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Synthesis of Benzofulvenes through Rhodium-Catalyzed Transannulation of Enynyl Triazoles

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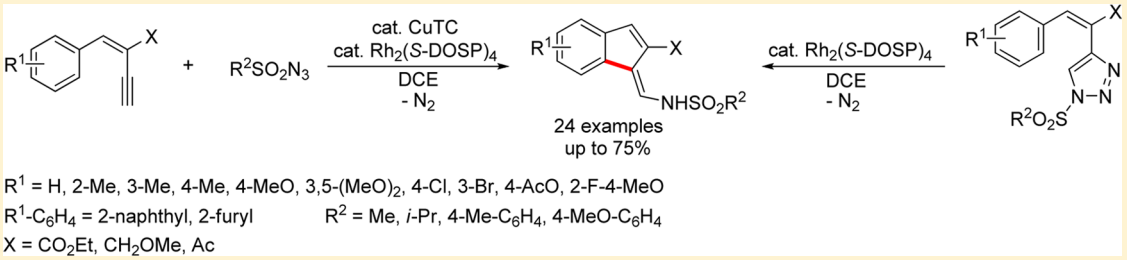
Supporting Information



ABSTRACT: Rhodium-catalyzed denitrogenative cyclization of (*E*)-ethyl 2-(1-alkyl and arylsulfonyl-1*H*-1,2,3-triazol-4-yl)-3-aryl acrylate generated from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides in the presence of a copper catalyst was developed for the synthesis of a large number of functionalized benzofulvenes. Moreover, the synthesis of benzofulvenes was demonstrated as a one-pot method through tandem copper-catalyzed [3 + 2] cycloaddition and rhodium-catalyzed denitrogenative cyclization from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides.

INTRODUCTION

Benzofulvenes are key privileged scaffolds present in natural products,[1] biologically and pharmacologically active molecules,[2] functional materials,[3] and metallocene catalysts.[4] Their importance has encouraged the development of new synthetic approaches for benzofulvenes. As a result, a large number of synthetic methods have been demonstrated for the synthesis of benzofulvenes, including the radical or Pd-catalyzed cyclization of enediynes (Scheme 1, **a**),[5] metal-catalyzed or photochemical cyclization of enynes (**b**),[6] Pd-catalyzed cyclization of homoallylic acetates or 1,3-dienes derived from Morita-Baylis-Hillman adducts (**c**),[7] thermal or photochemical cyclization of enyne-allenes (**d**),[8] domino Heck C−H activation reaction of unsymmetrically substituted [3]cumulenes (**e**),[9] $(CuOTf)_2 \cdot C_6H_6$-catalyzed reactions of vinylidene cyclopropane with *N*-Ts-iminophenyliodinanes (**f**),[10] Au-catalyzed isomerization of cyclopropenes (**g**),[11] Ag and Brønsted acid catalyzed Nazarov-type cyclization (**h**),[12] and Pd-catalyzed tandem reactions of 1-(2,2-dibromovinyl)-2-alkynylbenzenes with arylboronic acids (**i**).[13] Due to its significance, it is still of considerable interest and necessity to develop efficient synthetic methods for functionalized benzofulvenes, especially in the field of organometallic chemistry and materials science.[14]

Recently, *N*-sulfonyl-1,2,3-triazoles, easily obtained from click reactions of terminal alkynes with *N*-sulfonyl azides,[15] have been used for the preparation of a large number of heterocyclic and carbocyclic compounds through Rh-catalyzed denitrogenative cyclization.[16] In this regard, we reported novel synthetic methods of a variety of *N*-heterocyclic and carbocyclic compounds with *N*-sulfonyl-1,2,3-triazoles and 1,2,3-thiadiazoles.[17] On the basis of these results, we conceived that the Rh-catalyzed denitrogenative cyclization of aryl triazoles would produce benzofulvene. To date, there have been reported Rh-catalyzed denitrogenative cyclization methods using a number of aryl triazoles including 4-(3-arylpropyl)-1-tosyl-1,2,3-triazole,[18] 4-(aryloxymethyl)-1-tosyl-1,2,3-triazole,[19] 4-(*N*-aryl-*N*-sulfonylaminomethyl)-1-tosyl-1,2,3-triazole,[19] 4-(*N*-aryl-*N*-alkylaminomethyl)-1-tosyl-1,2,3-triazole,[20] *N*-sulfonyl-4-biaryl-1-tosyl-1,2,3-triazole,[17c] and *N*-phenyl-2-(1-sulfonyl-1*H*-1,2,3-triazole-4-yl)aniline[21] for the synthesis of *N*-heterocyclic and carbocyclic compounds (Figure 1).

As a consequence, the design of new substrates having an aryl triazole moiety for intramolecular denitrogenative cyclization has become an active field of research. To the best of our knowledge, a synthetic approach for benzofulvene skeletons with appropriate aryl triazoles has never been reported. Inspired by our recent interest in 1,2,3-triazole compounds,[17] we decided to examine the efficacy of Rh-catalyzed denitrogenative cyclization, with a variety of aryl triazoles having a two-carbon atom linker between aryl and triazole groups, for the synthesis of benzofulvene. However, the Rh-catalyzed denitrogenative cyclization of 4-phenethyl-1-tosyl-1*H*-1,2,3-triazole (**A**) did not proceed due to the unfavorable conformation. Although double bonds between aryl and triazole groups were introduced as a linker for suppressing free rotation of the C−C bond, the Rh-catalyzed denitrogenative cyclization using (*Z*)-4-styryl-1-tosyl-1*H*-1,2,3-triazole (**B**), triazole (**C**) generated from 1,2-diphenyl

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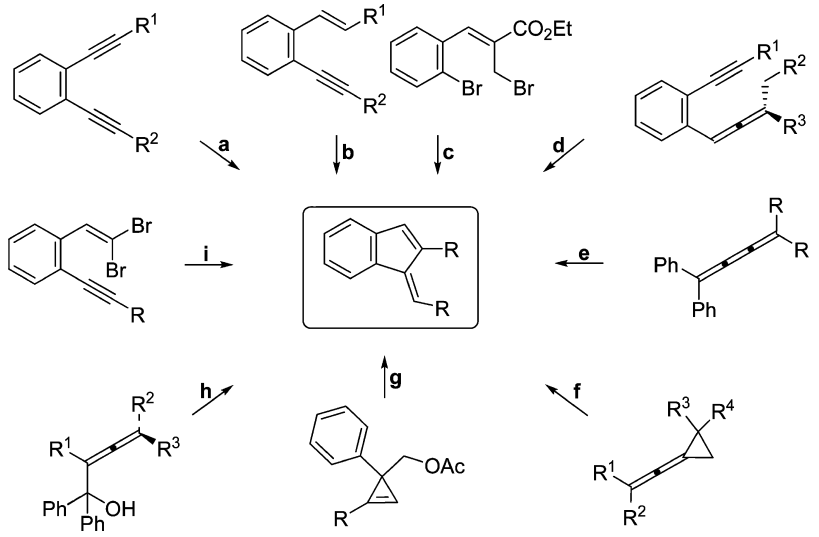
Scheme 1. Approaches for the Synthesis of the Benzofulvene Skeleton



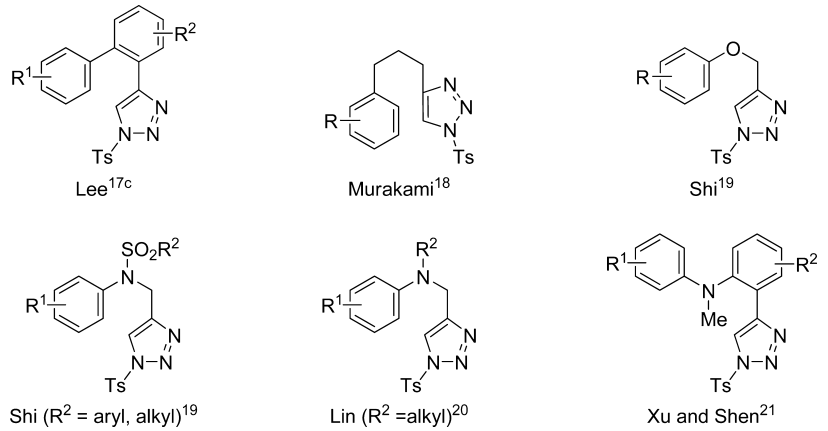


Figure 1. Previously reported aryl triazoles for intramolecular denitrogenative cyclization.

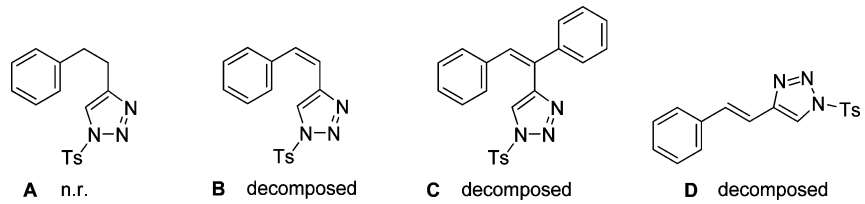
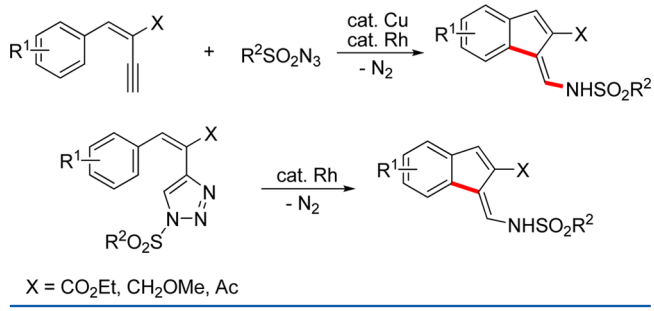


Figure 2. Failed aryl triazoles for denitrogenative cyclization.

(*E*)-1,3-enyne, and (*E*)-4-styryl-1-tosyl-1*H*-1,2,3-triazole (**D**) did not occur due to isomerization and substrate instability (Figure 2).

Thus, we envisioned that if the stereochemistry of the double bond in aryl triazoles having two-carbon linkers between aryl and triazole groups was fixed to the *cis*, and the substrate stability was increased, the denitrogenative cyclization would occur, leading to the formation of benzofulvenes. Herein, we report a synthetic method for the synthesis of benzofulvenes via Rh-catalyzed cyclization of (*E*)-ethyl 2-(1-alkyl and arylsulfonyl-1*H*-1,2,3-triazol-4-yl)-3-aryl acrylate (Scheme 2). In addition, tandem Cu-catalyzed [3 + 2] cycloaddition and Rh-catalyzed cyclization from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides were developed for the synthesis of a wide range of functionalized benzofulvenes. Methoxymethyl- and acetyl-substituted enynyl triazoles were also converted to the corresponding benzofulvenes.

Scheme 2. Synthesis of Benzofulvenes from Arylethenyl Triazoles



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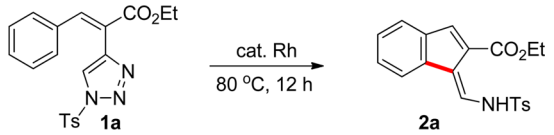
A large number of (*E*)-ethyl 2-(1-alkyl and arylsulfonyl-1*H*-1,2,3-triazol-4-yl)-3-aryl acrylates were prepared from the reaction of the corresponding (*E*)-ethyl 2-arylmethylidenebut-3-ynoate[22] with sulfonyl azide in the presence of copper(I) thiophene-2-carboxylate in toluene at room temperature.

RESULTS AND DISCUSSION

We started our investigation with (*E*)-ethyl 3-phenyl-2-(1-tosyl-1*H*-1,2,3-triazol-4-yl)acrylate (**1a**) (Table 1). To our delight,

Table 1. Reaction Optimization[a]



entry	cat.	solvent	yield (%)[b]
1	$Rh_2(OAc)_4$	DCE	41
2	$Rh_2(Oct)_4$	DCE	21
3	$Rh_2(esp)_2$	DCE	41
4	$Rh_2(OPiv)_4$	DCE	24
5	Rh_2(*S*-PTAD)$_4$	DCE	49
6	Rh_2(*S*-DOSP)$_4$	DCE	50
7	Rh_2(*S*-DOSP)$_4$	xylene	20
8	Rh_2(*S*-DOSP)$_4$	$CHCl_3$	43
9	Rh_2(*S*-DOSP)$_4$	hexane	0
10	Rh_2(*S*-DOSP)$_4$	THF	10
11	Rh_2(*S*-DOSP)$_4$	benzene	26
12	Rh_2(*S*-DOSP)$_4$	DCE	62 (56)[c]

[a]Reactions were performed with **1a** (0.2 mmol, 1.0 equiv) in the presence of a Rh catalyst (2.0 mol %) in solvent (1.0 mL, 0.2 M) at 80 °C for 12 h. [b]NMR yield using CH_2Br_2 as an internal standard. [c]Isolated yield. Rh catalyst (1.0 mol %) was used.

when **1a** was treated with $Rh_2(OAc)_4$ (2.0 mol %) in dichloroethane (DCE) at 80 °C for 12 h, the denitrogenative cyclization proceeded, producing the desired benzofulvene **2a** in 41% yield (entry 1). Thus, a large number of Rh(II) catalysts such as $Rh_2(Oct)_4$, $Rh_2(esp)_2$, $Rh_2(OPiv)_4$, Rh_2(*S*-PTAD)$_4$, and Rh_2(*S*-DOSP)$_4$ were examined, with the result being that Rh_2(*S*-DOSP)$_4$ (2.0 mol %) was the catalyst of choice (entries 2−6). DCE gave the best result among the solvents studied, including DCE, xylene, chloroform, hexane, tetrahydrofuran, and benzene (entries 6−11). We were pleased to observe that high yields were obtained even with a low loading of the Rh catalyst (1.0 mol %). The best result was obtained by using Rh_2(*S*-DOSP)$_4$ (1.0 mol %) in DCE at 80 °C after 12 h, which produced **2a** in 56% yield (entry 12). The formation of (*Z*)-enamine products could be explained from hydrogen bonding between the NH and the CO_2Et group.

Next, the effects of sulfonyl groups at N1 on the Rh-catalyzed denitrogenative cyclization were examined (Scheme 3). Methanesulfonyl triazoles **1b** provided the desired benzofulvene **2b** in 60% yield. However, isopropanesulfonyl triazoles **1c** lowered the product yield to 44% due to steric congestion. *N*-[(4-Methoxybenzene)sulfonyl]triazole **1d** was smoothly converted to benzofulvene **2d** in 63% yield under the optimized conditions. *N*-Benzenesulfonyl triazoles with electron-withdrawing groups such as chloride and trifluoromethyl were totally ineffective. Because triazole **1d**, generated from enynyl ester and 4-methoxyphenylsulfonyl azide, gave the best results, a wide range of arylethenyl triazoles **1** bearing a *N*-[(4-methoxybenzene)sulfonyl group at N1 were subjected to Rh_2(*S*-DOSP)$_4$ catalysis (1.0 mol %) under the optimized conditions.

Having established the optimized conditions, we next investigated the scope and limitation of the Rh-catalyzed denitrogenative cyclization by testing a wide range of functional groups on the aryl group of the arylethenyl triazoles **1** (Scheme 3). Electronic variation of substituents at the aryl group of **1** slightly influenced the reaction efficiency. Arylethenyl triazoles bearing electron-donating substituents such as methyl, methoxy, and methylenedioxy smoothly participated in the denitrogenative cyclization. For example, *ortho*- and *para*-methyl-substituted arylethenyl triazoles were converted to the desired benzofulvenes **2e** (50%) and **2f** (67%). Unexpectedly, *meta*-methyl-substituted arylethenyl triazole underwent the Rh-catalyzed denitrogenative cyclization at the sterically hindered site to provide predominantly benzofulvene **2g**. These results indicate that the cyclization was largely influenced by the electronic effect rather than a steric one. Unfortunately, the silica gel column chromatography failed to separate the two isomers. Exposure of *para*-methoxy-substituted arylethenyl triazole to a Rh catalyst afforded benzofulvene **2i** in 65% yield. The arylethenyl triazoles having 3,5-dimethoxy groups are good substrates for the present transformation, affording **2j** in 54% yield. NOE experiments suggest that the major isomer of **2j** is the *Z*-form (see the Supporting Information). Likewise, in the case of methylenedioxy-substituted arylethenyl triazoles, intramolecular cyclization at the sterically hindered position is the major pathway, delivering mainly the benzofulvene **2k**. In general, the denitrogenative cyclization took place with substrates possessing electron-withdrawing substituents at the aryl moiety of the arylethenyl triazoles. Substrates having electron-withdrawing chloride and bromide groups underwent the Rh-catalyzed cyclization, resulting in the formation of benzofulvenes in acceptable yields. Acetoxy-substituted triazoles turned out to be compatible with the optimized conditions. Arylethenyl triazoles bearing fluoride as well as methoxy substituents were subjected to the Rh-catalyzed denitrogenative cyclization reaction, producing **2q** in 75% yield. The 2-naphthyl-substituted triazole was selectively cyclized to produce sterically congested **2r**. Gratifyingly, the Rh-catalyzed denitrogenative cyclization using 2-furyl-substituted arylethenyl triazole took place to provide **2s** in 50% yield. Methoxymethyl and acetyl-substituted arylethenyl triazoles were also converted to the corresponding benzofulvenes **2t** (52%) and **2u** (46%). These results indicate that oxygen in ethoxycarbonyl, methoxymethyl, and acetyl groups could stabilize the Rh-carbene intermediate via chelation effect.

Because (*E*)-ethyl 2-(1-alkyl and arylsulfonyl)-1*H*-1,2,3-triazol-4-yl-3-aryl acrylate was prepared from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides in the presence of a copper catalyst, we next tried to develop a synthetic method for benzofulvenes from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides in one pot (Scheme 4). After (*E*)-ethyl 2-benzylidenebut-3-ynoates were treated with *N*-4-methoxyphenylsulfonyl azides in the presence of Cu(I) thiophene-2-carboxylate (10 mol %) in DCE at 25 °C for 2 h, Rh_2(*S*-DOSP)$_4$ (1.0 mol %) was added to the reaction mixture at 80 °C and reacted for 12 h, leading to the formation of benzofulvenes **2d** in 49% yield. Enynyl esters bearing 4-methylphenyl and 2-fluoro-4-methoxyphenyl substituents were smoothly converted to the corresponding benzofulvenes **2f** and **2q** in 54% and 62% yields, respectively.

Next, we investigated the synthetic utility of functionalized benzofulvenes. The reduction of benzofulvene **2d** using DIBAL-H in dichloromethane afforded the corresponding alcohol **2v**

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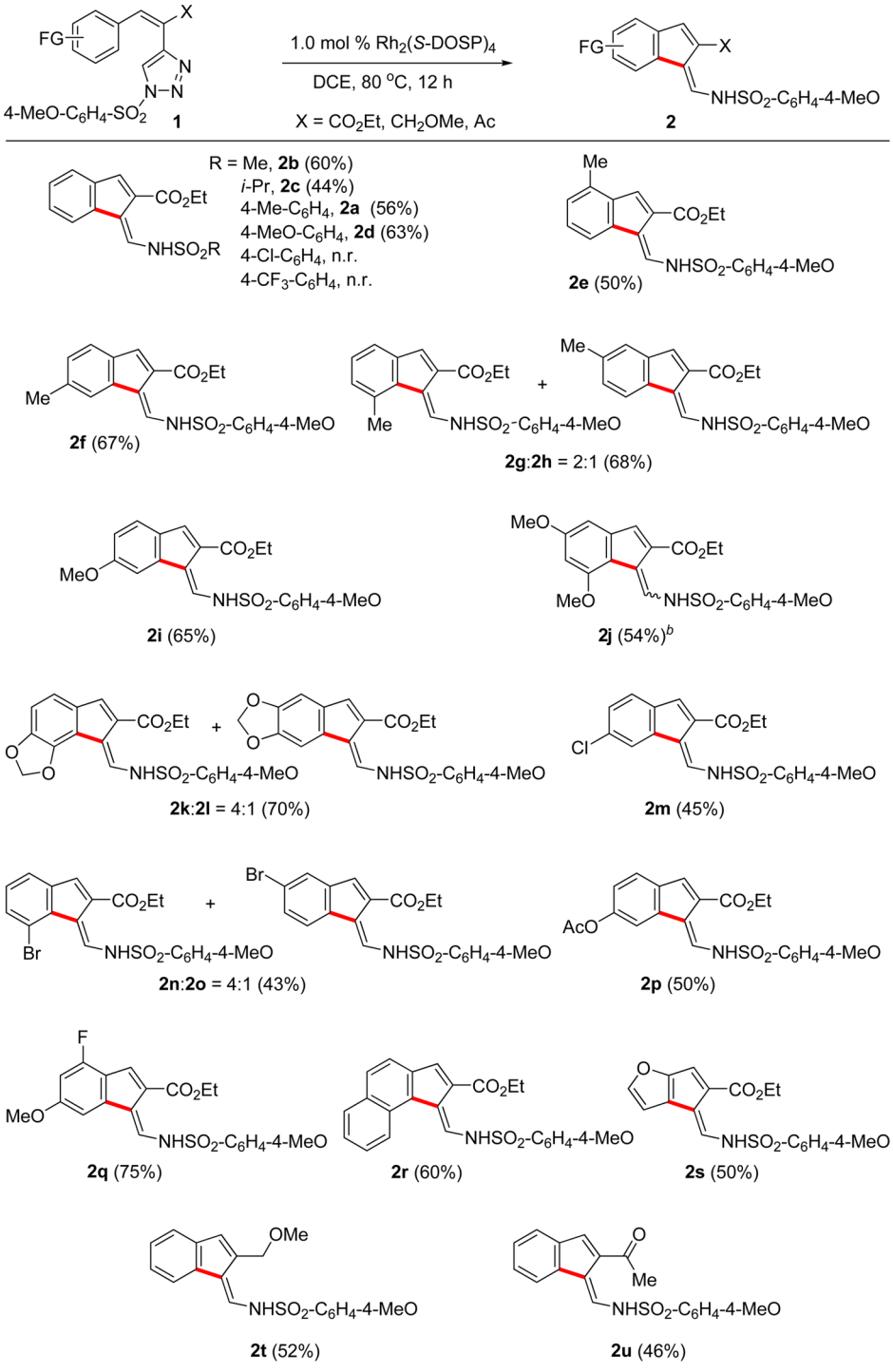
Scheme 3. Scope of Arylethenyl Triazoles[a]



[a]Reactions were performed with **1** (0.2 mmol, 1.0 equiv) in the presence of 1.0 mol % Rh_2(*S*-DOSP)$_4$ in DCE (0.7 mL, 0.3 M) at 80 °C for 12 h. [b]Ratio of *Z*/*E* = 2.5:1.

in 85% yield (eq 1). When **2d** was treated with *m*-CPBA in dichloromethane, the electron-rich alkene was selectively oxidized, leading to the formation of **2w** in 52% yield (eq 2).

A plausible mechanism for the formation of benzofulvenes through tandem Cu-catalyzed [3 + 2] cycloaddition and Rh-catalyzed denitrogenative cyclization from ethyl (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-tosyl azides is proposed in Scheme 5. After a reversible ring−chain tautomerization of *N*-sulfonyl-1,2,3-triazole **1** generated from enynyl esters and *N*-sulfonyl azides in the presence of a Cu catalyst furnishes *α*-diazo imine **I**,[15,16,23] the subsequent treatment of **I** with a rhodium(II) catalyst gives imino rhodium(II) carbenoid **II** along with release of nitrogen gas. It is possible that oxygen in ethoxycarbonyl, methoxymethyl, and acetyl groups could stabilize the Rh-carbene intermediate via chelation effect. Intramolecular nucleophilic addition of aryl group to the electrophilic carbene center provides the Rh-bound zwitterionic intermediate **III**. Aromatization via deprotonation followed by

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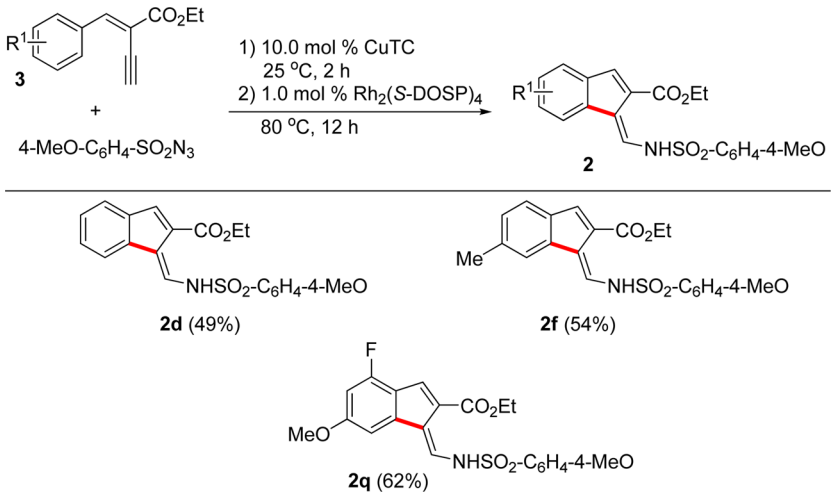
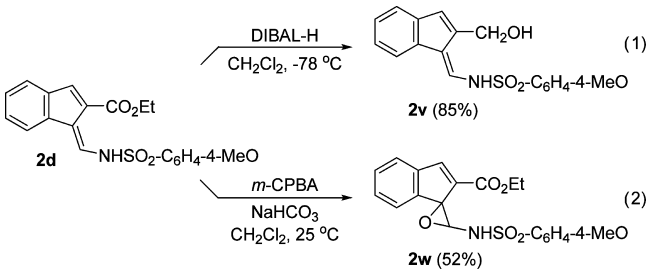
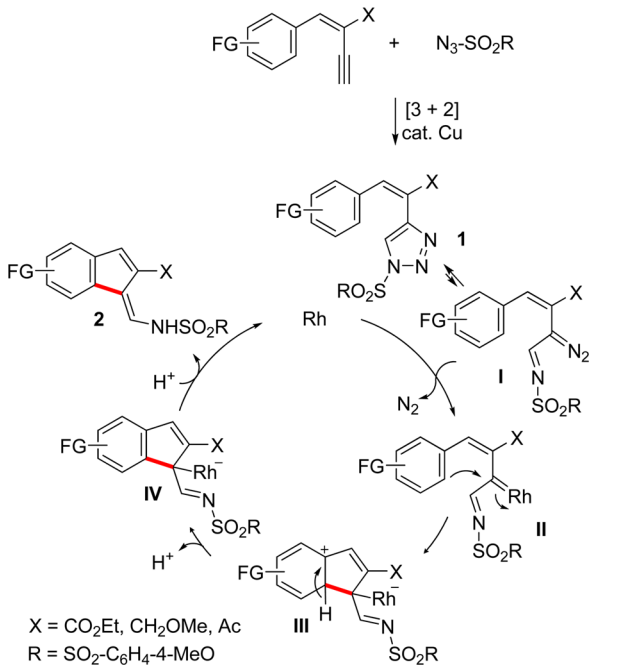
Scheme 4. Synthesis of Benzofulvenes from Ethyl (*E*)-2-Ethynyl Cinnamates and *N*-Sulfonyl Azides in a One-Pot[a]



[a]Reactions were performed with **3** (0.2 mmol, 1.0 equiv) and sulfonyl azide (1.1 equiv) in the presence of 10.0 mol % CuTC in toluene (1 mL) and then 1.0 mol % Rh_2(*S*-DOSP)$_4$ in DCE (0.7 mL).



Scheme 5. A Plausible Mechanism



proto-derhodation affords benzofulvenes **2** with regeneration of the Rh-catalyst.

CONCLUSION

In conclusion, Rh-catalyzed denitrogenative cyclization of (*E*)-ethyl 2-(1-alkyl and arylsulfonyl-1*H*-1,2,3-triazol-4-yl)-3-aryl acrylate generated from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides in the presence of a copper catalyst was demonstrated for the synthesis of a wide range of functionalized benzofulvenes. Additionally, we have developed straightforward synthetic procedures for three benzofulvenes through tandem Cu-catalyzed [3 + 2] cycloaddition and Rh-catalyzed denitrogenative cyclization from (*E*)-ethyl 2-benzylidenebut-3-ynoates and *N*-sulfonyl azides in a one-pot.

EXPERIMENTAL SECTION

General. Reactions were carried out in oven-dried glassware under N_2 conditions. $Rh_2(OAc)_4$, $Rh_2(esp)_2$, $Rh_2(OPiv)_4$, $Rh_2(Oct)_4$, Rh_2(*S*-PTAD)$_4$, and Rh_2(*S*-DOSP)$_4$ were purchased. Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were 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) and ^{13}C{^{1}H} NMR (100 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 77.16 for ^{13}C{^{1}H} (chloroform-*d*)]. Infrared spectra were recorded on an 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 fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and an electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer). Melting points were determined in an open capillary tube.

Synthetic Procedure of (E)-Ethyl 2-(1-(Sulfonyl)-1H-1,2,3-triazol-4-yl)-3-phenyl Acrylates.[15] To a solution of Cu(I) thiophene-2-carboxylate (9.5 mg, 0.05 mmol, 10 mol %) and 1,3-enyne (0.5 mmol), in toluene (2.5 mL), was added sulfonyl azide (0.65 mmol, 1.3 equiv) under a nitrogen atmosphere. The mixture was stirred at rt for 2 h, at which time 1,3-enyne was completely comsumed by TLC. The mixture was diluted with saturated aq NH_4Cl (10 mL) and extracted with ether (10 mL × 3). The collected organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, and the residue was purified via silica gel flash column chromatography using EtOAc/hexane to give the product **1**.

*(E)-Ethyl 3-Phenyl-2-(1-tosyl-1H-1,2,3-triazol-4-yl)acrylate (**1a**).* 163.0 mg, 82%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow solid, melting

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point 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.03 (s, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.30−7.27 (m, 1H), 7.18 (t, J = 7.7 Hz, 2H), 7.10 (d, J = 7.2 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 2.47 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 147.3, 145.0, 141.3, 133.8, 133.2, 130.5, 130.1, 129.9, 128.6, 128.4, 123.7, 120.5, 61.7, 21.9, 14.2; IR (film) 3146, 3059, 1712, 1594, 1394, 1254 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{20}H_{20}N_3O_4S$ 398.1176, found 398.1175.

*(E)-Ethyl 2-(1-(Methylsulfonyl)-1H-1,2,3-triazol-4-yl)-3-phenyl Acrylate (**1b**).* 128.5 mg, 80%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow solid, melting point 79−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.10 (s, 1H), 7.32−7.28 (m, 3H), 7.21−7.19 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.54 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 145.3, 141.4, 133.8, 130.1, 130.1, 128.5, 123.6, 120.2, 61.8, 42.7; IR (film) 3146, 2959, 1723, 1621, 1408, 1222 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd for $C_{14}H_{16}N_3O_4S$ 322.0863, found 322.0862.

*(E)-Ethyl 2-(1-(Isopropylsulfonyl)-1H-1,2,3-triazol-4-yl)-3-phenyl Acrylate (**1c**).* 134.5 mg, 77%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow oli. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.03 (s, 1H), 7.33−7.23 (m, 3H), 7.19−7.17 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.84 (nonet, J = 6.9 Hz, 1H), 1.41 (s, 3H), 1.40 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 145.4, 141.2, 133.8, 130.1, 130.0, 128.5, 125.2, 61.7, 57.5, 15.9, 14.2; IR (film) 3145, 2984, 1713, 1635, 1383, 1255 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{19}N_3O_4S$ 349.1096, found 349.1093.

*(E)-Ethyl 2-(1-((4-Methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-3-phenyl Acrylate (**1d**).* 173.6 mg, 84%, R_f = 0.3 (EtOAc/hexane = 1:3); ivory solid, melting point 98−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.05−8.01 (m, 3H), 7.29−7.27 (m, 1H), 7.21−7.17 (m, 2H), 7.18−7.10 (m, 2H), 7.03 (dt, J = 10.0, 2.6 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 165.4, 145.0, 141.2, 133.9, 131.2, 130.1, 129.9, 128.4, 127.1, 123.6, 120.6, 115.1, 61.7, 56.0, 14.2; IR (film) 3149, 2982, 1714, 1633, 1255 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{20}H_{20}N_3O_5S$ 414.1125, found 414.1124.

*(E)-Ethyl 2-(1-((4-Methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-3-(o-tolyl)acrylate (**1e**).* 188.0 mg, 88%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.98 (s, 1H), 7.95 (dt, J = 10.1, 2.6 Hz, 2H), 7.17 (s, 1H), 7.16 (d, J = 0.8 Hz, 1H), 7.00 (dt, J = 10.1, 2.6 Hz, 2H), 6.89 (m, 1H), 6.80 (d, J = 7.7 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 2.31 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 165.3, 143.8, 141.2, 137.1, 133.8, 131.1, 130.3, 129.1, 128.7, 127.1, 125.5, 123.5, 122.2, 115.0, 61.7, 56.0, 20.0, 14.2; IR (film) 3147, 2981, 1714, 1632, 1392, 1254, 1092 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{21}H_{22}N_3O_5S$ 428.1282, found 428.1283.

*(E)-Ethyl 2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-3-(p-tolyl)acrylate (**1f**).* 179.5 mg, 84%, R_f = 0.3 (EtOAc/hexane = 1:3); ivory solid, melting point 121−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.03 (dt, J = 10.0, 2.6 Hz, 2H), 8.00 (s, 1H), 7.04 (dt, J = 10.0, 2.6 Hz, 2H), 7.00−6.99 (m, 4H), 4.26 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 165.3, 145.1, 141.4, 140.4, 131.2, 131.0, 130.3, 129.2, 127.2, 123.5, 119.4, 115.1, 61.5, 56.0, 21.5, 14.2; IR (film) 3144, 2981, 1708, 1593, 1442, 1267 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{21}H_{22}N_3O_5S$ 428.1282, found 428.1281.

*(E)-Ethyl 2-(1-((4-Methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-3-(m-tolyl)acrylate (**1g**).* 192.4 mg, 90%, R_f = 0.3 (EtOAc/hexane = 1:3); white solid, melting point 115−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 (dt, J = 10.0, 2.5 Hz, 2H), 8.01 (s, 1H), 7.07 (t, J = 7.7 Hz, 2H), 7.04 (t, J = 1.9 Hz, 1H), 7.02 (t, J = 2.5 Hz, 1H), 6.91 (s, 1H), 6.87 (d, J = 6.9 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.17 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 145.3, 141.3, 138.0, 133.8, 131.2, 130.9, 130.7, 128.3, 127.2, 123.4, 120.3, 115.1, 61.6, 56.0, 21.2, 14.2; IR (film) 2980, 1712, 1633, 1394, 1264, 1065 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{21}H_{22}N_3O_5S$ 428.1282, found 428.1282.

*(E)-Ethyl 3-(4-Methoxyphenyl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-acrylate (**1i**).* 179.6 mg, 81%, R_f = 0.25 (EtOAc/hexane = 1:3); white soild, melting point 120−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.05 (dt, J = 10.0, 2.6 Hz, 2H), 7.98 (s, 1H), 7.06 (m, 4H), 6.70 (dt, J = 9.8, 2.5 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.79 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.4, 165.3, 161.2, 144.8, 141.6, 132.3, 131.2, 127.2, 126.3, 123.5, 117.7, 115.1, 113.1, 61.5, 56.0, 55.3, 14.2; IR (film) 3073, 2979, 1707, 1635, 1340, 1258 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{21}H_{22}N_3O_6S$ 444.1231, found 444.1227.

*(E)-Ethyl 3-(3,5-Dimethoxyphenyl)-2-(1-((4-methoxyphenyl)-sulfonyl)-1H-1,2,3-triazol-4-yl)-acrylate (**1j**).* 201.2 mg, 85%, R_f = 0.2 (EtOAc/hexane = 1:3); pale yellow solid, melting point 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.03 (d, J = 9.0 Hz, 2H), 7.97 (s, 1H), 7.03 (d, J = 9.0 Hz, 2H), 6.37 (t, J = 2.0 Hz, 1H), 6.23 (d, J = 2.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 3.53 (s, 6H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 165.4, 160.4, 145.2, 141.1, 135.5, 131.2, 127.0, 123.4, 121.1, 115.1, 107.7, 102.8, 61.7, 56.0, 55.29, 55.15, 14.21; IR (film) 3142, 2938, 1712, 1632, 1392, 1240, 1092 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{22}H_{24}N_3O_7S$ 474.1337, found 474.1335.

*(E)-Ethyl 3-(Benzo[d][1,3]dioxol-5-yl)-2-(1-((4-methoxyphenyl)-sulfonyl)-1H-1,2,3-triazol-4-yl)-acrylate (**1k**).* 201.3 mg, 88%, R_f = 0.2 (EtOAc/hexane = 1:3); ivory solid, melting point 120−123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.04 (d, J = 8.9 Hz, 2H), 7.93 (s, 1H), 7.04 (d, J = 9.0 Hz, 2H), 6.77 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.1 Hz, 2H), 6.50 (s, 1H), 5.94 (s, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 165.4, 149.3, 147.7, 144.7, 141.3, 131.1, 127.9, 127.1, 126.7, 123.6, 118.2, 115.1, 109.4, 108.3, 101.5, 61.5, 56.0, 14.2; IR (film) 3144, 2982, 1706, 1593, 1467, 1235 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{19}N_3O_7S$: 457.0944, found 457.0947.

*(E)-Ethyl 3-(4-Chlorophenyl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)acrylate (**1m**).* 176.9 mg, 79%, R_f = 0.3 (EtOAc/hexane = 1:3); white solid, melting point 127−128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.03 (dt, 10.0, 2.5 Hz, 2H), 7.97 (s, 1H), 7.15 (dt, J = 9.0, 2.2 Hz, 2H), 7.05 (m, 4H), 4.28 (q, 7.1 Hz, 2H), 3.91 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{ ^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 143.4, 140.9, 135.8, 132.4, 131.3, 131.2, 128.7, 127.0, 123.7, 121.1, 115.1, 61.8, 56.0, 14.2; IR (film) 3146, 2981, 1711, 1636, 1393, 1253, 1092, 883, 678 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{20}H_{19}ClN_3O_5S$ 448.0736, found 448.0732.

*(E)-Ethyl 3-(3-Bromophenyl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)acrylate (**1n**).* 184.6 mg, 75%, R_f = 0.3 (EtOAc/hexane = 1:3); brown soild, melting point 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.04 (dt, J = 10.0, 2.5 Hz, 2H), 7.93 (s, 1H), 7.39 (m, 1H), 7.26 (s, 1H), 7.07 (d, J = 1.6 Hz, 1H), 7.06 (d, J = 0.8 Hz, 1H), 7.03 (dt, J = 10.0, 2.5 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 165.4, 142.8, 140.6, 136.1, 132.8, 132.5, 131.2, 129.9, 128.4, 126.9, 123.7, 122.3, 122.0, 115.2, 61.9, 56.0, 14.2; IR (film) 3060, 2920, 1714, 1642, 1370, 1254, 1072, 802, 684 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{20}H_{19}BrN_3O_5S$ 492.0231, found 492.0226.

*(E)-Ethyl 3-(4-Acetoxyphenyl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)acrylate (**1p**).* 191.0 mg, 81%, R_f = 0.3 (EtOAc/hexane = 1:3); brown solid, melting point 129−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.03 (dt, J = 10.0, 2.5 Hz, 2H), 8.00 (s, 1H), 7.15 (d, J = 8.6 Hz, 2H), 7.04 (dt, J = 10.1, 2.5 Hz, 2H), 6.93 (dt, J = 9.5, 2.2 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.29 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{ ^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.0, 166.0, 165.4, 151.6, 143.8, 141.0, 131.5, 131.2, 127.1, 123.6, 121.6, 120.6, 115.1, 61.7, 56.0, 21.2, 14.2; IR (film) 3144, 2983, 1765, 1635, 1417, 1196 cm^{-1}; HRMS (FAB) [M + H]$^+$ m/z calcd $C_{22}H_{22}N_3O_7S$ 472.1180, found 472.1181.

*(E)-Ethyl 3-(2-Fluoro-4-methoxyphenyl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)acrylate (**1q**).* 191.5 mg, 83%, R_f = 0.3 (EtOAc/hexane = 1:3); pale green solid, melting point 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.08 (s, 1H), 8.04 (dt, J = 10.1, 2.6 Hz, 2H), 7.03 (dt, J = 10.1, 2.6 Hz, 2H), 6.91 (t, J = 8.7 Hz, 1H), 6.56 (dd, J = 12.2, 2.5 Hz, 2H), 6.44 (dd, J = 8.8,

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2.5 Hz, 2H), 4.28 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.78 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.0, 165.3, 162.5 (d, J_{CF} = 11.4 Hz), 162.1 (d, J_{CF} = 252.9 Hz), 141.4, 136.6 (d, J_{CF} = 4.5 Hz), 131.2, 131.1 (d, J_{CF} = 4.1 Hz), 127.1, 123.6, 119.8, 115.1, 114.6, 110.2, 101.5 (d, J_{CF} = 25.7 Hz), 61.6, 56.0, 55.7, 14.2; IR (film) 3100, 2980, 1710, 1443, 1166, 679, 551 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd $C_{21}H_{21}FN_3O_6S$ 462.1137, found 462.1134.

*(E)-Ethyl 2-(1-((4-Methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-3-(naphthalen-2-yl)acrylate (**1r**).* 185.4 mg, 80%, R_f = 0.2 (EtOAc/hexane = 1:3); white solid, melting point 123−125 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.12 (s, 1H), 8.02 (dt, J = 10.1, 2.6 Hz, 2H), 7.75 (d, J = 8.1 Hz, 1H), 7.70 (s, 1H), 7.61 (d, 8.0 Hz, 1H), 7.56 (d, J = 8.6 Hz, 1H), 7.46 (m, 2H), 7.03 (m, 3H), 4.30 (q, J = 7.1 Hz, 2H), 3.91 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.4, 145.0, 141.4, 133.7, 132.9, 131.4, 131.4, 131.2, 128.6, 127.9, 127.6, 127.4, 127.2, 126.5, 126.2, 123.6, 120.6, 115.1, 61.7, 56.0, 14.2; IR (film) 2979, 1708, 1624, 1392, 1243, 1091 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd $C_{24}H_{22}N_3O_5S$ 464.1282, found 464.1277.

*(E)-Ethyl 3-(Furan-2-yl)-2-(1-((4-methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)acrylate (**1s**).* 147.2 mg, 73%, R_f = 0.3 (EtOAc/hexane = 1:3); pale yellow soild, melting point 121−123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.81 (s, 1H), 7.35 (d, J = 1.3 Hz, 1H), 7.05 (d, J = 9.0 Hz, 2H), 6.82 (d, J = 3.5 Hz, 1H), 6.40 (q, J = 1.7 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.2, 165.3, 150.7, 145.6, 141.1, 131.2, 130.5, 127.2, 123.7, 118.2, 115.5, 115.1, 112.6, 61.6, 56.0, 14.2; IR (film) 3147, 2982, 1708, 1632, 1392, 1256, 1091 cm^{-1}; HRMS (FAB) $[M + H]^+$ m/z calcd $C_{18}H_{18}N_3O_6S$: 404.0918, found 404.0918.

*(E)-4-(3-Methoxy-1-phenylprop-1-en-2-yl)-1-((4-methoxyphenyl)-sulfonyl)-1H-1,2,3-triazole (**1t**).* 39.6 mg, 33%, Rf = 0.3 (EtOAc/hexane = 1:2); red oil, ^1H NMR (400 MHz, $CDCl_3$) δ 7.9 (d, J = 9.0 Hz, 2H), 7.57 (s, 1H), 7.27−7.22 (m, 3H), 7.13−7.11 (m, 2H) 7.01 (d, J = 9.1 Hz, 2H), 6.93 (s, 1H), 4.42 (d, J = 1.3 Hz, 2H), 3.89 (s, 3H), 3.43 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.3, 142.8, 135.3, 131.1, 130.1, 127.5, 127.5, 126.8, 126.1, 126.0, 121.0, 114.0, 74.2, 57.3, 54.9; IR (film) 3068, 1714, 1643, 1263, 1067, 671 cm^{-1}; HRMS (EI) m/z calcd $C_{19}H_{19}N_3O_4S$ 385.1096, found 385.1094.

*(E)-3-(1-((4-Methoxyphenyl)sulfonyl)-1H-1,2,3-triazol-4-yl)-4-phenylbut-3-en-2-one (**1u**).* 57.5 mg, 30%, Rf = 0.3 (EtOAc/hexane = 1:3); yellow soild, melting point 92−93 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.03 (d, J = 9.1 Hz, 2H), 7.84 (s, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.20 (t, J = 7.6 Hz, 2H), 7.09 (d, J = 7.2 Hz, 2H), 7.04 (d, J = 9.1 Hz, 2H), 3.91 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.1, 165.4, 144.3, 141.1, 133.9, 131.2, 130.2, 130.0, 129.1, 128.5, 127.1, 123.7, 115.1, 56.0, 27.1; IR (film) 3415, 1673, 1597, 1234, 026, 695 cm^{-1}; HRMS (EI) m/z calcd $C_{19}H_{17}N_3O_4S$ 383.0940, found 383.0943.

Synthetic Procedure of Benzofulvene Derivatives. $Rh_2(S\text{-}DOSP)_4$ (3.75 mg, 0.002 mmol) and (*E*)-ethyl 2-(1-(sulfonyl)-1*H*-1,2,3-triazol-4-yl)-3-phenyl acrylate (0.2 mmol) in DCE (0.7 mL) was added to an oven-dried test tube equipped with a stir bar under a nitrogen atmosphere. The mixture was stirred at 80 °C for 12 h, at which time **1** was completely comsumed by TLC. The mixture was concentrated under reduced pressure, and the residue was purified via silica gel flash column chromatography using EtOAc/hexane to give benzofulvenes **2**.

*(Z)-Ethyl 1-((4-Methylphenylsulfonamido)methylene)-1H-indene-2-carboxylate (**2a**).* 41.4 mg, 56%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.36 (d, J = 11.0 Hz, 1H), 7.84 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 0.4 Hz, 1H), 7.71 (dd, J = 11.1, 1.3 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.36−7.20 (m, H), 7.27−7.23 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 144.2, 139.7, 137.5, 136.7, 130.1, 128.4, 127.5, 126.7, 126.0, 123.4, 118.2, 115.3, 61.7, 21.6, 14.3; IR (film) 3033, 2954, 1765, 1613, 1432, 1251 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{19}NO_5S$ 385.0984, found 385.0987.

*(Z)-Ethyl 1-(Methylsulfonamidomethylene)-1H-indene-2-carboxylate (**2b**).* 35.2 mg, 60%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.3 (d, J = 10.9 Hz, 1H), 7.86 (d, J = 0.6 Hz, 1H), 7.69 (d, J = 1.2 Hz, 1H), 7.68−7.66 (m, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.37 (td, J = 7.5, 7.5, 1.1 Hz, 1H), 7.28 (td, J = 7.4, 7.4, 0.9 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 3.19 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 140.1, 139.7, 136.8, 128.1, 127.7, 126.2, 126.0, 123.5, 118.2, 115.2, 61.8, 42.7, 14.3; IR (film) 3283, 3066, 1713, 1660, 1512, 1377 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{15}NO_4S$ 293.0722, found 293.0726.

*(Z)-Ethyl 1-((1-Methylethylsulfonamido)methylene)-1H-indene-2-carboxylate (**2c**).* 28.3 mg, 44%, R_f = 0.4 (EtOAc/hexane = 1:5); brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.1 (d, J = 11.0 Hz, 1H), 7.86 (d, J = 0.7 Hz, 1H), 7.70−7.67 (m, 2H), 7.53 (d, J = 7.6 Hz, 1H), 7.36 (td, J = 7.5, 7.5, 1.1 Hz, 1H), 7.30−7.27 (q, J = 7.1 Hz, 2H), 3.38 (nonet, J = 6.8 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.7, 139.9, 139.6, 136.7, 129.5, 127.5, 126.0, 123.4, 118.2, 114.4, 61.8, 55.7, 16.6, 14.3; IR (film) 3069, 2983, 1715, 1659, 1375, 1267 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{19}NO_4S$ 321.1035, found 321.1037.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-1H-indene-2-carboxylate (**2d**).* 48.6 mg, 63%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.3 (d, J = 11.1, 1H), 7.89 (dt, J = 9.9, 2.5 Hz, 2H), 7.80 (d, J = 0.6 Hz, 1H), 7.72 (dd, J = 11.1, 1.4 Hz, 1H), 7.68 (dd, J = 7.8, 0.5 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.34 (td, J = 7.6, 7.6, 1.1 Hz, 1H), 7.28−7.24 (m, 1H), 6.98 (dt, J = 9.9, 2.5 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 163.3, 139.8, 139.6, 136.7, 132.0, 128.9, 128.5, 127.4, 126.0, 126.0, 123.4, 118.2, 115.1, 114.6, 61.7, 55.7, 14.2; IR (film): 3066, 2938, 1713, 1660, 1240; HRMS (EI) m/z calcd for $C_{20}H_{19}NO_5$ S 385.0984, found 385.0983.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-4-methyl-1H-indene-2-carboxylate (**2e**).* 39.9 mg, 50%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow solid, melting point 143−146 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.35 (d, J = 11.1 Hz, 1H), 7.91−7.87 (m, 3H), 7.70 (dd, J = 11.1, 1.4 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 6.97 (dt, J = 9.9, 2.5 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 2.48 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 163.3, 139.8, 137.9, 136.0, 132.9, 132.1, 128.9, 128.5, 127.7, 126.8, 125.2, 115.7, 115.6, 114.6, 61.7, 55.7, 18.3, 14.3; IR (film): 3059, 2973, 1659, 1439, 1293, 1158 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}NO_5$ S 399.1140, found 399.1141.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-6-methyl-1H-indene-2-carboxylate (**2f**).* 53.5 mg, 67%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow solid, Melting poing: 58−61 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.3 (d, J = 11.1 Hz, 1H), 7.89 (dt, J = 9.6, 2.5 Hz, 2H), 7.76 (s, 1H), 7.68 (d, J = 11.1 Hz, 1H), 7.48 (s, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.98 (dt, J = 9.9, 2.4 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 2.45 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 163.3, 140.2, 139.8, 137.8, 134.4, 132.1, 128.9, 127.9, 127.3, 125.3, 123.1, 118.7, 115.2, 114.6, 61.6, 55.7, 22.0, 14.3; IR (film): 3059, 2978, 1643, 1441, 1218 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}NO_5$ S 399.1140, found 399.1143.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-7-methyl-1H-indene-2-carboxylate (**2g**), (Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-5-methyl-1H-indene-2-carboxylate (**2h**).* 54.3 mg, 68%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.65 (d, J = 11.0 Hz, 1H), 12.28 (d, J = 11.0 Hz, 0.5H), 7.91−7.87 (m, 4.3H), 7.83 (d, J = 1.3 Hz, 1H), 7.73 (d, J = 0.7 Hz, 0.5H), 7.64 (dd, J = 11.1, 1.4 Hz, 0.5 Hz), 7.56 (d, J = 8.0 Hz, 0.5H), 7.41−7.39 (m, 1H), 7.28 (s, 0.5H), 7.18−7.16 (m, 2.5H), 7.00−6.96 (m, 3.25H), 4.38−4.31 (m, 3.25H), 3.84 (s, 3H), 3.83 (s, 1.5H), 2.63 (s, 3H), 2.40 (s, 1.5H), 1.41−1.37 (m, 4.5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.8, 167.6, 163.3, 163.3, 140.2, 139.7, 137.3, 137.2, 137.0, 136.7, 135.8, 132.1, 131.9, 131.3, 131.2, 128.9, 128.7, 127.7, 126.1, 126.0, 125.5, 123.6, 122.0, 118.0, 117.2, 115.3, 114.6, 114.6, 61.8, 61.7, 55.7, 22.3, 21.5, 14.3; IR (film): 3114,

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2980, 1660, 1410, 1235 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}NO_5$ S 399.1140, found 399.1139.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-6-methyl-1H-indene-2-carboxylate (**2i**).* 54.0 mg, 65%, R_f = 0.4 (EtOAc/hexane = 1:4); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.43 (d, J = 11.0, 1H), 7.89 (dt, J = 9.8, 2.5 Hz, 2H), 7.73 (d, J = 0.8 Hz, 1H), 7.67 (dd, J = 11.0, 1.4 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.16 (d, J = 2.2 Hz, 1H), 6.98 (dt, J = 9.9, 2.6 Hz, 2H), 6.84 (dd, J = 8.4, 2.3 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 163.3, 160.3, 142.0, 139.9, 132.1, 130.4, 128.9, 128.0, 124.4, 124.3, 115.5, 114.6, 102.5, 61.5, 55.7, 55.7, 14.3; IR (film) 3057, 2987, 1722, 1617, 1422, 1231 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}NO_6S$ 415.1090, found 415.1087.

*Ethyl 5,7-Dimethoxy-1-((4-methoxyphenylsulfonamido)-methylene)-1H-indene-2-carboxylate (**2j**).* 48.1 mg, 54%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow solid, melting point 121−124 °C. ^1H NMR 400 MHz, $CDCl_3$) data for the major isomer; δ 12.37 (d, J = 11.4 Hz, 1H), 8.38 (dd, J = 11.4, 1.3 Hz, 1H), 7.89 (dt, J = 9,9 2.5 Hz, 2H), 7.69 (d, J = 1.3 Hz, 1H), 6.97 (dt, J = 9.9, 2.5 Hz, 2H), 6.64 (d, J = 2.0 Hz, 1H), 6.50 (d, J = 2.0 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); data for the minor isomer; 10.58 (d, J = 12.0 Hz, 1H), 8.30 (d, J = 12.1 Hz, 1H), 7.88 (d, J = 9.0 Hz, 2H), 7.40 (s, 1H), 6.98 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 2.6 Hz, 1H), 6.43 (d, J = 2.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.99 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 164.5, 163.3, 163.2, 160.5, 159.3, 159.3, 155.5, 153.0, 142.3, 139.0, 138.6, 134.2, 132.3, 132.3, 131.8, 130.8, 130.5, 128.9, 128.8, 126.5, 120.1, 116.1, 115.3, 114.6, 114.5, 100.3, 99.3, 98.6, 61.6, 60.3, 56.3, 55.6, 55.5, 29.7, 14.36, 14.26; IR (film) 3095, 2928, 1699, 1498, 1262 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{23}NO_7S$ 445.1195, found 445.1197.

*(Z)-Ethyl 8-((4-Methoxyphenylsulfonamido)methylene)-8H-indeno[4,5-d][1,3]dioxole-7-carboxylate (**2k**).* 48.0 mg, 56%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow solid, melting point 63−65 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.15 (d, J = 11.2 Hz, 1H), 7.90 (dt, J = 9.9, 2.5 Hz, 2H), 7.79 (dd, J = 11.2, 1.2 Hz, 1H), 7.71 (d, J = 1.2 Hz, 1H), 7.04 (d, J = 7.0 Hz, 1H), 6.98 (dt, J = 9.9, 2.4 Hz, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.13 (s, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 163.2, 148.2, 140.1, 140.0, 132.5, 132.1, 130.6, 128.8, 125.0, 121.7, 117.5, 114.5, 113.6, 106.7, 101.9, 61.6, 55.6, 14.3; IR (film) 3069, 2981, 1697, 1634, 1415, 1235 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{19}NO_7S$ 429.0882, found 429.0881.

*(Z)-Ethyl 5-((4-Methoxyphenylsulfonamido)methylene)-5H-indeno[5,6-d][1,3]dioxole-6-carboxylate (**2l**).* 12.0 mg, 14%, R_f = 0.3 (EtOAc/hexane = 1:3); yellow solid, melting point 70−72 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.49 (d, J = 11.0 Hz, 1H), 7.88 (d, J = 8.8 Hz, 2H), 7.67 (s, 1H), 7.56 (dd, J = 11.0, 0.7 Hz, 1H), 7.11 (s, 1H), 6.98 (dt, J = 8.8 Hz, 2H), 6.89 (s, 1H), 5.99 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 163.3, 148.7, 147.1, 139.5, 135.5, 132.0, 131.0, 128.9, 128.5, 124.0, 115.3, 114.6, 102.6, 101.4, 99.0, 61.4, 55.7, 14.3; IR (film) 3069, 2981, 1697, 1634, 1415, 1235 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{19}NO_7S$ 429.0882, found 429.0881.

*(Z)-Ethyl 6-Chloro-1-((4-methoxyphenylsulfonamido)-methylene)-1H-indene-2-carboxylate (**2m**).* 37.8 mg, 45%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.39 (d, J = 11.2 Hz, 1H), 7.90 (dt, J = 10.0, 2.6 Hz, 2H), 7.74 (s, 1H), 7.70 (dd, J = 11.2, 1.3 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.41 (d, J = 8.2 Hz, 1H), 7.21 (dd, J = 8.2, 1.8 Hz, 1H), 7.00 (dt, J = 9.9, 2.5 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 163.5, 141.7, 138.3, 134.9, 133.6, 131.7, 129.6, 129.0, 126.5, 126.2, 124.2, 118.5, 114.7, 114.1, 61.8, 55.7, 14.2; IR (film) 3062, 2973, 1659, 1439, 1262, 879, 559 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{18}ClNO_5S$ 419.0594, found 419.0590.

*(E)-Ethyl 7-Bromo-1-((4-methoxyphenylsulfonamido)methylene)-1H-indene-2-carboxylate (**2n**), (Z)-Ethyl 5-Bromo-1-((4-methoxyphenylsulfonamido)methylene)-1H-indene-2-carboxylate (**2o**).* 39.9 mg, 43%, R_f = 0.4 (EtOAc/hexane = 1:5); brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.67 (d, J = 11.4 Hz, 1H), 12.37 (d, J = 11.1 Hz, 0.3H), 9.16 (dd, J = 11.4, 1.1 Hz, 1H), 7.94 (dt, J = 10.0, 2.5 Hz, 2H), 7.89 (dt, J = 9.9, 2.5 Hz, 0.6H), 7.73−7.70 (m, 1.6H), 7.62 (d, J = 1.6 Hz, 0.3H), 7.54 (d, J = 7.9 Hz, 1.3H), 7.49 (d, J = 7.3 Hz, 1H), 7.43 (d, J = 8.3, 1.7 Hz, 0.3H), 7.10 (t, J = 7.7 Hz, 1H), 7.01−6.98 (m, 2.6H), 4.39−4.34 (m, 2.6H), 3.85 (s, 3.9H), 1.40 (t, J = 7.1 Hz, 3.9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 167.3, 163.5, 163.4, 139.4, 138.3, 138.2, 137.7, 137.5, 135.5, 133.7, 133.1, 131.8, 131.7, 130.0, 129.7, 129.0, 127.1, 127.1, 126.2, 126.0, 122.9, 119.6, 119.4, 115.2, 114.7, 114.7, 114.6, 114.1, 62.0, 61.9, 55.7, 14.2; IR (film): 3095, 2981, 1714, 1413, 868, 647, 547 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{18}BrNO_5$ S 463.0089, found 463.0092.

*(Z)-Ethyl 6-Acetoxy-1-((4-methoxyphenylsulfonamido)-methylene)-1H-indene-2-carboxylate (**2p**).* 44.3 mg, 50%, R_f = 0.4 (EtOAc/hexane = 1:4); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.37 (d, J = 11.2 Hz, 1H), 7.88 (dt, J = 9.9, 2.5 Hz, 2H), 7.76 (dd, J = 11.1, 1.3 Hz, 1H), 7.48 (d, J = 8.3 Hz, 1H), 7.39 (d, J = 2.0 Hz, 1H), 7.00−6.96 (m, 3H), 4.35 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.35 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 167.4, 163.4, 150.5, 141.1, 138.6, 134.4, 131.8, 129.4, 129.4, 128.9, 126.5, 124.1, 119.7, 114.7, 111.6, 61.8, 55.7, 21.2, 14.2; IR (film) 3061, 2982, 1760, 1440, 1242 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{21}NO_7S$ 443.1039, found 443.1042.

*(Z)-Ethyl 4-Fluoro-6-methoxy-1-((4-methoxyphenyl-sulfonamido)methylene)-1H-indene-2-carboxy-late (**2q**).* 65.0 mg, 75%, R_f = 0.4 (EtOAc/hexane = 1:4); brown soild, melting point 129−132 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.49 (d, J = 11.1 Hz, 1H), 7.91−7.87 (m, 2H), 7.79 (d, J = 0.8 Hz, 1H), 7.71 (dd, J = 11.1, 1.3 Hz, 1H), 7.01−6.96 (m, 3H), 6.54 (dd, J = 11.0, 1.9 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 163.4, 161.5 (d, J = 10.2 Hz), 157.7 (d, J = 252.37 Hz), 143.4 (d, J = 7.5 Hz), 134.2, 131.9, 129.7, 128.9, 124.0, 118.3, 115.1, 114.6, 100.2, 98.8 (d, J = 3.2 Hz), 61.7, 56.1, 55.1, 14.3; IR (film) 3062, 2980, 1714, 1448, 1237, 832, 571 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{20}FNO_6S$ 433.0995, found 433.0997.

*(Z)-Ethyl 1-((4-Methoxyphenylsulfonamido)methylene)-1H-cyclopenta[a]naphthalene-2-carboxylate (**2r**).* 52.3 mg, 60%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow solid, melting point 199−203 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 13.20 (d, J = 11.0 Hz, 1H), 11.96 (d, J = 11.1 Hz, 0.1H), 8.54 (dd, J = 11.1, 1.3 Hz, 1H), 8.34 (s, 1H), 8.08 (s, 0.1H), 7.94−7.85 (m, 4.8H), 7.72 (dd, J = 11.1, 1.4 Hz, 0.1H), 7.65 (d, J = 8.3 Hz, 1H), 7.63−7.59 (m, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.50−7.46 (m, 1.1H), 7.45−7.44 (m, 0.1H), 7.43−7.40 (m, 0.1H), 4.40−4.34 (m, 2.2H), 3.83 (s, 3.3H), 1.43−1.39 (m, 3.3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.9, 167.3, 163.4, 163.2, 140.0, 139.9, 137.5, 136.0, 135.4, 135.0, 134.3, 134.2, 133.8, 133.1, 132.3, 132.3, 131.9, 130.0, 128.8, 128.3, 127.5, 127.3, 126.3, 125.3, 125.1, 123.6, 122.4, 121.6, 117.5, 116.4, 114.7, 114.6, 71.4, 61.9, 55.7, 42.6, 14.3, 14.2; IR (film) 3051, 2981, 2940, 1652, 1435, 1262 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{21}NO_5S$ 435.1140, found 435.1139.

*(Z)-Ethyl 4-((4-Methoxyphenylsulfonamido)methylene)-4H-cyclopenta[b]furan-5-carboxylate (**2s**).* 37.5 mg, 50%, R_f = 0.4 (EtOAc/hexane = 1:5); yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 12.98 (d, J = 11.1 Hz, 1H), 7.89 (dt, J = 9.9, 2.6 Hz, 2H), 7.59 (dd, J = 11.1, 1.3 Hz, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.40 (t, J = 0.9 Hz, 1H), 6.99 (dt, J = 9.9, 2.6 Hz, 2H), 6.59 (dd, J = 2.0, 0.7 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 163.5, 156.8, 148.9, 134.3, 131.7, 131.4, 129.0, 125.0, 121.0, 114.6, 109.2, 104.9, 61.3, 55.7, 14.33; IR (film) 3059, 2982, 1644, 1402, 1262 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{17}NO_6S$ 375.0777, found 375.0774.

*(Z)-4-methoxy-N-((2-(methoxymethyl)-1H-inden-1-ylidene)methyl)benzenesulfonamide (**2t**).* 37.2 mg, 52%, R_f = 0.5 (EtOAc:hexane = 1:2); yellow liquid, ^1H NMR (400 MHz, $CDCl_3$) 10.12 (d, J = 11.0 Hz, 1H), 7.84 (d, J = 9.00 Hz, 2H), 7.55−7.53 (m, 1H), 7.43 (dd, J = 11.0 Hz, 4.4 Hz, 1H), 7.29−4.25 (m, 1H), 7.19−7.16 (m, 2H), 6.97 (d, J = 9.0 Hz, 2H), 6.73 (s, 1H), 4.45 (d, J = 0.8 Hz, 2H), 3.84 (s, 3H), 3.32 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 139.1,

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137.9, 133.3, 132.0, 130.8, 128.7, 126.0, 125.3, 124.9, 121.0,120.4, 118.0, 114.6, 69.5, 56.7, 55.7; IR (film) 2930, 1597, 1446, 1234, 1027, 685 cm^{-1}; HRMS (EI) m/z calcd $C_{19}H_{19}NO_4S$ 357.1035, found 357.1031.

*(Z)-N-((2-Acetyl-1H-inden-1-ylidene)methyl)-4-methoxybenzenesulfonamide (**2u**).* 31.4 mg, 46%, R_f = 0.3 (EtOAc/hexane = 1:5); yellow solid, melting point 110−1112 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.77 (d, J = 10.9 Hz, 1H), 7.89 (d, J = 9.1 Hz, 2H), 7.82 (s, 1H), 7.80 (dd, J = 10.9 Hz, 1.4 Hz, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.39 (td, J = 15.1 Hz, 1.1 Hz, 1H), 7.29 (td, J = 14.9 Hz, 1.0 Hz, 1H), 6.97 (d, J = 9.1 Hz, 2H), 3.84 (s, 3H), 2.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 197.9, 163.4, 141.6, 140.4, 136.5, 134.8, 132.1, 130.0, 128.9, 128.4, 126.0, 123.8, 118.5, 114.6, 114.4, 55.7, 27.5; IR (film) 3449, 2927, 1746, 1633, 1241, 1050 cm^{-1}; HRMS (EI) m/z calcd $C_{19}H_{17}NO_4S$ 355.0878, found 355.0878.

Semi-One-Pot Synthesis of Benzofulvene Derivatives. A mixture of CuTC (0.02 mmol, 10 mol %), 1,3-enyne (0.2 mmol, 1.0 equiv), toluene (1.0 mL) and 4-methoxyphenylsulfonyl azide (0.22 mmol, 1.1 equiv) were added to an oven-dried test tube under nitrogen atmosphere. The mixture was stirred at rt for 2 h, at which time 1,3-enyne was completely comsumed by TLC. The reaction mixture was filtered through short pad of Celite with methylene chloride. The filtrate was concentrated under reduced pressure and then a solution of Rh_2(*S*-DOSP)$_4$ (0.002 mmol, 1.0 mol %) in DCE (0.7 mL) was added to the filtrate under nitrogen atmosphere. The mixture was stirred at 80 °C for 12 h. The mixture was concentrated under reduced pressure and the residue was purified via silica gel flash column chromatography to give benzofulvenes (**2d**, **2f**, and **2q**).

*Synthetic Procedure of (Z)-N-((2-(Hydroxymethyl)-1H-inden-1-ylidene)methyl)-4-methoxybenzenesulfonamide (**2v**).*[24] Benzofulvene **2d** (0.2 mmol, 77.1 mg) were added to an oven-dried test tube equipped with a stir bar under nitrogen atmosphere. Anhydrous methylene chloride (2 mL) was added and the solution was stirred for 10 min at rt. The the reaction solution was cooled −78 °C and DIBAL-H (0.4 mL, 1.0 M in THF) was added. The mixture was stirred at −78 °C for 20 min at which time benzofulvene **2d** was completely comsumed by TLC. The mixture was diluted with saturated aq NaCl (5 mL) and extracted with methylene chloride (10 mL × 3). The collected organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, and the residue was purified by silica gel flash column chromatography using EtOAc/hexane = 1:3 to give the product **2v**: 58.4 mg, 85%, R_f = 0.3 (EtOAc/hexane = 1:3); colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (d, J = 11.0 Hz, 1H), 7.83 (dt, J = 9.9, 2.5 Hz, 2H), 7.53−7.51 (m, 1H), 7.41 (dd, J = 11.0, 1.2 Hz, 1H), 7.27−7.15 (m, 2H), 6.94 (dt, J = 9.9, 2.5 Hz, 2H), 6.67 (s, 1H), 4.61 (s, 2H), 3.83 (s, 3H), 2.63 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3, 139.0, 137.8, 135.4, 131.8, 129.3, 128.8, 126.8, 125.0, 124.9, 121.2, 120.5, 118.0, 114.6, 60.6, 55.7; IR (film) 3477, 3279, 3071, 2943, 2255, 1709, 1415, 1235 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{17}NO_4S$ 343.0878, found 343.0876.

*Synthetic Procedure of Ethyl 3′-(4-Methoxyphenylsulfonamido)-spiro[indene-1,2′-oxirane]-2-carboxylate (**2w**).*[24] Benzofulvene **2d** (0.2 mmol, 77.1 mg) was added to an oven-dried test tube equipped with a stir bar under a nitrogen atmosphere. Anhydrous methylene chloride (10 mL) was added, and the solution was stirred for 5 min. Aqueous $NaHCO_3$ solution (0.5 M, 10 mL) was added afterward. *m*-CPBA (0.4 mmol, 69 mg) was added to the biphasic solution, and the solution was maintained at rt for 24 h. Then the mixture was diluted with H_2O (5 mL) and extracted with methylene chloride (10 mL × 3). The collected organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, and the residue was purified silica gel flash column chromatography using EtOAc/hexane = 1:7 to give the product **2w**: 41.7 mg, 52%, R_f = 0.5 (EtOAc/hexane = 1:7); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dt, J = 10.1, 2.6 Hz, 2H), 7.71 (s, 1H), 7.51−7.49 (m, 1H), 7.47−7.38 (m, 3H), 7.05 (dt, J = 9.7, 2.5 Hz, 2H), 4.58 (s, 1H), 4.45−4.30 (m, 2H), 3.91 (s, 3H), 3.57 (s, 1H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.9, 163.4, 144.1, 143.8, 139.3, 137.6, 131.8, 130.4, 129.8, 125.6, 124.8, 124.5, 114.6, 80.3, 79.5, 61.4, 55.8, 14.2; IR (film) 3471, 3060, 2930, 1713, 1162 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{19}NO_6S$ 401.0933, found 401.0933.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02140.

^{1}H and ^{13}C{^{1}H} NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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