

# Modulation of Photo-deprotection by the Sunscreen Protocol

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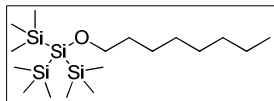
## EXPERIMENTAL SECTION/SUPPORTING INFORMATION

General Remarks. All commercially available solvents and reagents were of reagent grade quality and used without further purification. NMR spectra were recorded on Bruker DPX 400 or DPX 500 instruments; chemical shifts, given in ppm, are relative to the residual solvent peak.<sup>1</sup> Gas chromatography data was obtained using an Agilent 6850 GC equipped with an Agilent 5973 MSD working under standard conditions and an Agilent HP5-MS column. A Thermoscientific LTQU XL Orbitrap was used for high resolution mass spectrometry. Purification by column chromatography was performed on Davisil Chromatographic silica media (40-60  $\mu$ m). TLC analyses were performed using Merck pre-coated silica gel (0.2 mm) aluminum sheets or glass plates. UV-VIS measurement performed on a JASCO V-550 UV-VIS spectrophotometer. Irradiation experiments were carried out using a Rayonet RPR-200 photoreactor with 253.7 nm lamps (Figure S1) and were carried out in a quartz vessels or a quartz 5mm NMR tube.

2537 Å	
Wave length (Å)	Intensity (microwatts/cm <sup>2</sup> )
2537	12800
2652	388
2804	14
2894	18
2967	66
3022	32
3129	250
3654	213
4047	250
4359	768
5461	418
5780	91

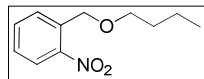
**Figure S1.** Lamps used in the Rayonet reactor: 2537Å lamps (approx. 35 watts. Photons  $1.6 \times 10^{16}$  / sec/cm<sup>3</sup>, intensity readings – at center of reactor).

### Synthesis of tris(trimethylsilyl)silyloxy octane (**1a**) :



To a solution of 1-octanol (0.190 mL, 1.2 equiv) and N,N dimethyl 4-aminopyridine (DMAP) (1.58 g, 1.3 equiv) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> a solution of tris(trimethylsilyl) silyl chloride (0.283 g, 1 mmol) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added under argon. The reaction was stirred overnight at room temperature. Water was added and the mixture extracted twice with CH<sub>2</sub>Cl<sub>2</sub>, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and solvent was evaporated to give a colorless oil which was purified using flash chromatography (Silica gel, 10% CH<sub>2</sub>Cl<sub>2</sub> in petroleum ether) to give 0.271 g of **1a** as colorless oil in 72% yield. <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>)  $\delta$  3.45 (2H, t,  $J$ = 6.5 Hz), 1.46 (2H, p,  $J$ = 6.5 Hz), 1.26 (10H, s (br)), 0.88 (3H, t,  $J$ = 6.5 Hz), 0.18 (27H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 68.3, 33.2, 32.0, 29.6, 29.5, 26.0, 22.8, 14.2, 0.4. UV-VIS:  $\lambda_{\text{max}}$  CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon_{254}$ ) 244nm, (925M<sup>-1</sup>cm<sup>-1</sup>) HR-MS (ESI) C<sub>17</sub>H<sub>44</sub>OSi<sub>4</sub> m/z: (M+H)<sup>+</sup> calculated: 377.2542 found: 377.2539, (M+Na)<sup>+</sup> calculated: 399.2361 found: 399.2361.

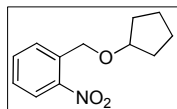
### Synthesis of o-nitro[pentyloxy (methyl)]benzene (**2a**):



This procedure relies on a general procedure offered by Madhavan *et al.* with several modifications.<sup>2</sup> To a

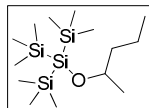
solution of 3.8 mL (35 mmol, 5 equiv) pentanol in 40 mL NaOH 10% and 80 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature, 2-nitrobenzylbromide (7 mmol) and tetrabutylammonium hydrogen sulfate (10 mmol) was added. The flask was covered with aluminum foil and the reaction was stirred for over 24 h, until GC-MS analysis indicated consumption of starting material. Water was added, and organic materials extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. Organic layers were combined, dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> and solvent was evaporated to leave yellow oil as residue, which was purified using flash chromatography (silica gel, 40% CH<sub>2</sub>Cl<sub>2</sub> in petroleum ether) to allow 0.480 g of **2a** as yellow oil in 31% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (1H, dd, J = 8.2, 1.3 Hz), 7.84 – 7.77 (1H, m), 7.69 – 7.56 (1H, m), 7.43 (1H, td, J = 7.4, 1.4 Hz), 4.87 (2H, s), 3.57 (2H, t, J = 6.6 Hz), 1.72 – 1.61 (2H, m), 1.48 – 1.27 (6H, m), 0.92 (3H, t, J = 7.1 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.4, 135.8, 133.8, 128.8, 127.9, 124.8, 76.8, 71.6, 69.5, 29.6, 28.5, 22.7, 14.2. UV-VIS: λ<sub>max</sub> CH<sub>2</sub>Cl<sub>2</sub> (ε<sub>254</sub>) 269nm, (3270M<sup>-1</sup>cm<sup>-1</sup>) HR-MS (ESI) C<sub>12</sub>H<sub>17</sub>NO<sub>3</sub> m/z: (M+H)<sup>+</sup> calculated: 224.1281 found : 224.1285, (M+Na)<sup>+</sup> calculated: 246.1101 found: 246.1100.

#### Synthesis of o-nitro[(cyclopentyloxy)methyl]benzene (**3a**):



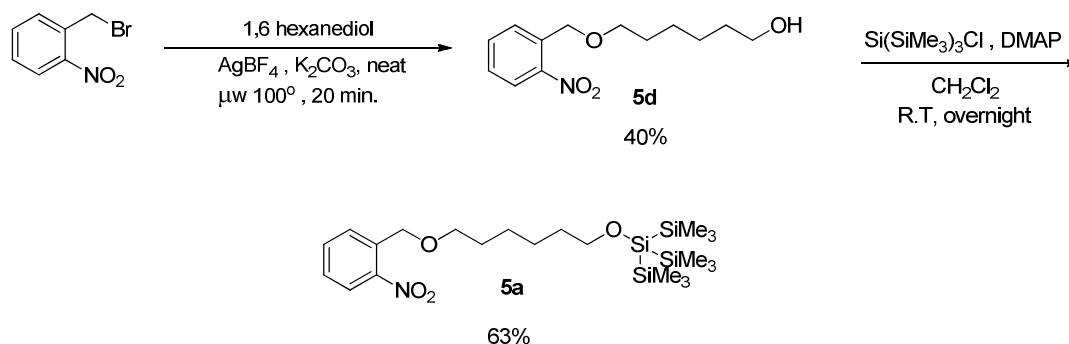
2.1 mL of cyclopentanol (23 mmol 10 equiv), 0.5g 2-nitrobenzyl bromide (2.3 mmol), 0.45 g silver tetrafluoroborate (2.3 mmol, 1 equiv) and 1.6 g potassium carbonate (5 equiv) were placed in a 35 mL Pyrex microwave tube equipped with a magnetic stirrer. The tube was heated in a CEM corporation Discover microwave reactor to 100 C° for 20 minutes (150 W, 150 PSI max. pressure). Ethyl acetate was added to the black residue and the mixture was filtered through Celite and washed thoroughly with water. Organic phase was dried with anhydrous MgSO<sub>4</sub> and solvent was evaporated to leave brown oil which was purified using flash chromatography (silica gel 3% ethyl acetate in petroleum ether) to afford 0.134 g of **3a** as yellow liquid in (27% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (1H, dd, J = 8, J=1.5 Hz), 7.85 – 7.75 (1H, bd, J = 8Hz), 7.63 (1H, m), 7.41 (1H, m), 4.84 (2H, s), 4.10 – 3.99 (1H, m), 1.84 – 1.68 (6H, m), 1.64 – 1.48 (2H, m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.5, 136.1, 133.7, 129.0, 127.8, 124.7, 82.1, 67.4, 32.4, 23.7. UV-VIS: λ<sub>max</sub> CH<sub>2</sub>Cl<sub>2</sub> (ε<sub>254</sub>) 269nm, (3377M<sup>-1</sup>cm<sup>-1</sup>) HR-MS (ESI) C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub> m/z: (M+H)<sup>+</sup> calculated: 222.1125 found : 222.1127, (M+Na)<sup>+</sup> calculated: 244.0944 found: 244.0942.

#### Synthesis of 2-tris(trimethylsilyl)silyloxy pentane (**4a**):



To a solution of 0.130 mL of 2-pentanol (1.2 equiv) and N,N dimethyl 4-aminopyridine (DMAP) (0.158 g, 1.3 equiv) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> a solution of tris(trimethylsilyl) Silyl chloride (0.283 g, 1 mmol) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added under Argon. The reaction was stirred overnight at room temperature. Water was added and the mixture extracted twice with CH<sub>2</sub>Cl<sub>2</sub>, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and solvent was evaporated to give a colorless oil which was purified by flash chromatography (Silica gel, 10% CH<sub>2</sub>Cl<sub>2</sub> in petroleum ether) to give 0.307 g **4a** as colorless oil which solidified to colorless amorphous solid in 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.48 (1H, sep, J=6Hz), 1.48 – 1.18 (4H, m), 1.07 (3H, d, J = 6Hz), 0.89 (3H, t, J = 6.9Hz), 0.18 (27H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 73.0, 42.1, 23.4, 18.9, 14.5, 0.6. UV-VIS: λ<sub>max</sub> CH<sub>2</sub>Cl<sub>2</sub>: (ε<sub>254</sub>) 246nm, (985M<sup>-1</sup>cm<sup>-1</sup>) HR-MS (ESI) C<sub>14</sub>H<sub>38</sub>OSi<sub>4</sub> m/z: (M+H)<sup>+</sup> calculated: 335.2072 found : 335.2071, (M+Na)<sup>+</sup> calculated: 357.1892 found: 357.1891

#### Synthesis of a silyl and nitro-protected hexane diol (**5a**):

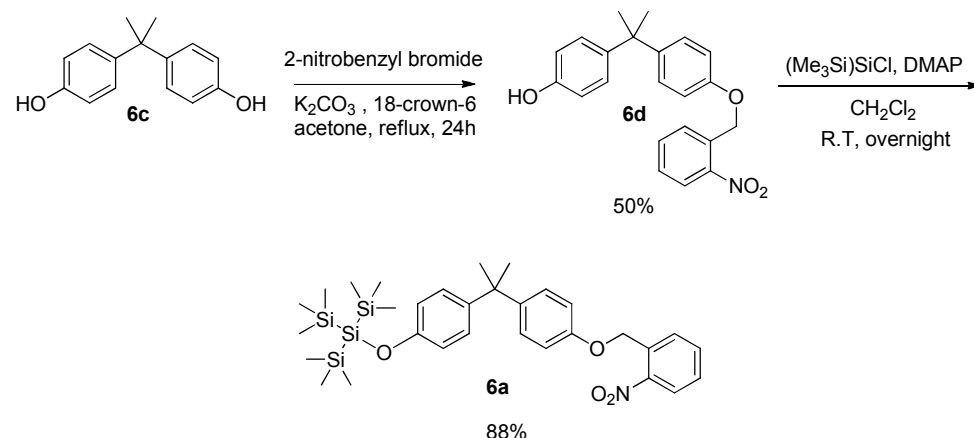


0.500 g of 2-nitrobenzyl bromide (2.3 mmol), 0.750 g of hexanediol (6.3 mmol), 0.450 g of silver tetrafluoroborate (2.3 mmol) and 1.60 g of potassium carbonate (11.5 mmol) was placed into 35 mL Pyrex microwave tube. The tube was heated in a CEM corporation microwave reactor to 100°C for 20 minutes (150 W, 150 PSI max. pressure). Ethyl acetate was added and the solution was filtered through Celite, washed extensively with water and dried on anhydrous MgSO<sub>4</sub>. Solvent was evaporated to leave brown oil which was purified using flash chromatography (silica gel, 100% CH<sub>2</sub>Cl<sub>2</sub> and then 30% ethyl acetate in petroleum ether) to give 0.235 g of **5d** as yellow oil in 40% yield for combined 2 reactions. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.05 (1H, dd, J = 8.0, 1.0 Hz), 7.79 (1H, dd, J = 8.0, 1.0 Hz), 7.64 (1H, td, J = 7.5, 1.0 Hz), 7.46 – 7.40 (1H, m), 4.87 (2H, s), 3.66 (2H, t, J = 6.5 Hz), 3.57 (2H, t, J = 6.5 Hz), 1.68 (2H, p, J = 6.5Hz), 1.59 (2H, p, J = 6.5 Hz), 1.49 – 1.36 (4H, m). <sup>13</sup>C NMR (125

MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 135.5, 133.7, 128.8, 128.0, 124.7, 71.4, 69.5, 63.0, 32.79, 29.8, 26.1, 25.7. HR-MS (ESI) C<sub>13</sub>H<sub>19</sub>NO<sub>4</sub> m/z: (M+H)<sup>+</sup> calculated: 254.1387 found : 254.1393, (M+Na)<sup>+</sup> calculated: 276.1206 found: 276.1209.

To a stirred solution of 0.230 g **5d** (0.9 mmol) and 0.133 g (1.1 mmol) of N,N dimethyl 4-aminopyridine (DMAP) in 0.9 mL of dry CH<sub>2</sub>Cl<sub>2</sub>, a solution of 0.283 g of tris(trimethylsilyl) silyl chloride (1 mmol) in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added. Reaction was covered with aluminum foil, and was stirred in room temperature under argon overnight. After completion (monitored by GC-MS), water was added and organics were extracted twice with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was dried on Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The yellow oil residue was purified using flash chromatography (silica gel, 5% diethyl ether in petroleum ether) to give 0.286 g of **5a** as yellow oil in 63% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (1H, dd, J = 8.0, 1.0 Hz), 7.81 (1H, d, J = 8.0 Hz), 7.64 (1H, t, J = 7.6 Hz), 7.42 (1H, m), 4.87 (2H, s), 3.56 (2H, t, J = 6.4 Hz), 3.46 (2H, t, J = 6.4 Hz), 1.66 (2H, p, J = 6.8), 1.49 (2H, p, J = 6.8), 1.45 – 1.30 (4H, m), 0.18 (27H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.4, 135.8, 133.8, 128.8, 127.9, 124.8, 71.5, 69.5, 68.1, 33.1, 29.9, 26.2, 25.9, 0.5. UV-VIS:  $\lambda_{\text{max}}$  CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon_{254}$ ) 268nm, (4011M<sup>-1</sup>cm<sup>-1</sup>). HR-MS (ESI) C<sub>22</sub>H<sub>45</sub>NO<sub>4</sub>Si<sub>4</sub>, m/z: (M+H)<sup>+</sup> calculated: 500.2498 found : 500.2495, (M+Na)<sup>+</sup> calculated: 522.2318 found: 522.2306.

#### Synthesis of a silyl and nitro-protected bisphenol A (**6a**):

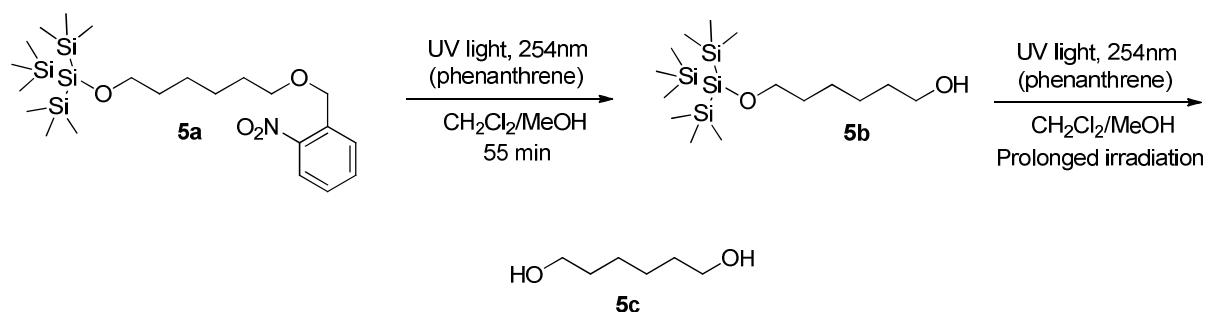


3.15 g of 2-nitrobenzyl bromide (13.8 mmol) and 3.00 g of bisphenol A (13.8 mmol) and 0.182 g of 18-crown 6 (5% mol) dissolved in 80 mL of acetone. 2.1 g of K<sub>2</sub>CO<sub>3</sub> (1.1 equiv) was added and the solution heated to reflux overnight. When GC-MS indicated that all of the bromide was consumed, reaction allowed to cool to room temperature and water was added. Organics were extracted twice to CH<sub>2</sub>Cl<sub>2</sub>, the combined organic phase was washed twice with water and dried with MgSO<sub>4</sub>, filtered and the solvent evaporated to leave a yellow/white solid which was purified by flash chromatography (silica gel, 50% CH<sub>2</sub>Cl<sub>2</sub> in petroleum ether until the double substituted bisphenol A is removed and then 100% CH<sub>2</sub>Cl<sub>2</sub>) to obtain 2.50 g of **6d** as a yellow solid in 50% yield.

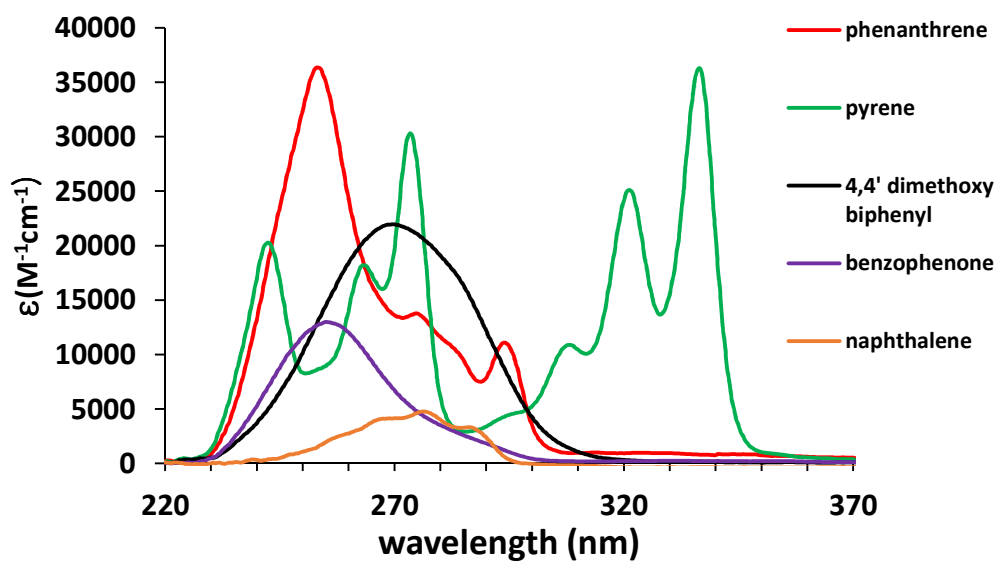
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (1H, dd, J = 8.0, 1.2 Hz), 7.91 (1H, dd, J = 8.0, 1.0 Hz), 7.68 (1H, td, J = 7.6, 1.2 Hz), 7.48 (1H, td, J = 8.0, 1.2 Hz), 7.20 – 7.05 (4H, m), 6.94 – 6.68 (4H, m), 5.46 (4H, s), 1.63 (6H, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 153.4, 147.1, 144.2, 143.3, 134.3, 134.1, 128.8, 128.4, 128.1, 128.0, 125.1, 114.9, 114.5, 67.0, 41.9, 31.2. HR-MS (ESI) C<sub>22</sub>H<sub>21</sub>NO<sub>4</sub>, m/z: (M+NH<sub>4</sub>)<sup>+</sup> calculated: 381.1809 found : 381.1815, (M+Na)<sup>+</sup> calculated: 386.1363 found: 386.1357.

To a stirred solution of 0.363 g (1 mmol) of **6d** and 0.158 g (1.3 mmol) of N,N dimethyl 4-aminopyridine (DMAP) dissolved in 1 mL of dry CH<sub>2</sub>Cl<sub>2</sub>, a solution of 0.283 g (1 mmol) of tris(trimethylsilyl) silyl chloride in 1 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added. Reaction was stirred overnight in room temperature under argon. After completion, water was added and organics were extracted twice to CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phase was dried using anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Solvent was evaporated to leave yellow oil which was purified using flash chromatography (silica gel, 20% CH<sub>2</sub>Cl<sub>2</sub> in petroleum ether) to yield 0.534 g **6a** as yellow solid in 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (1H, dd, J = 8.0, 1.2 Hz), 7.92 (1H, dd, J = 8.0, 1.0 Hz), 7.68 (1H, td, J = 8.0, 1.2 Hz), 7.48 (1H, tm, J = 8.0 Hz), 7.18 – 7.09 (2H, m), 7.09 – 7.02 (2H, m), 6.92 – 6.84 (2H, m), 6.76 – 6.63 (2H, m), 5.46 (2H, s), 1.62 (6H, s), 0.18 (27, s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.7, 156.1, 147.1, 144.6, 143.4, 134.4, 134.1, 128.8, 128.3, 128.1, 127.8, 125.1, 119.2, 114.4, 67.0, 42.0, 31.2, 0.2. UV-VIS:  $\lambda_{\text{max}}$  CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon_{254}$ ) 274nm, (4629M<sup>-1</sup>cm<sup>-1</sup>) HR-MS (ESI) C<sub>31</sub>H<sub>47</sub>NO<sub>4</sub>Si<sub>4</sub>, m/z: (M+H)<sup>+</sup> calculated: 610.2655 found : 610.2664, (M+Na)<sup>+</sup> calculated: 632.2474 found: 632.2466.

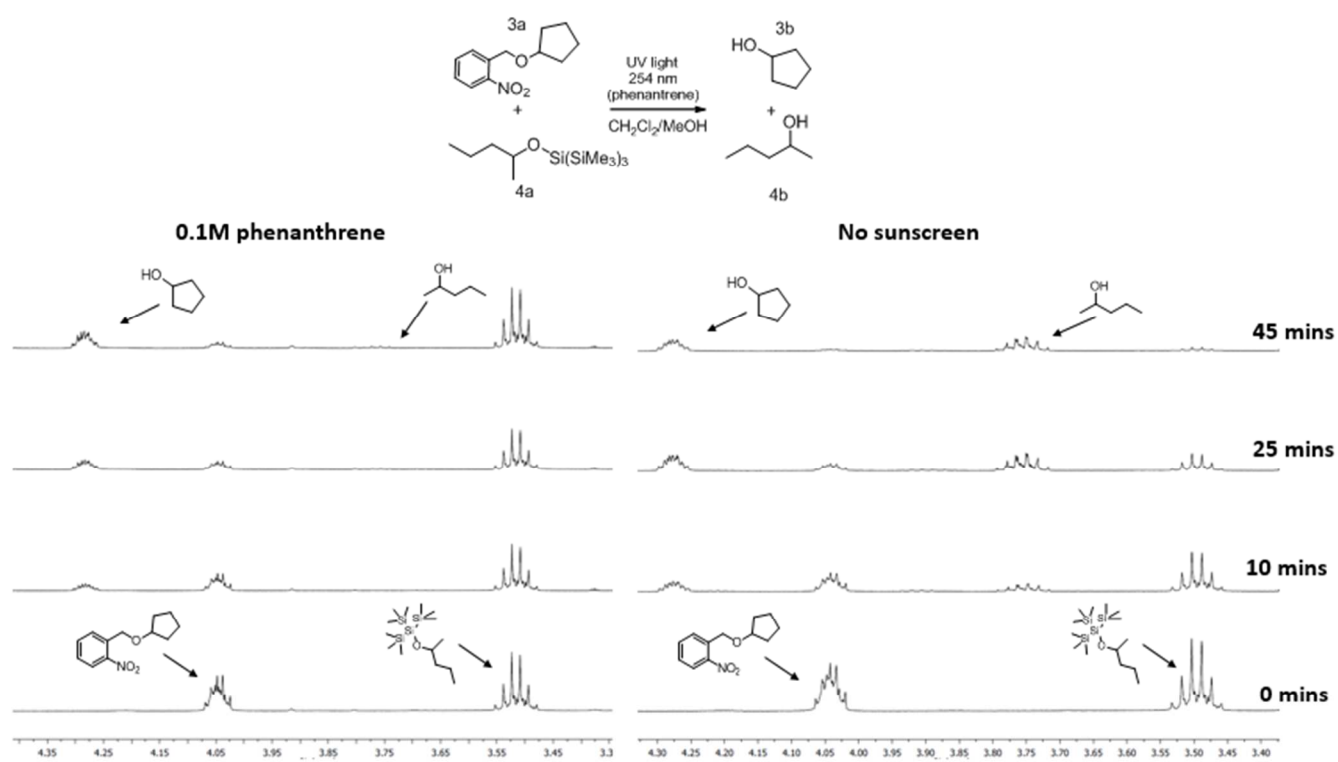
Representative preparative single wavelength selective photo-deprotection using a sunscreen:



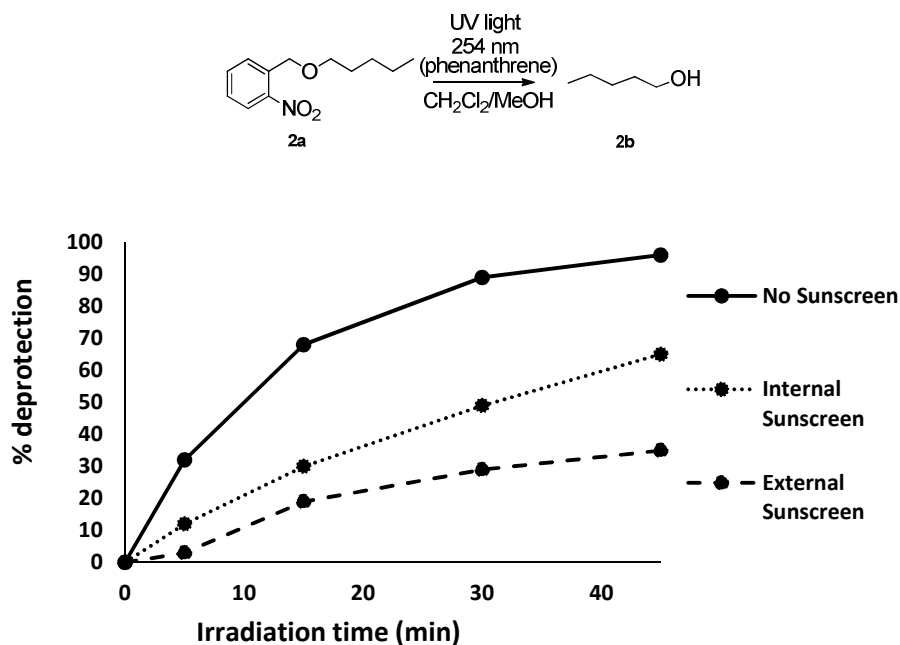
To a quartz vessel equipped with a stirring bar, 0.150 g of compound **5a** (0.3 mmol) was dissolved in 20 mL  $\text{CH}_2\text{Cl}_2$  (0.015 M) 24  $\mu\text{L}$  of methanol and 1.06 g phenanthrene (0.3 M) was added. The vessel was capped and irradiated by 254 nm UV light for 55 minutes, reaction progress was monitored by  $^1\text{H}$ -NMR. The quartz vessel content was transferred to a 50 mL round bottom flask, and the solvent was evaporated. The residue was then purified by flash chromatography (silica-gel, 40%  $\text{CH}_2\text{Cl}_2$  in petroleum ether and then 20% diethyl ether in petroleum ether) to afford 0.09026 g of compound **5b** as yellowish oil, in 82% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.59 (2H, t (br),  $J = 6.5$  Hz), 3.43 (2H, t,  $J = 6.5$  Hz), 1.83 (1H, s(br), OH) 1.54 (2H, p,  $J=6.5$  Hz), 1.46 (2H, p,  $J=6.5$  Hz), 1.38 – 1.25 (m, 4H), 0.16 (27H, s).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.2, 62.8, 33.0, 32.8, 25.74, 25.68, 0.4. UV-VIS:  $\lambda_{\text{max}}$  ( $\epsilon_{254}$ )  $\text{CH}_2\text{Cl}_2$ : 266 nm (1202  $\text{M}^{-1}\text{cm}^{-1}$ ) HR-MS (ESI)  $\text{C}_{15}\text{H}_{40}\text{O}_2\text{Si}_4$ ,  $m/z$ : ( $\text{M}+\text{H}$ ) $^+$  calculated: 365.2178 found : 365.2186, ( $\text{M}+\text{Na}$ ) $^+$  calculated: 387.1998 found: 387.1997.



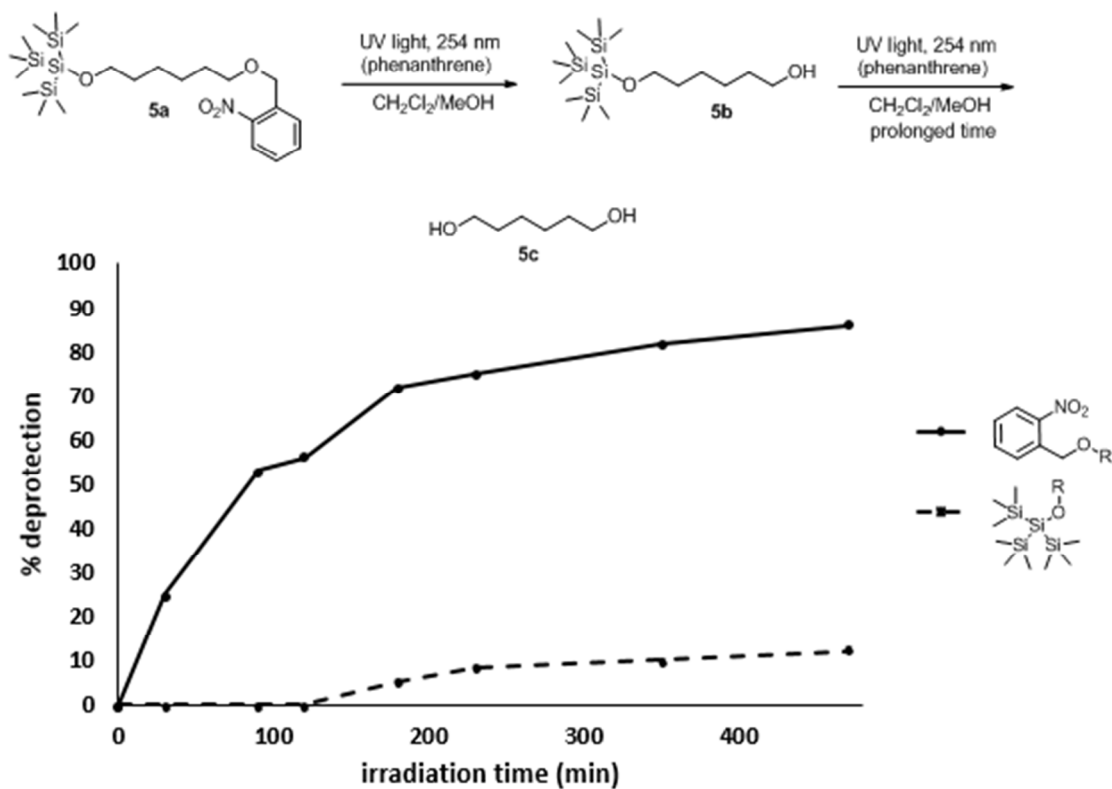
**Figure S2.** UV spectra of different sunscreen molecules in  $\text{CH}_2\text{Cl}_2$ .



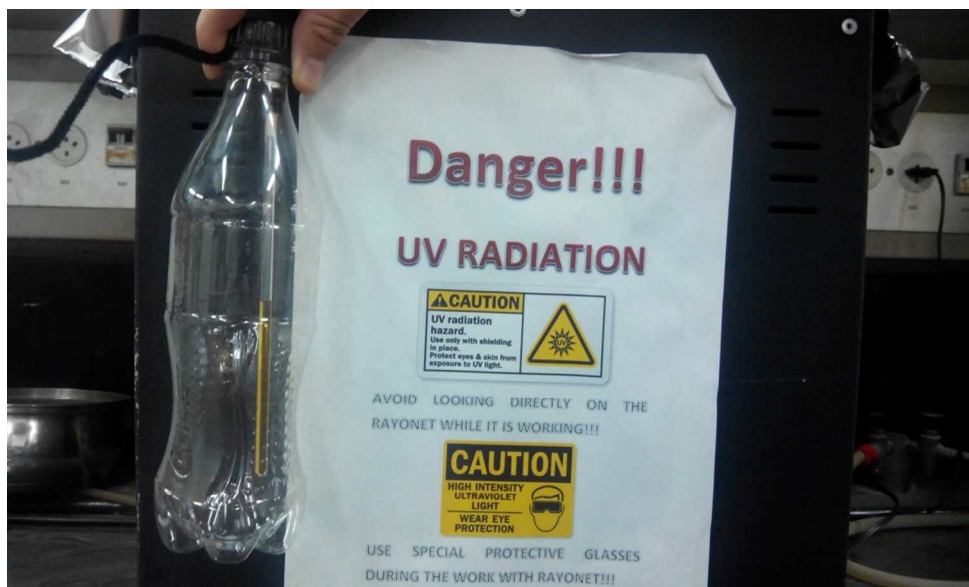
**Figure S3.**  $^1\text{H}$ -NMR analysis for sunscreen mediated single wavelength selective deprotection of tris(trimethylsilyl) silyloxy 2-pentane and 2-[(cyclopentyloxy)methyl] nitrobenzene. Signals are respective to the  $\alpha$  proton of the protected or free alcohol.



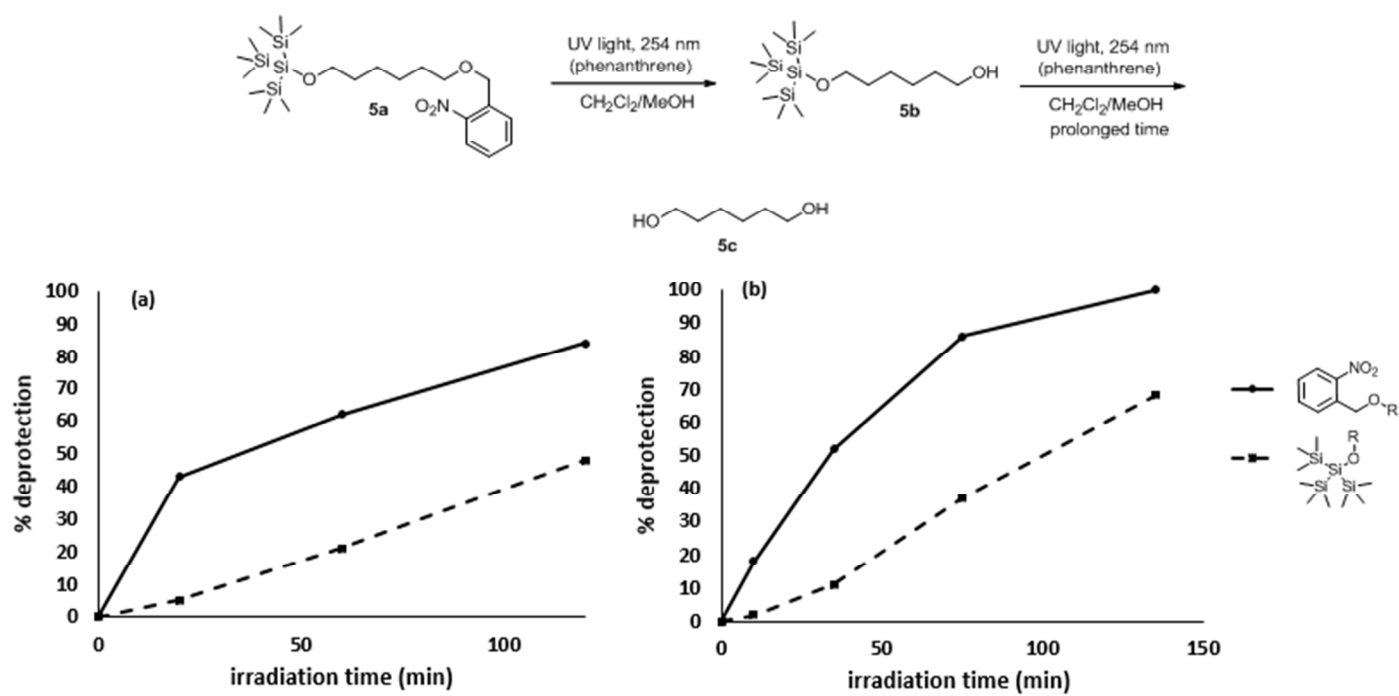
**Figure S4.** Photodeprotection of o-nitro[(pentyloxy)methyl] benzene in presence of phenanthrene. Phenanthrene concentrations; internal: 0.1M phenanthrene, external:  $1 \times 10^{-3}$  M phenanthrene. Reaction conditions: 0.03 M of protected alcohol, specified concentration of sunscreen, methanol-  $d_4$  (10 equiv), in 1 mL of  $\text{CD}_2\text{Cl}_2$ , irradiated by 254 nm light. Deprotection conversion measured by  $^1\text{H}$ -NMR. Phenanthrene Concentrations: internal: 0.1 M phenanthrene, external:  $1 \times 10^{-3}$  M phenanthrene For external sunscreen: 14 mL of solution of phenanthrene in  $\text{CH}_2\text{Cl}_2$  in the desired concentration was poured into a 15 mL Quartz test tube (15 mm diameter), 5 mm quartz NMR tube was fixed in center using aluminum foil (also used for capping).



**Figure S5.** Intramolecular selective photolysis on a 1,6 hexanediol linker protected with tris(trimethylsilyl) and 2-nitrobenzyl group (**5a**) using a PET bottle as sunscreen. Reaction conditions: 0.015 M of protected diol, 2 equiv of methanol- $d_4$ , in 1 mL of  $\text{CD}_2\text{Cl}_2$  were placed in a quartz NMR tube which was inserted into a PET bottle (Coca-Cola, see image below) and irradiated by 254 nm UV lamps. Deprotection conversion measured by  $^1\text{H}$ -NMR.



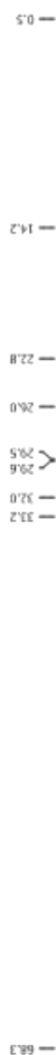




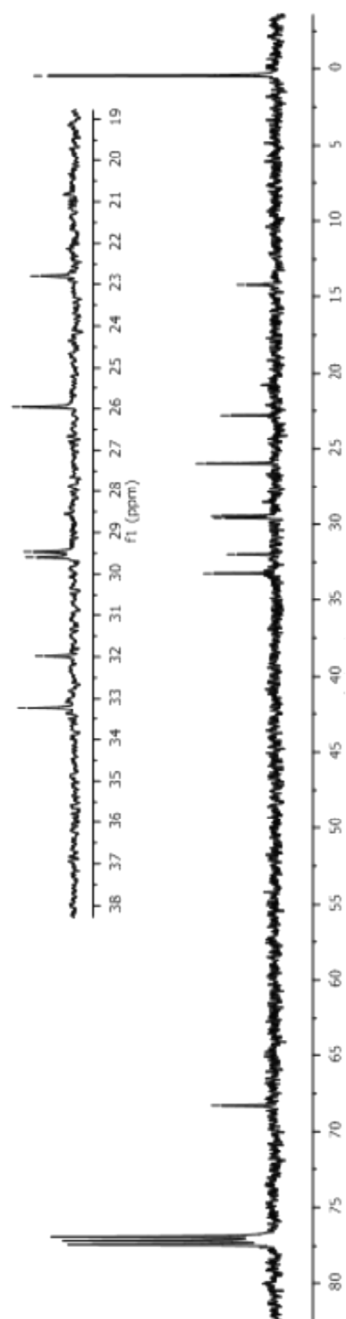
**Figure S6.** Control experiment for intramolecular selective photo-deprotection on a 1,6 hexanediol linker protected with tris(trimethylsilyl) and 2-nitrobenzyl group (**5a**) using low power UV source. Reaction conditions: 0.015 M of protected diol, 2 equiv of methanol- $d_4$ , in 1 mL of  $\text{CD}_2\text{Cl}_2$  irradiated by 254 nm UV source. (a) Simple TLC UV lamp (b) 2\*RPR-200 lamps in a Rayonet reactor.

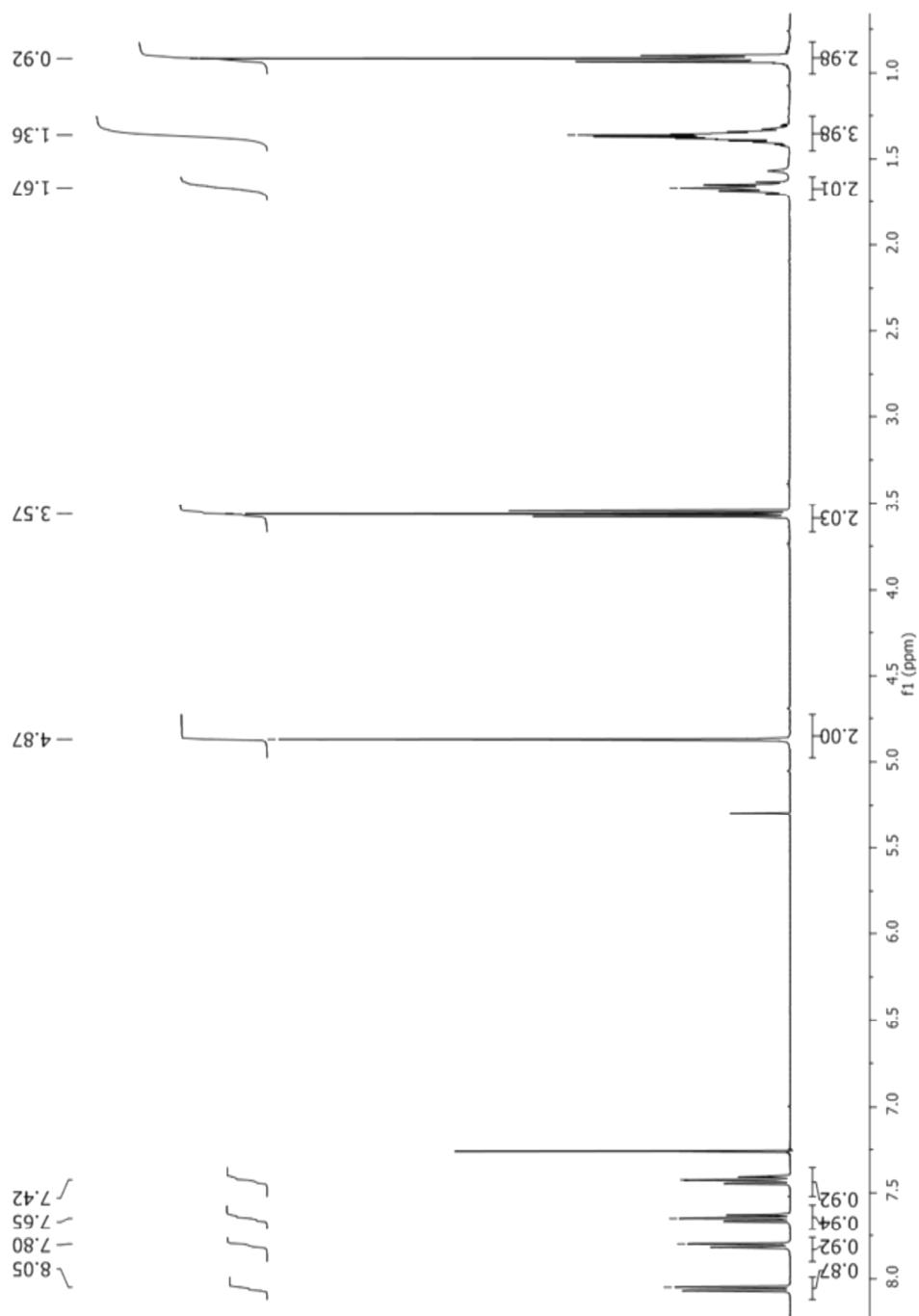


125MHz, CDCl<sub>3</sub>, <sup>13</sup>C-NMR

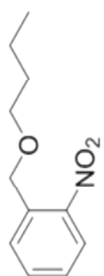


S11

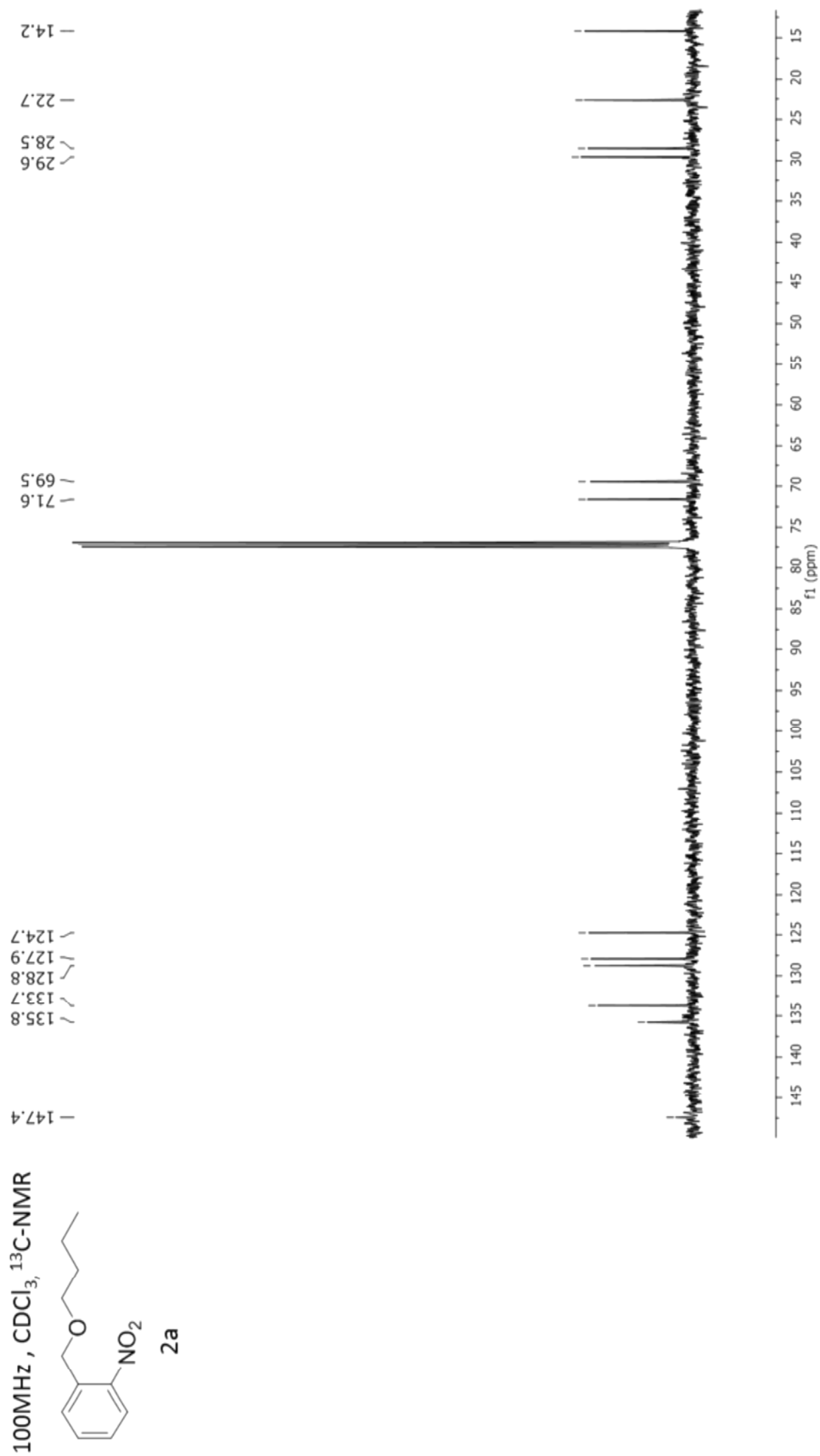


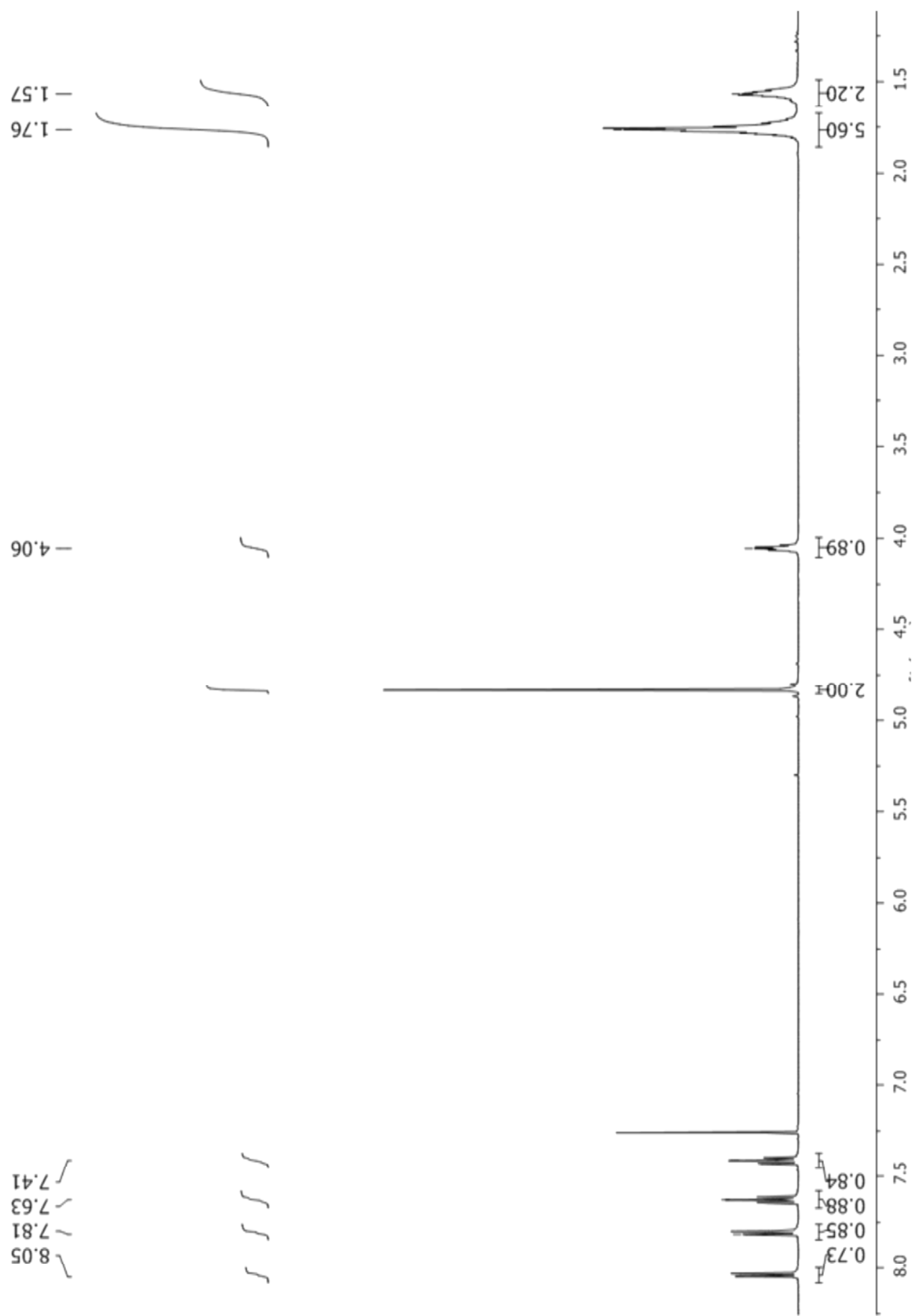
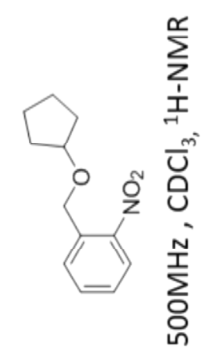


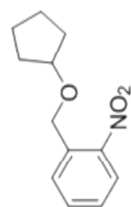
400MHz,  $\text{CDCl}_3$ ,  $^1\text{H-NMR}$



2a







125MHz, CDCl<sub>3</sub>, <sup>13</sup>C-NMR

3a

136.1  
133.7  
129.0  
127.8  
124.7

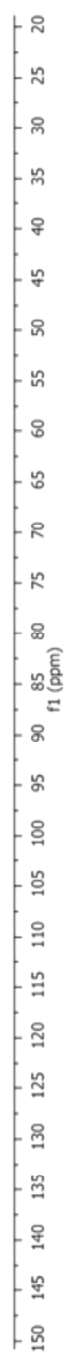
147.5

82.1

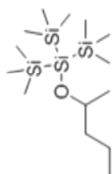
67.4

32.4

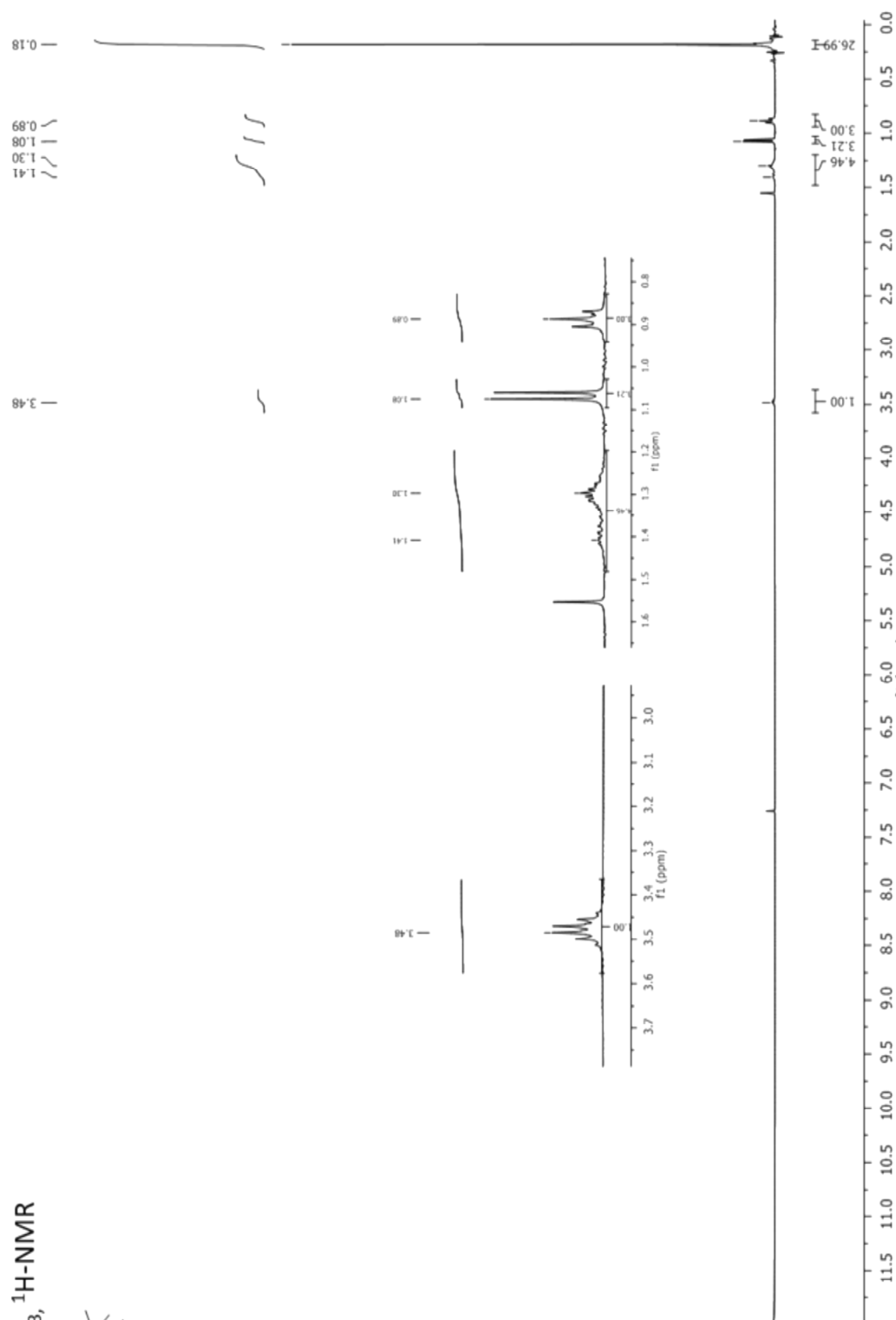
23.7



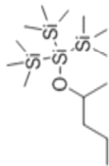
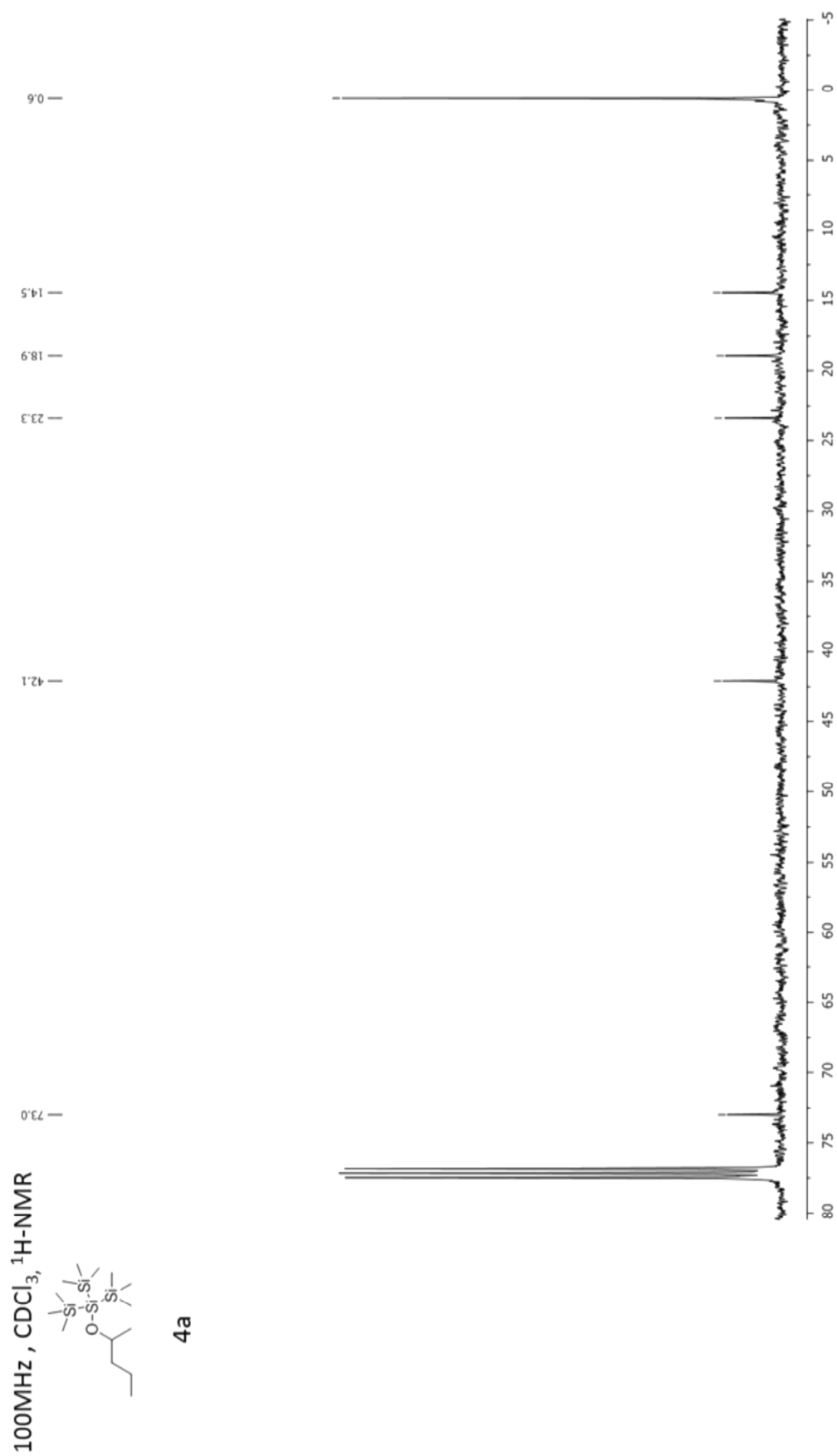
400MHz, CDCl<sub>3</sub>, <sup>1</sup>H-NMR



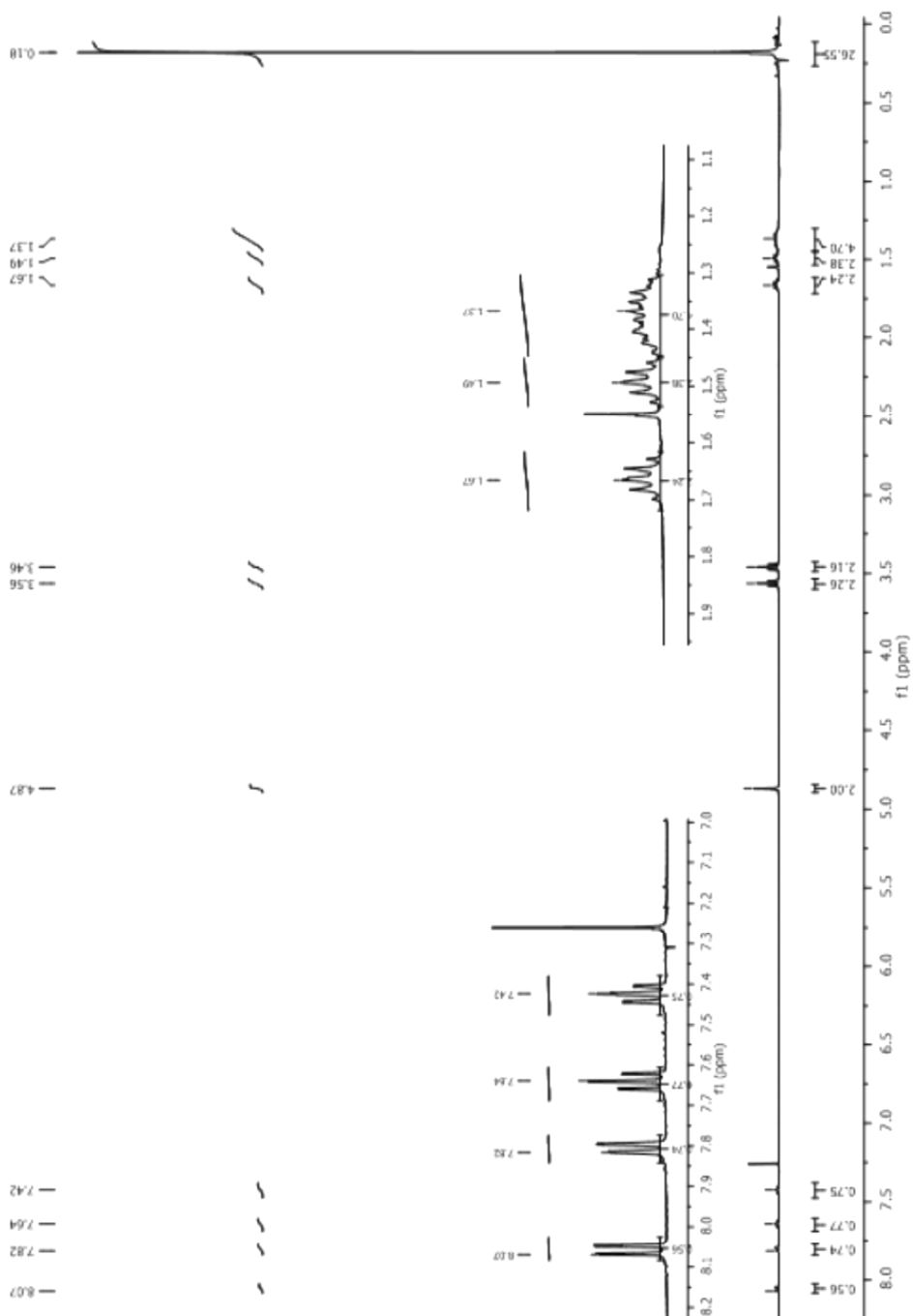
**4a**







4a



100MHz, CDCl<sub>3</sub>, <sup>13</sup>C-NMR



5a

147.4

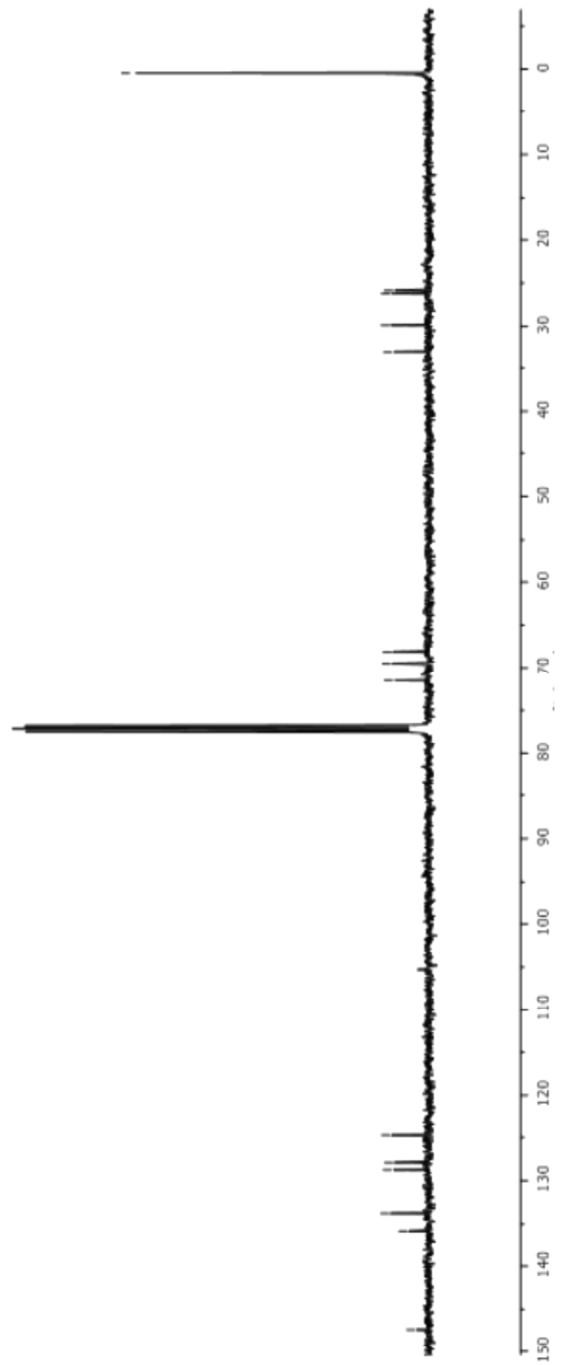
135.8  
133.8

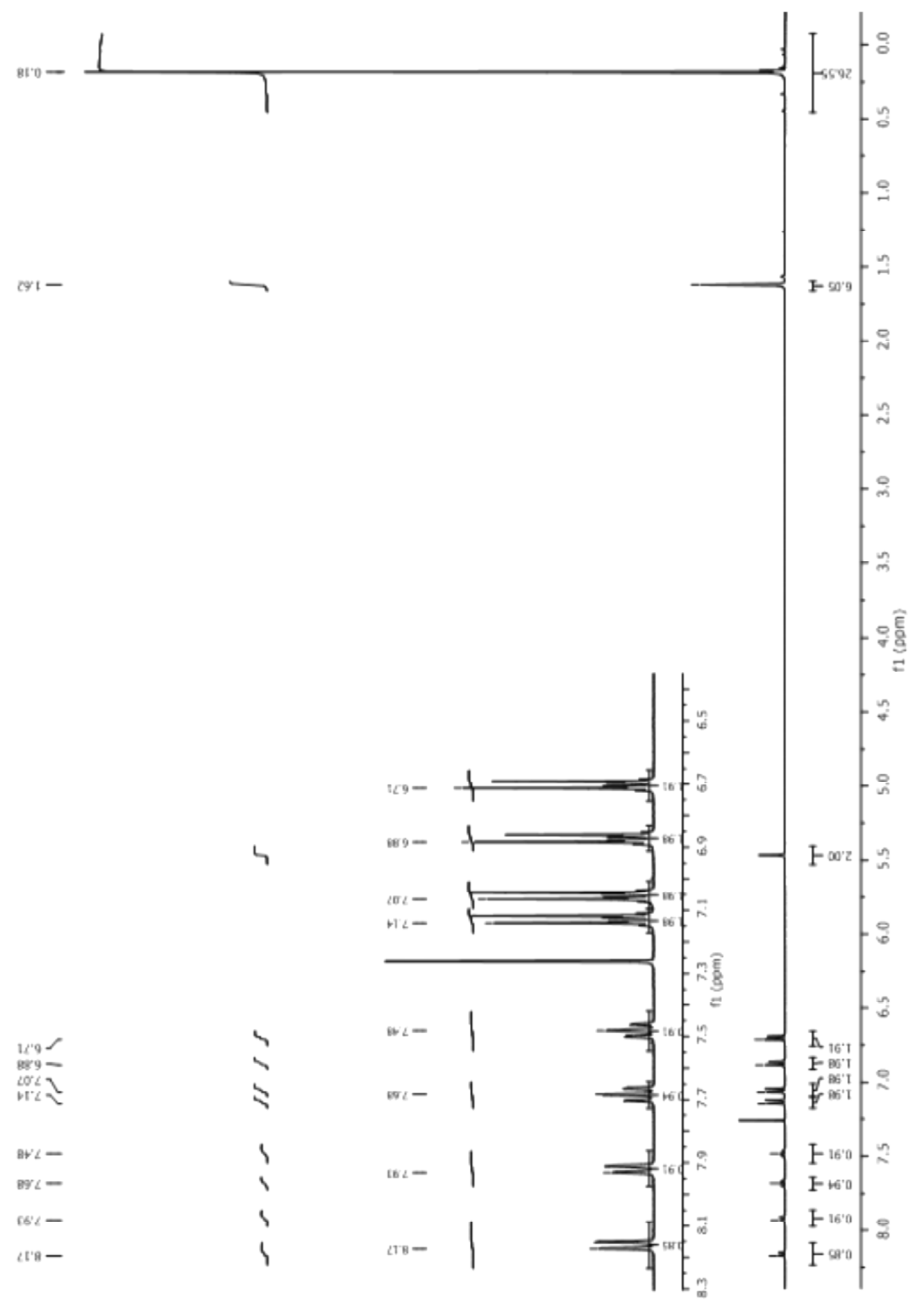
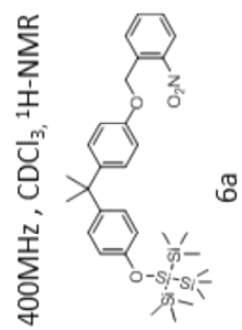
128.7  
127.9  
124.7

71.5  
69.5  
68.1

33.1  
29.9  
26.2  
25.9

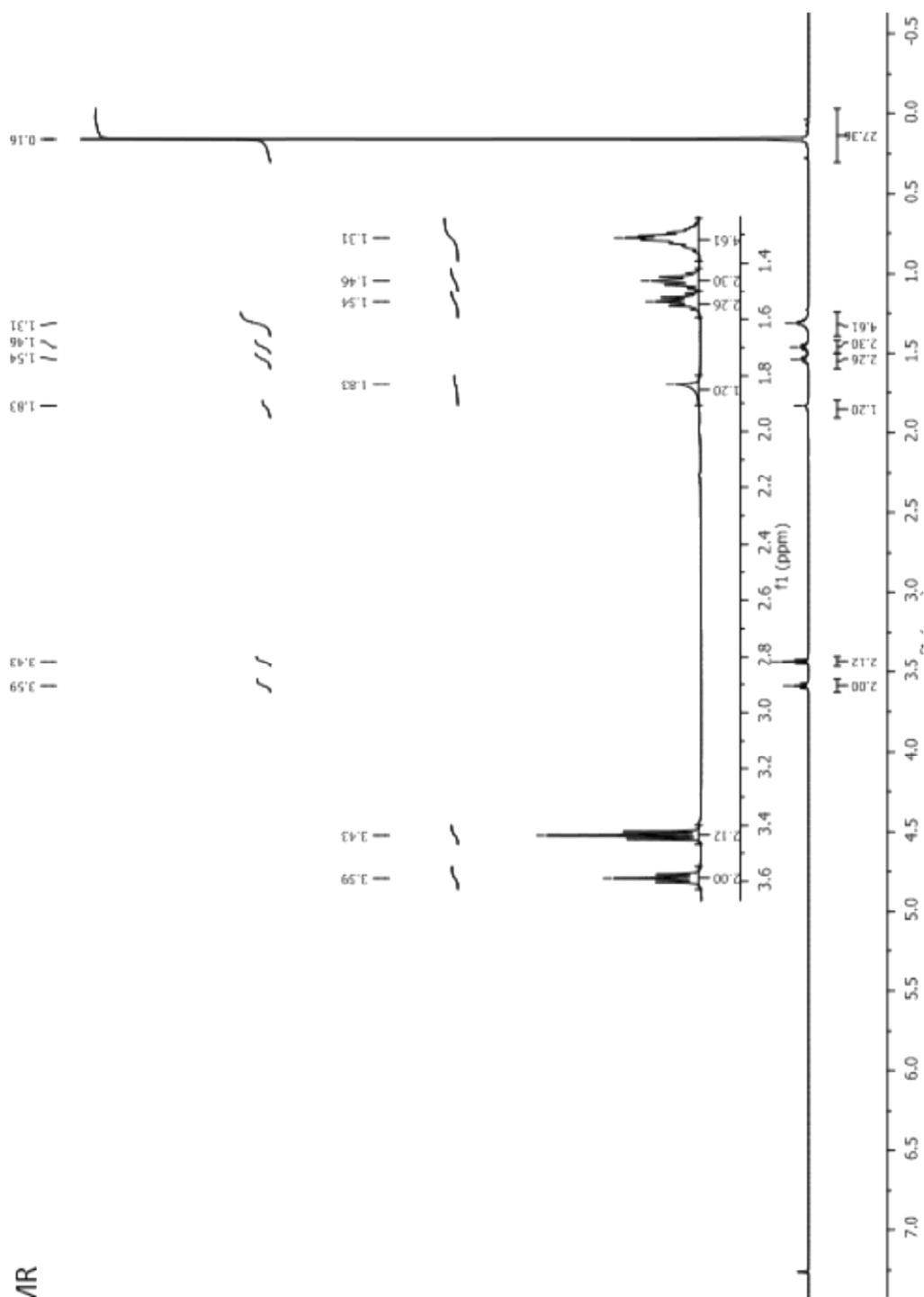
0.5

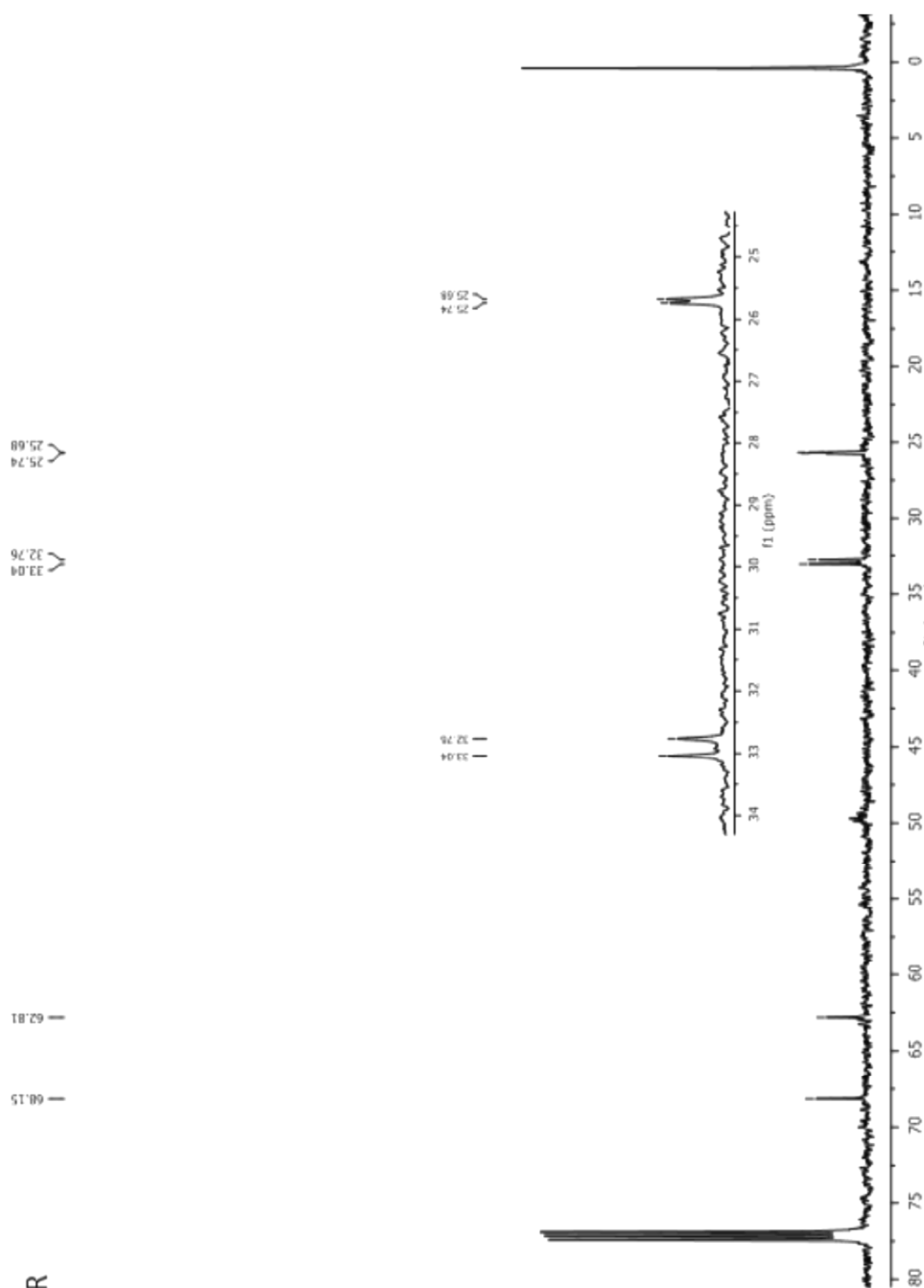
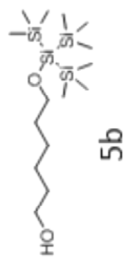






500MHz, CDCl<sub>3</sub>, <sup>1</sup>H-NMR



125MHz,  $\text{CDCl}_3$ ,  $^{13}\text{C}$ -NMR

References:

(1)Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, 29, 2176.

(2)Madhavan, N.; Gin, M. S. *Chem. Comm.* **2004**, 2728.