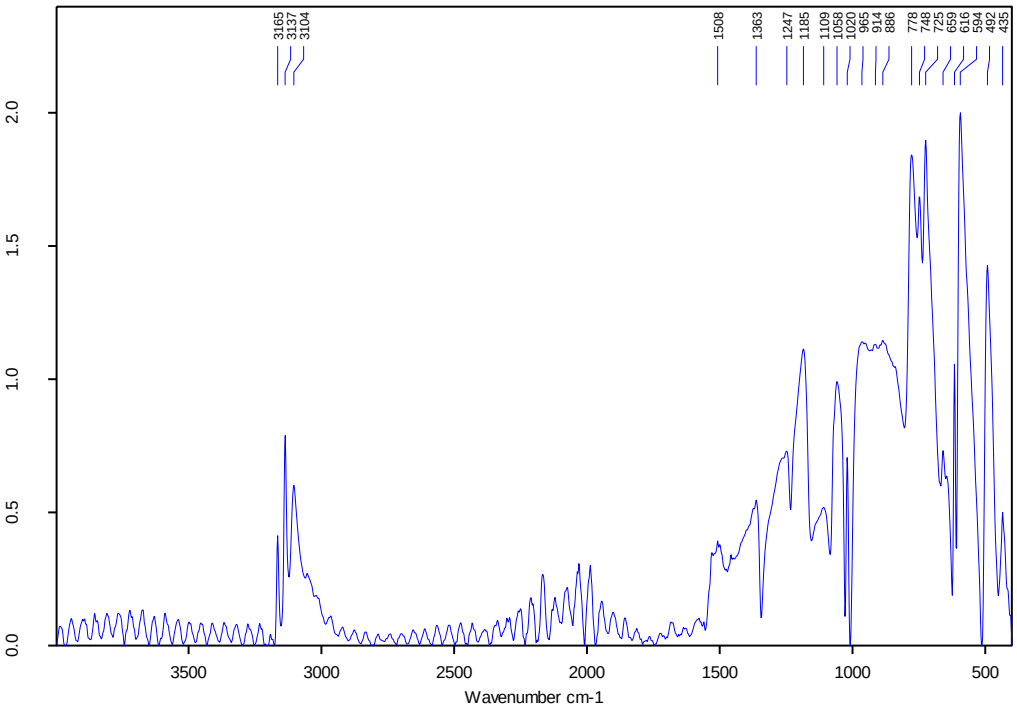

Figure S8. IR- absorption spectra (neat) of 1-hydroxyimidazole 3-oxide [35321-46-1]

2-Bromo-1,3-dimethoxyimidazolium tribromide (1)

^{1}H NMR (300 MHz, DMSO-d_6-slight dissociation) δ = 8.51 (s, 2H), 4.23 (s, 6H) ppm.

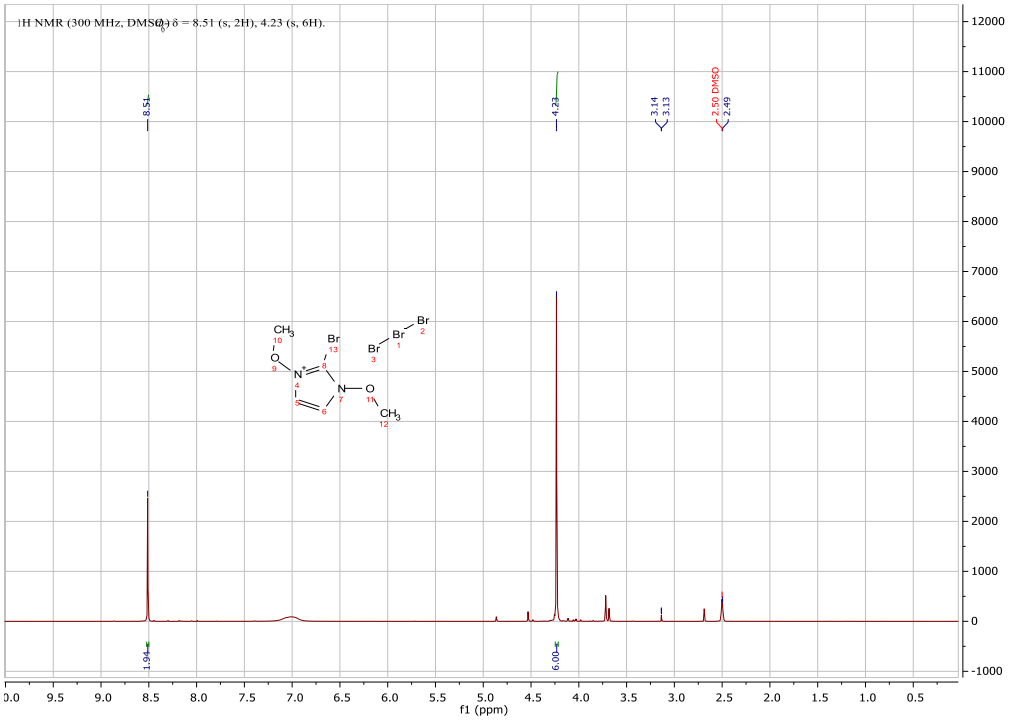

Figure S9. ^{1}H-NMR (DMSO-d_6) of 2-bromo-1,3-dimethoxyimidazolium tribromide (**1**)

^{13}C NMR (75 MHz, DMSO-d_6- slight dissociation) δ = 118.24 (2C), 117.31, 69.12 (2C) ppm.

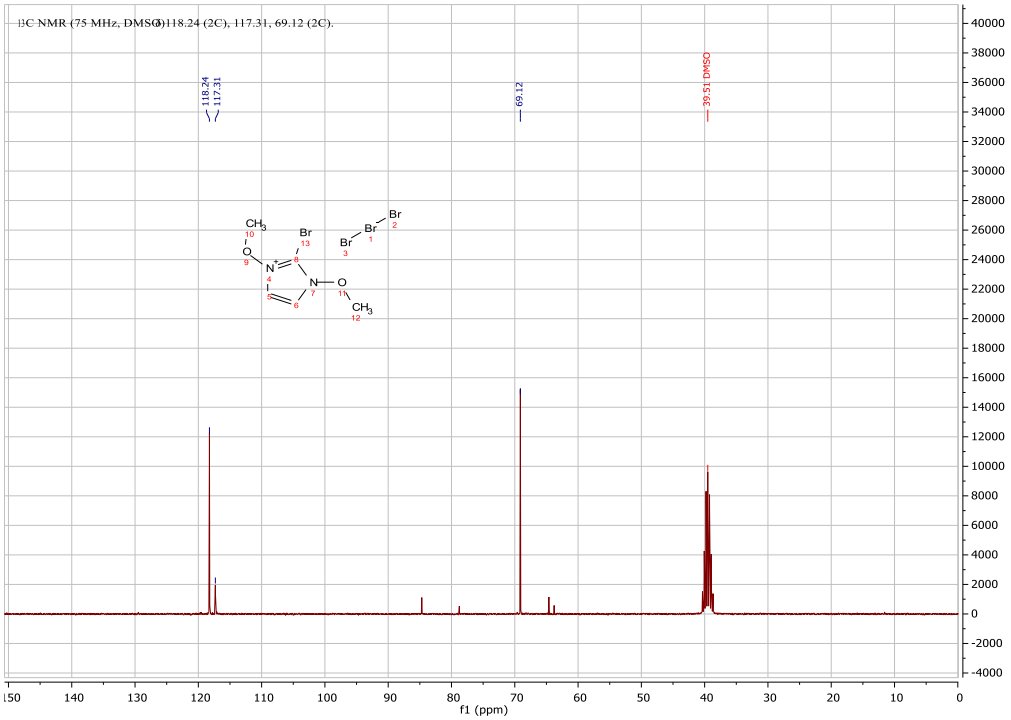

Figure S10. ^{13}C-NMR (DMSO-d_6) of 2-bromo-1,3-dimethoxyimidazolium tribromide (**1**)

IR(neat): ν = 3148 (w), 3117 (m), 3081 (w), 2942 (w), 1651 (w), 1546 (m), 1446 (m), 1435 (m), 1352 (w), 1322 (w), 1191 (w), 1151 (w), 1117 (m), 1040 (s), 931 (vs), 733 (m), 704 (s), 657 (m), 594 (s), 523 (w), 454 (w) cm^{-1}.

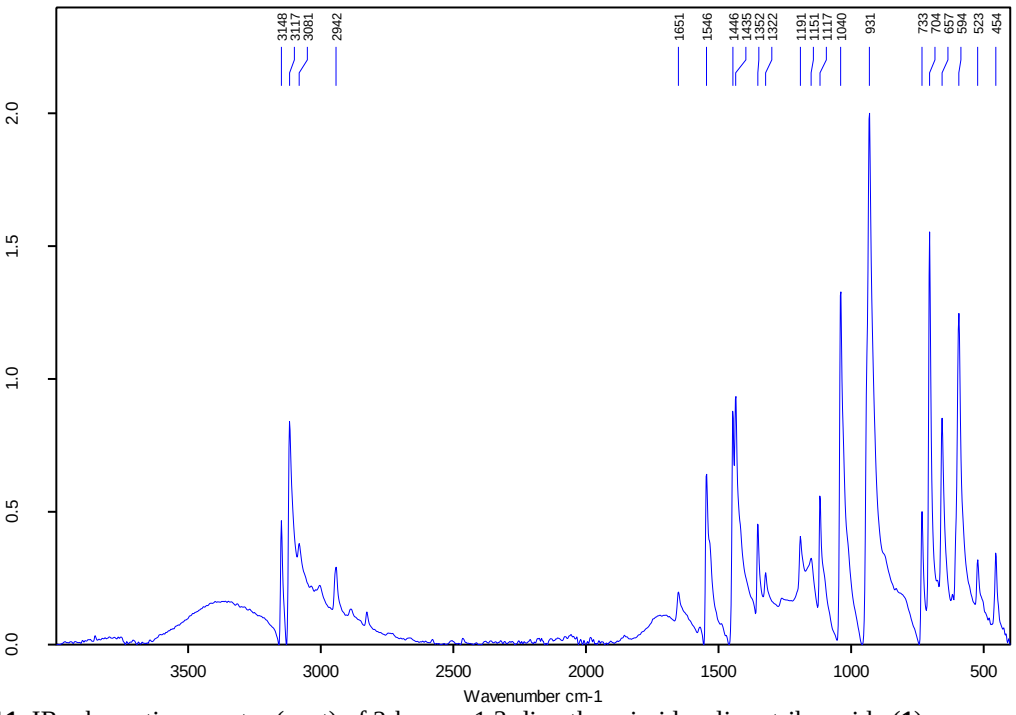

Figure S11. IR- absorption spectra (neat) of 2-bromo-1,3-dimethoxyimidazolium tribromide (**1**)

2-Bromo-1,3-dimethoxyimidazolium bromide (2)

^{1}H NMR (300 MHz, MeOH-*d*$_4$) δ = 8.32 (s, 2H), 4.34 (s, 6H) ppm.

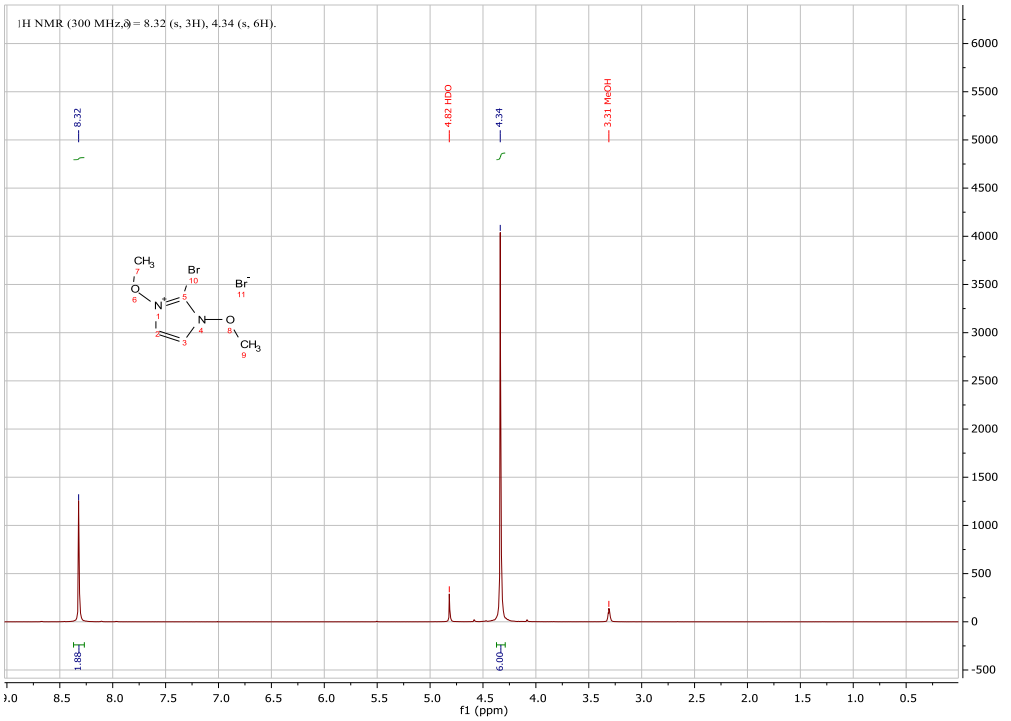

Figure S12. ^{1}H-NMR (MeOH-*d*$_4$) of 2-bromo-1,3-dimethoxyimidazolium bromide (**2**)

^{13}C NMR (75 MHz, MeOH-*d*$_4$) δ = 119.91 (2C), 118.24, 70.14 (2C) ppm.

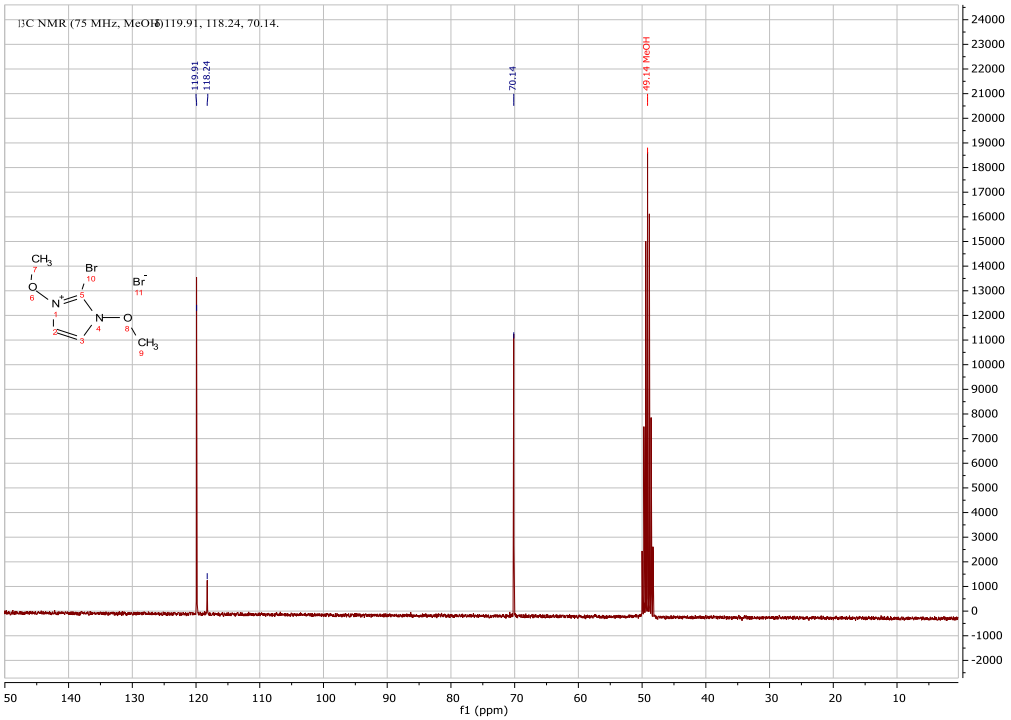

Figure S13. ^{13}C-NMR (MeOH-*d*$_4$) of 2-bromo-1,3-dimethoxyimidazolium bromide (**2**)

IR(neat): ν = 3148 (w), 3117 (m), 3081 (w), 2942 (w), 1651 (w), 1546 (m), 1446 (m), 1435 (m), 1352 (w), 1322 (w), 1191 (w), 1151 (w), 1117 (m), 1040 (s), 931 (vs), 733 (m), 704 (s), 657 (m), 594 (s), 523 (w), 454 (w) cm^{-1}.

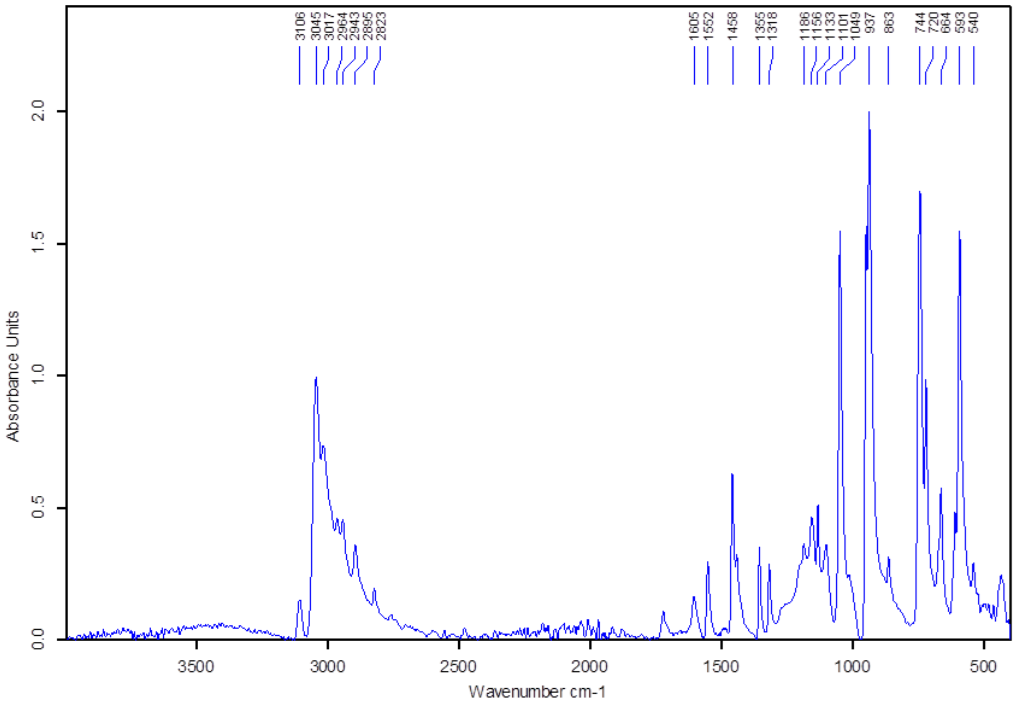

Figure S14. IR- absorption spectra (neat) of 2-bromo-1,3-dimethoxyimidazolium bromide (**2**)

2-Bromo-1,3-dimethoxyimidazolium hexafluorophosphate (3)

^{1}H NMR (300 MHz, acetone-d_6) δ = 8.30 (s, 2H), 4.38 (s, 6H) ppm.

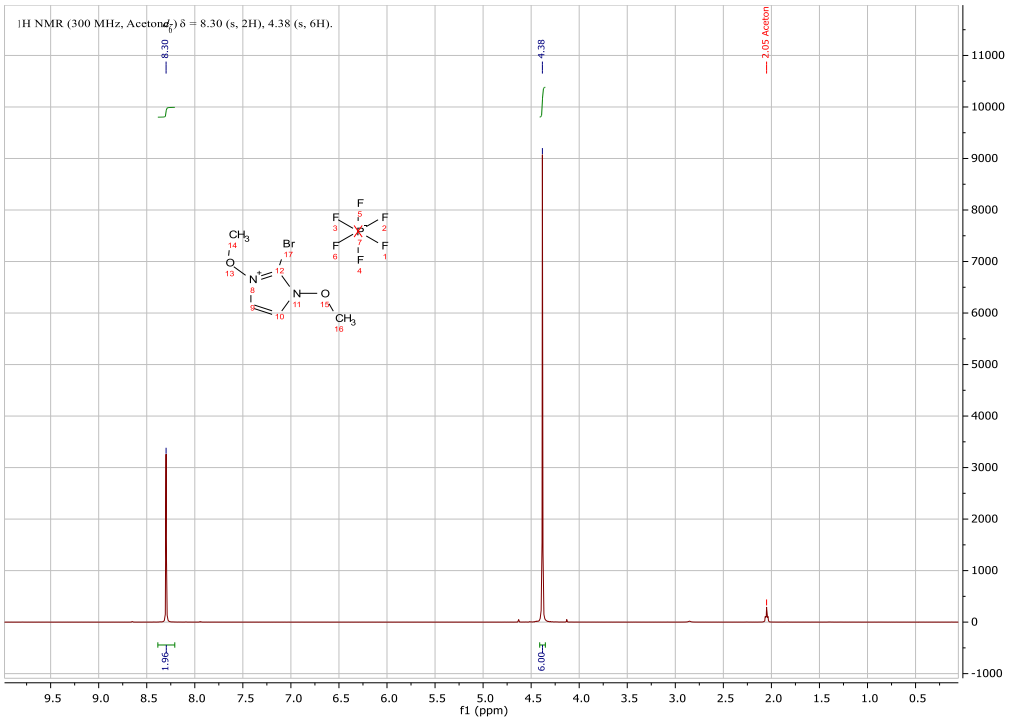

Figure S15. ^{1}H-NMR (acetone-d_6) of 2-bromo-1,3-dimethoxyimidazolium hexafluorophosphate (**3**)

^{13}C NMR (75 MHz, acetone-d_6) δ = 119.66 (2C), 117.09, 70.05 (2C) ppm.

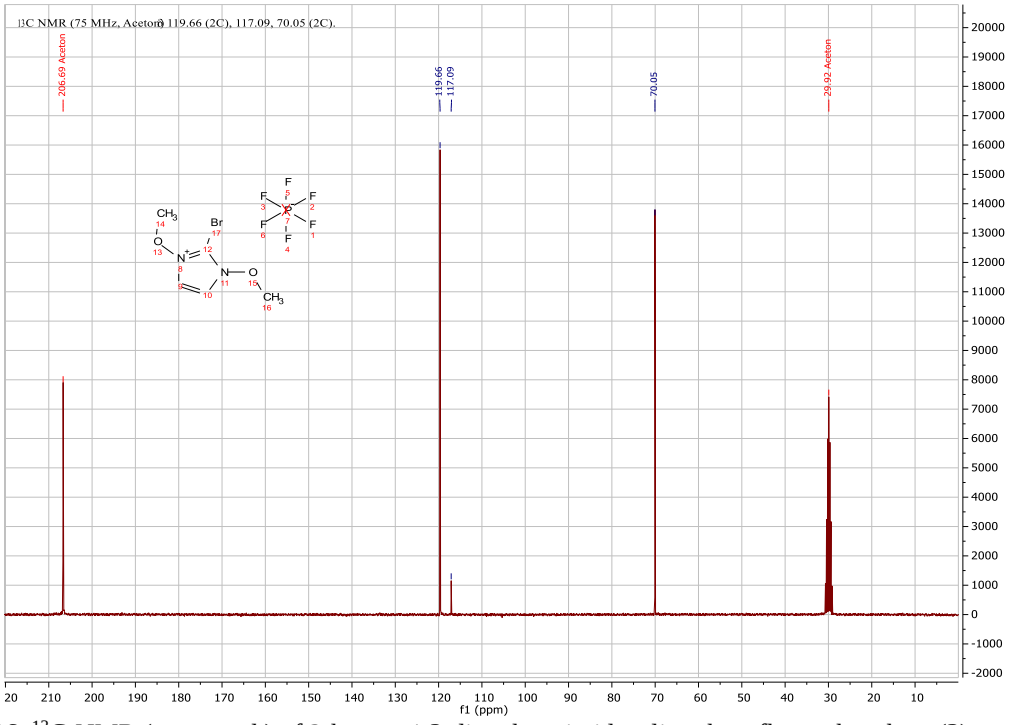

Figure S16. ^{13}C-NMR (acetone-d_6) of 2-bromo-1,3-dimethoxyimidazolium hexafluorophosphate (**3**)

IR(neat): ν = 3170 (w), 3150 (w), 1557 (w), 1458 (w), 1441 (w), 1049 (m), 940 (m), 826 (vs), 732 (m), 650 (m), 556 (s) cm^{-1}.

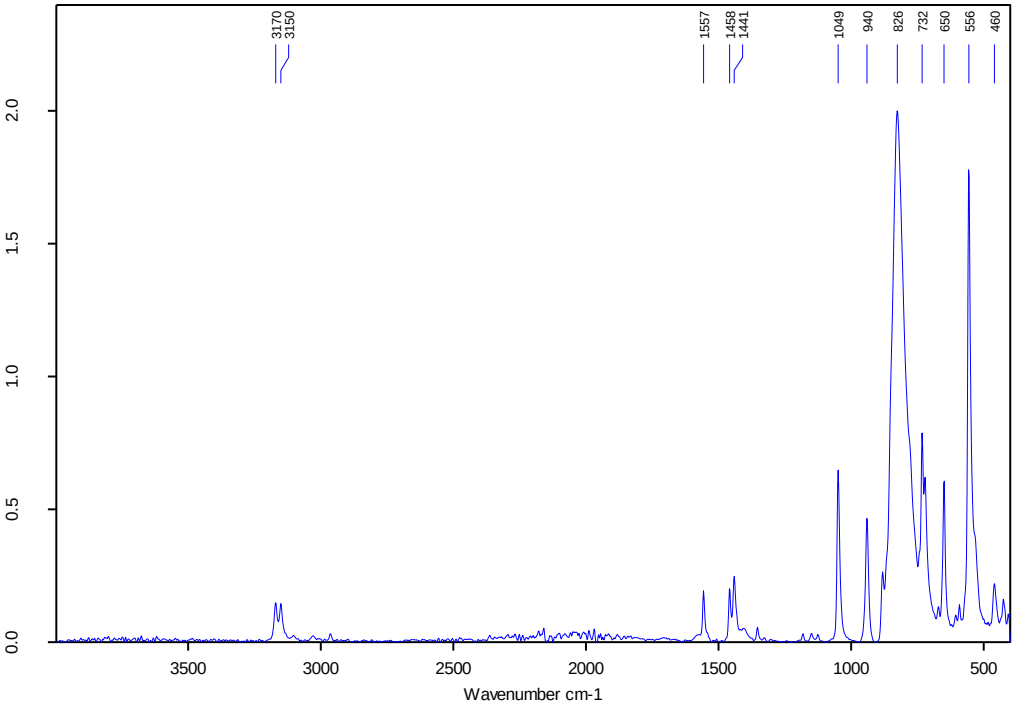

Figure S17. IR- absorption spectra (neat) of 2-bromo-1,3-dimethoxyimidazolium hexafluorophosphate (**3**)

2-((4-Bromophenyl)thio)-1,3-dimethoxyimidazolium bromide (4)

^{1}H NMR (300 MHz, MeOH-*d*$_4$) δ = 8.31 (s, 2H), 7.74 – 7.45 (m, 4H), 4.27 (s, 6H) ppm.

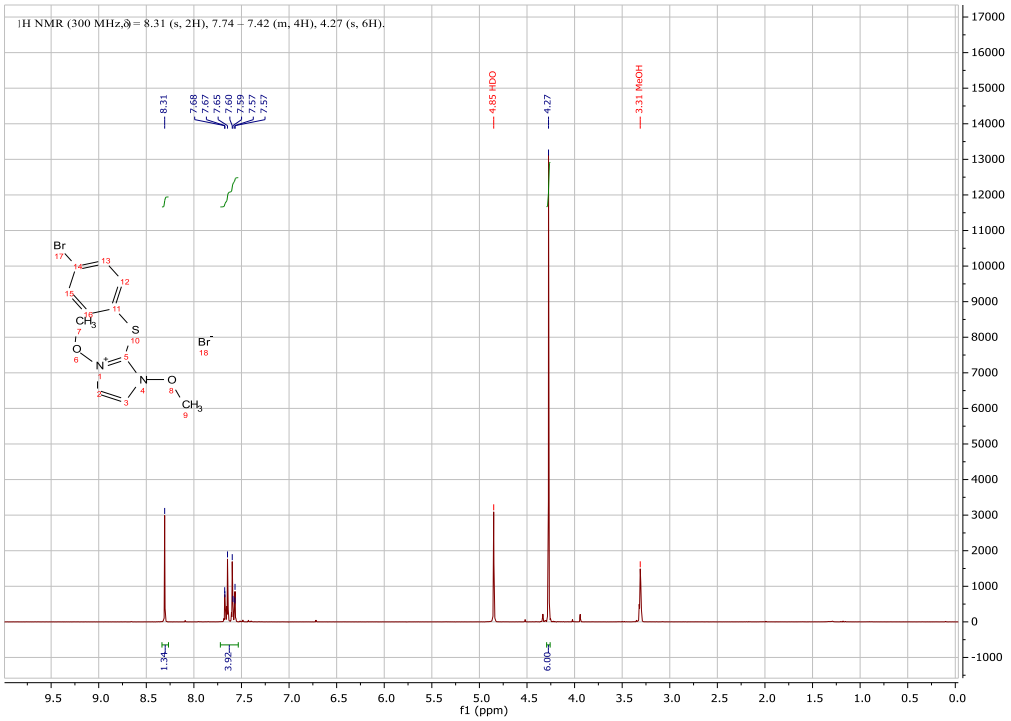

Figure S18. ^{1}H-NMR (MeOH-*d*$_4$) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium bromide (**4**)

^{13}C NMR (75 MHz, MeOH-*d*$_4$) δ = 136.05 (2C), 134.77 (2C), 127.17, 126.35, 120.29, 70.31(2C) ppm.

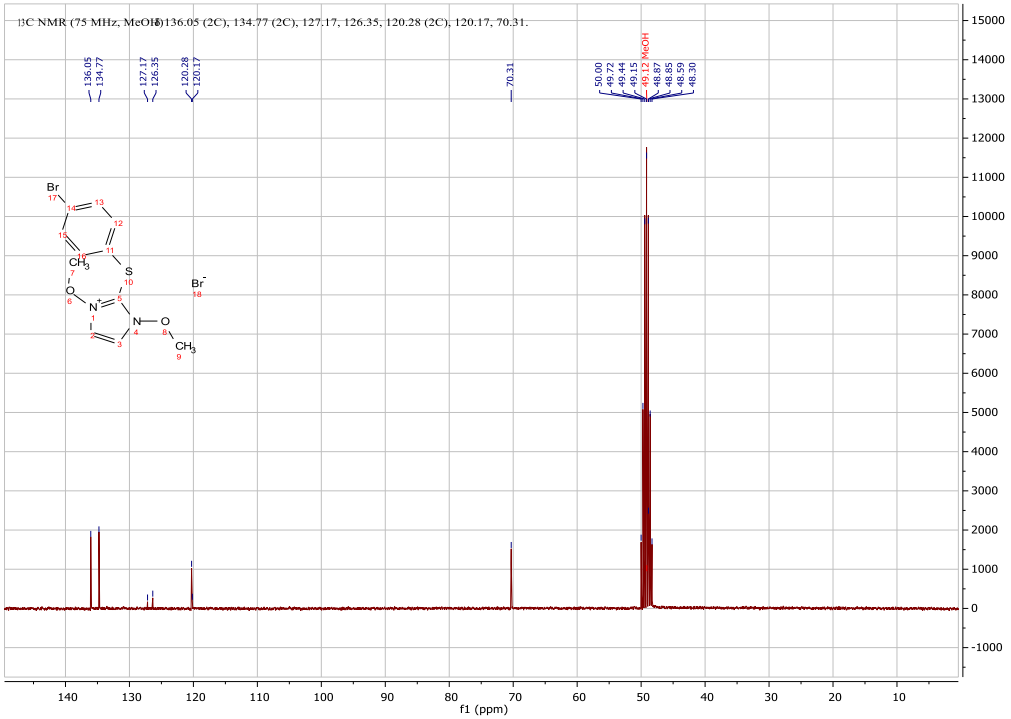

Figure S19. ^{13}C-NMR (MeOH-*d*$_4$) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium bromide (**4**)

IR(neat): ν = 3091 (w), 3026 (s), 2993 (m), 2913 (w), 1546 (m), 1470 (s), 1457 (s), 1443 (m), 1383 (m), 1155 (w), 1116 (w), 1078 (s), 1069 (m), 1046 (s), 1000 (s), 952 (s), 933 (vs), 801 (vs), 777 (s), 721 (m), 688 (w), 619 (m), 551 (w), 478 (s) cm^{-1}.

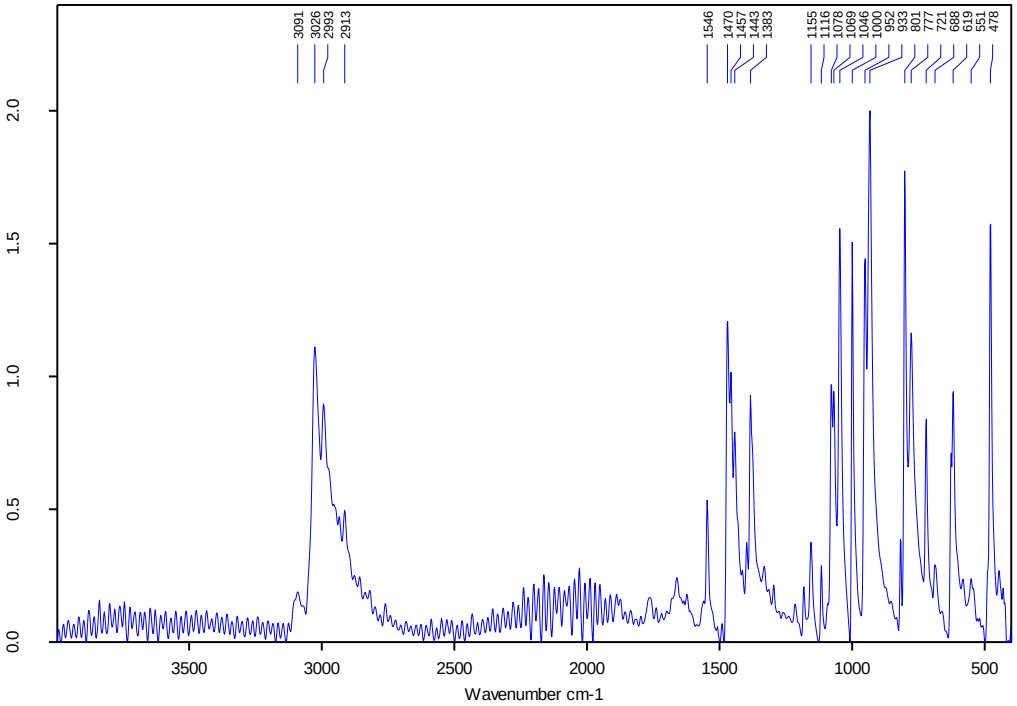

Figure S20. IR- absorption spectra (neat) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium bromide (**4**)

2-((4-Bromophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (5)

^{1}H NMR (300 MHz, acetone-d_6) δ = 8.34 (s, 2H), 7.75 – 7.66 (m, 4H), 4.36 (s,6H) ppm.

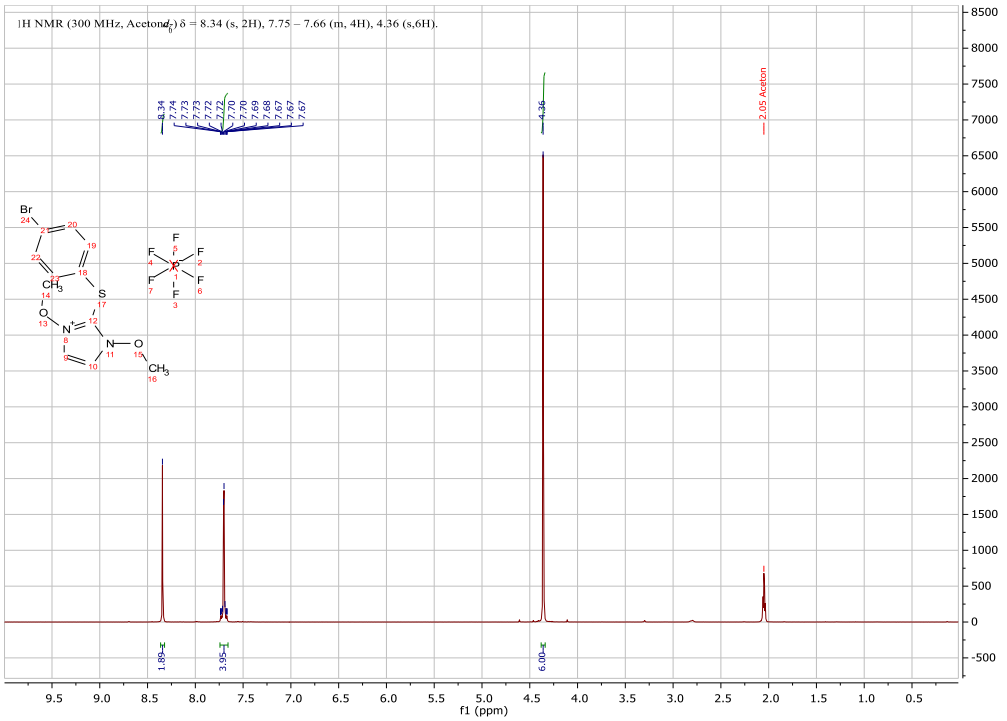

Figure S21. ^{1}H-NMR (acetone-d_6) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**5**)

^{13}C NMR (75 MHz, acetone-d_6) δ = 135.96 (2C), 134.26 (2C), 126.88, 125.53, 120.12 (2C), 105.39, 70.30 (2C) ppm.

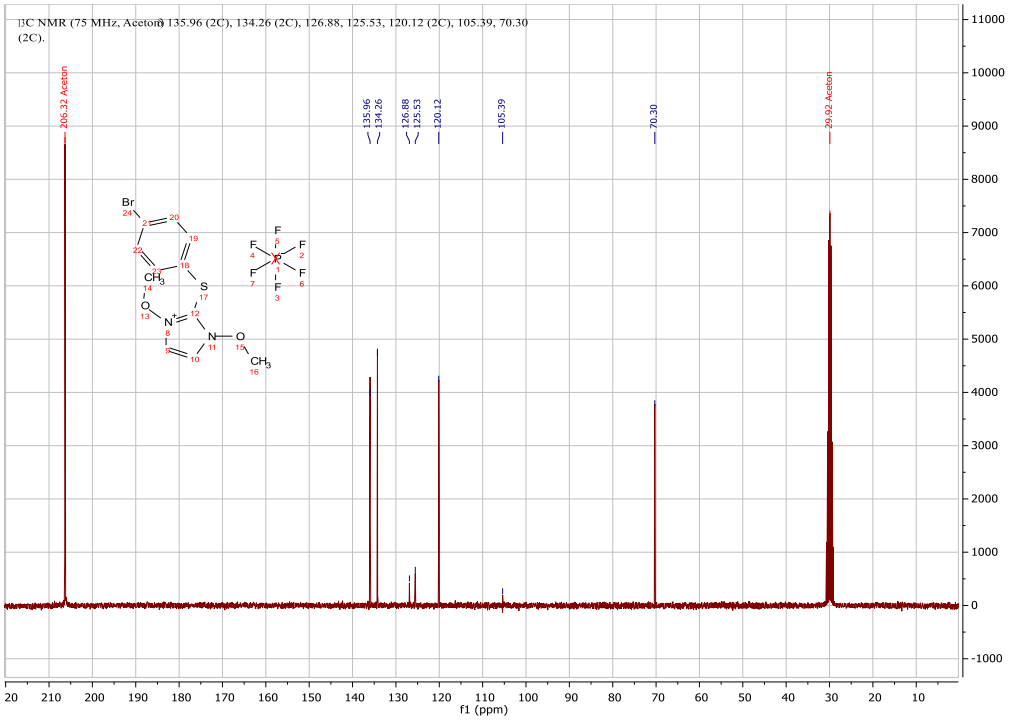

Figure S22. ^{13}C-NMR (acetone-d_6) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**5**)

IR(neat): ν = 3170 (w), 3152 (w), 3088 (w), 1549 (w), 1473 (w), 1458 (w), 1444 (w), 1386 (w), 1082 (w), 1042 (m), 1004 (m), 939 (w), 825 (vs), 801 (s), 741 (s), 690 (w), 620 (w), 555 (s), 475 (m) cm^{-1}.

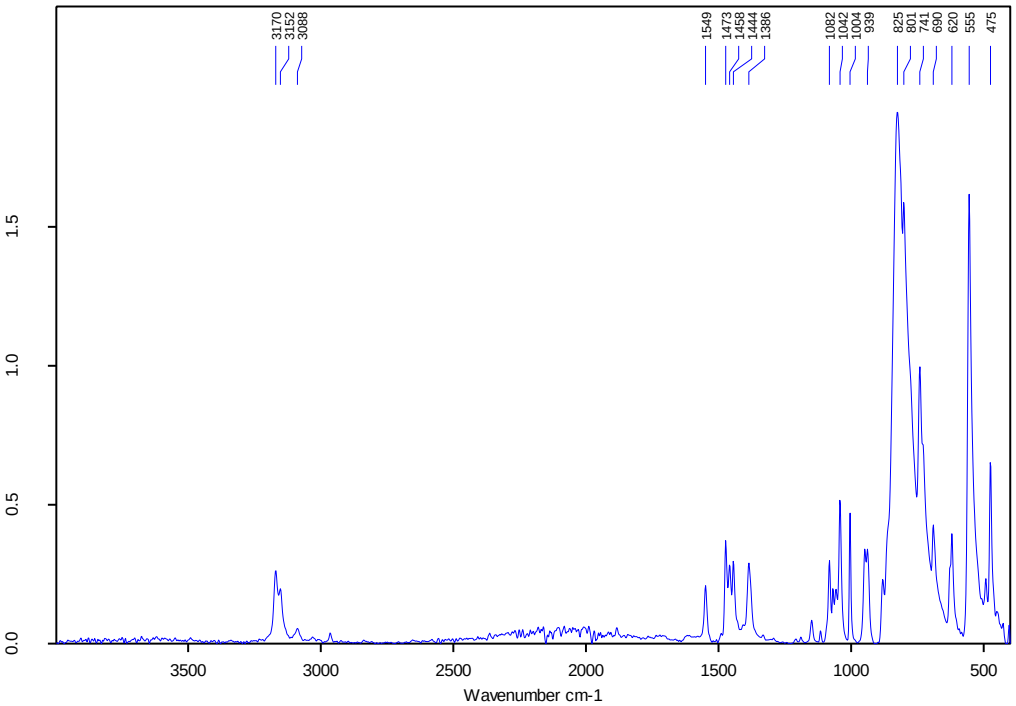

Figure S23. IR- absorption spectra (neat) of 2-((4-bromophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**5**)

2-((4-Chlorophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (6)

^{1}H NMR (300 MHz, acetone-d_6) δ = 8.34 (s, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 4.36 (s, 6H) ppm.

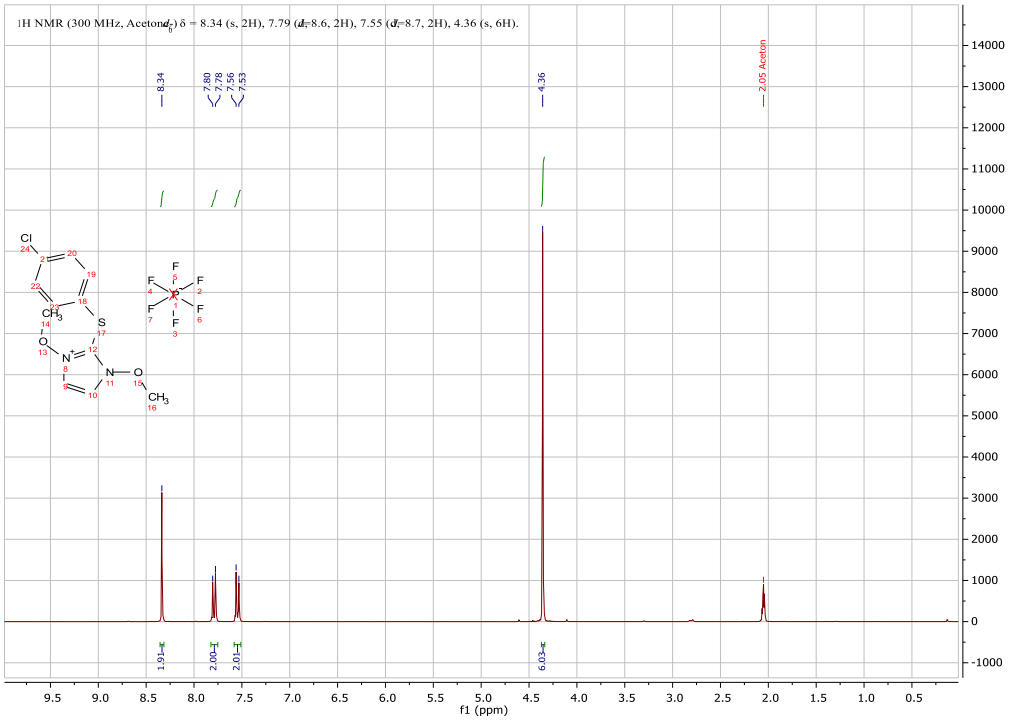

Figure S24. ^{1}H-NMR (acetone-d_6) of 2-((4-chlorophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**6**)

^{13}C NMR (75 MHz, acetone-d_6) δ = 137.37, 135.91 (2C), 134.39, 131.25 (2C), 126.20, 120.09 (2C), 70.28 (2C) ppm.

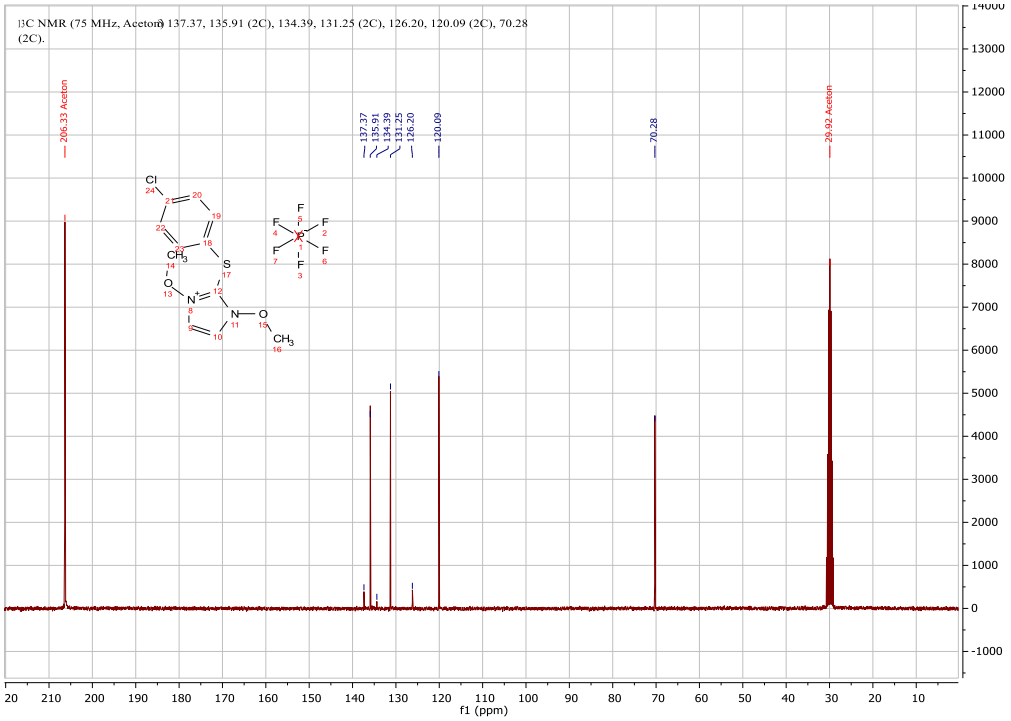

Figure S25.^{13}C-NMR (acetone-d_6) of 2-((4-chlorophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**6**)

IR(neat): ν = 3170 (w), 3152 (w), 3088 (w), 1549 (w), 1473 (w), 1458 (w), 1444 (w), 1386 (w), 1082 (w), 1042 (m), 1004 (m), 939 (w), 825 (vs), 801 (s), 741 (s), 690 (w), 620 (w), 555 (s), 475 (m) cm^{-1}.

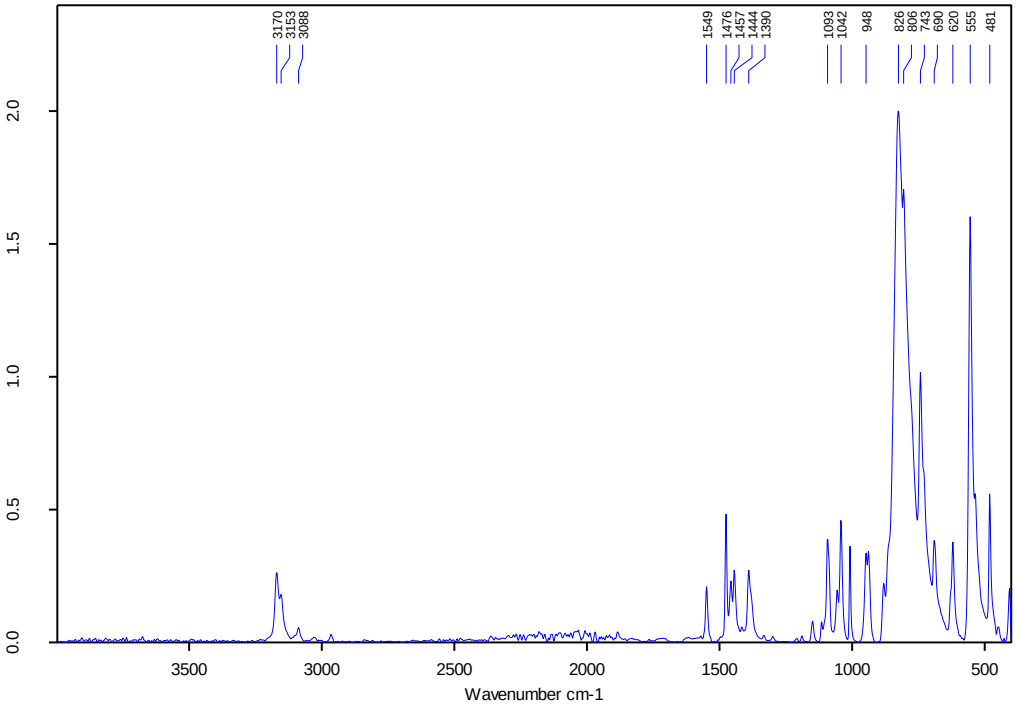

Figure S26. IR- absorption spectra (neat) of 2-((4-chlorophenyl)thio)-1,3-dimethoxyimidazolium hexafluorophosphate (**6**)

2-(Benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium hexafluorophosphate (7)

^{1}H NMR (300 MHz, acetone-d_6) δ = 8.62 (s, 2H), 8.17 – 8.09 (m, 1H), 7.96 – 7.90 (m, 1H), 7.63 – 7.49 (m, 2H), 4.47 (s, 6H) ppm.

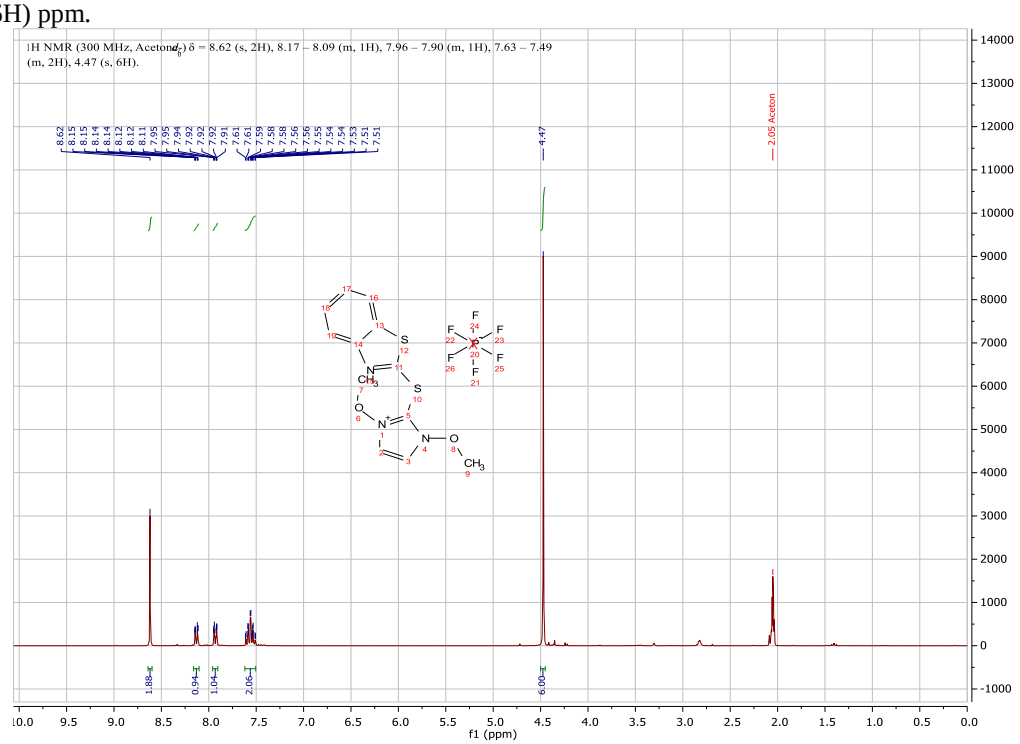

Figure S27. ^{1}H-NMR (acetone-d_6) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium hexafluorophosphate (**7**)

^{13}C NMR (75 MHz, acetone-d_6) δ = 157.79, 153.24, 137.60, 128.11, 127.34, 123.69, 123.10, 121.15 (2C), 71.00 (2C) ppm.

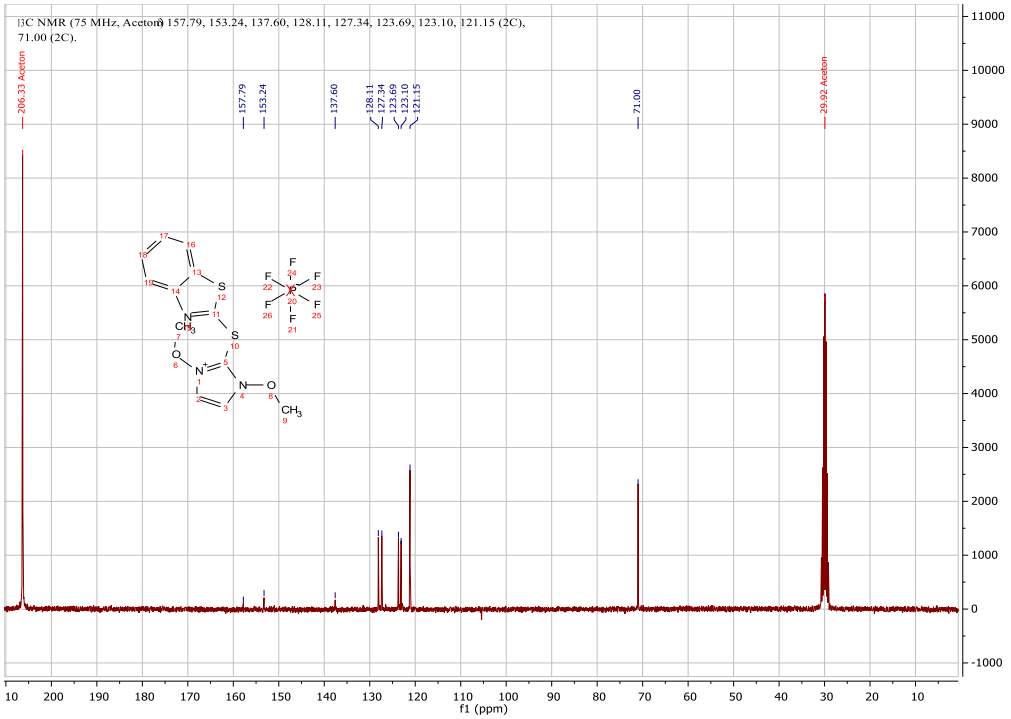

Figure S28. ^{13}C-NMR (acetone-d_6) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium hexafluorophosphate (**7**)

IR(neat): ν = 3170 (w), 3149 (w), 1549 (w), 1468 (w), 1447 (w), 1427 (w), 1394 (w), 1309 (w), 1236 (w), 1044 (w), 1005 (w), 950 (w), 860 (m), 826 (vs), 755 (s), 741 (m), 725 (m), 705 (w), 672 (w), 617 (w), 555 (s) cm^{-1}.

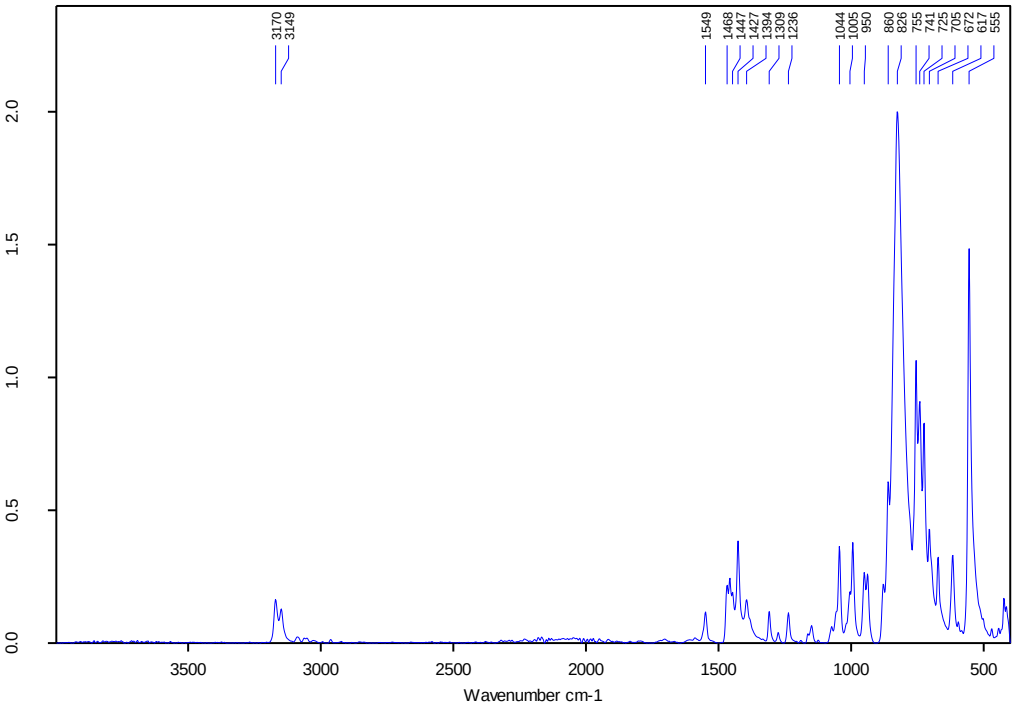

Figure S29. IR- absorption spectra (neat) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium hexafluorophosphate (**7**)

2-(Benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium bromide (8)

^{1}H NMR (300 MHz, MeOH-d_4) δ = 8.57 (s, 2H), 8.03 – 7.97 (m, 1H), 7.89 – 7.83 (m, 1H), 7.58 – 7.43 (m, 2H), 4.37 (s, 6H) ppm.

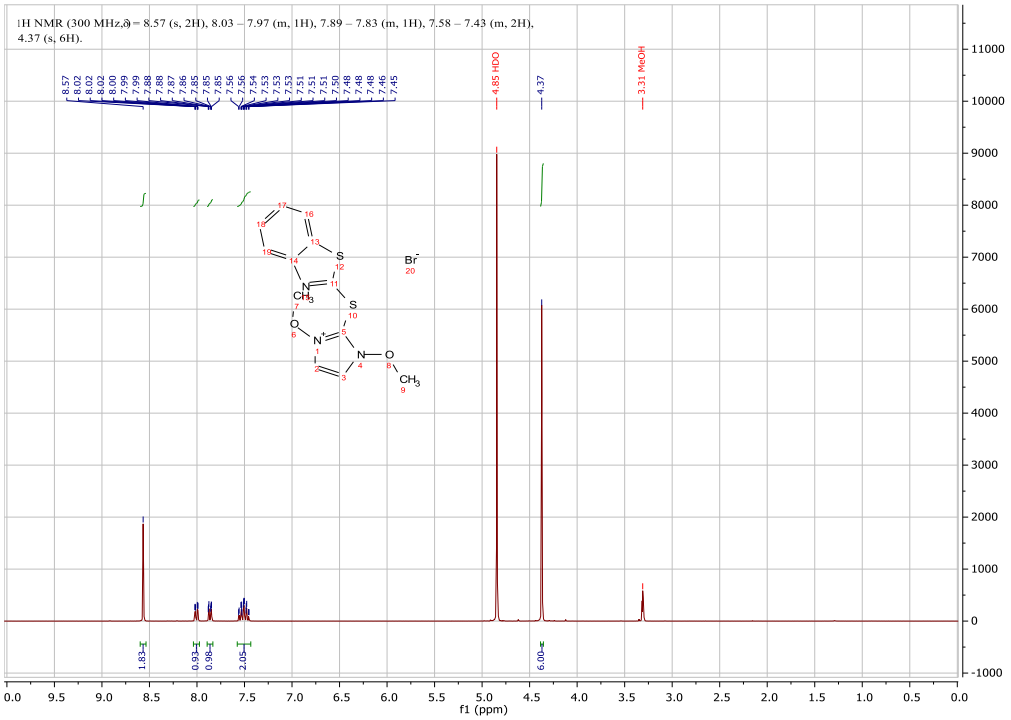

Figure S30. ^{1}H-NMR (MeOH-d_4) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium bromide (**8**)

^{13}C NMR (75 MHz, MeOH-d_4) δ = 158.91, 153.63, 137.92, 132.39, 128.41, 127.59, 123.79, 123.17, 121.26 (2C), 70.92 (2C) ppm.

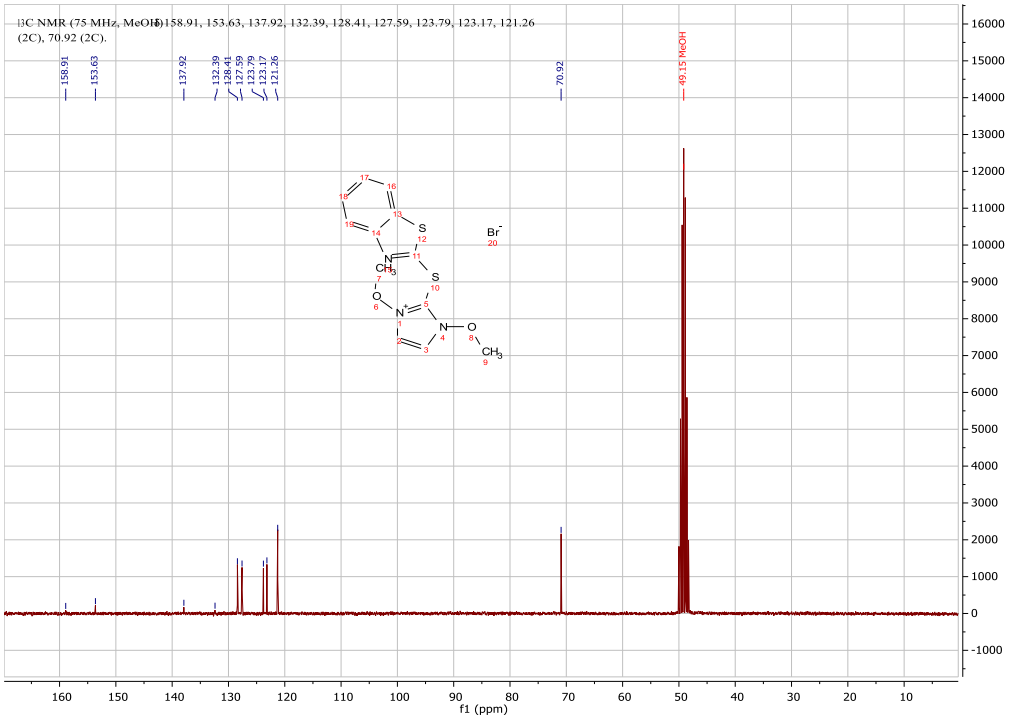

Figure S31.^{13}C-NMR (MeOH-d_4) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium bromide (**8**)

IR(neat): ν =3389 (broad; H_2O), 3108 (w), 3077 (w), 3026 (m), 3026 (m), 2941 (w), 1543 (w), 1454 (m), 1416 (m), 1397 (w), 1311 (m), 1234 (w), 1040 (m), 987 (s), 931 (vs), 888 (w), 847 (w), 779 (m), 762 (vs), 724 (s), 705 (w), 675 (m), 636 (w), 618 (m), 592 (m), 540 (m), 504 (w), 437 (w), 408 (m) cm^{-1}.

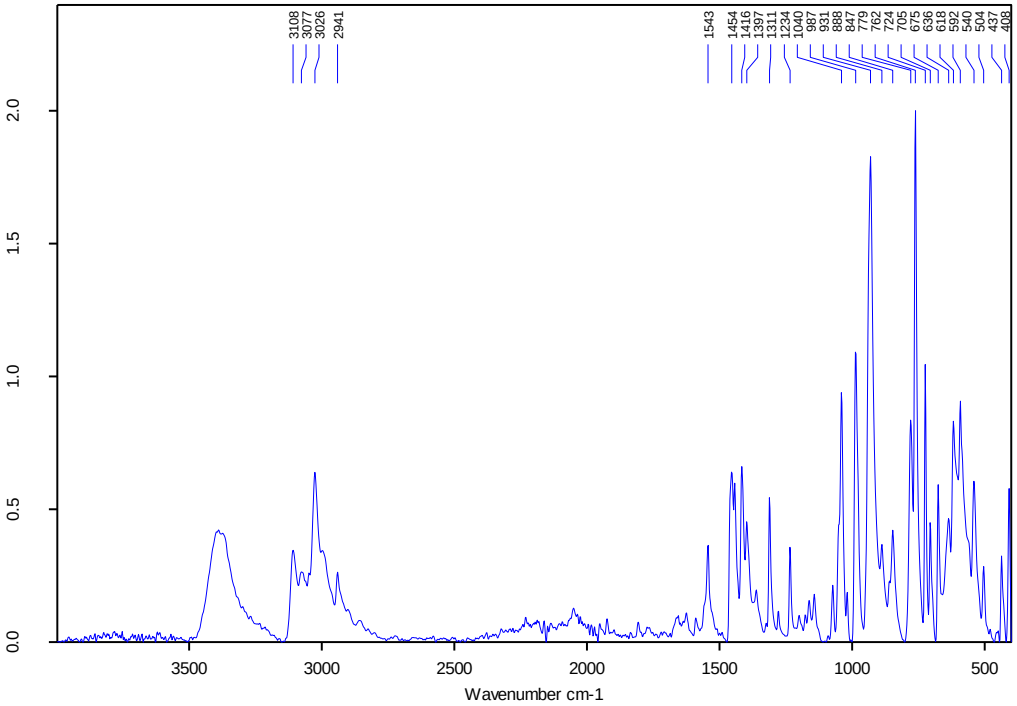

Figure S32. IR- absorption spectra (neat) of 2-(benzo[*d*]thiazol-2-ylthio)-1,3-dimethoxyimidazolium bromide (**8**)

1,3-Dimethoxy-2-((1-methyl-1*H*-imidazol-2-yl)thio)-imidazolium bromide (9)

^{1}H NMR (300 MHz, MeOH-*d*$_4$) δ = 8.33 (s, 2H), 7.46 (d, *J* = 1.3 Hz, 1H), 7.15 (d, *J* = 1.3 Hz, 1H), 4.30 (s, 6H), 3.97 (s, 3H) ppm.

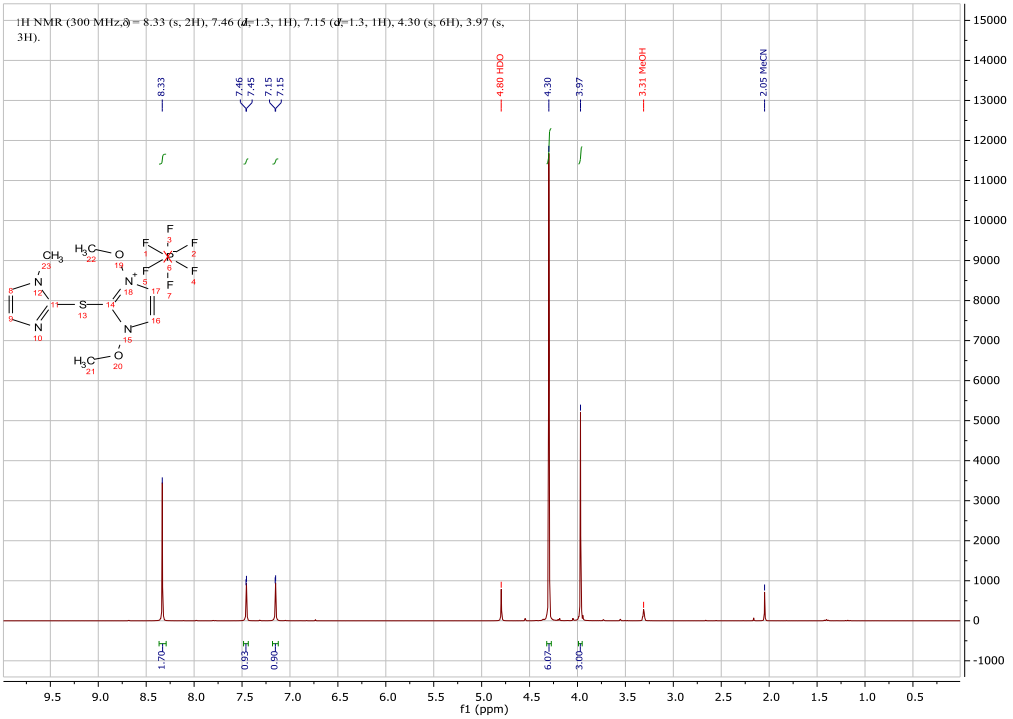

Figure S33. ^{1}H-NMR (MeOH-*d*$_4$) of 1,3-dimethoxy-2-((1-methyl-1*H*-imidazol-2-yl)thio)-imidazolium bromide (**9**)

^{13}C NMR (75 MHz, MeOH-*d*$_4$) δ = 133.82, 131.96, 131.32, 127.88, 120.16 (2C), 70.66 (2C), 35.33 ppm.

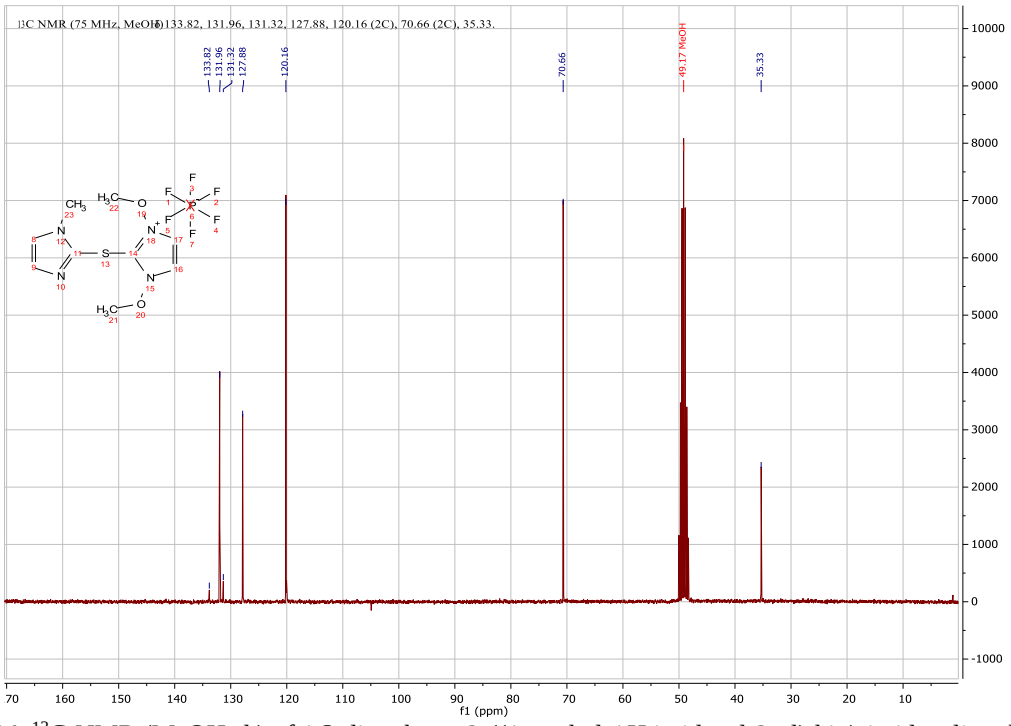

Figure S34. ^{13}C-NMR (MeOH-*d*$_4$) of 1,3-dimethoxy-2-((1-methyl-1*H*-imidazol-2-yl)thio)-imidazolium bromide (**9**)

IR(neat): ν = 3090 (w), 3016 (m), 2942 (w), 1543 (m), 1506 (w), 1457 (m), 1406 (w), 1364 (w), 1280 (m), 1124 (m), 1086 (w), 1039 (s), 934 (vs), 914 (s), 849 (w), 780 (s), 766 (s), 749 (s), 729 (m), 696 (w), 681 (m), 657 (m), 618 (m), 480 (w), 428 (m), 416 (w) cm^{-1}.

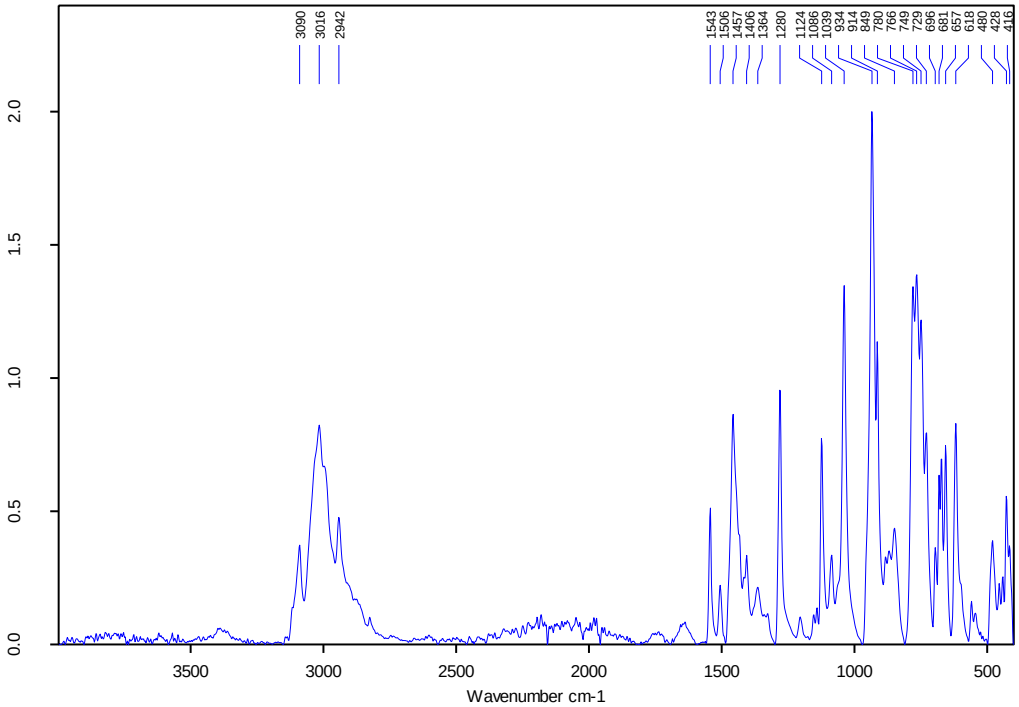

Figure S35. IR- absorption spectra (neat) of 1,3-dimethoxy-2-((1-methyl-1*H*-imidazol-2-yl)thio)-imidazolium bromide (**9**)

2,2'-((1,3,4-Thiadiazol-2,5-diyl)bis(sulfandiyl))bis(1,3-dimethoxyimidazolium) bromide (10)

^{1}H NMR (300 MHz, MeOH-d_4- slight dissociation) δ = 8.49 (s, 4H), 4.35 (s, 12H) ppm.

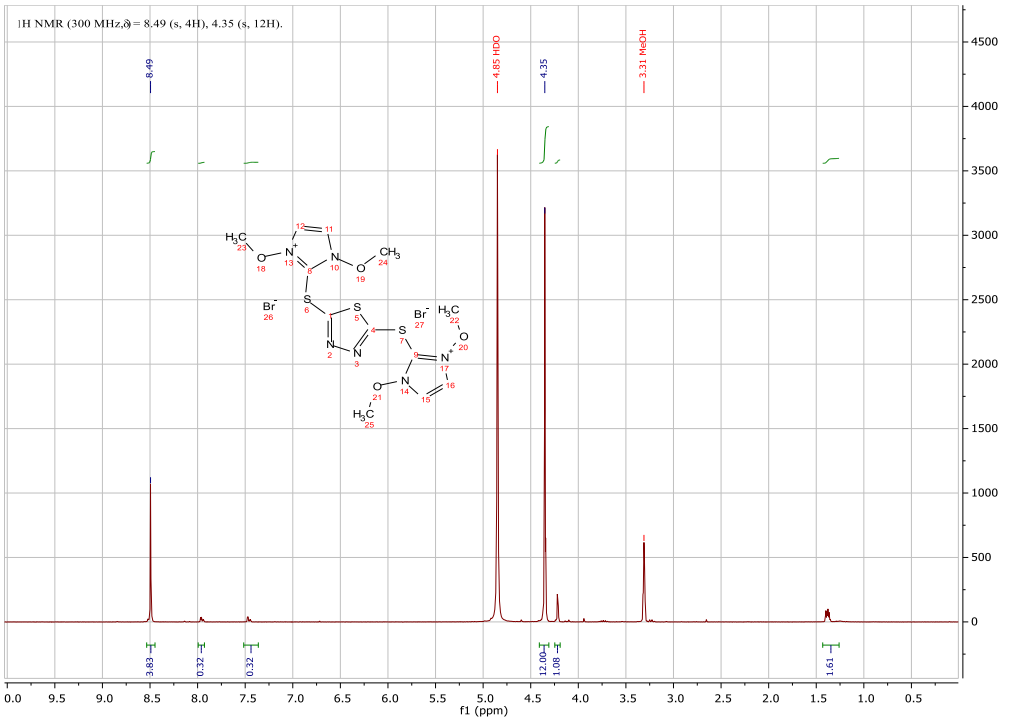

Figure S36. ^{1}H-NMR (MeOH-d_4) of 2,2'-((1,3,4-thiadiazol-2,5-diyl)bis(sulfandiyl))bis(1,3-dimethoxyimidazolium) bromide (**10**)

^{13}C NMR (75 MHz, MeOH-d_4- slight dissociation) δ = 163.62 (2C), 131.81 (2C), 121.21 (4C), 70.93 (4C) ppm.

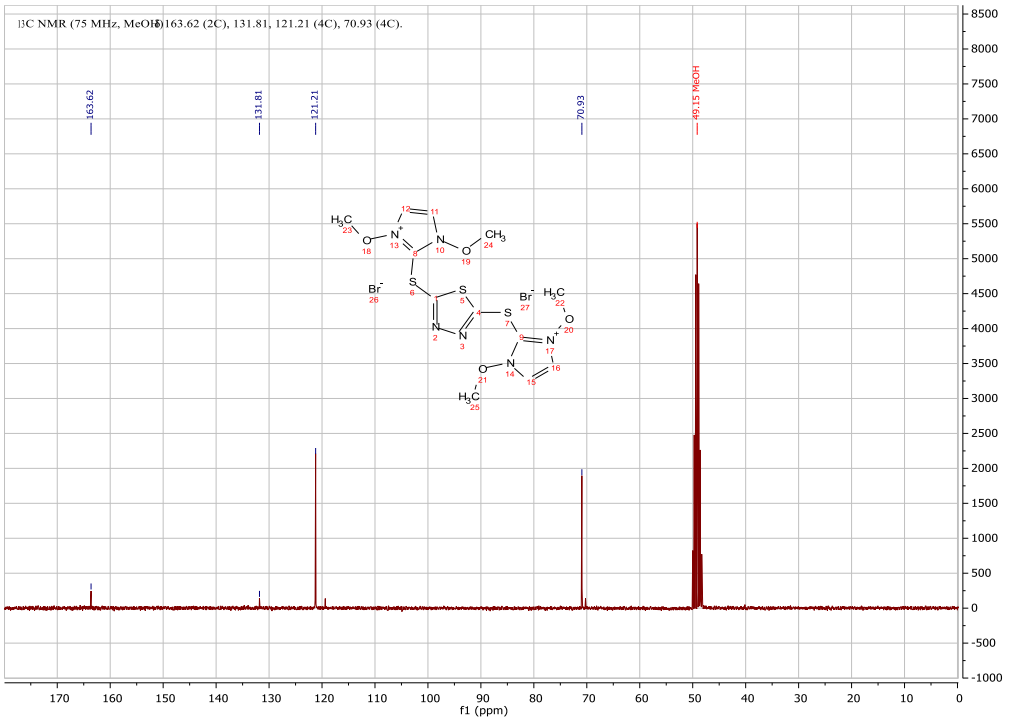

Figure S37. ^{13}C-NMR (MeOH-d_4) of 2,2'-((1,3,4-thiadiazol-2,5-diyl)bis(sulfandiyl))bis(1,3-dimethoxyimidazolium) bromide (**10**)

IR(neat): ν = 3035 (w), 2994 (w), 1544 (w), 1440 (m), 1378 (m), 1306 (m), 1204 (w), 1146 (w), 1035 (vs), 933 (s), 880 (w), 837 (s), 757 (s), 728 (s), 647 (m), 617 (w), 602 (w), 557 (m), 497 (m), 433 (w) cm^{-1}.

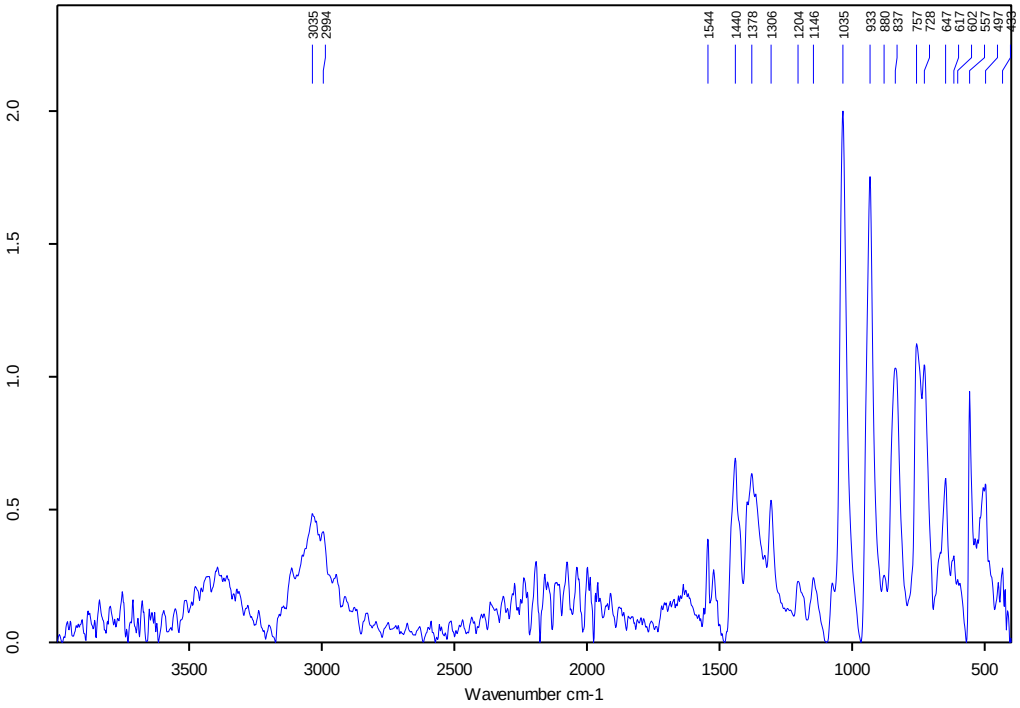

Figure S38. IR- absorption spectra (neat) of 2,2'-((1,3,4-thiadiazol-2,5-diyl)bis(sulfandiyl))bis(1,3-dimethoxyimidazolium) bromide (**10**)