Electronic Supporting Information for

"The impact of structure upon the acidity of triazolium salts in dimethyl sulfoxide"

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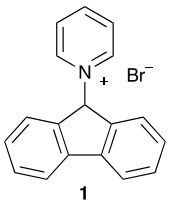
Synthesis of the fluorenes **1-4**

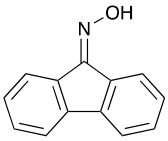
9-Pyridinium-9*H*-fluorene bromide 1[1]



1

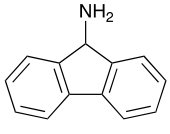
In an adaptation of a literature procedure,[1] 9-bromofluorene (0.6770 g, 2.762 mmol) was dissolved in pyridine (5 mL) and stirred at room temperature for 18 hours. The solvent was then removed under reduced pressure and the resultant pale brown solid was recrystallised from dichloromethane/ethyl acetate to give the product **1** as a beige solid (0.4282 g, 1.321 mmol, 48%). m.p. 197-200 °C. (lit.[1] 204-206 °C). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.98 (d, J = 5.8 Hz, 2H, Ar-H), 8.69 (t, J = 7.7 Hz, 1H, Ar-H), 8.17 (t, J = 7.1 Hz, , 2H, Ar-H), 8.07 (d, J = 7.6 Hz, 2H, Ar-H), 7.64-7.57 (m, 4H, Ar-H), 7.42 (t, J = 7.6 Hz, 2H, Ar-H), 7.21 (s, 1H, H9).

9*H*-Fluoren-9-one oxime[2]



In a method analogous to literature,[2,3] a solution of fluorenone (10.02 g, 55.60 mmol) and hydroxylamine hydrochloride (10.35 g, 155.7 mmol) in ethanol (100 mL) was heated to reflux for two hours before being stirred at room temperature overnight. Water (100 mL) was added and the resulting mixture was filtered to give the title compound as a yellow crystalline solid (10.85 g, 55.58 mmol, 100%). m.p. 198-200 °C (lit.[3] 192-194 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.53 (br s, 1H, OH), 8.34 (dt, J = 7.5, 0.8 Hz, 1H, H1/8), 7.88 (dt, J = 7.5, 0.8 Hz, 1H, Ar-H), 7.84 (dt, J = 7.5, 0.8 Hz, 1H, Ar-H), 7.70 (dt, J = 7.5, 0.8 Hz, 1H, Ar-H), 7.50 (td, J = 7.5, 1.0 Hz, 1H, Ar-H), 7.43 (td, J = 7.5, 1.0 Hz, 1H, Ar-H), 7.38 (td, J = 7.5, 1.0 Hz, 1H, Ar-H), 7.33 (td, J =7.5, 1.0 Hz, 1H, Ar-H).

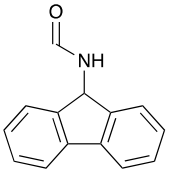
9*H*-Fluoren-9-amine[3]



In a method analogous to literature,[3] zinc powder (14.29 g, 218.5 mmol) was added portionwise to a solution of 9*H*-fluoren-9-one oxime (7.28 g, 37.3 mmol) in acetic acid (112 mL) and water (5.6 mL) over 20 minutes. The mixture was then heated to reflux for one

hour, was allowed to cool to room temperature and was filtered. The majority of the solvent was removed from the filtrate under reduced pressure until approximately 30 mL of solution remained. The residue was then cooled to 0 °C prior to the addition of hydrochloric acid (5 M, 125 mL) and the resulting mixture was left to stir overnight. The resulting precipitate was removed through filtration and the pH of the filtrate was adjusted to 10.5 with concentrated aqueous ammonia solution (28%). The aqueous phase was then extracted with dichloromethane (3 x 75 mL) and the organic phases were combined, washed with water (150 mL), dried over magnesium sulfate and filtered before the solvent was removed under reduced pressure to give the title compound as a pale yellow solid (5.02 g, 27.6 mmol, 74%). m.p. 57-59 °C (lit.[3] 61-63 °C). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.70 (d, J = 7.4 Hz, 2H, Ar-H), 7.61 (d, J = 7.4 Hz, 2H, Ar-H), 7.38 (t, J = 7.4 Hz, 2H, Ar-H), 7.33 (t, J = 7.4 Hz, 2H, Ar-H), 4.87 (s, 1H, H9).

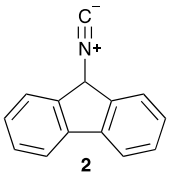
9-Formylamino-9*H*-fluorene[4,5]



In a method analogous to literature,[5] acetic anhydride (2.92 g, 28.6 mmol) and formic acid (1.48 g, 32.2 mmol) were heated at 60 °C for two hours in order to form acetic formic anhydride. The solution was cooled to room temperature and added dropwise over ten minutes to a solution of 9-amino-9*H*-fluorene (1.51 g, 8.30 mmol) in dichloromethane (90 mL). The resulting solution was stirred at room temperature for one hour before the solvent was removed under reduced pressure. The crude residue was recrystallised from ethanol to give the title compound as a white crystalline solid (1.51 g, 7.24 mmol, 88%). m.p. 210-212 °C (lit.[5] not reported). The ^{1}H NMR spectrum indicated the presence of two rotameric species at room temperature in chloroform-*d*. The ratio was found to be 10 : 1. Major rotamer: ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.51 (s, 1H, CHO), 7.70 (d, J = 7.5 Hz, 2H, Ar-H), 7.58 (d, J = 7.5 Hz, 2H, Ar-H), 7.41 (t, J = 7.5 Hz, 2H, Ar-H), 7.32 (t, J = 7.5 Hz, 2H, Ar-H), 6.30 (d, J = 9.1 Hz, 1H, H9), 5.77 (br s, 1H, NH). Minor rotamer: ^{1}H NMR (600 MHz, chloroform-*d*) δ 8.56 (d, J = 11.9 Hz, 1H, CHO), 7.72 (d, J =

7.5 Hz, 2H, Ar-H), 7.52 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.45 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.36 (t, *J* = 7.5 Hz, 2H, Ar-H), 5.65 (br s, 1H, NH), 5.47 (d, *J* = 10.2 Hz, 1H, H9).

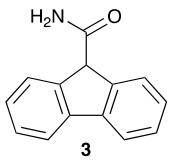
9-Isocyano-9*H*-fluorene 2[5]



2

In an adaptation of literature procedures,[5,6] 9-formylamino-9*H*-fluorene (0.308 g, 1.47 mmol) was dried under reduced pressure for one hour and then dissolved in SPS dichloromethane (10 mL) under nitrogen. Freshly distilled diisopropylamine (1.2 mL, 0.87 g, 8.6 mmol) was then added in one portion. The solution was then cooled to 0 °C using an ice bath and stirred for 15 minutes prior to the dropwise addition of freshly distilled phosphoryl chloride (0.35 mL, 0.58 g, 3.7 mmol) over approximately one minute. The solution was stirred at 0 °C for one hour before being stirred at room temperature for 24 hours; at this point the consumption of the starting material was confirmed using TLC. Aqueous sodium carbonate solution (1.5 M, 20 mL) was then added and the mixture was stirred for two hours. The organic layer was then separated and the aqueous layer was extracted with dichloromethane (3 x 40 mL). The combined organic phases were dried over magnesium sulfate and filtered before the solvent was removed under reduced pressure. The residue was subsequently purified using flash column chromatography (5% ethyl acetate in hexane) and recrystallised from hexane to give the product **2** as a red crystalline solid (0.038 g, 0.20 mmol, 14%). m.p. 113-115 °C (lit.[7] 113-115 °C). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.73-7.70 (m, 4H, Ar-H), 7.47 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.40 (t, *J* = 7.5 Hz, 2H, Ar-H), 5.64 (s, 1H, H9).

9-Carboxamido-9*H*-fluorene 3[8]

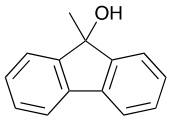


3

In an adaptation of a literature procedure,[8] 9*H*-fluorene-9-carboxylic acid (1.09 g, 5.19 mmol) was dissolved in thionyl chloride (35 mL) and the mixture was heated at reflux under nitrogen for four hours. Concentrated aqueous ammonia solution (28%, 50 mL) was then added dropwise over 10 minutes at 0 °C with stirring. Water (100 mL) was then

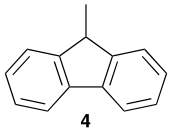
added and the mixture was then extracted with ethyl acetate (3 x 100 mL). The organic layers were combined, washed with hydrochloric acid (0.2 M, 3 x 60 mL) and saturated sodium bicarbonate solution (3 x 100 mL), dried over magnesium sulfate and filtered before the solvent was removed under reduced pressure. Multiple recrystallisations of the resulting yellow solid from ethanol gave the product **3** as white crystals (0.170 g, 0.812 mmol, 16%). m.p. 260.1-263.9 °C (lit.[8] 255-256 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.87 (d, J = 7.4 Hz, 2H, Ar-H), 7.76 (br s, 1H, NH), 7.53 (d, J = 7.4 Hz, 2H, Ar-H), 7.40 (t, J = 7.4 Hz, 2H, Ar-H), 7.32 (t, J = 7.4 Hz, 2H, Ar-H), 7.24 (br s, 1H, NH), 4.78 (s, 1H, H9).

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



Methylmagnesium bromide in diethyl ether (10 cm^3, 3 M, 30 mmol) was added to diethyl ether (50 cm^3) at 0 °C. To this solution, fluorenone (4.52 g, 25.1 mmol) in diethyl ether (40 cm^3) 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 cm^3). The reaction mixture was extracted with diethyl ether (30 cm^3), the organic phase was collected and dried with magnesium sulfate and volatiles were removed under reduced pressure. The resulting solid was recrystallised from isooctane to give the title compound as a white solid (2.40 g, 12.2 mmol, 49%) m.p. 173-174 °C (lit.[9] 174-175 °C). ^{1}H NMR (300 MHz, chloroform-d) 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 4[10]



A solution of 9-methylfluorenol (906 mg, 1.25 mmol) in dichloromethane (10 cm^3) was cooled at 0 °C, 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 cm^3). The resulting mixture was extracted with diethyl ether (60 cm^3), the organic phase collected and washed with brine (60 cm^3), dried over magnesium sulfate and the solvent removed under reduced pressure. The resulting solid was recrystallised from ethanol to give the title compound **4** 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*) 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).

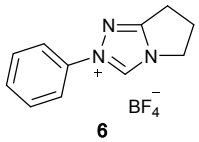
Absorbance data for the deprotonated form of each of the indicators **1-5**

Indicator	**pK_a**	**Wavelength λ_{max} / nm**
9-Pyridinium-9*H*-fluorene bromide **1**	11.8[1]	590
9-Isocyano-9*H*-fluorene **2**	12.3[1]	458
9-Carboxamido-9*H*-fluorene **3**	14.8[1]	428
9-Methylfluorene **4**	22.3[1]	515
Fluorene **5**	22.6[1]	484

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

Synthesis of the triazolium salt **6** and pK_a data

6,7-Dihydro-2-phenyl-5*H*-pyrrolo-1,2,4-triazolium tetrafluoroborate 6[14]



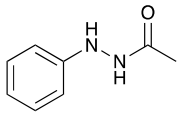
6

To a solution of 2-pyrrolidinone **6** (0.850 mL, 0.950 g, 11.2 mmol) in dry dichloromethane (50 mL), trimethyloxonium tetrafluoroborate (1.73 g, 11.7 mmol) was added in one portion. The resulting mixture was stirred at room temperature for 18 hours. To this solution phenylhydrazine (1.15 mL, 1.26 g, 11.7 mmol) was added resulting in a bright orange solution that was stirred at room temperature overnight. The mixture was concentrated under reduced pressure resulting in a yellow oil. Diethyl ether (30 mL) was added, the solid that formed was triturated with ethyl acetate, collected using filtration then dried under reduced pressure to give the hydrazone intermediate an off-white solid. This solid was placed under an atmosphere of argon. Dry toluene (15 mL) and triethyl orthoformate (4.80 mL, 4.28 g, 28.9 mmol) were added under argon and the mixture was heated at reflux for 48 hours. The mixture was then cooled to room temperature and concentrated under reduced pressure to give a dark red oil. To this diethyl ether (30 mL) was added, the solid that formed was triturated with ethyl acetate and then collected using filtration. The resulting off-white solid was recrystallized from ethanol to give the title compound **6** as a light orange crystalline solid (1.20 g, 1.85 mmol, 4.39 mmol, 38%). m.p. 160-162 °C (lit.[15] 154-156 °C). ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.69 (s, 1H, C5-H), 7.90-7.86 (m, 2H, Ar-H), 7.72-7.68 (m, 2H, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 4.41 (t, J = 7.5 Hz, 2H, NCH_2), 3.21 (t, J = 7.5 Hz, 2H, CCH_2), 2.75 (quin, J = 7.5 Hz, 2H, $CH_2CH_2CH_2$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.5 (C5), 138.8 (C3), 136.1 (C1'), 130.9 (C4'), 130.7 (Ar-C), 121.1 (Ar-CH), 47.4 (NCH_2), 27.1 ($CH_2CH_2CH_2$), 21.7 (CCH_2). ^{19}F NMR (282 MHz, DMSO-d_6): δ -148.36 (s, 4F, BF_4^-), -148.31 (s, 1F, BF_4^-).

Indicator	**pK_a of indicator**	**Measured K**	**pK_a**
9-isocyano-9*H*-fluorene **2**	12.3	0.01285	14.19
9-carboxamido-9*H*-fluorene **3**	14.8	3.990	14.20
9-carboxamido-9*H*-fluorene **3**	14.8	3.961	14.20
9-carboxamido-9*H*-fluorene **3**	14.8	3.243	14.29
9-carboxamido-9*H*-fluorene **3**	14.8	3.459	14.26
		Overall	**14.23 ± 0.12**

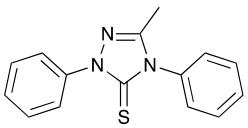
Synthesis of the thione **11**

1-Acetyl-2-phenylhydrazine[16]



Phenylhydrazine (4.04 g, 37.3 mmol) was added to acetic acid (40.0 mL) and the mixture was heated at 80 °C for 1.5 hours. The acetic acid was removed through distillation at atmospheric pressure to leave a viscous yellow oil. To this residue was added diethyl ether (40 mL) and the mixture was stirred overnight at room temperature. The suspension was filtered and the residue was washed with diethyl ether (2 x 20 mL) and recrystalised from dichloromethane to give the title compound as a white solid (3.38 g, 22.5 mmol, 60%). m.p. 127-129 °C (lit.[17] 129 °C). ^{1}H NMR data indicates the presence of two rotameric species at room temperature in chloroform-*d* - the ratio of these was found to be 0.7 : 0.3. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.67 (broad s, 0.7H, NH), 7.22-7.28 (m, 2H, Ar-H), 7.20 (broad s, 0.3H, NH), 6.92-6.95 (m, 1H, Ar-H), 6.85 (d, *J* = 7.8 Hz, 1.4H, Ar-H), 6.76 (d, *J* = 7.8 Hz, 0.6H, Ar-H), 5.84 (broad s, 1H, NH), 2.10 (s, 0.9H, CH_3), 2.04 (s, 2.1H, CH_3).

2,4-Dihydro-5-methyl-2, 4-diphenyl-3*H*-1,2,4-triazolethione 11[18]

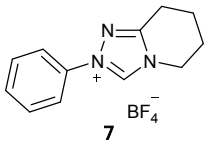


11

To a solution of potassium hydroxide (2.22 g, 39.6 mmol) in ethanol (30 mL), 1-acetyl-2-phenylhydrazine[16] (3.00 g, 20.0 mmol) was added. To this mixture, phenylisothiocyanate (3.27 g, 24.2 mmol) was added dropwise over five minutes; this process was exothermic. The solution was stirred at room temperature for 45 minutes during which time a white solid precipitated. This mixture was filtered and the collected solid dried under reduced pressure over 30 minutes to give the title thione **11** as an off-white solid (3.02 g, 11.3 mmol, 57%). m.p. 128-131 °C (lit.[18] 130-132 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.02 (m, 2H, Ar-H), 7.57 (m, 7H, Ar-H), 7.43 (m, 1H, Ar-H), 2.20 (s, 3H, CH_3).

pK_a Data for triazolium salts **7**, **8** and **10**

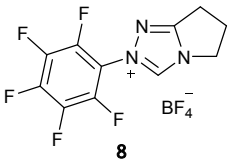
6,7,8,9-Tetrahydro-2-phenyl-5*H*-1,2,4-triazolo[4,3-*a*]azepinium tetrafluoroborate 7



7

Indicator	pK_a of indicator	Measured K	pK_a
9-isocyano-9*H*-fluorene **2**	12.3	0.005579	14.55
9-carboxamido-9*H*-fluorene **3**	14.8	2.120	14.47
9-carboxamido-9*H*-fluorene **3**	14.8	1.887	14.42
9-carboxamido-9*H*-fluorene **3**	14.8	2.140	14.47
9-carboxamido-9*H*-fluorene **3**	14.8	1.775	14.55
		Overall	**14.49 ± 0.16**

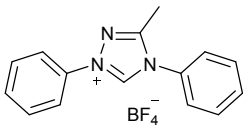
6,7-Dihydro-2-pentafluorophenyl-5*H*-pyrrolo-1,2,4-triazolium tetrafluoroborate 8



8

Indicator	pK_a of indicator	Measured K	pK_a
9-pyridinium-9*H*-fluorene bromide **1**	11.8	7.456	10.93
9-pyridinium-9*H*-fluorene bromide **1**	11.8	6.804	10.98
9-isocyano-9*H*-fluorene **2**	12.3	22.25	10.95
9-isocyano-9*H*-fluorene **2**	12.3	22.32	10.97
9-carboxamido-9*H*-fluorene **3**	14.8	>100.0	<12.8
		Overall	**10.95 ± 0.06**

3-Methyl-1,4-diphenyl-4*H*-1,2,4-triazolium tetrafluoroborate 10



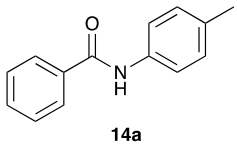
10

Indicator	pK_a of indicator	Measured K	pK_a
9-isocyano-9*H*-fluorene **2**	12.3	0.06830	13.47
9-isocyano-9*H*-fluorene **2**	12.3	0.06292	13.50
9-carboxamido-9*H*-fluorene **3**	14.8	22.61	13.45
9-carboxamido-9*H*-fluorene **3**	14.8	22.40	13.45
		Overall	**13.47 ± 0.08**

General procedure for synthesis of the *N*-phenylbenzamides **14a-e**

In a fashion analogous to that described in the literature,[19] to a solution of the appropriate aniline (1 equiv.) and triethylamine (0.15 equiv.) in dichloromethane (1.67 mL / mmol aniline), benzoyl chloride (1 equiv.) was added dropwise over 10 minutes, immediately affording a precipitate. The mixture was stirred at room temperature for 72 hours and then the volatiles were removed under reduced pressure. The resultant solid was recrystallised from ethanol affording the corresponding benzamide **14**.

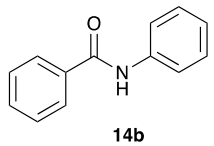
N-(4'-Methylphenyl)benzamide 14a



14a

4-Toluidine (5.00 g, 46.7 mmol), triethylamine (0.710 g, 7.02 mmol), benzoyl chloride (6.57 g, 46.7 mmol). Isolated as white crystals (5.24 g, 53%). m.p. 155-156 °C (lit.[20] 158 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.15 (s, 1H, NH), 7.94 (m, 2H, H2), 7.65 (d, 2H, J = 8.4 Hz, H2'), 7.55 (m, 3H, H3, H4), 7.15 (d, 2H, J = 8.4 Hz, H3'), 2.28 (s, 3H, 4'-Me).

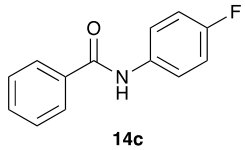
N-Phenylbenzamide 14b



14b

Aniline (2.79 g, 30.0 mmol), triethylamine (0.460 g, 4.55 mmol), benzoyl chloride (4.22 g, 30.0 mmol). Isolated as fine white crystals (4.73 g, 80%). m.p. 164 °C (lit.[21] 163-164 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.25 (s, 1H, NH), 7.96, (m, 2H, H2), 7.78 (m, 2H, H2'), 7.56 (m, 3H, H3, H4), 7.36 (t, 2H, J = 7.5 Hz, H3'), 7.10 (t, 1H, J = 7.5 Hz, H4').

N-(4'-Fluorophenyl)benzamide 14c

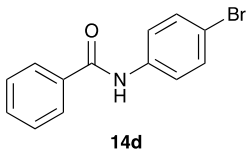


14c

4-Fluoroaniline (3.33 g, 30.0 mmol), triethylamine (0.460 g, 4.55 mmol), benzoyl chloride (4.22 g, 30.0 mmol). Isolated as fine white crystals (6.03 g,

93%). m.p. 184-185 °C (lit.[22] 184-185 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.30 (s, 1H, NH), 7.95 (m, 2H, H2), 7.79 (m, 2H, H2'), 7.56 (m, 3H, H3, H4), 7.19 (t, 2H, J = 9.3 Hz, H3').

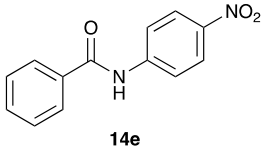
_N_-(4'-Bromophenyl)benzamide 14d



14d

4-Bromoaniline (5.14 g, 30.0 mmol), triethylamine (0.460 g, 4.55 mmol), benzoyl chloride (4.22 g, 30.0 mmol). Isolated as fine white crystals (5.64 g, 68%). m.p. 206 °C (lit.[23] 203 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.36 (s, 1H, NH), 7.94 (m, 2H, H2), 7.77 (d, 2H, J = 9.0 Hz, H2'), 7.50-7.64 (m, 5H, H3, H4, H3').

_N_-(4'-Nitrophenyl)benzamide 14e

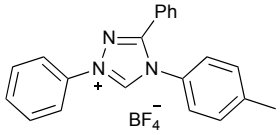


14e

4-Nitroaniline (2.19 g, 15.9 mmol), triethylamine (0.380 g, 3.75 mmol), benzoyl chloride (3.39 g, 24.1 mmol). Isolated as a pale yellow powder (2.34 g, 61%). m.p. 203 °C (lit.[24] 199-200 °C). ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.81 (s, 1H, NH), 8.27 (d, 2H, J = 9.4 Hz, H3'), 8.07 (d, 2H, J = 9.4 Hz, H2'), 7.98 (m, 2H, H2), 7.53-7.68 (m, 3H, H3, H4).

pK_a Data for triazolium salts **9a-e**

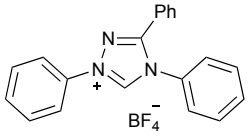
4-(4'-Methylphenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate 9a



9a

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-isocyano-9*H*-fluorene **2**	12.3	0.1366	13.16
9-isocyano-9*H*-fluorene **2**	12.3	0.1540	13.11
9-carboxamido-9*H*-fluorene **3**	14.8	46.80	13.13
9-carboxamido-9*H*-fluorene **3**	14.8	53.95	13.07
		Overall	**13.12 ± 0.12**

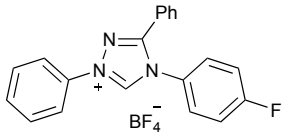
1,3,4-Triphenyl-4*H*-1,2,4-triazol-1*H*-ium tetrafluoroborate 9b



9b

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-pyridinium-9*H*-fluorene bromide **1**	11.8	0.09020	12.84
9-pyridinium-9*H*-fluorene bromide **1**	11.8	0.09614	12.82
9-isocyano-9*H*-fluorene **2**	12.3	0.2236	12.95
9-isocyano-9*H*-fluorene **2**	12.3	0.2262	12.95
9-isocyano-9*H*-fluorene **2**	12.3	0.2734	12.86
9-isocyano-9*H*-fluorene **2**	12.3	0.5876	12.92
9-carboxamido-9*H*-fluorene **3**	14.8	57.54	13.04
9-carboxamido-9*H*-fluorene **3**	14.8	57.80	13.04
9-carboxamido-9*H*-fluorene **3**	14.8	82.31	12.88
9-carboxamido-9*H*-fluorene **3**	14.8	58.85	13.03
		Overall	**12.93 ± 0.19**

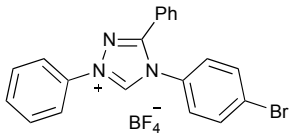
4-(4'-Fluorophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate 9c



9c

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-pyridinium-9*H*-fluorene bromide **1**	11.8	0.1490	12.63
9-pyridinium-9*H*-fluorene bromide **1**	11.8	0.1515	12.62
9-isocyano-9*H*-fluorene **2**	12.3	0.5207	12.58
9-isocyano-9*H*-fluorene **2**	12.3	0.4375	12.66
		Overall	**12.62 ± 0.10**

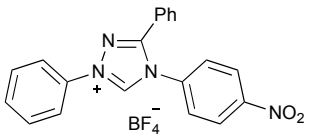
4-(4'-Bromophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate 9d



9d

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-pyridinium-9*H*-fluorene bromide **1**	11.8	0.3499	12.26
9-isocyano-9*H*-fluorene **2**	12.3	0.9007	12.35
9-isocyano-9*H*-fluorene **2**	12.3	0.9682	12.31
9-isocyano-9*H*-fluorene **2**	12.3	0.8140	12.39
		Overall	**12.33 ± 0.18**

4-(4'-Nitrophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate 9

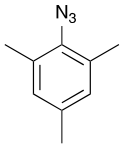


9e

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-pyridinium-9*H*-fluorene bromide **1**	11.8	1.726	11.56
9-pyridinium-9*H*-fluorene bromide **1**	11.8	1.376	11.66
9-pyridinium-9*H*-fluorene bromide **1**	11.8	1.766	11.55
9-isocyano-9*H*-fluorene **2**	12.3	6.062	11.52
9-isocyano-9*H*-fluorene **2**	12.3	5.223	11.58
9-isocyano-9*H*-fluorene **2**	12.3	5.591	11.55
9-isocyano-9*H*-fluorene **2**	12.3	7.036	11.45
		Overall	**11.55 ± 0.15**

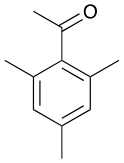
Synthesis of the triazolium salt **19** and pK_a data

2-Azido-1,3,5-trimethylbenzene[25]



A solution of 2,4,6-trimethylaniline (1.05 g, 7.76 mmol) in water (8.5 mL) was stirred rapidly and 32% hydrochloric acid (11.6 mL, 100 mmol) was added portionwise over several minutes, which resulted in the formation of a pale yellow solid and the evolution of heat, and the mixture was stirred for a further 16 hours at room temperature. The mixture was then cooled to *ca.* -5 °C and sodium nitrite (0.630 g, 9.13 mmol) was added portionwise to avoid bumping. The resulting yellow, oily suspension was stirred for 1.5 hours at 0ºC, then treated with a solution of sodium acetate (12.4 g, 170 mmol) and sodium azide (0.973 g, 15.0 mmol) in water (35 mL), which was cautiously added portionwise to prevent excess frothing. The stirred reaction mixture was warmed to room temperature to afford a colourless solution and a yellow oil. The mixture was extracted with pentane (3 x 20 mL), the combined organic extracts were then washed with brine (60 mL) and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded the title compound as a yellow oil (0.93 g, 75%) that was used without further purification.* ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.86 (s, 2H, 2,4-H), 2.35 (s, 6H, 1,5-CH_3), 2.28 (s, 3H, 3-CH_3).[26]

2',4',6'-Trimethyl acetophenone[27]

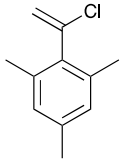


Acetyl chloride (42.7 mL, 0.600 mol) was added with stirring to a mixture of iron(III) oxide (10.3 g, 64.2 mmol) in mesitylene (60.5 mL, 0.503 mol) and the resulting mixture was stirred at room temperature for four days with a drying tube of colour indicating silica gel. Aqueous hydrogen peroxide (30% v/v, 5 mL, 7 mmol) was then added to the opaque blood-red suspension and the resulting mixture was filtered through a plug of celite. The celite was subsequently washed with ethyl acetate (50 mL), and the filtrates were combined and neutralised with saturated aqueous sodium hydrogen carbonate solution (to pH 7 as determined using a pH indicating strip).

*No further purification was attempted and care was taken when handling this azide as it has the smallest ratio of carbon to nitrogen (Sharpless index) advisable for handling and storage.[28]

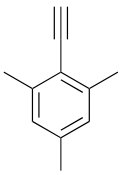
This aqueous phase was separated and then extracted with further ethyl acetate (3 x 100 mL). The combined organic layers were dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure to yield a yellow oil. Distillation under reduced pressure (60 °C, 5 mbar) afforded the title compound as a clear yellow oil (33.7 g, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (m, 2H, 3′,5′-H), 2.46 (s, 3H, C(O)CH_3), 2.28 (s, 3H, 4′-CH_3), 2.22 (s, 6H, 2′,6′-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 209.8 (CO), 138.5 (1′-C), 132.5 (2′,6′-C), 128.5 (4-CH), 126.9 (3′,5′-CH), 32.2 (C(O)CH_3), 21.3 (4′-CH_3), 19.3 (2′,6′-CH_3).

1-(1-Chlorovinyl)-2′,4′,6′-trimethylbenzene 11[28]



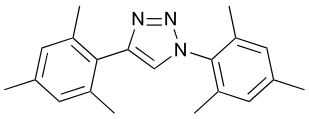
Oven-dried glassware was assembled as if for a reduced pressure distillation, with a pressure equalising dropping funnel in place of the thermometer and gas outlet on top bubbling through saturated aqueous sodium carbonate to neutralise hydrochloric acid produced in the reaction. The system was flushed with nitrogen. Phosphorus pentachloride (48.0 g, 0.231 mol) was added under nitrogen. Degassed 2',4',6'-trimethylacetophenone (33.7 g, 0.211 mol) was added dropwise to the cooled reaction flask at such a rate that the flask did not warm above 0 °C. The resulting yellow solution was heated at 70ºC overnight, resulting in a dark brown/red solution. The pressure equalising dropping funnel was replaced with a thermometer and the phosphoryl chloride produced in the reaction was distilled off at atmospheric pressure (86 °C), then the residue heated to 104 °C to ensure no low boiling substances remained. The residue was then distilled (0.9-1.3 mbar, 61-70 °C) to yield the desired 1-(1-chlorovinyl)-2′,4′,6′-trimethylbenzene **11** as a colourless liquid (26 g, 0.14 mol, 68%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.88 (s, 2H, 2,4-H), 5.70 (d, $^{2}J_{H\text{-}H}$ 1.1 Hz, 1H, vinyl-H, *trans* to Cl), 5.25 (d, $^{2}J_{H\text{-}H}$ 1.1 Hz, 1H, vinyl-H, *cis* to Cl), 2.33 (s, 6H, 2′,6′-CH_3), 2.29 (s, 3H, 4′-CH_3).

1-Ethynyl-2,4,6-trimethylbenzene[28]



Potassium hydroxide (44.3 g, 0.790 mol) was dissolved in 95% ethanol (125 mL) and the solution cooled to *ca.* 0 °C. 1-(1-Chlorovinyl)-2′,4′,6′-trimethylbenzene (26 g, 0.14 mol) was added dropwise over several minutes and the resulting opaque yellow mixture was stirred as it was allowed to warm to room temperature, after which it was heated at reflux for 24 hours. After cooling to room temperature, the resulting mixture was added to an ice/water mixture (400 g) and the biphasic system extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with brine (50 mL), then dried over anhydrous sodium sulfate and the volatile components removed under reduced pressure. The residue was distilled under reduced pressure (23-25 °C, 0.12 mbar) to afford the desired product as a colourless liquid that solidifies at -10 °C (16 g, 58%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.88 (br s, 2H, 3′,5′-CH), 3.46 (s, 1H, C≡CH), 2.42 (s, 6H, 2′,6′-CH_3), 2.29 (s, 3H, 4′-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.8 (s, 1-C_q), 138.1 (s, 4-C_q), 127.6 (s, 2,6-Ar-C_q), 119.0 (s, Ar-CH), 84.5 (s, C≡CH), 81.4 (s, C≡CH), 21.3 (s, 4-CH_3), 20.9 (s, 2′,6′-CH_3).

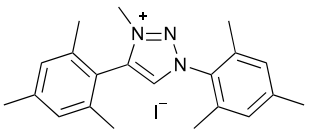
1,4-Dimesityl-1,2,3-triazole 12[29]



Copper sulfate pentahydrate (0.936 g, 3.75 mmol) was added to a suspension of 1-ethynyl-2,4,6-trimethylbenzene (3.61 g, 25.0 mmol), 2-azido-1,3,5-trimethylbenzene **8** (2.87 g, 24.7 mmol) and sodium ascorbate (0.995 g, 5.03 mmol) in methanol (50 mL). The mixture was stirred at room temperature for 14 days at which point a ^{1}H NMR spectrum ($CDCl_3$) of a vacuum dried aliquot of reaction mixture indicated incomplete conversion as determined by resonances attributable to the starting materials, noting protons at δ 6.90 (azide starting material) and *ca.* 7.0 (alkyne starting material). No further reaction was observed over a period of an additional three days. Additional copper sulfate pentahydrate (0.460 g, 1.85 mmol) and sodium ascorbate (0.990 g, 5.00 mmol) were added and the mixture stirred for a further 10 days at which point complete consumption of the azide starting material was was achieved, as determined

using ^{1}H NMR spectroscopy noting particularly the absence of the singlet at δ *ca.* 6.9. The reaction mixture was poured into water (500 mL) and the resulting mixture extracted with ethyl acetate (3 x 500 mL). The combined extracts were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified using flash column chromatography (silica, 10% ethyl acetate in hexane) to afford the title compound as a white crystalline solid (1.8 g, 28%). m.p. 134-137 °C (lit.[30] 152-154 °C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (s, 1H, 5-H), 6.98 (s, 2H, 3",5"-H), 6.78 (s, 2H, 3',5'-H), 2.37 (s, 3H, 4"-CH_3), 2.34 (s, 3H, 4'-CH_3), 2.17 (s, 6H, 2",6"-CH_3), 2.04 (s, 6H, 2',6'-CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.5 (4-C),140.1 (Ar-C), 138.4 (Ar-C), 137.9 (Ar-C), 135.3 (Ar-C), 129.2 (3″,5″-CH), 128.5 (3′,5′-CH), 124.6 (5-CH), 21.3 (2″,6″-CH_3), 20.8 (4′-CH_3), 17.4 (2′,6′-CH_3).

1,4-Dimesityl-3-methyl-1,2,3-triazolium iodide 19[31,32]



19

A mixture of 1,4-dimesityl-1,2,3-triazole (1.73 g, 5.65 mmol) and methyl iodide (1.00 g, 7.06 mmol) in acetonitrile (25 mL) was heated at 50 °C overnight, yielding a pale yellow solution. Additional methyl iodide (1.00 mL) was added each day for three days. The volatile components were removed under reduced pressure and the white powder was triturated with 5% ethyl acetate/hexane (20 mL) and dried *in vacuo* to afford the azolium salt **19** as a white powder (2.29 g, 91%). m.p. 148 °C to 149 °C. (lit. 185 °C,[33] 200-202 °C[30]). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.34 (s, 1H, H2), 7.06 (s, 2H, H3',5'), 7.05 (s, 2H, H3",5"), 4.25 (s, 3H, 3-Me), 2.37 (s, 3H, 4"-Me), 2.35 (s, 3H, 4'-Me), 2.18 (s, 6H, 2',6'-Me), 2.17 (s, 6H, 2",6"-Me). ^{13}C NMR (100 MHz, CDCl3): δ 142.0 (C4'), 141.7 (C4"), 141.0 (C4), 138.4 (C2',6'), 134.3 (C2",6"), 132.6 (C5), 131.2 (C1'), 129.5 (C3',5'), 128.8 (C3",5"), 118.0 (C1"), 38.3 (3-Me), 20.9 (4'-Me), 20.7 (4"-Me), 19.6 (2',6'-Me), 16.7 (2",6"-Me).

Indicator	**pK_a of indicator**	**Measured *K***	**pK_a**
9-Methyl-9*H*-fluorene **4**	22.3	1.105	22.26
9-Methyl-9*H*-fluorene **4**	22.3	1.125	22.25
Fluorene **5**	22.6	1.998	22.30
Fluorene **5**	22.6	2.278	22.24

	Overall	**22.26 ± 0.09**

Hammett analysis of series **12**, **13** and **16**

Using the data presented in Cheng *et al.*,[34] the slopes of the plots of the pK_a values of the triazolium salt series **12** and **13** in DMSO *vs* the Hammett σ parameters of the *para*-aryl substituents were determined to be (-2.12 ± 0.10) and (-1.87 ± 0.17).

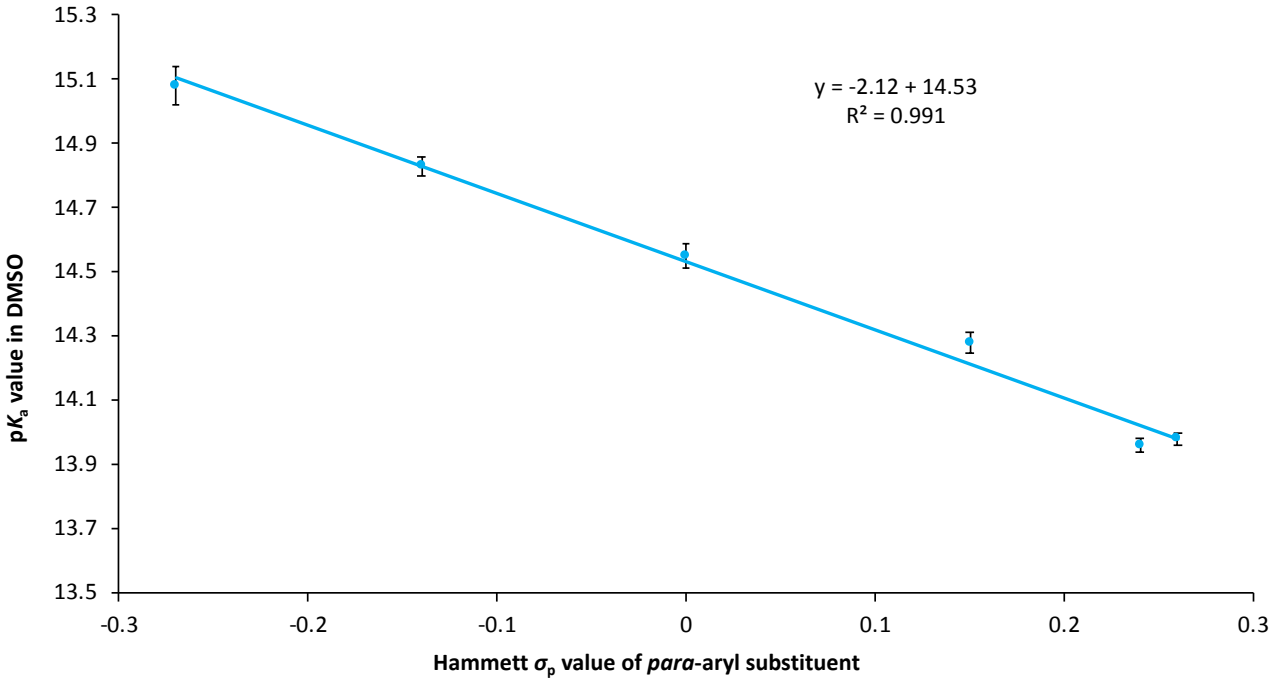


Figure S1. The correlation between the pK_a values of the triazolium salts **12** in DMSO at 25 °C and the Hammett σ_p value of the 4-aryl substituent.[35] The original data is reproduced from Cheng *et al.*[34]

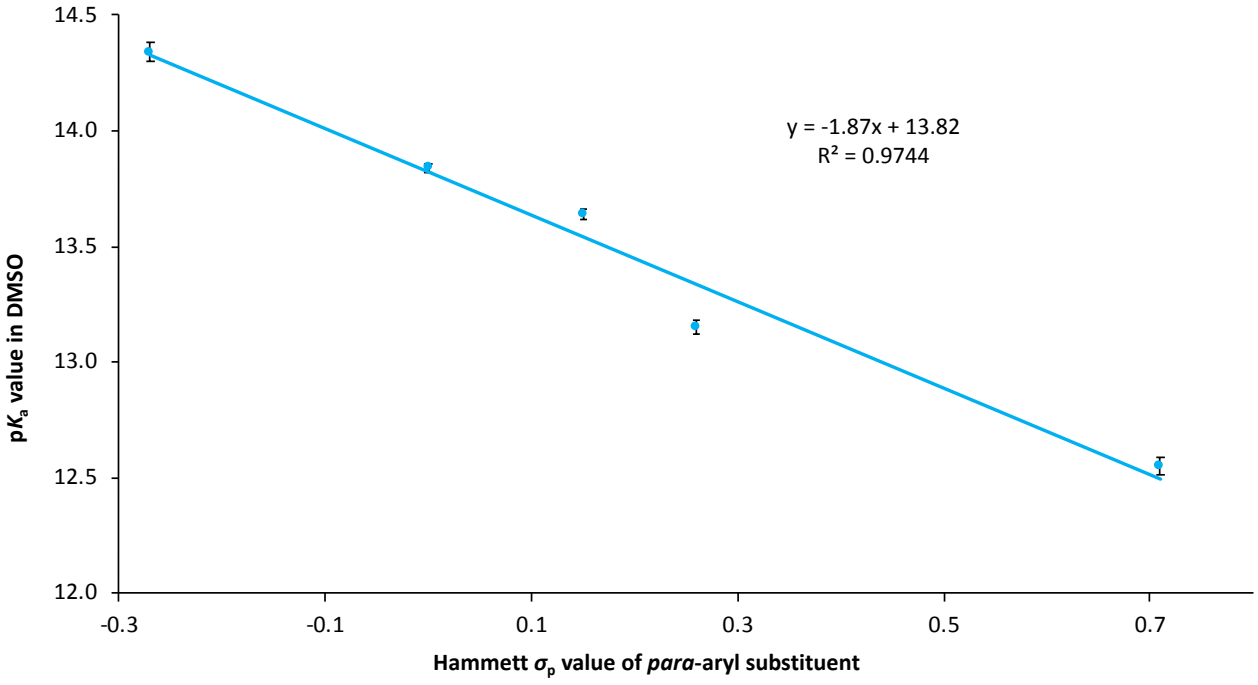


Figure S2. The correlation between the pK_a values of the triazolium salts **13** in DMSO at 25 °C and the Hammett σ_p value of the 4-aryl substituent.[35] The original data is reproduced from Cheng *et al.*[34]

Using the data presented in O'Donoghue *et al.*,[36] the slopes of the plots of the pK_a values of the triazolium salt series **12** and **16** in water *vs* the Hammett σ parameters of the *para*-aryl substituents were determined to be (-0.93 ± 0.05) and (-0.19 ± 0.17).

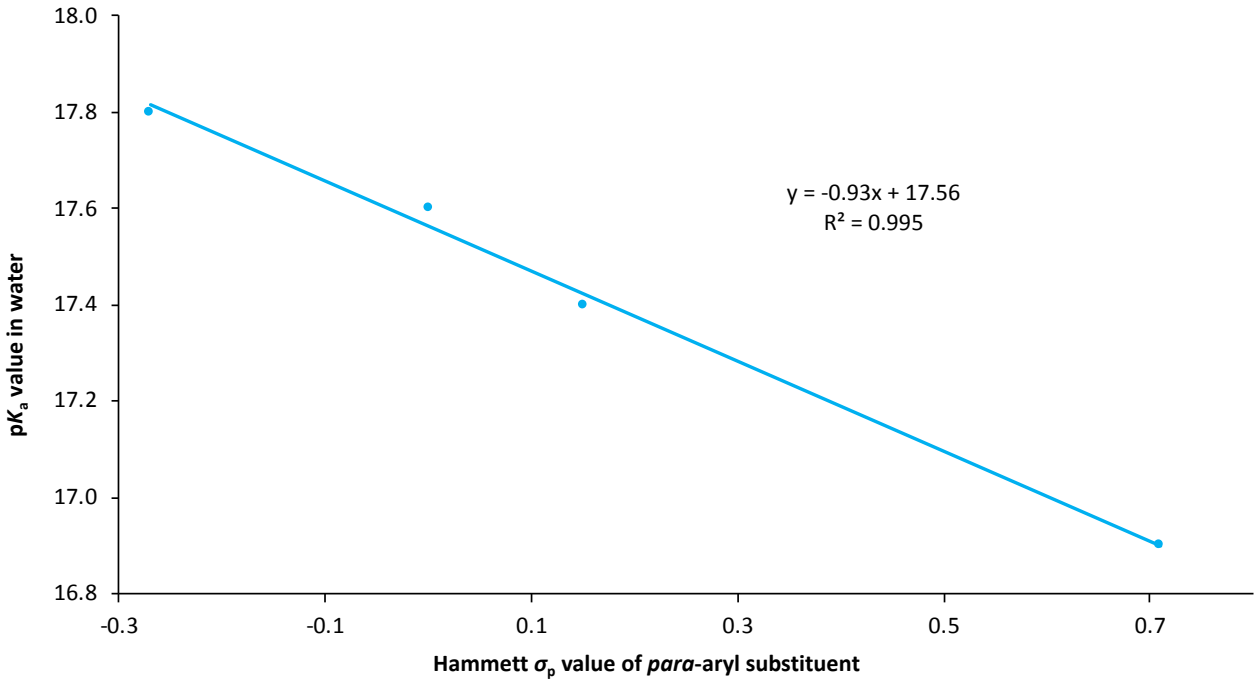


Figure S3. The correlation between the pK_a values of the triazolium salts **12** in water at 25 °C and the Hammett σ_p value of the 4-aryl substituent.[35] The original data is reproduced from O'Donoghue *et al.*[36]

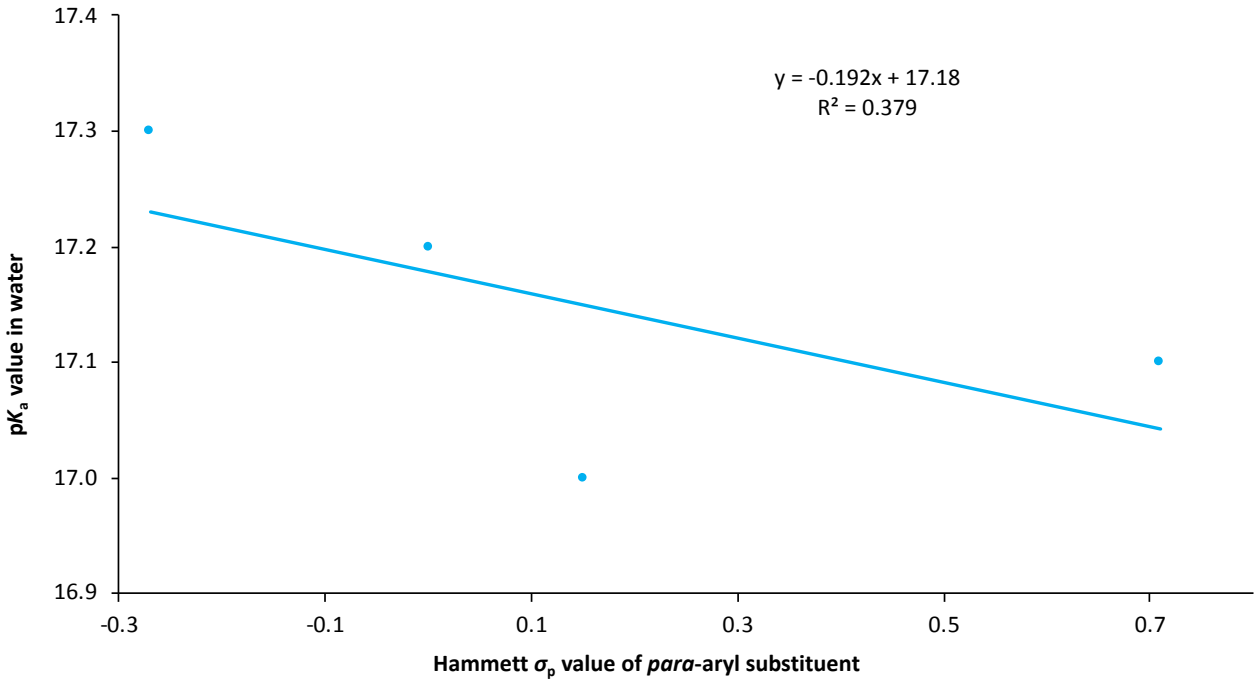
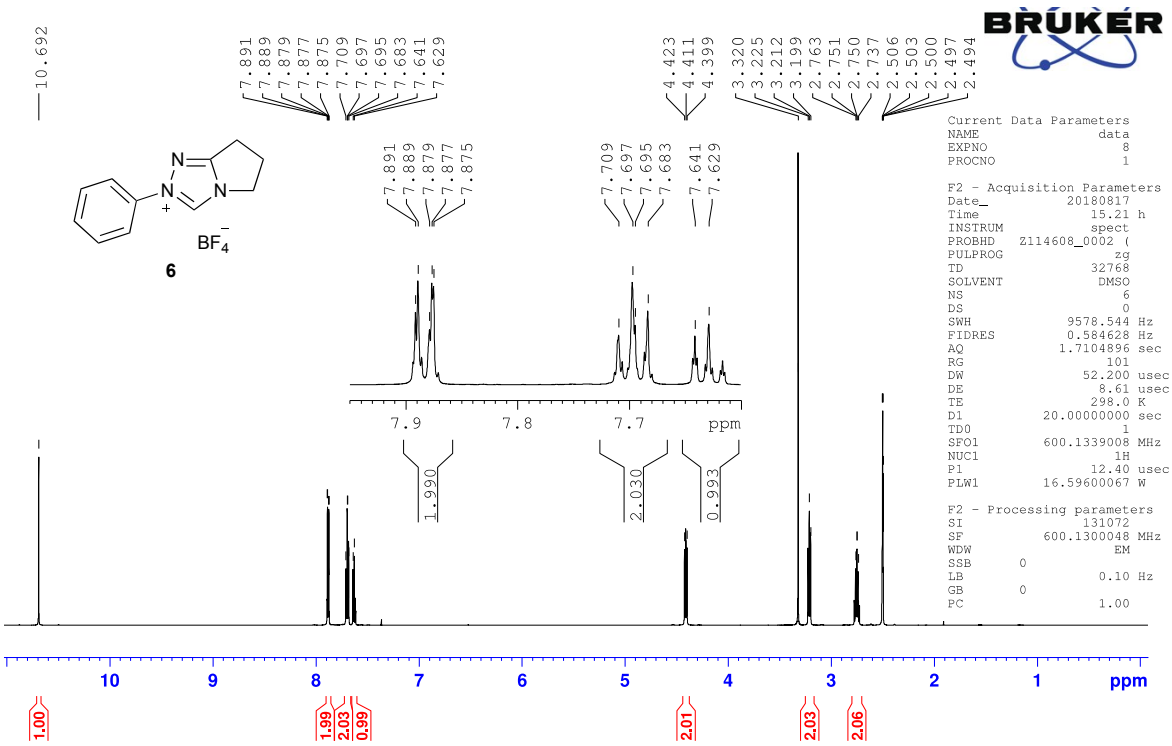


Figure S4. The correlation between the pK_a values of the triazolium salts **16** in water at 25 °C and the Hammett σ_p value of the 4-aryl substituent.[35] The original data is reproduced from O'Donoghue *et al.*[36]

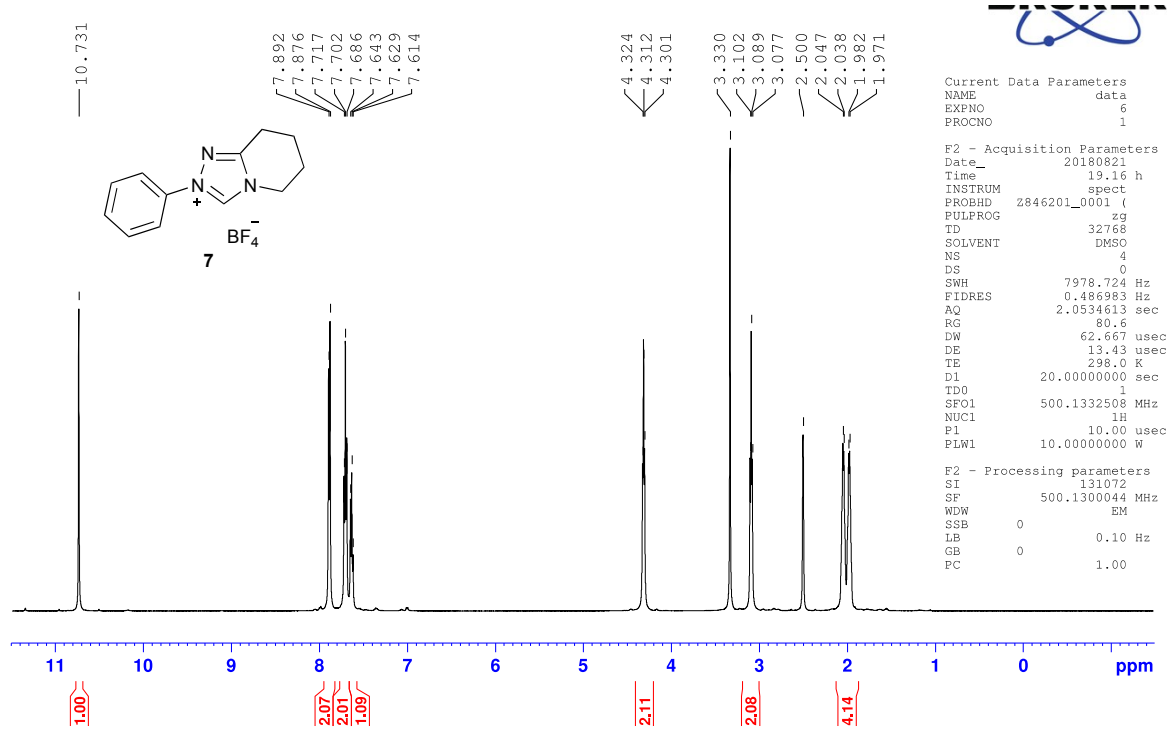
NMR spectra of all prepared triazolium salts

All NMR spectra for characterisation of synthesised compounds were obtained using a Bruker Avance III spectrometer 400. Spectra were processed using the Bruker Topspin 4.0.6 software.

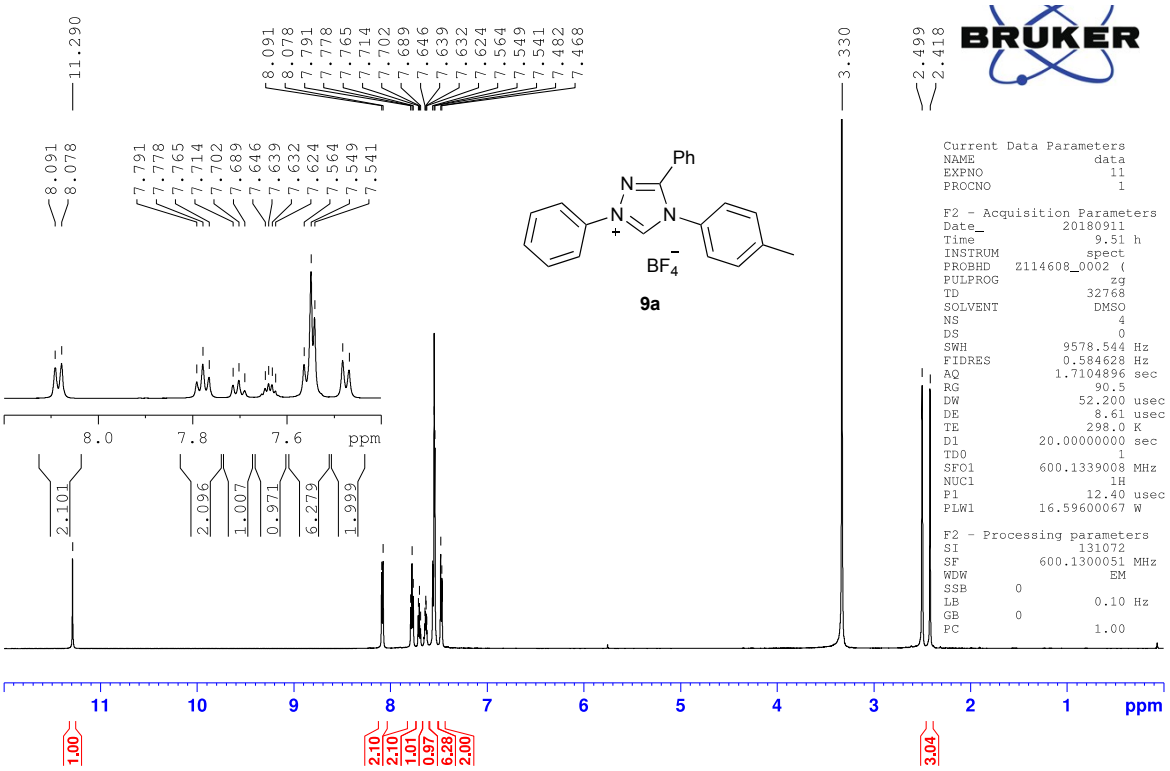
6,7-Dihydro-2-phenyl-5*H*-pyrrolo-1,2,4-triazolium tetrafluoroborate **6**



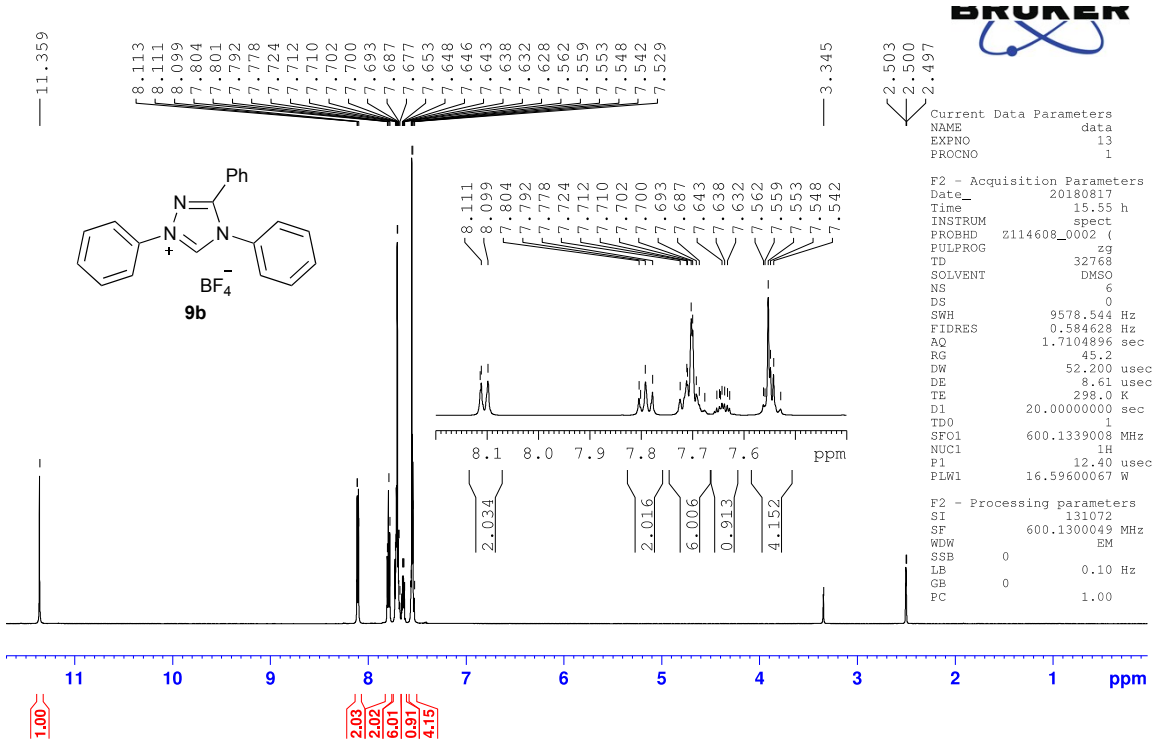
6,7,8,9-Tetrahydro-2-phenyl-5*H*-1,2,4-triazolo[4,3-*a*]azepinium tetrafluoroborate **7**



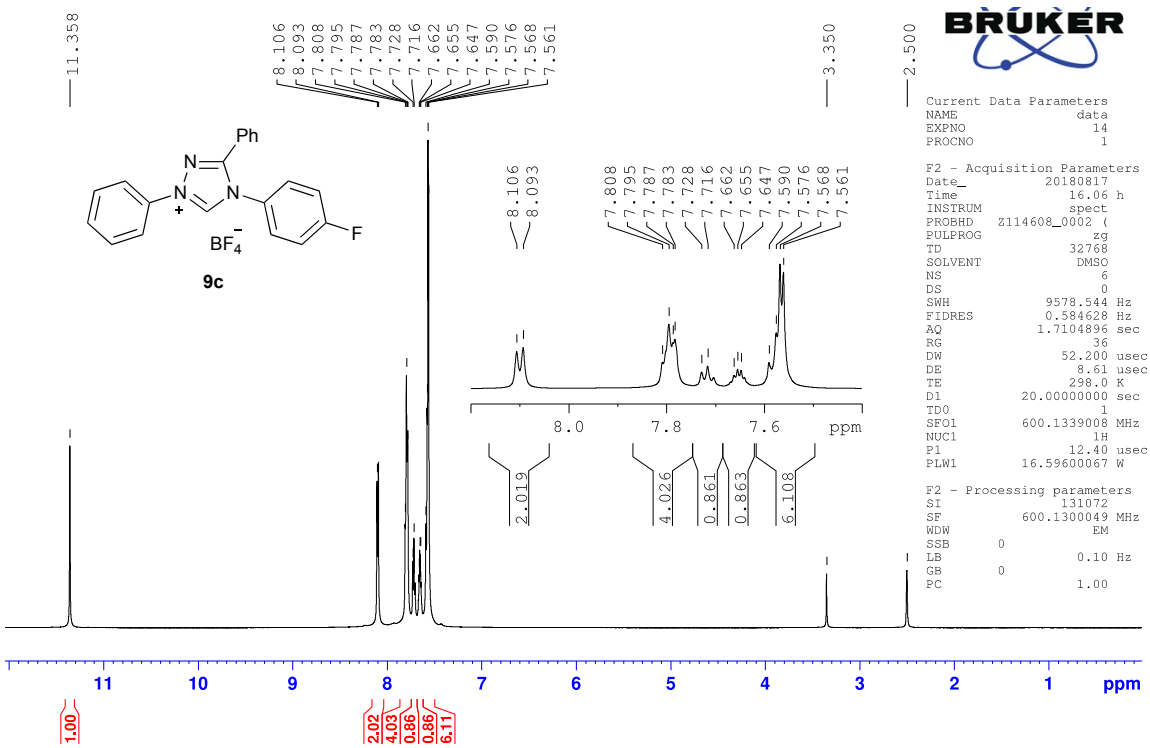
4-(4'-Methylphenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate **9a**



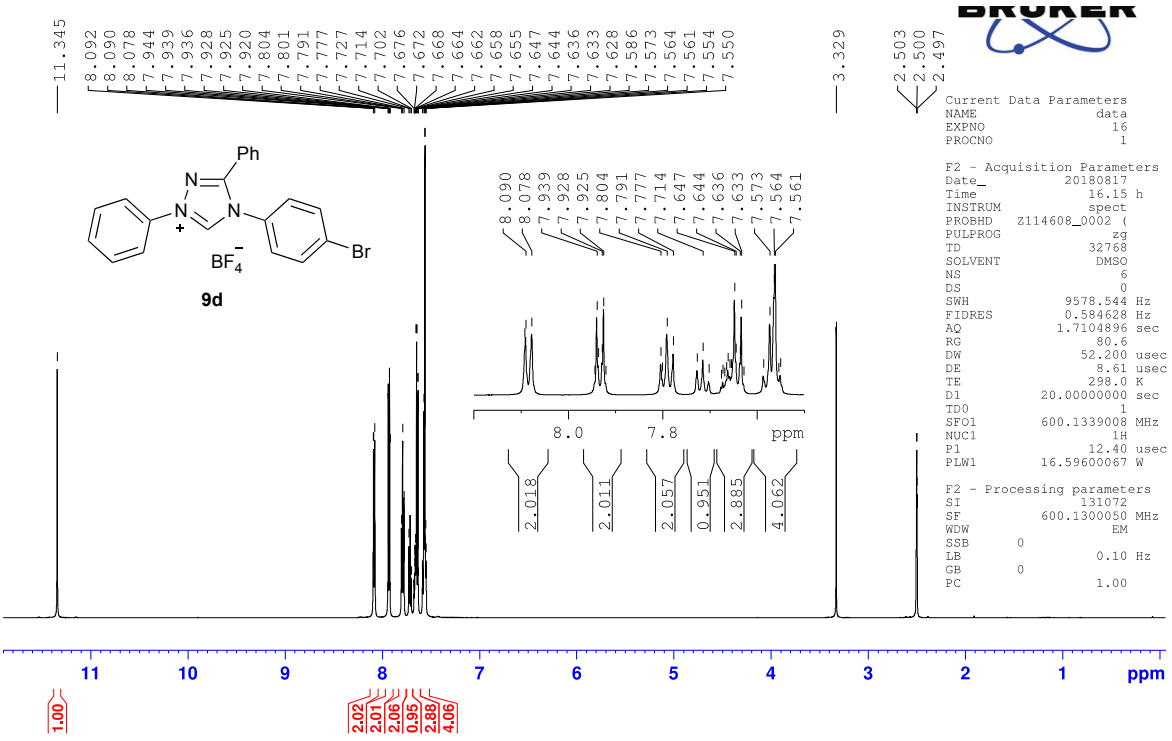
1,3,4-Triphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate **9b**



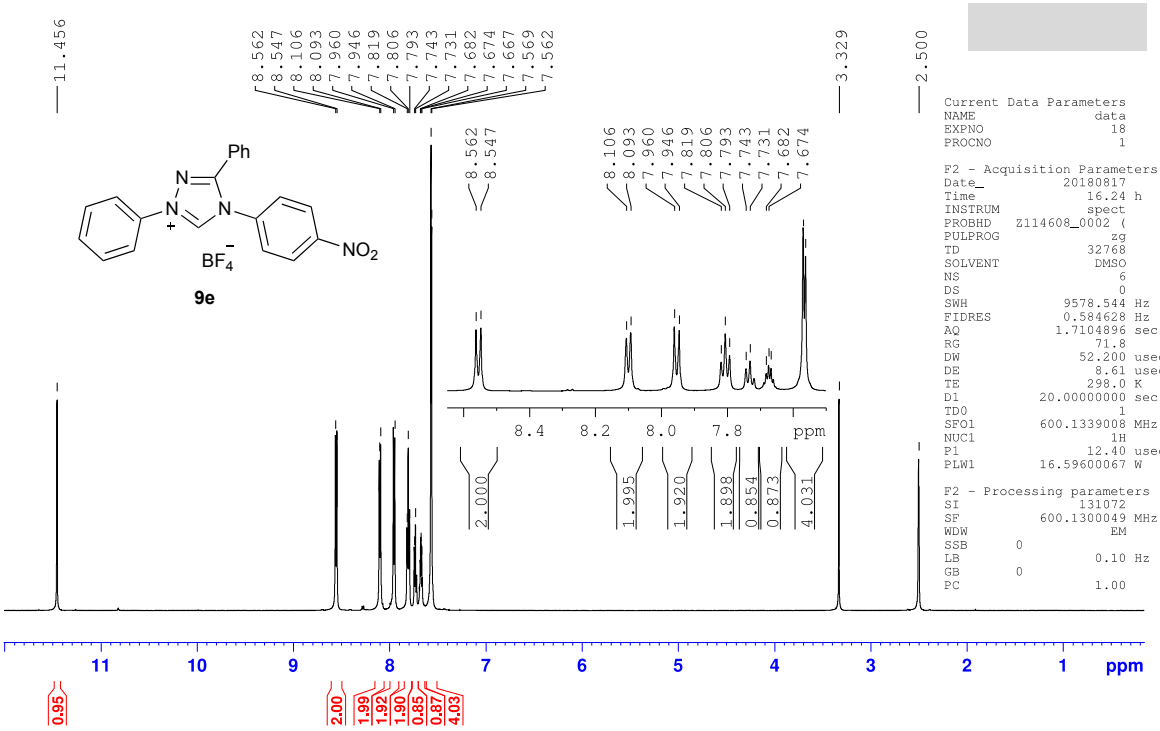
4-(4'-Fluorophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate **9c**



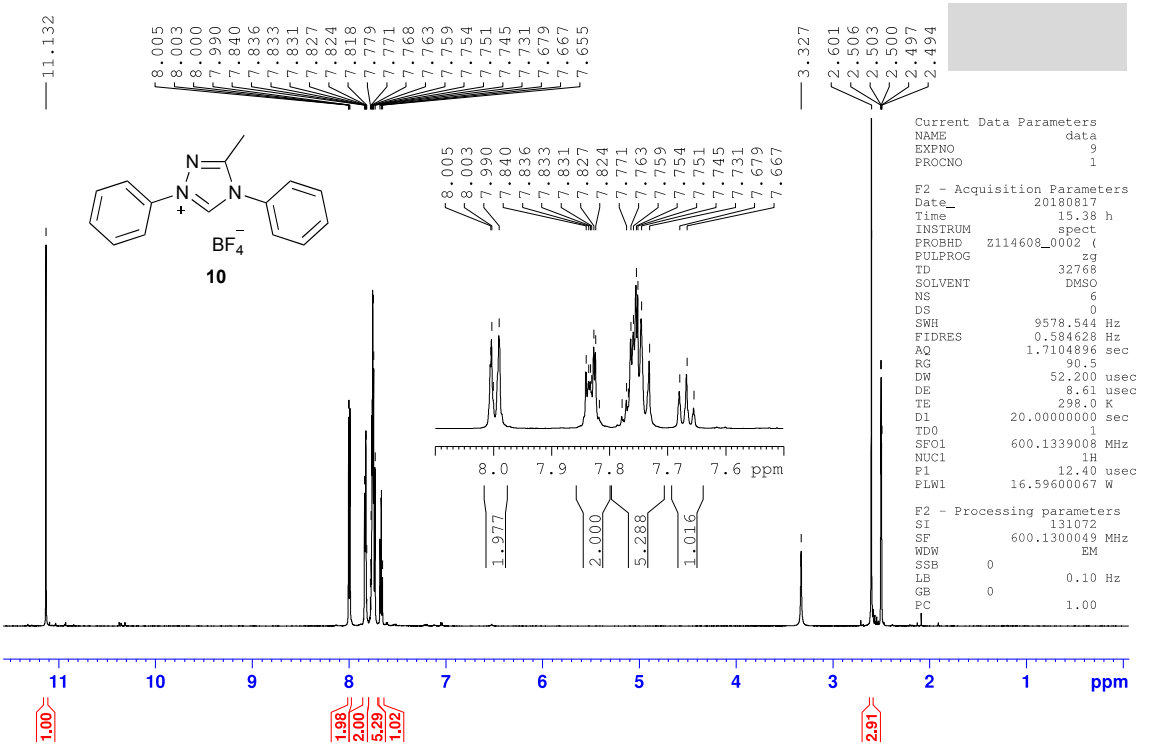
4-(4'-Bromophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate **9d**



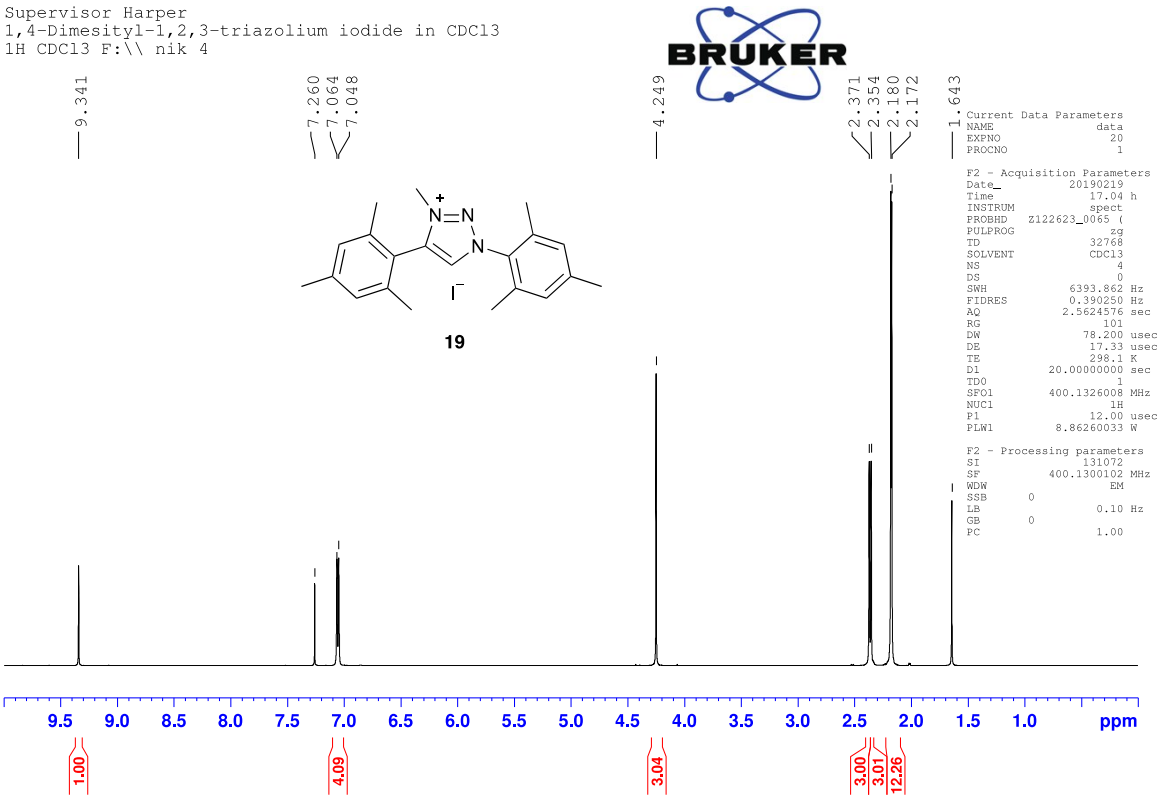
4-(4'-Nitrophenyl)-1,3-diphenyl-4*H*-1,2,4-triazol-1-ium tetrafluoroborate **9e**



3-Methyl-1,4-diphenyl-4*H*-1,2,4-triazolium tetrafluoroborate **10**



1,4-Dimesityl-3-methyl-1,2,3-triazolium iodide **19**



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