

# Stable Radicals During Photodecarbonylations of Trityl-alkyl Ketones Enable Solid State Reactions through Primary and Secondary Radical Centers

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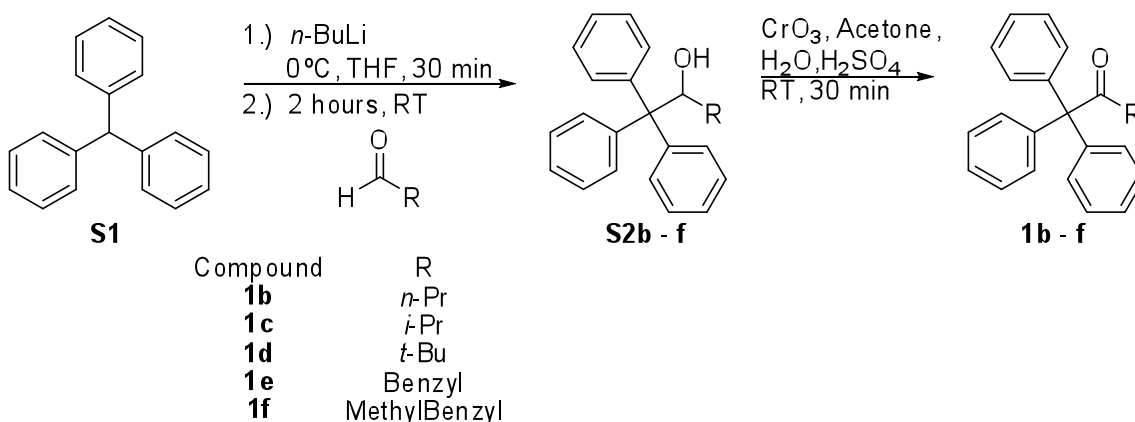
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**General Methods:** All chemicals were purchased from Sigma-Aldrich Co. Inc. and used without further purification. Anhydrous THF was acquired via distillation from sodium. Silica used for purification was Silica-P flash silica gel (40-62 Å), purchased from SiliCycle Inc. <sup>1</sup>H and <sup>13</sup>C NMR was acquired on a Bruker Advance AV300, AV400, or DRX500. IR spectra were obtained with a Perkin-Elmer Spectrum instrument equipped with a universal attenuated total reflectance (ATR) accessory. Mass spectra was acquired on an Applied Biosystems Voyager DE-STR-MALDI-TOF. Gas Chromatography data was acquired on a Hewlett-Packard 5890 Series II Gas Chromatography equipped with an HP3396 Series II integrator and HP-5 capillary column of dimension 25 m × 0.2 mm with a film thickness of 0.11 mm. UV-vis spectra were taken on an Ocean Optics USB2000.

**Scheme S1. Synthesis of Trityl ketones 1b – f.**



**General Synthesis of S2b – f.**

Following a modified procedure by Seebach,<sup>1</sup> to a flame-dried, 100 mL round bottom flask, 30 mL of anhydrous THF and 2.5 grams of **S1** (1 eq, 10 mmol) were added under an Argon atmosphere. The solution was cooled to 0 °C, and *n*-BuLi (1.6 M in hexanes) was added (1.2 eq, 7.7 mL, 12 mmol). This was allowed to stir for 30 minutes at 0 °C during which time it developed a deep red color. To the red solution, freshly distilled aldehyde (2 eq., 20 mmol) was added and the solution was allowed to warm to room temperature. After stirring for two hours at room temperature, the reaction was quenched by slow addition of 0.1 M HCl, and extracted with diethyl ether (4 X 15 ml). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvents were removed under reduced pressure, and subjected to column chromatography (1:9 diethyl ether:hexane). The resulting crystalline solid was further recrystallized from ethanol. All characterization agreed well with reported literature values.

**Characterization of S2b – f.**

**1,1,1-triphenyl-2-pentanol (S2b).<sup>1</sup>**

Yield 78%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.57 (m, 6H), 7.31 (m, 9H), 4.46 (m, 1H), 2.43 (br. s, 1H), 1.54 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.6, 129.6, 127.6, 126.6, 82.9, 60.8, 39.5, 20.2, 13.7; FTIR (solid, HATR, cm<sup>-1</sup>): 3054, 2966, 1597, 1493, 1444, 1122, 757, 728, 704; MS (EI): calcd. 316; found 243 (triphenylmethyl), 316 (M<sup>+</sup>).

**1,1,1-triphenyl-3-methyl-2-butanol (S2c).<sup>1</sup>**

Yield 31%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.59 (m, 6H), 7.25 (m, 9H), 4.21 (dd, *J* = 3 Hz, 1H), 2.24 (br. s, 1H), 1.96 (m, 1H), 1.01 (d, *J* = 7.0, 3H), 0.90 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 147.7, 129.7, 128.0, 126.0, 83.2, 59.6, 33.7, 20.7, 17.6; FTIR (solid, HATR, cm<sup>-1</sup>): 3552, 3061, 2975, 1594, 1493, 1465, 1447, 1442, 757, 746, 705; MS (EI): calcd. 316; found 244 (triphenylmethyl), 316 (M<sup>+</sup>).

**1,1,1-triphenyl-3,3-dimethyl-2-butanol (S2d).**

Yield 61%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.57 (m, 6H), 7.25 (m, 9H), 5.42(s, 1H), 2.02 (br. s, 1H), 0.69 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 148.3, 141.6, 131.1, 129.5, 128.5, 127.8, 126.7, 126.6, 80.5, 61.6, 43.3; FTIR (solid, HATR, cm<sup>-1</sup>): 3556, 3060, 2983, 2970, 2934, 1596, 1583, 1494, 1477, 1446, 1398, 1366, 856, 744, 728, 705; MS (EI): calcd. 330; found 243 (triphenylmethyl), 330 (M<sup>+</sup>).

### 1,1,1,3-tetraphenyl-2-propanol (S2e).

Yield 66%; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.25-7.55 (m, 20H), 5.51 (d, *J* = 9.6 Hz, 1H), 3.13 (d, *J* = 9.6, 2H), 1.75 (br. s, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 140.3, 130.1, 129.7, 129.3, 128.6, 128.1, 126.5, 126.4, 75.7, 62.6, 40.7; FTIR (solid, HATR, cm<sup>-1</sup>): 3564, 3551, 3056, 3026, 2932, 1599, 1494, 1447, 766, 745, 705; MS (EI): calcd. 364; found 243 (triphenylmethyl), 364 (M<sup>+</sup>).

### 1,1,1,3-tetraphenyl-3-methyl-2-propanol (S2f).

Yield 56%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25-7.55 (m, 20H), 5.78 (d, *J* = 7.5 Hz, 1H), 3.15 (dd, *J* = 7.5 and 7.3 Hz, 1H), 2.69 (br. s, 1H), 0.31 (d, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.7, 131.1, 129.6, 129.1, 128.9, 128.1, 126.6, 126.1, 76.1, 63.7, 41.6, 16.7.

### General Synthesis of 1b – f.

Following a modified procedure by Seebach,<sup>1</sup> to a 100 mL round bottom flask, alcohol **S2b – f** (1 eq) was added to 30 mL of acetone at 0 °C. To this solution, CrO<sub>3</sub> (1.25 eq) dissolved in 2 mL of H<sub>2</sub>O and 0.5 mL H<sub>2</sub>SO<sub>4</sub> was added over 20 minutes. When the reaction was complete, as monitored by TLC, the solution was filtered through cotton and 20 mL of H<sub>2</sub>O was added and extracted with diethyl ether (4 X 15 ml). The combined organic layers were washed with brine and dried over magnesium sulfate. The solvents were removed under reduced pressure, and subjected to column chromatography (1:9 diethyl ether:hexane). The resulting crystalline solid was further recrystallized from ethanol. All characterization agreed well with reported literature values.

### Characterization of 1b – f.

#### 1,1,1-triphenyl-2-pentanone (1b).<sup>1</sup>

Yield 98%; m.p. 115-116 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.29 (m, 6H), 7.28 (m, 9H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.38 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 208.5, 142.4, 130.4, 128.0, 126.7, 73.2, 43.7, 19.2, 13.8; FTIR (solid, HATR, cm<sup>-1</sup>): 3054, 2964, 1711, 1598, 1495, 1445, 1122, 1086, 1059, 1036, 758, 727; MS (EI): calcd. 314; found 243 (triphenylmethyl), 314 (M<sup>+</sup>); UV-Vis (hexane), λ<sub>Max</sub> = 300.1 nm, ε = 336.6 cm<sup>-1</sup>M<sup>-1</sup>.

#### 1,1,1-triphenyl-3-methyl-2-butanone (1c).<sup>1</sup>

Yield 98%; m.p. 79-80 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.41 (m, 6H), 7.33 (m, 6H), 7.24 (m, 3H), 3.08 (m, 1H), 0.80 (d, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 213.6, 142.5, 130.7, 128.3, 126.9, 74.5, 38.6, 22.1; FTIR (solid, HATR, cm<sup>-1</sup>): 3060, 2974, 1703, 1596, 1493, 1466, 1447, 1442, 1380, 1088, 1052, 1037, 756, 745, 704; MS (EI): calcd. 314; found 243 (triphenylmethyl), 314 (M<sup>+</sup>); UV-Vis (hexane), λ<sub>Max</sub> = 305.1 nm, ε = 404.3 cm<sup>-1</sup>M<sup>-1</sup>.

#### 1,1,1-triphenyl-3,3-dimethyl-2-butanone (1d).

Yield 95%; m.p. 94-95 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.31 (m, 12H), 7.22 (m, 3H), 1.02 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 213.5, 142.3, 131.0, 127.8, 126.7, 74.2, 47.3, 31.1; FTIR (solid, HATR, cm<sup>-1</sup>): 3061, 2982, 2969, 2934, 1687, 1596, 1583, 1494, 1476, 1462, 1446, 1398, 1367, 1087, 1052, 856, 752, 728, 705. MS (EI): calcd. 328; found 243 (triphenylmethyl), 328 (M<sup>+</sup>); UV-Vis (hexane), λ<sub>Max</sub> = 309.9 nm, ε = 967 cm<sup>-1</sup>M<sup>-1</sup>.

#### 1,1,1,3-tetraphenyl-2-propanone (1e).<sup>2</sup>

Yield 40%; m.p. 115-116 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.32-7.18 (m, 18H), 6.96 (dd, 2H), 3.66 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 205.6, 142.0, 135.3, 130.8, 129.6, 128.4, 128.2, 127.1, 126.7, 73.6, 47.6; FTIR (solid, HATR, cm<sup>-1</sup>): 3067, 3024, 2934, 1712, 1602, 1494, 1449, 1303, 1094, 1033, 1003, 764, 751, 743, 704, 617; MS (EI): calcd. 362; found 243 (triphenylmethyl), 362 (M<sup>+</sup>); UV-Vis (hexane), λ<sub>Max</sub> = 305.1 nm, ε = 330.6 cm<sup>-1</sup>M<sup>-1</sup>.

#### 1,1,1,3-tetraphenyl-3-methyl-2-propanone (1f).

Yield 66%; m.p. 109-110 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (m, 6H), 7.36 (m, 14H), 4.32 (d, *J* = 6.5 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 209.7, 142.7, 131.9, 130.8, 128.2, 128.1, 127.5, 126.8, 126.4, 74.6, 50.4, 24.3; FTIR (solid, HATR, cm<sup>-1</sup>): 3055, 3015, 2924, 2865, 1701, 1597, 1491, 1448, 1370, 1104, 1062, 1043, 1002, 867, 764, 669; HRMS (MALDI-TOF): calcd. 376.1827 (M<sup>+</sup>), 399.1725 (M + Na<sup>+</sup>); found 272.9716 (triphenylmethyl + Na<sup>+</sup>), 399.0543 (M + Na<sup>+</sup>); UV-Vis (hexane), λ<sub>Max</sub> = 307.0 nm, ε = 637.9 cm<sup>-1</sup>M<sup>-1</sup>.

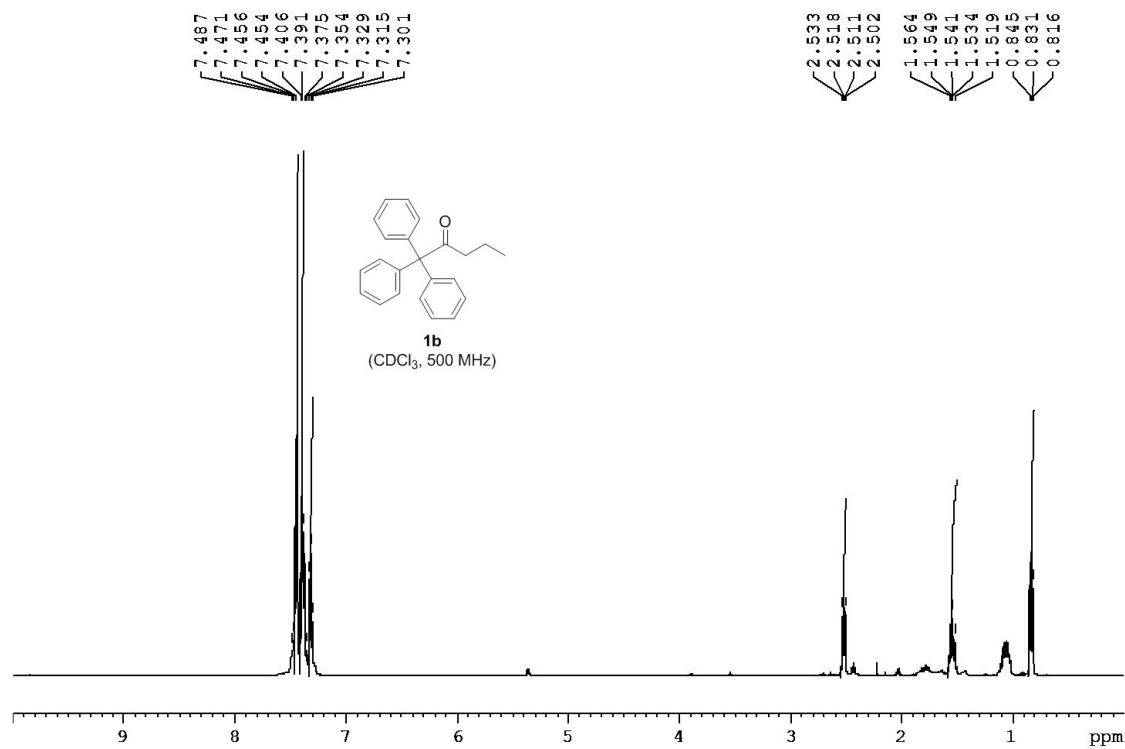


Figure S1. <sup>1</sup>H NMR spectra of **1b** in CDCl<sub>3</sub>.

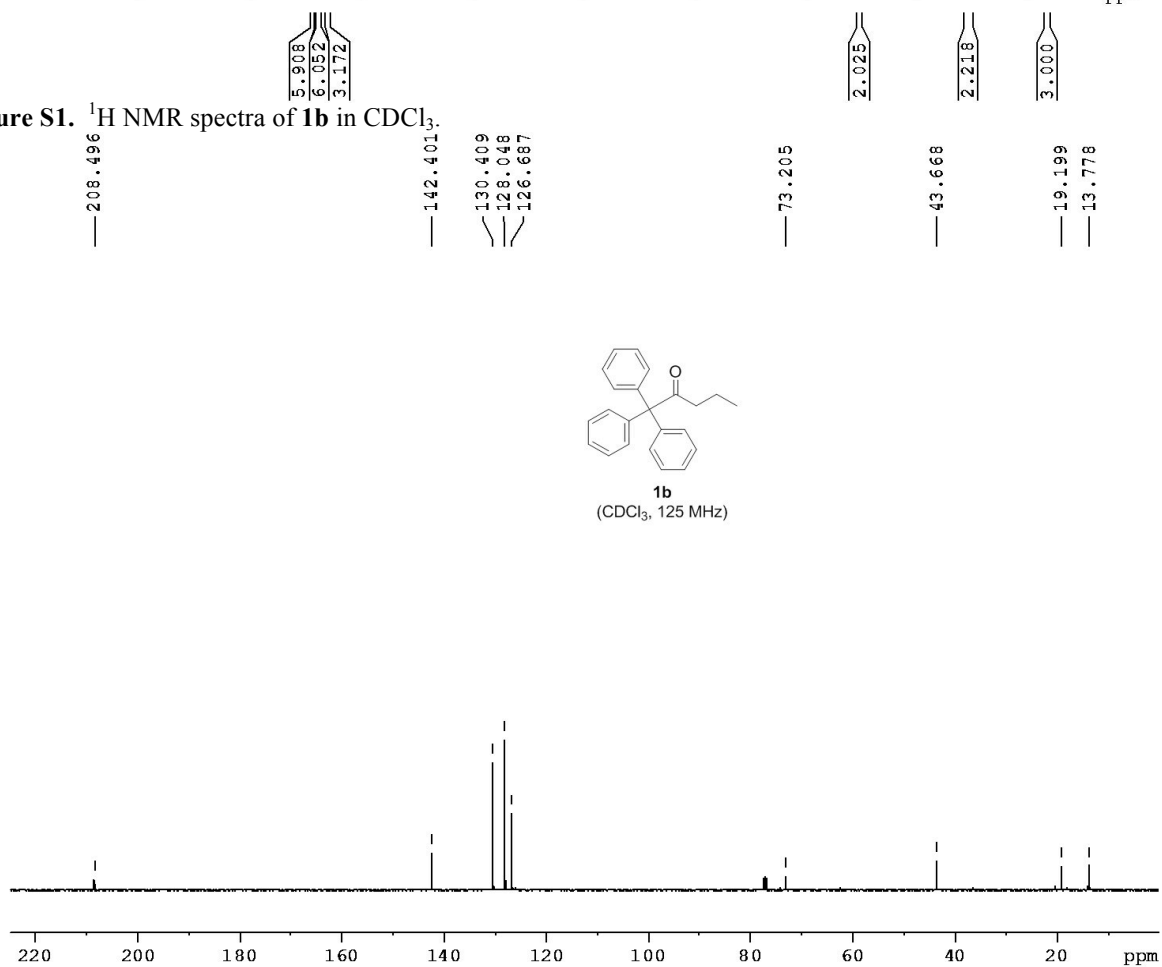


Figure S2. <sup>13</sup>C NMR spectra of **1b** in CDCl<sub>3</sub>.

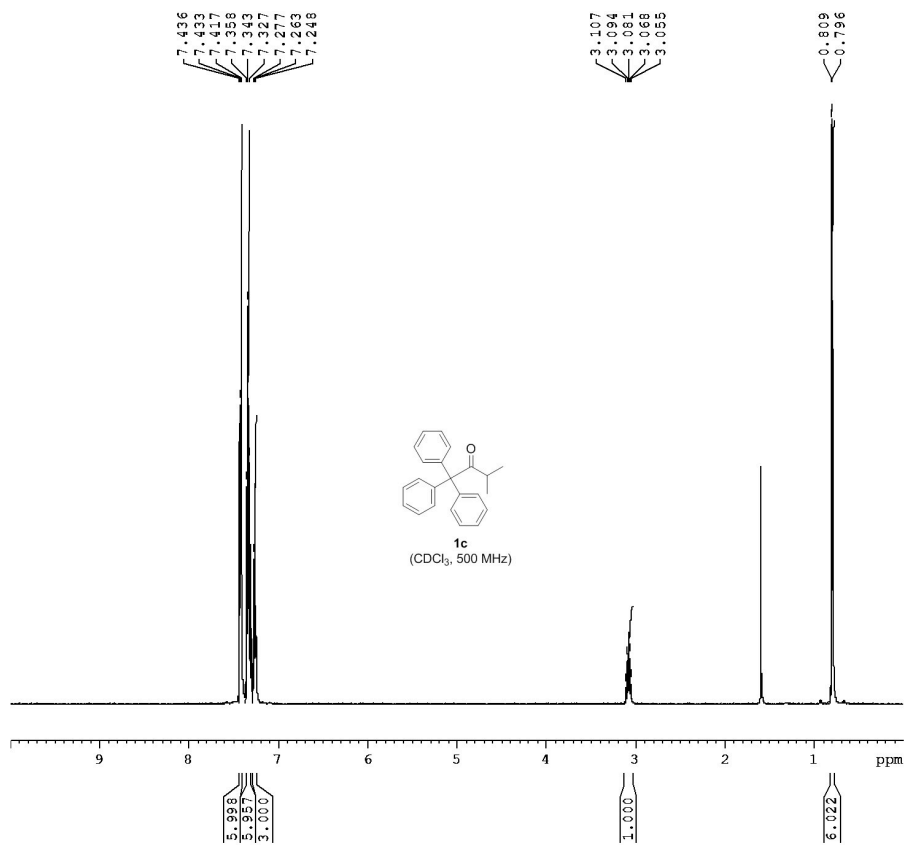


Figure S3. <sup>1</sup>H NMR spectra of **1c** in CDCl<sub>3</sub>.

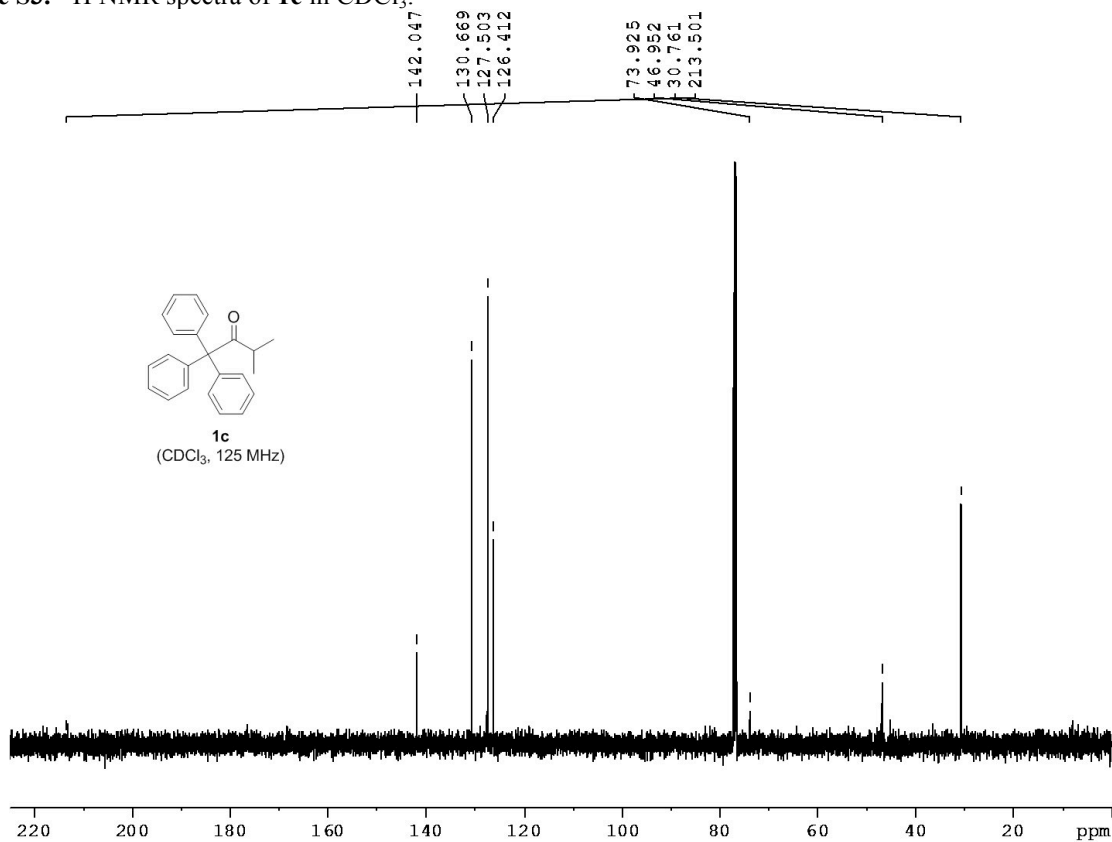


Figure S4. <sup>13</sup>C NMR spectra of **1c** in CDCl<sub>3</sub>.

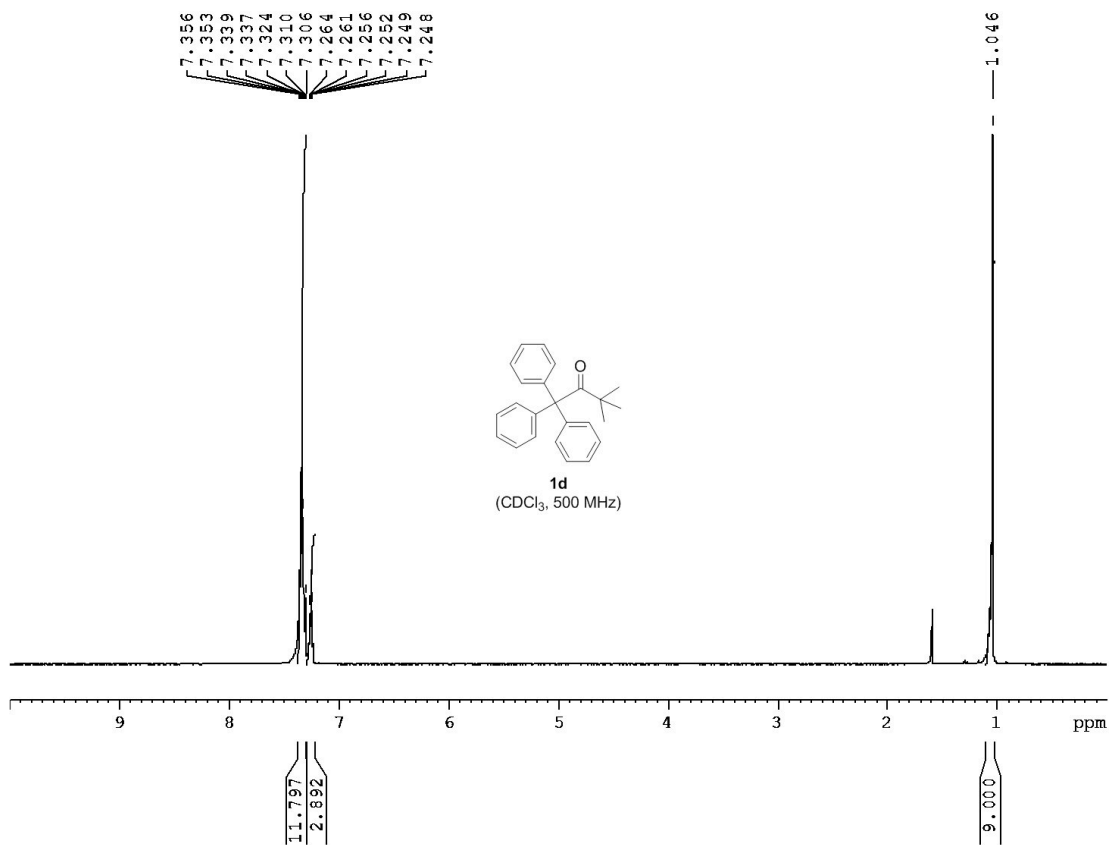


Figure S5. <sup>1</sup>H NMR spectra of **1d** in CDCl<sub>3</sub>.

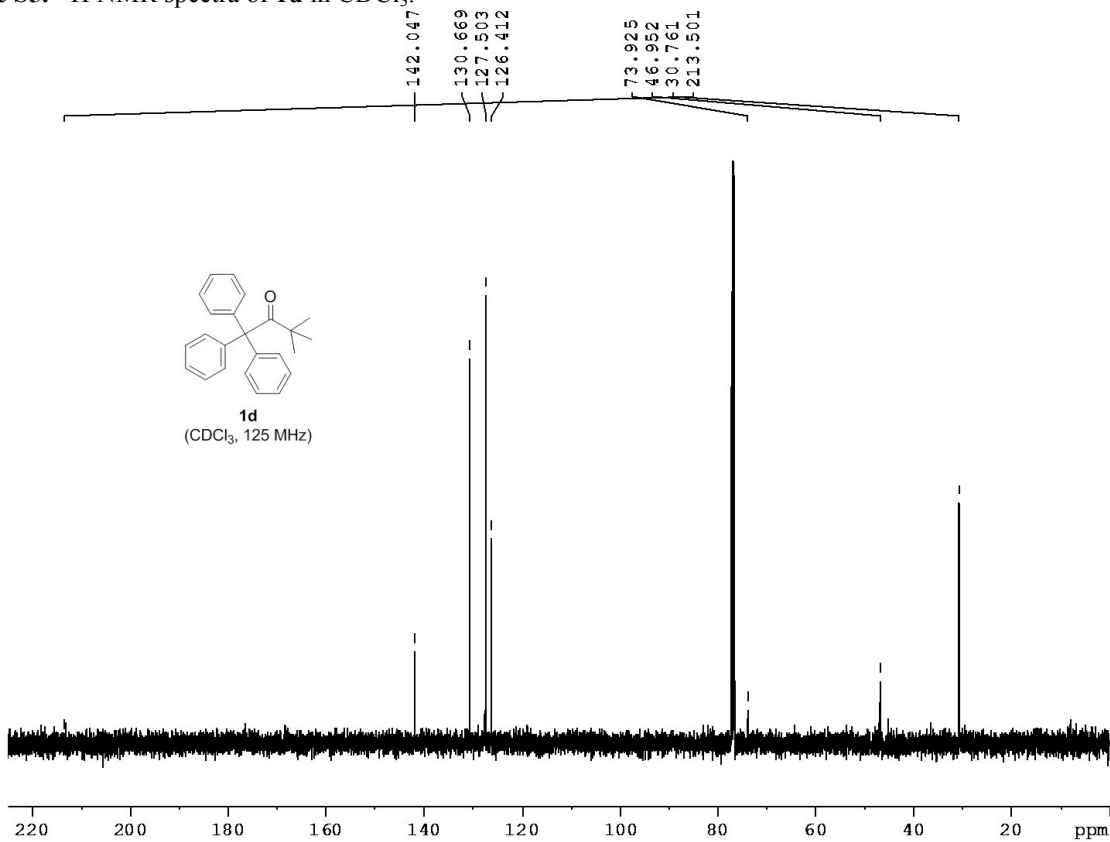


Figure S6. <sup>13</sup>C NMR spectra of **1d** in CDCl<sub>3</sub>.

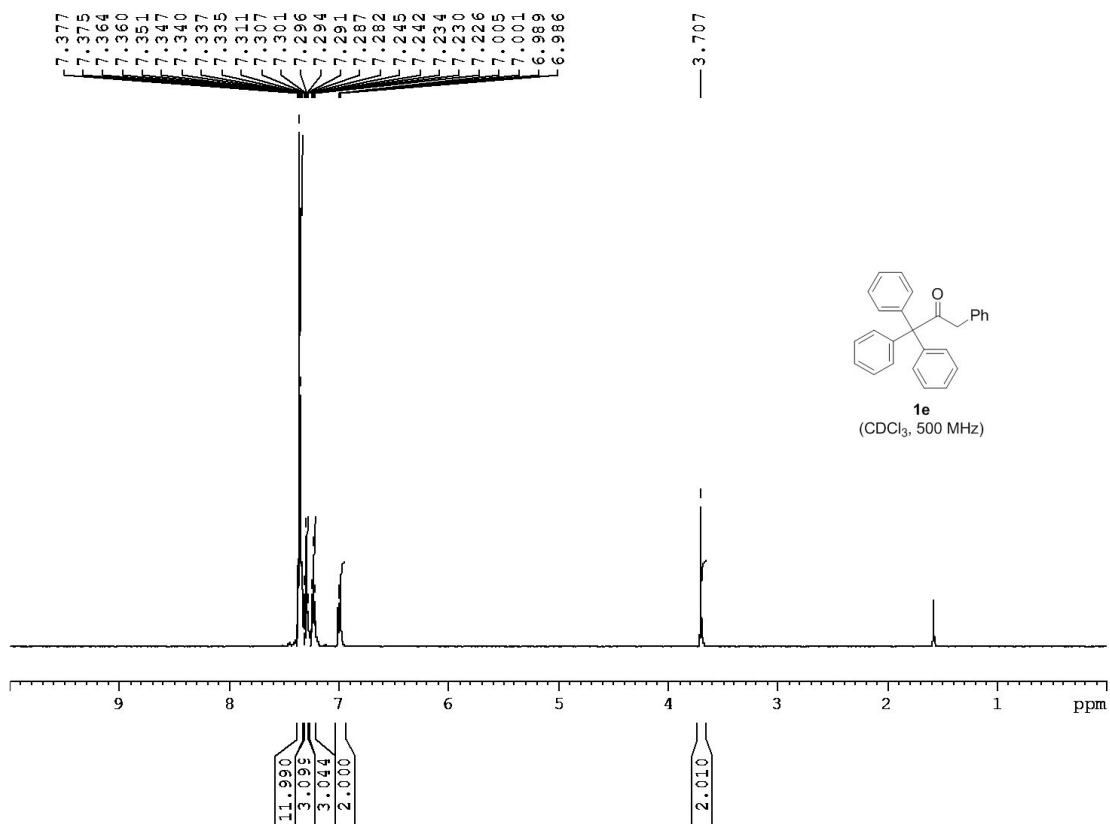


Figure S7. <sup>1</sup>H NMR spectra of **1e** in CDCl<sub>3</sub>.

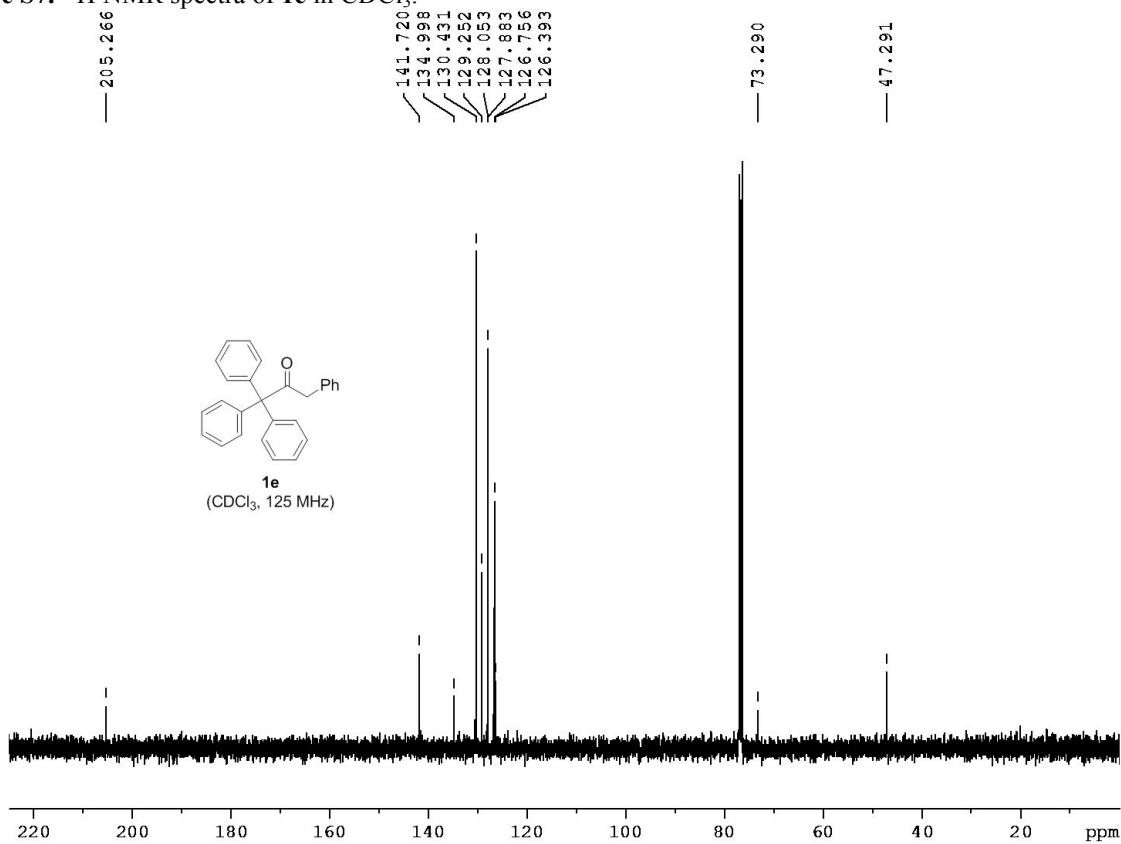


Figure S8. <sup>13</sup>C NMR spectra of **1e** in CDCl<sub>3</sub>.

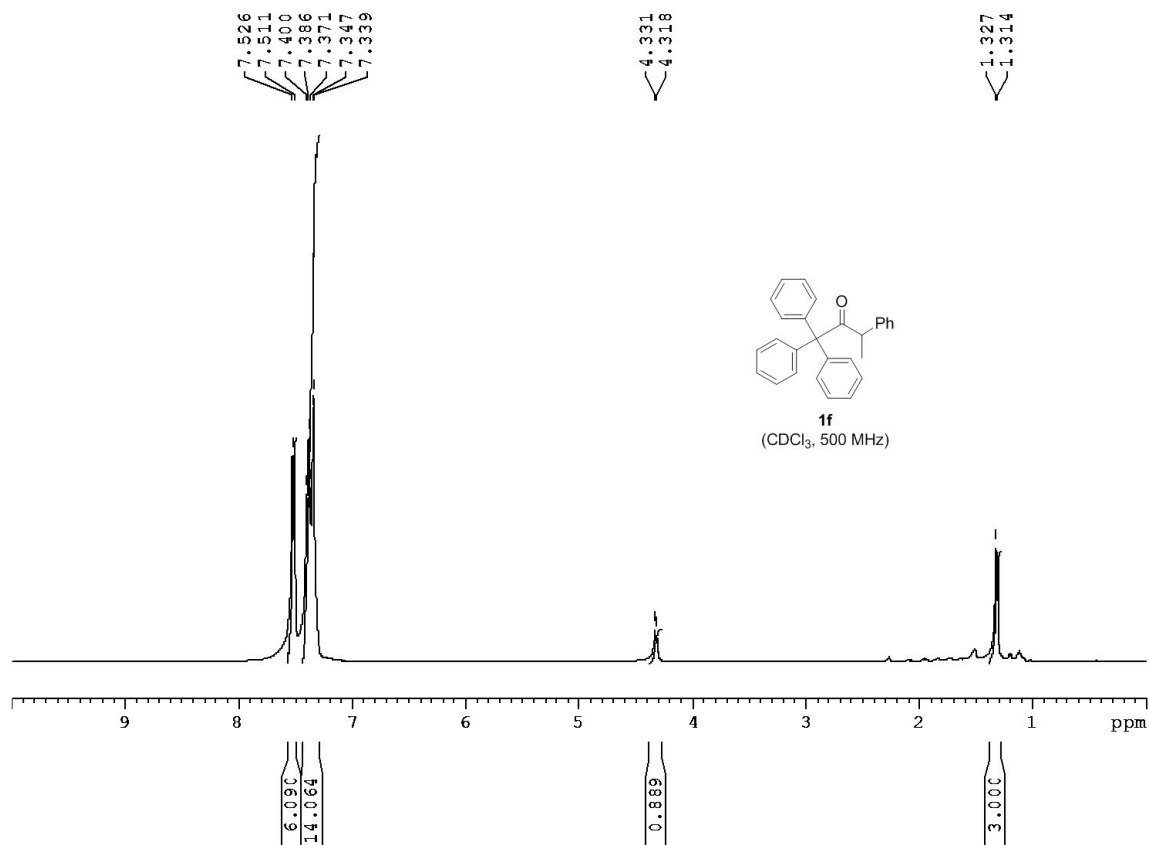


Figure S9. <sup>1</sup>H NMR spectra of **1f** in CDCl<sub>3</sub>.

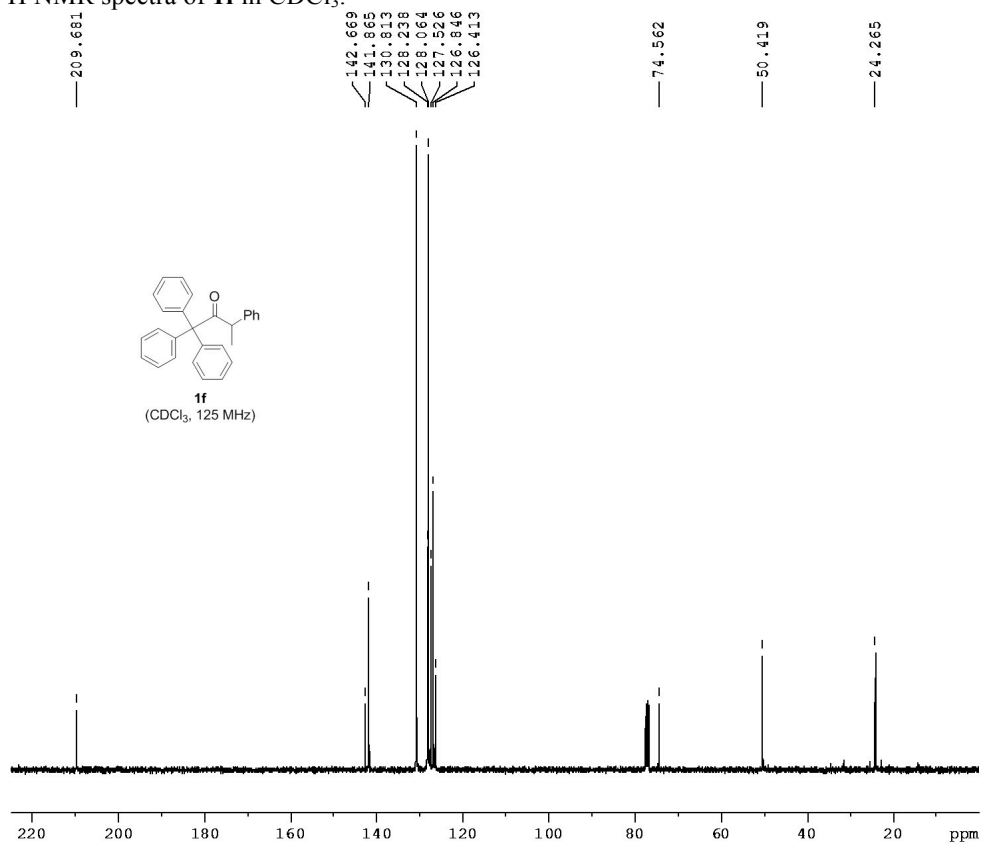


Figure S10. <sup>13</sup>C NMR spectra of **1f** in CDCl<sub>3</sub>.



**Photolysis in Benzene.**

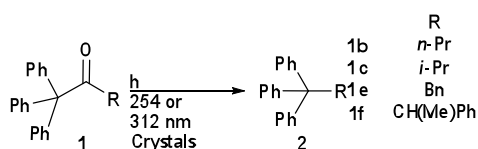
Compounds **1a - f** were dissolved in benzene (0.1 M) and degassed for 15 minutes with Argon. Samples were then irradiated at 312 nm using a Rayonet photochemical reactor (BLE-8T312). Aliquots were removed every 10 minutes and reaction progress was monitored by gas chromatography. Because the reactions produced numerous products in minor yields, the exact identification of the products was not attempted.

**Photolysis of Bulk Crystalline Samples.**

Powdered samples (ca. 5 mg) of crystalline material were acquired by crushing large single crystals with two pyrex plates, such that the powder remained on the plates. Plates were then irradiated at room temperature, without a Pyrex filter, at 254 nm (Hanovia 400W mercury-vapor lamp) or 312 nm (in a Rayonet photochemical reactor using 312 nm lamps [BLE-8T312]). Aliquots were removed hourly and reaction progress was monitored by gas chromatography. Moderate quantities of crystals (ca. 30 mgs) were irradiated for extended periods of time and subjected to column chromatography (20:1 hexane:diethyl ether) to isolate the major product.

## Characterization of photolyzed products.

### Scheme S2.



#### 1,1,1-triphenylbutane (2b).<sup>3</sup>

Yield 100%; m.p. 58-60 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 (m, 6H), 7.23 (m, 6H), 7.15 (m, 3H), 2.52 (t, *J*=8.0 Hz, 2H), 1.05 (m, 2H), 0.90 (t, *J*= 7.3, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.9, 129.4, 127.9, 125.9, 56.9, 43.0, 19.3, 14.9; MS (EI): calcd. 286; found 243 (triphenylmethyl), 286 (M<sup>+</sup>).

#### 1,1,1-triphenyl-*i*-butane (2c).<sup>4</sup>

Yield 100%; m.p. 92-94 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (m, 6H), 7.27 (m, 6H), 7.14 (m, 3H), 3.59 (m, 1H), 0.83 (d, *J*=6.6 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.8, 129.7, 128.5, 125.7, 61.7, 30.7, 19.3; MS (EI): calcd. 286; found 243 (triphenylmethyl), 286 (M<sup>+</sup>).

#### 1,1,1,2-tetraphenylethane (2e).<sup>5</sup>

Yield 100%; m.p. 106-108 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.0-7.48 (m, 18H), 6.99 (m, 2H), 3.96 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 146.8, 138.7, 131.3, 130.0, 127.8, 127.5, 126.2, 126.1, 58.7, 46.5; MS (EI): calcd. 334; found 243 (triphenylmethyl), 334 (M<sup>+</sup>).

#### 1,1,1,3-tetraphenyl-3-methyl-2-propane (2f).

Yield 100%; m.p. 119-121 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.34-7.42 (m, 6H), 7.11-7.42 (m, 9H), 6.97-7.09 (m, 3H), 6.65-6.72 (m, 2H), 4.79 (q, *J* = 7.5 Hz, 1H), 1.33 (d, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.4, 143.0, 131.2, 130.8, 127.2, 126.9, 126.1, 125.7, 63.1, 43.6, 19.3. FTIR (solid, HATR, cm<sup>-1</sup>): 3059.5, 2992.1, 1595.6, 1490.5, 1445.8, 1193.2, 1087.6, 772.2, 738.7. MS (MALDI-TOF): calcd. 348; found 243 (triphenylmethyl), 371 (M + Na<sup>+</sup>);.

**Synthesis of Nanocrystalline Suspensions.** Samples to be used for actinometry experiments were prepared by injecting a solution of **1** in acetone (ca. 10  $\mu$ L of a ca. 1M) into 3 mL of vortexing water (millipore). The resulting suspension (ca.  $1 \times 10^{-3}$  M) was sonicated three times at room temperature for 4 min, allowing for 2 min rest between runs.

**Quantum Yield Determination for Nanocrystalline Suspension.** Relative quantum yield determinations were performed with dicumyl ketone ( $\phi = 0.18$ ) as an internal standard in a Rayonet photochemical reactor using 312 nm lamps (BLE-8T312). Quantum yields were determined with equimolar, optically dense suspensions. Two independent suspensions of actinometer and substrate were independently synthesized. The samples were then combined immediately prior to irradiation in a 50 mL quartz Erlenmeyer flask and irradiated for 10 min. Every 2 minutes, an aliquot was removed (approximately one-twentieth of the suspension). The aliquots were subjected to gas chromatography to determine the extent of reaction.

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