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Visible-Light-Mediated Cyclopropanation Reactions of 3-Diazooxindoles with Arenes

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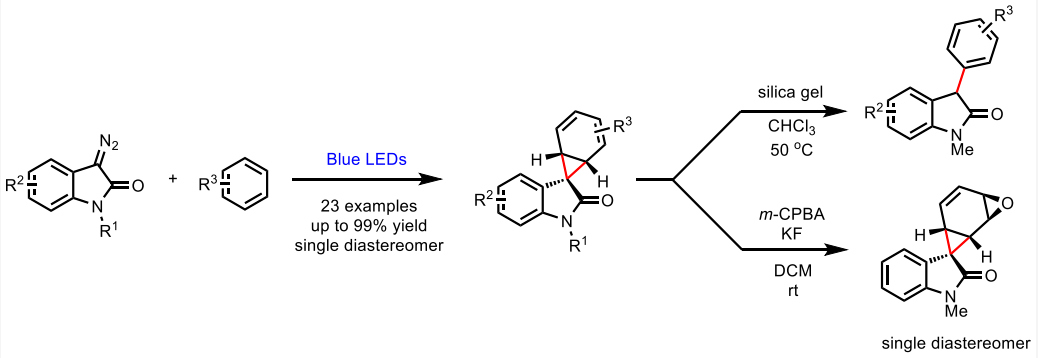

ABSTRACT: The cyclopropanation reaction of 3-diazooxindoles with arenes was first accomplished using visible-light irradiation. A series of spiro[norcaradiene-7,3′-indolin]-2′-ones were synthesized for the first time in high yields and with excellent diastereoselectivities. The synthetic usefulness of this catalyst-free photochemical methodology is illustrated by the further controllable rearrangement and epoxidation reactions.

INTRODUCTION

Carbenes represent some of the most important synthetic intermediates in modern organic chemistry. The multifarious transformations of carbenes, including cycloaddition reactions and C−H and X−H bond insertion reactions, provide an efficient way to construct complex molecules. Transition-metal-catalyzed carbene transfer reactions have made great progress over the past few decades.[1] However, the development of practical, sustainable, and environment-friendly metal-free carbene transfer reactions is in high demand today. Recently, visible-light-mediated metal-free carbene transfer reactions have attracted a lot of attention due to their simple operation and tolerance for moisture and oxygen.[2] Typical carbene transfer reactions, such as cycloaddition, C−H and X−H bond insertion, olefination, and rearrangement reactions, have been successfully accomplished under visible-light irradiation.[3] Compared to the conventional metal-free carbene transfer reactions mediated by UV light irradiation,[4] these approaches could decompose the diazo compound under mild conditions without side reactions related to the high-energy UV light. Nevertheless, visible-light-mediated carbene transfer reactions are so far mainly limited to the application of aryl diazoacetates,[3a] thus restricting their application in the construction of complex scaffolds.

The addition of diazo compounds to arenes, providing monocyclic cycloheptatriene via the ring expansion of bicyclic norcaradiene, was first described by Buchner in 1885.[5] Since then, the norcaradiene−cycloheptatriene (NCD−CHT) equilibrium has been extensively studied to understand its mechanism and the factors that influence the ratio of the two tautomers (Scheme 1a).[6] The Buchner reaction represents one of the most powerful methods of transforming stable aromatic rings to much more reactive systems.[7] Typically, precious transition-metal catalysts are required to access a metal carbene intermediate, which then undergoes a cyclopropanation reaction with arenes.[8] In contrast, the visible-light-mediated metal-free Buchner reaction has remained vastly underexplored until very recently. Koenigs and co-workers reported the metal-free visible light photolysis of aryl diazoacetates with arenes as the solvents (Scheme 1b).[3b] The norcaradiene-type products could be obtained in moderate yields and with excellent diastereoselectivities. According to the literature, the slow addition of the diazo components is crucial to obtain satisfactory results,[3d−f] which is probably due to the side reactions caused by the photolysis of aryl diazoacetates. We wonder whether norcaradiene

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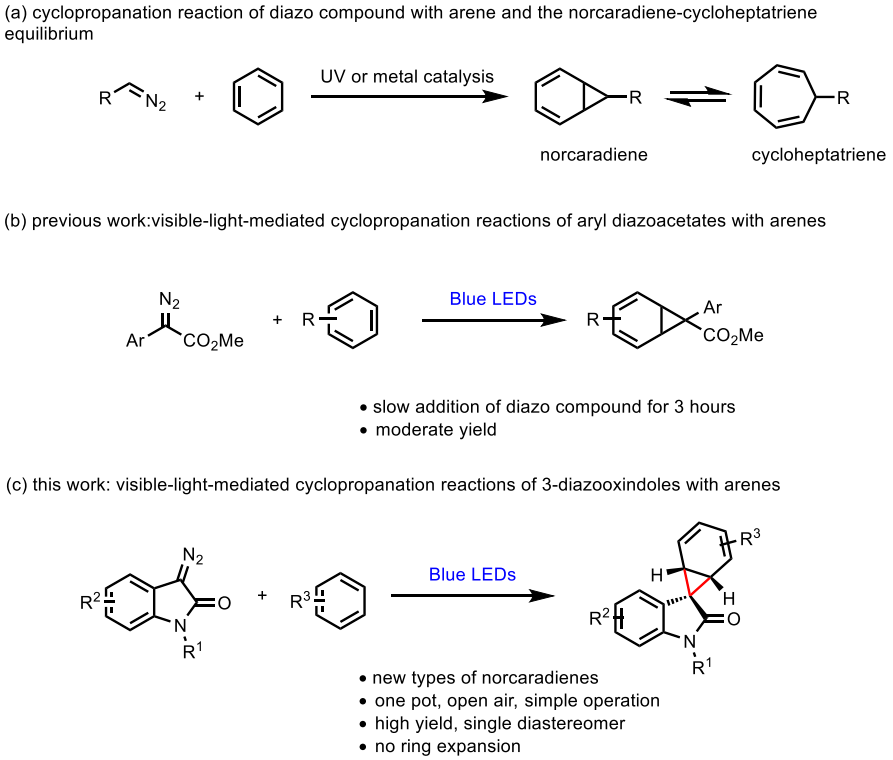
Scheme 1. Cyclopropanation Reactions of Diazo Compounds with Arenes



products could be obtained in higher yields and in a one-pot approach if more stable diazoalkanes, such as cyclic 3-diazooxindole **1**, were used.[9] Novel and interesting spiro-[norcaradiene-7,3′-indolin]-2′-one will be identified for the first time (Scheme 1c). Recently, Koenigs and co-workers described the photochemical O−H functionalization reaction of acidic alcohols with 3-diazooxindoles, which was the first application of this cyclic diazoamide in a visible-light-mediated carbene transfer reaction.[3a]

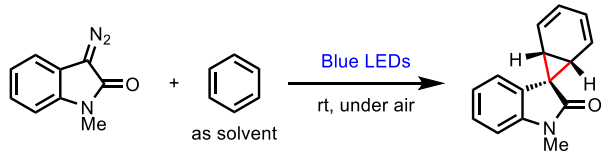
Spiro cyclopropyl oxindoles have stimulated intense research interest[10] for their potentially interesting biological activities[11] and utilities as synthetic intermediates.[12] 3-Diazooxindoles have been used in different metal-catalyzed carbene transfer reactions to give spirooxindoles.[13] However, the cyclopropanation reactions between 3-diazooxindoles and arenes have never been studied before. With our strong interest in developing practical methods to construct spirooxindoles[14] and inspiration from the fast growth of visible-light-mediated carbene transfer reactions, we began to study the visible-light-mediated cyclopropanation reaction between 3-diazooxindoles and arenes.

Herein we report the first example of a cyclopropanation reaction of 3-diazooxindole with an arene. The spiro-[norcaradiene-7,3′-indolin]-2′-ones were synthesized by visible-light-mediated carbene transfer reactions in moderate to high yields and with excellent diastereoselectivities. The ring-expansion products, cycloheptatrienes, could not be detected in this methodology.

RESULTS AND DISCUSSION

We initiated the study by investigating the reaction of 3-diazooxindole **1a** with 5 equiv of benzene **2a** in CH_2Cl_2 under the irradiation of blue LEDs (470 nm) at room temperature (Table 1, entry 1). After 24 h, no cyclopropanation product was detected, and most of the diazooxindole was recovered. Then, we tried to use benzene **2a** both as the reactant and the solvent. The cyclopropanation product **3a** was successfully obtained, albeit in a low yield, when the concentration of **1a** was 0.1 M (Table 1, entry 2). This novel spiro[norcaradiene-7,3′-indolin]-2′-one was synthesized for the first time, and the diastereoselectivity was very high. Then, different concen-

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3a**

entry	concentration (mol/L)	t (h)	yield (%)[b]
1[c]	0.1	24	NR
2	0.1	12	23
3	0.2	12	19
4	0.05	12	32
5	0.02	12	59
6	0.01	12	64
7	**0.01**	**24**	**82**
8[d]	0.01	24	84
9[e]	0.1	24	27
10[f]	0.01	24	NR

[a]Unless otherwise noted, **1a** (0.1 mmol) was dissolved in benzene (**2a**), and the mixture was stirred at room temperature under irradiation of blue LEDs (470 nm, 6 W). [b]Isolated yield. [c]The reaction was carried out with **1a** (0.1 mmol) and benzene (**2a**, 0.5 mmol) in 1 mL of CH_2Cl_2. [d]The reaction was carried out under a N_2 atmosphere. [e]The reaction was carried out with a slow addition of **1a** (0.1 mmol in 0.5 mL benzene) to benzene (0.5 mL) for 3 h. [f]The reaction was carried out in the dark.

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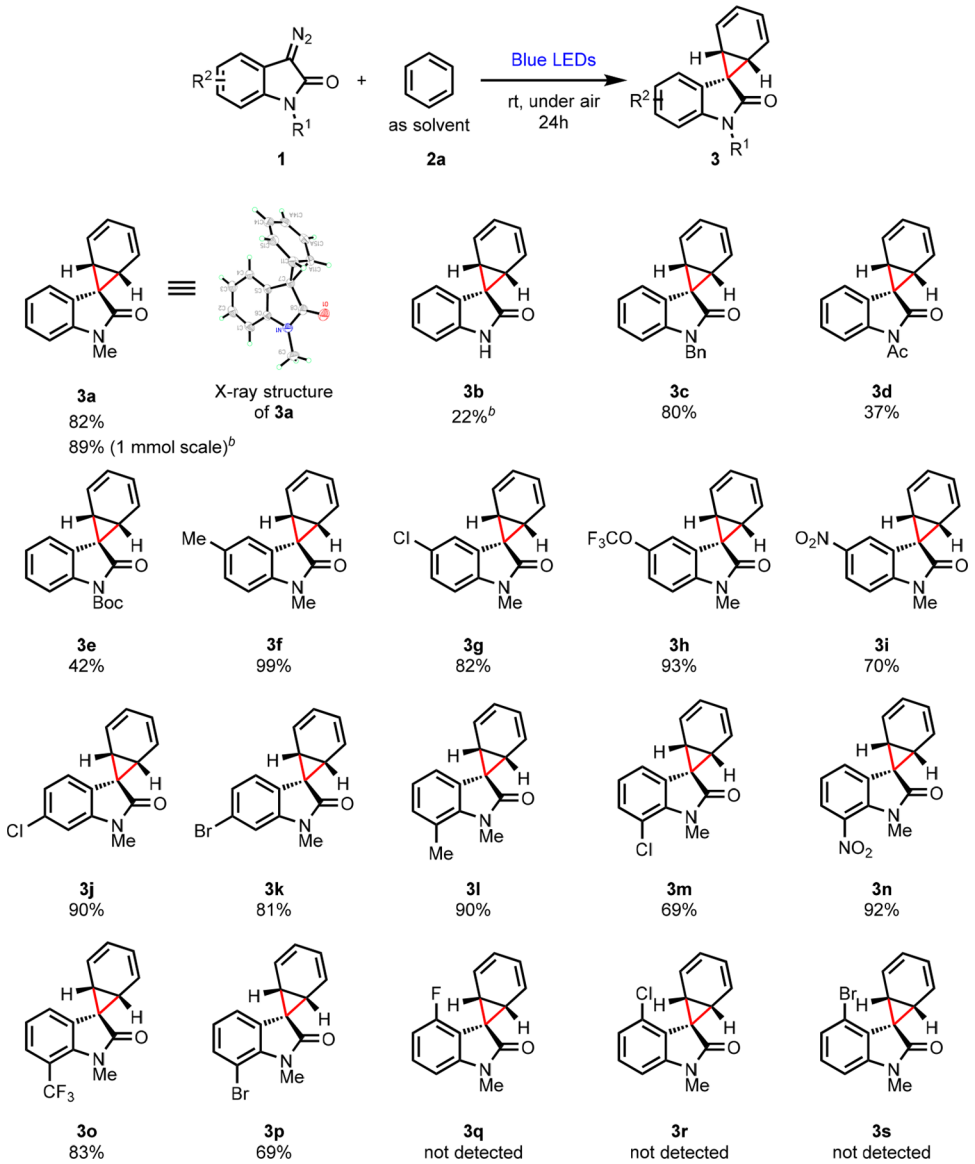
Scheme 2. Scope of 3-Diazooxindoles[a]



[a]Reaction conditions are as follows: **1** (0.1 mmol) was dissolved in benzene (**2a**, 10 mL), and the mixture was stirred at room temperature under irradiation of blue LEDs (470 nm, 6 W). Yields refer to isolated products. [b]Yield of 72 h.

trations of **1a** were screened to increase the yield. It was found that a lower concentration was more suitable for the cyclopropanation reaction, and **3a** could be isolated in 64% yield after 12 h when 0.01 M of **1a** was used (Table 1, entry 6). This is probably because of the higher equivalent of benzene at a lower concentration of **3a**. Extending the reaction time to 24 h gave **3a** in 82% yield and with an excellent diastereoselectivity (Table 1, entry 7). Notably, the norcaradiene-type product **3a** was the sole reaction product, and no cycloheptatriene formation was observed. The competing sp^2 C−H insertion product was also not detected. For comparison, the reaction was also conducted under a N_2 atmosphere (Table 1, entry 8). The desired product was isolated in almost the same yield with the reaction under air, which showed that this cyclopropanation reaction had a good tolerance for air and moisture. We also tried Koenigs' conditions[3b] by adding the diazo **1a** to benzene for 3 h (Table 1, entry 9). The yield was very low after another 21 h stirring. Importantly, the control experiment showed that no product was detected when the reaction was conducted in the dark (Table 1, entry 10).

With the optimal reaction conditions established, the substrate scope of this photochemical cyclopropanation reaction was investigated. The reaction time was set to 24 h for comparison unless otherwise noted, although the reaction could not go to completion in some cases. The *N*-substituents of the 3-diazooxindoles **1** have a great impact on the reaction. Substrates with electron-donating *N*-substituents gave much higher yields than those with electron-withdrawing ones (**3a** and **3c** versus **3d** and **3e**). The best yield was obtained using the *N*-methyl substrate (**3a**). With this substrate, a 1 mmol scale reaction was conducted. The desired product could be obtained in 89% yield, although a longer reaction time was needed. 3-Diazooxindole without any *N*-substituent gave only a 22% yield of the cyclopropanation product after 72 h due to the massive amount of diazo substrate left (**3b**). The absolute configuration of this novel spiro[norcaradiene-7,3′-indolin]-2′-

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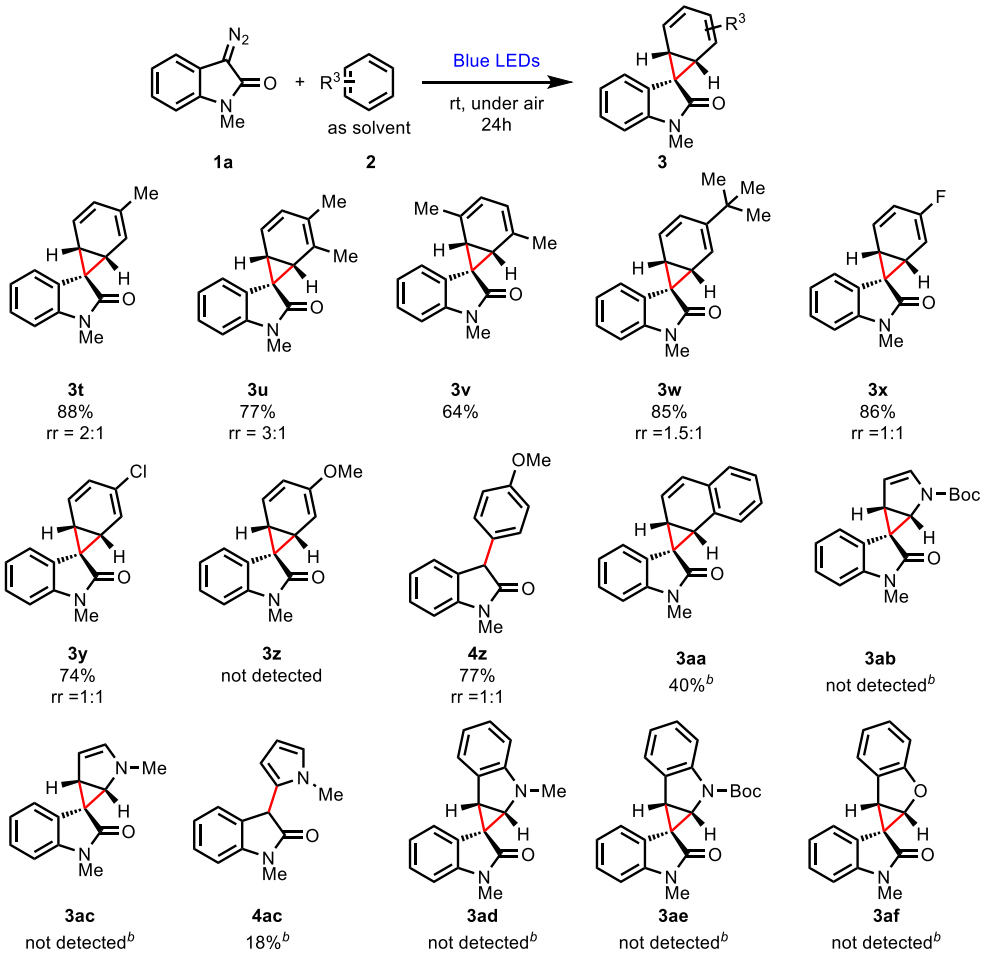
Scheme 3. Scope and Limitations of Arenes[a]



[a]Reaction conditions are as follows: **1a** (0.1 mmol) was dissolved in the arene (**2**, 10 mL), and the mixture stirred at room temperature under irradiation of blue LEDs (470 nm, 6 W). Yields refer to isolated products, and rr is short for regioisomer ratio, which was determined by ^{1}H NMR. [b]The reaction was carried out with **1a** (0.1 mmol) and arene (**2**, 0.5 mmol) in 1 mL of CH_2Cl_2 for 72 h.

one was unambiguously determined by X-ray crystallography (Scheme 2). Then 3-diazooxindoles with different substituents on the phenyl ring were investigated under the optimal reaction conditions. Substituents on the 5, 6, or 7 position of 3-diazooxindoles **1** had little influence on the cyclopropanation reaction (**3f**−**3p**). Additionally, the norcaradiene-type products were obtained in high yields and with excellent diastereoselectivities. However, when 4-substituted diazooxindoles were used, the desired cyclopropanation products could not be detected (**3q**−**3s**). This is probably because of the large steric hindrance from 4-substituents, which could be easily predicted from the X-ray crystallography of **3a**.

Then, the scope of the arenes was investigated with 3-diazooxindole **1a** (Scheme 3). The substituents of the arenes have significant effects on the regioselectivity of this photochemical carbene transfer reaction. Moreover, competing C−H insertion reactions can also occur. When alkyl-substituted benzenes were used, the cyclopropanation products could be obtained in moderate to high yields and with excellent diastereoselectivities (**3t**−**3w**). However, the regioselectivity of this reaction was very low, except for *p*-xylene (**3v**). Halo-substituted substrates also gave the desired products in high yields, albeit with no regioselectivity (**3x** and **3y**). Interestingly, when anisole was used, the C−H insertion product **4z** was obtained instead of the cyclopropanation product **3z**. This is probably due to the activation effect of the methoxy group toward the electrophile. However, we could not completely rule out the possibility that cyclopropane **3z** was indeed formed and rearranged to **4z** under the reaction conditions. Notably, no cycloheptatriene formation was observed for any of the substrates.

Next, other arenes besides benzene were examined (Scheme 3). Because they were all solid at room temperature, CH_2Cl_2 was used as the reaction solvent. The cyclopropanation of diazooxindole **1a** with naphthalene furnished the desired product **3aa** in moderate yield with an excellent diastereoselectivity and regioselectivity after 72 h. However, none of the tested heteroaromatic substrates could give the expected norcaradiene type products, and most of them remained intact under the reaction conditions. Only a small amount of the C−H insertion product **4ac** was isolated. In contrast, Davies and co-workers have reported the cyclopropanation or C−H insertion reactions of aryldiazoacetate with these heteroaromatic substrates in CH_2Cl_2 under blue light irradiation.[3g] These results suggest that diazooxindoles are less reactive carbene precursors than aryldiazoacetate under photochemical catalysis.

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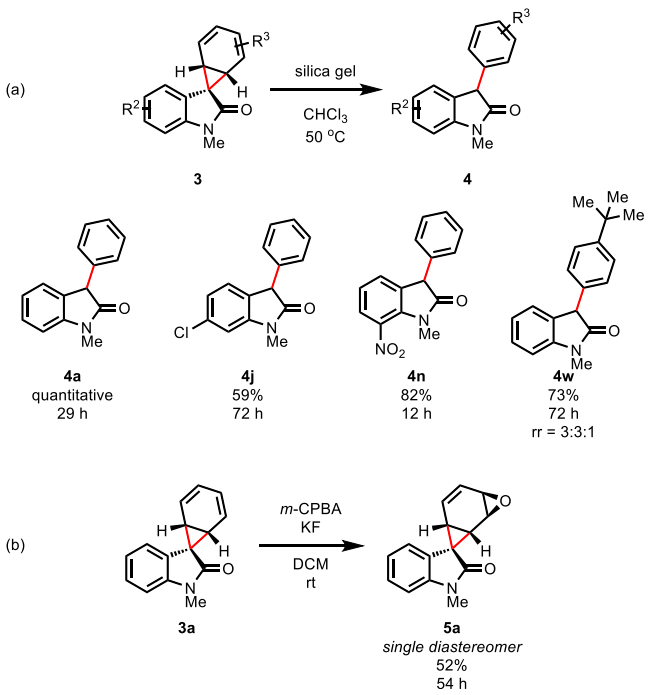
Then, the stability and synthetic utility of these novel spiro[norcaradiene-7,3′-indolin]-2′-ones were studied. Norcaradiene is well-known for undergoing a Buchner ring-expansion reaction to give cycloheptatriene. However, substituents with a strong π-acceptor at C-7 tend to shift this equilibrium to the norcaradiene side.[6] In this work, all the norcaradiene-type products **3** are quite stable, and no cycloheptatriene was detected. In addition, norcaradiene has been reported to rearrange to the C−H insertion product in thermal, photochemical, or acid conditions.[15] We have noticed that norcaradiene **3n** was partially converted to the C−H insertion product **4n** in the process of silica gel column chromatography purification.[15c] This result indicates that silica gel might assist the cyclopropane opening. Additionally, the subsequent proton transfer gave the product. Therefore, the silica gel-promoted cyclopropane-opening reaction of selected norcaradienes was studied in detail, and the results are outlined in Scheme 4. The

Scheme 4. (a) Silica Gel-Promoted Cyclopropane-Opening Reaction of Norcaradienes and (b) Monoepoxidation of Norcaradiene 3a



C−H insertion product **4a** was obtained in quantitative yield after 29 h. Unsurprisingly, norcaradiene **3n** was the most unstable substrate under this condition and gave the C−H insertion product **4n** in 82% yield after 12 h. Obviously, the substituents of the norcaradienes **3** have a great impact on this silica gel-promoted cyclopropane-opening reaction. Moreover, treating **3a** with the Camps condition[16] (*m*-CPBA/KF) gave the monoepoxidation product **5a** as a single diastereomer.[8g] By using this nonacidic epoxidation condition, possible rearrangement reactions of norcaradiene **3a** and epoxide **5a** were avoided.

Finally, based on the experimental results and literature reports,[3d,g,h] a plausible mechanism for this cyclopropanation reaction is postulated in Scheme 5. The irradiation of 3-diazooxindole **1a** with blue LEDs gives excited state **1a***, which expels dinitrogen to afford a singlet carbene ^{1}**A**. The intersystem crossing (ISC) of ^{1}**A** gives a triplet carbene ^{3}**A**, which is an unproductive and reversible pathway. Then, the electrophilic singlet carbene ^{1}**A** is trapped by an aromatic ring to produce norcaradiene **3a**.

CONCLUSIONS

In conclusion, we have developed the first examples of cyclopropanation reactions of 3-diazooxindoles with arenes. A series of novel spiro[norcaradiene-7,3′-indolin]-2′-ones were produced in moderate to high yields and with excellent diastereoselectivities by visible light irradiation. The synthetic application of this methodology is well demonstrated by the controllable rearrangement and epoxidation reactions. Moreover, this work will broaden the application of visible-light-mediated carbene transfer reactions.

EXPERIMENTAL SECTION

General Information. All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light or staining with phosphomolybdic acid, followed by heating on a hot plate. Flash chromatography was carried out using silica gel (160−200 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AV-300, AV-400, and AV-500 spectrometers. Chemical shifts (δ)are given in parts per million relative to tetramethylsilane (TMS). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet), integration, coupling constant (Hz), and assignment. The spectra were recorded in either $CDCl_3$ or $(CD_3)_2SO$ as the solvent at room temperature. TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR, and $CDCl_3$ served as an internal standard (δ = 77.00 ppm) for ^{13}C{H} NMR. High-resolution mass spectra were acquired on a Thermo Orbitrap Elite instrument (Agilent, Palo Alto, CA).

Synthesis of Diazo Substrates 1. Diazo substrates **1** were prepared with modified methods according to the literatures.[17] A mixture of isatin (147 mg, 1 mmol) and $TsNHNH_2$ (205 mg, 1.1 mmol, 1.1 equiv) in THF (5 mL) was stirred at 60 °C (oil bath) for 2 h. Then, the mixture was filtered. The filter cake was stirred in a 0.2 N NaOH aqueous solution at 60 °C (oil bath) for 1 h. The reaction mixture was extracted with EtOAc. The combined organic layers were dried by Na_2SO_4 and then concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:3) to afford 3-diazoindolin-2-one.

To a stirred solution of 3-diazoindolin-2-one (159 mg, 1 mmol) in CH_3CN (5 mL) was added K_2CO_3 (414 mg, 3 mmol, 3 equiv) at room temperature. After 5 min, CH_3I (156 mg, 1.1 mmol, 1.1 equiv) was added via syringe. The reaction mixture was stirred at room temperature until 3-diazoindolin-2-one was fully consumed (monitored by TLC). The reaction was then diluted with EtOAc and H_2O. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:5) to give *N*-methyl-3-diazoindolin-2-one **1**.

1a−**1m**, **1p**, **1r**, and **1s** are known compounds, and their spectra are all consistent with literature values.

*3-Diazo-1-methyl-7-nitroindolin-2-one (**1n**).* Yellow solid, 73% yield (159.7 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, J_1 = 8.32 Hz, J_2 = 0.9 Hz, 1H), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 0.9 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 3.36 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 166.6, 135.6, 127.6, 121.6, 121.5, 121.4, 120.6, 120.5, 30.5. HRMS (ESI) *m*/*z*: calcd for $C_9H_7N_4O_3$ $[M + H]^+$ 219.0513, found 219.0511.

*3-Diazo-1-methyl-7-(trifluoromethyl)indolin-2-one (**1o**).* Yellow solid, 76% yield (183.3 mg), R_f = 0.2 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 3.50 (d, J = 2.4 Hz, 3H).

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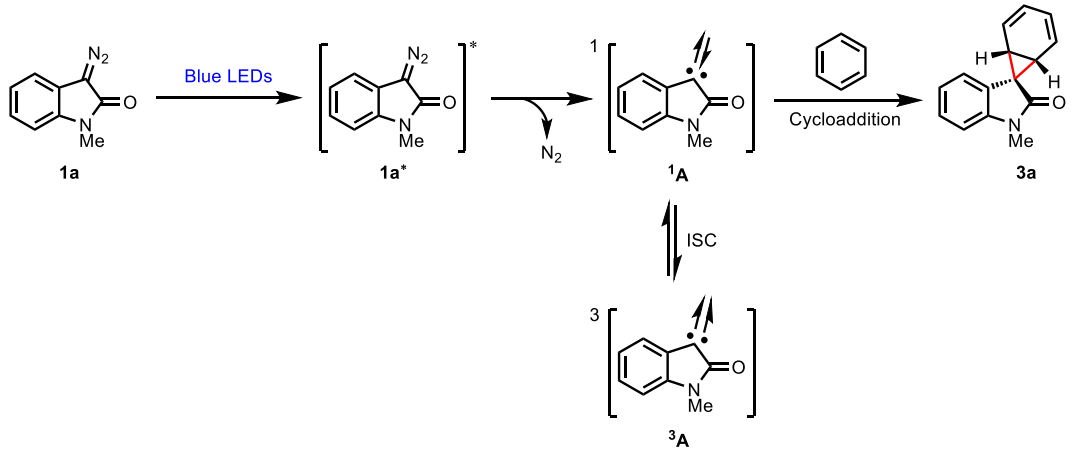
Scheme 5. Postulated Mechanism of the Cyclopropanation Reaction



$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.9, 131.8, 123.6, 123.5, 123.4, 123.3, 122.3, 121.4, 119.1, 113.3, 112.9, 29.5, 29.4. HRMS (ESI) m/z: calcd for $C_{10}H_7F_3N_3O$ $[M + H]^+$ 242.0536, found 242.0534.

*3-Diazo-4-fluoro-1-methylindolin-2-one (**1q**).* Red solid, 85% yield (162.9 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.22 (dd, J_1 = 13.9 Hz, J_2 = 8.0 Hz, 1H), 7.01−6.93 (m, 2H), 3.25 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $(CD_3)_2SO$): δ 165.7, 156.9, 136.4, 136.3, 126.8, 126.7, 108.8, 108.5, 105.9, 105.8, 103.1, 102.9, 27.2. HRMS (ESI) m/z: calcd for $C_9H_7FN_3O$ $[M + H]^+$ 192.0568, found 192.0567.

General Procedure for the Visible-Light-Mediated Cyclopropanation Reactions of 3-Diazooxindoles with Arenes. *Procedure A.* In a test tube and under air, 3-diazooxindole **1** (0.1 mmol) was dissolved in benzene **2** (10 mL), and the reaction mixture stirred at room temperature under irradiation of blue LEDs (470 nm, 6W) for 24 h. Then, the reaction mixture was concentrated and directly purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:5) to give products **3** or **4**.

Procedure B. In a test tube and under air, 3-diazooxindole **1** (0.1 mmol) and arene **2** (0.5 mmol, 5 equiv) were dissolved in DCM (1 mL), and the reaction mixture was stirred at room temperature under irradiation of blue LEDs (470 nm, 6W) for 24 h. Then, the reaction mixture was concentrated and directly purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:5) to give products **3** or **4**.

The procedure for the 1 mmol scale reaction is as follows: in a 250 mL round-bottomed flask and under air, 3-diazooxindole **1a** (1 mmol) was dissolved in benzene **2** (100 mL), and the reaction mixture was stirred at room temperature under irradiation of blue LEDs (470 nm, 6W) for 72 h. Then, the reaction mixture was concentrated and directly purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:5) to give product **3a** (89% yield, 189.7 mg).

*1′-Methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3a**).* Procedure A, red solid, 82% yield (18.3 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^1H NMR (500 MHz, $CDCl_3$): δ 7.23 (t, J = 7.7 Hz, 1H), 6.93−6.90 (m, 2H), 6.70 (d, J = 7.8 Hz, 1H), 6.48 (dd, J_1 = 2.9 Hz, J_2 = 7.3 Hz, 2H), 6.13−6.09 (m, 2H), 3.33 (s, 3H), 3.23 (t, J = 3.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz $CDCl_3$): δ 179.2, 144.6, 126.3, 126.2, 126.1, 123.9, 122.9, 121.5, 107.6, 41.4, 27.0, 16.0. HRMS (ESI) m/z: calcd for $C_{15}H_{13}NNaO$ $[M + Na]^+$ 246.0899, found 246.0904.

*Spiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3b**).* Procedure A, red solid, 22% yield (4.6 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 7.16 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.50 (dd, J_1 = 7.4 Hz, J_2 = 2.8 Hz, 2H), 6.15−6.11 (m, 2H), 3.25 (t, J = 2.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 181.7, 141.8, 126.5, 126.4, 126.2, 123.9, 123.2, 121.5, 109.5, 41.1, 16.4. HRMS (ESI) m/z: calcd for $C_{14}H_{12}NO$ $[M + H]^+$ 210.0913, found 210.0915.

*1′-Benzylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3c**).* Procedure A, red solid, 80% yield (23.9 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35−7.24 (m, 5H), 7.11 (t, J = 7.7 Hz, 1H), 6.87 (t, J = 7.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.49 (dd, J_1 = 7.3 Hz, J_2 = 2.9 Hz, 2H), 6.16−6.12 (m, 2H), 5.02 (s, 2H), 3.29 (t, J = 3.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 179.4, 143.8, 136.4, 128.8, 127.6, 127.5, 126.3, 126.2, 126.1, 124.0, 122.9, 121.6, 108.6, 44.5, 41.5, 15.9. HRMS (ESI) m/z: calcd for $C_{21}H_{18}NO$ $[M + H]^+$ 300.1383, found 300.1384

*1′-Acetylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3d**).* Procedure A, white solid, 37% yield (9.3 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, J = 8.2 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 6.55 (dd, J_1 = 7.4 Hz, J_2 = 2.9 Hz, 2H), 6.16−6.12 (m, 2H), 3.28 (t, J = 2.6 Hz, 2H), 2.73 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 180.3, 170.8, 140.8, 127.2, 126.7, 125.6, 124.4, 123.8, 122.3,115.9, 42.4, 26.9, 15.9. HRMS (ESI) m/z: calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$ 252.1019, found 252.1018.

*tert-Butyl 2′-Oxospiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-diene-1′-carboxylate (**3e**).* Procedure A, red solid, 42% yield (13.0 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.2 Hz, 1H), 7.26−7.22 (m, 1H), 7.00 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 7.7 Hz, 1H), 6.52 (dd, J_1 = 7.4 Hz, J_2 = 2.9 Hz, 2H), 6.13−6.09 (m, 2H), 3.26 (t, J = 3.0 Hz, 2H), 1.66 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 178.1, 149.3, 140.5, 126.9, 126.4, 125.4, 123.9, 123.6, 122.6, 84.3, 42.1, 28.3, 15.6. HRMS (ESI) m/z: calcd for $C_{19}H_{19}NNaO_3$ $[M + Na]^+$ 332.1257, found 332.1254.

*1′,5′-Dimethylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3f**).* Procedure A, red solid, 99% yield (23.5 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (dd, J_1 = 7.9 Hz, J_2 = 0.8 Hz, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.52 (s, 1H), 6.48 (dd, J_1 = 7.3 Hz, J_2 = 2.9 Hz, 2H), 6.13−6.09 (m, 2H), 3.3 (s, 3H), 3.22 (dd, J_1 = 3.6 Hz, J_2 = 2.6 Hz, 2H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 179.2, 142.3, 130.9, 126.5, 126.4, 126.3, 124.0, 123.8, 107.3, 41.9, 21.1, 21.5, 16.2. HRMS (ESI) m/z: calcd for $C_{16}H_{15}NNaO$ $[M + Na]^+$ 260.1046, found 260.1060.

*5′-Chloro-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3g**).* Procedure A, red solid, 82% yield (21.1 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 6.51 (dd, J_1 = 7.4 Hz, J_2 = 2.9 Hz, 2H), 6.13−6.09 (m, 2H), 3.31 (s, 3H), 3.24 (t, J = 3.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.7, 143.2, 127.6, 126.9, 126.5, 125.9, 123.8, 123.2, 108.2, 41.3, 27.1, 15.5. HRMS (ESI) m/z: calcd for $C_{15}H_{12}ClNNaO$ $[M + Na]^+$ 280.0500, found 280.0506.

*1′-Methyl-5′-(trifluoromethoxy)spiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3h**).* Procedure A, colorless oil, 93% yield

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(28.6 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (dd, J_1 = 8.5 Hz, J_2 = 1.4 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.56 (d, J = 1.0 Hz, 1H), 6.50 (dd, J_1 = 5.9 Hz, J_2 = 2.4 Hz, 2H), 6.13−6.10 (m, 2H), 3.33 (s, 3H), 3.26 (t, J = 2.4 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 178.9, 144.0, 143.9, 143.2, 127.2, 126.4, 123.8, 118.9, 116.9, 107.4, 40.9, 27.1, 15.4. HRMS (ESI) m/z: calcd for $C_{16}H_{13}F_3NO_2$ [M + H]$^+$ 308.0893, found 308.0895.

*1′-Methyl-5′-nitrospiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3i**).* Procedure A, yellow solid, 70% yield (18.8 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (dd, J_1 = 8.6 Hz, J_2 = 2.2 Hz, 1H), 7.49 (d, J = 2.1 Hz, 1H), 6.94 (d, J = 8.6 Hz, 1H), 6.62 (dd, J_1 = 7.4 Hz, J_2 = 2.8 Hz, 2H), 6.18−6.14 (m, 2H), 3.39 (s, 3H), 3.34 (t, J = 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 179.4, 150.1, 142.7, 127.1, 126.3, 123.7, 123.4, 118.5, 106.8, 41.2, 27.4, 15.2. HRMS (ESI) m/z: calcd for $C_{15}H_{13}N_2O_3$ [M + H]$^+$ 269.0921, found 269.0913.

*6′-Chloro-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3j**).* Procedure A, red solid, 90% yield (23.2 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.87 (td, J_1 = 9.2 Hz, J_2 = 2.3 Hz, 2H), 6.56 (d, J = 8.08 Hz, 1H), 6.47 (dd, J_1 = 9.2 Hz, J_2 = 3.6 Hz, 2H), 6.13−6.08 (m, 2H), 3.30 (s, 3H), 3.22 (t, J = 3.8 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 179.2, 145.8, 132.4, 126.3, 124.4, 123.9, 123.6, 121.3, 108.3, 41.1, 27.1, 15.8. HRMS (ESI) m/z: calcd for $C_{15}H_{12}ClNNaO$ [M + Na]$^+$ 280.0500, found 280.0504.

*6′-Bromo-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3k**).* Procedure A, white solid, 81% yield (24.5 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (d, J = 11.0 Hz, 2H), 6.48 (t, J = 9.7 Hz, 3H), 6.10 (d, J = 4.0 Hz, 2H), 3.30 (s, 3H), 3.22 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.9, 145.9, 126.3, 124.9, 124.2, 124.0, 123.9, 120.2, 111.0, 40.9, 27.1, 15.7. HRMS (ESI) m/z: calcd for $C_{15}H_{13}BrNO$ [M + H]$^+$ 302.0174, found 302.0173.

*1′,7′-Dimethylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3l**).* Procedure A, red solid, 90% yield (21.4 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, J = 7.7 Hz, 1H), 6.79 (t, J = 7.7 Hz, 1H), 6.55 (d, J = 7.4 Hz, 1H), 6.47 (dd, J_1 = 7.3 Hz, J_2 = 2.9 Hz, 2H), 6.12−6.06 (m, 2H), 3.62 (s, 3H), 3.22 (dd, J_1 = 3.6 Hz, J_2 = 2.6 Hz, 2H), 2.62 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.9, 142.4, 130.1, 126.9, 126.4, 124.0, 121.4, 120.7, 119.2, 42.5, 30.6, 19.5, 15.2. HRMS (ESI) m/z: calcd for $C_{16}H_{16}NO$ [M + H]$^+$ 238.1227, found 238.1228.

*7′-Chloro-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3m**).* Procedure A, yellow solid, 69% yield (17.8 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 8.2 Hz, 1H), 6.79 (t, J = 7.9 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.49 (dd, J_1 = 7.4 Hz, J_2 = 2.9 Hz, 2H), 6.12−6.09 (m, 2H), 3.71 (s, 3H), 3.24 (t, J = 3.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.4, 140.3, 128.8, 128.5, 126.6, 123.9, 122.1, 121.1, 115.1, 42.0, 30.5, 15.1. HRMS (ESI) m/z: calcd for $C_{15}H_{13}ClNO$ [M + H]$^+$ 258.0680, found 258.0681.

*1′-Methyl-7′-nitrospiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3n**).* Procedure A, colorless oil, 92% yield (24.7 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.2 Hz, 1H), 6.93 (t, J = 8.0 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.53 (dd, J_1 = 7.4 Hz, J_2 = 2.4 Hz, 2H), 6.16−6.12 (m, 2H), 3.23 (s, 3H), 3.32−3.28 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.74, 138.0, 135.1, 129.5, 126.9, 126.2, 123.9, 121.7, 121.0, 41.9, 30.5, 14.3. HRMS (ESI) m/z: calcd for $C_{15}H_{13}N_2O_3$ [M + H]$^+$ 269.0921, found 269.0920.

*1′-Methyl-7′-(trifluoromethyl)spiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3o**).* Procedure A, red solid, 83% yield (24.2 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.1 Hz, 1H), 6.95 (t, J = 7.9 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.52 (dd, J_1 = 7.4 Hz, J_2 = 2.8 Hz, 2H), 6.15−6.12 (m, 2H), 3.54 (d, J = 2.2 Hz, 3H), 3.28 (t, J = 2.9 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.9, 128.5, 126.8, 125.9, 124.0, 123.8, 123.7, 120.7, 112.1, 42.2, 29.8, 29.7, 13.9. HRMS (ESI) m/z: calcd for $C_{16}H_{13}F_3NO$ [M + H]$^+$ 292.0944, found 292.0945.

*7′-Bromo-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3p**).* Procedure A, white solid, 69% yield (20.8 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 8.2 Hz, 1H), 6.73 (t, J = 7.9 Hz, 1H), 6.58 (d, J = 7.6 Hz, 1H), 6.49 (dd, J_1 = 7.5 Hz, J_2 = 2.5 Hz, 2H), 6.11−6.09 (m, 2H), 3.73 (s, 3H), 3.25 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.6, 141.7, 131.8, 129.2, 126.7, 123.9, 122.6, 121.6, 102.0, 42.1, 30.8, 14.9. HRMS (ESI) m/z: calcd for $C_{15}H_{13}BrNO$ [M + H]$^+$ 302.0175, found 302.0174.

*1′,3-Dimethylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3t**).* Procedure A, colorless oil, 88% yield (20.9 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 2:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 6.93−6.89 (m, 3H), 6.66 (d, J = 7.4 Hz, 1H), 6.50 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 0.5H), 6.4 (dd, J_1 = 9.4 Hz, J_2 = 6.1 Hz, 1H), 6.33 (dd, J_1 = 9.5 Hz, J_2 = 1.1 Hz, 0.5H), 6.24 (d, J = 6 Hz, 1H), 6.09 (dd, J_1 = 9.4 Hz, J_2 = 5.1 Hz, 0.5H), 5.94 (dd, J_1 = 9.3 Hz, J_2 = 5.4 Hz, 1H), 5.83−5.82 (m, 0.5 H), 3.34 (s, 3H), 3.32 (s, 1.5H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 179.4, 179.0, 144.6, 144.5, 134.3, 133.6, 130.1, 126.9, 126.2, 126.1, 126.0, 125.6, 124.0, 122.6, 122.5, 121.7, 121.6, 121.5, 120.6, 119.1, 107.6, 107.5, 41.8, 40.3, 40.0, 39.3, 27.0, 26.9, 23.7, 21.8, 17.5, 16.2. HRMS (ESI) m/z: calcd for $C_{16}H_{15}NNaO$ [M + Na]$^+$ 260.1046, found 260.1061.

*1′,2,3-Trimethylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3u**).* Procedure A, white solid, 77% yield (19.4 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 3:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, J = 7.7 Hz, 1.3H), 6.91−6.88 (m, 2.7H), 6.46 (d, J = 7.5 Hz, 1H), 6.34 (d, J = 7.4 Hz, 0.3H), 6.30 (d, J = 9.4 Hz, 1H), 5.92−5.86 (m, 1.6H), 3.33 (s, 3H), 3.32 (s, 1H), 3.15−3.12 (m, 1.6H), 3.06 (d, J = 8.7 Hz, 1H), 2.03 (s, 2H), 1.99 (s, 3H), 1.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.3, 179.1, 144.6, 144.5, 136.1, 132.0, 127.7, 126.6, 126.3, 125.8, 122.3, 122.2, 121.5, 121.4, 120.4, 107.6, 107.5, 43.1, 39.9, 39.4, 26.9, 20.0, 19.9, 18.4, 17.8, 17.6. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO$ [M + H]$^+$ 252.1383, found 252.1384.

*1′,2,5-Trimethylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3v**).* Procedure A, red solid, 64% yield (16.1 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (td, J_1 = 7.7 Hz, J_2 = 0.8 Hz, 1H), 6.92−6.87 (m, 2H), 6.63 (d, J = 7.5 Hz, 1H), 6.2 (s, 2H), 3.84 (s, 3H), 3.01 (s, 2H), 1.84 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 179.6, 144.4, 130.1, 125.9, 125.3, 122.4, 122.3, 121.6, 107.5, 42.5, 27.0, 23.2, 17.0. HRMS (ESI) m/z: calcd for $C_{17}H_{18}NO$ [M + H]$^+$ 252.1383, found 252.1385.

*3-(tert-Butyl) 1′-Methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3w**).* Procedure A, colorless oil, 85% yield (23.7 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 1.5:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.18 (m, 2.5H), 6.91−6.86 (m, 5H), 6.64−6.60 (m, 2.5H), 6.55 (d, J = 7.4 Hz, 1H), 6.44 (dd, J_1 = 9.2 Hz, J_2 = 6.3 Hz, 1.5H), 6.28 (d, J = 6.3 Hz, 1.5H), 6.12 (dd, J_1 = 9.8 Hz, J_2 = 5.1 Hz, 1H), 5.92 (dd, J_1 = 9.2 Hz, J_2 = 5.0 Hz, 1.5H), 5.88 (d, J = 5.5 Hz, 1H), 3.34 (s, 4.5H), 3.32 (s, 3H), 3.24−3.21 (m, 2H), 3.20−3.11 (m, 3H), 1.21 (s, 9H), 0.96 (s, 14H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 179.4, 179.0, 146.3, 144.6, 146.4, 144.3, 127.2, 127.1, 126.2, 125.9, 125.8, 123.9, 122.9, 122.6, 121.5, 121.1, 120.9, 117.6, 115.3, 107.5, 107.4, 39.6, 38.4, 35.8, 34.8, 29.3, 28.0, 27.0, 26.9, 16.9, 16.5. HRMS (ESI) m/z: calcd for $C_{19}H_{21}NNaO$ [M + Na]$^+$ 302.1515, found 302.1520.

*3-Fluoro-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3x**).* Procedure A, colorless oil, 86% yield (20.7 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28−7.24 (m, 2H), 6.97−6.91 (m, 4H), 6.75 (dd, J_1 = 7.2 Hz, J_2 = 5.2 Hz, 2H), 6.44−6.37 (m, 2H), 6.25−6.26 (m, 1H), 6.06−6.02 (m, 1H), 5.89 (dd, J_1 = 9.3 Hz, J_2 = 5.2 Hz, 1H), 5.68−5.65 (m, 1H), 3.40−3.34 (m, 2H), 3.33 (s, 3H), 3.31 (s, 3H), 3.29−3.22 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 178.4, 177.9, 160.5, 159.6, 158.6, 157.5, 144.6, 144.4, 128.0, 127.9, 126.8, 126.3, 126.2, 126.1, 125.5, 122.7, 122.6, 122.2, 122.0, 121.9, 121.4, 121.1, 119.3, 119.2, 1183, 108.7, 107.9, 103.9, 103.8, 102.5, 102.3, 27.1, 26.9. HRMS (ESI) m/z: calcd for $C_{15}H_{12}FNNaO$ [M + Na]$^+$ 264.0795, found 264.0797.

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*3-Chloro-1′-methylspiro[bicyclo[4.1.0]heptane-7,3′-indoline]-2,4-dien-2′-one (**3y**).* Procedure A, red solid, 74% yield (19.1 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 1:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 7.6 Hz, 2H), 6.98−6.91 (m, 4H), 6.65 (dd, J_1 = 13.4 Hz, J_2 = 7.5 Hz, 2H), 6.53 (d, J = 6.5 Hz, 1H), 6.43−6.38 (m, 2H), 6.19−6.14 (m, 2H), 6.04 (dd, J_1 = 9.3 Hz, J_2 = 5.3 Hz, 1H), 3.34 (s, 3H), 3.32 (s, 3H), 3.28−3.19 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 178.0, 177.9, 144.7, 144.6, 131.1, 130.9, 128.7, 126.7, 126.6, 126.5, 126.1,125.6, 124.6, 123.0, 122.6, 122.4, 122.1, 122.0, 121.9, 120.4, 107.9, 107.8, 42.4, 42.0, 40.6, 40.3, 27.1, 27.0, 18.2, 15.5. HRMS (ESI) m/z: calcd for $C_{15}H_{13}ClNO$ [M + H]$^+$ 258.0680, found 258.0679.

*3-(4-Methoxyphenyl)-1-methylindolin-2-one (**4z**).* Procedure A, colorless oil, 77% yield (19.5 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 1:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.7 Hz, 1H), 7.29−7.24 (m, 2H), 7.16 (d, J = 7.3 Hz, 1H), 7.12 (d, J = 7.9 Hz, 2H), 7.09−7.05 (m, 3H), 6.97 (t, J = 7.5 Hz, 1H), 6.93−6.84 (m, 6H), 4.88 (s, 1H), 4.55 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.29 (s, 3H), 3.24 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.9, 176.4, 159.1, 157.6, 144.5, 144.4, 130.1, 129.9, 129.6, 129.2, 129.0, 128.7, 128.4, 127.9, 126.1, 125.1, 124.2, 122.8, 122.5, 121.1, 114.4, 111.5, 108.2, 107.8, 55.9, 55.4, 51.3, 48.0, 26.6, 26.5. HRMS (ESI) m/z: calcd for $C_{16}H_{16}NO_2$ [M + H]$^+$ 254.1176, found 254.1176.

*1′-Methyl-1a,7b-dihydrospiro[cyclopropa[a]naphthalene-1,3′-indolin]-2′-one (**3aa**).* Procedure B, red solid, 40% yield (10.9 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.29 (m, 3H), 7.26−7.22 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 6.89−6.86 (m, 2H), 6.72 (t, J = 7.8 Hz, 1H), 6.27 (d, J = 7.6 Hz, 1H), 6.11 (dd, J_1 = 9.5 Hz, J_2 = 5.2 Hz, 1H), 3.66 (d, J = 8.6 Hz, 1H), 3.34 (s, 3H), 3.22 (dd, J_1 = 8.7 Hz, J_2 = 5.3 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 178.4, 144.6, 132.6, 130.5, 129.6, 129.4, 128.7, 128.0, 127.9, 126.4, 124.9, 122.4, 122.0, 121.7, 107.8, 37.6, 36.7, 27.0, 21.6. HRMS (ESI) m/z: calcd for $C_{19}H_{16}NO$ [M + H]$^+$ 274.1226, found 274.1229.

*1-Methyl-3-(1-methyl-1H-pyrrol-2-yl)indolin-2-one (**4ac**).* Procedure B, colorless oil, 18% yield (4.1 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 7.7 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.63 (t, J = 2.1 Hz, 1H), 6.03 (t, J = 3.1 Hz, 1H), 5.78−5.77 (m, 1H), 4.74 (s, 1H), 3.69 (s, 3H), 3.22 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 175.0, 144.4, 128.6, 127.6, 126.6, 125.2, 123.7, 122.9, 108.5, 108.3, 107.0, 44.8, 34.6, 26.5. HRMS (ESI) m/z: calcd for $C_{14}H_{15}N_2O$ [M + H]$^+$ 227.1179, found 227.1181.

General Procedure for Silica Gel-Promoted Ring Opening of Norcaradiene 3. Silica gel (160−200 mesh, 40 mg) was added into a solution of norcaradiene **3** (0.1 mmol) in $CHCl_3$ (2 mL). The mixture was heated to 50 °C (oil bath) for specific time. Then, the mixture was filtered and concentrated to give product **4** in a pure form.

*1-Methyl-3-phenylindolin-2-one (**4a**).* Red solid, quantitative yield (29 h, 22.3 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.24 (m, 4H), 7.21−7.05 (m, 3H), 7.05 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 4.60 (s, 1H), 3.24 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.1, 144.6, 136.7, 129.0, 128.9, 128.5, 127.6, 125.1, 122.8, 108.3, 52.1, 26.6. HRMS (ESI) m/z: calcd for $C_{15}H_{14}NO$ [M + H]$^+$ 224.1070, found 224.1069.

*6-Chloro-1-methyl-3-phenylindolin-2-one (**4j**).* Colorless oil, 59% yield (72 h, 15.2 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.26 (m, 3H), 7.17 (d, J = 6.8 Hz, 2H), 7.09−7.03 (m, 2H), 6.90 (d, J = 1.3 Hz, 1H), 4.57 (s, 1H), 3.23 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.03, 145.8, 136.1, 134.3, 129.1, 128.5, 127.9, 127.2, 126.1, 122.7, 109.0, 51.7, 26.7. HRMS (ESI) m/z: calcd for $C_{15}H_{13}ClNO$ [M + H]$^+$ 258.0680, found 258.0678.

*1-Methyl-7-nitro-3-phenylindolin-2-one (**4n**).* Colorless oil, 82% yield (12 h, 22.0 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.3 Hz, 1H), 7.38−7.30 (m, 4H), 7.17 (d, J = 6.6 Hz, 2H), 7.11 (t, J = 7.9 Hz, 1H), 4.65 (s, 1H), 3.28 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 176.5, 138.0, 135.4, 135.3, 132.6, 129.3, 129.0, 128.5, 128.3, 124.5, 122.4, 50.9, 30.1. HRMS (ESI) m/z: calcd for $C_{15}H_{13}N_2O_3$ [M + H]$^+$ 269.0921, found 269.0915.

*3-(4-(tert-Butyl)phenyl)-1-methylindolin-2-one (**4w**).* Colorless oil, 73% yield (72 h, 20.4 mg), R_f = 0.3 (EtOAc/petroleum ether 1:5), regioisomer ratio 3:3:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 1H), 7.35−7.28 (m, 5.2H), 7.19−7.12 (m, 4.5 H), 7.07−6.99 (m, 4.3H), 6.90 (dd, J_1 = 11.1 Hz, J_2 = 7.9 Hz, 2.6H), 6.52 (d, J = 7.6 Hz, 1H), 5.42 (s, 1H), 4.61 (s, 0.3H), 4.58 (s, 1H), 3.29 (s, 3H), 3.25 (s, 1H), 3.24 (s, 3H), 1.59 (s, 9H), 1.30 (s, 3H), 1.29 (s, 9H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 177.1, 176.3, 176.2, 151.7, 150.4, 148.9, 144.6, 144.5, 136.3, 136.2, 133.5, 131.9, 130.2, 129.0, 128.6, 128.4, 128.2, 128.1, 127.3, 126.8, 126.5, 126.3, 125.9, 125.2, 125.2, 125.1, 124.7, 124.6, 122.9, 122.8, 108.2, 108.1, 107.6, 60.5, 52.3, 51.6, 49.7, 35.4, 34.8, 34.6, 32.4, 31.5, 31.4, 29,8, 26.5, 21.2, 14.3. HRMS (ESI) m/z: calcd for $C_{19}H_{22}NO$ [M + H]$^+$ 280.1696, found 280.1695.

Procedure for the Monoepoxidation of Norcaradiene 3a. A dram vial was charged with *m*-CPBA (27 mg, 0.12 mmol, 1.2 equiv), KF (7 mg, 0.12 mmol, 1.2 equiv), and CH_2Cl_2 (500 μL). The resulting mixture was stirred for 20 min before adding **3a** (23 mg, 0.1 mmol) as a solution in 1 mL of CH_2Cl_2. The reaction mixture was stirred at ambient temperature for 59 h. Then, the reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (eluted with EtOAc/petroleum ether 1:5) to afford the product **5a**.

*1-Methyl-8′-oxaspiro[indoline-3,3′-tricyclo[5.1.0.02,4]octan]-5′-en-2-on (**5a**).* Red solid, 52% yield (12.4 mg), R_f = 0.4 (EtOAc/petroleum ether 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.16 (dd, J_1 = 9.6 Hz, J_2 = 3.7 Hz, 1H), 5.85 (dd, J_1 = 9.5 Hz, J_2 = 4.6, 1H), 3.49 (d, J = 2.5 Hz, 1H), 3.35 (s, 1H), 3.29 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 174.6, 144.7, 128.0, 127.5, 124.9, 124.5, 122.4, 121.8, 108.5, 51.5, 47.9, 37.8, 29.8, 29.4, 26.8. HRMS (ESI) m/z: calcd for $C_{15}H_{14}NO_2$ [M + H]$^+$ 240.1019, found 240.1016.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00418.

Copies of NMR spectra and crystal data (PDF)

Accession Codes

CCDC 2052276 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

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