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ICl-Mediated Intramolecular Twofold Iodoarylation of Diynes and Diynyl Diethers and Amines: Synthesis of Bis(2*H*-hydronaphthalene and chromene) and 2*H*-Quinoline Bearing an Alkenyl Iodide Moiety

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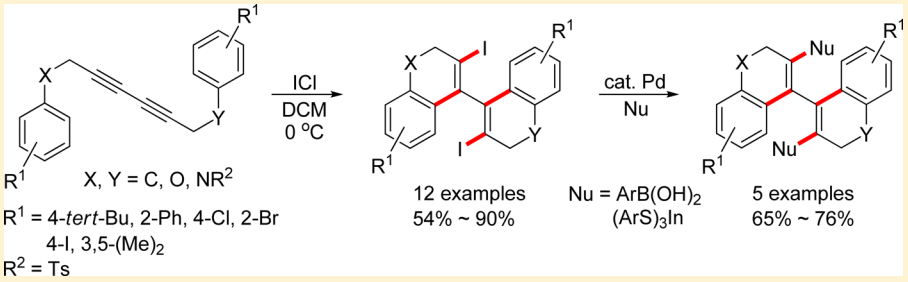
Supporting Information



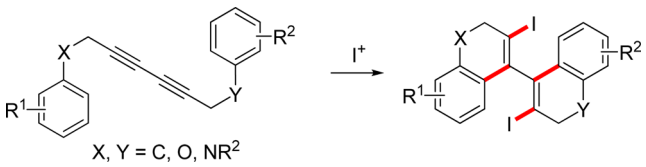
ABSTRACT: Electrophilic intramolecular twofold iodoarylation was developed from the reaction of diynes and diynyl diethers and amines with iodine monochloride under mild conditions, which produced bis(2*H*-hydronaphthalene and chromene) and 2*H*-quinoline bearing an alkenyl iodide moiety in good to excellent yields. These compounds underwent Pd-catalyzed cross-coupling reactions with arylboronic acid and indium tris(arylthiolate) to produce the functionalized styrene derivatives.

INTRODUCTION

Intramolecular hydroarylation of alkynyl arenes has emerged as an extremely useful method for the synthesis of a wide range of carbocyclic and heterocyclic compounds, which are valuable in the preparation of natural products and biologically active compounds.[1] In general, these methods can be accomplished either by transition-metal or Lewis acid catalysts. Alternatively, electrophilic addition reactions of polarized reagents to functionalized alkynyl arenes are good approaches to prepare carbocycles and heterocycles through hydroarylation. In comparison to hydroarylation using transition-metal and Lewis acid catalysts, intramolecular iodoarylation of alkynyl arenes using the iodonium ion has advantages such as further functionalization due to giving carbocycles and heterocycles possessing an alkenyl or aryl iodide moiety.[2] This method has been studied in detail by Barluenga,[3] Larock,[4] and others[5] and has thus been used as a widely applicable strategy for the efficient synthesis of target molecules.

Recently, we developed the intramolecular hydroarylation of aryl enynes and aryl alkynyl sulfides, amines, selenides, and tellurides.[6] In addition, we reported Au-catalyzed intramolecular 2-fold hydroarylation that allows an efficient synthesis of bis(2*H*-chromene and quinoline) from diyne diethers and diamines.[7] These results and the current importance of hydroarylation stimulated us to search for an intramolecular iodoarylation based on iodonium reagents. Herein, we report that electrophilic intramolecular 2-fold iodoarylation of diynes and diynyl diethers and amines with iodonium ion provides an efficient synthetic method of bis(2*H*-hydronaphthalene and chromene) and 2*H*-quinoline bearing an alkenyl iodide moiety, compounds which have potential for further functionalization (Scheme 1).

Scheme 1. Twofold Iodoarylation



RESULTS AND DISCUSSION

First, a variety of functionalized diynyl diethers and amines were prepared by treatment of phenol and *N*-tosylaniline derivatives with propargyl bromide in the presence of potassium carbonate followed by CuCl-catalyzed oxidative homo- or heterocoupling reactions using TMEDA and pyridine in DMF under oxygen (Scheme 2).[8]

We studied the reaction of 1,6-bis(phenoxy)-2,4-hexadiyne **1a** with NIS in various solvents (DCE, DCM, and AcOH) at

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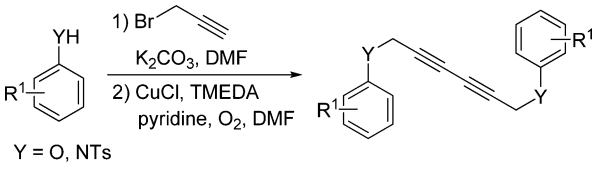
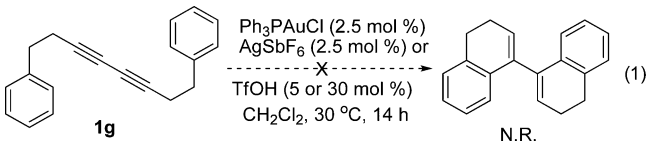
Scheme 2. Preparation of Diynyl Diethers and Amines



−78 °C. However, only the iodination product **3a** was obtained together with the starting material **1a** (Table 1, entries 1−3). The use of IPy_2BF_4 is totally ineffective for iodoarylation (entry 4). In general, the iodine molecule (I_2) shows electrophilic properties, but its reactivity in the iodoarylation reaction is low, thus producing 2-fold iodoarylated product **2a** in 17% yield (entry 5). Low temperature and addition of $NaHCO_3$ are not effective for intramolecular iodoarylation (entries 6 and 7). When iodine monochloride (ICl) was used as an electrophilic reagent in DCM at 25 °C, **1a** disappeared on TLC, but a complex mixture was obtained (entry 8). The best result was obtained with ICl (2 equiv) in DCM at 0 °C after 10 min, producing **2a** in 76% yield (entry 9). The iodoarylarion reaction was not complete at −78 °C (entry 10). Use of an increased amount (3 equiv) of ICl at 0 °C (10 min) and at −78 °C (30 min) gave **1a** in 71% yield (entry 11). On the whole, 1,6-bis(phenoxy)-2,4-hexadiyne (**1a**) and the twofold iodoarylated product **2a** are sensitive to the temperature and amount of iodine monochloride.

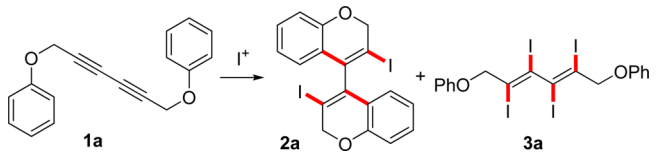
With this newly developed protocol in hand, we applied the optimum reaction conditions of intramolecular 2-fold iodoarylation of 1,6-bis(phenoxy)-2,4-hexadiyne (**1a**) to a wide range of diynes and diynyl diethers and amines **1** to demonstrate the efficiency and scope of the present method (Table 2). Treatment of 1,6-bis(*p*-*tert*-butylphenoxy)-2,4-hexadiyne (**1b**) with ICl (2 equiv) in DCM at 0 °C after 10 min produced the 4,4′-bis(2*H*-chromene) **2b** bearing an alkenyl iodide moiety in 60% yield (entry 2). The 2,4-hexadiyne **1c**, having an *o*-phenylphenoxy group at the 1,6-positions was reacted with ICl to afford the desired iodoarylated product **2c** in 90% yield (entry 3). 1,6-Bis(*p*-chlorophenoxy)-2,4-hexadiyne (**1d**) underwent the intramolecular twofold iodoarylation using ICl (4 equiv) to provide the 4,4′-bis(2*H*-chromene) **2d** having both iodo and chloro groups in 66% yield (entry 4). Exposure of the *o*-bromo-substituted diynyl diether **1e** to ICl (2 equiv) afforded the iodoarylated compound **2e** in 87% yield (entry 5). 1,6-Bis(*p*-iodophenoxy)-2,4-hexadiyne (**1f**) turned out to be compatible with the reaction conditions using 4 equiv of ICl (entry 6). The tolerance of chlodide, bromide, and iodide groups on the phenyl ring is especially valuable, affording an opportunity for further functionalization. In addition, reaction of 1,8-bis(phenyl)-3,5-octadiyne (**1g**) with ICl led to the formation of the 4,4′-bis(2*H*-hydronaphthalene) **2g** in 90% yield (entry 7). In contrast, **1g** was not cyclized with either Ph_3PAuCl and $AgSbF_6$ (5 mol % each) or trifluoromethanesulfonic acid (5 or 30 mol %) (eq 1). These results indicate that



the existence of the phenoxy and phenylamino moieties in ICl-mediated intramolecular 2twofold iodoarylation is not critical, while the presence of oxygen and nitrogen atoms having nonbonding electrons in Au-catalyzed 2-fold hydroarylation is critical (eq 1).[7]

In the case of unsymmetrical 1-(*o*-phenylphenoxy)-7-phenyl-2,4-heptadiyne (**1h**), intramolecular 2-fold iodoarylation proceeded efficiently to give **2h** in 81% yield in DCE at 0 °C after 10 min (entry 8). 1-(*o*-Bromophenoxy)-7-phenyl-2,4-heptadiyne (**1i**) worked equally well (entry 9). When the unsymmetrical diyne **1j** having phenoxy and *N*-phenyl-*N*-tosylamino groups was treated with ICl (2 equiv) in DCM at 0 °C, the intramolecular twofold iodoarylated compound **2j** was obtained in 53% yield (entry 10). In addition, phenoxy- and *N*-(3,5-dimethylphenyl)-*N*-tosylamino-substituted diyne **1k** was cyclized to produce **2k** in 55% yield (entry 11).

Table 1. Optimization of Intramolecular Twofold Iodoarylation[a]



entry	I^+ (amt (equiv))	additive (amt (equiv))	temp (°C)	solvent	time	yield (%) 2a	yield (%) 3a
1	NIS (3)		−78	DCE	10 h	0	28 (31)[b]
2	NIS (3)		−78	CH_2Cl_2	12 h	0	38 (30)[b]
3	NIS (3)		−78	AcOH	8 h	0	34 (12)[b]
4	IPy_2BF_4 (3)	HBF_4 (6)	−78	CH_2Cl_2	12 h	0	46 (45)[b]
5	I_2 (4)		25	CH_2Cl_2	1 h	17	8
6	I_2 (4)		−78	CH_2Cl_2	24 h	0	67
7	I_2 (4)	$NaHCO_3$ (2)	25	CH_2Cl_2	12 h	0	64
8	ICl (2)		25	CH_2Cl_2	10 min	0	0
9	ICl (2)		0	CH_2Cl_2	10 min	76	0
10	ICl (2)		−78	CH_2Cl_2	2 h	47	0 (46)[b]
11	ICl (3)		0	CH_2Cl_2	10 min	71	0
12	ICl (3)		−78	CH_2Cl_2	30 min	71	0

[a]Reaction conditions: **1a** (0.2 mmol) in solvent (0.1 M). [b]Recovery yields of **1a**.

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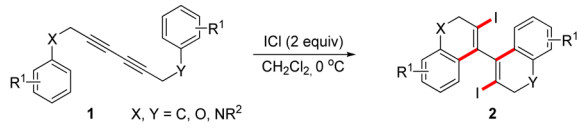
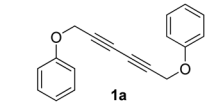
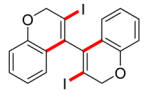
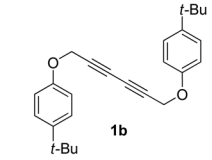
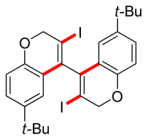
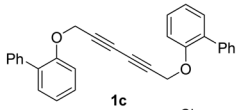
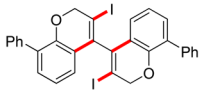
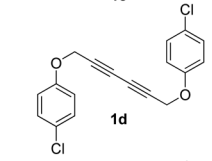
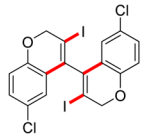
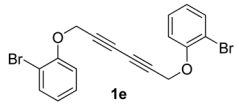
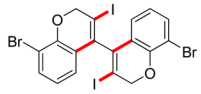
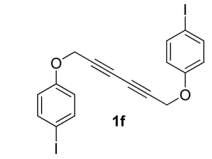
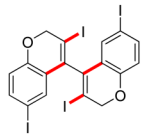
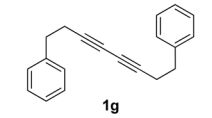
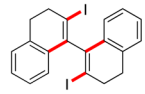
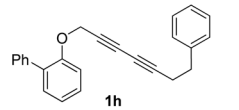
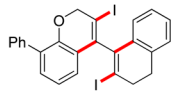
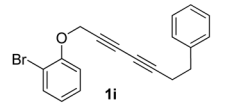
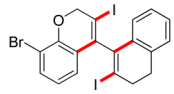
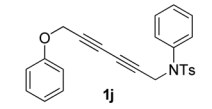
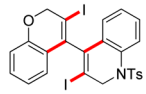
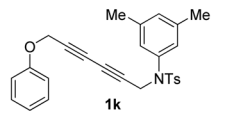
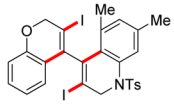
Table 2. Twofold Iodoarylation of Diyne and Diynyl Diethers and Diamines[a]



entry	1	time (min)	2	yield (%)
1	 1a	10	 2a	76
2	 1b	10	 2b	60
3	 1c	20	 2c	90
4	 1d	40	 2d	66[b]
5	 1e	20	 2e	87
6	 1f	40	 2f	70[b]
7	 1g	10	 2g	90
8	 1h	10	 2h	81
9	 1i	10	 2i	88
10	 1j	30	 2j	53
11	 1k	30	 2k	55

[a]Reaction conditions: **1** (0.2 mmol), ICl (0.4 mmol), 0 °C, CH_2Cl_2. [b]ICl (0.8 mmol) was used.

Because 4,4′-bis(2*H*-chromenes) bearing an alkenyl iodide moiety were now in hand, we investigated the feasibility of further transformation through cross-coupling reactions (Table 3). Reaction of **2a** with (4-Me-C_6H_4)$B(OH)_2$ in the presence of $Pd(OAc)_2$ catalyst and CsF in THF proceeded smoothly to afford the coupling product **4a** in 75% yield. We were pleased to obtain **4b,c** in 66% and 67% yields, respectively, from the treatment of **2a** with the corresponding boronic acids (4-MeO-C_6H_4)$B(OH)_2$ and (3-Cl-C_6H_4)$B(OH)_2$.

Next, a Pd-catalyzed cross-coupling reaction using indium tris(arylthiolate) was applied to **2a** (Table 4).[9] Subjecting **2a** to (4-Me-C_6H_4S)$_3$In in the presence of $Pd(OAc)_2$ (4 mol %), Xantphos (4.2 mol %), and DIPEA (0.2 mmol) in DMF (100 °C, 2 h) gave the desired product **5a** in 71% yield. Treatment of **2a** with (4-MeO-C_6H_4S)$_3$In resulted in the formation of C−S coupling product **5b** in 75% yield.

A possible reaction mechanism is described in Scheme 3. Activation of the iodonium cation to triple bond in diyne **1** results in the formation of the intermediate **I**, which upon nucleophilic attack of the carbon on the aromatic ring is cyclized, leading to the intermediates **II** and **V**.[3,4] Subsequent aromatization might deliver the iodoarylated compounds **IV** and **VI**. The repeated intramolecular iodoarylation of intermediates **IV** and **VI** with iodonium cation would provide the twofold iodoarylation product **2**. Because the rate of the iodoarylation reaction is fast, the first iodoarylated products **IV** and **VI** are not detected in TLC as well as NMR studies. In the case of unsymmetrical diynes, we cannot determine which side nucleophilic attack of the phenyl ring occurs first.

CONCLUSION

In conclusion, we developed herein electrophilic intramolecular twofold iodoarylation from the reaction of diynes and diynyl diethers and amines with iodine monochloride under mild conditions (DCE, 0 °C, 10−40 min), which produced bis(2*H*-hydronaphthalene and chromene) and 2*H*-quinoline bearing an alkenyl iodide moiety in good to excellent yields. These compounds underwent Pd-catalyzed cross-coupling reactions with arylboronic acid and indium tris(arylthiolate) to produce the functionalized styrene derivatives.

EXPERIMENTAL SECTION

General Considerations. Reactions were carried out in oven-dried glassware under a nitrogen atmosphere. $Pd(OAc)_2$, Xantphos, and ICl (1.0 M in CH_2Cl_2) were purchased. Commercially available reagents were used without purification. DCE, dichloromethane, and DMF were dried with CaH_2. THF was dried with Na−benzophenone. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light and then developed using either iodine or a solution of anisaldehyde. Flash column chromatography was carried out using silica gel (230−400 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on an NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.26 for ^{1}H and δ 77.0 for ^{13}C). Infrared spectra were recorded on an FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Mass spectrometry was performed on a GC/HRMS spectrometer by electron impact (EI) ionization techniques (magnetic sector−electric sector double focusing mass analyzer). Melting points were determined in open capillary tubes.

General Procedure for the Preparation of 1,6-Bis(phenoxy)-2,4-hexadiyne Derivatives. (Prop-2-ynyloxy)benzene derivatives were prepared from the reaction of the appropriate phenol (1 equiv) with propargyl bromide (1.5 equiv) at room temperature in DMF in

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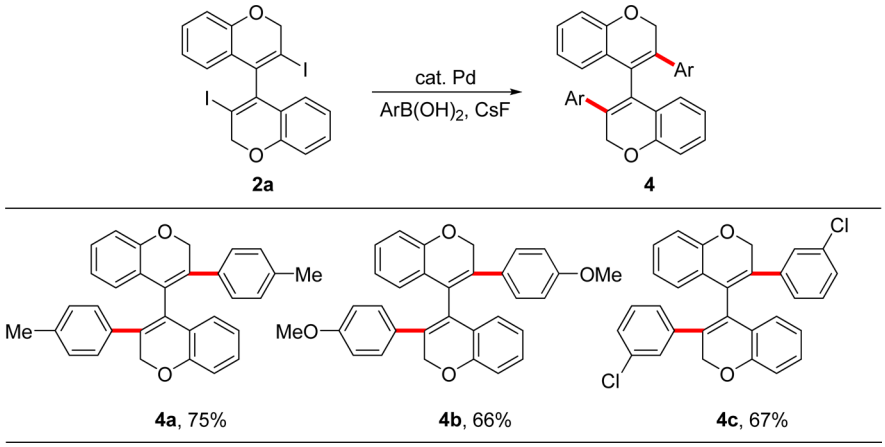
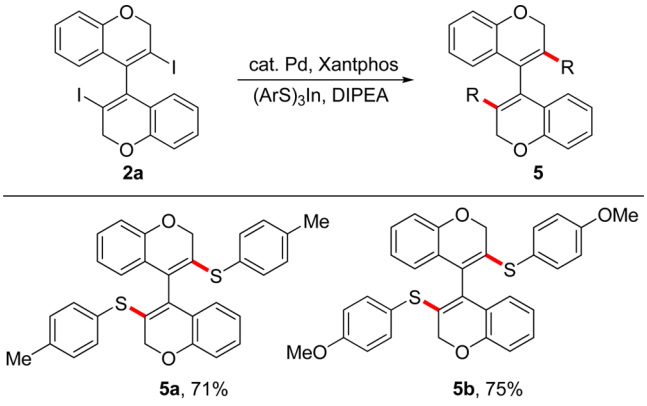
Table 3. Pd-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction using 2a[a]



[a]Reaction conditions: **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), $ArB(OH)_2$ (1.2 mmol), and CsF (1.6 mmol), in THF (4 mL) at 70 °C for 12 h.

Table 4. Pd-Catalyzed Cross-Coupling Reactions using Indium Tris(arylthiolate)[a]



[a]Reaction conditions: **2a** (0.2 mmol), $(ArS)_3In$ (0.28 mmol), $Pd(OAc)_2$ (4 mol %), Xantphos (4.2 mol %), and DIPEA (diisopropylethylamine) (0.2 mmol) in DMF (2 mL) at 100 °C for 2 h.

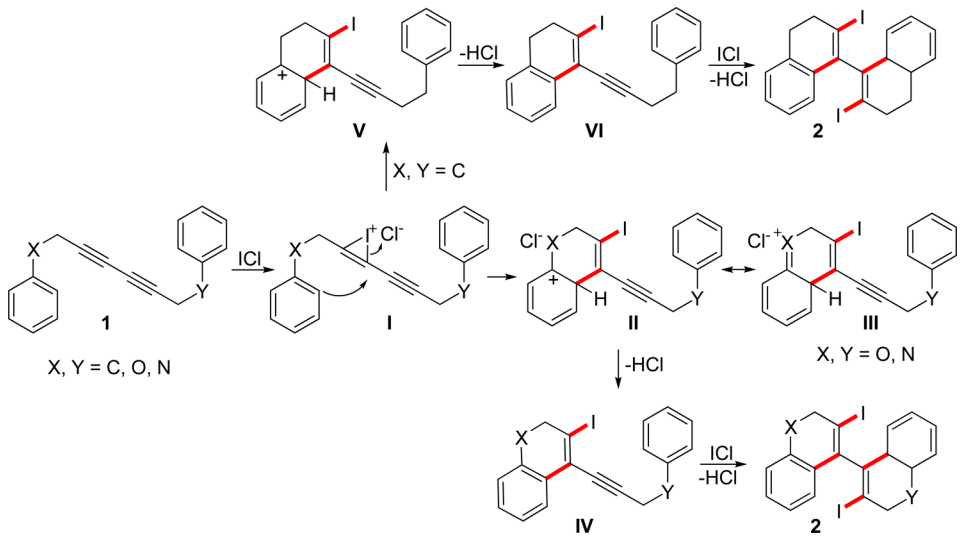
the presence of potassium carbonate (2 equiv). Purification of the crude product was achieved via flash column chromatography. Then, in a 50 mL flask were dissolved (prop-2-ynyloxy)benzene derivatives (6 mmol) in 4 mL of DMF. To the solution were added copper(I) chloride (30 mg, 5 mol %), 0.1 mL (10 mol %) of *N,N,N′,N′*-tetramethylethylenediamine, and 0.1 mL (10 mol %) of pyridine. The mixture was bubbled with oxygen and stirred at room temperature for 6–12 h. A 30 mL portion of DMF was added, and the mixture was filtered through a short silica column to remove copper. The filtrate was poured into 100 mL of water. The resultant precipitate was filtered, washed with water, and dried under vacuum to afford a beige powder (36–96%).

*1,6-Bis(phenoxy)-2,4-hexadiyne (**1a**):*[10] white solid (96%, 980 mg); mp 61–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 4H), 7.02–6.93 (m, 6H), 4.75 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 130.0, 122.2, 115.3, 75.0, 71.4, 56.6; IR (pellet) 3062, 3041, 2912, 1598, 1494, 1361, 1211, 1034 cm^{-1}.

*1,6-Bis(4-tert-butylphenoxy)-2,4-hexadiyne (**1b**):*[7] white solid (88%, 825 mg); mp 78–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 8.9 Hz, 4H), 6.88 (d, J = 8.8 Hz, 4H), 4.73 (s, 4H), 1.30 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 144.5, 126.4, 114.3, 74.8, 71.0, 56.3, 34.1, 31.5; IR (pellet) 2962, 2904, 2868, 1512, 1363, 1297, 1221 cm^{-1}.

*1,6-Bis(biphenyl-2-yloxy)-2,4-hexadiyne (**1c**):*[7] pale yellow solid (89%, 1.0 g); mp 102–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–

Scheme 3. Plausible Mechanism



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7.48 (m, 4H), 7.40 (t, J = 6.7 Hz, 4H), 7.35−7.31 (m, 6H), 7.10 (t, J = 8.1 Hz, 4H), 4.71 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 138.6, 132.1, 131.7, 130.1, 129.1, 128.6, 127.6, 122.7, 114.0, 75.5, 71.7, 57.2; IR (pellet) 3542, 3060, 3027, 1597, 1583, 1503, 1480, 1208 cm^{-1}.

*1,6-Bis(4-chlorophenoxy)-2,4-hexadiyne (**1d**):* white solid (89%, 730 mg); mp 140−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.23 (m, 4H), 6.89−6.85 (m, 4H), 4.73 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 129.5, 126.8, 116.3, 74.4, 71.2, 56.5; IR (pellet) 3094, 2906, 2860, 1493, 1370, 1244, 1031, 819 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{12}Cl_2O_2$ 330.0214, found 330.0213.

*1,6-Bis(2-bromophenoxy)-2,4-hexadiyne (**1e**):*[7] white solid (90%, 945 mg); mp 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.29 (t, J = 7.9 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.90 (t, J = 7.6 Hz, 2H), 4.84 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 134.1, 128.9, 123.6, 114.6, 112.9, 74.7, 71.9, 57.7; IR (pellet) 3064, 2912, 1476, 1277, 1224, 1051, 1031, 1017 cm^{-1}.

*1,6-Bis(4-iodophenoxy)-2,4-hexadiyne (**1f**):*[7] pale yellow solid (88%, 1.1 g); mp 164−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.9 Hz, 4H), 6.72 (d, J = 8.8 Hz, 4H), 4.72 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 138.3, 117.2, 84.2, 74.3, 71.2, 56.2; IR (pellet) 1571, 1484, 1284, 1236, 1026, 823, 797 cm^{-1}.

*1,8-Bis(phenyl)-3,5-octadiyne (**1g**):* white solid (94%, 608 mg); mp 66−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.28 (m, 4H), 7.24−7.20 (m, 6H), 2.84 (t, J = 7.5 Hz, 4H), 2.54 (t, J = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 128.5, 128.4, 126.4, 76.9, 65.9, 34.7, 21.5; IR (pellet) 3028, 2927, 2256, 1603, 1453, 1424, 1227, 1032, 699, 511 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}$ 258.1409, found 258.1407.

*2-((7-Phenylhepta-2,4-diyn-1-yl)oxy)-1,1′-biphenyl (**1h**):* pale yellow oil (48%, 403 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.51 (m, 2H), 7.43−7.39 (m, 2H), 7.35−7.28 (m, 5H), 7.24−7.18 (m, 3H), 7.12−7.07 (m, 2H), 4.70 (s, 2H), 2.84 (t, J = 7.5 Hz, 2H), 2.56 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 139.9, 138.2, 131.5, 131.1, 129.6, 128.5, 128.3, 128.0, 127.0, 126.5, 122.0, 113.6, 80.9, 72.1, 71.0, 65.2, 56.8, 34.4, 21.5; IR (film) 3060, 3022, 2928, 2255, 1480, 1209, 1018, 751, 698 cm^{-1}; HRMS (FAB) calcd for $C_{25}H_{20}O$ 336.1514, found 336.1511.

*1-Bromo-2-((7-phenylhepta-2,4-diyn-1-yl)oxy)benzene (**1i**):* yellow oil (43%, 365 mg), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.9, 1.6 Hz, 1H), 7.30−7.27 (m, 3H), 7.25−7.23 (m, 1H), 7.21−7.17 (m, 2H), 7.02 (dd, J = 8.2, 1.2 Hz, 1H), 6.87 (td, J = 7.7, 1.3 Hz, 1H), 4.79 (s, 2H), 2.82 (t, J = 7.5, Hz, 2H), 2.55 (t, J = 7.5, Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 139.9, 133.3, 128.5, 128.5, 128.4, 126.6, 122.9, 114.3, 112.5, 81.4, 72.8, 70.1, 65.1, 57.5, 34.4, 21.5; R (film) 3062, 3027, 2927, 2860, 2256, 1585, 1476, 1225, 1031, 748 cm^{-1}; HRMS (FAB) calcd for $C_{19}H_{15}BrO$ 338.0306, found 338.0302.

*4-Methyl-N-(6-phenoxyhexa-2,4-diyn-1-yl)-N-phenylbenzenesulfonamide (**1j**):* brown solid (36%, 374 mg); mp 51−56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.51 (d, J = 8.3 Hz, 2H), 7.34−7.29 (m, 5H), 7.22−7.17 (m, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.94 (d, J = 7.6 Hz, 2H), 4.73 (s, 2H), 4.51 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 144.2, 139.8, 135.7, 129.9, 129.7, 129.5, 128.6, 128.4, 122.2, 115.3, 74.7, 74.0, 71.4, 69.9, 56.5, 42.2, 21.9; IR (pellet) 3063, 1597, 1493, 1351, 1212, 1163, 754, 694 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{21}NO_3S$ 415.1242, found 415.1239.

*N-(3,5-Dimethylphenyl)-4-methyl-N-(6-phenoxyhexa-2,4-diyn-1-yl)benzenesulfonamide (**1k**):* colorless oil (40%, 443 mg), ^{1}H NMR (400 MHz, $CDCl_3$) 7.54 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 8.2 Hz, 3H), 6.78 (s, 2H), 4.73 (s, 2H), 4.46 (s, 2H), 2.39 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.6, 140.0, 139.6, 136.4, 130.9, 130.3, 130.0, 128.8, 126.7, 122.6, 115.5, 75.0, 73.9, 71.6, 69.7, 56.5, 42.2, 21.7, 21.4; IR (film) 2955, 2919, 1597, 1494, 1350, 1162, 1034, 664 cm^{-1}; HRMS (EI) calcd for $C_{27}H_{25}NO_3S$ 443.1555, found 443.1553.

General Procedure for the Preparation of Diiodo-2*H*,2′*H*-4,4′-bichromene Derivatives. To a solution of 1,6-bis(phenoxy)-2,4-hexadiyne (**1a**; 52.5 mg, 0.2 mmol) in CH_2Cl_2 (1.6 mL) was slowly added ICl (1.0 M in CH_2Cl_2, 0.4 mL) dropwise at 0 °C. The resulting solution was stirred at 0 °C for 10 min. The reaction mixture was quenched with 10 mol % KI aqueous (2 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic layers were washed with $Na_2S_2O_3{\cdot}5H_2O$ and water, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Silica gel column chromatography (acetone/hexane 1/9) gave 5,5′-diiodo-2*H*,2′*H*-4,4′-bichromene **2a** (77.5 mg, 76%) as a white solid.

*5,5′-Diiodo-2H,2′H-4,4′-bichromene (**2a**):* white solid (76%, 78 mg); mp 101−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 2H), 6.92−6.87 (m, 4H), 6.84−6.80 (m, 2H), 5.11−5.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 140.2, 130.2, 125.1, 122.1, 120.9, 116.3, 93.4, 74.4; IR (pellet) 3067, 2832, 1598, 1481, 1455, 1221, 1036, 993 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{12}I_2O_2$ 513.8927, found 513.8930.

*3,3′-Diiodo-8,8′-diphenyl-2H,2′H-4,4′-bichromene (**2b**):* white solid (60%, 75 mg); mp 111−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J = 8.5, 2.4 Hz, 2H), 6.88 (d, J = 2.4, 2H), 6.83 (d, J = 8.4, 2H), 5.04 (s, 4H), 1.14 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 144.7, 140.8, 126.9, 122.4, 120.7, 115.5, 92.6, 74.5, 34.1, 31.3; IR (pellet) 2961, 2904, 2867, 1606, 1490, 1363, 1004, 952 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{28}I_2O_2$ 626.0179, found 626.0176.

*6,6′-Di-tert-butyl-3,3′-diiodo-2H,2′H-4,4′-bichromene (**2c**):* white solid (90%, 120 mg); mp 97−100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 4H), 7.46−7.42 (m, 4H), 7.38−7.36 (m, 2H), 7.28−7.24 (m, 2H), 7.00−6.97 (m, 2H), 6.94−6.90 (m, 2H), 5.10−5.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 140.7, 137.4, 131.6, 130.1, 129.5, 128.1, 127.3, 124.6, 122.1, 121.7, 93.7, 74.4; IR (pellet) 3057, 2835, 1456, 1428, 1264, 1210, 1072, 1003 cm^{-1}; HRMS (EI) calcd for $C_{30}H_{20}I_2O_2$ 665.9553, found 665.9556.

*6,6′-Dichloro-3,3′-diiodo-2H,2′H-4,4′-bichromene (**2d**):* white solid (66%, 76.8 mg); mp 220−223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.6, 2.5 Hz, 2H), 6.83 (d, J = 12.5 Hz, 2H), 6.82 (d, J = 1.2 Hz, 2H), 5.12−5.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 138.8, 130.1, 127.1, 124.4, 121.7, 117.9, 95.7, 74.4; IR (pellet) 2848, 1479, 1404, 1260, 1093, 999, 817, 732 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{10}Cl_2I_2O_2$ 581.8147, found 581.8146.

*8,8′-Dibromo-3,3′-diiodo-2H,2′H-4,4′-bichromene (**2e**):* white solid (87%, 116.5 mg), 166−169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.96, 1.44 Hz, 2H), 6.84−6.82 (m, 2H), 6.73−6.69 (m, 2H), 5.22−5.14 (m, 4H);^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 139.4, 133.9, 124.2, 123.0, 121.8, 110.4, 94.8, 74.8; IR (pellet) 3069, 2844, 1635, 1588, 1556, 1457, 1440, 1233, 997, 907, 778 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{10}Br_2I_2O_2$ 669.7137, found 669.7141.

*3,3′,6,6′-Tetraiodo-2H,2′H-4,4′-bichromene (**2f**):* white solid (70%, 107.2 mg), 110−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.09 (s, 2H), 6.67 (d, J = 8.5 Hz, 2H), 5.13−5.02 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 139.2, 138.5, 132.8, 122.6, 118.8, 95.6, 84.4, 74.3; IR (pellet) 2831, 1473, 1394, 1265, 1228, 1073, 997, 815, 736 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{10}I_4O_2$ 765.6860, found 765.6856.

*2,2′-Diiodo-3,3′,4,4′-tetrahydro-1,1′-binaphthalene (**2g**):* white solid (90%, 91.8 mg); mp 111−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.15 9 (m, 4H), 7.08−7.04 (m, 2H), 6.98−6.96 (m, 2H), 3.10−3.05 (m, 4H), 3.03−2.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.7, 132.5, 127.8, 127.6, 127.0, 125.2, 103.2, 39.1, 29.9; IR (pellet) 3061, 2934, 2884, 2827, 1482, 1449, 1422, 907 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{16}I_2$ 509.9341, found 509.9344.

*3-Iodo-4-(2-iodo-3,4-dihydronaphthalen-1-yl)-8-phenyl-2H-chromene (**2h**):* white solid (81%, 95.2 mg); mp 107−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.45−7.41 (m, 2H), 7.37−7.32 (m, 1H), 7.26−7.24 (m, 1H), 7.20−7.16 (m, 2H), 7.12−7.08 (m, 1H), 7.04−7.02 (m, 1H), 7.00−6.95 (m, 1H), 6.90−6.88 (m, 1H), 5.08−5.00 (m, 2H), 3,14−3.09 (m, 2H), 3.04−2.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 143.1, 142.7, 137.5, 134.5, 132.0, 131.3, 130.0, 129.5, 128.1, 128.0, 127.7, 127.2, 127.1, 125.0, 124.8, 122.1, 121.9, 103.4, 93.4, 74.4, 39.1, 29.8; IR (pellet) 2925, 14555, 1428, 1213, 1002, 907 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{18}I_2O$ 587.9447, found 587.9448.

*8-Bromo-3-iodo-4-(2-iodo-3,4-dihydronaphthalen-1-yl)-2H-chromene (**2i**):* white solid (88%, 103.8 mg); mp 169−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 7.8 Hz, 1H), 7.21−7.15 (m, 2H),

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7.09−7.06 (m, 1H), 6.95−6.93 (m, 1H), 6.87−6.84 (m, 1H), 6.68 (t, *J* = 7.8 Hz, 1H), 5.22−5.13 (m, 2H), 3.10−3.08 (m, 2H), 3.01−2.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 142.2, 134.4, 133.5, 131.7, 128.5, 128.1, 127.8, 127.1, 124.8, 124.6, 122.8, 122.5, 110.2, 103.6, 94.4, 74.9, 39.1, 29.6; IR (pellet) 3060, 2946, 2886, 2829, 1479, 1456, 1441, 1232, 1088, 998 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{13}BrI_2O$ 589.8239, found 589.8242.

3-Iodo-4-(3-iodo-2H-chromen-4-yl)-1-tosyl-1,2-dihydroquinoline ***(2j):*** white solid (53%, 71 mg); mp 99−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.89 (m, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.36−7.31 (m, 1H), 7.26−7.24 (m, 2H), 7.12−7.06 (m, 2H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.42 (t, *J* = 7.6 Hz, 1H), 5.49 (d, *J* = 6.2 Hz, 1H), 5.27 (d, *J* = 17.9 Hz, 1H), 5.02−4.93 (m, 2H), 4.69 (d, *J* = 17.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.9, 141.7, 140.5, 137.2, 134.0, 130.2, 129.8, 129.1, 127.6, 127.1, 126.7, 126.4, 126.0, 125.6, 121.7, 120.8, 116.2, 95.2, 74.4, 56.2, 21.8; IR (pellet) 3058, 2923, 2845, 1597, 1482, 1452, 1353, 1220, 1161 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{19}I_2NO_3S$ 666.9175, found 666.9179.

3-Iodo-4-(3-iodo-2H-chromen-4-yl)-5,7-dimethyl-1-tosyl-1,2-dihydroquinoline ***(2k):*** white solid (55%, 76.5 mg); mp 98−101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3, 2H), 7.66 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.12−7.07 (m, 1H), 6.79−6.77 (m, 1H), 6.74 (s, 1H), 6.44 (t, *J* = 7.6 Hz, 1H), 5.71 (t, *J* = 7.7 Hz, 1H), 5.17 (d, *J* = 17.2 Hz, 1H), 4.97−4.85 (m, 2H), 4.65 (d, *J* = 17.2 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 144.2, 138.8, 138.3, 137.4, 137.1, 136.5, 136.1, 131.6, 130.2, 129.9, 128.6, 127.4, 125.7, 125.6, 125.1, 123.7, 121.9, 119.8, 116.7, 65.4, 45.3, 21.9, 21.6, 21.4; IR (pellet) 3063, 2922, 2840, 1481, 1452, 1357, 1164, 1089, 1035; HRMS (EI) calcd for $C_{27}H_{23}I_2NO_3S$ 694.9488, found 694.9490.

(((2E,4E)-2,3,4,5-Tetraiodohexa-2,4-diene-1,6-diyl)bis(oxy))-dibenzene ***(3a):*** white solid (67%, 103.1 mg); mp 169−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.25 (m, 5H), 6.98−6.94 (m, 5H), 4.84−4.80 (m, 2H), 4.71−4.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 129.6, 121.9, 115.9, 104.4, 103.6, 77.7; IR (pellet) 3038, 2919, 1596, 1492, 1210, 689 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{14}I_4O_2$ 769.7173, found 769.7169.

Typical Experimental Procedures for Palladium-Catalyzed Suzuki−Miyaura Cross-Coupling Reactions. A suspension of $Pd(OAc)_2$ (4.5 mg, 10 mol %), (4-methoxyphenyl)boronic acid (182 mg, 1.2 mmol), and CsF (243 mg, 1.6 mmol) in THF (4 mL) was stirred at 25 °C for 5 min. To this suspension was added 3,3′-diiodo-2*H*,2′*H*-4,4′-bichromene (0.2 mmol). The resulting mixture was stirred under a nitrogen atmosphere at 70 °C (bath temperature) for 12 h. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel with a gradient eluent of EtOAc/hexane to give the corresponding 3,3′-diaryl-2*H*,2′*H*-4,4′-bichromene.

3,3′-Di-p-tolyl-2H,2′H-4,4′-bichromene ***(4a):*** white solid (75%, 66.4 mg); mp 136−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.12 (m, 2H), 7.09−7.06 (m, 2H), 6.93−6.82 (m, 8H), 6.60−6.58 (m, 4H), 4.87−7.78 (m, 4H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 136.9, 135.0, 132.4, 128.9, 128.4, 127.4, 126.3, 126.2, 124.5, 121.8, 115.8, 69.2, 21.2; IR (pellet) 3027, 2920, 2828, 2248, 1600, 1485, 1218, 1038, 908, 813, 756 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{26}O_2$ 442.1933, found 442.1935.

3,3′-Bis(4-methoxyphenyl)-2H,2′H-4,4′-bichromene ***(4b):*** white solid (66%, 62.6 mg); mp 78−81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16−7.12 (m, 2H), 7.07−7.05 (m, 2H), 6.93−6.91 (m, 2H), 6.85−6.81 (m, 2H), 6.67−6.61 (m, 8H), 4.87−4.77 (m, 4H), 3.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.4, 132.0, 130.5, 128.9, 127.6, 127.1, 126.2, 124.5, 121.8, 115.8, 113.1, 69.1, 55.2; IR (pellet) 2955, 2835, 1607, 1512, 1248, 1179, 1034, 827, 757 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{26}O_4$ 474.1831, found 474.1832.

3,3′-Bis(3-chlorophenyl)-2H,2′H-4,4′-bichromene ***(4c):*** white solid (67%, 64.8 mg); mp 65−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.17 (m, 2H), 7.16−7.13 (m, 2H), 7.07−7.03 (m, 4H), 6.97−6.94 (m, 2H), 6.88−6.84 (m, 2H), 6.67−6.64 (m, 2H), 6.51−6.50 (m, 2H), 4.84−4.75 (m, 4H); ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 139.4, 133.9, 131.3, 129.8, 129.1, 128.9, 127.5, 126.4, 126.0, 124.6, 123.9, 122.1, 116.2, 68.6; IR (pellet) 3027, 2920, 2828, 2248, 1600, 1485, 1218, 1038, 908, 813, 756 cm^{-1}; HRMS (EI) calcd for $C_{30}H_{20}Cl_2O_2$ 482.0840, found 482.0839.

Typical Experimental Procedures for Palladium-Catalyzed C−S Bond Formation Cross-Coupling Reactions. A suspension of $Pd(OAc)_2$ (1.8 mg, 4 mol %) and Xantphos (4.8 mg, 4.2 mol %) in DMF (1 mL) was stirred at 25 °C for 5 min. To this suspension was added 3,3′-diiodo-2*H*,2′*H*-4,4′-bichromene (0.2 mmol) in DMF (1 mL) at 25 °C under a nitrogen atmosphere. After the mixture was stirred for 10 min, $(ArS)_3In$ (0.28 mmol) and DIPEA (34.8 μL, 0.2 mmol) in DMF (1 mL) were transferred via a double-ended needle, and this mixture was stirred at 100 °C for 2 h. The reaction mixture was quenched with $NaHCO_3$ (1 mL). The aqueous layer was extracted with ether (3 × 10 mL), and the combined organic layers were washed with water and brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography on silica gel with a gradient eluent of EtOAc/hexane to give the corresponding 3,3′-bis(arylthio)-2*H*,2′*H*-4,4′-bichromene.

3,3′-Bis((4-methylphenyl)thio)-2H,2′H-4,4′-bichromene ***(5a):*** yellow solid (71%, 71.9 mg); mp 77−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 4H), 7.14−7.09 (m, 6H), 6.98−6.96 (m, 2H), 6.87−6.85 (m, 4H), 4.76−4.66 (m, 4H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 138.0, 132.2, 130.6, 130.0, 129.2, 128.3, 128.0, 124.9, 123.0, 121.9, 116.1, 67.6, 21.1; IR (pellet) 3032, 2921, 2838, 1901, 1598, 1482, 1125, 1038, 755 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{26}O_2S_2$ 506.1374, found 506.1378.

3,3′-Bis((4-methoxyphenyl)thio)-2H,2′H-4,4′-bichromene ***(5b):*** pale yellow solid (75%, 80.7 mg); mp 88−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.41 (m, 4H), 7.13−7.09 (m, 2H), 6.96−6.94 (m, 2H), 6.86−6.83 (m, 8H), 4.74−4.63 (m, 4H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 153.1, 134.7, 129.2, 129.0, 128.7, 124.8, 129.9, 121.9, 121.9, 116.0, 114.9, 67.5, 55.4; IR (pellet) 2937, 2835, 1683, 1590, 1493, 1247, 1173, 1032, 756 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{26}O_4S_2$ 538.1273, found 538.1270.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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