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Synthesis of a Class of Fused δ-Sultone Heterocycles *via* DBU-Catalyzed Direct Annulative SuFEx Click of Ethenesulfonyl Fluorides and Pyrazolones or 1,3-Dicarbonyl Compounds

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Abstract. (*E*)-2-(hetero)arylethenesulfonyl fluorides and (*E*,*E*)-1,3-dienylsulfonyl fluorides are bis-electrophiles and rare members of the sulfonyl fluoride family with limited information being known of their reactivity and synthetic utility. The direct annulation reaction of these 2-substituted ethenesulfonyl fluorides with medicinally important enolizable pyrazolones and 1,3-dicarbonyl compounds utilizing catalytic DBU in DCM under mild conditions leads to over 50 structurally diverse δ-sultone fused heterocycles with a pyrazolone ring or a cyclic enone, respectively, in good to excellent yield. The double bond at the 1-position adjacent to the sulfonyl fluoride group in 1,3-dienylsulfonyl fluoride is the chemoselective site of reactivity but is less reactive than the double bond of arylethenesulfonyl fluoride. High turnover and robustness of construction for these fused heterocycles, including the novel fused pyrazolone δ-sultone heterocycle series, may make compounds like these attractive to drug discovery, development and material science.

Keywords: DBU; Ethenesulfonyl fluorides; Fused δ-sultone; Pyrazolones

Sulfonyl fluorides are an essential sulfur-containing functional group that serve utilities in a broad range of chemical disciplines. For example, in industrial chemistry, DOW AgroSciences-produced Vikane® (sulfuryl fluoride) is used as a fumigant gas,[1] in chemical biology, sulfonyl fluorides comprise warheads in irreversible probes and inhibitors of proteins,[2] and in organic chemistry they are identified as connectors for SuFEx-based click chemistry.[3] Although Truce and Hoerger reported over one half-century ago the first synthesis of 2-phenylethenesulfonyl fluoride from the action of boiling aqueous potassium fluoride on the corresponding sulfonyl chloride precursor, this class

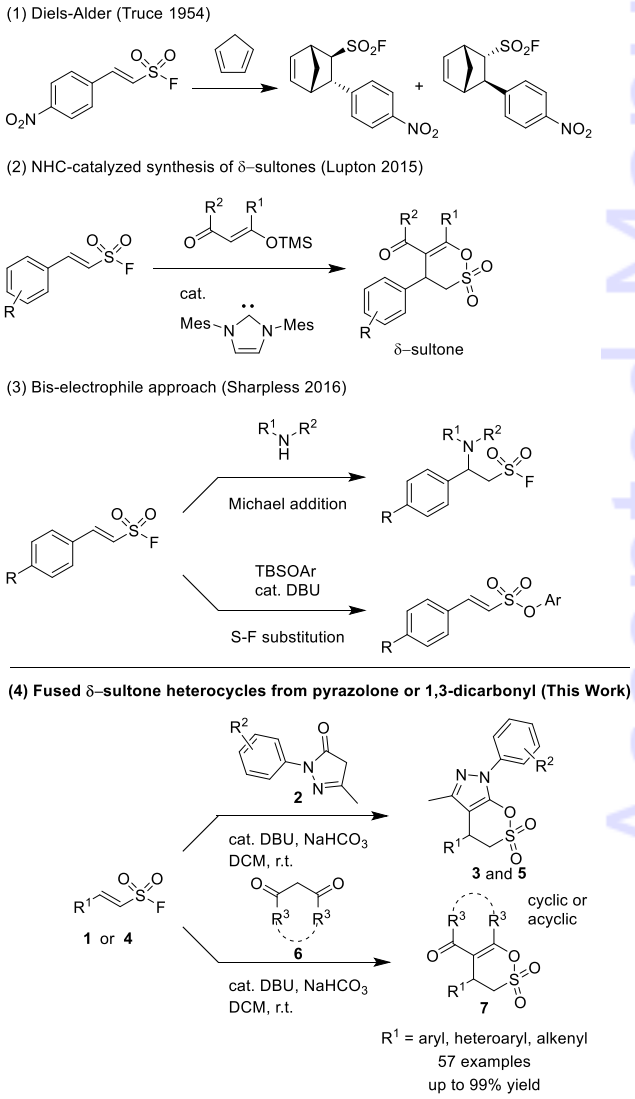

Figure 1. Reactions of substituted ethenesulfonyl fluorides.

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of sulfonyl fluoride remains the least studied, although several methods have been developed for the accessibility of nearly 100 structurally diverse (*E*)-2-(hetero)arylethenesulfonyl fluorides. [4-9]

The attractiveness of arylethenesulfonyl fluoride as a useful synthetic intermediate in organic chemistry lies in their unusual simultaneous incorporation of two chemoselective electrophilic sites: a Michael acceptor olefinic site and a latent S−F bond that may be activated toward substitution *via* DBU catalysis and the presence of aryl silyl ethers (Figure 1).[7] Thus, the vinyl sulfonyl fluoride group is preloaded for initial Michael addition and subsequent intramolecular cyclizations at the sulfur center. The synthesis of fused 1,2,4-thiadiazine 1,1-dioxides from the reaction of ESF and heterocyclic amines in good yield by Krutag and Hyatt in 1979 provides the oldest example.[10] ESF holds one of the highest positions on the Michael acceptor reactivity scale although β-substitution modulates its potential to undergo attack by a significant magnitude.[7,11] Ungureanu et al. in 2015 showed one of the best to date examples of arylethenesulfonyl fluoride reactivity in the synthesis of δ-sultones through N-heterocyclic carbene (NHC) catalysis of trimethylsilylated 1,3-dicarbonyl compounds and arylethenesulfonyl fluorides.[5a] The trimethylsilyl group serves necessary dual roles in this case by preloading the enol while becoming available to scavenge the fluoride leaving group. The sultones, in turn are oxidized sulfur analogues of lactones first reported by Erdmann in 1888, and considerable advances have been made in their synthesis and application.[12] Only a few other reactions of arylethenesulfonyl fluorides are known such as the participation of electon-deficient 2-*p*-nitrophenylethenesulfonyl fluoride as a dienophile in a Diels−Alder[4] reaction with cyclopentadiene and in a Friedal−Crafts[7] like reaction with *p*-xylene and stoichiometric aluminum trichloride.

We were inspired together by elucidating the reactivity of the ethenesulfonyl fluoride family and by a long withstanding problem in the field of medicinal chemistry. Large data cluster analysis going back four decades in drug discovery and manufacturing points to an invariable bias toward certain reaction types, particularly amide bond formation, Suzuki−Miyaura coupling, and S_NAr N-arylation.[13] Heterocyclic synthesis on the other hand is comparatively underutilized[13c-d] or has observed a dramatic decrease in use in this context.[13b] Consequently, developing efficient methods that include a high degree of functional group tolerance, robustness, and easy availability of diverse starting materials for the synthesis of difficult to access or otherwise novel heterocyclic scaffolds is an attractive goal to overcome constraints on chemical space. We hypothesized that Michael reaction between an enolizable substrate and a 2-substituted ethenesulfonyl fluoride using weak base while leaving the S−F bond intact followed by DBU activation of fluoride and cyclization could be achieved synthetically in one reaction flask. A survey of intriguing substrates attracted us to functionalized pyrazoles, which represent the core motif of numerous biologically active molecules and have been widely used in pharmaceuticals, agrochemicals, and in other functional materials.[14] Many pyrazole derivatives have been successfully developed as drugs or drug candidates for the treatment of a variety of diseases (Figure 2).[15] Among various types of py-

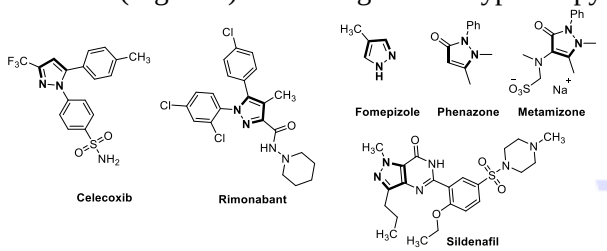

Figure 2. Representative drugs containing pyrazole moities.

razoles, enolizable pyrazolones have been particularly recognized as outstanding scaffolds for the discovery and development of new drugs, therefore, the development of efficient methods for the synthesis of novel pyrazolone heterocycles is of great significance.[16] Herein, we report a DBU-catalyzed direct annulation of (*E*)-2-(hetero)arylethenesulfonyl fluorides and (*E*,*E*)-1,3-dienylsulfonyl fluorides with pyrazolones (or 1,3-dicarbonyl compounds) for the synthesis of a class of novel δ-sultone fused pyrazolones (or δ-sultones fused cyclic enones). These reactions proceed under mild conditions of DBU catalysis and $NaHCO_3$ in DCM at room temperature with good to excellent yield without the need for preformed silylated enols.

It has been reported that the δ-sultones fused cyclic enones are accessible through a N-heterocyclic carbene (NHC) catalyzed reaction of trimethylsilylated 1,3-dicarbonyl compounds and arylethenesulfonyl fluorides[5a] or *via* a stoichiometric amount of triethylamine promoted procedure.[11] DBU, an abundant and inexpensive unique base has been widely used as nucleophilic catalyst for activation of a variety of nucleophiles.[17] It will be of great advantage if the δ-sultones fused heterocycles can be directly furnished through the reaction of arylethenesulfonyl fluorides and carbonyl compounds with catalytic amount of DBU. Accordingly, the reaction of (*E*)-2-phenylethenesulfonyl fluoride **1a** and enolizable pyrazolone **2a** in the presence of nitrogenous catalyst and stoichiometric $NaHCO_3$ to form fused δ-sultone heterocycle **3a** was initially investigated (Table 1). Extensive screening of catalyst (entries 1−4), catalytic loading (entries 2, 5−8), stoichiometric equivalents (entries 9−11), and solvent (entries 12−15) revealed that equimolar amounts of both pyrazolone and $NaHCO_3$ and 5 mol% DBU in DCM at room temperature for 24 h were required to afford the optimized isolated yield of 94% of **3a** (entry 15). Next, we turned our attention to the evaluation of functional group tolera-

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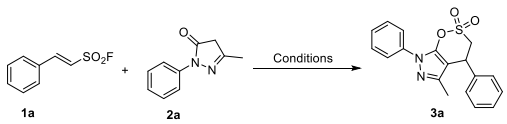
Table 1. Screening of reaction conditions of annulative δ-sultonation.[a]

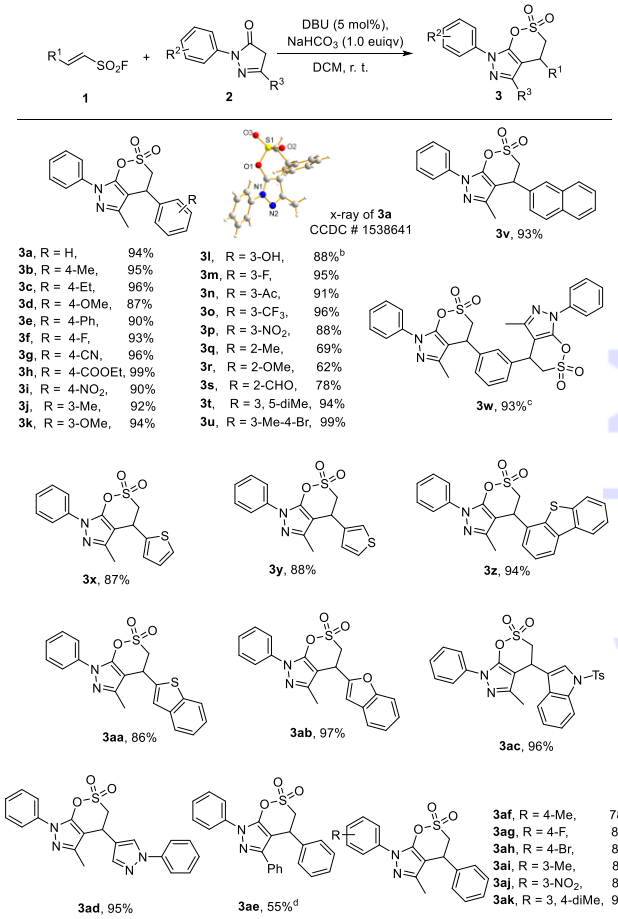


Entry	Solvent	Base (mol%)	Ratio (**1a**: **2a**)	$NaHCO_3$ (equiv)	Yield [b] (**3a**, %)
1	DCM	Et_3N (20)	1 : 2	2	88 (82)
2	DCM	DBU (20)	1 : 2	2	97
3	DCM	DABCO (20)	1 : 2	2	96
4	DCM	Na_2CO_3 (20)	1 : 2	2	9
5	DCM	DBU (1)	1 : 2	2	11
6	DCM	DBU (5)	1 : 2	2	97
7	DCM	DBU (10)	1 : 2	2	94
8	DCM	DBU (50)	1 : 2	2	43
9	DCM	DBU (5)	1 : 2	1	98
10	DCM	DBU (5)	1 : 2	/	17
11	DCM	DBU (5)	1 : 1	1	95
12	CH_3CN	DBU (5)	1 : 1	1	65
13	Acetone	DBU (5)	1 : 1	1	45
14	DMSO	DBU (5)	1 : 1	1	75
15[c]	DCM	DBU (5)	1 : 1	1	97 (94)

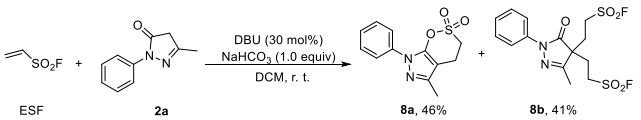
[a] Reaction conditions: (E)-2-phenylethene-1-sulfonyl fluoride (**1a**, 0.1 mmol), 3-methyl-1-phenyl-2-pyrazolin-5-one (**2a**) , base, $NaHCO_3$, solvent (1 mL) were added in a reaction tube (20 mL) and reacted at the corresponding condition for 24 h at room temperature. [b] The yield was determined by HPLC using **3a** as the external standard (t_R = 4.4 min, λ_{max} = 247.6 nm, methanol/water = 80 : 20 (v / v)). Isolated yield is reported in parenthesis. [c] 0.4 M.

nce and scope for the reaction of substituted (hetero)arylethenesulfonyl fluorides **1** and pyrazolones **2** under the optimized reaction conditions (Table 2). Yields were found to typically be excellent (>85%) for a wide range of electron-withdrawing and electron-donating groups in the *para*- or *meta*- positions of both the ethenesulfonyl fluorides (**3a**–**p**; **3t**–**u**) or the pyrazolones (**3af**–**ak**). Yields suffered somewhat for *ortho*- substitution on either substrate, possibly attributed to sterics (**3q**–**s**; **3ae**). Heteroarylethenesulfonyl fluorides with nitrogen, oxygen, and sulfur in the ring were well tolerated (**3x**–**ad**). Notably, an x-ray crystallographic structure of fused heterocycle **3a** showed the phenyl of the pyrazolone to be close to coplanar with the pyrazolone/δ-sultone ring system while the phenyl stemming from the ethenesulfonyl fluoride to be approximating an orthogonal conformation (Table 2). In comparison ESF, whose reactivity as a Michael acceptor has been measured recently as 4.5 orders of magnitude larger than **1a**,[11] when used in the reaction with pyrazolone **2a** forms approximate amounts the cyclized δ-sultone product **8a** (46%) and the bis-Michael adduct **8b** (41%) (Scheme 1). This observation provides important mechanistic insight that presumably in this case 1) Michael addition proceeds before substitution at sulfur and 2) that the rate of the second intermolecular Michael addition of ESF is competitive with the rate of intramolecular cyclization at the S–F bond.

Table 2. Annulative δ-sultonation of pyrazolones with (hetero)arylethenesulfonyl fluorides.[a]



[a] Reaction conditions: 2-(hetero)arylethenesulfonyl fluoride (**1**, 1.0 mmol), pyrazolone (**2**, 1.0 mmol), DBU (5 mol%), $NaHCO_3$ (1.0 mmol, 1.0 equiv), DCM (2.0 mL), reaction for 24 h at room temperature. [b] 60 mol% DBU was used. [c] 6.0 equiv **2a** and 2.0 equiv $NaHCO_3$ were used. [d] 20 mol% DBU was used.



Scheme 1. Reaction of ESF and pyrazolone **2a**.

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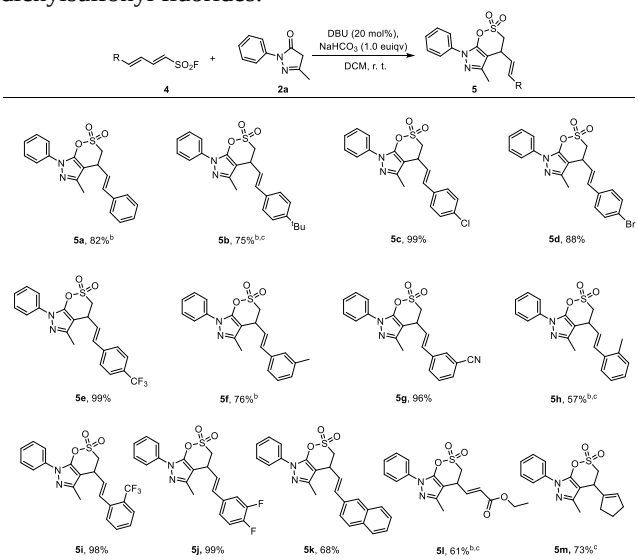
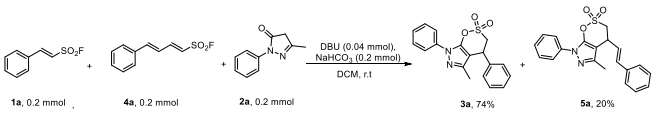
Since 1,3-dienylsulfonyl fluorides **4** possess two conjugated double bonds with the sulfonyl fluoride group, they are a scaffold with the propensity to undergo chemoselective reaction (Table 3). Indeed, in the presence of 20 mol% DBU catalyst good to excellent yields (57-99%) for 13 substrates with pyrazolone **2a** were obtained for the δ-sultone products **5** and not of the hypothetical 8-membered sultone or 6-membered ether ring products stemming

Table 3. Annulative δ-sultonation of pyrazolones with dienylsulfonyl fluorides.[a]



a) Reaction conditions: diethenesulfonyl fluoride (**4**, 1.0 mmol), pyrazolone (**2a**, 1.0 mmol), DBU (20 mol%), $NaHCO_3$ (1.0 mmol, 1.0 equiv), DCM (2.0 mL), reaction for 24 h at room temperature. b) Reaction for 48 h. c) 30 mol% DBU was used.

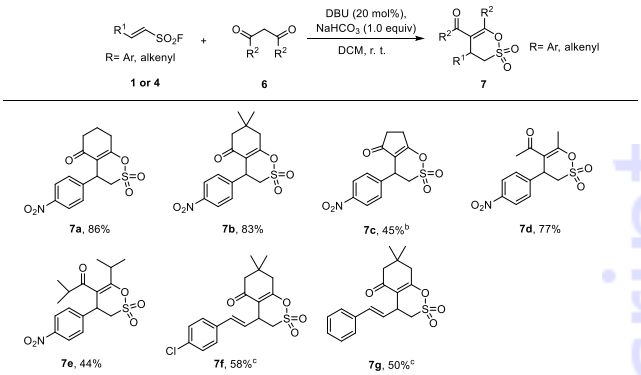
from addition at the distal double bond and then cyclization. This is the first reported reaction as far as we know of the novel 1,3-dienylsulfonyl fluorides, which supports their synthetic usefulness. A competition experiment between equimolar amounts of 2-phenylethenesulfonyl fluoride **1a**, and 4-phenyl-1,3-dienylsulfonyl fluoride **4a**, for pyrazolone **2a** demonstrated the reactivity to be greater for the single double bonded sulfonyl fluoride **1a** (Scheme 2).



Scheme 2. Competition between ethenesulfonyl fluorides for annulative δ-sultonation.

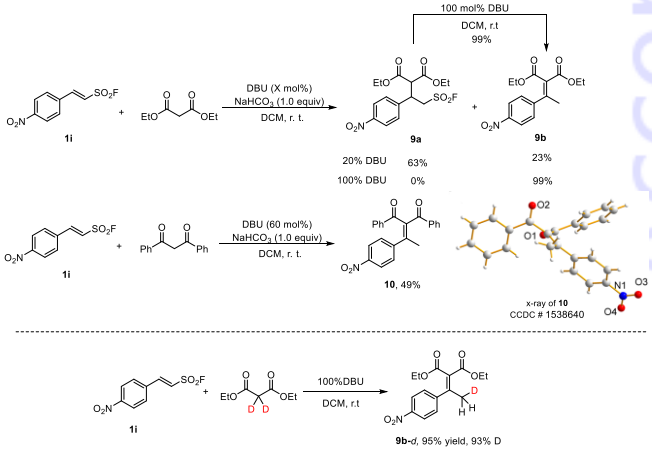
The cyclic symmetrical 1,3-dicarbonyl compounds (**6a−c**) were found to form fused cyclic enone δ-sultone heterocycles (**7a−c**) when reacted with *p*-nitrophenylethenesulfonyl fluoride **1i**, whereas less sterically hindered acyclic substrates (**6d, 6e**) form δ-sultone heterocycles (**7d, 7e**) (Table 4). Furthermore, 1,3-dienylethenesulfonyl fluorides also form fused cyclic enone δ-sultone heterocycles (**7f, 7g**) chemoselectively from a cyclic 1,3-dicarbonyl.

Table 4. δ-Sultonation of ketones with *p*-nitrophenylethenesulfonyl fluoride **1i** or diethenesulfonyl fluorides.[a]

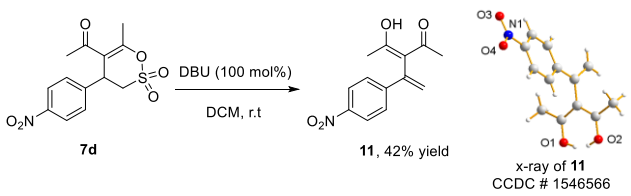


a) Reaction conditions: 2-(hetero)arylethenesulfonyl fluoride or diethenesulfonyl fluoride (**1** or **4**, 1.0 mmol), ketone (**6**, 1.0 mmol), DBU (20 mol%), $NaHCO_3$ (1.0 mmol, 1.0 equiv), DCM (2.0 mL), reaction for 24 h at room temperature. b) DMSO (2.0 mL) as the solvent. c) 40 mol% DBU was used and reacted for 96 h.

On the other hand, *p*-nitrophenylethenesulfonyl fluoride **1i** and diethyl malonate (or dibenzoylmethane) under catalytic DBU and $NaHCO_3$ in DCM afford the Michael adduct **9a** without cyclization which can then be driven to eliminate sulfonyl fluoride to form enedione **9b** (or **10**) when DBU approaches one equivalent (Scheme 3). A deuterium labeling experiment is consistent with **9a** undergoing a benzylic hydride shift with elimination of SO_2 and HF. Decomposition and loss of SO_2 was also observed for δ-sultone **7d** in the presence of stoichiometric DBU (Scheme 4).



Scheme 3. Reaction of arylethenesulfonyl fluoride **1i** and acyclic 1,3-dicarbonyls and a deuterium labeling experiment.



Scheme 4. Decomposition experiment of fused cyclic enone δ-sultone **7d**.

In conclusion, we have demonstrated here that the rare 2-(hetero)arylethenesulfonyl fluorides and 1,3-dienylsulfonyl fluorides, whose wider synthesis and reactivity has remained elusive until very recently, are versatile substrates for the synthesis of many fused δ-sultone-based heterocycles with pyrazolones or directly from 1,3-dicarbonyl compounds. The reactions described herein are characterized by heterocyclic novelty, high functional group tolerance, operation under mild conditions, and accessibility of starting materials lending them to high turnover and product structural diversity. These features may be advantageous to the search and development of new molecular-based medicines, which has observed limitations on chemical space and reaction usage over time.

Experimental Section

General procedure for compound 3.

An oven-dried reaction tube (20 mL) was charged with (hetero)arylethenesulfonyl fluoride (**1**, 1.0 mmol), pyrazolone (**2**, 1.0 mmol, 1.0 equiv), DBU solution (38 mg dissolved in 10 mL DCM, 2 mL, 5 mol%), and $NaHCO_3$ (84 mg, 1.0 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 3-24 h with monitoring by TLC. The crude products were purified by column chromatography on silica gel to give **3**.

General procedure for compound 5.

An oven-dried reaction tube (20 mL) was charged with dienylsulfonyl fluoride (**4**, 1.0 mmol), pyrazolone (**2a**, 1.0 mmol, 1.0 equiv), DBU (31 mg, 20 mol%), $NaHCO_3$ (84 mg, 1.0 mmol, 1.0 equiv), and DCM (2 mL). The resulting mixture was stirred at room temperature for 6-48 h with monitoring by TLC. The crude products were purified by column chromatography on silica gel to give **5**

General procedure for compound 7.

An oven-dried reaction tube (20 mL) was charged with *p*-nitrophenylethenesulfonyl fluoride **1i** or dienylsulfonyl fluorides (**1** or **4**, 1.0 mmol), ketone (**6**, 1.0 mmol, 1.0 equiv), DBU (31 mg, 20 mol%), $NaHCO_3$ (84 mg, 1.0 mmol, 1.0 equiv), and DCM (2 mL). The resulting mixture was stirred at room temperature for 24-96 h with monitoring by TLC. The crude products were purified by column chromatography on silica gel to give **7**.

CCDC-1538641, 1538640, and 1546566 contains the supplementary crystallographic data for compounds **3a**, **10** and **11**, respectively, in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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UPDATE

Synthesis of a Class of Fused δ-Sultone Heterocycles *via* DBU-Catalyzed Direct Annulative SuFEx Click of Ethenesulfonyl Fluorides and Pyrazolones or 1,3-Dicarbonyl Compounds

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