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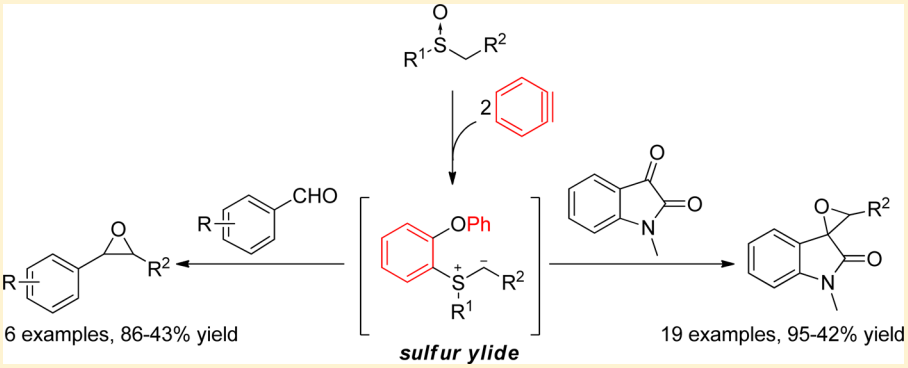
The Epoxidation of Carbonyl Compounds with a Benzyne-Triggered Sulfur Ylide

Mei-Mei Lou,[†] Han Wang,[†] Li Song,[†] Hong-Yi Liu,[†] Zhong-Qiu Li,[†] Xiao-Shuang Guo,[†] Fu-Geng Zhang,*[,‡] and Bin Wang*[,†]

[†]State Key Laboratory of Medicinal Chemical Biology, College of Pharmacy and Tianjin Key Laboratory of Molecular Drug Research, Nankai University, Haihe Education Park, 38 Tongyan Road, Tianjin 300353, People's Republic of China

[‡]Tianjin Key Laboratory of Cerebral Vascular and Neurodegenerative Diseases, Tianjin Huanhu Hospital, Tianjin 300060, People's Republic of China

Supporting Information



ABSTRACT: An efficient method for the synthesis of epoxides from carbonyl compounds, sulfoxides, and benzyne is presented. The strategy involved an epoxidation by a sulfur ylide which is formed in situ from sulfoxide and benzyne through the S−O bond insertion and deprotonation. This one-pot reaction proceeds under mild and base-free conditions, providing a convenient way to introduce the substituted methylene groups onto the carbonyl carbon.

INTRODUCTION

Since the early 1960s, sulfur ylides have emerged as reactive nucleophilic alkylidene transfer agents in organic syntheses.[1−5] This class of intermediates has been found to have wide applications in the synthesis of epoxides,[6,7] cyclopropanes,[8] aziridines,[9−11] terminal alkenes,[12] and organoboron compounds.[13,14] The most common method of sulfur ylide generation consists of proton abstraction from the corresponding sulfonium salts, which are available by the direct alkylation of thioethers (Scheme 1, method A, path 1).[15,16] A less common but exceedingly useful approach for the generation of sulfur ylides involves the reaction of a thioether with a carbene or a metal carbenoid (Scheme 1, method A, path 2).[15] Forbes and co-workers developed a new strategy for the synthesis of sulfur ylides, which is based on the alkylation of thioethers with 2-bromoacetic acid and the decarboxylation of in situ generated sulfonium (Scheme 1, method A, path 3).[17,18] Since the early 1960s, the benzyne-triggered method for the preparation of sulfur ylides has emerged (Scheme 1, method A, path 4).[19−21] The ylide was generated in situ from a thioether with benzyne, and the trapping of ylide with *N*-methyl isatins gave the corresponding spiroepoxy oxindoles.[22] Besides thioethers, a practical alternative approach utilizing sulfoxides as the starting materials for the generation of stable ylides was chosen (Scheme 1, method B).[2] However, the direct alkylation of sulfoxides to generate the sulfoxonium salts is essentially limited to the reaction of methyl halide with dimethyl sulfoxide (DMSO), and the subsequent deprotonation requires the use of strong bases such as sodium hydride,[2,3,23−26] sodium methylsulfinylmethylide,[27−32] and *n*-butyllithium.[33] In addition, the ylide generated from DMSO transfers only the methylene group to the electrophiles. Very recently, Xiao and our group independently reported a S−O bond insertion of sulfoxides with arynes (Scheme 1).[34,35] The reaction mechanism involves a benzannulated four-membered ring intermediate that leads to the formation of a sulfur ylide via deprotonation and S−O bond cleavage. This benzyne-triggered method for the production of sulfur ylides from sulfoxides is free of bases. Moreover, the introduction of substituted methylene units into an electrophilic carbon to prepare highly substituted epoxides is achieved in a facile manner. Herein, we describe the epoxidation of carbonyl compounds with a benzyne-triggered sulfur ylide.

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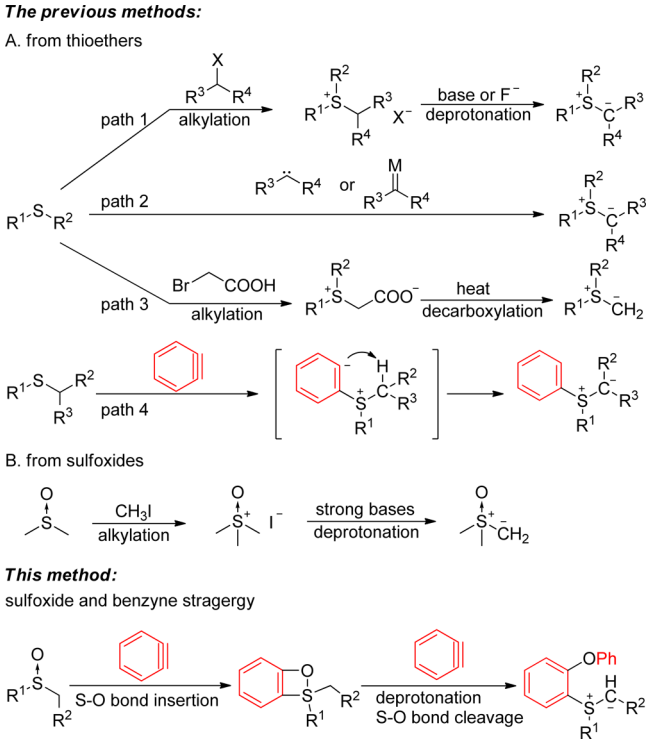
Scheme 1. Preparation of Sulfur Ylides

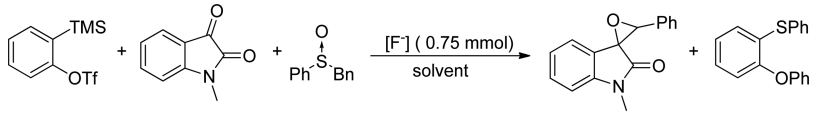


RESULTS AND DISCUSSION

Kobayashi benzyne precursor **1**, *N*-methyl isatin **2** and benzyl phenyl sulfoxide **3a** were chosen as model substrates in the optimization of reaction conditions yielding the epoxide **4a.** The insertion reaction also produced phenyl(2-phenoxyphenyl) sulfane **5a**, whose structure and generation mechanism were established in our earlier work.[34] An initial solvent screening with CsF as an aryne initiator revealed that 1,4-dioxane, toluene, and hexane failed to undergo the epoxidation within 6 h at 25 °C (Table 1, entries 1−3). Further examination indicated that the expoxidation was performed in 65% yield in THF (Table 1, entry 4); DME was more efficient, and the reaction afforded **4a** in 93% yield within 4 h (Table 1, entry 5). We were delighted to discover that the reaction in acetonitrile went to completion within 1 h to give an excellent yield of **4a** (Table 1, entry 6). When the reaction temperature was increased to 50 °C, the yield of **4a** was further increased to 98% within a shorter reaction time (Table 1, entry 7). Screening of other fluoride showed that both KF and Bu_4NF were less effective in the epoxidation, while NH_4F was completely ineffective under these conditions (Table 1, entries 8−10). The molar ratio of substrates of **1**, **2**, and **3a** was also investigated, and the results indicated that the yield of **4a** was significantly decreased (from 98% to 50% and 63%) if the molar ratio was changed from 4:1:2 to 2:1:1 or 3:1:2 (Table 1, entry 7 vs entries 11 and 12, respectively).

The scope of the benzyne-triggered epoxidation of *N*-methyl isatin **2** with CsF in acetonitrile was next examined with a diverse array of sulfoxides. As summarized in Table 2, these epoxidations could be applied to sulfoxides containing a variety of different groups, including aryl, benzyl, and alkyl groups. It should be noted that most of the epoxidations gave products as a mixture of two diastereoisomers which were successfully purified by column chromatography on silica gel and isolated. Sulfoxides **3e**, **3h**, **3k**, **3l**, **3o**, and **3q** afforded the corresponding two diastereoisomers in which the major diastereoisomers had *cis* stereochemistry, while sulfoxide **3g** favored the *trans* product. Other sulfoxides **3a−d**, **3m**, and **3n** led to both diastereoisomeric epoxides in roughly equal yields. The stereochemistry of these epoxides was readily determined by examination of the NMR spectra (HMQC and two-dimensional (2D) $^1H-^1H$ NOESY) for the corresponding *cis* and *trans* isomers, consistent with literature examples.[22,36−38] The epoxidation of *N*-methyl isatin **2** with benzyne-triggered sulfur ylides proceeded efficiently in sulfoxides containing a benzylic group with both electron-withdrawing (Table 2, **3b−g**, **3i**, and **3j**) and electron-donating (Table 2, **3k−n**) substituents. Functional groups such as fluoro, chloro, bromo, nitro, cyano, methoxy, and naphthyl groups were tolerated under the reaction conditions. Furthermore, sulfoxides with aliphatic

Table 1. Optimization of the Reaction Conditions[a]



1 2 3a 4a 5a

	solvent	[F⁻]	*T* (°C)	time (h)	**4a** yield (%)
1	1,4-dioxane	CsF	25	6	0
2	toluene	CsF	25	6	0
3	hexane	CsF	25	6	0
4	THF	CsF	25	6	65
5	DME	CsF	25	4	93
6	CH_3CN	CsF	25	1	96
7	CH_3CN	CsF	50	0.5	98
8	CH_3CN	KF	50	2.5	25
9	CH_3CN	Bu_4NF	50	2.0	41
10	CH_3CN	NH_4F	50	2.5	0
11	CH_3CN	CsF	50	0.5	50[b]
12	CH_3CN	CsF	50	0.5	63[c]

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.125 mmol), and **3a** (0.25 mmol) in 1 mL of solvent under air; isolated full yield of two isomers of **4a**. [b]Molar ratio = 2:1:1 **1**:**2**:**3a**. [c]Molar ratio = 3:1:2 **1**:**2**:**3a**.

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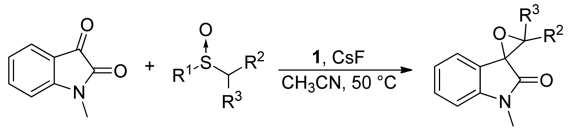
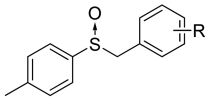
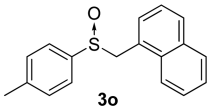
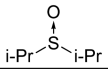
Table 2. Substrate Scope of Various Sulfoxides[a]



2 3a-s 4a-s

entry	sulfoxide 3	time (h)	yield of 4 (%)
1	**3a**	0.5	**4aa** (*cis*-), 50 **4ab** (*trans*-), 45
			
2	**3b**, R = 3-F	1	**4ba** (*cis*-), 38 **4bb** (*trans*-), 44
3	**3c**, R = 3-Cl	1	**4ca** (*cis*-), 36 **4cb** (*trans*-), 32
4	**3d**, R = 3-Br	1	**4da** (*cis*-), 39 **4db** (*trans*-), 36
5	**3e**, R = 3,4-di-Cl	1.5	**4ea** (*cis*-), 40 **4eb** (*trans*-), 21
6	**3f**, R = 2,5-di-F	1	**4f**, 61
7	**3g**, R = 2-fluoro-4-chloro-	0.5	**4ga** (*cis*-), 36 **4gb** (*trans*-), 49
8	**3h**, R = 3-CH_2Br	0.5	**4ha** (*cis*-), 31 **4hb** (*trans*-), 23
9	**3i**, R = 4-NO_2	1.5	**4i**, 42
10	**3j**, R = 4-CN	0.5	**4j**, 42
11	**3k**, R = 3-OCH_3	1	**4ka** (*cis*-), 59 **4kb** (*trans*-), 33
12	**3l**, R = 4-OCF_3	1.5	**4la** (*cis*-), 41 **4lb** (*trans*-), 27
13	**3m**, R = 4-tBu	1	**4ma** (*cis*-), 35 **4mb** (*trans*-), 33
14	**3n**, R = 4-Me	1	**4na** (*cis*-), 35 **4nb** (*trans*-), 32
15	 **3o**	1	**4oa** (*cis*-), 60 **4ob** (*trans*-), 27
			
16	**3p**, R = $CH_2CH_2OCH_3$,	1	**4p** 54
17	**3q**, R = Et	1	**4qa** (*cis*-), 47 **4qb** (*trans*-), 32
18	**3r**, R = Me	0.5	**4r** 92
19	**3s** 	1.5	**4s** 48

[a]Reaction conditions: **1** (1 mmol), **2** (0.25 mmol), **3a**−**s** (0.5 mmol), and CsF (1.5 mmol) in CH_3CN (1 mL); isolated yield.

chains (Table 2, **3p**−**s**), including alkoxyl, ethyl, methyl, and isopropyl substituent, could also produce the corresponding epoxides in 48−92% yield. It is noteworthy that the bromomethyl group was well-tolerated in sulfoxide **3h**, leading to the valuable bromo-substituted epoxides **4ha** and **4hb**, which could not be prepared by the standard alkylation/deprotonation methodology with sulfides.

The reaction scope was subsequently explored using benzyl phenyl sulfoxide **3a** and aromatic aldehydes **6a**−**f** (Table 3). Epoxidation of 4-nitrobenzaldehyde **6a** resulted in a good total yield of isomers **7aa** and **7ab**. Likewise, 2-nitrobenzaldehyde **6b** can easily be used in the epoxidation reaction albeit in a moderate yield of 65%. When the aromatic aldehyde contains other electron-withdrawing groups such as COOMe, Br, I, and CN, the epoxidation also happened under these conditions (Table 3, **6c**−**6f**). Unfortunately, benzaldehyde and aldehydes with electron-donating groups failed to undergo the epoxidation, most likely due to the unreactive nature of these substrates. An insertion reaction of sulfoxide and benzyne occurred instead, as described in our previous report.[34]

CONCLUSION

In summary, we developed a new method for sulfur ylide generation by the insertion reaction of benzynes with sulfoxides. In comparison to current alternative methods for epoxidation of sulfur ylides, this system reacts under milder conditions free of bases in a one-pot operation. Moreover, the substituted methylene groups can be readily introduced onto the carbonyl carbon of *N*-methyl isatin and activated aromatic aldehydes. The methodology is expected to be of high utility in sulfur ylide chemistry. Researchers can devise some asymmetric synthesis based on this strategy. Further studies on the mechanistic aspects of this reaction as well as related benzyne-triggered reactions are ongoing in our laboratory.

EXPERIMENTAL SECTION

1. General Remarks. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer (400 MHz for H and 100 MHz for C) using $CDCl_3$ as a solvent. Signal positions were recorded in ppm with the abbreviations s, d, t, q, and m denoting singlet, doublet, triplet, quartet, and multiplet, respectively. All NMR chemical shifts were referenced to residual solvent peaks or to TMS as an internal standard. NMR spectra recorded in $CDCl_3$ were referenced to residual $CHCl_3$ at 7.26 ppm for ^1H or 77.0 ppm for ^{13}C. All coupling constants *J* were quoted in Hz. Data were reported as follows: chemical shift, multiplicity, coupling constant, and integration. HRMS were measured using Q-TOF LC−MS and the ESI-FTICR technique. Elemental analysis was carried out on a Vario EL cube analyzer. The melting point of the product was measured with a microscopic melting point meter. Reactions were monitored by TLC on 0.25 mm silica gel glass plates coated with 60 F254. Column chromatography was performed on silica gel (200−300 mesh) using a mixture of petroleum ether (60−90 °C) and ethyl acetate as eluent. All commercially available reagents were used as received without further purification.

2. Experimental Procedures. *General Procedure for the Preparation of Product* ***4****.* A Schlenk tube was charged with 1-methylisatin **2** (0.25 mmol, 40.2 mg, 1 equiv), sulfoxide **3** (0.5 mmol, 2 equiv), and CsF (1.5 mmol, 228 mg, 6 equiv) under air at room temperature, and then 2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1** (1 mmol, 240 μL, 4 equiv) and CH_3CN (1 mL) were added. After the mixture was stirred at 50 °C for a certain time, the residue was mixed with silica gel and concentrated. The resulting mixture was purified by silica gel column chromatography on silica gel with petroleum ether:ethyl acetate (80:1) as eluent to give the desired product **4**.

General Procedure for the Preparation of Product ***7****.* A Schlenk tube was charged with benzyl phenyl sulfoxide **3a** (0.5 mmol, 108 mg, 2 equiv) and aldehyde **6** (0.25 mmol, 1 equiv) under air at room temperature, and then CsF (1.5 mmol, 228 mg, 6 equiv), 18-crown-6 (0.25 mmol, 66 mg, 1 equiv), 2-(trimethylsilyl) phenyl trifluoromethanesulfonate **1** (1 mmol, 240 μL, 4 equiv), and CH_3CN (1 mL) were added. After the mixture was stirred at 50 °C for a certain time, the residue was mixed with silica gel and concentrated. The resulting mixture was purified by silica gel column chromatography on silica gel with petroleum ether:ethyl acetate (800:1) as eluent to give the desired product **7**. The reaction times of **6a** and **6b**−**6f** were 0.25 and 0.5 h, respectively.

*1-Methyl-3′-phenylspiro[indoline-3,2′-oxiran]-2-one (cis-) (****4aa****)..*[36,38] Yellow solid (31.3 mg, 50%). Mp: 136−137 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.41−7.35 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.13 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.67 (s, 1H), 3.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8,

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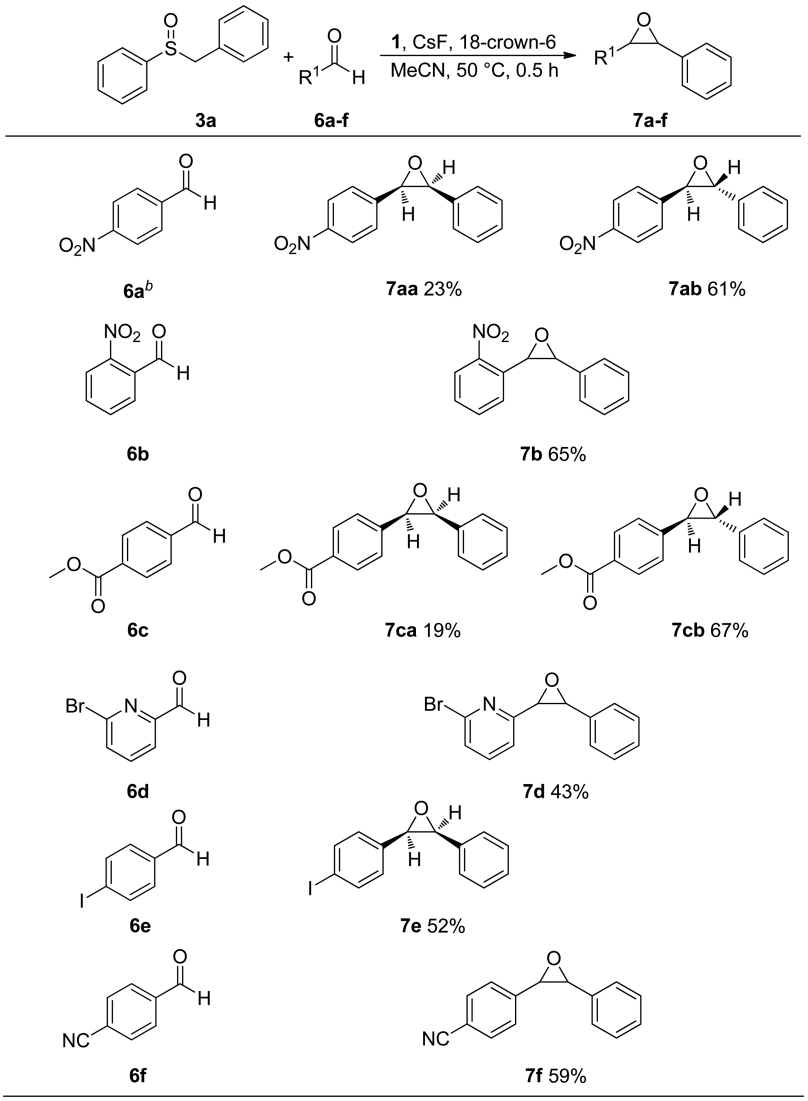
Table 3. Substrate Scopes of Various Aromatic Aldehyde[a]



[a]Reaction conditions: **1** (1 mmol), **3a** (0.5 mmol), **6a–f** (0.25 mmol), 18-crown-6 (0.25 mmol), and CsF (1.5 mmol) in CH_3CN (1 mL); isolated yields. [b]0.25 h.

144.5, 131.6, 130.2, 128.7, 127.7, 127.4, 123.5, 122.6, 121.6, 108.6, 67.4, 61.9, 26.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NO_2^+$ $[M + H]^+$: 252.1019, found 252.1021.

*1-Methyl-3′-phenylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4ab**).*[36] White solid (28.2 mg, 45%). Mp: 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.37 (m, 5H), 7.28 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.77 (t, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.83 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 145.2, 133.2, 130.1, 128.6, 128.4, 126.7, 123.6, 122.4, 120.9, 108.6, 65.0, 61.6, 26.6. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NO_2^+$ $[M + H]^+$: 252.1019, found 252.1022.

*3′-(3-Fluorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ba**).* Yellowish solid (25.7 mg, 38%). Mp: 107–108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.34 (m, 4H), 7.23 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.07–7.02 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 4.65 (s, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 162.7 (d, $^1J_{C-F}$ = 241.5 Hz), 145.3, 135.8, 135.7, 130.4, 130.3, 130.2, 123.5, 122.6, 122.5, 122.4, 120.5, 115.8, 115.6, 113.9, 113.7, 108.7, 64.3, 64.2, 61.6, 26.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}FNO_2^+$ $[M + H]^+$: 270.0925, found 270.0926.

*3′-(3-Fluorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4bb**).* White solid (29.5 mg, 44%). Mp: 136–137 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.28 (m, 2H), 7.24–7.17 (m, 2H), 7.07 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 4.0 Hz, 1H), 6.80 (t, J = 8.0 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 4.79 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 162.3 (d, $^1J_{C-F}$ = 251.5 Hz), 144.6, 134.3, 134.2, 130.4, 129.3, 129.2, 123.1, 123.0, 122.7, 121.6, 115.8, 115.6, 114.7, 114.5, 108.7, 66.6, 66.5, 61.8, 26.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}FNO_2^+$ $[M + H]^+$: 270.0925, found 270.0925.

*3′-(3-Chlorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ca**).* Yellow solid (25.6 mg, 36%). Mp: 135–136 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1H), 7.51–7.50 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 4.0 Hz, 2H), 7.22 (d, J = 4.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 4.63 (s, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 144.6, 133.8, 133.7, 130.4, 128.9, 128.9, 127.6, 125.6, 123.1, 122.7, 121.6, 108.7, 66.4, 61.8, 26.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}ClNO_2^+$ $[M + H]^+$: 286.0635, 287.0668, 288.0605, 289.0639, found 286.0626, 287.0654, 288.0601, 289.0633.

*3′-(3-Chlorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4cb**).* White solid (22.5 mg, 32%). Mp: 86–87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.35–7.28 (m, 4H), 6.89 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.78 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 145.3, 135.3, 134.6, 130.4, 129.8, 128.9, 126.8, 124.9, 123.5, 122.6, 120.4, 108.8, 64.2, 61.6, 26.7. HRMS (ESI): *m/z* calcd for $C_{16}H_{13}ClNO_2^+$ [M

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+ H]$^+$: 286.0635, 287.0668, 288.0605, 289.0639, found 286.0627, 287.0659, 288.0585, 289.0615.

*3′-(3-Bromophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4da**).* Yellowish solid (31.8 mg, 39%). Mp: 145−146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.28−7.21 (m, 2H), 7.13 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 4.62 (s, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 144.6, 134.0, 131.8, 130.4, 130.4, 129.2, 126.1, 123.1, 122.7, 121.8, 121.6, 108.7, 66.3, 61.8, 26.5. HRMS (ESI): m/z calcd for $C_{16}H_{13}BrNO_2^+$ [M + H] $^+$: 330.0130, 331.0163, 332.0109, 333.0143, found 330.0119, 331.0153, 332.0102, 333.0136.

*3′-(3-Bromophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4db**).* Yellowish solid (29.8 mg, 36%). Mp: 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 6,81 (t, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.77 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 145.3, 135.5, 131.9, 130.4, 130.1, 129.7, 125.3, 124.7, 123.5, 122.6, 120.4, 108.8, 64.1, 61.6, 26.7. HRMS (ESI): m/z calcd for $C_{16}H_{13}BrNO_2^+$ [M + H]$^+$: 330.0130, 331.0163, 332.0109, 333.0143, found 330.0122, 331.0164, 332.0099, 333.0134.

*3′-(3,4-Dichlorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ea**).* White solid (28.7 mg, 40%). Mp: 151−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.46−7.40 (m, 3H), 7.22 (d, J = 4.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 4.60 (s, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 144.6, 132.8, 132.0, 131.9, 130.5, 129.7, 129.5, 126.8, 123.4, 122.8, 121.7, 108.8, 65.9, 61.8, 26.5. HRMS (ESI) m/z calcd for $C_{16}H_{12}Cl_2NO_2^+$ [M + H]$^+$: 320.0245, 321.0279, 322.0216, 323.0249, found 320.0243, 321.0271, 322.0215, 323.0245.

*3′-(3,4-Dichlorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4eb**).* White solid (16.8 mg, 21%). Mp: 80−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.50 (d, J = 8.0 Hz,1H), 7.35−7.29 (m, 2H), 6.91−6.83 (m, 2H), 6.47 (d, J = 8.0 Hz, 1H), 4.74 (s, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 145.3, 133.5, 133.0, 132.9, 130.6, 130.5, 128.7, 126.0, 123.4, 122.7, 120.1, 108.9, 63.7, 61.7, 26.7. HRMS (ESI) m/z calcd for $C_{16}H_{12}Cl_2NO_2^+$ [M + H]$^+$: 320.0245, 321.0279, 322.0216, 323.0249, found 320.0240, 321.0273, 322.0212, 323.0259.

*3′-(2,5-Difluorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (**4f**).* White solid (43.7 mg, 61%). Mp: 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.37 (m, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.08−6.96 (m, 2H), 6.90(d, J = 8.0 Hz, 1H), 6.82 (t, J = 8.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 4.80 (s, 1H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 158.6 (d, $^1J_{C-F}$ = 251.5 Hz), 157.0 (d, $^1J_{C-F}$ = 221.3 Hz), 145.4, 130.6, 129.7, 128.5, 123.0, 122.7, 120.3, 117.1, 117.0, 116.9, 116.9, 116.8, 116.8, 116.7, 115.0, 114.8, 114.8, 108.9, 61.3, 60.5, 60.5, 26.8. HRMS (ESI): m/z calcd for $C_{16}H_{12}F_2NO_2^+$ [M + H]$^+$: 288.0831, found 288.0834.

*3′-(4-Chloro-2-fluorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ga**).* Yellow solid (27.2 mg, 36%). Mp: 146−147 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, J = 8.0 Hz, 1H), 7.28−7.20 (m, 2H), 7.00 (d, J = 12.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 8.0 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 4.73 (s, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 160.7 (d, $^1J_{C-F}$ = 251.5 Hz), 145.3, 135.6, 135.5, 130.5, 129.1, 129.0, 124.6, 124.6, 123.0, 122.6, 120.3, 120.0, 119.9, 116.5, 116.3, 108.9, 61.2, 60.5, 60.5, 26.7. HRMS (ESI): m/z calcd for $C_{16}H_{12}ClFNO_2^+$ [M + H]$^+$: 304.0541, 305.0574, 306.0511, 307.0545, found 304.0536, 305.0568, 306.0509, 307.0530.

*3′-(4-Chloro-2-fluorophenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4gb**).* White solid (37.1 mg, 49%). Mp: 151−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (t, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.14 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.76 (s, 1H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 160.7 (d, $^1J_{C-F}$ = 241.5 Hz), 144.6, 135.4, 135.3, 130.6, 130.5, 124.0, 123.9, 122.9, 122.7, 121.9, 118.4, 118.3, 115.7, 115.5, 108.8, 61.6, 61.5, 61.4, 26.5. HRMS (ESI): m/z calcd for $C_{16}H_{12}ClFNO_2^+$ [M + H]$^+$: 304.0541, 305.0574, 306.0511, 307.0545, found 304.0537, 305.0559, 306.0506, 307.0535.

*3′-(3-(Bromomethyl)phenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ha**).* White solid (26.3 mg, 31%). Mp: 194−195 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.55 (s, 1H), 7.41 (t, J = 8.0 Hz, 3H), 7.24 (d, J = 12.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 4.0 Hz, 1H), 4.66 (s, 1H), 4.53 (s, 2H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 144.5, 137.1, 132.4, 130.3, 129.4, 128.2, 128.1, 127.5, 123.3, 122.7, 121.6, 108.6, 67.0, 61.8, 33.3, 26.5. HRMS (ESI): m/z calcd for $C_{17}H_{15}BrNO_2^+$ [M + H]$^+$: 344.0286, 345.0320, 346.0266, 347.0299, found 344.0283, 345.0308, 346.0262, 347.0289.

*3′-(3-(Bromomethyl)phenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4hb**).* White solid (19.3 mg, 23%). Mp: 94−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.38 (s, 3H), 7.29 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 4.81 (s, 1H), 4.51 (q, J = 8.0 Hz, 2H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 145.2, 138.1, 133.9, 130.2, 129.2, 129.0, 127.2, 126.8, 123.6, 122.5, 120.5, 108.6, 64.6, 61.6, 32.9, 26.6. HRMS (ESI): m/z calcd for $C_{17}H_{15}BrNO_2^+$ [M + H]$^+$: 344.0286, 345.0320, 346.0266, 347.0299, found 344.0283, 345.0325, 346.0265, 347.0292.

*1-Methyl-3′-(4-nitrophenyl)spiro[indoline-3,2′-oxiran]-2-one (**4i**).* Yellowish solid (30.6 mg, 42%). Mp: 104−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 4.73 (s, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 148.1, 144.7, 139.0, 130.8, 128.4, 123.0, 122.6, 121.8, 108.9, 65.9, 62.0, 26.6. HRMS (ESI): m/z calcd for $C_{16}H_{13}N_2O_4^+$ [M + H]$^+$: 297.0870, found 297.0869.

*4-(1-Methyl-2-oxospiro[indoline-3,2′-oxiran]-3′-yl) Benzonitrile (**4j**).* Yellow solid (29 mg, 42%). Mp: 151−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (q, J = 8.0 Hz, 4H), 7.43 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.68 (s, 1H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 144.6, 137.0, 131.4, 130.6, 128.1, 122.9, 121.7, 118.6, 112.3, 108.8, 66.0, 61.9, 26.5. HRMS (ESI): m/z calcd for $C_{17}H_{13}N_2O_2^+$ [M + H]$^+$: 277.0972, found 277.0976.

*3′-(3-Methoxyphenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ka**).* White solid (41.5 mg, 59%). Mp: 97−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.21 (s, 2H), 7.13 (t, J = 8.0 Hz, 2H), 6.90 (d, J = 4.0 Hz, 2H), 4.64 (s, 1 H), 3.84 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 159.0, 144.5, 133.2, 130.1, 128.7, 123.5, 122.5, 121.5, 119.7, 114.8, 112.5, 108.5, 67.4, 61.9, 55.2, 26.4. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_3^+$ [M + H]$^+$: 282.1125, found 282.1126.

*3′-(3-Methoxyphenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4kb**).* Yellow oily liquid (22.8 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 8.0 Hz, 2H), 7.01 (d, J = 12.0 Hz, 2H), 6.88 (t, J = 8.0 Hz, 2H), 6.79 (t, J = 8.0 Hz, 1H), 6.55 (d, J = 8.0 Hz, 1H), 4.80 (s, 1 H), 3.81 (s, 3H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 159.7, 145.2, 134.7, 130.2, 129.7, 123.7, 122.6, 120.9, 119.0, 114.5, 112.0, 108.7, 65.0, 61.6, 55.4, 26.7. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_3^+$ [M + H]$^+$: 282.1125, found 282.1128.

*1-Methyl-3′-(4-(trifluoromethoxy)phenyl)spiro[indoline-3,2′-oxiran]-2-one (cis-) (**4la**).* Yellow solid (34.2 mg, 41%). Mp: 112−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 3H), 7.14 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 4.65 (s, 1H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, CDC_{l3}): δ 169.7, 149.3, 144.5, 132.9, 130.4, 129.0, 123.1, 122.7, 121.6, 120.0, 108.7, 66.6, 61.9, 26.5. HRMS (ESI): m/z calcd for $C_{17}H_{13}F_3NO_3^+$ [M + H]$^+$: 336.0842, found 336.0840.

*1-Methyl-3′-(4-(trifluoromethoxy)phenyl)spiro[indoline-3,2′-oxiran]-2-one (trans-) (**4lb**).* White solid (22.6 mg, 27%). Mp: 148−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 3H), 6.89 (d, J = 8.0 Hz, 1H), 6.80 (t, J = 8.0 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 4.81 (s, 1H), 3.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 149.3, 145.3, 131.9, 130.4, 128.3, 123.4, 122.5, 120.9, 120.5, 108.8, 64.2, 61.6, 26.7. HRMS (ESI): m/z calcd for $C_{17}H_{13}F_3NO_3^+$ [M + H]$^+$: 336.0842, found 336.0845.

*3′-(4-(tert-Butyl)phenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4ma**).* Yellowish solid (26.9 mg, 35%). Mp: 106−107 °C.

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^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.43−7.37 (m, 3H), 7.24 (t, J = 4.0 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 4.63 (s, 1H), 3.16 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 151.6, 144.5, 130.1, 128.7, 127.3, 124.7,123.7, 122.6, 121.5, 108.5, 67.7, 62.1, 34.7, 31.3, 26.5. HRMS (ESI): m/z calcd for $C_{20}H_{22}NO_2^+$ $[M + H]^+$: 308.1645, found 308.1647.

*3′-(4-(tert-Butyl)phenyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4mb**).* Yellowish solid (25 mg, 33%). Mp: 75−76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.37 (m, 4H), 7.29 (d, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 4.80 (s, 1H), 3.30 (s, 3H), 1.33 (s, 9 H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 151.8, 145.2, 130.1, 130.0, 126.4, 125.3, 123.7, 122.4, 121.1, 108.5, 65.2, 61.7, 34.7, 31.3, 26.6. HRMS (ESI): m/z calcd for $C_{20}H_{22}NO_2^+$ $[M + H]^+$: 308.1645, found 308.1650.

*1-Methyl-3′-(p-tolyl)spiro[indoline-3,2′-oxiran]-2-one (cis-) (**4na**).* White solid (22.9 mg, 35%). Mp: 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.24−7.11 (m, 4H), 6.90 (d, J = 4.0 Hz, 1H), 4.65 (s, 1H), 3.16 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 144.5, 138.6, 130.1, 128.7, 128.4, 127.3, 123.7, 122.6, 121.5, 108.5, 67.6, 61.9, 26.5, 21.4. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176, found 266.1181.

*1-Methyl-3′-(p-tolyl)spiro[indoline-3,2′-oxiran]-2-one (trans-) (**4nb**).* Yellow solid (20.8 mg, 32%). Mp: 94−95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 4.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 4.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 6.52 (d, J = 8.0 Hz, 1H), 4.79 (s, 1H), 3.30 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 145.2, 138.5, 130.1, 130.0, 129.1, 126.6, 123.7, 122.4, 121.2, 108.5, 65.1, 61.6, 26.6, 21.3. HRMS (ESI): m/z calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176, found 266.1179.

*1-Methyl-3′-(naphthalen-2-yl)spiro[indoline-3,2′-oxiran]-2-one (cis-) (**4oa**).* Yellowish solid (44.7 mg, 60%). Mp: 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (t, J = 8.0 Hz, 3H), 7.49−7.42 (m, 4H), 7.35 (t, J = 8.0 Hz, 1H), 7.20−7.13 (m, 3H), 4.80 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 144.8, 135.0, 133.6, 132.0, 130.5, 129.6, 129.4, 128.6, 128.5, 126.5, 125.8, 125.0, 124.6, 123.6, 121.8, 108.7, 65.5, 59.8, 21.5. HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_2^+$ $[M + H]^+$: 302.1176, found 302.1178.

*1-Methyl-3′-(naphthalen-2-yl)spiro[indoline-3,2′-oxiran]-2-one (trans-) (**4ob**).* White solid (20.1 mg, 27%). Mp: 86−87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90−7.83 (m, 3H), 7.73 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.47−7.38 (m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.61 (t, J = 8.0 Hz, 1H), 6.32 (t, J = 8.0 Hz, 1H), 5.26 (s, 1H), 3.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 145.0, 133.1, 130.8, 130.1, 129.3, 129.1, 128.6, 126.6, 126.1, 125.0, 124.5, 123.2, 122.7, 122.4, 120.8, 108.5, 64.0, 61.6, 26.7. HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_2^+$ $[M + H]^+$: 302.1176, found 302.1175.

*3′-(Methoxymethyl)-1-methylspiro[indoline-3,2′-oxiran]-2-one (**4p**).* White solid (29.4 mg, 54%). Mp: 83−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.35 (m, 1H), 7.08 (t, J = 4.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 4.09 (dd, J = 12.0 Hz, 8.0 Hz, 1H), 4.01−3.98 (m, 1H), 3.84−3.82 (m, 1H), 3.45 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 144.5, 130.3, 123.1, 122.9, 121.8, 108.7, 68.5, 64.3, 59.2, 58.9, 26.6. HRMS (ESI): m/z calcd for $C_{12}H_{14}NO_3^+$ $[M + H]^+$: 220.0968, found 220.0969.

*1,3′-Dimethylspiro[indoline-3,2′-oxiran]-2-one (cis-) (**4qa**)..*[34,39] White solid (22.2 mg, 47%). Mp: 104−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.34 (m, 1H), 7.07 (t, J = 4.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 1H), 3.76−3.72 (m, 1H), 3.26 (s, 3H), 1.73 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 144.4, 129.9, 124.1, 122.6, 121.5, 108.5, 63.1, 59.6, 26.6, 12.2. HRMS (ESI): m/z calcd for $C_{11}H_{12}NO_2^+$ $[M + H]^+$: 190.0863, found 190.0864.

*1,3′-Dimethylspiro[indoline-3,2′-oxiran]-2-one (trans-) (**4qb**).* Yellow oil (14.8 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.38 (m, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.76 (dd, J = 12 Hz, 8 Hz, 1H), 3.26 (s, 3H), 1.59 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 145.3, 130.0, 124.7, 124.0, 122.5, 108.8, 61.3, 60.5, 26.6, 13.6. HRMS (ESI): m/z calcd for $C_{11}H_{12}NO_2^+$ $[M + H]^+$: 190.0863, found 190.0866.

*1-Methylspiro[indoline-3,2′-oxiran]-2-one (**4r**)..*[34,36] Yellow solid (40.01 mg, 92%). Mp: 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, J = 8.0 Hz, 1H), 7.10−7.05 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 3.57 (d, J = 4.0 Hz, 1H), 3.42 (d, J = 8.0 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 145.0, 130.3, 122.8, 122.6, 122.0, 108.8, 56.3, 54.0, 26.6. HRMS (ESI): m/z calcd for $C_{10}H_9NO_2Na^+$ $[M + Na]^+$: 198.0525, found 198.0525.

*1,3′,3′-Trimethylspiro[indoline-3,2′-oxiran]-2-one (**4s**).* White solid (12.2 mg, 48%). Mp: 85−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.08−7.05 (m, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.25 (s, 3H), 1.77 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.9, 145.0, 129.6, 124.5, 123.4, 122.1, 108.4, 66.7, 64.8, 26.6, 21.1, 18.6. HRMS (ESI): m/z calcd for $C_{12}H_{14}NO_2^+$ $[M + H]^+$: 204.1019, found 204.1017.

*2-(4-Nitrophenyl)-3-phenyl-oxirane (cis-) (**7aa**).* White solid (13.6 mg, 23%). Mp: 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 4.0 Hz, 5H), 4.46 (d, J = 4.0 Hz, 1H), 4.41 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 142.0, 133.2, 128.0, 128.0, 127.6, 126.6, 123.0, 60.0, 58.8. MS: m/z 241.0. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81; O, 19.90. Found C, 69.72; H, 4.61; N, 5.82; O, 19.92.

*2-(4-Nitro-phenyl)-3-phenyl-oxirane (trans-) (**7ab**).* Colorless oil (36.7 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.41−7.35 (m, 5H), 3.99 (s, 1H), 3.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 144.4, 136.0, 128.8, 128.7, 126.2, 125.5, 123.8, 63.3, 61.6. MS: m/z 241.1.

*2-(2-Nitrophenyl)-3-phenyloxirane (**7b**).*[40] Yellow solid (38.8 mg, 65%). Mp: 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.0 Hz, 1H), 7.72(d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 5H), 4.51 (s, 1H), 3.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 134.3, 133.9, 130.3, 128.6, 128.6, 127.0, 125.8, 124.7, 120.4, 62.2, 59.9. HRMS (ESI): m/z calcd for $C_{14}H_{12}NO_3^+$ $[M + H]^+$: 242.0812, found 242.0806.

*Methyl 4-(3-Phenyloxiran-2-yl)benzoate (cis-) (**7ca**).*[37] White solid (12 mg, 19%). Mp: 85−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.24 (s, 2H), 7.15 (s, 5H), 4.40 (d, J = 4.0 Hz, 1H), 4.37 (d, J = 4.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 139.6, 133.7, 129.3, 129.0, 127.8, 127.7, 126.7, 126.7, 59.8, 59.3, 52.0. HRMS (ESI): m/z calcd for $C_{16}H_{15}O_3^+$ $[M + H]^+$: 255.1016, found 255.1015.

*Methyl 4-(3-Phenyloxiran-2-yl)benzoate (trans-) (**7cb**).* White solid (42.6 mg, 67%). Mp: 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 2H), 7.43−7.34 (m, 7H), 3.93 (s, 4H), 3.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 142.2, 136.6, 130.0, 129.8, 128.6, 128.5, 125.5, 125.4, 63.0, 62.2, 52.1. MS: m/z 254.1. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55; O, 18.88. Found C, 75.59; H, 5.56; O, 18.92.

*1-Bromo-6-(3-phenyloxiran-2-yl) Pyridine (**7d**).* White oil (29.6 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.39−7.29 (m, 6H), 4.05 (s, 1H), 3.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 141.8, 139.2, 136.0, 128.6, 128.5, 127.6, 125.7, 118.3, 62.2, 62.1. HRMS (ESI): m/z calcd for $C_{13}H_{11}BrNO^+$ $[M + H]^+$: 276.0024, 277.0058, 278.0004, 279.0037, found 276.0021, 277.0051, 278.0003, 279.0031.

*2-(4-Iodophenyl)-3-phenyloxirane (cis-) (**7e**).* White oil (41.7 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.0 Hz, 2H), 7.21−7.15 (m, 5H), 6.91 (d, J = 8.0 Hz, 2H), 4.36 (d, J = 4.0 Hz, 1H), 4.28 (d, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 134.1, 133.9, 128.7, 127.9, 127.7, 126.7, 93.2, 59.7, 59.2. MS: m/z 322.1. Anal. Calcd for $C_{14}H_{11}IO$: C, 52.20; H, 3.44; O, 4.97. Found C, 52.21; H, 3.40; O, 4.96.

*3-(3-Phenyloxiran-2-yl) Benzonitrile (**7f**).* Yellow solid (32.2 mg, 59%). Mp: 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.58 (m, 3H), 7.50 (t, J = 8.0 Hz, 1H), 7.40−7.33 (m, 5H), 3.91 (s, 1H), 3.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 136.1, 131.8, 129.8, 129.4, 129.0, 128.7, 128.7, 125.5, 118.5, 112.9, 63.1, 61.5. MS: m/z 221.1. Anal. Calcd for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33; O, 7.23. Found C, 81.46; H, 5.03; N, 6.34; O, 7.26.

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■ ASSOCIATED CONTENT

Supporting Information

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^{1}H and ^{13}C NMR and MS spectra for products **4** and **7**. HMQC and 2D ^{1}H−^{1}H NOESY spectra for products **4aa**, **4ab**, **4ca**, **4cb**, **7aa**, **7ab**, **7ca**, and **7cb** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: clare2006@163.com.

*E-mail: wangbin@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

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