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PAPER

Assisted tandem catalytic RCM-aromatization in the synthesis of pyrroles and furans†

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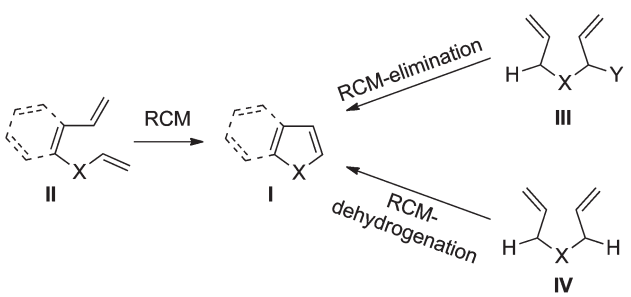
An assisted tandem catalytic transformation of diallyl amines and diallyl ethers into *N*-aryl pyrroles and furans, respectively, is described. The sequence relies on ring closing metathesis followed by dehydrogenation of the initially formed dihydropyrroles and dihydrofurans. Both steps are Ru-catalyzed, but the sequence requires only one precatalyst, because conversion of the metathesis catalyst into the dehydrogenation catalyst is achieved *in situ*, triggered by the oxidant *tert*-butyl hydroperoxide.

Introduction

Over the past few years the development of strategies for the incorporation of olefin metathesis steps in the synthesis of aromatic carba- and heterocycles has attracted considerable interest.[1–4] From a synthetic point of view, metathesis based routes to heteroaromatic compounds are particularly attractive, because due to the ubiquitous occurrence of aromatic heterocycles in medicinal and natural products chemistry there is a constant need for novel synthetic methods in this field.[5] However, examples for the straightforward synthesis of heteroaromatic compounds (**I**) through ring closing olefin metathesis of dienes **II** are normally limited to benzoannellated systems, in particular indoles[6–9] or benzo[*b*]furans.[10–14] In most other cases, two-step sequences are necessary that comprise an RCM step followed by elimination of H–Y or dehydrogenation (Scheme 1).

Several examples for the RCM-elimination approach, pioneered by Donohoe and coworkers, were published, in particular for the synthesis of pyrroles[15–17] and furans,[18,19] but pyridines and pyridones[20–23] have also been synthesized along these lines. The synthetic value of this approach to heteroaromatics has very recently been impressively demonstrated by synthesis of the natural product streptonigrin.[24] The first examples of RCM-dehydrogenation reactions reported in the literature were discovered by chance. For example, beginning in the late 1990s several independent reports were published describing the formation of pyrroles[25–28] and furans[29] during RCM reactions intended to deliver 2,5-dihydropyrroles and -furans,[30,31] respectively. Soon after these discoveries, strategies were developed to obtain these aromatic heterocycles in a selective, reproducible and predictable way from diallyl amines and ethers. Stevens *et al.* introduced the co-catalytic system of first generation Grubbs' catalyst, to achieve the RCM, and $RuCl_3$ as a dehydrogenation catalyst, for the selective synthesis of pyrroles.[32] Shortly afterwards, the same authors reported a one-flask RCM-aromatization sequence, using chloranil as a stoichiometric oxidant.[33,34] For the synthesis of *N*-aryl pyrroles, a subsequent dehydrogenation catalyzed by Pd/C has been described for one example,[35] and it has been reported that conducting the RCM under microwave conditions results in remarkably high yields of pyrroles in most cases.[36,37] In the furan series, one-flask sequences consisting of diallyl ether RCM and stoichiometric oxidation using NiO_2 [38] or benzoquinones[39,40] have been described.

In continuation of projects in our group directed at the development of novel "assisted tandem catalytic transformations"[41] involving olefin metathesis and at least one catalytic non-metathesis step, we investigated a sequential RCM-oxidative aromatization approach to furans and pyrroles along these lines. The results of this investigation are disclosed herein. Assisted tandem RCM sequences[42,43] coupled with reductive, *e.g.* hydrogenation,[44–46] as well as oxidative steps, *e.g.* di-[47,48] or ketohydroxylation,[49,50] have been developed over the past few years. An extension of the latter class of sequences has recently



Scheme 1 Metathesis-based synthesis of heteroaromatics.

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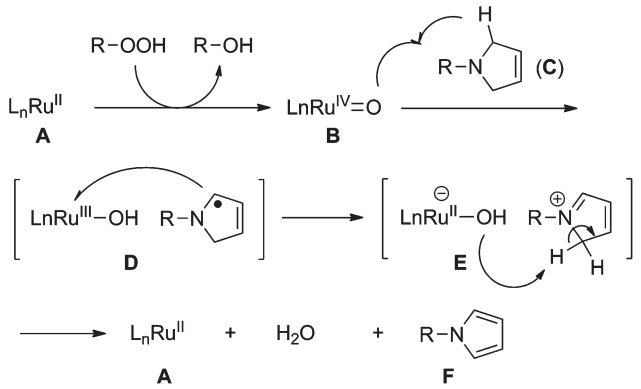


Scheme 2 Mechanistic rationale for the oxidative aromatization with Ru-(II)-precatalysts and hydroperoxides.

been published by us. We found that the addition of hydroperoxides to the RCM reaction of styrenyl ethers triggers the conversion of the metathesis catalyst into a catalyst for allylic oxidation, resulting in the formation of cumarins.[51] Shortly after and independent from our initial report on the RCM-allylic oxidation sequence, Arisawa *et al.* disclosed a similar approach to quinolones starting from styrenyl allyl amines.[52]

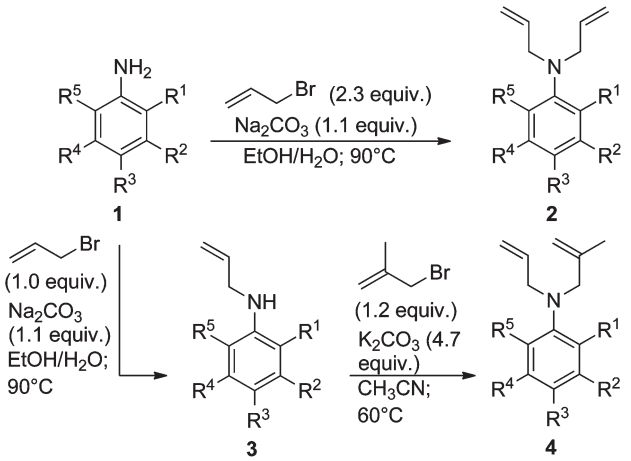
Results and discussion

Initial considerations

Several reports describe the oxidative aromatization of *N*-aryl dihydropyrroles upon prolonged exposure to air,[53] by treatment with stoichiometric amounts of benzoquinones[53] or MnO_2,[54,55] or during Pd-catalyzed Heck reactions at the endocyclic dihydropyrrole C–C-double bond.[37] In light of our successful RCM-allylic oxidation sequence for the synthesis of cumarins,[51] triggered by the addition of hydroperoxides to the RCM reaction, we speculated that the use of this chemical trigger in RCM reactions leading to five membered heterocycles might result in oxidative aromatization, rather than allylic oxidation. This assumption is based on the observation that many Ru-(II)-complexes (**A**) are known to react with hydroperoxides under formation of Ru-(IV)–oxo complexes (**B**), *i.e.* complexes comprising a Ru–oxygen double bond,[56] which are capable of cleaving C–H-bonds homolytically.[57] Following Murahashi's mechanistic proposals for the Ru-catalyzed oxidation of alkanes and other substrates with hydroperoxides[58] or peracids,[59] we assumed that a Ru–oxo complex **B** would abstract a hydrogen radical from a dihydropyrrol **C**, giving the radical pair **D**. Within this radical pair **D**, oxidation of the dihydropyrrole radical might occur by electron transfer to the Ru, if the oxidation potential is sufficiently low (which will most likely be the case with an adjacent donor such as a tertiary amine). As the cation in ion pair **E** is highly acidic, the resulting pyrrole **F** will be formed rapidly with concomitant formation of water and regeneration of the Ru-II-complex **A** (Scheme 2).

Synthesis of RCM precursors

A set of eleven *N*-aryldiallyl amines (**2**) was synthesized from the corresponding anilines (**1**) by allylation with excess allyl bromide in the presence of Na_2CO_3 in ethanol–water (Scheme 3 and Table 1).[60] Unsymmetrical *N*-aryl diallyl amines **4** were obtained by stepwise allylation. The anilines **1** were first monoallylated to secondary amines **3**, using one equivalent of allyl bromide, with the formation of minor amounts of diallylated products **2**. Subsequent allylation of **3** with methallyl bromide to the required unsymmetrical precursors **4** was achieved under conditions similar to those previously used for the allylation of *para*-toluenesulfonyl amide[61] (Scheme 3 and Table 2).



Scheme 3 Synthesis of RCM precursors. See Tables 1 and 2 for details.

Table 1 Synthesis of symmetrical diallyl amines **2**[a]

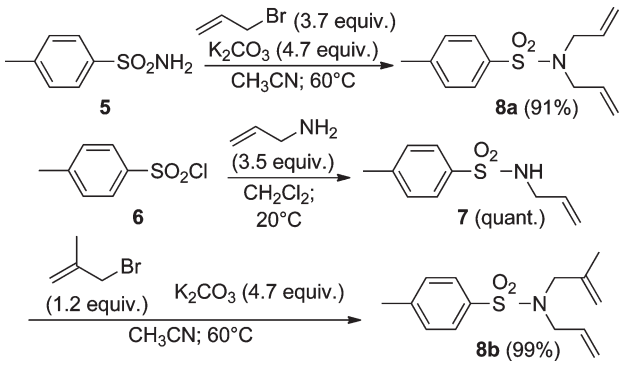
Entry	**1**	R^1	R^2	R^3	R^4	R^5	**2**	Yield
1	**1a**	H	H	Cl	H	H	**2a**	86%
2	**1b**	H	H	H	H	H	**2b**	90%
3	**1c**	CH_3	Cl	H	H	H	**2c**	72%
4	**1d**	OCH_3	H	H	Cl	H	**2d**	93%
5	**1e**	CH_3	H	H	H	CH_3	**2e**	67%
6	**1f**	H	F	H	H	H	**2f**	79%
7	**1g**	H	NO_2	H	H	H	**2g**	61%[b]
8	**1h**	H	NHAc	H	H	H	**2h**	52%
9	**1i**	H	OCH_3	H	H	H	**2i**	78%
10	**1j**	H	H	OCH_3	H	H	**2j**	86%
11	**1k**	H	H	Ac	H	H	**2k**	45%

[a] See Scheme 3 for details. [b] Isolated along with monoallylated amine **3g** (34%).

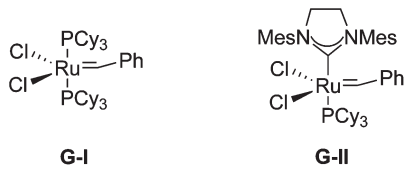
Table 2 Synthesis of allyl amines **3** and unsymmetrical diallyl amines **4**[a]

Entry	Starting material	R^1	R^2	R^3	R^4	R^5	Product(s)	Yield
1	**1a**	H	H	Cl	H	H	**3a**	46%
							2a	29%
2	**3a**	H	H	Cl	H	H	**4a**	68%
3	**1f**	H	F	H	H	H	**3f**	46%
							2f	16%
4	**3f**	H	F	H	H	H	**4f**	90%

[a] See Scheme 3 for details.



Scheme 4 Synthesis of *para*-tosyl diallyl amines **8a,b**.



G-I **G-II**

Fig. 1 First (**G-I**) and second (**G-II**) generation Grubbs'catalyst.

In addition to the precursors **2a–k** and **4a,f** described above, we synthesized two precursors **8a,b** with an electron withdrawing group attached to the nitrogen, starting from *para*-toluenesulfonyl amide **5**[61] and *para*-toluenesulfonyl chloride **6**,[62,63] respectively, as outlined in Scheme 4.

Pyrroles *via* RCM-oxidative aromatization

The conditions required for an efficient RCM-oxidative aromatization were optimized for substrate **2a**. For this particular substrate, Xiao *et al.* described the selective formation of the corresponding pyrrole **10a** rather than the expected dihydropyrrole **9a** under microwave assisted RCM conditions[36] in the presence of first generation Grubbs' catalyst **G-I** (Fig. 1).[64]

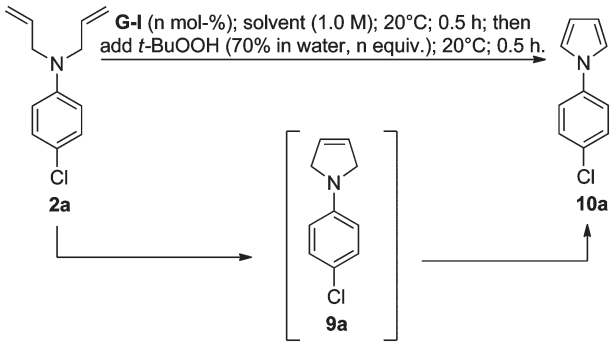
To the best of our knowledge, the RCM of **2a** had not been investigated under thermal conditions before, and we therefore started our investigation with this experiment. In the presence of 2.5 mol% of **G-I** we were indeed able to isolate the dihydropyrrole **9a** in quantitative yield, indicating that the spontaneous aromatization observed by Xiao *et al.*[36] is not specific for this particular substrate but most likely caused by the microwave conditions. Remarkably, the ring closing metathesis reaction proceeds efficiently in spite of the rather high initial substrate concentration of 1.0 M (Table 3, entry 1). In the next step, a commercially available aqueous solution of *t*-BuOOH was added to the RCM reaction after complete consumption of the starting material **2a**. Under these conditions, the pyrrole **10a** was isolated in 79% yield, along with minor amounts of the RCM product **9a** (Table 3, entry 2). By increasing the catalyst loading to 5 mol%, pyrrole **10a** could be obtained in 92% yield with an almost quantitative conversion to the desired product (Table 3, entry 3). Further optimization included a variation of the solvent. Both dichloromethane and ethyl acetate resulted in a significantly diminished yield of 71% (Table 3, entries 4 and 5), whereas toluene gave an even better yield than benzene (Table 3, entry 6). Having identified these optimized conditions, we checked whether or not the aromatization step is indeed Ru-catalyzed. To this end, dihydropyrrole **9a** was carefully purified by repeated chromatography to remove any Ru-residues and then subjected to the reaction conditions as stated in Table 3. Analysis of the crude reaction mixture by ^{1}H-NMR spectroscopy after a reaction time of 15 h revealed the presence of **9a** and **10a** in a ratio of 45 to 55 (Table 3, entry 7). This result points to a slow uncatalyzed background reaction, which presumably proceeds *via* a *tert*-butoxide or a *tert*-butylperoxide radical. To provide further proof that this pathway contributes only a minor amount to the overall conversion, the oxidative aromatization was repeated with isolated dihydropyrrole **9a** under the optimized conditions but in the presence of one equivalent of the radical scavenger 3,5-di-*t*-butyl-4-hydroxytoluene (BHT).[65] This experiment resulted in an only slightly decreased conversion of 82% to pyrrole **10a**, indicating that the oxidative step most likely proceeds *via* a Ru–oxo species **B**, as previously suggested by Murahashi *et al.* for the Ru-catalyzed oxidation of alkanes, based on a similar line of argumentation (Table 3, entry 8).[65] With these results in hand, we applied the optimized conditions to other *N*-aryl diallylamines listed in Table 4.

For almost all examples listed in Table 4 excellent yields were obtained using the standard conditions identified for the conversion of **2a** to **10a** (Table 3). Apparently, the electronic conditions of the *N*-aryl substituent have no significant influence on the reaction, as electron rich and electron deficient aryl groups give comparable yields. Conversion of substrates **4a,f**, containing one geminally disubstituted double bond, required the second generation catalyst **G-II**, elevated temperatures for the RCM step, and a lower initial substrate concentration (Table 4, entries 12, 13). Two notable exceptions are substrates **2e** and **2h**. In the case of **2h** a switch to the less suitable solvent ethyl acetate was required, because this precursor, with an acetamide substituent, is only sparingly soluble in benzene or toluene. For **2e**, the reaction failed completely, because the RCM step did not take place under these conditions. An analysis of the reaction mixture revealed that, apart from unreacted **2e** (35%), a deallylated secondary amine **3e** (see Scheme 3, $R^1 = R^5 = CH_3$, R^2–$R^4 = H$) was formed in 27% yield. This deallylation occurs *via* a Ru–hydride catalyzed isomerization[66] of the double bond to an enamine,[67] which is hydrolyzed upon addition of the aqueous solution of the oxidant.

Finally, the oxidative aromatization of the electron deficient RCM-precursors **8a,b** was investigated. It was previously mentioned in the literature that strongly electron withdrawing groups attached to the nitrogen of dihydropyrroles reduce the tendency towards aromatization.[32,68] For these reasons, we expected tosyl amides **8a,b** to be rather challenging substrates that might possibly require special optimization (Table 5).

Under the standard conditions established for the *N*-aryl derivatives **2** and **4**, a fair yield of 62% of pyrrole **12a** was obtained (Table 5, entry 1). Remarkably, this yield could be significantly improved when toluene was replaced by benzene and when a slightly higher amount of oxidant was used as a solution in decane, which is also commercially available (Table 5, entry 2). Further increasing the amount of oxidant resulted in significantly lower yields (Table 5, entries 3 and 4), presumably due to decomposition of the pyrrole. It is not clear

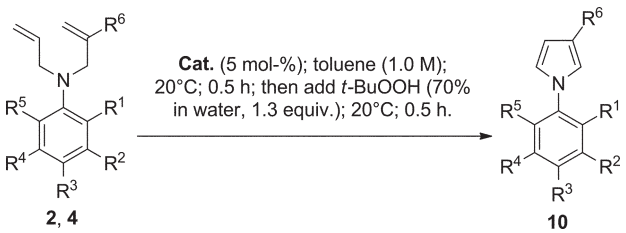
Table 3 Optimization of RCM-oxidative aromatization



Entry	Solvent	Starting material	Cat. loading	Equiv. of oxidant	Product	Yield[a]
1	Benzene	**2a**	2.5 mol%	—	**9a**	99%
2	Benzene	**2a**	2.5 mol%	1.3	**10a**	79%
3	Benzene	**2a**	5.0 mol%	1.3	**10a**	92%
4	CH_2Cl_2	**2a**	5.0 mol%	1.3	**10a**	71%
5	Ethyl acetate	**2a**	5.0 mol%	1.3	**10a**	71%
6	Toluene	**2a**	5.0 mol%	1.3	**10a**	96%
7	Toluene	**9a**	—	1.3	**10a**	55%[b]
8[c]	Toluene	**9a**	5.0 mol%	1.3	**10a**	82%[d]

[a] Isolated yields of pure product, unless otherwise stated. [b] Conversion after 15 h at 20 °C, determined *via* ^{1}H-NMR spectroscopy. [c] Reaction run in the presence of 3,5-di-*t*-butyl-4-hydroxytoluene (BHT, 1.0 equiv.). [d] Conversion after 2 h determined *via* ^{1}H-NMR spectroscopy.

Table 4 *N*-Aryl pyrroles **10** *via* RCM-oxidative aromatization

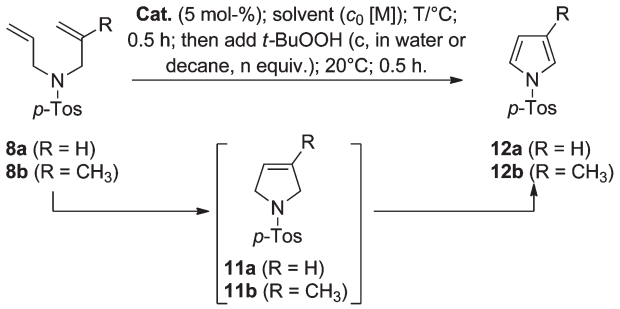


Entry	Starting material	Cat.	R^1	R^2	R^3	R^4	R^5	R^6	**10**	Yield
1	**2a**	**G-I**	H	H	Cl	H	H	H	**10a**	96%
2	**2b**	**G-I**	H	H	H	H	H	H	**10b**	86%
3	**2c**	**G-I**	CH_3	Cl	H	H	H	H	**10c**	98%
4	**2d**	**G-I**	OCH_3	H	H	Cl	H	H	**10d**	90%
5	**2e**	**G-I**	CH_3	H	H	H	CH_3	H	**10e**	—[a]
6	**2f**	**G-I**	H	F	H	H	H	H	**10f**	94%
7	**2g**	**G-I**	H	NO_2	H	H	H	H	**10g**	89%
8	**2h**	**G-I**	H	NHAc	H	H	H	H	**10h**	55%[b]
9	**2i**	**G-I**	H	OCH_3	H	H	H	H	**10i**	93%
10	**2j**	**G-I**	H	H	OCH_3	H	H	H	**10j**	87%
11	**2k**	**G-I**	H	H	Ac	H	H	H	**10k**	88%
12	**4a**	**G-II**	H	H	Cl	H	H	CH_3	**10l**	87%[c]
13	**4f**	**G-II**	H	F	H	H	H	CH_3	**10m**	92%[c]

[a] Unreacted **2e** (35%) and monoallyl amine **3e** (27%) were isolated. [b] Reaction was performed in ethyl acetate, initial substrate concentration 0.5 M. [c] Initial substrate concentration was 0.1 M; RCM conducted at 80 °C, oxidative aromatization at 20 °C.

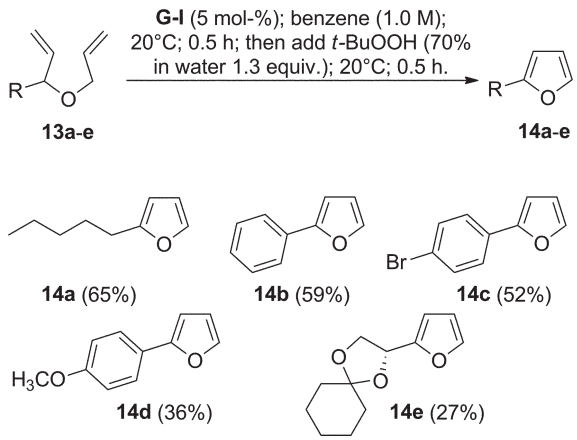
whether or not the decomposition of the pyrrole is further accelerated by the presence of a Ru–oxo species in this case, however, the sensitivity of pyrroles towards oxidation even in the absence of transition metal catalysts has precedence in the literature.[69] For successful conversion of the methyl substituted derivative **8b**, the second generation Grubbs' catalyst **G-II** was required. In these experiments, **12b** was isolated in yields between 40% and 50%, along with varying amounts of the primary RCM product **11b**. Unfortunately, the yield of **12b** could not be improved by increasing the amount of oxidant, although the

Table 5 RCM-oxidative aromatization for *N*-tosyl derivatives **8**



Entry	Starting material	Cat.	Solvent	c_0 [M]	T	Equiv. *t*BuOOH	Yield of **11**	Yield of **12**
1	**8a**	**G-I**	Toluene	1.0	20 °C	1.3[a]	—	62%
2	**8a**	**G-I**	Benzene	1.0	20 °C	2.0[b]	—	77%
3	**8a**	**G-I**	Benzene	1.0	20 °C	4.0[b]	—	50%
4	**8a**	**G-I**	Benzene	0.1	20 °C	4.0[b]	—	49%
5	**8b**	**G-II**	Toluene	0.1	80 °C	1.3[a]	42%	44%
6	**8b**	**G-II**	Benzene	0.1	80 °C	2.0[b]	16%	50%
7	**8b**	**G-II**	Toluene	0.1	80 °C	3.0[b]	—	45%

[a] 70% aqueous solution. [b] 5.5 M solution in decane.



Scheme 5 Furans through RCM oxidative aromatization.

yield of **11b** was significantly lower with 2.0 or 3.0 equivalents of *t*-BuOOH (Table 5, entries 6 and 7). This observation also points to a decomposition of the pyrrole in the presence of larger amounts of oxidant.

Furans *via* RCM-oxidative aromatization

In the following, we extended the RCM-oxidative aromatization approach to the synthesis of furans **14**, starting from various diallyl ethers **13**. The required diallyl ethers **13** were synthesized from aldehydes in two steps as previously described in the literature.[70] Application of the optimized conditions for the RCM-oxidative aromatization of *N*-aryl diallyl amines **2** gave furans in lower, but still preparatively useful yields, except for **13e**, which probably undergoes partial cleavage of the acetal and subsequent consecutive oxidation of the resulting diol (Scheme 5).

Conclusions

In summary, we developed a Ru catalyzed RCM-oxidative aromatization sequence for the synthesis of various pyrroles and furans. The synthesis starts from conveniently available diallyl amines or ethers and can be classified as an assisted tandem catalytic transformation, because the Ru metathesis catalyst is converted *in situ* to a catalyst for the aromatization step, using *tert*-butyl hydroperoxide as a chemical trigger and as an oxidant.

Experimental

General remarks

All experiments were conducted in dry reaction vessels under an atmosphere of dry nitrogen. Solvents were purified by standard procedures. ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ with tetramethylsilane (δ = 0.00 ppm) as an internal standard. Coupling constants (J) are given in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ with $CDCl_3$ (δ = 77.0 ppm) as an internal standard. The number of coupled protons was analyzed by APT-experiments and is denoted by a number in parentheses following the chemical shift value. IR spectra were recorded neat as films on NaCl or KBr plates. Wavenumbers (ν) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70 eV.

General procedure for the synthesis of *N*-aryl diallylamines 2

The appropriate aniline **1** (20 mmol) was dissolved in a mixture of ethanol (64 mL) and water (16 mL). Then Na_2CO_3 (2.12 g, 20 mmol) and allyl bromide (4.0 mL, 5.66 g, 46 mmol) were added. The solution was stirred at 80 °C until the starting material was fully consumed, as indicated by TLC (approx. 4 h).

After cooling to ambient temperature most of the ethanol was removed *in vacuo*. The residue was extracted three times with MTBE (50 mL each). The combined organic layers were dried with $MgSO_4$, filtered and all volatiles were removed *in vacuo*. The residue was purified by column chromatography.

***N,N*-Diallyl-4-chloroaniline (2a).** Following the general procedure, **2a** was obtained from **1a** (2.54 g, 20 mmol) as a colorless liquid (3.60 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (dd, 2H, J = 9.2, 0.8), 6.59 (d, 2H, J = 8.6), 5.89–5.74 (2H), 5.19–5.15 (2H), 5.15–5.09 (2H), 3.91–3.85 (4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3 (0), 133.6 (1, 2C), 128.8 (1, 2C), 121.2 (0), 116.2, (2, 2C), 113.6 (1, 2C), 53.0 (2, 2C); IR: $\tilde{\nu}$ = 3082 (w), 3007 (w), 2980 (w), 2863 (w), 1596 (m), 1497 (s), 1387 (m), 1355 (m), 1233 (m); HRMS (EI) calcd for $C_{12}H_{14}N$ [35]Cl $[M]^+$: 207.0815, found: 207.0827; MS (EI) *m/z* 207 (M^+, 26), 180 (19), 138 (19), 130 (21), 111 (26), 75 (20), 41 (100), 39 (48).

***N,N*-Diallylaniline (2b).** Following the general procedure, **2b** was obtained from **1b** (1.86 g, 20 mmol) as a colorless liquid (3.11 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, 1H, J = 7.2), 7.18 (d, 1H, J = 7.2), 6.74–6.63 (3H), 5.86 (ddt, 2H, J = 17.3, 10.0, 4.9), 5.18 (dddd, 2H, J = 17.2, 1.8, 1.8, 1.7), 5.15 (dddd, 2H, J = 9.9, 1.7, 1.7, 1.5), 3.92 (ddd, 4H, J = 4.8, 1.7, 1.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7 (0), 134.1 (1, 2C), 129.0 (1, 2C), 116.4 (1), 115.9 (2, 2C), 112.5 (1, 2C), 52.8 (2, 2C); IR: $\tilde{\nu}$ = 3062 (w), 2978 (w), 2908 (w), 1597 (s), 1503 (s), 1386 (m), 1351 (m); HRMS (EI) calcd for $C_{12}H_{15}N$ $[M]^+$: 173.1204, found: 173.1219; MS (EI) *m/z* 173 (M^+, 30), 146 (65), 130 (42), 77 (28), 41 (63), 39 (50).

***N,N*-Diallyl-3-chloro-2-methylaniline (2c).** Following the general procedure, **2c** was obtained from **1c** (2.82 g, 20 mmol) as a colorless liquid (3.18 g, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, 1H, J = 7.9, 1.7), 7.08 (dd, 1H, J = 7.9, 7.5), 6.91 (dd, 1H, J = 7.5, 1.7), 5.76 (ddt, 2H, J = 17.2, 10.3, 6.2), 5.20–5.07 (4H), 3.55 (d (br), 4H, J = 6.2), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5 (0), 135.6 (0), 134.8 (1, 2C), 132.4 (0), 126.1 (1), 124.2 (1), 120.6 (1), 117.3 (2, 2C), 55.9 (2, 2C), 15.4 (3); IR: $\tilde{\nu}$ = 3076 (w), 2979 (w), 2922 (w), 2815 (w), 1644 (w), 1586 (m), 1565 (m), 1458 (s), 1363 (w); HRMS (EI) calcd for $C_{13}H_{16}N$[35]Cl $[M]^+$: 221.0971, found: 221.0962; (EI) *m/z* 221 (M^+, 17), 117 (20), 43 (20), 41 (100), 39 (47).

***N,N*-Diallyl-5-chloro-2-methoxyaniline (2d).** Following the general procedure, **2d** was obtained from **1d** (3.14 g, 20 mmol) as a colorless liquid (4.40 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (dd, 1H, J = 8.5, 2.5), 6.84 (d, 1H, J = 2.4), 6.74 (d, 1H, J = 8.5), 5.80 (ddt, 2H, J = 17.2, 10.2, 6.3), 5.24–5.13 (4H), 3.83 (s, 3H), 3.74 (d (br), 4H, J = 6.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3 (0), 140.9 (0), 134.8 (1, 2C), 125.6 (0), 121.4 (1), 120.9 (1), 117.4 (2, 2C), 112.6 (1), 55.8 (3), 54.2 (2, 2C); IR: $\tilde{\nu}$ = 3076 (w), 2936 (w), 2833 (w), 1588 (m), 1495 (s), 1458 (m), 1409 (m), 1239 (s), 1214 (s); HRMS (EI) calcd for $C_{13}H_{16}NO$[35]Cl $[M]^+$: 237.0920, found: 237.0936; MS (EI) *m/z* 237 (M^+, 20), 154 (20), 41 (100), 39 (55).

***N,N*-Diallyl-2,6-dimethylaniline (2e).** Following the general procedure, **2e** was obtained from **1e** (2.42 g, 20 mmol) as a colorless liquid (2.70 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02–6.90 (3H), 5.83 (ddt, 2H, J = 17.1, 10.0, 6.5), 5.10 (dddd, 2H, J = 17.1, 1.8, 1.4, 1.4), 5.04–4.97 (2H), 3.62 (d (br), 4H, J = 6.5), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1 (0), 137.5 (0, 2C), 136.9 (1, 2C), 128.7 (1, 2C), 125.0 (1), 115.9 (2, 2C), 56.0 (2, 2C), 19.6 (3, 2C); IR: $\tilde{\nu}$ = 3072 (w), 2919 (w), 2821 (w), 1684 (w), 1641 (w), 1473 (m), 1415 (m); HRMS (EI) calcd for $C_{14}H_{19}N$ $[M]^+$: 201.1517, found: 201.1514; MS (EI) *m/z* 201 (M^+, 30), 144 (26), 132 (36), 117 (20), 77 (28), 41 (100), 29 (54).

***N,N*-Diallyl-3-fluoroaniline (2f).** Following the general procedure, **2f** was obtained from **1f** (2.22 g, 20 mmol) as a colorless liquid (3.00 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (m, 1H), 6.45–6.29 (3H), 5.80 (ddt, 2H, J = 17.7, 9.9, 4.8), 5.19–5.09 (4H), 3.87 (d (br), 4H, J = 4.7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (0, d, ^1J = 242.6), 150.5 (0, d, ^3J = 10.7), 133.5 (1, 2C), 130.0 (1, d, ^3J = 10.4), 116.2 (2, 2C), 107.9 (1, d, ^4J = 2.0), 102.7 (1, d, ^2J = 21.7), 99.3 (1, d, ^2J = 26.1), 52.8 (2, 2C); IR: $\tilde{\nu}$ = 3083 (w), 2981 (w), 2864 (w), 1617 (s), 1577 (m), 1498 (s), 1388 (w), 1355 (w); HRMS (EI) calcd for $C_{12}H_{14}NF$ $[M]^+$: 191.1110, found: 191.1101; MS (EI) *m/z* 191 (M^+, 100), 164 (46), 95 (32), 41 (44), 39 (38).

***N,N*-Diallyl-3-nitroaniline (2g) and *N*-allyl-3-nitroaniline (3g).** Following the general procedure, **2g** was obtained from **1g** (2.76 g, 20 mmol) as a yellow liquid (2.66 g, 61%). **2g** could be separated from *N*-allyl-3-nitroaniline (**3g**), which was isolated as an orange solid (1.21 g, 34%). *Analytical data of N,N-diallyl-3-nitroaniline* (**2g**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.44 (2H), 7.26 (dd, 1H, J = 8.5, 8.3), 6.93 (ddd, 1H, J = 8.7, 2.1, 1.3), 5.84 (ddt, 2H, J = 17.7, 9.9, 4.8), 5.20 (dddd, 2H, J = 9.2, 1.6, 1.5, 1.5), 5.17 (dddd, 2H, J = 17.0, 1.6, 1.4, 1.4), 3.98 (dt, J = 4.7, 2.1); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (0), 149.2 (0), 132.6 (1, 2C), 129.6 (1), 117.7 (1), 116.6 (2, 2C), 110.7 (1), 106.4 (1), 52.9 (2, 2C); IR: $\tilde{\nu}$ = 3085 (w), 2981 (w), 2866 (w), 1616 (m), 1522 (s), 1494 (m), 1389 (m), 1342 (s), 1236 (m); HRMS (EI) calcd for $C_{12}H_{14}N_2O_2$ $[M]^+$: 218.1055, found: 218.1064; MS (EI) *m/z* 218 (M^+, 30), 191 (32), 171 (20), 130 (28), 41 (100), 39 (27). *Analytical data of N-allyl-3-nitroaniline* (**3g**): Mp: 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, 1H, J = 8.0, 1.2), 7.41 (dd, 1H, J = 2.1, 2.0), 7.28 (dd, 1H, J = 8.2, 8.1), 6.90 (dd, 1H, J = 1.9, 1.9), 5.93 (ddt, 1H, J = 17.2, 10., 5.2), 5.32 (m, 1H), 5.23 (m, 1H), 4.26 (s (br), 1H), 3.85 (d (br), 2H, J = 5.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (0), 148.7 (0), 134.0 (1), 129.6 (1), 118.8 (2), 116.9 (1), 111.9 (1), 106.5 (1), 46.1 (2).

***N*-(3-(Diallylamino)phenyl)acetamide (2h).** Following the general procedure, **2h** was obtained from **1h** (3.00 g, 20.0 mmol) as a colorless solid (3.39 g, 52%). Mp: 70–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, (br), 1H), 7.12 (dd, 1H, J = 8.1, 8.1), 7.05 (m, 1H), 6.74 (d (br), 1H, J = 7.8), 6.46 (dd, 1H, J = 8.3, 2.0), 5.86 (ddt, 2H, J = 17.2, 10.0, 4.8), 5.23–5.13 (4H), 3.92 (d (br), 4H, J = 4.7), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2 (0), 149.4 (0), 138.9 (0), 133.8 (1, 2C), 129.4 (1), 116.1 (2, 2C), 108.6 (1), 108.0 (1), 104.1 (1), 52.8 (2, 2C), 24.6 (3); IR: $\tilde{\nu}$ = 3301 (m), 3081 (w), 2979 (w), 2922 (w), 1663 (s), 1610 (s), 1583 (s), 1551 (s), 1496 (s), 1434 (m); HRMS (EI) calcd for $C_{14}H_{18}N_2O$ $[M]^+$: 230.1419, found: 230.1412; MS (EI) *m/z* 230 (M^+, 100), 215 (31), 161 (29), 145 (20).

***N*,*N*-Diallyl-3-methoxyaniline (2i).** Following the general procedure, **2i** was obtained from **1i** (2.46 g, 20 mmol) as a colorless liquid (3.16 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, 1H, J = 8.6, 8.3), 6.32 (ddd, 1H, J = 8.9, 1.9, 1.2), 6.27–6.21 (2H), 6.32 (ddt, 2H, J = 17.1, 10.1, 4.9), 5.17 (dddd, 2H, J = 17.2, 1.8, 1.5, 1.5), 5.13 (dddd, 2H, J = 10.3, 1.7, 1.2, 1.2), 3.98 (dt, 4H, J = 4.9, 1.8), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8 (0), 150.2 (0), 134.1 (1, 2C), 129.7 (1), 116.0 (2, 2C), 105.6 (1), 101.3 (1), 99.1 (1), 55.0 (3), 52.9 (2, 2C); IR: $\tilde{\nu}$ = 3080 (w), 2935 (w), 2833 (w), 1608 (s), 1573 (s), 1497 (s), 1462 (m), 1330 (w), 1263 (m), 1202 (s), 1165 (s); HRMS (EI) calcd for $C_{13}H_{17}NO$ $[M]^+$: 203.1310, found: 203.1301; MS (EI) m/z 203 (M^+, 22), 77 (22), 41 (100), 39 (47).

***N*,*N*-Diallyl-4-methoxyaniline (2j).** Following the general procedure, **2j** was obtained from **1j** (2.46 g, 20 mmol) as a colorless liquid (3.49 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 (d, 2H, J = 9.2), 6.66 (d, 2H, J = 9.2), 5.82 (ddt, 2H, J = 17.2, 10.3, 5.0), 5.16 (dddd, 2H, J = 17.2, 1.6, 1.3, 1.3), 5.12 (dddd, 2H, J = 10.3, 1.6, 1.2, 1.2), 3.82 (dt, 4H, J = 5.0, 1.5), 3.68 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7 (0), 143.4 (0), 134.6 (1, 2C), 115.9 (2, 2C), 114.6 (1, 2C), 55.5 (3), 53.6 (2, 2C); IR: $\tilde{\nu}$ = 3076 (w), 2979 (w), 2904 (w), 2830 (w), 1639 (w), 1508 (s), 1441 (w), 1418 (w), 1230 (s); HRMS (EI) calcd for $C_{13}H_{17}NO$ $[M]^+$: 203.1310, found: 203.1304; MS (EI) m/z 203 (M^+, 46), 135 (46), 134 (49), 120 (34), 92 (24), 77 (32), 41 (100), 39 (56).

1-(4-(Diallylamino)phenyl)ethanone (2k). Following the general procedure, **2k** was obtained from **1k** (2.70 g, 20.0 mmol) as a colorless liquid (1.94 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, 2H, J = 9.1), 6.65 (d, 2H, J = 9.1), 5.84 (ddt, 2H, J = 17.0, 10.4, 4.7), 5.24–5.10 (4H), 3.98 (d (br), 4H, J = 4.7), 2.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1 (0), 152.1 (0), 132.7 (1, 2C), 130.5 (1, 2C), 125.9 (0), 111.0 (1, 2C), 52.6 (2, 2C) 25.8 (3); IR: $\tilde{\nu}$ = 3082 (w), 2980 (w), 2914 (w), 1660 (m), 1589 (s), 1553 (m), 1521 (m), 1395 (m), 1355 (m), 1279 (s), 1236 (s), 1188 (s); HRMS (EI) calcd for $C_{14}H_{17}NO$ $[M]^+$: 215.1310, found: 215.1312; MS (EI) m/z 215 (M^+, 100), 200 (22), 188 (26), 146 (26), 130 (18).

***N*-Allyl-4-chloroaniline (3a).** Aniline **1a** (2.54 g, 20 mmol) was dissolved in a mixture of ethanol (64 mL) and water (16 mL). Then Na_2CO_3 (2.12 g, 20 mmol) and allyl bromide (1.74 mL, 2.42 g, 20 mmol) were added. The solution was stirred at 80 °C for 4 h. After cooling to ambient temperature most of the ethanol was removed *in vacuo*. The residue was extracted three times with MTBE (50 mL each). The combined organic layers were dried over $MgSO_4$, filtered and all volatiles were removed *in vacuo*. The residue was purified by column chromatography. The title compound **3a** was isolated as a colorless liquid (1.54 g, 46%). **3a** could be separated from *N*,*N*-diallyl-4-chloroaniline (**2a**), which was isolated as a colorless liquid (1.20 g, 29%). Analytical data for **2a** synthesized *via* this protocol are identical to those reported above. *Analytical data of N-allyl-4-chloroaniline* (**3a**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, 2H, J = 8.7), 6.52 (d, 2H, J = 8.7), 5.91 (ddt, 1H, J = 17.1, 10.3, 5.3), 5.26 (m, 1H), 5.16 (m, 1H), 3.80 (s (br), 1H), 3.73 (ddd, 2H, J = 5.3, 1.6, 1.6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6 (0), 135.0 (1), 129.0 (1, 2C), 122.1 (0), 116.4 (2), 114.0 (1, 2C), 46.6 (2); IR: $\tilde{\nu}$ = 3419 (m), 3080 (w), 2848 (w), 1862 (w), 1598 (m), 1497 (s), 1315 (m), 1259 (m); HRMS (EI) calcd for $C_9H_{10}N[35]Cl$ $[M]^+$: 167.0496, found: 167.0497; MS (EI) m/z 167 (M^+, 32), 140 (46), 130 (28), 75 (32), 111 (26), 43 (44), 41 (100), 39 (70).

***N*-Allyl-4-chloro-*N*-(2-methylallyl)aniline (4a).** Aniline **3a** (835 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K_2CO_3 (3.24 g, 23.5 mmol) and methallyl bromide (570 µL, 810 mg, 6.0 mmol) were added. The solution was stirred at 60 °C for 12 h. After cooling to ambient temperature it was filtered over celite. All volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica. The title compound **4a** was isolated as a colorless liquid (750 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, 2H, J = 8.9), 6.56 (d, 2H, J = 9.1), 5.82 (ddt, 1H, J = 16.9, 10.4, 4.7), 5.19–5.08 (2H), 4.85 (m, 1H), 4.78 (m, 1H), 3.90 (dt, 2H, J = 4.7, 2.4), 3.75 (s, 2H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4 (0), 140.6 (0), 133.4 (1), 128.7 (1, 2C), 121.0 (0), 116.2 (2), 113.3 (1, 2C), 110.6 (2), 56.5 (2), 53.1 (2), 20.0 (3); IR: $\tilde{\nu}$ = 3082 (w), 2976 (w), 2911 (w), 1648 (w), 1596 (m), 1497 (s), 1442 (w), 1389 (w), 1231 (s); HRMS (EI) calcd for $C_{13}H_{16}N[35]Cl$ $[M]^+$: 221.0971, found: 221.0951; MS (EI) m/z 223 (M^+, 26), 221 (M^+, 100), 182 (25), 180 (88), 138 (34), 130 (27), 111 (27), 55 (26), 43 (28), 41 (41), 39 (26).

***N*-Allyl-3-fluoroaniline (3f).** Aniline **1f** (2.22 g, 20 mmol) was dissolved in a mixture of ethanol (64 mL) and water (16 mL). Then Na_2CO_3 (2.12 g, 20 mmol) and allyl bromide (1.74 mL, 2.42 g, 20 mmol) were added. The solution was stirred at 80 °C for 4 h. After cooling to ambient temperature most of the ethanol was removed *in vacuo*. The residue was extracted three times with MTBE (50 mL each). The combined organic layers were dried over $MgSO_4$, filtered and all volatiles were removed *in vacuo*. The residue was purified by column chromatography. The title compound **3f** was isolated as a colorless liquid (1.39 g, 46%). **3f** could be separated from *N*,*N*-diallyl-3-fluoroaniline (**2f**), which was isolated as a colorless liquid (620 mg, 16%). Analytical data for **2f** synthesized *via* this protocol are identical to those reported above. *Analytical data of N-allyl-3-fluoroaniline* (**3f**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (ddd, 1H, J = 8.1, 8.1, 6.8), 6.50–6.40 (2H), 6.37 (ddd, 1H, J = 11.6, 2.3, 2.3), 5.25 (ddt, 1H, J = 17.1, 10.4, 5.3), 5.35 (dddd, 1H, J = 17.2, 1.7, 1.6, 1.6), 5.25 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5), 3.94 (s (br), 1H), 3.79 (dt, 2H, J = 5.3, 1.6); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (0, d, ^1J = 242.4), 149.9 (0, d, ^3J = 10.8), 134.9 (1), 130.2 (1, d, ^3J = 10.3), 116.3 (2), 108.8 (1, d, ^4J = 2.3), 103.8 (1, d, ^2J = 21.6), 99.6 (1, d, ^2J = 25.4), 46.3 (2); IR: $\tilde{\nu}$ = 3421 (m), 3081 (w), 2843 (w), 1616 (s), 1587 (s), 1508 (s), 1495 (s), 1435 (m); HRMS (EI) calcd for $C_9H_{10}NF$ $[M]^+$: 151.0792, found: 151.0784; MS (EI) m/z 151 (M^+, 100), 150 (30), 124 (35), 43 (78), 41 (96).

***N*-Allyl-3-fluoro-*N*-(2-methylallyl)aniline (4f).** Aniline **3f** (756 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K_2CO_3 (3.24 g, 23.5 mmol) and methallyl bromide (570 µL, 810 mg, 6.0 mmol) were added. The solution was stirred at 60 °C for 12 h. After cooling to ambient temperature it was filtered over celite. All volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica.

The title compound **4f** was isolated as a colorless liquid (920 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (m, 1H), 6.44–6.28 (3H), 5.84 (ddt, 1H, J = 16.8, 10.6, 4.8), 5.16 (m, 1H), 5.15 (m, 1H), 4.86 (m, 1H), 4.79 (m, 1H), 3.91 (ddd, 2H, J = 4.7, 2.4, 2.4), 3.76 (s (br), 2H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (0, d, ^1J = 241.3), 150.6 (0, d, ^3J = 10.8), 140.3 (0), 133.2 (1), 129.9 (1, d, ^3J = 10.4), 116.2 (2), 110.5 (2), 107.6 (1, d, ^4J = 2.0), 102.6 (1, d, ^2J = 21.7), 99.1 (1, d, ^2J = 26.2), 56.2 (2), 52.9 (2), 20.0 (3); IR: $\tilde{\nu}$ = 3084 (w), 2912 (w) 1617 (s), 1577 (m), 1498 (s), 1444 (w), 1389 (w); HRMS (EI) calcd for $C_{13}H_{16}NF$ $[M]^+$: 205.1267, found: 205.1262; MS (EI) m/z 205 (M^+, 2), 134 (14), 98 (26), 84 (24), 74 (27), 71 (27), 69 (26), 57 (56), 55 (42), 43 (100), 41 (68).

***N,N*-Diallyl-4-methylbenzenesulfonamide (8a).** *p*-Toluenesulfonamide (**5**) (6.34 g, 36.4 mmol) was dissolved in acetonitrile (200 mL). Then K_2CO_3 (23.8 g, 171 mmol) and allyl bromide (12.0 mL, 16.6 g, 137 mmol) were added. The solution was stirred at 60 °C for 12 h. After cooling to ambient temperature it was filtered over celite. All volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica. The title compound **8a** was isolated as a colorless liquid (8.30 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.4), 7.30 (d, 2H, J = 8.0), 5.62 (ddt, 2H, J = 17.4, 9.8, 6.3), 5.19–5.09 (4H), 3.80 (d (br), 4H, J = 6.2), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (0), 137.6 (0), 132.7 (1, 2C), 129.6 (1, 2C), 127.2 (1, 2C), 118.8 (2, 2C), 49.3 (2, 2C), 21.4 (3); HRMS (EI) calcd for $C_{13}H_{17}NO_2[32]S$ $[M]^+$: 251.0980, found: 251.0975; MS (EI) m/z 251 (M^+, 12), 186 (11), 155 (40), 96 (54), 91 (100), 65 (39), 41 (84), 39 (41).

***N*-Allyl-4-methylbenzenesulfonamide (7).** Allyl amine (6.00 g, 105 mmol) was dissolved in dichloromethane (180 mL). Then a solution of tosyl chloride (**6**) (5.70 g, 30.0 mmol) in dichloromethane (20 mL) was added dropwise. The solution was stirred for 12 h, before water (150 mL) was added. After phase separation the organic layer was extracted three times with dichloromethane (50 mL each). The combined organic layers were dried over $MgSO_4$, filtered and all volatiles were removed *in vacuo*. The title compound **7** was isolated as a colorless solid (6.55 g, >98%) and was used without further purification. Mp: 65–67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 2H, J = 8.3), 7.31 (d, 2H, J = 8.0), 5.71 (ddt, 1H, J = 17.1, 10.3, 5.8), 5.16 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5), 5.08 (dddd, 1H, J = 10.2, 1.3, 1.2, 1.2), 4.98 (t (br), 1H, J = 6.0), 3.57 (tt, 2H, J = 6.0, 1.5), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (0), 137.1 (0), 133.0 (1), 129.6 (1, 2C), 127.1 (1, 2C), 117.5 (2), 45.6 (2), 21.4 (3); HRMS (EI) calcd for $C_{10}H_{13}NO_2[32]S$ $[M]^+$: 211.0667, found: 211.0680; MS (EI) m/z 211 (M^+, 5), 155 (22), 91 (100), 65 (39), 56 (47).

***N*-Allyl-4-methyl-*N*-(2-methylallyl)benzenesulfonamide (8b).** Amine **7** (1.27 g, 6.0 mmol) was dissolved in acetonitrile (33 mL). Then potassium carbonate (3.90 g, 28.3 mmol) and methallyl bromide (684 μL, 972 mg, 7.2 mmol) were added. The solution was stirred at 60 °C for 12 h. After cooling to ambient temperature it was filtered over celite. All volatiles were removed *in vacuo* and the residue was purified by column chromatography on silica. The title compound **8b** was isolated as a colorless liquid (1.59 g, >98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 8.3), 7.30 (d, 2H, J = 8.2), 5.52 (ddt, H, J = 17.1, 9.8, 6.5), 5.09 (m, 1H), 5.08 (m, 1H), 4.91 (s, 1H), 4.85 (s, 1H), 3.77 (d (br), 2H, J = 6.5), 3.70 (s, 2H), 2.43 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (0), 140.1 (0), 137.6 (0), 132.4 (1), 129.6 (1, 2C), 127.2 (1, 2C), 119.0 (2), 114.2 (2), 52.8 (2), 49.4 (2), 21.4 (3), 19.8 (3); HRMS (EI) calcd for $C_{14}H_{19}NO_2[32]S$ $[M]^+$: 265.1137, found: 265.1146; MS (EI) m/z 265 (M^+,1), 155 (15), 110 (16), 91 (48), 55 (34), 43 (44), 41 (100), 39 (46).

1-(4-Chlorophenyl)-2,5-dihydro-1*H*-pyrrole (9a). To a solution of diallylaniline **2a** (1040 mg, 5.0 mmol) in toluene (10 mL) was added catalyst **G-I** (51.4 mg, 1.3 mol%). The solution was stirred for 1 h at 40 °C. After cooling to ambient temperature all volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica. The title compound was isolated as a colorless solid (655 mg, 73%).

Mp: 113–115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, 2H, J = 9.0), 6.41 (d, 2H, J = 9.0), 5.94–5.89 (2H), 4.04 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6 (0), 129.0 (1, 2C), 126.3 (1, 2C), 120.4 (0), 112.1 (1, 2C), 54.5 (2, 2C); IR: $\tilde{\nu}$ = 3083 (w), 3017 (w), 2941 (w), 2821 (m), 1598 (m), 1501 (s), 1475 (m), 1377 (s); HRMS (EI) calcd for $C_{10}H_{10}N[35]Cl$ $[M]^+$: 179.0502, found: 179.0495; MS (EI) m/z 179 (M^+, 100), 178 (82), 143 (47), 138 (80), 115 (15), 111 (22).

General procedure for the RCM-aromatization of diallyl amines 2 and diallyl ethers 13 to pyrroles 10a–k and furans 14

To a solution of the appropriate precursor **2** or **13** (1.0 mmol) in benzene (1.0 mL, in the case of precursors **2**) or in toluene (1.0 mL, in the case of precursors **13**) was added catalyst **G-I** (41.1 mg, 5 mol%). The solution was stirred for 0.5 h at ambient temperature, before *tert*-butyl hydroperoxide (70% in water, 150 μL, 1.3 mmol) was added dropwise. After stirring for 0.5 h at ambient temperature the product was purified by column chromatography without further work-up.

1-(4-Chlorophenyl)-1*H*-pyrrole (10a). Following the general procedure, **10a** was obtained from **2a** (207 mg, 1.0 mmol) as a colorless solid (170 mg, 96%). Mp: 88–89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, 2H, J = 9.0), 7.28 (d, 2H, J = 9.1), 7.01 (dd, 2H, J = 2.2, 2.2), 6.33 (dd, 2H, J = 2.2, 2.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3 (0), 131.0 (0), 129.5 (1, 2C), 121.5 (1, 2C), 119.2 (1, 2C), 110.8 (1, 2C); IR: $\tilde{\nu}$ = 3131 (w), 3105 (w), 2927 (w), 2246 (w), 1596 (w), 1504 (s), 1471 (w), 1330 (m); HRMS (EI) calcd for $C_{10}H_8N[35]Cl$ $[M]^+$: 177.0345, found: 177.0343; MS (EI) m/z 177 (M^+, 42), 154 (40), 134 (100), 112 (50), 111 (50), 98 (98), 84 (55), 83 (55), 74 (55), 71 (52), 57 (86), 55 (68), 43 (86).

1-Phenyl-1*H*-pyrrole (10b). Following the general procedure, **10b** was obtained from **2b** (173 mg, 1.0 mmol) as a colorless solid (123 mg, 86%). Mp: 58–61 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.35 (4H), 7.23 (m, 1H), 7.11–7.05 (2H), 6.37–6.32 (2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8 (0), 129.5 (1, 2C), 125.6 (1), 120.5 (1, 2C), 119.3 (1, 2C), 110.4 (1, 2C); IR: $\tilde{\nu}$ = 3141 (w), 2827 (w), 1599 (m), 1555 (w), 1510 (s), 1469 (w), 1327 (s); HRMS (EI) calcd for $C_{10}H_9N$ $[M]^+$: 143.0735, found: 143.0733; MS (EI) m/z 143 (M^+, 100), 115 (46).

1-(3-Chloro-2-methylphenyl)-1*H*-pyrrole (10c). Following the general procedure, **10c** was obtained from **2c** (221 mg, 1.0 mmol) as a colorless liquid (188 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 1H), 7.17 (d, 1H, J = 4.1), 7.17 (d, 1H, J = 5.1), 6.75 (dd, 2H, J = 2.1, 2.1), 6.31 (dd, 2H, J = 2.1, 2.1), 2.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.9 (0), 135.6 (0), 133.0 (0), 128.5 (1), 126.7 (1), 125.3 (1), 122.2 (1, 2C), 109.1 (1, 2C), 15.3 (3); IR: $\tilde{\nu}$ = 2924 (w), 2361 (w), 1574 (m), 1492 (s), 1448 (m), 1327 (m); HRMS (EI) calcd for $C_{11}H_{10}N[35]Cl$ $[M]^+$: 191.0496, found: 191.0499; MS (EI) *m*/*z* 193 (M^+, 32), 192 (32), 191 (M^+, 100), 190 (68), 156 (25), 155 (28), 154 (32).

1-(5-Chloro-2-methoxyphenyl)-1*H*-pyrrole (10d). Following the general procedure, **10d** was obtained from **2d** (237 mg, 1.0 mmol) as a colorless liquid (187 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, 1H, J = 2.6), 7.22 (d, 1H, J = 8.8, 2.6), 6.98 (dd, 2H, J = 2.2), 6.94 (d, 1H, J = 8.8), 6.31 (dd, 2H, J = 2.2), 3.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3 (0), 131.1 (0), 126.9 (1), 125.7 (0), 125.1 (1), 121.8 (1, 2C), 113.5 (1), 109.3 (1, 2C), 56.1 (3); IR: $\tilde{\nu}$ = 2936 (w), 1597 (w), 1596 (s), 1479 (m), 1319 (m), 1244 (s); HRMS (EI) calcd for $C_{11}H_{10}ON[35]Cl$ $[M]^+$: 207.0445, found: 207.0444; MS (EI) *m*/*z* 209 (M^+, 26), 208 (23), 207 (M^+, 100), 206 (48).

***N*-Allyl-2,6-dimethylaniline (3e).** Following the general procedure for the RCM-oxidative aromatization of *N*-aryl diallyl amines **2**, substrate **2e** (201 mg, 1.0 mmol) did not react to the desired pyrrole **10e**. Instead, unreacted starting material **2e** (70 mg, 35%) and the deallylation product **3e** (44 mg, 27%) were isolated as colorless liquids. *Analytical data of N-allyl-3-fluoroaniline* (**3e**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, 2H, J = 7.5), 6.82 (dd, 1H, J = 7.7, 7.2), 5.98 (ddt, 1H, J = 17.1, 10.2, 6.1), 5.26 (dddd, 1H, J = 17.1, 1.6, 1.6, 1.6), 5.11 (dddd, 1H, J = 10.1, 1.6, 1.2, 1.2), 3.59 (ddd, 2H, J = 6.0, 1.4, 1.4), 2.92 (s (br), 1H), 2.28 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.9 (0), 136.8 (1), 129.5 (0, 2C), 128.8 (1, 2C), 121.9 (1), 115.9 (2), 51.2 (2), 18.4 (3, 2C).

1-(3-Fluorophenyl)-1*H*-pyrrole (10f). Following the general procedure, **10f** was obtained from **2f** (191 mg, 1.0 mmol) as a colorless liquid (151 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (ddd, 1H, J = 10.0, 6.3, 6.4), 7.18 (ddd, 1H, J = 8.1, 1.9, 0.7), 7.10 (ddd, 1H, J = 10.1, 2.2, 2.2), 7.08 (dd, 2H, J = 2.2, 2.2), 6.93 (dddd, 1H, J = 8.3, 8.2, 2.4, 0.8), 6.35 (dd, 2H, J = 2.2, 2.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (0, d, ^1J = 246.6), 142.2 (1, d, ^3J = 9.8), 130.8 (1, d, ^3J = 9.3), 119.2 (1, 2C), 115.7 (1, d, ^4J = 2.9), 112.3 (d, ^2J = 21.2), 111.0 (1, 2C), 107.8 (1, d, ^2J = 25.1); IR: $\tilde{\nu}$ = 3106 (w), 1612 (s), 1597 (m), 1502 (s), 1455 (m), 1342 (s); HRMS (EI) calcd for $C_{10}H_8NF$ $[M]^+$: 161.0641, found: 161.0640; MS (EI) *m*/*z* 161 (M^+, 18), 133 (15), 83 (21), 75 (24), 71 (34), 69 (36), 57 (98), 55 (100), 43 (86), 41 (36).

1-(3-Nitrophenyl)-1*H*-pyrrole (10g). Following the general procedure, **10g** was obtained from **2g** (218 mg, 1.0 mmol) as a colorless solid (167 mg, 89%). Mp: 73–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (dd, 1H, J = 2.2, 2.1), 8.06 (ddd, 1H, J = 8.1, 2.1, 1.0), 7.71 (ddd, 1H, J = 8.1, 2.2, 0.9), 7.59 (dd, 1H, J = 8.1, 8.1), 7.14 (dd, 2H, J = 2.2, 2.2), 6.40 (dd, 2H, J = 2.2, 2.2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1 (0), 141.5 (0), 130.4 (1), 125.4 (1), 119.9 (1), 119.1 (1, 2C), 114.8 (1), 111.9 (1, 2C); IR: $\tilde{\nu}$ = 3089 (w), 2924 (w), 2653 (w), 1527 (s), 1498 (s), 1343 (s); HRMS (EI) calcd for $C_{10}H_8N_2O_2$ $[M]^+$: 188.0586, found: 188.0576; MS (EI) *m*/*z* 188 (M^+, 88), 142 (74), 141 (80), 115 (100), 114 (28), 89 (25), 76 (25), 63 (28), 51 (30), 50 (45), 39 (47).

***N*-(3-(1*H*-Pyrrol-1-yl)phenyl)acetamide (10h).** To a solution of diallylaniline **2h** (230 mg, 1.0 mmol) in ethyl acetate (5.0 mL) was added catalyst **G-I** (30.5 mg, 5 mol%). The solution was stirred for 0.5 h. During the reaction a solid was formed, which was dissolved after the addition of ethyl acetate (3 mL). Then *tert*-butyl hydroperoxide (70% in water, 112 μL, 0.97 mmol) was added dropwise. After stirring for 0.5 h at this temperature all volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica. The title compound **10h** was isolated as a yellowish solid (109 mg, 55%). Mp: 137–139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s (br), 1H), 7.71 (s (br), 1H), 7.34–7.26 (2H), 7.10 (ddd, 1H, J = 6.7, 2.2, 1.9), 7.05 (dd, 2H, J = 2.2, 2.2), 6.31 (dd, 2H, J = 2.2, 2.2), 2.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7 (0), 141.3 (0), 139.1 (0), 129.9 (1), 119.2 (1, 2C), 116.7 (1), 116.0 (1), 112.0 (1), 110.5 (1, 2C), 24.5 (3); IR: $\tilde{\nu}$ = 3270 (w), 3097 (w), 1666 (m), 1605 (s), 1552 (m), 1495 (s), 1443 (m); HRMS (EI) calcd for $C_{12}H_{12}ON_2$ $[M]^+$: 200.0950, found: 200.0932; MS (EI) *m*/*z* 200 (M^+, 100), 158 (80), 130 (29), 43 (30).

1-(3-Methoxyphenyl)-1*H*-pyrrole (10i). Following the general procedure, **10i** was obtained from **2i** (203 mg, 1.0 mmol) as a colorless liquid (161 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (dd, 1H, J = 8.2, 8.0), 7.07 (dd, 2H, J = 2.2, 2.1), 6.98 (ddd, 1H, J = 7.9, 1.2, 1.0), 6.93 (dd, 1H, J = 1.3, 1.1), 6.78 (ddd, 1H, J = 8.3, 2.3, 2.3), 6.33 (dd, 2H, J = 2.1, 2.0), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (0), 142.0 (0), 130.3 (1), 119.4 (1, 2C), 112.9 (1), 110.9 (1), 110.4 (1, 2C), 106.8 (1), 55.4 (0); IR: $\tilde{\nu}$ = 3100 (w), 3002 (w), 2958 (w), 2836 (w), 1600 (s), 1501 (s), 1482 (w); HRMS (EI) calcd for $C_{11}H_{11}NO$ $[M]^+$: 173.0835, found: 173.0839; MS (EI) *m*/*z* 173 (M^+, 82), 130 (100), 115 (26), 103 (38), 77 (44), 63 (27), 51 (26), 43 (24), 39 (40).

1-(4-Methoxyphenyl)-1*H*-pyrrole (10j). Following the general procedure, **10j** was obtained from **2j** (203 mg, 1.0 mmol) as a colorless solid (150 mg, 87%). Mp: 110–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, 2H, J = 8.9), 7.01–6.96 (2H), 6.93 (d, 2H, J = 8.9), 6.42–6.35 (2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7 (0), 134.5 (0), 122.1 (1, 2C), 119.6 (1, 2C), 114.6 (1, 2C), 109.8 (1, 2C), 55.5 (3); IR: $\tilde{\nu}$ = 3142 (w), 3013 (w), 2961 (w), 2838 (w), 1517 (m), 1463 (w), 1441 (w), 1254 (m); HRMS (EI) calcd for $C_{11}H_{11}NO$ $[M]^+$: 173.0835, found: 173.0834; MS (EI) *m*/*z* 173 (M^+, 80), 158 (100), 130 (58), 103 (18), 77 (22).

1-(4-(1*H*-Pyrrol-1-yl)phenyl)ethanone (10k). Following the general procedure, **10k** was obtained from **2k** (215 mg, 1.0 mmol) as a colorless liquid (163 mg, 88%). Mp: 120–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 8.8), 7.45 (d, 2H, J = 8.8), 7.16 (dd, 2H, J = 2.3, 2.1), 6.38 (dd, 2H, J = 2.3, 2.1), 2.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)

δ 196.6 (0), 144.0 (0), 134.0 (0), 130.1 (1, 2C), 119.3 (1, 2C), 118.9 (1, 2C), 111.6 (1, 2C), 26.4 (0); IR: $\tilde{\nu}$ = 3338 (w), 3139 (w), 3110 (w), 3060 (w), 3006 (w), 1680 (s), 1598 (s), 1520 (m), 1468 (m), 1426 (m), 1360 (m); HRMS (EI) calcd for $C_{12}H_{11}NO$ $[M]^+$: 185.0841, found: 185.0849; MS (EI) *m*/*z* 185 (M^+, 100), 170 (74), 142 (42), 141 (24), 115 (32).

2-Pentylfuran (14a). Following the general procedure, **14a** was obtained from **13a** (168 mg, 1.0 mmol) as a colorless liquid (90 mg, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 1H), 6.27 (dd, 1H, J = 2.0, 1.9), 5.97 (m, 1H), 2.61 (t, 2H, J = 7.6), 1.70–1.57 (2H), 1.39–1.23 (4H), 0.96–0.84 (3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (0), 140.6 (1), 110.0 (1), 104.5 (1), 31.4 (2), 28.0 (2), 27.7 (2), 22.4 (2), 14.0 (3); IR: $\tilde{\nu}$ = 2957 (s), 2927 (s), 2858 (m), 1797 (w), 1720 (w), 1467 (w).

2-Phenylfuran (14b). Following the general procedure, **14b** was obtained from **13b** (174 mg, 1.0 mmol) as a colorless liquid (85 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70–7.64 (2H), 7.46 (m, 1H), 7.41–7.33 (2H), 7.24 (m, 1H), 6.64 (d, 1H, J = 3.4), 6.46 (dd, 1H, J = 3.4, 1.7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0 (0), 142.0 (1), 130.9 (0), 128.6 (1, 2C), 127.3 (1), 123.8 (1, 2C), 111.6 (1), 104.9 (1).

2-(4-Bromophenyl)furan (14c). Following the general procedure, **14c** was obtained from **13c** (252 mg, 1.0 mmol) as a colorless solid (114 mg, 52%). Mp: 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.50 (4H), 7.50 (dd, 1H, J = 1.8, 0.7), 6.68 (dd, 1H, J = 3.4, 0.6), 6.50 (dd, 1H, J = 3.4, 1.8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0 (0), 142.4 (1), 131.8 (1, 2C), 129.8 (0), 125.3 (1, 2C), 121.1 (0), 111.8 (1), 105.5 (1); IR: $\tilde{\nu}$ = 2927 (w), 1729 (w), 1495 (m), 1469 (m), 1405 (w), 1220 (w), 1157 (m), 1072 (w), 1009 (s).

2-(4-Methoxyphenyl)furan (14d). Following the general procedure, **14d** was obtained from **13d** (204 mg, 1.0 mmol) as a colorless solid (62 mg, 36%). Mp: 54–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, 2H, J = 8.8), 7.41 (d, 1H, J = 1.2), 6.91 (d, 2H, J = 8.9), 6.40 (d (br), 1H, J = 3.2), 6.43 (dd, 1H, J = 3.3, 1.8), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1 (0), 154.1 (0), 141.4 (1), 125.2 (1, 2C), 124.1 (0), 114.1 (1, 2C), 111.5 (1), 103.4 (1), 55.3 (3); IR: $\tilde{\nu}$ = 3004 (w), 2958 (w), 2837 (w), 1613 (w), 1513 (s), 1484 (w), 1297 (m), 1247 (s).

(*R*)-2-(Furan-2-yl)-1,4-dioxaspiro[4.5]decane (14e). Following the general procedure, **14e** was obtained from **13e** (238 mg, 1.0 mmol) as a colorless liquid (56 mg, 27%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, 1H, J = 1.5, 1.0), 6.38–6.33 (2H), 5.09 (dd, 1H, J = 7.1, 6.7), 4.22 (dd, 1H, J = 8.3, 6.4), 4.08 (dd, 1H, J = 8.2, 7.4), 1.80–1.30 (10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2 (0), 142.7 (1), 110.5 (0), 110.3 (1), 108.1 (1), 71.0 (1), 67.7 (2), 35.9 (2), 35.5 (2), 25.1 (2), 23.9 (2), 23.9 (2); IR: $\tilde{\nu}$ = 2934 (m), 2859 (w), 1449 (w), 1366 (w), 1336 (w), 1279 (w), 1161 (m), 1101 (s).

General procedure for the RCM-aromatization of *N*-aryl diallyl amines 4a,f

To a solution of the appropriate *N*-aryl diallylamine **4** (0.75 mmol) in toluene (7.5 mL) was added catalyst **G-II** (30.5 mg, 5 mol%). The solution was stirred for 0.5 h at 80 °C. After cooling to ambient temperature *tert*-butyl hydroperoxide (70% in water, 112 μL, 0.97 mmol) was added dropwise. After stirring for 0.5 h at this temperature all volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica.

1-(4-Chlorophenyl)-3-methyl-1*H*-pyrrole (10l). Following the general procedure, **10l** was obtained from **4a** (166 mg, 0.75 mmol) as a colorless solid (124 mg, 87%). Mp: 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, 2H, J = 9.0), 7.26 (d, 2H, J = 9.0), 6.94 (dd, 1H, J = 2.6, 2.5), 6.82 (m, 1H), 6.18 (dd, 1H, J = 2.2, 2.0), 2.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.3 (0), 130.4 (0), 129.5 (1, 2C), 121.6 (0), 121.0 (1, 2C), 118.9 (1), 117.0 (1), 112.4 (1), 11.9 (3); IR: $\tilde{\nu}$ = 2923 (w), 2923 (w), 1714 (m), 1598 (m), 1504 (s), 1495 (s), 1454 (m), 1386 (m), 1349 (m); HRMS (EI) calcd for $C_{11}H_{10}N$[35]Cl $[M]^+$: 191.0502, found: 191.0496; MS (EI) *m*/*z* 191 (M^+, 68), 190 (70), 138 (18), 127 (22), 111 (44), 75 (54), 69 (44), 53 (30), 51 (34), 41 (34), 39 (100).

1-(3-Fluorophenyl)-3-methyl-1*H*-pyrrole (10m). Following the general procedure, **10m** was obtained from **4f** (154 mg, 0.75 mmol) as a colorless solid (121 mg, 92%). Mp: 57–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (ddd, 1H, J = 10.0, 6.3, 6.3), 7.17 (ddd, 1H, J = 8.1, 2.1, 0.8), 7.10 (ddd, 1H, J = 10.3, 2.3, 2.2), 7.02 (dd, 1H, J = 2.6, 2.5), 6.93 (dddd, 1H, J = 8.3, 8.3, 2.4, 0.9), 6.90 (m, 1H), 6.23 (dd, 1H, J = 2.3, 1.9), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (0, d, ^1J = 246.2), 142.2 (0, d, ^3J = 10.2), 130.7 (1, d, ^3J = 9.4), 121.7 (0), 118.8 (1), 116.9 (1), 115.1 (1, d, ^4J = 2.9), 112.6 (1), 111.7 (1, d, ^2J = 21.2), 107.1 (1, d, ^2J = 25.0), 11.9 (3); IR: $\tilde{\nu}$ = 3092 (w), 2923 (w), 2359 (w), 1713 (m), 1612 (s), 1596 (s), 1502 (s), 1455 (m), 1387 (m), 1352 (s); HRMS (EI) calcd for $C_{11}H_{10}NF$ $[M]^+$: 175.0797, found: 175.0799; MS (EI) *m*/*z* 175 (M^+, 10), 122 (30), 95 (58), 75 (56), 69 (92), 68 (34), 57 (35), 43 (64), 41 (78), 39 (100).

1-Tosyl-1*H*-pyrrole (12a). To a solution of the RCM precursor **8a** (251 mg, 1.0 mmol) in benzene (1.0 mL) was added catalyst **G-I** (41.1 mg, 5 mol%). The solution was stirred for 0.5 h at ambient temperature, before *tert*-butyl hydroperoxide (5.5 M in decane, 360 μL, 2.0 mmol) was added dropwise. After stirring for 0.5 h at ambient temperature the product was purified by column chromatography without further work-up. The title compound was isolated as a colorless solid (170 mg, 77%). Mp: 99–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, 2H, J = 8.4), 7.27 (d, 2H, J = 8.1), 7.15 (dd, 2H, J = 2.3, 2.3), 6.27 (dd, 2H, J = 2.3, 2.3), 2.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9 (0), 136.1 (0), 129.9 (1, 2C), 126.7 (1, 2C), 120.7 (1, 2C), 113.4 (1, 2C), 21.5 (3); IR: $\tilde{\nu}$ = 3140 (w), 1594 (w), 1536 (w), 1457 (w), 1359 (s), 1308 (m); HRMS (EI) calcd for $C_{11}H_{11}NO_2$[32]S $[M]^+$: 221.0511, found: 221.0508; MS (EI) *m*/*z* 221 (M^+, 100), 155 (58), 91 (100), 65 (21), 39 (14).

3-Methyl-1-tosyl-1*H*-pyrrole (12b) and 3-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (11b). To a solution of the RCM precursor **8b** (199 mg, 0.75 mmol) in toluene (7.5 mL) was added catalyst **G-II** (30.5 mg, 5 mol%). The solution was stirred for 0.5 h at 80 °C. After cooling to ambient temperature *tert*-butyl hydroperoxide (5.5 M in decane, 270 μL, 1.5 mmol) was added dropwise.

After stirring for 0.5 h at this temperature all volatiles were removed *in vacuo*. The residue was purified by column chromatography on silica. Compound **12b** was isolated as a colorless solid (88 mg, 50%). **12b** could be separated from 3-methyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (**11b**), which was isolated as a colorless solid (29 mg, 16%). *Analytical data for 3-methyl-1-tosyl-1H-pyrrole* (**12b**): Mp: 62–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.4), 7.27 (d, 2H, J = 8.5), 7.05 (dd, 1H, J = 2.8, 2.6), 6.88 (m, 1H), 6.11 (dd, 1H, J = 3.1, 1.6), 2.38 (s, 3H), 2.01 (d, 3H, J = 0.9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6 (0), 136.4 (0), 129.8 (1, 2C), 126.7 (1, 2C), 124.4 (0), 120.8 (1), 117.8 (1), 115.7 (1), 21.5 (3), 11.8 (3); IR: $\tilde{\nu}$ = 3136 (w), 2925 (w), 1596 (w), 1472 (w), 1364 (s), 1261 (s); HRMS (EI) calcd for $C_{12}H_{13}NO_2[32]S$ $[M]^+$: 235.0662, found: 235.0665; MS (EI) *m*/*z* 235 (M^+, 75), 155 (46), 91 (100), 65 (20). *Analytical data for 3-methyl-1-tosyl-2,5-dihydro-1H-pyrrole* (**11b**): Mp: 96–98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, 2H, J = 8.3), 7.32 (d, 2H, J = 8.3), 5.26 (m, 1H, J = 2.8, 2.6), 4.11–4.04 (2H), 4.01–3.94 (2H), 2.43 (s, 3H), 1.69–1.64 (3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.3 (0), 135.0 (0), 134.4 (0), 129.7 (1, 2C), 127.4 (1, 2C), 119.0 (1), 120.8 (1), 57.6 (2), 55.1 (2), 21.4 (3), 14.0 (3).

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