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Rhodium-Catalyzed Transannulation of 1,2,3-Triazoles to Polysubstituted Pyrroles

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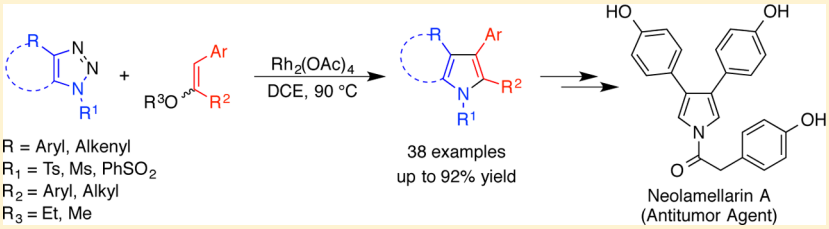
Supporting Information



ABSTRACT: Rhodium-catalyzed transannulation of *N*-sulfonyl-1,2,3-triazoles with vinyl ether has been accomplished for the synthesis of various polysubstituted pyrroles. The present method allows the synthesis of mono-, di-, and trisubstituted pyrroles with appropriate substitutions. Furthermore, the developed methodology was applied in the formal synthesis of neolamellarin A, an antitumor agent.

Pyrroles are ubiquitous subunits present in various bioactive natural products and pharmaceutically important molecules.[1] They exhibit a wide range of bioactivities such as antitumor, anti-inflammatory, and antibiotic activities (Figure 1). Furthermore, pyrroles also serves as vital intermediates in

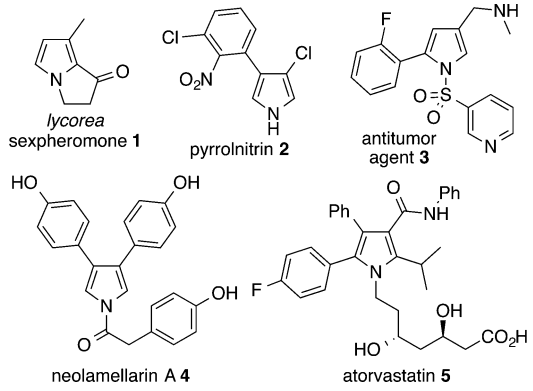


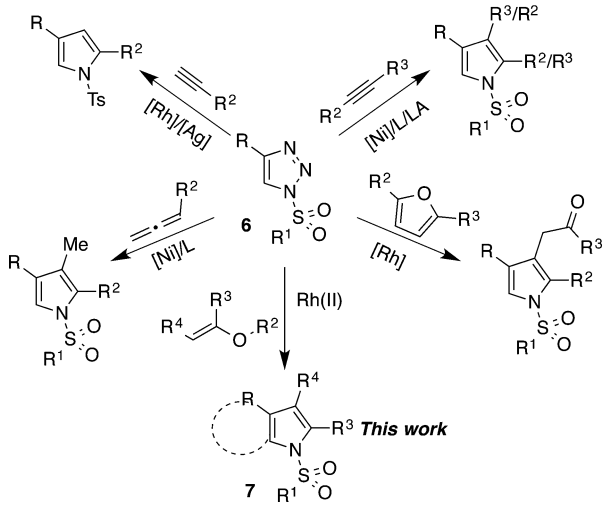
Figure 1. Representative examples of pyrrole-containing natural products and pharmaceuticals.

the synthesis of flavoring components,[2] dyes,[3] and organic functional materials.[4] Having mentioned these potentials, the synthesis of polysubstituted pyrroles has been an attractive field in organic synthesis and medicinal chemistry.

Typically, pyrroles are synthesized through classical Paal–Knorr,[5] Huisgen,[6] and Hantzsch[7] processes. During the last decades, various approaches have been documented for the synthesis of pyrrole through both metal-catalyzed inter-[8] and intramolecular[9] cyclization strategies. However, these strategies require multiple steps and prefunctionalized substrates. Most recently, readily accessible 1,2,3-triazoles, an efficient source of α-diazoimines,[10] were employed as starting material for the synthesis of pyrroles[11] using Rh and Ni catalysts and various coupling partners, such as alkynes,[12] allenes,[13] and furans[14] (Scheme 1).

Most of these reactions often produce the mixture of regioisomers, presumably due to the lack of directing ability in the coupling partners, and also have limitations on the kind of substitution that can be introduced on the pyrrole motif. Thus, the development of highly amenable and efficient synthesis of

Scheme 1. Transition-Metal-Catalyzed Transannulation of 1,2,3-Triazoles to Pyrroles



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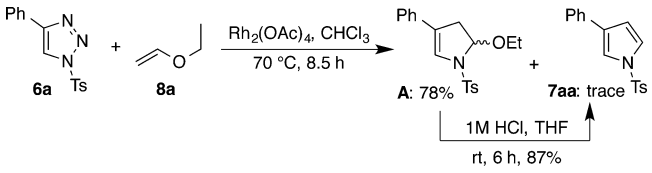
polysubstituted pyrroles with appropriate coupling partners is highly desirable.[15] Continuing our constant efforts in the functionalization of 1,2,3-triazoles[16] and inspired by the potential of polysubstituted pyrroles, we herein disclose the rhodium-catalyzed transannulation of 1,2,3-triazoles to pyrroles with substituted vinyl ethers.

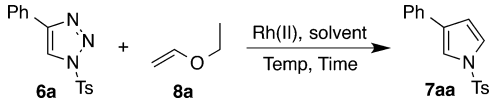
Initially, we focused on the optimization of suitable reaction conditions for the rhodium-catalyzed transannulation of 1,2,3-triazole **6a** to pyrrole **7aa** with ethylvinyl ether **8a**. Reaction of **6a** with 2 equiv of **8a** with 2 mol % of $Rh_2(OAc)_4$ in $CHCl_3$ at 70 °C in 8.5 h afforded 78% of unaromatized product **A** along with a detectable amount of pyrrole **7aa** (Scheme 2). The product **A** can be converted to pyrrole **7aa** in 87% yield utilizing acid-mediated elimination of ethanol.

Scheme 2. Rhodium-Catalyzed Transannulation of Triazole 6a with 8a



Interestingly, prolonging the reaction time (20 h) also afforded the pyrrole **7aa** in 82% yield (Table 1, entry 1).

Table 1. Rhodium-Catalyzed Transannulation of 6a with 8a: Optimization[a]



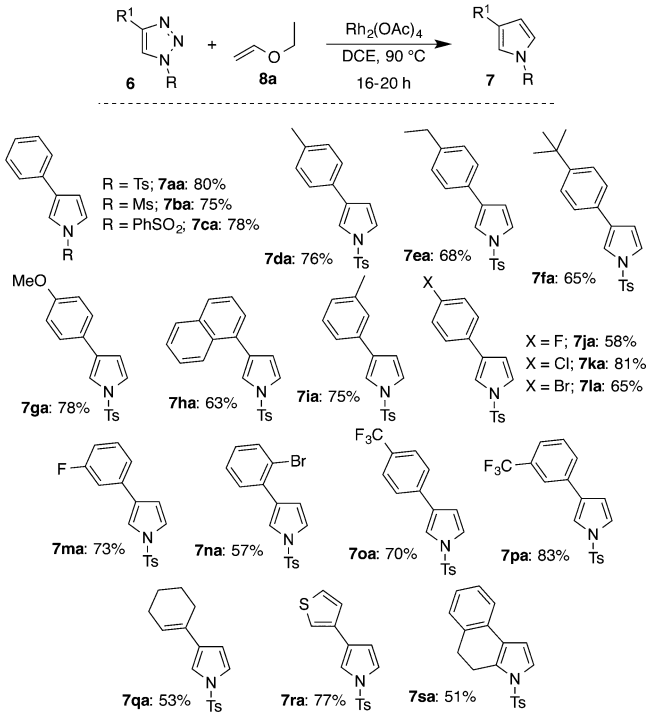
entry	Rh(II) cat.	solvent	temp (°C)	time (h)	yield (%)[b]
1	$Rh_2(OAc)_4$	$CHCl_3$	70	20	82
2	$Rh_2(OAc)_4$	DCE	90	16	80
3	$Rh_2(OAc)_4$	DCM	45	22	0
4	$Rh_2(OAc)_4$	DCM	70	20	63
5	$Rh_2(OAc)_4$	C_6H_5Cl	70	22	80
6	$Rh_2(Oct)_4$	DCE	90	16	92
7	$Rh_2(Oct)_4$	$CHCl_3$	70	20	91

[a]Reaction conditions: **6a** (1 equiv), **8a** (2 equiv), Rh(II) cat. (2 mol %), solvent (2 mL for 0.16 mmol), temp, time. [b]All are isolated yields.

Changing the solvent to 1,2-dichloroethane (DCE) along with an increase in temperature (90 °C) showed the similar result in 16 h (Table 1, entry 2). However, no formation of pyrrole was observed at decreased temperature (45 °C) in dichloromethane (DCM) (Table 1, entry 3). Screening solvents (DCM and chlorobenzene) at 70 °C gave the product **7aa** in 63% and 80% yield (Table 1, entries 4 and 5). Best results were observed when the catalyst was changed to $Rh_2(Oct)_4$ (Table 1, entries 6 and 7). However, due to the ready availability of $Rh_2(OAc)_4$ compared to $Rh_2(Oct)_4$, we used $Rh_2(OAc)_4$ as catalyst for the substrate studies. Similarly, chloroform at 70 °C and DCE at 90 °C gave the similar result, but the latter was opted since the latter gave the best result in substrate scope.

After identifying the suitable reaction conditions for the transannulation of triazole to pyrrole, the generality of the method was investigated. As shown in Scheme 3, various 1,3-disubstituted pyrroles were achieved from triazoles **6** and ethylvinyl ether **8a** employing the rhodium-catalyzed trans-

Scheme 3. Rhodium-Catalyzed Synthesis of 1,3-Disubstituted Pyrroles from Triazole 6 and 8a



annulation conditions. Replacement of the *p*-toluenesulfonyl moiety with mesyl and phenylsulfonyl gave the pyrroles **7ba** and **7ca** in comparable yield. Simple alkyl substituted aryl-containing pyrroles (**7da**, **7ea**, **7fa**, and **7ia**) were achieved in good yield from the corresponding 1,2,3-triazoles. Sterically hindered, naphthalene substituted triazole under the rhodium-catalyzed transannulation conditions afforded the pyrrole in 63% yield. Electron-poor, halogen and trifluoromethyl substituted aryl-containing triazoles furnished the pyrroles (**7ja**–**7pa**) in moderate to good yield. Interestingly, electron-rich, *p*-anisyl substituted triazole also underwent smooth reaction and pyrrole **7ga** was isolated in 78% yield. Thiophene, heteroarene substituted pyrrole (**7ra**), and cyclohexenyl substituted pyrrole (**7qa**) were also synthesized in good yield. Next, reaction of 1,4,5-trisubstituted triazoles and ethylvinyl ether **8a** gave the 1,2,3-trisubstituted pyrrole **7sa** in 51% yield.

Subsequently, the potential of the methodology was extended to the synthesis of tri- and tetrasubstituted pyrroles employing different triazoles and substituted enol ethers (Scheme 4). Reaction of *β*-aryl substituted enol ethers (**8b**–**8j**) with **6a** afforded the 1,3,4-trisubstituted pyrroles (**7ab**–**7ai**) in moderate to good yield. Interestingly, both sterically and electronically different aryl substituted enol ethers were tolerated under the optimized conditions. However, the reaction of a highly electron-withdrawing nitro group substituted *β*-arylenol ether with **6a** afforded the corresponding dihydropyrrole as the major product, even at a prolonged reaction time. Consequently, the corresponding pyrrole **7aj** was obtained in 48% yield after the treatment of dihydropyrrole with TMSOTf. Similarly, reaction of *α*-aryl substituted enol ethers (**8k**–**8m**) with triazoles (**6b** and **6c**) furnished the 1,2,4-trisubstituted pyrroles (**7bk**, **7bi**, and **7cm**) in good yield. The *α*-methyl substituted enol ether also underwent a smooth reaction to afford the pyrrole **7an** in 75% yield. Furthermore, the present strategy also allows the synthesis of 1,2,3,5-

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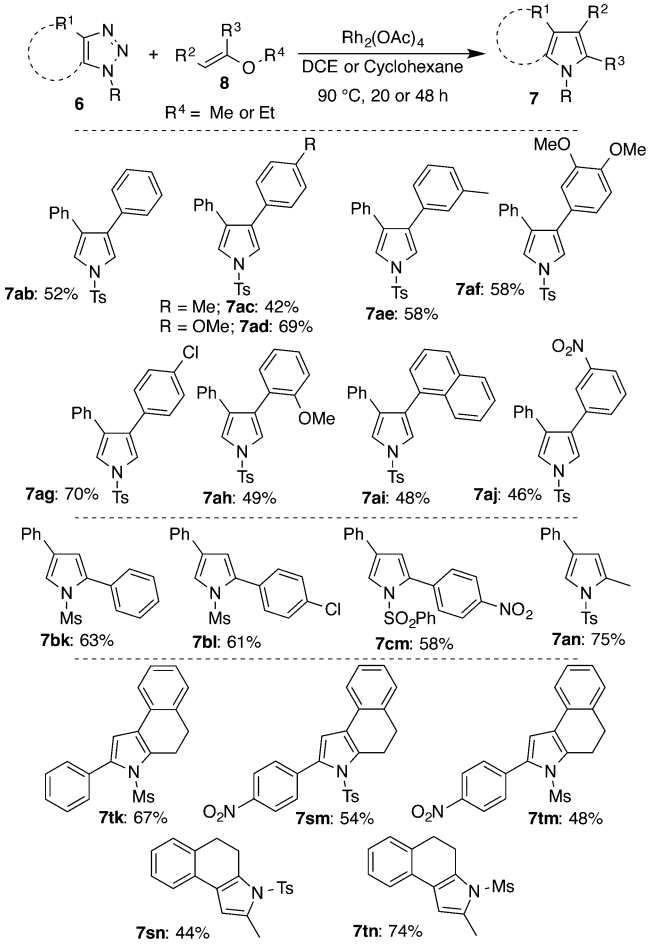
Scheme 4. Rhodium-Catalyzed Synthesis of Tri- and Tetrasubstituted Pyrroles

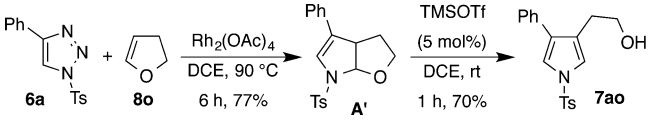


tetrasubstituted pyrroles in good yield. Reaction of 4,5-disubstituted triazoles (**7s** and **7t**) with α-aryl enol ethers (**8k** and **8m**) and α-alkyl enol ether **8n** gave the tetrasubstituted pyrroles (**7tk**, **7sm**, **7tm**, **7sn**, and **7tn**) in good to excellent yield.

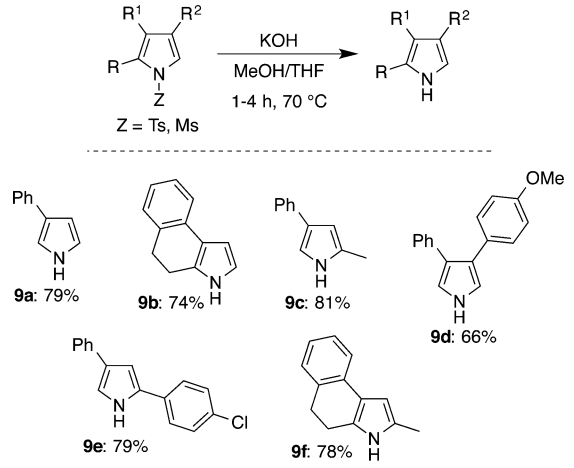
Next, transannulation of triazole **6a** with cyclic enol ether **8o** under the optimized conditions afforded the bicyclic compound **A′** in 77% yield, a potential motif present in a number of bioactive molecules, along with a detectable amount of pyrrole **7ao** (Scheme 5). Since prolonging the reaction time did not improve the pyrrole yield, the bicyclic compound **A′** was treated with a catalytic amount of TMSOTf to give pyrrole **7ao** in good yield.

Next, the conversion of synthesized *N*-sulfonyl pyrrole derivatives **7** to the polysubstituted pyrroles **9** were investigated. Treatment of *N*-sulfonyl pyrrole with KOH in methanol/THF afforded the free pyrroles (**9a**–**9f**) in excellent yield (Scheme 6). It is interesting to know that various mono-, di- (2,3-, 2,4-, and 3,4-), and tri (2,3,5)-substituted pyrroles can

Scheme 5. Rhodium-Catalyzed Transannulation of 6a with 8o



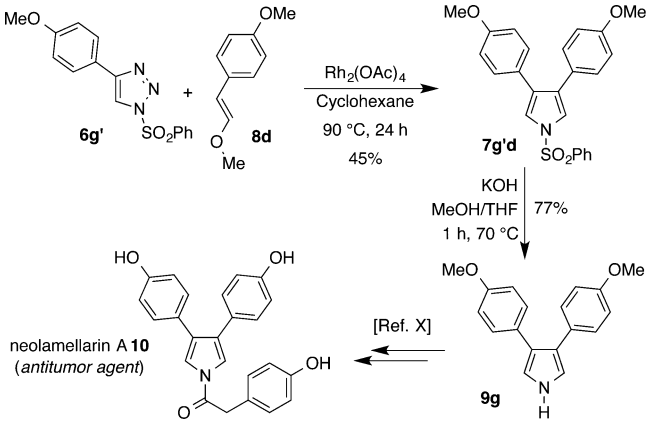
Scheme 6. Synthesis of Polysubstituted Pyrroles



be synthesized with high regioselectivity employing the present strategy.

After demonstrating the potential of the present strategy for the synthesis of pyrroles, we were interested in the application of the developed method in the formal synthesis of neolamellarin A (**4**). Neolamellarin A was isolated from a crude extract of the sponge *Dendrilla nigra*[17] and exhibits antitumor activity. The key intermediate 3,4-dianisylpyrrole **9g**[18] for the synthesis of **4** could be readily accessible through the present protocol (Scheme 7). Thus, the rhodium-catalyzed trans-

Scheme 7. Formal Synthesis of Neolamellarin A



annulation of triazole **6g′** with enol ether **8d** under the optimized conditions afforded the pyrrole, which, on subsequent reaction with KOH, furnished the key intermediate **9g** in two steps.

We postulate the following mechanism for the formation of pyrrole **7** from triazole **6** and enol ether **8** (Scheme 8). The reactive rhodium carbenoid **II** could be generated from **6** through the formation of α-diazoimine **I**. Reaction of **II** with **8** through a nucleophilic addition pathway would form zwitter ion **III**, which, on cyclization, would afford the intermediate **A** and reactive rhodium species. On the other hand, formation of **A** could be achieved from **II** and **8** via the cyclopropanated product **IV** and subsequent Cloke rearrangement.[19] Finally, aromatization of **A** through elimination of alcohol would furnish the pyrrole **7**.

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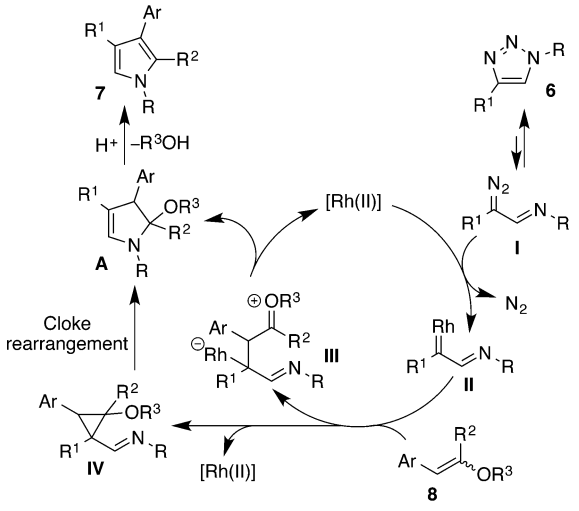
Scheme 8. Plausible Mechanism



In conclusion, we developed a highly efficient and amenable strategy for the synthesis of polysubstituted pyrroles from readily accessible triazoles and enol ethers. Employing the developed methodology, mono-, di-, and trisubstituted pyrroles can be achieved with high regioselectivity. Furthermore, the utility of the present method was demonstrated in the synthesis of the key intermediate for the synthesis of an antitumor agent, neolamellarin A.

EXPERIMENTAL SECTION

Synthesis of 2-Ethoxy-4-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole (A). 1,2,3-Triazoles **6a** (50 mg, 0.17 mmol) and $Rh_2(OAc)_4$ (1.4 mg, 0.003 mmol, 2 mol %) were added under a nitrogen atmosphere to an over-dried 5 mL reaction tube equipped with a stir bar. Subsequently, a solution of ethylvinyl ether **8a** (21.6 mg, 0.032 mL, 0.34 mmol) in $CHCl_3$ (2 mL) was introduced through a syringe. The reaction tube was sealed and kept at 90 °C for 8.5 h. After the TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture as eluent to afford the 2-ethoxy-4-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrole **A** (45 mg, 78% yield) as a colorless viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): 7.70 (d, 2H, J = 8.3 Hz), 7.30−7.20 (m, 7H), 6.79 (d, 1H, J = 2.5 Hz), 5.34 (d, 1H, J = 6.7 Hz), 3.93 (dq, 1H, J = 9.5, 7.0 Hz), 3.62 (dq, 1H, J = 9.5, 7.0 Hz), 2.77 (ddd, 1H, J = 16.8, 7.1, 2.7 Hz), 2.68−2.63 (m, 1H), 2.38 (s, 3H), 1.19 (t, 3H, J = 7.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 144.0, 135.8, 133.4, 129.9, 128.7, 127.5, 127.2, 126.1, 125.1, 123.4, 89.9, 63.0, 38.7, 21.6, 15.0.

Synthesis of 3-Phenyl-1-tosyl-1*H*-pyrrole (7aa). Dihydropyrrole **A** (44 mg, 0.13 mmol) and 3 mL of THF were added in a 10 mL round-bottom flask equipped with a stir bar. Subsequently, 1 M HCl (0.1 mL) was added, and the mixture was stirred at room temperature for 6 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexanes/ethyl acetate as eluent to afford the pyrrole **7aa** (34 mg, 87% yield) as a white solid. mp: 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, 2H, J = 7.6 Hz), 7.47 (d, 2H, J = 7.6 Hz), 7.41 (m, 1H), 7.34 (t, 2H, J = 7.3 Hz), 7.26−7.19 (m, 4H), 6.59 (m, 1H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.2, 136.2, 133.6, 130.2, 129.7, 128.9, 127.2, 127.1, 125.7, 121.8, 116.4, 112.2, 21.7; HRMS: calcd. for $C_{17}H_{15}NO_2S$+H: 298.0902; found: 298.0901.

General Procedure for the Synthesis of Substituted Pyrrole from 4-Substituted-*N*-sulfonyl-1,2,3-triazole 6 and Ethylvinyl Ether 8a. 4-Substituted-*N*-sulfonyl-1,2,3-triazoles **6** (50 mg, 0.14−0.17 mmol) and $Rh_2(OAc)_4$ (1.4 mg, 0.003 mmol, 2 mol %) were added under a nitrogen atmosphere to an over-dried 5 mL reaction tube equipped with a stir bar. Subsequently, a solution of ethyl vinyl ether **8a** (0.028−0.032 mL, 0.28−0.34 mmol) in DCE (2 mL) was introduced through a syringe. The reaction tube was sealed and stirred at 90 °C for 16−20 h. After the TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture as eluent to furnish the pyrroles (**7aa**−**7sa**).

7ba: 37 mg, 74% yield; colorless gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.52 (d, 2H, J = 7.4 Hz), 7.40−7.36 (m, 3H), 7.29 (d, 1H, J = 7.3 Hz), 7.18−7.16 (m, 1H), 6.69 (m, 1H), 3.18 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.4, 129.8, 129.0, 127.4, 125.8, 121.6, 116.2, 112.3, 43.0; HRMS: calcd. for $C_{11}H_{11}NO_2S$ + H: 222.0589; found: 222.0587.

7ca: 40 mg, 79% yield; brown gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.85 (m, 2H), 7.57−7.53 (m, 1H), 7.48−7.42 (m, 4H), 7.39 (t, 1H, J = 2 Hz), 7.31−7.28 (m, 2H), 7.21−7.19 (m, 1H), 7.17−7.16 (m, 1H), 6.6 (dd, 1H, J = 3.3, 1.7 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 139.1, 134.1, 133.5, 129.9, 129.6, 128.9, 127.6, 126.9, 125.7, 121.8, 116.5, 112.5; HRMS: calcd. for $C_{16}H_{13}NO_2S$ + H: 284.0745; found: 284.0743.

7da: 38 mg, 76% yield; white solid; mp: 109 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, 2H, J = 8.4 Hz), 7.38−7.37 (d, 3H), 7.28 (d, 2H, J = 8.1 Hz), 7.18−7.17 (m, 1H), 7.14 (d, 2H, J = 8.0), 6.58 (dd, 1H, J = 3.3, 1.7 Hz), 2.39 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.1, 136.9, 136.2, 135.7, 130.1, 129.7, 129.6, 127.0, 125.6, 121.7, 116.1, 112.2, 21.7, 21.3; HRMS: calcd. for $C_{18}H_{17}NO_2S$ + Na: 334.0878; found: 334.0880.

7ea: 34 mg, 68% yield; gummy solid; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, 2H, J = 8.4 Hz), 7.39−7.38 (m, 3H), 7.28 (d, 2H, J = 8.1 Hz), 7.18−7.16 (m, 3H), 6.58 (dd, 1H, J = 3.2, 1.6 Hz), 2.64 (q, 2H, J = 7.6 Hz), 2.39 (s, 3H), 1.23 (t, 3H, J = 7.6 Hz); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 145.2, 143.4, 136.2, 130.9, 130.1, 129.7, 128.4, 127.0, 125.7, 121.7, 116.1, 112.4, 28.7, 21.8, 15.7; HRMS: calcd. for $C_{19}H_{19}NO_2S$ + H: 326.1215; found: 326.1218.

7fa: 32 mg, 65% yield; white solid; mp: 135 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): 7.76 (d, 2H, J = 8.4 Hz), 7.41−7.35 (m, 5H), 7.27 (d, 2H, J = 8.1 Hz), 7.18 (dd, 1H, J = 3.5, 2.6 Hz), 6.58 (dd, 1H, J = 1.6, 3.3 Hz), 2.39 (s, 3H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 150.3, 145.1, 136.2, 130.7, 130.1, 129.6, 127.0, 125.8, 125.4, 121.7, 116.2, 112.4, 34.6, 31.4, 21.7; HRMS: calcd. for $C_{21}H_{23}NO_2S$ + H: 354.1528; found: 354.1516.

7ga: 38 mg, 78% yield; brown solid; mp: 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, 2H, J = 8.3 Hz), 7.39 (d, 2H, J = 8.8 Hz), 7.33−7.32 (m, 1H), 7.28 (d, 2H, J = 8.3 Hz), 7.18−7.17 (m, 1H,), 6.88 (d, 2H, J = 8.8 Hz), 6.54 (dd, 1H, J = 3.12, 1.6 Hz), 3.8 (s, 3H), 2.39 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.9, 145.1, 136.1, 130.1, 129.4, 127.0, 126.8, 126.3, 121.7, 115.5, 114.3, 112.2, 55.5, 21.7; HRMS: calcd. for $C_{18}H_{17}NO_3S$ + Na: 350.0827; found: 350.0842.

7ha: 33 mg, 66% yield; gummy liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.08 (d, 1H, J = 8.0 Hz), 7.88−7.79 (m, 4H), 7.50−7.43 (m, 4 H), 7.37 (t, 1H, J = 1.8 Hz), 7.32 (d, 2H, J = 8.2 Hz), 7.29 (t,1H, J = 3.0 Hz), 6.58 (dd, 1H, J = 3.14, 1.6 Hz), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.2, 136.2, 134.0, 132.2, 131.6, 130.2, 128.5, 128.3, 127.9, 127.1, 126.9, 126.3, 125.9, 125.6, 125.5, 120.9, 119.1, 115.8, 21.8; HRMS: calcd. for $C_{21}H_{17}NO_2S$ + Na: 370.0878; found: 370.0869.

7ia: 37 mg, 75% yield; gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (2H, d, J = 6.7 Hz), 7.39−7.4 (m, 1H), 7.29−7.27 (m, 4H), 7.23 (t, 1H, J = 5.9 Hz), 7.19−7.18 (m, 1H), 7.05 (d, 1H, J = 5.8 Hz), 6.59 (dd, 1H, J = 2.12, 1.3 Hz), 2.39 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.1, 138.5, 136.1, 133.5, 130.2, 129.8, 128.8, 127.9, 127.0, 126.5, 122.8, 121.7, 116.4, 112.3, 21.7, 21.6; HRMS: calcd. for $C_{18}H_{17}NO_2S$ + K: 350.0617; found: 350.0625.

7ja: 29 mg, 58% yield; gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, 2H, J = 8.4 Hz), 7.43−7.40 (m, 2H), 7.35 (t, 1H, J = 1.88 Hz), 7.30 (d, 2H, J = 8.08 Hz), 7.19 (dd, 1H, J = 3.2, 2.2 Hz), 7.02 (t, 2H, J = 8.7 Hz), 6.54 (dd, 1H, J = 3.2, 1.6 Hz), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 162.2 (d, J = 244.4 Hz), 145.3, 136.1, 130.2, 129.8 (d, J = 2.4 Hz), 128.8, 127.3 (d, J = 7.9 Hz),

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127.1, 121.9, 116.2, 115.8 (d, J = 21.4 Hz), 112.2, 21.7; HRMS: calcd. for $C_{17}H_{14}NO_2FS$ + H: 316.0808; found: 316.0816.

7ka: 40 mg, 81% yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, 2H, J = 8.4 Hz), 7.39−7.37 (m, 3H), 7.3 (d, 4H, J = 8.5 Hz), 7.2−7.19 (m, 1H), 6.55 (dd, 1H, J = 3.2, 1.6 Hz), 2.4 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.4, 135.9, 132.8, 132.2, 130.2, 129.1, 128.5, 127.1, 126.9, 121.9, 116.5, 112.0, 21.8; HRMS: calcd. for $C_{17}H_{14}ClNO_2S$ + H: 332.0512; found: 332.0511.

7la: 33 mg, 65% yield; white solid; mp: 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, 2H, J = 8.4 Hz), 7.46−7.44 (m, 2H), 7.39 (t, 1H, J = 1.96 Hz), 7.33−7.28 (m, 4H), 7.20−7.18 (m, 1H), 6.55 (dd, 1H, J = 3.1, 1.7 Hz), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.4, 136.0, 132.6, 132.0, 130.2, 128.5, 127.3, 127.1, 121.9, 120.8, 116.5, 111.9, 21.8; HRMS: calcd. for $C_{17}H_{14}NO_2S^{79}Br$ + H: 376.0007; found: 376.0005.

7ma: 37 mg, 73% yield; white solid; mp: 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, 2H, J = 8.4 Hz), 7.41 (t, 1H, J = 3.8 Hz), 7.32−7.29(m, 1H), 7.15 (td, 1H, J = 10.1, 2.3 Hz), 6.99−6.95 (m, 1H), 6.57 (dd, 1H, J = 3.2, 1.7 Hz), 2.4 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 163.3 (d, J = 243.7 Hz), 145.4, 135.9 (d, J = 4.2 Hz), 135.4, 130.4 (d, J = 34.4 Hz), 130.2, 128.5, 127.1, 121.9, 121.3 (d, J = 3.0 Hz), 116.9, 113.9 (d, J = 21.2 Hz), 112.5 (d, J = 22.1 Hz), 112.0, 21.8; HRMS: calcd. for $C_{17}H_{14}NO_2FS$ + H: 316.0808; found: 316.0817.

7na: 29 mg, 58% yield; brown gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.79 (d, 2H, J = 8.4 Hz), 7.61 (dd, 1H, J = 7.8, 1 Hz), 7.48 (t, 1H, J = 2.12 Hz), 7.35−7.28 (m, 4H), 7.18−7.17 (m, 1H), 7.11 (td, 1H, J = 7.7, 1.7 Hz), 6.57 (dd, 1H, J = 3.2, 1.6 Hz), 2.4 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.3, 136.1, 134.8, 133.7, 130.9, 130.2, 128.6, 128.2, 127.6, 127.1, 122.4, 120.3, 119.7, 115.1, 21.8; HRMS: calcd. for $C_{17}H_{14}NO_2S^{79}Br$ + H: 376.0007; found: 375.9995.

7oa: 35 mg, 70% yield; white solid; mp: 123 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.79 (d, 2H, J = 8.4 Hz), 7.60−7.55 (m, 4H), 7.48 (t, 1H, J = 1.9 Hz), 7.31 (d, 2H, J = 8.2 Hz), 7.23−7.22 (m, 1H), 6.61 (dd, 1H, J = 3.2, 1.7 Hz), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 145.4, 137.1, 135.7, 130.2, 128.9 (q, J = 32 Hz), 128.1, 127.0, 125.8 (q, J = 3.6 Hz), 125.7, 124.2 (q, J = 269.9 Hz), 121.1, 117.2, 111.8, 21.7; HRMS: calcd. for $C_{18}H_{14}NO_2SF_3$ + Na: 388.0595; found: 388.0608.

7pa: 41 mg, 83% yield; viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.80 (d, 2H, J = 8.4 Hz), 7.69 (s, 1H), 7.64−7.62 (m, 1H), 7.47−7.45 (m, 3H), 7.32 (d, 2H, J = 8.2 Hz), 7.24−7.22 (m, 1H), 6.61 (dd, 1H, J = 1.7, 3.2 Hz), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.5, 135.9, 134.5, 131.3 (q, J = 31.9 Hz), 130.3, 129.3, 128.9, 128.3, 127.1, 123.7 (q, J = 3.7 Hz,), 122.8, 122.4 (q, J = 3.8 Hz), 116.9, 111.9, 21.8; HRMS: calcd. for $C_{18}H_{14}F_3NO_2S$ + H: 366.0776; found: 366.0783.

7qa: 26 mg, 53% yield; white solid; mp: 151 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.72 (d, 2H, J = 8.4 Hz), 7.27 (d, 2H, J = 7.3 Hz), 7.09−7.07 (m, 1H), 7.02 (m, 1H), 7.02 (m, 1H), 6.42 (dd, 1H, J = 3.3, 1.6 Hz), 2.39 (s, 3H), 2.23−2.20 (m, 2H), 2.15−2.12 (m, 2H), 1.73−1.67 (m, 2H), 1.64−1.59 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 144.9, 136.3, 131.5, 130.0, 129.6, 126.9, 123.2, 121.4, 115.3,110.8, 26.7, 25.6, 22.7, 22.4, 21.7; HRMS: calcd. for $C_{17}H_{19}NO_2S$ + H: 302.1215; found: 302.1205.

7ra: 38 mg, 77% yield; brown solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C):δ 7.77 (d, 2H J = 8.4 Hz), 7.32−7.27 (m, 5H), 7.19 (dd, 1H, J = 5.0 1.2 Hz), 7.16−7.15 (m, 1H), 6.51 (dd, 1H, J = 3.2, 1.6 Hz), 2.4 (s, 3H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 145.2, 136.1, 134.9, 130.2, 127.0, 126.3, 125.9, 125.1, 121.7, 119.4, 116.4, 112.7, 21.8; HRMS: calcd. for $C_{15}H_{13}NO_2S_2$ + Na: 326.0285; found: 326.0284.

7sa: 25 mg, 51% yield; gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.63 (d, 2H, J = 8.3 Hz), 7.23−7.18 (m, 4H), 7.12−6.98 (m, 3H), 6.5 (d, 1H, J = 3.4 Hz), 2.92 (t, 2H, J = 6.8 Hz), 2.86 (t, 2H, J = 6.8 Hz), 2.32 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.1, 136.3, 133.3, 131.3, 130.2, 130.1, 128.0, 126.9, 126.8, 126.3, 124.2, 122.3, 122.2, 107.9, 29.2, 21.7, 21.4; HRMS: calcd. for $C_{19}H_{17}NO_2S$ + H: 324.1058; found: 324.1072.

General Procedure for the Synthesis of 3,4-Diaryl-1-tosyl-1*H*-pyrroles (7ab−7aj). 4-Phenyl-*N*-sulfonyl-1,2,3-triazoles **6a** (50 mg, 0.17 mmol) and $Rh_2(OAc)_4$ (1.4 mg, 0.003 mmol, 2 mol %) were added under a nitrogen atmosphere to an over-dried 10 mL reaction tube equipped with a stir bar. Subsequently, a solution of vinyl ether **8b−8j** (44−64 mg, 0.33 mmol) in cyclohexane (2 mL) was introduced through a syringe. The reaction tube was sealed and stirred at 90 °C for 48 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture as eluent to afford pyrroles **7ab−7aj**.

7ab: 33 mg, 52% yield; white solid; mp: 125 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.77 (d, 2H, J = 8.4 Hz), 7.25 (d, 2H, J = 8.2 Hz), 7.18−7.16 (m, 8H), 7.11−7.09 (m, 4H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.3, 136.1, 133.7, 130.3, 128.7, 128.6, 128.4, 127.2, 127.1, 119.0, 21.8; HRMS: calcd. for $C_{23}H_{19}NO_2S$ + H: 374.1215; found: 374.1231.

7ac: 27 mg, 42% yield; white solid; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.82 (d, 2H, J = 8.3 Hz), 7.32 (d, 2H, J = 8.3 Hz), 7.25−7.21 (m, 6H), 7.19−7.17 (m, 2H), 7.06 (m, 4H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 145.3, 136.8, 136.1, 133.8, 130.7, 130.2, 129.2, 128.7, 128.5, 128.4, 127.2, 127.0, 119.0, 118.8, 21.8, 21.3; HRMS: calcd. for $C_{24}H_{21}NO_2S$ + H: 388.1371; found: 388.1375.

7ad: 46 mg, 69% yield; yellow gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.75 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.17−7.09 (m, 7H), 7.02 (d, 2H, J = 8.4 Hz), 6.71 (d, 2H, J = 8.5 Hz), 3.7 (s, 3H), 2.34 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.8, 145.3, 136.1, 133.8, 130.2, 129.8, 128.7, 128.6, 128.4, 127.2, 126, 118.9, 118.5, 113.9, 55.3, 21.8; HRMS: calcd. for $C_{24}H_{21}NO_3S$ + H: 404.1320; found: 404.1305.

7ae: 37 mg, 57% yield; brown gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.76 (d, 2H, J = 8.4 Hz), 7.24 (d, 2H, J = 8.0 Hz), 7.17−7.15 (m, 5H), 7.11−7.09 (m, 2H), 7.06−7.02 (m, 1H), 6.97−6.95 (m, 2H), 6.87 (d, 2H, J = 7.04 Hz), 2.34 (s, 3H), 2.2 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.3, 138.0, 136.1, 133.7, 133.5, 130.2, 129.3, 128.8, 128.7, 128.6, 128.4, 128.2, 127.8, 127.2, 127.0, 125.8, 119.0, 118.9, 21.8, 21.5; HRMS: calcd. for $C_{24}H_{21}NO_2S$ + H: 388.1371; found: 388.1363.

7af: 42 mg, 58 yield; yellow solid; mp: 142 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.82 (d, 2H, J = 8.4 Hz), 7.31 (d, 2H, J = 8.1 Hz), 7.23−7.20 (m, 5H), 7.18−7.16 (m, 2H), 6.75 (m, 2H), 6.59 (s, 1H), 3.83 (s, 3H), 3.58 (s, 3H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 24 °C): δ 148.6, 148.2, 145.3, 136.1, 133.8, 130.3, 128.8, 128.7, 128.5, 128.4, 127.2, 127.1, 126.3, 120.7, 118.9, 112.1, 111.2, 55.9, 55.7, 21.8; HRMS: calcd. for $C_{25}H_{23}NO_4S$ + H: 434.1426; found: 434.1415.

7ag: 48 mg, 70% yield; gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.83 (d, 2H, J = 8.4 Hz), 7.32(d, 2H, J = 8.1 Hz), 7.24 (m, 5H), 7.20 (d, 2H, J = 8.5 Hz), 7.16−7.14 (m, 2H), 7.09 (2H, J = 8.5 Hz), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.5, 136.1, 133.4, 133.1, 132.2, 130.9, 130.3, 129.9, 128.7, 128.6, 127.5, 127.3, 119.2, 119.1, 21.8; HRMS: calcd. for $C_{23}H_{18}NO_2ClS$ + H: 408.0825; found: 408.0824.

7ah: 33 mg, 49% yield; yellow viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.83 (d, 2H, J = 8.4 Hz), 7.32−7.29 (m, 3H), 7.26−7.24 (m, 2H), 7.22−7.16 (m, 3H), 7.13−7.10 (m, 3H), 6.87 (td, 1H, J = 7.4, 1.0 Hz), 6.80 (d, 1H, J = 8.2 Hz), 3.38 (s, 3H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 156.9, 145.1, 136.3, 134.9, 131.4, 130.2, 129.8, 128.9, 128.2, 127.5, 127.2, 126.7, 124.8, 122.8, 120.6, 120.3, 120.3, 118.0, 111.3, 55.1, 21.8; HRMS: calcd. for $C_{24}H_{21}NO_3S$ + H: 404.1320; found: 404.1312.

7ai: 34 mg, 48% yield; brown gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.87 (d, 2H, J = 8.2 Hz), 7.81 (t, 2H, J = 7.8 Hz), 7.68 (d, 1H, J = 8.4 Hz), 7.44−7.34 (m, 5H), 7.29−7.25 (m, 3H), 7.03 (m, 5H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.4, 136.1, 133.8, 133.5, 132.4, 131.7, 130.3, 128.3, 128.29, 128.2, 128.1, 127.5, 126.8, 126.7, 126.2, 126.0, 125.8, 125.4, 121.0, 118.1, 21.8; HRMS: calcd. for $C_{27}H_{21}NO_2S$ + H: 424.1371; found: 424.1388.

7aj: 27 mg, 46% yield; white gummy liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.08−8.06 (m, 2H), 7.87 (d, 2H, J = 8.4 Hz), 7.43−

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7.35 (m, 5H), 7.28−7.26 (m, 4H), 7.15−7.13 (m, 2H), 2.44 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 148.5, 145.7, 135.8, 135.6, 134.7, 132.9, 130.5, 129.3, 128.75, 128.70, 128.5, 127.6, 127.4, 126.3, 123.1, 121.9, 119.6, 119.5, 21.8; HRMS: calcd. for $C_{23}H_{18}N_2O_4S$ + H: 419.1066; found: 419.1062.

Typical Procedure for the Synthesis of 1,2,4-Tri- and 1,2,3,5-Tetrasubstituted Pyrrole. 1,2,3-Triazoles (50 mg, 0.15−0.2 mmol) and $Rh_2(OAc)_4$ (1.4−1.8 mg, 0.003−0.004 mmol, 2 mol %) were added under a nitrogen atmosphere to an over-dried 5 mL reaction tube equipped with a stir bar. Subsequently, a solution of vinyl ether (22−73 mg, 0.32−0.51 mmol) in DCE (2 mL) was introduced through a syringe. The reaction tube was sealed and stirred at 90 °C for 24 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexanes/ethyl acetate mixture as eluent to afford the pyrrole.

7bk: 41 mg, 63% yield; gummy solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.58−7.54 (m, 5H), 7.43−7.36 (m, 5H), 7.29−7.24 (m, 1H), 6.65 (d, 1H, *J* = 2.0 Hz), 2.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 136.5, 133.3, 131.1, 130.9, 129.0, 128.0, 127.5, 127.3, 125.7, 119.3, 114.5, 42.4; HRMS: calcd. for $C_{17}H_{15}NO_2S$ + H: 298.0902; found: 298.0890.

7bl: 44 mg, 61 yield; white viscous liquid; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.58 (d, 1H, *J* = 2.0 Hz), 7.54 (d, 2H, *J* = 7.8 Hz), 7.5 (d, 2H, *J* = 8.6 Hz), 7.40−7.37 (m, 4H), 7.30−7.25 (m, 1H), 6.65 (d, 1H, *J* = 2.0 Hz), 2.89 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 135.3, 135.2, 133.0, 132.1, 129.4, 129.0, 128.4, 127.9, 127.5, 119.8, 115.0, 42.5; HRMS: calcd. for $C_{17}H_{14}ClNO_2S$ + H: 332.0512; found: 332.0523.

7cm: 25 mg, 58% yield; yellow solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.21 (d, 2H, *J* = 9.1 Hz), 7.78 (d, 1H, *J* = 2.0 Hz), 7.56−7.49 (m, 5H), 7.42−7.25 (m, 7H), 6.61 (d, 1H, *J* = 1.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 147.7, 138.2, 137.8, 134.9, 134.3, 132.7, 131.4, 129.3, 129.1, 128.8, 127.7, 126.9, 125.7, 122.9, 121.9, 116.6; HRMS: calcd. for $C_{22}H_{16}N_2O_4S$ + H: 405.0909; found: 405.0901.

7an: 39 mg, 75% yield; white solid; mp: 113 °C; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.70 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 1H, *J* = 1.9 Hz), 7.48−7.46 (m, 2H), 7.35 (t, 2H, *J* = 7.4 Hz), 7.3 (d, 2H, *J* = 8.0 Hz), 7.44−7.20 (m, 1H), 6.28−6.27 (m, 1H), 2.4 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.0, 136.4, 133.8, 131.9, 130.2, 128.9, 127.0, 126.9, 125.5, 117.7, 111.9, 21.7, 13.9; HRMS: calcd. for $C_{18}H_{17}NO_2S$ + H: 312.1058; found: 312.1059.

7tk: 45 mg, 69% yield; white solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): 7.54−7.51 (m, 2H), 7.44−7.38 (m, 4H), 7.20−7.18 (m, 1H), 6.6 (s, 3H), 3.25 (t, 2H, *J* = 7.8 Hz), 3.11 (t, 2H, *J* = 7.6 Hz), 2.92 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 137.8, 133.9, 133.8, 132.5, 130.8, 130.6, 128.6, 128.1, 127.8, 126.9, 126.7, 124.0, 122.5, 111.9, 42.2, 29.5, 23.1; HRMS: calcd. for $C_{19}H_{17}NO_2S$ + H: 324.1058; found: 324.1073.

7sm: 36 mg, 54% yield; yellow solid ; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.27 (d, 2H, *J* = 8.7 Hz), 7.64 (d, 2H, *J* = 8.8 HZ), 7.36 (d, 2H, J = 8.4 Hz), 7.31−7.28 (m, 1H), 7.24−7.16 (m, 5H), 6.63 (s, 1H), 3.28 (t, 2H, *J* = 7.8 Hz), 3.03 (t, 2H, *J* = 7.8 Hz), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 147.2, 145.2, 139.3, 136.0, 135.5, 135.4, 133.8, 130.7, 130.1, 129.8, 127.9, 126.9, 126.8, 126.4, 124.9, 122.8, 122.4, 114.4, 29.3, 23.1, 21.6; HRMS: calcd. for $C_{25}H_{20}N_2O_4S$ + H: 445.1222; found: 445.1237.

7tm: 34 mg, 48% yield; white solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.27 (d, 2H, *J* = 8.9 Hz), 7.68 (d, 2H, *J* = 8.9 Hz), 7.42−7.39 (m, 1H), 7.30−7.19 (m, 3H), 6.77 (s, 1H), 3.25 (t, 2H, *J* = 7.8 Hz), 3.12 (t, 2H, *J* = 7.8 Hz), 2.93 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 147.5, 138.9, 135.8, 135.2, 133.8, 130.8, 130.1, 128.2, 127.3, 127.1, 125.1, 123.1, 122.6, 114.2, 42.0, 29.3, 23.0; HRMS: calcd. for $C_{19}H_{16}N_2O_4S$ + H: 369.0909; found: 369.0917.

7sn: 23 mg, 44% yield; gummy solid; ^1H NMR (500 MHz, $CDCl_3$, 24 °C): δ 7.6 (d, 2H, *J* = 6.7 Hz), 7.27−7.23 (m, 3H), 7.18−7.14 (m, 2H), 7.04 (td, 1H, *J* = 7.3, 1.3 Hz), 6.27 (d, 1H), 3.13 (t, 2H, *J* = 7.8 Hz). 2.96 (t, 2H, *J* = 7.8 Hz), 2.46 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 144.8, 137.2, 133.7, 132.9, 131.6, 131.3, 130.1, 127.8, 126.8, 126.4, 126.1, 122.4, 122.2, 108.7, 29.6, 22.8, 21.7, 15.4; HRMS: calcd. for $C_{20}H_{19}NO_2S$ + H: 338.1215; found: 338.1211.

7tn: 38 mg, 74% yield; white gummy solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.22−7.16 (m, 2H), 7.13−7.08 (m, 1H), 6.33 (s, 1H), 3.11 (t, 2H, *J* = 7.6 Hz), 3.09 (s, 3H), 3.00 (t, 2H, *J* = 7.6 Hz), 2.47 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.6, 132.5, 131.1, 130.4, 127.9, 123.9, 126.3, 122.6, 122.3, 108.7, 42.7, 29.5, 22.7, 15.3; HRMS: calcd. for $C_{14}H_{15}NO_2S$ + H: 262.0902; found: 262.0903.

Synthesis of 7ao. 4-Phenyl-*N*-tosyl-1,2,3-triazoles **6a** (75 mg, 0.25 mmol) and $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol, 2 mol %) were added under a nitrogen atmosphere to an over-dried 10 mL reaction tube equipped with a stir bar. Subsequently, a solution of cyclic vinyl ether **8o** (35 mg, 0.5 mmol) in dichloroethane (3 mL) was introduced through a syringe. The reaction tube was sealed and stirred at 90 °C for 6 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture (3:17) as eluent to afford dihydropyrrole **A′** (65 mg, 77% yield) as a white gummy solid. ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.78 (d, 2H, *J* = 8.4 Hz), 7.33−7.26 (m, 6H), 7.23−7.18 (m, 1H), 6.91 (d, 1H, *J* = 1.2 Hz), 3.96−3.92 (m, 1H), 3.87−3.83 (m, 1H), 3.49−3.42 (m, 1H), 3.87−3.83 (m, 1H), 2.41 (s, 3H), 2.16−2.01 (m, 1H), 1.77 (dd, 1H, *J* = 12.3, 5.2 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 144.0, 136.3, 132.9, 129.9, 128.9, 127.4, 127.2, 125.1, 122.9, 94.7, 66.6, 48.6, 30.9, 21.7; HRMS: calcd. for $C_{19}H_{19}NO_3S$ + H: 342.1164; found: 342.1158.

Dihydropyrrole **A′** (65 mg, 0.19 mmol) and 4 mL of DCE were added in a 10 mL round-bottom flask equipped with a stir bar. Subsequently, TMSOTf (2 mg, 5 mol %) was added, and the mixture was stirred at room temperature for 1 h. After the TLC analysis, the reaction mixture was quenched with water, extracted with dichloromethane (2 × 10 mL), and dried over Na_2SO_4. Evaporation of solvent, followed by purification of the crude by column chromatography using hexanes/ethyl acetate as eluent, afforded the pyrrole **7ao** (45 mg, 70% yield) as a white gummy solid. ^1H NMR (400 MHz, $CDCl_3$, 24 °C): 7.78 (d, 2H, *J* = 8.4 Hz), 7.37−7.25 (m, 7H), 7.18 (d, 1H, *J* = 1.2 Hz), 7.09−7.08 (m, 1H), 3.68 (t, 3H, *J* = 6.6 Hz), 2.77 (t, 2H, *J* = 6.6 Hz), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 145.2, 136.2, 133.9, 130.2, 128.7, 128.4, 127.3, 127.1, 124.0, 119.1, 118.6, 62.3, 29.2, 21.8; HRMS: calcd. for $C_{19}H_{19}NO_3S$ + H: 342.1164; found: 342.1172.

Typical Procedure for the Synthesis of Polysubstituted Pyrroles. In a 25 mL round-bottom flask equipped with a stir bar, 1-tosyl-1*H*-pyrrole **7** (0.07−0.1 mmol) and KOH (11−16 mg, 0.21−0.3 mmol) were added. Subsequently, 4 mL (1:1 ratio) of THF and methanol was added, and the mixture was kept at 70 °C for 4 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture as eluent to furnish the polysubstituted pyrroles.

9a: 12 mg, 79% yield; colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): 8.30 (brs, 1H), 7.55−7.53 (m, 2H), 7.38−7.30 (m, 2H), 7.2−7.16 (m, 1H), 7.10−7.09 (m, 1H), 6.84−6.82 (m, 1H), 6.57−6.55 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 136.0, 128.7, 125.6, 125.4, 125.2, 119.0, 114.7, 106.7.

9b: 12 mg, 74% yield; colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.95 (brs, 1H), 7.37 (d, 1H, *J* = 7.4 Hz), 7.21−7.15 (m, 2H), 7.04−7.00 (m, 1H), 6.69 (t, 1H, *J* = 2.6 Hz), 6.48 (t, 1H, *J* = 2.6 Hz), 3.01 (t, 2H, *J* = 7.3 Hz), 2.8 (t, 2H, *J* = 7.3 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.3, 132.9, 129.1, 127.9, 126.7, 124.4, 121.6, 118.3, 116.9, 103.6, 29.7, 21.8.

9c: 13 mg, 81% yield; brown liquid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): 7.91 (brs, 1H), 7.51−7.48 (m, 2H), 7.32 (t, 2H, *J* = 7.5 Hz), 7.17−7.12 (m, 1H), 6.23−6.21 (m, 1H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 136.2, 128.9, 128.7, 128.6, 125.4, 125.2, 113.0, 104.5, 13.2.

9d: 12 mg, 66% yield; brown solid; ^1H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.25 (brs, 1H), 7.28−7.22 (m, 5H), 7.19 (d, 2H, *J* = 8.8 Hz), 6.90 (t, 1H,*J* = 2.5 Hz), 6.85 (t, 1H, *J* = 2.5 Hz), 6.83−6.78 (m, 2H), 3.8 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158, 136.0,

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129.8, 128.6, 128.4, 128.3, 125.8, 123.6, 123.4, 117.4, 117.1, 113.8, 55.4.

9e: 18 mg, 79% yield; gummy solid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.41 (brs, 1H), 7.56 (d, 2H, J = 7.16 Hz), 7.43 (d, 2H, J = 8.6 Hz), 7.38−7.34 (m, 4H), 7.25−7.18 (m, 1H), 7.16−7.12 (m, 1H), 6.81−6.80 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 135.4, 132.2, 132.1, 131.2, 129.3, 128.8, 127.0, 126.0, 125.3, 125.2, 116.0, 104.6.

9f: 13 mg, 78% yield; brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.61 (brs, 1H), 7.32−7.29 (m, 1H), 7.20−7.14 (m, 2H), 7.03−6.99 (m, 1H), 6.14 (m, 1H), 2.99 (t, 2H, J = 8.0 Hz), 2.76 (t, 2H, J = 8.0 Hz), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 133.5, 132.8, 127.8, 127.1, 126.6, 124.0, 121.3,118.5, 101.2, 29.8, 21.8, 13.1; HRMS: calcd. for $C_{13}H_{13}N$ + H: 184.1126; found: 184.1121.

Synthesis of 9g. 4-(4-Methoxyphenyl)-1-(phenylsulfonyl)-1*H*-1,2,3-triazole (50 mg, 0.16 mmol) and $Rh_2(OAc)_4$ (1.4 mg, 0.003 mmol, 2 mol %) were added under a nitrogen atmosphere to an oven-dried 5 mL reaction tube equipped with a stir bar. Subsequently, a solution of 1-methoxy-4-(2-methoxyvinyl) benzene (53 mg, 0.32 mmol) in cyclohexane (2 mL) was introduced through a syringe. The reaction tube was sealed and stirred at 90 °C for 24 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using hexanes/ethyl acetate (17:3) as eluent to afford the 3,4-bis(4-methoxyphenyl)-1-(phenylsulfonyl)-1*H*-pyrrole **7g′d** (30 mg, 45% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.94 (d, 2H, J = 7.2 Hz), 7.64−7.60 (m, 1H), 7.55−7.51 (m, 2H), 7.18 (s, 2H), 7.10 (d, 4H, J = 8.8 Hz), 6.79 (d, 4H, J = 8.5 Hz), 3.79 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.8, 139.2, 134.0, 129.8, 129.6, 128.63, 127.1, 126.1, 118.4, 113.9, 55.3; HRMS: calcd. for $C_{24}H_{21}NO_4S$ + H: 420.1270; found: 420.1255. 3,4-Bis(4-methoxyphenyl)-1-(phenylsulfonyl)-1*H*-pyrrole (30 mg, 0.1 mmol) and KOH (16 mg, 0.3 mmol) were added in a round-bottom flask equipped with a stir bar. Subsequently, 4 mL of a mixture of THF and methanol in a 1:1 ratio was added, and it was kept at 70 °C for 4 h. After the TLC analysis, it was cooled to room temperature and purified by column chromatography using a hexanes/ethyl acetate mixture as eluent to afford the 3,4-bis(4-methoxyphenyl)-1*H*-pyrrole **9g** (22 mg, 77% yield) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.24 (br. s, 1H), 7.19 (d, 4H, J = 8.8 Hz), 6.85 (d, 2H, J = 2.7 Hz), 6.82 (d, 4H, J = 8.8 Hz), 3.8 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.0, 129.7, 128.6, 123.3, 116.9, 113.8, 55.4.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information containing ^{1}H and ^{13}C NMR spectra of all the new 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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