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$AlCl_3$-Promoted Selective Michael Addition with Allenoate and Methyleneindolinone: Synthesis of Spirocyclic Oxindole by Using Allenoate as a Four-Carbon Component Building Block

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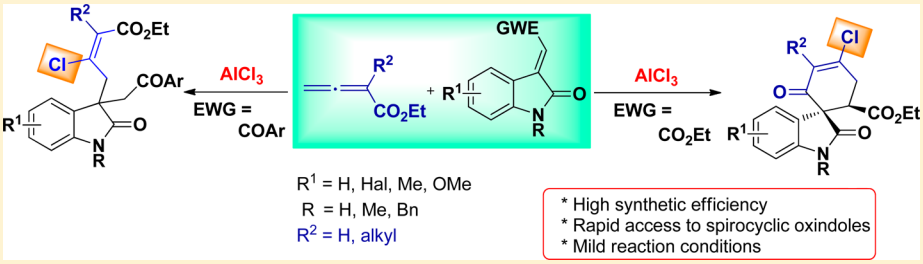
Supporting Information

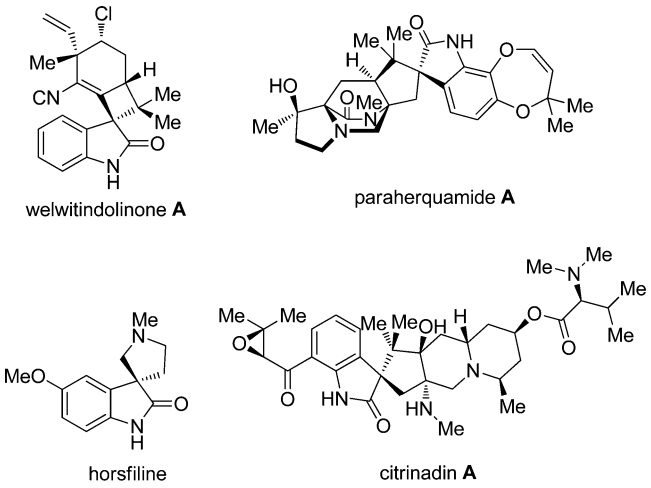


ABSTRACT: The $AlCl_3$-promoted cyclization of readily available allenoates with methyleneindolinone is disclosed. The present strategy provides a rapid access to spirocyclic oxindole-cyclohexenones in an efficient manner. Remarkably, the allenoate is implemented as a four-carbon (4C) component to form the ring, which shows high synthetic efficiency. Flexibility of this method allows quick synthesis of spirocyclic oxindole-dihydropyrans by varying one of the components. It is also noteworthy that $AlCl_3$ serves as the chlorine source as well as an effective catalyst to facilitate this interesting transformation.

INTRODUCTION

Spirocyclic oxindole represents a privileged synthetic motif in a large family of clinical pharmaceuticals and natural products including welwitindolinone A, horsfiline, paraherquamide A, and citrinadin A (Scheme 1).[1] These compounds often showed a broad range of biological activities such as insecticidal, antitumor, and antibacterial properties.[2] Enormous efforts have been dedicated to the efficient and selective construction of this core skeleton. As such, transition metal-catalyzed synthesis involving a domino approach, as well as C−H activation, has been widely documented.[3] More recently, organocatalyzed reactions and Lewis acid-promoted annulation have emerged as attractive synthetic strategies.[4,5] Although considerable progress has been described toward their syntheses, developing a novel method to efficiently synthesize this core structure remains valuable.

Scheme 1. Natural Products Possessing Spirooxindole as a Core Structure



In recent decades, allenoate has received significant interests in organic synthesis due to its facile preparation and versatile reactivity.[6] For instance, nucleophilic addition and electrophilic addition reactions with a wide range of substances, as well as rearrangements, have been well-documented.[7,8] In particular, they were proven to be valuable building blocks in many types of cycloaddition reactions.[9] In this field, the phosphine-catalyzed cycloaddition reaction is of great interest due to simple reagents and structural diversity of the adduct (Scheme 2a).[10] The first example of phosphine-catalyzed [3 + 2] cycloaddition reaction could be dated back to the work of Zhang and Lu in 1995.[11] Following this pioneering work, Zhu et al.[12] reported another important variant [4 + 2] cycloaddition. After that, a large number of asymmetric versions as

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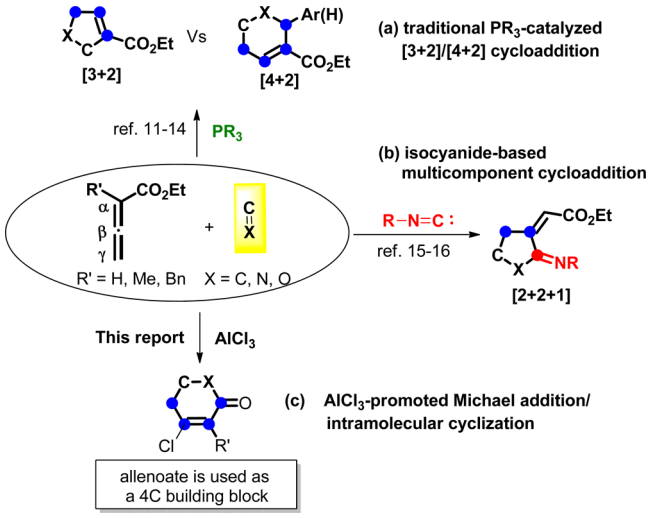
Scheme 2. Representative Cyclization Reactions Involving Allenoate and Electron-Deficient Species with Different Reagents

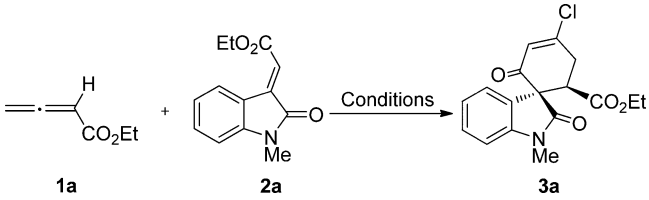


well as applications in natural product synthesis were fully investigated.[13,14] In 2011, we reported an unprecedented [2 + 2 + 1] cycloaddition involving allenoate by using isocyanide as nucleophile instead of phosphine (Scheme 2b).[15] In such case, the allenoate and electron-deficient carbonyl-containing isatin in the presence of isocyanide gave quick access to spirooxindole. Replacement of the carbonyl group with reactive carbon−carbon double bond also worked well,[16a,b] and thus a new class of multicomponent [2 + 2+1] cycloaddition reaction was successfully developed. More recently, we also found a novel [1,5]-hydride shift when α-substituted allenoate was used.[16c] Mechanistically, the above-mentioned cycloaddition reactions begin with nuclophilic addition toward allenoate, while isocyanide or phosphine acts as a good nucleophile to trigger the subsequent annulation. We thus envisioned that other nucleophiles may also be used to react with allenoate to bring us structurally novel skeletons.[16d,e] Herein we report that, in the presence of $AlCl_3$, an unexpected cyclization of allenoate and methyleneindolinone takes place to afford spirocyclic oxindole (Scheme 2c).

RESULTS AND DISCUSSION

Treatment of ethyl 2,3-butadienoate **1a** and methyleneindolinone **2a** with $AlCl_3$ and dichloroethylene (DCE) afforded a new cyclization product **3a** in 38% yield (Table 1, entry 1). Following this encouraging result, several chloride-containing Lewis acids, such as $FeCl_3$, $BiCl_3$, and trimethylsilyl chloride (TMSCl) as well as $ZnCl_2$, were subsequently evaluated. However, replacement of $AlCl_3$ with these metal chlorides did not display any reactivity and no desired product was obtained (Table 1, entries 2−7). The use of $InCl_3$ resulted in only a trace amount of **3a** (Table 1, entry 8). Further experiments also demonstrated that the amount of $AlCl_3$ had a significant influence. The isolated yield was improved to 53% when 1.5 equiv of $AlCl_3$ was used (Table 1, entry 10). Lower temperature (80 °C or room temperature) dramatically decreased the efficiency of the annulation. Subsequent solvent screening revealed that DCE was the most suitable medium for the reaction while toluene gave lower efficiency; other polar solvents such as tetrahydrofuran (THF) and CH_3CN resulted in either a trace amount or none of the desired product.

Table 1. Optimization for Cyclization of Allenoate 1a with Methyleneindolinone 2a[a]

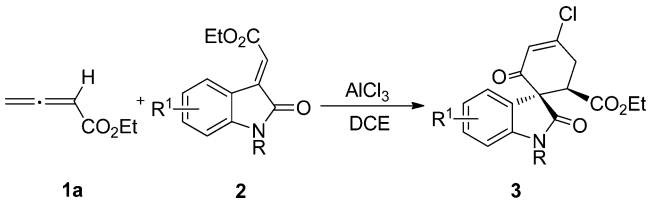


entry	Lewis acid	MXn (equiv)	solvent	temp (°C)	yield[b] (%)
1	$AlCl_3$	1.0	DCE	reflux	38
2	$FeCl_3$	1.0	DCE	reflux	*c*
3	$CuCl_2$	1.0	DCE	reflux	*d*
4	$SnCl_2{\cdot}2H_2O$	1.0	DCE	reflux	NR
5	$BiCl_3$	1.0	DCE	reflux	*c*
6	TMSCl	1.0	DCE	reflux	*d*
7	$ZnCl_2$	1.0	DCE	reflux	NR
8	$InCl_3$	1.0	DCE	reflux	trace
9	$AlCl_3$	1.2	DCE	reflux	46
10	$AlCl_3$	1.5	DCE	reflux	53
11	$AlCl_3$	1.5	DCE	80	33
12	$AlCl_3$	1.5	DCE	rt	trace
13	$AlCl_3$	1.5	CH_3CN	reflux	trace
14	$AlCl_3$	1.5	toluene	reflux	35
15	$AlCl_3$	1.5	THF	reflux	NR

[a]Reaction conditions: allenoate **1a** (0.6 mmol), methyleneindolinone **2a** (0.5 mmol), and Lewis acid in 5 mL of solvent. [b]Yield of product after silica gel chromatography. [c]Complex mixture was detected. [d]Isomerization of substrate **2a** was detected.

With the optimal reaction conditions in hand, we sought to briefly investigate the feasibility of methyleneindolinone **2** bearing different substitution patterns. As shown in Table 2, various methyleneindolinones **2** having electron-neutral (Table 2, entry 1), electron-deficient (Table 2, entries 2−4, 7, and 8), and electron-rich substituents (Table 2, entries 5 and 6) on the

Table 2. $AlCl_3$-Promoted Cyclization of Allenoate 1a with Substituted Methyleneindolinone 2[a]



entry	R^1	R	time (h)	product	yield[b] (%)
1	H	Me	20	**3a**	53
2	5-F	Me	12	**3b**	56
3	5-Cl	Me	15	**3c**	61
4	5-Br	Me	12	**3d**	50
5	5-CH_3	Me	12	**3e**	46
6	5-CH_3O	Me	12	**3f**	49
7	4-Br	Me	12	**3g**	60
8	6-Br	Me	12	**3h**	68
9	H	H	20	**3i**	32
10	H	Bn	20	**3j**	43
11	H	Ac	20		NR

[a]Reaction conditions: allenoate **1a** (0.6 mmol), 0.5 mmol methyleneindolinone **2** (0.5 mmol), and 1.5 equiv of $AlCl_3$in DCE (5 mL) under reflux. [b]Isolated yields.

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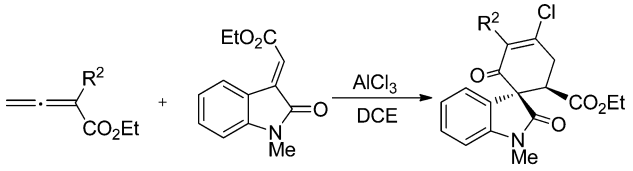
aryl ring were employed to correlate with the substitution effect. Gratifyingly, all substrates performed well with allenoate **1a** under optimal conditions (see Supporting Information for details). The structure of **3a** (CCDC 1014495) was unambiguously confirmed by single-crystal X-ray analysis (see Supporting Information).[17] Experiments to examine the influence of different protecting groups at the nitrogen of methyleneindolinone **2** were also conducted (Table 2, entries 9−11). Lower yield was obtained when methyleneindolinone **2** was free of a protecting group, while a complex mixture was found if the nitrogen was masked with an acetyl group (Table 2, entry 11).

To further demonstrate the scope and limitations of the above formal [4 + 2] annulation, we then focused our attention on the utilization of allenoates bearing different substitution patterns. As shown in Table 3, a series of structurally varied

Table 3. $AlCl_3$-Promoted Cyclization of Methyleneindolinone 2a with Substituted Allenoate 1[a]



1 2a 4

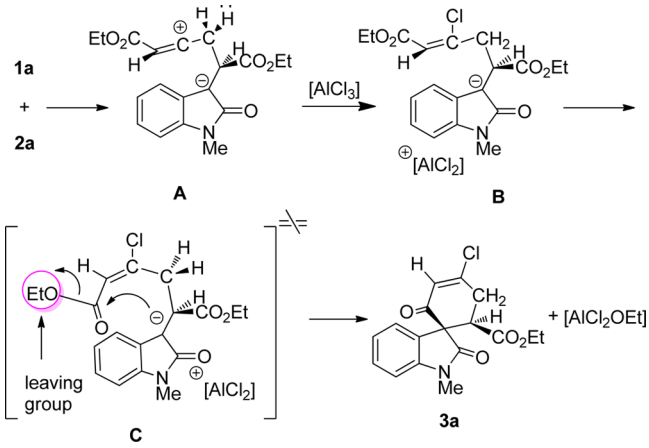
entry	R^2	time (h)	product	yield[b] (%)
1	CH_3	24	**4a**	57
2	Bn	24	**4b**	50
3	4-NO_2Bn	36	**4c**	75
4	3-NO_2Bn	24	**4d**	73
5	2-NO_2Bn	24	**4e**	45
6	3-FBn	36	**4f**	55
7	3-ClBn	36	**4g**	51
8	4-BrBn	36	**4h**	63
9	4-CH_3Bn	36	**4i**	43
10	2-CH_3Bn	24	**4j**	60

[a]Reaction conditions: allenoate **1** (0.6 mmol), methyleneindolinone **2a** (0.5 mmol), and 1.5 equiv of $AlCl_3$ in DCE (5 mL) under reflux. [b]Isolated yields.

allenoates **1** were used under the standard reaction conditions. To our delight, all reactions proceeded well to produce the corresponding products **4** (Table 3). When R^2 was changed from Me to CH_2Ph (Bn) and other substituents, the yields did not decreased significantly. For instance, the reaction of 4-NO_2Bn-substituted allenoate and methyleneindolinone **2a** produced **4c** in 75% yield (Table 3, entry 3). Moreover, the structure of **4c** (CCDC 1014497) was unambiguously confirmed by single-crystal X-ray analysis (see Supporting Information).[18]

Although the mechanism of the above cyclization reaction has not been unequivocally established, one reasonable pathway is outlined in Scheme 3. The beginning of the cyclization involves Michael addition of allenoate **1** and methyleneindolinone **2**. From a mechanistic standpoint, both the external and internal site of allenoate can be approached in the Michael addition. But the present transformation is obviously highlighted by the excellent regioselectivity observed. As shown in Scheme 3, only the more electron-rich external bond of the allenic fragment is used to furnish the cyclization. Then the in situ generated carbocation **A** is trapped by a chloride anion

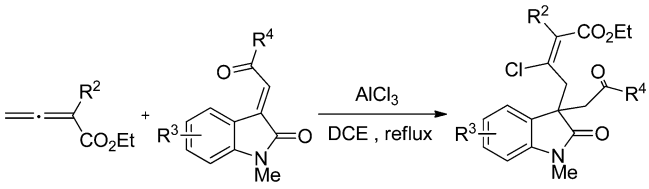
Scheme 3. Proposed Mechanism



derived from $AlCl_3$. With the aid of aluminum, the ethoxy group can act as a leaving group to facilitate the key Dieckmann-type transformation, presented in the proposed transition state **C**, which leads to the final cyclization product **3**.

To further demonstrate the versatility of the present method, the structurally varied methyleneindolinones **5** were also tested under standard reaction conditions. In this case, however, no corresponding cyclization product was obtained (Table 4). In

Table 4. $AlCl_3$-Promoted Michael Addition of Methyleneindolinone 5 with Allenoate 1[a]



1 5 6

entry	R^2	R^3	R^4	time (h)	product	yield[b] (%)
1	H	H	Ph	20	**6a**	72
2	H	H	4-FPh	15	**6b**	73
3	H	H	4-ClPh	15	**6c**	75
4	H	H	4-BrPh	20	**6d**	61
5	H	5-Cl	Ph	20	**6e**	79
6	H	5-Br	Ph	20	**6f**	75
7	H	5-Me	Ph	20	**6g**	66
8	Me	H	Ph	24	**6h**	61
9	Bn	H	Ph	24	**6i**	72

[a]Reaction conditions: allenoate **1** (0.6 mmol), methyleneindolinone **5** (0.5 mmol), and 1.5 equiv of $AlCl_3$ in DCE (5 mL) under reflux. [b]Isolated yields.

contrast, a different Michael addition took place to give rise to a new product **6**, thus constituting a novel carbon−carbon bond-forming method. During this process, the structure of **6e** (CCDC 1014496) was also confirmed by X-ray analysis (see Supporting Information).[19] The substitution patterns of R^4 bearing the carbonyl group were first investigated (Table 4, entries 1−4). Then the possibilities with electron-deficient and -rich substituents on the aromatic ring of the oxindole skeleton were subsequently verified (Table 4, entries 5−7). Substituted allenoates were also included to further establish the scope and limitations (Table 4, entries 8 and 9).

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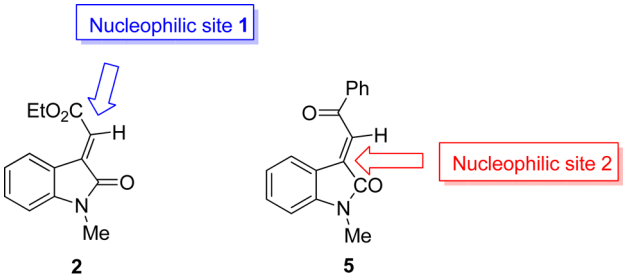
From the above-mentioned experimental results, we can see that two kinds of Michael addition patterns exist (Scheme 4).

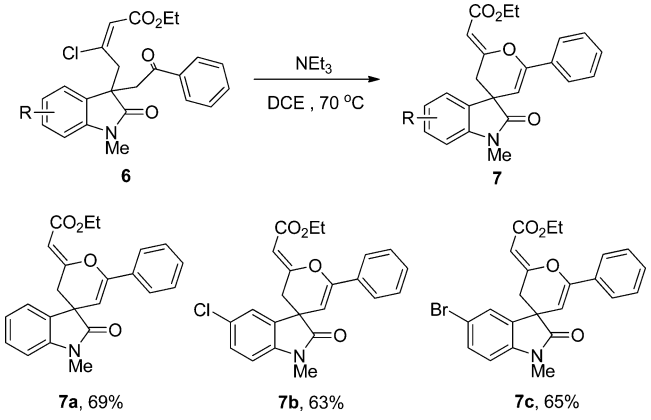
Scheme 4. Regioselective Michael (1,4-) Addition of Allenoate



When substrate **2** bearing an ester group was used, nuclophilic addition started from the exocyclic vinyl carbon. In contrast, the nucleophilic site transferred to the internal position of the double bond when methyleneindolinone **5**, having a more electron-deficient carbonyl group, was employed. These experimental results also imply that the reaction behavior is heavily dependent on the electron-deficient degree of the carbon−carbon double bond. Remarkably, no cyclization products were obtained in reactions involving substrates **5**, which may result from the different addition patterns in the first step.

Subsequently, **6** was further converted to other ring systems for the illustration of its potential applications (Scheme 5).

Scheme 5. Further Application of 6

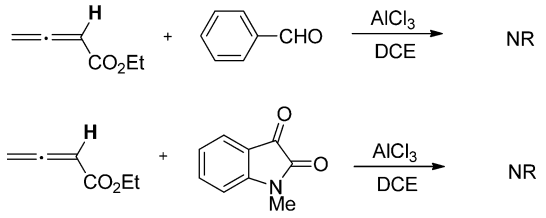


Treatment of **6** with Et_3N as base essentially resulted in the cyclization product **7**. The nucleophilic addition followed by cyclization enabled rapid access to spirocyclic oxindole-dihydropyrans, which may require tedious synthetic steps by traditional methods.

After the successful development of the regioselective Michael reactions involving methyleneindolinones, we were also interested in further application of the present strategy. In this process, however, no reactions occurred when carbonyl-containing substrates benzaldehyde and isatin were used (Scheme 6). The reasons are not clear at present, but one possibility may be insufficient reactivity of the corresponding carbonyl group. Further experiments are still underway in our laboratory.

In conclusion, we have disclosed a novel, efficient cyclization reaction to generate functionalized spirocyclic oxindole-cyclohexenones from readily available starting materials. Flexibility of this method also allows the rapid synthesis of spirocyclic oxindole-dihydropyrans by varying one of the components. The mechanistic proposal indicates that two kinds of Michael addition can take place depending on the electron-deficient degree of methyleneindolinone. Moreover, $AlCl_3$ acts as a chlorine source as well as catalyst, which is quite interesting. Another remarkable characteristic of this strategy is that substituted allenoate is used as four-carbon component (4C) to form the ring, which is very rare. This method is also distinguished by its convenient experimental setup and excellent regioselectivity. As a result, the present protocol has potential to be applied in medicinal and synthetic chemistry.

Scheme 6. Controlled Experiments with Carbonyl Compounds



EXPERIMENTAL SECTION

General Information. NMR spectra were recorded on a 500 MHz spectrometer (500 MHz for ^1H NMR and 125 MHz for ^{13}C NMR) with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal reference. ^1H NMR spectral data are reported as follows: chemical shift (δ in parts per million, ppm), multiplicity, integration, and coupling constant (in hertz). ^{13}C NMR spectral data were reported in terms of the chemical shift. The following abbreviations are used to indicate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. IR spectra were recorded on a Fourier transform infrared (FT-IR) spectrometer. High-resolution mass spectra (HRMS) were recorded on a FTMS instrument in electrospray ionization (ESI) mode and reported as m/z. Melting points were obtained on a digital melting point apparatus without correction. Unless otherwise stated, all reagents were commercially purchased and used without further purification. All allenoates **1** were synthesized according to procedures reported previously.[20,12] Substrate oxindolylidene acetates **2** and arenacylideneoxindoles **5** were synthesized according to procedures reported previously.[21−24]

Typical Procedures for Preparation of Allenoate 1a. Triphenylphosphine (131.0 g, 500 mmol) was dissolved in benzene (500 mL), and ethyl bromoacetate (83.5 g, 500 mmol) was added. The reaction mixture was vigorously stirred at room temperature and monitored (by thin-layer chromatography, TLC) for disappearance of the substrate. The resulting white precipitate was filtered off and washed with benzene to give the phosphonium salt in quantitative yield. Residual benzene was removed under vacuum, and a mixture of dichloromethane and *n*-hexane (2:1, 1.2 L) was subsequently added. The flask was cooled in an ice bath, followed by the addition of triethylamine (72.7 mL, 523 mmol). The mixture was stirred for 2 h, at which point triethylamine (72.7 mL, 523 mmol) was added, and then acetyl chloride (37.1 mL, 523 mmol) was added dropwise over 2 h. The reaction mixture was stirred in its ice bath overnight. The copious precipitate was filtered and rinsed with a mixture of *n*-hexane and dichloromethane (3:1). The resulting crude allenoate solution was concentrated to 300 mL; additional solid precipitate was filtered off after the addition of hexane (300 mL). The resulting solution was concentrated at room temperature and the residue was further distilled under reduced pressure (10 mmHg) to give the desired allenoate **1a**.[20]

Typical Procedure for Preparation of Substituted Allenoate 1. To a stirred solution of (carbethoxymethylene)triphenylphosphorane (10.0 g, 27.27 mmol) in chloroform (80 mL) was added 1.27

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equiv of (bromomethyl)benzene at room temperature. The reaction mixture was refluxed until (carbethoxymethylene)triphenylphosphorane (monitored by TLC) disappeared. The solvent and excess (bromomethyl)benzene were evaporated under reduced pressure. To the resulting phosphornium salt were added dichloromethane (100 mL) and 2.2 equiv of triethylamine (8.4 mL). After the mixture was stirred for about 1 h, 1.0 equiv of acetyl chloride (1.96 mL) was added dropwise over 30 min. Then the reaction mixture was stirred overnight. The resulting mixture was poured into a Buchner funnel that was packed with silica gel and was washed with dichloromethane for several times. The combined filtrate was carefully concentrated, and the residue was subjected to flash column chromatography (20:1 petroleum ether/ethyl acetate eluent) to provide allenoate **1c**.[12]

Representative Procedures for Preparation of Methyleneindolinone. *a. General Procedure for Synthesis of N-methylisatins.* Isatin (3.0 mmol) was dissolved in anhydrous *N*,*N*-dimethylformamide (DMF, 15 mL), and the resultant solution was cooled to 0 °C (ice bath), whereupon sodium hydride 80% dispersion in oil (105 mg, 3.5 mmol) was added in one portion and stirred for 5 min. Iodomethane (3.5 mmol) was added and the reaction was stirred at 0 °C for 30 min. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic portions were washed with water and brine, dried ($MgSO_4$), filtered, and concentrated to give the crude product, which was used without further purification.

b. General Procedure for Synthesis of Methyleneindolinone ***2****.* To a stirred solution of Wittig reagent (10 mmol) in dichloromethane (DCM, 5 mL) at 0 °C, was slowly added the solution of the appropriate isatin crude product (10 mmol) in DCM. The resulting mixture was stirred at room temperature for 2 h and then concentrated under reduced vacuum. The residue was purified by column chromatography (petroleum ether/dichloromethane = 10/1) to give oxindolylidene acetates **2**.

General Procedure for Syntheses of Spirocyclic Oxindoles 3 and 4. Allenoate **1** (0.6 mmol) and methyleneindolinone **2** (0.5 mmol) were placed in 5 mL of DCE in a flask. Then $AlCl_3$ (1.5 equiv) was added to this solution under nitrogen atmosphere. The mixture was stirred under reflux for several hours, and the reation progress was monitored by TLC detection. After completion, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (silica 200−300, eluent petroleum ether/ethyl acetate) to afford the product **3** or **4**.

Ethyl 4-Chloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3a)****.* 88.2 mg, 53% yield; white solid, mp 158−160 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.34 (td, 1H, J = 8.0, 1.5 Hz), 7.10−7.05 (m, 2H), 6.85 (d, 1H, J = 8.0 Hz), 6.37 (d, 1H, J = 2.0 Hz), 3.83 (ddd, 1H, J = 18.0, 11.5, 2.5 Hz), 3.72 (dd, 1H, J = 11.5, 5.0 Hz), 3.20 (s, 3H), 2.99 (dd, 1H, J = 18.0, 5.0 Hz), 0.97 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.7, 171.6, 169.2, 158.1, 144.9, 129.4, 127.5, 126.6, 123.2, 122.9, 108.4, 61.4, 59.6, 47.2, 33.8, 26.5, 13.7. HRMS (ESI) calcd for $C_{17}H_{17}ClNO_4$ $[M + H]^+$ 334.0846, found 334.0841.

Ethyl 4-Chloro-5′-fluoro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3b)****.* 98.3 mg, 56% yield; white solid, mp 137−139 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.04 (td, 1H, J = 8.5, 2.0 Hz), 6.82 (dd, 1H, J = 7.5, 2.5 Hz), 6.78 (dd, 1H, J = 8.5, 4.0 Hz), 6.37 (d, 1H, J = 2.5 Hz), 4.01−3.90 (m, 2H), 3.84 (ddd, 1H, J = 18.0, 11.5, 2.0 Hz), 3.69 (dd, 1H, J = 12.0, 5.5 Hz), 3.19 (d, 3H, J = 0.5 Hz), 3.00 (dd, 1H, J = 18.5, 5.5 Hz), 1.03 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.1, 171.3, 159.2 (d, $^1J_{C-F}$ = 240.0 Hz), 158.4, 141.0 (d, $^4J_{C-F}$ = 1.3 Hz), 129.2 (d, $^3J_{C-F}$ = 8.8 Hz), 126.4, 115.5 (d, $^2J_{C-F}$ = 22.5 Hz), 111.5 (d, $^2J_{C-F}$ = 25.0 Hz), 108 (d, $^3J_{C-F}$ = 8.8 Hz), 61.6, 60.0, 47.0, 33.7, 27.0, 13.8. HRMS (ESI) calcd for $C_{17}H_{15}ClFNNaO_4$ $[M + Na]^+$ 374.0571, found 374.0585.

(E)-Ethyl 4,5′-Dichloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3c)****.* 111.9 mg, 61% yield; white solid, mp 139−141 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.31 (dd, 1H, J = 8.5, 2.0 Hz), 7.03 (d, 1H, J = 2.0 Hz), 6.78 (d, 1H, J = 8.5 Hz), 6.36 (d, 1H, J = 2.0 Hz), 4.00−3.92 (m, 2H), 3.82 (ddd, 1H, J = 18.5, 12.0, 2.5 Hz), 3.69 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.01 (dd, 1H, J = 18.0, 5.5 Hz), 1.03 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 188.9, 171.3, 169.0, 158.4, 143.7, 129.4, 129.3, 128.2, 126.4, 123.7, 109.3, 61.7, 59.8, 46.9, 33.7, 26.7, 13.8. HRMS (ESI) calcd for $C_{17}H_{16}Cl_2NO_4$ $[M + H]^+$ 368.0456, found 368.0462.

Ethyl 5′-Bromo-4-chloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3d)****.* 102.8 mg, 50% yield; white solid, mp 138−139 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.46 (dd, 1H, J = 8.0, 1.5 Hz), 7.16 (d, 1H, J = 2.0 Hz), 6.73 (d, 1H, J = 7.5 Hz), 8.36 (d, 1H, J = 2.0 Hz), 4.01−3.91 (m, 2H), 3.81 (ddd, 1H, J = 18.5, 12.0, 2.5 Hz), 3.69 (dd, 1H, J = 11.5, 5.0 Hz), 3.18 (s, 3H), 3.01 (dd, 1H, J = 18.0, 5.0 Hz), 1.04 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 188.9, 171.2, 169.0, 158.4, 144.2, 132.2, 129.8, 126.4, 115.4, 109.8, 61.7, 59.7, 46.9, 33.7, 26.6, 13.8. HRMS (ESI) calcd for $C_{17}H_{16}BrClNO_4$ $[M + H]^+$ 411.9951, found 411.9962.

Ethyl 4-Chloro-1′,5′-dimethyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3e)****.* 79.8 mg, 46% yield; white solid, mp 139−142 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.12 (dd, 1H, J = 8.0, 1.0 Hz), 6.87 (s, 1H), 6.74 (d, 1H, J = 8.0 Hz), 6.37 (d, 1H, J = 2.0 Hz), 3.98−3.89 (m, 2H), 3.84 (ddd, 1H, J = 18.0, 11.5, 2.5 Hz), 3.70 (dd, 1H, J = 11.5, 5.0 Hz), 3.17 (s, 3H), 2.98 (dd, 1H, J = 18.0, 5.0 Hz), 2.32 (s, 3H), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.9, 171.6, 169.2, 158.1, 142.5, 132.4, 129.7, 127.5, 126.6, 124.0, 108.2, 61.4, 59.7, 47.2, 33.8, 26.5, 21.2, 13.7. HRMS (ESI) calcd for $C_{18}H_{19}ClNO_4$ $[M + H]^+$ 348.1003, found 348.0998.

Ethyl 4-Chloro-5′-methoxy-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3f)****.* 88.9 mg, 49% yield; white solid, mp 145−147 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 6.85 (dd, 1H, J = 8.5, 2.5 Hz), 6.76 (d, 1H, J = 8.5 Hz), 6.66 (d, 1H, J = 2.5 Hz), 6.37 (d, 1H, J = 2.0 Hz), 3.98−3.90 (m, 2H), 3.84 (ddd, 1H, J = 18.0, 11.5, 2.5 Hz), 3.77 (s, 3H), 3.69 (dd, 1H, J = 11.5, 5.0 Hz), 3.17 (s, 3H), 2.99 (dd, 1H, J = 18.5, 5.0 Hz), 1.00 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.7, 171.3, 169.1, 158.2, 156.1, 138.5, 128.9, 126.6, 113.3, 110.9, 108.7, 61.5, 60.0, 55.8, 47.1, 33.9, 26.6, 13.8. HRMS (ESI) calcd for $C_{18}H_{19}ClNO_5$ $[M + H]^+$ 364.0952, found 364.0953.

Ethyl 4′-Bromo-4-chloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3g)****.* 123.3 mg, 60% yield; white solid, mp 127−129 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.23−7.17 (m, 2H), 6.79 (dd, 1H, J = 7.5, 1.5 Hz), 6.40 (d, 1H, J = 2.0 Hz), 4.61−4.58 (m, 1H), 3.99−3.92 (m, 2H), 3.86 (ddd, 1H, J = 18.5, 12.0, 2.5 Hz), 3.18 (s, 3H), 3.02 (dd, 1H, J = 18.5, 5.5 Hz), 1.02 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 187.5, 170.9, 169.3, 158.5, 147.0, 130.8, 126.9, 126.6, 126.5, 118.7, 107.4, 61.5, 61.1, 43.8, 33.4, 26.7, 13.8. HRMS (ESI) calcd for $C_{17}H_{16}BrClNO_4$ $[M + H]^+$ 411.9951, found 411.9960.

Ethyl 6′-Bromo-4-chloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3h)****.* 139.7 mg, 68% yield; white solid, mp 143−144 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.21 (dd, 1H, J = 8.0, 1.5 Hz), 7.00 (d, 1H, J = 1.5 Hz), 6.90 (d, 1H, J = 8.0 Hz), 6.36 (d, 1H, J = 2.0 Hz), 4.01−3.90 (m, 2H), 3.81 (ddd, 1H, J = 18.0, 11.5, 2.5 Hz), 3.70 (dd, 1H, J = 11.5, 5.0 Hz), 3.18 (s, 3H), 2.99 (dd, 1H, J = 18.0, 5.0 Hz), 1.04 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.0, 171.5, 169.0, 158.3, 146.4, 126.6, 126.4, 125.7, 124.4, 123.1, 112.0, 61.7, 59.4, 46.9, 33.7, 26.7, 13.8. HRMS (ESI) calcd for $C_{17}H_{16}BrClNO_4$ $[M + H]^+$ 411.9951, found 411.9959.

Ethyl 4-Chloro-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3i)****.* 51.0 mg, 32% yield; white solid, mp 136−138 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.83 (s, 1H), 7.29−7.25 (m, 1H), 7.08−7.04 (m, 2H), 6.87 (d, 1H, J = 8.0 Hz), 6.39 (d, 1H, J = 2.0 Hz), 4.00−3.93 (m, 2H), 3.83 (ddd, 1H, J = 18.0, 11.5, 2.5 Hz), 3.73 (dd, 1H, J = 11.5, 5.0 Hz), 2.99 (dd, 1H, J = 18.0, 5.0 Hz), 1.00 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.4, 173.1, 169.3, 158.1, 141.8, 129.4, 128.1, 126.5, 123.5, 122.9, 110.0, 61.6, 60.0, 47.2, 33.7, 13.7. HRMS (ESI) calcd for $C_{16}H_{15}ClNO_4$ $[M + H]^+$ 320.0690, found 320.0683.

Ethyl 1′-Benzyl-4-chloro-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate ***(3j)****.* 87.9 mg, 43% yield; white oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.45 (d, 2H, J = 7.5 Hz), 7.34 (t, 2H, J

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= 7.0 Hz), 7.27 (t, 1H, J = 7.5 Hz), 7.18 (td, 1H, J = 8.0, 1.0 Hz), 7.09 (d, 1H, J = 7.0 Hz), 6.95 (td, 1H, J = 7.5, 0.5 Hz), 6.71 (d, 1H, J = 7.5 Hz), 6.40 (d, 1H, J = 2.0 Hz), 5.23 (d, 1H, J = 15.5 Hz), 4.76 (d, 1H, J = 15.5 Hz), 4.07−4.04 (m, 1H), 3.99−3.92 (m, 1H), 3.86−3.80 (m, 1H), 3.43 (ddd, 1H, J = 20.0, 11.5, 2.5 Hz), 3.28 (dd, 1H, J = 20.0, 6.5 Hz), 0.90 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.7, 174.9, 168.9, 156.7, 144.1, 135.2, 129.5, 128.8, 127.6, 127.4, 127.0, 125.9, 123.1, 122.6, 110.0, 61.5, 60.2, 44.3, 44.0, 33.3, 13.7. HRMS (ESI) calcd for $C_{23}H_{21}ClNO_4$ $[M + H]^+$ 410.1159, found 410.1155.

*Ethyl 4-Chloro-1′,3-dimethyl-2,2′-dioxospiro[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4a**).* 98.9 mg, 57% yield; white solid, mp 120−122 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.32 (td, 1H, J = 7.5, 2.0 Hz), 7.09−7.04 (m, 2H), 6.84 (d, 1H, J = 8.0 Hz), 3.96−3.83 (m, 3H), 3.70 (dd, 1H, J = 11.5, 5.0 Hz), 3.19 (s, 3H), 3.02 (ddd, 1H, J = 18.0, 5.5, 1.5 Hz), 1.97−1.96 (m, 3H), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.7, 171.8, 169.4, 152.9, 144.8, 132.1, 129.2, 128.3, 123.0, 122.8, 108.4, 61.3, 59.8, 46.6, 33.9, 26.5, 13.8, 13.2. HRMS (ESI) calcd for $C_{18}H_{19}ClNO_4$ $[M + H]^+$ 348.1003, found 348.0998.

*Ethyl 3-Benzyl-4-chloro-1′-methyl-2,2′-dioxospiro[cyclohex[3]-ene-1,3′-indoline]-6-carboxylate (**4b**).* 105.8 mg, 50% yield; white solid, mp 172−174 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.31 (td, 1H, J = 7.5, 1.5 Hz), 7.25−7.24 (m, 4H), 7.18−7.15 (m, 1H), 7.05 (td, 1H, J = 7.5, 0.5 Hz), 7.01 (dd, 1H, J = 7.0, 1.0 Hz), 6.83 (d, 1H, J = 8.0 Hz), 3.97−3.89 (m, 3H), 3.84 (s, 2H), 3.70 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.07 (dd, 1H, J = 18.0, 5.5 Hz), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.5, 171.5, 169.4, 154.3, 144.8, 138.2, 135.2, 129.3, 128.6, 128.4, 128.1, 126.2, 123.1, 122.8, 108.4, 61.4, 59.9, 46.6, 34.2, 33.0, 26.5, 13.7. HRMS (ESI) calcd for $C_{24}H_{23}ClNO_4$ $[M + H]^+$ 424.1316, found 424.1330.

*Ethyl 4-Chloro-1′-methyl-3-(4-nitrobenzyl)-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4c**).* 175.5 mg, 75% yield; white solid, mp 176−178 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 8.08 (d, 2H, J = 9.0 Hz), 7.38 (d, 2H, J = 9.0 Hz), 7.32 (td, 1H, J = 7.5, 1.5 Hz), 7.06 (td, 1H, J = 7.5, 1.0 Hz), 7.02 (dd, 1H, J = 7.5, 1.0 Hz), 6.83 (d, 1H, J = 8.0 Hz), 3.97−3.88 (m, 5H), 3.72 (dd, 1H, J = 11.5, 5.5 Hz), 3.17 (s, 3H), 3.10 (ddd, 1H, J = 18.5, 5.5, 0.5 Hz), 0.96 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.5, 171.2, 169.1, 155.4, 146.6, 145.9, 144.7, 133.9, 129.5, 129.3, 127.5, 123.7, 123.2, 122.9, 108.5, 61.5, 59.8, 46.5, 34.2, 33.0, 26.6, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}ClN_2O_6$ $[M + H]^+$ 469.1166, found 469.1162.

*Ethyl 4-Chloro-1′-methyl-3-(3-nitrobenzyl)-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4d**).* 170.8 mg, 73% yield; white solid, mp 167−169 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 8.06 (t, 1H, J = 1.5 Hz), 8.01 (dd, 1H, J = 8.0, 1.5 Hz), 7.55 (d, 1H, J = 7.5 Hz), 7.39 (t, 1H, J = 8.0 Hz), 7.32 (td, 1H, J = 7.5, 1.5 Hz), 7.08−7.02 (m, 2H), 6.83 (d, 1H, J = 7.5 Hz), 3.97−3.88 (m, 5H), 3.72 (dd, 1H, J = 11.5, 5.5 Hz), 3.17 (s, 3H), 3.13−3.08 (m, 1H), 0.97 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.5, 171.2, 169.2, 155.3, 148.3, 144.7, 140.2, 134.7, 134.0, 129.4, 129.3, 127.5, 123.5, 123.2, 122.9, 121.5, 108.5, 61.5, 59.9, 46.5, 34.2, 32.7, 26.6, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}ClN_2O_6$ $[M + H]^+$ 469.1166, found 469.1159.

*Ethyl 4-Chloro-1′-methyl-3-(2-nitrobenzyl)-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4e**).* 105.3 mg, 45% yield; white solid, mp 141−143 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.89 (dd, 1H, J = 8.0, 1.0 Hz), 7.49 (td, 1H, J = 7.5, 1.0 Hz), 7.33−7.29 (m, 3H), 7.07−7.06 (m, 2H), 6.82 (d, 1H, J = 8.0 Hz), 4.24 (d, 1H, J = 16.5 Hz), 4.12 (d, 1H, J = 16.5 Hz), 4.02−3.90 (m, 3H), 3.76 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.11 (ddd, 1H, J = 18.5, 5.5, 1.0 Hz), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.1, 171.4, 169.2, 156.2, 149.2, 144.7, 133.5, 133.2, 132.9, 129.6, 129.4, 127.6, 127.1, 124.7, 123.3, 123.0, 108.4, 61.5, 59.8, 46.7, 34.3, 29.7, 26.6, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}ClN_2O_6$ $[M + H]^+$ 469.1166, found 469.1166.

*Ethyl 4-Chloro-3-(3-fluorobenzyl)-1′-methyl-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4f**).* 121.3 mg, 55% yield; white solid, mp 138−139 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.32 (td, 1H, J = 7.5, 1.5 Hz), 7.21−7.17 (m, 1H), 7.06 (td, 1H, J = 7.5, 1.0 Hz), 7.02−7.00 (m, 2H), 6.94 (dd, 1H, J = 10.0, 2.0 Hz), 6.87−6.82 (m, 2H), 3.97−3.89 (m, 3H), 3.85−3.79 (m, 2H), 3.70 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.08 (dd, 1H, J = 18.0, 5.5 Hz), 0.97 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.4, 171.4, 169.3, 162.8 (d, $^1J_{C-F}$ = 242.5 Hz), 154.6, 144.7, 140.6 (d, $^3J_{C-F}$ = 7.5 Hz), 134.6, 129.7 (d, $^3J_{C-F}$ = 8.8 Hz), 129.3, 127.8, 124.2 (d, $^4J_{C-F}$ = 3.8 Hz), 123.2, 122.9, 115.4 (d, $^2J_{C-F}$ = 22.5 Hz), 113.1 (d, $^2J_{C-F}$ = 21.3 Hz), 108.4, 61.4, 59.8, 46.5, 34.2, 32.7, 32.7, 30.9, 26.5, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}ClFNO_4$ $[M + H]^+$ 442.1221, found 442.1224.

*Ethyl 4-Chloro-3-(3-chlorobenzyl)-1′-methyl-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4g**).* 116.5 mg, 51% yield; white solid, mp 183−185 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.32 (td, 1H, J = 7.5, 1.5 Hz), 7.21 (s, 1H), 7.18−7.10 (m, 3H), 7.06 (td, 1H, J = 7.5, 0.5 Hz), 7.02 (dd, 1H, J = 7.5, 1.0 Hz), 6.83 (d, 1H, J = 8.0 Hz), 3.98−3.87 (m, 3H), 3.83−3.77 (m, 2H), 3.70 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.08 (dd, 1H, J = 18.5, 5.5 Hz), 0.98 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.4, 171.4, 169.3, 154.6, 144.7, 140.2, 134.6, 134.1, 129.6, 129.3, 128.7, 127.8, 126.7, 126.5, 123.2, 122.9, 108.4, 61.4, 59.9, 46.5, 34.2, 32.7, 26.5, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}Cl_2NO_4$ $[M + H]^+$ 458.0926, found 458.0934.

*Ethyl 3-(4-Bromobenzyl)-4-chloro-1′-methyl-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4h**).* 157.8 mg, 63% yield; white solid, mp 181−183 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.36−7.34 (m, 2H), 7.32 (td, 1H, J = 8.0, 1.5 Hz), 7.11 (d, 2H, J = 8.5 Hz), 7.06 (td, 1H, J = 7.5, 1.0 Hz), 7.01 (dd, 1H, J = 7.5, 1.0 Hz), 6.83 (d, 1H, J = 8.0 Hz), 3.97−3.87 (m, 3H), 3.80−3.74 (m, 2H), 3.69 (dd, 1H, J = 11.5, 5.5 Hz), 3.17 (s, 3H), 3.07 (dd, 1H, J = 18.0, 5.5 Hz), 0.97 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.4, 171.4, 169.2, 154.5, 144.7, 137.2, 134.7, 131.4, 130.3, 129.3, 127.8, 123.2, 122.9, 120.1, 108.4, 61.4, 59.8, 46.5, 34.2, 32.5, 26.6, 13.7. HRMS (ESI) calcd for $C_{24}H_{22}BrClNO_4$ $[M + H]^+$ 502.0421, found 502.0414.

*Ethyl 4-Chloro-1′-methyl-3-(4-methylbenzyl)-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4i**).* 94.0 mg, 43% yield; white solid, mp 195−196 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.31 (td, 1H, J = 8.0, 1.0 Hz), 7.13 (d, 2H, J = 8.0 Hz), 7.06−7.04 (m, 3H), 7.01 (d, 1H, J = 7.0 Hz), 6.82 (d, 1H, J = 8.0 Hz), 3.96−3.88 (m, 3H), 3.79 (s, 2H), 3.69 (dd, 1H, J = 11.5, 5.5 Hz), 3.18 (s, 3H), 3.05 (dd, 1H, J = 18.0, 5.5 Hz), 2.29 (s, 3H), 0.97 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.4, 171.5, 169.4, 154.1, 144.8, 135.6, 135.4, 135.1, 129.2, 129.1, 128.4, 128.1, 123.1, 122.8, 108.3, 61.4, 59.9, 46.6, 34.2, 32.6, 26.5, 21.0, 13.7. HRMS (ESI) calcd for $C_{25}H_{25}ClNO_4$ $[M + H]^+$ 438.1472, found 438.1463.

*Ethyl 4-Chloro-1′-methyl-3-(2-methylbenzyl)-2,2′-dioxospiro-[cyclohex[3]ene-1,3′-indoline]-6-carboxylate (**4j**).* 131.1 mg, 60% yield; white solid, mp 139−141 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.32−7.29 (m, 1H), 7.09−7.02 (m, 6H), 6.81 (d, 1H, J = 8.0 Hz), 4.04−3.90 (m, 3H), 3.84−3.72 (m, 3H), 3.18 (s, 3H), 3.11 (dd, 1H, J = 18.0, 5.5 Hz), 2.33 (s, 3H), 0.99 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 189.2, 171.5, 169.3, 154.9, 144.8, 136.1, 135.9, 134.9, 130.0, 129.2, 128.0, 126.8, 126.1, 126.0, 123.2, 122.8, 108.3, 61.4, 60.0, 46.8, 34.2, 30.0, 26.5, 19.8, 13.8. HRMS (ESI) calcd for $C_{25}H_{25}ClNO_4$ $[M + H]^+$ 438.1472, found 438.1468.

General Procedure for Syntheses of Oxindole 6. Allenoate **1** (0.6 mmol) and arenacylideneoxindoles **4** (0.5 mmol) were placed in 5 mL of DCE in a flask. Then $AlCl_3$ (1.5 equiv) was added to this solution under nitrogen atmosphere. The mixture was stirred under reflux for several hours, and the reaction progress was monitored by TLC detection. After completion, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (silica 200−300; eluant petroleum ether/ethyl acetate) to afford the product **6**.

*Ethyl 3-Chloro-4-[1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)-indolin-3-yl]but-2-enoate (**6a**).* 148.0 mg, 72% yield; pale yellow oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.83 (d, 2H, J = 7.0 Hz), 7.51 (t, 1H, J = 7.5 Hz), 7.39 (t, 2H, J = 8.0 Hz), 7.24 (td, 1H, J = 8.0, 1.0 Hz), 7.11 (dd, 1H, J = 7.5, 1.0 Hz), 6.89−6.87 (m, 2H), 5.95 (s,

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1H), 4.21 (d, 1H, J = 13.5 Hz), 4.08 (q, 2H, J = 7.0 Hz), 3.91 (d, 1H, J = 18.0 Hz), 3.74 (d, 1H, J = 18.0 Hz), 3.30 (s, 3H), 3.20 (d, 1H, J = 13.5 Hz), 1.23 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.5, 178.8, 164.2, 149.8, 144.6, 136.3, 133.3, 129.7, 128.5, 128.4, 128.0, 123.1, 122.4, 121.7, 108.1, 60.6, 49.2, 45.5, 41.9, 26.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{23}ClNO_4$ $[M + H]^+$ 412.1316, found 412.1311.

*Ethyl 3-Chloro-4-{3-[2-(4-fluorophenyl)-2-oxoethyl]-1-methyl-2-oxoindolin-3-yl}but-2-enoate (**6b**).* 156.6 mg, 73% yield; white solid, mp 159−161 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.86−7.83 (m, 2H), 7.24 (td, 1H, J = 8.0, 1.0 Hz), 7.10 (dd, 1H, J = 8.0, 1.0 Hz), 7.05 (t, 2H, J = 8.5 Hz), 6.88 (t, 2H, J = 7.0 Hz), 5.94 (s, 1H), 4.20 (d, 1H, J = 13.5 Hz), 4.09−4.05 (m, 2H), 3.85 (d, 1H, J = 18.0 Hz), 3.71 (d, 1H, J = 18.0 Hz), 3.29 (s, 3H), 3.19 (d, 1H, J = 13.5 Hz), 1.22 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 193.9, 178.7, 165.8 (d, $^1J_{C-F}$ = 252.5 Hz), 164.2, 149.7, 144.6, 132.7 (d, $^4J_{C-F}$ = 2.5 Hz), 130.6 (d, $^3J_{C-F}$ = 8.8 Hz), 129.6, 128.5, 123.1, 122.5, 121.7, 115.6 (d, $^2J_{C-F}$ = 22.5 Hz), 108.1, 60.6, 49.1, 45.3, 41.9, 26.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}ClFNO_4$ $[M + H]^+$ 430.1221, found 430.1225.

*Ethyl 3-Chloro-4-{3-[2-(4-chlorophenyl)-2-oxoethyl]-1-methyl-2-oxoindolin-3-yl}but-2-enoate (**6c**).* 166.9 mg, 75% yield; white solid, mp 144−146 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.75 (d, 2H, J = 8.5 Hz), 7.35 (d, 2H, J = 9.5 Hz), 7.23 (t, 1H, J = 8.0 Hz), 7.10 (d, 1H, J = 7.0 Hz), 6.88 (t, 2H, J = 8.0 Hz), 5.93 (s, 1H), 4.20 (d, 1H, J = 13.5 Hz), 4.09−4.04 (m, 2H), 3.84 (d, 1H, J = 17.5 Hz), 3.70 (d, 1H, J = 18.0 Hz), 3.28 (s, 3H), 3.18 (d, 1H, J = 13.5 Hz), 1.22 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 194.3, 178.7, 164.2, 149.7, 144.6, 139.7, 134.6, 129.5, 129.4, 128.8, 128.5, 123.1, 122.5, 121.7, 108.1, 60.6, 49.1, 45.4, 41.9, 26.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}Cl_2NO_4$ $[M + H]^+$ 446.0926, found 446.0929.

*Ethyl 4-{3-[2-(4-Bromophenyl)-2-oxoethyl]-1-methyl-2-oxoindolin-3-yl}-3-chlorobut-2-enoate (**6d**).* 149.1 mg, 61% yield; white solid, mp 123−125 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.67 (d, 2H, J = 8.5 Hz), 7.52 (d, 2H, J = 8.5 Hz), 7.24 (td, 1H, J = 8.0, 1.0 Hz), 7.10 (d, 1H, J = 7.0 Hz), 6.88 (t, 2H, J = 8.0 Hz), 5.93 (s, 1H), 4.20 (d, 1H, J = 14.0 Hz), 4.09−4.04 (m, 2H), 3.83 (d, 1H, J = 18.0 Hz), 3.69 (d, 1H, J = 18.0 Hz), 3.28 (s, 3H), 3.18 (d, 1H, J = 13.5 Hz), 1.22 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 194.5, 178.6, 164.2, 149.7, 144.6, 135.0, 131.8, 129.5, 128.5, 123.1, 122.5, 121.7, 108.1, 60.6, 49.1, 45.3, 41.9, 26.6, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}BrClNO_4$ $[M + H]^+$ 490.0421, found 490.0418.

*Ethyl 3-Chloro-4-[5-chloro-1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl]but-2-enoate (**6e**).* 175.8 mg, 79% yield; white solid, mp 148−149 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.84 (dd, 2H, J = 8.0, 1.0 Hz), 7.53 (t, 1H, J = 7.5 Hz), 7.41 (t, 2H, J = 7.5 Hz), 7.21 (dd, 1H, J = 8.5, 2.0 Hz), 7.08 (d, 1H, J = 2.0 Hz), 6.80 (d, 1H, J = 8.5 Hz), 5.96 (s, 1H), 4.25 (d, 1H, J = 13.5 Hz), 4.17−4.06 (m, 2H), 3.88 (d, 1H, J = 18.0 Hz), 3.78 (d, 1H, J = 18.0 Hz), 3.28 (s, 3H), 3.15 (d, 1H, J = 14.0 Hz), 1.25 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.2, 178.3, 164.3, 149.2, 143.3, 136.0, 133.5, 131.5, 128.6, 128.3, 128.0, 127.0, 123.6, 122.7, 109.0, 60.8, 49.3, 45.5, 41.9, 26.8, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}Cl_2NO_4$ $[M + H]^+$ 446.0926, found 446.0916.

*Ethyl 4-[5-Bromo-1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)-indolin-3-yl]-3-chlorobut-2-enoate (**6f**).* 183.4 mg, 75% yield; white solid, mp 160−162 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.84 (dd, 2H, J = 8.0, 1.0 Hz), 7.21 (d, 1H, J = 2.0 Hz), 6.76 (d, 1H, J = 8.5 Hz), 5.96 (s, 1H), 4.24 (d, 1H, J = 13.5 Hz), 4.19−4.07 (m, 2H), 3.87 (d, 1H, J = 18.0 Hz), 3.78 (d, 1H, J = 18.0 Hz), 3.28 (s, 3H), 3.14 (d, 1H, J = 13.5 Hz), 1.26 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.2, 178.3, 164.3, 149.2, 143.8, 136.0, 133.5, 131.9, 131.2, 128.6, 128.0, 126.3, 122.7, 114.3, 109.5, 60.9, 49.3, 45.6, 41.9, 26.7, 14.1. HRMS (ESI) calcd for $C_{23}H_{22}BrClNO_4$ $[M + H]^+$ 490.0421, found 490.0407.

*Ethyl 3-Chloro-4-[1,5-dimethyl-2-oxo-3-(2-oxo-2-phenylethyl)-indolin-3-yl]but-2-enoate (**6g**).* 140.3 mg, 66% yield; white solid, mp 126−127 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.84 (dd, 2H, J = 8.5, 1.0 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.40 (t, 2H, J = 8.0 Hz), 7.03 (dd, 1H, J = 8.0, 1.0 Hz), 6.91 (t, 1H, J = 1.0 Hz), 6.76 (d, 1H, J = 8.0 Hz), 5.95 (s, 1H), 4.18 (d, 1H, J = 13.5 Hz), 4.07 (q, 2H, J = 7.0 Hz), 3.88 (d, 1H, J = 18.0 Hz), 3.74 (d, 1H, J = 18.0 Hz), 3.28 (s, 3H), 3.19 (d, 1H, J = 13.5 Hz), 2.20 (s, 3H), 1.23 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.4, 178.7, 164.2, 150.0, 142.2, 136.3, 133.2, 131.0, 129.7, 128.6, 128.5, 128.0, 124.0, 122.4, 107.8, 60.5, 49.2, 45.4, 42.0, 26.7, 21.0, 14.1. HRMS (ESI) calcd for $C_{24}H_{25}ClNO_4$ $[M + H]^+$ 426.1472, found 426.1465.

*Ethyl 3-Chloro-2-methyl-4-[1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl]but-2-enoate (**6h**).* 129.6 mg, 61% yield; pale yellow oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.82 (d, 2H, J = 7.0 Hz), 7.51 (t, 1H, J = 7.5 Hz), 7.39 (t, 2H, J = 8.0 Hz), 7.23 (td, 1H, J = 7.5, 1.0 Hz), 7.06 (dd, 1H, J = 7.0, 0.5 Hz), 6.90−6.85 (m, 2H), 4.05 (q, 2H, J = 7.0 Hz), 3.91 (d, 1H, J = 18.0 Hz), 3.86 (d, 1H, J = 14.0 Hz), 3.73 (d, 1H, J = 18.0 Hz), 3.32 (dd, 1H, J = 14.0, 1.0 Hz), 3.29 (s, 3H), 1.89 (s, 3H), 1.24 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.7, 179.2, 166.6, 144.6, 141.5, 136.4, 133.2, 130.2, 129.4, 128.5, 128.2, 128.0, 123.2, 121.7, 107.9, 61.1, 49.3, 45.2, 43.4, 26.6, 17.8, 14.0. HRMS (ESI) calcd for $C_{24}H_{25}ClNO_4$ $[M + H]^+$ 426.1472, found 426.1464.

*Ethyl 2-Benzyl-3-chloro-4-[1-methyl-2-oxo-3-(2-oxo-2-phenylethyl)indolin-3-yl]but-2-enoate (**6i**).* 180.4 mg, 72% yield; pale yellow oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.82 (dd, 2H, J = 8.0, 1.0 Hz), 7.51 (t, 1H, J = 7.5 Hz), 7.39 (t, 2H, J = 8.0 Hz), 7.29 (td, 1H, J = 7.5, 1.0 Hz), 7.17−7.14 (m, 4H), 6.89−6.86 (m, 2H), 6.78 (dd, 2H, J = 8.0, 2.0 Hz), 4.15 (d, 1H, J = 14.0 Hz), 4.04 (q, 2H, J = 7.0 Hz), 3.88 (d, 1H, J = 17.5 Hz), 3.80 (d, 1H, J = 15.0 Hz), 3.73−3.66 (m, 2H), 3.27 (s, 3H), 3.22 (d, 1H, J = 18.5 Hz), 1.14 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 195.6, 179.3, 166.0, 144.8, 143.0, 137.8, 136.4, 133.2, 132.4, 129.8, 128.5, 128.3, 128.2, 128.1, 128.0, 126.1, 123.7, 121.9, 108.1, 61.1, 49.3, 45.8, 43.7, 37.2, 26.6, 13.9. HRMS (ESI) calcd for $C_{30}H_{29}ClNO_4$ $[M + H]^+$ 502.1785, found 502.1781.

General Procedure for Syntheses of Spirocyclic Oxindole 7. To a solution of **6** (0.5 mmol) in 5 mL of DCE was added NEt_3 (0.2 mL, 3.0 equiv). The stirred mixture was heated at 70 °C for several hours, and the reaction progress was monitored by TLC detection. After completion, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (silica 200−300; eluant petroleum ether/ethyl acetate) to afford the desired product **7**.

*Ethyl 2-{1-Methyl-2-oxo-6′-phenylspiro[indoline-3,4′-pyran]-2′(3′H)-ylidene}acetate (**7a**).* 129.4 mg, 69% yield; yellow oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.58−7.56 (m, 2H), 7.33−7.28 (m, 5H), 7.10 (t, 1H, J = 7.5 Hz), 6.84 (d, 1H, J = 7.5 Hz), 5.12 (d, 1H, J = 2.0 Hz), 4.66 (d, 1H, J = 2.5 Hz), 4.22 (q, 2H, J = 7.0 Hz), 3.38 (d, 1H, J = 16.0 Hz), 3.28 (d, 1H, J = 16.0 Hz), 3.24 (s, 3H), 1.30 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 178.5, 169.1, 150.8, 147.4, 142.1, 135.7, 133.3, 128.9, 128.8, 128.2, 125.7, 124.8, 123.3, 108.0, 99.5, 96.3, 61.2, 48.7, 39.6, 26.7, 14.2. HRMS (ESI) calcd for $C_{23}H_{22}NO_4$ $[M + H]^+$ 376.1549, found 376.1555.

*Ethyl 2-{5-Chloro-1-methyl-2-oxo-6′-phenylspiro[indoline-3,4′-pyran]-2′(3′H)-ylidene}acetate (**7b**).* 128.8 mg, 63% yield; pale yellow oil. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.58−7.56 (m, 2H), 7.35−7.33 (m, 3H), 7.29−7.25 (m, 3H), 6.76 (d, 1H, J = 8.0 Hz), 5.09 (d, 1H, J = 2.0 Hz), 4.65 (d, 1H, J = 2.0 Hz), 4.22 (q, 2H, J = 7.0 Hz), 3.38 (d, 1H, J = 16.0 Hz), 3.29 (d, 1H, J = 16.0 Hz), 3.23 (s, 3H), 1.31 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 178.1, 168.9, 151.2, 147.8, 140.7, 137.2, 133.1, 129.1, 128.8, 128.7, 128.3, 126.1, 124.9, 109.0, 98.9, 95.6, 61.3, 48.9, 39.5, 26.8, 14.2. HRMS (ESI) calcd for $C_{23}H_{21}ClNO_4$ $[M + H]^+$ 410.1159, found 410.1159.

*Ethyl 2-{5-Bromo-1-methyl-2-oxo-6′-phenylspiro[indoline-3,4′-pyran]-2′(3′H)-ylidene}acetate (**7c**).* 147.2 mg, 65% yield; white solid, mp 128−130 °C. ^{1}H NMR (500 MH_Z, $CDCl_3$) δ (ppm) = 7.58−7.56 (m, 2H), 7.42 (dd, 1H, J = 8.5, 2.0 Hz), 7.38 (d, 1H, J = 2.0 Hz), 7.34 (dd, 3H, J = 5.0, 2.0 Hz), 6.72 (d, 1H, J = 8.0 Hz), 5.08 (d, 1H, J = 2.0 Hz), 4.65 (d, 1H, J = 2.0 Hz), 4.22 (q, 2H, J = 7.0 Hz), 3.38 (d, 1H, J = 16.0 Hz), 3.29 (d, 1H, J = 16.0 Hz), 3.22 (s, 3H), 1.31 (t, 3H, J = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 177.9, 168.9, 151.2, 147.8, 141.2, 137.5, 133.0, 131.7, 129.1, 128.9, 128.3,

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124.9, 116.0, 109.5, 98.9, 95.6, 61.3, 48.8, 39.5, 26.7, 14.2. HRMS (ESI) calcd for $C_{23}H_{21}BrNO_4$ $[M + H]^+$ 454.0654, found 454.0644.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra of all compounds; three figures and six tables with single-crystal X-ray structures, crystal data and structure refinement, and atomic coordinates and equivalent isotropic displacement parameters for **3a**, **4c**, and **6e** (PDF). Crystallographic information files for **3a**, **4c**, and **6e** (CIF). 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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