

Supporting Information

Title: Ultrafast Time-Resolved Transient Absorption and Resonance Raman Spectroscopy Study of the Photodeprotection and Rearrangement Reactions of *p*-Hydroxyphenacyl Caged Phosphates

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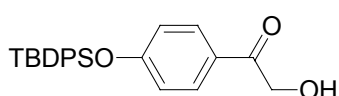
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Table 2S. Time dependent DFT (B3LYP/6-311G**) RPA calculated result obtained for excited state energies and oscillator strengths from the ground state of the spiroketone species. S13

Complete of Ref. 47 S13

was stirred at rt for 3 h. At this time the reaction mixture was concentrated in vacuo and H₂O (15 mL) was added. The mixture was extracted with diethyl ether (3 x 20 mL). The combined organic extracts were washed with brine (15 mL), dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (hexanes:EtOAc, 3:1) to afford **B** (3.97 g, 8.8 mmol, 78%) as a thick yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 9H), 4.32-4.57 (d, *J* = 75.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 7.37-7.40 (m, 6H), 7.68-7.75 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 19.4, 26.3 (3C), 30.8, 120.0 (2C), 127.3 (4C), 130.2 (2C), 130.6 (2C), 131.0 (2C), 131.9, 135.3 (4C), 160.7, 189.9; MS (m/z) calcd for C₂₄H₂₅O₂BrSi (M⁺) 452.0807, found, 452.0794.

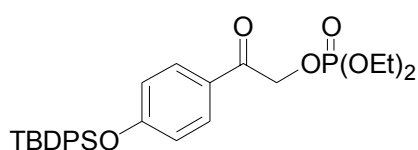
4-*tert*-butyldiphenylsilyloxy- α -hydroxyacetophenone (**C**):



Sodium formate (1.71 g, 25.2 mmol) was stirred in ethanol (120 mL) for 15 min and **B** (3.80 g, 8.5 mmol) was added. The mixture was stirred at 70 °C overnight. At this time the reaction was judged to be complete by TLC analysis. The solution was filtered hot and concentrated in vacuo. The crude residue was purified by silica gel chromatography (n-hexane:EtOAc, 6:1) to afford **C** (2.4 g, 6.1 mmol, 73%) as a viscous yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 9H), 3.51 (br, s, 1H), 4.73 (s, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 7.37-7.40 (m, 6H), 7.67-7.71 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 19.4, 26.3 (3C), 64.9, 120.1 (2C), 128.0 (4C), 129.7 (2C), 130.2 (2C), 130.3 (2C), 131.9, 135.3 (4C), 161.0, 196.7; MS (m/z) calcd for C₂₄H₂₆O₃Si (M⁺) 390.1651, found, 390.1655.

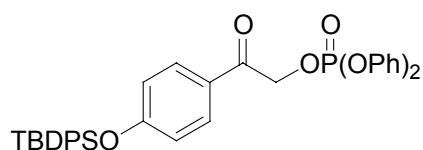
General procedure for the synthesis of dialkyl phosphates **D**, (Procedure A):

4-*tert*-Butyldiphenylsilyloxyphenacyl diethyl phosphate (**D1**):



To a solution of **C** (0.71 g, 1.8 mmol) in pyridine (5 ml) was added diethyl phosphoryl chloride (0.65 g, 3.8 mmol) dropwise at -5 °C with constant stirring. The mixture was allowed to warm to rt and stir under nitrogen for 4 h. At this time diethyl ether (10 ml) and water (5 ml) were added to the mixture. The aqueous layer was separated and extracted with additional diethyl ether (2 x 10 mL). The combined organic extracts were washed sequentially with 1N HCl (10 mL), NaHCO₃ (10 mL) and water (10 mL), dried over MgSO₄, filtered and concentrated in vacuo to afford **D1** (0.56 g, 1.1 mmol, 58%) as a viscous yellow oil after silica gel chromatography (n-hexane:EtOAc, 1:1). ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 9H), 1.33 (t, *J* = 7.0 Hz, 6H), 4.18 (m, *J* = 7.3 Hz, 4H), 5.17 (d, *J* = 9.9 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.37-7.40 (m, 6H), 7.66-7.70 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 16.0 (2C), 19.4, 26.3 (3C), 64.2, 68.3 (2C), 120.0 (2C), 127.9 (4C), 129.8 (2C), 130.2 (2C), 130.3 (2C), 131.9, 135.3 (4C), 160.7, 196; MS (m/z) calcd for C₂₈H₃₅PO₆Si (M⁺) 526.1941, found, 526.1938.

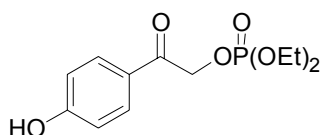
4-*tert*-Butyldiphenylsilyloxyphenacyl diphenyl phosphate (D2):



This was prepared by procedure **A** using **C** (1.10 g, 2.9 mmol), diphenyl phosphoryl chloride (1.81 g, 6.7 mmol) and pyridine (0.30 g, 4.4 mmol) in CH₂Cl₂ (25 mL) to afford **D2** as white solid (1.4 g, 2.2 mmol, 75%) after silica gel chromatography (n-hexanes:EtOAc, 9:1). ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 9H), 5.31 (d, *J* = 9.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 7.25–7.40 (m, 16H), 7.66–7.69 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 19.4, 26.3 (3C), 69.6, 120.0 (4C), 120.1 (2C), 125.4 (2C), 127.0, 127.9 (4C), 129.7 (4C), 129.8 (2C), 130.2 (2C), 131.8 (2C), 135.3 (4C), 150.4 (2C), 160.8, 190.0; MS (m/z) calcd for C₃₆H₃₅O₆PSi (M⁺ - *t*-butyl), 566.1236, found, 566.1248.

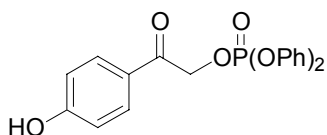
General procedure for the synthesis of 4-hydroxyphenacyl dialkyl phosphate **6**, (Procedure B):

4-Hydroxyphenacyl diethyl phosphate (HPDP):



Tetrabutylammonium fluoride (TBAF) (1.2 mL of 1.0 M solution in THF, 1.2 mmol) was added to a solution of **D1** (0.56 g, 1.1 mmol) in THF (6 mL). The reaction mixture was stirred at rt for 30 min. At this time the reaction was judged to be complete by TLC analysis. The reaction mixture was quenched with water, extracted with EtOAc, washed with satd NH₄Cl, dried over MgSO₄, filtered and concentrated in vacuo to give a crude pale yellow solid. The crude product was washed with n-hexane, filtered and concentrated in vacuo to afford **HPDP** (0.25 g, 0.86 mmol, 79 %) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 1.41 (t, *J* = 7.0 Hz, 6H), 4.28 (m, *J* = 7.3 Hz, 4H), 7.57 (d, *J* = 9.2 Hz, 2H), 5.17 (d, *J* = 11.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 9.08 (s, br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 16.1, 64.9, 68.8 (2C), 115.9 (2C), 125.5, 130.0 (2C), 162.6, 189.9; MS (m/z) calcd for C₁₂H₁₇PO₆ (M⁺) 288.0763, found, 288.0760.

4-Hydroxyphenacyl diphenyl phosphate (HPPP):



This was prepared by procedure **B** using **D2** (4.21 g, 6.8 mmol) and tetrabutylammonium fluoride (TBAF) (5.3 mL of 1.0 M solution in THF, 3.3 mmol) in THF (40 mL) to afford **HPPP** as pale yellow solid (1.90 g, 4.9 mmol, 73%) after silica gel chromatography (CH₂Cl₂:MeOH, 18:1). ¹H NMR (300 MHz, CDCl₃) δ 1.82 (br, 1H), 5.31 (d, *J* = 11.3 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 7.22–7.37 (m, 10H), 7.58 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 70.0, 115.8 (4C), 120.2 (2C), 125.7 (2C), 129.7, 129.9 (4C), 130.2 (2C), 150.3 (2C), 161.9, 189.1; MS (m/z) calcd for C₂₀H₁₇O₆P (M⁺ - OPh), 292.0500, found, 292.0458.

Figure 1S

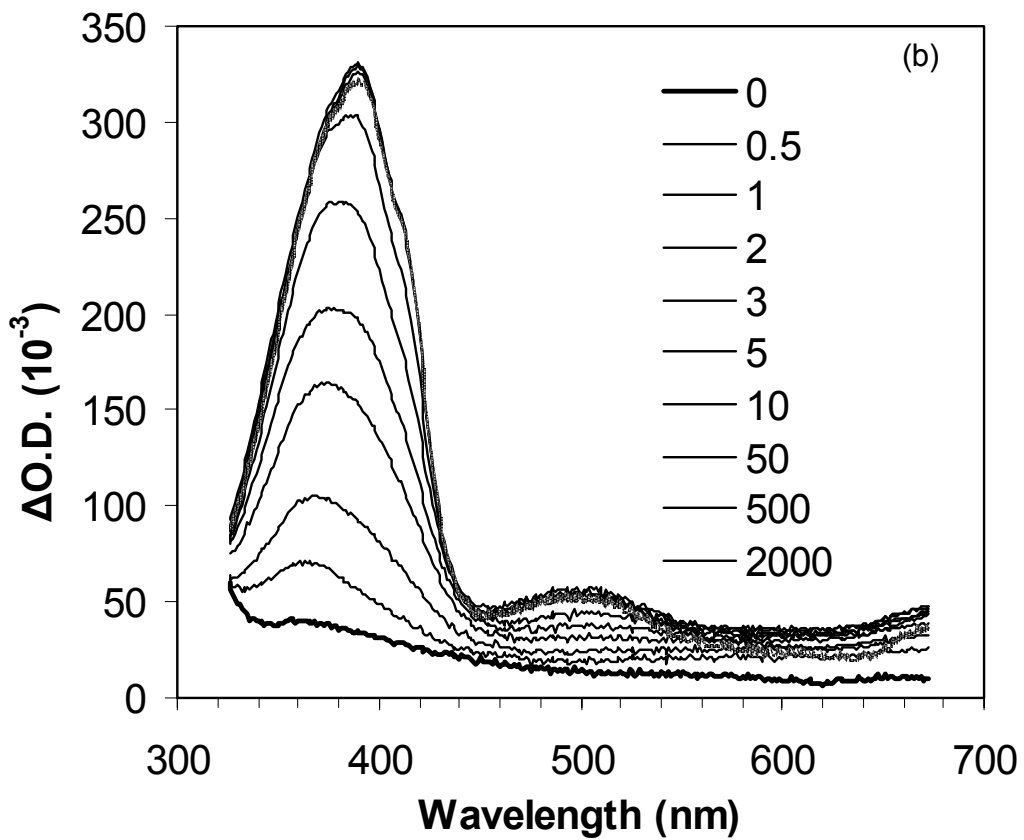
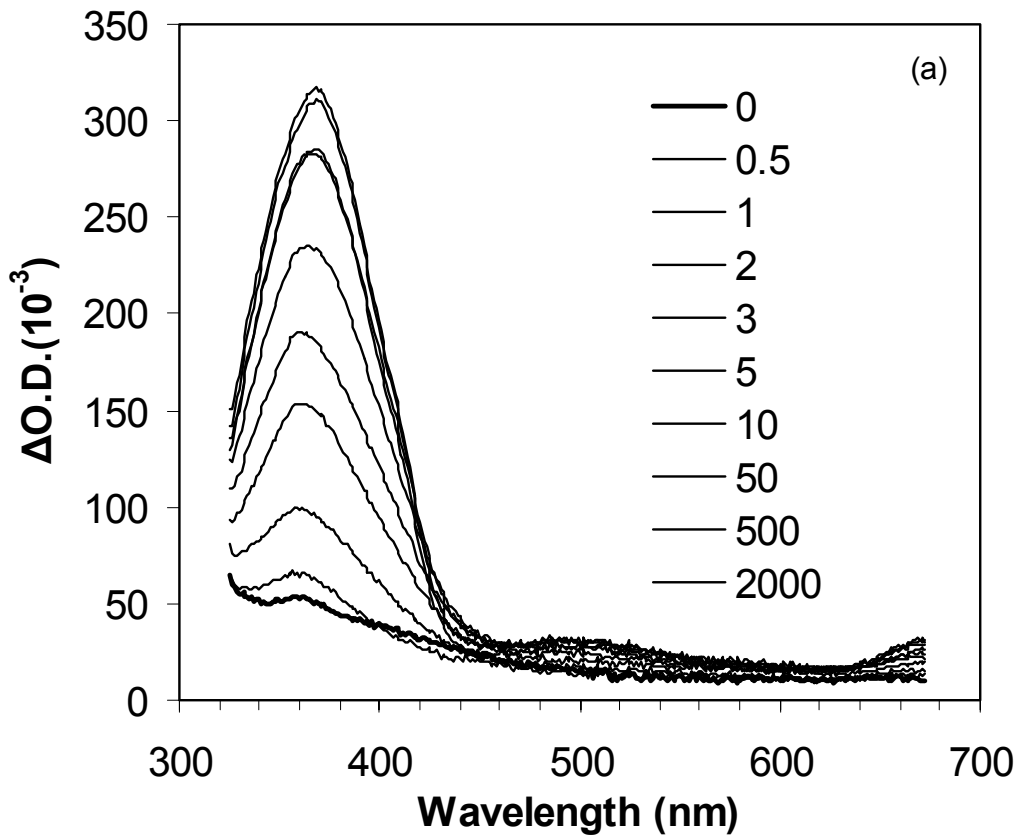


Figure 2S

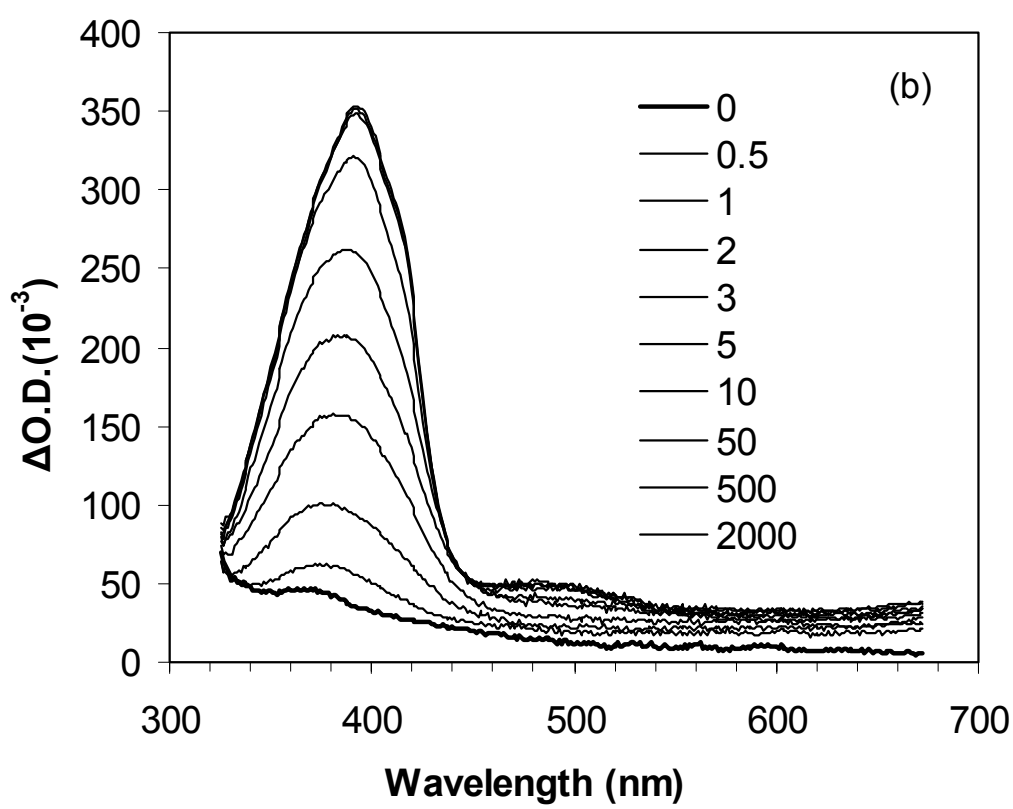
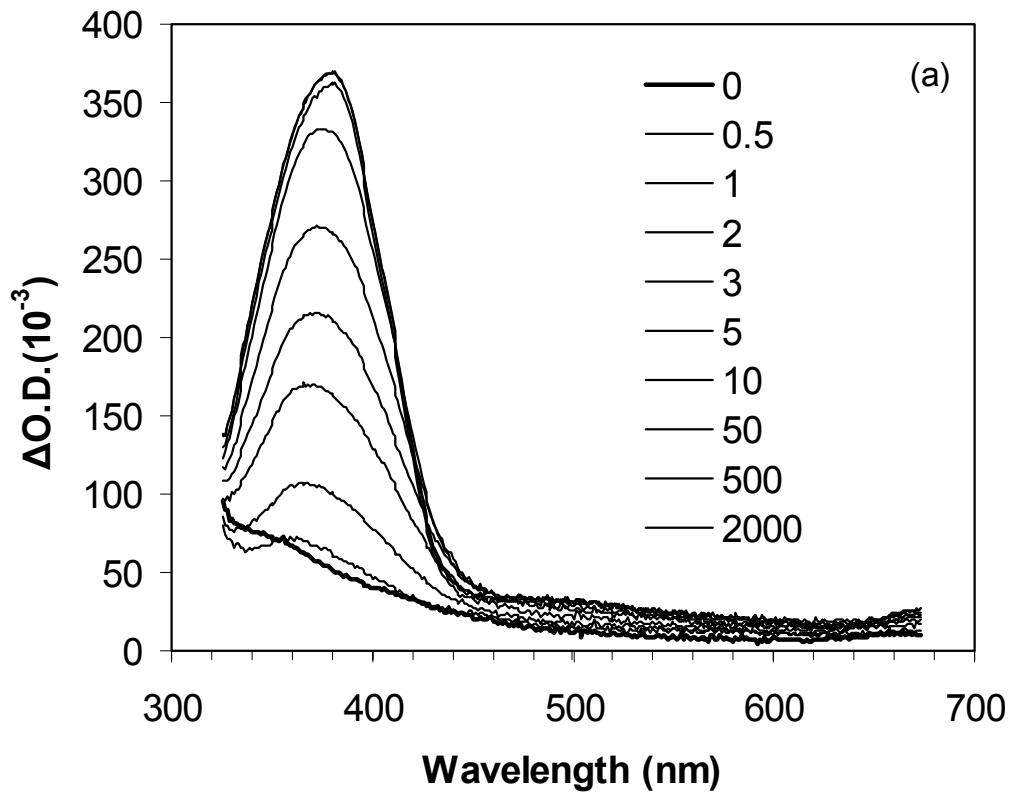


Figure 3S

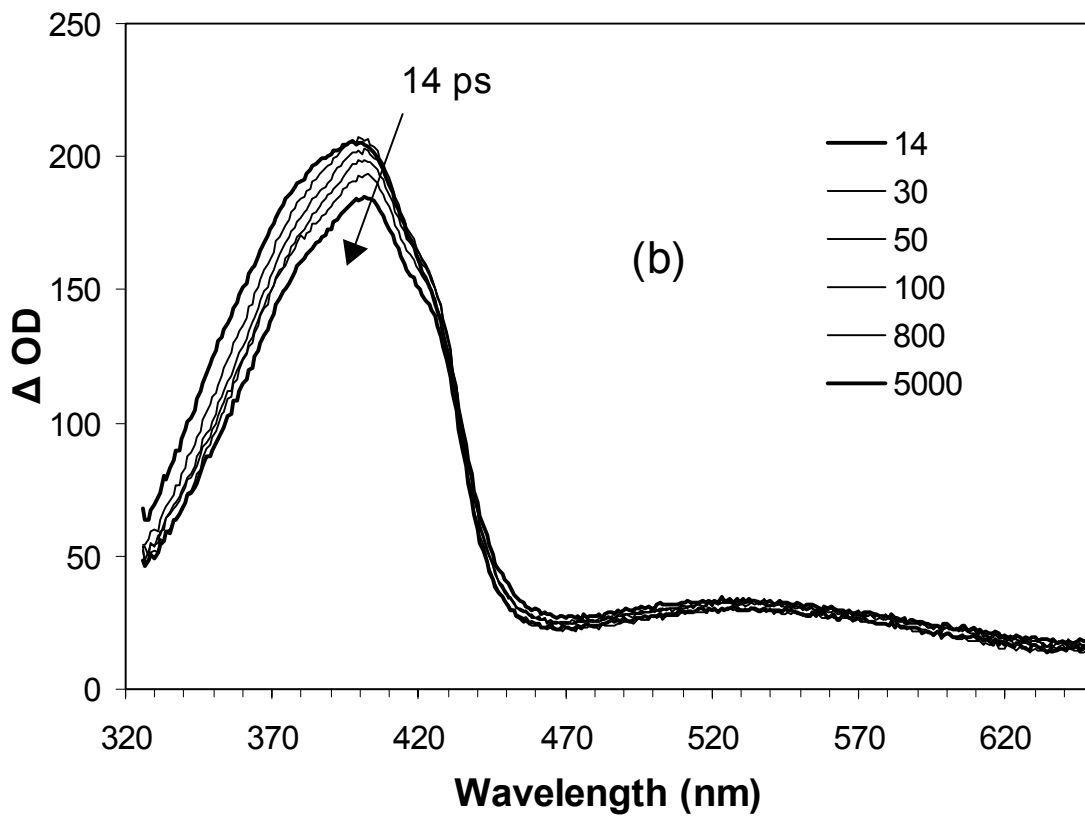
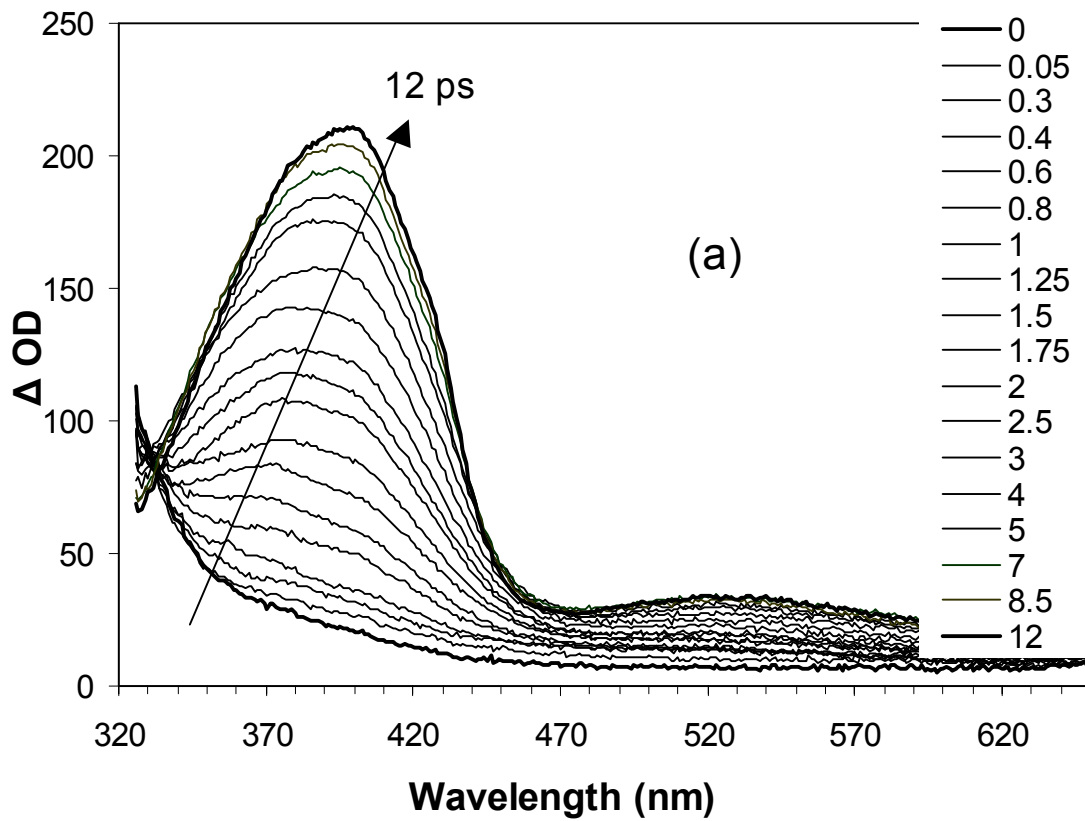


Figure 4S

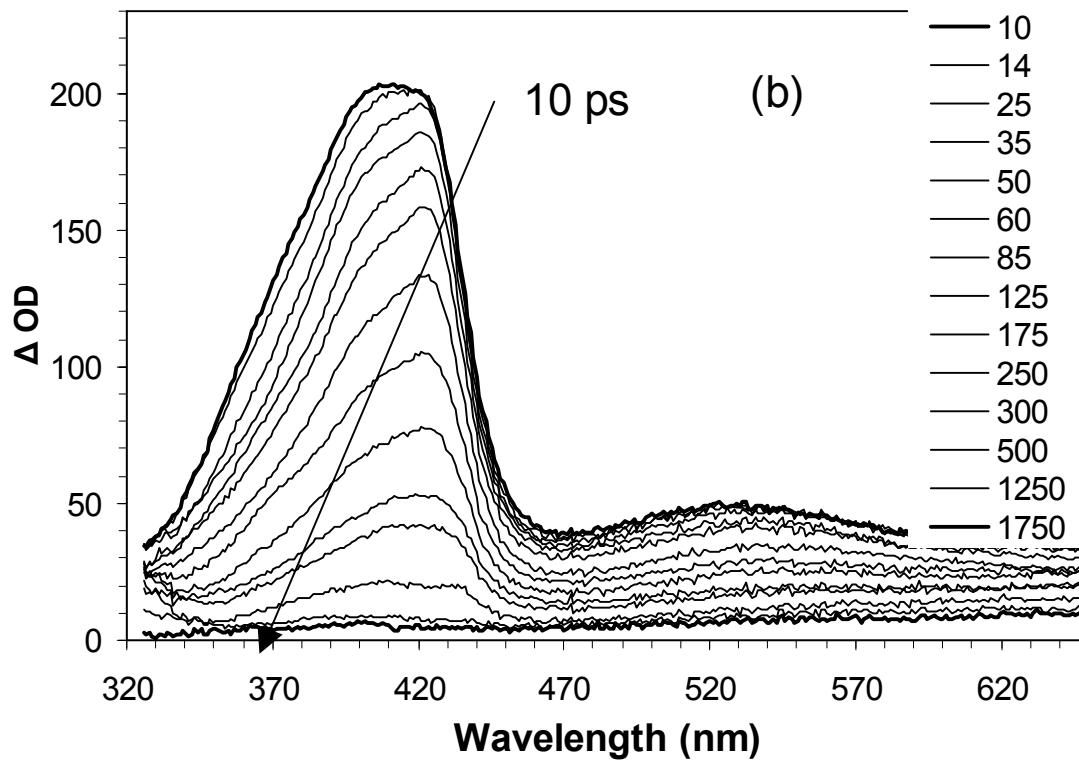
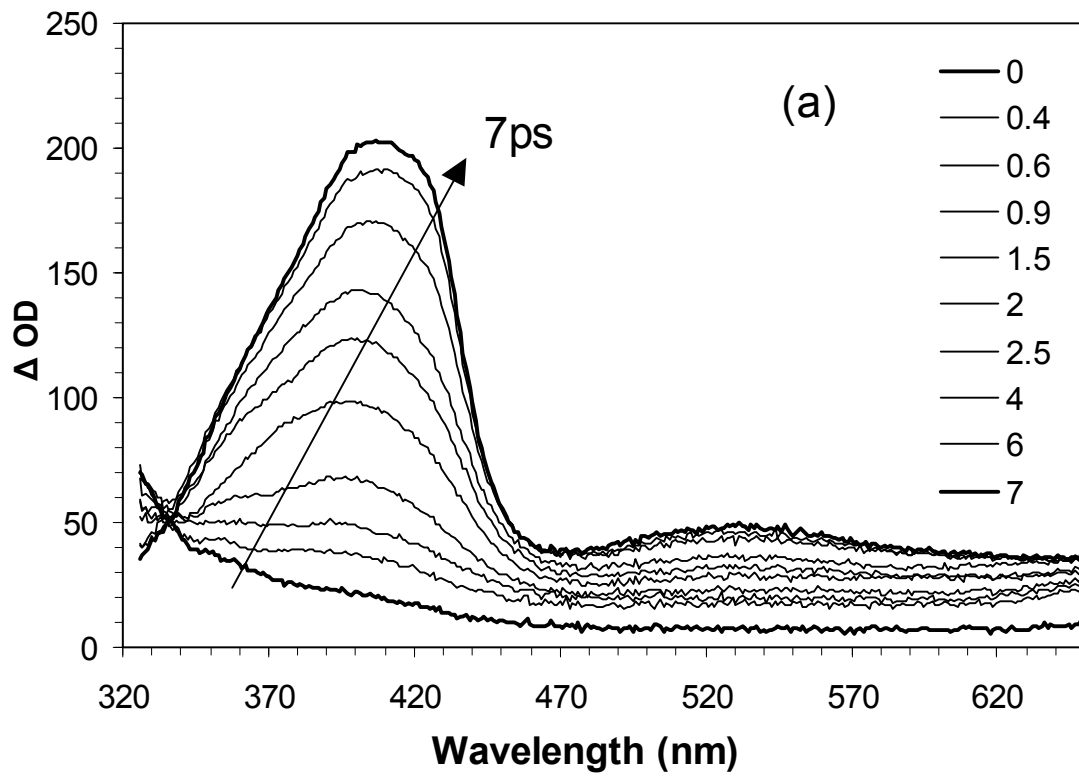


Figure 5S.

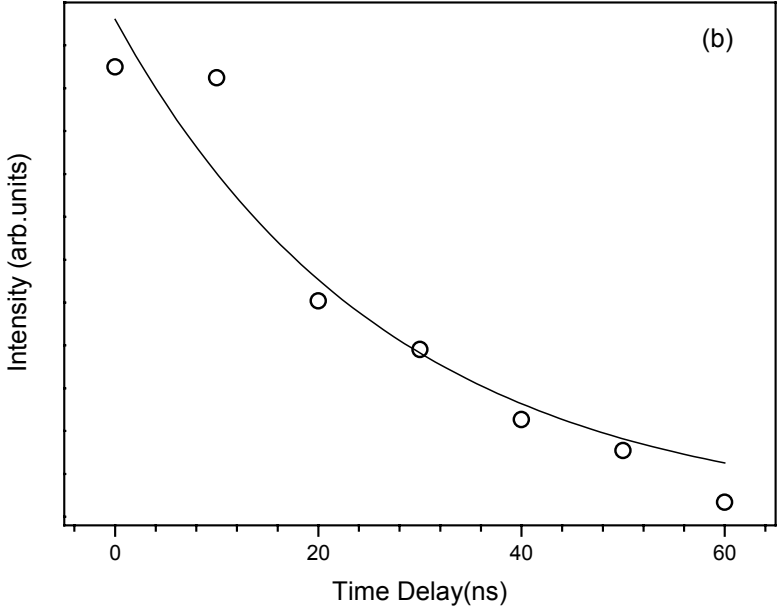
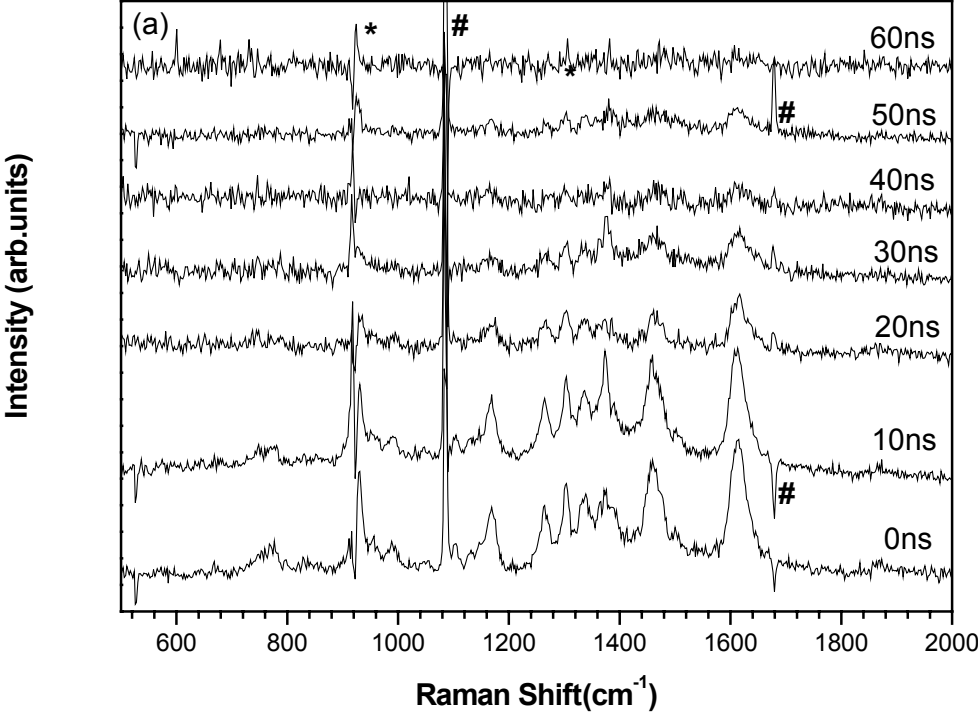


Figure 6S.

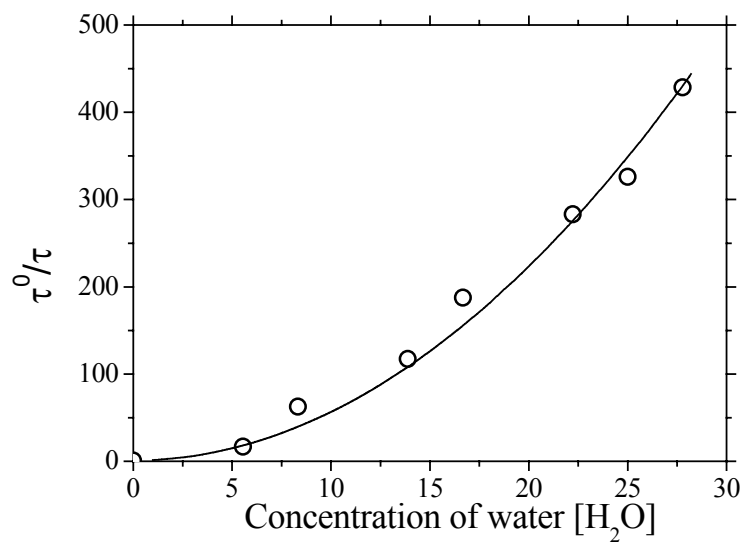


Figure 7S

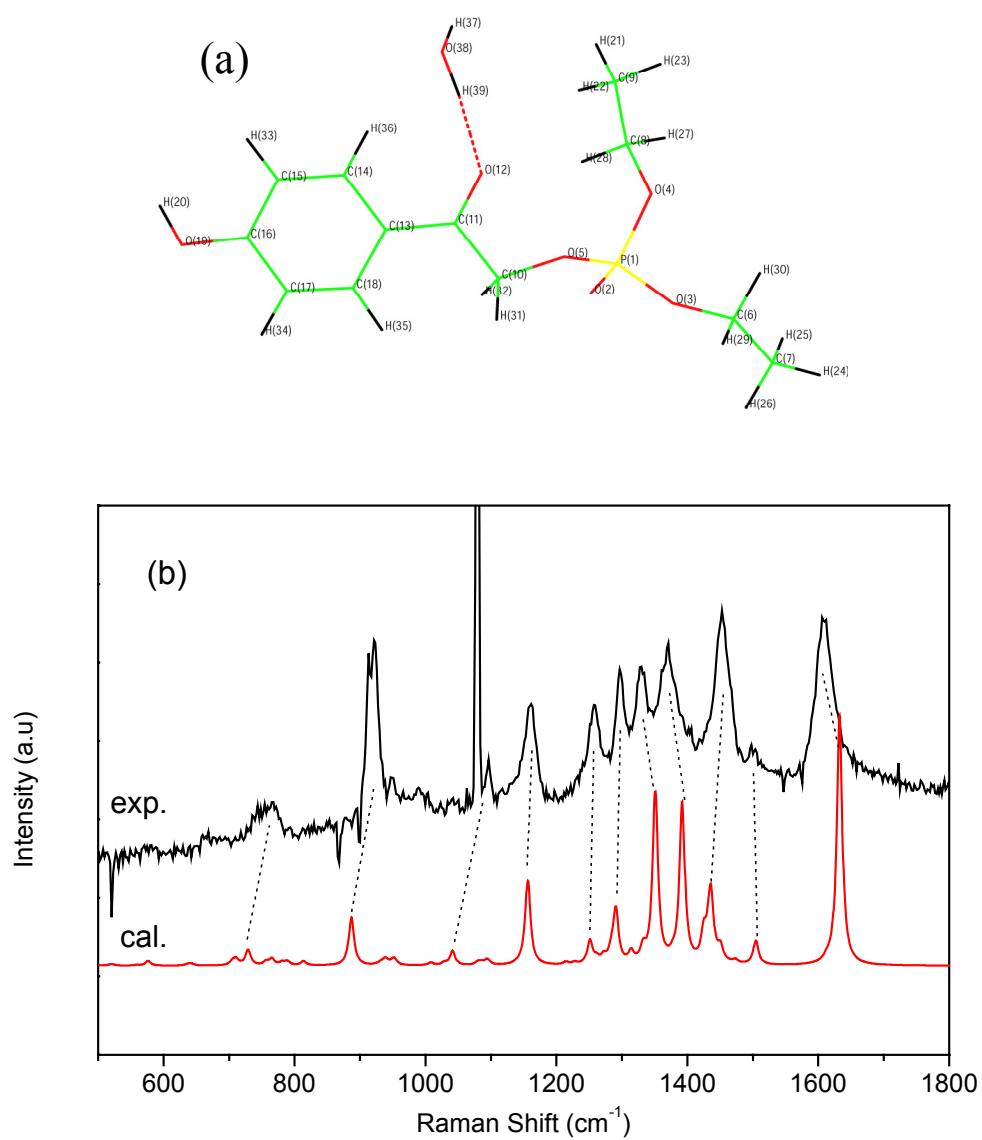


Figure 8S.

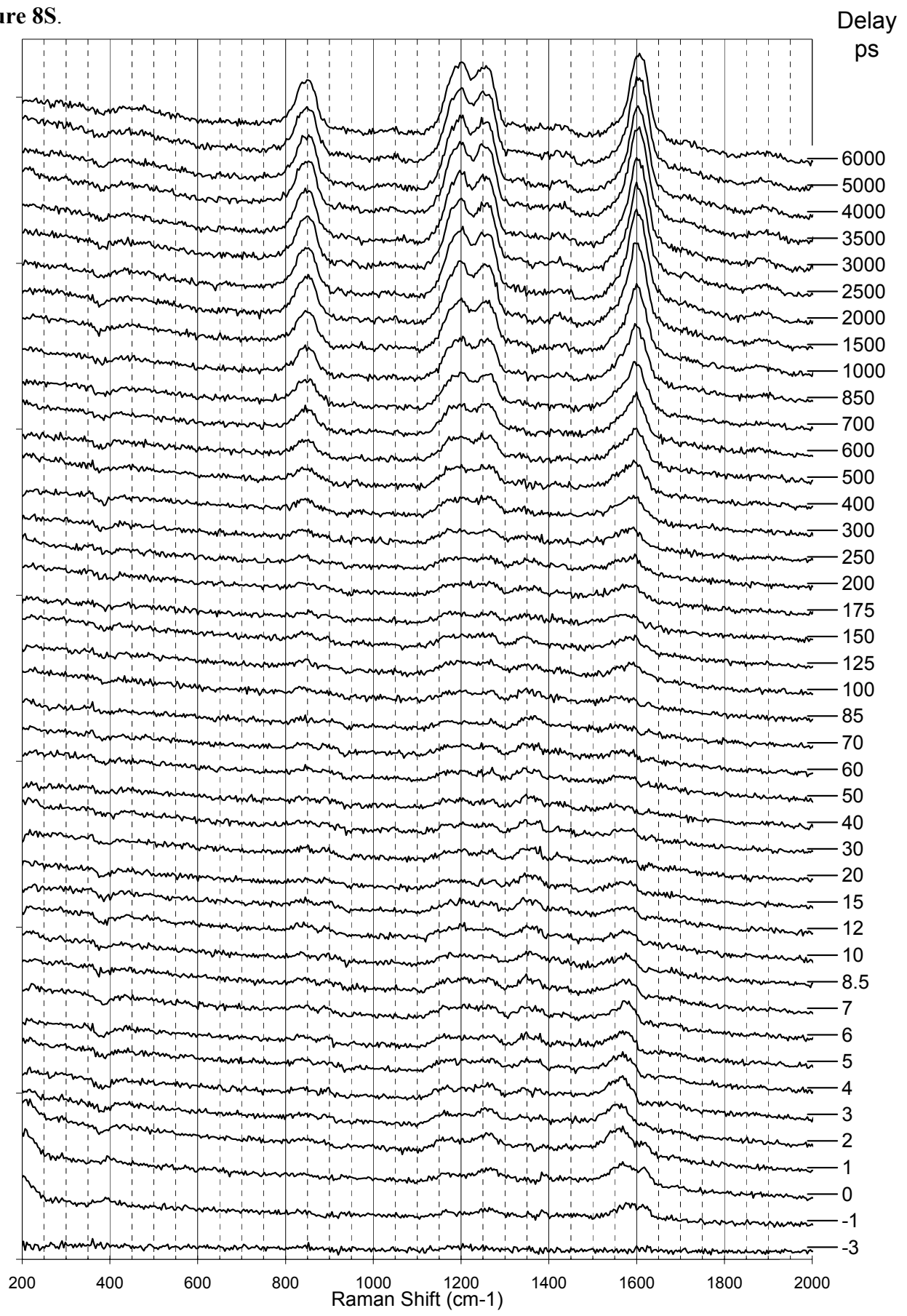


Figure 9S

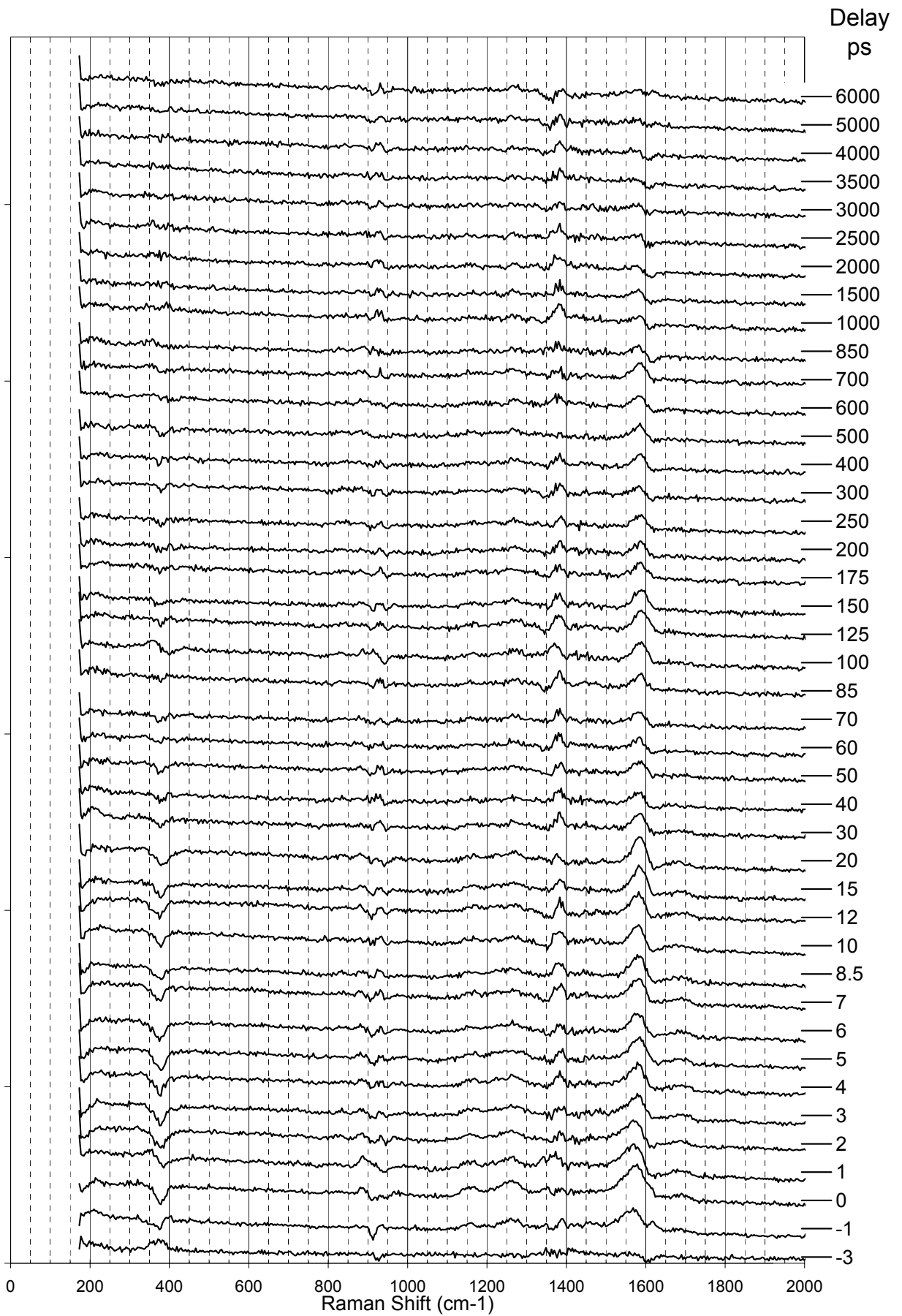


Table 1S

| Bond length (Å) | | Bond angle (degree) | | Dihedral angle (degree) | |
|-----------------|-------|---------------------|-------|-------------------------|--------|
| P1=O2 | 1.479 | O2=P1-O3 | 117.2 | O2=P1-O3-C6 | -59.4 |
| P1-O3 | 1.601 | O2=P1-O4 | 116.3 | O2=P1-O4-C8 | -37.4 |
| P1-O4 | 1.597 | O2=P1-O5 | 114.6 | O2=P1-O5-C10 | -0.3 |
| P1-O5 | 1.610 | P1-O3-C6 | 119.9 | P1-O3-C6-C7 | 173.6 |
| O3-C6 | 1.449 | P1-O4-C8 | 122.3 | P1-O4-C8-C9 | -125.7 |
| O4-C8 | 1.459 | P1-O5-C10 | 120.9 | P1-O5-C10-C11 | 91.3 |
| O5-C10 | 1.426 | O3-C6-C7 | 107.7 | O5-P1-O3-C6 | 176.8 |
| C6-C7 | 1.515 | O4-C8-C9 | 109.0 | O5-P1-O4-C8 | 91.6 |
| C8-C9 | 1.514 | O5-C10-C11 | 111.3 | O3-P1-O5-C10 | 125.4 |
| C10-C11 | 1.528 | O3-P1-O5 | 99.2 | O4-P1-O5-C10 | -130.2 |
| C11-C13 | 1.424 | O4-P1-O5 | 106.4 | O5-C10-C11-O12 | -17.1 |
| C11=O12 | 1.262 | C10-C11-C13 | 119.7 | O5-C10-C11-O13 | 164.5 |
| C13-C14 | 1.480 | C10-C11=O12 | 119.2 | C10-C11-C13-C14 | -178.2 |
| C14-C15 | 1.356 | O12=C11-C13 | 121.1 | O12=C11-C13-C14 | 3.5 |
| C15-C16 | 1.428 | C11-C13-C14 | 119.5 | C11-C13-C14-C15 | 179.5 |
| C16-C17 | 1.441 | C13-C14-C15 | 120.6 | C13-C14-C15-C16 | 0.3 |
| C17-C18 | 1.354 | C14-C15-C16 | 120.7 | C14-C15-C16-O19 | 179.8 |
| C13-C18 | 1.466 | C16-C17-C18 | 120.5 | C15-C16-O19-H20 | -0.3 |
| C16-O19 | 1.350 | C13-C18-C17 | 120.8 | C11-C13-C18-C17 | -179.4 |
| | | C14-C13-C18 | 117.4 | C10-C11-C13-C18 | 2.6 |
| | | C15-C16-O19 | 123.3 | C10-C11=O12-H39 | -175.4 |
| | | C16-O19-H20 | 110.0 | C13-C11=O12-H39 | 3.0 |
| | | C11=O12-H39 | 140.6 | C11-O12-H39-O38 | -65.5 |
| | | O12-H39-O38 | 165.0 | O12-H39-O38-H37 | -40.6 |

Total Energy (including ZPE): -1336.611877 (Hartree)

H-bond Energy: 5.74 kcal/mol

Table 2S

| | excitation energy (nm) | oscillator strength (f) |
|-----------------|------------------------|-------------------------|
| Excited state 1 | 369.13 | 0.0000 |
| Excited state 2 | 354.08 | 0.0007 |
| Excited state 3 | 298.83 | 0.0000 |
| Excited state 4 | 273.63 | 0.2155 |
| Excited state 5 | 249.06 | 0.0034 |
| Excited state 6 | 235.06 | 0.0448 |
| Excited state 7 | 233.26 | 0.0273 |
| Excited state 8 | 231.28 | 0.0000 |

Completion of Ref. 47

[47] Gaussian 98, Revision A.7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr. J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh PA, **1998**.