– Supplementary Material –

Nucleophilicities and Carbon Basicities of DBU and DBN

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Materials

Commercially available acetonitrile (VWR, Prolabo, HPLC-gradient grade) was used without further purification for all kinetic experiments and determinations of equilibrium constants. Commercially available CH_2Cl_2 (VWR) was distilled over CaH_2 just before experiments. DBU (Acros, 98%) and DBN (Acros, 98%) were freshly distilled under nitrogen before all the kinetics and equilibrium experiments. DMAP (Aldrich, >99%) was used without further purification. The benzhydrylium tetrafluoroborates Ar_2CH^+ BF_4^- (**1**-BF_4^-) were prepared as described before.[S1] The Michael acceptors (**2**) were prepared according to literature procedures[S22] (for UV-Vis spectrocopic data see Table S1).

Table S1. Molar absorption coefficients ε of the Michael acceptors **2** in CH_3CN.

Michael acceptor	λ_{max} (nm)	ε (M^{-1} cm^{-1})
2a	340	3.51×10^4
2c	360	2.58×10^4
2e	370	3.09×10^4
2f	400	3.62×10^4

Product Characterization by NMR Spectroscopy

Under an atmosphere of nitrogen, one equivalent (or little excess) of DBU, DBN, or DMAP was added directly to the $CDCl_3$ solution of **1** or **2** in an NMR tube. After few minutes of shaking, the NMR study was performed.

Adducts from the reactions of **1a** with DBU and **2f** with DMAP (**2´f**) were characterized in detail by different NMR techniques (^1H and ^{13}C NMR, gHSQC). The products of the several other (analogous) addition reactions of DBU and DMAP with benzhydrylium tetrafluoroborates (**1**-BF_4^-) and DBU, DBN and DMAP with Michael acceptors (**2**) were characterized by ^1H NMR spectroscopy. The characteristic δ_H shifts are listed below (Tables S2 and S3).

Some of the combinations of Michael acceptors with DBU and DMAP are reversible which prevented product study.

[S1] H. Mayr, T. Bug, M. F. Gotta, N. Hering, B. Irrgang, B. Janker, B. Kempf, R, Loos, A. R. Ofial, G. Remennikov, H. Schimmel, *J. Am. Chem. Soc*., 2001, **123**, 9500; B. Kempf, H. Mayr, *Chem. Eur. J*., 2005, **11**, 917; F. Brotzel, B. Kempf, T. Singer, H. Zipse, H. Mayr, *Chem. Eur. J*., 2007, **13**, 336.

[S2] a) Y. Xu, W. R. Dolbier, *Tetrahedron*, 1998, **54**, 6319; b) S. T. A. Berger, F. H. Seeliger, F. Hofbauer, H. Mayr, *Org. Biomol. Chem.*, 2007, **5**, 3020; c) F. Seeliger, S. T. A. Berger, G. Y. Remennikov, K. Polborn, H. Mayr, *J. Org. Chem.*, 2007, **72**, 9170; d) O. Kaumanns, H. Mayr, *J Org. Chem*., in print; e) characterization of **2f** will be published separately.

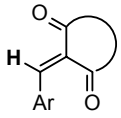
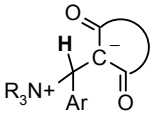
1a-DBU: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.45-2.00 (m, 8 H), 2.9 (m, 2 H, CH_2), 2.97 (s, 12 H, 2 × NMe_2), 3.15 (m, 2 H, CH_2), 3.56 (m, 2 H, CH_2), 3.76 (m, 2 H, CH_2), 6.26 (s, 1 H, Ar_2CHN^+), 6.70 (d, 4 H, *J* = 8.7 Hz, CH arom), 7.01 ppm (d, 4H, *J* = 8.7 Hz, CH arom); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.3 (CH_2), 25.1 (CH_2), 27.9 (CH_2), 29.6 (CH_2), 40.6 (CH_3), 41.6 (CH_2), 44.0 (CH_2), 49.6 (CH_2), 55.4 (CH_2), 68.6 (Ar_2C), 112.6 (CH arom), 124.1 (C arom), 128.2 (CH arom), 150.6 (C arom), 167.8 ppm.

Table S2. δ_H shift (ppm) of the benzhydryl proton in Ar_2CH^+ **1** and its adducts with DBU and DBN ($CDCl_3$, 200 MHz):

Ar_2CH^+	$Ar_2C\mathbf{H}^+BF_4^-$	$Ar_2C\mathbf{H}$-DBU$^+$	$Ar_2C\mathbf{H}$-DBN$^+$
1a	7.40	6.26	
1b	7.71	6.22	
1c	overlapping	6.10	5.86
1d	overlapping	6.15	5.94
1e	7.31	5.96	5.77
1f	7.38	6.06	5.87

2'f (for DMAP): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.17 (s, 6 H, 2 × CH_3), 3.71 (s, 6 H, 2 × CH_3), 3.76 (s, 3 H, OCH_3), 6.59 (d, 2H, *J* = 7.4 Hz, CH arom), 6.83 (d, *J* = 8.8, 2H, CH arom), 6.95 (s, 1 H, N^+-CH), 7.18 (d, 2 H, *J* = 8.8 Hz, CH arom), 8.25 ppm (d, 2 H, *J* = 7.6 Hz, CH arom); ^{13}C NMR (75.5 MHz, $CDCl_3$): 35.4 (NMe_2), 40.3 (NMe_2), 55.5 (OMe), 69.7 (N^+-CH), 89.8 (C^-), 106.7 (CH arom), 114.3 (CH arom), 128.8 (C arom), 129.7 (CH arom), 142.7 (CH arom), 156.4 (C arom), 159.6 (C arom), 162.5 (CO), 177.9 ppm (CS).

Table S3. δ_H shift (ppm) of benzylidene proton of Michael acceptors **2** and its adducts with DBU and DBN ($CDCl_3$, 200 MHz):

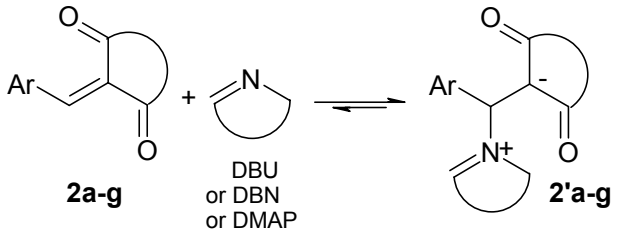
Michael acceptor				
		DBU	DBN	DMAP
2f	8.53	6.52		6.95
2e	8.51	6.51	6.38	
2c	8.37	6.34	6.14	

Determination of the Rate Constants for the Reactions of Amines with Benzhydrylium Ions 1 and Michael Acceptors 2

Apart from few reactions, which were carried out in CH_2Cl_2, most of the reactions of amines with **1** and **2** were performed in acetonitrile at 20°C. The kinetics were followed photometrically using the stopped-flow technique described previously.[S1] The kinetic runs were performed by mixing equal volumes of acetonitrile solutions of the amines with acetonitrile solutions of **1** or **2** and monitoring the decrease of absorbances at wavelenghts close to the absorption maxima of **1** or **2**. In general, amines were applied in high excess over **1** and **2** to achieve pseudo-first-order conditions. The first-order rate constants k_{obs} (s^{-1}) were obtained by least-squares fitting of the absorbances (averaged from at least 10 kinetic runs) to the single exponential function $A = A_0 \exp(-k_{obs}t) + C$. Second-order rate constants k ($M^{-1}\,s^{-1}$) were then obtained from the slope of the k_{obs} vs [amine] plot.

Determination of the Equilibrium Constants for the Reactions of Amines with Michael Acceptors 2

Because Michael acceptors **2** are colored and their reaction with colorless amines yields zwitterions **2´** which are either colorless or have different absorption maxima, the equilibrium constants can be determined by UV-vis spectroscopy as described before using the following equation.[S33]



$$\mathbf{2} + NR_3 \underset{}{\overset{K}{\rightleftharpoons}} \mathbf{2}\text{-}NR_3^+$$

$$K = \frac{[\mathbf{2}\text{-}NR_3^+]}{[\mathbf{2}]\,[NR_3]} = \frac{(A_0 - A)}{A\,[NR_3]} = \frac{(A_0 - A)}{A\,\{[NR_3]_0 - (A_0 - A)/\varepsilon d\}}$$

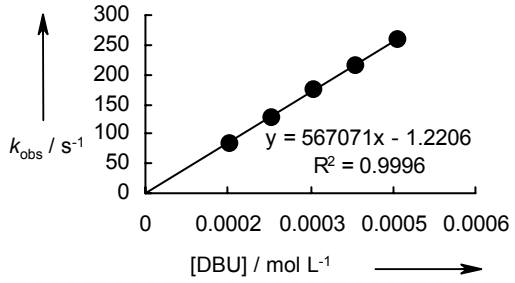
where $[NR_3] = [NR_3]_0 - [\mathbf{2}\text{-}NR_3^+]$

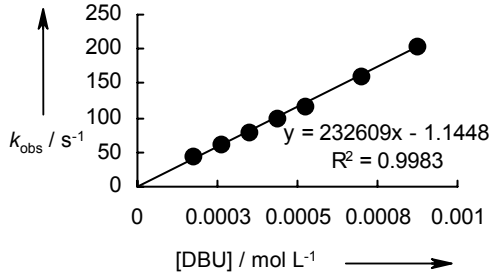
where A_0 = absorbance before addition of amine, A = absorbance after addition of amine, ε = molar absorption coefficient and d = path length. The amines were added to solutions of the Michael acceptors and after a few seconds when the equilibrium was reached, the absorbance of the solutions was determined photometrically and converted into concentrations of Michael acceptors using the molar absorption coefficients ε listed in Table S1. Their combination with initial concentrations of the amines yields the equilibrium constant K. Because $[NR_3]_0 >> [(A_0 - A)/\varepsilon d]$, inaccuracies in ε will have little influence on the equilibrium constants. Equilibrium constants K have been measured with variable concentrations of **2** and NR_3 at 20°C.

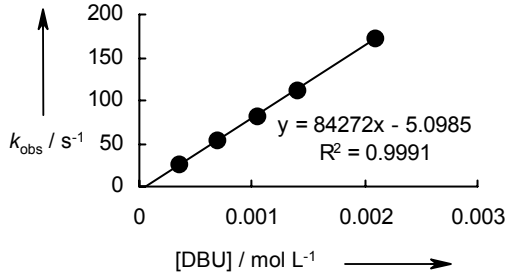
[S3] M. Baidya, S. Kobayashi, F. Brotzel, U. Schmidhammer, E. Riedle, H. Mayr, *Angew. Chem. Int. Ed.*, 2007, **46**, 6176.

Table S4. Kinetics of the Reactions of DBU with Ar_2CH^+ **1** (20°C, CH_3CN)

[**1**] (mol L^{-1})	[DBU] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**1a**] = 1.41E-05, λ_{max} = 605 nm				
	1.53E-04	84.76		5.67E+05
	3.07E-04	174.60		
	2.30E-04	128.85		
	3.83E-04	217.00		
	4.60E-04	258.01		
[**1b**] = 1.71E-05, λ_{max} = 612 nm				
	1.75E-04	42.24		2.33E+05
	2.62E-04	60.87		
	3.50E-04	79.44		
	4.37E-04	98.67		
	5.24E-04	117.08		
	6.99E-04	161.23		
	8.74E-04	204.93		
[**1c**] = 3.92E-05, λ_{max} = 620 nm				
	3.50E-04	25.66		8.43E+04
	6.99E-04	54.61		
	1.05E-03	81.00		
	1.40E-03	111.37		
	2.10E-03	173.26		
[**1d**] = 1.12E-05, λ_{max} = 616 nm				
	6.99E-04	24.18		3.17E+04
	1.40E-03	48.37		
	2.10E-03	68.56		
	2.80E-03	91.42		
	3.50E-03	113.33		







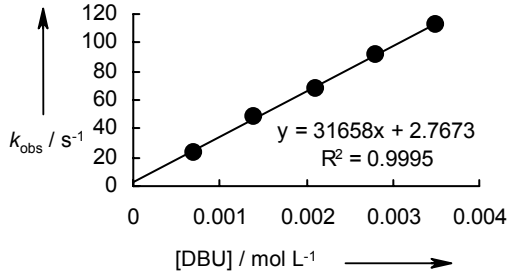
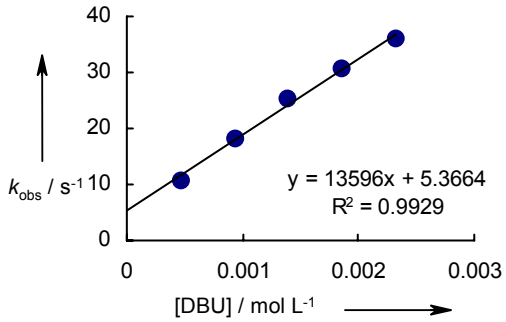
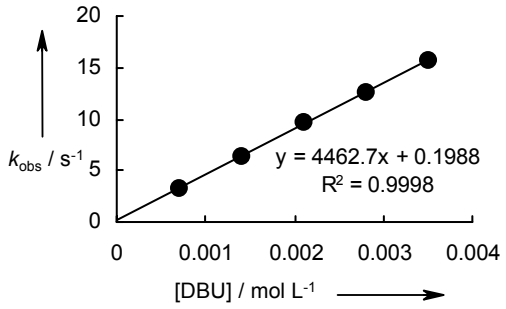


Table S4. (continued)

[**1**] (mol L^{-1})	[DBU] (mol L^{-1})	k_{obs} (s^{-1})	k_2 (L mol^{-1} s^{-1})
[**1e**] = 1.08E-05, λ_{max} = 635 nm			
	4.64E-04	10.84	1.36E+04
	9.28E-04	18.25	
	1.39E-03	25.45	
	1.86E-03	30.85	
	2.32E-03	36.09	

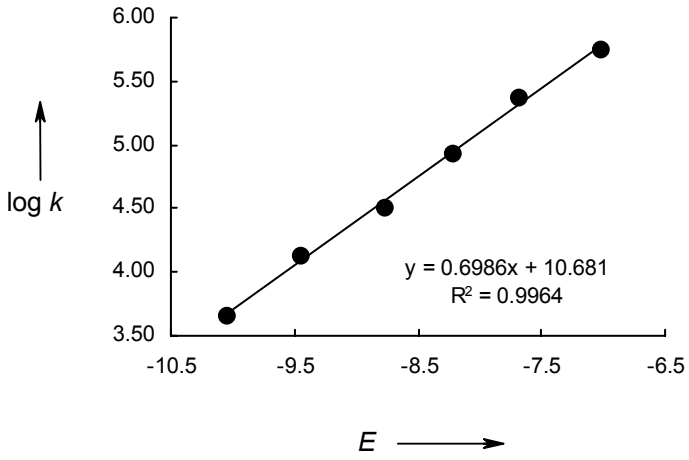


[**1f**] = 1.15E-05, λ_{max} = 632nm			
	6.99E-04	3.27	4.46E+03
	1.40E-03	6.50	
	2.10E-03	9.63	
	2.80E-03	12.59	
	3.50E-03	15.82	



Determination of the Nucleophilicity Parameters *N* and *s* for DBU in Acetonitrile

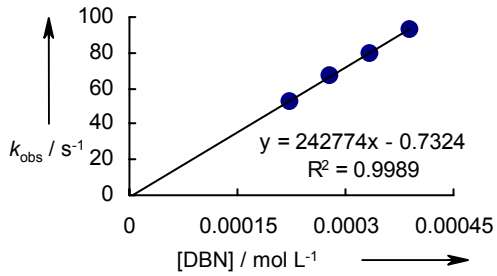
Ar_2CH^+	*E*	k_2 (L mol^{-1} s^{-1})	log *k*
1a	–7.02	5.67E+05	5.75
1b	–7.69	2.33E+05	5.37
1c	–8.22	8.43E+04	4.93
1d	–8.76	3.17E+04	4.50
1e	–9.45	1.36E+04	4.13
1f	–10.04	4.46E+03	3.65

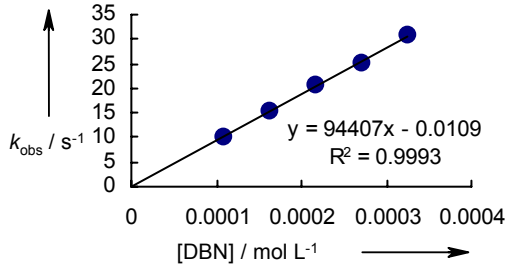


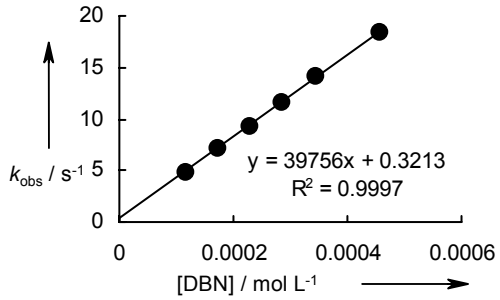
Nucleophilicity parameters for **DBU (in MeCN): *N* = 15.29, *s* = 0.70**

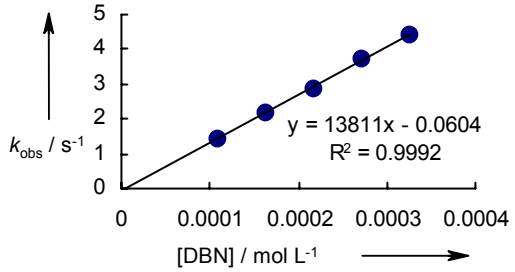
Table S5. Kinetics of the Reactions of DBN with Ar_2CH^+ **1** (20°C, CH_3CN)

[**1**] (mol L^{-1})	[DBN] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**1c**] = 3.92E-05, λ_{max} = 620 nm				
	2.21E-04	52.52		2.43E+05
	2.77E-04	67.01		
	3.32E-04	80.33		
	3.88E-04	92.88		
[**1d**] = 1.05E-05, λ_{max} = 616 nm				
	1.09E-04	10.16		9.44E+04
	1.63E-04	15.31		
	2.17E-04	20.82		
	2.71E-04	25.35		
	3.26E-04	30.75		
[**1e**] = 1.08E-05, λ_{max} = 635 nm				
	1.14E-04	4.87		3.98+04
	1.72E-04	7.14		
	2.29E-04	9.37		
	2.86E-04	11.62		
	3.43E-04	14.13		
	4.57E-04	18.43		
[**1f**] = 1.10E-05, λ_{max} = 632nm				
	1.09E-04	1.46		1.38E+04
	1.63E-04	2.18		
	2.17E-04	2.89		
	2.71E-04	3.73		
	3.26E-04	4.43		



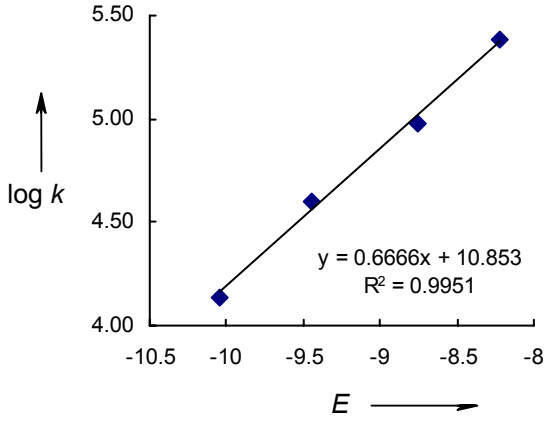






Determination of the Nucleophilicity Parameters *N* and *s* for DBN in Acetonitrile

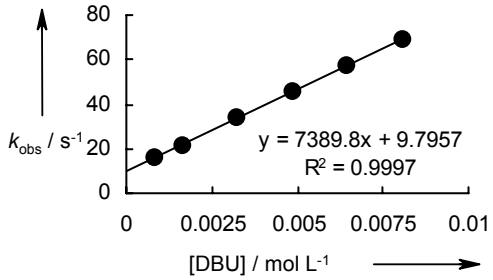
Ar_2CH^+	*E*	k_2 (L mol^{-1} s^{-1})	log *k*
1c	–8.22	2.43E+05	5.39
1d	–8.76	9.44E+04	4.98
1e	–9.45	3.98E+04	4.60
1f	–10.04	1.38E+04	4.14

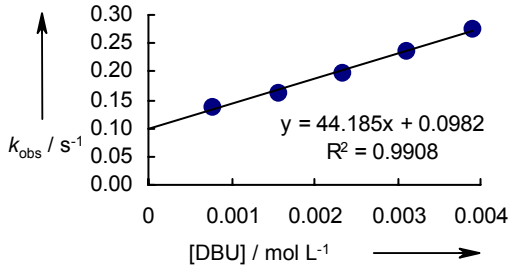


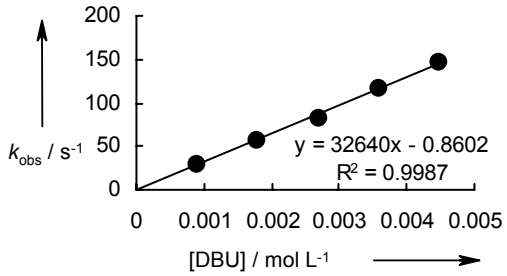
Nucleophilicity parameters for **DBN (in MeCN): *N* = 16.28, *s* = 0.67**

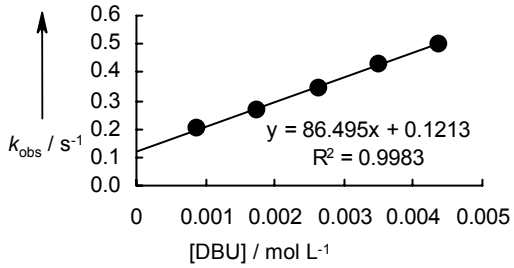
Table S6. Kinetics of the Reactions of DBU with Michael Acceptors **2** (20°C, CH_3CN)

[**2**] (mol L^{-1})	[DBU] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**2a**] = 3.21E-05, λ_{max} = 340 nm				
	8.05E-04	15.77		7.39E+03
	1.61E-03	21.21		
	3.22E-03	33.87		
	4.83E-03	45.96		
	6.44E-03	57.52		
	8.05E-03	68.93		
[**2b**] = 4.73E-05, λ_{max} = 385 nm				
	7.79E-04	0.14		4.42E+01
	1.56E-03	0.16		
	2.34E-03	0.20		
	3.12E-03	0.24		
	3.90E-03	0.27		
[**2c**] = 8.63-05, λ_{max} = 360 nm				
	8.93E-04	29.72		3.26E+04
	1.79E-03	57.26		
	2.68E-03	83.88		
	3.57E-03	116.16		
	4.47E-03	146.05		
[**2d**] = 1.69E-05, λ_{max} = 450 nm				
	8.74E-04	0.201		8.65E+01
	1.75E-03	0.268		
	3.50E-03	0.430		
	2.62E-03	0.343		
	4.37E-03	0.499		
[**2e**] = 5.89E-05, λ_{max} = 370 nm				
	7.79E-04	13.17		1.62E+04
	1.56E-03	26.55		
	2.34E-03	38.75		
	3.12E-03	51.67		
	3.90E-03	63.60		









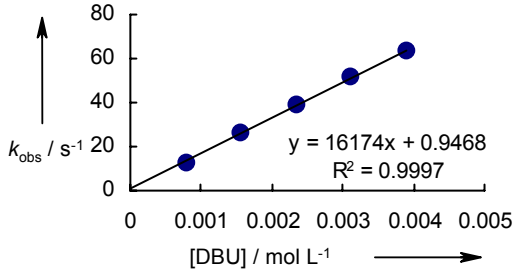
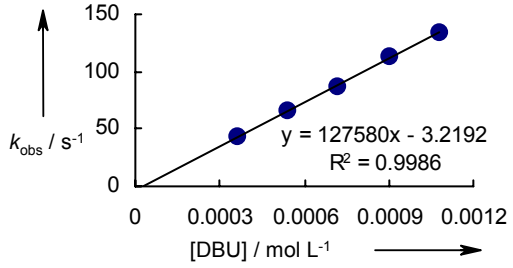


Table S6. (continued)

[**2**] (mol L^{-1})	[DBU] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**2f**] = 4.07E-05, λ_{max} = 400 nm				
	3.60E-04	42.884		1.28E+05
	5.40E-04	66.741		
	7.21E-04	86.435		
	1.08E-03	134.84		
	9.01E-04	112.654		
[**2g**] = 1.23E-05, λ_{max} = 500 nm, CH_2Cl_2				
	8.95E-03	1.97		2.61E+02
	1.34E-02	3.00		
	1.61E-02	3.86		
	1.79E-02	4.29		
	2.24E-02	5.42		



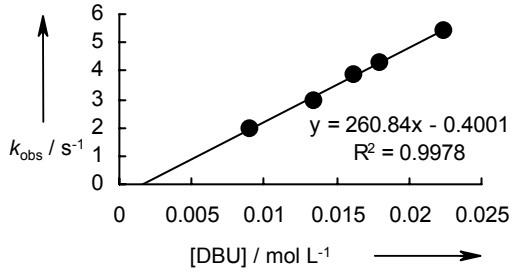
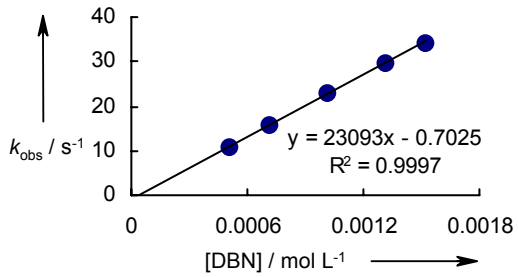
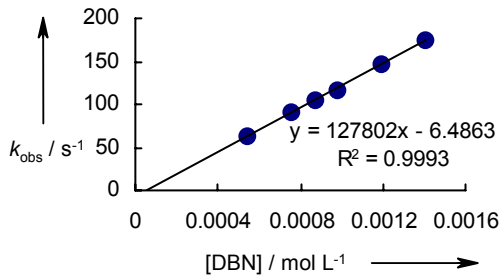


Table S7. Kinetics of the Reactions of DBN with Michael Acceptors **2** (20°C, CH_3CN)

[**2**] (mol L^{-1})	[DBN] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**2a**] = 5.12E-05, λ_{max} = 340 nm				
	5.07E-04	10.91		2.31E+04
	7.10E-04	15.65		
	1.01E-03	23.01		
	1.32E-03	29.76		
	1.52E-03	34.30		
[**2c**] = 5.86E-05, λ_{max} = 360 nm				
	5.43E-04	63.38		1.28E+05
	7.60E-04	91.626		
	8.68E-04	103.798		
	9.77E-04	116.79		
	1.19E-03	145.466		
	1.41E-03	174.966		
[**2e**] = 6.56E-05, λ_{max} = 370 nm				
	6.09E-04	26.71		4.43E+04
	8.12E-04	36.31		
	1.01E-03	45.23		
	1.22E-03	54.35		
	1.42E-03	62.67		





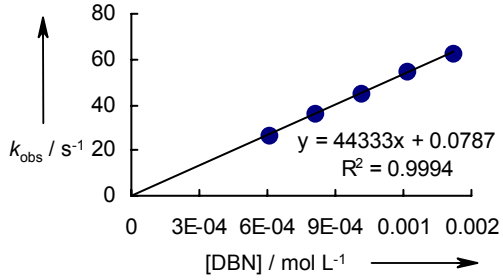
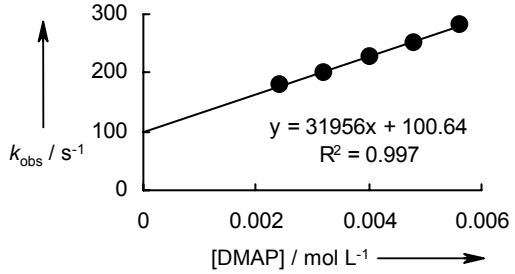
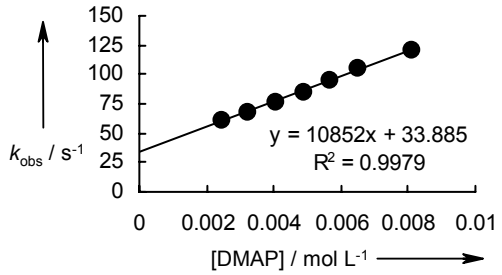
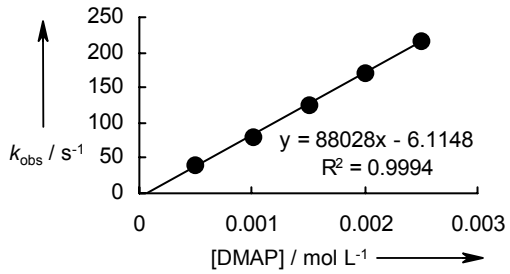


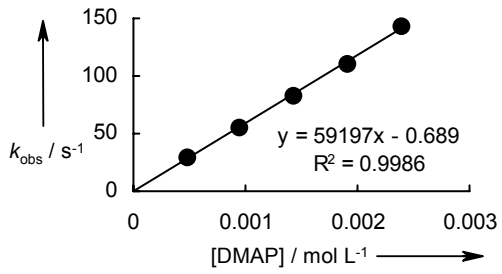
Table S8. Kinetics of the Reactions of DMAP with Michael Acceptors **2** (20°C, CH_3CN)

[**2**] (mol L^{-1})	[DMAP] (mol L^{-1})	k_{obs} (s^{-1})		k_2 (L mol^{-1} s^{-1})
[**2c**] = 8.63E-05, λ_{max} = 360 nm				
	2.41E-03	179.74		3.20E+04
	3.21E-03	200.35		
	4.01E-03	229.37		
	4.81E-03	252.49		
	5.61E-03	281.79		
[**2e**] = 6.07E-05, λ_{max} = 370 nm				
	2.43E-03	60.98		1.09E+04
	3.24E-03	69.03		
	4.05E-03	77.40		
	4.86E-03	85.26		
	5.67E-03	95.18		
	6.48E-03	105.88		
	8.10E-03	121.43		
[**2f**] = 3.59E-05, λ_{max} = 400 nm				
	5.02E-04	40.12		8.80E+04
	1.00E-03	80.76		
	1.51E-03	124.20		
	2.01E-03	171.05		
	2.51E-03	215.82		
[**2f**] = 2.06E-05, λ_{max} = 410 nm, CH_2Cl_2				
	4.78E-04	29.34		5.92E+04
	9.55E-04	54.79		
	1.43E-03	82.88		
	1.91E-03	111.08		
	2.39E-03	142.56		









Equilibrium Constants for the Reactions of Amines with Michael acceptors 2

Equilibrium constant for the reaction of **2a** with DBU (20 °C, in acetonitrile)
ε [**2a** at 340 nm] = 3.51 × 10^4 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DBU]_0$ (mol L^{-1})	A	$[\mathbf{2a}]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.942	5.360E-05	
1	6.050E-05	0.755	4.296E-05	4.36E+03
2	1.159E-04	0.693	3.944E-05	2.94E+03
3	1.691E-04	0.642	3.653E-05	2.47E+03
4	2.204E-04	0.596	3.394E-05	2.25E+03
5	2.699E-04	0.556	3.166E-05	2.13E+03
6	3.176E-04	0.520	2.962E-05	2.05E+03
7	3.636E-04	0.487	2.773E-05	2.02E+03
0	0	0.857	4.879E-05	
1	5.893E-05	0.686	3.903E-05	4.49E+03
2	1.156E-04	0.623	3.545E-05	3.10E+03
3	1.700E-04	0.575	3.275E-05	2.58E+03
4	2.224E-04	0.535	3.042E-05	2.32E+03
5	2.729E-04	0.498	2.832E-05	2.19E+03
6	3.215E-04	0.465	2.646E-05	2.11E+03
0	0	0.512	2.913E-05	
1	3.988E-05	0.327	1.862E-05	1.73E+04
2	7.766E-05	0.296	1.683E-05	9.56E+03
3	1.135E-04	0.270	1.536E-05	7.37E+03
4	1.476E-04	0.248	1.411E-05	6.34E+03
5	1.800E-04	0.227	1.294E-05	5.85E+03
6	2.108E-04	0.209	1.190E-05	5.56E+03
0	0	0.515	2.931E-05	
1	4.007E-05	0.323	1.838E-05	1.84E+04
2	7.803E-05	0.295	1.679E-05	9.75E+03
3	1.140E-04	0.268	1.527E-05	7.55E+03
4	1.482E-04	0.247	1.404E-05	6.46E+03
5	1.808E-04	0.226	1.288E-05	5.94E+03
6	2.117E-04	0.209	1.192E-05	5.57E+03
0	0	0.519	2.952E-05	
1	4.047E-05	0.325	1.849E-05	1.83E+04
2	7.878E-05	0.296	1.683E-05	9.76E+03
3	1.151E-04	0.270	1.539E-05	7.44E+03
4	1.496E-04	0.247	1.408E-05	6.45E+03
5	1.824E-04	0.226	1.287E-05	5.97E+03
6	2.136E-04	0.206	1.175E-05	5.75E+03
0	0	0.320	1.820E-05	
1	2.364E-05	0.233	1.326E-05	1.92E+04
2	4.690E-05	0.206	1.174E-05	1.29E+04
3	6.979E-05	0.190	1.080E-05	1.03E+04
4	9.232E-05	0.177	1.009E-05	8.81E+03
5	1.145E-04	0.167	9.477E-06	7.95E+03
6	1.363E-04	0.157	8.960E-06	7.33E+03
0	0	0.332	1.888E-05	
1	2.398E-05	0.243	1.386E-05	1.84E+04
2	4.757E-05	0.217	1.238E-05	1.21E+04
3	7.078E-05	0.201	1.144E-05	9.58E+03
4	9.363E-05	0.189	1.073E-05	8.18E+03
5	1.161E-04	0.177	1.008E-05	7.41E+03
6	1.382E-04	0.169	9.597E-06	6.74E+03

Equilibrium constant for the reaction of **2c** with DBU (20 °C, in acetonitrile)

ε [**2c** at 360 nm] = 2.58 × 10^4 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DBU]_0$ (mol L^{-1})	A	$[\mathbf{2c}]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.916	7.098E-05	
1	1.498E-04	0.339	2.627E-05	1.61E+04
2	2.244E-04	0.232	1.796E-05	1.71E+04
3	2.989E-04	0.164	1.273E-05	1.89E+04
4	3.733E-04	0.122	9.450E-06	2.07E+04
0	0	0.864	6.698E-05	
1	7.123E-05	0.497	3.850E-05	1.72E+04
2	1.423E-04	0.321	2.484E-05	1.69E+04
3	2.133E-04	0.221	1.709E-05	1.78E+04
4	2.841E-04	0.160	1.239E-05	1.91E+04
5	3.548E-04	0.119	9.224E-06	2.09E+04
0	0	0.907	7.028E-05	
1	7.497E-05	0.522	4.044E-05	1.63E+04
2	1.498E-04	0.334	2.590E-05	1.62E+04
3	2.244E-04	0.226	1.752E-05	1.75E+04
4	2.989E-04	0.162	1.252E-05	1.90E+04
5	3.733E-04	0.119	9.261E-06	2.09E+04
0	0	0.897	6.952E-05	
1	7.380E-05	0.521	4.041E-05	1.61E+04
2	1.475E-04	0.336	2.605E-05	1.60E+04
3	2.210E-04	0.230	1.779E-05	1.71E+04
4	2.943E-04	0.165	1.275E-05	1.86E+04
5	3.675E-04	0.122	9.422E-06	2.06E+04
0	0	0.423	3.277E-05	
1	4.112E-05	0.235	1.819E-05	2.91E+04
2	8.141E-05	0.169	1.310E-05	2.33E+04
3	1.209E-04	0.131	1.013E-05	2.16E+04
4	1.596E-04	0.105	8.127E-06	2.11E+04
5	1.976E-04	0.087	6.747E-06	2.09E+04
0	0	0.203	1.577E-05	
1	2.406E-05	0.096	7.418E-06	7.05E+04
2	4.783E-05	0.067	5.165E-06	5.39E+04
3	7.133E-05	0.051	3.967E-06	4.86E+04
4	9.455E-05	0.042	3.224E-06	4.59E+04

Equilibrium constant for the reaction of **2e** with DBU (20 °C, in acetonitrile)

ε [**2e** at 370 nm] = 3.09 × 10^4 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DBU]_0$ (mol L^{-1})	A	$[\mathbf{2e}]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.812	5.258E-05	
1	5.832E-05	0.445	2.883E-05	2.24E+04
2	1.148E-04	0.281	1.821E-05	2.19E+04
3	1.695E-04	0.195	1.263E-05	2.25E+04
4	2.225E-04	0.149	9.619E-06	2.26E+04
5	2.739E-04	0.121	7.832E-06	2.23E+04
0	0	0.547	3.544E-05	
1	4.772E-05	0.263	1.706E-05	3.60E+04
2	9.488E-05	0.174	1.125E-05	2.97E+04
3	1.415E-04	0.126	8.168E-06	2.84E+04
4	1.875E-04	0.100	6.449E-06	2.74E+04
5	2.331E-04	0.081	5.271E-06	2.71E+04
0	0	0.559	3.618E-05	
1	4.870E-05	0.268	1.737E-05	3.55E+04
2	9.681E-05	0.177	1.148E-05	2.91E+04
3	1.443E-04	0.129	8.352E-06	2.78E+04
4	1.913E-04	0.100	6.494E-06	2.73E+04
5	2.377E-04	0.081	5.259E-06	2.73E+04
0	0	0.549	3.553E-05	
1	4.796E-05	0.263	1.703E-05	3.62E+04
2	9.535E-05	0.173	1.118E-05	3.00E+04
3	1.422E-04	0.126	8.132E-06	2.85E+04
4	1.885E-04	0.097	6.293E-06	2.82E+04
5	2.342E-04	0.079	5.141E-06	2.79E+04
0	0	0.304	1.971E-05	
1	2.190E-05	0.177	1.145E-05	5.17E+04
2	4.353E-05	0.128	8.306E-06	4.16E+04
3	6.490E-05	0.100	6.479E-06	3.82E+04
4	8.602E-05	0.082	5.278E-06	3.67E+04
5	1.069E-04	0.068	4.428E-06	3.60E+04
0	0	0.199	1.291E-05	
1	1.467E-05	0.114	7.399E-06	8.01E+04
2	2.922E-05	0.082	5.300E-06	6.52E+04
3	4.366E-05	0.064	4.146E-06	5.93E+04
4	5.798E-05	0.053	3.402E-06	5.62E+04

Equilibrium constant for the reaction of **2a** with DBN (20 °C, in acetonitrile)

ε [**2a** at 340 nm] = 3.51 × 10^4 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DBN]_0$ (mol L^{-1})	A	$[\mathbf{2a}]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.400	2.277E-05	
1	2.819E-05	0.132	7.495E-06	1.53E+05
2	5.584E-05	0.055	3.102E-06	1.69E+05
3	8.294E-05	0.035	1.986E-06	1.61E+05
0	0	0.394	2.241E-05	
1	2.764E-05	0.129	7.354E-06	1.58E+05
2	5.474E-05	0.054	3.062E-06	1.72E+05
3	8.133E-05	0.034	1.935E-06	1.67E+05
0	0	0.407	2.314E-05	
1	2.878E-05	0.134	7.627E-06	1.48E+05
2	5.698E-05	0.057	3.227E-06	1.61E+05
3	8.461E-05	0.041	2.311E-06	1.35E+05
0	0	0.400	2.277E-05	
1	2.744E-05	0.137	7.802E-06	1.49E+05
2	5.433E-05	0.057	3.250E-06	1.66E+05
3	8.070E-05	0.036	2.066E-06	1.60E+05

Equilibrium constant for the reaction of **2c** with DMAP (20 °C, in acetonitrile)
ε [**2c** at 360 nm] = 2.58 × 10^4 M^{-1} cm^{-1} and *d* = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[\mathbf{2c}]_{eq}$ (mol L^{-1})	*K* (L mol^{-1})
0	0	1.228	9.522E-05	
1	3.084E-04	1.150	8.915E-05	2.11E+02
2	6.144E-04	1.086	8.419E-05	2.02E+02
3	9.178E-04	1.028	7.971E-05	1.99E+02
4	1.518E-03	0.906	7.022E-05	2.20E+02
5	2.108E-03	0.828	6.416E-05	2.13E+02
6	2.689E-03	0.762	5.909E-05	2.09E+02
7	3.260E-03	0.706	5.473E-05	2.06E+02
8	3.823E-03	0.658	5.101E-05	2.04E+02
0	0	0.628	4.865E-05	
1	6.125E-04	0.557	4.319E-05	1.93E+02
2	1.215E-03	0.501	3.885E-05	1.92E+02
3	1.808E-03	0.458	3.547E-05	1.89E+02
4	2.392E-03	0.418	3.238E-05	1.91E+02
5	2.967E-03	0.386	2.989E-05	1.91E+02
6	3.532E-03	0.359	2.784E-05	1.90E+02
7	4.089E-03	0.337	2.609E-05	1.88E+02
8	4.638E-03	0.317	2.457E-05	1.86E+02
9	5.178E-03	0.301	2.330E-05	1.83E+02
0	0	0.618	4.790E-05	
1	6.093E-04	0.549	4.253E-05	1.94E+02
2	1.209E-03	0.493	3.822E-05	1.94E+02
3	1.799E-03	0.449	3.482E-05	1.92E+02
4	2.380E-03	0.413	3.202E-05	1.90E+02
5	2.952E-03	0.381	2.957E-05	1.90E+02
6	3.515E-03	0.354	2.743E-05	1.90E+02
7	4.069E-03	0.330	2.554E-05	1.91E+02
8	4.615E-03	0.308	2.390E-05	1.92E+02
9	5.153E-03	0.292	2.267E-05	1.89E+02

K_{av}(20 °C) = 1.96 × 10^2 L mol^{-1}

Equilibrium constant for the reaction of **2e** with DMAP (20 °C, in acetonitrile)
ε [**2e** at 370 nm] = 3.09 × 10^4 M^{-1} cm^{-1} and *d* = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[\mathbf{2e}]_{eq}$ (mol L^{-1})	*K* (L mol^{-1})
0	0	0.543	3.518E-05	
1	2.436E-04	0.512	3.314E-05	2.37E+02
2	8.441E-04	0.446	2.890E-05	2.39E+02
3	1.433E-03	0.396	2.562E-05	2.40E+02
4	2.010E-03	0.355	2.301E-05	2.39E+02
5	2.577E-03	0.323	2.089E-05	2.39E+02
6	3.132E-03	0.295	1.913E-05	2.39E+02
7	3.678E-03	0.272	1.761E-05	2.40E+02
0	0	0.553	3.582E-05	
1	6.053E-04	0.478	3.095E-05	2.43E+02
2	1.199E-03	0.421	2.728E-05	2.41E+02
3	1.781E-03	0.376	2.432E-05	2.43E+02
4	2.352E-03	0.340	2.201E-05	2.42E+02
5	2.911E-03	0.309	2.003E-05	2.43E+02
6	3.461E-03	0.285	1.845E-05	2.42E+02

K_{av}(20 °C) = 2.41 × 10^2 L mol^{-1}

Equilibrium constant for the reaction of **2f** with DMAP (20 °C, in acetonitrile)
ε [**2f** at 400 nm] = 3.77 × 10^4 M^{-1} cm^{-1} and d = 0.5 cm

Entry	$[DMAP]_0$ (mol L^{-1})	A	$[\mathbf{2f}]_{eq}$ (mol L^{-1})	K (L mol^{-1})
0	0	0.507	2.688E-05	
1	3.01E-05	0.234	1.24E-05	7.48E+04
2	6.01E-05	0.129	6.83E-06	7.30E+04
3	9.00E-05	0.086	4.56E-06	7.20E+04
4	1.20E-04	0.060	3.17E-06	7.73E+04
0	0	0.496	2.626E-05	
1	2.92E-05	0.232	1.23E-05	7.46E+04
2	5.83E-05	0.127	6.75E-06	7.42E+04
3	8.73E-05	0.084	4.47E-06	7.41E+04
4	1.16E-04	0.062	3.28E-06	7.46E+04
5	1.45E-04	0.049	2.61E-06	7.42E+04
0	0	0.567	3.002E-05	
1	2.86E-05	0.273	1.45E-05	8.16E+04
2	5.72E-05	0.150	7.97E-06	7.84E+04
3	8.57E-05	0.098	5.19E-06	7.83E+04
4	1.14E-04	0.072	3.82E-06	7.74E+04
0	0	0.554	2.935E-05	
1	2.82E-05	0.276	1.46E-05	7.43E+04
2	5.63E-05	0.150	7.93E-06	7.70E+04
3	8.44E-05	0.098	5.19E-06	7.69E+04
4	1.12E-04	0.073	3.86E-06	7.55E+04

K_{av}(20 °C) = 7.58 × 10^4 L mol^{-1}