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Photochemical Synthesis of 1,4-Dicarbonyl Bifluorene Compounds via Oxidative Radical Coupling Using TEMPO as the Oxygen Atom Donor

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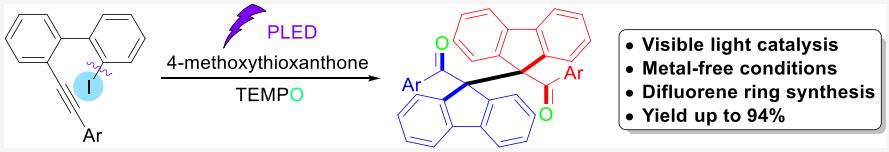


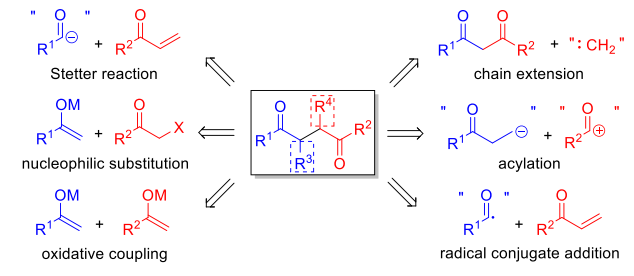
ABSTRACT: A visible-light-induced metal-free synthesis of 1,4-dicarbonyl compounds from alkyne-containing aryl iodides via photochemical C–I bond cleavage, intramolecular cyclization, oxidation, and intermolecular radical coupling sequence is reported. TEMPO was employed as the oxygen atom donor in this transformation. This protocol provided a new strategy for the synthesis of 1,4-dicarbonyl bifluorene compounds.

The 1,4-dicarbonyl motif widely exists in various bioactive natural products and pharmaceuticals.[1,2] As a versatile building block, it is also quite useful in organic synthesis.[3,4] Thus, the syntheses of 1,4-dicarbonyl compounds have attracted attention of chemists widely. Several strategies have been developed in this field (Scheme 1A), including (i) Stetter reaction of aldehydes with Michael acceptors,[5] (ii) nucleophilic substitution of enolates with α-haloketones,[6] (iii) oxidative coupling of enolates,[7] (iv) chain extension of 1,3-diketones,[8] (v) acylation of homoenolate equivalents with acyl chlorides,[9] and (vi) radical conjugate addition of acyl radicals with Michael acceptors.[10] However, to the best of our knowledge, there have been few reports[7] on radical coupling targeting the formation of 1,4-dicarbonyl compounds so far. In general, radical coupling reaction needs a highly functional group tolerant and mild synthetic strategy to access various organic molecules.[11,12] Therefore, it is promising to develop a new method for the synthesis of 1,4-dicarbonyl compounds via a radical coupling process, which provides more choice for synthesizing these compounds.

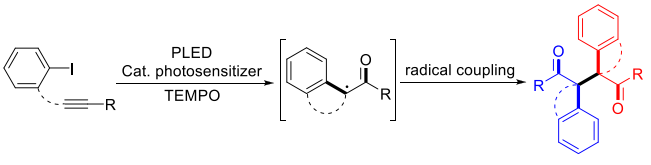
Recently, we developed an intramolecular iodine-atom transfer radical addition of alkyne under visible light irradiation.[13] This method showed precise control of the C_{aryl}–I bond cleavage and $C_{alkenyl}$–I bond formation tuned by a photosensitizer. It also provided a convenient and atom-economic way to synthesize vinyl iodide compounds. During the mechanistic studies, the observation indicated that TEMPO could significantly inhibit this transformation. As a result, conversion and yield decreased dramatically. However, side products formed under such conditions received less attention. With our continuous interest in this reaction, further investigation revealed that the main byproduct in the presence of TEMPO was a dimeric 1,4-dicarbonyl bifluorene compound, which showed several applications in the field of functional materials[14] and potential photosensitizer (*vide infra*). On the basis of this discovery, more explorations in this field were carried out. Herein, we wish to report a new

Scheme 1. Synthesis of 1,4-Dicarbonyl Compounds

A) Previous work: Strategies for the synthesis of 1,4-dicarbonyl compounds



B) This work: Photochemical synthesis of 1,4-dicarbonyl compounds via radical coupling process



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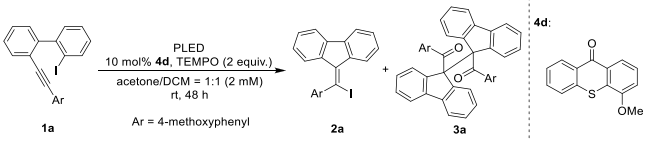
synthetic protocol for 1,4-dicarbonyl bifluorene compounds via a radical coupling process (Scheme 1B).

Initially, we used 2-iodo-2′-[(4-methoxyphenyl)ethynyl]-1,1′-biphenyl (**1a**) as the model substrate and TEMPO as the oxygen atom donor.[15] The reaction was irradiated by a purple light-emitting diode (PLED) at room temperature. A series of reaction parameters were tested, and the optimized reaction condition was obtained (Table 1, entry 1) (for detailed screening, see Table S1 in the Supporting Information). Control experiments indicated that light was essential for the formation of **3a** (Table 1, entry 2). Without photoirradiation, even though the reaction mixture was heated at 60 °C, no reaction occurred (Table 1, entry 3), which meant that the reaction was not thermally initiated. Finally, no products **2a** and **3a** were formed in the absence of **4d**, which revealed that **4d** was necessary for this transformation (Table 1, entry 4). Thus, Condition A (**4d** (10 mol %), TEMPO (2 equiv), acetone/DCM = 1:1, PLED, and rt) was applied as the optimized condition for further studies.

Table 1. Investigation of Reaction Parameters

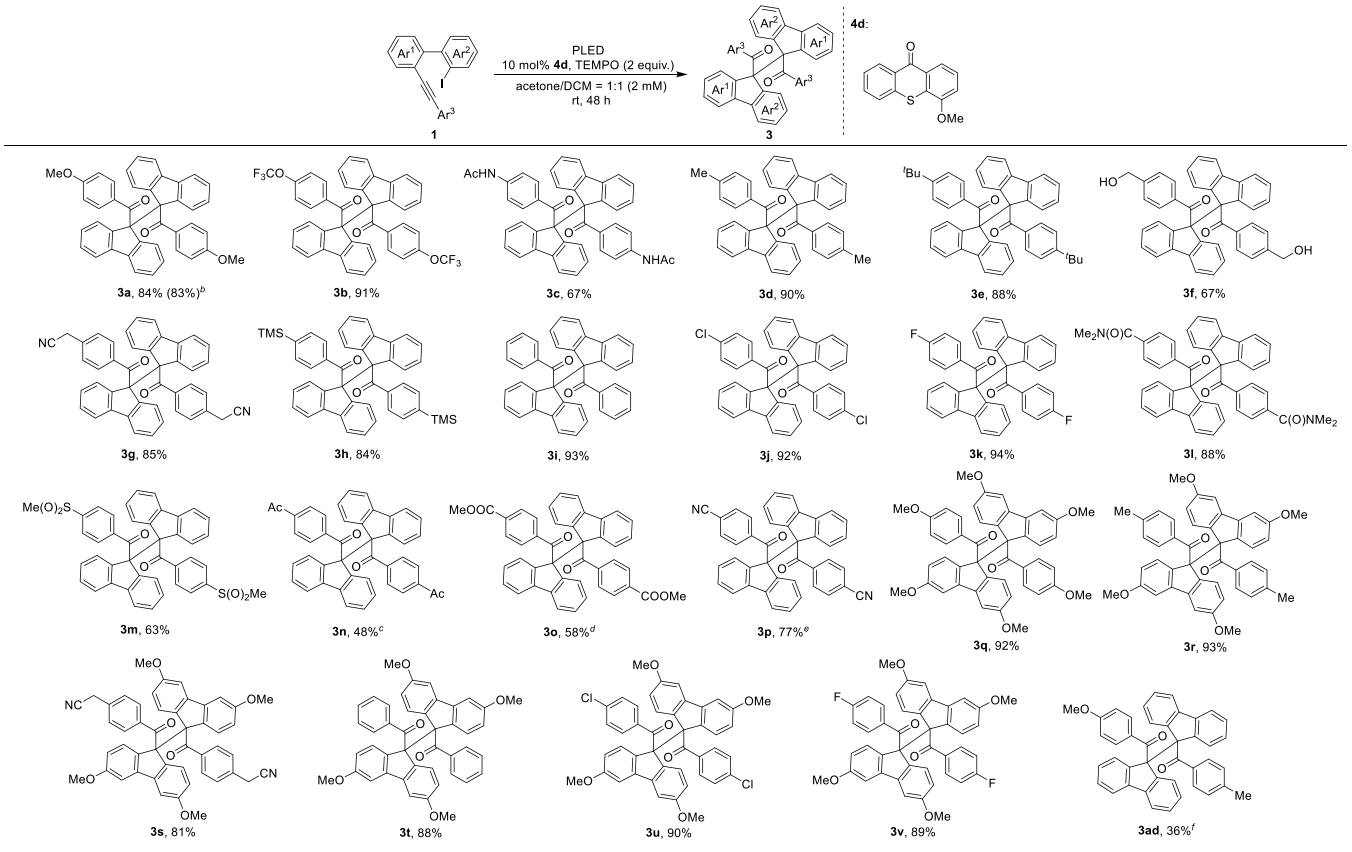


entry	variation from Condition A[a]	NMR yield (%)[b] 1a	2a	3a
1	none	0	0	86 (84)[c]
2	without light	99	0	0
3	without light, 60 °C instead of rt	99	0	0
4	without **4d**	99	0	0

[a]**1a** (0.1 mmol), **4d** (10 mol %), and TEMPO (2 equiv) in anhydrous acetone/DCM = 1:1 (50 mL) was irradiated by PLED for 48 h at rt under an argon atmosphere. [b]Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 (0.1 mmol) as internal standard. [c]Isolated yield.

With the optimized reaction condition in hand, the substrate scope was then investigated. As shown in Scheme 2, a variety of alkyne-containing aryl iodides reacted under our established condition. Reactants with a strong electron donating group (**1a**–**c**), a weak electron donating group (**1d**–**h**), a weak electron withdrawing group (**1j**–**k**), or no substitution (**1i**) in Ar^3 were converted into the desired products in good to excellent yields. Strong electron withdrawing groups (**1l**–**p**) had a negative influence on this reaction. The yields were a little lower. Notably, for acetyl (**1n**) or methoxycarbonyl (**1o**) substituted substrates, longer reaction time was required, while, for a substrate with a cyano group (**1p**), higher temperature was necessary. Next, some trisubstituted reactants were investigated under the optimized reaction conditions (**1q**–**v**). All the tested substrates showed decent reactivity. The desired products were generated in good to excellent yields,

Scheme 2. Substrate Scope[a]



[a]All reactions were carried out using **1** (0.1 mmol), **4d** (10 mol %), and TEMPO (2 equiv) in anhydrous acetone/DCM = 1:1 (50 mL) irradiated by PLED for 48 h at rt under an argon atmosphere. Isolated yield was reported. [b]Gram-scale reaction. [c]The reaction was carried out for 72 h. [d]The reaction was carried out for 120 h. [e]The reaction was carried out at 60 °C. [f]The reaction was carried out using **1a** (0.1 mmol), **1d** (0.1 mmol), **4d** (20 mol %), and TEMPO (4 equiv) in anhydrous acetone/DCM = 1:1 (50 mL).

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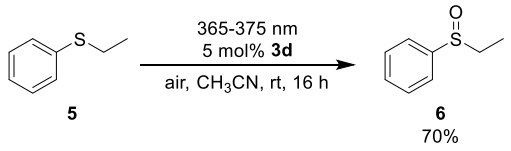
respectively. Importantly, a variety of functional groups, such as alkoxy (**1a**–**b**, **1q**–**v**), acetylamino (**1c**), alkyl (**1d**, **1e**, **1r**), hydroxy (**1f**), cyano (**1g**, **1p**, **1s**), trimethylsilyl (**1h**), halogen atom (**1j**–**k**, **1u**–**v**), dimethylcarbamoyl (**1l**), methylsulfonyl (**1m**), acetyl (**1n**), and methoxycarbonyl (**1o**), were all tolerated in this reaction, which showed very good functional group tolerance. A hetero-coupled product **3ad** was successfully prepared in a 36% isolated yield when the same amount of **1a** and **1d** was applied (Scheme 2). Meanwhile, two homo-coupled products **3a** and **3d** were produced inevitably, and the ratio of **3a**:**3ad**:**3d** was 1:2.1:1.2. To explore the synthetic utility of this method, a gram-scale reaction using **1a** (2.5 mmol, 1.028 g) was carried out under the standard conditions, and the desired product **3a** was obtained in an 83% isolated yield.

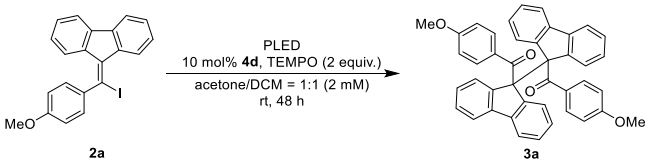
Then, the practical utility of these 1,4-dicarbonyl bifluorenes was further explored. According to the structure analysis, these compounds may have the potential to be a photosensitizer. We tried to use these compounds as the photosensitizers in the photo-oxidation of thioether. Excitingly, the selective oxidation of thioether into sulfoxide proceeded smoothly under the catalysis of **3d** under 365–375 nm UV light irradiation at room temperature under an air atmosphere (Scheme 3). Sulfoxide was generated in a 70% isolated yield. No sulfone product was found in the reaction.

Scheme 3. Selective Oxidation of Thioether 5 Using 3d as the Photosensitizer



To investigate the mechanism of the reaction, some control experiments were carried out (Table 2). Since alkenyl iodide **2a** was observed in the process of this reaction, we hypothesized that it might be an intermediate of this transformation. Thus, **2a** was employed under Condition A. Indeed, **3a** was generated in 92% NMR yield (Table 2, entry 1). Then the reaction was carried out in the absence of catalyst **4d** (Table 2, entry 2); **3a** was also formed in 93% NMR yield, which meant that **4d** was not essential for the transformation from **2a** to **3a**. When the reaction was conducted without photo-irradiation, **3a** was not formed and **2a** was stoichiometrically recovered (Table 2, entry 3), which suggested that light was necessary for this step.

Table 2. Control Experiments



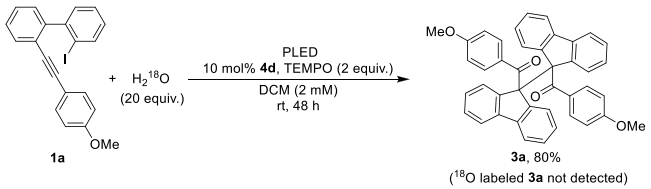
entry	variation from Condition A[a]	NMR yield (%)[b]
1	none	92
2	without **4d**	93
3	without light	0 (99)[c]

[a]**2a** (0.1 mmol), **4d** (10 mol %), and TEMPO (2 equiv) in anhydrous acetone/DCM = 1:1 (50 mL) was irradiated by PLED for 48 h at rt under argon atmosphere. [b]Yield was determined by ^{1}H NMR analysis of the crude reaction mixture using CH_2Br_2 (0.1 mmol) as internal standard. [c]Recovery yield of **2a**.

As shown in Figure S3 (see Supporting Information), intermediate **2a** has a wide and strong absorption band below 440 nm in the UV–vis absorption spectra, which indicates that light (λ < 440 nm) might directly activate **2a**. **1a** has no obvious absorption in this wavelength range of light (350–500 nm). Thus, **1a** needs to gain energy from the excited **4d** to reach its excited state to accomplish the following transformation. Next, calculations of triplet energies of **1a** and **4d** were conducted. The triplet energy of **4d** (267 kJ/mol) is higher than that of **1a** (252 kJ/mol), which indicates that the energy transfer process occurring between **4d** (T_1) and substrate **1a** (S_0) might be possible.

To diagnose the oxygen atom source of the target product **3**, $H_2{}^{18}O$ was subjected into the reaction mixture (Scheme 4).

Scheme 4. ^{18}O Labeling Experiment



Moreover, to avoid possible interference of the oxygen atom from acetone, DCM was used as the solvent instead of mixed solvent. The result showed that no ^{18}O incorporation was observed in **3a**, which indicated that the oxygen atom should not stem from the trace amount of water in the reaction mixture.

HRMS analysis of the crude reaction mixture confirmed the formation of 2,2,6,6-tetramethylpiperidine (Figure S4), which indicated that TEMPO might be the oxygen source of product **3** in this transformation. On the basis of the experimental results and previous reports, a plausible mechanism is proposed (Scheme 5). Under visible light irradiation, the photosensitizer **4d** is converted to a long-lived excited state **4d*** which sensitizes substrate **1** into its triplet state **1***. The ground state **4d** is regenerated for another catalytic cycle. Reversible homolytic cleavage[13,16,17] of the aryl C–I bond of **1*** and the subsequent intramolecular radical cyclization afford alkenyl radical intermediate **8**. Then, the radical intermediate **8** is trapped by an iodine radical to form vinyl iodide intermediate **2**. Meanwhile, reversible heterolytic cleavage of the aryl C–I bond of **1*** and the following intramolecular carbo-iodination also yield vinyl iodide **2** which can be converted into **8** by photoinduced reversible homolytic cleavage of the alkenyl C–I bond in the absence of photosensitizer. UV–vis absorption spectra of **2a** (Figure S3) indicated that vinyl iodide might be directly excited under PLED irradiation. Then, **8** is trapped by TEMPO to form the TEMPO adduct **11**[18] which can be excited under PLED irradiation. A single-electron transfer from excited **11*** to the iodine atom occurs to form *N* radical cation **12** and an iodine anion.

An intermolecular nucleophilic attack of iodine anion to **12** leads to the N–O bond cleavage,[15c,f] affording an amino radical which can be quenched by the hydrogen atom from the solvent molecules. The resulting benzyl iodide **13** is excited by PLED irradiation to provide an α-acyl radical species **14** via

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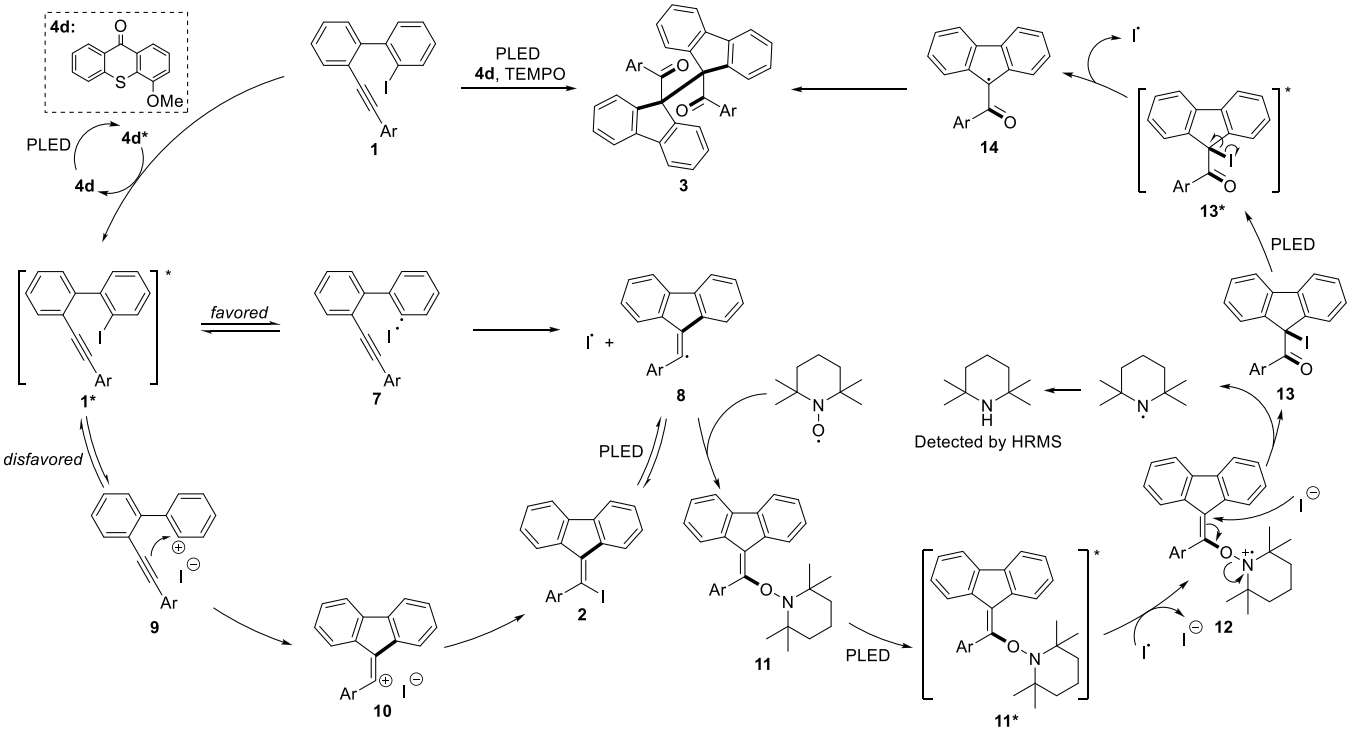
Scheme 5. Plausible Mechanism



C−I bond homolysis. Ultimately, two C-central radicals **14** undergo an intermolecular radical-radical coupling reaction to yield the final product **3**.

On the basis of the above reaction mechanism (Scheme 5), TEMPO might serve a dual function. First, TEMPO coupled with alkenyl radical **8** and then provided an oxygen atom by N−O bond cleavage. Second, TEMPO quenched the *in situ* generated iodine radical,[19] which promoted the reaction. Therefore, 2 equiv of TEMPO was consumed in the reaction process. The C−X bond cleavage types of haloarenes depend on the electronegativity of the halogen atom, electronic properties of the substituent groups in the haloarene, and solvent.[16] Although homolysis and heterolysis may occur at the same time, homolysis is favored in iodoarenes due to the lower electronegativity of the iodine atom. In our previous reports,[13] the transformation from **1a** to **2a** was evidently inhibited when 5 equiv of TEMPO was applied. Such a result should be due to the fact that the remaining excess TEMPO in the reaction mixture inhibited the radical reaction, even though some TEMPO was consumed in the reaction process. These two results could be complemented mutually.

In conclusion, we have developed a visible-light-induced synthetic method of 1,4-dicarbonyl bifluorene compounds under metal-free and mild conditions. In this transformation, TEMPO was used as the oxygen atom donor. Further studies in this field are being carried out in our group.

EXPERIMENTAL SECTION

General Information. All the photoreactions were carried out using PLED (2 × 1 m strip, Greethink 5050, 12 V/m) at a distance of 8−10 cm at rt unless stated otherwise. Pyrex flasks were used for all photoreactions without any filters. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376 MHz) NMR spectra of samples in $CDCl_3$ or DMSO-d_6 were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on an Avatar 360 FT-IR spectrometer. HRMS (ESI) determinations were performed on a Bruker micrOTOF II spectrometer (TOF analyzer). Melting points were determined on a WRS-2 apparatus. X-ray crystallographic structure determination was carried out on a Bruker SMART CCD. Anhydrous DCM was distilled with CaH_2. Anhydrous acetone was distilled with $CaSO_4$. 2,2′-Diiodo-5,5′-dimethoxy-1,1′-biphenyl,[20] 2,2′-diiodo-1,1′-biphenyl,[21] **1a**,[17] **1d**,[17] **1i**,[17] **1j**,[17] **1k**,[13] **1o**,[13] **1p**,[17] **1q**,[17] **1r**,[17] **1t**,[17] **1u**,[17] and **1v**[13] were synthesized according to literature procedures.

Procedure I for the Synthesis of 4-(Dimethylcarbamoyl)-phenylacetylene (1l′). To a stirred suspension of 4-ethynylbenzoic acid (2.926 g, 20 mmol) in dry DCM (40 mL) was added thionyl chloride (2.2 mL, 30 mmol) at 0 °C. Then the ice bath was removed and the reaction mixture was stirred at room temperature. After 5 h, Et_3N (8.3 mL, 60 mmol) and Me_2NH (2 M in THF) (12 mL, 24 mmol) were added dropwise into the reaction mixture subsequently. The reaction was stirred for another 5 h at room temperature. Then, the reaction mixture was washed with H_2O and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Further purification by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3:1) afforded **1l′** as a solid (2.340 g, 68%); mp 118.5−118.6 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.8 Hz, 2 H), 3.14 (s, 1 H), 3.11 (s, 3 H), 2.97 (s, 1 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.8, 136.5, 132.1, 127.1, 123.4, 82.9, 78.5, 39.4, 35.3; IR (neat) 1614, 1512, 1482, 1453, 1394 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{11}H_{12}NO$: 174.0913, found: 174.0917.

Typical Procedure II for the Synthesis of ((4-(Trifluoromethoxy)phenyl)ethynyl) Copper and Its Derivatives. *((4-(Trifluoromethoxy)phenyl)ethynyl)copper.* A solution of cuprous iodide (1.908 g, 10 mmol) in aqueous ammoniacal (28 mL) was poured into a solution of 4-(trifluoromethoxy)penylacetylene (1.5 mL, 10 mmol) in ethanol (80 mL). The reaction mixture was allowed to stir at room temperature overnight. The bright chartreuse precipitate was filtered off and washed three times with water, ethanol, and ethyl acetate. The bright canary green solid was dried at 60 °C under reduced pressure with oil pump. The crude product was used without further purification.

The Following Compounds Were Prepared According to Typical Procedure II. *((4-(Acetylamino)phenyl)ethynyl)copper.* The reaction of 4-(acetylamino)phenylacetylene (1.593 g, 10

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mmol), cuprous iodide (1.917 g, 10 mmol), aqueous ammoniacal (28 mL), and ethanol (80 mL) afforded ((4-(acetylamino)phenyl)-ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-(tert-Butyl)phenyl)ethynyl)copper. The reaction of 4-(*tert*-butyl)phenylacetylene (3.6 mL, 20 mmol), cuprous iodide (3.826 g, 20 mmol), aqueous ammoniacal (56 mL), and ethanol (160 mL) afforded ((4-(*tert*-butyl)phenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-(Hydroxymethyl)phenyl)ethynyl)copper. The reaction of 4-(hydroxymethyl)phenylacetylene (1.326 g, 10 mmol), cuprous iodide (1.917 g, 10 mmol), aqueous ammoniacal (28 mL), and ethanol (80 mL) afforded ((4-(hydroxymethyl)phenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-(Cyanomethyl)phenyl)ethynyl)copper. The reaction of 4-(cyanomethyl)phenylacetylene (2.7 mL, 20 mmol), cuprous iodide (3.823 g, 20 mmol), aqueous ammoniacal (56 mL), and ethanol (160 mL) afforded ((4-(cyanomethyl)phenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-(Trimethylsilyl)phenyl)ethynyl)copper. The reaction of 4-(trimethylsilyl)phenylacetylene (1.201 g, 7 mmol), cuprous iodide (1.342 g, 7 mmol), aqueous ammoniacal (20 mL), and ethanol (56 mL) afforded ((4-(trimethylsilyl)phenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-(Dimethylcarbamoyl)phenyl)ethynyl)copper. The reaction of 4-(dimethylcarbamoyl)phenylacetylene (1.735 g, 10 mmol), cuprous iodide (1.921 g, 10 mmol), aqueous ammoniacal (28 mL), and ethanol (80 mL) afforded ((4-(dimethylcarbamoyl)phenyl)ethynyl) copper as a dark green solid. The crude product was used without further purification.

((4-(Methylsulfonyl)phenyl)ethynyl)copper. The reaction of 4-(methylsulfonyl)phenylacetylene (1.069 g, 6 mmol), cuprous iodide (1.151 g, 6 mmol), aqueous ammoniacal (17 mL), and ethanol (48 mL) afforded ((4-(methylsulfonyl)phenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

((4-Acetylphenyl)ethynyl)copper. The reaction of 4-acetylphenylacetylene (871 mg, 6 mmol), cuprous iodide (1.159 g, 6 mmol), aqueous ammoniacal (17 mL), and ethanol (48 mL) afforded ((4-acetylphenyl)ethynyl)copper as a bright canary yellow solid. The crude product was used without further purification.

Typical Procedure III for the Synthesis of 2-((4-(Trifluoromethoxy)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (1b) and Its Derivatives. *2-((4-(Trifluoromethoxy)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1b**).* To a 120 mL of dry Pyrex sealed tube was added 2,2′-diiodo-1,1′-biphenyl (1.223 g, 3.0 mmol), ((4-(trifluoromethoxy)-phenyl)ethynyl)copper (0.830 g, 3.3 mmol), triethylamine (7.5 mL), and butyl acetate (15 mL). The mixture was stirred in an oil bath at 140 °C for 36 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1b** as an oil (0.488 g, 35%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.0, 1.2 Hz, 1 H), 7.65−7.58 (m, 1 H), 7.45−7.37 (m, 3 H), 7.36−7.32 (m, 1 H), 7.29−7.26 (m, 1 H), 7.18−7.13 (m, 2 H), 7.12−7.05 (m, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.70, 148.68, 146.9, 145.7, 138.8, 132.8, 131.6, 130.3, 129.5, 129.0, 128.3, 127.9, 127.7, 124.2 (C-F, $J_{C\text{-}F}$ = 256.1 Hz), 122.4, 122.0, 121.6 (C-F, $J_{C\text{-}F}$ = 256.1 Hz), 120.7, 119.1 (C-F, $J_{C\text{-}F}$ = 256.1 Hz), 116.5 (C-F, $J_{C\text{-}F}$ = 256.1 Hz), 99.4, 91.6, 89.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.8; IR (neat) 1581, 1508, 1460, 1440, 1430 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{21}H_{13}F_3IO$: 464.9958, found: 464.9962.

The Following Compounds Were Prepared According to Typical Procedure III. *2-((4-(Acetylamino)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1c**).* The reaction of ((4-(acetylamino)phenyl)-ethynyl)copper (0.745 g, 3.3 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.223 g, 3.0 mmol) in pyridine (20 mL) was stirred in an oil bath at 130 °C for 48 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 2:1) afforded **1c** as an oil (0.566 g, 43%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.0, 0.8 Hz, 1 H), 7.61−7.57 (m, 1 H), 7.44−7.32 (m, 6 H), 7.28−7.24 (m, 1 H), 7.12−7.05 (m, 3 H), 2.15 (s, 3 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.2, 146.7, 145.8, 138.8, 137.7, 132.1, 131.5, 130.3, 129.4, 129.0, 127.9, 127.8, 127.7, 122.8, 119.2, 118.9, 99.5, 92.8, 88.1, 24.7; IR (neat) 1668, 1592, 1530, 1514, 1460, 1447, 1404 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{22}H_{17}INO$: 438.0349, found: 438.0348.

*2-((4-(tert-Butyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1e**).* The reaction of ((4-(*tert*-butyl)phenyl)ethynyl)copper (0.985 g, 4.4 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.627 g, 4.0 mmol) in triethylamine (10 mL) and butyl acetate (20 mL) was stirred in an oil bath at 140 °C for 48 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1e** as an oil (0.729 g, 42%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1 H), 7.64−7.58 (m, 1 H), 7.44−7.32 (m, 4 H), 7.28−7.23 (m, 3 H), 7.11−7.05 (m, 3 H), 1.27 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.3, 146.8, 145.9, 138.8, 131.6, 131.1, 130.4, 129.4, 128.9, 127.8, 127.7, 125.2, 123.1, 120.2, 99.5, 93.3, 87.8, 34.7, 31.1; IR (neat) 1516, 1460, 1442, 1430, 1365 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{24}H_{22}I$: 437.0761, found: 437.0762.

*2-((4-(Hydroxymethyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1f**).* The reaction of ((4-(hydroxymethyl)phenyl)ethynyl)copper (0.641 g, 3.3 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.220 g, 3.0 mmol) in triethylamine (7.5 mL) and butyl acetate (15 mL) was stirred in an oil bath at 140 °C for 60 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 5:1) afforded **1f** as an oil (0.357 g, 29%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.0, 0.8 Hz, 1 H), 7.65−7.59 (m, 1 H), 7.45−7.33 (m, 4 H), 7.30−7.26 (m, 1 H), 7.25−7.21 (m, 2 H), 7.16−7.12 (m, 2 H), 7.11−7.06 (m, 1 H), 4.64 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.8, 145.8, 140.8, 138.8, 131.6, 131.5, 130.3, 129.4, 129.0, 128.0, 127.8, 127.7, 126.7, 122.7, 122.5, 99.5, 92.9, 88.5, 64.9; IR (neat) 3355, 1582, 1556, 1511, 1460, 1438, 1427, 1413 cm^{-1}; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{21}H_{15}INaO$: 433.0060, found: 433.0063.

*2-((4-(Cyanomethyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1g**).* The reaction of ((4-(cyanomethyl)phenyl)ethynyl)copper (0.905 g, 4.4 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.626 g, 4.0 mmol) in triethylamine (10 mL) and butyl acetate (20 mL) was stirred in an oil bath at 140 °C for 64 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 5:1) afforded **1g** as a solid (0.561 g, 33%); mp 99.7−99.9 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 1 H), 7.62 (d, J = 6.8 Hz, 1 H), 7.46−7.37 (m, 3 H), 7.35 (d, J = 7.6 Hz, 1 H), 7.28 (d, J = 7.2 Hz, 1 H), 7.20 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 7.09 (t, J = 7.6 Hz, 1 H), 3.70 (s, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.9, 145.8, 138.8, 132.0, 131.7, 130.3, 129.6, 129.5, 129.0, 128.3, 127.85, 127.78, 127.7, 123.3, 122.5, 117.4, 99.4, 92.1, 89.3, 23.5; IR (neat) 1511, 1460, 1442, 1414 cm^{-1}; HRMS (ESI) m/z: [M + NH_4]$^+$ calcd for $C_{22}H_{18}IN_2$: 437.0509, found: 437.0511.

*2-((4-(Trimethylsilyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1h**).* The reaction of ((4-(trimethylsilyl)phenyl)ethynyl)copper (0.780 g, 3.3 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.219 g, 3.0 mmol) in triethylamine (7.5 mL) and butyl acetate (15 mL) was stirred in an oil bath at 140 °C for 36 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether) afforded **1h** as an oil (0.652 g, 48%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 8.0, 1.2 Hz, 1 H), 7.65−7.59 (m, 1 H), 7.44−7.33 (m, 6 H), 7.29−7.25 (m, 1 H), 7.14−7.05 (m, 3 H), 0.23 (s, 9 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.9, 145.8, 140.8, 138.8, 133.0, 131.6, 130.4, 130.3, 129.4, 128.9, 128.0, 127.8, 127.7, 123.5, 122.8, 99.5, 93.3, 88.8, −1.3; IR

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(neat) 1602, 1505, 1459, 1443, 1429, 1392 cm^{-1}; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{21}INaSi$: 475.0349, found: 475.0347.

*2-((4-(Dimethylcarbamoyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1l**).* The reaction of ((4-(dimethylcarbamoyl)phenyl)ethynyl)copper (0.781 g, 3.3 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.219 g, 3.0 mmol) in triethylamine (7.5 mL) and butyl acetate (15 mL) was stirred in an oil bath at 140 °C for 42 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 2:1) afforded **1l** as an oil (0.627 g, 46%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J = 8.0, 0.8 Hz, 1 H), 7.66−7.59 (m, 1 H), 7.45−7.33 (m, 4 H), 7.31−7.26 (m, 3 H), 7.19−7.14 (m, 2 H), 7.12−7.06 (m, 1 H), 3.08 (s, 3 H), 2.93 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 146.9, 145.7, 138.8, 135.6, 131.7, 131.2, 130.3, 129.4, 129.0, 128.3, 127.8, 127.7, 127.0, 124.5, 122.4, 99.4, 92.3, 89.7, 39.5, 35.3; IR (neat) 1633, 1609, 1561, 1493, 1462, 1442, 1393 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}INO$: 452.0506, found: 452.0517.

*2-((4-(Methylsulfonyl)phenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1m**).* The reaction of ((4-(methylsulfonyl)phenyl)ethynyl)copper (0.796 g, 3.3 mmol) and 2,2′-diiodo-1,1′-biphenyl (1.217 g, 3.0 mmol) in triethylamine (7.5 mL) and butyl acetate (15 mL) was stirred in an oil bath at 140 °C for 60 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 5:1) afforded **1m** as a solid (0.466 g, 35%); mp 169.9−170.1 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 8.0, 1.2 Hz, 1 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.67−7.62 (m, 1 H), 7.50−7.40 (m, 3 H), 7.36−7.26 (m, 4 H), 7.14−7.08 (m, 1 H), 3.02 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.3, 145.5, 139.3, 138.8, 131.9, 131.8, 130.3, 129.5, 129.2, 129.1, 128.9, 127.9, 127.8, 127.2, 121.8, 99.3, 92.5, 91.2, 44.4; IR (neat) 1592, 1499, 1462, 1439 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{16}IO_2S$: 458.9910, found: 458.9904.

*2-((4-Acetylphenyl)ethynyl)-2′-iodo-1,1′-biphenyl (**1n**).* The reaction of ((4-acetylphenyl)ethynyl)copper (0.468 g, 2.2 mmol) and 2,2′-diiodo-1,1′-biphenyl (0.819 g, 2.0 mmol) in pyridine (10 mL) was stirred in an oil bath at 115 °C for 60 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 20:1) afforded **1n** as a solid (0.228 g, 27%); mp 117.5−117.8 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 1 H), 7.82 (d, J = 7.6 Hz, 2 H), 7.64 (d, J = 6.8 Hz, 1 H), 7.48−7.38 (m, 3 H), 7.35 (d, J = 7.6 Hz, 1 H), 7.29 (d, J = 7.2 Hz, 1 H), 7.21 (d, J = 8.0 Hz, 2 H), 7.10 (t, J = 7.6 Hz, 1 H), 2.56 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.2, 147.1, 145.6, 138.9, 136.0, 131.8, 131.4, 130.3, 129.5, 129.1, 128.6, 128.1, 127.9, 127.7, 122.2, 99.4, 92.2, 91.8, 26.5; IR (neat) 1682, 1600, 1558, 1459, 1427, 1402 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{16}IO$: 423.0240, found: 423.0247.

*2-((4-(Cyanomethyl)phenyl)ethynyl)-2′-iodo-5,5′-dimethoxy-1,1′-biphenyl (**1s**).* The reaction of ((4-(cyanomethyl)phenyl)-ethynyl)copper (0.681 g, 3.3 mmol) and 2,2′-diiodo-5,5′-dimethoxy-1,1′-biphenyl (1.399 g, 3.0 mmol) in triethylamine (7.5 mL) and butyl acetate (15 mL) was stirred in an oil bath at 140 °C for 72 h under an argon atmosphere. The solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 5:1) afforded **1s** as a solid (0.455 g, 32%); mp 177.1−177.2 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.4 Hz, 1 H), 7.54 (d, J = 8.8 Hz, 1 H), 7.22−7.14 (m, 4 H), 6.96−6.90 (m, 2 H), 6.81 (d, J = 2.4 Hz, 1 H), 6.70 (dd, J = 8.8, 3.2 Hz, 1 H), 3.86 (s, 3 H), 3.79 (s, 3 H), 3.70 (s, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.5, 159.4, 148.2, 146.4, 139.4, 133.1, 131.8, 129.2, 127.8, 123.6, 117.4, 115.9, 115.7, 115.0, 114.7, 113.8, 90.7, 89.4, 87.7, 55.5, 55.4, 23.5; IR (neat) 1601, 1561, 1513, 1464, 1415 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{19}INO_2$: 480.0455, found: 480.0449.

Typical Procedure IV for the Photoreactions. *9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-methoxyphenyl)methanone) (**3a**).* **1a** (41 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) were added subsequently into a 120 mL dry Pyrex sealed tube. The reaction mixture was degassed with three freeze-pump-thaw cycles (15 min per cycle). Then, the reaction mixture was irradiated by PLED at rt under an argon atmosphere. The reaction was completed after 48 h as monitored by TLC (eluent: petroleum ether:ethyl acetate = 20:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 10:1) to afford **3a** as a solid (25 mg, 84%); mp 219.6−220.1 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 2 H), 7.46 (d, J = 7.6 Hz, 2 H), 7.35 (t, J = 7.4 Hz, 2 H), 7.28−7.21 (m, 4 H), 7.06−6.97 (m, 6 H), 6.56 (t, J = 7.6 Hz, 2 H), 6.46 (d, J = 8.0 Hz, 4 H), 5.92 (d, J = 7.6 Hz, 2 H), 3.64 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.6, 161.7, 147.4, 143.2, 142.7, 141.1, 131.05, 130.95, 130.6, 128.3, 127.8, 126.7, 126.4, 125.6, 119.3, 118.6, 112.6, 73.8, 55.1; IR (neat) 1667, 1601, 1574, 1510, 1448 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{42}H_{31}O_4$: 599.2217, found: 599.2222. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC: 2004217; see Supporting Information.

The Following Compounds Were Prepared According to Typical Procedure IV. *9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(trifluoromethoxy)phenyl)methanone) (**3b**).* The reaction of **1b** (46 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3b** as a solid (32 mg, 91%); mp 197.3−198.1 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 2 H), 7.50 (d, J = 7.6 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 2 H), 7.32−7.22 (m, 4 H), 7.12−7.00 (m, 6 H), 6.81 (d, J = 8.0 Hz, 4 H), 6.59 (t, J = 7.4 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.4, 150.9, 146.1, 143.2, 141.6, 141.1, 136.8, 130.7, 130.0, 128.8, 128.3, 126.9, 126.3, 126.0, 124.0 (C-F, $J_{C\text{-}F}$ = 256.7 Hz), 121.4 (C-F, $J_{C\text{-}F}$ = 256.7 Hz), 119.6, 119.3, 118.9, 116.3 (C-F, $J_{C\text{-}F}$ = 256.7 Hz), 73.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −57.7; IR (neat) 1676, 1601, 1502, 1476, 1447 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{42}H_{25}F_6O_4$: 707.1652, found: 707.1657.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(acetylamino)phenyl)-methanone) (**3c**).* The reaction of **1c** (44 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3c** as a solid (22 mg, 67%); mp 238.3−238.6 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6) δ 9.97 (s, 2 H), 8.02 (d, J = 8.0 Hz, 2 H), 7.69 (d, J = 7.6 Hz, 2 H), 7.52−7.39 (m, 4 H), 7.30 (t, J = 7.6 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 4 H), 7.08 (t, J = 7.6 Hz, 2 H), 6.83 (d, J = 8.4 Hz, 4 H), 6.58 (t, J = 7.6 Hz, 2 H), 5.80 (d, J = 7.6 Hz, 2 H), 1.96 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 202.6, 173.1, 150.8, 147.3, 146.4, 146.3, 145.4, 136.8, 134.6, 133.3, 133.2, 132.7, 131.1, 130.1, 130.0, 124.5, 123.9, 121.7, 77.5, 28.5; IR (neat) 1666, 1593, 1523, 1445, 1403, 1370 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{44}H_{33}N_2O_4$: 653.2435, found: 653.2424.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis(p-tolylmethanone) (**3d**).* The reaction of **1d** (40 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3d** as a solid (26 mg, 90%); mp 231.5−231.8 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 7.6 Hz, 2 H), 7.36 (t, J = 7.4 Hz, 2 H), 7.29−7.20 (m, 4 H), 7.03 (t, J = 7.4 Hz, 2 H), 6.92 (d, J = 7.6 Hz, 4 H), 6.77 (d, J = 7.6 Hz, 4 H), 6.56 (t, J = 7.4 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H), 2.15 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 146.9, 143.3, 142.4, 141.3, 141.2, 135.9, 130.9, 128.3, 128.1, 127.8, 126.6, 126.4, 125.7, 119.3, 118.6, 73.8, 21.3; IR (neat) 1735, 1671, 1607, 1448 cm^{-1}; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{42}H_{31}O_2$: 567.2319, found: 567.2325.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(tert-butyl)phenyl)-methanone) (**3e**).* The reaction of **1e** (44 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3e** as a solid (29 mg, 88%); mp 200.1−200.5 °C (petroleum

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ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 2 H), 7.48 (d, J = 7.2 Hz, 2 H), 7.36 (t, J = 7.2 Hz, 2 H), 7.29−7.20 (m, 4 H), 7.07−6.94 (m, 10 H), 6.56 (t, J = 7.4 Hz, 2 H), 5.92 (d, J = 8.0 Hz, 2 H), 1.14 (s, 18 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.8, 154.3, 147.0, 143.2, 142.5, 141.2, 135.7, 131.0, 128.3, 127.8, 126.6, 126.5, 125.6, 124.3, 119.2, 118.5, 73.8, 34.7, 30.9; IR (neat) 1671, 1605, 1448 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{48}H_{43}O_2$: 651.3258, found: 651.3244.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(hydroxymethyl)phenyl)-methanone) (**3f**).* The reaction of **1f** (41 mg, 0.1 mmol), 4-methoxythioxanthone (3 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3f** as a solid (20 mg, 67%); mp 185.3−186.0 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 7.2 Hz, 2 H), 7.36 (t, J = 7.2 Hz, 2 H), 7.29−7.18 (m, 4 H), 7.07−6.92 (m, 10 H), 6.56 (t, J = 7.4 Hz, 2 H), 5.91 (d, J = 8.0 Hz, 2 H), 4.49 (s, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.4, 146.5, 143.7, 143.2, 142.1, 141.2, 137.9, 130.8, 128.5, 128.4, 128.0, 126.7, 126.4, 125.8, 125.6, 119.4, 118.7, 73.7, 64.6; IR (neat) 3397, 1667, 1610, 1572, 1476, 1450, 1413 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{42}H_{31}O_4$: 599.2217, found: 599.2218.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(cyanomethyl)phenyl)-methanone) (**3g**).* The reaction of **1g** (43 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3g** as a solid (27 mg, 85%); mp 203.5−204.0 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2 H), 7.50 (d, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 2 H), 7.31−7.22 (m, 4 H), 7.09−6.99 (m, 6 H), 6.97−6.93 (m, 4 H), 6.59 (t, J = 7.4 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H), 3.57 (s, 4 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.1, 146.1, 143.2, 141.7, 141.2, 138.4, 132.5, 130.7, 128.8, 128.7, 128.2, 127.0, 126.8, 126.3, 125.9, 119.6, 118.8, 117.1, 73.6, 23.3; IR (neat) 1677, 1607, 1448, 1417 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{44}H_{29}N_2O_2$: 617.2224, found: 617.2249.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(trimethylsilyl)phenyl)-methanone) (**3h**).* The reaction of **1h** (46 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3h** as a solid (29 mg, 84%); mp 189.4−190.1 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2 H), 7.49 (d, J = 7.6 Hz, 2 H), 7.37 (t, J = 7.4 Hz, 2 H), 7.29−7.20 (m, 4 H), 7.16−7.09 (m, 4 H), 7.07−6.95 (m, 6 H), 6.56 (t, J = 7.6 Hz, 2 H), 5.91 (d, J = 8.0 Hz, 2 H), 0.11 (s, 18 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.6, 146.6, 144.3, 143.2, 142.2, 141.2, 138.7, 132.4, 130.8, 128.4, 127.9, 127.1, 126.7, 126.4, 125.7, 119.3, 118.6, 73.8, −1.4; IR (neat) 1673, 1594, 1446, 1384 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{46}H_{43}O_2Si_2$: 683.2796, found: 683.2794.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis(phenylmethanone) (**3i**).* The reaction of **1i** (38 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3i** as a solid (25 mg, 93%); mp 172.0−172.5 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2 H), 7.48 (d, J = 7.2 Hz, 2 H), 7.36 (t, J = 7.4 Hz, 2 H), 7.29−7.20 (m, 4 H), 7.16 (t, J = 7.0 Hz, 2 H), 7.07−6.94 (m, 10 H), 6.57 (t, J = 7.4 Hz, 2 H), 5.93 (d, J = 7.6 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.0, 146.5, 143.3, 142.1, 141.3, 138.9, 130.8, 128.5, 128.0, 127.4, 126.7, 126.4, 125.8, 119.4, 118.7, 73.8; IR (neat) 1675, 1599, 1580, 1448 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{27}O_2$: 539.2006, found: 539.2007.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-chlorophenyl)-methanone) (**3j**).* The reaction of **1j** (41 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3j** as a solid (28 mg, 92%); mp 227.4−227.7 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 2 H), 7.49 (d, J = 7.2 Hz, 2 H), 7.39 (t, J = 7.2 Hz, 2 H), 7.30−7.22 (m, 4 H), 7.05 (t, J = 7.4 Hz, 2 H), 6.99−6.90 (m, 8 H), 6.58 (t, J = 7.4 Hz, 2 H), 5.90 (d, J = 7.6 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.6, 146.2, 143.2, 141.7, 141.2, 137.2, 136.9, 130.7, 129.5, 128.7, 128.2, 127.8, 126.9, 126.3, 125.9, 119.6, 118.8, 73.6; IR (neat) 1680, 1590, 1485, 1451 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{25}Cl_2O_2$: 607.1226, found: 607.1217.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-fluorophenyl)-methanone) (**3k**).* The reaction of **1k** (40 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3k** as a solid (27 mg, 94%); mp 202.7−202.8 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2 H), 7.48 (d, J = 7.6 Hz, 2 H), 7.38 (t, J = 7.4 Hz, 2 H), 7.30−7.22 (m, 4 H), 7.08−6.99 (m, 6 H), 6.65 (t, J = 8.2 Hz, 4 H), 6.58 (t, J = 7.6 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.3, 165.4, 162.9, 146.5, 143.2, 141.9, 141.1, 134.8, 130.8, 130.7, 130.6, 128.6, 128.1, 126.8, 126.3, 125.9, 119.6, 118.8, 114.6, 114.4, 73.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −107.9; IR (neat) 1676, 1601, 1507, 1447 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{40}H_{25}F_2O_2$: 575.1817, found: 575.1810.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(dimethylcarbamoyl)-phenyl)methanone) (**3l**).* The reaction of **1l** (45 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3l** as a solid (30 mg, 88%); mp 180.1−180.7 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.6 Hz, 2 H), 7.49 (d, J = 7.6 Hz, 2 H), 7.37 (t, J = 7.4 Hz, 2 H), 7.31−7.20 (m, 4 H), 7.10−6.99 (m, 10 H), 6.58 (t, J = 7.4 Hz, 2 H), 5.90 (d, J = 8.0 Hz, 2 H), 3.00 (s, 6 H), 2.76 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.5, 170.6, 145.8, 143.2, 141.6, 141.2, 139.7, 138.3, 130.6, 128.7, 128.1, 128.0, 126.8, 126.3, 126.2, 125.9, 119.5, 118.8, 73.6, 39.2, 35.2; IR (neat) 1673, 1633, 1510, 1490, 1447, 1397 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{46}H_{37}N_2O_4$: 681.2748, found: 681.2734.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-(methylsulfonyl)phenyl)-methanone) (**3m**).* The reaction of **1m** (46 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3m** as a solid (22 mg, 63%); mp 247.7−248.2 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.6 Hz, 2 H), 7.58 (d, J = 8.8 Hz, 4 H), 7.53 (d, J = 7.6 Hz, 2 H), 7.42 (t, J = 7.4 Hz, 2 H), 7.34−7.26 (m, 4 H), 7.15 (d, J = 8.4 Hz, 4 H), 7.09 (t, J = 7.4 Hz, 2 H), 6.62 (t, J = 7.4 Hz, 2 H), 5.90 (d, J = 8.0 Hz, 2 H), 2.90 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.2, 145.0, 143.4, 143.3, 142.0, 141.2, 140.8, 130.4, 129.3, 128.6, 127.1, 126.7, 126.26, 126.24, 119.9, 119.1, 73.5. 44.2; IR (neat) 1679, 1481, 1447, 1393 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{42}H_{31}O_6S_2$: 695.1557, found: 695.1547.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-acetylphenyl)-methanone) (**3n**).* The reaction of **1n** (42 mg, 0.1 mmol), 4-methoxythioxanthone (3 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) was completed after 72 h to afford **3n** as a solid (15 mg, 48%); mp 239.3−240.1 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.6 Hz, 2 H), 7.60−7.54 (m, 4 H), 7.51 (d, J = 7.6 Hz, 2 H), 7.39 (t, J = 7.4 Hz, 2 H), 7.32−7.22 (m, 4 H), 7.10−7.03 (m, 6 H), 6.60 (t, J = 7.4 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H), 2.45 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.8, 197.4, 145.5, 143.3, 142.7, 141.31, 141.28, 138.2, 130.5, 128.9, 128.3, 128.0, 127.5, 126.9, 126.3, 126.0, 119.7, 118.9, 73.6, 26.6; IR (neat) 1687, 1604, 1445, 1400, 1356 cm^{-1}; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{44}H_{30}NaO_4$: 645.2036, found: 645.2025.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-methoxycarbonylphenyl)methanone) (**3o**).* The reaction of **1o** (44 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) was completed after 120 h to afford **3o** as a solid (19 mg, 58%); mp 222.3−222.9 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2 H), 7.65 (d, J = 8.0 Hz, 4 H), 7.50 (d, J = 7.6 Hz, 2 H), 7.38 (t, J = 7.2 Hz, 2 H), 7.31−7.20 (m, 4 H), 7.09−7.01 (m, 6 H), 6.59 (t, J = 7.6 Hz, 2 H), 5.91 (d, J = 7.6 Hz, 2 H), 3.80 (s, 6 H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.0,

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166.3, 145.6, 143.3, 142.8, 141.3, 131.7, 130.6, 128.9, 128.8, 128.3, 127.7, 126.9, 126.3, 126.0, 119.6, 118.9, 73.6, 52.1; IR (neat) 1729, 1679, 1450, 1437 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{44}H_{31}O_6$: 655.2115, found: 655.2111.

*9H,9′H-[9,9′-Bifluorene]-9,9′-diylbis((4-cyanophenyl)-methanone) (**3p**).* The reaction of **1p** (41 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) was carried out in an oil bath at 60 °C to afford **3p** as a solid (23 mg, 77%); mp 206.2−206.8 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.6 Hz, 2 H), 7.52 (d, J = 7.2 Hz, 2 H), 7.42 (t, J = 7.2 Hz, 2 H), 7.33−7.23 (m, 8 H), 7.12−7.02 (m, 6 H), 6.61 (t, J = 7.2 Hz, 2 H), 5.89 (d, J = 7.6 Hz, 2 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 145.1, 143.3, 142.4, 141.2, 140.8, 131.4, 130.4, 129.2, 128.6, 128.2, 127.1, 126.2, 119.9, 119.1, 118.0, 114.3, 73.4; IR (neat) 1684, 1607, 1474, 1450, 1400 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{42}H_{25}N_2O_2$: 589.1911, found: 589.1900.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis((4-methoxyphenyl)methanone) (**3q**).* The reaction of **1q** (47 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3q** as a solid (33 mg, 92%); mp 219.2−219.7 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2 H), 7.01 (d, J = 8.8 Hz, 4 H), 6.97 (d, J = 2.0 Hz, 2 H), 6.80−6.74 (m, 4 H), 6.47 (d, J = 8.4 Hz, 4 H), 6.17 (dd, J = 8.4, 2.0 Hz, 2 H), 5.88 (d, J = 8.4 Hz, 2 H), 3.88 (s, 6 H), 3.71 (s, 6 H), 3.66 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.3, 161.5, 160.0, 159.6, 144.5, 142.5, 140.9, 136.0, 131.7, 131.3, 130.5, 127.2, 112.63, 112.58, 112.0, 104.5, 103.9, 72.7, 55.5, 55.3, 55.1; IR (neat) 1601, 1578, 1512, 1495, 1466, 1431 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{46}H_{39}O_8$: 719.2639, found: 719.2632.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis(p-tolylmethanone) (**3r**).* The reaction of **1r** (46 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3r** as a solid (32 mg, 93%); mp 228.8−229.4 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2 H), 6.97 (d, J = 2.0 Hz, 2 H), 6.91 (d, J = 8.0 Hz, 4 H), 6.81−6.74 (m, 8 H), 6.17 (dd, J = 8.8, 2.0 Hz, 2 H), 5.88 (d, J = 8.8 Hz, 2 H), 3.88 (s, 6 H), 3.71 (s, 6 H), 2.16 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.8, 160.0, 159.7, 144.5, 142.6, 141.0, 140.4, 136.2, 135.7, 131.6, 128.2, 128.1, 127.2, 112.6, 112.1, 104.4, 103.9, 72.7, 55.5, 55.2, 21.3; IR (neat) 1669, 1609, 1578, 1495, 1468, 1435 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{46}H_{39}O_6$: 687.2741, found: 687.2745.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis((4-(cyanomethyl)phenyl)methanone) (**3s**).* The reaction of **1s** (48 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3s** as a solid (30 mg, 81%); mp 132.9−133.6 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2 H), 7.06−6.93 (m, 10 H), 6.83−6.74 (m, 4 H), 6.20 (d, J = 8.4 Hz, 2 H), 5.88 (d, J = 8.4 Hz, 2 H), 3.89 (s, 6 H), 3.72 (s, 6 H), 3.58 (s, 4 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.7, 160.2, 159.8, 144.6, 142.7, 139.5, 138.7, 134.9, 132.2, 131.3, 128.7, 127.1, 127.0, 117.2, 112.8, 112.4, 104.6, 104.0, 72.5, 55.5, 55.2, 23.3; IR (neat) 1673, 1611, 1580, 1493, 1469, 1432 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{48}H_{37}N_2O_6$: 737.2646, found: 737.2631.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis-(phenylmethanone) (**3t**).* The reaction of **1t** (44 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3t** as a solid (29 mg, 88%); mp 191.5−191.7 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2 H), 7.19−7.11 (m, 2 H), 7.03−6.93 (m, 10 H), 6.82−6.73 (m, 4 H), 6.19 (d, J = 8.4 Hz, 2 H), 5.90 (d, J = 8.8 Hz, 2 H), 3.88 (s, 6 H), 3.71 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.6, 160.1, 159.7, 144.5, 142.7, 139.9, 139.2, 135.4, 131.5, 130.6, 127.9, 127.4, 127.2, 112.6, 112.2, 104.5, 103.9, 72.6, 55.5, 55.2; IR (neat) 1671, 1609, 1578, 1495, 1466 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{44}H_{35}O_6$: 659.2428, found: 659.2424.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis((4-chlorophenyl)methanone) (**3u**).* The reaction of **1u** (48 mg, 0.1 mmol), 4-methoxythioxanthone (3 mg, 0.01 mmol), TEMPO (33 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3u** as a solid (33 mg, 90%); mp 230.4−230.7 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2 H), 7.00−6.89 (m, 10 H), 6.81−6.75 (m, 4 H), 6.19 (d, J = 8.4 Hz, 2 H), 5.87 (d, J = 8.4 Hz, 2 H), 3.89 (s, 6 H), 3.71 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.3, 160.2, 159.9, 144.5, 142.6, 139.5, 137.2, 136.9, 134.9, 131.4, 129.4, 127.8, 127.1, 112.8, 112.3, 104.7, 104.1, 72.5, 55.5, 55.3; IR (neat) 1675, 1611, 1580, 1495, 1468, 1433 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{44}H_{33}Cl_2O_6$: 727.1649, found: 727.1627.

*(3,3′,6,6′-Tetramethoxy-9H,9′H-[9,9′-bifluorene]-9,9′-diyl)bis((4-fluorophenyl)methanone) (**3v**).* The reaction of **1v** (46 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) afforded **3v** as a solid (31 mg, 89%); mp 220.8−221.0 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2 H), 7.04−6.96 (m, 6 H), 6.82−6.75 (m, 4 H), 6.66 (t, J = 8.6 Hz, 4 H), 6.19 (d, J = 8.4 Hz, 2 H), 5.88 (d, J = 8.8 Hz, 2 H), 3.89 (s, 6 H), 3.71 (s, 6 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.9, 165.2, 162.7, 160.2, 159.8, 144.5, 142.6, 139.9, 135.14, 135.06, 131.4, 130.6, 130.5, 127.1, 114.6, 114.4, 112.7, 112.3, 104.6, 104.0, 72.6, 55.5, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −108.5; IR (neat) 1671, 1599, 1578, 1495, 1468, 1435 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{44}H_{33}F_2O_6$: 695.2240, found: 695.2228.

Gram-Scale Synthesis of 9*H*,9′*H*-[9,9′-Bifluorene]-9,9′-diylbis((4-methoxyphenyl)methanone) (3a). **1a** (1.028 g, 2.5 mmol), 4-methoxythioxanthone (61 mg, 0.25 mmol), TEMPO (784 mg, 5 mmol), anhydrous acetone (625 mL), and anhydrous DCM (625 mL) were added subsequently into a 2 L dry Pyrex flask. The reaction mixture was bubbled with argon for 30 min. Then, the reaction mixture was irradiated by PLED at rt under an argon atmosphere. The reaction was completed after 48 h as monitored by TLC (eluent: petroleum ether:ethyl acetate = 20:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 10:1) to afford **3a** as a solid (0.622 g, 83%).

Synthesis of Ethyl Phenyl Sulfoxide (6). **5** (69 mg, 0.5 mmol), **3d** (12 mg, 0.025 mmol), and CH_3CN (5 mL) were added subsequently into a 25 mL dry Pyrex flask. The reaction mixture was irradiated by 365−375 nm UV light at rt under an air atmosphere. The reaction was completed after 16 h as monitored by TLC (eluent: petroleum ether:ethyl acetate = 2:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 1:1) to afford **6**[22] as an oil (54 mg, 70%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66−7.57 (m, 2 H), 7.56−7.46 (m, 3 H), 2.97−2.71 (dm, 2 H), 1.20 (t, J = 7.4 Hz, 3 H).

Detection of the Fragment Tetramethylpiperidine. Aryl iodide **1a** (41 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) were added subsequently into a 120 mL dry Pyrex sealed tube. The reaction mixture was degassed with three freeze-pump-thaw cycles (15 min per cycle). Then, the reaction mixture was irradiated by PLED for 48 h at rt under an argon atmosphere. The fragment tetramethylpiperidine was detected by HRMS analysis of the crude reaction mixture (see Figure S3 in Supporting Information). HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_{20}N$: 142.1590, found: 142.1595.

Oxygen Labeling Experiment. Aryl iodide **1a** (41 mg, 0.1 mmol), 4-methoxythioxanthone (2 mg, 0.01 mmol), TEMPO (32 mg, 0.2 mmol), $H_2{}^{18}O$ (36 μL, 2 mmol), and anhydrous DCM (50 mL) were added subsequently into a 120 mL dry Pyrex sealed tube. The reaction mixture was degassed with three freeze-pump-thaw cycles (15 min per cycle). Then, the reaction mixture was irradiated by PLED at rt under an argon atmosphere. The reaction was completed after 48 h as monitored by TLC (eluent: petroleum ether:ethyl

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acetate = 20:1). The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 10:1) to afford **3a** as a solid (24 mg, 80%). HRMS analysis indicated that no ^{18}O atom was transferred into the product **3a**.

Crossover Experiment. **1a** (41 mg, 0.1 mmol), **1d** (39 mg, 0.1 mmol), 4-methoxythioxanthone (5 mg, 0.02 mmol), TEMPO (64 mg, 0.4 mmol), anhydrous acetone (25 mL), and anhydrous DCM (25 mL) were added subsequently into a 120 mL dry Pyrex sealed tube. The reaction mixture was degassed with three freeze-pump-thaw cycles (15 min per cycle). Then, the reaction mixture was irradiated by PLED at rt under an argon atmosphere. The reaction was completed after 48 h as monitored by TLC (eluent: petroleum ether:ethyl acetate = 5:1). The ratio of **3a**:**3ad**:**3d** was determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 (0.1 mmol) as internal standard. The solvent was removed, and the residue was purified by flash chromatography on silica gel (eluent: petroleum ether:ethyl acetate = 10:1) to afford (9′-(4-methoxybenzoyl)-9*H*,9′*H*-[9,9′-bifluoren]-9-yl)(*p*-tolyl)methanone **3ad** as a solid (21 mg, 36%); mp 225.7−226.5 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1 H), 8.07 (d, J = 8.0 Hz, 1 H), 7.49−7.43 (m, 2 H), 7.39−7.30 (m, 2 H), 7.29−7.16 (m, 4 H), 7.07−6.97 (m, 4 H), 6.91 (d, J = 8.0 Hz, 2 H), 6.77 (d, J = 8.0 Hz, 2 H), 6.59 (t, J = 7.4 Hz, 1 H), 6.52 (t, J = 7.4 Hz, 1 H), 6.45 (d, J = 8.8 Hz, 2 H), 5.98 (d, J = 7.6 Hz, 1 H), 5.85 (d, J = 7.6 Hz, 1 H), 3.62 (s, 3 H), 2.15 (s, 3 H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.4, 198.3, 161.9, 147.3, 147.0, 143.3, 143.1, 142.9, 142.1, 141.2, 141.1, 141.0, 136.5, 131.1, 130.84, 130.79, 130.4, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 126.7, 126.6, 126.4, 125.7, 125.6, 119.31, 119.27, 118.6, 112.7, 74.5, 73.1, 55.1, 21.3; IR (neat) 1667, 1600, 1573, 1508, 1473, 1446 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{42}H_{31}O_3$: 583.2268, found: 583.2278.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02781.

Figures S1−S5, Tables S1−S2, copies of NMR spectra data of all compounds, and crystal information for compound **3a** (PDF)

Accession Codes

CCDC 2004217 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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