Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.202001082

Link to VoR: https://doi.org/10.1002/adsc.202001082

10.1002/adsc.202001082

DOI: 10.1002/adsc.202((will be filled in by the editorial staff))

Regioselective and Chemodivergent Synthesis of Azulenolactones and Azulenolactams from Rhodium(III)-Catalyzed Reactions of Azulenecarboxamides with Sulfoxonium Ylides

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Received: ((will be filled in by the editorial staff))

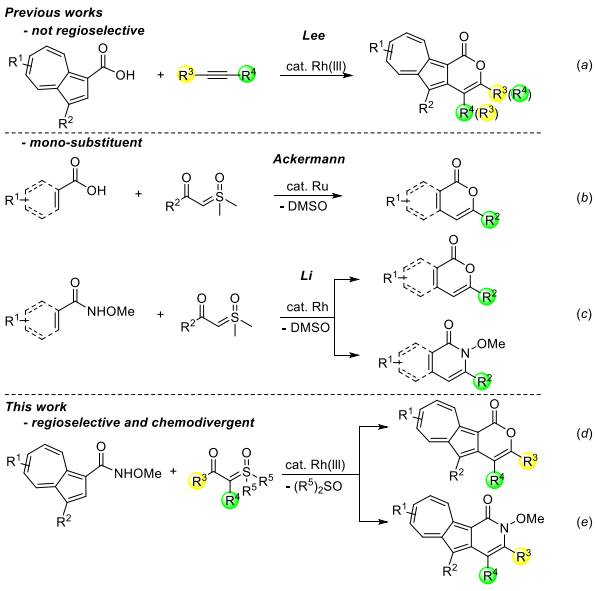
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A regioselective and chemodivergent synthetic approach for azulenolactones and azulenolactams as a new scaffold was demonstrated through Rh(III)-catalyzed reaction of *N*-methoxyazulene-1-carboxamides with sulfoxonium ylides. Sulfoxonium ylides that act as a precursor of secondary carbene was described, leading to the selective formation of azulenolactones and azulenolactams bearing two substituents on a newly introduced double bond. This method demonstrated functionalization of less reactive 2-position of azulene to overcome the natural reactivity.

Keywords: azulene; rhodium; azulenolactone; azulenolactam; sulfoxonium ylide

Introduction

Because azulene derivatives have been found in natural products, pharmacologically active substances, and functional materials,[1] the establishment of a new synthetic approach is required. To date, C−H activation has received considerable attention in the development of new synthetic methods for valuable compounds that could not be synthesized by conventional methods.[2,3] In particular, transition metal-catalyzed cyclization reactions of aromatic compounds with a large number of coupling partners have been reported.[3] Despite great progress, this promising C−H activation is mainly applied to benzenoid aromatic compounds. Therefore, C–H activation using nonbenzenoid aromatic compounds is challenging.[4,5a] Moreover, because azulene has a dipole moment of 1.08 D as a result of an electron-poor seven-membered ring and an electron-rich five-membered ring, 2-position of azulene is less reactive than 1,3-position, and then introduction of substituents into 2-position has been an irresistible synthetic challenge.[5] In this regard, we have developed a Rh(III)-catalyzed cyclization *via* the C−H activation of azulene carboxylic acids with alkynes, leading to the formation of azulenolactones (Scheme 1*a*).[6] Although these methods provided new scaffolds with nonbenzenoid aromatic azulene moiety, the formation of regioisomeric mixtures



Scheme 1. Cyclization Reactions Using Sulfoxonium Ylides and Synthetic Approaches for Azulenolactones and Azulenolactams.

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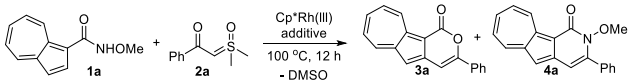
cannot be avoided when unsymmetrical internal alkynes are employed. Also, it cannot be applied to terminal alkynes. Thus, the establishment of a regioselective and chemodivergent synthetic approach for azulenolactone and azulenolactam to overcome these shortcomings is in high demand. Recently, the Aïssa and Li groups reported Rh(III)-catalyzed carbenoid insertion reactions into benzenoid aromatic C−H functionalization with sulfoxonium ylides,[7] and various synthetic methods have also been described by other groups (Scheme 1*b*).[8] In addition, Li and coworkers have developed Rh(III)-catalyzed chemodivergent reactions between benzamides and sulfoxonium ylides, regioselectively producing isocoumarins and isoquinolones (Scheme 1*c*).[9] However, sulfoxinium ylides to act as precursor of primary carbene have been investigated in the main to date. Thus, the reported methods could largely be used for the synthesis of cyclic compounds with one substituent in a newly introduced double bond.[10] Therefore, it is necessary to expand synthetic utility of a sulfoxonium ylide that acts as a precursor of secondary carbene to selectively introduce two substituents into a newly introduced double bond.[7a,11] To continue our recent studies on the functionalization of nonbenzenoid aromatic azulenes,[6,12] we envisioned that the reaction of *N*-methoxyazulene-1-carboxamides with sulfoxonium ylides would selectively provide azulenolactones and azulenolactams. Herein, we demonstrated a regioselective and chemodivergent synthetic method for azulenolactones and azulenolactams with mono- and di-substituents on a newly introduced double bond via tandem Rh(III)-catalyzed alkylation and cyclization reaction of *N*-methoxyazulene-1-carboxamides with sulfoxonium ylides (Scheme 1*d* and 1*e*). Therefore, challenging functionalization of less reactive 2-position of azulene to overcome the natural reactivity was achieved.

Results and Discussion

First, we investigated Rh-catalyzed reaction of *N*-methoxyazulene-1-carboxamide (**1a**) with phenylsulfoxonium ylide (**2a**) to selectively obtain azulenolactone (**3a**) and azulenolactam (**4a**) (Table 1). When **1a** (0.1 mmol, 1.0 equiv) reacted with **2a** (1.5 equiv) in the presence of $[Cp^*RhCl_2]_2$(4.0 mol %) and CsOAc (0.3 equiv) in DCE, reaction took place through C−H activation followed by cyclization, leading to the formation of the desired compounds **3a** and **4a** in 45 and 39% yields, respectively (entry 1). Fortunately, the addition of pivalic acid (2.0 equiv) increased the selectivity of **3a** and **4a** to 3.25:1 (entry 2). In addition, when $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (4.0 mol %) was used as a catalyst in the presence of KOAc and pivalic acid, azulenolactone (**3a**) was selectively obtained in 78% yield (entry 4). Among the solvents tested in this study, toluene gave the best results, although DCE and *tert*-amyl alcohol were also effective to some extent (entries 4-6). The best result was obtained from the reaction of **1a** (0.1 mmol, 1.0 equiv) with **2a** (1.2 equiv) in the presence of $[Cp^*Rh(MeCN)_3][(SbF_6)_2]$ (4.0 mol %), KOAc (0.3 equiv), and PivOH (2.0 equiv) in toluene at 100 °C for 12 h under a nitrogen atmosphere, providing azulenolactone (**3a**) in 92% yield (entry 6). Next, optimization of the formation of azulenolactam (**4a**) was attempted with $[Cp^*RhCl_2]_2$ (4.0 mol %) as a catalyst. Among the additives [$Zn(OTf)_2$, CsOAc, KOAc, and CsOAc/KOAc] screened in toluene, CsOAc/KOAc (1.0 equiv, each) gave the best results, producing **3a** and **4a** in 26 and 70% yields,

Table 1. Reaction optimization.[a]



Entry	Additive (equiv)	Solvent	Yield [%][b] 3a	4a
1[c]	CsOAc (0.3)	DCE	45	39
2[c]	CsOAc (0.3)/ PivOH (2.0)	DCE	65	20
3[d]	CsOAc (0.3)/ PivOH (2.0)	DCE	70	14
4[d]	KOAc (0.3)/ PivOH (2.0)	DCE	78	14
5[d]	KOAc (0.3)/ PivOH (2.0)	*t*-AmOH	73	17
6[d]	KOAc (0.3)/ PivOH (2.0)	toluene	92 (92)[e]	5
7[c]	$Zn(OTf)_2$ (1.0)	toluene	0	0
8[c]	CsOAc (1.0)	toluene	33	56
9[c]	KOAc (1.0)	toluene	21	36 (22)[f]
10[c]	CsOAc (1.0)/ KOAc (1.0)	toluene	26	70
11[c]	CsOAc (1.0)/ KOAc (1.0)	MeCN	8	60
12[d]	CsOAc (1.0)/ KOAc (1.0)	toluene	34	30 (16)[f]
13[d]	CsOAc (1.0)/ KOAc (1.0)	MeCN	5	66 (28)[g]
14[d,h]	CsOAc (1.0)/ KOAc (1.0)	MeCN	5	91 (90)[e]
15[d]	CsOAc (2.0)	MeCN	5	50 (20)[g]
16[d]	KOAc (2.0)	MeCN	19	17 (30)[g]

[a] **1a** (0.10 mmol, 1.0 equiv) reacted with **2a** (1.5 equiv) in the presence of a catalyst and additive in solvent (0.5 mL) at 100 °C for 12 h under N_2.
[b] NMR yields using CH_2Br_2 as an internal standard.
[c] $[Cp^*RhCl_2]_2$ (4.0 mol %).
[d] $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (4.0 mol %).
[e] Isolated yield.
[f] *N*-methoxy-3-hydroxy-3-phenyl-3,4-dihydroazulenolactam (**5**).
[g] Recovered yield of **1a**.
[h] 16 h.

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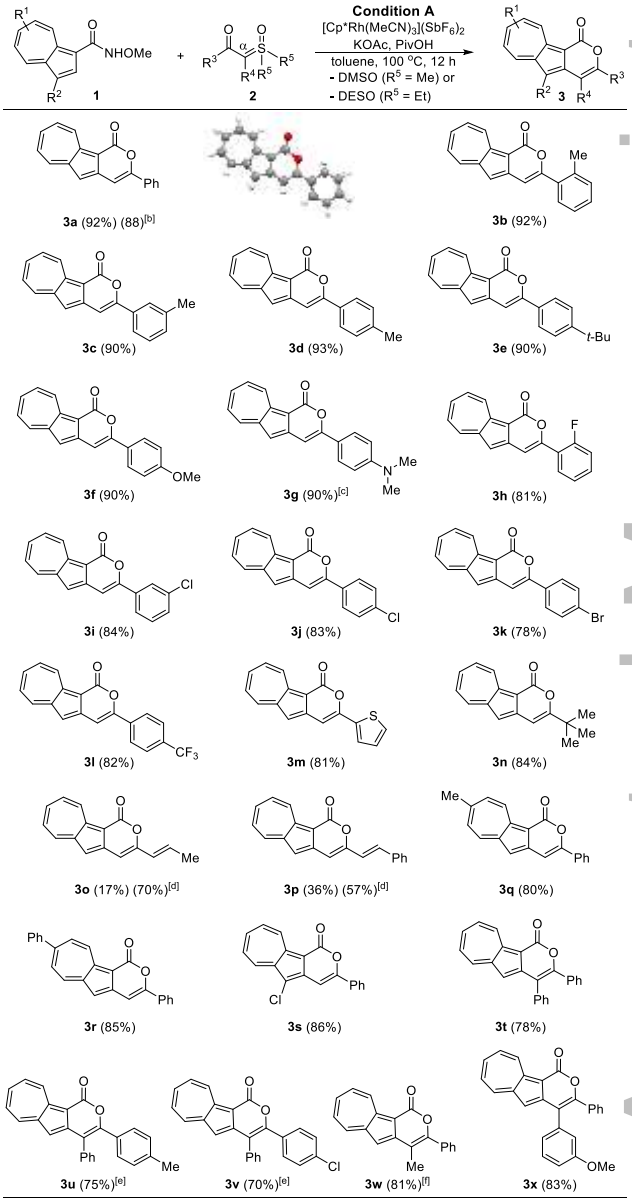
respectively (entries 7-10). The use of acetonitrile substantially increased the selectivity (**3a**:**4a** = 1:7.5) despite a slight decrease in yield (entry 11). Although $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (4.0 mol %) was used in the presence of CsOAc and KOAc (1.0 equiv, each) in toluene or acetonitrile, inferior results were obtained (entries 12 and 13). Based on the fact that **1a** was recovered in 28% (entry 13), optimum reaction conditions for azulenolactam (**4a**) were obtained when the reaction time was extended to 16 h, providing **4a** in 90% yield (entry 14). The use of CsOAc or KOAc (2.0 equiv, each) gave inferior results (entries 15 and 16). However, *N*-methoxyazulene-2-carboxamide was not effective.

With the optimum reaction conditions in hand, we examined the substrate scope of azulenecarboxamides (**1**) and sulfoxonium ylides (**2**) (Table 2). The reaction efficiency was not influenced by the electronic properties of the azulenes and sulfoxonium ylides. Electron-donating methyl and *tert*-butyl groups on the phenyl ring of sulfoxonium ylides afforded the corresponding compounds (**3b**-**3e**). Substrate bearing a strongly electron-donating 4-methoxy group on the phenyl ring underwent C−H activation followed by cyclization, producing **3f** in 90% yield. Because 4-(*N*,*N*-dimethylamino)phenyl-substituted sulfoxonium ylide has a slightly low reactivity, the reaction conditions were modified, and the desired product **3g** was produced in 90% yield with 3.0 equivalents of sulfoxonium ylide. In addition, halogenated aryl sulfoxonium ylides bearing fluoro, chloro, and bromo groups were well tolerated in the reaction conditions to afford the corresponding azulenolactones (**3h**-**3k**). The azulenolactone **3l** was produced in 82% yield despite the presence of a strong electron-withdrawing trifluoromethyl group. Also, a sulfoxonium ylide containing a thiophenyl group underwent cyclization reaction, providing **3m** in 81% yield. Although the sulfoxonium ylides bearing an ethyl and *n*-butyl group provided unexpectedly the corresponding lactams (**4l** and **4m**) in quantitative yield instead of lactones under condition A, the sulfoxonium ylide bearing a *tert*-butyl group provided the desired lactone (**3n**) in 84% yield. When sulfoxonium ylides obtained from (*E*)-but-2-enoyl chloride and cinnamoyl chloride were used, the desired lactones (**3o** and **3p**) were produced in 17 and 36%, respectively, together with lactam compounds (**4n** and **4o**) in major under condition A. Gratifyingly, Rh-catalyzed cyclization reaction using 6-methyl and 6-phenyl-substituted azulenes produced the corresponding azelenolactones **3q** and **3r** in 80 and 85% yields, respectively. Additionally, azulene-1-carboxamide bearing a 3-chloro group was applicable in the present transformation. Stimulated by these results, regioselective synthesis of 3,4-disubstituted azulenolactones was attempted with *α*,*β*-disubstituted sulfoxonium ylides. For example, when *α*,*β*-diphenyl sulfoxonium ylide was treated with **1a**, the corresponding diphenyl-substituted azulenolactone **3t** was obtained in 78% yield. Next, we investigated the scope of Rh-catalyzed regioselective annulation of **1a** by variation at the *α*-position of the sulfoxonium ylides **2**. The reaction efficiency was not influenced by the electronic properties of the aryl ring of *α*,*β*-diaryl sulfoxonium ylides. Electron-donating methyl and methoxy groups on the phenyl ring of sulfoxonium ylides regioselectively yielded the corresponding disubsititued azulenolactones (**3u** and **3x**) in 75 and 83%, respectively. *α*,*β*-Diphenyl sulfoxonium ylide possessing a 4-chloro group was

Table 2. Scope of Azulenes and Sulfoxonium Ylides for the Synthesis of Azulenolactones.[a]



[a] **Condition A**: **1a** (0.2 mmol, 1.0 equiv), **2** (1.5 equiv), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (4.0 mol %), KOAc (0.3 equiv), and PivOH (2.0 equiv) in toluene (1.0 mL) at 100 °C for 12 h. R^5 = Me.
[b] 1.0 mmol scale of **1a**.
[c] Sulfoxonium ylide (3.0 equiv).
[d] Isolated yields of **4n** and **4o**.
[e] $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (8.0 mol %).
[f] R^5 = Et.

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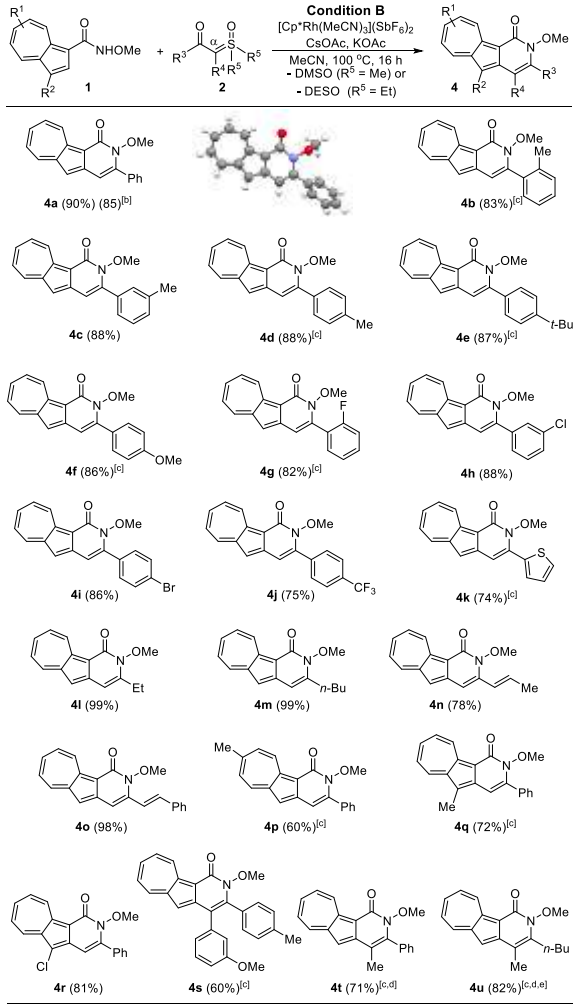
smoothly cyclized to produce **3v** in 70% yield. Gratifyingly, sulfoxonium ylide with phenyl and methyl groups was subjected to a Rh-catalyzed cyclization reaction, regioselectively producing the desired aznulenolactone (**3w**) in 81% yield. To demonstrate the applicability of the present method to larger scale processes, a 1.0 mmol scale reaction of **1a** (0.20 g) was attempted with **2a** (1.5 equiv), thus affording the desired azulenolactone **3a** in 88% yield (0.24 g).

We next attempted the selective synthesis of azulenolactams from the reaction of *N*-methoxyazulene-1-carboxamides (**1**) with sulfoxonium ylides (**2**) under the optimum condition **B** (Table 3). Electronic variation of the substituents did not largely influence the reaction efficiency. The sulfoxonium ylides bearing electron-donating methyl, *tert*-butyl, and methoxy groups were smoothly converted to the desired azulenolactams (**4b**-**4f**) in good yields. When sulfoxonium ylides bearing electron-withdrawing fluoro, chloro, bromo, and trifluoromethyl groups were used, the corresponding azulenolactams (**4g**-**4j**) were selectively obtained in good yields varying from 75 to 88%. Notably, ylide with a 2-thiophenyl group was successfully applied to the current method, producing **4k** in 74% yield. The cyclization was highly selective and useful, as proven by the quantitative reaction using ethyl- and *n*-butyl-sulfoxonium ylides (**4l** and **4m**). In the case of sulfoxonium ylides obtained from (*E*)-but-2-enoyl chloride and cinnamoyl chloride, the desired lactams (**4n** and **4o**) were produced in 78 and 98% yields, respectively, under condition B. However, the sulfoxonium ylide bearing a *tert*-butyl group did not react with *N*-methoxyazulene-1-carboxamide (**1a**) under condition B. In addition, substrates having 6-methyl, 3-methyl, and 3-chloro groups on the azulene ring worked well with phenyl sulfoxonium ylide, providing azulenolactams **4p**-**4r** in good yields. Since the Pd-catalyzed reaction of *N*-methoxyazulene-1-carboxamides (**1a**) with unsymmetrical alkynes provided regioisomeric products, a regioselective synthetic method is extremely needed. Thus, we investigated the Rh-catalyzed regioselective reaction of **1a** with sulfoxonium ylide **2** having substituents at the *α*-position. When sulfoxonium ylide bearing electron-donating methyl and methoxy groups on each phenyl ring was treated with **1a**, the desired diaryl-substituted azulenolactam **4s** was regioselectively obtained in 60% yield. Gratifyingly, sulfoxoniumylides having not only aryl groups but also alkyl groups were subjected to Rh-catalyzed reactions, regioselectively providing the corresponding azulenolactams (**4t** and **4u**)in 71% and 82% yields, respectively.

A catalytic C−H activation in toluene:D_2O (5:1) and MeCN:D_2O (5:1) was conducted, affording a significant D/H exchange at 2- and 8-position of product **1a**-[$\mathbf{D_2}$] (Scheme 2*a* and 2*b*). These results suggest that the C−H activation step is reversible. H/D exchange in the substrates did not occur in the absence of a catalyst, indicating that the regioselective and chemodivergent synthesis of azulenolactones and azulenolactams took place through Rh(III)-catalyzed C−H activation reactions of azulenecarboxamides with sulfoxonium ylides. Also, H/D scrambling at the 8-position of *N*-methoxyazuleneamide was observed, indicating that 8-position of nonbenzenoid aromatic compounds can be used as a reactive site for C−H activation reaction. Next, we performed kinetic isotope effect (KIE) studies to obtain insight into the reaction mechanism (Scheme 2*c* and 2*d*). The KIE was observed (K_H/K_D = 1.62, 1.60) by independent reactions using **1a** or **1a**-[$\mathbf{D_3}$] as the substrate under condition A and B, respectively (see the Supporting Information for details). Also, the KIE was obtained (K_H/K_D = 1.54, 1.57) *via* parallel reactions. Then, the KIE was

Table 3. Scope of Azulenes and Sulfoxonium Ylides for the Synthesis of Azulenolactams.[a]



[a] **Condition B**: **1a** (0.2 mmol, 1.0 equiv), **2** (1.5 equiv), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (4.0 mol %), CsOAc (1.0 equiv), and KOAc (1.0 equiv) in MeCN (1.0 mL) at 100 °C for 16 h. R^5 = Me.

[b] 1.0 mmol scale of **1a**.

[c] [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (8.0 mol %).

[d] R^5 = Et.

[e] Sulfoxonium ylide (2.0 equiv).

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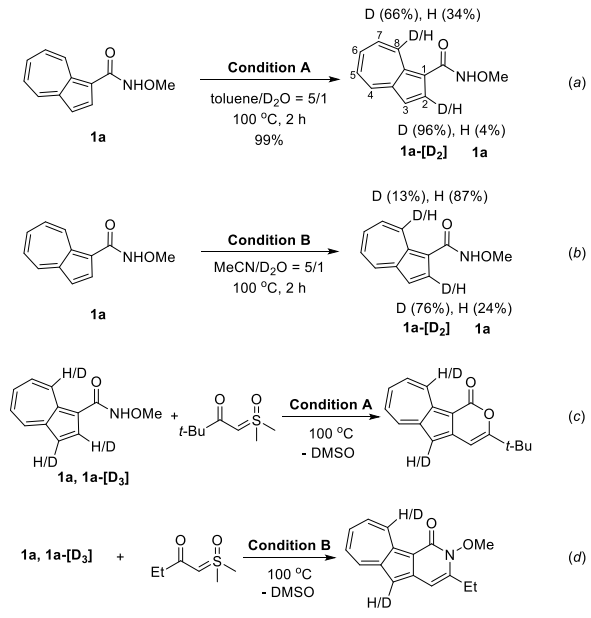
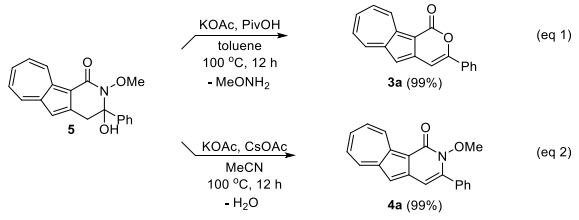


Reaction condition	Isotope experiments	Condition A	Condition B
1a or **1a-[D$_3$]**	*kinetic measurement*	K_H/K_D = 1.62	K_H/K_D = 1.60
1a or **1a-[D$_3$]**	*parallel reactions*	K_H/K_D = 1.54	K_H/K_D = 1.57
1a + **1a-[D$_3$]**	*intermolecular competition*	K_H/K_D = 2.13	K_H/K_D = 2.13

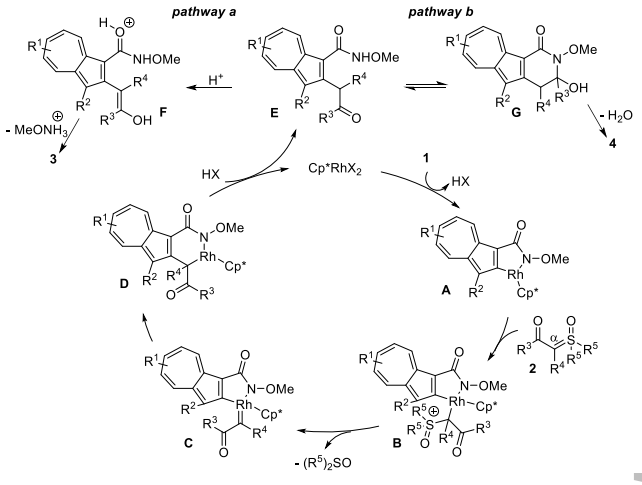
Scheme 2. Deuterium-Labeling Experiments.

measured (K_H/K_D = 2.13) from intermolecular competition reaction using **1a** and **1a**-[**D$_3$**] due to H/D scrambling. These results suggested that the cleavage of C−H bond at the 2-position of *N*-methoxyazuleneamide is not involved in the rate-determining step.

When *N*-methoxy-3-hydroxy-3-phenyl-3,4-dihydroazulenolactam (**5**) was treated with KOAc and PivOH in toluene at 100 °C for 12 h, azulenolactone (**3a**) was obtained in quantitative yield with the release of methoxyamine, indicating that ring-opening followed by ring-closing reaction occurred smoothly under the equilibrium conditions (eq 1). Additionally, when **5** was treated with KOAc and CsOAc in acetonitrile at 100 °C for 12 h, azulenolactam (**4a**) was produced in quantitative yield through dehydration (eq 2).



A proposed mechanism for the Rh-catalyzed reaction is illustrated in Scheme 3. Rhodacyclic intermediate **A** is generated through C–H activation from *N*-methoxyazulene-1-carboxamide (**1**) with a Rh(III) catalyst. Sulfoxonium ylide **2** is coordinated



Scheme 3. A Proposed Mechanism.

with **A** to generate rhodium alkyl species **B**, and the subsequent α-elimination of DMSO from **B** affords Rh-carbene intermediate **C**. Then, it would undergo migratory insertion of the Rh–C bond to give six-membered rhodacycle **D**, and protonolysis would afford acylmethylated intermediate **E**. Next, two pathways are possible. In pathway **a**, PivOH activates the amide group toward a nucleophilic attack by the enol oxygen, leading to the formation of azulenolactones **3** with the elimination of NH_2OMe. In contrast, in pathway **b**, the intramolecular nucleophilic addition followed by dehydration produces azulenolactam **4**.

Conclusion

In conclusion, we have developed a regioselective and chemodivergent reaction of *N*-methoxyazulene-1-carboxamides with sulfoxonium ylides, leading to the selective formation of azulenolactones and azulenolactams from the same starting materials. Sulfoxonium ylides that act as a precursor of secondary carbene was investigated, providing azulenolactones and azulenolactams bearing two substituents on a newly introduced double bond. The present method demonstrated functionalization of less reactive 2-position of azulene to overcome the natural reactivity.

Experimental Section

Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. For reactions that require heating, oil bath was used as the source of heating. Flash column chromatography was carried out using silica gel (230-400 mesh). ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz), and ^{19}F NMR (377 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform, dimethyl sulfoxide, and acetone

were used as the solvents, and chemical shift values (δ) are reported in parts per million relative to the residual signals of these solvent [δ 7.26 for ^{1}H (chloroform-*d*), δ 2.50 for ^{1}H (DMSO-d_6), δ 77.2 for ^{13}C{^{1}H} (chloroform-*d*), δ 39.5 for ^{13}C{^{1}H} (DMSO-d_6)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by electron impact (EI) ionization technique (magnetic sector - electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute Daegu Center). Melting points were determined in open capillary tube.

1. General Procedure for the Starting Material

(a) Synthetic Procedure for Azulene-1-carboxylic Acid[2b,13]

Phosphoryl trichloride (1.1 mL, 12 mmol) was added to anhydrous DMF (5.0 mL) very slowly at 0 °C and the mixture was stirred for 30 min. After 30 min, a solution of azulene (1.28 g, 10 mmol) in DMF was added to reaction mixture slowly at 25 °C. The reaction mixture was stirred at 25 °C for 2 h. The mixture was quenched by addition of 10 % aqueous NaOH (20 mL). Then, the mixture was extracted with ethyl acetate (3 x 30 mL) and the combined organic phase was washed with brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure to afford the azulene-1-carboxaldehyde as an oil (1.48 g, 95%). To a solution of azulene-1-carboxaldehyde (0.109 g, 0.70 mmol) and Na_2CO_3 in acetone/H_2O 5:1 (13.5 mL) were added $KMnO_4$ (0.283 g, 1.79 mmol) in H_2O at 25 °C for 5 min. The mixture was stirred for 4 h at 25 °C. The suspension was then treated with 5% aq. HCl and acetone was removed by evaporation. Then, the mixture was extracted with ethyl acetate (3 x 15 mL). After drying over $MgSO_4$, the desired product was obtained (91.6 mg, 76%, red-violet crystals).

(b) Synthetic Procedure for Azulene-1-*N*-methoxyamide[14]

1) To a solution of the azulene-1-carboxaldehyde (10.0 mmol, 1.0 equiv) in dry DCM (50 mL) at 0°C under a nitrogen atmosphere was dropwise added oxalyl chloride (1.0 mL, 12.0 mmol, 1.2 equiv) followed by a catalytic amount of dry DMF (10 drops). The reaction was stirred at 25 °C for 2 h. The solvent was then removed under reduce pressure.

2) After methoxyamine hydrochloride (1.7 g, 20.0 mmol, 2.0 equiv) and triethylamine (3.5 mL, 25.0 mmol, 2.5 equiv) in DCM (80 mL) was stirred for 10 min, the resulting solution was cooled to 0°C followed by a dropwise addition of the unpurified azulene-1-carbonyl chloride dissolved in a DCM (20 mL). The reaction was stirred at 25 °C for 1 h. Afterwards, the reaction was quenched with aqueous NH_4Cl solution and extracted with dichloromethane (3 x 30 mL). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The pure products were purified by column chromatography on silica gel (ether : DCM : hexane = 1 : 4 : 1) to afford *N*-methoxyazuleneamide (1.4g, 74%). Violet solid.

(c) Synthetic Procedure for 3-Chloro-*N*-methoxyazulene-1-carboxamide

NCS (133.5 mg, 1.0 mmol) was added to a stirred solution of azulene-1-*N*-methoxyamide (201.2 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C. After being stirred for 10 min, the cooling bath was removed, and the reaction mixture was stirred at 25 °C for 30 min. Next, the reaction mixture was evaporated to a small volume (~ 2 mL), and the residue was diluted with hexane (15 mL). As a result, a precipitate of succinimide formed was filtered off. The volatiles were evaporated, and the residue was purified by column chromatography (hexane) to afford the 3-chloro-*N*-methoxyazulene-1-carboxamide as a blue solid (233.3 mg, 99%).

(d) Synthetic Procedure for Sulfoxonium Ylides[11,15]

To a stirred solution of potassium *tert*-butoxide (3.0 g, 27.2 mmol) in THF (30 mL) was added trimethylsulfoxonium iodide (5.0 g, 20.6 mmol) at 25 °C. The resulting mixture is refluxed for 2 h. Then, reaction mixture was cooled to 0 °C, followed by addition of acyl chlorides (7.0 mmol) in THF (5 mL). The reaction was allowed to 25 °C and stirred for 3 h. Next, the solvent was evaporated and water (15 mL) and ethyl acetate (20 mL) were added to the resulting slurry. The layers were separated and the aqueous layer was washed with ethyl acetate (2 x 30 mL) and the organic layers were combined. The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by recrystalization using EtOAc and hexane to afford the corresponding sulfoxonium ylide.

(e) Synthetic Procedure for α-Aryl-β-keto Sulfoxonium Ylides[15,16]

To an oven dried 25 mL round bottom flask containing a magnetic stirrer, β-ketosulfoxonium ylide (1.0 equiv, 1.0 mmol), activated molecular sieves 4 Å powder (200 mg), CsF (4.0 equiv, 607.6 mg, 4.0 mmol), and dry acetonitrile (8.0 mL) were added. Under vigorous stirring, the appropriate precursor of aryne (1.5 equiv, 1.5 mmol) was added in three portions at intervals of 1 h at 65 °C. After 3 h, the organic solvent was removed into rotary evaporator and the crude product purified by column chromatography, employing the basic silica gel (MeOH : DCM = 1 : 50) to afford the corresponding α-aryl-β-keto sulfoxonium ylides.

(f) Procedure for the Triethylsulfoxonium chloride[11,15]

Diethyl sulfide (2.0 g, 22.7 mmol, 1.0 equiv) was added to a flame-dried schlenk tube, followed by iodoethane (3.9 g, 25.0 mmol, 1.1 equiv) and iodine (2.9 g, 11.4 mmol, 0.5 equiv) under nitrogen condition. The tube was sealed and the mixture was stirred at 70 °C overnight. Then, the mixture was transferred at 25 °C to a conical flask with water (70 mL), DCM (46 mL) and tributylbenzylammonium chloride (7.1 g, 22.7 mmol, 1.0 equiv). The mixture was protected from light and stirred overnight at 25 °C. The two layers were separated and the aqueous layer was washed with 5 times with DCM (30 mL). The aqueous layer was evaporated to give triethylsulfonium chloride as hygroscopic white solid.

Triethylsulfonium chloride was dissolved with water (112 mL) in a round bottom flask, the resulting solution was cooled to 0 °C and NaOH (5.4 g, 0.13 mol, 6 equiv) was added. The mixture was stirred at 0 °C until homogeneous. *m*CPBA (22.2 g, 90.0 mmol, 4 equiv (77% grade)) was added in portions and the mixture was stirred at 50 °C for 30 minutes. Then the pH was adjusted to pH = 1 with 6 M HCl (20 mL) at 0 °C. The precipitate was filtered off and washed with water. The corresponding filtrate was concentrated to 60 mL and washed with DCM (20 mL). The pH of the aqueous layer was adjusted to pH = 5-6 with saturated Na_2CO_3 and evaporated to dryness. The resulting solid was dispersed in warm *i*PrOH (40 mL) and the mixture was filtered. All volatiles were removed and the crude product was recrystallized from *i*PrOH to give triethylsulfoxonium chloride as white solid.

2. General Procedure for Rh-Catalyzed Tandem Annulation Reaction of *N*-Methoxyazuleneamides with Sulfoxonium Ylides

(a) Synthesis of azulenolactone

To an oven-dried test tube charged with *N*-methoxyazuleneamide **1** (40.1 mg, 0.2 mmol), $[Cp^*Rh(MeCN)_3]_2$ (6.7 mg, 0.008 mmol, 4.0 mol %), KOAc (5.9 mg, 0.06 mmol), PivOH (40.8 mg, 0.4 mmol), sulfoxonium ylide **2** (58.9 mg, 0.3 mmol), and toluene (1.0 mL). The reaction mixture was stirred at 100 °C for 12 h under a nitrogen atmosphere. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane : hexane = 4:1.

(b) Synthesis of azulenolactam

To an oven-dried test tube charged with *N*-methoxyazuleneamide **1** (40.1 mg, 0.2 mmol), $[Cp^*Rh(MeCN)_3]_2$ (6.7 mg, 0.008 mmol, 4.0 mol %), KOAc (19.6 mg, 0.2 mmol), CsOAc (38.4 mg, 0.2 mmol), sulfoxonium ylide **2** (58.9 mg, 0.3 mmol) and MeCN (1.0 mL). The reaction mixture was stirred at 100 °C for 16 h under a nitrogen condition. Then, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using acetone : hexane = 1 : 7.

3. Characterization data

3-Phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3a) : Yield : 50.1 mg (92%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 192-194 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, J = 9.2 Hz, 1H), 8.4 (d, J = 10.2 Hz, 1H), 8.01 (d, J = 7.0 Hz, 1H), 7.76 (t, J = 9.7 Hz, 1H), 7.65 (t, J = 9.7 Hz, 1H), 7.54-7.43 (m, 4H), 7.31 (s, 1H), 7.25 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 157.5, 149.3, 146.3, 141.6 137.8, 136.9, 135.9, 132.7, 130.2, 129.9, 128.9, 128.8, 125.9, 112.2, 107.6; IR (film): 3059, 1711, 1607, 1017, 914, 686 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{19}H_{12}O_2$ 272.0837; Found 272.0838.

3-(*o*-Tolyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3b) : Yield : 52.6 mg (92%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, J = 9.3 Hz, 1H), 8.42 (d, J = 10.2 Hz, 1H), 7.78 (t, J = 9.8 Hz, 1H), 7.67 (t, J = 9.8 Hz, 1H), 7.60 (d, J = 4.5 Hz, 1H), 7.53 (t, J = 9.7 Hz, 1H), 7.38-7.27 (m, 4H), 7.25 (s, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 159.8, 149.4, 146.3, 141.6, 138.0, 137.03, 137.02, 136.2, 133.7, 131.2, 130.0, 129.9, 129.5, 128.9, 126.1, 112.1, 107.5, 103.6, 21.1; IR (film) : 3062, 1712, 1612, 1012, 915, 640 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0992.

3-(*m*-Tolyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3c) : Yield : 51.5 mg (90%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 200-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 9.2 Hz, 1H), 8.39 (d, J = 10.2 Hz, 1H), 7.85 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.75 (t, J = 10.5 Hz, 1H), 7.64 (t, J = 9.8 Hz, 1H), 7.50 (t, J = 9.7 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.29 (s, 1H), 7.26 (d, J = 7.5, 1H), 7.24 (s, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 157.8, 149.5, 146.4, 141.7, 138.7, 137.8, 136.9, 135.9, 132.7, 131.1, 130.0, 128.8, 128.8, 126.6, 123.1, 112.2, 107.7, 99.4, 21.6; IR (film): 3027, 1710, 1611, 1023, 934, 794 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0995.

3-(*p*-Tolyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3d) : Yield : 53.2 mg (93%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, J = 9.2 Hz, 1H), 8.36 (d, J = 10.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.72 (t, J = 9.7 Hz, 1H), 7.62 (t, J = 9.7 Hz, 1H), 7.48 (t, J = 9.7 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.24 (s, 1H), 7.21 (s, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 158.0, 149.7, 146.4, 141.8, 140.7, 137.7, 136.8, 135.8, 130.1, 130.0, 129.7, 128.8, 126.0, 112.2, 107.7, 98.8, 21.6; IR (film): 3027, 1710, 1611, 1023, 934, 608 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0996.

3-(4-(*tert*-Butyl)phenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3e) : Yield : 59.1 mg (90%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 9.2 Hz, 1H), 8.37 (d, J = 10.2 Hz, 1H), 7.94 (d, J = 8.5Hz, 2H), 7.73 (t, J = 9.7 Hz, 1H), 7.63 (t, J = 9.7 Hz, 1H), 7.51-7.47 (m, 3H), 7.27 (s, 1H), 7.23 (s, 1H), 1.37 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 157.9, 153.8, 149.7, 146.4, 141.8, 137.7, 136.8, 135.8, 130.0, 130.0, 128.8, 125.9, 125.8, 112.2, 107.7, 98.9, 35.0, 31.3; IR (film): 3069, 1709, 1608, 1021, 915, 640 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{23}H_{20}O_2$ 328.1463; Found 328.1460.

3-(4-Methoxyphenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3f) : Yield : 54.3 mg (90%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, J = 9.2 Hz, 1H), 8.34 (d, J = 10.2 Hz, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.70 (tt, J = 2.7 Hz, 1H), 7.61 (t, J = 9.7 Hz, 1H), 7.50-7.45 (m, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 6.99 (d, H = 9.0 Hz, 2H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 160.2, 157.9, 149.9, 146.5, 141.9, 137.4, 136.6, 135.5, 130.0, 128.8, 127.6, 125.4, 114.4, 112.1, 107.4, 98.0, 55.6; IR (film): 3076, 1715, 1604, 1258, 1177, 913, 631 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}O_3$ 302.0943; Found 302.0945.

3-(4-(Dimethylamino)phenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3g) : Yield : 56. 7 mg (90%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 250-252 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 9.0 Hz, 1H), 8.29 (d, J = 10.2 Hz, 1H), 7.90 (d, J = 9.0 Hz, 2H), 7.64 (t, J = 9.5 Hz, 1H), 7.58 (t, J = 9.6 Hz, 1H), 7.43 (t, J = 9.6, Hz, 1H), 7.15 (s, 1H), 7.11 (s, 1H), 6.75 (d, J = 9.0 Hz, 2H), 3.05 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 159.2, 152.0, 150.7, 146.7, 142.3, 136.6, 135.9, 134.7, 130.0, 128.6, 127.5, 120.5, 112.1, 111.9, 107.3, 96.3, 40.3; IR (film): 3056, 1703, 1598, 1373, 1197, 945, 635 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1256.

3-(2-Fluorophenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3h) : Yield : 47.0 mg (81%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 202-204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (d, J = 9.2 Hz, 1H), 8.41 (d, J = 10.2 Hz, 1H), 8.15 (td, J = 3.5 Hz, 1H), 7.77 (t, J = 9.8 Hz, 1H), 7.65 (t, J = 9.8 Hz, 1H), 7.54-7.49 (m, 2H), 7.43-7.38 (m, 1H), 7.31-7.27 (m, 1H), 7.22-7.17 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4 (d, J = 253.3 Hz), 160.0, 152.1, 152.0, 149.3, 146.3, 141.6, 138.2, 137.3, 136.4, 131.4 (d, J = 9.2 Hz), 130.0, 129.4, 128.9, 124.7 (d, J = 3.5 Hz), 121.1, 121.0, 116.6 (d, J = 23.2 Hz), 112.7, 108.1, 104.9, 104.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.5; IR (film): 3064, 1731, 1604, 1215, 1018, 944, 629 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{19}H_{11}FO_2$ 290.0743; Found 290.0743.

3-(3-Chlorophenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3i) : Yield : 51.4 mg (84%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 219-221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, J = 9.3 Hz, 1H), 8.42 (d, J = 10.1 Hz, 1H), 7.99 (s, 1H), 7.89-7.86 (m, 1H), 7.79 (t, J = 9.8 Hz, 1H), 7.67 (t, J = 9.8 Hz, 1H), 7.53 (t, J = 9.7, Hz, 1H), 7.42-7.41 (m, 1H), 7.30 (s, 1H), 7.26 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 156.0, 148.9, 146.5, 141.7, 138.3, 137.3, 136.5, 135.2, 134.6, 130.22, 130.18, 130.17, 129.1, 126.1, 124.0, 112.4, 107.8, 100.3; IR (film): 3089, 1710, 1609, 1030, 950, 787, 671 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{19}H_{11}ClO_2$ 306.0448; Found 306.0450.

3-(4-Chlorophenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3j) : Yield : 50.8 mg (83%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 230-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 9.3 Hz, 1H), 8.38 (d, J = 10.2 Hz, 1H), 7.91 (d, J = 8.5, 1H), 7.76 (t, J = 9.7 Hz, 1H), 7.64 (t, J = 9.8 Hz, 1H), 7.51 (t, J = 9.7 Hz, 1H), 7.43 (d, J = 8.6, Hz, 1H), 7.25 (s, 1H), 7.22 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 156.4, 149.0, 146.4, 141.7, 138.1, 137.1, 136.3, 136.3, 131.3, 130.1, 129.2, 129.0, 127.2, 112.3, 107.7, 99.7; IR (film): 3091, 1710, 1611, 1091, 913, 828, 673 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{19}H_{11}ClO_2$ 306.0448; Found 306.0451.

3-(4-Bromophenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3k) : Yield : 54.8 mg (78%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 239-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, J = 9.3 Hz, 1H), 8.40 (d, J = 10.2 Hz, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.78 (t, J = 9.8 Hz, 1H), 7.66 (t, J = 9.8 Hz, 1H), 7.60 (d, J = 8.6 Hz, 2H), 7.52 (t, J = 9.8, Hz, 1H), 7.28 (s, 1H), 7.24 (s, 1H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 156.5, 149.0, 146.5, 141.7, 138.2, 137.2, 136.3, 132.2, 131.8, 130.2, 129.1, 127.4, 124.7, 112.3, 107.7, 99.7; IR (film): 3054, 1708, 1610, 1025, 948, 671, 607 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{11}Br^{79}O_2$ 349.9942, $C_{19}H_{11}Br^{81}O_2$ 351.9922; Found 349.9945, 351.9940.

3-(4-(Trifluoromethyl)phenyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3l) : Yield : 55.8 mg (82%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 240-242 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (d, *J* = 9.2 Hz, 1H), 8.43 (d, *J* = 10.2 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.81 (t, *J* = 9.7 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (t, *J* = 10.3 Hz, 1H), 7.55 (t, *J* = 9.7, Hz, 1H), 7.37 (s, 1H), 7.28 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.7, 155.8, 148.6, 146.5, 141.7, 138.6, 137.5, 136.7, 136.1, 131.7 (q, *J* = 31.7 Hz), 130.2, 129.2, 124.0 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 169.0 Hz), 112.5, 107.9, 101.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; IR (film): 3090, 1714, 1615, 1169, 1118, 955, 669 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{11}F_3O$ 340.0711; Found 340.0713.

3-(Thiophen-2-yl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3m) : Yield : 45.0 mg (81%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 220-222 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 9.3 Hz, 1H), 8.36 (d, *J* = 10.2 Hz, 1H), 7.75-7.70 (m, 2H), 7.63 (t, *J* = 9.7, 1H), 7.49 (t, *J* = 9.7 Hz, 1H), 7.44 (dd, *J* = 2.0 Hz, 1H), 7.18 (s, 1H), 7.13 (dd, *J* = 2.9 Hz, 1H), 7.11 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.5, 153.4, 149.2, 146.6, 142.0, 137.8, 136.9, 136.8, 135.8, 130.2, 129.1, 128.4, 128.2, 127.0, 112.1, 107.4, 98.7; IR (film): 3073, 1799, 1710, 1603, 1115, 946, 666 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{10}O_2S$ 278.0402; Found 278.0405.

3-(*tert*-Butyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3n) : Yield : 42.3 mg (84%); R_f = 0.3 (acetone: hexane = 1:7); Red solid; Melting point : 87-89 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 9.3 Hz, 1H), 8.37 (d, *J* = 10.2 Hz, 1H), 7.73 (t, *J* = 9.8 Hz, 1H), 7.62 (t, *J* = 9.8 Hz, 1H), 7.48 (t, *J* = 9.7 Hz, 1H), 7.14 (s, 1H), 6.68 (s, 1H), 1.40 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1, 160.8, 150.1, 146.2, 141.6, 137.5, 136.6, 135.7, 129.8, 128.6, 111.8, 107.4, 97.4, 36.4, 28.4; IR (film): 3070, 1708, 1616, 1094, 940, 693 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{16}O_2$ 252.1150; Found 252.1147.

(*E*)-3-(prop-1-en-1-yl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3o) : Yield : 8.0 mg (17%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 102-104 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 9.2 Hz, 1H), 8.35 (d, *J* = 10.2 Hz, 1H), 7.72 (t, *J* = 9.8 Hz, 1H), 7.62 (t, *J* = 9.8 Hz, 1H), 7.48 (t, *J* = 9.7 Hz, 1H), 7.15 (s, 1H), 6.87-6.78 (m, 1H), 6.59 (s, 1H), 6.19 (dd, *J* = 5.7 Hz, 1H), 1.96 (dd, *J* = 2.7 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 156.6, 149.7, 146.5, 141.9, 137.6 136.7 135.7 133.4 130.1 128.9 124.4 112.0 101.4 77.5 77.2 76.9, 18.7; IR (film): 3060, 1681, 1556, 1211, 1148, 928, 641 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{16}H_{12}O_2$ 236.2700; Found 236.2701.

(*E*)-3-styryl-1*H*-azuleno[1,2-*c*]pyran-1-one (3p) : Yield : 21.5 mg (36%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 203-205 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 9.2 Hz, 1H), 8.36 (d, *J* = 10.1 Hz, 1H), 7.73 (t, *J* = 9.8 Hz, 1H), 7.65-7.55 (m, 4H), 7.49 (t, *J* = 9.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 5.5 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 156.6, 149.2, 146.5, 142.0, 137.9, 137.0, 136.2, 136.0, 134.2, 130.2, 129.1, 129.0, 129.0, 127.5, 120.5, 112.3, 108.0, 103.9; IR (film): 3058, 1706, 1621, 1032, 926, 634 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{14}O_2$ 298.0994; Found 298.0995.

8-Methyl-3-phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3q) : Yield : 45.8 mg (80%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 238-240 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 9.8 Hz, 1H), 8.26 (d, *J* = 10.6 Hz, 1H), 8.01-7.98 (m, 2H), 7.54 (d, *J* = 9.9 Hz, 1H), 7.50-7.41 (m, 4H), 7.28 (s, 1H), 7.17 (s, 1H), 2.73 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 157.1, 150.4, 148.3, 145.2, 140.1, 136.1, 135.5, 133.0, 131.2, 130.7, 130.1, 128.9, 126.0, 112.0, 107.9, 99.5, 28.3; IR (film): 3031, 1705, 1613, 1016, 915, 663 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0994.

3,8-Diphenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3r) : Yield : 59.2 mg (85%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 241-243 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, *J* = 10.0 Hz, 1H), 8.43 (d, *J* = 10.8 Hz, 1H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 9.9 Hz, 1H), 7.75 (d, *J* = 10.8 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 2H), 7.54-7.43 (m, 6H), 7.32 (s, 1H), 7.25 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 157.6, 151.8, 149.2, 145.1, 144.3, 140.5, 136.3, 135.4, 132.9, 130.3, 130.0, 129.9, 129.2, 129.0,128.8, 128.7, 126.0, 112.4, 108.1, 99.7; IR (film): 3047, 1712, 1609, 1016, 913, 631 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{25}H_{16}O_2$ 348.1150; Found 348.1147.

5-Chloro-3-phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3s) : Yield : 52.6 mg (86%); R_f = 0.3 (dichloromethane : hexane = 4:1); Green solid; Melting point : 247-249 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (d, *J* = 8.8 Hz, 1H), 8.46 (d, *J* = 10.2 Hz, 1H), 8.06-8.04 (m, 2H), 7.80 (t, *J* = 9.8 Hz, 1H), 7.66 (t, *J* = 9.8 Hz, 1H), 7.59 (t, *J* = 9.8 Hz, 1H), 7.53-7.46 (m, 3H), 7.36 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 158.8, 146.0, 140.1, 139.9, 138.8, 136.4, 134.0, 132.5, 130.8, 130.5, 129.3, 129.1, 126.2, 111.3, 105.6, 96.7; IR (film): 3061, 1737, 1611, 1014, 913, 761, 601 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{11}ClO_2$ 306.0448; Found 306.0445.

3,4-Diphenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3t) : Yield : 54.3 mg (78%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 207-209 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 9.3 Hz, 1H), 8.33 (d, *J* = 10.1 Hz, 1H), 7.78 (t, *J* = 9.8 Hz, 1H), 7.68 (t, *J* = 9.7 Hz, 1H), 7.48-7.45 (m, 3H), 7.44-7.37 (m, 5H), 7.30-7.21 (m, 2H), 7.00 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 154.6, 151.3, 145.9, 141.9, 138.2, 137.3, 136.7, 135.6, 133.4, 130.6, 130.1, 129.9, 129.3, 129.1, 128.9, 128.0, 127.9, 116.0, 112.5, 107.5; IR (film): 3059, 1700, 1586, 1147, 963, 634 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{25}H_{16}O_2$ 348.1150; Found 348.1151.

4-(3-Methoxyphenyl)-3-phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3u) : Yield : 62.8 mg (83%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 188-190 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 9.2 Hz, 1H), 8.34 (d, *J* = 10.2 Hz, 1H), 7.79 (t, *J* = 9.8 Hz, 1H), 7.68 (t, *J* = 9.7 Hz, 1H), 7.52-7.48 (m, 3H), 7.36-7.23 (m, 4H), 7.05 (s, 1H), 6.98-6.94 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 160.0, 154.6, 151.2, 145.9, 141.9, 138.2, 137.4, 136.9, 136.7, 133.4, 130.1, 130.1, 129.8, 129.3, 128.8, 128.1, 123.1, 116.1, 115.9, 113.6, 112.6, 107.5, 55.4; IR (film): 3061, 1705, 1586, 1290, 1243, 923, 634 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{18}O_3$ 378.1256; Found 378.1253.

4-Phenyl-3-(*p*-tolyl)-1*H*-azuleno[1,2-*c*]pyran-1-one (3v): Yield : 54.3 mg (75%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 244-246 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J* = 9.2 Hz, 1H), 8.31 (d, *J* = 10.2 Hz, 1H), 7.76 (td, *J* = 3.9 Hz, 1H), 7.67 (t, *J* = 9.7 Hz, 1H), 7.48 (t, *J* = 9.8 Hz, 1H), 7.45-7.36 (m, 7H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 2.31 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 154.9, 151.5, 145.9, 142.0, 139.5, 138.0, 137.2, 136.5, 135.9, 130.6, 130.5, 130.1, 129.8, 129.1, 128.8, 128.8, 127.9, 115.6, 112.5, 107.5, 21.5; IR (film): 3060, 1714, 1605, 1202, 913, 644 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{18}O_2$ 362.1307; Found 362.1307.

3-(4-Chlorophenyl)-4-phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3w) : Yield : 53.5 mg (70%); R_f = 0.3

(dichloromethane : hexane = 4:1); Red solid; Melting point : 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, J = 9.3 Hz, 1H), 8.34 (d, J = 10.1 Hz, 1H), 7.80 (t, J = 9.8 Hz, 1H), 7.69 (t, J = 9.7 Hz, 1H), 7.51 (t, J = 9.8 Hz, 3H), 7.46-7.37 (m, 7H), 7.21 (dd, J = 2.9 Hz, 2H), 7.00 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 153.3, 151.0, 146.0, 141.9, 138.5, 137.5, 136.9, 135.4, 135.3, 131.9, 131.1, 130.5, 130.2, 129.3, 129.0, 128.4, 128.2, 116.4, 112.6, 107.5; IR (film): 3058, 1714, 1607, 1091, 914, 832, 663 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{25}H_{15}ClO_2$ 382.0761; Found 382.0761.

4-Methyl-3-phenyl-1*H*-azuleno[1,2-*c*]pyran-1-one (3x) : Yield : 46.3 mg (81%); R_f = 0.3 (dichloromethane : hexane = 4:1); Red solid; Melting point : 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 9.3 Hz, 1H), 8.45 (d, J = 10.1 Hz, 1H), 7.79 (t, J = 9.8 Hz, 1H), 7.72-7.70 (m, 2H), 7.67 (t, J = 9.7 Hz, 1H), 7.54 (t, J = 10.1 Hz, 1H), 7.51-7.42 (m, 3H), 7.29 (s, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 154.7, 152.0, 146.0, 141.8, 138.0, 137.2, 136.5, 133.7, 129.9, 129.6, 129.4, 128.8, 128.4, 111.1, 108.9, 107.8, 14.2; IR (film): 3060, 1703, 1612, 1211, 917, 605 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0991.

2-Methoxy-3-phenylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4a) : Yield : 54.8 mg (91%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 162-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, J = 9.0 Hz, 1H), 8.33 (d, J = 10.4 Hz, 1H), 7.73-7.69 (m, 2H), 7.66 (t, J = 9.8, 1H), 7.57 (t, J = 9.7, 1H), 7.50-7.48 (m, 3H), 7.38 (t, J = 3.2, 1H), 7.24 (s, 1H), 6.77 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 147.1, 145.9, 144.7, 141.3, 136.9, 136.4, 135.6, 133.6, 129.6, 129.4, 129.1, 128.3, 127.2, 114.5, 112.2, 103.0, 64.0; IR (film): 3060, 1651, 1530, 1196, 1108, 932, 642 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{15}NO_2$ 301.1103; Found 301.1105.

2-Methoxy-3-(*o*-tolyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4b) : Yield : 52.3 mg (83%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 10.4 Hz, 1H), 7.67 (t, J = 9.7 Hz, 1H), 7.59 (t, J = 9.7, 1H), 7.44-7.37 (m, 3H), 7.33-7.28 (m, 2H), 7.24 (s, 1H), 6.66 (s, 1H), 3.76 (s, 3H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.7, 147.2, 146.1, 144.7, 141.2, 138.1, 136.9, 136.4, 135.6, 133.6, 130.0, 129.5, 129.4, 129.0, 127.2, 125.5, 114.6, 112.1, 102.4, 64.2, 20.1; IR (film): 3053, 1653, 1530, 1200, 1111, 932, 681 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1259.

2-Methoxy-3-(*m*-tolyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4c) : Yield : 55.5 mg (88%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (d, J = 8.9 Hz, 1H), 8.32 (d, J = 10.4 Hz, 1H), 7.65 (t, J = 9.7 Hz, 1H), 7.56 (t, J = 9.7, 1H), 7.51-7.49 (m, 2H), 7.40-7.35 (m, 3H), 7.31-7.29 (m, 2H), 7.23 (s, 1H), 6.80 (s, 1H), 3.77 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 147.1, 146.1, 144.7, 141.3, 138.0, 136.8, 136.4, 135.4, 133.5, 130.2, 130.1, 129.0, 128.2, 127.2, 126.7, 114.4, 112.1, 102.8, 64.0, 21.6; IR (film): 3046, 1653, 1601, 1530, 1200, 1109, 917, 646 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1257.

2-Methoxy-3-(*p*-tolyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4d) : Yield : 55.5 mg (88%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 8.9 Hz, 1H), 8.31 (d, J = 10.4 Hz, 1H), 7.66-7.53 (m, 4H), 7.36 (t, J = 9.6 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (s, 1H), 6.75 (s, 1H), 3.75 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 147.2, 146.1, 144.7, 141.3, 139.5, 136.7, 136.3, 135.4, 130.7, 129.5, 129.04, 129.03, 127.2, 114.4, 112.1, 102.7, 63.9, 21.5; IR (film): 3032, 1651, 1600, 1530, 1189, 1110, 971, 618cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1255.

3-(4-(*tert*-Butyl)phenyl)-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4e) : Yield : 62.2 mg (87%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (d, J = 8.8 Hz, 1H), 8.30 (d, J = 10.4 Hz, 1H), 7.65-7.60 (m, 3H), 7.55 (t, J = 9.7 Hz, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.35 (t, J = 9.6 Hz, 1H), 7.21 (s, 1H), 6.75 (s, 1H), 3.77 (s, 3H), 1.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 152.6, 147.2, 146.0, 144.7, 141.3, 136.6, 136.3, 135.3, 130.6, 129.2, 129.0, 127.2, 125.3, 114.4, 112.1, 102.8, 63.9, 34.9, 31.4; IR (film): 3054, 1654, 1530, 1198, 1102, 932, 623 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{24}H_{23}NO_2$ 357.1729; Found 357.1728.

2-Methoxy-3-(4-methoxyphenyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4f) : Yield : 56.9 mg (86%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 196-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 8.9 Hz, 1H), 8.31 (d, J = 10.4 Hz, 1H), 7.68-7.61 (m, 3H), 7.56 (t, J = 9.6 Hz, 1H), 7.36 (t, J = 9.6 Hz, 1H), 7.22 (s, 1H), 7.03-6.99 (m, 2H), 6.74 (s, 1H), 3.90 (s, 3H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.5, 157.8, 147.2, 145.7, 144.7, 141.3, 136.6, 136.2, 135.2, 131.0, 129.0, 127.2 125.8, 114.2, 113.8, 112.1, 102.5, 63.8, 55.5; IR (film): 3061, 1650, 1530, 1251, 1180, 1110, 931, 619 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{21}H_{17}NO_3$ 331.1208; Found 331.1208.

3-(2-Fluorophenyl)-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4g) : Yield : 52.3 mg (82%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 9.0 Hz, 1H), 8.33 (d, J = 10.4 Hz, 1H), 7.66 (t, J = 9.4 Hz, 1H), 7.59-7.46 (m, 3H), 7.37 (t, J = 9.7 Hz, 1H), 7.29-7.20 (m, 3H), 6.76 (s, 1H), 3.83 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2 (d, J = 250.2 Hz), 157.6, 146.7, 144.6, 141.1, 140.3, 137.1, 136.7, 135.9, 131.5, 131.4 (d, J = 10.9 Hz), 129.0, 127.2, 124.0 (d, J = 3.6 Hz), 121.9, 121.7, 115.9 (d, J = 21.6 Hz), 115.0, 112.1, 103.7, 64.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6; IR (film): 3060, 1652, 1530, 1424, 1206, 1126, 933, 645 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}FNO_2$ 319.1009; Found 319.1010.

3-(3-Chlorophenyl)-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4h) : Yield : 59.0 mg (88%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 10.4 Hz, 1H), 7.71-7.66 (m, 2H), 7.61-7.56 (m, 2H), 7.48-7.38 (m, 3H), 7.24 (s, 1H), 6.77 (s, 1H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 146.7, 144.7, 144.3, 141.2, 137.2, 136.7, 136.0, 135.2, 134.3, 129.6, 129.5, 129.5, 129.1, 127.8, 127.4, 114.6, 112.2, 103.3, 64.1; IR (film): 3063, 1653, 1529, 1200, 1111, 931, 795, 680 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}ClNO_2$ 335.0713; Found 335.0712.

3-(4-Bromophenyl)-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4i) : Yield : 65.4 mg (86%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (d, J = 8.9 Hz, 1H), 8.35 (d, J = 10.4 Hz, 1H), 7.70-7.56 (m, 6H), 7.40 (t, J = 9.6 Hz, 2H), 7.24 (s, 1H), 6.76 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 146.8, 144.7 144.6, 141.2, 137.1, 136.6, 135.8, 132.4, 131.6, 131.1, 129.1, 127.4, 123.9, 114.5, 112.1, 103.0, 64.0; IR (film): 3068, 1652, 1530, 1201, 1106, 931, 733, 614 cm^{-1}; HRMS (EI) *m/z*: [M]$^+$ Calcd for $C_{20}H_{14}Br^{79}NO_2$ 379.0208, $C_{20}H_{14}Br^{81}NO_2$ 381.0188; Found 379.0208, 381.0184.

2-Methoxy-3-(4-(trifluoromethyl)phenyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4j) : Yield : 55.4 mg (75%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 185-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (d, J = 9.0 Hz, 1H), 8.35 (d, J = 10.2 Hz, 1H), 7.83 (d, J = 7.3 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.69 (t, J = 8.6 Hz, 1H), 7.58 (t, J = 9.2 Hz, 1H), 7.40 (t, J = 9.0 Hz, 1H), 7.25 (s, 1H), 6.78 (s,1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 146.6, 144.7, 144.1, 141.1, 137.4, 137.0, 136.8,

136.1, 131.3 (q, J = 32.8 Hz), 129.9, 129.2, 127.5, , 125.3 (q, J = 3.7 Hz), 124.1 (q, J = 272.3 Hz), 114.6, 112.2, 103.5, 64.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (film): 3060, 1655, 1530, 1324, 1166, 1125, 932, 622 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{14}F_3NO_2$ 369.0977; Found 369.0974.

2-Methoxy-3-(thiophen-2-yl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4k) : Yield : 45.5 mg (74%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 159-161 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (d, J = 9.0 Hz, 1H), 8.30 (d, J = 10.3 Hz, 1H), 7.71 (dd, J = 1.6 Hz, 1H), 7.63 (t, J = 9.7 Hz, 1H), 7.56 (d, J = 9.4 Hz, 1H), 7.53 (dd, J = 2.1 Hz, 1H), 7.36 (t, J = 9.6 Hz, 1H), 7.23 (s, 1H), 7.17 (dd, J = 3.0 Hz, 1H), 7.07 (s, 1H), 4.00 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.7, 146.9, 144.8, 141.3, 139.1, 136.8, 136.3, 135.4, 133.8, 129.5, 129.3, 129.2, 127.5, 127.4, 114.0, 112.2, 101.4, 64.2; IR (film): 3072, 1652, 1530, 1295, 1206, 1112, 928, 634 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{13}NO_2S$ 307.0667; Found 307.0669.

3-Ethyl-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4l) : Yield : 50.1 mg (99%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 133-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, J = 8.9 Hz, 1H), 8.27 (d, J = 10.4 Hz, 1H), 7.59 (t, J = 9.7 Hz, 1H), 7.51 (t, J = 9.6 Hz, 1H), 7.32 (t, J = 9.6 Hz, 1H), 7.15 (s, 1H), 6.57 (s, 1H), 4.17 (s, 3H), 2.90 (t, J = 7.40 Hz, 2H), 1.39 (q, J = 4.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 148.9, 147.6, 144.6, 141.3, 136.2, 136.0, 134.7, 128.9, 127.0, 114.0, 111.7, 98.8, 64.4, 24.6, 12,8; IR (film): 3082, 1650, 1531, 1197, 1119, 921, 621 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{16}H_{15}NO_2$ 253.1103; Found 253.1099.

3-Butyl-2-methoxyazuleno[1,2-*c*]pyridin-1(2*H*)-one (4m) : Yield : 55.7 mg (99%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 97-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, J = 8.9 Hz, 1H), 8.26 (d, J = 10.5 Hz, 1H), 7.61-7.56 (m, 1H), 7.51 (t, J = 9.6 Hz, 1H), 7.32 (td, J = 4.0 Hz, 1H), 7.13 (s, 1H), 6.56 (s, 1H), 4.16 (s, 3H), 2.85 (t, J = 7.70 Hz, 2H), 1.81-1.73 (m, 2H), 1.52-1.43 (m, 2H), 1.01-0.97 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.0, 147.6, 147.5, 144.5, 141.2, 136.1, 135.9, 134.5, 128.8, 126.9, 113.9, 111.6, 99.7, 64.3, 31.3, 30.6, 22.5, 14.0; IR (film): 3060, 1652, 1531, 1205, 1141, 921, 627 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{19}NO_2$ 281.1416; Found 281.1416.

(*E*)-2-methoxy-3-(prop-1-en-1-yl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4n) : Yield : 36.9 mg (78%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 130-132 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 10.4 Hz, 1H), 7.60-7.48 (m, 3H), 7.31 (t, J = 9.6 Hz, 1H), 7.15 (s, 1H), 6.85 (s, 1H), 6.73 (d, 1H), 6.62-6.53 (m, 1H), 4.09 (s, 3H), 2.01 (dd, J = 5.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 147.3, 144.7, 143.6, 141.4, 136.3, 136.0, 134.8, 133.9, 129.0, 127.1, 122.4, 114.1, 112.1, 98.1, 64.2, 19.2; IR (film): 3060, 1652, 1531, 1205, 1141, 921, 627 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{15}NO_2$ 265.1103; Found 265.1105.

(*E*)-2-methoxy-3-styrylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4o) : Yield : 64.2 mg (98%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 171-173 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (d, J = 8.9 Hz, 1H), 8.28 (d, J = 10.4 Hz, 1H), 7.62-7.58 (m, 3H), 7.52 (t, J = 9.7 Hz, 1H), 7.45-7.41 (m, 4H), 7.38-7.31 (m, 2H), 7.21 (s, 1H), 7.10 (s, 1H), 4.13 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 146.9, 144.8, 143.2, 141.4, 136.6, 136.4, 136.2, 135.3, 135.2, 129.2, 129.1, 129.1, 127.4, 127.3, 119.1, 114.4, 112.2, 98.7, 64.4; IR (film): 3060, 1652, 1531, 1205, 1141, 921, 627 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{17}NO_2$ 327.1259; Found 327.1261.

2-Methoxy-8-methyl-3-phenylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4p) : Yield : 37.8 mg (60%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 201-203 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, J = 9.6 Hz, 1H), 8.20 (d, J = 10.8 Hz, 1H), 7.71-7.68 (m, 2H), 7.49-7.44 (m, 4H), 7.29 (d, J = 10.8 Hz, 1H), 7.16 (s, 1H), 6.74 (s, 1H), 3.75 (s, 3H), 2.69 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 148.9, 146.1, 145.3, 143.6, 139.5, 135.5, 135.2, 133.7, 129.9, 129.6, 129.2, 128.3, 128.3, 114.7, 111.9, 103.0, 63.9, 28.3; IR (film): 3061, 1651, 1536, 1198, 1085, 920, 642 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1258.

2-Methoxy-5-methyl-3-phenylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4q) : Yield : 45.4 mg (72%); R_f = 0.3 (acetone : hexane = 1:7); Green solid; Melting point : 215-217 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (dd, J = 3.3 Hz, 1H), 8.21 (d, J = 10.6 Hz, 1H), 7.73-7.71 (m, 2H), 7.56 (t, J = 9.7 Hz, 1H), 7.52-7.49 (m, 3H), 7.46 (t, J = 9.8 Hz, 1H), 7.30 (t, J = 9.7 Hz, 1H), 6.76 (s, 1H), 3.76 (s, 3H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 146.7, 145.7, 141.0, 139.9, 136.4, 134.5, 133.7, 133.5, 129.6, 129.4, 128.5, 128.3, 125.8, 119.1, 113.0, 101.3, 63.9, 10.0; IR (film): 3054, 1651, 1527, 1296, 1192, 929, 644 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1262.

5-Chloro-2-methoxy-3-phenylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4r) : Yield : 57.5 mg (81%); R_f = 0.3 (acetone : hexane = 1:7); Green solid; Melting point : 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (dd, J = 3.4 Hz, 1H), 8.37 (d, J = 10.5 Hz, 1H), 7.76-7.72 (m, 2H), 7.70-7.65 (m, 1H), 7.56 (t, J = 9.8 Hz, 1H), 7.53-7.50 (m, 3H), 7.48-.743 (m, 1H), 6.84 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.0, 147.0, 143.4797, 139.2, 137.9, 137.5, 135.7, 133.3, 133.2, 129.7, 129.6, 129.5, 128.4, 127.7, 112.3, 111.3, 100.1, 64.1; IR (film): 3057, 1658, 1525, 1180, 1126, 938, 769, 610 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{14}ClNO_2$ 335.0713; Found 355.0715.

2-Methoxy-4-(3-methoxyphenyl)-3-(*p*-tolyl)azuleno[1,2-*c*]pyridin-1(2*H*)-one (4s) : Yield : 50.5 mg (60%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 188-190 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (d, J = 8.9 Hz, 1H), 8.25 (d, J = 10.4 Hz, 1H), 7.66 (t, J = 9.7 Hz, 1H), 7.59 (t, J = 9.7 Hz, 1H), 7.35 (t, J = 9.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 2H), 7.19 (t, J = 7.9 Hz, 1H), 7.10-7.08 (m, 3H), 6.84 (d, J = 7.5 Hz, 1H), 6.80-6.77 (m, 1H), 6.73 (s, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 157.3, 147.9, 144.0, 143.4, 141.4, 138.5, 138.0, 137.0, 136.8, 136.1, 130.9, 129.2, 129.1, 129.1, 128.5, 127.1, 123.7, 116.5, 115.5, 114.0, 112.9, 112.5, 64.0, 55.3, 21.5; IR (film): 3051, 1653, 1508, 1236, 1036, 942, 656 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{28}H_{23}NO_3$ 421.1678; Found 421.1680.

2-Methoxy-4-methyl-3-phenylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4t) : Yield : 44.7 mg (71%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 168-170 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (d, J = 9.0 Hz, 1H), 8.39 (d, J = 10.3 Hz, 1H), 7.69 (t, J = 9.8 Hz, 1H), 7.59 (t, J = 9.7 Hz, 1H), 7.54-7.45 (m, 5H), 7.40 (t, J = 9.7 Hz, 1H), 7.31 (s, 1H), 3.8 (s, 3H), 2.22 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.3, 148.7, 144.1, 142.7, 141.3, 137.0, 136.7, 136.0, 132.7, 130.2, 129.0, 128.9, 128.3, 127.1, 114.2, 110.9, 108.6, 63.9, 14.9; IR (film): 3056 1649, 1531, 1340, 1206, 948, 647 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{17}NO_2$ 315.1259; Found 315.1260.

3-Butyl-2-methoxy-4-methylazuleno[1,2-*c*]pyridin-1(2*H*)-one (4u) : Yield : 48.4 mg (82%); R_f = 0.3 (acetone : hexane = 1:7); Brown solid; Melting point : 137-139 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (d, J = 8.9 Hz, 1H), 8.30 (d, J = 10.4 Hz, 1H), 7.60 (t, J = 9.7 Hz, 1H), 7.52 (t, J = 9.6 Hz, 1H), 7.33 (t, J = 9.6 Hz, 1H), 7.23 (s, 1H), 4.16 (s, 3H), 2.89 (t, J = 7.9 Hz, 2H), 2.42 (s, 3H), 1.73-1.65 (m, 2H), 1.52-1.43 (m, 2H), 1.69 (t, J = 3.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.5, 149.0, 144.2, 144.0, 141.4, 136.2, 136.1, 135.0, 128.9, 126.9, 113.5, 110.6, 106.6, 64.4, 31.3, 28.2, 22.9, 14.0, 13.9; IR (film): 3076, 1648, 1532,

1383, 1293, 920, 627 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{21}NO_2$ 295.1572; Found 295.1571.

CCDC-1923064 (**3a**) and CCDC-1946573 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (2011-0018355).

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10.1002/adsc.202001082

FULL PAPER

Regioselective and Chemodivergent Synthesis of Azulenolactones and Azulenolactams from Rhodium(III)-Catalyzed Reactions of Azulenecarboxamides with Sulfoxonium Ylides

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