

## Supporting Information for

### Direct Detection of 1,1-Diphenyl-2-neopentylsilene and the Effects of Solvent Polarity on its Reactivity with Nucleophiles

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**Figure 1.** Concentration vs. time plots for the photolysis (254 nm) of a 0.05 M solution of *trans*-**5** in cyclohexane-*d*<sub>12</sub> containing 0.09 M MeOH: (a) 0-12 minutes; (b) 0-180 minutes. Product yields were calculated from the relative slopes of the plots shown in (a).

**Figure 2.** Concentration vs. time plots for the photolysis (254 nm) of a 0.05 M solution of *cis*-**5** in cyclohexane-*d*<sub>12</sub> containing 0.09 M MeOH: (a) 0-12 minutes; (b) 0-180 minutes. Product yields were calculated from the relative slopes of the plots shown in (a).

**Figure 3.** Plot of  $k_{\text{decay}}$  vs  $[\text{O}_2]$  for the transient observed from laser flash photolysis of *trans*-**5** in hexane solution at 24.5 °C.

**Figure 4.** The decay of silene **4** in deoxygenated Na/K-distilled hexane at 25 °C. The solid line represents the best fit of the data to mixed first- and second-order exponential decay kinetics (equation 5), which yields 1<sup>st</sup> and 2<sup>nd</sup> order rate coefficients of  $1660 \pm 80 \text{ s}^{-1}$  and  $4520 \pm 280 \text{ s}^{-1}$ , respectively ( $r^2$  0.9925).

**Table 1.** Rate constants for reaction of acetone with 1,1-diphenyl-2-neopentylsilene (**4**) in hexane solution over the 0-53 °C temperature range.

**Table 2.** Rate constants for reaction of acetone with 1,1-diphenyl-2-neopentylsilene (**4**) in acetonitrile solution over the 7-57 °C temperature range.

**Table 3.** Rate constants for reaction of acetone with 1,1-diphenyl-2-neopentylsilene (**4**) in tetrahydrofuran solution over the 6-53 °C temperature range.

**Table 4.** Rate constants for addition of methanol to 1,1-diphenyl-2-neopentylsilene (**4**) in hexane solution over the 5-58 °C temperature range.

**Table 5.** Rate constants for addition of methanol to 1,1-diphenyl-2-neopentylsilene (**4**) in acetonitrile solution over the 7-56 °C temperature range.

**Table 6.** Rate constants for addition of methanol to 1,1-diphenyl-2-neopentylsilene (**4**) in THF solution over the 1-54 °C temperature range.

**Table 7.** Rate constants for addition of methanol to 1,1-diphenyl-2-neopentylsilene (**4**) in 1,2-dichloroethane (DCE) solution over the 2-58 °C temperature range.

**Table 8.** Rate constants for addition of 2,2,2-trifluoroethanol (TFE) to 1,1-diphenyl-2-neopentylsilene (**4**) in hexane solution over the 1-59 °C temperature range.

**Table 9.** Rate constants for addition of 2,2,2-trifluoroethanol (TFE) to 1,1-diphenyl-2-neopentylsilene (**4**) in acetonitrile solution over the 6-55 °C temperature range.

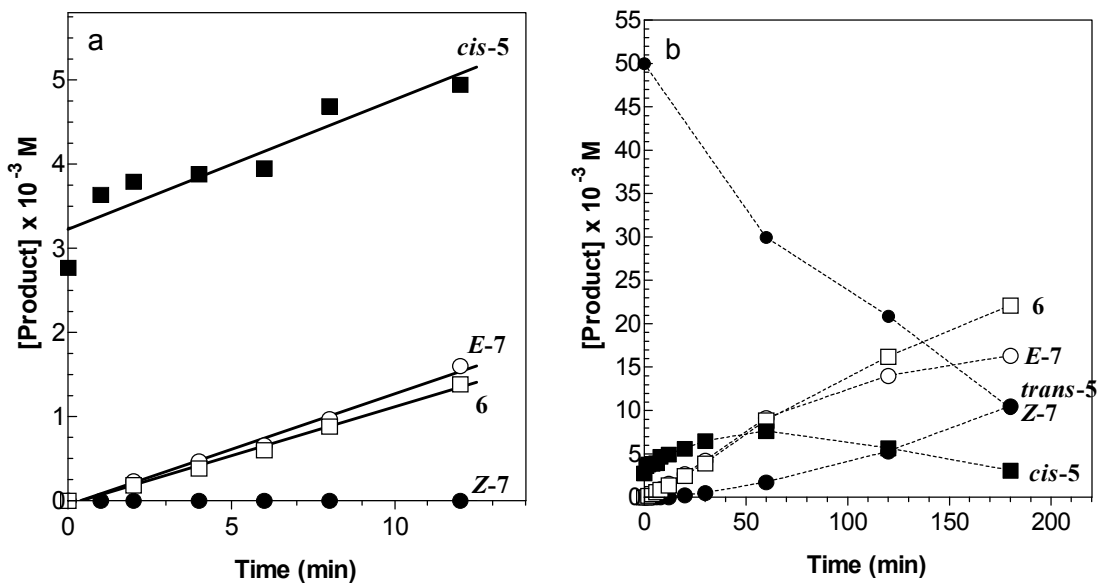
**Table 10.** Rate constants for addition of acetic acid to 1,1-diphenyl-2-neopentylsilene (**4**) in acetonitrile solution over the 7-58 °C temperature range.

**Table 11.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with 1,1-diphenyl-2-neopentylsilene (**4**) in tetrahydrofuran solution over the 2-55 °C temperature range.

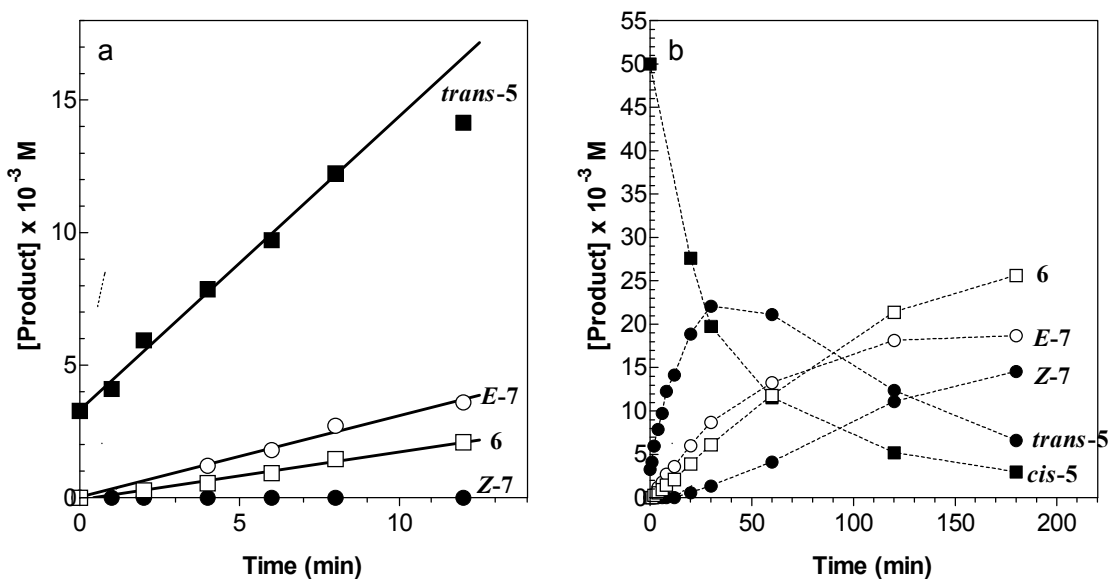
**Table 12.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with 1,1-diphenyl-2-neopentylsilene (**4**) in acetonitrile solution over the 6-56 °C temperature range.

**Table 13.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with 1,1-diphenyl-2-neopentylsilene (**4**) in hexane solution over the 6-56 °C temperature range.

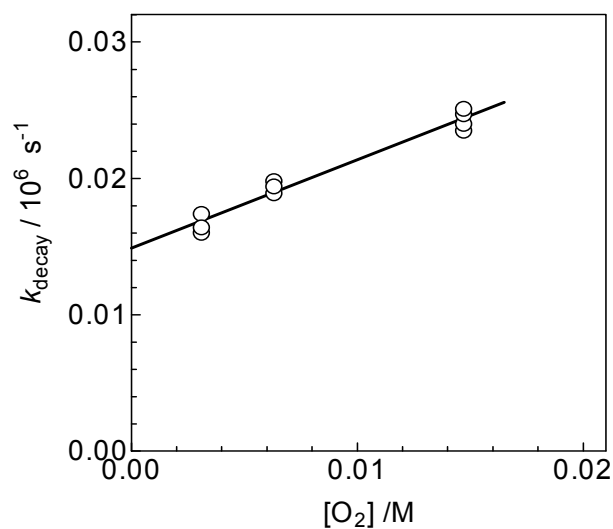
**Figure 1.** Concentration vs. time plots for the photolysis (254 nm) of a 0.05 M solution of *trans*-5 in cyclohexane- $d_{12}$  containing 0.09 M MeOH: (a) 0-12 minutes; (b) 0-180 minutes. Product yields were calculated from the relative slopes of the plots shown in (a).



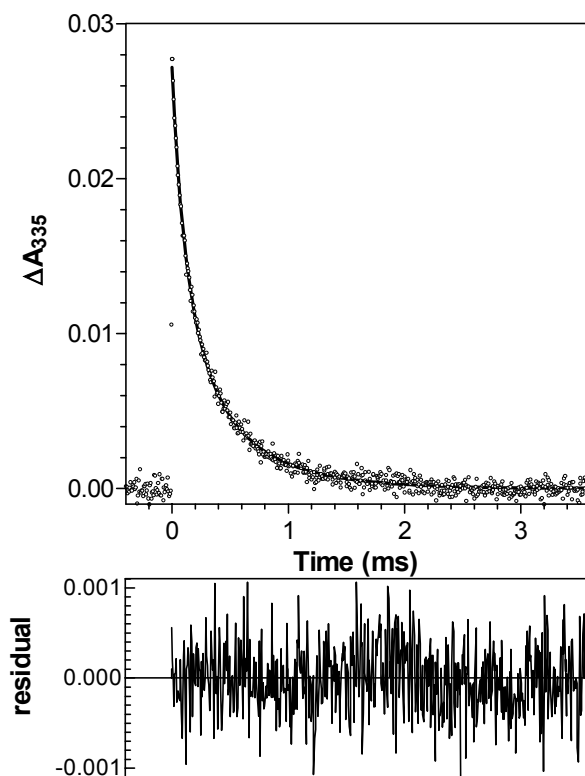
**Figure 2.** Concentration vs. time plots for the photolysis (254 nm) of a 0.05 M solution of *cis*-5 in cyclohexane- $d_{12}$  containing 0.09 M MeOH: (a) 0-12 minutes; (b) 0-180 minutes. Product yields were calculated from the relative slopes of the plots shown in (a).



**Figure 3.** Plot of  $k_{\text{decay}}$  vs  $[\text{O}_2]$  for the transient observed from laser flash photolysis of *trans*-5 in hexane solution at 24.5 °C.



**Figure 4.** The decay of silene 4 in deoxygenated Na/K-distilled hexane at 25 °C. The solid line represents the best fit of the data to mixed first- and second-order exponential decay kinetics (equation 5), which yields rate coefficients of  $1660 \pm 80 \text{ s}^{-1}$  and  $4520 \pm 280 \text{ s}^{-1}$  for the 1<sup>st</sup> and 2<sup>nd</sup> order components, respectively ( $r^2$  0.9925).



**Table 1.** Rate constants for reaction of acetone with **4** in hexane solution over the 0-53 °C temperature range.

Temp. °C	$k_0 / 10^4 \text{ s}^{-1}$	$k_{\text{acetone}} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$R^2$	Conc. Range (mM)
0.6	$3.9 \pm 0.5$	$13.99 \pm 0.60$	.9922	0 – 1.5
9.1	$2.5 \pm 0.7$	$11.44 \pm 0.59$	.9893	0 – 2.2
24.5	$3.0 \pm 1.0$	$10.13 \pm 0.36$	.9910	0 – 3.3
42.0	$3.2 \pm 0.3$	$9.60 \pm 0.23$	.9978	0 – 1.76
53.0	$2.9 \pm 0.4$	$9.22 \pm 0.24$	.9965	0 – 1.5

**Table 2.** Rate constants for reaction of acetone with **4** in MeCN solution over the 7-57 °C temperature range.

Temp. °C	$k_0 / 10^4 \text{ s}^{-1}$	$k_{\text{acetone}} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$R^2$	Conc. Range (mM)
7.0	$3.3 \pm 0.4$	$2.86 \pm 0.17$	.9941	0 – 4.5
18.6	$2.5 \pm 0.6$	$2.98 \pm 0.18$	.9955	0 – 6.1
24.8	$2.2 \pm 0.6$	$3.05 \pm 0.34$	.9871	0 – 3.0
32.5	$3.0 \pm 0.6$	$3.18 \pm 0.20$	.9893	0 – 4.4
45.5	$2.8 \pm 0.3$	$3.17 \pm 0.10$	.9932	0 – 3.1
56.9	$2.7 \pm 0.6$	$3.27 \pm 0.26$	.9934	0 – 3.7

**Table 3.** Rate constants for reaction of acetone with **4** in THF solution over the 6-53 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{acetone}} / 10^6 \text{ M}^{-1}\text{s}^{-1}$	$R^2$	Conc. Range (mM)
6.4	$2.1 \pm 0.1$	$7.47 \pm 0.44$	.9954	0 – 4.8
16.3	$1.7 \pm 0.1$	$7.56 \pm 0.58$	.9924	0 – 5.8
24.4	$4.1 \pm 0.1$	$7.93 \pm 0.32$	.9969	0 – 7.3
31.0	$2.3 \pm 0.1$	$8.04 \pm 0.36$	.9979	0 – 5.1
41.5	$3.1 \pm 0.1$	$8.10 \pm 0.22$	.9990	0 - 4.5
53.4	$2.1 \pm 0.1$	$8.20 \pm 0.4$	.9963	0 – 4.2

**Table 4.** Rate constants for addition of methanol to **4** in hexane solution over the 5-58 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{MeOH}} / 10^6$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{2\text{MeOH}} / 10^6$ ( $\text{M}^{-2}\text{s}^{-1}$ )	$R^2$	Conc. Range (mM)
5.2	$3.7 \pm 1.1$	$71.6 \pm 15.6$	$8880 \pm 4008$	.9921	0 – 3.5
10.6	$4.2 \pm 0.1$	$53.3 \pm 2.0$	$6758 \pm 467$	.9998	0 – 4.1
24.6	$2.5 \pm 0.9$	$43.8 \pm 6.7$	$5407 \pm 995$	.9959	0 – 6.6
35.0	$3.3 \pm 0.4$	$41.9 \pm 5.2$	$4998 \pm 1221$	.9983	0 – 4.2
43.1	$3.3 \pm 0.3$	$38.5 \pm 3.5$	$2937 \pm 680$	.9989	0 – 5.0
58.3	$2.3 \pm 0.4$	$31.8 \pm 4.2$	$1947 \pm 825$	.9966	0 – 4.9

**Table 5.** Rate constants for addition of methanol to **4** in MeCN solution over the 7-56 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{MeOH}} / 10^6$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{2\text{MeOH}} / 10^6$ ( $\text{M}^{-2}\text{s}^{-1}$ )	$R^2$	Conc. Range (mM)
7.6	$0.4 \pm 0.1$	$1.03 \pm 0.84$	$571.8 \pm 30.6$	.9989	0 – 30
15.0	$0.4 \pm >0.1$	$2.11 \pm 0.98$	$534.6 \pm 36.7$	.9983	0 – 30
24.6	$0.3 \pm 0.1$	$4.34 \pm 1.12$	$306.4 \pm 28.0$	.9986	0 – 37
32.4	$0.2 \pm 0.1$	$5.71 \pm 1.21$	$186.2 \pm 26.08$	.9961	0 – 43
43.4	$0.2 \pm >0.1$	$6.59 \pm 0.79$	$71.85 \pm 18.74$	.9964	0 – 39
55.7	$0.1 \pm >0.1$	$8.37 \pm 0.69$	$55.38 \pm 16.09$	.9978	0 – 39

**Table 6.** Rate constants for addition of methanol to **4** in THF solution over the 1-54 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{MeOH}} / 10^6$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{2\text{MeOH}} / 10^6$ ( $\text{M}^{-2}\text{s}^{-1}$ )	$R^2$	Conc. Range (mM)
1.0	$3.6 \pm 0.4$	$51.8 \pm 5.7$	$135 \pm 143$	.9961	0 – 39
8.2	$2.6 \pm 0.1$	$21.6 \pm 1.7$	$191 \pm 61$	.9983	0 – 28
24.2	$0.2 \pm >0.1$	$18.7 \pm 2.8$	$228 \pm 83$	.9952	0 – 34
24.5	$0.4 \pm >0.1$	$15.5 \pm 1.6$	$301 \pm 40$	.9966	0 – 39
42.8	$1.7 \pm 0.1$	$5.8 \pm 1.1$	$105 \pm 23$	.9955	0 – 68
54.4	$1.6 \pm 0.1$	$7.3 \pm 0.9$	$89.1 \pm 11.9$	.9981	0 – 78

**Table 7.** Rate constants for addition of methanol to **4** in 1,2-dichloroethane (DCE) solution over the 2-58 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{MeOH}} / 10^6$ ( $\text{M}^{-1}\text{s}^{-1}$ )	$k_{2\text{MeOH}} / 10^6$ ( $\text{M}^{-2}\text{s}^{-1}$ )	$R^2$	Conc. Range (mM)
2.2	$2.4 \pm 0.2$	$11.5 \pm 2.1$	$445 \pm 52$	.9979	0 – 40
11.5	$1.9 \pm 0.2$	$9.07 \pm 1.45$	$114 \pm 25$	.9971	0 – 55
23.3	$2.4 \pm 0.2$	$12.2 \pm 2.4$	$158 \pm 40$	.9966	0 – 56
32.7	$1.3 \pm 0.2$	$11.6 \pm 2.6$	$404 \pm 47$	.9984	0 – 53
42.7	$1.3 \pm 0.1$	$11.9 \pm 1.5$	$368 \pm 34$	.9990	0 – 43
58.0	$3.5 \pm 0.2$	$8.01 \pm 2.19$	$274 \pm 43$	.9966	0 – 49

**Table 8.** Rate constants for addition of 2,2,2-trifluoroethanol (TFE) to **4** in hexane solution over the 1-59 °C temperature range.

Temp. °C	$k_0 / 10^4 \text{ s}^{-1}$	$k_{\text{TFE}} / 10^6 \text{ M}^{-1}\text{s}^{-1}$	$k_{2\text{TFE}} / 10^6 \text{ M}^{-2}\text{s}^{-1}$	$R^2$	Conc. Range (mM)
1.9	$2.1 \pm 0.3$	$1.71 \pm 0.41$	$64.6 \pm 9.7$	.9954	0 – 35
15.7	$2.6 \pm 0.2$	$1.54 \pm 0.24$	$128 \pm 6$	.9996	0 – 43
25.2	$1.6 \pm 0.1$	$1.35 \pm 0.13$	$15.3 \pm 2.5$	.9984	0 – 52
36.2	$1.4 \pm 0.7$	$2.14 \pm 0.91$	$100.5 \pm 20.9$	.9935	0 – 42
42.3	$1.7 \pm 0.5$	$1.43 \pm 0.52$	$69.0 \pm 10.8$	.9957	0 – 46
49.5	$2.7 \pm 0.2$	$0.50 \pm 0.24$	$20.7 \pm 5.5$	.9897	0 – 42
59.4	$2.0 \pm 0.8$	$0.52 \pm 0.07$	$4.0 \pm 1.0$	.9967	0 – 67



**Table 9.** Rate constants for addition of 2,2,2-trifluoroethanol (TFE) to **4** in MeCN solution over the 6-55 °C temperature range.

Temp. °C	$k_0 / 10^4 \text{ s}^{-1}$	$k_{\text{TFE}} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$R^2$	Conc. Range (mM)
6.4	$-0.3 \pm 0.7$	$87.6 \pm 2.3$	.9959	0 – 6.3
12.1	$1.2 \pm 0.4$	$76.8 \pm 2.2$	.9959	0 – 4.2
24.7	$0.2 \pm 0.6$	$86.2 \pm 2.8$	.9925	0 – 4.2
39.9	$1.8 \pm 0.2$	$64.0 \pm 1.2$	.9984	0 – 3.9
55.4	$2.0 \pm 0.2$	$53.0 \pm 1.0$	.9979	0 – 4.2

**Table 10.** Rate constants for addition of acetic acid to **4** in MeCN solution over the 7-58 °C temperature range.

Temp. °C	$k_0 / 10^5 \text{ s}^{-1}$	$k_{\text{AcOH}} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$R^2$	Conc. Range (mM)
7.3	$0.3 \pm >0.1$	$133.4 \pm 4.6$	.9991	0 – 2
14.7	$0.18 \pm 0.1$	$224.1 \pm 11.44$	.9897	0 – 1
16.1	$0.2 \pm 0.1$	$154.3 \pm 25.2$	.9738	0 – 2
24.9	$0.6 \pm 0.4$	$218.4 \pm 20.6$	.9907	0 – 1
31.6	$0.3 \pm >0.1$	$322.1 \pm 13.2$	.9975	0 – 1
39.9	$0.2 \pm >0.1$	$370.3 \pm 12.8$	.9982	0 – 1
47.0	$0.1 \pm >0.1$	$441.8 \pm 31.8$	.9935	0 – 1
51.9	$0.1 \pm >0.1$	$447.3 \pm 12.6$	.9988	0 – 1
57.5	$0.2 \pm >0.1$	$427.2 \pm 29.9$	.9951	0 – 1
57.8	$0.1 \pm >0.1$	$471.4 \pm 28.2$	.9937	0 – 1

**Table 11.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with **4** in THF solution over the 2-55 °C temperature range.

Temp. °C	$k_0 / 10^6 \text{ s}^{-1}$	$k_{n\text{-BuNH}_2} / 10^6 \text{ M}^{-1}\text{s}^{-1}$	R <sup>2</sup>	Conc. Range (mM)
1.8	0.44 ± 0.01	2110 ± 71	.9955	0 – 0.20
12.5	0.18 ± 0.01	2027 ± 102	.9900	0 – 0.24
25.1	0.12 ± 0.01	1887 ± 67	.9949	0 – 0.19
33.6	0.21 ± 0.01	1748 ± 71	.9918	0 – 0.23
43.2	0.12 ± 0.01	1712 ± 26	.9989	0 – 0.29
55.1	0.13 ± 0.01	1674 ± 43	.9961	0 – 0.21

**Table 12.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with **4** in MeCN solution over the 6-56 °C temperature range.

Temp. °C	$k_0 / 10^6 \text{ s}^{-1}$	$k_{n\text{-BuNH}_2} / 10^6 \text{ M}^{-1}\text{s}^{-1}$	R <sup>2</sup>	Conc. Range (mM)
6.5	-0.01 ± 0.02	1910 ± 200	.9590	0 – 0.15
16.3	0.004 ± 0.006	1919 ± 55	.9968	0 – 0.19
24.4	0.01 ± 0.01	2239 ± 129	.9901	0 – 0.14
33.8	0.01 ± 0.01	2200 ± 81	.9946	0 – 0.15
42.2	0.01 ± >0.01	2216 ± 35	.9990	0 – 0.14
56.3	0.01 ± 0.01	2496 ± 89	.9949	0 – 0.15

**Table 13.** Rate constants for reaction of *n*-BuNH<sub>2</sub> with **4** in hexane solution over the 6-56 °C temperature range.

Temp. °C	$k_0 / 10^4 \text{ s}^{-1}$	$k_{n\text{-BuNH}_2} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	R <sup>2</sup>	Conc. Range (mM)
5.7	0.29 ± 0.02	962.0 ± 75.9	.9757	0 – 0.46
13.0	0.01 ± >0.01	716.1 ± 22.6	.9960	0 – 0.60
23.6	1.6 ± 0.1	440.9 ± 6.7	.9991	0 – 0.47
37.0	0.02 ± >0.01	260.3 ± 3.4	.9993	0 – 0.71
45.7	0.01 ± >0.01	206.8 ± 9.6	.9915	0 – 1.1
56.0	1.5 ± 0.2	137.8 ± 3.1	.9979	0 – 0.98