Copper(I)-catalyzed Cyclization Reactions of Ethyl (*E*)-α-Ethynyl-β-Aryl-α,β-Unsaturated Esters with *N*-Sulfonyl Azides: Synthesis of 1-Aminonaphthalene, 3-Aminobenzofuran, and 3-Aminothiobenzofuran Derivatives

Jeong-Yu Son, Gi Uk Han, Gi Hoon Ko, Chanyoung Maeng, Seohyun Shin, and Phil Ho Lee*

Department of Chemistry, Kangwon National University, Chuncheon 24341, Republic of Korea.
**E-mail: phlee@kangwon.ac.kr*
Received March 5, 2019, Accepted April 17, 2019

A synthetic method for ethyl 4-(alkyl or arylsulfonamido)-2-naphthoates from ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters (**1**) and *N*-sulfonyl azides (**2**) in the presence of 2,6-lutidine in THF at 60 °C for 3 h was developed in one step, in which a copper(I)-catalyzed 1,3-dipolar cycloaddition, ketenimine formation, and 6π-electrocyclization followed by [1,3]-H shift tandem reaction took place. This method enabled efficient synthesis of a wide range of 1-aminonaphthalene and 3-aminobenzofuran and 3-aminobenzothiophene derivatives with the release of molecular nitrogen.

Keywords: Aminonaphthalene, Dipolar cycloaddition, Ketenimine, Cyclization, Copper

Introduction

The structural motif of 1-aminonaphthalenes exists broadly in biologically active compounds used as a protein kinase and angiogenesis inhibitors for the treatment of cancer,[1] Mcl-1 inhibitors,[2] p38 inhibitors,[3] and BRAF inhibitors (Figure 1).[4] Accordingly, development of efficient synthetic method for functionalized 1-aminonaphthalene derivatives is of great importance.

Normally, functionalized 1-aminonaphthalene derivatives were prepared by nucleophilic aromatic substitution reaction of 1-halonaphthalene derivatives with primary amines.[5] High reaction temperature and boring purification steps were frequently demanded in this method. Pd-catalyzed Buchwald–Hartwig amination reaction was demonstrated to be a suitable alternative approach to 1-aminonaphthalene derivatives from 1-halonaphthalene derivatives.[6] However, some functionalized 1-halonaphthalene derivatives are not commercially available.

Recently, we developed Rh-catalyzed denitrogenative cyclization of (*E*)-ethyl 2-(1-alkyl and arylsulfonyl-1*H*-1,-2,3-triazol-4-yl)-3-arylacrylate obtained from ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters and *N*-sulfonyl azides with a copper(I) catalyst for the synthesis of a variety of functionalized benzofulvenes (Scheme 1, Eq. 1).[7] In addition, the synthesis of benzofulvenes was proved as a one-pot method through tandem Cu(I)-catalyzed [3 + 2] cycloaddition followed by Rh(II)-catalyzed denitrogenative

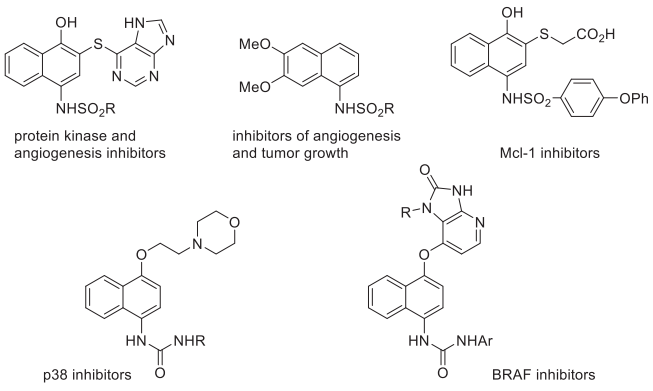
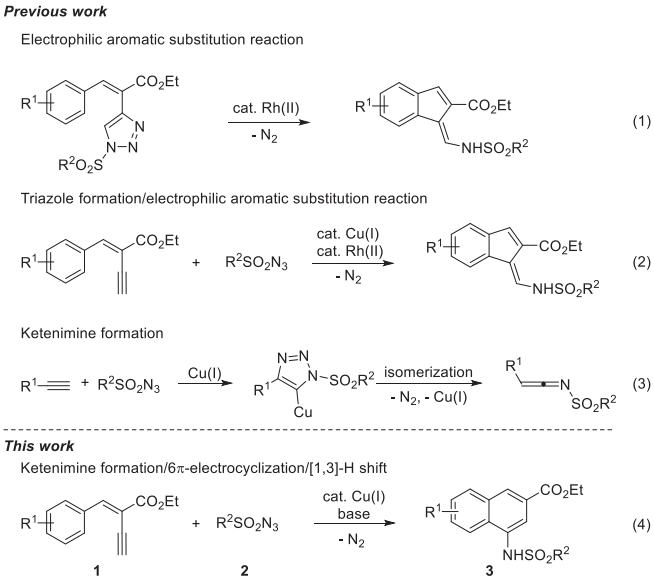


Figure 1. Bioactive 1-aminonaphthalene derivatives.



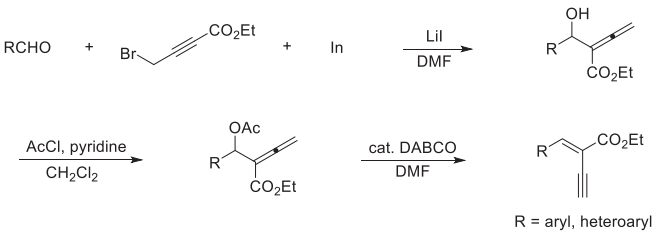
Scheme 1. Intramolecular cyclization of ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters.

cyclization from ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters and *N*-sulfonyl azides (Eq. 2).[7] Moreover, a Cu(I)-catalyzed 1,3-dipolar cycloaddition followed by ring-chain isomerization to ketenimine formation tandem process was reported by Chang *et al*. (Eq. 3).[8] Taking the progress of Rh(II)-catalyzed denitrogenative cyclization and Cu(I)-catalyzed ketenimine formation in mind, we envisaged that ethyl 4-(alkyl or aryl)sulfonamido-2-naphthoate (**3**) could be synthesized through a tandem reaction of ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters (**1**) with *N*-sulfonyl azides (**2**). Furthermore, the sulfonamide skeleton is frequently utilized in the design of bioactive compounds.[9] Many drugs bearing *N*-arylsulfonamides are in clinical use as HIV-1 protease inhibitors,[10] non-nucleotide reverse transcriptase inhibitors,[11] anti-bacterials,[12] and antitumor agents.[13] Herein, we develop a very practical method to synthesize ethyl 4-(alkyl or arylsulfonamido)-2-naphthoates from ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters (**1**) in one step, in which a Cu(I)-catalyzed 1,3-dipolar cycloaddition, ketenimine formation, and 6π-electrocyclization followed by [1,3]-H shift tandem reaction took place (Eq. 4).

Results and Discussion

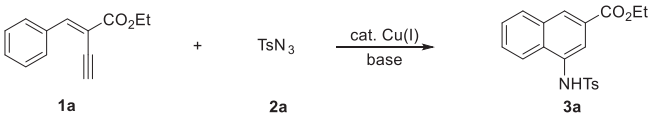
Ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters were prepared in good to excellent yields from treatment of a variety of allenyl acetates, which were prepared from the reaction of aldehydes with organoindium reagent *in situ* generated from ethyl 4-bromobutynoate and indium in the presence of lithium iodide in DMF and subsequent acetylation, with 10.0 mol % DABCO in DMF at room temperature (Scheme 2).[14]

First, we investigated the reaction of ethyl 2-ethynylcinnamate (**1a**) with *N*-tosyl azide (**2a**) using a variety of Cu catalysts (10.0 mol%), bases (1.5 equiv), and solvents (Table 1). Potassium and sodium carbonate in the presence of CuI were not effective in tetrahydrofuran (THF) at 60 °C for 12 h (entries 1 and 2). When pyridine was used, the cyclized product, ethyl 4-((4-methylphenyl) sulfonamido)-2-naphthoate (**3a**), was obtained in 22% yield with the release of molecular nitrogen (entry 3). A variety of bases, such as triethylamine, diisopropylethylamine, and 2,6-lutidine, in THF were screened to reveal that 2,6-lutidine was the best performing base, providing **3a** in



Scheme 2. Preparation of ethyl (*E*)-α-ethynyl-β-aryl-α,-β-unsaturated esters.

Table 1. Reaction optimization.[a]



1a 2a 3a

Entry	Cat.	Base	Solvent	Time (h)	Yield (%)[b]
1	CuI	K_2CO_3	THF	12	0
2	CuI	Na_2CO_3	THF	12	0
3	CuI	Pyridine	THF	5	22
4	CuI	Et_3N	THF	3	10
5	CuI	DIPEA	THF	3	28
6	CuI	2,6-lutidine	THF	3	80 (74)[c]
7	CuI	2,6-lutidine	DCE	3	40
8	CuI	2,6-lutidine	CH_3CN	3	26
9	CuI	2,6-lutidine	Toluene	3	24
10	CuBr	2,6-lutidine	THF	3	30
11	CuCl	2,6-lutidine	THF	3	28

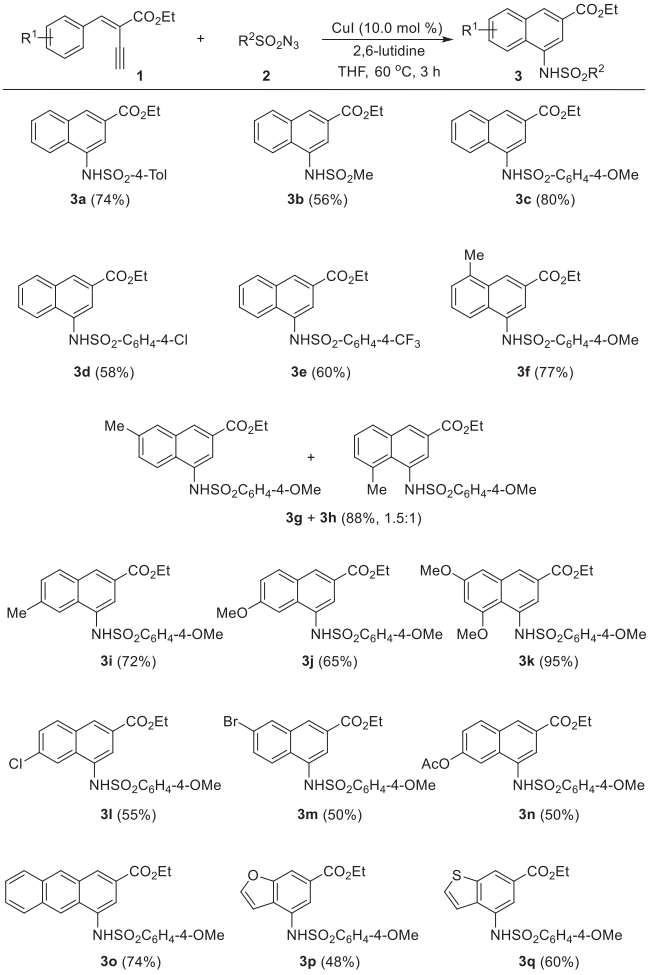
[a] Reactions were carried out with (*E*)-ethyl 2-ethynylcinnamate **1a** (0.2 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (2.0 equiv), CuI (10.0 mol%), and base (1.5 equiv) in solvent (1.0 mL, 0.2 M) at 60 °C.
[b] NMR yield using dibromomethane as an internal standard.
[c] Isolated yield.

80% yield (entries 4, 5, and 6). Further examination of the solvents indicated that tetrahydrofuran (THF) was the optimum solvent, and the other solvents, such as dichloroethane, acetonitrile, and toluene, gave inferior results (entries 6–9). Based on these results, CuBr and CuCl in the presence of 2,6-lutidine in THF were examined to determine that CuI (10.0 mol%) was the best catalyst (entries 6, 10, and 11).

With these optimized reaction conditions, we first examined the substrate scope of *N*-sulfonyl azides (Table 2). Variation of the sulfonyl group in the *N*-sulfonyl azides (**2**) slightly affected the efficiency of the reaction. When *N*-methanesulfonyl azide was used, the desired product, ethyl 4-(methylsulfonamido)-2-naphthoate (**3b**), was obtained in 56% yield. *N*-4-methoxybenzenesulfonyl azide was treated with **1a** under the optimum reaction conditions, the desired cyclized product (**3c**) was obtained in 80% yield with the release of molecular nitrogen. *N*-4-chlorosulfonyl and 4-trifluoromethylsulfonyl azide were reacted with ethyl 2-ethynylcinnamate (**1a**) to produce the corresponding naphthalene derivatives **3d** and **3e** in 58% and 60% yields, respectively.

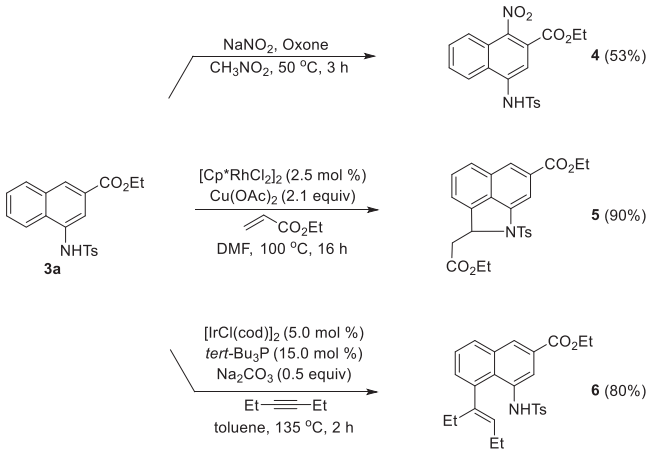
Next, the substrate scope of ethyl (*E*)-α-ethynyl-β-aryl-α,-β-unsaturated esters (**1**) were investigated. Electronic modification of the substituents on the aryl group of ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters (**1**) slightly influenced the reaction efficiency. An electron-donating 2-methyl group provided the desired naphthalene derivative **3f** in 77% yield. *Meta*-methyl-substituted substrate underwent the Cu(I)-catalyzed cyclization reaction at the sterically less hindered

Table 2. Substrate scope of ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters and *N*-sulfonyl azides.[a]



[a] Reactions were carried out with **1** (0.2 mmol, 1.0 equiv), **2** (2.0 equiv), CuI (10.0 mol%), and 2,6-lutidine (1.5 equiv) in THF (1.0 mL, 0.2 M) at 60 °C for 3 h.

site to provide predominantly naphthalene derivative **3g**. These results indicate that the cyclization was influenced by the steric effect rather than an electronic one. Exposure of *para*-methyl- and methoxy-substituted substrate to a CuI catalyst provided naphthalene derivatives **3i** and **3j** in 72% and 65% yields. The ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters having 3,5-dimethoxy groups are good substrate for the present transformation, producing **3k** in 95% yield. Substrates bearing electron-withdrawing chloride and bromide groups underwent the Cu(I)-catalyzed cyclization reaction, leading to the formation of naphthalene derivatives in moderate yields. Regioselective formation of **3m** from *meta*-bromo-substituted substrate indicates that the cyclization was largely effected by the steric effect. Acetoxy-substituted substrate turned out to be compatible with the optimized conditions, providing the corresponding product **3n** in 50% yield. The 2-naphthyl-substituted substrate was selectively cyclized to produce sterically less hindered anthracene derivative **3o**.

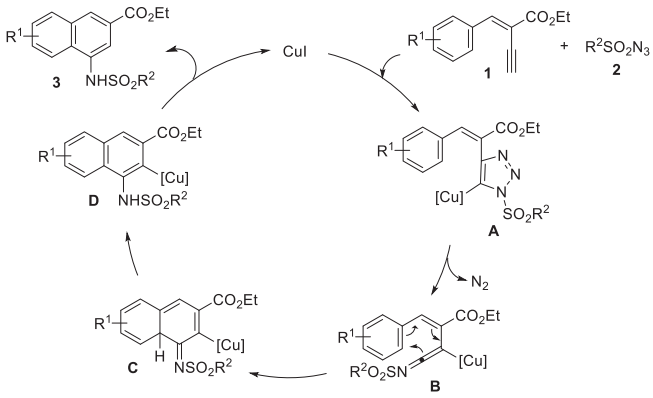


Scheme 3. Nitration and C—H activation using ethyl 4-((4-methylphenyl)sulfonamido)-2-naphthoate.

Gratifyingly, the Cu(I)-catalyzed denitrogenative cyclization reaction using furan-2-yl- and thiophen-2-yl-substituted substrates took place to provide **3p** and **3q** in 48% and 60% yields, respectively.

Next, we investigated the synthetic application of ethyl 4-((4-methylphenyl)sulfonamido)-2-naphthoate (**3a**) on nitration and C—H activation (Scheme 3). When **3a** was treated with sodium nitrate and oxone in nitromethane at 50 °C for 3 h, the nitrated naphthalene derivative **4** was obtained in 53% yield.[15] Additionally, the Rh-catalyzed C—H activation reaction of **3a** with ethyl acrylate in the presence of $Cu(OAc)_2$ in DMF at 100 °C for 16 h produced the isoindole **5** in 90% yield through the alkenylation followed by Michael addition.[16] The Ir-catalyzed alkenylation of **3a** with 3-hexyne in the presence of tri(*tert*-butyl)phosphine and sodium carbonate in toluene at 135 °C for 2 h was successful and produced **6** in 80% yield.[17]

The possible mechanism for this cyclization reaction is described in Scheme 4. As reported by Chang and Wang,[8,18] the reactive ketenimine **B** would be generated by the ring-opening rearrangement of triazole intermediate **A**, which was formed from alkyne **1** and *N*-sulfonyl azide **2** in the presence of CuI and 2,6-lutidine. Subsequently the



Scheme 4. A plausible mechanism.

intramolecular 6π-electrocyclization occurred and provided the intermediate **C**. The following [1,3]-H shift and protodecupration produced the final product, ethyl 4-(alkyl or arylsulfonamido)-2-naphthoate **3**, with regeneration of the copper(I) catalyst.

Experimental

General. Commercial available reagents were used without purification. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light and then, developed using either iodine or a solution of anisaldehyde. 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 NMR spectrometer. Deuterated chloroform was used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-*d*) and δ 77.2 for ^{13}C{^{1}H} (chloroform-*d*). Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) were obtained by electron impact (EI) ionization technique (magnetic sector—electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute Daegu Center). Melting points were determined in open capillary tube.

Synthetic Procedure of Ethyl 4-(4-methylphenylsulfonamido)-2-naphthoate (3a). A mixture of (*E*)-ethyl 2-ethynylcinnamate **1a** (0.2 mmol, 40.0 mg, 1.0 equiv), 4-methylbenzenesulfonyl azide **2a** (0.4 mmol, 78.9 mg, 2.0 equiv), CuI (3.8 mg, 10.0 mol%), and 2,6-lutidine (32.1 mg, 1.5 equiv) was stirred in THF (1.0 mL) at 60 °C for 3 h under N_2. After cooling to room temperature and evaporation of the solvents *in vacuo,* the crude product was purified by column chromatography on silica gel using EtOAc:hexane = 1:2. The desired product was obtained in 74% (34.9 mg) yield.

Ethyl 4-(4-methylphenylsulfonamido)-2-naphthoate (3a). Yield: 34.9 mg (74%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 156–158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.95–7.92 (m, 2H), 7.84 (d, *J* = 1.4 Hz, 1H), 7.67 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.59–7.52 (m, 2H), 7.20 (d, *J* = 7.1 Hz, 2H), 6.69 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 144.0, 136.1, 133.4, 131.9, 131.2, 130.0, 129.9, 129.7, 129.0, 127.5, 127.5, 127.2, 121.9, 61.3, 21.6, 14.3; IR (film) 3255, 1717, 1460, 1400, 780 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{20}H_{19}NO_4S$: 369.1035; Found: 369.1039.

Ethyl 4-(methylsulfonamido)-2-naphthoate (3b). Yield: 33 mg (56%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.19–8.16 (m, 2H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.74–7.70 (m, 1H), 7.64–7.61 (m, 1H), 7.20 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.10 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.6, 131.9, 131.2, 130.4, 130.2, 129.4, 127.8, 127.4, 122.0, 121.9, 61.7, 40.1, 14.4; IR (film) 3263, 1715, 1400, 1629, 775, cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{14}H_{15}NO_4S$: 293.0722; found: 293.0721.

Ethyl 4-(4-methoxyphenylsulfonamido)-2-naphthoate (3c). Yield: 62 mg (80%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.93–7.90 (m, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.71 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.58–7.50 (m, 2H), 7.24 (s, 1H), 6.84 (dt, *J* = 9.9, 2.5 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.2, 133.4, 132.1, 131.1, 130.6, 129.9, 129.8, 129.6, 128.9, 127.5, 127.1, 122.0, 121.7, 114.2, 61.3, 55.6, 14.3; IR (film) 3258, 1716, 1628, 1348, 732 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{20}H_{19}NO_5S$: 385.0984; found: 385.0982.

Ethyl 4-(4-chlorophenylsulfonamido)-2-naphthoate (3d). Yield: 45 mg (58%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 147–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 1.2 Hz, 1H), 7.96–7.93 (m, 2H), 7.83 (d, *J* = 1.4 Hz, 1H), 7.71 (dt, *J* = 9.2, 2.2 Hz, 2H), 7.60–7.53 (m, 2H), 7.37 (dt, *J* = 9.2, 2.2 Hz, 2H), 7.12 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.7, 137.5, 133.5, 131.4, 131.3, 130.5, 130.0, 129.4, 129.2, 128.9, 127.5, 127.3, 122.5, 121.9, 61.5, 14.3; IR (film) 3257, 1718, 1628, 1376, 774, 737 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{16}ClNO_4S$: 389.0489; found: 389.0488.

Ethyl 4-(4-(trifluoromethyl)phenylsulfonamido)-2-naphthoate (3e). Yield: 51 mg (60%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 170–171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.97–7.95 (m, 1H), 7.89 (d, *J* = 8.1 Hz, 3H), 7.81 (d, *J* = 1.4 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.58–7.54 (m, 2H), 6.97 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 142.6, 134.8 (q, J_{CF} = 33.0 Hz), 133.5, 131.5, 131.1, 130.8, 130.0, 129.2, 128.0, 127.6, 127.4, 126.2 (q, J_{CF} = 3.7 Hz), 123.0, 121.7, 61.5, 14.3; IR (film) 3255, 1718, 1629, 1404, 1370, 775 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{20}H_{16}F_3NO_4S$: 423.0752; found: 423.0754.

Ethyl 4-(4-methoxyphenylsulfonamido)-8-methyl-2-naphthoate (3f). Yield: 61.5 mg (77%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 175–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.88 (d, *J* = 1.4 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.70 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.37 (d, *J* = 7.0 Hz, 1H), 6.85 (dt, *J* = 9.9, 2.5 Hz, 2H), 6.77 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.74 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 163.2, 136.7, 132.8, 132.3, 131.4, 130.7, 129.6, 128.6, 127.9, 127.1, 126.1, 121.7, 120.0, 114.2, 61.3, 55.6,

19.8, 14.3; IR (film) 3246, 1713, 1619, 1374, 772 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{21}H_{21}NO_5S$: 399.1140; found: 399.1139.

Ethyl 4-(4-methoxyphenylsulfonamido)-7-methyl-2-naphthoate (3g) and Ethyl 4-(4-methoxyphenylsulfonamido)-5-methyl-2-naphthoate (3h). Yield: 70.2 mg (88%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 167–168 °C; data for the major ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.79–7.76 (m, 1H), 7.70 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.67 (s, 1H), 7.41–7.36 (m, 1H), 7.15 (s, 1H), 6.84 (dt, *J* = 9.9, 2.5 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.49 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); data for the minor ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 1.8 Hz, 1H), 7.79–7.76 (m, 1H), 7.64 (dt, *J* = 9.7, 2.5 Hz, 2H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.41–7.36 (m, 2H), 6.98 (s, 1H), 6.89 (dt, *J* = 9.8, 2.5 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.01 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15, 165.72, 163.18, 163.10, 137.05, 135.17, 133.74, 133.68, 133.08, 132.69, 131.98, 131.94, 131.71, 131.22, 130.91, 130.61, 129.81, 129.63, 129.42, 129.22, 129.05, 128.79, 127.47, 126.72, 126.47, 124.81, 121.87, 120.80, 114.18, 114.15, 61.26, 61.20, 55.60, 55.58, 25.28, 21.47, 14.32, 14.24; IR (film) 3253, 1716, 1596, 1371, 774 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{21}H_{21}NO_5S$: 399.1140; found: 399.1143.

Ethyl 4-(4-methoxyphenylsulfonamido)-6-methyl-2-naphthoate (3i). Yield: 57.5 mg (72%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 171–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.72 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.68 (d, *J* = 0.5 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.90 (s, 1H), 6.86 (dt, *J* = 9.9, 2.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.47 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.2, 139.4, 131.7, 131.4, 131.3, 130.7, 129.8, 129.7, 129.4, 126.6, 122.2, 121.1, 114.1, 61.2, 55.6, 22.2, 14.3; IR (film) 3249, 1715, 1630, 1378, 763 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{21}H_{21}NO_5S$: 399.1140; found: 399.1139.

Ethyl 6-methoxy-4-(4-methoxyphenylsulfonamido)-2-naphthoate (3j). Yield: 54.1 mg (65%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 172–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.78 (d, *J* = 1.4 Hz, 1H), 7.71 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.04 (s, 1H), 6.86 (dt, *J* = 10.0, 2.5 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.2, 160.3, 133.5, 131.4, 130.7, 130.0, 129.6, 128.8, 125.1, 123.6, 120.2, 114.2, 100.8, 61.1, 55.6, 55.7, 14.3; IR (film) 3258, 1714, 1626, 1380, 766 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{21}NO_6S$: 415.1090; found: 415.1092.

Ethyl 5,7-dimethoxy-4-(4-methoxyphenylsulfonamido)-2-naphthoate (3k). Yield: 81.9 mg (95%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 171–173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.07 (d, *J* = 1.5 Hz, 1H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.74 (dt, *J* = 9.9, 2.5 Hz, 2H), 6.81 (dt, *J* = 9.9, 2.6 Hz, 2H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.52 (d, *J* = 2.3 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 3.87 (s, 3H), 3.76 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 163.0, 158.0, 156.6, 136.5, 134.6, 130.8, 129.6, 128.8, 125.4, 114.4, 113.9, 113.5, 101.2, 101.0, 61.2, 56.4, 55.5, 55.4, 14.4; IR (film) 3293, 1714, 1626, 1383, 768 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{22}H_{23}NO_7S$: 445.1195; found: 445.1192.

Ethyl 6-chloro-4-(4-methoxyphenylsulfonamido)-2-naphthoate (3l). Yield: 46.1 mg (55%); R_f = 0.2 (EtOAc:hexane = 1:2); yellow solid, melting point: 174–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.89–7.83 (m, 3H), 7.69 (dt, *J* = 9.9, 2.5 Hz, 2H), 7.47 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.89 (dt, 2H), 6.71 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.4, 135.4, 132.5, 131.7, 131.3, 131.3, 130.4, 130.0, 129.7, 128.2, 127.9, 124.1, 121.7, 114.3, 61.5, 55.6, 14.3; IR (film) 3249, 1718, 1624, 1376, 763, 731 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{20}H_{18}ClNO_5S$: 419.0594; found: 419.0598.

Ethyl 7-bromo-4-(4-methoxyphenylsulfonamido)-2-naphthoate (3m). Yield: 46.5 mg (50%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 179–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.09 (d, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 1.2 Hz, 1H), 7.69–7.63 (m, 3H), 6.88 (dt, *J* = 9.9, 2.4 Hz, 2H), 6.78 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.4, 134.6, 132.4, 132.2, 131.6, 130.2, 130.2, 129.7, 129.0, 128.7, 124.2, 122.7, 121.5, 114.3, 61.5, 55.6, 14.3; IR (film) 3251, 1727, 1592, 1399, 811, 761 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{18}BrNO_5S$: 463.0089 found: 463.0090.

Ethyl 6-acetoxy-4-(4-methoxyphenylsulfonamido)-2-naphthoate (3n). Yield: 44.3 mg (50%); R_f = 0.3 (EtOAc:hexane = 1:2); yellow solid, melting point: 140–142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 1.3 Hz, 1H), 7.71–7.67 (m, 3H), 7.29 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.89 (s, 1H), 6.86 (dt, *J* = 9.9, 2.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.36 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 165.7, 163.3, 150.9, 132.6, 131.9, 131.4, 131.3, 130.5, 129.8, 129.7, 127.4, 123.3, 122.7, 114.2, 114.0, 61.4, 55.6, 21.1, 14.3; IR (film) 3250, 1716, 1632, 1371, 763 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{22}H_{21}NO_7S$: 443.1039; found: 443.1041.

Ethyl 4-(4-methoxyphenylsulfonamido)anthracene-2-carboxylate (3o). Yield: 64.4 mg (74%); R_f = 0.4 (EtOAc:hexane = 1:2); yellow solid, melting point: 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69–9.65 (m,

1H), 8.45 (d, J = 1.8 Hz, 1H), 7.90–7.86 (m, 1H), 7.77–7.70 (m, 3H), 7.67–7.62 (m, 4H), 6.88–6.83 (m, 3H), 4.38 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 163.3, 134.1, 134.1, 133.3, 130.5, 130.2, 129.9, 129.6, 129.1, 129.0, 128.9, 127.9, 127.5, 127.3, 127.3, 126.8, 126.2, 114.1, 61.3, 55.6, 14.3; IR (film) 3250, 1715, 1594, 1375, 767 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{24}H_{21}NO_5S$: 435.1140 found: 435.1141.

Ethyl 4-(4-methoxyphenylsulfonamido)benzofuran-6-carboxylate (3p). Yield: 36.0 mg (48%); R_f = 0.3 (EtOAc:hexane = 1:2); brown solid, melting point: 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, J = 1.1 Hz, 1H), 7.72 (dt, J = 10.1, 2.6 Hz, 2H), 7.70 (d, J = 1.2 Hz, 1H), 7.69 (d, J = 2.2 Hz, 1H), 7.16 (s, 1H), 6.89 (dd, J = 2.3, 1.0 Hz, 1H), 6.87 (dt, J = 9.7, 2.4 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.3, 155.0, 147.8, 130.2, 129.6, 129.1, 127.3, 126.8, 117.9, 114.3, 111.0, 104.7, 61.3, 55.6, 14.3; IR (film) 3254, 1714, 1621, 1371, 1305, 769 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{18}H_{17}NO_6S$: 375.0777 found: 375.0775.

Ethyl 4-(4-methoxyphenylsulfonamido)benzo[b]-thiophene-6-carboxylate (3q). Yield: 46.9 mg (60%); R_f = 0.3 (EtOAc:hexane = 1:2); brown solid, melting point: 178–179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, J = 1.0 Hz, 1H), 7.82 (d, J = 1.3 Hz, 1H), 7.73 (dt, J = 9.9, 2.5 Hz, 2H), 7.59 (d, J = 5.6 Hz, 1H), 7.41 (dd, J = 5.6, 0.8 Hz, 1H), 7.26 (s, 1H), 6.86 (dt, J = 9.9, 2.5 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.3, 140.7, 137.8, 130.8, 130.8, 130.3, 129.6, 127.1, 122.5, 120.4, 119.6, 114.3, 61.3, 55.6, 14.3; IR (film) 3263, 1713, 1595, 1367, 772 cm^{-1}; HRMS (EI): $[M]^+$ calcd for $C_{18}H_{17}NO_5S_2$: 391.0548 found: 391.0545.

Synthetic Procedure of Ethyl 4-((4-methylphenyl)sulfonamido)-1-nitro-2-naphthoate (4). A mixture of ethyl 4-(4-methylphenylsulfonamido)-2-naphthoate **3a** (0.2 mmol, 73.9 mg, 1.0 equiv), $NaNO_2$ (27.6 mg, 2.0 equiv), and oxone (60.9 mg, 2.0 equiv) was stirred in nitromethane (1.0 mL) at 50 °C for 3 h under air. After the reaction was concentrated, the residue was purified by flash column chromatography using EtOAc:hexane = 1:5. The desired product was obtained in 53% (43.9 mg) yield.

Ethyl 4-((4-methylphenyl)sulfonamido)-1-nitro-2-naphthoate (4). Yield: 43.9 mg (53%); R_f = 0.3 (EtOAc:hexane = 1:5); white solid, melting point: 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.01 (m, 1H), 7.90 (s, 1H), 7.76–7.73 (m, 3H), 7.68–7.73 (m, 3H), 7.54 (br, NH), 7.25 (d, J = 8.0 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.39 (t, J = 7.16 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 146.5, 144.8, 135.5, 133.9, 129.9, 129.6, 127.5, 125.0, 123.4, 121.8, 119.6, 119.1, 62.7, 21.6, 13.8; IR (film) 3210, 1690, 1440, 1397, 780 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{20}H_{18}N_2O_6S$: 414.4320; found: 414.4320.

Synthetic Procedure of Ethyl 2-(2-ethoxy-2-oxoethyl)-1-tosyl-1,2-dihydrobenzo[*cd*]indole-7-carboxylate (5). A Schlenk tube was charged with $Cu(OAc)_2$ (76.3 mg, 2.1 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol%), and ethyl 4-(4-methylphenylsulfonamido)-2-naphthoate **3a** (0.2 mmol, 73.9 mg, 1.0 equiv). After purged with nitrogen, DMF (0.4 mL) and ethyl acrylate (32.7 μL, 1.5 equiv) were added. The mixture was stirred at 100 °C for 16 h, followed by dilution CH_2Cl_2 and filtration through celite. All volatiles were removed under reduced pressure. The purification was performed by flash column chromatography on silica gel using EtOAc:hexane = 1:5. The desired product was obtained in 90% (84.1 mg) yield.

Ethyl 2-(2-ethoxy-2-oxoethyl)-1-tosyl-1,2-dihydrobenzo[*cd*]indole-7-carboxylate (5). Yield: 84.1 mg (90%); R_f = 0.3 (EtOAc:hexane = 1:5); white solid, melting point: 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 0.8 Hz, 1H), 8.11 (d, J = 0.8 Hz, 1H), 7.75–7.70 (m, 3H), 7.50–7.46 (m, 1H), 7.31–7.30 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 5.73–5.59 (m, 1H), 4.51–4.42 (m, 2H), 4.24–4.19 (m, 2H), 3.65–3.59 (m,. 1H), 2.95–2.89 (m, 1H), 2.29 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 166.7, 144.7, 142.3, 138.8, 133.8, 131.4, 131.2, 130.2, 129.9, 129.2, 127.3, 125.4, 123.3, 120.2, 107.8, 65.1, 61.4, 60.9, 42.1, 21.5, 14.4, 14.1; IR (film) 3300, 1725, 1550, 1390, 1377, 1280, 780 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{25}H_{25}NO_6S$: 467.1403; found: 467.1403.

Synthetic Procedure of Ethyl (*E*)-5-(hex-3-en-3-yl)-4-((4-methylphenyl)sulfonamido)-2-naphthoate (6). A mixture of ethyl 4-(4-methylphenylsulfonamido)-2-naphthoate **3a** (0.2 mmol, 73.9 mg, 1.0 equiv), 3-hexyne (22.7 μL, 1.0 equiv), $[IrCl(cod)]_2$ (6.7 mg, 5.0 mol%), P(*t*-Bu)$_3$ (6.1 mg, 15.0 mol%), and Na_2CO_3 (10.6 mg, 0.5 equiv) was stirred in toluene (0.5 mL) at 135 °C for 2 h under nitrogen. After cooling to room temperature and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel using EtOAc:hexane = 1:6. The desired product was obtained in 80% (72.2 mg) yield.

Ethyl-5-(hex-3-en-3-yl)-4-((4-methylphenyl)sulfonamido)-2-naphthoate (6). Yield: 72.2 mg (80%); R_f = 0.3 (EtOAc:hexane = 1:6); brown solid, melting point: 104–106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.24 (d, J = 1.6 Hz, 1H), 7.99 (d, J = 1.6 Hz, 1H), 7.83–7.78 (m, 3H), 7.43–7.39 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.18–7.16 (m, 1H), 5.76–5.72 (m, 1H), 4.40 (q, J = 7.1 Hz, 2H), 2.95–2.43 (m, 2H), 2.37–2.15(m, 2H), 2.35 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H), 1.23 (t. J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 144.0, 143.9, 138.4, 136.6, 134.7, 134.6, 134.4, 131.2, 129.8, 129.6, 127.7, 127.3, 127.0, 125.9, 123.9, 113.1, 61.2, 26.5, 21.6, 21.5, 14.4, 13.9, 12.2; IR (film) 3285, 1737, 1420, 1395, 795 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{26}H_{29}NO_4S$: 451.1817; found: 451.1817.

Conclusion

In conclusion, we developed a Cu(I)-catalyzed cyclization reaction of ethyl (*E*)-α-ethynyl-β-aryl-α,β-unsaturated esters with *N*-sulfonyl azides in the presence of 2,6-lutidine in THF at 60 °C for 3 h. This method enabled efficient synthesis of a wide range of 1-aminonaphthalene and 3-aminobenzofuran and 3-aminobenzothiophene derivatives with the release of molecular nitrogen.

Acknowledgments. This paper is dedicated to Professor Hong-Seok Kim (Kyungpook National University) for his honorable retirement. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (2011-0018355 and 2017R1A4A1015405) and by 2017 Research Grant from Kangwon National University (No. 520170529).

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra for all products (PDF) is available in the online version of this article.

References

1. (a) F. Xu, H. Xu, X. Wang, L. Zhang, Q. Wen, Y. Zhang, W. Xu, *Bioorg. Med. Chem.* **2014**, *22*, 1487. (b) G. Xu, Y. Zhou, S. Zhang, S. Ma, F. Xu, H. Xu, W. Xu, *Med. Chem.* **2014**, *4*, 598.
2. F. A. Abulwerdi, C. Liao, A. S. Mady, J. Gavin, C. Shen, T. Cierpicki, H. D. H. Showalter, Z. Nikolovska-Coleska, *J. Med. Chem.* **2014**, *57*, 4111.
3. D. R. Goldberg, M.-H. Hao, K. C. Qian, A. D. Swinamer, D. A. Gao, Z. Xiaon, C. Sarko, A. Berry, J. Lord, R. L. Magolda, T. Fadra, R. R. Kroe, A. Kukulka, J. B. Madwed, L. Martin, C. Pargellis, D. Skow, J. J. Song, Z. Tan, C. A. Torcellini, C. S. Zimmitti, N. K. Yee, N. Moss, *J. Med. Chem.* **2007**, *50*, 4016.
4. D. Ménard, I. Niculescu-Duvaz, H. P. Dijkstra, D. Niculescu-Duvaz, B. M. J. M. Suijkerbuijk, A. Zambon, A. Nourry, E. Roman, L. Davies, H. A. Manne, F. Friedlos, R. Kirk, S. Whittaker, A. Gill, R. D. Taylor, R. Marais, C. J. Springer, *J. Med. Chem.* **2009**, *52*, 3881.
5. (a) B. Riegel, G. R. Lappin, *J. Am. Chem. Soc.* **1946**, *68*, 1229. (b) P. B. Madrid, N. T. Wilson, J. L. DeRisi, R. K. Guy, *J. Comb. Chem.* **2004**, *6*, 437. (c) O. Dechy-Cabaret, F. Benoit-Vical, C. Loup, A. Robert, H. Gornitzka, A. Bonhoure, H. Vial, J. F. Magnaval, J. P. Seguela, B. Meunier, *Chem. Eur. J.* **2004**, *10*, 1625. (d) S. Melato, P. Coghi, N. Basilico, D. Prosperi, D. Monti, *Eur. J. Org. Chem.* **2007**, *2007*, 6118. (e) E. Paunescu, N. Matuszak, P. Melnyk, *Tetrahedron* **2007**, *63*, 12791. (f) S. Gemma, G. Kukreja, P. Tripaldi, M. Altarelli, M. Bernetti, S. Franceschini, L. Savini, G. Campiani, C. Fattorusso, S. Butini, *Tetrahedron Lett.* **2008**, *49*, 2074. (g) M. J. Mphahlele, *Tetrahedron* **2010**, *66*, 8261.
6. (a) G. Burton, P. Cao, G. Li, R. Rivero, *Org. Lett.* **2003**, *5*, 4373. (b) C. Wolf, R. Lerebours, *J. Org. Chem.* **2003**, *68*, 7077. (c) T. H. Jonckers, B. U. W. Maes, G. L. F. Lemiere, G. Rombouts, L. Pieters, A. Haemers, R. A. Dommisse, *Synlett* **2003**, 615. (d) S. Jaime-Figueroa, Y. Z. Liu, J. M. Muchowski, D. G. Putman, *Tetrahedron Lett.* **1998**, *39*, 1313. (e) B. J. Margolis, K. A. Long, D. L. T. Laird, J. C. Ruble, S. R. Pulley, *J. Org. Chem.* **2007**, *72*, 2232. (f) C. Ronco, L. Jean, H. Outaabout, P.-Y. Renard, *Eur. J. Org. Chem.* **2011**, *2011*, 302.
7. S. Shin, J.-Y. Son, C. Choi, S. Kim, P. H. Lee, *J. Org. Chem.* **2016**, *81*, 11706.
8. (a) S. H. Cho, S. Chang, *Angew. Chem. Int. Ed.* **2008**, *47*, 2836. (b) E. J. Yoo, S. Chang, *Org. Lett.* **2008**, *10*, 1163. (c) E. J. Yoo, S. Chang, *Curr. Org. Chem.* **2009**, *13*, 1766. (d) S. H. Kim, S. H. Park, J. H. Choi, S. Chang, *Chem. Asian J.* **2011**, *6*, 2618.
9. (a) A. Casini, A. Scozzafava, C. T. Supuran, *Expert Opin. Ther. Pat.* **2002**, *12*, 1307. (b) A. Scozzafava, T. Owa, A. Mastrolorenzo, C. T. Supuran, *Curr. Med. Chem.* **2003**, *10*, 925.
10. S. R. Turner, J. W. Strohbach, R. A. Tommasi, P. A. Aristoff, P. D. Johnson, H. I. Skulnick, L. A. Dolak, E. P. Seest, P. K. Tomich, M. J. Bohanan, M. M. Horng, J. C. Lynn, K. T. Chong, R. R. Hinshaw, K. D. Watenpaugh, M. N. Janakiraman, S. Thaisrivongs, *J. Med. Chem.* **1998**, *41*, 3467.
11. J. Drews, *Science* **2000**, *287*, 1960.
12. C. Hansch, P. G. Sammes, J. B. Taylor, *Comprehensive Medicinal Chemistry*, Vol. *2*, Pergamon Press, Oxford, **1990** Chapter 7.
13. T. Owa, T. Nagasu, *Expert Opin. Ther. Pat.* **2000**, *10*, 1725.
14. (a) Y. Choe, P. H. Lee, *Org. Lett.* **2009**, *11*, 1445. (b) C. Park, P. H. Lee, *Org. Lett.* **2008**, *10*, 3359. (c) K. Lee, P. H. Lee, *Bull. Korean Chem. Soc.* **2008**, *29*, 487.
15. Y. X. Li, L. H. Li, Y. F. Yang, H. L. Hua, X. B. Yan, L. B. Zhao, J. B. Zhang, F. J. Ji, Y. M. Liang, *Chem. Commun.* **2014**, *50*, 9936.
16. (a) X. Li, X. Gong, M. Zhao, G. Song, J. Deng, X. Li, *Org. Lett.* **2011**, *13*, 5808. (b) T. Ryu, J. Kim, Y. Park, S. Kim, P. H. Lee, *Org. Lett.* **2013**, *15*, 3986. (c) S. Park, B. Seo, S. Shin, J.-Y. Son, P. H. Lee, *Chem. Commun.* **2013**, *49*, 8671. (d) J. Mo, S. Lim, S. Park, T. Ryu, S. Kim, P. H. Lee, *RSC Adv.* **2013**, *3*, 18296. (e) L. Y. Chan, S. Kim, T. Ryu, P. H. Lee, *Chem. Commun.* **2013**, *49*, 4682. (f) W. H. Jeon, J.-Y. Son, S.-E. Kim, P. H. Lee, *Adv. Synth. Catal.* **2015**, *357*, 811.
17. (a) Y. Nishinaka, T. Satoh, M. Miura, H. Morisaka, M. Nomura, H. Matsui, C. Yamaguchi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1727. (b) J. Seo, Y. Park, I. Jeon, T. Ryu, S. Park, P. H. Lee, *Org. Lett.* **2013**, *15*, 3358. (c) Y. Park, J. Seo, S. Park, E. J. Yoo, P. H. Lee, *Chem. Eur. J.* **2013**, *19*, 16461. (d) Y. Park, I. Jeon, S. Shin, J. Min, P. H. Lee, *J. Org. Chem.* **2013**, *78*, 10209.
18. (a) I. Bae, H. Han, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 2038. (b) S. H. Cho, E. J. Yoo, I. Bae, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 16046. (c) P. Lu, Y.-G. Wang, *Synlett* **2010**, 165. (d) Y. Shen, S. Cui, J. Wang, X. Chen, P. Lu, Y.-G. Wang, *Adv. Synth. Catal.* **2010**, *352*, 1139. (e) W. Yao, L. Pan, Y. Zhang, G. Wang, X. Wang, C. Ma, *Angew. Chem. Int. Ed.* **2010**, *49*, 9210. (f) S. L. Cui, J. Wang, Y.-G. Wang, *Tetrahetron* **2008**, *64*, 487. (g) J. She, Z. Jiang, Y.-G. Wang, *Synlett* **2009**, 2023. (h) F. Wang, H. Fu, Y. Jiang, Y. Zhao,

Adv. Synth. Catal. **2008**, *350*, 1830. (i) S. Maisonneuve, J. Xie, *Synlett* **2009**, 2977. (j) Y. Shang, X. He, J. Hu, J. Wu, M. Zhang, S. Yu, Q. Zhang, *Adv. Synth. Catal.* **2009**, *351*, 2709. (k) W. Lu, W. Z. Song, D. Hong, P. Lu, Y.-G. Wang, *Adv. Synth. Catal.* **2009**, *351*, 1768. (l) H. Jin, X. Xu, J. Gao, J. Zhong, Y.-G. Wang, *Adv. Synth. Catal.* **2010**, *352*, 347.

