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Halogen-Mediated Cascade Cyclization Reaction of Aryldiynes to Indeno[1,2-*c*]chromene Derivatives

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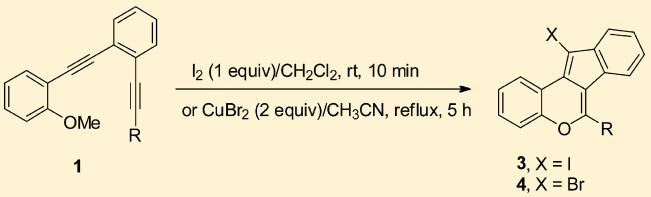
Supporting Information

ABSTRACT: The halogen-mediated cyclization reaction of aryldiynes to produce halogenated indeno[1,2-*c*]chromene derivatives is described. Treatment of aryldiynes **1** with one equivalent of iodine gave iodinated indeno[1,2-*c*]chromenes **3** in good chemical yields. When two equivalents of iodine were employed into the reaction mixture, dimer **9** was obtained as the major products. On the other hand, reaction of two equivalents of $CuBr_2$ with compounds **1** gave the brominated indeno[1,2-*c*]chromenes **4**. The DFT calculation of the iodine-mediated cyclization reactions for molecules containing methoxy, carboxy, amino, and sulfide substituents were carried out in order to understand how the substituent affects the cyclization pathway.



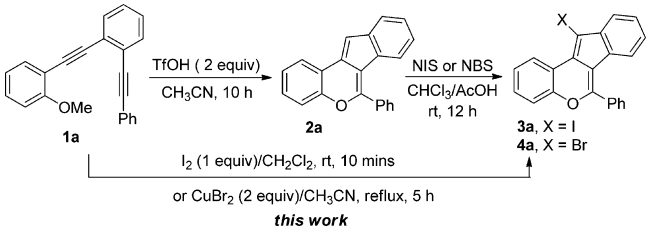
INTRODUCTIONS

Natural and synthetic chromenes and fused chromenes have attracted much attention due to their bioactivities and pharmaceutical applications.[1] A tetracyclic-, indeno[1,2-*c*]-chromene that contains a [6−5−6−6] moiety is a unique skeleton. One of the natural products, *Gnetuhainin S*, isolated from *Gnetum macrostachyum* lianas exhibits antioxidant activity as a radical scavenger against DPPH (2,2-diphenyl-1-picrylhydrazyl).[2] However, synthetic methods to construct the indeno[1,2-*c*]chromene core structure and its derivatives are limited.[3] Recently a series of transition-metal-catalyzed or halo-mediated cyclizations of enediynes and aryldiynes to give benzofulvenes,[4] dibenzo[*b*,*d*]pyran-6-ones,[5] benzo[*a*]-carbazoles,[6] and benzo[*b*]naphtho[2,1-*d*]thiophenes[7] have been reported. Other related cyclization reaction of enediyne and aryldiynes to polyaromatic compounds have also been widely studied.[8]

In a continuation of our interest in the cyclization reaction of enediynes and aryldiynes, the halogen-mediated cyclization of anisole containing aryldiyne was investigated. Recently, Jin reported the triflic acid-mediated cylization of **1a** to give indeno[1,2-*c*]chromene **2a**.[9] Compound **2a** can be converted to iodinated indeno[1,2,-*c*]chromene **3a** or brominated indeno-[1,2-*c*]chromene **3b** by the reaction with NIS or NBS, respectively. An alternative cyclization of aryldiynes using gold catalyst to produce benzofuran derivatives was reported by Alabugin.[10] The iodine-mediated cyclization reaction of alkynes to give heterocyclic compounds has been investigated widely during the past two decades.[11]

Cupric halide-mediated halocyclization reactions have also been reported by several research groups.[12] When we attempted the reaction of iodine (one equivalent) with compound **1a** in CH_2Cl_2 at room temperature for 5 min **3a** was produced in 76% yield and reaction of **1a** with two equivalents of $CuBr_2$ at refluxing CH_3CN for 5 h gave **4a** in 77% yield. (Scheme 1) The anisole containing aryldiynes proceed by a different cyclization pathway than the carboxy, sulfide, and amino containing molecules, however, the indeno[1,2,-*c*]chromenes have been shown not only to exhibit good biological activities but also have been shown to be a good electron push subunit for the solar cell materials. Therefore, we investigated in more detail the one-step synthesis of halogenated indeno[1,2-*c*]chromenes and the results are reported.

Scheme 1. I_2 or $CuBr_2$-Mediated Cascade Cyclization Reaction to Halogenated Indeno[1,2,-*c*]chromene 3 and 4



RESULTS AND DISCUSSIONS

The synthesis of anisole containing aryldiynes **1a**−**p** was carried out by a synthetic pathway reported by us[5−7] and Jin[9] starting from 2-iodoanisoles **4a**−**g** and summarized in Scheme 2. For instance, the synthesis of **1a** was carried out by the Sonogashira

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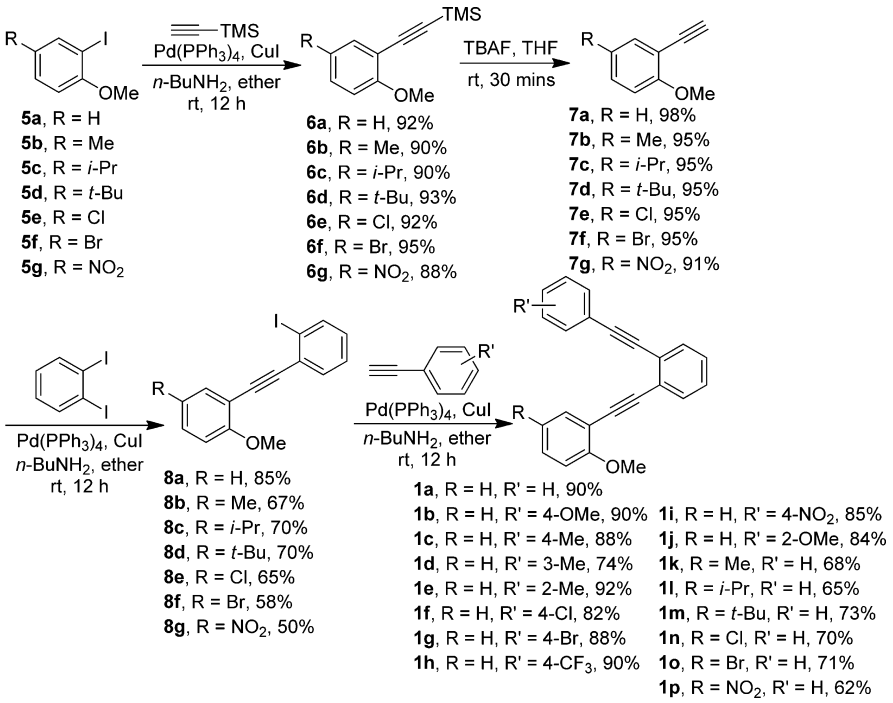
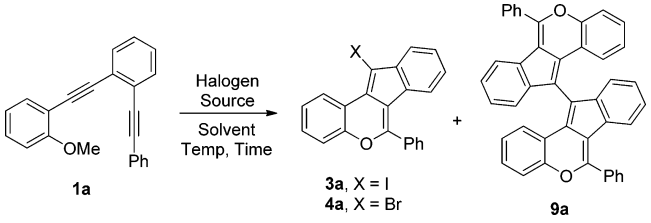
Scheme 2. Preparation of Aryldiynes 1a to 1p



coupling reaction of **4a** with trimethylsilylacetylene using $Pd(PPh_3)_4$ as catalyst to give compound **5a** in 92% yield. Desilylation of **5a** using TBAF in THF gave **6a** in 98% yield. Compound **6a** was coupled with 1,2-diiodobenzene under Sonogashira coupling reaction conditions to give **7a** in 85% yield. Finally, another Sonogashira coupling reaction of compound **7a** with phenyl acetylene gave **1a** in 90% yield.

Our initial attempt for the iodo-cyclization of **1a** was carried out under the optimized reaction condition of our previous carbazole synthesis.[6b] Thus, treatment of **1a** with one equivalent of iodine in CH_2Cl_2 at room temperature for 10 min gave iodinated indeno[1,2,-*c*]chromene **3a** in 76% yield. (Table 1, entry 1) We also screened different solvents, such as CH_3CN, toluene, Et_2O, and THF, for this cyclization reaction (Table 1, entries 2−5). Using CH_3CN as the solvent, product **3a** was isolated in 69% yield. The other three solvents are not effective in carrying out the reaction to completion and gave principally recovered materials. When two equivalents of iodine were introduced into the reaction, dimer **9a** was obtained in 70% yield as the major product. (Table 1, entry 6) For the bromo-cyclization of **1a**, it was found that the optimized reaction conditions are the treatment of two equivalents of $CuBr_2$ with **1a** in refluxing CH_3CN, for 5 h, to give brominated indeno[1,2,-*c*]chromene **4a** in 77% yield. (Table 1, entry 8) $PdBr_2$ catalyst seems to be unnecessary in this cyclization reaction. (Table 1, entry 7) Other solvents, such as CH_2Cl_2 or THF, are inferior to CH_3CN (Table 1, entries 9 and 10).

Table 1. Optimization of Halocyclization of 1a



entry	halogen source (equiv)	solvent	temp	time	products/yields (%)
1	I_2 (1)	CH_2Cl_2	rt	0.5 h	**3a**/76
2	I_2 (1)	CH_3CN	rt	0.5 h	**3a**/69
3	I_2 (1)	toluene	rt	0.5 h	**3a**/25 (**1a**/62)
4	I_2 (1)	Et_2O	rt	0.5 h	**3a**/15 (**1a**/55)
5	I_2 (1)	THF	rt	0.5 h	**3a**/18 (**1a**/57)
6	I_2 (2)	CH_2Cl_2	rt	4 h	**3a**/11; **9a**/82
7	$CuBr_2$ (2); $PdBr_2$ (0.1)	CH_3CN	reflux	5 h	**4a**/75
8	$CuBr_2$ (2)	CH_3CN	reflux	5 h	**4a**/77
9	$CuBr_2$ (2)	CH_2Cl_2	reflux	5 h	NR
10	$CuBr_2$ (2)	THF	reflux	5 h	**4a**/15

With the optimized reaction conditions in hand, we then explore the scope of the iodine-mediated cyclization reactions. Thus, compounds **1b−i** bearing either electron-donating or -withdrawing group were subjected to the optimized reaction conditions and the results are summarized in Table 2. The results indicate that all the reactions undergo cyclization smoothly with one equivalent of iodine to give the iodinated indeno[1,2-*c*]chromenes **3b−i** in 65−85% yields. The reactions were complete within 30 min except for compound **1i** that required 12 h to go to completion. However, treatment of **1c** with two equivalents of iodine for 4 h gave dimer **9c** in 78% yield along with **3c** in 14% yield. Similar results were observed with compound **1f**. Dimer **9f** was isolated in 36% yield as the major product. The structure of compound **3g** was unambiguously determined by single X-ray crystallography.

The scope of the bromo-cyclization reaction under the optimized reaction conditions was also investigated. The results are summarized in Table 3. Again, all the reactions proceeded very smoothly to give the brominated products in good chemical yields except for compound **1i** bearing a strong electron-withdrawing nitro group (Table 3, entry 8). We also introduced different substituents in the 4-position of the anisole

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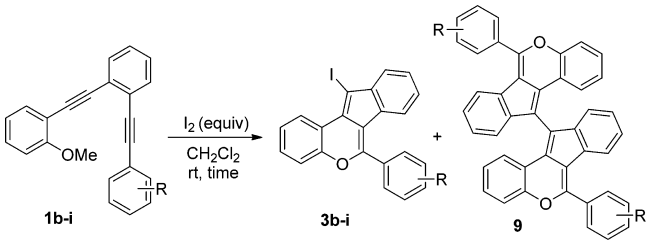
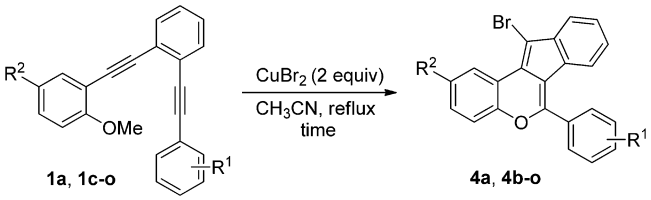
Table 2. Iodine-Mediated Cyclization Reactions of 1b−i



entry	compounds	I_2 (equiv)	time (h)	products/yields (%)
1	**1b**, R = 4-OMe	1	0.5	**3b**/65
2	**1c**, R = 4-Me	1	0.5	**3c**/72
3	**1d**, R = 3-Me	1	0.5	**3d**/65
4	**1e**, R = 2-Me	1	0.5	**3e**/70
5	**1f**, R = 4-Cl	1	0.5	**3f**/78
6	**1g**, R = 4-Br	1	0.5	**3g**/72
7	**1h**, R = 4-CF_3	1	0.5	**3h**/84
8	**1i**, R = 4-NO_2	1	12	**3i**/70
9	**1c**, R = 4-Me	2	4	**3c**/14; **9c**/78
10	**1f**, R = 4-Cl	2	4	**3f**/22; **9f**/36

Table 3. Cyclization Reaction of 1a, 1c−o with $CuBr_2$ to the Brominated Indeno[1,2-*c*]chromenes 4a, 4c−o



entry	compounds	time	products/yields (%)
1	**1a**, R^1 = H, R^2 = H	4 h	**4a**/77
2	**1c**, R^1 = 4-Me, R^2 = H	2 h	**4c**/90
3	**1d**, R^1 = 3-Me, R^2 = H	2 h	**4d**/90
4	**1e**, R^1 = 2-Me, R^2 = H	2 h	**4e**/93
5	**1f**, R^1 = 4-Cl, R^2 = H	5 h	**4f**/90
6	**1g**, R^1 = 4-Br, R^2 = H	5 h	**4g**/90
7	**1h**, R^1 = 4-CF_3, R^2 = H	5 h	**4h**/65
8	**1i**, R^1 = 4-NO_2, R^2 = H	15 h	**4i**/25
9	**1j**, R^1 = 2-OMe, R^2 = H	1 h	**4j**/91
10	**1k**, R^1 = H, R^2 = Me	5 min	**4k**/90
11	**1l**, R^1 = H, R^2 = *i*-Pr	5 min	**4l**/80
12	**1m**, R^1 = H, R^2 = *t*-Bu	5 min	**4m**/85
13	**1n**, R^1 = H, R^2 = Cl	24 h	**4n**/88
14	**1o**, R^1 = H, R^2 = Br	24 h	**4o**/87

ring. The compounds bearing electron-donating substituents undergo the cyclization reaction very rapidly and go to completion within 5 min (Table 3, entries 10−12). However, compounds **1n** and **1o**, which contain chloro or bromo groups at the 4-position, required 24 h to go to completion, but the yields were excellent.

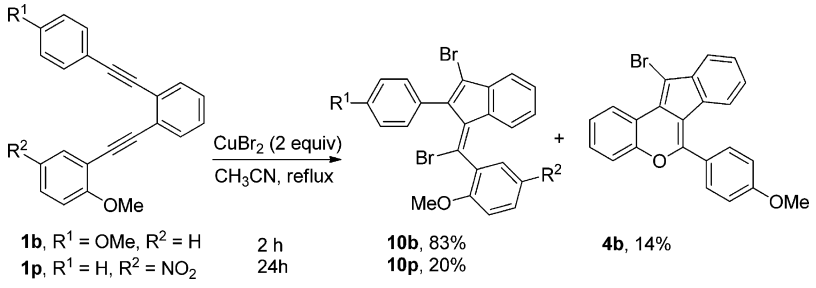
Interestingly, treatment of compound **1b** with two equivalents of $CuBr_2$ under the optimized reaction conditions gave the dibromobenzofulvene adduct **10b** in 83% yield as the major product.[13] Compound **1p** bearing nitro group at the 4-position of the anisole ring undergoes the bromo-cyclization very slowly. The only product that was isolated was **10p** in 20% yield, structure **10p** was characterized as a dibromobenzofulvene as shown in Scheme 3.

To explain the different modes of cyclization of aryldiynes bearing different substituents, we proposed a plausible mechanism for the electrophile mediated cyclization reactions as shown in Scheme 4. Generally, the iodine or bromine generated by heating $CuBr_2$ in refluxing acetonitrile[14] would coordinate to the more electron rich alkyne that is attached to the anisole ring followed by intramolecular cyclization by electron transformation from the other triple bond to form intermediate **I**. The methoxy group would attack the carbocation to generate intermediate **II**. Finally the iodide or bromide would remove the methyl group to give compound **3a** or **4a**, respectively. When introducing a strong electron-donating methoxy group into the molecule, such as compound **1b**, the electrophile, cupric bromide, would coordinate to the alkyne adjacent to the *para*-methoxy phenyl group, followed by intramolecular cyclization. At this point, the *ortho*-methoxy group would not be able to attack the carbocation, however the bromide generated from another $CuBr_2$ molecule would attack the carbocation to form **10b**.

To investigate the dimerization of the brominated indeno-[1,2-*c*]chromenes, compounds **4a**, **4c**, **4f**, **4k**, **4l**, and **4n** were treated with two equivalents of $CuBr_2$ in refluxing CH_3CN for 24 h. Compounds **4a**, **4c**, **4f**, and **4n** were recovered in 75, 70, 73, and 77% yields, respectively. Only compounds **4k** and **4l** were converted to the dimers in 72% and 65% overall yields (Scheme 5). This result indicates that the rate of dimerization is strongly dependent upon the electron density of the chromene ring although the mechanism of the dimerization is not clear at this stage. Since we are able to control the further bromination of the dimer, compound **4k** was treated with six equivalents of $CuBr_2$ in CH_3CN at reflux for 24 h to give compound **12k** in 68% yield as the only product. The structure of compound **12k** was unambiguously determined by single X-ray crystallography as shown in Figure S2.

The present results in conjunction with the previous results[5−7] reveal that the cyclization behavior of aryldiynes bearing *ortho*-methoxy substituted is different than that of aryldiynes bearing carboxy, amino, and sulfide substituents. The

Scheme 3. Cyclization of 1b and 1p to Dibromobenzofulvenes 10b and 10p



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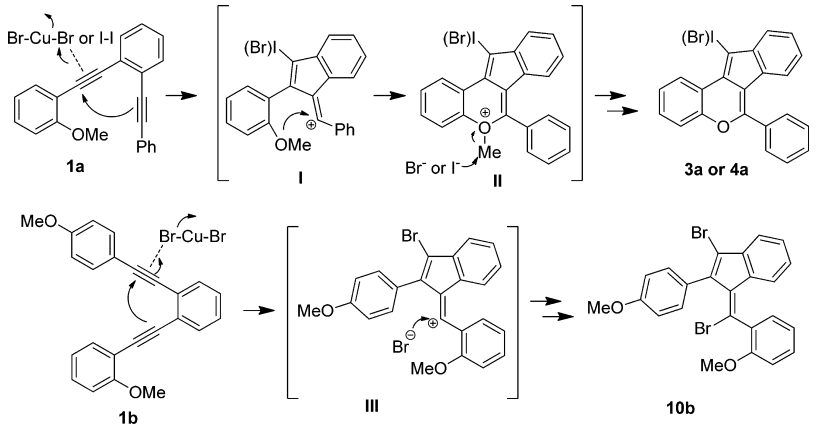
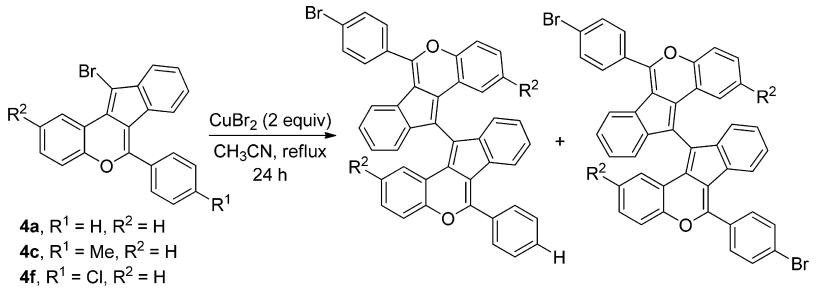
Scheme 4. Plausible Mechanism of Cyclization Reaction



Scheme 5. $CuBr_2$-Mediated Dimerization of the Brominated Indeno[1,2-*c*]chromenes

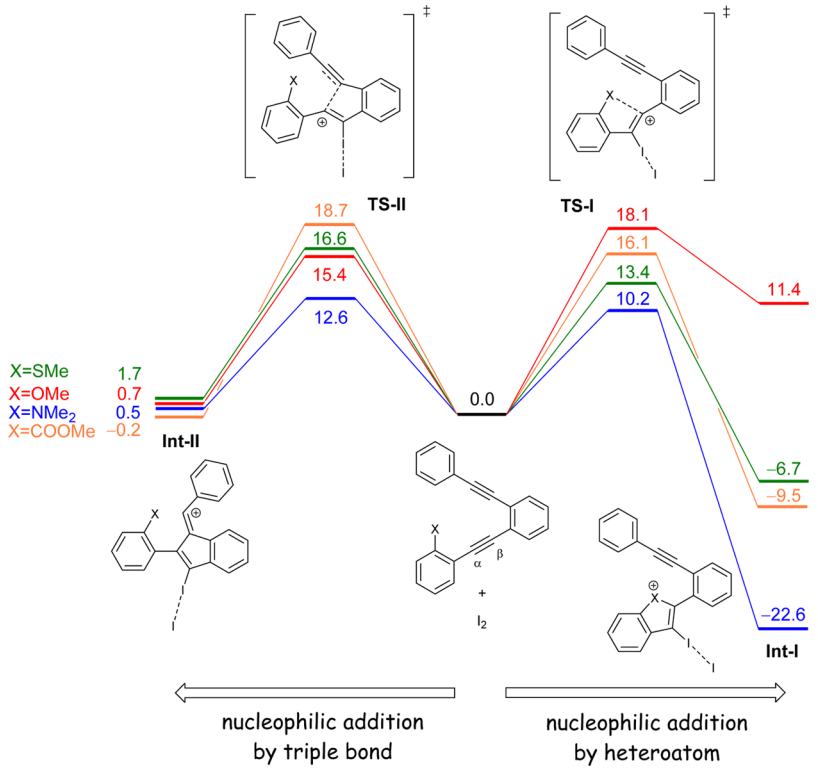


4a, R^1 = H, R^2 = H
4c, R^1 = Me, R^2 = H
4f, R^1 = Cl, R^2 = H
4k, R^1 = H, R^2 = Me
4l, R^1 = H, R^2 = *i*-Pr
4n, R^1 = H, R^2 = Cl

11k, R^2 = Me, 35%
11l, R^2 = *i*-Pr 30%

12k R^2 = Me, 37%
12l, R^2 = *i*-Pr, 35%

Scheme 6. DFT Calculation for the Cyclization Pathways[a]



[a]The unit of free energy is kcal/mol.

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cyclization reactions of aryldiynes could proceed by two distinct pathways: (i) nucleophilic addition by a heteroatom following iodine coordination to C_α or (ii) nucleophilic addition by the other triple bond upon iodine coordination to C_β (Scheme 6). The methoxy-substituted aryldiynes prefer path-II whereas the others prefer path-I. We therefore carried out the DFT calculation on iodine-mediated cyclization reaction for all of these molecules to understand how the substituent affects the mode of cyclization pathway. The calculated free energy profile and the transition-state structures are depicted in Scheme 6 and Figure S2, respectively. For the compounds bearing carboxy, amino, and sulfide groups, the free energies of activation of the addition by the heteroatom (**TS-I**) were estimated to be 2−3 kcal/mol lower than those of the addition by the other triple bond (**TS-II**). In addition, the former reactions were exergonic while the latter reactions were thermodynamically neutral or slightly endergonic. In contrast, the compound bearing methoxy group at the *ortho*-position displayed an opposite trend. In particular, intermediate **Int-I** for the methoxy-substituted compound was relatively thermodynamically unstable that prohibits this pathway. This can be rationalized by the fact that the oxygen of methoxyl group is the most electronegative and least nucleophilic atom of these functional groups.

To verify that these computational results are not basis set dependence, additional single point energy calculations with a larger basis set were performed. It turned out that while the predicted activation energies and reaction energies are somewhat different, the above-mentioned trend for different substituents is not altered (Figure S3).

CONCLUSION

In conclusion, we have developed the directed iodine and bromine mediated cyclization reaction of aryldiynes to produce halogenated indeno[1,2-*c*]chromene derivatives. We have also observed the electronic effects upon the dimerization of the brominated indeno[1,2-*c*]chromenes. Since the indeno[1,2-*c*]chromenes have been shown to be a good electron push subunit for the solar cell materials,[9] we believe that the reported synthetic methods will have a strong impact not only on synthetic organic chemistry but also on material chemistry. Through the DFT calculation of the activation energy difference for the iodine-mediated cyclization reaction of the aryldiynes bearing carboxy, amino, sulfide, and methoxy, we are able to understand more clearly the electron effect upon the mode of cyclization of these diyne derivatives.

EXPERIMENTAL SECTION

Procedure for Sonogashira Coupling Reactions of Aryl Iodides 5a−g, 1,2-Diiodobenezene, and 8a−g to Compounds 6a−g, 8a−g, and 1a−p. *Represented Reaction Conditions for Preparation of ((2-Methoxyphenyl)ethynyl)trimethylsilane (**6a**).* To a solution of 2-iodoanisole **5a** (2.0 g, 8.6 mmol) in Et_2O (50 mL) containing $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol) was added trimethylsilylacetylene (1.0 g, 10.3 mmol), CuI (49 mg, 0.3 mmol), and *n*-$BuNH_2$ (749 mg, 10.3 mmol). The resulting solution was stirred at room temperature for 4 h, quenched by saturated aqueous NH_4Cl (100 mL), and extracted by EtOAc (100 mL × 2). The combined organic layers were dried over $MgSO_4$. After filtration and removal of EtOAc, the residue was purified by column chromatography on silica gel to give ((2-methoxyphenyl)ethynyl)trimethylsilane **6a** (1.6 g. 92%).

*General Procedure for the Desilylation of ((2-Methoxyphenyl)-ethynyl)trimethylsilane **6a** To Give Compound **7a**.* To a solution of ((2-methoxyphenyl)ethynyl)trimethylsilane **6a** (1.0 g, 4.9 mmol) in THF (30 mL) was added tetra-*n*-butylammonium fluoride (1.9 g, 7.35 mmol). The resulting solution was stirred at room temperature for 0.5 h, quenched by brine (50 mL), and extracted with EtOAc (two 50 mL portions). The combined organic layers were dried over $MgSO_4$. After filtration and removal of solvent, the residue further purified by column chromatography on silica gel to give 1-ethynyl-2-methoxybenzene **7a** (0.63 g, 98%).

*1-Methoxy-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (**1a**).* Yielded 0.20 g, 76%; as a dark brown oil; R_f= 0.51 (50:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.90 (d,*J* = 8.0 Hz, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 7.30−7.35 (m, 6H), 7.55−7.62 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.7, 88.4, 90.4, 92.2, 93.4, 110.7, 112.5, 120.4, 123.4, 125.6, 126.2, 127.8, 127.9, 128.2, 128.2, 129.9, 131.7, 131.8, 131.9, 133.8, 160.0; MS (70 eV) *m*/*z* (%): 308 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{16}O$, 308.1201; Found, 308.1203.

*1-Methoxy-2-((2-((4-methoxyphenyl)ethynyl)phenyl)ethynyl)-benzene (**1b**).* Yielded 0.26 g, 90%; as a brown solid; R_f= 0.50 (10:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$)δ 3.82 (s, 6H), 6.86 (d,*J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.27−7.33 (m, 3H), 7.51−7.61 (m, 5H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.3, 55.8, 87.2, 89.9, 92.4, 93.6, 110.7, 112.6, 113.9, 115.6, 120.4, 125.9, 126.0, 127.5, 127.8, 129.8, 131.5, 131.9, 133.2, 133.8, 159.6, 160.0; mp 63−64 °C; MS (70 eV) *m*/*z* (%): 338 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O_2$, 338.1307; Found, 338.1305.

*1-Methoxy-2-((2-(p-tolylethynyl)phenyl)ethynyl)benzene (**1c**).* Yielded 0.23 g, 83%; as a brown solid; R_f = 0.50 (50:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.82 (s, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.95 (t,*J* = 7.5 Hz, 1H), 7.15 (d,*J* = 8.5 Hz, 2H), 7.28−7.34 (m, 3H), 7.51 (d,*J* = 8.0 Hz, 2H), 7.55−7.64 (m, 3H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.5, 55.7, 87.8, 89.9, 92.3, 93.7, 110.7, 112.5, 120.3, 120.4, 125.8, 126.0, 127.7, 127.8, 129.0, 129.8, 131.6, 131.6, 131.9, 133.7, 138.4, 160.0; mp 66−67 °C; MS (70 eV) *m*/*z* (%): 322 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O$, 322.1358; Found, 322.1357.

*1-Methoxy-2-((2-(m-tolylethynyl)phenyl)ethynyl)benzene (**1d**).* Yielded 0.24 g, 85%; as a yellow solid; R_f = 0.5 (50:1 Hex/EA);^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.82 (s, 3H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.94 (td, *J* = 7.5. One Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.29−7.34 (m, 3H), 7.40−7.43 (m, 2H), 7.55−7.63 (m, 3H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.2, 55.7, 88.1, 90.0, 92.3, 93.7, 110.7, 112.5, 120.4, 123.2, 125.8, 126.2, 127.8, 127.8, 128.1, 129.1, 131.6, 131.8, 132.4, 133.8, 137.8, 160.0; mp 65−66 °C; MS (70 eV) *m*/*z* (%): 322 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O$, 322.1358; Found, 322.1357.

*1-Methoxy-2-((2-(o-tolylethynyl)phenyl)ethynyl)benzene (**1e**).* Yielded 0.23 g, 83%; as a yellow solid; R_f = 0.5 (50:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.05 (s, 3H), 3.31 (s, 3H), 6.42 (d, *J* = 8.0 Hz, 1H), 6.46 (td, *J* = 7.5, 1.0 Hz, 1H), 6.69 (td, *J* = 7.5, 2.5 Hz, 1H), 6.73−6.77 (m, 2H), 6.82−6.86 (m, 3H), 7.05 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.09−7.16 (m, 3H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 20.7, 55.6, 89.8, 92.2, 92.3, 92.3, 110.6, 112.5, 120.3, 123.2, 125.4, 125.8, 125.9, 127.8, 127.8, 128.3, 129.3, 129.8, 131.8, 132.1, 132.1, 133.7, 140.1, 160.0; mp 65−66 °C; MS (70 eV) *m*/*z* (%): 322 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O$, 322.1358; Found, 322.1358.

*1-((4-Chlorophenyl)ethynyl)-2-((2-methoxyphenyl)ethynyl)-benzene (**1f**).* Yielded 0.23 g, 78%; as a yellow solid; R_f = 0.49 (25:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.28−7.34 (m, 5H), 7.50−7.56 (m, 4H), 7.61−7.62 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.7, 89.4, 90.2, 92.1, 92.2, 110.7, 112.4, 120.5, 121.9, 125.2, 126.2, 127.8, 128.1, 128.5, 130.0, 131.6, 131.9, 132.9, 133.7, 134.2, 160.0; mp 82−83 °C; MS (70 eV) *m*/*z* (%): 344 (M+2, 32), 342 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}OCl$, 342.0811; Found, 342.0808.

*1-((4-Bromophenyl)ethynyl)-2-((2-methoxyphenyl)ethynyl)-benzene (**1g**).* Yielded 0.23 g, 70%; as a yellow solid; R_f = 0.5 (25:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.28−7.35 (m, 3H), 7.43−7.48

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J. Org. Chem. 2017, 82, 6071−6081

(m, 4H), 7.53−7.56 (m, 2H), 7.60−7.62 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.7, 89.6, 90.2, 92.1, 92.3, 110.7, 112.4, 120.5, 122.4, 122.5, 125.2, 126.2, 127.8, 128.1, 130.0, 131.5, 131.6, 131.9, 133.1, 133.7, 159.9; mp: 83−84 °C; MS (70 eV) *m*/*z* (%): 388 (M+2, 100), 386 (M^+, 100), 263 (43); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}OBr$, 386.0306; Found, 386.0305.

*1-Methoxy-2-((2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)-ethynyl)benzene (**1h**).* Yielded 0.23 g, 70%; as a brown solid; R_f = 0.5 (25:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 7.30−7.36 (m, 3H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.57−7.60 (m, 3H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 2H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.7, 90.3, 90.8, 91.9, 92.0, 110.8, 112.3, 120.5, 124.9, 125.1, 125.1, 125.2, 126.5, 127.9, 128.5, 130.1, 131.8, 131.9, 132.0, 133.7, 160.0; mp: 80−81 °C; MS (70 eV) *m*/*z* (%): 376 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{15}OF_3$, 376.1075; Found, 376.1074.

*1-Methoxy-2-((2-((4-nitrophenyl)ethynyl)phenyl)ethynyl)benzene (**1i**).* Yielded 0.19 g, 62%; as a yellow solid; R_f = 0.48 (10:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.92−6.97 (m, 2H), 7.30−7.38 (m, 3H), 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.57 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.62 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.69 (dt, *J* = 9.0, 2.0 Hz, 2H), 8.18 (dt, *J* = 9.0, 2.0 Hz, 2H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.7, 90.6, 91.4, 91.7, 93.8, 110.8, 112.1, 120.5, 123.5, 124.3, 126.7, 127.9, 128.9, 130.2, 130.4, 131.9, 132.0, 132.3, 133.6, 146.9, 159.9; mp: 82−83 °C; MS (70 eV) *m*/*z* (%): 353 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}O_3N$, 353.1052; Found, 353.1054.

*1,2-Bis((2-methoxyphenyl)ethynyl)benzene (**1j**).* Yielded 0.25 g, 87%; as a dark brown oil; R_f = 0.5 (15:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 6H), 6.88−6.92 (m, 4H), 7.28−7.32 (m, 4H), 7.56 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.59−7.60 (m, 2H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.7, 89.9, 92.4, 110.7, 112.7, 120.3, 126.0, 127.7, 129.7, 131.8, 133.9, 160.0; MS (70 eV) *m*/*z* (%): 338 (100) $[M^+]$, 321 (42), 308 (59); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O_2$, 338.1307; Found, 338.1305.

*1-Methoxy-4-methyl-2-((2-(phenylethynyl)phenyl)ethynyl)-benzene (**1k**).* Yielded 0.65 g, 65%; as a yellow solid; R_f= 0.6 (12:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.79 (s, 3H), 6.80 (d, *J* = 8.5 Hz, 1H), 7.11 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.29−7.38 (m, 6H), 7.54−7.63 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 20.1, 55.8, 88.5, 90.4, 92.0, 93.4, 110.7, 112.1, 123.4, 125.7, 126.3, 127.7, 127.8, 128.2, 128.3, 129.6, 130.4, 131.6, 131.8, 134.3, 157.9; mp 64−65 °C; MS (70 eV) *m*/*z* (%): 328 (100) $[M^+]$, 292 (44), 146 (40); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{24}H_{18}O$, 322.1358; Found 322.1358.

*4-Isopropyl-1-methoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-benzene (**1l**).* Yielded 0.65 g, 65%; as a brown solid; R_f = 0.6 (12:1 Hex/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.9 Hz, 6H), 2.81 (p, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 6.82 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.27−7.34 (m, 5H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.54−7.61 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 24.0, 33.1, 55.9, 88.5, 90.6, 91.8, 93.4, 110.7, 112.1, 123.5, 125.7, 126.3, 127.7, 127.9, 128.0, 128.2, 128.2, 131.6, 131.7, 131.8, 140.9, 158.1; mp 63−64 °C; MS (70 eV) *m*/*z* (%): 350 (100) $[M^+]$, 335 (32); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{26}H_{22}O$,350.1671; Found350.1671.

*4-(tert-Butyl)-1-methoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-benzene (**1m**).* Yielded 0.71 g, 73%; as a brown oil; R_f = 0.6 (13:1 Hex/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (d, *J* = 6.0 Hz, 10H), 3.80 (s, 3H), 6.84 (d, *J* = 9.0 Hz, 1H), 7.28−7.34 (m, 6H), 7.55−7.61 (m, 5H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 31.3, 34.0, 55.8, 88.4, 90.6, 91.6, 93.4, 110.3, 111.8, 123.5, 125.6, 126.3, 126.9, 127.7, 127.9, 128.2, 130.8, 131.6, 131.8, 131.9, 143.2, 157.8; MS (70 eV) *m*/*z* (%): 364 (100) $[M^+]$, 349 (87), 334 (36); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{27}H_{24}O$, 364.1827; Found, 364.1830.

*4-Chloro-1-methoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-benzene (**1n**).* Yielded 0.68 g, 70%; as a brown solid; R_f= 0.5 (10:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (s, 3H), 6.81 (d, *J* = 9.0 Hz, 1H), 7.25 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.31−7.36 (m, 5H), 7.52−7.60 (m, 5H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 56.1, 88.2, 88.7, 93.3, 93.6, 111.9, 111.4, 123.3, 125.2, 125.7, 125.8, 127.9, 128.2, 128.3, 128.4, 129.6, 131.8, 131.9, 133.2, 158.6; mp 63−64 °C; MS (70 eV) *m*/*z* (%): 342 (100) $[M^+]$, 292 (57), 263 (43), 132 (50); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}ClO$, 342.0811; Found, 342.0814.

*4-Bromo-1-methoxy-2-((2-(phenylethynyl)phenyl)ethynyl)-benzene (**1o**).* Yielded 0.69 g, 71%; as a brown solid; R_f= 0.5 (10:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$)δ 3.77 (s, 3H), 6.76 (d, *J* = 9.0 Hz, 1H), 7.31−7.40 (m, 6H), 7.56−7.60 (m, 4H), 7.67 (d, *J* = 2.5 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 56.0, 88.2, 88.5, 93.4, 93.6, 112.2, 112.3, 114.6, 123.3, 125.7, 125.8, 127.9, 128.2, 128.3, 131.7, 131.7, 131.9, 132.5, 136.0, 159.1; mp: 64−65 °C; MS (70 eV) *m*/*z* (%):388 (84) [M+2], 386 (80) $[M^+]$, 305 (44), 292 (100), 263 (78), 132 (72); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO$, 386.0306; Found, 386.0309.

*1-Methoxy-4-nitro-2-((2-(phenylethynyl)phenyl)ethynyl)benzene (**1p**).* Yielded 58 mg, 62%; As a yellow oil: R_f= 0.5 (5:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.95 (d, *J* = 9.2 Hz, 1H), 7.33−7.38 (m, 5H), 7.57−7.62 (m, 4H), 8.22 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.45 (d, *J* = 2.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.6, 87.4, 88.8, 93.8, 94.2, 110.3, 113.7, 123.2, 125.1, 125.7, 126.0, 128.0, 128.4, 128.6, 128.6, 129.3, 131.8, 131.9, 132.1, 164.4; mp: 110−112 °C; MS (70 eV) *m*/*z* (%): 353 (22) $[M^+]$, 57 (100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}NO_3$, 353.1052; Found, 353.1049.

*2-Iodo-1-methoxy-4-methylbenzene (**5b**).* Yielded 2.71 g, 64%; as a yellow oil; R_f = 0.7 (Hex); ^{1}HNMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.85 (s, 3H), 6.72 (d, *J* = 8.8 Hz, 1H), 7.08−7.11 (m, 1H), 7.60−7.61 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 19.9, 56.4, 85.7, 110.7, 129.9, 132.0, 139.8, 156.0; MS (70 eV) *m*/*z* (%): 248 (100) $[M^+]$, 121 (45), 106 (48), 78 (44); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for C_8H_9IO, 247.9698; Found,247.9695.

*2-Iodo-4-isopropyl-1-methoxybenzene (**5c**).* Yielded 2.53 g, 60%; As a brown oil; R_f = 0.7 (Hex); ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.21−1.23 (m, 6H), 2.82 (p, *J* = 7.2 Hz, 1H), 3.85 (s, 3H), 6.76 (d, *J* = 8.4 Hz, 1H), 7.16 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.64 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 24.0, 24.1, 32.9, 56.4, 85.9, 110.8, 127.3, 137.4, 143.2, 156.2; MS (70 eV) *m*/*z* (%): 276 (100) $[M^+]$, 261 (75),134 (55); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{10}H_{13}IO$, 276.0011; Found, 276.0011.

*4-(tert-Butyl)-2-iodo-1-methoxybenzene (**5d**).* Yielded 2.6 g, 62%; as a brown oil; R_f= 0.7 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (s, 9H), 3.86 (s, 3H), 6.77 (d, *J* = 8.8 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 31.1, 31.4, 33.9, 56.3, 85.8, 110.4, 126.3, 136.5, 145.5, 155.8; MS (70 eV) *m*/*z* (%): 290 (47) $[M^+]$, 275 (100), 148 (52); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{11}H_{15}IO$, 290.0168; Found, 290.0165.

*4-Chloro-2-iodo-1-methoxybenzene (**5e**).* Yielded 2.5 g, 58%; as a yellow oil; R_f= 0.7 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.72 (d, *J* = 8.8 Hz, 1H), 7.27 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.6, 86.1, 111.3, 126.3, 129.2, 138.6, 157.0; MS (70 eV) *m*/*z* (%): 268 (100) $[M^+]$, 253 (41), 126 (36); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for C_7H_6ClIO, 267.9152; Found, 267.9153.

*4-Bromo-2-iodo-1-methoxybenzene (**5f**).* Yielded 2.39 g, 57%; as a brown oil; R_f= 0.7 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.67 (d,*J* = 8.8 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.86 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.5, 86.6, 111.9, 113.3, 132.1, 141.0, 157.3; MS (70 eV) *m*/*z* (%): 314 (92) [M+2], 312 (100) $[M^+]$, 170 (56), 63 (64); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for C_7H_6BrIO, 311.8647; Found, 311.8647.

*2-Iodo-1-methoxy-4-nitrobenzene (**5g**).* Yielded 1.37 g, 65%; As a yellow solid: R_f= 0.55 (10:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 3.99 (s, 3H), 6.87 (d, *J* = 9.2 Hz, 1H), 8.25 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.66 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 57.1, 85.1, 109.6, 125.7, 135.1, 163.0; mp: 89−90 °C; MS (70 eV) *m*/*z* (%): 279 (100) $[M^+]$; HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for for $C_7H_6INO_3$, 278.9392; Found, 278.9392.

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J. Org. Chem. 2017, 82, 6071−6081

*((2-Methoxyphenyl)ethynyl)trimethylsilane (**6a**).* Yielded 1.60 g, 92%; As a yellow oil; R_f= 0.78 (20:1 Hex/EA); ^{1}HNMR (500 MHz, $CDCl_3$) δ 0.27 (s, 9H), 3.88 (s, 3H), 6.85 (d,*J* = 8.5 Hz, 1H), 6.88 (td, *J* = 7.5, 0.5 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 7.5, 2.0 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 0.1, 55.8, 101.2, 110.6, 112.4, 120.3, 129.9, 134.1, 160.3; MS (70 eV) *m*/*z* (%): 204 (47) [M^+], 189 (100), 159 (35); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{16}OSi$, 204.0970; Found, 204.0969.

*((2-Methoxy-5-methylphenyl)ethynyl)trimethylsilane (**6b**).* Yielded 1.51 g, 92%; as a yellow oil; R_f= 0.6 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 2.25 (s, 3H), 3.85 (s, 3H), 6.73−7.75 (m, 1H), 7.06−7.09 (m 1H), 7.26 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 0.1, 19.9, 20.2, 55.9, 56.4, 98.1, 101.4, 110.6, 110.7, 130.5, 134.6, 139.8, 158.3; MS (70 eV) *m*/*z* (%): 218 (96) [M^+], 203 (100), 175 (67), 129 (80); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{13}H_{18}OSi$, 218.1127; Found, 218.1130.

*((5-Isopropyl-2-methoxyphenyl)ethynyl)trimethylsilane (**6c**).* Yielded 1.51 g, 90%; as a yellow oil; R_f= 0.6 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 9H), 1.20−1.22 (m, 6H), 2.82 (p,*J* = 7.2 Hz, 1H), 3.85 (s, 3H), 6.77 (d, *J* = 8.4 Hz, 1H), 7.12 (dd,*J* = 8.4, 2.4 Hz, 1H), 7.30 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 0.11, 24.0, 33.1, 55.9, 97.9, 101.7, 110.7, 128.0, 132.0, 140.7, 158.5; MS (70 eV) *m*/*z* (%): 246 (82) [M^+], 231 (100), 115 (43); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{15}H_{22}OSi$, 246.1440; Found,246.1440.

*((5-(tert-Butyl)-2-methoxyphenyl)ethynyl)trimethylsilane (**6d**).* Yielded 1.6 g, 93%; as a brown oil; R_f= 0.6 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 9H), 1.29 (s, 9H), 3.85 (s, 3H), 6.7 (d, *J* = 8.8 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 0.1, 31.3, 34.0, 55.9, 97.7, 101.9, 110.4, 111.5, 126.9, 131.1, 143.0, 158.2; MS (70 eV) *m*/*z* (%): 260 (37) [M^+], 245 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{16}H_{24}OSi$, 260.1596; Found, 260.1595.

*((5-Chloro-2-methoxyphenyl)ethynyl)trimethylsilane (**6e**).* Yielded 1.51 g, 90%; as a yellow oil; R_f= 0.6 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 3.84 (s, 3H), 6.75 (d, *J* = 8.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.40 (d, *J* = 2.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ −0.1, 56.1, 99.7, 99.9, 111.8, 113.8, 125.0, 129.6, 133.4, 158.9; MS (70 eV) *m*/*z* (%): 238 (82) [M^+], 223 (100), 195 (52), 149 (36); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{15}ClOSi$,238.0581; Found, 238.0583.

*((5-Bromo-2-methoxyphenyl)ethynyl)trimethylsilane (**6f**).* Yielded 1.56 g, 91%; as a yellow oil; R_f= 0.6 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 9H), 3.83 (s, 3H), 6.70 (d, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 8.8, 2 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ −0.1, 56.0, 99.5, 100.0, 112.0, 112.2, 114.2, 114.3, 132.5, 136.2, 159.4; MS (70 eV) *m*/*z* (%): 284 (88) [M+2], 282 (85) [M^+], 267 (100), 188 (64), 173 (84); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{15}BrOSi$, 282.0076; Found, 282.0079.

*((2-Methoxy-5-nitrophenyl)ethynyl)trimethylsilane (**6g**).* Yielded 0.79 g, 88%; As a yellow solid: R_f= 0.56 (10:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.27 (s, 9H), 3.98 (s, 3H), 6.92 (d, *J* = 9.2 Hz, 1H), 8.17 (dd, *J* = 9.2, 2.8 Hz, 1H), 8.31 (d, *J* = 2.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ −0.2, 56.6, 98.4, 101.3, 110.2, 113.4, 114.0, 125.7, 129.6, 164.8; mp: 74−75 °C; MS (70 eV) *m*/*z* (%): 249 (19) [M^+], 234 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{15}NO_3Si$, 249.0821; Found, 249.0821.

*1-Ethynyl-2-methoxybenzene (**7a**).* Yielded 0.63 g, 98%; As a brown oil; R_f= 0.50 (20:1 Hex/EA);^{1}HNMR (500 MHz, $CDCl_3$) δ 3.01 (s, 1H), 3.90 (s, 3H), 6.88−6.93 (m, 2H), 7.32 (td, *J* = 8.5, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.5, 1.0 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.8, 80.1, 81.1, 110.6, 111.1, 120.4, 130.3, 134.1, 160.5; MS (70 eV) *m*/*z* (%):132 (100) [M^+], 89 (61); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for C_9H_8O, 132.0575; Found, 132.0578.

*2-Ethynyl-1-methoxy-4-methylbenzene (**7b**).* Yielded 0.9 g, 95%; As a yellow oil; R_f= 0.5 (20:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.28 (s, 1H), 3.85 (s, 3H), 6.76 (d, *J* = 8.4 Hz, 1H), 7.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 20.1, 55.8, 80.2, 80.7, 110.5, 110.7, 129.6, 130.7, 134.4, 158.5; MS (70 eV) *m*/*z* (%): 146 (100) [M^+], 145 (74); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{10}H_{10}O$, 146.0732; Found, 146.0733.

*2-Ethynyl-4-isopropyl-1-methoxybenzene (**7c**).* Yielded 1.0 g, 95%; As a brown oil; R_f= 0.5 (20:1 Hex/EA); ^{1}HNMR (400 MHz, $CDCl_3$) δ 1.21−1.22 (m, 6H), 2.83 (p, *J* = 6.8 Hz, 1H), 3.30 (s, 1H), 3.87 (s, 3H), 6.81 (d, *J* = 8.8 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 23.9, 33.0, 55.8, 80.4, 80.6, 110.5, 110.6, 128.2, 131.9, 140.8, 158.6; MS (70 eV) *m*/*z* (%): 174 (68) [M^+], 159 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{12}H_{14}O$, 174.1045; Found, 174.1047.

*4-(tert-Butyl)-2-ethynyl-1-methoxybenzene (**7d**).* Yielded 0.98 g, 95%; as a brown oil; R_f= 0.5 (20:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.30 (s, 1H), 3.88 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 31.3, 34.0, 55.8, 80.5, 80.6, 110.2, 127.2, 131.1, 143.2, 158.4; MS (70 eV) *m*/*z* (%): 188 (32) [M^+], 173 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{13}H_{16}O$, 188.1201; Found, 188.1198.

*4-Chloro-2-ethynyl-1-methoxybenzene (**7e**).* Yielded 1.0 g, 95%; as a yellow oil; R_f= 0.5 (20:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 1H), 3.89 (s, 3H), 6.81 (d, *J* = 9.2 Hz, 1H), 7.26−7.29 (m, 1H), 7.42 (d, *J* = 2.4 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.2, 78.7, 82.2, 111.8, 112.7, 125.2, 130.1, 133.6, 159.3; MS (70 eV) *m*/*z* (%): 166 (82) [M^+], 123 (39); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for C_9H_7ClO, 166.0185; Found,166.0186.

*4-Bromo-2-ethynyl-1-methoxybenzene (**7f**).* Yielded 1.0 g, 95%; as a brown oil; R_f= 0.5 (20:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 1H), 3.85 (s, 3H), 6.74 (d, *J* = 9.2 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.54 (d, *J* = 2.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.0, 78.5, 82.3, 112.0, 112.2, 113.1, 132.9, 136.3, 159.6; MS (70 eV) *m*/*z* (%): 212 (96) [M+2], 210 (100) [M^+], 167 (41), 88 (57); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for C_9H_7BrO, 209.9680; Found, 209.9683.

*2-Ethynyl-1-methoxy-4-nitrobenzene (**7g**).* Yielded 0.32 g, 91%; As a brown solid: R_f= 0.45 (5:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 3.39 (s, 1H), 4.01 (s, 3H), 6.97 (d, *J* = 9.2 Hz, 1H), 8.24 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.36 (d, *J* = 1.2 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.7, 77.6, 83.3, 110.4, 126.2, 129.8, 165.1; mp: 88−89 °C; MS (70 eV) *m*/*z* (%): 177 (43) [M^+], 88 (49), 61 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_9H_7NO_3$, 177.0426; Found, 177.0426.

*1-Iodo-2-((2-methoxyphenyl)ethynyl)benzene (**8a**).* Yielded 1.08 g, 85%; as a yellow oil; R_f= 0.62 (20:1 Hex/EA); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.98 (qd, *J* = 7.5, 1.0 Hz, 2H), 7.31−7.35 (m, 2H), 7.58 (td, *J* = 8.0, 1.5 Hz, 2H), 7.88 (dd, *J* = 8.0, 0.5 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ55.8, 89.6, 95.4, 100.9, 110.8, 112.1, 120.5, 127.7, 129.1, 130.1, 130.1, 132.5, 133.6, 138.6, 160.0; MS (70 eV) *m*/*z* (%): 334 (100)[M^+]; HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{15}H_{11}IO$, 333.9855; Found, 333.9858.

*2-((2-Iodophenyl)ethynyl)-1-methoxy-4-methylbenzene (**8b**).* Yielded 1.37 g, 67%; as a yellow oil; R_f= 0.5 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H),3.90 (s, 3H), 6.81 (d, *J* = 8.4 Hz, 1H), 7.04 (td, *J* = 7.6, 1.6 Hz, 1H), 7.12(d, *J* = 8.4, 1.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.88 (dd, *J* = 8.0, 0.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 20.2, 55.9, 89.8, 95.0, 100.9, 110.8, 111.7, 127.6, 129.0, 129.7, 130.1, 130.7, 132.5, 133.9, 138.6, 158.0; MS (70 eV) *m*/*z* (%): 348 (100) [M^+], 178 (82), 145 (55); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{16}H_{13}OI$, 348.0011; Found, 348.0010.

*2-((2-Iodophenyl)ethynyl)-4-isopropyl-1-methoxybenzene (**8c**).* Yielded 1.42 g, 70%; as a brown oil; R_f= 0.5 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25−1.27 (m, 6H), 2.89 (p, *J* = 6.8 Hz, 1H), 3.91 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 1H), 7.00 (td, *J* = 7.2,1.6 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.32 (td, *J* = 7.2, 1.2 Hz, 1H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.2 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 24.0, 33.1, 55.9, 90.0, 94.9, 100.8, 110.8, 111.7, 127.6, 128.1, 129.0, 130.1, 131.4, 132.5, 138.6, 140.8, 158.2; MS (70 eV) *m*/*z* (%): 376.0 (92) [M^+], 361

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J. Org. Chem. 2017, 82, 6071−6081

(100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{18}H_{17}IO$, 376.0324; Found, 376.0326.

*4-(tert-Butyl)-2-((2-iodophenyl)ethynyl)-1-methoxybenzene (**8d**).* Yielded 1.4 g, 70%; as a brown oil; R_f= 0.5 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 9H), 3.91 (s, 3H), 6.85 (d, J = 8.8 Hz, 1H), 6.99 (td, J = 7.6, 1.6 Hz, 1H), 7.30−7.36 (m, 2H), 7.57−7.59 (m, 2H), 7.88 (dd, J = 8.0, 0.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 31.4, 34.0, 56.0, 90.2, 94.8, 100.9, 110.6, 111.4, 127.2, 127.7, 129.1, 130.2, 130.6, 132.5, 138.7, 143.2, 158.0; MS (70 eV) m/z (%): 390 (67) [M^+], 375 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{19}H_{19}IO$, 390.0481; Found, 390.0483.

*4-Chloro-2-((2-iodophenyl)ethynyl)-1-methoxybenzene (**8e**).* Yielded 1.36 g, 65%; as a yellow oil; R_f= 0.5 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 6.83 (d, J = 8.8 Hz, 1H), 7.02 (td, J = 7.6, 2.0 Hz, 1H), 7.28 (dd, J = 8.8, 2.0 Hz, 1H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.54−7.57 (m, 2H), 7.88 (dd, J = 8.0, 1.2 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.1, 88.1, 96.3, 100.9, 112.0, 113.7, 125.2, 127.7, 129.5, 129.6, 129.8, 132.6, 132.8, 138.7, 158.7; MS (70 eV) m/z (%): 368 (100) [M^+], 205 (82), 178 (79), 163 (52); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{15}H_{10}ClIO$, 367.9465; Found, 367.9466.

*4-Bromo-2-((2-iodophenyl)ethynyl)-1-methoxybenzene (**8f**).* Yielded 1.24 g, 68%; as a yellow oil; R_f= 0.5 (50:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.78 (d, J = 8.8 Hz, 1H), 7.01 (td, J = 7.2, 1.6 Hz, 1H), 7.32 (td, J = 7.6, 1.2 Hz, 1H), 7.41 (dd, J = 8.8, 2.4 Hz, 1H), 7.55 (dd, J = 7.2, 1.2 Hz, 1H), 7.67 (d, J = 2.8 Hz, 1H), 7.87 (dd, J = 8.4, 0.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.1, 88.0, 96.4, 100.9, 112.2, 112.4, 127.7, 129.5, 129.6, 132.6, 132.7, 135.7, 138.7, 159.2; MS (70 eV) m/z (%):414 (40) [M+2], 412 (42) [M^+], 205 (100), 178 (57), 163 (66); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{15}H_{10}BrIO$, 411.8960; Found, 411.8957.

*2-((2-Iodophenyl)ethynyl)-1-methoxy-4-nitrobenzene (**8g**).* Yielded0.21 g, 50%; As a yellow solid: R_f= 0.52 (10:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H), 6.98 (d, J = 9.2 Hz, 1H), 7.05 (td, J = 7.6, 1.6 Hz, 1H), 7.36 (td, J = 7.6, 1.2 Hz, 1H), 7.57 (dd, J = 7.6, 1.6 Hz, 1H), 7.90 (dd, J = 8.0, 0.8 Hz, 1H), 8.24 (dd, J = 9.2, 2.8 Hz, 1H), 8.44 (d, J = 2.8 Hz, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 56.6, 86.9, 97.1, 100.8, 110.4, 113.4, 125.9, 127.8, 129.0, 129.2, 129.9, 132.9, 138.9, 164.6; mp: 96−97 °C; MS (70 eV) m/z (%): 379 (84) [M^+], 61 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{15}H_{10}INO_3$, 378.9705; Found, 378.9705.

General Procedure for Iodine-Mediated Cyclization Reactions. *Represented Procedure for Preparation of Compounds **3a** and **9a**.* To a solution of compound **1a** (50 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) was added iodine (81 mg, 0.32 mmol). The resulting solution was stirred at room temperature for 4 h, quenched by 10% of $Na_2S_2O_{3(aq)}$ (30 mL) and extracted by EtOAc (two 30 mL portions). The combined organic layers were dried over $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography on silica gel to give **3a** (7.5 mg, 11%) and **9a** (39 mg, 82%).

General Procedure for $CuBr_2$-Mediated Cyclization Reaction. *Represented Procedures for the Preparation of Compound **4a**.* To a solution of compound **1a** (50 mg, 0.16 mmol) in CH_3CN (5 mL) was added $CuBr_2$ (71 mg, 0.32 mmol). The resulting solution was stirred at reflux for 4 h, quenched by brine (30 mL), and extracted by EtOAc (30 mL × 2). The combined organic layers were dried over $MgSO_4$. After filtration and removal of solvent, the residue was purified by column chromatography on silica gel to give **4a** (47 mg, 77%).

*11-Iodo-6-phenylindeno[1,2-c]chromene (**3a**).* Yielded 51 mg, 75%; as a yellow solid: R_f = 0.60 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.45−7.55 (m, 4H), 7.59−7.67 (m, 4H), 7.83−7.86 (m, 2H), 9.37−9.41 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 73.0, 117.8, 119.6, 121.1, 121.8, 123.6, 123.7, 124.2, 127.2, 128.7, 128.7, 128.9, 129.6, 129.6, 130.8, 133.3, 144.2, 150.3, 151.8; mp: 106−106 °C; MS (70 eV) m/z (%): 420 (M^+,8), 61 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{22}H_{13}OI$, 420.0011; Found, 420.0014.

*11-Iodo-6-(4-methoxyphenyl)indeno[1,2-c]chromene (**3b**).* Yielded 43 mg, 65%; as a yellow solid: R_f = 0.60 (10:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.10−7.16 (m, 3H), 7.45−7.54 (m, 5H), 7.63 (d, J = 8.0 Hz, 1H), 7.78−7.82 (m, 2H), 9.37−9.40 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 55.5, 72.5, 114.2, 114.3, 117.7, 17.8, 119.6, 121.0, 121.7, 123.5, 123.6, 124.0, 125.4, 127.0, 128.6, 128.8, 129.7, 131.2, 144.1, 150.2, 152.0, 161.5; mp: 140−142 °C; MS (70 eV) m/z (%): 450 (M^+, 100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{23}H_{15}O_2I$, 450.0117; Found, 450.0115.

*11-Iodo-6-(p-tolyl)indeno[1,2-c]chromene (**3c**).* Yielded 49 mg, 72%; as a yellow oil: R_f = 0.61 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.13 (t, J = 8.4 Hz, 1H), 7.41−7.53 (m, 7H), 7.63 (d, J = 6.8 Hz, 1H), 7.73−7.75 (m, 2H), 9.38−9.40 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 21.7, 72.7, 117.8, 118.0, 119.6, 121.1, 123.6, 123.6, 124.1, 127.0, 128.6, 129.5, 129.5, 130.4, 141.1, 144.1, 150.3, 152.1; mp: 164−166 °C; MS (70 eV) m/z (%): 434 (M^+, 100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{23}H_{15}OI$, 434.0168; Found, 434.0168.

*11-Iodo-6-(m-tolyl)indeno[1,2-c]chromene (**3d**).* Yielded 45 mg, 65%; as a yellow oil: R_f = 0.58 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 7.12 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.43−7.54 (m, 6H), 7.61−7.63 (m, 3H), 9.37−9.40 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 21.4, 72.8, 117.8, 118.1, 119.6, 121.1, 121.7, 123.6, 123.7, 124.1, 126.7, 127.1, 128.7, 128.7, 129.7, 130.0, 131.5, 133.1, 138.7, 144.2, 150.3, 152.1; mp: 203−205 °C; MS (70 eV) m/z (%): 434(M^+, 7), 61 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{23}H_{15}OI$, 434.0168; Found, 434.0169.

*11-Iodo-6-(o-tolyl)indeno[1,2-c]chromene (**3e**).* Yielded 47 mg, 70%; as a yellow oil: R_f = 0.60 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33(s, 3H), 6.83 (d, J = 8.0 Hz, 1H), 7.11 (t, J = 6.8 Hz, 1H), 7.42−7.59 (m, 8H), 7.64 (d, J = 7.6 Hz, 1H), 9.41−9.43 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 19.4, 73.0, 117.8, 119.0, 119.8, 120.8, 121.6, 123.6, 123.9, 124.2, 126.3, 127.1, 128.4, 128.7, 129.6, 129.8, 130.6, 130.8, 132.6, 137.5, 144.1, 150.4, 151.5; mp: 170−172 °C; MS (70 eV) m/z (%): 434 (M^+,28),61 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{23}H_{15}OI$, 434.0168; Found, 434.0171.

*6-(4-Chlorophenyl)-11-iodoindeno[1,2-c]chromene (**3f**).* Yielded 52 mg, 78%; as a yellow solid: R_f = 0.50 (20:1 Hex/EtOAc);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.46−7.52 (m, 4H), 7.58−7.64 (m, 3H), 7.77−7.81 (m, 2H), 9.36−9.40 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 73.5, 117.7, 119.5, 120.9, 121.9, 123.6, 123.9, 124.3, 127.4, 128.6, 128.8, 129.2, 129.3, 131.0, 131.6, 137.0, 144.3, 150.1; mp: 160−162 °C; MS (70 eV) m/z (%): 456 (M+2, 32), 454 (M^+,100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{22}H_{12}OClI$, 453.9621; Found, 453.9621.

*6-(4-Bromophenyl)-11-iodoindeno[1,2-c]chromene (**3g**).* Yielded 46 mg, 72%; as a brown solid: R_f = 0.50 (20:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 6.8 Hz, 1H) 7.36 (d, J = 8.4 Hz, 1H), 7.47−7.52 (m, 4H), 7.63 (d, J = 7.6 Hz, 1H), 7.71−7.77 (m, 4H), 9.36−9.39 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 73.8, 117.7, 118.4, 119.5, 121.0, 121.9, 123.6, 123.9, 124.3, 125.3, 127.4, 128.6, 128.8, 129.3, 131.2, 132.1, 132.2, 144.3, 150.1, 150.4; mp: 158−160 °C; MS (70 eV) m/z (%): 500 (M+2, 34), 498 (M^+, 34), 454 (50), 57 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{22}H_{12}OBrI$, 497.9116; Found, 497.9117.

*11-Iodo-6-(4-(trifluoromethyl)phenyl)indeno[1,2-c]chromene (**3h**).* Yielded 55 mg, 84%; As a brown solid: R_f= 0.50 (20:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.48−7.52 (m, 4H), 7.64 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 9.37−9.40 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 74.1, 117.7, 119.5, 120.9, 122.0, 123.6, 124.0, 124.4, 125.8, 125.9, 125.9, 127.6, 128.6, 128.9, 129.1, 130.1, 144.4, 150.1; mp: 120−122 °C; MS (70 eV) m/z (%): 488 (M^+, 13), 61 (100); HRMS (EI-magnetic sector) m/z: $[M]^+$ Calcd for $C_{23}H_{12}OF_3I$, 487.9885; Found, 487.9884.

*11-Iodo-6-(4-nitrophenyl)indeno[1,2-c]chromene (**3i**).* Yielded 46.1 mg, 70%; As a brown solid: R_f= 0.52 (10:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.15 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.49−7.54 (m, 4H), 7.64 (d, J = 8.0 Hz, 1H), 8.04−8.08 (m, 2H), 8.46−8.50 (m, 2H), 9.37−9.40 (m, 1H); ^{13}C{H}NMR (100

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J. Org. Chem. 2017, 82, 6071−6081

MHz, $CDCl_3$) δ 74.8, 117.7, 119.4, 120.8, 122.2, 123.7, 124.1, 124.2, 124.6, 127.9, 128.5, 128.8, 129.0, 130.9, 139.4, 144.6, 148.5, 150.0; mp: 142−144 °C; MS (70 eV) *m*/*z* (%): 465 (M^+, 100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{12}O_3NI$, 464.9862; Found, 464.9865.

11-Bromo-6-phenylindeno[1,2-c]chromene (***4a***). Yield 47 mg, 77%; As an orange solid; R_f= 0.5 (25:1 Hex/EA); ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.8 Hz, 1H), 7.39−7.50 (m, 5H), 7.61−7.70 (m, 4H), 7.82−7.85 (m, 2H), 9.08−9.11 (m, 1H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 102.5, 116.5, 117.6, 119.3, 121.2, 123.7, 124.3, 124.6, 124.7, 127.1, 128.5, 128.8, 129.0, 129.5, 130.8, 133.4; mp: 83−84 °C; MS (70 eV) *m*/*z* (%): 374 (98) [M+2], 372 (100) [M^+], 292 (85), 263 (62), 146 (65); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{13}BrO$, 372.0150; Found, 372.0150.

11-Bromo-6-(4-methoxyl)indeno[1,2-c]chromene (***4b***). Yielded 17 mg, 14%; as an orange solid; R_f= 0.5 (25:1 Hex/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (s, 3H), 7.10−7.17 (m, 3H), 7.43−7.53 (m, 5H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 6.9 Hz, 2H), 9.08 (dd, *J* = 6.6, 2.4 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.5, 102.0, 114.2, 116.1, 117.6, 119.2, 119.3, 121.2, 123.5, 124.5, 124.7, 125.6, 126.9, 128.4, 129.1, 131.2, 141.6, 150.1, 152.3, 161.5; mp 151−152 °C; MS (70 eV) *m*/*z* (%): 404 (84) [M+2], 402 (85) [M^+], 280 (100); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO_2$, 402.0255; Found, 402.0258.

11-Bromo-6-(p-tolyl)indeno [1,2-c]chromene (***4c***). Yielded 108 mg, 90%; as an orange solid; R_f= 0.6 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (s, 3H), 7.13 (td, *J* = 7.5, 0.6 Hz, 1H), 7.40−7.50 (m, 7H), 7.67−7.75 (m, 3H), 9.07−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.7, 102.2, 116.3, 117.6, 119.2, 119.3, 121.3, 123.6, 124.4, 124.5, 124.7, 127.0, 128.5, 129.1, 129.5, 129.5, 130.5, 141.1, 141.6, 150.2, 152.5; mp 151−152 °C; MS (70 eV) *m*/*z* (%): 388 (100) [M+2], 386 (98) [M^+];HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO$, 386.0306; Found, 386.0307.

11-Bromo-6-(m-tolyl)indeno[1,2-c]chromene (***4d***). Yielded 108 mg, 90%; as a yellow solid; R_f= 0.5 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 7.13 (td, *J* = 7.2, 0.9 Hz, 1H), 7.40−7.51 (m, 7H), 7.51−7.69 (m, 3H), 9.07−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.4, 102.3, 116.4, 117.6, 119.2, 119.3, 121.2, 123.6, 124.3, 124.5, 124.7, 126.7, 127.0, 128.5, 128.7, 129.0, 130.0, 131.5, 133.2, 138.7, 141.6, 150.1, 152.4; mp 114−115 °C; MS (70 eV) *m*/*z* (%): 388 (100) [M+2], 386 (98) [M^+]; HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO$, 386.0306; Found, 386.0304.

11-Bromo-6-(o-tolyl)indeno[1,2-c]chromene (***4e***). Yielded 111 mg, 93%; as a yellow oil; R_f= 0.5 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 6.85 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.09 (td, *J* = 7.2, 1.2 Hz, 1H), 7.40−7.56 (m, 8H), 7.67 (dt, *J* = 7.6, 0.8 Hz, 1H), 9.08−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 19.4, 102.4, 117.7, 119.2, 119.4, 121.0, 123.9, 124.0, 124.6, 124.8, 126.3, 127.0, 128.5, 129.0, 129.9, 130.6, 130.8, 131.0, 132.7, 137.6, 141.6, 150.3, 151.9; MS (70 eV) *m*/*z* (%): 388 (100) [M+2], 386 (98) [M^+]; HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO$, 386.0306; Found, 386.0303.

11-Bromo-6-(4-chlorophenyl)indeno[1,2-c]chromene (***4f***). Yielded 106 mg, 90%; as an orange solid; R_f= 0.6 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (td, *J* = 9.0, 0.9 Hz, 1H), 7.40−7.45 (m, 5H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 9.07−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 102.9, 116.8, 117.5, 119.2, 119.4, 121.1, 123.8, 124.2, 124.7, 124.7, 127.4, 128.6, 128.7, 129.2, 131.0, 131.8, 137.0, 141.8, 150.0, 150.7; mp 181−182 °C; MS (70 eV) *m*/*z* (%): 410 (24) [M+4], 408 (94) [M +2], 406 (72) [M^+], 292 (100), 263 (70), 146 (70); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{12}BrClO$, 405.9760; Found, 405.9760.

11-Bromo-6-(4-bromophenyl)indeno[1,2-c]chromene (***4g***). Yielded 101 mg, 90%; as an orange solid; R_f= 0.6 (Hex);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 8.0, 1.2 Hz, 1H), 7.41−7.50 (m, 5H), 7.68−7.77 (m, 5H), 9.07−9.09 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 103.0, 116.8, 117.5, 119.2, 119.5, 121.1, 123.9, 124.3, 124.7, 124.8, 125.3, 127.4, 128.6, 128.7, 131.0, 131.2, 132.2, 132.3, 141.8, 150.0, 150.7; mp 141−142 °C; MS (70 eV) *m*/*z* (%): 454 (38) [M+4], 452 (81) [M+2], 450 (38) [M^+], 292 (100), 263 (62), 146 (78), 132 (42); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{12}Br_2O$, 449.9255; Found, 449.9256.

11-Bromo-6-(4-(trifluoromethyl)phenyl)indeno[1,2-c]chromene (***4h***). Yielded 77 mg, 65%; as an orange solid; R_f= 0.6 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (td, *J* = 8.4, 1.2 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.44−7.51 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 9.07−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 103.4, 117.5, 117.6, 119.2, 119.6, 120.8, 121.0, 123.9, 124.0, 124.2, 124.8, 125.1, 125.9, 127.6, 128.5, 128.7, 129.0, 130.0, 130.1, 130.4, 141.9, 150.0; mp 177−178 °C; MS (70 eV) *m*/*z* (%): 442 (98) [M+2], 440 (100) [M^+], 360 (43), 292 (81), 263 (60), 146 (42); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{12}BrF_3O$, 440.0024; Found, 440.0026.

11-Bromo-6-(4-nitrophenyl)indeno [1,2-c]chromene (***4i***). Yielded 29 mg, 25%; as an orange solid; R_f= 0.5 (20:1 Hex/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.46−7.53 (m, 4H), 7.70 (d, *J* = 7.8 Hz, 1H), 8.03−8.08 (m, 2H), 8.46−8.51 (m, 2H), 9.07−9.10 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ104.0, 117.5, 119.1, 119.7, 120.9, 121.0, 124.1, 124.2, 124.2, 124.8, 125.0, 127.9, 128.2, 128.9, 130.8, 130.9, 139.5, 142.1, 148.9, 149.1, 149.9; mp 210−211 °C; MS (70 eV) *m*/*z* (%):419 (79) [M+2], 417 (80) [M^+], 373 (42), 292 (100), 263 (69), 207 (69); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{22}H_{12}BrNO_3$, 417.0001; Found, 417.0002.

11-Bromo-6-(2-methoxyphenyl)indeno[1,2-c]chromene (***4j***). Yielded 110 mg, 91%; as a yellow solid; R_f= 0.5 (15:1 Hex/EA); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 6.97 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.11 (td, *J* = 7.2, 1.2 Hz, 1H), 7.13−7.20 (m, 2H), 7.43−7.69 (m, 7H), 9.08−9.11 (m, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.8, 102.1, 111.8, 117.8, 117.9, 119.1, 119.5, 120.9, 121.1, 122.3, 123.6, 124.2, 124.4, 124.7, 126.8, 128.4, 129.2, 131.3, 132.2, 141.5, 149.7, 150.5, 157.8; mp 48−49 °C; MS (70 eV) *m*/*z* (%): 404 (100) [M+2], 402 (98) [M^+]; HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO_2$, 402.0255; Found, 402.0258.

11-Bromo-2-methyl-6-phenylindeno[1,2-c]chromene (***4k***). Yielded 108 mg, 90%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.11 (td, *J* = 7.2, 1.2 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38−7.47 (m, 3H), 7.60−7.69 (m, 4H), 7.82−7.84 (m, 2H), 8.87 (s, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.5, 102.0, 117.3, 119.0, 119.2, 121.2, 123.5, 124.4, 124.5, 127.0, 128.8, 128.9, 129.0, 129.4, 129.6, 130.7, 134.2, 148.3, 152.2; mp 155−156 °C; MS (70 eV) *m*/*z* (%): 388 (98) [M+2], 386 (100) [M^+]; HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{15}BrO$, 386.0306; Found, 386.0307.

11-Bromo-2-isopropyl-6-phenylindeno[1,2-c]chromene (***4l***). Yielded 96 mg, 80%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (d, *J* = 6.9 Hz, 6H), 3.11 (p, *J* = 6.9 Hz, 1H), 7.11 (td, *J* = 7.8, 0.9 Hz, 1H), 7.34−7.48 (m, 4H), 7.58−7.69 (m, 4H), 7.81−7.84 (m, 2H), 8.96 (d, *J* = 7.8 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 24.2, 34.1, 101.9, 116.4, 117.4, 119.2, 119.2, 121.2, 122.0, 123.5, 124.6, 127.0, 127.0, 128.8, 129.5, 130.7, 133.5, 141.7, 145.3, 148.5, 152.2; mp 92−93 °C; MS (70 eV) *m*/*z* (%): 416 (100) [M+2], 414 (96) [M^+], 401 (40), 320 (78); HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{25}H_{19}BrO$, 414.0619; Found, 414.0620.

11-Bromo-2-(tert-butyl)-6-phenylindeno[1,2-c]chromene (***4m***). Yielded 98 mg, 85%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 9H), 7.11 (td, *J* = 8.1, 0.9 Hz, 1H); 7.37−7.47 (m, 3H), 7.53 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.59−7.70 (m, 4H), 7.80−7.84 (m, 2H), 9.15 (d, *J* = 2.1 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 31.5, 35.0, 101.8, 116.4, 117.7, 118.5, 119.2, 121.0, 121.2, 123.5, 124.8, 126.2, 127.0, 128.8, 129.0, 129.5, 130.7, 133.5, 141.7, 147.6, 148.2, 152.2; mp 110−111 °C; MS (70 eV) *m*/*z* (%): 430 (100) [M+2], 428 (96) [M^+], 415 (58), 334 (63), 153 (100);HRMS (EI-magnetic sector) *m*/*z*: $[M]^+$ Calcd for $C_{26}H_{21}BrO$, 428. 0776; Found, 428.0774.

11-Bromo-2-chloro-6-phenylindeno[1,2-c]chromene (***4n***). Yielded 104 mg, 88%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.8, 0.9 Hz, 1H), 7.40−7.50 (m, 5H), 7.59−7.70 (m, 4H), 7.81−7.84 (m, 2H), 9.04−9.15 (m, 1H);

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^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 103.7, 116.4, 119.0, 119.6, 120.6, 121.3, 123.2, 124.0, 124.1, 127.4, 128.5, 128.9, 128.9, 129.5, 129.8, 130.9, 133.0, 141.5, 148.5, 152.0; mp 160−161 °C; MS (70 eV) *m*/*z* (%): 410 (25) [M+4], 408 (100) [M+2], 406 (75) [M$^+$], 292 (79), 263 (70), 132 (55); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{22}H_{12}BrClO$, 405.9760; Found, 405.9762.

*2,11-Dibromo-6-phenylindeno[1,2-c]chromene (**4o**).* Yielded 102 mg, 87%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (td,*J* = 8.1, 1.2 Hz, 1H), 7.36−7.50 (m, 3H), 7.54−7.70 (m, 5H), 7.81−7.84 (m, 2H), 9.20 (d,*J* = 2.1 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 103.8, 116.5, 117.4, 119.3, 119.6, 121.0, 121.3, 123.0, 124.1, 127.0, 127.4, 128.9, 129.5, 130.9, 131.3, 133.0, 141.5, 149.0, 151.9; mp 160−161 °C; MS (70 eV) *m*/*z* (%): 454 (50) [M +4], 452 (100) [M+2], 450 (50) [M$^+$], 292 (94), 263 (100), 132 (84); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{22}H_{12}$ Br_2O, 449.9255 Found, 449.9258.

*6,6′-Diphenyl-11,11′-biindeno[1,2-c]chromene (**9a**).* Yielded 39 mg, 82%; As a yellow solid: R_f= 0.35 (50:1 Hex/EtOAc); ^{1}HNMR (400 MHz, $CDCl_3$) δ 6.93 (t, *J* = 7.8 Hz, 2H), 7.09−7.13 (m, 2H), 7.19−7.28 (m, 6H), 7.47 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.62−7.70 (m, 10H), 8.01−8.04 (m, 4H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 117.2, 117.9, 120.0, 120.5, 121.6, 122.8, 124.8, 125.8, 126.0, 126.7, 127.6, 128.8, 129.7, 130.3, 130.6, 134.0, 134.4, 150.2, 152.5; mp: 102−105 °C; MS (70 eV) *m*/*z* (%): 586 (1) [M$^+$], 85 (100), 71 (100), 57 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{44}H_{26}O_2$, 586.1933; Found, 586.1935.

*6,6′-Di-p-tolyl-11,11′-biindeno[1,2-c]chromene (**9c**).* Yielded 41 mg, 78%; As a yellow solid: R_f= 0.30 (50:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 6H), 6.93 (t, *J* = 7.6 Hz, 2H), 7.11−7.15 (m, 2H), 7.20−7.28 (m, 6H), 7.45−7.50 (m, 6H), 7.65 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.92−7.94 (m, 4H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 21.7, 117.2, 117.7, 119.8, 120.5, 120.5, 121.6, 122.7, 124.7, 125.8, 126.0, 126.6, 127.5, 129.5, 129.6, 130.4, 131.1, 140.8, 143.3, 150.2, 152.7; mp: 268−270 °C; MS (70 eV) *m*/*z* (%): 614 (100) [M$^+$], 322 (43); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{46}H_{30}O_2$, 614.2246; Found, 614.2245.

*6,6′-Bis(4-chlorophenyl)-11,11′-biindeno[1,2-c]chromene (**9f**).* Yielded 20 mg, 36%; As a yellow solid: R_f= 0.36 (20:1 Hex/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (t, *J* = 8.0 Hz, 2H), 7.14−7.15 (m, 2H), 7.22−7.28 (m, 6H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.61−7.68 (m, 8H), 7.96−7.99 (m, 4H); ^{13}C{H}NMR (100 MHz, $CDCl_3$) δ 117.2, 120.1, 120.6, 121.5, 123.1, 124.9, 125.9, 127.0, 127.8, 129.2, 130.1, 131.2, 132.4, 136.7, 143.4, 150.3, 151.1; mp: 103−105 °C; MS (70 eV) *m*/*z* (%): 656 (19) [M+2], 654 (25) [M$^+$], 57 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{44}H_{24}Cl_2O_2$, 654.1153; Found, 654.1153.

*(Z)-3-Bromo-1-(bromo(2-methoxyphenyl)methylene)-2-(4-methoxyphenyl)-1H-indene (**10b**).* Yielded 124 mg, 83%; as a yellow solid; R_f= 0.5 (10:3:3 Hex/DCM/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 3.69 (s, 3H), 6.36−6.49 (m, 3H), 6.60−6.61 (m, 2H), 6.87−6.97 (m, 3H), 7.34−7.46 (m, 3H), 8.75 (d,*J* = 7.5 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 55.0, 55.1, 110.2, 120.0, 120.4, 124.8, 125.5, 126.6, 126.7, 127.0, 128.0, 130.2, 130.3, 130.5, 131.0, 131.6, 135.3, 139.1, 140.3, 141.3, 154.8, 158.2; mp48−49 °C; MS (70 eV) *m*/*z* (%): 450 (3) [M+4], 498 (7) [M+2], 496 (3) [M$^+$], 338 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{24}H_{18}Br_2O_2$, 495.9674;Found, 495.9674.

*(Z)-3-Bromo-1-(bromo(2-methoxy-5-nitrophenyl)methylene)-2-phenyl-1H-indene (**10p**).* Yielded 29 mg, 20%; as a green oil; R_f= 0.5 (10:1 Hex/EA); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 3H), 6.47 (d, *J* = 9.0 Hz, 1H), 6.88−6.96 (m, 4H), 7.35−7.51 (m, 3H), 7.76−7.85 (m, 2H), 8.72 (d, *J* = 9.0 Hz, 1H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 56.1, 110.3, 120.8, 121.9, 124.9, 126.2, 127.0, 127.2, 127.2, 127.3, 127.3, 128.7, 129.4, 130.4, 130.6, 134.8, 160.2; MS (70 eV) *m*/*z* (%): 515 (2) [M+4], 513 (4) [M+2], 511 (2) [M$^+$], 353 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{23}H_{15}Br_2NO_3$, 510.9419; Found, 510.9422.

*6-(4-Bromophenyl)-2,2′-dimethyl-6′-phenyl-11,11′-biindeno[1,2-c]chromene (**11k**).* Yielded 43 mg, 35%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ1.97 (s, 3H), 2.01 (s, 3H), 7.09−7.14 (m, 4H), 7.22−7.23 (m, 2H), 7.35−7.41 (m, 5H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.69−7.75 (m, 7H), 8.01−8.05 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.1, 21.2, 116.3, 116.9, 116.9, 117.7, 119.0, 119.0, 119.9, 120.0, 120.5, 121.5, 121.8, 122.7, 124.4, 125.9, 126.2, 134.0, 134.1, 134.3, 141.9, 143.1, 148.4, 148.4, 152.6, 153.5; mp 263−264 °C; MS (70 eV) *m*/*z* (%): 694 (8) [M+2], 692 (6) [M$^+$], 136 (44), 95 (78), 69 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{46}H_{29}BrO_2$, 692.1351; Found, 692.1354.

*6-(4-Bromophenyl)-2,2′-diisopropyl-6′-phenyl-11,11′-biindeno-[1,2-c]chromene (**11l**).* Yielded 45 mg, 30%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.67−0.73 (m, 12H), 2.52 (q, *J* = 6.9 Hz, 2H), 7.10−7.39 (m, 9H), 7.47 (d, *J* = 1.8 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.62−7.72 (m, 7H), 7.95−7.98 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 23.0, 23.2, 23.3, 33.1, 33.1, 116.2, 116.7, 116.8, 117.6, 119.1, 119.1, 119.9, 119.9, 120.8, 121.6, 122.2, 122.7, 123.3, 123.6, 124.4, 126.1, 126.3, 126.6, 126.7, 126.9, 128.8, 129.0, 129.2, 129.5, 129.7, 130.2, 130.5, 130.9, 131.9, 133.6, 134.1, 142.0, 143.2, 144.7, 144.9, 148.6, 148.6, 152.6, 153.6; mp 263−264 °C; MS (70 eV) *m*/*z* (%): 750 (23) [M+2], 748 (19) [M$^+$], 109 (52), 81 (91), 69 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{50}H_{37}BrO_2$, 748.1977 Found, 748.1979.

*6,6′-Bis(4-bromophenyl)-2,2′-dimethyl-11,11′-biindeno[1,2-c]-chromene (**12k**).* Yielded 44 mg, 37%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 6H), 7.07−7.14 (m, 4H), 7.32−7.35 (m, 4H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.72−7.75 (m, 8H), 8.00−8.03 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 21.2, 116.4, 116.8, 117.0, 118.3, 119.8, 121.6, 124.4, 125.9, 126.3, 129.0, 129.1, 129.3, 129.6, 131.0, 131.8, 133.5, 134.5, 141.7, 148.4, 153.7; mp 124−125 °C; MS (70 eV) *m*/*z* (%): 774 (2) [M+4], 772 (4) [M+2], 770 (2) [M$^+$], 81 (85), 55 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{46}H_{28}Br_2O_2$, 770.0456; Found, 770.0457.

*6,6′-Bis(4-bromophenyl)-2,2′-diisopropyl-11,11′-biindeno[1,2-c]-chromene (**12l**).* Yielded 36 mg, 35%; as an orange solid; R_f= 0.7 (Hex); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74 (dd, *J* = 6.6, 1.2 Hz, 12H), 2.52 (q, *J* = 6.9 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 4H), 7.33−7.40 (m, 4H), 7.46 (d, *J* = 2.1 Hz, 2H), 7.70−7.72 (m, 8H), 7.94−7.97 (m, 4H); ^{13}C{H}NMR (125 MHz, $CDCl_3$) δ 23.0, 23.3, 33.1, 116.3, 116.8, 116.8, 118.4, 119.8, 122.0, 123.3, 124.5, 126.5, 127.1, 129.0, 129.3, 129.5, 131.0, 131.9, 133.5, 141.8, 145.1, 148.6, 153.8; mp 271−272 °C; MS (70 eV) *m*/*z* (%): 830 (6) [M+4], 828 (12) [M+2], 826 (6) [M$^+$], 81 (85), 55 (100); HRMS (EI-magnetic sector) *m*/*z*: [M]$^+$ Calcd for $C_{50}H_{36}Br_2O_2$, 826.1082; Found, 826.1084.

Computational Methods. All the DFT calculations were accomplished with the Gaussian 09 program.[15] The M06-2X functional[16] combined with the 6-31G* basis set for hydrogen, carbon, nitrogen, oxygen, sulfur, and MIDI! basis set for iodine were adopted in the present calculations. The full-electron basis MIDI! was selected for iodine since it is superior to commonly used pseudopotential basis LANL2DZ and SDDALL in reproducing experimental bond length of iodine−iodine and carbon−iodine bonds (Figure S1). Numerical integrations were done using ultrafine grid. Geometry optimization and frequency analysis were performed in the solution environment (solvent = THF, ε = 7.4257) simulated by the integral equation formalism variant of polarizable continuum model (IEF-PCM).[17] The obtained equilibrium and transition-state structures have been confirmed to be characterized by all positive vibrational frequencies and one imaginary vibrational mode, respectively. The adequacy of the transition states can be distinctly identified by visualizing the imaginary modes, which clearly display a nuclear motion along the ring-closure coordinate. Free energy corrections were made at the standard conditions of 1 atm and 298.15 K.

■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR spectra for all new compounds; crystallographic data of compounds **3g** and **12k**; and DFT optimized geometries and energies (PDF)

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Notes

The authors declare no competing financial interest.

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