Supporting Information File

Early Events in the Photochemistry of 1,2,3-Thiadiazole Studied by Ultrafast Time Resolved UV−Vis and IR Spectroscopies

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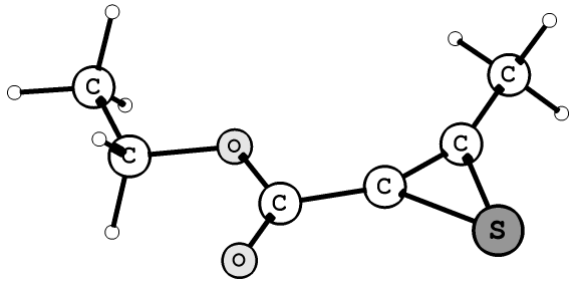
Table S1. Optimized structure of thiirene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



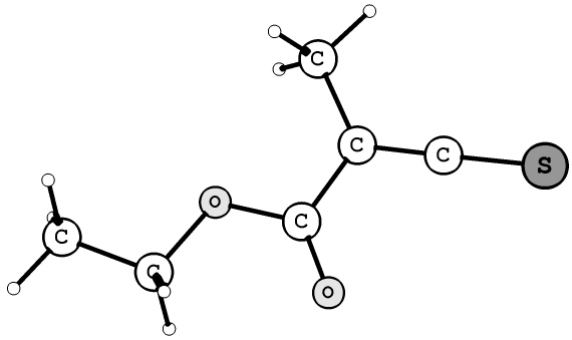
Energy = -782.0374661 Hartree

C	0.874453000	-0.213639000	-0.000097000
C	1.686016000	0.790595000	-0.000044000
C	1.963371000	2.235430000	-0.000108000
H	1.029374000	2.806523000	-0.000233000
H	2.554932000	2.503644000	0.883980000
H	2.555175000	2.503566000	-0.884037000
C	-0.463486000	-0.786036000	-0.000115000
O	-1.396895000	0.196140000	-0.000302000
C	-2.780766000	-0.244594000	-0.000231000
H	-2.945618000	-0.866631000	0.885187000
H	-2.945914000	-0.865894000	-0.886126000
C	-3.653790000	0.995978000	0.000411000
H	-4.709445000	0.700574000	0.000429000
H	-3.468223000	1.607748000	0.889732000
H	-3.468466000	1.608518000	-0.888429000
O	-0.707328000	-1.976867000	0.000015000
S	2.654824000	-0.776165000	0.000181000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
38	0.4	713	15.5	1427	13.1
73	0.2	787	0.1	1434	16.5
75	0.5	819	9.1	1451	8.0
88	1.9	875	24.0	1461	3.7
147	0.0	992	28.2	1476	5.7
188	0.7	1015	0.8	1691	350.8
191	4.0	1032	16.8	1860	256.8
222	4.5	1040	150.8	2928	9.5
252	0.5	1097	5.0	2938	19.7
307	7.8	1139	3.9	2957	16.5
375	7.0	1197	790.0	2985	2.6
382	2.7	1254	1.0	2993	0.5
471	16.8	1355	1.5	3003	26.1
548	9.4	1365	1.6	3013	4.7
693	21.3	1389	11.5	3017	39.6

1860 cm^{-1}, C=C (ring) stretching (similarly substituted cyclopropene – 1840 cm^{-1} ref. 17)
1691 cm^{-1}, C=O stretching

Table S2. Optimized structure of thioketene at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



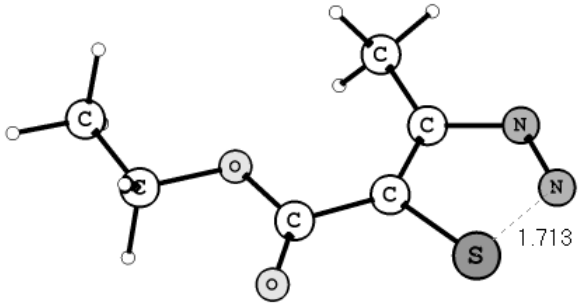
Energy = -782.0852237 Hartree

C	0.729441000	0.592481000	-0.000451000
C	1.970541000	0.124109000	-0.000626000
C	0.456804000	2.087105000	-0.000208000
H	-0.121740000	2.371959000	0.885422000
H	1.391851000	2.654174000	-0.000896000
H	-0.123080000	2.371840000	-0.884931000
C	-0.366810000	-0.404346000	-0.000376000
O	-1.575705000	0.207624000	0.000501000
C	-2.731975000	-0.666656000	0.000881000
H	-2.681662000	-1.308176000	0.886356000
H	-2.681168000	-1.309717000	-0.883474000
C	-3.969644000	0.211161000	-0.000133000
H	-4.866341000	-0.419605000	0.000337000
H	-3.999967000	0.851615000	0.887986000
H	-3.999728000	0.849957000	-0.889453000
O	-0.223162000	-1.615002000	-0.001044000
S	3.433914000	-0.404134000	0.000530000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
41	0.7	766	5.4	1444	7.6
79	1.8	787	0.1	1451	14.8
84	0.5	843	5.8	1451	9.8
120	2.6	930	1.0	1461	2.3
131	0.0	1011	18.6	1477	6.4
157	2.4	1015	0.0	1662	303.0
225	0.2	1092	346.4	1756	532.3
258	1.9	1095	214.5	2936	7.3
260	0.3	1121	17.3	2937	40.5
334	14.7	1140	3.8	2957	16.2
412	0.5	1234	580.3	2991	0.3
450	0.1	1253	0.9	2995	11.3
465	1.1	1355	1.4	3001	28.9
604	10.5	1377	53.2	3015	42.4
724	15.7	1389	3.4	3017	13.0

1756 cm^{-1}, asymmetric C=O stretching, C=C=S stretching
1662 cm^{-1}, symmetric C=O stretching, C=C=S stretching

Table S3. Optimized structure of **MCT** at the B3LYP/6-31+G(d) level of theory (frequencies scaled by 0.9614)



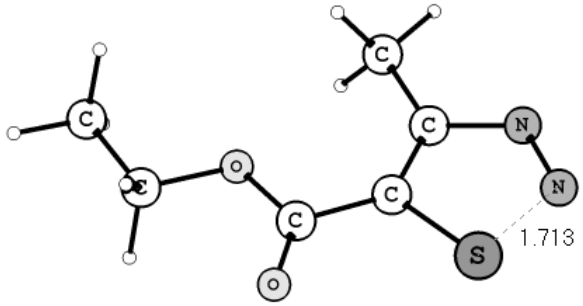
Energy = -891.5914872 Hartree

C	-0.686966000	-0.207006000	-0.000065000
C	-1.067284000	1.126126000	-0.000095000
S	-2.100106000	-1.185285000	-0.000165000
N	-2.435544000	1.283370000	-0.000288000
N	-3.114899000	0.194651000	-0.000307000
C	-0.211821000	2.357569000	0.000061000
H	0.436597000	2.392445000	0.881388000
H	0.438186000	2.391584000	-0.880106000
H	-0.860265000	3.237090000	-0.000902000
C	0.648492000	-0.841817000	0.000182000
O	1.648399000	0.059213000	0.000035000
C	2.998157000	-0.484565000	0.000327000
H	3.112449000	-1.117434000	-0.884939000
H	3.112365000	-1.116688000	0.886137000
C	3.962860000	0.685463000	-0.000120000
H	4.992020000	0.308398000	0.000193000
H	3.827123000	1.309711000	-0.889628000
H	3.826897000	1.310567000	0.888753000
O	0.815200000	-2.048197000	0.000487000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
20	0.0	737	15.7	1383	6.1
66	1.1	778	14.9	1388	6.4
85	0.0	785	0.0	1445	28.3
95	0.1	813	5.5	1445	8.0
101	0.2	841	17.6	1451	13.0
167	10.0	954	11.0	1460	1.7
215	4.4	982	12.5	1473	1.6
238	0.2	1020	42.1	1483	31.9
269	1.4	1028	1.7	1693	309.0
291	0.1	1081	166.8	2939	15.7
321	18.6	1101	22.7	2949	12.5
382	2.2	1139	3.9	2961	12.9
468	3.9	1208	235.2	2997	0.0
488	0.6	1255	1.2	3004	7.0
546	13.9	1291	54.3	3004	24.6
599	2.6	1310	252.4	3020	36.2
638	0.0	1359	23.1	3032	7.7

1693 cm^{-1}, C=O stretching

Table S4. TD DFT of **MCT** at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

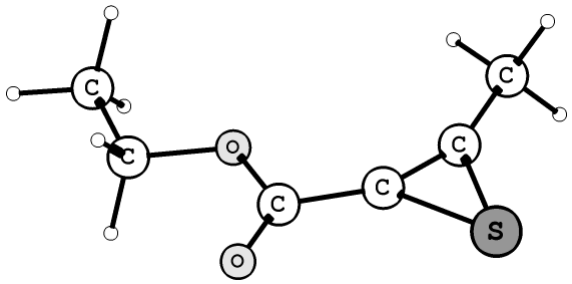


Energy = -891.5914872 Hartree

Wavelength (nm)	*f*
348.6	0.0009
269.6	0.0001
268.1	0.0810
229.1	0.1657
217.3	0.0028
216.3	0.0378
210.6	0.0022
209.9	0.0026
207.0	0.0482
188.8	0.0447

C	-0.686966000	-0.207006000	-0.000065000
C	-1.067284000	1.126126000	-0.000095000
S	-2.100106000	-1.185285000	-0.000165000
N	-2.435544000	1.283370000	-0.000288000
N	-3.114899000	0.194651000	-0.000307000
C	-0.211821000	2.357569000	0.000061000
H	0.436597000	2.392445000	0.881388000
H	0.438186000	2.391584000	-0.880106000
H	-0.860265000	3.237090000	-0.000902000
C	0.648492000	-0.841817000	0.000182000
O	1.648399000	0.059213000	0.000035000
C	2.998157000	-0.484565000	0.000327000
H	3.112449000	-1.117434000	-0.884939000
H	3.112365000	-1.116688000	0.886137000
C	3.962860000	0.685463000	-0.000120000
H	4.992020000	0.308398000	0.000193000
H	3.827123000	1.309711000	-0.889628000
H	3.826897000	1.310567000	0.888753000
O	0.815200000	-2.048197000	0.000487000

Table S5. TD DFT of thiirene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -782.0374661 Hartree

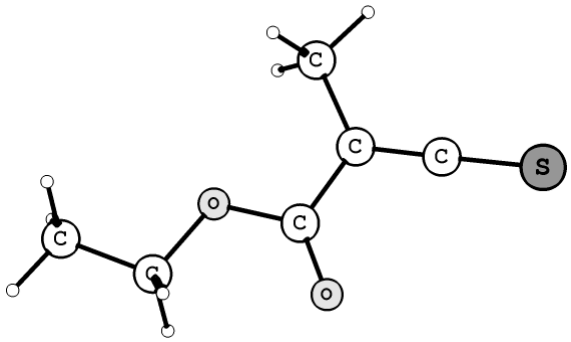
Wavelength (nm)	f
429.3	0.0622
340.5	0.0003
267.0	0.0033
266.5	0.0025
258.5	0.0090
235.5	0.0031
223.8	0.0007
219.0	0.0129
213.8	0.0125
209.4	0.0001

C	0.874453000	−0.213639000	−0.000097000
C	1.686016000	0.790595000	−0.000044000
C	1.963371000	2.235430000	−0.000108000
H	1.029374000	2.806523000	−0.000233000
H	2.554932000	2.503644000	0.883980000
H	2.555175000	2.503566000	−0.884037000
C	−0.463486000	−0.786036000	−0.000115000
O	−1.396895000	0.196140000	−0.000302000
C	−2.780766000	−0.244594000	−0.000231000
H	−2.945618000	−0.866631000	0.885187000
H	−2.945914000	−0.865894000	−0.886126000
C	−3.653790000	0.995978000	0.000411000
H	−4.709445000	0.700574000	0.000429000
H	−3.468223000	1.607748000	0.889732000
H	−3.468466000	1.608518000	−0.888429000
O	−0.707328000	−1.976867000	0.000015000
S	2.654824000	−0.776165000	0.000181000

TD DFT B3LYP/6-311+G(d,p) using PCM model to include presence of solvent (acetonitrile):

Wavelength (nm)	f
407.9	0.0861
330.3	0.0002
255.4	0.0027
255.0	0.0057
244.2	0.0220
221.1	0.0000
214.2	0.0062
206.9	0.0157
206.1	0.0726
199.3	0.0372

Table S6. TD DFT of thioketene at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

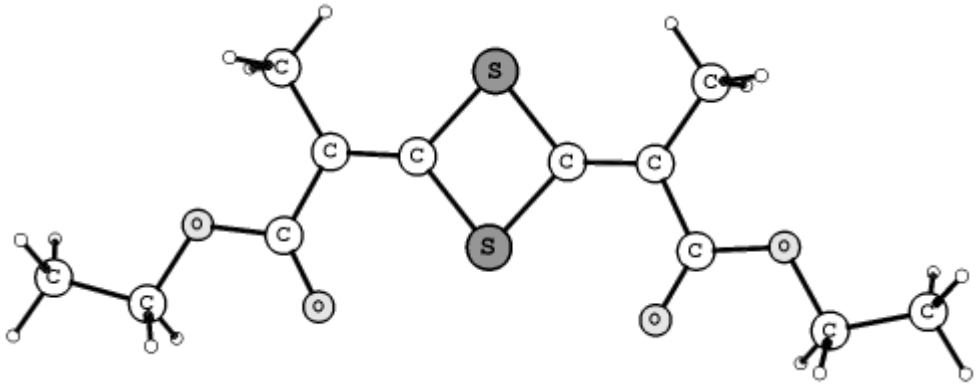


Energy = -782.0852237 Hartree

Wavelength (nm)	f
501.3	0.000
298.0	0.000
256.9	0.229
248.5	0.000
247.0	0.000
222.1	0.011
219.9	0.000
202.3	0.005
196.8	0.543
194.3	0.001

C	0.729441000	0.592481000	-0.000451000
C	1.970541000	0.124109000	-0.000626000
C	0.456804000	2.087105000	-0.000208000
H	-0.121740000	2.371959000	0.885422000
H	1.391851000	2.654174000	-0.000896000
H	-0.123080000	2.371840000	-0.884931000
C	-0.366810000	-0.404346000	-0.000376000
O	-1.575705000	0.207624000	0.000501000
C	-2.731975000	-0.666656000	0.000881000
H	-2.681662000	-1.308176000	0.886356000
H	-2.681168000	-1.309717000	-0.883474000
C	-3.969644000	0.211161000	-0.000133000
H	-4.866341000	-0.419605000	0.000337000
H	-3.999967000	0.851615000	0.887986000
H	-3.999728000	0.849957000	-0.889453000
O	-0.223162000	-1.615002000	-0.001044000
S	3.433914000	-0.404134000	0.000530000

Table S7. TD DFT of dimer D_1 at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

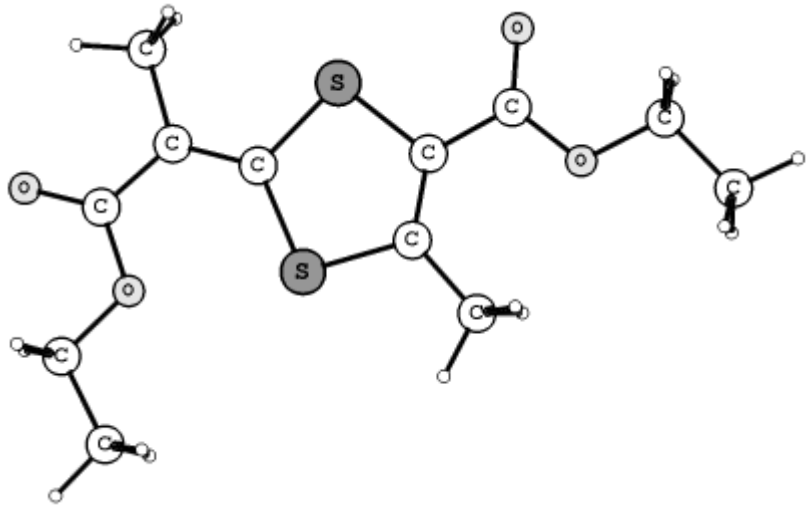


Energy = -1564.4595737 Hartree

Wavelength (nm)	f
323	0
314.83	0.7558
279.89	0.0091
272.51	0
266.58	0.0191
258.16	0.0001
257.92	0
238.77	0.0066
224.13	0.0658
221.13	0

S	0.000007000	2.175163000	0.000003000
S	-0.000023000	-0.533222000	0.000115000
C	1.158000000	0.820933000	0.000012000
C	-1.157993000	0.820950000	0.000041000
C	2.505516000	0.842865000	-0.000066000
C	-2.505515000	0.842883000	0.000032000
C	3.315484000	2.114164000	-0.000092000
H	2.673185000	3.000347000	-0.000971000
H	3.965133000	2.166460000	0.880881000
H	3.966410000	2.165581000	-0.880145000
C	-3.315484000	2.114177000	0.000004000
H	-3.966064000	2.165845000	-0.880301000
H	-3.965504000	2.166205000	0.880714000
H	-2.673199000	3.000369000	-0.000359000
C	3.176519000	-0.471429000	-0.000001000
C	-3.176505000	-0.471399000	0.000084000
O	-2.595340000	-1.547135000	0.000167000
O	2.595331000	-1.547152000	-0.000108000
O	-4.523590000	-0.358516000	0.000100000
O	4.523585000	-0.358522000	0.000052000
C	-5.259530000	-1.603148000	0.000130000
H	-4.970586000	-2.182716000	-0.882520000
H	-4.971174000	-2.182313000	0.883246000
C	-6.736798000	-1.258221000	-0.000413000
H	-7.002922000	-0.675971000	-0.888506000
H	-7.332075000	-2.177786000	-0.000165000
H	-7.003373000	-0.675203000	0.887042000
C	5.259551000	-1.603150000	-0.000001000
H	4.970959000	-2.182514000	0.882901000
H	4.970855000	-2.182517000	-0.882866000
C	6.736810000	-1.258190000	-0.000089000
H	7.003039000	-0.675386000	-0.887788000
H	7.003257000	-0.675719000	0.887761000
H	7.332108000	-2.177744000	-0.000339000

Table S8. TD DFT of dimer D_2 at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

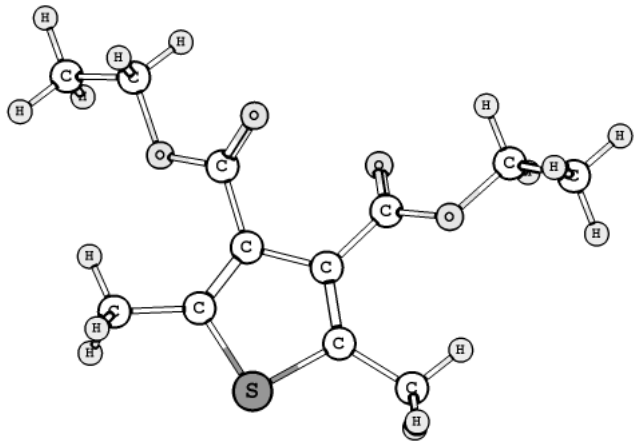


Energy = -1564.4709831Hartree

Wavelength (nm)	*f*
366.75	0.0939
309.92	0.0007
302.73	0.3869
256.55	0.0001
256.06	0.006
254.19	0.0001
237.52	0.0028
233.02	0
230.56	0.0005
227.79	0.135

C	1.011304000	-0.738433000	-0.000005000
S	0.719359000	1.015866000	-0.000131000
S	-0.487740000	-1.683349000	0.000116000
C	2.216187000	-1.377874000	0.000000000
C	-1.742115000	2.275741000	-0.000212000
H	-1.021750000	3.098790000	0.000092000
H	-2.382998000	2.374922000	-0.880818000
H	-2.383563000	2.374758000	0.879994000
C	-1.037192000	0.942700000	-0.000110000
C	-1.590152000	-0.294413000	0.000012000
C	-3.014094000	-0.680984000	0.000085000
O	-3.381012000	-1.841977000	0.000268000
O	-3.858727000	0.373083000	-0.000097000
C	-5.269180000	0.038582000	-0.000020000
H	-5.483489000	-0.570914000	-0.883251000
H	-5.483404000	-0.570884000	0.883250000
C	-6.046893000	1.340493000	-0.000010000
H	-7.121299000	1.127570000	0.000021000
H	-5.815644000	1.937036000	0.888388000
H	-5.815694000	1.937015000	-0.888436000
C	2.267602000	-2.887750000	0.000126000
H	1.769706000	-3.309113000	-0.883849000
H	3.308074000	-3.215423000	0.000085000
H	1.769823000	-3.308948000	0.884247000
C	3.517206000	-0.690211000	-0.000153000
O	4.599121000	-1.252991000	-0.000247000
O	3.406254000	0.666351000	-0.000185000
C	4.649810000	1.400885000	-0.000292000
H	5.228002000	1.111188000	-0.883488000
H	5.228820000	1.110089000	0.881992000
C	4.314769000	2.880616000	0.000753000
H	3.735206000	3.151247000	0.889245000
H	5.239412000	3.468263000	0.000623000
H	3.734294000	3.152303000	-0.886822000

Table S9. TD DFT of dimer D_3 at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

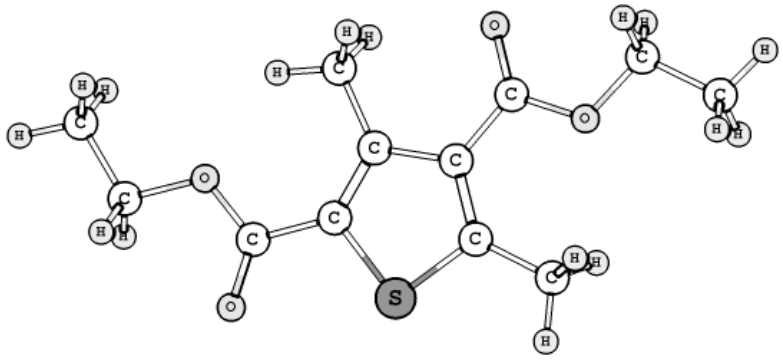


Energy = -1166.0251225 Hartree

Wavelength (nm)	f
256.87	0.0214
251.76	0
240.21	0.1002
238.58	0.0352
231.2	0.0437
224.75	0.0207
220.05	0.1129
214.6	0.0006
212.26	0.0901
208.73	0.1336

C	-1.250641000	1.777939000	-0.213762000
C	-0.713538000	0.518354000	-0.120656000
C	0.713905000	0.519438000	0.122882000
C	1.249690000	1.779675000	0.212997000
S	-0.001094000	2.981691000	-0.001790000
C	-2.650435000	2.220136000	-0.525976000
H	-3.318099000	1.359106000	-0.561639000
H	-3.026541000	2.908144000	0.240523000
H	-2.698503000	2.743502000	-1.488837000
C	2.649068000	2.223408000	0.524854000
H	2.697737000	2.742486000	1.490033000
H	3.318446000	1.363474000	0.555660000
H	3.022596000	2.915593000	-0.239102000
C	-1.440395000	-0.750499000	-0.416255000
O	-0.983249000	-1.641507000	-1.100777000
O	-2.669242000	-0.796648000	0.146607000
C	-3.422220000	-2.007316000	-0.107085000
H	-3.573306000	-2.110770000	-1.186692000
H	-2.826043000	-2.861633000	0.226902000
C	-4.733919000	-1.896019000	0.646697000
H	-5.319148000	-1.038268000	0.298790000
H	-5.328429000	-2.802699000	0.489790000
H	-4.558040000	-1.780738000	1.720863000
C	1.443029000	-0.747515000	0.421843000
O	0.990541000	-1.634487000	1.114539000
O	2.668537000	-0.796015000	-0.147990000
C	3.423845000	-2.004788000	0.107881000
H	2.824579000	-2.861585000	-0.213952000
H	3.585035000	-2.099939000	1.186810000
C	4.728420000	-1.899267000	-0.658972000
H	5.316542000	-1.038480000	-0.323657000
H	5.324729000	-2.804447000	-0.500238000
H	4.542390000	-1.792836000	-1.732337000

Table S10. TD DFT of dimer D_4 at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.

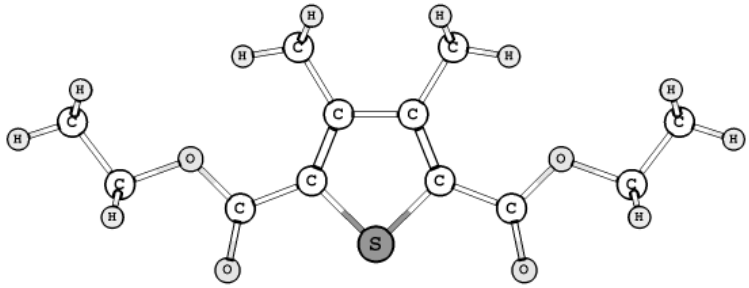


Energy = -1166.033364 Hartree

Wavelength (nm)	*f*
267.8	0.1053
260.73	0.1198
255.41	0
249.16	0
232.84	0.1593
224.29	0.0003
223.65	0.5092
213.96	0.0001
208.1	0
207.35	0

C	-1.128057000	1.364186000	0.000105000
C	-1.019635000	-0.022259000	0.000015000
C	0.349627000	-0.492722000	-0.000109000
C	1.242483000	0.563050000	-0.000105000
S	0.424558000	2.109048000	0.000007000
C	-2.338330000	2.255182000	0.000265000
H	-2.962497000	2.067787000	0.878939000
H	-2.043343000	3.308750000	0.000450000
H	-2.962491000	2.068114000	-0.878487000
C	-2.167869000	-0.960664000	0.000082000
O	-2.080371000	-2.175005000	0.000181000
O	-3.367035000	-0.325390000	-0.000014000
C	-4.528480000	-1.186092000	0.000010000
H	-4.488813000	-1.832524000	-0.882431000
H	-4.488908000	-1.832349000	0.882586000
C	-5.757617000	-0.296402000	-0.000136000
H	-5.779869000	0.343636000	-0.888191000
H	-6.661887000	-0.914682000	-0.000131000
H	-5.779968000	0.343787000	0.887808000
C	0.731111000	-1.948717000	-0.000306000
H	0.307244000	-2.455334000	0.872075000
H	0.306658000	-2.455225000	-0.872455000
H	1.811744000	-2.068724000	-0.000642000
C	2.712190000	0.671007000	-0.000133000
O	3.286941000	1.747007000	-0.000206000
O	3.365942000	-0.510476000	-0.000041000
C	4.811204000	-0.422951000	-0.000027000
H	5.128543000	0.140464000	0.882949000
H	5.128586000	0.140026000	-0.883268000
C	5.352991000	-1.839795000	0.000342000
H	5.021209000	-2.387521000	-0.887588000
H	6.448204000	-1.815936000	0.000381000
H	5.021130000	-2.387067000	0.888519000

Table S11. TD DFT of dimer D_5 at the B3LYP/6-311+G(d,p)//B3LYP/6-31+G(d) level of theory.



Energy = -1166.0322398 Hartree

Wavelength (nm)	f
294.53	0.0583
282.09	0.4165
273.99	0
268.77	0
214.45	0.001
212.59	0.0583
212.11	0.0599
205.79	0.1882
205.69	0.0047
204.98	0

C	-1.237797000	-0.262285000	-0.000086000
C	-0.718190000	1.023400000	-0.000052000
C	0.718201000	1.023391000	0.000003000
C	1.237787000	-0.262304000	-0.000002000
S	0.000007000	-1.481981000	-0.000062000
C	1.495849000	2.312335000	0.000052000
H	1.241852000	2.916937000	-0.880280000
H	1.241620000	2.917008000	0.880265000
H	2.569301000	2.138614000	0.000195000
C	2.617491000	-0.793388000	0.000028000
O	2.864528000	-1.985707000	0.000111000
O	3.577367000	0.157814000	-0.000002000
C	4.939825000	-0.333943000	0.000034000
H	5.084800000	-0.963715000	-0.883081000
H	5.084783000	-0.963597000	0.883234000
C	5.859515000	0.872435000	-0.000026000
H	5.695993000	1.490991000	0.888366000
H	6.903417000	0.540509000	0.000032000
H	5.696046000	1.490844000	-0.888529000
C	-1.495821000	2.312355000	-0.000048000
H	-1.241834000	2.916907000	0.880322000
H	-1.241564000	2.917073000	-0.880222000
H	-2.569275000	2.138649000	-0.000220000
C	-2.617497000	-0.793375000	-0.000132000
O	-2.864532000	-1.985694000	-0.000040000
O	-3.577379000	0.157822000	0.000030000
C	-4.939833000	-0.333946000	0.000161000
H	-5.084831000	-0.963806000	-0.882885000
H	-5.084759000	-0.963514000	0.883430000
C	-5.859533000	0.872425000	0.000010000
H	-6.903433000	0.540490000	0.000123000
H	-5.695995000	1.491061000	0.888343000
H	-5.696090000	1.490756000	-0.888552000

Fig. S1. Time-resolved infrared transient absorption spectra produced in acetonitrile after photoexcitation of **MCT** at 266 nm.

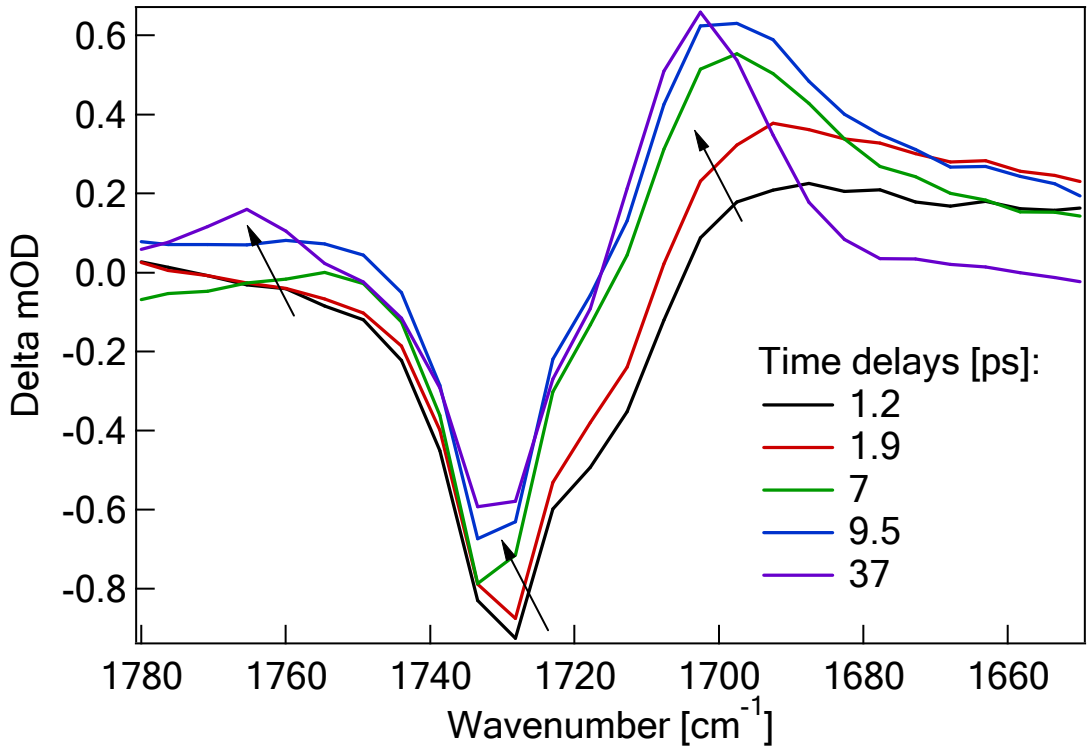


Fig. S2. Kinetic traces for **MCT** in chloroform photoexcited at 266 nm and recorded at 1661, 1690, 1726 and 1763 cm^{-1} (points) and approximated by one-exponential fitting function (solid lines). Global fitting results in a characteristic time constant of 12 ± 2 ps.

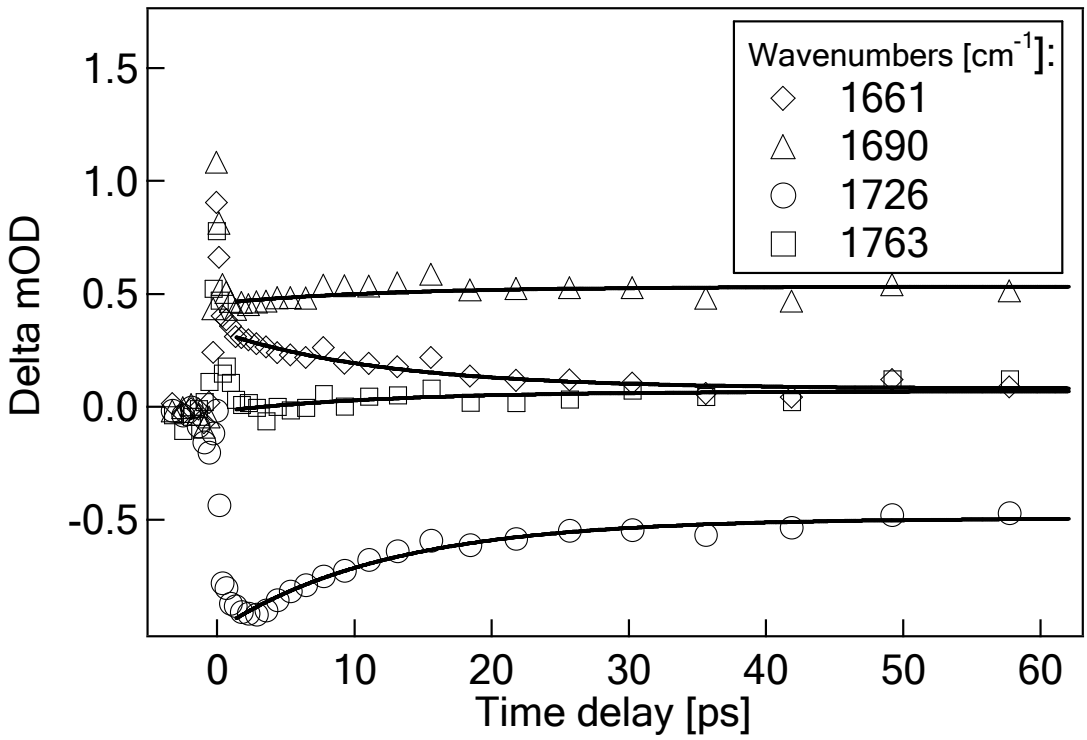


Fig. S3. Time-resolved infrared transient absorption spectra obtained in chloroform after photoexcitation of **MCT** at 266, with initial bleach contribution subtracted for all delays. Dotted line shows stationary IR spectrum of **MCT** in chloroform.

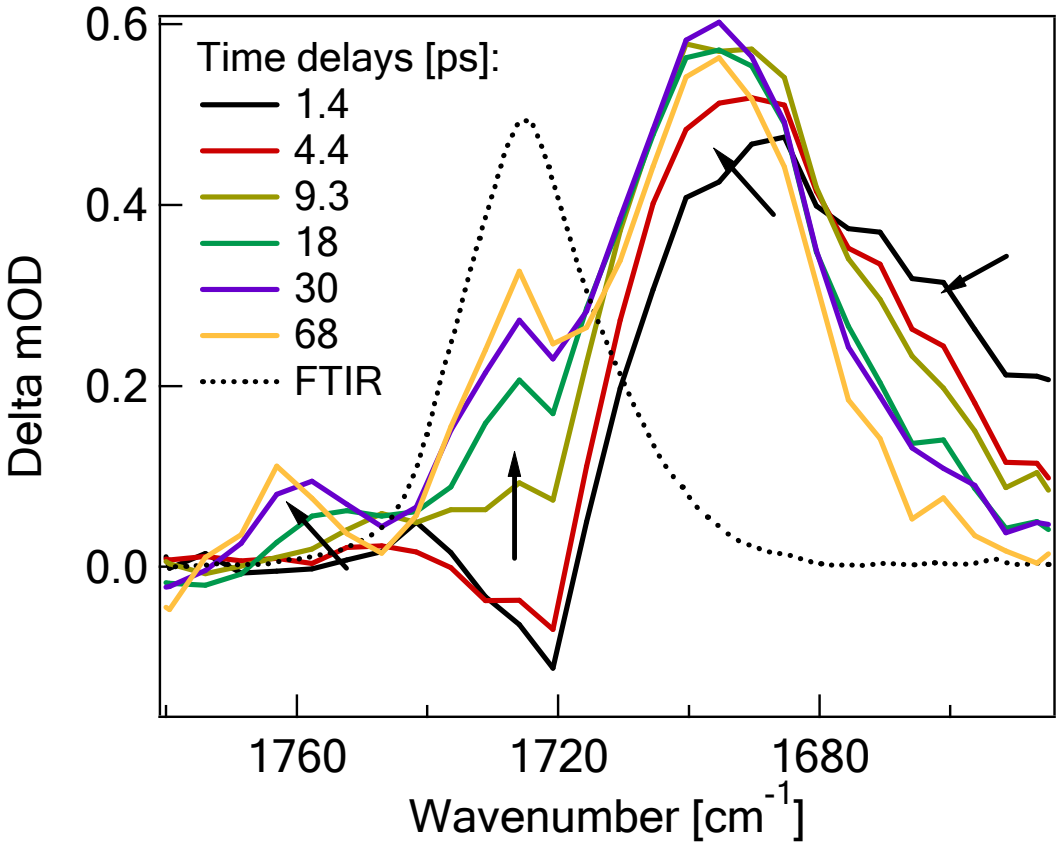
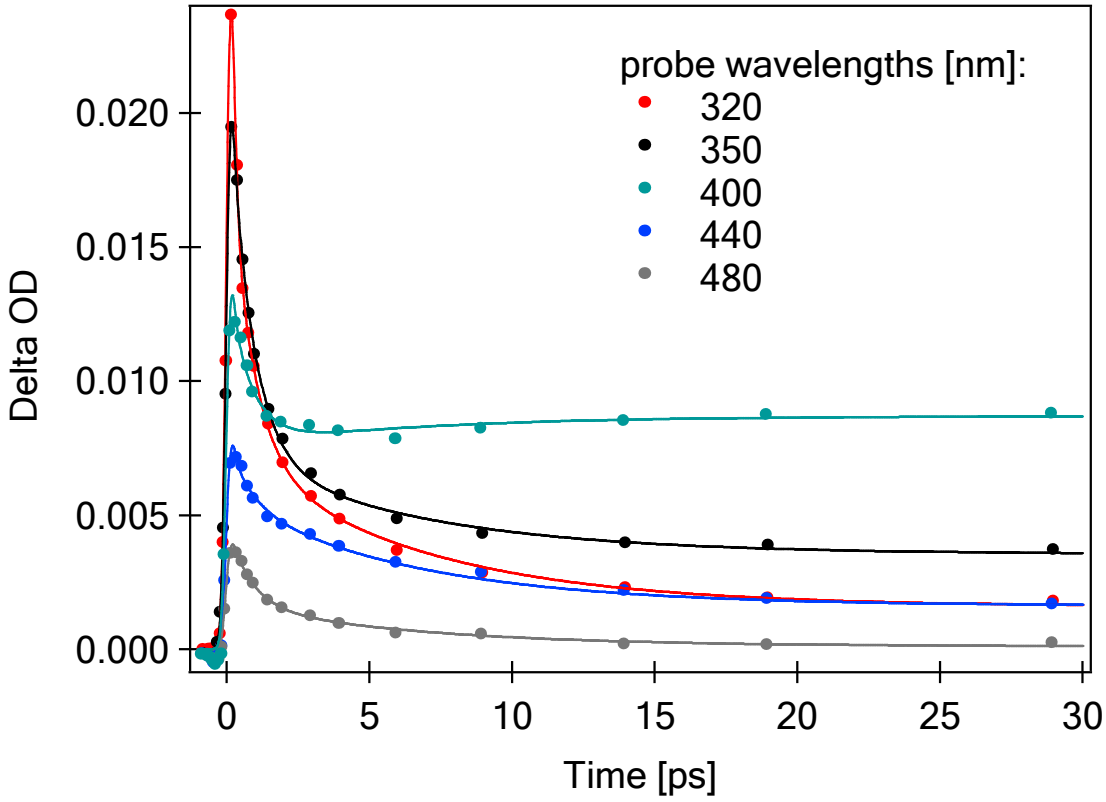


Fig. S4. Kinetic traces at 320, 350, 400, 440 and 480 nm (points) fitted to a three exponential function (solid lines). Global fitting convolved by a 300 fs Gaussian IRF yields 100 fs, 800 fs and 6.5 ps time constants.



Probe [nm]	A1	A2	A3	Offset
320	0.046	0.012	0.006	0.0016
350	0.013	0.015	0.004	0.0035
400	0.010	0.006	-0.001	0.0087
440	0.006	0.002	0.004	0.0016
480	0.001	0.003	0.002	0

Fig. S5. The wavelength-dependant amplitudes of the time constants (given in the inset) obtained by 4 exponential global fit. The FWHM of the instrumental function used for convolution with the exponential functions was set as 300 fs.

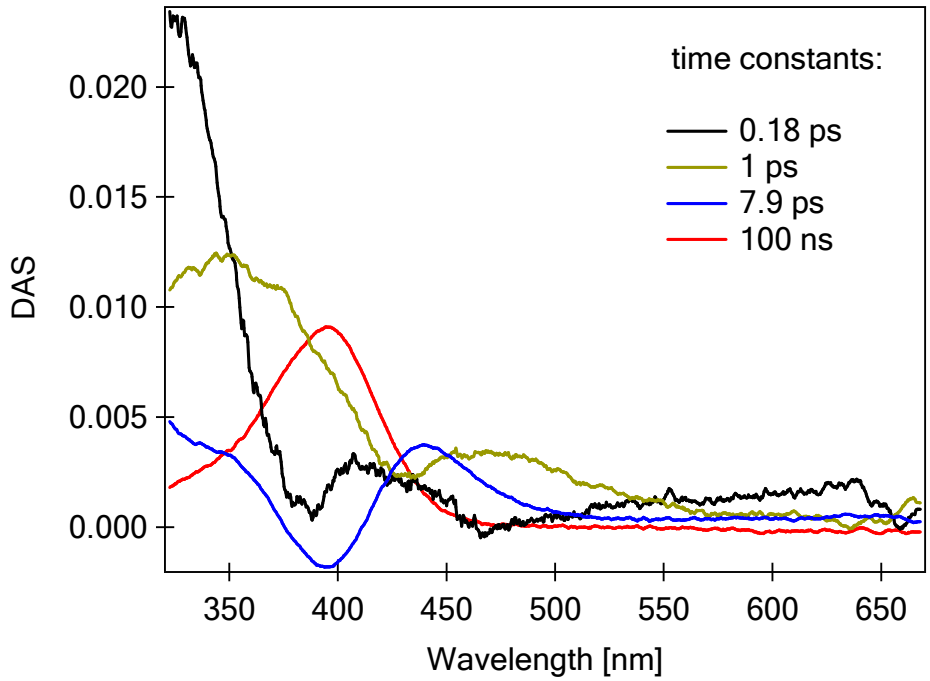


Fig. S6. Relative Gibbs free energies of the stationary points on the PES for isomerization of the thiirene to thioketene.

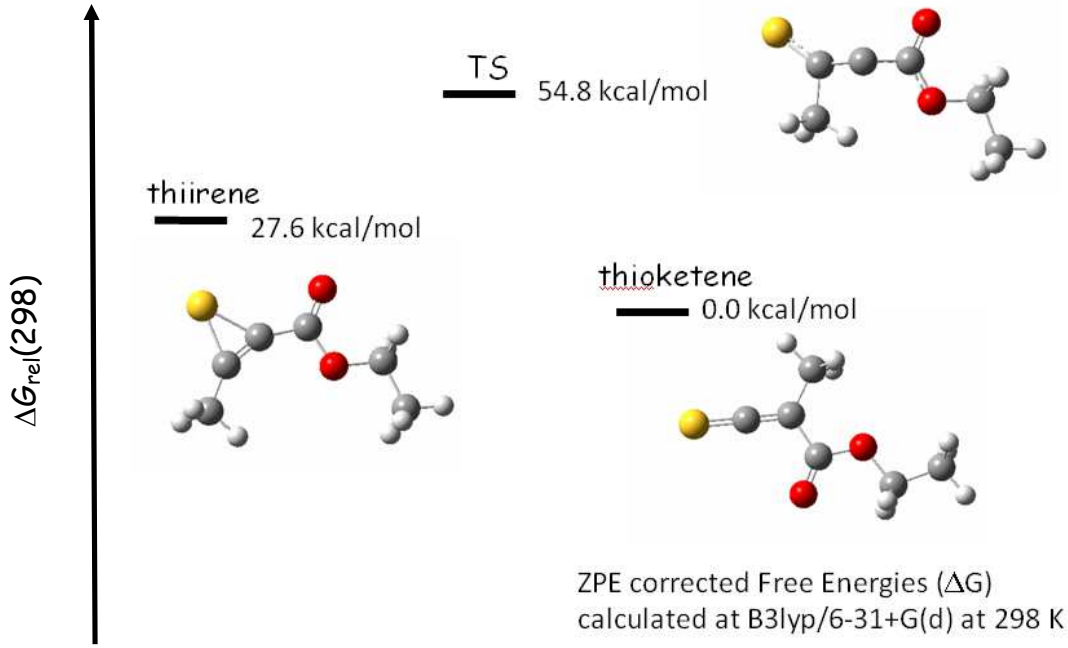
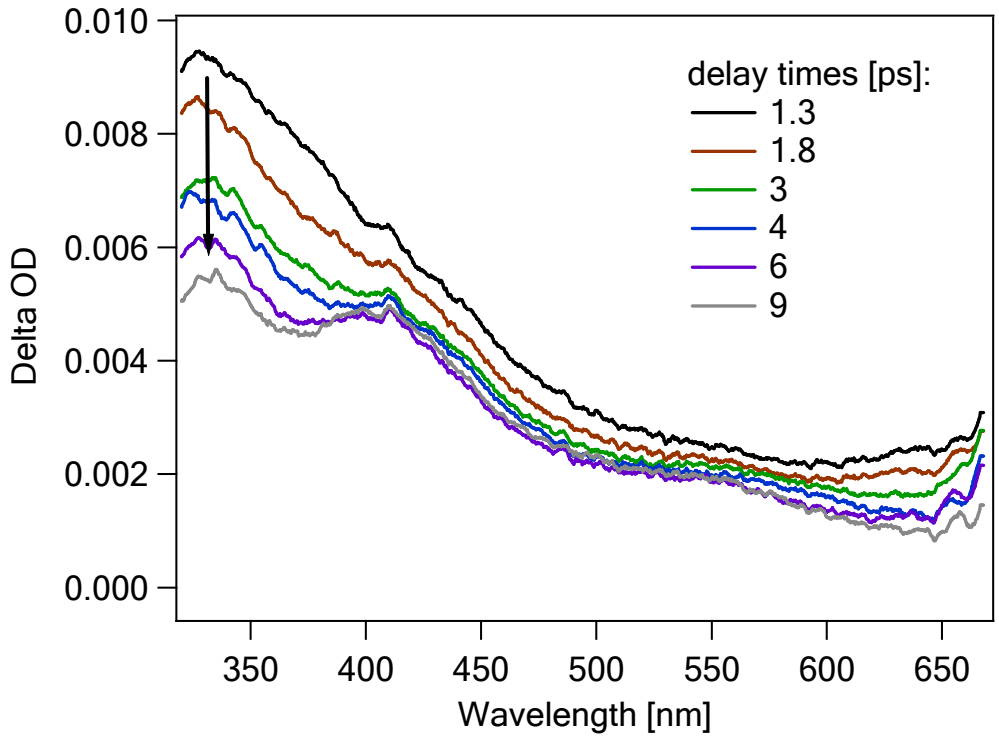


Fig. S7. Transient absorption spectra recorded in chloroform over a 0.8 – 9 ps time window following photoexcitation at 266 nm (a) for **MCT** (b) solvent only.

(a)



(b)

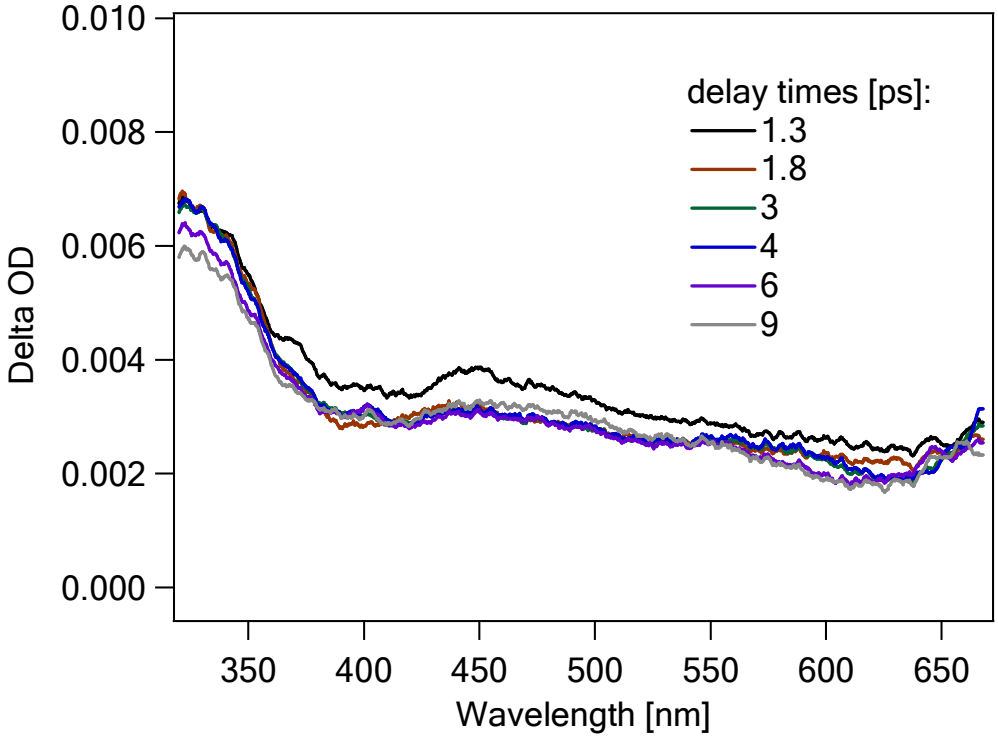
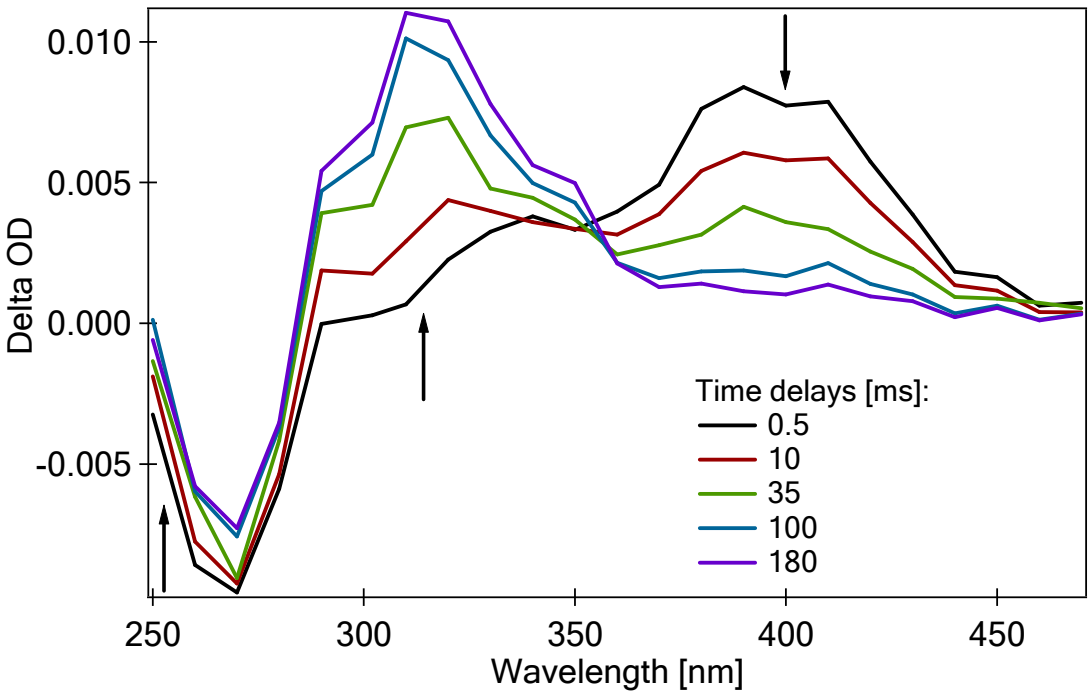


Figure S8. (a) Nanosecond laser flash photolysis studies for **MCT** in acetonitrile (λ_{ex} = 266 nm, 0.75 mJ/pulse). (b) Absorption UV-vis spectra changes upon irradiation (λ = 266 nm) in acetonitrile.

(a)



(b)

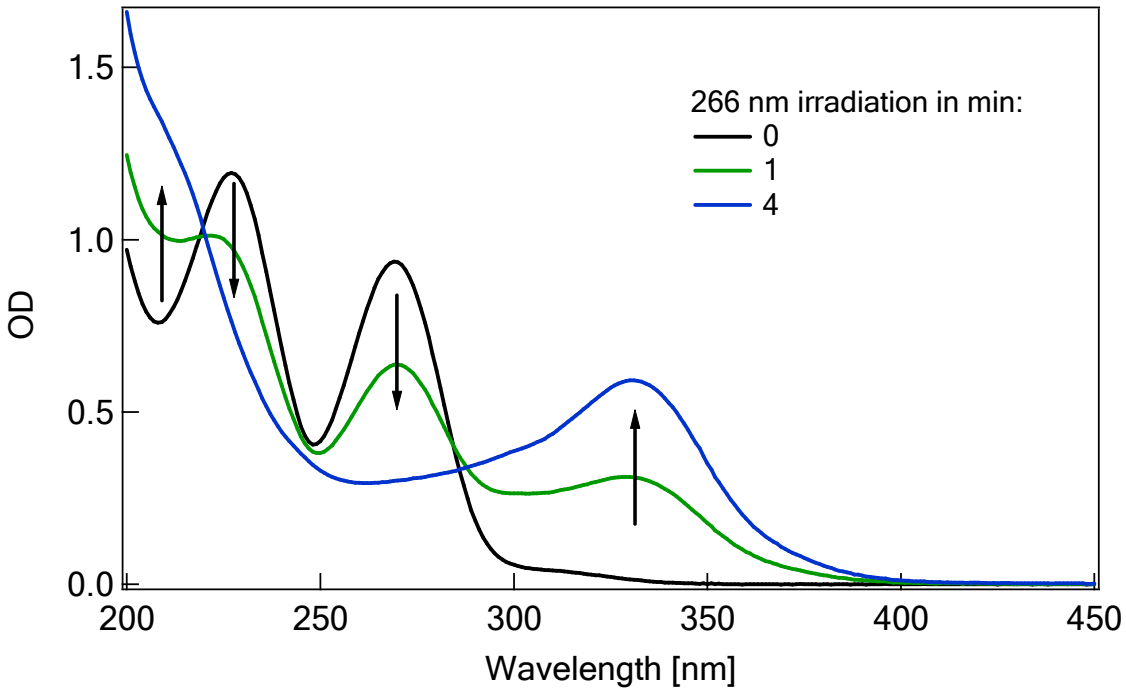


Fig. S9. Signal comparison recorded in nanosecond transient absorption experiments (λ_{exc} = 266 nm) for solutions of benzophenone **BP** and **MCT** in acetonitrile with equal absorbance.

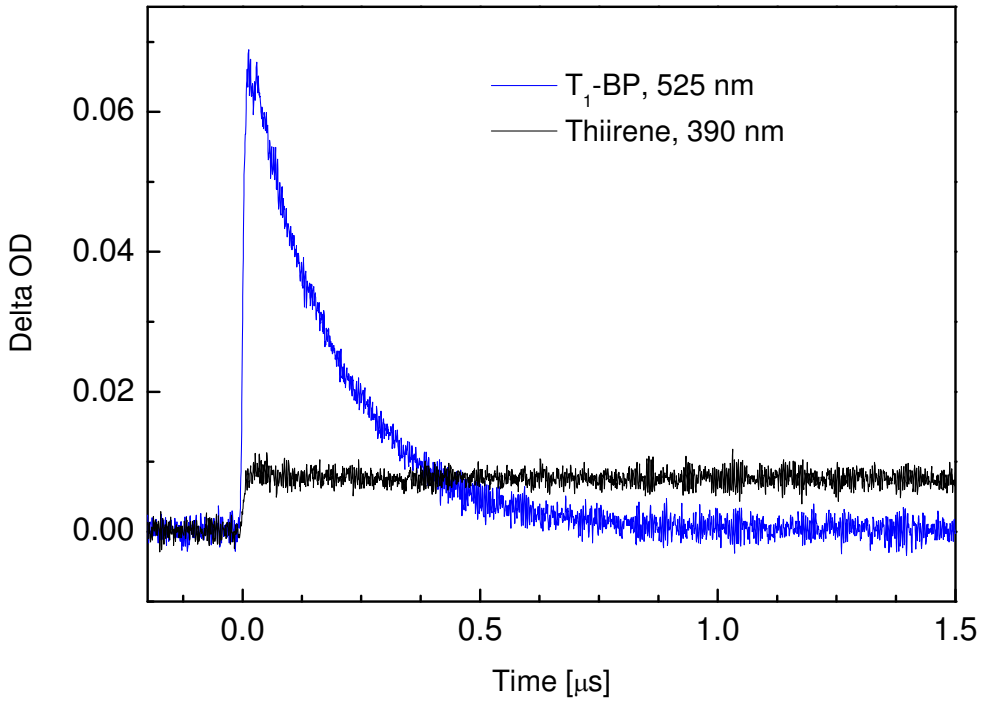
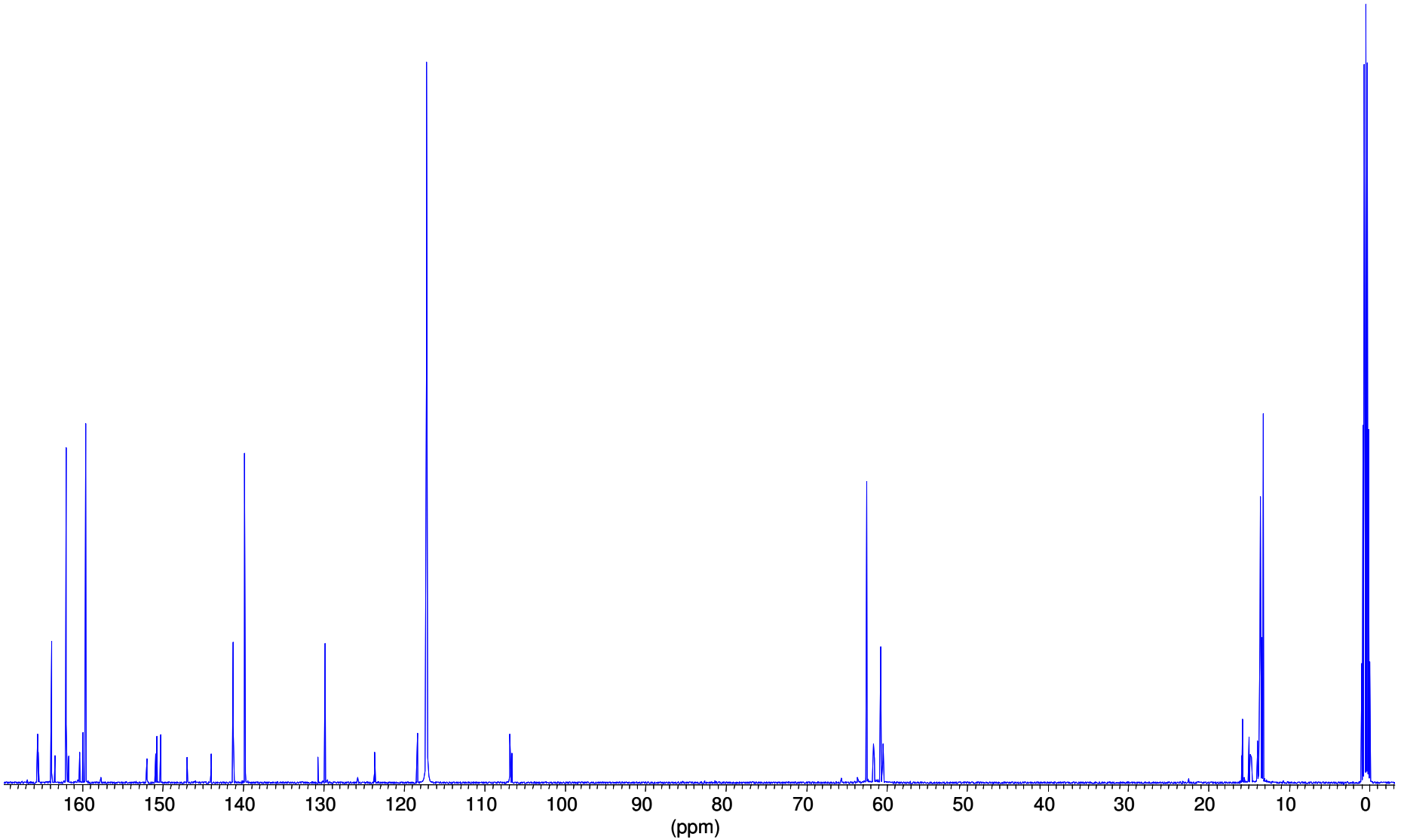
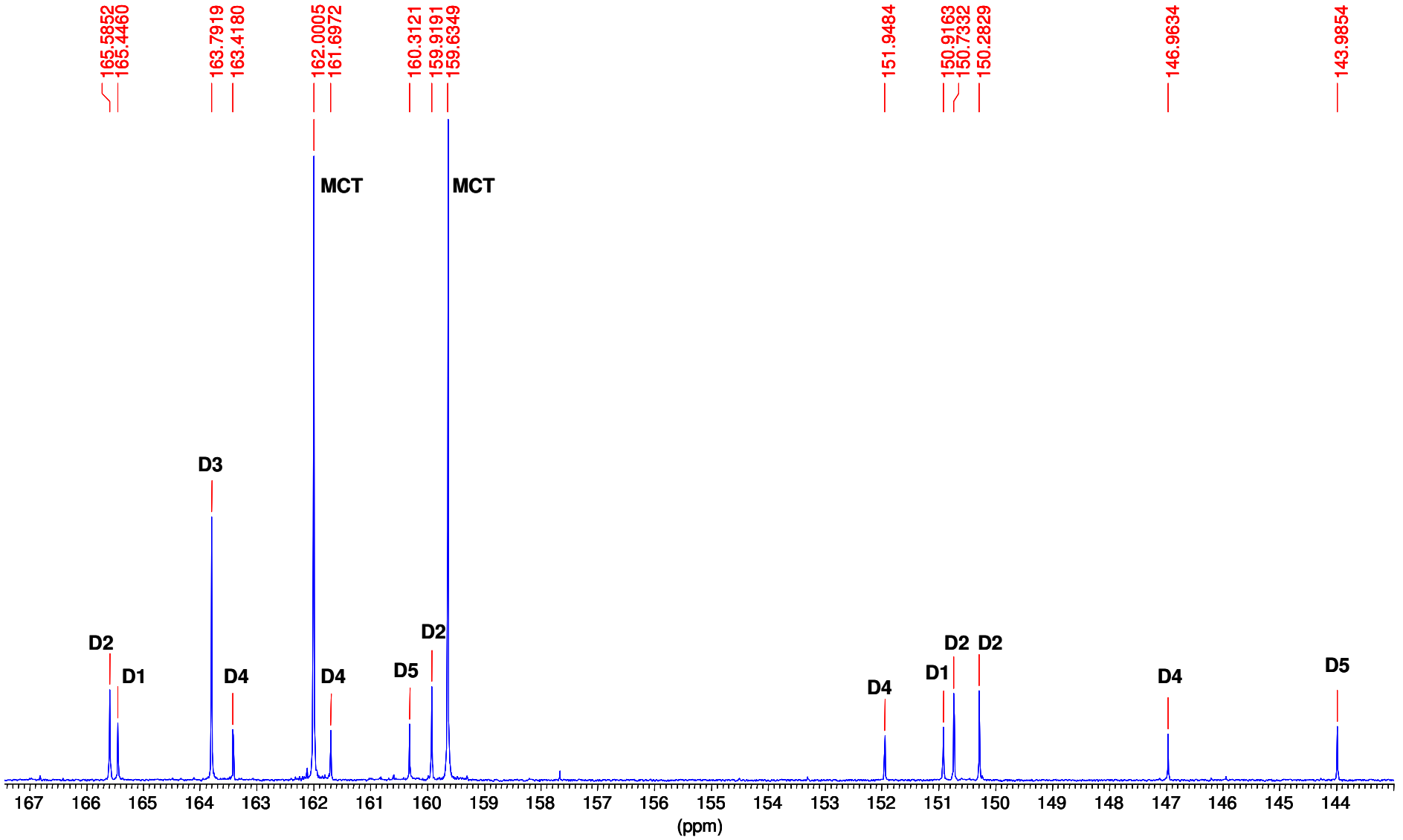
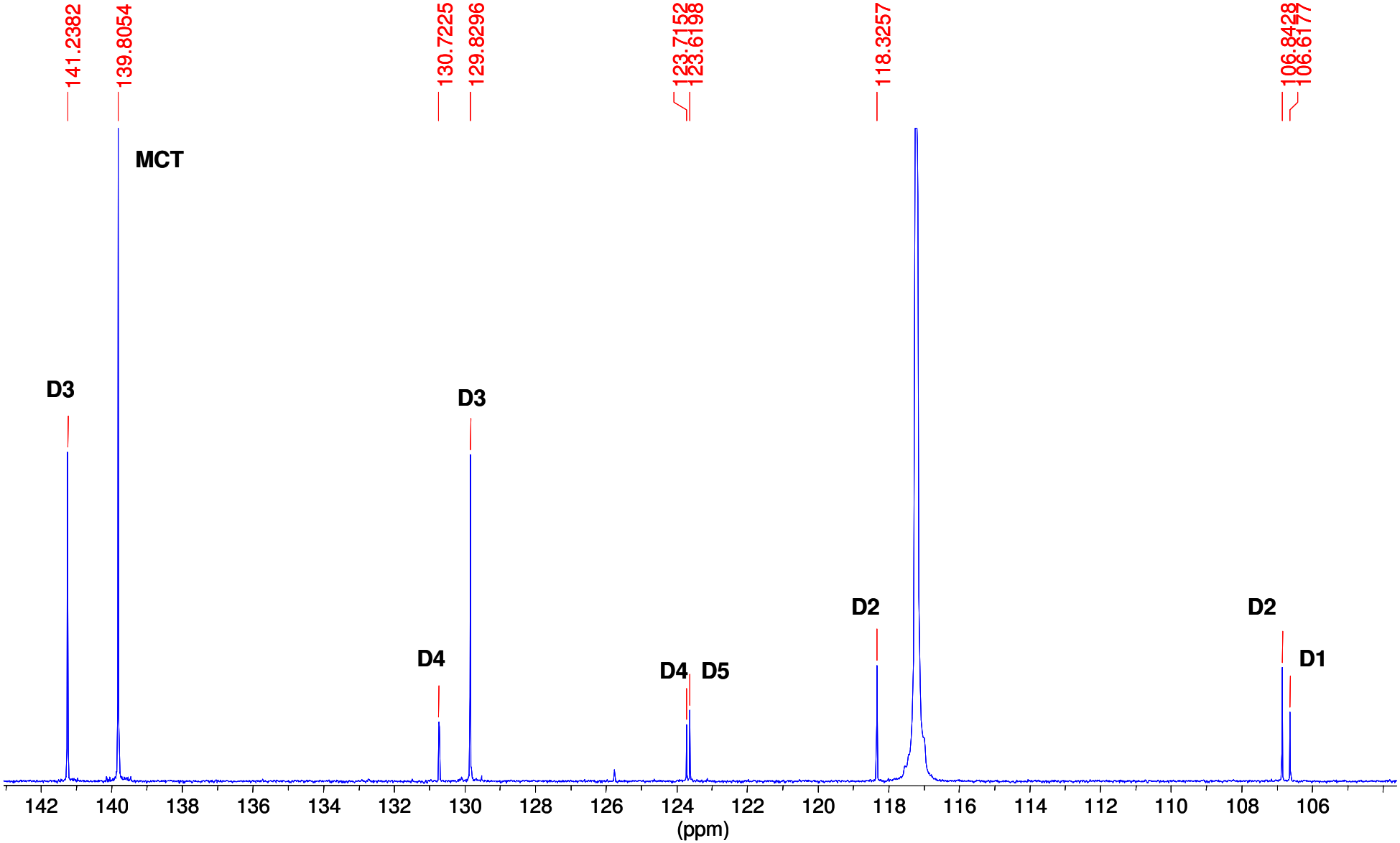
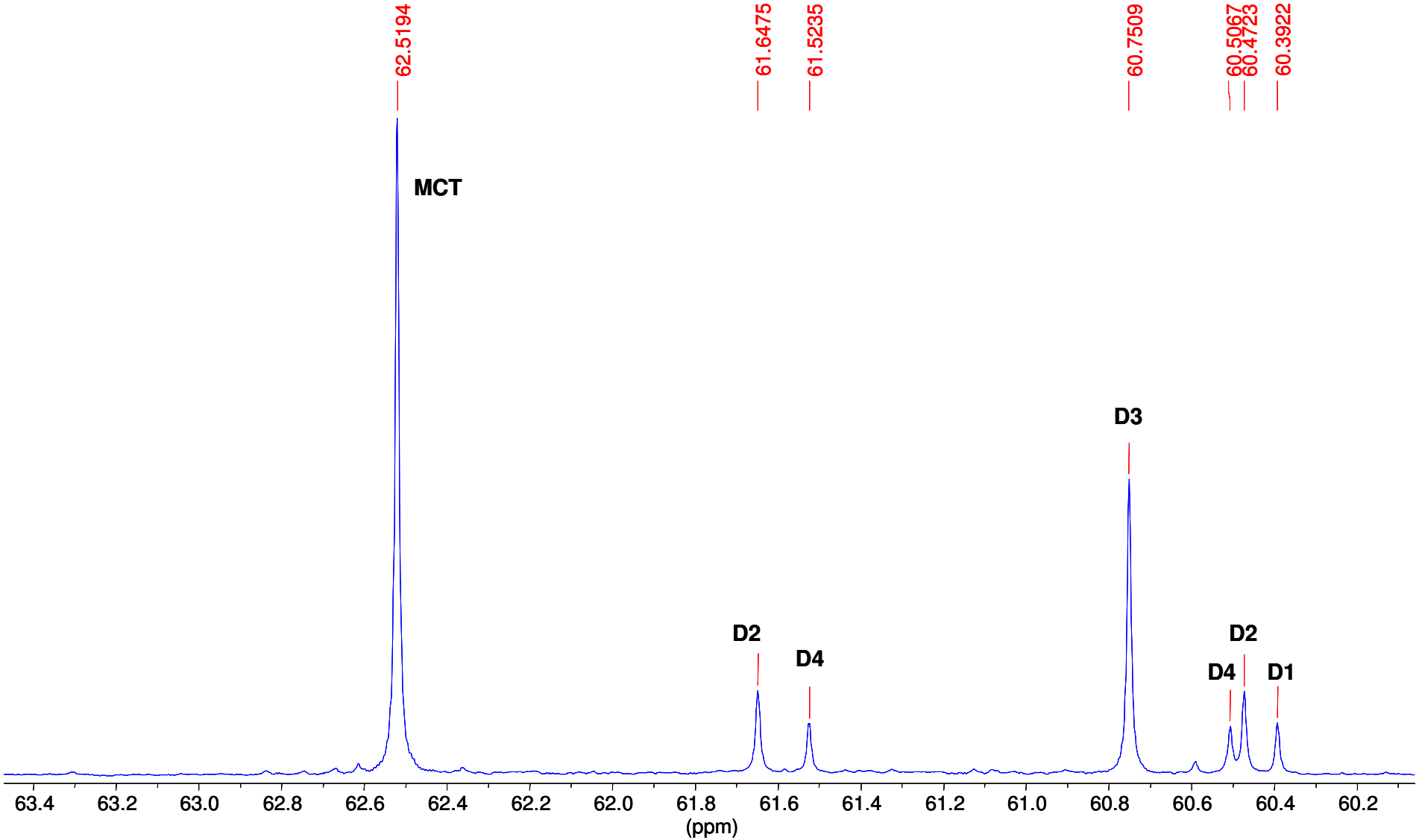


Fig. S10. ^{13}C NMR spectrum (Inverse gated decoupling) of **MCT** after irradiation.




165.5852
165.4460
163.7919
163.4180
162.0005
161.6972
160.3121
159.9191
159.6349
151.9484
150.9163
150.7332
150.2829
146.9634
143.9854
MCT
MCT
D3
D2
D1
D4
D4
D5
D2
D4
D1
D2
D2
D4
D5
167
166
165
164
163
162
161
160
159
158
157
156
155
154
153
152
151
150
149
148
147
146
145
144
(ppm)


141.2382
139.8054
130.7225
129.8296
123.7152
123.6198
118.3257
106.8428
106.6177
MCT
D3
D3
D4
D4
D5
D2
D2
D1
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
(ppm)


62.5194
61.6475
61.5235
60.7509
60.5067
60.4723
60.3922
MCT
D3
D2
D4
D2
D4
D1
63.4
63.2
63.0
62.8
62.6
62.4
62.2
62.0
61.8
61.6
61.4
61.2
61.0
60.8
60.6
60.4
60.2
(ppm)

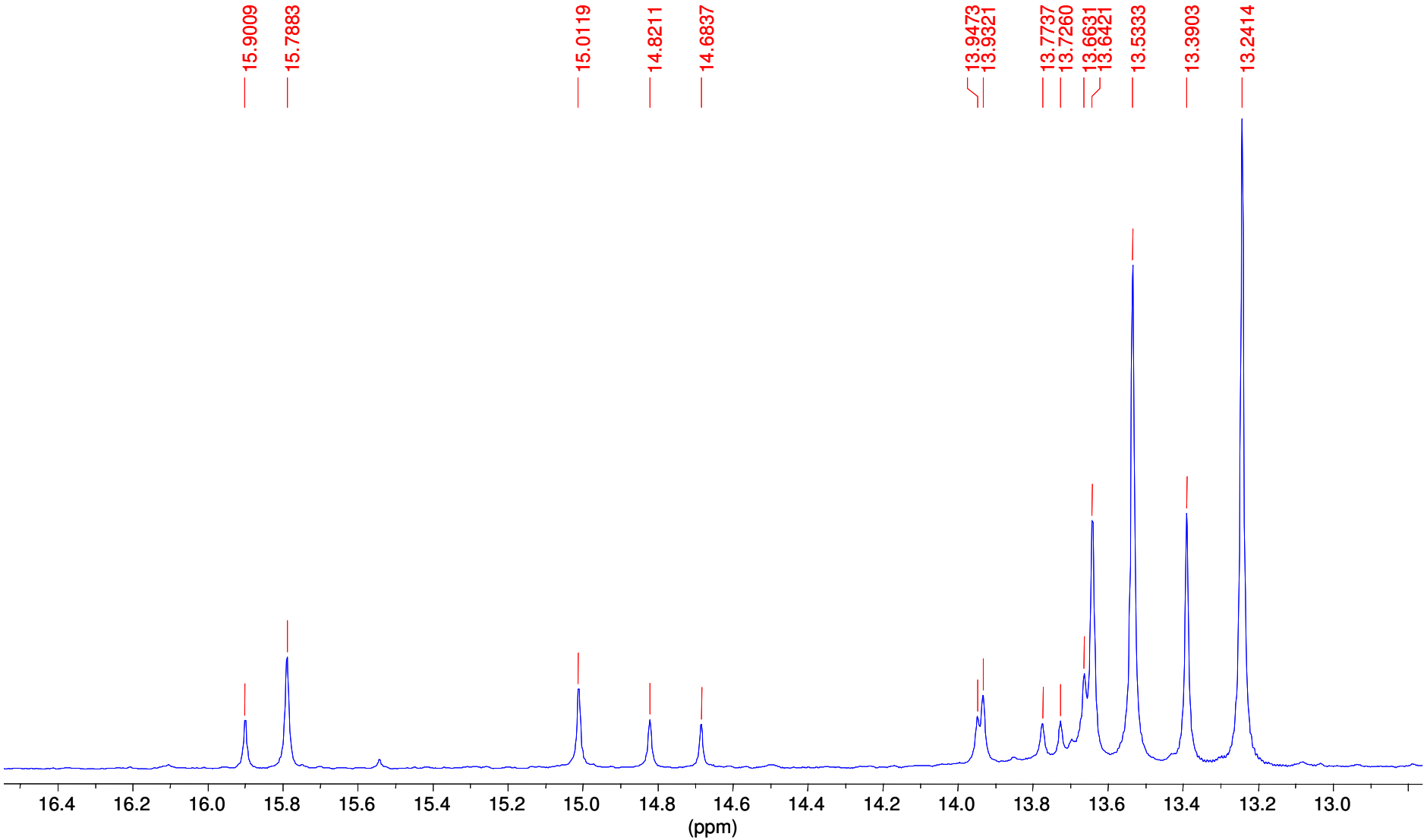

15.9009
15.7883
15.0119
14.8211
14.6837
13.9473
13.9321
13.7737
13.7260
13.6631
13.6421
13.5333
13.3903
13.2414
16.4
16.2
16.0
15.8
15.6
15.4
15.2
15.0
14.8
14.6
14.4
14.2
14.0
13.8
13.6
13.4
13.2
13.0
(ppm)

Fig. S11. ^{1}H-^{13}C NMR HSQC spectrum (Heteronuclear Single Quantum Coherence) of **MCT** after irradiation.

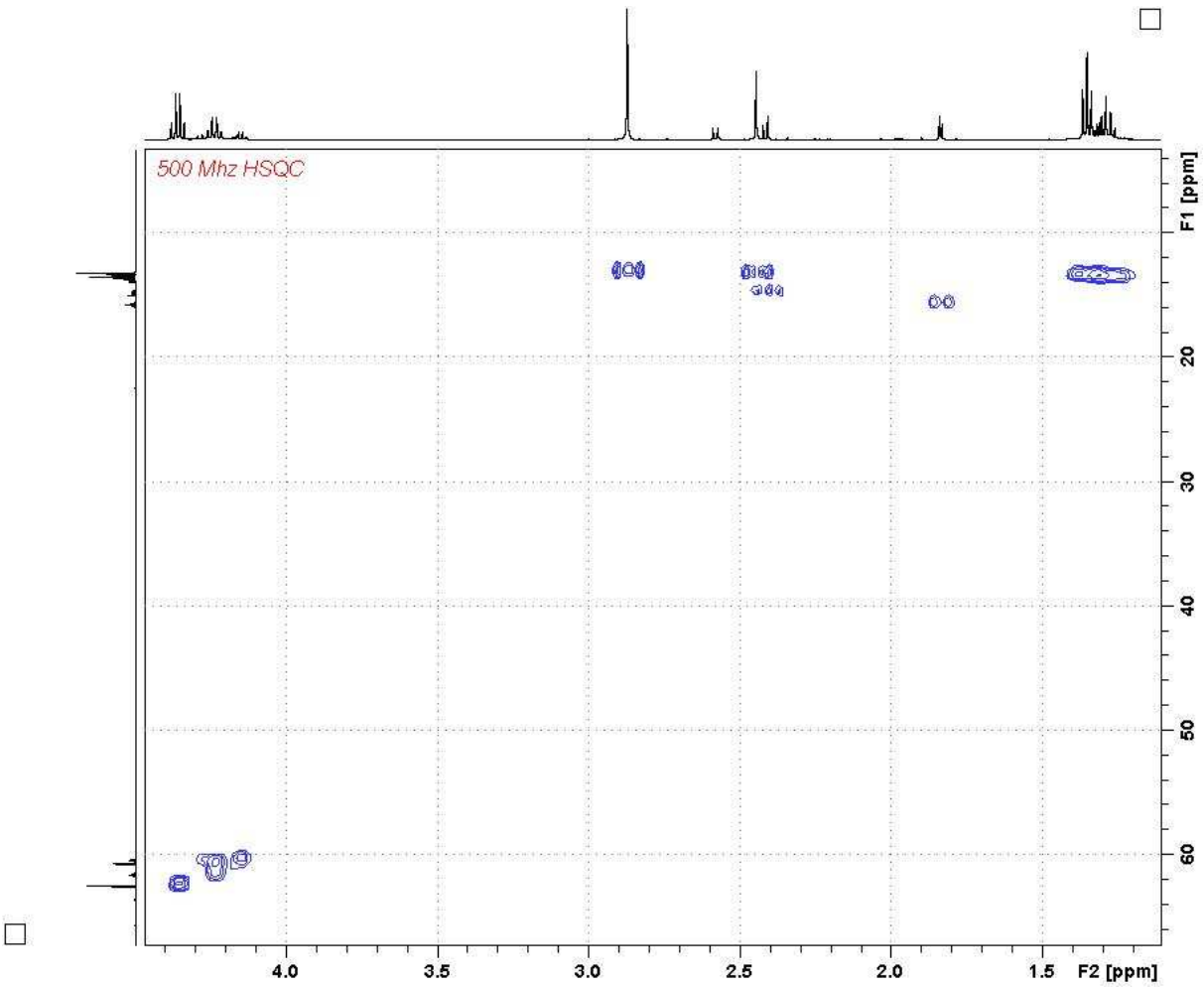


Fig. S12. ^{1}H-^{13}C NMR HMBC (heteronuclear Multiple Bond Correlations) of **MCT** after irradiation.