JOC The Journal of Organic Chemistry

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Expansion of Azulenes as Nonbenzenoid Aromatic Compounds for C−H Activation: Rhodium- and Iridium-Catalyzed Oxidative Cyclization of Azulene Carboxylic Acids with Alkynes for the Synthesis of Azulenolactones and Benzoazulenes

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Cite This: https://dx.doi.org/10.1021/acs.joc.9b03448 Read Online

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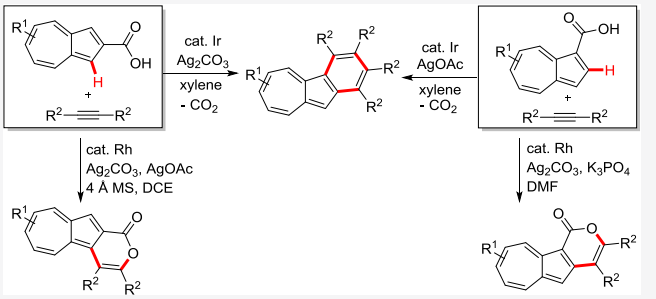
ABSTRACT: Rhodium-catalyzed oxidative [4 + 2] cyclization reactions through the C−H activation of azulene carboxylic acids as nonbenzenoid aromatic compounds with symmetrical and unsymmetrical alkynes were developed under aerobic conditions, which produced azulenolactone derivatives with a wide substrate scope and excellent functional group tolerance. Interestingly, azulenic acids in reaction with alkynes underwent iridium-catalyzed [2 + 2 + 2] cyclization accompanied by decarboxylation to afford tetra(aryl)-substituted benzoazulene derivatives. The reactivity order for C−H activation reaction is greater toward azulene-6-carboxylic acid, azulene-1-carboxylic acid, and azulene-2-carboxylic acid. For the first time, the expansion of azulenes having directing group as nonbenzenoid aromatic compounds for C−H activation was successful, indicating that nonbenzenoid aromatic compounds can be used as good substrates for the C−H activation reaction. Therefore, the research area of C−H activation will certainly expand to nonbenzenoid aromatic compounds in future.



INTRODUCTION

Azulene derivatives, which are well known as representative compounds of nonbenzenoid aromatic hydrocarbons, have been attracting attention in various fields because they exist in natural products, pharmacologically active substances, and functional materials.[1] Because azulene, a nonbenzenoid aromatic compound, has a dipole moment of 1.08 D, which is different from the general benzenoid aromatic compound (e.g., dipole moment of naphthalene = 0), various organic reactions that apply to benzenoid aromatic compounds are often not applied to the functionalization of azulene.[2] Therefore, the development of a novel synthetic method that applies to azulene derivatives is very important and meaningful.

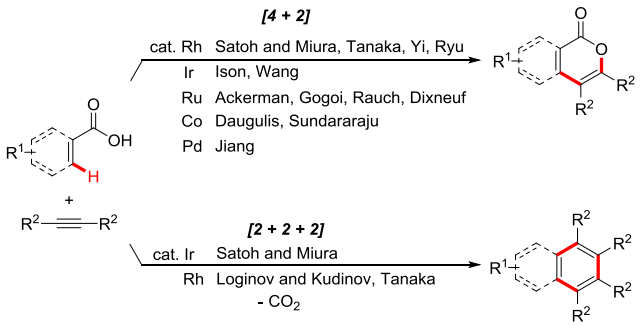
Recently, diverse studies on C−H activation have been reported, and thus it is possible to synthesize various compounds that could not be synthesized by conventional methods.[3] However, these investigations have mainly been carried out on benzenoid aromatic hydrocarbons, which could introduce a large number of substituents on the aryl ring or expand the additional ring. To the best of our knowledge, there are few examples of the application of nonbenzenoid aromatic hydrocarbon compounds in C−H activation reactions to date.[4] Moreover, no studies on C−H activation using directing group have been reported for azulene, a nonbenzenoid aromatic compound. Therefore, we thought that developing a new C−H activation reaction using azulene having a directing group would be very meaningful and important for the expansion of the research area of C−H activation. Initially, we decided to study the C−H activation reaction of azulene carboxylic acid in which the acid group, a good directing group, was introduced into the 5-membered ring of azulene.

In recent years, there has been significant interest in transition-metal-catalyzed oxidative cyclization reactions of benzenoid aromatic carboxylic acids with alkynes. For example, Miura, Satoh, and co-workers have developed an efficient oxidative cyclization reaction with rhodium and iridium catalysts.[5] It was demonstrated that rhodium(III) catalysts in the presence of copper salts were effective in the oxidative [4 + 2] annulation of benzoic acids with alkynes to provide isocoumarins. Interestingly, when iridium(III) catalysts were used in the presence of silver salts for the same reaction, the oxidative [2 + 2 + 2] annulation reaction accompanied by decarboxylation leads to the formation of substituted naphthalenes instead of isocoumarins. More recently, Tanaka,

Received: December 22, 2019

Miura, and co-workers have reported an electron-deficient Cp^E rhodium(III)-catalyzed oxidative [4 + 2] cyclization reaction of substituted benzoic and acrylic acids with alkynes to produce the corresponding substituted isocoumarins and α-pyrones.[6] In addition, similar oxidative [4 + 2] and [2 + 2 + 2] cyclization reactions of benzenoid aromatic carboxylic acids with alkynes using Ru (Ackermann, Gogoi, Rauch, Dixneuf, and Gogoi),[7] Pd (Jiang),[8] and Co (Daugulis and Sundararaju)[9] catalysts have been reported (Scheme 1).[10]

Scheme 1. Transition-Metal-Catalyzed Oxidative [4 + 2] and [2 + 2 + 2] Cyclization Reactions of Benzenoid Aromatic and Alkenyl Acids with Alkynes

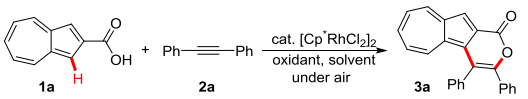


No studies on C−H activation using directing group followed by functionalization have been reported for azulene, a nonbenzenoid aromatic compound. Since the reactivity of nonbenzenoid aromatic compounds is quite different from that of benzenoid aromatic compounds, it is not easy to introduce functional groups into azulene rings. Therefore, if azulene is applied to the C−H activation followed by functionalization, a general oxidative cyclization reaction that can apply to all of aromatic compounds, including benzenoid and nonbenzenoid aromatic compounds, would be developed. Herein, we demonstrated universal Rh- and Ir-catalyzed oxidative [4 + 2] and [2 + 2 + 2] cyclization reactions of azulene-1-carboxylic acid and azulene-2-carboxylic acid, which are nonbenzenoid aromatic acids, with symmetrical and unsymmetrical alkynes, leading to the formation of a variety of azulenolactones and tetra(aryl)benzoazulenes with novel azulene skeletons (Scheme 2).

RESULTS AND DISCUSSION

At the outset of this study, the optimum reaction conditions were examined for the C−H activation followed by cyclization reactions of azulene-2-carboxylic acid (**1a**) with diphenylacetylene (**2a**) in the presence of catalysts and oxidants (Table 1). A variety of catalysts, including $[Cp^*RhCl_2]_2$, $[Cp^*IrCl_2]_2$, $[Cp^*Co(CO)I_2]$, and $[Ru(p\text{-cymene})Cl_2]_2$, were screened, and $[Cp^*RhCl_2]_2$ was the catalyst of choice (see the Supporting Information). Although the reaction of **1a** with **2a** using $[Cp^*RhCl_2]_2$ (4.0 mol %) and Ag_2CO_3 (1.0 equiv) was not effective in dimethyl sulfoxide (DMSO) (120 °C, 16 h) (entry 1), the desired C−H cyclized product **3a** was gratifyingly produced, ranging from 14 to 36% yield in *N*,*N*-dimethylformamide (DMF), *tert*-amyl alcohol, and dichloroethane (DCE) (entries 2, 3, and 4). Chlorobenzene, 1,4-dioxane, acetonitrile, trifluoroethanol, *o*-xylene, *tert*-butyl alcohol, tetrahydrofuran (THF), DMSO, and hexafluoroisopropanol were inferior to DCE. The structure of **3a** was confirmed by X-ray crystallography (see the Supporting Information). These results indicate that the C−H bonds in azulene, as a nonbenzenoid aromatic compound, can undergo C−H activation followed by cyclization reactions such as those in benzenoid aromatic compounds. Stimulated by these important clues, a variety of reaction parameters, such as the temperature and oxidant, were explored. Heating to 80 °C in DCE for 8 h gave the same result (entry 4 *vs* 5). Other additives, such as AgOTf, AgOAc, Ag_2O, $Cu(OAc)_2{\cdot}H_2O$, $Ag_2CO_3/Cu(OAc)_2{\cdot}H_2O$, and Ag_2CO_3/AgOAc, were screened, and Ag_2CO_3/AgOAc provided **3a** in 66% yield

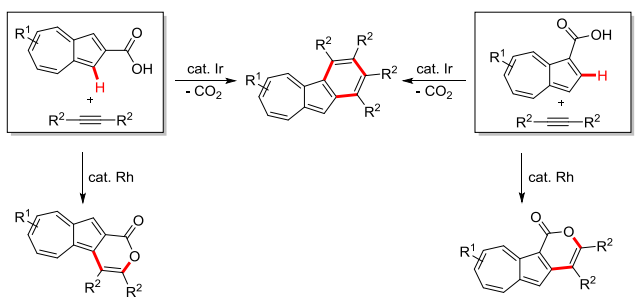
Table 1. Optimization of Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-2-carboxylic Acid with Diphenylacetylene[a]



entry	oxidant (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1	Ag_2CO_3 (1.0)	DMSO	120	16	0
2	Ag_2CO_3 (1.0)	DMF	120	16	14
3	Ag_2CO_3 (1.0)	*t*-AmOH	120	16	19
4	Ag_2CO_3 (1.0)	DCE	120	16	36 (16)[c]
5	Ag_2CO_3 (1.0)	DCE	80	8	36 (16)[c]
6	Ag_2CO_3 (2.0)	DCE	80	8	36 (15)[c]
7	AgOTf (1.0)	DCE	80	8	0
8	AgOAc (1.0)	DCE	80	8	34 (10)[c]
9	Ag_2O (1.0)	DCE	80	8	30 (10)[c]
10	$Cu(OAc)_2{\cdot}H_2O$ (1.0)	DCE	80	8	27
11	Ag_2CO_3 (1.0)/$Cu(OAc)_2{\cdot}H_2O$ (1.0)	DCE	80	8	55
12	Ag_2CO_3 (1.0)/AgOAc (1.0)	DCE	80	8	66
13[d]	Ag_2CO_3 (1.0)/AgOAc (1.0)	DCE	80	8	76
14[d,e]	Ag_2CO_3 (1.0)/AgOAc (1.0)	DCE	80	8	81 (78)[f]

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv) was reacted with **2a** (1.2 equiv), $[Cp^*RhCl_2]_2$ (4.0 mol %), oxidant, and solvent (0.75 mL) under air. [b]NMR yield using dibromomethane as an internal standard. [c]Numbers in parenthesis are the NMR yields of 2-chloroethyl azulene-2-carboxylate (**4**). [d]4 Å MS (30.0 mg) was added. [e]**1a** (1.2 equiv) and **2a** (0.15 mmol, 1.0 equiv) were used. [f]Isolated yield of **3a**.

Scheme 2. Rh- and Ir-Catalyzed Oxidative [4 + 2] and [2 + 2 + 2] Cyclization Reactions of Azulenic Acids (Nonbenzenoid Aromatic Acids) with Alkynes



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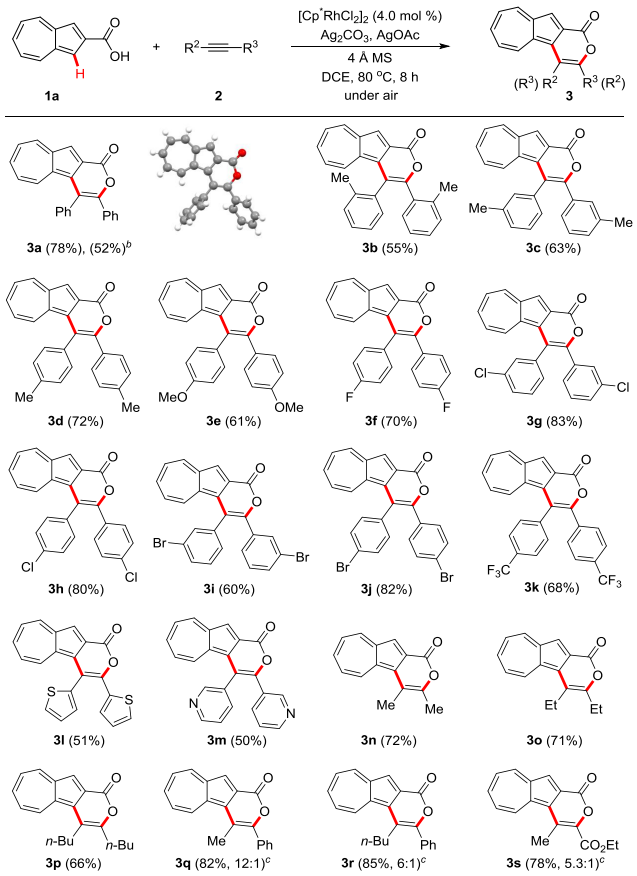
(entries 7−12). The addition of 4 Å molecular sieve increased the product yield to 76% (entry 12 *vs* 13). The best result of the cyclization reaction was obtained from the reaction of **1a** (1.2 equiv) with **2a** (0.15 mmol, 1.0 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4.0 mol %), Ag_2CO_3/AgOAc (1.0 equiv each), and a 4 Å molecular sieve in DCE at 80 °C for 6 h under aerobic conditions, providing **3a** in 78% yield (entry 14).

With the optimum reaction conditions in hand ($[Cp^*RhCl_2]_2$ (4.0 mol %) and Ag_2CO_3/AgOAc (1.0 equiv each)), the scope and limitations of the alkynes (**2**) in the reaction with azulene-2-carboxylic acid (**1a**) were scrutinized (Table 2). With respect to the alkyne substituent, the C−H activation followed by cyclization reaction displays a wide substrate tolerance. Compound **1a** smoothly cyclized with a wide range of symmetrical electron-rich diarylacetylenes **2**, as with diphenylacetylene, to afford 3,4-diarylazulenolactones **3b−e** in moderate to good yields under aerobic conditions. Moreover, symmetrical electron-deficient diarylacetylenes with fluoro, chloro, bromo, and trifluoromethyl groups were more reactive, and the corresponding 3,4-diarylazulenolactones **3f−k** were isolated in good yields, ranging from 60 to 83%. Symmetrical di(heteroaryl)acetylenes with thiophen-2-yl and pyridin-3-yl substituents are also applicable to the present method, providing the corresponding 3,4-di(heteroaryl)-azulenolactones (**3l** and **3m**) in 51 and 50% yields, respectively. Dialkyl-substituted alkynes, including but-2-yne, hex-3-yne, and dec-5-yne, were cyclized to afford the desired 3,4-dialkylazulenolactones **3n−p** in good yields. The unsymmetrical disubstituted alkynes could be used to demonstrate the unique reactivity and effectiveness of the developed reaction. 1-Phenyl-1-propyne and 1-phenyl-1-hexyne delivered the desired products **3q** (82%, 12:1) and **3r** (85%, 6:1), respectively, indicating that the regioselectivity of the C−H activation/cyclization reaction is affected by the steric effects of the unsymmetrical disubstituted alkynes. Ethyl but-2-ynoate reacted with **1a** to provide **3s** in 78% yield (5.3:1). To demonstrate the applicability of the present method to larger-scale processes, a 1.0 mmol scale of diphenylacetylene (**2a**) (0.18 g) was treated with azulene-2-carboxylic acid (**1a**) (1.2 equiv) under optimal reaction conditions, providing the corresponding compound **3a** (0.18 g, 52%).

Next, the scope of azulene-2-carboxylic acids **1** was examined (Table 3). Azulene-2-carboxylic acids with a 6-methyl or 6-phenyl on the 7-membered ring worked equally well with diphenylacetylene and di(3-chlorophenyl)acetylene, leading to the formation of 3,4-diarylazulenolactones **3t−w** in good yields ranging from 58 to 66% under aerobic conditions. Electron-deficient azulene-2-carboxylic acid with a 1-chloro group on the 5-membered ring efficiently underwent C−H activation, followed by cyclization with diphenylacetylene, affording the desired 3,4-diphenylazulenolactone **3x** in 78% yield under aerobic conditions.

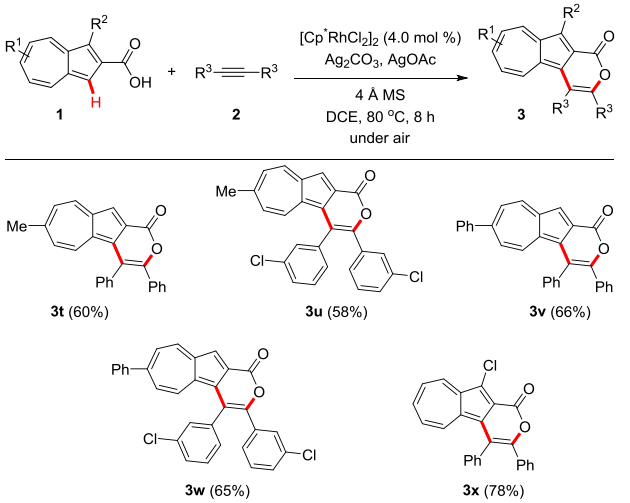
Competition experiments between alkynes were also investigated (Scheme 3). Azulene-2-carboxylic acid **1a** reacted with diphenylacetylene and dec-5-yne (1.2 equiv each) to provide 3,4-diphenylazulenolactone **3a** in 46% yield together with 3,4-di(*n*-butyl)azulenolactone **3p** in 19% yield, indicating that diphenylacetylene is more reactive than dec-5-yne

Table 2. Scope of Alkynes in the Rh-Catalyzed [4 + 2] Cyclization Reactions of Azulene-2-carboxylic Acids with Alkynes[a,b,c]



[a]Reaction conditions: **1a** (1.2 equiv) reacted with **2** (0.2 mmol, 1.0 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4.0 mol %), Ag_2CO_3 (1.0 equiv), AgOAc (1.0 equiv), and 4 Å MS (30.0 mg) in DCE (0.75 mL) at 80 °C for 8 h under air. [b]Reaction scale is 1.0 mmol. [c]Ratios in parentheses indicate the isomeric ratio.

Table 3. Scope of Acids in the Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-2-carboxylic Acids with Alkynes[a]



[a]Reaction conditions: **1** (1.2 equiv) reacted with **2** (0.2 mmol, 1.0 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4.0 mol %), Ag_2CO_3 (1.0 equiv), AgOAc (1.0 equiv), and 4 Å MS (30.0 mg) in DCE (0.75 mL) at 80 °C for 8 h under air.

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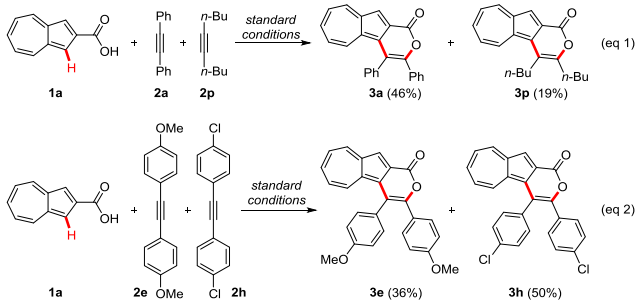
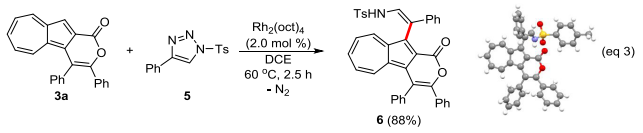
Scheme 3. Competition Experiments of Alkynes



(Scheme 3, eq 1). A competition experiment between the electron-rich 4-methoxy and electron-deficient 4-chloro-substituted diphenylacetylenes furnished mainly 3,4-di(4-chlorophenyl)azulenolactone **3h**, which was obtained from the electron-deficient alkyne (**2h**) (Scheme 3, eq 2).

Next, we explored the synthetic application of 3,4-diphenylazulenolactone (**3a**) in electrophilic aromatic substitution (Scheme 4). When **3a** was treated with *N*-sulfonyl-4-

Scheme 4. Applications of 3,4-Diphenylazulenolactone for Alkylation

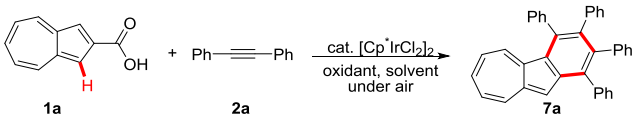


phenyl-1,2,3-triazole (**5**) in the presence of $Rh_2(oct)_4$ (2.0 mol %), *N*-tosylaminoethenyl azulenolactone **6** was obtained in 88% yield (Scheme 4, eq 3).[11] The structure of **6** was confirmed by X-ray crystallography (see the Supporting Information).

With these results in hand, we next attempted to synthesize 3,4-diphenylazulenolactone by reacting azulene-2-carboxylic acid (**1a**) with diphenylacetylene (**2a**) using an iridium catalyst through C−H activation followed by cyclization (Table 4). Although the best oxidants Ag_2CO_3 and AgOAc (1.0 equiv each) using a rhodium catalyst ($[Cp^*RhCl_2]_2$ (4.0 mol %)) in DCE (Table 1, entry 14) were applied to the cyclization reaction, the cyclized azulenolactone (**3a**) was not produced (entry 1). Thus, the optimum reaction conditions were reexamined. When **1a** reacted with **2a** in the presence of $[Cp^*IrCl_2]_2$ (4.0 mol %) and Ag_2CO_3 (1.0 equiv), a variety of solvents, including DMF, toluene, and xylene, were examined. Although DMF was not effective at 160 °C for 6 h, toluene and xylene afforded the unexpected [2 + 2 +2] cyclized product **7a** in 45 and 56% yield, respectively, instead of 3,4-diphenylazulenolactone (entries 2−4). The structure of **7a** was confirmed by X-ray crystallography (see the Supporting Information). Other oxidants, including AgOTf, AgOAc, Ag_2O, $Cu(OAc)_2\cdot H_2O$, and $PhI(OAc)_2$, were inferior to Ag_2CO_3 (entries 5−9). The best result was obtained with $[Cp^*IrCl_2]_2$ (4.0 mol %) and Ag_2CO_3 (2.0 equiv) in xylene at 160 °C for 6 h, affording **7a** in 74% yield (entry 10).

With the optimum reaction conditions in hand ($[Cp^*IrCl_2]_2$ (4.0 mol %) and Ag_2CO_3 (2.0 equiv)), the scope and limitation of azulene-2-carboxylic acids (**1**) and diarylacetylenes (**2**) were examined under aerobic conditions (Table 5). Modification of the substituents on the aryl group was explored and found to have little effect on the efficiency of the [2 + 2 +

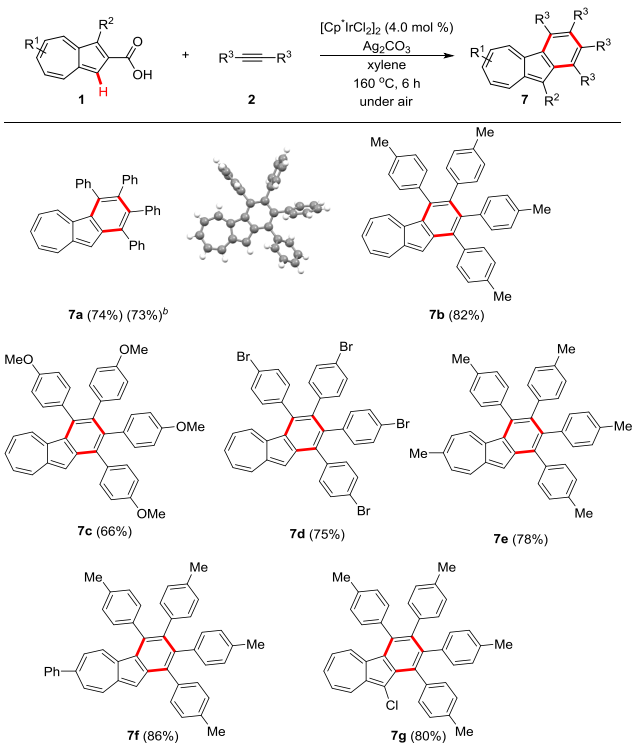
Table 4. Optimization of the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-2-carboxylic Acid with Diphenylacetylene[a]



entry	oxidant (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1[c]	Ag_2CO_3 (1.0)/ AgOAc (1.0)	DCE	120	6	0
2	Ag_2CO_3 (1.0)	DMF	160	6	0
3	Ag_2CO_3 (1.0)	toluene	160	6	45
4	Ag_2CO_3 (1.0)	xylene	160	6	56
5	AgOTf (1.0)	xylene	160	6	0
6	AgOAc (1.0)	xylene	160	6	40
7	Ag_2O (1.0)	xylene	160	6	26
8	$Cu(OAc)_2\cdot H_2O$ (1.0)	xylene	160	6	18
9	$PhI(OAc)_2$ (1.0)	xylene	160	6	0
10	Ag_2CO_3 (2.0)	xylene	160	6	80 (74)[d]

[a]Reaction conditions: **1a** (0.15 mmol, 1.0 equiv) reacted with **2a** (2.0 equiv), $[Cp^*IrCl_2]_2$ (4.0 mol %), oxidant, and solvent (1.5 mL) at 160 °C for 6 h under air. [b]NMR yield using dibromomethane as an internal standard. [c]**1a** (1.2 equiv) reacted with **2** (0.2 mmol, 1.0 equiv) in the presence of $[Cp^*IrCl_2]_2$ (4.0 mol %), Ag_2CO_3 (1.0 equiv), AgOAc (1.0 equiv), and 4 Å MS (30.0 mg) in DCE (0.75 mL) at 120 °C for 6 h under air. [d]Isolated yield.

Table 5. Substrate Scope in the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-2-carboxylic Acids with Alkynes[a]



[a]Reaction conditions: **1a** (0.2 mmol, 1.0 equiv) reacted with **2** (2.0 equiv) in the presence of $[Cp^*IrCl_2]_2$ (4.0 mol %) and Ag_2CO_3 (2.0 equiv) in xylene (1.5 mL) at 160 °C for 6 h under air. [b]Reaction scale is 1.0 mmol.

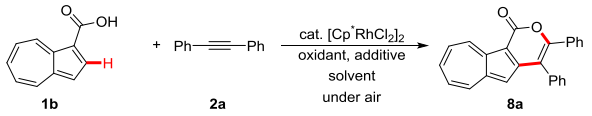
https://dx.doi.org/10.1021/acs.joc.9b03448
J. Org. Chem. XXXX, XXX, XXX−XXX

2] cyclization reaction accompanied by decarboxylation to deliver benzoazulene derivatives **7**. Tetra(aryl)-substituted benzoazulenes (**7b** and **7c**) were produced in good yields from diarylacetylenes (**2**) with electron-donating 4-methyl and 4-methoxy groups on the aryl ring. When di(4-bromophenyl)-acetylene was exposed to azulene-2-carboxylic acid (**1a**), the [2 + 2 + 2] cyclized product (**7d**) was obtained in 75% yield with the release of carbon dioxide. Azulene-2-carboxylic acids bearing 6-methyl and 6-phenyl groups on the 7-membered ring underwent a C−H activation/cyclization reaction accompanied by decarboxylation with di(4-methylphenyl)-acetylene under aerobic conditions, resulting in the production of tetra(4-methylphenyl)-substituted benzoazulenes **7e** and **7f** in 78 and 86% yields, respectively. Azulene-2-carboxylic acid, with a 1-chloro group on the 5-membered ring, is amenable to the present [2 + 2 + 2] cyclization reaction, providing the desired product **7g** in 80% yield. Dec-5-yne did not react with azulene-2-carboxylic acid under the optimum reaction conditions. To demonstrate the applicability of the present method to a larger-scale process, a 1.0 mmol scale of azulene-2-carboxylic acid (**1a**) (0.17 g) was treated with diphenylacetylene (**2a**) (2.0 equiv) under the optimum reaction conditions, affording the corresponding compound **7a** (0.35 g, 73%). Unfortunately, when unsymmetrical prop-1-yn-1-ylbenzene was used with the iridium catalyst, the mixture of [2 + 2 + 2] cyclization products was obtained together with the oxidative [4 + 2] cyclization product (**3q**, 21%).

Based on the above results produced from azulene-2-carboxylic acid (**1a**) with diphenylacetylene (**2a**), we next attempted C−H activation followed by cyclization using azulene-1-carboxylic acid (**1b**) (Table 6). First, when the optimum reaction conditions obtained from azulene-2-carboxylic acid (**1a**) were applied to the cyclization reaction of azulene-1-carboxylic acid (**1b**) with diphenylacetylene (**2a**), the desired cyclized azulenolactone (**8a**) was produced in only 11% yield (entry 1). Thus, the optimum reaction conditions were reexamined. In general, the reactivity of azulene-1-carboxylic acid (**1b**) was inferior to that of azulene-2-carboxylic acid (**1a**). These results coincide with the fact that the electron density of the 2-position on azulene-1-carboxylic acid is lower than that on the 1-position of azulene-2-carboxylic acid. A variety of oxidants, including Ag_2CO_3, AgOAc, AgOTf, Ag_2O, and $Cu(OAc)_2{\cdot}H_2O$, and additives, including K_3PO_4, KH_2PO_4, NaH_2PO_4, and LiH_2PO_4, were screened, and Ag_2CO_3 (2.0 equiv) and K_3PO_4, (1.0 equiv) gave the desired azulenolactone **8a** in 36% yield (entry 9) (see the Supporting Information).

Diarylacetylene with an electron-withdrawing 3-chloro group on the aryl ring underwent Rh-catalyzed oxidative [4 + 2] cyclization reactions with azulene-1-carboxylic acid (**1b**) to provide the corresponding 3,4-di(3-chlorophenyl)-azulenolactone **8b** in 39% yield (Scheme 5).

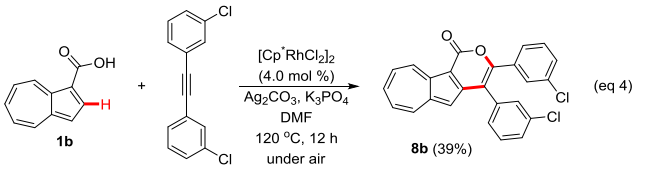
Table 6. Optimization of the Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with Diphenylacetylene[a,b,c,d]



entry	oxidant/additive (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1[c]	Ag_2CO_3 (1.0)/AgOAc (1.0)	DCE	80	12	11
2	Ag_2CO_3 (2.0)	xylene	120	12	0
3	Ag_2CO_3 (2.0)	*t*-BuOH	120	12	10
4	Ag_2CO_3 (2.0)	DMF	120	12	29
5	AgOAc (2.0)	DMF	120	12	0
6	AgOTf (2.0)	DMF	120	12	0
7	Ag_2O (2.0)	DMF	120	12	4
8	$Cu(OAc)_2{\cdot}H_2O$ (2.0)	DMF	120	12	5
9	Ag_2CO_3 (2.0)/ K_3PO_4 (1.0)	DMF	120	12	40 (36)[d]
10	Ag_2CO_3 (2.0)/ KH_2PO_4 (1.0)	DMF	120	12	12
11	Ag_2CO_3 (2.0)/ NaH_2PO_4 (1.0)	DMF	120	12	28
12	Ag_2CO_3 (2.0)/ LiH_2PO_4 (1.0)	DMF	120	12	20

[a]Reaction conditions: **1b** (0.15 mmol, 1.0 equiv) reacted with **2a** (1.2 equiv), $[Cp^*RhCl_2]_2$ (4.0 mol %), oxidant, and additive in solvent (0.75 mL) for 12 h under air. [b]NMR yield using dibromomethane as an internal standard. [c]**1b** (1.2 equiv) was reacted with **2a** (0.15 mmol, 1.0 equiv) and 4 Å MS (30.0 mg). [d]Isolated yield.

Scheme 5. Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with 1,2-bis(3-chlorophenyl)ethyne[a]



[a]Reaction conditions: **1b** (0.2 mmol, 1.0 equiv) reacted with **2** (1.2 equiv) in the presence of $[Cp^*RhCl_2]_2$ (4.0 mol %), Ag_2CO_3 (2.0 equiv), and K_3PO_4 (1.0 equiv) in DMF (0.75 mL) at 120 °C for 12 h under air.

Next, the [2 + 2 + 2] cyclization reaction of azulene-1-carboxylic acid (**1b**) with diphenylacetylene (**2a**) was attempted (Table 7). First, when the optimum reaction conditions of the [2 + 2 + 2] cyclization reaction obtained from azulene-2-carboxylic acid (**1a**) were applied to azulene-1-carboxylic acid (**1b**), the desired tetra(phenyl)azulene (**7a**) was produced in 70% yield (entry 1). Screening of solvents, including toluene, mesitylene, and DMF, gave inferior results to xylene (entries 2−4). A variety of oxidants, including AgOAc, AgOTf, Ag_2O, $Cu(OAc)_2{\cdot}H_2O$, and $PhI(OAc)_2$, were reexamined (entries 5−9), and AgOAc (3.0 equiv) was the oxidant of choice, affording **7a** in 80% yield (entry 10).

When azulene-1-carboxylic acid (**1b**) was treated with a wide range of diarylacetylenes, including 3-methylphenyl, 4-chlorophenyl, 4-trifluoromethylphenyl, and thiophen-2-yl, under the optimum reaction conditions, the desired tetra(aryl or heteroaryl)benzoazulenes (**7h−k**) were produced in good to excellent yields varying from 61 to 92% (Table 8).

On the basis of Rh-catalyzed oxidative [4 + 2] cyclization reactions and Ir-catalyzed [2 + 2 + 2] cyclization reaction accompanied by decarboxylation using azulene-1- and 2-carboxylic acids, azulene-6-carboxylic acid (**1c**) was applied to the corresponding reaction. Although Rh-catalyzed oxidative [4 + 2] cyclization reactions of azulene-6-carboxylic acid (**1c**) have been tried with varying various reaction parameters such as oxidant, solvent, additive, and temperature, the desired azulenolactone (**9**) was obtained in only 9% yield together

https://dx.doi.org/10.1021/acs.joc.9b03448
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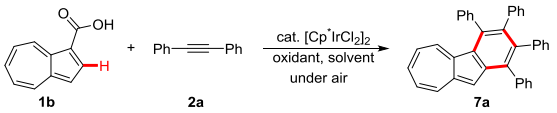
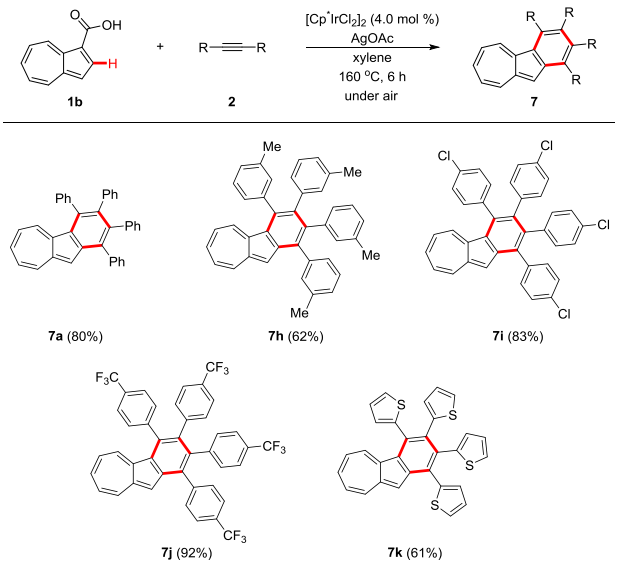
Table 7. Optimization of the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with Diphenylacetylene[a]



entry	oxidant (equiv)	solvent	temp (°C)	time (h)	yield (%)[b]
1	Ag_2CO_3 (2.0)	xylene	160	6	70
2	Ag_2CO_3 (2.0)	toluene	160	6	61
3	Ag_2CO_3 (2.0)	mesitylene	160	6	59
4	Ag_2CO_3 (2.0)	DMF	160	6	0
5	AgOAc (2.0)	xylene	160	6	73
6	AgOTf (2.0)	xylene	160	6	0
7	Ag_2O (2.0)	xylene	160	6	44
8	$Cu(OAc)_2·H_2O$ (2.0)	xylene	160	6	20
9	$PhI(OAc)_2$ (2.0)	xylene	160	6	0
10	AgOAc (3.0)	xylene	160	6	85 (80)[c]

[a]Reaction conditions: **1b** (0.15 mmol, 1.0 equiv) reacted with **2a** (2.0 equiv) in the presence of $[Cp^*IrCl_2]_2$ (4.0 mol %), oxidant, and solvent (1.5 mL) at 160 °C for 6 h under air. [b]NMR yield using dibromomethane as an internal standard. [c]Isolated yield.

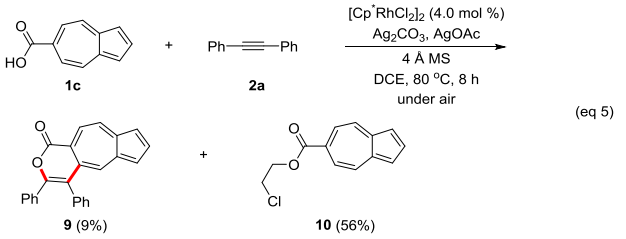
Table 8. Scope of Alkynes in the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with Alkynes[a]

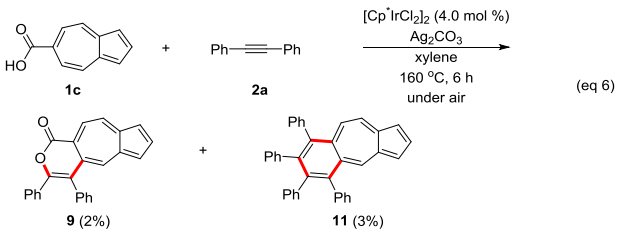


[a]Reaction conditions: **1b** (0.2 mmol, 1.0 equiv) reacted with **2** (2.0 equiv) in the presence of $[Cp^*IrCl_2]_2$ (4.0 mol %) and AgOAc (3.0 equiv) in xylene (1.5 mL) at 160 °C for 6 h under air.

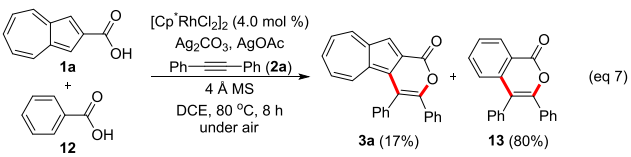
with 2-chloroethyl azulene-6-carboxylate (**10**) in 56% yield (eq 5). In addition, when **1c** was applied to the Ir-catalyzed [2 + 2 + 2] cyclization reaction accompanied by decarboxylation, the corresponding 5,6,7,8-tetraphenylbenzo[*f*]azulene (**11**) and azulenolactone (**9**) were produced in 3 and 2% yields, respectively, and most of **1c** was decomposed (Scheme 6, eq 6).

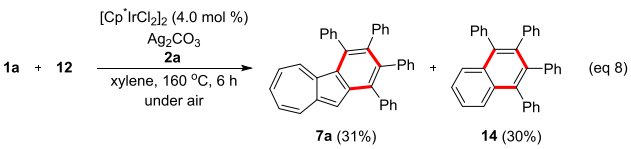
We conducted a series of investigations to establish the mechanism of C−H activation followed by cyclization. First, competition experiments with **1a** and **1b** were carried out to gain insight into the innate ability of azulene carboxylic acid

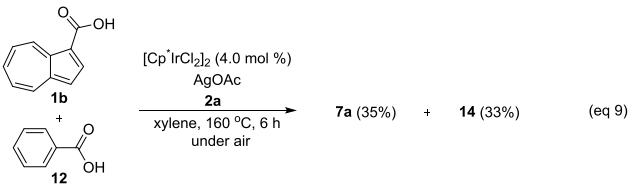




Scheme 6. Competition Experiments of C−H Activation/Cyclization between Azulene Carboxylic Acids and Benzoic Acids







compared to benzoic acid in C−H activation (eq 6). Treatment of azulene-2-carboxylic acid (**1a**) and benzoic acid (**12**) (1.0 equiv each) with diphenylacetylene (**2a**) (1.0 equiv) under optimum reaction conditions gave **3a** and **13** in 17 and 80% yields, respectively (Scheme 6, eq 7). These results indicate that the ability of azulene-2-carboxylic acid to activate the C−H bond is weak compared to its ability to activate the C−H bond of benzoic acid. However, because **3a** was obtained in 78% yield when **1a** is used alone (Table 1, entry 14), the C−H activation ability of azulene-2-carboxylic acid is still useful. Azulene-2-carboxylic acid (**1a**) and benzoic acid (**12**) (1.0 equiv each) were treated with diphenylacetylene (2.0 equiv) in the presence of an iridium catalyst to give tetra(phenyl)azulene **7a** (31%) and tetraphenylnaphthalene **14** (30%), suggesting that the ability of C−H activation and decarboxylation of azulene-2-carboxylic acid is the same as that of benzoic acid (Scheme 6, eq 8). Then, a competition experiment between azulene-1-carboxylic acid (**1b**) and **12** afforded **7a** (35%) and **14** (33%) (Scheme 6, eq 9). These results imply that the ability of C−H activation and decarboxylation of azulene-1-carboxylic acid is similar to that of benzoic acid.

https://dx.doi.org/10.1021/acs.joc.9b03448
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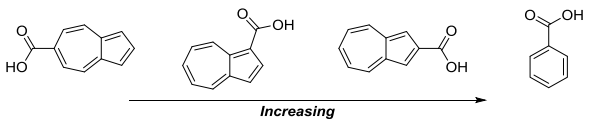
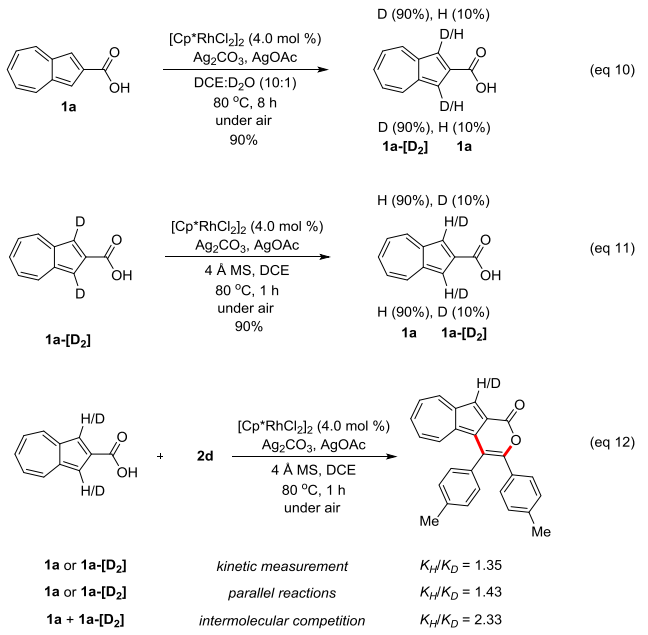
These results indicate that the reactivity order for the C−H activation reaction is greater toward azulene-6-carboxylic acid, azulene-1-carboxylic acid, azulene-2-carboxylic acid, and benzoic acid (Scheme 7). The fact that azulene-2-carboxylic acid is the most reactive among azulenic acids in the C−H activation reaction coincides with the fact that azulene has a resonance structure in which the 5-membered ring is anionic and the 7-membered ring is cationic.

Scheme 7. Reactivity Order for C−H Activation Reaction



A catalytic C−H activation in DCE/D_2O (10:1) was conducted, affording a significant D/H exchange at the *ortho*-position of the product **1a**-[$\mathbf{D_2}$] (Scheme 8, eq 10).

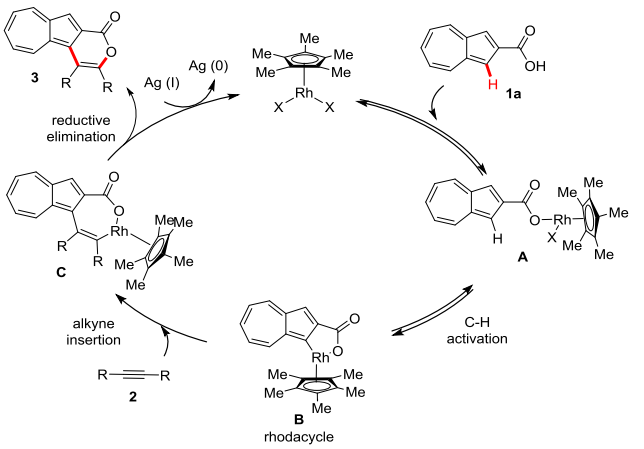
Scheme 8. Experiments with an Isotopically Labeled Compound



These results suggest that the C−H activation step is reversible. Also, when **1a**-[$\mathbf{D_2}$] was treated with optimum reaction conditions, 90% protonation of *ortho*-position was observed in 1 h, indicating that the protonation of the C−H activation step is much faster than the oxidative [4 + 2] cyclization with alkyne (Scheme 8, eq 11). Next, we performed kinetic isotope effect (KIE) studies to obtain insight into the cyclization mechanism (Scheme 8, eq 12). The KIE was observed (K_H/K_D = 2.33) from the intermolecular competition reaction using **1a** and **1a**-[$\mathbf{D_2}$] due to H/D scrambling. The KIE was observed (K_H/K_D = 1.35) by independent reactions using **1a** or **1a**-[$\mathbf{D_2}$] as the substrate (see the Supporting Information for details). Also, the KIE was observed (K_H/K_D = 1.43) via parallel reactions. These results suggested that the C−H bond cleavage at the 1-position of azulene-2-carboxylic acid is not involved in the rate-determining step.

A proposed mechanism for the C−H activation followed by cyclization of azulene-2-carboxylic acid (**1a**) with alkynes **2** is described in Scheme 9. Coordination of the carboxylate to Cp*RhX_2(III) provides rhodium(III) azulene-2-carboxylate **A**.

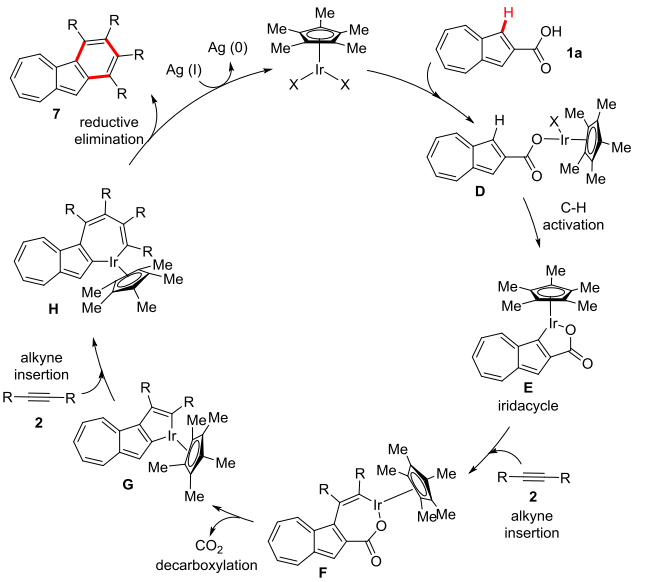
Scheme 9. Proposed Mechanism of the [4 + 2] Cyclization Reaction



ortho-Rhodation provides rhodacycle **B**,[12] and alkyne insertion followed by reductive elimination delivers azulenolactone **3**. Finally, the oxidation of Rh(I) by the silver(I) salt regenerates the catalytically active Rh(III) species.

A proposed mechanism for the C−H activation followed by the [2 + 2 + 2] cyclization of azulene-2-carboxylic acid (**1a**) with alkynes **2** is illustrated in Scheme 10. The 7-membered iridacycle intermediate **F** formed via a method similar to the rhodacycle **C** in Scheme 9 was subjected to decarboxylation, rather than reductive elimination, to afford 5-membered iridacycle intermediate **G**, which is the favored pathway in rhodium catalysis. Next, the second alkyne insertion and reductive elimination take place to provide tetra(aryl)-benzoazulene **7**. The resulting Ir(I) species are oxidized in the presence of the silver(I) salt to regenerate Ir(III).

Scheme 10. Proposed Mechanism for the [2 + 2 + 2] Cyclization Reaction



In conclusion, we have developed a Rh-catalyzed oxidative [4 + 2] cyclization reaction through the C−H activation of

https://dx.doi.org/10.1021/acs.joc.9b03448
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nonbenzenoid aromatic azulene carboxylic acids with symmetrical as well as unsymmetrical alkynes under aerobic conditions, providing azulenolactone derivatives with a wide substrate scope and excellent functional group tolerance. Moreover, the treatment of azulenic acids with alkynes underwent an iridium-catalyzed [2 + 2 + 2] cyclization reaction accompanied by decarboxylation to provide tetra(aryl)-substituted benzoazulene derivatives. The reactivity order for C−H activation reaction is greater toward azulene-6-carboxylic acid, azulene-1-carboxylic acid, and azulene-2-carboxylic acid. The expansion of azulenes having directing group as nonbenzenoid aromatic compounds for C−H activation was accessed for the first time, indicating that nonbenzenoid aromatic compounds can be used as good substrates for the C−H activation reaction. Therefore, the research area of C−H activation will certainly expand to nonbenzenoid aromatic compounds in future.

EXPERIMENTAL SECTION

General. Commercial available reagents were used without purification. Azulene-2-carboxylic acids (**1**)[4b,13] azulene-1-carboxylic acid (**1b**),[14] and azulene-6-carboxylic acid (**1c**)[15] were prepared by the reported method. All reaction mixtures were stirred magnetically, monitored by thin-layer chromatography using silica gel precoated glass plates, which were visualized with UV light, and then developed using either iodine or a solution of anisaldehyde. 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 an NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-*d*), and δ 77.2 for ^{13}C{^{1}H} (chloroform-*d*)]. Infrared spectra were recorded on a Fourier transform infrared (FT-IR) spectrometer either as 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 the 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 an open capillary tube.

General Procedure for the Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-2-carboxylic Acids with Alkynes. To a screw-top V-vial were added azulene-2-carboxylic acid (**1**) (0.18 mmol, 1.2 equiv), alkyne (**2**) (0.15 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.7 mg, 4.0 mol %), Ag_2CO_3 (1.0 equiv), AgOAc (1.0 equiv), and 4 Å MS (30.0 mg) in DCE (0.75 mL). The resulting mixture was stirred at 80 °C (bath temperature) for 8 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 2:1).

3,4-Diphenyl-1H-azuleno[2,1-c]pyran-1-one (**3a**). Yield: 54.3 mg (78%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); Green solid; Melting point: 245−247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 10.0 Hz, 1H), 7.90 (s, 1H), 7.56−7.35 (m, 9H), 7.20−7.16 (m, 3H), 7.06 (t, J = 9.7 Hz, 1H), 6.74 (t, J = 10.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.4, 149.5, 142.6, 142.4, 141.5, 140.8, 136.5, 135.9, 133.7, 131.3, 130.5, 129.39, 129.38, 128.5, 128.3, 128.0, 127.9, 124.7, 124.6, 116.8, 115.8; IR (film): 3055, 2964, 2924, 1721, 1570, 1391, 1185, 698 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{25}H_{16}O_2$ 348.1150; Found 348.1152.

3,4-Di-o-tolyl-1H-azuleno[2,1-c]pyran-1-one (**3b**). Yield: 41.4 mg (55%); R_f = 0.4 (CH_2Cl_2/hexane = 2:1); Brown solid; Melting point: 189−191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 10.0 Hz, 1H), 7.91 (s, 1H), 7.58 (d, J = 9.5 Hz, 1H), 7.53 (t, J = 6.6 Hz, 1H), 7.37 (t, J = 7.8 Hz, 1H), 7.32−7.28 (m, 2H), 7.23−7.21 (m, 2H), 7.10−7.00 (m, 4H), 6.76 (t, J = 10.0 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 149.5, 142.5, 142.3, 141.7, 140.8, 139.1, 137.5, 136.6, 135.8, 133.6, 131.7, 130.9, 130.0, 129.20, 129.15, 129.1, 128.3, 128.0, 127.6, 126.5, 124.7, 124.5, 116.8, 115.8, 21.6, 21.5; IR (film): 3046, 2916, 1718, 1566, 1394, 1372, 1137, 717 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{27}H_{20}O_2$ 376.1463; Found 376.1461.

3,4-Di-m-tolyl-1H-azuleno[2,1-c]pyran-1-one (**3c**). Yield: 47.4 mg (63%); R_f = 0.4 (CH_2Cl_2/hexane = 2:1); Brown solid; Melting point: 193−195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 10.0 Hz, 1H), 7.90 (s, 1H), 7.58 (d, J = 9.5 Hz, 1H), 7.52 (t, J = 9.9 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.32−7.27 (m, 2H), 7.22−7.21 (m, 2H), 7.09−7.00 (m, 4H), 6.76 (t, J = 10.0 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 149.5, 142.5, 142.3, 141.7, 140.8, 139.1, 137.5, 136.6, 135.8, 133.6, 131.7, 130.8, 130.0, 129.2, 129.1, 129.0, 128.3, 127.9, 127.6, 126.5, 124.7, 124.5, 116.8, 115.7, 21.6, 21.5; IR (film): 3046, 2914, 1718, 1566, 1394, 922, 787, 718 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{27}H_{20}O_2$ 376.1463; Found 376.1462.

3,4-Di-p-tolyl-1H-azuleno[2,1-c]pyran-1-one (**3d**). Yield: 54.2 mg (72%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); Green solid; Melting point: 259−261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 10.0 Hz, 1H), 7.89 (s, 1H), 7.59 (d, J = 9.5 Hz, 1H), 7.51 (t, J = 6.6 Hz, 1H), 7.28−7.26 (m, 6H), 7.06−6.99 (m, 3H), 6.75 (t, J = 10.0 Hz, 1H), 2.47 (s, 3H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 149.7, 142.5, 142.3, 141.6, 140.7, 138.2, 138.1, 136.6, 132.8, 131.1, 131.0, 130.9, 130.1, 129.2, 128.6, 127.8, 124.6, 124.4, 116.3, 115.7, 21.6, 21.4; IR (film): 3102, 2920, 1720, 1508, 1394, 1186, 828, 740 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{27}H_{20}O_2$ 376.1463; Found 376.1465.

3,4-Bis(4-methoxyphenyl)-1H-azuleno[2,1-c]pyran-1-one (**3e**). Yield: 49.8 mg (61%); R_f = 0.2 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 237−239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 10.0 Hz, 1H), 7.87 (s, 1H), 7.64 (d, J = 9.5 Hz, 1H), 7.50 (t, J = 9.8 Hz, 1H), 7.32−7.28 (m, 4H), 7.04−6.99 (m, 3H), 6.78−6.71 (m, 3H), 3.91 (s, 3H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.5, 159.6, 159.4, 149.7, 142.5, 142.3, 141.5, 140.6, 136.6, 132.4, 131.3, 130.7, 128.0, 127.6, 126.3, 124.6, 124.3, 115.7, 115.4, 114.9, 113.4, 55.5, 55.3; IR (film): 3049, 2835, 1719, 1571, 1508, 1247, 1028, 835 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{27}H_{20}O_4$ 408.1362; Found 408.1364.

3,4-Bis(4-fluorophenyl)-1H-azuleno[2,1-c]pyran-1-one (**3f**). Yield: 53.8 mg (70%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 264−266 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 10.1 Hz, 1H), 7.91 (s, 1H), 7.61−7.56 (m, 2H), 7.40−7.36 (m, 2H), 7.33−7.30 (m, 2H), 7.20 (t, J = 8.6 Hz, 2H), 7.11 (t, J = 9.6 Hz, 1H), 6.90 (t, J = 8.7 Hz, 2H), 6.82 (t, J = 10.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J = 248.8 Hz), 162.7 (d, J = 249.8 Hz), 161.0, 149.1, 142.8, 142.5, 141.2, 141.0, 136.5, 133.1 (d, J = 7.9 Hz), 131.8(d, J = 3.6 Hz), 131.4 (d, J = 8.4 Hz), 130.1, 129.9 (d, J = 3.6 Hz), 128.2, 124.80, 124.76, 116.7 (d, J = 21.4 Hz), 116.1, 115.7, 115.2 (d, J = 21.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.15, −112.47; IR (film): 3049, 2850, 1725, 1504, 1186, 844, 813 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{25}H_{14}F_2O_2$ 384.0962; Found 384.0962.

3,4-Bis(3-chlorophenyl)-1H-azuleno[2,1-c]pyran-1-one (**3g**). Yield: 69.1 mg (83%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 238−240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 10.0 Hz, 1H), 7.93 (s, 1H), 7.64−7.60 (m, 2H), 7.52−7.42 (m, 4H), 7.33 (dt, J = 7.4 Hz, J = 1.3 Hz, 1H), 7.21 (dt, J = 7.1 Hz, J = 2.0 Hz, 1H), 7.17−7.10 (m, 3H), 6.87 (t, J = 9.9 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.8, 148.0, 143.0, 142.7, 141.3, 141.2, 137.4, 136.2, 135.4, 135.0, 134.1, 131.1, 130.8, 129.5, 129.4, 129.20, 129.18, 129.1, 128.7, 128.1, 127.4, 125.14, 125.11, 116.2, 116.1; IR (film): 3053, 2885, 1721, 1567, 1393, 792, 704, 675 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{25}H_{14}Cl_2O_2$ 416.0371; Found 416.0373.

3,4-Bis(4-chlorophenyl)-1H-azuleno[2,1-c]pyran-1-one (**3h**). Yield: 66.6 mg (80%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 219−221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 10.0 Hz, 1H), 7.92 (s, 1H), 7.64−7.58 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 7.27−7.24 (m, 2H), 7.20−7.18 (m, 2H), 7.13 (t, J = 9.6 Hz, 1H), 6.86 (t, J = 10.0 Hz, 1H);

https://dx.doi.org/10.1021/acs.joc.9b03448
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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 148.5, 143.0, 142.7, 141.3, 141.1, 136.3, 134.8, 134.5, 134.1, 132.6, 131.9, 130.6, 129.9, 129.5, 128.3, 128.0, 125.0, 124.95, 116.0, 115.9; IR (film): 2642, 1641, 1573, 1322, 1161, 1065, 717 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{14}Cl_2O_2$ 416.0371; Found 416.0367.

3,4-Bis(3-bromophenyl)-1H-azuleno[2,1-c]pyran-1-one (**3i**). Yield: 60.5 mg (60%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 239−241 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 10.0 Hz, 1H), 7.93 (s, 1H), 7.68−7.59 (m, 5H), 7.41−7.35 (m, 3H), 7.19−7.13 (m, 2H), 7.06 (t, J = 7.9 Hz, 1H), 6.87 (t, J = 10.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 147.9, 143.1, 142.7, 141.4, 141.2, 137.7, 136.2, 135.2, 134.0, 132.3, 132.0, 131.6, 131.0, 130.0, 129.4, 129.1, 128.1, 127.9, 125.2, 125.1, 123.4, 122.2, 116.2, 116.1; IR (film): 3052, 2359, 1721, 1644, 1568, 1391, 761, 566 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{14}{}^{79}Br_2O_2$ 503.9361, $C_{25}H_{14}{}^{81}Br_2O_2$ 507.9321; Found 503.9358, 507.9306.

3,4-Bis(4-bromophenyl)-1H-azuleno[2,1-c]pyran-1-one (**3j**). Yield: 82.6 mg (82%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 269−271 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 10.0 Hz, 1H), 7.91 (s, 1H), 7.65−7.58 (m, 4H), 7.35 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.13 (t, J = 9.7 Hz, 1H), 6.87 (t, J = 10.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 148.4, 143.0, 142.7, 141.3, 141.1, 136.3, 134.6, 132.90, 132.85, 132.4, 131.3, 130.9, 129.4, 128.0, 125.04, 124.99, 123.0, 122.9, 116.1, 116.0; IR (film): 2359, 1644, 1483, 1391, 1181, 1009, 743, 606 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{14}{}^{79}Br_2O_2$ 503.9361, $C_{25}H_{14}{}^{81}Br_2O_2$ 507.9321; Found 503.9359, 507.9323.

3,4-Bis(4-(trifluoromethyl)phenyl)-1H-azuleno[2,1-c]pyran-1-one (**3k**). Yield: 65.8 mg (68%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 244−246 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 10.0 Hz, 1H), 7.95 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.64 (t, J = 9.8 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.51−7.41 (m, 5H), 7.19 (t, J = 9.7 Hz, 1H), 6.86 (t, J = 10.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.7, 147.9, 143.2, 142.9, 141.4, 141.1, 139.5, 136.8, 136.2, 131.8, 130.8 (q, J = 61.3 Hz), 130.7 (q, J = 39.4 Hz), 129.6, 128.7, 128.3, 124.0 (q, J = 272.3 Hz), 126.6 (q, J = 3.6 Hz), 125.4, 125.2, 125.1 (q, J = 3.7 Hz), 122.6, 116.7, 116.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.49, −62.82; IR (film): 2908, 1718, 1636, 1568, 1488, 1182, 1015, 764 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{27}H_{14}F_6O_2$ 484.0898; Found 484.0900.

3,4-Di(thiophen-2-yl)-1H-azuleno[2,1-c]pyran-1-one (**3l**). Yield: 36.7 mg (51%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 241−243 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 10.0 Hz, 1H), 7.85 (s, 1H), 7.71 (d, J = 5.0 Hz, 1H), 7.58−7.52 (m, 2H), 7.40 (d, J = 2.3 Hz, 1H), 7.34 (t, J = 4.1 Hz, 1H), 7.27−7.26 (m, 2H), 7.05 (t, J = 9.5 Hz, 1H), 6.97 (t, J = 4.2 Hz, 1H), 6.84 (t, J = 9.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 146.9, 143.0, 142.6, 141.7, 141.0, 136.3, 135.53, 135.50, 130.8, 130.7, 129.3, 128.8, 128.7, 128.5, 127.1, 127.0, 125.3, 124.8, 116.0, 107.1; IR (film): 2359, 1791, 1638, 1428, 1222, 1017, 778 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{12}O_2S_2$ 360.0279; Found 360.0281.

3,4-Di(pyridin-3-yl)-1H-azuleno[2,1-c]pyran-1-one (**3m**). Yield: 35.0 mg (50%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 252−254 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (dd, J = 4.9 Hz, J = 1.7 Hz, 1H), 8.69 (dd, J = 2.2 Hz, J = 0.8 Hz, 2H), 8.50−8.45 (m, 3H), 7.95 (s, 1H), 7.78 (dt, J = 7.8 Hz, J = 2.0 Hz, 1H), 7.69 (dt, J = 8.0 Hz, J = 2.0 Hz, 1H), 7.67−7.62 (m, 1H), 7.60 (d, J = 9.6 Hz, 1H), 7.47 (ddd, J = 7.8 Hz, J = 4.9 Hz, J = 0.8 Hz, 1H), 7.22−7.17 (m, 2H), 6.87 (t, J = 9.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.6, 151.7, 150.2, 150.1, 149.3, 147.6, 143.3, 142.9, 141.3, 141.0, 138.8, 136.6, 136.2, 131.3, 129.4, 128.7, 128.1, 125.4, 125.2, 124.1, 123.0, 116.2, 114.6; IR (film): 3082, 2359, 1720, 1568, 1393, 1194, 1020, 721 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{14}N_2O_2$ 350.1055; Found 350.1053.

3,4-Dimethyl-1H-azuleno[2,1-c]pyran-1-one (**3n**). Yield: 32.3 mg (72%); R_f = 0.1 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 226−228 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 9.4 Hz, 1H), 8.32 (d, J = 10.0 Hz, 1H), 7.76 (s, 1H), 7.59 (t, J = 9.8 Hz, 1H), 7.09 (t, J = 9.9 Hz, 1H), 7.02 (t, J = 9.7 Hz, 1H), 2.57 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 149.1, 142.3, 142.2, 141.1, 139.6, 136.8, 131.4, 127.8, 124.2, 123.8, 115.8, 108.7, 17.2, 15.3; IR (film): 2952, 1706, 1615, 1574, 1195, 1092, 738 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{15}H_{12}O_2$ 224.0837; Found 224.0834.

3,4-Diethyl-1H-azuleno[2,1-c]pyran-1-one (**3o**). Yield: 35.8 mg (71%); R_f = 0.2 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 135−137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 9.5 Hz, 1H), 8.34 (d, J = 10.0 Hz, 1H), 7.81 (s, 1H), 7.61 (t, J = 9.8 Hz, 1H), 7.13 (t, J = 10.0 Hz, 1H), 7.04 (t, J = 9.6 Hz, 1H), 3.00 (q, J = 7.5 Hz, 2H), 2.74 (q, J = 7.5 Hz, 2H), 1.37 (t, J = 7.5 Hz, 3H), 1.32 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 154.1, 142.3, 142.2, 140.7, 140.0, 135.7, 130.0, 128.5, 124.2, 123.9, 116.3, 114.1, 23.9, 20.8, 14.5, 13.4; IR (film): 2967, 1713, 1643, 1391, 1190, 990, 735 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{16}O_2$ 252.1150; Found 252.1152.

3,4-Dibutyl-1H-azuleno[2,1-c]pyran-1-one (**3p**). Yield: 40.7 mg (66%); R_f = 0.4 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 90−92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 9.5 Hz, 1H), 8.33 (d, J = 10.0 Hz, 1H), 7.81 (s, 1H), 7.61 (t, J = 9.8 Hz, 1H), 7.12 (t, J = 9.9 Hz, 1H), 7.03 (t, J = 7.0 Hz, 1H), 2.94 (t, J = 8.1 Hz, 2H), 2.70 (t, J = 7.8 Hz, 2H), 1.78−1.68 (m, 4H), 1.60−1.51 (m, 2H), 1.48−1.39 (m, 2H), 1.03 (t, J = 7.3 Hz, 3H), 0.97 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 153.3, 142.3, 142.2, 140.7, 140.0, 135.8, 130.2, 128.5, 124.1, 123.9, 116.3, 113.2, 31.9, 30.8, 30.4, 27.4, 22.9, 22.7, 14.1, 14.0; IR (film): 2956, 2929, 2870, 2359, 1718, 1572, 1187, 735 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{24}O_2$ 308.1776; Found 308.1773.

4-Methyl-3-phenyl-1H-azuleno[2,1-c]pyran-1-one (**3q**). Yield: 46.9 mg (82%); data for the major isomer **3r-1**; R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 208−210 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 9.4 Hz, 1H), 8.35 (d, J = 10.0 Hz, 1H), 7.81 (s, 1H), 7.65−7.59 (m, 3H), 7.49−7.39 (m, 3H), 7.15 (t, J = 9.9 Hz, 1H), 7.07 (t, J = 9.7 Hz, 1H), 2.68 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 150.5, 142.5, 142.3, 141.2, 140.3, 137.3, 133.8, 131.1, 130.0, 128.9, 128.28, 128.27, 124.6, 124.4, 116.0, 110.0, 16.7; IR (film): 3064, 2921, 2851, 1722, 1643, 1572, 1185, 703 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0992. Data for the minor isomer **3r-2**; R_f = 0.4 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 208−210 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 9.9 Hz, 1H), 7.84 (s, 3H), 7.57−7.51 (m, 3H), 7.47 (d, J = 9.5 Hz, 2H), 7.41−7.38 (m, 2H), 7.01 (t, J = 9.7 Hz, 1H), 6.70 (t, J = 9.9 Hz, 1H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.9, 150.4, 142.4, 142.3, 141.4, 139.9, 136.2 135.6, 130.8, 130.5, 129.4 128.4, 127.4, 124.4, 124.0, 115.7, 115.5, 17.7; IR (film): 2359, 2088, 1643, 1499, 1183, 1085, 770 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O_2$ 286.0994; Found 286.0993.

4-Butyl-3-phenyl-1H-azuleno[2,1-c]pyran-1-one (**3r**). Yield: 55.8 mg (85%); Data for the major isomer **3s-1**; R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 147−149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 9.5 Hz, 1H), 8.42 (d, J = 10.0 Hz, 1H), 7.90 (s, 1H), 7.68 (t, J = 9.8 Hz, 1H), 7.59−7.56 (m, 2H), 7.49−7.43 (m, 3H), 7.20 (t, J = 9.9 Hz, 1H), 7.13 (t, J = 9.7 Hz, 1H), 3.02 (t, J = 8.0 Hz, 2H), 1.80−1.72 (m, 2H), 1.43−1.37 (m, 2H), 0.88 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 150.7, 142.6, 142.4, 140.9, 140.6, 136.2, 134.2, 129.8, 129.6, 129.2, 129.0, 128.4, 124.5, 124.4, 116.5, 115.0, 32.1, 28.0, 22.6, 13.9; IR (film): 2359, 1868, 1639, 1466, 1293, 1183, 771 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{20}O_2$ 328.1463; Found 328.1465. Data for the minor isomer **3s-2**; R_f = 0.4 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 147−149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 10.0 Hz, 1H), 7.84 (s, 1H), 7.56−7.37 (m, 7H), 7.00 (t, J = 9.7 Hz, 1H), 6.69 (t, J = 9.9 Hz, 1H), 2.42 (t, J = 7.6 Hz, 2H), 1.70−1.58 (m, 2H), 1.32-1.22 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 154.1, 142.4, 142.2, 141.4, 140.0, 136.1, 135.8, 130.9, 130.6, 129.3, 128.4, 127.4, 124.0, 115.6, 115.5, 30.8, 30.5, 22.4, 13.9; IR (film): 2958, 2869, 2339, 1724, 1643, 1180, 1017, 703 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{23}H_{20}O_2$ 328.1463; Found 328.1465.

Ethyl 4-methyl-1-oxo-1H-azuleno[2,1-c]pyran-3-carboxylate (**3s**). Yield: 44.0 mg (78%); data for the major isomer **3q-1**; R_f =

https://dx.doi.org/10.1021/acs.joc.9b03448
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0.1 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 175−177 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.19 (d, J = 9.6 Hz, 1H), 8.54 (d, J = 10.0 Hz, 1H), 7.92 (s, 1H), 7.83 (t, J = 9.9 Hz, 1H), 7.39 (t, J = 9.9 Hz, 1H), 7.32 (t, J = 9.7 Hz, 1H), 4.43 (q, J = 7.1 Hz, 2H), 3.11 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.2, 159.6, 143.1, 142.6, 142.1, 141.4, 138.4, 137.9, 130.3, 128.2, 126.1, 126.0, 121.7, 116.7, 61.7, 15.2, 14.4; IR (film): 3100, 2984, 1698, 1274, 1196, 723, 571 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_4$ 282.0892; Found 282.0895. Data for the minor isomer **3q-2**; R_f = 0.2 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 304−306 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 9.2 Hz, 1H), 8.44 (d, J = 10.0 Hz, 1H), 7.83 (s, 1H), 7.71 (t, J = 9.6 Hz, 1H), 7.20−7.14 (m, 2H), 4.56 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.47 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 160.4, 153.4, 143.0, 142.7, 140.6, 140.4, 133.8, 126.9, 125.7, 124.7, 124.6, 115.6, 109.5, 62.0, 18.5, 14.2; IR (film): 2978, 2359, 1715, 1575, 1270, 1151, 1049, 736 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{17}H_{14}O_4$ 282.0892; Found 282.0889.

7-Methyl-3,4-diphenyl-1H-azuleno[2,1-c]pyran-1-one (**3t**). Yield: 43.5 mg (60%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 209−211 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 10.4 Hz, 1H), 7.84 (s, 1H), 7.47−7.45 (m, 3H), 7.42−7.35 (m, 5H), 7.20−7.16 (m, 3H), 6.98 (d, J = 10.4 Hz, 1H), 6.67 (d, J = 9.9 Hz, 1H), 2.52 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5, 155.7, 149.3, 141.2, 140.7, 139.7, 136.1, 134.7, 133.8, 131.3, 130.8, 129.4, 129.3, 128.4, 128.2, 127.9, 126.9, 126.8, 125.5, 116.8, 115.8, 28.3; IR (film): 2922, 2852, 1722, 1573, 1242, 1158, 1024, 697 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{26}H_{18}O_2$ 362.1307; Found 362.1304.

3,4-Bis(3-chlorophenyl)-7-methyl-1H-azuleno[2,1-c]pyran-1-one (**3u**). Yield: 49.9 mg (58%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 206−208 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 10.4 Hz, 1H), 7.86 (s, 1H), 7.51−7.41 (m, 5H), 7.32 (dt, J = 7.4 Hz, J = 1.4 Hz, 1H), 7.20 (dt, J = 7.3 Hz, J = 1.9 Hz, 1H), 7.16−7.05 (m, 3H), 6.79 (d, J = 9.9 Hz, 1H), 2.56 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.0, 156.3, 147.8, 141.5, 140.5, 140.0, 137.6, 135.4, 135.1, 134.4, 134.1, 131.2, 130.7, 129.51, 129.47, 129.4, 129.2, 129.0, 128.6, 127.4, 127.3, 127.0, 126.0, 116.3, 116.1, 28.4; IR (film): 3064, 2970, 2853, 1726, 1572, 1404, 1159, 796, 699 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{26}H_{16}Cl_2O_2$ 430.0527; Found 430.0529.

3,4,7-Triphenyl-1H-azuleno[2,1-c]pyran-1-one (**3v**). Yield: 56.0 mg (66%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 219−221 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 10.6 Hz, 1H), 7.90 (s, 1H), 7.57−7.53 (m, 3H), 7.48−7.41 (m, 8H), 7.38−7.36 (m, 2H), 7.29 (dd, J = 10.6 Hz, J = 1.5 Hz, 1H), 7.20−7.16 (m, 3H), 6.94 (dd, J = 10.1 Hz, J = 1.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.4, 156.4, 149.4, 143.9, 141.5, 140.7, 139.5, 135.9, 134.9, 133.7, 131.3, 130.9, 129.37, 129.36, 129.1, 129.0, 128.5, 128.4, 128.3, 127.9, 127.7, 125.5, 124.8, 116.8, 116.1; IR (film): 2922, 2852, 1722, 1573, 1242, 1158, 1024, 697 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{31}H_{20}O_2$ 424.1463; Found 424.1465.

3,4-Bis(3-chlorophenyl)-7-phenyl-1H-azuleno[2,1-c]pyran-1-one (**3w**). Yield: 64.0 mg (65%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 226−228 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 10.6 Hz, 1H), 7.91 (s, 1H), 7.61 (d, J = 10.2 Hz, 1H), 7.58−7.55 (m, 2H), 7.52−7.42 (m, 7H), 7.38−7.33 (m, 2H), 7.20 (dt, J = 7.5 Hz, J = 1.8 Hz, 1H), 7.16−7.04 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 156.9, 148.0, 143.7, 141.8, 140.5, 139.9, 137.5, 135.4, 135.1, 134.6, 134.1, 131.1, 130.8, 129.6, 129.5, 129.4, 129.3, 129.2, 129.09, 129.05, 128.6, 128.5, 127.7, 127.4, 125.9, 125.5, 116.4, 116.2; IR (film): 3064, 2975, 2096, 1727, 1572, 1149, 762, 699 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{31}H_{18}Cl_2O_2$ 492.0684; Found 492.0681.

10-Chloro-3,4-diphenyl-1H-azuleno[2,1-c]pyran-1-one (**3x**). Yield: 59.6 mg (78%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 284−286 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 10.3 Hz, 1H), 7.54−7.46 (m, 5H), 7.40−7.34 (m, 4H), 7.20−7.16 (m, 3H), 7.10 (t, J = 9.7 Hz, 1H), 6.69 (t, J = 9.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 150.4, 143.7, 142.1, 139.3, 135.6, 134.8, 134.7, 133.3, 131.3, 129.6, 129.5, 129.4, 128.7, 128.6, 127.9, 125.2, 124.8, 122.5, 116.2, 115.9; IR (film): 2360, 1717, 1637, 1385, 1069, 743, 693 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{15}ClO_2$ 382.0761; Found 382.0757.

2-Chloroethyl azulene-2-carboxylate (**4**). Yield: 7.5 mg (16%); R_f = 0.5 (CH_2Cl_2/hexane = 1:1); blue solid; melting point: 246−248 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 9.1 Hz, 2H), 7.82 (s, 2H), 7.67 (t, J = 9.9 Hz, 1H), 7.20 (t, J = 9.8 Hz, 2H), 4.62 (t, J = 5.8 Hz, 2H), 3.86 (t, J = 5.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.4, 141.0, 140.8, 140.1, 137.5, 124.2, 119.2, 64.4, 41.9; IR (film): 3045, 2961, 1713, 1321, 1194, 765, 736 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{11}ClO_2$ 234.0448; Found 234.0448.

General Procedure for the Alkenylation of 3,4-Diphenylazulenolactone.[11] $Rh_2(oct)_4$ (2 mol %), 3,4-diphenylazulenolactone (**3a**) (0.3 mmol, 1.5 equiv), *N*-sulfonyl-4-phenyl-1,2,3-triazole (**4**) (0.2 mmol, 1.0 equiv), and DCE (1.0 mL) were added to an oven-dried test tube equipped with a stirring bar. The mixture was stirred at 60 °C for 2.5 h under nitrogen. The residue was passed through a pad of celite and eluted with CH_2Cl_2. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel fresh column chromatography (EtOAc/hexane = 1:5) to give **6** (76.7 mg, 88%) as a deep-blue solid.

(Z)-4-Methyl-N-(2-(1-oxo-3,4-diphenyl-1H-azuleno[2,1-c]pyran-10-yl)-2-phenylvinyl) benzenesulfonamide (**6**). Yield: 109.0 mg (88%); R_f = 0.2 (EtOAc/hexane = 1:5); blue solid; melting point: 274−276 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, J = 10.6 Hz, 1H), 7.83 (d, J = 10.1 Hz, 1H), 7.68−7.64 (m, 3H), 7.54 (s, 4H), 7.49 (d, J = 9.6 Hz, 1H), 7.44−7.43 (m, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.33−7.30 (m, 2H), 7.25−7.23 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 7.16−7.12 (m, 2H), 7.03 (d, J = 7.3 Hz, 2H), 6.93 (t, J = 9.7 Hz, 1H), 6.85 (t, J = 10.0 Hz, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.6, 148.4, 143.5, 143.0, 140.4, 140.0, 139.5, 138.1, 137.6, 135.7, 135.2, 133.3, 131.1, 130.7, 129.6, 129.4, 129.24, 129.16, 128.9, 128.5, 128.2, 127.8, 126.2, 126.0, 125.14, 125.05, 124.7, 124.1, 122.8, 116.2, 116.0, 20.9; IR (film): 2924, 1725, 1637, 1337, 1164, 850, 696 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{40}H_{29}NO_4S$ 619.1817; Found 619.1817.

General Procedure for the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-2-carboxylic Acids with Alkynes. To a screw-top V-vial were added azulene-2-carboxylic acid (**1**) (0.15 mmol, 1.0 equiv), alkyne (**2**) (0.3 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (4.0 mol %), and Ag_2CO_3 (0.3 mmol, 2.0 equiv) in xylene (1.5 mL). The resulting mixture was stirred at 160 °C (bath temperature) for 6 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 1:20).

1,2,3,4-Tetraphenylbenzo[a]azulene (**7a**). Yield: 71.4 mg (74%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 235−237 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 10.8 Hz, 1H), 7.32−7.24 (m, 8H), 7.22−7.15 (m, 4H), 7.01 (dd, J = 11.0 Hz, J = 8.5 Hz, 1H), 6.89−6.82 (m, 10H), 6.72 (dd, J = 10.8 Hz, J = 8.4 Hz, 1H), 6.54 (dd, J = 10.9 Hz, J = 9.0, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6, 141.4, 140.9, 140.69, 140.66, 140.61, 140.58, 140.2, 137.3, 136.7, 136.4, 135.0, 132.8, 132.7, 132.1, 131.7, 131.3, 130.3, 128.4, 127.8, 127.7, 126.9, 126.7, 126.5, 126.3, 125.9, 125.5, 125.2, 123.8, 116.4; IR (film): 3055, 2930, 1645, 1585, 1440, 1391, 737, 699 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{38}H_{26}$ 482.2035; Found 482.2037.

1,2,3,4-Tetra-p-tolylbenzo[a]azulene (**7b**). Yield: 88.3 mg (82%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 194−196 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 10.9 Hz, 1H), 7.18−7.05 (m, 10H), 6.97 (dd, J = 10.9 Hz, J = 8.6 Hz, 1H), 6.77−6.66 (m, 9H), 6.53 (dd, J = 10.9 Hz, J = 9.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.7, 141.6, 140.8, 140.3, 138.1, 137.8, 137.5, 137.4, 137.0, 136.3, 136.1, 135.5, 134.6, 134.5, 134.2, 132.6, 132.5, 131.8, 131.6, 131.1, 130.1, 129.1, 128.40, 128.39, 128.0, 127.4, 127.2, 125.8, 123.5, 116.6, 21.5, 21.4, 21.27, 21.23; IR (film): 3047, 2919, 1646, 1514, 1390, 1021, 815, 740 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{42}H_{34}$ 538.2661; Found 538.2659.

https://dx.doi.org/10.1021/acs.joc.9b03448
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*1,2,3,4-Tetrakis(4-methoxyphenyl)benzo[a]azulene (**7c**).* Yield: 94.0 mg (78%); R_f = 0.1 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 267−269 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 11.0 Hz, 1H), 7.23−7.17 (m, 3H), 7.14 (d, J = 8.7 Hz, 2H), 6.99 (dd, J = 11.1 Hz, J = 8.4 Hz, 1H), 6.86−6.67 (m, 10H), 6.56 (dd, J = 11.0 Hz, J = 8.9 Hz, 1H), 6.48−6.43 (m, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 3.65 (s, 3H), 3.64 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 157.9, 157.1, 156.9, 141.8, 141.7, 140.7, 140.4, 137.2, 137.0, 136.3, 134.7, 133.7, 133.5, 133.2, 132.92, 132.85, 132.7, 132.5, 132.4, 132.3, 131.1, 128.1, 125.9, 123.6, 116.6, 113.9, 113.2, 112.4, 112.2, 55.30, 55.28, 55.1, 55.0; IR (film): 3034, 2957, 2834, 1609, 1515, 1244, 828 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{42}H_{34}O_4$ 602.2457; Found 602.2461.

*1,2,3,4-Tetrakis(4-bromophenyl)benzo[a]azulene (**7d**).* Yield: 119.1 mg (75%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 334−336 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 10.8 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.8 Hz, 1H), 7.14−7.05 (m, 10H), 6.80 (dd, J = 10.8 Hz, J = 8.3 Hz, 1H), 6.73−6.63 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.7, 141.1, 140.9, 139.14, 139.09, 138.97, 138.87, 138.6, 136.7, 136.3, 135.8, 134.9, 133.38, 133.35, 133.1, 132.7, 132.0, 131.9, 131.8, 131.3, 130.5, 130.3, 127.8, 126.1, 124.6, 121.5, 121.0, 120.4, 120.1, 115.7; IR (film): 2972, 1987, 1645, 1489, 1389, 1070, 736, 666 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{38}H_{22}{}^{79}Br_4$ 793.8455, $C_{38}H_{22}{}^{81}Br_4$ 801.8375; Found 793.8459, 801.8510.

*7-Methyl-1,2,3,4-tetra-p-tolylbenzo[a]azulene (**7e**).* Yield: 86.2 mg (78%); R_f = R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 256−258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 11.2 Hz, 1H), 7.18−7.00 (m, 10H), 6.77−6.65 (m, 8H), 6.60 (dd, J = 11.2 Hz, J = 1.3 Hz, 1H), 6.44 (d, J = 9.2 Hz, 1H), 2.34-2.32 (m, 9H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.6, 141.2, 140.3, 139.5, 139.4, 138.2, 137.94, 137.92, 137.92, 137.6, 137.1, 136.8, 136.0, 135.4, 135.1, 134.4, 134.1, 132.6, 132.3, 131.8, 131.6, 131.1, 130.1, 129.1, 128.4, 128.3, 127.4, 127.2, 126.7, 124.8, 116.4, 27.6, 21.5, 21.4, 21.3, 21.2; IR (film): 3048, 2920, 2359, 1983, 1646, 1515, 1021, 817, 740 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{43}H_{36}$ 552.2817; Found 552.2814.

*7-Phenyl-1,2,3,4-tetra-p-tolylbenzo[a]azulene (**7f**).* Yield: 105.7 mg (86%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 256−258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 11.4 Hz, 1H), 7.50 (d, J = 7.0 Hz, 2H), 7.39−7.32 (m, 3H), 7.20−7.14 (m, 6H), 7.10−7.05 (m, 3H), 6.98 (dd, J = 11.3 Hz, J = 1.4 Hz, 1H), 6.78−6.64 (m, 10H), 2.34 (s, 3H), 2.33 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.8, 144.8, 141.7, 140.8, 140.41, 140.36, 139.2, 138.13, 138.08, 137.8, 137.5, 137.4, 137.0, 136.1, 135.7, 135.5, 134.5, 134.2, 132.8, 131.9, 131.8, 131.6, 131.43, 131.42, 131.13, 130.1, 129.2, 128.7, 128.4, 128.3, 128.0, 127.9, 127.4, 127.3, 127.2, 125.3, 125.1, 116.9, 21.5, 21.4, 21.3, 21.2; IR (film): 3022, 2919, 1713, 1586, 1398, 1021, 815, 700 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{48}H_{38}$ 614.2974; Found 614.2977.

*10-Chloro-1,2,3,4-tetra-p-tolylbenzo[a]azulene (**7g**).* Yield: 91.6 mg (80%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 259−261 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 11.1 Hz, 1H), 7.11−7.05 (m, 7H), 6.98−6.93 (m, 3H), 6.77 (dd, J = 11.2 Hz, J = 8.3 Hz, 1H), 6.72−6.64 (m, 8H), 6.50 (dd, J = 11.1 Hz, J = 8.9 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 139.4, 137.7, 137.58, 137.57, 137.5, 137.1, 136.4, 136.1, 135.7, 135.3, 134.80, 134.79, 134.7, 134.4, 134.3, 132.60, 132.57, 131.8, 131.62, 131.57, 131.2, 130.0, 129.2, 127.4, 127.24, 127.19, 126.6, 124.6, 116.6, 21.50, 21.49, 21.24, 21.22; IR (film): 2924, 1640, 1541, 1387, 1020, 776, 669 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{42}H_{33}Cl$ 572.2271; Found 572.2274.

General Procedure for the Rh-Catalyzed [4 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with Alkynes. To a screw-top V-vial were added azulene-1-carboxylic acid (**1b**) (0.15 mmol, 1.0 equiv), alkyne (**2**) (0.18 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (4.0 mol %), Ag_2CO_3 (0.3 mmol, 2.0 equiv), and K_3PO_4 (0.15 mmol, 1.0 equiv) in DMF (0.75 mL). The resulting mixture was stirred at 120 °C (bath temperature) for 12 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 2:1).

*3,4-Diphenyl-1H-azuleno[1,2-c]pyran-1-one (**8a**).* Yield: 25.1 mg (36%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); red solid; melting point: 207−209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, J = 9.3 Hz, 1H), 8.33 (d, J = 10.1 Hz, 2H), 7.78 (t, J = 6.5 Hz, 1H), 7.68 (t, J = 9.7 Hz, 1H), 7.52−7.37 (m, 8H), 7.30−7.21 (m, 3H), 7.00 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 154.7, 151.4, 146.0, 142.0, 138.2, 137.3, 136.7, 135.7, 133.5, 130.7, 130.1, 129.9, 129.3, 129.1, 128.8, 128.1, 128.0, 116.1, 112.6, 107.6; IR (film): 2388, 1771, 1645, 1505, 1426, 1015, 889, 702 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{25}H_{16}O_2$ 348.1150; Found 348.1153.

*3,4-Bis(3-chlorophenyl)-1H-azuleno[1,2-c]pyran-1-one (**8b**).* Yield: 32.5 mg (39%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); brown solid; melting point: 229−231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (d, J = 9.3 Hz, 1H), 8.39 (d, J = 10.1 Hz, 1H), 7.85 (t, J = 9.8 Hz, 1H), 7.73 (t, J = 9.7 Hz, 1H), 7.58−7.53 (m, 2H), 7.43−7.36 (m, 3H), 7.30−7.27 (m, 1H), 7.25−7.23 (m, 2H), 7.16 (t, J = 7.9 Hz, 1H), 7.00 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 153.2, 150.1, 146.1, 141.9, 138.9, 137.8, 137.3, 137.1, 135.1, 134.7, 134.4, 130.5, 130.44, 130.37, 129.74, 129.68, 129.4, 129.2, 128.9, 128.5, 128.0, 115.5, 112.3, 107.4; IR (film): 1703, 1644, 1506, 1427, 1103, 958, 742, 635 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{25}H_{14}Cl_2O_2$ 416.0371; Found 416.0368.

General Procedure for the Ir-Catalyzed [2 + 2 + 2] Cyclization Reaction of Azulene-1-carboxylic Acid with Alkynes. To a screw-top V-vial were added azulene-1-carboxylic acid (**1b**) (0.15 mmol, 1.0 equiv), alkyne (**2**) (0.3 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (4.0 mol %), and AgOAc (0.45 mmol, 3.0 equiv) in xylene (1.5 mL). The resulting mixture was stirred at 160 °C (bath temperature) for 6 h under air. After celite filtration and evaporation of the solvent in vacuo, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 1:20).

*1,2,3,4-Tetra-m-tolylbenzo[a]azulene (**7h**).* Yield: 66.7 mg (62%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 109−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 10.9 Hz, 1H), 7.22−6.95 (m, 11H), 6.79−6.60 (m, 9H), 6.54 (t, J = 9.9 Hz, 1H), 2.27 (s, 3H), 2.25 (s, 3H), 2.02−2.01 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.53, 141.50, 140.8, 140.7, 140.6, 140.5, 140.3, 140.2, 137.8, 137.7, 137.3, 136.9, 136.3, 135.7, 135.4, 134.7, 133.0, 132.7, 132.0, 131.1, 130.9, 129.0, 128.7, 128.3, 128.2, 128.1, 127.7, 127.4, 127.3, 127.2, 126.9, 126.3, 126.1, 126.0, 125.9, 125.7, 123.5, 116.6, 21.6, 21.5, 21.3, 21.2; IR (film): 3036, 2919, 1698, 1585, 1389, 1087, 783, 706 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{42}H_{34}$ 538.2661; Found 538.2661.

*1,2,3,4-Tetrakis(4-chlorophenyl)benzo[a]azulene (**7i**).* Yield: 102.6 mg (83%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 302−304 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 10.9 Hz, 1H), 7.3−7.27 (m, 3H), 7.23−7.07 (m, 8H), 6.92 (dd, J = 11.7 Hz, J = 8.4 Hz, 4H), 6.82−6.73 (m, 5H), 6.64 (dd, J = 10.9 Hz, J = 9.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.8, 141.1, 141.0, 139.1, 138.8, 138.7, 138.6, 138.1, 136.7, 136.4, 135.7, 135.1, 133.34, 133.31, 133.0, 132.74, 132.73, 132.4, 132.1, 132.0, 131.8, 131.5, 129.1, 128.3, 127.9, 127.5, 127.3, 126.1, 124.5, 115.8; IR (film): 2925, 2853, 1731, 1637, 1492, 1089, 1014, 755 cm^{-1}; HRMS (EI) m/z: [M]$^+$ Calcd for $C_{38}H_{22}Cl_4$ 618.0476; Found 618.0479.

*1,2,3,4-Tetrakis(4-(trifluoromethyl)phenyl)benzo[a]azulene (**7j**).* Yield: 138.8 mg (92%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); blue solid; melting point: 299−301 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 10.9 Hz, 1H), 7.61 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 4H), 7.23−7.11 (m, 7H), 7.00 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 10.8 Hz, J = 8.5 Hz, 1H), 6.63 (dd, J = 10.9 Hz, J = 9.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.8, 143.6, 143.5, 143.1, 141.8, 141.6, 140.7, 136.9, 136.3, 135.2 (q, J = 227.6 Hz), 133.8, 132.1, 131.7, 131.4, 130.6, 129.9 (q, J = 33.7 Hz), 128.6 (q, J = 29.1 Hz), 128.4, 128.3 (q, J = 32.6 Hz), 128.1, 125.8 (q, J = 3.7 Hz), 125.7, 125.5, 125.4, 125.3 (q, J = 170.6 Hz), 125.1 (q, J = 4.2 Hz), 124.3 (q, J = 3.6 Hz), 124.0 (q, J = 3.6 Hz), 123.0, 122.8, 120.3, 120.1, 120.0, 115.5; ^{19}F NMR (376

https://dx.doi.org/10.1021/acs.joc.9b03448
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MHz, $CDCl_3$) δ −62.46, −62.54, −62.69, −62.74; IR (film): 2937, 1771, 1645, 1326, 1124, 1066, 848, 741 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{42}H_{22}F_{12}$ 754.1530; Found 754.1533.

*2,2′,2″,2‴-(Benzo[a]azulene-1,2,3,4-tetrayl)tetrathiophene (**7k**).* Yield: 61.7 mg (61%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 164−166 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 10.9 Hz, 1H), 7.40−7.34 (m, 4H), 7.15−7.03 (m, 6H), 6.99 (d, J = 3.4 Hz, 1H), 6.82 (dd, J = 10.8 Hz, J = 8.5 Hz, 1H), 6.74-6.64 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.8, 141.4, 141.3, 141.0, 140.6, 140.5, 136.8, 135.9, 135.2, 133.8, 131.6, 131.3, 129.7, 129.5, 129.1, 128.6, 128.1, 127.7, 127.0, 126.6, 126.4, 126.34, 126.26, 126.25, 125.79, 125.77, 125.5, 124.6, 116.0; IR (film): 2958, 1764, 1638, 1415, 1205, 815, 695 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{30}H_{18}S_4$ 506.0291; Found 506.0294.

*3,4-Diphenyl-1H-azuleno[6,5-c]pyran-1-one (**9**).* Yield: 6.3 mg (9%); R_f = 0.3 (CH_2Cl_2/hexane = 2:1); green solid; melting point: 245−247 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (q, J = 12.3 Hz, 2H), 8.30 (s, 1H), 7.97 (t, J = 3.7 Hz, 1H), 7.48−7.45 (m, 4H), 7.33−7.28 (m, 4H), 7.23−7.17 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.1, 150.5, 143.5, 141.4, 138.4, 135.6, 135.3, 134.1, 133.8, 133.2, 131.9, 129.5, 129.3, 129.0, 128.6, 128.0, 125.1, 122.3, 121.4, 120.7, 120.0; IR (film): 3059, 3024, 1713, 1414, 1211, 760, 707 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{16}O_2$ 348.1150; Found 348.1149.

*2-Chloroethyl azulene-6-carboxylate (**10**).* Yield: 26.2 mg (56%); R_f = 0.5 (CH_2Cl_2/hexane = 1:1); blue solid; melting point: 204−206 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 10.7 Hz, 2H), 8.08−8.05 (m, 3H), 7.48 (d, J = 3.7 Hz, 2H), 4.64 (t, J = 5.6 Hz, 2H), 3.88 (t, J = 5.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 168.1, 141.6, 140.7, 135.6, 134.9, 123.2, 119.2, 65.6, 41.8; IR (film): 3023, 2898, 1584, 1474, 1222, 1011, 721 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{13}H_{11}ClO_2$ 234.0448; Found 234.0448.

*5,6,7,8-Tetraphenylbenzo[f]azulene (**11**).* Yield: 2.9 mg (3%); R_f = 0.2 (CH_2Cl_2/hexane = 1:20); green solid; melting point: 235−237 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.66 (d, J = 11.8 Hz, 1H), 7.45 (t, J = 3.5 Hz, 1H), 7.23−7.13 (m, 12H), 6.92 (d, J = 4.3 Hz, 1H), 6.84−6.78 (m, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.0, 143.4, 142.4, 141.3, 141.2, 140.8, 140.7, 140.5, 140.2, 139.4, 137.2, 134.5, 133.6, 131.5, 131.4, 131.2, 130.9, 130.0, 129.4, 127.9, 127.8, 126.86, 126.85, 126.72, 126.69, 126.6, 125.6, 125.5, 124.0, 122.2; IR (film): 3054, 3022, 1612, 1440, 1374, 1025, 698 cm^{-1}; HRMS (EI) m/z: $[M]^+$ Calcd for $C_{38}H_{26}$ 482.2035; Found 482.2034.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.9b03448.

Crystallographic data of **3a** (CIF)

Crystallographic data of **6** (CIF)

Crystallographic data of **7a** (CIF)

General procedure for the starting materials; additional data for optimization of reaction conditions; X-ray crystallography; optimization of Rh-catalyzed [4 + 2] cyclization reaction of azulene-2-carboxylic acid with diphenylacetylene; optimization of the Ir-catalyzed [2 + 2 + 2] cyclization reaction of azulene-2-carboxylic acid with diphenylacetylene (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This paper is dedicated to Prof. Chang Ho Oh (Hanyang University) on the occasion of his 60th birthday. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (2011-0018355).

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