

HETEROCYCLES, Vol. 95, No. 1, 2017, pp. 232-242. © 2017 The Japan Institute of Heterocyclic Chemistry
Received, 9th June, 2016, Accepted, 29th June, 2016, Published online, 28th July, 2016
DOI: 10.3987/COM-16-S(S)8

***N*-HETEROCYCLIC CARBENE-PROMOTED [3+2] CYCLOADDITION OF ALLENYL SULFONE AND ARYLIDENEMALONONITRILES**

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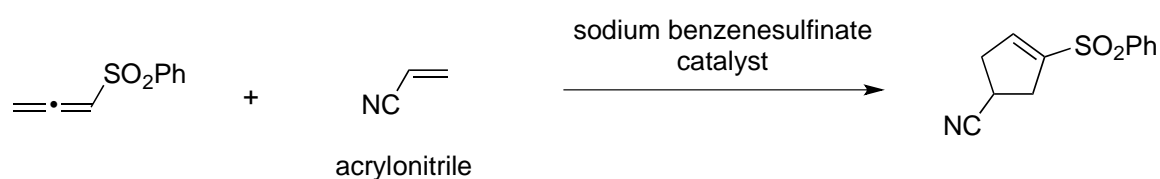
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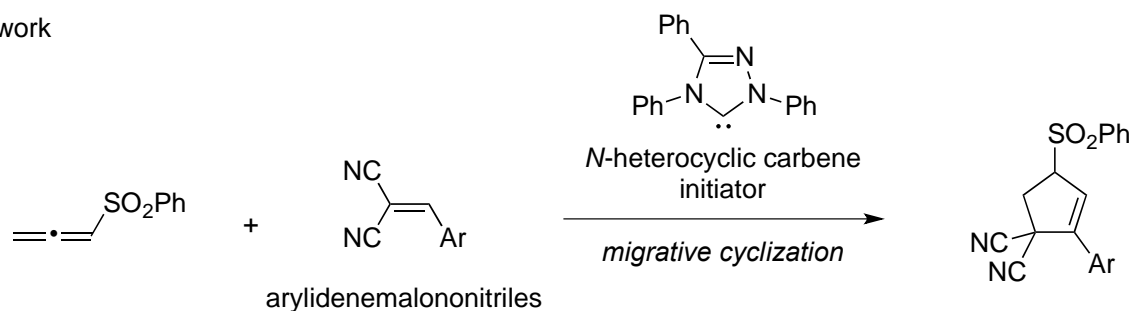
Abstract – *N*-Heterocyclic carbenes promote the [3+2] cycloaddition of allenyl sulfone and arylidenemalononitriles, accompanied by 1,2-migration of the sulfonyl group. This reaction provides a new route to highly substituted cyclopentenes.

INTRODUCTION

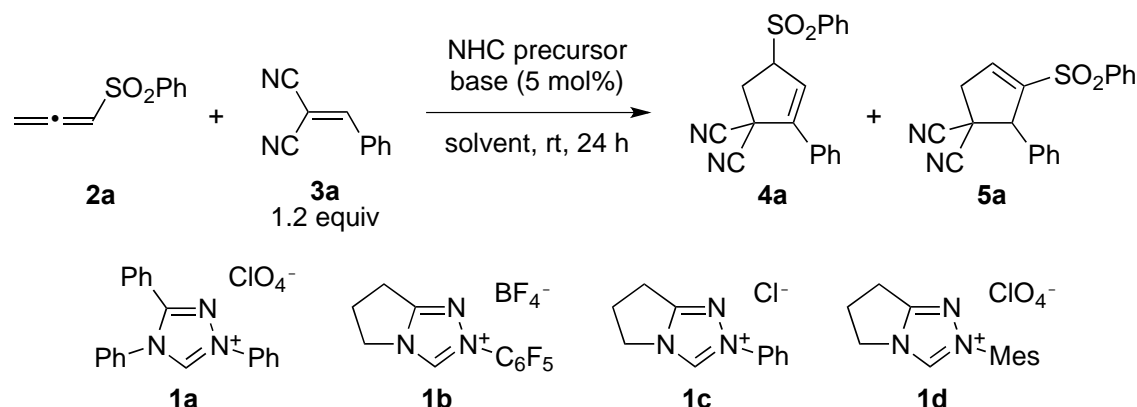
The widespread occurrence of cyclopentene rings in synthetic and natural biologically active molecules has stimulated the extensive development of various strategies for the preparation of these five-membered carbocyclic skeletons.¹ Among the proposed routes, [3+2] cycloaddition is advantageous as it allows the formation of multiple bonds in a single operation and to date, has played an essential role in the construction of a range of five-membered rings. For example, Padwa *et al.* reported the sodium benzenesulfinate-catalyzed [3+2] cycloaddition of allenyl sulfone and acrylonitrile to afford a cyclopentene derivative (Scheme 1).² We envisaged that this type of reaction may also be promoted by *N*-heterocyclic carbenes (NHC),³ which are nucleophilic catalysts whose electronic and steric environments are easily manipulated. We herein chose to investigate the [3+2] cycloaddition reaction between allenyl sulfone⁴ and arylidenemalononitriles in the presence of a catalytic amount of various NHCs. We observed an unexpected cyclization process along with formal 1,2-migration of the sulfonyl group. Thus, we herein report a new type of [3+2] cycloaddition to yield the cyclopentene skeleton in good yields.

Padwa *et al.* (1988)

This work

**Scheme 1.** Reactions of allenyl sulfone with acrylonitrile and arylidenemalononitriles**RESULTS AND DISCUSSION**

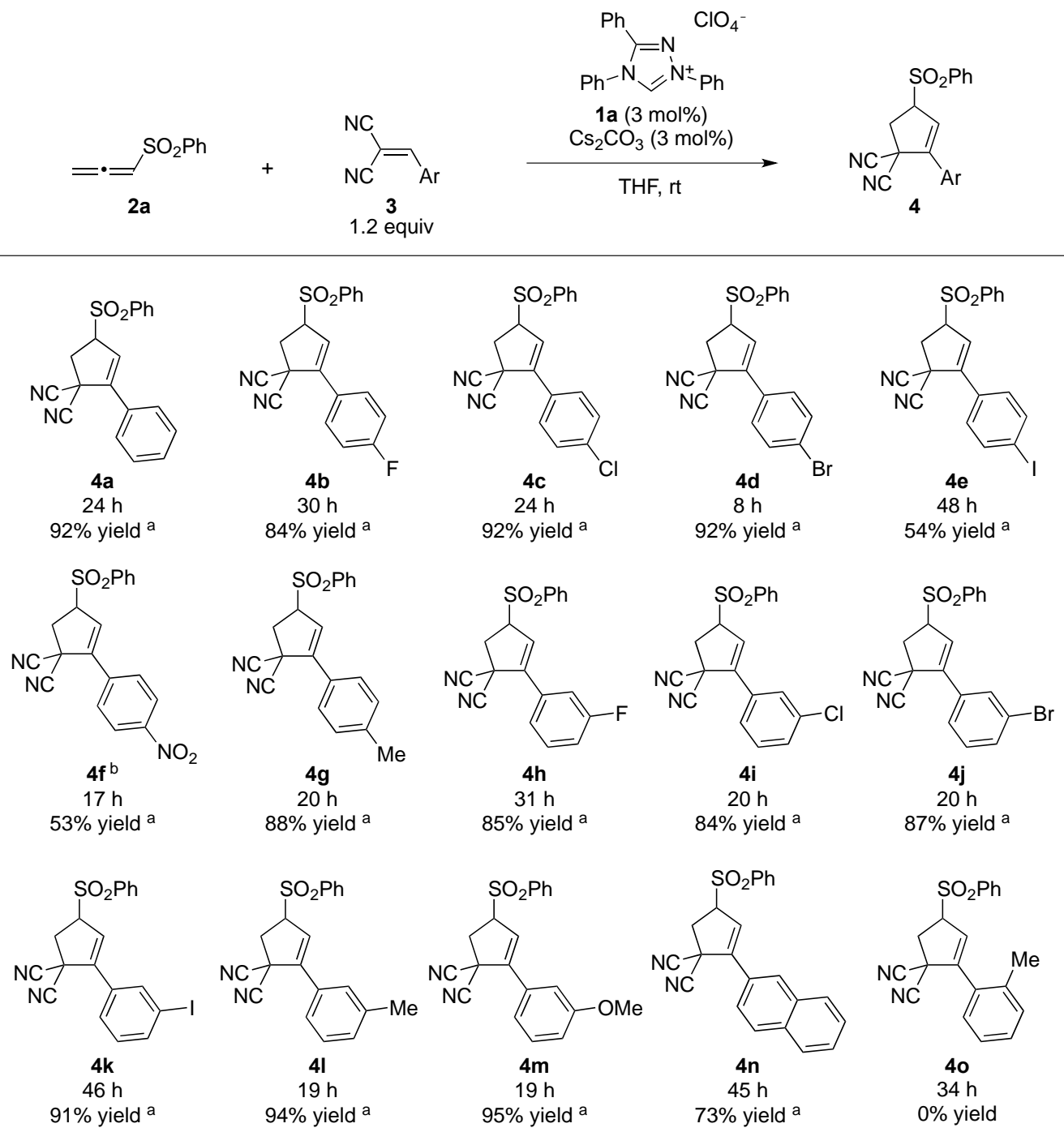
A mixture of allenyl sulfone **2a** (0.1 mmol) and benzylidenemalononitrile **3a** (0.12 mmol) was stirred at ambient temperature in the presence of NHC precursor **1a** (5 mol%) and K₃PO₄ (5 mol%) in acetonitrile. After 24 h, instead of the expected product **5a**, cyclopentene **4a** was produced in 58% yield via 1,2-migration of the sulfonyl group (Table 1, entry 1). Although **4a** was not the expected product, it also contained a highly substituted cyclopentene ring, and so we investigated the effects of a range of bases, azolium salts, and solvents to improve the yield of **4a**. We initially examined a series of NHC precursors. While **1a**, **1c**, and **1d** gave similar results (55–58% yields), the fluorine-containing **1b** was not suitable for this reaction, giving only a trace amount of product (entries 1–4). In the absence of NHC, **4a** was not obtained (entry 5). Among the various bases examined, Cs₂CO₃ was the most effective, with organic bases tending to give poor yields (entries 6–11). Furthermore, in cyclic ether solvents, such as THF and 1,4-dioxane, the reaction proceeded smoothly (entries 12–17). Interestingly, although the yield decreased to 79% in the presence of 10 mol% **1a** (entry 18), the use of 3 mol% **1a** was sufficient, giving **4a** in 91% yield (entry 19). The formation of product **5a** was not observed in any reaction.

Table 1. Optimization of reaction conditions

entry	NHC precursor (mol%)	base	solvent	4a (% yield) ^a
1	1a (5)	K ₃ PO ₄	MeCN	58
2	1b (5)	K ₃ PO ₄	MeCN	trace
3	1c (5)	K ₃ PO ₄	MeCN	55
4	1d (5)	K ₃ PO ₄	MeCN	57
5	none	none	MeCN	0
6	1a (5)	Na ₂ CO ₃	MeCN	18
7	1a (5)	K ₂ CO ₃	MeCN	32
8	1a (5)	Cs ₂ CO ₃	MeCN	83
9	1a (5)	Et ₃ N	MeCN	14
10	1a (5)	DBU	MeCN	8
11	1a (5)	proton-sponge	MeCN	trace
12	1a (5)	Cs ₂ CO ₃	EtOAc	55
13	1a (5)	Cs ₂ CO ₃	toluene	7
14	1a (5)	Cs ₂ CO ₃	CHCl ₃	4
15	1a (5)	Cs ₂ CO ₃	CH ₂ Cl ₂	26
16	1a (5)	Cs ₂ CO ₃	THF	86
17	1a (5)	Cs ₂ CO ₃	1,4-dioxane	68
18	1a (10)	Cs ₂ CO ₃	THF	79
19	1a (3)	Cs ₂ CO ₃	THF	91

^a Yield was determined by ¹H NMR analysis using triphenylmethane as the internal standard.

Under the optimized reaction conditions (Table 1, entry 19), the generality of the NHC-promoted migrative [3+2] cycloaddition of allenyl sulfone **2a** with various arylidene malononitriles **3** was examined (Table 2). With respect to the Ar moiety of the arylidene malononitrile substrate **3**, both electron withdrawing and electron donating substituents at the *para*- and *meta*-positions were compatible, giving cyclized products in moderate to high yields. However, the arylidene malononitrile bearing a methyl substituent at the *ortho*-position gave poor results, failing to yield the desired cyclopentene **4o**.

Table 2. NHC-promoted [3+2] cycloaddition of allenyl sulfone and arylidenemalononitriles^a Isolated yield^b **1a** (6 mol%) and Cs₂CO₃ (6 mol%) were used.

The structure of the migrative [3+2] cycloaddition product was confirmed by the X-ray crystallographic analysis of **4d** (Figure 1).

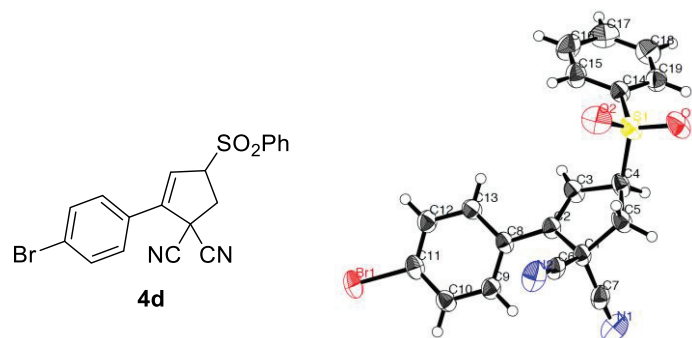
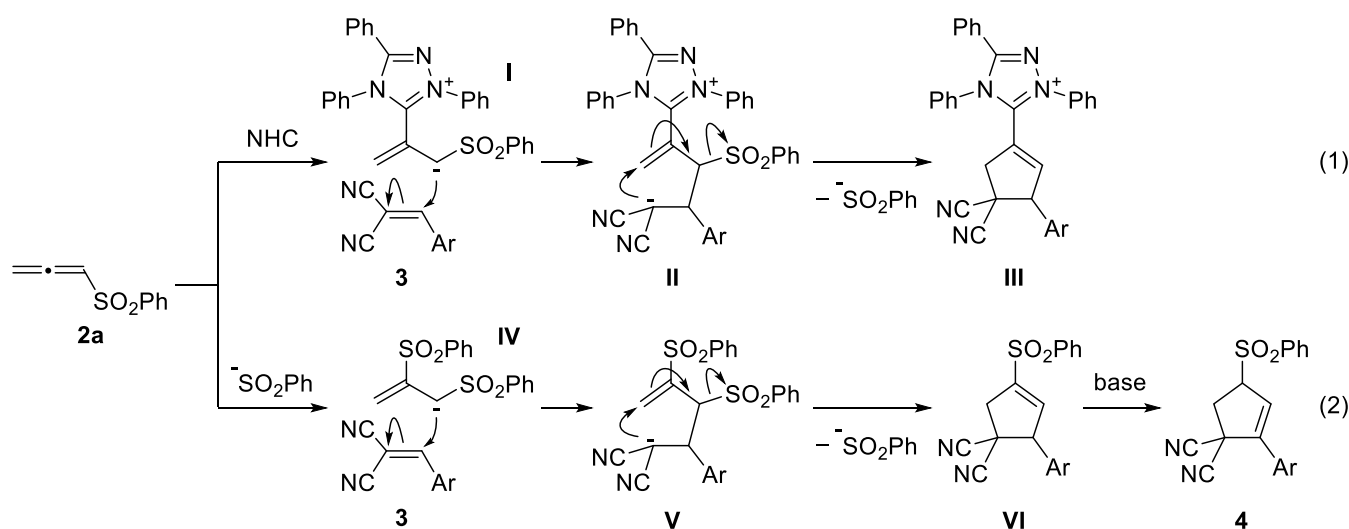
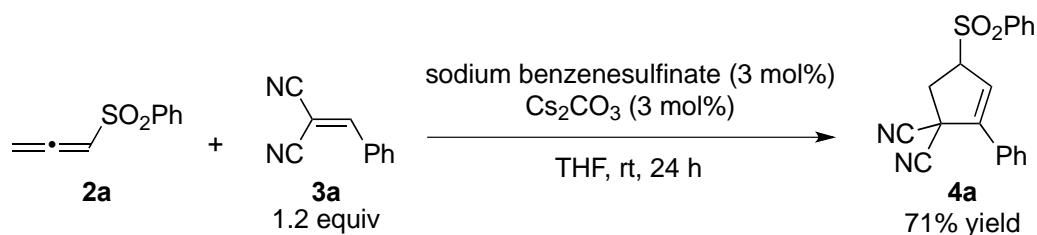


Figure 1. Crystal structure of **4d** determined by X-ray crystallography

A plausible reaction pathway for this transformation is shown in Scheme 2. Pathway 1 (top line, Scheme 2) would initially involve the conjugate addition of NHC to the allenyl sulfone **2a** to yield the zwitterionic intermediate **I**.⁵ A [3+2] cycloaddition between **I** and arylidenemalononitrile **3** would then proceed in a stepwise manner. Following the conjugate addition of **I** to **3**, the intramolecular cyclization of anion **II** would be followed by proton transfer, NHC regeneration, and ultimately, the formation of product **5** (not shown). However, the pathway involving S_N2' -cyclization of **II** and release of the sulfinate anion to give **III** is dominant. As the released sulfinate anion becomes a good nucleophile for **2a**, further [3+2] cycloadditions could take place between disulfone **IV** and **3** (bottom line, pathway 2, Scheme 2), and the subsequent S_N2' -cyclization of **V** would yield **VI**.⁶ Finally, the olefin isomerization of **VI** would give cyclopentene **4**. This scenario is supported by the result that, in the presence of 3 mol% sodium benzenesulfinate, the reaction proceeded and gave **4a** in 71% yield (Scheme 3). The scenario is also supported by the lower yield (79%) of **4a** using 10 mol% of **1a** when compared to the yield obtained (91%) using 3 mol% of **1a** (*c.f.*, entries 18 and 19, Table 1).



Scheme 2. Plausible reaction pathway to the formation of cyclopentene **4**



Scheme 3. [3+2] cycloaddition in the presence of sodium benzenesulfinate

In conclusion, we successfully developed an NHC-promoted [3+2] cycloaddition of allenyl sulfone with a range of arylidenemalononitriles. This cyclization was accompanied by a formal 1,2-migration of the sulfonyl group. This reaction provides a new route to functionalized cyclopentene derivatives.

EXPERIMENTAL

1. General

Dry solvents were purchased from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). Silica gel column chromatography was performed on Kanto silica gel 60 (spherical, 100-210 μm). IR spectra were recorded on JASCO FT/IR-4100 using ATR. ¹H-NMR spectra were recorded on JEOL ECS-400 (400 MHz) spectrometers. Chemical shifts of ¹H-NMR spectra were reported relative to tetramethyl silane (δ 0) or acetone-*d*₆ (δ 2.05). ¹³C-NMR spectra were recorded on JEOL ECS-400 (100 MHz) spectrometers. Chemical shifts of ¹³C-NMR spectra were reported relative to CDCl₃ (δ 77.0) or acetone-*d*₆ (δ 29.84). Splitting patterns were reported as s, singlet; d, doublet; t, triplet; m, multiplet.

2. Preparation of arylidenemalononitriles

Arylidenemalononitriles **3b–n** were prepared through Knoevenagel condensation of the corresponding aldehydes with malononitrile and recrystallized from EtOH and hexane, according to the literature.⁷

3. NHC-promoted [3+2] cyclization of allenyl sulfone and arylidenemalononitrile

a. General procedure for *N*-heterocyclic carbene-promoted [3+2] cyclization of allenyl sulfone and arylidenemalononitriles

A 10 mL flame-dried test tube with a magnetic stirring bar was charged with **1a** (1.2 mg, 0.003 mmol), Cs₂CO₃ (1.0 mg, 0.003 mmol), allenyl sulfone **2a** (18 mg, 0.1 mmol), and arylidenemalononitrile **3** (0.12 mmol). The test tube was filled with argon by the evacuation–refill process. After addition of THF (0.5 mL), the mixture was stirred at ambient temperature until TLC monitoring showed that **2a** was completely consumed. After evaporation of THF in vacuo, the residue was purified by silica gel column chromatography to give product **4**.

b. Analytical data for product 4**2-Phenyl-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4a)**

According to the General Procedure, the title compound was obtained after 24 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 2:1) gave the product as pale green oil (31 mg, 92% yield). $R_f=0.30$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.93 (m, 2H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.67-7.59 (m, 4H), 7.49-7.46 (m, 3H), 6.44 (d, $J = 2.8$ Hz, 1H), 4.67 (ddd, $J = 2.8, 5.6, 8.4$ Hz, 1H), 3.26 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.20 (dd, $J = 8.4, 15.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 142.8, 135.9, 135.0, 130.7, 129.8, 129.2, 129.1, 128.9, 126.7, 125.9, 114.5, 113.4, 69.7, 40.0, 38.2; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2\text{S} [\text{M}+\text{NH}_4]^+$: 352.1120, found: m/z 352.1118; IR (neat) 2241, 1585, 1497, 1448, 1308, 1224, 1089 cm^{-1} .

2-(4-Fluorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4b)

According to the General Procedure, the title compound was obtained after 30 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 3:1) gave the product as pale green oil (30 mg, 84% yield). $R_f=0.30$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.93 (m, 2H), 7.76 (tt, $J = 1.2, 7.6$ Hz, 1H), 7.67-7.59 (m, 4H), 7.19-7.15 (m, 2H), 6.38 (d, $J = 2.8$ Hz, 1H), 4.66 (ddd, $J = 2.4, 5.6, 8.4$ Hz, 1H), 3.26 (dd, $J = 5.6, 15.2$ Hz, 1H), 3.18 (dd, $J = 8.8, 15.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.9 (d, $^1J_{\text{CF}} = 256.5$ Hz), 141.9, 135.9, 135.0, 129.9, 128.93, 128.86 (d, $^3J_{\text{CF}} = 6.7$ Hz), 125.9, 125.5, 116.6 (d, $^2J_{\text{CF}} = 22.9$ Hz), 114.3, 113.3, 69.7, 40.2, 38.3; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}_2\text{S} [\text{M}+\text{NH}_4]^+$: 370.1026, found: m/z 370.1028; IR (neat) 2283, 1604, 1512, 1447, 1321, 1239, 1150, 1085 cm^{-1} .

2-(4-Chlorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4c)

According to the General Procedure, the title compound was obtained after 24 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 3:1) gave the product as pale green oil (34 mg, 92% yield). $R_f=0.33$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.92 (m, 2H), 7.76 (t, $J = 7.6$ Hz, 1H), 7.67-7.63 (m, 2H), 7.56-7.53 (m, 2H), 7.46-7.44 (m, 2H), 6.44 (d, $J = 2.8$ Hz, 1H), 4.66 (ddd, $J = 2.8, 5.6, 8.4$ Hz, 1H), 3.26 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.18 (dd, $J = 8.4, 15.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.7, 136.9, 135.8, 135.0, 129.9, 129.6, 128.9, 128.0, 127.6, 126.6, 114.2, 113.2, 69.7, 40.0, 38.2; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_3\text{O}_2\text{S} [\text{M}+\text{NH}_4]^+$: 386.0730, found: m/z 386.0736; IR (neat) 2262, 1494, 1448, 1405, 1311, 1266, 1219, 1154, 1096 cm^{-1} .

2-(4-Bromophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4d)

According to the General Procedure, the title compound was obtained after 8 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 3:1) gave the product as pale green solids (38 mg, 92% yield). $R_f=0.33$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.92 (m, 2H), 7.77 (tt, $J = 7.6, 1.2$ Hz, 1H), 7.67-7.55 (m, 4H), 7.49-7.45 (m, 2H), 6.44 (d, $J = 2.8$ Hz, 1H), 4.66 (ddd, $J = 2.8, 5.6, 8.4$ Hz, 1H), 3.26 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.18 (dd, $J = 8.4, 15.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.8,

135.8, 135.0, 132.5, 129.9, 128.9, 128.1, 128.0, 126.7, 125.2, 114.2, 113.2, 69.7, 39.9, 38.2; HRMS calcd for $C_{19}H_{17}BrN_3O_2S [M+NH_4]^+$: 430.0225, found: m/z 430.0226; IR (neat) 2233, 1492, 1447, 1322, 1276, 1266, 1152, 1085 cm^{-1} . Single crystals were obtained by recrystallization from acetone and hexane.

2-(4-Iodophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4e)

According to the General Procedure, the title compound was obtained after 48 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 2:1) gave the product as gray solids (25 mg, 54% yield). $R_f=0.33$ (hexane:EtOAc = 2:1); 1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.76 (t, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 6.47 (d, $J = 2.8$ Hz, 1H), 4.64 (ddd, $J = 2.4, 5.6, 8.4$ Hz, 1H), 3.25 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.18 (dd, $J = 8.4, 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 138.5, 135.8, 135.1, 129.9, 128.9, 128.6, 128.1, 126.7, 114.2, 113.2, 97.3, 69.7, 39.9, 38.2; HRMS calcd for $C_{19}H_{17}IN_3O_2S [M+NH_4]^+$: 478.0086, found: m/z 478.0081; IR (neat) 2256, 1583, 1488, 1447, 1397, 1309, 1155, 1085, 1005 cm^{-1} .

2-(4-Nitrophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4f)

A 10 mL flame-dried test tube with a magnetic stirring bar was charged with **1a** (1.2 mg, 0.003 mmol), Cs_2CO_3 (1.0 mg, 0.003 mmol), allenyl sulfone **2a** (18 mg, 0.1 mmol), and **3f** (24 mg, 0.12 mmol). The test tube was filled with argon by the evacuation–refill process. After addition of THF (0.5 mL), the mixture was stirred at ambient for 12 h. To the suspension, additional **1a** (1.2 mg, 0.003 mmol) and Cs_2CO_3 (1.0 mg, 0.003 mmol) were added and the mixture was stirred for 5 h. After evaporation of THF *in vacuo*, the residue was purified by silica-gel column chromatography (hexane:EtOAc = 4:1 to 1:2) to give product **4f** as white solids (20 mg, 53% yield). $R_f=0.24$ (hexane:EtOAc = 2:1); 1H NMR (400 MHz, $CDCl_3$) δ 8.36–8.33 (m, 2H), 7.97–7.94 (m, 2H), 7.82–7.77 (m, 3H), 7.70–7.66 (m, 2H), 6.64 (d, $J = 2.4$ Hz, 1H), 4.71 (ddd, $J = 2.8, 5.6, 8.4$ Hz, 1H), 3.32 (dd, $J = 5.6, 15.2$ Hz, 1H), 3.21 (dd, $J = 8.8, 15.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 140.9, 135.9, 135.2, 135.1, 130.4, 130.0, 128.8, 127.8, 124.5, 113.9, 112.9, 69.7, 40.1, 38.2; HRMS calcd for $C_{19}H_{17}N_4O_4S [M+NH_4]^+$: 397.0971, found: m/z 397.0968; IR (neat) 2249, 1598, 1516, 1447, 1352, 1155, 1084 cm^{-1} .

4-(Phenylsulfonyl)-2-(*p*-tolyl)cyclopent-2-ene-1,1-dicarbonitrile (4g)

According to the General Procedure, the title compound was obtained after 20 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 2:1) gave the product as pale yellow oil (31 mg, 88% yield). $R_f=0.39$ (hexane:EtOAc = 2:1); 1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.92 (m, 2H), 7.75 (tt, $J = 1.6, 7.2$ Hz, 1H), 7.66–7.62 (m, 2H), 7.51–7.49 (m, 2H), 7.27–7.25 (m, 2H), 6.39 (d, $J = 2.4$ Hz, 1H), 4.66 (ddd, $J = 2.4, 5.6, 8.4$ Hz, 1H), 3.24 (dd, $J = 5.2, 15.6$ Hz, 1H), 3.18 (dd, $J = 8.8, 15.2$ Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.1, 135.8, 134.9, 129.9, 129.8, 128.9, 126.6, 126.3, 124.7, 114.6, 113.5, 69.7, 39.9, 38.2, 21.3; HRMS calcd for $C_{20}H_{20}N_3O_2S [M+NH_4]^+$: 366.1276, found: m/z 366.1275; IR (neat) 2260, 1509, 1447, 1309, 1152, 1085 cm^{-1} .

2-(3-Fluorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4h)

According to the General Procedure, the title compound was obtained after 31 h. Silica gel column chromatography (hexane:EtOAc = 4:1) gave the product as pale green oil (30 mg, 85% yield). $R_f=0.33$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97-7.93 (m, 2H), 7.77 (tt, $J = 1.2, 7.6$ Hz, 1H), 7.68-7.62 (m, 2H), 7.48-7.39 (m, 2H), 7.32-7.16 (m, 2H), 6.45 (d, $J = 2.8$ Hz, 1H), 4.67 (ddd, $J = 2.8, 5.6, 8.4$ Hz, 1H), 3.27 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.19 (dd, $J = 8.8, 15.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 162.8 (d, $^1J_{\text{CF}} = 252.8$ Hz), 141.7, 135.8, 135.0, 131.2 (d, $^3J_{\text{CF}} = 7.6$ Hz), 131.1 (d, $^3J_{\text{CF}} = 8.6$ Hz), 129.9, 128.9, 127.6, 122.5, 117.8 (d, $^2J_{\text{CF}} = 22.0$ Hz), 114.2, 113.9 (d, $^2J_{\text{CF}} = 23.8$ Hz), 113.2, 69.6, 40.1, 38.2; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{FN}_3\text{O}_2\text{S}$ $[\text{M}+\text{NH}_4]^+$: 370.1026, found: m/z 370.1021; IR (neat) 2225, 1446, 1322, 1266, 1153, 1085 cm^{-1} .

2-(3-Chlorophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4i)

According to the General Procedure, the title compound was obtained after 20 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 3:1) gave the product as pale green oil (31 mg, 84% yield). $R_f=0.33$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.93 (m, 2H), 7.78 (tt, $J = 1.2, 7.6$ Hz, 1H), 7.70-7.64 (m, 2H), 7.55-7.40 (m, 4H), 6.45 (d, $J = 2.8$ Hz, 1H), 4.67 (ddd, $J = 2.4, 5.2, 8.4$ Hz, 1H), 3.28 (dd, $J = 5.2, 15.2$ Hz, 1H), 3.19 (dd, $J = 8.8, 15.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.6, 135.9, 135.3, 135.1, 130.9, 130.8, 130.6, 129.9, 128.9, 127.7, 126.9, 124.7, 114.2, 113.2, 69.6, 40.0, 38.2; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{ClN}_3\text{O}_2\text{S}$ $[\text{M}+\text{NH}_4]^+$: 386.0730, found: m/z 386.0732; IR (neat) 2278, 1567, 1447, 1321, 1268, 1085 cm^{-1} .

2-(3-Bromophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4j)

According to the General Procedure, the title compound was obtained after 20 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 3:1) gave the product as pale green oil (36 mg, 87% yield). $R_f=0.32$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.77 (t, $J = 7.2$ Hz, 1H), 7.70-7.55 (m, 5H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.45 (d, $J = 2.4$ Hz, 1H), 4.67 (ddd, $J = 2.4, 5.6, 8.4$ Hz, 1H), 3.27 (dd, $J = 5.2, 15.2$ Hz, 1H), 3.19 (dd, $J = 8.8, 15.6$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 141.5, 135.9, 135.1, 133.7, 131.2, 130.8, 129.9, 129.8, 128.9, 127.7, 125.1, 123.3, 114.1, 113.1, 69.6, 40.0, 38.2; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_3\text{O}_2\text{S}$ $[\text{M}+\text{NH}_4]^+$: 430.0225, found: m/z 430.0223; IR (neat) 2229, 1560, 1447, 1322, 1085 cm^{-1} .

2-(3-Iodophenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4k)

According to the General Procedure, the title compound was obtained after 46 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 2:1) gave the product as pale yellow oil (42 mg, 91% yield). $R_f=0.32$ (hexane:EtOAc = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.95-7.93 (m, 2H), 7.89-7.87 (m, 1H), 7.82-7.76 (m, 2H), 7.68-7.58 (m, 2H), 7.36 (t, $J = 8.0$ Hz, 1H), 6.44 (d, $J = 2.4$ Hz, 1H), 4.66 (ddd, $J = 2.8, 5.2, 8.4$ Hz, 1H), 3.27 (dd, $J = 5.6, 15.6$ Hz, 1H), 3.18 (dd, $J = 8.8, 15.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz,

CDCl₃) δ 141.4, 139.6, 135.9, 135.7, 135.1, 131.2, 130.8, 129.9, 128.9, 127.5, 125.6, 114.1, 113.1, 94.9, 69.6, 40.0, 38.3; HRMS calcd for C₁₉H₁₇IN₃O₂S [M+NH₄]⁺: 478.0086, found: *m/z* 478.0087; IR (neat) 2249, 1554, 1447, 1309, 1151, 1082 cm⁻¹.

4-(Phenylsulfonyl)-2-(*m*-tolyl)cyclopent-2-ene-1,1-dicarbonitrile (4l)

According to the General Procedure, the title compound was obtained after 19 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 1:1) gave the product as pale green oil (31 mg, 88% yield). *R_f*=0.32 (hexane:EtOAc = 2:1); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.93 (m, 2H), 7.75 (tt, *J* = 1.2, 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 2H), 7.42-7.25 (m, 4H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.66 (ddd, *J* = 2.4, 5.6, 8.4 Hz, 1H), 3.24 (dd, *J* = 5.6, 15.2 Hz, 1H), 3.18 (dd, *J* = 8.8, 15.6 Hz, 1H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.0, 139.1, 135.9, 134.9, 131.5, 129.8, 129.10, 129.08, 128.9, 127.3, 125.6, 123.8, 114.5, 113.5, 69.7, 40.0, 38.3, 21.4; HRMS calcd for C₂₀H₂₀N₃O₂S [M+NH₄]⁺: 366.1276, found: *m/z* 366.1272; IR (neat) 2283, 1585, 1448, 1322, 1267, 1153, 1086 cm⁻¹.

2-(3-Methoxyphenyl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4m)

According to the General Procedure, the title compound was obtained after 19 h. Silica gel column chromatography (hexane:EtOAc = 3:1) gave the product as pale yellow oil (35 mg, 95% yield). *R_f*=0.26 (hexane:EtOAc = 2:1); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 7.75 (tt, *J* = 1.2, 7.2 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.20-7.19 (m, 1H), 7.09-7.08 (m, 1H), 7.02-6.99 (m, 1H), 6.42 (d, *J* = 2.8 Hz, 1H), 4.66 (ddd, *J* = 2.4, 5.6, 8.0 Hz, 1H), 3.85 (s, 3H), 3.25 (dd, *J* = 5.6, 15.6 Hz, 1H), 3.18 (dd, *J* = 8.4, 15.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 142.7, 135.8, 135.0, 130.4, 130.3, 129.8, 128.9, 126.3, 119.0, 116.2, 114.5, 113.4, 112.3, 69.6, 55.3, 40.1, 38.2; HRMS calcd for C₂₀H₂₀N₃O₃S [M+NH₄]⁺: 382.1225, found: *m/z* 382.1223; IR (neat) 2256, 1601, 1580, 1491, 1447, 1319, 1217, 1151, 1085, 1038 cm⁻¹.

2-(Naphthalen-2-yl)-4-(phenylsulfonyl)cyclopent-2-ene-1,1-dicarbonitrile (4n)

According to the General Procedure, the title compound was obtained after 45 h. Silica gel column chromatography (hexane:EtOAc = 4:1 to 1:3) gave the product as pale yellow solids (28 mg, 73% yield). *R_f*=0.29 (hexane:EtOAc = 2:1); ¹H NMR (400 MHz, acetone-*d*₆) δ 8.29 (d, *J* = 1.6 Hz, 1H), 8.06-7.90 (m, 6H), 7.83 (tt, *J* = 1.6, 7.6 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.65-7.60 (m, 2H), 6.91 (d, *J* = 2.8 Hz, 1H), 5.15 (ddd, *J* = 2.8, 4.4, 8.8 Hz, 1H), 3.57 (dd, *J* = 8.8, 15.6 Hz, 1H), 3.43 (dd, *J* = 4.4, 15.6 Hz, 1H); ¹³C NMR (100 MHz, acetone-*d*₆) δ 142.8, 138.1, 135.7, 134.9, 134.0, 130.8, 130.2, 130.1, 129.7, 129.3, 128.8, 128.4, 128.2, 127.4, 124.9, 116.3, 115.5, 71.0, 41.2, 39.1; HRMS calcd for C₂₃H₂₀N₃O₂S [M+NH₄]⁺: 402.1276, found: *m/z* 402.1273; IR (neat) 2229, 1315, 1146 cm⁻¹.

Deposition number CCDC-1485660 for compound **4d**. Free copies of the data can be obtained via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

This work was financially supported by JSPS KAKENHI (15K18841).

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