

– Supporting Information –

**Can One Predict Changes from S<sub>N</sub>1 to S<sub>N</sub>2 Mechanisms?**

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# Table of Contents

	<b>Content</b>	<b>Page</b>
<b>1</b>	<b>Chemicals</b>	S3
<b>2</b>	<b>Determination of Amine Nucleophilicities in DMSO</b>	S4
2.1	Method	S4
2.2	2-Aminobutan-1-ol (in DMSO)	S6
2.3	Benzylamine (in DMSO)	S7
2.4	1-Aminopropan-2-ol (in DMSO)	S8
2.5	Diethanolamine (in DMSO)	S9
2.6	Ethanolamine (in DMSO)	S10
<b>3</b>	<b>Determination of the Nucleophilicity of DMSO (in MeCN)</b>	S11
<b>4</b>	<b>Reactions of Benzhydryl Bromides with Amines in DMSO</b>	S16
4.1	Method	S16
4.2	4-Methyl-benzhydryl bromide	S17
4.3	Benzhydryl bromide	S19
4.4	4,4'-Dichlorobenzhydryl bromide	S21
4.5	4-Trifluoromethyl-benzhydryl bromide	S26
4.6	4,4'-Bis(trifluoromethyl)benzhydryl bromide	S28
<b>5</b>	<b>Product Studies</b>	S30
5.1	Method	S30
5.2	Synthesis of Compounds for GC Calibrations	S31
5.3	Standardization	S35
5.4	Analysis of Product Mixtures	S40
<b>6</b>	<b>Hammett Plots for the Kinetics of the Reactions of Substituted Benzyl Bromides with Pyridine</b>	S43

## 1 Chemicals

**Solvents:** Reagent grade DMSO (>99.8 %, Acros, extra dry).

**Electrophiles:** Benzhydrylium tetrafluoroborates (Table S1) were prepared as described before.<sup>S1</sup>. The benzhydryl bromides were prepared by refluxing the corresponding benzhydrols in solution of HBr in glacial acetic acid in the presence of acetyl bromide.<sup>S2</sup>

**Nucleophiles.** 2-Amino-1-butanol (>99.5 %, Aldrich), 1-aminopropan-2-ol (>99.5 %, Aldrich), ethanolamine (>99.5 %, Acros), diethanolamine (>99.5 %, Acros), *n*-propylamine (>99.5 %, Fluka), Piperidine (>99 %, Lancaster), morpholine (>99 %, Lancaster), benzylamine (>99 %, Fluka), were purchased and freshly distilled before use.

**Benzophenones and Benzhydrols.** The following benzophenones and benzhydrols for GC calibration and synthesis were commercially available and used as received: benzhydrol (99%, Acros), benzophenone (99%, Acros), 4,4-dichlorobenzhydrol (98%, Aldrich), 4,4-dichlorobenzophenone (99%, Acros), 4-methylbenzhydrol (>98%, Alfa Aesar), 4-methylbenzophenone (98%, Molekula).

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(S1) Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, G.; Schimmel, H., *J. Am. Chem. Soc.* **2001**, *123*, 9500–9512.

(S2) (a) Weber, E.; Seichter, W.; Goldberg, I. *Chem. Ber.* **1990**, *123*, 811–820. (b) Bachmann, W. E. *J. Am. Chem. Soc.* **1933**, *55*, 2135–2139.

## 2 Determination of Amine Nucleophilicities in DMSO

### 2.1 Method

The reactivity parameters  $N$  and  $s$  of various amines in DMSO were determined on the basis of Equation (S1) using benzhydrylium ions (Table S1) as reference electrophiles.

$$\log k(20\text{ }^\circ\text{C}) = s(N + E) \quad (\text{S1})$$

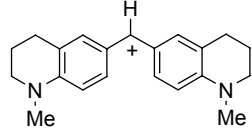
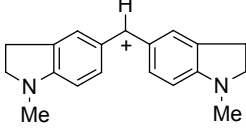
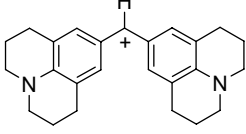
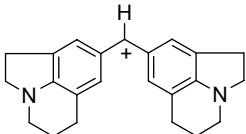
Since the reactions of the colored reference electrophiles with nucleophiles gave rise to colorless products, the decay of the absorptions of the electrophiles was followed by UV-Vis spectroscopy.

Stopped-flow spectrophotometer systems (Hi-Tech SF-61DX2 controlled by Hi-Tech KinetAsyst2 software) were used for the investigation of the reactions. The temperature of the solutions during all kinetic studies was kept constant ( $20.0 \pm 0.1\text{ }^\circ\text{C}$ ) by using a circulating bath thermostat.

The concentrations of the amines ( $[\text{Nu}]$ ) were at least ten times as high as those of the electrophiles, resulting in pseudo-first-order kinetics with an exponential decay of the electrophile concentrations. The pseudo-first-order rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) were obtained by least-squares fitting of the absorbance  $A$  of the electrophiles to the single-exponential  $A_t = A_0 \exp(-k_{\text{obs}}t) + C$ . Because of  $k_{\text{obs}} = k_2[\text{Nu}]$ , second-order rate constants  $k_2$  ( $\text{M}^{-1} \text{s}^{-1}$ ) were derived from the slopes of the linear plots of  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ) vs.  $[\text{Nu}]$ .

The linear plots of  $\log k_2$  vs. the electrophilicity parameters  $E$  (Table S1) of the benzhydrylium ions yield the nucleophilicity parameters  $N$  and  $s$  of the nucleophiles in DMSO according to Equation (S1).

**Table S1.** Benzhydrylium ions ( $\text{Ar}_2\text{CH}^+$ ) used as reference electrophiles in this work.

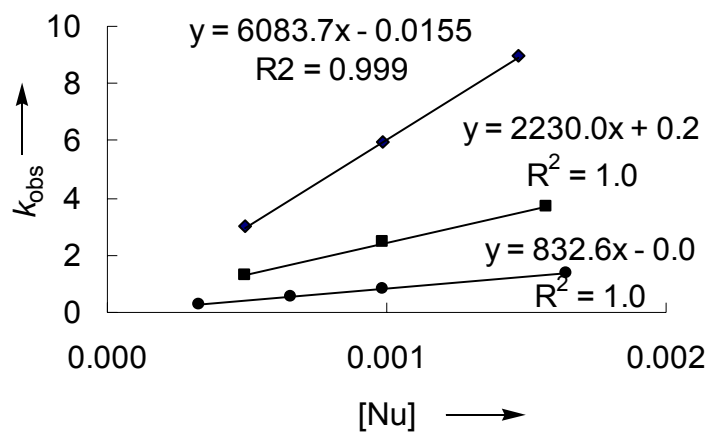
Benzhydrylium Ion ( $\text{Ar}_2\text{CH}^+$ )	$E^a$	$\lambda^b / \text{nm}$
$(\text{thq})_2\text{CH}^+$ 	-8.22	618
$(\text{ind})_2\text{CH}^+$ 	-8.76	615
$(\text{jul})_2\text{CH}^+$ 	-9.45	632
$(\text{lil})_2\text{CH}^+$ 	-10.04	629

<sup>a</sup> From ref. S1 ; <sup>b</sup> Wavelengths used for the evaluation of the kinetic experiments.

## 2.2 2-Aminobutan-1-ol (in DMSO)

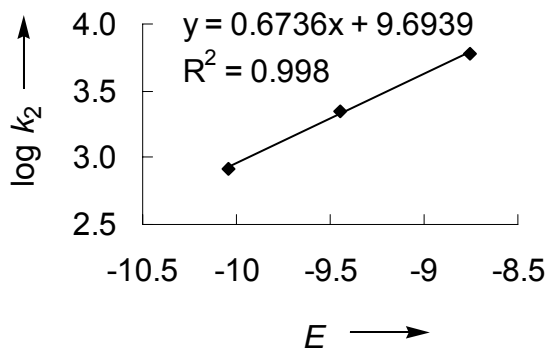
Kinetics of the reactions with benzhydrylium ions ( $\text{Ar}_2\text{CH}^+ \text{BF}_4^-$ , 20 °C, in DMSO, stopped-flow)

$\text{Ar}_2\text{CH}^+$	$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{Nu}] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
$(\text{ind})_2\text{CH}^+$	$1.02 \times 10^{-5}$	$4.92 \times 10^{-4}$	2.99
	$1.02 \times 10^{-5}$	$9.83 \times 10^{-4}$	5.94
	$1.02 \times 10^{-5}$	$1.47 \times 10^{-3}$	8.94
$(\text{jul})_2\text{CH}^+$	$9.15 \times 10^{-6}$	$4.92 \times 10^{-4}$	1.29
	$9.15 \times 10^{-6}$	$9.83 \times 10^{-4}$	2.49
	$9.15 \times 10^{-6}$	$1.57 \times 10^{-3}$	3.70
$(\text{lil})_2\text{CH}^+$	$8.55 \times 10^{-6}$	$3.28 \times 10^{-4}$	0.271
	$8.55 \times 10^{-6}$	$6.57 \times 10^{-4}$	0.535
	$8.55 \times 10^{-6}$	$9.85 \times 10^{-4}$	0.819
	$8.55 \times 10^{-6}$	$1.64 \times 10^{-3}$	1.36



Determination of reactivity parameters  $N$  and  $s$ :

electrophile	$E$	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
$(\text{ind})_2\text{CH}^+$	-8.76	$6.08 \times 10^3$	3.78
$(\text{jul})_2\text{CH}^+$	-9.45	$2.23 \times 10^3$	3.35
$(\text{lil})_2\text{CH}^+$	-10.04	$8.33 \times 10^2$	2.92

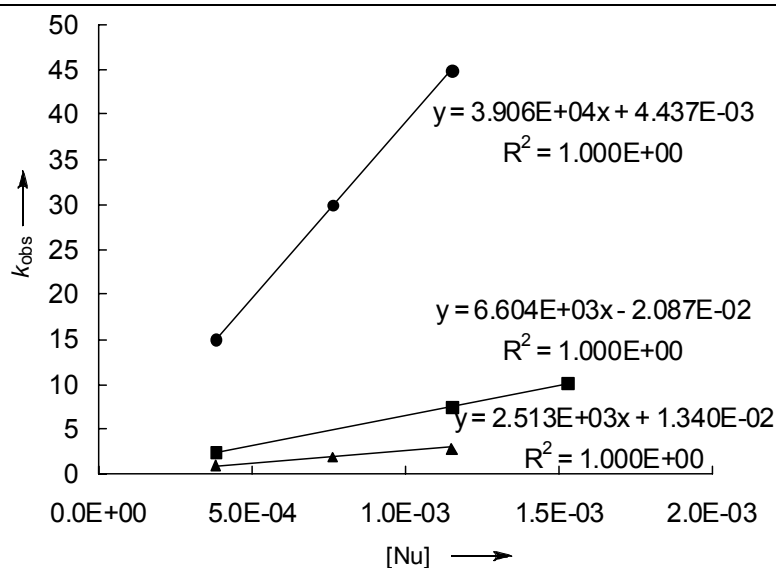


$$N = 14.39, s = 0.67$$

## 2.3 Benzylamine (in DMSO)

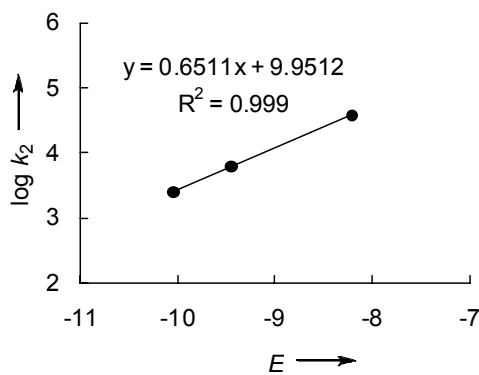
Kinetics of the reactions with benzhydrylium ions ( $\text{Ar}_2\text{CH}^+ \text{BF}_4^-$ , 20 °C, in DMSO, stopped-flow)

$\text{Ar}_2\text{CH}^+$	$[\text{Ar}_2\text{CH}^+]_0 / \text{M}$	$[\text{Nu}] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$
$(\text{thq})_2\text{CH}^+$	$4.50 \times 10^{-7}$	$3.82 \times 10^{-4}$	14.9
	$4.50 \times 10^{-7}$	$7.64 \times 10^{-4}$	29.9
	$4.50 \times 10^{-7}$	$1.15 \times 10^{-3}$	44.9
$(\text{jul})_2\text{CH}^+$	$8.70 \times 10^{-7}$	$3.82 \times 10^{-4}$	2.51
	$8.70 \times 10^{-7}$	$1.15 \times 10^{-3}$	7.55
	$8.70 \times 10^{-7}$	$1.53 \times 10^{-3}$	10.1
$(\text{lil})_2\text{CH}^+$	$6.20 \times 10^{-7}$	$3.82 \times 10^{-4}$	0.970
	$6.20 \times 10^{-7}$	$7.64 \times 10^{-4}$	1.94
	$6.20 \times 10^{-7}$	$1.15 \times 10^{-3}$	2.90



Determination of reactivity parameters  $N$  and  $s$ :

electrophile	$E$	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
$(\text{thq})_2\text{CH}^+$	-8.22	$3.91 \times 10^4$	4.59
$(\text{jul})_2\text{CH}^+$	-9.45	$6.60 \times 10^3$	3.82
$(\text{lil})_2\text{CH}^+$	-10.04	$2.51 \times 10^3$	3.40

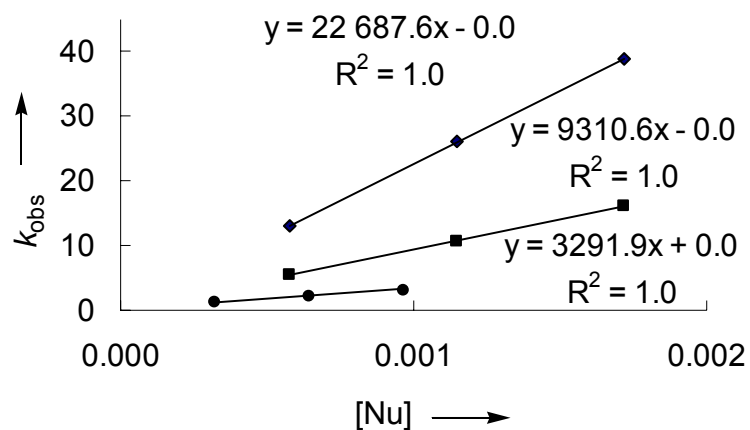


$$N = 15.28, s = 0.65$$

## 2.4 1-Aminopropan-2-ol (in DMSO)

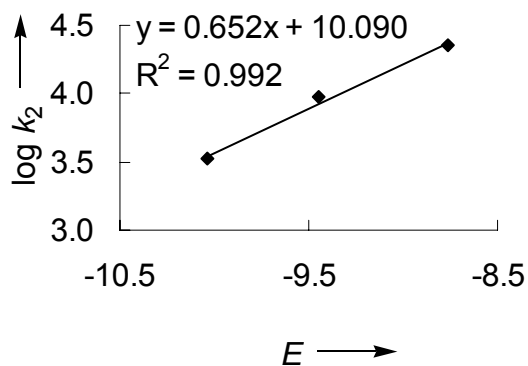
Kinetics of the reactions with benzhydrylium ions (20 °C, in DMSO; stopped-flow)

Ar <sub>2</sub> CH <sup>+</sup>	[Ar <sub>2</sub> CH <sup>+</sup> ] <sub>0</sub> / M	[Nu] / M	k <sub>obs</sub> / s <sup>-1</sup>
(ind) <sub>2</sub> CH <sup>+</sup>	7.90 × 10 <sup>-7</sup>	5.74 × 10 <sup>-4</sup>	13.0
	7.90 × 10 <sup>-7</sup>	1.15 × 10 <sup>-3</sup>	26.1
	7.90 × 10 <sup>-7</sup>	1.72 × 10 <sup>-3</sup>	39.0
(jul) <sub>2</sub> CH <sup>+</sup>	7.70 × 10 <sup>-7</sup>	5.74 × 10 <sup>-4</sup>	5.33
	7.70 × 10 <sup>-7</sup>	1.15 × 10 <sup>-3</sup>	10.7
	7.70 × 10 <sup>-7</sup>	1.72 × 10 <sup>-3</sup>	16.0
(lil) <sub>2</sub> CH <sup>+</sup>	1.15 × 10 <sup>-5</sup>	3.22 × 10 <sup>-4</sup>	1.07
	1.15 × 10 <sup>-5</sup>	6.44 × 10 <sup>-4</sup>	2.14
	1.15 × 10 <sup>-5</sup>	9.66 × 10 <sup>-4</sup>	3.19



Determination of reactivity parameters  $N$  and  $s$ :

electrophile	$E$	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
(ind) <sub>2</sub> CH <sup>+</sup>	-8.76	2.27 × 10 <sup>4</sup>	4.36
(jul) <sub>2</sub> CH <sup>+</sup>	-9.45	9.31 × 10 <sup>3</sup>	3.97
(lil) <sub>2</sub> CH <sup>+</sup>	-10.04	3.29 × 10 <sup>3</sup>	3.52

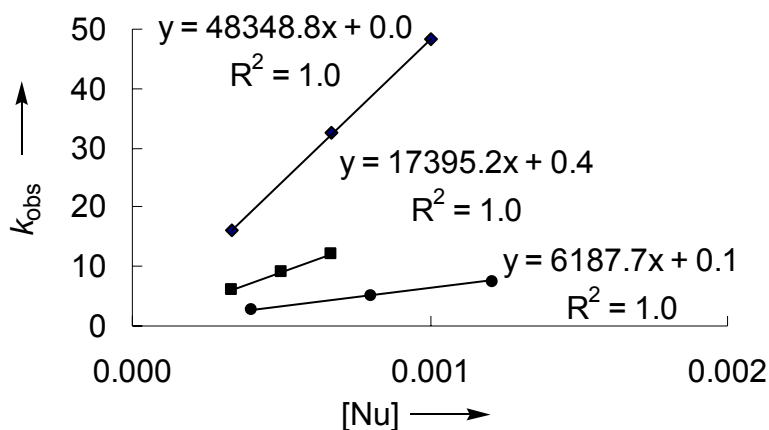


$$N = 15.47, s = 0.65$$

## 2.5 Diethanolamine (in DMSO)

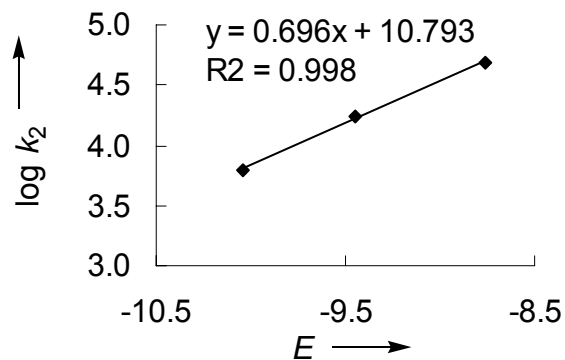
Kinetics of the reactions with benzhydrylium ions (20 °C, in DMSO; stopped-flow)

Ar <sub>2</sub> CH <sup>+</sup>	[Ar <sub>2</sub> CH <sup>+</sup> ] <sub>0</sub> / M	[Nu] / M	k <sub>obs</sub> / s <sup>-1</sup>
(ind) <sub>2</sub> CH <sup>+</sup>	1.08 × 10 <sup>-5</sup>	3.34 × 10 <sup>-4</sup>	16.1
	1.08 × 10 <sup>-5</sup>	6.68 × 10 <sup>-4</sup>	32.4
	1.08 × 10 <sup>-5</sup>	1.00 × 10 <sup>-3</sup>	48.3
(jul) <sub>2</sub> CH <sup>+</sup>	8.05 × 10 <sup>-6</sup>	3.34 × 10 <sup>-4</sup>	6.18
	8.05 × 10 <sup>-6</sup>	5.01 × 10 <sup>-4</sup>	9.10
	8.05 × 10 <sup>-6</sup>	6.68 × 10 <sup>-4</sup>	12.0
(lil) <sub>2</sub> CH <sup>+</sup>	1.15 × 10 <sup>-5</sup>	4.02 × 10 <sup>-4</sup>	2.52
	1.15 × 10 <sup>-5</sup>	8.04 × 10 <sup>-4</sup>	5.12
	1.15 × 10 <sup>-5</sup>	1.21 × 10 <sup>-3</sup>	7.52



Determination of reactivity parameters *N* and *s*:

electrophile	<i>E</i>	k <sub>2</sub> / M <sup>-1</sup> s <sup>-1</sup>	log k <sub>2</sub>
(ind) <sub>2</sub> CH <sup>+</sup>	-8.76	4.83 × 10 <sup>4</sup>	4.68
(jul) <sub>2</sub> CH <sup>+</sup>	-9.45	1.74 × 10 <sup>4</sup>	4.24
(lil) <sub>2</sub> CH <sup>+</sup>	-10.04	6.19 × 10 <sup>3</sup>	3.79

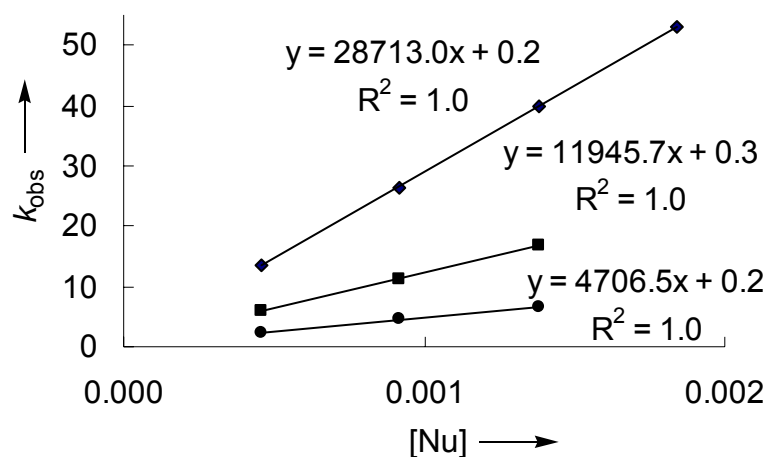


$$N = 15.51, s = 0.70$$

## 2.6 Ethanolamine (in DMSO)

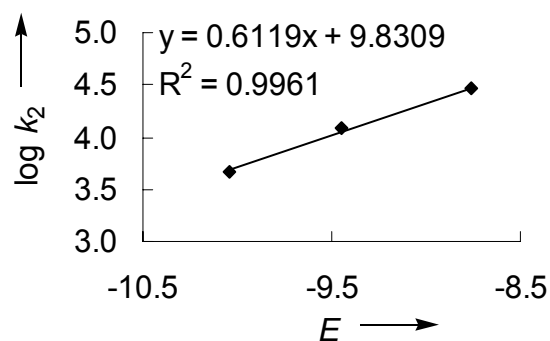
Kinetics of the reactions with benzhydrylium ions (20 °C, in DMSO; stopped-flow)

Ar <sub>2</sub> CH <sup>+</sup>	[Ar <sub>2</sub> CH <sup>+</sup> ] <sub>0</sub> / M	[Nu] / M	k <sub>obs</sub> / s <sup>-1</sup>
(ind) <sub>2</sub> CH <sup>+</sup>	7.15 × 10 <sup>-6</sup>	4.60 × 10 <sup>-4</sup>	13.5
	7.15 × 10 <sup>-6</sup>	9.20 × 10 <sup>-4</sup>	26.5
	7.15 × 10 <sup>-6</sup>	1.38 × 10 <sup>-3</sup>	40.0
	7.15 × 10 <sup>-6</sup>	1.84 × 10 <sup>-3</sup>	53.0
(jul) <sub>2</sub> CH <sup>+</sup>	8.05 × 10 <sup>-6</sup>	4.60 × 10 <sup>-4</sup>	5.81
	8.05 × 10 <sup>-6</sup>	9.20 × 10 <sup>-4</sup>	11.3
	8.05 × 10 <sup>-6</sup>	1.38 × 10 <sup>-3</sup>	16.8
(lil) <sub>2</sub> CH <sup>+</sup>	6.77 × 10 <sup>-6</sup>	4.60 × 10 <sup>-4</sup>	2.37
	6.77 × 10 <sup>-6</sup>	9.20 × 10 <sup>-4</sup>	4.50
	6.77 × 10 <sup>-6</sup>	1.38 × 10 <sup>-3</sup>	6.70



Determination of reactivity parameters  $N$  and  $s$ :

electrophile	$E$	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
(ind) <sub>2</sub> CH <sup>+</sup>	-8.76	$2.87 \times 10^4$	4.46
(jul) <sub>2</sub> CH <sup>+</sup>	-9.45	$1.19 \times 10^4$	4.08
(lil) <sub>2</sub> CH <sup>+</sup>	-10.04	$4.71 \times 10^3$	3.67



$$N = 16.07, s = 0.61$$

### 3 Determination of the Nucleophilicity of DMSO (in MeCN)

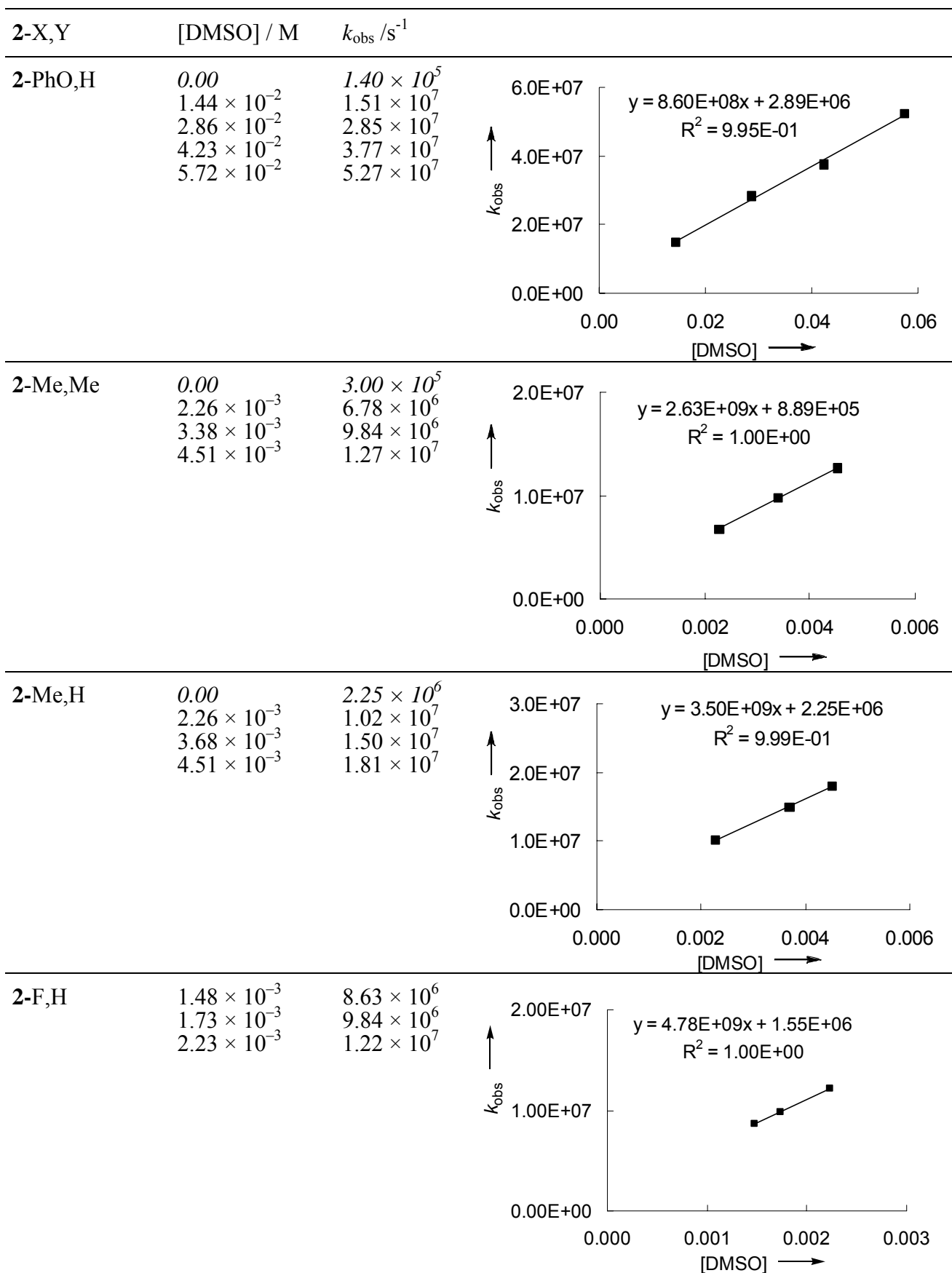
**Laser Flash Photolysis.** The laser pulse (7 ns pulse width, 266 nm, 40-60 mJ/pulse) originates from a Nd-YAG laser (Innolas SpitLight 600) with second (532 nm) and fourth (266 nm) harmonic generators. The UV-visible detection unit of the laser flash photolysis setup comprises a Xe-light source (Osram XBO 150 W/CR OFR in a Hamamatsu E7536 housing with Hamamatsu C8849 power supplier), a spectrograph (Acton Spectra Pro 2300i from Princeton Instruments), a photomultiplier (Hamamatsu H-7332-10 with C7169 power supply) with amplifier (Stanford Research Systems SR445A), and a pulse generator (Berkeley Nucleonics Corp. BNC 565). For the data acquisition a 350 MHz-oscilloscope (Tektronix DPO 4032) was used. The sample was kept in a temperature controlled fluorescence cell, the temperature of which was maintained at 20 °C by a circulating bath thermostat. A shutter was used to prevent the long exposure of the sample to the light from the Xe-lamp.

The less stabilized benzhydrylium ions ( $E \geq 0$ ) were generated from the corresponding benzhydryl chlorides (**2**-Me,H from the bromide **1**-Me,H and **2**-MeO,MeO from bis(*p*-anisyl)methyl acetate) by the laser pulse. The decay of their absorbance was monitored by UV/Vis spectroscopy at their absorption maxima. The resulting pseudo-first-order rate constants  $k_{\text{obs}}$  were obtained from at least five runs at each DMSO concentration. The absorbance-time curves were fitted to the single exponential,  $A = A_0 \exp(-k_{\text{obs}}t) + C$  to yield the rate constants  $k_{\text{obs}}$  ( $\text{s}^{-1}$ ).

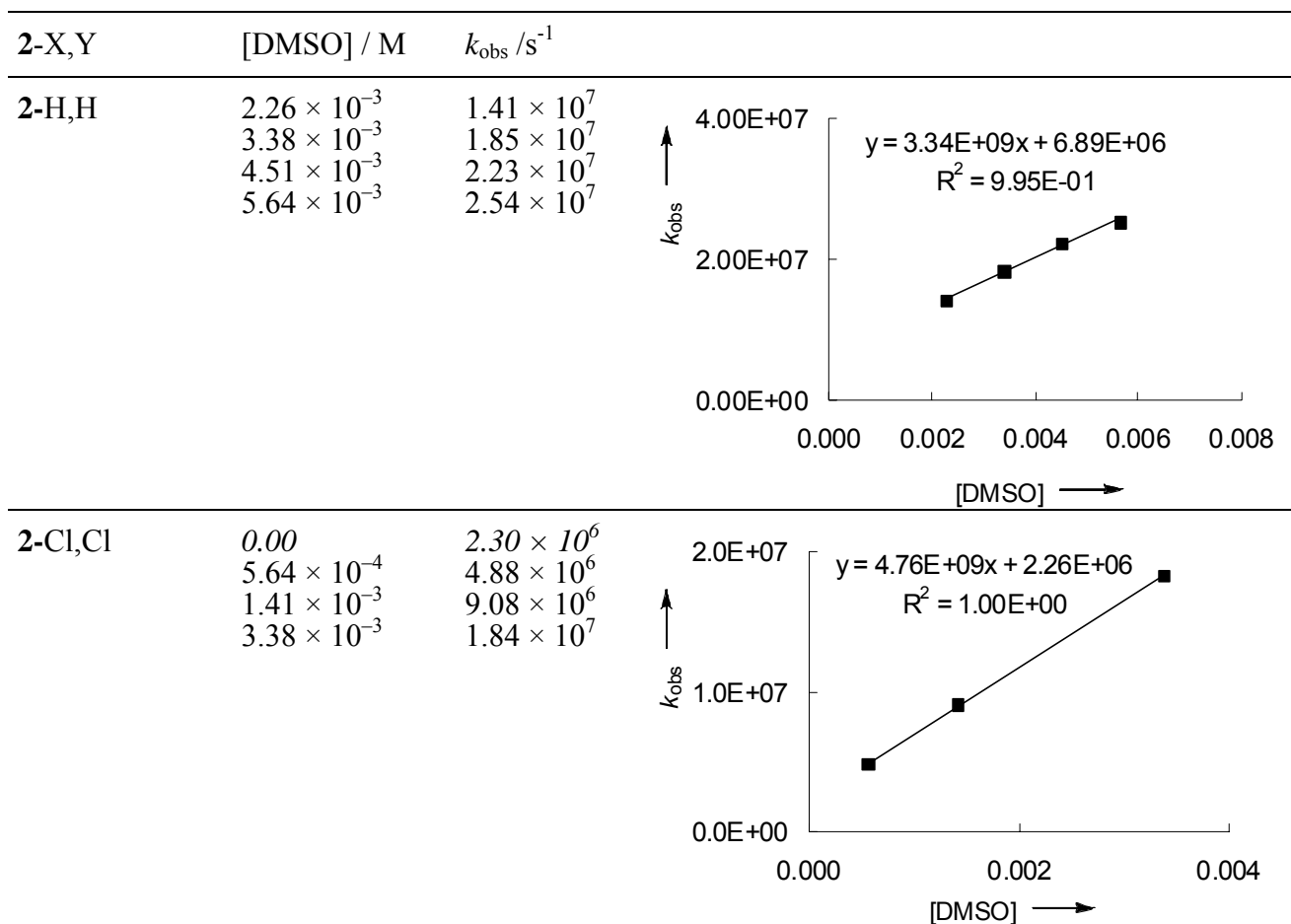
## Kinetics of the reactions of DMSO with benzhydrylium ions (20°C, in MeCN; laser flash photolysis)

2-X,Y	[DMSO] / M	$k_{\text{obs}} / \text{s}^{-1}$	
2-MeO,MeO	$1.86 \times 10^{-1}$	$3.17 \times 10^6$	
	$3.25 \times 10^{-1}$	$5.69 \times 10^6$	
	$4.75 \times 10^{-1}$	$8.05 \times 10^6$	
2-MeO,PhO	0.00	$1.75 \times 10^5$	
	$5.64 \times 10^{-2}$	$3.67 \times 10^6$	
	$1.13 \times 10^{-1}$	$6.51 \times 10^6$	
	$1.69 \times 10^{-1}$	$9.32 \times 10^6$	
2-MeO,H	0.00	$7.76 \times 10^5$	
	$2.45 \times 10^{-2}$	$1.51 \times 10^7$	
	$4.99 \times 10^{-2}$	$3.06 \times 10^7$	
	$7.23 \times 10^{-2}$	$4.43 \times 10^7$	
2-PhO,Me	0.00	$3.04 \times 10^5$	
	$1.13 \times 10^{-2}$	$8.05 \times 10^6$	
	$2.17 \times 10^{-2}$	$1.54 \times 10^7$	
	$3.12 \times 10^{-2}$	$2.20 \times 10^7$	

Continued.



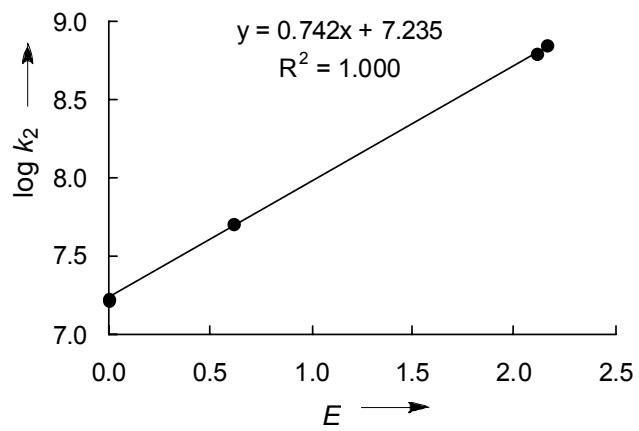
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For the determination of the nucleophilicity parameter of DMSO (in acetonitrile) only the second-order rate constants of the reactions of DMSO with the four benzhydrylium ions of lowest reactivity ( $E < 2.2$ ) were employed because the second-order rate constants for the reactions of DMSO with the more electrophilic benzhydrylium ions were already influenced by their vicinity to the diffusion limit.

Determination of reactivity parameters  $N$  and  $s$  of DMSO (in acetonitrile):

electrophile	$E$	$k_2 / \text{M}^{-1} \text{s}^{-1}$	$\log k_2$
2-MeO,MeO	0.00	$1.69 \times 10^7$	7.23
2-MeO,PhO	0.61	$5.00 \times 10^7$	7.70
2-MeO,H	2.11	$6.13 \times 10^8$	8.79
2-PhO,Me	2.16	$7.04 \times 10^8$	8.85



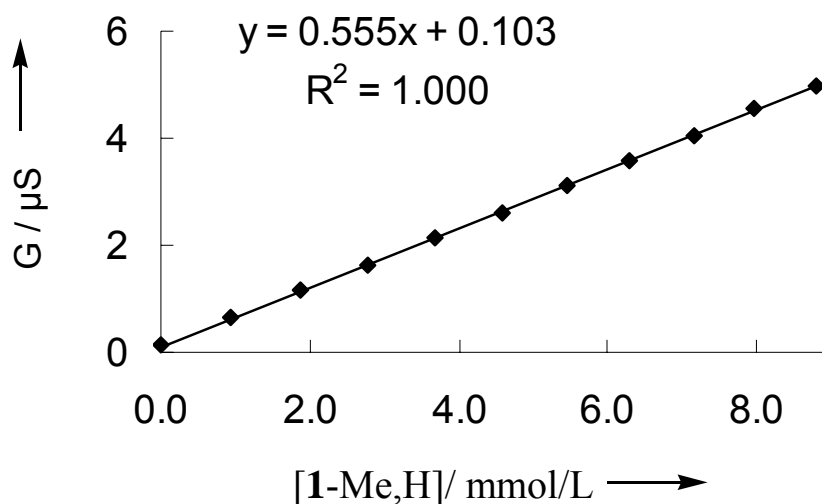
$N = 9.75, s = 0.74$

## 4 Reactions of Benzhydryl Bromides with Amines in DMSO

### 4.1 Method

The reactions of the benzhydryl bromides (**1-X,Y**) with amines in DMSO were followed by conductometry (conductimeters: Radiometer Analytical CDM 230 or Tacussel CD 810, Pt electrode: WTW LTA 1/NS). The temperature of the solutions during all kinetic studies was kept constant ( $\pm 0.1^\circ\text{C}$ ) by using a circulating bath thermostats.

A calibration was performed to test the dependance of the conductance on the concentration of liberated HBr. For this purpose, 0.25 mL of a 0.11 M solution of the benzhydryl bromide **1-Me,H** in acetonitrile was injected to a 0.34 M solution of piperidine in DMSO. After the conductivity had increased to a constant value another portion of the benzhydryl bromide **1-Me,H** was added. As shown in Figure S1, the conductivity depended linearly on the concentration of added **1-Me,H**, i. e., released HBr.



**Figure S1.** Initial concentration of the benzhydryl bromide [**1-Me,H**] vs. conductance at  $t_\infty$ . After the addition of a portion of **1-Me,H**, the next conductivity value was taken when the conductivity remained constant for at least 300 s.

The first order rate constants  $k$  ( $\text{s}^{-1}$ ) were obtained by least squares fitting of the increasing conductance to a single-exponential equation (S2)

$$dG/dt = G_{\max}[1 - \exp(-k_{\text{obs}}t)] + C \quad (\text{S2})$$

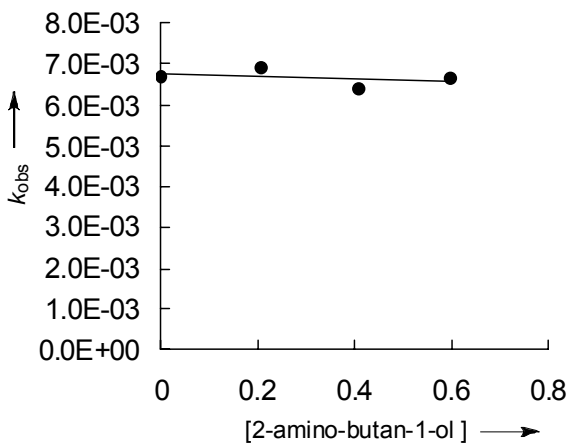
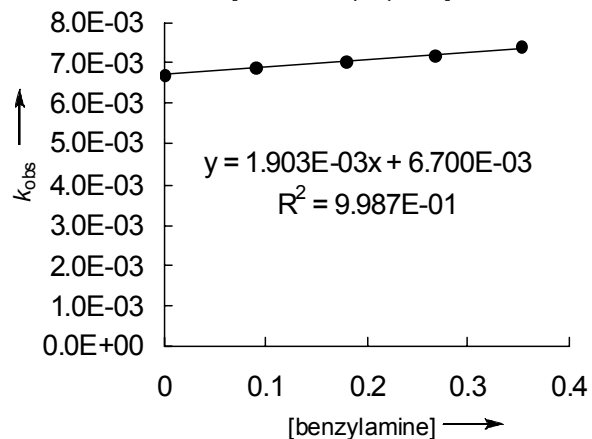
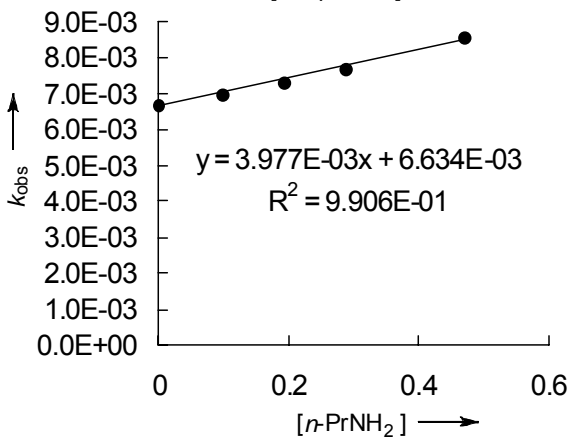
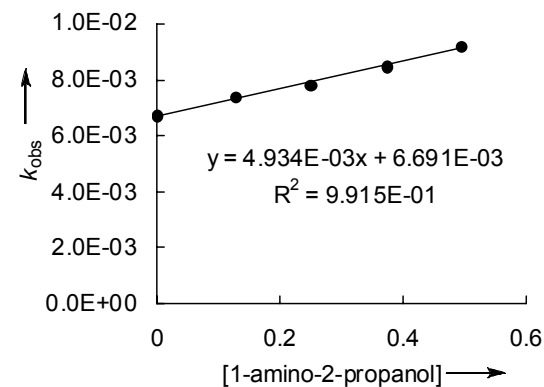
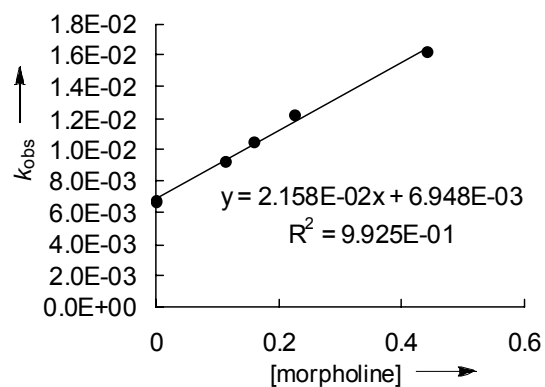
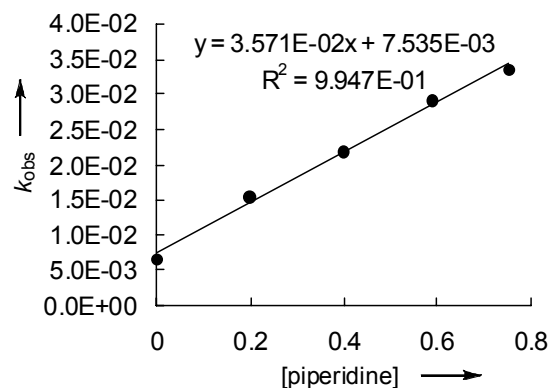
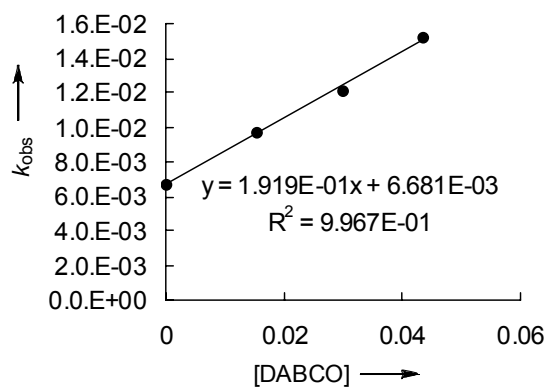
Second-order rate constants  $k_2$  ( $\text{M}^{-1} \text{s}^{-1}$ ) were obtained from the slopes of linear plots of  $k_{\text{obs}}$  vs. the concentrations of the amines [Nu].

## 4.2 4-Methyl-benzhydryl bromide

20 °C, in DMSO, conductometry

Nu	[1-Me,H] <sub>0</sub> / M	[Nu] / M	<i>k</i> <sub>obs</sub> / s <sup>-1</sup>	<i>k</i> <sub>2</sub> / M <sup>-1</sup> s <sup>-1</sup>
DABCO	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>1.92 × 10<sup>-1</sup></b>
	4.76 × 10 <sup>-4</sup>	1.51 × 10 <sup>-2</sup>	9.68 × 10 <sup>-3</sup>	
	1.29 × 10 <sup>-3</sup>	2.98 × 10 <sup>-2</sup>	1.21 × 10 <sup>-2</sup>	
	9.28 × 10 <sup>-4</sup>	4.35 × 10 <sup>-2</sup>	1.52 × 10 <sup>-2</sup>	
piperidine	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>3.57 × 10<sup>-2</sup></b>
	3.03 × 10 <sup>-3</sup>	1.99 × 10 <sup>-1</sup>	1.55 × 10 <sup>-2</sup>	
	9.04 × 10 <sup>-4</sup>	3.99 × 10 <sup>-1</sup>	2.19 × 10 <sup>-2</sup>	
	2.92 × 10 <sup>-3</sup>	5.89 × 10 <sup>-1</sup>	2.92 × 10 <sup>-2</sup>	
	2.93 × 10 <sup>-3</sup>	7.52 × 10 <sup>-1</sup>	3.36 × 10 <sup>-2</sup>	
morpholine	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>2.16 × 10<sup>-2</sup></b>
	2.31 × 10 <sup>-3</sup>	1.14 × 10 <sup>-1</sup>	9.31 × 10 <sup>-3</sup>	
	2.65 × 10 <sup>-3</sup>	1.59 × 10 <sup>-1</sup>	1.05 × 10 <sup>-2</sup>	
	3.52 × 10 <sup>-3</sup>	2.26 × 10 <sup>-1</sup>	1.23 × 10 <sup>-2</sup>	
	2.84 × 10 <sup>-3</sup>	4.41 × 10 <sup>-1</sup>	1.62 × 10 <sup>-2</sup>	
1-aminopropan-2-ol	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>4.93 × 10<sup>-3</sup></b>
	1.12 × 10 <sup>-3</sup>	1.28 × 10 <sup>-1</sup>	7.40 × 10 <sup>-3</sup>	
	1.52 × 10 <sup>-3</sup>	2.50 × 10 <sup>-1</sup>	7.79 × 10 <sup>-3</sup>	
	7.25 × 10 <sup>-4</sup>	3.72 × 10 <sup>-1</sup>	8.49 × 10 <sup>-3</sup>	
	9.28 × 10 <sup>-4</sup>	4.93 × 10 <sup>-1</sup>	9.20 × 10 <sup>-3</sup>	
<i>n</i> -PrNH <sub>2</sub>	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>3.98 × 10<sup>-3</sup></b>
	2.38 × 10 <sup>-3</sup>	9.65 × 10 <sup>-2</sup>	7.00 × 10 <sup>-3</sup>	
	3.25 × 10 <sup>-4</sup>	1.92 × 10 <sup>-1</sup>	7.34 × 10 <sup>-3</sup>	
	1.56 × 10 <sup>-3</sup>	2.86 × 10 <sup>-1</sup>	7.70 × 10 <sup>-3</sup>	
	4.52 × 10 <sup>-3</sup>	4.69 × 10 <sup>-1</sup>	8.57 × 10 <sup>-3</sup>	
benzylamine	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	<b>1.90 × 10<sup>-3</sup></b>
	1.25 × 10 <sup>-3</sup>	9.02 × 10 <sup>-2</sup>	6.86 × 10 <sup>-3</sup>	
	1.08 × 10 <sup>-3</sup>	1.79 × 10 <sup>-1</sup>	7.04 × 10 <sup>-3</sup>	
	1.78 × 10 <sup>-3</sup>	2.67 × 10 <sup>-1</sup>	7.20 × 10 <sup>-3</sup>	
	1.64 × 10 <sup>-3</sup>	3.53 × 10 <sup>-1</sup>	7.38 × 10 <sup>-3</sup>	
2-aminobutan-1-ol	1.15 × 10 <sup>-4</sup>	0.00	6.71 × 10 <sup>-3</sup>	not determined
	4.71 × 10 <sup>-4</sup>	2.08 × 10 <sup>-1</sup>	6.91 × 10 <sup>-3</sup>	
	8.51 × 10 <sup>-4</sup>	4.06 × 10 <sup>-1</sup>	6.40 × 10 <sup>-3</sup>	
	8.29 × 10 <sup>-4</sup>	5.95 × 10 <sup>-1</sup>	6.67 × 10 <sup>-3</sup>	

$k_{\text{obs}}$  vs. [Nu] correlations for the reactions of amines with 1-Me,H in DMSO

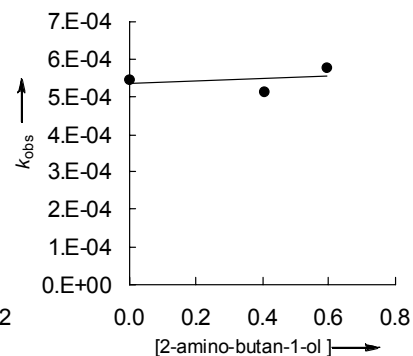
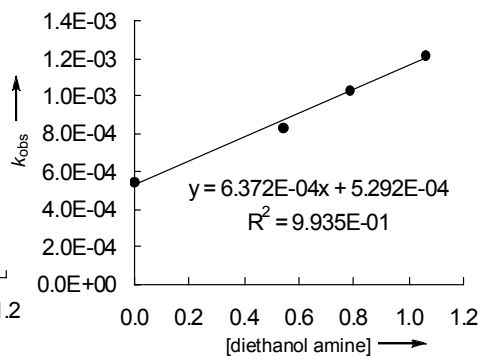
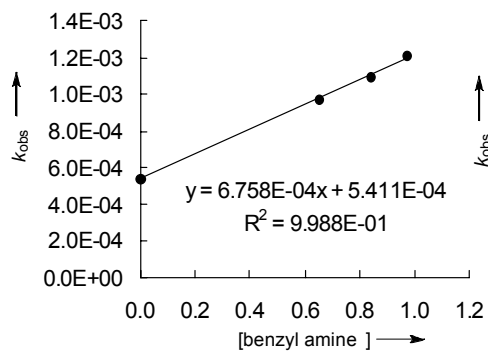
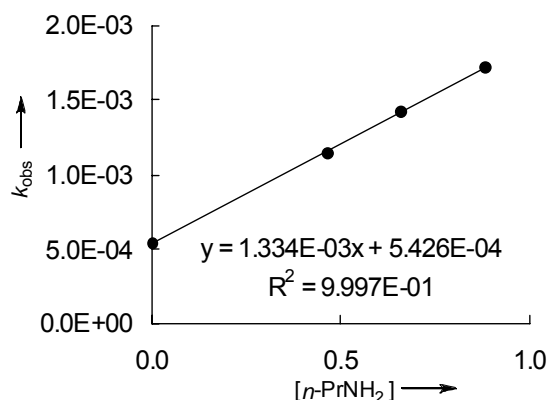
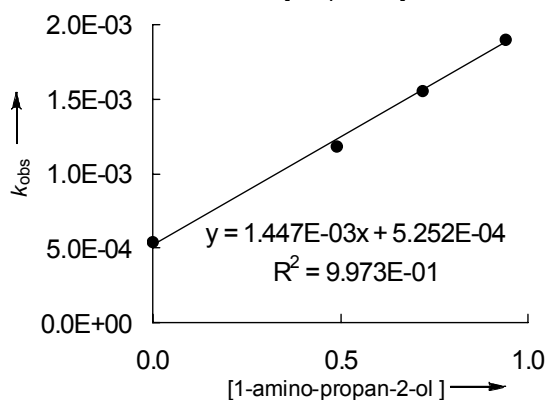
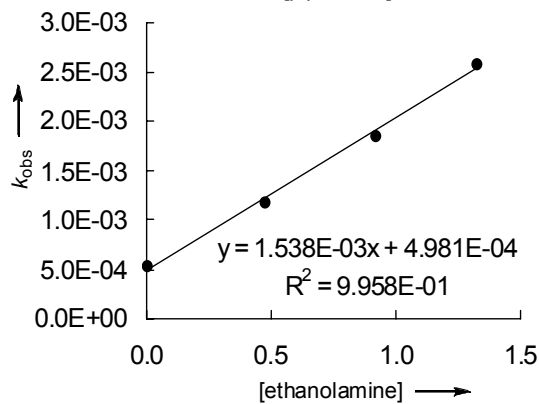
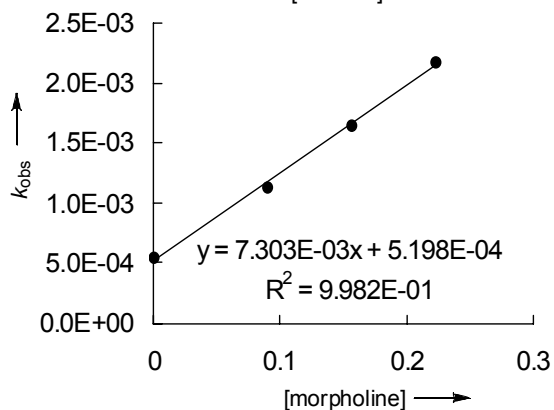
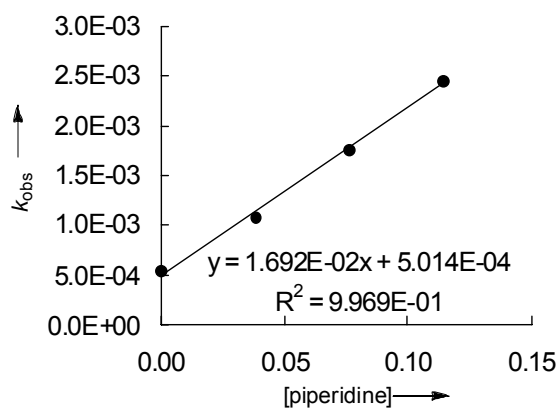
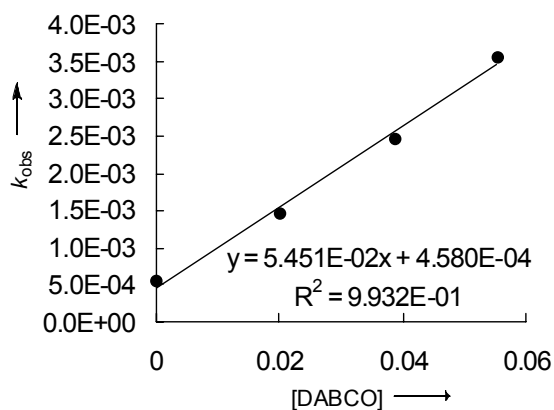


### 4.3 Benzhydryl bromide

20 °C, in DMSO, conductometry

Nu	[1-H <sub>2</sub> H] <sub>0</sub> / M	[Nu] / M	<i>k</i> <sub>obs</sub> / s <sup>-1</sup>	<i>k</i> <sub>2</sub> / M <sup>-1</sup> s <sup>-1</sup>
DABCO	2.50 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>5.45 × 10<sup>-2</sup></b>
	3.55 × 10 <sup>-4</sup>	1.99 × 10 <sup>-2</sup>	1.45 × 10 <sup>-3</sup>	
	3.52 × 10 <sup>-4</sup>	3.86 × 10 <sup>-2</sup>	2.47 × 10 <sup>-3</sup>	
	3.02 × 10 <sup>-4</sup>	5.51 × 10 <sup>-2</sup>	3.56 × 10 <sup>-3</sup>	
piperidine	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>1.69 × 10<sup>-2</sup></b>
	4.12 × 10 <sup>-4</sup>	3.82 × 10 <sup>-2</sup>	1.09 × 10 <sup>-3</sup>	
	4.41 × 10 <sup>-4</sup>	7.59 × 10 <sup>-2</sup>	1.77 × 10 <sup>-3</sup>	
	4.02 × 10 <sup>-4</sup>	1.14 × 10 <sup>-1</sup>	2.46 × 10 <sup>-3</sup>	
morpholine	2.50 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>7.30 × 10<sup>-3</sup></b>
	4.11 × 10 <sup>-4</sup>	9.01 × 10 <sup>-2</sup>	1.14 × 10 <sup>-3</sup>	
	4.01 × 10 <sup>-4</sup>	1.56 × 10 <sup>-1</sup>	1.65 × 10 <sup>-3</sup>	
	4.08 × 10 <sup>-4</sup>	2.23 × 10 <sup>-1</sup>	2.17 × 10 <sup>-3</sup>	
ethanolamine	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>1.54 × 10<sup>-3</sup></b>
	3.82 × 10 <sup>-4</sup>	4.76 × 10 <sup>-1</sup>	1.18 × 10 <sup>-3</sup>	
	3.75 × 10 <sup>-4</sup>	9.17 × 10 <sup>-1</sup>	1.86 × 10 <sup>-3</sup>	
	3.80 × 10 <sup>-4</sup>	1.32	2.58 × 10 <sup>-3</sup>	
1-aminopropan-2-ol	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>1.45 × 10<sup>-3</sup></b>
	3.69 × 10 <sup>-4</sup>	4.90 × 10 <sup>-1</sup>	1.19 × 10 <sup>-3</sup>	
	3.72 × 10 <sup>-4</sup>	7.18 × 10 <sup>-1</sup>	1.57 × 10 <sup>-3</sup>	
	3.68 × 10 <sup>-4</sup>	9.37 × 10 <sup>-1</sup>	1.90 × 10 <sup>-3</sup>	
<i>n</i> -PrNH <sub>2</sub>	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>1.33 × 10<sup>-3</sup></b>
	4.81 × 10 <sup>-4</sup>	4.63 × 10 <sup>-1</sup>	1.15 × 10 <sup>-3</sup>	
	4.85 × 10 <sup>-4</sup>	6.58 × 10 <sup>-1</sup>	1.43 × 10 <sup>-3</sup>	
	4.90 × 10 <sup>-4</sup>	8.84 × 10 <sup>-1</sup>	1.72 × 10 <sup>-3</sup>	
benzyl amine	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>6.76 × 10<sup>-4</sup></b>
	3.58 × 10 <sup>-4</sup>	6.50 × 10 <sup>-1</sup>	9.72 × 10 <sup>-4</sup>	
	3.70 × 10 <sup>-4</sup>	8.39 × 10 <sup>-1</sup>	1.10 × 10 <sup>-3</sup>	
	3.57 × 10 <sup>-4</sup>	9.71 × 10 <sup>-1</sup>	1.21 × 10 <sup>-3</sup>	
diethanolamine	2.51 × 10 <sup>-4</sup>	0.00	5.45 × 10 <sup>-4</sup>	<b>6.37 × 10<sup>-3</sup></b>
	3.15 × 10 <sup>-4</sup>	5.42 × 10 <sup>-1</sup>	8.41 × 10 <sup>-4</sup>	
	3.07 × 10 <sup>-4</sup>	7.82 × 10 <sup>-1</sup>	1.03 × 10 <sup>-3</sup>	
	3.02 × 10 <sup>-3</sup>	1.06	1.22 × 10 <sup>-3</sup>	
2-aminobutan-1-ol	2.51 × 10 <sup>-4</sup>	0.00	5.46 × 10 <sup>-4</sup>	not determined
	3.87 × 10 <sup>-4</sup>	4.05 × 10 <sup>-1</sup>	5.14 × 10 <sup>-4</sup>	
	3.80 × 10 <sup>-4</sup>	5.95 × 10 <sup>-1</sup>	5.78 × 10 <sup>-4</sup>	

$k_{obs}$  vs. [Nu] correlations for the reactions of amines with 1-H,H in DMSO

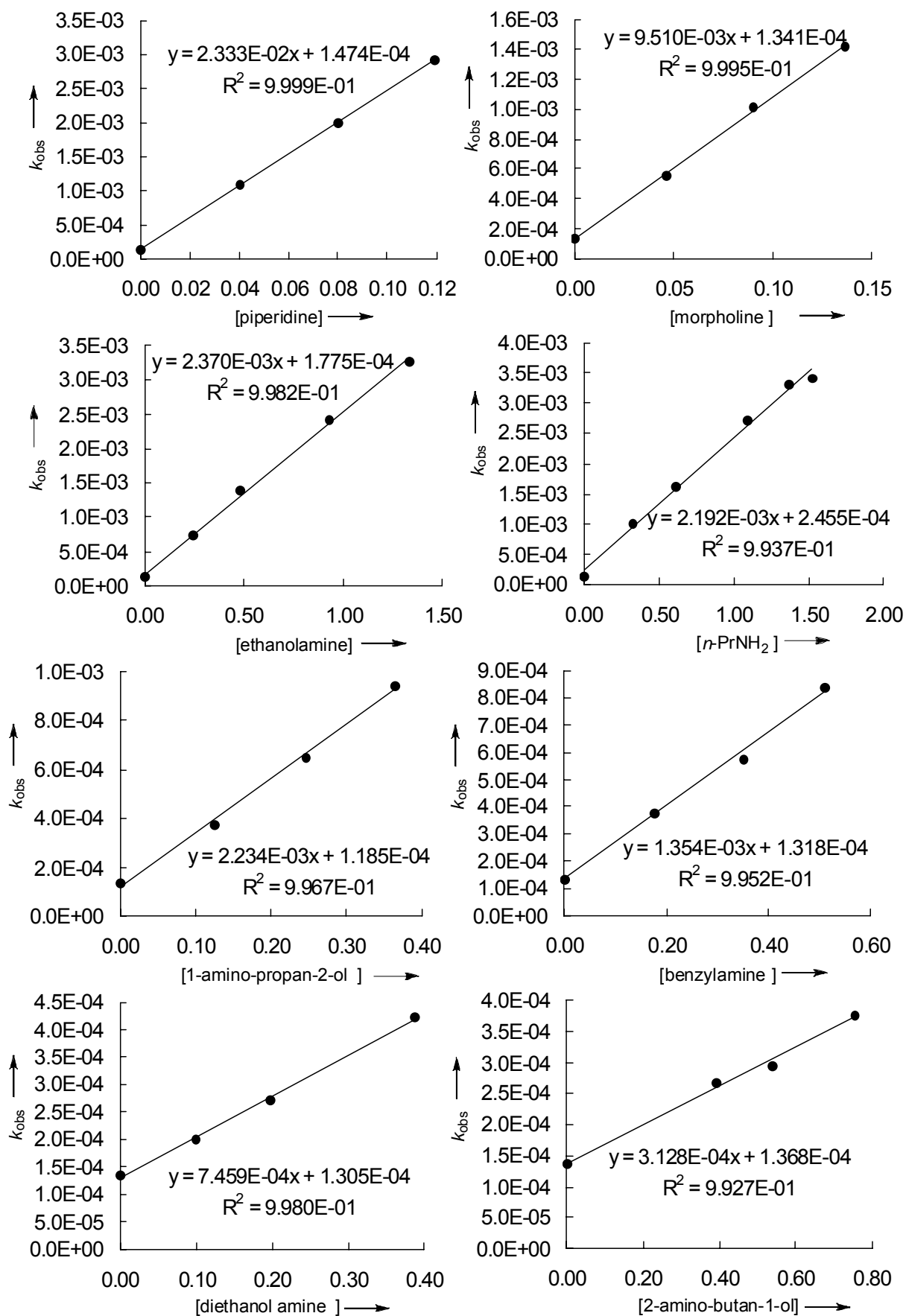


#### 4.4 4,4'-Dichlorobenzhydryl bromide

20 °C, in DMSO, conductometry

Nu	[1-Cl,Cl] <sub>0</sub> / M	[Nu] / M	k <sub>obs</sub> / s <sup>-1</sup>	k <sub>2</sub> / M <sup>-1</sup> s <sup>-1</sup>
piperidine	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>2.33 × 10<sup>-2</sup></b>
	4.83 × 10 <sup>-4</sup>	4.00 × 10 <sup>-2</sup>	1.10 × 10 <sup>-3</sup>	
	4.85 × 10 <sup>-4</sup>	7.96 × 10 <sup>-2</sup>	2.00 × 10 <sup>-3</sup>	
	4.82 × 10 <sup>-4</sup>	1.19 × 10 <sup>-1</sup>	2.92 × 10 <sup>-3</sup>	
morpholine	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>9.51 × 10<sup>-3</sup></b>
	4.85 × 10 <sup>-4</sup>	4.60 × 10 <sup>-2</sup>	5.60 × 10 <sup>-4</sup>	
	4.81 × 10 <sup>-4</sup>	9.03 × 10 <sup>-2</sup>	1.01 × 10 <sup>-3</sup>	
	4.86 × 10 <sup>-4</sup>	1.36 × 10 <sup>-1</sup>	1.42 × 10 <sup>-3</sup>	
ethanolamine	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>2.37 × 10<sup>-3</sup></b>
	6.77 × 10 <sup>-4</sup>	2.45 × 10 <sup>-1</sup>	7.36 × 10 <sup>-4</sup>	
	6.15 × 10 <sup>-4</sup>	4.80 × 10 <sup>-1</sup>	1.39 × 10 <sup>-3</sup>	
	6.65 × 10 <sup>-4</sup>	9.26 × 10 <sup>-1</sup>	2.41 × 10 <sup>-3</sup>	
	6.62 × 10 <sup>-4</sup>	1.33	3.28 × 10 <sup>-3</sup>	
n-PrNH <sub>2</sub>	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>2.19 × 10<sup>-3</sup></b>
	5.93 × 10 <sup>-5</sup>	3.20 × 10 <sup>-1</sup>	1.01 × 10 <sup>-3</sup>	
	5.51 × 10 <sup>-5</sup>	6.10 × 10 <sup>-1</sup>	1.63 × 10 <sup>-3</sup>	
	7.21 × 10 <sup>-5</sup>	1.09	2.72 × 10 <sup>-3</sup>	
	7.18 × 10 <sup>-5</sup>	1.36	3.30 × 10 <sup>-3</sup>	
	7.10 × 10 <sup>-5</sup>	1.52	3.42 × 10 <sup>-3</sup>	
1-aminopropan-2-ol	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>2.23 × 10<sup>-3</sup></b>
	4.68 × 10 <sup>-4</sup>	1.24 × 10 <sup>-1</sup>	3.77 × 10 <sup>-4</sup>	
	4.69 × 10 <sup>-4</sup>	2.46 × 10 <sup>-1</sup>	6.52 × 10 <sup>-4</sup>	
	4.71 × 10 <sup>-4</sup>	3.64 × 10 <sup>-1</sup>	9.49 × 10 <sup>-4</sup>	
benzylamine	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>1.35 × 10<sup>-3</sup></b>
	4.51 × 10 <sup>-4</sup>	1.76 × 10 <sup>-1</sup>	3.78 × 10 <sup>-4</sup>	
	4.45 × 10 <sup>-4</sup>	3.50 × 10 <sup>-1</sup>	5.76 × 10 <sup>-4</sup>	
	4.55 × 10 <sup>-4</sup>	5.10 × 10 <sup>-1</sup>	8.40 × 10 <sup>-4</sup>	
diethanolamine	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>7.46 × 10<sup>-4</sup></b>
	3.47 × 10 <sup>-4</sup>	9.92 × 10 <sup>-2</sup>	2.01 × 10 <sup>-4</sup>	
	3.49 × 10 <sup>-4</sup>	1.96 × 10 <sup>-1</sup>	2.71 × 10 <sup>-4</sup>	
	3.28 × 10 <sup>-4</sup>	3.87 × 10 <sup>-1</sup>	4.23 × 10 <sup>-4</sup>	
2-aminobutan-1-ol	3.42 × 10 <sup>-4</sup>	0.00	1.36 × 10 <sup>-4</sup>	<b>3.13 × 10<sup>-4</sup></b>
	3.77 × 10 <sup>-4</sup>	3.92 × 10 <sup>-1</sup>	2.68 × 10 <sup>-4</sup>	
	3.80 × 10 <sup>-4</sup>	5.39 × 10 <sup>-1</sup>	2.94 × 10 <sup>-4</sup>	
	3.82 × 10 <sup>-4</sup>	7.56 × 10 <sup>-1</sup>	3.77 × 10 <sup>-4</sup>	

$k_{\text{obs}}$  vs. [Nu] correlations for the reactions of amines with 1-Cl<sub>2</sub>C in DMSO



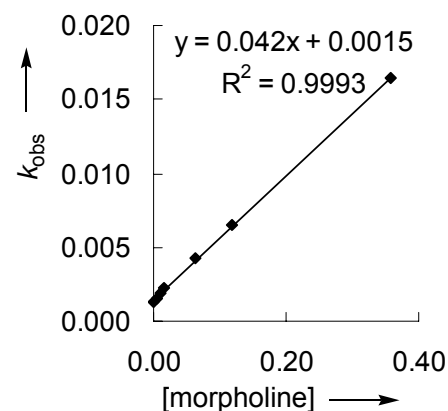
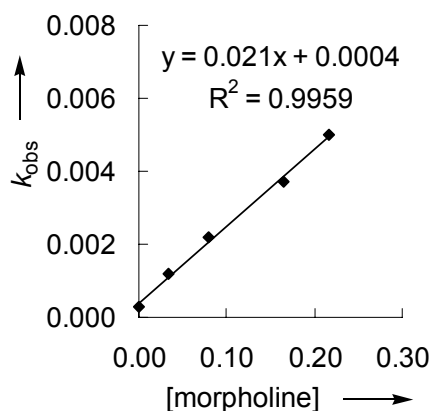
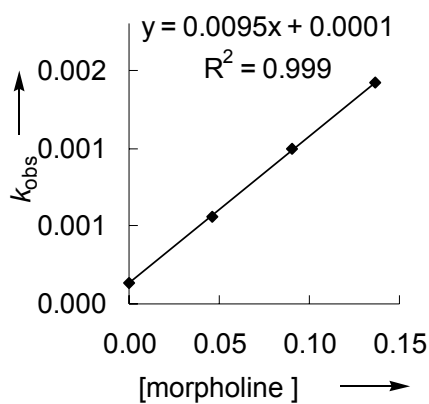
## Temperature Dependent Kinetics of the Reaction of 4,4'-Dichlorobenzhydryl Bromide with Morpholine (in DMSO, conductometry)

### Kinetics

For the measurements with  $[\text{morpholine}] = 0 \text{ mol L}^{-1}$  an excess of at least 5 equiv 2,6-lutidine was added in order to quench released HBr and avoid autocatalysis. The rates of the investigated solvolysis reactions were found to be independent of the concentration of 2,6-lutidine.

$T / ^\circ\text{C}$	$[\mathbf{1-Cl,Cl}]_0 / \text{M}$	$[\text{morpholine}] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$	$k_2 / \text{M}^{-1} \text{s}^{-1}$
20	$3.42 \times 10^{-4}$	0.00	$1.36 \times 10^{-4}$	$9.50 \times 10^{-3}$
	$4.85 \times 10^{-4}$	$4.60 \times 10^{-2}$	$5.60 \times 10^{-4}$	
	$4.81 \times 10^{-4}$	$9.03 \times 10^{-2}$	$1.00 \times 10^{-3}$	
	$4.86 \times 10^{-4}$	$1.36 \times 10^{-1}$	$1.42 \times 10^{-3}$	
35	$2.76 \times 10^{-4}$	0.00	$3.02 \times 10^{-4}$	$2.10 \times 10^{-2}$
	$2.70 \times 10^{-4}$	$1.65 \times 10^{-1}$	$3.69 \times 10^{-3}$	
	$2.90 \times 10^{-4}$	$3.46 \times 10^{-2}$	$1.18 \times 10^{-3}$	
	$2.85 \times 10^{-4}$	$8.03 \times 10^{-2}$	$2.18 \times 10^{-3}$	
	$2.84 \times 10^{-4}$	$2.16 \times 10^{-1}$	$5.02 \times 10^{-3}$	
50	$2.83 \times 10^{-4}$	$5.98 \times 10^{-3}$	$1.60 \times 10^{-3}$	$4.20 \times 10^{-2}$
	$2.67 \times 10^{-4}$	$1.06 \times 10^{-2}$	$1.87 \times 10^{-3}$	
	$2.74 \times 10^{-4}$	$1.51 \times 10^{-2}$	$2.22 \times 10^{-3}$	
	$2.73 \times 10^{-4}$	$5.47 \times 10^{-2}$	$1.25 \times 10^{-3}$	
	$2.89 \times 10^{-4}$	$6.37 \times 10^{-2}$	$4.26 \times 10^{-3}$	
	$2.88 \times 10^{-4}$	$1.18 \times 10^{-1}$	$6.56 \times 10^{-3}$	
	$2.49 \times 10^{-4}$	$3.58 \times 10^{-1}$	$1.64 \times 10^{-2}$	

$k_{\text{obs}}$  vs [morpholine] plots:

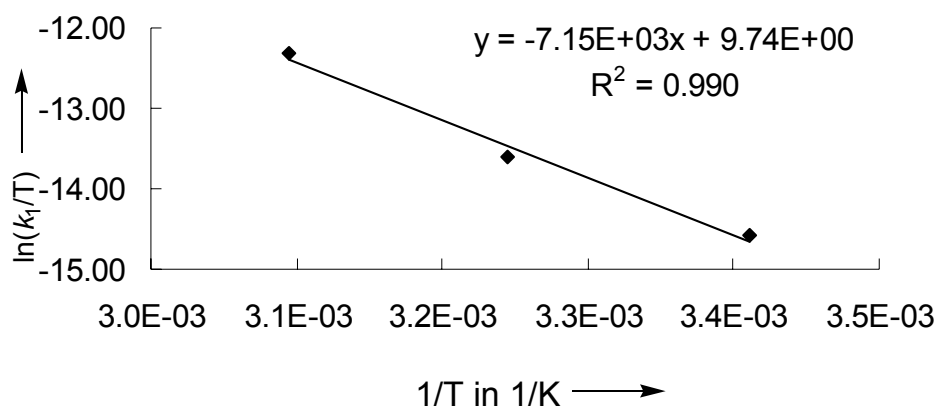


## Determination of the Eyring and Arrhenius activation parameters

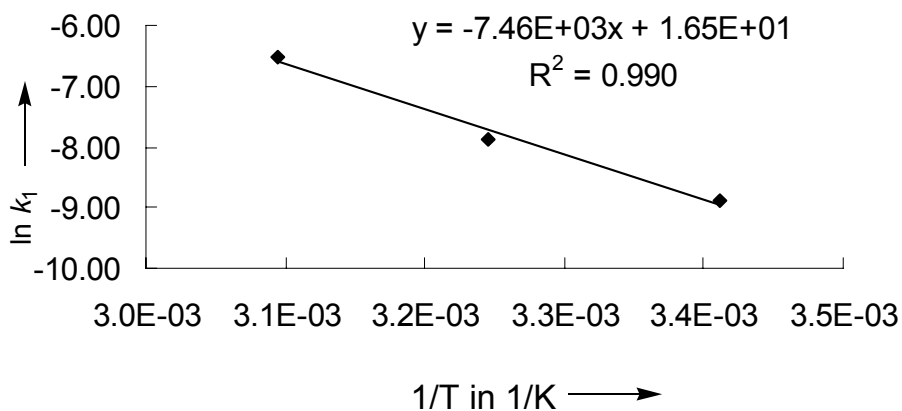
Eyring and Arrhenius plots for the rate constants  $k_1$  and  $k_2$  of the solvolysis of 4,4'-dichlorobenzhydryl bromide in DMSO ( $k_1$ ) and the reaction with morpholine ( $k_2$ ); both rate constants were derived from the linear fit of  $k_{\text{obs}}$  vs. [morpholine].

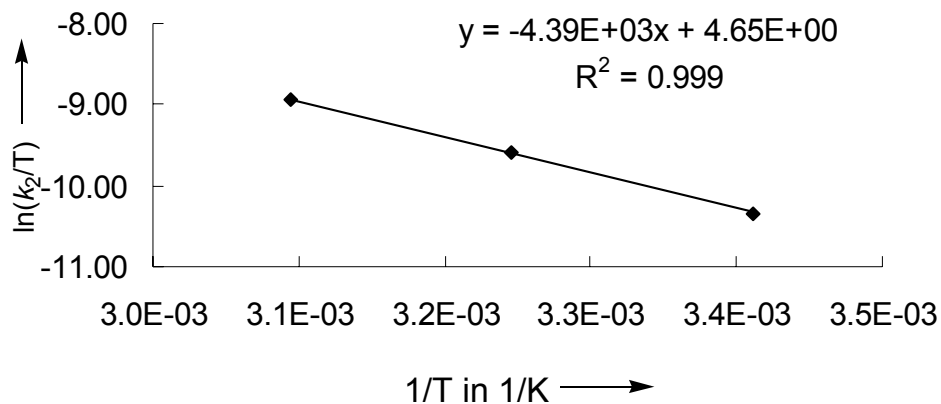
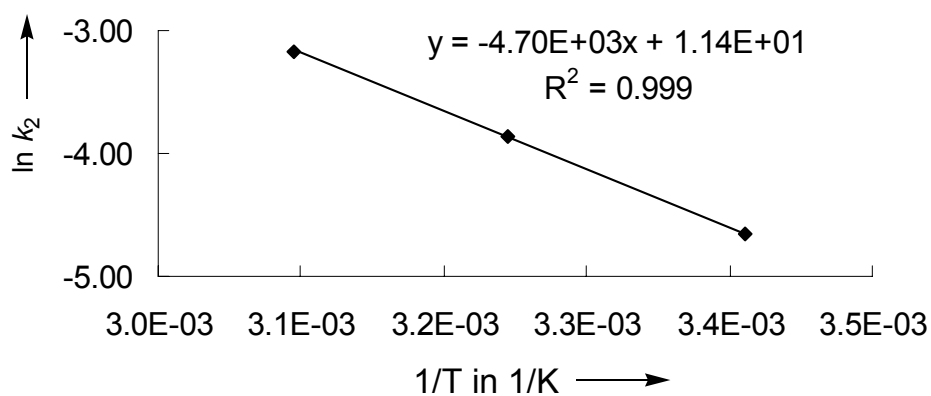
$T / \text{C}$	$k_1 / \text{s}^{-1}$	$k_2 / \text{M}^{-1}\text{s}^{-1}$
20	$1.36 \times 10^{-4}$	$9.50 \times 10^{-3}$
35	$3.85 \times 10^{-4}$	$2.10 \times 10^{-2}$
50	$1.45 \times 10^{-3}$	$4.20 \times 10^{-2}$

Eyring plot for  $k_1$



Arrhenius plot for  $k_1$



Eyring plot for  $k_2$ Arrhenius plot for  $k_2$ 

Eyring and Arrhenius activation parameters for the rate constants  $k_1$  and  $k_2$  of the solvolysis of 4,4'-dichlorobenzhydryl bromide in DMSO ( $k_{-1}$ ) and the reaction with morpholine ( $k_2$ ).

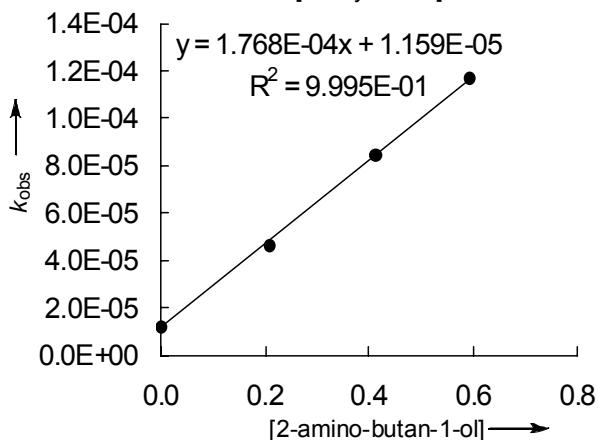
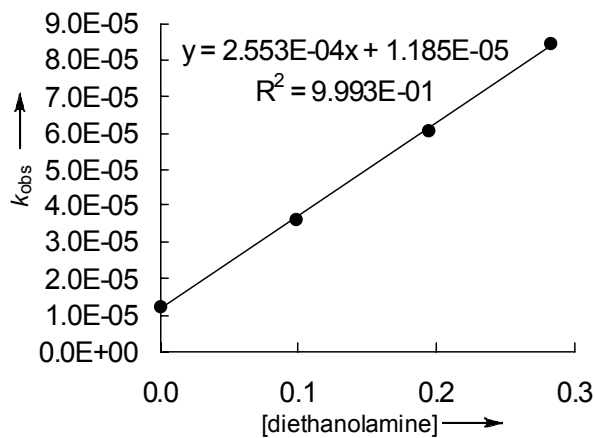
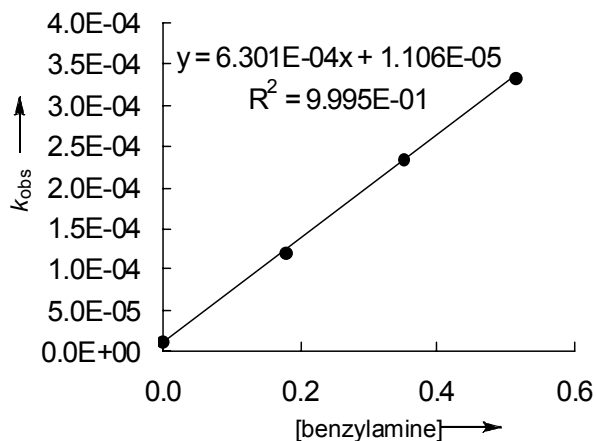
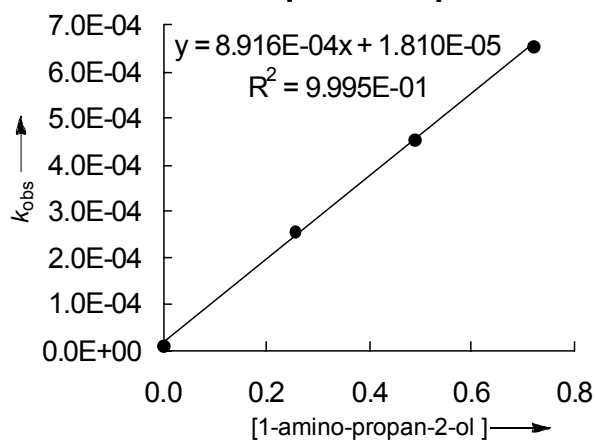
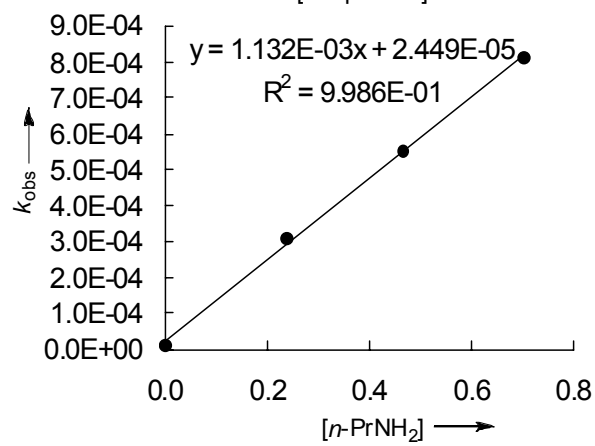
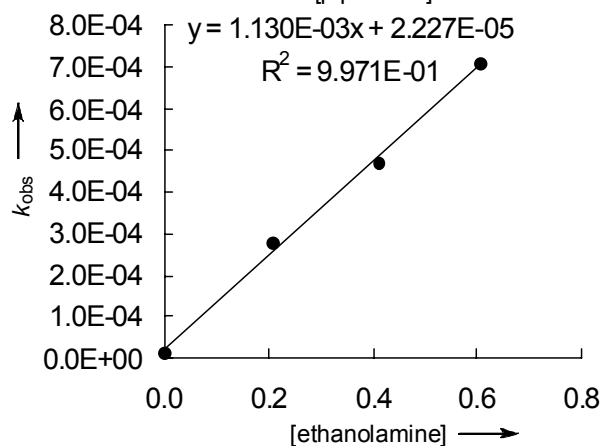
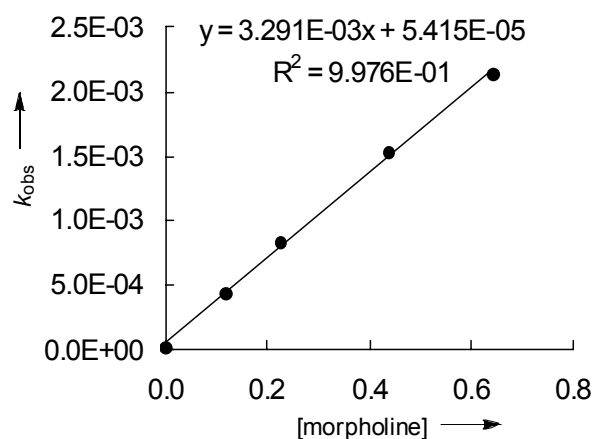
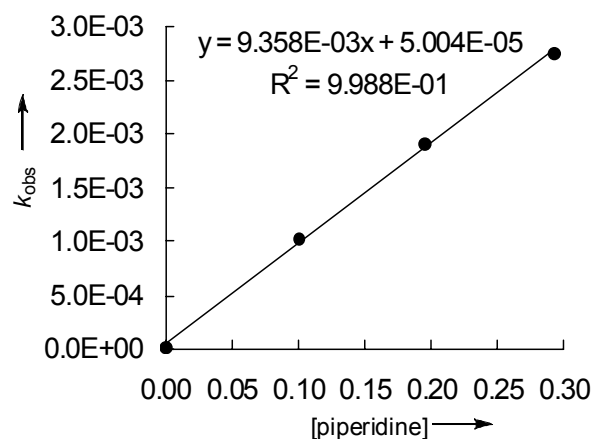
	for $k_1$	for $k_2$
$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$59.4 \pm 6.1$	$36.5 \pm 0.6$
$\Delta S^\ddagger / \text{J mol}^{-1} \text{K}^{-1}$	$-116.7 \pm 19.8$	$-159.0 \pm 1.8$
$E_a / \text{kJ mol}^{-1}$	$62.0 \pm 6.1$	$39.0 \pm 0.5$
$\ln A$	$16.4 \pm 2.4$	$11.4 \pm 0.2$

## 4.5 4-Trifluoromethyl-benzhydryl bromide

20 °C, in DMSO, conductometry

Nu	[1-CF <sub>3</sub> H] <sub>0</sub> / M	[Nu] / M	k <sub>obs</sub> / s <sup>-1</sup>	k <sub>2</sub> / M <sup>-1</sup> s <sup>-1</sup>
piperidine	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>9.36 × 10<sup>-3</sup></b>
	2.35 × 10 <sup>-4</sup>	1.00 × 10 <sup>-1</sup>	1.03 × 10 <sup>-3</sup>	
	2.37 × 10 <sup>-4</sup>	1.95 × 10 <sup>-1</sup>	1.90 × 10 <sup>-3</sup>	
	2.36 × 10 <sup>-4</sup>	2.93 × 10 <sup>-1</sup>	2.76 × 10 <sup>-3</sup>	
morpholine	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>3.29 × 10<sup>-3</sup></b>
	2.45 × 10 <sup>-4</sup>	1.16 × 10 <sup>-1</sup>	4.41 × 10 <sup>-4</sup>	
	2.41 × 10 <sup>-4</sup>	2.24 × 10 <sup>-1</sup>	8.27 × 10 <sup>-4</sup>	
	2.47 × 10 <sup>-4</sup>	4.38 × 10 <sup>-1</sup>	1.54 × 10 <sup>-3</sup>	
	2.44 × 10 <sup>-4</sup>	6.44 × 10 <sup>-1</sup>	2.13 × 10 <sup>-3</sup>	
ethanolamine	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>1.13 × 10<sup>-3</sup></b>
	5.53 × 10 <sup>-4</sup>	2.08 × 10 <sup>-1</sup>	2.79 × 10 <sup>-4</sup>	
	5.50 × 10 <sup>-4</sup>	4.11 × 10 <sup>-1</sup>	4.73 × 10 <sup>-4</sup>	
	5.28 × 10 <sup>-4</sup>	6.05 × 10 <sup>-1</sup>	7.08 × 10 <sup>-4</sup>	
n-PrNH <sub>2</sub>	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>1.13 × 10<sup>-3</sup></b>
	2.39 × 10 <sup>-4</sup>	2.38 × 10 <sup>-1</sup>	3.10 × 10 <sup>-4</sup>	
	2.41 × 10 <sup>-4</sup>	4.66 × 10 <sup>-1</sup>	5.56 × 10 <sup>-4</sup>	
	2.45 × 10 <sup>-4</sup>	7.02 × 10 <sup>-1</sup>	8.11 × 10 <sup>-4</sup>	
1-aminopropan-2-ol	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>8.92 × 10<sup>-4</sup></b>
	5.51 × 10 <sup>-4</sup>	2.57 × 10 <sup>-1</sup>	2.55 × 10 <sup>-4</sup>	
	5.49 × 10 <sup>-4</sup>	4.89 × 10 <sup>-1</sup>	4.56 × 10 <sup>-4</sup>	
	5.48 × 10 <sup>-4</sup>	7.20 × 10 <sup>-1</sup>	6.56 × 10 <sup>-4</sup>	
benzylamine	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>6.30 × 10<sup>-4</sup></b>
	2.37 × 10 <sup>-4</sup>	1.79 × 10 <sup>-1</sup>	1.20 × 10 <sup>-4</sup>	
	2.49 × 10 <sup>-4</sup>	3.50 × 10 <sup>-1</sup>	2.35 × 10 <sup>-4</sup>	
	2.48 × 10 <sup>-4</sup>	5.14 × 10 <sup>-1</sup>	3.34 × 10 <sup>-4</sup>	
diethanolamine	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>2.55 × 10<sup>-4</sup></b>
	3.83 × 10 <sup>-4</sup>	9.78 × 10 <sup>-2</sup>	3.62 × 10 <sup>-5</sup>	
	3.85 × 10 <sup>-4</sup>	1.94 × 10 <sup>-1</sup>	6.06 × 10 <sup>-5</sup>	
	3.82 × 10 <sup>-4</sup>	2.82 × 10 <sup>-1</sup>	8.46 × 10 <sup>-5</sup>	
2-aminobutan-1-ol	2.55 × 10 <sup>-4</sup>	0.00	1.25 × 10 <sup>-5</sup>	<b>1.77 × 10<sup>-4</sup></b>
	5.42 × 10 <sup>-4</sup>	2.07 × 10 <sup>-1</sup>	4.70 × 10 <sup>-5</sup>	
	5.46 × 10 <sup>-4</sup>	4.13 × 10 <sup>-1</sup>	8.42 × 10 <sup>-5</sup>	
	5.45 × 10 <sup>-4</sup>	5.92 × 10 <sup>-1</sup>	1.17 × 10 <sup>-4</sup>	

$k_{\text{obs}}$  vs. [Nu] correlations for the reactions of amines with **1**-CF<sub>3</sub>H in DMSO

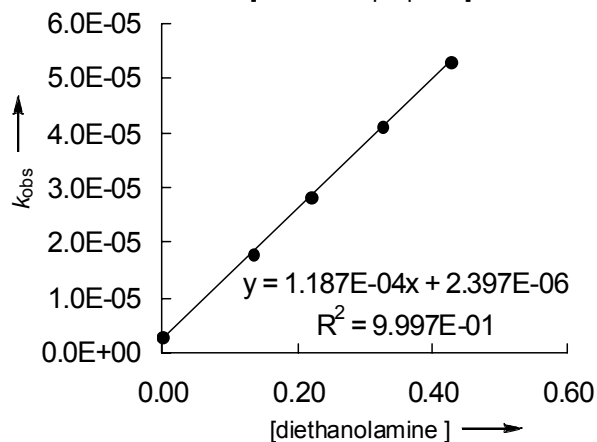
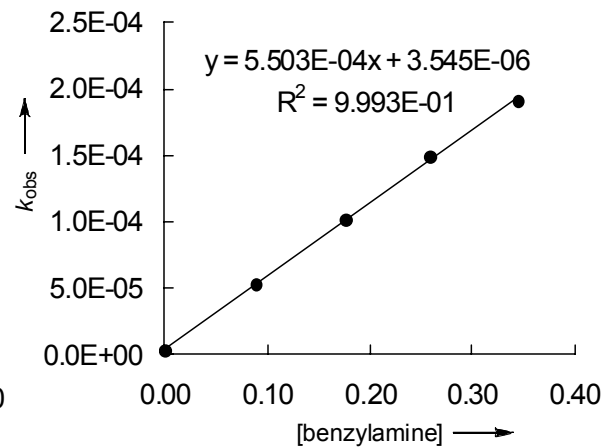
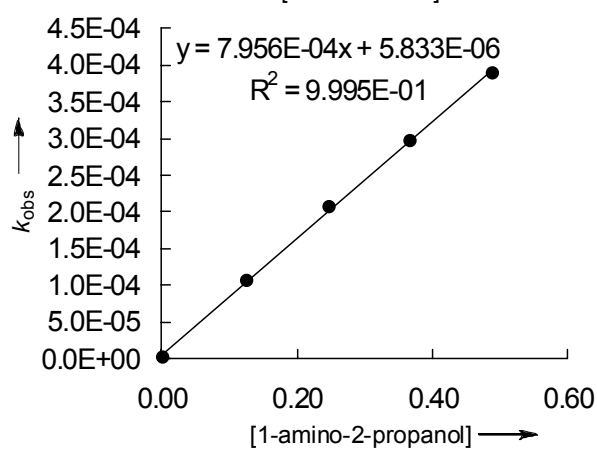
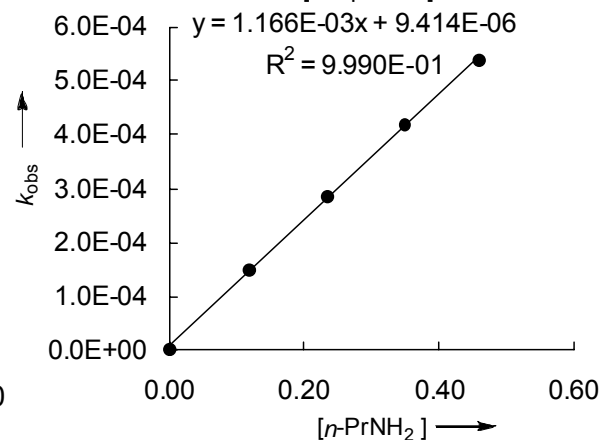
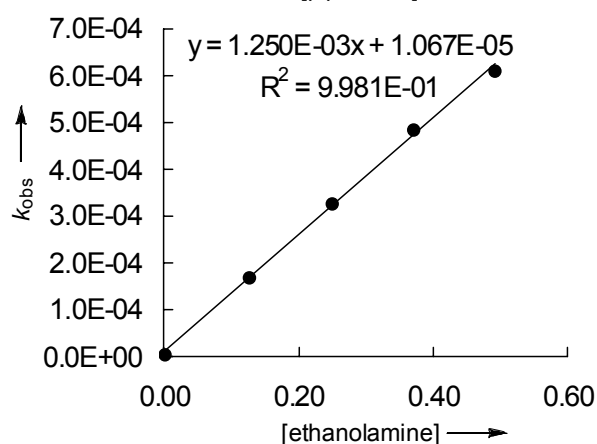
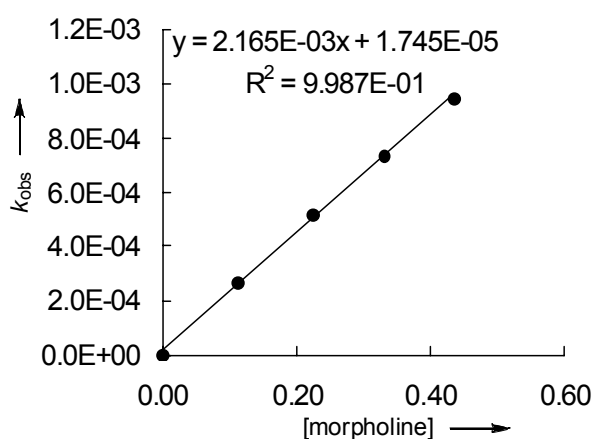
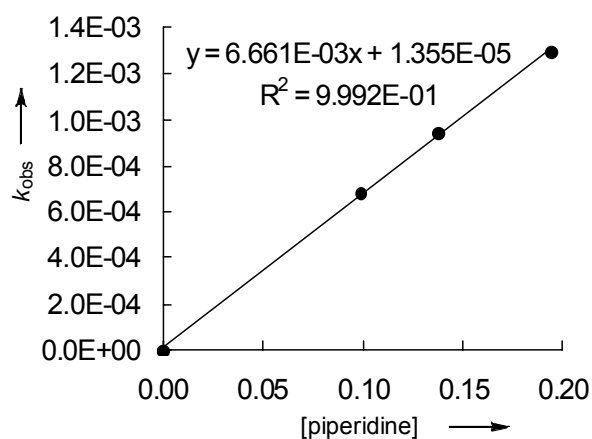


#### 4.6 4,4'-Bis(trifluoromethyl)benzhydryl bromide

20 °C, in DMSO, conductometry

Nu	$[1\text{-CF}_3\text{,CF}_3]_0 / \text{M}$	$[\text{Nu}] / \text{M}$	$k_{\text{obs}} / \text{s}^{-1}$	$k_2 / \text{M}^{-1} \text{s}^{-1}$
piperidine	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>6.66 \times 10^{-3}</math></b>
	$7.96 \times 10^{-5}$	$9.85 \times 10^{-2}$	$6.85 \times 10^{-4}$	
	$4.95 \times 10^{-4}$	$1.38 \times 10^{-1}$	$9.44 \times 10^{-4}$	
	$5.01 \times 10^{-4}$	$1.94 \times 10^{-1}$	$1.29 \times 10^{-3}$	
morpholine	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>2.17 \times 10^{-3}</math></b>
	$7.96 \times 10^{-5}$	$1.11 \times 10^{-1}$	$2.66 \times 10^{-4}$	
	$6.95 \times 10^{-5}$	$2.23 \times 10^{-1}$	$5.16 \times 10^{-4}$	
	$7.94 \times 10^{-5}$	$3.29 \times 10^{-1}$	$7.34 \times 10^{-4}$	
	$7.95 \times 10^{-5}$	$4.34 \times 10^{-1}$	$9.44 \times 10^{-4}$	
ethanolamine	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>1.25 \times 10^{-3}</math></b>
	$3.96 \times 10^{-4}$	$1.26 \times 10^{-1}$	$1.71 \times 10^{-4}$	
	$3.95 \times 10^{-4}$	$2.49 \times 10^{-1}$	$3.27 \times 10^{-4}$	
	$3.94 \times 10^{-4}$	$3.70 \times 10^{-1}$	$4.86 \times 10^{-4}$	
	$3.93 \times 10^{-4}$	$4.91 \times 10^{-1}$	$6.11 \times 10^{-4}$	
<i>n</i> -PrNH <sub>2</sub>	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>1.17 \times 10^{-3}</math></b>
	$3.97 \times 10^{-4}$	$1.19 \times 10^{-1}$	$1.52 \times 10^{-4}$	
	$3.98 \times 10^{-4}$	$2.34 \times 10^{-1}$	$2.87 \times 10^{-4}$	
	$3.98 \times 10^{-4}$	$3.48 \times 10^{-1}$	$4.21 \times 10^{-4}$	
	$3.99 \times 10^{-4}$	$4.61 \times 10^{-1}$	$5.39 \times 10^{-4}$	
1-aminopropan-2-ol	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>7.96 \times 10^{-4}</math></b>
	$2.85 \times 10^{-4}$	$1.25 \times 10^{-1}$	$1.06 \times 10^{-4}$	
	$3.46 \times 10^{-4}$	$2.47 \times 10^{-1}$	$2.07 \times 10^{-4}$	
	$3.03 \times 10^{-4}$	$3.66 \times 10^{-1}$	$2.98 \times 10^{-4}$	
	$3.05 \times 10^{-4}$	$4.87 \times 10^{-1}$	$3.90 \times 10^{-4}$	
benzylamine	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>5.50 \times 10^{-4}</math></b>
	$3.59 \times 10^{-4}$	$8.88 \times 10^{-2}$	$5.21 \times 10^{-5}$	
	$3.61 \times 10^{-4}$	$1.76 \times 10^{-1}$	$1.01 \times 10^{-4}$	
	$3.62 \times 10^{-4}$	$2.59 \times 10^{-1}$	$1.49 \times 10^{-4}$	
	$3.60 \times 10^{-4}$	$3.45 \times 10^{-1}$	$1.91 \times 10^{-4}$	
diethanolamine	$2.46 \times 10^{-4}$	0.00	$2.76 \times 10^{-6}$	<b><math>1.19 \times 10^{-4}</math></b>
	$2.85 \times 10^{-4}$	$1.35 \times 10^{-1}$	$1.79 \times 10^{-5}$	
	$3.46 \times 10^{-4}$	$2.21 \times 10^{-1}$	$2.85 \times 10^{-5}$	
	$3.03 \times 10^{-4}$	$3.26 \times 10^{-1}$	$4.13 \times 10^{-5}$	
	$3.05 \times 10^{-4}$	$4.25 \times 10^{-1}$	$5.29 \times 10^{-5}$	

$k_{\text{obs}}$  vs. [Nu] correlations for the reactions of amines with **1**-CF<sub>3</sub>,CF<sub>3</sub> in DMSO



## 5 Product Studies

### 5.1 Method

The product studies were carried out for several representative systems to examine the ratios of the products formed during the reactions of benzhydryl bromides with 0.2 M solutions of amines in DMSO.

The concentrations of the components in the reaction mixtures were determined by GC with a flame ionization detector (FID) using n-hexadecane (C16) as an internal standard.

The ratio of the peak area of a compound ( $A_{Cpd}$ ) to the peak area of a given standard ( $A_{Std}$ ), is not equal to the ratio of the molar amount of the compound [ $Cpd$ ] to the molar amount of the standard [ $Std$ ]. Therefore, the specific sensitivity of the FID for different molecules was accounted for by defining relative molar response (RMR) factors (equation S3) for each of the possible products which were synthesized independently (Section 5.2).

$$\frac{[Cpd]}{[Std]} = RMR \frac{A_{Cpd}}{A_{Std}} \quad (S3)$$

In Section 5.3, the retention times ( $t_R$  in min) and the  $RMR$  values for each product with respect to C16 (= Std) were determined from the peak areas in chromatograms with known [ $Cpd$ ] and [ $Std$ ] (equation S4).

$$RMR = \frac{[Cpd]A_{Std}}{[Std]A_{Cpd}} \quad (S4)$$

Thus, the product concentrations tabulated in Section 5.4 were calculated according to equation (S5)

$$[Cpd] = RMR[Std] \frac{A_{Cpd}}{A_{Std}} \quad (S5)$$

in which  $A_{Cpd}$  and  $A_{Std}$  are the peak areas of the compound and the standard C16, respectively, and [ $Std$ ] is the known concentration of the internal standard C16.

## 5.2 Synthesis of Compounds for GC Calibrations

*General Procedure A (GP A):* A solution of the amine (20 equiv) in DMSO (10 mL) was mixed with the benzhydryl bromide (1 equiv.). The solution was stirred at room temperature for 12 h, then poured on water (100 mL) and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic phases were washed with water (25 mL) and dried with MgSO<sub>4</sub>. Evaporation of the solvent in the vacuum gave the crude product which was purified as described below.

*General Procedure B (GP B):* A solution of the benzhydryl bromide in CH<sub>3</sub>CN (10 mL) was prepared. After addition of amine (2.5 equiv), the solution was stirred at room temperature for 12 h, then poured on water (100 mL) and extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic phases were washed with water (25 mL) and dried with MgSO<sub>4</sub>. Evaporation of the solvent in the vacuum gave the crude product which was purified as described below.

**(4,4'-Dichlorobenzhydryl)-propyl-amine** (GP A) was obtained from 4,4'-dichlorobenzhydryl bromide (3.0 g, 9.5 mmol) and n-propylamine (11.2 g, 189 mmol). The crude product was distilled in the vacuum (127–137 °C/1 × 10<sup>-3</sup> mbar): colorless oil (1.6 g, 57 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.30 (d, *J* = 8.7 Hz, 4 H, ArH), 7.24 (d, *J* = 8.7 Hz, 4 H, ArH), 4.74 (s, 1 H, CHN), 2.49 (t, *J* = 6.9 Hz, 2 H), 1.51 (sext, *J* = 7.2 Hz, 2 H), 1.47 (br s, 1 H, NH), 0.90 ppm (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 142.5, 132.8, 128.7, 128.5, 66.3, 50.0, 23.3, 11.8 ppm; MS (EI): *m/z* = 295, 293, 235; HR-MS (EI): Calcd *m/z* for C<sub>16</sub>H<sub>17</sub><sup>35</sup>Cl<sub>2</sub>N: 293.0740, Found: 293.0732.

***N*-(4,4'-Dichlorobenzhydryl)-piperidine** (GP A) was obtained from 4,4'-dichlorobenzhydryl bromide (3.5 g, 11 mmol) and piperidine (18.9 g, 221 mmol) after purification of the crude product by crystallization from methanol: colorless crystals (3.0 g, 85 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.28 (d, *J* = 8.5 Hz, 4 H, ArH), 7.21 (d, *J* = 8.6 Hz, 4 H, ArH), 4.18 (s, 1 H), 2.26–2.25 (m, 4 H), 1.57–1.50 (m, 4 H), 1.44–1.38 ppm (m, 2 H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 141.2, 132.5, 129.2, 128.6, 75.1, 52.9, 26.2, 24.5 ppm. MS (EI): *m/z* = 321, 319, 235; HR-MS (EI): Calcd *m/z* for C<sub>18</sub>H<sub>19</sub><sup>35</sup>Cl<sub>2</sub>N: 319.0895, Found: 319.0885.

***N*-(4,4'-Dichlorobenzhydryl)-morpholine** (GP A) was obtained from 4,4'-dichlorobenzhydryl bromide (2.5 g, 7.9 mmol) and morpholine (13.8 g, 158 mmol) after purification of the crude product by crystallization from methanol: colorless crystals.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32 (d,  $J = 8.4$  Hz, 4 H, ArH), 7.24 (d,  $J = 8.7$  Hz, 4 H, ArH), 4.16 (s, 1 H), 3.71–3.68 (m, 4 H), 2.36–2.33 ppm (m, 4 H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.4, 133.0, 129.1, 128.9, 77.1, 67.1, 52.5 ppm; MS (EI):  $m/z = 322, 323$ ; HR-MS (EI): Calcd  $m/z$  for  $\text{C}_{17}\text{H}_{17}^{35}\text{Cl}_2\text{NO}$ : 321.0687, Found: 321.0680.

**Benzhydryl-propyl-amine** (GP B) was obtained from benzhydryl bromide (3.0 g, 12 mmol) and propylamine (1.8 g, 30 mmol). The crude product was distilled in the vacuum (150-152 °C /  $2.1 \times 10^{-2}$  mbar): colorless oil (1.85 g, 68 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J = 7.4$  Hz, 4 H), 7.27 (t,  $J = 7.2$  Hz, 4 H), 7.17 (t,  $J = 7.0$  Hz, 2 H), 4.80 (s, 1 H), 2.53 (t,  $J = 7.0$  Hz, 2 H), 1.52 (sext,  $J = 7.3$  Hz, 2 H), 1.46 (br s, 1 H, NH), 0.90 ppm (s,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.4, 128.4, 127.2, 126.8, 67.5, 50.2, 23.3, 11.8 ppm; MS (EI):  $m/z = 225, 196$ ; HR-MS (EI): Calcd  $m/z$  for  $\text{C}_{16}\text{H}_{19}\text{N}$ : 225.1518, Found: 225.1504.

***N*-Benzhydryl-piperidine** (GP B) was obtained from benzhydryl bromide (2.5 g, 10 mmol) and piperidine (2.2 g, 26 mmol) after purification of the crude product by crystallization from methanol: colorless crystals (1.6 g, 64 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J_{\text{HH}} = 7.3$  Hz, 4 H), 7.23 (t,  $J = 7.3$  Hz, 4 H), 7.13 (t,  $J = 7.2$  Hz, 2 H), 4.22 (s, 1 H), 2.35–2.28 (m, 4 H), 1.59-1.51 (m, 4 H), 1.45–1.37 ppm (m, 2 H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 128.3, 128.0, 126.6, 76.7, 53.1, 26.3, 24.7 ppm; MS (EI):  $m/z = 252, 251, 174, 167$ ; HR-MS (EI): Calcd  $m/z$  for  $\text{C}_{18}\text{H}_{21}\text{N}$ : 251.1674, Found: 251.1663.

***N*-Benzhydryl-morpholine** (GP B) was obtained from benzhydryl bromide (2.0 g, 8.1 mmol) and morpholine (1.8 g, 21 mmol) after purification of the crude product by crystallization from methanol: colorless crystals (1.6 g, 78 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (d,  $J = 7.2$  Hz, 4 H), 7.24 (t,  $J = 7.2$  Hz, 4 H), 7.14 (t,  $J = 7.3$  Hz, 2 H), 4.80 (s, 1 H), 3.70–3.67 (m, 4 H), 2.38–2.35 ppm (m, 4 H);  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.3, 128.5, 127.9, 126.9, 76.6, 67.1, 52.6 ppm; MS (EI):  $m/z = 254, 253, 176, 167$ ; HR-MS (EI): Calcd  $m/z$  for  $\text{C}_{16}\text{H}_{19}\text{N}$ : 253.1467, Found: 253.1461.

**(4-Methylbenzhydryl)-propyl-amine** (GP B) was obtained from 4-methylbenzhydryl bromide (1.5 g (5.7 mmol) and *n*-propylamine (0.85 g, 14 mmol) after purification of the crude product by chromatography (silica gel, 10/1 → 5/1 *n*-pentane/ethyl acetate, v/v): colorless oil (0.70 g, 51 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.38 (d, *J* = 7.4 Hz, 2 H), 7.28-7.14 (m, 5 H), 7.08 (d, *J* = 7.8 Hz, 2 H), 4.77 (s, 1 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H, CH<sub>3</sub>), 1.52 (sext, *J* = 7.2 Hz, 2 H), 1.46 (s, 1 H, NH), 0.90 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 144.7, 141.6, 136.5, 129.2, 128.5, 127.3, 127.2, 126.8, 67.3, 50.3, 23.4, 21.1, 11.9; MS (EI): *m/z* = 240, 239, 181; HR-MS (EI): Calcd *m/z* for C<sub>17</sub>H<sub>21</sub>N: 239.1674, Found: 239.1670.

***N*-(4-Methylbenzhydryl)-piperidine** (GP B) was obtained from 4-methylbenzhydryl bromide (1.5 g, 5.7 mmol) and piperidine (1.2 g, 14 mmol) after purification of the crude product by chromatography (silica gel, 15/1 *n*-pentane/ethyl acetate, v/v): colorless oil (0.79 g, 52 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.46 (d, *J* = 7.5 Hz, 2 H), 7.36–7.18 (m, 5 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 4.26 (s, 1 H), 2.38 (br t, 4 H), 2.34 (br s, 3 H), 1.66–1.59 (m, 4 H), 1.52-1.45 ppm (m, 2 H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 143.5, 140.2, 136.1, 129.0, 128.3, 127.9, 126.5, 76.4, 53.1, 26.3, 24.7, 21.0 ppm; MS (EI): *m/z* = 266, 265, 181; HR-MS (EI): Calcd *m/z* for C<sub>19</sub>H<sub>23</sub>N: 265.1831, Found: 265.1828.

***N*-(4-Methylbenzhydryl)-morpholine** (GP B) was obtained from 4-methylbenzhydryl bromide (1.5 g, 5.7 mmol) and morpholine (1.3 g, 15 mmol) after purification of the crude product by chromatography (silica gel, 20/1 *n*-pentane/ethyl acetate, v/v): colorless oil (1.1 g, 72 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.41 (d, *J* = 7.5 Hz, 2 H), 7.40–7.12 (m, 5 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 4.15 (s, 1 H), 3.69 (br t, *J* = 4.6 Hz, 4 H), 2.37 (br t, *J* = 4.2 Hz, 4 H), 2.26 ppm (s, 3 H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ 142.5, 139.3, 136.5, 129.2, 128.5, 127.8, 127.8, 126.9, 76.4, 67.1, 52.6, 21.0 ppm.

**Benzhydryl Methyl Ether** was synthesized in analogy to a procedure by Olah and Welch.<sup>S3</sup> Benzhydrol (10 g) was dissolved in methanol (120 mL). After addition of a catalytic amount of trifluoromethanesulfonic acid (approximately 0.5 mL) the mixture was heated to reflux for 2.5 h. Then

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(S3) Olah, G. A.; Welch, J. *J. Am. Chem. Soc.* **1978**, *100*, 5396–5402.

the solvent was removed under reduced pressure. The resulting oil was poured on water (100 mL) and a spatula tip of  $K_2CO_3$  was added. The mixture was extracted with 1/1 n-pentane/diethylether ( $3 \times 50$  mL). The combined organic phases were dried over  $MgSO_4$ . Evaporation of the solvent gave the crude product as a colorless oil. For purification the product was distilled from sodium in the vacuum (83–84 °C/ $1 \times 10^{-3}$  mbar) to give a colorless oil (7.8 g, 72 %).  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.34–7.16 (m, 10 H, ArH), 5.20 (s, 1 H, CHOMe), 3.33 ppm (s, 3 H, Me);  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ ):  $\delta$  142.0, 128.3, 126.8, 127.3, 85.3, 56.8 ppm; MS (EI):  $m/z$  = 199, 198 [ $M^+$ ], 167; HR-MS (EI): Calcd  $m/z$  for  $C_{14}H_{14}O$ : 198.1045, Found: 198.1056.

### 5.3 Standardization

As defined in equation (S4) the relative molar response (*RMR*) factors of benzophenone, benzhydrol, and several representative benzhydryl amines was determined by GC with respect to *n*-hexadecane (C<sub>16</sub>) used as an internal standard.

**X,Y = Me,H**

	<i>c</i> / mol L <sup>-1</sup>	average A	RMR	<i>t<sub>R</sub></i> / min	average <i>RMR</i>
C16	1.46 × 10 <sup>-3</sup>	18252107		5.20	1.29
4-methylbenzhydrol <sup>a</sup>	6.21 × 10 <sup>-3</sup>	59502760	1.31	9.84	
C16	1.46 × 10 <sup>-3</sup>	17548737			1.28
4-methylbenzhydrol <sup>a</sup>	1.24 × 10 <sup>-2</sup>	116746533	1.28		
C16	1.46 × 10 <sup>-3</sup>	17516347			1.29
4-methylbenzhydrol <sup>a</sup>	1.86 × 10 <sup>-2</sup>	173877367	1.29		
	<i>c</i> / mol L <sup>-1</sup>	average A	RMR	<i>t<sub>R</sub></i> / min	average <i>RMR</i>
C16	1.46 × 10 <sup>-3</sup>	17991280			1.29
4-methylbenzophenone <sup>a</sup>	5.72 × 10 <sup>-3</sup>	55033793	1.28	9.96	
C16	1.46 × 10 <sup>-3</sup>	18125710			1.29
4-methylbenzophenone <sup>a</sup>	1.14 × 10 <sup>-2</sup>	110819800	1.29		
C16	1.46 × 10 <sup>-3</sup>	17433973			1.29
4-methylbenzophenone <sup>a</sup>	1.72 × 10 <sup>-2</sup>	159565800	1.29		
	<i>c</i> / mol L <sup>-1</sup>	average A	RMR	<i>t<sub>R</sub></i> / min	average <i>RMR</i>
C16	1.46 × 10 <sup>-3</sup>	18392697		5.22	1.07
<i>N</i> -(4-methylbenzhydryl)morpholine	1.85 × 10 <sup>-3</sup>	22421527	1.04	13.1	
C16	1.46 × 10 <sup>-3</sup>	17689997			1.09
<i>N</i> -(4-methylbenzhydryl)morpholine	7.41 × 10 <sup>-3</sup>	82840557	1.09		
C16	1.46 × 10 <sup>-3</sup>	17577083			1.12
<i>N</i> -(4-methylbenzhydryl)morpholine	1.48 × 10 <sup>-2</sup>	159630267	1.12		
C16	1.46 × 10 <sup>-3</sup>	17779833			1.03
<i>N</i> -(4-methylbenzhydryl)morpholine	3.70 × 10 <sup>-3</sup>	44007437	1.03		

**X,Y = Me,H** (Continued)

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average <i>RMR</i>
C16	$1.46 \times 10^{-3}$	18424133		5.22	1.07
<i>N</i> -(4-methylbenzhydryl)-propyl-amine	$2.69 \times 10^{-3}$	33041727	1.03	10.14	
C16	$1.46 \times 10^{-3}$	17794760			1.07
<i>N</i> -(4-methylbenzhydryl)-propyl-amine	$5.38 \times 10^{-3}$	61645867	1.07		
C16	$1.46 \times 10^{-3}$	18698703			1.08
<i>N</i> -(4-methylbenzhydryl)-propyl-amine	$1.08 \times 10^{-2}$	127503300	1.08		
C16	$1.46 \times 10^{-3}$	18647680			1.11
<i>N</i> -(4-methylbenzhydryl)-propyl-amine	$1.61 \times 10^{-2}$	185498700	1.11		

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average <i>RMR</i>
C16	$1.46 \times 10^{-3}$	17841197		5.22	1.06
<i>N</i> -(4-methylbenzhydryl)piperidine	$1.78 \times 10^{-3}$	22589587	0.96	12.24	
C16	$1.46 \times 10^{-3}$	18263093			1.15
<i>N</i> -(4-methylbenzhydryl)piperidine	$3.70 \times 10^{-3}$	40523610	1.15		
C16	$1.46 \times 10^{-3}$	18352357			1.06
<i>N</i> -(4-methylbenzhydryl)piperidine	$7.41 \times 10^{-3}$	88217353	1.06		
C16	$1.46 \times 10^{-3}$	17164033			1.06
<i>N</i> -(4-methylbenzhydryl)piperidine	$1.48 \times 10^{-2}$	165438033	1.06		

<sup>a</sup> In the case of 4-methylbenzophenone and 4-methylbenzhydrol the retention time and *RMR* value were almost identical.

**X,Y = H,H**

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.08 \times 10^{-3}$	12616997		5.18	
benzhydrol	$5.13 \times 10^{-4}$	5118717	1.17	8.34	1.17
benzophenone	$2.36 \times 10^{-3}$	21475193	1.28	7.98	1.34
<i>N</i> -benzhydrylpiperidine	$1.35 \times 10^{-3}$	18003217	0.88	11.12	0.90
C16	$1.08 \times 10^{-3}$	12787997			
benzhydrol	$1.03 \times 10^{-3}$	10627827	1.14		
benzophenone	$5.90 \times 10^{-4}$	5126065	1.36		
<i>N</i> -benzhydrylpiperidine	$4.51 \times 10^{-4}$	5675417	0.94		
C16	$1.08 \times 10^{-3}$	13296300			
benzhydrol	$1.54 \times 10^{-3}$	16139817	1.17		
benzophenone	$1.18 \times 10^{-3}$	10621647	1.37		
<i>N</i> -benzhydrylpiperidine	$9.02 \times 10^{-4}$	12755333	0.87		
C16	$1.08 \times 10^{-3}$	13162683			
benzhydrol	$2.56 \times 10^{-4}$	2615610	1.19		
benzophenone	$1.89 \times 10^{-3}$	17007627	1.35		

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.09 \times 10^{-3}$	12668245		5.18	
benzhydryl-propyl-amine	$7.55 \times 10^{-3}$	76862430	1.14	9.12	1.11
C16	$1.09 \times 10^{-3}$	13187900			
benzhydryl-propyl-amine	$1.13 \times 10^{-2}$	117953400	1.16		
C16	$1.09 \times 10^{-3}$	13471903			
benzhydryl-propyl-amine	$5.66 \times 10^{-3}$	63520567	1.10		
C16	$1.09 \times 10^{-3}$	13104907			
benzhydryl-propyl-amine	$1.89 \times 10^{-3}$	22196133	1.02		

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.09 \times 10^{-3}$	13028710		5.18	
<i>N</i> -benzhydrylmorpholine	$1.47 \times 10^{-3}$	16938615	1.04	12.00	1.04
C16	$1.09 \times 10^{-3}$	13394560			
<i>N</i> -benzhydrylmorpholine	$2.21 \times 10^{-3}$	25147613	1.08		
C16	$1.09 \times 10^{-3}$	12996903			
<i>N</i> -benzhydrylmorpholine	$1.10 \times 10^{-3}$	13195633	1.00		
C16	$1.09 \times 10^{-3}$	13028693			
<i>N</i> -benzhydrylmorpholine	$5.15 \times 10^{-3}$	59620750	1.03		

**X,Y = H,H** (Continued)

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.16 \times 10^{-3}$	14734243		5.22	1.02
benzhydryl methyl ether	$4.64 \times 10^{-3}$	59440763	0.99	6.94	
C16	$1.16 \times 10^{-3}$	15104223			1.01
benzhydryl methyl ether	$9.27 \times 10^{-3}$	119391333	1.01		
C16	$1.16 \times 10^{-3}$	14696190			1.02
benzhydryl methyl ether	$1.39 \times 10^{-2}$	172305233	1.02		
C16	$1.16 \times 10^{-3}$	15661193			1.04
benzhydryl methyl ether	$1.85 \times 10^{-2}$	239973200	1.04		

**X,Y = Cl,Cl**

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.13 \times 10^{-3}$	13573363		5.18	1.52
4,4'-dichlorobenzhydrol	$1.23 \times 10^{-3}$	9333182	1.59	14.38	
4,4'-dichlorobenzophenone	$2.49 \times 10^{-3}$	19730167	1.52	12.68	
C16	$1.13 \times 10^{-3}$	13929460			1.45
4,4'-dichlorobenzhydrol	$2.47 \times 10^{-3}$	20626030	1.48		
4,4'-dichlorobenzophenone	$4.99 \times 10^{-3}$	42420953	1.45		
C16	$1.13 \times 10^{-3}$	13556390			1.39
4,4'-dichlorobenzhydrol	$4.94 \times 10^{-3}$	40377470	1.47		
4,4'-dichlorobenzophenone	$1.25 \times 10^{-3}$	10769563	1.39		
C16	$1.13 \times 10^{-3}$	12544883			1.42
4,4'-dichlorobenzhydrol	$9.88 \times 10^{-3}$	74436677	1.48		
4,4'-dichlorobenzophenone	$4.99 \times 10^{-3}$	39232363	1.42		
C16	$1.13 \times 10^{-3}$	13118177			1.48
4,4'-dichlorobenzhydrol	$7.41 \times 10^{-3}$	55738440	1.55		
4,4'-dichlorobenzophenone	$9.98 \times 10^{-3}$	78744740	1.48		
C16	$1.13 \times 10^{-3}$	12947747			1.44
4,4'-dichlorobenzhydrol	$4.94 \times 10^{-3}$	37237693	1.52		
4,4'-dichlorobenzophenone	$7.48 \times 10^{-3}$	59802570	1.44		

**X,Y = Cl,Cl (Continued)**

	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.08 \times 10^{-3}$	12483880		5.18	0.96
<i>N</i> -(4,4'-dichlorobenzhydryl)morpholine	$1.34 \times 10^{-3}$	13539817	0.94	17.14	
C16	$1.08 \times 10^{-3}$	13943160			0.99
<i>N</i> -(4,4'-dichlorobenzhydryl)morpholine	$1.78 \times 10^{-3}$	19422840	0.99		
C16	$1.08 \times 10^{-3}$	12387687			0.90
<i>N</i> -(4,4'-dichlorobenzhydryl)morpholine	$1.51 \times 10^{-3}$	15393007	0.90		
C16	$1.08 \times 10^{-3}$	13861360			1.00
<i>N</i> -(4,4'-dichlorobenzhydryl)morpholine	$8.91 \times 10^{-4}$	9667222	1.00		

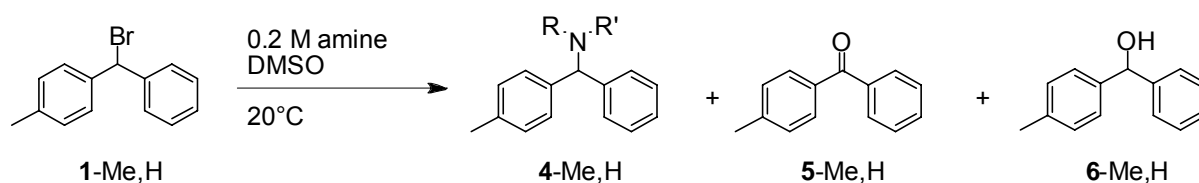
	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$9.30 \times 10^{-4}$	13933403		5.20	1.41
(4,4'-dichlorobenzhydryl)-propylamine	$7.44 \times 10^{-3}$	79286523	1.41	14.48	
C16	$9.30 \times 10^{-4}$	13766470			1.46
(4,4'-dichlorobenzhydryl)-propylamine	$1.12 \times 10^{-2}$	113108667	1.46		
C16	$9.30 \times 10^{-4}$	13741350			1.37
(4,4'-dichlorobenzhydryl)-propylamine	$3.72 \times 10^{-3}$	40173987	1.37		

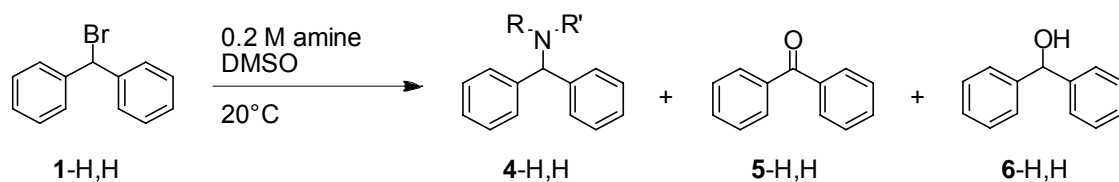
	$c / \text{mol L}^{-1}$	average A	RMR	$t_R / \text{min}$	average RMR
C16	$1.16 \times 10^{-3}$	14842043		5.18	1.14
<i>N</i> -(4,4'-dichlorobenzhydryl)piperidine	$6.09 \times 10^{-3}$	70046967	1.11	16.52	
C16	$1.16 \times 10^{-3}$	17969947			1.12
<i>N</i> -(4,4'-dichlorobenzhydryl)piperidine	$2.03 \times 10^{-3}$	28178667	1.12		
C16	$1.16 \times 10^{-3}$	15486927			1.11
<i>N</i> -(4,4'-dichlorobenzhydryl)piperidine	$4.06 \times 10^{-3}$	48926543	1.11		
C16	$1.16 \times 10^{-3}$	14583050			1.22
<i>N</i> -(4,4'-dichlorobenzhydryl)piperidine	$3.05 \times 10^{-3}$	31454863	1.22		

## 5.4 Analysis of Product Mixtures

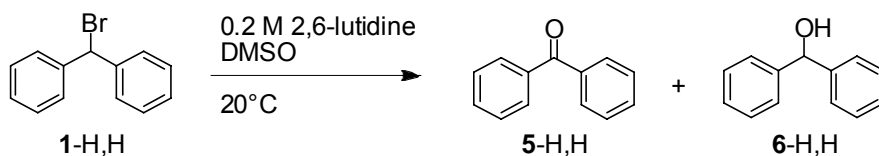
A 0.2 M solution of the amine in DMSO (25 mL) was prepared in a volumetric flask and kept at 20°C. Then this solution was added to a corresponding benzhydrylbromide (0.5 mmol) and stirred for 24 h. After addition of water (50 mL) the solution was extracted with Et<sub>2</sub>O (3 × 50 mL). The combined organic phases were dried (MgSO<sub>4</sub>). After evaporation of the solvent the remaining oil was dissolved in acetone (ca. 20 mL) and transferred into a 25 mL-volumetric flask. Then a defined amount of an acetone stock solution containing the hexadecane standard (C16) was added, to give a C16 concentration of about 1 mM. The volumetric flask was then filled up to 25 mL with acetone, and aliquots were subjected to GC analysis (*t<sub>R</sub>* = retention time; peak areas are the average of 3 separate GC runs for each sample). Concentrations of **4**, **5**, and **6** were calculated by using equation (S3) and refer to the known concentration of the standard (C16).



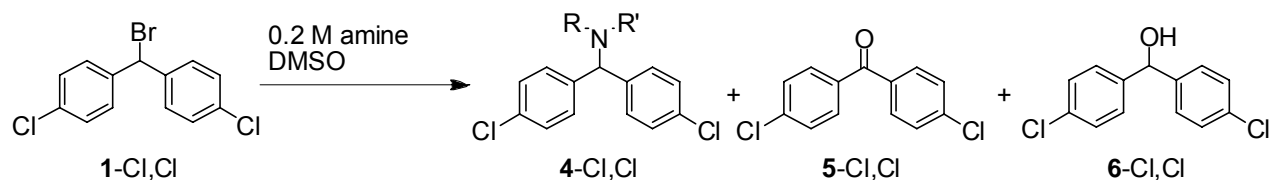
RR'NH	compound	<i>t<sub>R</sub></i> / min	peak area	RMR	<i>c</i> / mol L <sup>-1</sup>	[ <b>4</b> ]/([ <b>5</b> ]+[ <b>6</b> ])
piperidine	C16	5.20	14371033		<b>1.16 × 10<sup>-3</sup></b>	
	<b>6-Me,H</b> + <b>5-Me,H</b>	9.84 / 9.96	67721127	1.29	7.08 × 10 <sup>-3</sup>	
	<b>4-Me,H</b>	12.56	97602543	1.06	8.35 × 10 <sup>-3</sup>	1.18
morpholine	C16	5.20	14378403		<b>1.11 × 10<sup>-3</sup></b>	
	<b>6-Me,H</b> + <b>5-Me,H</b>	9.84 / 9.96	99732157	1.29	9.96 × 10 <sup>-3</sup>	
	<b>4-Me,H</b>	13.32	65561753	1.07	5.43 × 10 <sup>-3</sup>	0.54
n-PrNH <sub>2</sub>	C16	5.20	13121633		<b>1.05 × 10<sup>-3</sup></b>	
	<b>6-Me,H</b> + <b>5-Me,H</b>	9.84 / 9.96	156201167	1.29	1.61 × 10 <sup>-2</sup>	
	<b>4-Me,H</b>	10.32	34093090	1.07	2.92 × 10 <sup>-3</sup>	0.18



RR'NH	compound	$t_R$ / min	peak area	RMR	$c$ / mol L <sup>-1</sup>	[4]/([5]+[6])
piperidine	C16	5.20	14843277		<b>1.16 × 10<sup>-3</sup></b>	
	<b>6-H,H</b>	8.34	1263792	1.17	1.16 × 10 <sup>-4</sup>	
	<b>5-H,H</b>	7.98	14133813	1.34	1.49 × 10 <sup>-3</sup>	
	<b>4-H,H</b>	11.6	198575867	0.90	1.40 × 10 <sup>-2</sup>	8.6
morpholine	C16	5.20	13262553		<b>1.04 × 10<sup>-3</sup></b>	
	<b>6-H,H</b>	8.34	5840434	1.17	5.34 × 10 <sup>-4</sup>	
	<b>5-H,H</b>	7.98	30709390	1.34	3.22 × 10 <sup>-3</sup>	
	<b>4-H,H</b>	12.48	172224433	1.04	1.40 × 10 <sup>-2</sup>	3.72
n-PrNH <sub>2</sub>	C16	5.20	13528813		<b>1.04 × 10<sup>-3</sup></b>	
	<b>6-H,H</b>	8.34	36709970	1.17	3.32 × 10 <sup>-3</sup>	
	<b>5-H,H</b>	7.98	51315043	1.34	5.33 × 10 <sup>-3</sup>	
	<b>4-H,H</b>	9.12	113360600	1.11	9.67 × 10 <sup>-3</sup>	1.12

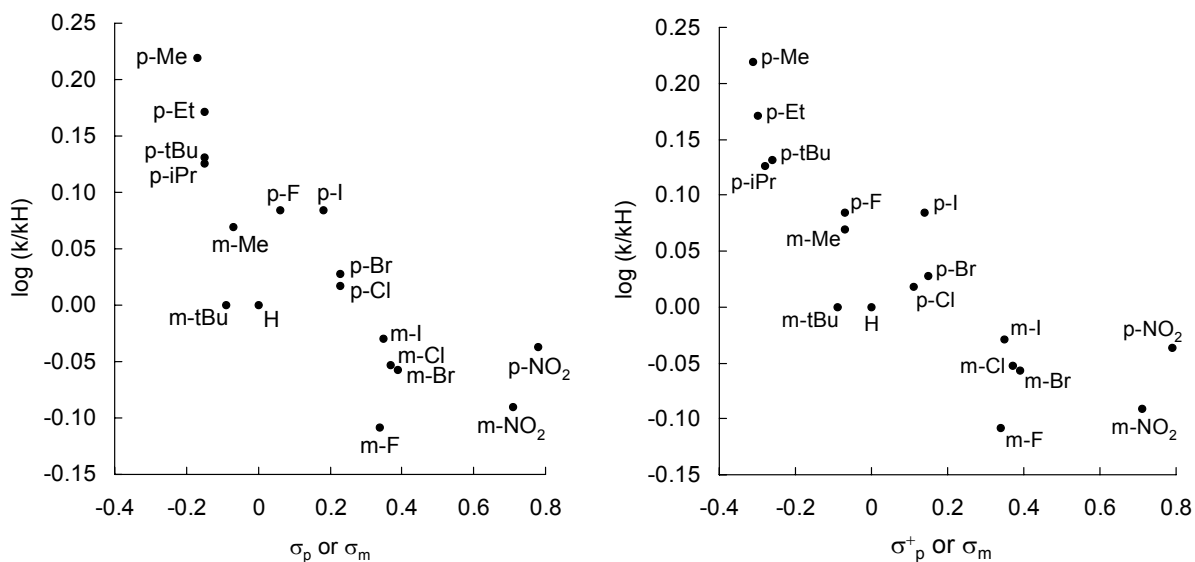


rxn time / min	compound	$t_R$ / min	peak area	RMR	$c$ / mol L <sup>-1</sup>	[5-H,H]/[6-H,H]
60	C16	5.20	13253270		<b>1.13 × 10<sup>-3</sup></b>	
	<b>5-H,H</b>	7.98	37614477	1.34	4.24 × 10 <sup>-3</sup>	
	<b>6-H,H</b>	8.34	112488067	1.17	1.11 × 10 <sup>-2</sup>	0.38
120	C16	5.20	12744147		<b>1.13 × 10<sup>-3</sup></b>	
	<b>5-H,H</b>	7.98	74312043	1.34	8.71 × 10 <sup>-3</sup>	
	<b>6-H,H</b>	8.34	77821767	1.17	7.95 × 10 <sup>-3</sup>	1.10
180	C16	5.20	13204473		<b>1.13 × 10<sup>-3</sup></b>	
	<b>5-H,H</b>	7.98	92219953	1.34	1.04 × 10 <sup>-2</sup>	
	<b>6-H,H</b>	8.34	63360827	1.17	6.25 × 10 <sup>-3</sup>	1.67
300	C16	5.20	13204473		<b>1.13 × 10<sup>-3</sup></b>	
	<b>5-H,H</b>	7.98	92219953	1.34	1.26 × 10 <sup>-2</sup>	
	<b>6-H,H</b>	8.34	63360827	1.17	3.75 × 10 <sup>-3</sup>	3.36
360	C16	5.20	13204473		<b>1.13 × 10<sup>-3</sup></b>	
	<b>5-H,H</b>	7.98	92219953	1.34	1.09 × 10 <sup>-2</sup>	
	<b>6-H,H</b>	8.34	63360827	1.17	2.76 × 10 <sup>-3</sup>	3.95



RR'NH	<i>T</i> / °C	compound	<i>t<sub>R</sub></i> / min	peak area	<i>RMR</i>	<i>c</i> / mol L <sup>-1</sup>	[4]/([5]+[6])
piperidine	20	C16	5.20	14845483		<b>1.16 × 10<sup>-3</sup></b>	36.7
		6-Cl,Cl	14.38	1001725	1.52	1.19 × 10 <sup>-4</sup>	
		5-Cl,Cl	12.68	2615282	1.45	2.98 × 10 <sup>-4</sup>	
		4-Cl,Cl	16.52	172146633	1.14	1.54 × 10 <sup>-2</sup>	
morpholine	20	C16	5.20	12987620		<b>1.04 × 10<sup>-3</sup></b>	11.0
		6-Cl,Cl	14.38	3263352	1.52	3.95 × 10 <sup>-4</sup>	
		5-Cl,Cl	12.68	4546383	1.45	5.26 × 10 <sup>-4</sup>	
		4-Cl,Cl	17.62	132638233	0.96	1.01 × 10 <sup>-2</sup>	
	35	C16	5.20	12923807		<b>1.13 × 10<sup>-3</sup></b>	7.13
		6-Cl,Cl	14.38	1700768	1.52	2.26 × 10 <sup>-4</sup>	
		5-Cl,Cl	12.68	9956992	1.45	1.27 × 10 <sup>-3</sup>	
		4-Cl,Cl	17.62	126759467	0.96	1.07 × 10 <sup>-2</sup>	
	50	C16	5.20	13748827		<b>1.13 × 10<sup>-3</sup></b>	4.13
		6-Cl,Cl	14.38	1862981	1.52	2.33 × 10 <sup>-4</sup>	
		5-Cl,Cl	12.68	15290797	1.45	1.83 × 10 <sup>-3</sup>	
		4-Cl,Cl	17.62	107793400	0.96	8.52 × 10 <sup>-3</sup>	

## 6 Hammett Plots for the Kinetics of the Reactions of Substituted Benzyl Bromides with Pyridine



Correlation of second-order rate constants determined by Baker for the reactions of substituted benzyl bromides + pyridine (20 °C, in acetone) with the Hammett  $\sigma$  and  $\sigma^+$  values, respectively (rate constants from: Baker, J. W. *J. Chem. Soc.* **1936**, 1448–1451; Baker, J. W. *Trans. Faraday Soc.* **1941**, 37, 632–644;  $\sigma$  and  $\sigma^+$  parameters from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, 91, 165–195.)