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Synthesis of Dibenzocyclohepten-5-ones by Electrophilic Iodocyclization of 1-([1,1′-Biphenyl]-2-yl)alkynones

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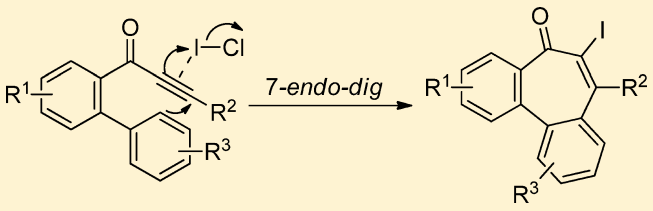
Supporting Information

ABSTRACT: A synthesis of iodo-substituted dibenzocyclohepten-5-ones by the iodine monochloride (or iodine)-induced intramolecular 7-endo-dig cyclization of 1-([1,1′-biphenyl]-2-yl)alkynones is reported. Detailed investigations on the substituent effects during the electrophilic iodocyclization of the alkynones show that they play a crucial role in determining the reaction pathways of the cyclization. By modifying the substitution pattern on the alkynone substrates, the cyclization takes place regioselectively, leading to either dibenzocyclohepten-5-ones, via a 7-endo-dig cyclization, or spiroconjugated compounds, via a 6-endo-dig cyclization.



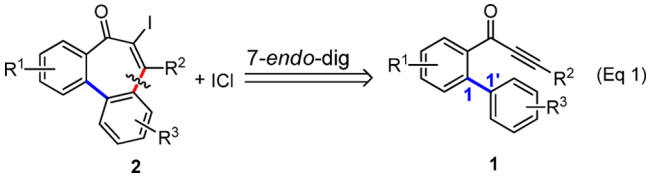
INTRODUCTION

Colchicine, a naturally occurring molecule isolated from meadow saffron (*Colchicum autumnale*), has long been known for its potent antitumor effects;[1] however, because of its cytotoxicity, its therapeutic applications have been rather limited. Allocolchicine, a degradation product of colchicine, has recently attracted the attention of medicinal chemists. Both allocolchicine and its derivatives display potent anticancer effects by inhibiting tubulin polymerization (Figure 1),[2] with the added benefit of having a more-limited toxicity than their parent molecule. Accordingly, various synthetic methods producing allocolchicine analogues have been developed, including Wulff's Diels–Alder reaction–aromatization approach,[3] Fagnou's palladium-catalyzed intramolecular direct arylation,[4] DeShong's phenanthrol ring expansion,[5] Green's intramolecular Nicholas reaction,[6] Leonard's Ziegler–Ullmann coupling process,[7] Kocienski's sequential Suzuki–Miyaura coupling–asymmetric reduction[8] preceded by his earlier synthesis involving an intramolecular biaryl oxidative coupling,[9] Hanna's sequential ring-closing enyne metathesis–Diels–Alder reactions,[10] and a thallium(III)-mediated intramolecular nonphenolic biaryl oxidative coupling originally developed by Sawyer[11] and utilized in the asymmetric synthesis of (−)-*N*-acetylcolchinol by Chong.[12]

From a synthetic point-of-view, dibenzocyclohepten-5-one is the core structure of allocolchicine. However, there are only a few known methods for the synthesis of dibenzocyclohepten-5-ones, these being limited to Choi's sequential Suzuki–Miyaura coupling–aldol condensation synthesis,[13] Satyanarayana's palladium-catalyzed domino homobiaryl coupling reaction,[14] and Waldvogel's oxidative aryl–aryl coupling of 1,3-diarylpropene derivatives.[15] A facile synthetic route toward this core structure is thus still in high demand.

Halogen-induced electrophilic cyclization reactions have emerged as an indispensable method for the synthesis of cyclic compounds, as they occur under relatively mild conditions. Moreover, these reactions provide a facile approach toward the synthesis of a variety of functionally substituted heterocyclic and carbocyclic compounds, by the ready modification of the halide functionality, and have therefore attracted a significant amount of attention from synthetic chemists.[16,17]

On the basis of our continuing interest in synthesizing biologically interesting cyclic compounds by the cyclization of functionally substituted alkynes,[18] our group has designed an ICl-induced intramolecular cyclization of 1-([1,1′-biphenyl]-2-yl)alkynones (**1**). From the outset of our experimentation, we envisioned that a 7-endo-dig cyclization of substrate **1** would take place in the presence of ICl, leading to the formation of 6-iododibenzocyclohepten-5-ones (**2**) (eq 1).



2 **1**

Our results reveal that the ICl-induced cyclization of **1** is strongly controlled by substituent effects. We show that the attachment of different functional groups on the phenyl group distal to the 1,1′-biphenyl bond modulates the electron density at both the ipso and ortho positions, influencing the relative nucleophilicity of the ipso and ortho sites on the distal phenyl

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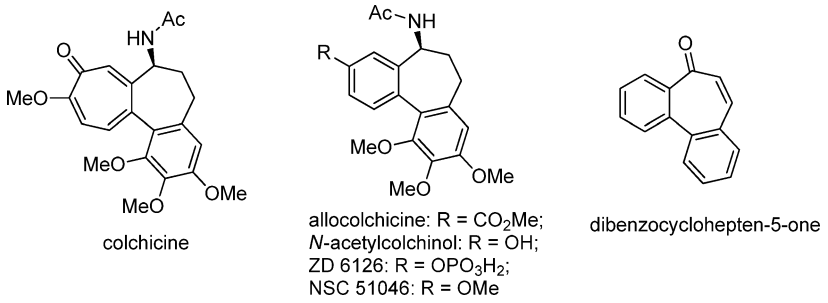
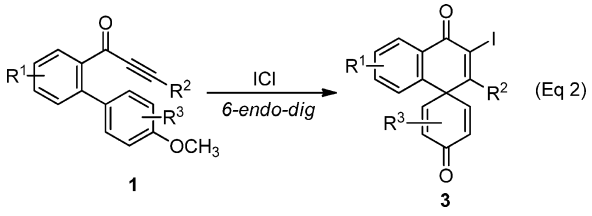


Figure 1. Colchicine, allocolchicine analogues, and dibenzocyclohepten-5-one.

ring. These substituent effects generate two alternative reaction pathways: a 6-endo-dig and a 7-endo-dig cyclization, which compete with each other during the process of the electrophilic cyclization. The outcome of which process predominates depends on the relative electron density at the ipso and ortho positions of the phenyl ring distal to the 1,1′-biphenyl bond. We show that when a strong electron-donating group such as a methoxy is present at the para position of the distal phenyl ring, a 6-endo-dig cyclization is favored, leading to the formation the spiroconjugated compounds **3** (eq 2).[19] Conversely, when the



strongly electron-donating group is removed from the para position, a 7-endo-dig cyclization predominates, producing dibenzocyclohepten-5-ones (**2**). Some of these results have been communicated previously.[19] Herein we report the full details of these electrophilic iodocyclization reactions.

RESULTS AND DISCUSSION

The starting materials 1-([1,1′-biphenyl]-2-yl)alkynones (**1**) were prepared from 1-(2-bromoaryl)alkynones (**4**) and boronic acids by a microwave-assisted Suzuki–Miyaura coupling.[20] The 1-(2-bromoaryl)alkynones (**4**) used in this first reaction were prepared from commercially available 2-bromobenzoyl chlorides (**5**) and terminal alkynes by a Sonogashira coupling (Scheme 1; see Experimental Section for details on the synthesis of compounds **1** and **4**).[21]

The resulting 1-([1,1′-biphenyl]-2-yl)alkynones (**1**) were then subjected to an ICl-induced cyclization under the optimal conditions established by our previous work.[19] Building on this work, we first studied the effect of the groups at the para position of the phenyl ring distal to the 1,1′-biphenyl bond. Following our study of the methoxy functionality,[19] we investigated the cyclization processes of the monosubstituted substrates bearing the following functionalizations at the para position of the distal phenyl ring: benzyloxy, phenoxy, fluorine, chlorine, thiomethyl, and methyl groups. Both benzyloxy- and phenoxy-substituted substrates (**1ab** and **1ac**) lead to the same spiroconjugated compound (**3aa**) as the methoxy-substituted substrate **1aa** (Table 1, entries 1–3). In the presence of a *p*-fluorine group (**1ad**), a mixture of dibenzocyclohepten-5-one (**2ad**) and the spiroconjugated compound (**3aa**) is obtained in an approximate 1:2 ratio (Table 1, entry 4), while dibenzocyclohepten-5-one (**2ae**) is obtained as the sole product when a *p*-chlorine group is present (Table 1, entry 5). The cyclization of *p*-thiomethyl-substituted substrate **1af** leads to an equal mixture of the spiroconjugated compound (**3aa**) and a chlorine-substituted dibenzocyclohepten-5-one (**2ae**) (Table 1, entry 6). When a methyl group is present at the para position, dibenzocyclohepten-5-one **2aga** is obtained together with the minor product **2agb** (Table 1, entry 7). The latter is presumably formed via chlorination of **2aga**.

Because an electron-donating group at the ortho position of the distal phenyl ring also enriches the electron-density at the ipso position, we examined the cyclization of substrate **1b** (Table 1, entry 8); a pair of spiroconjugated compounds, **3b** and **3c**, results from this reaction. The structures of **3b** and **3c** were characterized by analysis of their ^{1}H and ^{13}C NMR and high resolution mass spectra. In addition, the structure of **3c** was further confirmed by comparison of its spectra with those of the regiospecific product from the cyclization of **1c** (Table 1, entry 9).

Alkynone substrates with polysubstituted distal phenyl rings were also investigated. In addition to the *p*-methoxy group, when a second methoxy group is present at the ortho position to the 1,1′-biphenyl bond, the cyclization leads exclusively to the spiro compound **3c** (Table 1, entry 9), by amplification of the electron density at the ipso position. When a second methoxy group is introduced at the meta position of the distal phenyl ring, a mixture of spiro compound **3d** and dibenzocyclohepten-5-one **2d** is produced (Table 1, entry 10). On the other hand, when both a second and third methoxy group are present at the meta positions, a 7-endo-dig cyclization takes place, leading exclusively to the dibenzocyclohepten-5-one product **2e** (Table 1, entry 11). However, when two more weakly electron-donating methyl

Scheme 1. Preparation of 1-([1,1′-Biphenyl]-2-yl)alkynones (1)

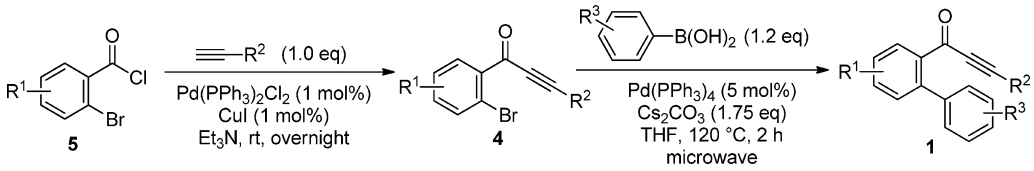


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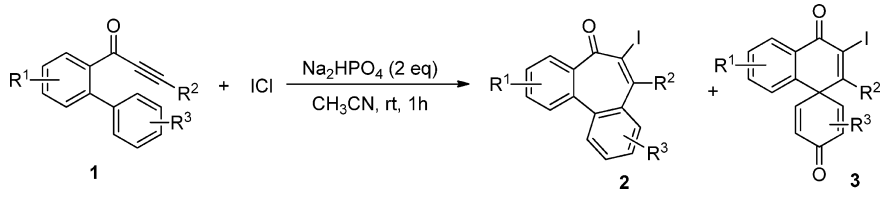
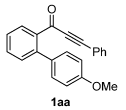
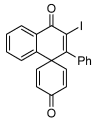
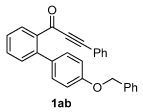
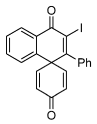
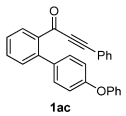
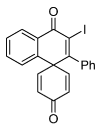
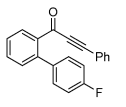
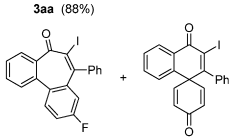
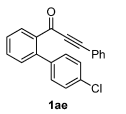
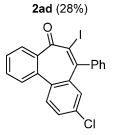
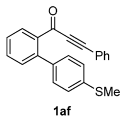
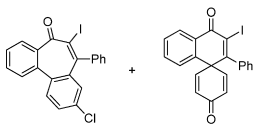
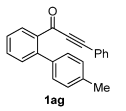
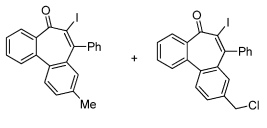
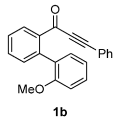
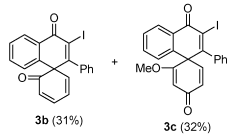
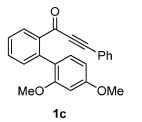
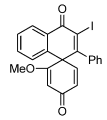
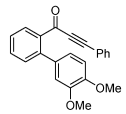
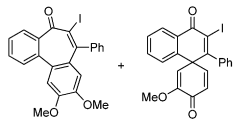
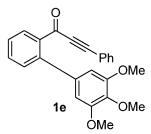
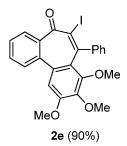
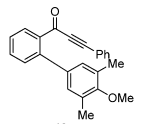
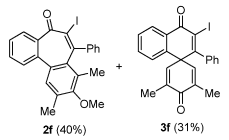
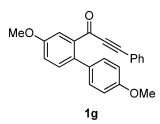
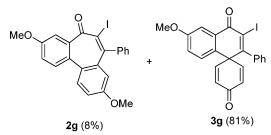
Table 1. Substituent Effects in the ICl-Induced Intramolecular Cyclization of 1-([1,1′-Biphenyl]-2-yl)alkynones[a]



entry	substrate **1**	product **2** + **3** (yield)[b]
1	 **1aa**	 **3aa** (99%)
2	 **1ab**	 **3aa** (83%)
3	 **1ac**	 **3aa** (88%)
4	 **1ad**	 **2ad** (28%) **3aa** (51%)
5	 **1ae**	 **2ae** (73%)
6	 **1af**	 **2ae** (29%) **3aa** (27%)
7	 **1ag**	 **2aga** (85%) **2agb** (11%)
8	 **1b**	 **3b** (31%) **3c** (32%)
9	 **1c**	 **3c** (86%)
10	 **1d**	 **2d** (58%) **3d** (18%)
11	 **1e**	 **2e** (90%)
12	 **1f**	 **2f** (40%) **3f** (31%)
13	 **1g**	 **2g** (8%) **3g** (81%)

[a]See Experimental Section for the general procedure. [b]Isolated yields after column chromatography.

groups are placed at the meta positions of the distal phenyl ring, a mixture of **3f** and **2f** is obtained (Table 1, entry 12). Our study has also revealed a mild substituent effect on the phenyl ring proximal to the 1,1′-biphenyl bond. When the proximal phenyl ring bears a methoxy group at the para position to the 1,1′-biphenyl bond, a mixture of dibenzocyclohepten-5-one **2g** and spiro compound **3g** is obtained in a 1:10 ratio (Table 1, entry 13).

To investigate the formation of dibenzocyclohepten-5-ones by a regioselective process, a variety of alkynone substrates were employed in this cyclization reaction. When no substituent is present at the distal phenyl ring (**1h**), dibenzocyclohepten-5-one (**2h**) is exclusively obtained (Table 2, entry 1). Additionally, substrates including 3′-methoxy-, 3′-fluoro-, 3′,5′-dimethyl-, 3′,5′-dimethoxy-, 2′,3′-dimethoxy-, and 3′-methoxy-4′-methyl-substituted distal phenyl rings all lead exclusively to the dibenzocyclohepten-5-one products, proceeding via a 7-endo-dig cyclization (Table 2, entries 1−7).

Mild electron-withdrawing substituents (such as fluorine) and strong electron-donating substituents (such as methoxy) are well accommodated on the proximal phenyl group at the position para to the 1,1′-biphenyl bond, with both leading to the dibenzocyclohepten-5-one products (Table 2, entries 8 and 9). The electronic effects of substituents at the distal position of the alkynone triple bond were also investigated. Both electron-rich and -deficient aryl, heteroaryl, and alkenyl groups are well accommodated at the distal position of the alkynone triple bond (Table 2, entries 10−14). It is worth noting that cyclization products **2l**, **2t**, and **2u** (Table 2, entries 5, 13, and 14) were produced from a cyclization reaction involving I_2, as the reaction with ICl produced an inseparable mixture of products.

Finally, it should be noted that the electrophilic cyclizations of the meta-substituted alkynones to give dibenzocyclohepten-5-one product **2** take place regiospecifically at the less-hindered 6′ ortho position of the 1,1′-biphenyl bond. This phenomenon is

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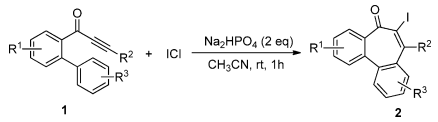
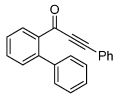
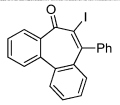
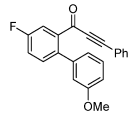
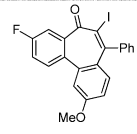
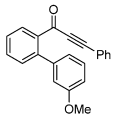
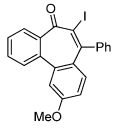
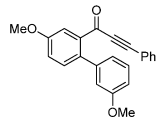
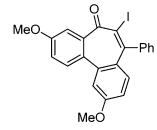
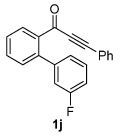
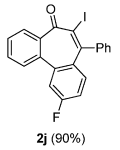
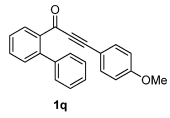
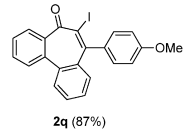
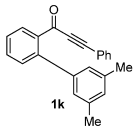
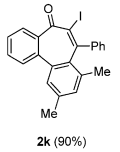
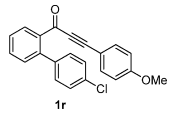
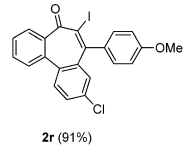
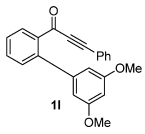
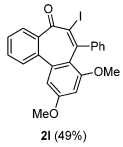
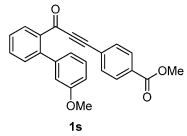
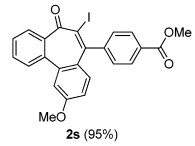
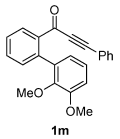
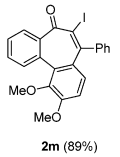
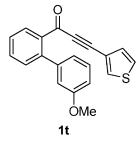
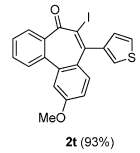
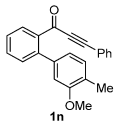
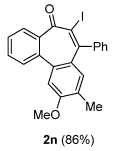
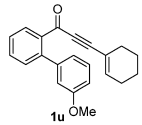
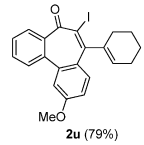
Table 2. Synthesis of Dibenzocyclohepten-5-ones by ICl-Induced Intramolecular Cyclization of 1-([1,1′-Biphenyl]-2-yl)alkynones[a]



entry	substrate **1**	product **2** (yield)[b]	entry	substrate **1**	product **2** (yield)[b]
1	 **1h**	 **2h** (90%)	8	 **1o**	 **2o** (88%)
2	 **1i**	 **2i** (87%)	9	 **1p**	 **2p** (96%)
3	 **1j**	 **2j** (90%)	10	 **1q**	 **2q** (87%)
4	 **1k**	 **2k** (90%)	11	 **1r**	 **2r** (91%)
5[c]	 **1l**	 **2l** (49%)	12	 **1s**	 **2s** (95%)
6	 **1m**	 **2m** (89%)	13[c]	 **1t**	 **2t** (93%)
7	 **1n**	 **2n** (86%)	14[c]	 **1u**	 **2u** (79%)

[a]See Experimental Section for the general procedure. [b]Isolated yields after column chromatography. [c]Three equivalents of I_2 was used instead of ICl, for the cyclization of these products.

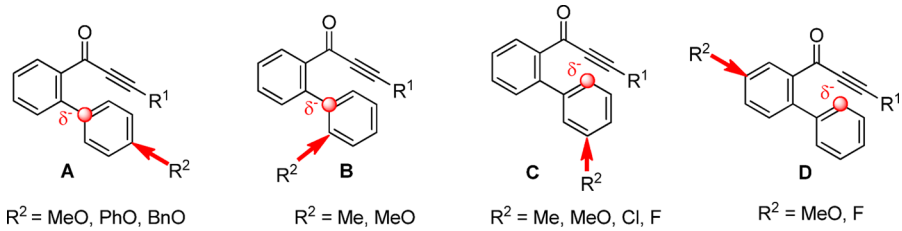


Figure 2. Position of electron density on the distal phenyl ring influenced by the substituent effects about the 1,1′-biphenyl bond.

supported by the ^{1}H NMR spectra of these compounds, where a proton doublet peak with long distance coupling of ^4J is observed on the original distal phenyl groups of **2i**, **2j**, **2o**, **2p**, **2s**, **2t**, and **2u** (Table 2, entries 2, 3, 8, 9, 12−14), and two isolated proton singlets are observed on the original distal phenyl group of **2n** (Table 2, entry 7). The regiospecificity observed during the cyclizations of alkynones **1i**, **1j**, **1n**, **1o**, **1p**, **1s**, **1t**, and **1u** is presumably due to the steric effects induced by the meta substituents on the distal phenyl ring.

On the basis of our results, the outcome of this regioselective cyclization primarily depends on whether the electron-density is concentrated at the ortho or ipso position of the phenyl ring

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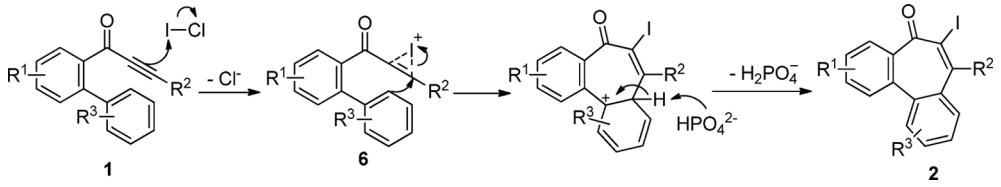
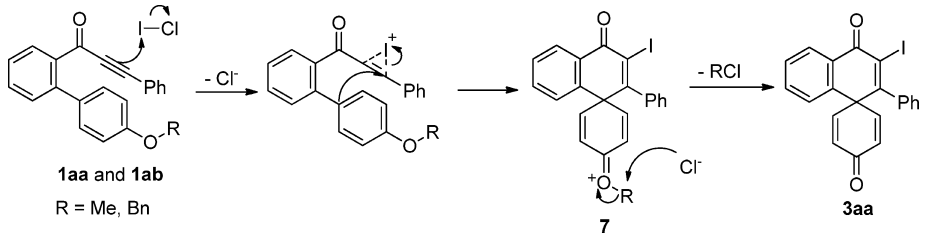
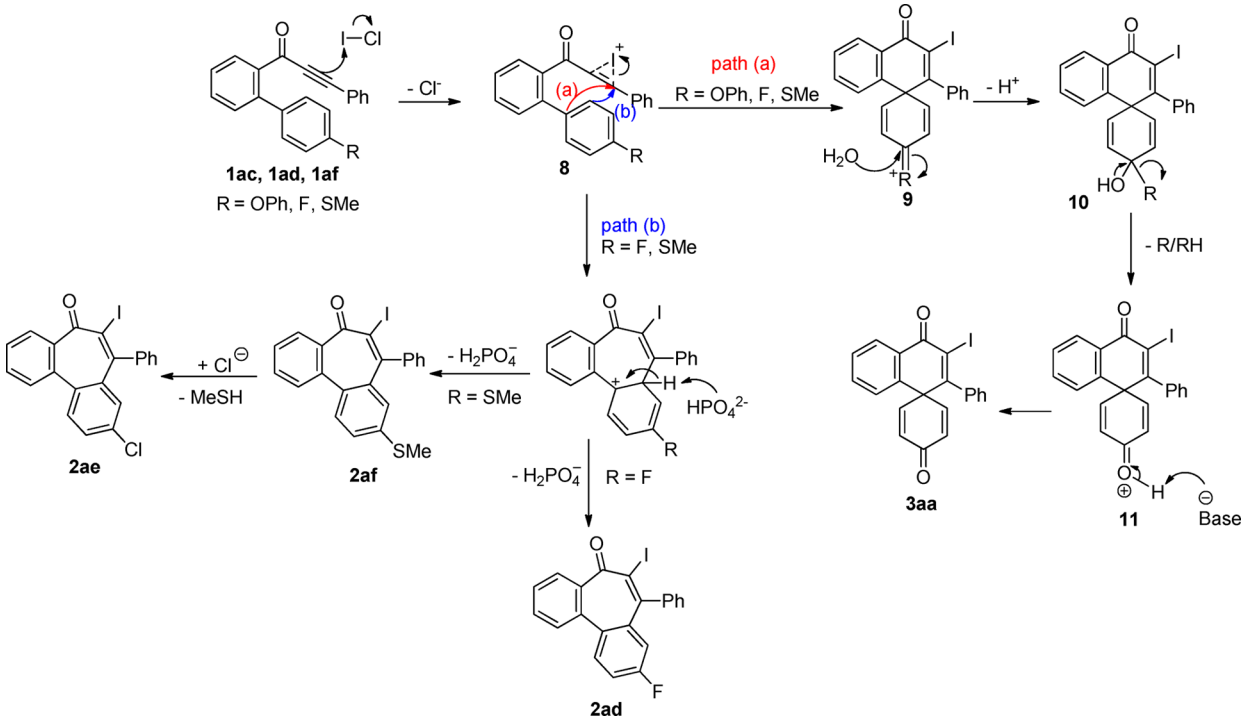
Scheme 2. A Plausible Mechanism for the Formation of Dibenzocyclohepten-5-ones by the ICl-Induced Electrophilic Cyclization of 1-([1,1′-Biphenyl]-2-yl)alkynones



Scheme 3. A Plausible Mechanism for the ICl-Induced Ipso-Electrophilic Cyclization of Alkynones 1aa and 1ab



Scheme 4. A Plausible Mechanism for the ICl-Induced Electrophilic Cyclization of Alkynones 1ac, 1ad, and 1af



distal to the 1,1′-biphenyl bond, which is in turn influenced by the substitution pattern of the alkynone substrate **1**. In the absence of any substituent on either the proximal or distal phenyl rings, a 7-endo-dig cyclization exclusively takes place, leading only to dibenzocyclohepten-5-one (**1h**) (Table 2, entry 1). When a strong electron-donating substituent such as methoxy is present at either the para or ortho position of the distal phenyl group, the ipso position on the phenyl ring becomes more electron-dense than the ortho position (Figure 2, structures **A** and **B**); therefore, only an ipso cyclization takes place. On the other hand, when the donor substituent is present at the meta position of the distal phenyl ring, or at the para position of the proximal phenyl ring, the ortho position of the distal phenyl ring becomes more electron-dense (Figure 2, structures **C** and **D**); therefore, an ortho electrophilic cyclization is favored. When the mild electron-withdrawing substituent fluorine or the electron-donating thiomethyl group is present at the para position of the distal phenyl ring, both ipso and ortho cyclizations take place, affording a mixture of the spiro compound and dibenzocyclohepten-5-one. Mesomeric effects presumably play a significant role in determining the reaction pathways during the cyclizations of **1ad** and **1ae**. The formation of a substantial amount of spiro compound from the cyclization of alkynone **1ad** but not for **1ae** is presumably due to the relatively stronger mesomeric effect displayed by the fluorine atom than the chlorine atom. Similar explanation also explicates the different outcome observed during the cyclizations of alkynones **1af** and **1ag**.

Our results also demonstrate that the functional group distal to the alkyne triple bond does not display any appreciable substituent effects during the cyclization process. Additionally,

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while functionalization of the phenyl ring proximal to the 1,1′-biphenyl bond induces a mild substituent effect, groups on the distal phenyl ring induce a much stronger effect, partially due to their proximity to the ortho and ipso positions.

When more than one substituent is present on the distal and proximal phenyl groups, the outcome of the reaction depends on the identity of the substituents, as well as on their positions. If all substituents reinforce each other, only one product predominates (e.g., Table 1, entry 9; Table 2, entries 4, 5, 8, and 9). However, if multiple substituents shift electron density to both the ipso and ortho positions, a mixture of both the dibenzocyclohepten-5-ones and the spiro compound is afforded (e.g., Table 1, entries 10, 12, and 13). The ratio of the mixture is in turn determined by the strength of each substituent's electron-donating ability, as well as their proximity to either the ipso or the ortho position of the distal phenyl ring. For instance, substrate **1g** generates a lower yield of a 7-endo-dig cyclization product than substrate **1d**, as the methoxy groups compete only in terms of their proximity to the ipso or ortho positions on the distal phenyl ring. The strength of the substituent groups also affects the cyclization process, as demonstrated by the reactions of **1e** and **1f**. While compound **2e** forms regiospecifically due to the significant amplification of the substituent effects of the two meta methoxy groups, a mixture of **2f** and **3f** is obtained when the milder electron-donating methyl groups replace the two meta methoxy groups in **1e**.

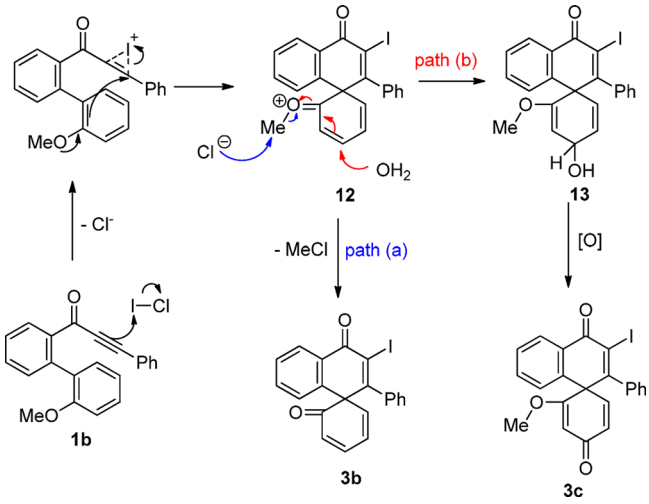
A plausible reaction mechanism is proposed to account for the formation of the dibenzocyclohepten-5-ones **2** (Scheme 2). First, the iodonium intermediate **6** forms upon the interaction of the electrophilic ICl with the alkynone (**1**) triple bond.[17b,22] A 7-endo-dig electrophilic aromatic substitution then takes place at the ortho position of the distal phenyl group to form compound **2**.

When a strong electron-donating group, such as a methoxy or a benzyloxy, is the only substituent present at the para position of the distal phenyl ring, a 6-endo-dig cyclization exclusively takes place at the ipso position to form oxonium ion intermediate **7**. The methyl or benzyl group on **7** is then removed, in situ, by a nucleophile such as chloride anion, and the spiro compound **3aa** forms.

Similarly, when a phenoxy is present at the para position of the distal phenyl ring, a 6-endo-dig ipso-cyclization takes place on intermediate **8**, leading to the spiro intermediate **9** (Scheme 4, path a). The nucleophilic addition of water to **9** leads to intermediate **10**. After the phenoxy group is expelled, a base abstracts a proton from intermediate **11**, generating the spiro compound **3aa**. When a fluorine or thiomethyl group is present at the para position of the distal phenyl ring, two reaction pathways are possible: (a) a 6-endo-dig ipso-cyclization similar to the reaction of the phenoxy-substituted substrate **1ac** (Scheme 4, path a), or (b) a 7-endo-dig ortho electrophilic aromatic substitution leading to dibenzocyclohepten-5-ones **2ad** and **2ae** (Scheme 4, path b). The formation of **2ae** from **1af** presumably occurs from a nucleophilic aromatic substitution on an intermediate compound **2af**, with chloride replacing the thiomethyl group. Our effort to trap the intermediate compound **2af** was, however, unsuccessful.

When a methoxy group is present at the ortho position of distal phenyl ring, a 6-endo-dig cyclization takes place at the ipso position, leading to the spiro intermediate **12**, which upon the loss of the methyl group forms spiro compound **3b** (Scheme 5, path a). Alternatively, intermediate **12** can also undergo a different reaction pathway, by a nucleophilic conjugate addition

Scheme 5. A Plausible Mechanism for the ICl-Induced Electrophilic Cyclization of Alkynone 1b



of water to form intermediate **13** (Scheme 5, path b), which leads to spiro compound **3c** after oxidation (presumably by air or ICl).

CONCLUSION

A synthesis of dibenzocyclohepten-5-ones, the core structure of allocolchicine, by the iodocyclization reaction of 1-([1,1′-biphenyl]-2-yl)alkynones under mild reaction conditions is described. Two reaction pathways were observed: a 7-endo-dig and a 6-endo-dig cyclization for the alkynone substrates. Substituent effects during the cyclization process have been studied in detail and play a crucial role in determining which reaction pathway predominates. By selecting the substituent pattern on the alkynone substrates, we are able to selectively prepare either dibenzocyclohepten-5-ones or spiroconjugated compounds. The iodine functional group in the produced compounds promises further elaboration of the core structure through well-known palladium-catalyzed coupling reactions. This method is particularly useful for combinatorial chemistry, as it provides a direct route toward the library synthesis of allocolchicine derivatives, potentiating the discovery of new anticancer medications. Synthesis of a molecular library of allocolchicine analogues using the developed method is currently underway in our group. We expect this facile synthetic route will soon find applications in high-throughput drug screening processes.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in sealed 6-dram vials, unless otherwise indicated. All microwave irradiation reactions were carried out in 20 mL Biotage microwave vials sealed with an aluminum/Teflon crimp cap, which can be exposed to a maximum of 250 °C and 20 bar internal pressure. The microwave irradiation reactions were run using a Biotage-EXP Microwave synthesis system, operating at a frequency of 2450 MHz, with continuous irradiation power from 0 to 300 W. An IR sensor within the apparatus measured the reaction temperatures by analysis of radiant heat from the outer surfaces of the process vials. All commercially available chemicals were used as received without further purification. All products were purified by flash column chromatography on silica gel (230−400 mesh). ^{1}H NMR spectra were recorded at 500 MHz using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded at either 125 or 100 MHz using $CDCl_3$ as the solvent. The chemical shifts of all ^{1}H and ^{13}C NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm for the ^{1}H NMR

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spectra, and δ 77.23 ppm for the ^{13}C NMR spectra). IR spectra were recorded on a FT-IR spectrometer, at a resolution of 4.0 cm^{-1}, with only major peaks reported. The high resolution mass spectra were recorded on a double focusing magnetic-sector mass spectrometer, using electrospray ionization. The melting points are uncorrected.

General Procedure for the Preparation of 1-(2-Bromophenyl)alkynones (4) from 2-Bromobenzoyl Chlorides (5) and Terminal Alkynes.[23] An oven-dried 6-dram vial was charged with 2-bromobenzoyl chloride or its derivative (**5**, 2.0 mmol), a terminal alkyne (2.0 mmol), $Pd(PPh_3)_2Cl_2$ (14.0 mg, 0.02 mmol), CuI (3.8 mg, 0.02 mmol), and anhydrous Et_3N (10 mL). The vial was then flushed with nitrogen and sealed. The reaction mixture was stirred at room temperature overnight, until the disappearance of starting material was observed, as monitored by thin layer chromatography. The reaction mixture was diluted with ethyl acetate (40 mL) and washed with brine (40 mL), and the aqueous phase was then extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg); the resulting residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate).

*1-(2-Bromophenyl)-3-phenylprop-2-yn-1-one (**4a**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (468.5 mg, 82% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.7, 1.8 Hz, 1H), 7.71 (dd, J = 7.9, 1.1 Hz, 1H), 7.64−7.66 (m, 2H), 7.37−7.50 (m, 5H). The ^1H NMR spectral data are in good agreement with the literature data.[18a]

*1-(2-Bromophenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (**4b**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a beige solid, mp 46.0−46.9 °C; (453.6 mg, 72% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.69 (dd, J = 8.0, 1.0 Hz, 1H), 7.60−7.62 (m, 2H), 7.45 (dt, J = 7.5, 1.1 Hz, 1H), 7.37 (dt, J = 7.8, 1.8 Hz, 1H), 6.91−6.93 (m, 2H), 3.85 (s, 3H). The ^1H NMR spectral data are in good agreement with the literature data.[24]

*Methyl 4-(3-(2-Bromophenyl)-3-oxoprop-1-yn-1-yl)benzoate (**4c**).*[25] Eluent of column chromatography: hexanes/ethyl acetate 5:1. This compound was obtained as a yellow solid, by reacting 2-bromobenzoyl chloride with methyl 4-ethynylbenzoate in the presence of 1 equiv of Et_3N in 10 mL of anhydrous THF (501.3 mg, 73% yield): mp 89.9−90.5 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.06−8.08 (m, 3H), 7.70−7.72 (m, 3H), 7.47 (dt, J = 7.6, 1.0 Hz, 1H), 7.40 (dt, J = 7.9, 1.7 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.4, 166.3, 137.3, 135.2, 133.8, 133.09, 133.06, 132.0, 129.9, 127.7, 124.6, 121.6, 92.5, 89.6, 52.7; IR ($CHCl_3$, cm^{-1}) ν 3012, 2960, 2204, 1723, 1640, 1587, 1436, 1278, 1203, 1004, 768, 734; HRMS (ESI) calcd for $C_{17}H_{12}BrO_3$ $(M + H)^+$ 342.9964, found 342.9966.

*1-(2-Bromophenyl)-3-(thiophen-3-yl)prop-2-yn-1-one (**4d**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a light brown oil (469.6 mg, 81% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.7, 1.4 Hz, 1H), 7.82−7.83 (m, 1H), 7.69 (d, J = 7.9 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.35−7.40 (m, 2H), 7.28−7.29 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7, 137.6, 135.1, 134.5, 133.5, 132.9, 130.4, 127.6, 126.5, 121.4, 119.4, 89.9, 88.4; IR ($CHCl_3$, cm^{-1}) ν 3018, 2197, 1644, 1290, 1216, 1012, 758; HRMS (ESI) calcd for $C_{13}H_8BrOS$ $(M + H)^+$ 290.9474, found 290.9473.

*1-(2-Bromophenyl)-3-(cyclohex-1-en-1-yl)prop-2-yn-1-one (**4e**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (324.0 mg, 56% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.7, 1.8 Hz, 1H), 7.66 (dd, J = 7.9, 1.1 Hz, 1H), 7.41 (dt, J = 7.5, 1.2 Hz, 1H), 7.34 (dt, J = 7.7, 1.8 Hz, 1H), 6.54−6.56 (m, 1H), 2.22−2.25 (m, 2H), 2.17−2.20 (m, 2H), 1.66−1.69 (m, 2H), 1.61−1.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8, 143.5, 137.8, 134.9, 133.2, 132.7, 127.4, 121.1, 119.2, 97.0, 86.5, 28.2, 26.3, 22.0, 21.2; IR ($CHCl_3$, cm^{-1}) ν 3019, 2940, 2864, 2182, 1650, 1430, 1293, 1246, 1026, 757; HRMS (ESI) calcd for $C_{15}H_{14}BrO$ $(M + H)^+$ 289.0223, found 289.0220.

*1-(2-Bromo-5-fluorophenyl)-3-phenylprop-2-yn-1-one (**4f**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow solid (357.3 mg, 59% yield): mp 59.2−60.1 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 8.8, 3.2 Hz, 1H), 7.60−7.64 (m, 3H), 7.45−7.48 (m, 1H), 7.37−7.40 (m, 2H), 7.07−7.11 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0 (d, J_{C-F} = 1.6 Hz), 161.4 (d, J_{C-F} = 250.5 Hz), 138.7 (d, J_{C-F} = 6.3 Hz), 136.4 (d, J_{C-F} = 7.2 Hz), 133.2, 131.3, 128.8, 120.7 (d, J_{C-F} = 21.3 Hz), 119.6, 119.5 (d, J_{C-F} = 24.4 Hz), 115.5 (d, J_{C-F} = 3.6 Hz), 95.0, 87.6; IR ($CHCl_3$, cm^{-1}) ν 3068, 2201, 1654, 1576, 1464, 1398, 1299, 1261, 1159, 758; HRMS (ESI) calcd for $C_{15}H_9BrFO$ $(M + H)^+$ 302.9815, found 302.9817.

*1-(2-Bromo-5-methoxyphenyl)-3-phenylprop-2-yn-1-one (**4g**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a light brown oil (500.8 mg, 78% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.58−7.60 (m, 2H), 7.54 (d, J = 3.2 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.41−7.45 (m, 1H), 7.34−7.37 (m, 2H), 6.89 (dd, J = 8.8, 3.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 158.7, 137.9, 135.6, 133.1, 131.1, 128.7, 119.8, 119.4, 117.9, 111.4, 94.4, 87.9, 55.7; IR ($CHCl_3$, cm^{-1}) ν 2936, 2838, 2199, 1653, 1468, 1286, 1240, 1172, 1031, 757; HRMS (ESI) calcd for $C_{16}H_{12}BrO_2$ $(M + H)^+$ 315.0015 found 315.0016.

General Procedure for the Preparation of 1-([1,1′-Biphenyl]-2-yl)alkynones (1) from 1-(2-Bromophenyl)alkynones (4) and Arylboronic Acids.[26] A 20 mL microwave vial was charged with 1-(2-bromophenyl)alkynone (**4**, 1.0 mmol), an arylboronic acid (1.2 mmol), $Pd(PPh_3)_4$ (57.7 mg, 0.05 mmol), Cs_2CO_3 (570.2 mg, 1.75 mmol), and THF (10 mL). The vial was flushed with nitrogen and sealed with an aluminum/Teflon crimp cap. The reaction mixture was stirred at 120 °C while undergoing microwave irradiation (300 W) for 2 h and then diluted with ethyl acetate (30 mL) and washed with brine (30 mL). The aqueous phase was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator, under reduced pressure (20 mmHg). The subsequent residue was then purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate).

*1-(4′-Methoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1aa**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (247.6 mg, 79% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.9 Hz, 1H), 7.41−7.45 (m, 2H), 7.34−7.35 (m, 3H), 7.26−7.29 (m, 4H), 6.94 (d, J = 7.2 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 159.7, 142.6, 138.1, 133.1, 132.9, 132.3, 131.1, 130.9, 130.5, 130.1, 128.4, 127.2, 120.3, 114.0, 93.8, 89.0, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3016, 2935, 2835, 2194, 1636, 1299, 1246, 759; HRMS (ESI) calcd for $C_{22}H_{17}O_2$ $(M + H)^+$ 313.1223, found 313.1223.

*1-(4′-(Benzyloxy)-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1ab**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow solid (310.1 mg, 80% yield): mp 104.4−105.3 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96−7.98 (m, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.46 (dd, J = 13.9, 7.7 Hz, 2H), 7.39−7.40 (m, 8H), 7.29−7.31 (m, 4H), 7.04−7.06 (m, 2H), 5.03 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 158.9, 142.5, 138.0, 136.9, 133.1, 132.3, 131.0, 130.9, 130.5, 130.1, 128.7, 128.4, 128.1, 127.5, 127.2, 120.3, 114.9, 93.8, 89.0, 70.2 (fewer ^{13}C signals were observed due to signal overlapping); IR ($CHCl_3$, cm^{-1}) ν 3063, 3017, 2196, 1639, 1516, 1300, 1240, 1009, 758; HRMS (ESI) calcd for $C_{28}H_{21}O_2$ $(M + H)^+$ 389.1536, found 389.1533.

*1-(4′-Phenoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1ac**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as an orange oil (322.8 mg, 86% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.44−7.49 (m, 2H), 7.42−7.43 (m, 1H), 7.39 (d, J = 8.4 Hz, 2H), 7.31−7.35 (m, 4H), 7.22 (t, J = 7.7 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.8, 157.5, 156.9, 142.2, 138.2, 135.3, 133.1, 132.3, 131.1, 131.0, 130.7, 130.1, 130.0, 128.6, 127.5, 123.6, 120.2, 119.2, 118.6, 93.8, 89.1; IR ($CHCl_3$, cm^{-1}) ν 3061, 2196, 1636, 1591, 1488, 1304, 1239, 758, 689; HRMS (ESI) calcd for $C_{27}H_{19}O_2$ $(M + H)^+$ 375.1380, found 375.1378.

*1-(4′-Fluoro-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1ad**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (251.5 mg, 84% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.31−7.35 (m, 4H), 7.25−7.26 (m, 4H), 7.05 (t,

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J = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.4, 162.7 (d, J_{C-F} = 247.0 Hz), 141.7, 137.9, 136.6 (d, J_{C-F} = 3.5 Hz), 133.0, 132.4, 131.20 (d, J_{C-F} = 1.9 Hz), 131.15, 130.6 (d, J_{C-F} = 36.4 Hz), 128.6, 127.7, 120.0, 115.5, 115.3, 94.0, 88.9; IR ($CHCl_3$, cm^{-1}) ν 3063, 3020, 2197, 1642, 1513, 1303, 1223, 1204, 1010, 837, 758; HRMS (ESI) calcd for $C_{21}H_{14}FO$ $(M + H)^+$ 301.1023, found 301.1023.

*1-(4′-Chloro-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1ae**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (233.2 mg, 74% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.7, 0.7 Hz, 1H), 7.60 (dt, J = 7.5, 1.2 Hz, 1H), 7.51 (dt, J = 7.7, 1.0 Hz, 1H), 7.38−7.42 (m, 4H), 7.29−7.35 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 141.6, 139.1, 137.7, 134.2, 133.0, 132.5, 131.2, 130.9, 130.8, 130.6, 128.64, 128.62, 128.0, 120.0, 94.3, 88.9; IR ($CHCl_3$, cm^{-1}) ν 3061, 3023, 2194, 1644, 1591, 1470, 1299, 1203, 1008, 758; HRMS (ESI) calcd for $C_{21}H_{14}ClO$ $(M + H)^+$ 317.0728, found 317.0726.

*1-(4′-(Methylthio)-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1af**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (241.8 mg, 74% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.8, 1.2 Hz, 1H), 7.55 (dt, J = 7.5, 1.3 Hz, 1H), 7.44 (dt, J = 7.6, 1.3 Hz, 1H), 7.38 (dd, J = 7.8, 1.1 Hz, 1H), 7.30−7.36 (m, 3H), 7.24−7.27 (m, 4H), 7.20−7.22 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6, 142.4, 138.7, 137.9, 137.3, 133.0, 132.5, 131.1, 130.6, 130.4, 130.2, 128.5, 127.6, 126.5, 120.2, 94.2, 89.0, 15.9; IR ($CHCl_3$, cm^{-1}) ν 3060, 2982, 2922, 2198, 1734, 1642, 1293, 1243, 1010, 824, 690; HRMS (ESI) calcd for $C_{22}H_{17}OS$ $(M + H)^+$ 329.0995, found 329.0994.

*1-(4′-Methyl-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1ag**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (228.1 mg, 77% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.7, 0.7 Hz, 1H), 7.59 (dt, J = 7.6, 1.2 Hz, 1H), 7.46 (dt, J = 7.6, 0.8 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.22−7.24 (m, 4H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 143.0, 138.1, 137.9, 137.7, 133.1, 132.4, 131.2, 130.5, 130.2, 129.7, 129.3, 128.4, 127.4, 120.4, 93.9, 89.0, 21.4; IR ($CHCl_3$, cm^{-1}) ν 3060, 3023, 2922, 2198, 1645, 1592, 1489, 1442, 1300, 1202, 1008, 819, 757, 690; HRMS (ESI) calcd for $C_{22}H_{17}O$ $(M + H)^+$ 297.1274, found 297.1273.

*1-(2′-Methoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1b**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (251.3 mg, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.8, 1.0 Hz, 1H), 7.61 (dt, J = 7.6, 1.3 Hz, 1H), 7.46 (dt, J = 7.7, 1.0 Hz, 1H), 7.37−7.40 (m, 3H), 7.29−7.34 (m, 5H), 7.10 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 8.3 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 156.5, 138.4, 138.3, 133.2, 132.6, 131.7, 130.60, 130.55, 129.8, 129.6, 129.3, 128.5, 127.6, 121.3, 120.4, 110.8, 92.0, 88.5, 55.3; IR ($CHCl_3$, cm^{-1}) ν 3064, 3014, 2960, 2935, 2836, 2198, 1645, 1487, 1299, 1025, 753; HRMS (ESI) calcd for $C_{22}H_{17}O_2$ $(M + H)^+$ 313.1223, found 313.1223.

*1-(2′,4′-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1c**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (257.9 mg, 75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.8, 0.8 Hz, 1H), 7.58 (dt, J = 7.5, 1.1 Hz, 1H), 7.43 (dt, J = 7.5, 0.7 Hz, 1H), 7.35−7.38 (m, 2H), 7.28−7.33 (m, 5H), 6.60 (dd, J = 8.3, 2.3 Hz, 1H), 6.45 (d, J = 2.3 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.3, 161.3, 157.7, 138.3, 138.2, 133.1, 132.6, 131.6, 131.1, 130.5, 129.2, 128.4, 127.2, 122.4, 120.5, 105.1, 98.7, 91.9, 88.5, 55.6, 55.3; IR ($CHCl_3$, cm^{-1}) ν 3009, 2958, 2935, 2834, 2198, 1610, 1461, 1304, 1207, 1158, 1034, 759; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1329.

*1-(3′,4′-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1d**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (256.6 mg, 75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.2, 1.4 Hz, 1H), 7.57 (dt, J = 7.5, 1.3 Hz, 1H), 7.43−7.46 (m, 2H), 7.34−7.35 (m, 1H), 7.23−7.29 (m, 4H), 6.88−6.98 (m, 3H), 3.88 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 149.1, 148.8, 142.6, 138.2, 133.2, 132.9, 132.2, 130.9, 130.5, 129.9, 128.4, 127.3, 122.3, 120.2, 113.0, 111.3, 93.6, 88.9, 56.1, 56.0; IR ($CHCl_3$, cm^{-1}) ν 3019, 2936, 2835, 2196, 1638, 1520, 1299, 1248, 1026, 758; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1332.

*3-Phenyl-1-(3′,4′,5′-trimethoxy-[1,1′-biphenyl]-2-yl)prop-2-yn-1-one (**1e**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a colorless crystal (223.4 mg, 60% yield): mp 121.0−122.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.9 Hz, 1H), 7.59 (dt, J = 7.7, 1.3 Hz, 1H), 7.46−7.50 (m, 2H), 7.35−7.38 (m, 1H), 7.25−7.30 (m, 4H), 6.63 (s, 2H), 3.86 (s, 6H), 3.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 153.3, 142.9, 138.5, 138.0, 136.3, 133.0, 132.3, 130.71, 130.69, 129.9, 128.6, 127.7, 120.3, 107.2, 93.7, 88.8, 60.9, 56.4; IR ($CHCl_3$, cm^{-1}) ν 3016, 2938, 2836, 2198, 1638, 1587, 1461, 1300, 1239, 1128, 1010, 760; HRMS (ESI) calcd for $C_{24}H_{21}O_4$ $(M + H)^+$ 373.1434, found 373.1436.

*1-(4′-Methoxy-3′,5′-dimethyl-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1f**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (239.6 mg, 70% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.41−7.45 (m, 2H), 7.34−7.36 (m, 1H), 7.23- 7.28 (m, 4H), 7.06 (s, 2H), 3.48 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 157.0, 142.9, 138.3, 136.1, 133.0, 132.2, 130.9, 130.5, 130.3, 129.8, 128.4, 127.3, 120.4, 93.6, 89.0, 59.5, 16.3 (fewer ^{13}C signals were observed due to signal overlapping); IR ($CHCl_3$, cm^{-1}) ν 3017, 2935, 2199, 1637, 1472, 1300, 1234, 1010, 760; HRMS (ESI) calcd for $C_{24}H_{21}O_2$ $(M + H)^+$ 341.1536, found 341.1536.

*1-(4,4′-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1g**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (212.0 mg, 62% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 2.7 Hz, 1H), 7.30−7.35 (m, 4H), 7.21−7.28 (m, 4H), 7.12 (dd, J = 8.5, 2.6 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 3.74(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 159.4, 158.7, 138.7, 135.4, 133.1, 132.7, 132.3, 131.0, 130.5, 128.4, 120.3, 119.1, 114.0, 113.9, 94.1, 89.0, 55.8, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3016, 2836, 2203, 1637, 1603, 1489, 1290, 1033, 757; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1332.

*1-([1,1′-Biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1h**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (208.3 mg, 74% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 7.7, 0.6 Hz, 1H), 7.56 (dt, J = 7.5, 1.1 Hz, 1H), 7.38−7.47 (m, 6H), 7.31−7.34 (m, 2H), 7.22−7.26 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 142.8, 140.4, 138.0, 133.0, 132.2, 131.1, 130.5, 130.1, 129.6, 128.44, 128.37, 127.9, 127.5, 120.1, 93.9, 88.9; IR ($CHCl_3$, cm^{-1}) ν 3060, 3020, 2196, 1642, 1303, 1202, 1010, 748, 697; HRMS (ESI) calcd for $C_{21}H_{15}O$ $(M + H)^+$ 283.1117, found 283.1124.

*1-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1i**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (214.1 mg, 69% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 1H), 7.59 (dt, J = 7.5, 1.0 Hz, 1H), 7.48 (dt, J = 7.6, 0.6, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36−7.39 (m, 1H), 7.28−7.34 (m, 5H), 6.98−7.00 (m, 2H), 6.87 (dd, J = 8.4, 1.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 159.7, 142.7, 142.0, 138.3, 133.1, 132.3, 131.0, 130.6, 130.0, 129.6, 128.5, 127.7, 122.5, 120.3, 115.2, 113.6, 93.9, 88.9, 55.5; IR ($CHCl_3$, cm^{-1}) ν 3061, 2956, 2935, 2834, 2196, 1641, 1299, 1209, 1008, 757, 693; HRMS (ESI) calcd for $C_{22}H_{17}O_2$ $(M + H)^+$ 313.1223, found 313.1226.

*1-(3′-Fluoro-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1j**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (230.7 mg, 77% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.39−7.42 (m, 2H), 7.30−7.37 (m, 5H), 7.15−7.19 (m, 2H), 7.03 (dt, J = 5.8, 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 162.7 (d, J_{C-F} = 246.2 Hz), 142.8 (d, J_{C-F} = 7.9 Hz), 141.4 (d, J_{C-F} = 1.6 Hz), 137.9, 133.0, 132.4, 131.0, 130.8, 130.4, 129.9 (d, J_{C-F} = 8.4 Hz), 128.6, 128.0, 125.6 (d, J_{C-F} = 2.7 Hz), 120.0, 116.3 (d, J_{C-F} = 21.8 Hz), 114.7 (d, J_{C-F} = 21.0 Hz), 94.0, 88.8; IR ($CHCl_3$, cm^{-1}) ν 3065, 2925, 2196, 1769, 1643, 1587, 1487, 1292, 1266, 757, 691; HRMS (ESI) calcd for $C_{21}H_{14}FO$ $(M + H)^+$ 301.1023, found 301.1026.

*1-(3′,5′-Dimethyl-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1k**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This compound was obtained as a yellow oil (255.0 mg, 82% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.56 (dt, J = 7.5, 1.0

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Hz, 1H), 7.41−7.46 (m, 2H), 7.35−7.38 (m, 1H), 7.23−7.29 (m, 4H), 7.03 (s, 2H), 6.95 (s, 1H), 2.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 143.3, 140.6, 138.3, 138.0, 133.0, 132.2, 131.1, 130.5, 130.0, 129.7, 128.4, 127.6, 127.4, 120.4, 93.7, 89.0, 21.5; IR ($CHCl_3$, cm^{-1}) ν 3020, 2920, 2198, 1644, 1594, 1301, 1204, 1010, 758, 693; HRMS (ESI) calcd for $C_{23}H_{19}O$ $(M + H)^+$ 311.1430, found 311.1428.

*1-(3′,5′-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1l**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (257.8 mg, 75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 1H), 7.58 (dt, J = 7.6, 1.1 Hz, 1H), 7.47 (dd, J = 16.0, 7.7 Hz, 2H), 7.36−7.39 (m, 1H), 7.27−7.32 (m, 4H), 6.57 (d, J = 2.2 Hz, 2H), 6.41−6.42 (m, 1H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6, 160.7, 142.7, 142.6, 138.3, 133.0, 132.1, 130.6, 130.5, 129.7, 128.4, 127.7, 120.2, 108.0, 100.0, 93.6, 88.7, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3011, 2961, 2938, 2838, 2198, 1638, 1590, 1458, 1420, 1300, 1204, 1156, 1063, 1027, 1013; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1329.

*1-(2′,3′-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1m**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (256.6 mg, 75% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.8 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.34−7.39 (m, 3H), 7.27−7.31 (m, 2H), 7.12 (t, J = 7.8 Hz, 1H), 6.92 (d, J = 7.1 Hz, 1H), 6.90 (d, J = 8.2 Hz, 1H), 3.81 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6, 152.7, 146.2, 138.4, 137.9, 134.8, 133.0, 132.2, 131.6, 130.4, 129.9, 128.4, 127.6, 124.2, 122.9, 120.4, 112.6, 92.5, 88.5, 60.4, 55.9; IR ($CHCl_3$, cm^{-1}) ν 3007, 2936, 2197, 1644, 1476, 1301, 1264, 1010, 690; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1330.

*1-(3′-Methoxy-4′-methyl-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1n**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (262.7 mg, 80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.3 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.46−7.49 (m, 2H), 7.36−7.38 (m, 1H), 7.29 (t, J = 7.7 Hz, 2H), 7.23−7.24 (m, 2H), 7.19 (d, J = 7.4 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.92 (s, 1H), 3.84 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.8, 157.6, 143.0, 139.2, 138.1, 132.8, 132.2, 130.9, 130.6, 130.4, 129.9, 128.4, 127.4, 126.5, 121.8, 120.2, 111.5, 93.7, 88.8, 55.4, 16.1; IR ($CHCl_3$, cm^{-1}) ν 3061, 3011, 2938, 2197, 1641, 1301, 1225, 1204, 1134, 1011; HRMS (ESI) calcd for $C_{23}H_{19}O_2$ $(M + H)^+$ 327.1380, found 327.1379.

*1-(4-Fluoro-3′-methoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1o**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as an orange oil (266.2 mg, 81% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 9.0, 2.7 Hz, 1H), 7.37−7.43 (m, 2H), 7.27−7.33 (m, 6H), 6.94−6.96 (m, 2H), 6.87 (dd, J = 8.5, 2.2 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2 (d, J_{C-F} = 1.7 Hz), 161.9 (d, J_{C-F} = 248.6 Hz), 151.6, 140.9, 139.5 (d, J_{C-F} = 6.3 Hz), 138.7 (d, J_{C-F} = 3.4 Hz), 133.1, 132.7 (d, J_{C-F} = 7.5 Hz), 130.8, 129.6, 128.4, 122.5, 119.9, 119.2 (d, J_{C-F} = 21.2 Hz), 116.5 (d, J_{C-F} = 23.5 Hz), 115.3, 113.6, 94.5, 88.5, 55.3; IR ($CHCl_3$, cm^{-1}) ν 3065, 3016, 2937, 2836, 2200, 1640, 1609, 1477, 1294, 1226, 1161, 1044, 758; HRMS (ESI) calcd for $C_{22}H_{16}FO_2$ $(M + H)^+$ 331.1129, found 331.1129.

*1-(3′,4-Dimethoxy-[1,1′-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1p**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as an orange oil (200.3 mg, 58% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 2.6 Hz, 1H), 7.36−7.39 (m, 2H), 7.25−7.32 (m, 5H), 7.14 (dd, J = 8.5, 2.8 Hz, 1H), 6.97−6.99 (m, 2H), 6.85 (dd, J = 8.4, 2.1 Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 159.6, 159.1, 141.8, 139.1, 135.5, 133.1, 132.2, 130.6, 129.5, 128.4, 122.7, 120.3, 118.9, 115.4, 114.0, 113.3, 94.1, 88.9, 55.8, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3001, 2938, 2835, 2202, 1639, 1604, 1476, 1290, 1231, 1029, 761, 687; HRMS (ESI) calcd for $C_{23}H_{19}O_3$ $(M + H)^+$ 343.1329, found 343.1329.

*1-([1,1′-Biphenyl]-2-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (**1q**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as an orange oil (285.5 mg, 91% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 1H), 7.59 (dt, J = 7.4, 0.6 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.40−7.46 (m, 5H), 7.33−7.36 (m, 1H), 7.21 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.9, 161.6, 142.7, 140.6, 138.3, 135.2, 132.1, 131.2, 130.1, 129.7, 128.5, 127.9, 127.5, 114.2, 112.0, 95.3, 89.0, 55.5; IR ($CHCl_3$, cm^{-1}) ν 3019, 2841, 2190, 1635, 1601, 1510, 1292, 1253, 1215, 1171, 1031, 760; HRMS (ESI) calcd for $C_{22}H_{17}O_2$ $(M + H)^+$ 313.1223, found 313.1222.

*1-(4′-Chloro-[1,1′-biphenyl]-2-yl)-3-(4-methoxyphenyl)prop-2-yn-1-one (**1r**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (231.9 mg, 67% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.7, 0.8 Hz, 1H), 7.58 (dt, J = 7.5, 1.1 Hz, 1H), 7.48 (dt, J = 7.5, 0.8 Hz, 1H), 7.33−7.38 (m, 5H), 7.24−7.26 (m, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 161.7, 141.4, 139.2, 137.8, 135.1, 134.0, 132.3, 131.1, 130.9, 130.5, 128.5, 127.8, 114.3, 111.7, 95.5, 88.9, 55.5; IR ($CHCl_3$, cm^{-1}) ν 3012, 2962, 2933, 2839, 2189, 1639, 1603, 1510, 1292, 1253, 1207, 1171, 1090, 1028, 833, 757; HRMS (ESI) calcd for $C_{22}H_{16}ClO_2$ $(M + H)^+$ 347.0833, found 347.0834.

*Methyl 4-(3-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-3-oxoprop-1-yn-1-yl)benzoate (**1s**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a yellow oil (237.0 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91−7.95 (m, 3H), 7.60 (dt, J = 7.5, 1.2 Hz, 1H), 7.48 (dt, J = 7.7, 1.0 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.29−7.33 (m, 3H), 6.98−6.99 (m, 2H), 6.85−6.88 (m, 1H), 3.91 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.5, 166.3, 159.7, 142.9, 141.9, 138.0, 132.8, 132.5, 131.4, 131.0, 130.0, 129.6, 129.4, 127.8, 124.8, 122.6, 115.2, 113.7, 91.9, 90.5, 55.5, 52.6; IR ($CHCl_3$, cm^{-1}) ν 3018, 2952, 2837, 2199, 1724, 1640, 1437, 1280, 1213, 1107, 1005, 758; HRMS (ESI) calcd for $C_{24}H_{19}O_4$ $(M + H)^+$ 371.1278, found 371.1272.

*1-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-3-(thiophen-3-yl)prop-2-yn-1-one (**1t**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as an orange oil (236.1 mg, 74% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 7.8, 0.9 Hz, 1H), 7.59 (dt, J = 7.5, 1.3 Hz, 1H), 7.48 (dd, J = 7.6, 1.1 Hz, 1H), 7.43−7.46 (m, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.22 (dd, J = 5.0, 3.1 Hz, 1H), 6.98−7.00 (m, 2H), 6.94 (dd, J = 5.0, 1.0 Hz, 1H), 6.88−6.90 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6, 159.6, 142.7, 142.0, 138.2, 133.3, 130.9, 130.4, 129.9, 129.5, 127.7, 125.9, 122.5, 119.6, 115.2, 113.6, 89.3, 89.1, 55.5, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3106, 3005, 2937, 2835, 2196, 1636, 1278, 1215, 1019, 787, 759; HRMS (ESI) calcd for $C_{20}H_{15}O_2S$ $(M + H)^+$ 319.0787, found 319.0788.

*3-(Cyclohex-1-en-1-yl)-1-(3′-methoxy-[1,1′-biphenyl]-2-yl)prop-2-yn-1-one (**1u**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (154.4 mg, 49% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 7.7, 1.2 Hz, 1H), 7.54 (td, J = 7.6, 1.2 Hz, 1H), 7.43 (td, J = 7.6, 1.2 Hz, 1H), 7.39 (dd, J = 7.7, 1.2 Hz, 1H), 7.30 (dd, J = 8.8, 7.6 Hz, 1H), 6.90−6.94 (m, 3H), 6.17−6.18 (m, 1H), 3.82 (s, 3H), 2.05−2.07 (m, 2H), 1.89−1.90 (m, 2H), 1.52−1.57 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0, 159.6, 142.4, 142.2, 142.0, 138.6, 131.9, 130.8, 129.9, 129.3, 127.5, 122.3, 119.1, 114.9, 113.5, 96.4, 87.3, 55.4, 28.2, 26.2, 22.0, 21.2; IR ($CHCl_3$, cm^{-1}) ν 3016, 2938, 2182, 1640, 1599, 1473, 1288, 1215, 1049, 757; HRMS (ESI) calcd for $C_{22}H_{21}O_2$ $(M + H)^+$ 317.1536, found 317.1535.

General Procedure for the ICl-Induced Intramolecular Electrophilic Cyclization of 1-([1,1′-Biphenyl]-2-yl)alkynones (1). A 4-dram vial was charged with 1-([1,1′-biphenyl]-2-yl)alkynones (**1**, 0.5 mmol, 1 equiv), Na_2HPO_4 (142.0 mg, 1.0 mmol, 2 equiv), ICl (243.6 mg, 1.5 mmol, 3 equiv), and acetonitrile (5 mL). The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with 25 mL of ethyl acetate and washed with a 0.5 M aqueous $Na_2S_2O_3$ solution (30 mL), and the aqueous phase was extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg). The subsequent residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the corresponding cyclization product.

*3′-Iodo-2′-phenyl-4′H-spiro[cyclohexa[2,5]diene-1,1′-naphthalene]-4,4′-dione (**3aa**).* Eluent of column chromatography: hexanes/ethyl acetate 3:1. This product was obtained as a white solid (208.9 mg, 99% yield): mp 228.2−229.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, J = 7.9, 1.3 Hz, 1H), 7.60 (dt, J = 7.5, 1.5 Hz, 1H), 7.53 (dt, J = 7.9,

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1.2 Hz, 1H), 7.32−7.38 (m, 3H), 7.28−7.30 (m, 1H), 6.99−7.03 (m, 2H), 6.73−6.76 (m, 2H), 6.29−6.33 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 178.8, 160.5, 147.8, 141.5, 138.4, 133.9, 130.3, 129.4, 129.14, 129.05, 128.25, 128.23, 127.4, 114.7, 53.3 (fewer ^{13}C signals were observed due to signal overlapping); IR ($CHCl_3$, cm^{-1}) ν 3048, 3024, 1659, 1620, 1594, 1570, 1393, 1300, 1243, 1219, 1174, 1126, 1029, 759; HRMS (ESI) calcd for $C_{21}H_{14}IO_2$ $(M + H)^+$ 425.0033, found 425.0030.

*9-Fluoro-6-iodo-7-phenyldibenzocyclohepten-5-one (**2ad**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a light yellow solid (58.9 mg, 28% yield); mp 160.8−162.0 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 1H), 7.71 (dt, J = 7.4, 1.6 Hz, 1H), 7.67 (dd, J = 8.9, 5.9 Hz, 1H), 7.62 (dd, J = 7.7, 1.3 Hz, 1H), 7.56 (dt, J = 7.5, 1.0 Hz, 1H), 7.42−7.47 (m, 3H), 7.21−7.22 (m, 2H), 7.10−7.14 (m, 1H), 6.81 (dd, J = 10.3, 2.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 161.4 (d, J_{C-F} = 248.8 Hz), 149.3, 145.0, 139.5, 136.3 (d, J_{C-F} = 7.7 Hz), 135.7, 133.9 (d, J_{C-F} = 3.0 Hz), 133.3 (d, J_{C-F} = 8.4 Hz), 131.9, 129.3, 129.2, 128.9, 128.82, 128.76, 127.2, 118.1 (d, J_{C-F} = 23.9 Hz), 116.3 (d, J_{C-F} = 21.6 Hz), 103.4; IR ($CHCl_3$, cm^{-1}) ν 3061, 3020, 2924, 2852, 1675, 1597, 1478, 1233, 1207, 756; HRMS (ESI) calcd for $C_{21}H_{13}FIO$ $(M + H)^+$ 426.9990, found 426.9993.

*9-Chloro-6-iodo-7-phenyldibenzocyclohepten-5-one (**2ae**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (160.5 mg, 73% yield) from **1ae**; mp 213.7−216.3 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.56−7.63 (m, 3H), 7.41−7.47 (m, 3H), 7.37 (dd, J = 8.4, 2.1 Hz, 1H), 7.22 (s, broad, 2H), 7.09 (d, J = 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 149.0, 144.8, 139.6, 136.0, 135.9, 135.5, 133.7, 132.7, 132.0, 131.3, 129.3, 129.1, 128.9, 128.8, 127.2, 103.5 (fewer ^{13}C signals were observed due to signal overlapping); IR ($CHCl_3$, cm^{-1}) ν 3061, 3020, 2925, 2853, 1676, 1590, 1475, 1437, 1258, 1108, 756, 702; HRMS (ESI) calcd for $C_{21}H_{13}ClIO$ $(M + H)^+$ 442.9694, found 442.9697.

*6-Iodo-9-methyl-7-phenyldibenzocyclohepten-5-one (**2aga**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a white solid (179.1 mg, 85% yield); mp 152.3−153.3 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.69 (td, J = 7.7, 1.8 Hz, 1H), 7.62 (dd, J = 7.7, 1.6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.39−7.46 (m, 3H), 7.22−7.25 (m, 3H), 6.91 (d, J = 1.8 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 150.4, 145.6, 139.5, 137.6, 136.5, 134.9, 134.3, 132.0, 131.7, 131.2, 129.8, 129.3, 129.1, 128.6, 128.41, 128.35, 127.0, 102.0, 21.3; IR ($CHCl_3$, cm^{-1}) ν 3058, 3022, 2920, 1676, 1592, 1478, 1439, 1294, 1260, 1218, 1114, 827, 755; HRMS (ESI) calcd for $C_{22}H_{16}IO$ $(M + H)^+$ 423.0240, found 423.0241.

*9-(Chloromethyl)-6-iodo-7-phenyldibenzocyclohepten-5-one (**2agb**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (25.6 mg, 11% yield); mp 170.8−172.0 °C: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.70−7.74 (m, 2H), 7.62 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.42−7.47 (m, 4H), 7.23−7.24 (m, 2H), 7.08 (d, J = 1.3 Hz, 1H), 4.45 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 149.7, 145.1, 139.8, 137.6, 137.0, 135.9, 134.8, 131.93, 131.90, 131.7, 129.4, 129.3, 129.1, 128.84, 128.78, 128.68, 127.2, 102.8, 45.5; IR ($CHCl_3$, cm^{-1}) ν 3020, 2928, 1679, 1440, 1217, 758; HRMS (ESI) calcd for $C_{22}H_{15}ClIO$ $(M + H)^+$ 456.9851, found 456.9853.

*3′-Iodo-2′-phenyl-4′H-spiro[cyclohexa[2,4]diene-1,1′-naphthalene]-4′,6-dione (**3b**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a yellow solid (66.3 mg, 31% yield): sublime at 189.0−190.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31−8.33 (m, 1H), 7.48−7.53 (m, 2H), 7.32−7.39 (m, 3H), 7.15−7.16 (m, 1H), 7.05 (s, 1H), 6.92−6.98 (m, 2H), 6.32−6.37 (m, 2H), 6.04 (d, J = 9.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 179.8, 159.4, 142.8, 141.8, 141.5, 139.3, 133.6, 129.2, 129.1, 128.9, 128.6, 127.5, 126.5, 126.3, 122.5, 114.6, 63.8 (fewer ^{13}C signals were observed due to signal overlapping); IR ($CHCl_3$, cm^{-1}) ν 3064, 3017, 2927, 1664, 1594, 1301, 1221, 1132, 753; HRMS (ESI) calcd for $C_{21}H_{14}IO_2$ $(M + H)^+$ 425.0033, found 425.0032.

*3′-Iodo-2-methoxy-2′-phenyl-4′H-spiro[cyclohexa[2,5]diene-1,1′-naphthalene]-4,4′-dione (**3c**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a yellow solid from **1c** (196.3 mg, 86% yield): mp 258.4−259.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, J = 7.8, 0.7 Hz, 1H), 7.59 (dt, J = 7.6, 1.0 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.31−7.36 (m, 3H), 7.23 (d, J = 7.7 Hz, 1H), 6.99 (d, J = 7.0 Hz, 1H), 6.92−6.93 (m, 1H), 6.43 (d, J = 9.6 Hz, 1H), 6.26 (dd, J = 9.7, 0.5 Hz, 1H), 5.56 (s, 1H), 3.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.2, 179.0, 172.8, 160.2, 143.5, 141.1, 139.2, 134.0, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 128.2, 127.2, 126.94, 126.91, 115.1, 105.1, 56.2, 55.5; IR ($CHCl_3$, cm^{-1}) ν 3017, 2941, 2846, 1655, 1592, 1453, 1338, 1302, 1221, 1080, 982, 856, 761; HRMS (ESI) calcd for $C_{22}H_{16}IO_3$ $(M + H)^+$ 455.0139, found 455.0138.

*6-Iodo-9,10-dimethoxy-7-phenyldibenzocyclohepten-5-one (**2d**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (135.4 mg, 58% yield): mp 187.5−188.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 1H), 7.69 (dt, J = 7.4, 1.4 Hz, 1H), 7.62 (dd, J = 7.7, 1.3 Hz, 1H), 7.53 (dt, J = 7.5, 1.0 Hz, 1H), 7.37−7.45 (m, 3H), 7.23−7.24 (m, 2H), 7.13 (s, 1H), 6.51 (s, 1H), 3.96 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 150.2, 149.0, 148.1, 145.8, 139.1, 136.3, 131.7, 131.4, 129.3, 128.9, 128.6, 128.43, 128.40, 127.8, 127.3, 114.3, 113.1, 100.1, 56.2, 55.8; IR ($CHCl_3$, cm^{-1}) ν 3020, 1669, 1516, 1262, 1216, 761; HRMS (ESI) calcd for $C_{23}H_{18}IO_3$ $(M + H)^+$ 469.0295, found 469.0298.

*3′-Iodo-3-methoxy-2′-phenyl-4′H-spiro[cyclohexa[2,5]diene-1,1′-naphthalene]-4,4′-dione (**3d**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a white solid (40.8 mg, 18% yield): mp 250.8−251.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, J = 7.9, 0.7 Hz, 1H), 7.59 (dt, J = 7.3, 1.1 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.32−7.34 (m, 3H), 7.29 (d, J = 7.8 Hz, 1H), 6.96−7.00 (m, 2H), 6.73 (dd, J = 9.8, 2.7 Hz, 1H), 6.33 (d, J = 9.8 Hz, 1H), 5.70 (d, J = 2.6 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.9, 178.8, 161.6, 152.2, 147.9, 141.5, 139.8, 133.9, 130.1, 129.2, 129.1, 129.0, 128.3, 128.2, 128.1, 128.0, 127.5, 127.4, 116.0, 114.0, 55.4, 53.6; IR ($CHCl_3$, cm^{-1}) ν 3021, 1667, 1637, 1215, 760; HRMS (ESI) calcd for $C_{22}H_{16}IO_3$ $(M + H)^+$ 455.0139, found 455.0138.

*6-Iodo-8,9,10-trimethoxy-7-phenyldibenzocyclohepten-5-one (**2e**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (223.7 mg, 90% yield): mp 172.4−173.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.65−7.68 (m, 1H), 7.49−7.51 (m, 2H), 7.31−7.34 (m, 2H), 7.24−7.28 (m, 3H), 6.85 (s, 1H), 3.94 (s, 3H), 3.74 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 153.9, 152.1, 144.79, 144.76, 141.9, 140.8, 136.8, 134.4, 131.6, 129.0, 128.5, 128.4, 127.8, 127.7, 126.5, 123.2, 108.7, 98.4, 60.7, 59.5, 56.2; IR ($CHCl_3$, cm^{-1}) ν 3017, 2940, 2848, 1691, 1588, 1480, 1384, 1348, 1215, 1122, 1107, 759; HRMS (ESI) calcd for $C_{24}H_{20}IO_4$ $(M + H)^+$ 499.0401, found 499.0403.

*6-Iodo-9-methoxy-8,10-dimethyl-7-phenyldibenzocyclohepten-5-one (**2f**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (93.9 mg, 40% yield): mp 165.2−165.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.62 (dt, J = 7.5, 1.0 Hz, 1H), 7.48 (d, J = 7.5 Hz,1H), 7.43 (t, J = 7.4 Hz, 1H), 7.25−7.29 (m, 6H), 3.58 (s, 3H), 2.33 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 156.9, 145.4, 142.8, 140.7, 137.3, 134.6, 134.0, 131.9, 131.5, 131.3, 131.0, 130.1, 128.4, 128.2, 127.9, 127.7, 126.3, 98.5, 60.0, 16.6, 15.9; IR ($CHCl_3$, cm^{-1}) ν 3019, 2963, 2934, 1694, 1592, 1471, 1444, 1254, 1202, 1117, 1072, 1003, 756; HRMS (ESI) calcd for $C_{24}H_{20}IO_2$ $(M + H)^+$ 467.0502, found 467.0504.

*3′-Iodo-3,5-dimethyl-2′-phenyl-4′H-spiro[cyclohexa[2,5]diene-1,1′-naphthalene]-4,4′-dione (**3f**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a yellow crystal (70.6 mg, 31% yield): mp 204.7−205.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, J = 8.0, 1.6 Hz, 1H), 7.57 (td, J = 7.5, 1.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.31−7.32 (m, 3H), 7.23 (d, J = 7.8 Hz, 1H), 6.92−6.94 (m, 2H), 6.48 (s, 2H), 1.81 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.9, 179.0, 162.1, 142.6, 141.7, 140.0, 136.9, 133.7, 129.0, 128.82, 128.80, 128.17, 128.14, 127.9, 127.3, 113.7, 53.3, 16.1; IR ($CHCl_3$, cm^{-1}) ν 3009, 2921, 1659, 1641, 1596, 1450, 1297, 1241, 1122, 1038, 756; HRMS (ESI) calcd for $C_{23}H_{18}IO_2$ $(M + H)^+$ 453.0346, found 453.0345.

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*6-Iodo-3,9-dimethoxy-7-phenyl-5H-dibenzocyclohepten-5-one (**2g**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow crystal (18.7 mg, 8% yield): mp 174.2−175.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.38−7.45 (m, 3H), 7.21−7.25 (m, 3H), 7.09 (d, J = 2.8 Hz, 1H), 6.96 (dd, J = 8.7, 2.6 Hz, 1H), 6.58 (d, J = 2.7 Hz, 1H), 3.92 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 159.6, 158.0, 150.6, 145.9, 140.0, 135.1, 132.2, 130.6, 130.5, 129.4, 129.3, 128.7, 128.4, 119.6, 116.8, 115.0, 110.1, 102.1, 55.9, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3021, 2955, 2833, 1662, 1603, 1483, 1338, 1280, 1218, 1130, 1051, 1038, 755; HRMS (ESI) calcd for $C_{23}H_{18}IO_3$ $(M + H)^+$ 469.0295, found 469.0296.

*3′-Iodo-6′-methoxy-2′-phenyl-4′H-spiro[cyclohexa[2,5]diene-1,1′-naphthalene]-4,4′-dione (**3g**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a light yellow solid (184.0 mg, 81% yield): mp 268.1−269.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 2.7 Hz, 1H), 7.32−7.37 (m, 3H), 7.14−7.20 (m, 2H), 6.99−7.01 (m, 2H), 6.68−6.71 (m, 2H), 6.27−6.30 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7, 178.7, 160.7, 160.2, 148.0, 141.5, 130.4, 130.1, 129.7, 129.4, 129.1, 128.2, 127.4, 122.5, 114.5, 110.6, 55.9, 53.0; IR ($CHCl_3$, cm^{-1}) ν 3055, 3019, 2968, 1670, 1648, 1493, 1345, 1288, 1239, 1039, 863, 829; HRMS (ESI) calcd for $C_{22}H_{16}IO_3$ $(M + H)^+$ 455.0139, found 455.0137.

*6-Iodo-7-phenyldibenzocyclohepten-5-one (**2h**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (183.7 mg, 90% yield): mp 131.5−132.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.71 (ddd, J = 7.7, 7.4, 1.4 Hz, 2H), 7.63 (dd, J = 7.4, 1.4 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.40−7.45 (m, 4H), 7.21−7.26 (m, 3H), 7.12 (dd, J = 8.1, 1.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 150.4, 145.6, 139.8, 137.6, 136.5, 134.6, 131.9, 131.8, 131.3, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 127.8, 127.1, 102.1; IR ($CHCl_3$, cm^{-1}) ν 3061, 3019, 1676, 1595, 1441, 1217, 760; HRMS (ESI) calcd for $C_{21}H_{14}IO$ $(M + H)^+$ 409.0084, found 409.0085.

*6-Iodo-10-methoxy-7-phenyldibenzocyclohepten-5-one (**2i**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as an orange oil (191.5 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.71 (dt, J = 7.6, 1.5 Hz, 1H), 7.63 (dd, J = 7.8, 1.4 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.39−7.44 (m, 3H), 7.22−7.23 (m, 2H), 7.17 (d, J = 2.6 Hz, 1H), 7.03 (d, J = 8.9 Hz, 1H), 6.77 (dd, J = 8.9, 2.7 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 159.2, 150.4, 145.9, 139.5, 139.2, 136.3, 134.0, 131.8, 129.4, 129.3, 129.0, 128.6, 128.4, 127.9, 127.3, 115.8, 113.9, 99.9, 55.7; IR ($CHCl_3$, cm^{-1}) ν 3009, 2840, 1671, 1602, 1490, 1338, 1282, 1232, 1071, 1037, 752, 701; HRMS (ESI) calcd for $C_{22}H_{16}IO_2$ $(M + H)^+$ 439.0189, found 439.0191.

*10-Fluoro-6-iodo-7-phenyldibenzocyclohepten-5-one (**2j**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (191.9 mg, 90% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 1H), 7.73 (t, J = 7.1 Hz, 1H), 7.58−7.64 (m, 2H), 7.38−7.45 (m, 4H), 7.22 (s, broad, 2H), 7.11 (dd, J = 8.9, 6.0 Hz, 1H), 6.90−6.94 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 161.8 (d, J_{C-F} = 252.5 Hz), 149.5, 145.4, 139.9 (d, J_{C-F} = 8.4 Hz), 139.6, 135.3 (d, J_{C-F} = 1.7 Hz), 134.5 (d, J_{C-F} = 8.4 Hz), 132.0, 131.0 (d, J_{C-F} = 3.1 Hz), 129.43, 129.36, 129.2, 128.8, 128.6, 127.3, 117.4 (d, J_{C-F} = 22.9 Hz), 115.2 (d, J_{C-F} = 21.5 Hz), 101.5; IR ($CHCl_3$, cm^{-1}) ν 3063, 3020, 1675, 1609, 1588, 1487, 1440, 1217, 753, 700; HRMS (ESI) calcd for $C_{21}H_{13}FIO$ $(M + H)^+$ 426.9990, found 426.9992.

*6-Iodo-8,10-dimethyl-7-phenyldibenzocyclohepten-5-one (**2k**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (196.3 mg, 90% yield): mp 218.0−219.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 1H), 7.62 (dt, J = 7.4, 1.5 Hz, 1H), 7.49 (dt, J = 7.0, 1.8 Hz, 1H), 7.43 (dt, J = 7.5, 1.3 Hz, 1H), 7.23−7.28 (m, 6H), 6.89 (d, J = 1.6 Hz, 1H), 2.33 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 145.6, 142.8, 140.9, 138.5, 138.33, 138.30, 137.5, 132.1, 131.8, 131.5, 130.0, 129.1, 128.6, 128.2, 128.1, 127.7, 126.1, 98.5, 23.2, 21.3; IR ($CHCl_3$, cm^{-1}) ν 3019, 2947, 2922, 1690, 1591, 1444, 1277, 1216, 756; HRMS (ESI) calcd for $C_{23}H_{18}IO$ $(M + H)^+$ 437.0397, found 437.0397.

*6-Iodo-8,10-dimethoxy-7-phenyldibenzocyclohepten-5-one (**2l**).* Three equivalents of I_2 was used instead of ICl. Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (114.0 mg, 49% yield): mp 180.5−181.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.9 Hz, 1H), 7.65−7.68 (m, 1H), 7.50−7.52 (m, 2H), 7.23−7.29 (m, 3H), 7.19−7.21 (m, 2H), 6.72 (d, J = 2.5 Hz, 1H), 6.37 (d, J = 2.5 Hz, 1H), 3.86 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 160.4, 159.3, 145.0, 144.8, 140.9, 140.0, 136.8, 131.6, 128.9, 128.8, 128.7, 127.4, 127.2, 126.5, 118.7, 106.7, 99.6, 98.1, 55.73, 55.66; IR ($CHCl_3$, cm^{-1}) ν 3015, 2936, 2839, 1688, 1600, 1456, 1338, 1208, 1026, 758; HRMS (ESI) calcd for $C_{23}H_{18}IO_3$ $(M + H)^+$ 469.0295, found 469.0285.

*6-Iodo-10,11-dimethoxy-7-phenyldibenzocyclohepten-5-one (**2m**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (207.3 mg, 89% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.50−7.55 (m, 2H), 7.37−7.42 (m, 3H), 7.22 (d, J = 6.3 Hz, 2H), 6.80 (q, J = 9.0 Hz, 2H), 3.87 (s, 3H), 3.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 152.9, 149.8, 146.9, 145.1, 140.8, 132.3, 132.0, 130.3, 129.8, 129.4, 128.9, 128.7, 128.5, 128.3, 127.7, 125.8, 111.6, 99.7, 60.5, 56.1; IR ($CHCl_3$, cm^{-1}) ν 3017, 2939, 2838, 1679, 1590, 1486, 1289, 1218, 1132, 1018, 758, 702; HRMS (ESI) calcd for $C_{23}H_{18}IO_3$ $(M + H)^+$ 469.0295, found 469.0298.

*6-Iodo-10-methoxy-9-methyl-7-phenyldibenzocyclohepten-5-one (**2n**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (194.7 mg, 86% yield): mp 172.2−173.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.9 Hz, 1H), 7.71 (td, J = 7.5, 1.5 Hz, 1H), 7.64 (dd, J = 7.4, 1.4 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.40−7.45 (m, 3H), 7.23 (s, broad, 2H), 7.07 (s, 1H), 6.85 (s, 1H), 3.91 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 157.7, 150.6, 145.9, 139.4, 136.9, 136.6, 134.1, 131.7, 129.4, 129.1, 128.64, 128.56, 128.3, 127.23, 127.21, 127.0, 111.7, 99.6, 55.7, 16.1; IR ($CHCl_3$, cm^{-1}) ν 3019, 1669, 1606, 1503, 1339, 1251, 1216, 1142, 1026, 761; HRMS (ESI) calcd for $C_{23}H_{18}IO_2$ $(M + H)^+$ 453.0346, found 453.0349.

*3-Fluoro-6-iodo-10-methoxy-7-phenyldibenzocyclohepten-5-one (**2o**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (201.7 mg, 88% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 8.7, 5.1 Hz, 1H), 7.38−7.45 (m, 4H), 7.33 (dd, J = 8.3, 2.7 Hz, 1H), 7.20−7.21 (m, 2H), 7.12 (d, J = 2.6 Hz, 1H), 7.02 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 8.9, 2.7 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 164.9 (d, J_{C-F} = 251.5 Hz), 159.3, 151.1, 145.8, 140.8 (d, J_{C-F} = 6.7 Hz), 138.3, 134.1, 132.6 (d, J_{C-F} = 3.0 Hz), 131.6 (d, J_{C-F} = 8.2 Hz), 129.3, 128.7, 128.5, 127.7, 119.1 (d, J_{C-F} = 21.6 Hz), 115.8, 113.8 (d, J_{C-F} = 3.0 Hz), 113.6, 98.9, 55.7; IR ($CHCl_3$, cm^{-1}) ν 3013, 2938, 2846, 1675, 1607, 1492, 1273, 1228, 832, 752; HRMS (ESI) calcd for $C_{22}H_{15}FIO_2$ $(M + H)^+$ 457.0095, found 457.0096.

*6-Iodo-3,10-dimethoxy-7-phenyldibenzocyclohepten-5-one (**2p**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (224.9 mg, 96% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.8 Hz, 1H), 7.37−7.44 (m, 3H), 7.24−7.26 (m, 1H), 7.20 (d, J = 5.6 Hz, 2H), 7.12 (dd, J = 4.2, 2.8 Hz, 2H), 7.00 (d, J = 8.9 Hz, 1H), 6.72 (dd, J = 8.9, 2.5 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 160.2, 159.2, 150.8, 146.2, 140.3, 139.0, 134.1, 131.0, 129.3, 129.2, 128.6, 128.3, 127.4, 119.4, 115.3, 113.3, 110.2, 99.5, 55.9, 55.6; IR ($CHCl_3$, cm^{-1}) ν 3013, 2963, 2937, 2838, 1668, 1600, 1489, 1335, 1294, 1226, 1042, 757; HRMS (ESI) calcd for $C_{23}H_{18}IO_3$ $(M + H)^+$ 469.0295, found 469.0297.

*6-Iodo-7-(4-methoxyphenyl)dibenzocyclohepten-5-one (**2q**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (191.2 mg, 87% yield): mp 132.9−133.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.67−7.71 (m, 2H), 7.63 (d, J = 7.4 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.17−7.22 (m, 3H), 7.12 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 8.1 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.7, 159.4, 150.0, 139.7, 137.8, 137.4, 136.3, 134.8, 132.0, 131.7, 131.1, 130.8, 129.2, 128.64, 128.59, 127.6, 126.9, 113.8, 101.7, 55.4; IR ($CHCl_3$, cm^{-1}) ν 3061, 3014, 2956, 2835, 1672, 1605, 1507,

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1296, 1248, 1174, 1031, 759; HRMS (ESI) calcd for $C_{22}H_{16}IO_2$ $(M + H)^+$ 439.0189, found 439.0190.

*9-Chloro-6-iodo-7-(4-methoxyphenyl)dibenzocyclohepten-5-one (**2r**).* Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (214.3 mg, 91% yield): mp 209.8−211.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.71 (dt, J = 7.2, 1.7 Hz, 1H), 7.59−7.62 (m, 2H), 7.56 (dt, J = 7.1, 0.9 Hz, 1H), 7.36 (dd, J = 8.5, 2.2 Hz, 1H), 7.15−7.16 (m, 2H), 7.08 (d, J = 2.3 Hz, 1H), 6.95−6.97 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 159.8, 148.7, 139.7, 137.1, 136.2, 136.1, 135.5, 133.6, 132.6, 131.9, 131.5, 130.9, 129.1, 129.0, 128.8, 127.1, 114.1, 103.1, 55.5; IR ($CHCl_3$, cm^{-1}) ν 3013, 2958, 2931, 2838, 1678, 1606, 1507, 1475, 1294, 1248, 1175, 1107, 1031, 830, 752; HRMS (ESI) calcd for $C_{22}H_{15}ClIO_2$ $(M + H)^+$ 472.9800, found 472.9801.

*Methyl 4-(6-Iodo-10-methoxy-5-oxo-dibenzocyclohepten-7-yl)-benzoate (**2s**).* Eluent of column chromatography: hexanes/ethyl acetate 5:1. This product was obtained as a yellow oil (234.7 mg, 95% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10−8.12 (m, 2H), 7.85 (d, J = 7.9 Hz, 1H), 7.70−7.73 (m, 1H), 7.62 (dd, J = 7.6, 1.4 Hz, 1H), 7.57 (dt, J = 7.5, 1.0 Hz, 1H), 7.31−7.32 (m, 2H), 7.18 (d, J = 2.8 Hz, 1H), 6.95 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 8.9, 2.7 Hz, 1H), 3.94 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 166.8, 159.4, 150.1, 149.5, 139.41, 139.39, 136.2, 133.6, 131.9, 130.02, 129.99, 129.6, 129.4, 129.1, 127.32, 127.30, 116.1, 113.9, 100.0, 55.7, 52.5; IR ($CHCl_3$, cm^{-1}) ν 3016, 2951, 2840, 1723, 1675, 1607, 1436, 1281, 1112, 1018, 757, 706; HRMS (ESI) calcd for $C_{24}H_{18}IO_4$ $(M + H)^+$ 497.0244, found 497.0231.

*6-Iodo-10-methoxy-7-(thiophen-3-yl)dibenzocyclohepten-5-one (**2t**).* Three equivalents of I_2 was used instead of ICl. Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow solid (206.1 mg, 93% yield): mp 155.0−156.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.37−7.38 (m, 1H), 7.31 (d, J = 1.5 Hz, 1H), 7.16 (d, J = 2.2 Hz, 1H), 7.06 (d, J = 8.9 Hz, 1H), 6.99 (d, J = 4.9 Hz, 1H), 6.79 (dd, J = 8.9, 2.3 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 159.2, 146.1, 145.3, 139.5, 138.9, 136.2, 133.6, 131.8, 129.2, 128.96, 128.89, 127.8, 127.1, 125.7, 125.6, 115.7, 113.9, 99.9, 55.6; IR ($CHCl_3$, cm^{-1}) ν 3016, 2939, 2837, 1672, 1605, 1280, 1212, 758; HRMS (ESI) calcd for $C_{20}H_{14}IO_2S$ $(M + H)^+$ 444.9754, found 444.9758.

*7-(Cyclohex-1-en-1-yl)-6-iododibenzocyclohepten-5-one (**2u**).* Three equivalents of I_2 was used instead of ICl. Eluent of column chromatography: hexanes/ethyl acetate 10:1. This product was obtained as a yellow oil (173.7 mg, 79% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.69 (d, J = 8.9 Hz, 1H), 7.65 (dt, J = 7.9, 1.4 Hz, 1H), 7.59 (dd, J = 7.6, 1.2 Hz, 1H), 7.52 (dt, J = 7.5, 0.8 Hz, 1H), 7.14 (d, J = 2.8 Hz, 1H), 6.93 (dd, J = 8.8, 2.7 Hz, 1H), 5.84−5.86 (m, 1H), 3.88 (s, 3H), 2.27−2.29 (m, 2H), 1.88−1.90 (m, 2H), 1.68−1.69 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 159.2, 152.1, 142.8, 139.5, 139.4, 136.2, 132.3, 131.5, 130.5, 129.2, 128.8, 127.2, 125.5, 116.1, 114.2, 98.2, 55.7, 27.6, 25.2, 22.8, 22.0; IR ($CHCl_3$, cm^{-1}) ν 3015, 2933, 2835, 1670, 1603, 1486, 1281, 1254, 1214, 755; HRMS (ESI) calcd for $C_{22}H_{19}IKO_2$ $(M + K)^+$ 481.0061, found 481.0046.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for the 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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