Supporting Information for:

Excited State Dynamics for Visible Light Sensitization of Fast Photochromic Phenoxyl-Imidazolyl Radical Complex with Aryl Ketone

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1. ^{1}H NMR Spectra

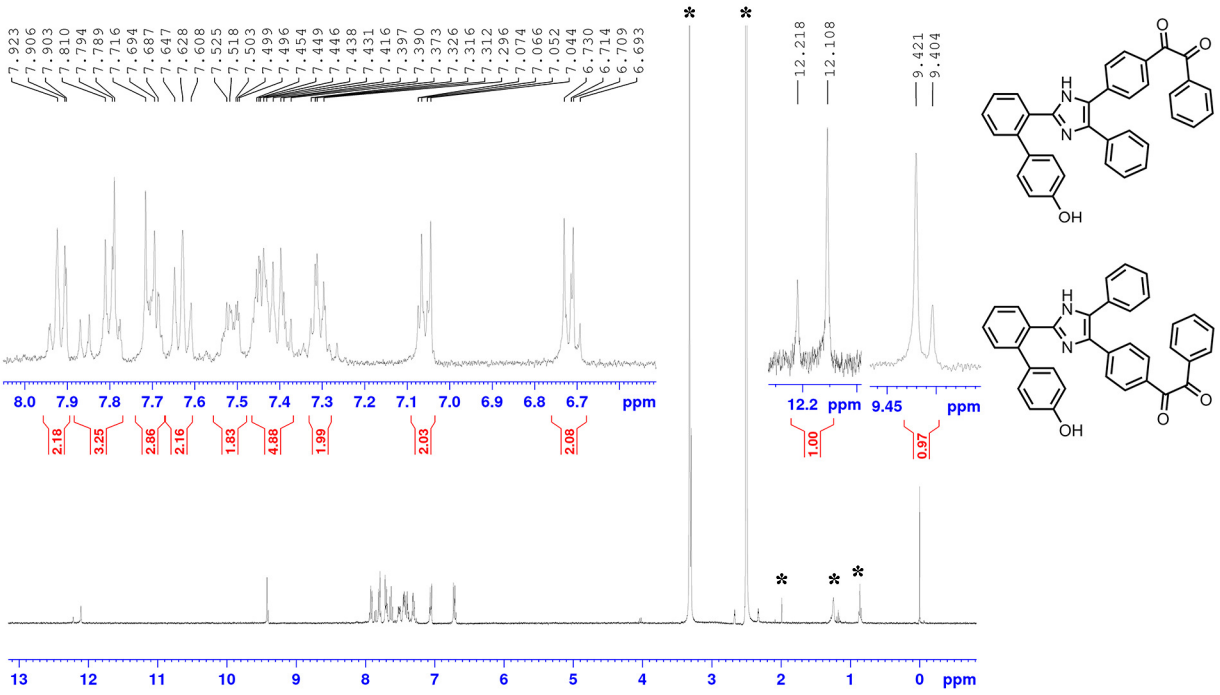


Figure S1. ^{1}H NMR spectrum of **2** in DMSO-d_6 (* solvent peaks).

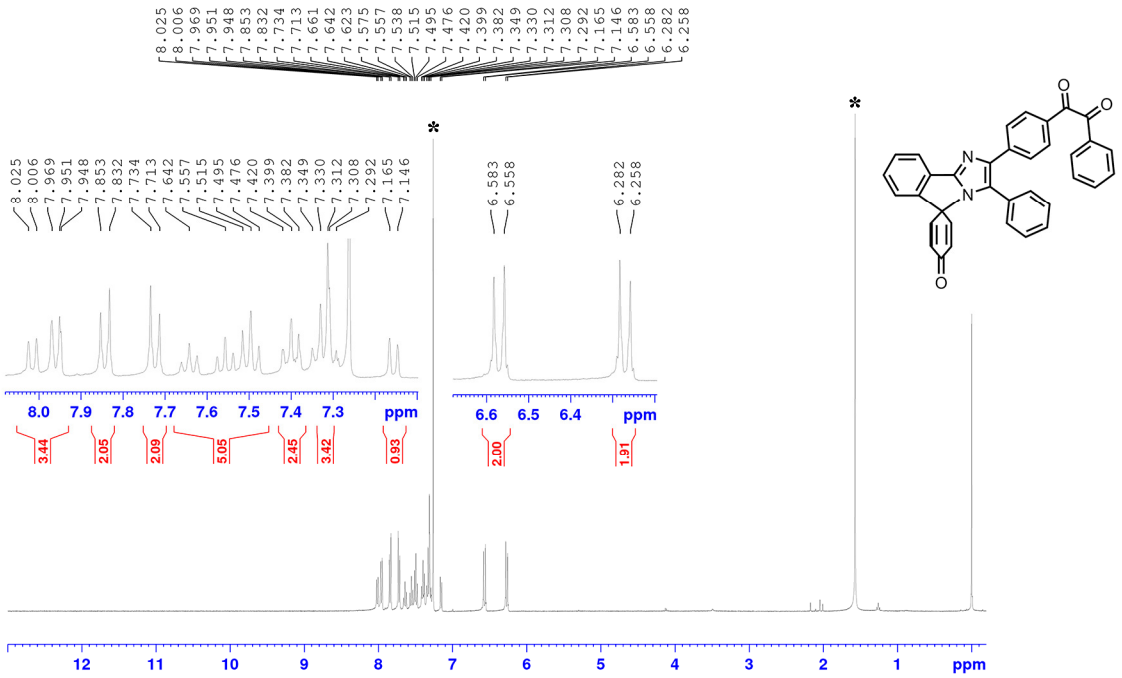


Figure S2. ^{1}H NMR spectrum of the isomer A of **Benzil-PIC** in $CDCl_3$ (* solvent peaks).

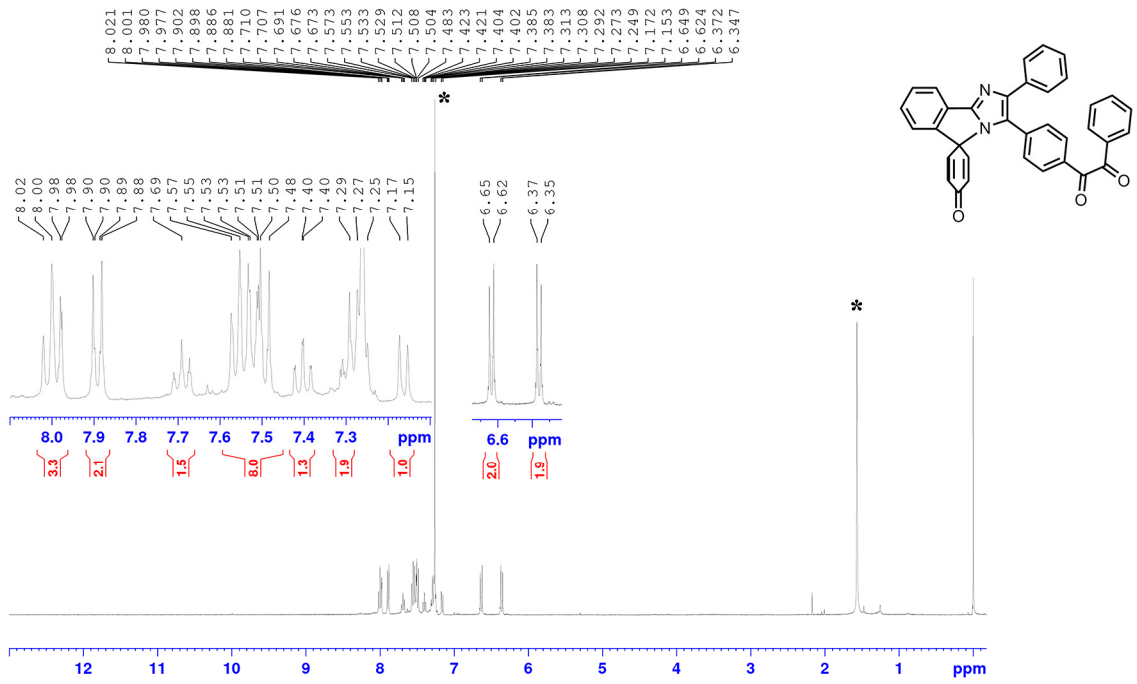


Figure S3. ^{1}H NMR spectrum of the isomer B of **Benzil-PIC** in $CDCl_3$ (* solvent peaks).

2. HR-ESI-TOF-MS Spectra

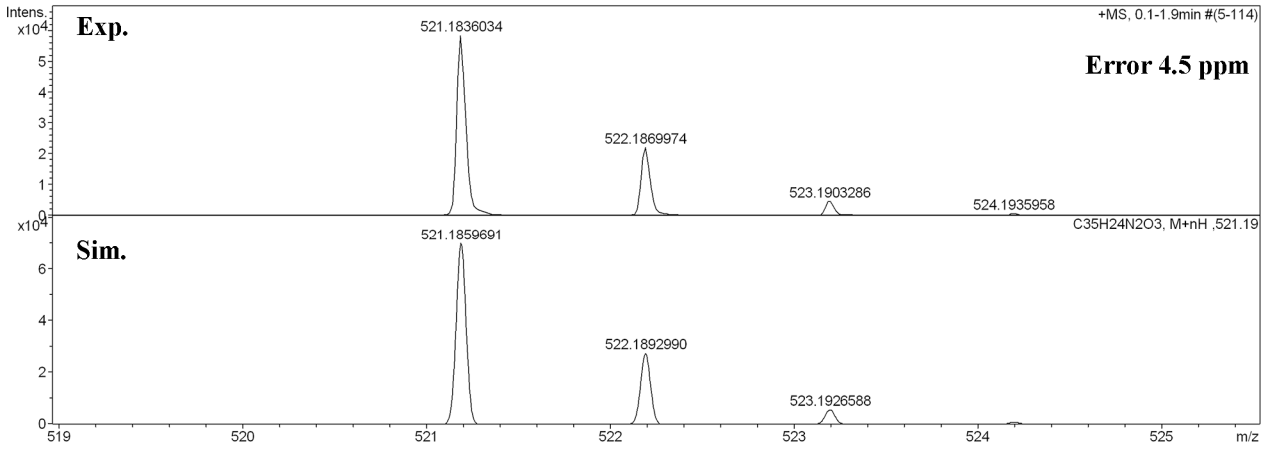


Figure S4. HR-ESI-TOF MS spectra of **2**.

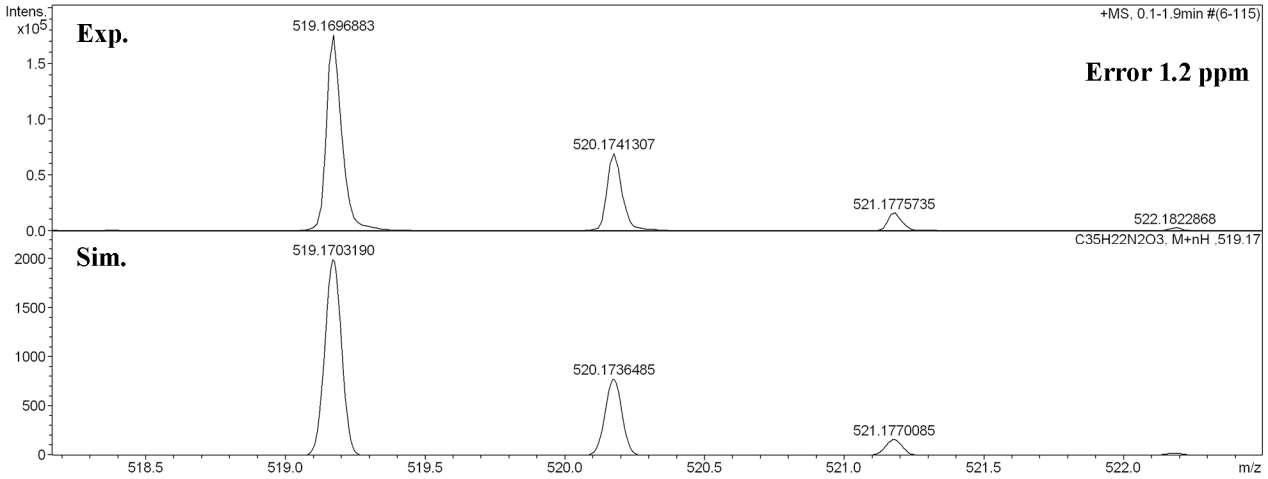
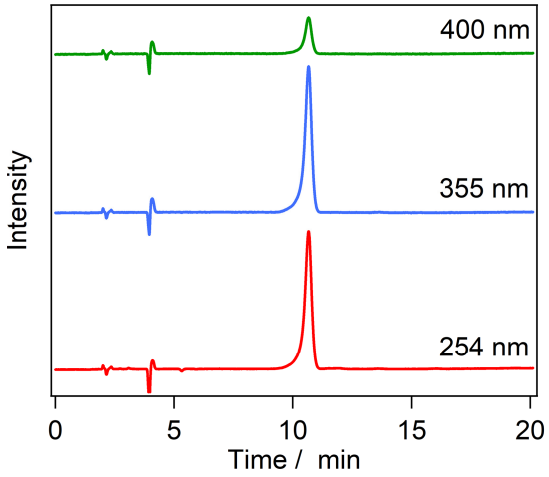
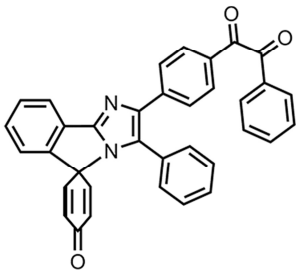


Figure S5. HR-ESI-TOF MS spectra of **Benzil-PIC**.

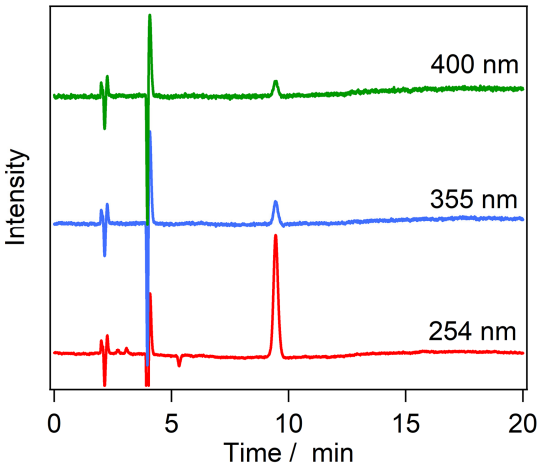
3. HPLC Chromatograms

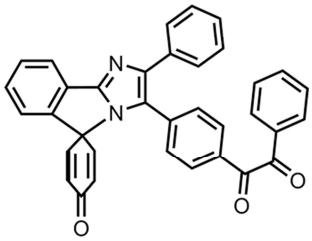




Bensil-PIC (isomer A)

Figure S6. HPLC chromatogram of ~~I~~isomer A of benzil-PIC; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5µm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was CH_3CN/H_3O = 3:1 with a flow rate of 1.0 mL/min (detection wavelength; 254, 355, and 400 nm).





Bensil-PIC (isomer B)

Figure S7. HPLC chromatogram of ~~isomer~~ Isomer B of benzil-PIC; 99% purity. HPLC analysis was performed using a reverse phase analytical column (Mightysil RP18, 25cm×4.6mm, 5µm particle) from Kanto Chemical Industries, equipped with a UV detector; the mobile phase was CH_3CN/H_3O = 3:1 with a flow rate of 1.0 mL/min (detection wavelength; 254, 355, and 400 nm).

4. Difference in the Thermal Back Reactions between Two Isomers of Benzil-PIC

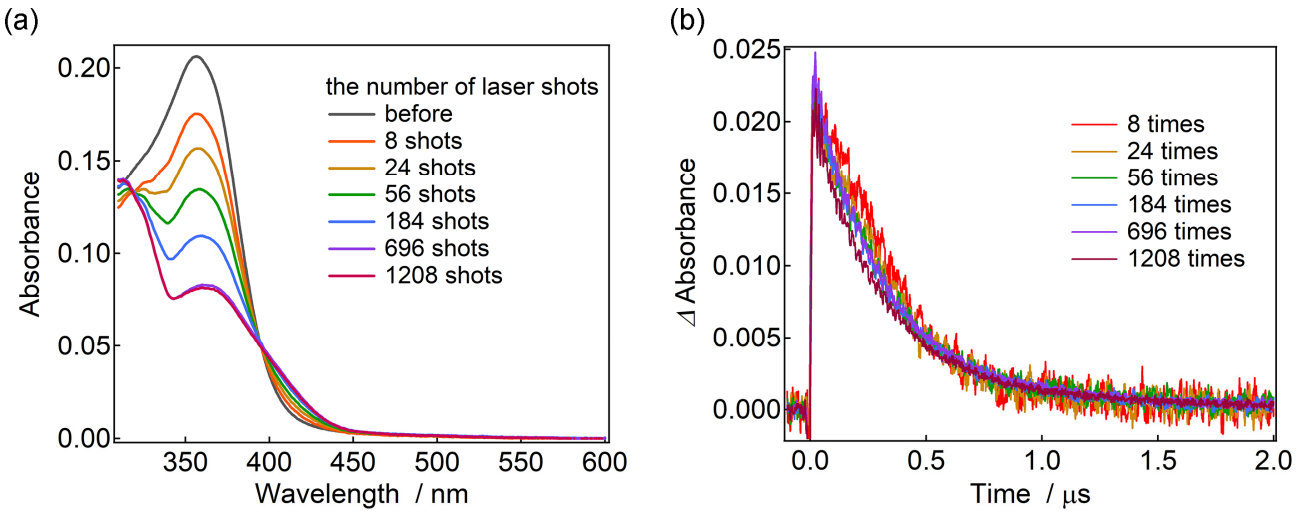


Figure S8. (a) Steady-state absorption spectra of Isomer A of Benzil-PIC in benzene upon repeated irradiation of 355-nm nanosecond laser pulses (355 nm, 7 mJ pulse^{-1}). (b) Nanosecond-to-microsecond transient absorption dynamics of Isomer A of Benzil-PIC in benzene at the same condition.

5. Estimation of the Ratio of Two Isomers at the Photostationary State

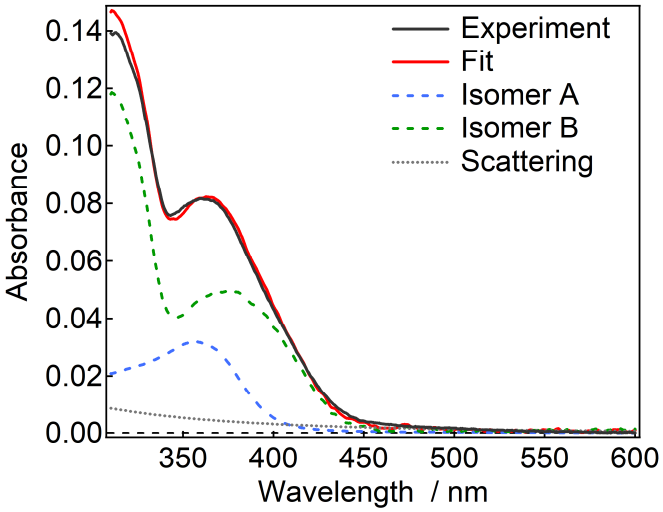


Figure S9. Absorption spectrum of Benzil-PIC at the photostationary state after the excitation with 355-nm nanosecond laser pulses. The absorption spectrum can be resolved into the two isomers by the curve fitting with pure absorption spectra of the two isomers and the small amount of the Rayleigh scattering component ($1/\lambda^4$).

6. Details of the SVD Global Analyses of benzil and Benzil-PIC

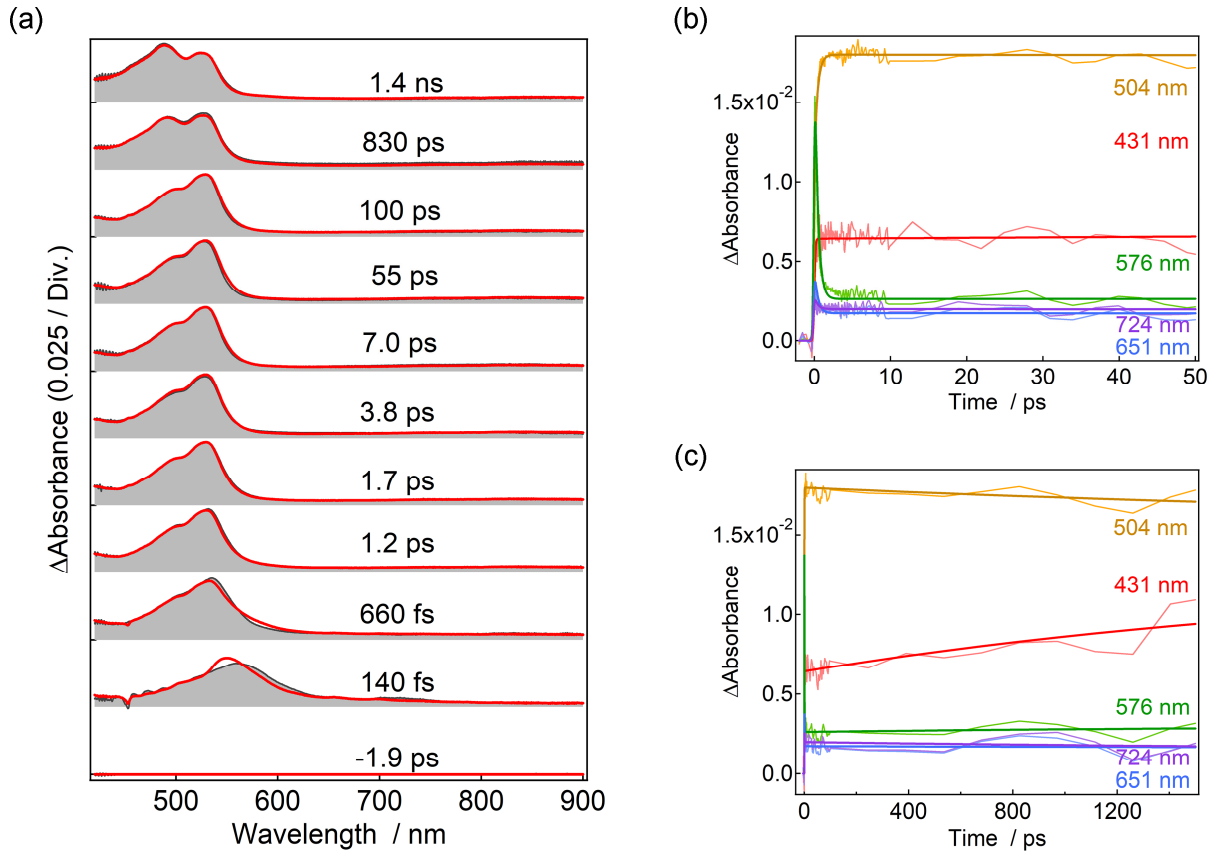


Figure S10. (a) Transient absorption spectra and fitted spectra of benzil in benzene excited at 400 nm. The red spectra show the fitted spectra by SVD global analyses assuming the three-state sequential kinetic model (b and c) Transient absorption dynamics of benzil at different time scales. Thick solid lines show the fitted dynamics.

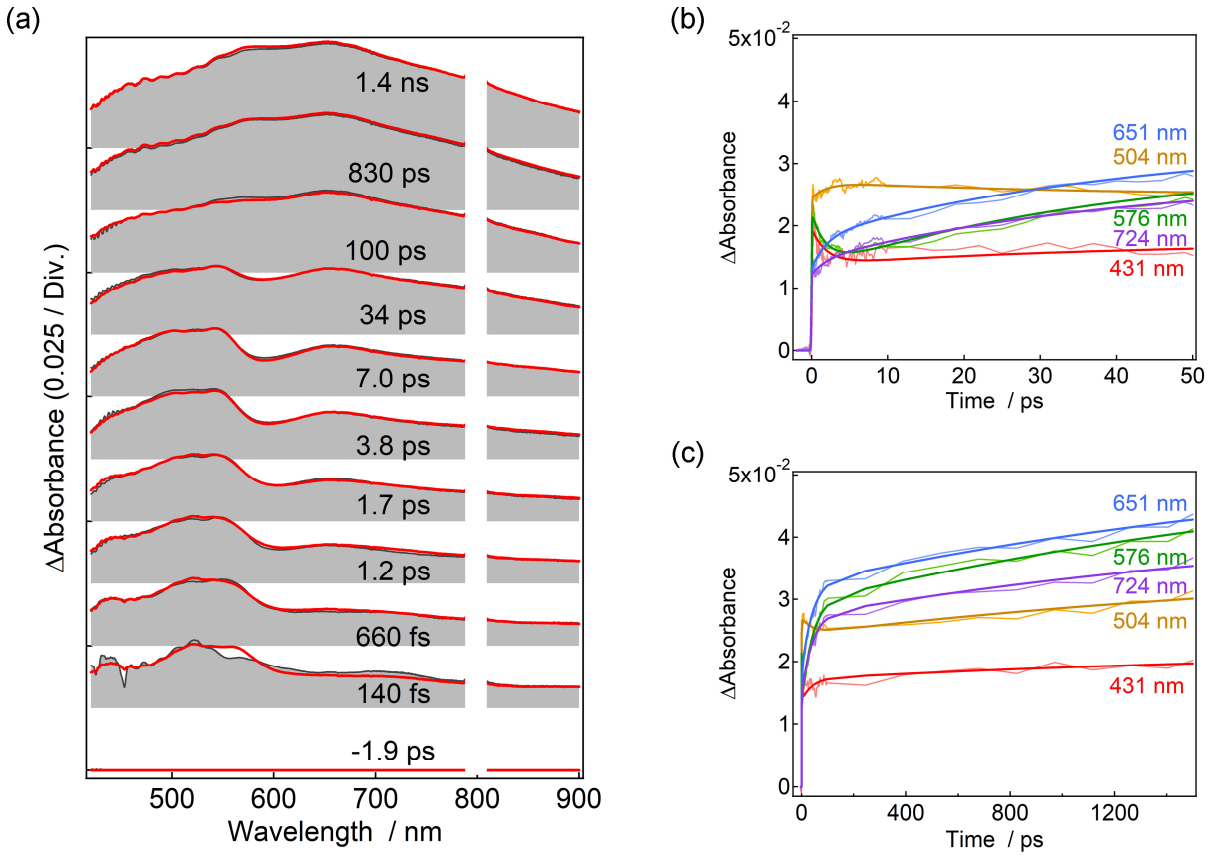


Figure S11. (a) Transient absorption spectra and fitted spectra of Benzil-PIC in benzene excited at 400 nm. The red spectra show the fitted spectra by SVD global analyses assuming the four-state sequential kinetic model (b and c) Transient absorption dynamics of Benzil-PIC at different time scales. Thick solid lines show the fitted dynamics.

7. Sensitization of Photochromic Reaction with Triplet Excited States

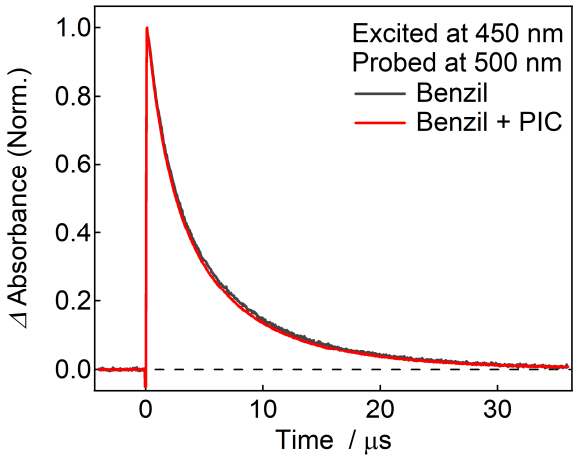


Figure S12. Microsecond transient absorption dynamics of Benzil in benzene (gray) and the mixture solution of benzil and PIC in benzene (red) excited and probed at 450 and 500 nm, respectively.

8. DFT Calculations

All calculations was carried out using the Gaussian 09 program (Revision D.01).[S1] The molecular structure was fully optimized at the M05-2X/6-31+G(d,p) level of theory, and analytical second derivative was computed using vibrational analysis to confirm each stationary point to be a minimum. TDDFT calculations were performed at the MPW1PW91/6-31+G(d,p) level of the theory for the optimized structures.

Table S1. Standard orientation of the optimized geometry for the closed-ring isomer of Isomer A of **Benzil-PIC**.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-4.5343040	4.8339550	-0.1087920
2	C	-5.7231620	4.0997860	-0.1233790
3	C	-5.7033220	2.7045910	-0.0563070
4	C	-4.4724650	2.0768440	0.0194500
5	C	-3.2797830	2.8107210	0.0385620
6	C	-3.2960610	4.1985250	-0.0279040
7	C	-2.1871820	1.8491060	0.1070340
8	C	-4.1894340	0.5652840	0.1168770
9	C	-4.6626950	-0.1533880	-1.1167110
10	C	-5.6317340	-1.0709760	-1.0921870
11	C	-6.2792230	-1.4787900	0.1754780
12	C	-5.7762550	-0.8511180	1.4194990
13	C	-4.7935480	0.0516020	1.3959970
14	N	-2.7219810	0.5944710	0.1722450
15	C	-1.6828470	-0.3046790	0.1123530
16	C	-0.5447700	0.4952940	0.0548370
17	N	-0.8826850	1.8345120	0.0443630
18	C	0.8636860	0.0818830	-0.0027350
19	C	-1.8938520	-1.7591180	-0.0038450
20	C	-1.4321630	-2.4279980	-1.1431540
21	C	-1.6515160	-3.7935340	-1.2908720
22	C	-2.3442940	-4.5008500	-0.3092460
23	C	-2.8017400	-3.8415200	0.8294570
24	C	-2.5700520	-2.4774480	0.9865140
25	C	1.8071290	0.9681240	-0.5366310
26	C	3.1448950	0.6075630	-0.6208350
27	C	3.5624040	-0.6459460	-0.1599780
28	C	2.6260220	-1.5260940	0.3955400
29	C	1.2906410	-1.1678190	0.4745130
30	C	4.9806680	-1.0644110	-0.1899970

31	O	5.3814070	-2.1146250	0.2786780
32	C	6.0014510	-0.1688320	-0.9034530
33	C	7.2011860	0.2919990	-0.1594610
34	O	5.8090470	0.0887740	-2.0763970
35	C	8.1512290	1.0460120	-0.8571890
36	C	9.2726070	1.5298590	-0.1976690
37	C	9.4464920	1.2665020	1.1623640
38	C	8.5007700	0.5188440	1.8599610
39	C	7.3761160	0.0284030	1.2025030
40	O	-7.1791920	-2.3012420	0.1983380
41	H	-4.5764180	5.9145840	-0.1620050
42	H	-6.6712220	4.6181560	-0.1883410
43	H	-6.6224290	2.1298460	-0.0661400
44	H	-2.3711160	4.7600690	-0.0170180
45	H	-4.1781050	0.1414200	-2.0414930
46	H	-5.9793190	-1.5671800	-1.9894170
47	H	-6.2345740	-1.1833430	2.3427670
48	H	-4.4089150	0.5037080	2.3045990
49	H	-0.9010670	-1.8693560	-1.9048360
50	H	-1.2888020	-4.3034800	-2.1745190
51	H	-2.5235150	-5.5618890	-0.4296530
52	H	-3.3331810	-4.3886270	1.5981380
53	H	-2.9057290	-1.9691320	1.8813820
54	H	1.4726060	1.9354000	-0.8864100
55	H	3.8570630	1.2938830	-1.0593470
56	H	2.9695920	-2.4835590	0.7659350
57	H	0.5767650	-1.8498520	0.9176240
58	H	7.9886320	1.2379520	-1.9101330
59	H	10.0101110	2.1108210	-0.7369100
60	H	10.3213980	1.6444870	1.6771310
61	H	8.6401430	0.3135660	2.9136400
62	H	6.6512840	-0.5678540	1.7402340

SCF Done: E(RM052X) = -1682.07194943

Zero-point correction = 0.484395 (Hartree/Particle)
Thermal correction to Energy = 0.514380
Thermal correction to Enthalpy = 0.515324
Thermal correction to Gibbs Free Energy = 0.419921

Sum of electronic and zero-point Energies	=	-1681.587555
Sum of electronic and thermal Energies	=	-1681.557569
Sum of electronic and thermal Enthalpies	=	-1681.556625
Sum of electronic and thermal Free Energies	=	-1681.652029

Low frequencies ---	-15.6158	-7.3907	-4.7849	-0.0025	-0.0020	-0.0015
Low frequencies ---	4.2114	17.0347	19.5463			

The Result for the TDDFT calculation of Isomer A of Benzil-PIC

Excited State 1: Singlet-A 2.9259 eV 423.75 nm f=0.0004 <S**2>=0.000
135 ->136 0.70311
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1681.71934799
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9476 eV 420.63 nm f=0.0019 <S**2>=0.000
134 ->137 0.67289

Excited State 3: Singlet-A 3.3545 eV 369.60 nm f=0.4650 <S**2>=0.000
135 ->137 0.69239

Excited State 4: Singlet-A 3.3566 eV 369.38 nm f=0.0009 <S**2>=0.000
127 ->136 -0.31432
128 ->136 0.61322

Excited State 5: Singlet-A 3.7322 eV 332.20 nm f=0.0367 <S**2>=0.000
121 ->137 0.16761
134 ->138 0.60262
134 ->141 0.11111
135 ->138 0.24962

Excited State 6: Singlet-A 3.9208 eV 316.23 nm f=0.0659 <S**2>=0.000
134 ->138 -0.19248
135 ->138 0.53794
135 ->139 -0.37383

Excited State 7: Singlet-A 3.9311 eV 315.39 nm f=0.3054 <S**2>=0.000
134 ->138 -0.12780
135 ->138 0.35971
135 ->139 0.57393
135 ->140 -0.10136

Excited State 8: Singlet-A 4.0772 eV 304.09 nm f=0.0015 <S**2>=0.000
134 ->136 0.69654

Excited State 9: Singlet-A 4.2382 eV 292.54 nm f=0.1177 <S**2>=0.000

126 ->139 -0.11429
133 ->137 -0.11417
135 ->139 0.11912
135 ->140 0.64432

Excited State 10: Singlet-A 4.2940 eV 288.74 nm f=0.0178 <S**2>=0.000
127 ->137 -0.10703
132 ->137 -0.27994
133 ->136 0.25554
133 ->137 0.47623
135 ->140 0.16842
135 ->142 0.14419
135 ->145 0.11100

Excited State 11: Singlet-A 4.3010 eV 288.27 nm f=0.0036 <S**2>=0.000
129 ->136 -0.12741
130 ->136 0.28202
132 ->136 0.32103
132 ->137 0.12595
133 ->136 0.43117
133 ->137 -0.22750

Excited State 12: Singlet-A 4.3666 eV 283.94 nm f=0.0064 <S**2>=0.000
126 ->136 0.20343
127 ->136 -0.30682
128 ->136 -0.18191
130 ->136 0.37678
132 ->136 0.21393
133 ->136 -0.35424

Excited State 13: Singlet-A 4.3972 eV 281.96 nm f=0.0022 <S**2>=0.000
126 ->136 -0.30892
129 ->136 0.45942
130 ->136 -0.15666
132 ->136 0.38259

Excited State 14: Singlet-A 4.4604 eV 277.97 nm f=0.0534 <S**2>=0.000
129 ->137 -0.18748
130 ->137 -0.19753

131 ->137 0.49445
131 ->138 0.13800
132 ->137 0.27604
133 ->137 0.19022

Excited State 15: Singlet-A 4.5055 eV 275.18 nm f=0.0227 <S**2>=0.000
126 ->136 0.53240
128 ->136 -0.11476
129 ->136 0.28749
130 ->136 -0.20491
133 ->136 0.16646
133 ->137 -0.10306

Excited State 16: Singlet-A 4.5102 eV 274.90 nm f=0.1750 <S**2>=0.000
126 ->136 0.16365
131 ->137 -0.37615
132 ->137 0.38534
133 ->137 0.25669
135 ->141 -0.25771

Excited State 17: Singlet-A 4.5650 eV 271.60 nm f=0.0120 <S**2>=0.000
132 ->137 0.11982
133 ->137 -0.12036
135 ->141 -0.10794
135 ->142 0.63092

Excited State 18: Singlet-A 4.5948 eV 269.83 nm f=0.0450 <S**2>=0.000
127 ->137 -0.10556
129 ->137 -0.12119
130 ->137 -0.18831
131 ->137 -0.17716
132 ->137 0.17914
135 ->141 0.54786

Excited State 19: Singlet-A 4.6289 eV 267.85 nm f=0.0006 <S**2>=0.000
126 ->136 0.17369
127 ->136 0.39423
128 ->136 0.18066
129 ->136 -0.15768

130 ->136 -0.14840
132 ->136 0.36624
133 ->136 -0.24380
135 ->141 0.14842

Excited State 20: Singlet-A 4.7094 eV 263.27 nm f=0.0329 <S**2>=0.000
127 ->137 0.24300
128 ->137 0.11313
129 ->137 0.30709
130 ->137 0.32937
131 ->137 0.18462
131 ->138 -0.10335
132 ->137 0.19268
133 ->137 0.19787
135 ->141 0.20342
135 ->142 0.10227

Excited State 21: Singlet-A 4.8499 eV 255.64 nm f=0.0087 <S**2>=0.000
127 ->137 -0.17793
128 ->137 -0.12202
129 ->137 0.54239
129 ->138 -0.12773
130 ->137 -0.30621

Excited State 22: Singlet-A 4.8600 eV 255.11 nm f=0.0002 <S**2>=0.000
131 ->136 0.70119

Excited State 23: Singlet-A 4.8641 eV 254.90 nm f=0.0102 <S**2>=0.000
127 ->137 -0.25149
127 ->138 0.12943
128 ->137 -0.14352
130 ->137 0.34893
132 ->137 0.18302
132 ->138 0.11354
133 ->137 -0.10872
133 ->138 -0.29273
135 ->145 0.28092

Excited State 24: Singlet-A 4.9117 eV 252.43 nm f=0.0574 <S**2>=0.000

121 ->137 -0.12296
127 ->137 0.35331
128 ->137 0.21273
130 ->137 -0.19630
132 ->138 0.25402
133 ->138 -0.32620
135 ->145 0.21308

Excited State 25: Singlet-A 4.9299 eV 251.49 nm f=0.0014 <S**2>=0.000
124 ->136 0.18117
125 ->136 -0.12341
127 ->136 0.29656
128 ->136 0.16714
129 ->136 0.36786
130 ->136 0.38104
132 ->136 -0.18410

Excited State 26: Singlet-A 4.9673 eV 249.60 nm f=0.0066 <S**2>=0.000
126 ->139 0.14492
135 ->144 0.63484

Excited State 27: Singlet-A 4.9900 eV 248.46 nm f=0.0026 <S**2>=0.000
134 ->139 0.68982

Excited State 28: Singlet-A 5.0255 eV 246.71 nm f=0.0051 <S**2>=0.000
121 ->137 0.11648
122 ->136 -0.10240
124 ->136 0.46768
125 ->136 -0.39911
127 ->136 -0.14649
129 ->136 -0.10884
130 ->136 -0.14101

Excited State 29: Singlet-A 5.0376 eV 246.12 nm f=0.0053 <S**2>=0.000
121 ->137 0.50752
122 ->137 0.19741
124 ->136 -0.11066
128 ->137 0.10803
131 ->138 0.16916

132 ->137	0.12221				
134 ->138	-0.20173				
Excited State 30:	Singlet-A	5.0903 eV	243.57 nm	f=0.0543	<S**2>=0.000
121 ->137	-0.10160				
127 ->137	0.10671				
129 ->138	-0.13754				
130 ->137	0.10434				
130 ->138	-0.17503				
131 ->137	-0.12435				
131 ->138	0.47643				
132 ->138	0.22320				
133 ->138	0.20685				
Excited State 31:	Singlet-A	5.1093 eV	242.66 nm	f=0.0009	<S**2>=0.000
127 ->137	-0.31187				
128 ->137	0.58459				
131 ->138	0.10720				
Excited State 32:	Singlet-A	5.1352 eV	241.44 nm	f=0.0646	<S**2>=0.000
128 ->137	0.11443				
131 ->138	-0.15104				
133 ->138	0.37550				
133 ->139	-0.15843				
135 ->143	0.21834				
135 ->145	0.39924				
135 ->146	0.10237				
Excited State 33:	Singlet-A	5.1828 eV	239.22 nm	f=0.0404	<S**2>=0.000
126 ->137	0.36871				
127 ->137	-0.16848				
131 ->138	-0.12848				
132 ->138	0.34148				
132 ->139	-0.13525				
133 ->138	0.11974				
135 ->144	0.10014				
135 ->145	-0.14110				
135 ->146	-0.22046				

Excited State 34:	Singlet-A	5.1969 eV	238.57 nm	f=0.0138	<S**2>=0.000
126 ->137	0.53132				
132 ->138	-0.22924				
135 ->145	0.16972				
135 ->146	0.27113				
Excited State 35:	Singlet-A	5.2307 eV	237.03 nm	f=0.0017	<S**2>=0.000
125 ->136	-0.10481				
132 ->138	-0.18689				
133 ->139	-0.27755				
134 ->143	0.11707				
135 ->143	0.38883				
135 ->146	-0.33684				
Excited State 36:	Singlet-A	5.2499 eV	236.16 nm	f=0.0470	<S**2>=0.000
128 ->139	0.12519				
132 ->139	0.24311				
133 ->138	0.13241				
133 ->139	0.48248				
135 ->143	0.25774				
135 ->146	-0.20751				
Excited State 37:	Singlet-A	5.2607 eV	235.68 nm	f=0.0351	<S**2>=0.000
132 ->138	0.21132				
133 ->138	-0.10580				
135 ->143	0.40958				
135 ->145	-0.22805				
135 ->146	0.39974				
Excited State 38:	Singlet-A	5.2742 eV	235.08 nm	f=0.0344	<S**2>=0.000
123 ->136	0.18925				
124 ->136	0.30554				
125 ->136	0.45356				
129 ->139	0.17958				
130 ->139	-0.16726				
132 ->138	-0.14374				
Excited State 39:	Singlet-A	5.3070 eV	233.62 nm	f=0.0055	<S**2>=0.000
125 ->136	0.12107				

126 ->139 0.23048
132 ->140 -0.13471
133 ->140 -0.11711
134 ->140 0.53356
134 ->142 -0.10516
135 ->144 -0.10384

Excited State 40: Singlet-A 5.3297 eV 232.63 nm f=0.0281 <S**2>=0.000
128 ->139 0.32059
128 ->140 -0.15109
129 ->138 0.19247
130 ->138 0.18280
130 ->139 -0.15970
131 ->138 0.11899
132 ->139 -0.25578
134 ->140 0.15082
135 ->145 0.10020
133 ->138 0.22100

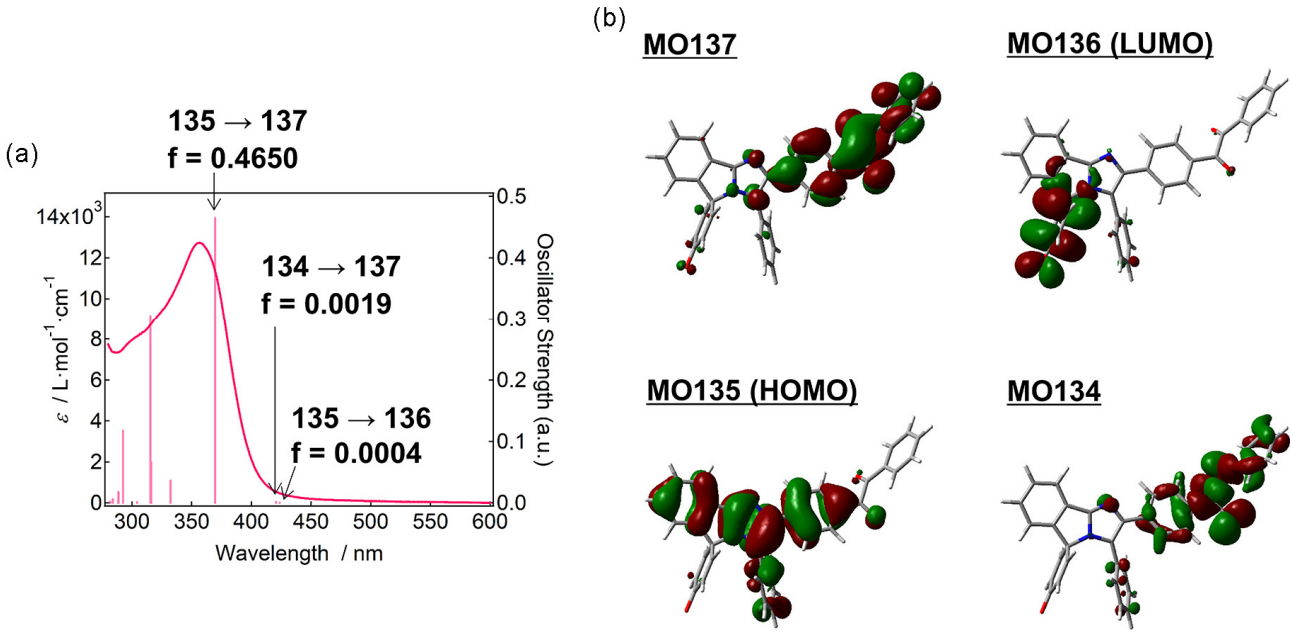


Figure S13. (a) UV-vis absorption spectrum of the closed-ring isomer of Isomer A of Benzil-PIC in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M05-2X/6-31+G(d,p) level of the theory) is shown by the vertical lines. (b) The relevant molecular orbitals of Isomer A of Benzil-PIC calculated at the M05-2X/6-31+G(d,p) level of the theory.

Table S2. Standard orientation of the optimized geometry for the closed-ring isomer of Isomer B of **Benzil-PIC**.

Tag	Symbol	Coordinates (Angstroms)		
		X	Y	Z
1	C	-7.2911450	-0.0734050	0.5917970
2	C	-6.9953580	-1.4392900	0.5947190
3	C	-5.6885720	-1.8887120	0.3916340
4	C	-4.7008270	-0.9398680	0.1947450
5	C	-4.9946510	0.4284170	0.1886290
6	C	-6.2937110	0.8792730	0.3891000
7	C	-3.7376390	1.1338130	-0.0187760
8	C	-3.2004740	-1.1793270	-0.0657180
9	C	-3.0762250	-1.9264700	-1.3667960
10	C	-2.6118700	-3.1757120	-1.4392430
11	C	-2.0954660	-3.8785860	-0.2409580
12	C	-2.0751500	-3.1152180	1.0283060
13	C	-2.5568550	-1.8725980	1.1031740
14	N	-2.7428000	0.2132520	-0.1766710
15	C	-1.5497600	0.9060640	-0.2274900

16	C	-1.9266470	2.2443190	-0.1473590
17	N	-3.2928230	2.3633260	-0.0094020
18	C	-1.0734110	3.4431170	-0.2044330
19	C	-0.2283030	0.2616310	-0.2335760
20	C	0.7209930	0.6467540	0.7211820
21	C	1.9738950	0.0492960	0.7498830
22	C	2.2903370	-0.9528200	-0.1738610
23	C	1.3470460	-1.3389590	-1.1316680
24	C	0.1002790	-0.7329290	-1.1646350
25	C	-1.4831080	4.6023200	0.4636110
26	C	-0.6998760	5.7513550	0.4242460
27	C	0.5008660	5.7586210	-0.2832960
28	C	0.9075550	4.6114700	-0.9620090
29	C	0.1237920	3.4622590	-0.9291660
30	O	-1.6962730	-5.0286230	-0.3022650
31	C	3.6253000	-1.6008130	-0.2171430
32	O	3.9269000	-2.4414760	-1.0423170
33	C	4.6597650	-1.2389270	0.8558790
34	O	4.3465550	-1.3950990	2.0206440
35	C	6.0017250	-0.7670200	0.4322890
36	C	6.3257740	-0.5528020	-0.9111830
37	C	7.5873380	-0.0700480	-1.2468990
38	C	8.5208250	0.1971960	-0.2484160
39	C	8.1982090	-0.0162120	1.0930000
40	C	6.9409860	-0.4953700	1.4336870
41	H	-8.3122390	0.2494520	0.7509040
42	H	-7.7883330	-2.1580920	0.7569020
43	H	-5.4534820	-2.9470220	0.3913090
44	H	-6.5138950	1.9387700	0.3874760
45	H	-3.4474940	-1.4007690	-2.2408480
46	H	-2.5737710	-3.7259210	-2.3712520
47	H	-1.6391290	-3.6172950	1.8826690
48	H	-2.5385570	-1.3073970	2.0290100
49	H	0.4664600	1.4163050	1.4392320
50	H	2.6907620	0.3451010	1.5035630
51	H	1.6149220	-2.1078820	-1.8453710
52	H	-0.6175500	-1.0165520	-1.9224520
53	H	-2.4204080	4.5879840	1.0047200
54	H	-1.0270510	6.6418600	0.9469150

55	H	1.1104300	6.6533330	-0.3129070
56	H	1.8306700	4.6139440	-1.5285040
57	H	0.4347300	2.5829710	-1.4796620
58	H	5.6085020	-0.7771490	-1.6889680
59	H	7.8417920	0.0927970	-2.2863820
60	H	9.5019520	0.5712090	-0.5142400
61	H	8.9265610	0.1919170	1.8665100
62	H	6.6631990	-0.6669360	2.4658600

SCF Done: E(RM052X) = -1682.06936648

Zero-point correction = 0.484362 (Hartree/Particle)
Thermal correction to Energy = 0.515169
Thermal correction to Enthalpy = 0.516114
Thermal correction to Gibbs Free Energy = 0.417471
Sum of electronic and zero-point Energies = -1681.585004
Sum of electronic and thermal Energies = -1681.554197
Sum of electronic and thermal Enthalpies = -1681.553253
Sum of electronic and thermal Free Energies = -1681.651895

Low frequencies --- -4.3160 -1.9542 -0.0022 -0.0021 -0.0008 2.7981
Low frequencies --- 9.0325 15.7886 20.1891

The Result for the TDDFT calculation of Isomer B of Benzil-PIC

Excited State 1: Singlet-A 2.8390 eV 436.72 nm f=0.0510 <S**2>=0.000

135 ->136 0.59567

135 ->137 -0.37415

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1681.72018008

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9139 eV 425.50 nm f=0.0005 <S**2>=0.000

134 ->136 0.61091

134 ->137 0.29730

Excited State 3: Singlet-A 3.0151 eV 411.21 nm f=0.1352 <S**2>=0.000

135 ->136 0.36705

135 ->137 0.59089

135 ->138 -0.10602

Excited State 4: Singlet-A 3.3406 eV 371.15 nm f=0.0000 <S**2>=0.000

131 ->136 -0.35930

131 ->137 0.58641

Excited State 5: Singlet-A 3.6321 eV 341.36 nm f=0.0668 <S**2>=0.000

134 ->138 0.10961

135 ->138 0.67919

Excited State 6: Singlet-A 3.7531 eV 330.35 nm f=0.0002 <S**2>=0.000

120 ->136 -0.13517

121 ->136 -0.10047

134 ->136 -0.13186

134 ->137 0.15289

134 ->138 0.60232

134 ->139 0.11434

135 ->138 -0.12011

Excited State 7: Singlet-A 3.9652 eV 312.68 nm f=0.1856 <S**2>=0.000

135 ->139 0.67109

135 ->140 0.17159

Excited State 8:	Singlet-A	4.1273 eV	300.40 nm	f=0.0011	<S**2>=0.000
133 ->136	0.64944				
135 ->140	-0.17365				
Excited State 9:	Singlet-A	4.1565 eV	298.29 nm	f=0.0162	<S**2>=0.000
132 ->136	0.31656				
134 ->136	-0.25569				
134 ->137	0.51977				
134 ->138	-0.13358				
Excited State 10:	Singlet-A	4.1697 eV	297.34 nm	f=0.2147	<S**2>=0.000
132 ->136	-0.12126				
133 ->136	0.16126				
135 ->139	-0.17387				
135 ->140	0.63007				
Excited State 11:	Singlet-A	4.1901 eV	295.90 nm	f=0.1010	<S**2>=0.000
132 ->136	0.53040				
132 ->137	-0.10029				
133 ->136	0.11233				
134 ->136	0.11975				
134 ->137	-0.31070				
134 ->138	0.12016				
135 ->140	0.11875				
135 ->141	-0.10282				
Excited State 12:	Singlet-A	4.3070 eV	287.87 nm	f=0.0288	<S**2>=0.000
127 ->136	-0.15075				
128 ->137	0.10459				
129 ->136	0.21410				
132 ->137	0.46372				
133 ->137	0.33595				
135 ->141	-0.20622				
Excited State 13:	Singlet-A	4.3575 eV	284.53 nm	f=0.0339	<S**2>=0.000
126 ->136	0.15027				
127 ->136	0.18269				
130 ->136	-0.15818				
132 ->136	0.22852				

133 ->136 -0.11694
133 ->137 0.36498
135 ->141 0.40636

Excited State 14: Singlet-A 4.3653 eV 284.02 nm f=0.0077 <S**2>=0.000
128 ->136 -0.10727
129 ->136 -0.23630
130 ->136 0.52495
130 ->137 0.22804
130 ->138 0.11679
133 ->137 0.19844

Excited State 15: Singlet-A 4.3917 eV 282.31 nm f=0.0449 <S**2>=0.000
127 ->136 -0.14918
128 ->136 0.21434
128 ->137 -0.27443
129 ->136 -0.20402
129 ->137 0.18329
130 ->136 -0.12206
132 ->137 -0.26510
133 ->137 0.31902
135 ->141 -0.24928

Excited State 16: Singlet-A 4.4173 eV 280.68 nm f=0.0135 <S**2>=0.000
127 ->136 0.10549
127 ->137 -0.12204
128 ->136 0.26904
128 ->137 -0.30900
129 ->136 -0.14192
129 ->137 0.23454
132 ->137 0.36487
133 ->137 -0.27187

Excited State 17: Singlet-A 4.4568 eV 278.19 nm f=0.1076 <S**2>=0.000
128 ->136 0.27798
129 ->136 0.45692
129 ->137 0.15937
130 ->136 0.28285
132 ->136 -0.11839

132 ->137 -0.17034

Excited State 18: Singlet-A 4.5165 eV 274.52 nm f=0.0142 <S**2>=0.000
126 ->136 0.18872
127 ->136 0.49605
135 ->141 -0.34116
135 ->142 -0.22136

Excited State 19: Singlet-A 4.5900 eV 270.12 nm f=0.0007 <S**2>=0.000
126 ->136 -0.10270
131 ->136 0.58438
131 ->137 0.34167
131 ->138 -0.10560

Excited State 20: Singlet-A 4.6058 eV 269.19 nm f=0.0267 <S**2>=0.000
126 ->136 0.48298
126 ->137 -0.14209
127 ->136 -0.21088
127 ->137 0.13911
128 ->137 0.18976
129 ->136 -0.11339
129 ->137 0.22575
130 ->136 0.10984
131 ->137 0.10148
135 ->141 -0.11060

Excited State 21: Singlet-A 4.6607 eV 266.02 nm f=0.1442 <S**2>=0.000
126 ->136 0.13067
126 ->137 0.18720
127 ->137 -0.28488
128 ->136 0.14681
129 ->137 -0.25884
135 ->141 -0.15148
135 ->142 0.44732
135 ->143 0.12532

Excited State 22: Singlet-A 4.7023 eV 263.67 nm f=0.0164 <S**2>=0.000
126 ->137 0.39630
127 ->137 0.48254

128 ->136 0.12999
129 ->137 -0.19765

Excited State 23: Singlet-A 4.7267 eV 262.31 nm f=0.0437 <S**2>=0.000
126 ->136 -0.13307
127 ->136 0.13399
127 ->137 0.27608
128 ->136 -0.20951
128 ->137 -0.10195
129 ->136 0.13251
129 ->137 0.25109
133 ->138 0.16089
135 ->142 0.39558

Excited State 24: Singlet-A 4.8270 eV 256.86 nm f=0.0195 <S**2>=0.000
126 ->136 -0.20090
126 ->137 -0.16553
127 ->136 0.12582
127 ->137 0.11500
128 ->136 0.36659
128 ->137 0.32811
128 ->138 -0.10127
129 ->136 -0.15495
133 ->138 0.25654
135 ->144 0.11290

Excited State 25: Singlet-A 4.8436 eV 255.97 nm f=0.0188 <S**2>=0.000
127 ->136 -0.12616
128 ->136 -0.10192
128 ->137 -0.11060
133 ->138 0.55737
133 ->142 -0.10712
135 ->145 -0.16769
135 ->146 0.14345

Excited State 26: Singlet-A 4.9080 eV 252.61 nm f=0.0189 <S**2>=0.000
129 ->138 -0.11723
130 ->136 -0.27318
130 ->137 0.52042

130 ->138	0.25265				
132 ->138	-0.15261				
Excited State 27:	Singlet-A	4.9346 eV	251.25 nm	f=0.0054	<S**2>=0.000
126 ->138	-0.10109				
130 ->137	0.13724				
132 ->138	0.51925				
135 ->144	-0.37240				
Excited State 28:	Singlet-A	4.9569 eV	250.12 nm	f=0.0221	<S**2>=0.000
124 ->136	-0.14875				
124 ->137	0.13653				
125 ->136	0.14341				
132 ->138	0.28994				
135 ->144	0.42355				
135 ->145	-0.22490				
135 ->146	0.11146				
Excited State 29:	Singlet-A	4.9700 eV	249.46 nm	f=0.0528	<S**2>=0.000
120 ->136	-0.24402				
120 ->137	-0.11533				
121 ->136	-0.17627				
126 ->136	0.10070				
126 ->137	-0.11474				
128 ->137	-0.12449				
129 ->136	0.10248				
132 ->138	0.18478				
133 ->138	0.14265				
133 ->142	0.13346				
134 ->138	-0.14576				
135 ->144	0.20566				
135 ->145	0.28507				
135 ->146	-0.17445				
Excited State 30:	Singlet-A	4.9843 eV	248.75 nm	f=0.0070	<S**2>=0.000
124 ->136	-0.17469				
124 ->137	0.20396				
125 ->136	0.24444				
125 ->137	-0.19594				

126 ->137 0.23062
128 ->137 0.15177
129 ->136 -0.13534
129 ->137 0.18628
130 ->137 0.13031
133 ->138 0.12424
133 ->142 0.10161
135 ->145 0.24172
135 ->146 -0.13241

Excited State 31: Singlet-A 5.0152 eV 247.22 nm f=0.0138 <S**2>=0.000
120 ->136 0.27557
120 ->137 0.12624
121 ->136 0.21868
121 ->137 0.11544
124 ->136 0.11118
124 ->137 -0.11219
125 ->136 -0.17360
125 ->137 0.17608
126 ->137 0.11061
132 ->138 0.10282
133 ->138 0.15429
134 ->138 0.14948
135 ->144 0.18228
135 ->145 0.16897
135 ->146 -0.11285

Excited State 32: Singlet-A 5.0190 eV 247.03 nm f=0.0013 <S**2>=0.000
120 ->136 -0.16148
121 ->136 -0.13769
124 ->136 0.10907
124 ->137 -0.13717
125 ->136 -0.25134
125 ->137 0.17217
126 ->136 -0.10825
126 ->137 0.25337
128 ->136 -0.10279
128 ->137 0.16522
129 ->137 0.18154

130 ->137 0.24172
130 ->138 -0.23198

Excited State 33: Singlet-A 5.0599 eV 245.03 nm f=0.0124 <S**2>=0.000
135 ->142 -0.15365
135 ->143 0.65899

Excited State 34: Singlet-A 5.0886 eV 243.65 nm f=0.0143 <S**2>=0.000
126 ->137 0.23768
127 ->137 -0.10148
128 ->137 0.18699
128 ->138 -0.11345
129 ->137 0.21261
129 ->138 -0.20637
130 ->137 -0.21910
130 ->138 0.42716

Excited State 35: Singlet-A 5.1578 eV 240.38 nm f=0.0151 <S**2>=0.000
124 ->136 0.26634
124 ->137 -0.17517
125 ->136 0.47589
125 ->137 0.19048
125 ->138 -0.14507
127 ->138 0.17939
132 ->139 -0.11001

Excited State 36: Singlet-A 5.1806 eV 239.32 nm f=0.0186 <S**2>=0.000
126 ->138 0.11737
127 ->138 0.19805
129 ->138 -0.11572
133 ->139 0.10712
135 ->145 0.32478
135 ->146 0.47820

Excited State 37: Singlet-A 5.2077 eV 238.08 nm f=0.0683 <S**2>=0.000
126 ->138 0.18327
127 ->138 0.39486
128 ->138 -0.12214
129 ->138 -0.17103

130 ->138 -0.11275
134 ->139 -0.21220
135 ->145 -0.26001
135 ->146 -0.19330

Excited State 38: Singlet-A 5.2318 eV 236.98 nm f=0.0045 <S**2>=0.000
124 ->136 -0.13366
124 ->137 0.10193
125 ->136 -0.12457
125 ->137 0.10040
127 ->138 0.20528
129 ->138 0.23288
131 ->138 0.18978
134 ->139 0.46421
134 ->141 -0.10496

Excited State 39: Singlet-A 5.2404 eV 236.59 nm f=0.0057 <S**2>=0.000
124 ->136 0.15819
125 ->137 -0.22260
127 ->138 -0.16217
129 ->138 -0.16008
131 ->138 0.39639
131 ->139 -0.25050
131 ->140 -0.17316
132 ->139 -0.14452
133 ->139 -0.18348

Excited State 40: Singlet-A 5.2538 eV 235.99 nm f=0.0083 <S**2>=0.000
124 ->136 0.16756
125 ->137 -0.24111
126 ->138 0.13569
129 ->138 -0.21236
131 ->138 -0.31070
131 ->139 0.15628
131 ->140 0.11376
134 ->139 0.34806

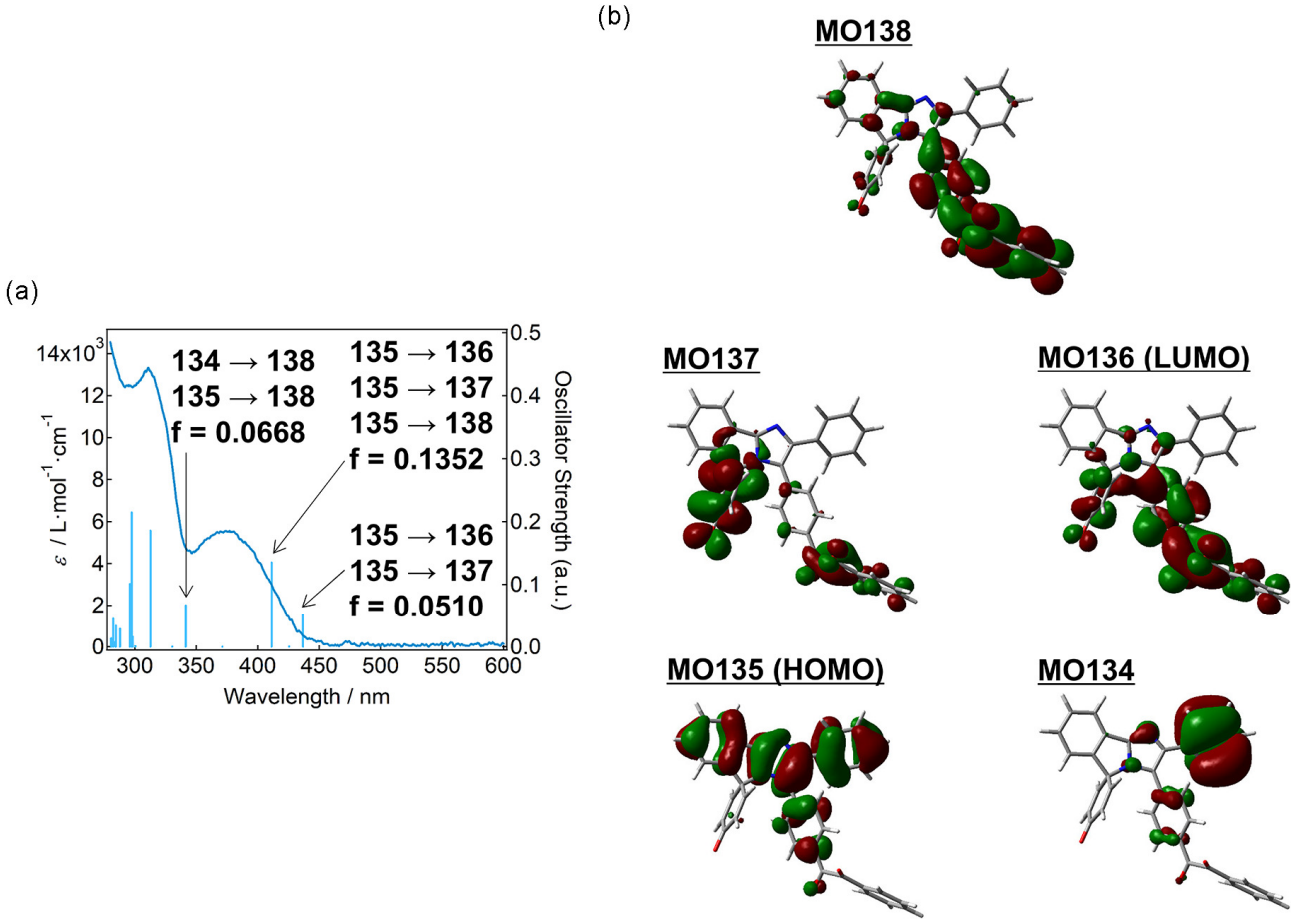


Figure S14. (a) UV-vis absorption spectrum of Isomer B of Benzil-PIC in benzene. The calculated spectrum (MPW1PW91/6-31+G(d,p)//M05-2X/6-31+G(d,p) level of the theory) is shown by the vertical lines. (b) The relevant molecular orbitals of Isomer B of Benzil-PIC calculated at the M05-2X/6-31+G(d,p) level of the theory.

9. Reference

S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; S. 50 Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford CT, 2009.