ELECTRONIC SUPPLEMENTARY INFORMATION

1 Preparation and characterisation of reaction media

1.1 Aqueous phosphate buffers used in preparation of reaction media

Phosphate buffers of a nominal pH were prepared in two ways: 1, by addition of a prescribed volume of standard NaOH solution to a known amount of KH_2PO_4 and dilution to a standard volume or 2, by making co-solutions of KH_2PO_4 and K_2HPO_4 or Na_2HPO_4 in prescribed ratio. Aqueous buffers of nominal pH 7, prepared by method 1 and having total phosphate concentrations, B_{aq}, of 0.150 mol dm^{-3} or 0.100 mol dm^{-3} were diluted to provide those with B_{aq} 0.075, 0.05 and 0.025 mol dm^{-3}. Mixed with MeCN, these were used for all spectrophotometric rate measurements except for those at variable pH and constant ionic strength where buffers prepared by method 2 were used. Buffer made by method 2 was also used to prepare the medium for investigation of factors affecting product distributions. Rates of nitrogen evolution were measured for aqueous MeCN buffers where the aqueous components were prepared by both methods.

1.2 Buffers in aqueous acetonitrile mixtures

The general procedure was to take a required volume (or, in the case of large quantities, weight) of MeCN and dilute it in a volumetric flask with the required aqueous buffer but, on account of the endothermic mixing, leaving sufficient space for expansion on re-warming. The temperature was allowed to recover to the ambient value before the final adjustment of volume with additional buffer. The pH values found for aqueous MeCN buffers were higher by up to ~1 unit than those measured for the aqueous buffers alone and varied with the buffer concentration, the ionic strength and the percentage of MeCN.

1.3 Standard buffers in mixed solvents

Standard buffers in aqueous MeCN mixtures were needed for pH-meter calibration when such mixtures were used for making measurements. Three buffer systems were used: potassium hydrogenphthalate (0.05 mol kg^{-1}), KH_2PO_4 and Na_2HPO_4 (each 0.025 mol kg^{-1}), and $Na_2B_4O_7.10H_2O$ (0.01 mol kg^{-1}); all three were used in the 50% v/v mixture and the latter two were also used in the 20 and 30% v/v mixtures. Solutions were prepared by dissolution of the buffer salt in less than the required amount of water followed by addition of the required volume of acetonitrile and final adjustment of volume with water, again allowing recovery from the endotherm. The weights of buffer salts used took account of the density of the final solvent mixture in order to obtain molal concentrations. The pH_S values ascribed to these

standard buffers were interpolated from the pH_S versus w/w composition data of Barbosa and co-workers (See Table 1 and ref. of 24 main paper).

1.4 pH Measurements

Measurements of the pH of aqueous acetonitrile reaction media were made on solutions separate from those used for kinetic measurements but of the same composition except for the presence of **1** and **2**. The pH values obtained for aqueous MeCN buffers using a meter calibrated with the above standards were similar to those obtained with a meter which had been calibrated using commercially available aqueous standard buffers. Solutions of variable ionic strength, whether intrinsic or due to added KNO_3, gave pH_{50} values greater by 0.04 to 0.06 units when recorded by a meter calibrated using mixed-solvent standards than when recorded by a meter calibrated with aqueous standards; solutions of fixed ionic strength but variable pH gave pH_{50} values differing by −0.03 to +0.06 units according to the method of calibration. Measurements of pH, made using Jenway 3305 and Jenway 3310 pH meters fitted with combination electrodes, were taken in triplicate and averaged.

1.5 Interpolation of properties of aqueous MeCN mixtures and derived buffers

Required properties of solutions formulated on a v/v basis were interpolated from published data given on a w/w basis (see ref. 24 and 25 of main paper). The general method was to find a polynomial $P_w = \sum a_n w^n$ which accurately expresses the published property in terms of the fractional weight, w, of MeCN in the solvent, to express v/v solution compositions of interest in terms of fractional weight and then to use the polynomial to infer the value of the required property. Coefficients, a_n, of the polynomials for the various properties are given in Table S1; the coefficient, a_0 was constrained to the pure water value in each case. For a solution of aqueous MeCN in which the percentage by volume of MeCN is V, the fractional weight was calculated as $(0.7766 \times V)/[0.7766 \times V + (100 - V) \times 0.9971]$ where 0.7766 and 0.9971 g cm^{-3} are the densities of MeCN and H_2O, respectively, at 298 K. The maximum value of w used (for 50% v/v solution) was 0.4378, *i.e. within* the range of the explanatory polynomial in all cases as required for *inter*polation.

2 Kinetic measurements

2.1 Spectrophotometric rate measurements at variable phosphate buffer concentration

Fig. S1 shows the decay in absorbance of **1** (initially 7.5×10^{-5} mol dm^{-3}) at 312 nm as a function of time t when treated with a 20-fold excess of **2** in an aqueous MeCN buffer, $B_{50} = 0.05$ mol dm^{-3}, $pH_{50} = 7.92$ [see Experimental (ii)]. Instrumental readings were taken at 1 s intervals but, for clarity in the figure, only one in five readings is plotted. The continuous line is the fitting of the data by eqn. (S1) allowing determination of k_{obs} for the particular run as $(3.15 \pm 0.01) \times 10^{-2}$ s^{-1}.

Table S1 Polynomials for interpolation of properties of aqueous MeCN mixtures and derived solutions at 298 K

Entry	*Property*	*Coefficients, a_n, of polynomials in fraction by weight, w, of MeCN*					*Range(N)*[a]	R^2 [b]	*Ref.*[c]
		a_0	a_1	a_2	a_3	a_4			
1	Density, ρ_V/g cm^{-3}	0.9971	−0.1399	−0.2369	+0.1858		0.70 (6)	1.0000	24(*a*)
2	Debye-Hückel coefficient, A_V/(mol kg^{-1})^{½}	0.5103	+0.2550	+0.6800			0.70 (6)	1.0000	24(*a*)(*b*)
3	Relative Permittivity, ε_{rV}	78.360	−35.774	−31.407	+24.892		0.70 (6)	0.9996	24(*a*)(*b*)
4	Viscosity, $10^4\eta$/kg m^{-1} s^{-1}	8.903	+10.453	−35.285	+19.405		0.9932 (10)	0.9998	25
5	Autoprotolysis, pK_{apV}	14.00	+2.3683	+2.3281			0.70 (6)	0.9996	24(*a*)(*b*)
6	$H_2PO_4^-$, pK_{aV}	7.20	+3.2339	−3.5200	+4.888		0.70 (6)	0.9992	24(*c*)
	Standard buffers								24(*d*)(*e*)
7	pH_{SV}(phthalate)[d]	4.005	+2.6458	+6.2171	−16.551	+13.333	0.70 (6)	1.0000	
8	pH_{SV}(phosphate)[e]	6.865	+1.3973	+23.266	−99.733	+113.42	0.50 (5)	1.0000	
9	pH_{SV}(borate)[f]	9.180	+4.3157	−0.5488			0.50 (5)	0.9999	

[a] *Range* is the upper limit of *w* used in defining the polynomial; *N* is the number of data points used in the definition. [b] *R* is the correlation coefficient. [c] See References and Notes. [d] Potassium hydrogenphthalate, 0.05 mol kg^{-1}. [e] KH_2PO_4 and Na_2HPO_4, each 0.025 mol kg^{-1}. [f] $Na_2B_4O_7.10H_2O$, 0.01 mol kg^{-1}

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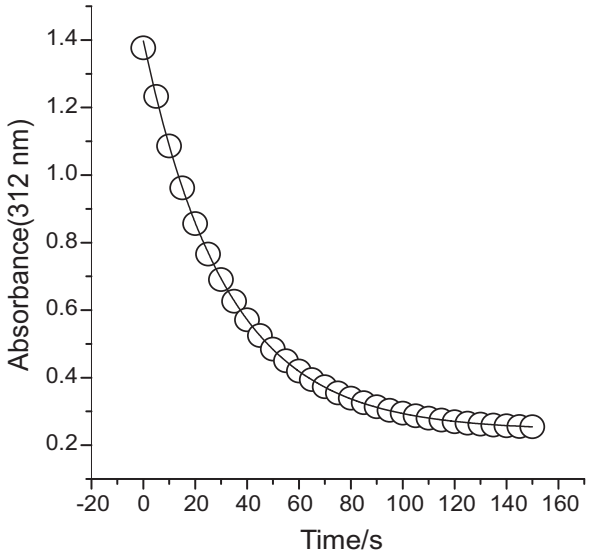

Fig. S1

Fig. S1 Variation in absorbance of **1** at λ_{max} = 312 nm as a function of time on treatment with a 20-fold excess of **2** in a phosphate buffer (B_{50} = 0.05 mol dm^{-3}) in 50% aqueous MeCN.

$$Abs = (1.153 \pm 0.001)\exp[-10^{-2} \times (3.146 \pm 0.005)t] + (0.244 \pm 0.0004) \qquad R^2 = 0.9999 \qquad \text{(S1)}$$

Fig. S2 illustrates the variation in k_{obs} as a function of the initial concentration of **2**; the linearity shows the observed reaction is of first order in Cu(I) and the separate plots for buffers differing in concentration implicates one or more buffer components as a reactant. Fig. S3 shows the variation in k_{obs} with $[HPO_4^{2-}]$ and the linearity demonstrates the first order dependence of the reaction on this species too.

2.2 Dependence of reaction rate on ionic strength

The linear dependence of log k_{obs} upon the square root of the ionic strength of the reaction medium is shown in Fig. S4. The negative sign of the gradient requires the rate-determining step in the reduction of **1** by **2** involves the reaction of an anion and a cation. After taking into account the Debye-Hückel constant of the reaction medium the magnitude of the gradient shows that one of these is doubly charged and one is singly charged. The only doubly charged ion is HPO_4^{2-} but at this juncture the identity of the singly charged cation with which it reacts is uncertain.

3 Measurements of nitrogen evolution

Table S2(i) presents the results of experiments which measured the evolution of N_2 as a function of time over 400 s. The volumes of N_2 measured are presented as percentages, Q, of the millimolar volume theoretically available in the quantity of diazonium ion used.

Towards the end of reaction when the gas-evolution rate is slow, the gas cell is insensitive to small volume changes and measurements become sporadic (indicated by two or three consecutive measurements being the same before reaction is complete). In extracting rate constants, $k_{obs}^{(g)}$, from the Q *vs* t curves, a curve fitting option was therefore taken which applied a statistical weighting in the minimisation of χ^2, according greater significance to the earlier points. Table S2(ii) presents the fittings of the data by $Q = q_1 - q_2\exp(-k_{obs}^{(g)}t)$ which may be re-written as $Q = q_2[1 - \exp(-k_{obs}^{(g)}t)] - (q_2 - q_1)$, [*cf.* eqn. (4)]. The mean value of $k_{obs}^{(g)}$ is $(1.024 \pm 0.114) \times 10^{-2}$ s^{-1}. Data set Q_1(A) and its fitting by the parameters of entry 3 of Table S2(ii) are given in Fig. 2a.

4 Product distributions

4.1 Organic products as a function of [2]/[1]

Table S3 gives the complete experimental distribution of products **3** – **10**.

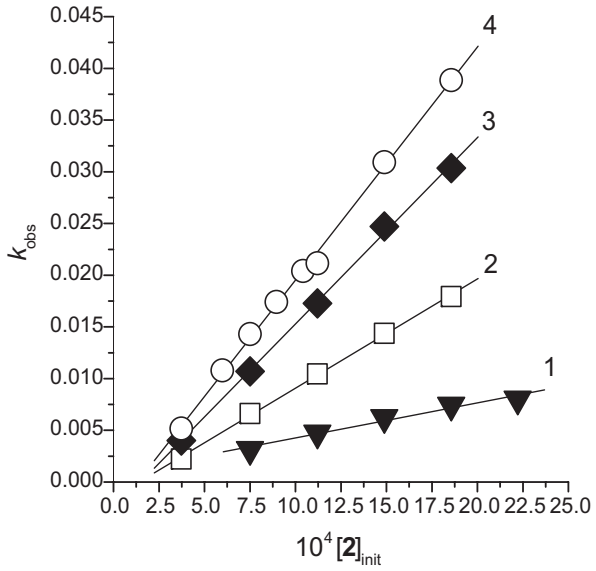

Fig. S2

Fig. S2 Variation of k_{obs} as a function of the initial concentration of **2** in phosphate buffers of different concentration, B_{50}, in 50% aqueous MeCN: 1, B_{50} = 0.0125 mol dm^{-3}; 2, B_{50} = 0.025 mol dm^{-3}; 3, B_{50} = 0.0375 mol dm^{-3}; 4, B_{50} = 0.05 mol dm^{-3}.

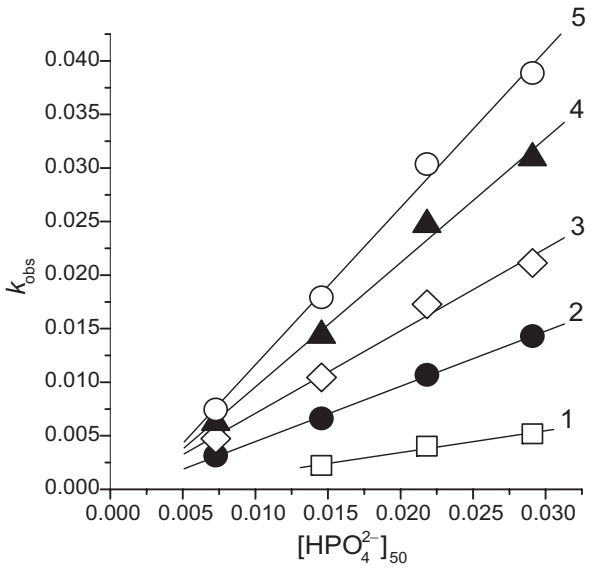

Fig. S3

Fig. S3 Variation of k_{obs} as a function of $[HPO_4^{2-}]_{50}$ for different initial concentrations of **2**: 1, $[\mathbf{2}]_{init} = 3.726 \times 10^{-4}$ mol dm^{-3}; 2, $[\mathbf{2}]_{init} = 7.505 \times 10^{-4}$ mol dm^{-3}; 3, $[\mathbf{2}]_{init} = 11.20 \times 10^{-4}$ mol dm^{-3}; 4, $[\mathbf{2}]_{init} = 14.89 \times 10^{-4}$ mol dm^{-3}; 5, $[\mathbf{2}]_{init} = 18.56 \times 10^{-4}$ mol dm^{-3}.

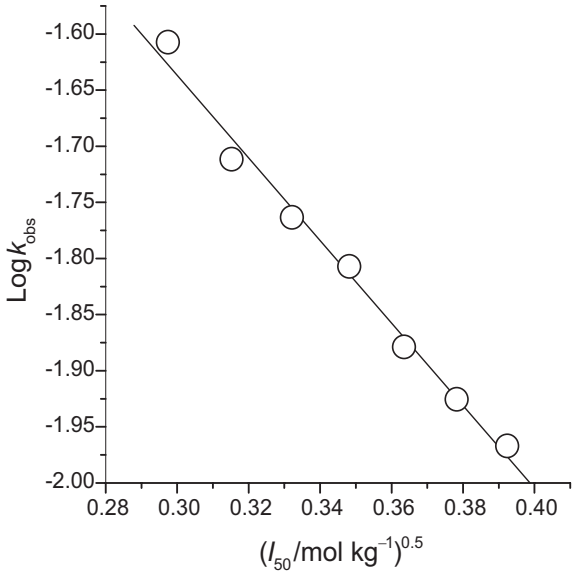

Fig. S4

Fig. S4 Plot of log k_{obs} *versus* (I_{50}/mol kg^{-1})^{½} for the reaction of **1** and **2** in phosphate buffer (B_{50} = 0.0375 mol dm^{-3}) in 50% aqueous MeCN.

Table S2(i) Evolution of N_2 as a percentage of available millimolar volume at SATP

Low phosphate

B_{50} = 0.025 mol dm^{-3}

Time/s	[**2**]/[**1**]$_{init}$ = 0.02/0.01 = 2		[**2**]/[**1**]$_{init}$ = 0.01/0.01 =1		[**2**]/[**1**]$_{init}$ = 0.01/0.02 = 0.5	
	Q_2(A)	Q_2(B)	Q_1(A)	Q_1(B)	$Q_{0.5}$(A)	$Q_{0.5}$(B)
10		2.70	1.25	3.43	2.08	0.22
20	5.85	8.19	6.05	7.46	4.92	3.51
30	11.54	14.16	11.29	11.25	7.85	7.20
40	16.34	20.37	15.89	14.84	10.73	10.69
50	21.10	24.12	19.69	18.31	13.09	13.80
60	24.53	27.91	23.44	21.50	15.63	16.36
70	27.87	30.25	26.10	24.57	17.85	18.39
80	30.74	34.05	29.25	26.50	19.69	20.33
90	33.20	35.50	31.14	28.88	21.18	21.58
100	35.38	38.97	33.08	31.71	22.99	22.95
110	36.63	41.15	35.01	33.68	24.49	24.02
120	38.73	43.53	36.43	35.26	25.21	24.61
130	39.90	45.42	38.08	36.51	26.93	25.94
140	41.23	46.83	39.29	38.00	28.00	26.24
150	42.19	48.08	40.54	38.68	28.72	27.55
160	43.28	49.33	41.67	39.90	30.35	28.00
170	44.82	50.26	42.88	41.23	30.76	28.02
180	45.66	51.31	43.69	41.71	31.77	29.47
190	46.59	52.20	44.37	42.68	31.99	29.79
200	47.40	52.96	45.18	44.05	33.30	30.21
210	47.88	53.69	46.11	44.05	33.68	30.56
220	48.73	54.34	47.04	45.54	34.39	30.80
230	49.33	55.02	47.04	45.58	34.93	30.80
240	49.66	55.55	47.76	45.58	35.58	31.73
250	50.58	56.07	47.76	46.75	35.60	31.75
260	51.31	56.43	48.93	46.99	36.59	32.31
270	51.80	56.92	49.21	47.20	36.67	32.71
280	52.24	57.40	49.62	48.12	36.67	32.92
290	52.24	57.77	50.42	48.12	37.82	33.32
300	52.56	58.13	50.42	48.16	37.82	33.32
310	53.21	58.61	50.99	48.16	38.00	33.72
320	53.25	58.85	50.99	50.06	38.91	33.72
330	54.09	59.26	50.99	50.30	39.27	33.78
340	54.09	59.26	51.96	50.30	39.65	34.07
350	54.62	59.54	51.96	50.30	39.85	34.25
360	54.62	59.78	51.96	50.30	40.04	34.25
370	55.10	60.06	52.64	51.92	40.30	34.57
380	55.10	60.31	52.68	51.96	40.72	34.85
390	56.07	60.63	52.68	51.96	40.74	34.87
400	56.07	60.87	52.68	51.96	41.21	35.07

High phosphate

B_{50} = 0.081 mol dm^{-3}

Time/s	[**2**]/[**1**]$_{init}$ = 0.01/0.01 =
	Q_1(C)
5	3.03
10	12.34
15	17.47
20	22.51
25	26.06
30	30.29
35	33.36
40	37.15
45	40.14
50	42.68
55	
60	46.67
70	50.34
80	53.05
90	56.11
100	
110	58.13
120	58.69
130	
140	
150	63.7
160	
170	
180	65.55
190	
200	
210	66.88
220	
230	
240	67.81
250	
260	
270	
280	
290	
300	68.78
310	
320	
330	
340	
350	
360	69.71
370	
380	
390	
400	69.71

Tables S4(i) – S4(iii) present the normalised percentage yields of **3** – **7** calculated by the model of Scheme 5; entries labelled A in the third column are the results for the scheme excluding reaction 22 whereas those marked B include it. Data in these tables are plotted as the curves in Fig. 3 – 5 of the main paper.

4.2 Nitrogen evolution as a function of time

Table S5 gives the evolution of nitrogen, as a function of time, calculated as the percentage of that theoretically available in the diazonium ion for different ratios $([\mathbf{2}]/[\mathbf{1}])_{init}$ at different concentrations of phosphate buffer. These simulated are plotted as the continuous curves in Fig. 6. The discrete points which these curves fit are taken from Table S2(i) columns Q_2(A) and Q_1(C).

5 Adaptation of Scheme 5 for change of substituent character

Applying Scheme 5 to a general diazonium ion ArN_2^+, the release of N_2 is governed by reactions 3 – 5 and occurs in the reaction sequence before the formation of any of the stable organic products. The yield of azoarene thus depends inversely on how much N_2 is released by reactions 3 – 5. Reaction 5 is merely the rapid irreversible fragmentation of $ArN_2\cdot$ thus reactions 3 and 4 are crucial in determining the partitioning of the nitrogen of the diazonium function between N_2 and azoarene. In order to reflect the increased electrophilic character of Ar (relative to An), k_3, k_{-3} and k_4 were set to 50 $dm^3\ mol^{-1}\ s^{-1}$, $1\times10^2\ s^{-1}$ and $1\times10^4\ dm^3\ mol^{-1}\ s^{-1}$, respectively. (The relative concentration of the intermediate A^- is thus increased but the equilibrium still lies to the left). The greater electrophilicity of Ar· relative to An· in reactions 6 and 9 was denoted by increasing k_6 and k_9 to 2×10^5 and $3\times10^9\ dm^3\ mol^{-1}\ s^{-1}$, respectively; conversely, the lower nucleophilicity of Ar· relative to An· in reaction 7 was denoted by decreasing k_7 to $5\times10^5\ dm^3\ mol^{-1}\ s^{-1}$. An increase of k_{14} to $1\times10^4\ s^{-1}$ adjusted the partitioning of $(Cu^{III}Ar_2)^+$ between (ArOH + ArH) and biaryl in favour of the latter. Initially, rate constants for reactions between cations (*i. e.* reactions 8, 11, 13 and 16) were not adjusted on the grounds that the effects of polarity variations due to different substituents would be small in comparison to that of the ionic charge.

With this extent of adjustment of rate constants, for $[\mathbf{2}]/[ArN_2^+]_{init}$ = 0.0926/0.01 = 9.26 (*cf.* entry 6 of Table 8), the calculated yields of azoarene and biaryl were 44.3%$_N$ and 47.1%$_N$, respectively; biaryl had become the dominant product but marginally so. However, it was also found that the model now predicted >0.1%$_N$ residual (Cu^IAr). In order to reduce this, variation in k_{11} and k_{12} was explored: lowering k_{11} to 1 $dm^3\ mol^{-1}\ s^{-1}$ and increasing k_{12} to $1\times10^7\ dm^3\ mol^{-1}\ s^{-1}$ reduced the residual (Cu^IAr) to <0.1%$_N$ and also reduced the yield of azoarene relative to biaryl. Thus for $[\mathbf{2}]/[ArN_2^+]_{init}$ = 9.26, the respective calculated yields of azoarene and biaryl became 3.9%$_N$ and 81.7%$_N$, *i. e.* inverting the ratio of entry 6 of Table 8. For

Table S2(ii) Curve fitting of nitrogen evolution data: $Q = q_1 - q_2\exp(-k_{obs}^{(g)}t)$

Entry	Data set	q_1 (%)	q_{1error} (%)	q_2 (%)	q_{2error} (%)	$k_{obs}^{(g)}/s^{-1}$	k_{error}/s^{-1}	χ^2/D of F	R^2
1	Q_2(A)	55.17953	2.50261	60.53995	3.30499	0.01085	0.00182	0.01868	0.99815
2	Q_2(B)	60.66302	2.43756	64.65899	2.51023	0.01096	0.00146	0.00855	0.99955
3	Q_1(A)	52.76453	2.31269	57.27708	2.19933	0.01064	0.00144	0.00967	0.99956
4	Q_1(B)	52.50754	2.73901	53.91272	2.63165	0.00917	0.00148	0.00818	0.99938
5	$Q_{0.5}$(A)	42.14488	2.84656	43.41812	2.56799	0.00800	0.00148	0.00525	0.99955
6	$Q_{0.5}$(B)	34.39192	1.68914	38.47039	1.50866	0.01182	0.00180	0.01583	0.99929

Table S3 Normalised percentage distribution of reaction products

Entry	$10^3 m_{Dz}$/mol [b]	$[\mathbf{2}]_{init}$/mol dm^{-3}	$([\mathbf{2}]/[\mathbf{1}])_{init}$	Acc Dz [c]	Normalised percentage yields (%$_N$) of products[a]							
					AnH, **3**	4,4′-An$_2$, **4**	4,4′-AnNNAn, **5**	AnOH, **6**	AnCH$_2$CN **7**	AnCN, **8**	2,4′-An$_2$, **9**	3,4′-An$_2$, **10**
Subset (a)												
1	0.4967	0.0019	0.193	4.94	29.78	0.00	70.22	0.00	0.00	0.00	0.00	0.00
2	0.5184	0.0039	0.371	11.68	60.49	4.46	33.56	0.00	1.50	0.00	0.00	0.00
3	0.5220	0.0096	0.922	48.85	46.85	6.73	26.53	8.40	6.08	trace	0.00	0.00
4	0.5130	0.0192	1.872	78.02	22.13	8.78	54.29	13.31	1.49	0.00	0.00	0.00
5	0.4882	0.0577	5.925	91.54	9.83	7.86	73.21	8.71	0.40	0.00	0.00	0.00
6	0.5202	0.0962	9.248	93.31	4.90	3.95	86.14	5.01	0.00	0.00	0.00	0.00
Subset (b)												
7	4.998	0.0577	0.577	32.81	40.91	16.25	20.56	13.22	2.06	5.36	0.41	1.24
8	3.994	0.0577	0.722	37.24	48.77	14.44	19.50	9.14	0.89	6.33	0.18	0.75
9	2.010	0.0577	1.435	76.79	40.74	13.10	30.19	9.74	0.73	4.63	0.13	0.74
5	0.4882	0.0577	5.925	91.54	9.83	7.86	73.21	8.71	0.40	0.00	0.00	0.00
10	0.2379	0.0577	12.13	94.12	3.46	4.05	86.10	6.39	0.00	0.00	0.00	0.00
Subset (c)												
11	4.002	0.0019	0.024	1.71	26.88	9.86	60.97	0.00	0.00	0.00	0.22	2.08
12	4.012	0.0039	0.048	3.57	36.74	10.52	36.89	0.00	3.58	5.09	1.54	5.64
13	3.993	0.0096	0.120	9.93	41.76	13.24	24.40	0.00	12.3	3.03	1.22	3.95
8	3.994	0.0577	0.722	37.24	48.77	14.44	19.5	9.14	0.89	6.33	0.18	0.75

[a] An is 4-methoxyphenyl. [b] Amounts of diazonium ion, **1**, reacted in 50 cm^3 solution: $[\mathbf{1}]_{init}$ = ~ 0.01 mol dm^{-3} in subset (a); $[\mathbf{1}]_{init}$ = ~ (0.005 – 0.1) mol dm^{-3} in subset (b); $[\mathbf{1}]_{init}$ = ~ 0.08 mol dm^{-3} in subset (c). [c] Percentage accountability of **1**, as products, *i. e.* $100\times[\sum(n \times m_n)]/m_{Dz}$ (see text).

Tables S4(i) - (iii) Product distributions calculated by the model of Scheme 5
A without reaction 22; B with reaction 22

Table S4(i) Distributions for subset (a): [1] = 0.01 mol dm^{-3}; [2] varied

[**2**]	[**2**]/[**1**]	Scheme 5	%AnOH(1)	%AnOH(2)	%AnOH(tot)	% AnH(1)	%AnH(2a)	%AnH(2b)	%AnH(2c)	%AnH(tot)	%AnNNAn(1)	%AnNNAn(2)	%AnNNAn(tot)	%4,4'-An$_2$	%AnCH$_2$CN	AccDz calc	AnH(1)/AnH(2)	Final pH
0.0005	0.05	A	0.02	0.24	0.26	66.81	0.02	0.24	0.01	67.08	32.33	0.06	32.39	0.02	0.35	3.01	247.44	7.92
0.0005	0.05	B	0.01	0.14	0.15	44.59	0.01	0.14	0.01	44.75	51.56	0.04	51.60	0.01	0.21	3.21	278.69	7.91
0.00075	0.075	A	0.06	0.46	0.52	61.86	0.06	0.46	0.02	62.40	36.21	0.12	36.33	0.05	0.66	4.68	114.56	7.93
0.00075	0.075	B	0.04	0.30	0.34	44.56	0.04	0.30	0.01	44.91	52.17	0.10	52.27	0.04	0.44	5.15	127.31	7.91
0.001	0.1	A	0.12	0.70	0.82	58.64	0.12	0.70	0.02	59.48	38.38	0.20	38.58	0.10	1.01	6.4	69.81	7.93
0.001	0.1	B	0.09	0.50	0.59	44.34	0.09	0.50	0.02	44.95	51.97	0.90	52.87	0.08	0.72	7.05	72.69	7.91
0.0025	0.25	A	0.89	2.23	3.12	48.96	0.89	2.23	0.04	52.12	39.80	0.98	40.78	0.77	3.23	17.69	15.49	7.94
0.0025	0.25	B	0.77	1.91	2.68	42.40	0.77	1.91	0.04	45.12	47.43	0.90	48.33	0.67	2.75	18.43	15.59	7.89
0.005	0.5	A	2.95	3.68	6.63	42.12	2.95	3.68	0.07	48.82	33.67	3.02	36.69	2.55	5.31	38.6	6.29	7.95
0.005	0.5	B	2.72	3.36	6.08	39.33	2.72	3.36	0.07	45.48	38.13	2.94	41.07	2.35	4.85	39.13	6.40	7.84
0.0075	0.75	A	5.06	4.12	9.18	38.74	5.06	4.12	0.09	48.01	26.78	5.69	32.47	4.39	5.94	60.17	4.18	7.96
0.0075	0.75	B	4.72	3.81	8.53	37.57	4.72	3.81	0.09	46.19	29.95	5.71	35.66	4.09	5.50	60.21	4.36	7.80
0.01	1	A	6.80	4.12	10.92	37.11	6.80	4.12	0.11	48.14	20.27	8.86	29.13	5.89	5.95	81.28	3.36	7.97
0.01	1	B	6.32	3.82	10.14	37.00	6.32	3.82	0.11	47.25	22.53	9.09	31.62	5.48	5.51	80.67	3.61	7.74
0.0125	1.25	A	8.08	3.84	11.92	36.44	8.08	3.84	0.13	48.49	14.28	12.75	27.03	7.00	5.55	100	3.02	7.98
0.0125	1.25	B	7.43	3.53	10.96	37.51	7.43	3.53	0.13	48.60	15.64	13.23	28.87	6.44	5.10	99.38	3.38	7.69
0.015	1.5	A	10.13	3.63	13.76	27.30	10.13	3.63	0.16	41.22	11.29	19.72	31.01	8.78	5.24	100	1.96	7.96
0.015	1.5	B	9.20	3.38	12.58	29.02	9.20	3.38	0.16	41.76	12.15	20.64	32.79	7.97	4.89	100	2.28	7.68
0.0175	1.75	A	11.34	3.12	14.46	21.12	11.34	3.12	0.16	35.74	9.16	26.32	35.48	9.82	4.51	100	1.44	7.95
0.0175	1.75	B	10.29	2.95	13.24	22.49	10.29	2.95	0.17	35.90	9.78	27.86	37.64	8.92	4.27	100	1.68	7.68
0.02	2	A	11.91	2.64	14.55	16.87	11.91	2.64	0.16	31.58	7.61	32.12	39.73	10.32	3.82	100	1.15	7.94
0.02	2	B	10.84	2.52	13.36	17.88	10.84	2.52	0.17	31.41	8.09	34.13	42.22	9.39	3.64	100	1.32	7.68
0.0225	2.25	A	12.09	2.24	14.33	13.83	12.09	2.24	0.16	28.32	6.45	37.18	43.63	10.48	3.24	100	0.95	7.94
0.0225	2.25	B	10.99	2.14	13.13	14.61	10.99	2.14	0.17	27.91	6.82	39.52	46.34	9.52	3.10	100	1.10	7.68
0.025	2.5	A	12.03	1.92	13.95	11.58	12.03	1.92	0.15	25.68	5.56	41.62	47.18	10.42	2.78	100	0.82	7.93
0.025	2.5	B	10.92	1.83	12.75	12.18	10.92	1.83	0.16	25.09	5.85	44.20	50.05	9.45	2.65	100	0.94	7.67
0.03	3	A	11.51	1.45	12.96	8.53	11.51	1.45	0.14	21.63	4.27	49.08	53.35	9.97	2.09	100	0.65	7.93
0.03	3	B	10.41	1.38	11.79	8.91	10.41	1.38	0.15	20.85	4.47	51.88	56.35	9.01	2.00	100	0.75	7.67
0.04	4	A	9.99	0.91	10.90	5.27	9.99	0.91	0.12	16.29	2.80	60.04	62.84	8.66	1.31	100	0.48	7.92
0.04	4	B	8.96	0.86	9.82	5.44	8.96	0.86	0.13	15.39	2.89	62.89	65.78	7.76	1.24	100	0.55	7.67
0.05	5	A	8.51	0.62	9.13	3.63	8.51	0.62	0.11	12.87	2.00	67.74	69.74	7.37	0.90	100	0.39	7.92
0.05	5	B	7.57	0.58	8.15	3.72	7.57	0.58	0.11	11.98	2.05	70.40	72.45	6.56	0.84	100	0.45	7.67
0.06	6	A	7.24	0.45	7.69	2.67	7.24	0.45	0.09	10.45	1.51	73.41	74.92	6.28	0.65	100	0.34	7.92
0.06	6	B	6.41	0.42	6.83	2.72	6.41	0.42	0.10	9.65	1.54	75.82	77.36	5.55	0.61	100	0.39	7.67
0.08	8	A	5.34	0.27	5.61	1.65	5.34	0.27	0.80	8.06	0.96	81.09	82.05	4.63	0.30	100	0.26	7.92
0.08	8	B	4.68	0.25	4.93	1.67	4.68	0.25	0.08	6.68	0.98	83.01	83.99	4.06	0.36	100	0.33	7.67
0.1	10	A	4.05	0.18	4.23	1.14	4.05	0.18	0.06	5.43	0.68	85.92	86.60	3.51	0.25	100	0.27	7.92
0.1	10	B	3.52	0.16	3.68	1.14	3.52	0.16	0.06	4.88	0.68	87.45	88.13	3.05	0.23	100	0.30	7.67

Table S4(ii) Distributions for subset (b): [2] = 0.0577 mol dm^{-3}; [1] varied

[**1**]	[**2**]/[**1**]	Scheme 5	%AnOH(1)	%AnOH(2)	%AnOH(tot)	% AnH(1)	%AnH(2a)	%AnH(2b)	%AnH(2c)	%AnH(tot)	%AnNNAn(1)	%AnNNAn(2)	%AnNNAn(tot)	%4,4'-An$_2$	%AnCH$_2$CN	AccDz calc	AnH(1)/AnH(2)	Final pH
0.005	11.54	A	4.85	0.38	5.23	2.79	4.85	0.38	0.10	8.12	0.82	81.07	81.89	4.21	0.55	100.00	0.52	7.92
0.005	11.54	B	4.56	0.36	4.92	2.81	4.56	0.36	0.10	7.83	0.83	81.94	82.77	3.95	0.52	100.00	0.56	7.81
0.0075	7.69	A	6.31	0.44	6.75	2.81	6.31	0.44	0.10	9.66	1.21	76.27	77.48	5.47	0.63	100.00	0.41	7.92
0.0075	7.69	B	5.76	0.42	6.18	2.85	5.76	0.42	0.10	9.13	1.23	77.87	79.10	4.99	0.60	100.00	0.45	7.75
0.01	5.77	A	7.51	0.48	7.99	2.85	7.51	0.48	0.10	10.94	1.60	72.25	73.85	6.51	0.70	100.00	0.35	7.92
0.01	5.77	B	6.66	0.45	7.11	2.91	6.66	0.45	0.10	10.12	1.64	74.71	76.35	5.77	0.65	100.00	0.40	7.67
0.015	3.85	A	9.45	0.55	10.00	2.98	9.45	0.55	0.09	13.07	2.41	65.53	67.94	8.19	0.80	100.00	0.30	7.92
0.015	3.85	B	7.86	0.50	8.36	3.10	7.86	0.50	0.10	11.56	2.50	70.05	72.55	6.81	0.73	100.00	0.37	7.48
0.02	2.89	A	10.99	0.62	11.61	3.16	10.99	0.62	0.09	14.86	3.25	59.86	63.11	9.53	0.89	100.00	0.27	7.92
0.02	2.89	B	8.49	0.54	9.03	3.39	8.49	0.54	0.10	12.52	3.45	66.87	70.32	7.36	0.78	100.00	0.37	7.20
0.025	2.31	A	12.29	0.69	12.98	3.40	12.29	0.69	0.09	16.47	4.16	54.75	58.91	10.66	0.99	100.00	0.26	7.93
0.025	2.31	B	8.73	0.56	9.29	3.80	8.73	0.56	0.11	13.20	4.54	64.61	69.15	7.56	0.81	100.00	0.40	6.89
0.03	1.92	A	13.41	0.76	14.17	3.27	13.41	0.76	0.09	17.53	5.14	49.98	55.12	11.62	1.10	100.00	0.23	7.93
0.03	1.92	B	8.71	0.58	9.29	4.38	8.71	0.58	0.11	13.78	5.83	62.72	68.55	7.55	0.84	100.00	0.47	6.65
0.04	1.44	A	15.16	0.98	16.14	4.76	15.16	0.98	0.09	20.99	7.52	40.81	48.33	13.14	1.41	100.00	0.29	7.93
0.04	1.44	B	8.48	0.64	9.12	6.17	8.48	0.64	0.13	15.42	9.53	57.65	67.18	7.35	0.93	100.00	0.67	6.38
0.045	1.28	A	15.74	1.14	16.88	5.69	15.74	1.14	0.09	22.66	9.03	36.15	45.18	13.64	1.65	100.00	0.34	7.94
0.045	1.28	B	8.11	0.68	8.79	8.45	8.11	0.68	0.14	17.38	12.00	53.83	65.83	7.03	0.98	100.00	0.95	6.31
0.05	1.15	A	15.97	1.37	17.34	7.25	15.97	1.37	0.08	24.67	10.93	31.26	42.19	13.84	1.97	100.00	0.42	7.95
0.05	1.15	B	7.81	0.73	8.54	11.97	7.81	0.73	0.14	20.65	15.59	47.41	63.00	6.77	1.05	99.97	1.38	6.28
0.055	1.05	A	15.58	1.56	17.14	10.20	15.58	1.56	0.08	27.42	13.54	26.15	39.69	13.50	2.26	99.49	0.59	7.99
0.055	1.05	B	7.77	0.75	8.52	12.27	7.77	0.75	0.12	20.91	20.69	42.05	62.74	6.73	1.09	95.55	1.42	6.25
0.06	0.96	A	15.76	1.53	17.29	8.67	15.76	1.53	0.07	26.03	17.11	23.69	40.80	13.66	2.22	92.96	0.50	7.97
0.06	0.96	B	7.88	0.76	8.64	10.67	7.88	0.76	0.11	19.42	25.15	38.85	64.00	6.83	1.10	88.90	1.22	6.22
0.08	0.72	A	15.65	1.19	16.84	5.90	16.84	1.19	0.05	23.98	26.66	18.44	45.10	13.56	1.72	70.81	0.33	7.95
0.08	0.72	B	8.05	0.70	8.75	7.24	8.05	0.70	0.08	16.07	36.47	30.70	67.17	6.98	1.01	68.76	0.82	6.16
0.1	0.58	A	15.18	0.98	16.16	4.72	15.18	0.98	0.04	20.92	32.81	15.55	48.36	13.15	1.41	56.92	0.29	7.94
0.1	0.58	B	8.02	0.63	8.65	5.64	8.02	0.63	0.07	14.36	43.22	25.92	69.14	6.95	0.91	55.72	0.65	6.13
0.2	0.29	A	12.70	0.56	13.26	2.79	12.70	0.56	0.02	16.07	43.39	9.28	52.67	11.00	0.81	28.67	0.21	7.92
0.2	0.29	B	7.22	0.42	7.64	2.89	7.22	0.42	0.04	10.57	59.54	15.38	74.92	6.26	0.60	28.42	0.38	6.09
0.5	0.12	A	8.41	0.26	8.67	1.63	8.41	0.26	0.01	10.31	67.79	4.42	72.21	7.29	0.38	11.43	0.19	7.90
0.5	0.12	B	5.20	0.22	5.42	1.29	5.20	0.22	0.02	6.73	75.63	7.41	83.04	4.50	0.31	11.36	0.24	6.07
1	0.06	A	5.37	0.14	5.51	0.84	5.37	0.14	0.10	6.45	77.68	2.35	80.03	4.65	0.20	5.72	0.15	7.87
1	0.06	B	3.44	0.12	3.56	0.70	3.44	0.12	0.01	4.27	85.04	3.99	89.03	2.98	0.17	5.75	0.20	6.06

Table S4(iii) Distributions for subset (c): [1] = 0.08 mol dm^{-3}; [2] varied

[**2**]	[**2**]/[**1**]	Scheme 5	%AnOH(1)	%AnOH(2)	%AnOH(tot)	% AnH(1)	%AnH(2a)	%AnH(2b)	%AnH(2c)	%AnH(tot)	%AnNNAn(1)	%AnNNAn(2)	%AnNNAn(tot)	%Azo+.	%4,4'-An_2	%$AnCH_2CN$	AccDz calc	AnH(1)/AnH(2)	Final pH
0.001	0.0125	A	0.06	0.14	0.20	25.14	0.06	0.14	0.01	25.35	73.63	0.05	73.68	0.56	0.05	0.20	1.06	119.71	7.92
0.001	0.0125	B	0.04	0.07	0.11	9.10	0.04	0.07	0.00	9.21	71.29	0.03	71.32	19.14	0.03	0.10	1.26	82.73	7.90
0.0025	0.03125	A	0.46	0.42	0.88	15.92	0.46	0.42	0.01	16.81	80.82	0.21	81.03	0.30	0.40	0.60	2.79	17.89	7.92
0.0025	0.03125	B	0.35	0.29	0.64	9	0.35	0.29	0.01	9.65	81.27	0.18	81.45	7.41	0.3	0.42	3.00	13.85	7.87
0.005	0.0625	A	1.65	0.83	2.48	12.20	1.65	0.83	0.02	14.70	79.33	0.63	79.96	0.16	1.43	1.20	5.77	4.88	7.92
0.005	0.0625	B	1.41	0.69	2.10	8.69	1.41	0.69	0.01	10.80	81.07	0.58	81.65	3.17	1.22	0.99	5.97	4.12	7.82
0.01	0.125	A	4.46	1.24	5.70	9.75	4.46	1.24	0.02	15.47	71.39	1.80	73.19	0.00	3.87	1.79	11.90	1.70	7.93
0.01	0.125	B	3.98	1.11	5.09	8.01	3.98	1.11	0.02	13.12	73.86	1.80	75.66	1.07	3.44	1.62	12.06	1.57	7.68
0.02	0.25	A	9.02	1.34	10.36	7.68	9.02	1.34	0.03	18.07	56.91	4.81	61.72	0.10	7.82	1.94	24.29	0.74	7.93
0.02	0.25	B	7.74	1.23	8.97	7.13	7.74	1.23	0.03	16.13	60.93	5.31	66.24	0.16	6.71	1.78	24.31	0.79	7.24
0.04	0.5	A	13.86	1.23	15.09	6.21	13.86	1.23	0.04	21.34	38.01	11.77	49.78	0.00	12.01	1.78	49.03	0.41	7.94
0.04	0.5	B	9.39	0.93	10.32	6.86	9.39	0.93	0.06	17.24	46.46	16.48	62.94	0.01	8.13	1.35	48.22	0.66	6.41
0.06	0.75	A	15.83	1.19	17.02	5.94	15.83	1.19	0.05	23.01	25.44	19.07	44.51	0.00	13.72	1.72	73.37	0.35	7.95
0.06	0.75	B	7.83	0.68	8.51	7.33	7.83	0.68	0.09	15.93	35.10	32.72	67.82	0.00	6.78	0.98	71.36	0.85	6.14
0.08	1	A	16.09	1.22	17.31	7.00	16.09	1.22	0.06	24.37	14.28	28.34	42.62	0.00	13.95	1.76	97.21	0.40	7.98
0.08	1	B	5.86	0.45	6.31	8.67	5.86	0.45	0.11	15.09	22.04	50.87	72.91	0.00	5.07	0.66	93.27	1.35	6.03
0.085	1.0625	A	16.17	1.10	17.27	6.13	16.17	1.10	0.07	23.47	11.58	32.05	43.63	0.00	14.02	1.60	100.00	0.35	7.97
0.085	1.0625	B	5.40	0.40	5.80	9.36	5.40	0.40	0.12	15.28	18.07	55.62	73.69	0.00	4.68	0.57	98.28	1.58	6.02
0.09	1.125	A	16.16	0.88	17.04	4.34	16.16	0.88	0.07	21.45	9.84	36.40	46.24	0.00	14.00	1.27	100.00	0.25	7.95
0.09	1.125	B	5.10	0.34	5.44	7.59	5.10	0.34	0.12	13.15	14.36	62.15	76.51	0.00	4.42	0.48	100.00	1.37	5.98
0.1	1.25	A	15.35	0.60	15.95	2.73	15.37	0.60	0.06	18.76	7.64	43.48	51.12	0.00	13.31	0.86	100.00	0.17	7.93
0.1	1.25	B	4.62	0.23	4.85	3.97	4.62	0.23	0.11	8.93	10.12	71.76	81.88	0.00	4.01	0.34	100.00	0.80	5.85

Table S5 Nitrogen evolution rates calculated by the model of Scheme 5 with inclusion of reactio

Time/s	LOW PHOSPHATE [Cu] = 2*[Dz] %N2calc(L)	HIGH PHOSPHATE [Cu] = [Dz] %N2calc(H)
0	0	0
5	3.71	8.45
10	6.93	15.29
15	9.80	21.02
20	12.35	25.94
25	14.69	30.12
30	16.84	33.91
35	18.78	36.89
40	20.63	40.26
45	22.34	42.83
50	23.88	44.96
55	25.37	47.04
60	26.70	48.75
70	29.14	51.76
80	31.41	54.24
90	33.43	56.29
100	35.19	58.00
110	36.83	59.43
120	38.27	60.63
130	39.56	61.65
140	40.63	62.51
150	41.85	63.40
160	42.85	64.13
170	43.81	64.65
180	44.71	65.08
190	45.57	65.46
200	46.35	65.78
210	47.10	66.07
220	47.82	66.34
230	48.49	66.54
240	49.12	66.72
250	49.72	66.88
260	50.28	
270	50.85	
280	51.35	
290	51.89	
300	52.36	67.41
310	52.82	
320	53.26	
330	53.68	
340	54.08	
350	54.46	67.66
360	54.84	
370	55.20	67.78
380	55.56	
390	55.91	
400	56.23	

[**2**]/[ArN_2^+]$_{init}$ = 0.0577/0.01, 0.02/0.01 and 0.01/0.01, the yields of azoarene and biaryl were, respectively, 2.4%$_N$ and 81.6%$_N$, 0.7%$_N$ and 70.2%$_N$, and 0.2%$_N$ and 44.6%$_N$ (see Table S6); *i.e*. across the range of [**2**]/[ArN_2^+]$_{init}$ biaryl predominates over azoarene even when its normalised yield declines due to the formation of other prdoucts. Provided that the electron-withdrawing substitution increases the electrophilicity of ArN_2^+, relative to AnN_2^+, more than it stabilises (Cu^IAr), relative to (Cu^IAn), an increase in value for k_{12} seems reasonable. Viewed as a simple electron transfer process, reaction 11 would to require an increased constant on introduction of an electrophilic substituent; however, the reaction might be a two-step process involving rate-determining prior formation of a binuclear di-cation followed by rapid electron transfer. That being the case, a reduced rate constant would be consistent with more electrophilic substitution.

Although we have not attempted to simulate the behaviour of a real example with an electron-withdrawing substituent, these findings indicate the model of Scheme 5 is consistent with known facts regarding the dependence of the azoarene/biaryl ratio on substituent character.

Table S6 Product distributions following model modifications to represent electron withdrawing substitution

[ArN_2^+]	[**2**]	[**2**]/[ArN_2^+]	Modification	%ArOH(1)	%ArOH(2)	%ArOH(tot)	% ArH(1)	%ArH(2a)	%ArH(2b)	%ArH(2c)	%ArH(tot)	%ArNNAr(1)	%ArNNAr(2)	%ArNNAr(tot)	$\%ArCu^I$	%4,4'-Ar_2	$\%ArCH_2CN$	AccDz calc	(%4,4'-Ar2)/(%ArNNAr(tot))
0.005	0.0577	11.54	1	3.42	0.45	3.87	2.02	3.42	0.45	0.05	5.94	0.00	39.71	39.71	0.52	49.33	0.64	100.00	1.24
0.005	0.0577	11.54	2	5.54	0.70	6.24	3.03	5.54	0.70	0.09	9.36	0.00	3.31	3.31	0.08	80.00	1.01	100.00	24.17
0.01	0.0926	9.26	1	3.26	0.25	3.51	1.04	3.26	0.25	0.04	4.59	0.00	44.30	44.30	0.15	47.10	0.36	100.00	1.06
0.01	0.0926	9.26	2	5.65	0.40	6.05	1.60	5.65	0.40	0.07	7.72	0.00	3.94	3.94	0.06	81.65	0.57	100.00	20.72
0.01	0.0577	5.77	1	3.89	0.49	4.38	2.00	3.89	0.49	0.40	6.78	0.00	32.08	32.08	0.16	56.24	0.70	100.00	1.75
0.01	0.0577	5.77	2	5.62	0.67	6.29	2.75	5.62	0.67	0.07	9.11	0.01	2.43	2.44	0.03	81.16	0.97	100.00	33.26
0.01	0.02	2.00	1	4.32	2.24	6.56	9.60	4.32	2.24	0.06	16.22	0.02	11.55	11.57	0.02	62.39	3.23	100.00	5.39
0.01	0.02	2.00	2	4.86	2.50	7.36	10.73	4.86	2.50	0.07	18.16	0.02	0.65	0.67	0.00	70.19	3.61	100.00	104.76
0.01	0.01	1.00	1	2.95	5.10	8.05	30.44	2.95	5.10	0.05	38.54	0.06	3.18	3.24	0.00	42.77	7.37	88.56	13.20
0.01	0.01	1.00	2	3.09	5.23	8.32	30.94	3.09	5.23	0.05	39.31	0.06	0.16	0.22	0.00	44.60	7.55	88.53	202.73
0.01	0.005	0.50	1	2.06	5.90	7.96	44.37	7.96	5.90	0.04	58.27	0.13	1.33	1.46	0.00	29.70	8.52	40.30	20.34
0.01	0.005	0.50	2	2.10	5.98	8.08	44.69	2.10	5.98	0.40	53.17	0.13	0.07	0.20	0.00	30.29	8.63	40.28	151.45