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Expeditious Access to Spiro-Fused 2,5-Cyclohexadienones *via* Thio(seleno)cyanative *ipso*-Cyclization

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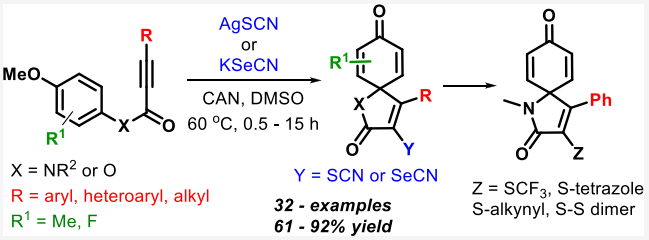
ABSTRACT: A facile oxidative dearomatization of *N*-(*p*-methoxyaryl)propiolamides has been established for the synthesis of spiro-fused 2,5-cyclohexadienone frameworks *via* thio(seleno)-cyanative *ipso*-cyclization in the presence of ceric ammonium nitrate (CAN) as the oxidant. The present method, involving the formation of C−S and C−C bonds, was also extended to (*p*-methoxyaryl)propiolates for thiocyanative *ipso*-cyclization. Furthermore, the obtained chalcogeno-spirocyclohexadienones were transformed into uniquely functionalized spirocyclohexadienone derivatives.



INTRODUCTION

Carbon−sulfur bond construction symbolizes one of the most prevailing approaches for the production of organosulfur compounds, which have found extensive applications in pharmaceuticals, agrochemicals, and materials science.[1] Among the organosulfur compounds, thiocyanates are ubiquitous motifs in bioactive compounds due to their stability and promising physiochemical properties.[2] They also serve as valuable intermediates in the synthesis of diverse organosulfur compounds such as thioethers,[3] thiols,[4] thiotetrazoles,[5] trifluoromethyl sulfides,[6] disulfides,[7] thiocarbamates,[8] alkynyl thioethers,[9] sulfonyl chlorides,[10] etc. Hence, numerous methods have been developed for the synthesis of alkyl, aryl, and vinyl thiocyanates.[11] Nevertheless, the construction of thiocyanated-cyclic compounds *via* a domino thiocyanation/annulation of unsaturated carbon−carbon bonds, in particular alkynes, is still underexplored.[12] Given the significant reactivity of alkynes in synthetic chemistry through difunctionalization,[13] the development of further conversions of alkynes is necessary to intensify their utility, precisely in domino reactions to make diversely functionalized annulated products.

Spirocyclohexadienones are found as a valuable motif of pharmaceutical chemistry in various natural products showing notable biological activities and serve as convenient forerunners toward the synthesis of natural products.[14] Hence, these scaffolds have drawn growing attention of synthetic organic chemists. In recent years, a common concise approach for the assembly of spirocyclohexanedienones from dearomatization of *N*-(*p*-methoxyaryl)propiolamides by a domino electrophilic or radical addition/*ipso*-spirocyclization method has attracted great attention. To accomplish this transformation by installing the number of functional groups, several efforts have been made using carbon-centered or heteroatom-centered electrophiles/radicals from their corresponding reagents for the addition reaction with the alkyne to initiate the domino process.[15] In this context, only two approaches were disclosed to access thiocyanato-containing spirocyclohexadienone *N*-(aryl)propiolamides. In 2008, Li and co-workers briefly studied the electrophilic *ipso*-cyclization involving an electrophile-exchange process, wherein only three substrates were studied using CuSCN in the presence of an electrophilic fluoride reagent, *N*-Fluoro-*N*′-(chloromethyl)-triethylenediamine bis(tetrafluoro-borate), in acetonitrile at 90 °C (Scheme 1a).[16a] Very recently, He and coworkers reported a visible-light-mediated thiocyanate radical addition/ipso-cyclization/oxidation cascade reaction of *N*-phenylpropanamides using ammonium thiocyanate in the presence of acridinium perchlorate as an organic photocatalyst in acetonitrile under irradiation of a 23 W compact fluorescent lamp (Scheme 1b).[16b] Despite the merits, these methods also suffer from either low yield of the products or a longer reaction time and may be inconvenient for large-scale reactions. Thus, the development of novel and efficient domino thiocyanation/*ipso*-cyclization under mild reaction conditions is still needed and a favorable alternative to make diverse SCN-containing spirocyclohexadienones is required. Recently, we developed a domino Ag-catalyzed oxidative *ipso*-cyclization of *N*-arylpropiolamides with α-keto acids/alkyl carboxylic acids to access 3-acyl/alkyl-spiro[4,5]-trienones *via* decarboxylative acylation/alkylation (Scheme 1c).[17a] In continuation of our work on

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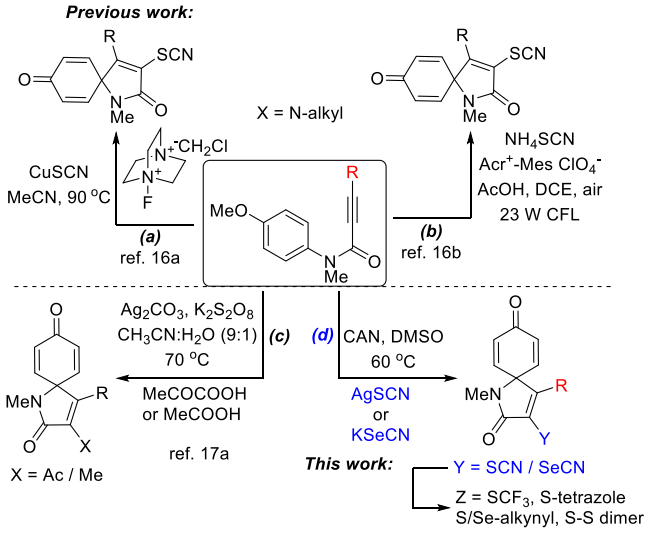
Scheme 1. Spirocyclohexadienones *via* Thio(seleno)cyanative or Oxidative *ipso*-Cyclization



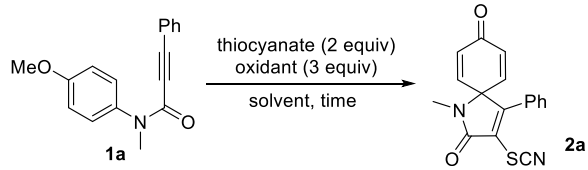
ipso-cyclization reactions,[17] herein, we disclose a facile synthesis of diversely substituted thiocyanato-spirocyclohexadienones from the domino thiocyanation/*ipso*-cyclization of *N*-(*p*-methoxyaryl)propiolamides in the presence of ceric ammonium nitrate (CAN) as the oxidant. The method is extended to an unprecedented domino selenocyanate radical addition/*ipso*-cyclization of *N*-(*p*-methoxyaryl)-propiolamides. Further, transformations of the thiocyanated-spirocyclohexadienones to their corresponding derivatives with unique structural motifs are established for the first time (Scheme 1d).

RESULTS AND DISCUSSION

To identify the optimal conditions, the reactions were carried out with *N*-(*p*-methoxyphenyl)-3-phenylpropiolamide (**1a**) as the model substrate, and the results are presented in Table 1. Primarily, the envisaged conversion was attempted using NH_4SCN as a thiocyanating agent in the presence of $K_2S_2O_8$ as an oxidant in acetonitrile and no progress was found in the reaction at room temperature. However, the formation of azaspirocyclohexadienone **2a** was observed at 60 °C after 12 h (entry 1, Table 1). When, the same reaction was carried out in dimethyl sulfoxide (DMSO), the yield of the product **2a** slightly improved to 24% (entry 2, Table 1). The replacement of the thiocyanating agent with AgSCN gave the product **2a** in 55% yield (entry 3). To our delight, the reaction of **1a** with AgSCN using a different oxidizing agent, CAN, in DMSO at 60 °C proceeded well and provided **2a** in 92% yield (entry 4, Table 1). The use of CAN in 2 equiv lowered the yield to 65% (entry 5). Later, the experiment was carried out in other solvents such as CH_3CN and DCE using CAN/AgSCN, and the results revealed that DMSO was the best solvent (entries 6 and 7). However, the results are inferior when NH_4SCN or KSCN was used in the presence of either 3 or 5 equiv of CAN (entry 8 and 9). Further studies using diverse oxidants such as TBHP and oxone were unsuccessful (entries 10 and 11), while $PhI(OAc)_2$ offered 14% of **2a** (entry 12, Table 1). As anticipated, no reaction progress was observed in the absence of CAN (entry 13, Table 1).

With the optimized conditions for the thiocyanative *ipso*-cyclization established, we then examined the substrate scope as presented in Scheme 2. First, we explored the choice of the

Table 1. Optimization of Conditions[a]



entry	oxidant	thiocyanate	solvent	time (h)	yield (%)[e]
1[b]	$K_2S_2O_8$	NH_4SCN	CH_3CN	12	10
2	$K_2S_2O_8$	NH_4SCN	DMSO	8	24
3	$K_2S_2O_8$	AgSCN	DMSO	4	55
4[b]	**CAN**	**AgSCN**	**DMSO**	**0.5**	**92**
5[c]	CAN	AgSCN	DMSO	5	65
6	CAN	AgSCN	CH_3CN	8	36
7	CAN	AgSCN	DCE	5	25
8	CAN	NH_4SCN	DMSO	10	17
9	CAN	KSCN	DMSO	10	32
10[d]	TBHP	AgSCN	DMSO	12	
11[d]	Oxone	AgSCN	DMSO	12	
12	$PhI(OAc)_2$	AgSCN	DMSO	4	14
13		AgSCN	DMSO	12	

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.3 mmol), thiocyanate (0.6 mmol), and oxidant (0.9 mmol) in 2 mL of the solvent for the specified time at 60 °C. [b]No progress in the reaction at room temperature. [c]Oxidant used in 2 equiv. [d]No product formation was observed. [e]Isolated yield.

substitutions on the alkyne of *N*-(*p*-methoxyphenyl)-propiolamides. The reactions of propiolamides bearing electron-donating groups, such as methyl and methoxyl, on the *para*-position of the phenyl ring attached to alkyne produced the desired spiro-compounds **2b** and **2c** in 88 and 85% yields, respectively. It was found that halide substituents, fluoro and chloro groups, were endured well under the CAN-mediated domino thiocyanation/*ipso*-cyclization to deliver the corresponding halo-spirocyclohexadienones **2d** (89%) and **2e** (86%), giving the opportunity for further structural elaboration. To our delight, the propiolamides with electron-withdrawing groups, such as nitro, cyano, and acyl groups, could also take part in this one-pot reaction to give the matching thiocyano-dearomative spiro-cyclized compounds **2f** (NO_2), **2g** (CN), and **2h** (COMe) in high yield. The applicability of this cascade reaction was also shown by varying the aryl as well as heteroaryl substituents on the alkyne, affording 3-thiocyanato-1-azaspiro-cyclohexadienones **2i** (3,5-dimethyl-phenyl), **2j** (3-trifluoromethylphenyl), **2k** (2-naphthyl), and **2l** (2-thiophenyl) in good yield. Notably, alkyl-propiolamides were also amenable to thiocyanative *ipso*-cyclization to provide the expected spiro-products **2m** (methyl, 81%) and **2n** (ethyl, 83%). Moreover, the replacement of methyl substitution (R^1) on the nitrogen of *N*-(*p*-methoxyphenyl)-propiolamides with benzyl (**2o**), 2-iodo-benzyl (**2p**), and 3-CF_3-benzyl (**2q**) groups was also feasible to give azaspirocyclohexadienones in decent yield. Likewise, the introduction of supplementary R^2 substituents such as 2-methyl, 3-methyl, and 3-fluoro on the *N*-(4-methoxyphenyl) group offered the required products **2q** to **2u** in high yields.

To further widen the substrate choice, we tested the reactivity of *N*-(alkynoyl)-6-methoxytetrahydroquinolines with AgSCN in the presence of CAN to get pyrrolo-[2,1-*j*]-quinolone, an inspiring structural motif found in tricyclic marine alkaloids.[18] Gratifyingly, the domino thiocyanative *ipso*-

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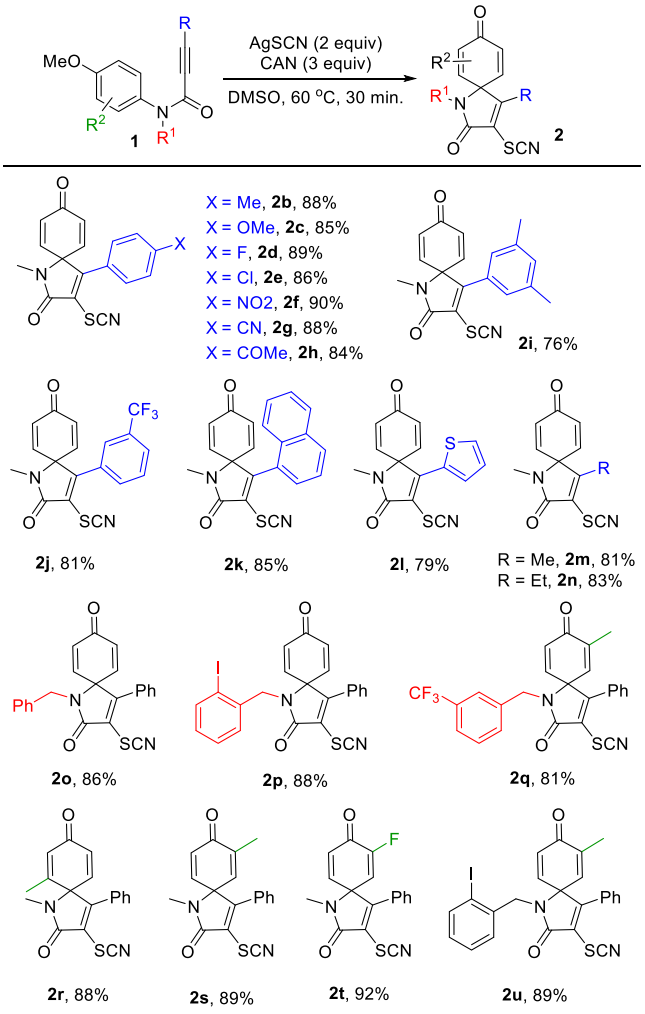
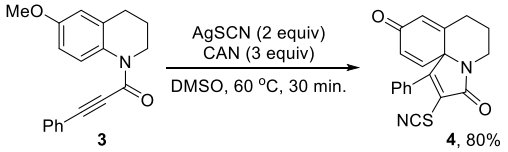
Scheme 2. Scope of *N*-(*p*-Methoxyaryl)propiolamides



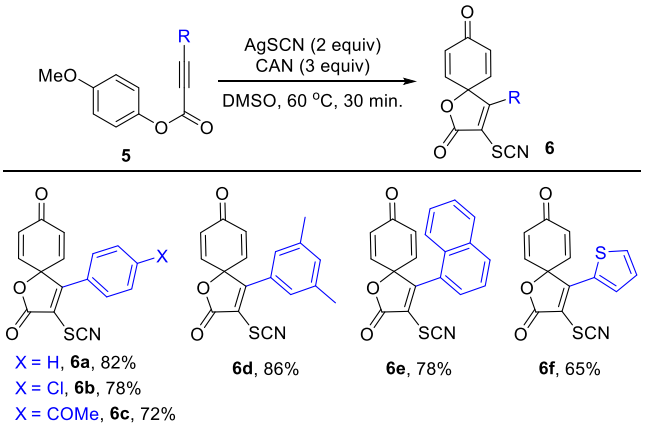
cyclization of **3** progressed well, giving the thiocyanato-pyrrolo-[2,1-*j*]-quinolone **4** in 80% yield (Scheme 3).

Scheme 3. Synthesis of Thiocyanato-pyrrolo-[2,1-*j*]quinolone 4



We next extended the scope of this thiocyanative *ipso*-cyclization to 4-methoxyphenyl propiolates (Scheme 4) and to the best of our knowledge, only one such example is known in the literature using the combination of bis(iodoarene) and mCPBA/*p*-TsOH.[19] Various 4-methoxyphenyl 3-aryl/hetero-arylpropiolates gave the corresponding thiocyanated products in good yield, regardless of the effect of a substituent on alkyne functionality. Substrates with electronically different substituents such as phenyl, 4-Cl-phenyl, and 4-COMe-phenyl gave the resultant products **6a**, **6b**, and **6c** in 82, 78, and 72% yields, respectively. 3,5-Dimethyl phenyl and 1-naphthyl groups on the alkyne were also compatible in this thiocyanative *ipso*-cyclization to give 3-thiocyanato-1-oxaspirocyclohexadienones

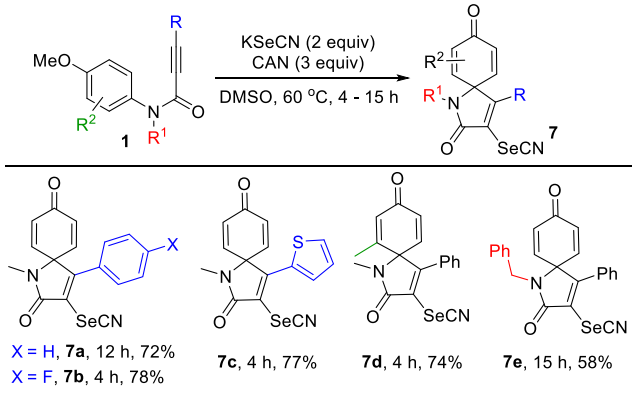
Scheme 4. Synthesis of 3-Thiocyanato-1-oxaspirocycles



6d (86%) and **6e** (78%). Likewise, the reaction effectively progressed with 4-methoxyphenyl propiolates having the heteroaryl group, 2-thiophenyl, delivering the product **6f** in 65% yield.

In the next part of this study, we turned our attention to verify the feasibility of this domino selenocyanation/*ipso*-cyclization, hitherto unknown transformation (Scheme 5).

Scheme 5. Domino Selenocyanation/*ipso*-Cyclization of *N*-(*p*-Methoxyphenyl)-propiolamides



Pleasantly, the selenocyanative cyclization of **1a** ensued cleanly to offer the selenocyanato azaspirocyclohexadienone **7a** (72%) in 12 h. The slower reactivity of a SeCN radical compared to a SCN radical might be due to the difference in redox potentials and sizes of these two chalcogen radicals.[20] The reaction tolerates the 4-fluoro-phenyl (**7b**) and 2-thiophenyl (**7c**) groups on the alkyne of propiolamides. Interestingly, other *N*-(*p*-methoxyphenyl)propiolamides having a methyl group on aryl and a benzyl group on nitrogen also underwent the *ipso*-cyclization successfully, furnishing the products **7d** and **7e** in 74 and 61% yields, respectively. Regrettably, selenocyanative *ipso*-cyclization of *N*-(*p*-methoxyphenyl)-propiolate **5a** was futile.

The scalability of the reaction was explored with 1.18 g (4.5mmol) of phenylpropiolamide **1a** under optimal conditions that provided the required product **2a** (1.2 g) in 92% yield (Scheme 6). In addition, the possible synthetic efficacies of thiocyanato-azaspirocyclohexadienones **2a** were also studied by the conversion of thiocyanate (SCN) into a wide variety of sulfur-containing useful frameworks (Scheme 6). For example, the SCN group of **2a** was efficiently transformed into

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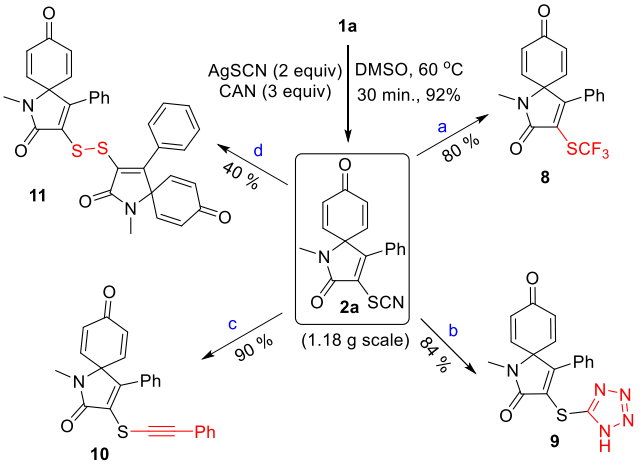
Scheme 6. Diversification of Thiocyanate 2a[a]

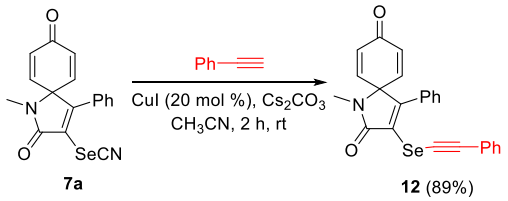


[a](a) CsF (1 equiv), $TMSSCF_3$ (2 equiv), CH_3CN, rt, 2 h; (b) NaN_3 (1.2 equiv), $ZnCl_2$ (1 equiv), ^iPrOH, 50 °C, 1.5 h; (c) phenlacetylene (1.5 equiv), CuI (0.2 equiv), Cs_2CO_3 (1 equiv), CH_3CN, 2 h rt; (d) *n*-BuLi (2 equiv), Et_2NH (3 equiv), THF, 0 °C-rt, 3 h.

trifluoromethylthiolate (SCF_3, ubiquitous lipophilic group), using $TMSSCF_3$ and CsF to obtain **8** in 80% yield (Scheme 6a).[12c] The click reaction of **2a** with NaN_3 in the presence of $ZnCl_2$ provided the corresponding thiotetrazole (metabolically stable substitute for the carboxyl) **9** in 84% yield.[5b] Interestingly, the thio-alkynylation of **2a** with phenylacetylene using CuI (20 mol %) and Cs_2CO_3 in CH_3CN at room temperature offered the alkynyl sulfide **10** in 90% yield.[9a] Pleasingly, the treatment of **2a** with *n*BuLi in the presence of Et_2NH in THF afforded the disulfide **11**, albeit in low yield (40%).[12c]

Further, the conversion of SeCN in **7a** into alkynyl selenide **12** with phenylacetylene using CuI (20 mol %) and Cs_2CO_3 in CH_3CN was also successful through seleno-alkynylation (Scheme 7).

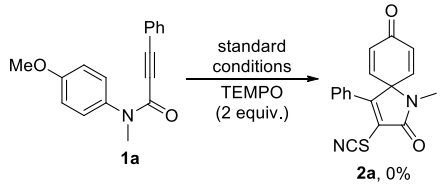
Scheme 7. Seleno-alkynylation of Selenide 7a



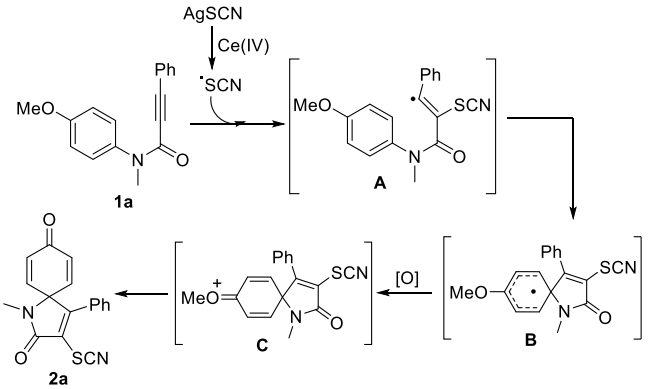
To gain mechanistic perception, we next executed a radical trap experiment. The treatment of **1a** using standard reaction conditions in the presence of radical scavenger 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) does not lead to formation of **2a** (Scheme 8), suggesting that the reaction pathway involves free radical intermediates.

According to the experimental outcomes and literature reports,[12a] a possible reaction mechanism for the CAN-mediated domino thiocyanation/*ipso*-cyclization/dearomatization is proposed (Scheme 9). Initially, CAN oxidizes AgSCN to generate a SCN radical, which attacks propiolamide **1a** regioselectively to produce radical **A**. Next, an *ipso*-carbacyclization of **A** affords intermediate **B**, which subsequently oxidizes to oxonium ion **C**. Finally, hydrolytic demethylation of **C** eventually delivers the desired azaspirocyclohexadienone **2a**.

Scheme 8. Outcome of the Control Experiment



Scheme 9. Possible Reaction Mechanism



CONCLUSIONS

In summary, earlier to this work, thiocyanative *ipso*-cyclizations were studied in the presence of either an electrophilic fluoride reagent or an acridinium perchlorate photocatalyst with limited substrates. In this paper, we successfully established a CAN mediated domino thiocyanation/*ipso*-cyclization/dearomatization of *N*-(*p*-methoxyphenyl)-propiolamides, leading to numerous spiro-fused 2,5-cyclohexadienones in good to excellent yields. The method was also extended to 4-methoxyphenyl propiolates. Another unprecedented transformation, selenocyanative *ipso*-cyclization of propiolamides, has also been demonstrated. Moreover, the resulting chalcogenocyanates were smoothly converted into unique azaspirocyclohexadienones bearing diverse frameworks for the first time. This method can be projected to find inclusive synthetic applications due to the mild reaction conditions, easy operation, high efficiency, and good yields.

EXPERIMENTAL SECTION

General Information. All of the reactions were performed in oven-dried glass apparatus. Reactions requiring anhydrous conditions were performed under a nitrogen atmosphere using freshly distilled anhydrous solvents. Commercially available reagents were used as received. All reactions were monitored by thin-layer chromatography (TLC) carried out on silica plates using UV light and anisaldehyde for visualization. Column chromatography was performed on silica gel (100−200 meshes) using hexane and ethyl acetate or methanol and dichloromethane as eluents. NMR spectra were reported in parts per million (δ) relative to tetramethylsilane (0.00 ppm) for protons and carbon. Coupling constants (J) are reported in hertz (Hz). ^1H NMR spectra were recorded in $CDCl_3$ or CD_3OD at 500, 400, and 300 MHz, and ^{13}C NMR spectra were recorded at 125, 100, and 75 MHz. δ 7.26 and δ 77.2 correspond to $CDCl_3$ in ^1H NMR and ^{13}C NMR, respectively.

All of the starting materials (**1a−1e**, **1g−1p**, **1r−1t**),[17a] (**1f**, **2b**, **2f**),[21a] and (**2a**, **2c−2e**)[21b] were prepared based on the literature reports, and spectral data was compared.

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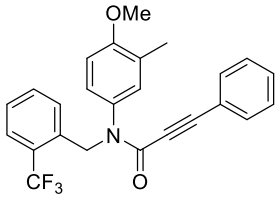
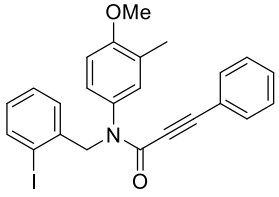
*N-(4-Methoxy-3-methylphenyl)-3-phenyl-N-(2-(trifluoromethyl)-benzyl)propiolamide (**1q**).*



To a stirred solution of phenylpropiolic acid (285 mg, 1.1 equiv) in CH_2Cl_2 under a nitrogen atmosphere at 0 °C was added 2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethylaminium hexafluorophosphate (HBTU, 877 mg, 1.5 equiv). After 30 min, 4-methoxy-3-methyl-*N*-(2-(trifluoromethyl)benzyl)aniline (500 mg, 1 equiv) and *N*,*N*-diisopropylethylamine (DIPEA, 0.9 ml, 3 equiv) were added drop wise for a period of 5 min. The reaction mixture was allowed to stir for 12 h at room temperature and quenched with water. The aqueous solution was extracted with dichloromethane (DCM, 3 × 50 mL), and the combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to get the crude product, which was purified by column chromatography on silica gel (100−200 meshes) using hexane and ethyl acetate as an eluent to obtain **1q** (as an equimolar ratio of rotamers) as a brown color oil (527 mg, 70% yield). R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.38 (m, 5H), 7.36−7.29 (m, 1H), 7.25−7.20 (m, 1H), 7.17−7.12 (m, 2H), 6.96−6.88 (m, 2H), 6.76 (d, J = 8.5 Hz, 1H), 4.99 (s, 2H), 3.84 (s, 3H), 2.19 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.5, 154.9, 137.9, 133.6, 132.5, 132.2, 130.4, 129.9, 129.0, 128.3, 127.6, 126.9, 125.6, 124.5, 124.4, 120.5, 109.9, 91.8, 82.5, 55.6, 52.1, 16.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.61; IR (neat): ν_{max} = 2218, 1638, 1328, 764 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{25}H_{21}F_3NO_2$ $(M + H)^+$ 424.1524, found 424.1513.

*N-(2-Iodobenzyl)-N-(4-methoxy-3-methylphenyl)-3-phenylpropiolamide (**1u**).*



To a stirred solution of phenylpropiolic acid (237 mg, 1.1 equiv) in DCM under a nitrogen atmosphere at 0 °C, HBTU (763 mg, 1.5 equiv) was added. After 30 min, *N*-(2-iodobenzyl)-4-methoxy-3-methylaniline (500 mg, 1 equiv) and DIPEA (0.8 ml, 3 equiv) were added dropwise for a period of 5 min at 0 °C. The reaction mixture was allowed to stir for 12 h at room temperature and quenched with water. The aqueous solution was extracted with DCM (3 × 50 mL), and the combined organic layers were washed with brine (50 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure to get the crude product, which was purified by column chromatography on silica gel (100−200 meshes) using hexane and ethyl acetate as an eluent to obtain **1u** (as an equimolar ratio of rotamers) as a red liquid (452 mg, 64% yield). R_f = 0.5 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79−7.76 (m, 1H), 7.43−7.38 (m, 1H), 7.35−7.30 (m, 2H), 7.27−7.23 (m, 2H), 7.19−7.16 (m, 2H), 7.06−7.00 (m, 2H), 6.96−6.92 (m, 1H), 6.74 (d, J = 8.5Hz, 1H), 5.04 (s, 2H), 3.82 (s, 3H), 2.18 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.4, 154.9, 139.5, 138.7, 133.7, 132.5, 130.4, 129.9, 129.3, 129.1, 128.5, 128.4, 127.3, 126.7, 120.6, 109.8, 99.0, 91.7, 82.7, 56.9, 55.6, 16.2; IR (neat): ν_{max} = 2951, 2217, 1638, 1437, 1134, 759 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{24}H_{21}INO_2$ $(M + H)^+$ 482.0617, found 482.0615.

General Procedure for Synthesis of 3-Thiocyanato [4,5] Spirotrienones (2). *N*-(4-Methoxyaryl)-propiolamide **1** (0.3 mmol), silver thiocyanate (0.6 mmol), and CAN (0.9 mmol) were taken in a reaction vessel, and DMSO (3 mL) was added. The reaction mixture was stirred at 60 °C (oil bath temperature) for 30 min. After completion of the reaction (monitored by TLC), water was added to the mixture, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to get the crude product, which was purified by column chromatography on silica gel using ethyl acetate and hexane as an eluent to afford the corresponding 3-thiocyanato[4,5] spirotrienones.

*1-Methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2a**).* Following the general procedure, *N*-(4-methoxyphenyl)propiolamide **1a** (80 mg, 0.3 mmol), AgSCN (112 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2a** as a white solid (85 mg, 92% yield). Mp: 150−152 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−7.40 (m, 3H), 7.28−7.25 (m, 2H), 6.55−6.49 (m, 4H), 2.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.3, 164.9, 157.0, 143.1, 134, 131.1, 129.1, 128.9, 127.8, 122.4, 106.3, 68.4, 26.6; IR (KBr): ν_{max} = 2925, 2162, 1709, 1629, 1268, 754 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{13}N_2O_2S$ $(M + H)^+$ 309.0698, found 309.0696.

*1-Methyl-3-thiocyanato-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2b**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(*p*-tolyl)propiolamide **1b** (85 mg, 0.3 mmol), AgSCN (103 mg, 0.6 mmol), and CAN (497 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2b** as a brown solid (85 mg, 88% yield). Mp: 125−127 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.15 (m, 4H), 6.55−6.47 (m, 4H), 2.94 (s, 3H), 2.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.4, 165.1, 157.3, 143.3, 141.8, 133.8, 129.8, 127.6, 126.0, 121.5, 106.4, 68.3, 26.5, 21.5; IR (KBr): ν_{max} = 2924, 2163, 1709, 1671, 1379, 758 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{15}N_2O_2S$ $(M + H)^+$ 323.0854, found 323.0856.

*4-(4-Methoxyphenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**2c**).* Following the general procedure, *N*-3-bis(4-methoxyphenyl)-*N*-methylpropiolamide **1c** (90 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatographic purification gave **2c** as a white solid (86 mg, 85% yield). Mp: 132−134 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.28 (m, 2H), 6.95−6.90 (m, 2H), 6.57−6.47 (m, 4H), 3.83 (s, 3H), 2.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.4, 165.3, 161.8, 157.0, 143.6, 133.7, 129.5, 121.1, 120.3, 114.6, 106.7, 68.1, 55.4, 26.4; IR (KBr): ν_{max} = 2927, 2163, 1706, 1671, 1258, 759 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{15}N_2O_3S$ $(M + H)^+$ 339.0803, found 339.0805.

*4-(4-Fluorophenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**2d**).* Following the general procedure, 3-(4-fluorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1d** (85 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **2d** as a brown solid (87 mg, 89% yield). Mp: 109−111 °C; R_f = 0.4 (hexane:ethyl acetate = 6:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32−7.27 (m, 2H), 7.16−7.11 (m, 2H), 6.56−6.53 (m, 2H), 6.51−6.47 (m, 2H), 2.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.1, 165.3, 164.8, 162.7, 155.6, 142.9, 134.1, 130.1, 130.0, 124.8, 122.7, 116.7, 116.5, 106.1, 68.4, 26.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ −107.20; IR (KBr): ν_{max} = 2924, 2164, 1705, 1668, 1232, 753 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{12}FN_2O_2S$ $(M + H)^+$ 327.0604, found 327.0602.

*4-(4-Chlorophenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**2e**).* Following the general procedure, 3-(4-chlorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1e** (91 mg, 0.3 mmol), AgSCN (103 mg, 0.6 mmol), and CAN (496 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2e** as a brown solid (90 mg, 86% yield). Mp: 167−169 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.39 (m, 2H), 7.25−7.21 (m, 2H), 6.57−6.53 (m, 2H), 6.51−6.47 (m, 2H), 2.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.1, 164.7, 155.4, 142.9, 137.6, 134.2, 129.6, 129.2, 127.2, 123.0, 105.9, 68.4, 26.6; IR (KBr): ν_{max} = 3023,

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2163, 1707, 1672, 1215, 745 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{12}N_2O_2SCl$ $(M + H)^+$ 343.0308, found 343.0308.

*1-Methyl-4-(4-nitrophenyl)-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2f**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(4-nitrophenyl)propiolamide **1f** (94 mg, 0.3 mmol), AgSCN (103 mg, 0.6 mmol), and CAN (495 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **2f** as a white solid (97 mg, 90% yield). Mp 160−162 °C; R_f = 0.4 (hexane:ethyl acetate = 5:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34−8.28 (m, 2H), 7.49−7.44 (m, 2H), 6.58−6.49 (m, 4H), 2.98 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 182.7, 164.3, 153.1, 149.1, 142.2, 134.7, 134.6, 129.3, 125.3, 124.3, 105.3, 68.6, 26.8; IR (KBr): ν_{max} = 2922, 2854, 2164, 1709, 1669, 1350 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{12}N_3O_4S$ $(M + H)^+$ 354.0549, found 354.0543.

*4-(1-Methyl-2,8-dioxo-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)benzonitrile (**2g**).* Following the general procedure, 3-(4-cyanophenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1g** (88 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (496 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2g** as a pale-yellow solid (89 mg, 88% yield). Mp: 173−175 °C; R_f = 0.4 (hexane:ethyl acetate = 5:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.72 (m, 2H), 7.43−7.38 (m, 2H), 6.58−6.49 (m, 4H), 2.97 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 182.8, 164.4, 153.7, 142.3, 134.5, 133.1, 132.8, 128.8, 124.7, 117.5, 114.9, 105.5, 68.5, 26.7; IR (KBr): ν_{max} = 2925, 2164, 1709, 1671, 1379, 1217, 751 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{12}N_3O_2S$ $(M + H)^+$ 334.0650, found 334.0653.

*4-(4-Acetylphenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2h**).* Following the general procedure, 3-(4-acetylphenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1h** (93 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (495 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **2h** as a white solid (89 mg, 84% yield). Mp: 179−181 °C; R_f = 0.4 (hexane:ethyl acetate = 5:5); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01−7.98 (m, 2H), 7.39−7.36 (m, 2H), 6.56−6.50 (m, 4H), 2.97 (s, 3H), 2.62 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 196.8, 183, 164.6, 155.2, 142.6, 138.7, 134.3, 133, 128.9, 128.3, 123.8, 105.8, 68.4, 26.7 (2C); IR (KBr): ν_{max} = 2921, 2165, 1679, 1630, 1371, 1265, 722 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{19}H_{15}N_2O_3S$ $(M + H)^+$ 351.0803, found 351.0804.

*4-(3,5-Dimethylphenyl)-1-methyl-3-thiocyanato-1-azaspiro-[4.5]deca-3,6,9-triene-2,8-dione (**2i**).* Following the general procedure, 3-(3,5-dimethylphenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1i** (89 mg, 0.3 mmol), AgSCN (103 mg, 0.6 mmol), and CAN (496 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2i** as a white solid (77 mg, 76% yield). Mp: 128−130 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09−7.08 (m, 1H), 6.83−6.81 (m, 2H), 6.54−6.51 (m, 2H), 6.50−6.47 (m, 2H), 2.94 (s, 3H), 2.30 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.5, 165.0, 157.6, 143.2, 138.9, 133.9, 132.9, 128.9, 125.3, 121.9, 106.5, 68.3, 26.6, 21.4 (2C); IR (KBr): ν_{max} = 2921, 2163, 1711, 1271, 1023, 760 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{19}H_{17}N_2O_2S$ $(M + H)^+$: 337.1011, found 337.1010.

*1-Methyl-3-thiocyanato-4-(3-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2j**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(3-(trifluoromethyl)-phenyl)propiolamide **1j** (100 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2j** as a white solid (92 mg, 81% yield). Mp: 102−104 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.9 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.52 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 6.58−6.51 (m, 4H), 2.97 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 182.9, 164.6, 154.5, 142.6, 134.4, 131.8, 131.5, 131.2, 129.9, 129.6, 127.8, 124.9, 124.8, 124.2, 121.9, 105.6, 68.5, 26.7; ^{19}F NMR (377 MHz, $CDCl_3$): δ −62.61; IR (KBr): ν_{max} = 2925, 2165, 1708, 1672, 1631, 1331, 1129, 758 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{12}F_3N_2O_2S$ $(M + H)^+$ 377.0572, found 377.0569.

*1-Methyl-4-(naphthalen-1-yl)-3-thiocyanato-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**2k**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(naphthalen-1-yl)propiolamide **1k** (95 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **2k** as a yellow solid (92 mg, 85% yield). Mp: 179−181 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97−7.91 (m, 2H), 7.61−7.54 (m, 2H), 7.51−7.42 (m, 2H), 7.25−7.22 (m, 1H), 6.72 (dd, J = 10.0, 3.0 Hz, 1H), 6.64 (dd, J = 10.0, 1.7 Hz, 1H), 6.52 (dd, J = 10.1, 3.0 Hz, 1H), 6.16 (dd, J = 10.1, 1.7 Hz, 1H), 3.04 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.1, 164.8, 154.5, 142.6, 142.5, 134.7, 133.7, 133.4, 131.3, 129.9, 129.6, 127.9, 126.9, 126.8, 125.8, 125.1, 124.6, 123.4, 105.4, 69.9, 27.1; IR (KBr): ν_{max} = 2924, 2164, 1708, 1671, 759 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{21}H_{15}N_2O_2S$ $(M + H)^+$ 359.0854, found 359.0854.

*1-Methyl-3-thiocyanato-4-(thiophen-2-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2l**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(thiophen-2-yl)propiolamide **1l** (82 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (494 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **2l** as a yellow solid (75 mg, 79% yield). Mp: 143−145 °C; R_f = 0.3 (hexane:ethyl acetate = 5:5); ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (dd, J = 5.1, 1.0 Hz, 1H), 7.53 (dd, J = 3.9, 1.0 Hz, 1H), 7.15 (dd, J = 5.1, 3.9 Hz, 1H), 6.67−6.63 (m, 2H), 6.55−6.52 (m, 2H), 2.92 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.5, 165.2, 150.8, 144.1, 133.8, 132.4, 131.7, 130.6, 128.3, 116.4, 106.4, 66.8, 26.1; IR (KBr): ν_{max} = 2924, 2160, 1702, 1630, 1374, 1269, 754 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{15}H_{11}N_2O_2S_2$ $(M + H)^+$ 315.0262, found 315.0259.

*1,4-Dimethyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2m**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methylbut-2-ynamide **1m** (61 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2m** as a white solid (60 mg, 81% yield). Mp: 146−148 °C; R_f = 0.3 (hexane:ethyl acetate = 5:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65−6.60 (m, 2H), 6.38−6.34 (m, 2H), 2.92 (s, 3H), 2.06 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.3, 165.4, 158.1, 143.5, 134.2, 121.4, 106.9, 68.8, 26.9, 12.3; IR (KBr): ν_{max} = 2958, 2170, 1713, 1674, 1388, 860 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{12}H_{11}N_2O_2S$ $(M + H)^+$ 247.0541, found 247.0542.

*4-Ethyl-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2n**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methylpent-2-ynamide **1n** (66 mg, 0.3 mmol), AgSCN (103 mg, 0.6 mmol), and CAN (497 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2n** as a white solid (66 mg, 83% yield). Mp: 128−130 °C; R_f = 0.3 (hexane:ethyl acetate = 5:5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (d, J = 10.0 Hz, 2H), 6.37 (d, J = 6.4 Hz, 2H), 2.90 (s, 3H), 2.39 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.5, 165.5, 162.9, 143.3, 134.2, 121.1, 106.8, 68.8, 26.8, 20.2, 13.4; IR (KBr): ν_{max} = 2980, 2163, 1708, 1603, 1382, 762 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{13}H_{13}N_2O_2S$ $(M + H)^+$ 261.0698, found 261.0698.

*1-Benzyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2o**).* Following the general procedure, *N*-benzyl-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **1o** (103 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2o** as a brown solid (100 mg, 86% yield). Mp: 108−110 °C; R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.42 (m, 1H), 7.42−7.36 (m, 2H), 7.30−7.23 (m, 5H), 7.19−7.14 (m, 2H), 6.35−6.27 (m, 4H), 4.59 (s, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.5, 165.2, 157.2, 143.3, 136.6, 133.1, 131.1, 129.0, 128.8, 128.7, 128.5, 128.3, 127.8, 122.4, 106.2, 68.9, 45.5; IR (KBr): ν_{max} = 2923, 2163, 1701, 1671, 754 cm^{-1}; HRMS

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(ESI/Q-TOF): m/z calcd for $C_{23}H_{17}N_2O_2S$ $(M + H)^+$ 385.1011, found 385.1013.

*1-(2-Iodobenzyl)-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2p**).* Following the general procedure, *N*-(2-iodobenzyl)-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **1p** (144 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (489 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2p** as a brown solid (131 mg, 86% yield). Mp: 113−115 °C; R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 1H), 7.47−7.35 (m, 4H), 7.30 (d, J = 7.4 Hz, 1H), 7.18 (d, J = 7.3 Hz, 2H), 6.97 (t, J = 7.4 Hz, 1H), 6.29 (q, J = 10.2 Hz, 4H), 4.77 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 183.5, 165.2, 157.7, 142.4, 139.7, 138.9, 133.5, 131.1, 130.3, 129.9, 129.0, 128.8, 128.6, 127.8, 122.2, 106.2, 99.7, 68.8, 49.7; IR (KBr): ν_{max} = 3055, 2163, 1709, 1389, 756 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{23}H_{16}N_2O_2SI$ $(M + H)^+$ 510.9977, found 510.9988.

*7-Methyl-4-phenyl-3-thiocyanato-1-(2-(trifluoromethyl)benzyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2q**).* Following the general procedure, *N*-(4-methoxy-3-methylphenyl)-3-phenyl-*N*-(2-(trifluoromethyl)benzyl)propiolamide **1q** (127 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (494 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2q** as a yellow solid (114 mg, 81% yield). Mp: 139−141 °C; R_f = 0.5 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (t, J = 8.5 Hz, 2H), 7.48−7.36 (m, 5H), 7.19−7.13 (m, 2H), 6.39−6.33 (m, 2H), 6.01 (dd, J = 2.4, 1.4 Hz, 1H), 4.78 (d, J = 15.1 Hz, 1H), 4.44 (d, J = 15.1 Hz, 1H), 1.74 (d, J = 1.5 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.0, 165.3, 158.3, 142.6, 140.7, 138.0, 137.8, 133.4, 132.6, 131.3, 131.1, 130.9, 129.4, 129.0, 128.7, 127.7, 125.7, 125.0, 121.7, 106.3, 69.2, 44.9, 15.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.99; IR (KBr): ν_{max} = 3063, 2164, 1700, 1670, 737 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{25}H_{18}F_3N_2O_2S$ $(M + H)^+$ 467.1041, found 467.1040.

*1,6-Dimethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2r**).* Following the general procedure, *N*-(4-methoxy-2-methylphenyl)-*N*-methyl-3-phenylpropiolamide **1r** (84 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (492 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2r** as a white solid (85 mg, 88% yield). Mp: 163-165 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50−7.46 (m, 1H), 7.45−7.41 (m, 2H), 7.28−7.27 (m, 1H), 7.26−7.25 (m, 1H), 6.54 (dd, J = 9.9, 1.7 Hz, 1H), 6.46 (d, J = 9.9 Hz, 1H), 6.40−6.38 (m, 1H), 2.86 (s, 3H), 1.76 (d, J = 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.1, 165.5, 157.4, 151.5, 143.2, 133.5, 132.6, 131.4, 129.3, 128.7, 127.6, 122.4, 106.3, 70.5, 26.2, 17.7; IR (KBr): ν_{max} = 3016, 2163, 1709, 1389, 757 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{15}N_2O_2S$ $(M + H)^+$ 323.0854, found 323.0858.

*1,7-Dimethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2s**).* Following the general procedure, *N*-(4-methoxy-3-methylphenyl)-*N*-methyl-3-phenylpropiolamide **1s** (84 mg, 0.3 mmol), AgSCN (112 mg, 0.6 mmol), and CAN (492 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2s** as a white solid (86 mg, 89% yield). Mp: 129−131 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49−7.44 (m, 1H), 7.44−7.39 (m, 2H), 7.24−7.21 (m, 2H), 6.51−6.45 (m, 2H), 6.28 (dd, J = 2.7, 1.4 Hz, 1H), 2.93 (s, 3H), 1.95 (d, J = 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.2, 165, 157.7, 142.9, 141.5, 137.7, 133.7, 131.0, 129.0 (2C), 127.8, 121.9, 106.5, 68.9, 26.5, 16; IR (KBr): ν_{max} = 2923, 2164, 1706, 1642, 1371, 750 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{15}N_2O_2S$ $(M + H)^+$ 323.0854, found 323.0858.

*7-Fluoro-1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2t**).* Following the general procedure, *N*-(3-fluoro-4-methoxyphenyl)-*N*-methyl-3-phenylpropiolamide **1t** (85 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2t** as a yellow solid (90 mg, 92% yield). Mp 125−127 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.43 (m, 3H), 7.25−7.22 (m, 2H), 6.57−6.51 (m, 2H), 6.12−6.08 (m, 1H), 2.98 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 176.3, 164.5, 157.4, 156.2, 144.3, 133.0, 133.0, 131.4, 129.3, 128.5, 127.7, 122.9, 119.3, 119.2, 105.9, 69.9, 26.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ −119.75; IR (KBr): ν_{max} = 3050, 2164, 1714, 1380, 1173, 760 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{12}FN_2O_2S$ $(M + H)^+$ 327.0604, found 327.0611.

*1-(2-Iodobenzyl)-7-methyl-4-phenyl-3-thiocyanato-1-azaspiro-[4.5]deca-3,6,9-triene-2,8-dione (**2u**).* Following the general procedure, *N*-(2-iodobenzyl)-*N*-(4-methoxy-3-methylphenyl)-3-phenylpropiolamide **1u** (128 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (494 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **2u** as a white solid (141 mg, 89% yield). Mp: 143−145 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, J = 8.0, 1.1 Hz, 1H), 7.45−7.41 (m, 2H), 7.39−7.35 (m, 2H), 7.31− 7.29 (m, 1H), 7.17−7.14 (m, 2H), 6.97−6.93 (m, 1H), 6.30−6.25 (m, 2H), 5.98−5.96 (m, 1H), 4.86 (d, J = 15.3 Hz, 1H), 4.68 (d, J = 15.3 Hz, 1H), 1.72 (d, J = 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 184.4, 165.2, 158.5, 142.2, 140.9, 139.6, 139.3, 137.3, 133.4, 131, 130.3, 129.9, 128.9, 128.9, 128.8, 127.7, 121.6, 106.4, 99.8, 69.2, 49.5, 16.0; IR (KBr): ν_{max} = 2923, 2167, 1707, 1643, 1386, 757 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{24}H_{18}N_2O_2SI$ $(M + H)^+$ 525.0134, found 525.0136.

*1-Phenyl-2-thiocyanato-6,7-dihydro-3H-pyrrolo[2,1-j]quinoline-3,9(5H)-dione (**4**).* Following the general procedure, 1-(6-methoxy-3,4-dihydroquinolin-1(2*H*)-yl)-3-phenylprop-2-yn-1-one **3** (88 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (489 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **4** as a brown solid (80 mg, 80% yield). Mp: 147−149 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47−7.43 (m, 1H), 7.41−7.37 (m, 2H), 7.08−7.05 (m, 2H), 6.54−6.52 (m, 1H), 6.40 (t, J = 1.5 Hz 1H), 6.28−6.24 (m, 1H), 4.28−4.22 (m, 1H), 2.90−2.82 (m, 1H), 2.59−2.50 (m, 2H), 2.08−2.00 (m, 1H), 1.94−1.87 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.9, 168.7, 158.6, 156.4, 144.5, 132.9, 131.0, 129.9, 128.9, 128.3, 127.9, 122.9, 106.2, 72.3, 37.2, 26.8, 26.2; IR (KBr): ν_{max} 2951, 2163, 1709, 1667, 1377, 753 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{19}H_{15}N_2O_2S$ $(M + H)^+$ 335.0854, found 335.0857.

*4-Phenyl-3-thiocyanato-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6a**).* Following the general procedure, 4-methoxyphenyl 3-phenylpropiolate **5a** (76 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **6a** as a brown liquid (73 mg, 82% yield), R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.52 (m, 1H), 7.51-7.45 (m, 2H), 7.36−7.31 (m, 2H), 6.71−6.65 (m, 2H), 6.50−6.43 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.1, 165.9, 165.7, 140.6, 139.7, 132.7, 132.3, 129.5, 127.5, 116.4, 105.2, 83.1; IR (neat): ν_{max} = 3058, 2924, 2105, 1772, 1672, 1214, 746 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{16}H_{10}NO_3S$ $(M + H)^+$ 296.0381, found 296.0383.

*4-(4-Chlorophenyl)-3-thiocyanato-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6b**).* Following the general procedure, 4-Methoxyphenyl 3-(4-chlorophenyl)propiolate **5b** (86 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (492 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **6b** as a white solid (77 mg, 78% yield). Mp: 137−139 °C; R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 10.1 Hz, 2H), 6.48 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.9, 165.7, 164.2, 140.4, 138.9, 132.9, 129.9, 128.9, 125.7, 116.9, 104.9, 83.0; IR (KBr): ν_{max} = 3058, 2166, 1766, 1674, 1216, 759 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{16}H_{12}ClN_2O_3S^+$ $(M + NH_4)^+$: 347.0257, Found: 347.0254.

*4-(4-Acetylphenyl)-3-thiocyanato-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6c**).* Following the general procedure, 4-methoxyphenyl 3-(4-acetylphenyl)propiolate **5c** (89 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (494 mg, 0.9 mmol) were reacted in

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DMSO (3 mL). After the workup, column chromatography purification gave **6c** as a brownish white solid (74 mg, 72% yield). Mp: 129−131 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.68 (d, J = 10.0 Hz, 2H), 6.47 (d, J = 10.0 Hz, 2H), 2.63 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 196.5, 182.7, 165.6, 164.1, 140.2, 139.4, 133.0, 131.4, 129.1, 127.9, 118, 104.6, 83.2, 26.7; IR (KBr): ν_{max} = 2924, 2168, 1778, 1681, 1632, 1267, 757 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{12}NO_4S$ (M + H)$^+$ 338.0487, found 338.0492.

*4-(3,5-Dimethylphenyl)-3-thiocyanato-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6d**).* Following the general procedure, 4-methoxyphenyl 3-(3,5-dimethylphenyl)propiolate **5d** (84 mg, 0.3 mmol), AgSCN (101 mg, 0.6 mmol), and CAN (490 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **6d** as a white solid (83 mg, 86% yield). Mp: 127−129 °C; R_f = 0.3 (hexane:ethyl acetate = 8:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 6.89 (s, 2H), 6.68−6.63 (m, 2H), 6.48−6.43 (m, 2H), 2.32 (s, 6H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.2, 166.3, 166.0, 140.8, 139.3, 134.0, 132.6, 127.5, 125.0, 115.8, 105.3, 83.0, 21.3 (2C); IR (KBr): ν_{max} = 2968, 2162, 2918, 1782, 1678, 1382 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{14}NO_3S$ (M + H)$^+$ 324.0694, found 324.0695.

*4-(Naphthalen-1-yl)-3-thiocyanato-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6e**).* Following the general procedure, 4-methoxyphenyl 3-(naphthalen-1-yl)propiolate **5e** (91 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (492 mg, 0.9 mmol) were reacted in DMSO (3 mL). Column chromatography purification gave **6e** as a brown solid (81 mg, 78% yield). Mp: 176−178 °C; R_f = 0.3 (hexane:ethyl acetate = 8:2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01−7.95 (m, 2H), 7.66−7.59 (m, 2H), 7.51−7.45 (m, 2H), 7.28−7.27 (m, 1H), 6.87 (dd, J = 10.1, 3.2 Hz, 1H), 6.68 (dd, J = 10.1, 3.2 Hz, 1H), 6.57 (dd, J = 10.1, 1.7 Hz, 1H), 6.09 (dd, J = 10.1, 1.7 Hz, 1H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 182.8, 165.8, 164.2, 140.3, 139.9, 133.4, 133.3, 132.3, 132.1, 129.7, 129.2, 128.4, 127.1, 126.4, 124.6, 123.7, 123.1, 120.2, 104.3, 84.8; IR (KBr): ν_{max} = 3055, 2167, 1779, 1673, 1222, 756 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{20}H_{12}NO_3S$ (M + H)$^+$ 346.0538, found 346.0539.

*3-Thiocyanato-4-(thiophen-2-yl)-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6f**).* Following the general procedure, 4-methoxyphenyl 3-(thiophen-2-yl)propiolate **5f** (78 mg, 0.3 mmol), AgSCN (102 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL). After the workup, column chromatography purification gave **6f** as a yellow liquid (59 mg, 65% yield). R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 4.9 Hz, 1H), 7.66 (d, J = 3.7 Hz, 1H), 7.25−7.21 (m, 1H), 6.70 (d, J = 10.0 Hz, 2H), 6.58 (d, J = 10.0 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.4, 166.4, 158.8, 141.8, 135.6, 134, 132.7, 129.1, 128.9, 108.8, 105.6, 80.8; IR (neat): ν_{max} = 2924, 2159, 1706, 1672, 1378, 758 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{14}H_8NO_3S_2$ (M + H)$^+$ 301.9946, found 301.9945.

General Procedure for Synthesis of 3-Selenocyanato[4,5]-spirotrienones (7). *N*-(4-Methoxyaryl)-propiolamide **1** (0.3 mmol), potassium selenocyanate (0.6 mmol), and ceric ammonium nitrate (0.9 mmol) were taken in a reaction vessel, and DMSO (3 mL) was added. The reaction mixture was stirred at 60 °C (oil bath temperature) for 4−15 h. After completion of the reaction (monitored by TLC), water was added to the mixture, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to get the crude product, which was purified by column chromatography on silica gel using ethyl acetate and hexane as an eluent to afford the corresponding 3-selenocyanato [4,5] spirotrienones.

*1-Methyl-4-phenyl-3-selenocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**7a**).* Following the general procedure, *N*-(4-methoxyaryl)-propiolamide **1a** (80 mg, 0.3 mmol), KSeCN (87 mg, 0.6 mmol), CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL) for 12 h. After the workup, column chromatography purification gave **7a** as a brown solid (78 mg, 72% yield). Mp: 140−142 °C; R_f = 0.3 (hexane:ethyl acetate = 6:4); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49−7.38 (m, 3H), 7.25−7.21 (m, 2H), 6.52 (s, 4H), 2.96 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 183.4, 166.2, 157.7, 143.2, 133.9, 131.0, 129.6, 129.1, 127.7, 122.3, 96.8, 69.7, 26.7; IR (KBr): ν_{max} = 3098, 1706, 1673, 1380, 1217, 767 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{13}N_2O_2Se$ (M + H)$^+$ 357.0142, found 357.0138.

*4-(4-Fluorophenyl)-1-methyl-3-selenocyanato-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**7b**).* Following the general procedure, 3-(4-fluorophenyl)-*N*-(4-methoxyphenyl)-*N*-methylpropiolamide **1d** (85 mg, 0.3 mmol), KSeCN (86 mg, 0.6 mmol), and CAN (491 mg, 0.9 mmol) were reacted in DMSO (3 mL) for 4 h. After the workup, column chromatography purification gave **7b** as a white solid (88 mg, 78% yield). Mp: 140−142 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.24 (m, 2H), 7.15−7.09 (m, 2H), 6.52 (s, 4H), 2.95 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 183.2, 166.1, 165.2, 162.7, 156.5, 143.1, 134.0, 130.1, 130.0, 125.6, 125.5, 122.7, 116.6, 116.3, 96.8, 69.8, 26.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ −107.72; IR (KBr): ν_{max} = 3016, 1696, 1667, 1373, 1280, 751 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{12}FN_2O_2Se$ (M + H)$^+$ 375.0048, found 375.0045.

*1-Methyl-3-selenocyanato-4-(thiophen-2-yl)-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**7c**).* Following the general procedure, *N*-(4-methoxyphenyl)-*N*-methyl-3-(thiophen-2-yl)propiolamide **1l** (82 mg, 0.3 mmol), KSeCN (86 mg, 0.6 mmol), and CAN (494 mg, 0.9 mmol) were reacted in DMSO (3 mL) for 4 h. After the workup, column chromatography purification gave **7c** as a yellow solid (84 mg, 77% yield). Mp: 133−135 °C; R_f = 0.2 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 5.1, 1.1 Hz, 1H), 7.46 (dd, J = 3.9, 1.1 Hz, 1H), 7.14 (dd, J = 5.1, 3.9 Hz, 1H), 6.65−6.62 (m, 2H), 6.56−6.53 (m, 2H), 2.93 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 183.6, 166.3, 151.5, 144.1, 133.8, 131.8, 131.3, 131.1, 128.2, 117.3, 97.4, 68.1, 26.2; IR (KBr): ν_{max} = 2924, 2158, 1696, 1584, 1373, 758 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{15}H_{11}N_2O_2SSe$ (M + H)$^+$ 362.9706, found 362.9702.

*1,6-Dimethyl-4-phenyl-3-selenocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**7d**).* Following the general procedure, *N*-(4-methoxy-2-methylphenyl)-*N*-methyl-3-phenylpropiolamide **1r** (84 mg, 0.3 mmol), KSeCN (86 mg, 0.6 mmol), and CAN (492 mg, 0.9 mmol) were reacted in DMSO (3 mL) for 4 h. After the workup, column chromatography purification gave **7d** as a white solid (82 mg, 74% yield). Mp: 158−160 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.40 (m, 3H), 7.23 (dd, J = 5.2, 3.3 Hz, 2H), 6.55−6.47 (m, 2H), 6.39−6.37 (m, 1H), 2.86 (s, 3H), 1.78 (d, J = 1.3 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 184.1, 166.6, 158.2, 151.6, 143.4, 133.4, 132.5, 131.2, 129.5, 129.2, 127.5, 122.2, 97.0, 71.9, 26.3, 17.7; IR (KBr): ν_{max} = 3015, 2161, 1655, 1648, 1374, 1277, 748 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{18}H_{15}N_2O_2Se$ (M + H)$^+$ 371.0299, found 371.0298.

*1-Benzyl-4-phenyl-3-selenocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**7e**).* Following the general procedure, *N*-benzyl-*N*-(4-methoxyphenyl)-3-phenylpropiolamide **1o** (103 mg, 0.3 mmol), KSeCN (86 mg, 0.6 mmol), and CAN (493 mg, 0.9 mmol) were reacted in DMSO (3 mL) for 15 h. After the workup, column chromatography purification gave **7e** as a white solid (75 mg, 58% yield). Mp: 95−97 °C; R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.31−7.22 (m, 5H), 7.14 (d, J = 7.4 Hz, 2H), 6.34 (d, J = 10.0 Hz, 2H), 6.28 (d, J = 10.1 Hz, 2H), 4.59 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 183.6, 166.4, 158.0, 143.4, 136.6, 133.0, 130.9, 129.4, 129.0, 128.9, 128.7, 128.3, 127.8, 122.2, 96.8, 70.2, 45.5; IR (KBr): ν_{max} = 3019, 2159, 1696, 1667, 1385, 738 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{23}H_{17}N_2O_2Se$ (M + H)$^+$ 433.0455, found 433.0456.

Gram-Scale Synthesis. *1-Methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2a**).* *N*-(4-Methoxyaryl)-propiolamide **1a** (1.18 g, 4.5 mmol), AgSCN (1.5 g, 9 mmol), and CAN (7.3 g, 13.5 mmol) were taken in a 100 mL round-bottomed flask, and 25 mL of DMSO was added. The round-bottomed flask was fitted with a condenser, and the reaction mixture was stirred at 60 °C (oil bath temperature) for 30 min. After completion of the reaction

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(monitored by TLC), water was added to the mixture, and the mixture was extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over Na_2SO_4. The organic layer was concentrated, and the crude reaction mixture was purified by column chromatography on silica gel by using ethyl acetate and hexane as an eluent to afford the corresponding product **2a** as a white solid (1.2 g) in 92% yield.

*1-Methyl-4-phenyl-3-((trifluoromethyl)thio)-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**8**).* A mixture of **2a** (50 mg, 0.16 mmol) and CsF (25 mg, 0.16 mmol) was taken in a 10 mL round-bottomed flask and dissolved in acetonitrile (3 mL) and cooled to 0 °C. Then, trifluoromethyl trimethylsilane (45 mg, 0.32 mmol) was added at once *via* a syringe and stirred at room temperature for 2 h. After completion of the reaction (indicated by TLC), the reaction mixture was filtered using a pad of Celite and extracted with ethyl acetate and concentrated. The residue was purified by column chromatography to obtain **8** as a white solid (46 mg, 80% yield). Mp: 105−107 °C; R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.37 (m, 3H), 7.27−7.23 (m, 2H), 6.51 (s, 4H), 2.95 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 183.4, 166.7, 165.1, 143.4, 133.8, 130.7, 129.8, 129.6, 128.7, 128.0, 126.8, 123.9, 68.4, 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −39.27; IR (KBr): ν_{max} = 3055, 1709, 1670, 1374, 1101, 759 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{13}F_3NO_2S$ $(M + H)^+$ 352.0619, found 352.0620.

*3-((1H-Tetrazol-5-yl)thio)-1-methyl-4-phenyl-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**9**).* A solution of **2a** (50 mg, 0.16 mmol), $ZnCl_2$ (22 mg, 0.16 mmol), and NaN_3 (13 mg, 0.19 mmol) was taken in a reaction vessel, and *i*-PrOH (3 mL) was added and left for stirring at 60 °C for 1.5 h. After completion of the reaction, the mixture was diluted with ethyl acetate and concentrated under vacuum. The residue was purified by column chromatography on silica gel using methanol and DCM as an eluent to provide **9** as a white solid (47 mg, 84% yield). Mp: 185−187 °C; R_f = 0.3 (DCM: MeOH = 7:3); ^{1}H NMR (500 MHz, CD_3OD) δ 7.37−7.30 (m, 5H), 6.93−6.89 (m, 2H), 6.49−6.46 (m, 2H), 2.92 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 184.4, 167.8, 155.4, 145.4, 132.7, 130.5, 129.4, 128.5, 128.1, 127.8, 115.8, 68.6, 25.4; IR (KBr): ν_{max} = 3437, 3377, 2924, 1668, 1384, 757 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{17}H_{14}N_5O_2S$ $(M + H)^+$ 352.0868, found 352.0866.

*1-Methyl-4-phenyl-3-((phenylethynyl)thio)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**10**).* An oven-dried 25 mL round-bottomed flask fitted with a stirring bar was charged with **2a** (50 mg, 0.16 mmol) in acetonitrile (4 mL), and phenylacetylene (24 mg, 0.24 mmol), CuI (20 mol %), and Cs_2CO_3 (52 mg, 0.16 mmol) were added successively to this solution at room temperature and stirred for 1.5 h. After confirming the completion of the reaction by TLC, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using ethyl acetate and hexane as an eluent to obtain the desired product **10** as a white solid (55 mg, 90% yield). Mp: 162−164 °C; R_f = 0.4 (hexane:ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34−7.28 (m, 5H), 7.27−7.23 (m, 1H), 7.21−7.17 (m, 2H), 7.04−7.01 (m, 2H), 6.55−6.51 (m, 2H), 6.48−6.44 (m, 2H), 2.93 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 183.9, 166.9, 148.9, 144.8, 133.3, 131.6, 129.9, 129.8, 129.1, 128.6, 128.4, 128.2, 128, 122.2, 97.7, 71.8, 68.4, 26.3; IR (KBr): ν_{max} = 3053, 1701, 1672, 1380, 1271, 758 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{24}H_{18}NO_2S$ $(M + H)^+$ 384.1058, found 384.1057.

*3,3′-Disulfanediylbis(1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione) (**11**).* To a stirred solution of Et_2NH (71 mg, 0.97 mmol) in dry THF at 0 °C under a N_2 atmosphere was added n-BuLi (0.2 mL, 0.65 mmol 2.5 M) in hexane dropwise, and the stirring was continued for 0.5 h. A solution of **2a** (100 mg, 0.33 mmol) in THF was added dropwise *via* a syringe to the reaction mixture and allowed to warm to room temperature, and the reaction was continued for 3 h. After completion of the reaction (confirmed by TLC), the reaction was quenched with a saturated solution of NH_4Cl, extracted with ethyl acetate and dried over Na_2SO_4. The concentrated residue was purified by silica gel column chromatography using ethyl acetate and hexane as an eluent to obtain **11** as a yellow solid (75 mg, 40% yield). Mp: 158−160 °C; R_f = 0.3 (hexane:ethyl acetate = 2:8); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.5 Hz, 5H), 7.28 (d, J = 6.0 Hz, 3H), 6.49−6.44 (m, 8H), 2.87 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 183.9, 167.7, 157.3, 144.7, 133.8, 133.2, 130.8, 130.2, 128.6, 128.4, 67.7, 26.2; IR (KBr): ν_{max} = 3094, 1707, 1672, 1218, 771 cm^{-1}; HRMS (ESI/Q-TOF): m/z calcd for $C_{32}H_{25}N_2O_4S_2$ $(M + H)^+$ 565.1256, found 565.1250.

*1-Methyl-4-phenyl-3-((phenylethynyl)selanyl)-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**12**).* Following the procedure used for the synthesis of **10**, 1-methyl-4-phenyl-3-selenocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **7a** (50 mg, 0.14 mmol) in acetonitrile (4 mL), phenylacetylene (22 mg, 0.21 mmol), CuI (20 mol %), and Cs_2CO_3 (46 mg, 0.14 mmol) were added sequentially at room temperature. After the workup, column chromatography purification gave the desired product **12** as a white solid (54 mg, 89% yield). Mp 169−171 °C; R_f = 0.4 (hexane:ethyl acetate = 6:34); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.30 (m, 2H), 7.30−7.25 (m, 3H), 7.25−7.16 (m, 3H), 7.03−6.99 (m, 2H), 6.55−6.51 (m, 2H), 6.48−6.43 (m, 2H), 2.93 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 183.9, 167.9, 151.8, 144.7, 133.3, 131.7, 130.3, 129.7, 128.5, 128.3, 128.2, 127.9, 126.9, 122.5, 103.3, 69.8, 65.0, 26.3; IR (KBr): ν_{max} = 3058, 1698, 1383, 1037, 760 cm^{-1}; HRMS (ESI/Q-OTF): m/z calcd for $C_{24}H_{18}NO_2Se$ $(M + H)^+$ 432.0503, found 432.0502.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02270.

Structures of propiolamides and propiolates; control experiment-procedure; copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra of all of the new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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