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Rhodium-Catalyzed Intramolecular Transannulation Reaction of Alkynyl Thiadiazole Enabled 5,*n*-Fused Thiophenes

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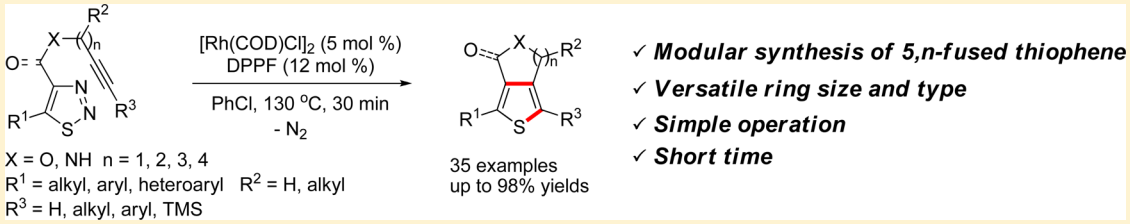
Supporting Information



ABSTRACT: A method for the synthesis of a wide range of fused thiophenes, including those fused with lactams, lactones, or cyclic ethers, was developed from a rhodium-catalyzed intramolecular transannulation reaction of alkynyl thiadiazoles. This transannulation reaction provides an efficient platform for the construction of a variety of 5,*n*-fused thiophenes from readily available starting materials together with the release of molecular nitrogen.

INTRODUCTION

Fused thiophenes have been recognized as very important scaffolds in the fields of pharmaceutical and functional materials sciences.[1] For this reason, the development of an efficient synthetic method for functionalized fused thiophenes is highly attractive and poses a significant challenge. To date, various synthetic methods of fused thiophenes from easily available compounds have been reported (Scheme 1a–g): (a) a one-pot, three-step reaction of 3,4-dibromothiophene using *n*-BuLi, 1-benzylpiperidin-4-one, CO_2, and Ac_2O,[2] (b) basic hydrolysis and subsequent ring closure of a dicarboxylic acid after a Rosenmund–von Braun reaction of 3,4-dibromothiophene,[3] (c) a Pd-catalyzed carbonylative amidation of 3,4-dibromothiophene,[4] (d) a condensation reaction of thiophene dicarbaldehydes and aromatic amines in the presence of 2-mercaptoethanol,[5] (e) Friedel–Crafts acylation of thiophene-3,4-dicarbonyl dichloride and benzene,[6] (f) Suzuki–Miyaura cross-coupling of bromoarylcarboxylate and *o*-hydroxyarylboronic acid,[7] and (g) reaction of *o*-hydroxyacetophenone with ethyl cyanoacetate and elemental sulfur under microwave conditions.[8] However, because some of the previously reported synthetic methods demand a strong base, long reaction times, and vigorous reaction conditions, the development of efficient synthetic approaches to overcome these shortcomings has been continuously required.

Recently, *N*-sulfonyl-1,2,3-triazoles were easily prepared through a Cu-catalyzed [3 + 2] cycloaddition reaction from 1-alkynes and *N*-sulfonyl azides[9] and have been used as α-imino carbene precursors.[10] These results showed that the α-imino carbene functions as a 1,3-dipole equivalent in transannulation reactions with diverse unsaturated compounds possessing carbon–carbon or carbon–heteroatom multiple bonds. Thus, intermolecular, as well as intramolecular, transannulation reactions using *N*-sulfonyl-1,2,3-triazoles have become valuable methods for preparing a wide variety of heterocyclic compounds.[11] More recently, Gevorgyan and co-workers developed Rh-catalyzed intermolecular transannulation reactions of 1,2,3-thiadiazoles with alkynes to produce thiophenes (Scheme 2a).[12a] In addition, Rh-catalyzed intermolecular transannulation reactions of 1,2,3-thiadiazoles with alkenes (Scheme 2b,c) and nitriles (Scheme 2d) were developed to produce sulfur-containing five-membered heterocyclic compounds, including thiophenes, dihydrothiophenes, and isothiazoles, through an α-thiavinyl carbene.[12b,c]

On the basis of these results and facts, we envisioned that if alkynyl thiadiazoles possessing a variety of linkers between the alkynyl group and the thiadiazole ring were treated with a transition-metal catalyst, an intramolecular transannulation reaction would occur, producing a large number of fused thiophenes together with the release of molecular nitrogen. Herein, we report for the first time that rhodium-catalyzed intramolecular transannulation reactions of alkynyl thiadiazoles including esters, amides, or ethers as linkers afford an excellent platform for the preparation of a wide range of 5,*n*-fused thiophenes (Scheme 1h).

RESULTS AND DISCUSSION

First, we commenced our study by optimizing an intramolecular transannulation reaction of alkynyl thiadiazole **1a** in the presence of a transition-metal catalyst (Table 1). $Rh_2(oct)_4$ (5 mol %) and $RhCl_3{\cdot}H_2O$ (5 mol %)/DPPF (12 mol %) were

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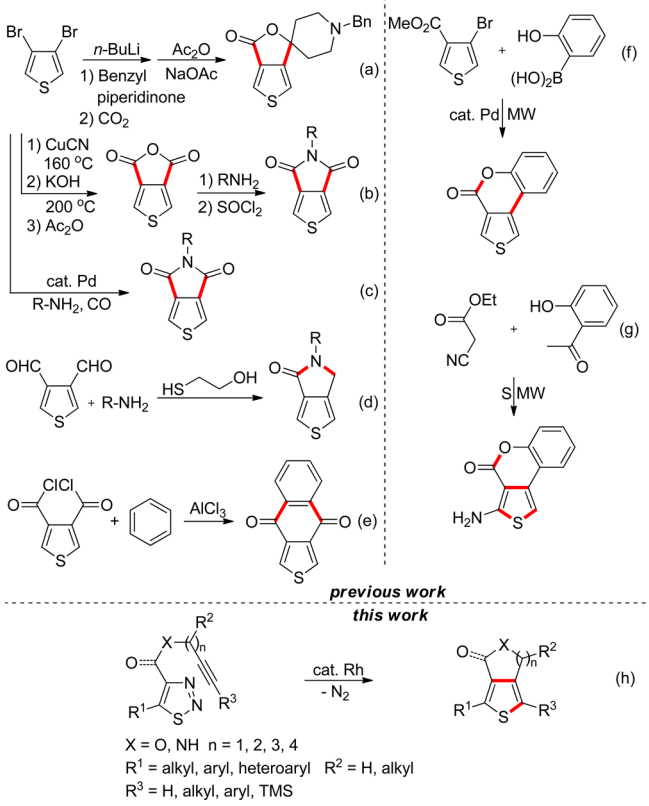
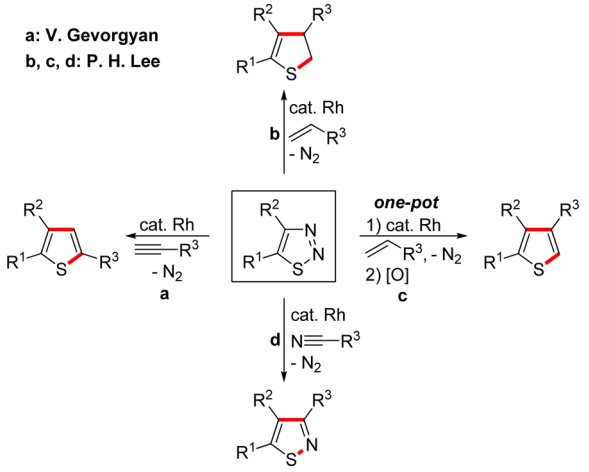
Scheme 1. Synthesis of the Fused Thiophenes

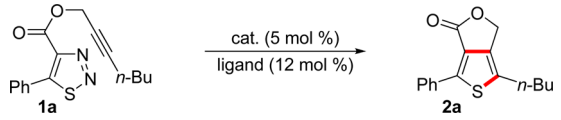


Scheme 2. Rh-Catalyzed Intermolecular Transannulation Reactions of 1,2,3-Thiadiazoles



totally ineffective for the transannulation (entries 2 and 3). However, $Rh(PPh)_3Cl$ and $[Ir(COD)Cl]_2$ (5 mol % each) in the presence of DPPF (12 mol %) afforded, gratifyingly, the desired transannulated product **2a** in 42% and 16% yields, respectively (entries 1 and 5). A quantitative yield of **2a** was obtained with $[Rh(COD)Cl]_2$ (5 mol %) and DPPF (12 mol %) together with the release of nitrogen gas (entry 4). The efficiency of the present transannulation was not greatly influenced by solvents. The desired product **2a** was produced in 65% yield in chloroform (entry 8). Moreover, the fused thiophene **2a** was obtained in good to excellent yields ranging from 87% to 90% in the solvents dichloromethane (DCM), dichloroethane (DCE), and toluene (entries 6, 7, and 9). The

Table 1. Reaction Optimization[a]



entry	cat. (mol %)	ligand (mol %)	solvent	temp (°C)	time (h)	yield[b] (%)
1	$Rh(PPh_3)Cl$ (5)	DPPF (12)	PhCl	130	12	42
2	$Rh_2(oct)_4$ (5)		PhCl	130	12	0
3	$RhCl_3·H_2O$ (5)	DPPF (12)	PhCl	130	12	0
4	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	130	0.5	99 (95)[c]
5	$[Ir(COD)Cl]_2$ (5)	DPPF (12)	PhCl	130	12	16
6	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	DCM	40	12	89
7	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	DCE	60	12	90
8	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	$CHCl_3$	60	12	65
9	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	toluene	130	12	87
10	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	60	12	29
11	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	25	12	5
12	$[Rh(COD)Cl]_2$ (2)	DPPF (5)	PhCl	130	12	36
13	$[Rh(COD)Cl]_2$ (5)		PhCl	130	2	0
14		DPPF (12)	PhCl	130	2	0
15			PhCl	130	2	0

[a]Reaction conditions: **1a** (0.2 mmol) was placed in solvent (1.0 mL) under N_2. [b]NMR yields using dibromomethane as an internal standard. [c]Isolated yield given in parentheses.

reaction temperature had an effect on the transannulation efficiency. A higher transannulation reaction took place at 130 °C (entries 4, 10, and 11). Use of a lesser amount of $[Rh(COD)Cl]_2$ (2 mol %) and DPPF (5 mol %) provided an inferior result (entry 12). Control experiments demonstrated that both $[Rh(COD)Cl]_2$ and DPPF were essential for the transannulation reaction (entries 13−15).

To demonstrate the efficiency and scope of the Rh-catalyzed transannulation reaction, we applied this catalytic system to a wide range of alkynyl thiadiazoles **1** with ester or amide groups as linkers between the thiadiazole ring and the alkynyl group, and the results are summarized in Scheme 3. The corresponding alkynyl thiadiazoles **1** were easily obtained from the coupling reactions of acids derived from the hydrolysis of ethyl 5-aryl-1,2,3-thiadiazole-4-carboxylate with alkynyl alcohols and amines (see the Supporting Information). Alkynyl thiadiazole **1b**, having a propargyl group, which is a terminal alkyne, was smoothly transannulated to give the fused thiophene **2b** in 72% yield. Alkynyl thiadiazoles **1c−e** obtained from 2-butyn-1-ol, 2-pentyn-1-ol, and 3-phenyl-2-propyn-1-ol, respectively, underwent the transannulation reaction, affording the fused thiophenes **2c−e** in high yields ranging from 87% to 89%. The structure of **2d** was confirmed by X-ray crystallography (see the Supporting Information). In particular, it is noteworthy that a trimethylsilyl group was compatible with the present reaction. In particular, trimethylsilyl-substituted propargyl thiadiazole **1f** is applicable to the present trans-

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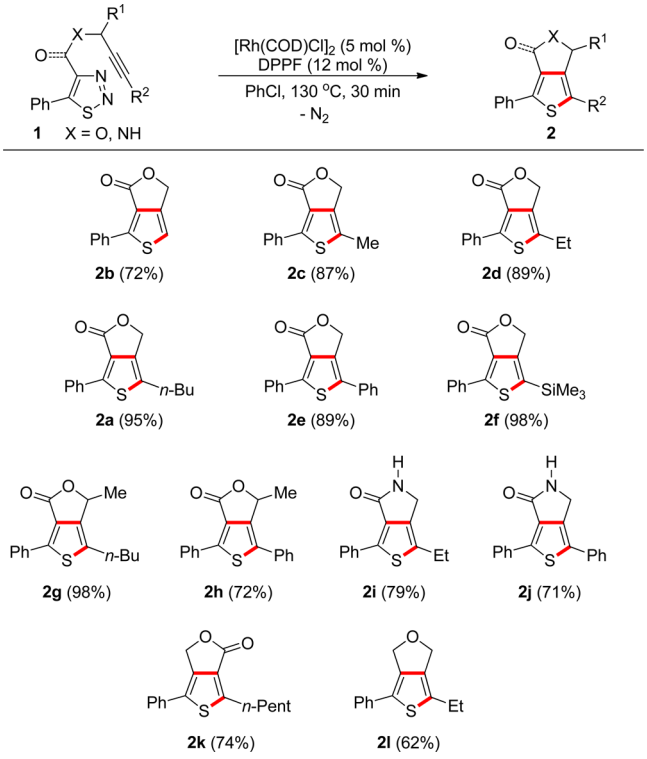
Scheme 3. Scope of Alkynyl Groups in the Transannulation of Alkynyl Thiadiazoles[a]

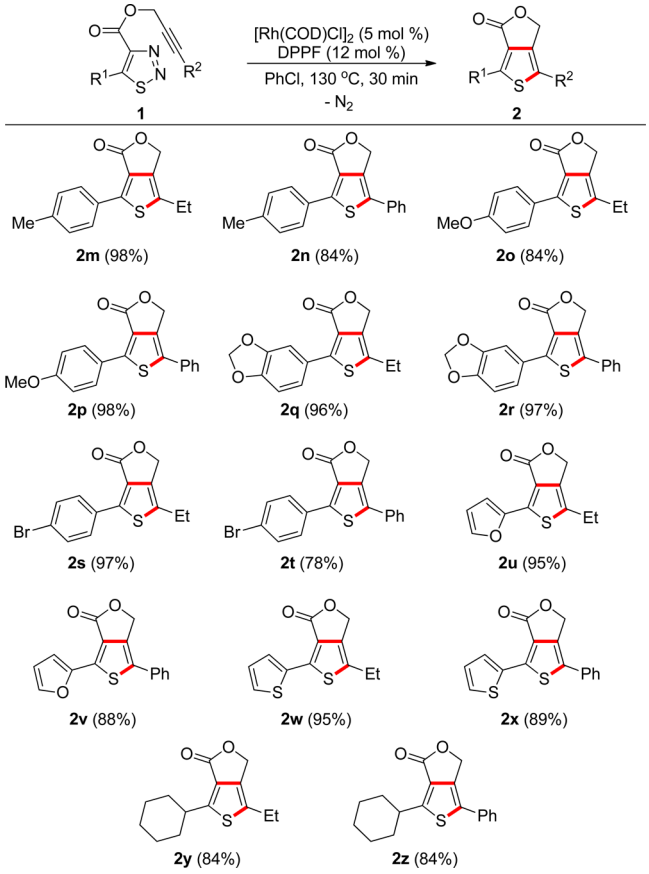


[a]Reaction conditions: **1** (0.2 mmol) was used in the presence of $[Rh(COD)Cl]_2$ (5 mol %) and DPPF (12 mol %) in PhCl (1.0 mL) under N_2 at 130 °C.

annulation reaction, providing **2f** in quantitative yield. Alkynyl thiadiazoles **1g,h** generated from internal alkynyl alcohols having a methyl substituent on the propargylic carbon worked equally well to give the fused thiophenes **2g** (98%) and **2h** (72%). To our satisfaction, amide-linked alkynyl thiadiazoles **1i,j**, which are easily prepared from the coupling reaction of a thiadiazolyl acid with 2-pentyn-1-amine and 3-phenyl-2-propyn-1-amine, turned out to be compatible with the reaction conditions, leading to the formation of γ-lactam fused thiophenes **2i,j** in good yields. Moreover, thiadiazolylmethyl octynoate (**1k**) was compatible with the reaction conditions, producing 5,5-fused thiophene **2k** in 74% yield. Thiadiazolylmethyl 2-pentyn-1-yl ether (**1l**) took part in the transannulation reaction to afford **2l** in 62% yield.

Encouraged by these results, we investigated the scope of a wide range of ester-linked alkynyl thiadiazoles **1** in the Rh-catalyzed intramolecular transannulation reaction (Scheme 4). Electronic variation of the thiadiazolyl ring did not greatly affect the efficiency of the transannulation reaction. Alkynyl thiadiazoles having an electron-donating methyl group on the 5-phenylthiadiazolyl ring efficiently underwent the intramolecular transannulation reaction to afford the desired fused thiophenes **2m,n**, in 98% and 84% yields, respectively, under the optimized conditions. Substrates **1o,p** obtained from 4-methoxyphenyl-substituted thiadiazolyl acid and 2-pentyn-1-ol and 3-phenyl-2-propyn-1-ol were smoothly converted to give the fused thiophenes **2o** (84%) and **2p** (98%). Methylenedioxy-substituted alkynyl thiadiazoles were efficiently subjected to the transannulation reaction, producing the desired fused thiophenes **2q,r** in quantitative yields. Substrates possessing an

Scheme 4. Scope of Thiadiazolyl and Alkynyl Groups in the Transannulation of Alkynyl Thiadiazoles[a]



[a]Reaction conditions: **1** (0.2 mmol) was used in the presence of $[Rh(COD)Cl]_2$ (5 mol %) and DPPF (12 mol %) in PhCl (1.0 mL) under N_2 at 130 °C.

electron-withdrawing bromo group on the 5-phenylthiadiazolyl ring delivered the desired γ-lactone fused thiophenes **2s,t** in good to excellent yields. Heteroaryl-substituted alkynyl thiadiazoles were easily transformed to the corresponding fused thiophenes. For example, furan-2-yl- and thiophen-2-yl-substituted alkynyl thiadiazoles are applicable to the present transannulation reaction, affording the corresponding fused thiophenes **2u−x** in good to excellent yields ranging from 88% to 95%. To our delight, cyclohexyl-substituted substrates took part in the transannulation reaction to afford **2y,z** in 84% yields.

With these results in hand, we next examined the Rh-catalyzed transannulation reaction of alkynyl thiadiazoles **3** in the case where the alkynyl chain was largely extended by carbon (Scheme 5). Alkynyl thiadiazole **3a**, obtained from the coupling reaction of 5-phenylthiadiazolyl acid with 3-butyn-1-ol, was exposed to the rhodium catalyst, leading to the formation of δ-lactone fused thiophene **4a** in 51% yield. Alkynyl thiadiazole **3b**, derived from 3-hexyn-1-ol, was converted to the desired product **4b** in 87% yield. Substrate **3c** was less reactive, and the corresponding δ-lactone fused diphenyl-substituted thiophene **4c** was produced in 62% yield in chlorobenzene at 130 °C after 3 h. Alkynyl thiadiazole **3d**, prepared from the coupling reaction of 5-phenylthiadiazolyl acid with 2-(hex-1-ynyl)phenol, was engaged in the Rh-catalyzed transannulation reaction, producing **4d** in 90% yield (130 °C, 5 h). When alkynyl thiadiazole **3e** was employed, the desired product **4e** was

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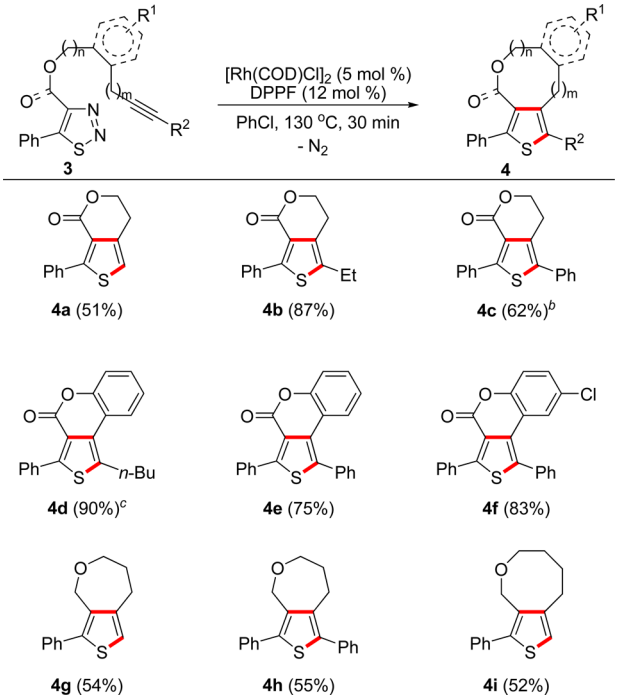
Scheme 5. Synthesis of 5,*n*-Fused Thiophenes via Transannulation of Alkynyl Thiadiazoles[a]

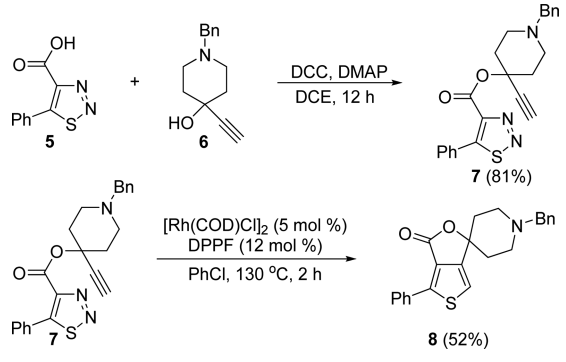


[a]Reaction conditions unless specified otherwise: **1** (0.2 mmol) was used in the presence of $[Rh(COD)Cl]_2$ (5 mol %) and DPPF (12 mol %) in PhCl (1.0 mL) under N_2 at 130 °C. [b]3 h. [c]5 h.

obtained in 75% yield. Substrate **3f**, possessing a 4-chlorophenyl group, was employed in the Rh-catalyzed transannulation reaction, providing **4f** in 83% yield. In addition, thiadiazolyl alkynyl ethers **3g,h** were compatible with the reaction conditions, producing 5,7-fused thiophenes **4g,h** in moderate yield. To our delight, 5,8-fused thiophene **4i** was obtained in 52% yield.

The present method was applied in the synthesis of spirocyclic fused thiophene, which has been known as a ligand to interact with σ_1 receptor protein and modulate σ_1 receptor activity for the treatment of neurological disorders (Scheme 6).[13] The corresponding alkynyl thiadiazole **7** was prepared from the esterification reaction of acid **5** derived from the hydrolysis of ethyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate with alkynyl alcohol **6** in 81% yield. Alkynyl thiadiazole **7** was

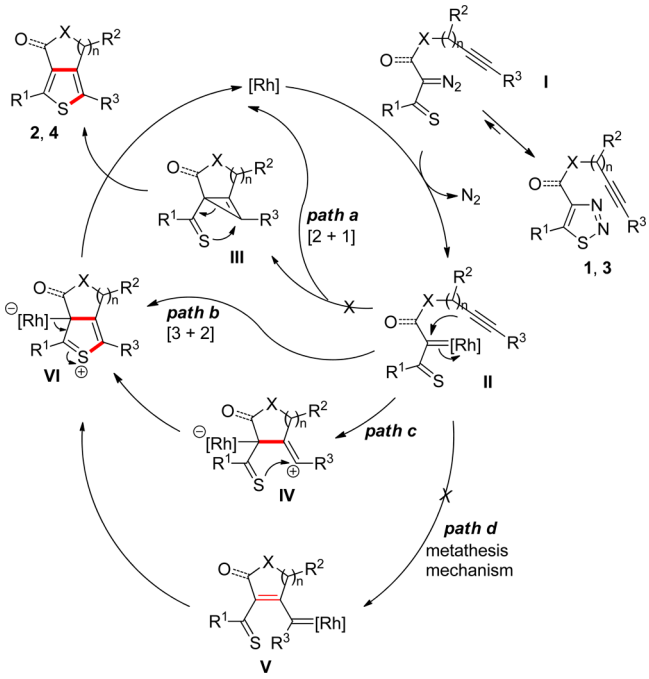
Scheme 6. Synthetic Application of Spirocyclic Fused Thiophene



transannulated under the optimized reaction conditions, producing the desired product **8** in 52% yield.[2]

A plausible reaction mechanism for the Rh-catalyzed intramolecular transannulation of alkynyl thiadiazoles is proposed in Scheme 7. First, a reversible ring−chain

Scheme 7. Proposed Mechanism



tautomerization of thiadiazole moieties in alkynyl thiadiazoles **1** and **3** provides the alkynyl-substituted α-diazo thiocarbonyl **I**. Next, exposure of α-diazo thiocarbonyl **I** to the Rh(I) catalyst affords the α-thiavinyl Rh carbenoid **II** together with the release of nitrogen gas.[12,14] The fused thiophenes **2** and **4** might be produced through cyclopropene intermediate **III** generated from the intramolecular [2 + 1] cycloaddition of **II** (path a). However, path a is ruled out in the catalytic cycle due to Bredt's rule and ring strain. In addition, the Rh carbenoid **II** reacts with the intramolecular triple bond to afford the zwitterionic intermediate **IV**, which then cyclizes to intermediate **VI** (path c). Alternatively, intermediate **VI** can be produced through the intramolecular [3 + 2] cycloaddition of the α-thiavinyl Rh carbenoid **II** (path b). A mechanism involving rhodium carbene−alkyne metathesis is not favored in the catalytic cycle due to an efficient intramolecular transannulation reaction of internal alkynyl thiadiazoles (path d). The elucidation of the detailed mechanism of the intramolecular transannulation reaction awaits further investigation.

CONCLUSION

In summary, a method for the synthesis of a wide range of thiophenes fused to lactams, lactones, and cyclic ethers was developed, employing a Rh-catalyzed intramolecular transannulation reaction of alkynyl thiadiazoles. This method provides an efficient platform for the construction of a wide range of 5,*n*-fused thiophenes from readily accessible starting materials.

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EXPERIMENTAL SECTION

General Considerations. Reactions were carried out in oven-dried glassware in an air atmosphere. $[Rh(COD)Cl]_2$, $Rh_2(oct)_4$, $RhCl_3·H_2O$, $Rh(PPh_3)_3Cl$, $[Ir(COD)Cl]_2$, and DPPF were purchased and used as received. Commercially available reagents were used without purification. Chlorobenzene was purified by distillation from $CaCl_2$ under nitrogen. 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). ^1H NMR (400 MHz) and $^{13}C\{^1H\}$ 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 ^1H (chloroform-*d*), δ 2.50 for ^1H (DMSO-d_6), δ 77.2 for $^{13}C\{^1H\}$ (chloroform-*d*), and δ 39.25 for $^{13}C\{^1H\}$ (DMSO-d_6)). 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 electron impact (EI) ionization techniques (magnetic sector−electric sector double-focusing mass analyzer). Melting points were determined in open capillary tubes.

Preparation of Alkynyl Thiadiazoles 1a−z. The thiadiazole[15] (4.4 mmol, 1.03 g) was added to a 10% aqueous methanolic solution (9.0 mL) of potassium hydroxide (8.8 mmol, 494.0 mg), and the mixture was heated for 2 h under reflux. After the solvent was evaporated, 10 mL of water was added to the residue and the mixture was acidified with dilute hydrochloric acid with vigorous stirring. The precipitate was filtered off, dried in air, and recrystallized from water. To a solution of the alcohol or amine (1.0 mmol), 4-dimethylaminopyridine (DMAP; 0.10 mmol, 36.7 mg), and thiadiazole-4-carboxylic acid (**5**;[16] 1.3 mmol, 822.8 mg) in dry DCE (10 mL) at 0 °C under a nitrogen atmosphere was added *N,N′*-dicyclohexylcarbodiimide (DCC; 1.3 mmol, 823.3 mg) in one portion. After it was stirred for 30 min at the same temperature, the reaction mixture was warmed to room temperature followed by stirring for another 3 h. Then, the reaction mixture was filtered through Celite and the mixture was washed with CH_2Cl_2 (3 × 10 mL). The combined filtrate was evaporated under reduced pressure to give the crude product, which was purified by silica gel chromatography (EtOAc/CH_2Cl_2/hexane = 1/5/15) to provide the pure product **1**.[17]

*Hept-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1a**):* yield 180.0 mg (75%); R_f = 0.3 (EtOAc/hexane = 1/9); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.46 (m, 5H), 4.95 (t, *J* = 2.2 Hz, 2H), 2.21 (tt, *J* = 10.4 Hz, 2.2 Hz, 2H), 1.52−1.45 (m, 2H), 1.43−1.34 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 160.0, 147.8, 130.9, 130.0, 128.8, 126.0, 88.7, 73.2, 54.4, 30.5, 22.0, 18.6, 13.7; IR (film) 2932, 2236, 1736, 1325, 1171, 984 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{16}H_{16}N_2O_2S$ 300.0932, found 300.0928.

*Prop-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1b**):* yield 102.6 mg (57%); R_f = 0.3 (EtOAc/hexane = 1/9); white solid; mp 62−64 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.46 (m, 5H), 4.95 (d, *J* = 2.4 Hz, 2H), 2.53 (t, *J* = 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9, 159.6, 147.3, 130.9, 129.9, 128.8, 125.7, 76.8, 75.8, 53.2; IR (film) 3287, 2948, 1737, 1281, 1172, 693 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{12}H_8N_2O_2S$ 244.0306, found 244.0306.

*But-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1c**).* yield 140.5 mg (68%); R_f = 0.3 (EtOAc/hexane = 1/9); ivory solid; mp 112−114 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.46 (m, 5H), 4.93 (q, *J* = 2.4 Hz, 2H), 1.85 (t, *J* = 2.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 160.0, 147.7, 130.9, 130.0, 128.8, 125.9, 84.2, 72.4, 54.3, 3.8; IR (film) 2910, 2238, 1731, 1326, 1172, 984 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{10}N_2O_2S$ 258.0463, found 258.0466.

*Pent-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1d**):* yield 736 mg (90%); R_f = 0.3 (EtOAc/hexane = 1/9); orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.46 (m, 5H), 4.95 (t, *J* = 2.2 Hz, 2H), 2.21 (qt, *J* = 12.5 Hz, 2.2 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.6, 160.0, 147.8, 130.9, 130.0, 128.8, 126.0, 89.9, 72.6, 54.3, 13.6, 12.6; IR (film) 2975, 2236, 1731, 1273, 1167, 934 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{14}H_{12}N_2O_2S$ 272.0619, found 272.0621.

*3-Phenylprop-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1e**):* yield 240.3 mg (75%); R_f = 0.3 (EtOAc/hexane = 1/9); white solid; mp 83−85 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.55 (m, 2H), 7.53−7.43 (m, 5H), 7.37−7.29 (m, 3H), 5.20 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.9, 159.9, 147.7, 132.1, 131.0, 130.0, 129.0, 128.9, 128.5, 125.9, 122.1, 87.4, 82.2, 54.3; IR (film) 3061, 2949, 2360, 2342, 1734, 1473, 1325, 1168, 690 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{18}H_{12}N_2O_2S$ 320.0619, found 320.0617.

*3-(Trimethylsilyl)prop-2-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1f**):* yield 167.7 mg (53%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.28 (m, 5H), 4.78 (s, 2H), 0.00 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7, 159.7, 147.6, 130.9, 129.9, 128.8, 125.9, 98.0, 93.1, 54.1, 0.3; IR (film) 3063, 2960, 2899, 2359, 2186, 1737, 1474, 1328, 1251, 1172, 1034, 846, 753, 694 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{15}H_{16}N_2O_2SSi$ 316.0702, found 316.0704.

*Oct-3-yn-2-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1g**):* yield 213.8 mg (68%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.45 (m, 5H), 5.68 (qt, *J* = 6.7 Hz, 2.0 Hz, 1H), 2.19 (td, *J* = 7.0 Hz, 1.9 Hz, 2H), 1.52 (d, *J* = 6.6 Hz, 3H), 1.49−1.33 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1, 159.6, 148.4, 130.7, 129.9, 128.7, 126.2, 86.7, 77.8, 62.9, 30.5, 22.6, 21.7, 18.5, 13.7; IR (film) 2957, 2934, 2871, 2247, 1733, 1472, 1330, 1280, 1182, 1165, 1058, 984, 846, 694 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{17}H_{18}N_2O_2S$ 314.1089, found 314.1092

*4-Phenylbut-3-yn-2-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1h**):* yield 217.4 mg (65%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.52−7.41 (m, 5H), 7.35−7.28 (m, 3H), 5.93 (q, *J* = 6.7 Hz, 1H), 1.65 (d, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.3, 159.6, 148.3, 132.0, 130.8, 129.9, 128.9, 128.8, 128.4, 126.1, 122.2, 86.6, 85.6, 62.8, 21.4; IR (film) 3060, 2989, 2935, 2359, 1733, 1473, 1443, 1328, 1280, 1175, 1084, 845, 755, 691 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{19}H_{14}N_2O_2S$ 334.0776, found 334.0778.

*N-(Pent-2-yn-1-yl)-5-phenyl-1,2,3-thiadiazole-4-carboxamide (**1i**):* yield 168.2 mg (62%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 109−111 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (brs, 1H), 7.66−7.63 (m, 2H), 7.52−7.44 (m, 3H), 4.25−4.23 (m, 2H), 2.19 (qt, *J* = 12.5 Hz, 2.3 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 159.0, 149.3, 130.6, 130.2, 128.5, 125.9, 85.9, 74.1, 29.8, 13.7, 12.4; IR (film) 3311, 2979, 1661, 1277, 1530, 826 cm^{-1}; HRMS (EI) *m*/*z* calcd. for $C_{14}H_{13}N_3OS$ 271.0779, found 271.0779.

*5-Phenyl-N-(3-phenylprop-2-yn-1-yl)-1,2,3-thiadiazole-4-carboxamide (**1j**):* yield 174.8 mg (71%); R_f = 0.3 (EtOAc/CH_2Cl_2/hexane = 1/5/15); orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (brs, 1H), 7.67−7.65 (m, 2H), 7.51−7.43 (m, 5H), 7.33−7.29 (m, 3H), 4.51 (d, *J* = 5.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.9, 159.1, 149.2, 131.8, 130.7, 130.2, 128.6, 128.5, 128.3, 125.9, 122.5, 84.1, 83.8, 30.1 ; IR (film) 3331, 3059, 1674, 1270, 756, 691 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{18}H_{13}N_3OS$ 319.0779, found 319.0782.

*(5-Phenyl-1,2,3-thiadiazol-4-yl)methyl oct-2-ynoate (**1k**):* yield 236.0 mg (97%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52−7.46 (m, 5H), 5.56 (s, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.62−1.54 (m, 2H), 1.42−1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.4, 153.3, 152.2, 130.6, 129.6, 129.5, 126.9, 91.4, 72.6, 58.8, 31.1, 27.2, 22.2, 18.8, 14.0; IR (film) 2932, 2861, 2232, 1715, 1238, 1072, 696 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{17}H_{18}N_2O_2S$ 314.1089, found 314.1093.

*Pent-2-yn-1-yl 5-(p-tolyl)-1,2,3-thiadiazole-4-carboxylate (**1m**):* yield 277.8 mg (97%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 68−70 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 2H), 7.30−7.28 (m, 2H), 4.95 (t, *J* = 2.2 Hz, 2H), 2.43 (s, 3H), 2.26−2.20 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100

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MHz, $CDCl_3$) δ 162.9, 160.1, 147.5, 141.4, 129.9, 129.6, 122.9, 89.9, 72.7, 54.3, 21.6, 13.6, 12.6; IR (film) 2920, 2227, 1735, 1478, 1442, 1375, 1324, 1281, 1166, 990, 829, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}N_2O_2S$ 286.0776, found 286.0777.

*3-Phenylprop-2-yn-1-yl 5-(p-tolyl)-1,2,3-thiadiazole-4-carboxylate (**1n**):* yield 317.7 mg (95%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (m, 4H), 7.37−7.28 (m, 5H), 5.20 (s, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1, 160.0, 147.4, 141.5, 132.0, 129.9, 129.6, 129.0, 128.4, 122.8, 122.1, 87.3, 82.2, 54.2, 21.5; IR (film) 2920, 2231, 1735, 1478, 1442, 1375, 1324, 1280, 1166, 990, 757, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}N_2O_2S$ 334.0776, found 334.0776.

*Pent-2-yn-1-yl 5-(4-methoxyphenyl)-1,2,3-thiadiazole-4-carboxylate (**1o**):* yield 124.0 mg (41%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 71−73 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.52 (m, 2H), 7.01−6.97 (m, 2H), 4.97 (t, J = 2.2 Hz, 2H), 3.87 (s, 3H), 2.27−2.20 (m, 2H), 1.14 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8, 161.9, 160.2, 147.0, 131.7, 117.9, 114.4, 89.8, 72.7, 55.6, 54.2, 13.6, 12.6; IR (film) 2976, 2938, 2839, 2239, 1732, 1605, 1476, 1257, 1168, 985, 835, 784 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}N_2O_3S$ 302.0725, found 302.0728.

*3-Phenylprop-2-yn-1-yl 5-(4-methoxyphenyl)-1,2,3-thiadiazole-4-carboxylate (**1p**):* yield 332.9 mg (95%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); orange solid; mp 87−89 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.46−7.44 (m, 2H), 7.37−7.29 (m, 3H), 7.00−6.95 (m, 2H), 5.21 (s, 2H), 3.82 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 161.9, 160.2, 146.9, 132.1, 131.7, 129.0, 128.4, 122.2, 117.8, 114.4, 87.3, 82.3, 55.5, 54.2; IR (film) 2936, 2837, 2233, 1732, 1604, 1475, 1294, 1256, 1165, 1030, 835, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}N_2O_3S$ 350.0725, found 350.0723.

*Pent-2-yn-1-yl 5-(benzo[d][1,3]dioxol-5-yl)-1,2,3-thiadiazole-4-carboxylate (**1q**):* yield 230.9 mg (73%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 88−90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08−7.05 (m, 2H), 6.90−6.88 (m, 1H), 6.06 (s, 2H), 4.97 (t, J = 2.2 Hz, 2H), 2.27−2.21 (m, 2H), 1.14 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5, 160.1, 150.1, 148.2, 147.3, 124.9, 119.1, 110.2, 108.7, 102.0, 89.9, 72.6, 54.3, 13.6, 12.6; IR (film) 2977, 2938, 2907, 2239, 1732, 1509, 1471, 1316, 1243, 1175, 1037, 973, 815 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{12}N_2O_4S$ 316.0518, found 316.0515.

*3-Phenylprop-2-yn-1-yl 5-(benzo[d][1,3]dioxol-5-yl)-1,2,3-thiadiazole-4-carboxylate (**1r**):* yield 164.0 mg (45%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1/5/15); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.44 (m, 2H), 7.37−7.29 (m, 3H), 7.09−7.05 (m, 2H), 6.89−6.87 (m, 1H), 6.00 (s, 2H), 5.21 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.8, 160.0, 150.2, 148.2, 147.2, 132.1, 129.0, 128.4, 124.8, 122.1, 119.0, 110.2, 108.7, 102.0, 87.4, 82.2, 54.3; IR (film) 2902, 2782, 2237, 1733, 1509, 1470, 1316, 1244, 1172, 1036, 963, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{12}N_2O_4S$ 364.0518, found 364.0515.

*Pent-2-yn-1-yl 5-(4-bromophenyl)-1,2,3-thiadiazole-4-carboxylate (**1s**):* yield 277.5 mg (79%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow solid; mp 91−93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.44−7.41 (m, 2H), 4.95 (t, J = 2.2 Hz, 2H), 2.27−2.20 (m, 2H), 1.14 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.4, 159.8, 147.9, 132.1, 131.5, 125.6, 124.9, 90.1, 72.4, 54.5, 13.6, 12.6; IR (film) 2976, 2937, 2239, 1732, 1587, 1470, 1375, 1320, 1172, 1071, 984, 831 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{11}{}^{79}BrN_2O_2S$ 349.9725, $C_{14}H_{11}{}^{81}BrN_2O_2S$ 351.9705, found 349.9724, 351.9703.

*3-Phenylprop-2-yn-1-yl 5-(4-bromophenyl)-1,2,3-thiadiazole-4-carboxylate (**1t**):* yield 167.7 mg (42%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63−7.59 (m, 2H), 7.46−7.42 (m, 4H), 7.37−7.30 (m, 3H), 5.19 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5, 159.7, 147.8, 132.1, 132.0, 131.4, 129.1, 128.5, 125.6, 124.8, 122.0, 87.5, 82.0, 54.4; IR (film) 3057, 2938, 2234, 1734, 1587, 1470, 1321, 1271, 1169, 981, 756, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{11}{}^{79}BrN_2O_2S$ 397.9725, $C_{18}H_{11}{}^{81}BrN_2O_2S$ 399.9705, found 397.9723, 399.9709.

*Pent-2-yn-1-yl 5-(furan-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1u**):* yield 175.7 mg (67%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 105−107 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 3.6 Hz, 0.6 Hz, 1H), 7.65 (dd, J = 1.8 Hz, 0.6 Hz, 1H), 6.65 (dd, J = 3.7 Hz, 1.8 Hz, 1H), 5.07 (t, J = 2.2 Hz, 2H), 2.29−2.23 (m, 2H), 1.16 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 151.3, 146.9, 144.4, 143.2, 117.6, 113.6, 90.1, 72.8, 54.4, 13.6, 12.7; IR (film) 3147, 2981, 2938, 2247, 1717, 1573, 1480, 1310, 1219, 1029, 981, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{10}N_2O_3S$ 262.0412, found 262.0409.

*3-Phenylprop-2-yn-1-yl 5-(furan-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1v**):* yield 214.1 mg (69%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); pale yellow solid; mp 88−90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 3.7 Hz, 0.6 Hz, 1H), 7.65 (dd, J = 1.8 Hz, 0.7 Hz, 1H), 7.50−7.46 (m, 2H), 7.37−7.29 (m, 3H), 6.65 (dd, J = 3.6 Hz, 1.8 Hz, 1H), 5.32 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 151.5, 147.0, 144.3, 143.1, 132.1, 129.0, 128.4, 122.1, 117.8, 113.7, 87.5, 82.4, 54.4; IR (film) 3050, 2938, 2233, 1725, 1488, 1312, 1223, 1172, 1031, 964, 879, 754 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}N_2O_3S$ 310.0412, found 310.0415.

*Pent-2-yn-1-yl 5-(thiophen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1w**):* yield 264.4 mg (95%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); ivory solid; mp 75−77 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 3.8 Hz, 1.2 Hz, 1H), 7.64 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.19−7.17 (m, 1H), 5.05 (t, J = 2.2 Hz, 2H), 2.28−2.22 (m, 2H), 1.15 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 155.8, 145.7, 133.5, 132.2, 128.5, 126.0, 90.0, 72.7, 54.5, 13.5, 12.6; IR (film) 3106, 2975, 2313, 2238, 1721, 1513, 1463, 1298, 1175, 1147, 959, 732, 652 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{10}N_2O_2S_2$ 278.0184, found 278.0184.

*3-Phenylprop-2-yn-1-yl 5-(thiophen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1x**):* yield 320.0 mg (98%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); white solid; mp 85−87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 3.8 Hz, 1.2 Hz, 1H), 7.64 (dd, J = 5.1 Hz, 1.2 Hz, 1H), 7.49−7.46 (m, 2H), 7.36−7.29 (m, 3H), 7.18−7.16 (m, 1H), 5.30 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 156.0, 145.6, 133.6, 132.3, 132.1, 129.0, 128.6, 128.4, 126.0, 122.1, 87.5, 82.3, 54.5; IR (film) 2920, 2850, 2330, 2230, 1726, 1466, 1273, 1210, 1165, 965, 755, 690 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}N_2O_2S_2$ 326.0184, found 326.0181.

*Pent-2-yn-1-yl 5-cyclohexyl-1,2,3-thiadiazole-4-carboxylate (**1y**):* yield 192.1 mg (69%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 5.03 (t, J = 2.2 Hz, 2H), 3.84−3.76 (m, 1H), 2.29−2.22 (m, 2H), 2.18−2.14 (m, 2H), 1.89−1.78 (m, 3H), 1.54−1.43 (m, 2H), 1.39−1.24 (m, 3H), 1.15 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.4, 160.3, 148.0, 89.8, 72.8, 54.1, 37.1, 36.2, 26.3, 25.6, 13.6, 12.6; IR (film) 2976, 2931, 2852, 2240, 2117, 1725, 1486, 1313, 1193, 1130, 997, 786 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{18}N_2O_2S$ 278.1089, found 278.1093.

*3-Phenylprop-2-yn-1-yl 5-cyclohexyl-1,2,3-thiadiazole-4-carboxylate (**1z**):* yield 267.7 mg (82%); R_f = 0.6 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.46 (m, 2H), 7.36−7.29 (m, 3H), 5.27 (s, 2H), 3.85−3.78 (m, 1H), 2.17 (d, J = 11.5 Hz, 2H), 1.89−1.78 (m, 3H), 1.55−1.43 (m, 2H), 1.39−1.23 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.6, 160.2, 147.8, 132.0, 128.9, 128.4, 122.1, 87.2, 82.4, 54.0, 37.1, 36.1, 26.3, 25.5; IR (film) 2929, 2852, 2235, 1727, 1488, 1444, 1313, 1192, 1129, 997, 757, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{18}N_2O_2S$ 326.1089, found 326.1086.

Preparation of Alkynyl Thiadiazoles 3a−f. To a solution of the alcohol[18] (1.0 mmol), 4-dimethylaminopyridine (DMAP; 0.10 mmol, 36.7 mg), and thiadiazole-4-carboxylic acid (**5**;[16] 1.3 mmol, 822.8 mg) in dry DCE (10 mL) at 0 °C under a nitrogen atmosphere was added *N,N′*-dicyclohexylcarbodiimide (DCC; 1.3 mmol, 823.3 mg) in one portion. After it was stirred for 30 min at the same temperature, the reaction mixture was allowed warmed to room temperature followed by stirring for another 3 h. Then, the reaction mixture was filtered through Celite and the mixture was washed with CH_2Cl_2 (3 × 10 mL). The combined filtrate was evaporated under reduced pressure to give

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the crude product, which was purified by silica gel chromatography (EtOAc/CH_2Cl_2/hexane = 1/5/15) to provide the pure product **3**.[17]

*But-3-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3a**):* yield 155.0 mg (60%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.46 (m, 5H), 4.47 (t, J = 7.0 Hz, 2H), 2.60 (td, J = 7.0 Hz, 2.7 Hz, 2H), 2.00 (t, J = 2.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 160.1, 148.0, 130.8, 129.8, 128.8, 126.0, 79.5, 70.5, 63.6, 18.9; IR (film) 3288, 2963, 2918, 1731, 1474, 1330, 1281, 1178, 1003, 840, 751, 694 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{10}N_2O_2S$ 258.0463, found 258.0459.

*Hex-3-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3b**):* yield 203.3 mg (71%); R_f = 0.5 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.46 (m, 5H), 4.42 (t, J = 7.2 Hz, 2H), 2.55 (tt, J = 7.2 Hz, 2.4 Hz, 2H), 2.13 (qt, J = 12.5 Hz, 2.4 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.2, 160.2, 148.2, 130.8, 129.9, 128.7, 126.1, 83.9, 74.3, 64.3, 19.2, 14.1, 12.4; IR (film) 2974, 2936, 1733, 1474, 1388, 1330, 1281, 1179, 1005, 845, 752, 694 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}N_2O_2S$ 286.0776, found 286.0779.

*4-Phenylbut-3-yn-1-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3c**):* yield 210.7 mg (63%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1/5/15); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.43 (m, 5H), 7.38−7.36 (m, 2H), 7.29−7.27 (m, 3H), 4.55 (t, J = 7.0 Hz, 2H), 2.82 (t, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4, 160.2, 148.2, 131.7, 130.8, 129.9, 128.8, 128.3, 128.1, 126.1, 123.3, 85.0, 82.5, 63.8, 19.9; IR (film) 3059, 2961, 2916, 2360, 2341, 1732, 1474, 1330, 1281, 1177, 1004, 755, 692 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}N_2O_2S$ 334.0776, found 334.0778.

*2-(Hex-1-yn-1-yl)phenyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3d**):* yield 235.6 mg (65%); R_f = 0.4 (EtOAc/hexane = 1/15); Yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.64 (m, 2H), 7.52−7.44 (m, 4H), 7.33−7.29 (m, 1H), 7.23 (m, 2H), 2.29 (t, J = 6.9 Hz, 2H), 1.39−1.25 (m, 4H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ; 163.6, 158.4, 151.1, 147.1, 133.1, 130.9, 130.0, 128.8, 128.7, 126.3, 125.7, 121.9, 118.2, 96.2, 75.5, 30.5, 21.8, 19.2, 13.5; IR (film) 3062, 2957, 2232, 1752, 1186, 752 cm^{-1}; HRMS (EI) m/z calcd. For $C_{21}H_{18}N_2O_2S$ 362.1089, found: 362.1087.

*2-(Phenylethynyl)phenyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3e**):* yield 290.6 mg (76%); R_f = 0.2 (EtOAc/CH_2Cl_2/hexane = 1/1/20); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 1H), 7.55−7.53 (m, 2H), 7.45−7.39 (m, 1H), 7.38−7.33 (m, 3H), 7.31−7.21 (m, 7H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.9, 158.5, 151.2, 147.1, 133.1, 131.5, 130.9, 129.9, 129.6, 128.7, 128.6, 128.3, 126.5, 125.6, 122.7, 122.2, 117.6, 94.9, 84.3; IR (film) 3060, 2220, 1752, 1195, 754, 691 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{14}N_2O_2S$ 382.0776, found 382.0776.

*4-Chloro-2-(phenylethynyl)phenyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**3f**):* yield 219.2 mg (58%); R_f = 0.3 (ether/hexane = 1/4); white solid; mp 127−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 2.5 Hz, 1H), 7.55−7.53 (m, 2H), 7.49−7.45 (m, 1H), 7.41−7.34 (m, 3H), 7.31−7.26 (m, 5H), 7.21 (d, J = 8.7 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 158.2, 149.7, 146.8, 132.6, 131.9, 131.6, 131.0, 129.9, 129.5, 128.9, 128.8, 128.4, 125.4, 123.4 122.2, 119.2, 96.0, 83.0; IR (film) 3060, 2223, 1753, 1140, 864, 690 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{13}ClN_2O_2S$ 416.0386, found 416.0384.

General Procedure for Alkynyl Thiadiazoles 1l and 3g−i. Compounds **1l** and **3g−i** were prepared from thiadiazoles[15] as shown. Thiadiazole was reacted with DIBAL-H to give (1,2,3-thiadiazol-4-yl)methanol[19] in THF. In an oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere was placed (1,2,3-thiadiazol-4-yl)methanol (1.0 mmol) and DMF (3.0 mL). Sodium hydride was added as a 95% suspension in mineral oil (3.0 mmol, 72 mg), and the mixture was stirred at room temperature for 30 min. Alkynyl halide (5.0 mmol, 0.51 mL) was added, and the mixture was stirred at 100 °C for 2 h. All volatiles were removed in vacuo, and the resulting residue was partitioned between water and ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine and then dried over $MgSO_4$. The solvent was removed in vacuo and purified by silica gel chromatography (EtOAc/hexane = 1/5) to provide products **1** and **3**.

*4-((Pent-2-yn-1-yloxy)methyl)-5-phenyl-1,2,3-thiadiazole (**1l**):* yield 194.1 mg (75%); R_f = 0.5 (EtOAc/hexane = 1/5); orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.63 (m, 2H), 7.51−7.49 (m, 3H), 4.98 (s, 2H), 4.33 (t, J = 2.2 Hz, 2H), 2.21 (qt, J = 12.5 Hz, 2.1 Hz, 2H), 1.13 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 154.8, 130.3, 129.8, 129.4, 127.6, 89.4, 74.8, 62.6, 58.6, 13.9, 12.6; IR (film) 3063, 2976, 2936, 1245, 1074, 697 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{14}N_2OS$ 258.0827, found 258.0830.

*4-((Pent-4-yn-1-yloxy)methyl)-5-phenyl-1,2,3-thiadiazole (**3g**):* yield 240.3 mg (93%); R_f = 0.6 (EtOAc/hexane = 1/5); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.52−7.49 (m, 3H), 4.91 (s, 2H), 3.74 (t, J = 6.1 Hz, 2H), 2.29 (td, J = 10.5 Hz, 2.7 Hz, 2H), 1.94 (t, J = 2.7 Hz, 1H), 1.85 (quintet, J = 6.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 155.2, 130.3, 129.6, 129.4, 127.7, 83.7, 68.86, 68.80, 64.1, 28.6, 15.3; IR (film) 3294, 3062, 2867, 1102, 697, 637 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{14}N_2OS$ 258.0827, found 258.0823.

*5-Phenyl-4-(((5-phenylpent-4-yn-1-yl)oxy)methyl)-1,2,3-thiadiazole (**3h**):* yield 138.2 mg (41%); R_f = 0.4 (EtOAc/hexane = 1/10); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.62 (m, 2H), 7.50−7.47 (m, 3H), 7.37−7.34 (m, 2H), 7.29−7.26 (m, 3H), 4.93 (s, 2H), 3.79 (t, J = 6.1 Hz, 2H), 2.52 (t, J = 7.0 Hz, 2H), 1.93 (quintet, J = 6.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 155.2, 131.7, 130.3, 129.6, 129.4, 128.3, 127.74, 127.69, 124.0, 89.3, 81.2, 69.1, 64.1, 28.9, 16.4; IR (film) 3059, 2865, 2233, 1101, 757, 693 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{18}N_2OS$ 334.1140, found 334.1142.

*4-((Hex-5-yn-1-yloxy)methyl)-5-phenyl-1,2,3-thiadiazole (**3i**):* yield 239.7 mg (88%); R_f = 0.6 (EtOAc/hexane = 1/5); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2H), 7.51−7.49 (m, 3H), 4.89 (s, 2H), 3.65 (t, J = 6.3 Hz, 2H), 2.20 (td, J = 10.6 Hz, 2.6 Hz, 2H), 1.94 (t, J = 2.6 Hz, 1H), 1.80−1.73 (m, 2H), 1.65−1.57 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.7, 155.3, 130.3, 129.6, 129.4, 127.7, 84.3, 70.2, 68.6, 64.0, 28.8, 25.2, 18.3; IR (film) 3294, 2939, 2865, 1092, 697, 635 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{16}N_2OS$ 272.0983, found 272.0984.

General Procedure for Transannulation of Alkynyl Thiadiazoles for the Synthesis of 5,5-Fused Thiophenes. In a test tube were placed $[Rh(COD)Cl]_2$ (0.01 mmol, 4.9 mg), DPPF (0.024 mmol, 13.3 mg), and alkynyl thiadiazoles **1** (0.2 mmol) in chlorobenzene (1.0 mL). The resulting mixture was stirred at 130 °C for 30 min under a nitrogen atmosphere. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel using Et_2O/hexane = 1/4.

*4-Butyl-6-phenylthieno[3,4-c]furan-1(3H)-one (**2a**):* yield 51.7 mg (95%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.99 (m, 2H), 7.44−7.40 (m, 2H), 7.37−7.33 (m, 1H), 5.13 (s, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.71−1.64 (m, 2H), 1.47−1.38 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 145.1, 144.1, 133.0, 131.7, 129.2, 129.0, 127.9, 125.7, 66.2, 32.8, 27.9, 22.4, 13.9; IR (film) 2955, 2929, 1751, 1090, 1020, 754 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{16}O_2S$ 272.0871, found 272.0868.

*6-Phenylthieno[3,4-c]furan-1(3H)-one (**2b**):*[12c] yield 31.1 mg (72%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 124−126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.04 (m, 2H), 7.47−7.43 (m, 2H), 7.41−7.37 (m, 1H), 6.98 (t, J = 1.4 Hz, 1H), 5.21 (d, J = 1.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.0, 148.6, 148.0, 131.1, 129.6, 129.0, 128.0, 126.1, 112.7, 66.5; IR (film) 3105, 2945, 1751, 1115, 1053, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_8O_2S$ 216.0245, found 216.0241.

*4-Methyl-6-phenylthieno[3,4-c]furan-1(3H)-one (**2c**):* yield 40.1 mg (87%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 111−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.44−7.40 (m, 2H), 7.37−7.33 (m, 1H), 5.11 (d, J = 1.1 Hz, 2H), 2.40 (t, J = 1.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 145.3, 144.8, 131.6, 129.3, 129.0, 127.8, 127.0, 125.8, 66.1, 13.0; IR (film) 3064, 2919, 1752, 1342, 1113, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{10}O_2S$ 230.0402, found 230.0400.

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*4-Ethyl-6-phenylthieno[3,4-c]furan-1(3H)-one (**2d**):* yield 43.5 mg (89%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 78−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.43−7.40 (m, 2H), 7.36−7.33 (m, 1H), 5.14 (s, 2H), 2.78 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 144.9, 143.7, 134.3, 131.6, 129.2, 129.0, 127.8, 125.7, 66.2, 21.7, 15.0; IR (film) 2973, 2959, 1746, 1588, 1454, 1116 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{12}O_2S$ 244.0558, found 244.0561.

*4,6-Diphenylthieno[3,4-c]furan-1(3H)-one (**2e**):*[20] yield 52.0 mg (89%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; mp 139−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 2H), 7.46−7.40 (m, 4H), 7.39−7.32 (m, 4H), 5.35 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.9, 146.1, 143.6, 132.1, 131.5, 131.2, 129.7, 129.5, 129.1, 128.3, 128.1, 127.0, 126.0, 67.2; IR (film) 3056, 2928, 1742, 1112, 1052, 755 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{12}O_2S$ 292.0558, found 292.0561.

*6-Phenyl-4-(trimethylsilyl)thieno[3,4-c]furan-1(3H)-one (**2f**):* yield 56.5 mg (98%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 154−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.05 (m, 2H), 7.46−7.42 (m, 2H), 7.40−7.36 (m, 1H), 5.18 (s, 2H), 0.36 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 156.2, 152.6, 131.5, 129.6, 129.1, 128.1, 127.9, 127.2, 67.3, −0.18; IR (film) 2966, 2888, 1764, 1246, 1016, 844 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{16}O_2SSi$: 288.0640, found 288.0641.

*4-Butyl-3-methyl-6-phenylthieno[3,4-c]furan-1(3H)-one (**2g**):* yield 56.1 mg (98%); R_f = 0.4 (ether/hexane = 1/4); Yellow solid; mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−8.00 (m, 2H), 7.43−7.39 (m, 2H), 7.36−7.32 (m, 1H), 5.41 (q, J = 6.6 Hz, 1H), 2.74 (td, J = 7.5 Hz, 2.5 Hz, 2H), 1.72−1.66 (m, 2H), 1.63 (d, J = 6.6 Hz, 3H), 1.48−1.39 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.8, 148.6, 144.7, 133.4, 131.7, 129.2, 129.0, 127.9, 126.1, 74.5, 33.6, 27.6, 22.4, 20.6, 13.9; IR (film) 2957, 2930, 1755, 1310, 1119, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{18}O_2S$ 286.1028, found 286.1025.

*3-Methyl-4,6-diphenylthieno[3,4-c]furan-1(3H)-one (**2h**):* yield 44.1 mg (72%); R_f = 0.4 (ether/hexane = 1/4); white solid; mp 131−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 2H), 7.48−7.43 (m, 6H), 7.41−7.36 (m, 2H), 5.80 (q, J = 6.5 Hz, 1H), 1.56 (d, J = 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.5, 148.4, 146.3, 131.9, 131.8, 131.3, 129.7, 129.4, 129.1, 128.5, 128.1, 127.2, 75.4, 19.2; IR (film) 3061, 2981, 1757, 1125, 1053, 758 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}O_2S$ 306.0715, found 306.0713.

*1-Ethyl-3-phenyl-5,6-dihydro-4H-thieno[3,4-c]pyrrol-4-one (**2i**):* yield 38.4 mg (79%); R_f = 0.4 (EtOAc/CH_2Cl_2/hexane = 1/1/2); ivory solid; mp 164−166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (m, 2H), 7.42−7.38 (m, 2H), 7.32−7.28 (m, 1H), 6.87 (brs, 1H), 4.26−4.25 (m, 2H), 2.78 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 141.3, 141.1, 135.0, 132.6, 131.4, 128.8, 128.3, 128.1, 41.7, 21.6, 15.2; IR (film) 3196, 3080, 2878, 1682, 1488, 754 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{13}NOS$ 243.0718, found 243.0716.

*1,3-Diphenyl-5,6-dihydro-4H-thieno[3,4-c]pyrrol-4-one (**2j**):* yield 41.4 mg; (71%); R_f = 0.4 (EtOAc/hexane = 1/1); ivory solid; mp 231−233 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.74 (s, 1H), 8.21 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.48 (q, J = 8.1 Hz, 4H), 7.38 (q, J = 6.5 Hz, 2H), 4.55 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 164.4, 142.5, 139.9, 134.4, 132.2, 131.7, 130.8, 129.4, 128.8, 128.7, 127.9, 127.7, 125.9, 42.5; IR (film) 3324, 3189, 2927, 1681, 1483, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{13}NOS$ 291.0718, found 291.0720.

*6-Pentyl-4-phenylthieno[3,4-c]furan-1(3H)-one (**2k**):* yield 42.4 mg (74%); R_f = 0.5 (ether/hexane = 1/4); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.39 (m, 2H), 7.33−7.28 (m, 3H), 5.33 (s, 2H), 3.10 (t, J = 7.6 Hz, 2H), 1.77 (quintet, J = 7.5 Hz, 2H), 1.43−1.34 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 149.6, 141.2, 132.6, 130.9, 129.4, 128.9, 127.9, 125.8, 67.5, 31.3, 31.2, 27.9, 22.5, 14.1; IR (film) 2954, 2929, 2857, 1760, 1541, 999, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{17}H_{18}O_2S$ 286.1028, found 286.1028.

*4-Ethyl-6-phenyl-1,3-dihydrothieno[3,4-c]furan (**2l**):* yield 28.7 mg (62%); R_f = 0.6 (ether/hexane = 1/4); pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.33 (m, 2H), 7.32−7.30 (m, 2H), 7.24−7.20 (m, 1H), 4.99 (s, 2H), 4.80 (s, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.1, 141.1, 134.2, 133.2, 129.1, 128.7, 126.8, 125.7, 69.0, 67.4, 22.4, 15.3; IR (film) 3025, 2966, 2851, 2360, 1489, 1034, 688 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{14}OS$ 230.0765, found 230.0762.

*4-Ethyl-6-(p-tolyl)thieno[3,4-c]furan-1(3H)-one (**2m**):* yield 50.6 mg (98%); R_f = 0.4 (ether/hexane = 1/4); white solid; mp 114−116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.88 (m, 2H), 7.22−7.20 (m, 2H), 5.11 (t, J = 0.9 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.30 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 145.2, 143.5, 139.4, 133.5, 129.6, 128.9, 127.7, 125.2, 66.1, 21.6, 21.5, 14.9; IR (film) 3076, 2974, 1743, 1345, 1082, 831 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}O_2S$ 258.0715, found 258.0716.

*4-Phenyl-6-(p-tolyl)thieno[3,4-c]furan-1(3H)-one (**2n**):* yield 51.5 mg (84%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; mp 174−176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2H), 7.45−7.41 (m, 2H), 7.37−7.31 (m, 3H), 7.26−7.24 (m, 2H), 5.36 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.0, 146.6, 143.5, 140.1, 132.3, 130.8, 129.8, 129.5, 128.6, 128.2, 128.0, 126.6, 125.9, 67.2, 21.6; IR (film) 3025, 2873, 1733, 1487, 1095, 761 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}O_2S$ 306.0715, found306.0714.

*4-Ethyl-6-(4-methoxyphenyl)thieno[3,4-c]furan-1(3H)-one (**2o**):* yield 46.1 mg (84%); R_f = 0.4 (ether/hexane = 1/4); white solid; mp 81−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.95 (m, 2H), 6.95−6.92 (m, 2H), 5.12 (s, 2H), 3.84 (s, 3H), 2.76 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.5, 160.5, 145.3, 143.3, 132.8, 129.4, 124.6, 124.5, 114.3, 66.1, 55.5, 21.6, 15.0; IR (film) 2968, 2839, 1744, 1499, 1254, 1023 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0664.

*6-(4-Methoxyphenyl)-4-phenylthieno[3,4-c]furan-1(3H)-one (**2p**):* yield 63.2 mg (98%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; mp 168−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.04 (m, 2H), 7.46−7.42 (m, 2H), 7.38−7.31 (m, 3H), 6.99−6.96 (m, 2H), 5.38 (s, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 160.9, 146.6, 143.5, 132.3, 130.0, 129.7, 129.5, 128.1, 125.84, 125.81, 124.2, 114.5, 67.2, 55.5; IR (film) 2934, 2839, 1744, 1497, 1258, 1095 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}O_3S$ 322.0664, found 322.0664.

*6-(Benzo[d][1,3]dioxol-5-yl)-4-ethylthieno[3,4-c]furan-1(3H)-one (**2q**):* yield 55.4 mg (96%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; 104−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 1.8 Hz, 1H), 7.52 (dd, J = 8.2 Hz, 1.9 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.00 (s, 2H), 5.13 (t, J = 1.0 Hz, 2H), 2.76 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.4, 148.6, 148.2, 145.1, 143.4, 133.1, 125.8, 124.8, 122.4, 108.7, 108.4, 101.6, 66.2, 21.6, 15.0; IR (film) 2969, 2887, 1749, 1484, 1233, 1025 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{12}O_4S$ 288.0456, found 288.0454.

*6-(Benzo[d][1,3]dioxol-5-yl)-4-phenylthieno[3,4-c]furan-1(3H)-one (**2r**):* yield 65.3 mg (97%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; mp 210−212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.61 (m, 2H), 7.46−7.42 (m, 2H), 7.37−7.31 (m, 3H), 6.88 (dd, J = 8.0 Hz, 0.4 Hz, 1H), 6.03 (s, 2H), 5.37 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.1, 149.1, 148.3, 146.3, 143.5, 132.2, 130.4, 129.5, 128.2, 126.1, 125.9, 125.5, 122.9, 108.9, 108.5, 101.7, 67.2; IR (film) 3078, 2920, 1742, 1479, 1256, 1090 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{12}O_4S$ 336.0456, found 336.0457.

*6-(4-Bromophenyl)-4-ethylthieno[3,4-c]furan-1(3H)-one (**2s**):* yield 62.7 mg (97%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 101−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.86 (m, 2H), 7.53−7.50 (m, 2H), 5.14 (s, 2H), 2.77 (q, J = 7.6 Hz, 2H), 1.33 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.2, 143.8, 143.2, 134.7, 132.1, 130.6, 129.2, 126.2, 123.3, 66.2, 21.7, 14.9; IR (film) 2978, 2936, 1746, 1482, 1078, 773 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{11}{}^{79}BrO_2S$ 321.9663, $C_{14}H_{11}{}^{81}BrO_2S$ 323.9643, found 321.9660, 323.9650.

*6-(4-Bromophenyl)-4-phenylthieno[3,4-c]furan-1(3H)-one (**2t**):* yield 57.9 mg (78%); R_f = 0.4 (ether/hexane = 1/4); yellow solid; mp 179−181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.96 (m, 2H),

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7.59−7.56 (m, 2H), 7.48−7.43 (m, 2H), 7.39−7.34 (m, 3H), 5.40 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.9, 144.5, 143.8, 132.3, 132.0, 130.2, 129.6, 129.5, 129.3, 128.6, 127.5, 126.1, 124.1, 67.3; IR (film) 3055, 2932, 1738, 1478, 1092, 753 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{11}{}^{79}BrO_2S$ 369.9663, $C_{18}H_{11}{}^{81}BrO_2S$ 371.9644, found 369.9665, 371.9637

4-Ethyl-6-(furan-2-yl)thieno[3,4-c]furan-1(3H)-one ***(2u)****:* yield 44.5 mg (95%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 109−111 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 3.4 Hz, 1H), 7.43−7.42 (m, 1H), 6.54 (dd, J = 3.5 Hz, 1.8 Hz, 1H), 5.14 (s, 2H), 2.77 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 147.1, 142.9, 142.7, 133.5, 132.6, 124.0, 112.9, 111.9, 66.5, 21.6, 14.9; IR (film) 3114, 2976, 1748, 1342, 1101, 773 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{10}O_3S$ 234.0351, found 234.0352.

6-(Furan-2-yl)-4-phenylthieno[3,4-c]furan-1(3H)-one ***(2v)****:* yield 49.7 mg (88%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 140−142 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 3.5 Hz, 0.6 Hz, 1H), 7.49−7.48 (m, 1H), 7.46−7.42 (m, 2H), 7.38−7.32 (m, 3H), 6.58 (dd, J = 3.5 Hz, 1.8 Hz, 1H), 5.39 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.7, 146.9, 143.4, 142.8, 133.6, 132.2, 130.7, 129.6, 128.3, 125.8, 125.2, 113.24, 113.22, 67.6; IR (film) 3140, 2940, 1744, 1520, 1057, 754 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}O_3S$ 282.0351, found 282.0350.

4-Ethyl-6-(thiophen-2-yl)thieno[3,4-c]furan-1(3H)-one ***(2w)****:* yield 47.6 mg (95%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 107−109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.90 (m, 1H), 7.32−7.31 (m, 1H), 7.07−7.06 (m, 1H), 5.11 (s, 2H), 2.73 (q, J = 7.6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 142.9, 137.6, 133.5, 133.3, 128.7, 128.4, 127.2, 124.9, 66.4, 21.6, 14.9; IR (film) 3107, 2962, 1744, 1345, 1092, 713 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{10}O_2S_2$ 250.0122, found 250.0120.

4-Phenyl-6-(thiophen-2-yl)thieno[3,4-c]furan-1(3H)-one ***(2x)****:* yield 53.1 mg (89%); R_f = 0.4 (ether/hexane = 1/4); Yellow solid; mp 158−160 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04−8.03 (m, 1H), 7.46−7.42 (m, 2H), 7.40−7.38 (m, 1H), 7.35−7.31 (m, 3H), 7.13−7.11 (m, 1H), 5.38 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.8, 143.0, 138.8, 133.3, 132.0, 130.3, 129.64, 129.56, 128.7, 128.3, 128.0, 126.2, 125.9, 67.5; IR (film) 3094, 2929, 1753, 1450, 1102, 682 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{10}O_2S_2$ 298.0122, found 298.0120.

6-Cyclohexyl-4-ethylthieno[3,4-c]furan-1(3H)-one ***(2y)****:* yield 42.1 mg (84%); R_f = 0.4 (ether/hexane = 1/4); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 2H), 3.33−3.27 (m, 1H), 2.72 (q, J = 7.6 Hz, 2H), 2.04−2.03 (m, 2H), 1.82−1.71 (m, 3H), 1.50−1.36 (m, 4H), 1.30−1.26 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.4, 154.4, 141.2, 132.4, 126.1, 66.6, 38.1, 35.1, 26.4, 25.8, 21.7, 15.0; IR (film) 2927, 2851, 1761, 1340, 1088, 1010 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{18}O_2S$ 250.1028, found 250.1029.

6-Cyclohexyl-4-phenylthieno[3,4-c]furan-1(3H)-one ***(2z)****:* yield 50.1 mg (84%); R_f = 0.4 (ether/hexane = 1/4); white solid; mp 139−141 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.39 (m, 2H), 7.34−7.28 (m, 3H), 5.33 (s, 2H), 3.42−3.35 (m, 1H), 2.12−2.09 (m, 2H), 1.86−1.75 (m, 3H), 1.54−1.40 (m, 4H), 1.35−1.25 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.0, 156.0, 141.4, 132.7, 130.3, 129.4, 27.8, 127.6, 125.8, 67.6, 38.3, 35.0, 26.4, 25.8; IR (film) 2926, 2851, 1758, 1446, 1096, 688 cm^{-1}; HRMS (EI) m/z calcd for $C_{18}H_{18}O_2S$ 298.1028, found 298.1028.

General Procedure for Transannulation of Diverse Alkynyl Thiadiazoles for the Synthesis of 5,*n*-Fused Thiophenes. In a test tube were placed $[Rh(COD)Cl]_2$ (0.01 mmol, 4.9 mg), DPPF (0.024 mmol, 13.3 mg), and alkynyl thiadiazoles **1** (0.2 mmol) in chlorobenzene (1.0 mL). The resulting mixture was stirred at 130 °C for 30 min under a nitrogen atmosphere. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel using Et_2O/hexane = 1/4.

3-Phenyl-6,7-dihydro-4H-thieno[3,4-c]pyran-4-one ***(4a)****:*[12c] yield 23.5 mg (51%); R_f = 0.4 (ether/hexane = 1/4); white solid; mp 118−120 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63−7.61 (m, 2H), 7.43−7.39 (m, 3H), 7.03 (t, J = 1.1 Hz, 1H), 4.49 (t, J = 5.8 Hz, 2H), 3.04−3.02 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 154.9, 139.2, 132.5, 129.8, 129.3, 128.4, 122.0, 118.3, 67.9, 26.4; IR (film) 2921, 2853, 1722, 1460, 1268, 751 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{10}O_2S$ 230.0402, found 230.0402.

1-Ethyl-3-phenyl-6,7-dihydro-4H-thieno[3,4-c]pyran-4-one ***(4b)****:* yield 45.0 mg (87%); R_f = 0.4 (ether/hexane = 1/4); Pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.59 (m, 2H), 7.42−7.37 (m, 3H), 4.48 (t, J = 5.8 Hz, 2H), 2.90 (t, J = 5.8 Hz, 2H), 2.80 (q, J = 7.5 Hz, 2H), 1.32 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 151.5, 139.0, 133.8, 132.7, 129.7, 129.0, 128.3, 121.8, 67.7, 24.7, 21.2, 15.8; IR (film) 2966, 2895, 1725, 1471, 1146, 753 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{14}O_2S$ 258.0715, found 258.0716.

1,3-Diphenyl-6,7-dihydro-4H-thieno[3,4-c]pyran-4-one ***(4c)****:* yield 38.0 mg (62%); R_f = 0.4 (ether/hexane = 1/4); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.65 (m, 2H), 7.47−7.46 (m, 4H), 7.45−7.37 (m, 4H), 4.46 (t, J = 5.8 Hz, 2H), 3.12 (t, J = 5.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0, 153.4, 136.4, 134.5, 132.7, 132.3, 129.8, 129.3, 129.2, 128.5, 128.39, 128.36, 122.8, 67.8, 26.2; IR (film) 3057, 2897, 1725, 1465, 1161, 694 cm^{-1}; HRMS (EI) m/z calcd for $C_{19}H_{14}O_2S$ 306.0715, found 306.0711.

1-Butyl-3-phenyl-4H-thieno[3,4-c]chromen-4-one ***(4d)****:* yield 59.9 mg (90%); R_f = 0.4 (ether/hexane = 1/4); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.91 (m, 1H), 7.64−7.60 (m, 2H), 7.46−7.43 (m, 3H), 7.40−7.32 (m, 2H), 7.30−7.25 (m, 1H), 3.23 (t, J = 7.8 Hz, 2H), 1.91−1.83 (m, 2H), 1.62−1.52 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 151.0, 150.7, 139.0, 132.4, 130.2, 130.1, 129.2, 128.6, 128.2, 124.5, 124.3, 119.9, 119.0, 117.7, 32.3, 30.1, 22.8, 14.0; IR (film) 2956, 2871, 1736, 1459, 1140, 747 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{18}O_2S$ 334.1028, found 334.1025.

1,3-Diphenyl-4H-thieno[3,4-c]chromen-4-one ***(4e)****:* yield 53.2 mg (75%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 166−168 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.67 (m, 2H), 7.59−7.56 (m, 2H), 7.54−7.52 (m, 3H), 7.49−7.46 (m, 3H), 7.41−7.39 (m, 1H), 7.30−7.28 (m, 2H), 6.95−6.91 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 153.8, 151.2, 136.7, 133.3, 132.1, 130.7, 130.4, 130.2, 129.50, 129.48, 129.3, 129.2, 128.4, 124.3, 123.9, 119.6, 118.0, 117.6; IR (film) 3058, 3022, 1739, 1459, 1134, 748 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{14}O_2S$ 354.0715, found 354.0712.

8-Chloro-1,3-diphenyl-4H-thieno[3,4-c]chromen-4-one ***(4f)****:* yield 64.6 mg (83%); R_f = 0.4 (ether/hexane = 1/4); ivory solid; mp 171−173 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.66 (m, 2H), 7.57 (s, 5H), 7.49−7.47 (m, 3H), 7.33 (dd, J = 2.1 Hz, 0.6 Hz, 1H), 7.26−7.21 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.6, 154.1, 149.7, 137.7, 132.6, 131.8 130.20, 130.18 (2C), 129.9, 129.7, 129.56, 129.53, 129.2, 128.4, 124.0, 119.24, 119.22, 118.9; IR (film) 3059, 1742, 1467, 1262, 1010, 747 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{13}ClO_2S$ 388.0325, found 388.0328.

3-Phenyl-4,6,7,8-tetrahydrothieno[3,4-c]oxepine ***(4g)****:* yield 24.8 mg (54%); R_f = 0.5 (ether/hexane = 1/4); pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.31 (m, 5H), 6.91 (s, 1H), 4.62 (s, 2H), 4.03−4.00 (m, 2H), 2.93−2.90 (m, 2H), 1.88−1.83 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.3, 141.0, 137.5, 134.3, 129.8, 128.7 127.8, 119.6, 76.0, 68.1, 31.1, 31.0; IR (film) 3059, 2933, 2842, 1251, 1105, 751, 699 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{14}OS$ 230.0765, found 230.0763.

1,3-Diphenyl-4,6,7,8-tetrahydrothieno[3,4-c]oxepine ***(4h)****:* yield 33.7 mg (55%); R_f = 0.5 (ether/hexane = 1/4); yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.40 (m, 8H), 7.38−7.33 (m, 2H), 4.66 (s, 2H), 4.05−4.02 (m, 2H), 2.99−2.96 (m, 2H), 1.87−1.82 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.6, 139.2, 138.4, 137.2, 134.5, 133.9, 129.82, 129.80, 128.72, 128.70, 127.9, 127.7, 75.8, 68.1, 30.9, 28.3; IR (film) 3056, 2935, 2842, 1116, 752, 698 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{18}OS$ 306.1078, found 306.1080.

3-Phenyl-6,7,8,9-tetrahydro-4H-thieno[3,4-c]oxocine ***(4i)****:* yield 25.2 mg (52%); R_f = 0.5 (ether/hexane = 1/4); pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.54 (m, 2H), 7.43−7.40 (m, 2H), 7.35−7.31 (m, 1H), 6.92 (s, 1H), 4.62 (s, 2H), 3.73 (t, J = 4.3 Hz, 2H), 2.90 (t, J = 5.6 Hz, 2H), 1.76−1.75 (m, 4H); $^{13}C\{^1H\}$ NMR

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(100 MHz, $CDCl_3$) δ 144.2, 142.3, 134.6, 134.2, 129.3, 128.8 127.8, 119.8, 69.1, 63.7, 29.7, 29.1, 28.1; IR (film) 3057, 2923, 2853, 1456, 1077, 698 cm^{-1}; HRMS (EI) m/z calcd for $C_{15}H_{16}OS$ 244.0922, found 244.0922.

Preparation of Alkynyl Thiadiazole 7. Thiadiazole[15] (4.4 mmol, 1.03 g) was added to a 10% aqueous methanolic solution (9.0 mL) of potassium hydroxide (8.8 mmol, 494.0 mg), and the mixture was heated for 2 h under reflux. After the solvent was evaporated, 10 mL of water was added to the residue and the mixture was acidified with dilute hydrochloric acid with vigorous stirring. The precipitate was filtered off, dried in air, and recrystallized from water. To a solution of 1-benzyl-4-ethynylpiperidin-4-ol (**6**;[21] 1.0 mmol), 4-dimethylaminopyridine (DMAP; 0.10 mmol, 36.7 mg), and thiadiazole-4-carboxylic acid (**5**;[16] 1.3 mmol, 822.8 mg) in dry DCE (10 mL) at 0 °C under a nitrogen atmosphere was added *N,N′*-dicyclohexylcarbodiimide (DCC; 1.3 mmol, 823.3 mg) in one portion. After it was stirred for 30 min at the same temperature, the reaction mixture was heated to 80 °C followed by stirring for another 12 h. Then, the reaction mixture was filtered through Celite and the mixture was washed with CH_2Cl_2 (3 × 10 mL). The combined filtrate was evaporated under reduced pressure to give the crude product, which was purified by silica gel chromatography (EtOAc/hexane = 1/4) to provide the pure product **7**.

*1-Benzyl-4-ethynylpiperidin-4-yl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**7**):* yield 326.8 mg (81%); R_f = 0.5 (EtOAc/hexane = 1/2); brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52−7.44 (m, 5H), 7.33−7.23 (m, 5H), 3.47 (s, 2H), 2.70 (s, 1H), 2.50−2.42 (m, 4H), 2.22−2.19 (m, 2H), 2.09−2.07 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.7, 158.6, 149.1, 138.5, 130.7, 129.9, 129.1, 128.8, 128.4, 127.2, 126.4, 82.3, 76.0 (2C), 62.7, 49.6, 36.6; IR (film) 3281, 2937, 2811, 1735, 1339, 1178 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{21}N_3O_2S$ 403.1354, found 403.1353.

General Procedure for Transannulation of Alkynyl Thiadiazole 7 for the Synthesis of Spirocyclic Fused Thiophene 8. In a test tube were placed $[Rh(COD)Cl]_2$ (0.01 mmol, 4.9 mg), DPPF (0.024 mmol, 13.3 mg), and alkynyl thiadiazole **7** (0.2 mmol) in chlorobenzene (1.0 mL). The resulting mixture was stirred at 130 °C for 2 h under a nitrogen atmosphere. After Celite filtration and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel using EtOAc/hexane = 1/2.

*1-Benzyl-4′-phenyl-3′H-spiro[piperidine-4,1′-thieno[3,4-c]furan]-3′-one (**8**):*[2] yield 35.3 mg (47%); R_f = 0.3 (EtOAc/hexane = 1/2); orange oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06−8.04 (m, 2H), 7.46−7.42 (m, 2H), 7.40−7.38 (m, 1H), 7.35−7.32 (m, 4H), 7.30−7.27 (m, 1H), 6.92 (s, 1H), 3.61 (s, 2H), 2.79−2.76 (m, 2H), 2.65−2.59 (m, 2H), 2.13−2.06 (m, 2H), 2.00−1.97 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.0, 156.6, 148.2, 138.3, 131.3, 129.7, 129.3, 129.1, 128.4, 128.1, 127.3, 126.5, 112.3, 82.2, 63.2, 49.7, 37.0; IR (film) 2916, 2811, 2360, 2341, 1749 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02614.

X-ray crystallographic data for **2d** and NMR spectra for all products (CIF)

X-ray crystallographic data for **2d** (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to Professor B. Moon Kim (Seoul National University) on the occasion of his 60th birthday.

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