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Electrochemical Oxidative Halogenation of *N*-Aryl Alkynamides for the Synthesis of Spiro[4.5]trienones

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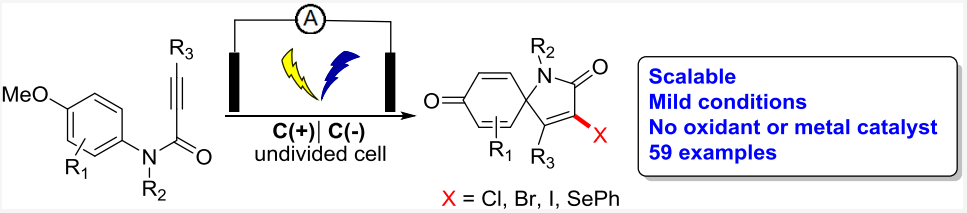


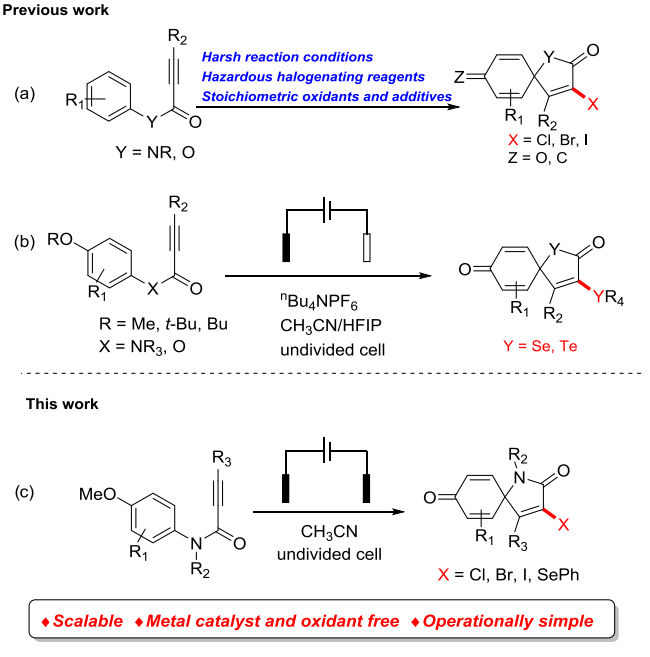
ABSTRACT: We developed a green method for the synthesis of spiro[4.5]trienones through an electrochemical oxidative halocyclization with *N*-aryl alkynamides. This reaction was conducted under metal-catalyst- and exogenous-oxidant-free conditions at room temperature. Using readily available LiCl, LiBr, and LiI as the halogen source, a variety of dearomative halo-spirocyclization products were obtained in good to excellent yields with a broad scope and functional group tolerance.

INTRODUCTION

Spirocyclic compounds are important structural motifs widely existing in many natural products and bioactive molecules.[1] Owing to their unique structure, they play a pivotal role in organic synthesis.[2] Consequently, great efforts have been devoted to the construction of a spirocyclic framework.[3] For example, methods including dearomatization of phenol derivatives,[4] electrophilic *ipso*-cyclization,[5] radical dearomatization tandem reaction,[6] etc.,[7] have been established for the synthesis of spiro[4.5]trienones. Moreover, the introduction of halogen atoms into the framework of organic compounds can greatly improve the pharmacological activities[8] and act as a versatile intermediate for further ample functionalization.[9] Over the past decade, a variety of halogenated spiro[4.5]-trienones have been constructed via alkymate or alkyamide intramolecular *ipso*-cyclization and coupling with iodine monochloride (ICl),[10] I_2,[10a,b] CuX (X = I, Br, SCN), and electrophilic fluoride reagents,[11] NXS,[12] or hypervalent iodine(III) reagent bis(trifluoroacetate) (PIFA)[13] (Scheme 1a). Despite the remarkable achievement, these strategies generally suffer from disadvantages such as exogenous additives,[13] stoichiometric oxidants,[14] and harsh reaction conditions.[10c,11,12,13b] Thus, the development of a green and environmentally friendly approach under mild conditions for the synthesis of halogenated spiro[4.5]trienones is still strongly desirable.

Electrochemistry has become a routine technique in organic synthesis due to its convenience and environmental sustainability as well as controllability simply by potential, current, or total charge.[15] Remarkable progress has been made to prompt the investigations of reactions for C−C,[16] C−O,[17] C−N,[18] and C−X[19] bond formation. In 2020, Guo's group developed a

Scheme 1. Synthesis of Spiro[4.5]trienones



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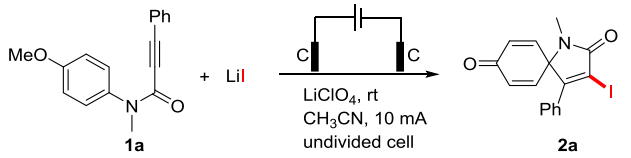
radical-initiated dearomative selenylative spirocyclization of alkynes through a direct constant current electrolysis[20] (Scheme 1b). Inspired by this and other electrochemical dearomatization studies,[21] we here for the first time report a clean halogenation through an electrochemical dearomative spirocyclization for the synthesis of spiro[4.5]trienones from readily available halide salts (LiX, X = Cl, Br, I). The reaction was conducted at room temperature without metal catalysts or exogenous oxidants.

RESULTS AND DISCUSSION

Initially, we chose *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropiolamide (**1a**) as the model substrate to explore the reaction conditions in an undivided cell (Table 1). After optimizations, we found that 86% isolated yield of desired product **2a** could be obtained at 10 mA constant current in CH_3CN using graphite electrodes as both the cathode and anode at room temperature (entry 1). A mixture of CH_3CN with H_2O or dichloroethane (DCE) gave lower yields (entries 2−4). Alternative iodine sources such as tetrabutylammonium iodide (TBAI) and potassium iodide (KI) were found less efficient (entries 5 and 6). Furthermore, LiBr or LiCl was found to be a good bromine or chloride source with yields as high as 87 or 82%. However, KBr afforded an obviously decreased yield (entries 7−9). Decreasing current to 5 mA led to no reaction, while increasing to 15 mA resulted in a quite close conversion (entries 10 and 11). Subsequently, replacing the electrolyte of $LiClO_4$ with *n*-Bu_4NPF_6, *n*-Bu_4NClO_4, or *n*-Bu_4NBF_4 afforded no reaction (entries 12−14). The reaction under a N_2 atmosphere displayed a lower yield relative to the air atmosphere (entry 15). This result indicated that the oxygen atom of the ketone group formed by dearomative spirocyclization was derived from the methoxy group of **1a**. No desired product was observed without the electrolyte or electricity (entries 16 and 17). In the end, we explored the electrode materials for this electrochemical dearomatization reaction. Pt (+)/Pt (−) and C (+)/Pt (−) electrodes both led to decreased yields, while the Pt (+)/C (−) combination gave a very similar yield (Table S1 in the Supporting Information).

Table 1. Optimization of Reaction Conditions[a]



entry	variation from standard conditions[a]	yield (%)[b]
1	none[a]	86
2	CH_3CN/H_2O = 9:1	52
3	CH_3CN/H_2O = 5:1	45
4	CH_3CN/DCE = 9:1	78
5	TBAI instead of LiI	74
6	KI instead of LiI	70
7	LiBr	87[c]
8	LiCl	82[d]
9	KBr instead of LiBr	41[c,e]
10	5 mA instead of 10 mA	NR[f]
11	15 mA instead of 10 mA	84
12	*n*-Bu_4NPF_6 instead of $LiClO_4$	NR[f]
13	*n*-Bu_4NClO_4 instead of $LiClO_4$	NR[f]
14	*n*-Bu_4NBF_4 instead of $LiClO_4$	NR[d]
15	N_2 atmosphere	76
16	no electrolyte	NR[d]
17	no electric current	NR[d]

[a]Reaction conditions: graphite anode and cathode (52.5 mm × 8.0 mm × 1.5 mm), constant current = 10 mA, **1a** (0.125 mmol), LiI (0.25 mmol), $LiClO_4$ (0.2 M), CH_3CN (4 mL), room temperature, undivided cell. [b]Isolated yield. [c]Product **3a**. [d]Product **4a**. [e]Constant current = 8 mA. [f]NR = no reaction.

With the optimized conditions in hand, we next investigated the substrate scope of iodinated and brominated spiro[4,5]-trienones (Scheme 2). First, the substitutes on the nitrogen such as methyl, ethyl, benzyl, and isopropyl groups all showed good tolerance with excellent yields of corresponding products ranging from 75 to 92% (**2a−d**, **3a−d**). It was pleasing to find that the *N*-allyl group also applies to this reaction, and the iodinated and brominated products could be obtained with yields of 56 and 70%, respectively (**2e**, **3e**). Sterically hindered electron-withdrawing groups such as *t*-butyloxycarbonyl (Boc) and benzyloxycarbonyl (Cbz) could take part in this transformation with moderate yields (**2f−g**, **3f−g**). Substrates bearing *ortho*-methyl and two *meta*-methoxy groups on the *N*-aryl ring also proceeded smoothly to give the desired products (71−92%, **2h−i**, **3h−i**). Aryl substituents at the terminal alkynes bearing halide (*p*-F, *p*-Cl, *p*-Br) groups were successfully coupled with **1a** with the yields of 70−90% (**2j−l**, **3j−l**). When strong electron-withdrawing groups (*p*-CF_3, *p*-CN) were installed, iodinated products were achieved in moderate yields (**2m−n**), and brominated products gave high yields (**3m−n**). In addition, methyl groups at different positions of the aryl ring afforded a decreasing yield from para to meta and to ortho due to the steric effect (**2o−r**, **3o−r**). Notably, heteroaromatic groups such as furan and thiophene were also suitable for this reaction (**2s−t**, **3s−t**).

Compared with iodination and bromination, there are very few examples reporting the chlorination of spirocyclization in the literature.[10] We here further evaluated the scope and generality of the chlorination of spiro[4,5]trienones (Scheme 3). Gratifyingly, when *N* was protected by electron-donating groups or sterically hindered electron-withdrawing groups, the corresponding products (**4a−g**) were obtained in moderate to excellent yields (52−91%). However, the substrate of *N*-allyl only gave a trace amount of the desired product (**4e**). It is interesting to find that the substrate with *ortho*-methyl groups on the aryl ring could get the desired chlorination product in 51% yield (**4h**), whereas substrates bearing two *meta*-methoxy groups only afforded a chlorinated quinolinone product (**4i′**). We speculate that this is due to the increased nucleophilicity of the aromatic ring. Moreover, the aryl substitutes at the terminal C−C triple bond showed good performance. Substrates with electron-withdrawing (*p*-Br, *p*-CN) and -donating (*p*-methoxy, *p*-methyl, *o*-methyl) groups were all tolerated under standard reaction conditions (**4j−n**). Unfortunately, no desired product was detected for the heterocycle furan group at the alkyne (**4o**). Finally, the *N*-H-substituted substrate failed to afford the desired halogenated products.

We continued to investigate the spirocyclization reaction of alkynamides with diphenyl selenium (Scheme 4). Both electron-withdrawing and electron-donating groups performed well under standard conditions (**5a−e**, 50−99%). Specifically, *N*-H-substituted alkynamides and the terminal terminal alkyne gave yields of 52 and 60%, respectively. Very recently, Guo and co-workers[20] reported the preparation of selenylated spiro-[4,5]trienones using electrochemistry in a mixture of solvents

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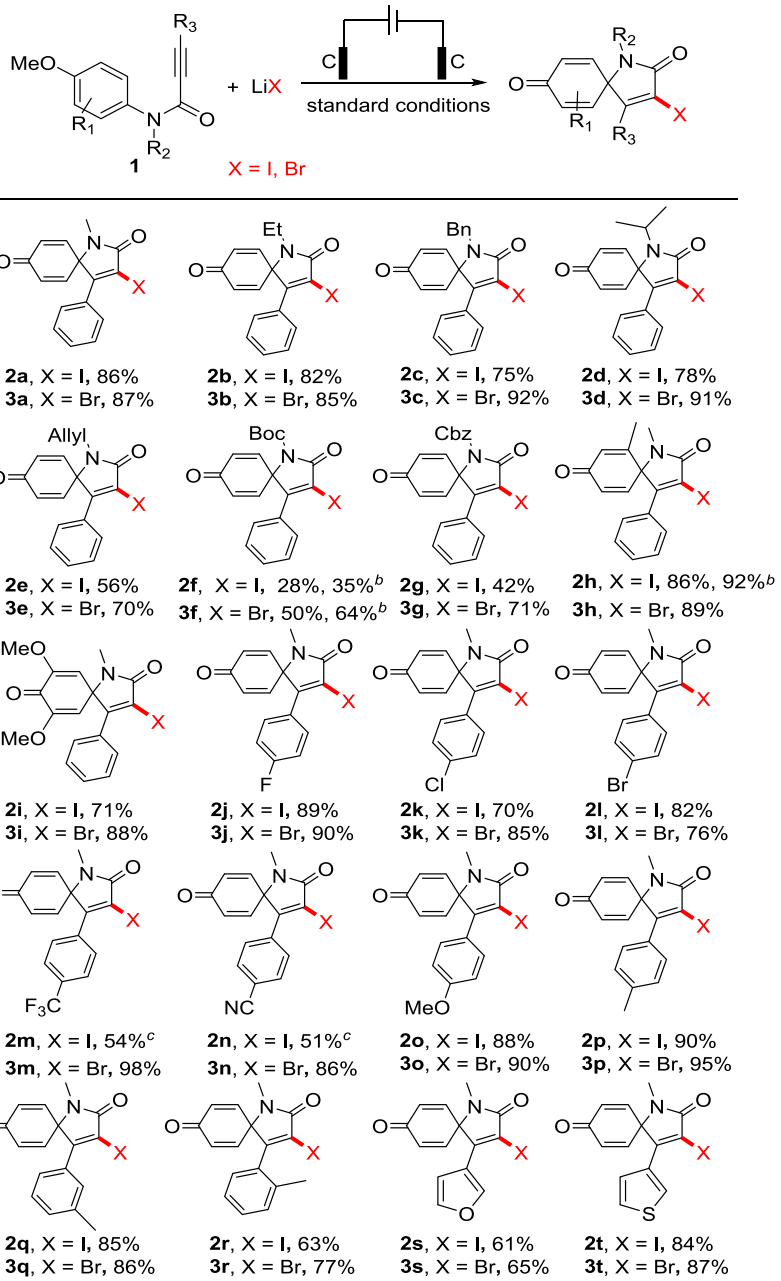
Scheme 2. Substrate Scope of Electrochemical Synthesis of Iodinated and Brominated Spiro[4,5]trienones[a,b,c]



[a]Reaction conditions: graphite anode and cathode (52.5 mm × 8.0 mm × 1.5 mm), constant current = 10 mA, **1a** (0.125 mmol), LiI or LiBr (0.25 mmol), $LiClO_4$ (0.2 M), CH_3CN (4 mL), room temperature, undivided cell, 2 h. [b]Pt anode (52.5 mm × 8.0 mm × 1.5 mm), graphite cathode (52.5 mm × 8.0 mm × 1.5 mm). [c]12 mA, 2 h.

CH_3CN/HFIP. Therefore, we here only present a few examples. Notably, diphenyldisulfane was also tried; however, no desired product was obtained. Similar results have been reported by Guo.[20a]

To evaluate the potential applicability of this electrochemical oxidative halogenation protocol, a scale-up reaction was conducted. As shown in Scheme 5, 4.0 mmol (1.06 g) of **1a** was electrolyzed at 40 mA for 10 h, and the corresponding brominated product could be obtained with a yield of 80% (1.05 g), indicating the potential industrial application prospects of this method. Subsequently, we performed derivatization experiments of product **2a**. The Sonogashira and Suzuki coupling reaction proceeded smoothly with desired products **6a** and **6b** in excellent yields (Scheme S1 in the Supporting Information).

To shed light on the reaction mechanism of this method, a series of control experiments were carried out. When *N*-methyl-*N*,3-diphenylpropiolamide **1b** and *N*-(4-fluorophenyl)-*N*-methyl-3-phenylpropiolamide **1c** were chosen to react with LiI, no reactions occurred under standard conditions. It should be noted that coupling of alkynamides **1a** with LiI gave a yield of 86% under the same condition (Table 1, entry 1). The above observation indicated that the methoxy group contributed to the formation of ketones. Furthermore, in the radical trapping experiments, by the addition of 3 equiv of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) or bu-

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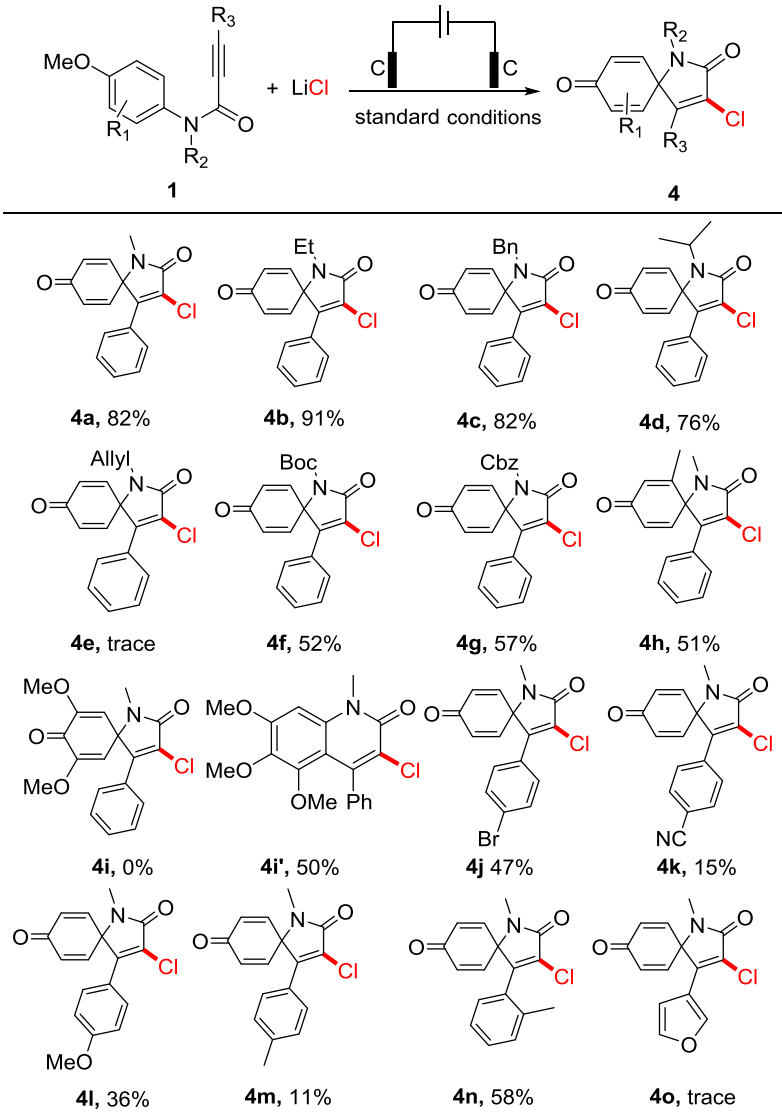
Scheme 3. Substrate Scope of Electrochemical Synthesis of Chlorinated Spiro[4,5]trienones[a]



[a]Reaction conditions: graphite anode and cathode (52.5 mm × 8.0 mm × 1.5 mm), constant current = 8 mA, **1a** (0.125 mmol), LiCl (0.25 mmol), $LiClO_4$ (0.2 M), CH_3CN (4 mL), room temperature, undivided cell, 2 h.

tylated hydroxytoluene (BHT) into the reaction system, the yields of iodinated and brominated products sharply decreased and the chlorinated product was completely suppressed (Schemes 5(b)2−3), suggesting that radical intermediates are probably involved in this process.

Cyclic voltammograms of related compounds were investigated on the glassy carbon electrode. As shown in Figure 1, LiI undergoes two oxidation processes at 0.44 and 0.76 V, while an oxidation peak for reactant **1a** is observed at 1.48 V.

Based on the above experiments and cyclic voltammetric results, a plausible mechanism was proposed in Scheme 6. First, the iodine anion lost electrons at the anode and became iodine cation **B**. Then, iodine cation **B** reacted with **1a** to form cyclic iodonium **C**. Subsequently, **C** underwent thermodynamically controlled *ispo*-electrophilic spirocyclization onto the aromatic ring to give oxonium ion **D**, which was followed by demethylation to the final product **2a**. On the other hand, iodine radical **E** might be produced by the iodine anion oxidation in path II. After combining with **1a**, vinyl radical species **F** could be generated and converted into intermediate **G** by intramolecular *ispo*-spirocyclization. The intermediate **G** underwent the same process as path I to form **2a**.

In summary, we have developed an environment-friendly and operationally simple electrocatalytic protocol for the synthesis of halogenated and selenylated spiro[4.5]trienones under metal-catalyst- and oxidant-free conditions. With cheap graphite electrodes and lithium salts, we can get a series of dearomatization products. The gram-scale experiment shows that this method has prospective applications.

EXPERIMENTAL SECTION

General Methods. Commercial reagents and solvents were purchased and used without further purification. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Alternatively, ^{1}H NMR chemical shifts were referenced to a tetramethylsilane signal (0 ppm). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (J) are reported in hertz (Hz). High

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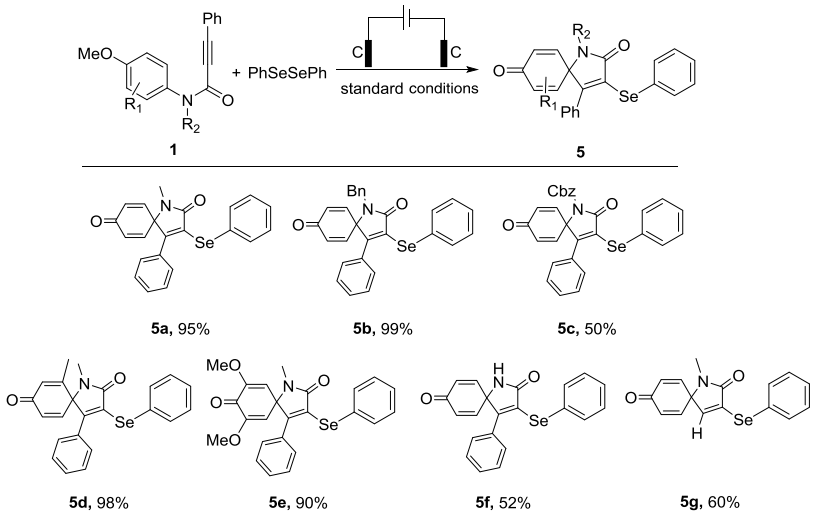
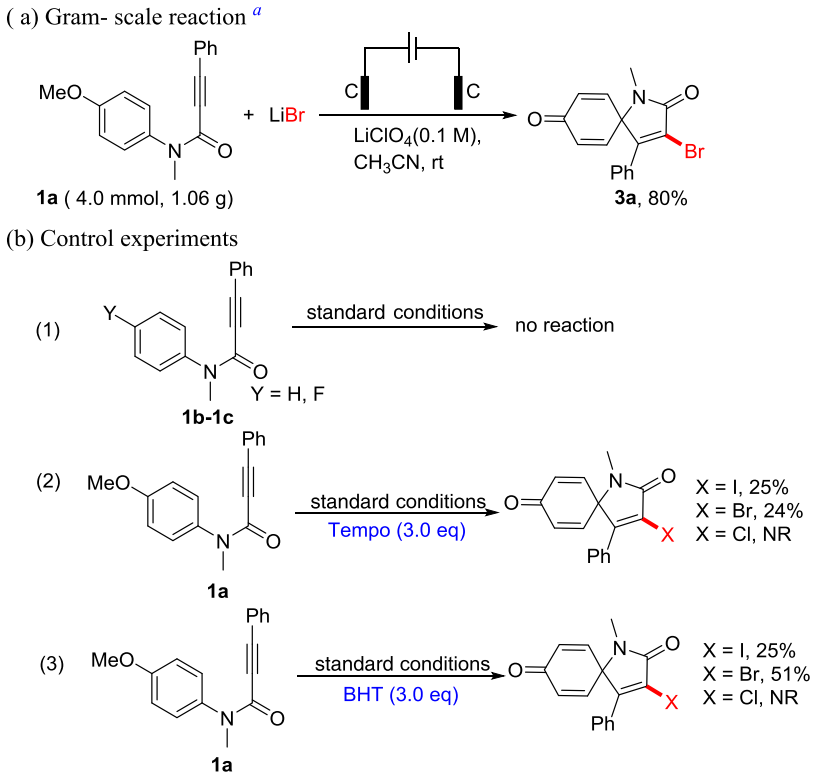
Scheme 4. Substrate Scope of Electrochemical Synthesis of Selenylated Spiro[4,5]trienones[a]



[a]Reaction conditions: graphite anode and cathode (52.5 mm × 8.0 mm × 1.5 mm), constant current = 10 mA, 1 (0.125 mmol), PhSeSePh (0.25 mmol), $LiClO_4$ (0.2 M), CH_3CN (4 mL), room temperature, undivided cell, 1 h.

Scheme 5. Gram-Scale Reaction and Control Experiments[a]



[a]Reaction conditions: carbon felt as the anode and cathode (4.0 cm × 4.0 cm), constant current = 40 mA, **1a** (4.0 mmol), LiBr (10.0 mmol), $LiClO_4$ (0.1 M), CH_3CN (80 mL), room temperature, undivided cell, 10 h.

resolution mass spectrometry (HRMS) was performed on a Thermo Scientific Q Exactive HF Orbitrap-FTMS apparatus.

General Procedure for the Synthesis of *N*-Aryl Alkynamides.[22] To an ice-bath-cooled solution of the relative aniline (5.0 mmol, 1.0 equiv) in dichloromethane (DCM; 30 mL) was added 3-phenylpropiolic acid (5.5 mmol, 1.1 equiv), and a mixture of *N*,*N*′-dicyclohexylcarbodiimide (DCC; 7.5 mmol, 1.5 equiv, 1.5 g) and 4-dimethyl- aminopyridine (DMAP; 0.5 mmol, 0.1 equiv, 60 mg) in DCM (15 mL) was added dropwise. Then, the mixture was stirred at room temperature overnight. The reaction was diluted with water and extracted with DCM. The organic layer was washed with brine and dried over Na_2SO_4. The obtained filtrate was concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc = 5:1) to afford the desired *N*,3-diphenylpropiolamide, which was used directly in the next step.

Under a N_2 atmosphere, to a solution of *N*,3-diphenylpropiolamide products (3.0 mmol) in anhydrous tetrahydrofuran (THF) or DCM (20 mL) was added NaH (60%, 4.5 mmol, 1.5 equiv, 180 mg) at 0 °C. After the mixture was stirred for 10 min at the same temperature, the corresponding halogenated hydrocarbon or acid chloride was

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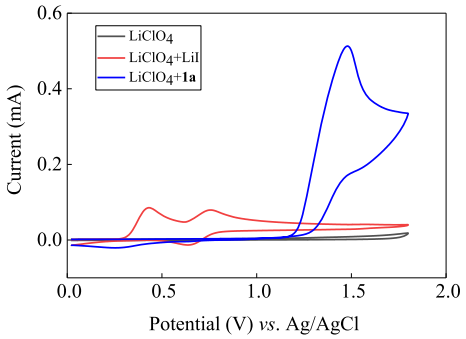


Figure 1. Cyclic voltammograms of a 0.1 M $LiClO_4$ solution in CH_3CN at room temperature; a 3 mm diameter glassy carbon electrode was used as the working electrode and Ag/AgCl and a carbon rod were used as the reference and counter electrode, respectively. Scan rate: 0.1 V/s. (a) Black line: background, 0.1 M $LiClO_4$; (b) red line: 0.1 M $LiClO_4$ + 10 mM LiI; (c) blue line: 0.1 M $LiClO_4$ + 10 mM **1a**.

added and the mixture was stirred for 15 min at 0 °C and then warmed up to room temperature. The reaction was diluted with water and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel.

N-Methyl-*N*-phenylpropiolamide (2 mmol), boronic acid (2.4 mmol), $Pd(OAc)_2$ (1 mol %), Ag_2O (3.0 mmol), K_2CO_3 (4 mmol), and CH_3CN (12 mL) were added to a Schlenk tube. Then, the solution was stirred at 70 °C in an oil bath for 12 h. After the reaction was finished, the mixture was filtered, extracted with EtOAc, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel to afford the desired product.

General Procedure for Electrochemical Oxidative Halogenation. An undivided cell was equipped with graphite electrodes as the anode and cathode (52.5 mm × 8.0 mm × 1.5 mm) and connected to an IKA power supply. Alkynamides (0.125 mmol), halogenated lithium salt (0.25 mmol), and $LiClO_4$ (0.2 M) were added into the cell with a 4.0 mL solution of CH_3CN. The mixture was electrolyzed using a constant current of 10 mA at room temperature under magnetic stirring. When the reaction was finished (witnessed by the disappearance of 1), the solvent was removed under vacuum and then extracted with DCM (3 × 5 mL), washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel.

Procedures for the Gram-Scale Reaction. In an oven-dried undivided bottle (100 mL) equipped with a stir bar, **1a** (4 mmol), LiBr (10 mmol), $LiClO_4$ (0.1 M), and CH_3CN (70 mL) were added. The bottle was equipped with a carbon felt as the anode and cathode (4.0 cm × 4.0 cm × 1 mm, approximately 3.0 cm immersed in the solvent). The reaction mixture was stirred at room temperature with a constant current of 40 mA for 10 h. When the reaction was finished, the solvent was removed under vacuum. The residue was then extracted with DCM and H_2O, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel.

3-Iodo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2a**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 86% yield (41 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 (dt, J = 14.8, 7.1 Hz, 3H), 7.30 (d, J = 7.3 Hz, 2H), 6.53 (d, J = 9.8 Hz, 2H), 6.48 (d, J = 10.2 Hz, 2H), 2.97 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 183.7, 167.4, 157.9, 144.1, 133.3, 131.9, 130.1, 128.7, 127.7, 98.2, 70.4, 27.0.

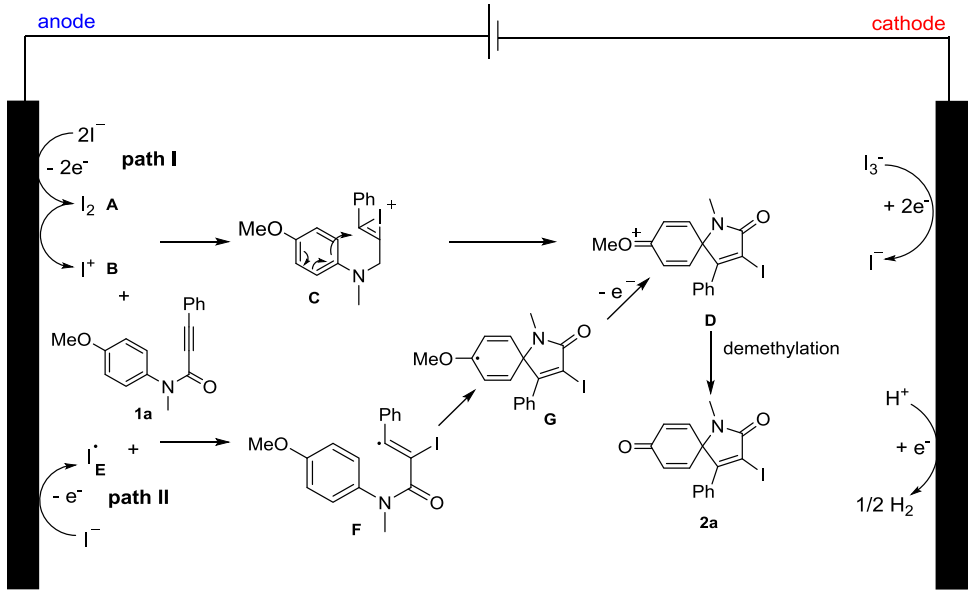
3-Iodo-1-ethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2b**).[6e] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 82% yield (40 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.44−7.34 (m, 3H), 7.29−7.25 (m, 2H), 6.57 (d, J = 10.1 Hz, 2H), 6.44 (d, J = 10.1 Hz, 2H), 3.42 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 184.0, 167.3, 157.8, 144.4, 132.8, 131.9, 130.0, 128.7, 127.8, 98.9, 70.8, 37.0, 15.2.

1-Benzyl-3-iodo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2c**).[11] Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 75% yield (43 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.4 Hz, 2H), 7.28 (tq, J = 4.8, 2.2, 1.6 Hz, 5H), 7.23−7.18 (m, 2H), 6.36 (d, J = 10.1 Hz, 2H), 6.26 (d, J = 10.1 Hz, 2H), 4.62 (s, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 184.0, 167.6, 158.4, 144.2, 137.1, 132.4, 131.8, 130.1, 129.0, 128.6, 128.0, 127.8, 98.2, 70.82, 45.8.

3-Iodo-1-isopropyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2d**).[13b] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 78% yield (40 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.44−7.33 (m, 3H), 7.27−7.22 (m, 2H), 6.61 (d, J = 10.1 Hz, 2H), 6.43 (d, J = 10.1 Hz, 2H), 3.50 (quint, J = 6.8 Hz, 1H), 1.46 (d, J = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 183.9, 166.8, 157.2, 144.3, 132.7, 132.0, 130.0, 128.7, 127.8, 100.6, 71.6, 47.4, 20.9.

1-Allyl-3-iodo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2e**). Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid, 56%

Scheme 6. Proposed Mechanism



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yield (28 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.36 (m, 3H), 7.30−7.24 (m, 2H), 6.55 (d, J = 10.1 Hz, 2H), 6.42 (d, J = 10.1 Hz, 2H), 5.88−5.77 (m, 1H), 5.20−5.15 (m, 2H), 4.01 (d, J = 6.3 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.0, 167.3, 158.3, 144.3, 132.8, 132.8, 131.8, 130.1, 128. 7, 127.8, 119.1, 98.4, 70.8, 44.5. HRMS (ESI+) m/z calcd for $C_{18}H_{15}O_2NI$ [M + H]$^+$: m/z 404.0138; found: 404.0142.

tert-Butyl 3-iodo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**2f**). Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid, 35% yield (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (m, J = 7.4 Hz, 1H), 7.37 (m, J = 7.4 Hz, 2H), 7.11 (d, J = 7.0 Hz, 2H), 6.64 (d, J = 10.0 Hz, 2H), 6.35 (d, J = 10.0 Hz, 2H), 1.45 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 164.8, 160.7, 147.4, 143.8, 132.0, 131.2, 130.3, 128.6, 128.1, 98.5, 85.0, 70.5, 27.8. HRMS (ESI+) m/z calcd for $C_{20}H_{18}O_4NINa$ [M + Na]$^+$: m/z 486.0170; found: 486.0173.

Benzyl 3-iodo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**2g**). Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 42% yield (26 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, J = 7.4 Hz, 1H), 7.42−7.33 (m, 7H), 7.14 (d, J = 7.0 Hz, 2H), 6.62 (d, J = 10.0 Hz, 2H), 6.34 (d, J = 10.0 Hz, 2H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.6, 164.2, 161.6, 149.2, 142.9, 134.3, 132.3, 131.0, 130.4, 128.7, 128.6, 128.3, 128.0, 97.8, 70.6, 69.0. HRMS (ESI+) m/z calcd for $C_{23}H_{16}O_4NINa$ [M + Na]$^+$: m/z 520.0013; found: 520.0016.

3-Iodo-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2h**).[12] Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 86% yield (46 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.49 (s, 2H), 6.34 (s, 1H), 2.87 (s, 3H), 1.77 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.5, 167.9, 157.9, 152.4, 144.3, 132.8, 132.1, 131.6, 130.3, 128.8, 127.4, 97.9, 72.6, 26.6, 17.7.

3-Iodo-7,9-dimethoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2i**). Eluent: petroleum ether/ethyl acetate (1:1). White solid, 71% yield (55 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43−7.34 (m, 3H), 7.27−7.23 (m, 2H), 5.42 (s, 2H), 3.69 (s, 6H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 175.2, 166.8, 160.5, 153.3, 132.3, 130.0, 128.7, 127.8, 127.6, 111.1, 96.8, 70.6, 55.9, 26.5. HRMS (ESI+) m/z calcd for $C_{18}H_{17}O_4NI$ [M + H]$^+$: m/z 438.0192; found: 438.0197.

4-(4-Fluorophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2j**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 89% yield (44 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.8, 5.2 Hz, 2H), 7.08 (t, J = 8.6 Hz, 2H), 6.51 (q, J = 10.3 Hz, 4H), 2.97 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.6, 167.3, 163.4 (d, J = 250.5 Hz), 156.8, 144.0, 133.4, 129.9 (d, J = 7.5 Hz), 127.8 (d, J = 4.5 Hz), 116.0 (d, J = 22.5 Hz), 98.7, 70.4, 27.1.

4-(4-Chlorophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2k**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 70% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.54−6.47 (m, 4H), 2.97 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 167.2, 156.7, 143.9, 136.4, 133.5, 130.2, 129.1, 129.1, 98.9, 70.3, 27.1.

4-(4-Bromophenyl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2l**).[13a] Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid, 82% yield (47 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.53−6.46 (m, 4H), 2.96 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 167.2, 156.7, 143.8, 133.5, 132.1, 130.7, 129.3, 124.7, 98.9, 70.2, 27.1.

3-Iodo-1-methyl-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**2m**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 54% yield (30 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 6.57−6.49 (m, 4H), 3.00 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.3, 167.0, 156.5, 143.5, 135.5, 133.6, 132.1(d, J = 22.0 Hz), 128.3, 125.8 (q, J = 3.0 Hz), 123.5 (q, J = 271.5 Hz), 99.8, 70.3, 27.1.

4-(3-Iodo-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)-benzonitrile (**2n**). Eluent: petroleum ether/ethyl acetate (2:1). White solid, 51% yield (26 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74−7.64 (d, J = 12 Hz, 2H), 7.48−7.37 (d, J = 12 Hz, 2H), 6.56−6.47 (m, 4H), 3.00 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.2, 166.8, 155.9, 143.3, 136.5, 133.7, 132.6, 128.7, 117.8, 114.0, 100.4, 70.2, 27.1. HRMS (ESI+) m/z calcd for $C_{17}H_{12}O_2N_2I$ [M + H]$^+$: m/z 402.9936; found: 402.9938.

3-Iodo-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2o**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 88% yield (42 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.51 (q, J = 10.3 Hz, 4H), 3.82 (s, 3H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 167.6, 160.9, 157.2, 144.6, 133.1, 129.2, 123.9, 114.1, 96.8, 70.2, 55.3, 26.9.

3-Iodo-1-methyl-4-(*p*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2p**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 90% yield (44 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25−7.07 (m, 4H), 6.59−6.40 (m, 4H), 2.96 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 167.6, 157.9, 144.3, 140.4, 133.2, 129.4, 128.9, 127.6, 97.6, 70.4, 27.0, 21.4.

3-Iodo-1-methyl-4-(m-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2q**). Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 85% yield (43 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.19 (m, 2H), 7.12−7.05 (m, 2H), 6.53 (d, J = 10.2 Hz, 2H), 6.47 (d, J = 10.1 Hz, 2H), 2.97 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 167.5, 158.172, 144.2, 138.4, 133.2, 131.8, 130.9, 128.6, 128.3, 124.7, 98.0, 70.4, 27.0, 21.4. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NI$ [M + H]$^+$: m/z 392.0137; found: 392.0142.

3-Iodo-1-methyl-4-(*o*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2r**).[11] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 63% yield (31 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32−7.28 (m, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.16 (t, J = 6.9 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 6.62 (dd, J = 10.0, 3.0 Hz, 1H), 6.55−6.51 (m, 2H), 6.33 (dd, J = 10.0, 1.8 Hz, 1H), 3.02 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.6, 167.2, 159.3, 143.7, 143.5, 135.6, 133.6, 133.0, 130.8, 130.6, 129.8, 128.1, 125.5, 100.6, 72.0, 27.4, 20.1.

4-(Furan-3-yl)-3-iodo-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2s**). Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid, 61% yield (28 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.47 (t, J = 1.8 Hz, 1H), 6.95 (d, J = 2.0 Hz, 1H), 6.60 (d, J = 10.1 Hz, 2H), 6.52 (d, J = 10.1 Hz, 2H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 167.7, 148.5, 145.3, 143.6, 142.7, 133.0, 117.3, 108.4, 93.7, 69.0, 26.5. HRMS (ESI+) m/z calcd for $C_{14}H_{11}O_3NI$ [M + H]$^+$: m/z 367.9775; found: 367.9778.

3-Iodo-1-methyl-4-(thiophen-3-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2t**). Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid, 84% yield (51 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, J = 2.9, 1.4 Hz, 1H), 7.55 (dd, J = 5.1, 1.4 Hz, 1H), 7.39 (dd, J = 5.1, 2.9 Hz, 1H), 6.62−6.47 (m, 4H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 167.7, 151.3, 145.1, 133.1, 131.6, 127.0, 126.4, 126.2, 95.2, 69.5, 26.6. HRMS (ESI+) m/z calcd for $C_{14}H_{11}O_2NIS$ [M + H]$^+$: m/z 383.9544; found: 383.9550.

3-Bromo-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3a**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 87% yield (36 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (m, 4.3 Hz, 5H), 6.59−6.45 (m, 4H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.7, 165.8, 151.3, 144.1, 133.5, 130.3, 130.2, 128.8, 127.8, 119.9, 68.3, 26.7.

3-Bromo-1-ethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3b**). Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 85% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.34 (m, 5H), 6.58 (d, J = 10.1 Hz, 2H), 6.47 (d, J = 10.1 Hz, 2H), 3.41 (q, J = 7.2 Hz, 2H), 1.24 (t, J = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183, 165.7, 151.2, 144.4, 132.9, 130.2, 130.2, 128.7, 127.8, 120.3, 68.8, 36.7, 15.2. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NBr$ [M + H]$^+$: m/z 344.0278; found: 344.0281.

1-Benzyl-3-bromo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3c**).[14] Eluent: petroleum ether/ethyl acetate (4:1). White solid, 92% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (t, J = 7.3 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.33−7.23 (m, 7H), 6.37 (d, J = 10.0 Hz, 2H), 6.28 (d, J = 10.0 Hz, 2H), 4.61 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 166.0, 151.9, 144.3, 137.0, 132.6, 130.2, 130.0, 128.9, 128.7, 128.6, 128.1, 127.8, 119.9, 68.1, 45.5.

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3-Bromo-1-isopropyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3d**). Eluent: petroleum ether/ethyl acetate (3:1). White solid, 91% yield (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.32 (m, 5H), 6.61 (d, J = 10.1 Hz, 2H), 6.46 (d, J = 10.1 Hz, 2H), 3.47 (quint, J = 6.8 Hz, 1H), 1.46 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.900, 165.2, 150.5, 144.4, 132.9, 130.3, 130.1, 128.7, 127.8, 121.3, 69.5, 47.2, 20.8. HRMS (ESI+) m/z calcd for $C_{18}H_{17}O_2NBr$ [M + H]$^+$: m/z 358.0435; found: 358.0437.

1-Allyl-3-bromo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3e**). Eluent: petroleum ether/ethyl acetate (4:1). White solid, 70% yield (31 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45−7.33 (m, 5H), 6.56 (d, J = 10.1 Hz, 2H), 6.45 (d, J = 10.1 Hz, 2H), 5.82 (ddt, J = 16.7, 10.3, 6.3 Hz, 1H), 5.22−5.12 (m, 2H), 3.99 (d, J = 6.3 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 165.6, 151.7, 144.3, 133.0, 132.6, 130.2, 130.1, 128.7, 127.8, 120.0, 119.2, 68.7, 44.2. HRMS (ESI+) m/z calcd for $C_{18}H_{15}O_2NBr$ [M + H]$^+$: m/z 356.0277; found: 356.0281.

tert-Butyl 3-bromo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**3f**). Eluent: petroleum ether/ethyl acetate (4:1). White solid, 64% yield (34 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (m, J = 7.9 Hz, 1H), 7.39 (m, J = 7.6 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 6.67 (d, J = 9.8 Hz, 2H), 6.39 (d, J = 9.8 Hz, 2H), 1.47 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 163.3, 154.4, 147.4, 143.7, 132.2, 130.4, 129.3, 128.6, 128.2, 120.0, 85.1, 68.6, 27.8. HRMS (ESI+) m/z calcd for $C_{20}H_{18}O_4NBrNa$ [M + Na]$^+$: m/z 438.0307; found: 438.0311.

Benzyl 3-bromo-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**3g**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 71% yield (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (t, J = 7.4 Hz, 1H), 7.41−7.33 (m, 7H), 7.22 (d, J = 7.0 Hz, 2H), 6.64 (d, J = 10.0 Hz, 2H), 6.35 (d, J = 10.0 Hz, 2H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.6, 162.8, 155.2, 149.1, 142.9, 134.2, 132.6, 130.5, 129.1, 128.7, 128.7, 128.6, 128.3, 128.1, 119.4, 69.0, 68.5. HRMS (ESI+) m/z calcd for $C_{23}H_{16}O_4NBrNa$ [M + Na]$^+$: m/z 472.0150; found: 472.0155.

3-Bromo-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3h**).[12] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 89% yield (37 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−7.35 (m, 5H), 6.53−6.48 (m, 2H), 6.38 (s, 1H), 2.86 (s, 3H), 1.76 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.4, 166.3, 152.6, 151.3, 144.4, 132.9, 132.2, 130.4, 129.9, 128.9, 127.5, 119.7, 70.4, 26.2, 17.7.

3-Bromo-7,9-dimethoxy-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3i**). Eluent: petroleum ether/ethyl acetate (1:1). White solid, 88% yield (49 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−7.32 (m, 5H), 5.42 (s, 2H), 3.70 (s, 6H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 175.2, 165.3, 153.6, 153.4, 130.5, 130.1, 128.7, 127.7, 118.6, 111.1, 68.7, 55.9, 26.1. HRMS (ESI+) m/z calcd for $C_{18}H_{17}O_4NBr$ [M + H]$^+$: m/z 390.0330; found: 390.0335.

3-Bromo-4-(4-fluorophenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3j**). Eluent: petroleum ether/ethyl acetate (3:1). White solid, 90% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−7.40 (m, 2H), 7.08 (t, J = 8.6 Hz, 2H), 6.53 (s, 4H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 163.5 (d, J = 250.5 Hz), 162.7, 150.2, 144.1, 133.6, 129.9 (d, J = 7.5 Hz), 126.2 (d, J = 4.5 Hz), 120.12, 116.1 (d, J = 21 Hz), 68.25, 26.67. HRMS (ESI+) m/z calcd for $C_{16}H_{12}O_2NBrF$ [M + H]$^+$: m/z 348.0027; found: 348.0030.

3-Bromo-4-(4-chlorophenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3k**).[13a] Eluent: petroleum ether/ethyl acetate (2:1). White solid, 85% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (s, 4H), 6.53 (s, 4H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 165.5, 150.0, 143.9, 136.5, 133.6, 129.2, 129.1, 128.5, 120.5, 68.2, 26.7.

3-Bromo-4-(4-bromophenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3l**).[13a] Eluent: petroleum ether/ethyl acetate (2:1). White solid, 76% yield (39 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 1.5 Hz, 4H), 2.95 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.4, 165.5, 150.1, 143.9, 133.6, 132.1, 129.3, 129.0, 124.9, 120.5, 68.1, 26.7.

3-Bromo-1-methyl-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**3m**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 98% yield (48 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H), 6.55 (s, 4H), 2.98 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.3, 165.3, 149.8, 143.5, 133.8, 132.1 (d, J = 33.0 Hz), 128.3, 125.8 (q, J = 3.0, 4.5 Hz), 123.5 (d, J = 271.5 Hz), 121.5, 68.2, 26.7.

4-(3-Bromo-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)benzonitrile (**3n**). Eluent: petroleum ether/ethyl acetate (2:1). White solid, 86% yield (38 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.7 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 6.54 (s, 3H), 2.97 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.1, 165.1, 149.3, 143.4, 134.7, 133.9, 132.6, 128.6, 122.0, 117.8, 114.1, 68.1, 26.8. HRMS (ESI+) m/z calcd for $C_{17}H_{12}O_2N_2Br$ [M + H]$^+$: m/z 355.0075; found: 355.0077.

3-Bromo-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3o**).[13a] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 90% yield (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 6.53 (s, 4H), 3.83 (s, 3H), 2.93 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 166.1, 161.0, 150.6, 144.7, 133.3, 129.3, 122.3, 118.3, 114.2, 68.1, 55.4, 26.5.

3-Bromo-1-methyl-4-(*p*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3p**).[14] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 95% yield (41 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 8.2 Hz, 2H), 7.24−6.99 (m, 2H), 6.68−6.28 (m, 4H), 2.94 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.9, 151.3, 144.4, 140.6, 133.3, 129.5, 127.6, 127.2, 119.2, 68.3, 26.6, 21.4.

3-Bromo-1-methyl-4-(*m*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3q**). Eluent: petroleum ether/ethyl acetate (3:1). White solid, 86% yield (38 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29−7.25 (m, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.20 (s, 1H), 7.17 (d, J = 7.6 Hz, 1H), 6.59−6.46 (m, 4H), 2.95 (s, 3H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.9, 151.6, 144.2, 138.5, 133.4, 131.1, 130.1, 128.6, 128.3, 124.7, 119.7, 68.4, 26.7, 21.4. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NBr$ [M + H]$^+$: m/z 344.0277; found: 344.0281.

3-Bromo-1-methyl-4-(*o*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3r**).[14] Eluent: petroleum ether/ethyl acetate (3:1). White solid, 77% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (td, J = 7.5, 1.4 Hz, 1H), 7.26 (d, J = 7.7 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.92 (dd, J = 7.7, 1.3 Hz, 1H), 6.64 (dd, J = 10.0, 3.0 Hz, 1H), 6.55 (dd, J = 10.0, 1.8 Hz, 1H), 6.52 (dd, J = 10.0, 3.0 Hz, 1H), 6.34 (dd, J = 10.0, 1.8 Hz, 1H), 3.01 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 165.6, 152.5, 143.5, 143.3, 136.1, 133.9, 133.2, 130.7, 129.9, 128.7, 128.1, 125.4, 122.1, 69.9, 27.2, 20.0.

3-Bromo-4-(furan-3-yl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3s**). Eluent: petroleum ether/ethyl acetate (2:1). White solid, 65% yield (26 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.47 (t, J = 1.7 Hz, 1H), 6.89 (dd, J = 2.0, 0.9 Hz, 1H), 6.62 (d, J = 10.1 Hz, 2H), 6.53 (d, J = 10.1 Hz, 2H), 2.91 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.8, 145.3, 143.7, 143.1, 142.5, 133.2, 116.4, 116.3, 108.3, 66.7, 26.1. HRMS (ESI+) m/z calcd for $C_{14}H_{11}O_3NBr$ [M + H]$^+$: m/z 319.9914; found: 319.9917.

3-Bromo-1-methyl-4-(thiophen-3-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3t**). Eluent: petroleum ether/ethyl acetate (2:1). White solid, 87% yield (36 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (dd, J = 2.9, 1.4 Hz, 1H), 7.61 (dd, J = 5.2, 1.4 Hz, 1H), 7.40 (dd, J = 5.2, 2.9 Hz, 1H), 6.62 (d, J = 10.1 Hz, 2H), 6.56 (d, J = 10.2 Hz, 2H), 2.93 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 166.0, 145.2, 144.9, 133.2, 130.4, 127.4, 126.4, 126.2, 117.1, 67.2, 26.2. HRMS (ESI+) m/z calcd for $C_{14}H_{11}O_2NBrS$ [M + H]$^+$: m/z 335.9683; found: 335.9688.

3-Chloro-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4a**).[13a] Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 82% yield (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51−7.44 (m, 2H), 7.45−7.35 (m, 3H), 6.54 (s, 4H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.7, 165.2, 147.3, 144.4, 133.5, 130.4, 129.3, 128.8, 128.5, 127. 8, 66.5, 26.4.

3-Chloro-1-ethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4b**). Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid,

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91% yield (32 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47−7.36 (m, 5H), 6.59 (d, J = 6.2 Hz, 2H), 6.51 (d, J = 6.0 Hz, 2H), 3.40 (q, J = 7.2 Hz, 2H), 1.25 (t, J = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 165.1, 147.2, 144.7, 133.0, 130.3, 129.3, 128.8, 127.8, 67.0, 36.5, 15.1. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NCl$ [M + H]$^+$: m/z 300.0782; found: 300.0786.

1-Benzyl-3-chloro-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4c**). Eluent: petroleum ether/ethyl acetate (4:1). White solid, 82% yield (37 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43−7.35 (m, 5H), 7.32−7.24 (m, 5H), 6.37 (d, J = 10.1 Hz, 2H), 6.31 (d, J = 10.1 Hz, 2H), 4.60 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 165.4, 147.9, 144.5, 136.9, 132.7, 130.3, 129.1, 128.9, 128.7, 128.6, 128.5, 128.0, 127.9, 67.1, 45.2. HRMS (ESI+) m/z calcd for $C_{22}H_{17}O_2NCl$ [M + H]$^+$: m/z 362.0938; found: 362.0942.

3-Chloro-1-isopropyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4d**). Eluent: petroleum ether/ethyl acetate (5:1). white solid, 76% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44−7.37 (m, 5H), 6.61 (d, J = 10.1 Hz, 2H), 6.50 (d, J = 10.1 Hz, 2H), 3.46 (quint, J = 6.9 Hz, 1H), 1.47 (d, J = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 164.6, 146.4, 144.7, 132.9, 130.2, 129.6, 129.4, 128.7, 127.8, 67.6, 47.0, 20.7. HRMS (ESI+) m/z calcd for $C_{18}H_{17}O_2NCl$ [M + H]$^+$: m/z 314.0938; found: 314.0942.

tert-Butyl 3-chloro-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**4f**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 52% yield (24 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (m, J = 7.4 Hz, 1H), 7.39 (m, J = 7.5 Hz, 2H), 7.25 (d, J = 9.8 Hz, 2H), 6.67 (d, J = 9.8 Hz, 2H), 6.41 (d, J = 9.8 Hz, 2H), 1.47 (s, 9H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 162.8, 150.6, 147.4, 143.9, 132.3, 130.5, 128.7, 128.6, 128.2, 85.2, 67.0, 27.8. HRMS (ESI+) m/z calcd for $C_{20}H_{18}O_4NClNa$ [M + Na]$^+$: m/z 394.0813; found: 394.0817.

Benzyl 3-chloro-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**4g**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 57% yield (29 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46−7.42 (m, 1H), 7.42−7.35 (m, 7H), 7.27 (d, J = 7.1 Hz, 2H), 6.63 (d, J = 10.0 Hz, 2H), 6.37 (d, J = 10.0 Hz, 2H), 5.30 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.6, 162.2, 151.4, 149.1, 143.0, 134.2, 132.7, 130.7, 128.7, 128.4, 128.2, 128.1, 69.0, 66.9. HRMS (ESI+) m/z calcd for $C_{23}H_{16}O_4NClNa$ [M + Na]$^+$: m/z 428.0656; found: 428.0660.

3-Chloro-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4h**). Eluent: petroleum ether/ethyl acetate (4:1). White solid, 51% yield (19 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53−7.49 (m, 2H), 7.44−7.37 (m, 3H), 6.55 (dd, J = 9.9, 1.7 Hz, 1H), 6.50 (d, J = 9.9 Hz, 1H), 6.42 (t, J = 1.5 Hz, 1H), 2.85 (s, 3H), 1.76 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.5, 165.6, 153.0, 147.3, 144.7, 132.9, 132.2, 130.5, 129.0, 127.5, 68.6, 25.9, 17.8, 17.7. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NCl$ [M + H]$^+$: m/z 300.0782; found: 300.0786.

3-Chloro-5,6,7-trimethoxy-1-methyl-4-phenylquinolin-2(1*H*)-one (**4i′**). Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 50% yield (45 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36−7.32 (t, J = 6.0 Hz, 1H), 7.24 (t, J = 6.0 Hz, 2H), 7.19−7.11 (d, J = 6.0 Hz, 2H), 6.77 (s, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.87 (s, 3H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 154.6, 152.3, 150.7, 143.6, 136.1, 132.4, 130.1, 128.4, 120.3, 120.1, 109.0, 90.1, 82.1, 61.4, 61.3, 56.4, 35.1. HRMS (ESI+) m/z calcd for $C_{19}H_{19}O_4NCl$ [M + H]$^+$: m/z 360.0993; found: 360.0994.

4-(4-Bromophenyl)-3-chloro-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4j**).[13a] Eluent: petroleum ether/ethyl acetate (5:1). White solid, 47% yield (21 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 6.59−6.50 (m, 4H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.4, 164.9, 146.1, 144.2, 133.7, 132.2, 129.3, 129.0, 128.1, 124.9, 66.4, 26.4.

4-(3-Chloro-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)benzonitrile (**4k**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 15% yield (6 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 6.56 (d, J = 10.1 Hz, 2H), 6.51 (d, J = 10.1 Hz, 2H), 2.94 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.1, 164.4, 145.1, 143.6, 133.9, 133.7, 132.6, 130.8, 128.6, 117.8, 114.1, 66.3, 26.5. HRMS (ESI+) m/z calcd for $C_{17}H_{11}O_2N_2Cl$ [M + H]$^+$: m/z 311.0580; found: 311.0582.

3-Chloro-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4l**).[13a] Eluent: petroleum ether/ethyl acetate (5:1). White solid, 36% yield (13 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.57−6.53 (m, 4H), 3.84 (s, 3H), 2.92 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.5, 161.0, 146.6, 145.0, 144.7, 133.3, 129.3, 126.7, 121.6, 114.3, 66.3, 55.4, 26.2.

3-Chloro-1-methyl-4-(*p*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4m**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 11% yield (4 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 3.1 Hz, 4H), 2.91 (s, 3H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.4, 147.2, 144.7, 140.8, 133.4, 132.4, 129.5, 127.6, 126.4, 66.5, 26.3, 21.4. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NCl$ [M + H]$^+$: m/z 300.0782; found: 300.0786.

3-Chloro-1-methyl-4-(*o*-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**4n**). Eluent: petroleum ether/ethyl acetate (5:1). White solid, 58% yield (25 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (td, J = 7.5, 1.3 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.95 (d, J = 6.4 Hz, 1H), 6.68−6.46 (m, 3H), 6.38−6.31 (m, 1H), 3.00 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.5, 164.9, 148.6, 143.6, 143.4, 136.5, 134.0, 133.4, 130.7, 130.6, 129.9, 128.2, 127.7, 125.5, 68.2, 27.1, 19.9. HRMS (ESI+) m/z calcd for $C_{17}H_{15}O_2NCl$ [M + H]$^+$: m/z 300.0782; found: 300.0786.

1-Methyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**5a**).[20a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 95% yield (48 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.2, 1.3 Hz, 2H), 7.30−7.24 (m, 1H), 7.23−7.16 (m, 3H), 7.12 (t, J = 7.9 Hz, 4H), 6.52 (d, J = 10.2 Hz, 2H), 6.44 (d, J = 10.1 Hz, 2H), 2.92 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.0, 168.8, 154.2, 145.1, 133.9, 133.1, 131.2, 130.1, 129.4, 129.0, 128.2, 128.0, 127.9, 127.1, 69.1, 26.4.

1-Benzyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**5b**).[20a] Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid, 99% yield (60 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.2, 1.3 Hz, 2H), 7.26 (tdt, J = 9.3, 6.5, 3.3 Hz, 5H), 7.23−7.17 (m, 2H), 7.17−7.11 (m, 4H), 7.05−6.96 (m, 2H), 6.35 (d, J = 10.1 Hz, 2H), 6.22 (d, J = 10.1 Hz, 2H), 4.58 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.2, 168.9, 154.5, 145.2, 137.4, 133.9, 132.2, 130.9, 130.1, 129.3, 129.0, 128.9, 128.5, 128.1, 128.1, 128.0, 127.9, 127.1, 69.5, 45.2.

Benzyl 2,8-dioxo-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-1-carboxylate (**5c**). Eluent: petroleum ether/ethyl acetate (4:1). Yellow solid, 50% yield (33 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39−7.33 (m, 7H), 7.28 (s, 1H), 7.20 (q, J = 7.4 Hz, 3H), 7.11 (t, J = 7.7 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 6.60 (d, J = 10.0 Hz, 2H), 6.27 (d, J = 10.0 Hz, 2H), 5.27 (s, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.8, 165.9, 157.8, 149.5, 143.8, 134.6, 134.4, 132.1, 130.2, 130.0, 129.7, 129.2, 128.7, 128.6, 128.4, 128.4, 128.3, 128.1, 126.3, 69.2, 68.7. HRMS (ESI+) m/z calcd for $C_{29}H_{21}O_4NSeNa$ [M + Na]$^+$: m/z 550.0522; found: 550.0528.

1,6-Dimethyl-4-phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**5d**). Eluent: petroleum ether/ethyl acetate (2:1). Yellow solid, 98% yield (51 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.2, 1.3 Hz, 2H), 7.30−7.24 (m, 1H), 7.23−7.16 (m, 3H), 7.14−7.11 (m, 4H), 6.48 (d, J = 9.9 Hz, 1H), 6.45 (dd, J = 9.9, 1.6 Hz, 1H), 6.33 (t, J = 1.5 Hz, 1H), 2.81 (s, 3H), 1.76 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.7, 169.2, 154.5, 153.3, 145.3, 133.7, 132.6, 132.0, 131.0, 130.4, 129.6, 129.0, 128.3, 127.9, 127.7, 127.5, 71.1, 26.0, 17.8. HRMS (ESI+) m/z calcd for $C_{23}H_{20}O_2NSe$ [M + H]$^+$: m/z 422.0647; found: 422.0654.

7,9-Dimethoxy-1-methyl-4-phenyl-3-(phenylselanyl)-1-azaspiro-[4.5]deca-3,6,9-triene-2,8-dione (**5e**). Eluent: petroleum ether/ethyl acetate (1:1). White solid, 90% yield (52 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45−7.40 (m, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.18 (t, J = 7.8 Hz, 3H), 7.13 (t, J = 7.4 Hz, 2H), 7.05 (d, J = 7.0 Hz, 2H), 5.40 (s, 2H), 3.66 (s, 6H), 2.88 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 175.3, 168.2, 157.1, 153.3, 134.0, 131.5, 129.3, 129.0, 128.5, 128.2,

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127.9, 127.9, 127.4, 112.0, 69.2, 55.9, 26.0. HRMS (ESI+) m/z calcd for $C_{24}H_{22}O_4NSe$ $[M + H]^+$: m/z 468.0702; found: 468.0709.

4-Phenyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**5f**).[20a] Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 52% yield (25 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, J = 8.0 Hz, 2H), 7.28−7.26 (m, 1H), 7.23−7.16 (m, 3H), 7.14−7.08 (m, 4H), 6.74 (s, 1H), 6.65 (d, J = 10.0 Hz, 2H), 6.32 (d, J = 10.0 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.1, 170.9, 157.6, 145.1, 133.7, 131.5, 131.0, 129.6, 129.6, 129.1, 128.2, 128.0, 127.9, 127.1, 65.1.

1-Methyl-3-(phenylselanyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**5g**). Eluent: petroleum ether/ethyl acetate (3:1). Yellow solid, 60% yield (27 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 4.0 Hz, 2H), 7.44−7.37 (m, 3H), 6.44−6.39 (d, J = 8.0 Hz, 2H), 6.38−6.32 (d, J = 8.0 Hz, 2H), 5.81 (s, 1H), 2.89 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 183.9, 168.5, 145.1, 138.6, 136.0, 133.4, 132.2, 130.0, 129.5, 124.8, 67.0, 26.2. HRMS (ESI+) m/z calcd for $C_{16}H_{14}O_2NSe$ $[M + H]^+$: m/z 332.0183; found: 332.0184.

1-Methyl-4-phenyl-3-(phenylethynyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6a**).[13a] Under a N_2 atmosphere, to a solution of **2a** (0.15 mmol) and phenylacetylene (0.2 mmol) in Et_3N (6 mL) and THF (6 mL), $PdCl_2(PPh_3)_2$ (0.005 mmol) and CuI (0.01 mmol) were added. The reaction mixture was heated to 70 °C in an oil bath and stirred overnight. Until the reaction was completed, the resulting mixture was cooled to room temperature. Then the residue was extracted with EtOAc, washed with brine, and dried over Na_2SO_4, and the solvent was evaporated. The given residue was purified by flash chromatography. Eluent: petroleum ether/ethyl acetate (5:1). Yellow solid, 88% yield (80 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J = 7.4 Hz, 2H), 7.55 (dt, J = 7.6, 2.1 Hz, 2H), 7.44−7.35 (m, 6H), 6.60 (s, 4H), 2.91 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.1, 167. 6, 153.6, 145.8, 132.9, 132.1, 131.2, 130.7, 129.3, 128.7, 128.4, 127.6, 122.2, 119.8, 100.4, 81.7, 66.2, 25.7.

3-(4-Methoxyphenyl)-1-methyl-4-phenyl-1 azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6b**).[1a] **2a** (0.15 mmol), 4-methoxyphenylboronic acid (0.3 mmol), $PdO(Ac)_2$ (0.015 mmol), and K_2CO_3 (0.30 mmol) were added in a Schlenk tube under a N_2 atmosphere, then DMF (3 mL) and H_2O (0.75 mL) were added in the system. The reaction mixture was stirred overnight at room temperature. Until the reaction was completed, the resulting mixture was cooled to room temperature. Then, the residue was extracted with EtOAc, washed with brine, and dried over Na_2SO_4, and the solvent was evaporated. The given residue was purified by flash chromatography. Eluent: petroleum ether/ethyl acetate (6:1). White solid, 92% yield (50 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 6.0 Hz, 2H), 7.34−7.24 (m, 4H), 7.14 (d, J = 7.2 Hz, 2H), 6.81 (d, J = 6.0 Hz, 2H), 6.60 (d, J = 10.0 Hz, 2H), 6.48 (d, J = 10.0 Hz, 2H), 3.79 (s, 3H), 2.98 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 184.3, 169.9, 159.8, 147.8, 146.0, 134.7, 133.1, 132.2, 130.9, 129.1, 128.7, 128.4, 122.9, 113.7, 67.0, 55.2, 26.2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02429.

Experimental procedure, compound characterization, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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