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Silyloxyamines as Sources of Silyl Radicals: ESR Spin Trapping, Laser Flash Photolysis Investigation and Photopolymerization Ability

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Supporting Information for:**Silyloxyamines as Sources of Silyl Radicals: ESR Spin Trapping, Laser Flash Photolysis Investigation and Photopolymerization Ability.**

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For purification, the chromatographic technique described by Still (J. Org. Chem. 1978, 43, 2923-2925) was selected.

Figures 1-3. ¹H (400M Hz), ¹³C (100M Hz) and DEPT NMR spectra for **SiN1**.

Figures 2-5. ¹H (400M Hz), ¹³C (100M Hz) NMR spectra for **SiN2**.

Z-Matrix for **SiN1** and **SiN2**.

Figure 1.

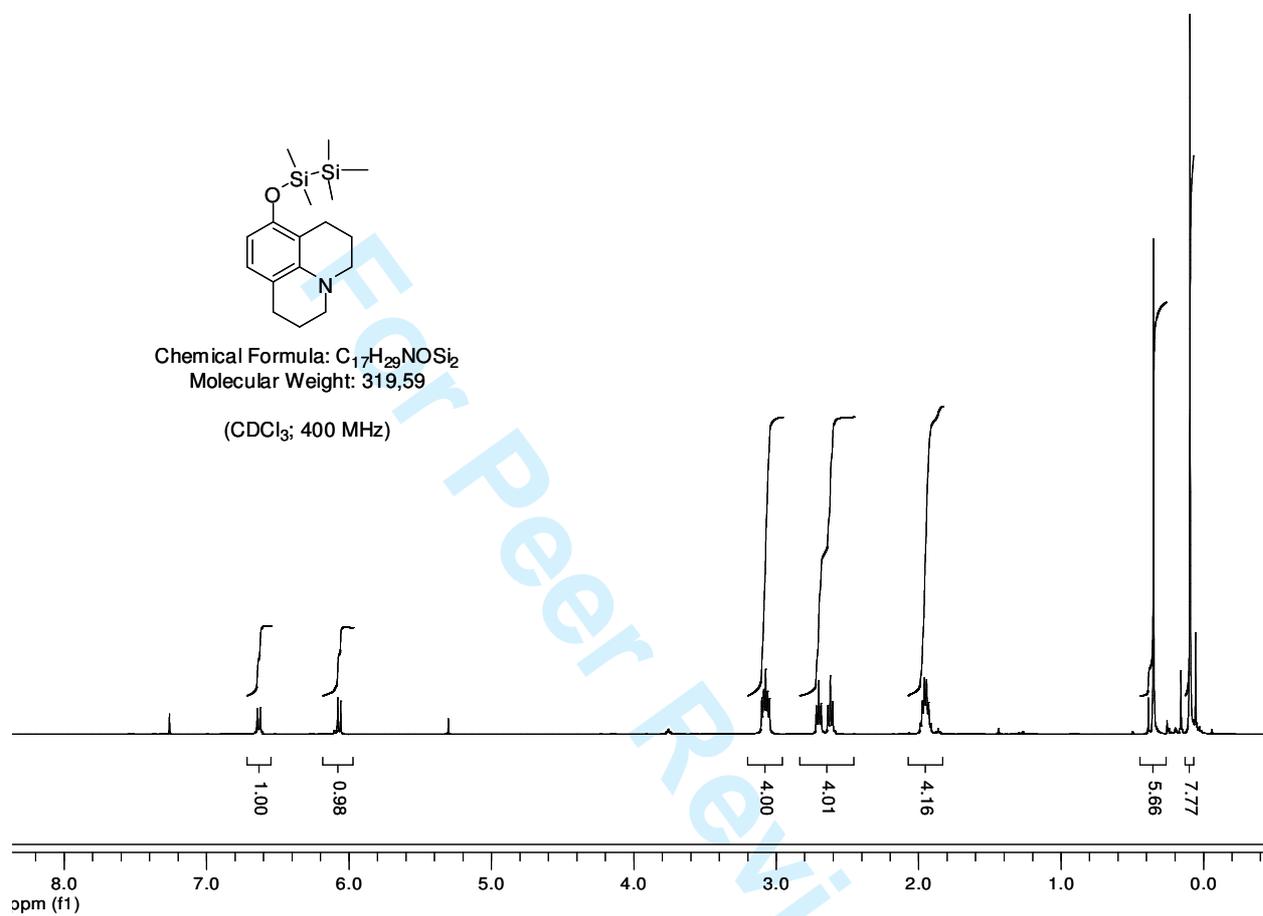


Figure 2.

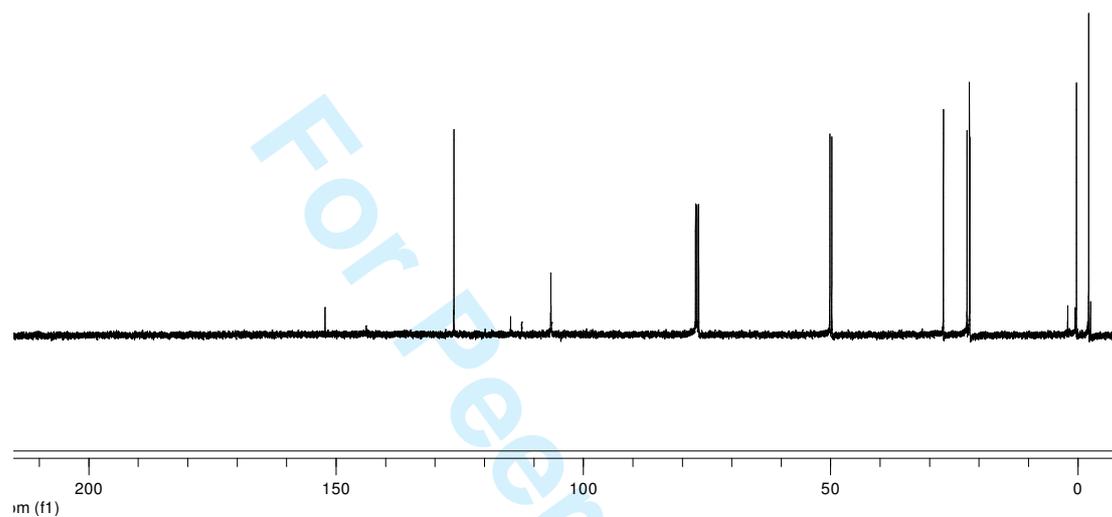


Figure 3.

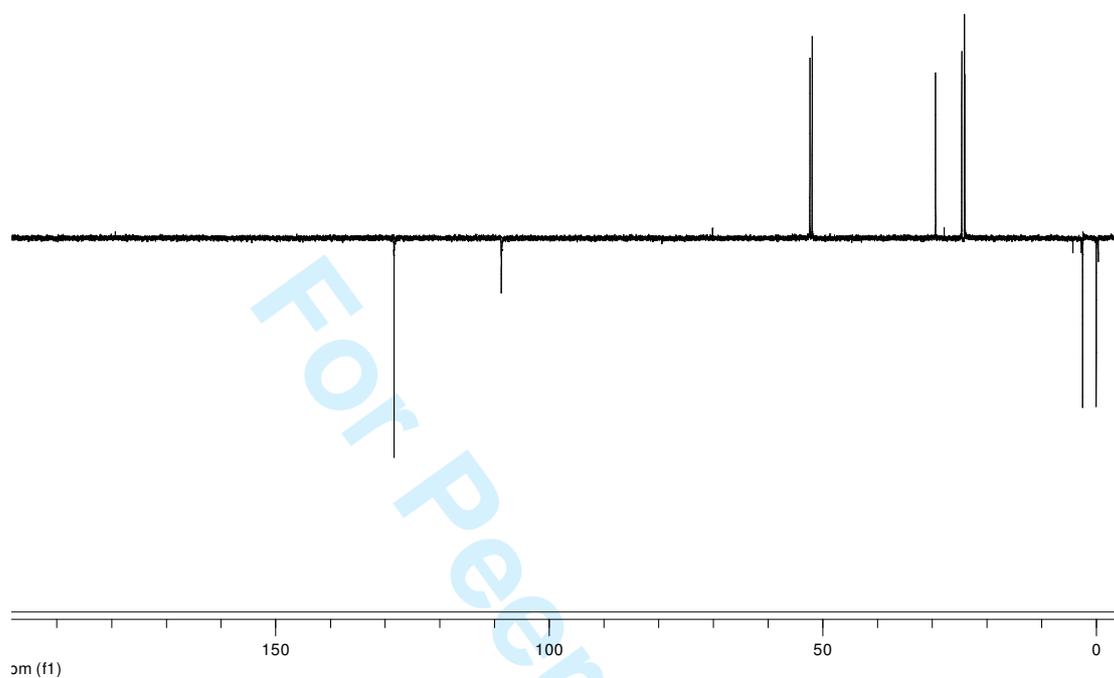


Figure 4.

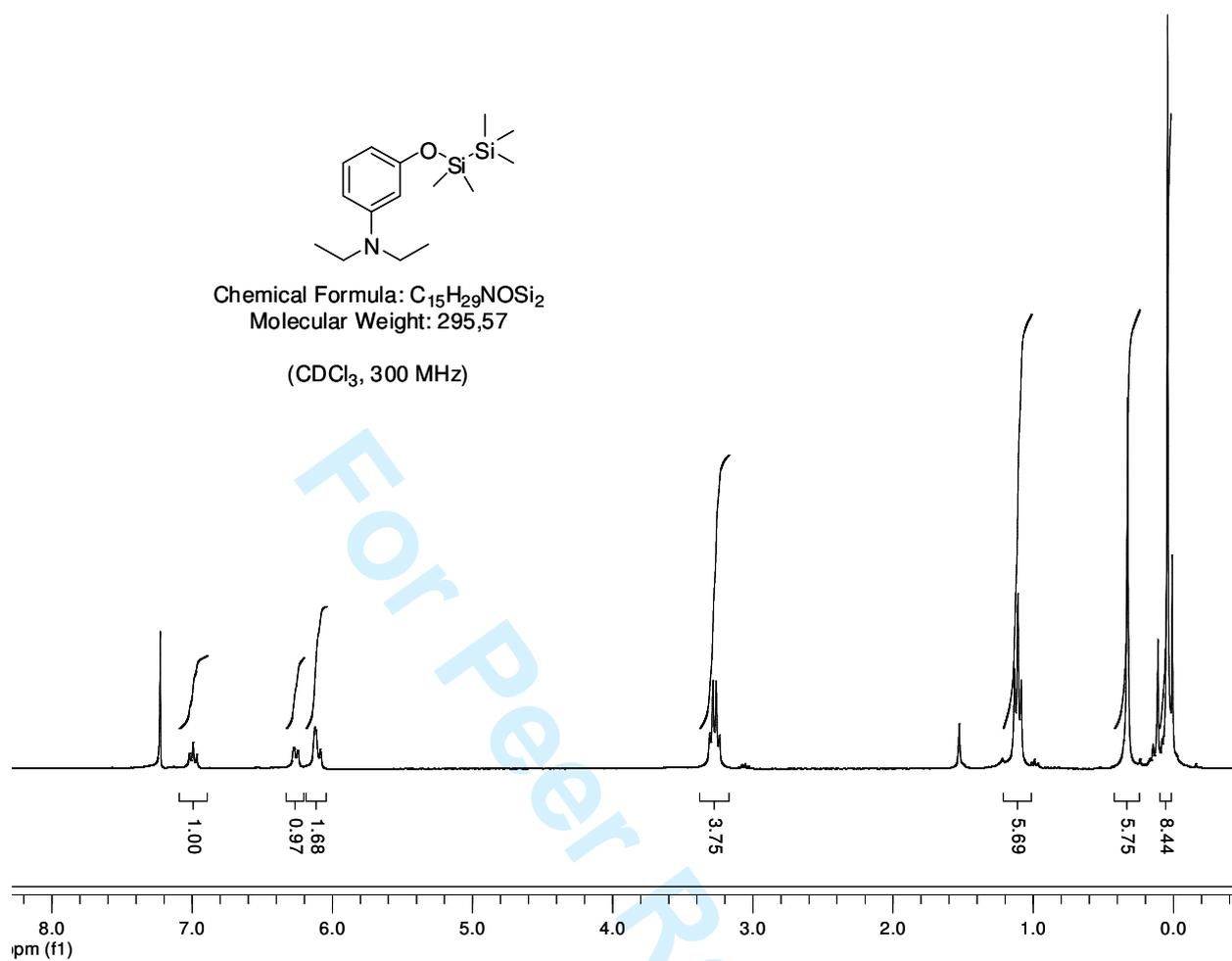
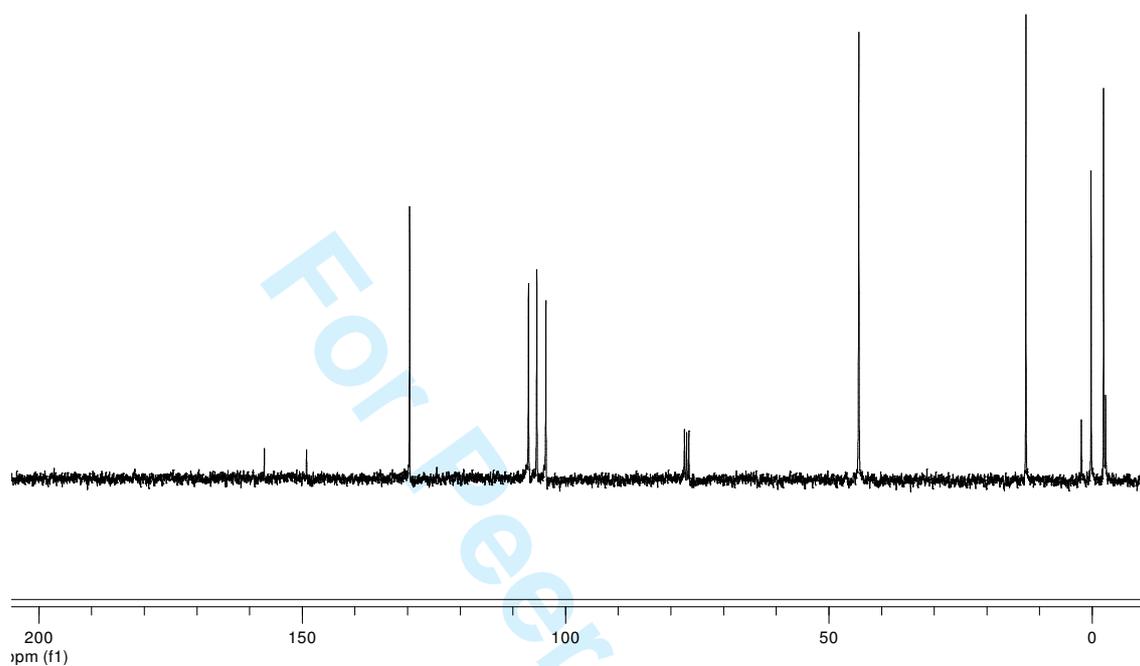


Figure 5.



Z-Matrix for SiN1 and SiN2:

C						
C	1	B1				
C	1	B2	2	A1		
H	1	B3	2	A2	3	D1
C	2	B4	1	A3	3	D2
C	3	B5	1	A4	2	D3
H	2	B6	1	A5	3	D4
H	3	B7	1	A6	2	D5
C	6	B8	3	A7	1	D6
N	5	B9	2	A8	1	D7
O	6	B10	3	A9	1	D8
C	10	B11	5	A10	2	D9
C	10	B12	5	A11	2	D10
Si	11	B13	6	A12	3	D11
H	9	B14	6	A13	3	D12
C	12	B15	10	A14	5	D13
C	13	B16	10	A15	5	D14
C	14	B17	11	A16	6	D15
C	14	B18	11	A17	6	D16
Si	14	B19	11	A18	6	D17
H	12	B20	10	A19	5	D18
H	12	B21	10	A20	5	D19
H	13	B22	10	A21	5	D20
H	13	B23	10	A22	5	D21
C	20	B24	14	A23	11	D22
C	20	B25	14	A24	11	D23
C	20	B26	14	A25	11	D24
H	16	B27	12	A26	10	D25
H	16	B28	12	A27	10	D26
H	16	B29	12	A28	10	D27
H	17	B30	13	A29	10	D28
H	17	B31	13	A30	10	D29
H	17	B32	13	A31	10	D30
H	18	B33	14	A32	11	D31
H	18	B34	14	A33	11	D32
H	18	B35	14	A34	11	D33
H	19	B36	14	A35	11	D34
H	19	B37	14	A36	11	D35
H	19	B38	14	A37	11	D36
H	25	B39	20	A38	14	D37
H	25	B40	20	A39	14	D38
H	25	B41	20	A40	14	D39
H	26	B42	20	A41	14	D40
H	26	B43	20	A42	14	D41
H	26	B44	20	A43	14	D42
H	27	B45	20	A44	14	D43
H	27	B46	20	A45	14	D44
H	27	B47	20	A46	14	D45
B1	1.39201640					
B2	1.39378782					
B3	1.09078921					
B4	1.41416569					
B5	1.39799046					
B6	1.08747125					
B7	1.08774922					
B8	1.39466637					
B9	1.39579082					
B10	1.38021659					
B11	1.45681053					
B12	1.45692757					
B13	1.69558897					
B14	1.08678969					
B15	1.53309618					
B16	1.53328407					
B17	1.89622017					

1		
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3	B18	1.89684001
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5	B20	1.09217964
6	B21	1.10110337
7	B22	1.09237008
8	B23	1.10102472
9	B24	1.90662791
10	B25	1.90222071
11	B26	1.90071664
12	B27	1.09688129
13	B28	1.09621048
14	B29	1.09621642
15	B30	1.09693896
16	B31	1.09612521
17	B32	1.09606987
18	B33	1.09840409
19	B34	1.09671481
20	B35	1.09721149
21	B36	1.09836505
22	B37	1.09715582
23	B38	1.09679370
24	B39	1.09832852
25	B40	1.09731825
26	B41	1.09715526
27	B42	1.09798477
28	B43	1.09705351
29	B44	1.09676968
30	B45	1.09804137
31	B46	1.09647633
32	B47	1.09712948
33	A1	121.72864056
34	A2	118.96964042
35	A3	120.49782825
36	A4	118.12096436
37	A5	119.30492526
38	A6	121.95878758
39	A7	121.09450848
40	A8	121.29457917
41	A9	119.91568473
42	A10	121.56022237
43	A11	121.70196996
44	A12	126.31119745
45	A13	117.78784528
46	A14	115.00603871
47	A15	115.07164457
48	A16	109.90152077
49	A17	109.83991705
50	A18	103.50037223
51	A19	108.08161520
52	A20	108.88821873
53	A21	108.01705494
54	A22	108.81604921
55	A23	109.17791337
56	A24	110.33516486
57	A25	110.17567822
58	A26	110.18579519
59	A27	111.99084817
60	A28	111.26496625
	A29	110.20668223
	A30	111.97766105
	A31	111.26876274
	A32	110.63530545
	A33	111.79612515
	A34	111.80021088
	A35	110.44165343
	A36	111.66252310
	A37	112.13783144
	A38	110.91323699
	A39	111.94515183
	A40	111.99063234
	A41	111.11711069

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4	A43	111.27580285
5	A44	111.24769763
6	A45	111.11951271
7	A46	111.84275563
8	D1	-179.16139097
9	D2	-0.98546026
10	D3	0.32709334
11	D4	177.25182173
12	D5	179.17564963
13	D6	0.73833927
14	D7	-178.79960837
15	D8	176.27270505
16	D9	21.11334167
17	D10	-159.57627998
18	D11	89.56785854
19	D12	175.07059065
20	D13	-103.73837100
21	D14	-102.66940907
22	D15	-65.14653065
23	D16	53.67606799
24	D17	174.48060511
25	D18	19.18406014
26	D19	133.23057885
27	D20	20.28672097
28	D21	134.30012114
29	D22	174.67998506
30	D23	-65.68378598
31	D24	54.93788535
32	D25	-179.84789861
33	D26	-60.44631633
34	D27	59.99156046
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37	D30	60.11471745
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42	D35	-62.26246844
43	D36	58.60477735
44	D37	179.69850955
45	D38	-60.63196627
46	D39	60.06478834
47	D40	178.87786606
48	D41	-61.12971887
49	D42	59.06811365
50	D43	-179.42556333
51	D44	-59.38776847

52	C				
53	C	1	B1		
54	C	1	B2	2	A1
55	H	1	B3	2	A2 3 D1
56	C	2	B4	1	A3 3 D2
57	C	3	B5	1	A4 2 D3
58	O	3	B6	1	A5 2 D4
59	H	2	B7	1	A6 3 D5
60	C	6	B8	3	A7 1 D6
	C	6	B9	3	A8 1 D7
	C	5	B10	2	A9 1 D8
	Si	7	B11	3	A10 1 D9
	C	10	B12	6	A11 3 D10
	N	9	B13	6	A12 3 D11
	C	11	B14	5	A13 2 D12
	C	12	B15	7	A14 3 D13
	C	12	B16	7	A15 3 D14
	Si	12	B17	7	A16 3 D15
	H	10	B18	6	A17 3 D16
	H	10	B19	6	A18 3 D17

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H	11	B20	5	A19	2	D18
H	11	B21	5	A20	2	D19
C	14	B22	9	A21	6	D20
C	14	B23	9	A22	6	D21
C	18	B24	12	A23	7	D22
C	18	B25	12	A24	7	D23
C	18	B26	12	A25	7	D24
H	13	B27	10	A26	6	D25
H	13	B28	10	A27	6	D26
H	15	B29	11	A28	5	D27
H	15	B30	11	A29	5	D28
H	16	B31	12	A30	7	D29
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H	17	B35	12	A34	7	D33
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H	23	B37	14	A36	9	D35
H	23	B38	14	A37	9	D36
H	24	B39	14	A38	9	D37
H	24	B40	14	A39	9	D38
H	25	B41	18	A40	12	D39
H	25	B42	18	A41	12	D40
H	25	B43	18	A42	12	D41
H	26	B44	18	A43	12	D42
H	26	B45	18	A44	12	D43
H	26	B46	18	A45	12	D44
H	27	B47	18	A46	12	D45
H	27	B48	18	A47	12	D46
H	27	B49	18	A48	12	D47

B1	1.39176070
B2	1.39682934
B3	1.08399236
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B7	1.08851536
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	D13	-70.70576050
	D14	49.11862850

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2		
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13	D25	-75.27670514
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15	D27	-168.54904969
16	D28	72.39744299
17	D29	-169.11476386
18	D30	-50.00843616
19	D31	71.42082545
20	D32	61.88432502
21	D33	-177.78504214
22	D34	-58.31962928
23	D35	168.37553697
24	D36	-74.57727096
25	D37	77.10040458
26	D38	-166.00991355
27	D39	-179.84327306
28	D40	-60.21486370
29	D41	60.44062153
30	D42	179.08691466
31	D43	-61.08262253
32	D44	59.24049388
33	D45	-177.92233658
34	D46	-57.85513639
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For Peer Review

Silyloxyamines as Sources of Silyl Radicals: ESR Spin Trapping, Laser Flash Photolysis Investigation and Photopolymerization Ability.

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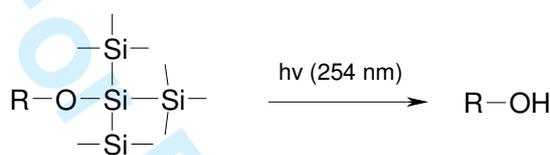
Abstract:

Two silyloxyamines derived from 8-(pentamethyldisilyloxy)-julolidine and diethyl 3-(pentamethyldisilyloxy)-aniline are proposed as new sources of silyl radicals. The decomposition mechanism, excited state processes and the radical generation are explored by steady state photolysis, laser flash photolysis, ESR and MO calculations. The Si-Si bond cleavage is clearly demonstrated. The formation of a radical cation on the amine moiety is also observed. Moreover, these compounds work as efficient Type I and Type II photoinitiators of free radical photopolymerization.

Keywords: Silyl Radicals, Laser Flash Photolysis, ESR spin-trapping, Photopolymerization, Photoinitiators.

Introduction:

The development of silyl functionalized compounds and silyl radical sources is now the subject of many efforts in organic chemistry.^[1-2] In particular, the bulky tris(trimethylsilyl)silyl group has been found to promote [2+2] cyclizations^[2b] and Mukaiyama aldol reactions.^[2c] In addition, the silyloxy compounds derived from tris(trimethylsilyl)silane ("super silyl ethers") can be used as interesting UV-labile silyl protecting groups of alcohols^[1-2] (Scheme 1 where R stands for a large diversity of substituents). This photocleavage provides an alternative approach to the classical thermal deprotection.³ However, little is known on the photochemical mechanisms associated with such a reaction; this process can involve photogeneration of silyl radicals.



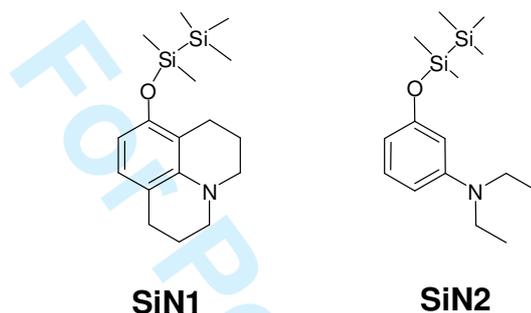
Scheme 1.

The silyl radical chemistry which is now the subject of numerous studies^[4-12] appears highly worthwhile for the development of new mono- and bi-component sources of silyl radicals $\text{R}_3\text{Si}^\bullet$ usable as photoinitiators (PI) for free radical photopolymerization (FRP): indeed, silyl radicals are highly valuable to overcome the oxygen inhibition usually observed in FRP.^[7-12] In this area, the production of $\text{R}_3\text{Si}^\bullet$ was first achieved through the photodegradation of polysilane polymers that occurs *via* a Si-Si bond cleavage^[4-6] or the use of photosensitizer/silane couples. New compounds based on Si-Si, C-Si or S-Si single bond cleavage and leading to $\text{R}_3\text{Si}^\bullet$ have been also recently proposed.^[7-12] On this occasion, their ability as Type I photoinitiating systems to initiate both FRP and free radical promoted cationic polymerization (FRPCP) was underlined.

The design and the development of new PIs from silyl containing compounds exhibiting novel properties remain of great interest. The aim of the present paper is to introduce new sources of silyl radicals based on the design of silyloxyamines having easy and convenient synthetic procedures. The new proposed structures could be useful for FRP. The limited access and stability of phenoxy tris(trimethylsilyl)silanes led us to investigate alternative compounds such as new silyloxyamines derived from pentamethyldisilane.^[3] Two starting structures (8-hydroxyjulolidine and 3-diethylaminophenol) have been selected for the synthesis of the corresponding silyloxyamines (Scheme 2): silyloxyjulolidine (**SiN1**), silyloxyaniline (**SiN2**). In contrast with other silyl sources previously developed and built on a carbonyl chromophore, these molecules are expected to possess a charge transfer transition

(the donor being the amine and the acceptor the silyl ether group) allowing a tunable red-shift of the absorption through a relatively easy introduction of various amine skeletons. This could help in the design of efficient longer wavelength absorbing PIs for less toxic irradiation lamps.^[11-12]

Through laser flash photolysis (LFP), Electron Spin Resonance Spin-Trapping (ESR-ST) and quantum mechanical calculations, we will evaluate the silyl radical formation upon UV irradiation, investigate the photopolymerization ability of these silyloxyamines by Real-Time FTIR and propose a mechanism for the initiation step of the acrylate photopolymerization.



Scheme 2.

Experimental part and computational procedure:

1/ Samples:

8-hydroxyjulolidine and 3-diethylaminophenol were purchased from Aldrich and used with the best purity available. Chloropentamethyldisilane was purchased from Aldrich and used as received. Benzophenone (BP) was used as reference type II photoinitiator (Aldrich). Ethyldimethylaminobenzoate (EDB-Esacure from Lamberti) and Tris(trimethylsilyl)silane (TTMSS - Aldrich) were chosen as reference co-initiators.

2/ Synthesis procedures for SiN1 and SiN2:

Synthesis of SiN1:

To a solution of 8-hydroxyjulolidine (0.1 g, 0.53 mmol) in CH_2Cl_2 (0.5 mL) were added DMAP (10 mol%, 6.5 mg), $i\text{-PrNEt}_2$ (0.18 mL, 1.06 mmol) and chloropentamethyldisilane (0.16 mL, 0.84 mmol). After 48 h, a conversion of 70% was reached as indicated by TLC analysis (cyclohexane/ethyl acetate = 85:15). The reaction mixture was concentrated under vacuum and the residual oil was adsorbed on silica gel using CH_2Cl_2 . The dried solid was then loaded on silica gel and eluted with cyclohexane/ethyl acetate = 100:3 following the

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3 rapid chromatographic technique (see supporting information). The desired product eluted
4 first (clearly different from 8-hydroxyjulolidine by silica coated thin layer chromatography
5 analysis) and was obtained as colorless oil (0.10 g, 59%). A copy of the ^1H and ^{13}C NMR
6 Spectra is provided as supplementary material. The estimated purity is > 95%. From the UV
7 spectra and taking into account that the visible absorption of the starting compound (8-
8 hydroxyjulolidine) completely disappears; the presence of this starting compound in the final
9 purified product is < 0.5%.

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14 ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.64 (d, J = 7.9 Hz, 1H); 6.07 (d, J = 7.9 Hz, 1H); 3.08
15 (p, J = 5.5 Hz, 4H), 2.71 (t, J = 6.5 Hz, 2H); 2.63 (t, J = 6.5 Hz, 2H); 1.99-1.92 (4H); 0.36 (s,
16 6H); 0.10 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3 , 298 K) δ 152.2; 146.1; 126.2; 114.7; 112.5;
17 106.6; 50.2; 49.8; 27.2; 22.4; 21.94; 21.86; 2.08; -2.2.

21 22 23 *Synthesis of SiN2:*

24 To a solution of 3-diethylaminophenol (0.15 g, 0.9 mmol) in CH_2Cl_2 (1 mL) were added
25 DMAP (10 mol%), $i\text{-PrNEt}_2$ (0.32 mL, 1.8 mmol) and chloropentamethyldisilane (0.2 mL, 1
26 mmol). Monitoring the progress of the reaction by silica gel thin layer chromatography was
27 difficult as SiN2 is prone to desilylation on prolonged contact with SiO_2 . Therefore, after 12h
28 the reaction mixture was concentrated under vacuum and the residual oil was adsorbed on
29 neutral alumina using CH_2Cl_2 . The dried solid was then loaded on a small pad of silica gel
30 and eluted quickly with cyclohexane/ethyl acetate = 100:5. The desired product eluted first
31 (clearly different from 3-diethylaminophenol by alumina coated thin layer chromatography
32 analysis) and was obtained as colorless oil (0.21 g, 79%). A copy of the ^1H and ^{13}C NMR
33 Spectra is provided as supplementary material. The estimated purity is > 95%. From the UV
34 spectra and taking into account that the visible absorption of the starting compound (3-
35 diethylaminophenol) completely disappears; the presence of this starting compound in the
36 final purified product is < 0.5%.

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46 ^1H NMR (CDCl_3 , 300 MHz, 298 K) δ 7.03 (t, J = 8.1 Hz, 1H); 6.30 (d, J = 7.2 Hz, 1H); 6.17-
47 6.12 (2H); 3.31 (q, J = 6.9 Hz, 4H); 1.15 (t, J = 6.9 Hz, 6H); 0.37 (s, 6H), 0.08 (s, 9H). ^{13}C
48 NMR (75 MHz, CDCl_3 , 298 K) δ 157.2; 149.2; 129.6; 107.0; 105.4; 103.7; 44.3; 12.6; 0.2; -
49 2.2.

50 51 52 53 54 **3/ Polymerization experiments:**

55 For the film photopolymerization (20 μm thick film), a given silyloxyamine photoinitiator
56 (3% w/w; weight concentration with respect to the monomer) was dissolved in the
57 polymerizable triacrylate monomer (trimethylolpropane triacrylate TMPTA from Cytec). The
58 laminated or oxygenated films deposited on a BaF_2 chip were irradiated with the
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3 polychromatic light of a Xe lamp (filtered at $\lambda > 390$ nm; light intensity = 60 mW/cm² in the
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5 390 < λ < 800 nm range) or a polychromatic light of a Xe-Hg lamp (L8252, Hamamasu; 150
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7 W; light intensity = 44 mW/cm² in the 300-400 nm range). The polymerization kinetics of
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9 TMPTA were examined by measuring the consumption of monomer in photoinitiated
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11 experiments. The polymerization efficiencies of the photoinitiating systems were studied by
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13 measuring the percent conversion of TMPTA as a function of time. The evolution of the
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15 monomer double bond absorption at about 1630 cm⁻¹ was continuously followed by Real-
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17 Time FTIR spectroscopy (Nexus 870, Nicolet) as described in [9-13 and references therein].

18 **4/ Silyloxyamines absorption spectra:**

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20 The UV-Visible absorption spectra (200-600 nm) in acetonitrile were performed in a
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22 Beckman DU-640 Spectrophotometer. Solutions were filled into a 1-cm UV path cell.

23 **5/ Laser Flash Photolysis:**

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25 The nanosecond transient absorption setup working at 355 nm is based on a
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27 nanosecond Nd:YAG laser (Powerlite 9010, Continuum) operating at 10 Hz with an energy
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29 decreased down to about 10 mJ/ pulse at 266 nm. The analyzing system (LP900, Edinburgh
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31 Instruments) used a 450-W pulsed xenon arc lamp, a Czerny-Turner monochromator, a fast
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33 photomultiplier and a transient digitizer (TDS 340, Tektronix). The beam irradiated a 1-cm
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35 cell containing the PI. Measurements were done at room temperature. Before each
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37 measurement, solutions were degassed by argon bubbling.^[8]

38 **6/ ESR Spin-Trapping:**

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40 Electron Spin Resonance (ESR)-Spin Trapping experiments were carried out using a
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42 X-Band spectrometer (MS 200 Magnetech). The radicals generated under light irradiation
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44 (Xe-Hg lamp –Hamamatsu L8252, 150 W; $\lambda > 310$ nm) were trapped by phenyl-N-
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46 tbutyl nitron (PBN, Assay ~98%, Aldrich). This technique is useful for the identification of the
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48 radical center.^[14a-b,d] The ESR spectra simulations were carried out with the PEST WINSIM
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50 program.^[14c]

51 **7/ Cyclic Voltammetry:**

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53 The redox potentials were measured in acetonitrile by cyclic voltammetry with tetrabutyl
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55 ammonium hexafluorophosphate (0.1 M) as a supporting electrolyte. The working electrode
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57 was a platinum disc and the reference one, a saturated calomel electrode (SCE). Ferrocene
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59 was used as a standard reference ($E_{ox} = + 0.44$ V/SCE). The free-energy changes (ΔG_{Et}) for
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the electron transfer from the free radical to the triplet energy acceptor can be calculated from the classical Rehm-Weller equation^[15] (Eq. 1) where E_{ox} is the oxidation potential of the donor, E_{red} the reduction potential of the acceptor, E_T the triplet state energy, C a coulombic term for the initially formed ion pair (C is neglected here as usually done in polar solvents).

$$\Delta G_{Et} = E_{Ox} - E_{Red} - E_T + C \quad \text{Eq. 1}$$

8/ Computational procedure:

All the calculations were performed using the hybrid functional B3LYP from the Gaussian 03 suite of program.^[16] The different structures were fully optimized in the Density Functional Theory framework. The Bond Dissociation Energies (BDE) and the triplet state energy (E_T) were calculated at the UB3LYP/6-31G* level. The electronic absorption spectra for the radical cations were calculated with the time-dependent density functional theory at UB3LYP/6-311G** level on the relaxed geometries.

Results and discussion:

1/ Absorption properties and molecular orbitals involved:

The UV absorption properties of **SiN1** and **SiN2** as well as 8-hydroxyjulolidine and 3-diethylaminophenol in acetonitrile are displayed in Figure 1. The maximum absorption wavelengths are summarized in Table 1. The starting amino alcohols show a broad band between 350 and 600 nm which disappears in silyloxyamines (Figure 1).

Figure 2 describes the HOMOs and LUMOs orbitals of **SiN1** and **SiN2**; the more red-shifted absorption band corresponding to a HOMO \rightarrow LUMO transition. The HOMO of the silyloxyamines involves the π -system and the nitrogen lone pair. Interestingly, the LUMO is also delocalized on the silyl ether group. This evidences a partial charge transfer transition between the donor (the amine) and the acceptor (the O-Si-Si group). Silyloxyamines behave therefore as donor- π -acceptor molecules.

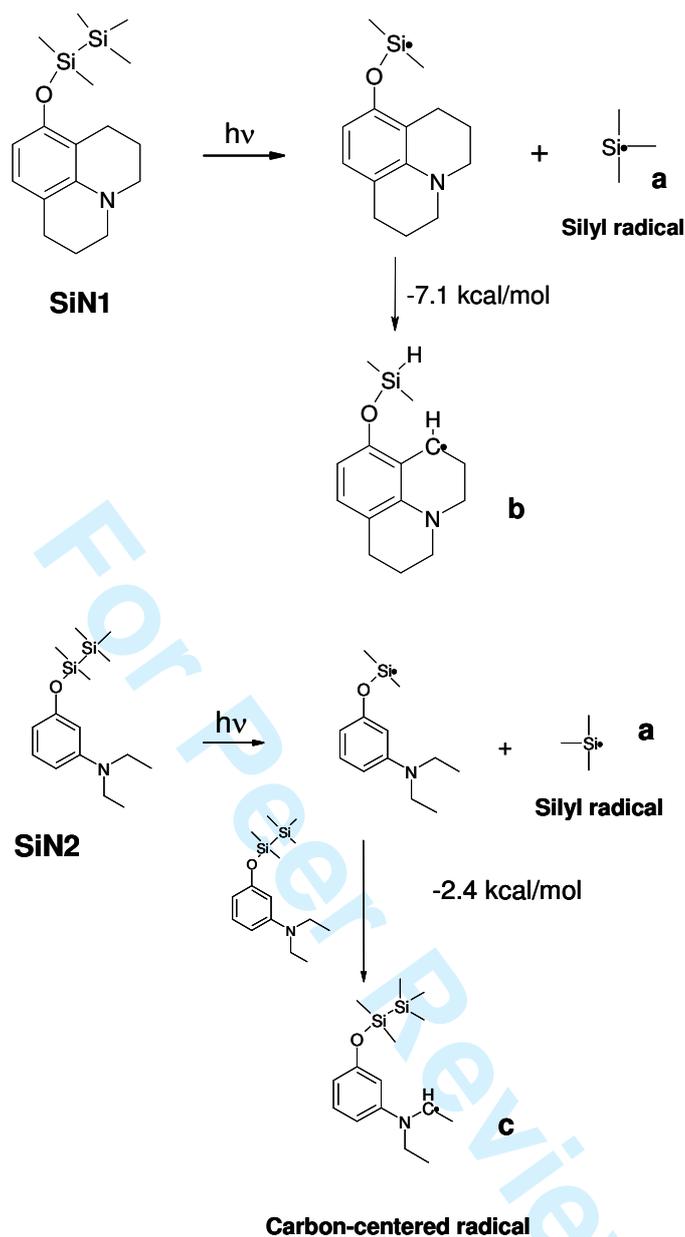
2/ Photolysis experiments:

It was reported^[1,2] that silyloxy compounds can be cleaved upon photolysis at 254 nm to give the starting alcohols with yields ranging from 62-95%. The photolysis of **SiN1** and **SiN2** in degassed acetonitrile under UV irradiation (Hg-Xe lamp; 220 mW/cm²) was thus examined as shown in Figure 3. **SiN1** and **SiN2** do not generate the corresponding alcohols

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3 as the typical absorption bands of the parent hydroxy compounds at 462 and 526 nm are not
4 observed. This behavior can suggest the occurrence of a Si-Si instead an O-Si bond
5 cleavage. An increase of a broad absorption band between 350 nm and 400 nm for both
6 silyloxyamines is also noted: it might correspond to the formation of a photolysis product
7 resulting from the attack of a silyl radical to the aromatic ring i.e. the addition of R_3Si^\bullet onto
8 aromatic rings is well documented.^[21]
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13 3/ ESR Spin-Trapping experiments:

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15 Under direct irradiation of **SiN1** and **SiN2**, two radicals are generated and trapped by
16 PBN (Figure 4). The hyperfine splitting constants for both the nitrogen (a_N) and the hydrogen
17 (a_H) of these adducts are reported in Table 2. They are assigned (Scheme 3) to the known
18 trimethylsilyl radical^[11] (**a**) and tentatively to the carbon centered radicals (**b** and **c**). *No*
19 *radicals are observed when irradiating the amino alcohols in the same conditions.* These
20 results clearly support the Si-Si cleavage; the O-Si bond cleavage can be probably ruled out
21 as the $(CH_3)_3Si-Si^\bullet(Me)_2$ radical is not observed here. Oxygen and carbon centered radicals
22 can exhibit in some case similar spectral parameters (a_N and a_H),^[14a] however, the oxygen
23 centered radicals will correspond here to phenoxy derived radicals which are fairly stable.
24 The addition of these radicals to PBN is probably not highly favorable. Moreover, in previous
25 works, the parameters for phenoxy derived radicals were found quite different to carbon
26 centered radicals.^[14b] Independently, phenoxy derived radicals can be easily characterized by
27 Laser Flash Photolysis experiments (intense absorption and specific reactivity – see below
28 the LFP data). This absorption is clearly not observed in our LFP experiments ruling out the
29 O-Si cleavage in agreement with the Molecular Orbital calculations and ESR spin trapping
30 results. The presence of **b** and **c** is accounted for by a hydrogen abstraction process. The
31 generation of these radicals is in good agreement with the high polymerization initiating
32 ability observed for **SiN1** and **SiN2** (see below) i.e. these latter radicals being good
33 polymerization initiating structures.^[8b] In **SiN1**, an intramolecular process ($\Delta H = -7.1$ kcal/mol;
34 from MO calculations) can be favorable as it involves the intermediate conformation of a six-
35 member ring. In **SiN2**, the **c** ($a_N = 14.4$; $a_H = 2.4G$ – Table 2) amount increases with the
36 irradiation time in line with a bimolecular process ($\Delta H = -2.4$ kcal/mol; MO calculations). The
37 hyperfine splitting constants for the adduct of **c** are in excellent agreement with those
38 observed recently for aminoalkyl radicals.^[14d]
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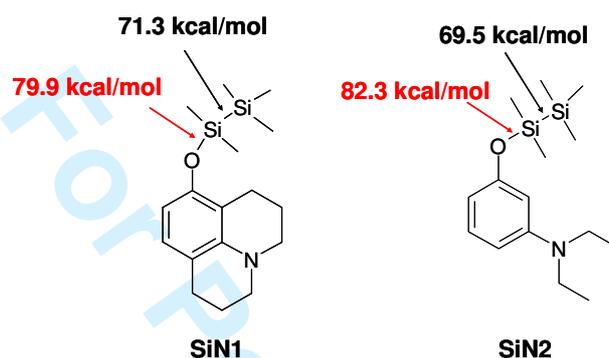
Scheme 3.

4/ Energetic Considerations:

The triplet energy levels (E_T) of **SiN1** and **SiN2** are calculated as 75.1 and 66 kcal/mol, respectively (at UB3LYP/6-31G* level). The different bond dissociation energies (BDE) associated with the cleavage of the Si-Si and Si-O bonds in **SiN1** and **SiN2** are summarized in Scheme 4. The BDEs(Si-O) are weaker than previously reported data (BDE(Si-OR)~110 kcal/mol with R=alkyl).^[28] In the present work, these weaker BDEs(Si-O) can be ascribed to the formation of stabilized phenoxy radicals. For BDEs(Si-Si) a good agreement with literature data is found.^[28]

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Interestingly, the cleavage of the Si-Si bond is energetically more favorable than that of the Si-O bond by about 9 and 13 kcal/mol for **SiN1** and **SiN2**, respectively; the (Si-Si) BDEs are lower than the (Si-O) BDEs for both compounds; the Si-Si triplet cleavage is exothermic for **SiN1** and athermic for **SiN2**; the Si-O triplet cleavage is endothermic. A singlet state cleavage should be obviously feasible in both **SiN1** and **SiN2** for the Si-Si bonds. The Si-O fragmentation is not, however, experimentally supported. The triplet state of **SiN1** and **SiN2** is not found dissociative in MO calculations but this does not exclude the possibility of a cleavage process.



Scheme 4.

5/ Laser flash photolysis (LFP) investigation:

The transient absorption spectra recorded immediately after the laser flash excitation (at 266 nm) of **SiN1** and **SiN2** as well as the corresponding starting amino alcohols (Figure 5) are similar. The 8-hydroxyjulolidine and **SiN1** absorption maximum wavelength is located at 470 nm whereas it shifts to a slightly higher wavelength (about 490 nm) for diethylaminophenol and **SiN2**. The transients decay in the 5-10 μ s range. They are ascribed to the radical cation centered on the N-atom and probably generated through a photoionization process. Indeed, this is consistent with the reported formation of a radical cation upon laser excitation of various aliphatic and aromatic amines in a freon glass,^[17,18] for triethylamine, 1-azabicyclo[3.3.3]undecane, 1-azabicyclo[2.2.2]octane or 1,4-diazabicyclo[2.2.2]octane) in acetonitrile solutions.^[19-20] Moreover, TD-DFT calculations on the possible radical cation (at the B3LYP/6-311G** level; after full geometry optimization) show here that the observed transient spectra for 8-hydroxyjulolidine and **SiN1**, 3-diethylaminophenol and **SiN2** quite satisfactorily correlate with the calculated spectra (vertical bars in Figure 5). Radicals **a**, **b** and **c** are not observed due to their lack of significant absorption.^[11,12,21] The phenoxy radicals usually characterized^[24] by an intense absorption at about 400 nm are not observed here in full agreement with ESR-ST results which have ruled out a O-Si cleavage for the investigated compounds.

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3 The formation of the radical cation can be assumed as a competitive pathway to the Si-
4 Si cleavage process since the absorption corresponding to this species is very similar for
5 both **SiN1**/8-hydroxyjulolidine and **SiN2**/diethylamino-phenol evidencing a weak influence of
6 the silyl moiety on this transient.
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10 The Si-Si cleavage can result from the significant electron density transfer from the
11 donor (julolidine for example) to the acceptor (silyl ether group) observed in the LUMOs. A
12 similar behavior has been pointed out ^[22] in a donor-acceptor molecule (3,5-dimethyl-4-(9-
13 anthracenyl)julolidine) where an intramolecular charge transfer occurs from julolidine to
14 anthracene.
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18 When exciting benzophenone (BP) in the presence of **SiN2**, the BP ketyl radical is
19 detected (ketyl radical quantum yield = 0.8; the procedure to measure this parameter is
20 presented in detail in [8c]). The BP/**SiN2** interaction rate constant is measured as $3.1 \cdot 10^9 \text{ M}^{-1}$
21 s^{-1} . The oxidation potentials of EDB and **SiN2** are 1.08 V and 0.77 V, respectively. Using a
22 reduction potential of -1.79 eV and a triplet state energy of 2.98 eV for BP, exothermic
23 electron-transfer reactions ($\Delta G = -0.11 \text{ eV}$ and -0.42 eV for BP/EDB and BP/**SiN2**,
24 respectively) are calculated from the Rehm-Weller equation (Eq 1). These results are in favor
25 of an usual electron transfer followed by a proton transfer observed for amines.^[11] An
26 aminoalkyl radical is concomitantly generated.
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34 **6/ Free Radical photopolymerization ability:**

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37 Interestingly, the **SiN1** and **SiN2** compounds proposed as Type I photoinitiators are
38 liquids: this improves their solubility in monomers compared to the starting alcohol powders.
39 The photopolymerization profiles of TMPTA in laminated (to avoid oxygen regeneration) and
40 aerated conditions under a polychromatic irradiation (Xe-Hg lamp) are shown in Figure 6.
41 The polymerization rates R_p and the final conversions after 400 s of irradiation are given in
42 Table 3. In laminate, **SiN1** and **SiN2** are better PIs than 8-hydroxyjulolidine where the
43 initiating radicals are presumably formed through unclear by-side interactions of this amino
44 alcohol with the monomer. Due to their quite low absorption (Figure 1) for the principal
45 emission bands of Hg-Xe lamp i.e. $\lambda > 300 \text{ nm}$, their efficiency is likely lower than that
46 encountered with other Type I PIs. **SiN2** is better than **SiN1** in agreement with the above
47 mentioned energetic considerations for a more efficient Si-Si cleavage process. Under air, as
48 expected in such a low viscosity matrix,^[25] the polymerization rate dramatically drops down.
49 However, interestingly, **SiN1** compared to 8-hydroxyjulolidine leads to a significant
50 polymerization process under air. This behavior is highly worthwhile since many classical PIs
51 do not allow initiation for these severe conditions. This evidences the formation of silyl
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3 radicals i.e. it is well known that these species are useful for polymerization in aerated
4 conditions (to overcome the oxygen inhibition).^[25]

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6 Under visible light (Xe lamp; $\lambda > 400$ nm), in an aerated matrix, both the rate of
7 polymerization and final conversion decrease (see Figure 7 for **SiN1**). To speed up the
8 polymerization, experiments were done using **SiN1** in the presence of tris(trimethylsilyl)silane
9 (TTMSS; 1 wt%) already shown as an excellent additive for photopolymerization under
10 air.^[7,23,25] A remarkable enhancement is noted as quite good photopolymerization profiles and
11 high conversion (~ 60%) were obtained (Figure 7). The better photoinitiating ability of **SiN1** in
12 the presence of TTMSS is full agreement with previous data on other photoinitiators. The
13 ability of TTMSS to overcome the oxygen inhibition in FRP process is already described in
14 [25].
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21 Based on the LFP experiments, silyloxyamines should also work as Type II PIs. This is
22 exemplified (Figure 8) by the benzophenone (BP)/**SiN2** system in laminated conditions using
23 a polychromatic light exposure (Xe-Hg lamp). Compared to the BP/EDB reference system, a
24 remarkable increase of the polymerization rate (R_p) is noted (Table 4). The direct light
25 absorption by **SiN2** leading to a silyl radical can contribute to the R_p enhancement.
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31 Conclusion:

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33 In the present paper, the photolysis of two new silyloxyamines derived from
34 pentamethyldisilane is investigated. Compared to usual super silyl ethers, they cannot be
35 deprotected upon photolysis as they do not yield the starting alcohol (the Si-Si bond is
36 weaker than the Si-O bond). On the opposite, the generation of the silyl radicals allows to
37 use of these compounds as photoinitiators. Some modifications of the chromophoric group
38 (for example by introducing more delocalized π systems) should allow tuning of the
39 absorption towards the visible due to the charge transfer character of the HOMO-LUMO
40 transition, enhance the light absorption properties and, hence, the polymerization ability of
41 these compounds: this new concept opens up a new way for the design of efficient visible-
42 near UV absorbing PIs in the Radiation Curing area.^[26] This concept might also be used in
43 non linear optics or two-photon absorption applications.^[27]
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Tables:

Table 1. Absorption maxima of 8-hydroxyjulolidine, 3-diethylaminophenol, **SiN1** and **SiN2** in acetonitrile.

	SiN1	8-hydroxyjulolidine	SiN2	3-diethylaminophenol
Absorption maximum (nm)	267, 303	267, 303, 462	262, 301	262, 301, 526

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Table 2. Hyperfine coupling constants for the radical adducts of **SiN1** and **SiN2** measured by ESR Spin-Trapping (PBN).

		$a_N(\text{G})$	$a_H(\text{G})$
SiN1	a	14.8	6.3
	b	14.4	2.5
SiN2	a	14.8	6.3
	c	14.4	2.4

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Table 3. Radical photopolymerization of TMPTA in the presence of different photoinitiating systems: polymerization rate ($R_p/[M_0]$ (s^{-1})) and final conversion after 400 s of irradiation.

Photoinitiators	In laminate		Under air	
	Final conversion (%)	$R_p / [M_0] \times 100$	Final conversion (%)	$R_p / [M_0] \times 100$
8-hydroxyjulolidine	62	1.4	-	-
SiN1	72	4.1	17	0.2
SiN2	68	2.2	-	-

(-) no photopolymerization

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Table 4. Radical photopolymerization of TMPTA in the presence of BP/SiN₂ and BP/EDB: polymerization rate $R_p/[M_0]$ (s^{-1}) and final conversion after 400 s of irradiation.

Photoinitiating systems	In laminate	
	Final conversion (%)	$R_p / [M_0] \times 100$
BP / EDB	71	16.7
BP / SiN ₂	80	23.3

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Captions of Figures:

Figure 1. UV absorption properties: (A) 8-hydroxyjulolidine (dash line) and **SiN1** (solid line); insert: zoom between 300 and 600 nm. (B) 3-diethylaminophenol (dash line) and **SiN2** (solid line). In acetonitrile.

Figure 2. HOMO and LUMO of **SiN1** (left) and **SiN2** (right). From DFT calculations.

Figure 3 . Photolysis of (A) **SiN1** and (B) **SiN2** in acetonitrile (Hg-Xe lamp irradiation).

Figure 4. ESR spin-trapping spectra using PBN. 1) **SiN1** and 2) **SiN2**. UV-light irradiation at $\lambda > 310$ nm: A) experimental and B) simulated spectra.

Figure 5. Transient absorption spectra of A) 8-hydroxyjulolidine and **SiN1** and B) 3-diethylamino-phenol and **SiN2** in acetonitrile ($\lambda_{exc} = 266$ nm). The oscillator strengths for the calculated UV-visible absorption spectra of the corresponding cations are given (sticks: see text).

Figure 6. Photopolymerization profiles of TMPTA in the presence of A) **SiN1** (1), 8-hydroxyjulolidine (2) and **SiN2** (3) in laminated conditions (1% w/w) and B) **SiN1** (1), 8-hydroxyjulolidine (2) in aerated conditions (1% w/w). Xe-Hg lamp; Lamp intensity = 44 mW/cm².

Figure 7. Photopolymerization profiles of TMPTA in the presence of 1) 8-hydroxyjulolidine, 2) **SiN1**, 3) 8-hydroxyjulolidine/TTMSS (1 wt%) and 4) **SiN1**/TTMSS (1 wt%). Under air. Xe lamp; $\lambda > 400$ nm. Intensity = 60 mW / cm².

Figure 8. Photopolymerization profiles of TMPTA in the presence of 1) BP (1wt%)/EDB (3 wt%) and 2) BP (1 wt%)/**SiN2** (3 wt%). In laminate. Hg-Xe lamp; polychromatic light; intensity = 44 mW/cm².

Figure 1.

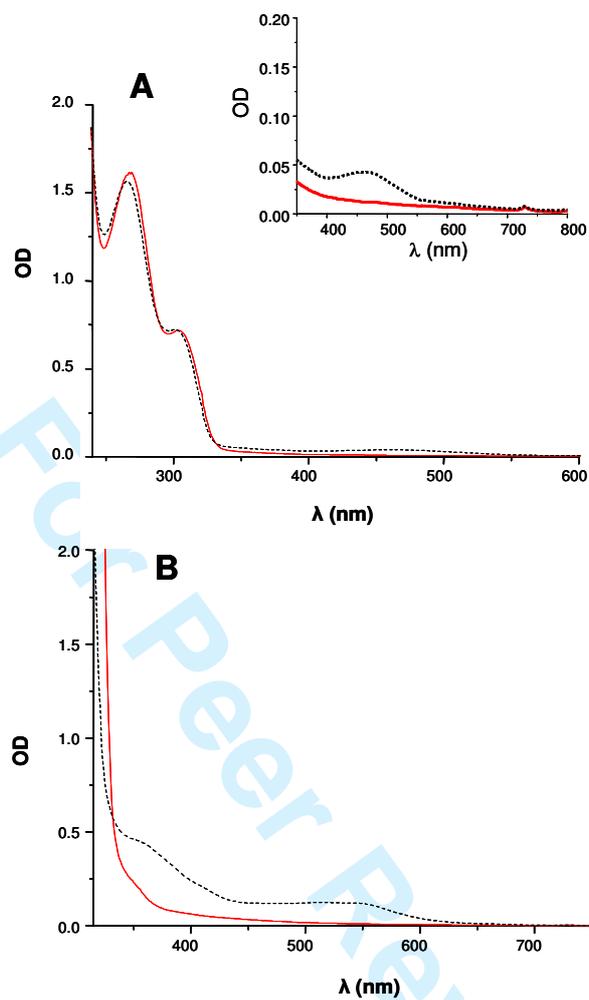


Figure 2.

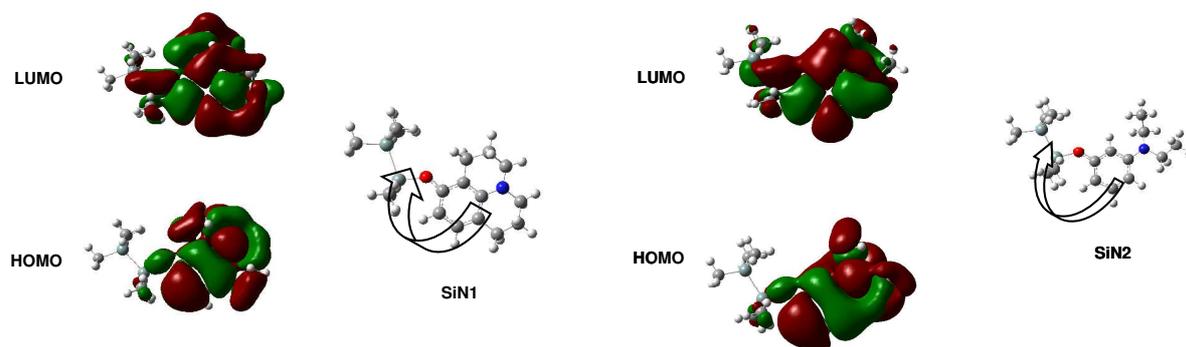


Figure 3.

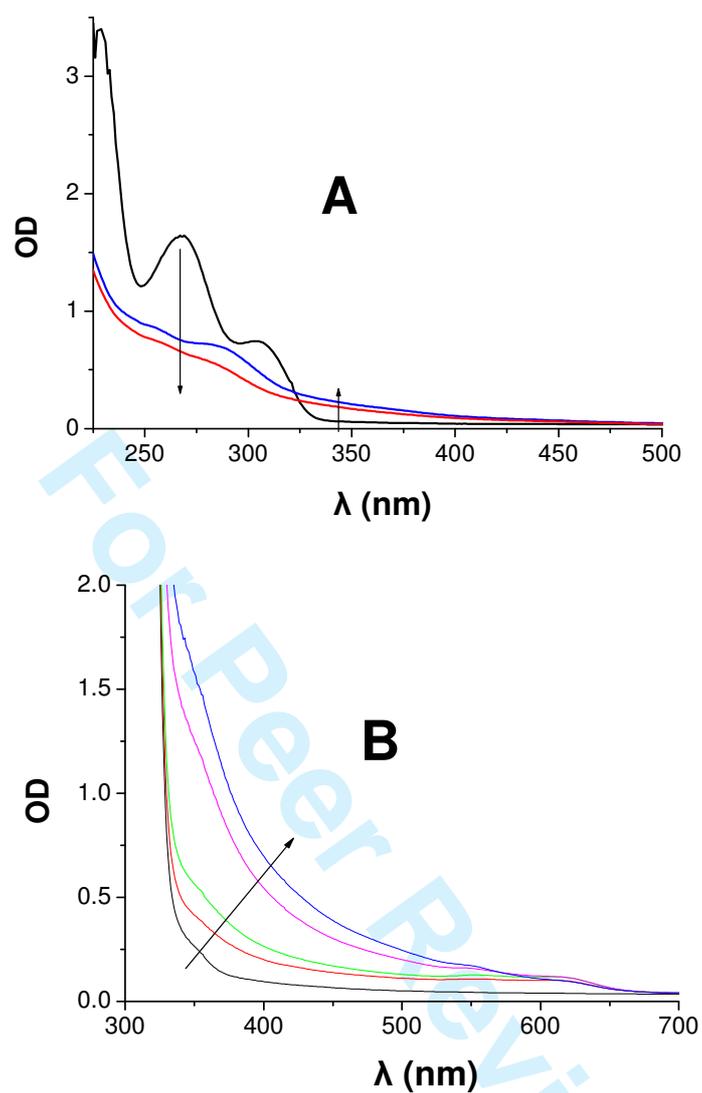


Figure 4.

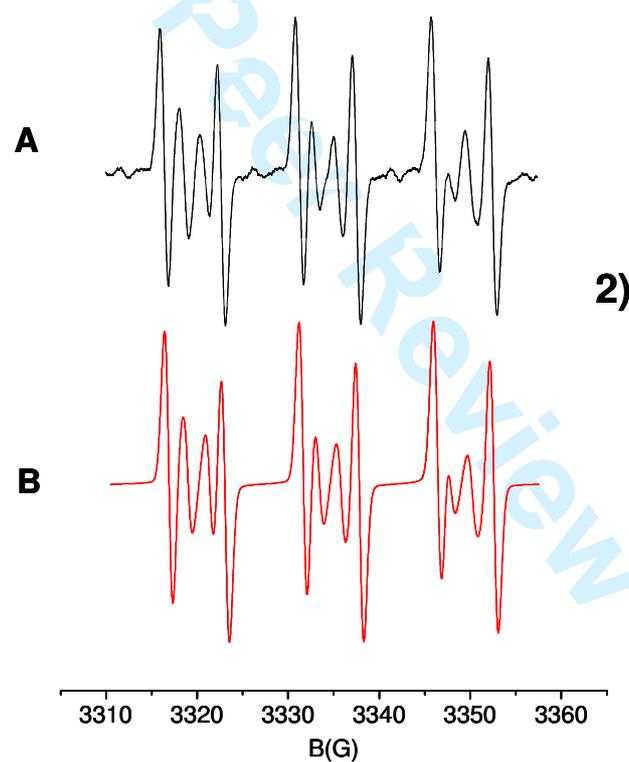
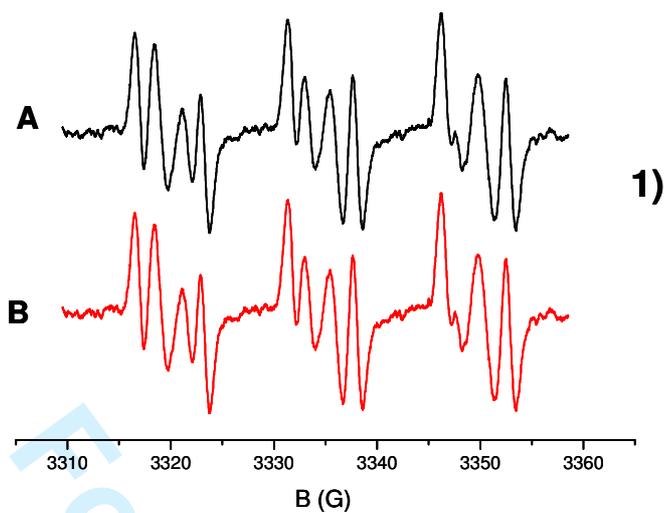


Figure 5.

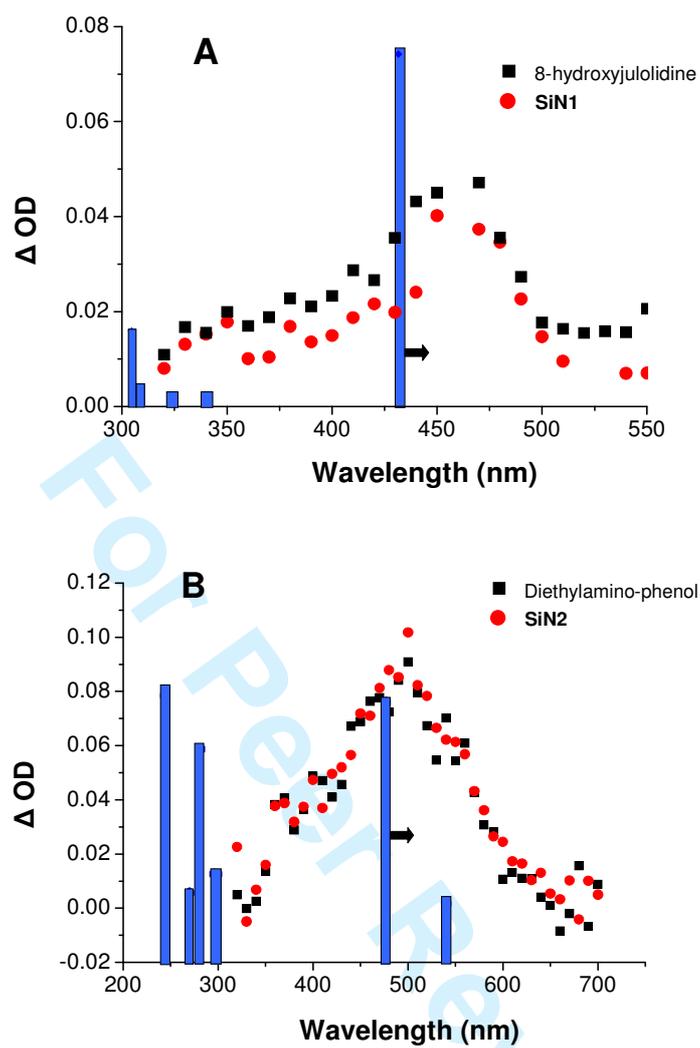


Figure 6.

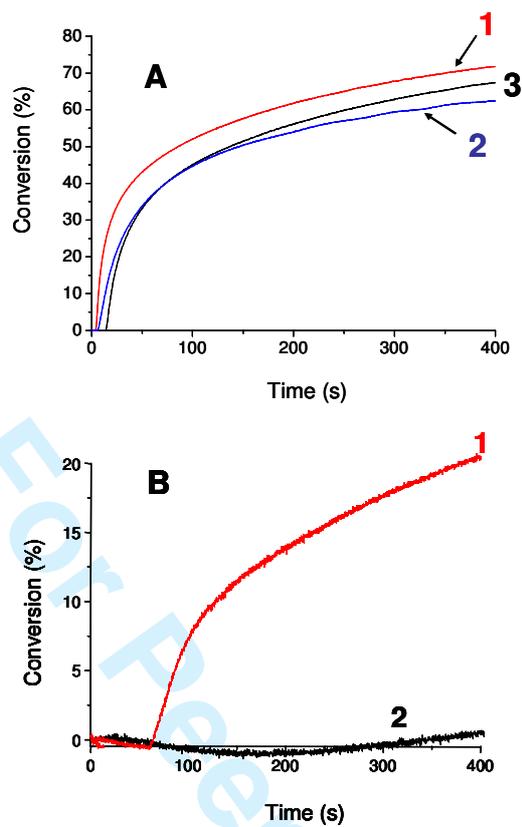
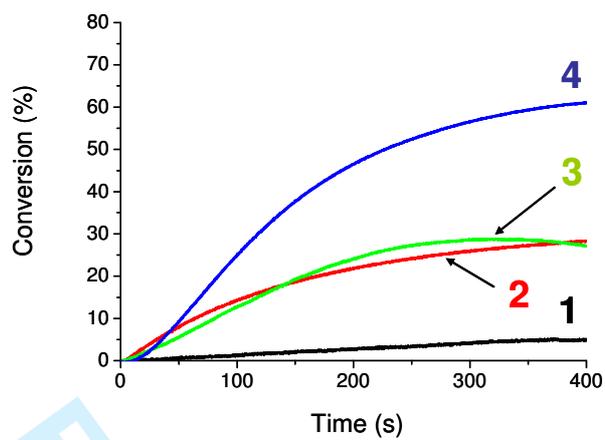
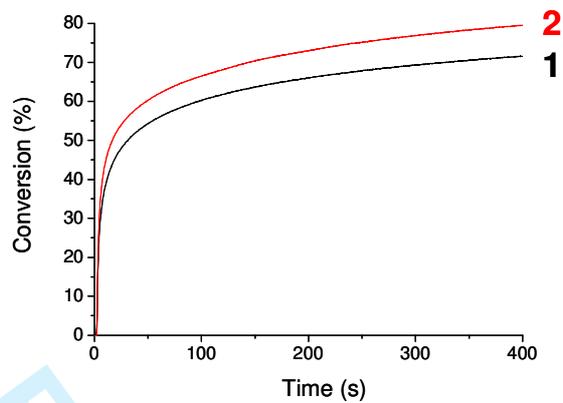


Figure 7.



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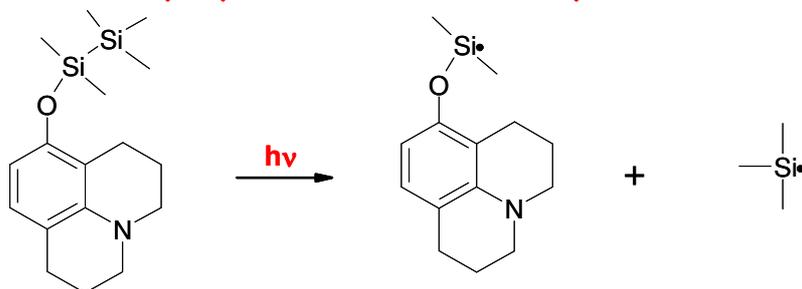
Figure 8.



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Silyloxyamines as Sources of Silyl Radicals



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