Electronic supporting information for

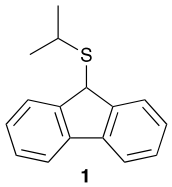
"The pK_a values of *N*-aryl imidazolinium salts, their higher homologues, and formamidinium salts in dimethyl sulfoxide"

Nicholas Konstandaras, Michelle H. Dunn, Ena T. Luis, Marcus L. Cole and Jason B. Harper

School of Chemistry, University of New South Wales, Sydney, NSW, 2052, Australia.

Synthesis of the fluorenes **1**, **2**, **3**, **5** and **7**

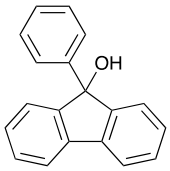
9-Isopropylsulfane-9*H*-fluorene 1[1]



1

In a method analogous to literature,[1] a solution of aqueous sodium hydroxide (0.57 g, 14 mmol, 14 M) was added in one portion to a solution of propanethiol (0.49 g 6.4 mmol) in THF (6 mL) under nitrogen. A solution of 9-bromo-9*H*-fluorene (1.56 g, 6.36 mmol) in THF (2 mL) was then added in one portion. The resulting emulsion was stirred vigorously for 21 hours. The volatile components were then removed under reduced pressure. Water (20 mL) was added and the mixture was extracted with dichloromethane (3 x 20 mL). The organic layers were then combined, dried over magnesium sulfate and filtered before the solvent was removed under reduced pressure. The product was then purified using flash column chromatography (hexane) to give the product **1** as a white crystalline solid (0.57 g, 2.4 mmol, 37%). m.p. 60-62 °C (lit.[2] 63-63.5 °C). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.73 (d, J = 7.4 Hz, 2H, Ar-H), 7.70 (d, J = 7.4 Hz, 2H, Ar-H), 7.38 (t, J = 7.4 Hz, 2H, Ar-H), 7.34 (t, J = 7.4 Hz, 2H, Ar-H), 4.94 (s, 1H, H9), 2.59 (sept, J = 6.7 Hz, 1H, $CH(CH_3)_2$), 0.98 (d, J = 6.7 Hz, 6H, $CH(CH_3)_2$).

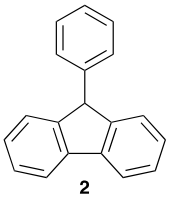
9-Phenyl-9*H*-fluoren-9-ol[3]



In an adaptation of a literature procedure,[4] 9-fluorenone (0.81 g, 4.5 mmol) was dissolved in anhydrous ether (70 mL). A solution of phenyllithium in dibutyl ether (1.9 M, 4.8 mL, 9.0 mmol) was added dropwise at 0 °C over two minutes resulting in the immediate formation of a white precipitate. The mixture was stirred for two hours at room temperature until the fluorenone was consumed as determined using TLC (3 : 7, dichloromethane : hexane). The reaction mixture was then quenched through the dropwise addition of water (10 mL) over two minutes before the further addition of water (65 mL). The aqueous layer was then separated and washed with ethyl acetate (2 x 65 mL). The organic layers were then combined, dried over magnesium sulfate and filtered before the solvent was removed under reduced

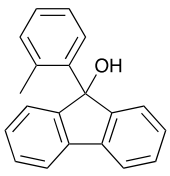
pressure. The resulting yellow oil was allowed crystallise overnight resulting in white crystals that were collected using suction filtration and triturated in hexane to give the title alcohol as a white solid (0.87 g, 3.4 mmol, 75%). m.p. 91-93 °C (lit.[5] 85 °C). ^{1}H NMR (600 MHz, dimethyl sulfoxide-d_6) δ 7.81 (d, J = 7.5 Hz, 2H, Ar-H), 7.38-7.34 (m, 2H, Ar-H), 7.27-7.21 (m, 8H, Ar-H), 7.20-7.15 (m, 1H, Ar-H), 6.29 (s, 1H, OH).

9-Phenyl-9*H*-fluorene 2[3]



In a method analogous to literature,[6] triethylsilane (0.70 g, 6.1 mmol) and boron trifluoride diethyl etherate (0.85 g, 6.0 mmol) were then each added in one portion to a solution of 9-phenyl-9*H*-fluoren-9-ol (0.70 g, 2.7 mmol) in dry dichloromethane (20 mL) maintained at 0 °C using an ice bath. The resultant solution was stirred at 0 °C for one hour. The reaction mixture was then quenched with saturated sodium bicarbonate solution (30 mL) and the resulting mixture was extracted with dichloromethane (3 x 30 mL). The organic layers were then dried over magnesium sulfate and filtered before the solvent was removed under reduced pressure to give the product **2** as a white solid (0.64 g, 2.6 mmol, 98%). m.p. 143-145 °C (lit.[7] 145 °C). ^{1}H NMR (600 MHz, acetone-d_6) δ 7.91 (dt, J = 7.6, 0.9 Hz, 2H, Ar-H), 7.42-7.38 (m, 2H, Ar-H), 7.32-7.26 (m, 6H, Ar-H), 7.25-7.21 (m, 1H, Ar-H), 7.12-7.09 (m, 2H, Ar-H), 5.16 (s, 1H, H9).

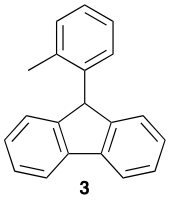
9-(*ortho*-Tolyl)-9*H*-fluorenol[3]



To a mixture of magnesium turnings (1.32 g, 54.3 mmol) and iodine (40.1 mg, 0.158 mmol) in diethyl ether (70 mL) under nitrogen, 2-bromotoluene (7.14 g, 41.7 mmol) was added dropwise using a syringe over 5 minutes. After five minutes of stirring at room temperature, the mixture had turned from orange to colourless, and was then heated at reflux for 1 hour. To this mixture, fluorenone (5.54 g, 30.7 mmol) was added and resulting mixture was heated at reflux for a further 3 hours. After cooling to room temperature, the reaction was quenched with water (60 mL) and the resulting mixture was extracted with diethyl ether (30 mL). The

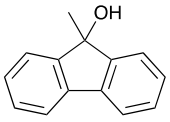
organic phase was collected, dried with magnesium sulfate and volatile components were removed under reduced pressure. The resulting solid was recrystallised from isooctane to give the title alcohol as a white solid (5.48 g, 20.1 mmol, 66%). m.p. 116-118 °C (lit.[8] 119-120 °C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 8.32 (d, J = 7.6 Hz, 1H, Ar-H), 7.69 (m, 2H, Ar-H), 7.33-7.41 (m, 3H, Ar-H), 7.16-7.25 (m, 5H, Ar-H), 6.95 (d, J = 7.4 Hz, 1H, Ar-H), 1.32 (s, 3H, CH_3).

9-(*ortho*-Tolyl)-9*H*-fluorene 3



A solution of 9-(*ortho*-tolyl)-9*H*-fluorenol (5.00 g, 18.4 mmol) in dichloromethane (40 mL) was cooled to 0 ^{o}C in an ice bath, after which triethylsilane (2.14 g, 18.4 mmol) was added, followed by boron trifluoride diethyl etherate (2.69 g, 19.0 mmol) in one portion. The reaction was stirred at 0 ^{o}C for one hour, before being quenched with saturated aqueous sodium bicarbonate solution (20 mL). The reaction mixture was extracted with diethyl ether (30 mL), the organic phase was collected, dried over magnesium sulfate and the solvent removed under reduced pressure. This gave the title compound **3** as a white solid (4.40 g, 17.2 mmol, 93%). m.p. 90-92 °C (lit.[2] 92-94.5 °C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 7.82 (d, J = 7.5 Hz, 2H, Ar-H), 7.62 (d, J = 7.5 Hz, 0.5 H, Ar-H), 6.84-7.44 (m, 9H), 6.37 (d, J = 7.5 Hz, 0.5H, Ar-H), 5.42 (s, 0.5H, C9-H), 5.03 (s, 0.5H, C9-H), 2.78 (s, 1.9 H, CH_3), 1.14 (s, 1.1H, CH_3). Note that there are two different isomers present, this is consistent with the literature.[2]

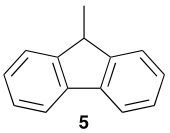
9-Methyl-9*H*-fluorenol[9]



Methylmagnesium bromide in diethyl ether (10 mL, 3 M, 30 mmol) was added to diethyl ether (50 mL) at 0°C. To this solution, fluorenone (4.52 g, 25.1 mmol) in diethyl ether (40 mL) was added under nitrogen over ten minutes. The reaction was allowed to warm to room temperature and was then stirred overnight before being quenched with water (60 mL). The reaction mixture was extracted with diethyl ether (30 mL), the organic phase was collected and dried with magnesium sulfate and volatile components were removed under reduced

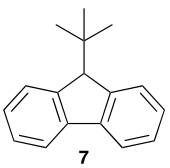
pressure. The resulting solid was recrystallised from isooctane to give the title alcohol as white solid (2.40 g, 12.2 mmol, 49%) m.p. 173-174 °C (lit.[10] 174-175 °C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 7.65 (d, J = 7.6 Hz, 2H, Ar-H), 7.60 (d, J = 7.6 Hz, 2H, Ar-H), 7.39 (m, 2H, Ar-H), 7.35 (m, 2H, Ar-H), 2.06 (s, 1H, OH), 1.76 (s, 3H, CH_3).

9-Methyl-9*H*-fluorene 5[3]


5

A solution of 9-methyl-9*H*-fluorenol **101** (906.3 mg, 1.25 mmol) in dichloromethane (10 mL) was cooled at 0 °C in an ice bath, after which triethylsilane (534 mg, 4.59 mmol) was added, followed by boron trifluoride diethyl etherate (676 mg, 4.76 mmol) in one portion. The reaction mixture was stirred at 0 °C for one hour before being allowed to warm to room temperature and stirred overnight. The reaction mixture was then quenched with saturated aqueous sodium bicarbonate solution (10 mL). The resulting mixture was extracted with diethyl ether (60 mL), the organic phase collected and washed with brine (60 mL), dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting solid was recrystallised from ethanol to give the title compound **5** as a white solid (202 mg, 1.12 mmol, 90%). m.p. 44-45 °C (lit.[11] 45-46 °C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 7.76 (d, J = 7.3 Hz, 2H, Ar-H), 7.51 (d, J = 7.3 Hz, 2H, Ar-H), 7.37 (m, 2H, Ar-H), 7.32 (m, 2H, Ar-H), 3.95 (quin, J = 7.5 Hz, 1H, C9-H), 1.53 (d, J = 7.5 Hz, 3H, CH_3).

9-(*tert*-Butyl)-9*H*-fluorene 7[3]


7

To a mixture of magnesium turnings (1.72 g, 70.8 mmol) and iodine (64.1 mg, 0.253 mmol) in dry tetrahydrofuran (60 mL) under nitrogen, 2-bromo-2-methylpropane (6.50 g, 47.4 mmol) in tetrahydrofuran (20 mL) was added dropwise over ten minutes. The reaction mixture was heated at reflux for 24 hours, after which the solution had turned colourless. To this mixture, fluorenone (7.12 g, 39.5 mmol) in dry tetrahydrofuran was added over 25 minutes and the resulting red solution was heated at reflux overnight. After cooling to room

temperature, the reaction was quenched with water (50 mL). The mixture was filtered and the filtrate was extracted with dichloromethane (50 mL). The organic phase was collected, dried with magnesium sulfate and volatile components were removed under reduced pressure. The resultant orange oil was purified using column chromatography (eluent: 1% ethyl acetate in hexane) to give 9-(*tert*-butyl)-9*H*-fluorenol as a white solid (0.500 g, 2.10 mmol, 5%). m.p. 92-94°C (lit.[12] 96°C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 7.60 (m, 2H, Ar-H), 7.58 (m, 2H, Ar-H), 7.34 (m, 2H, Ar-H), 7.23 (m, 2H, Ar-H), 1.88 (br s, 1H, OH), 1.02 (s, 9H, $C(CH_3)_3$).

A solution of 9-(*tert*-butyl)-9*H*-fluorenol (99.6 mg, 0.418 mmol) in dichloromethane (2 mL) was cooled to 0 ^{o}C in an ice bath, after which triethylsilane (58.9 mg, 0.507 mmol) was added, followed by boron trifluoride diethyl etherate (72.3 mg, 0.635 mmol) in one portion. The reaction was stirred at 0 ^{o}C for one hour, before being allowed to warm to room temperature and stirred overnight. The reaction was then quenched with saturated aqueous sodium bicarbonate solution (5 mL). The resultant mixture was extracted with diethyl ether (20 mL), the organic phase was collected, washed with brine (20 mL), dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting solid was recrystallised from ethanol to give the title compound **7** as a white solid (78.6 mg, 0.354 mmol, 85%) m.p. 103-105 °C (lit.[13] 101-101.5 °C). ^{1}H NMR (300 MHz, chloroform-d_1) δ 7.72 (d, J = 7.6 Hz, 2H, Ar-H), 7.59 (d, J = 7.6 Hz, 2H, Ar-H), 7.34 (m, 2H, Ar-H), 7.23 (m, 2H, Ar-H), 3.76 (s, 1H, C9-H), 1.00 (s, 9H, $C(CH_3)_3$).

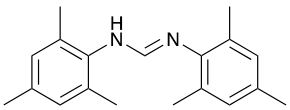
Absorbance data for the deprotonated form of each of the indicators **1-7**

Indicator	**pK_a**	**Wavelength λ_{max} /**
9-Isopropylsulfane-9*H*-fluorene **1**	16.9[14]	466
9-Phenyl-9*H*-fluorene **2**	17.9[15]	489
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8[14]	490
Carbazole **4**	19.9[16]	393
9-Methyl-9*H*-fluorene **5**	22.3[15]	515
Fluorene **6**	22.6[15]	484
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96[2]	509

Table S1: The pK_a values of the indicators used herein, and the absorbance maxima of their deprotonated form.

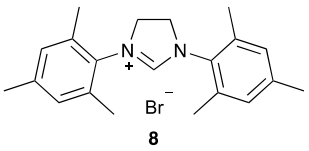
Synthesis of the salts **8-11** and pK_a data

***N*, *N*'-bis(2',4',6'-Trimethylphenyl)formamidine[17, 18]**



To a mixture of mesaniline (5.42 g, 40.1 mmol) and triethyl orthoformate (2.97 g, 20.0 mmol), glacial acetic acid (0.10 mL, 1.8 mmol) was added. The clear mixture was heated at reflux for one hour, whereupon the solution had turned red; the mixture was further heated at reflux overnight. The resulting solution was allowed to cool to room temperature, a white precipitate formed which was collected using filtration, washed with cold hexane (2 x 10 mL) and air dried over an hour. This gave the title formamidine as a white solid (5.12 g, 18.26 mmol, 91%). m.p. 207-208 °C (lit.[18] 208-210 °C). ^{1}H NMR (300 MHz, benzene-d_6) Isomer 1 δ 6.98 (d, J = 11.7 Hz, 1H, NC(H)N), 6.94 (s, 2H, Ar-H), 6.58 (s, 2H, Ar-H), 5.03 (d, J = 11.7 Hz, 1H, NH), 2.35 (s, 6H, C2"-CH_3), 2.27 (s, 3H, C4"-CH_3), 2.06 (s, 3H, C4'-CH_3), 1.89 (s, 6H, C2'-CH_3). Isomer 2: δ 6.86 (s, 1H, NC(H)N), 6.79 (s, 4H, Ar-H), 2.19 (s, 12H, C2'-CH_3), 2.16 (s, 6H, C4'-CH_3).

1,3-bis(2',4',6'-Trimethylphenyl)-4,5-dihydroimidazolium bromide 8[19]

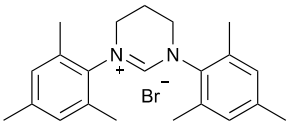


8

A solution of 2,4,6-trimethylphenylformamidine (2.49 g, 8.88 mmol), 1,2-dibromoethane (1.92 g, 10.2 mmol) and potassium carbonate (0.71 g, 5.14 mmol) in acetonitrile (125 mL) was heated at reflux for three days. The reaction mixture was allowed to cool to room temperature and the precipitate that formed was collected through filtration, was washed with hexane and air-dried to yield the title product **8** as a white solid (3.10 g, 8.00 mmol, 90%). m.p. 296-299 °C (lit.[20] 314-316 °C dec.). ^{1}H NMR (300 MHz, chloroform-d_1) δ 8.79 (s, 1H, C2-H), 6.98 (s, 4H, Ar-H), 4.67 (s, 4H, NCH_2), 2.41 (s, 12H, C2-CH_3), 2.30 (s, 6H, C4'-CH_3). ^{1}H NMR (400 MHz, dimethyl sulfoxide-d_6) δ 9.00 (s, 1H, C2-H), 7.09 (s, 4H, Ar-H), 4.44 (s, 4H, NCH_2), 2.35 (s, 12H, C2'-CH_3), 2.29 (s, 6H, C4'-CH_3).

1,3-*bis*(2',4',6'-Trimethylphenyl)-4,5-dihydroimidazolium bromide 8			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.1993	19.50
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.1785	19.55
Carbazole **4**	19.9	2.249	19.55
Carbazole **4**	19.9	2.700	19.47
Fluorene **6**	22.6	>100	<20.6
Fluorene **6**	22.6	>100	<20.6
		Overall	**19.52 ± 0.12**

1,3-bis(2',4',6'-Trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide 9[19]

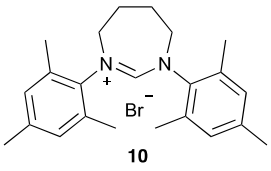


9

To a stirred solution of 2,4,6-trimethylphenylformamidine (2.32 g, 8.27 mmol) and 1,3-dibromopropane (1.75 g, 8.67 mmol) in acetonitrile (150 mL), sodium carbonate (2.05 g, 19.3 mmol) was added. The reaction mixture was heated at reflux for three days. The reaction was allowed to cool to room temperature and the solvent removed under reduced pressure, resulting in the title compound **9** as a white solid (3.11 g, 7.75 mmol, 94%). m.p. 250-254 °C (lit.[19] not reported). ^{1}H NMR (400 MHz, chloroform-d_1) δ 7.60 (s, 1H, C2-H), 6.90 (s, 4H, Ar-H), 4.13 (t, J = 5.6 Hz, 4H, NCH_2), 2.57 (quin, J = 5.6 Hz, 2H, CH_2), 2.30 (s, 12H, C2'-CH_3), 2.22 (s, 6H, C2'-CH_3). ^{1}H NMR (400 MHz, dimethyl sulfoxide-d_6) δ 8.64 (s, 1H, C2-H), 7.06 (s, 4H, Ar-H), 3.81 (t, J = 5.5 Hz, 4H, NCH_2), 2.37 (quin, J = 5.5 Hz, CH_2), 2.26-2.26 (m, 18H, C4'-CH_3, C2'-CH_3).

1,3-bis(2',4',6'-Trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide 9			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
Carbazole **4**	18.8	0.02176	21.56
Carbazole **4**	18.8	0.02085	21.58
Fluorene **6**	22.6	12.06	21.52
Fluorene **6**	22.6	8.759	21.65
		Overall	**21.58 ± 0.17**

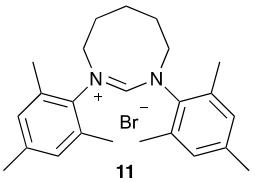
1,3-*bis*(2',4',6'-Trimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 10[21]



To a stirred mixture of 2',4',6'-trimethylphenylformamidine (2.01 g, 7.17 mmol) and 1,4-dibromobutane (1.57 g, 7.27 mmol) in acetonitrile (100 mL), potassium carbonate (0.57 g, 7.8 mmol) was added. The reaction mixture was heated at reflux for 48 hours before being allowed to cool to room temperature. The volatile components were removed under reduced pressure and the residue recrystallised from dichloromethane/diethyl ether to give the title compound **10** as a white solid (1.15 g, 2.77 mmol, 39%). m.p. 184 °C (lit.[22] 204-205 °C). ^{1}H NMR (400 MHz, chloroform-d_1) δ 7.22 (s, 1H, C2-H), 6.92 (s, 4H, Ar-H), 4.58-4.51 (m, 4H, NCH_2), 2.56-2.52 (m, 4H, CH_2), 2.46 (s, 12H, C2'-CH_3), 2.31 (s, 6H, C4'-CH_3). ^{1}H NMR (400 MHz, dimethyl sulfoxide-d_6) δ 8.27 (s, 1H, C2-H), 7.04 (s, 4H, Ar-H), 4.20-4.13 (m, 4H, NCH_2), 2.35-2.29 (m, 16H, CH_2, C2'-CH_3), 2.25 (s, 6H, C4'-CH_3).

1,3-*bis*(2',4',6'-Trimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 10			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
Carbazole **4**	19.9	0.09140	20.94
Carbazole **4**	19.9	0.07930	21.00
Fluorene **6**	22.6	41.18	20.99
Fluorene **6**	22.6	37.23	21.03
Fluorene **6**	22.6	46.17	20.94
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	77.70	21.07
		Overall	**20.99 ± 0.13**

1,3-*bis*(2',4',6'-trimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocinium bromide 11[23]



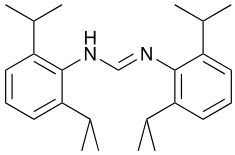
To a stirred mixture of 2',4',6'-trimethylphenylformamidine (2.78 g, 9.91 mmol) and 1,5-dibromopentane (2.30 g, 10.0 mmol) in acetonitrile (250 mL), *N*,*N*-diisopropylethylamine (1.50 g, 11.6 mmol) was added. The reaction mixture was heated at reflux for 12 days, allowed to cool to room temperature and the volatile components were removed under reduced pressure. Recrystallisation of the residue from dichloromethane/diethyl ether gave the title compound **11** as a white solid (1.18 g, 2.75 mmol, 28%). m.p. 224-226 °C (lit.[23] not reported). ^{1}H NMR (600 MHz, dimethyl sulfoxide-d_6) δ 7.39 (s, 1H, C2-H), 6.93 (s, 4H, Ar-H), 3.77 (s, br, 4H, NCH_2), 2.40 (s, 12H, C2'-CH_3), 2.31-2.24 (m, 4H,

NCH_2CH_2), 2.25 (s, 6H, C4'-CH_3), 2.01 (m, 2H, CH_2). ^{1}H NMR (400 MHz, dimethyl sulfoxide-d_6) δ 8.46 (s, 1H, C2-H), 7.03 (s, 4H, Ar-H), 4.40-4.30 (m, NCH_2), 2.30 (s, 12H, C2'-CH_3), 2.25 (s, 6H, C4'-CH_3), 2.16-2.05 (m, 4H, NCH_2CH_2), 2.05-1.95 (m, 2H, CH_2).

1,3-*bis*(2',4',6'-trimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocinium bromide 11			
Indicator	**pK_a of indicator**	**Measured K**	**pK_a**
Carbazole **4**	19.9	0.06114	21.11
Carbazole **4**	19.9	0.05698	21.14
Fluorene **6**	22.6	30.36	21.12
Fluorene **6**	22.6	25.24	21.20
Fluorene **6**	22.6	21.65	21.26
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	52.62	21.24
		Overall	**21.18 ± 0.16**

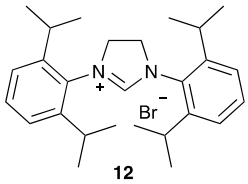
Synthesis of the salts **12-14** and pK_a data

N, *N*'-Diisopropylformamidine[18]



To a mixture of diisopropylaniline (5.35 g, 30.2 mmol) and triethyl orthoformate (2.36 g, 15.92 mmol), glacial acetic acid (0.50 mL, 8.74 mmol) was added. The clear mixture was heated at reflux, whereupon a white precipitate had formed after 4 hours and the reaction mixture was further heated at reflux overnight. The precipitate was collected through filtration, was washed with cold ethyl acetate (2 x 15 mL) and air dried. This gave the product title formamidine as a white solid (3.44 g, 9.44 mmol, 63%). m.p. 202-204 °C (lit.[18] 202-203 °C). ^{1}H NMR (400 MHz, benzene-d_6) Major isomer δ 7.09-7.02 (m, 6H, Ar-H), 3.43 (sept, J = 6.7 Hz, 4H, CH), 1.11 (d, J =6.7 Hz, 24H, CH_3).

1,3-*bis*(2',6'-Diisopropylphenyl)-4,5-dihydroimidazolium bromide 12[19]

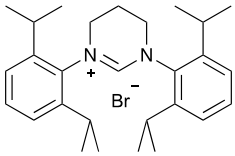


12

To a stirred solution of 2,6-diisopropylformamidine (1.87 g, 5.13 mmol) and 1,2-dibromoethane (2.98 g, 15.9 mmol) in acetonitrile (70 mL), potassium carbonate (0.38 g, 2.75 mmol) was added in one portion. The reaction mixture was heated at reflux until the formamidine was consumed as determined using TLC (ten days). The reaction mixture was allowed to cool to room temperature and filtration of the mixture allowed isolation of the title compound **12** as a white solid (2.14 g, 4.54 mmol, 88%). m.p. 280 °C (lit.[19] not reported). ^{1}H NMR (400 MHz, chloroform-d_1) δ 8.13 (s, 1H, C2-H), 7.48 (t, J = 7.8 Hz, 2H, Ar-H), 7.29 (d, J = 7.8 Hz, 4H, Ar-H), 4.88 (s, 4H, NCH_2), 3.06 (sept, J = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.41 (d, J = 6.8, 12H, $CH(CH_3)_2$), 1.25 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$)

1,3-*bis*(2',6'-Diisopropylphenyl)-4,5-dihydroimidazolium bromide 12			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	3.950	19.30
Carbazole **4**	19.9	3.220	19.39
Carbazole **4**	19.9	3.426	19.36
Carbazole **4**	19.9	0.3516	19.25
		Overall	**19.33 ± 0.20**

1,3-b*is*(2',6'-Diisopropylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide 13[19]

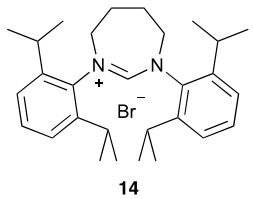


13

To a stirred solution of 2,6-diisopropylformamidine (2.60 g, 7.13 mmol) and 1,3-dibromopropane (2.20 g, 10.9 mmol) in acetonitrile (100 mL), potassium carbonate (0.54 g, 4.70 mmol) was added in one portion. The reaction mixture was heated at reflux until the formamidine was consumed as determined using TLC (four days). The reaction mixture was allowed to cool to room temperature and filtration of the mixture allowed isolation of the title compound **13** as a white solid (3.30 g, 4.79 mmol, 93%). m.p. 290-295 °C (lit. 269-270 °C (EtOAc);[22] 300-301 °C (dec.)[24]) ^{1}H NMR (600 MHz, chloroform-d_1) δ 7.54 (s, 1H, C2-H), 7.44 (t, J = 7.7 Hz, 2H, C4'-H), 7.25 (d, J = 7.7 Hz, 4H, C3'-H), 4.27 (t, J = 5.6 Hz, 4H, NCH_2), 3.05 (sept, J = 6.8 Hz, m, 4H, $CH(CH_3)_2$), 2.76 (pent, J = 5.6 Hz, 2H, NCH_2CH_2), 1.40 (d, J = 6.8, 12H, $CH(CH_3)_2$), 1.28 (d, J = 6.8 Hz, 12H, $CH(CH_3)_2$).

1,3-*bis*(2',6'-Diisopropylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide 13			
Indicator	**pK_a of indicator**	**Measured K**	**pK_a**
Fluorene **6**	22.6	3.475	22.06
Fluorene **6**	22.6	3.858	22.01
Fluorene **6**	22.6	4.377	21.96
Fluorene **6**	22.6	4.418	21.95
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	11.06	21.92
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	10.24	21.95
		Overall	**21.98 ± 0.13**

1,3-*bis*(2',6'-Diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 14[22]



14

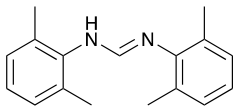
To a stirred mixture of 2,6-diisopropylformamidine (3.27 g, 12.4 mmol) and 1,4-dibromobutane (2.20 g, 11.7 mmol), *N*,*N*-diisopropylethylamine (0.723 g, 5.59 mmol) was added. The reaction mixture was heated at reflux for three hours, was allowed to cool to room temperature and the volatile components were removed under reduced pressure. The residue was dissolved in dichloromethane (16 mL) and the solution was washed with saturated aqueous potassium carbonate (2 x 5 mL). The organic solvent was removed under reduced pressure to give a white residue, which was recrystallised from dichloromethane/toluene to give the title compound **14** as a white crystalline solid (3.54 g, 7.09

mmol, 61%). m.p. 246-248 °C (lit.[22] 254-256 °C). ^{1}H NMR (600 MHz, dimethyl sulfoxide-d_6) δ 7.40 (t, J = 7.8 Hz, 2H, C4'-H), 7.27 (s, 1H, C2-H), 7.24 (d, J = 7.8 Hz, 4H, C3'-H), 4.70-4.66 (m, 4H, NCH_2), 3.22 (sept, J = 6.7 Hz, 4H, $CH(CH_3)_2$), 2.65-2.61 (m, 4H, NCH_2CH_2), 1.39 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$), 1.24 (d, J = 6.7 Hz, 12H, $CH(CH_3)_2$).

1,3-*bis*(2',6'-Diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 14			
Indicator	**pK_a of indicator**	**Measured K**	**pK_a**
Carbazole **4**	19.9	0.01530	21.72
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	15.00	21.78
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	18.02	21.70
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	15.51	21.77
		Overall	**21.74 ± 0.13**

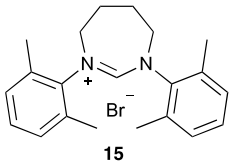
Synthesis of the salt **15** and pK_a data

***N*,*N*'-(2',6'-Dimethylphenyl)formamidine[25]**



To a mixture of 2,6-dimethylaniline (7.28 g, 60.1 mmol) and triethyl orthoformate (5.61 g, 37.9 mmol), glacial acetic acid (0.10 mL, 1.8 mmol) was added dropwise over ten minutes. The solution was heated at reflux overnight. Upon cooling the reaction mixture to room temperature, a white solid precipitated from the solution. This solid was collected through filtration, washed with cold hexane (2 x 10 mL) and air dried over an hour to give the title formamidine as a white solid (6.17 g, 24.5 mmol, 81%). m.p. 181-184 °C (lit.[25] 181 °C). ^{1}H NMR (300 MHz, dimethyl sulfoxide-d_6) δ 6.50 (s, 1H, NC(H)N), 6.21 (m, 6H Ar-H), 1.54 (s, 6H, 2'-CH_3), 1.39 (s, 6H, C2'-CH_3).

1,3-*bis*(2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 15[22]



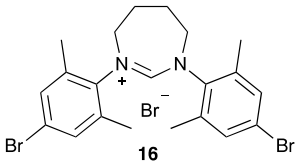
15

To a stirred solution of 2,6-dimethylformamidine (3.00 g, 11.9 mmol) and 1,4-dibromobutane (7.74 g, 4.63 mmol) in acetonitrile (200 mL), potassium carbonate (4.95 g, 35.8 mmol) was added in one portion. The reaction mixture was heated at reflux until the formamidine was consumed as determined using TLC (eight days). The reaction mixture was allowed to cool to room temperature and volatile components were removed under reduced pressure. The residue was dissolved in dichloromethane (100 mL) and diethyl ether (50 mL) was added. The precipitate that formed was collected using filtration and was recrystallised from ethanol/diethyl ether to give the title compound **15** as a white solid (2.16 g, 5.58 mmol, 47%). m.p. 236-238 °C (lit.[22] not reported). ^{1}H NMR (600 MHz, dimethyl sulfoxide-d_6) δ 7.28 (s, 1H, C2-H), 7.21-7.17 (m, 2H, C4-H), 7.11 (d, J = 7.6 Hz, 4H, C3-H), 4.61-4.58 (m, 4H, NCH_2), 2.56-2.53 (m, 4H, NCH_2CH_2), 2.37 (s, 12H, Ar-CH_3).

1,3-*bis*(2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 15			
Indicator	**pK_a of indicator**	**Measured K**	**pK_a**
Fluorene **6**	22.6	12.48	21.50
Fluorene **6**	22.6	11.64	21.53
Fluorene **6**	22.6	11.78	21.53
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	33.74	21.43
		Overall	**21.50 ± 0.15**

pK_a Data for salt **16**

1,3-*bis*(4'-Bromo, 2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 16



16

1,3-*bis*(4'-bromo, 2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide 16			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
Carbazole **4**	19.9	0.2142	20.57
Carbazole **4**	19.9	0.1628	20.69
Fluorene **6**	22.6	84.90	20.67
Fluorene **6**	22.6	78.43	20.71
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	>100	<20.96
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	>100	<20.96
9-(*tert*-Butyl)-9*H*-fluorene **7**	22.96	>100	<20.96
		Overall	**20.69 ± 0.19**

NMR experiments to determine the relative acidity of salts **10** and **15**

General conditions: Sodium hydride (60% dispersion in oil, 10 equiv) was washed with *n*-pentane (3 x 3 mL) and dried under vacuum. A solution of salt **10** (1 equiv.) in dry DMSO (2 mL) was then added under nitrogen and the resultant mixture was stirred for ten minutes, before the solution was transferred under nitrogen into a dried flask *via* filter cannula. Half of this solution was transferred to a Young's tap NMR tube and subjected to ^{1}H NMR analysis (resulting in the green spectra in Figures S3 and S4 below). To the remainder of the solution was added a solution of salt **15** (0.5 equiv.) in dry DMSO (1 mL). The resultant solution was stirred for five minutes and then transferred into a Young's tap tube and subjected to ^{1}H NMR analysis.

Competition 1: Salt **10** (8.7 mg, 0.021 mmol), sodium hydride (60% dispersion in oil, 92.9 mg, 2.32 mmol), salt **15** **(3.9** mg, 0.010 mmol).

Competition 2: Salt **10** (0.121 g, 0.290 mmol), sodium hydride (60% dispersion in oil, 0.108 g, 2.72 mmol), salt **15** (56.3 mg, 0.146 mmol).

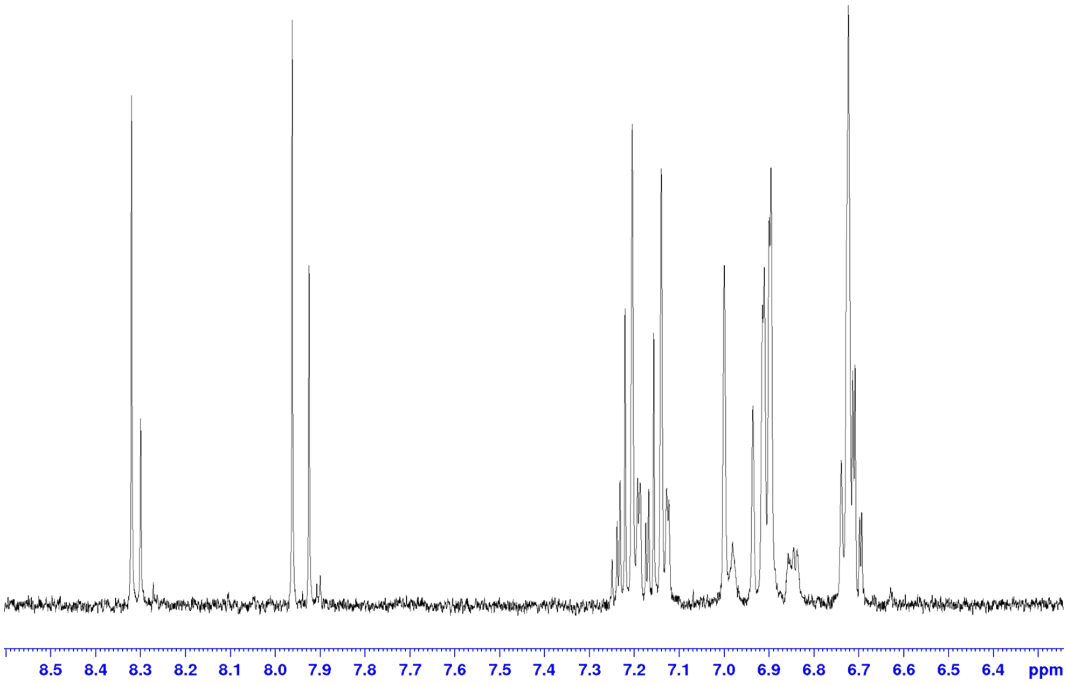


Figure S1. A portion of the ^{1}H NMR spectrum (600 MHz, dry DMSO) for competition 1. Key signals include salt **15,** δ 8.32 (s, C2-H) and 7.25-7.16 (m, Ar-H), the carbene formed from salt 10 δ 8.30 (s), 7.92 (s), 7.01-6.97 (m), 6.94-6.89 (m) and 6.75-6.71 (m). Other signals in this region δ 7.96 (s), 7.16-7.11 (s), 6.92-6.89 (m) and 6.71-6.69 (m) are assumed to be the result of deprotonation of salt **15** by excess base.

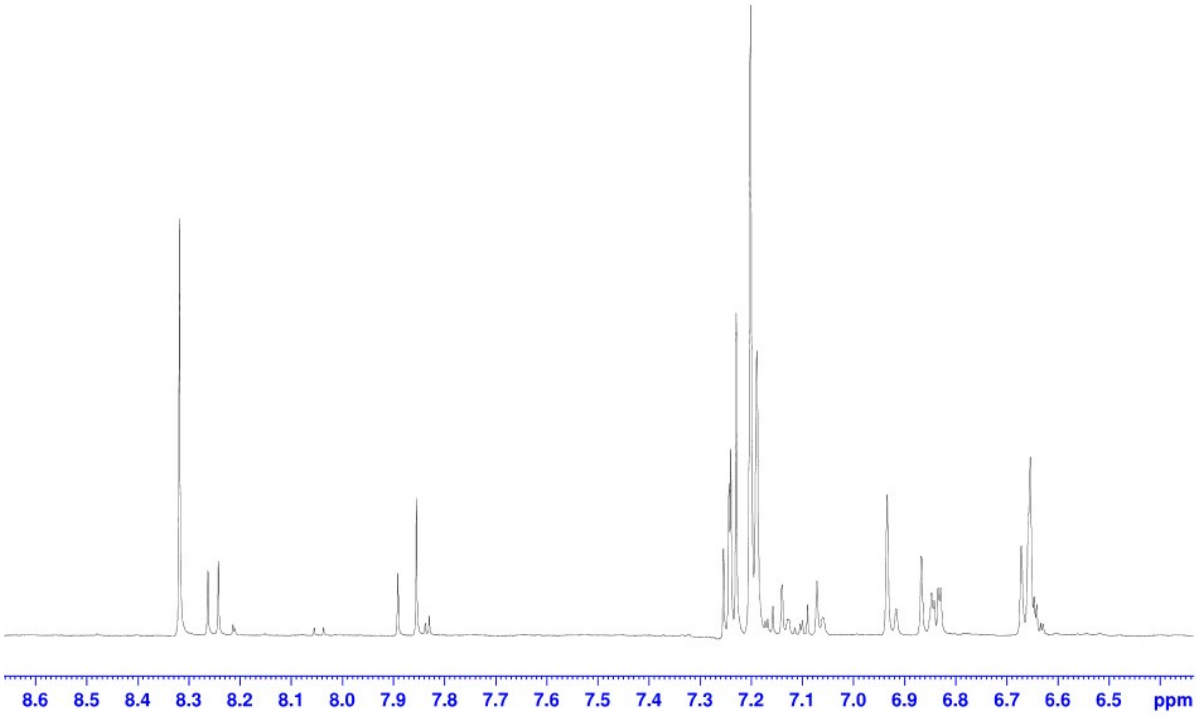


Figure S2. A portion of the ^{1}H NMR spectrum (600 MHz, dry DMSO) for competition 2. Key signals include salt **15,** δ 8.32 (s, C2-H) and 7.26-7.18 (m, Ar-H), the carbene formed from salt 10 δ 8.24 (s), 7.86 (s), 6.93-6.91 (m), 6.87-6.84 (m) and 6.68-6.64 (m). Other signals in this region δ 8.26 (s), 7.89 (s), 7.16-7.05 (m) and 6.85-6.81 (m) are assumed to be the result of deprotonation of salt **15** by excess base.

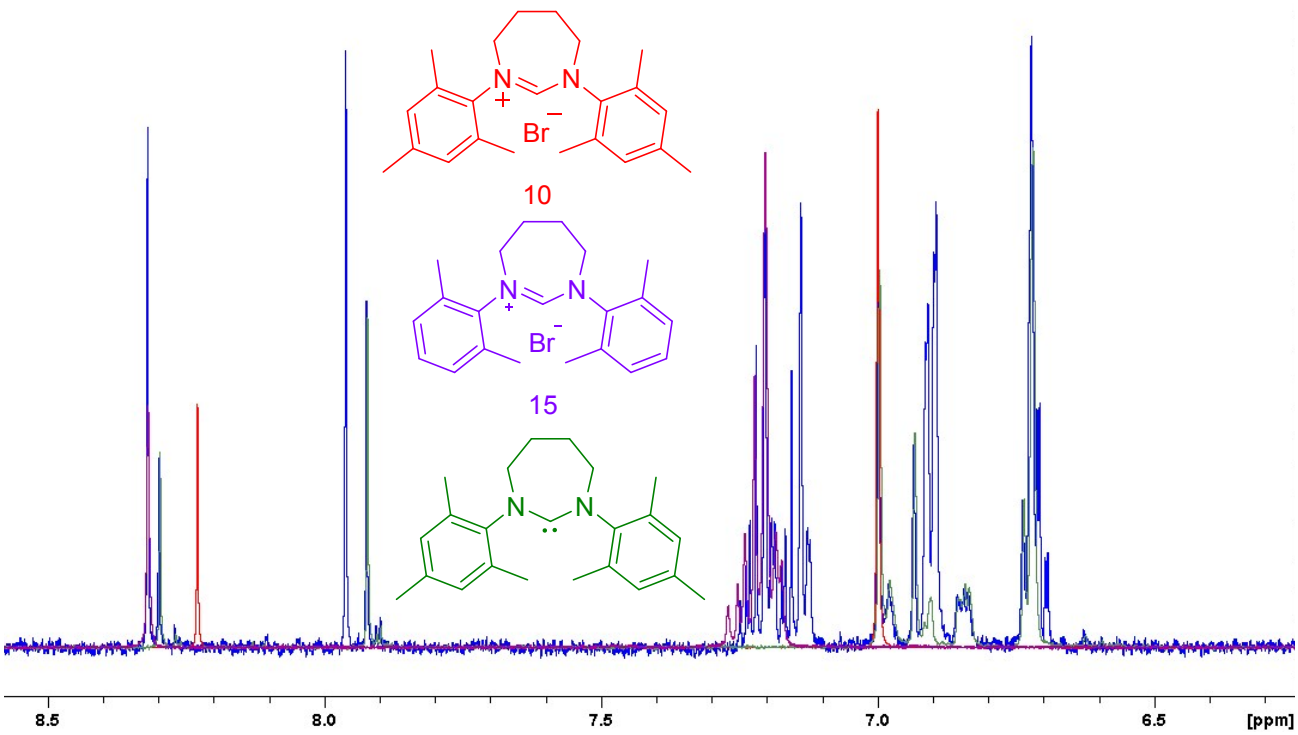


Figure S3. An overlay of portions of several ^{1}H NMR spectra (600 MHz, dry DMSO). Red = Salt **10**. Purple = Salt **15**. Green = The carbene generated from salt **10**. Blue = Competition experiment 1.

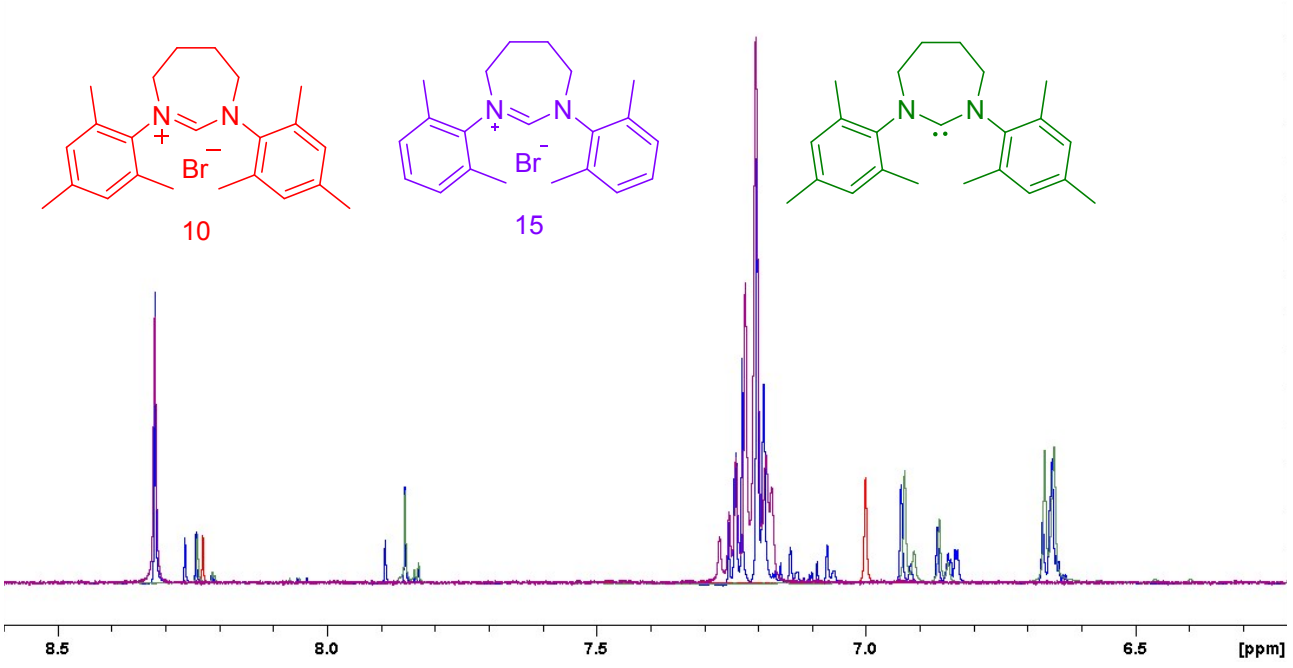


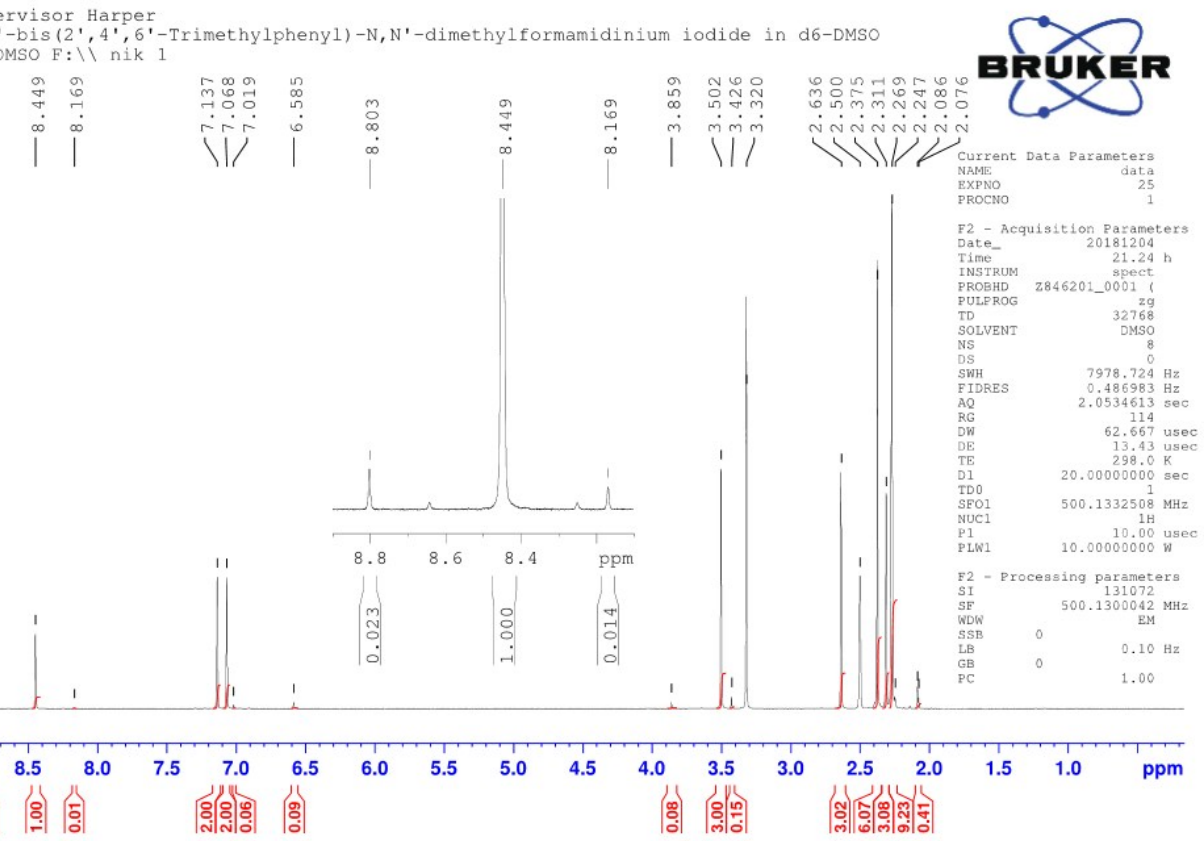
Figure S4. An overlay of portions of several ^{1}H NMR spectra (600 MHz, dry DMSO). Red = Salt **10**. Purple = Salt **15**. Green = The carbene generated from salt **10**. Blue = Competition experiment 2.

Figures S3 and S4 demonstrate that combining solutions of the carbene derived from the salt **10** and the salt **15** results in a mixture of the salt **15** and the carbene generated from salt **10**. Any additional signals in the spectrum are assumed to be the result of deprotonation of salt **15** by small

amounts of excess base (sodium dimsyl) generated upon the treatment of DMSO with excess sodium hydride. Most telling, is the fact that no signals due to the salt **10** can be seen in the spectra of the final mixtures, noting the distinct lack of signals at δ 8.23 in Figure S3 or at either δ 8.23 or 7.00 in Figure S4.

Identifying conformers in NMR spectra of the formamidinium salts **19-22**

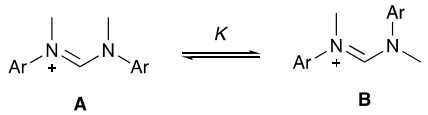
For the formamidinium salts **19-22** detailed herein, multiple conformers were noted in the ^{1}H NMR spectra* and were identified and assigned as follows. Conformer B was identified through the presence of two separare *N*-methyl signals at δ *ca*. 3.6 and 2.7, as conformer B is the only non-symmetrical conformer. The next most numerous conformer was assumed to be conformer A as the steric hindrance between the two phenyl rings in conformer C would likely disfavour its formation in solution.



* A recycle time of 20 s was used to ensure complete relaxation of the nuclei considered.

Figure S5 A ^{1}H NMR spectrum of the mesityl substituted formamidinium iodide **19** in d_6-DMSO. The expansion highlights the C2-H proton signals for the three conformers **A**, **B** and **C**, respectively.

With this data, the position of equilibrium for the reaction shown in Scheme S1 was determined (Table S2). A conservative estimate of uncertainty (10%) was assumed for each integral in determining the position of equilibrium; this uncertainty was considered more realistic than the comparatively small (generally 2-5%) reproducibility uncertainties from replicate experiments.



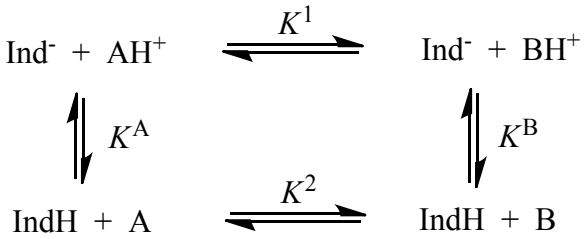
Scheme S1. The equilibrium between the two conformers **A** and **B** of formamidinium cations.

Compoun	*K*
19	44 ± 4
20	54 ± 6
21	38± 4
22	1.46 ±

Table S2. Equilibrium constants between conformers **A** and **B** for the formamidinium salts **19**-**22**, determined in d_6-DMSO using ^{1}H NMR spectroscopy. Uncertainties are based on 10% uncertainties in the integrals on which the ratios are based.

Determination of pK_a values for formadinium salts **19-22**

The pK_a values reported herein were determined following the methodology we have outlined previously,[26,27] with the exception of the phenyl formamidinium salt **22**, as this compound exhibited significant portions of conformers **A** and **B**, and so the pK_a values of both conformers was considered.



Scheme S2: AH^+ and BH^+ / A and B' are two conformers (protonated and deprotonated forms) with K^1 being the equilibrium constant for the interconversion of the protonated conformers, while K^2 is the equilibrium constant for the interconversion of the deprotonated conformers. K^A and K^B are the equilibrium constants for reaction of the protonated forms with a given indicator (Ind^-).

From the various equilibria introduced in Scheme S2.

$$K^1 = \frac{[BH^+]}{[AH^+]} \Rightarrow [BH^+] = K^1[AH^+]$$

$$K^2 = \frac{[B]}{[A]} \Rightarrow [B] = K^2[A]$$

$$K^A = \frac{[A][IndH]}{[AH^+][Ind^-]}$$

$$K^B = \frac{[B][IndH]}{[BH^+][Ind^-]}$$

therefore

$$K^B = \frac{K^2[A][IndH]}{K^1[AH^+][Ind^-]} \Rightarrow \frac{K^1K^B}{K^2} = \frac{[A][IndH]}{[AH^+][Ind^-]}$$

$$K^A = \frac{[A][IndH]}{[AH^+][Ind^-]}$$

$$K^A = \frac{K^1K^B}{K^2}$$

$$therefore\ K^2 = \frac{K^1K^B}{K^A}$$

Importantly, the apparent position of equilibrium, K_{app}, which is the effective equilibrium constant obtained utilising the UV-vis titration methodology we have reported previously,[26,27] can be correlated to the total amount of protonated ([A_{tot}]) and deprotonated ([AH_{tot}]) formamidinium salt.

$$K_{app} = \frac{[A_{tot}][IndH]}{[AH_{tot}][Ind^-]}$$

$$K_{app} = \frac{([A] + [B])}{([AH^+] + [BH^+])} . \frac{[IndH]}{[Ind^-]}$$

$$= \frac{([A] + [B])}{([AH^+] + [BH^+])} . \frac{1/[AH^+]}{1/[AH^+]} . \frac{[IndH]}{[Ind^-]}$$

$$= \frac{([A] + [B])/[AH^+]}{\frac{[AH^+]}{[AH^+]} + \frac{[BH^+]}{[AH^+]}} . \frac{[IndH]}{[Ind^-]}$$

$$= \frac{([A] + [B])/[AH^+]}{1 + \frac{[BH^+]}{[AH^+]}} . \frac{[IndH]}{[Ind^-]}$$

$$= \frac{([A] + [B])/[AH^+]}{1 + K^1} . \frac{[IndH]}{[Ind^-]}$$

$$= \frac{([A] + [B])}{[AH^+]} . \frac{1}{1 + K^1} . \frac{[IndH]}{[Ind^-]}$$

$$= \left(\frac{[A][IndH]}{[AH^+][Ind^-]} + \frac{[B][IndH]}{[AH^+][Ind^-]}\right) . \frac{1}{1 + K^1}$$

$$= \left(K^A + \frac{[B][IndH]}{[AH^+][Ind^-]}\right) . \frac{1}{1 + K^1}$$

$$= \left(K^A + \frac{[B][IndH]}{[AH^+][Ind^-]}\right) . \frac{[BH^+]}{[BH^+]} . \frac{1}{1 + K^1}$$

$$= \left(K^A + \frac{[B][IndH]}{[AH^+][Ind^-]}\right) . \frac{[BH^+]}{[BH^+]} . \frac{1}{1 + K^1}$$

$$= \left(K^A + \frac{[B][IndH]}{[BH^+][Ind^-]} . \frac{[BH^+]}{[AH^+]}\right) . \frac{1}{1 + K^1}$$

$$= (K^A + K^B K^1).\frac{1}{1 + K^1}$$

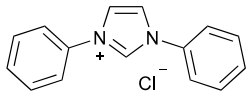
$$K_{app} = \frac{K^A + K^B K^1}{1 + K^1}$$

$$K^B = \frac{K_{app}(1 + K^1) - K^A}{K^1}$$

Note that the value of K^1 for salts **19-21** was quite large (see Table S2) such that $K^B \approx K_{app}$ for all but the most extreme values of K^A.

For the diphenyl salt **22**, K^1 was determined to be 1.46 ± 0.15 from ^{1}H NMR studies in d_6-DMSO (see Table S2). K^A is the acid dissociation constant for conformer **A**. As the value for K^A (the equilibrium constants for reaction of that conformer with a given indicator) cannot be explicitly measured, it was assumed that the pK_a value of conformer **A** of salt **22** is identical to that for the corresponding six-membered heterocyclic system; unfortunately, that data is unavaible so it was determined to be approximately 20.3. This is approximation based on the fact the pK_a value of salt **S1** (Figure S6) is known (allowing the effect of the three methyl groups to be taken into account and serving as a staring point), that salts **8** and **17** have the same pK_a value (such that the removal of aromaticity from salt **S1** has no effect on acidity) and that salts **8** and **9** differ in pK_a value by 2 (such that the effect of ring size is taken into account). Thus,

Given the large difference in the pK_a values between the conformers of salt **22**, it is worth noting that comparatively large (±1) changes in the estimate of K^A have a neglibible impact upon the K^B, and therefore upon the pK_a of formamidinium salt **22**.



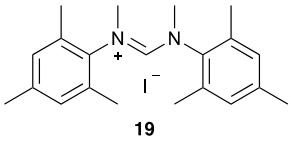
S1

pK_a = 18.33 ± 0.09

Figure S6. The pK_a value of the phenyl imidazolium salt **S1** in DMSO at 25 °C reported previously.[26]

Synthesis of the formamidinium salts **19-22** and pK_a data

N,*N*'-*bis*(2',4',6'-Trimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide 19[28]



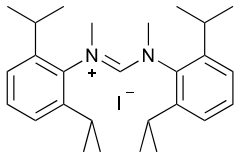
19

To a slurry of trimethylformamidine (1.38 g, 4.92 mmol) and sodium bicarbonate (2.12 g, 25.2 mmol) in acetonitrile (10 mL), methyl iodide (2.37 g, 16.7 mmol) was added in one portion. The reaction mixture was heated at reflux until the formamidine was consumed as determined using TLC (two days). The reaction mixture was diluted with acetonitrile (20 mL) and filtered to remove excess base. The filtrate was concentrated under reduced pressure to give a yellow oil. Addition of ethyl acetate (10 mL) precipitated a white solid that was recrystallised from dichloromethane/ethyl acetate to give the title compound **19** as a white solid (0.450 g, 1.03 mmol, 21%). m.p. 220-222 °C (lit.[28] not reported). ^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6) Conformer A: δ 8.80 (s, 1H, C2-H), 6.59 (s, 4H, 3□-Ar-H), 3.43 (s, 6H, NCH_3), 2.08 (s, 12H, C2□-CH_3), 2.08 (s, 6H, C4□-CH_3). Conformer B: δ 8.45 (s, 1H, C2-H), 7.13 (s, 2H, Ar-H), 7.07 (s, 2H, Ar-H), 3.50 (s, 3H, NCH_3), 2.64 (s, 3H, NCH_3), 2.37 (s, 6H, 2'-CH_3), 2.31 (s, 3H, C4'-CH_3), 2.27 (s, 9H, C2',4'-CH_3). Conformer C: δ 8.17 (s, 1H, C2-H), 7.02 (s, 4H, 3□-Ar-H), 3.86 (s, 6H, NCH_3), 2.27 (s, 12H, C2-CH_3),† 2.25 (s, 6H, C4□-CH_3). Ratio A : B : C is 0.02 : 1 : 0.01.

***N*,*N*'-*bis*(2',4',6'-Trimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide 19**			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.1120	19.76
Carbazole **4**	19.9	1.865	19.63
Carbazole **4**	19.9	1.667	19.68
Carbazole **4**	19.9	1.379	19.77
Carbazole **4**	19.9	1.835	19.64
Carbazole **4**	19.9	1.674	19.68
Fluorene **6**	22.6	>100	<20.6
		Overall	**19.69 ± 0.16**

† This signal was obscured by a larger methyl signal seen for conformer B.

***N*,*N*'-*bis*(2',6'-Diisopropylphenyl)-*N*,*N*'-dimethylformamidinium iodide 20[28]**

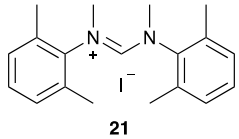


20

To a slurry of diisopropylphenylformamidine (1.71 g, 4.70 mmol) and sodium bicarbonate (2.23 g, 26.5 mmol) in acetonitrile (10 mL), methyl iodide (2.43 g, 17.1 mmol) was added in one portion. The reaction mixture was heated at reflux until the formamidine was consumed as determined using TLC (two days). The reaction mixture was diluted with acetonitrile (20 mL) and filtered to remove excess base. The filtrate was concentrated under reduced pressure to give an off-white solid. The resulting solid was recrystallised from dichloromethane/ethyl acetate to give the title compound **20** as a white solid (1.22 g, 2.34 mmol, 50%). m.p. 201-204 °C (lit.[28] not reported). ^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6) Conformer A: δ 8.52 (s, 1H, C2-H), 7.32 (d, J = 7.7 Hz, 4H, C3-Ar-H), 3.96 (s, 6H, NCH_3), 3.13 (sept, J = 6.6 Hz, 4H, $CH(CH_3)_2$).Conformer B: δ 8.92 (s, 1H, C2-H), 7.65-7.60 (m, 1H, Ar-H), 7.56-7.50 (m, 3H, Ar-H), 7.42 (d, J = 7.8 Hz, 2H, Ar-H), 3.60 (s, 3H, NCH_3), 3.01 (sept, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.80 (sept, J = 6.8 Hz, 2H, $CH(CH_3)_2$), 2.70 (s, 3H, NCH_3), 1.39 (d, J = 6.8, 6H, CH_3), 1.36-1.30 (m, 12H, CH_3), 1.23 (d, 6H, J = 6.8, CH_3). Conformer C: δ 8.80 (s, 1H, C2-H). Ratio A : B : C is 0.02 : 1 : 0.01.‡

N,N'-*bis*(2',6'-diisopropylphenyl)-N,N'-dimethylformamidinium iodide 20			
Indicator	**pK_a of indicator**	**Measured K_a**	**pK_a**
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.3515	19.21
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.3361	19.27
Carbazole **4**	19.9	3.508	19.36
Carbazole **4**	19.9	3.842	19.32
		Overall	**19.29 ± 0.20**

***N*,*N*'-*bis*(2',6'-Dimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide 21**



21

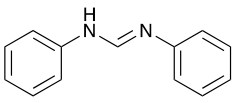
To a slurry of dimethylformamidine (1.25 g, 4.95 mmol) and sodium bicarbonate (2.43 g, 28.9 mmol) in acetonitrile (10 mL), methyl iodide (2.46 g, 17.3 mmol) was added in one portion. The reaction mixture was heated at reflux until the

‡ Other signals for conformer C are presumed to be obscured by larger signals in the ^{1}H NMR spectrum.

formamidine was consumed as determined using TLC (two days). The reaction mixture was diluted with acetonitrile (20 mL) and filtered to remove excess base. The filtrate was concentrated under reduced pressure to give an off-white solid. The resulting solid was recrystallised from dichloromethane/diethyl ethyl acetate to give the title compound **21** as a white solid (0.79 g, 1.93 mmol, 39%) m.p. 211-214 °C. ^{1}H NMR (600 MHz, dimethyl sulfoxide-d_6) Conformer A: δ 8.87 (s, 1H, C2-H), 6.93 (t, J = 7.5 Hz, 4-Ar-H), 6.80 (d, J = 7.5 Hz, 3-Ar-H), 3.46 (s, 6H, NCH_3), 2.14 (s, 12H, C2-CH_3). Conformer B: δ 8.50 (s, 1H, C2-H), 7.44-7.40 (m, 1H, Ar-H), 7.35-7.30 (m, 3H, Ar-H), 7.27 (d, J = 7.7 Hz, 2H, Ar-H), 3.54 (s, 3H, NCH_3), 2.65 (s, 3H, NCH_3), 2.43 (s, 6H, C2'-CH_3), 2.33 (s, 6H, C2'-CH_3). Conformer C: δ 8.26 (s, 1H, C2-H), 7.22 (d, J = 7.4 Hz, 4H, Ar-H), 3.90 (s, 6H, NCH_3), 2.33 (s, 12H, C2-CH_3).[§] Ratio A : B : C is 0.02 : 1 : 0.01. ^{13}C NMR (150 MHz, dimethyl sulfoxide-d_6) δ 156.2 (C2-H), 143.1 (Ar-H), 136.6 (Ar-H), 134.8 (Ar-H), 134.2 (Ar-H), 130.2 (Ar-H), 129.5 (Ar-H), 129.1 (Ar-H), 128.9 (Ar-H), 45.5 (NCH_3), 37.1 (NCH_3), 17.3 (C2-CH_3), 17.0 (C2-CH_3). IR (Solid): ν_{max} 3481 (m), 3421 (m), 3020 (w), 2935 (w), 1665 (sh, s), 1468 (sh, m), 1409 (sh, m), 1280 (sh, w), 1124 (m), 1085 (m), 1037 (m), 953 (sh, w), 770 (sh,s) cm^{-1}. Found HR-MS (ESI) *m/z*: 281.2011 (M+, 100%). $C_{19}H_{25}N_2^+$ requires *m/z*: 281.2012 (M+, 100%).

***N*,*N*'-*bis*(2',6'-Dimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide 21**			
Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	0.3781	19.22
Carbazole **4**	19.9	4.901	19.21
Carbazole **4**	19.9	4.587	19.24
Carbazole **4**	19.9	5.218	19.18
Carbazole **4**	19.9	5.796	19.13
		Overall	**19.19 ± 0.11**

N,*N*'-Diphenylformamidine[29]

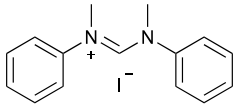


To a mixture of aniline (5.50 mL, 5.61 g, 60.2 mmol) and triethyl orthoformate (5.00 mL, 4.90 g, 33.1 mmol), glacial acetic acid (0.10 mL, 1.8 mmol) was added dropwise over ten minutes. The solution was heated at reflux overnight. Upon cooling the

[§] The remainder of the aromatic signals of conformer C are presumed to be obscured by the aromatic signals of the major conformer.

reaction mixture to room temperature, a white solid precipitated from the solution. This solid was collected through filtration, washed with cold hexane (2 x 10 mL) and air dried over an hour to give the title formamidine as a white solid (1.49 g, 7.59 mmol, 25%). m.p.139-140 °C (lit.[29] 64-65 °C). ^{1}H NMR (300 MHz, dimethyl sulfoxide-d_6) δ 7.36 (s, 1H, NC(H)N), 6.49 (m, 4H, Ar-H), 6.35 (m, 4H, Ar-H), 6.23 (m, 2H, Ar-H).

***N*,*N*'-*bis*(Phenyl)-*N*,*N*'-dimethylformamidinium iodide 22[30]**



22

To a slurry of diphenylformamidine (1.39 g, 7.10 mmol) and sodium bicarbonate (3.31 g, 39.4 mmol) in acetonitrile (16 mL) was added methyl iodide (4.14 g, 29.2 mmol) in one portion. The reaction mixture was heated until the formamidine was consumed as determined by TLC (112 h). The resultant material was purified through multiple recrystallisations in ethyl acetate to give the title compound **22** as a white solid (0.339 g, 0.963 mmol, 14%). m.p. 163-165 °C (lit.[31] 162-164 °C). ^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6) Conformer A: δ 8.83 (s, 1H, C2-H), 7.11-7.01 (m, 10H, Ar-H), 3.61 (s, 6H, NCH_3). Conformer B: δ 8.64 (s, 1H, C2-H), 7.73-7.45 (m, 10H, Ar-H), 3.68 (s, 3H, NCH_3), 2.85 (s, 3H, NCH_3). Ratio A : B is 0.7 : 1

***N*,*N*'-*bis*(Phenyl)-*N*,*N*'-dimethylformamidinium iodide 22**				
Indicator	**pK_a of indicator**	**K_{app}**	**K^B**	**pK_a of conformer B**
9-Isopropylsulfane-9*H*-fluorene **1**	16.9	81.82	137.9	14.76
9-Isopropylsulfane-9*H*-fluorene **1**	16.9	84.44	142.3	14.75
9-Isopropylsulfane-9*H*-fluorene **1**	16.9	95.22	160.4	14.69
9-Isopropylsulfane-9*H*-fluorene **1**	16.9	91.52	154.2	14.71
9-Phenyl-9*H*-fluorene **2**	17.9	>100	>100	<15.9
9-Phenyl-9*H*-fluorene **2**	17.9	>100	>100	<15.9
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	>100	>100	<16.8
9-(*ortho*-Tolyl)-9*H*-fluorene **3**	18.8	>100	>100	<16.8
9-Methyl-9*H*-fluorene **6**	22.3	>100	>100	<20.3
			Overall	**14.73 ± 0.10**

Crystal structure data for compounds **21** and **22**

Crystalline samples of the compounds were mounted on MiTeGen micromounts in type NVH immersion oil at 150(2) K. A summary of crystallographic data can be found in the Table S3 below. Data were collected using a Bruker Quazar Multilayer Optics MoKα X-ray micro source (λ = 0.71073 Å) on a Bruker Apex II CCD diffractometer, and were corrected for absorption using SADABS.[32] Unit cell parameters were determined for collection employing software defaults and optimized upon completion of data collection. Structure solution and refinement was carried out using the SHELX suite of programs[33, 34] with the OLEX2 GUI.[35] For compound **21**, all hydrogen atoms were located in difference maps and refined isotropically, excepting the lattice solvent (riding model).** For compound **22**, all hydrogen atoms were located in difference maps and refined isotropically, excepting those of the *N*-methyl substituents (riding model).

** The lattice dichloromethane of salt **19** lies on a special position with disorder of the methylene C(1S) over two sites of partial occupancy. Symmetry necessitates that these exist with 50:50 occupancy.

	Compound 21	**Compound 22**
Mol. Formula	$C_{19}H_{25}N_2I$ (0.5 CH_2Cl_2)	0.5($C_{15}H_{17}N_2I$)
Formula Weight	450.77	176.10
Crystal System	monoclinic	orthorhombic
Space Group	*C*2/*c*	*Pccn*
a, Å	16.6780(5)	7.3978(4)
b, Å	26.8240(8)	11.4140(4)
c, Å	11.0601(3)	17.0191(8)
α, deg	90	90
β, deg	124.7010(10)	90
γ, deg	90	90
Volume, Å^3	4067.9(2)	1437.07(11)
Z	8	8
Description	trapezoid plate	truncated block
Colour	colourless	colourless
D_c, g cm^{-3}	1.472	1.628
F(000)	1816	696
μ, mm^{-1}	1.709	2.213
Reflections Collected	18215	7072
R(int)	0.0336	0.0185
R(sigma)	0.0275	0.0184
Unique Reflections	5670	2114
Parameters Varied	318	106
R_1	0.0297	0.0186
wR_2 (all data)	0.0689	0.0482
GooF	1.033	1.049
Δ*ρ*/e Å^{-3}	0.873/-0.645	0.477/-0.344
CCDC Number	1973199	1973198

Table S3: Collection parameters for the crystal structures of salts **21** and **22**.

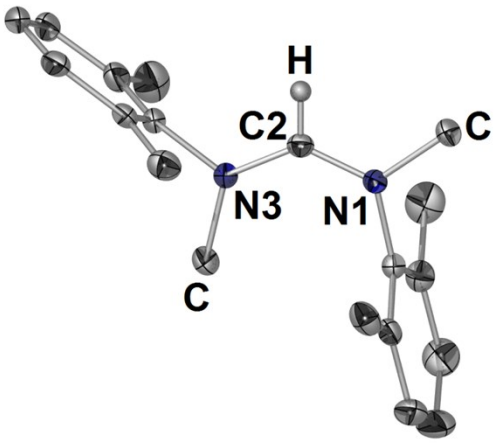


Figure S7: Crystal structure of the cation of salt **21** (50% thermal ellipsoids). All hydrogens atoms except NC(H)N are omitted for clarity. Salient lengths (Å) and angles (°): N1-C2 1.313(2), C2-N3 1.316(3), C2-H 0.90(2), N1-C2-N3 130.4(2), H-C2-N3 114.7(14), H-C2-N1 115.0(14), $CN3C_{Xy}$: $CN1C_{Xy}$ torsion angle 7.9(3), Xy_{N3}:N3C2N1 torsion angle 80.3(2), Xy_{N1}:N1C2N3 torsion angle 84.9(1), $CN3C_{Xy}$:N3C2N1 5.8(4), $CN1C_{Xy}$:N1C2N3 2.7(5).

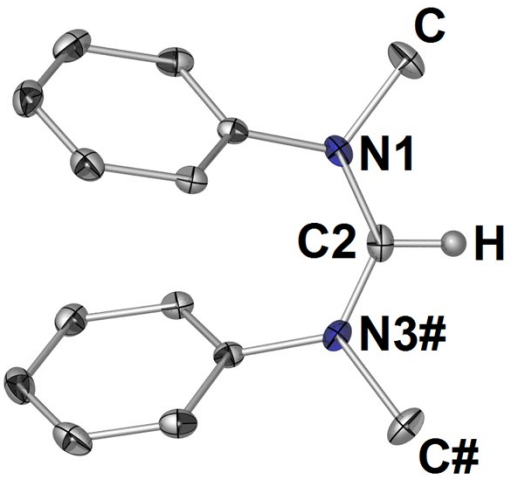


Figure S8: Crystal structure of the cation of salt **22** (50% thermal ellipsoids). All hydrogens atoms except NC(H)N are omitted for clarity. Symmetry equivalent C# and N3# generated by the operation 3/2-z, 1/2-y, z. Salient lengths (Å) and angles (°): N1-C2 1.3153(16), C2-N3# 1.3153(16), C2-H 0.94(3), C-C# 4.73(3), N1-C2-N3# 130.2(2), H-C2-N3# 114.88(10), H-C2-N1 114.88(10), C#N3#C_{Ph}: $CN1C_{Ph}$ torsion angle 22.4(2), $Ph_{N3\#}$:N3C2N1 torsion angle 55.28(5), $CN1C_{Ph}$:N1C2N3# 11.19(2), Ph_{N1}:N1C2N3# torsion angle 55.28(5), C#N3#C_{Ph}:N1C2N3# torsion angle 55.28(5).

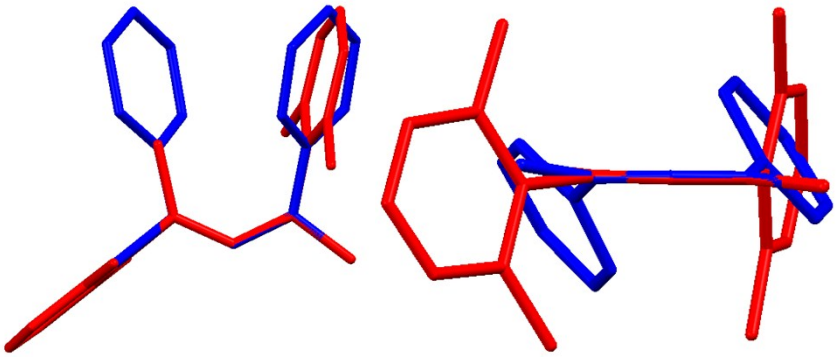
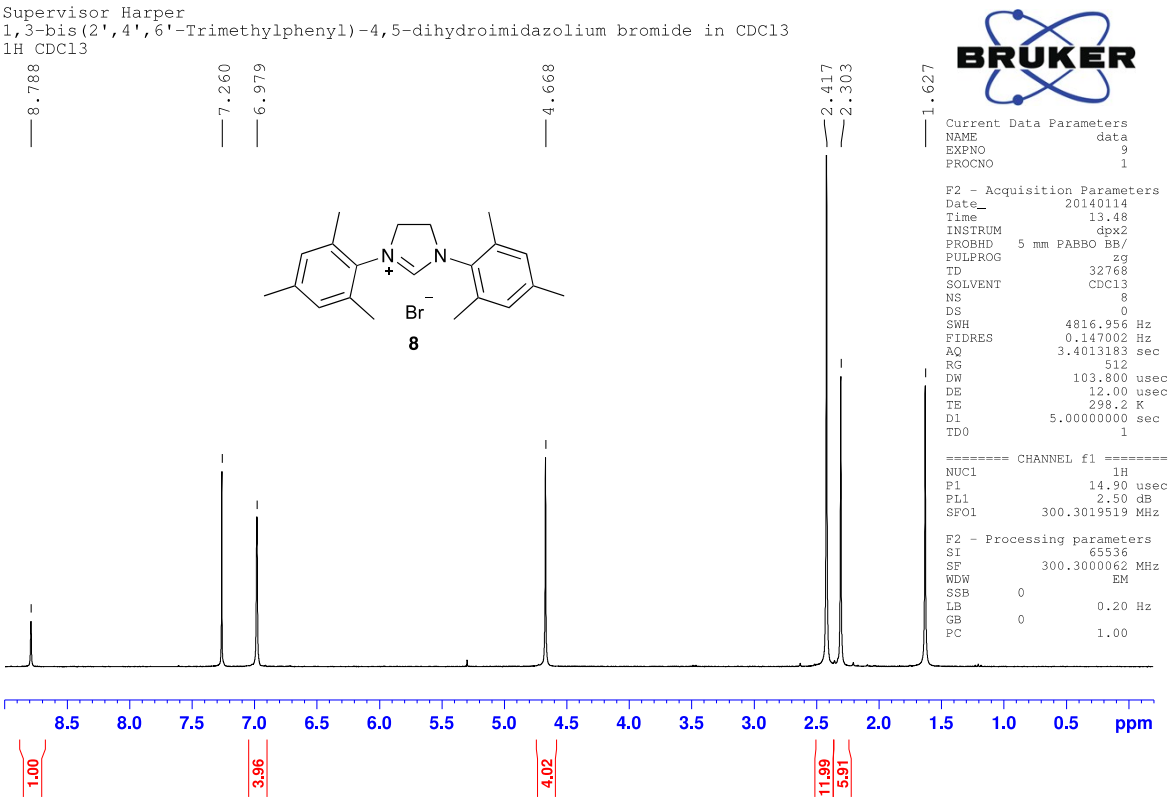


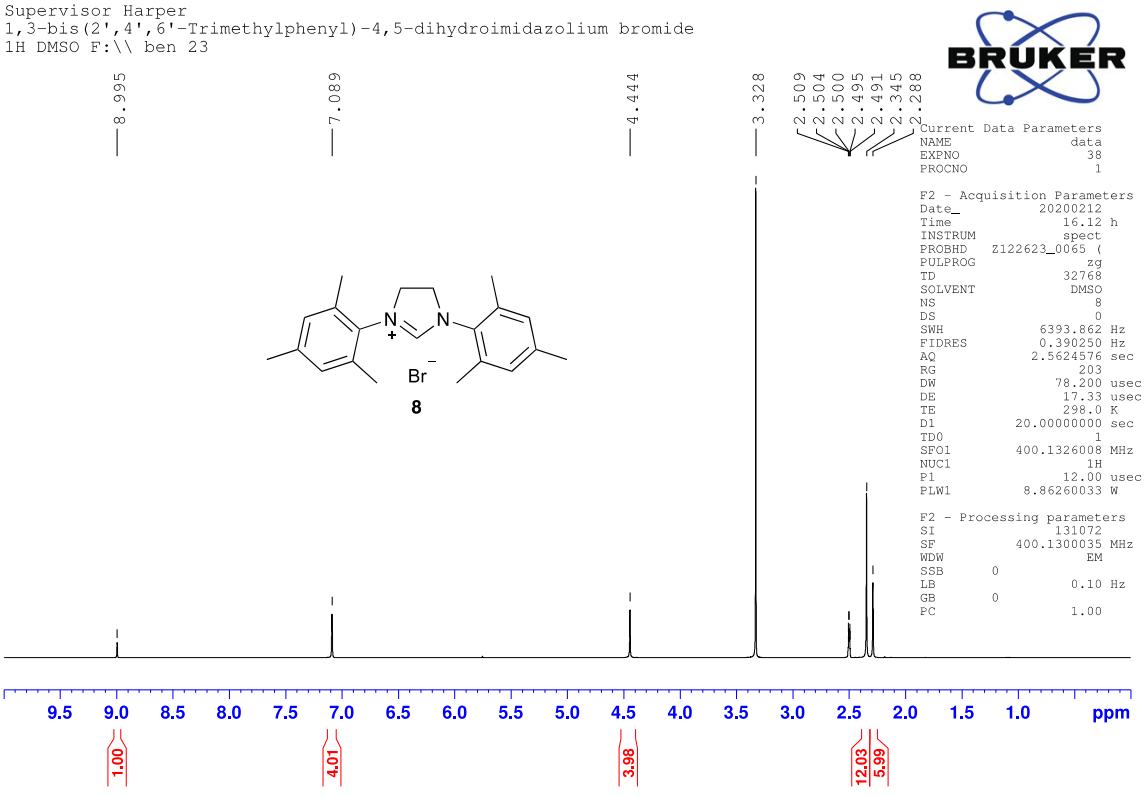
Figure S9: Overlay of crystal structures of the phenyl formamidinium cation of salt **22** in conformer C (blue) and the xylyl formamidinium cation of salt **21** in conformer A. Left = normal to NCN plane, right = along CH of NCN vector.

NMR spectra of prepared salts

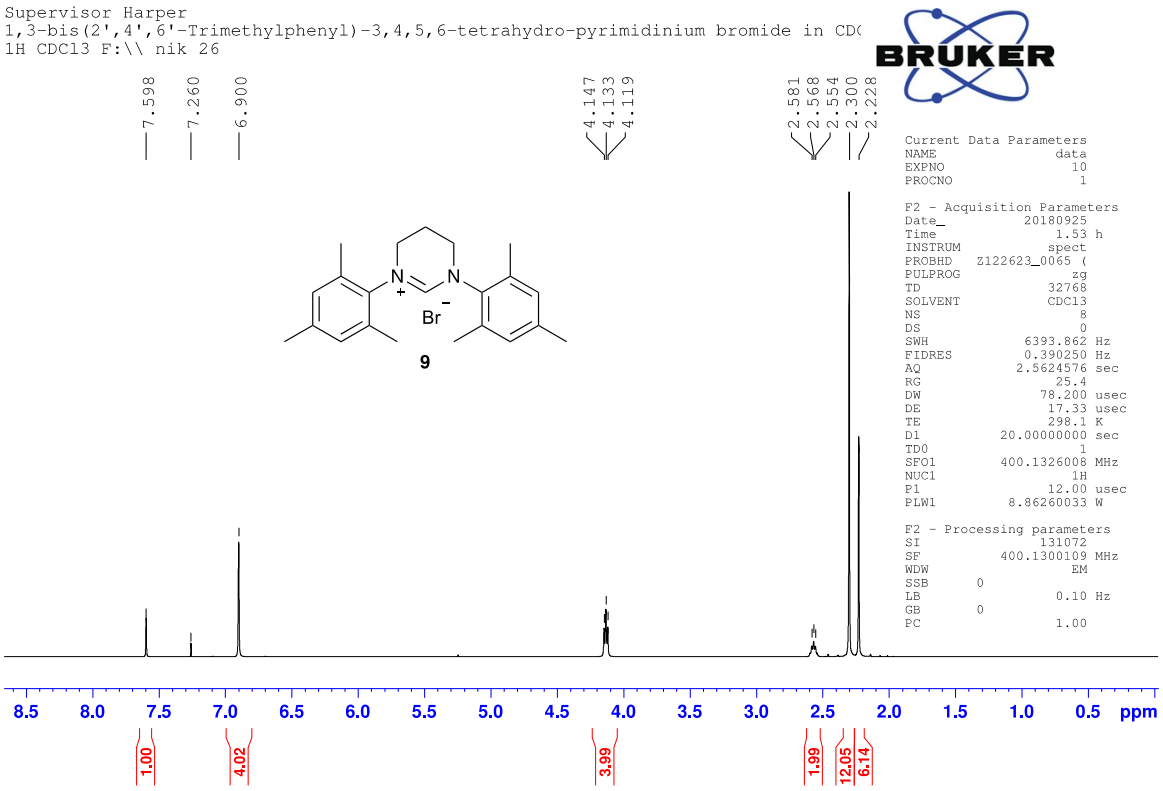
^{1}H and ^{13}C NMR spectra were recorded on either a Bruker Advance III 300 MHz NMR (^{1}H: 300 MHz, ^{13}C: 75 MHz), a Bruker Advance III 400 MHz NMR (^{1}H: 400 MHz and ^{13}C: 100 MHz), a Bruker Advance III 500 MHz NMR (^{1}H: 500 MHz) or a Bruker Advance III 600 MHz NMR (^{1}H: 600 MHz and ^{13}C: 150 MHz) spectrometer at 298 K. All spectra were recorded in the solution state using the deuterated solvent specified, with chemical shifts referenced to residual non-deuterated solvent resonances (see Gottlieb *et al.*[36]) and reported in parts per million (ppm). Signals are reported to either two decimal places (^{1}H) or one decimal place (^{13}C), unless greater accuracy is required for signal delineation. Multiplicities are denoted as singlet (s), doublet (d), triplet (t), quartet (q), pentet (pen), septet (sept) and multiplet (m) (or combinations thereof). Broad signals have the prefix br. Unless otherwise specified, all reported coupling constants refer to proton-proton couplings. Note that when two nuclei have the same environment (e.g. the 2'- and 6'-methyl groups in a mesityl derivative) only one of the two groups is listed in the assignment. NMR spectra were processed using the Bruker TOPSPIN 4.0.3 software. All reported ^{13}C NMR resonances are singlets.

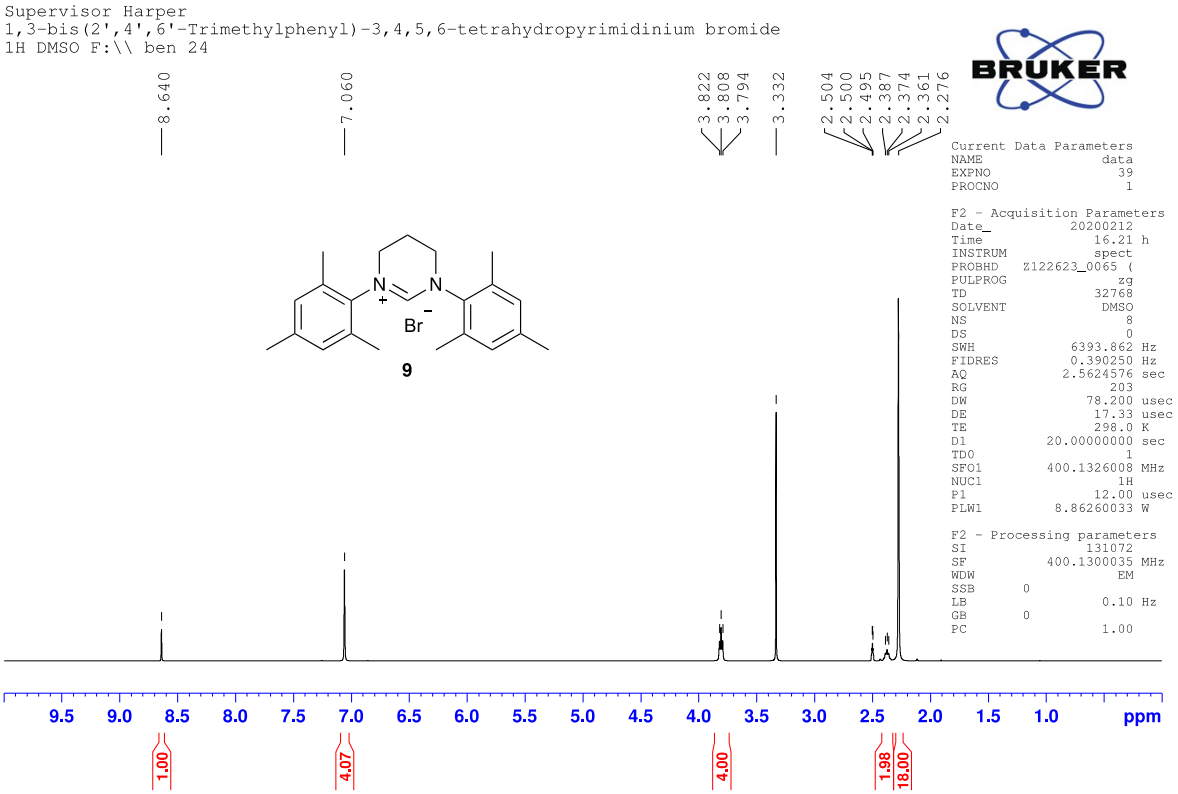
1,3-bis(2',4',6'-Trimethylphenyl)-4,5-dihydroimidazolium bromide **8**



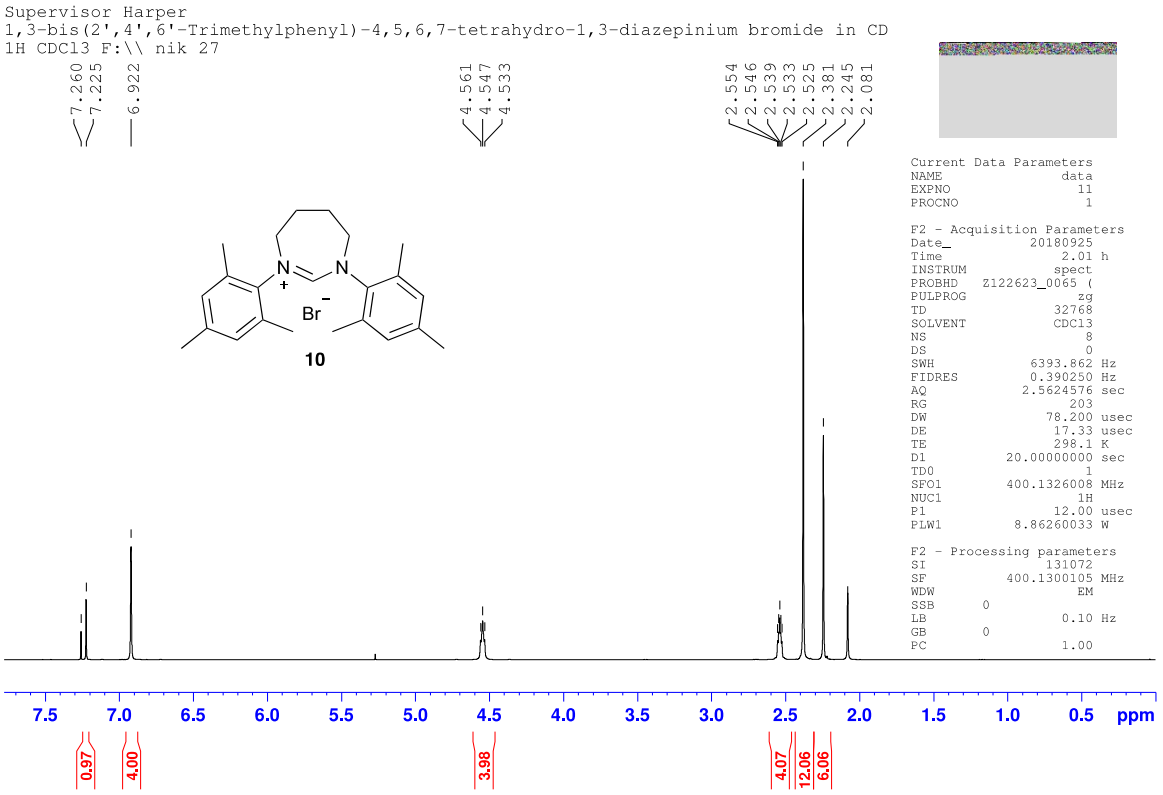


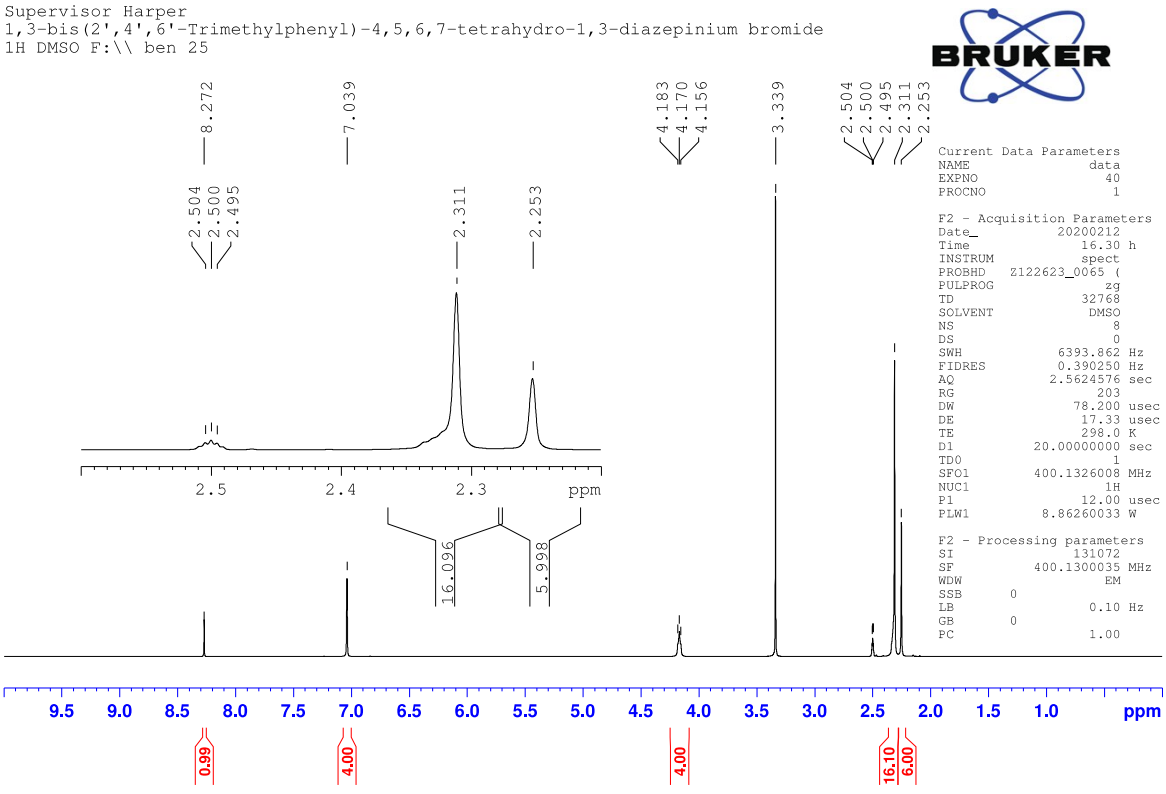
1,3-bis(2',4',6'-Trimethylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide **9**



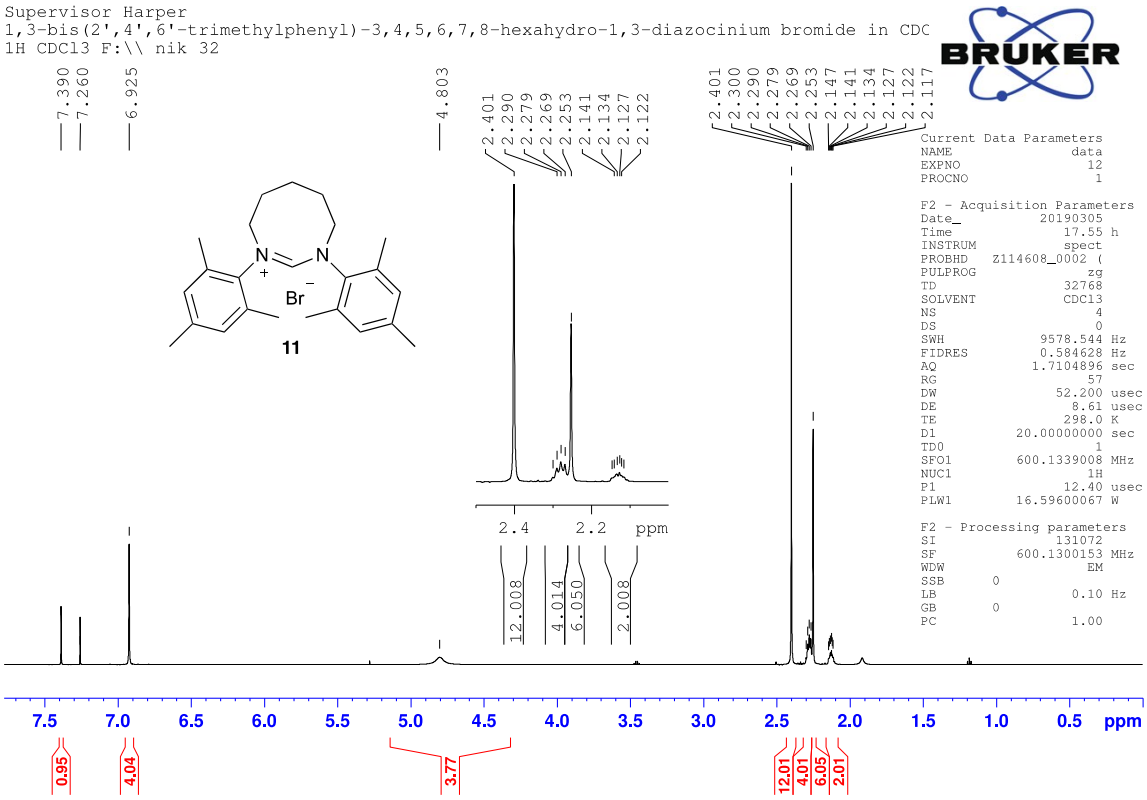


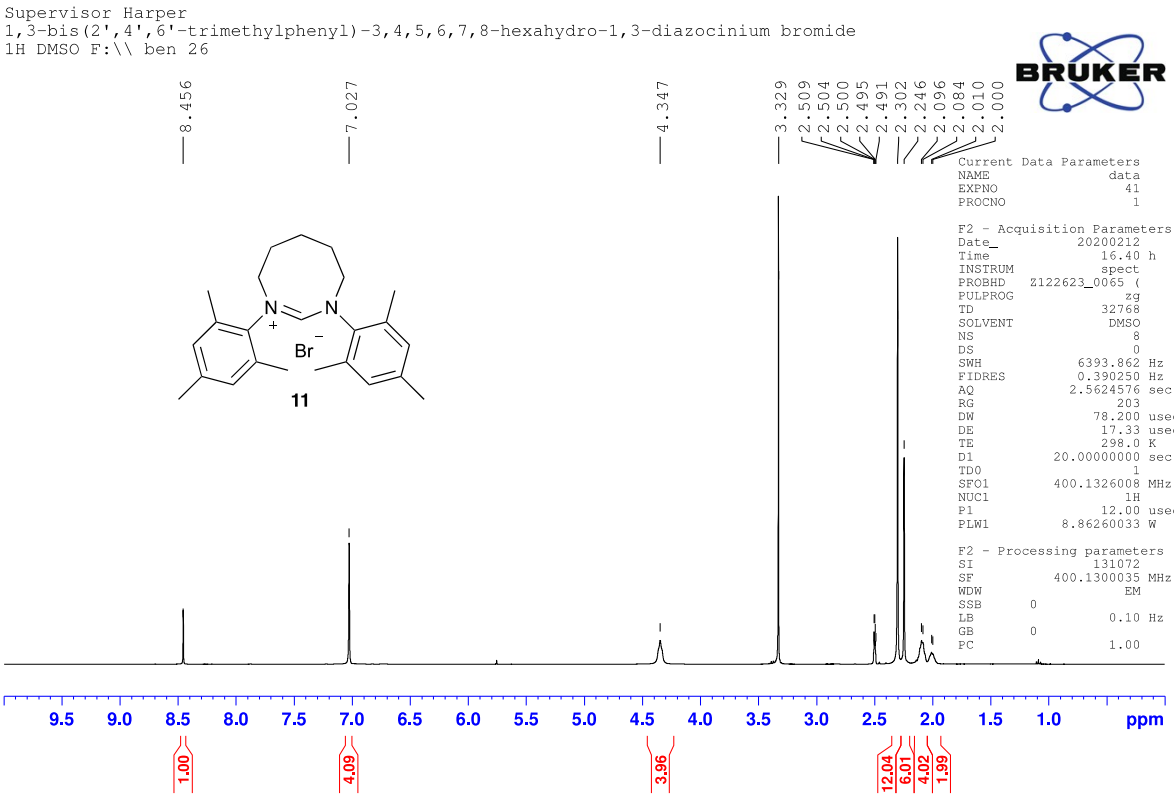
1,3-*bis*(2',4',6'-Trimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide **10**



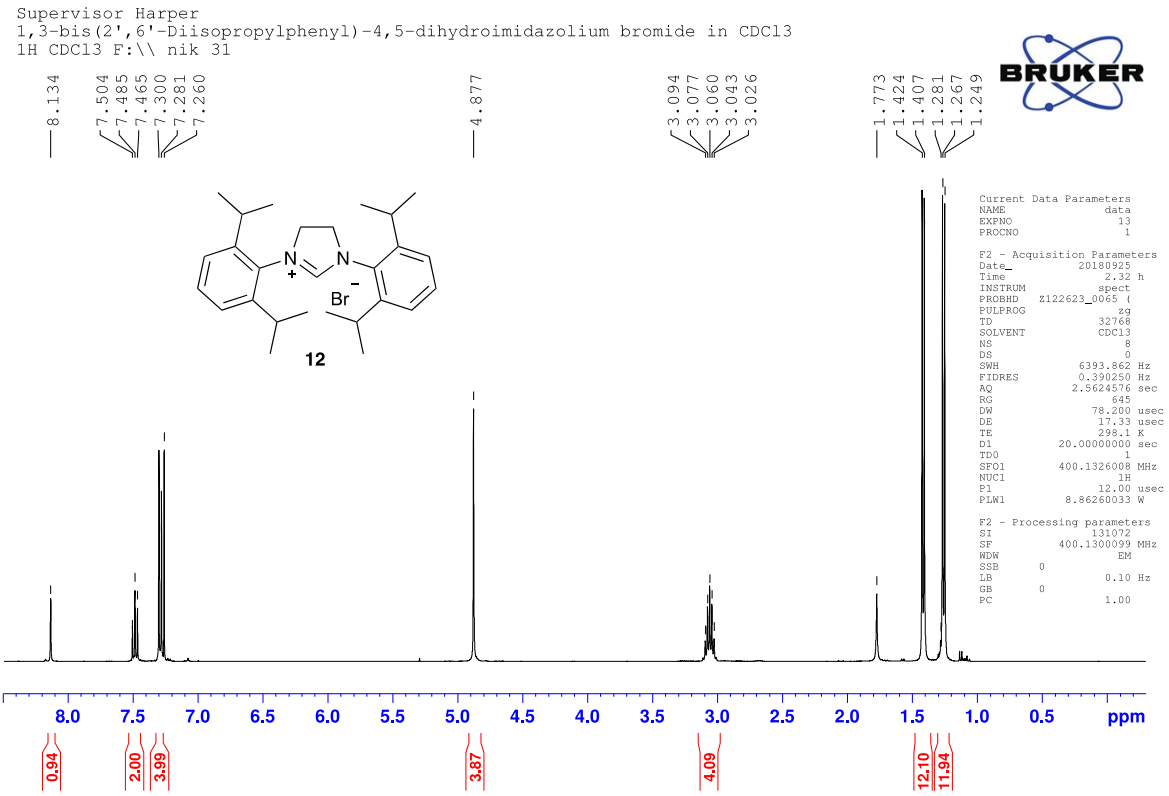


1,3-*bis*(2',4',6'-trimethylphenyl)-3,4,5,6,7,8-hexahydro-1,3-diazocinium bromide **11**

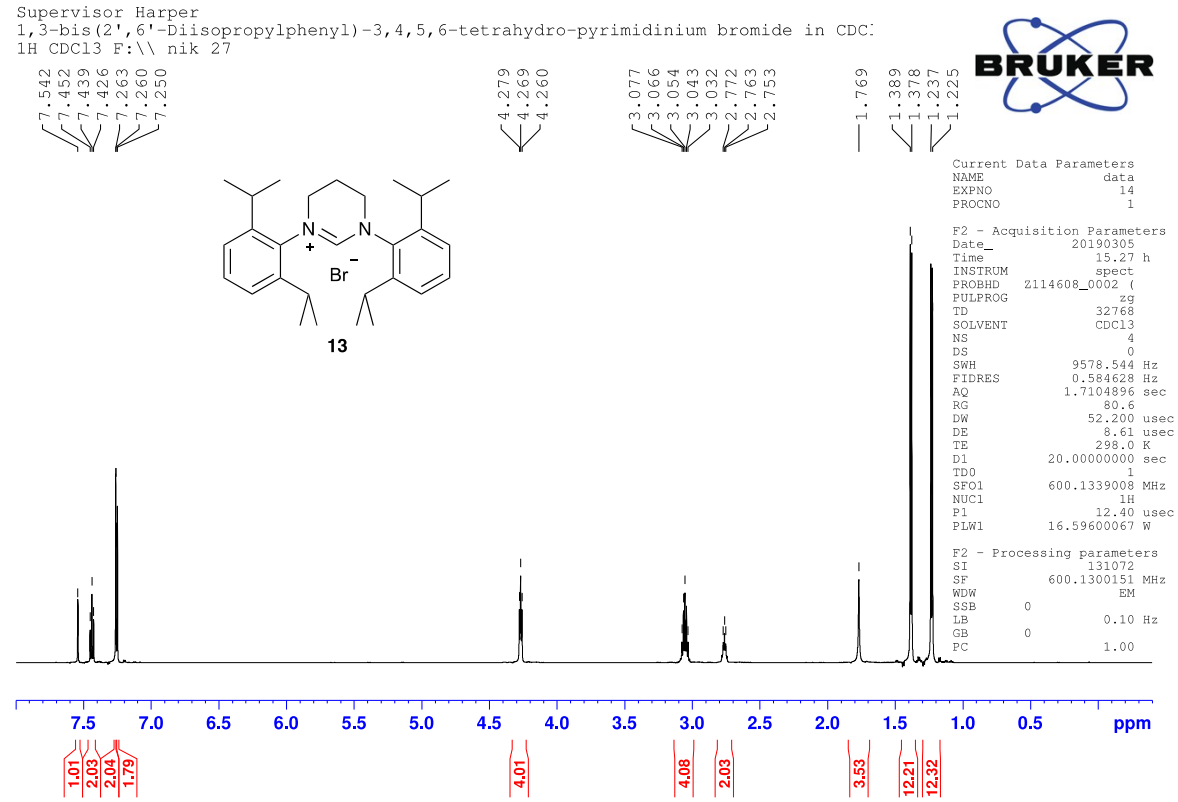




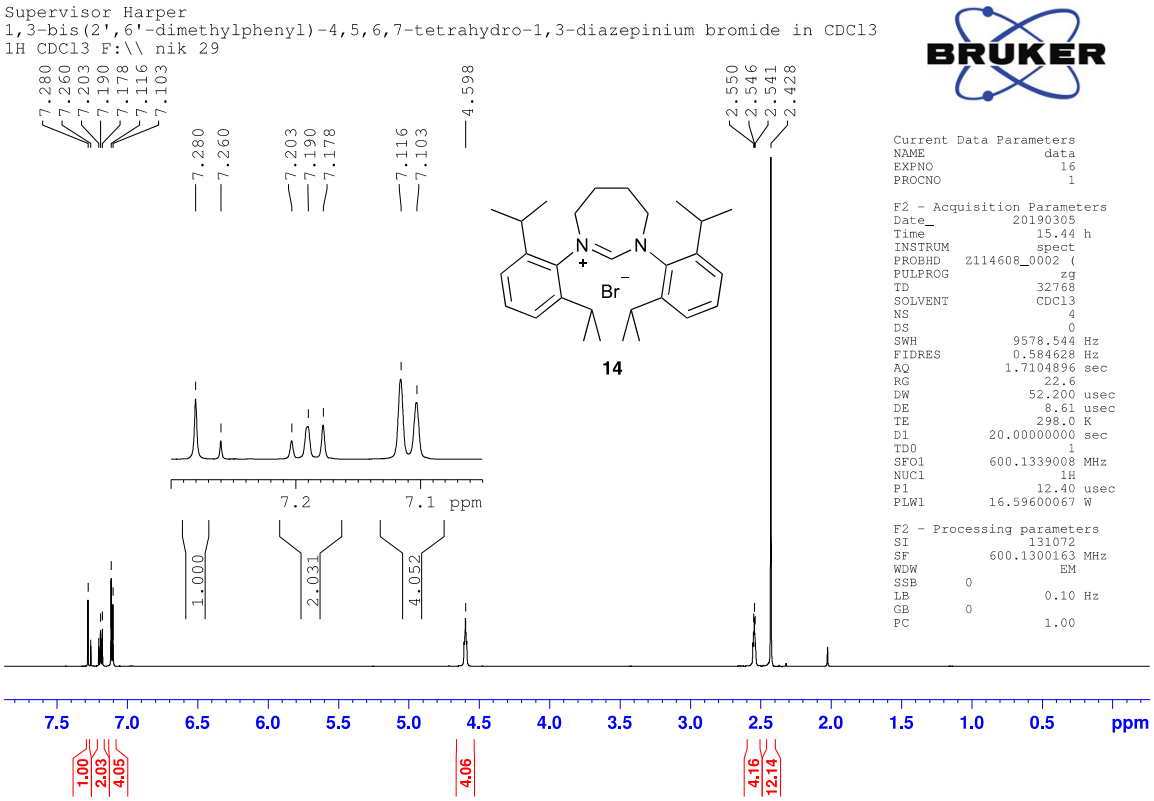
1,3-*bis*(2',6'-Diisopropylphenyl)-4,5-dihydroimidazolium bromide **12**



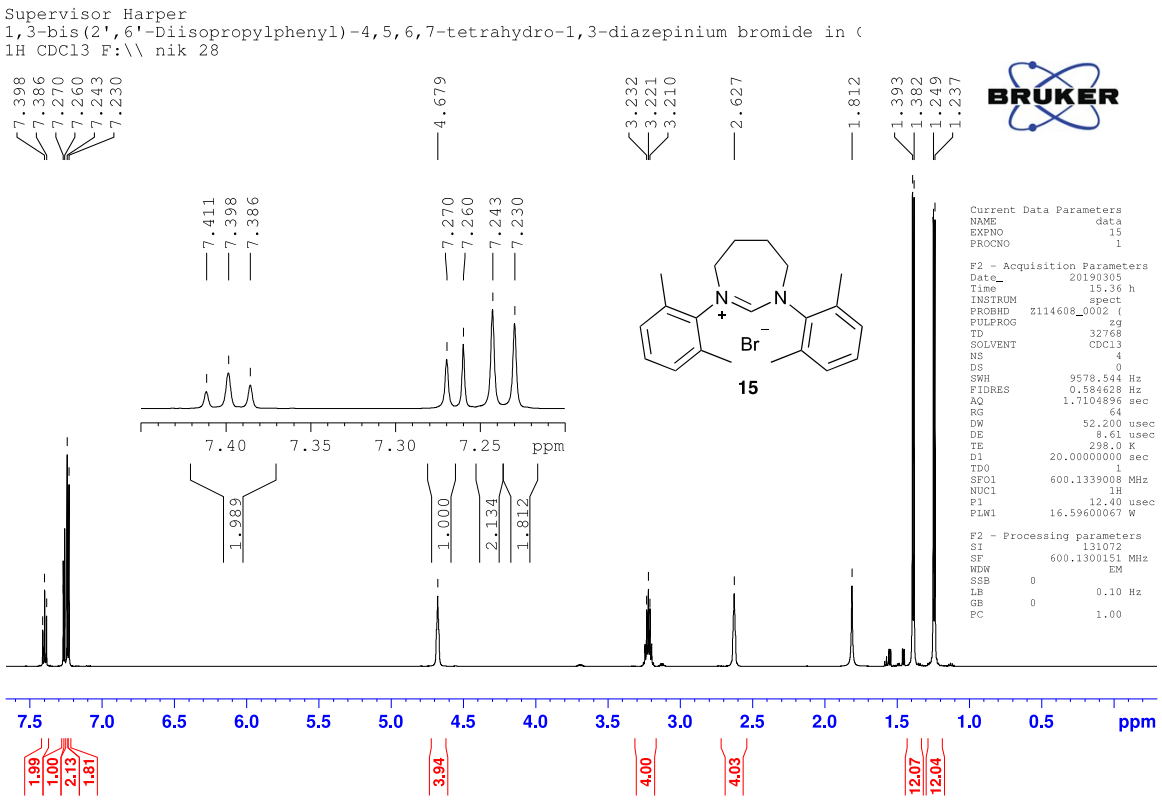
1,3-b*is*(2',6'-Diisopropylphenyl)-3,4,5,6-tetrahydropyrimidinium bromide **13**



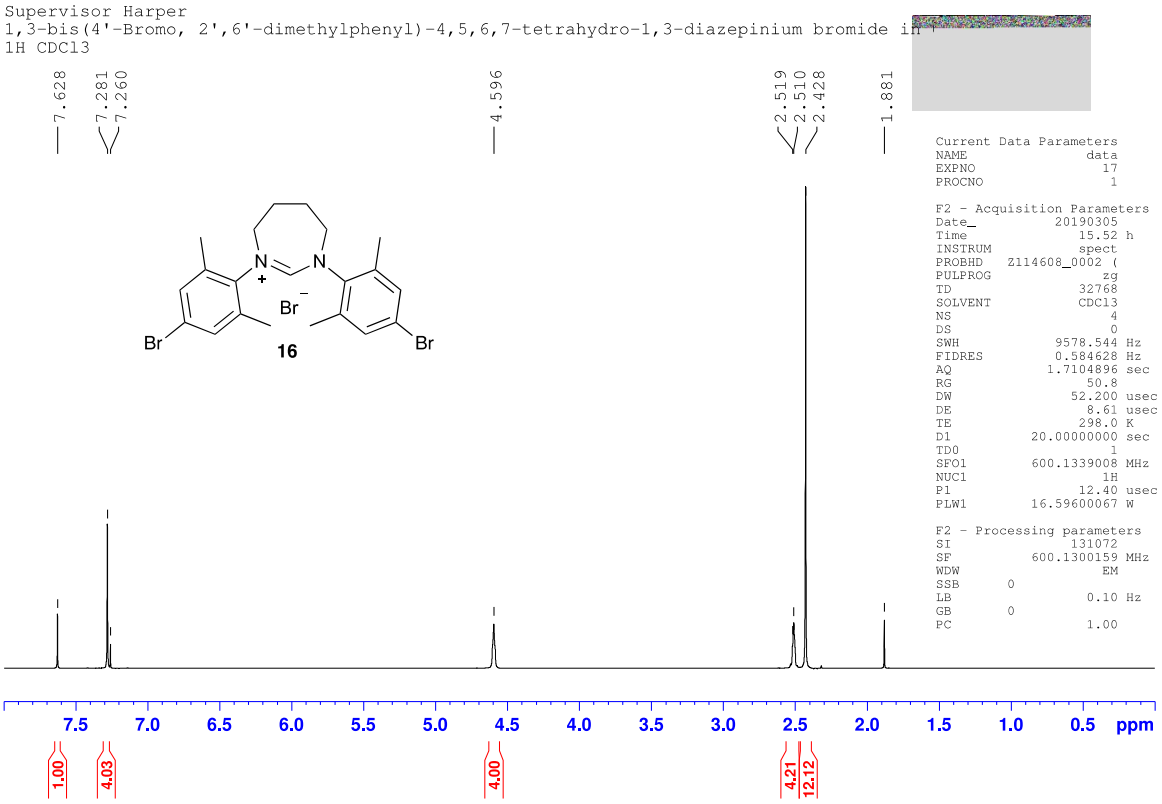
1,3-*bis*(2',6'-Diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide **14**



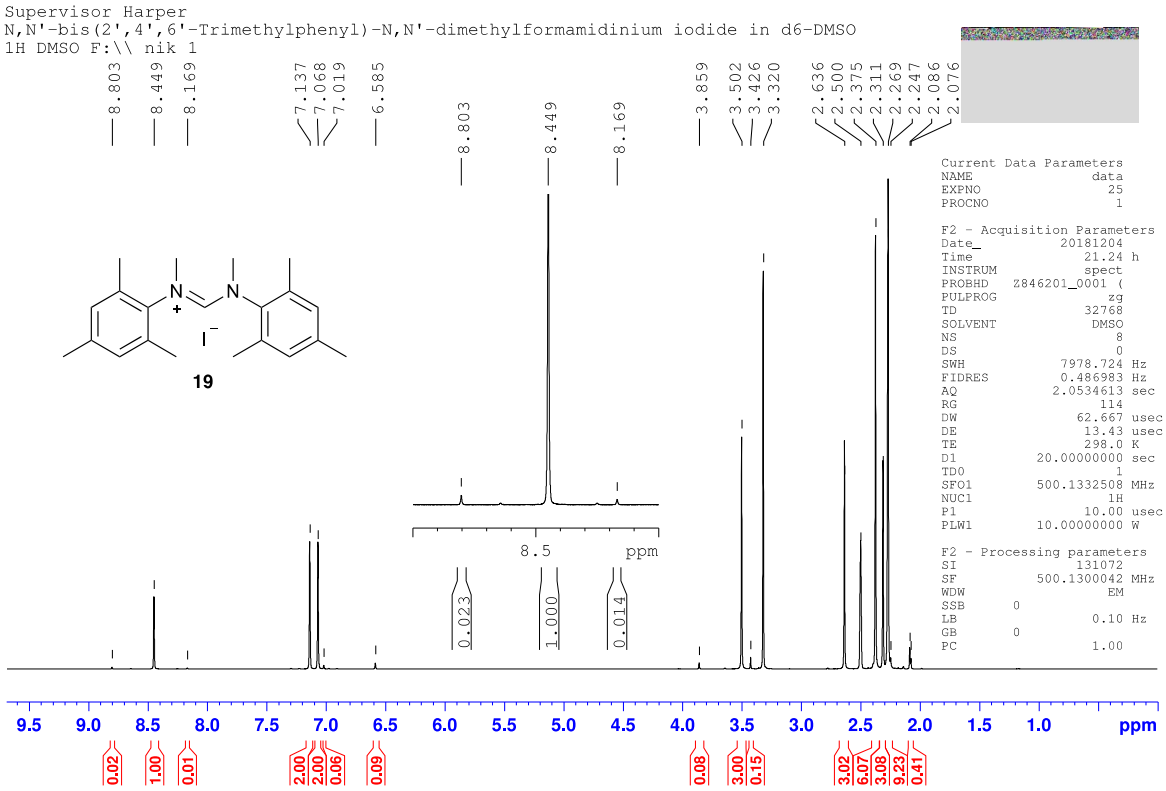
1,3-*bis*(2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide **15**



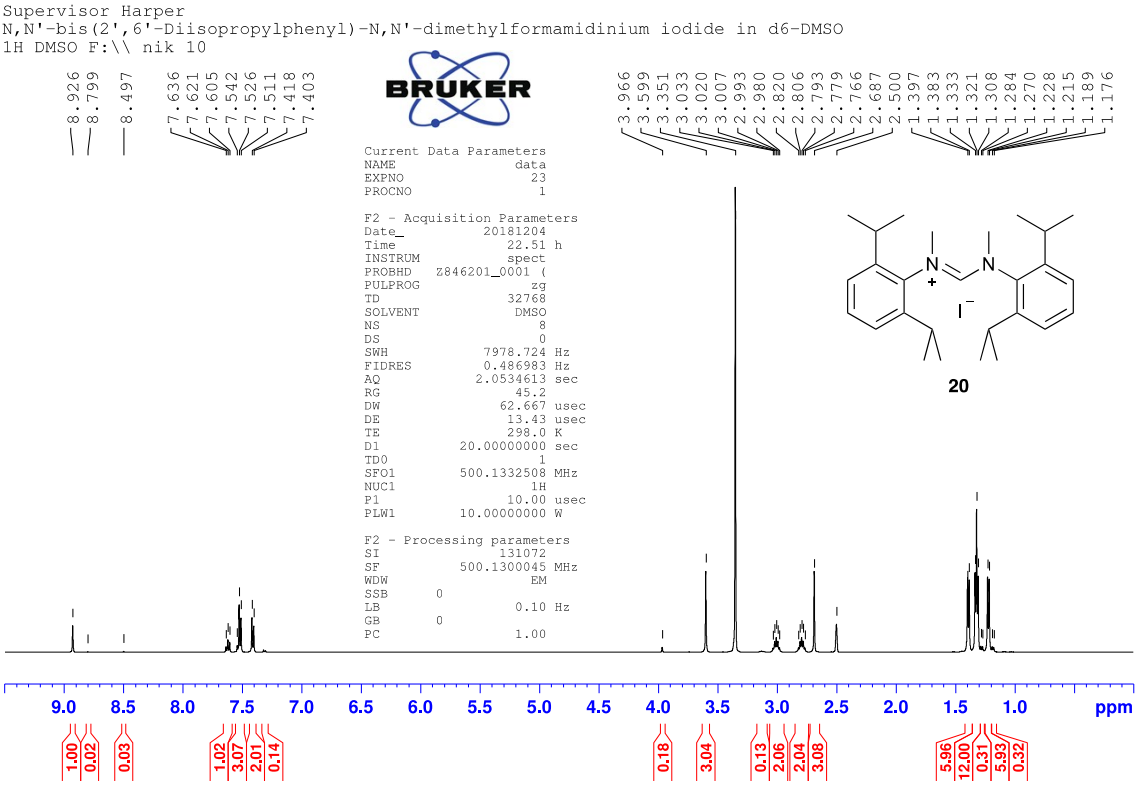
1,3-*bis*(4'-Bromo, 2',6'-dimethylphenyl)-4,5,6,7-tetrahydro-1,3-diazepinium bromide **16**



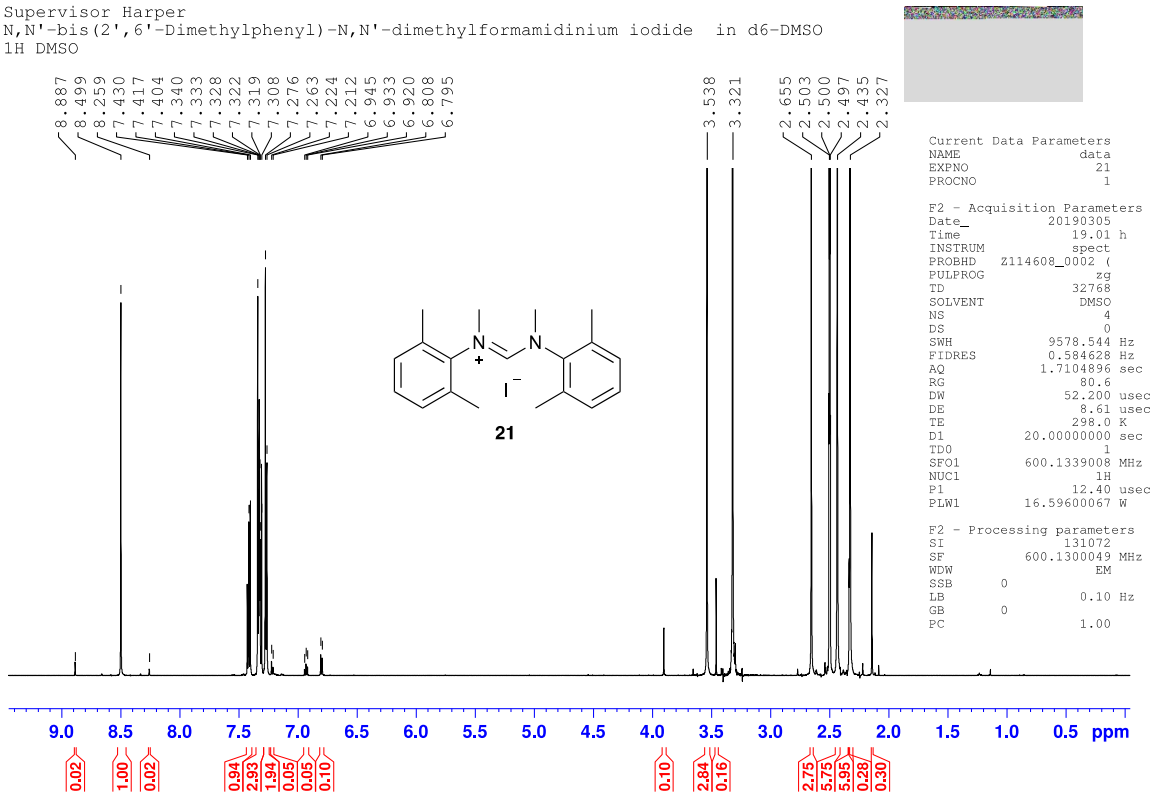
N,*N*'-*bis*(2',4',6'-Trimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide **19**



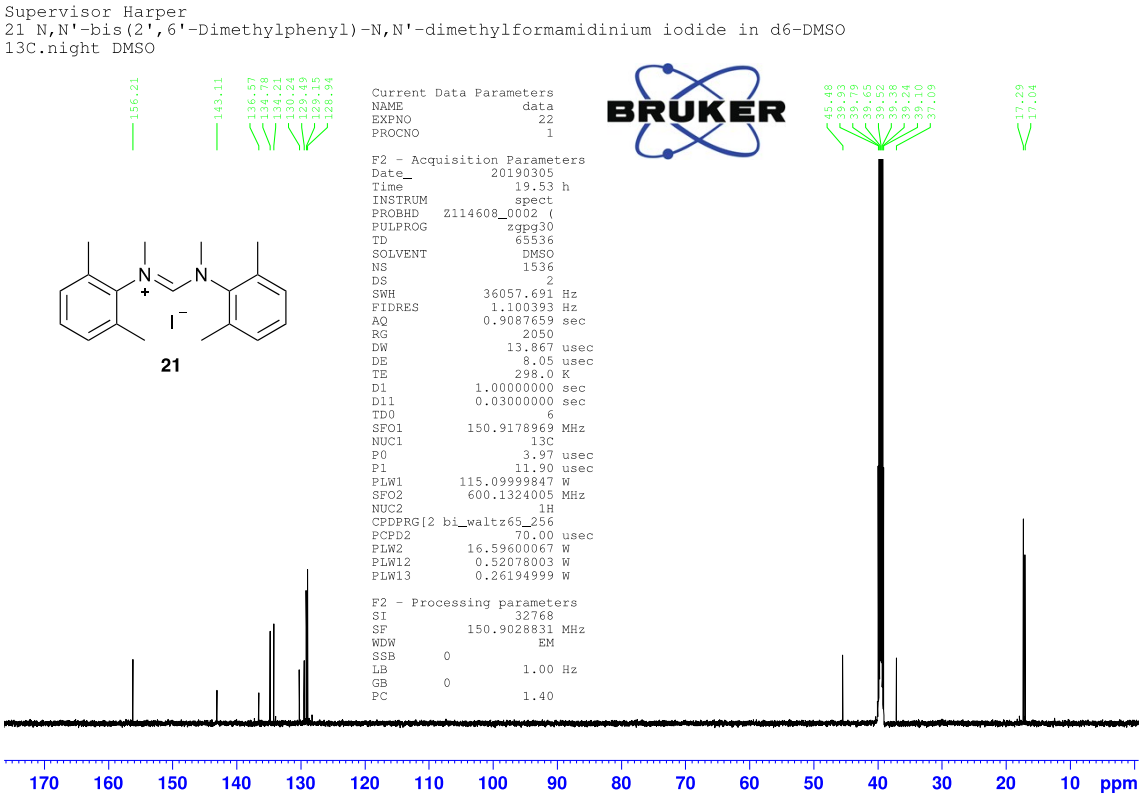
N,*N*'-*bis*(2',6'-Diisopropylphenyl)-*N*,*N*'-dimethylformamidinium iodide **20**



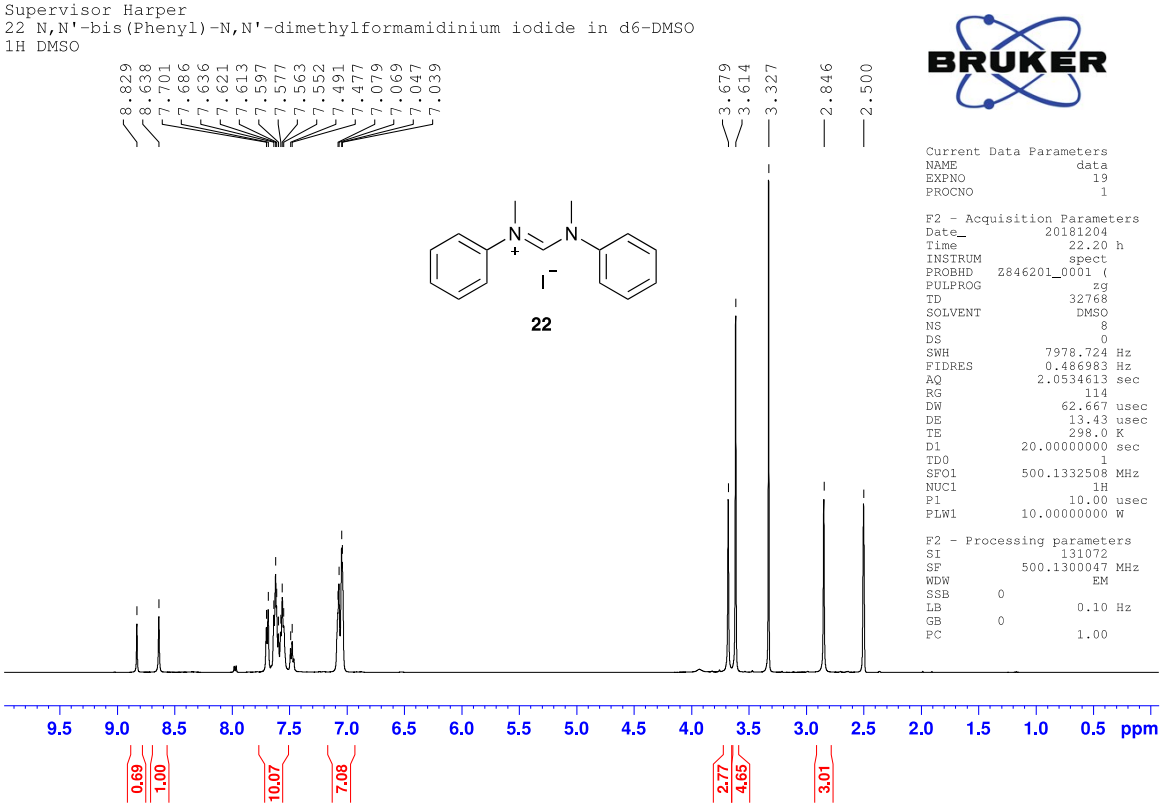
N,*N*'-*bis*(2',6'-Dimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide **21**



N,*N*'-*bis*(2',6'-Dimethylphenyl)-*N*,*N*'-dimethylformamidinium iodide **21**



N,*N*'-*bis*(Phenyl)-*N*,*N*'-dimethylformamidinium iodide **22**



References

1. M. Blain, H. Yau, L. Jean-Gerard, R. Auvergne, D. Benazet, P. R. Schreiner, S. Caillol and B. Andrioletti, *ChemSusChem*, 2016, **9**, 2269-2272.
2. F. G. Bordwell, G. E. Drucker and G. J. McCollum, *J. Org. Chem.*, 1982, **47**, 2504-2510.
3. G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, *J. Org. Chem.*, 2010, **75**, 4124-4130.
4. K. Albert, *Chem. Ber.*, 1977, **110**, 1804-1822.
5. R. M. Bolton, R. S.; Williams, G. H., *J. Chem. Soc., Perkin Trans. 2*, 1986, 405-408.
6. G. C. Vougioukalakis and M. Orfanopoulos, *Tetrahedron Lett.*, 2003, **44**, 8649-8652.
7. W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, *J. Am. Chem. Soc.*, 1975, **97**, 7006-7014.
8. C. Y. Meyers, P. D. Robinson and A. W. McLean, *Acta Crystallogr. C*, 2003, **59**, o712-o714.
9. M. E. Bowen, B. R. Aavula and E. A. Mash, *J. Org. Chem.*, 2002, **67**, 9087-9088.
10. M. E. Bowen, B. R. Aavula and E. A. Mash, *J. Org. Chem.*, 2002, **67**, 9087-9088.
11. J. J. Eisch, C. A. Kovacs and P. Chobe, *J. Org. Chem.*, 1989, **54**, 1275-1284.
12. C. L. Arcus and E. A. Lucken, *J. Chem. Soc.*, 1955, 1634.
13. F. A. Anet and P. M. G. Bavin, *Can. J. Chem.*, 1956, **34**, 991-1005.
14. F. G. Bordwell and H. J. Reich, Bordwell pK_a Table (Acidity in DMSO), http://www.chem.wisc.edu/areas/reich/pkatable/, Accessed 31/12/2019.
15. F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin and W. S. Matthews, *J. Am. Chem. Soc.*, 1975, **97**, 3226-3227.
16. F. G. Bordwell, G. E. Drucker and H. E. Fried, *J. Org. Chem.*, 1981, **46**, 632-635.
17. K. M. Kuhn and R. H. Grubbs, *Org. Lett.*, 2008, **10**, 2075-2077.
18. E. M. McGarrigle, S. P. Fritz, L. Favereau, M. Yar and V. K. Aggarwal, *Org. Lett.*, 2011, **13**, 3060-3063.
19. M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, 2008, **27**, 3279-3289.
20. A. Aidouni, S. Bendahou, A. Demonceau and L. Delaude, *J. Comb. Chem.*, 2008, **10**, 886-892.
21. J. J. Dunsford, K. J. Cavell and B. Kariuki, *J. Organomet. Chem.*, 2010, **696**, 188-194.
22. E. L. Kolychev, I. A. Portnyagin, V. V. Shuntikov, V. N. Khrustalev and M. S. Nechaev, *J. Organomet. Chem.*, 2009, **694**, 2454-2462.
23. W. Y. Lu, K. J. Cavell, J. S. Wixey and B. Kariuki, *Organometallics*, 2011, **30**, 5649-5655.
24. S. Flügge, A. Anoop, R. Goddard, W. Thiel and A. Fürstner, *Chem. Eur. J.*, 2009, **15**, 8558-8565.
25. P. Grammaticakis, *C. R. Acad. Sci.*, 1957, **245**, 2307-2310.
26. M. H. Dunn, N. Konstandaras, M. L. Cole and J. B. Harper, *J. Org. Chem.*, 2017, **82**, 7324-7331.
27. N. Konstandaras, L. Matto, M. Bhadbhade, L. Hunter and J. B. Harper, *ChemistrySelect*, 2017, **2**, 7018-7023.
28. K. Denk, P. Sirsch and W. A. Herrmann, *J. Organomet. Chem.*, 2002, **649**, 219-224.
29. M. Wakae and K. Konishi, *Rep. Ind. Res. Inst., Osaka Prefect*, 1963, **29**, 47-50.
30. C. Jutz and H. Amschler, *Chem. Ber.*, 1963, **96**, 2100-2108.
31. D. H. Clemens and W. D. Emmons, *J. Am. Chem. Soc.*, 1961, **83**, 2588-2589.
32. SADABS.
33. G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122.
34. G. M. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3-8.
35. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
36. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.