

Supporting Information for

Photophysical Studies and Submicron Ring Formation of Morpholino U-Nucleoside Monomer

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Experimental:

All reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Petroleum ether (PE) refers to the fraction of petroleum boiling between 60-80 °C. All reactions were carried out in oven-dried glassware under an argon atmosphere using anhydrous solvents, standard syringe and septum techniques unless otherwise indicated. MeOH was dried over sodium before use. DMF was dried over CaH₂ under vacuum. Et₃N was dried over KOH and CaH₂. Organic extracts were dried over anhydrous Na₂SO₄ and then filtered prior to removal of all volatiles under reduced pressure on rotary evaporation. Chromatographic purification of products was accomplished using column chromatography on silica gels (mesh 100 ~ 200). Thin-layer chromatography (TLC) was carried out on aluminum sheets, Silica Gel 60 F254 (Merck; layer thickness 0.25 mm). Visualization of the developed chromatogram was performed by UV light and /or CAM stains. ¹H and ¹³C NMR spectra were recorded at 500 MHz and 125 MHz, respectively using CDCl₃ or DMSO as solvent. Chemical shifts (δ) are given in ppm relative to the solvent residual peak or TMS as internal standard. The following abbreviations are used for multiplicity of NMR signals: s = singlet, d = doublet, t = triplet, m = multiplet, br s = broad singlet, dd = doublet of doublet.

UV-Visible Absorption Spectroscopy

UV-vis measurements were taken with a Shimadzu UV 2550 spectrophotometer. Photoluminescence spectra were collected using a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer.

Temperature dependent UV Spectroscopy

This experiment was carried out using Agilent 8453 spectrophotometer and temperature was controlled using Agilent 89090H machine.

Luminescence Spectroscopy

We have used Horiba Jobin Yvon Fluoromax -4 spectrofluorometer for all the steady-state PL and PLE measurements. PL lifetime has been studied using time correlated single photon counting (TCSPC) technique equipped with a picosecond laser source.

Transmission Electron Microscopy (TEM)

TEM images were taken on a JEOL-JEM 2010 electron microscopy using 200 kV electron source. Specimens were prepared by dropping a drop of compound solution in chloroform on a carbon coated copper grid, and the grids were dried in air.

Atomic Force Microscopy (AFM)

A diluted purified sample was first dispersed in chloroform. Then a droplet of this solution was deposited on a clean silicon wafer or mica surface and AFM was measured using VEECO dICP-II autoprobe (model AP 0100). The AFM images were created using WSxM software.

Thermo Gravimetric Analysis (TGA)

TGA experiments were carried out using SDT Q 600 machine.

Compound 3. Compound **1** (0.184 g, 0.31 mmol) was dissolved in dry DMF (4.0 mL) followed by the addition of 1-ethynyl-4-methoxy benzene (0.121 g, 0.92 mmol) and Et₃N (85 μ L, 0.62 mmol). The reaction mixture was degassed with argon for 15 mins. To the reaction mixture was added Pd(PPh₃)₄ (0.036 g, 0.031 mmol) and CuI (0.012 g, 0.062 mmol) and stirred under argon atmosphere for a period of 1.5 h. The reaction mixture was diluted with EtOAc (10 mL), washed with water (3 \times 10 mL), brine (5 mL). The reaction mixture was dried over Na₂SO₄, concentrated *in vacuo* and purified by column chromatography (100-200 mesh silica gel) using MeOH in CH₂Cl₂ as eluent to get compound **3** (0.146 g, 77%) as brown solid. R_f (19:1, CH₂Cl₂/MeOH)= 0.51.

IR (neat/CHCl₃): ν = 3387, 3057, 2833, 2145, 1712, 1693, 1484, 1263, 711 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.40-1.44 (1H, t, *J* = 12 Hz), 1.44-1.49 (1H, t, *J* = 11.0 Hz), 1.84 (1H, br s), 2.52 (1H, br s), 3.09-3.11 (1H, d, *J* = 12 Hz), 3.39-3.42 (1H, d, *J* = 11.0 Hz), 3.62 (2H, m), 3.78 (3H, s), 4.30-4.32 (1H, br s), 6.15-6.17 (1H, dd, *J* = 9.5, 1.5 Hz), 6.78-6.80 (2H, d, *J* = 8.5 Hz), 7.17-7.50 (17H, m), 9.16 (1H, s); ¹³C NMR (125 MHz, CDCl₃): δ = 48.89, 52.42, 55.36, 63.69, 78.10, 78.74, 81.19, 94.06, 100.57, 114.02, 114.64, 126.72, 128.08, 129.28, 133.34, 141.68, 148.77, 159.96, 161.36; HRMS (ESI) (M + Na)⁺ calculated for C₃₇H₃₃N₃O₅Na⁺ = 622.1318 found 622.2318.

Compound 4: Following the general procedure, compound **4** was obtained after 1 h stirring in 78% yield. R_f (19:1, CH₂Cl₂/MeOH) 0.48, IR (neat/CHCl₃): ν 3387, 3057, 2833, 2145, 1712, 1693, 1527, 1484, 1263, 711 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.42-1.46 (1H, t, *J* = 10.5 Hz), 1.49-1.53 (1H, t, *J* = 11.5 Hz), 3.09-3.12 (1H, d, *J* = 12 Hz), 3.42-3.45 (1H, d, *J* = 11.5 Hz), 3.64-3.65 (2H, d, *J* = 4.5 Hz), 4.31-4.33 (1H, m), 6.14-6.16 (1H, d, *J* = 9.0 Hz), 7.11- 7.59 (16H, m), 7.65 (1H, s), 7.69-7.70 (1H, d, *J* = 7.5 Hz), 8.02-8.03 (1H, d, *J* = 8.0 Hz), 9.18 (1H, br s); ¹³C NMR (125 MHz, CDCl₃): δ 48.85, 52.47, 63.70, 78.32, 81.55, 88.30, 89.54, 99.62, 118.37, 124.80, 126.81, 129.13, 128.91, 129.28, 133.12, 135.2, 143.62, 148.72, 149.01, 160.93; HRMS (ESI) (M + Na)⁺ calculated for C₃₆H₃₀N₄O₆Na⁺ = 637.2063 found 637.2063.

Compound 5: Following the general procedure compound **5** was synthesized after 1 h stirring in 81% yield. R_f (1:1, PE/EtOAc) 0.52, IR (neat/CHCl₃): ν 3401, 3089, 2824, 1705, 1680, 1445, 1263, 759 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 1.46-1.54 (2H, m), 3.12-3.15 (1H, d, *J* = 11.5 Hz), 3.46-3.49 (1H, d, *J* = 11.5 Hz), 3.67-3.68 (2H, m), 4.36-4.38 (1H, m), 6.22-6.24 (1H, d, *J* = 9.0 Hz), 7.19-7.69 (24H, m), 7.99 (1H, s); ¹³C NMR (125 MHz, CDCl₃): δ 48.9, 52.5, 63.7, 78.2, 81.4, 84.7, 92.9, 100.6, 119.0, 122.55, 122.60, 126.74, 126.84, 127.10, 127.22, 127.33, 127.50, 128.09, 128.61, 129.27, 129.91, 130.36, 130.85, 131.03, 131.80, 141.7, 148.8, 161.5; HRMS (ESI) (M + Na)⁺ calculated for C₄₄H₃₅N₃O₄Na⁺ = 692.2525 found 692.2526.

Compound 6: Following the general procedure, after 1.5 h stirring, compound **6** was synthesized from **1** in 77% yield. R_f (19:1, CH₂Cl₂/MeOH) 0.54, IR (neat/CHCl₃): ν 3390, 2841, 2141, 1712, 1263, 711 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.43-1.49 (2H, m), 3.10-3.12 (1H, d, *J* = 12.0 Hz), 3.42-3.44 (1H, d, *J* = 11.5 Hz), 3.63-3.64 (2H, m), 3.91 (3H, s), 4.29-4.32 (1H, m), 6.16-6.19 (1H, dd, *J* = 9.2, 2.5 Hz), 7.06-7.64 (20H, m), 7.91 (1H, s), 8.47 (1H, s); ¹³C NMR (75 MHz, CDCl₃): δ 48.9, 52.4, 55.5, 63.8, 78.1, 79.6, 81.3, 94.7, 100.6, 105.9, 117.4, 119.6, 126.8, 126.9, 128.13, 128.46, 128.92, 129.29, 129.54, 131.7, 131.77, 134.44, 141.8, 141.92, 148.6, 158.6, 160.9; HRMS (ESI) (M + Na)⁺ calculated for C₄₁H₃₅N₃O₅Na⁺ = 672.2474 found 672.2476.

Compound 7: To silyl protected N-tritylated uracil morpholino (1.8 g, 3.87 mmol) in dry dimethylformamide (6 mL) was added triethylamine (1.34 mL, 9.67 mmol) followed by portion wise addition of trityl chloride (1.30 g, 4.6 mmol) at 0 °C. After one hour the reaction mixture was concentrated in reduced pressure. This was diluted with chloroform (50 mL) and washed with water (3 \times 20 mL) and brine (30 mL). Solvent was removed *in vacuo*, and the residue was purified by SiO₂ column

chromatography (0 - 2 % MeOH/CH₂Cl₂) to obtain the product **7** as a colorless solid (2.33 g, overall yield 55% from uridine). IR (neat/CHCl₃): ν 3188, 3034, 2930, 1692, 1464, 1265, 1109, 708 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.93-1.01 (9H, s), 1.30-1.34 (1H, t, J = 11.0 Hz), 1.51-1.55 (1H, t, J = 11.0 Hz), 3.25-3.27 (1H, d, J = 11.5 Hz), 3.34-3.36 (1H, d, J = 11.5 Hz), 3.59-3.62 (1H, m), 3.72-3.75 (1H, m), 4.24-4.26 (1H, m), 5.52-5.53 (1H, d, J = 8.5 Hz), 6.10-6.12 (1H, dd, J = 10.5, 1.0 Hz), 7.00-7.02 (1H, d, J = 8.0 Hz), 7.21-7.59 (25H, m), 9.13 (1H, s); ¹³C NMR (75 MHz, CDCl₃): δ 19.34, 26.86, 49.80, 52.35, 64.71, 80.76, 102.11, 126.62, 127.36, 127.79, 127.84, 128.00, 129.35, 129.84, 129.94, 133.13, 133.50, 135.62, 135.69, 139.99, 149.90, 163.18; HRMS (ESI) (M + Na)⁺ calculated for C₄₄H₄₅N₃O₄SiNa⁺ = 730.3077 found 730.3077.

Compound 8: To a stirred solution of O-silylated uracil morpholino monomer (0.772 g, 1.66 mmol) in dry CH₂Cl₂ (5.0 mL) was added triethylamine (0.58 mL, 4.2 mmol) followed by addition of acetic anhydride (0.63 mL, 6.63 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for a period of 1 h. After completion, the reaction mixture was diluted with CH₂Cl₂ (15 mL), washed with water (2 × 10 mL) and brine (5 mL). Organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel (100-200 mesh) column chromatography to obtain compound (**8**) as colorless solid. Yield: 0.82 g, 98%. IR (neat/CHCl₃): ν 2931, 1695, 1427, 1112, 704, 505 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.99-1.02 (9H, m), 2.02 (3H, s), 2.06-2.08 (3H, d, J = 10.0 Hz), 2.42-2.47 (0.4H, t, J = 11.5 Hz), 2.68-2.72 (0.6H, dd, J = 13.3, 11.0 Hz), 2.82-2.89 (0.6H, m), 2.99-3.05 (0.4H, t, J = 12.0 Hz), 3.67-3.77 (3.4H, m), 3.93-3.96 (0.6H, d, J = 13.0 Hz), 4.55-4.57 (0.6H, d, J = 13.5 Hz), 4.63-4.65 (0.4H, d, J = 12.5 Hz), 5.49-5.59 (1H, m), 5.64-5.65 (1H, d, J = 8.0 Hz), 7.19-7.38 (6H, m), 7.56-7.58 (4H, m); ¹³C NMR (125 MHz, CDCl₃): δ 19.4, 20.9, 21.4, 26.87, 26.90, 42.3, 44.3, 47.4, 49.5, 64.03, 64.31, 79.2, 80.0, 102.75, 102.93, 127.92, 127.99, 130.06, 130.19, 132.93, 132.99, 133.2, 135.6, 139.26, 139.51, 149.80, 149.97, 163.7, 169.92, 169.98; HRMS (ESI) (M + Na)⁺ calculated for C₂₇H₃₃N₃O₅SiNa⁺ = 530.2087 found 530.2087.

Compound 9: To a stirred solution of morpholine (0.734 g, 8.43 mmol) in dry DMF (4.0 mL) was added triethylamine (3.0 mL, 21.1 mmol) followed by addition of tritylchloride (2.6 g, 9.3 mmol) at 0 °C. Reaction mixture was stirred at 0 °C for 1 h then at room temperature for 2 h. Organic layer was evaporated to dryness. Diluted with EtOAc (20 mL), washed with water (2 × 10 mL) and brine (5 mL). Ethylacetate layer was concentrated *in vacuo* and purified by silica gel (100-200 mesh) column chromatography to obtain compound (**9**) as colorless solid. Yield: 2.59 g, 94%. IR (neat/CHCl₃): ν 2837, 1415, 1112, 717, 490 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 3.99-4.04 (4H, m), 7.29-7.35 (3H, m), 7.37-7.48 (7H, m), 7.71 (5H, br s); ¹³C NMR (125 MHz, CDCl₃): δ 48.6, 67.5, 81.7, 126.1, 126.9, 127.5, 127.7, 127.9, 129.3, 147.2.

Compound 10: Compound **7** (0.126 g, 0.18 mmol) was dissolved in a mixture of DMF:acetone (1:1, 4.0 mL), followed by addition of potassium carbonate (0.05 g, 0.36 mmol) and methyl iodide (0.017 mL, 0.27 mmol). The reaction mixture was heated at 100 °C for a period of 5 h. The reaction mixture was evaporated to dryness and diluted with ethylacetate (10 mL). Organic layer was washed with water (2 × 10 mL), brine (5 mL) and dried over Na₂SO₄. Ethylacetate layer was concentrated *in vacuo* and purified by silica gel (100-200 mesh) column chromatography to obtain compound **10** as colorless solid. Yield: 0.12 g, 89%. IR (neat/CHCl₃): ν 2929, 1712, 1660, 1448, 1112, 759 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 0.97 (9H, s), 1.31-1.35 (1H, t, J = 10.0 Hz), 1.50-1.54 (1H, t, J = 11.0 Hz), 3.25-3.34 (5H, m), 3.58-3.61 (1H, dd, J = 11.0, 5.5 Hz), 3.72-3.75 (1H, m, J = 11.0, 4.5 Hz), 4.24-4.26 (1H, m), 5.56-5.58 (1H, d, J = 8.5 Hz), 6.12-6.14 (1H, dd, J = 9.3, 2.0 Hz), 6.98-7.00 (1H, d, J = 8.0 Hz), 7.19-7.59 (25H, m); ¹³C NMR (125 MHz, CDCl₃): δ 19.3, 26.9, 27.8, 49.8, 52.3, 64.7, 81.4, 101.4, 126.6, 127.78, 127.82, 127.99, 129.35, 129.82, 129.90, 133.2, 135.62, 135.68, 137.8, 150.6, 162.8; HRMS (ESI) (M + Na)⁺ calculated for C₄₄H₄₇N₃O₄SiNa⁺ = 744.3234 found 744.3236.

Compound	Absorption band edge (nm)	First absorption maxima (nm)	Emission maxima (nm)	Quantum yield (%)
3	368	320	412	34
4	418	353	442	~4
5	388	338	410	36
6	375	336	420	48

Table 1 Optical data of compounds 3-6

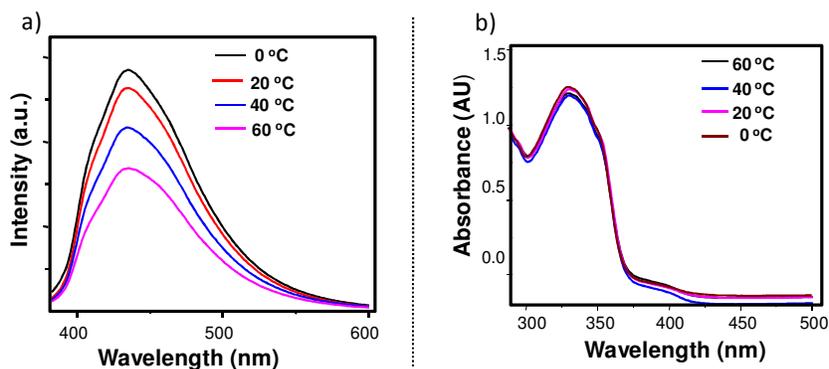


Fig. S1 Temperature dependent a) PL spectra of compound 6 in toluene and b) UV-Vis spectra of compound 6 in chloroform

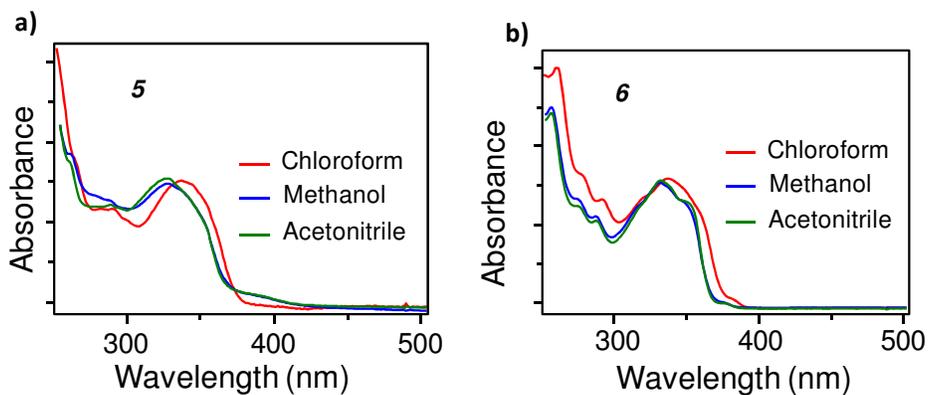


Fig. S2 Solvent dependent UV-vis spectra of a) compound 5 and b) compound 6

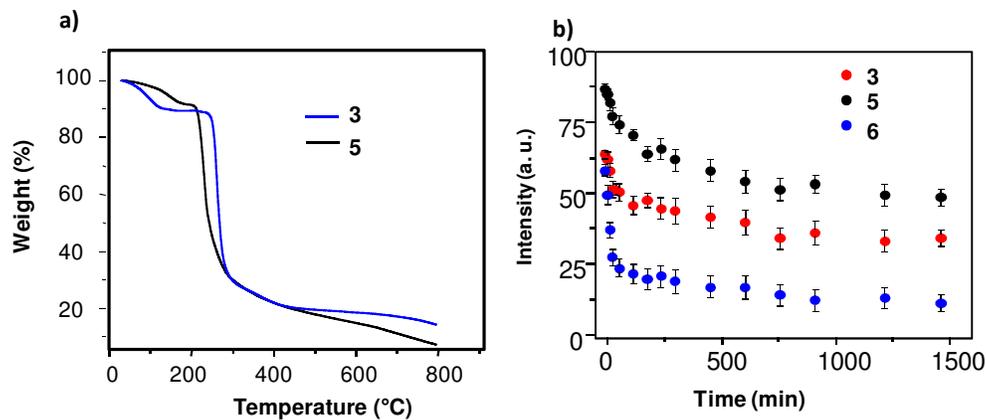


Fig. S3 a) TGA analysis of compound **3** and **5**; b) Stability of compound **3**, **5** and **6** when irradiated under 365 nm UV lamp (6 mW).

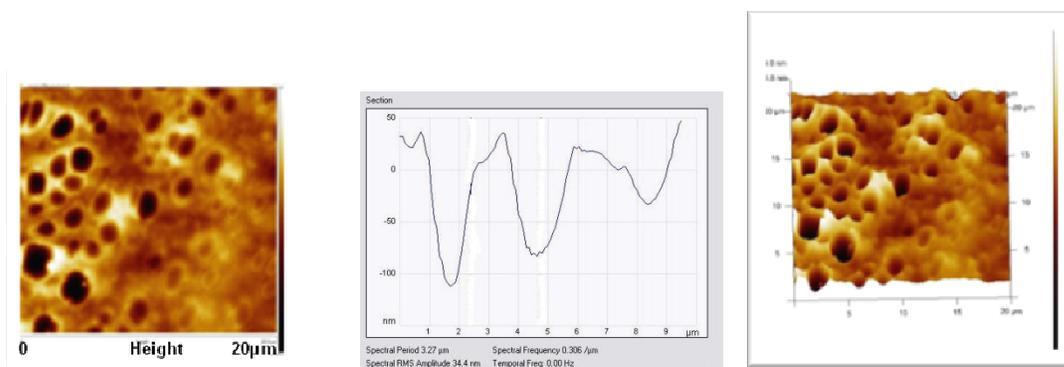


Fig. S4 a) AFM images of Compound **6** on mica surface b) Depth profile
Average depth ~ 60 nm
Average diameter ~ 2 µm

c) 3D profile of compound **6**

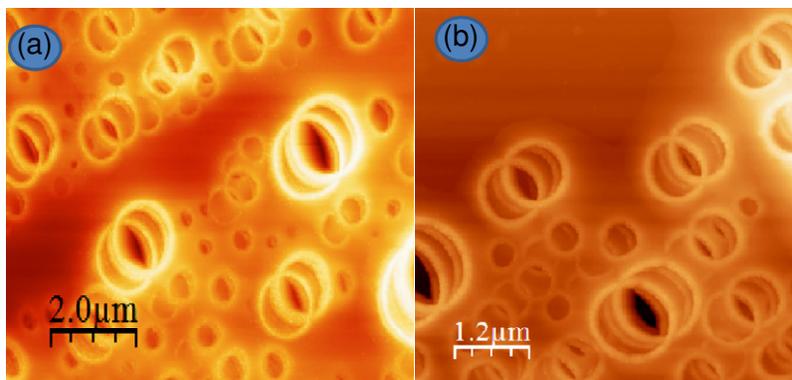


Fig. S5 AFM images of a) compound **1** and b) compound **7** in 3×10^{-3} M concentration

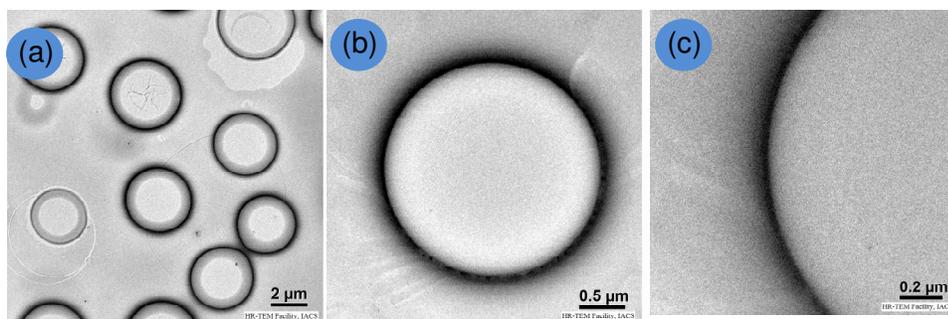


Fig. S6 HRTEM analysis of compound **6**, scale bar at a) 2 μm, b) 0.5 μm and c) 0.2 μm

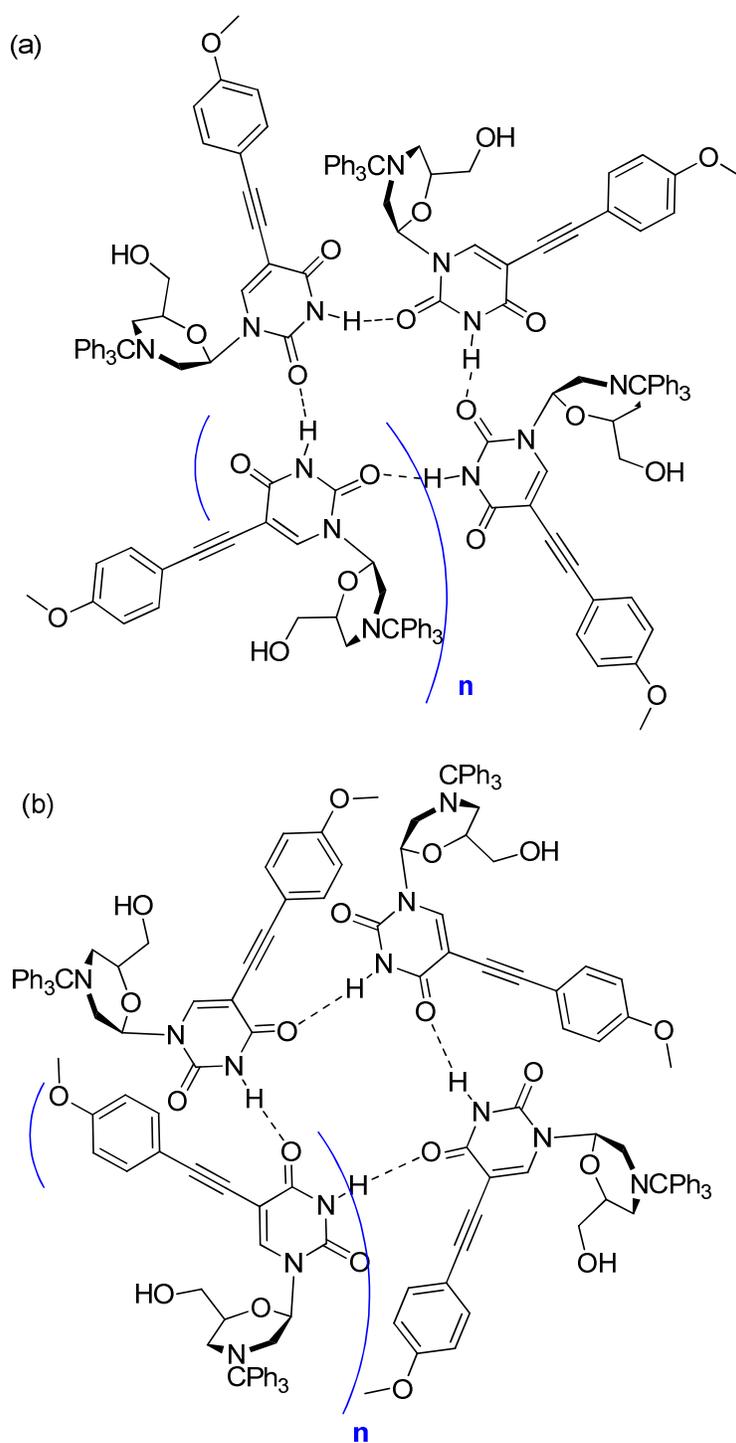
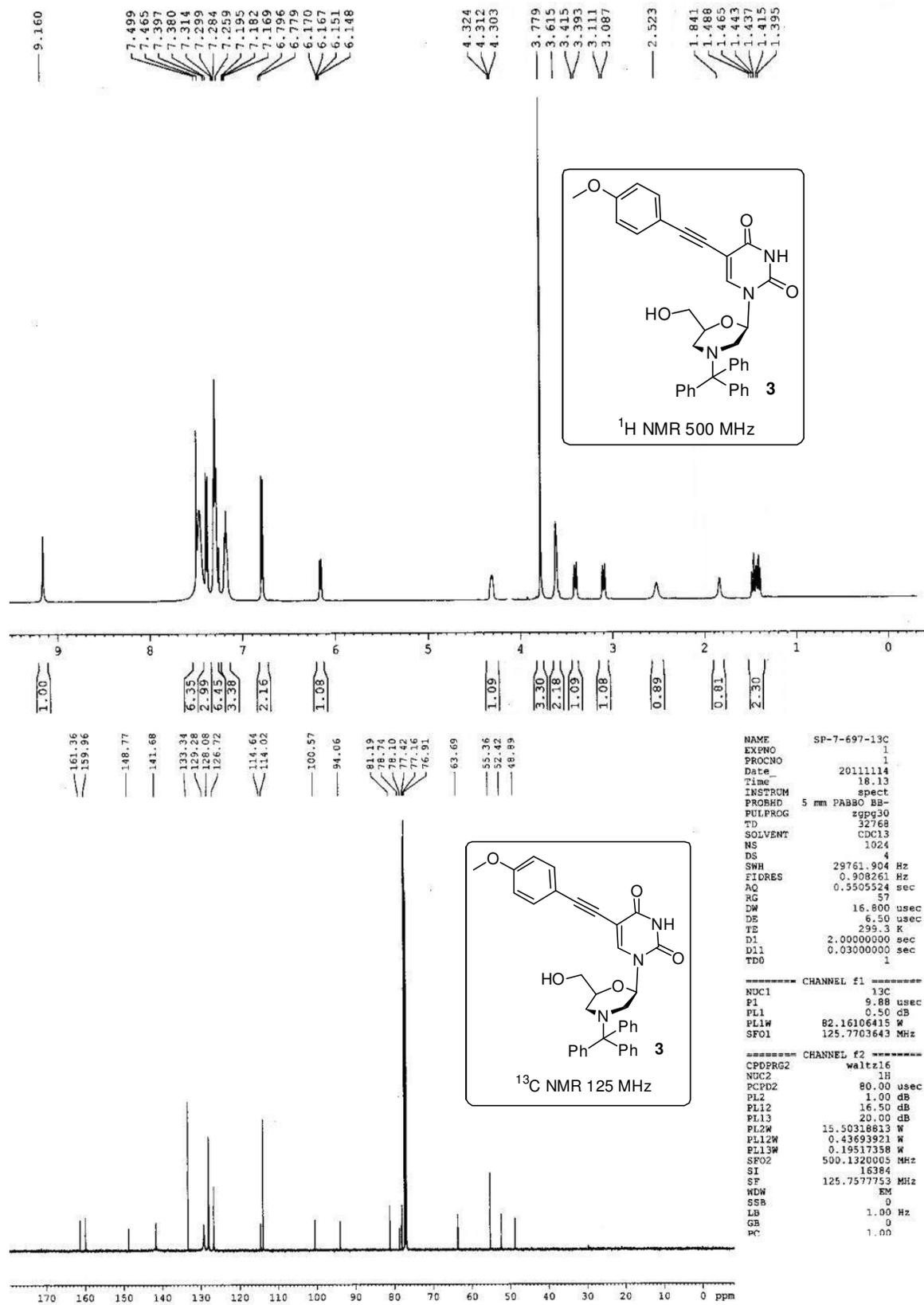
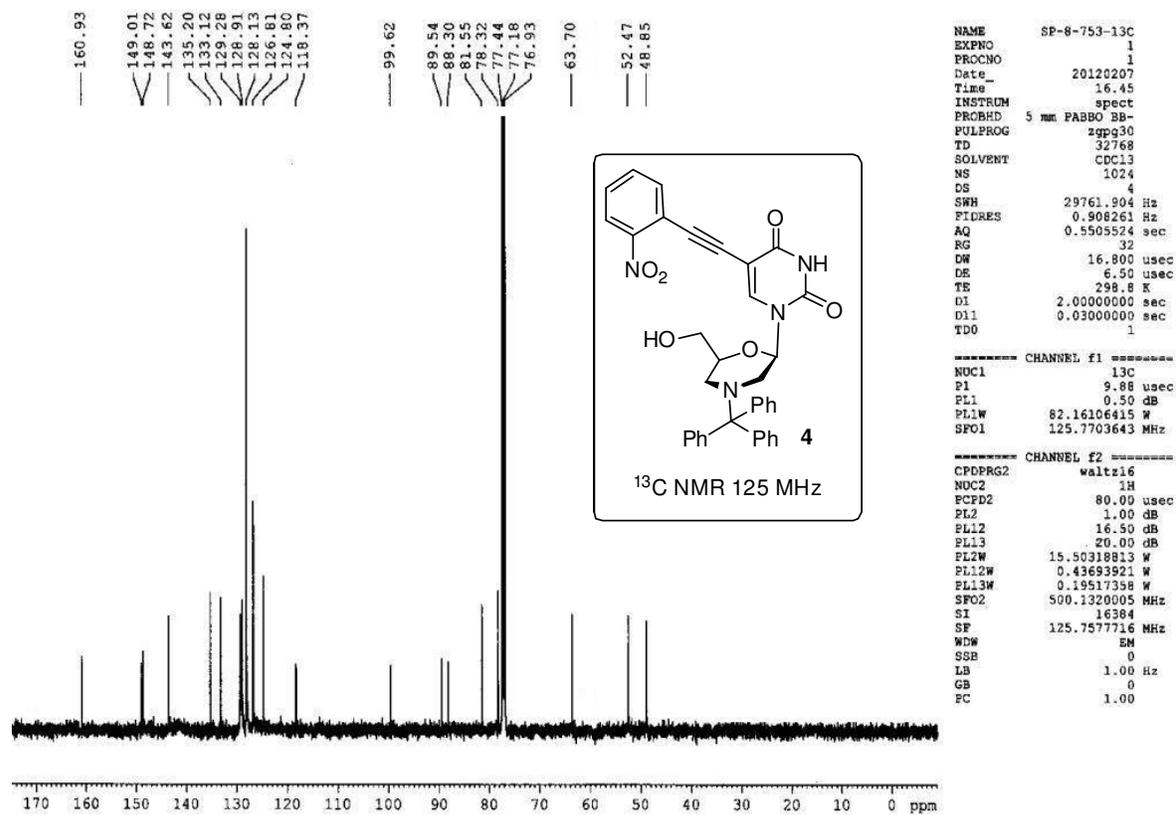
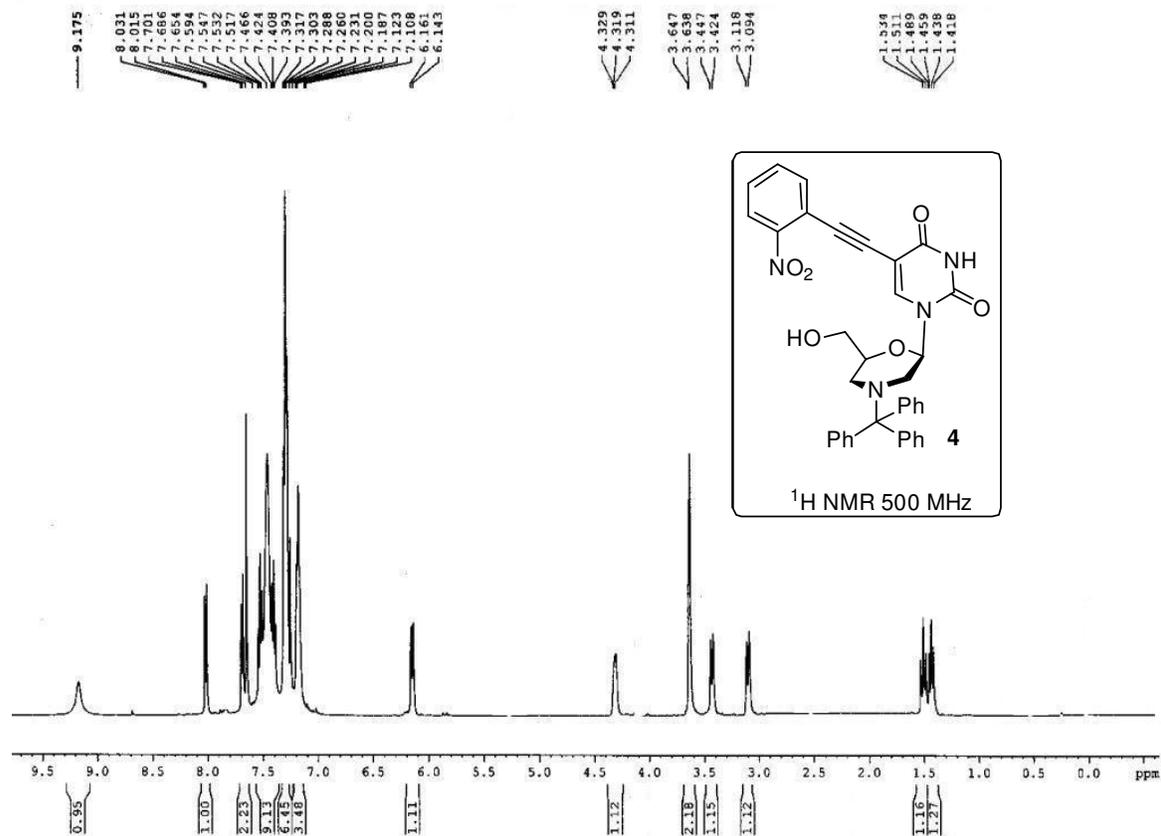
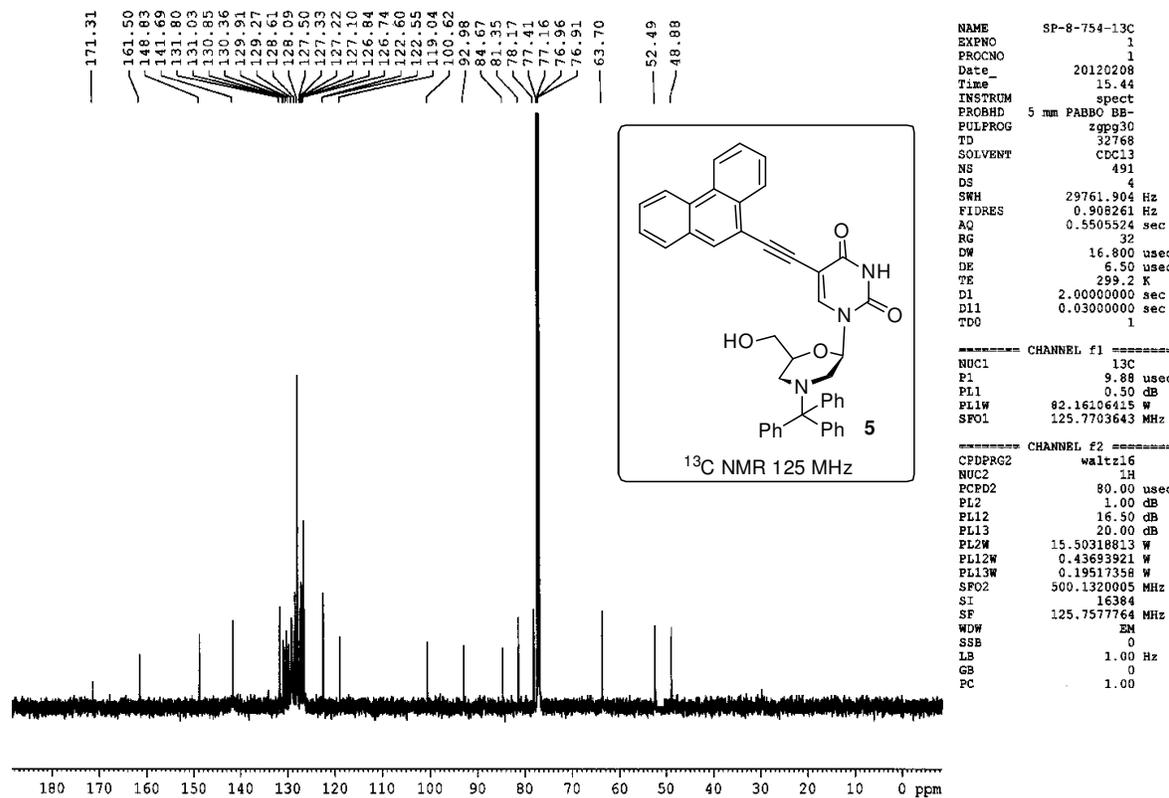
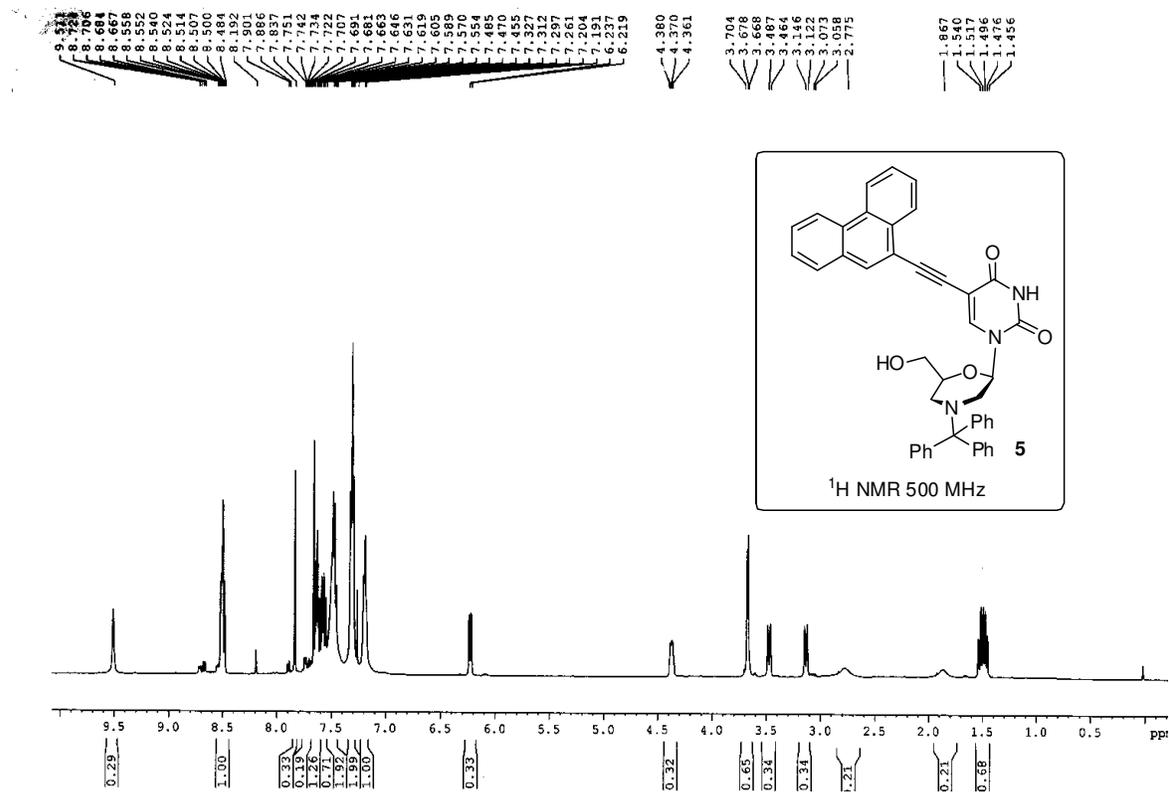
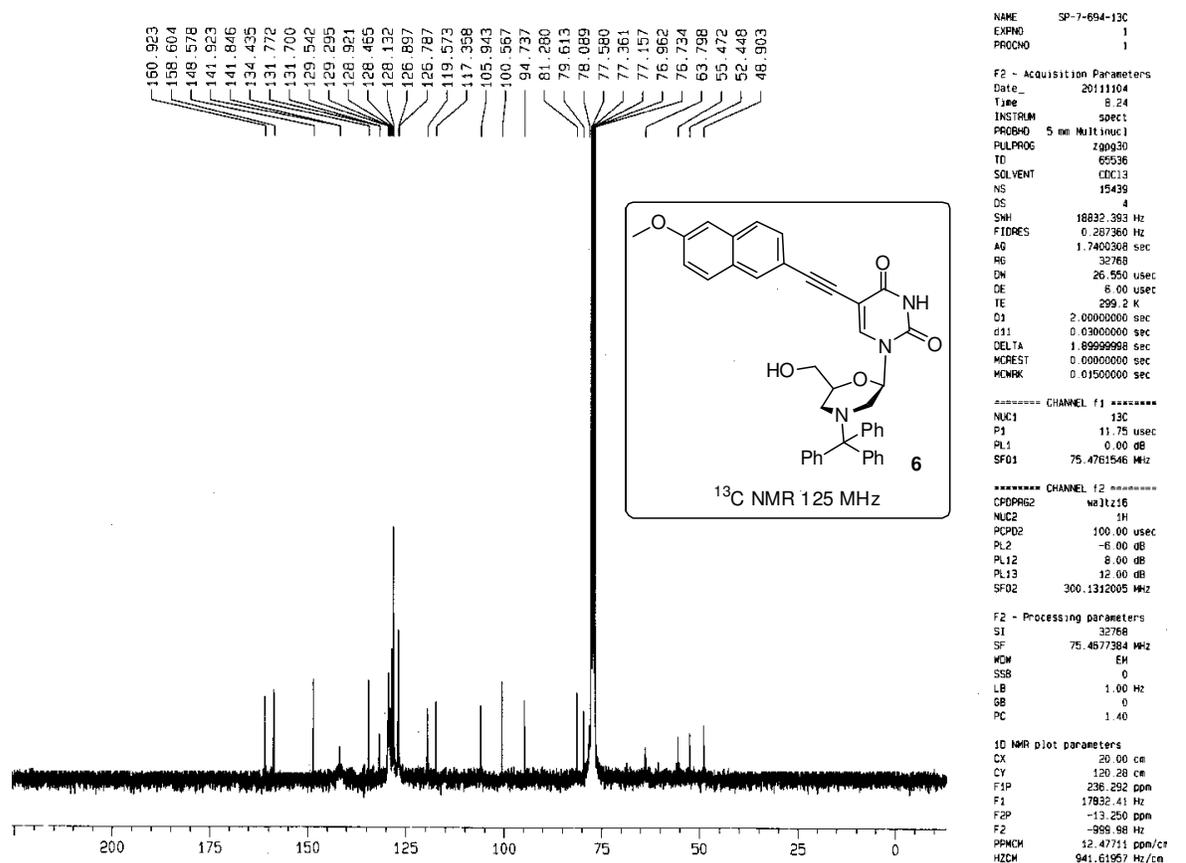
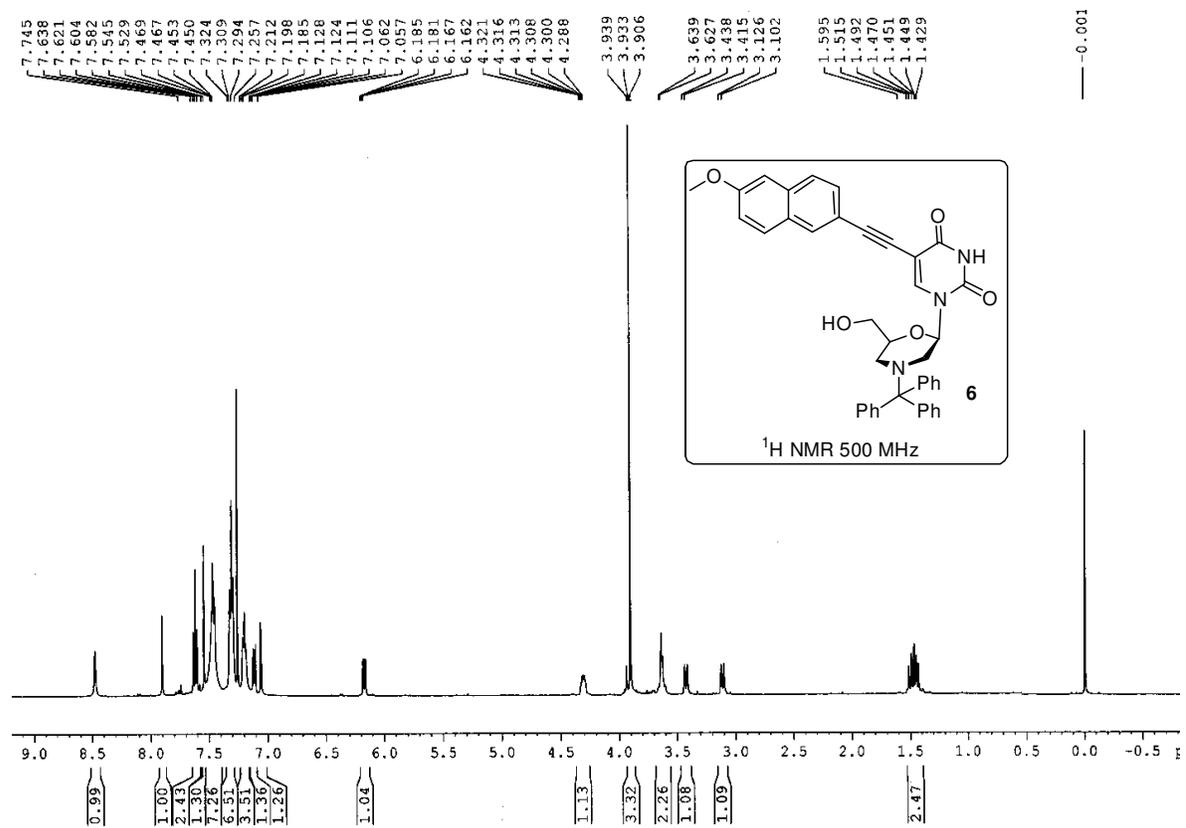


Fig. S7 Possibilities of two types of hydrogen bonding for ring formation









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PROCNO 1

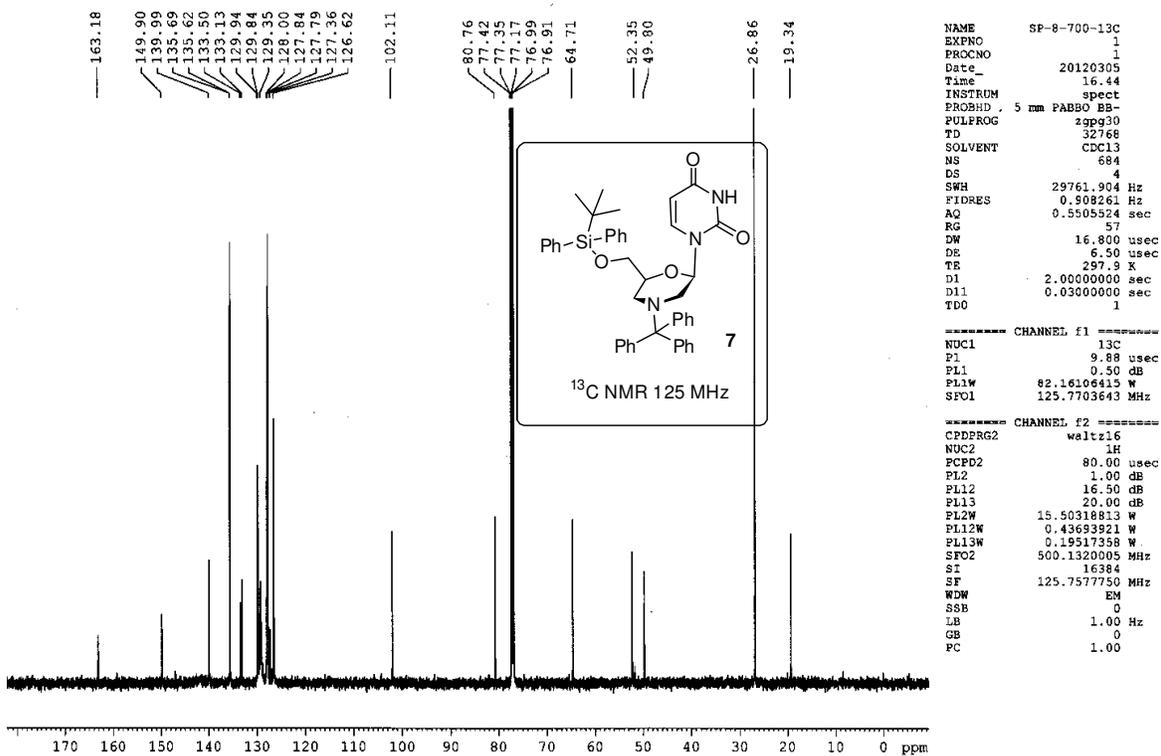
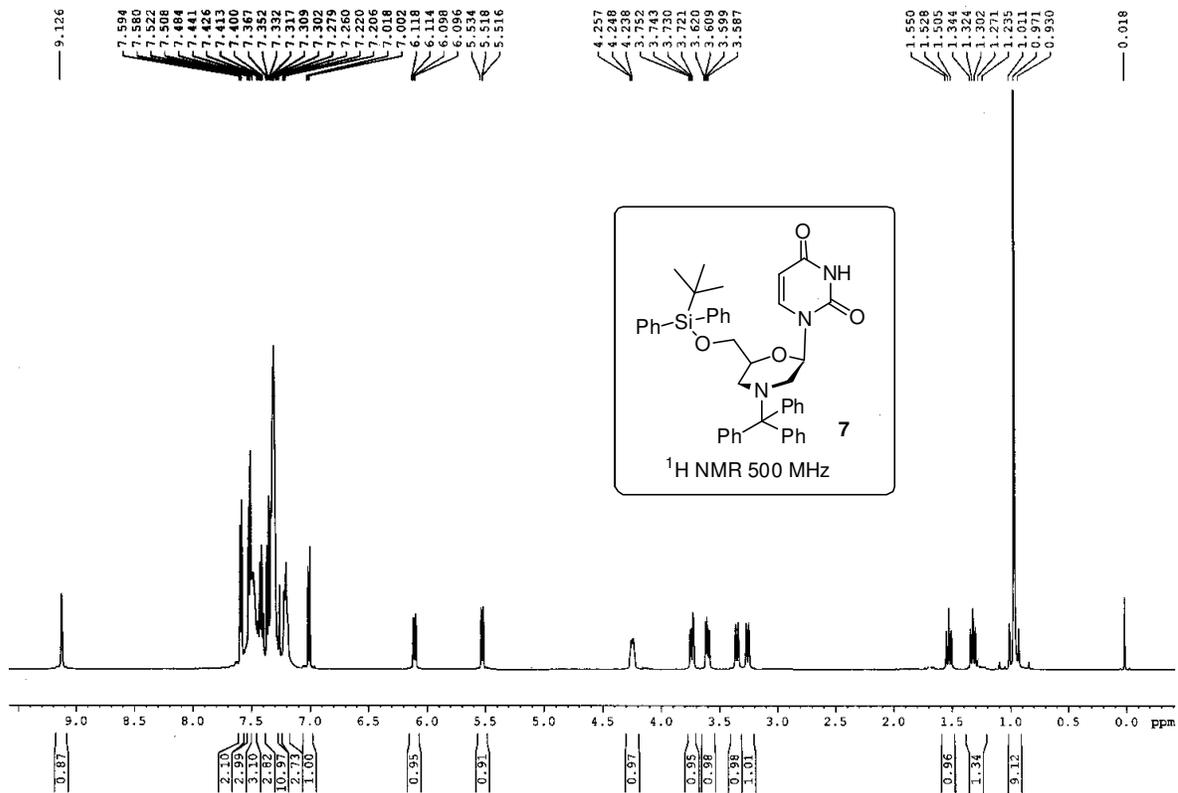
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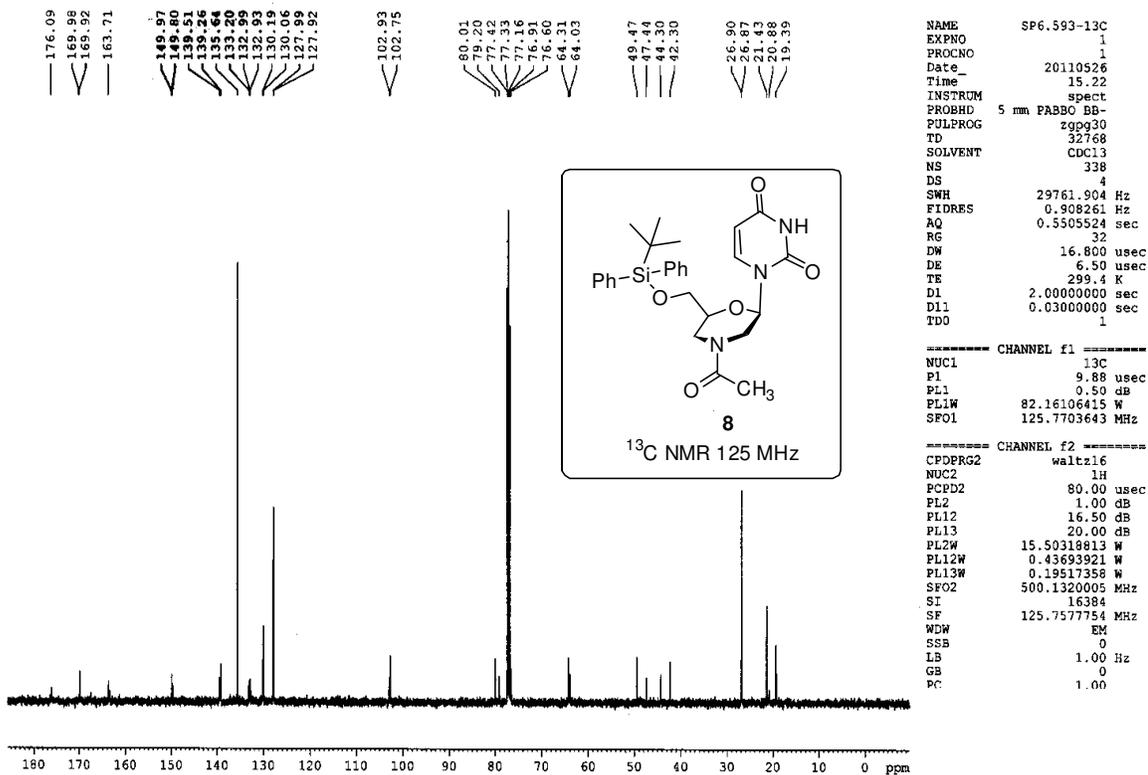
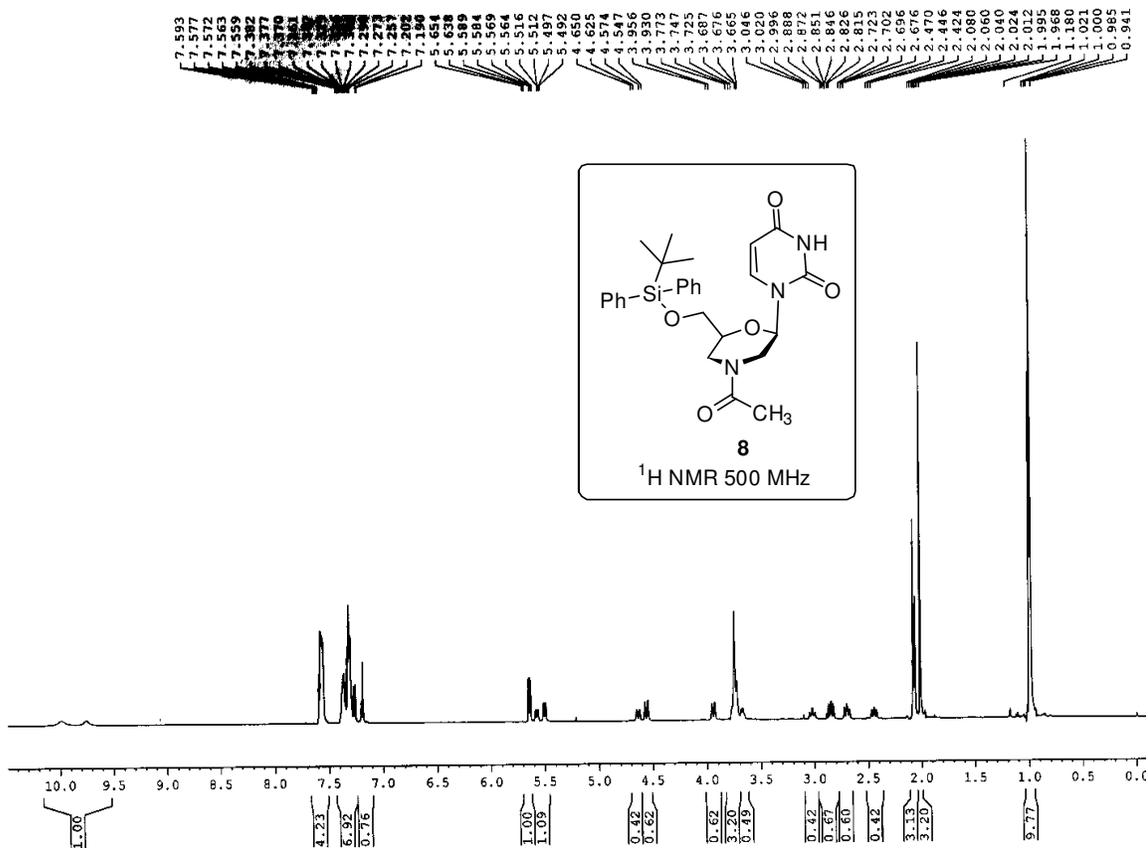
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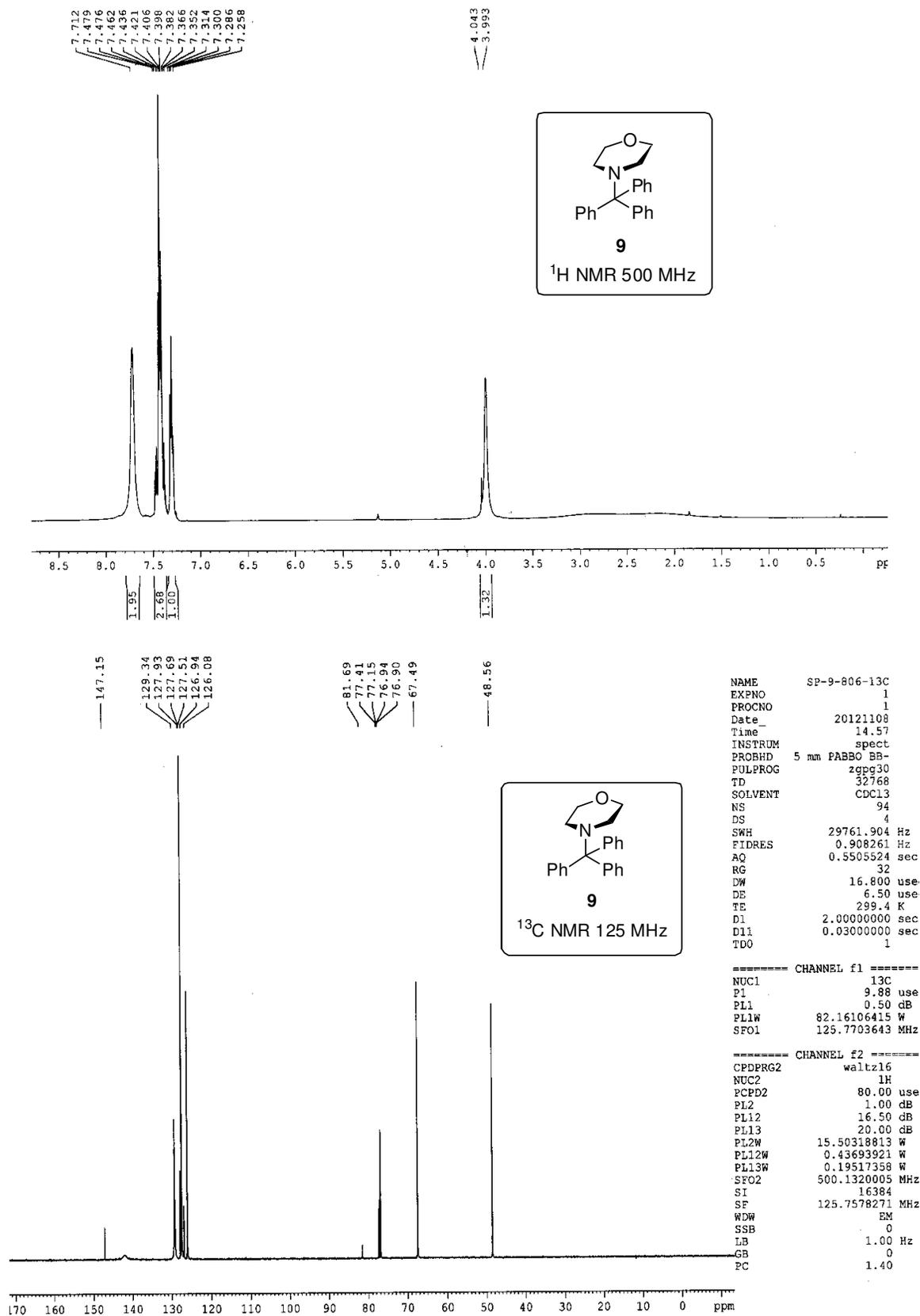
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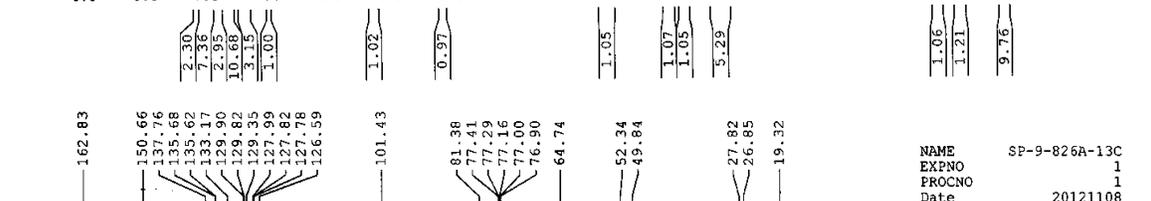
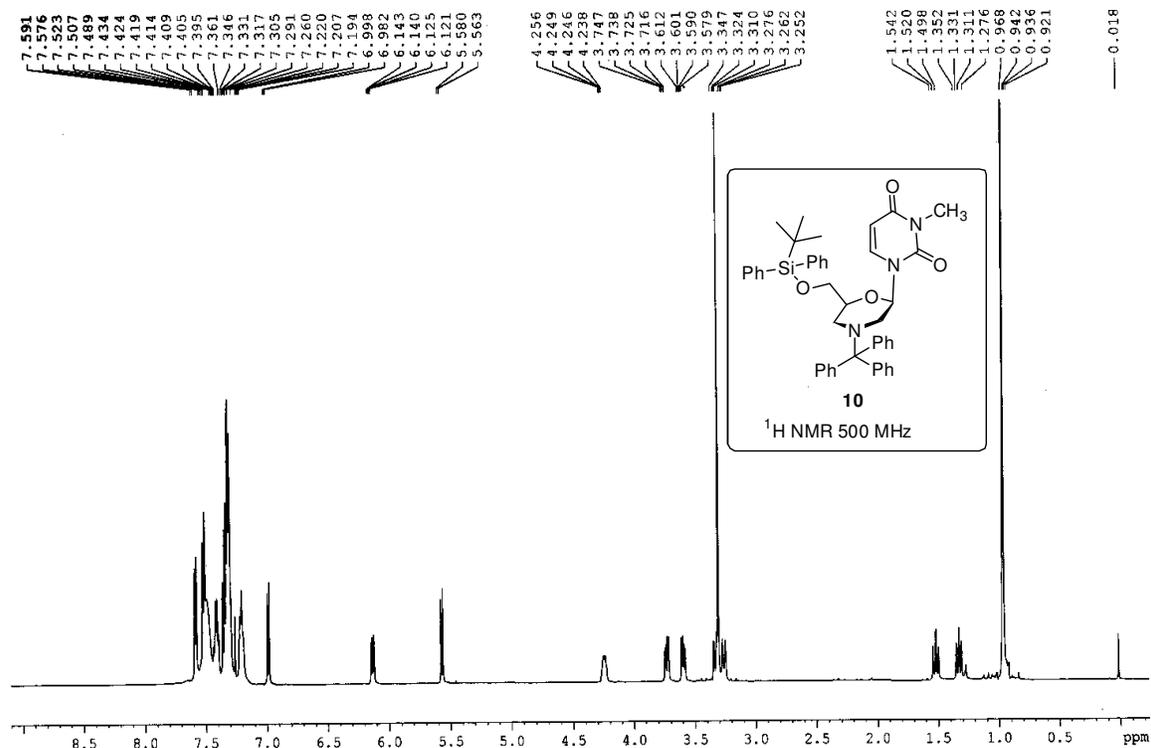
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