Supplemental material for:

One-Pot Synthesis of *N*-Heterocyclic Carbene Ligands From a N-(2-iodoethyl)arylamine salts

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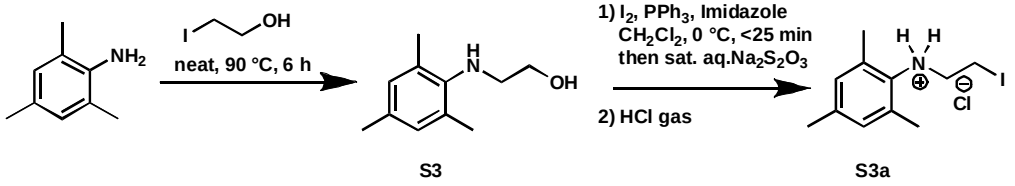
Table of Contents:

General Experimental: All air or moisture sensitive reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using dry, deoxygenated solvents. Methylene chloride was distilled under nitrogen from calcium hydride prior to use. All reagents were purchased from Aldrich and Acros and used without further purification. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} pre-coated plates (0.25 mm) from EMD Chemical Inc. and components were visualized by ultraviolet light (254 nm) and/or phosphomolybdic acid, anisaldehyde stain. Silicycle silica gel 230-400 (particle size 40-63 μm) mesh was used for all column chromatography. NHC-ligand syntheses were performed in Chemglass airfree sealed tubes. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer (at 300 MHz and 75 MHz respectively) in chloroform-*d* and DMSO-*d*6 at 23 $^{\circ}$C. Chemical shifts were referenced to the residual chloroform-H peak, which was set at 7.26 ppm for ^{1}H and 77.0 ppm (center peak) for ^{13}C spectra. In DMSO-*d*6, chemical shifts were referenced to the residual DMSO at 2.50 ppm for ^{1}H and 39.5 ppm (center peak) for ^{13}C spectra. Chemical shifts are reported in ppm, multiplicities are indicated by s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br = broad resonance), coupling constants, *J*, are reported in Hz. Data for ^{13}C NMR are reported in terms of chemical shift. High resolution mass spectral data were obtained from the Ohio State University, Mass Spectrometry & Proteomics Facility, Columbus, OH.

SM Scheme 1: Synthesis of 2-amino alcohols and their *N*(2-iodoethyl)aryl amine salts from *N*-arylamines.



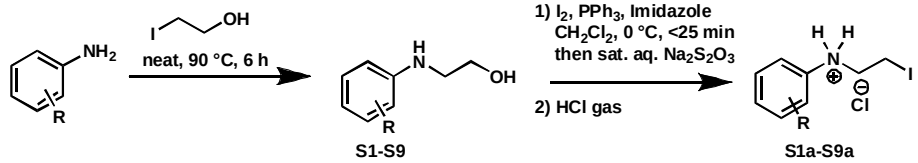
S3 S3a

Representative Procedure for the Synthesis of N(2-iodoethyl)aryl amine salts (SM Table 1, entry S4a):

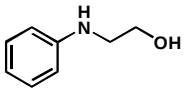
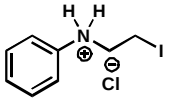
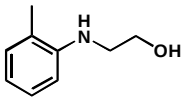
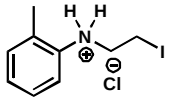
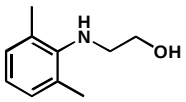
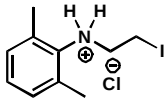
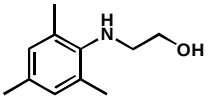
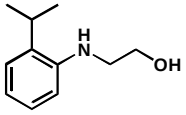
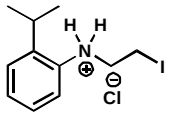
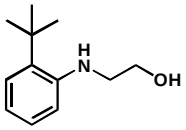
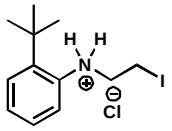
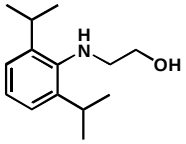
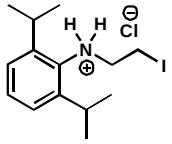
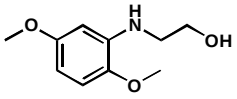
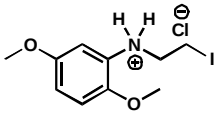
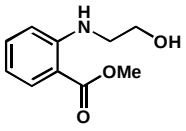
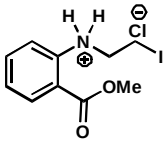
A mixture of 2,4,6-trimethylaniline (5.00 g, 37.03 mmol) and 2-iodoethanol (4.25 g, 24.69 mmol) was heated at 90 ºC under nitrogen atmosphere for 6 h, then the resulting solid was dissolved in ethyl acetate (100 mL) and washed with 2M aqueous NaOH solution (3 × 20 mL), brine solution (1 × 20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the concentrate mixture was purified by flash column chromatography (3:2 hexanes:EtOAc) to obtain the pure amino alcohol **S4** (8.95 g, 95% yield).

To a solution of triphenylphosphine (9.88 g, 37.68 mmol) in dry methylene chloride (330 mL) was added iodine (9.56 g, 37.68 mmol) and imidazole (2.56 g, 37.68 mmol) at 0 ºC. The resulting solution was stirred for 10 min, before a solution of amino alcohol **S4** (4.50 g, 25.12 mmol) in dry methylene chloride (105 mL) was added. The reaction mixture was then quenched with sat. aqueous $Na_2S_2O_3$ solution (150 mL) after 30 min. The organic layer was separated, and washed with brine and dried over $MgSO_4$. After removing the solvent under reduced pressure, the solid residue was dissolved in minimum amount of diethyl ether. The insoluble excess triphenylphosphine and the by-product triphenylphosphine oxide were filtered off through a Buchner funnel and the filtrate was evaporated under reduced pressure. This process was repeated another time to remove the left out unwanted phosphine impurities. The solid residue was fully dissolved in minimum amount of ethyl acetate, and then HCl gas was passed through it for about 5-10 min., the resulted solid was then filtered and washed with ethyl acetate, diethyl ether and then dried to obtain the pure 2-iodo amine hydrochloride salt **S4a** as a pale yellow crystalline solid (7.59 g, 93%).

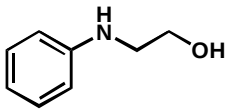
SM Table 1: Synthesis of *N*(2-iodoethyl)aryl amine salts from aryl amines



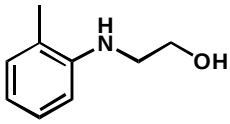
S1-S9 S1a-S9a

entry	Compund (S1-S8)		yield(%)	compound (S1a-S8a)		yield(%)
1		S1	90		S1a	87
2		S2	88		S2a	88
3		S3	88		S3a	88
4		S4	95		S4a	94
5		S5	86		S5a	90
6		S6	84		S6a	91
7		S7	84		S7a	87
8		S8	90		S8a	92
9		S9	58		S9a	80

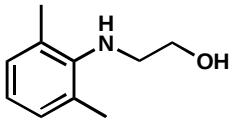
Spectral Data for the Substrates (Table 1):



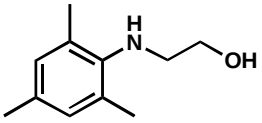
2-(Phenylamino)ethanol(S1, SM Table 1): Colorless liquid; R_F 0.38 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 3.34 (m, 2H), 3.52 (br, 1H), 3.86 (m, 2H), 6.72(m, 2H), 6.86 (m, 1H), 7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 147.8, 129.1, 117.7, 113.1, 60.9, 46.5; HRMS (EI^+) calc'd for $[C_8H_{11}NO+H]^+$: *m/z*, 138.1092 found 138.1101.



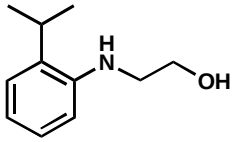
2-(o-Tolylamino)ethanol(S2, SM Table 1): Colorless dense liquid; R_F 0.36 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.16 (s, 3H), 3.24 (m, 2H), 3.46 (br, 1H), 3.76 (m, 2H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 6.9 Hz, 1H), 7.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 145.9, 130.2, 127.1, 122.6, 117.6, 110.2, 61.1, 46.1, 17.7; HRMS (EI^+) calc'd for $[C_9H_{13}NO+H]^+$: *m/z*, 152.0994 found 152.0999.



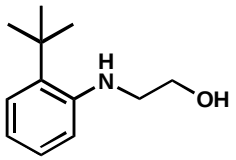
2-(2,6-Dimethylphenylamino)ethanol (S3, SM Table 1): Colorless dense liquid; R_F 0.32 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.33 (s, 6H), 2.83 (br, 1H), 3.15 (t, *J* = 5.1 Hz, 2H), 3.79 (t, *J* = 5.1 Hz, 2H), 6.86 (t, *J* = 6.9 Hz, 1H), 7.01 (dd, *J* = 6.9, 0.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 145.1, 129.8, 128.7, 122.3, 62.2, 50.3, 18.5; HRMS (EI^+) calc'd for $[C_{10}H_{15}NO+H]^+$: *m/z*, 166.1232 found 166.1248.



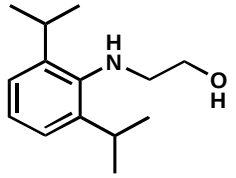
2-(2,4,6-Trimethylphenylamino)ethanol, (S4, SM Table 1): White solid; R_F 0.37 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.30 (s, 3H), 2.33 (s, 6H), 3.11 (m, 2H), 3.33 (br, 1H), 3.79 (m, 2H), 6.87 (d, *J* = 0.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 143.0, 132.0, 130.3, 129.7, 62.3, 50.9, 21.0, 18.6; HRMS (EI^+) calc'd for $[C_{11}H_{17}NO+H]^+$: *m/z*, 180.1388 found 180.1370.



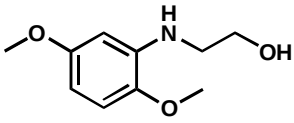
2-(2-Isopropylphenylamino)ethanol (S5, SM Table 1): Colorless dense liquid; R_F 0.43 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.24 (d, *J* = 6.6 Hz, 6H), 2.89 (sep, *J* = 6.6 Hz, 1H), 3.24 (m, 3H), 3.29 (br, 1H), 3.77 (m, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.74 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 144.5, 132.7, 126.5, 124.8, 117.7, 110.8, 60.9, 46.2, 27.0, 22.3; HRMS (EI^+) calc'd for $[C_{11}H_{17}NO+H]^+$: *m/z*, 180.1388 found 180.1372.



2-(2-*tert*-Butylphenylamino)ethanol (S6, SM Table 1): Colorless dense liquid; R_F 0.42 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.47 (s, 9H), 3.36 (t, *J* = 5.1 Hz, 2H), 3.92 (t, *J* = 5.1, 2H), 6.74 (m, 2H), 7.15 (m, 1H), 7.27 (dd, *J* = 7.8, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 146.1, 133.9, 127, 126.2, 117.6, 112.3, 61.27, 46.8, 34.3, 30.0; HRMS (EI^+) calc'd for $[C_{12}H_{19}NO+H]^+$: *m/z*, 194.1467 found 194.1459, HRMS (EI^+) calc'd for $[C_{12}H_{19}NO+Na]^+$: *m/z*, 216.1364 found 216.1345.

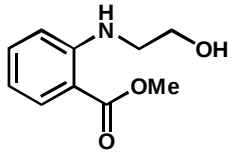


2-(2,6-Diisopropylphenylamino)ethanol (S7, SM Table 1): White crystalline solid; R_F 0.42 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$- *d*) δ 1.27 (d, *J* = 6.9 Hz, 12H), 3.07 (m, 2H), 3.33 (sep, *J* = 6.9 Hz, 2H), 3.85 (m, 2H), 7.11 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 142.5, 142.4, 123.9, 123.5, 62.3, 53.5, 27.6, 24.3; HRMS (EI^+) calc'd for $[C_{14}H_{23}NO+Na]^+$: *m/z*, 244.1677 found 244.1656.

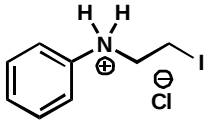


2-(2,5-Dimethoxyphenylamino)ethanol (S8, SM Table 1): Gray powder; R_F 0.32 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 3.29 (m, 2H), 3.76 (s, 3H), 3.8 (s, 3H),

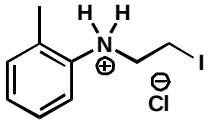
3.81 (m, 3H), 6.18 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.25 (d, *J* = 3.0 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 154.4, 141.6, 138.7, 109.8, 99.1, 98.4, 61.1, 55.3, 55.5, 45.8; HRMS (EI^+) calc'd for $[C_{10}H_{15}NO_3+H]^+$: *m/z*, 198.1052 found 198.1124.



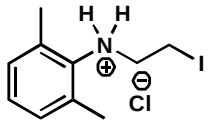
Methyl 2-(2-hydroxyethylamino)benzoate (S9, SM Table 1): Colorless dense liquid; R_F 0.38 (3:2 hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 3.43 (t, *J* = 5.7 Hz, 2H), 3.87 (s, 3H), 3.89 (t, *J* = 5.4 Hz, 2H), 6.63 (dt, *J* = 7.8, 0.6 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 1H), 7.36 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 168.8, 150.8, 134.4, 131.5, 114.6, 111.1, 110.0, 60.9, 51.4, 44.9; HRMS (EI^+) calc'd for $[C_{10}H_{13}NO_3+H]^+$: *m/z*, 196.0895 found 196.0889.



***N*-(2-Iodoethyl)benzenaminium chloride (S1a, SM Table 1):** White powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 3.39 (m, 2H), 3.58 (m, 2H), 7.19 (m, 1H), 7.34-7.43 (m, 4H), 4.91 (br, 2H); ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ 129.5, 129.4, 126.0, 119.7, 51.7, -4.7; HRMS (EI^+) calc'd for $[C_8H_{11}ClIN\text{-}Cl+H]^+$: *m/z*, 248.0166 found 248.01891.

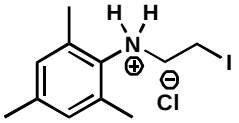


***N*-(2-iodoethyl)-2-methylbenzenaminium chloride (S2a, SM Table 1):** White powder; ^{1}H NMR (300 MHz, $CHCl_3$-*d*) δ 2.27 (s, 3H), 3.31 (m, 4H), 6.91-7.06 (m, 3H), 7.34 (m, 1H), 10.91 (br, 2H); ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ 132.7, 132.5, 131.7, 129.9, 127.7, 124.2, 53.6, 18.2, -6.8; HRMS (EI^+) calc'd for $[C_9H_{13}ClIN\text{-}Cl]^+$: *m/z*, 262.0899 found 262.0891.

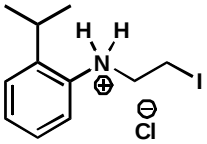


***N*-(2-iodoethyl)-2,6-dimethylbenzenaminium chloride (S3a, SM Table 1):** Pale pink powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.81 (s, 6H), 3.87 (m, 4H), 7.26 (m, 2H), 7.33 (m, 1H), 11.27 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 132.2, 132.0, 130.1, 129.3,

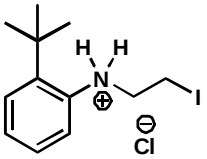
52.9, 19.0, -6.0; HRMS (EI^+) calc'd for $[C_{10}H_{15}ClIN\text{-}Cl]^+$: *m/z*, 276.0243 found 276.0249.



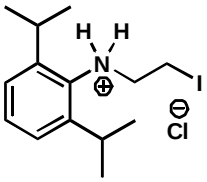
***N*-(2-iodoethyl)-2,4,6-trimethylbenzenaminium chloride (S4a, SM Table 1):** Pale yellow crystalline solid; ^1H NMR (300 MHz, $CDCl_3$-*d*) δ 2.28 (s, 3H), 2.63 (s, 6H), 3.63-3.81 (m, 4H), 6.91 (s, 2H), 11.05 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 139.4, 132.0, 130.8, 129.5, 53.2, 20.8, 19.1, -6.7; HRMS (EI^+) calc'd for $[C_{11}H_{17}ClIN\text{-}Cl]^+$: *m/z*, 290.0402 found 290.0410.



***N*-(2-iodoethyl)-2-isopropylbenzenaminium chloride (S5a, SM Table 1):** Colorless dense liquid; ^1H NMR (300 MHz, $CDCl_3$-*d*) δ 1.32 (d, *J* = 6.6 Hz, 6H), 3.35 (sep, *J* = 6.6 Hz, 1H), 3.62 (br, 4H), 7.25 (m, 1H), 7.42 (m, 2H), 7.67 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 143.3, 131.7, 130.8, 128.9, 128, 124.8, 55.5, 28.5, 25.1, -6.7; HRMS (EI^+) calc'd for $[C_{11}H_{17}ClIN\text{-}Cl]^+$: *m/z*, 290.0403 found 290.0409.

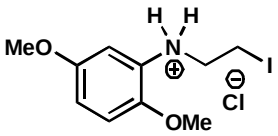


2-*tert*-butyl-*N*-(2-iodoethyl)benzenaminium chloride (S6a, SM Table 1): White powder; ^1H NMR (300 MHz, $CDCl_3$-*d*) δ 1.55 (s, 9H), 3.82 (m, 4H), 7.33 (m, 2H), 7.48 (m, 1H), 7.69 (m, 1H), 10.23 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 143.3, 133.5, 129.8, 128.9, 128.3, 126.1, 57, 35.5, 32.2, -4.8; HRMS (EI^+) calc'd for $[C_{12}H_{19}ClIN\text{-}Cl]^+$: *m/z*, 304.0562 found 304.0567.

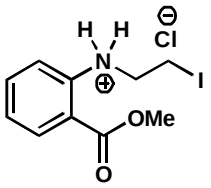


***N*-(2-iodoethyl)-2,6-diisopropylbenzenaminium chloride (S7a, SM Table 1):** Yellow solid; ^1H NMR (300 MHz, $CDCl_3$-*d*) δ 1.33 (d, *J* = 6.6 Hz, 12H), 3.59 (sep, *J* = 6.6 Hz, 2H), 3.64-3.83 (m, 4H), 7.25 (m, 2H), 7.39 (m, 1H), 11.2 (br, 2H); ^{13}C NMR (75 MHz,

$CDCl_3$-*d*) δ 143.3, 130.0, 128.6, 125.7, 55.3, 28.5, 25.0, -5.9; HRMS (EI^+) calc'd for $[C_{14}H_{23}ClIN\text{-}Cl]^+$: *m/z*, 332.0872 found 332.0891.

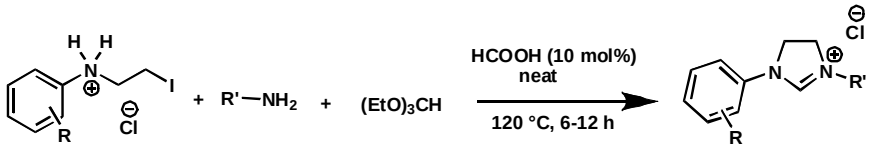


***N*-(2-iodoethyl)-2,5-dimethoxybenzenaminium chloride (S8a, SM Table 1):** White powder; ^1H NMR (300 MHz, $CHCl_3$-*d*) δ 3.56 (m, 2H), 3.69 (m, 2H), 3.78 (s, 3H), 3.92 (s, 3H), 6.91 (d, *J* = 2.7 Hz, 1H), 6.93 (s, 1H), 7.35 (dd, *J* = 0.6, 2.7 Hz, 1H), 9.01 (br, 2H); ^{13}C NMR (75 MHz, $CHCl_3$-*d*) δ 153.6, 146.3, 123.3, 116.2, 113.6, 109.9, 56.9, 56.0, 52.9, -5.7; HRMS (EI^+) calc'd for $[C_{10}H_{15}ClINO_2\text{-}Cl]^+$: *m/z*, 308.0142 found 308.0148.



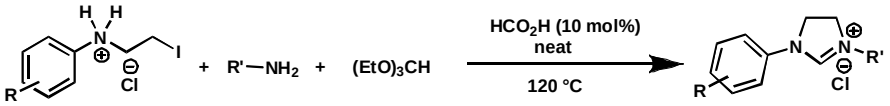
***N*-(2-iodoethyl)-2-(methoxycarbonyl)benzenaminium chloride (S9a, SM Table 1):** White crystalline powder; ^1H NMR (300 MHz, $CDCl_3$-*d*) δ 3.39 (m, 2H), 3.58 (m, 2H), 3.79 (s, 3H), 6.61 (m, 1H), 7.79 (m, 1H), 7.38 (m, 1H), 7.66 (br, 1H), 7.79 (dd, *J* = 7.8, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 166.6, 140.0, 134.8, 131.9, 125.5, 121.2, 118.9, 53.0, 52.3, -2.7; HRMS (EI^+) calc'd for $[C_{10}H_{13}ClINO_2\text{-}Cl]^+$: *m/z*, 306.0868 found 306.0786.

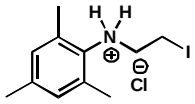
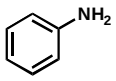
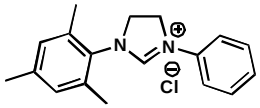
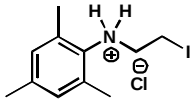
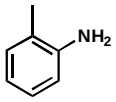
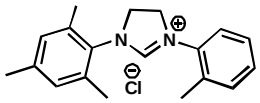
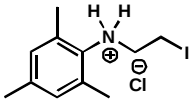
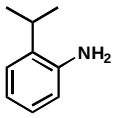
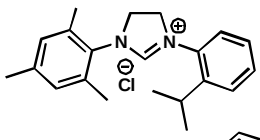
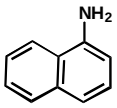
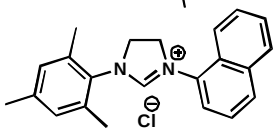
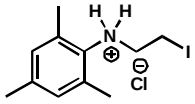
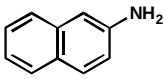
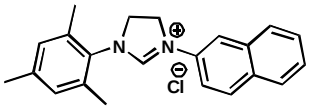
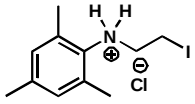
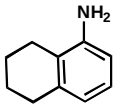
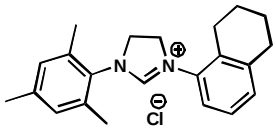
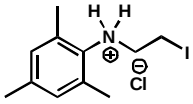
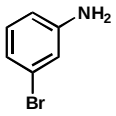
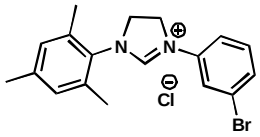
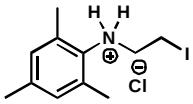
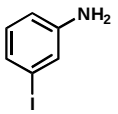
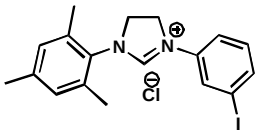
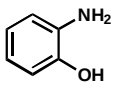
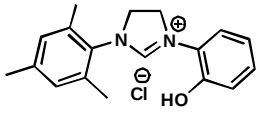
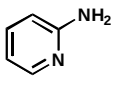
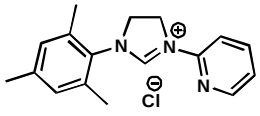
SM Scheme 2: Synthesis of symmetrical, unsymmetrical and chiral NHC-ligands

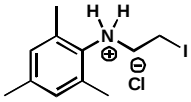
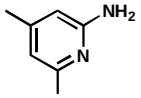
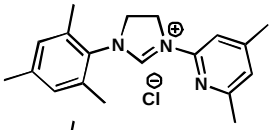
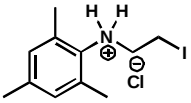
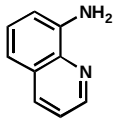
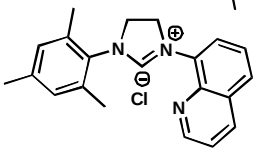
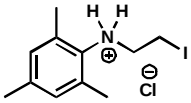
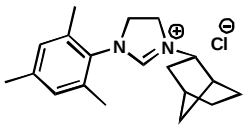
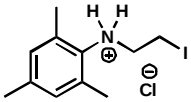
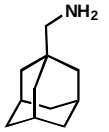
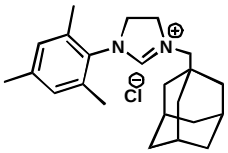
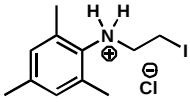
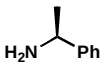
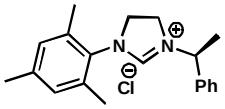
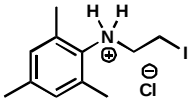
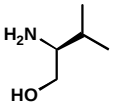
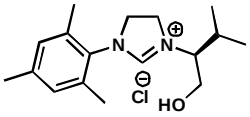
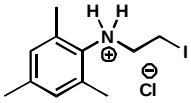
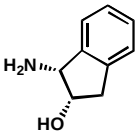
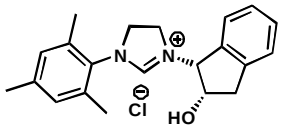
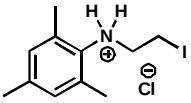
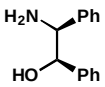
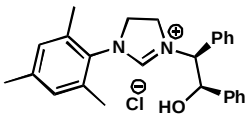
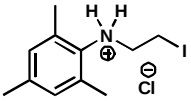
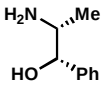
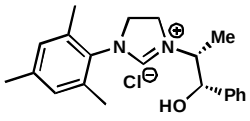
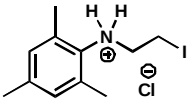
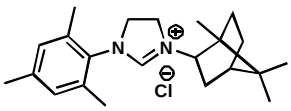


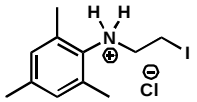
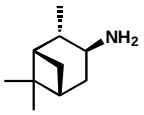
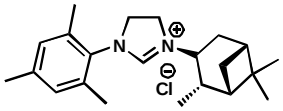
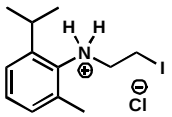
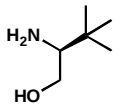
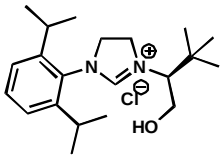
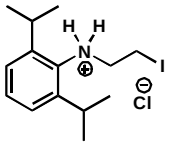
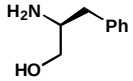
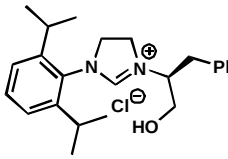
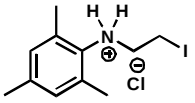
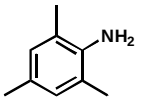
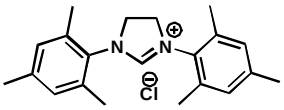
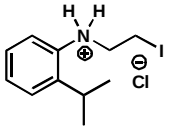
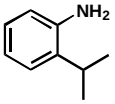
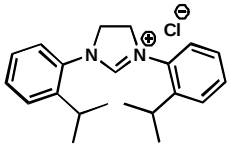
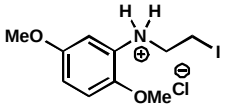
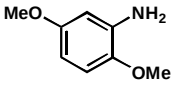
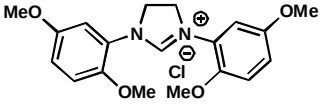
General Procedure for synthesis of *N*-heterocyclic carnbene ligands: To a mixture of *N*(2-iodoethyl)aryl amine salt (10 mmol), amine (10 mmol), and triethylorthoformate (20 mmol), few drops of formic acid (10 mol%) was added and heated to 120 ºC in a sealed tube for 6-12 h. (a) The resulting precipitate was isolated and washed with toluene (2 × 6 mL) and diethyl ether (2 × 6 mL) to obtain the pure *N*-heterocyclic carbene compound in moderate to good yields. (b) If the resulting product is a gummy compound, few drops of acetone was added and then triturated with diethyl ether or 20% diethyl ether in hexanes until the pure solid product was obtained.

SM Table 2: Synthesis of various symmetrical, unsymmetrical and chiral NHC-ligands

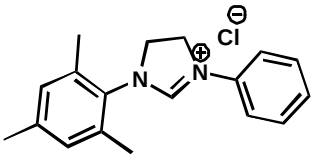


entry	amine salt		amine (R'-NH_2)	NHC-ligand		yield(%)
1		S3a			S3a.1	76
2		S3a			S3a.2	71
3		S3a			S3a.3	67
4		S3a			S3a.4	72
5		S3a			S3a.5	77
6		S3a			S3a.6	60
7		S3a			S3a.7	72
8		S3a			S3a.8	70
9		S3a			S3a.9	65
10		S3a			S3a.10	72

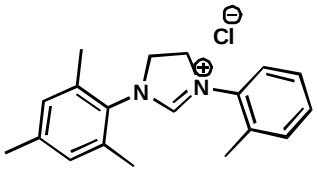
entry	amine salt		amine (R-NH_2)	NHC-ligand		yield(%)
11		S3a			S3a.11	94
12		S3a			S3a.12	83
13		S3a			S3a.13	72
14		S3a			S3a.14	89
15		S3a			S3a.15	29
16		S3a			S3a.16	32
17		S3a			S3a.17	56
18		S3a			S3a.18	50
19		S3a			S3a.19	66
20		S3a			S3a.20	76

entry	amine salt		amine (R-NH_2)	NHC-ligand		yield(%)
21		S3a			S3a.21	62
22		S7a			S7a.1	31
23		S7a			S7a.2	35
24		S3a			S3a.22	83
25		S5a			S5a.1	68
26		S8a			S8a.1	80

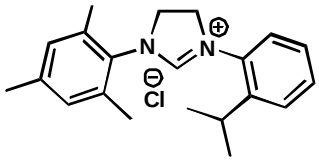
Spectral Data for the NHC-ligands (SM Table 2)



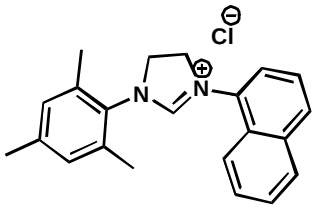
1-(2,3,6-Trimethylphenyl)-3-phenyl-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.1, SM Table 2): Pale orange powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.30, (s, 3H), 2.33 (s, 6H), 4.38 (m, 2H), 4.66 (m, 2H), 7.08 (s, 2H), 7.34 (m, 1H), 7.52 (m, 4H), 9.62 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 155.8, 139.9, 136, 135.2, 131, 129.5, 129.2, 126.5, 117.9, 50.7, 48.5, 20.6, 17.3; HRMS (EI^+) calc'd for $[C_{18}H_{21}ClN_2\text{-}Cl]^+$: *m/z*, 265.1705 found 265.1697.



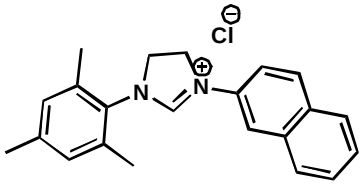
1-(2,4,6-Trimethylphenyl)-3-*o*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.2, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.31 (s, 3H), 2.45 (s, 6H), 2.49 (s, 3H), 4.62 (m, 2H), 4.91 (m, 2H), 6.95 (s, 2H), 7.31 (m, 3H), 7.77 (d, 6.3 Hz), 8.46 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 157.2, 140.6, 135, 133.7, 133.1, 131.8, 130.2, 130.1, 130.0, 128.8, 126.6, 53.7, 52.3, 21.1, 19.9, 18.7; HRMS (EI^+) calc'd for $[C_{19}H_{23}ClN_2\text{-}Cl]^+$: *m/z*, 279.1861 found 279.1852.



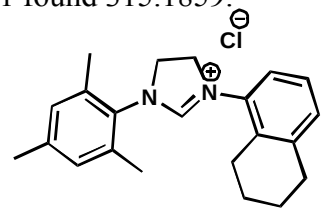
3-(2-Isopropylphenyl)-1-(2,4,6-trimethylphenyl-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.3, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 1.27 (d, *J* = 6.9 Hz, 6H), 2.29 (s, 3H), 2.36 (s, 6H), 3.18 (sep, *J* = 6.9 Hz, 1H), 4.37-4.56 (m, 4H), 7.07 (s, 2H), 7.40 (m, 1H), 7.58 (m, 3H), 9.11 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 159.4, 144.9, 139.4, 135.1, 133.2, 130.8, 130.6, 129.3(d) 127.2, 127.1, 53.6, 51.2, 27.5, 23.8, 20.6, 17.3; HRMS (EI^+) calc'd for $[C_{21}H_{27}ClN_2\text{-}Cl]^+$: *m/z*, 307.2174 found 307.2161.



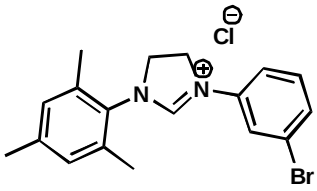
1-(2,4,6-Trimethylpheny)-3-(naphthalen-1-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.4, SM Table 2): off white powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.30 (s, 3H), 2.45 (s, 6H), 4.52 (m, 2H), 4.72 (m, 2H), 7.09 (s, 2H), 7.66-7.79 (m, 3H), 7.89 (dd, *J* = 7.5, 0.9 Hz, 1H), 8.14 (m, 3H), 9.29 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 159.9, 139.4, 135.2, 133.7, 132.0, 130.9, 130.0, 129.3, 128.5, 128.0, 127.9, 127.3, 125.6, 124.6, 121.7, 53.3, 51.4, 20.6, 17.5; HRMS (EI^+) calc'd for $[C_{22}H_{23}ClN_2\text{-}Cl]^+$: *m/z*, 315.1866 found 315.1857.



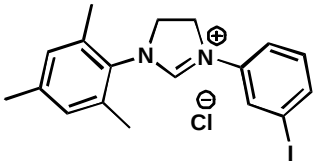
1-(2,4,6-Trimethylpheny)-3-(naphthalen-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.5, SM Table 2): Pale brown powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.31 (s, 3H), 2.37 (s, 6H), 4.45 (m, 2H), 4.79 (m, 2H), 7.58 (m, 2H), 7.09 (s, 2H), 7.83 (dd, *J* = 9, 2.4 Hz, 1H), 7.98 (m, 3H), 8.09 (d, *J* = 9 Hz, 1H), 9.78 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 155.9, 139.5, 135.3, 133.6, 132.7, 131.0, 130.8, 129.5, 129.2, 127.6, 127.5, 127.4, 126.1, 117.0, 115.0, 50.8, 48.7, 20.6, 17.3; HRMS (EI^{+}) calc'd for $[C_{22}H_{23}ClN_2\text{-}Cl]^{+}$: *m/z*, 315.1861 found 315.1859.



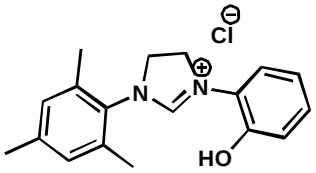
1-(2,4,6-Trimethylpheny)-3-(5,6,7,8-tetrahydronaphthalen-1-yl)-4,5-dihydro-1H-imidazol-3-ium chloride (S3a.6, SM Table 2): Brown powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.93 (m, 4H), 2.39 (s, 3H), 2.52 (s, 6H), 2.90 (m, 4H), 4.65-4.73 (m, 2H), 4.90-4.97 (m, 2H), 7.03 (s, 2H), 7.25 (m, 2H), 7.59 (m, 1H), 8.48 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 157.2, 140.3, 139.7, 134.9, 133.4, 132.7, 131.1, 129.9, 129.8, 126.6, 123.8, 53.5, 52.2, 29.3, 25.5, 22.5, 22.1, 21.0, 18.8; HRMS (EI^{+}) calc'd for $[C_{22}H_{27}ClN_2\text{-}Cl]^{+}$: *m/z*, 319.2174 found 319.2166



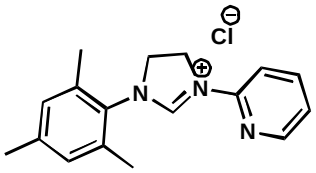
3-(3-Bromophenyl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.7, SM Table 2): Red crystalline solid; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.3 (s, 3H), 2.32 (s, 6H), 4.39 (m, 2H), 4.63 (m, 2H), 7.07 (s, 2H), 7.52 (m, 3H), 7.86 (s, 1H), 9.62 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 157.1, 140.4, 138.2, 136.0, 132.1, 131.6, 130.0, 129.8, 123.1, 121.6, 117.7, 51.7, 49.3, 21.4, 18.1; HRMS (EI^{+}) calc'd for $[C_{18}H_{20}BrClN_2\text{-}Cl]^{+}$: *m/z*, 343.0801 found 343.0805.



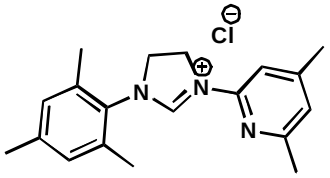
3-(3-Iodophenyl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.8, SM Table 2): White powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.3 (s, 3H), 2.32 (s, 6H), 4.36 (m, 2H), 4.62 (m, 2H), 7.07 (s, 2H), 7.30 (t, *J* = 8.4 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.98 (t, *J* = 2.4 Hz, 1H), 9.59 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 156.3, 139.4, 137.3, 135.2, 134.8, 131.1, 130.8, 129.2, 129.1, 126.2, 117.3, 50.7, 48.4, 20.6, 17.3; HRMS (EI^{+}) calc'd for $[C_{18}H_{20}ClIN_2]^{+}$: *m/z*, 391.0338 found 391.0345.



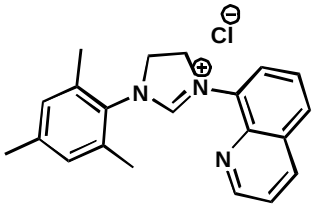
3-(2-Hydroxyphenyl)-1-(2,4,6-trimethylpheny)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.9, SM Table 2): Brown powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.29 (s, 3H), 2.32 (s, 6H), 4.32 (m, 2H), 4.62 (m, 2H), 6.95 (m, 1H), 7.05 (m, 2H), 7.06 (s, 2H), 7.24 (m, 1H), 7.41 (dd, *J* = 7.8, 1.2 Hz, 1H), 9.22 (s, 1H), 10.8 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 158.3, 149.7, 139.0, 134.9, 130.7, 128.9, 128.9, 128.6, 123.1, 119.1, 116.2, 50.4, 49.9, 20.2, 16.9; HRMS (EI^{+}) calc'd for $[C_{18}H_{21}ClN_2O\text{-}Cl]^{+}$: *m/z*, 281.1654 found 281.1644.



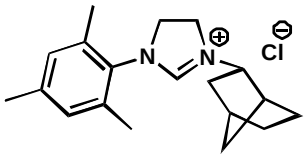
1-(2,4,6-Trimethylpheny)-3-(pyridin-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.10, SM Table 2): White powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.30 (s, 3H), 2.34 (s, 6H), 4.32 (m, 2H), 4.68 (m, 2H), 7.08 (s, 2H), 7.39 (t, *J* = 6.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 8.02 (t, *J* = 7.5 Hz, 1H), 8.48 (d, *J* = 3.6 Hz, 1H), 9.87 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 156, 147.9, 139.2, 138.8, 134.6, 130.5, 128.8, 121.4, 111.6, 51.2, 46.8, 20.3, 17.0; HRMS (EI^{+}) calc'd for $[C_{17}H_{20}ClN_3\text{-}Cl]^{+}$: *m/z*, 266.1657 found 266.1647.



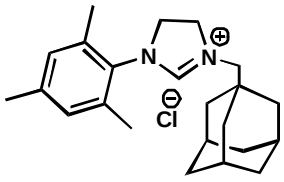
3-(4,6-Dimethylpyridin-2-yl)-1-(2,4,6-Trimethylpheny)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.11, SM Table 2): Brown powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.3 (s, 3H), 2.37 (s, 6H), 2.4 (s, 3H), 4.71 (m, 2H), 5.03 (m, 2H), 6.90 (s, 1H), 6.95 (s, 2H), 7.14 (s, 1H), 9.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7, 153.7, 151.4, 146.4, 140.5, 134.4, 129.9, 129.7, 123.0, 109.3, 53.0, 48.0, 23.7, 20.9, 20.9, 18.4; HRMS (EI^+) calc'd for $[C_{19}H_{24}ClN_3\text{-}Cl]^+$: *m/z*, 294.1970 found 294.1963.



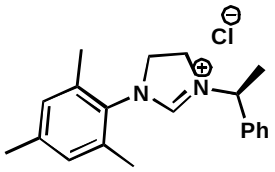
1-(2,4,6-Trimethylpheny)-3-(quinolin-8-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.12, SM Table 2): Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 2.34 (s, 3H), 2.49 (s, 6H), 4.65 (m, 2H), 5.26 (m, 2H), 7.01 (s, 2H), 7.54 (dd, *J* = 3.9, 4.2 Hz, 1H), 7.65 (t, *J* = 8.1 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.30 (dd, *J* = 6.9, 1.5 Hz, 1H), 8.83 (dd, *J* = 2.7, 1.5 Hz, 1H), 9.71 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 158.1, 150.2, 140.8, 140.0, 137.3, 135.3, 131.7, 130.6, 130.0, 129.1, 127.6, 126.8, 122.3, 122.0, 52.9, 51.0, 21.1, 18.6; HRMS (EI^+) calc'd for $[C_{21}H_{22}ClN_3\text{-}Cl]^+$: *m/z*, 316.1814 found 316.1809.



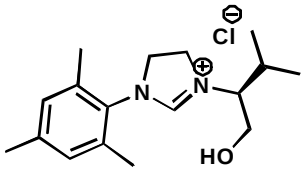
3-*exo*-Bicyclo[2.2.1]heptan-2-yl-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.13, SM Table 2): White crystalline powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.31-1.88 (m, 8H), 2.27 (s, 3H), 2.31 (s, 6H), 2.43 (br, 1H), 2.62 (d, *J* = 4.2 Hz, 1H), 4.11 (dd, *J* = 7.8, 4.5 Hz, 1H), 4.31 (m, 4H), 6.89 (s, 2H), 8.69, (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 156.0, 139.8, 135.4, 130.4, 129.6, 61.7, 51.0, 48.4, 40.7, 37.1, 36.2, 36.1, 27.5, 26.8, 21.0, 18.6; HRMS (EI^+) calc'd for $[C_{19}H_{27}ClN_2\text{-}Cl]^+$: *m/z*, 283.2174 found 283.2170.



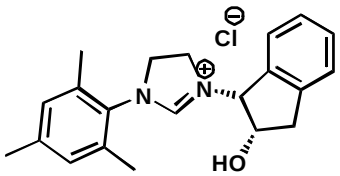
3-(1-Adamantanemethyl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.14, SM Table 2): White crystalline powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.63 (s, 6H), 1.69 (m, 6H), 2.05 (br, 3H), 2.29 (s, 3H), 2.33 (s, 6H), 3.64 (s, 2H), 4.12 (m, 2H), 4.29 (m, 2H), 6.91 (s, 2H), 9.5 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 160.6, 140.1, 135.1, 130.4, 129.8, 60.2, 52.5, 50.8, 40.4, 36.5, 34.5, 28.1, 21.1, 18.1; HRMS (EI^+) calc'd for $[C_{23}H_{33}ClN_2\text{-}Cl]^+$: *m/z*, 337.2644 found 337.2636.



(*S*)-1-(2,4,6-Trimethylpheny)-3-(1-phenylethyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.15, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.79 (d, *J* = 6.9 Hz, 3H), 2.22 (s, 3H), 2.28 (br, 6H), 4.17 (m, 4H), 5.59 (q, *J* = 6.9 Hz, 1H), 6.93 (s, 3H), 7.41 (m, 5H), 8.87 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 156.6, 140.0, 136.8, 134.9, 130.3, 129.7, 129.1, 128.9, 126.9, 57.5, 51.0, 47.2, 20.9, 19.1, 18.5; HRMS (EI^+) calc'd for $[C_{20}H_{25}ClN_2\text{-}Cl]^+$: *m/z*, 293.2018 found 293.2007.

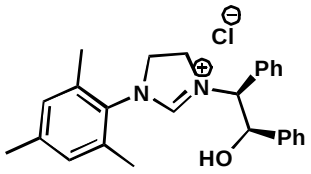


(*S*)-3-(1-Hydroxy-3,3-dimethylbutan-2-yl)-1-(2,4,6-Trimethylpheny)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.16, SM Table 2): Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.02 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.91 (sep, *J* = 6.6 Hz, 1H), 2.29 (br, 9H), 3.68-4.50 (m, 8H), 6.92 (s, 2H), 8.43 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 158.8, 140.3, 130.1, 129.9, 129.7, 66.8, 58.2, 50.7, 45.9, 27.6, 21.1, 20.3, 19.0; HRMS (EI^+) calc'd for $[C_{17}H_{27}ClN_2O\text{-}Cl]^+$: *m/z*, 275.2112 found 275.2116.

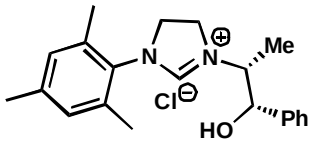


3-((1*R*,2*S*)-2-Hydroxy-2,3-dihydro-1*H*-inden-1-yl)-1-(2,4,6-trimethylpheny)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.17, SM Table 2): Brown solid; ^{1}H NMR

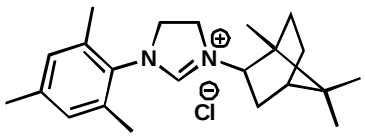
(300 MHz, $CDCl_3$-*d*) δ 2.26 (s, 3H), 2.36 (s, 6H), 3.03 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.26 (dd, *J* = 16.8, 6.9 Hz, 1H), 4.09-4.43 (m, 4H), 4.89 (br, 1H), 5.05 (d, *J* = 4.8 Hz, 1H), 5.44 (d, *J* = 6 Hz, 1H), 6.88 (s, 2H), 7.24-7.4 (m, 3H), 7.41 (d, *J* = 6.9 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 158.4, 141.7, 140.3, 135.5, 130.3, 129.8, 129.7, 127.6, 127.6, 125.7, 125.1, 70.0, 65.2, 50.9, 49.7, 39.0, 21.0, 18.7; HRMS (EI^+) calc'd for $[C_{21}H_{25}ClN_2O\text{-}Cl]^+$: *m/z*, 321.1967 found 321.1962.



3-((1*S*,2*R*)-2-Hydroxy-1,2-diphenylethyl)-1-(2,4,6-Trimethylpheny)-4,5-dihydro-1H-imidazol-3-ium chloride (S3a.18, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.13 (s, 3H), 2.23 (s, 6H), 3.75-4.22 (m, 4H), 5.12 (d, *J* = 8.4 Hz, 1H), 5.46 (d, *J* = 8.1 Hz, 1H), 5.99 (br, 1H), 6.97 (s, 2H), 7.29-7.53 (m, 10H), 8.79 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 157.9, 141.5, 139.2, 135.0, 130.7, 129.1, 128.8, 128.4, 128.3, 128.3, 127.9, 126.8, 71.3, 66.1, 49.9, 47.2, 20.5, 17.0; HRMS (EI^+) calc'd for $[C_{26}H_{29}ClN_2O\text{-}Cl]^+$: *m/z*, 385.2280 found 385.2269.

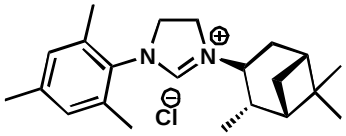


3-((1*S*,2*R*)-1-Hydroxy-1-phenylpropan-2-yl)-1-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.19, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.26 (d, *J* = 7.2 Hz, 3H), 2.30 (s, 3H), 2.36 (br, 6H), 3.80-4.06 (m, 2H), 4.28 (m, 1H), 4.50-4.63 (m, 2H), 5. 38 (m, 1H), 6.93 (s, 2H), 7.27-7.37 (m, 3H), 7.46 (m, 2H), 8.47 (s, 1H); HRMS (EI^+) calc'd for $[C_{21}H_{27}ClN_2O\text{-}Cl]^+$: *m/z*, 323.2123 found 323.2114.

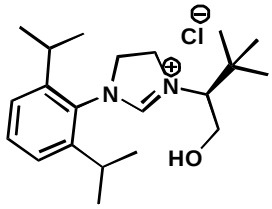


1-(2,4,6-Trimethylphenyl)-3-(*endo*-(1*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.20, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 8.95 (s, 1H), 6.92 (s, 2H), 4.53-4.20 (m, 5H), 2.50-2.42 (m,

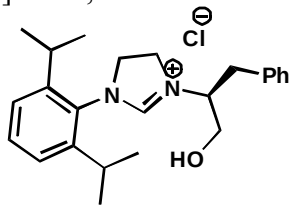
1H), 2.35 (br, 6H), 2.29 (s, 3H), 1.85 (m, 2H), 1.56-1.33 (m, 4H), 1.03 (s, 3H), 0.99 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 158.9, 140.2, 135.1, 130.5, 129.8, 64.8, 50.9, 50.7, 50.7, 49.0, 44.5, 32.8, 28.5, 28.0, 21.1, 19.7, 18.7, 18.3, 14.5; HRMS (EI^+) calc'd for $[C_{22}H_{33}ClN_2O\text{-}Cl]^+$: *m/z*, 325.2644 found 325.2633.



1-Mesityl-3-((1S,2S,3R,5R)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)-4,5-dihydro-1H-imidazol-3-ium chloride(S3a.21, SM Table 1): White crystalline powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 0.85 (d, *J* = 9.9 Hz, 1H), 1.0 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.16 (s, 3H), 1.96-1.81 (m, 3H), 2.21 (s, 6H), 2.24 (br, 4H), 2.39 (m, 1H), 2.54 (m, 1H), 4.37-4.19 (m, 4H), 4.93 (m, 1H), 6.82 (s, 2H), 9.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 157.6, 139.7, 135, 130.3, 129.5, 56.8, 50.9, 46.8, 44.6, 40.9, 39.6, 38.2, 34.7, 31.5, 27.8, 23.6, 20.9, 19.9, 18.2; HRMS (EI^+) calc'd for $[C_{22}H_{33}ClN_2\text{-}Cl]^+$: *m/z*, 325.2647 found 325.2678.

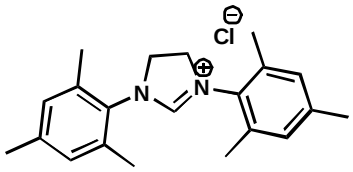


(*S*)-1-(2,6-Diisopropylphenyl)-3-(1-hydroxy-3,3-dimethylbutan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S7a.1, SM Table 2): Yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.10 (s, 9H), 1.26 (d, *J* = 5.4 Hz, 3H), 1.28 (d, *J* = 5.1 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.33 (d, *J* = 6.3 Hz, 3H), 2.88 (sep, *J* = 6.9 Hz, 1H), 3.16 (sep, *J* = 6.6 Hz, 1H), 3.98 (m, 2H), 4.17-4.35 (m, 3H), 4.45 (m, 1H), 4.72 (m, 1H), 7.24 (m, 2H), 7.44 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 159.3, 147.1, 146.0, 131.1, 129.4, 125.1, 124.5, 70.1, 56.0, 53.4, 48.5, 33.4, 28.9, 28.7, 27.5, 25.3, 25.2, 24.1, 24.0; HRMS (EI^+) calc'd for $[C_{21}H_{35}ClN_2O\text{-}Cl]^+$: *m/z*, 331.2749 found 331.2737.

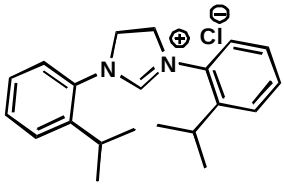


(*S*)-1-(2,6-Diisopropylphenyl)-3-(1-hydroxy-3-phenylpropan-2-yl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S7a.2, SM Table 2): White crystalline powder; ^{1}H NMR (300

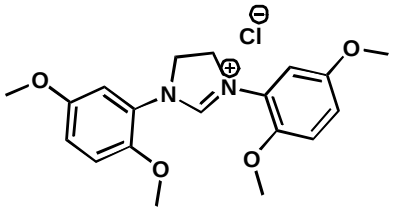
MHz, $CDCl_3$-*d*) δ 1.03 (d, *J* = 6.9 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.6 Hz, 3H), 2.31 (sep, *J* = 6.9 Hz, 1H), 2.86 (m, 1H), 3.08 (m, 2H), 3.95 (m, 3H), 4.17 (m, 1H), 4.33 (m, 1H), 4.49 (m, 1H), 4.62 (m, 1H), 4.86 (m, 1H), 7.25 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 157.9, 147.0, 146.0, 135.6, 131.1, 129.1, 128.5, 127.3, 125.0, 124.5, 62.0, 59.7, 52.9, 45.8, 34.2, 28.7, 28.5, 25.3, 25.0, 24.2, 24.0; HRMS (EI^+) calc'd for $[C_{24}H_{33}ClN_2O\text{-}Cl]^+$: *m/z*, 365.2593 found 365.2585.



1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S3a.22, SM Table 2): Gray powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 2.29 (s, 3H), 2.35 (s, 6H), 4.44 (s, 4H), .7.07 (s, 2H), 8.97 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 160.0, 139.4, 135.2, 130.7, 129.2, 51.0, 20.6, 17.3; HRMS (EI^+) calc'd for $[C_{21}H_{27}ClN_2\text{-}Cl]^+$: *m/z*, 307.2174 found 307.2164.



1,3-Bis(2-isopropylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (S5a.1, SM Table 2): White powder; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 1.43 (d, *J* = 6.6 Hz, 12H), 3.12 (sep, *J* = 6.6 Hz, 2H), 4.84 (s, 4H), 7.31-7.49 (m, 6H), 7.85 (s, 1H), 8.21 (dd, *J* = 7.8, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$-*d*) δ 156.7, 144.4, 132.3, 130.9, 128.1, 127.8, 126.9, 54.7, 28.4, 24.3; HRMS (EI^+) calc'd for $[C_{21}H_{27}ClN_2\text{-}Cl]^+$: *m/z*, 307.1863 found 307.1877.

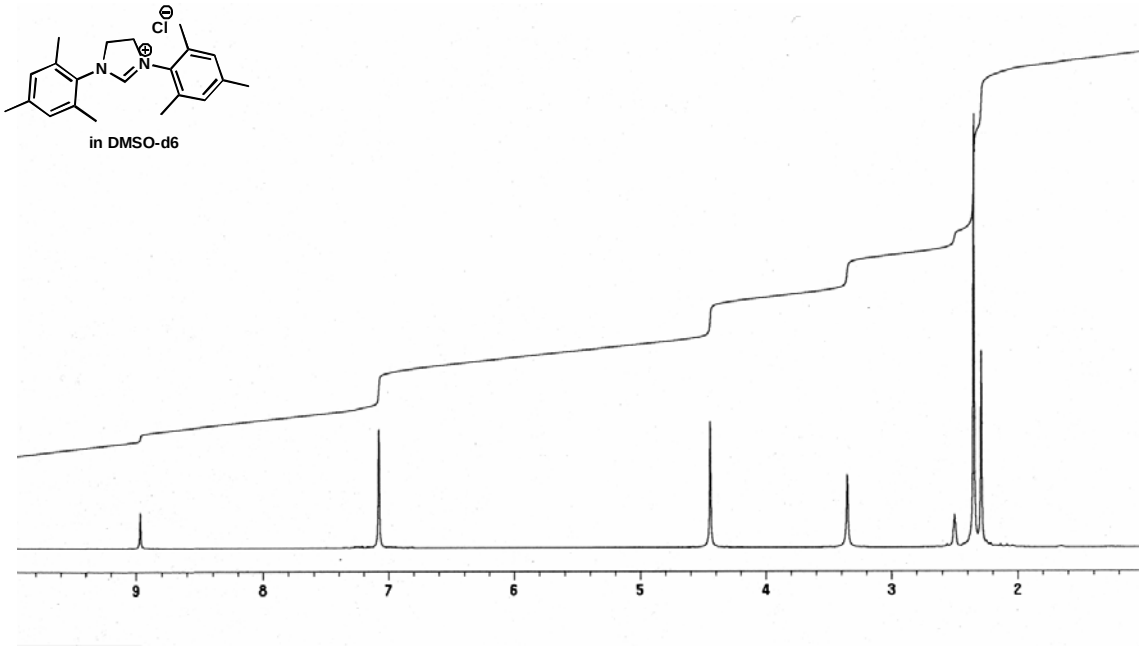


1,3-Bis(2,5-dimethoxyphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (S8a.1, SM Table 2): white crystalline powder; ^{1}H NMR (300 MHz, DMSO-*d*6) δ 3.77 (s, 6H), 3.88 (s, 6H), 4.56 (s, 4H), 6.98 (dd, *J* = 9.3, 3.0 Hz, 2H), 7.16 (d, *J* = 2.7 Hz, 2H), 7.21 (d, *J* =

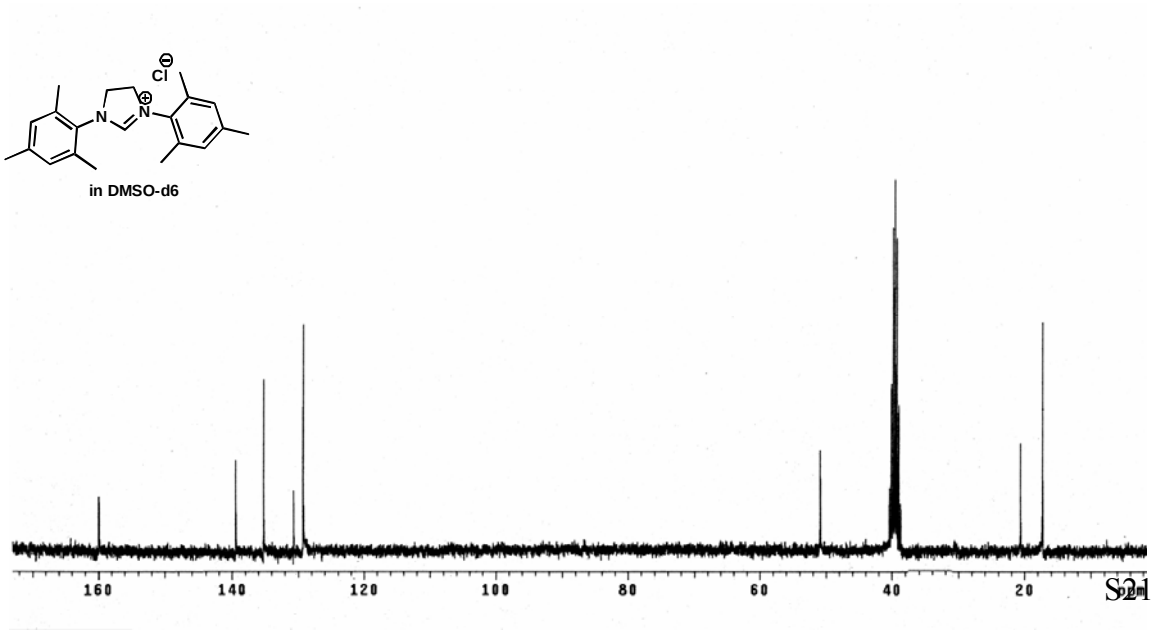
9.3 Hz, 2H), 9.47 (s, 1H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ 157.1, 153.1, 145.5, 124.9, 113.8, 113.6, 109.7, 56.7, 55.9, 49.9; HRMS (EI^+) calc'd for $[C_{19}H_{23}ClN_2O_4\text{-}Cl]^+$: *m/z*, 343.1658 found 343.1650.

Selected ^{1}H and ^{13}C NMR Spectral Data:

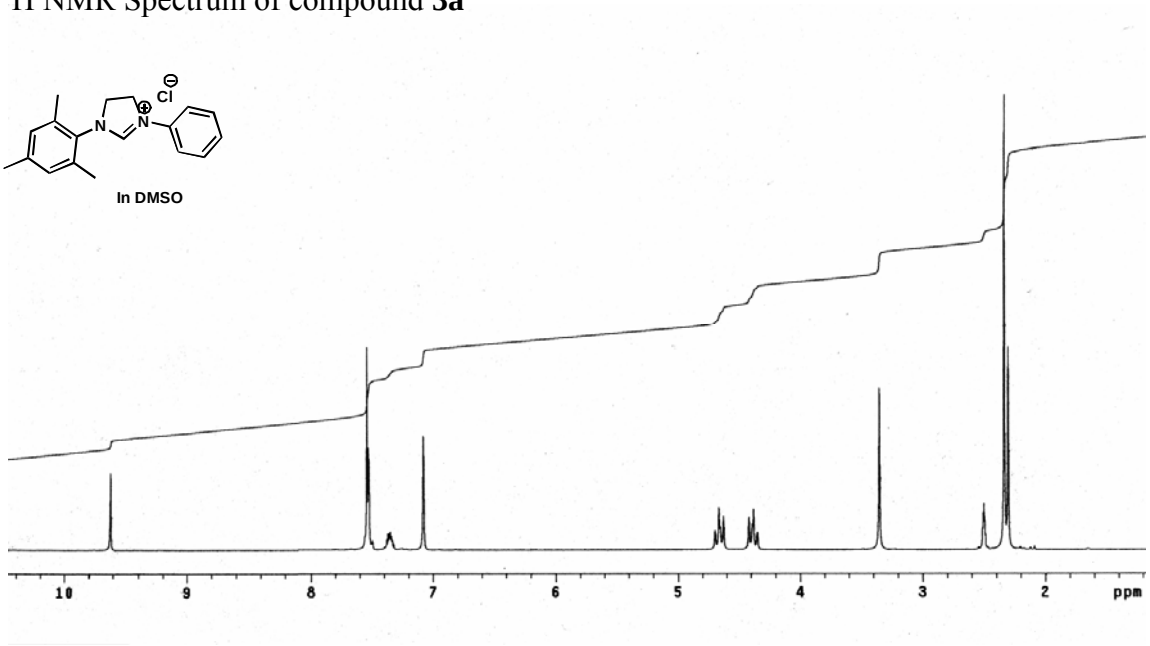
^{1}H NMR Spectrum of compound **3d**



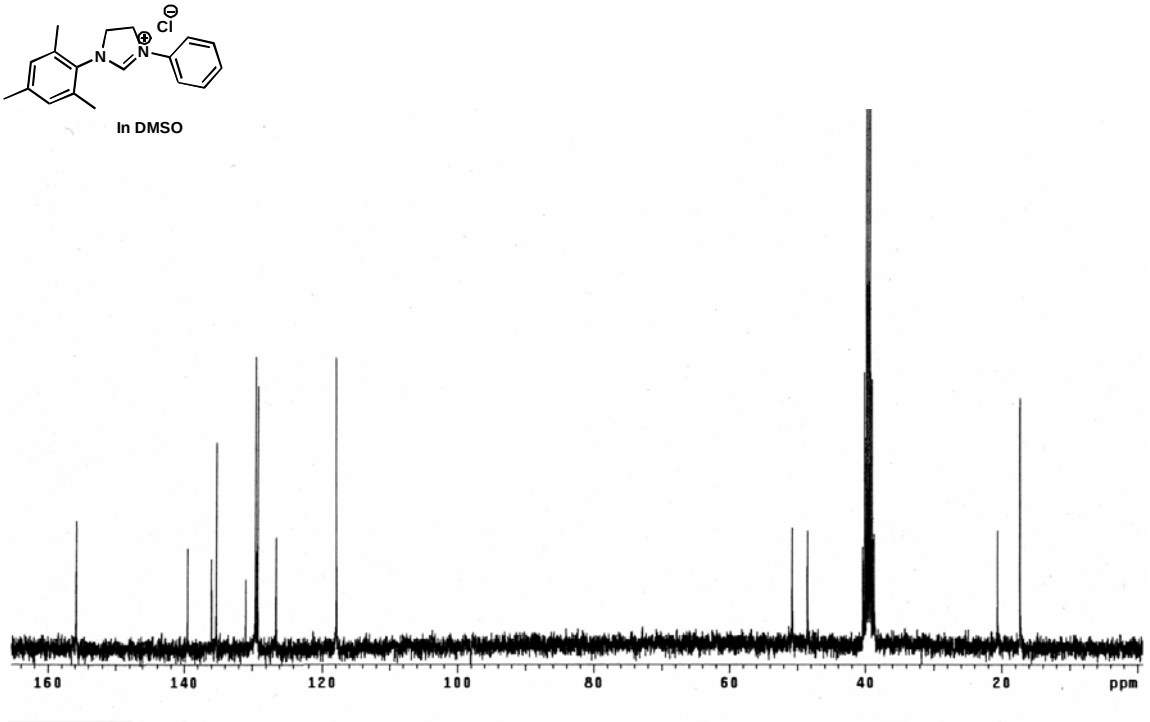
^{13}C NMR Spectrum of compound **3d**



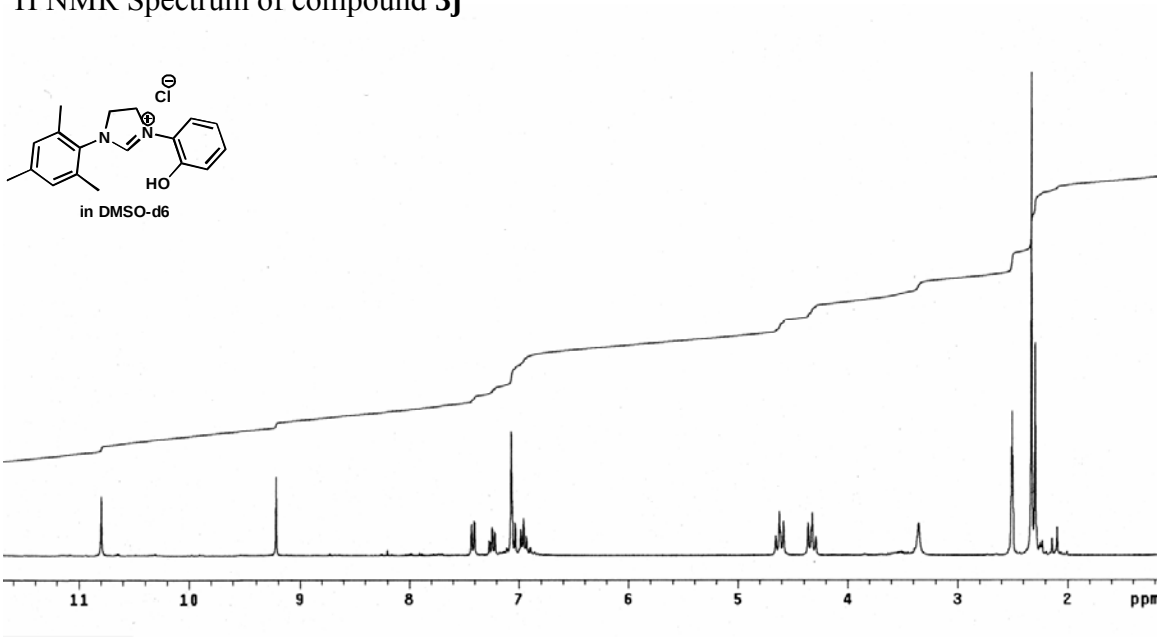
^{1}H NMR Spectrum of compound **3a**



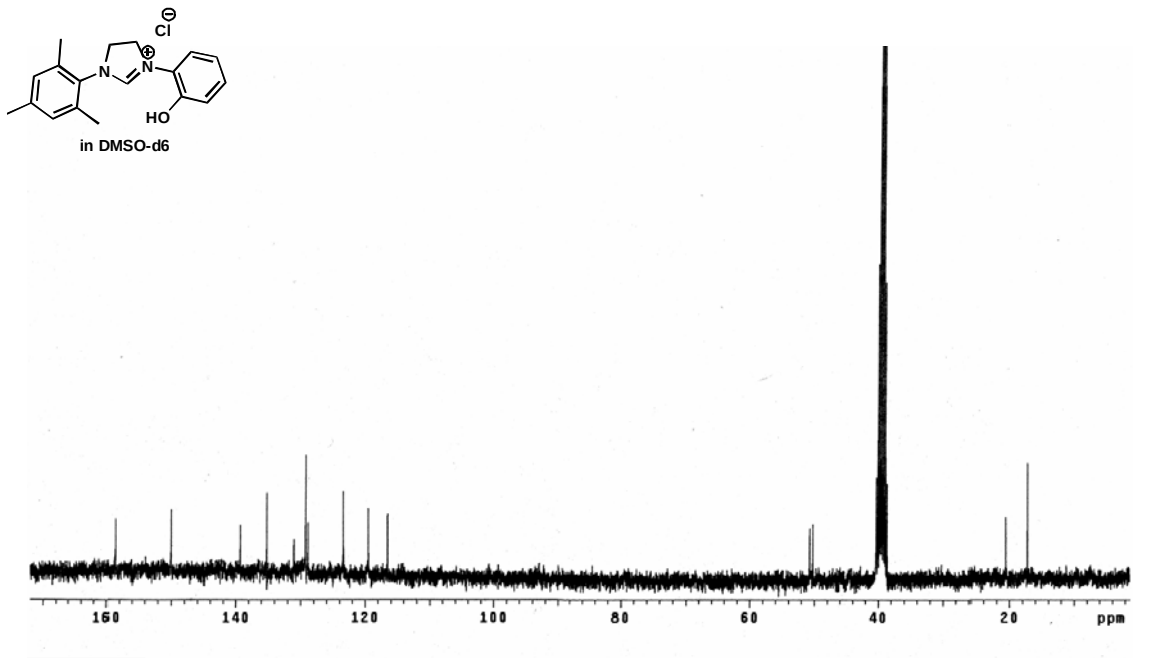
^{13}C NMR Spectrum of compound **3a**



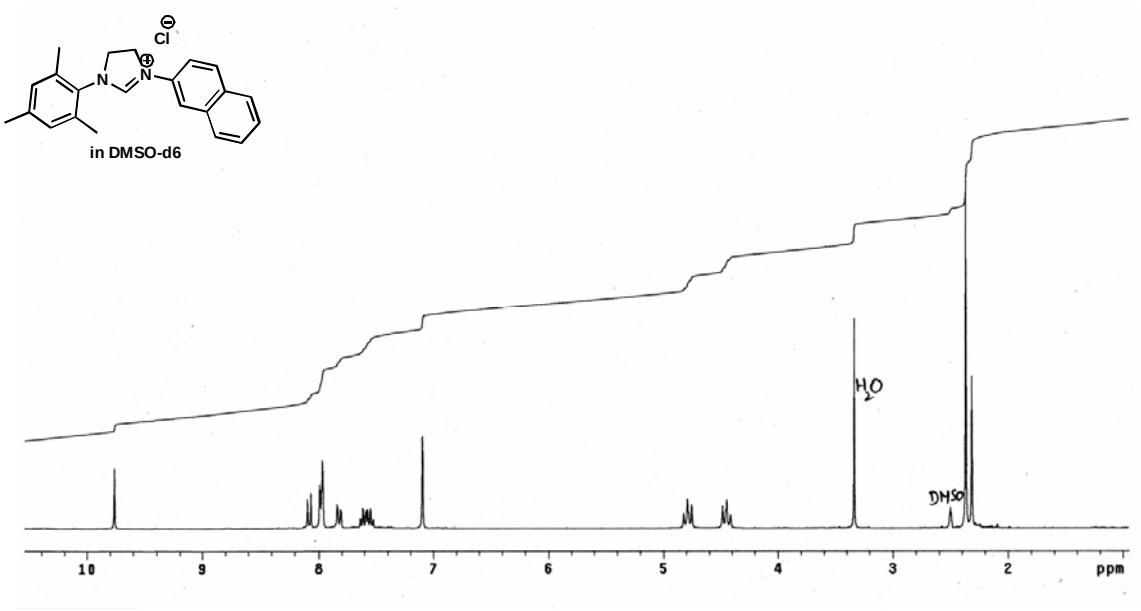
^{1}H NMR Spectrum of compound **3j**



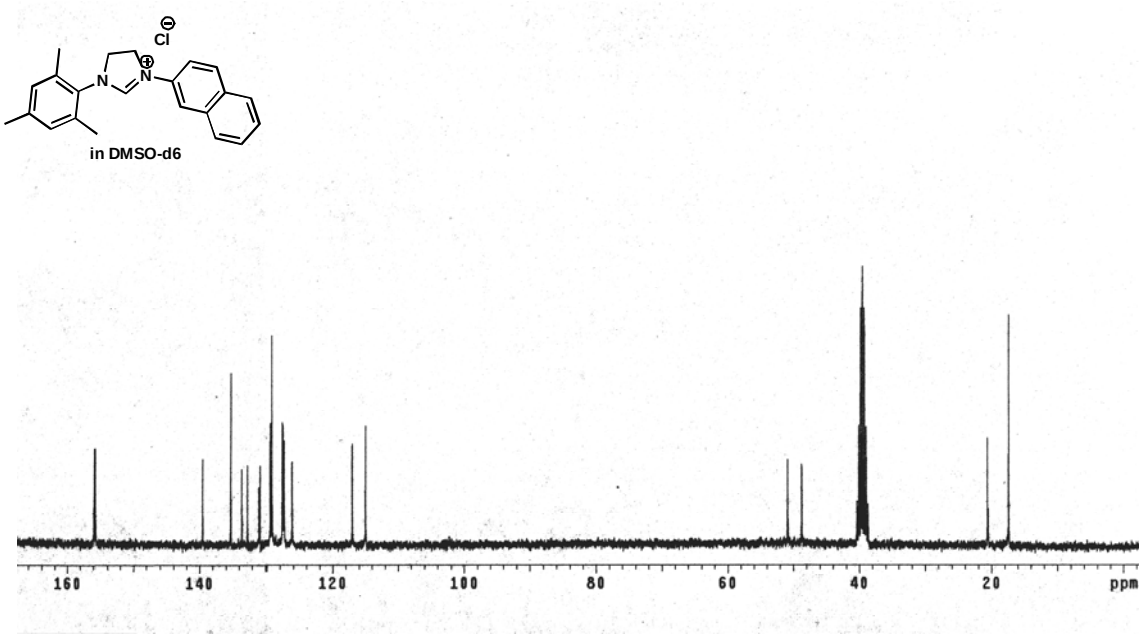
^{13}C NMR Spectrum of compound **3j**



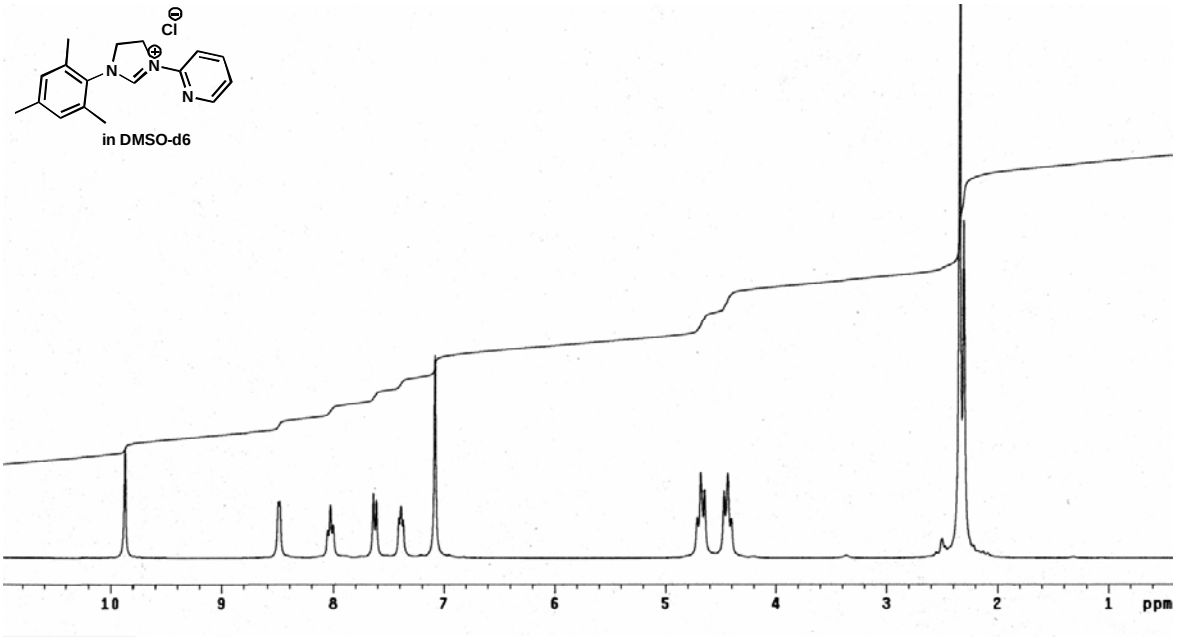
^{1}H NMR Spectrum of compound **3f**



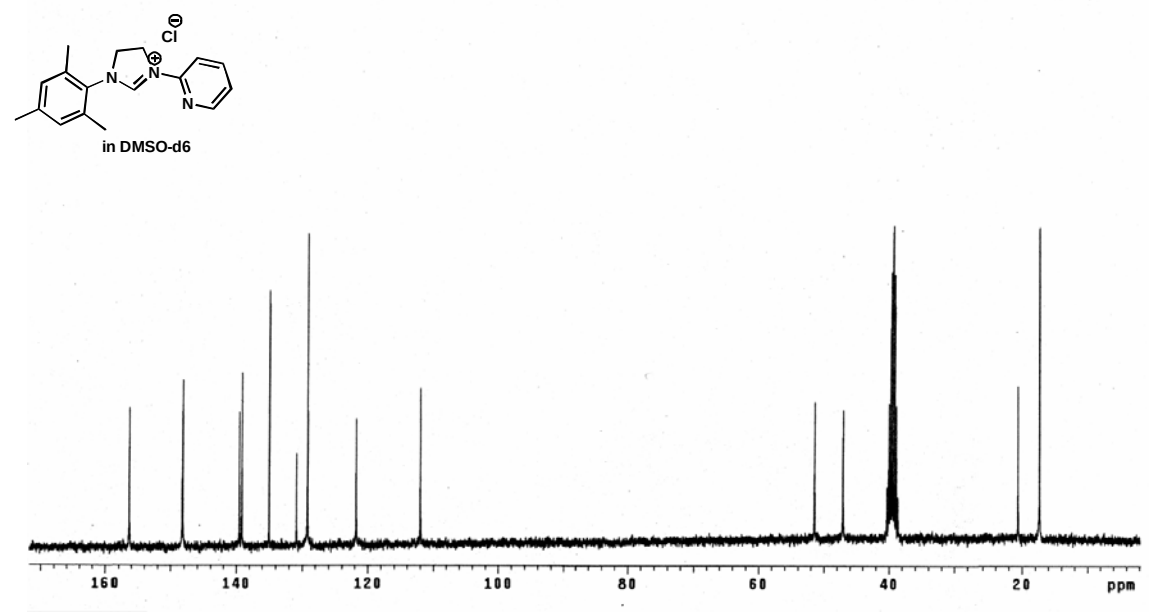
^{13}C NMR Spectrum of compound **3f**



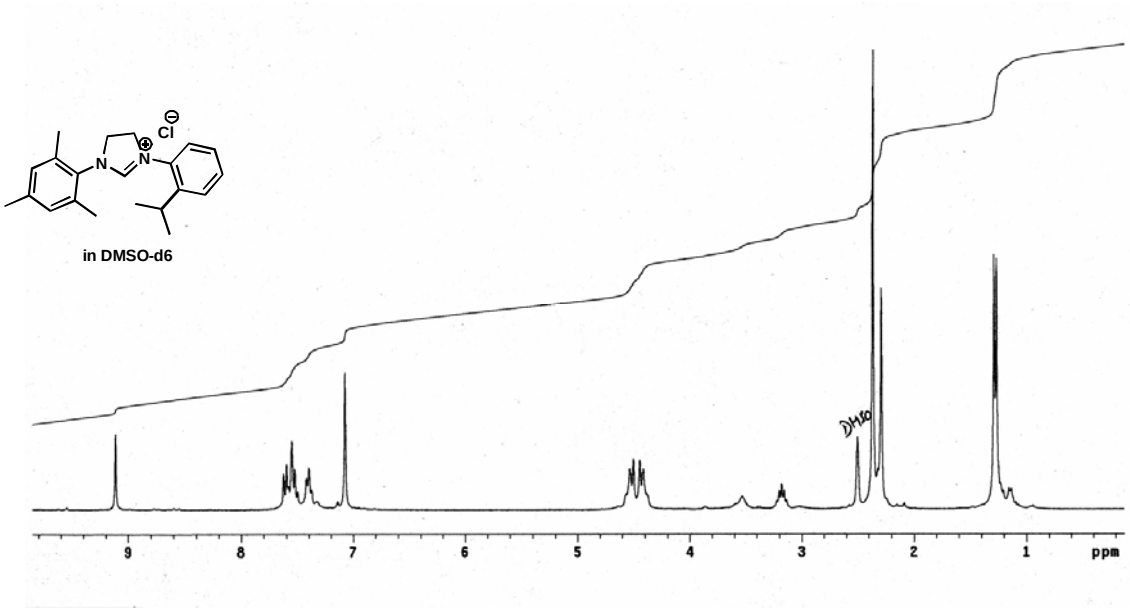
^{1}H NMR Spectrum of compound **3k**



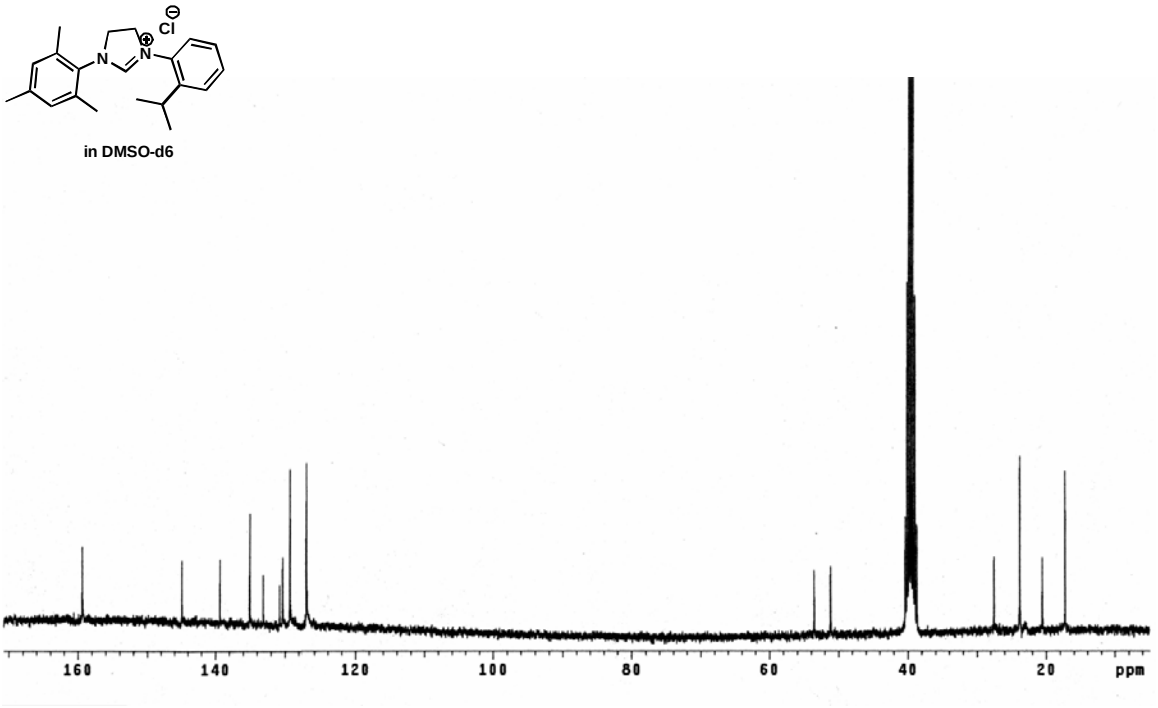
^{13}C NMR Spectrum of compound **3k**



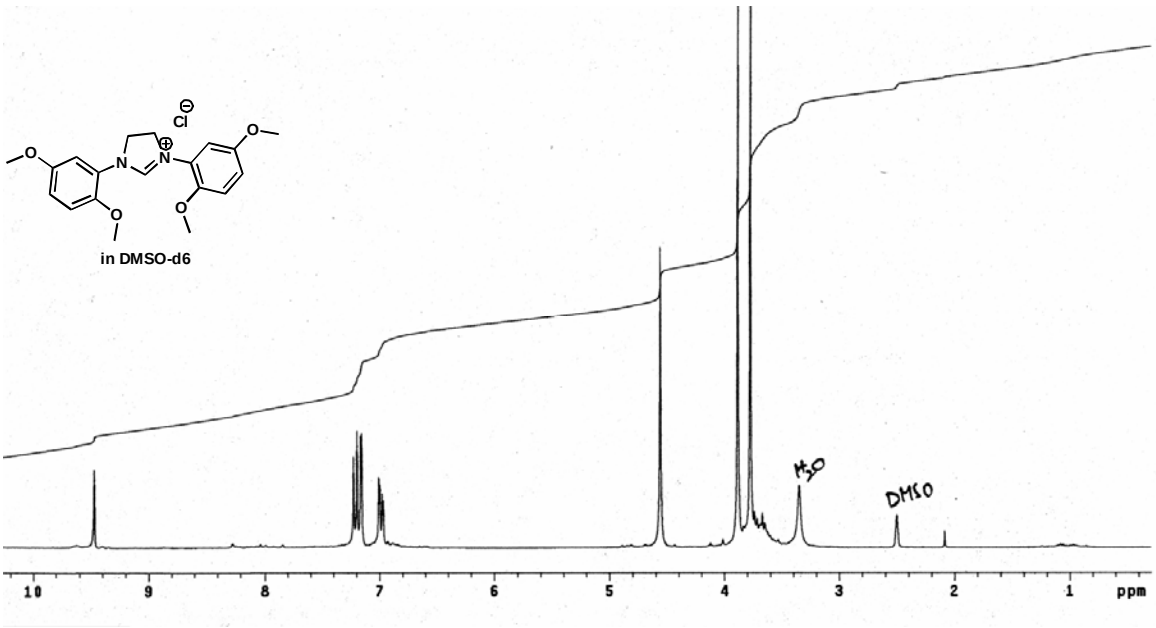
^{1}H NMR Spectrum of compound **3c**



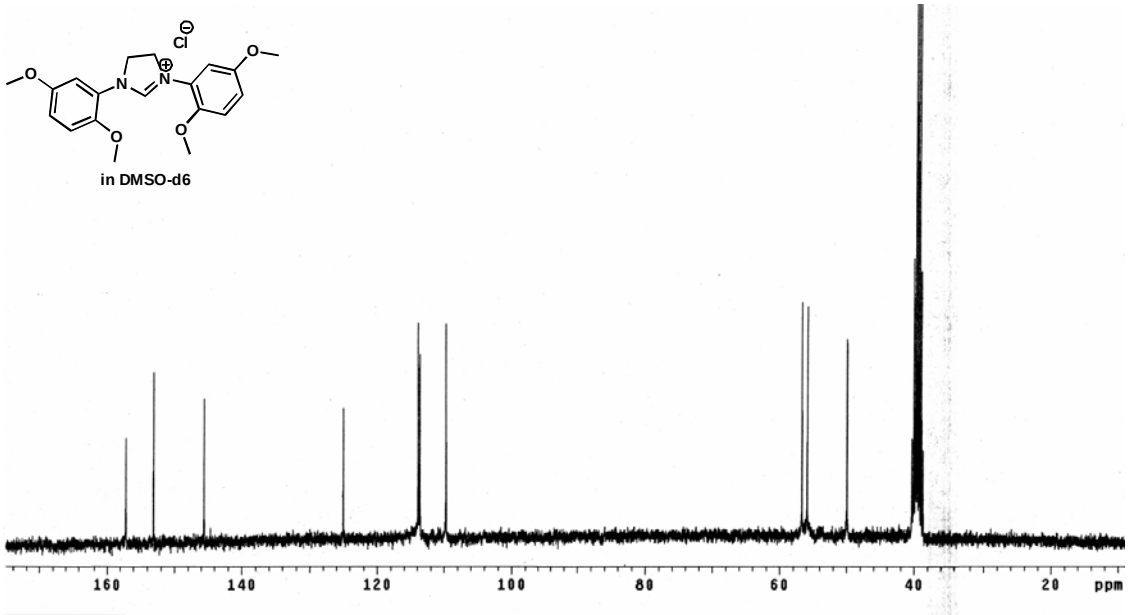
^{13}C NMR Spectrum of compound **3c**



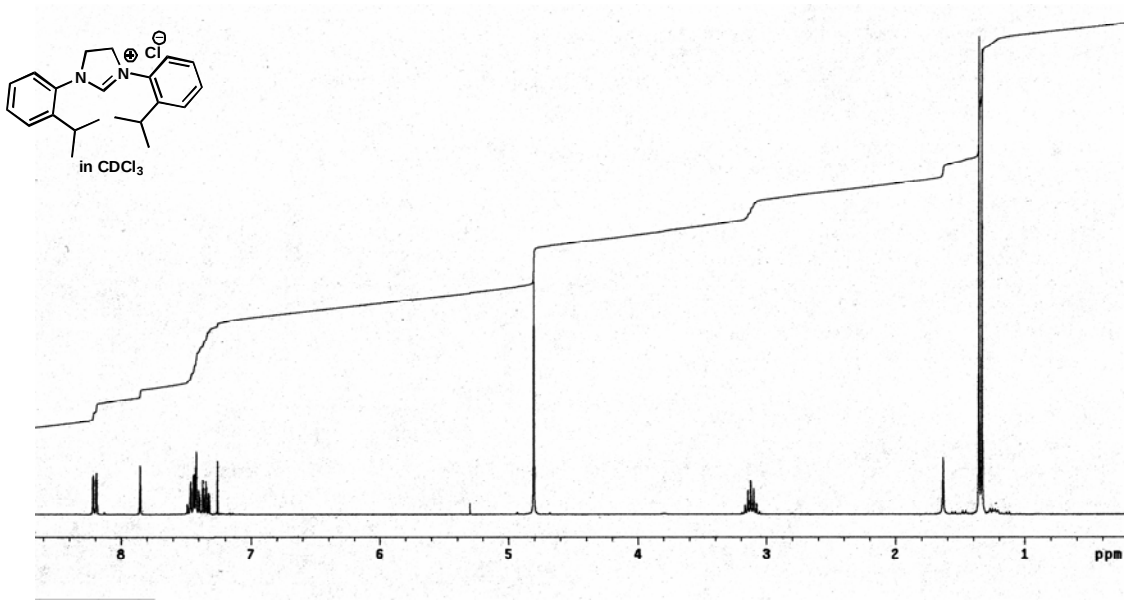
^{1}H NMR Spectrum of compound **3q**



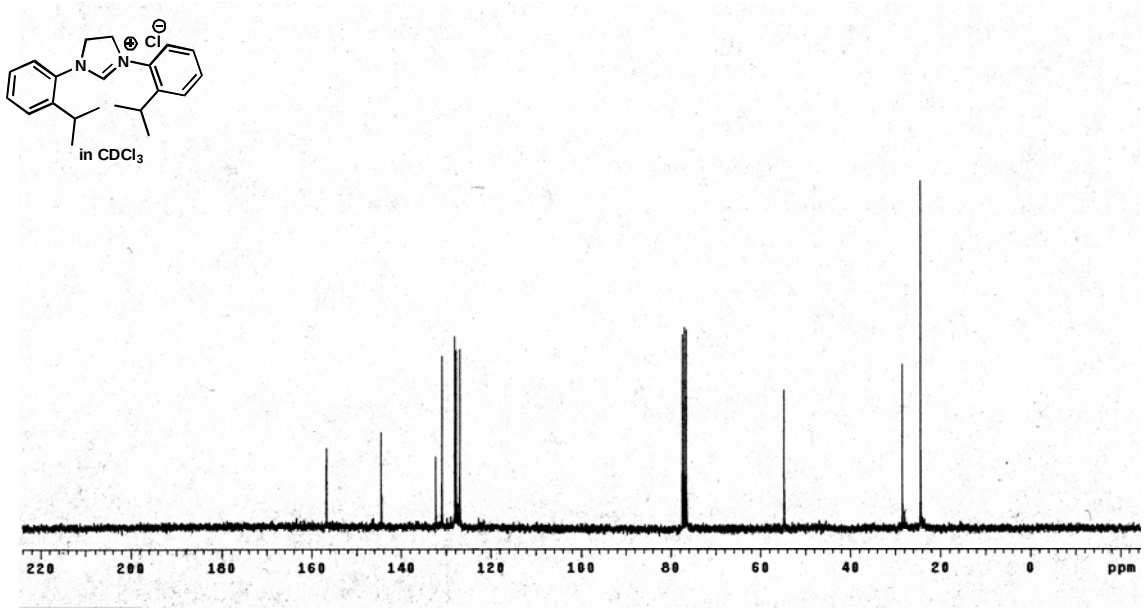
^{13}C NMR Spectrum of compound **3q**



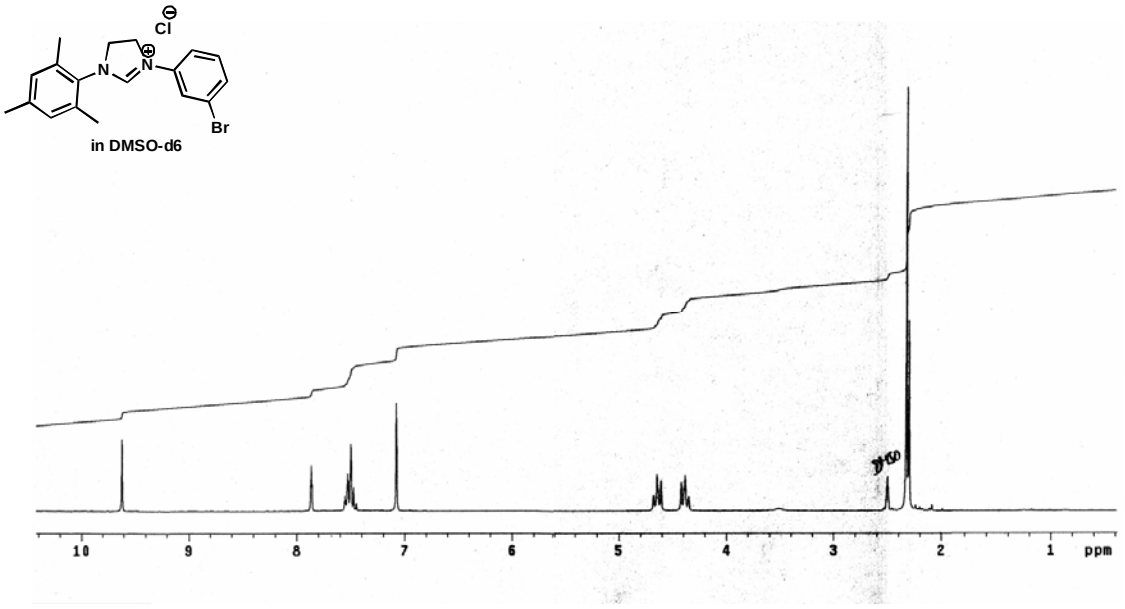
^{1}H NMR Spectrum of compound **3p**



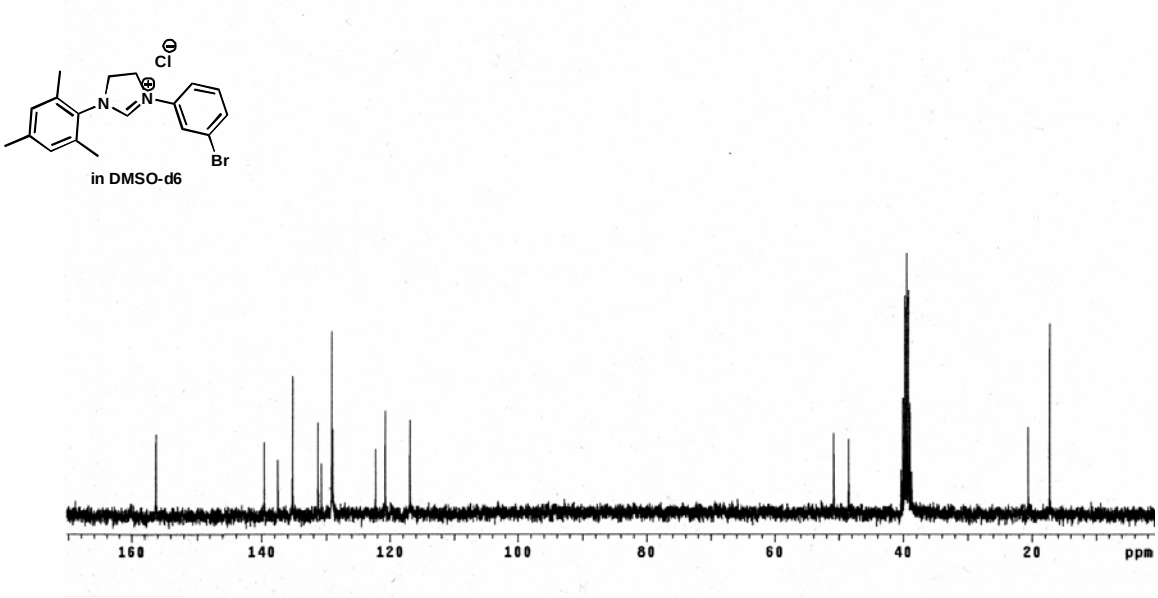
^{13}C NMR Spectrum of compound **3p**



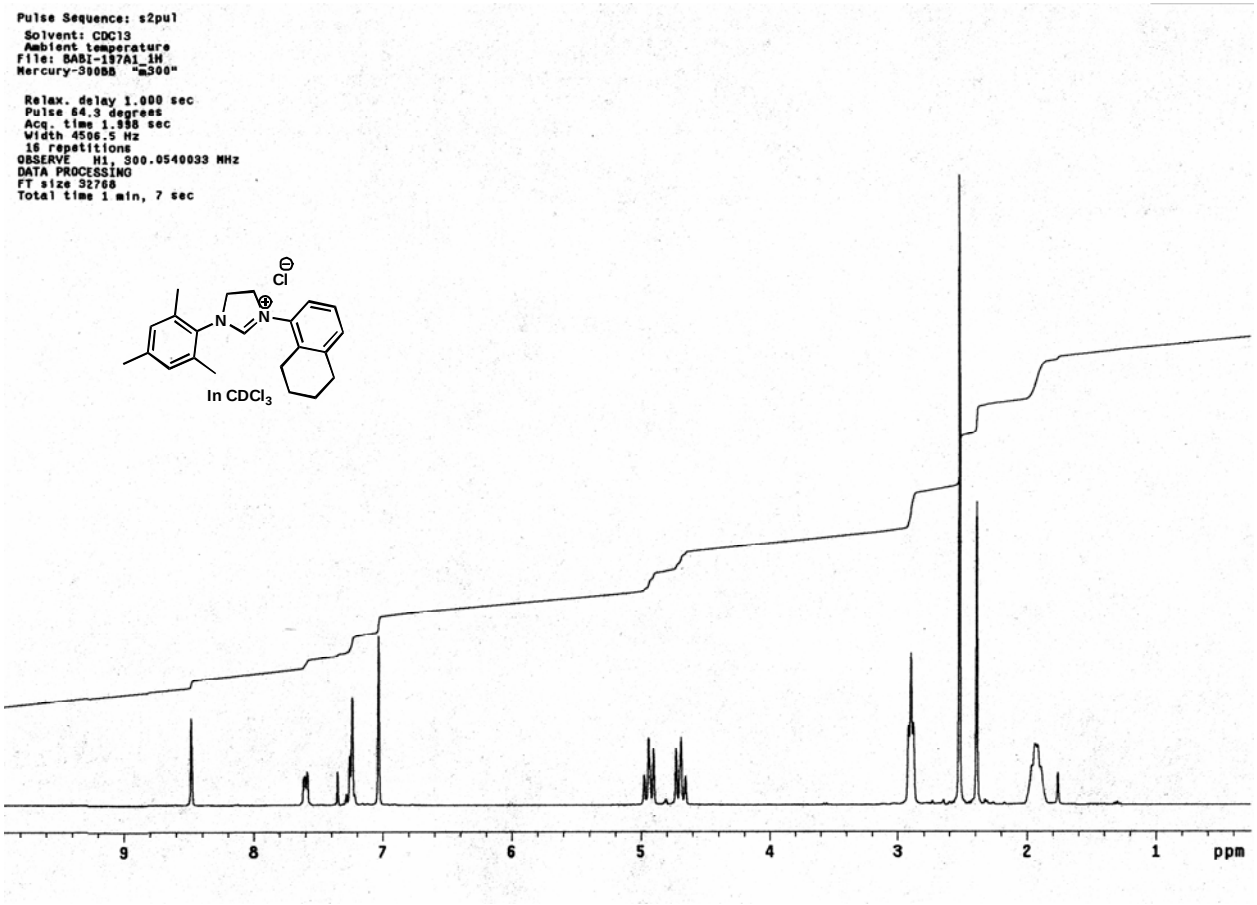
^{1}H NMR Spectrum of compound **3h**



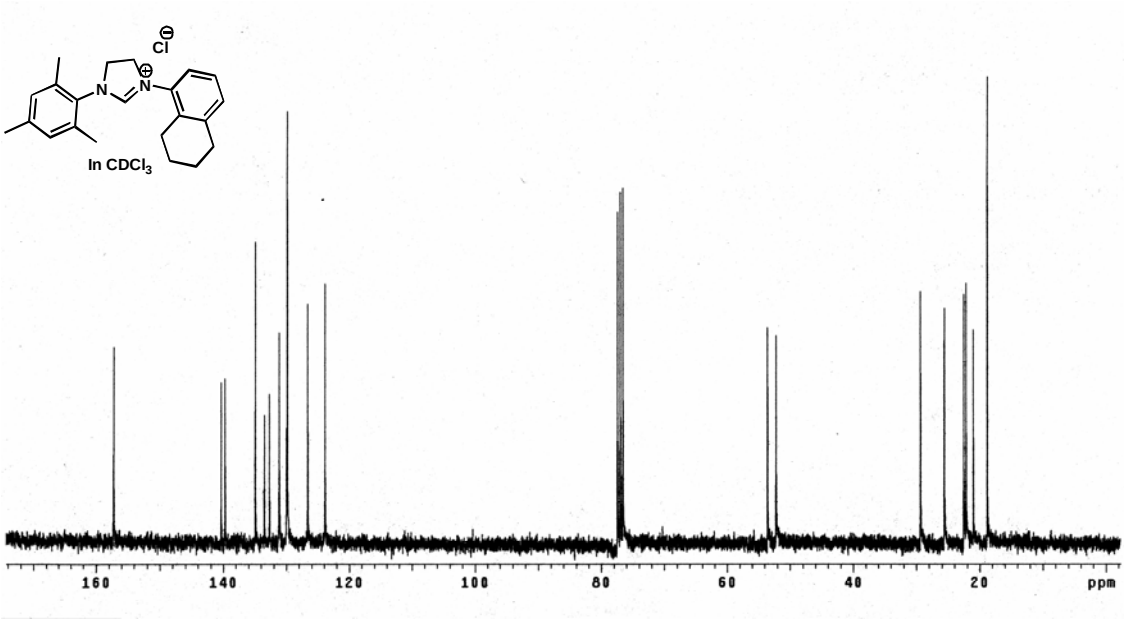
^{13}C NMR Spectrum of compound **3h**



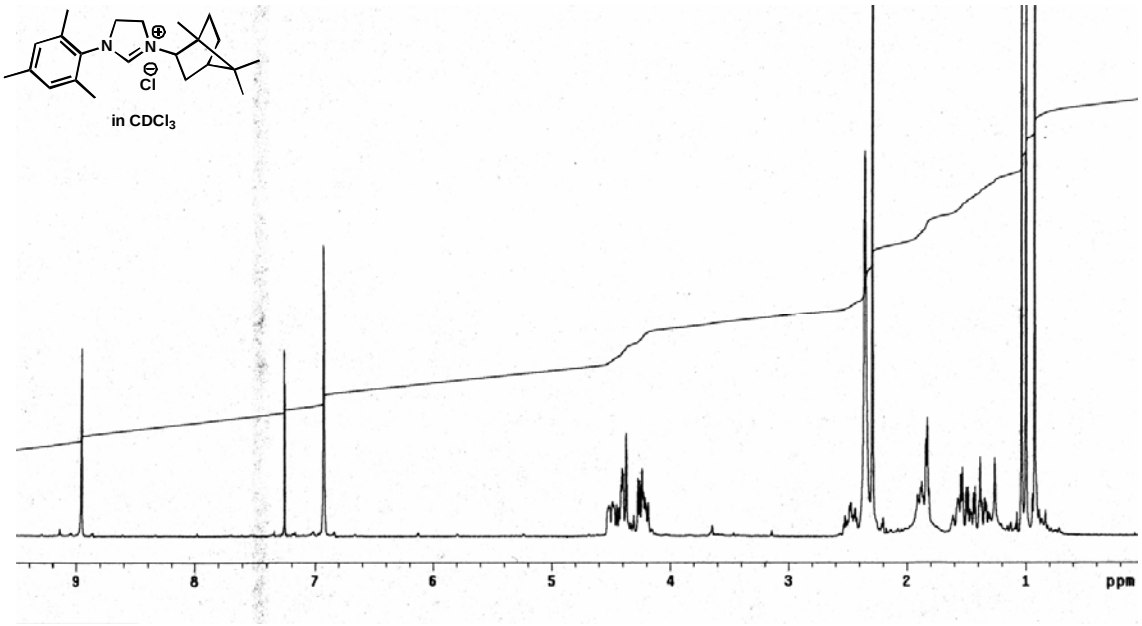
^{1}H NMR Spectrum of compound **3g**



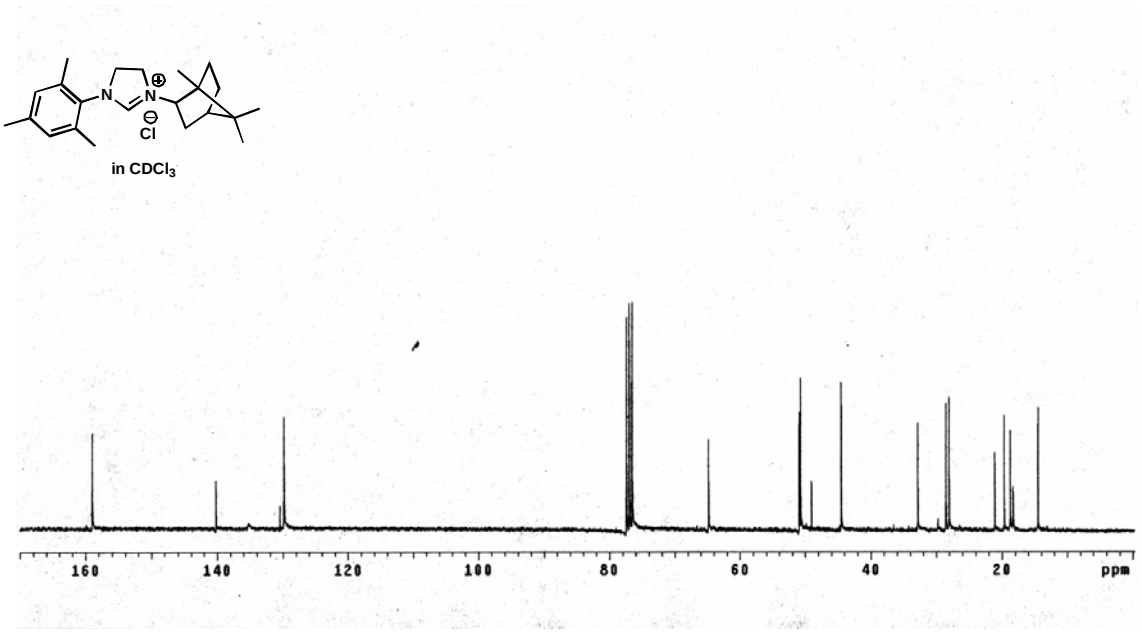
^{13}C NMR Spectrum of compound **3g**



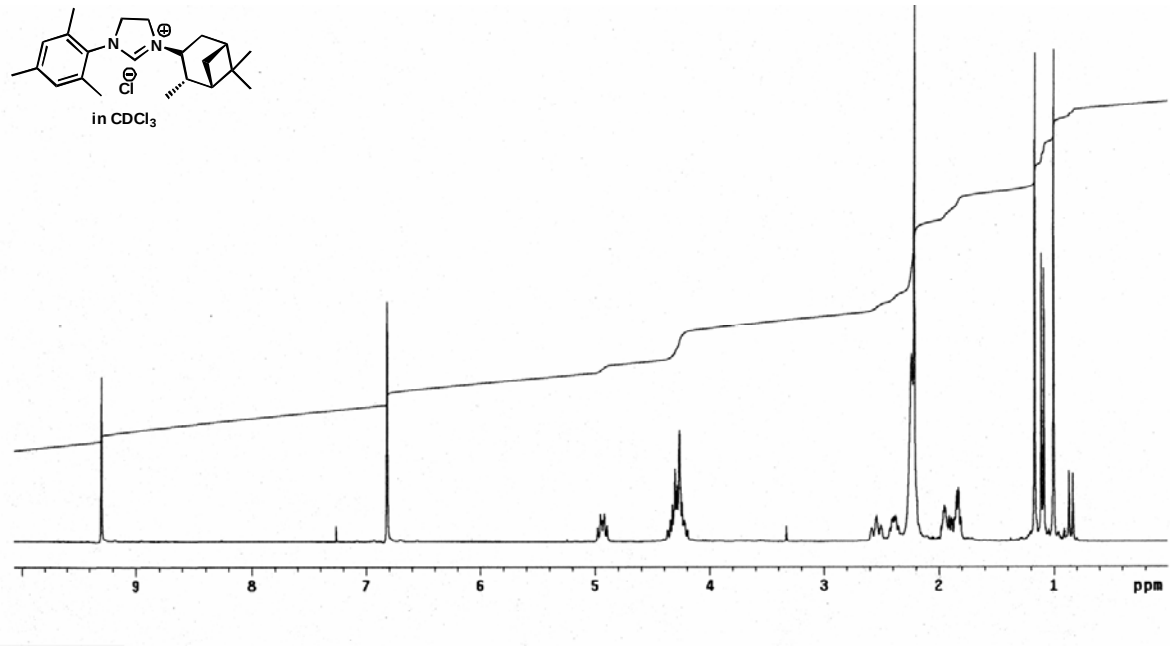
^{1}H NMR Spectrum of compound **3w**



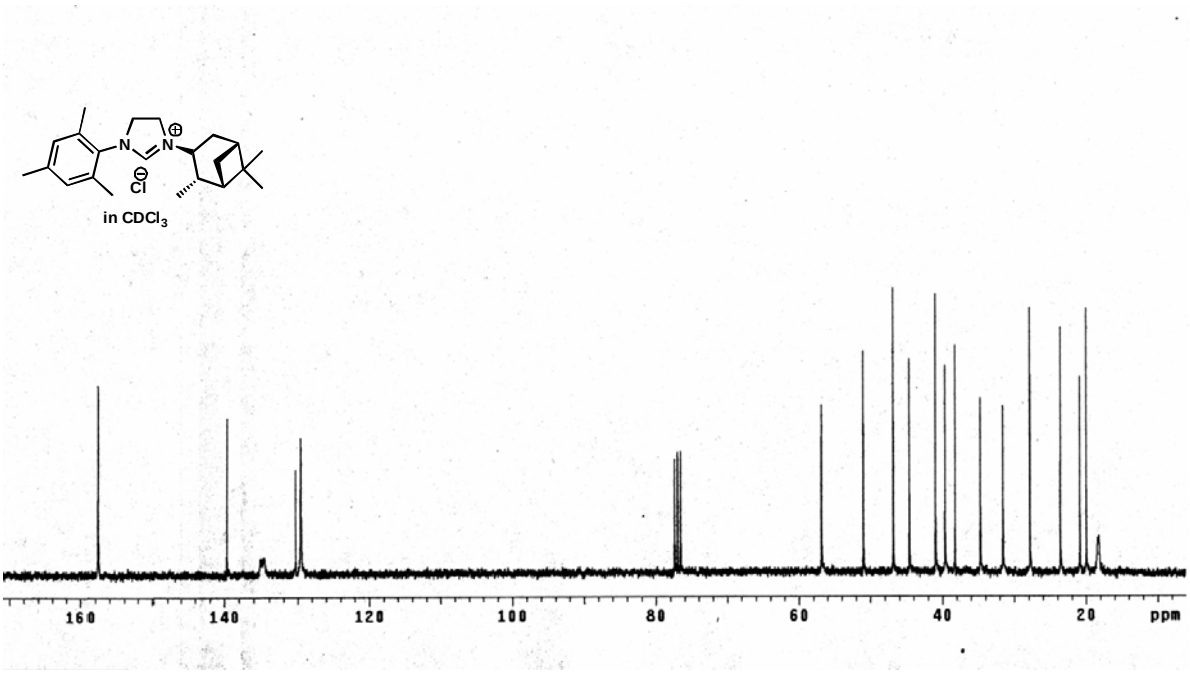
^{13}C NMR Spectrum of compound **3w**



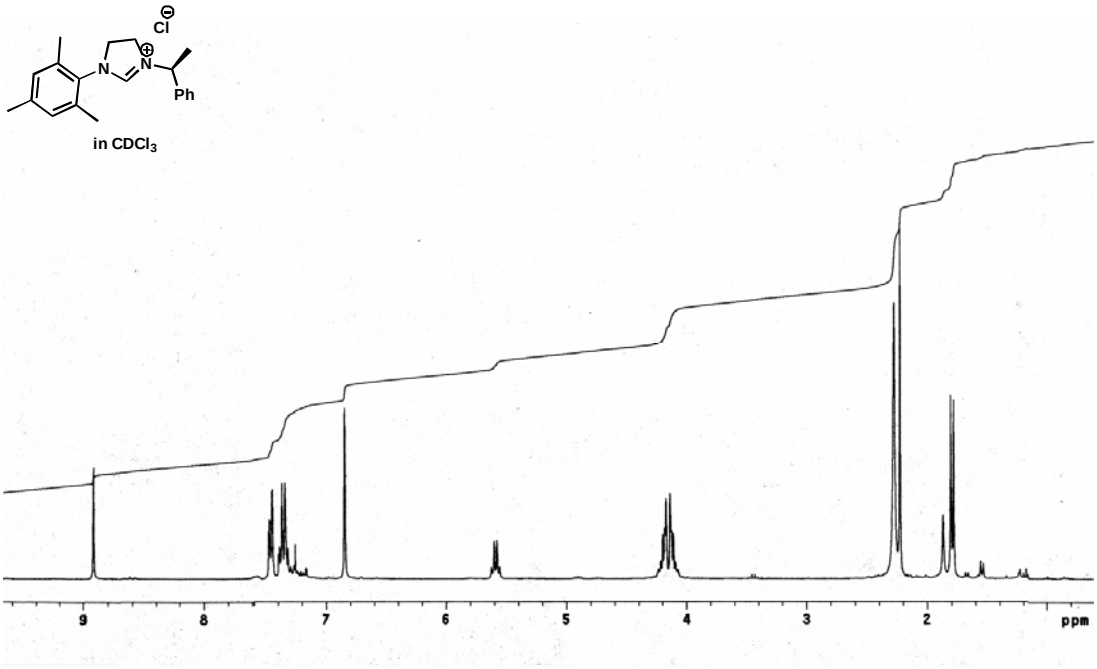
^{1}H NMR Spectrum of compound **3z**



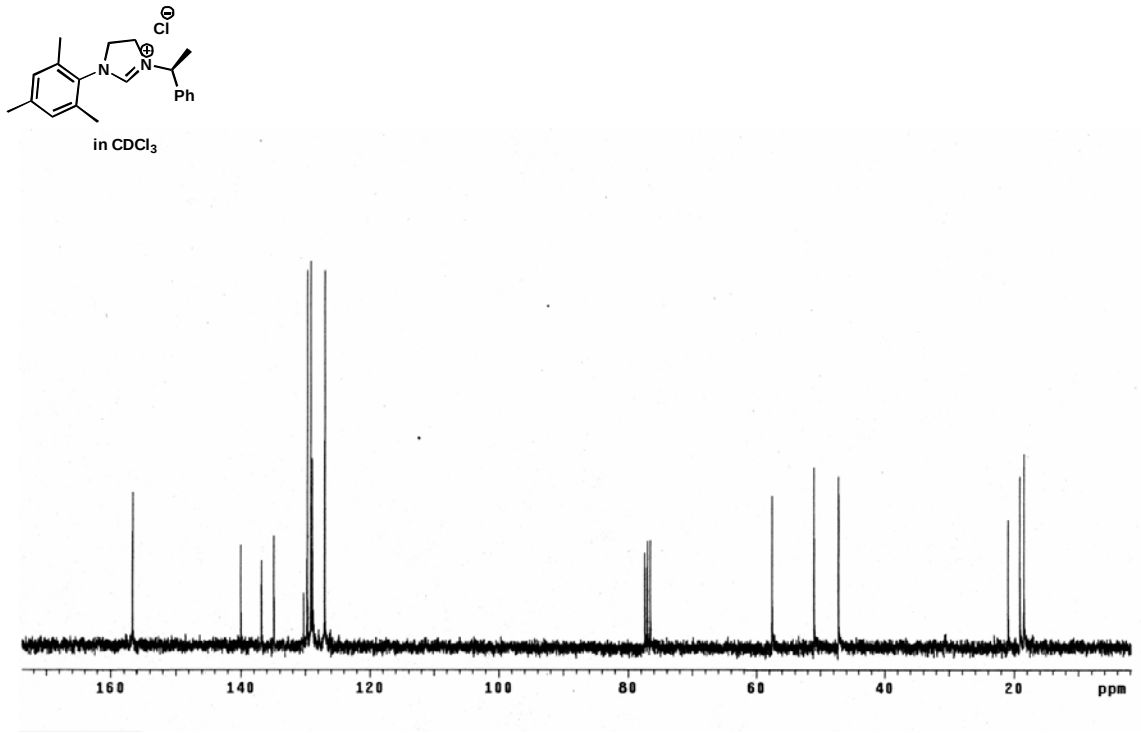
^{13}C NMR Spectrum of compound **3z**



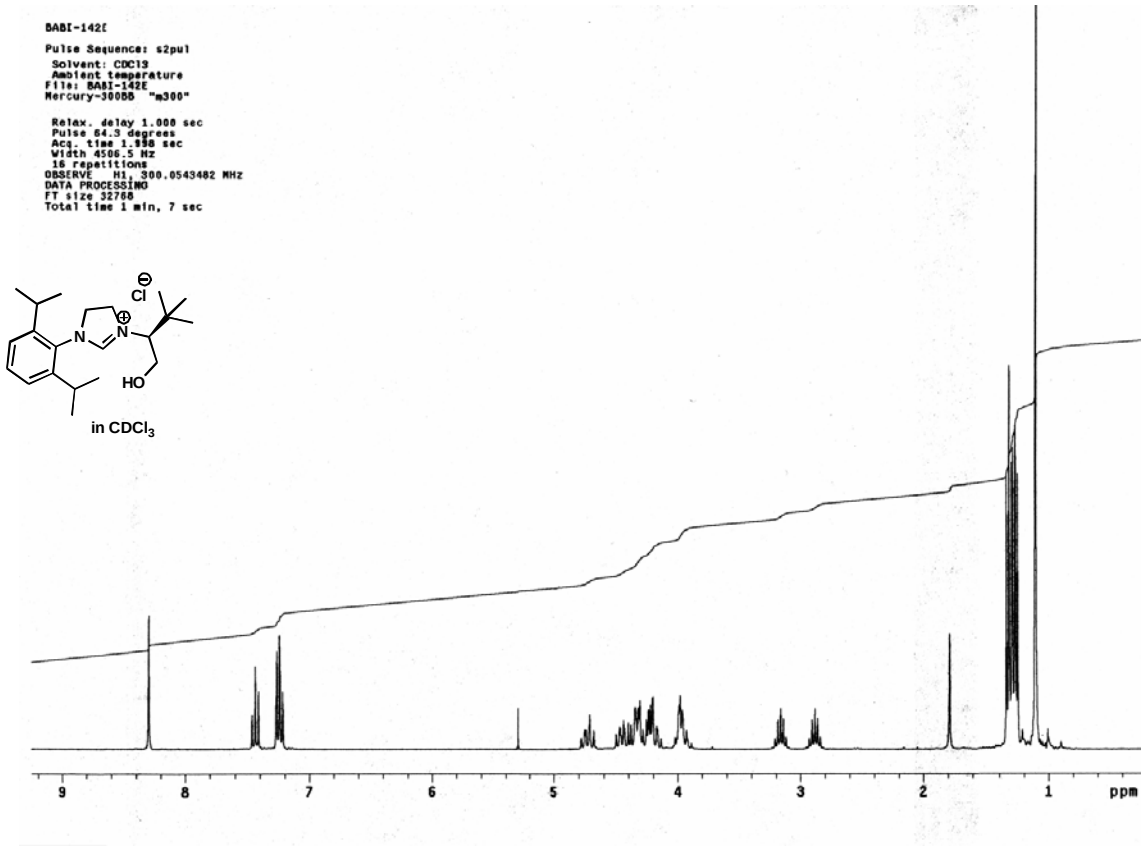
^{1}H NMR Spectrum of compound **3r**



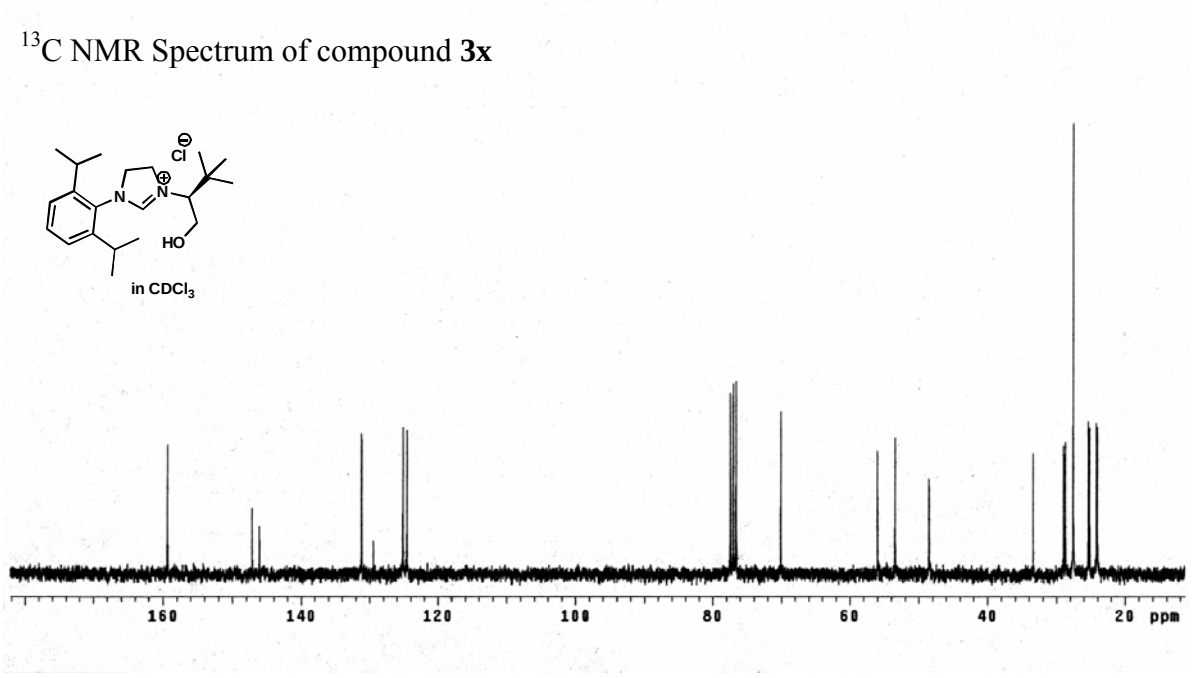
^{13}C NMR Spectrum of compound **3r**



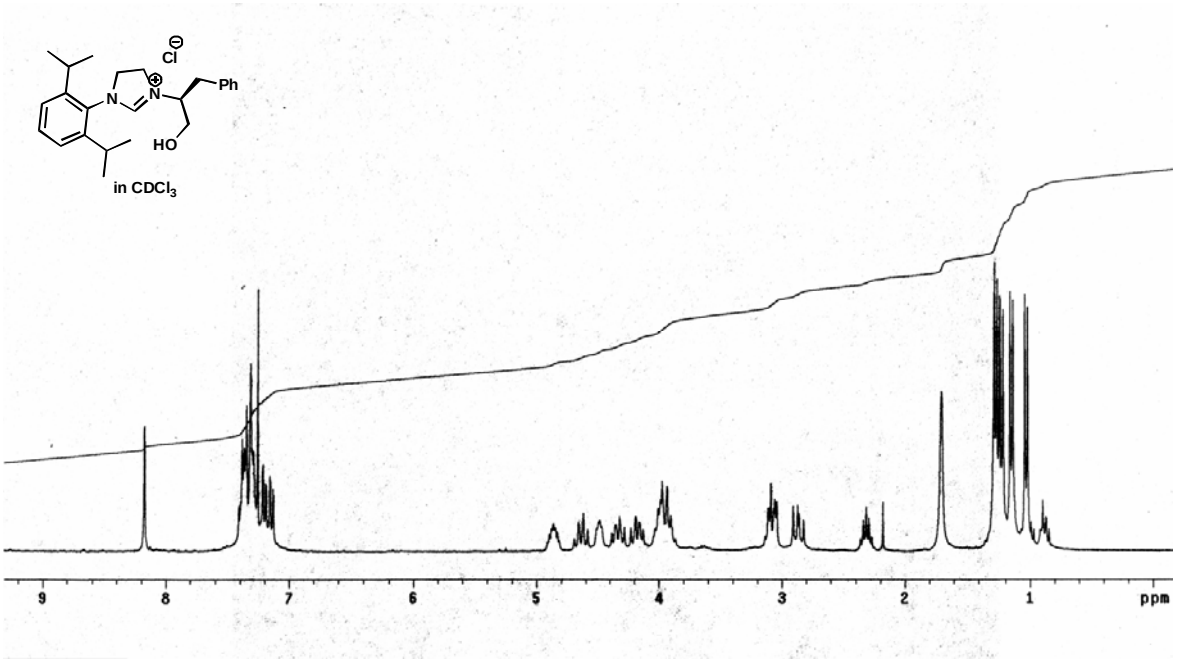
^{1}H NMR Spectrum of compound **3x**



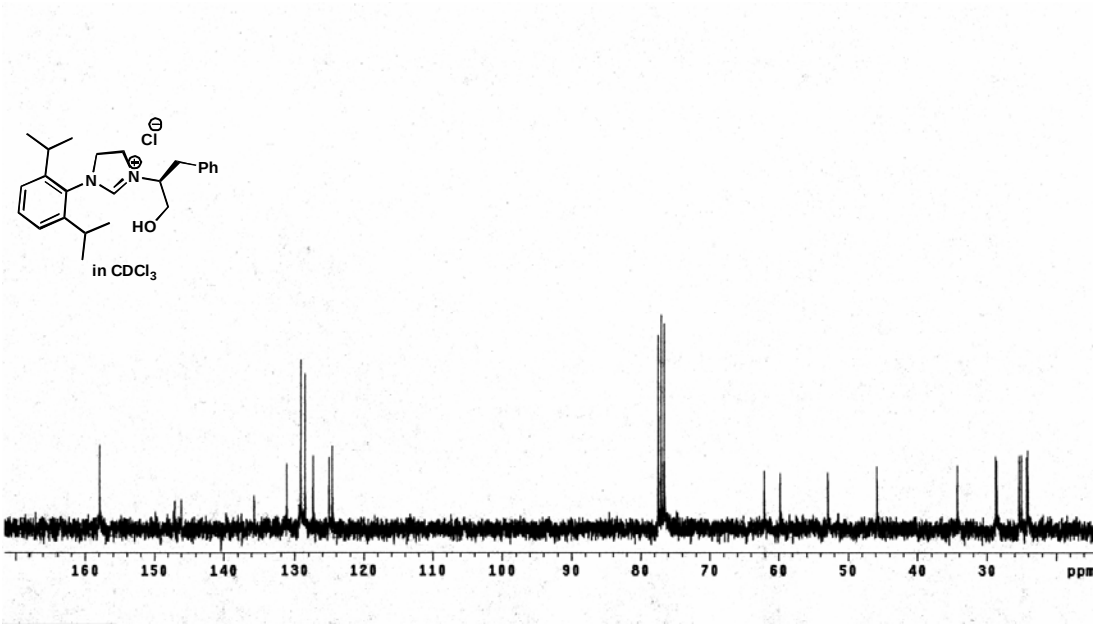
^{13}C NMR Spectrum of compound **3x**



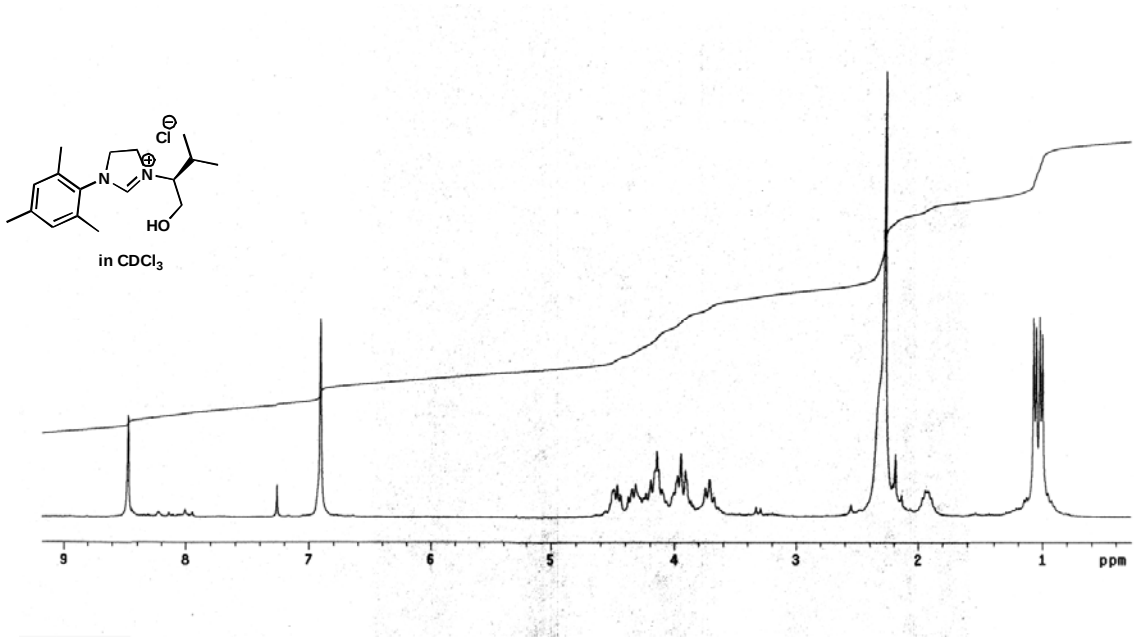
^{1}H NMR Spectrum of compound **3y**



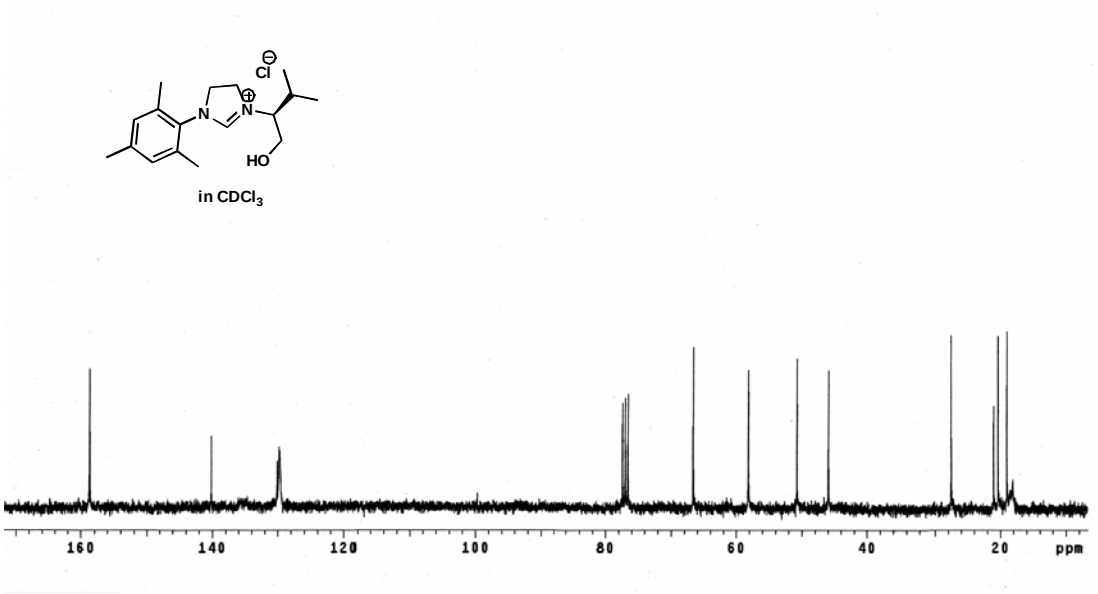
^{13}C NMR Spectrum of compound **3y**



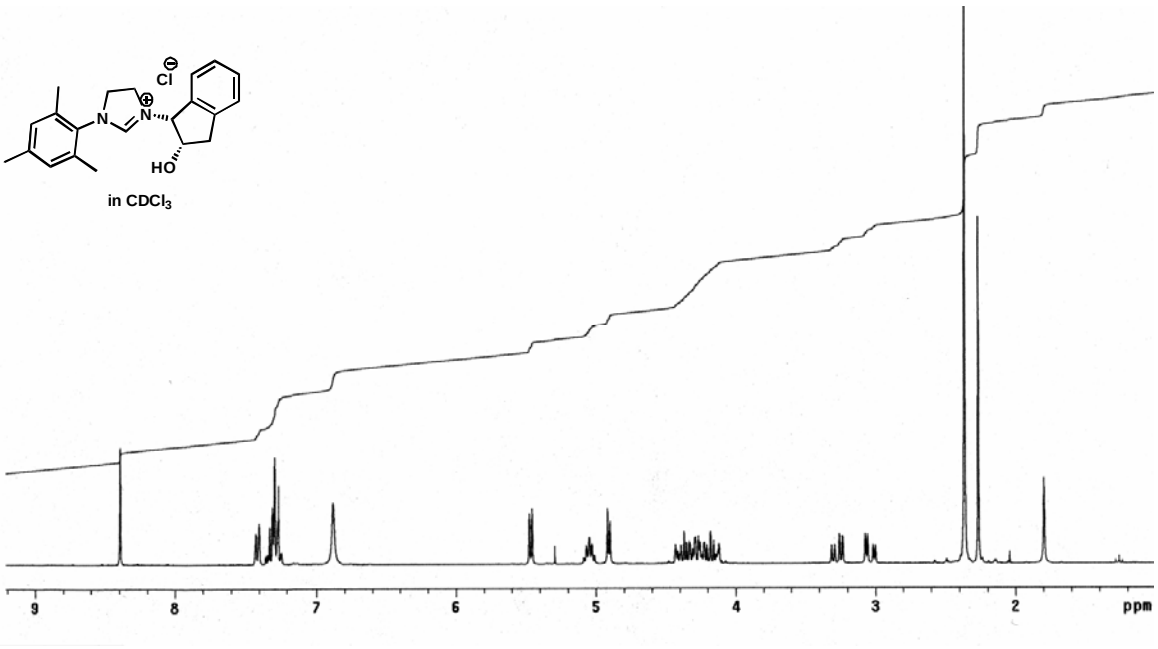
^{1}H NMR Spectrum of compound **3s**



^{13}C NMR Spectrum of compound **3s**



^{1}H NMR Spectrum of compound **3t**



^{13}C NMR Spectrum of compound **3t**