Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

The interplay between hydrogen bonding and π-π stacking interactions in the crystal packing of N(1)-thyminyl derivatives, and implications to the photo-chemical [2π+2π]-cycloaddition of thyminyl compounds

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Supplementary Information

Table S1. Geometry parameters of the optimized transition states for the concerted mechanism

		TA	TS	CA	CS
Acetate (**3**)	R(HC···C-CH_3), Å	2.119 2.279		2.031 2.291	
	R(HC···C-H), Å		2.109		2.186
	R(H_3C-C···C-CH_3), Å		2.309		2.225
	α(N-C=C··C(=O)), °	17.4 9.2	18.3 5.7	7.0 0.1	12.3 0.8
Propanoate (**5**)	R(HC···C-CH_3), Å	2.082 2.332		2.157 2.157	
	R(HC···C-H), Å		2.104		2.150
	R(H_3C-C···C-CH_3), Å		2.296		2.275
	α(N-C=C··C(=O)), °	16.4 11.5	15.7 2.3	54.5 9.5	14.5 5.4
Propanoic acid (**6**)	R(HC···C-CH_3), Å	2.029 2.381		2.178 2.178	
	R(HC···C-H), Å		2.243		2.152
	R(H_3C-C···C-CH_3), Å		2.222		2.275
	α(N-C=C··C(=O)), °	15.9 9.6	12.5 2.7	9.6 9.5	14.6 5.4
Propanoamide (**7**)	R(HC···C-CH_3), Å	1.966 2.474		2.185 2.185	
	R(HC···C-H), Å		2.096		2.159
	R(H_3C-C···C-CH_3), Å		2.301		2.274
	α(N-C=C··C(=O)), °	22.6 1.1	15.6 4.2	12.0 12.0	16.6 6.8

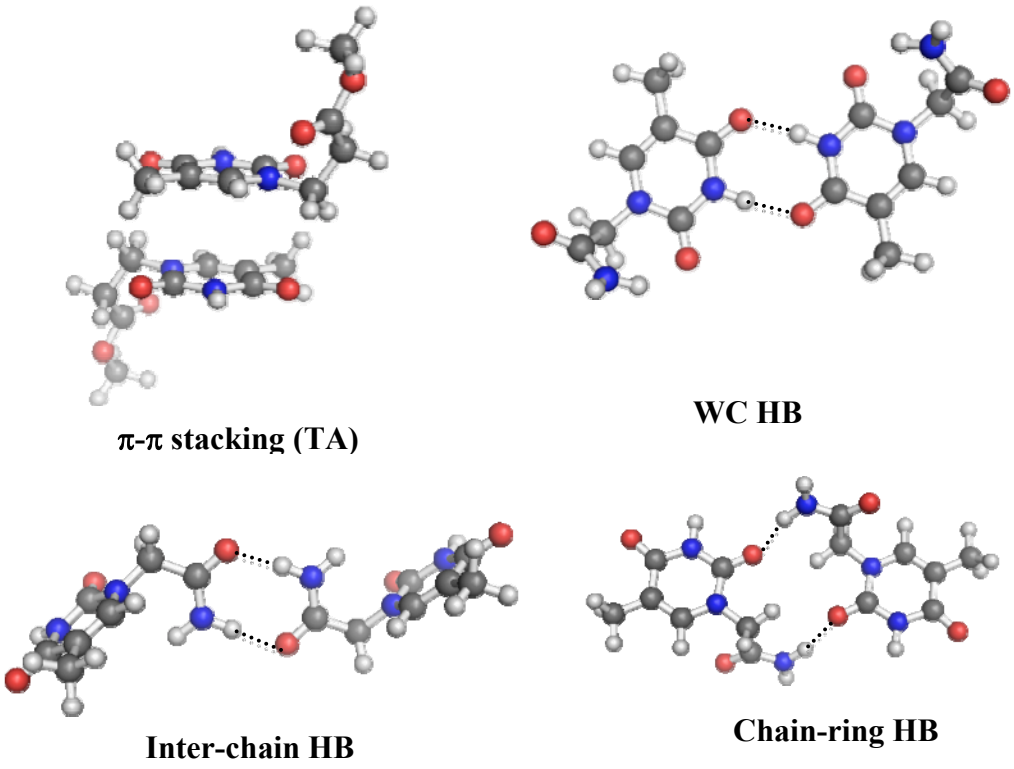


Figure S1. Examples of B3LYP optimised structures for each type of the four specific interactions as discussed in the paper.

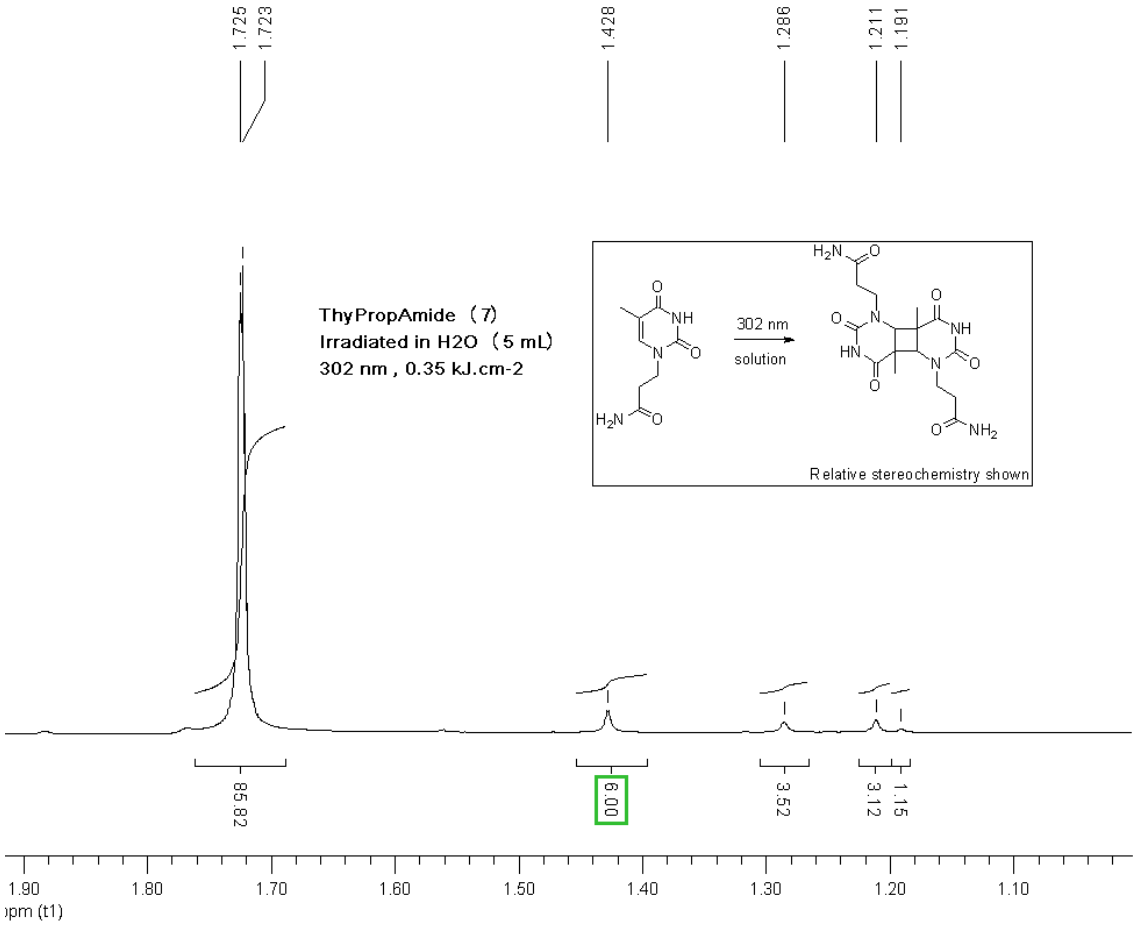
Table S2. Calculated number of interactions occurring in a unit cell and between eight molecules

	Acetic (**2**)	Acetate (**3**)	Acetamide (**4**)	PropOate (**5**)	PropOic (**6**)	PropAmide (**7**)
Z	4	4	4	4	4	8
WC HB	4	4	0	4	4	0
Ring-ring	0	0	4	0	0	4
pi-pi stacking	2	2	2	2	2	4
Chain-chain	0	0	4	0	0	8
Chain-ring	4	4	4	0	4	12
Total per unit cell	10	10	14	6	10	28
Number of molecules	8	8	8	8	8	8
Total interactions for 8 molecules	20	20	28	12	20	28

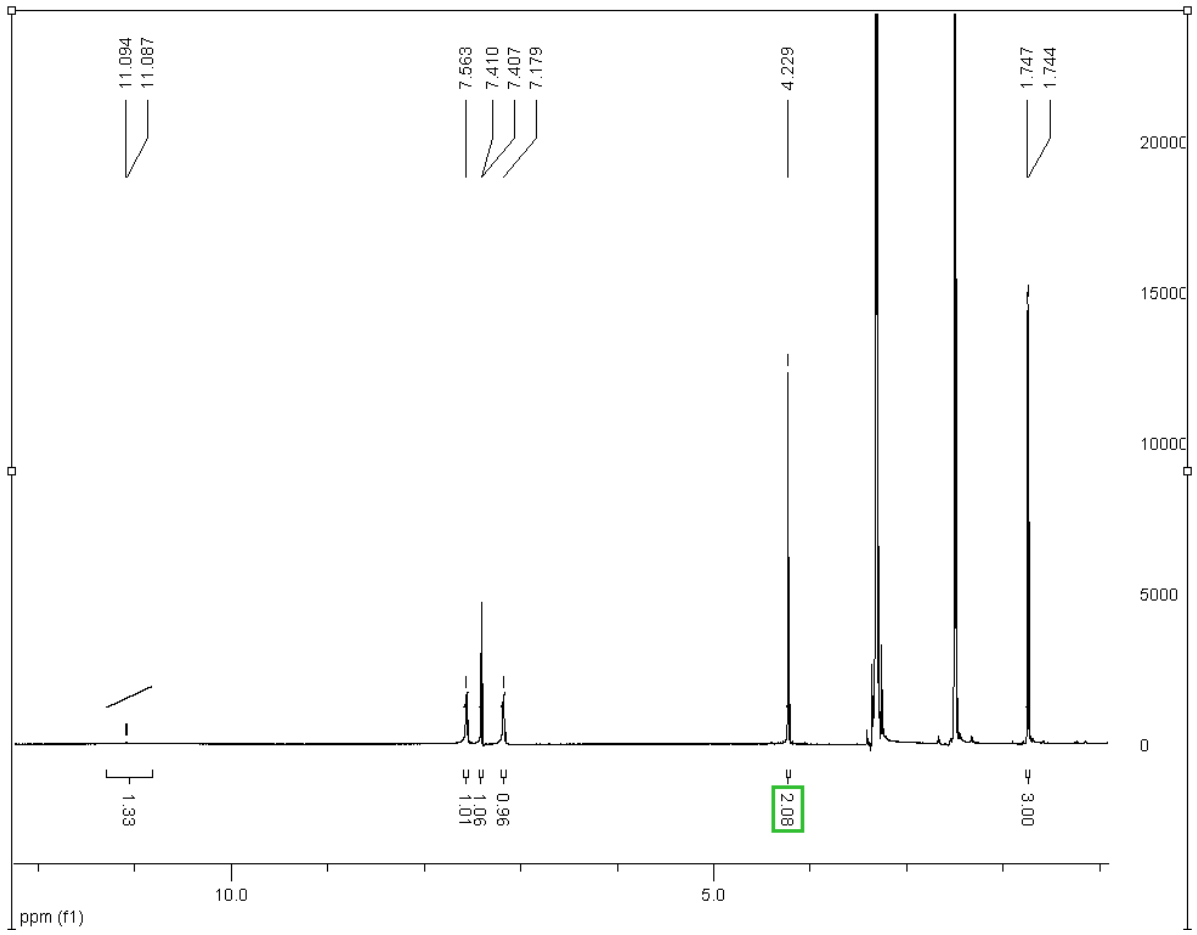
Table S3. Photo-dimerization and selectivity yields determined by ^{1}H NMR analysis (in D_6-DMSO) of the products generated from solution-phase and solid-phase irradiations of **7**. The ^{1}H NMR spectra obtained for the irradiated monomer samples were used to determine the percentage conversion of thyminyl units to cyclobutane units, by comparing the integration values of (non-reacted) thyminyl C5-CH_3 methyl protons (δ 1.72 ppm) and (reacted) cyclobutane C5-CH_3 methyl protons (δ 1.19, 1.21, 1.29, 1.43 ppm).

Chemical shift	Solution-phase		Solid-phase	
δ (ppm)	Mol. Equiv.	Specificity	Mol. Equiv	Specificity
Monomer (7)				
1.72	28.6	NA	1.00	NA
Dimer				
1.19 (TS)	0.19	8%	1.02	80%
1.21	0.52	23%	0.09	7%
1.29	0.59	26%	0.04	3%
1.43	1.00	43%	0.12	10%
Cyclobutane yield %	7.4%	NA	56%	NA

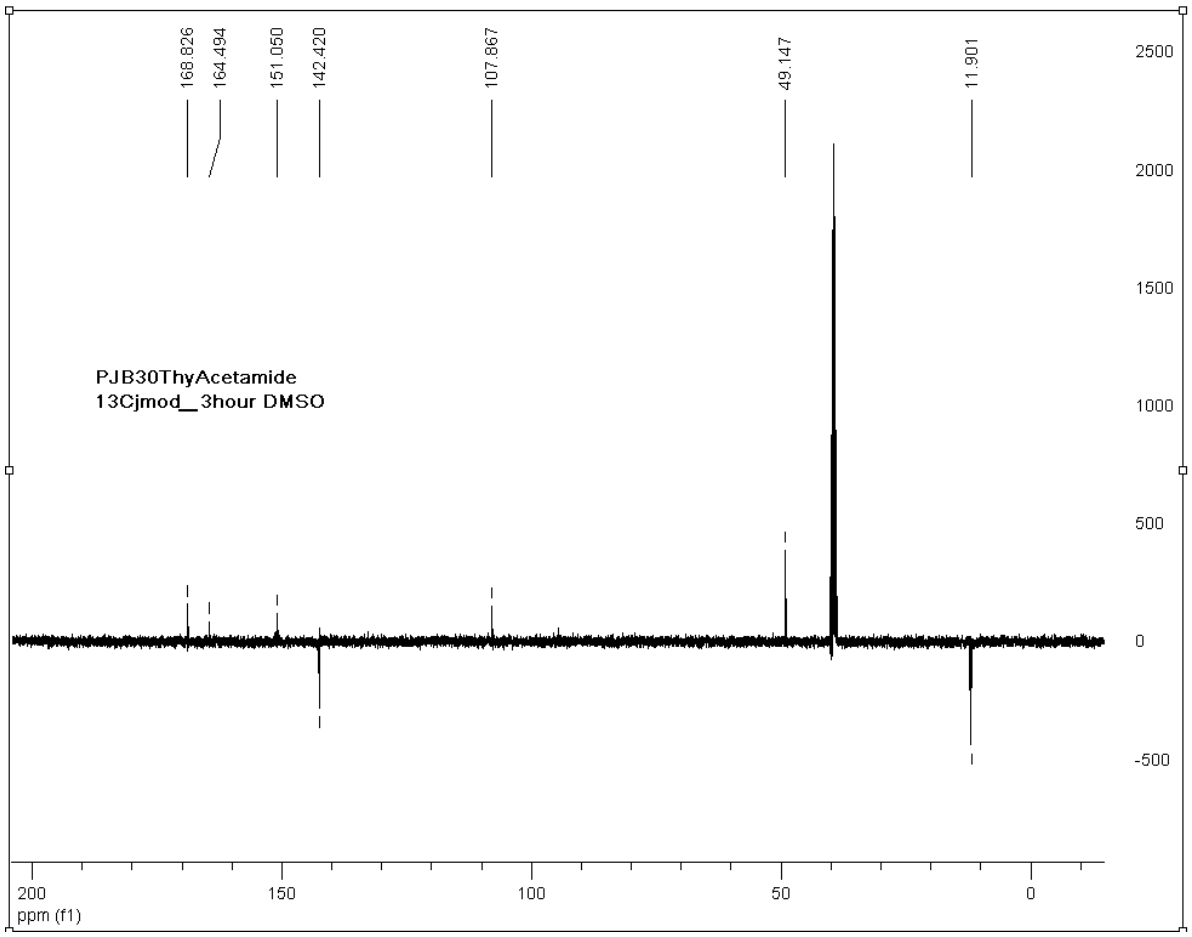
Partial ^{1}H NMR spectrum of the crude photo-products generated from the solution-phase irradiation of **7**.



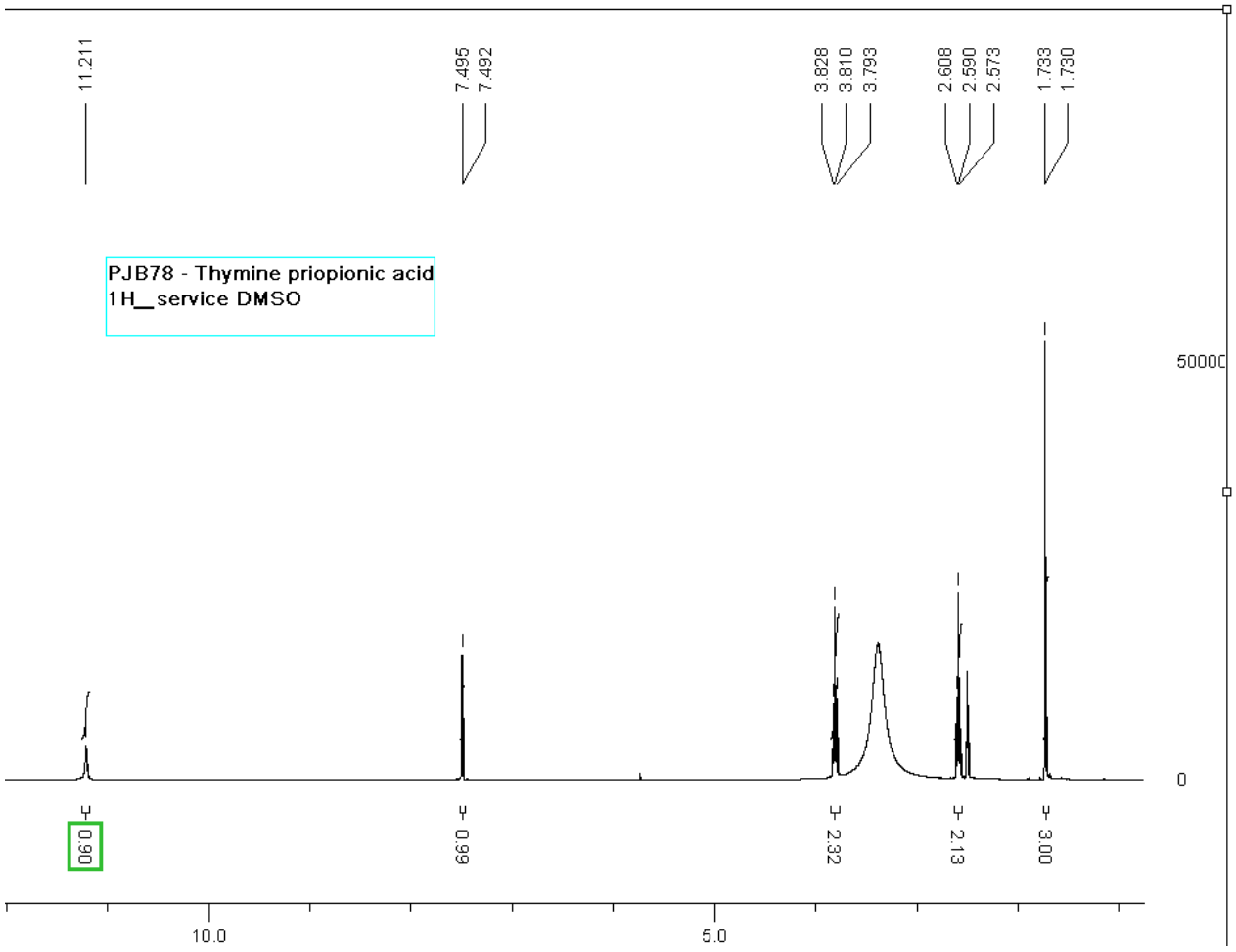
^{1}H NMR spectrum of **4**



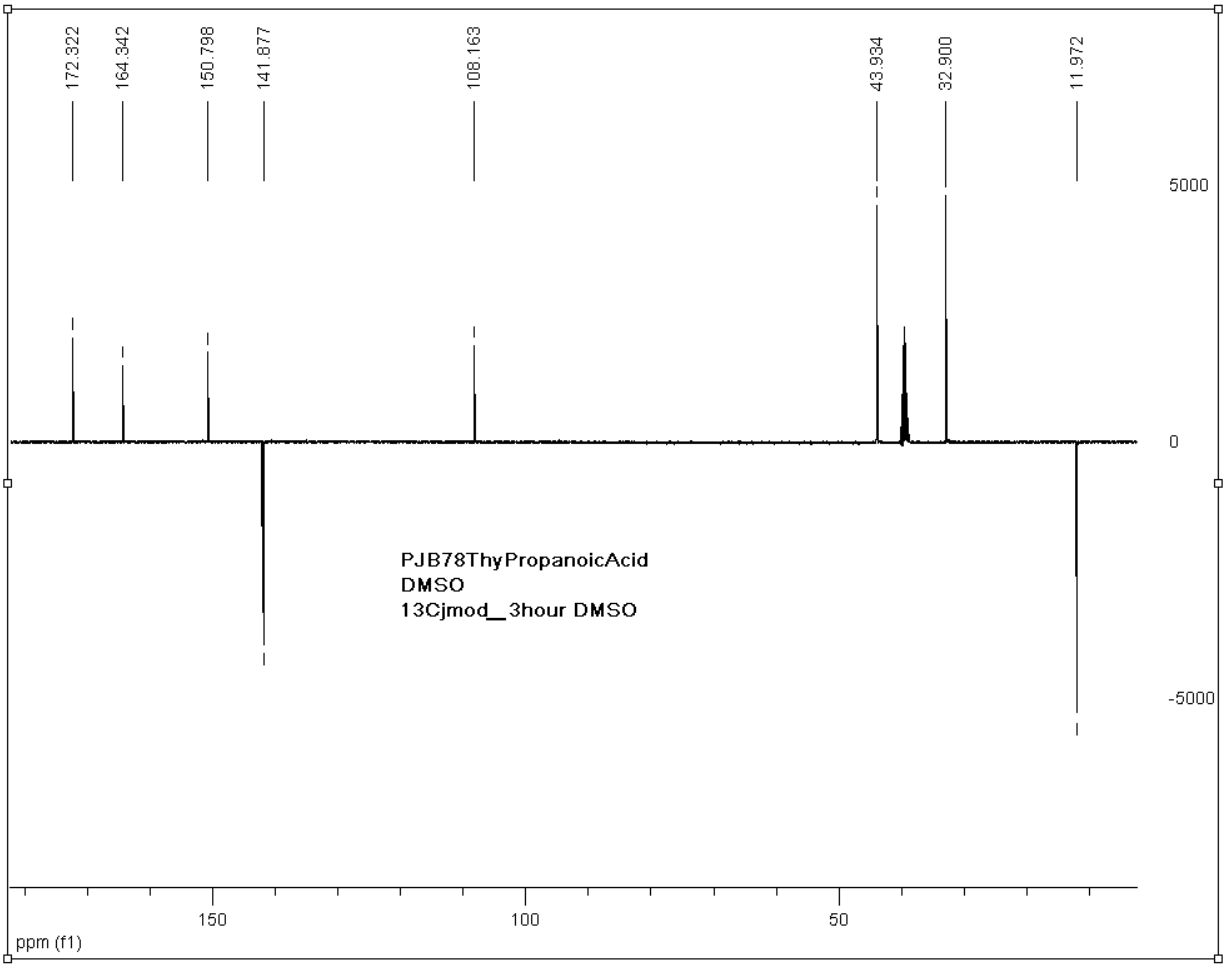
^{13}C NMR spectrum of **4**



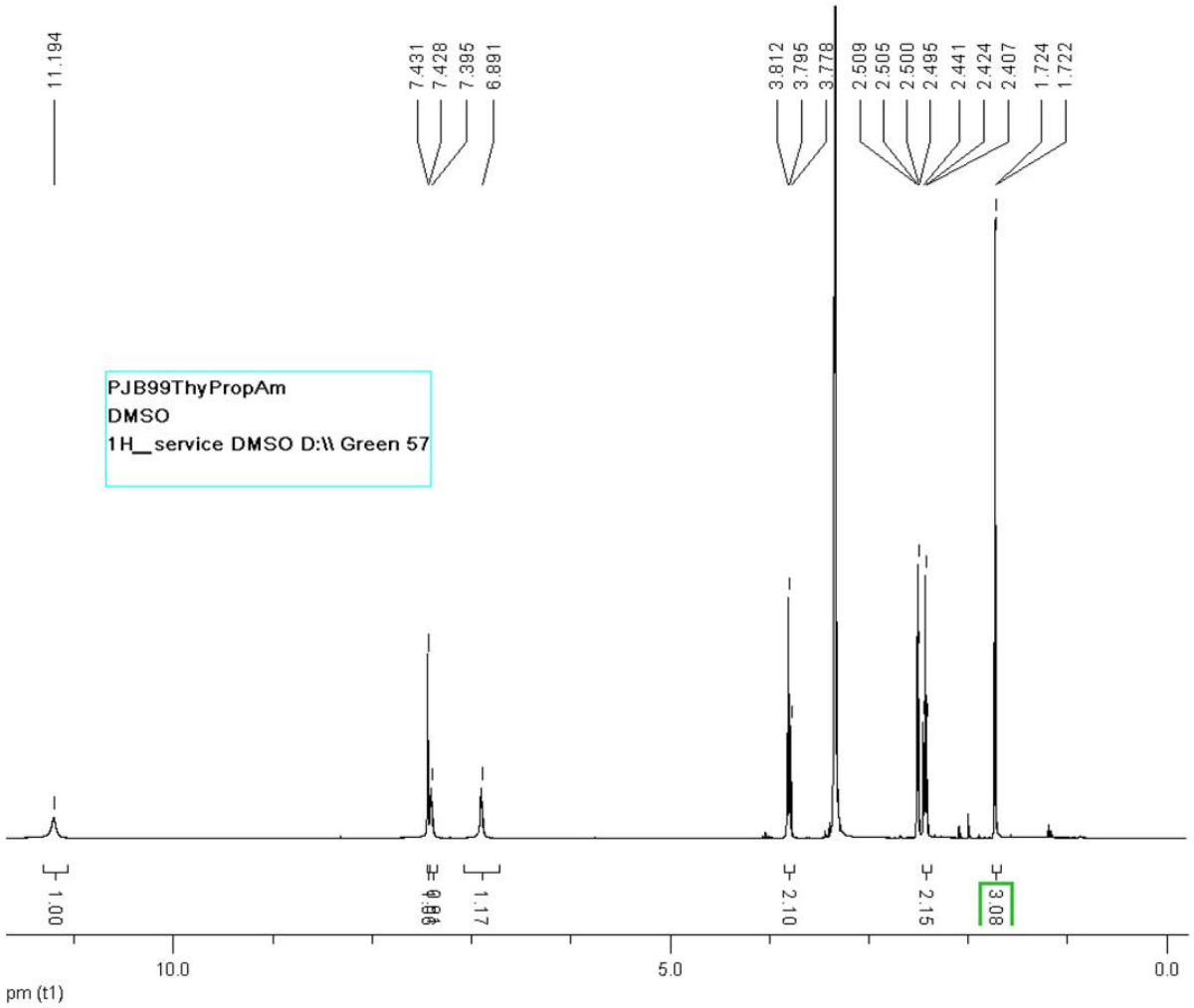
^{1}H NMR spectrum of **6**



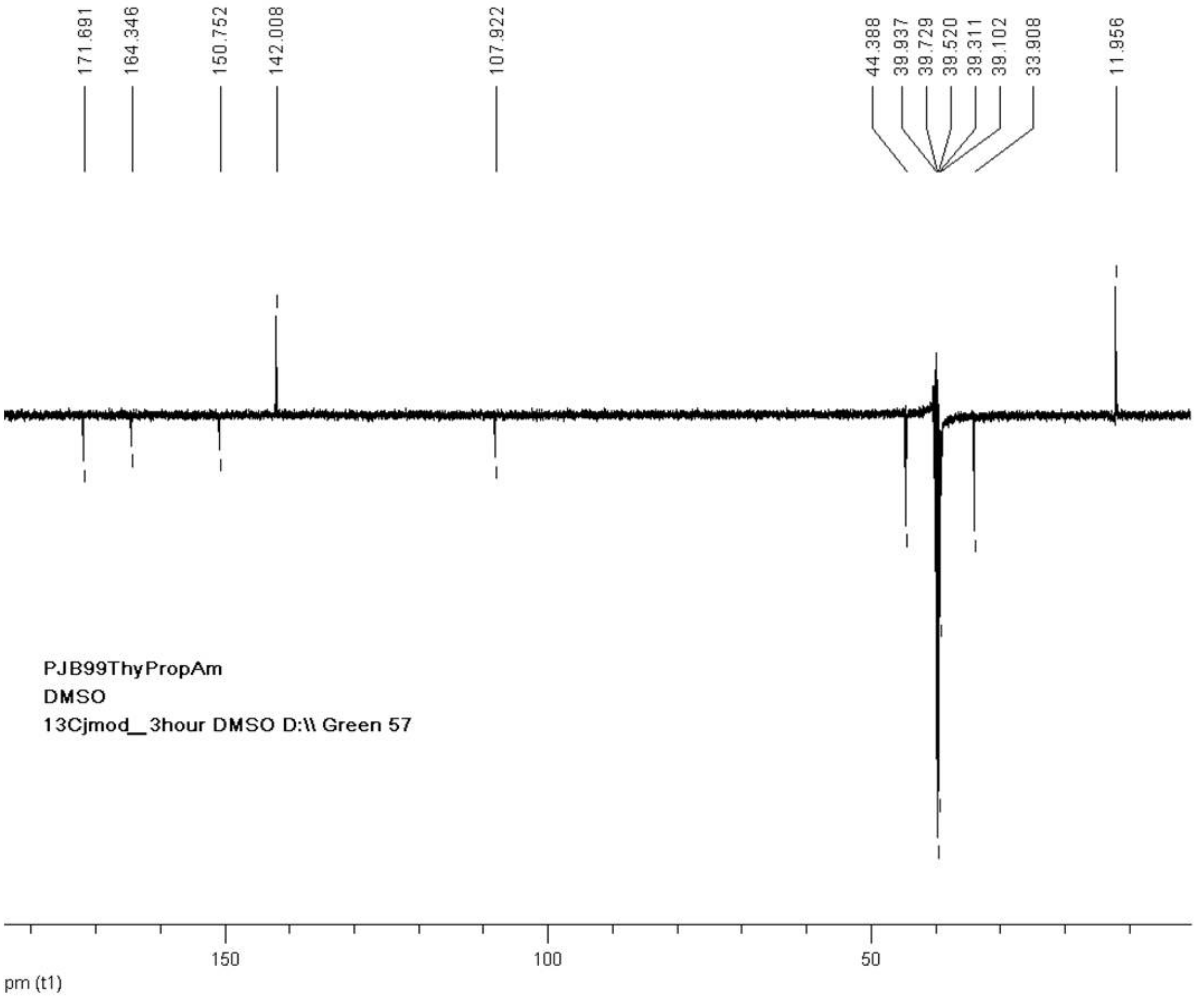
^{13}C NMR spectrum of **6**



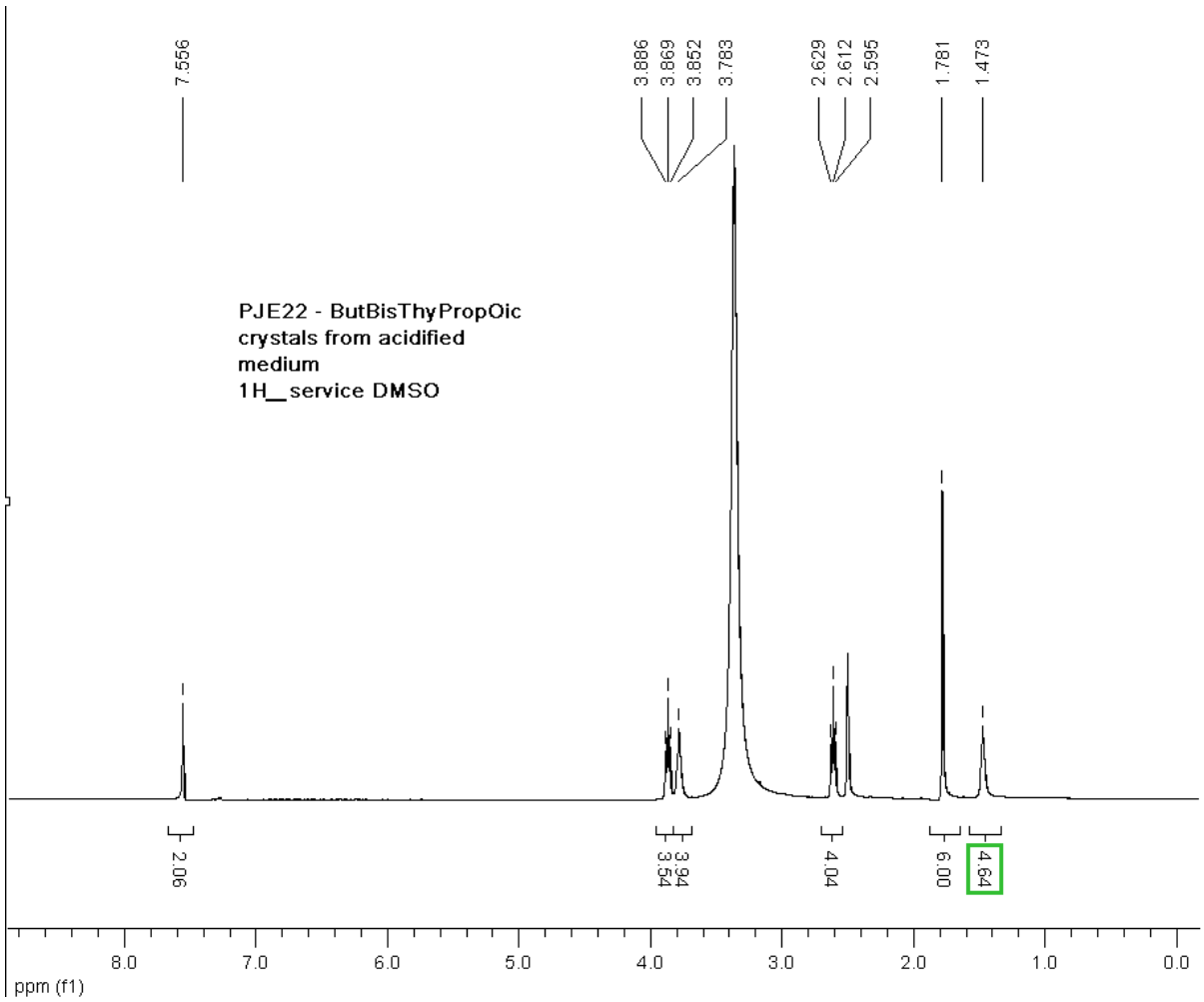
^{1}H NMR spectrum of **7**



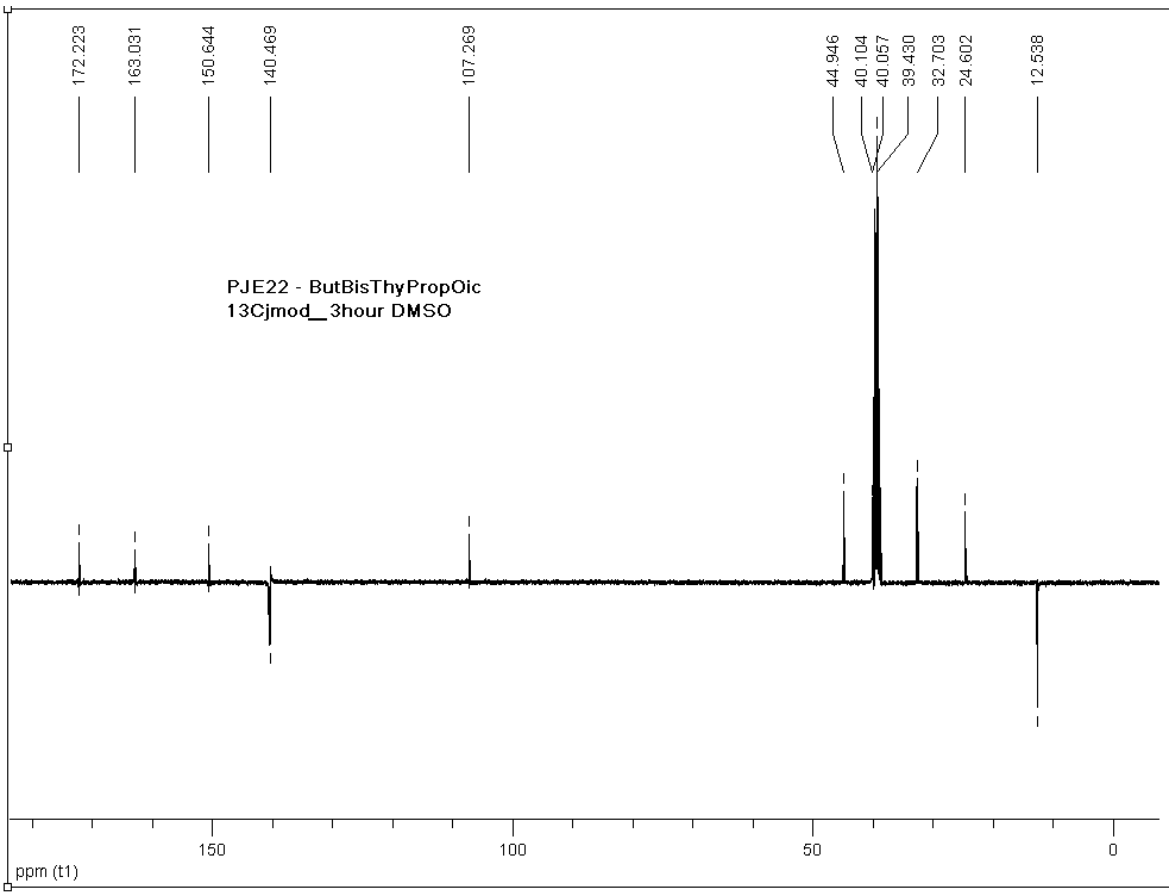
^{13}C NMR spectrum of **7**



^{1}H NMR spectrum of **9**



^{13}C NMR spectrum of **9**



Partial ^{1}H NMR spectrum of irradiated crystals of **9.** The ^{1}H NMR spectrum (400 MHz, DMSO) of the crude products was used to determine the percentage conversion of thyminyl units to cyclobutane units, by comparing the integration values of (non-reacted) thyminyl C5-CH_3 methyl protons (δ 1.78 ppm) and (reacted) cyclobutane C5-CH_3 methyl protons (δ 1.24 ppm). Thyminyl conversion = 80.6%.