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Synthesis of N-Sulfonyl- and N-Acylpyrroles via a Ring-Closing Metathesis/Dehydrogenation Tandem Reaction

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Abstract *N*-Sulfonyl- and *N*-acylpyrroles were synthesized via olefin ring-closing metathesis of diallylamines and in situ oxidative aromatization in the presence of the ruthenium Grubbs catalyst and a suitable copper catalyst. In the presence of $Cu(OTf)_2$ and $CuBr_2$, the reaction afforded *N*-sulfonyl- and *N*-acylpyrroles, respectively, in one pot. Under an oxygen atmosphere, the reaction went smoothly without the need of hydroperoxide oxidants. This protocol possesses many advantages, such as using a nonhazardous oxidant and readily available starting materials, operating in one pot, and showing a broad substrate scope.

Key words *N*-substituted pyrroles, ring-closing methathesis, Grubbs catalyst, Oxydehydrogenation, tandem reactions

Olefin ring-closing metathesis (RCM) is a powerful tool for the construction of C-C double bonds in the field of organic chemistry, biology, and pharmaceutical sciences,¹ especially for the synthesis of functionalized pyrroles from acyclic precursors.²⁻⁴ The significance of the ring-closing metathesis reaction has been witnessed in the facile synthesis of the aromatic ring of streptonigrin.⁵ Donohoe reported the first RCM-elimination approach to pyrroles,⁶ which was subsequently used for pyrrole syntheses by other groups.⁷ It was discovered by chance that olefin ringclosing metathesis of diallylamines afforded traces of unexpected pyrrole byproducts along with the 2,5-dihydro-1Hpyrrole products.⁸ Soon after this discovery, Stevens developed a straightforward protocol for pyrrole synthesis using a co-catalytic system of the ruthenium Grubbs catalyst I in combination with RuCl₃ (Scheme 1a).^{9a} Since this seminal work reported by Stevens, many alternative methods have been developed for the construction of pyrroles using a one-pot combination of ring-closing metathesis and in situ oxidative aromatization. Pujol and Wang synthesized Narylpyrroles with the use of Pd/C^{9b} and $FeCl_3$, ^{9c} respectively, as the dehydrogenation catalysts (Scheme 1a). Castagnolo used monoamine oxidase enzymes (MAO-N and 6-HDNO) to convert 2,5-dihydro-1*H*-pyrroles into pyrroles.^{9d} These synthetic methods could afford useful pyrroles,¹⁰⁻¹² but often suffer from certain drawbacks such as relying on the use of expensive metal compounds (RuCl₃, Pd/C) or nontraditional energy sources (assisted by microwave irradiation or ultrasound). Moreover, the synthetic approaches mentioned above have not been used for the synthesis of N-sulfonylpyrroles and *N*-acylpyrroles,^{9a,b,d} or failed^{9c} to give these pyrroles, such as *N*-Ts-pyrrole (Scheme 1a). However, N-sulfonyl- and N-acylpyrroles are useful heterocyclic compounds that can be used in organic functional materials¹³ and various organic reactions.¹⁴ Inspiringly, Schmidt and Evans reported a synthesis of pyrroles, including an N-Tspyrrole, by a Ru-catalyzed RCM/oxidative aromatization sequence with the use of stoichiometric TBHP or MnO₂ as the oxidant (Scheme 1b).¹⁵ Compared with other oxidation agents, O_2 is undoubtedly the most appealing oxidant, because it is abundant, inexpensive, and non-hazardous. In this context, we would like to report here the one-pot synthesis of N-sulfonyl- and N-acylpyrroles via olefin ring-closing metathesis of diallylamines and in situ oxidative aromatization with the use of O_2 as the oxidant (Scheme 1c).

N,N-Diallyl-*p*-methylbenzenesulfonamide (1a) was used as a probe for optimizing the reaction conditions, and representative results are summarized in Table 1. Initially, reaction of the substrate 1a was conducted in the presence of Grubbs catalyst I/II in toluene at 110 °C for 24 h under a N₂ atmosphere (1 atm). Then, the N₂ protective atmosphere was changed to an O₂ atmosphere. No desired pyrrole product 2a was observed (entries 1–3), or a trace of 2a was obtained (entry 4). Subsequently, the reaction of substrate 1a was conducted under an O₂ atmosphere (1 atm). The major product of this reaction was the ring-closing product 3a, and a small amount of the desired pyrrole product 2a was

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observed with the use of FeCl₃-6H₂O and CuCl₂-2H₂O as the additives (entries 5 and 6). The yield of 2a was increased to 27% when Cu(OAc)₂·H₂O was used instead of CuCl₂·2H₂O (entry 7). Then, several other copper salts [CuBr₂, $CuSO_4 \cdot 5H_2O$, $Cu(BF_4)_2 \cdot xH_2O$, $Cu(NO_3)_2 \cdot 3H_2O$] were investigated as the additive in combination with the Grubbs II catalyst under an O₂ atmosphere (entries 8–11), but 2a was still obtained in low yield. We were pleased that pyrrole product **2a** was obtained in 62% yield when Cu(OTf)₂ was used in combination with the Grubbs II catalyst (entry 12). Subsequently, other triflate salts were investigated as additives in combination with the Grubbs II catalyst under otherwise identical conditions. Traces of 2a were obtained when $Zn(OTf)_2$, $Mg(OTf)_2$, AgOTf, or $Bi(OTf)_3$ was used as the additive (entries 14, 15, 17, and 18). In contrast, Fe(OTf)₃, Al(OTf)₃, and Sn(OTf)₂ were relatively effective additives for the dehydrogenation process (entries 13, 16, and 19). However, Cu(OTf)₂ was chosen in our investigations, because it led to the best yield. The yield of 2a further increased to 87%, and 3a was nearly completely consumed, when the loading of Cu(OTf)₂ was increased from 20 mol% to 50 mol% (entry 20). No further increase was observed when the loading of Cu(OTf)₂ exceeded 50 mol%. The yield of 2a decreased to 69% and 80% when the Grubbs I and Hoveyda-Grubbs II catalysts were used instead of the Grubbs II catalyst (entries 21 and 22). When the O_2 atmosphere was changed to air, the yield of 2a also decreased (entry 23). Furthermore, scaling up the reaction (1a, 0.125 g) provided the product at good yield (entry 24). Thus, the combination of the Grubbs II catalyst (5 mol%) with Cu(OTf)₂ (50 mol%) at 110 °C under an atmosphere of oxygen (1 atm) was selected as the optimized reaction conditions for the transformation of sulfonyldiallylamines to the corresponding pyrrole products.

Table 1 Screening the Reaction Conditions for the RCM/Dehydroge	<u>-</u>
nation of N-Ts-Substituted Diallylamine (1a) ^a	

	Ts-N 1a [Ru] Cat., A Toluene, 1 24 h, 0	$\begin{array}{c} \text{Additive} \\ 10 ^{\circ}\text{C} \\ D_2 \\ 2a \end{array} + 2a \\ 2a \end{array}$	Ts-N
Entry	[Ru] Cat.	Additive	Yield of 2a/3a^b (%)
1 ^c	Grubbs I	-	0/91
2 ^c	Grubbs II	-	0/89
3 ^d	Grubbs I	-	0/81
4 ^d	Grubbs II	-	<5/73
5	Grubbs II	FeCl ₃ ⋅6H ₂ O	10/82
6	Grubbs II	CuCl ₂ ·2H ₂ O	18/73
7	Grubbs II	Cu(OAc) ₂ ·H ₂ O	27/66
8	Grubbs II	CuBr ₂	38/53
9	Grubbs II	CuSO ₄ ·5H ₂ O	19/73
10	Grubbs II	Cu(BF ₄) ₂ ·xH ₂ O	21/71
11	Grubbs II	$Cu(NO_3)_2 \cdot 3H_2O$	25/63
12	Grubbs II	Cu(OTf) ₂	62/30
13	Grubbs II	Fe(OTf) ₃	36/54
14	Grubbs II	Zn(OTf) ₂	<5/89
15	Grubbs II	Mg(OTf) ₂	<5/65
16	Grubbs II	Al(OTf) ₃	39/51
17	Grubbs II	AgOTf	12/80
18	Grubbs II	Bi(OTf) ₃	<5/<5
19	Grubbs II	Sn(OTf) ₂	51/36
20 ^e	Grubbs II	Cu(OTf) ₂	87/<5
21 ^e	Grubbs I	Cu(OTf) ₂	69/20
22 ^e	Hoveyda–Grubbs II	Cu(OTf) ₂	80/9
23 ^f	Grubbs II	Cu(OTf) ₂	51/29
24 ^g	Grubbs II	Cu(OTf) ₂	82/8

^a Reaction conditions: **1a** (0.20 mmol), [Ru] Cat. (0.01 mmol, 5 mol%), additive (0.04 mmol, 20 mol%), toluene (2.0 mL), 110 $^{\circ}$ C, 24 h, under O₂ (1 atm).

^b Isolated yields.

 $^{\rm c}$ Reaction conditions: [Ru] Cat. (0.01 mmol, 5 mol%), toluene (2.0 mL), 110 $^{\circ}C$, 24 h, under N $_2$ (1 atm).

 d Reaction conditions: [Ru] Cat. (0.01 mmol, 5 mol%), toluene (2.0 mL), 110 °C, 24 h, under O_2 (1 atm).

 $^{\rm e}$ Reaction conditions: [Ru] Cat. (0.01 mmol, 5 mol%), additive (0.10 mmol, 50 mol%), toluene (2.0 mL), 110 °C, 24 h, under O_2 (1 atm).

^f Reaction conditions: [Ru] Cat. (0.01 mmol, 5 mol[®]), additive (0.10 mmol, 50 mol[®]), toluene (2.0 mL), 110 °C, 24 h, under air.

^g Reaction was carried out on a 0.125 g scale of **1a** (0.50 mmol).

With the optimized reaction conditions in hand, the scope and limitations of the reaction were subsequently investigated, and representative results are summarized in Table 2. With *N*,*N*-diallylbenzenesulfonamide (**1b**) the reaction proceeded smoothly under the optimized reaction

Grubbs II (5 mol%)

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conditions to afford pyrrole **2b** in 80% yield (entry 2). The reaction of sulfonyldiallylamines **1a**, **1c**, **1d**, and **1f**, each bearing an electron-donating group on its phenyl group, proceeded smoothly in the presence of the Grubbs II catalyst (5 mol%) and Cu(OTf)₂ (50 mol%) in toluene at 110 °C under an oxygen atmosphere (1 atm) to generate pyrroles **2a**, **2c**, **2d**, and **2f** in good yields (87%, 86%, 83%, and 75%,

respectively) within 24 h (entries 1, 3, 4, and 6). When relatively sterically hindered diallylamine **1e** was used as the substrate, pyrrole **2e** was obtained in only moderate yield, indicating a steric effect on the tandem reaction (entry 5). With the aromatic rings bearing weak electron-withdrawing groups (entries 7 and 9–12), diallylamines **1g** and **1i–l** underwent the RCM/dehydrogenation tandem reaction un-

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Table 2 RCM/Dehydrogenation of Sulfonyl Diallylamines^a

$\begin{pmatrix} u_1(1) & U_2(1) & &$					
Entry	Product 2	Yield of 2/3 ^b (%)	Entry	Product 2	Yield of 2/3 ^b (%)
1		87/5	11	Br 2k	66/29
2	⊘ S S S S S S S S S S S S S S S S S S S	80/8	12		70/23
3	MeO	86/6	13	2m	60/32
4	t-Bu→OH-N→ SH-N→ 2d	83/9	14	°→{⊂> ⁰ N⊂⊃ 2n	54/30
5		59/32	15	0 ₂ N- S S O S S O S S O S S O S S S O S S S O S S S S S S S S S S S S S	51/39
6	0 − 2f	75/19	16	O ₂ N O ₂ N 2 p	43/50
7	Ph	72/20	17		50/41
8	F	50/40	18	2r	54/39
9		63/30	19	CS −N S −N 2s	50/38
10	Br - S - N 3	69/26	20		45/45

^a Reaction conditions: **1** (0.20 mmol), Grubbs II (0.01 mmol, 5 mol%), Cu(OTf)₂ (0.10 mmol, 50 mol%), toluene (2.0 mL), 110 °C, 24 h, under O₂ (1 atm). ^b Isolated yields.

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der the standard conditions well to give pyrroles 2g and 2il in 63–72% yield. Diallylamines 1h and 1n-p, each bearing an electron-withdrawing group, gave pyrroles **2h** and **2n-p** in moderate yields (entries 8 and 14-16). The results indicate that electron-withdrawing groups are unfavorable for the formation of iminium ion intermediates. Pleasingly, reaction of diallylamine 1m, bearing an electron-donating group and an electron-withdrawing group, underwent the RCM/dehydrogenation tandem reaction smoothly to generate pyrrole **2m** as the major product in 60% yield (entry 13). Diallylamines **1g** and **1r**, each bearing a naphthyl group, also gave the corresponding pyrroles **2g** and **2r** in 50% and 54% yield, respectively (entries 17 and 18). The thiophene substrates 1s and 1t were also investigated; they were converted into the corresponding products 2s and 2t in moderate yields under the optimized reaction conditions (entries 19 and 20). These reactions are extremely easy to perform without the need of using hazardous oxidation agents. However, the reaction was complex when N,N-diallylcyclopropanesulfonamide was used as the substrate and the expected pyrrole product was not obtained, indicating that the reaction conditions are not suitable for alkyl-substituted sulfonyl diallylamines.

Subsequently, the RCM/dehydrogenation reaction of acyldiallylamines for the synthesis of *N*-acylpyrroles was also investigated. The reaction of *N*,*N*-diallylbenzamide (**1aa**) was examined in the presence of the Grubbs II catalyst (5 mol%) and Cu(OTf)₂ (50 mol%) in toluene at 110 °C

 Table 3
 Conditions for the RCM/Dehydrogenation of N,N-Diallylbenzamide (1aa)^a

	Ph N A Toluc 1aa	ul Cat. dditive ne, 110 °C 24 h, O ₂ 2a	→ → + Ph N → 3aa
Entry	[Ru] Cat.	Additive	Yield of 2aa/3aa ^b (%)
1 ^c	Grubbs II	Cu(OTf) ₂	61/30
2	Grubbs II	Cu(OTf) ₂	36/54
3	Grubbs II	CuCl ₂ ·2H ₂ O	83/16
4	Grubbs II	Cu(OAc) ₂ ·H ₂ O	69/22
5	Grubbs II	CuBr ₂	91/0
6	Grubbs II	CuSO ₄ ·5H ₂ O	29/62
7	Grubbs II	Cu(BF ₄) ₂ ·xH ₂ O	45/51
8	Grubbs II	Cu(NO ₃) ₂ ·3H ₂ O	<5/90
9	Grubbs I	CuBr ₂	73/20
10	Hoveyda–Grubbs II	CuBr ₂	81/11

^a Reaction conditions: **1aa** (0.20 mmol), [Ru] Cat. (0.01 mmol, 5 mol%), additive (0.04 mmol, 20 mol%), toluene (2.0 mL), 110 °C, 24 h, under O_2 (1 atm).

^b Isolated yields.

^c Reaction conditions: additive (0.10 mmol, 50 mol%), toluene (2.0 mL),

110 °C, 24 h, under O₂ (1 atm).

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under an oxygen atmosphere (1 atm); this gave *N*-acylpyrrole 2aa in moderate yield (Table 3, entry 1). Then 1aa was used as a probe to evaluate the reaction conditions, and the results are shown in Table 3. Given the importance of copper salts, a series of copper salts was examined for optimizing the reaction conditions. N-Acylpyrrole 2aa was obtained in low to moderate yields with the use of $Cu(OTf)_2$, $Cu(OAc)_2 \cdot H_2O$, $CuSO_4 \cdot 5H_2O_1$ $Cu(BF_4)_2 \cdot xH_2O_1$ and $Cu(NO_3)_2 \cdot 3H_2O$ as the additive in combination with the Grubbs II catalyst under an O₂ atmosphere (entries 2, 4, and 6-8). The additive CuCl₂·2H₂O improved the reaction yield to 83% (entry 3). The most favorable additive was CuBr₂, which gave the desired product **2aa** in 91% yield (entry 5). The yield of 2aa decreased to 73% and 81% when the Grubbs I and Hovevda-Grubbs II catalysts were used instead of the Grubbs II catalyst (entries 9 and 10). Therefore, the combination of the Grubbs II catalyst (5 mol%) and CuBr₂ (20 mol%) at 110 °C under an O₂ atmosphere (1 atm) for 24 h was used as the optimum reaction conditions for the current transformation.

Next, the scope of the RCM/dehydrogenation reaction of acyldiallylamines under the optimized reaction conditions was investigated, and representative results are summarized in Table 4. Acyldiallylamines 1aa-ee, each bearing an electron-donating group, underwent the RCM/dehydrogenation tandem reaction smoothly in the presence of the Grubbs II catalyst (5 mol%) and CuBr₂ (20 mol%) in toluene at 110 °C under an oxygen atmosphere (1 atm) to give Nacylpyrroles 2aa-ee in 90%-93% yields (entries 1-5). Sterically hindered acyldiallylamine 1ff was also a well-tolerated substrate for the RCM/dehydrogenation tandem reaction to afford N-acylpyrrole 2ff in 87% yield (entry 6). With electron-withdrawing groups on the aromatic ring, acyldiallylamines 1gg-oo also gave good results in the RCM/dehydrogenation tandem reaction under the standard conditions, to generate N-acylpyrroles 2gg-oo in good yields (entries 7-15). Furanyl- and thiophenyl-containing diallylamines **1pp**tt were also found to be suitable substrates for the RCM/dehydrogenation tandem reaction, providing the corresponding N-acylpyrroles **2pp-tt** in excellent yields (entries 16– 20). Notably, this protocol is also suitable for the N-alkylsubstituted substrates 1uu and 1vv, which could be converted into pyrroles 2uu and 2vv in 80% and 82% yield, respectively (entries 21 and 22).

The reaction mechanism of this pyrrole synthetic method was next studied, with representative results illustrated in Scheme 2. By treating the ring-closing products **3a** and **3aa** in the presence of the Grubbs II catalyst (5 mol%) in toluene at 110 °C under an atmosphere of oxygen (1 atm) for 24 h, pyrroles **2a** and **2aa** were obtained in trace and 8% yield, respectively (Schemes 2a and 2b). With the use of Cu(OTf)₂ (50 mol%) or CuBr₂ (20 mol%) instead of the Grubbs II catalyst (5 mol%) under otherwise identical conditions, the reactions of **3a** and **3aa** proceeded well to afford the desired pyrroles **2a** and **2aa** in 82% and 80% yields, re-

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Table 4 RCM/Dehydrogenation of Acyldiallylamines^a

$R \xrightarrow{O} R \xrightarrow{Grubbs II (5 mol%)} (20 mol%) \xrightarrow{CuBr_2 (20 mol%)} R \xrightarrow{O} R $					
Entry	Product	Yields of 2/3 ^b (%)	Entry	Product	Yields of 2/3 ^b (%)
1	C Zaa	91/0	12		82/8
2	Et N	90/0	13	O ₂ N 2mm	80/10
3	MeO N N	92/0	14	2nn	80/12
4	MeO 2dd	93/0	15		83/10
5	2ee	90/0	16		82/9
6	2ff	87/0	17		81/12
7	2gg	87/5	18	2rr	80/10
8	Br 2hh	86/9	19		66/26
9	Bry N 2ii	87/9	20		72/16
10		83/10	21		80/12
11		80/11	22	۲۰۷۰ ۲۰۷۰	82/10

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^a Reaction conditions: **1** (0.20 mmol), Grubbs II (0.01 mmol, 5 mol%), Cu(OTf)₂ (0.10 mmol, 50 mol%), toluene (2.0 mL), 110 °C, 24 h, under O₂ (1 atm). ^b Isolated yields.

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spectively (Schemes 2c and 2d). However, the yields of **2a** and **2aa** in the control experiments were all lower than those obtained when a combination of the Grubbs II catalyst/Cu(OTf)₂ or the Grubbs II catalyst/CuBr₂ was used.



Based on the above results and related reports in the literature,^{9d,15a} a plausible pathway for this RCM/dehydrogenation tandem reaction is illustrated in Scheme 3. First, the diallylamines 1 undergo cyclization to form ring-closing products 3 in the presence of the ruthenium Grubbs catalyst. Meanwhile, Ru-oxo complexes form from the ruthenium Grubbs catalyst by oxidation.¹⁶ In path A, the ring-closing products **3** are oxidized to the iminium ion intermediates **4** by the Ru–oxo complexes.^{15a} The ring-closing products 3 can also be converted into the final products under the catalysis of Cu(OTf)₂ or CuBr₂, respectively. Accordingly, intermediates 4 are formed in the presence of Cu(OTf)₂ or CuBr₂ in path B. The control experiment data (Scheme 2) indicate that path A is the minor catalytic pathway and that path B is the major pathway. Finally, an oxidation-aromatization reaction of the ring-closing products 3 gives the desired pyrrole products **2**.



In summary, a RCM/dehydrogenation tandem reaction of diallylamines has been developed, which provides a variety of *N*-sulfonyl- and *N*-acylpyrrole derivatives in moderate to good yields under the optimized reaction conditions. The corresponding pyrrole products are obtained via iminium ion intermediates, which lead, in turn, to pyrroles by aromatization. $Cu(OTf)_2$ and $CuBr_2$ played a critical role in the high conversions of the ring-closing products to pyrroles. This is a straightforward one-pot synthetic pathway for the synthesis of *N*-sulfonyl- and *N*-acylpyrroles based on the RCM reaction. Further applications of this tandem reaction for the diversity-oriented synthesis of *N*-substituted pyrroles are currently under investigation, and will be reported in due course.

All reactions were carried out under an O₂ atmosphere except when noted otherwise. CH₂Cl₂ and toluene were distilled prior to use under a N₂ atmosphere. Silica gel (200–300 mesh) was used for flash chromatography. The sulfonyl- and acyldiallylamines were prepared according to literature procedures.^{17–22} Sulfonyl chloride, formyl chloride, diallylamine, and other reagents were purchased from commercial sources and used as received. High-resolution mass spectra were recorded by using an Electrothermal LTQ-Orbitrap mass spectrometer. Melting points were measured by using a Gongyi X-5 microscopy digital melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 MHz NMR spectrometer with CDCl₃ (δ = 7.26) for ¹H NMR and relative to the central CDCl₃ resonance (δ = 77.0) for ¹³C NMR. NMR data of known compounds are in agreement with literature values.

Sulfonyldiallylamines 1a–t; General Procedure^{17–19}

Et₃N (116 mg, 1.15 mmol) was added dropwise to a stirred solution of diallylamine (100 mg, 1.03 mmol) in anhyd CH_2Cl_2 (3.0 mL) at 0 °C. After 0.5 h, the appropriate sulfonyl chloride (1.0 mmol) was slowly added to the mixture. The solution was allowed to warm to room temperature and stirred overnight. The reaction mixture was poured into a separation funnel containing H_2O (3.0 mL). The aqueous phase was removed and the organic phase was subsequently washed with 1 M aq HCl (3.0 mL) and brine (3.0 mL), dried over Na_2SO_4 , and filtered. The volatiles were removed in vacuo and the residue was subjected to flash column chromatography to give the corresponding sulfonyldiallylamine.

N,N-Diallyl-p-methylbenzenesulfonamide (1a)

Compound **1a** was prepared according to a literature procedure.¹⁷ Yield: 225.9 mg (90%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.70 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 5.65–5.55 (m, 2 H), 5.16–5.11 (m, 4 H), 3.79 (d, *J* = 6.0 Hz, 4 H), 2.42 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 143.2, 137.4, 132.6, 129.6, 127.1, 118.9, 49.3, 21.5.

N,N-Diallylbenzenesulfonamide (1b)

Compound **1b** was prepared according to a literature procedure.¹⁷ Yield: 208.6 mg (88%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.83–7.81 (m, 2 H), 7.59–7.48 (m, 3 H), 5.65–5.55 (m, 2 H), 5.16–5.11 (m, 4 H), 3.82 (d, *J* = 6.4 Hz, 4 H). ¹³C NMR (100 MHz, CDCl₃): δ = 140.4, 132.5, 129.0, 127.1, 119.0, 49.3.

N,N-Diallyl-p-methoxybenzenesulfonamide (1c)

Compound 1c was prepared according to a literature procedure.¹⁷

Yield: 243.0 mg (91%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 9.2 Hz, 2 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 5.66–5.56 (m, 2 H), 5.16–5.11 (m, 4 H), 3.86 (s, 3 H), 3.78 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 162.7, 132.7, 132.0, 129.2, 118.9, 114.1, 55.5, 49.3.

N,N-Diallyl-p-tert-butylbenzenesulfonamide (1d)

Compound **1d** was prepared according to a literature procedure.¹⁸ Yield: 254.9 mg (87%); white solid; mp 53–54 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, *J* = 8.8 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 5.68–5.58 (m, 2 H), 5.16–5.13 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H), 1.34 (s, 9 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 156.2, 137.3, 132.8, 127.0, 126.0, 118.9, 49.4, 35.1, 31.1.

N,N-Diallyl-2,4-dimethylbenzenesulfonamide (1e)

Compound 1e was prepared according to a literature procedure.¹⁸

Yield: 235.9 mg (89%); colorless oil.

¹H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 5.69–5.59 (m, 2 H), 5.18–5.12 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H), 2.55 (s, 3 H), 2.36 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 143.3, 137.4, 135.1, 133.3, 132.7, 130.2, 126.6, 119.2, 48.3, 21.2, 20.2.

N,N-Diallyl-2,3-dihydrobenzofuran-5-sulfonamide (1f)

Compound **1f** was prepared according to a literature procedure.¹⁷ Yield: 226.0 mg (81%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.62–7.58 (m, 2 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 5.67–5.57 (m, 2 H), 5.16–5.11 (m, 4 H), 4.66 (t, *J* = 8.8 Hz, 2 H), 3.77 (d, J = 6.4 Hz, 4 H), 3.25 (t, *J* = 8.8 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 163.6, 132.8, 131.8, 128.6, 128.2, 124.4, 118.8, 109.4, 72.2, 49.3, 29.0.

N,N-Diallyl-p-phenylbenzenesulfonamide (1g)

Compound **1g** was prepared according to a literature procedure.¹⁷ Yield: 272.3 mg (87%); white solid; mp 68–69 °C.

¹H NMR (400 MHz, CDCl3): δ = 7.89 (d, *J* = 8.8 Hz, 2 H), 7.72 (d, *J* = 8.8 Hz, 2 H), 7.63–7.61 (m, 2 H), 7.51–7.40 (m, 3 H), 5.70–5.60 (m, 2 H), 5.19–5.15 (m, 4 H), 3.86 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 145.3, 139.3, 139.0, 132.6, 129.0, 128.4, 127.7, 127.3, 119.1, 49.4.

N,N-Diallyl-p-fluorobenzenesulfonamide (1h)

Compound **1h** was prepared according to a literature procedure.¹⁷ Yield: 204.0 mg (80%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.85–7.82 (m, 2 H), 7.20–7.15 (m, 2 H), 5.65–5.55 (m, 2 H), 5.17–5.12 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 166.2, 163.7, 136.6, 136.5, 132.3, 129.8, 129.7, 119.2, 116.3, 116.1, 49.2.

N,*N*-Diallyl-*p*-chlorobenzenesulfonamide (1i)

Compound **1i** was prepared according to a literature procedure.¹⁷ Yield: 241.2 mg (89%); colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 5.65–5.55 (m, 2 H), 5.17–5.12 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 139.0, 138.9, 132.2, 129.3, 128.5, 119.3, 49.3.

N,N-Diallyl-p-bromobenzenesulfonamide (1j)

Compound **1j** was prepared according to a literature procedure.¹⁷ 90% yield; 284.4mg; colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.69–7.62 (m, 4 H), 5.65–5.55 (m, 2 H), 5.17–5.12 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 139.5, 132.3, 132.2, 128.6, 127.3, 119.3, 49.3.

N,N-Diallyl-m-bromobenzenesulfonamide (1k)

Compound **1k** was prepared according to a literature procedure.¹⁷ Yield: 259.1 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.96 (t, *J* = 2.2 Hz, 1 H), 7.75–7.67 (m, 2 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 5.65–5.55 (m, 2 H), 5.18–5.13 (m, 4 H), 3.82 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 142.3, 135.5, 132.1, 130.6, 130.0, 125.6, 123.0, 119.3, 49.3.

N,N-Diallyl-p-iodobenzenesulfonamide (11)

Compound **11** was prepared according to a literature procedure.¹⁷

Yield: 294.0 mg (81%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 5.66–5.56 (m, 2 H), 5.18–5.14 (m, 4 H), 3.82 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 140.1, 138.2, 132.1, 128.5, 119.2, 99.7, 49.2.

N,N-Diallyl-3-fluoro-4-methylbenzenesulfonamide (1m)

Compound **1m** was prepared according to a literature procedure.¹⁷ Yield: 239.4 mg (89%): colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.51–7.44 (m, 2 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 5.66–5.56 (m, 2 H), 5.17–5.12 (m, 4 H), 3.81 (d, *J* = 6.4 Hz, 4 H), 2.34 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 162.0, 159.5, 139.6, 139.5, 132.3, 132.1, 132.0, 130.4, 130.2, 122.6, 122.5, 119.2, 114.2, 113.9, 49.3, 14.7, 14.6.

N,N-Diallyl-p-acetylbenzenesulfonamide (1n)

Compound ${\bf 1n}$ was prepared according to a literature procedure. $^{\rm 19}$

Yield: 239.9 mg (86%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.05 (d, *J* = 8.8 Hz, 2 H), 7.90 (d, *J* = 8.8 Hz, 2 H), 5.63–5.53 (m, 2 H), 5.16–5.11 (m, 4 H), 3.83 (d, *J* = 6.4 Hz, 4 H), 2.64 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 196.7, 144.4, 139.8, 132.0, 128.9, 127.3, 119.4, 49.3, 26.8.

N,N-Diallyl-p-nitrobenzenesulfonamide (10)

Compound **10** was prepared according to a literature procedure.¹⁹ Yield: 231.2 mg (82%); white solid; mp 65–66 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 9.2 Hz, 2 H), 8.01 (d, *J* = 8.8 Hz, 2 H), 5.65–5.55 (m, 2 H), 5.20–5.15 (m, 4 H), 3.87 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 149.9, 146.5, 131.7, 128.3, 124.4, 119.8, 49.3.

N,N-Diallyl-m-nitrobenzenesulfonamide (1p)

Compound **1p** was prepared according to a literature procedure.¹⁹

Yield: 228.4 mg (81%); yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.65 (t, *J* = 2.0 Hz, 1 H), 8.43–8.40 (m, 1 H), 8.16–8.13 (m, 1 H), 7.73 (t, *J* = 8.0 Hz, 1 H), 5.66–5.56 (m, 2 H), 5.20–5.15 (m, 4 H), 3.87 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 148.2, 142.8, 132.6, 131.7, 130.4, 126.9, 122.3, 119.7, 49.4.

N,N-Diallyl-1-naphthalenesulfonamide (1q)

Compound ${\bf 1q}$ was prepared according to a literature procedure. $^{\rm 17}$

Yield: 246.8 mg (86%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.63 (d, *J* = 8.8 Hz, 1 H), 8.27–8.25 (m, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.68–7.50 (m, 3 H), 5.62–5.52 (m, 2 H), 5.13–5.09 (m, 4 H), 3.90 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 134.9, 134.3, 134.2, 132.5, 130.1, 128.9, 128.4, 128.0, 126.7, 124.9, 124.0, 119.2, 48.4.

N,N-Diallyl-2-naphthalenesulfonamide (1r)

Compound **1r** was prepared according to a literature procedure.¹⁷ Yield: 252.6 mg (88%): colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.41 (s, 1 H), 7.97–7.90 (m, 3 H), 7.81– 7.78 (m, 1 H), 7.66–7.59 (m, 2 H), 5.67–5.57 (m, 2 H), 5.17–5.12 (m, 4 H), 3.88 (d, *I* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 137.3, 134.7, 132.6, 132.2, 129.4, 129.2, 128.7, 128.4, 127.9, 127.5, 122.5, 119.1, 49.3.

N,N-Diallyl-2-thiophenesulfonamide (1s)

Compound **1s** was prepared according to a literature procedure.¹⁷ Yield: 194.4 mg (80%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.58–7.56 (m, 2 H), 7.10–7.08 (m, 1 H), 5.70–5.60 (m, 2 H), 5.19–5.15 (m, 4 H), 3.83 (d, J = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 140.9, 132.2, 131.7, 131.5, 127.3, 119.2, 49.7.

N,N-Diallyl-5-chlorothiophene-2-sulfonamide (1t)

Compound **1t** was prepared according to a literature procedure.¹⁷ Yield: 227.1 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.34 (d, *J* = 4.0 Hz, 1 H), 6.92 (d, *J* = 4.0 Hz, 1 H), 5.72–5.62 (m, 2 H), 5.21–5.17 (m, 4 H), 3.82 (d, *J* = 6.4 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 139.0, 136.8, 132.0, 131.1, 126.7, 119.5, 49.6.

N,N-Diallylcyclopropanesulfonamide

This compound was prepared according to a literature procedure.¹⁷ Yield: 138.7 mg (69%); yellow oil. ^1H NMR (400 MHz, CDCl_3): δ = 5.86–5.76 (m, 2 H), 5.27–5.22 (m, 4 H), 3.86 (d, J = 6.0 Hz, 4 H), 2.35–2.28 (m, 1 H), 1.18–1.15 (m, 2 H), 1.00–0.94 (m, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 132.9, 118.9, 49.1, 30.2, 5.3.

Acyldiallylamines 1aa-vv; General Procedure²⁰⁻²²

Et₃N (126 mg, 1.25 mmol) was added dropwise to a stirred solution of diallylamine (107 mg, 1.10 mmol) in anhyd CH₂Cl₂ (3.0 mL) at 0 °C. Then the appropriate formyl chloride (1.00 mmol) was slowly added to the mixture. The solution was allowed to warm to room temperature and stirred until the end of the reaction. The reaction mixture was poured into a separation funnel containing H₂O (3.0 mL). The aqueous phase was removed and the organic phase was subsequently washed with 1 M aq HCl (3.0 mL) and brine (3.0 mL), dried over Na₂-SO₄, and filtered. The volatiles were removed in vacuo and the residue was subjected to flash column chromatography to give the corresponding acyldiallylamine.

N,N-Diallylbenzamide (1aa)

Compound **1aa** was prepared according to a literature procedure.²⁰ Yield: 180.9 mg (90%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.44–7.34 (m, 5 H), 5.86 (br s, 1 H), 5.72 (br s, 1 H), 5.24–5.16 (m, 4 H), 4.13 (br s, 2 H), 3.82 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 136.2, 133.1, 132.7, 129.5, 128.3, 126.5, 117.6, 50.7, 46.9.

N,N-Diallyl-p-ethylbenzamide (1bb)

Compound **1bb** was prepared according to a literature procedure.²⁰

Yield: 203.8 mg (89%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.35 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 5.86 (br s, 1 H), 5.75 (br s, 1 H), 5.24–5.16 (m, 4 H), 4.12 (br s, 2 H), 3.86 (br s, 2 H), 2.65 (q, *J* = 7.6 Hz, 2 H), 1.23 (t, *J* = 7.6 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.9, 145.9, 133.5, 127.7, 126.7, 117.5, 50.8, 46.9, 28.7, 15.3.

N,N-Diallyl-m-methoxybenzamide (1cc)

Compound **1cc** was prepared according to a literature procedure.²⁰ Yield: 205.6 mg (89%); colorless oil.

 1H NMR (400 MHz, CDCl₃): δ = 7.29–7.25 (m, 1 H), 6.99–6.91 (m, 3 H), 5.86 (br s, 1 H), 5.73 (br s, 1 H), 5.24–5.16 (m, 4 H), 4.11 (br s, 2 H), 3.83 (br s, 2 H), 3.79 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 171.4, 159.4, 137.4, 133.2, 132.7, 129.4, 118.6, 117.5, 115.6, 111.8, 55.3, 50.6, 46.9.

N,N-Diallyl-p-methoxybenzamide (1dd)

Compound **1dd** was prepared according to a literature procedure.²⁰ Yield: 203.3 mg (88%); white solid; mp 39–40 °C.

¹H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 5.81 (br s, 2 H), 5.23–5.16 (m, 4 H), 3.98 (br s, 4 H), 3.80 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 160.6, 133.1, 128.6, 128.3, 117.4, 113.5, 55.2, 50.7, 47.4.

N,N-Diallyl-o-methylbenzamide (1ee)

Compound **1ee** was prepared according to a literature procedure.²¹ Yield: 195.7 mg (91%); colorless oil.

 ^1H NMR (400 MHz, CDCl₃): δ = 7.27–7.23 (m, 1 H), 7.20–7.15 (m, 3 H), 5.92–5.83 (m, 1 H), 5.67–5.57 (m, 1 H), 5.26–5.05 (m, 4 H), 3.68 (br s, 4 H), 2.30 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 136.3, 134.0, 132.8, 132.7, 130.3, 128.8, 125.7, 125.5, 117.8, 50.1, 46.1, 19.0.

N,N-Diallyl-2,4,6-trimethylbenzamide (1ff)

Compound 1ff was prepared according to a literature procedure.²¹

Yield: 199.3 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 6.83 (s, 2 H), 5.93–5.83 (m, 1 H), 5.66– 5.56 (m, 1 H), 5.27–5.22 (m, 2 H), 5.14–5.01 (m, 2 H), 4.19 (d, *J* = 6.4 Hz, 2 H), 3.66 (d, *J* = 6.0 Hz, 2 H), 2.26 (s, 3 H), 2.20 (s, 6 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 171.0, 137.9, 133.4, 132.9, 132.8, 128.2, 118.5, 118.4, 50.0, 45.8, 21.0, 19.0.

N,N-Diallyl-p-iodobenzamide (1gg)

Compound **1gg** was prepared according to a literature procedure.²²

Yield: 284.5 mg (87%); white solid; mp 50-51 °C.

 1H NMR (400 MHz, CDCl₃): δ = 7.72 (d, J = 8.4 Hz, 2 H), 7.16 (d, J = 8.4 Hz, 2 H), 5.84 (br s, 1 H), 5.70 (br s, 1 H), 5.28–5.15 (m, 4 H), 4.10 (br s, 2 H), 3.80 (br s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 170.7, 137.4, 135.5, 132.9, 132.5, 128.3, 117.7, 95.8, 50.6, 47.1.

N,N-Diallyl-p-bromobenzamide (1hh)

Compound **1hh** was prepared according to a literature procedure.²² Yield: 249.2 mg (89%): white solid: mp 55–56 °C.

 ^1H NMR (400 MHz, CDCl₃): δ = 7.51 (d, J = 8.4 Hz, 2 H), 7.30 (d, J = 8.4 Hz, 2 H), 5.84 (br s, 1 H), 5.71 (br s, 1 H), 5.28–5.16 (m, 4 H), 4.10 (br s, 2 H), 3.80 (br s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 170.6, 135.0, 132.9, 132.5, 131.5, 128.3, 123.9, 117.8, 50.6, 47.1.

N,N-Diallyl-m-bromobenzamide (1ii)

Compound **1ii** was prepared according to a literature procedure.²²

Yield: 232.4 mg (83%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.57–7.52 (m, 2 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.27–7.23 (m, 1 H), 5.85 (br s, 1 H), 5.72 (br s, 1 H), 5.29–5.17 (m, 4 H), 4.11 (br s, 2 H), 3.81 (br s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 170.0, 138.1, 132.8, 132.7, 132.4, 129.9, 129.7, 125.0, 122.4, 117.9, 53.4, 50.7, 47.1.

N,N-Diallyl-p-chlorobenzamide (1jj)

Compound **1jj** was prepared according to a literature procedure.²² Yield: 202.1 mg (86%); white solid; mp 58–59 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.39–7.34 (m, 4 H), 5.85 (br s, 1 H), 5.72 (br s, 1 H), 5.29–5.16 (m, 4 H), 4.11 (br s, 2 H), 3.81 (br s, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ = 170.6, 135.7, 134.5, 132.9, 132.5, 128.6, 128.1, 117.7, 50.6, 47.2.

N,N-Diallyl-m-fluorobenzamide (1kk)

Compound **1kk** was prepared according to a literature procedure.²² Yield: 194.9 mg (89%); colorless oil. ^1H NMR (400 MHz, CDCl₃): δ = 7.38–7.33 (m, 1 H), 7.21–7.07 (m, 3 H), 5.86 (br s, 1 H), 5.72 (br s, 1 H), 5.29–5.17 (m, 4 H), 4.12 (br s, 2 H), 3.82 (br s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 170.2, 163.6, 161.1, 138.1, 132.8, 132.5, 130.2, 130.1, 122.2, 122.1, 117.8, 116.7, 116.5, 114.0, 113.8, 53.4, 50.6, 47.0.

2-(Diallylcarbamoyl)phenyl Acetate (111)

Compound **1ll** was prepared according to a literature procedure.²²

Yield: 207.2 mg (80%); colorless oil.

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 ^1H NMR (400 MHz, CDCl_3): δ = 7.42–7.37 (m, 1 H), 7.32–7.30 (m, 1 H), 7.24–7.20 (m, 1 H), 7.16–7.14 (m, 1 H), 5.87–5.77 (m, 1 H), 5.71–5.61 (m, 1 H), 5.28–5.10 (m, 4 H), 4.11 (br s, 2 H), 3.75 (br s, 2 H), 2.25 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 169.0, 167.9, 146.9, 133.0, 132.4, 130.1, 129.7, 127.0, 125.8, 122.9, 117.7, 117.6, 50.4, 46.3, 20.8.

N,N-Diallyl-m-nitrobenzamide (1mm)

Compound **1mm** was prepared according to a literature procedure.²² Yield: 216.5 mg (88%); yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 8.31 (t, *J* = 1.8 Hz, 1 H), 8.28–8.25 (m, 1 H), 7.79–7.76 (m, 1 H), 7.59 (t, *J* = 7.8 Hz, 1 H), 5.87 (br s, 1 H), 5.74 (br s, 1 H), 5.28–5.20 (m, 4 H), 4.15 (br s, 2 H), 3.82 (br s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 169.1, 147.9, 137.7, 132.6, 129.6, 124.4, 121.8, 118.3, 118.0, 50.7, 50.6, 47.4.

N,N-Diallyl-1-naphthamide (1nn)

Compound **1nn** was prepared according to a literature procedure.²²

Yield: 200.8 mg (80%); colorless oil.

 ^1H NMR (400 MHz, CDCl_3): δ = 7.87–7.84 (m, 3 H), 7.55–7.41 (m, 4 H), 6.06–5.96 (m, 1 H), 5.64–5.55 (m, 1 H), 5.34–5.28 (m, 2 H), 5.14–5.04 (m, 2 H), 4.56 (br s, 1 H), 4.03 (br s, 1 H), 3.66 (d, J = 5.6 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 170.7, 134.2, 133.4, 133.0, 132.8, 129.5, 129.0, 128.3, 126.9, 126.3, 124.9, 124.7, 123.4, 118.0, 117.9, 50.6, 46.3.

N,*N*-Diallyl-2-naphthamide (100)

Compound **100** was prepared according to a literature procedure.²² Yield: 205.8 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.94 (d, J = 1.6 Hz, 1 H), 7.87–7.83 (m, 3 H), 7.55–7.50 (m, 3 H), 5.93 (br s, 1 H), 5.77 (br s, 1 H), 5.28–5.21 (m, 4 H), 4.19 (br s, 2 H), 3.89 (br s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 171.7, 133.6, 133.5, 132.6, 128.3, 128.2, 127.7, 126.9, 126.6, 126.2, 124.0, 117.6, 50.8, 47.1.

N,N-Diallylfuran-2-carboxamide (1pp)

Compound **1pp** was prepared according to a literature procedure.²² Yield: 152.8 mg (80%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.47 (d, *J* = 0.8 Hz, 1 H), 7.02 (d, *J* = 3.6 Hz, 1 H), 6.45–6.44 (m, 1 H), 5.91–5.83 (m, 2 H), 5.22–5.17 (m, 4 H), 4.11 (br s, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 160.0, 147.7, 143.9, 133.3, 132.8, 117.5, 116.1, 111.2, 49.8, 48.4.

N,N-Diallylfuran-3-carboxamide (1qq)

Compound **1qq** was prepared according to a literature procedure.²²

Yield: 154.7 mg (81%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.75–7.74 (m, 1 H), 7.38 (t, *J* = 1.8 Hz, 1 H), 6.63–6.62 (m, 1 H), 5.88–5.78 (m, 2 H), 5.22 (br s, 4 H), 4.04 (s, 4 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 164.8, 143.4, 142.7, 133.0, 121.0, 117.5, 117.1, 110.3, 50.0, 47.9.

N,N-Diallylthiophene-2-carboxamide (1rr)

Compound **1rr** was prepared according to a literature procedure.²² Viold: 160.7 mg (82%): colorloss oil

Yield: 169.7 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.44–7.42 (m, 1 H), 7.39–7.38 (m, 1 H), 7.01–6.99 (m, 1 H), 5.92–5.82 (m, 2 H), 5.28–5.21 (m, 4 H), 4.10 (d, *J* = 5.2 Hz, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 164.4, 137.7, 132.8, 129.1, 128.4, 126.7, 117.6, 49.6.

N,N-Diallyl-3-methylthiophene-2-carboxamide (1ss)

Compound **1ss** was prepared according to a literature procedure.²² Yield: 179.0 mg (81%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.22 (d, *J* = 4.8 Hz, 1 H), 6.82 (d, *J* = 4.8 Hz, 1 H), 5.83–5.73 (m, 2 H), 5.22–5.14 (m, 4 H), 4.01 (br s, 4 H), 2.26 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 165.8, 137.5, 132.9, 129.9, 129.6, 125.2, 117.8, 49.1, 14.5.

$\textit{N,N-Diallyl-5-chlorothiophene-2-carboxamide}\ (1tt)$

Compound **1tt** was prepared according to a literature procedure.²²

Yield: 197.6 mg (82%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.18 (d, *J* = 4.0 Hz, 1 H), 6.82 (d, *J* = 4.0 Hz, 1 H), 5.90–5.80 (m, 2 H), 5.28–5.20 (m, 4 H), 4.08 (d, *J* = 5.2 Hz, 4 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 163.1, 136.5, 134.5, 132.6, 128.2, 126.1, 117.7, 49.7.

N,N-Diallylcyclohexanecarboxamide (1uu)

Compound **1uu** was prepared according to a literature procedure.²²

Yield: 165.6 mg (80%); colorless oil.

 ^1H NMR (400 MHz, CDCl_3): δ = 5.82–5.67 (m, 2 H), 5.19–5.05 (m, 4 H), 3.95–3.86 (m, 4 H), 2.42–2.35 (m, 1 H), 1.78–1.64 (m, 5 H), 1.59–1.49 (m, 2 H), 1.29–1.16 (m, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 176.3, 133.5, 133.4, 116.7, 116.3, 48.9, 47.6, 40.8, 29.6, 25.7.

N,N-Diallylacetamide (1vv)

Compound **1vv** was prepared according to a literature procedure.²² Yield: 125.1 mg (90%); colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 5.78–5.69 (m, 2 H), 5.18–5.06 (m, 4 H), 3.94 (d, *J* = 6.0 Hz, 2 H), 3.83–3.82 (m, 2 H), 2.06 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 170.5, 133.2, 132.6, 117.1, 116.5, 49.8, 47.6, 21.2.

N-Sulfonylpyrroles 2a-t; General procedure I

A Schlenk tube equipped with a magnetic stir bar was charged with the Grubbs II cat. (8.5 mg, 0.01 mmol), $Cu(OTf)_2$ (36.2 mg, 0.10 mmol), the appropriate sulfonyldiallylamine **1** (1.0 equiv, 0.20 mmol), and toluene (2.0 mL). The tube was under an O₂ balloon and the mixture was stirred at 110 °C in an oil bath for 24 h, after which the mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to give the desired product.

1-[(4-Methylphenyl)sulfonyl]-1H-pyrrole (2a)

The synthesis was carried out according to general procedure I.

Yield: 38.5 mg (87%); white solid; mp 96–98 $^\circ\text{C}.$

IR (film): 1596, 1455, 1364, 1187, 1168, 1057, 734, 673 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.15 (s, 2 H), 6.28 (s, 2 H), 2.40 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 144.9, 136.1, 129.9, 126.8, 120.7, 113.5, 21.6.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{11}H_{11}NNaO_2S$: 244.0403; found: 244.0400.

These spectral data correspond to previously reported data.²³

1-(Phenylsulfonyl)-1H-pyrrole (2b)

The synthesis was carried out according to general procedure I.

Yield: 33.1 mg (80%); white solid; mp 87–89 $^\circ\text{C}.$

IR (film): 1449, 1368, 1190, 1170, 1057, 728, 685 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.17 (s, 2 H), 6.30 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 139.1, 133.8, 129.3, 126.7, 120.8, 113.7.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₀H₉NNaO₂S: 230.0246; found: 230.0243.

These spectral data correspond to previously reported data.²³

1-[(4-Methoxyphenyl)sulfonyl]-1H-pyrrole (2c)

The synthesis was carried out according to general procedure I. Yield: 40.8 mg (86%); white solid; mp 100–103 °C.

IR (film): 1595, 1499, 1456, 1361, 1183, 1162, 1057, 735, 679 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.80 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 0.8 Hz, 2 H), 6.94 (d, *J* = 8.0 Hz, 2 H), 6.27 (d, *J* = 0.8 Hz, 2 H), 3.84 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 163.7, 130.6, 129.1, 120.6, 114.5, 113.4, 55.7.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₁₁NnaO₃S: 260.0352; found: 260.0350.

These spectral data correspond to previously reported data.²³

1-[(4-*tert*-Butylphenyl)sulfonyl]-1*H*-pyrrole (2d)

The synthesis was carried out according to general procedure I.

Yield: 43.7 mg (83%); white solid; mp 86–89 °C.

IR (film): 1594, 1455, 1370, 1186, 1171, 1057, 837, 734 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.0 Hz, 2 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 1.6 Hz, 2 H), 6.30 (d, *J* = 2.0 Hz, 2 H), 1.31 (s, 9 H). ¹³C NMR (100 MHz, CDCl₃): δ = 157.8, 136.1, 126.6, 126.4, 120.7, 113.4, 35.2, 30.9.

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HRMS (ESI): $m/z \ [M + Na]^+$ calcd for $C_{14}H_{17}NNaO_2S$: 286.0872; found: 286.0880.

1-[(2,4-Dimethylphenyl)sulfonyl]-1H-pyrrole (2e)

The synthesis was carried out according to general procedure I.

Yield: 27.7 mg (59%); white solid; mp 58-60 °C.

IR (film): 1602, 1455, 1355, 1173, 1057, 823, 745, 670 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.60 (d, J = 8.4 Hz, 1 H), 7.14–7.08 (m, 4 H), 6.30 (d, J = 1.6 Hz, 2 H), 2.52 (s, 3 H), 2.35 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 144.9, 137.8, 134.8, 133.6, 128.7, 127.2, 121.0, 112.6, 21.3, 20.0.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₂H₁₃NNaO₂S: 258.0559; found: 258.0568.

1-[(2,3-Dihydrobenzofuran-5-yl)sulfonyl]-1H-pyrrole (2f)

The synthesis was carried out according to general procedure I.

Yield: 37.3 mg (75%); white solid; mp 136-139 °C.

IR (film): 1604, 1484, 1456, 1357, 1180, 1151, 1053, 891, 822, 745, 702 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, *J* = 8.0 Hz, 2 H), 7.14 (s, 2 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 6.28 (s, 2 H), 4.66 (t, *J* = 8.8 Hz, 2 H), 3.23 (t, *J* = 8.8 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 164.8, 130.4, 128.8, 128.7, 124.1, 120.5, 113.2, 109.8, 72.5, 28.9.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₂H₁₁NNaO₃S: 272.0352; found: 272.0360.

1-([1,1'-Biphenyl]-4-ylsulfonyl)-1H-pyrrole (2g)

The synthesis was carried out according to general procedure I.

Yield: 40.8 mg (72%); white solid; mp 109-112 °C.

IR (film): 1593, 145, 1367, 1188, 1168, 1057, 840, 736, 678 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.92 (d, *J* = 7.6 Hz, 2 H), 7.69 (d, *J* = 7.6 Hz, 2 H), 7.56 (d, *J* = 7.2 Hz, 2 H), 7.49–7.42 (m, 3 H), 7.21 (d, *J* = 1.6 Hz, 2 H), 6.33 (d, *J* = 1.6 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 146.8, 138.8, 137.5, 129.1, 128.7, 127.9, 127.3, 120.8, 113.7.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₆H₁₃NNaO₂S: 306.0559; found: 306.0567.

1-[(4-Fluorophenyl)sulfonyl]-1H-pyrrole (2h)

The synthesis was carried out according to general procedure I.

Yield: 22.5 mg (50%); yellowish solid; mp 96-99 °C.

IR (film): 1590, 1493, 1373, 1189, 1173, 1057, 835, 741, 678 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.89–7.86 (m, 2 H), 7.19–7.15 (m, 4 H), 6.31 (d, *J* = 1.6 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.9, 164.4, 135.1, 135.0, 129.7, 129.6, 120.7, 116.8, 116.6, 113.9.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₀H₈FNNaO₂S: 248.0152; found: 248.0154.

These spectral data correspond to previously reported data.²⁴

1-[(4-Chlorophenyl)sulfonyl]-1H-pyrrole (2i)

The synthesis was carried out according to general procedure I. Yield: 30.4 mg (63%); white solid; mp 106–108 °C. IR (film): 1585, 1477, 1456, 1365, 1187, 1173, 1057, 829, 757 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, *J* = 7.6 Hz, 2 H), 7.47 (d, *J* = 7.6 Hz, 2 H), 7.14 (d, *J* = 1.2 Hz, 2 H), 6.31 (d, *J* = 1.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 140.5, 137.5, 129.7, 128.2, 120.8, 114.1.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{10}H_8$ ClNNaO₂S: 263.9856; found: 263.9860.

These spectral data correspond to previously reported data.²³

1-[(4-Bromophenyl)sulfonyl]-1H-pyrrole (2j)

The synthesis was carried out according to general procedure I. Yield: 39.5 mg (69%); white solid; mp 113-116 °C.

IR (film): 1574, 1456, 1364, 1186, 1173, 1058, 821, 743, 700 cm⁻¹.

 ^1H NMR (400 MHz, CDCl_3): δ = 7.71 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.14 (s, 2 H), 6.32 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 138.0, 132.7, 129.1, 128.2, 120.8, 114.1.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₀H₈BrNNaO₂S: 307.9351; found: 307.9359.

These spectral data correspond to previously reported data.²³

1-[(3-Bromophenyl)sulfonyl]-1H-pyrrole (2k)

The synthesis was carried out according to general procedure I. Yield: 37.8 mg (66%); white solid; mp 90–93 °C.

IR (film): 1572, 1456, 1375, 1191, 1172, 1057, 735, 676 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.99 (s, 1 H), 7.77 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 1 H), 7.16 (s, 2 H), 6.33 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 140.7, 136.9, 130.8, 129.6, 125.3, 123.2, 120.8, 114.2.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₀H₈BrNNaO₂S: 307.9351; found: 307.9360.

1-[(4-Iodophenyl)sulfonyl]-1H-pyrrole (2l)

The synthesis was carried out according to general procedure I.

Yield: 46.6 mg (70%); white solid; mp 125–127 °C.

IR (film): 1568, 1456, 1386, 1363, 1188, 1170, 1054, 818, 735 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, J = 8.0 Hz, 2 H), 7.55 (d, J = 8.0 Hz, 2 H), 7.13 (s, 2 H), 6.31 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 138.7, 128.0, 120.8, 114.1, 101.7.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₀H₈INNaO₂S: 355.9213; found: 355.9209.

These spectral data correspond to previously reported data.²⁵

1-[(3-Fluoro-4-methylphenyl)sulfonyl]-1H-pyrrole (2m)

The synthesis was carried out according to general procedure I. Yield: 28.7 mg (60%); yellowish solid; mp 102–105 °C.

IR (film): 1490, 1456, 1364, 1186, 1165, 1058, 822, 751, 680 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.54 (d, *J* = 8.0 Hz, 1 H), 7.48 (d, *J* = 8.8 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.14 (d, *J* = 1.6 Hz, 2 H), 6.30 (d, *J* = 1.6 Hz, 2 H), 2.32 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 161.9, 159.4, 138.0, 137.9, 132.5, 132.4, 132.3, 132.1, 122.4, 122.3, 120.8, 113.9, 113.6, 14.9, 14.8.

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HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₁₁H₁₀FNNaO₂S: 262.0308; found: 262.0316.

1-[(4-Acetylphenyl)sulfonyl]-1*H*-pyrrole (2n)

The synthesis was carried out according to general procedure I.

Yield: 26.9 mg (54%); yellowish solid; mp 133–136 °C.

IR (film): 2922, 1688, 1456, 1372, 1260, 1192, 1171, 1061, 837, 748 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, *J* = 8.0 Hz, 2 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 0.8 Hz, 2 H), 6.32 (d, *J* = 1.2 Hz, 2 H), 2.62 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 196.3, 142.7, 140.8, 129.1, 127.1, 120.9, 114.3, 26.8.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{12}H_{11}NNaO_3S$: 272.0352; found: 272.0360.

1-[(4-Nitrophenyl)sulfonyl]-1*H*-pyrrole (20)

The synthesis was carried out according to general procedure I.

Yield: 25.7 mg (51%); yellowish solid; mp 129–132 °C.

IR (film): 1533, 1456, 1378, 1349, 1192, 1171, 1057, 855, 739 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.33 (d, *J* = 8.0 Hz, 2 H), 8.02 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 1.2 Hz, 2 H), 6.36 (d, *J* = 1.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 150.6, 144.4, 128.1, 124.6, 120.9, 114.9.

HRMS (ESI): $m/z \ [M + Na]^+$ calcd for $C_{10}H_8N_2NaO_4S$: 275.0097; found: 275.0105.

These spectral data correspond to previously reported data.²³

1-[(3-Nitrophenyl)sulfonyl]-1*H*-pyrrole (2p)

The synthesis was carried out according to general procedure I.

Yield: 21.7 mg (43%); yellow solid; mp 81-84 °C.

IR (film): 1535, 1379, 1352, 1193, 1174, 1056, 878, 733, 664 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.68 (s, 1 H), 8.44 (d, J = 8.0 Hz, 1 H), 8.16 (d, J = 8.0 Hz, 1 H), 7.74 (t, J = 8.0 Hz, 1 H), 7.19 (s, 2 H), 6.36 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 148.3, 141.0, 132.1, 130.9, 128.2, 122.1, 120.9, 114.8.

HRMS (ESI): m/z [M + Na] * calcd for $C_{10}H_8N_2NaO_4S$: 275.0097; found: 275.0106.

1-(1-Naphthylsulfonyl)-1*H*-pyrrole (2q)

The synthesis was carried out according to general procedure I.

Yield: 25.7 mg (50%); white solid; mp 130–133 °C.

IR (film): 1508, 1454, 1363, 1182, 1163, 1056, 831, 797, 765, 731, 681 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 8.74 (d, *J* = 8.4 Hz, 1 H), 8.11 (d, *J* = 8.0 Hz, 1 H), 7.99–7.93 (m, 2 H), 7.71 (t, *J* = 7.6 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.54 (t, *J* = 7.8 Hz, 1 H), 7.27 (d, *J* = 1.2 Hz, 2 H), 6.32 (d, *J* = 0.8 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 135.5, 134.7, 134.1, 129.1, 128.8, 128.6, 128.0, 127.3, 124.2, 123.9, 121.2, 113.0.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₁NNaO₂S: 280.0403; found: 280.0406.

These spectral data correspond to previously reported data.²³

1-(2-Naphthylsulfonyl)-1*H*-pyrrole (2r)

The synthesis was carried out according to general procedure I.

Yield: 27.8 mg (54%); white solid; mp 125–127 $^\circ C.$

IR (film): 1589, 1455, 1361, 1185, 1167, 1060, 859, 813, 738, 667 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.48 (s, 1 H), 7.98–7.87 (m, 3 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.68–7.60 (m, 2 H), 7.23 (d, *J* = 1.6 Hz, 2 H), 6.29 (d, *J* = 1.6 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 135.9, 135.2, 131.9, 129.8, 129.5, 129.4, 128.5, 127.9, 127.8, 121.5, 120.8, 113.7.

HRMS (ESI): $m/z \,[M + Na]^+$ calcd for $C_{14}H_{11}NNaO_2S$: 280.0403; found: 280.0409.

These spectral data correspond to previously reported data.²³

1-(2-Thiophenesulfonyl)-1*H*-pyrrole (2s)

The synthesis was carried out according to general procedure I.

Yield: 21.3 mg (50%); yellowish solid; mp 81–83 °C. IR (film): 1455, 1373, 1189, 1166, 1057, 857, 733, 672 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.67–7.63 (m, 2 H), 7.18 (d, *J* = 0.8 Hz, 2 H), 7.06 (s, 1 H), 6.32 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 133.8, 133.4, 127.5, 120.8, 113.9.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₈H₇NNaO₂S₂: 235.9810; found: 235.9816.

These spectral data correspond to previously reported data.²⁶

1-[(5-Chlorothiophen-2-yl)sulfonyl]-1*H*-pyrrole (2t)

The synthesis was carried out according to general procedure I. Yield: 22.2 mg (45%); yellowish solid; mp 89–92 °C.

IR (film): 1456, 1409, 1380, 1191, 1167, 1057, 994, 736, 681 cm⁻¹.

 ^1H NMR (400 MHz, CDCl_3): δ = 7.46 (s, 1 H), 7.14 (s, 2 H), 6.90 (s, 1 H), 6.34 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 132.8, 132.0, 126.9, 120.7, 119.5, 114.3.

HRMS (ESI): *m*/*z* [M + Na]⁺ calcd for C₈H₆ClNNaO₂S₂: 269.9421; found: 269.9430.

N-Acylpyrroles 2aa-vv; General Procedure II

A Schlenk tube equipped with a magnetic stir bar was charged with the Grubbs II cat. (8.5 mg, 0.01 mmol), $CuBr_2$ (8.9 mg, 0.04 mmol), the appropriate acyldiallylamine **1** (1.0 equiv, 0.20 mmol), and toluene (2.0 mL). The tube was under an O₂ balloon and the mixture was stirred at 110 °C in an oil bath for 24 h, after which the mixture was cooled to room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to give the desired product.

Phenyl(1H-pyrrol-1-yl)methanone (2aa)

The synthesis was carried out according to general procedure II.

Yield: 31.1 mg (91%); yellow oil.

IR (film): 2925, 1692, 1466, 1324, 1089, 1072, 879, 719, 696 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 7.6 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 2 H), 7.29 (d, *J* = 1.6 Hz, 2 H), 6.35 (d, *J* = 1.6 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 167.7, 133.2, 132.2, 129.4, 128.4, 121.2, 113.1.

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HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₉NNaO: 194.0576; found: 194.0571.

These spectral data correspond to previously reported data.²⁷

(4-Ethylphenyl)(1H-pyrrol-1-yl)methanone (2bb)

The synthesis was carried out according to general procedure II.

Yield: 35.8 mg (90%); yellowish oil.

IR (film): 2931, 1691, 1465, 1325, 1087, 1073, 881, 736 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.69 (d, J = 7.6 Hz, 2 H), 7.34–7.30 (m, 4 H), 6.34 (s, 2 H), 2.75 (q, J = 7.4 Hz, 2 H), 1.29 (t, J = 7.4 Hz, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 167.7, 149.2, 130.5, 129.8, 127.9, 121.3, 112.9, 28.9, 15.2.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₃H₁₃NNaO: 222.0889; found: 222.0896.

(3-Methoxyphenyl)(1*H*-pyrrol-1-yl)methanone (2cc)

The synthesis was carried out according to general procedure II.

Yield: 37.0 mg (92%); yellowish oil.

IR (film): 2924, 1694, 1466, 1326, 1074, 1047, 793, 737 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.41 (t, *J* = 8.0 Hz, 1 H), 7.31–7.27 (m, 4 H), 7.15–7.12 (m, 1 H), 6.35 (t, *J* = 2.2 Hz, 2 H), 3.86 (s, 3 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 167.5, 159.5, 134.4, 129.5, 121.7, 121.3, 118.4, 114.3, 113.1, 55.5.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{12}H_{11}NNaO_2$: 224.0682; found: 224.0686.

These spectral data correspond to previously reported data.²⁷

(4-Methoxyphenyl)(1H-pyrrol-1-yl)methanone (2dd)

The synthesis was carried out according to general procedure II.

Yield: 37.4 mg (93%); yellowish oil.

IR (film): 2931, 1685, 1464, 1326, 1088, 1073, 881, 737 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 8.4 Hz, 2 H), 7.29 (t, *J* = 2.0 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 6.34 (t, *J* = 2.0 Hz, 2 H), 3.89 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 167.1, 163.0, 132.0, 125.2, 121.3, 113.8, 112.7, 55.5.

HRMS (ESI): $m/z \ [M + Na]^+$ calcd for $C_{12}H_{11}NNaO_2$: 224.0682; found: 224.0687.

These spectral data correspond to previously reported data.²⁷

(1H-Pyrrol-1-yl)(o-tolyl)methanone (2ee)

The synthesis was carried out according to general procedure II. Yield: 33.3 mg (90%); yellowish oil.

IR (film): 2925, 1702, 1466, 1326, 1083, 1072, 882, 737, 664 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.44–7.39 (m, 2 H), 7.30 (t, *J* = 6.6 Hz, 2 H), 7.15 (s, 2 H), 6.31 (d, *J* = 1.2 Hz, 2 H), 2.34 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 168.2, 136.4, 133.7, 130.8, 130.7, 127.8, 125.5, 120.6, 113.4, 19.3.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₂H₁₁NNaO: 208.0733; found: 208.0730.

These spectral data correspond to previously reported data.²⁷

Mesityl(1H-pyrrol-1-yl)methanone (2ff)

The synthesis was carried out according to general procedure II.

Yield: 37.1 mg (87%); yellowish oil.

IR (film): 2922, 1702, 1465, 1325, 1070, 866, 850, 738 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.66 (s, 1 H), 6.91 (s, 2 H), 6.51 (s, 1 H), 6.38 (s, 1 H), 6.21 (s, 1 H), 2.33 (s, 3 H), 2.17 (s, 6 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 169.0, 139.6, 134.7, 131.8, 128.2, 121.1, 118.3, 113.7, 113.4, 21.2, 19.0.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₄H₁₅NNaO: 236.1046; found: 236.1041.

(4-Iodophenyl)(1H-pyrrol-1-yl)methanone (2gg)

The synthesis was carried out according to general procedure II. Yield: 51.7 mg (87%); white solid; mp 69–70 °C.

IR (film): 2925, 1694, 1466, 1329, 1089, 1074, 878, 739 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, J = 8.4 Hz, 2 H), 7.47 (d, J = 8.4 Hz, 2 H), 7.25 (t, J = 1.8 Hz, 2 H), 6.36 (t, J = 2.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.9, 137.7, 132.5, 130.9, 121.1, 113.4, 99.6.

HRMS (ESI): $m/z \ [M + Na]^+$ calcd for $C_{11}H_8INNaO:$ 319.9543; found: 319.9540.

These spectral data correspond to previously reported data.²⁸

(4-Bromophenyl)(1H-pyrrol-1-yl)methanone (2hh)

The synthesis was carried out according to general procedure II. Yield: 42.8 mg (86%); white solid; mp 68–69 °C.

IR (film): 2925, 1694, 1466, 1329, 1089, 1070, 878, 738 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.70–7.64 (m, 4 H), 7.27 (t, *J* = 2.2 Hz, 2 H), 6.38 (t, *J* = 2.4 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.7, 132.0, 131.8, 131.0, 127.2, 121.1, 113.4.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{11}H_8BrNNaO$: 271.9681; found: 271.9687.

These spectral data correspond to previously reported data.²⁹

(3-Bromophenyl)(1H-pyrrol-1-yl)methanone (2ii)

The synthesis was carried out according to general procedure II. Yield: 43.3 mg (87%); yellowish oil.

IR (film): 2924, 1694, 1466, 1327, 1088, 1075, 889, 729 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.91 (s, 1 H), 7.77–7.68 (m, 2 H), 7.42 (t, *J* = 7.8 Hz, 1 H), 7.28 (s, 2 H), 6.39 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.1, 135.2, 135.1, 132.3, 130.0, 127.9, 122.6, 121.1, 113.6.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₈BrNNaO: 271.9681; found: 271.9689.

(4-Chlorophenyl)(1H-pyrrol-1-yl)methanone (2jj)

The synthesis was carried out according to general procedure II. Yield: 34.0 mg (83%); yellowish oil.

IR (film): 2925, 1698, 1465, 1328, 1091, 1075, 880, 741 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.70 (d, *J* = 8.4 Hz, 2 H), 7.49 (d, *J* = 8.8 Hz, 2 H), 7.25 (t, *J* = 2.4 Hz, 2 H), 6.36 (t, *J* = 2.4 Hz, 2 H). ¹³C NMP (100 MHz, CDCl): δ = 166 C, 128 7, 121 5, 120 0, 128 8

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.6, 138.7, 131.5, 130.9, 128.8, 121.1, 113.4.

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HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₈ClNNaO: 228.0187; found: 228.0181.

(3-Fluorophenyl)(1H-pyrrol-1-yl)methanone (2kk)

The synthesis was carried out according to general procedure II. Yield: 30.2 mg (80%); yellowish oil.

IR (film): 2925, 1695, 1467, 1327, 1091, 1073, 815, 736 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.54–7.44 (m, 3 H), 7.33–7.28 (m, 1 H), 7.27 (t, J = 2.2 Hz, 2 H), 6.36 (t, J = 2.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 166.2, 163.5, 161.0, 135.2, 135.1, 130.3, 130.2, 125.2, 125.1, 121.1, 119.4, 119.2, 116.7, 116.4, 113.5.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₈FNNaO: 212.0482; found: 212.0490.

2-(1H-Pyrrole-1-carbonyl)phenyl Acetate (2ll)

The synthesis was carried out according to general procedure II.

Yield: 37.6 mg (82%); yellowish oil.

IR (film): 2925, 1767, 1700, 1467, 1332, 1178, 1084, 1073, 886, 738 $\rm cm^{-1}.$

¹H NMR (400 MHz, CDCl₃): δ = 7.60–7.54 (m, 2 H), 7.37–7.33 (m, 1 H), 7.27–7.25 (m, 1 H), 7.17 (t, *J* = 2.4 Hz, 2 H), 6.32 (t, *J* = 2.4 Hz, 2 H), 2.12 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 168.8, 164.8, 148.3, 132.4, 129.6, 126.9, 125.7, 123.4, 120.7, 113.4, 20.6.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₃H₁₁NNaO₃: 252.0631; found: 252.0639.

(3-Nitrophenyl)(1H-pyrrol-1-yl)methanone (2mm)

The synthesis was carried out according to general procedure II.

Yield: 34.6 mg (80%); yellow oil.

IR (film): 2923, 1697, 1467, 1329, 1099, 1075, 852, 741, 713 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.63 (s, 1 H), 8.49 (d, J = 8.0 Hz, 1 H), 8.11 (d, J = 7.6 Hz, 1 H), 7.77 (t, J = 7.8 Hz, 1 H), 7.27 (s, 2 H), 6.44 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 165.2, 148.0, 134.9, 134.8, 129.9, 126.7, 124.3, 121.0, 114.2.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{11}H_8N_2NaO_3$: 239.0427; found: 239.0421.

These spectral data correspond to previously reported data.³⁰

Naphthalen-1-yl(1H-pyrrol-1-yl)methanone (2nn)

The synthesis was carried out according to general procedure II. Yield: 35.4 mg (80%); yellowish oil.

IR (film): 2922, 1694, 1465, 1321, 1105, 1068, 887, 737 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, *J* = 8.0 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.67–7.65 (m, 1 H), 7.59–7.52 (m, 3 H), 7.22 (s, 2 H), 6.33 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 167.6, 133.4, 131.4, 131.2, 130.4, 128.4, 127.6, 126.9, 126.7, 125.0, 124.4, 121.0, 113.4.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₅H₁₁NNaO: 244.0733; found: 244.0737.

These spectral data correspond to previously reported data.³¹

Naphthalen-2-yl(1H-pyrrol-1-yl)methanone (200)

The synthesis was carried out according to general procedure II.

Yield: 36.7 mg (83%); white solid; mp 85-87 °C.

IR (film): 2923, 1695, 1465, 1325, 1087, 1074, 830, 746 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.27 (s, 1 H), 7.98–7.92 (m, 3 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.66–7.58 (m, 2 H), 7.36 (s, 2 H), 6.39 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 167.8, 134.9, 132.2, 130.7, 130.4, 129.1, 128.5, 128.4, 127.9, 127.1, 125.5, 121.4, 113.1.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₅H₁₁NNaO: 244.0733; found: 244.0739.

Furan-2-yl(1H-pyrrol-1-yl)methanone (2pp)

The synthesis was carried out according to general procedure II. Yield: 26.4 mg (82%); yellowish oil.

IR (film): 2926, 1682, 1461, 1330, 1100, 1074, 837, 734 cm⁻¹.

 ^{1}H NMR (400 MHz, CDCl_3): δ = 7.69–7.66 (m, 3 H), 7.43–7.42 (m, 1 H), 6.63–6.62 (m, 1 H), 6.36 (t, J = 2.4 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 155.5, 146.7, 146.5, 121.2, 120.7, 113.2, 112.4.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₉H₇NNaO₂: 184.0369; found: 184.0378.

Furan-3-yl(1H-pyrrol-1-yl)methanone (2qq)

The synthesis was carried out according to general procedure II.

Yield: 26.1 mg (81%); yellowish oil.

IR (film): 2924, 1691, 1465, 1335, 1074, 875, 837, 735 cm⁻¹.

 ^{1}H NMR (400 MHz, CDCl_3): δ = 8.02 (s, 1 H), 7.53 (s, 1 H), 7.40 (s, 2 H), 6.86 (s, 1 H), 6.37 (s, 2 H).

 ^{13}C NMR (100 MHz, CDCl_3): δ = 161.1, 147.2, 143.9, 120.6, 120.4, 113.3, 110.8.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₉H₇NNaO₂: 184.0369; found: 184.0373.

These spectral data correspond to previously reported data.²⁸

(1H-Pyrrol-1-yl)(thiophen-2-yl)methanone (2rr)

The synthesis was carried out according to general procedure II. Yield: 28.3 mg (80%); yellowish oil.

IR (film): 2924, 1665, 1464, 1318, 1070, 816, 719 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.77–7.76 (m, 1 H), 7.72–7.71 (m, 1 H), 7.47 (t, *J* = 2.4 Hz, 2 H), 7.20–7.18 (m, 1 H), 6.38 (t, *J* = 2.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 160.6, 135.8, 134.0, 133.3, 127.7, 121.0, 113.2.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₉H₇NNaOS: 200.0141; found: 200.0138.

(3-Methylthiophen-2-yl)(1*H*-pyrrol-1-yl)methanone (2ss)

The synthesis was carried out according to general procedure II. Yield: 25.2 mg (66%); white solid; mp 70–71 °C.

IR (film): 2924, 1675, 1466, 1320, 1073, 866, 741 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.50 (d, *J* = 5.2 Hz, 1 H), 7.40 (t, *J* = 2.2 Hz, 2 H), 6.99 (d, *J* = 4.8 Hz, 1 H), 6.34 (t, *J* = 2.4 Hz, 2 H), 2.45 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 161.7, 145.8, 131.3, 129.9, 127.6, 121.1, 113.0, 15.8.

HRMS (ESI): $m/z [M + Na]^+$ calcd for $C_{10}H_9NNaOS$: 214.0297; found: 214.0305.

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(5-Chlorothiophen-2-yl)(1H-pyrrol-1-yl)methanone (2tt)

The synthesis was carried out according to general procedure II.

Yield: 30.4 mg (72%); white solid; mp 39–40 $^\circ \text{C}.$

IR (film): 2925, 1670, 1464, 1417, 1331, 1073, 1010, 824, 727 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, *J* = 3.6 Hz, 1 H), 7.41 (d, *J* = 1.2 Hz, 2 H), 7.02 (d, *J* = 3.6 Hz, 1 H), 6.38 (d, *J* = 1.2 Hz, 2 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 159.4, 139.0, 134.3, 133.7, 127.2, 120.8, 113.5.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₉H₆ClNNaOS: 233.9751; found: 233.9756.

Cyclohexyl(1H-pyrrol-1-yl)methanone (2uu)

The synthesis was carried out according to general procedure II. Yield: 28.3 mg (80%); white solid; mp 54–55 °C.

IR (film): 2929, 1714, 1466, 1336, 1272, 1112, 1072, 924, 741 cm⁻¹.

¹H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, *J* = 2.0 Hz, 2 H), 6.29 (t, *J* = 2.4 Hz, 2 H), 2.96–2.89 (m, 1 H), 1.97–1.85 (m, 4 H), 1.76–1.58 (m, 3 H), 1.43–1.24 (m, 3 H).

 ^{13}C NMR (100 MHz, CDCl₃): δ = 173.8, 118.9, 112.9, 42.8, 29.6, 25.6, 25.5.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₁₁H₁₅NNaO: 200.1046; found: 200.1041.

These spectral data correspond to previously reported data.²⁹

1-(1*H*-Pyrrol-1-yl)ethan-1-one (2vv)

The synthesis was carried out according to general procedure II. Yield: 17.9 mg (82%); yellowish oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.29 (s, 2 H), 6.30 (t, *J* = 2.2 Hz, 2 H), 2.53 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 167.7, 119.3, 113.2, 22.3.

HRMS (ESI): m/z [M + Na]⁺ calcd for C₆H₇NNaO: 132.0420; found: 132.0426.

These spectral data correspond to previously reported data.³²

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690002.

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