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Metal-Free Oxidative *Ipso*-Carboacylation of Alkynes: Synthesis of 3-Acylspiro[4,5]trienones from *N*-Arylpropiolamides and Aldehydes

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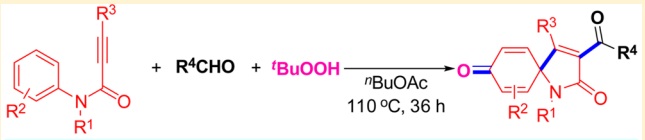
Supporting Information

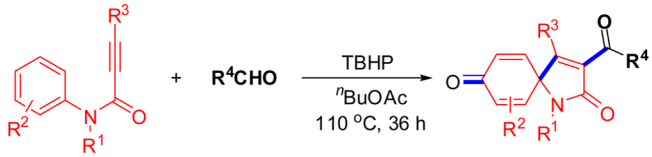
ABSTRACT: A general and metal-free radical route to synthesis of 3-acylspiro[4,5]trienones is established that utilizes TBHP (*tert*-butyl hydrogenperoxide) as an oxidation and a reaction partner to trigger the oxidative *ipso*-carboacylation of *N*-arylpropiolamides with aldehydes. This method offers a new difunctionalization of alkynes through oxidative cross coupling of the aldehyde C(sp^2)−H bond with an *ipso*-aromatic carbon.



INTRODUCTION

The introduction of a carbonyl group into the organic frameworks is one of the most popularly fundamental processes in organic synthesis and chemical industries. Traditionally, the frequently utilized method for the carbonyl introduction purpose is the carbonylation reaction that employs the toxic CO gas as the carbonyl resource.[1] However, the reaction suffers from the storage and transport of the toxic CO gas, thereby limiting their wide application in fine chemistry research and industry. Alternatively, the acylation reaction is becoming a major topic of research in the carbonyl introduction by direct functionalization of the carbonyl C−H bond.[2−5] In this field, acylation of alkynes with aldehydes to versatile α-alkenyl ketones as one of the most elegant examples has received considerable attention in recent years with the inherent advantages: high atom economy and avoidance of using the toxic CO gas. Generally, the method is initially performed via the addition of the metal catalyst into the carbonyl C−H bond leading to an acylmetal hydride intermediate, followed by 1,2-hydroacylation of an alkyne with the acylmetal hydride intermediate that furnishes an α-alkenyl ketone.[2,3] To our knowledge, however, difunctionalization of alkynes using the acylation strategy to simultaneously introduce an acyl group and another non-hydrogen group remains an unexplored area. Herein, we report a novel metal-free TBHP-mediated oxidative *ipso*-carboacylation of alkynes with aldehydes to synthesize 3-acylspiro[4,5]trienones (Scheme 1); this new oxidative tandem method is achieved by sequential acylation, *ipso*-carbocylation, dearomatization, and hydration, thus providing the first example of alkyne difunctionalization for the simultaneous formation of two new carbon−carbon bonds through an oxidative cross coupling strategy.[4a−g,5] Notably, the spirocycle unit is the common core structure in many natural products and pharmaceuticals as well as a versatile building block in organic synthesis.[6]

Scheme 1. *Ipso*-Carboacylation of Alkynes with Aldehydes



Recently, oxidative cross coupling involving a C−H functionalization process has attracted increasing interest because it offers an ideal process to overcome the disadvantages of the classical cross-coupling reactions, particularly avoiding prefunctionalization of the coupling partners.[4,5] Among them, oxidative coupling with an aldehyde C(sp^2)−H bond holds a particular fascination to organic synthesis because it provides an efficient way to both form new carbon−carbon bonds and incorporate an acyl group into the products.[4] In light of these findings, we reason that the oxidative coupling reactions between alkynes and aldehydes can be realized under metal-free conditions using a single-electron-transfer (SET) strategy because the reported transition-metal-free cross-coupling[7] and some transition-metal-catalyzed oxidative coupling have been proven to include a radical process.[4,5]

RESULTS AND DISCUSSION

To test our hypothesis, the reaction between *N*-methyl-*N*,3-diphenylpropiolamide (**1a**) and 4-methoxybenzaldehyde (**2a**) was initially selected (Table 1).[8] As expected, treatment of substrate **1a** with aldehyde **2a** and TBHP (*tert*-butyl hydrogen peroxide, anhydrous, 5 M in decane) at 110 °C for 36 h afforded the desired 3-acylspiro[4,5]trienone **3aa** in 68% yield (entry 1). However, the yield was lowered slightly using

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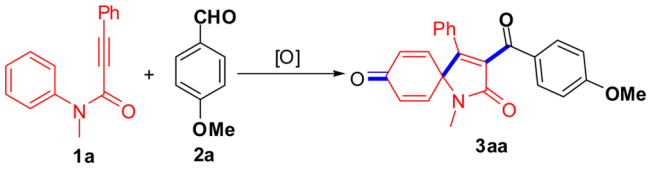
Table 1. Screening Optimal Conditions[a]



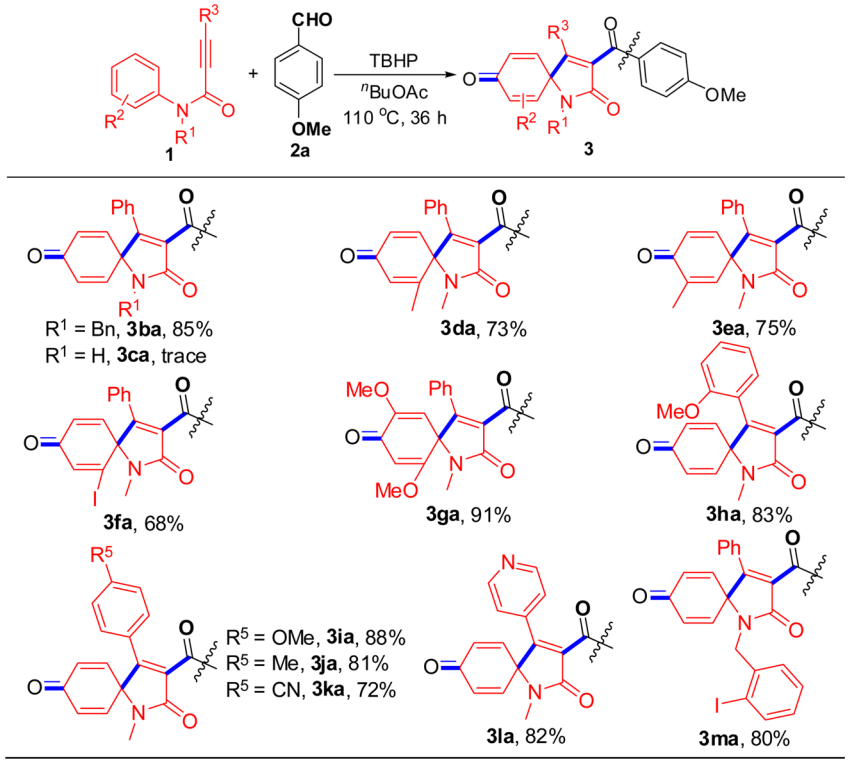
entry	[O]	solvent	T (°C)	yield[b] (%)
1	TBHP	neat	110	68
2[c]	TBHP	neat	110	63
3	TBHP	neat	80	15
4	TBHP	neat	130	65
5	TAHP	neat	110	38
6	CHP	neat	110	18
7[d]	DTBP	neat	110	0
8[e]	DTBP	neat	110	0
9[f]	DCP	neat	110	0
10[g]	BPO	neat	110	0
11	TBHP	^{n}BuOAc	110	86
12[g]	TBHP	^{n}BuOAc	110	57
13[h]	TBHP	^{n}BuOAc	110	68
14[i]	TBHP	^{n}BuOAc	110	83

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (2 equiv), [O] (2 equiv), and solvent (2 mL) under argon atmosphere for 36 h. Some byproducts, including 4-methoxybenzoic acid, C−N bond decomposition products, and hydroacylation product, were observed by GC−MS analysis. [b]Isolated yield. [c]TBHP (70% in water) was added. [d]>90% of both **1a** and **2a** were recovered. [e]2 equiv of H_2O was added: >90% of **1a** was recovered, and aldehyde **2a** was completely converted to acid. [f]An unidentified product was isolated in 52% yield. [g]Under oxygen atmosphere. [h]Under air atmosphere. [i]**1a** (5 mmol, 1.175 g).

aqueous TBHP (entry 2). We found that the reaction temperature played an important role in the reaction, and the reaction at 110 °C gave the best results (entries 1, 3, and 4). Subsequently, a series of other oxidants, including TAHP (*tert*-amyl hydroperoxide), CHP (cumene hydroperoxide), DTBP (di-*tert*-butyl peroxide), DCP (dicumyl peroxide), and BPO (benzoyl peroxide), were investigated (entries 5−10). We were surprised to find that only hydroperoxides, TAHP and CHP, effected the reaction (entries 5 and 6), and the other oxidants, DTBP, DCP, and BPO, have no reactivity for the reaction (entries 7−10). Notably, aldehyde **2a** was completely transferred into 4-methoxybenzoic acid using DTBP combined with 2 equiv of H_2O, resulting in no detectable 3-acylspiro[4,5]trienone **3aa** (entry 8). Among the effect of solvents examined, it turned out that ^{n}BuOAc was the most efficient, increasing the yield to 86% (entry 11).[8] However, the reaction was suppressed under either O_2 or air atmosphere (entry 12 and 13). The reason is that aldehyde **2a** is readily converted to acid under the conditions. Noteworthy is that the reaction can be performed on gram scale of propiolamide **1a** (5 mmol), and good yield is still achieved (entry 14).

With the optimal conditions in hand, we first investigated the scope of *N*-arylacrylamides **1** with respect to 4-methoxybenzaldehyde (**2a**) for this new *ipso*-carboacylation process (Table 2). We were pleased to find that analogous amide with *N*-Bn was a viable substrate for the reaction (product **3ba**), but changing to *N*-H resulted in a lower reactivity (product **3ca**). Subsequently, the substitution effect of the *N*-aryl moiety was tested (products **3da−ha**). For example, substrates **1d** or **1e**, bearing a *o*-Me group or a *m*-Me group on the aromatic ring of the *N*-aryl moiety, were

Table 2. Screening Scope of *N*-Arylacrylamides (1)[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (2 equiv), TBHP (2 equiv), and ^{n}BuOAc (2 mL) at 110 °C under argon atmosphere for 36 h.

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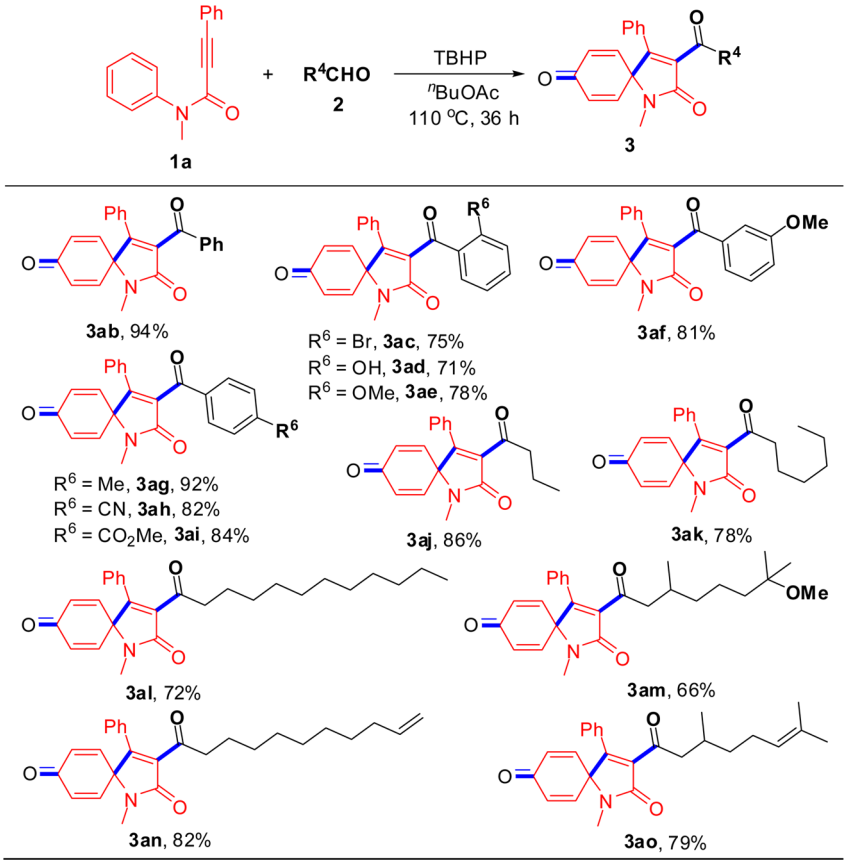
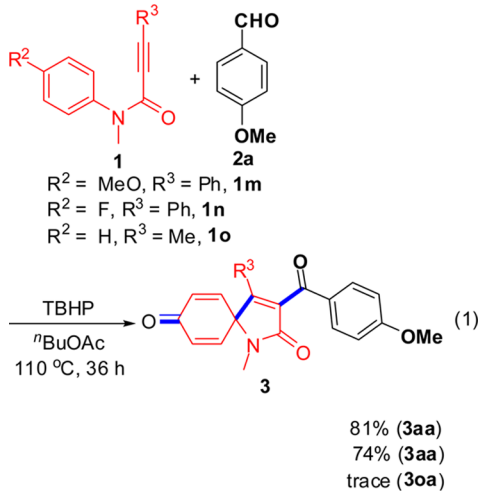
Table 3. Screening Scope of Aldehydes (2)[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (2 equiv), TBHP (2 equiv), and ^{n}BuOAc (2 mL) at 110 °C under argon atmosphere for 36 h.

successfully reacted with aldehyde **2a** and TBHP in good yields (products **3da** and **3ea**). Importantly, the iodo group was found to be well tolerated (product **3fa**). Substrate **1g** with two MeO groups was also consistent with the optimal conditions (product **3ga**). Extensive screening revealed that several substituents, including MeO, Me, and CN groups, on the aromatic ring at the terminal alkyne were tolerated well, and the electron-donating groups displayed higher reactivity than the electron-withdrawing groups in terms of the yields (products **3ha**–**ka**). Using pyridin-2-yl-susbtituted substrate **1l**, a good yield of the desired 3-acylspiro[4,5]trienones **3la** was still isolated. Notably, the *ipso*-carboacylation process could toleratethe iodo group: *N*-(2-iodobenzyl)-*N*,3-diphenylpropiolamide (**1m**) delivered iodo-substituted spiro[4,5]-trienone **2ma** in 80% yield. Unfortunately, both *N*-methyl-*N*-(naphthalen-1-yl)-3-phenylpropiolamide and *N*-methyl-*N*-(naphthalen-2-yl)-3-phenylpropiolamide were not suitable substrates for the reaction.

To our surprise, substrates **1** with a substituent, MeO or F, at the *para*-position of the *N*-phenyl moiety furnished 3-acylspiro[4,5]trienone **3aa** in good yield by releasing *para*-substituents (eq 1). However, aliphatic alkyne **1o** was not a suitable substrate (product **3oa**).



As shown in Table 3, we next set out to explore the scope of alkyl **2** in the presence of *N*-methyl-*N*,3-diphenylpropiolamide (**1a**) and TBHP. The results demonstrated that this process could be applied to *ipso*-carboacylation of a wide range of aldehydes **2b**–**o**, including functionalized aryl and aliphatic aldehydes. Using fresh benzaldehyde **2b**, for instance, the desired 3-benzoyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **3ab** was obtained in 94% yield. The optimal conditions were compatible with various arylaldehydes having substituents, such as Br, OH, MeO, Me, CN, and CO_2Me, on the aryl ring, and the reactivity order is *para* > *meta* > *ortho* (products **3ac**–**ai**). To our delight, aliphatic aldehydes **2j**–**o**, even with a MeO group or an olefin group, were viable for the reaction with substrate **1a** and TBHP, offering 3-acylspiro[4,5]-trienones **3aj**–**ao** in good yields. Notably, aldehydes **2m**–**o**, important components in flavors and fragrances as well as having strong antifungal qualities,[9] could be easily introduced into the spiro[4,5]trienone frameworks (products **3am**–**ao**),

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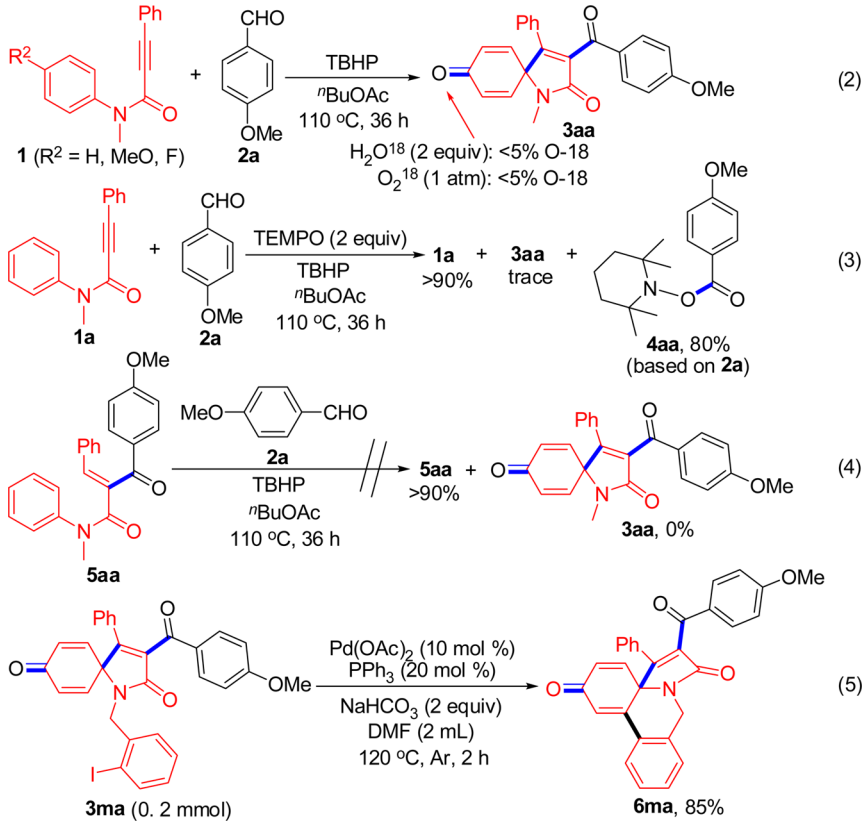
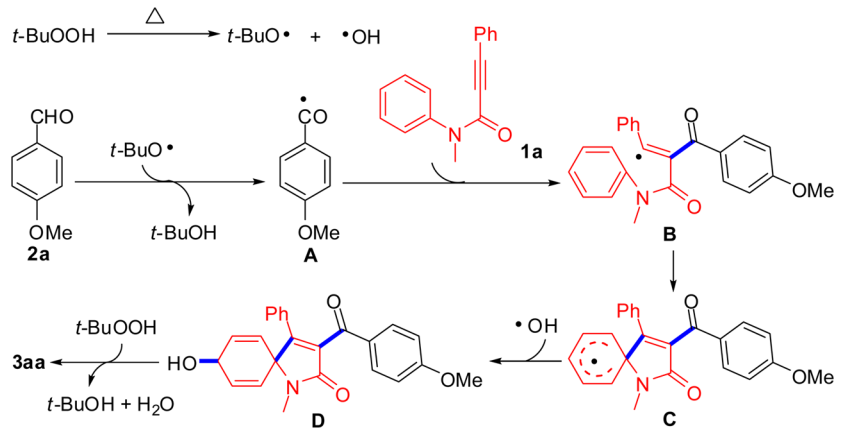
Scheme 2. Control Experiments and Utilization of Product 3ma



Scheme 3. Possible Mechanisms



thereby making this methodology more useful in organic synthesis.

The results in Table 1 showed that the presence of either H_2O or O_2 disfavored the reaction (entries 1, 2, 12, and 13). Thus, some control experiments in the presence of 2 equiv of $H_2{}^{18}O$ or 1 atm of $^{18}O_2$ were performed, and the results indicated that the amount of ^{18}O in 3-acylspiro[4,5]trienones **3aa** did not increase obviously (eq 2, Scheme 2). These suggest that the oxygen atom of the new formed carbonyl group is not from either H_2O or O_2. We carefully checked the results in Table 1 again, and we found that only hydroperoxides displayed catalytic activity for the current reaction (entries 1−2, 5, 6 vs entries 7−10). In light of these, we deduce that the oxygen atom of the new formed carbonyl group is from TBHP. Screening disclosed that a stoichiometric amount of radical inhibitor (2 equiv), TEMPO or 2,6-di-*tert*-butylphenol, resulted in no conversion of substrate **1a**; moreover, aldehyde **2a** was converted into 2,2,6,6-tetramethylpiperidin-1-yl 4-methoxybenzoate by reacting with TEMPO (eq 3, Scheme 2). It was noted that substrate **5aa**, a hydroacylation product, is inert for the reaction (eq 4, Scheme 2). Interestingly, treatment of product **3ma** with $Pd(OAc)_2$, PPh_3 and $NaHCO_3$ delivered anthor polycyclic compound **6ma** in 85% yield (eq 5, Scheme 2).[6n]

Consequently, a work mechanism outlined in Scheme 3 is proposed on the basis of the present results and the literature reports.[2−5,7] Initially, carbonyl radical **A** is formed from aldehyde **1a** by a single-electron transfer (SET) with TBHP.[5] Subsequently, acylation of alkyne **2a** with carbonyl radical **A** yields vinyl radical intermediate **B**, followed by selective *ipso*-

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carbocyclization to give intermediate **C**. Intermediate **C** selectively undergoes the addition with $^{\bullet}$OH to afford intermediate **D**. Finally, oxidation of intermediate **D** by TBHP results in the desired 3-acylspiro[4,5]trienone **3aa**.

CONCLUSIONS

In summary, we have illustrated an unprecedented metal-free TBHP-mediated *ipso*-carboacylation of alkynes with aldehydes through sequential aldehyde C(sp^2)−H oxidation, acylation, *ipso*-carbocyclization, dearomatization, hydration, and hydroxyl group oxidation processes. This method is the first example of alkyne difunctionalization to simultaneously form two carbon−carbon bonds using the oxidative cross-coupling strategy and provides valuable access to 3-acylspiro[4,5]-trienones. Applications of this oxidative cross-coupling method in organic synthesis are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Considerations. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. LRMS was performed on a GC−MS instrument and HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

Caution. Organic peroxides are dangerous under heating because they may cause a fire or explosion.

Preparation of *N*-Arylpropiolamides (1). All *N*-arylpropiolamides (**1**) were synthesized according to the known methods.[10]

Typical Experimental Procedure for the TBHP-Mediated Synthesis of 3-Acylspiro[4,5]trienone from *N*-Arylpropiolamides with Aldehydes. To a Schlenk tube were added *N*-arylpropiolamides **1** (0.3 mmol), aldehydes **2** (2 equiv), TBHP (anhydrous, 2 equiv) and ^{n}BuOAc (2 mL). Then the tube was charged with argon, and was stirred at 110 °C for 36 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was washed with brine. The aqueous phase was re-extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product.

*3-(4-Methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3aa**):* 99.3 mg, 86%; yellow solid; mp 171.2−172.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 2H), 7.230−7.25 (m, 3H), 7.21−7.20 (m, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 10.0 Hz, 2H), 6.58 (d, J = 10.0 Hz, 2H), 3.82 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 183.8, 167.3, 164.4, 153.6, 144.8, 136.3, 133.4, 131.9, 130.4, 130.1, 128.7 (2C), 127.7, 114.0, 67.1, 55.5, 25.8; IR (KBr, cm^{-1}) 1628, 1658, 1699; LRMS (EI, 70 eV) m/z 385 (M$^+$, 13), 384 (8), 263 (25), 135 (100); HRMS m/z (ESI) calcd for $C_{24}H_{20}NO_4$ ([M + H]$^+$) 386.1387, found 386.1403.

*1-Benzyl-3-(4-methoxybenzoyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ba**):* 117.6 mg, 85%; yellow solid; mp 133.5−135.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.8 Hz, 2H), 7.27−7.16 (m, 10H), 6.87 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 10.0 Hz, 2H), 6.34 (d, J = 10.0 Hz, 2H), 4.58 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 184.0, 167.5, 164.4, 154.2, 145.0, 137.2, 136.2, 132.6, 131.9, 130.4, 130.0, 128.9, 128.8, 128.6 (2C), 127.9, 127.8, 114.0, 67.6, 55.5, 44.6; IR (KBr, cm^{-1}) 1629, 1678, 1708; LRMS (EI, 70 eV) m/z 461 (M$^+$, 13), 135 (100); HRMS m/z (ESI) calcd for $C_{30}H_{24}NO_4$ ([M + H]$^+$) 462.1700, found 462.1720.

*3-(4-Methoxybenzoyl)-1,6-dimethyl-4-phenyl-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**3da**):* 87.4 mg, 73%; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 9.0 Hz, 2H), 7.27−7.25 (m, 3H), 7.18 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.64 (d, J = 10.0 Hz, 1H), 6.54 (d, J = 10.0 Hz, 1H), 6.45 (s, 1H), 3.82 (s, 3H), 2.89 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.8, 184.6, 167.3, 164.4, 154.0, 144.7, 140.6, 139.5, 136.1, 133.1, 131.9, 130.3, 130.2, 128.8, 128.6, 127.7, 113.9; IR (KBr, cm^{-1}) 1632, 1668, 1699; LRMS (EI, 70 eV) m/z 399 (M$^+$, 21), 384 (8), 263 (18), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{21}NO_4$ ([M + H]$^+$) 400.1543, found 400.1558.

*3-(4-Methoxybenzoyl)-1,7-dimethyl-4-phenyl-1-azaspiro[4.5]-deca-3,6,9-triene-2,8-dione (**3ea**):* 89.8 mg, 75%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 7.2 Hz, 3H), 7.20 (d, J = 6.4 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.66−6.63 (m, 1H), 6.56−6.45 (m, 1H), 6.45 (d, J = 1.6 Hz, 1H), 3.83 (s, 3H), 2.90 (s, 3H), 2.00 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 184.7, 167.4, 164.4, 154.1, 144.7, 140.7, 139.5, 136.0, 133.1, 131.9, 130.3, 128.8, 128.7, 128.2, 127.7, 114.0, 67.7, 55.5, 25.8, 15.9; IR (KBr, cm^{-1}) 1628, 1679, 1699; LRMS (EI, 70 eV) m/z 399 (M$^+$, 13), 398 (5), 263 (23), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{21}NO_4$ ([M + H]$^+$) 400.1543, found 400.1556.

*6-Iodo-3-(4-methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro-[4.5]deca-3,6,9-triene-2,8-dione (**3fa**):* 104.3 mg, 68%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 1.2 Hz, 1H), 7.32−7.00 (m, 5H), 6.93−6.87 (m, 3H), 6.64−6.61 (m, 1H), 3.84 (s, 3H), 2.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 180.8, 167.3, 164.5, 153.7, 145.2, 144.2, 138.2, 132.3, 132.2, 130.6, 129.5, 128.9, 128.8, 127.9, 124.3, 114.0, 71.9, 55.5, 25.6; IR (KBr, cm^{-1}) 1630, 1672, 1708; LRMS (EI, 70 eV) m/z 511 (M$^+$, 12), 385 (87), 135 (100); HRMS m/z (ESI) calcd for $C_{24}H_{19}INO_4$ ([M + H]$^+$) 512.0359, found 512.0363.

*6,9-Dimethoxy-3-(4-methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ga**):* 121.5 mg, 91%; yellow solid; mp 204.5−205.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 2H), 7.28−7.18 (m, 5H), 6.86 (d, J = 8.8 Hz, 2H), 5.91 (s, 1H), 5.26 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.67 (s, 3H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 180.9, 168.9, 167.8, 164.3, 154.0, 153.2, 136.1, 132.0, 130.2, 130.0, 128.9, 128.7, 127.5, 113.9, 106.6, 105.8, 69.5, 55.9, 55.8, 55.4, 25.2; IR (KBr, cm^{-1}) 1611, 1646, 1663, 1689; LRMS (EI, 70 eV) m/z 445 (M$^+$, 12), 430 (3), 263 (15), 135 (100); HRMS m/z (ESI) calcd for $C_{26}H_{23}NO_6$ ([M + H]$^+$) 446.1598, found 446.1593.

*3-(4-Methoxybenzoyl)-4-(2-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ha**):* 103.3, 83%; yellow solid; mp 127.5−128.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 7.13−7.11 (m, 1H), 6.86 (d, J = 9.2 Hz, 2H), 6.84−6.80 (m, 1H), 6.71−6.66 (m, 3H), 6.46 (d, J = 10.4 Hz, 2H), 3.84 (s, 3H), 3.45 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 184.1, 167.6, 164.0, 155.9, 152.6, 144.9, 138.1, 132.8, 131.9, 131.4, 129.0, 128.9, 120.2, 118.7, 113.5, 111.0, 68.2, 55.5, 54.7, 26.2; IR (KBr, cm^{-1}) 1658, 1663, 1699; LRMS (EI, 70 eV) m/z 415 (M$^+$, 7), 385 (12), 263 (21), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{22}NO_5$ ([M + H]$^+$) 416.1492, found 416.1496.

*3-(4-Methoxybenzoyl)-4-(4-methoxyphenyl)-1-methyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ia**):* 109.6 mg, 88%; yellow solid; mp 121.4−123.2 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.71−6.68 (m, 4H), 6.59 (d, J = 10.0 Hz, 2H), 3.83 (s, 3H), 3.72 (s, 3H), 2.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 183.9, 167.6, 164.4, 161.2, 153.0, 145.4, 134.3, 133.2, 131.9, 129.4, 128.8, 122.5, 114.3, 114.0, 66.8, 55.5, 55.2, 25.7; IR (KBr, cm^{-1}) 1658, 1672, 1708; LRMS (EI, 70 eV) m/z 415 (M$^+$, 31), 263 (18), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{22}NO_5$ ([M + H]$^+$) 416.1492, found 416.1477.

*3-(4-Methoxybenzoyl)-1-methyl-4-p-tolyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ja**):* 97 mg, 81%; yellow solid; mp 119.6−121.0 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 10.0 Hz, 2H), 6.58 (d, J = 10.0 Hz, 2H), 3.83 (s, 3H), 2.90 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 183.9, 167.5, 164.4, 153.6, 145.1, 140.9, 135.5, 133.2, 131.9, 129.5, 128.8, 127.6, 127.3, 114.0, 67.0, 55.5, 25.8, 21.2;

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IR (KBr, cm^{-1}) 1628, 1664, 1699; LRMS (EI, 70 eV) m/z 399 (M^+, 12), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{22}NO_4$ ($[M + H]^+$) 400.1543, found 400.1563.

*4-(3-(4-Methoxybenzoyl)-1-methyl-2,8-dioxo-1-azaspiro[4.5]deca-3,6,9-trien-4-yl)benzonitrile (**3ka**):* 88.6 mg, 72%; yellow solid; mp 179.6−181.0 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 10.0 Hz, 2H), 6.60 (d, J = 10.40 Hz, 2H), 3.86 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 183.2, 166.7, 164.9, 151.5, 144.0, 138.8, 134.5, 133.9, 132.4, 132.0, 128.5, 128.4, 117.6, 114.2, 114.1, 67.1, 55.6, 26.0; IR (KBr, cm^{-1}) 1639, 1678, 1702; LRMS (EI, 70 eV) m/z 410 (M^+, 17), 288 (37), 135 (100); HRMS m/z (ESI) calcd for $C_{25}H_{19}N_2O_4$ ($[M + H]^+$) 411.1339, found 411.1349.

*3-(4-Methoxybenzoyl)-1-methyl-4-(pyridin-4-yl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3la**):* 95 mg, 82%; yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 4.5 Hz, 2H), 7.81 (d, J = 7.0 Hz, 2H), 7.17 (d, J = 5.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 11.0 Hz, 2H), 6.61 (d, J = 10.5 Hz, 2H), 3.85 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 183.2, 166.5, 164.8, 150.5, 150.2, 143.8, 138.9, 137.7, 133.8, 131.9, 128.4, 121.8, 114.2, 66.9, 55.5, 25.9; IR (KBr, cm^{-1}) 1634, 1662, 1698; LRMS (EI, 70 eV) m/z 386 (M^+, 26), 385 (30), 264 (23), 135 (100); HRMS m/z (ESI) calcd for $C_{23}H_{19}N_2O_4$ ($[M + H]^+$) 387.1345, found 387.1336.

*1-(2-Iodobenzyl)-3-(4-methoxybenzoyl)-4-phenyl-1-azaspiro-[4.5]deca-3,6,9-triene-2,8-dione (**3ma**):* 140.9 mg, 80%; yellow solid; mp 233.1−234.6 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.2 Hz, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.29−7.16 (m, 6H), 7.00 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.0 Hz, 2H), 6.32 (d, J = 10.0 Hz, 2H), 4.75 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 184.0, 167.4, 164.4, 154.6, 144.1, 139.5, 139.4, 136.0, 132.9, 131.9, 130.3, 130.2, 129.9, 129.6, 128.7, 128.6 (2C), 127.7, 114.0, 99.4, 67.5, 55.5, 48.9; IR (KBr, cm^{-1}) 1630, 1669, 1697, 1703; HRMS m/z (ESI) calcd for $C_{30}H_{23}INO_4$ ($[M + H]^+$) 588.0666, found 588.0657.

*3-Benzoyl-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ab**):* 100.1 mg, 94%; yellow solid; mp 108.2−110.0 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.51−7.50 (m, 1H), 7.40−7.39 (m, 2H), 7.27 (t, J = 3.6 Hz, 3H), 7.26−7.20 (m, 2H), 6.70 (d, J = 10.0 Hz, 2H), 6.59 (d, J = 10.8 Hz, 2H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 183.7, 167.2, 154.5, 144.6, 136.0, 135.5, 134.2, 133.5, 130.5, 130.0, 129.4, 128.7 (2C), 127.7, 67.2, 25.9; IR (KBr, cm^{-1}) 1573, 1597, 1669, 1699; LRMS (EI, 70 eV) m/z 355 (M^+, 27), 233 (17), 105 (100); HRMS m/z (ESI) calcd for $C_{23}H_{18}NO_3$ ($[M + H]^+$) 356.1281, found 356.1272.

*3-(2-Bromobenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ac**):* 97.9 mg, 75%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.41 (m, 2H), 7.26−7.15 (m, 7H), 6.64 (d, J = 10.4 Hz, 2H), 6.51 (d, J = 10.4 Hz, 2H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 183.6, 166.5, 157.3, 143.7, 139.0, 135.8, 133.7, 133.3, 132.9, 131.3, 130.2, 129.8, 128.3, 127.7, 127.4, 120.6, 67.4, 26.0; IR (KBr, cm^{-1}) 1568, 1603, 1688, 1701; LRMS (EI, 70 eV) m/z 435 (M^++2, 13), 433 (M^+, 13), 354 (100), 326 (70); HRMS m/z (ESI) calcd for $C_{23}H_{17}BrNO_3$ ($[M + H]^+$) 434.0392, found 434.0383.

*3-(2-Hydroxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ad**):* 79.0, 71%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 7.6 Hz, 1H), 7.67−7.62 (m, 2H), 7.56 (d, J = 6.4 Hz, 1H), 7.51−7.47 (m, 2H), 7.39−7.33 (m, 3H), 6.45 (d, J = 8.8 Hz, 2H), 6.31 (d, J = 7.6 Hz, 2H), 3.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 165.5, 160.5, 155.8, 134.1, 132.1, 131.5, 129.0, 128.6, 128.4, 126.6, 125.9, 125.4, 122.5, 120.6, 118.0, 115.6, 60.5, 37.3; IR (KBr, cm^{-1}) 1572, 1600, 1682, 1700; LRMS (EI, 70 eV) m/z 371 (M^+, 14), 261 (12), 135 (100); HRMS m/z (ESI) calcd for $C_{23}H_{18}NO_4$ ($[M + H]^+$) 372.1230, found 372.1220.

*3-(2-Methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ae**):* 90.1 mg, 78%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 1H), 7.51−7.47 (m, 1H), 7.29−7.18 (m, 5H), 7.01 (t, J = 8.4 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 10.4 Hz, 2H), 6.53 (d, J = 10.0 Hz, 2H), 3.85 (s, 3H), 2.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 183.9, 167.3, 159.6, 152.3, 144.9, 139.5, 135.2, 133.3, 131.1, 130.4, 129.9, 128.5, 127.8, 126.78, 121.1, 111.9, 66.9, 55.8, 25.7; IR (KBr, cm^{-1}) 1570, 1608, 1660, 1698; LRMS (EI, 70 eV) m/z 385 (M^+, 3), 367 (14), 354 (41), 135 (100); HRMS m/z (ESI) calcd for $C_{24}H_{20}NO_4$ ($[M + H]^+$) 386.1387, found 386.1400.

*3-(3-Methoxybenzoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3af**):* 93.6, 81%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.30−7.26 (m, 4H), 7.22−7.18 (m, 2H), 7.09 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 10.0 Hz, 2H), 6.58 (d, J = 10.0 Hz, 2H), 3.81 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 183.7, 167.1, 159.9, 154.2, 144.7, 136.8, 136.2, 133.5, 130.5, 130.1, 129.7, 128.8, 127.8, 122.7, 121.0, 112.9, 67.2, 55.4, 25.9; IR (KBr, cm^{-1}) 1582, 1599, 1663, 1697; LRMS (EI, 70 eV) m/z 385 (M^+, 22), 263 (45), 135 (100); HRMS m/z (ESI) calcd for $C_{24}H_{20}NO_4$ ($[M + H]^+$) 386.1387, found 386.1403.

*1-Methyl-3-(4-methylbenzoyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ag**):* 101.8 mg, 92%; yellow solid; mp 123.1−124.9 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 2H), 7.28 (d, J = 7.6 Hz, 3H), 7.20 (t, J = 7.6 Hz, 4H), 6.69 (d, J = 9.6 Hz, 2H), 6.58 (d, J = 9.6 Hz, 2H), 2.92 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 183.8, 167.3, 154.0, 145.4, 144.8, 136.3, 133.4, 133.2, 130.5, 130.1, 129.6, 129.4, 128.8, 127.8, 67.2, 25.9, 21.8; IR (KBr, cm^{-1}) 1589, 1645, 1668, 1697; LRMS (EI, 70 eV) m/z 369 (M^+, 20), 247 (25), 119 (100); HRMS m/z (ESI) calcd for $C_{24}H_{20}NO_3$ ($[M + H]^+$) 370.1438, found 370.1427.

*4-(1-Methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trienecarbonyl)benzonitrile (**3ah**):* 93.5 mg, 82%; yellow solid; mp 183.4−184.6 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.31 (t, J = 4.4 Hz, 1H), 7.22 (d, J = 4.0 Hz, 4H), 6.69−6.65 (m, 2H), 6.62−6.59 (m, 2H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 183.5, 166.7, 156.8, 144.0, 138.4, 135.0, 133.8, 132.5, 131.0, 129.7, 129.0, 127.7, 117.7, 117.21, 67.4, 26.0; IR (KBr, cm^{-1}) 1575, 1602, 1669, 1694; LRMS (EI, 70 eV) m/z 380 (M^+, 43), 252 (24), 102 (49), 129 (100); HRMS m/z (ESI) calcd for $C_{24}H_{17}N_2O_3$ ($[M + H]^+$) 381.1239, found 381.1230.

*Methyl 4-(1-methyl-2,8-dioxo-4-phenyl-1-azaspiro[4.5]deca-3,6,9-trienecarbonyl)benzoate (**3ai**):* 104.1 mg, 84%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.26−7.17 (m, 5H), 6.70 (d, J = 10.0 Hz, 2H), 6.60 (d, J = 9.6 Hz, 2H), 3.92 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 183.6, 166.9, 165.9, 155.6, 144.3, 138.6, 135.5, 134.6, 133.6, 130.8, 129.8, 129.3, 128.9, 127.7, 67.3, 52.5, 25.9; IR (KBr, cm^{-1}) 1499, 1572, 1631, 1669, 1706; LRMS (EI, 70 eV) m/z 413 (M^+, 32), 384 (11), 291 (16), 163 (100); HRMS m/z (ESI) calcd for $C_{25}H_{20}NO_5$ ($[M + H]^+$) 414.1336, found 414.1314.

*3-Butyryl-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3aj**):* 82.8 mg, 86%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.18 (m, 3H), 7.19 (d, J = 8.8 Hz, 2H), 6.55−6.48 (m, 4H), 2.90 (s, 3H), 2.72 (t, J = 7.2 Hz, 2H), 1.63−1.57 (m, 2H), 0.87 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 183.6, 167.1, 157.0, 144.0, 136.2, 133.6, 130.3, 130.2, 128.5, 127.7, 67.3, 45.0, 26.0, 16.7, 13.5; IR (KBr, cm^{-1}) 1633, 1670, 1697; LRMS (EI, 70 eV) m/z 321 (M^+, 57), 251 (65), 129 (100); HRMS m/z (ESI) calcd for $C_{20}H_{20}NO_3$ ($[M + H]^+$) 322.1443, found 322.1434.

*3-Heptanoyl-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ak**):* 84.9 mg, 78%; yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, J = 7.2 Hz, 1H), 7.34−7.29 (m, 2H), 7.19 (d, J = 7.6 Hz, 2H), 6.54 (d, J = 10.0 Hz, 2H), 6.49 (d, J = 10.0 Hz, 2H), 2.89 (s, 3H), 2.73 (t, J = 7.2 Hz, 2H), 1.57−1.52 (m, 2H), 1.21 (s, 6H), 0.84 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 183.5, 167.0, 156.8, 143.9, 136.2, 133.6, 130.2, 130.1, 128.4, 127.7, 67.3, 43.0, 31.4, 28.5, 25.9, 23.1, 22.3, 13.9; IR (KBr, cm^{-1}) 1460, 1631, 1670, 1697; LRMS (EI, 70 eV) m/z 363 (M^+, 34), 292

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(58), 207 (100); HRMS *m*/*z* (ESI) calcd for $C_{23}H_{26}NO_3$ ([M + H]$^+$) 364.1913, found 364.1904.

*3-Dodecanoyl-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3al**):* 93.5 mg, 72%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.28 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.55−6.48 (m, 4H), 2.89 (s, 3H), 2.75−2.71 (m, 2H), 1.55 (t, *J* = 7.2 Hz, 2H), 1.24−1.21 (m, 16H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 183.5, 167.0, 156.8, 144.0, 136.2, 133.6, 130.2, 130.1, 128.5, 127.7, 67.3, 43.0, 31.8, 29.5 (2C), 29.3, 29.2, 28.9, 25.9, 23.1, 22.6, 14.0; IR (KBr, cm^{-1}) 1638, 1671, 1697; LRMS (EI, 70 eV) *m*/*z* 433 (M$^+$, 38), 207 (100); HRMS *m*/*z* (ESI) calcd for $C_{28}H_{36}NO_3$ ([M + H]$^+$) 434.2695, found 434.2687.

*3-(7-Methoxy-3,7-dimethyloctanoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3am**):* 79.8 mg, 66%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.56−6.47 (m, 4H), 3.15 (s, 3H), 2.89 (s, 3H), 2.74−2.68 (m, 1H), 2.56−2.52 (m, 1H), 2.05−1.98 (m, 1H), 1.26−1.17 (m, 2H), 1.13−1.10 (m, 4H), 1.10 (s, 6H), 0.84 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 183.6, 167.0, 156.7, 144.0 (2C), 136.5, 133.7 (2C), 130.3, 130.1, 128.5, 127.8, 67.4, 50.3, 49.0, 39.9, 37.2, 28.8, 26.0, 24.9 (2C), 21.1, 19.7; IR (KBr, cm^{-1}) 1630, 1678, 1699; LRMS (EI, 70 eV) *m*/*z* 403 (M$^+$, 14), 363 (5), 320 (16), 73 (100); HRMS *m*/*z* (ESI) calcd for $C_{27}H_{34}NO_4$ ([M + H]$^+$) 436.2488, found 436.2480.

*1-Methyl-4-phenyl-3-undec-10-enoyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3an**):* 102.6 mg, 82%; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 2H), 6.55−6.51 (m, 4H), 5.83−5.77 (m, 1H), 5.01−4.91 (m, 2H), 2.90 (s, 3H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.05−1.99 (m, 2H), 1.56 (t, *J* = 7.2 Hz, 2H), 1.36−1.22 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 183.6, 167.1, 156.9, 144.0, 139.1, 136.2, 133.6, 130.3, 130.1, 128.5, 127.8, 114.1, 67.3, 43.1, 33.7, 29.2, 29.0, 28.9, 28.8, 26.0, 23.2; IR (KBr, cm^{-1}) 1635, 1678, 1697; LRMS (EI, 70 eV) *m*/*z* 417 (M$^+$, 48), 292 (99), 129 (100), 55 (71); HRMS *m*/*z* (ESI) calcd for $C_{27}H_{32}NO_3$ ([M + H]$^+$) 418.2378, found 418.2371.

*3-(3,7-Dimethyloct-6-enoyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**3ao**):* 95.5 mg, 79%; yellow oil; the ratio of two diastereomers is 2:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.28 (s, 1.6H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.54−6.47 (m, 5H), 6.30 (d, *J* = 10.0 Hz, 1H), 5.02 (S, 1H), 3.88−3.85 (m, 0.5H), 2.89 (s, 3H), 2.83 (m, 1.5H), 2.73−2.68 (m, 1.5H), 2.58−2.52 (m, 1.5H), 2.01−1.99 (m, 1.5H), 1.91−1.88 (m, 3H), 1.66 (s, 4.5H), 1.56 (s, 3H), 1.42−1.40 (m, 1.5H), 1.16−1.10 (m, 2H), 0.99 (d, *J* = 6.4 Hz, 1.5H), 0.85 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 198.8, 183.6, 166.8, 156.7, 146.7, 146.3, 145.7, 144.0, 136.5, 133.6, 133.0, 132.7, 131.4, 130.3, 130.1, 128.5, 128.1, 128.0, 124.2, 99.9, 67.9, 67.3, 54.1, 51.4, 50.3, 38.2, 36.7, 35.5, 34.2, 28.5, 27.2, 26.7, 26.2, 26.0, 25.6, 25.3, 22.9, 22.3, 19.6, 17.6; IR (KBr, cm^{-1}) 1633, 1673, 1697; LRMS (EI, 70 eV) *m*/*z* 403 (M$^+$, 72), 292 (100), 265 (65); HRMS *m*/*z* (ESI) calcd for $C_{26}H_{30}NO_3$ ([M + H]$^+$) 404.2220, found 404.2201.

*6-(4-Methoxybenzoyl)-5-phenyl-2H-pyrrolo[2,1-e]phenanthridine-2,7(9H)-dione (**6ma**):* 78.0 mg, 85%; yellow solid; mp 193.7−196.1 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.6 Hz, 1H), 7.49 (t, *J* = 2.8 Hz, 2H), 7.39−7.37 (m, 3H), 7.29−7.20 (m, 3H), 7.03 (d, *J* = 2.8 Hz, 2H), 6.87 (d, *J* = 4.8 Hz, 1H), 6.69 (d, *J* = 4 Hz, 2H), 6.49 (s, 1H), 6.26 (d, *J* = 4.8 Hz, 1H), 5.18 (d, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 184.3, 173.7, 164.2, 159.7, 151.1, 146.5, 138.5, 136.4, 132.9, 131.7, 131.5, 130.9, 129.9, 129.0, 128.7(2C), 128.6, 128.1, 126.3, 125.0, 113.7, 72.0, 55.45, 44.5; HRMS *m*/*z* (ESI) calcd for $C_{30}H_{22}NO_4$ ([M + H]$^+$) 460.1543, found 460.1533.

■ ASSOCIATED CONTENT

Supporting Information

Screening of the optimal conditions (Table S1) and copies of ^{1}H and ^{13}C spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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