Electronic Supplimentary Information for:

Tuning N-Heterocyclic Carbene Wingtips to Form Electrochemically Stable Adlayers on Metals

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Electrochemical Methods

Chemicals and Materials

6-Mercapto-1-hexanol (MCH, PN 725226-1G) was purchased from Sigma-Aldrich (St. Louis, MO). Phosphate buffered saline (1X PBS, 11.9 mM HPO_3 2- ; 137 mM NaCl; 2.7 mM KCl; pH = 7.4), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) were purchased from Fisher-Scientific (Waltham, MA). All aqueous solutions were prepared using deionized water from a Milli-Q Direct purification system, with a resistivity of 18 MΩ. Gold disk electrodes (PN 002314, diameter 1.6 mm), platinum disk electrodes (PN 002013, diameter 1.6 mm) and coiled platinum wire counter electrodes (PN 012961) were purchased from ALS Inc. (Tokyo, Japan). Silver/silver chloride reference electrodes (PN CHI111) and glassy carbon working electrode (PN CHI104, diameter 3.0 mm) were purchased from CH instruments (Austin, TX). For polishing electrodes 0.1 μM diamond slurry was purchased from Buehler (Lake Bluff, IL) and cloth pads (PN MF-1040) were purchased from BASi (West Lafayette, IN).

Preparation of NHC Functionalized Electrodes.

Electrodes were first cleaned by a 30 second placement into a thiourea based gold surface cleaning solution (Mettler Toledo, Leicester, UK) with constant swirling. We then polished the gold electrodes on a cloth pad with a 0.1 μM diameter diamond slurry for 2 min per electrode. Electrodes were then placed in a beaker of PBS and cycled using cyclic voltammetry from -0.1 V – 0.3 V (vs Ag|AgCl) to confirm removal of NHCs with a return to bare gold baseline voltammograms. Following PBS scans, electrodes were electrochemically roughened via chronoamperometry to increase electroactive surface area following previously published protocols.[11] In short, 320 pulses (0.01 s pulse width) from 0 to 2 V (vs Ag|AgCl), was repeated 50 times for a total of 16,000 pulses in 0.5 M H_2SO_4. Immediately following roughening, electrodes were placed in 0.05 M H_2SO_4 and cycled once to ascertain the active surface area of each electrode. After surface area determination, electrodes were placed upright in a beaker and 1 mM of NHC methanol solution was drop casted on the electrode surface and allowed to evaporate for 10 min. Electrodes were then wrapped in aluminum foil and placed in a vacuum oven (Thermo Scientific, 3618-1CE) at 120 °C, 10 inHg (30 inHg room pressure, vacuumed to -20 inHg) for 25 min. Electrodes were then allowed to slowly to room temperature on the benchtop prior to electrochemical characterization. To reduce contamination, the oven was left under constant heat and pressure, and the aluminum foil was discarded after every functionalization.

Electrochemical Measurements.

CH Instruments Electrochemical Analyzer (CHI 1040C, Austin, TX) multichannel potentiostats and associated software were used for all electrochemical measurements. A three-electrode cell configuration consisting of a working electrode, a coiled platinum wire counter electrode, and an Ag/AgCl reference electrode was used. For the continuous voltammetric interrogation found in Figures 2, 3, 4 and 6, all cyclic voltammetry measurements used a voltage window beginning at 0 V sweeping to 0.3 V, returning to −0.1 V, and concluding at 0 V for 3 total sweep segments with a scanning rate of 0.1V/s after a quiet time of 2 s. Cyclic voltammetry measurements found in figure 5 used a voltage window beginning at 0 V sweeping to 0.3 V, returning to −0.4 V, and concluding at 0 V for 3 total sweep segments with a scanning rate of 0.1V/s after a quiet time of 2 s.

Data Analysis.

To process the files generated during the continuous voltametric interrogation, we used a Python-based custom script previously reported by our group (SACMES).[12] SACMES allows for the rapid extraction of capacitive currents from voltammograms, thus enabling batch analysis of the thousands of files generated during measurements.

EChem SI Figures

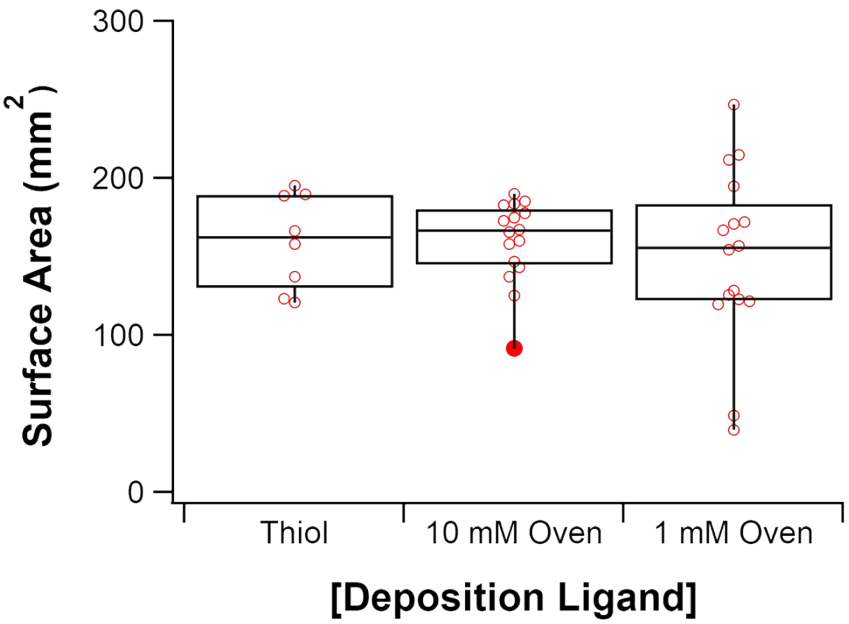


Figure S1. Surface area of electrodes after functionalization. Regardless of functionalization technique, thiol deposition, 10 mM NHC deposition, or 1 mM NHC deposition, the surface area of the electrodes are returned to similar topography following cleaning protocol (see Methods).

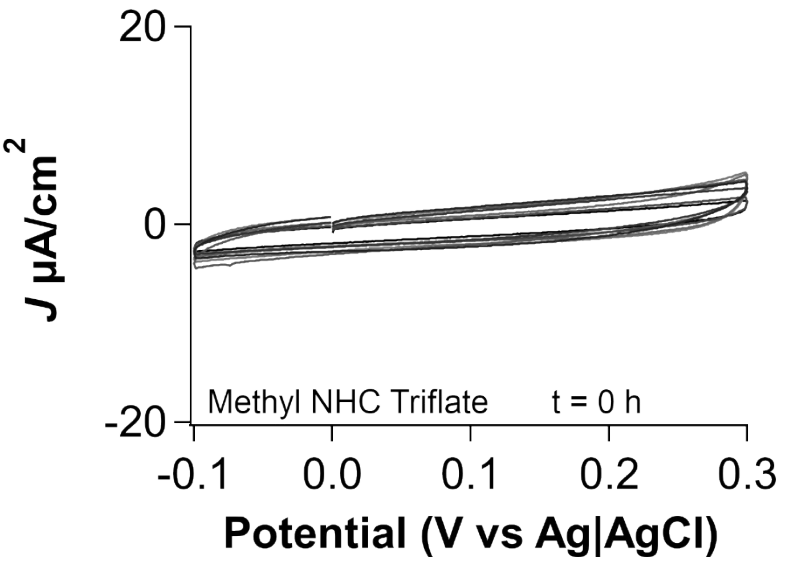


Figure S2. Voltammograms of (**1-H**)(**OTf**) deposited onto gold electrodes at t = 0 h from Figure 2B.

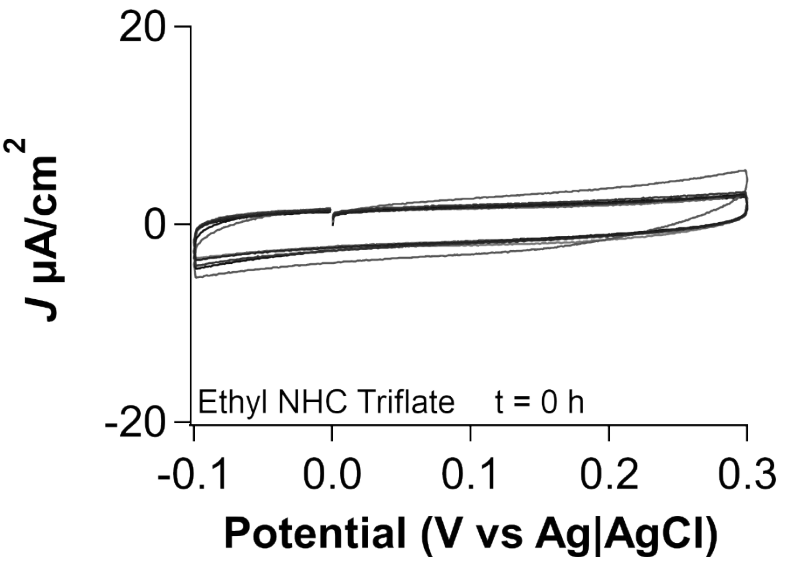


Figure S3. Voltammograms of (**2-H**)(**OTf**) deposited onto gold electrodes at t = 0 h from Figure 2C.

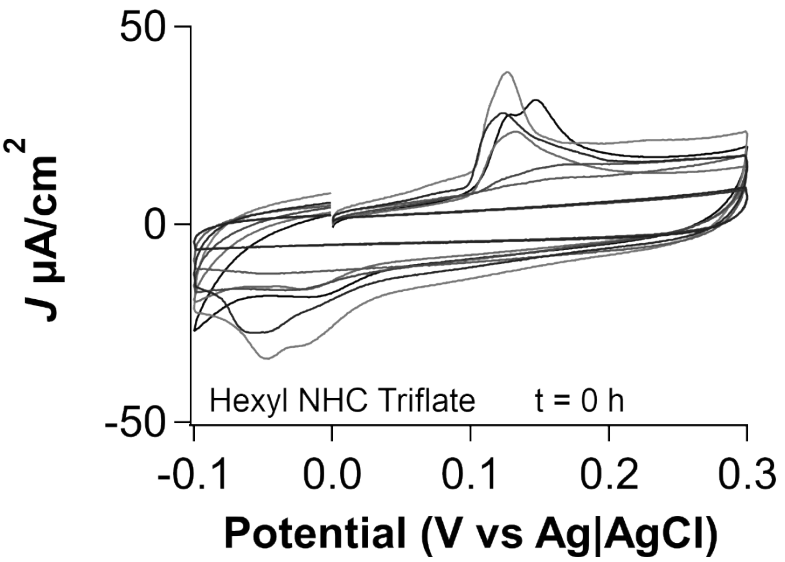


Figure S4. Voltammograms of (**3-H**)(**OTf**) deposited onto gold electrodes at t = 0 h from Figure 2D.

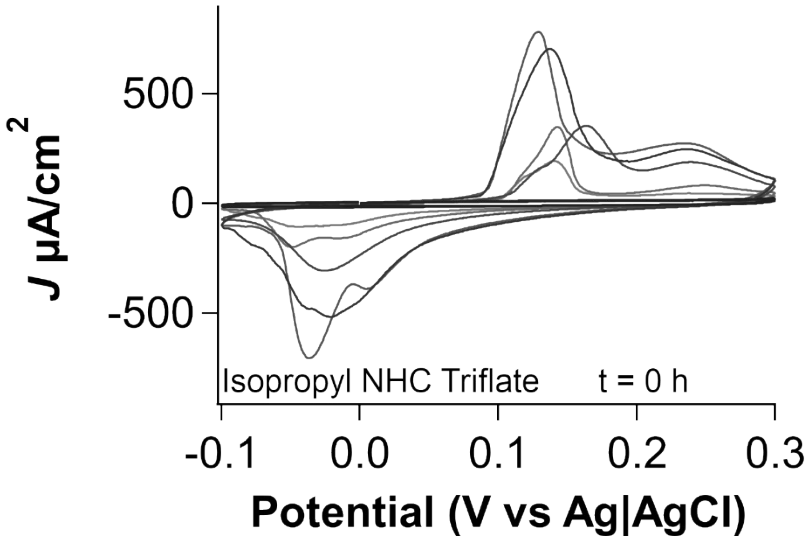


Figure S5. Voltammograms of (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h from Figure 2E.

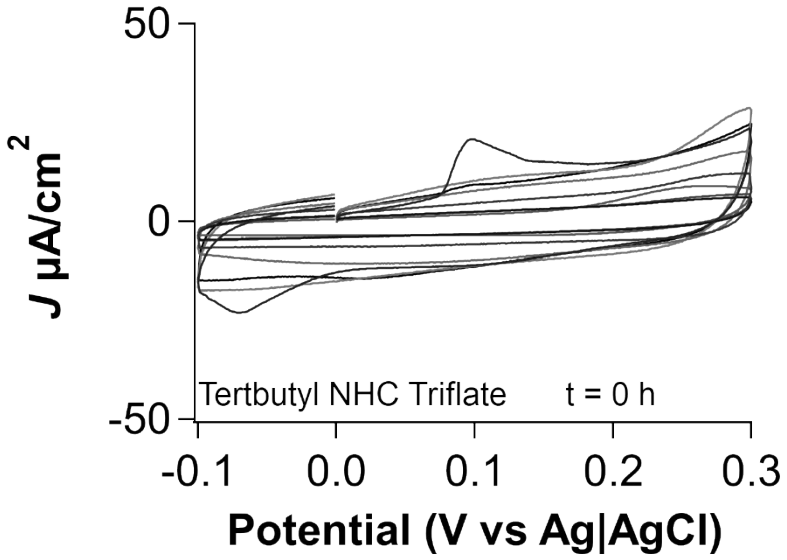


Figure S6. Voltammograms of (**5-H**)(**OTf**) deposited onto gold electrodes at t = 0 h from Figure 2F.

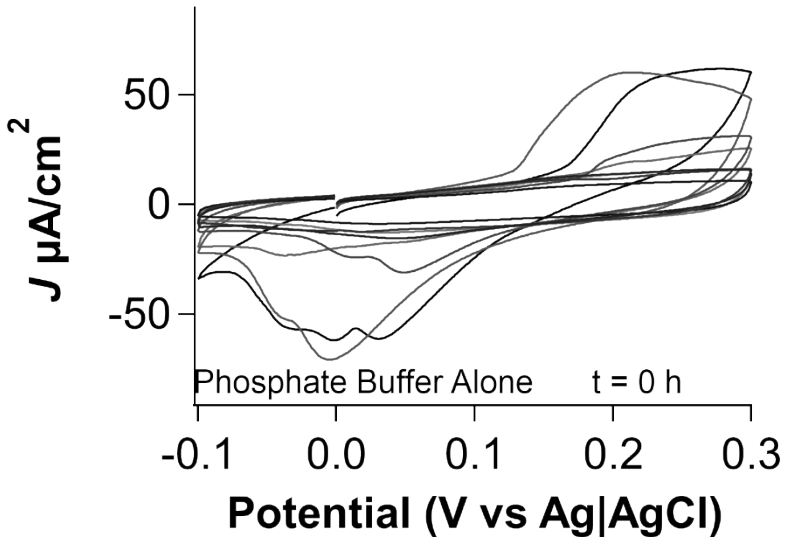


Figure S7. Voltammograms of (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h in phosphate buffer alone from Figure 3A.

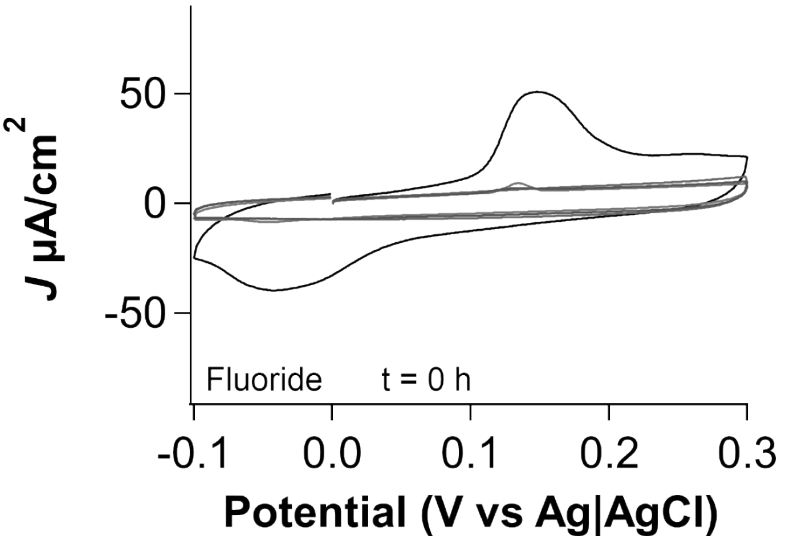


Figure S8. Voltammograms of (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h in phosphate buffer with 137 mM fluoride from Figure 3B.

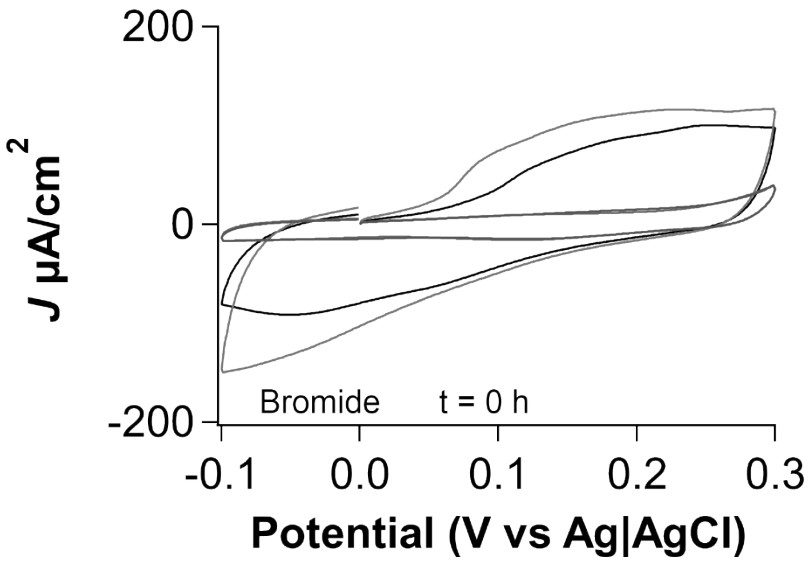


Figure S9. Voltammograms of (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h in phosphate buffer with 137 mM bromide from Figure 3D.

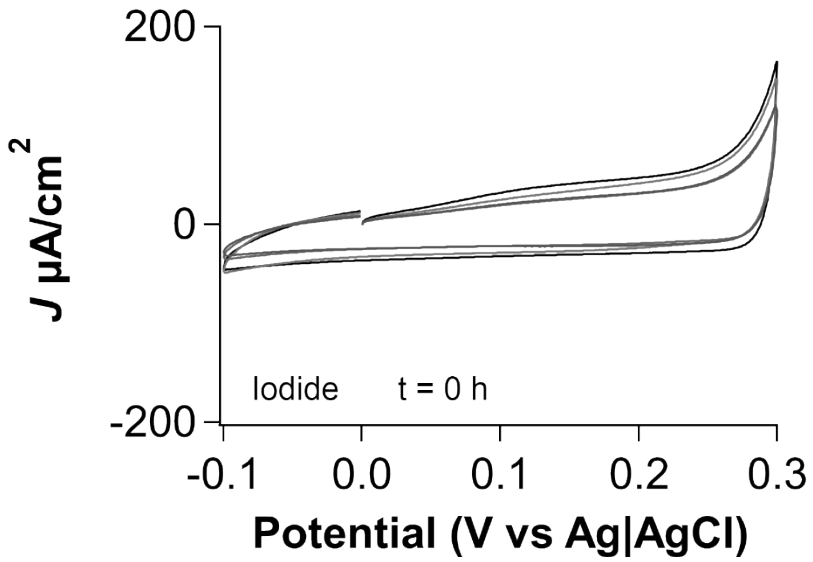


Figure S10. Voltammograms (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h in phosphate buffer with 137 mM iodide from Figure 3E.

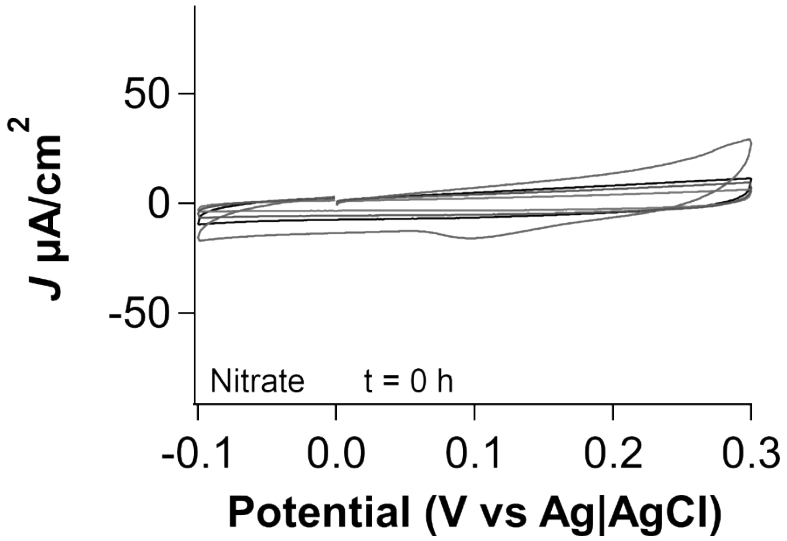


Figure S11. Voltammograms of (**4-H**)(**OTf**) deposited onto gold electrodes at t = 0 h in phosphate buffer with 137 mM nitrate from Figure 3F.

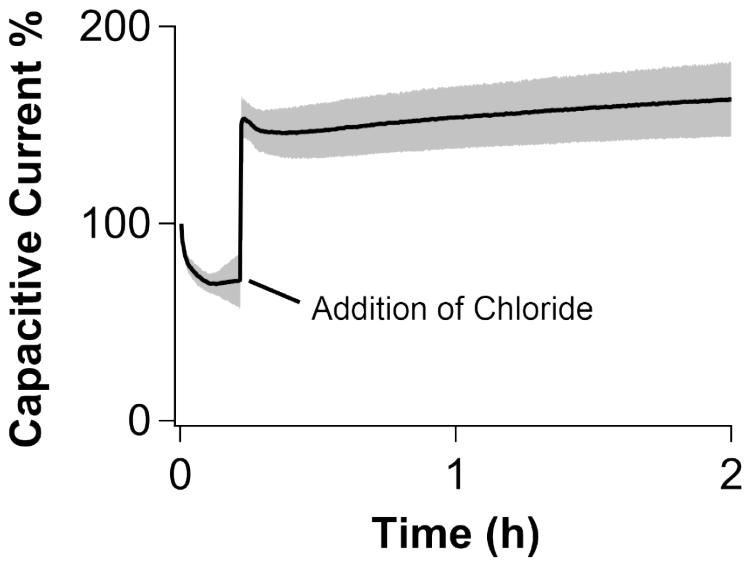


Figure S12. Addition of chloride ions into nitrate-containing phosphate buffer results in the reappearance of transitional features of voltammograms. Electrodes were scanned in conditions presented in Fig 3F, with an addition of 137 mM chloride ions.

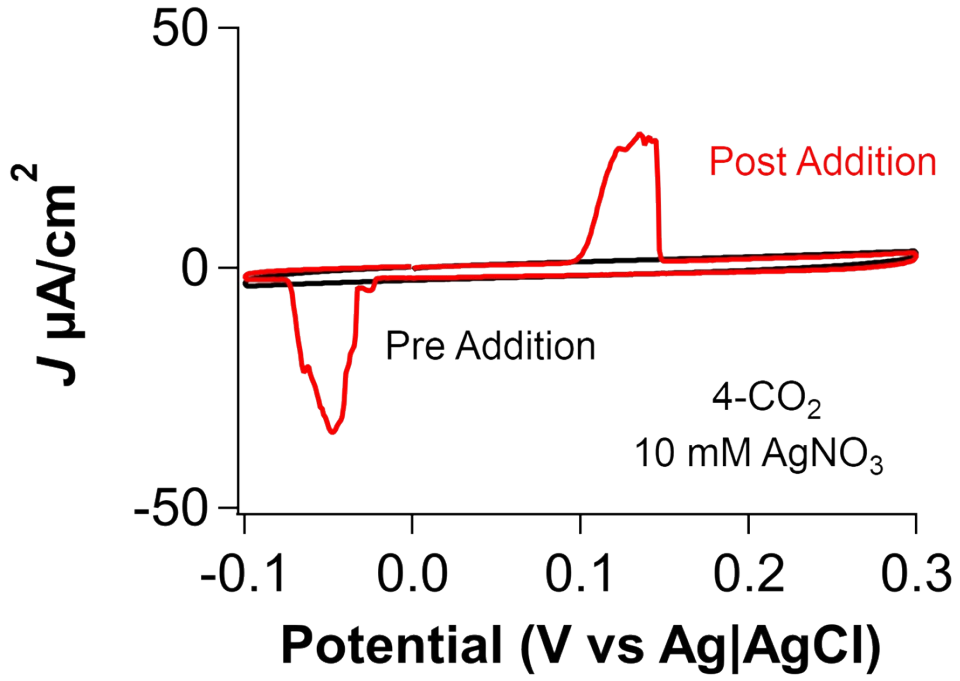


Figure S13. Addition of silver ions to phosphate-buffered saline causes the appearance of redox peaks similar to those observed in Figure 3D-F and Figure 4. Electrodes were scanned using cyclic voltammetry at 0.1 V/s. Although we added sodium nitrate, the buffered saline contains 137 mM Cl^- ions, causing the sharper redox peaks as seen in Figure 4C.

Synthetic Methods

General Considerations for Synthesis:

All reactions and workups were conducted under air unless otherwise stated. All reagents and solvents were purchased from commercial vendors and used as received. All reactions were stirred vigorously with magnetic stirrers. Air-sensitive reactions were done using an Mbraun Unilab Glovebox under N_2. Solvents used under N_2 atmosphere were dried on an Innovative Technologies Pure Solv MD-7 Solvent Purification System, degassed by freeze-pump-thaw cycles on a Schlenk line to remove dioxygen and stored over activated 4 Å molecular sieves prior to use.

NHC-triflate salts (**2-H**)(**OTf**), (**3-H**)(**OTf**), and (**5-H**)(**OTf**), and NHC CO_2-adduct (**5-CO$_2$**) are completely original syntheses, denoted by (❖).

Characterization of compound (**1-H**)(**OTf**) has been previously reported, but no synthetic conditions were published, denoted by (✣).

Compounds (**2-1**), (**3-1**), and (**3-H**)(**I**) have been previously synthesized and published via an entirely different synthetic method reported here, denoted by (§)

Compounds (**4-H**)(**I**), (**4-CO$_2$**), and (**5-1**) were prepared according to modified published procedures described below, and their syntheses are denoted by a pound sign (#).

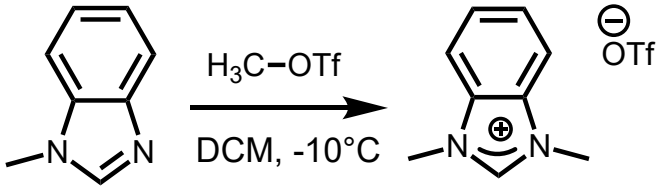
Compounds (**2-2**) and **(5-H)(Cl)** have been previously reported, but are lacking some characterization; their syntheses are denoted by a double dagger (‡). This additional characterization that was not previously published, including ^{1}H and ^{13}C spectra, as well as IR spectra and mass spectrometry data, has been included.

The synthesis and characterization of compound (**4-H**)(**OTf**) was reported in our previous publication.[1]

General Considerations for Molecular Characterization:

Solution ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR were performed on a Bruker Avance 500 MHz narrow-bore broadband system at 298 K. All ^{1}H and ^{13}C shifts were referenced to the residual solvent. Infrared Spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance (ATR) using neat compounds. All mass spectrometry analyses were conducted at the Biological and Small Molecule Mass Spectrometry Core Facility located in the Department of Chemistry at the University of Tennessee, Knoxville. The analysis of NHC-triflate salt species were performed using a Waters Synapt G2-S*i* qTOF instrument with ESI ion source. The reflector was set to positive mode and data were collected from 100-1000 Daltons. The analysis of (**3-H**) and (**5-1**) were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). Solutions for mass spectrometry were prepared in methanol for all compounds.

Synthesis of N,N-di-methyl-benzimidazolium Trifluoromethanesulfonate, (1-H)(OTf).[‡]



This compound was prepared with modifications from a previously published procedure for a similar compound.[2] In a glovebox, dichloromethane (10 mL) was added to N-methyl-benzimidazole (1.54 g, 11.6 mmol), and the solution was placed in the glovebox freezer at -35°C for one hour. Previously cooled methyl triflate (2.42 g, 14.8 mmol) was added and the solution was stirred at -10 °C for one hour. The solution continued to stir overnight while warming to room temperature. During this time, the solution changed from yellow to brown and solids precipitated. The mixture was then removed from the glovebox and filtered over Celite. The filtrate was concentrated to dryness on the rotary evaporator. The crude product was dissolved in dichloromethane (5 mL) and triturated into a stirring solution of diethyl ether at -10 °C to give **(1-H)(OTf)** as a white solid (1.01 g, 30.0% yield).

[‡]This compound was initially described by Dodević and Huynh via an unknown literature procedure.[3]

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.61 (s, 1H), 8.01 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.71 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.08 (s, 6H)

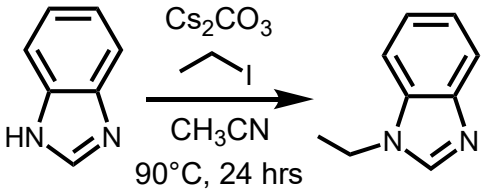
^{13}C NMR (126 MHz, DMSO-d_6): δ 143.13, 131.66, 126.40, 120.67 (q, *J* = 309 Hz, $SO_3\underline{\mathbf{C}}F_3$ of OTf^-), 113.35, 33.07

^{19}F NMR (471 MHz, DMSO-d_6) δ -77.73

IR: 3164, 3108, 3047, 1623, 1577, 1494, 1468, 1421, 1364, 1349, 1261, 1223, 1149, 1108, 1025, 956, 871, 775, 756, 633, 601, 572, 562, 541

ESI HR-MS (m/z): $[M]^+$: 147.0917 (found), $[C_9H_{11}N_2]^+$: 147.0917 (calculated)

Synthesis of N-ethyl-benzimidazole, (2-1)[§]



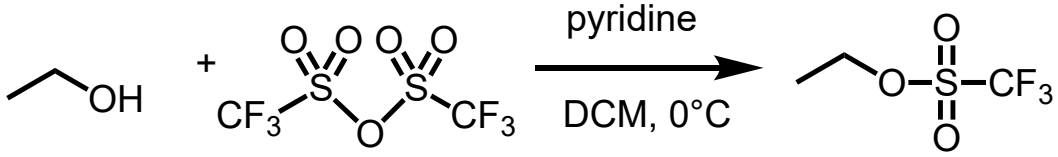
This compound was prepared with modifications from a previously published procedure for a similar compound.[2] Benzimidazole (1.51 g, 12.7 mmol), cesium carbonate (4.14 g, 12.7 mmol), 1-iodoethane (3.58 g, 2.29 mmol), and acetonitrile (100 mL) were added to a 250 mL round bottom flask. The reaction mixture was then refluxed overnight. After cooling to room temperature, the mixture was filtered over Celite, and the filtrate was concentrated to dryness. Water (100 mL) was added to the residue, and the solution was extracted with dichloromethane (3 x 30 mL). The organic phase was separated and dried with anhydrous magnesium sulfate. After filtration, dichloromethane was removed via rotary evaporator, and the crude product was obtained as a pale-yellow liquid. The crude material was purified using flash chromatography (R_f = 0.35, 0% to 5% ^{i}PrOH in EtOAc) on silica gel, yielding **(2-1)** as yellow oil (0.54 g, 29.2%).

[§]This compound's synthesis was initially described by Pilarski via a different synthetic approach.[4]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.82 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 2H), 4.25 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.99, 142.38, 133.71, 122.88, 122.13, 120.44, 109.65, 39.92, 15.34

Synthesis of Ethyl Trifluoromethanesulfonate, (2-2)‡



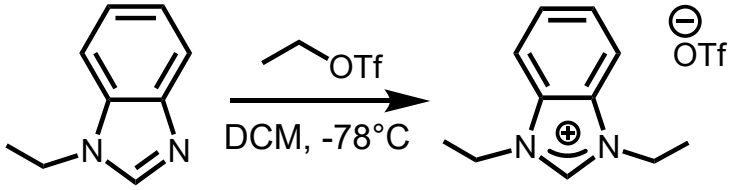
This compound was prepared according to previously published procedure.[5] A mixture of ethanol (3.06 g, 66.0 mmol) and pyridine (5.18 g, 65.5 mmol) in CH_2Cl_2 (6 mL) was added dropwise to a solution of trifluoromethanesulfonic anhydride (18.46 g, 65.4 mmol) in dichloromethane (60 mL) cooled to 0 °C in an ice bath. After 30 minutes of stirring at 0 °C, the reaction mixture was poured into water (50 mL) and the solution was extracted with dichloromethane (3 x 20 mL). The organic layers were combined and dried with magnesium sulfate, filtered, and concentrated on a rotary evaporator to give **(2-2)** as a colorless oil (4.97 g, 42.1%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 4.32 (q, *J* = 7.0 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (126 MHz, DMSO-d_6): δ 120.68 (q, *J* = 322 Hz), 72.69, 15.22

^{19}F NMR (471 MHz, DMSO-d_6): δ -77.75.

Synthesis of N,N-di-ethyl-benzimidazolium trifluoromethanesulfonate, (2-H)(OTf)❖



Dichloromethane (10 mL) was added to N-ethyl-benzimidazole (0.52 g, 3.53 mmol) and the solution was cooled to -78 °C in an isopropanol/dry ice bath. Ethyl triflate (0.80 g, 4.47 mmol) was diluted in dichloromethane (5 mL) and slowly added to the N-ethyl-benzimidazole solution. The reaction mixture was stirred at -78 °C for 1 h before the dry ice bath was removed and the solution was allowed to warm to room temperature overnight. The solution was then concentrated on a rotary evaporator and redissolved in dichloromethane (5 mL). This solution was added dropwise to a stirring solution of diethyl ether at 0 °C and the precipitate was collectedto give **(2-H)(OTf)** as a light purple solid (1.07 g, 93.4%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.75 (s, 1H), 8.08 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.70 (dd, *J* = 6.3, 3.2 Hz, 2H), 4.50 (q, *J* = 7.3 Hz, 4H), 1.54 (t, *J* = 7.2 Hz, 6H).

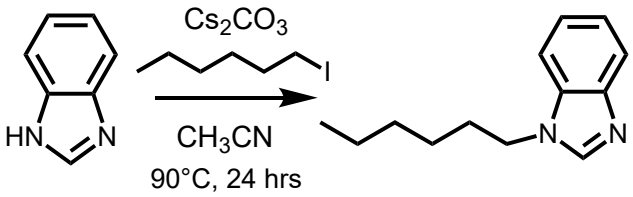
^{13}C NMR (126 MHz, DMSO-d_6): δ 141.55, 130.97, 126.45, 113.60, 41.98, 14.11

^{19}F NMR (471 MHz, DMSO-d_6): δ -77.72

IR: 3152, 3081, 2982, 1617, 1573, 1490, 1454, 1430. 1391, 1348, 1329, 1251, 1223, 1152, 1085, 1028, 903, 764, 638, 603, 572, 522

ESI HR-MS (m/z): $[M]^+$: 175.1229 (found), $[C_{11}H_{15}N_2]^+$: 175.1230 (calculated)

Synthesis of N-Hexyl-benzimidazole, (3-1)[§]



This compound was prepared with modifications from a previously published procedure for a similar compound.[6] Benzimidazole (0.51 g, 4.30 mmol), cesium carbonate (1.39 g, 4.26 mmol), 1-iodohexane (1.64 g, 7.72 mmol) and acetonitrile (80 mL) were added to a 250 mL round bottom flask and the reaction mixture was refluxed overnight. After cooling to room temperature, the mixture was filtered over Celite, and the filtrate was concentrated. Water (100 mL) was added to the dark red residue, and the solution was extracted with dichloromethane (3 x 30 mL). The organic layers were then combined and dried with anhydrous magnesium sulfate. The solution was filtered over Celite and the filtrate was concentrated to dryness before purification via flash chromatography (0% to 5% iPrOH in EtOAc) on silica to give **(3-1)** as a red oil (0.31 g, 35.4%).

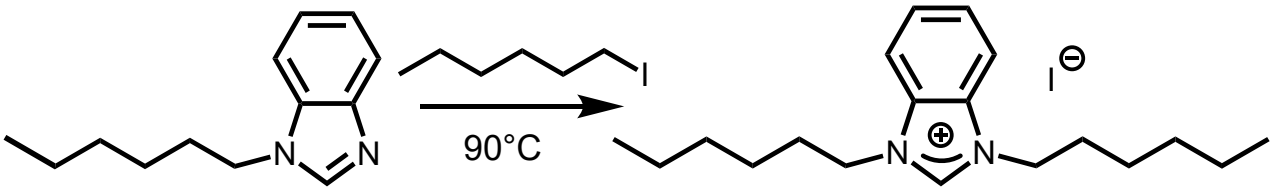
[§]This compound was originally synthesized by Dissanayake and Vannucci via a different synthetic approach.[7]

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.87 (s, 1H), 7.72 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.31 – 7.20 (m, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 1.87 (p, *J* = 7.2 Hz, 2H), 1.38 – 1.24 (m, 6H), 0.91 – 0.83 (m, 3H)

^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.41, 143.47, 134.45, 122.93, 122.10, 120.41, 110.20, 45.49, 31.69, 30.19, 26.89, 22.90, 14.13.

DART HR-MS (m/z): $[M+H]^+$: 203.1532 (found), $[C_{13}H_{19}N_2]^+$: 203.1543 (calculated)

Synthesis of N,N-di-hexyl-benzimidazolium iodide, (3-H)(I)[§]



This compound was prepared with modifications from a previously published procedure for a similar compound.[8] To a 100 mL pressure flask were added n-hexyl-benzimidazole (2.26 g, 11.9 mmol) and 1-iodohexane (30.0 g, 142 mmol). The flask was sealed with a Teflon cap and heated at 90°C for 5 days. After cooling to room temperature, the solution was diluted with toluene, filtered over Celite, and the filtrate was concentrated to dryness via rotary evaporator. The resulting residue was dissolved in dichloromethane (5 mL) and triturated into n-pentane (300 mL). The solids were filtered and washed with additional n-pentane to give **(3-H)(I)** as an orange solid (1.75 g, 35.5%).

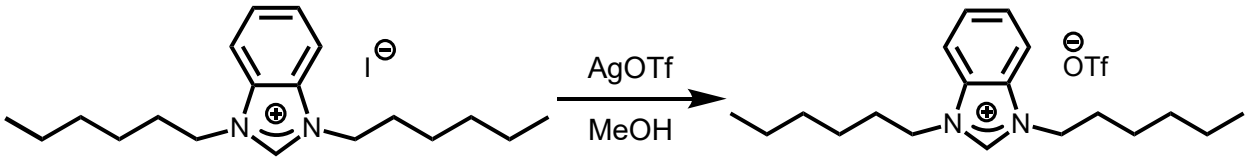
[§]This compound was initially synthesized by Lee via a different synthetic approach.[9]

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.96 (s, 1H), 7.73 (dd, *J* = 6.3, 3.2 Hz, 2H), 7.68 (dd, *J* = 6.4, 3.2 Hz, 2H), 4.62 (t, *J* = 7.5 Hz, 4H), 2.08 (p, *J* = 7.6 Hz, 4H), 1.52 – 1.23 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 6H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.08, 131.55, 127.49, 113.31, 48.04, 31.29, 29.65, 26.43, 22.59, 14.10

ESI HR-MS (m/z): $[M]^+$: 287.2473 (found), $[C_{19}H_{31}N_2]^+$: 287.2482 (calculated)

Synthesis of N,N-di-hexyl-benzimidazolium trifluoromethanesulfonate, (3-H)(OTf)❖



N,N-di-hexyl-benzimidazolium iodide (0.51 g, 1.21 mmol) was dissolved in methanol (2 mL) in a 25 mL Erlenmeyer flask. With minimal exposure to light, silver triflate (0.66 g, 2.42 mmol) was added, and exchange occurred immediately with precipitation of a yellow solid out of the solution. The mixture was filtered over Celite, and the filtrate was dried to give **(3-H)(OTf)** as a dark orange semi-solid (0.541 g, 99%).

^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.72 (dt, *J* = 7.0, 3.5 Hz, 2H), 7.67 (dt, *J* = 6.3, 3.6 Hz, 2H), 4.50 (t, *J* = 7.5 Hz, 4H), 2.00 (septet, *J* = 7.0 Hz, 4H), 1.45 – 1.26 (m, 12H), 0.87 (t, *J* = 7.0 Hz, 6H)

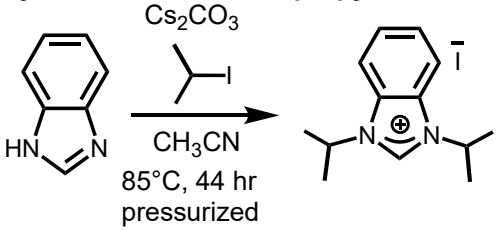
^{13}C NMR ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.17, 131.59, 127.29, 113.28, 47.95, 31.18, 29.40, 26.25, 22.48, 13.98

^{19}F NMR ^{19}F NMR (471 MHz, $CDCl_3$) δ -78.33

IR: 3141, 3077, 2931, 2859, 1565, 1458, 1380, 1254, 1223, 1167, 1027, 896, 757, 731, 625, 574, 553

ESI HR-MS (m/z): $[M]^+$: 287.2473 (found), $[C_{19}H_{31}N_2]^+$: 287.2482 (calculated)

Synthesis of N,N-di-isopropyl-benzimidazolium iodide, (4-H)(I)[#]

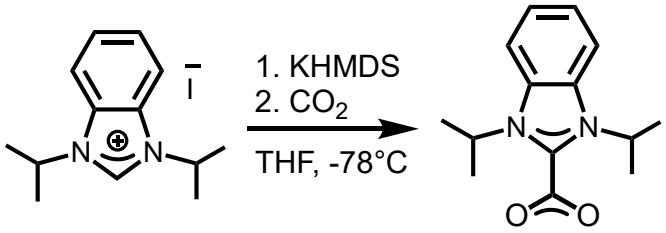


This compound was prepared according to previously published procedure with modifications.[6] 10.0 g (84.6 mmol) benzimidazole, 34.0 g (0.104 mol) cesium carbonate, 80.6 g (0.474 mol), 2-iodopropane and 70 mL acetonitrile were added to a 350 mL pressure tube with Teflon screw-cap and O-ring. The reaction mixture was stirred at 85 °C in the pressure tube for 44 hours. The reaction mixture was then cooled to room temperature and the volatiles were removed. The solids were extracted with dichloromethane, filtered over Celite, and dried. The solids were dissolved in minimal acetonitrile, triturated with diethyl ether, then filtered over a fine frit to afford **(4-H)(I) as** a white powder (26.49 g, 95%).

^{1}H NMR ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.83 (s, 1H), 7.81 (dd, J = 6.3, 3.1 Hz, 1H), 7.67 (dd, J = 6.4, 3.1 Hz, 1H), 5.16 (p, J = 6.8 Hz, 1H), 1.86 (d, J = 6.9 Hz, 7H).

^{13}C NMR ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.98, 131.35, 127.36, 114.23, 52.75, 22.44.

Synthesis of N,N-di-isopropyl-benzimidazole CO_2 adduct, (4-CO_2)[#]

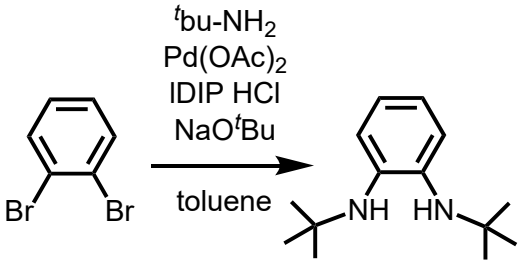


This compound was prepared according to a previously published procedure with modifications.[6] 2.05 g (6.20 mmol) N,N-di-isopropyl-benzimidazolium iodide and 1.25 g (6.25 mmol) potassium hexamethyldisilazane were added to THF under inert atmosphere and stirred for 5 days. The reaction mixture was then filtered over Celite and the free carbene solution was transferred to a Schlenk flask. The flask was removed from the glovebox, transferred to a Schlenk line, and cooled to -78 °C with isopropanol/dry ice bath for 30 minutes. The headspace of the flask was evacuated and purged with CO_2 while stirring at -78°C. The product precipitated from solution as a white solid. The flask was then returned to the glovebox and cooled to -35 °C in the glovebox freezer for one hour. The mixture was then triturated with diethyl ether and filtered over a fine frit to afford **(4-CO_2)** as a white powder (0.950 g, 62%).

^{1}H NMR ^{1}H MR (500 MHz, CD_3OD) δ 8.05 (dd, J = 6.3, 3.2 Hz, 2H), 7.73 (dd, J = 6.4, 3.1 Hz, 2H), 5.10 (p, J = 6.8 Hz, 2H), 1.75 (d, J = 6.8 Hz, 12H)

^{13}C NMR ^{13}C NMR (126 MHz, CD_3OD) δ 161.34, 139.06, 132.57, 128.15, 114.99, 52.83, 22.11.

Synthesis of 1,2-di-*tert*-butylaminobenzene, (5-1)[#]



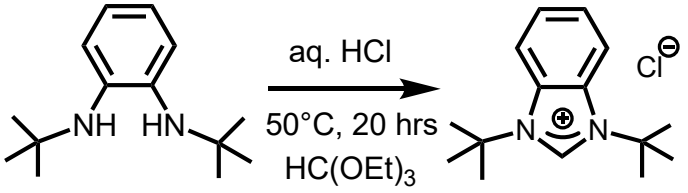
This compound was first synthesized by Hadei, and prepared with modification to the published procedure.[10] The catalyst was prepared by adding 1,3-bis-(2', 6'-di-isopropylphenyl)imidazolium chloride (42.5 mg, 0.10 mmol), sodium *tert*-butoxide (13.4 mg, 0.14 mmol), palladium acetate (8.20 mg, 0.04 mmol), and toluene (10 mL) to a pressure flask. This mixture was heated at 135 °C and stirred under nitrogen for 15 minutes. After cooling to room temperature, the catalyst was added to a mixture of *o*-dibromobenzene (501 mg, 1.90 mmol), *tert*-butylamine (309 mg, 4.22 mmol), and sodium *tert*-butoxide (548 mg, 5.68 mmol) in toluene (40 mL). This mixture was then refluxed overnight. After cooling to room temperature, saturated ammonium chloride solution (30 mL), water (30 mL) and additional toluene (50 mL) were added, and the phases were separated. The organic phase was washed with water (2 x 30 mL) and brine (30 mL) before drying with anhydrous sodium sulfate and concentrating. The crude residue was purified via flash chromatography on silica (0% to 25% acetonitrile in dichloromethane) to afford **(5-1)** as a dark brown oil (167 mg, 40.0%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (dd, *J* = 5.9, 3.5 Hz, 2H), 6.76 (dd, *J* = 5.9, 3.5 Hz, 2H), 1.28 (s, 18H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.63, 120.77, 120.32, 52.11, 30.04

DART HR-MS (m/z): $[M+H]^+$: 221.2005 (found), $[C_{14}H_{25}N_2]^+$: 221.2013 (calculated)

Synthesis of N,N-di-*tert*-butyl-benzimidazolium Chloride, (5-H)(Cl)‡

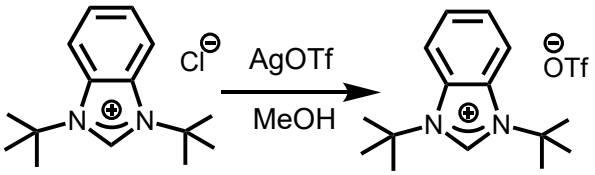


This compound was prepared according to a previously published procedure.[11] Crude 1,2-di-tert-butylaminobenzene (108 mg, 0.49 mmol) was treated with aq. HCl (55.0 µL, 0.65 mmol) in triethyl orthoformate (2.56 mL, 15.4 mmol). The resulting reaction mixture was stirred overnight at 50°C and then concentrated to ~1 mL. The precipitated solids were then collected by filtration before washing with diethyl ether (10 mL) to afford **(5-H)(Cl)** as a tan powder (86.3 mg, 66%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.86 (s, 1H), 8.32 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.65 (dd, *J* = 6.4, 3.2 Hz, 2H), 1.82 (s, 18H)

^{13}C NMR (126 MHz, DMSO-d_6): δ 138.79, 130.87, 125.81, 116.62, 60.95, 28.08

Synthesis of N,N-di-*tert*-butyl-benzimidazolium Trifluoromethanesulfonate, (5-H)(OTf)❖



N,N-di-*tert*-butyl-benzimidazolium chloride (409.2 mg, 1.54 mmol) was dissolved in methanol (5 mL). With minimal exposure to light, silver triflate (483 mg, 1.88 mmol) was added to this solution and exchange was observed to occur immediately with precipitation of a gray solid out of the solution. The mixture was filtered through Celite, and the filtrate was concentrated to dryness to afford **(5-H)(OTf)** as a pink solid (516.0 mg, 88%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.02 (s, 1H), 7.96 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.61 (dd, *J* = 6.4, 3.2 Hz, 2H), 1.96 (s, 18H)

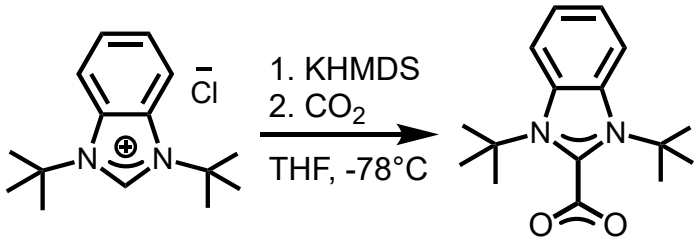
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.14, 131.78, 126.29, 116.58, 62.20, 29.04

^{19}F NMR (471 MHz, $CDCl_3$): δ -78.32.

IR: 3470, 2993, 1610, 1551, 1481, 1404, 1378, 1336, 1255, 1207, 1144, 1027, 986, 862, 782, 751, 626, 572

ESI HR-MS (m/z): $[M]^+$: 231.1848 (found), $[C_{15}H_{23}N_2]^+$: 231.1856 (calculated)

Synthesis of N,N-di-*tert*-butyl-benzimidazole CO_2 adduct, (5-CO_2)❖



N,N-di-*tert*-butyl-benzimidazolium chloride (1.00 g, 4.41 mmol) and 0.880 g (4.45 mmol) potassium hexamethyldisilazane were added to THF under inert atmosphere and stirred for 1 hour at room temperature. The mixture was then filtered over Celite to remove potassium salts and isolate the free carbene, which was transferred to Strauss tube. The tube was removed from the glovebox, transferred to a Schlenk line, and cooled to -78 °C with a isopropanol/dry ice bath for 30 minutes while being added to Schlenk line. The headspace of the tube was evacuated and purged with CO_2 was added while stirring at -78°C. The product precipitated from solution as a white solid. The Strauss tube was then returned to the glovebox and cooled in the glovebox freezer at -35°C for one hour. The mixture was triturated with diethyl ether and filtered over a fine frit to afford **(5-CO_2)** as a white powder (0.0635 g, 5.2%). NMR spectra were recorded in anhydrous $CDCl_3$ stored in a glovebox over 4 Å molecular sieves

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (m, 2H), 7.57 (m, 2H), 2.01 (s, 18H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 131.79, 125.94, 116.47, 62.22, 29.28. Incredibly poor solubility precluded finding all carbons for **5-CO_2.**

5-CO_2 was subjected to benchtop CD_3OD to show the decomposition to the bicarbonate salt version (**5-H)(HCO_3)**, which has been previously reported by Crudden[12] and Taton[13]—synthesized via anion exchange resin or anion metathesis, respectively.

^{1}H NMR (500 MHz, CD_3OD): δ 8.26 (dd, *J* = 6.4, 3.2 Hz, 2H), 7.69 (dd, *J* = 6.5, 3.2 Hz, 2H), 1.91 (s, 18H)

^{13}C NMR (126 MHz, CD_3OD): δ 161.46, 132.92, 127.40, 117.85, 62.82, 28.91.

Annotated NMRs, IRs, and MS for NHC-triflate salts and CO_2-adducts

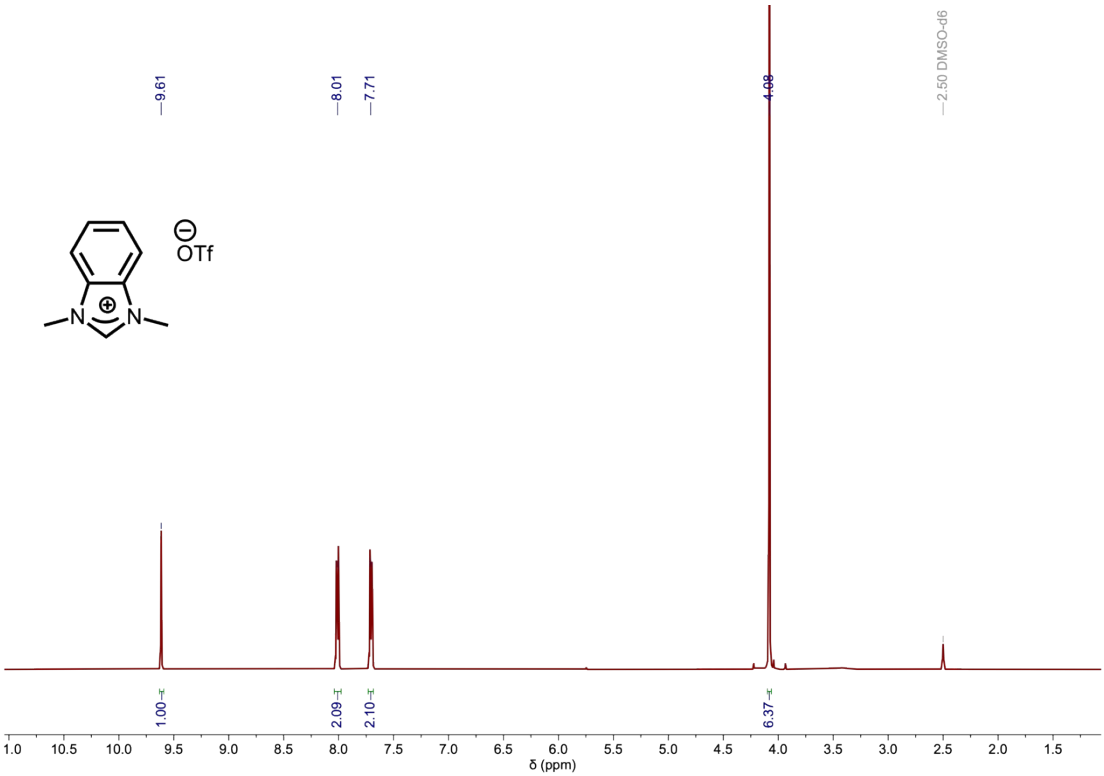


Figure S14. ^{1}H NMR of N,N-di-methyl-benzimidazolium triflate **(1-H)(OTf)** in DMSO-d_6.

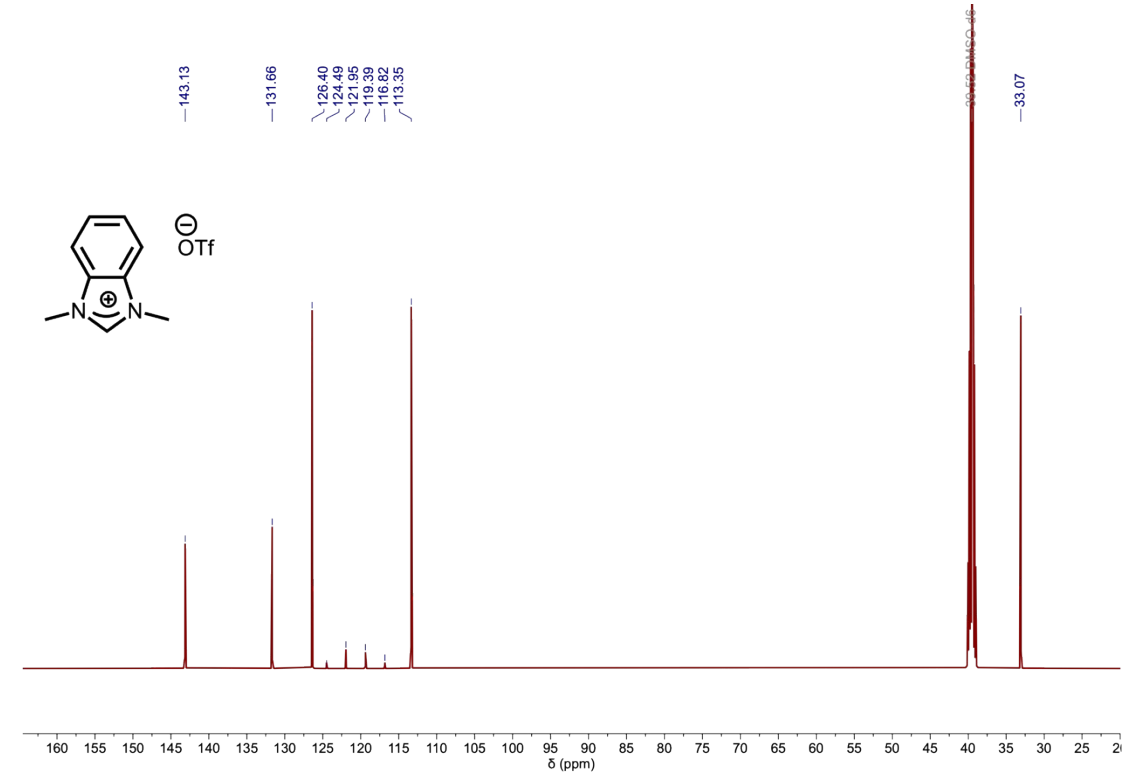


Figure S15. ^{13}C NMR of N,N-di-methyl-benzimidazolium triflate **(1-H)(OTf)** in DMSO-d_6.

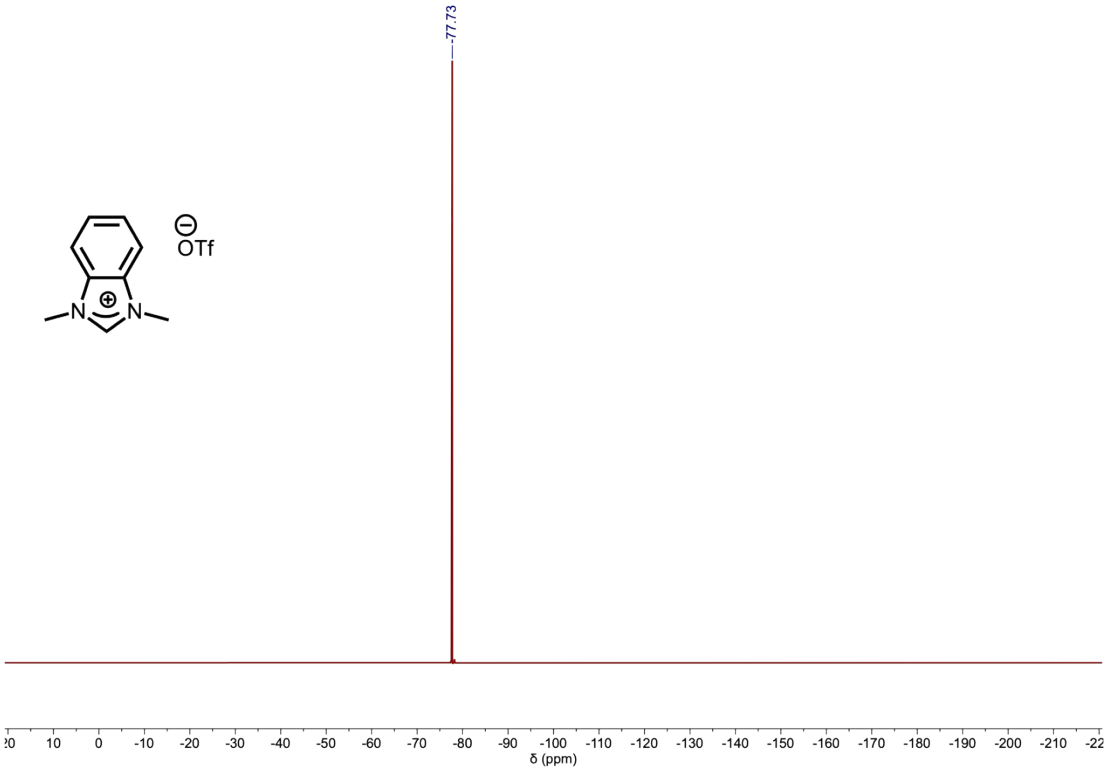


Figure S16. ^{19}F NMR of N,N-di-methyl-benzimidazolium triflate **(1-H)(OTf)** in DMSO-d_6.

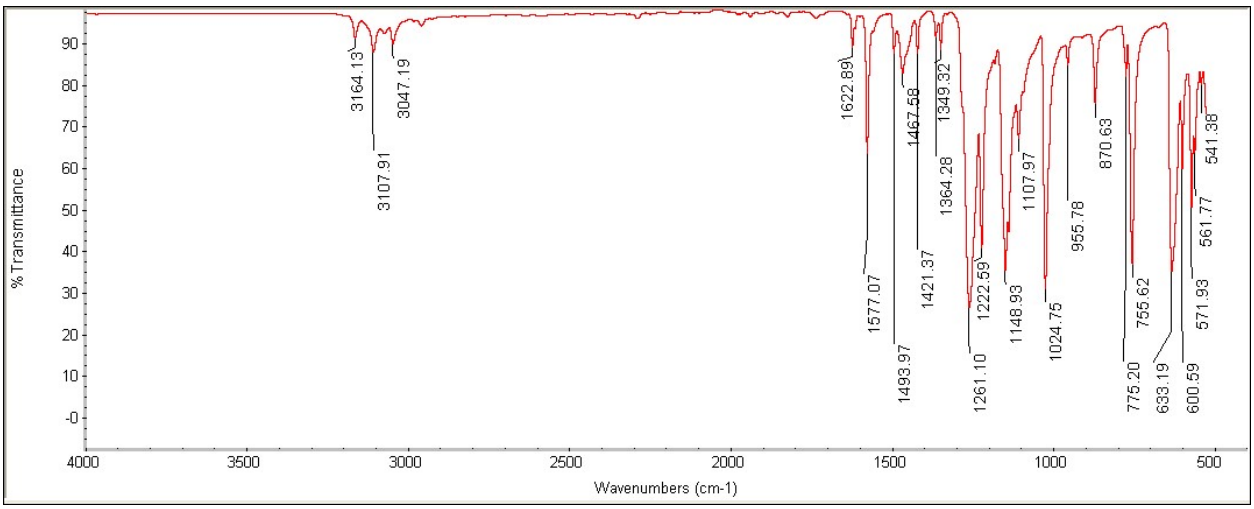


Figure S17. IR of N,N-di-methyl-benzimidazolium triflate, **(1-H)(OTf)**.

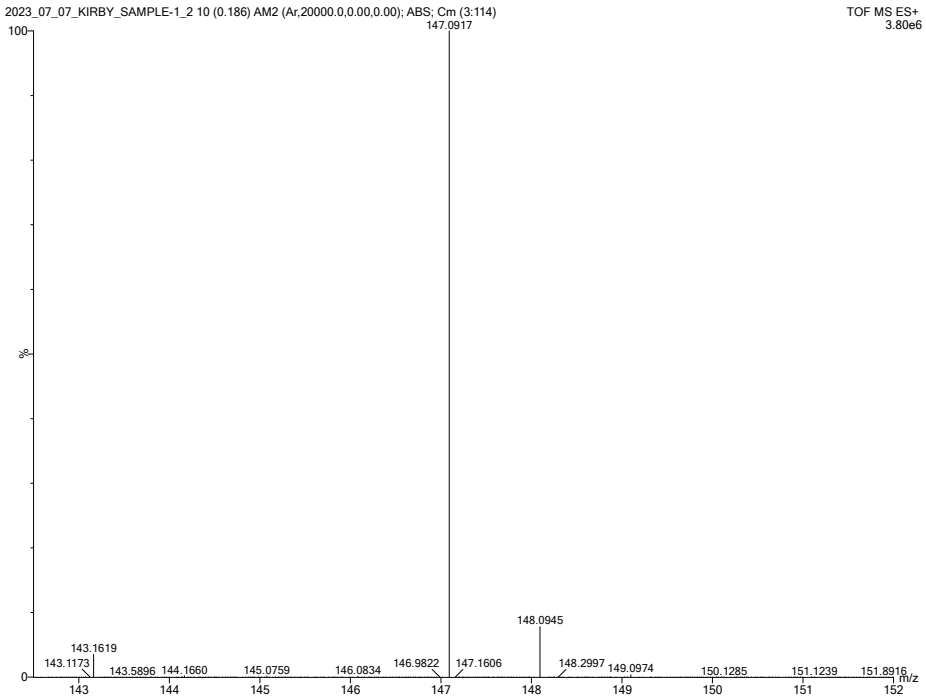


Figure S18. ESI HR-MS of N,N-di-methyl-benzimidazolium triflate, **(1-H)(OTf)**.

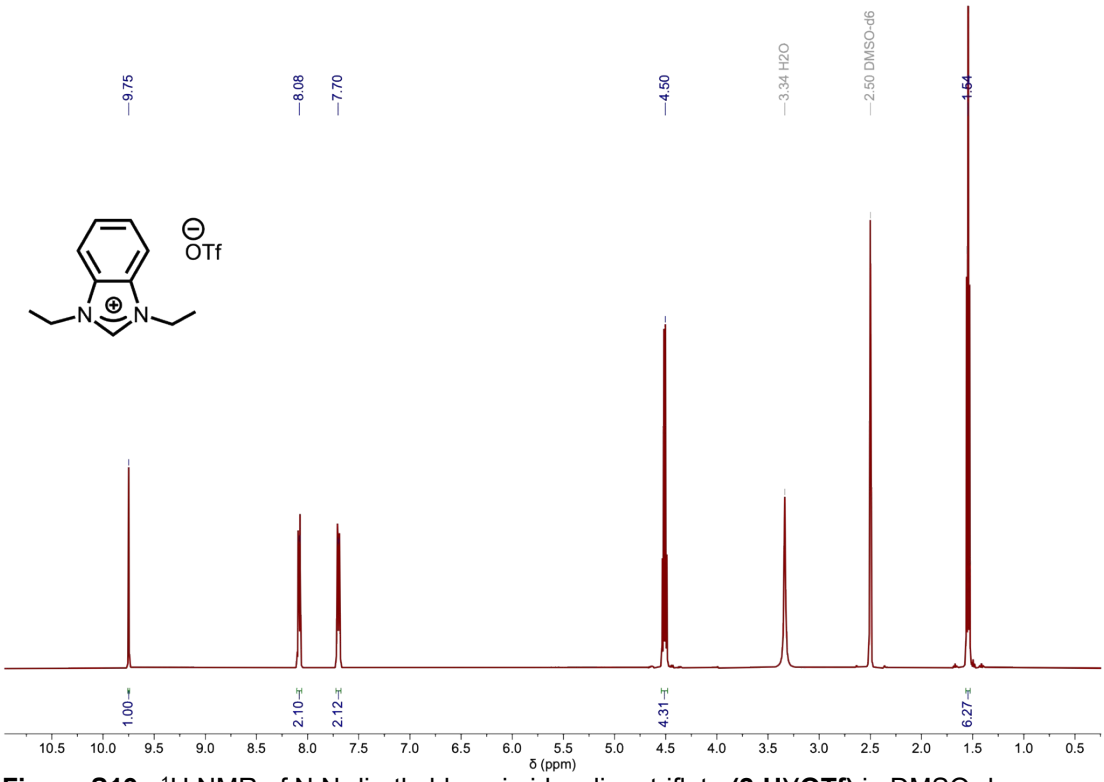


Figure S19. ^{1}H NMR of N,N-di-ethyl-benzimidazolium triflate **(2-H)(OTf)** in DMSO-d_6.

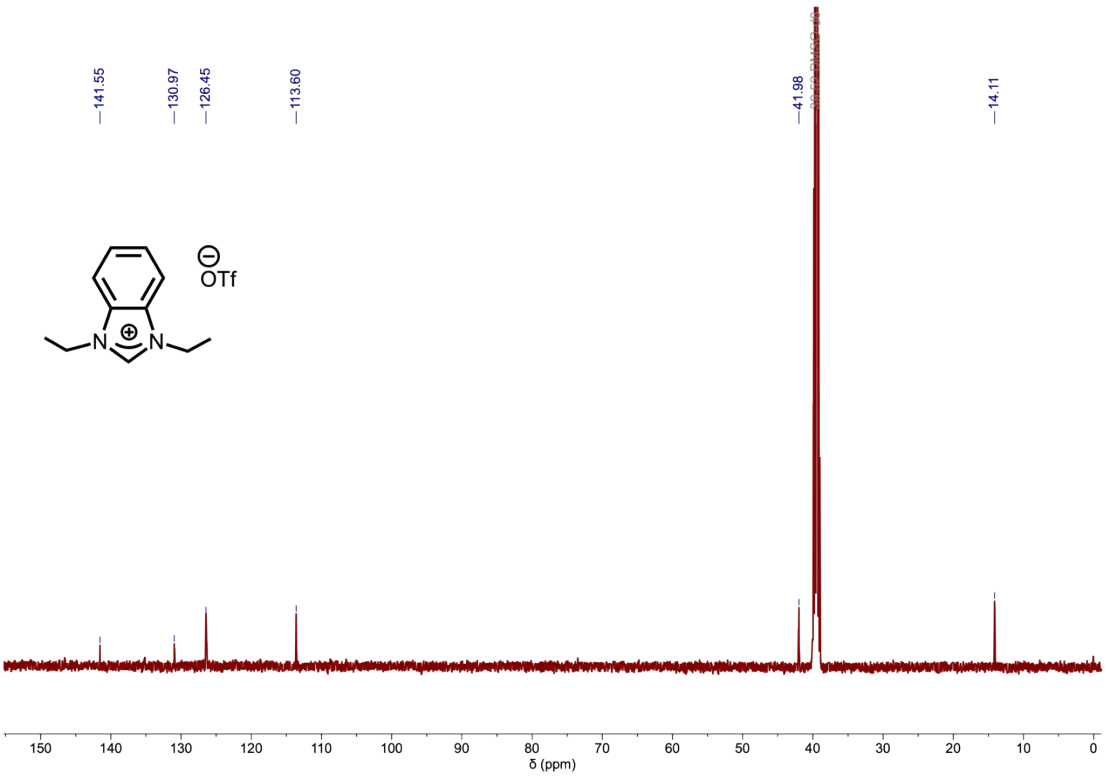


Figure S20. ^{13}C NMR of N,N-di-ethyl-benzimidazolium triflate **(2-H)(OTf)** in DMSO-d_6.

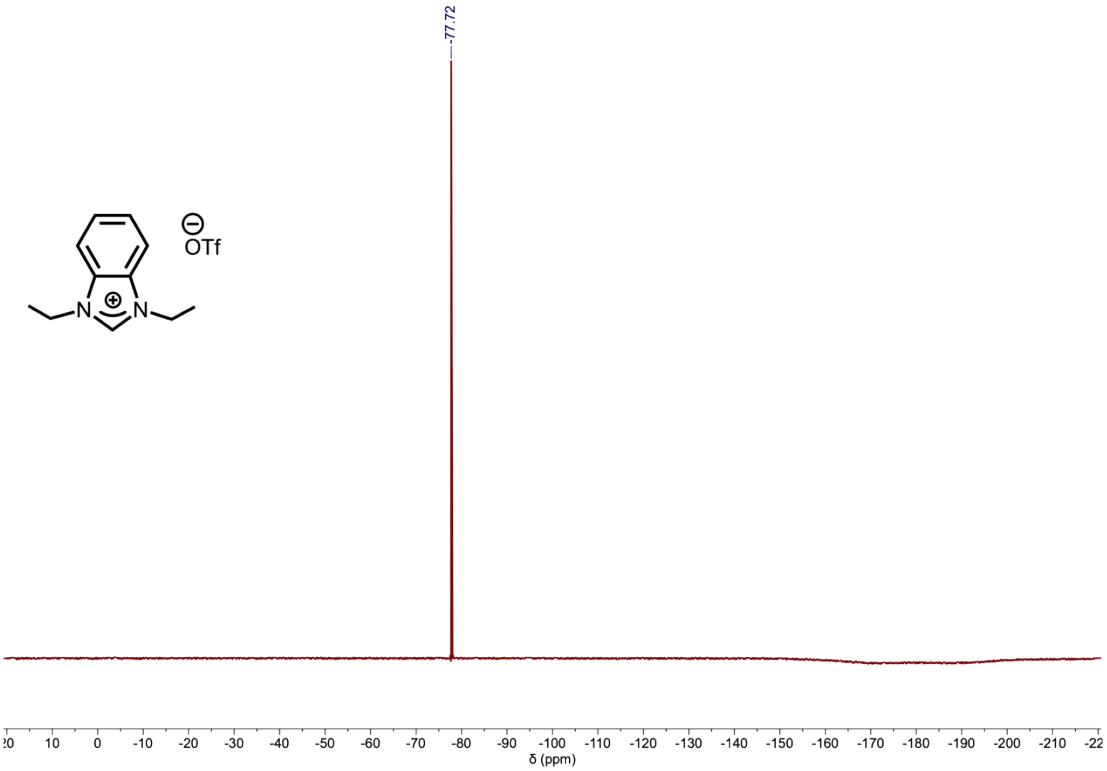


Figure S21. ^{19}F NMR of N,N-di-ethyl-benzimidazolium triflate **(2-H)(OTf)** in DMSO-d_6.

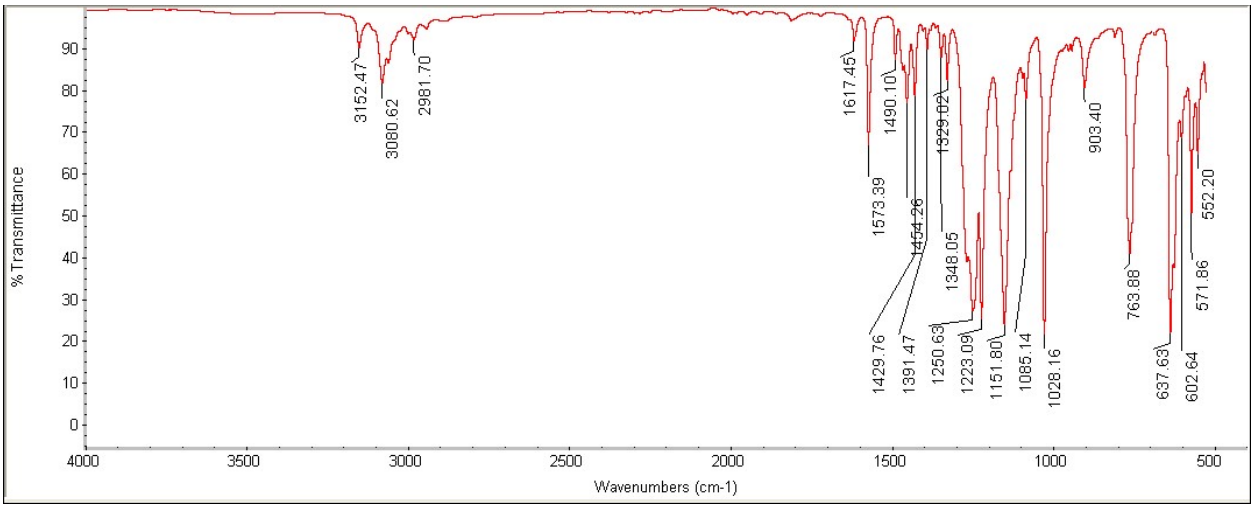


Figure S22. IR of N,N-di-ethyl-benzimidazolium triflate, **(2-H)(OTf)**.

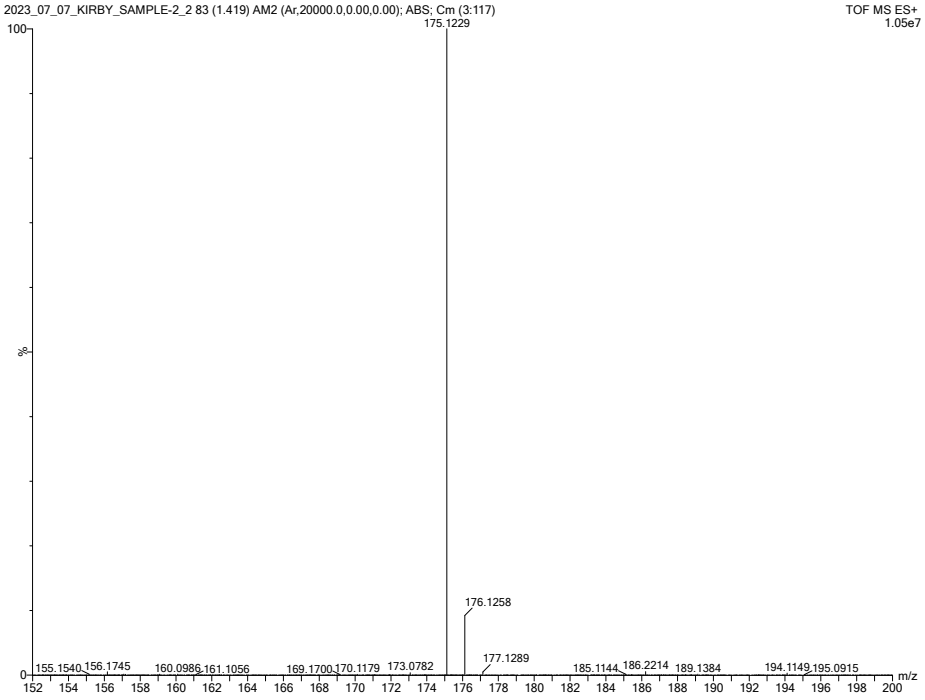


Figure S23. ESI HR-MS of N,N-di-ethyl-benzimidazolium triflate, **(2-H)(OTf)**.

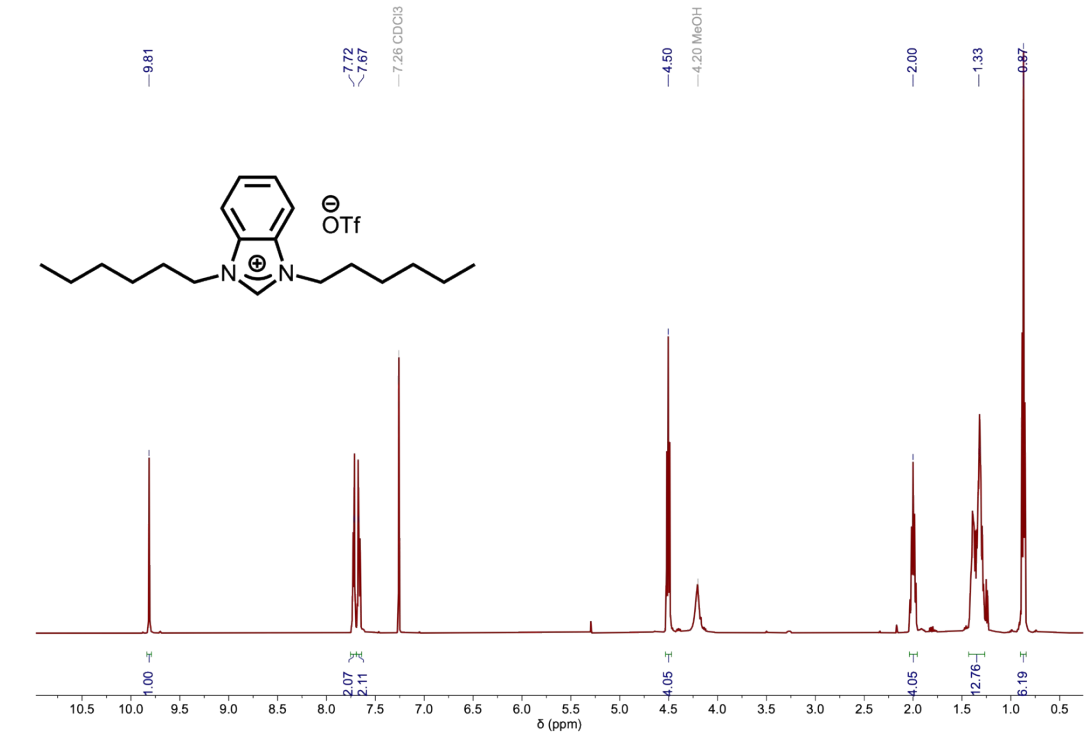


Figure S24. ^{1}H NMR of N,N-di-hexyl-benzimidazolium triflate **(3-H)(OTf)** in $CDCl_3$.

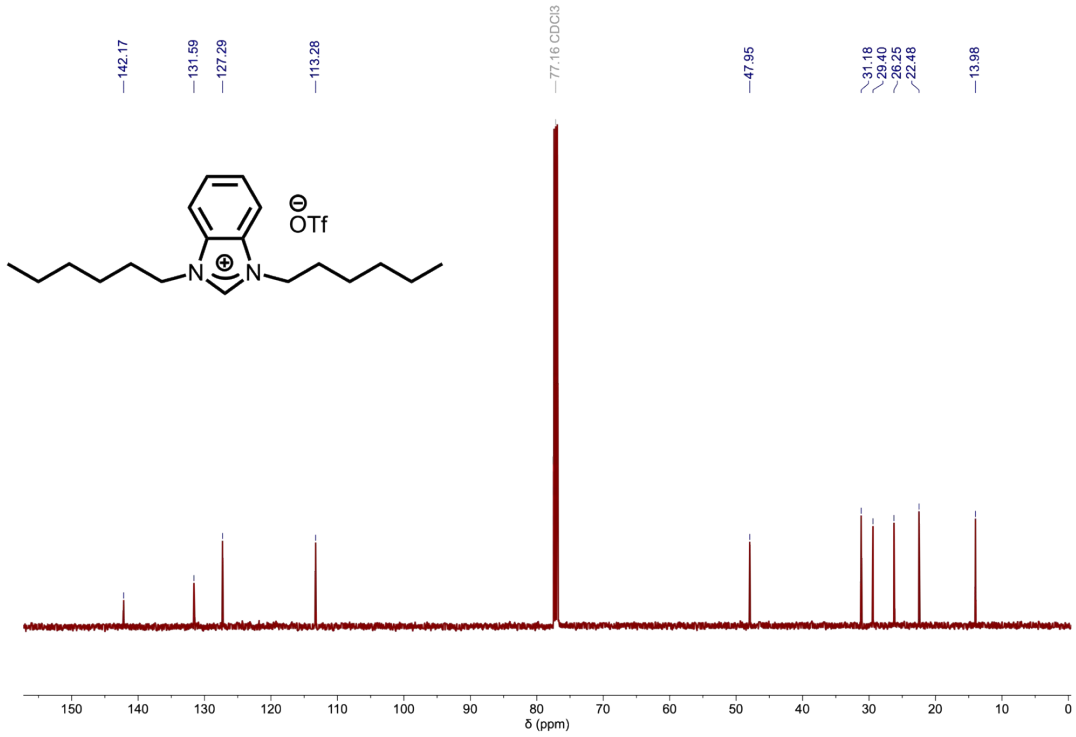


Figure S25. ^{13}C NMR of N,N-di-hexyl-benzimidazolium triflate **(3-H)(OTf)** in $CDCl_3$.

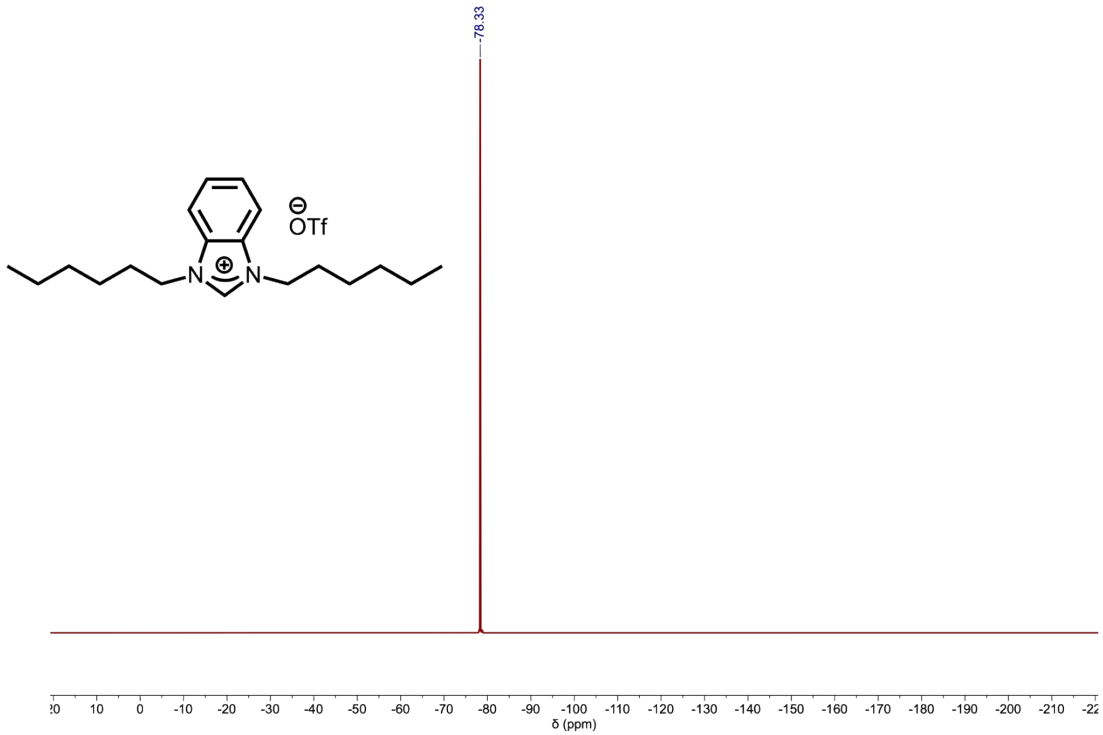


Figure S26. ^{19}F NMR of N,N-di-hexyl-benzimidazolium triflate **(3-H)(OTf)** in $CDCl_3$.

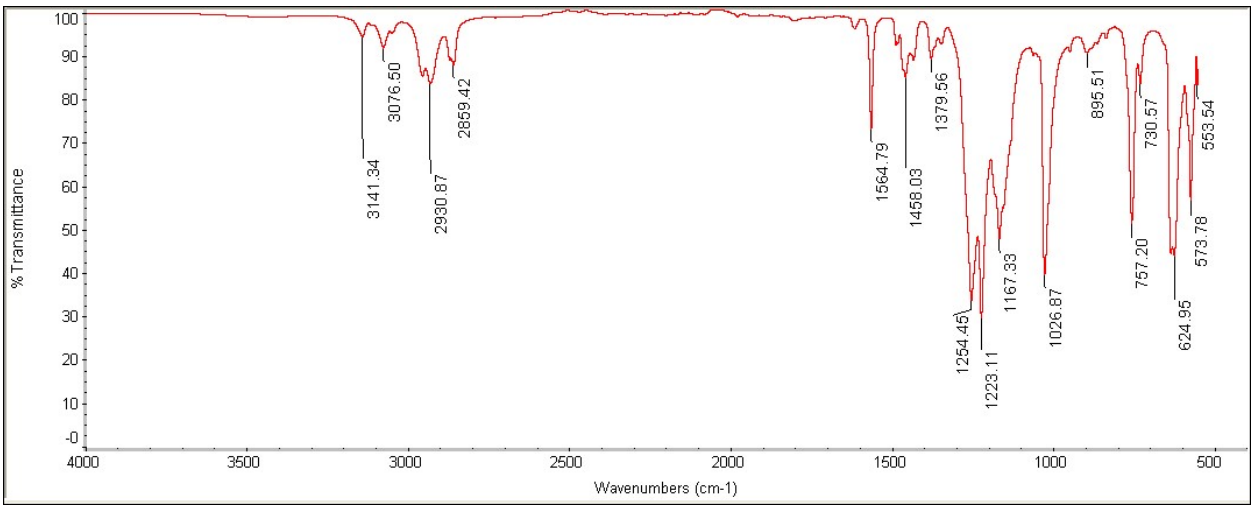


Figure S27. IR of N,N-di-hexyl-benzimidazolium triflate, **(3-H)(OTf)**.

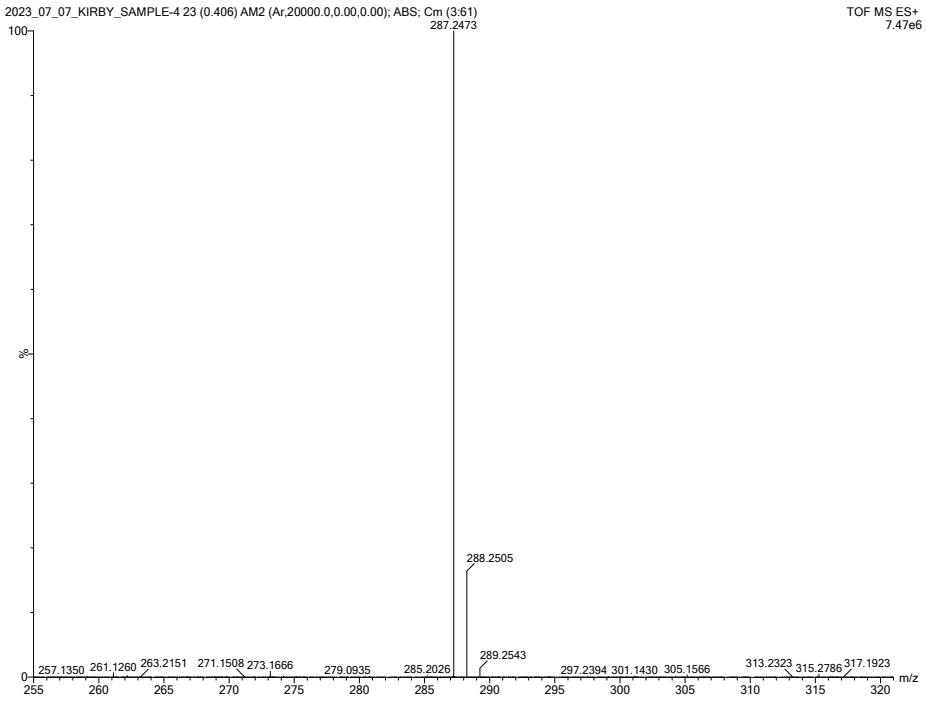


Figure S28. ESI HR-MS of N,N-di-hexyl-benzimidazolium triflate, **(3-H)(OTf)**.

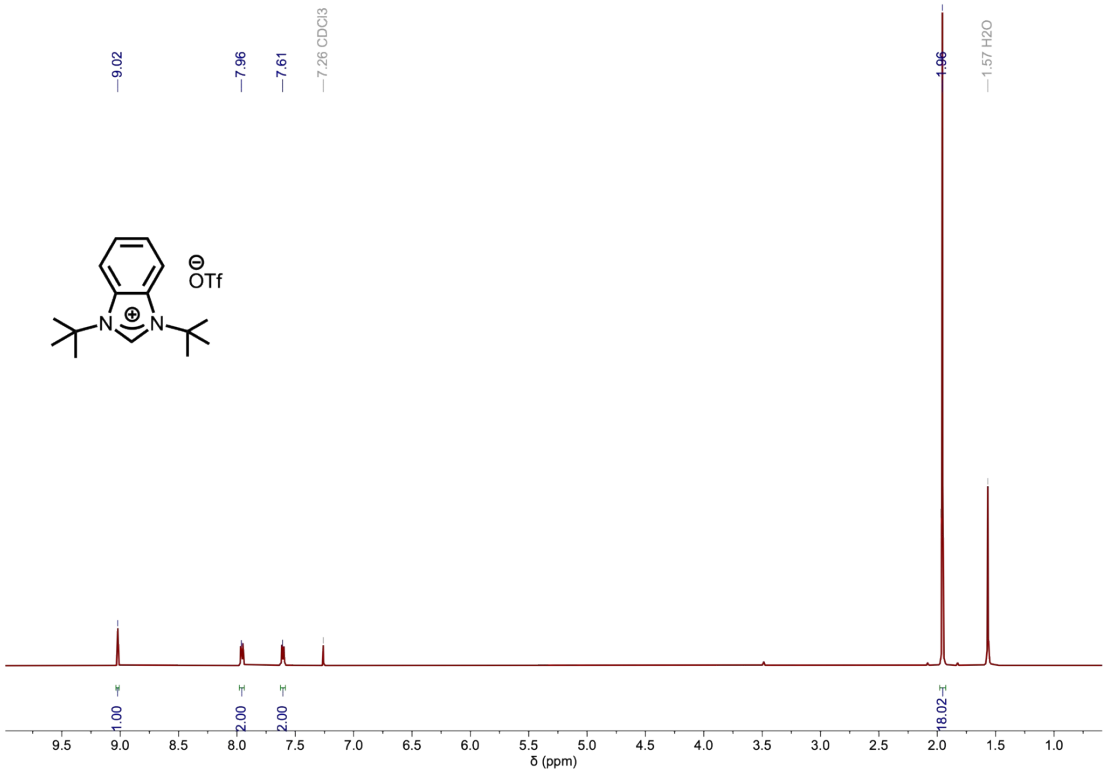


Figure S29. ^{1}H NMR of N,N-di-*tert*-butyl-benzimidazolium triflate **(5-H)(OTf)** in $CDCl_3$.

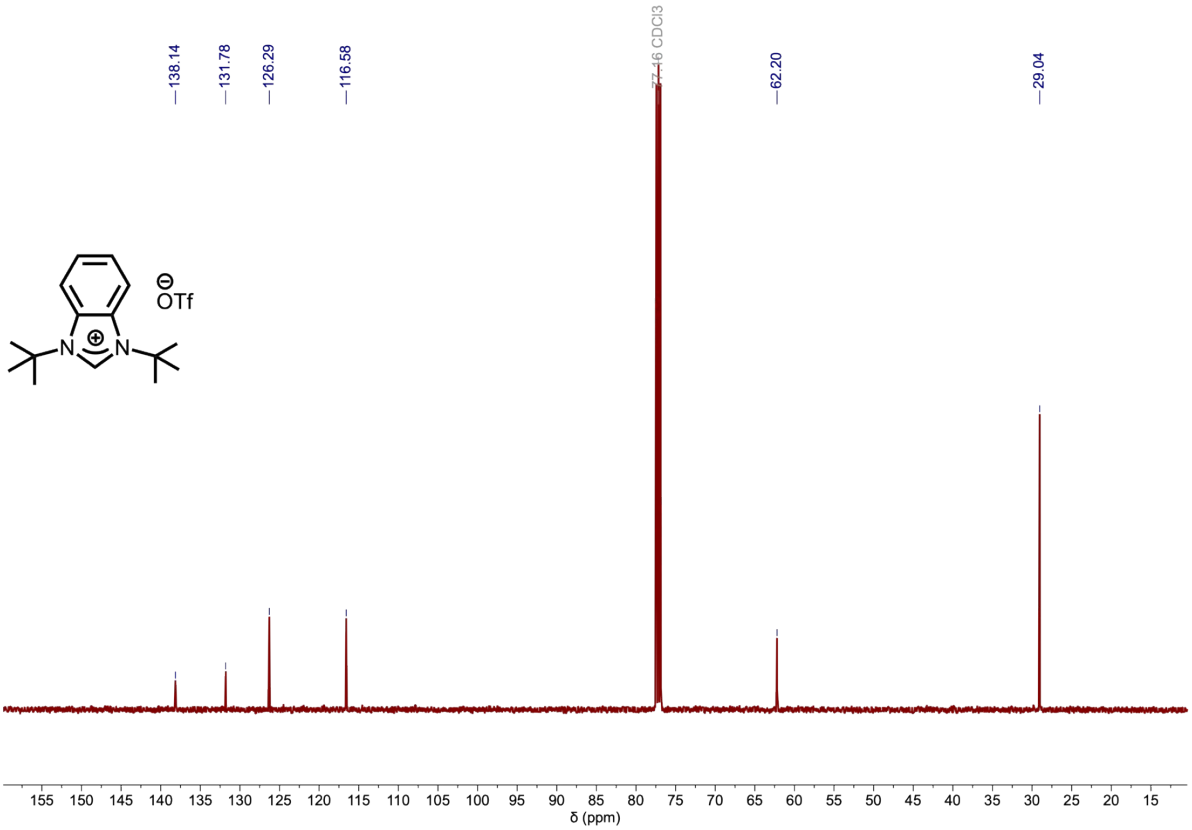


Figure S30. ^{13}C NMR of N,N-di-*tert*-butylbenzimidazolium triflate **(5-H)(OTf)** in $CDCl_3$.

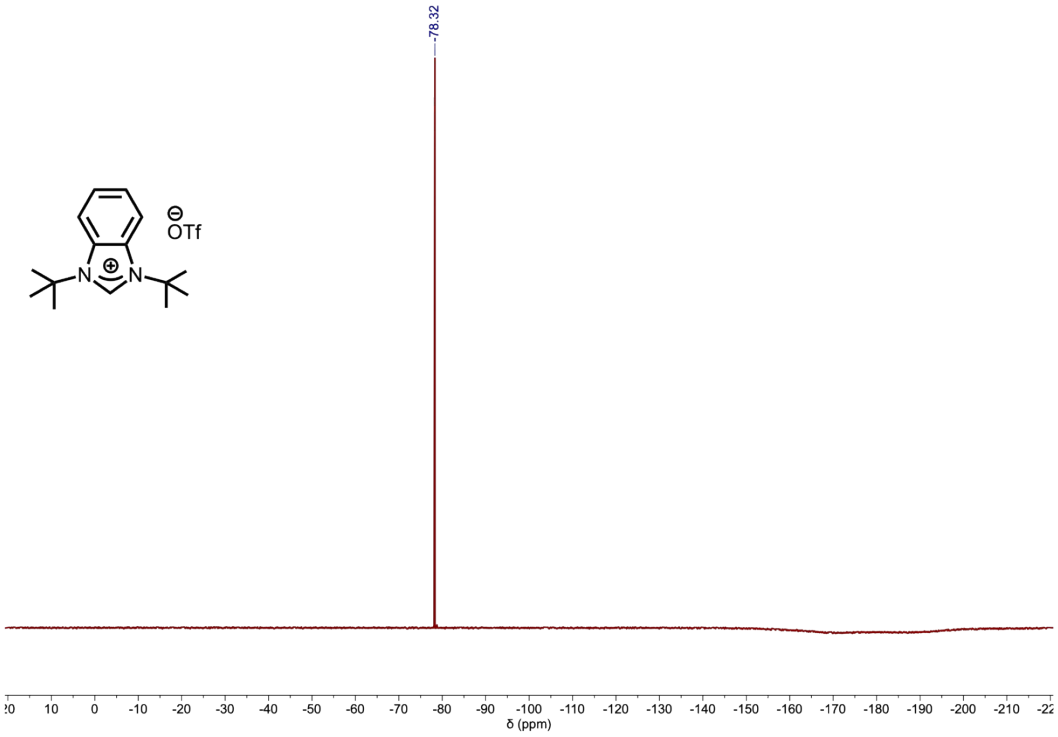


Figure S31. ^{19}F NMR of N,N-di-*tert*-butyl-benzimidazolium triflate **(5-H)(OTf)** in $CDCl_3$.

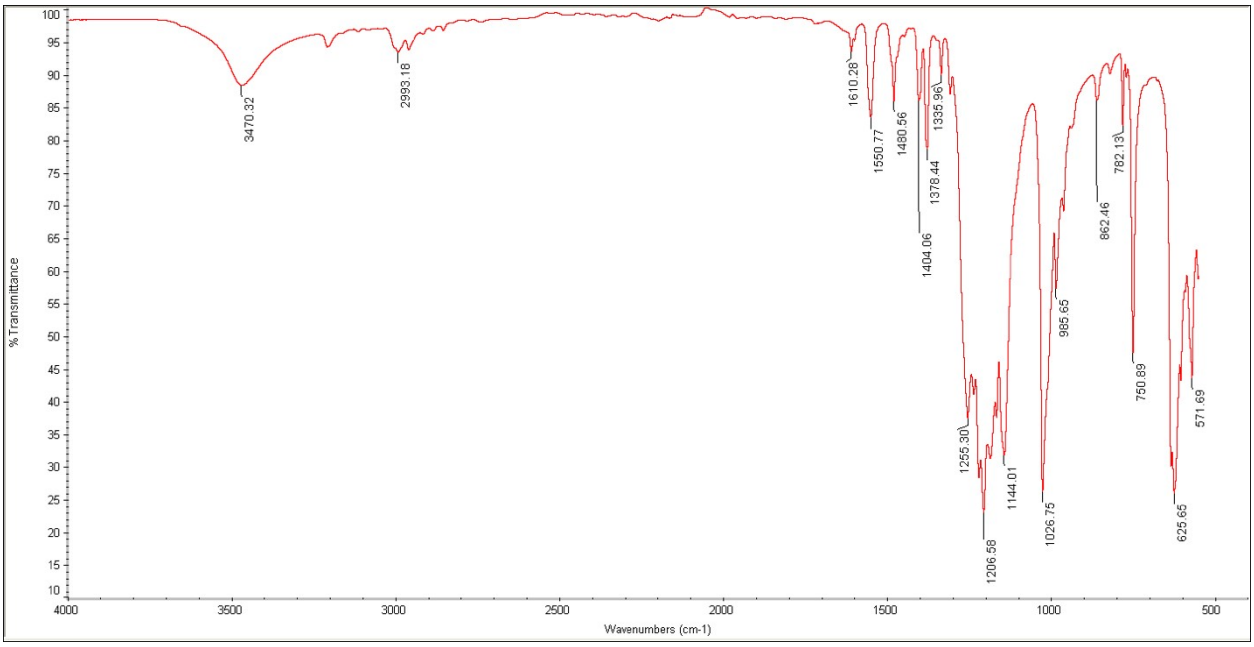


Figure S32. IR of N,N-di-*tert*-butyl-benzimidazolium triflate, **(5-H)(OTf)**.

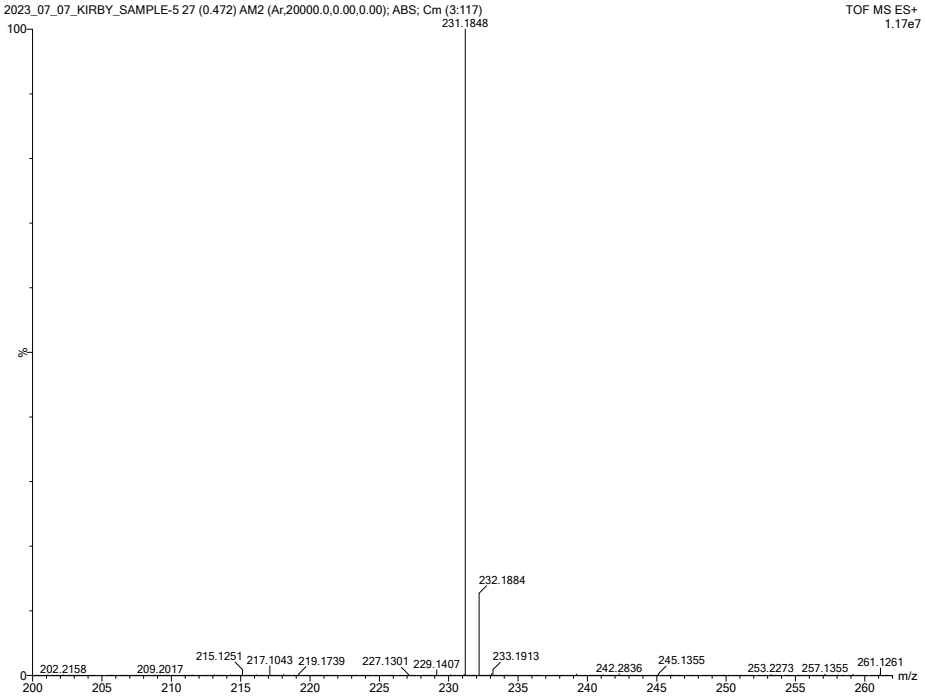


Figure S33. ESI HR-MS of N,N-di-*tert*-butylbenzimidazolium triflate, **(5-H)(OTf)**.

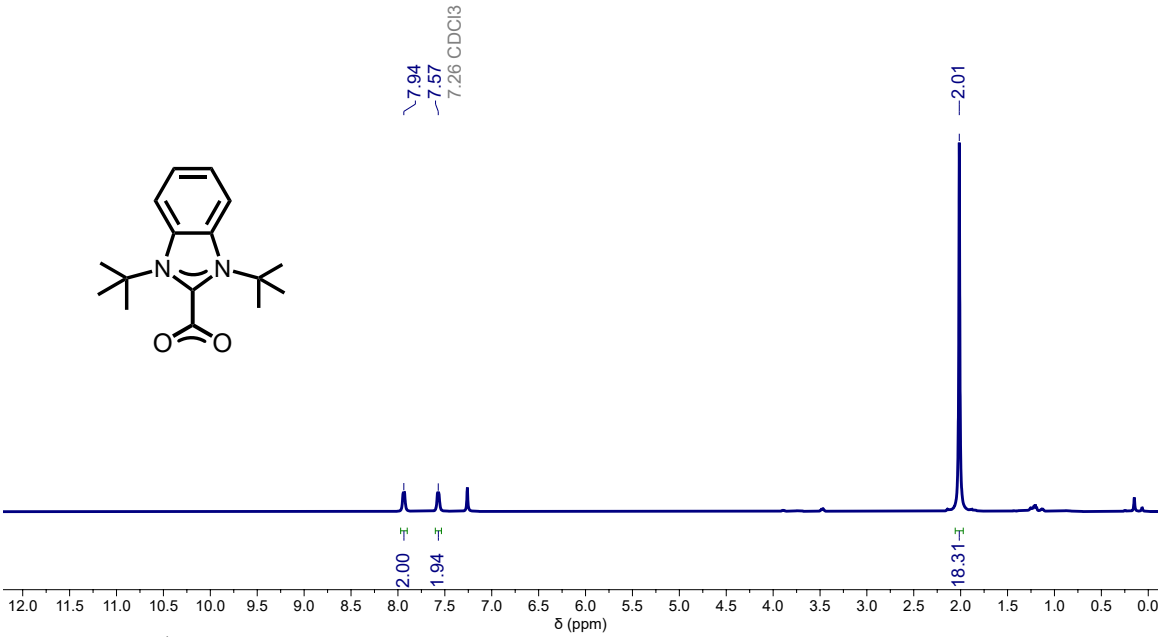


Figure S34. ^{1}H NMR of N,N-di-*tert*-butyl-benzimidazole CO_2-adduct (**5-CO$_2$**) in $CDCl_3$.

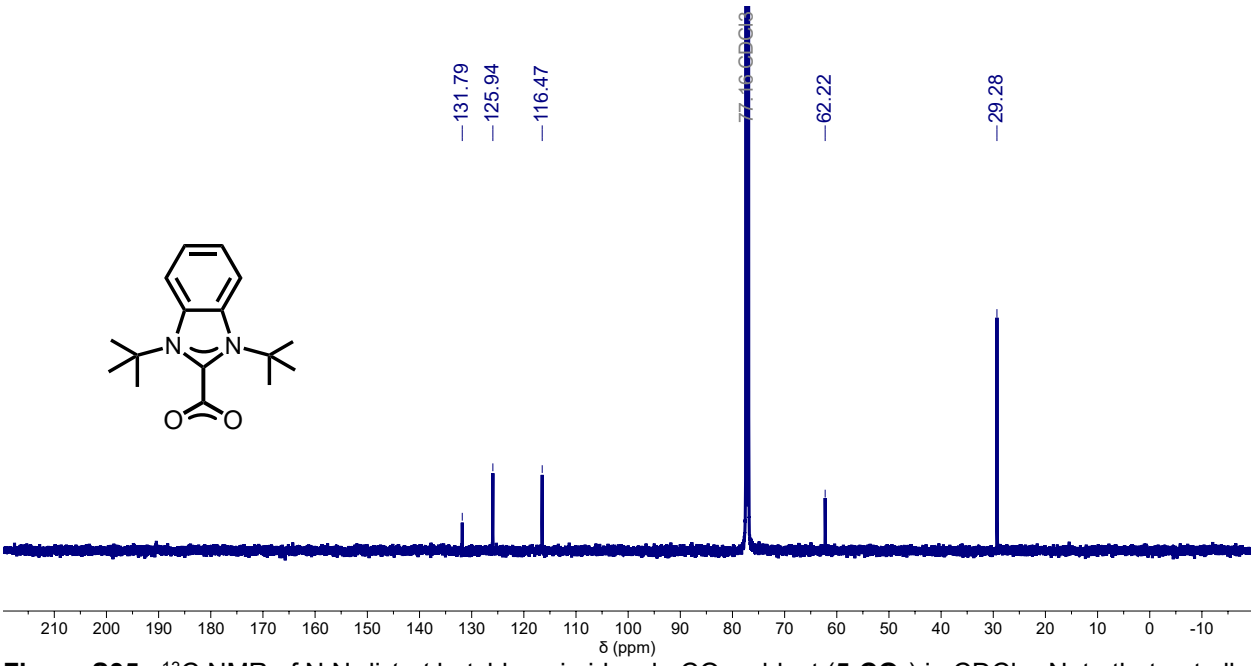


Figure S35. ^{13}C NMR of N,N-di-*tert*-butyl-benzimidazole CO_2-adduct (**5-CO$_2$**) in $CDCl_3$. Note that not all carbons are observed due to incredibly poor solubility.

Annotated NMR and MS for precursor compounds (incl. previously published).

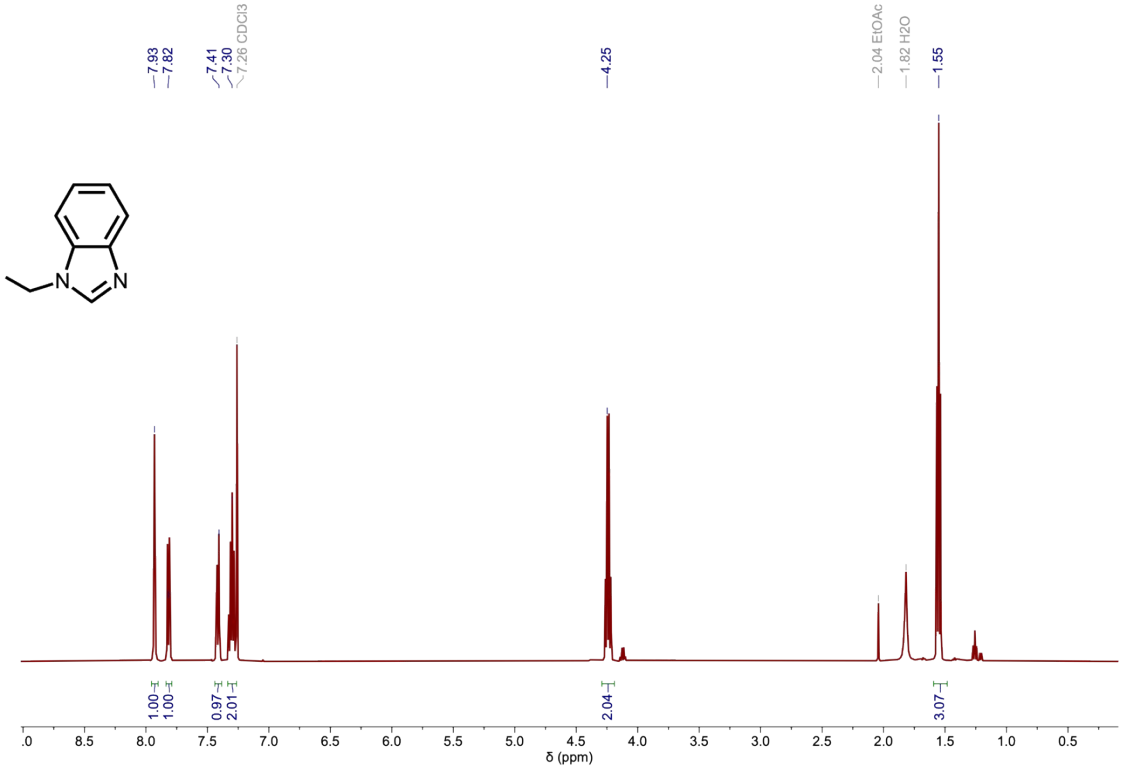


Figure S36. ^{1}H NMR of N-ethyl-benzimidazole (**2-1**) in $CDCl_3$.

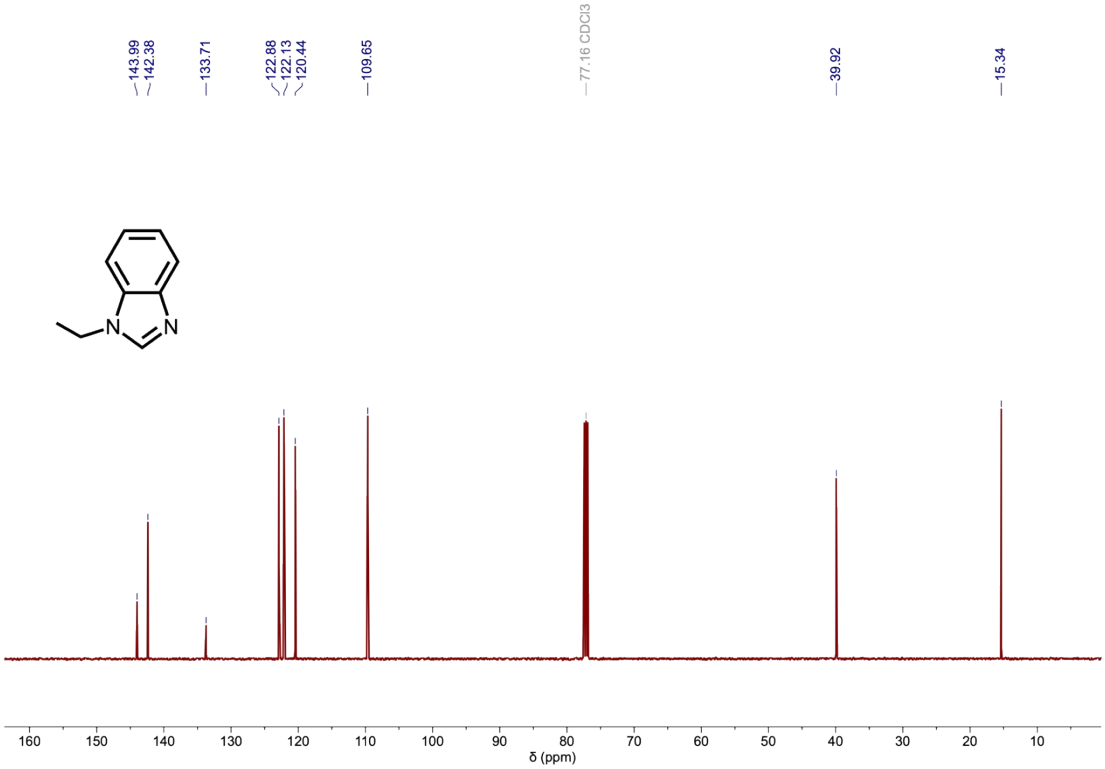


Figure S37. ^{13}C NMR of N-ethyl-benzimidazole (**2-1**) in $CDCl_3$.

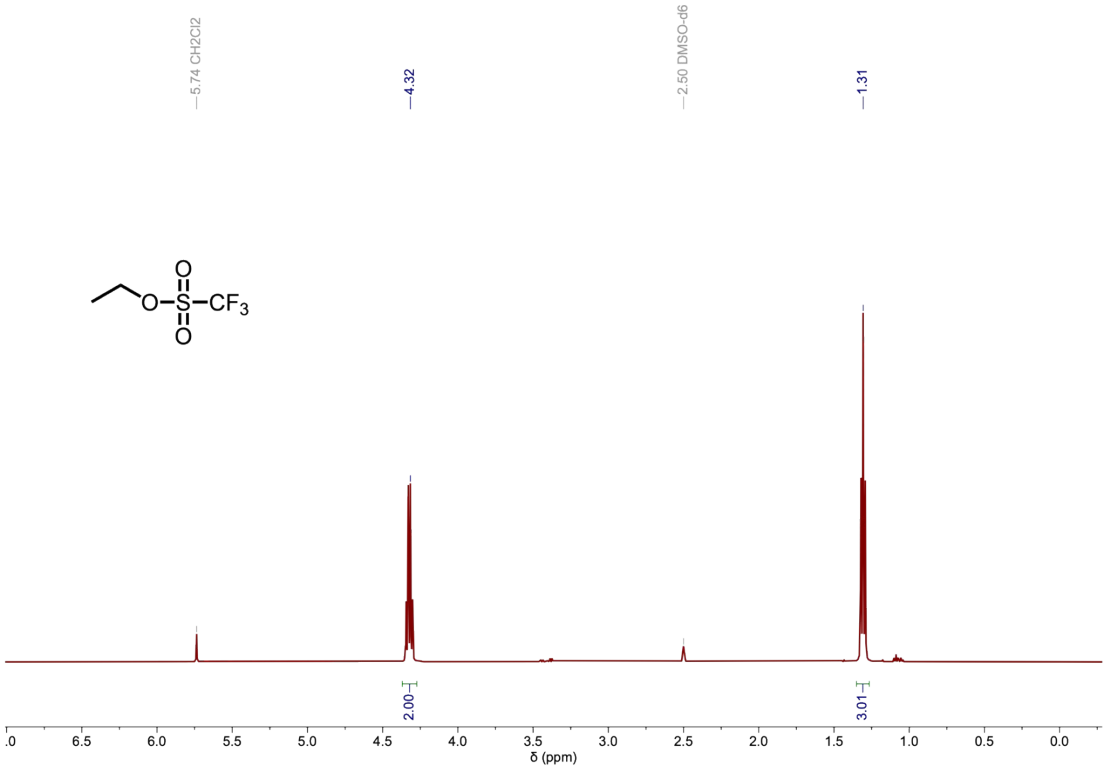


Figure S38. ^{1}H NMR of Ethyl triflate (**2-2**) in DMSO-d_6.

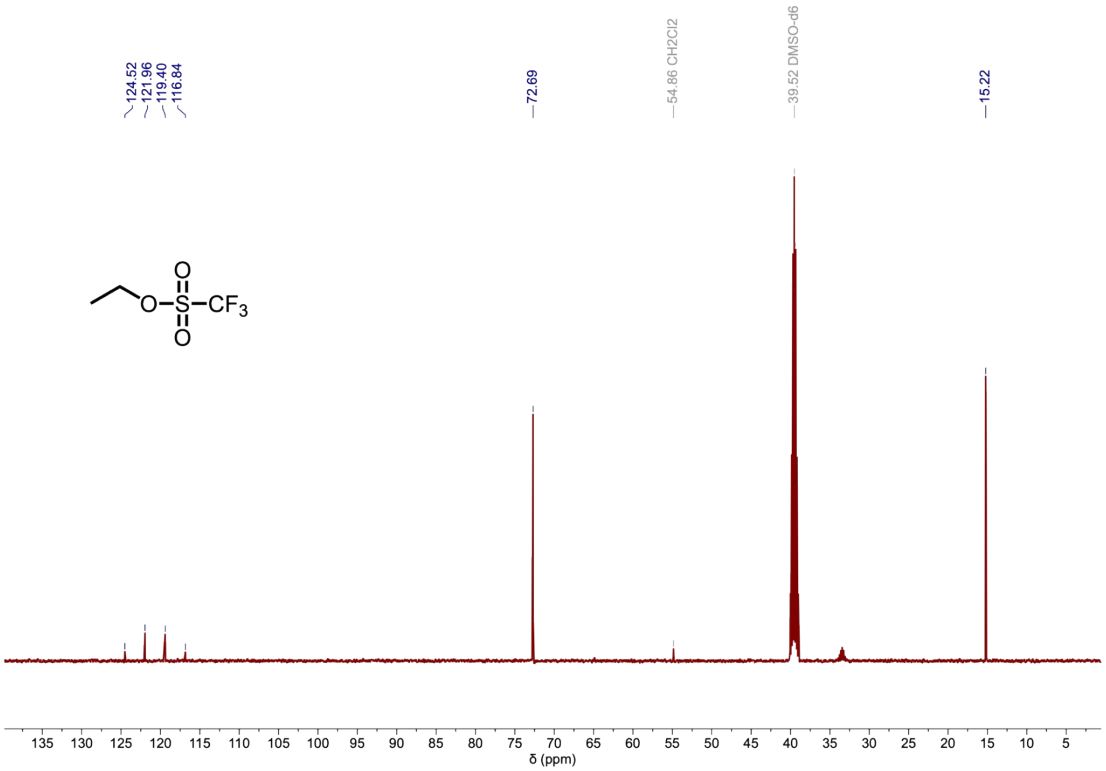


Figure S39. ^{13}C NMR of Ethyl triflate (**2-2**) in DMSO-d_6.

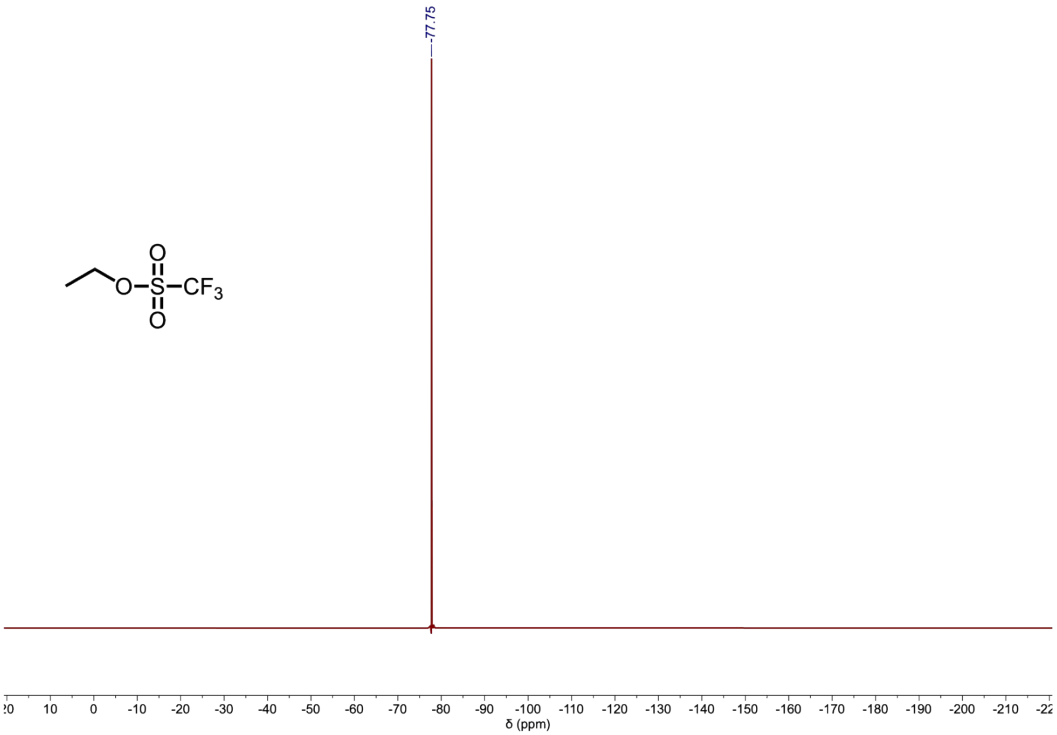


Figure S40. ^{19}F NMR of Ethyl triflate (**2-2**) in DMSO-d_6.

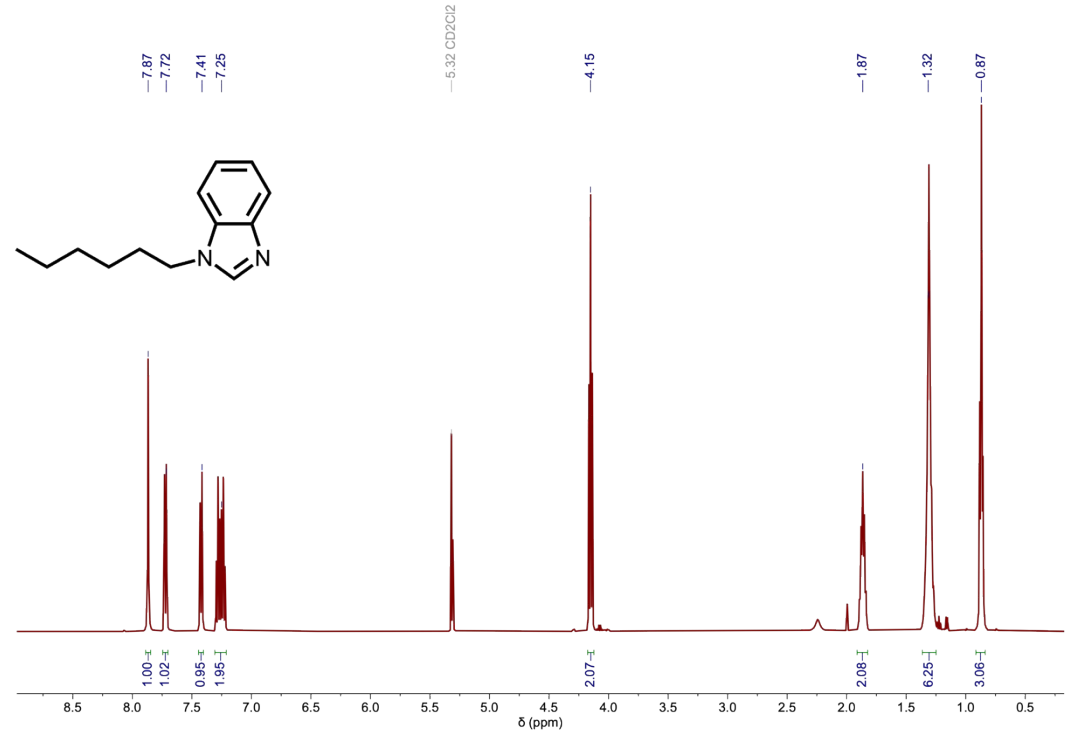


Figure S41. ^{1}H NMR of N-hexyl-benzimidazole (**3-1**) in CD_2Cl_2.

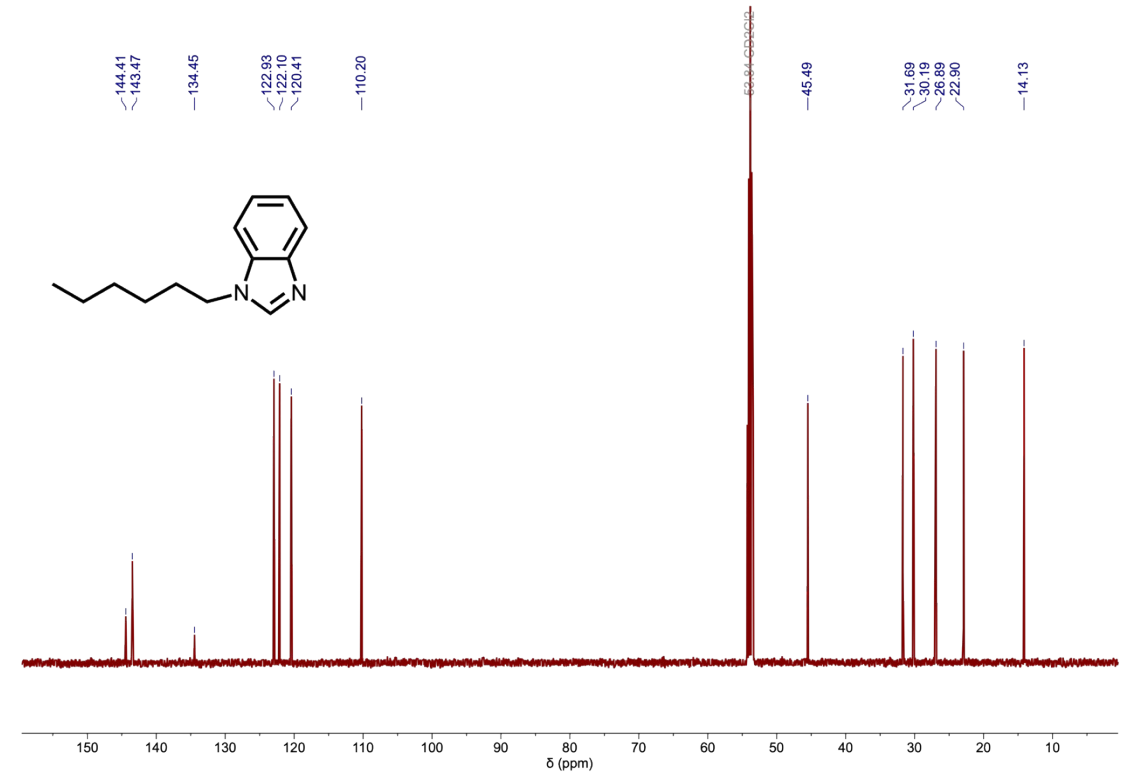


Figure S42. ^{13}C NMR of N-hexyl-benzimidazole (**3-1**) in CD_2Cl_2.

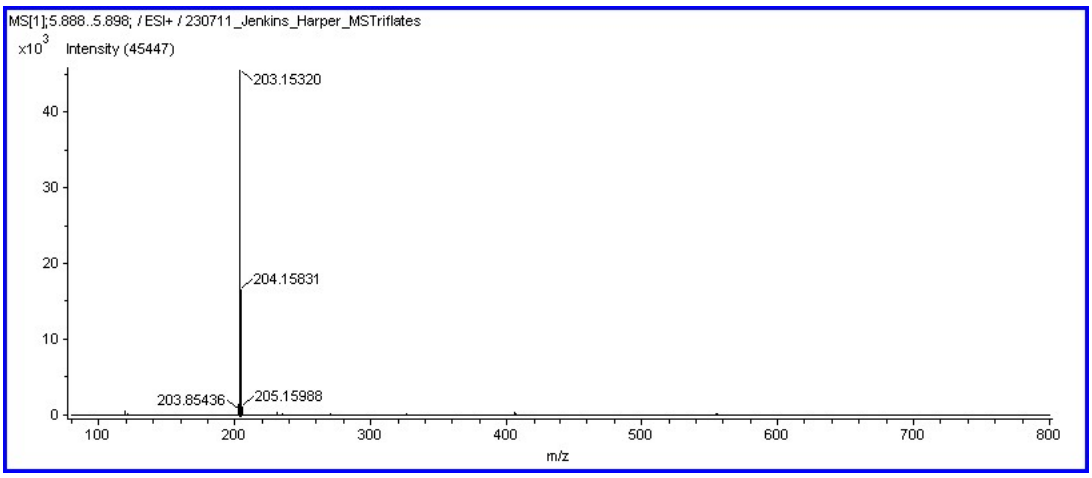


Figure S43. DART HR-MS of N-hexyl-benzimidazole (**3-1**).

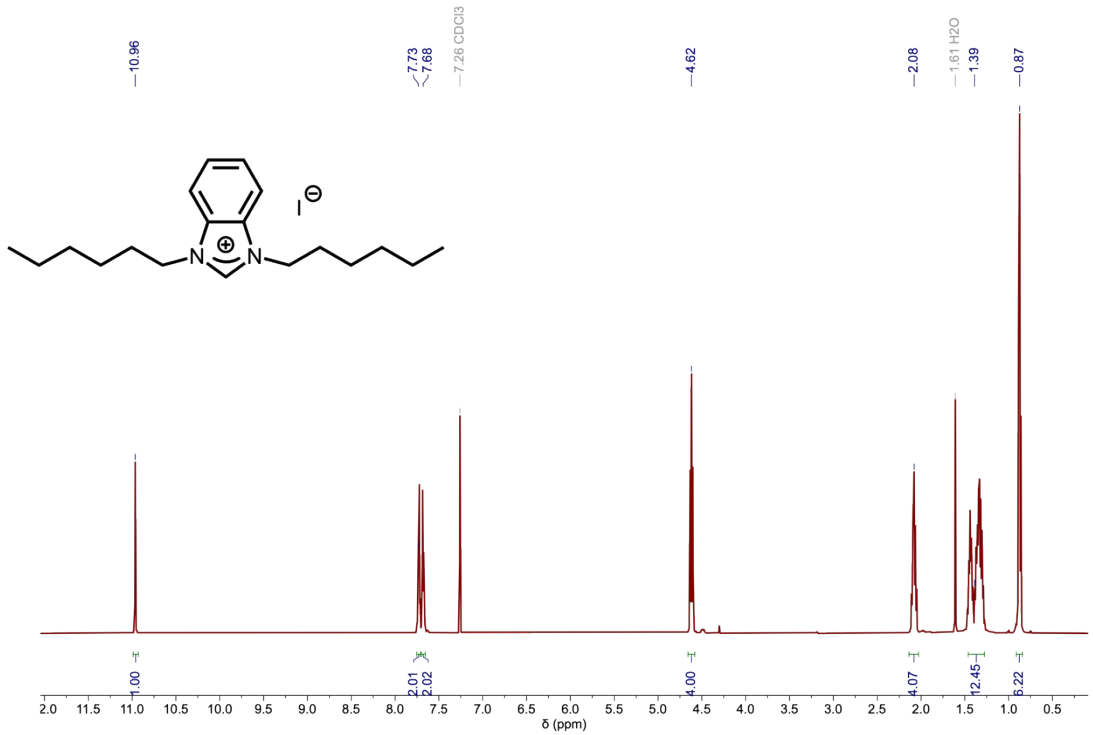


Figure S44. ^{1}H NMR of N,N-di-hexyl-benzimidazolium Iodide **(3-H)(I)** in $CDCl_3$.

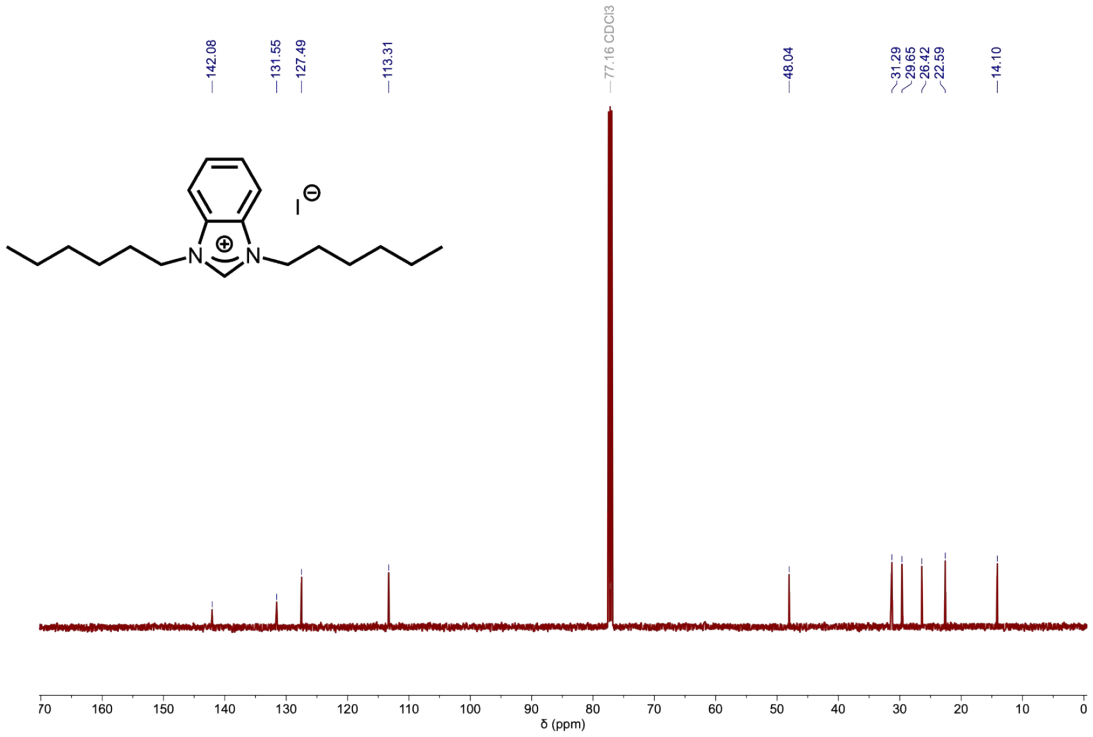


Figure S45. ^{13}C NMR of N,N-di-hexyl-benzimidazolium Iodide **(3-H)(I)** in $CDCl_3$.

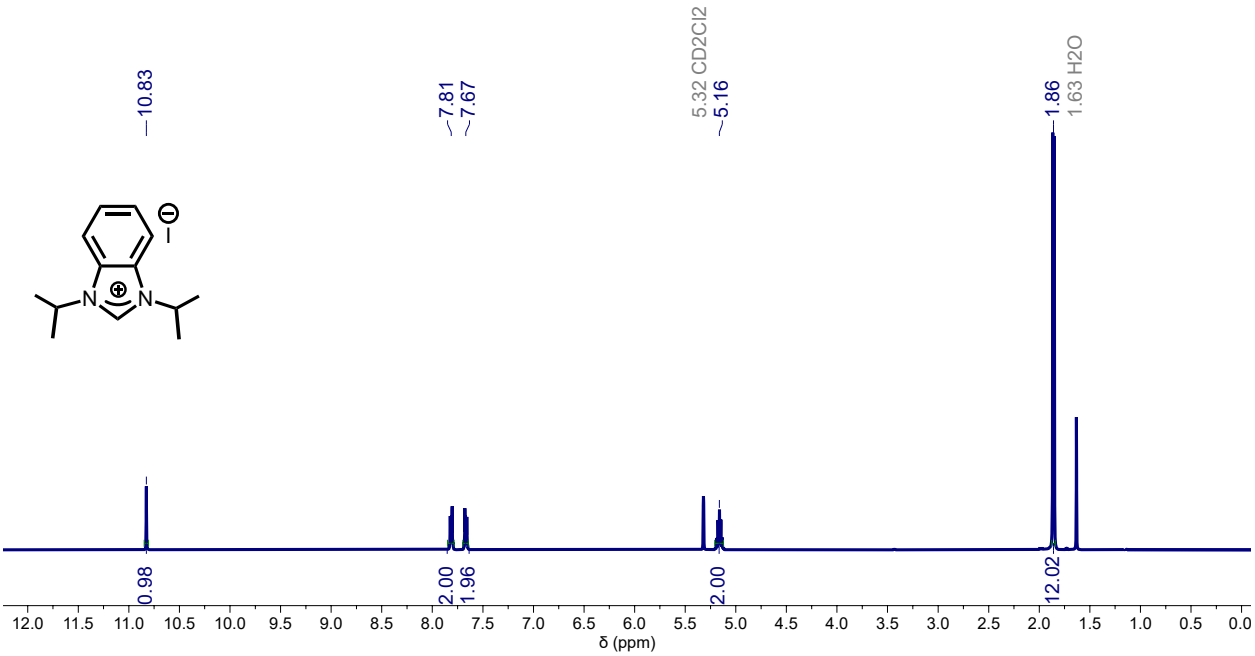


Figure S46. ^{1}H NMR of N,N-di-*iso*-propyl-benzimidazolium iodide **(4-H)(I)** in CD_2Cl_2.

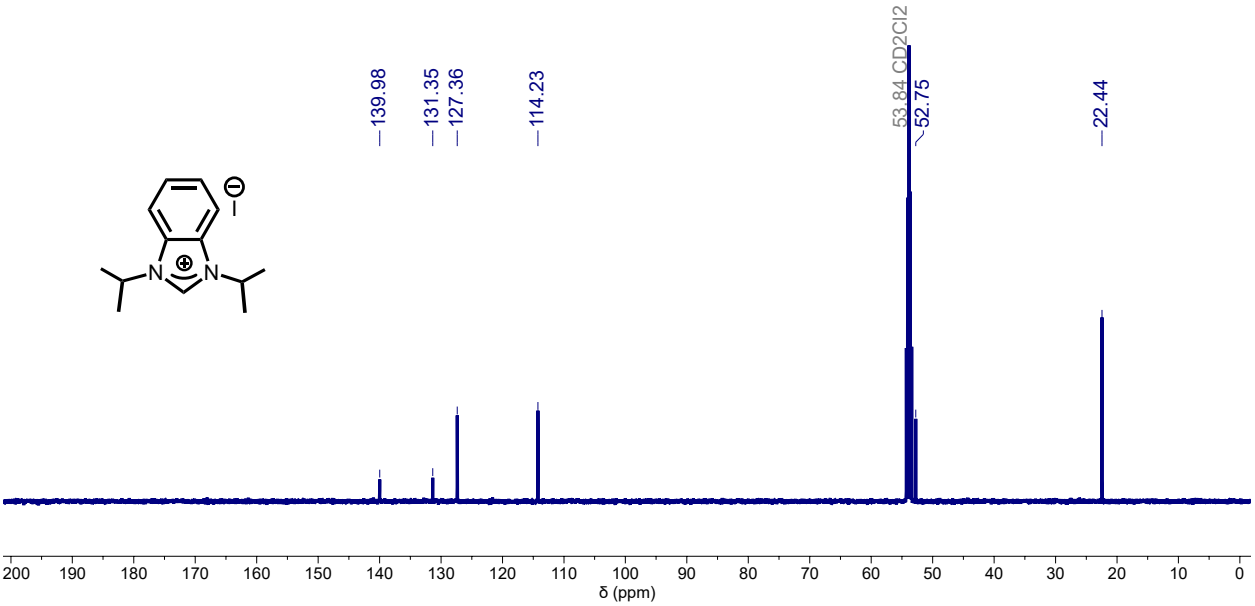


Figure S47. ^{13}C NMR of N,N-di-*iso*-propyl-benzimidazolium iodide **(4-H)(I)** in CD_2Cl_2.

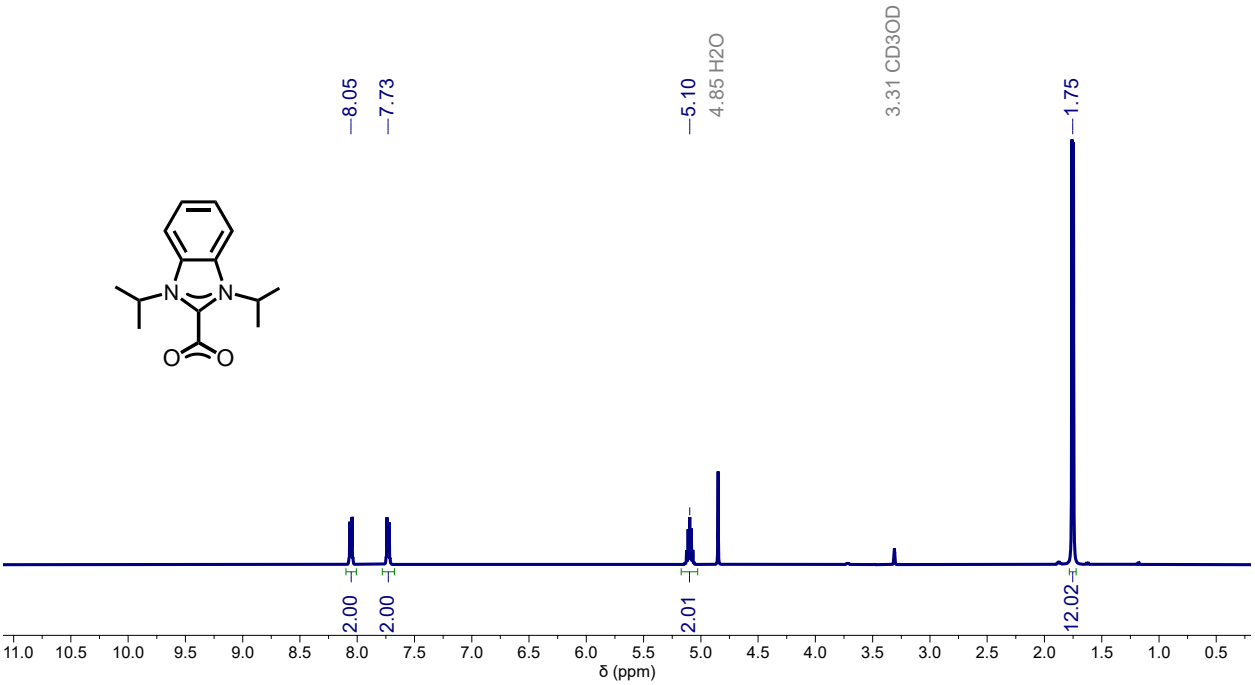


Figure S48. ^{1}H NMR of N,N-di-*iso*-propyl-benzimidazole CO_2-adduct (**4-CO_2**) in CD_3OD.

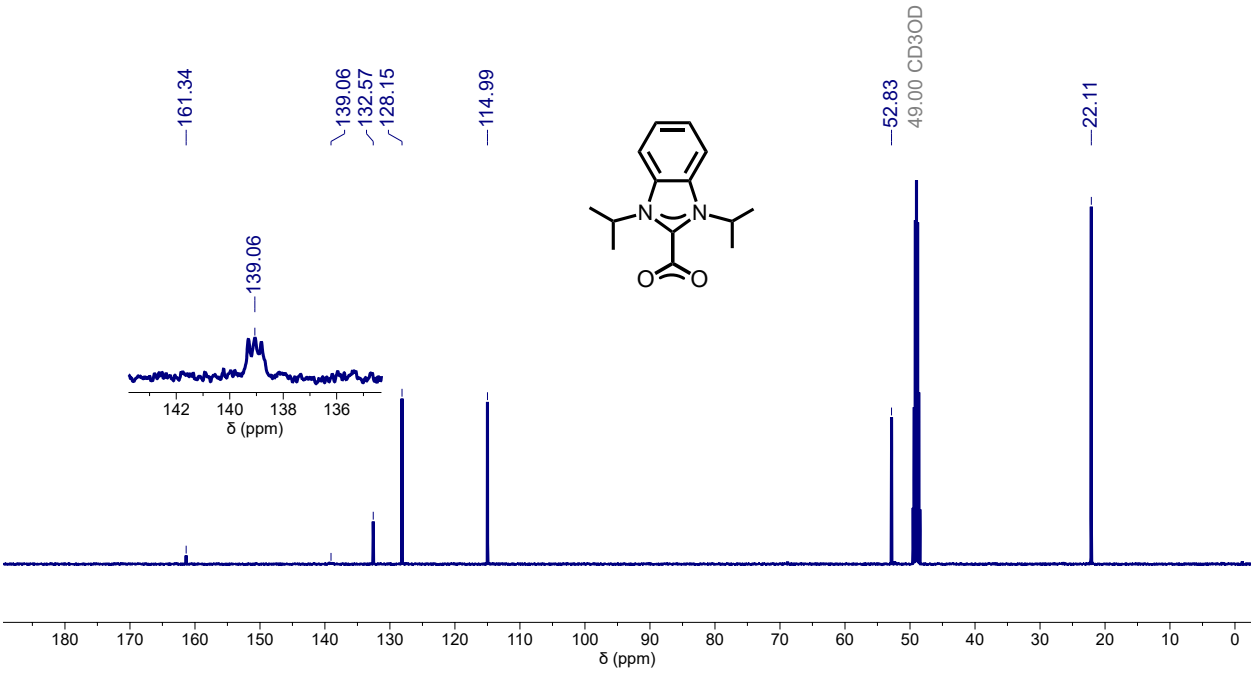


Figure S49. ^{13}C NMR of N,N-di-*iso*-propyl-benzimidazole CO_2-adduct (**4-CO_2**) in CD_3OD.

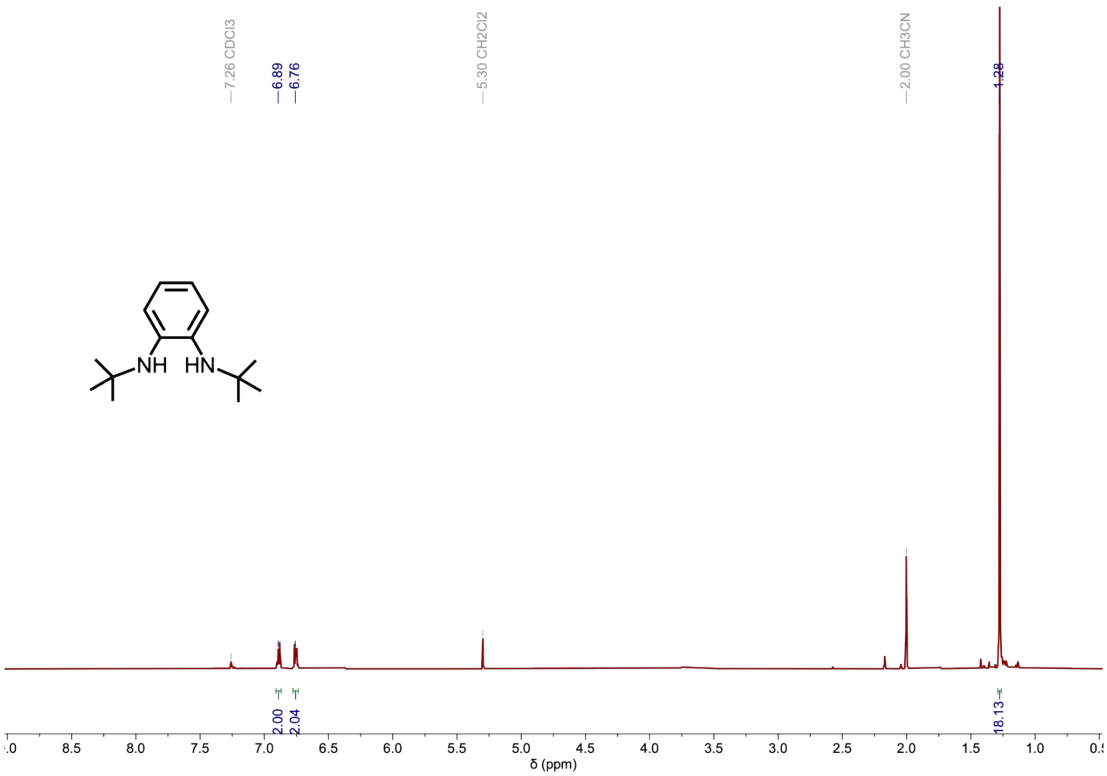


Figure S50. ^{1}H NMR of 1,2-di-*tert*-butylaminobenzene (**5-1**) in $CDCl_3$.

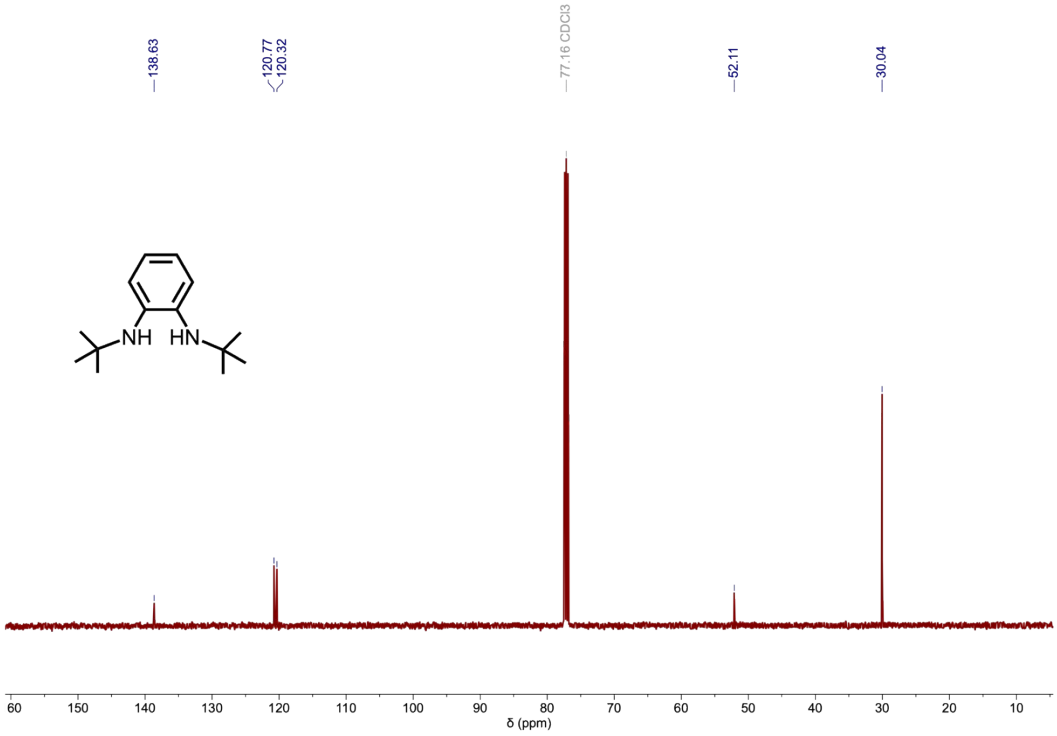


Figure S51. ^{13}C NMR of 1,2-di-*tert*-butylaminobenzene (**5-1**) in $CDCl_3$.

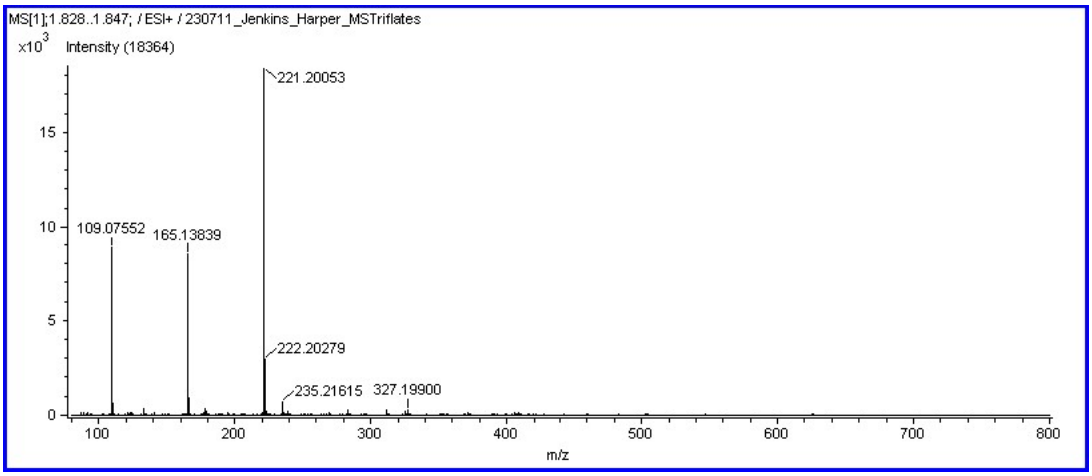


Figure S52. DART HR-MS of 1,2-di-*tert*-butylaminobenzene (**5-1**).

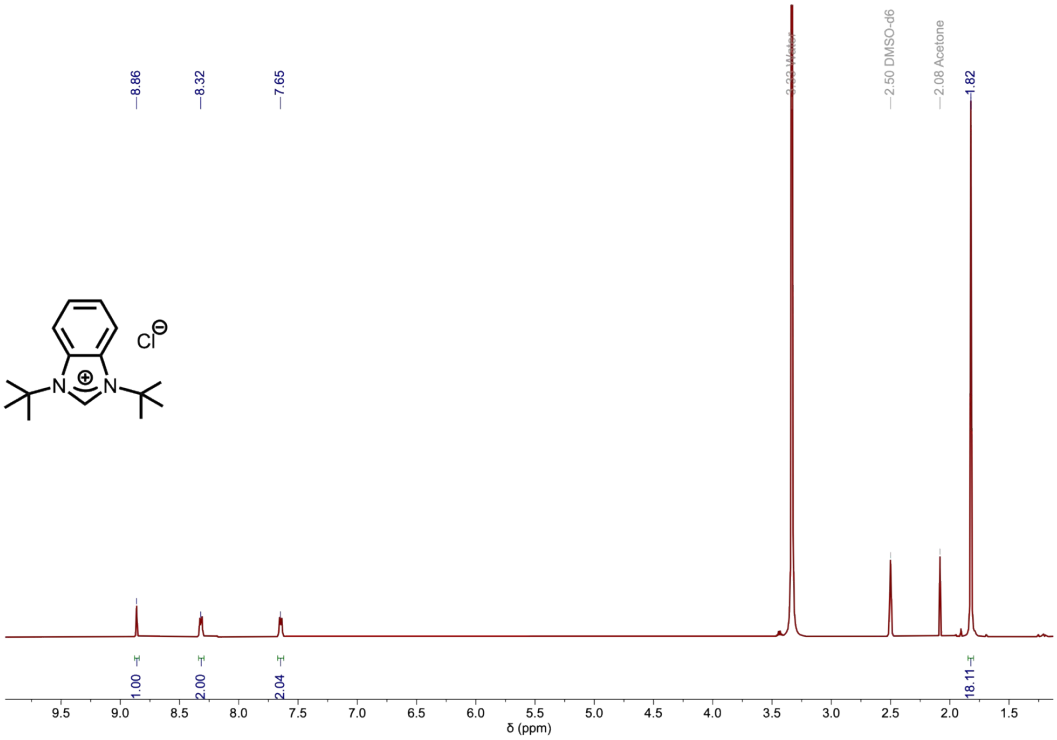


Figure S53. ^{1}H NMR of N,N-di-*tert*-butyl-benzimidazolium chloride (**4-H**)(**OTf**) in DMSO-d_6.

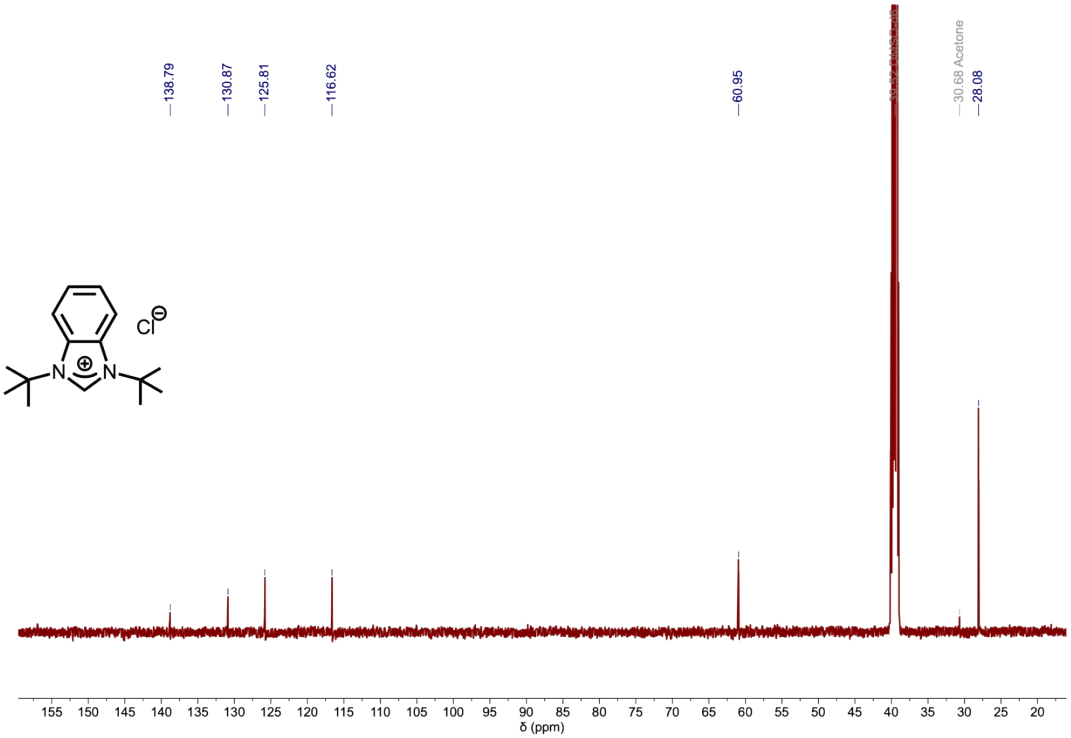


Figure S54. ^{13}C NMR of N,N-di-*tert*-butyl-benzimidazolium chloride (**4-H**)(**OTf**) in DMSO-d_6.

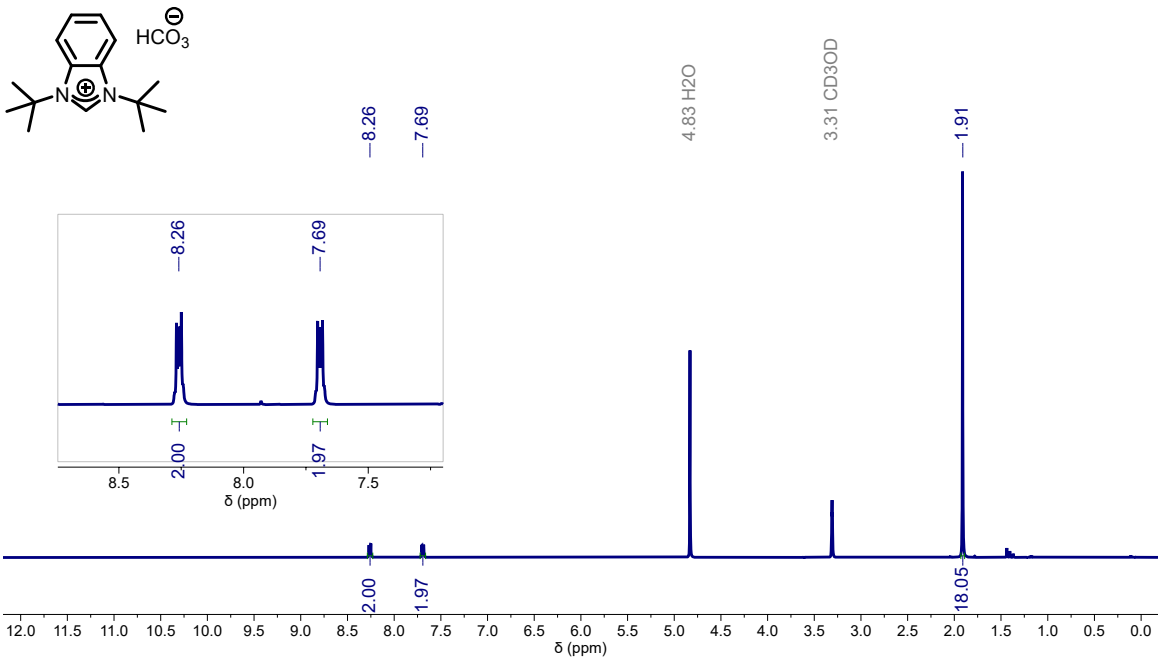


Figure S55. ^{1}H NMR of N,N-di-*tert*-butyl-benzimidazolium bicarbonate (**5-H**)(**HCO_3**) in CD_3OD.

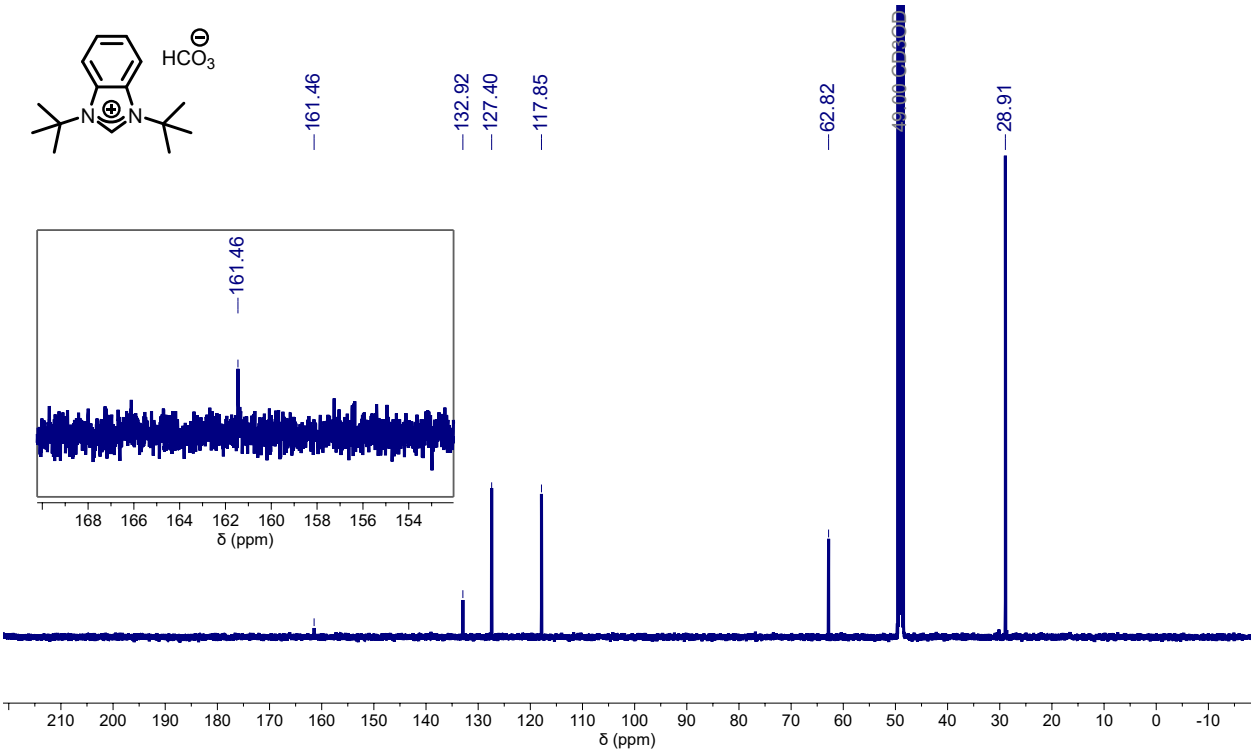


Figure S56. ^{13}C NMR of N,N-di-*tert*-butyl-benzimidazolium bicarbonate (**5-H**)(**HCO_3**) in CD_3OD.

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