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Note

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Photoredox Reaction of 2-Mercaptothiazolinium Salts with Silyl Enol Ethers

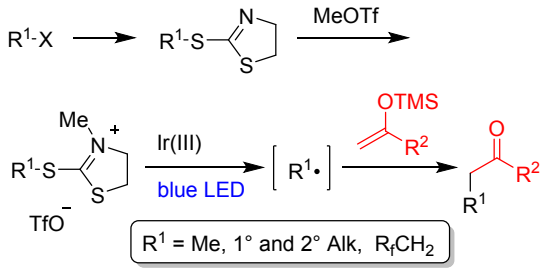
Artem A. Zemtsov,[†] Salavat S. Ashirbaev,[†] Vitalij, V. Levin,[†] Vladimir A. Kokorekin,[†,‡] Alexander A. Korlyukov,[§,¶] Alexander D. Dilman,[†,*]

[†]*N. D. Zelinsky Institute of Organic Chemistry, 119991 Moscow, Leninsky prosp. 47, Russian Federation, Fax: +7 499 135-53-28, E-mail: adil25@mail.ru*

[‡]*Sechenov First Moscow State Medical University, 119991 Moscow, Trubetskaya st. 8-2, Russian Federation*

[§]*A. N. Nesmeyanov Institute of Organoelement Compounds, 119991 Moscow, Vavilov str. 28, Russian Federation*

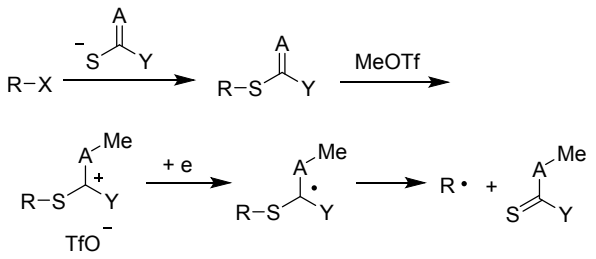
[¶]*N. I. Pirogov Russian National Research Medical University, Ostrovitianov str., 1, 117997 Moscow, Russian Federation*



Abstract A method for the generation of free radicals from thiazolinium salts upon photocatalytic reduction, is described. The thiazolinium salts are generated by treatment with methyl triflate of 2-mercaptothiazolines, which can be readily obtained from alkyl bromides and tosylates via nucleophilic substitution reaction, or by hydrothiolation of alkenes. Silyl enol ethers were used to trap the radicals furnishing ketones after successive single electron oxidation and elimination of the silyl cation.

Photoredox catalysis has emerged as a powerful methodology for carrying out reactions involving free radicals.[1] A radical species is generated with the aid of a catalyst, which after activation by light serves as one-electron reductant or oxidant. The reductive pathway is typically applied for the cleavage of carbon-heteroatom bond thereby providing carbon-centered radicals.

However, this process efficiently works with certain types of substrates, prone to SET reduction such as α-halocarbonyl compounds,[2] perfluorinated compounds,[3] and benzyl halides.[4] At the same time, the generation of unstabilized alkyl radicals from conventional alkyl halides with this method is less frequent, apparently, because of their unfavorable redox potential.[5,6] Herein we report that alkylthio-substituted dihydrothiazolinium salts, which can be readily accessed from corresponding alkyl halides and tosylates, or by an acid-promoted addition of 2-mercaptothiazoline to alkenes, serve as excellent sources of alkyl radicals under standard photoredox conditions. Our idea is to convert a poorly reducible neutral substrate into a cationic species capable of facile single electron reduction with subsequent dissociation of the C-S bond (Scheme 1). As acceptors of alkyl radicals, silyl enol ethers were selected, since they are known to be good components in photoredox reactions.[7,8]

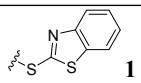
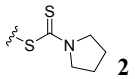
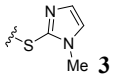
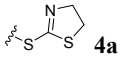


Scheme 1. Generation of radicals.

A series of thio-substituted starting compounds were prepared from cyclopentyl bromide and corresponding S-centered nucleophiles. Treatment of these compounds with methyl triflate for 15 min at 70 °C in dichloroethane generated triflate salts. Then, dichloroethane was evaporated under vacuum, which also removed the excess of the volatile methylating agent. After addition of another solvent, a photocatalyst (0.25 mol %) and silyl enol ether **5a**, the mixture was irradiated with blue light for 18 hours at room temperature (Table 1). N,N′-Dimethylpropyleneurea (DMPU, 1.2 equiv) was also added as a basic scavenger of trimethylsilyltriflate formed as a by-product. Derivatives of 2-mercaptobenzothiazole (entries 1-3), dithiocarbamic acid (entry 4), and 2-mercaptoimidazole (entry 5) in the presence of iridium and ruthenium catalysts showed moderate efficiency. The best results were achieved using the derivative of 2-mercapto-thiazoline in combination with a cationic

iridium complex. The use of a cheaper methylating agent, dimethylsulfate, gave inferior results (entry 8). The coupling was successfully performed in dichloromethane and acetonitrile with yields of 86% and 82%, respectively (entries 6 and 11). However, in all reactions using chlorinated solvents, small amounts of trapping of the radicals (i.e. cyclopentyl) by chlorine were observed by GC-MS analysis, and, for this reason, acetonitrile was used as solvent for further experiments.

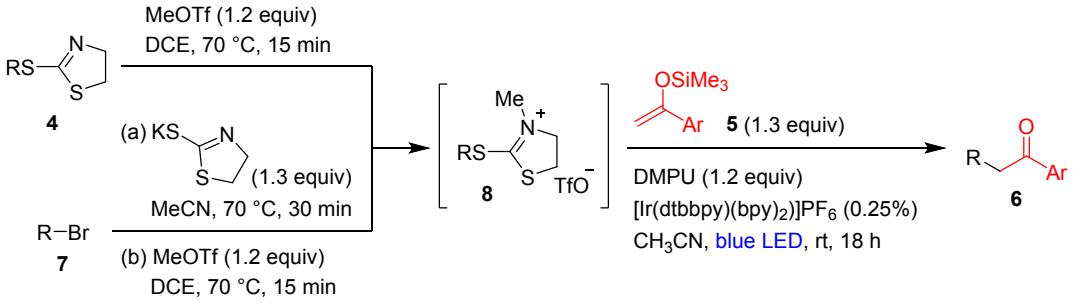
Table 1. Optimization studies.

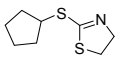
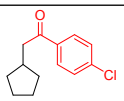
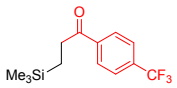
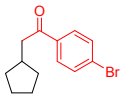
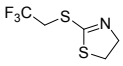
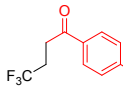
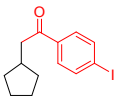
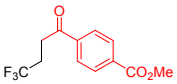
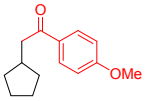
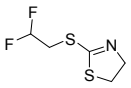
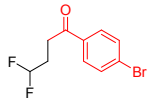
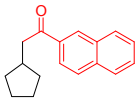
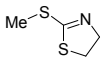
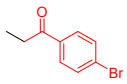
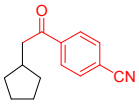
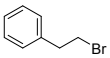
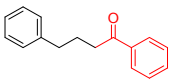
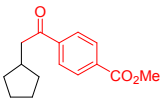
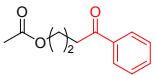
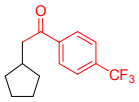
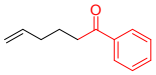
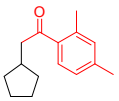
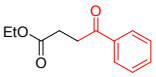
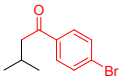
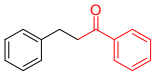
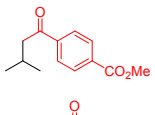
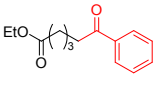
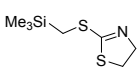
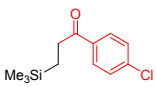
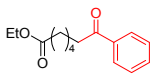
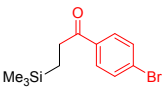
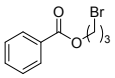
#	X	Solv.	Cat.	Y., %
1	 **1**	$ClCH_2CH_2Cl$	$[Ir(dtbbpy)(ppy)_2]PF_6$	40
2	**1**	$ClCH_2CH_2Cl$	$Ru(bpy)_3(PF_6)_2$	(25)[a]
3	**1**	CH_2Cl_2	$[Ir(dtbbpy)(ppy)_2]PF_6$	60
4	 **2**	CH_2Cl_2	$[Ir(dtbbpy)(ppy)_2]PF_6$	53
5[b,c]	 **3**	CH_2Cl_2	$Ir(ppy)_3$	(18)[b]
6	 **4a**	CH_2Cl_2	$[Ir(dtbbpy)(ppy)_2]PF_6$	86
7[c]	**4a**	CH_2Cl_2	$[Ir(dtbbpy)(ppy)_2]PF_6$	84
8[d]	**4a**	CH_2Cl_2	$[Ir(dtbbpy)(ppy)_2]PF_6$	60
9	**4a**	CH_2Cl_2	$Ru(phen)_3(BF_4)_2$	(29)[a]
10[e]	**4a**	CH_2Cl_2	xantphos(neocup)$CuBF_4$	78
11	**4a**	**CH_3CN**	**$[Ir(dtbbpy)(ppy)_2]PF_6$**	**82**
12[f]	**4a**	CH_3CN	$[Ir(dtbbpy)(ppy)_2]PF_6$	35
13[g]	**4a**	CH_3CN	$[Ir(dtbbpy)(ppy)_2]PF_6$	53
14[b,c]	**4a**	CH_3CN	$Ir(ppy)_3$	71
15[b,c,h]	**4a**	CH_3CN	$Ir(ppy)_3$	n.r.

[a]GC yield. [b]400 nm LED. [c]PPh_3 (0.1 equiv) added. [d]Me_2SO_4 (1.2 equiv) instead of MeOTf. [e]0.5% of cat. [f]No DMPU. [g]4 hours. [h]$BF_3{\cdot}OEt_2$ (1.2 equiv) instead of MeOTf.

We evaluated a series of such transformations starting either from 2-mercaptothiazolines **4** or from primary alkyl bromides **7** (Table 2). In the latter case, the corresponding derivatives **4** were prepared from **7** by brief heating with a potassium salt of 2-mercaptothiazoline for 70 °C in acetonitrile and used without further purification. The light-induced reaction of thiazolinium salts **8** proceeded smoothly with the sources of secondary radicals such as cyclopentyl (products **6b-e,j**) or isopropyl (products **6k,l**). Non-stabilized primary radicals including methyl, di- and trifluorinated ethyl radicals, as well as (trimethylsilyl)methyl radical, gave products **6** in reasonable yields. For stabilized radicals, the satisfactory results were obtained starting from ethyl bromoacetate (product **6w**), while the reaction with benzyl bromide was notably less efficient affording product **6x** in only 38% yield. Concerning the silyl enol ether counterpart, derivatives of aromatic ketones worked well. However, the enolates derived from aliphatic ketones proved to be not suitable for this process. For example, the reactions of enol ether obtained from methyl *tert*-butyl ketone resulted in complex mixtures, while the enol ether derived from α-tetralone gave 1-silyloxynaphtalene as the major product. For enolates bearing the naphthalene group or containing strong electron-withdrawing trifluoromethyl or ester groups in the aromatic ring, reactions proceeded very slowly under standard conditions. Fortunately, the replacement of the photocatalyst by more reducing $Ir(ppy)_3$ in combination with substoichiometric amounts of triphenylphosphine (0.2 equiv) allowed successful preparation of expected products **6f-i,o** in good yields. Though the exact nature of the such effect remains unknown, the ability of the phosphine to improve the efficiency of photoredox reactions has been noted earlier.[8b,c,9] Presumably, the role of phosphine is to negate the deleterious effect of oxygen on photocatalyst performance.

Table 2. Reactions of 2-Mercaptothiazolinium Salts

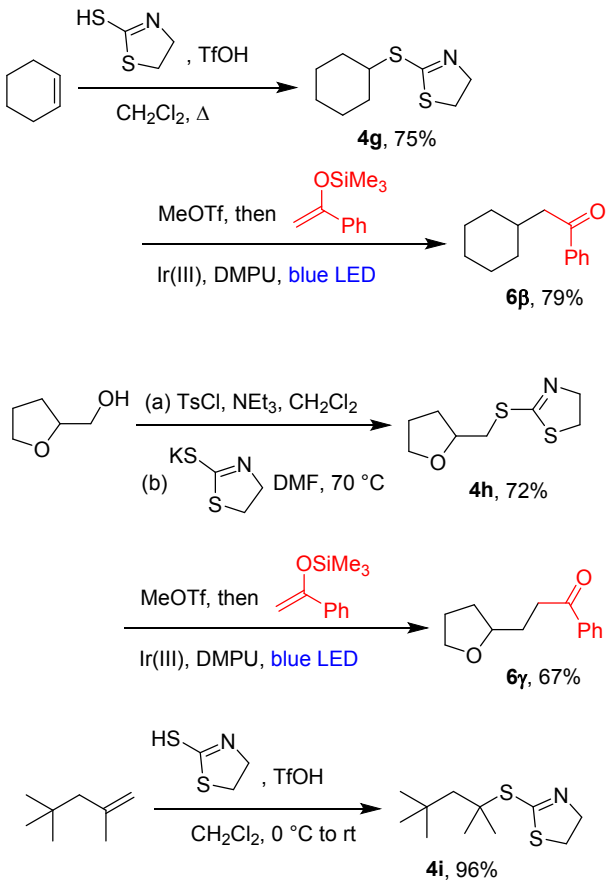


Starting		Product		Y, %	Starting		Product		Y, %
	**4a**		**6b**	93		**4c**		**6o**	82[a]
	4a		**6c**	73		**4d**		**6p**	99
	4a		**6d**	75		**4d**		**6q**	71
	4a		**6e**	56		**4e**		**6r**	63
	4a		**6f**	64[a]		**4f**		**6s**	80
	4a		**6g**	68[a]		**7a**		**6t**	70
	4a		**6h**	91[a]		**7b**		**6u**	46
	4a		**6i**	81[a]		**7c**		**6v**	41
	4a		**6j**	53		**7d**		**6w**	75
	**4b**		**6k**	85		**7e**		**6x**	38
	4b		**6l**	68		**7f**		**6y**	57
	**4c**		**6m**	77		**7g**		**6z**	57
	4c		**6n**	58		**7h**		**6α**	71

[a]$Ir(ppy)_3$ instead of $[Ir(dtbbpy)(ppy)_2]PF_6$. Ph_3P (0.2 equiv) was added.

2-Mercaptothiazoline derivatives **4** may be easily synthesized by different pathways, which greatly increase their applicability. We showed two examples of such transformations involving hydrothiolation of the double bond and tosylation/substitution of the hydroxy group (Scheme 2). These reactions starting from cyclohexene and (tetrahydrofuran-2-yl)methanol furnished thiazolines **4** in good yields, which were coupled with a silyl enol ether. Overall, this process may be considered as a method for the generation of radicals from alkenes or alcohols. The double bond addition reaction was also used to obtain thiazoline **4i** containing a tertiary substituent at sulfur. However, attempted generation of the corresponding thiazolinium salt by methylation of **4i** with methyl triflate failed, presumably, owing its facile decomposition.

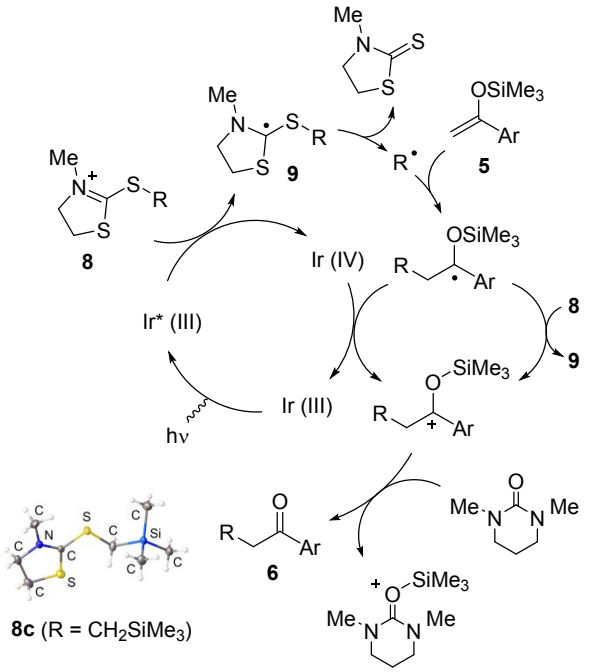
Scheme 2. Synthesis and Reactions of 2-Mercaptothiazolines.



The photoredox reaction likely proceeds via typical mechanism shown in Scheme 3. Thiazolinium salt **8** is reduced by photoexcited iridium (III) catalyst to give, after cleavage of the C-S bond, the free radical. The latter attacks at the double bond of the enol ether followed by

oxidation of the silyloxy-substituted radical. At the final step, the carbocation expels the silyl group, which is trapped by DMPU.[10] Several thiazolinium salts (**8a,c,f**) were characterized in solution by ^{1}H and ^{13}C NMR. Moreover, salt **8c** derived from thiazoline **4c** (R = CH_2SiMe_3) was isolated in individual state, and its structure was confirmed by single-crystal X-ray analysis. According to cyclic voltammetry, the reduction of compound **8c** begins at a potential of –0.82 V (vs. SCE, see Supporting Information for details). The values of oxidative potentials of photoexcited iridium complexes $[Ir(dtbbpy)(ppy)_2]PF_6$ (–0.96 V)[11] and $Ir(ppy)_3$ (–1.73 V)[11] suggest that the direct electron transfer between these two species is possible. We also performed Stern-Volmer experiments to test the interaction of salt **8c** with iridium complexes. While **8c** quenched the fluorescence of $Ir(ppy)_3$, no quenching of the fluorescence was observed for $Ir[(dtbbpy)(ppy)_2]PF_6$. The absence of quenching means that the interaction of cationic **8c** with cationic iridium $Ir[(dtbbpy)(ppy)_2]$ complex is problematic. In this case, the chain mechanism involving oxidation of silyloxy-substituted radical by the starting cation **8** may be operative, but the nature of the reaction initiation and the details of the electron transfer event from the cationic iridium complex are not clear.

Scheme 3. Proposed Mechanism.



In summary, a method for the photoinduced coupling of 2-mercaptothiazolinium salts, generated by alkylation of thiazolines, with silyl enol ethers is described. The thiazolinium salts behave as precursors of free radicals upon single electron reduction. The starting thiazolines can be readily accessed from corresponding alkyl halides, tosylates or alkenes.

EXPERIMENTAL SECTION

General Methods. Column chromatography was carried out employing silica gel (230−400 mesh). Precoated silica gel plates F254 were used for thin-layer analytical chromatography, and UV light and/or acidic aq KMnO4 solution was used for visualization. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer (Bruker MicrOTOF II). The measurements were done in a positive-ion mode (interface capillary voltage −4500 V) or in a negative-ion mode (3200 V); the mass ranged from m/z 50 to m/z 3000. For NMR measurements, a Bruker AM300 spectrometer was used. Fluorescence and absorption spectra were recorded on a Fluorat-02-Panorama spectrofluorometer (Lumex Instruments). For irradiation, a strip of light-emitting diodes (SMD2835-120 LED 1M Blue, 12 V, 24W/m, 465 nm) was used. Photo-induced reactions were performed in Duran culture tubes (Roth

cat. no K248.1, outside diameter = 12 mm); the distance from light source to the reaction vessel was 5 mm; during irradiation, the tube was cooled with room temperature water. 2-Mercaptothiazoline, acetophenones, compounds **7a** and **7c-e** were purchased from Acros. Compounds 2-(cyclopentylthio)-1,3-benzothiazole **1**,[12] 2-(methylthio)-4,5-dihydro-1,3-thiazole **4f**,[13] silyl enol ethers **5**,[14] 2-bromoethyl acetate **7b**,[15] ethyl 4-bromobutanoate **7f**,[16] ethyl 5-bromopentanoate **7g**,[17] 3-bromopropyl benzoate **7h**[18] were prepared according to literature procedures.

Potassium 4,5-dihydrothiazole-2-thiolate. Potassium hydroxide (4.48 g, 80.0 mmol) was added to a stirred solution of 2-mercaptothiazoline (10.0 g, 84.0 mmol) in ethanol (20 mL) at room temperature. The resulting suspension was stirred until complete dissolution of solid components (about 0.5 h; mild heating of the reaction mixture was observed; however, no temperature control was used). The solvent was evaporated under vacuum, the residue was dissolved in a small amount of methanol (5 mL) under reflux, and the hot solution was quickly diluted with boiling isopropanol (30 mL). The stirring was immediately discontinued, and the mixture was left to crystallize overnight at room temperature. The crystals were filtered and dried. Yield 11.52 g (77%). White crystals. Mp 193 – 195 °C. ^{1}H NMR (300 MHz, DMSO-d6): δ 3.84 (t, *J* = 7.7 Hz, 1H), 3.02 (t, *J* = 7.7 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d6): δ 177.7, 64.4, 35.7. HRMS (ESI): calcd for $C_3H_6NS_2$ [Anion + 2H$^+$], 119.9934; found, 119.9936.

*Cyclopentyl pyrrolidine-1-carbodithioate (**2**).* Cyclopentyl bromide (536 μL, 5.0 mmol) was added to a stirred solution of potassium pyrrolidine-1-carbodithioate (971 mg, 5.25 mmol) in DMF (5 mL) at room temperature. The resulting white suspension was stirred overnight, then diluted with water (15 mL), and extracted with hexane (3×5 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and the residue was crystallized from hexane (2 mL) at –20 °C. Yield 753 mg (70%). Pale-yellow crystals. Mp 45 – 47 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 – 4.08 (m, 1H), 3.90 (t, *J* = 6.7 Hz, 2H), 3.59 (t, *J* = 6.7 Hz, 2H), 2.32 – 2.13 (m, 2H), 2.05 (tt, *J* = 7.8, 6.7 Hz, 2H), 1.95 (tt, *J* = 7.8, 6.7 Hz, 2H), 1.79 – 1.54 (m, 6H). ^{13}C{^{1}H} NMR (75

MHz, $CDCl_3$): δ 193.4, 54.6, 50.6, 49.4, 33.0, 26.1, 24.9, 24.3. HRMS (ESI): calcd for $C_{10}H_{18}NS_2$ [M + H], 216.0875; found, 216.0880.

*2-(Cyclopentylthio)-1-methyl-1H-imidazole (**3**).* 1-Methyl-1H-imidazole-2-thiol (1.2 g, 10.5 mmol) was added to a stirred solution of potassium *tert*-butoxide (1.18 g, 10.5 mmol) in DMF (10 mL) [the addition was performed at such a rate to maintain the reaction temperature below 30 °C]. Then, cyclopentyl bromide (1.07 mL, 10.0 mmol) was added slowly and the resulting suspension was stirred for 4 hours at 70 °C (water bath). The mixture was diluted with water (20 mL) and extracted with hexane (3×10 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and the residue was distilled under vacuum (10 Torr) using Hickman distilling head (180 – 200 °C bath temp.). Yield 546 mg (30%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (d, J = 0.9 Hz, 1H), 6.87 (d, J = 0.9 Hz, 1H), 3.71 – 3.60 (m, 1H), 3.58 (s, 3H), 2.05 – 1.89 (m, 2H), 1.80 – 1.64 (m, 2H), 1.62 – 1.46 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 141.8, 129.2, 122.0, 47.6, 33.5, 33.3, 24.4. HRMS (ESI): calcd for $C_9H_{15}N_2S$ [M + H], 183.0950; found, 183.0951.

*2-(Cyclopentylthio)-4,5-dihydrothiazole (**4a**).* Potassium hydroxide (2.26 g, 40.3 mmol) was rapidly added to a stirred solution of 2-mercaptothiazoline (4.79 g, 40.3 mmol) in ethanol (20 mL), and the resulting suspension was stirred until complete dissolution of solid components (about 0.5 h). Then, cyclopentyl bromide (3.4 mL, 33.6 mmol) was added and the mixture was refluxed for 1 hour (water bath). The mixture was cooled to room temperature, diluted with water (30 mL) and extracted with MTBE (3×10 mL). The combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and the residue was distilled under vacuum (10 Torr) using Hickman distilling head (180 – 200 °C bath temp.). Yield 4.83 g (77%). Yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.21 (t, J = 8.0 Hz, 2H), 3.81 (sept, J = 6.8 Hz, 1H), 3.34 (t, J = 8.0 Hz, 2H), 1.37 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.7, 64.5, 45.7, 35.1, 33.6, 24.6. HRMS (ESI): calcd for $C_8H_{14}NS_2$ [M + H], 188.0562; found, 188.0562.

*Synthesis of 2-mercaptothiazoline derivatives **4b-e** (General Procedure **I**).* Alkyl halide (6 mmol) to a stirred suspension of 2-mercaptothiazoline potassium salt (1.22 g, 7.8 mmol) in acetonitrile (6 mL) was added [a quaternary ammonium salt was also added for the synthesis of **4c,e**: for **4c,** Bu_4NBr (97 mg, 0.3 mmol); for **4e**, Bu_4NI (111 mg, 0.3 mmol)]. The mixture was stirred in a closed vial at 75 °C (water bath), and the reaction progress was monitored by GC analysis. After completion (1-3 hours), the solvent was evaporated under reduced pressure, the residue was diluted with water (10 mL) and extracted with hexane (3×5 mL). The combined organic phases were filtered through a small pad of Na_2SO_4, concentrated under reduced pressure, and the residue was distilled under vacuum (10 Torr) using Hickman distilling head (140 – 170 °C bath temp.).

*2-(Isopropylthio)-4,5-dihydrothiazole (**4b**).* Synthesized according to General Procedure **I** from isopropyl bromide. Yield 705 mg (73%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.21 (t, J = 8.0 Hz, 1H), 3.81 (sept, J = 6.8 Hz, 1H), 3.34 (t, J = 8.0 Hz, 1H), 1.37 (d, J = 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 165.2, 64.5, 38.2, 35.0, 23.2. HRMS (ESI): calcd for $C_9H_{12}NS_2$ [M + H], 162.0406; found, 162.0402.

*2-{[(Trimethylsilyl)methyl]thio}-4,5-dihydrothiazole (**4c**)*. Synthesized according to General Procedure **I** from (bromomethyl)trimethylsilane. Yield 1.03 g (84%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17 (t, J = 7.9 Hz, 2H), 3.37 (t, J = 7.9 Hz, 2H), 2.36 (s, 2H), 0.09 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 168.1, 64.2, 35.8, 18.2, -1.8. HRMS (ESI): calcd for $C_7H_{16}NS_2Si$ [M + H], 206.0488; found, 206.0487.

*2-[(2,2,2-Trifluoroethyl)thio]-4,5-dihydrothiazole (**4d**).* Synthesized according to General Procedure **I** from 1,1,1-trifluoro-2-iodoethane. Yield 856 mg (71%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.21 (t, J = 8.0 Hz, 1H), 3.87 (q, J = 9.8 Hz, 1H), 3.47 (t, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 162.7, 124.77 (q, J = 276.1 Hz), 63.7, 36.4, 33.6 (q, J = 34.2 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): -66.55 (t, J = 9.5 Hz). HRMS (ESI): calcd for $C_5H_7F_3NS_2$ [M + H], 201.9967; found, 201.9960.

*2-[(2,2-Difluoroethyl)thio]-4,5-dihydrothiazole (**4e**).* Synthesized according to General Procedure **I** from 1,1-difluoro-2-iodoethane. Yield 889 mg (81%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.00 (tt, *J* = 56.7, 4.4 Hz, 1H), 4.19 (t, *J* = 8.0 Hz, 2H), 3.58 – 3.34 (m, 4H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 163.7, 114.3 (t, *J* = 242.3 Hz), 63.9, 36.2, 34.5 (t, *J* = 25.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -115.59 (dt, *J* = 56.8, 14.8 Hz). HRMS (ESI): calcd for $C_5H_8F_2NS_2$ [M + H], 184.0061; found, 184.0059.

*2-(Cyclohexylthio)-4,5-dihydrothiazole (**4g**).* Cyclohexene (505 μL, 5.0 mmol) and triflic acid (441 μL, 5.0 mmol) were added to a stirred solution of 2-mercaptothiazoline (714 mg, 6.0 mmol) in CH_2Cl_2 (3 mL) at room temperature. The mixture was refluxed for 48 hours (heating mantle), then immersed in a water bath at room temperature and quenched by dropwise addition of saturated aq. $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with hexane (2×5 mL). The combined organic phases were filtered through a small pad of Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography. Yield 753 mg (75 %). Colorless oil. Chromatography: hexanes/EtOAc, 4/1. R_f 0.45 (hexanes/EtOAc, 4/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.20 (t, *J* = 7.9 Hz, 2H), 3.74 – 3.60 (m, 1H), 3.33 (t, *J* = 7.9 Hz, 2H), 2.14 – 1.99 (m, 2H), 1.79 – 1.65 (m, 2H), 1.64 – 1.18 (m, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 165.1, 64.5, 46.0, 35.0, 33.3, 25.8, 25.6. HRMS (ESI): calcd for $C_9H_{16}NS_2$ [M + H], 202.0719; found, 202.0715.

*2-{[(Tetrahydrofuran-2-yl)methyl]thio}-4,5-dihydrothiazole (**4h**).* Triethylamine (1.0 ml, 7.2 mmol) and (tetrahydrofuran-2-yl)methanol (581 μL, 6.0 mmol) were added successively to a stirred suspension of 4-methylbenzenesulfonyl chloride (1.24 g, 6.5 mmol) in CH_2Cl_2 (6 mL) at 0 °C. The cooling bath was removed, the reaction vessel was left to warm to room temperature, and the resulting homogenous mixture was stirred overnight. After the completion (monitored by GC analysis), the mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3×5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in DMF (4 mL) and charged with 2-mercaptothiazoline potassium salt (1.26

g, 8.0 mmol). The resulting suspension was stirred for 3 hours at 70 °C (water bath), then diluted with water (10 mL) and extracted with hexane (3×5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography. Yield 877 mg (72%). Pale-yellow oil. Chromatography: hexanes/EtOAc, 2/1. R_f 0.21 (hexanes/EtOAc, 2/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 – 4.06 (m, 3H), 3.86 (dd, J = 14.2, 7.4 Hz, 1H), 3.73 (dd, J = 14.2, 7.6 Hz, 1H), 3.40 – 3.17 (m, 4H), 2.10 – 1.95 (m, 1H), 1.97 – 1.78 (m, 2H), 1.69 – 1.55 (m, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.5, 77.3, 68.3, 64.1, 37.4, 35.6, 30.7, 25.8. HRMS (ESI): calcd for $C_8H_{14}NOS_2$ [M + H], 204.0511; found, 204.0513.

*2-[(2,4,4-Trimethylpentan-2-yl)thio]-4,5-dihydrothiazole (**4i**).* 2,4,4-Trimethylpent-1-ene (633 μL, 4.0 mmol) was added dropwise to a stirred solution of 2-mercaptothiazoline (571 mg, 4.8 mmol) and TfOH (354 μL, 4.0 mmol) in CH_2Cl_2 (2 mL) at 0 °C. The reaction mixture was stirred for 20 minutes at 0 °C, then warmed to room temperature and kept for additional 10 minutes. The resulting mixture was quenched with saturated aqueous $NaHCO_3$ (7 mL), then the organic layer was separated, and the aqueous layer was washed with methyl *tert*-butyl ether (2×5 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under reduced pressure, and the residue was filtered through a pad of silica gel (~ 3 cm) eluting with hexane/ethyl acetate (6/1). Yield 887 mg (96%). Colorless oil. R_f 0.47 (hexanes/EtOAc, 6/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.26 (t, J = 7.6 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H), 1.89 (s, 2H), 1.64 (s, 6H), 1.04 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 163.9, 65.3, 54.8, 54.0, 34.1, 32.8, 31.7, 30.3. HRMS (ESI): calcd for $C_{11}H_{21}NS_2Na$ [M + Na], 254.1008; found, 254.1000.

*Reaction of 2-mercaptothiazolines **4** (General Procedure **II**).* 2-Mercaptothiazoline **4** (1.0 mmol) was placed into a sealed tube and diluted with dichloroethane (100 μL). Then, methyl triflate (131 μL, 1.2 mmol) was added at room temperature. The resulting viscous mixture was stirred for 15 minutes at 70 °C (water bath), then cooled down to room temperature, and volatile components were evaporated under vacuum. The residue was diluted with acetonitrile (1.5 mL), then DMPU (144 μL, 1.2 mmol), silyl enol ether **5** (1.33 mmol), a photocatalyst [for **6a-e,j-n,p-s**,

Ir(dtbbpy)(ppy)$_2$]PF$_6$ (2.4 mg, 0.25 mol %); for **6f-i,o**, Ir(ppy)$_3$ (1.6 mg, 0.25 mol %) and triphenylphosphine (52.0 mg, 0.2 mmol)] were successively added. The reaction tube was cooled to –20 °C, and a vacuum of 10 Torr was briefly applied with intense stirring followed by filling with argon (three times), and the tube was warmed to room temperature. The mixture was irradiated with blue LEDs upon for 16 hours while maintaining the reaction temperature around 20 °C. The mixture was diluted with water (10 mL) and extracted with hexane (3×5 mL). The combined organic phases were filtered through a small pad of Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography.

*2-Cyclopentyl-1-phenylethan-1-one (**6a**).*[19] General Procedure **II**. Yield 154 mg (82%). Slightly-yellow oil. Chromatography: hexanes/EtOAc, 40/1. R_f 0.27 (hexanes/EtOAc, 40/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 – 7.93 (m, J = 5.3, 3.4 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.50 – 7.40 (m, 2H), 2.98 (d, J = 7.1 Hz, 2H), 2.39 (tp, J = 8.3, 7.3 Hz, 1H), 1.96 – 1.78 (m, 2H), 1.72 – 1.48 (m, 4H), 1.28 – 1.11 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.3, 137.3, 132.8, 128.5, 128.1, 44.8, 36.1, 32.8, 25.0.

*1-(4-Chlorophenyl)-2-cyclopentylethan-1-one (**6b**).* General Procedure **II**. Yield 207 mg (93%). White crystals. Mp 63 – 64 °C. Chromatography: hexanes/EtOAc, 30/1. R_f 0.19 (hexanes/EtOAc, 30/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 2.95 (d, J = 7.2 Hz, 2H), 2.36 (tp, J = 8.6, 7.2 Hz, 1H), 1.95 – 1.79 (m, 2H), 1.75 – 1.46 (m, 4H), 1.28 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.1, 139.3, 135.6, 129.6, 128.9, 44.8, 36.1, 32.8, 25.0. HRMS (ESI): calcd for $C_{13}H_{16}ClO$ [M + H], 223.0884; found, 223.0891.

*1-(4-Bromophenyl)-2-cyclopentylethan-1-one (**6c**).* General Procedure **II**. Yield 195 mg (73%). Colorless crystals. Mp 69 – 70 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.27 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 2.94 (d, J = 7.3 Hz, 2H), 2.36 (tp, J = 8.6, 7.3 Hz, 1H), 1.97 – 1.76 (m, 2H), 1.73 – 1.46 (m, 4H), 1.28 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.3, 136.0, 131.9, 129.7, 128.0,

44.8, 36.0, 32.8, 25.0. HRMS (ESI): calcd for $C_{13}H_{15}BrONa$ [M + Na], 289.0198/291.0178; found, 289.0208/291.0188.

*2-Cyclopentyl-1-(4-iodophenyl)ethan-1-one (**6d**)*. General Procedure **II**. Yield 238 mg (75%). White crystals. Mp 66 – 67 °C. Chromatography: hexanes/EtOAc, 30/1. R_f 0.24 (hexanes/EtOAc, 30/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 2.93 (d, *J* = 7.2 Hz, 2H), 2.36 (tp, *J* = 8.5, 7.2 Hz, 1H), 1.95 – 1.79 (m, 2H), 1.73 – 1.46 (m, 4H), 1.26 – 1.07 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.6, 137.9, 136.6, 129.6, 100.8, 44.8, 36.1, 32.8, 25.0. HRMS (ESI): calcd for $C_{13}H_{16}IO$ [M + H], 315.0240; found, 315.0240.

*2-Cyclopentyl-1-(4-methoxyphenyl)ethan-1-one (**6e**)*.[20] General Procedure **II**. Yield 122 mg (56%). Colorless oil. Chromatography: hexanes/EtOAc, 12/1. R_f 0.27 (hexanes/EtOAc, 12/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 4H), 2.89 (d, *J* = 7.3 Hz, 2H), 2.35 (tp, *J* = 8.5, 7.3 Hz, 1H), 1.95 – 1.75 (m, 2H), 1.73 – 1.43 (m, 4H), 1.27 – 1.06 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 198.9, 163.3, 130.4, 130.3, 113.6, 55.4, 44.4, 36.3, 32.7, 25.0.

*2-Cyclopentyl-1-(naphthalen-2-yl)ethan-1-one (**6f**)*. General Procedure **II**. Yield 152 mg (64%). Slightly-yellow oil. Chromatography: hexanes/EtOAc, 25/1. R_f 0.23 (hexanes/EtOAc, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (s, 1H), 8.10 – 7.97 (m, 1H), 8.01 – 7.92 (m, 1H), 7.96 – 7.80 (m, 2H), 7.66 – 7.46 (m, 2H), 3.12 (d, *J* = 7.4 Hz, 2H), 2.47 (sept, *J* = 7.4 Hz, 1H), 2.02 – 1.86 (m, 2H), 1.78 – 1.50 (m, 3H), 1.34 – 1.16 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.3, 135.5, 134.7, 132.6, 129.7, 129.5, 128.4, 128.3, 127.8, 126.7, 124.0, 44.9, 36.3, 32.8, 25.1. HRMS (ESI): calcd for $C_{17}H_{19}O$ [M + H], 239.1430; found, 239.1432.

*4-(2-Cyclopentylacetyl)benzonitrile (**6g**)*. General Procedure **II**. Yield 145 mg (68%). Colorless crystals. Mp 57 – 58 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.25 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 2.98 (d, *J* = 7.3 Hz, 2H), 2.34 (sept, *J* = 7.3 Hz, 1H), 1.94 – 1.80 (m, 2H), 1.71 – 1.45 (m, 4H), 1.24 – 1.06 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 198.8, 140.1, 132.4, 128.5, 117.9, 116.1, 45.0, 35.7, 32.6, 24.9. HRMS (ESI): calcd for $C_{14}H_{15}NONa$ [M + Na], 236.1046; found, 236.1046.

*Methyl 4-(2-cyclopentylacetyl)benzoate (**6h**)*. General Procedure **II**. Yield 224 mg (91%). White crystals. Mp 67 – 68 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.25 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 2.99 (d, J = 7.2 Hz, 2H), 2.36 (tp, J = 8.6, 7.2 Hz, 1H), 1.95 – 1.79 (m, 2H), 1.72 – 1.45 (m, 4H), 1.29 – 1.07 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 199.8, 166.2, 140.5, 133.7, 129.8, 128.0, 52.4, 45.2, 35.9, 32.7, 25.0. HRMS (ESI): calcd for $C_{15}H_{19}O_3$ [M + H], 247.1329; found, 247.1335.

*2-Cyclopentyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**6i**)*. General Procedure **II**. Yield 207 mg (81%). Colorless crystals. Mp 34 – 35 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.27 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 3.01 (d, J = 7.1 Hz, 2H), 2.39 (sept, J = 7.6 Hz, 1H), 1.97 – 1.81 (m, 2H), 1.75 – 1.48 (m, 4H), 1.27 – 1.10 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 199.3, 140.0, 134.0 (q, J = 32.6 Hz), 128.5, 125.7 (q, J = 3.7 Hz), 123.7 (q, J = 273.2 Hz), 45.2, 36.0, 32.8, 25.0. ^{19}F NMR (282 MHz, Chloroform-*d*): δ -63.91. HRMS (ESI): calcd for $C_{14}H_{15}F_3ONa$ [M + Na], 279.0967; found, 279.0965.

*2-Cyclopentyl-1-(2,4-dimethylphenyl)ethan-1-one (**6j**)*. General Procedure **II**. Yield 114 mg (53%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1. R_f 0.27 (hexanes/EtOAc, 15/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 5.7 Hz, 2H), 2.90 (d, J = 7.2 Hz, 2H), 2.49 (s, 3H), 2.35 (s, 3H), 2.34 – 2.28 (m, 1H), 1.93 – 1.78 (m, 2H), 1.71 – 1.47 (m, 4H), 1.26 – 1.09 (m, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 204.1, 141.5, 138.3, 135.6, 132.8, 128.9, 126.2, 47.7, 36.3, 32.7, 25.0, 21.4, 21.3. HRMS (ESI): calcd for $C_{15}H_{21}O$ [M + H], 217.1587; found, 217.1589.

*1-(4-Bromophenyl)-3-methylbutan-1-one (**6k**)*. General Procedure **II**. Yield 204 mg (85%). Colorless crystals. Mp 48 – 49 °C. Chromatography: hexanes/EtOAc, 40/1. R_f 0.17 (hexanes/EtOAc, 40/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5

Hz, 2H), 2.79 (d, J = 6.8 Hz, 2H), 2.27 (m, J = 6.8 Hz, 1H), 0.99 (d, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.1, 136.1, 131.9, 129.7, 128.0, 47.5, 25.2, 22.8. HRMS (ESI): calcd for $C_{11}H_{14}{}^{79}BrO$ [M + H], 241.0223; found, 241.0227; calcd for $C_{11}H_{14}{}^{81}BrO$ [M + H], 243.0202; found, 243.0208.

*Methyl 4-(3-methylbutanoyl)benzoate (**6l**)*.[21] General Procedure **II**. Yield 150 mg (68%). White solid. Mp 37 – 38 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.25 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H), 2.79 (d, J = 6.7 Hz, 2H), 2.23 (nonet, J = 6.7 Hz, 1H), 0.93 (d, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.4, 166.1, 140.5, 133.6, 129.7, 127.8, 52.3, 47.6, 24.9, 22.6.

*1-(4-Chlorophenyl)-3-(trimethylsilyl)propan-1-one (**6m**)*.[22] General Procedure **II**. Yield 185 mg (77%). Yellowish oil. Chromatography: hexanes/EtOAc, 30/1. R_f 0.22 (hexanes/EtOAc, 30/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 2.97 – 2.85 (m, 2H), 0.97 – 0.85 (m, 2H), 0.05 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.0, 139.3, 135.2, 129.6, 128.9, 33.2, 10.9, -1.7.

*1-(4-Bromophenyl)-3-(trimethylsilyl)propan-1-one (**6n**)*.[22] General Procedure **II**. Yiled 165 mg (58%). Slightly-yellow solid. Mp 23 – 24 °C. Chromatography: hexanes/EtOAc, 40/1. R_f 0.28 (hexanes/EtOAc, 40/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 2.94 – 2.82 (m, 2H), 0.93 – 0.81 (m, 2H), 0.03 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.0, 135.5, 131.8, 129.6, 127.8, 33.1, 10.8, -1.7.

*1-(4-(Trifluoromethyl)phenyl)-3-(trimethylsilyl)propan-1-one (**6o**)*.[22] General Procedure **II**. Yield 225 mg (82%). Colorless oil. Chromatography: hexanes/EtOAc, 25/1. R_f 0.27 (hexanes/EtOAc, 25/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 3.02 – 2.90 (m, 2H), 0.97 – 0.84 (m, 2H), 0.05 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.1, 139.6, 134.2 (q, J = 32.5 Hz), 125.7 (q, J = 3.8 Hz), 123.7 (q, J = 271.1 Hz), 33.6, 10.8, -1.8.

*1-(4-Chlorophenyl)-4,4,4-trifluorobutan-1-one (**6p**)*.[23] General Procedure **II**. Yield 234 mg (99%). White solid. Mp 66 – 67 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.21 (hexanes/EtOAc,

20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 3.29 – 3.15 (m, 2H), 2.59 (qt, *J* = 10.8, 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.1, 140.2, 134.5, 129.5, 129.2, 127.1 (q, *J* = 275.7 Hz), 31.3 (q, *J* = 2.6 Hz), 28.3 (q, *J* = 29.9 Hz). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ -67.24 (t, *J* = 10.8 Hz).

*Methyl 4-(4,4,4-trifluorobutanoyl)benzoate (**6q**)*.[24] General Procedure **II**. Yield 185 mg (71%). White crystals. Mp 75 – 77 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.28 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 3H), 3.35 – 3.20 (m, 2H), 2.71 – 2.49 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 195.8, 166.1, 139.3, 134.4, 130.0, 128.0, 127.1 (q, *J* = 276.1 Hz), 52.5, 31.7 (q, *J* = 2.6 Hz), 28.3 (q, *J* = 29.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -66.46 (t, *J* = 10.5 Hz).

*1-(4-bromophenyl)-4,4-difluorobutan-1-one (**6r**)*.[23] General Procedure **II**. Yield 165 mg (63%). White solid. Mp 29 – 30 °C. Chromatography: hexanes/EtOAc, 12/1. R_f 0.22 (hexanes/EtOAc, 12/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 6.01 (tt, *J* = 57.1, 4.1 Hz, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.28 (ttd, *J* = 18.1, 7.2, 4.1 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 196.8, 135.1, 132.0, 129.5, 128.6, 116.4 (t, *J* = 238.8 Hz), 30.8 (t, *J* = 5.3 Hz), 28.3 (t, *J* = 22.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ -117.86 (dt, *J* = 57.1, 18.1 Hz).

*1-(4-Bromophenyl)propan-1-one (**6s**)*.[25] General Procedure **II**. Yield 170 mg (80%). White crystals. Mp 44 – 45 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.25 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 2.91 (q, *J* = 7.2 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.5, 135.5, 131.7, 129.4, 127.9, 31.7, 8.0.

*Reaction with primary bromides 7 (General Procedure **III**)*. 2-Mercaptothiazoline potassium salt (209 mg, 1.33 mmol) was added to a stirred solution of bromide **7** (1.0 mmol) in acetonitrile (1 mL), and the suspension was stirred for 30 minutes at 70 °C (water bath). After completion (monitored by GC), the solvent was evaporated under reduced pressure, the residue was diluted with water (10 mL) and extracted with hexane (3×5 mL). The combined organic phases were

filtered through a small pad of Na_2SO_4 and concentrated under reduced pressure. Then, dichloroethane (100 μL) and MeOTf (131 μL, 1.2 mmol) were added. The resulting viscous mixture was stirred for 15 minutes at 70 °C (water bath), then cooled down to room temperature, and all the volatile components were evaporated in vacuum. The residue was dissolved in acetonitrile (1.5 mL), then DMPU (144 μL, 1.2 mmol), silyl enol ether of acetophenone (255 mg, 1.33 mmol) and $[Ir(dtbbpy)(ppy)_2]PF_6$ (2.4 mg, 0.25 mol%) were successively added. The reaction tube was cooled to –20 °C, and a vacuum of 10 Torr was briefly applied with intense stirring followed by filling with argon (three times), and the tube was warmed to room temperature. The mixture was irradiated with blue LEDs upon for 16 hours while maintaining the reaction temperature around 20 °C. The mixture was diluted with water (10 mL) and extracted with hexane (3×5 mL). The combined organic phases were filtered through a small pad of Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography.

*1,4-Diphenylbutan-1-one (**6t**)*.[26] General Procedure **III**. Yield 157 mg (70%). Yellowish solid. Mp 53 – 54 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.26 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 – 7.94 (m, 2H), 7.63 – 7.54 (m, 1H), 7.54 – 7.44 (m, 2H), 7.39 – 7.21 (m, 5H), 3.03 (t, J = 7.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 2H), 2.15 (p, J = 7.5, 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.9, 141.7, 137.0, 132.9, 128.6, 128.5, 128.4, 128.0, 125.9, 37.6, 35.2, 25.7.

*4-Oxo-4-phenylbutyl acetate (**6u**)*.[27] General Procedure **III**. Yield 95 mg (46%). Yellowish oil. Chromatography: hexanes/EtOAc, 1/1. R_f 0.28 (hexanes/EtOAc, 1/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 – 7.90 (m, 2H), 7.57 – 7.49 (m, 1H), 7.47 – 7.39 (m, 2H), 4.15 (t, J = 6.5 Hz, 2H), 3.03 (t, J = 7.1 Hz, 2H), 2.06 (tt, J = 7.1, 6.5 Hz, 2H), 2.00 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 198.9, 170.9, 136.8, 133.0, 128.5, 127.9, 63.7, 34.8, 23.2, 20.8.

*1-Phenylhex-5-en-1-one (**6v**)*.[28] General Procedure **III**. Yield 71 mg (41%). Yellowish oil. Chromatography: hexanes/EtOAc, 20/1. R_f 0.27 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (dd, J = 7.0, 1.7 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 5.83 (ddt, J =

17.0, 10.1, 7.4 Hz, 1H), 5.05 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.00 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.86 (p, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 138.1, 137.1, 132.9, 128.6, 128.0, 115.3, 37.7, 33.2, 23.3.

*Ethyl 4-oxo-4-phenylbutanoate (**6w**)*.[29] General Procedure **III**. Yield 155 mg (75%). Slightly-yellow oil. Chromatography: hexanes/EtOAc, 4/1. R_f 0.30 (hexanes/EtOAc, 4/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.44 – 7.34 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.24 (t, *J* = 6.6 Hz, 2H), 2.69 (t, *J* = 6.6 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 197.9, 172.6, 136.4, 133.0, 128.4, 127.8, 60.4, 33.2, 28.1, 14.0.

*1,3-Diphenylpropan-1-one (**6x**)*.[30] General Procedure **III**. Yield 80 mg (38%). White crystals. Mp 65 – 66 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.29 (hexanes/EtOAc, 20/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 – 7.97 (m, 2H), 7.62 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 7.38 – 7.21 (m, 5H), 3.34 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.1, 141.3, 136.9, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.2.

*Ethyl 6-oxo-6-phenylhexanoate (**6y**)*.[31] General Procedure **III**. Yield 133 mg (57%). Colorless crystals. Mp 20 – 21 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.21 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.59 – 7.47 (m, 1H), 7.51 – 7.37 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.97 (t, *J* = 6.8 Hz, 2H), 2.34 (t, *J* = 6.9 Hz, 2H), 1.85 – 1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.8, 173.4, 136.9, 132.9, 128.6, 128.0, 60.2, 38.1, 34.1, 24.6, 23.6, 14.2.

*Ethyl 7-oxo-7-phenylheptanoate (**6z**)*.[32] General Procedure **III**. Yield 141 mg (57%). Colorless oil. Chromatography: hexanes/EtOAc, 10/1. R_f 0.21 (hexanes/EtOAc, 10/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 7.2, 1.3 Hz, 2H), 7.60 – 7.48 (m, 1H), 7.44 (dd, *J* = 8.2, 6.6 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 1.75 (p, *J* = 7.4 Hz, 2H), 1.68 (p, *J* = 7.4 Hz, 2H), 1.48 – 1.35 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.1, 173.6, 137.0, 132.9, 128.6, 128.0, 60.2, 38.3, 34.2, 28.8, 24.8, 23.9, 14.3.

*5-Oxo-5-phenylpentyl benzoate (**6α**).*[33] General Procedure **III**. Yield 200 mg (71%). Yellow oil. Chromatography: hexanes/EtOAc, 4/1. R_f 0.27 (hexanes/EtOAc, 4/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.35 (m, 6H), 4.36 (t, *J* = 5.8 Hz, 2H), 3.04 (t, *J* = 6.6 Hz, 2H), 1.99 – 1.79 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 199.5, 166.4, 136.9, 132.9, 132.8, 130.3, 129.4, 128.5, 128.2, 127.9, 64.5, 37.8, 28.2, 20.7.

*2-Cyclohexyl-1-phenylethan-1-one (**6β**).*[34] General Procedure **III**. Yield 159 mg (79%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1. R_f 0.20 (hexanes/EtOAc, 30/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 7.0, 1.6 Hz, 2H), 7.57 – 7.47 (m, 1H), 7.42 (dd, *J* = 8.3, 6.6 Hz, 2H), 2.80 (d, *J* = 6.8 Hz, 2H), 1.97 (ttt, *J* = 10.5, 6.8, 3.5 Hz, 1H), 1.81 – 1.58 (m, 5H), 1.39 – 0.91 (m, 5H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.0, 137.4, 132.7, 128.4, 128.0, 46.1, 34.4, 33.4, 26.2, 26.1.

*1-Phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (**6γ**).*[35] General Procedure **III**. Yield 137 mg (67%). Colorless oil. Chromatography: hexanes/EtOAc, 6/1. R_f 0.16 (hexanes/EtOAc, 6/1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 – 7.94 (m, 2H), 7.59 – 7.50 (m, 1H), 7.50 – 7.41 (m, 2H), 3.97 – 3.82 (m, 2H), 3.73 (td, *J* = 7.7, 6.5 Hz, 1H), 3.18 (ddd, *J* = 17.2, 9.0, 5.7 Hz, 1H), 3.05 (ddd, *J* = 17.2, 8.8, 6.3 Hz, 1H), 2.10 – 1.79 (m, 5H), 1.53 (ddd, *J* = 15.6, 11.7, 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 200.1, 137.1, 133.0, 128.6, 128.1, 78.5, 67.8, 35.5, 31.5, 30.0, 25.8.

*Generation of salts **8a,f**.* A mixture of thiazoline **4a,f** (0.2 mmol) and dichloroethane (50 μL) in NMR tube was treated with MeOTf (26μL, 0.24 mmol). The tube was heated at 70 °C (water bath) for 15 minutes, then cooled to room temperature, and all the volatile components were evaporated under vacuum. The residue was dissolved in $CDCl_3$.

*2-Cyclopentylthio-3-methyl-4,5-dihydro-1,3-thiazol-3-ium triflate **8a**.* ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.51 (t, *J* = 8.7 Hz, 2H), 3.85 – 3.71 (m, 3H), 3.32 (s, 3H), 2.34 – 2.14 (m, 2H), 1.84 – 1.58 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 190.8, 120.4 (q, *J* = 320.6 Hz), 61.9, 50.5, 38.4, 33.8, 30.4, 24.6.

3-Methyl-2-methylthio-4,5-dihydro-1,3-thiazol-3-ium triflate ***8f***. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.44 (t, *J* = 8.8 Hz, 2H), 3.67 (t, *J* = 8.8 Hz, 2H), 3.25 (s, 3H), 2.70 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 192.2, 120.3 (q, *J* = 320.7 Hz), 62.3, 37.9, 30.1, 18.2.

*3-Methyl-2-{[(trimethylsilyl)methyl]thio}-4,5-dihydro-1,3-thiazol-3-ium triflate (**8c**)*. Methyl triflate (131 μL, 1.2 mmol) was added to a stirred mixture of thiazoline **4c** (205 mg, 1.0 mmol) and dichloroethane (100 μL). The resulting viscous solution was stirred for 15 minutes at 70 °C (water bath), then cooled down to room temperature, and all volatile components were evaporated under vacuum. The residue was dissolved in chloroform (0.5 mL) and crystallized overnight by slow diffusion with methyl *tert*-butyl ether at room temperature. The resulting white crystals were washed with cold (–20 °C) methyl *tert*-butyl ether (3×2 mL) and dried under vacuum. Yield 296 mg (80 %). Mp 80 – 81 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.66 (t, *J* = 8.8 Hz, 2H), 3.82 (t, *J* = 8.8 Hz, 2H), 3.41 (s, 3H), 2.49 (s, 2H), 0.21 (s, 9H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 195.3, 63.5, 38.4, 30.4, 22.2, -1.9. HRMS (ESI): calcd for $C_8H_{18}NS_2Si$ [Cation], 220.0644; found 220.0635.

ASSOCIATED CONTENT

Supporting Information. CV curve and X-ray structure for **8c** and copies of NMR spectra for all compounds (PDF). Stern-Volmer plots. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

* E-mail: adil25@mail.ru

Author Contributions

All authors have given approval to the final version of the manuscript.

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