Metal-Free Hydrogen Evolution Cross-Coupling Enabled by Synergistic Photoredox and Polarity Reversal Catalysis

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I. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ¹H NMR, ¹³C NMR spectra were recorded on a Bruker AV-III400 (400 MHZ) spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (CDCl₃: 7.26 ppm ¹H NMR, 77.0 ppm ¹³C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). All high resolution mass spectra (HRMS) were obtained by either ESI mode with the mass analyzer of TOF used or by MALDI-TOF. The Blue LED strips were used in 2 meter, 18 W (maximum Emission at around 470 nm). Further visualization was achieved by staining with KMnO₄.

II. Survey of Reaction Conditions

Table S1. Survey of conditions for silanol formation via Si-H activation^[a]



Entry	Deviation from the standard conditions	Yield of 12 (%) ^[b]
1	none	72
2	DCM instead of CH ₃ CN	14
3	THF instead of CH ₃ CN	53
4	DCE instead of CH ₃ CN	36
5	CH ₃ Cl instead of CH ₃ CN	6
6	PhMe instead of CH ₃ CN	16
7	PhCl instead of CH ₃ CN	23
8	C ₆ D ₆ instead of CH ₃ CN	16
9	PC 4 instead of 1	<5
10	PC 5 instead of 1	<5

11	PC 6 instead of 1	10
12	PC 7 instead of 1	13
13	HAT cat.3 instead of 2	43
14	HAT cat.8 instead of 2	60
15	HAT cat.9 instead of 2	50
16	HAT cat.10 instead of 2	56
17	HAT cat.11 instead of 2	43
18	H ₂ O 20 equiv. instead of 50 equiv.	40
19	without PC or HAT cat. or light	N.D.

[a] Reaction conditions: dimethylphenylsilane (0.2 mmol), H₂O (10 mmol), 4CzIPN (PC 1, 0.006 mmol), ethyl
2-mercaptopropanoate (HAT cat. 2, 0.02 mmol), CH₃CN (2 mL), 18 W blue LED, RT, 24 h. [b] Isolated yield.

Table S2. Survey of conditions for silane with alcohol or phenol via Si–H activation ^[a]

	Ph	PC HAT-C	(3 mol %) at (10 mol%)	Ph 	Ha + Ha
		Solvent (0).1 M), RT, Time	e (h) Ph	113 · · ·2
	FII	blue L	ED ((1))	45	
Entry	РС	HAT-Cat	Solvent	Time (h)	Yield of 45 (%) ^[b]
1	PC 1	HAT cat.2	CH ₃ CN	16	67
2	PC 1	HAT cat.2	DCM	16	47
3	PC 1	HAT cat.2	THF	16	30
4	PC 1	HAT cat.2	dioxane	16	64
5	PC 1	HAT cat.3	CH ₃ CN	16	71
6	PC 1	HAT cat.8	CH ₃ CN	16	28
7	PC 1	HAT cat.9	CH ₃ CN	16	42
8	PC 1	HAT cat.10	CH ₃ CN	16	9
9	PC 4	HAT cat.3	CH ₃ CN	16	17
10	PC 5	HAT cat.3	CH ₃ CN	16	34
11	PC 6	HAT cat.3	CH ₃ CN	16	17
12	PC 7	HAT cat.3	CH ₃ CN	16	24
13	PC 1	HAT cat.3	CH ₃ CN	24	80
14 ^[c]	PC 1	HAT cat.3	CH ₃ CN	24	N.D.
15	-	HAT cat.3	CH ₃ CN	24	N.D.
16	PC 1	-	CH ₃ CN	24	N.D.

[a] Reaction conditions: triphenylsilane (0.2 mmol), CH₃OH (4 mmol), PC (0.006 mmol), HAT-Cat (0.02 mmol), CH₃CN (2.0 mL), 18 W blue LED, RT, 16 h. [b] Isolated yield. [c] No light.

III. Typical Procedure for Dehydrogenative Cross-coupling of Silane with H₂O

$$\begin{array}{c} \text{PC 1 (3 mol \%)} \\ \text{R}^{1-}\text{Si-H} + \text{H}_{2}\text{O} \\ \text{R}^{3} \end{array} \xrightarrow{\text{HAT cat. 2 (10 mol\%)}} \text{CH}_{3}\text{CN, RT, 24-36 h} \\ \begin{array}{c} \text{Blue LED } \end{array} \xrightarrow{\text{R}^{1-}\text{Si-OH}} \text{H}_{2} \\ \text{Blue LED } \end{array}$$

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous acetonitrile (2.0 mL), H_2O (10 mmol), silane (0.2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **2**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24-36 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (30:1–15:1) or by prepared TLC to give the silanol product.

IV. Typical Procedure for Dehydrogenative Cross-coupling of

Silane with Alcohol or Phenol

$$\begin{array}{c} R^{2} \\ R^{1}-S_{i}-H \\ R^{3} \end{array} + HO-R \\ R^{3} \end{array} \xrightarrow{PC 1 (3 \text{ mol }\%)}_{\begin{array}{c} HAT \text{ cat. } 3 (10 \text{ mol}\%) \\ \hline CH_{3}CN, RT, 24-36 \text{ h} \\ \hline blue \text{ LED } \textcircled{O} \end{array}} \xrightarrow{R^{1}-S_{i}-OR}_{R^{3}} + H_{2}$$

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous acetonitrile (1.0–2.0 mL), silane (0.2 mmol), alcohol (2–17 mmol) or phenol (0.6 mmol), *tert*-dodecanethiol (HAT cat. **3**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24-36 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane to hexane / ethyl acetate (150:1) or by prepared TLC to give the product.

V. Mechanistic Investigations

1) Radical inhibition experiments



When 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 1.0 equiv.) was introduced into the model reactions, the desired triphenylsilanol was isolated in 51% yield after column chromatography separation. Whereas the presence of 1,1-diphenylethene (DPE, 1.0 equiv.) inhibited the reaction completely. These results suggest the involvement of radical species in this cross-coupling process.

2)Light on-off experiments





with H₂O

3) Stern-Volmer fluorescence quenching experiments

In a typical experiment, a solution of photocatalyst **1** 4CzIPN in anhydrous acetonitrile $(1.25 \times 10^{-4} \text{ M})$ was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 554 nm was collected with excited wavelength of 360 nm.



Figure S2. Stern-Volmer fluorescence quenching studies

4) Determination of quantum yields by standard ferrioxalate actinometry

Determination of the light intensity at 470 nm: Following Yoon's procedure,^[S1] the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepapred by dissoving 50 mg of phenanthroline and 11.25 g of sodium aceate in 50 mL of 0.5 M H₂SO₄. Both solution were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed solution was placed in a cuvette and irradiated for 90.0 second at $\lambda = 470$ nm with an emssion slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradinated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculates using eq (1).

$$\mathrm{mol}Fe^{2^{+}} = \frac{V \ \Delta A}{l \ \varepsilon} \tag{1}$$

Where V is the total volume (0.00235 L) of the solution after of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solution, I is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹). The photon flux can be calculated using eq (2).

photo flux =
$$\frac{\text{mol}Fe^{2^+}}{\Phi t f}$$
 (2)

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at λ = 468 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 470 nm (0.648, vide infra). The photo flux was calculated (average of three experiments) to be 5.489 × 10⁻⁹ einstein⁻¹.

$$molFe^{2+} = \frac{0.00235 \ L \cdot 1.391}{1.000 \ cm \cdot 11100 \ L \ mol^{-1}cm^{-1}} = 2.945 \times 10^{-7} \ mol$$

photo flux = $\frac{2.945 \times 10^{-7} \ mol}{0.92 \cdot 90.0 \ s \cdot 0.648} = 5.489 \times 10^{-9} \ mol$

Determination of quantum yield:

$$\begin{array}{c} PC \ \mathbf{1} \ (3 \ mol \ \%) \\ Ph - Si - H \ + \ H_2O \\ Me \end{array} \xrightarrow{\begin{array}{c} \text{PC } \mathbf{1} \ (3 \ mol \ \%) \\ \text{HAT cat. } \mathbf{2} \ (10 \ mol \ \%) \\ \hline CH_3CN, RT, 2.1 \ h \\ \hline blue \ LED \end{array} \xrightarrow{\begin{array}{c} Ph \\ \text{Ph - Si - OH } \\ Me \end{array}} \xrightarrow{\begin{array}{c} Ph \\ \text{Ph - Si - OH } \\ \text{Me } \end{array} + H_2 \\ \hline Me \\ \hline \mathbf{12}, 12\% \end{array}$$

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that acetonitrile- d_3 (2.0 mL), H₂O (10 mmol), methyldiphenylsilane (40 µL, 0.2 mmol) and ethyl 2-mercaptopropanoate (HAT cat. **2**, 2.6 µL, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated ($\lambda = 470$ nm, slit width = 10.0 nm) for 7560 s (126 min). After irradiation, the solvent was removed. The yield of product **12** was determined as 12% by crude ¹H NMR base on a 1,3,5-trimethoxybenzene standard. The quantum yield was determined using eq (3). Essentially all incident light (f > 0.999, vide infra) is absorbed by the 4CzIPN at the reaction conditions described above. $\Phi = 0.578$.

$$\Phi = \frac{\text{mol product}}{\text{flux } t \ f}$$
(3)

$$\Phi = \frac{2.4 \times 10^{-5} \text{ mol}}{5.489 \times 10^{-9} \text{ einstein s} \cdot 7560 \text{ s} \cdot 1.00} = 0.578$$

5)KIE studies

The deuterated triphenylsilane Ph₃SiD (96%-*D* incorporation) was prepared according to a known method. ^[S2]

$$\begin{array}{c} PC \ \mathbf{1} \ (3 \ mol \ \%) \\ Ph \\ Ph \\ Ph \\ n_{H}:n_{D} = 1:1 \end{array} \xrightarrow{PC \ \mathbf{1} \ (3 \ mol \ \%)} \begin{array}{c} PC \ \mathbf{1} \ (3 \ mol \ \%) \\ HAT \ cat. \ \mathbf{2} \ (10 \ mol \ \%) \\ CH_{3}CN, RT, 4 \ h \\ blue \ LED \ \textcircled{h} \\ \textcircled{h} \\ \textcircled{h} \\ (1)$$

To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), triphenylsilane (26 mg, 0.1 mmol), and triphenylsilane- d_1 (26 mg, 0.1 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous acetonitrile (2.0 mL), H₂O (10 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **2**, 2.6 µL, 0.02 mmol) were added sequentially by

means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 4 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (30:1–15:1) to give the recovered silane and the silanol product. A remained Si–H/D ratio was observed in the recovered silane according to ¹H NMR.



Figure S3. ¹H NMR spectra of the starting silane ($Ph_3SiH/Ph_3SiD = 1:1$)



Figure S4. ¹H NMR spectra of the recovered silane ($Ph_3SiH/Ph_3SiD = 1:1$)

6) Trapping the silyl cation with fluorine anion

To a 25 mL Schlenk tube equipped with a magnetic stir bar were added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol) and triphenylsilane (52 mg, 0.2 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous acetonitrile (2.0 mL), fluorine anion source (potassium bifluoride or tetrabutylammomiumfluoride, 0.8 mmol), and ethyl 2-mercaptopropanoate (HAT cat. **2**, 2.6 μ L, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 hrs. The solvent was removed on a rotary evaporator under reduced pressure and the crude product was purified by column chromatography isolation on silica gel via gradient elution with hexane / ethyl acetate (100:1–50:1) to give the fluorotriphenylsilane.



Figure S5. ¹H NMR spectra of Ph₃SiF

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.7 Hz, 6H), 7.49 (t, *J* = 7.1 Hz, 3H), 7.41 (t, *J* = 7.4 Hz, 6H) ppm.



Figure S6. ¹⁹F NMR of Ph₃SiF

¹⁹F NMR (376 MHz, CDCl₃): δ -169.6 (s) ppm.

7) Silyl cation mediated hydrodefluorination



To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequent backfill with argon for three times. After that anhydrous acetonitrile (2.0 mL), methyldiphenylsilane (60 mg, 0.3 mmol), trifluoromethylbenzene (0.2 mmol) and *tert*-dodecanethiol (HAT cat. **3**, 0.02 mmol) were added sequentially by means of syringe. Then the reaction was placed under a blue LED (2 meter strips, 18 W) with an argon balloon and irradiated for 24 hrs. The crude mixture was then analysis by GC-MS and ¹H NMR (1,3,5-trimethoxybenzene as a internal standard) analysis, indicating the formation of the hydrodefluorination product, toluene (18%), as well as the methyldiphenylfluorosilane.

VI. Preparation of the Starting Silanes

The silanes were prepared according to the literature procedures.^[S3]

1) Synthesis of organosilanes (13-26, 35, 36, 41)

In a 100 mL two-necked round-bottom flask, chlorodimethylsilane (0.89 mL, 8 mmol) in THF (6 mL) was cooled to 0 °C under a nitrogen atmosphere. A solution of a Grignard reagent (10 mL, 1.0 M in THF) was added dropwise slowly over 15 min. Then the reaction was allowed to warm to room temperature and stirred for 4 h. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by silica column chromatography with hexane to afford the desired silanes.

2) Synthesis of silane 43 from PhSiCl₃

In a 100 mL two-necked round-bottom flask, phenyltrichlorosilane (1.60 mL, 10 mmol) in THF (10 mL) was cooled to -78 °C under nitrogen atmosphere. A solution of Grignard reagent (10 mL, 1.0 M in THF) was added dropwise slowly over 60 min. Then the reaction was allowed to warm to room temperature and stirred for 12 h. The reaction was cooled down to -78 °C and Lithium aluminum hydride (LAH) (2.5 M in THF, 12 mL, 30 mmol) was added dropwise. After warming to room temperature, the soultion was stirred for an additional 3 h. The reaction mixture was quenched with saturated NH₄Cl solution and extracted with Et₂O (25 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over Na₂SO₄, filtered and concentrated. The crude product was purified by silica column chromatography with hexane to afford the desired silane .

VII. Alternative Mechanistic Proposal



Scheme S1. Proposed mechanism involving the formation of PC 1^{2-}

We also questioned whether the silvl radical II could be oxidized by the reduced photocatalyst 1^{•-} to afford the silvl cation III and 1²⁻, and then the resulting 1²⁻ reduced the two protons to molecular hydrogen. However, DFT calculation indicated that the 1^{•-} ($E^{\text{red}} = -2.31 \text{ V} vs$ SCE in MeCN] is not oxidative enough to support the SET process from silvl radical II to 1^{•-}

VIII. DFT Calculation Results

To determine the mechanism of the dehydrogenation cross-coupling reaction catalyzed by 4CzIPN, density functional theory (DFT) calculations were performed to investigate the thermodynamic properties of the photocatalyst (PC 1), the silane radical as well as their redox species, using the Gaussian 09 program package.^{S4} Geometries were first optimized using the unrestricted hybrid density functional UB3LYP^{S5} including empirical dispersion correction computed with Grimme's D3 formula^{S6} and the 6-31g(d)^{S7} basis set (BSI). Based on the optimized geometries, vibrational frequency analyses were conducted at the same theoretical level to ensure that each stationary point truly represented a minimum (zero imaginary frequencies), and to obtain the thermodynamic energy corrections at 298.15 K and 1 atm. The electronic energies were then refined with the UM06-2X-D3^{S8} exchange-correlation functional and a larger def2-TZVP^{S9} basis set (BSII). The polarizable continuum model (PCM)^{S10} was employed to consider the solvent effect of acetonitrile (ϵ =36.6) for all computations. Finally, the reduction free energy changes between the oxidized species (**S**) and the reduced species (**S**^{-•}) in solution, ΔG^0 (sol, red) can be calculated using eq. 1^{S11}

$\Delta G^{0}(\text{sol,red}) = \Delta G^{0}(\text{gas,red}) + G^{0}(\text{sol}, S^{-*}) - G^{0}(\text{gas}, S)$ (1)

the standard absolute potentials (E^0) in the ground state were obtained from Nernst equation,

$$E_{abs,red}^{0} = -\Delta G^{0} (\text{sol}, \text{red}) / nF$$
⁽²⁾

where *F* is the Faraday constant (96485.3 C/mol) and *n* is the number of electrons transferred in the reduction reaction. To mimic the liquid environment of experimental procedures, the standard calomel electrode (SCE) in acetonitrile solution $[E^0(SCE)= 4.522 \text{ V}]^{S12}$ was adopted with consideration of the correction term for the liquid junction potential in MeCN (0.093 V)^{S13} as the reference value in calculating absolute potentials. For the calculation of proton reduction potential, the standard free energy of proton in solution is needed. Since the proton is a Fermion, the Fermi–Dirac statistical mechanics is the suitable formalism to be used.^[S11] Thus, in this work, a value of -266.5 kcal/mol was used, which is obtained by adding the statistical gas-phase Gibbs free energy of proton of 6.3 kcal/mol^[S14-S16] and the absolute solvation free energy of the proton in acetonitrile of 260.2 kcal/mol reported by Truhlar et al.^[S17] Meanwhile, the free Gibbs energy of the H₂(g) was obtained at the CCSD/def2-QZVPP level of theory, that is -1.175328 Hartree.

 Table S3.
 Summary of calculated thermodynamic properties of the dehydrogenation

 cross-coupling reaction.
 Image: Coupling reaction

 G_{corr} (Hartree) is the thermodynamic energy corrections obtained at the BS1 level of theory; E (Hartree) is the refined electron energy calculated at the BS2 level of theory; G_{sol}^0 (Hartree) is the absolute Gibbs free energy for each species involved in different redox reaction steps; $\Delta G_{\text{sol, red}}^0$ (eV) is the Gibbs free energy changes in acetonitrile solution; $E_{\text{abs, red}}^0$ (V) is the calculated absolute reduction potential; $E_{\text{red vs SCE}}^0$ (V) is the relative reduction potential versus the aqueous saturated calomel electrode (SCE) potential.

	G _{corr} (Hartree)	E (Hartree)	G ⁰ _{sol} (Hartree)	$\Delta G^0_{ m sol, red}$ (eV)	E ⁰ abs, red (V)	E ⁰ _{red vs SCE} (V)
PC 1	0.64648	-2481.75817	-2481.11168	2 20	2 20	1 1 4
PC 1 ^{-•}	0.64109	-2481.87364	-2481.23255	-3.29	3.29	-1.14
PC 1 ^{-•}	0.64109	-2481.87364	-2481.23255	2.12	2.12	2.21
PC 1 ²⁻	0.63647	-2481.94699	-2481.31052	-2.12	2.12	-2.31

Ph_3Si^{\oplus}	0.22993	-984.21195	-983.98203	-4.20	4.20	0.22
Ph ₃ Si•	0.22776	-984.36410	-984.13635		4.20	-0.23
PhMe ₂ Si [⊕]	0.12831	-600.75607	-600.62776	4.04	4.04	0.20
PhMe ₂ Si•	0.12792	-600.90401	-600.77609	-4.04	4.04	-0.39
H^{+}	-	-	-0.42469	4 42	4 42	0.01
$1/2 \ \mathrm{H_2}$	-	-	-0.58766	-4.43	4.43	0.01

Cartesian Coordinates

PC 1

С	5.84784000	-5.39672600	4.18962700
С	7.25278100	-5.41622500	4.15994000
С	7.95132800	-4.19696700	4.15326900
С	7.25999800	-2.96469500	4.14546900
С	5.84621400	-2.94921500	4.20380000
С	5.13994700	-4.17488700	4.24030300
Ν	7.94794600	-6.63518600	4.14023800
С	8.76342700	-7.09913100	3.09243700
С	9.28173100	-8.36544400	3.45380700
С	9.04027000	-6.50482300	1.86196500
С	10.11815100	-9.04333200	2.55952700
С	8.76322600	-8.67998100	4.77163600
С	9.87824400	-7.19853100	0.98904800
Н	8.61534600	-5.54480600	1.58750900
С	10.41495800	-8.45207300	1.33283400
Н	10.52418000	-10.01673900	2.81968900
С	7.94447500	-7.59593400	5.16713800
С	8.93079900	-9.76386900	5.64122600
Н	10.11611600	-6.75935300	0.02470600
Н	11.06419100	-8.96616000	0.63036400
С	7.30968100	-7.55573500	6.40771900
С	8.28782200	-9.74282900	6.87757600
Н	9.55666500	-10.60437300	5.35497400
С	7.48959500	-8.64846900	7.25564500
Н	6.70723100	-6.70473200	6.70844400
Н	8.40780100	-10.57813100	7.56102100
Н	7.00429400	-8.64858500	8.22718300
Ν	3.73735300	-4.20823800	4.28842100
Ν	5.15102400	-1.72762000	4.22180200
Ν	8.00229700	-1.77387700	4.11903300
С	2.86234900	-3.55316300	3.40038600
С	1.54881000	-3.63061900	3.91773100
С	3.13911100	-2.96044100	2.17048900
С	0.49273400	-3.05481000	3.20311900
С	1.62251900	-4.36731600	5.16454900
С	2.07384900	-2.38434200	1.47922100
Н	4.14304600	-2.94063600	1.76381700
С	0.76509000	-2.42294600	1.99089400
Н	-0.52161000	-3.10452600	3.58861400
С	2.97784300	-4.71806800	5.36455300
С	0.66903500	-4.72863100	6.12202600

Н	2.26486100	-1.90013600	0.52604900
Н	-0.04334200	-1.96543000	1.42834600
С	3.40284500	-5.40285700	6.50243600
С	1.08150800	-5.42263500	7.25816600
Н	-0.37468000	-4.46194000	5.98228700
С	2.43478800	-5.75186200	7.44470600
Н	4.44648700	-5.65120600	6.66199900
Н	0.35207500	-5.70917400	8.00978000
Н	2.73924200	-6.28837100	8.33844000
С	5.19038000	-0.74601900	3.21482500
С	4.35447000	0.32902600	3.59745500
С	5.85289200	-0.76339200	1.98884800
С	4.21279300	1.42913600	2.74455200
С	3.78083100	-0.01340500	4.88378200
С	5.70130900	0.34488600	1.15593600
Н	6.46363300	-1.60468500	1.68446400
С	4.89574400	1.43449400	1.52954500
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С	4.29109500	-1.28322400	5.24285000
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Н	6.21812300	0.35945500	0.20086000
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С	3.10300200	-1.20927900	7.30998300
Н	4.39829400	-2.84209700	6.74614000
Η	1.88447700	0.54190900	7.64190800
Η	2.83546100	-1.66370600	8.25941800
С	7.90332000	-0.71470000	5.04170400
С	8.64747900	0.38383500	4.55314800
С	7.26362800	-0.68325500	6.27881300
С	8.71233200	1.56065000	5.30734600
С	9.22838300	-0.02152300	3.28770000
С	7.33302700	0.50222100	7.00979600
Η	6.72796200	-1.54341900	6.66193700
С	8.04333100	1.61599000	6.52887100
Η	9.27918200	2.41358400	4.94512400
С	8.82414900	-1.35564000	3.04947500
С	10.02480800	0.63554700	2.34390700
Η	6.82909800	0.55888800	7.97013800
Η	8.07953300	2.52482700	7.12219000
С	9.18267000	-2.03940000	1.88829200
С	10.39735400	-0.04228800	1.18444500

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Н	8.85396800	-3.05569000	1.70015200
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Н	10.27254000	-1.87565200	0.04955200
С	5.13021200	-6.62621300	4.05472400
С	9.37629900	-4.20918100	4.27144900
Ν	4.55314000	-7.62750800	3.93118800
Ν	10.53315900	-4.22543000	4.38211900

PC 1^{-•}

С	1.58770300	1.14440200	0.40680400
С	2.27167600	-0.00990700	-0.00482500
С	1.57657900	-1.15803300	-0.41462100
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С	-0.56561600	0.00227000	-0.00064700
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Ν	3.68915100	-0.01642000	-0.00570200
С	4.50211900	-0.82496200	0.79703800
С	5.86001800	-0.53665600	0.50971700
С	4.13452300	-1.76329700	1.76332700
С	6.86929100	-1.21610100	1.20307400
С	5.86517200	0.48696200	-0.51596500
С	5.15716900	-2.42597400	2.43998500
Н	3.09043300	-1.96866600	1.97382700
С	6.51149000	-2.15923400	2.16433700
Н	7.91475000	-1.00571000	0.99399900
С	4.51022300	0.78585200	-0.80643700
С	6.88138500	1.15891600	-1.20640600
Н	4.89993800	-3.16396600	3.19466100
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Н	4.93226200	3.12318000	-3.20162400
Ν	-0.54024000	2.37476900	0.66637700
Ν	-1.98733400	0.00928800	-0.00086300
Ν	-0.56227000	-2.37164600	-0.66444600
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С	-2.84603800	4.34159700	2.62894700
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С	-2.67729300	2.17207500	3.71959900
Н	-1.35074700	0.71542400	2.82181900
С	-3.21761000	3.47038800	3.65141600
Н	-3.25436800	5.34780300	2.58198300
С	-0.47427600	3.55457600	-0.08181100
С	-1.44207700	5.78739000	-0.09365600
Н	-2.97454000	1.50956400	4.52799100
Н	-3.92756000	3.79580900	4.40656000
С	0.26364600	3.82091700	-1.23774100
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Н	0.90881900	3.06471200	-1.67306400
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Н	0.69768500	5.31885900	-2.71006500
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С	-2.45700600	-1.63094200	1.86023400
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Н	-3.23532100	-2.95420200	3.35509500
Н	-5.61674100	-2.50918200	2.82181500
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Н	-6.21293200	0.94940400	-1.04892000
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С	-2.90947300	-4.31381100	-2.60292300
С	-1.37876200	-4.51005800	-0.48532400
С	-2.71866300	-2.15111100	-3.70301600
Н	-1.36271800	-0.71093700	-2.82305900

С	-3.27745000	-3.44102600	-3.62523400
Н	-3.33118400	-5.31409100	-2.54880800
С	-0.50728900	-3.54971400	0.08793500
С	-1.50483500	-5.76956200	0.11306200
Н	-3.01269300	-1.48740400	-4.51161100
Н	-3.99837200	-3.75886800	-4.37318200
С	0.23404800	-3.82227700	1.24028400
С	-0.76696400	-6.05009300	1.26188000
Н	-2.17231200	-6.51456900	-0.31217100
С	0.09242800	-5.08332800	1.81735800
Н	0.89177000	-3.07366500	1.66978500
Н	-0.85482300	-7.02376000	1.73544200
Н	0.65814500	-5.32187300	2.71382600
С	2.29456700	2.23181200	0.96398800
С	2.27276300	-2.25098000	-0.97448100
N	2.86654000	3.14516100	1.42203900
N	2.83786600	-3.16725700	-1.43506000

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С	-1.46021300	0.88988200	-0.81863100
С	-2.14182900	-0.02558800	-0.00172200
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С	0.05436500	-1.04493100	0.60328100
С	0.70715100	0.01691600	-0.01328300
С	0.01853500	1.06039100	-0.62686900
Ν	-3.57425100	-0.04875800	0.00264900
С	-4.37740800	-1.14809400	-0.31279300
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С	-4.00439900	-2.43707500	-0.70782900
С	-6.74539300	-1.70678600	-0.49634300
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С	-6.79127300	1.51956400	0.49709600
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Н	-7.24915400	3.52719100	1.12024700
Н	-4.87503100	4.22119500	1.30790600
Ν	0.53714100	2.39895800	-0.56465700
Ν	2.15447400	0.03578800	-0.02456900
Ν	0.61986000	-2.36424700	0.56741600
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С	1.65960900	4.33994200	-1.07425200
С	1.93716500	2.46547000	-2.64852900
С	2.51023200	5.13722500	-1.85140200
С	0.93670000	4.54459500	0.16407200
С	2.77882100	3.27891400	-3.40338700
Н	1.72269000	1.43886400	-2.92524900
С	3.06572400	4.60336900	-3.01327800
Н	2.73518200	6.15745100	-1.54911600
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С	0.80730300	5.61536700	1.05848300
Н	3.22832300	2.88147200	-4.31017400
Н	3.73061000	5.20988100	-3.62251400
С	-0.50655600	3.14690400	1.59278200
С	0.02441600	5.45379000	2.20140400
Н	1.31486600	6.55780200	0.86597200
С	-0.62186400	4.22902900	2.46422900
Н	-0.98240300	2.19199100	1.79360200
Н	-0.08492800	6.27785800	2.90133000
Η	-1.21901700	4.12346200	3.36649700
С	2.95892700	-0.52988500	-1.00061200
С	4.32548600	-0.33820300	-0.65360100
С	2.58418400	-1.20926600	-2.16458200
С	5.32656600	-0.83950900	-1.49620300
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С	3.59932800	-1.69793800	-2.98361100
Η	1.53707300	-1.35570300	-2.40398100
С	4.95885600	-1.51663500	-2.65745800
Η	6.37544900	-0.70127300	-1.24492600
С	2.96667300	0.59341900	0.94962500
С	5.33958500	0.87548800	1.43992100
Η	3.33519800	-2.23350400	-3.89192900
Η	5.72577700	-1.91139200	-3.31833100
С	2.60344300	1.27941100	2.11351800
С	4.98297300	1.55628400	2.60247600
Н	6.38610000	0.72447400	1.18601500
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Η	3.37065700	2.29373600	3.83942000
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С	2.89585800	-3.11001100	3.41733300
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С	3.23518100	-4.42772300	3.04731400
Н	2.96256600	-6.01791800	1.61028200
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Н	3.33000400	-2.68048000	4.31691700
Н	3.92448900	-4.99753600	3.66478400
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С	0.21758000	-5.48317800	-2.14391200
Н	1.55386800	-6.51369200	-0.79509700
С	-0.47723100	-4.28923700	-2.42475900
Н	-0.91138000	-2.25508700	-1.78739100
Н	0.13798600	-6.32274900	-2.82926300
Н	-1.08086000	-4.22241600	-3.32639500
С	-2.10817800	1.57625400	-1.85673700
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Ν	-2.52818600	-2.29459900	2.71337900

Ph₃Si[⊕]

Si	-0.00037700	-0.00019200	0.00048800
С	1.45811600	-1.09058400	0.00075300
С	1.37862000	-2.39734100	0.53824300
С	2.68828400	-0.64385900	-0.53757600
С	2.49707700	-3.22530900	0.53926200
Н	0.44899700	-2.75873300	0.96714500
С	3.79875100	-1.48248800	-0.54133100
Н	2.77158000	0.35072000	-0.96502900
С	3.70368700	-2.76953700	-0.00193300
Н	2.43065600	-4.22326800	0.96090500
Н	4.73655600	-1.13588000	-0.96385700
Η	4.57346600	-3.41987700	-0.00322700
С	-1.67377700	-0.71836600	0.00222600
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С	-1.90159700	-2.00911400	-0.53137000
С	-4.04304400	-0.54693600	0.53444400
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С	-3.18356500	-2.55044800	-0.53653000
Н	-1.08085800	-2.58069000	-0.95374700
С	-4.25137500	-1.82152400	-0.00270500
Η	-4.87471500	0.01175600	0.95200800
Η	-3.35210800	-3.53736500	-0.95571700
Н	-5.24991200	-2.24857000	-0.00515300
С	0.21471300	1.80826900	-0.00007400
С	-0.78733100	2.65183200	-0.53562100
С	1.38780400	2.39084500	0.53574300
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Н	-1.69126400	2.22781400	-0.96204400
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Η	-1.38403300	4.67292900	-0.95825200
Η	2.44532600	4.21330600	0.95980900
Η	0.67765200	5.67037900	0.00123800

Ph₃Si[•]

Si	0.00063800	-0.00142000	-0.79858100
С	1.74558000	-0.46450300	-0.28540600
С	2.02634200	-1.63134300	0.45573000
С	2.83524800	0.34976900	-0.66460100
С	3.33491900	-1.96291900	0.81113900
Н	1.21413900	-2.28266300	0.76656600
С	4.14259300	0.02349300	-0.30422300
Н	2.65967600	1.25296200	-1.24516300
С	4.39682200	-1.13655100	0.43386900
Н	3.52529000	-2.86451000	1.38772200
Н	4.96347600	0.67018800	-0.60289400
Н	5.41523400	-1.39459600	0.71142700
С	-1.27476800	-1.27915800	-0.28558200
С	-2.42575700	-0.93540700	0.45376400
С	-1.11637800	-2.63091800	-0.66204500
С	-3.36889400	-1.90066900	0.81063200
Н	-2.58247200	0.09471200	0.76157700
С	-2.05427900	-3.59782000	-0.30008300
Н	-0.24670500	-2.93269300	-1.24194000
С	-3.18573700	-3.23464400	0.43678500
Н	-4.24491800	-1.61217900	1.38590000
Н	-1.90595700	-4.63295600	-0.59629400
Н	-3.91958400	-3.98589900	0.71587800
С	-0.46977300	1.74208000	-0.28637200
С	-1.71734400	2.28158700	-0.66934300

С	0.39853600	2.56525600	0.46057300
С	-2.08788900	3.57668000	-0.30731500
Н	-2.41033000	1.68022400	-1.25394200
С	0.03205400	3.86406400	0.81768700
Н	1.36651600	2.18503800	0.77484500
С	-1.21216800	4.37343300	0.43656000
Н	-3.05659100	3.96649500	-0.60881400
Н	0.71614900	4.47708600	1.39888400
Н	-1.49749800	5.38409700	0.71577700

PhMe₂Si[⊕]

Si	-1.59292500	-0.00253700	0.00054400
С	0.21791000	-0.00586300	0.00318400
С	0.93437700	1.21671500	-0.00565200
С	0.94021200	-1.22490900	0.01066100
С	2.32442700	1.21560000	-0.00823500
Н	0.40572800	2.16485600	-0.00898000
С	2.33024500	-1.21670300	0.00684000
Н	0.41683800	-2.17590700	0.01812600
С	3.01982000	0.00110300	-0.00288600
Н	2.86773400	2.15504300	-0.01526700
Н	2.87816300	-2.15347300	0.01155100
Н	4.10586100	0.00368300	-0.00611700
С	-2.52522800	1.59141000	0.00541200
Н	-1.92633900	2.43297300	-0.35077700
Н	-3.42438300	1.49450700	-0.61227900
Η	-2.85169600	1.80661300	1.03213700
С	-2.55119000	-1.58012100	-0.00987900
Η	-3.01453400	-1.70168800	-0.99840400
Н	-1.93670900	-2.45786800	0.20195800
Н	-3.36315300	-1.51661300	0.72376300

PhMe₂Si[•]

Si	1.66529100	-0.00166500	-0.42523500
С	-0.19552900	0.00014400	-0.17128000
С	-0.92499700	-1.20614800	-0.09650400
С	-0.92333600	1.20695100	-0.08961900
С	-2.31099500	-1.20765700	0.06475000
Н	-0.40412300	-2.15908500	-0.15794000
С	-2.30937900	1.20924200	0.07179400
Н	-0.40145400	2.15968500	-0.14546700
С	-3.00873400	0.00104100	0.14972600
Н	-2.84762200	-2.15112100	0.12666800
Н	-2.84490000	2.15294300	0.13929800

Н	-4.08823200	0.00136900	0.27514000
С	2.45882200	-1.56675800	0.29586300
Н	2.04642500	-2.47839300	-0.14938800
Н	3.53952400	-1.56439800	0.11567100
Н	2.29570200	-1.61526800	1.38115200
С	2.46292800	1.56628800	0.28530900
Н	3.54432000	1.55633300	0.10944100
Н	2.05742300	2.47556800	-0.17100400
Н	2.29617700	1.62705900	1.36947400

IX. Analytical Data of the Products

12; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, dimethyl(phenyl)silane (31 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **12** (22 mg) in 72% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.57 (m, 2H), 7.43 – 7.37 (m, 3H), 1.77 (s, 1H), 0.41 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 139.1, 133.0, 129.6, 127.9, 0 ppm.

13; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, (4-methoxyphenyl)dimethylsilane (33 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **13** (25 mg) in 69% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 1.88 (s, 1H), 0.38 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 160.8, 134.6, 130.1, 113.6, 55.0, 0 ppm.

14; Following the typical procedure III, (3-methoxyphenyl)dimethylsilane (33 mg, 0.2 mmol),

H₂O (180 μL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **14** (27 mg) in 75% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.28 (m, 1H), 7.17 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 2.6 Hz, 1H), 6.94 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 3.83 (s, 3H), 1.91 (s, 1H), 0.40 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 140.7, 129.2, 125.3, 118.4, 115.0, 55.1, 0 ppm; HRMS–ESI m/z: [M – H]⁻ calcd for C₉H₁₃O₂Si 181.0690, found 181.0685.

15; A known compound and the characterization data are in accordance with the literature.^[S18] Following the typical procedure **III**, (4-butylphenyl)dimethylsilane (38 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **15** (29 mg) in 70% yield as a colorless oil.¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 2.71 – 2.54 (m, 2H), 1.81 (s, 1H), 1.60 (dt, *J* = 15.3, 7.5 Hz, 2H), 1.36 (dd, *J* = 14.9, 7.4 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.40 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 144.6, 135.8, 133.1, 128.1, 35.7, 33.5, 22.4, 13.9, 0 ppm.

16; Following the typical procedure **III**, [1,1'-biphenyl]-4-yldimethylsilane (42 mg, 0.2 mmol), H_2O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **16** (39 mg) in 86% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.63 – 7.57 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 1.93 (s, 1H), 0.44 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 141,0, 137.7, 133.6, 128.8, 127.5, 127.2, 126.6, 0 ppm; HRMS–ESI *m/z*: [M – H]⁻ calcd for C₁₄H₁₅OSi 227.0898, found 227.0881.

17; Following the typical procedure III, (3,5-dimethoxyphenyl)dimethylsilane (39 mg, 0.2 mmol),

H₂O (180 μL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02mmol) in acetonitrile (2.0 mL) were employed to give the product **17** (28 mg) in 65% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.65 (d, J = 2.2 Hz, 2H), 6.42 (t, J = 2.1 Hz, 1H), 3.74 (s, 6H), 1.83 (s, 1H), 0.32 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 160.5, 141.5, 110.4, 101.5, 55.3, 0 ppm; GCMS–EI (M⁺) calcd for C₁₀H₁₆O₃Si 212.086, found 212.086.



18; Following the typical procedure **III**, (2,4,6-trimethylphenyl)dimethylsilane (36 mg, 0.2 mmol), H_2O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **18** (26 mg) in 67% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.82 (s, 2H), 2.46 (s, 6H), 2.25 (s, 3H), 1.90 (s, 1H), 0.47 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 139.1, 132.4, 129.1, 24.2, 20.9, 4.0 ppm; GCMS–EI (M⁺) calcd for C₁₁H₁₈OSi 194.112, found 194.112.



19; Following the typical procedure **III**, silane (36 mg, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **19** (31 mg) in 78% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.11 – 7.00 (m, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.95 (s, 2H), 1.82 (s, 1H), 0.38 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 148.8, 147.4, 132.2, 127.2, 112.5, 108.6, 100.6, 0 ppm; GCMS–EI *m/z*: [M – OH]⁺ calcd for C₉H₁₁O₂Si 179.052, found 179.052.

20; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, (4-chlorophenyl)dimethylsilane (34 mg, 0.2 mmol), H_2O (180

 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **20** (36 mg) in 96% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 1.93 (s, 1H), 0.39 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 137.3, 135.9, 134.4, 128.1, 0 ppm.

21; Following the typical procedure **III**, (3-chlorophenyl)dimethylsilane (34 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **21** (21 mg) in 56% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dd, *J* = 1.3, 0.5 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.38 – 7.34 (m, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 2.32 (s, 1H), 0.39 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 134.3, 132.9, 130.9, 129.6, 129.4, -0.1 ppm; HRMS–ESI *m/z*: [M – H]⁻ calcd for C₈H₁₀ClOSi 185.0195, found 185.0179.

22; Following the typical procedure **III**, (4-fluorophenyl)dimethylsilane (31 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **22** (18 mg) in 53% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.07 (t, *J* = 8.9 Hz, 2H), 2.01 (s, 1H), 0.40 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 165.2, 162.8, 135.1, 135.0, 115.1, 114.9, 0.1 ppm; HRMS–MALDI–TOF *m/z*: [M + K]⁺ calcd for C₈H₁₁FKOSi 209.0195, found 209.0195.



23; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure III, dimethyl(naphthalen-1-yl)silane (37 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst 1 4CzIPN (4.7 mg, 0.006 mmol), and ethyl

2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **23** (27 mg) in 67% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 2H), 7.77 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.56 – 7.42 (m, 3H), 2.04 (s, 1H), 0.58 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 136.9, 136.6, 133.4, 133.2, 130.4, 129.0, 128..1, 126.0, 125.5, 125.0, 1.3 ppm.



24; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, dimethyl(naphthalen-2-yl)silane (37 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **24** (30 mg) in 73% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.89 – 7.81 (m, 3H), 7.66 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 1.90 (s, 1H), 0.49 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 136.5, 134.0, 133.9, 132.8, 129.1, 128.2, 127.7, 127.2, 126.6, 126.0, 0.1 ppm.

25; A known compound and the characterization data are in accordance with the literature.^[S18] Following the typical procedure **III**, dimethyl(thiophen-2-yl)silane (32 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **25** (26 mg) in 83% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 4.6, 0.6 Hz, 1H), 7.37 (dd, *J* = 3.3, 0.7 Hz, 1H), 7.21 (dd, *J* = 4.6, 3.4 Hz, 1H), 2.06 (s, 1H), 0.46 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 138.5, 134.7, 131.1, 128.2, 0.9 ppm.

26; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, dimethyl(3-methylthiophen-2-yl)silane (34 mg, 0.2 mmol),

H₂O (180 μL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **26** (27 mg) in 78% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 4.6 Hz, 1H), 7.00 (d, *J* = 4.6 Hz, 1H), 2.40 (s, 3H), 2.13 (s, 1H), 0.46 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 145.5, 132.0, 131.8, 129.9, 16.4, 1.3 ppm.



27; Following the typical procedure **III**, 1,4-bis(dimethylsilyl)benzene (45 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **27** (29 mg) in 70% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.47 (m, 4H), 4.35 (dt, *J* = 7.5, 3.7 Hz, 1H), 1.95 (s, 1H), 0.32 (s, 6H), 0.27 (d, *J* = 3.8 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 140.0, 139.1, 133.4, 132.4, -0.1, -3.9 ppm; GCMS–EI *m/z*: (M⁺) calcd for C₁₀H₁₈OSi₂ 210.089, found 210.085.

28; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, methyldiphenylsilane (40 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **28** (32 mg) in 75% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.54 (m, 4H), 7.42 – 7.30 (m, 6H), 2.35 (s, 1H), 0.63 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 137.0, 133.9, 129.9, 127.9, -1.3 ppm.

29; Following the typical procedure **III**, silane (58 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **29** (47 mg) in 78% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 7.8, 1.5 Hz, 4H), 7.44 – 7.34 (m, 6H),

7.24 (dd, J = 14.5, 7.6 Hz, 2H), 7.19 – 7.13 (m, 3H), 2.82 – 2.71 (m, 2H), 2.19 (s, 1H), 1.55 – 1.45 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 144.4, 135.8, 134.1, 129.9, 128.4, 127.9, 127.8, 125.7, 29.0, 17.0 ppm; GCMS–EI *m/z*: (M – Ph(CH₂)₂)⁺ calcd for C₁₂H₁₁OSi 199.057, found 199.057.

30; Following the typical procedure **III**, silane (61 mg, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **30** (32 mg) in 50% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.45 – 7.34 (m, 6H), 7.06 (s, 4H), 2.77 – 2.68 (m, 2H), 2.30 (s, 3H), 2.11 (s, 1H), 1.54 – 1.44 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 135.9, 135.2, 134.1, 129.9, 129.1, 127.9, 127.7, 28.6, 20.9, 17.2. ppm; GCMS–EI *m/z*: (M – *p*-MePh(CH₂)₂)⁺ calcd for C₁₂H₁₁OSi 199.057, found 199.057.



31; Following the typical procedure **III**, silane (64 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **31** (38 mg) in 57% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.57 (m, 4H), 7.45 – 7.34 (m, 6H), 7.10 – 7.04 (m, 2H), ppm; ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 136.5, 135.9, 134.1, 129.9, 128.7, 127.9, 113.8, 55.2, 28.1, 17.3 ppm; GCMS–EI *m/z*: (M⁺) calcd for C₂₁H₂₂O₂Si 324.138, found 324.138.



32; Following the typical procedure **III**, silane (69 mg, 0.2 mmol), H₂O (180 μ L,10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **32** (54 mg) in 75% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.45 – 7.34 (m, 6H),

7.29 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 2.81 – 2.71 (m, 2H), 2.08 (s, 1H), 1.55 – 1.49 (m, 2H), 1.30 (s, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 148.6, 141.3, 135.9, 134.1, 129.9, 128.0, 127.4, 125.3, 34.3, 31.4, 28.4, 16.9 ppm; GCMS–EI *m/z*: (M – ^{*t*}BuPh(CH₂)₂)⁺ calcd for C₁₂H₁₁OSi 199.057, found 199.057.



33; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, silane (50 mg, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **33** (34 mg) in 64% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.75 (m, 3H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.32 (m, 6H), 2.48 (s, 1H), 0.80 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 137.6, 136.7, 134.8, 134.7, 133.9, 133.4, 130.7, 129.9, 128.9, 128.4, 128.0, 126.0, 125.5, 125.0, 0 ppm.

34; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, triphenylsilane (52 mg, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **34** (53 mg) in 96% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 6.6 Hz, 6H), 7.41 (t, *J* = 7.3 Hz, 3H), 7.34 (t, *J* = 7.2 Hz, 6H), 2.84 (s, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.1, 135.0 130.1, 127.9 ppm.

Si OH Me

35; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, benzyldimethylsilane (30 mg, 0.2 mmol), H_2O (180 μ L, 10

mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **35** (11 mg) in 34% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, *J* = 7.6 Hz, 2H), 7.14 – 7.05 (m, 3H), 2.20 (s, 2H), 1.65 (s, 1H), 0.16 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 139.0, 128.4, 128.1, 124.3, 28.0, -0.7 ppm.



36; A known compound and the characterization data are in accordance with the literature.^[S18] Following the typical procedure **III**, dimethyl(4-methylbenzyl)silane (33 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **36** (17 mg) in 48% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.13 (s, 2H), 1.66 (s, 1H), 0.13 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.6, 133.6, 129.1, 128.0, 27.4, 20.9, -0.7 ppm.

37; A known compound and the characterization data are in accordance with the literature.^[S19] Following the typical procedure **III**, trihexylsilane (40 µL, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **37** (27 mg) in 45% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.48 (s, 1H), 1.39 – 1.22 (m, 24H), 0.88 (t, *J* = 6.9 Hz, 9H), 0.66 – 0.53 (m, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 33.3, 31.6, 23.0, 22.6, 15.1, 14.1 ppm.

38; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, tributylsilane (51 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02

mmol) in acetonitrile (2.0 mL) were employed to give the product **38** (34 mg) in 79% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.48 (s, 1H), 1.39 – 1.28 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 9H), 0.66 – 0.55 (m, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 26.5, 25.3, 14.7, 13.8 ppm.

39; A known compound and the characterization data are in accordance with the literature.^[S19] Following the typical procedure **III**, triisopropylsilane (41 µL, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **39** (19 mg) in 53% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.41 (s, 1H), 1.05 (d, *J* = 1.5 Hz, 21H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 17.7, 12.7 ppm.

40; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, triethylsilane (32 µL, 0.2 mmol), H₂O (180 µL, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **40** (13 mg) in 51% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.50 (s, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 6.6, 5.8 ppm.

41; A known compound and the characterization data are in accordance with the literature.^[S19] Following the typical procedure **III**, cyclohexyldimethylsilane (35 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **41** (10 mg) in 32% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.78 – 1.69 (m, 5H), 1.44 (s, 1H), 1.29 – 1.10 (m, 6H), 0.09 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 27.8, 27.4, 26.9, 26.6, -2.3 ppm.



42; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, diphenylsilane (37 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and quinuclidine (2.2 mg, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **42** (26 mg) in 61% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.0, 1.4 Hz, 4H), 7.33 (ddd, *J* = 7.1, 4.2, 1.4 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 4H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 134.4, 134.3, 130.0, 127.6 ppm.



43; A known compound and the characterization data are in accordance with the literature.^[S3] Following the typical procedure **III**, (4-Methoxyphenyl)(phenyl)silane (43 mg, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and quinuclidine (2.2 mg, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **43** (15 mg) in 31% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.43 (m, 2H), 7.39 – 7.29 (m, 3H), 7.19 (dt, *J* = 13.4, 6.6 Hz, 2H), 6.74 – 6.65 (m, 2H), 3.77 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 161.0, 136.0, 135.0, 134.3, 129.8, 127.5, 125.8, 113.3, 55.0 ppm.



44; A known compound and the characterization data are in accordance with the literature.^[S20] Following the typical procedure III, di-*tert*-butylsilane (40 μ L, 0.2 mmol), H₂O (180 μ L, 10 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and quinuclidine (2.2 mg, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product 44 (17 mg) in 47% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 2.03 (s, 2H), 1.05 (s, 18H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 27.2, 19.8 ppm.

45; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), methanol (162 μ L, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.84 mL) were employed to give the product **45** (47 mg) in 80% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.36 – 7.27 (m, 9H), 3.55 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 133.9, 130.0, 127.9, 51.8 ppm.

46; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), alcohol (1.0 mL, 17.1 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.0 mL) were employed to give the product **46** (36 mg) in 60 % yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.45 – 7.35 (m, 9H), 3.87 (q, *J* = 7.0 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.4, 129.9, 127.8, 59.7, 18.4 ppm.



47; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), alcohol (0.4 mL, 4.4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **47** (60 mg) in 90% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.46 – 7.34 (m, 9H), 3.79 (t, *J* = 6.5 Hz, 2H), 1.61 – 1.52 (m, 2H), 1.38 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.5, 129.9, 127.8, 63.7, 34.7, 19.0, 13.8 ppm.
48; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), *n*-hexanol (0.5 mL, 4.0mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.5 mL) were employed to give the product **48** (47 mg) in 67% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.47 –7.30 (m, 9H), 3.79 (t, *J* = 6.6 Hz, 2H), 1.57 (td, *J* = 13.7, 7.0 Hz, 2H), 1.37 – 1.19 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.5, 129.9, 127.8, 64.0, 32.5, 31.5, 25.4, 22.6, 14.0 ppm; GCMS–EI *m/z*: (M – C₆H₁₃O) calcd for C₁₈H₂₃OSi 259.094, found 259.094.

49; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), 1-nonanol (0.4 mL, 2.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **49** (60 mg) in 75% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.8, 1.3 Hz, 6H), 7.45 – 7.35 (m, 9H), 3.78 (t, *J* = 6.6 Hz, 2H), 1.62 – 1.53 (m, 2H), 1.38 – 1.15 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.5, 129.9, 127.8, 64.0, 32.5, 31.9, 29.5, 29.3, 29.3, 25.7, 22.7, 14.1 ppm; HRMS–ESI [M + Na]⁺ *m/z*: calcd for C₂₇H₃₄OSiNa 425.2271, found 425.2271.

50; A known compound and the characterization data are in accordance with the literature.^[S22] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), 3-chloro-1-propanol (0.5 mL, 5.9 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.5 mL) were employed to give the product **50** (53 mg) in 75% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.60 (m, 5H), 7.41 (qd, *J* = 7.7, 2.9 Hz, 10H), 3.93 (t, *J* = 5.8 Hz, 2H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.04 – 1.97 (m, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 133.9, 130.1, 127.9, 60.4, 41.7, 35.2 ppm.

51; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), 2,2,2-trifluoroethanol (151 μ L, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.85 mL) were employed to give the product **51** (54 mg) in 76% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.9, 1.4 Hz, 6H), 7.49 – 7.37 (m, 9H), 4.04 (q, *J* = 8.5 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 132.5, 130.5, 128.1, 62.6, 62.2, 61.9, 61.5 ppm; GCMS-EI *m/z*: (M⁺) calcd for C₂₀H₁₇F₃OSi 358.100, found 358.099.

52; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), methanol- d_4 (162 µL, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol) in acetonitrile (1.85 mL) were employed to give the product **52** (31 mg) in 54% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.59 (m, 6H), 7.47 – 7.36 (m, 9H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 133.9, 130.0, 127.9, 51.0 ppm; GCMS–EI *m/z*: (M⁺) calcd for C₁₉H₁₅D₃OSi 293.131, found 293.131.

53; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), cyclopropanemethanol (0.5 mL, 6 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.5 mL) were employed to give the product **52** (60.6 mg) in 92 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.3 Hz, 6H), 7.48 – 7.33 (m, 9H), 3.65 (d, *J* = 6.5 Hz, 2H), 1.17 – 1.02 (m, 1H), 0.43 (d, *J* = 7.8 Hz, 2H), 0.13 (d, *J* = 4.6 Hz, 2H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.4, 129.9, 127.8, 68.3, 13.2, 2.8 ppm; HRMS–ESI *m/z*: [M + Na]⁺ calcd for C₂₂H₂₂NaOSi 353.1332, found 353.1334.



54; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), isopropanol (0.4 mL, 4.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μL, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **54** (38.4 mg) in 58 % yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.9, 1.4 Hz, 6H), 7.45 – 7.35 (m, 9H), 3.55 (d, *J* = 6.4 Hz, 2H), 1.83 (dq, *J* = 13.2, 6.6 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 134.5, 129.9, 127.8, 70.3, 30.8, 19.1 ppm.



55; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), isopropanol (0.4 mL, 5.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **55** (33 mg) in 52 % yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 7.8, 1.4 Hz, 6H), 7.44 – 7.33 (m, 9H), 4.22 – 4.12 (m, 1H), 1.18 (d, *J* = 6.1 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 135.0, 129.8, 127.7, 66.3, 25.7 ppm.



56; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), cyclobutanol (0.4 mL, 5 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **56** (58 mg) in 88% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.8, 1.4 Hz, 6H), 7.42 – 7.32 (m, 9H), 4.42 – 4.34 (m, 1H), 2.12 – 1.99 (m, 4H), 1.63 – 1.52 (m, 1H), 1.35 – 1.22 (m, 1H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 134.6, 129.9, 127.8, 68.0, 33.8, 12.2 ppm; HRMS – ESI *m/z*: [M + Na]⁺ calcuted for C₂₂H₂₂NaOSi 353.1332, found 353.1336.



57; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), cyclohexanol (0.4 mL, 3.8 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (1.6 mL) were employed to give the product **57** (61 mg) in 85% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.45 – 7.32 (m, 9H), 3.83 (ddd, *J* = 12.7, 8.9, 3.5 Hz, 1H), 1.80 – 1.64 (m, 4H), 1.46 (dt, *J* = 19.2, 11.2 Hz, 3H), 1.27 – 1.09 (m, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.4, 135.1, 129.8, 127.7, 71.8, 35.6, 25.6, 23.9 ppm.



58; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), *L*-Menthol (63 mg, 0.4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **58** (34 mg) in 41% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, *J* = 7.9, 1.5 Hz, 6H), 7.44 – 7.34 (m, 9H), 3.58 – 3.48 (m, 1H), 2.45 – 2.30 (m, 1H), 1.95 – 1.81 (m, 1H), 1.54 (s, 1H), 1.37 – 1.08 (m, 5H), 0.88 (d, *J* = 7.1 Hz, 3H), 0.79 (d, *J* = 6.0 Hz, 3H), 0.38 (d, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.6, 135.2, 129.7, 127.7, 73.9, 50.2, 45.3, 34.4, 31.6, 25.3, 22.6, 22.2, 21.3, 15.3 ppm; GCMS–EI *m/z*: [M – C₁₀H₁₉O]⁺ calcd for C₁₈H₁₅Si 259.094, found 259.094.

60; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, methyldiphenylsilane (40 μ L, 0.2 mmol), isopropanol (0.4 mL, 5.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol), and DBU (30 μ L, 0.2 mmol) in acetonitrile (1.6 mL) were employed to give the product **53** (38.4 mg) in 58 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (dd,

J = 7.6, 1.8 Hz, 4H), 7.30 (dd, *J* = 8.4, 6.7 Hz, 6H), 4.02 (dt, *J* = 12.1, 6.1 Hz, 1H), 1.10 (d, *J* = 6.1 Hz, 6H), 0.57 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 136.8, 134.3, 129.6, 127.7, 65.8, 25.7, -2.4 ppm.

61; Following the typical procedure **IV**, phenethyldiphenylsilane (57.6 mg, 0.2 mmol), isopropanol (0.4 mL, 5.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol), and DBU (30 µL, 0.2 mmol) in acetonitrile (1.6 mL) were employed to give the product **61** (55 mg) in 79% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 4H), 7.40 (dq, *J* = 13.8, 6.8 Hz, 6H), 7.28 (s, 1H), 7.24 (s, 1H), 7.17 (dd, *J* = 14.6, 7.1 Hz, 3H), 4.11 (dt, *J* = 12.0, 6.0 Hz, 1H), 2.75 – 2.68 (m, 2H), 1.51 (dd, *J* = 8.9, 4.4 Hz, 2H), 1.18 (d, *J* = 6.0 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 135.4, 134.7, 129.7, 128.3, 127.8, 127.7, 125.6, 65.9, 29.1, 25.7, 16.4 ppm; HRMS–ESI *m/z*: [M + Na]⁺ calcd for C₂₃H₂₆NaOSi 369.1645, found 369.1645.



62; Following the typical procedure **IV**, (4-(*tert*-butyl)phenethyl)diphenylsilane (68.9 mg, 0.2 mmol), isopropanol (0.4 mL, 5.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol), and DBU (30 µL, 0.2 mmol) in acetonitrile (1.6 mL) were employed to give the product **62** (73 mg) in 91% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.60 (m, 4H), 7.41 – 7.28 (m, 8H), 7.14 – 7.10 (m, 2H), 4.10 (dt, *J* = 12.1, 6.0 Hz, 1H), 2.79 – 2.63 (m, 2H), 1.61 – 1.47 (m, 2H), 1.29 (s, 9H), 1.17 (d, *J* = 6.1 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 148.3, 141.8, 135.5, 134.7, 129.7, 127.8, 127.4, 125.2, 65.9, 34.3, 31.4, 28.5, 25.7, 16.2 ppm; HRMS–MALDI–TOF *m/z*: [M + Na]⁺ calcd for C₂₇H₃₄NaOSi 425.2271, found 425.2274.

63; Following the typical procedure **IV**, diphenylsilane (37 ul, 0.2 mmol), 1-hexanol (0.5 mL, 4 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μ L, 0.02 mmol), and DBU (30 μ L, 0.2 mmol) in acetonitrile (1.5 mL) were employed to give the product **63** (65 mg) in 85 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.60 (m, 4H), 7.41 – 7.30 (m, 6H), 3.82 – 3.71 (m, 4H), 1.63 – 1.56 (m, 4H), 1.39 – 1.24 (m, 12H), 0.87 (t, J = 5.6 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 134.9, 133.3, 130.1, 127.7, 63.2, 32.5, 31.6, 25.5, 22.6, 14.0 ppm; GCMS–EI m/z: [M – C₆H₁₃O]⁺ calcd for C₁₈H₂₃OSi 283.151, found 283.151.



64; Following the typical procedure **IV**, diphenylsilane (37 μL, 0.2 mmol), isopropanol (0.4 mL, 5.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μL, 0.02 mmol), and DBU (30 μL, 0.2 mmol) in acetonitrile (1.6 mL) were employed to give the product **64** (54 mg) in 90 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 6.7 Hz, 4H), 7.39 – 7.29 (m, 6H), 4.21 (dt, J = 12.1, 6.1 Hz, 2H), 1.20 (d, J = 6.1 Hz, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.0, 134.3, 129.9, 127.6, 65.6, 25.6 ppm; GCMS–EI *m/z*: [M–C₃H₇O]⁺ calcd for C₁₅H₁₇OSi 241.104, found 241.104.



65; Following the typical procedure **IV**, diphenylsilane (37 µL, 0.2 mmol), cyclohexanol (0.5 mL, 4.7 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol), and DBU (30 µL, 0.2 mmol) in acetonitrile (1.5 mL) were employed to give the product **65** (68 mg) in 86 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (t, *J* = 8.5 Hz, 4H), 7.42 – 7.25 (m, 6H), 3.96 – 3.77 (m, 2H), 1.77 (dd, *J* = 19.7, 12.2 Hz, 8H), 1.51 – 1.35 (m, 6H), 1.23 (d, *J* = 22.6 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 135.0, 134.7, 129.8, 127.6, 71.0, 35.5, 25.6, 23.9 ppm; GCMS–EI *m/z*: [M – C₆H₁₁O] calcd for C₁₈H₂₁OSi 281.136, found 281.136.



66; Following the typical procedure **IV**, (4-Methoxyphenyl)(phenyl)silane (64 mg, 0.2 mmol), cyclohexanol (0.5 mL, 4.7 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μL, 0.02 mmol), and DBU (30 μL, 0.2 mmol) in acetonitrile (1.5 mL) were employed to give the product **66** (27 mg) in 41% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (dd, J = 24.9, 7.9 Hz, 4H), 7.45 – 7.29 (m, 3H), 6.90 (d, J = 8.1 Hz, 2H), 4.19 (dt, J = 12.1, 6.0 Hz, 2H), 3.81 (s, 3H), 1.19 (d, J = 6.0 Hz, 12H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 161.1, 136.6, 135.0, 134.6, 129.8, 127.6, 125.2, 113.4, 65.5, 55.0, 25.6 ppm; GCMS–EI m/z: [M – Me]⁺ calcd for C₁₈H₂₃O₃Si 315.141 found 315.141.

67; A known compound and the characterization data are in accordance with the literature.^[S21] Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), phenol (214 mg, 2.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μL, 0.02 mmol), and DBU (30 μL, 0.2 mmol) in acetonitrile (1.8 mL) were employed to give the product **67** (27 mg) in 38 % yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.71 – 7.63 (m, 6H), 7.41 (dt, J = 26.8, 7.1 Hz, 9H), 7.12 (t, J = 7.9 Hz, 2H), 6.88 (dd, J = 15.6, 7.9 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 155.0, 135.5, 133.5, 130.3, 129.3, 127.9, 121.5, 120.0 ppm.



68; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), *m*-cresol (220 mg, 2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 μL, 0.02 mmol), and DBU (30 μL, 0.2 mmol) in acetonitrile (1.8 mL) were employed to give the product **68** (47 mg) in 62 % yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.65 (m, 6H), 7.46 – 7.35 (m, 9H), 6.98 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 6.6 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 1H), 2.19 (s, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 139.3, 135.5, 133.7, 130.2, 128.9,

127.9, 122.3, 120.8, 116.8, 21.3 ppm; GCMS-EI m/z: $[M - C_7H_7O]^+$ calcd for $C_{18}H_{15}OSi$, 259.094, found 259.094.



69; Following the typical procedure **IV**, triphenylsilane (52 mg, 0.2 mmol), 4-ethylphenol (202 mg, 1.65 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol), and DBU (30 µL, 0.2 mmol) in acetonitrile (2.0 mL) were employed to give the product **69** (24 mg) in 31% yield as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 6.7 Hz, 6H), 7.40 (dt, *J* = 26.5, 7.2 Hz, 9H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 152.9, 137.1, 135.5, 130.2, 128.5, 127.9, 119.7, 28.0, 15.6 ppm; HRMS–ESI *m*/*z*: [M + Na]⁺ calcd for C₂₆H₂₄NaOSi 403.1489, found 403.1492.



70; Following the typical procedure **IV**, diphenylsilane (37 µL, 0.2 mmol), phenol (214 mg, 2.3 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), *tert*-dodecanethiol (HAT cat. **3**, 4.7 µL, 0.02 mmol), and DBU (30 µL, 0.2 mmol) in acetonitrile (1.8 mL) were employed to give the product **70** (31 mg) in 42% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.73 (m, 4H), 7.47 – 7.34 (m, 7H), 7.16 (t, *J* = 7.5 Hz, 4H), 6.99 – 6.90 (m, 5H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 154.0, 135.0, 131.3, 130.9, 129.5, 128.0, 122.1, 119.8 ppm; GCMS–EI *m/z*: [M⁺] calcd for C₂₄H₂₀O₂Si 368.123, found 328.123.

71; Following the typical procedure **III**, triethylsilane (48 μ L, 0.3 mmol), methyldiphenylsilanol (43 mg, 0.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 μ L, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **71** (25 mg) in 38% yield as a colorless oil together with the dimmer byproduct **71**' in 22% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 7.7, 1.8 Hz, 4H), 7.41 – 7.31 (m, 6H), 0.90 (t, *J*

= 7.9 Hz, 9H), 0.61 (s, 3H), 0.55 (q, J = 7.9 Hz, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 138.4, 133.8, 129.4, 127.7, 6.8, 6.3, -0.5 ppm; GCMS–EI m/z: [M – Et]⁺ calcd for C₁₇H₂₃OSi₂ 299.128, found 299.128.

72; Following the typical procedure **III**, triethylsilane (48 µL, 0.2 mmol), dimethyl(phenyl)silanol (31 mg, 0.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol) in acetonitrile (2.0 mL) were employed to give the product **72** (19 mg) in 36% yield as a colorless oil together with the dimmer byproduct **72**' in 26% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.36 (dd, *J* = 5.0, 1.8 Hz, 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.9 Hz, 6H), 0.32 (s, 6H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 132.9, 129.1, 127.6. 6.8, 6.3, 0.9 ppm; GCMS–EI *m/z*: [M – Et]⁺ calcd for C₁₂H₂₁OSi₂ 237.113, found 237.112.



73; Following the typical procedure **III**, 1,4-bis(dimethylsilyl)benzene (67 µL, 0.3 mmol), 1,4-phenylenebis(dimethylsilanol) (45 mg,0.2 mmol), photocatalyst **1** 4CzIPN (4.7 mg, 0.006 mmol), and ethyl 2-mercaptopropionate (2.6 µL, 0.02 mmol)in acetonitrile (2.0 mL) were employed to give the product **73** (65 mg) in 77% yield as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.48 (m, 36H), 4.42 (dt, *J* = 7.4, 3.7 Hz, 2H), 0.34 (d, *J* = 4.9 Hz, 108H) ppm; ¹³C NMR (101 MHz, CDCl₃) δ 140.8, 138.5, 133.3, 132.2, 0.9, -3.9 ppm; HRMS–MALDI-TOF *m/z*: [M + K]⁺ calcd for C₉₀H₁₄₆KO₁₈Si₁₈ 1897.6496, found 1897.6496.

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XI. ¹H, ¹³C NMR Spectra of Products























S57











































































































S110



























S121















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S127













S132



S133






























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S155















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S161













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