Supplementary Material (ESI) for Photochemical & Photobiological Sciences


**Supporting Information**

# Observation of the two triplet state conformations of alkyl phenylglyoxylates.

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# I. Synthetic Procedures

## Experimental Part

**Materials and Solvents.**

The following chemicals were commercially available and were used as received: Methyl phenylglyoxylate (Aldrich), ethyl phenylglyoxylate (Aldrich), benzoylformic acid (Aldrich), *N,N'*–dicyclohexylcarbodiimide (DCC) (Acros), methyl–$d_3$ alcohol–*d* (Acros), ethyl–$d_3$ alcohol–*d* (Acros), 2-propanol–$d_8$ (Aldrich), 4–*tert*–butylcyclohexanone (Aldrich), lithium trisiamylborohydride (1M in THF) (Acros), 4–*tert*–butyltoluene (Avocado), benzeneseleninic anhydride (Acros). Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone ketyl. Dichloromethane and acetone were distilled from calcium hydride and calcium chloride respectively prior to use. Pyridine was distilled from potassium hydroxide and stored over potassium hydroxide. Benzene was distilled from sodium and stored over sodium.

***cis*–4–*tert*–Butylcyclohexanol** was prepared according to a literature procedure.[1] M.p. 80 – 81°C (lit.[1] m.p. 80°C). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 0.86 (s, 9H), 0.91 – 1.08 (m, 1H), 1.32 – 1.60 (m, 7H), 1.75 – 1.91 (m, 2H), 4.04 (m, 1H); EI–MS (70 *eV*) 156 ($M^+$), 141 ($M^+$–$CH_3$), 123 ($M^+$–$CH_3$–$H_2O$), 99, 80–83, 67, 57, 41.

**General Methods:**

Melting points were determined with a Fisher–John's melting point apparatus and are uncorrected. NMR spectra were obtained using a Varian Gemini 200 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard. GC/MS and MS spectra were obtained either with a Hewlett–Packard (HP) 5997 mass spectrometer coupled to an HP5880A GC or a Shimadzu QP5050A mass spectrometer coupled to a Shimadzu GC-17A. Aldrich silica gel 60 Å (70 – 270 mesh) was used in chromatography. Elemental analysis was performed by Atlanta Microlab, Inc.

**General procedure for synthesis of alkyl phenylglyoxylates:**

Alkyl phenylglyoxylates were prepared by DCC esterification of the benzoylformic acid according to a literature procedure,[2] except for a modification in the separation step: after the precipitated urea was filtered off, the resulting solution was washed sequently with 10% acetic acid and 5% potassium carbonate and then dried over $Na_2SO_4$. After the solvent was removed under reduced pressure, the residue was passed through a small layer of silica gel using hexane as eluent.

**Isopropylphenylglyoxylate.** Yield – 78%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.39 (d, $J$ = 6.2 Hz, 6H), 5.31 (septet, $J$ = 6.3 Hz, 1H), δ 7.43 – 7.54 (m, 2H), 7.57 – 7.69 (m, 1H), 7.92 – 8.01 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) δ 21.6, 70.6, 128.8, 129.8, 132.4, 134.8, 163.5, 186.6; EI–MS (70 *eV*) 192 ($M^+$), 164 ($M^+$–CO), 123, 105 ($PhCO^+$), 77, 51.

***tert*-Butyl phenylglyoxylate.** Yield – 71%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.60 (s, 9H), δ 7.46 – 7.56 (m, 2H), 7.61 – 7.71 (m, 1H), 7.95 – 8.20 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) δ 28.0, 84.8, 128.8, 129.8, 132.4, 134.6, 163.7, 186.8; EI–MS (70 *eV*) 105 ($PhCO^+$), 77, 57, 41.

**Neopentylphenylglyoxylate**. Yield – 65%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.00 (s, 9H), 4.09 (s, 2H), 7.43 – 7.65 (m, 3H), 7.93 – 8.02 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 26.3, 31.5, 75.1, 128.8, 129.9, 132.4, 134.8, 164.1, 186.5; EI–MS (70 *eV*) 220 ($M^+$), 205 ($M^+$–$CH_3$), 150, 105 ($PhCO^+$), 77, 51.

**Cyclohexylphenylglyoxylate**. Yield – 64%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.18 – 2.08 (m, 10H), 4.98 – 5.17 (m, 1H), 7.40 – 7.71 (m, 3H), 7.88 – 8.05 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 23.5, 25.1, 31.3, 75.3, 128.8, 129.8, 132.4, 134.7, 163.6, 186.7; EI–MS (70 *eV*) 187, 170, 147, 133, 105 ($PhCO^+$), 83, 77, 55, 41.

***cis*–4–(*tert*–Butyl)cyclohexylphenylglyoxylate**. Yield – 75%. M.p. 60 – 61$^o$C. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 0.84 (s, 9H), 0.97 – 1.72 (m, 7H), 2.05 – 2.21 (m, 2H),

5.31 – 5.37 (m, 1H), 7.46 – 7.56 (m, 2H), 7.61 – 7.71 (m, 1H), 7.96 – 8.04 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 21.5, 27.3, 30.5, 32.5, 47.3, 72.6, 128.8, 129.9, 132.5, 134.7, 163.8, 186.8; EI–MS (70 *eV*) 232 ($M^+$–$C_4H_8$), 193, 163, 152, 139, 123, 105 ($PhCO^+$), 83, 77, 57, 41; Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.71; H, 8.42.

**Methyl–*$d_3$* phenylglyoxylate**. Yield – 80%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 7.46 – 7.56 (m, 2H), 7.61 – 7.71 (m, 1H), 7.98 – 8.06 (m, 2H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 52.2 (septet, $J_{C–D}$ = 22.8 Hz), 128.6, 129.7, 132.1, 134.7, 163.8, 185.9; EI–MS (70 *eV*) 167 ($M^+$), 139 ($M^+$–CO), 105 ($PhCO^+$), 77, 51.

**Ethyl–*$d_5$* phenylglyoxylate**. Yield – 40%. $^1$H NMR (200 MHz, acetone–*$d_6$*) $\delta$ (ppm) 7.55 – 7.81 (m, 3H), 7.97 – 8.07 (m, 2H); $^{13}$C NMR (50 MHz, acetone–*$d_6$*) $\delta$ (ppm) 15.24 (septet, $J_{C–D}$ =19.2 Hz), 64.2 (quintet, $J_{C–D}$ =22.8 Hz), 129.8, 130.3, 133.0, 135.7, 164.8, 187.5; EI–MS (70 *eV*) 183 ($M^+$), 155 ($M^+$–CO), 123, 105 ($PhCO^+$), 77, 51.

**Isopropyl–*$d_7$* phenylglyoxylate**. Yield – 72%. $^1$H NMR (200 MHz, acetone–*$d_6$*) $\delta$ (ppm) 7.56 – 7.82 (m, 3H), 7.96 – 8.06 (m, 2H); $^{13}$C NMR (50 MHz, acetone–*$d_6$*) $\delta$ (ppm) 20.8 (septet, $J_{C–D}$ = 19.1 Hz), 70.7 (t, $J_{C–D}$ = 22.8 Hz), 130.0, 130.4, 133.1, 135.8, 164.6, 187.8; EI–MS (70 *eV*) 199 ($M^+$), 171 ($M^+$–CO), 153, 125, 105 ($PhCO^+$), 77, 51.

**Synthesis of the 6–*tert*–Butylisochroman–3,4–dione:**

**2–Bromo–4–*tert*–butylmethylbenzene**. The synthesis was performed according to a literature procedure.[3] Yield – 88%.

**5–*tert*–Butyl–2–methylbenzoic acid** was synthesized from 2–bromo–4–*tert*–butylmethylbenzene according to a literature procedure.[4] Yield – 59%. M.p. 96 – 97$^o$C (lit.[4] m.p. 98$^o$C). EI–MS (70 *eV*) 192 ($M^+$), 177 ($M^+$–$CH_3$), 149, 131, 115, 105, 91.

**Methyl 5–*tert*–butyl–2–methylbenzoate.** This synthesis was performed based on a literature procedure,[5] starting from 5–*tert*–butyl–2–methylbenzoic acid (24.3 g, 0.36 mol) and $Me_2SO_4$ in $K_2CO_3$/acetone system. After work-up, the residue was purified by silica gel flash chromatography using hexane as eluent to yield the product, which was sufficiently pure for the next purposes. Yield – 28.42 g (91%). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.33 (s, 9H), 2.56 (s, 3H), 3.90 (s, 3H), 7.18 (d, $J$ = 8.2 Hz, 1H), 7.44 (dd, $J$ = 8.2, 2.2 Hz, 1H), 7.93 (d, $J$ = 2.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 21.2, 31.2, 34.4, 51.8, 127.3, 129.0, 129.1, 131.4, 137.0, 148.6, 168.5; EI–MS (70 *eV*) 206 ($M^+$), 191 ($M^+$–$CH_3$), 175, 159, 131, 115, 105, 91, 79.

**Methyl 2–bromomethyl–5–*tert*–butylbenzoate**. The bromination of the methyl 5–*tert*–butyl–2–methylbenzoate with NBS was performed according to the standard procedure.[6] The reaction was monitored by GC/MS. The precipitate was filtered off and washed with $CH_2Cl_2$ (2×50 ml), the filtrate was washed with 5% sodium carbonate, dried over $Na_2SO_4$ and concentrated under the vacuum. The residue was passed through a small layer of silica gel using hexane as eluent. After solvent evaporation, the product was sufficiently pure for the next step. Yield – 97%. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.34 (s, 9H), 3.96 (s, 3H), 4.94 (s, 2H), 7.39 (d, $J$ = 8.0 Hz, 1H), 7.52 (dd, $J$ = 8.0, 2.2 Hz, 1H), 7.98 (d, $J$ = 2.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 31.1, 34.7, 38.4, 52.3, 126.8, 128.2, 129.6, 131.5, 136.1, 151.8, 167.4; EI–MS (70 *eV*) 284/286 ($M^+$), 269/271 ($M^+$–$CH_3$), 253/255, 237/239, 205, 190, 175, 145, 131, 115, 105, 91.

**Methyl 5–*tert*–butyl–2–methoxymethylbenzoate**. To a stirred solution of sodium methoxide (prepared by dissolving sodium (6.43 g, 0.28 mol) in 100 ml of the methanol) at 0$^o$C, solution of the methyl 2–bromomethyl–5–*tert*–butylbenzoate (38.2 g, 0.134 mol) in dry THF (40 ml) was added dropwise over 1.5 h. The reaction mixture then was stirred for 4 h at room temperature and left overnight at 35 – 40$^o$C. The resulting mixture was poured into crushed ice, extracted with $CH_2Cl_2$, dried ($Na_2SO_4$) and concentrated under vacuum. The residue was purified on small layer if silica gel using hexane as eluent. Yield – 25.4 g (79%). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.34 (s, 9H), 5.70 (s, 2H), 7.31 (d, $J$ = 7.6 Hz, 1H), 8.80 (dd, $J$ = 7.6 Hz, 1H); $^{13}$C NMR (50

MHz, $CDCl_3$) $\delta$ (ppm) 31.2, 34.5, 51.9, 58.6, 72.4, 127.3, 127.5, 127.8, 129.3, 137.6, 150.0, 167.9; EI–MS (70 *eV*) 236 ($M^+$), 221 ($M^+ - CH_3$), 205 ($M^+ - OCH_3$), 189, 174, 159, 131, 115, 105, 91, 77.

**5–*tert*–Butyl–2–methoxymethylbenzyl alcohol**. Reduction of the methyl 5–*tert*–butyl–2–methoxymethylbenzoate (25 g, 0.106 mol) with $LiAlH_4$ was performed according to the standard procedure.[7] After aqueous/acid work-up the resulting alcohol was used in the next step without additional purification. Yield – 21.6 g (98%). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.33 (s, 9H), 3.42 (s, 3H), 4.55 (s, 2H), 4.66 (d, $J$ = 6.2 Hz, 2H), 7.26 (d, $J$ = 8 Hz, 1H), 7.33 (dd, $J$ = 7.8, 2.0 Hz, 1H), 7.43 (d, $J$ = 2.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 31.3, 34.6, 58.0, 64.4, 73.7, 124.8, 127.0, 130.0, 132.9, 140.1, 152.1; EI–MS (70 *eV*) 208 ($M^+$), 207 ($M^+$–H), 193 ($M^+$–$CH_3$), 190 ($M^+$–$H_2O$), 176, 161, 133, 115, 105, 91, 77.

**5–*tert*–Butyl–2–methoxymethylbenzyl chloride**. This synthesis was performed base on a literature procedure describing the synthesis of the *o*–methoxymethylbenzyl chloride,[8] starting from 21 g (0.1 mol) of 5–*tert*–butyl–2–methoxymethylbenzyl alcohol. The reaction was monitored by GC/MS. After aqueous work-up, 22.7 g (99%) of the crude product was obtained, which according to GC was sufficiently pure for the next step. EI–MS (70 *eV*) 226/228 ($M^+$), 211/213 ($M^+$–$CH_3$), 194/196, 179, 159, 145, 131, 115, 105, 91, 45.

**2–[5–*tert*–Butyl–2–methoxymethylphenyl]acetonitrile**. The vigorously stirred mixture of 5–*tert*–butyl–2–methoxymethylbenzyl chloride (22.6 g, 99.7 mmol), $CH_2Cl_2$ (50 ml), MeCN (15 ml), NaCN (8.82 g, 0.18 mol), water (40 ml) and benzyltriethylammonium chloride (TEBAC) (400 mg, 1.76 mmol) was heated at 45 – 50$^o$C until starting chloride was completely converted to product (~ 1.5 day), according to GC/MS. The product was extracted with $CH_2Cl_2$, dried over $Na_2SO_4$, and the solvent was evaporated under the reduced pressure. The residue was passed trough small layer of silica gel using hexane as eluent to give pure product (16.47 g, 76%). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.32 (s, 9H), 3.36 (s, 3H), 3.85 (s, 2H), 4.46 (s, 2H), 7.23 (d, $J$ =

8.2 Hz, 1H), 7.32 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.44 (d, $J$ = 1.8 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 21.0, 31.1, 34.6, 58.0, 72.7, 117.9, 124.9, 126.2, 128.9, 129.8, 132.5, 152.1; EI–MS (70 *eV*) 217 ($M^+$), 202 ($M^+ - CH_3$), 185, 170, 160, 143, 115, 91.

**6–*tert*–Butylisochroman–3–one**. The cyclization of the 2–[5–*tert*–butyl–2–methoxymethylphenyl]acetonitrile (5 g, 23.0 mmol) was performed according to a literature procedure[8] describing the synthesis of the isochroman–3–one with modification on the separation step: the product was purified on a small layer of silica gel using sequentially hexane, hexane/$CH_2Cl_2$ (12/1) and hexane/$CH_2Cl_2$ (5/1) as an eluent. Yield – 3.81 g (81%). $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.33 (s, 9H), 3.72 (s, 2H), 5.30 (s, 2H), 7.19 (d, $J$ = 7.8 Hz, 1H), 7.23 (d, $J$ = 1.8 Hz, 1H), 7.34 (dd, $J$ = 7.6, 1.8 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 31.2, 34.7, 36.5, 69.9, 124.0, 124.2, 124.3, 128.6, 130.6, 152.1, 170.9; EI–MS (70 *eV*) 204 ($M^+$), 189 ($M^+ - CH_3$), 161, 160, 145, 133, 131, 115, 105, 91, 77.

**6–*tert*–Butylisochroman–3,4–dione**. This synthesis was performed based on the literature procedure describing the synthesis of the isochroman–3,4–dione.[9] In the case below, we started from 1.8 g, (8.8 mmol) of the 6–*tert*–butylisochroman–3–one. After aqueous work-up, the product was subjected to column chromatography using sequentially hexane (to remove diphenyl diselenide), hexane/$CH_2Cl_2$ (5/1) (to remove ureacted starting material and the rest of the diphenyl diselenide) and hexane/$CH_2Cl_2$ (1/1) as an eluent. Yield – 1.17 g (61%). Analytical sample was additionally recrystallized from hexane – $CH_2Cl_2$ (12 : 1). M.p. 156 – 157$^o$C. $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ (ppm) 1.34 (s, 9H), 5.70 (s, 2H), 7.31 (d, $J$ = 7.8 Hz, 1H), 7.80 (dd, $J$ = 8.1, 2.0 Hz, 1H), 8.11 (d, $J$ = 2.2 Hz, 1H); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ (ppm) 30.9, 35.0, 69.3, 124.2, 124.3, 129.6, 133.7, 136.0, 152.8, 157.1, 173.8; EI–MS (70 *eV*) 218 ($M^+$), 203 ($M^+ - CH_3$), 174 ($M^+ - CO_2$), 159, 146, 115, 102, 91, 77, 65. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.28; H, 6.45.

**References.**

(1) Krishnamurthy, S.; Brown, H. C. *J. Am. Chem. Soc.*, **1976**, *98*, 3383 – 3384

(2) Hu, S.; Neckers, D. C. *J. Org. Chem.*, **1996**, *61*, 6407 – 6415

(3) Tashiro, M.; Yamato, T *J. Chem. Soc. Perkin Trans. 1*, **1979**, 176 – 179

(4) Royals, E. E.; Prasad, R. N. *J. Am. Chem. Soc.*, **1955**, *77*, 1696 – 1697

(5) Giles, R. G. F.; Mitchell, P. R. K. *J. Chem. Soc. Perkin Trans. 1*, **1983**, 2147

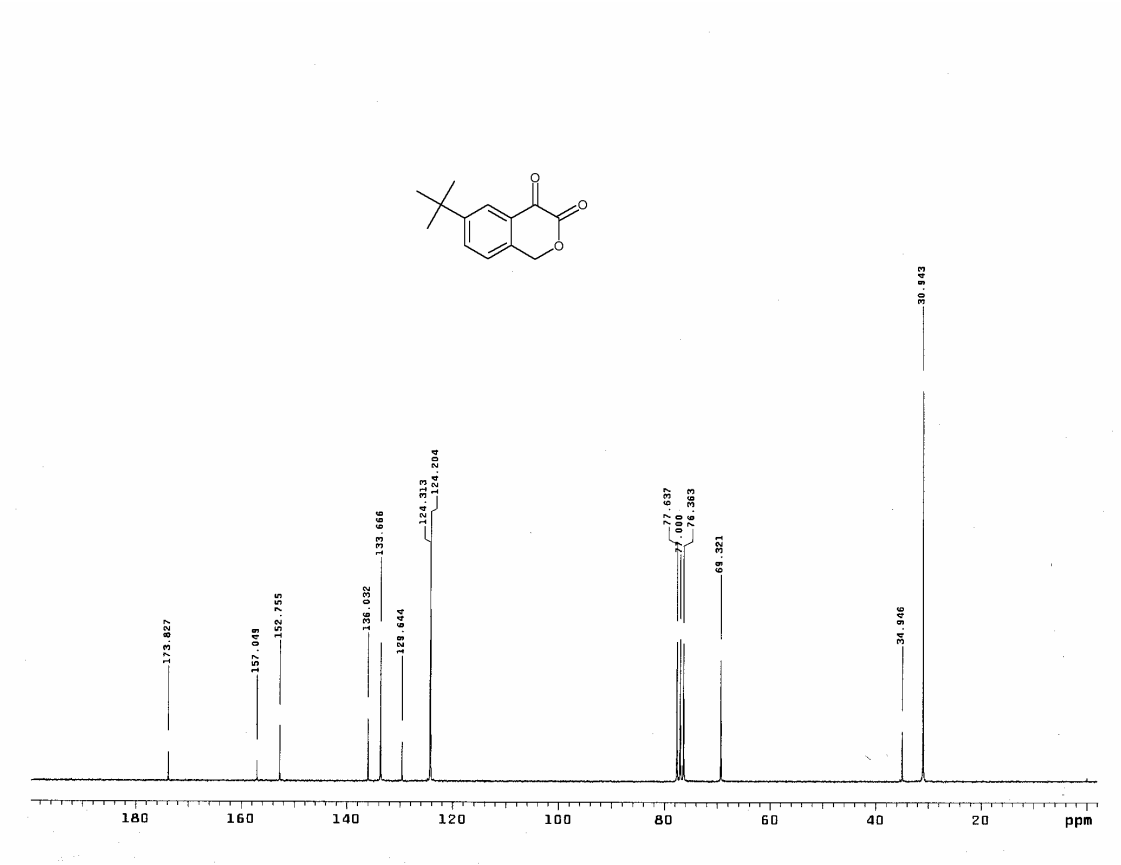
(6) Kalir, A. *Organic Syntheses*, **1973**, *Coll. Vol. V*, 825

(7) Moffett, R. B. *Organic Syntheses*, **1963**, *Coll. Vol. IV*, 834

(8) Mann, F. G.; Stewart, F. H. C. *J. Chem. Soc.*, **1954**, 2819 – 2826

(9) Barbier, M. *Synth. Commun.*, **1988**, *18 (11)*, 1253.

**Spectra.**



## II. Spectroscopic Data

**Figure S1.Time-resolved infrared spectra of various APGs and structural analogs The spectra shown are averaged over 200 ns time intervals.**

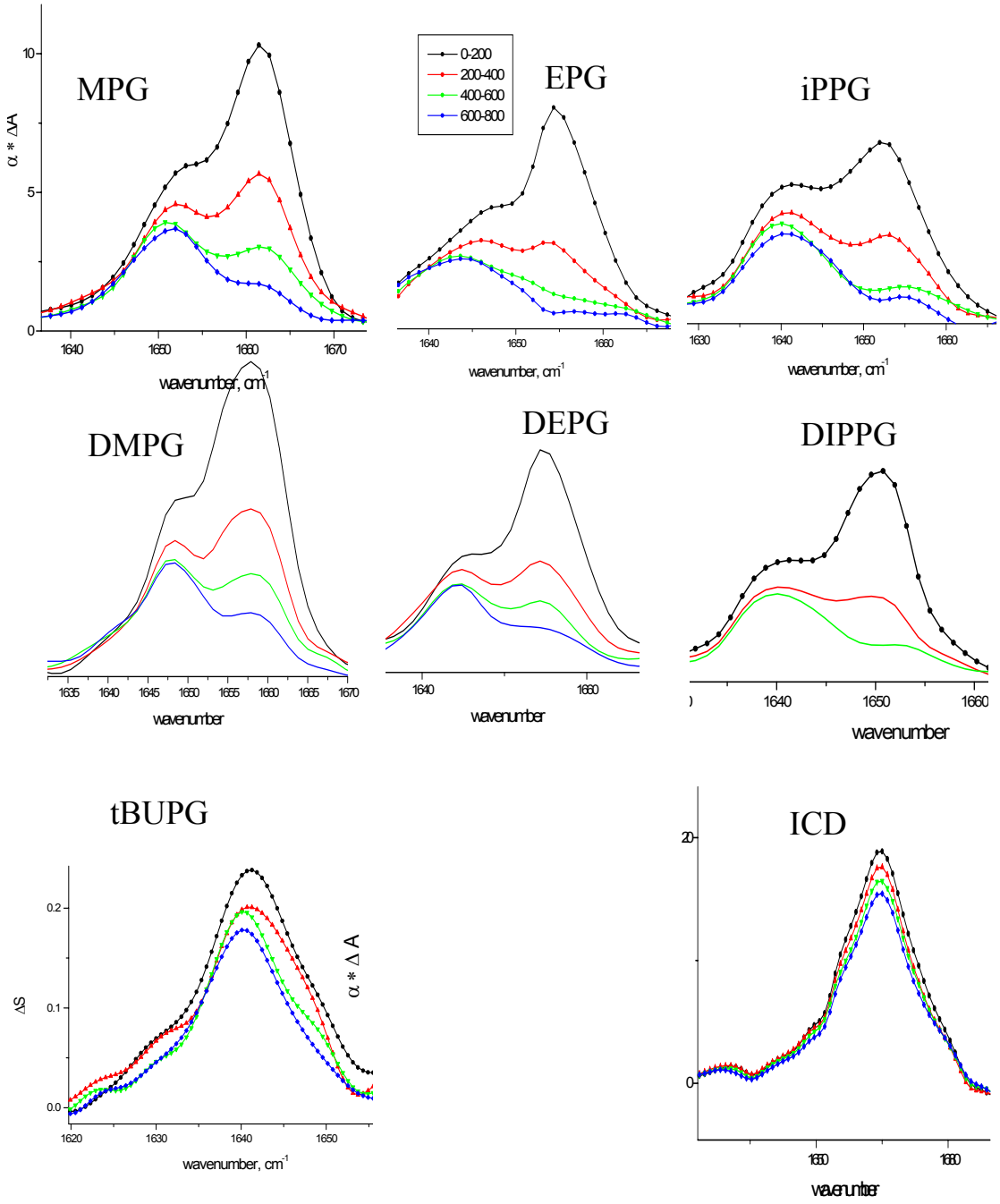


**Figure S2. Kinetics of Deuterated Compounds. D-isotope effect on the photolysis of 40 mM solution of MPG in hexane**

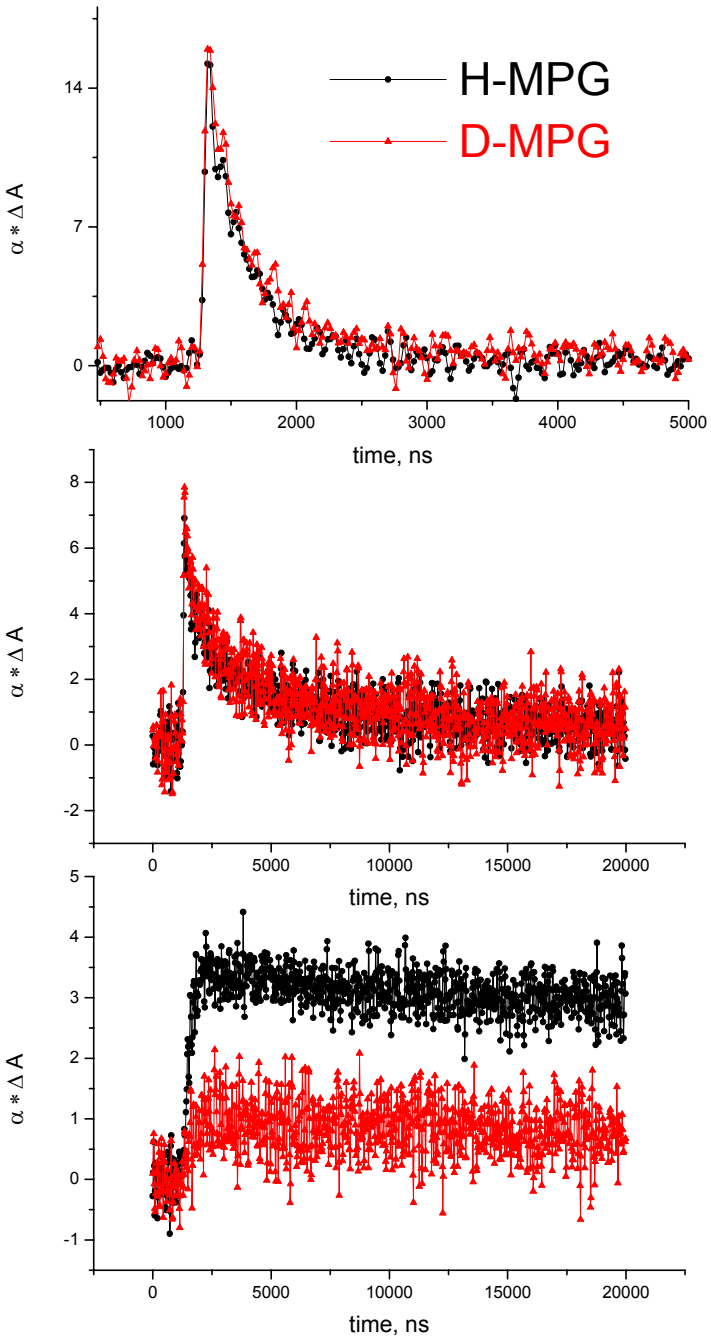
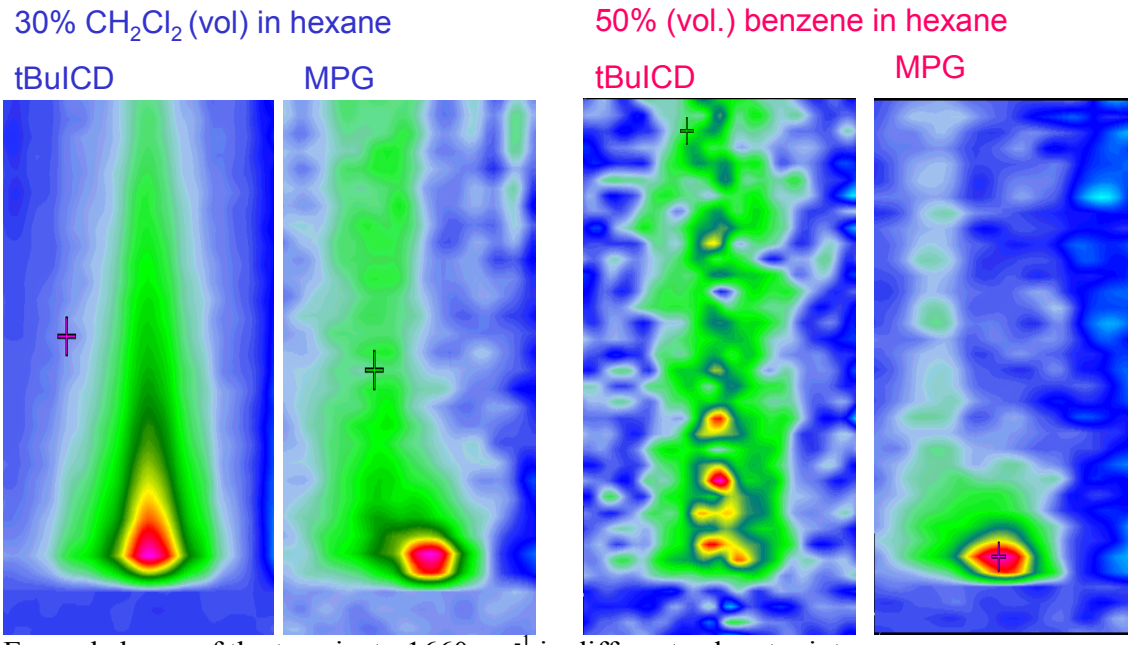


**Figure S3. Colormaps of triplet peaks of tBuICD and MPG in various solvent systems. Two components are observed in the case of MPG. Only one component is present in the spectra of tBuICD.**




Expanded area of the transient ~1660 $cm^{-1}$ in different solvent mixtures.

**Figure S4. Transient profiles observed in tBuCHPG (red) and CHPG (blue) in hexane. Transients are Triplet B (top left); Triplet A (top right); Ketene (bottom)**

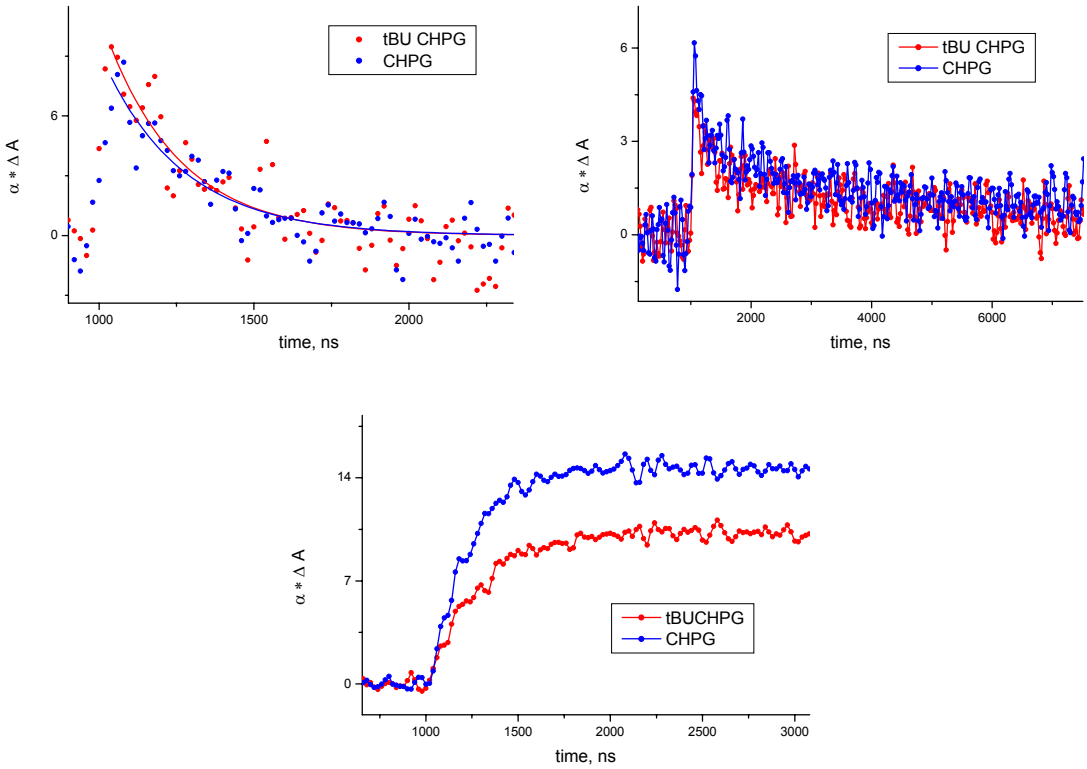
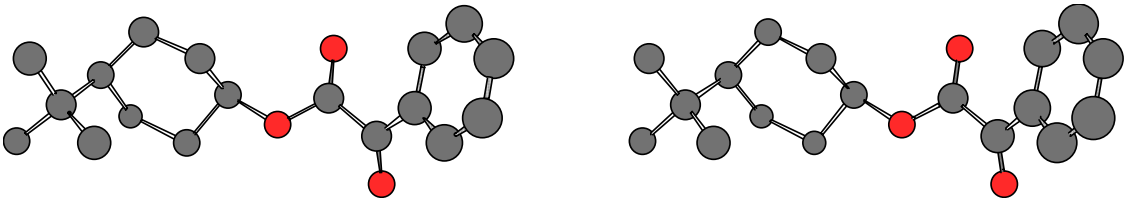


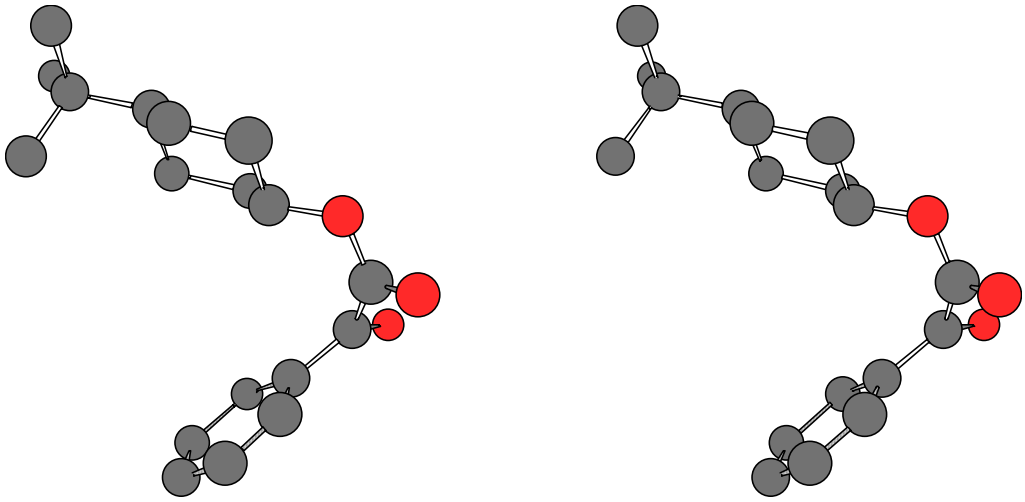

**Table S1. Semi-empirical calculation (PM3) of the properties of tBuCHPG and CHPG.**

| Compound | Parameter | Z | E | Δ |
|---|---|---|---|---|
| **tBuCHPG** | O=C-C-O angle | -144° | -1.4° | 142.6° |
| | $\Delta H_f$, kcal mol$^{-1}$ | -121.98 | -122.06 | -0.12 |
| **CHPG** | O=C-C-O angle | -110° | 1.1° | 111.1° |
| | $\Delta H_f$, kcal mol$^{-1}$ | -99.42 | -104.21 | 4.8 |

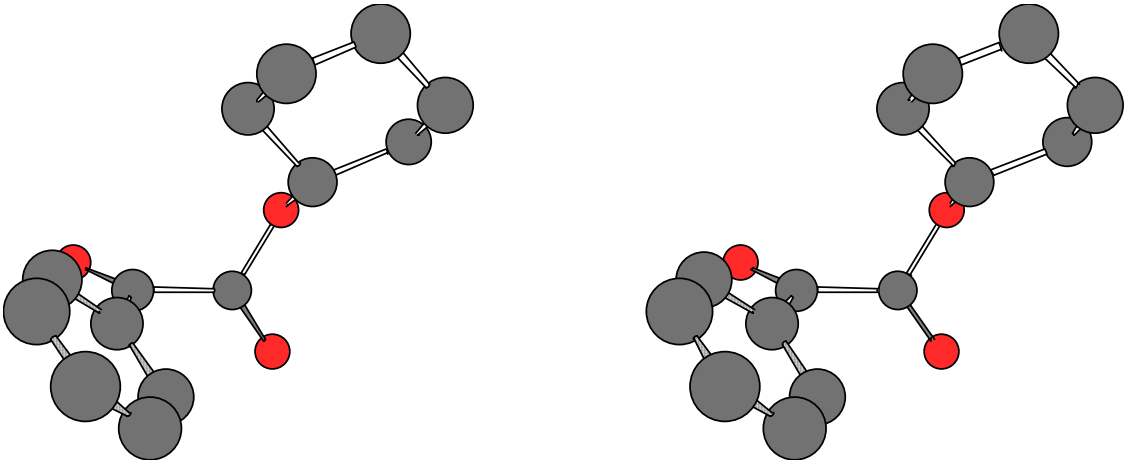
**Figure S5. Stereoimages of the structures corresponding to the minima in table Singlet state.**



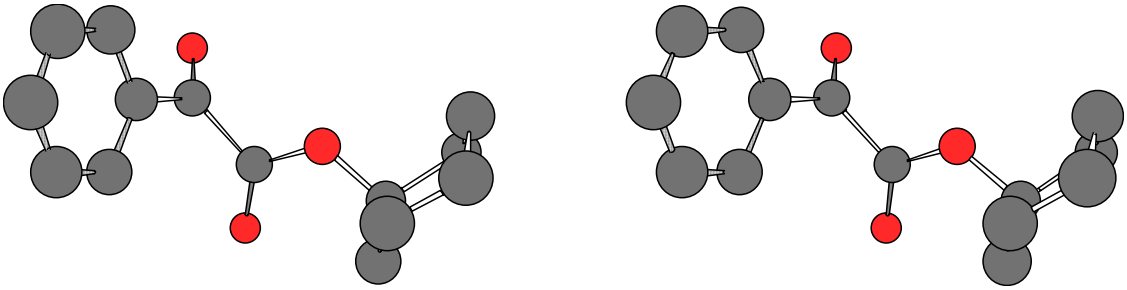
*tBuCHPG E-isomer*



*tBuCHPG Z-isomer*



*CHPG Z-isomer*



*CHPG E-isomer*

**III. Computational Details**

The results of ground state rotational barrier calculations are presented in Figure S6. The activation energy for the rotation around the ester C—O bond was calculated to be 10-11 kcal $mol^{-1}$. The energy difference between the two conformers was ~7 kcal $mol^{-1}$ and ~5.1 kcal $mol^{-1}$ in favor of the E-conformer according to RHF and DFT, respectively. These values are slightly higher than the values obtained for the simple ester rotamers, which are approximately 3-4 kcal $mol^{-1}$ (Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935). The predicted ground state geometry involves almost

planar benzil and ester moieties at the minima on the potential energy curve. The angle between the two carbonyl groups changes as a function of the ester torsional angle.

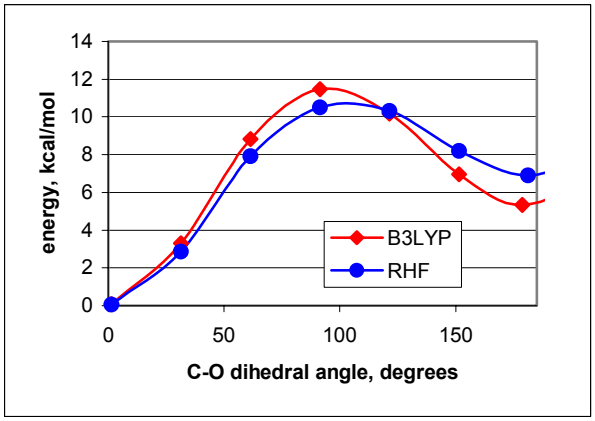



**Figure S6.** Barrier for the rotation around C-O ester bond calculated using B3LYP/6-31G* (squares) and RHF/6-31G* (dots). 0 and 180 degrees correspond to E- and Z-conformers, respectively. The molecular geometry was optimized at each step with the dihedral angle of the ester C-O bond frozen.

The rotation barriers in the triplet excited state were calculated using CI-singles method. These calculations show that the lowest excited triplet state $T_1$ (HOMO to LUMO excitation) has a π–π* character, and the second excited triplet state $T_2$ has an n–π* character (HOMO-2 to LUMO excitation). It was previously shown that APG triplet has an n-π* character (Wagner, P. J.; Park, B.-S. *Org. Photochem.* Padwa, A., Ed.; Marcel Dekker, Inc.; New York, 1991; Vol. 11, p 227), which closely corresponds to the computed $T_2$ state.

The relative energies, energy barriers (Table S2), and carbonyl vibrational frequencies (Table S3) were calculated for the conformational isomers of $T_1$ and $T_2$ formed by rotation around diketone C—C and ester C—O bonds (E-, Z-, and syn-). Both in $T_1$ and

$T_2$, the minima corresponding to the E-, Z- and *syn*-rotamers were found. In both excited states, the syn- and Z-conformers are higher in energy than the conformer E-. The rotational barriers, however, are different for $T_1$ and $T_2$. In the lowest triplet excited state, the rotation from syn- to E- conformation was essentially uninhibited. The rotation barrier between the E- and Z- conformations is almost identical to that one for the ground state (10-10.5 kcal $mol^{-1}$). The situation reverses in the second excited state (n–π*) with the substantial energy barrier between the syn- and E- conformers. The magnitude of the barrier between the E- and Z- does not change significantly; however, because of the higher energy of the Z-conformer in this excited state, the rotation of Z into the E conformation is virtually free.

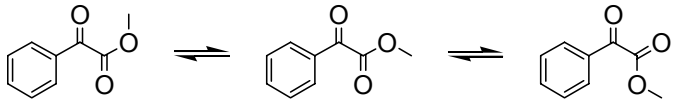



**Table S2. Relative energies of the conformers and rotational barrier in the excited and ground states.**

| | Syn, kcal/mol | E to Syn Barrier,** kcal/mol | E,* Kcal/mol | E to Z Barrier,** kcal/mol | Z, Kcal/mol |
|---|---|---|---|---|---|
| Ground | - | - | 0 | 10.5 | 6.9 |
| $T_1$ | 2.3 | 2.3 | 0 | 10.3 | 7.2 |
| $T_2$ | 5.2 | ~14 | 0 | 10.1 | 10.1 |

* E is the lowest-energy conformation for each of the electronic states

** the energy of the highest-energy transition structure calculated

The calculated vibrational frequencies of the β-carbonyl group are provided in the Table S3. The scaling coefficient (0.85) was selected to match one of the frequencies to the observed value, and the agreement between the observed and calculated frequency of the second rotamer's vibration was analyzed.

**Table S3. Calculated unscaled (scaled) and observed frequencies of the carbonyl group vibrations in different conformations of the triplet excited states***

| **State** | **syn** | **E** | **Z** |
|---|---|---|---|
| $T_1$ | 2033(1728) | 1995(1696) | 2018(1715) |
| $T_2$ | 1953(1660) | 1949(1657) | 1924(1635) |
| Experimental | 1655 | | 1662 |

* Values calculated by CIS/6-31G*

The experimental data imply that the band that belongs to the Z-conformation appears at a higher frequency than the band of the Norrish Type II inactive conformation. In $T_1$, the calculations predict the frequency of Z-conformer to be higher than the frequency of the E-conformer and lower than the frequency of the syn-conformer. In $T_2$, the signals from both inactive conformations are calculated to have the higher frequency than that of the Z-conformer.

According to both DFT and HF calculations, the ground state molecule of MPG contains planar benzoyl and ester moieties, tilted with respect to each other. The dihedral angle between the two carbonyl groups thus adequately describes the geometry of a molecule. Upon excitation, an electron is promoted to a π* molecular orbital (LUMO)

which introduces a π-character into the diketone C-C bond, thus making a molecule more planar (Figure S7). Accordingly, the diketone dihedral angle changes from ~ 127 in the ground state to ~ 155$^{o}$ in $T_1$ and to 180$^{o}$ in $T_2$ (data shown are for the E-conformer of MPG). The molecules in Z-conformation were less planar than the corresponding E-conformations. Both calculated molecular geometries and vibrational frequencies did not allow us to unambiguously attribute the Norrish Type II inactive conformer to either E- or syn-conformer of the APGs.

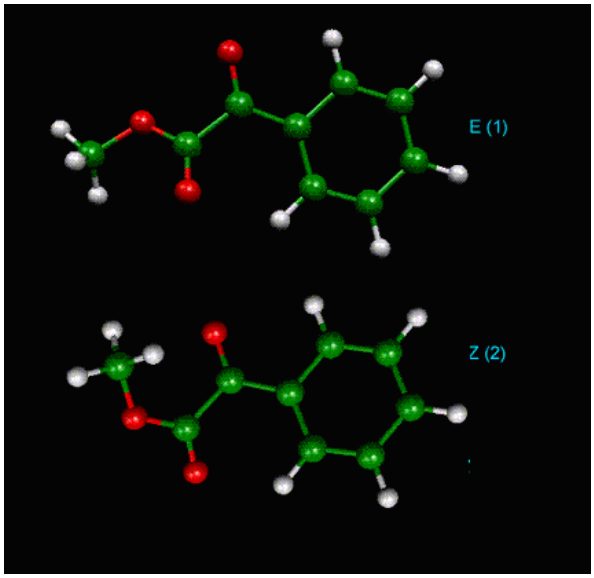



**Figure S7**. Z and E conformers of methyl phenylglyoxylate calculated using CIS/6-31G