Electronic Supplementary information

3-Ketoquinolones as new photoinitiators for free radical photopolymerization under LED.

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1/ Synthesis procedures.

All chemicals used were of reagent grade. The yields refer to the purified products and are not optimized. Merck silica gel 60 (230−400 mesh) was used for column chromatography. Merck thin-layer chromatography (TLC) plates (silica gel 60 F_{254}) were used for TLC. NMR spectra were recorded by a Bruker Avance 400 MHz or a Bruker DMX 500 MHz or Bruker DMX 600 MHz spectrometer in the indicated solvents; the values of the chemical shifts (δ) were expressed in ppm.

N-(3-methoxyphenyl)-3-oxo-3-phenylpropanamide, (**KQ1-1b**)

19.22 g (156.06 mmoles) of m-Anisidine and 25.00 g (130.07 mmoles) of Ethyl benzoylacetate were dissolved in 75 mL of N,N-Dimethylformamide. The reaction mixture was stirred at 150°C for 4 hours, eliminating ethanol by distillation. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 625 mL of 6M hydrochloric acid and extracted with 375 mL of diethyl ether. The organic layer was washed with 375 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 27.92 g of a yellow oil (yield 80%).

^{1}H-NMR ($CDCl_3$, δ ppm): 3.80 (s, 3H), 4.10 (s, 2H), 6.68 (d, 1H), 7.08 (d, 1H), 7.22 (t, 1H), 7.31 (s, 1H), 7.51 (t, 2H), 7.64 (t, 1H), 8.02 (d, 2H), 9.30 (br s, 1H).

3-[4-(2-methylpropyl)phenyl]-3-oxo-N-phenylpropanamide, (**KQ2-1a**)

2.38 g (25.56 mmoles) of Aniline and 5.00 g (21.34 mmoles) of Methyl 3[4(2methylpropyl)phenyl]3oxopropanoate were dissolved in 60 mL of N,N-Dimethylformamide. The reaction mixture was stirred at 150°C for 3.5 hours, eliminating methanol by distillation. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 300 mL of 6M hydrochloric acid and extracted with 250 mL of diethyl ether. The organic layer was washed with 250 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 5.97 g of an off-white solid (yield 95%).

^{1}H-NMR ($CDCl_3$, δ ppm): 0.90 (d, 6H), 1.90 (m, 1H), 2.54 (d, 2H), 4.07 (s, 2H), 7.10 (t, 1H), 7.25 (d, 2H), 7.35 (t, 2H), 7.60 (d, 2H), 7.95 (d, 2H), 9.35 (br s, 1H).

3-[4-(2-methylpropyl)phenyl]-N-[3-(methylsulfanyl)phenyl]-3-oxopropanamide, (**KQ3-1d**)

4.95 g (35.55 mmoles) of 3-(Methylthio)aniline and 7.57 g (32.31 mmoles) of Methyl 3[4(2methylpropyl)phenyl]3oxopropanoate were dissolved in 80 mL of N,N-Dimethylformamide. The reaction mixture was stirred at 150°C for 4 hours, eliminating methanol by distillation. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 400 mL of 6M hydrochloric acid and extracted with 300 mL of diethyl ether. The organic layer was washed with 300 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 10.37 g of a yellow oil (yield 94%).

^{1}H-NMR ($CDCl_3$, δ ppm): 0.90 (d, 6H), 1.90 (m, 1H), 2.47 (s, 3H), 2.54 (d, 2H), 4.07 (s, 2H), 7.00 (d, 1H), 7.21 (t, 1H), 7.27 (d, 2H), 7.32 (d, 1H), 7.55 (s, 1H), 7.93 (d, 2H), 9.40 (br s, 1H).

N-(3,5-dimethoxyphenyl)-3-[4-(2-methylpropyl)phenyl]-3-oxopropanamide, (**KQ4-1e**)

8.05 g (52.55 mmoles) of 3,5-Dimethoxyaniline and 11.20 g (47.80 mmoles) of Methyl 3[4(2methylpropyl)phenyl]3oxopropanoate were dissolved in 100 mL of N,N-Dimethylformamide. The reaction mixture was stirred at 150°C for 4 hours, eliminating methanol by distillation. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 500 mL of 6M hydrochloric acid and extracted with 250 mL of ethyl acetate/tolune (1:1). The organic layer was separated and washed with 300 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 16.88 g of an off-white solid (yield 99%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.87 (d, 6H), 1.89 (m, 1H), 2.53 (d, 2H), 3.71 (s, 6H), 4.10 (s, 2H), 6.23 (t, 1H), 6.84 (d, 2H), 7.33 (d, 2H), 7.93 (d, 2H).

N-(3,4-dimethoxyphenyl)-3-[4-(2-methylpropyl)phenyl]-3-oxopropanamide, (**KQ5-1c**)

8.20 g (53.53 mmoles) of 3,4-Dimethoxyaniline and 11.40 g (48.66 mmoles) of Methyl 3[4(2methylpropyl)phenyl]3oxopropanoate were dissolved in 120 mL of N,N-Dimethylformamide. The reaction mixture was stirred at 150°C for 3 hours, eliminating methanol by distillation. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, diluted with 300 mL of toluene/ethyl acetate (60:40) and poured into 500 mL of 6M hydrochloric acid. The organic layer was separated and washed with 500 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 17.00 g of a grey solid (yield 98%).

^{1}H-NMR ($CDCl_3$, δ ppm): 0.90 (d, 6H), 1.90 (m, 1H), 2.52 (d, 2H), 3.84 (s, 3H), 3.87 (s, 3H), 4.07 (s, 2H), 6.80 (d, 1H), 7.01 (dd, 1H), 7.27 (d, 2H), 7.30 (d, 1H), 7.93 (d, 2H), 9.25 (br s, 1H).

(4E)-2-[(E)-benzoyl]-N-(3-methoxyphenyl)-5-phenylpenta-2,4-dienamide, (**KQ1-2b**)

To a warm solution of 22.06 g (81.92 mmoles) of **KQ1-1b** and 10.83 g (81.95 mmoles) of trans-Cinnamaldehyde in 220 mL of toluene were added in sequence 0.698 g (8.197 mmoles) of piperidine, 0.492 g (8.193 mmoles) of acetic acid and 11.03 g of anhydrous sodium sulfate. The reaction mixture was refluxed for 1 hour under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 300 mL of brine and extracted with 220 mL of ethyl acetate. The organic layer was washed with 300 mL (x3) of water, dried

over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 31.40 g of crude as a mixture of two regioisomers. The crude was used in the next step without any further purification.

(4E)-2-[(E)-4-(2-methylpropyl)benzoyl]-N,5-diphenylpenta-2,4-dienamide, (**KQ2-2a**)

To a warm solution of 5.90 g (19.97 mmoles) of **KQ2-1a** and 2.64 g (19.98 mmoles) of trans-Cinnamaldehyde in 70 mL of toluene were added in sequence 0.170 g (2.00 mmoles) of piperidine, 0.120 g (2.00 mmoles) of acetic acid and 2.95 g of anhydrous sodium sulfate. The reaction mixture was refluxed for 1 hour under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 175 mL of brine and extracted with 70 mL (x2) of dichloromethane. The organic layer was washed with 175 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 8.17 g of crude as a mixture of two regioisomers. The crude was used in the next step without any further purification.

(4E)-2-[(E)-4-(2-methylpropyl)benzoyl]-N-[3-(methylsulfanyl)phenyl]-5-phenylpenta-2,4-dienamide, (**KQ3-2d**)

To a warm solution of 10.00 g (29.29 mmoles) of **KQ3-1d** and 3.87 g (29.28 mmoles) of trans-Cinnamaldehyde in 120 mL of toluene were added in sequence 0.249 g (2.92 mmoles) of piperidine, 0.175 g (2.91 mmoles) of acetic acid and 5.00 g of anhydrous sodium sulfate. The reaction mixture was refluxed for 1 hour under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 250 mL of brine and extracted with 150 mL (x2) of dichloromethane. The organic layer was washed with 150 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 13.00 g of crude as a mixture of two regioisomers. The crude was used in the next step without any further purification.

(4E)-N-(3,5-dimethoxyphenyl)-2-[(E)-4-(2-methylpropyl)benzoyl]-5-phenylpenta-2,4-dienamide, (**KQ4-2e**)

To a warm solution of 16.88 g (47.49 mmoles) of **KQ4-1e** and 6.28 g (47.52 mmoles) of trans-Cinnamaldehyde in 170 mL of toluene were added in sequence 0.405 g (4.76 mmoles) of piperidine, 0.285 g (4.75 mmoles) of acetic acid and 8.44 g of anhydrous sodium sulfate. The reaction mixture was refluxed for 1 hour under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 200 mL of brine and extracted with 200 mL of ethyl acetate. The organic layer was washed with 200 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 22.30 g of crude as a mixture of two regioisomers. The crude was used in the next step without any further purification.

(4E)-N-(3,4-dimethoxyphenyl)-2-[(E)-4-(2-methylpropyl)benzoyl]-5-phenylpenta-2,4-dienamide, (**KQ5-2c**)

To a warm solution of 17.00 g (47.83 mmoles) of **KQ5-1c** and 6.32 g (47.82 mmoles) of trans-Cinnamaldehyde in 200 mL of tolune were added in sequence 0.407 g (4.78 mmoles) of piperidine, 0.287 g (4.78 mmoles) of acetic acid and 8.50 g of anhydrous sodium sulfate. The reaction mixture was refluxed for 1 hour under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 400 mL of brine and extracted with 200 mL (x2) of dichloromethane. The organic layer was washed with 200 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 22.40 g of crude as a mixture of two regioisomers. The crude was used in the next step without any further purification.

(4E)-2-[(E)-benzoyl]-N-(3-methoxyphenyl)-N-methyl-5-phenylpenta-2,4-dienamide, (**KQ1-3b**)

9.66 g (86.09 mmoles) of Potassium tert-butoxide were slowly added in portions under stirring to an ice-cooled solution of 31.40 g (81.89 mmoles as crude) of **KQ1-2b** in 310 mL of anhydrous Tetrahydrofuran. After stirring for 10 minutes, 12.81 g (90.25 mmoles) of Iodomethane were cautiously added to the reaction. Then the resulting mixture was stirred at room temperature for 1.5 hours under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 150 mL of ammonium chloride saturated solution, diluted with 150 mL of water and extracted with 300 mL of ethyl acetate. The organic layer was washed with 300 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 32.12 g of crude. The crude was used in the next step without any further purification.

(4E)-N-methyl-2-[(E)-4-(2-methylpropyl)benzoyl]-N,5-diphenylpenta-2,4-dienamide, (**KQ2-3a**)

2.35 g (20.94 mmoles) of Potassium tert-butoxide were slowly added in portions under stirring to an ice-cooled solution of 8.17 g (19.95 mmoles as crude) of **KQ2-2a** in 125 mL of anhydrous Tetrahydrofuran. After stirring for 10 minutes, 3.11 g (21.91 mmoles) of Iodomethane were cautiously added to the reaction. Then the resulting mixture was stirred at room temperature for 1.5 hours under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 50 mL of ammonium chloride saturated solution, diluted with 100 mL of water and extracted with 150 mL of ethyl acetate. The organic layer was washed with 150 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 8.45 g of crude. The crude was used in the next step without any further purification.

(4E)-N-methyl-2-[(E)-4-(2-methylpropyl)benzoyl]-N-[3-(methylsulfanyl)phenyl]-5-phenylpenta-2,4-dien amide, (**KQ3-3d**)

3.36 g (29.94 mmoles) of Potassium tert-butoxide were slowly added in portions under stirring to an ice-cooled solution of 13.00 g (28.53 mmoles as crude) of **KQ3-2d** in 180 mL of anhydrous Tetrahydrofuran. After stirring for 10 minutes, 4.45 g (31.35 mmoles) of Iodomethane were cautiously added to the reaction. Then the resulting mixture was stirred at room temperature for 1.5 hours under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 100 mL of ammonium chloride saturated solution, diluted with 100 mL of water and extracted with 200 mL of ethyl acetate. The organic layer was washed with 200 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under

vacuum obtaining 13.40 g of crude. The crude was used in the next step without any further purification.

(4E)-N-(3,5-dimethoxyphenyl)-N-methyl-2-[(E)-4-(2-methylpropyl)benzoyl]-5-phenylpenta-2,4-dienamide, (**KQ4-3e**)

5.60 g (49.91 mmoles) of Potassium tert-butoxide were slowly added in portions under stirring to an ice-cooled solution of 22.30 g (47.49 mmoles as crude) of **KQ4-2e** in 223 mL of anhydrous Tetrahydrofuran. After stirring for 10 minutes, 7.41 g (52.21 mmoles) of Iodomethane were cautiously added to the reaction. Then the resulting mixture was stirred at room temperature for 1.5 hours under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 100 mL of ammonium chloride saturated solution, diluted with 100 mL of water and extracted with 150 mL of ethyl acetate. The organic layer was washed with 100 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 22.26 g of crude. The crude was used in the next step without any further purification.

(4E)-N-(3,4-dimethoxyphenyl)-N-methyl-2-[(E)-4-(2-methylpropyl)benzoyl]-5-phenylpenta-2,4-dienamide, (**KQ5-3c**)

5.77 g (51.42 mmoles) of Potassium tert-butoxide were slowly added in portions under stirring to an ice-cooled solution of 22.40 g (47.70 mmoles as crude) of **KQ5-2c** in 300 mL of anhydrous Tetrahydrofuran. After stirring for 10 minutes, 7.65 g (53.90 mmoles) of Iodomethane were cautiously added to the reaction. Then the resulting mixture was stirred at room temperature for 1.5 hours under nitrogen atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 200 mL of ammonium chloride saturated solution, diluted with 200 mL of water and extracted with 300 mL of ethyl acetate. The organic layer was washed with 400 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum obtaining 23.00 g of crude. The crude was used in the next step without any further purification.

3-benzoyl-7-hydroxy-1-methyl-1,2-dihydroquinolin-2-one, (**KQ1-4b**)

9.16 g (68.70 mmoles) of aluminum chloride were slowly added in portions under stirring to a solution of 4.55 g (11.45 mmoles as crude) of **KQ1-3b** in 135 mL of chlorobenzene. The resulting mixture was gradually heated to 120°C and then stirred at this temperature for 1.5 hours. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 450 mL of ice-water and extracted with 100 mL (x4) of dichloromethane/methanol (80:20). The organic layers were collected and the solvent removed by distillation under vacuum. The crude product was treated with 55 mL of toluene/cyclohexane (30:70), made to solidify and the solid washed under stirring at 100°C for 15 minutes. Then the mixture was allowed to cool and the solid recovered by filtration obtaining 2.56 g of an off-white solid (yield 80%).

^{1}H-NMR (DMSO-d_6, δ ppm): 3.55 (s, 3H), 6.82 (dd, 1H), 6.88 (d, 1H), 7.50 (t, 2H), 7.62 (t, 1H), 7.70 (d, 1H), 7.79 (d, 2H), 8.10 (s, 1H).

6,7-dimethoxy-1-methyl-3-[4-(2-methylpropyl)benzoyl]-4-[(1E)-2-phenylethenyl]-1,2,3,4-tetrahydroquinolin-2-one, (**KQ5-4c**)

34.06 g (354.39 mmoles) of Methanesulfonic acid were slowly added under stirring to a solution of 23.00 g (47.56 mmoles as crude) of **KQ5-3c** in 460 mL of dichloromethane. After stirring for 10-15 minutes at room temperature, the reaction mixture was poured into 800 mL of water. The organic layer was separated and washed with 800 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (toluene/ethyl acetate 90:10) followed by crystallization from cyclohexane obtaining 10.11 g of an off-white solid (yield 44%).

^{1}H-NMR ($CDCl_3$, δ ppm): 0.90 (d, 6H), 1.90 (m, 1H), 2.52 (d, 2H), 3.46 (s, 3H), 3.83 (s, 3H), 3.95 (s, 3H), 4.15 (t, 1H), 4.68 (d, 1H), 6.22 (dd, 1H), 6.48 (d, 1H), 6.67 (s, 1H), 6.71 (s, 1H), 7.22-7.35 (m, 7H), 7.91 (d, 2H).

3-benzoyl-7-[(2-ethylhexyl)oxy]-1-methyl-1,2-dihydroquinolin-2-one, (**KQ1**)

To a solution of 3.20 g (11.46 mmoles) of **KQ1-4b** in 35 mL of N,N-Dimethylformamide were added in sequence 4.75 g (34.37 mmoles) of potassium carbonate, 0.34 g (2.27 mmoles) of sodium iodide and 4.43 g (22.94 mmoles) of 2-Ethylhexyl bromide. The reaction mixture was stirred at 80°C for 8 hours. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 200 mL of water and extracted with 100 mL of toluene. The organic layer was washed with 100 mL (x3) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 80:20) followed by crystallization from cyclohexane obtaining 2.50 g of a white solid (yield 56%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.92 (m, 6H), 1.23-1.58 (m, 8H), 1.74 (m, 1H), 3.64 (s, 3H), 1.99 (d, *J* = 5.7 Hz, 2H), 6.94 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.79 (m, 3H), 8.13 (s, 1H).

^{13}C-NMR (DMSO-d_6, δ ppm): 11.37, 14.38, 22.99, 23.80, 28.94, 29.81, 30.41, 39.17, 71.07, 99.63, 111.72, 113.56, 127.77, 128.92 (2C), 129.62 (2C), 132.13, 133.56, 137.56, 140.38, 143.02, 159.99, 162.99, 194.50.

1-methyl-3-[4-(2-methylpropyl)benzoyl]-1,2-dihydroquinolin-2-one, (**KQ2**)

8.40 g (19.83 mmoles) of **KQ2-3a** were dissolved under vigorous stirring into 51.80 g (538.97 mmoles) of Methanesulfonic acid. The reaction mixture was stirred at 55°C for 1.5 hours. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 600 mL of water and extracted with 300 mL of dichloromethane. The organic layer was washed with 300 mL (x2) of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (toluene/ethyl acetate 85:15) followed by crystallization from cyclohexane/ethyl acetate (90:10) obtaining 2.58 g of a white solid (yield 41%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.88 (d, *J* = 6.6 Hz, 6H), 1.88 (m, 1H), 2.53 (d, *J* = 6.9 Hz, 2H), 3.67 (s, 3H), 7.28-7.37 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.70-7.78 (m, 3H), 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.16 (s, 1H).

^{13}C-NMR (DMSO-d_6, δ ppm): 22.58 (2C), 29.76, 29.97, 44.99, 115.36, 119.61, 122.90, 129.68 (2C), 129.83 (2C), 130.26, 131.89, 132.52, 134.75, 139.25, 140.74, 148.05, 159.65, 193.87.

1-methyl-3-[4-(2-methylpropyl)benzoyl]-7-(methylsulfanyl)-1,2-dihydroquinolin-2-one, (**KQ3**)

18.06 g (135.44 mmoles) of aluminum chloride were slowly added in portions under stirring to a solution of 10.60 g (22.57 mmoles as crude) of **KQ3-3d** in 300 mL of chlorobenzene. The resulting mixture was gradually heated to 120°C and then stirred at this temperature for 1 hour. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was allowed to cool, poured into 1000 mL of ice-water and extracted with 300 mL dichloromethane. The organic layer was washed with 800 mL of water/brine (75:25), dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (toluene/ethyl acetate 90:10) followed by crystallization from cyclohexane/ethyl acetate (75:25) obtaining 1.07 g of a white solid (yield 13%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.88 (d, *J* = 6.6 Hz, 6H), 1.88 (m, 1H), 2.54 (d, *J* = 6.6 Hz, 2H), 2.64 (s, 3H), 3.66 (s, 3H), 7.23 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.30 (m, 3H), 7.75 (m, 3H), 8.11 (s, 1H).

^{13}C-NMR (DMSO-d_6, δ ppm): 14.72, 22.60 (2C), 29.71, 29.97, 44.99, 110.67, 116.66, 120.34, 129.63 (2C), 129.80 (2C), 130.11, 130.43, 134.94, 139.36, 141.25, 145.11, 147.90, 159.74, 193.88.

5,7-dimethoxy-1-methyl-3-[4-(2-methylpropyl)benzoyl]-1,2-dihydroquinolin-2-one, (**KQ4**)

22.26 g (46.03 mmoles) of **KQ4-3e** were dissolved under vigorous stirring into 164.39 g (1710.44 mmoles) of Methanesulfonic acid. The reaction mixture was stirred at room temperature for 24 hours. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 500 mL of cold water and extracted with 250 mL of dichloromethane. The organic layer was washed in with 300 mL of water and brine, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (toluene/ethyl acetate 75:25) followed by crystallization from cyclohexane/ethyl acetate (71:29) obtaining 1.71 g of a white solid (yield 10%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.88 (d, *J* = 6.6 Hz, 6H), 1.87 (m, 1H), 2.51 (d, *J* = 6.3 Hz, 2H), 3.60 (s, 3H), 3.91 (s, 3H), 3.95 (s, 3H), 6.50 (s, 1H), 6.58 (s, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 8.13 (s, 1H).

^{13}C-NMR (DMSO-d_6, δ ppm): 22.59 (2C), 29.95, 30.15, 44.99, 56.37, 56.69, 91.69, 93.74, 104.41, 126.15, 129.40 (2C), 129.69 (2C), 134.25, 135.45, 143.72, 147.40, 158.51, 160.06, 164.65, 194.06.

6,7-dimethoxy-1-methyl-3-[4-(2-methylpropyl)benzoyl]-1,2-dihydroquinolin-2-one, (**KQ5**)

8.00 g (16.54 mmoles) of **KQ5-4c** were dissolved under vigorous stirring into 59.20 g (615.96 mmoles) of Methanesulfonic acid. The reaction mixture was stirred at room temperature for 4 hours. Progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured into 800 mL of water and extracted with 300 mL of dichloromethane. The organic layer was washed in sequence with 300 mL of sodium hydrogen carbonate saturated solution and then with 300 mL of water, dried over anhydrous sodium sulfate, filtered and the solvent removed by distillation under vacuum. The crude product was purified by flash column chromatography on silica gel (toluene/ethyl

acetate 65:35) followed by crystallization from cyclohexane/ethyl acetate (75:25) obtaining 1.85 g of a white-yellow solid (yield 29%).

^{1}H-NMR (DMSO-d_6, δ ppm): 0.88 (d, *J* = 6.3 Hz, 6H), 1.86 (m, 1H), 2.52 (d, *J* = 6.3 Hz, 2H), 3.67 (s, 3H), 3.81 (s, 3H), 3.99 (s, 3H), 7.03 (s, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.39 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 8.04 (s, 1H).

^{13}C-NMR (DMSO-d_6, δ ppm): 22.54 (2C), 26.77, 29.95, 44.98, 56.26, 56.58, 98.42, 110.91, 112.71, 128.33, 129.52 (2C), 129.79 (2C), 135.26, 137.15, 139.40, 145.51, 147.53, 153.78, 159.53, 194.18.

2/ NMR spectra.

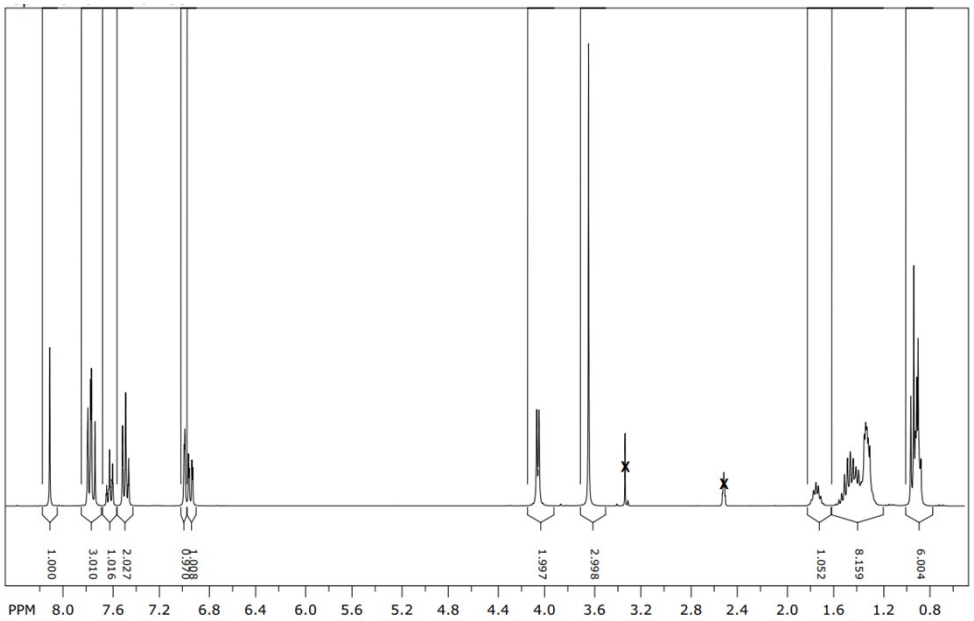

Figure SI1. ^{1}H NMR spectrum for KQ1.

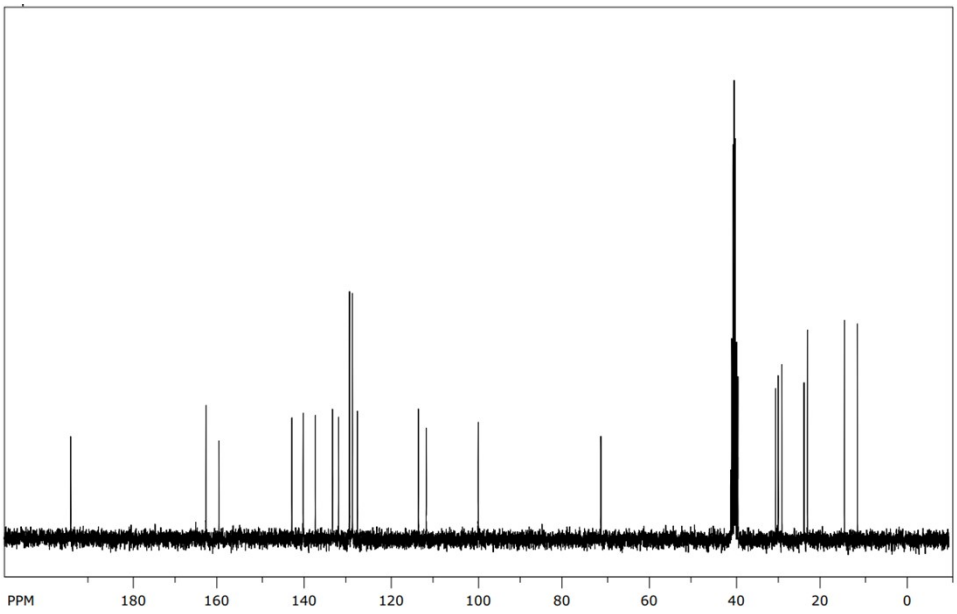

Figure SI2. ^{13}C NMR spectrum for KQ1.

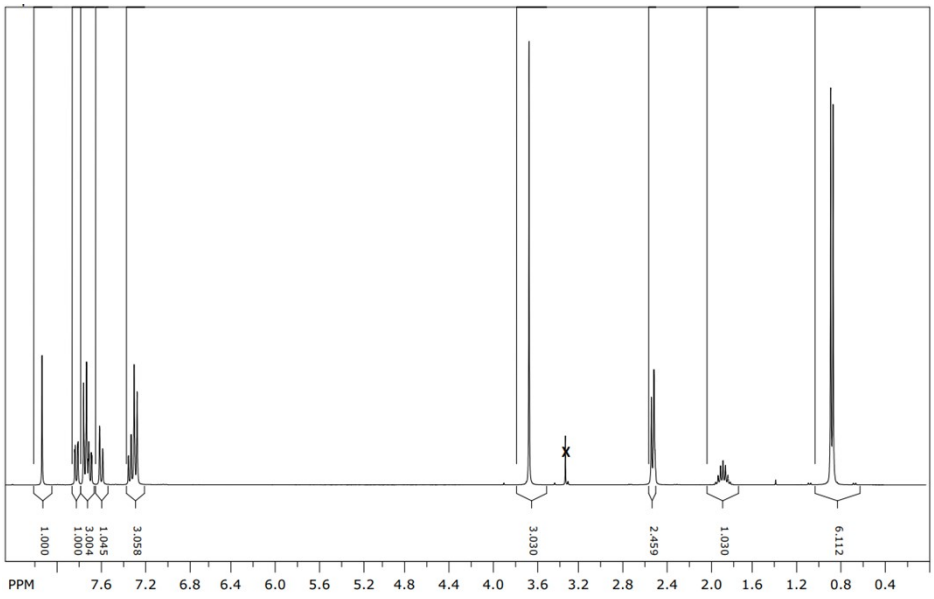

Figure SI3. ^{1}H NMR spectrum for KQ2.

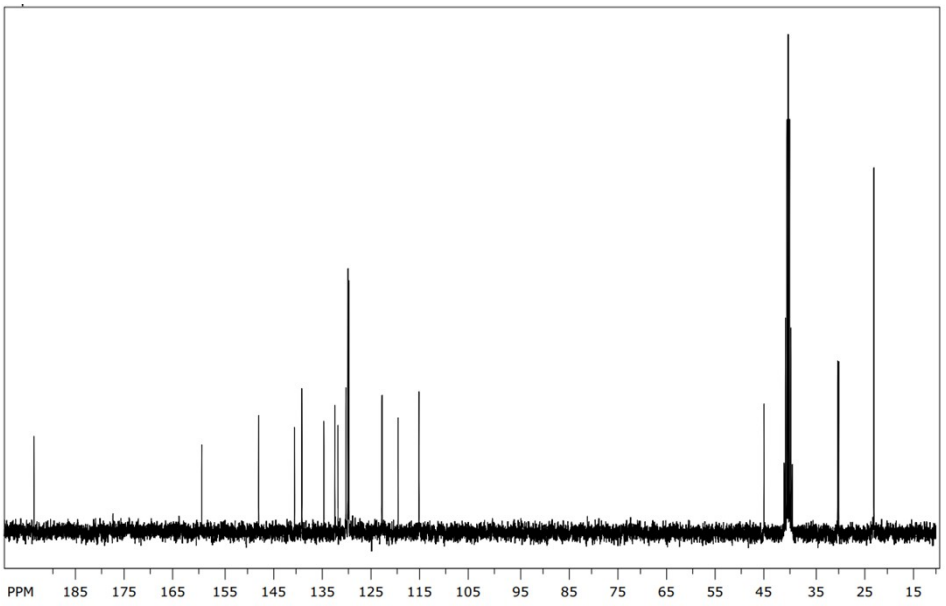

Figure SI4. ^{13}C NMR spectrum for KQ2.

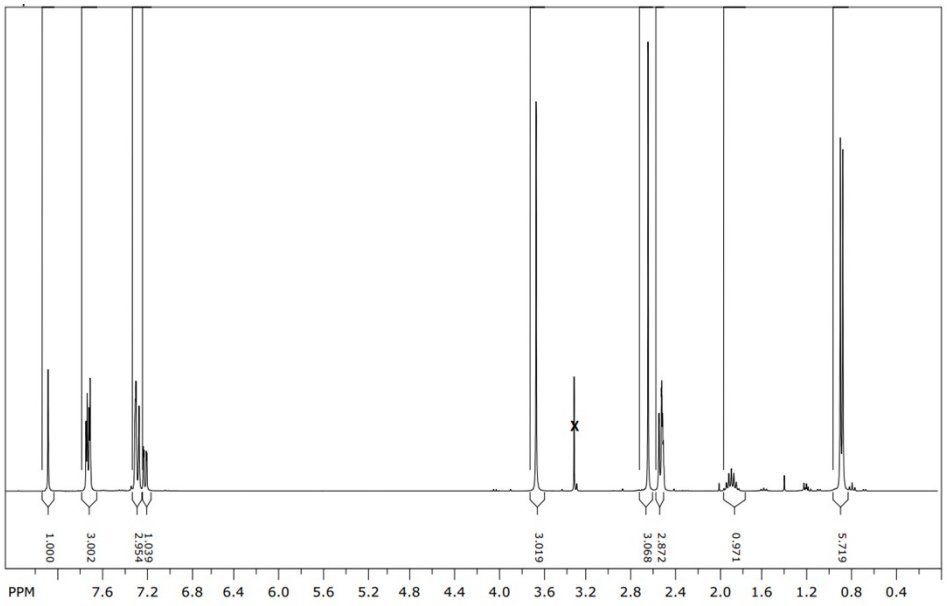

Figure SI5. ^{1}H NMR spectrum for KQ3.

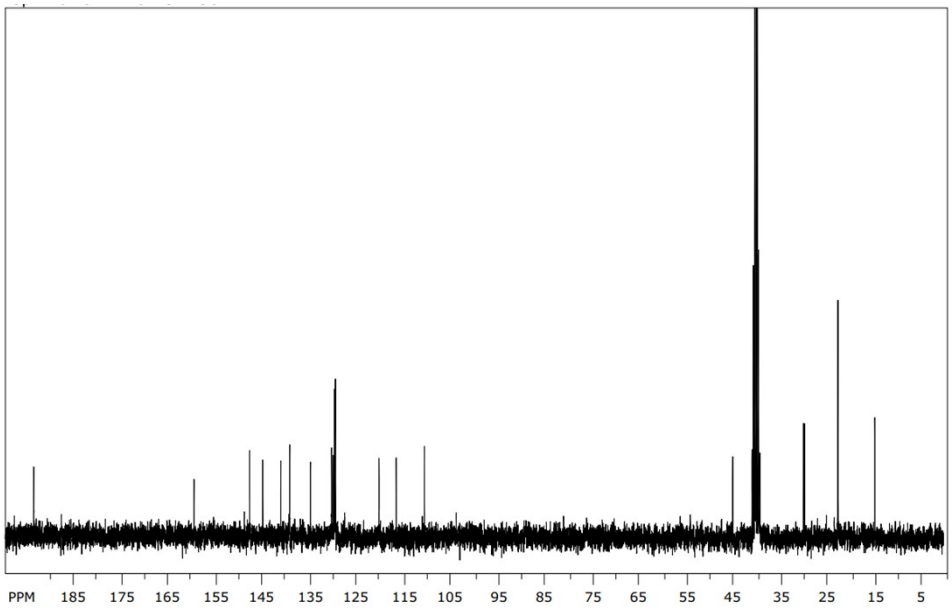

Figure SI6. ^{13}C NMR spectrum for KQ3.

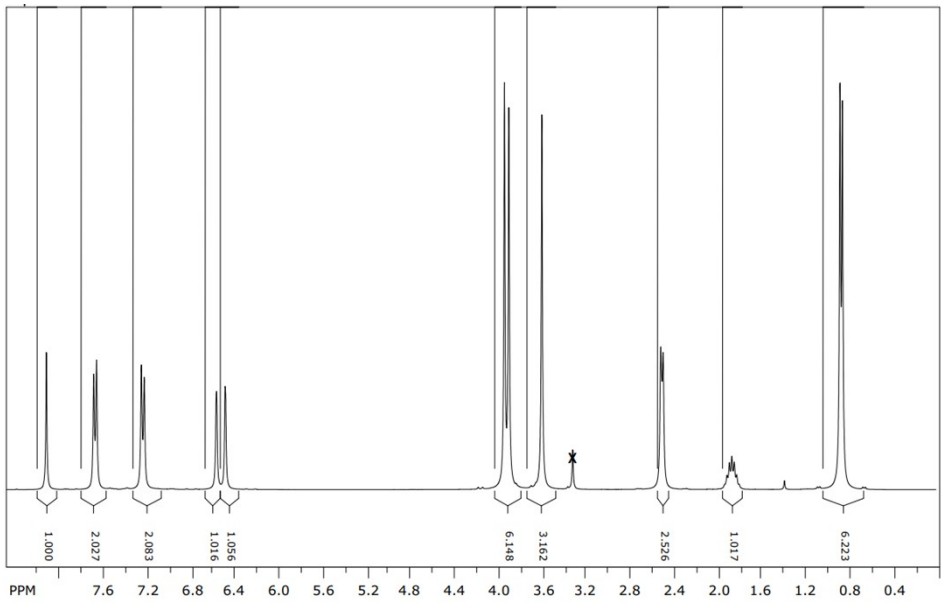

Figure SI7. ^{1}H NMR spectrum for KQ4.

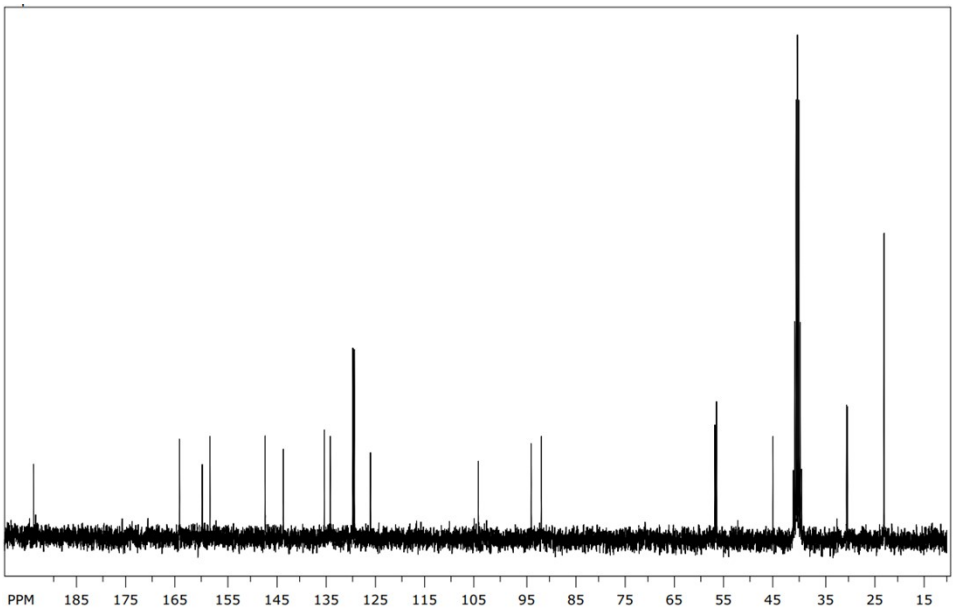

Figure SI8. ^{13}C NMR spectrum for KQ4.

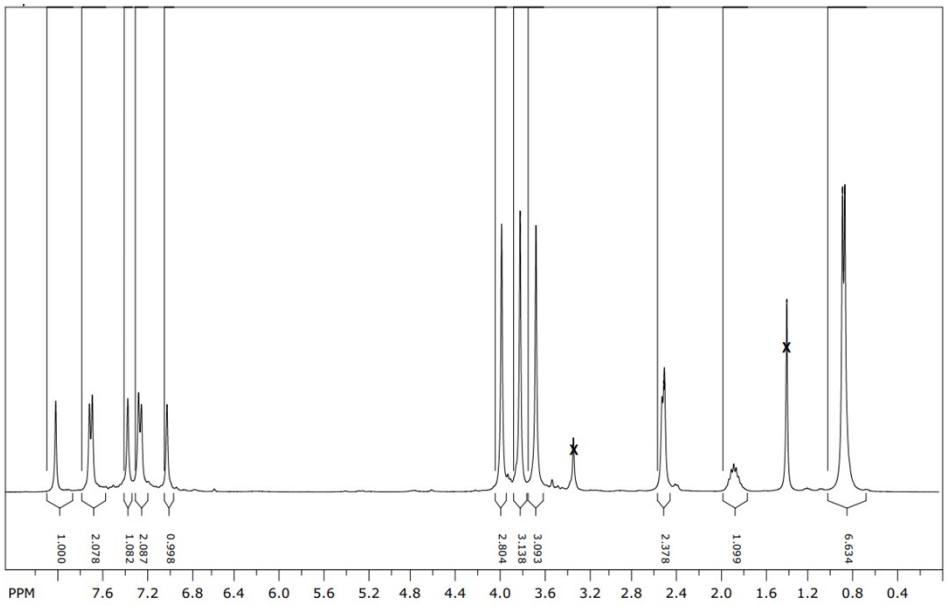

Figure SI9. ^{1}H NMR spectrum for KQ5.

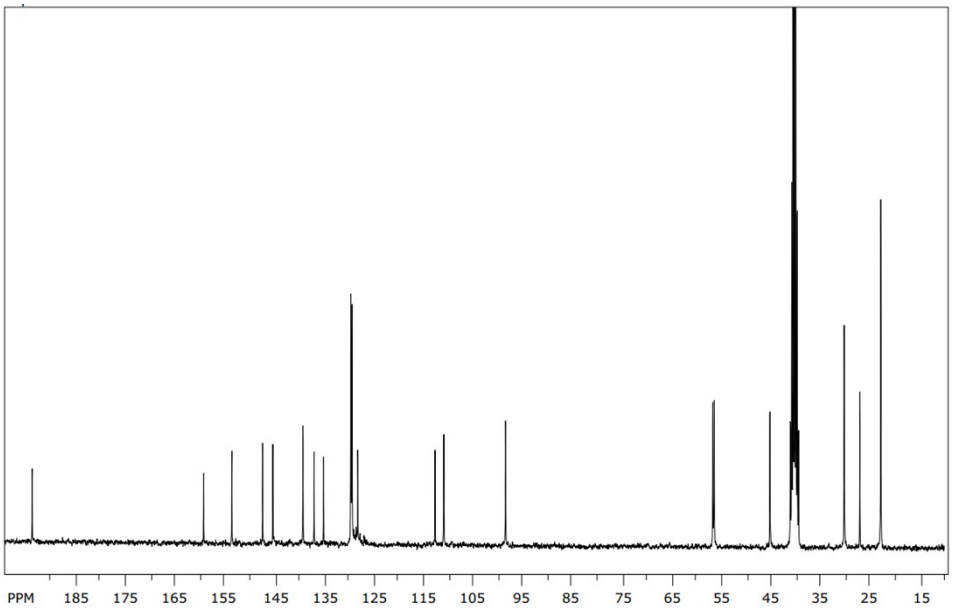

Figure SI10. ^{13}C NMR spectrum for KQ5.

3/ Laser flash photolysis

Table SI 1. Lifetimes τ_T, maximum absorption (λ_{max}^{T-T}) and rate constant of quenching k_q by 1-methylnaphtalene of 3-ketoquinolone triplet states.

Molecule	τ_T (µs)	λ_{max}^{T-T} (nm)[a]	k_q (M^{-1} s^{-1})
KQ1	1.0	560	$1.1\ 10^{10}$
KQ3	5.6	560	$3.2\ 10^{8}$
KQ4	5.2	460	$3.7\ 10^{8}$
KQ5	19.5	540	$5.4\ 10^{7}$

Figure SI11. Transient absorption of KQ1 in deoxygenated solution in acetonitrile at 425 and 525 nm and at different concentration of 1MeN.

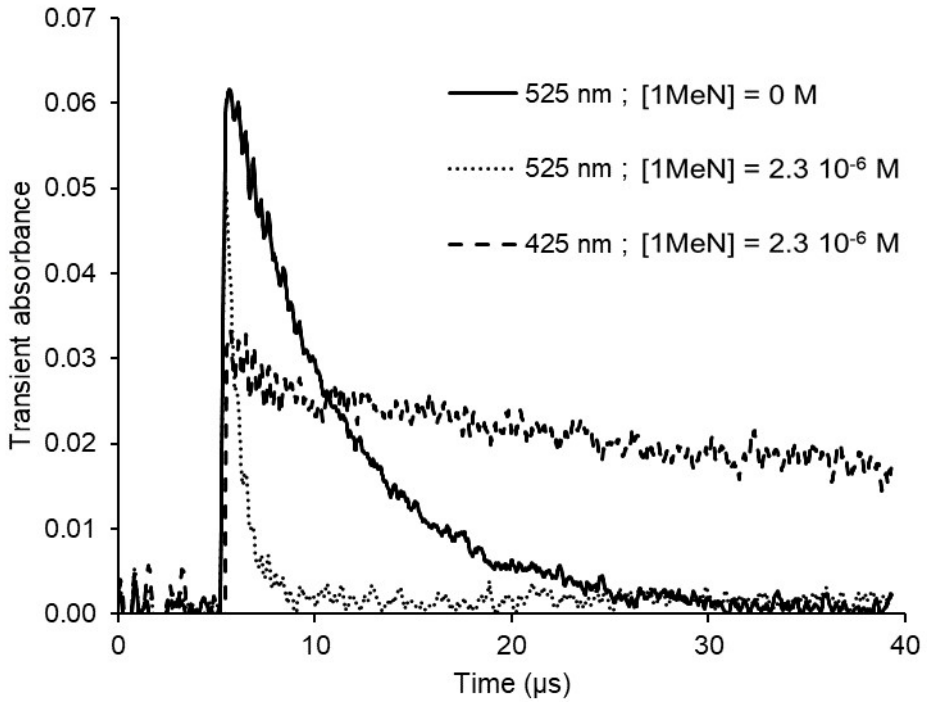

Figure SI12. Transient absorption of KQ1 in deoxygenated solution in acetonitrile at 580 nm in the absence and in the presence of 10^{-5}M of EDB.