Electronic Supplementary Material (ESI) for Chemical Communications

- Supplementary Information -

Controlling stereoselectivity of solid-state photoreactions by co-crystal formation

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Experimental Section

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Materials and instruments.

All chemicals and solvents were purchased from Kanto Chemical Co., Ltd., Wako Pure Chemical Co., Ltd., and Tokyo Kasei Kogyo Co., Ltd., and were used without further purification. Compounds **1**–**3** were synthesized according to procedures reported by Schultz et.al.[1] Melting points were measured on Yanaco Micro Melting Point Apparatus 3120. ^{1}H NMR (500MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a JEOL α-500 spectrometer. In addition to $CHCl_3$ in $CDCl_3$ solution, fluorene was selected as the internal standard (see Fig. S8c) because its methylene singlet peak at 3.8 ppm does not overlap with other relevant peaks. The chemical shift values reported here are with respect to an external tetramethylsilane (TMS) standard. IR data were recorded on a JASCO FT/IR-350 spectrometer. EI-MS was acquired on JEOL JMS-600H MSroute.

X-ray crystallography.

X-ray crystallographic data of **X(1)**, **X(2)**, **X(3)**, **X_3(1:3**=1:1**)** and **3c** were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 103 K. X-ray crystallographic data of **X_3(2:3**=1:1**)**, **X_3(1:3**=9:1**)** and **1t** were collected on a Rigaku RAXIS-RAPID imaging plate area detector using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 153 K or 103 K. Crystallographic parameters are summarized in Table S1. The crystal structures were solved by the direct method using *SHELXS-97* program and refined by the successive differential Fourier syntheses and full-matrix least-squares procedure using *SHELXL-97* program.[2] Anisotropic thermal factors were applied to all non-hydrogen atoms. All hydrogen atoms were generated geometrically. The occupancy factors of the disordered atoms in **X_3(2:3**=1:1**)** and **X_3(1:3**=9:1**)** were fixed to 0.5:0.5 and 0.9:0.1, respectively. The occupancy factors of the disordered atoms in **X_3(1:3**=1:1**)** were estimated by *SHELXL-97* program.[2] Computer graphics of ORTEP drawing of the X-ray crystal structures were portrayed with Mercury 2.3 program.[3]

Stereochemistry.

The stereochemistry of the photochemical reaction products (the *trans* and the *cis* isomers) were determined by single crystal X-ray diffraction analysis. Crystal and molecular structures of **1t** (*trans* isomer) and **3c** (*cis* isomer) are shown in Fig. S4 and S5, respectively. They are representatives of the *trans* isomers (**1t**, **2t**, and **3t**) and the *cis* isomers (**1c**, **2c**, and **3c**).

Experimental procedure of the photochemical reactions.

A single crystal of a reactant (ca. 1.6~2 mg) was stored in a NMR sampling tube (KUSANO SCIENCE Corp., hard glass, ϕ5 mm). The NMR sampling tube was degassed and then filled with dry argon (this process was repeated three times). The single crystal was irradiated at 365 nm with SPOT CURE SP-V (USHIO SCIENCE Corp.) using a cut-filter (λ < 350 nm). After irradiation, the sample was dissolved in $CDCl_3$ and then subjected to ^{1}H NMR measurement.

Table S1 Crystallographic parameters

Crystal	**X(1)**	**X(2)**	**X(3)**	**X$_3$(2:3**=1:1**)**
Compound	**1**	**2**	**3**	**2** + **3**
Ratio	-	-	-	**2** : **3** = 0.52 : 0.48
Formula	$C_{14}H_{16}OS$	$C_{13}H_{13}OSCl$	$C_{13}H_{13}OSBr$	$C_{13}H_{13}OSCl_{0.5}Br_{0.5}$
Formula weight	232.3	252.7	297.2	275.0
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*P* $\bar{1}$ (#2)	*Pbca* (#61)	*Pbca* (#61)	*Pbca* (#61)
a/ Å	7.923(2)	15.596(3)	15.730(5)	15.8902(4)
b/ Å	10.418(2)	14.935(3)	15.142(5)	15.2239(3)
c/ Å	15.473(3)	20.531(4)	20.590(6)	20.6540(5)
α/ º	91.07 (3)	90	90	90
β/ º	102.32(3)	90	90	90
γ/ º	104.43(3)	90	90	90
V/ Å^3	1204.9(4)	4782.2(2)	4904(3)	4996.4(2)
$D_{calc.}$ /g cm^{-3}	1.28	1.40	1.61	1.46
Z	4	16	16	16
$2\theta_{max}$/º	55.6	55.8	55.8	54.8
μ (MoKα) /mm^{-1}	0.244	0.468	3.498	1.941
Temperature /*K*	103	103	103	153
Crystal form	block	block	block	block
Crystal size /mm	0.40×0.35×0.20	0.40×0.40×0.20	0.40×0.40×0.20	0.60 × 0.52 × 0.42
Crystal colourless	colourless	colourless	colourless	colourless
h range	−9 → 10	−20 → 20	−11 → 20	0 → 20
k range	−10 → 13	−19 → 19	−19 → 16	0 → 19
l range	−20 → 14	−26 → 26	−26 → 25	−26 → 0
# of total reflections	7394	39673	28443	43366
# of unique reflections	5205	5630	5696	5653
# of observed reflections	4521	4938	4446	2699
R_{int}	0.0230	0.0412	0.0461	0.0406
Criterion for observed reflections	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$
X-ray apparatus	SMART-CCD	SMART-CCD	SMART-CCD	Rigaku-IP
*R*1 (observed)	0.0423	0.0393	0.0345	0.0413
*wR*2 (observed)	0.1066	0.0930	0.0771	0.0969
G. O. F.	1.035	1.063	1.014	0.815
# of parameters used	293	291	291	309
$\Delta\rho_{max}$ (eÅ^{-3})	+0.403	+0.452	+0.754	+0.360
$\Delta\rho_{min}$ (eÅ^{-3})	−0.282	−0.323	−0.627	−0.297
CCDC number	679703	679704	679705	679709

Table S1 Crystallographic parameters (continued)

Crystal	**X_3(1:3**=1:1**)**	**X_3(1:3**=9:1**)**	-	-
Compound	**1** + **3**	**1** + **3**	**1t**	**3c**
Ratio	**1** : **3** = 0.49 : 0.51	**1** : **3** = 0.9 : 0.1	-	-
Formula	$C_{27.18}H_{29.54}O_2S_2Br_{0.82}$	$C_{13.9}H_{15.7}OSBr_{0.1}$	$C_{14}H_{16}OS$	$C_{13}H_{13}OSBr$
Formula weight	517.8	238.8	232.3	297.2
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca* (#61)	*Pbca* (#61)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a/ Å	15.591(3)	15.5798(4)	6.9911(2)	9.607(2)
b/ Å	15.064(3)	15.0633(4)	17.8652(4)	7.577(2)
c/ Å	20.669(4)	20.6424(5)	9.4401(2)	17.375(4)
α/ º	90	90	90	90
β/ º	90	90	96.020(1)	103.40(3)
γ/ º	90	90	90	90
V/ Å^3	4854.4(2)	4844.4(2)	1172.54(5)	1230.3(4)
$D_{calc.}$ /g cm^{-3}	1.42	1.32	1.32	1.60
Z	8	16	4	4
$2\theta_{max}$/º	55.8	59.8	59.8	55.8
μ (MoKα) /mm^{-1}	1.590	0.573	0.251	3.486
Temperature /*K*	103	103	153	103
Crystal form	plate	block	block	block
Crystal size /mm	0.20×0.20×0.05	0.52×0.50×0.46	0.25×0.25×0.05	0.40×0.10×0.10
Crystal colourless	colourless	colourless	colourless	colourless
h range	−20 → 20	−20 → 21	0 → 9	−12 → 12
k range	−19 → 19	−21 → 21	0 → 25	−9 → 9
l range	−26 → 26	−28 → 28	−13 → 13	−22 → 22
# of total reflections	40034	53767	13602	10251
# of unique reflections	5714	6998	3385	2840
# of observed reflections	4730	5748	2475	2553
R_{int}	0.0502	0.0551	0.0331	0.0387
Criterion for observed reflections	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$	$I > 2\sigma(F_o)$
X-ray apparatus	SMART-CCD	Rigaku-IP	Rigaku-IP	SMART-CCD
*R*1 (observed)	0.0464	0.0517	0.0380	0.0317
*wR*2 (observed)	0.1092	0.1215	0.0923	0.0793
G. O. F.	1.112	1.193	1.003	1.066
# of parameters used	301	299	146	145
$\Delta\rho_{max}$ (eÅ^{-3})	+0.520	+1.461	+0.491	+0.923
$\Delta\rho_{min}$ (eÅ^{-3})	−0.318	−1.142	−0.282	−0.351
CCDC number	679710	801654	679706	679707

Physical properties of 2-(2-methylphenylthio)-3-methyl-2-cyclohexene-1-one (1)

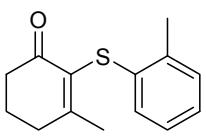
^{1}H NMR (500 MHz, $CDCl_3$): 2.06 (m, 2H), 2.23 (s, 3H,), 2.41 (s, 3H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 6.79 (m, 1H), 7.01 (m, 2H), 7.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.3, 21.9, 24.5, 24.5. 34.4, 38.4, 124.9, 125.7, 126.1, 129.4, 130.0, 135.6, 169.3, 194.3; MS (EI, 70 eV, *m/z*): 232 (M+); Elemental Analysis calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; N, 0. Found: C, 72.40; H, 7.07; N, 0.; Melting Point: 103.0 – 103.5 ºC.

Physical properties of 2-(2-chlorophenylthio)-3-methyl- 2-cyclohexene-1-one (2)

^{1}H NMR (500 MHz, $CDCl_3$): 2.08 (m, 2H), 2.27 (s, 3H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 6.1 Hz, 2H), 6.82 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.03 (ddd, *J* = 1.5, 7.6, 7.9 Hz, 1H), 7.08 (ddd, *J* = 1.2, 7.6, 7.9 Hz, 1H), 7.31 (dd, *J* = 1.2, 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 21.7, 24.4, 34.4, 38.2, 126.0, 126.9, 127.0, 129.5, 129.6, 131.9, 135.7, 170.7, 194.1; MS (EI, 70 eV, *m/z*): 254 (M+, ^{37}Cl), 252 (M+, ^{35}Cl); Elemental Analysis calcd. for $C_{13}H_{13}OSCl$: C, 61.77; H, 5.18; N, 0. Found: C, 61.70; H, 5.30; N, 0.; Melting Point: 94.0 – 95.0 ºC.

Physical properties of 2-(2-bromophenylthio)-3-methyl- 2-cyclohexene-1-one (3)

^{1}H NMR (500 MHz, $CDCl_3$): 2.09 (m, 2H), 2.26 (s, 3H,), 2.59 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 6.1 Hz, 2H), 6.78 (dd, *J* = 1.5, 7.9 Hz, 1H), 6.95 (ddd, *J* = 1.5, 7.3, 7.9 Hz, 1H), 7.12 (ddd, *J* = 1.2, 7.3, 7.9 Hz, 1H), 7.48 (dd, *J* = 1.2, 7.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 21.7, 24.5, 34.4, 38.2, 121.5, 126.1, 126.7, 127.5, 128.9, 132.9, 137.7, 170.8, 194.1; MS (EI, 70 eV, *m/z*): 298 (M+, ^{81}Br), 296 (M+, ^{79}Br); Elemental Analysis calcd. for $C_{13}H_{13}OSBr$: C, 52.54; H, 4.41; N, 0. Found: C, 52.60; H, 4.47; N, 0.; Melting Point: 99.0 – 100.0 ºC.



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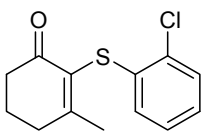

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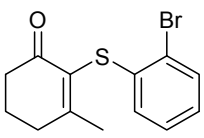


3

Physical properties of *trans*-6,9b-dimethyl-2,3,4a,9b-tetrahydro-1*H*- dibenzothiophene-4-one (1t)

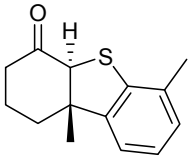
^{1}H NMR (500 MHz, $CDCl_3$): 1.13 (s, 3H), 2.06 (m, 1H), 2.17 (m, 1H), 2.24 (m, 1H), 2.27 (s, 3H), 2.37 (m, 1H), 2.45 (m, 1H), 2.54 (m, 1H), 4.61 (s, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H) ; ^{13}C NMR (125 MHz, $CDCl_3$): 18.8, 20.6, 23.2, 34.0, 40.4, 55.0, 70.5, 118.9, 125.3, 128.6, 133.5, 138.9, 147.5, 204.9; MS (EI, 70 eV, *m/z*): 232 (M+); Elemental Analysis calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; N, 0. Found: C, 72.36; H, 6.98; N, 0.; Melting Point: 161.0-163.5 ºC.

Physical properties of *trans*-6-chloro-9b-methyl-2,3,4a,9b-tetrahydro-1*H*-dibenzothiophene-4-one (2t)

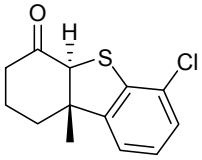
^{1}H NMR (500 MHz, $CDCl_3$): 1.15 (s, 3H), 2.08 (m, 1H), 2.17 (m, 1H), 2.25 (m, 1H), 2.38 (m, 1H), 2.46 (m, 1H), 2.55 (m, 1H), 4.66 (s, 1H), 6.95 (dd, *J* = 1.2, 7.3 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 1.2, 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 18.8, 23.0, 33.9, 40.3, 55.7, 70.3, 119.6, 126.5, 128.0, 149.5, 204.1; MS (EI, 70 eV, *m/z*): 254 (M+, ^{37}Cl), 252 (M+, ^{35}Cl); Elemental Analysis calcd. for $C_{13}H_{13}OSCl$: C, 61.77; H, 5.18; N, 0. Found: C, 61,63; H, 5.32; N, 0.; Melting Point: 148.0 – 149.5 ºC.

Physical properties of *trans*-6-bromo-9b-methyl-2,3,4a,9b-tetrahydro-1*H*-dibenzothiophene-4-one (3t)

^{1}H NMR (500 MHz, $CDCl_3$): 1.16 (s, 3H), 2.05 (m, 1H,), 2.10 (m, 1H), 2.26 (m, 1H), 2.34 (m, 1H), 2.46 (m, 1H), 2.55 (m, 1H), 4.67 (s, 1H), 6.99 (m, 2H), 7.31 (dd, J = 2.4, 6.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 18.9, 23.0, 34.0, 40.3, 56.1, 69.9, 118.2, 120.2, 126.6, 131.0, 141.7, 149.2, 204.1; MS (EI, 70 eV, *m/z*): 298 (M+, ^{81}Br), 296 (M+, ^{79}Br); Elemental Analysis calcd. for $C_{13}H_{13}OSBr$: C, 52.54; H, 4.41; N, 0. Found: C, 52.44; H, 4.45; N, 0.; Melting Point: 129.0 – 130.5 ºC.



1t



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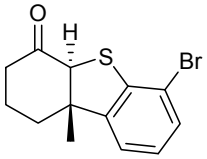


3t

Physical properties of *cis*-6,9b-dimethyl-2,3,4a,9b-tetrahydro-1*H*- dibenzothiophene-4-one (1c)

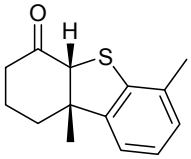
^{1}H NMR (500 MHz, $CDCl_3$): 1.45 (s, 3H), 1.66 (m, 1H), 1.87 (m, 1H), 2.18 (s, 3H), 2.36 (m, 1H), 2.79 (m, 1H), 3.93 (s, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.5, 21.1, 25.8, 34.3, 37.5, 54.5, 64.4, 120.0, 125.4, 128.7, 132.2, 138.9, 145.9, 208.5; MS (EI, 70 eV, *m/z*): 232 (M+); Elemental Analysis calcd. for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; N, 0. Found: C, 72.18; H, 7.15; N, 0.; Melting Point: 99.0 – 100.0 ºC.

Physical properties of *cis*-6-chloro-9b-methyl-2,3,4a,9b-tetrahydro-1*H*-dibenzothiophene-4-one (2c)

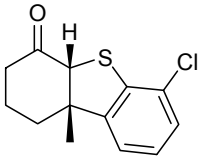
^{1}H NMR (500 MHz, $CDCl_3$): 1.47 (s, 3H), 1.67 (m, 1H), 1.87 (m, 1H), 2.17 (m, 1H), 2.37 (m, 1H), 2.80 (m, 1H), 3.97 (s, 1H), 6.92 (dd, *J* = 1.1, 7.5 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.18 (dd, *J* = 1.1, 7.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 21.0, 25.8, 34.4, 37.4, 64.8, 120.7, 126.6, 128.1, 148.0, 207.5; MS (EI, 70 eV, *m/z*): 254 (M+, ^{37}Cl), 252 (M+, ^{35}Cl); Elemental Analysis calcd. for $C_{13}H_{13}OSCl$: C, 61.77; H, 5.18; N, 0. Found: C, 61.71; H, 5.24; N, 0.; Melting Point: 65.0 – 66.0 ºC.

Physical properties of *cis*-6-bromo-9b-methyl-2,3,4a,9b-tetrahydro-1*H*-dibenzothiophene-4-one (3c)

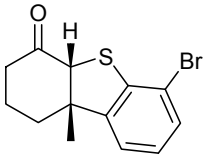
^{1}H NMR (500 MHz, $CDCl_3$): 1.46 (s, 3H), 1.66 (m, 1H), 1.87 (m, 1H), 2.18 (m, 1H), 2.37 (m, 1H), 2.80 (m, 1H), 3.97 (s, 1H), 6.99 (m, 2H), 7.33 (dd, *J* = 1.5, 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 20.9, 25.9, 34.5, 37.4, 55.8, 63.6, 116.3, 121.2, 126.6, 131.0, 141.5, 147.6, 207.5; MS (EI, 70 eV, *m/z*): 298 (M+, ^{81}Br), 296 (M+, ^{79}Br); Elemental Analysis calcd. for $C_{13}H_{13}OSBr$: C, 52.54; H, 4.41; N, 0. Found: C, 52.65; H, 4.57; N, 0.; Melting Point: 73.0 – 74.0 ºC.



1c



2c



3c

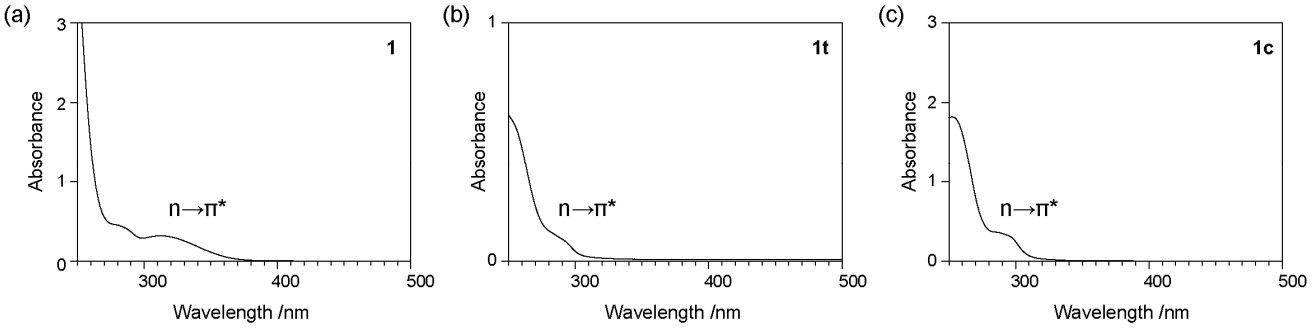


Fig. S1 Typical UV/vis absorption spectra (CH_2Cl_2) of (a) the reactant (**1**), (b) the *trans* isomer (**1t**) and (c) the *cis* isomer (**1c**).

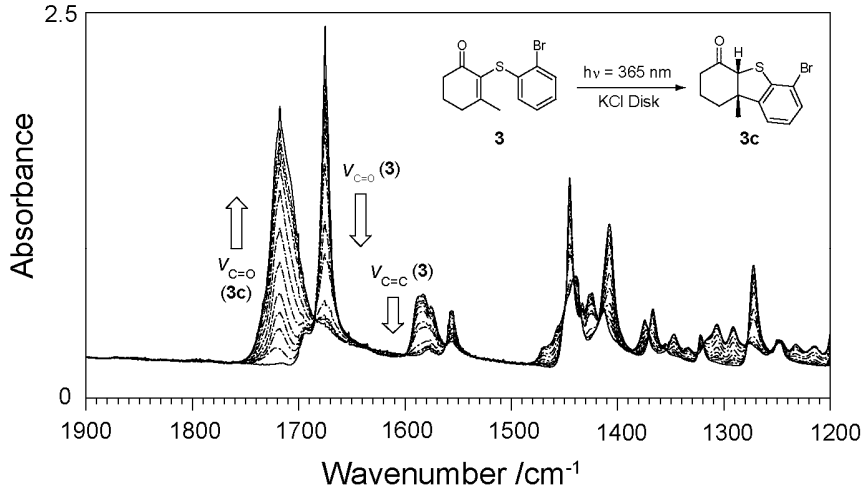


Fig. S2 The change of IR spectra of **X(3)** in a KCl disk upon UV irradiation at rt. Reaction time: 0 – 960 s.

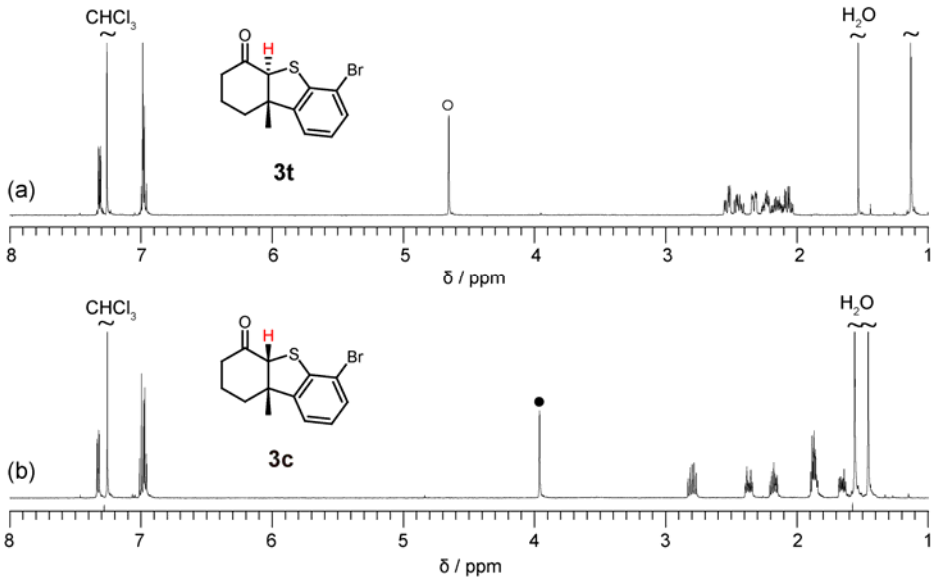


Fig. S3 Typical ^{1}H NMR spectra (500 MHz, 293 K, $CDCl_3$) of (a) the *trans* isomer (**3t**) and (b) the *cis* isomer (**3c**). (●) and (○) denote the methine proton of **3t** and the methine proton of **3c**, respectively.

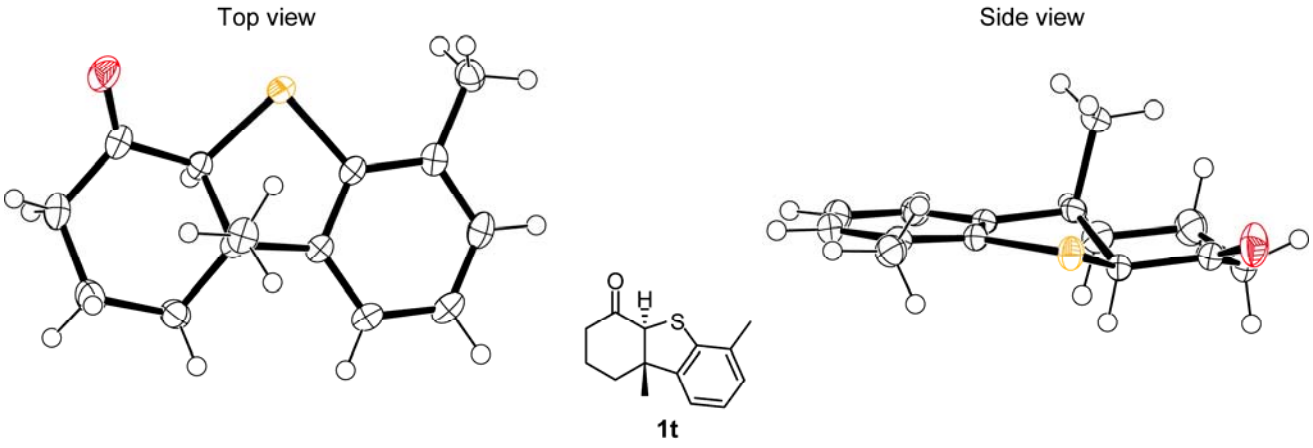


Fig. S4 ORTEP drawing (50 % probability ellipsoids) of top (left) and side (right) views of **1t**. Colour scheme: black (carbon), black (hydrogen), red (oxygen), orange (sulphur).

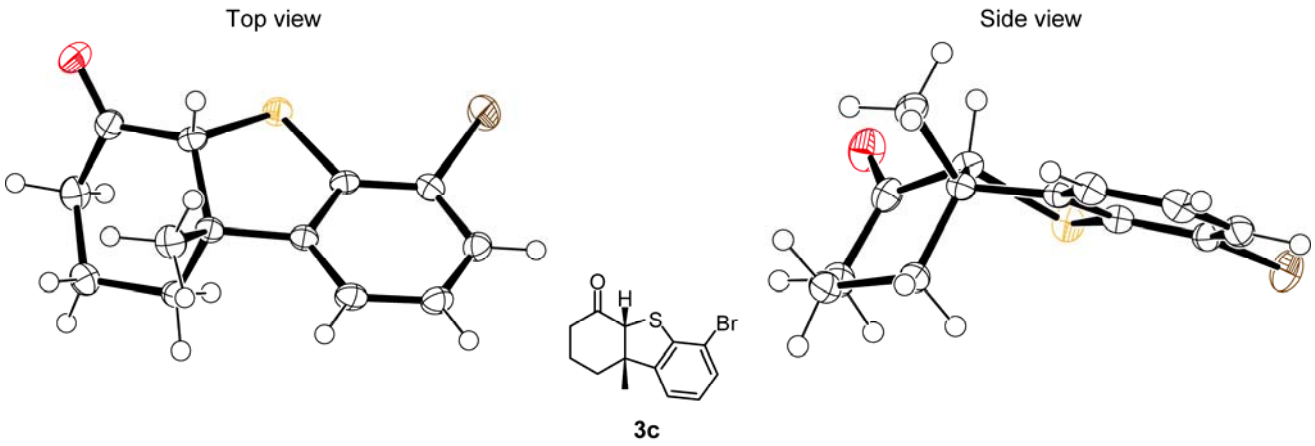


Fig. S5 ORTEP drawing (50 % probability ellipsoids) of top (left) and side (right) views of **3c**. Colour scheme: black (carbon), black (hydrogen), red (oxygen), orange (sulphur), brown (bromine).

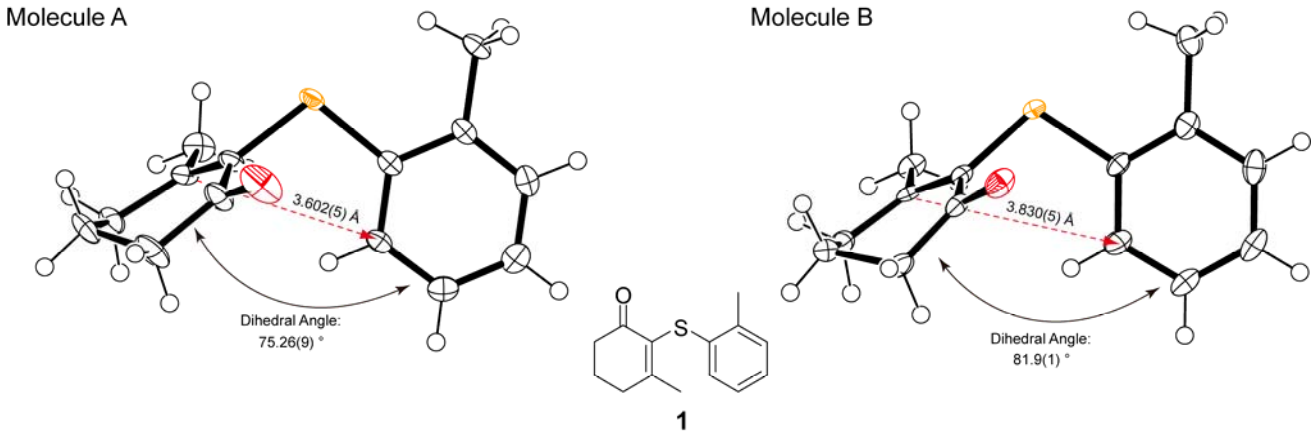


Fig. S6 ORTEP drawing (50 % probability ellipsoids) of the two independent molecules (Molecule A and B) of **1** in **X(1)**. Colour scheme: black (carbon), black (hydrogen), red (oxygen), orange (sulphur).

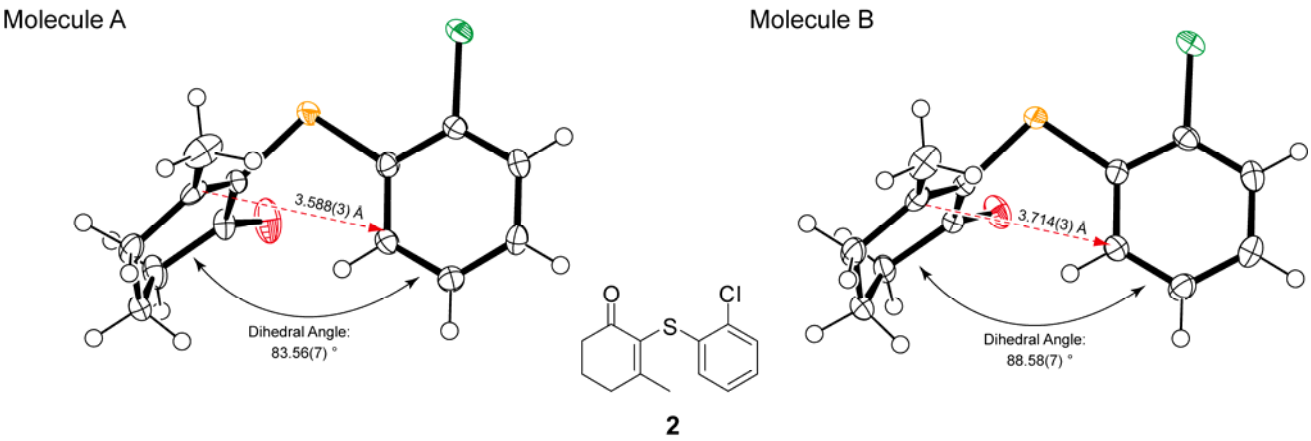


Fig. S7 ORTEP drawing (50 % probability ellipsoids) of the two independent molecules (Molecule A and B) of **2** in **X(2)**. Colour scheme: black (carbon), black (hydrogen), red (oxygen), orange (sulphur), green (chorine).

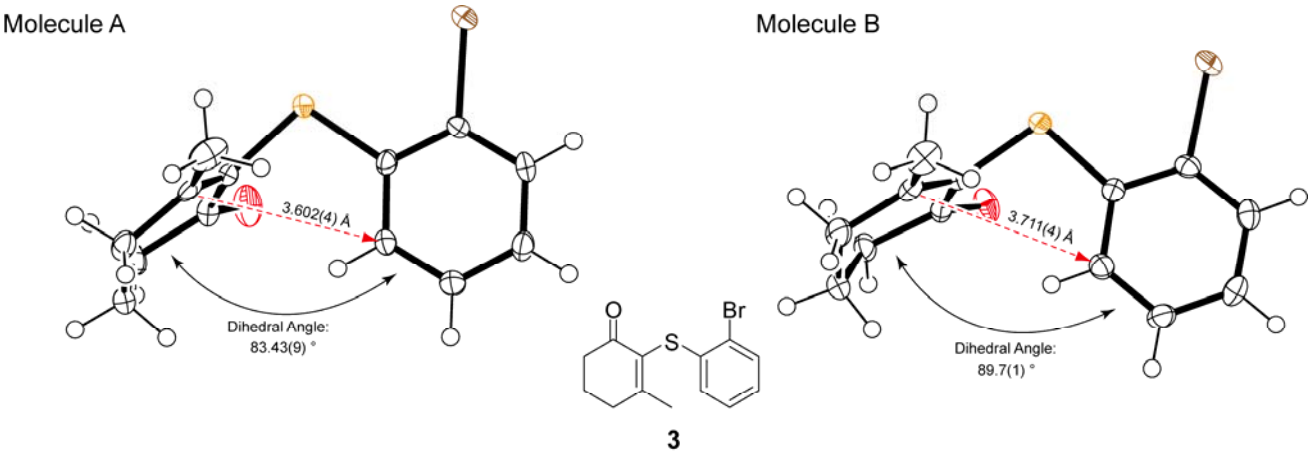


Fig. S8 ORTEP drawing (50 % probability ellipsoids) of the two independent molecules (Molecule A and B) of **3** in **X(3)**. Colour scheme: black (carbon), black (hydrogen), red (oxygen), orange (sulphur), brown (bromine).

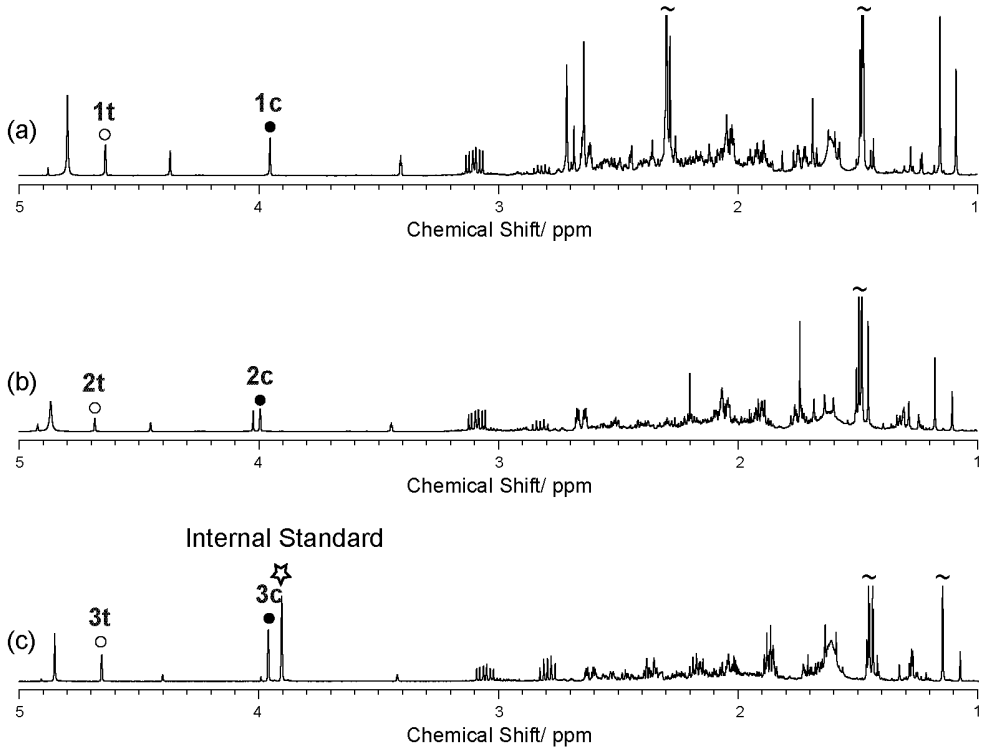


Fig. S9 Photochemical reaction products of (a) compound **1**, (b) compound **2** and (c) compound **3** in degassed benzene solution after UV irradiation (λ = 365 nm) for 2.0 *h*. (●) and (○) denote the *cis* and the *trans* isomers, respectively.

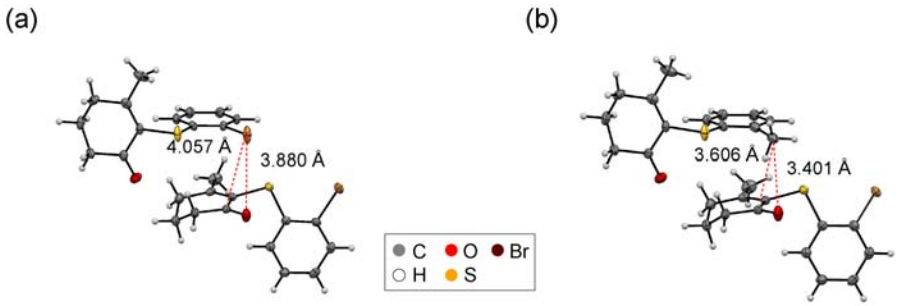


Fig. S10 Intermolecular carbonyl-Br (a) and carbonyl-Me (b) contacts found in **X(3)** and **X_3(1:3**=1:9**)**, respectively.

There are two independent molecules in crystals **X(3)** and **X_3(1:3**=1:9**).** Contacts for one molecule are shown in Fig. 3 and those for the other are shown in this Figure.

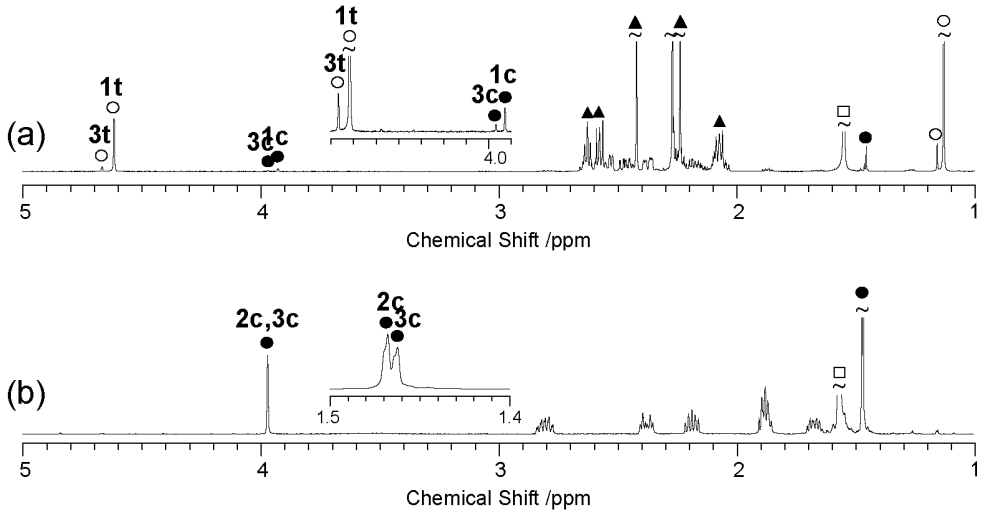


Fig. S11 The photochemical reaction products after UV irradiation for 0.5 *h* on single crystals of **X_3(1:3**=9:1**)** (a) and **X_3(2:3**=1:1**)** (b). (●), (○), (▲) and (□) denote the *cis* isomer, the *trans* isomer, the reactant and H_2O, respectively.

References

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2 G. M. Sheldrick, A short history of SHELX, *Acta. Cryst.* 2008, **A64**, 112.

3 See: http://www.ccdc.cam.ac.uk/products/mercury/