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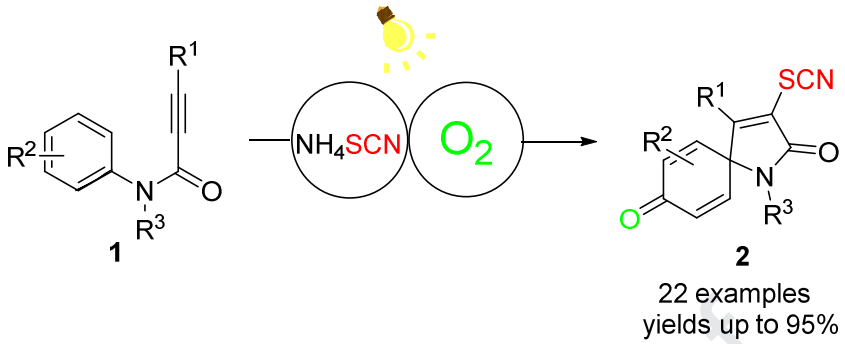
Graphical Abstract



A visible-light-mediated metal-free thiocyanate radical addition/*ipso*-cyclization/oxidation cascade reaction for the synthesis of thiocyanato-containing azaspirotrienediones from N-phenylpropynamides is described.

Visible-light-mediated selective thiocyanation/*ipso*-cyclization/oxidation cascade for the synthesis of thiocyanato-containing azaspirotrienediones

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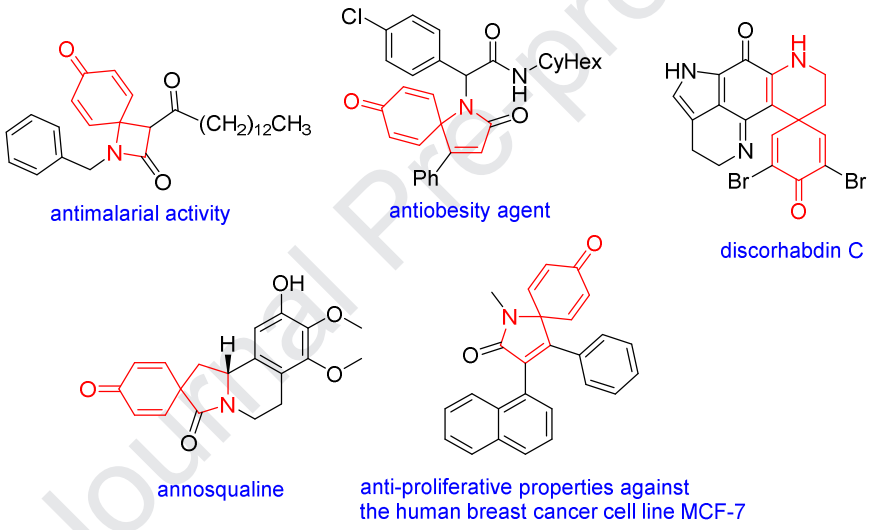
Abstract: A visible-light-mediated metal-free thiocyanate radical addition/*ipso*-cyclization/oxidation cascade reaction for the synthesis of thiocyanato-containing azaspirotrienediones from *N*-phenylpropynamides is described. Cheap and readily available ammonium thiocyanate was used as a precursor to the thiocyanate free radical, which undergoes a radical addition reaction with the alkyne, followed by selective *ipso*-cyclization and oxidation to afford the dearomatized products. No product of *ortho*-cyclization was detected. The reaction completes the synthesis of C-S, C-C, and C=O bonds in one pot, with abundant and renewable air oxygen as the sole sacrificial reagent and oxygen source.

Key words: photocatalysis; organic dye; thiocyanation; *ipso*-cyclization, dearomatization

1. Introduction

A spirocyclic compound is a compound in which two monocyclic rings share the same quaternary carbon atom in one molecule, and the shared carbon atom is called a spiro carbon atom [1]. Spirocyclic compounds are widely used in polymer binders/expanders and fireproofing materials due to their stable rigid structure [2]. Chiral spirocyclic compounds play an important role as good chiral ligands in asymmetric catalysis owing to their difficulty in racemization [3]. In addition, when the spiro ring system contains two π systems that are approximately perpendicular

to each other, the interesting spiroconjugation phenomenon occurs [4]. This special homoconjugation makes it an important direction for cutting-edge materials [5]. The azaspirohexadienone moiety is one of the most important structures in the biological and pharmaceutical fields [6]. It can be found in many drug molecules and natural products, such as antimalarial molecule [7], antiobesity agent [8], alkaloid discorhabdin C from sponges [9], alkaloid annosqualine from the stems of *Annona squamosa*, and molecule with anti-proliferative properties against the human breast cancer cell line MCF-7 [6b] **(Scheme 1)**. Moreover, some azaspirohexadienone-containing molecules are important intermediates in organic synthesis and have been extensively used to construct high-value macromolecular compounds [10].



Scheme 1. Drugs and natural products containing azaspirohexadienone moiety

The synthesis of spirohexadienones is mainly realized through de-aromatization of the aromatic rings by *ipso* nucleophilic or electrophilic addition [11]. Recently, a number of synthetic methods for spirodihexenones have been developed. However, in most cases, phenol, a phenol derivative or an excess of *t*-butylhydroperoxide is required as a source of carbonyl oxygen, which not only limits the scope of application but is also harmful to the environment. Therefore, it is still necessary to develope more green and mild synthetic methods for the synthesis of spirohexadienones.

Some organic thiocyanates have been found in natural products [12]. Moreover, thiocyanato is a valuable group with many functions in organic synthesis, so it has attracted increasing

attention from chemists in recent decades [13]. For example, thiocyanates can be used as precursors to other thio functional groups [14]. Since the nitrile moiety acts as a leaving group, the sulfur atom of the thiocyanate has an electrophilic property. Thiocyanate has the opposite reactivity because it can be nucleophilic at its sulfur or its nitrogen end, which can be readily used to convert organic thiocyanates to isothiocyanates by simple molecular rearrangement. Due to the specific polarization of the electron-rich nitrile moiety of thiocyanate, these compounds represent attractive cycloaddition partners to produce heterocycles and are therefore useful as precursors for heterocycles. Additionally, thiocyanates can also be used as a source of cyanides [15]. Therefore, the introduction of versatile thiocyanate into the spirohexadienone framework to obtain highly functionalized novel compounds is of great significance for the study of spiro compounds. In 2008 [11e], Li's group reported the electrophilic spirocyclization reaction catalyzed by electrophilic fluorination reagents at 90 ^{o}C. The halogenated and thiocyanated spirocyclohexenylenediones were synthesized by using CuX (X = I, Br, SCN) to provide functional groups, wherein four thiocyanate products were obtained in moderate yields.

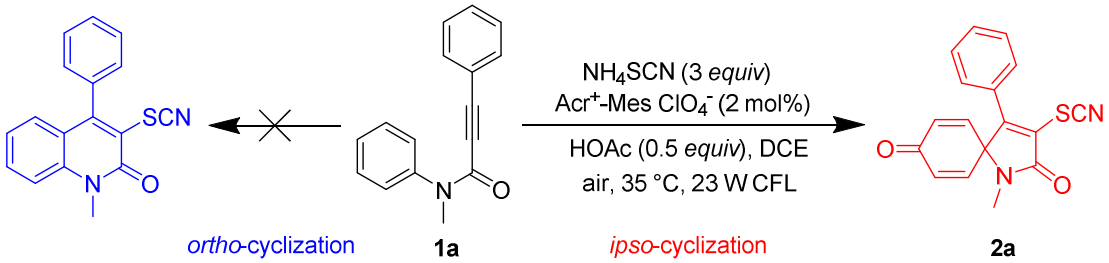
Visible light is a clean energy source that is inexpensive, easy to obtain, rich in source, green and renewable. Photoredox catalysis has been effectively used to drive chemical conversion in organic synthesis and to construct molecules that are difficult to prepare by other methods [16]. Recently, it has been reported that thiocyanate radicals can be produced from thiocyanates by photocatalysis, which can be combined with unsaturated compounds including indoles and imidazoles to form various organic thiocyanates [17]. Inspired by previous work, we decided to introduce thiocyanate group into spirocyclic skeleton by photocatalysis. Herein, we report the synthesis of thiocyanato-containing azaspirotrienediones by cascade thiocyanate radical addition/*ipso*-cyclization/oxidation. To the best of our knowledge, this is the first photocatalytic reaction of thiocyanate with an alkyne. The reaction was carried out under mild and metal-free conditions using acridinium perchlorate as an organic photocatalyst. The oxygen atom of the newly formed carbonyl comes from the air oxygen, so there is no need to pre-functionalize the benzene ring or add additional oxygen source. The air oxygen is also the only sacrificial agent in the reaction.

2. Results and discussion

In our initial study, ammonium thiocyanate (NH_4SCN) was used as the source of thiocyanate and its reaction with N-phenylpropynamide (**1a**) was chosen as the model reaction. The reaction was carried out using rose Bengal (2 mol%) as a photocatalyst in acetonitrile (MeCN, 1 mL) under irradiation of a 23 W compact fluorescent lamp (CFL) at 35 °C for 48 h. The desired product **2a** was obtained in 11% yield and by-product **3a** was isolated in 10% yield (see The Supporting Information (SI), **Table S1**, entry 1) while the substrates were not completely consumed. After screening some commonly used photocatalysts (SI, **Table S1**), acridinium perchlorate was selected as the photocatalyst for the reaction (SI, **Table S1**, entry 2). The results of solvent screening showed that in 1,2-dichloroethane (DCE), **2a** was isolated as a single product in 41% yield, while by-product **3a** was only observed in a trace amount (SI, **Table S2**, entry 1). Next, the effects of additives, photocatalyst loading and the molar ratio of **1a** and NH_4SCN on the reaction were investigated (SI, **Tables S3-S5**). Ultimately, the desired product **2a** was cheeringly obtained in 85% yield (**Table 1**, entry 1) under the optimal conditions consisting of the following: **1a** (0.2 mmol, 1 *equiv.*), NH_4SCN (0.6 mmol, 3 *equiv.*), AcOH (6 μL, 0.5 *equiv.*), Acr^+-Mes ClO_4^- (2 mol%), DCE (1 mL), in air atmosphere at 35 ^oC under irradiation of a 23 W CFL (SI, **Table S5**, entry 4).

In order to confirm this photocatalyzed reaction, some control experiments were conducted (**Table 1**). The experimental results showed that both light and photocatalyst are indispensable for the reaction (**Table 1**, entries 2 and 3). When the reaction was carried out under argon instead of air, only a trace amount of product **2a** was observed (**Table 1**, entry 4), indicating that air (O_2) is necessary in the reaction. To verify whether the reaction undergoes a radical pathway, radical scavengers 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO) and butylated hydroxytoluene (BHT) were separately added to the reaction system. It was found that in the presence of these radical scavengers, the reaction was completely inhibited (**Table 1**, entries 5 and 6), indicating that the reaction may involve a radical process. It is noteworthy that this reaction only selectively produced the *ipso*-cyclized product and no *ortho*-cyclized product was observed.

Table 1. Control experiments [a]

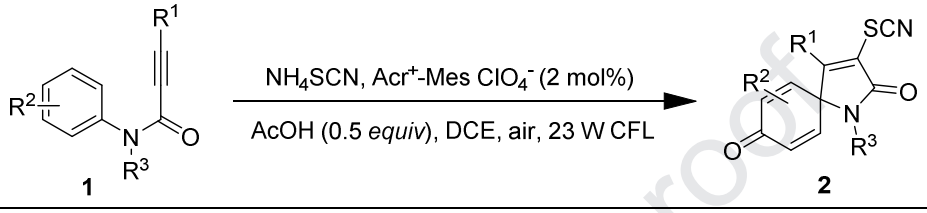


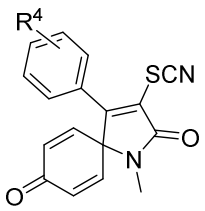
Entry	Variation from standard conditions	Yield of **2a** (%) [b]
1	--	85
2	Without photocatalyst	Trace
3	Without light	Not detected
4	Under argon instead of air	Trace
5	With BHT (1.5 *equiv.*)	Trace [c]
6	With TEMPO (1.5 *equiv.*)	Not detected

[a] Unless otherwise noted, reaction conditions: A mixture of **1a** (0.2 mmol), NH_4SCN (0.6 mmol), AcOH (0.1 mmol), and Acr^+-Mes ClO_4^- (2 mol%) in DCE (1.0 mL) was irradiated by a 23 W CFL in air atmosphere at 35 °C for 24 h. [b] Isolated yield. [c] **4a** was detected by high resolution mass spectrometry (HRMS) (for the structure of **4a**, see **Scheme 5**; for HRMS spectrum, See SI).

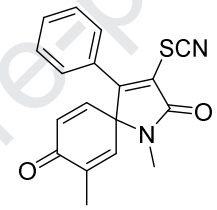
Employing the optimized conditions, we investigated the substrate scope of this tandem reaction and the results are listed in **Scheme 2**. A series of N-arylpropynamides could react smoothly with NH_4SCN under the optimal conditions to give the corresponding spirocyclic products in moderate to good yields. The effect of the substituents at the phenyl ring attached to the alkynyl group on the reaction was first investigated. The substrates with electron-donating groups (methyl, methoxy) or electron-withdrawing groups (trifluoromethyl, halogen) on the benzene rings reacted smoothly to give the corresponding products in satisfactory yields (**2b-2h**), wherein the *p*-methyl substituted **1b** provided the product **2b** in 95% yield. The electronic nature of the substituents on the N-phenyl moiety has a significant effect on the yield of the reaction. The substrates with electron-donating groups (3-methyl, 2-methyl and 2-methoxy) gave corresponding products with decent yields (**2i, 2j** and **2l**), and those with electron-withdrawing groups (2-phenyl, 3-chloro, 3-bromo and 2-chloro) gave lower yields (**2k** and **2m-2o**). This reaction was also applicable to N-naphthylpropynamide, which gave the corresponding product **2p** in 50% yield. When the methyl group on the N atom was replaced with other alkyl groups such as ethyl, isopropyl and benzyl, these substrates were also compatible with the reaction, giving the

corresponding products in satisfactory yields (**2q**-**2s**). When the N atom was bonded to the electron-withdrawing group acetyl, the reaction required a longer time to obtain **2t** in 45% yield, and the substrate **1t** could not be completely consumed. Further, in addition to the aryl alkyne, an alkyl alkyne was also suitable for the reaction, which gave the corresponding product **2u** in 57% yield. It is worth noting that this reaction could also be used to construct the tricyclic structure (**2v**).

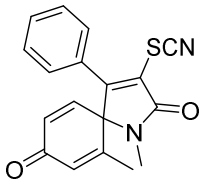




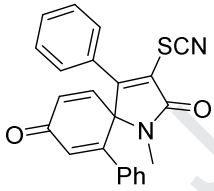
2a, R^4 = H, 85%
2b, R^4 = 4-Me, 95%
2c, R^4 = 4-OMe, 75%
2d, R^4 = 3-OMe, 73%
2e, R^4 = 4-CF_3, 85%
2f, R^4 = 4-F, 78%
2g, R^4 = 4-Cl, 76%
2h, R^4 = 4-Br, 55%



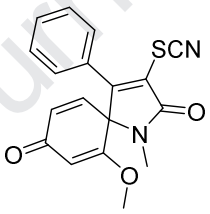
2i 77%



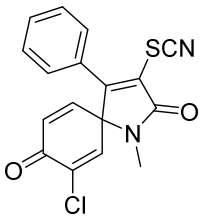
2j 75%



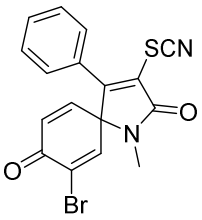
2k 61%



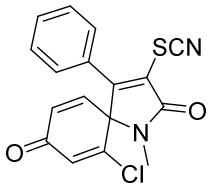
2l 72%



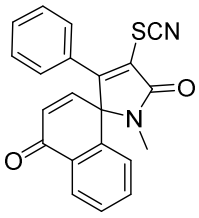
2m 40%



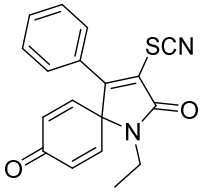
2n 51%



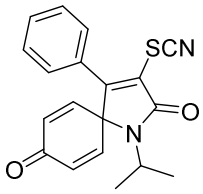
2o 60%



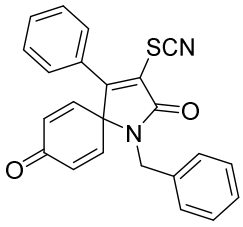
2p 50%



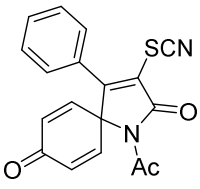
2q 78%



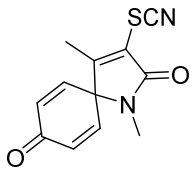
2r 88%



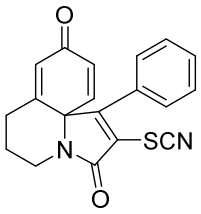
2s 72%



2t 45%[b]



2u 57%[b]

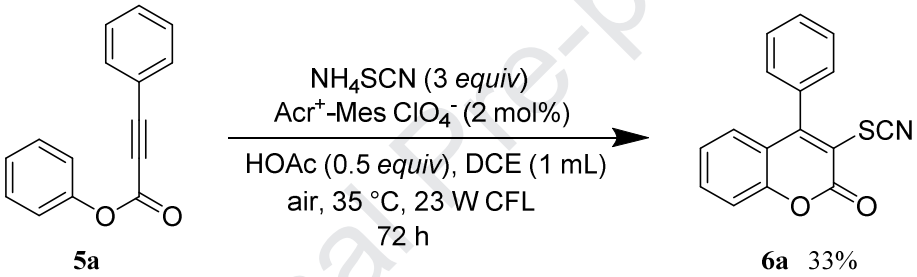


2v 50%[b]

Scheme 2. Substrate scope [a]

[a] Unless otherwise noted, reaction conditions: A mixture of **1** (0.2 mmol), NH_4SCN (0.6 mmol), AcOH (0.1 mmol), and Acr^+-Mes ClO_4^- (2 mol%) in DCE (1.0 mL) was irradiated by a 23 W CFL in an air atmosphere at 35 ^oC for 15-36 h. Isolated yield. [b] 48 h.

Next, we investigated the reaction efficiency when the amide group of **1a** was replaced with the ester group (**5a**) under standard conditions. Interestingly, the reaction gave the *ortho*-cyclized product **6a** in 33% yield instead of the desired *ipso*-cyclized product. Even after 72 h of reaction, there was still a large amount of starting material remaining (**Scheme 3**).



5a **6a** 33%

Scheme 3. The reaction using phenyl 3-phenylpropiolate (**5a**)

To further understand the reaction mechanism, a series of experiments were carried out. The fluorescence quenching experiments (Stern-Volmer studies) of Acr^+-Mes ClO_4^- were performed to verify which substrate first reacts with the excited photocatalyst. The results showed that NH_4SCN effectively quenched the excited Acr^+-Mes ClO_4^- but **1a** did not show significant quenching (**Figure 1**, for details, see SI, **Figures S1** and **S2**). Next, the cyclic voltammetry experiments were conducted, and the oxidation potentials of **1a** and NH_4SCN were determined as: **1a** had no apparent oxidation peak in the range of 0-2.4 V (SI, **Figure S3**) and NH_4SCN had an obvious oxidation peak (E_{ox} = +0.729 V in MeCN) (SI, **Figure S4**). The data indicated that NH_4SCN instead of **1a** can be oxidized by the excited Acr^+-Mes ClO_4^- ($E_{[Acr+-Mes]^*/[Acr^{\bullet}-Mes]}$ = +2.08 V vs. SCE in MeCN).[11a] In addition, to verify whether a radical chain propagation process is involved, an on/off visible light irradiation experiment was performed. The results showed that even if the light was turned off, the yield of the reaction continued to increase slightly, so we speculate that

there may be radical chain propagation during the reaction (SI, **Figure S5**).

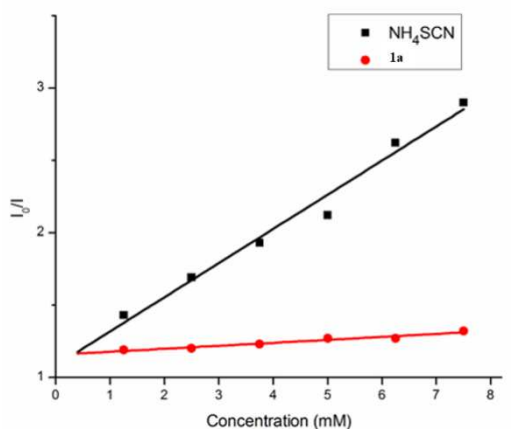
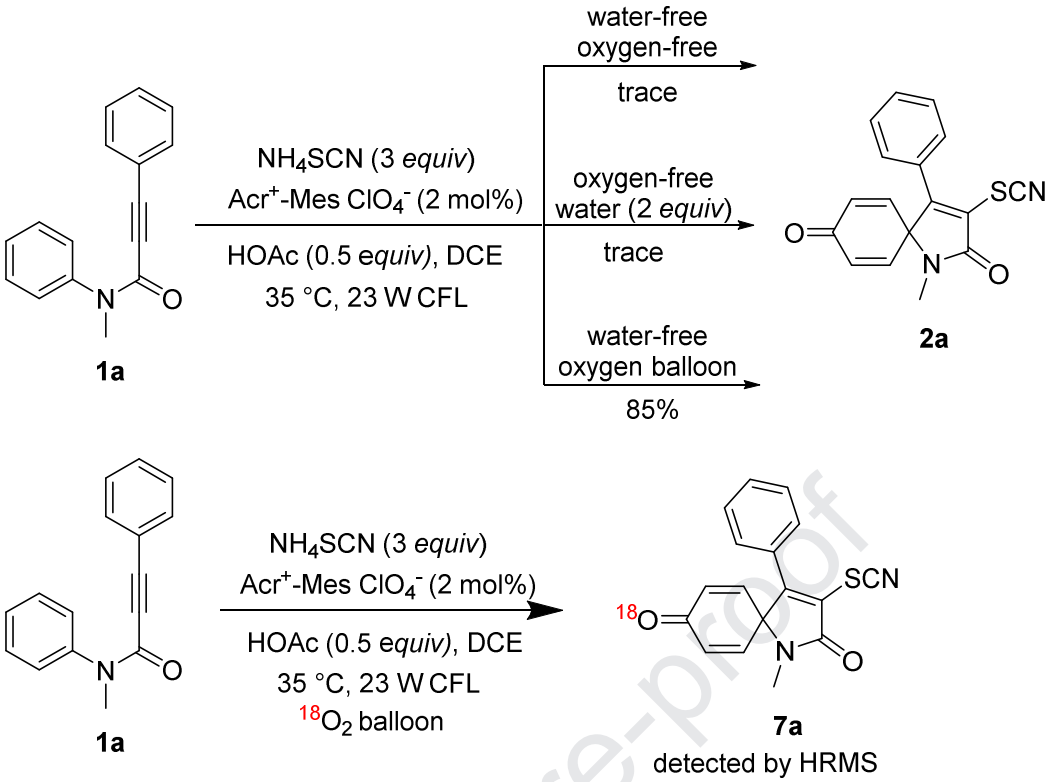


Figure 1. Stern–Volmer plots of fluorescence quenching of $5*10^{-4}$ M Acr^{+}-Mes ClO_4^{-}

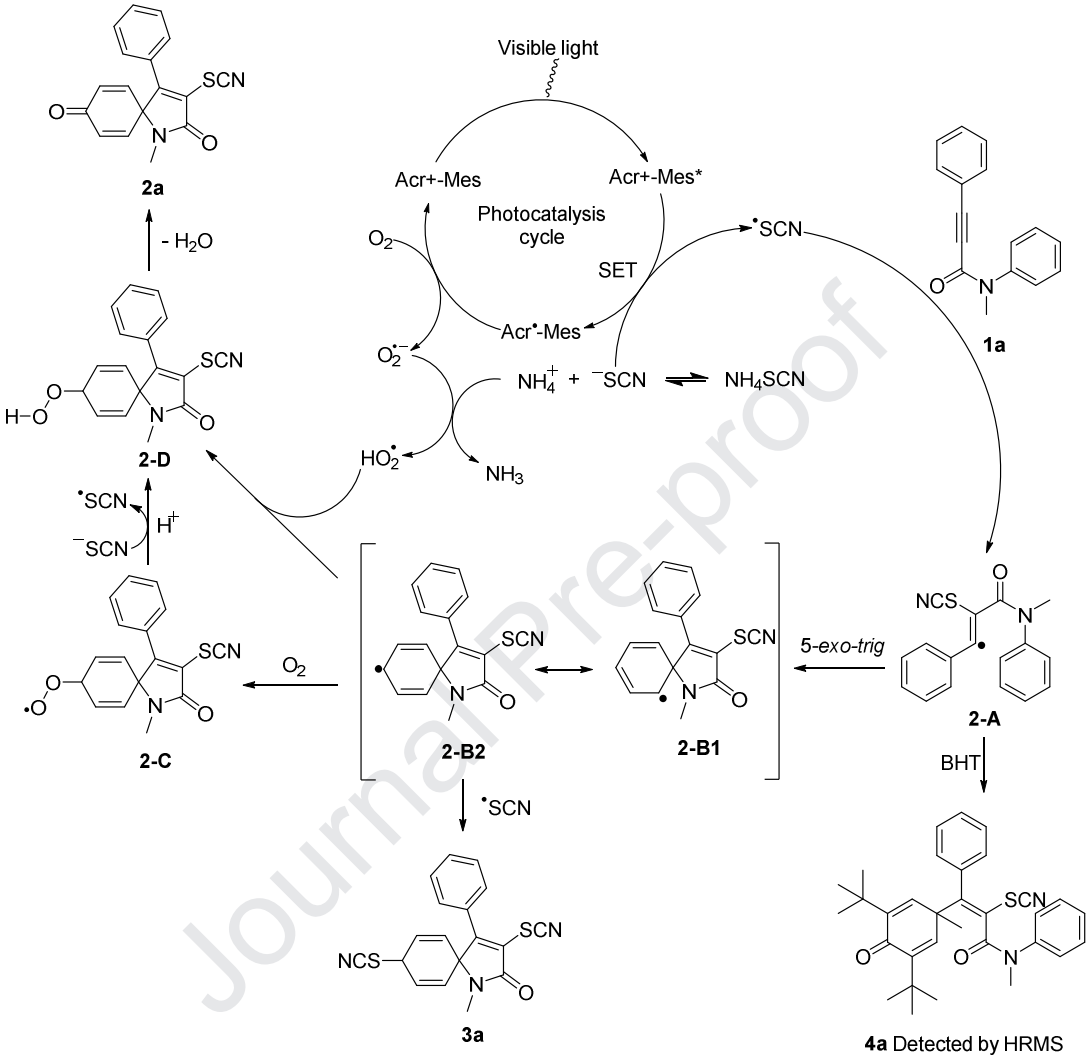
We then explored the oxygen atom source of the newly formed carbonyl group. Since the above reactions were carried out under ambient conditions, both water and oxygen can be a source of oxygen. Thus, we investigated the effect of water and oxygen on the reaction (**Scheme 4**). Firstly, under anhydrous and anaerobic conditions, the model reaction was completely inhibited. Secondly, without oxygen, in the presence of 2 equivalents of water, the reaction also could not proceed. Finally, under anhydrous conditions in the presence of oxygen (oxygen balloon), the reaction proceeded smoothly to give the product **2a** in 85% yield. The results of these experiments indicated that oxygen participates in the reaction while water does not, so we speculated that the oxygen atom of the newly formed carbonyl in **2a** is derived from oxygen in the air. To further confirm this speculation, we performed an ^{18}O labeling experiment. The model reaction was carried out under $^{18}O_2$ conditions ($^{18}O_2$ balloon) to give the ^{18}O-labeled product **7a** (detected by HRMS), which clearly demonstrated the reliability of our conclusion.



Scheme 4. Effect of water and oxygen on the reaction

Based on our control experiments and previous literatures [18], we proposed a possible mechanism for the reaction (**Scheme 5**). Under visible light irradiation, Acr^+-Mes is excited to Acr^+-Mes* and then undergoes single electron transfer (SET) with thiocyanate anion to produce thiocyanate radical and $Acr^{\bullet}$-Mes. $Acr^{\bullet}$-Mes is oxidized back to Acr^+-Mes by air oxygen to complete the photocatalytic cycle, and simultaneously the superoxide anion radical ($O_2^{\bullet-}$) is produced, which obtains a proton from NH_4^+ to form the hydrogen peroxy radical ($HO_2^{\bullet}$). The addition of thiocyanate radical to alkyne **1a** forms a C-S bond to give the alkenyl radical intermediate **2-A**, which was captured by BHT (**4a** was detected by HRMS). **2-A** undergoes 5-*exo*-*trig* *ipso*-cyclization to give the dearomatized intermediate **2-B1**, and there is resonance between **2-B1** and **2-B2**. **2-B2** can undergoes three possible reaction pathways: (i) **2-B2** can be coupled with the thiocyanate radical to give **3a** which was isolated as a by-product during the optimization of the reaction conditions. (ii) **2-B** can be captured by hydroperoxy radical ($HO_2^{\bullet}$) to form peroxide intermediate **2-D**. (iii) **2-B** can be captured by air oxygen to give the intermediate **2-C**. **2-C** undergoes a SET with the thiocyanate anion and then combines with a proton to form

2-D, which results in radical chain propagation. Finally, dehydration of **2-D** gives the desired product **2a**.



Scheme 5. Proposed reaction mechanism

3. Conclusion

We have successfully developed a metal-free photocatalytic thiocyanate radical addition/*ipso*-cyclization/oxidation cascade reaction for the synthesis of thiocyanato-containing azaspirotrienediones from N-phenylpropynamides. The organic dye acridinium perchlorate was used as a photocatalyst. Cheap and readily available ammonium thiocyanate was used as a precursor to the thiocyanate free radical, which undergoes a radical addition reaction with the alkyne, followed by selective *ipso*-cyclization to afford the dearomatized products. No product of

ortho-cyclization was detected. Twenty-two products were synthesized with yields of up to 95%, of which eighteen are new compounds. The reaction completes the synthesis of C-S, C-C and C=O bonds in one pot. Abundant and renewable air oxygen acts as the sole sacrificial reagent and oxygen source, so there is no need to pre-functionalize the benzene ring or add additional oxygen source. The reaction has the advantages of mild reaction conditions, simple operation, good functional group compatibility and wide range of substrate scope.

4. Experimental section

4.1 General experimental details

Acr^+-Mes ClO_4^- was purchased from TCI industrial corporation Shanghai, China. The anhydrous 1,2-dichloroethane (DCE) (99.5%, SafeDry, with molecular sieves, water ≤50 ppm (by K.F., SafeSeal) was purchased from Adamas Reagent, Ltd. Other solvents were dried by molecular sieves. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz and 150 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (J) were reported in Hz. High-resolution mass spectra (HRMS) were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS), ESI-TOF and Q-TOF. Melting points were taken on a WPX-4 apparatus (Yice instrument equipment Co Ltd, Shanghai) and were uncorrected.

4.2 General procedure for the synthesis of products 2

A 10 mL round-bottomed glass flask was charged with **1** (0.20 mmol, 1.0 *equiv.*), NH_4SCN (0.60 mmol, 3.0 *equiv.*), Acr^+-Mes ClO_4^- (2 mol%), AcOH (6 μL, 0.5 *equiv*.) and DCE (1 mL). The mixture was stirred at 35 ^oC under irradiation of a 23 W CFL (Philips) in an air atmosphere. After completion of the reaction (monitored by TLC), the DCE was removed from the reaction mixture. The residue was diluted with EtOAc (20 mL) and washed with saturated brine (10 mL). The organic layers were dried over anhydrous Na_2SO_4 and evaporated in vacuo. The residue was

purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (10:1 to 2:1) as the eluent to give the desired product **2**.

*4.2.1 1-Methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione[11e] (**2a**)* White solid (53.3 mg, 85%); Melting range: 157.8-158.6 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 6.53 (s, 4H), 2.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.2, 164.9, 157.0, 143.1, 134.0, 131.1, 129.1, 128.9, 127.8, 122.4, 106.2, 68.4, 26.6. IR (KBr) ν 3076, 2168, 1715, 1671, 1659, 1617, 1563, 1493, 1459, 1367, 1275, 873, 736, 690 cm^{-1}. HRMS m/z 331.0515 (M + Na^+), Cal. $C_{17}H_{12}N_2O_2SNa^+$, 331.0512.

*4.2.2 1-Methyl-3-thiocyanato-4-(p-tolyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2b**)* White solid (60.1 mg, 95%); Melting range: 140.5-141.9 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 17.6 Hz, 4H), 6.53 (d, *J* = 1.4 Hz, 4H), 2.94 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4, 165.1, 157.4, 143.3, 141.7, 133.8, 129.8, 127.7, 126.1, 121.5, 106.4, 68.3, 26.5, 21.4. IR (KBr) ν 3126, 2178, 1713, 1673, 1640, 1605, 1583, 1497, 1457, 1397, 1358, 864, 755 cm^{-1}. HRMS m/z 345.0664 (M + Na^+), Cal. $C_{18}H_{14}N_2O_2SNa^+$, 345.0668.

*4.2.3 4-(4-Methoxyphenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione [11e] (**2c**)* White solid (51.0 mg, 75%); Melting range: 154.9-155.7 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.55 (d, *J* = 10.2 Hz, 2H), 6.52 (d, *J* = 10.3 Hz, 2H), 3.83 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4, 165.3, 161.8, 157.1, 143.6, 133.7, 129.5, 121.2, 120.3, 114.6, 106.6, 68.2, 55.4, 26.4. IR (KBr) ν 3145, 2168, 1722, 1678, 1635, 1605, 1575, 1506, 1457, 1398, 1363, 874, 825 cm^{-1}. HRMS m/z 361.0620 (M + Na^+), Cal. $C_{18}H_{14}N_2O_3SNa^+$, 361.0617.

*4.2.4 4-(3-Methoxyphenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2d**)* White solid (51.3 mg, 76%); Melting range: 156.9-158.2 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 6.54 (d, *J* = 10.6 Hz, 2H), 6.52 (d, *J* = 10.6 Hz, 2H), 3.78 (s, 3H), 2.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.3, 164.9, 159.8, 156.8, 143.1, 133.9, 130.3, 130.1, 122.4, 120.0, 116.3, 113.7, 106.2, 68.3, 55.4, 26.5. IR (KBr) ν 3136, 2168, 1710, 1654, 1643, 1609, 1586, 1506, 1467, 1358, 1298, 854, 795, 746, 706 cm^{-1}. HRMS m/z 361.0620 (M + Na^+), Cal. $C_{18}H_{14}N_2O_3SNa^+$, 361.0617.

4.2.5

1-Methyl-3-thiocyanato-4-(4-(trifluoromethyl)phenyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2e)*** White solid (69.9 mg, 85%); Melting range: 158.9-160.8 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.54 (s, 4H), 2.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.8, 164.5, 155.0,142.5, 134.3, 132.9 (q, *J* = 33.5 Hz), 132.4, 128.5, 126.1 (d, *J* = 3.7 Hz), 124.2, 122.4, 105.6, 68.4, 26.7. IR (KBr) ν 3116, 2168, 1733, 1635, 1601, 1567, 1500, 1442, 1342, 1319, 874, 844 cm^{-1}. HRMS m/z 399.0381 (M + Na^+), Cal. $C_{18}H_{11}F_3N_2O_2SNa^+$, 399.0386.

4.2.6 4-(4-Fluorophenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2f)*** White solid (53.9 mg, 78%); Melting range: 127.0-128.3 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.3, 5.2 Hz, 2H), 7.13 (t, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 10.4 Hz, 2H), 6.52 (d, *J* = 10.5 Hz, 2H), 2.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.1, 164.9, 164.0 (d, *J* = 252 Hz), 163.2, 155.7, 143.0, 134.1, 130.1 (d, *J* = 8.7 Hz), 124.9 (d, *J* = 3.5 Hz), 122.8, 116.6, 116.4, 106.0, 68.4, 26.6. IR (KBr) ν 3116, 2168, 1733, 1635, 1601, 1567, 1500, 1442, 1342, 1319, 874, 844 cm^{-1}. HRMS m/z 349.0420 (M + Na^+), Cal. $C_{17}H_{11}FN_2O_2SNa^+$, 349.0417.

4.2.7 4-(4-Chlorophenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2g)*** White solid (58.6 mg,76%); Melting range: 177.9-179.3 ^{o}C; 1H NMR (600 MHz, CDCl3) δ 7.41 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.54 (d, J = 9.9 Hz, 2H), 6.51 (d, J = 10.1 Hz, 2H), 2.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.0, 164.7, 155.5, 142.8, 137.5, 134.2, 129.5, 129.2, 127.2, 123.0, 105.9, 68.4, 26.6. IR (KBr) ν 3096, 2168, 1713, 1674, 1644, 1607, 1585, 1476, 1427, 1348, 1278, 835, 766 cm^{-1}. HRMS m/z 365.0120 (M + Na^+), Cal. $C_{17}H_{11}ClN_2O_2SNa^+$, 365.0122.

4.2.8 4-(4-Bromophenyl)-1-methyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2h)*** White solid (43.1 mg, 55%); Melting range: 173.5-174.7 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 10.1 Hz, 2H), 6.51 (d, *J* = 10.3 Hz, 2H), 2.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.0, 164.7, 155.6, 142.8, 134.2, 132.5, 129.3, 127.7, 125.8, 123.0, 105.9, 68.3, 26.6. IR (KBr) ν 3102, 2148, 1721, 1681, 1642, 1602, 1582, 1504, 1461, 1403, 1383, 846, 827 cm^{-1}. HRMS m/z 408.9618 (M + Na^+), Cal. $C_{17}H_{11}BrN_2O_2SNa^+$, 408.9617.

4.2.9 1,7-Dimethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2i)*** White solid (50.5 mg, 77%); Melting range: 165.2-166.9 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.27 (d, *J* = 6.7 Hz, 2H), 6.54 (d, *J* = 9.7 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 6.39 (s, 1H), 2.86 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.0, 165.4, 157.4, 151.5, 143.2, 133.5, 132.6, 131.3, 129.2, 128.8, 127.6, 122.5, 106.2, 70.6, 26.1, 17.6. IR (KBr) ν 3122, 2168, 1731, 1673, 1635, 1612, 1575, 1486, 1447, 1384, 1363, 896, 746, 696 cm^{-1}. HRMS m/z 345.0666 (M + Na^+), Cal. $C_{18}H_{14}N_2O_2SNa^+$, 345.0668.

4.2.10 1,6-Dimethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2j)*** White solid (49.2 mg, 75%); Melting range: 142.3-143.3 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.40 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.49 (s, 2H), 6.30 (s, 1H), 2.93 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.1, 164.9, 157.8, 142.9, 141.4, 137.8, 133.7, 130.9, 129.1, 129.0, 127.8, 121.9, 106.4, 69.0, 26.5, 15.8. IR (KBr) ν 3150, 2160, 1710, 1668, 1632, 1607, 1571, 1501, 1457, 1405, 1374, 899, 755, 694 cm^{-1}. HRMS m/z 345.0666 (M + Na^+), Cal. $C_{18}H_{14}N_2O_2SNa^+$, 345.0668.

4.2.11 1-Methyl-4,6-diphenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione （***2k***） Yellow solid (46.7 mg, 61%); Melting range: 54.2-55.8 ^{o}C;^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.33 (m, 6H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.63-6.62 (m, 2H), 6.49 (d, *J* = 9.5 Hz, 1H), 2.94 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.3, 165.5, 158.1, 152.8, 144.5, 135.1, 133.1, 132.7, 131.4, 130.6, 129.2, 129.1, 129.0, 128.0, 126.9, 122.2, 106.0, 70.1, 26.5. IR (KBr) ν 3057, 2164, 1706, 1672, 1649, 1603, 1580, 1500, 1454, 1374, 1362, 904, 769, 689 cm^{-1}. HRMS m/z 407.0829 (M + Na^+), Cal. $C_{23}H_{16}N_2O_2SNa^+$, 407.0825.

4.2.12 6-Methoxy-1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2l)*** White solid (50.5 mg, 77%); Melting range: 231.8-232.9 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.19-7.11 (m, 2H), 6.44 (d, *J* = 9.8 Hz, 1H), 6.30 (d, *J* = 9.8 Hz, 1H), 5.77 (s, 1H), 3.74 (s, 3H), 2.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.4, 167.0, 165.7, 156.9, 138.9, 133.1, 131.0, 129.1, 128.7, 127.6, 122.4, 106.6, 106.3, 69.7, 56.5, 26.2. IR (KBr) ν 3145, 2158, 1713, 1654, 1624, 1605, 1586, 1496, 1447, 1368, 1230, 992, 736, 687 cm^{-1}. HRMS m/z 361.0620 (M + Na^+), Cal. $C_{18}H_{14}N_2O_3SNa^+$, 361.0617.

4.2.13 7-Chloro-1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2m)*** White solid (27.5 mg, 40%); Melting range: 155.8-157.2 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.43 (m, 3H), 7.22 (d, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 1.7 Hz, 1H), 6.60-6.54 (m, 2H), 2.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.5, 164.6, 155.9, 143.6, 138.7, 137.4, 132.9, 131.3, 129.3, 128.4, 127.8, 123.0, 105.8, 70.1, 26.8. IR (KBr) ν 3136, 2158,1730, 1675, 1624, 1595, 1578, 1497, 1447, 1378, 1328, 845, 736, 696 cm^{-1}. HRMS m/z 365.0121 (M + Na^+), Cal. $C_{17}H_{11}ClN_2O_2SNa^+$, 365.0122.

4.2.14 7-Bromo-1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2n)*** White solid (41.8 mg, 54%); Melting range: 177.7-178.5 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.43 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.60-6.56 (m, 2H), 2.99 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.4, 164.6 155.7, 143.6, 143.0, 132.3, 131.3, 129.2, 129.1,

128.4, 127.8, 123.0, 105.8, 70.7, 26.8. IR (KBr) ν 3126, 2158, 1703, 1674, 1605, 1586, 1497, 1457, 1387, 1315, 884, 746, 696 cm^{-1}. HRMS m/z 408.9619 ($M + Na^+$), Cal. $C_{17}H_{11}BrN_2O_2SNa^+$, 408.9617.

*4.2.15 6-Chloro-1-methyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2o**)*
Yellowish solid (41.0 mg, 60%); Melting range: 187.1-188.8 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 9.8 Hz, 1H), 6.56 (d, *J* = 9.6 Hz, 1H), 2.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.2, 165.2, 155.3, 149.1, 142.3, 133.4, 133.0, 131.3, 129.2, 128.1, 127.8, 124.1, 105.8, 71.5, 26.2. IR (KBr) ν 3136, 2148, 1703, 1674, 1632, 1619, 1586, 1497, 1447, 1368, 973, 736, 696 cm^{-1}. HRMS m/z 365.0124 ($M + Na^+$), Cal. $C_{17}H_{11}ClN_2O_2SNa^+$, 365.0122.

*4.2.16 1'-Methyl-3'-phenyl-4'-thiocyanato-4H-spiro[naphthalene-1,2'-pyrrole]-4,5'(1'H)-dione (**2p**)*
White solid (36.3 mg, 50%); Melting range: 218.1-218-9 ^oC**;** ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.7 Hz, 1H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.25-7.21 (m, 3H), 6.76 (d, *J* = 7.4 Hz, 2H), 6.65 (d, *J* = 10.1 Hz, 1H), 6.56 (d, *J* = 10.1 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.5, 165.5, 160.8, 143.2, 135.6, 134.1, 133.8, 132.6, 130.8, 130.1, 128.9, 128.8, 127.8, 127.7, 125.8, 121.2, 106.5, 69.6, 26.3. IR (KBr) ν 3044, 2155, 1729, 1668, 1656, 1607, 1583, 1510, 1449, 1364, 1291, 840, 767, 709 cm^{-1}. HRMS m/z 381.0668 ($M + Na^+$), Cal. $C_{21}H_{14}N_2O_2SNa^+$, 381.0667.

*4.2.17 1-Ethyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione[11e] (**2q**)*
White solid (50.6 mg, 78%); Melting range: 142.3-144.2 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, *J* = 28.3, 3H), 7.23 (d, *J* = 7.3 Hz, 2H), 6.56 (d, *J* = 10.0 Hz, 2H), 6.49 (d, *J* = 9.9 Hz, 2H), 3.41 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4, 164.9, 156.6, 143.4, 133.5, 131.0, 129.0, 128.9, 127.8, 122.8, 106.1, 68.9, 36.8, 15.0. IR (KBr) ν 3126, 2158, 1694, 1664, 1644, 1615, 1586, 1498, 1457, 1378, 1308, 865, 735, 696 cm^{-1}. HRMS m/z 345.0665 ($M + Na^+$), Cal. $C_{18}H_{14}N_2O_2SNa^+$, 345.0668.

*4.2.18 1-Isopropyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**2r**)*
Yellowish solid (59.4 mg, 88%); Melting range: 170.1-171.8 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 7.47-7.70 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.60 (d, *J* = 10.0 Hz, 2H), 6.48 (d, *J* = 9.7 Hz, 2H), 3.53-3.47 (m, 1H), 1.46 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4, 164.4, 155.7, 143.4, 133.4, 130.9, 129.0, 129.0 127.8, 123.6, 106.2, 69.6, 47.4, 20.8. IR (KBr) ν 3145, 2929, 2158, 1704, 1656, 1632, 1586, 1497, 1457, 1097, 1338, 865, 736, 696 cm^{-1}. HRMS m/z 359.0827 ($M + Na^+$), Cal. $C_{19}H_{16}N_2O_2SNa^+$, 359.0825.

4.2.19 1-Benzyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione[11e] ***(2s)*** White solid (49.6 mg, 78%); Melting range: 142.1-143.7 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45-7.16 (m, 11H), 6.33 (d, *J* = 9.9 Hz, 2H), 6.29 (d, *J* = 9.9 Hz, 2H), 4.59 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4, 165.1, 157.3, 143.2, 136.6, 133.1, 131.0, 129.0, 129.0 128.7, 128.7, 128.2, 127.8, 122.5, 106.1, 68.7, 45.5. IR (KBr) ν 3166, 2929, 2168, 1717, 1656, 1632, 1583, 1497, 1447, 1387, 865, 736, 687 cm^{-1}. HRMS m/z 407.0824 (M + Na^+), Cal. $C_{23}H_{16}N_2O_2SNa^+$, 407.0825.

4.2.20 1-Acetyl-4-phenyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2t)*** Yellow solid (30.2 mg, 45%); Melting range: 209.3-210.8 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.54 (d, *J* = 9.9 Hz, 2H), 6.43 (d, *J* = 9.8 Hz, 2H), 2.66 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.3, 168.4, 163.8, 161.6, 141.9, 133.0, 131.5, 129.0, 128.0, 127.6, 122.3, 105.5, 68.6, 25.6. IR (KBr) ν 3145, 2168, 1729, 1693, 1680, 1619, 1607, 1583, 1506, 1447, 1387, 1328, 1259, 874, 844, 746, 687 cm^{-1}. HRMS m/z 359.0464 (M + Na^+), Cal. $C_{18}H_{12}N_2O_3SNa^+$, 359.0461.

4.2.21 1,4-Dimethyl-3-thiocyanato-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione ***(2u)*** Yellow solid (32.9 mg, 57%); Melting range: 139.1-140.9 ^{o}C ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.62 (d, *J* = 9.7 Hz, 2H), 6.36 (d, *J* = 9.8 Hz, 2H), 2.92 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (150MHz, $CDCl_3$) δ 183.2, 165.4, 158.0, 143.5, 134.2, 121.4, 106.9, 68.8, 26.8, 12.2. IR (KBr) ν 3048, 2190, 1722, 1678, 1635, 1417, 1363, 1353, 863 cm^{-1}. HRMS m/z 269.0365 (M + Na^+), Cal. $C_{12}H_{10}N_2O_2SNa^+$, 269.0366.

4.2.22 1-Phenyl-2-thiocyanato-6,7-dihydro-3H-pyrrolo[2,1-j]quinoline-3,9(5H)-dione ***(2v)*** Yellow solid (39.4 mg, 50%); Melting range: 99.4-100.5 ^{o}C**;** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56-7.53 (m, 3H), 7.40-7.39 (m, 1H), 7.27-7.26 (m, 2H), 7.07-7.04 (m, 2H), 4.38-4.36 (m, 2H), 3.05 (t, *J* = 6.0 Hz, 2H), 2.21-2.17 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 155.5, 136.9, 135.4, 131.9, 129.3, 128.9, 128.5, 127.2 125.2, 122.3, 120.8, 117.1, 109.3, 43.8, 27.7, 20.6. IR (KBr) ν 3068, 2143, 1717, 1658, 1644, 1595, 1583, 1498, 1449, 1388, 899,731,694 cm^{-1}. HRMS m/z 357.0667 (M + Na^+), Cal. $C_{19}H_{14}N_2O_2SNa^+$, 357.0668.

4.2.23 1-methyl-4-phenyl-3,8-dithiocyanato-1-azaspiro[4.5]deca-3,6,9-trien-2-one ***(3a)*** Yellow solid; ^{1}H NMR (600 MHz, DMSO-d^6) δ 7.46-7.45 (m, 3H), 7.33-7.32(m, 2H), 6.32 (dd, *J* = 10.1, 3.1 Hz, 2H), 5.81 (dd, *J* = 10.1, 1.8 Hz, 2H), 4.52 (d, *J* = 1.7 Hz, 1H), 2.88 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d^6) δ 165.0, 162.6, 131.8, 130.5, 129.0, 128.6, 127.4, 120.4, 111.9, 108.9, 66.8, 42.8,

26.6. IR (KBr) ν 3298, 2146, 2178, 1711, 1689, 1624, 1581, 1483, 1428, 1363, 1276, 831, 744, 690 cm^{-1}. HRMS m/z 352.0572 ($M + H^+$), Cal. $C_{18}H_{13}N_3OS_2H^+$, 351.0573.

*4.2.24 4-phenyl-3-thiocyanato-2H-chromen-2-one (**6a**)* [19] White solid; ^1H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 4H), 7.46 (d, J = 8.3, 1H), 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.16 (d, J = 8.0, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.8, 157.3, 153.6, 134.0, 133.2, 130.3, 129.6, 128.7, 128.0, 125.0, 119.9, 117.3, 112.9, 108.1 . IR (KBr) ν 3051, 2171, 1731, 1595, 1542, 1479, 1448, 1301, 987, 768, 694 cm^{-1}.

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Highlights

- A visible-light-mediated metal-free thiocyanate radical addition/*ipso*-cyclization/oxidation cascade reaction is described.
- With this reaction, various thiocyanato-containing azaspirotrienediones were synthesized from *N*-phenylpropynamides.
- Cheap and readily available ammonium thiocyanate was used as a precursor to the thiocyanate free radical.
- The reaction completes the formation of C-S, C-C and C=O bonds in one pot, with air oxygen as oxidant and oxygen source.

Declaration of Interest Statement

We declare no conflicts of interest.