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Palladium-Catalyzed Divergent Reactions of 1,6-Enyne Carbonates: Synthesis of Vinylidenepyridines and Vinylidenepyrrolidines

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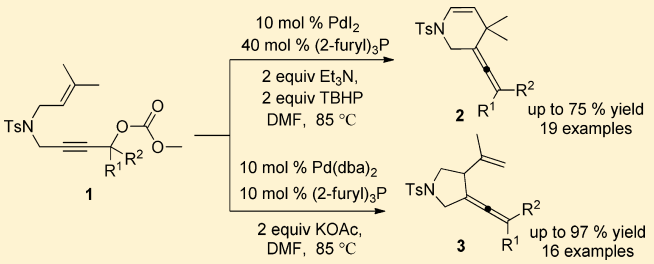
Supporting Information

ABSTRACT: A method for preparing five- or six-membered heterocyclic compounds from enyne carbonates via palladium catalysis was developed. Enyne carbonates were transformed into 3-vinylidene-1-tosylpyridines **2** in the presence of PdI_2 as the catalyst. Using $Pd(dba)_2$ as the catalyst, 3-vinylidene-1-tosylpyrrolidines **3** were obtained. Further functionalizations of compounds **3** were carried out in a one-pot manner.



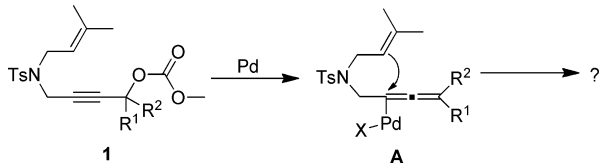
INTRODUCTION

The construction of carbon−carbon and carbon−heteroatom bonds via palladium catalysis from propargylic compounds with nucleophiles has developed tremendously over the past few years.[1] Since the first report of Tsuji in 1985, many interesting reactions in this family have been shown to be very effective for organic synthesis,[2] including the efforts of our group.[3] Olefins as nucleophiles are well-known to react with allenylpalladium to form carbon−carbon bonds.[4] However, much less attention has been paid to the propargylic substitution reactions of propargylic carbonates with olefins as nucleophiles via palladium catalysis because most of these reactions give rise to corresponding allenic systems and subsequent rearranged derivatives.[5] Thus, allenes that can be prepared by isomerization, metal-mediated reactions, transition-metal-catalyzed reactions, and other reactions[6] continue to attract considerable attention due to their extraordinary properties, such as strained structure and high reactivity.[7]

Very recently, our group has reported a concise synthesis of five-membered allenes **3** from hydroxylated enynes using Brønsted acids as catalysts.[8] This synthesis was performed in the context of our ongoing efforts to construct various functionalized heterocyclic structures, as well as to form carbon−carbon and carbon−heteroatom bonds from propargylic compounds with nucleophiles using palladium as the catalyst. The vision was that 1,6-enyne carbonates would first generate an intermediate allenylpalladium **A** by facile decarboxylation, which would be subsequently trapped by an olefin in an intramolecular fashion to form the putative products (Scheme 1).[9]

In the current study, a novel strategy for the construction of heterocyclic allenes from 1,6-enyne carbonates **1** using palladium as the catalyst is reported. Not only 3-vinylidene-1-tosylpyridines but also 3-vinylidene-1-tosylpyrrolidines were obtained in moderate to good yields.

Scheme 1. Design of the Proposed Palladium-Catalyzed Process



RESULTS AND DISCUSSION

To explore the proposed intramolecular cyclization reaction, a model enyne carbonate **1a** was treated with 5 mol % $Pd(OAc)_2$, 20 mol % PPh_3, 2 equiv of KI, and 2 equiv of Et_3N in DMF as the solvent under oxygen. After the mixture was stirred at 80 °C for 2 h, only a 20% yield of **2a** and trace amounts of **3a** were isolated (Table 1, entry 1). Further investigation revealed that a larger catalyst loading and higher reaction temperature gave a higher yield of **2a** (entries 2, 4, and 5). When a monodentate phosphine ligand such as $P(2\text{-furyl})_3$ was used, a moderate yield of **2a** was obtained (entry 3). When PdI_2 was used as the catalyst, **2a** was the sole product (entry 6).

Other bases were screened (entries 7 and 8), but Et_3N was proven to be the best. The influences of the reaction additive and solvent were also screened (entries 9−11). The combination of DMF and TBHP was found to give the best result (entry 10). The cyclization of a six-membered ring gave a low yield without an additive, revealing that the additive played an important role in this reaction system. The reason may be the formation of I_3^- upon the addition of KI or TBHP. I_3^- had a spatial interaction with the palladium catalyst; thus, less catalyst was available for the formation of intermediate **B** (in

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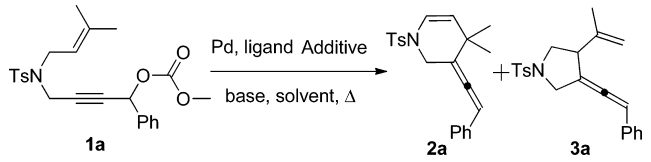
Table 1. Palladium-Catalyzed Synthesis of Heterocyclic Allenes from 1,6-Enyne Carbonate 1a[a]



entry	catalyst (mol %)	base (equiv)	ligand (mol %)	solvent	T (°C)	additive (equiv)	Yield (%) 2a	Yield (%) 3a
1	$Pd(OAc)_2$ (5)	Et_3N (2)	PPh_3 (20)	DMF	80	KI (2)[b]	20	trace
2	$Pd(OAc)_2$ (10)	Et_3N (2)	PPh_3 (40)	DMF	80	KI (2)[b]	41	trace
3	$Pd(OAc)_2$ (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMF	80	KI (2)[b]	48	trace
4	$Pd(OAc)_2$ (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMF	85	KI (2)[b]	60	14
5	$Pd(OAc)_2$ (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMF	95	KI (2)[b]	50	trace
6	PdI_2 (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMF	85	KI (2)[b]	54	–
7	PdI_2(10)	KOH (2)	P(2-furyl)$_3$ (40)	DMF	85	KI (2)[b]	10	–
8	PdI_2 (10)	KOAc (2))	P(2-furyl)$_3$ (40)	DMF	85	KI (2)[b]	45	–
9	PdI_2 (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMSO	85	TBHP (2)[c,d]	59	–
10	**PdI_2 (10)**	**Et_3N (2)**	**P(2-furyl)$_3$ (40)**	**DMF**	**85**	**TBHP (2)[c]**	**75**	–
11	PdI_2 (10)	Et_3N (2)	P(2-furyl)$_3$ (40)	DMF	85	–[c]	40	–
12	$Pd(OAc)_2$ (5)	KOAc (2)	PPh_3 (20)	DMF	80	–[c]	trace	13
13	$Pd(OAc)_2$ (5)	KOAc (2)	P(*o*-tolyl)$_3$ (20)	DMF	80	–[c]	trace	47
14	$Pd(OAc)_2$ (5)	KOAc (2)	P(2-furyl)$_3$ (10)	DMF	80	–[c]	12	70
15	$Pd_2(dba)_3$ (5)	KOAc (2)	P(2-furyl)$_3$ (10)	DMF	80	–[c]	–	57
16	$Pd(dba)_2$ (10)	KOAc (2)	P(2-furyl)$_3$ (10)	DMF	80	–[c]	–	80
17	**$Pd(dba)_2$ (10)**	**KOAc (2)**	**P(2-furyl)$_3$ (10)**	**DMF**	**85**	–[c]	–	**97**
18	$Pd(dba)_2$ (10)	KOAc (2)	P(2-furyl)$_3$ (10)	DMF	90	–[c]	–	78
19	$Pd(dba)_2$ (10)	Et_3N (2)	P(2-furyl)$_3$ (10)	DMF	85	–[c]	–	52
20	$Pd(dba)_2$ (10)	KOH (2)	P(2-furyl)$_3$ (10)	DMF	85	–[c]	–	55

[a]Unless otherwise specified, the reaction was carried out by using **1a** (0.20 mmol), Pd catalysts (10 mol %), and bases in solvent (2 mL) for 2 h. [b]Under oxygen. [c]Under an argon atmosphere. [d]TBHP = *tert*-butyl hydroperoxide.

Scheme 3), which selectively favored a six-membered ring formation. Ultimately, the use of 10 mol % PdI_2, 40 mol % P(2-furyl)$_3$, 2 equiv of Et_3N, and 2 equiv of TBHP in DMF at 85 °C under an argon atmosphere was found to be the most efficient and used as the standard conditions for **2a**.

Without using the additive TBHP, only trace amounts of **2a** and a 13% yield of **3a** (entry 12) were obtained when **1a** was treated with $Pd(OAc)_2$ in the presence of 2 equiv of KOAc and PPh_3 (20 mol %) in DMF as the solvent, and when the mixture was stirred at 80 °C for 2 h under an argon atmosphere. The use of phosphine ligand P(2-furyl)$_3$ gave a higher yield of **3a** (entries 13 and 14). $Pd_2(dba)_3$ and $Pd(dba)_2$, as convenient sources of palladium(0), were found to be effective for selectively generating **3a** (entries 15 and 16). With increased temperature to 85 °C, the desired product **3a** was obtained in the highest yield (entries 17 and 18). Compared with KOAc, an organic base such as Et_3N and a stronger inorganic base such as KOH were less effective (entries 19 and 20). Thus, the optimized reaction conditions for **3a** were $Pd(dba)_2$ (10 mol %), P(2-furyl)$_3$ (10 mol %), KOAc (2 equiv), and DMF (2 mL) at 85 °C.

Under the optimized conditions, various representative enyne carbonates **1a**−**1u** were then subjected to the optimized conditions selected for **2a**, as shown in Table 2. The reaction was found to tolerate a variety of functional groups at the ortho-, meta-, and para-positions of the phenyl moiety in substituted enyne carbonates, indicating that the steric effect has little impact on this transformation. The substrates with a 2-naphthyl or a heterocyclic ring can also afford the desired product (e.g., **2n** in 53% yield and **2o** in 57% yield). The substrate scope can also be extended to vinyl enyne carbonates, such as **1q**. Substrates with a hydrogen atom and aliphatic substitution under the standard reaction conditions were also investigated, and the corresponding products were obtained in 49%, 31%, and 70% yields. However, some oxygenated enyne carbonates such as **1t** and amines such as **1u** cannot afford the desired products.

Subsequently, the scope of 3-vinylidene-1-tosylpyrrolidines **3** was examined. Under the optimized conditions for **3a**, a wide range of 1,6-enyne carbonates **1a**−**1u** in the presence of 10 mol % $Pd(dba)_2$ at 85 °C in DMF was also investigated. The substrates **1a**−**o** and **1s** were found to be effectively converted into the corresponding five-member heterocyclic allenes **3** in moderate to good yields, as shown in Table 2. Enyne carbonates with a heterocyclic ring, such as the thiophene nucleus, can also afford the desired product (e.g., **3o** in 40% yield). The substrates with aliphatic R^1 and R^2 groups can also afford the desired product (e.g., **3s** in 45% yield). The results revealed that electron-donating groups favored product formation (**1f**−**1m**), whereas electron-withdrawing groups (e.g., Cl and Br) hindered product formation (**1b**−**1e**).

To develop a method for a one-pot cyclization/Suzuki coupling,[10] aryl boronic acids were added to the reaction mixture under the optimized conditions selected for **3a**. The Suzuki coupling products **3aa** and **3ab**, highly functionalized 3-vinylidene-1-tosylpyrrolidines, were obtained in moderate yields (Scheme 2).

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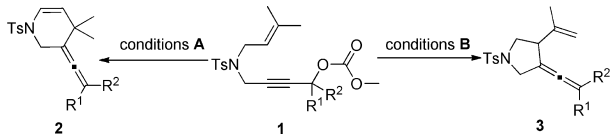
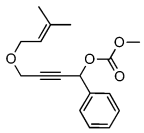
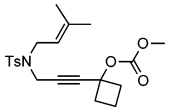
Table 2. PdI_2-Catalyzed Synthesis of 3-Vinylidene-1-tosylpyridines 2 and $Pd(dba)_2$-Catalyzed Synthesis of 3-Vinylidene-1-tosylpyrrolidines 3 from 1,6-Enyne Carbonates 1



Entry	1	R^1	R^2	Yield [%]	
				2[a]	3[b]
1	1a	H	Ph	75	96
2	1b	H	*p*-ClC_6H_4	66	55
3	1c	H	*m*-ClC_6H_4	64	79
4	1d	H	*o*-ClC_6H_4	63	67
5	1e	H	*p*-BrC_6H_4	36	56
6	1f	H	*p*-MeC_6H_4	61	86
7	1g	H	*m*-MeC_6H_4	64	94
8	1h	H	*o*-MeC_6H_4	56	94
9	1i	H	3,4-dimethylphenyl	62	65
10	1j	H	*p*-$MeOC_6H_4$	62	70
11	1k	H	*m*-$MeOC_6H_4$	61	85
12	1l	H	*o*-$MeOC_6H_4$	55	93
13	1m	H	2,6-dimethoxyphenyl	50	79
14	1n	H	2-naphthyl	53	73
15	1o	H	Thienyl	57	40
16	1p	H	Propyl	49	-[c]
17	1q	H	Styryl	30	-[c]
18	1r	H	H	31	-[c]
19	1s	Me	Me	70	45
20	1t			-[c]	-[c]
21	1u			-[d]	-[c]

[a]Condition **A**: The reaction was carried out by using **1** (0.2 mmol), PdI_2 (10 mol %), P(2-furyl)$_3$ (40 mol %), Et_3N (2 equiv), and TBHP (2 equiv) in DMF (2 mL) at 85 °C under an argon atmosphere. [b]Condition **B**: The reaction was carried out by using **1** (0.2 mmol), $Pd(dba)_2$ (10 mol %), P(2-furyl)$_3$ (10 mol %), and KOAc (2 equiv) in DMF (2 mL) at 85 °C under an argon atmosphere. [c]Decomposed. [d]No gain.

Based on the above observations, the following plausible mechanisms for palladium-catalyzed intramolecular cyclization reactions (Scheme 3) are proposed. PdI_2 is initially reduced to Pd(0) by a ligand, and both routes 1 and 2 are catalyzed by Pd(0) via the following steps: (a) The Pd(0)-catalyzed transformation of 1,6-enyne carbonates generates allenylpalladium intermediate **A** or **C**, which is readily attacked by an olefin nucleophile to form intermediate **B** or **D**.[11] I_3^- may have a strong spatial interaction with the palladium catalyst and induces more hindered catalysts to form five-membered ring **B**, which selectively favors six-membered ring formation **D**. The stability of the formation of intermediates **D** and **B** determines the regioselective insertion of olefin into the C−Pd bond in the allenylpalladium intermediate to form five- or six-membered rings. (b) The β-hydrogen elimination[3h] of intermediate **D** or **B** would give six-membered heterocyclic allenes **2** or five-membered heterocyclic allenes **3**.

CONCLUSION

In summary, Pd-catalyzed divergent cyclizations of 1,6-enyne carbonates were developed. The cyclizations provide a versatile cascade reaction for the synthesis of heterocyclic allenes. The method can be combined with Suzuki coupling to prepare highly functionalized 3-vinylidene-1-tosylpyrrolidines in a one-pot manner.

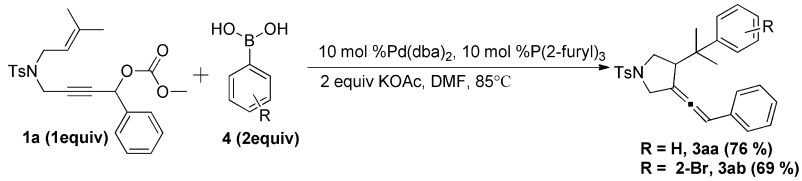
EXPERIMENTAL SECTION

Typical Procedure for the Preparation of Enyne Carbonates 1a−1u. *Method A.*[12] To a stirred solution of the appropriate terminal alkyne **A** (1.2 equiv) in THF (1.0 M) was added ethyl magnesium bromide (1.0 M in THF, 1.1 equiv) at room temperature. The resulting solution was stirred at 50 °C for 1 h. Then **B** (1.0 equiv) in THF (0.35 M) was added slowly by syringe to the resulting solution at room temperature and stirred for 3 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride (40 mL) and extracted with ethyl ether (2 × 40 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was purified by flash column chromatography to obtain the pure propargylic alcohols **C** in quantitative yield.

To a mixture of propargylic alcohol **C** (2.37 mmol) and pydrine (19 mmol) in methylene chloride (30 mL) was added methyl chloroformate (7.11 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2.5 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride and extracted with ethyl ether. The combined organic layers were washed with water and brine and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The concentrate was purified by flash column chromatography to obtain the desired propargylic esters **1**.

Method B.[13] To a solution of **A** (22 mmol) in THF (100 mL) was added *n*-BuLi (2.2 M in hexane, 10.9 mL, 24 mmol) at −20 °C, and the mixture was stirred at the same temperature for 5 min. To this solution was added ketone or aldehyde (20 mmol) in a dropwise manner, and the mixture was then stirred at −20 °C for 30 min. To this solution was slowly added methyl chloroformate (3.9 mL, 50

Scheme 2. One-Pot Cyclization/Suzuki Coupling of 1,6-Enyne 1a with Aryl Boronic Acids 4



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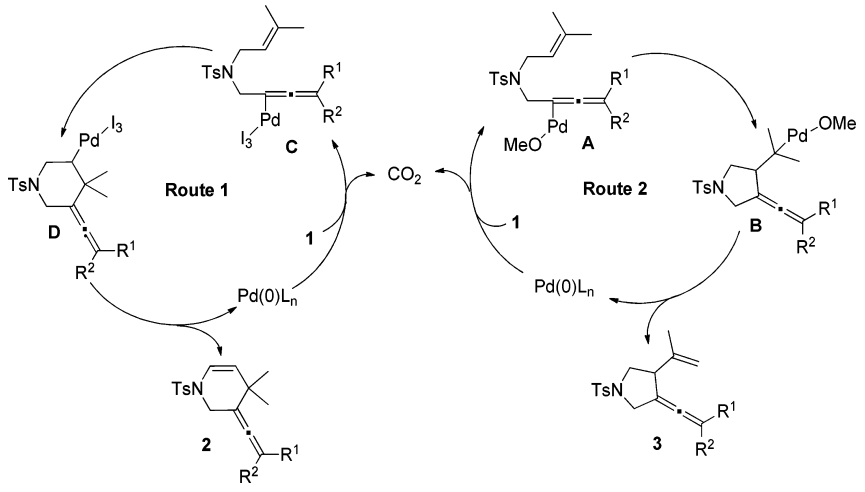
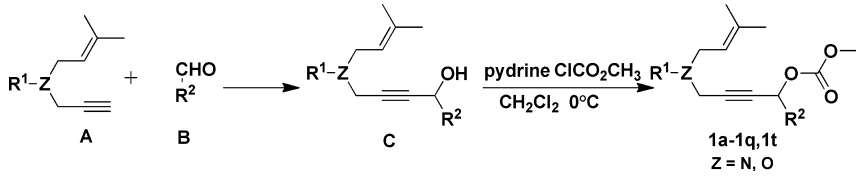
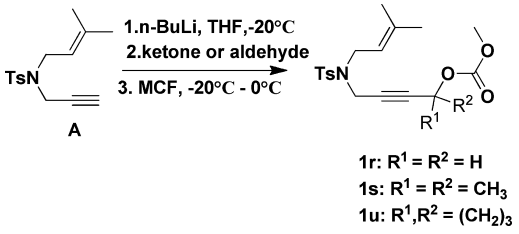
Scheme 3. Proposed Mechanism







mmol), and the mixture was warmed up to 0 °C and stirred at the same temperature for 2 h. The reaction was quenched with a saturated solution of ammonium chloride and extracted with ether (3 × 60 mL). The combined organic layer was washed with brine (2 × 10 mL) and dried over anhydrous sodium sulfate. The solvent was removed under vacuum, and the concentrate was purified by flash column chromatography to obtain **1r–s**.

Characterization Data of Enyne Carbonates 1a–1u. **1a:** Compound **1a** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (d, J = 8.0 Hz, 2H), 7.37–7.30 (m, 3H), 7.23–7.25 (m, 2H), 7.20–7.18 (m, J = 8.0 Hz, 2H), 5.60 (s, 1H), 5.11–5.07 (t, J = 7.2 Hz, 1H), 4.23–4.11 (m, 2H), 3.83–3.70 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H), 1.69 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.4, 139.1, 135.8, 135.7, 129.4, 129.1, 128.5, 127.6, 127.4, 117.7, 81.5, 81.2, 69.2, 54.9, 44.0, 35.6, 25.7, 21.4, 17.6; IR (neat, cm^{-1}) 3399, 2922, 2868, 1751, 1597, 1441, 1346, 1258, 1161. Anal. Calcd for $C_{24}H_{27}NO_5S$: C, 65.28; H, 6.16; N, 3.17. Found: C, 65.30; H, 6.18; N, 3.13.

1b: Compound **1b** was prepared according to the method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (d, J = 8.0 Hz, 2H), 7.30–7.27 (m, 2H), 7.22–7.17 (m, 4H), 5.97 (s, 1H), 5.10–5.06 (m, 1H), 4.22–4.11 (m, 2H), 3.82–3.70 (m, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.4, 139.0, 135.8, 135.0, 134.4, 129.3, 128.7, 128.6, 127.6, 117.6, 81.9, 80.7, 68.3, 54.9, 44.0, 35.5, 25.7, 21.3, 17.6; IR (neat, cm^{-1}) 3395, 2922, 2359, 1751, 1383. Anal. Calcd for $C_{24}H_{26}ClNO_5S$: C, 60.56; H, 5.51; N, 2.94. Found: C, 60.51; H, 5.49; N, 2.99.

1c: Compound **1c** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.69 (d, J = 8.0 Hz, 2H), 7.35–7.31 (m, 1H), 7.28–7.14 (m, 4H), 7.13–7.12 (m, 1H), 5.95 (s, 1H), 5.11–5.06 (m, 1H), 4.23–4.10 (m, 2H), 3.83–3.69 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H), 1.70 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 143.4, 139.2, 137.7, 135.7, 134.4, 129.8, 129.5, 129.3, 127.7, 127.5, 125.5, 117.7, 82.1, 80.6, 68.3, 55.1, 44.1, 35.6, 25.8, 21.4, 17.6; IR (neat, cm^{-1}) 3398, 2923, 2359, 1753, 1440, 1260. Anal. Calcd for $C_{24}H_{26}ClNO_5S$: C, 60.56; H, 5.51; N, 2.94. Found: C, 60.58; H, 5.48; N, 2.93.

1d: Compound **1d** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.69 (d, J = 8.4 Hz, 2H), 7.37–7.35 (m, 2H), 7.30–7.19 (m, 4H), 6.35 (s, 1H), 5.10–5.06 (t, J = 7.2 Hz, 1H), 4.22–4.11 (m, 2H), 3.83–3.71 (m, 2H), 3.81 (s, 3H), 2.34 (s, 3H), 1.68 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.3, 138.9, 135.6, 133.3, 132.8, 130.3, 129.4, 129.3, 128.8, 127.5, 126.9, 117.6, 81.6, 80.2, 65.9, 55.0, 43.9, 35.5, 25.6, 21.2, 17.4; IR (neat, cm^{-1}) 3396, 2922, 2359, 1754, 1441, 1256. Anal. Calcd for $C_{24}H_{26}ClNO_5S$: C, 60.56; H, 5.51; N, 2.94. Found: C, 60.55; H, 5.53; N, 2.94.

1e: Compound **1e** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (d, J = 8.4 Hz, 2H), 7.46–7.44 (d, J = 8.4 Hz, 2H), 7.22–7.19 (d, J = 8.0 Hz, 2H), 7.13–7.10 (d, J = 8.4 Hz, 2H), 5.95 (s, 1H), 5.11–5.06 (m, 1H), 4.23–4.11 (m, 2H), 3.82–3.69 (m, 2H), 3.79 (s, 3H), 2.36 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.4, 139.1, 135.8, 134.9, 131.7, 129.4, 129.1, 127.7, 123.4, 117.7, 82.1, 80.7, 68.5, 55.1, 44.1, 35.6, 25.8, 21.5, 17.7; IR (neat, cm^{-1}) 3396, 2957, 2923, 2359, 1752, 1257, 1161. Anal. Calcd for $C_{24}H_{26}BrNO_5S$: C, 55.39; H, 5.04; N, 2.69. Found: C, 55.37; H, 5.05; N, 2.68.

1f: Compound **1f** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (d, J = 8.4 Hz, 2H), 7.20–7.18 (m, 3H), 7.13 (s, 3H), 5.95 (s, 1H), 5.11–5.07 (t, J = 7.2 Hz, 1H), 4.23–4.10 (m, 2H), 3.80–3.73 (m, 2H), 3.78 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.3, 139.1, 139.0, 135.8, 132.9, 129.4, 129.2, 127.7, 127.4, 117.8, 81.4, 81.3, 69.1, 54.9, 44.0, 35.7, 25.8, 21.4, 21.2, 17.7; IR (neat, cm^{-1}) 3410, 2922, 2851, 1749, 1383, 1257. Anal. Calcd for $C_{25}H_{29}NO_5S$: C, 65.91; H, 6.42; N, 3.07. Found: C, 65.93; H, 6.41; N, 3.05.

1g: Compound **1g** was prepared according to method A. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.69 (d, J = 8.4 Hz, 2H), 7.23–7.03 (m, 6H), 5.95 (s, 1H), 5.11–5.07 (m, 1H), 4.23–3.10 (m, 2H), 3.82–3.70 (m, 2H), 3.78 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.3, 139.0, 138.3, 135.7, 129.9, 129.4, 128.4, 128.0, 127.6, 124.4, 117.8, 81.4, 81.3, 69.2,

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54.9, 44.0, 35.7, 25.7, 21.4, 21.2, 17.6; IR (neat, cm^{-1}) 3403, 2922, 2851, 1751, 1597, 1346, 1259. Anal. Calcd for $C_{25}H_{29}NO_5S$: C, 65.91; H, 6.42; N, 3.07. Found: C, 65.90; H, 6.44; N, 3.06.

1h: Compound **1h** was prepared according to the method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.68 (d, J = 8.4 Hz, 2H), 7.26−7.12 (m, 6H), 6.15 (s, 1H), 5.10−5.05 (t, J = 7.2 Hz, 1H), 4.22−4.10 (m, 2H), 3.81−3.69 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H), 2.28 (s, 3H), 1.68 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.3, 138.9, 135.8, 133.9, 130.6, 129.3, 129.0, 127.6, 127.5, 126.1, 117.7, 81.4, 81.0, 67.1, 54.9, 43.9, 35.6, 25.7, 21.3, 15.7, 17.5; IR (neat, cm^{-1}) 3405, 2923, 2359, 1751, 1598, 1346, 1258. Anal. Calcd for $C_{25}H_{29}NO_5S$: C, 65.91; H, 6.42; N, 3.07. Found: C, 65.89; H, 6.42; N, 3.08.

1i: Compound **1i** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72−7.69 (d, J = 8.4 Hz, 2 H), 7.20−7.17 (d, J = 8.4 Hz, 2H), 7.09−7.04 (m, 2H), 6.99−6.96 (m, 1H), 5.92 (s, 1H), 5.11−5.07 (m, 1H), 4.23−4.10 (m, 2H), 3.82−3.70 (m, 2H), 3.78 (s, 3 H), 2.34 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.3, 139.1, 137.8, 136.8, 135.7, 133.3, 129.7, 129.4, 128.6, 127.7, 124.9, 117.8, 81.5, 81.2, 69.2, 54.9, 44.0, 35.7, 25.8, 21.4, 19.7, 19.6, 17.6; IR (neat, cm^{-1}) 3395, 2922, 1750, 1597, 1257. Anal. Calcd for $C_{26}H_{31}NO_5S$: C, 66.50; H, 6.65; N, 2.98. Found: C, 66.49; H, 6.63; N, 3.01.

1j: Compound **1j** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72−7.69 (d, J = 8.0 Hz, 2H), 7.21−7.17 (m, 4H), 6.84−6.82 (d, J = 8.8 Hz, 1H), 5.95 (s, 1H), 5.11−5.07 (t, J = 7.2 Hz, 1H), 4.23−4.11 (m, 2H), 3.83−3.71 (m, 2H), 3.80 (s, 3H), 3.78 (s, 3H), 2.35 (s, 3H), 1.69 (s, 3 H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 154.7, 143.3, 139.1, 135.8, 131.7, 129.6, 129.4, 129.1, 128.0, 127.7, 117.7, 113.8, 81.4, 81.3, 68.9, 55.3, 54.9, 44.0, 35.7, 25.8, 21.4, 17.7; IR (neat, cm^{-1}) 3396, 2924, 2359, 1748, 1383, 1249. Anal. Calcd for $C_{25}H_{29}NO_6S$: C, 63.67; H, 6.20; N, 2.97. Found: C, 63.64; H, 6.18; N, 2.99.

1k: Compound **1k** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71−7.68 (d, J = 8.0 Hz, 2H), 7.27−7.18 (m, 3H), 6.90−6.82 (m, 3H), 5.96 (s, 1H), 5.11−5.07 (t, J = 7.2 Hz, 1H), 4.22−4.10 (m, 2H), 3.84−3.71 (m, 8H), 2.34 (s, 3H), 1.69 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.6, 143.4, 139.1, 137.2, 135.7, 129.6, 129.4, 127.6, 119.5, 117.7, 114.5, 112.9, 81.4, 81.1, 69.0, 55.2, 54.9, 44.0, 35.6, 25.7, 21.4, 17.5; IR (neat, cm^{-1}) 3394, 2921, 1751, 1383, 1257. Anal. Calcd for $C_{25}H_{29}NO_6S$: C, 63.67; H, 6.20; N, 2.97. Found: C, 63.69; H, 6.19; N, 2.95.

1l: Compound **1l** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72−7.69 (d, J = 8.4 Hz, 2H), 7.34−7.32 (t, J = 4.4 Hz 13H), 7.30−7.17 (m, 3H), 6.91−6.84 (m, 2H), 6.41 (s, 1H), 5.11−5.07 (t, J = 7.2 Hz, 1H), 4.24−4.11 (m, 2H), 3.85−3.70 (m, 8H), 2.32 (s, 3H), 1.69 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 154.6, 143.3, 139.0, 135.8, 130.5, 129.4, 128.7, 127.6, 123.8, 120.4, 117.8, 114.5, 110.6, 81.4, 80.7, 63.9, 55.5, 54.8, 44.0, 35.7, 25.8, 21.4, 17.6; IR (neat, cm^{-1}) 3404, 2922, 1751, 1383, 1260. Anal. Calcd for $C_{25}H_{29}NO_6S$: C, 63.67; H, 6.20; N, 2.97. Found: C, 63.66; H, 6.20; N, 2.98.

1m: Compound **1m** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71−7.69 (d, J = 8.4 Hz, 2H), 7.20−7.18 (d, J = 8.0 Hz, 2H), 6.89−6.78 (m, 3H), 6.39−6.37 (t, J = 1.4 Hz, 1H), 5.11−5.07 (t, J = 7.4 Hz, 1H), 4.22−4.10 (m, 2H), 3.83−3.71 (m, 11H), 2.33 (s, 3H), 1.69 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 153.4, 150.6, 143.4, 139.1, 135.7, 129.4, 127.6, 124.8, 117.8, 114.9, 114.5, 111.8, 81.3, 80.8, 63.8, 56.1, 55.6, 54.8, 43.9, 35.7, 25.7, 21.3, 17.6; IR (neat, cm^{-1}) 3413, 2956, 2829, 1752, 1500, 1256. Anal. Calcd for $C_{26}H_{31}NO_7S$: C, 62.26; H, 6.23; N, 2.79. Found: C, 62.24; H, 6.24; N, 2.80.

1n: Compound **1n** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74−7.61 (m, 7H), 7.54−7.47 (m, 2H), 7.35−7.32 (m, 1H), 7.11−7.09 (d, J = 8.0 Hz, 2H), 6.16 (s, 1H), 5.12−5.08 (t, J = 7.2 Hz, 1H), 4.26−4.14 (m, 2H), 3.84−3.72 (m, 5H), 2.18 (s, 3H), 1.68 (s, 3H), 1.55 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 143.4, 139.2, 135.8, 133.5, 133.2, 132.8, 129.4, 128.6, 128.2, 127.6, 126.9, 126.8, 126.5, 124.6, 117.8, 81.9, 81.3, 69.4, 55.1, 44.1, 35.7, 25.8, 21.3, 17.7; IR (neat, cm^{-1}) 3398, 2922, 2362, 1750, 1381, 1258. Anal. Calcd for $C_{28}H_{29}NO_5S$: C, 68.41; H, 5.95; N, 2.85. Found: C, 68.43; H, 5.93; N, 2.84.

1o: Compound **1o** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72−7.69 (d, J = 8.0 Hz, 2H), 7.33−7.31 (m, 1H), 7.26−7.18 (m, 2H), 7.01−7.00 (d, J = 3.6 Hz, 1H), 6.95−6.92 (m, 1H), 6.22 (s, 1H), 5.14−5.10 (m, 1H), 4.23−4.11 (m, 2H), 3.86−3.75 (m, 5H), 2.34 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 143.5, 139.3, 138.5, 135.8, 129.5, 127.9, 127.7, 127.4, 126.6, 117.8, 81.2, 80.6, 64.2, 55.1, 44.2, 35.6, 25.8, 21.5, 17.8; IR (neat, cm^{-1}) 3397, 2922, 1749, 1381, 1258, 1159. Anal. Calcd for $C_{22}H_{25}NO_5S_2$: C, 59.04; H, 5.63; N, 3.13. Found: C, 59.02; H,5.65; N, 3.13.

1p: Compound **1p** was prepared according to method A. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73−7.71 (d, J = 8.0 Hz, 2H), 7.31−7.28 (m, 2H), 5.12−5.08 (m, 1H), 4.96−4.92 (t, J = 6.6 Hz, 1H), 4.12−4.11 (d, J = 1.6 Hz, 2H), 3.79−3.77 (m, 5H), 2.43 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H), 1.58−1.40 (m, 2H), 1.30−1.21 (m, 2H), 0.89−0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 143.3, 138.9, 136.0, 129.4, 127.6, 117.8, 82.1, 79.4, 67.5, 54.8, 43.9, 36.4, 35.5, 25.8, 21.4, 18.0, 17.7, 13.4; IR (neat, cm^{-1}) 3398, 2961, 1751, 1382, 1348, 1266, 1161. Anal. Calcd for $C_{21}H_{29}NO_5S$: C, 61.89; H, 7.17; N, 3.44. Found: C, 61.87; H,7.18; N, 3.43.

1q: Compound **1q** was prepared according to method **A**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75−7.69 (m, 2H), 7.39−7.29 (m, 5H), 7.26−7.20 (m, 2H), 6.62 −6.58(d, J = 7.6 Hz, 1H), 6.03−5.96 (m, 1H), 5.63−5.61 (m, 1H), 5.14−5.10 (t, J = 7.2 Hz, 1H), 4.18−4.14 (m, 2H), 3.83−3.74 (m, 5H), 2.30 (s, 3H), 1.72 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 143.5, 139.2, 135.8, 135.3, 134.9, 129.5, 129.3, 128.8, 128.7, 127.8, 127.7, 127.0, 126.9, 122.6, 117.8, 81.5, 80.3, 67.9, 55.0, 44.1, 35.7, 25.8, 21.4, 17.8; IR (neat, cm^{-1}) 3493, 3029, 2959, 2925, 1750, 1689, 1490, 1597, 1263, 1160. Anal. Calcd for $C_{26}H_{29}NO_5S$: C, 66.79; H, 6.25; N, 3.00. Found: C, 66.77; H, 6.25; N, 3.01.

1r: Compound **1r** was prepared according to method **B**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74−7.72 (d, J = 8.0 Hz, 2H), 7.32−7.29 (d, J = 8.4 Hz, 2H), 5.11−5.07 (m, 1H), 4.44−4.43 (t, J = 2.0 Hz, 2H), 4.10−4.08 (t, J = 2.2 Hz, 2H), 3.79−3.76 (m, 5H), 2.43 (s, 3H), 1.72 (s, 3H), 1.65−1.63 (d, J = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 143.4, 139.1, 135.9, 129.3, 127.8, 117.8, 80.8, 78.6, 55.2, 55.1, 44.1, 35.6, 25.8, 21.5, 17.7; IR (neat, cm^{-1}) 3395, 2922, 1754, 1443, 1379, 1346, 1265, 1158. Anal. Calcd for $C_{18}H_{23}NO_5S$: C, 59.16; H, 6.34; N, 3.83. Found: C, 59.15; H, 6.33; N, 3.85.

1s: Compound **1s** was prepared according to method **B**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74−7.72 (d, J = 8.4 Hz, 2H), 7.30−7.28 (d, J = 8.0 Hz, 2H), 5.14−5.09 (m, 1H), 4.12 (s, 2H), 3.83−3.81 (d, J = 7.2 Hz, 2H), 3.72 (s, 3H), 2.42 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 143.2, 138.9, 136.4, 129.4, 127.7, 118.1, 85.5, 77.9, 73.6, 54.2, 43.9, 35.6, 28.4, 25.8, 21.4, 17.7; IR (neat, cm^{-1}) 3393, 2922, 1752, 1596, 1381. Anal. Calcd for $C_{20}H_{27}NO_5S$: C, 61.05; H, 6.92; N, 3.56. Found: C, 61.06; H, 6.91; N, 3.55.

1t: Compound **1t** was prepared according to method **A**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54−7.52 (m, 2H), 7.41−7.33 (m, 3H), 6.34 (s, 1H), 5.35 −5.30 (m, 1H), 4.22−4.21 (d, J = 1.6 Hz, 2H), 4.05−4.03 (d, J = 7.2 Hz, 2H), 3.79 (s, 3H), 1.75 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 138.5, 136.2, 129.2, 128.6, 127.6, 120.1, 84.7, 81.9, 69.6, 65.9, 56.9, 55.0, 25.7, 17.9; IR (neat, cm^{-1}) 3398, 2921, 2359, 1751, 1258. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.83; H, 6.97.

1u: Compound **1u** was prepared according to method **B**. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75−7.73 (d, J = 8.0 Hz, 2H), 7.31−7.29 (d, J = 7.6 Hz, 2H), 5.14−5.11 (m, 1H), 4.15 (s, 2H), 3.83−3.81 (d, J = 7.2 Hz, 2H), 3.73−3.72 (t, J = 1.4 Hz, 3H), 2.40 (s, 3H), 2.32−2.25 (m, 2H), 2.20−2.15 (m, 2H), 1.83−1.79 (m, 1H), 1.78 (s, 3H), 1.72 (s, 3H), 1.67−1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 143.2, 138.7, 136.2, 129.4, 127.5, 117.9, 84.8, 78.2, 73.1, 54.3, 43.8, 35.8, 35.6, 25.7, 21.3, 17.6, 13.7; IR (neat, cm^{-1}) 3393, 2922, 1752, 1596, 1381. Anal. Calcd for $C_{21}H_{27}NO_5S$: C, 62.20; H, 6.71; N, 3.45. Found: C, 62.22; H, 6.70; N, 3.43.

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General Procedure for the Palladium Catalyzed Cyclization Reactions of Enyne Carbonates 1 To Form 3-Vinylidene-1-tosylpyridines 2. A mixture of methyl 4-(4-methyl-*N*-(3-methylbut-2-enyl)phenylsulfonamido)-1-phenylbut-2-ynyl carbonate **1a** (88.3 mg, 0.2 mmol), PdI_2 (7.2 mg, 10 mol %), Et_3N (40 mg, 0.4 mmol), $P(2\text{-furyl})_3$ (18.6 mg, 40 mol %), TBHP (0.08 mL, 0.4 mmol), and DMF (2 mL) was added to a 20 mL tube under an argon atmosphere. The resulting mixture was then stirred at 85 °C. When the reaction was considered complete as determined by TLC, the reaction mixture was allowed to cool to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and extracted with ethyl acetate. The combined organic extracts were washed with water and saturated brine, dried over Na_2SO_4, and filtered. Solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel using mixtures of hexanes and EtOAc to afford **2a** (54.8 mg, 75%).

Characterization Data of Six-Membered Heterocycles 2a–2q, 2r, 2s. 2a: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 54.8 mg (75%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (d, J = 8.0 Hz, 2H), 7.29–7.16 (m, 5H), 7.11–7.08 (t, J = 4.2 Hz, 1H), 6.62–6.60 (d, J = 8.0 Hz, 1H), 6.08 (s, 1H), 4.97–4.94 (d, J = 8.0 Hz, 1H), 4.16–4.06 (m, 2H), 2.42 (s, 3H), 1.14 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 143.6, 135.2, 134.1, 129.6, 128.6, 127.2, 127.1, 126.6, 122.9, 119.5, 106.2, 97.1, 44.7, 33.8, 29.7, 29.0, 21.6; IR (neat, cm^{-1}) 3398, 2963, 2361, 1948, 1644, 1355, 1164, 771, 680. ESIHRMS: Found: m/z 388.1331. Calcd for $C_{22}H_{23}NNaO_2S$: $(M + Na)^+$ 388.1342.

2b: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 52.8 mg (66%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.28–7.26 (d, J = 8.0 Hz, 2H), 7.20–7.18 (d, J = 8.4 Hz, 2H), 7.00–6.98 (d, J = 8.4 Hz, 2H), 6.05 (s, 1H), 4.96–4.94 (d, J = 8.4 Hz, 1H), 4.14–4.06 (m, 2H), 2.42 (s, 3H), 1.12 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 143.7, 135.2, 132.7, 132.6, 129.6, 128.7, 127.7, 127.2, 122.9, 119.3, 106.7, 96.2, 44.6, 33.9, 29.6, 29.1, 21.6; IR (neat, cm^{-1}) 3424, 2963, 2923, 1955, 1490, 1355, 1165, 679, 547. ESIHRMS: Found: m/z 422.0957. Calcd for $C_{22}H_{22}ClNNaO_2S$: $(M + Na)^+$ 422.0952.

2c: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 51.5 mg (64%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.30–7.27 (d, J = 8.4 Hz, 2H), 7.19–7.14 (m, 2H), 7.09 (s, 1H), 7.00–6.96 (m, 1H), 6.62–6.60 (d, J = 8.4 Hz, 1H), 6.03 (s, 1H), 4.96–4.94 (d, J = 8.4 Hz, 1H), 4.16–4.04 (m, 2H), 2.42 (s, 3H), 1.14 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 143.7, 136.2, 135.1, 134.5, 129.8, 129.6, 127.2, 127.1, 126.4, 124.7, 123.0, 119.2, 106.8, 96.2, 44.5, 33.8, 29.8, 28.9, 21.6; IR (neat, cm^{-1}) 3433, 2964, 1924, 1956, 1593, 1354, 1165, 680, 545. ESIHRMS: Found: m/z 422.0954. Calcd for $C_{22}H_{22}ClNNaO_2S$: $(M + Na)^+$ 422.0952.

2d: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 50.4 mg (63%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (d, J = 8.0 Hz, 2H), 7.33–7.28 (m, 3H), 7.14–7.07 (m, 3H), 6.63–6.60 (d, J = 8.4 Hz, 1H), 6.46–6.45 (d, J = 1.8 Hz, 1H), 4.99–4.96 (d, J = 8.4 Hz, 1H), 4.16–4.07 (m, 2H), 2.43 (s, 3H), 1.15 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 143.7, 136.2, 135.1, 134.5, 129.8, 129.6, 127.2, 127.1, 126.4, 124.7, 123.0, 119.2, 106.8, 96.2, 44.5, 33.8, 29.8, 28.9, 21.6; IR (neat, cm^{-1}) 3395, 2964, 2923, 1956, 1644, 1355, 1193, 1028, 754, 679, 547. ESIHRMS: Found: m/z 422.0958. Calcd for $C_{22}H_{22}ClNNaO_2S$: $(M + Na)^+$ 422.0952.

2e: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 32.0 mg (36%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.36–7.32 (m, 2H), 7.28–7.25 (m, 2H), 6.94–6.90 (m, 2H), 6.63–6.61 (d, J = 8.0 Hz, 1H), 6.04–6.03 (t, J = 1.6 Hz, 1H), 4.96–4.94 (d, J = 8.4 Hz, 1H), 4.15–4.06 (m, 2H), 2.43 (s, 3H), 1.12 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 143.7, 135.2, 133.1, 131.7, 129.7, 128.1, 127.2, 123.0, 120.7 119.2, 106.8, 96.3, 44.5, 33.9, 29.6, 29.2, 21.6; IR (neat, cm^{-1}) 3396, 2962, 2923, 1355, 1165, 681, 547. ESIHRMS: Found: m/z 466.0444. Calcd for $C_{22}H_{22}BrNNaO_2S$: $(M + Na)^+$ 466.0447.

2f: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 47.8 mg (61%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.28–7.26 (d, J = 8.0 Hz, 2H), 7.06–7.04 (d, J = 8.0 Hz, 2H), 7.00–6.97 (d, J = 8.4 Hz, 2H), 6.62–6.59 (d, J = 8.4 Hz, 1H), 6.05 (s, 1H), 4.96–4.94 (d, J = 8.0 Hz, 1H), 4.15–4.05 (m, 2H), 2.43 (s, 3H), 2.32 (s, 3H), 1.13 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 143.6, 136.9, 135.2, 131.1, 129.6, 129.3, 127.2, 126.5, 122.9, 119.6, 106.0, 96.9, 44.8, 33.8, 29.8, 29.0, 21.6, 21.4; IR (neat, cm^{-1}) 3443, 2963, 2923, 1955, 1712, 1355, 1166, 681, 548. ESIHRMS: Found: m/z 402.1487. Calcd for $C_{23}H_{25}NNaO_2S$: $(M + Na)^+$ 402.1498.

2g: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 48.6 mg (64%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.29–7.26 (d, J = 8.0 Hz, 2H), 7.15–7.11 (t, J = 7.6 Hz, 1H), 7.01–6.99 (d, J = 8.4 Hz, 1H), 6.96 (s, 1H), 6.92–6.89 (d, J = 8.4 Hz, 1H), 6.61–6.59 (d, J = 8.4 Hz, 1H), 6.04 (s, 1H), 4.96–4.94 (d, J = 8.0 Hz, 1H), 4.16–4.04 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 1.15 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 143.6, 138.2, 135.2, 134.0, 129.6, 128.5, 127.9, 127.4, 127.2, 123.7, 123.0, 119.6, 106.0, 97.2, 44.8, 33.8, 29.9, 28.9, 21.6, 21.3; IR (neat, cm^{-1}) 3412, 2963, 2923, 1955, 1354, 1165, 679, 547. ESIHRMS: Found: m/z 402.1492. Calcd for $C_{23}H_{25}NNaO_2S$: $(M + Na)^+$ 402.1498.

2h: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 42.5 mg (56%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.28–7.26 (d, J = 8.0 Hz, 2H), 7.13–7.03 (m, 4H), 6.61–6.59 (d, J = 8.0 Hz, 1H), 6.23 (s, 1H), 4.97–4.94 (d, J = 8.0 Hz, 1H), 4.16–4.03 (m, 2H), 2.42 (s, 3H), 2.31 (s, 3H), 1.14 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 143.6, 135.2, 134.9, 132.2, 130.5, 129.6, 127.3, 126.9, 126.1, 123.0, 119.6, 104.9, 94.3, 44.9, 33.6, 29.6, 28.9, 21.6, 19.8; IR (neat, cm^{-1}) 2963, 2924, 1953, 1355, 1165, 680, 548. ESIHRMS: Found: m/z 402.1494. Calcd for $C_{23}H_{25}NNaO_2S$: $(M + Na)^+$ 402.1498.

2i: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 48.8 mg (62%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.0 Hz, 2H), 7.29–7.26 (d, J = 8.0 Hz, 2H), 7.01–6.99 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.85–6.82 (d, J = 7.6 Hz, 1H), 6.61–6.58 (d, J = 8.4 Hz, 1H), 6.03 (s, 1H), 4.97–4.94 (d, J = 8.4 Hz, 1H), 4.16–4.03 (m, 2H), 2.42 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 1.14 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 143.6, 136.7, 135.6, 135.2, 131.5, 129.9, 129.6, 127.9, 127.3, 124.0, 122.9, 119.7, 105.9, 96.9, 44.9, 33.8, 29.9, 28.9, 21.5, 19.7, 19.6; IR (neat, cm^{-1}) 3403, 2963, 2922, 1955, 1355, 1166, 1026, 679, 545. ESIHRMS: Found: m/z 416.1668. Calcd for $C_{24}H_{27}NNaO_2S$: $(M + Na)^+$ 416.1655.

2j: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 49.0 mg (62%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.65 (d, J = 8.4 Hz, 2H), 7.29–7.27 (d, J = 8.0 Hz, 2H), 7.04–7.01 (d, J = 8.8 Hz, 2H), 6.80–6.77 (d, J = 8.8 Hz, 2H), 6.61–6.59 (d, J = 8.0 Hz, 1H), 6.05 (s, 1H), 4.96–4.93 (d, J = 8.4 Hz, 1H), 4.14–4.04 (m, 2H), 3.79 (s, 3H), 2.43 (s, 3H), 1.12 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 158.9, 143.6, 135.2, 129.6, 127.7, 127.2, 126.4, 122.9, 119.6, 114.1, 106.1, 96.6, 55.3, 44.9, 33.8, 29.8, 29.1, 21.6; IR (neat, cm^{-1}) 3411, 2962, 2924, 1954, 1510, 1353, 1247, 1165, 1028, 680, 547. ESIHRMS: Found: m/z 418.1438. Calcd for $C_{23}H_{25}NNaO_3S$: $(M + Na)^+$ 418.1447.

2k: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 48.3 mg (61%) of the indicated compound after 2 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.65 (d, J = 8.0 Hz, 2H), 7.29–7.26 (d, J = 8.0 Hz, 2H), 7.19–7.14 (t, J = 4.0 Hz, 1H), 6.76–6.70 (m, 3H), 6.61–6.58 (d, J = 8.0 Hz, 1H), 6.05 (s, 1H), 4.96–4.94 (d, J = 8.4 Hz, 1H), 4.16–4.04 (m, 2H), 3.76 (s, 3H), 2.42 (s, 3H), 1.15 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 159.8, 143.7, 135.6, 135.2, 129.6, 129.5, 127.2, 123.0, 119.5,

119.3, 112.6, 112.1, 106.3, 97.1, 55.1, 44.7, 33.8, 29.9, 28.9, 21.5; IR (neat, cm^{-1}) 3403, 2963, 2926, 1956, 1598, 1354, 1165, 1028, 681, 546. ESIHRMS: Found: m/z 418.1440. Calcd for $C_{23}H_{25}NNaO_3S$: $(M + Na)^+$ 418.1447.

2l: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 43.5 mg (55%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68−7.65 (d, J = 8.0 Hz, 2H), 7.28−7.26 (d, J = 8.0 Hz, 2H), 7.18−7.14 (m, 1H), 7.06−7.04 (m, 1H), 6.85−6.79 (m, 2H), 6.61−6.58 (d, J = 8.4 Hz, 1H), 6.45 (s, 1H), 4.97−4.94 (d, J = 8.4 Hz, 1H), 4.15−4.05 (m, 2H), 3.83 (s, 3H), 2.43 (s, 3H), 1.13 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 155.9, 143.6, 135.3, 129.6, 128.1, 127.5, 127.2, 123.0, 122.5, 120.7, 119.9, 110.9, 105.1, 91.1, 55.5, 44.9, 33.7, 29.7, 28.9, 21.6; IR (neat, cm^{-1}) 3410, 2962, 2923, 1954, 1354, 1246, 1165, 1027, 680, 547. ESIHRMS: Found: m/z 418.1442. Calcd for $C_{23}H_{25}NNaO_3S$: $(M + Na)^+$ 418.1447.

2m: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 42.3 mg (50%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.64 (d, J = 8.4 Hz, 2H), 7.29−7.25 (t, J = 5.6 Hz, 2H), 6.79−6.77 (t, J = 4.6 Hz, 1H), 6.73−6.70 (t, J = 5.4 Hz, 2H), 6.59−6.56 (d, J = 8.4 Hz, 2H), 6.42−6.41 (d, J = 1.6 Hz, 1H), 4.96−4.94 (d, J = 8.4 Hz, 1H), 4.15−4.04 (m, 2H), 3.79 (s, 3H), 3.71 (s, 3H), 2.42 (s, 3H), 1.15 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 153.6, 150.6, 143.7, 135.1, 129.6, 127.2, 123.5, 123.0, 119.8, 113.1, 112.8, 112.3, 105.5, 91.2, 56.3, 55.5, 44.9, 33.7, 29.9, 28.8, 21.5; IR (neat, cm^{-1}) 3394, 2961, 2924, 1955, 1501, 1354, 1166, 1026, 680, 546. ESIHRMS: Found: m/z 448.1556. Calcd for $C_{24}H_{27}NNaO_4S$: $(M + Na)^+$ 448.1553.

2n: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 45.1 mg (53%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78−7.73 (m, 2H), 7.69−7.65 (t, J = 7.8 Hz, 3H), 7.55 (s, 1H), 7.48−7.40 (m, 2H), 7.28−7.25 (d, J = 8.0 Hz, 2H), 7.19−7.17 (m, 1H), 6.65−6.62 (d, J = 8.0 Hz, 1H), 6.26 (s, 1H), 4.99−4.96 (d, J = 8.4 Hz, 1H), 4.21−4.11 (m, 2H), 2.38 (s, 3H), 1.17 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 143.7, 135.2, 133.6, 132.7, 131.6, 129.6, 128.3, 127.7, 127.6, 127.2, 126.3, 125.7, 125.6, 124.2, 123.0, 119.5, 106.4, 97.5, 44.8, 33.8, 29.8, 29.1, 21.5; IR (neat, cm^{-1}) 3395, 2963, 2924, 1954, 1355, 1165, 1026, 679, 547. ESIHRMS: Found: m/z 438.1502. Calcd for $C_{26}H_{25}NNaO_2S$: $(M + Na)^+$ 438.1498.

2o: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 42.4 mg (57%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68−7.65 (d, J = 8.4 Hz, 2H), 7.30−7.27 (d, J = 8.0 Hz, 2H), 7.12−7.10 (d, J = 5.2 Hz, 1H), 6.93−6.90 (m, 1H), 6.82−6.81 (d, J = 3.2 Hz, 1H), 6.60−6.58 (d, J = 8.0 Hz, 1H), 6.29 (s, 1H), 4.96−4.93 (d, J = 8.0 Hz, 1H), 4.18−4.14 (m, 2H), 2.43 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 143.6, 138.5, 135.2, 129.6, 127.4, 127.3, 124.9, 124.4, 123.0, 119.6, 106.5, 91.4, 44.7, 34.0, 29.9, 28.7, 21.6; IR (neat, cm^{-1}) 3408, 2964, 2924, 1955, 1355, 1166, 1026, 681, 546. ESIHRMS: Found: m/z 394.0899. Calcd for $C_{20}H_{21}NNaO_2S_2$: $(M + Na)^+$ 394.0906.

2p: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 32.5 mg (49%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.64 (d, J = 8.0 Hz, 2H), 7.29−7.27 (d, J = 8.0 Hz, 2H), 6.54−6.52 (d, J = 8.0 Hz, 1H), 5.08−5.04 (m, 1H), 4.91−4.89 (d, J = 8.4 Hz, 1H), 4.02−3.91 (m, 2H), 2.42 (s, 3H), 1.90−1.75 (m, 2H), 1.37−1.28 (m, 2H), 1.01 (s, 3H), 0.96 (s, 3H), 0.90−0.86 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 143.4, 135.4, 129.5, 127.3, 122.9, 120.3, 101.9, 93.8, 45.4, 32.9, 31.9, 30.9, 29.7, 29.0, 22.4, 21.5, 13.7; IR (neat, cm^{-1}) 3412, 2959, 2921, 1712, 1382, 1358, 1165, 1029, 756, 672, 547. ESIHRMS: Found: m/z 354.1497. Calcd for $C_{19}H_{25}NNaO_2S$: $(M + Na)^+$ 354.1498.

2q: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 23.5 mg (30%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.69−7.66 (d, J = 8.0 Hz, 2H), 7.36−7.29 (m, 6H), 7.25−7.21 (m, 1H), 6.58−6.56 (d, J = 8.0 Hz, 1H), 6.49−6.45 (d, J = 15.6 Hz, 1H), 6.34−6.27 (m, 1H), 5.94−5.91 (d, J = 10.4 Hz, 1H), 4.97−4.94 (d, J = 8.0 Hz, 1H), 4.09−4.02 (m, 2H), 2.42 (s, 3H), 1.06 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 143.6, 137.1, 135.3, 131.1, 129.6, 128.6, 127.5, 127.3, 126.2, 124.5, 123.1, 120.2, 103.8, 97.2, 44.9, 33.6, 29.7, 29.5, 29.1, 21.6; IR (neat, cm^{-1}) 3411, 2959, 2923, 1948, 1355, 1165, 1025, 746, 680, 547. ESIHRMS: Found: m/z 414.1502. Calcd for $C_{24}H_{25}NNaO_2S$: $(M + Na)^+$ 414.1499.

2r: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 17.9 mg (31%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66−7.64 (d, J = 8.0 Hz, 2H), 7.28−7.27 (d, J = 8.0 Hz, 2H), 6.53−6.50 (d, J = 8.4 Hz, 1H), 4.95−4.92 (d, J = 8.4 Hz, 1H), 4.61−4.60 (t, J = 2.0 Hz, 2H), 4.01−3.99 (t, J = 2.0 Hz, 1H), 2.42 (s, 3H), 0.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 143.6, 135.1, 129.4, 127.4, 123.2, 120.9, 101.1, 45.1, 32.5, 28.9, 21.5; IR (neat, cm^{-1}) 3397, 2962, 2924, 1960, 1454, 1382, 1355, 1165, 1029, 675, 545. ESIHRMS: Found: m/z 312.1021. Calcd for $C_{16}H_{19}NNaO_2S$: $(M + Na)^+$ 312.1029.

2s: The reaction mixture was chromatographed using 50:1 hexanes/EtOAc to afford 44.5 mg (70%) of the indicated compound after 2 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68−7.65 (d, J = 8.4 Hz, 2H), 7.29−7.26 (d, J = 8.4 Hz, 2H), 6.55−6.52 (d, J = 8.4 Hz, 1H), 4.90−4.88 (d, J = 8.0 Hz, 1H), 3.94 (s, 2H), 2.40 (s, 3H), 1.54 (s, 6H), 0.97 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 143.4, 135.5, 129.5, 127.2, 122.7, 120.2, 100.0, 98.1, 45.3, 33.3, 29.4, 21.5, 20.4; IR (neat, cm^{-1}) 3406, 3020, 2962, 2925, 1711, 1219, 759, 667, 547. ESIHRMS: Found: m/z 340.1344. Calcd for $C_{18}H_{23}NNaO_2S$: $(M + Na)^+$ 340.1342.

General Procedure for the Palladium-Catalyzed Cyalization Reactions of Enyne Carbonates 1 To Form 3-Vinylidene-1-tosylpyrrolidines 3. A mixture of 1,6-enyne carbonate **1a** (88.3 mg, 0.2 mmol), $Pd(dba)_2$ (11.5 mg, 10 mol %), KOAc (39 mg, 0.4 mmol), P(2-furyl)$_3$ (4.6 mg, 10 mol %), and DMF (2 mL) was added to a 20 mL tube under an argon atmosphere. The resulting mixture was then stirred at 85 °C. When the reaction was considered complete as determined by TLC, the reaction mixture was allowed to cool to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and extracted with ethyl acetate. The combined organic extracts were washed with water and saturated brine, dried over Na_2SO_4, and filtered. Solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel using mixtures of hexanes and EtOAc to afford **3a** (70.2 mg, 96%).

Characterization Data of Five-Membered Heterocycles 3a−3o, 3s. 3a: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 70.2 mg (96%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76−7.71 (m, 2H), 7.38−7.35 (d, J = 8.4 Hz, 2H), 7.29−7.25 (m, 1H), 7.22−7.19 (m, 1H), 7.18−7.15 (d, J = 7.2 Hz, 2H), 6.29−6.25 (m, 1H), 4.84−4.77 (m, 1H), 4.13−3.89 (m, 2H), 3.62−3.42 (m, 2H), 3.29−3.18 (m, 1H), 2.42 (s, 3H), [1.68(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 143.8, 142.5, 133.7, 132.8, 129.7, 128.6, 127.9, 127.4, 127.0, 113.3, 105.0, 99.4, 99.3, 52.3, 49.8, 49.5, 49.0, 21.6, 19.8; IR (neat, cm^{-1}) 3420, 2924, 1722, 1346, 1163, 1093, 767, 666, 548. ESIHRMS: Found: m/z 366.1524. Calcd for $C_{22}H_{24}NO_2S$: $(M + H)^+$ 366.1522.

3b: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 44.0 mg (55%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76−7.73 (d, J = 7.6 Hz, 2H), 7.38−7.36 (d, J = 7.6 Hz, 2H), 7.25−7.22 (m, 2H), 7.10−7.07 (d, J = 8.4 Hz, 2H), 6.25−6.22 (m, 1H), 4.83−4.77 (m, 1H), 4.12−3.88 (m, 2H), 3.62−3.45 (m, 2H), 3.30−3.13 (m, 1H), 2.47 (s, 3H), [1.67(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 197.9, 143.9, 142.4, 142.0, 133.0, 132.7, 132.4, 132.3, 129.8, 128.8, 128.7, 128.2, 128.1, 127.9, 113.4, 113.3, 105.5, 105.4, 98.5, 98.4, 52.2, 49.7, 49.5, 49.1, 21.6, 19.8, 19.5; IR (neat, cm^{-1}) 3408, 2925, 1721, 1594, 1346, 1163, 1092, 816, 768, 667, 548. ESIHRMS: Found: m/z 400.1132. Calcd for $C_{22}H_{23}ClNO_2S$: $(M + H)^+$ 400.1133.

3c: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 63.2 mg (79%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78−7.73 (m, 2H), 7.39−7.31 (m, 2H), 7.25−7.10 (m, 3H), 7.06−7.02 (m, 1H), 6.23−6.19 (m, 1H), 4.83−4.78 (m, 1H), 4.41−3.87 (m, 2H), 3.61−3.50 (m, 2H), 3.47−3.16 (m, 1H), 2.46 (s, 3H), [1.68(s), 1.66(s), 3H]; ^{13}C NMR (100

MHz, $CDCl_3$) δ 198.3, 198.1, 144.0, 143.9, 142.4, 142.0, 138.6, 135.9, 135.7, 134.6, 132.6, 129.9, 129.8, 129.8, 127.8, 127.5, 127.4, 127.3, 126.9, 126.7, 126.1, 125.2, 125.1, 124.8, 122.0, 118.1, 113.5, 105.7, 105.6, 98.5, 52.2, 52.1, 49.7, 49.5, 49.1, 22.7, 21.6, 19.8, 19.5; IR (neat, cm^{-1}) 3410, 2925, 2924, 2858, 1594, 1457, 1346, 1164, 1094, 816, 755, 666, 547. ESIHRMS: Found: m/z 400.1136. Calcd for $C_{22}H_{23}ClNO_2S$: $(M + H)^+$ 400.1133.

3d: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 53.6 mg (67%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78–7.73 (m, 2H), 7.38–7.34 (m, 2H), 7.33–7.30 (m, 2H), 7.26–7.10 (m, 2H), 6.76–6.68 (m, 1H), 4.84–4.77 (m, 2H), 4.14–3.89 (m, 2H), 3.63–3.45 (m, 2H), 3.33–3.15 (m, 1H), [2.46(s), 2.43(s), 3H], [1.68(s), 1.67(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 198.8, 143.9, 143.6, 142.6, 141.9, 132.6, 132.2, 131.6, 131.5, 130.6, 129.9, 129.8, 129.7, 128.9, 128.6, 128.4, 128.4, 127.9, 127.5, 127.3, 126.9, 126.8, 126.3, 113.5, 113.3, 105.2, 105.1, 95.8, 95.7, 52.2, 49.8, 49.4, 49.2, 21.6, 19.8, 19.5; IR (neat, cm^{-1}) 3396, 2922, 2848, 1382, 1346, 1162, 1093, 1036, 815, 757, 665, 547. ESIHRMS: Found: m/z 400.1138. Calcd for $C_{22}H_{23}ClNO_2S$: $(M + H)^+$ 400.1133.

3e: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 49.8 mg (56%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.53 (d, J = 8.0 Hz, 2H), 7.39–7.35 (t, J = 7.0 Hz, 4H), 7.03–7.01 (d, J = 8.4 Hz, 2H), 6.22–6.20 (t, J = 3.6 Hz, 1H), 4.82–4.77 (m, 2H), 4.12–3.88 (m, 2H), 3.62–3.46 (m, 2H), 3.30–3.14 (m, 1H), 2.47 (s, 3H), [1.67(s), 1.65(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 198.0, 143.9, 142.4, 142.0, 132.9, 132.8, 132.7, 131.8, 131.7, 129.8, 128.5, 128.4, 127.9, 121.1, 121.1, 113.4, 113.3, 105.6, 105.5, 98.6, 98.5, 52.2, 49.7, 49.5, 49.1, 21.6, 19.8, 19.5; IR (neat, cm^{-1}) 3417, 2924, 2858, 1486, 1347, 1163, 1093, 1035, 816, 756, 665, 548. ESIHRMS: Found: m/z 444.0615. Calcd for $C_{22}H_{23}BrNO_2S$: $(M + H)^+$ 444.0627.

3f: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 65.3 mg (86%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.73 (t, J = 4.0 Hz, 2H), 7.37–7.35 (d, J = 8.0 Hz, 2H), 7.09–7.03 (m, 4H), 6.26–6.22 (m, 1H), 4.83–4.76 (m, 2H), 4.11–3.87 (m, 2H), 3.61–3.43 (m, 2H), 3.31–3.14 (m, 1H), 2.46 (s, 3H), [2.32(s), 2.31(s), 3H], [1.68(s), 1.65(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 197.6, 143.8, 142.6, 142.2, 137.3, 132.7, 130.8, 130.6, 129.7, 129.7, 129.3, 129.3, 127.8, 126.9, 113.1, 104.8, 104.7, 99.2, 99.1, 52.2, 49.8, 49.5, 49.0, 21.6, 21.2, 19.8, 19.5; IR (neat, cm^{-1}) 3407, 2923, 2361, 1721, 1382, 1346, 1162, 1092, 1037, 814, 771, 666, 548. ESIHRMS: Found: m/z 380.1683. Calcd for $C_{23}H_{26}NO_2S$: $(M + H)^+$ 380.1679.

3g: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 71.3 mg (94%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–7.73 (m, 2H), 7.38–7.32 (m, 2H), 7.18–7.02 (m, 1H), 6.99–6.96 (m, 3H), 6.26–6.21 (m, 1H), 4.84–4.76 (m, 2H), 4.13–3.87 (m, 2H), 3.61–3.46 (m, 2H), 3.30–3.13 (m, 1H), 2.46 (s, 3H), [2.34(s), 2.31(s), 3H], [1.69(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 197.8, 143.8, 143.3, 142.6, 142.2, 138.3, 138.2, 134.8, 133.7, 133.5, 132.7, 132.6, 130.5, 129.8, 129.7, 129.6, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 125.4, 124.2, 124.1, 113.2, 104.8, 104.7, 99.4, 99.3, 52.2, 49.8, 49.7, 49.5, 49.0, 21.6, 21.3, 19.8, 19.5; IR (neat, cm^{-1}) 3433, 2923, 2361, 1720, 1345, 1163, 1093, 1037, 816, 755, 666, 548. ESIHRMS: Found: m/z 380.1674. Calcd for $C_{23}H_{26}NO_2S$: $(M + H)^+$ 380.1679.

3h: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 71.3 mg (94%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.73 (d, J = 8.0 Hz, 2H), 7.38–7.35 (d, J = 8.0 Hz, 2H), 7.18–7.07 (m, 4H), 6.47–6.44 (m, 1H), 4.82–4.76 (m, 2H), 4.09–3.90 (m, 2H), 3.70–3.45 (m, 2H), 3.29–3.16 (m, 1H), 2.46 (s, 3H), [2.29(s), 2.28(s), 3H], [1.67(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 198.5, 143.8, 142.6, 142.2, 135.4, 135.2, 132.6, 132.1, 131.9, 131.7, 130.6, 130.5, 129.7, 127.8, 127.7, 127.4, 127.3, 126.0, 113.3, 113.2, 103.9, 103.6, 96.9, 96.7, 52.2, 49.9, 49.9, 49.5, 49.3, 21.6, 19.9, 19.8, 19.7, 19.5; IR (neat, cm^{-1}) 3432, 2923, 1598, 1345, 1163, 1093, 1036, 816, 754, 665, 548. ESIHRMS: Found: m/z 380.1683. Calcd for $C_{23}H_{26}NO_2S$: $(M + H)^+$ 380.1679.

3i: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 51.2 mg (65%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.73 (t, J = 4.0 Hz, 2H), 7.37–7.35 (d, J = 8.0 Hz, 2H), 7.04–7.01 (m, 1H), 6.95–6.89 (m, 2H), 6.23–6.20 (t, J = 4.0 Hz, 1H), 4.84–4.76 (m, 2H), 4.12–3.86 (m, 2H), 3.59–3.47 (m, 2H), 3.31–3.00 (m, 1H), 2.46 (s, 3H), [2.22(s), 2.20(s), 6H], [1.69(s), 1.65(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 197.6, 143.8, 142.6, 142.2, 136.8, 136.7, 136.0, 132.6, 131.2, 131.0, 129.9, 129.7, 128.3, 128.1, 127.8, 124.5, 124.4, 113.1, 104.6, 104.5, 99.2, 99.1, 52.2, 52.1, 49.8, 49.4, 48.9, 21.6, 19.7, 19.5; IR (neat, cm^{-1}) 3418, 2923, 1641, 1348, 1163, 1093, 1034, 814, 753, 665, 548; ESIHRMS: Found: m/z 394.1826. Calcd for $C_{24}H_{28}NO_2S$: $(M + H)^+$ 394.1835.

3j: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 55.4 mg (70%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.73 (t, J = 4.0 Hz, 2H), 7.37–7.35 (d, J = 8.0 Hz, 2H), 7.10–7.07 (d, J = 8.4 Hz, 2H), 6.83–6.79 (m, 2H), 6.26–6.21 (m, 1H), 4.84–4.76 (m, 2H), 4.11–3.86 (m, 2H), [3.79(s), 3.78(s), 3H], 3.61–3.43 (m, 2H), 3.29–3.15 (m, 1H), 2.46 (s, 3H), [1.68(s), 1.65(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 197.2, 159.1, 159.0, 143.8, 142.6, 142.3, 132.7, 129.7, 128.1, 127.8, 126.0, 125.9, 114.1, 113.1, 104.8, 104.7, 98.8, 98.7, 52.2, 52.1, 49.8, 49.5, 48.9, 21.5, 19.8, 19.5; IR (neat, cm^{-1}) 3434, 2927, 1602, 1345, 1164, 1093, 1032, 817, 756, 665, 549. ESIHRMS: Found: m/z 396.1618. Calcd for $C_{23}H_{26}NO_3S$: $(M + H)^+$ 396.1628.

3k: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 67.2 mg (85%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.79–7.73 (m, 2H), 7.38–7.33 (m, 2H), 7.24–7.11 (m, 1H), 6.82–6.72 (m, 3H), 6.26–6.23 (t, J = 3.0 Hz, 1H), 4.85–4.77 (m, 2H), 4.11–3.89 (m, 2H), [3.79(s), 3.77(s), 3H], 3.59–3.47 (m, 2H), 3.30–3.15 (m, 1H), 2.46 (s, 3H), [1.70(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 197.9, 159.8, 159.7, 143.8, 142.7, 142.2, 135.3, 135.1, 132.6, 129.8, 129.7, 129.6, 127.9, 119.7, 113.3, 113.2, 112.7, 112.6, 112.1, 105.1, 104.9, 99.4, 99.3, 55.2, 55.1, 52.3, 52.2, 49.8, 49.5, 49.0, 21.6, 19.9, 19.5; IR (neat, cm^{-1}) 3407, 2926, 1597, 1346, 1162, 1092, 1040, 815, 754, 666, 548. ESIHRMS: Found: m/z 413.1896. Calcd for $C_{23}H_{29}N_2O_3S$: $(M + NH_4)^+$ 413.1893.

3l: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 73.6 mg (93%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.73 (d, J = 8.0 Hz, 2H), 7.37–7.34 (d, J = 8.0 Hz, 2H), 7.25–7.13 (m, 2H), 6.88–6.81 (m, 2H), 6.67–6.64 (t, J = 4.2 Hz, 1H), 4.83–4.75 (m, 2H), 4.11–3.85 (m, 2H), [3.80(s), 3.79(s), 3H], 3.60–3.45 (m, 2H), 3.31–3.14 (m, 1H), 2.45 (s, 3H), [1.67(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 198.3, 156.1, 143.7, 142.8, 142.3, 132.9, 132.8, 129.7, 128.5, 128.0, 127.8, 122.2, 122.0, 120.6, 113.1, 112.9, 103.9, 103.8, 93.4, 93.3, 55.5, 55.4, 52.3, 49.9, 49.8, 49.4, 49.1, 22.6, 21.5, 19.8, 19.5; IR (neat, cm^{-1}) 3407, 2924, 1595, 1346, 1163, 1095, 1028, 817, 755, 665, 548. ESIHRMS: Found: m/z 396.1622. Calcd for $C_{23}H_{26}NO_3S$: $(M + H)^+$ 396.1628.

3m: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 67.2 mg (79%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.75–7.72 (d, J = 7.6 Hz, 2H), 7.38–7.34 (m, 2H), 6.80–6.70 (m, 3H), 6.65–6.62 (m, 1H), 4.85–4.76 (m, 2H), 4.09–3.88 (m, 2H), [3.77(s), 3.74(s), 6H], 3.57–3.44 (m, 2H), 3.30–3.15 (m, 1H), 2.45 (s, 3H), [1.71(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 198.2, 153.5, 150.6, 143.8, 142.9, 142.2, 132.6, 132.5, 129.8, 129.7, 127.8, 127.5, 123.3, 122.9, 113.9, 113.7, 113.2, 112.9, 112.8, 112.2, 104.3, 104.2, 93.5, 93.4, 56.2, 56.1, 55.6, 55.5, 52.3, 52.2, 49.8, 49.4, 48.9, 21.5, 19.9, 19.5; IR (neat, cm^{-1}) 3415, 2924, 1642, 1382, 1162, 1092, 1043, 811, 707, 665, 549. ESIHRMS: Found: m/z 426.1730. Calcd for $C_{24}H_{28}NO_4S$: $(M + H)^+$ 426.1734.

3n: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 60.7 mg (73%) of the indicated compound after 4 h. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–7.69 (m, 5H), 7.57 (s, 1H), 7.46–7.41 (m, 2H), 7.37–7.34 (d, J = 7.6 Hz, 2H), 7.30–7.27

(d, J = 8.8 Hz, 2H), 6.45−6.43 (t, J = 3.2 Hz, 1H), 4.86−4.76 (m, 2H), 4.17−3.92 (m, 2H), 3.64−3.43 (m, 2H), 3.34−3.17 (m, 1H), 2.46 (s, 3H), [1.70(s), 1.67(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 198.3, 143.8, 142.5, 142.1, 133.5, 132.7, 131.3, 131.2, 129.7, 128.2, 127.9, 127.7, 127.6, 127.5, 126.3, 126.1, 126.0, 125.9, 124.6, 124.5, 113.3, 105.2, 105.1, 99.7, 99.6, 52.2, 49.8, 49.5, 49.1, 22.6, 21.5, 19.8, 19.6; IR (neat, cm^{-1}) 3400, 2923, 1599, 1382, 1162, 1092, 1038, 816, 715, 666, 548. ESIHRMS: Found: m/z 438.1503. Calcd for $C_{26}H_{25}NNaO_2S$: $(M + Na)^+$ 438.1498.

3o: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 29.7 mg (40%) of the indicated compound after 4 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.70 (m, 2H), 7.37−7.33 (m, 2H), 7.18−7.14 (m, 1H), 6.94−6.90 (m, 1H), 6.86−6.85 (d, J = 3.6 Hz, 1H), 6.51−6.47 (m, 1H), 4.86−4.78 (m, 2H), 4.10−3.87 (m, 2H), 3.64−3.39 (m, 2H), 3.26−3.17 (m, 1H), [2.46(s), 2.45(s), 3H], [1.72(s), 1.66(s), 3H]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 197.2, 143.8, 143.6, 142.3, 142.1, 137.9, 132.7, 131.6, 129.8, 129.7, 127.9, 127.5, 127.4, 126.8, 126.5, 125.7, 125.5, 125.1, 123.3, 113.5, 113.3, 105.3, 105.2, 93.5, 93.4, 52.2, 51.3, 49.8, 49.7, 49.1, 21.6, 19.7, 19.6; IR (neat, cm^{-1}) 3409, 2925, 1647, 1345, 1162, 1094, 1041, 815, 753, 666, 549. ESIHRMS: Found: m/z 372.1082. Calcd for $C_{20}H_{22}NO_2S_2$: $(M + H)^+$ 372.1086.

3s: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 28.6 mg (45%) of the indicated compound after 4 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73−7.70 (d, J = 8.4 Hz, 2H), 7.35−7.32 (d, J = 8.0 Hz, 2H), 4.76−4.74 (m, 2H), 3.87−3.74 (m, 2H), 3.48−3.43 (m, 1H), 3.34−3.29 (t, J = 7.4 Hz, 1H), 3.13−3.08 (m, 1H), 2.44 (s, 3H), 1.63(s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 143.6, 143.2, 133.0, 129.6, 127.7, 112.5, 100.8, 98.5, 52.1, 49.9, 48.8, 21.5, 20.5, 20.2, 19.4; IR (neat, cm^{-1}) 3403, 2919, 1347, 1164, 1092, 1035, 816, 706, 663, 550. ESIHRMS: Found: m/z 318.1529. Calcd for $C_{18}H_{24}NO_2S$: $(M + H)^+$ 318.1523.

General Procedure for the Palladium-Catalyzed Suzuki Reactions of Enyne Carbonates 1. 1,6-Enyne carbonate **1a** (88.3 mg, 0.2 mmol), $Pd(dba)_2$ (11.5 mg, 10 mol %), KOAc (39 mg, 0.4 mmol), P(2-furyl)$_3$ (4.6 mg, 10 mol %), $PhB(OH)_2$ (48.8 mg, 0.4 mmol), and DMF (2 mL) were added to a 20 mL tube under an argon atmosphere. The resulting mixture was stirred at 85 °C. When the reaction was considered complete as determined by TLC, the reaction mixture was allowed to cool to room temperature, quenched with a saturated aqueous solution of ammonium chloride, and extracted with ethyl acetate. The combined organic extracts were washed with water and saturated brine, dried over Na_2SO_4, and filtered. Solvent was evaporated under reduced pressure. The residue was purified by chromatography on silica gel using mixtures of hexanes and EtOAc to afford **3aa** (70.9 mg, 80%).

Characterization Data of Products 3aa, 3ab. 3aa: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 67.4 mg (76%) of the indicated compound after 4 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.65 (d, J = 8.4 Hz, 2H), 7.51−7.48 (d, J = 7.6 Hz, 2H), 7.35−7.30 (m, 2H), 7.29−7.19 (m, 8H), 6.36 (s, 1H), 4.96−4.92 (t, J = 6.8 Hz, 1H), 4.52−4.47 (m, 1H), 3.29−3.24 (m, 1H), 3.89−3.74 (m, 2H), 2.41 (s, 3H), 1.55(s, 3H), 1.54(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 142.9, 137.2, 136.4, 133.8, 133.4, 129.4, 128.7, 128.6, 127.6, 127.5, 127.4, 127.0, 126.5, 106.0, 98.9, 47.1, 44.8, 25.6, 21.5, 17.8; IR (neat, cm^{-1}) 3399, 2920, 1382, 1158, 1093, 1023, 771, 553. ESIHRMS: Found: m/z 444.1987. Calcd for $C_{28}H_{30}NO_2S$: $(M + H)^+$ 444.1992.

3ab: The reaction mixture was chromatographed using 30:1 hexanes/EtOAc to afford 71.9 mg (69%) of the indicated compound after 4 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61−7.58 (d, J = 8.0 Hz, 2H), 7.55−7.52 (d, J = 8.0 Hz, 1H), 7.38−7.24 (m, 6H), 7.22−7.10 (m, 4H), 6.23−6.21 (t, J = 2.4 Hz, 1H), 4.98−4.94 (t, J = 7.0 Hz, 1H), 4.36−4.30 (m, 1H), 4.21−4.16 (m, 1H), 3.90−3.79 (m, 2H), 2.39 (s, 3H), 1.62(s, 3H), 1.59(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 142.8, 137.4, 136.9, 135.8, 133.4, 132.9, 130.9, 129.4, 129.1, 128.6, 127.5, 127.4, 127.3, 127.2, 123.2, 118.8, 106.2, 97.4, 48.7, 45.2, 25.8, 21.4, 17.9; IR (neat, cm^{-1}) 3398, 2923, 1354, 1164, 1090, 1023, 771, 683, 547. ESIHRMS: Found: m/z 522.1199. Calcd for $C_{28}H_{30}BrNO_2S$: $(M + H)^+$ 522.1197.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The detailed experimental procedure and copies of ^{1}H and ^{13}C NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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