Supporting information

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

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A 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 ($\delta = 0.00$ 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$_3$ ($\delta = 77.0$ 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 in substance on NaCl or KBr plates. Wavenumbers ($\nu$) are given in cm$^{-1}$. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70eV.
Experimental procedures, analytical data and copies of NMR-spectra

B1 General procedure for the Synthesis of N-aryl diallylanilines 2 from anilines 1

The appropriate Aniline 1 (20 mmol) was dissolved in a mixture of ethanol (64 mL) and water (16 mL). Then Na₂CO₃ (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 over MgSO₄, filtered and all volatiles were removed in vacuo. The residue was purified by column chromatography.
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$_3$) $\delta$ 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$_3$) $\delta$ 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\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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).
$^1$H NMR spectrum of 2b

$^{13}$C NMR spectrum of 2b
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$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^1$H NMR spectrum of 2c

$^{13}$C NMR spectrum of 2c
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$_3$) $\delta$ 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$_3$) $\delta$ 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), 2976 (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$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^1$H NMR spectrum of 2e

$^{13}$C NMR spectrum of 2e
$N,N$-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$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu$ = 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).
1H NMR spectrum of 2f

13C NMR spectrum of 2f
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): ¹H NMR (300 MHz, CDCl₃) 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 (ddddd, 2H, J = 9.2, 1.6, 1.5, 1.5), 5.17 (ddd, 2H, J = 17.0, 1.6, 1.4, 1.4), 3.98 (dt, J = 4.7, 2.1); ¹³C NMR (75 MHz, CDCl₃) 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: ν = 3085 (w), 2981 (w), 2866 (w), 1616 (m), 1522 (s), 1494 (m), 1389 (m), 1342 (s), 1236 (m); HRMS (EI) calcd for C₁₂H₁₄N₂O₂ [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 (2g): Mp: 66 – 68 °C; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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).
$^1$H NMR spectrum of 3g

$^{13}$C NMR spectrum of 3g
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, 1H NMR (300 MHz, CDCl₃) 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); 13C NMR (75 MHz, CDCl₃) 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: υ = 3301 (m), 3081 (w), 2979 (w), 2922 (w), 1663 (s), 1610 (s), 1583 (s), 1551 (s), 1496 (s), 1434 (m); HRMS (EI) calcd for C₁₄H₁₈N₂O [M⁺]: 230.1419, found: 230.1412; MS (EI) m/z 230 (M⁺, 100), 215 (31), 161 (29), 145 (20).
**¹H NMR spectrum of 2h**

**¹³C NMR spectrum of 2h**
**N,N-Diallyl-3-methoxyaniline (2i)**

Following the general procedure, 2i was obtained from 1i (2.46 g, 20mmol) as a colorless liquid (3.16 g, 78%). $^1$H NMR (300 MHz, CDCl₃) $\delta$ 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 (ddddd, 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, CDCl₃) $\delta$ 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 C₁₃H₁₇NO [M$^+$]: 203.1310, found: 203.1301; MS (EI) $m/z$ 203 (M$^+$, 22), 77 (22), 41 (100), 39 (47).
$^1$H NMR spectrum of 2i

$^{13}$C NMR spectrum of 2i
$N,N$-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$_3$) $\delta$ 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 (ddddd, 2H, $J = 17.2, 1.6, 1.3, 1.3$), 5.12 (ddddd, 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$_3$) $\delta$ 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).
$^1$H NMR spectrum of 2j

$^{13}$C NMR spectrum of 2j
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$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^{1}H$ NMR spectrum of 2k

$^{13}C$ NMR spectrum of 2k
**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 Na₂CO₃ (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 MgSO₄, 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% d. Th.). Analytical data for 2a synthesized via this protocol are identical to those reported above. **Analytical data of N-Allyl-4-chloroaniline (3a):** ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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: \( \nu = 3419 \) (m), 3080 (w), 2848 (w), 1862 (w), 1598 (m), 1497 (s), 1315 (m), 1259 (m); HRMS (EI) caled for C₉H₁₀N[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).
**^1H NMR spectrum of 3a**

**^13C NMR spectrum of 3a**
**N-Allyl-4-chloro-N-(2-methylallyl)aniline (4a)**

Aniline 3a (835 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K$_2$CO$_3$(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), 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 Na₂CO₃ (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 MgSO₄, 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% d. Th.). Analytical data for 2f synthesized via this protocol are identical to those reported above. *Analytical data of N-Allyl-3-fluoroaniline (3f):* 

**1H NMR (300 MHz, CDCl₃)** \( \delta \): 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, \( J = 10.3, 1.5, 1.5, 1.5 \)), 3.94 (s (br), 1H), 3.79 (dt, 2H, \( J = 5.3, 1.6 \)); **13C NMR (75 MHz, CDCl₃)** \( \delta \): 164.1 (0, d, \( J = 242.4 \)), 149.9 (0, d, \( J = 10.8 \)), 134.9 (1), 130.2 (1, d, \( J = 10.3 \)), 116.3 (2), 108.8 (1, d, \( J = 2.3 \)), 103.8 (1, d, \( J = 21.6 \)), 99.6 (1, d, \( J = 25.4 \)), 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 C₉H₁₀NF [M]⁺: 151.0792, found: 151.0784; **MS (EI)** \( m/z \): 151 (M⁺, 100), 150 (30), 124 (35), 43 (78), 41 (96).
$^{1}$H NMR spectrum of 3f

$^{13}$C NMR spectrum of 3f
N-Allyl-3-fluoro-N-(2-methylallyl)aniline (4f)

Aniline 3f (756 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K$_2$CO$_3$ (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$_3$) $\delta$ 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$_3$) $\delta$ 164.1 (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: $\nu$ = 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).
$^1$H NMR spectrum of 4f

$^{13}$C NMR spectrum of 4f
**N- Allyl-2,6-dimethylaniline (3e)**

After applying the conditions of the general procedure B2 for substrate **2e** (201mg, 1.0mmol), the desired pyrrole **10e** could not be isolated. Instead unreacted starting material **2e** (70 mg, 35%) and the secondary amine **3e** (44 mg, 27%) were isolated as a colorless liquids. Analytical data for **2e** are identical to those reported above. *Analytical data of N- Allyl-3-fluoroaniline (3e):* \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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 (ddddd, 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\(_3\)) \(\delta\) 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).
$^{1}H$ NMR spectrum of 3e

$^{13}C$ NMR spectrum of 3e
**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 MgSO₄, 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; ¹H NMR (300 MHz, CDCl₃) 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 (ddddd, 1H, J = 17.1, 1.5, 1.5, 1.5, 1.5), 5.08 (ddddd, 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₀H₁₃NO₂S [M]+: 211.0667, found: 211.0680; MS (EI) m/z 211 (M⁺, 5), 155 (22), 91 (100), 65 (39), 56 (47).
$^1$H NMR spectrum of 7

$^{13}$C NMR spectrum of 7
**N,N-Diallyl-4-methylbenzenesulfonamide (8a)**

*p*-Toluenesulfonamide (5) (6.34 g, 36.4 mmol) was dissolved in acetonitrile (200 mL). Then K₂CO₃ (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%). **¹H NMR** (300 MHz, CDCl₃) 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); **¹³C NMR** (75 MHz, CDCl₃) 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 C₁₃H₁₇NO₂[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).

**Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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$^1$H NMR spectrum of 8a

$^{13}$C NMR spectrum of 8a
**N- Allyl-4-methyl-N-(2-methylallyl)benzenesulfonamide (8b)**

Amine 7 (1.27 g, 6.0 mmol) was dissolved in acetonitrile (33 mL). Then K₂CO₃ (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%). ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 C₁₄H₁₉NO₂[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).
$^1$H NMR spectrum of 8b

$^{13}$C NMR spectrum of 8b
B2 General procedure for the RCM-aromatization

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 0.5 h at ambient temperature the product was purified by column chromatography without further work up.

B3 General procedure for the synthesis of disubstituted pyrrolo 10l and 10m via RCM-aromatization

To a solution of the appropriate Diallylaniline 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 hydperoxide (70% in water, 112 μL, 0.97 mmol) was added dropwise. After stirring 0.5 h at this temperature all volatiles were removed in vacuo. The residue was purified by column chromatography on silica.
1-(4-Chlorophenyl)-2,5-dihydro-1H-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: ν = 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).
$^1$H NMR spectrum of 9a

$^{13}$C NMR spectrum of 9a
1-(4-Chlorophenyl)-1H-pyrrole (10a)

Following the general procedure B2, 10a was obtained from 2a (207mg, 1.0mmol) as a colorless solid (170 mg, 96%). Mp: 88 – 89°C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 139.3 (0), 131.0 (0), 129.5 (1, 2C), 121.5 (1, 2C), 119.2 (1, 2C), 110.8 (1, 2C); IR: \(\nu = 3131\) (w), 3105 (w), 2927 (w), 2246 (w), 1596 (w), 1504 (s), 1471 (w), 1330 (m); HRMS (EI) calcd for C\(_{10}\)H\(_8\)N[35]Cl \([\text{M}]^+\): 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).
$^{1}H$ NMR spectrum of 10a

$^{13}C$ NMR spectrum of 10a
1-Phenyl-1H-pyrrole (10b)

Following the general procedure B2, 10b was obtained from 2b (173mg, 1.0mmol) as a colorless solid (123 mg, 86%). Mp: 58 – 61 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 140.8 (0), 129.5 (1, 2C), 125.6 (1), 120.5 (1, 2C), 119.3 (1, 2C), 110.4 (1, 2C); IR: $\nu$ = 3141 (w), 2827 (w), 1599 (m), 1555 (w), 1510 (s), 1469 (w), 1327 (s); HRMS (EI) calcd for C$_{10}$H$_9$N [M$^+$]: 143.0735, found: 143.0733; MS (EI) $m$/z 143 (M$^+$, 100), 115 (46).
$^{1}H$ NMR spectrum of 10b

$^{13}C$ NMR spectrum of 10b
1-(3-Chloro-2-methylphenyl)-1H-pyrrole (10c)

Following the general procedure B2, 10c was obtained from 2c (221 mg, 1.0 mmol) as a colorless liquid (188 mg, 98%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu$ = 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).
$^{1}$H NMR spectrum of 10c

$^{13}$C NMR spectrum of 10c
1-(5-Chloro-2-methoxyphenyl)-1H-pyrrole (10d)

Following the general procedure B2, 10d was obtained from 2d (237mg, 1.0mmol) as a colorless liquid (187 mg, 90%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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: \(\nu\) = 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).
$^1$H NMR spectrum of 10d

$^{13}$C NMR spectrum of 10d
Following the general procedure B2, 10f was obtained from 2f (191mg, 1.0mmol) as a colorless liquid (151 mg, 94%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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 (ddddd, 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$_3$) $\delta$ 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: $\bar{v}$ = 3106 (w), 1612 (s), 1597 (m), 1502 (s), 1455 (m), 1342 (s); HRMS (EI) calcd for C$_{10}$H$_8$NF [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).
$^{1}$H NMR spectrum of 10f

$^{13}$C NMR spectrum of 10f
1-(3-Nitrophenyl)-1H-pyrrole (10g)

Following the general procedure B2, 10g was obtained from 2g (218mg, 1.0mmol) as a colorless solid (167 mg, 89%). Mp: 73 – 74 °C; $^1$H NMR (300 MHz, CDCl3) $\delta$ 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, CDCl3) $\delta$ 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: $\nu$ = 3089 (w), 2924 (w), 2653 (w), 1527 (s), 1498 (s), 1343 (s); HRMS (EI) calcd for C$_{10}$H$_8$N$_2$O$_2$ [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).
$^1$H NMR spectrum of 10g

$^{13}$C NMR spectrum of 10g
**N-(3-(1H-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 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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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: ʋ = 3270 (w), 3097 (w), 1666 (m), 1605 (s), 1552 (m), 1495 (s), 1443 (m); HRMS (EI) calcd for C₁₂H₁₂O₂N₂ [M⁺]: 200.0950, found: 200.0932; MS (EI) m/z 200 (M⁺, 100), 158 (80), 130 (29), 43 (30).
$^{1}H$ NMR spectrum of 10h

$^{13}C$ NMR spectrum of 10h
1-(3-Methoxyphenyl)-1H-pyrrole (10i)

Following the general procedure B2, 10i was obtained from 2i (203mg, 1.0mmol) as a colorless liquid (161 mg, 93%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu$ = 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).
$^1$H NMR spectrum of 10i

$^{13}$C NMR spectrum of 10i
1-(4-Methoxyphenyl)-1H-pyrrole (10j)

Following the general procedure B2, 10j was obtained from 2j (203mg, 1.0mmol) as a colorless solid (150 mg, 87%). Mp: 110 – 111 °C; 1H NMR (300 MHz, CDCl3) 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); 13C NMR (75 MHz, CDCl3) 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: ν = 3142 (w), 3013 (w), 2961 (w), 2838 (w), 1517 (m), 1463 (w), 1441 (w), 1254 (m); HRMS (EI) calcd for C11H11NO [M]+: 173.0835, found: 173.0834; MS (EI) m/z 173 (M+, 80), 158 (100), 130 (58), 103 (18), 77 (22).
\(^1\)H NMR spectrum of 10j

\(^13\)C NMR spectrum of 10j
1-(4-(1H-Pyrrol-1-yl)phenyl)ethanone (10k)

Following the general procedure B2, 10k was obtained from 2k (215mg, 1.0mmol) as a colorless liquid (163 mg, 88%). Mp: 120 – 122 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu$ = 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).
$^1$H NMR spectrum of 10k

$^{13}$C NMR spectrum of 10k
1-(4-Chlorophenyl)-3-methyl-1H-pyrrole (10l)

Following the general procedure B3, 10l was obtained from 4a (166mg, 0.75mmol) as a colorless solid (124 mg, 87%). Mp: 80 – 82 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^1$H NMR spectrum of 10l

$^{13}$C NMR spectrum of 10l
1-(3-Fluorophenyl)-3-methyl-1H-pyrrole (10m)

Following the general procedure B3, 10m was obtained from 4f (154mg, 0.75mmol) as a colorless solid (121 mg, 92%). Mp: 57 – 59 °C; 1H NMR (300 MHz, CDCl3) 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 (ddddd, 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); 13C NMR (75 MHz, CDCl3) δ 163.4 (0, d, 3J = 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: v = 3092 (w), 2923 (w), 2359 (w), 1713 (m), 1612 (s), 1596 (s), 1502 (s), 1455 (m), 1387 (m), 1352 (s); HRMS (EI) calcd for C11H10NF [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).
\(^1\)H NMR spectrum of 10m

\(^{13}\)C NMR spectrum of 10m
1-Tosyl-1H-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 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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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: ν = 3140 (w), 1594 (w), 1536 (w), 1457 (w), 1359 (s), 1308 (m); HRMS (EI) calcd for C₁₁H₁₁NO₂[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-1H-pyrrole (12b) and 3-Methyl-1-tosyl-2,5-dihydro-1H-pyrrole (11b)

To a solution 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 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-1H-pyrrole (11b), which was isolated as a colorless solid (29 mg, 16% d. Th.).

**Analytical data for 3-Methyl-1-tosyl-1H-pyrrole (12b):** Mp: 62 – 64 °C; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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: ν = 3136 (w), 2925 (w), 1596 (w), 1472 (w), 1364 (s), 1261 (s); HRMS (EI) calcd for C₁₂H₁₃NO₂S[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; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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).
$^1$H NMR spectrum of 12b

$^{13}$C NMR spectrum of 12b
$^1$H NMR spectrum of 11b

$^{13}$C NMR spectrum of 11b
2-Pentylfuran (14a)

Following the general procedure B2, 14a was obtained from 13a (168 mg, 1.0 mmol) as a colorless liquid (90 mg, 65%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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).
\(^1\)H NMR spectrum of 14a

\(^13\)C NMR spectrum of 14a
2-Phenylfuran (14b)

Following the general procedure B2, 14b was obtained from 13b (174mg, 1.0mmol) as a colorless liquid (85 mg, 59%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^1$H NMR spectrum of 14b

$^{13}$C NMR spectrum of 14b
2-(4-Bromophenyl)furan (14c)

Following the general procedure B2, 14c was obtained from 13c (252mg, 1.0mmol) as a colorless solid (114 mg, 52%). Mp: 78 – 80 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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).
$^{1}$H NMR spectrum of 14c

$^{13}$C NMR spectrum of 14c
2-(4-Methoxyphenyl)furan (14d)

Following the general procedure B2, 14d was obtained from 13d (204mg, 1.0mmol) as a colorless solid (62 mg, 36%). Mp: 54 – 55 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu = 3004$ (w), 2958 (w), 2837 (w), 1613 (w), 1513 (s), 1484 (w), 1297 (m), 1247 (s).
$^1$H NMR spectrum of 14d

$^{13}$C NMR spectrum of 14d
(R)-2-(Furan-2-yl)-1,4-dioxaspiro[4.5]decane (14e)

Following the general procedure B2, 14e was obtained from 13e (238mg, 1.0mmol) as a colorless liquid (56 mg, 27%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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: $\nu$ = 2934 (m), 2859 (w), 1449 (w), 1366 (w), 1336 (w), 1279 (w), 1161 (m), 1101 (s).
$^1$H NMR spectrum of 14e

$^{13}$C NMR spectrum of 14e
B4 Control experiment 1: aromatization in the absence of Ru-catalyst

Purified (via repeated column chromatography) dihydropyrrole 9a (179 mg, 1.0 mmol) was dissolved in toluene (1.0 mL) To this solution 1BuOOH (70% in water, 150 µL, 1.3 mmol) was added dropwise. The reaction mixture was stirred for 15 h. Then all volatiles were removed in vacuo. The residue was immediately subjected to NMR spectroscopy. Ratios of product 10a to starting material 9a were determined by the integration of two baseline separated signals.

B5 Control experiment 2: aromatization in the presence of BHT

Purified (via repeated column chromatography) dihydropyrrole 9a (179 mg, 1.0 mmol) and 3,5-di-t-butyl-4-hydroxytoluene (BHT) were dissolved in toluene (1.0 mL) To this solution 1BuOOH (70% in water, 150 µL, 1.3 mmol) was added dropwise. The reaction mixture was stirred for 2 h. Then all volatiles were removed in vacuo. The residue was immediately subjected to NMR spectroscopy. Ratios of product 10a to starting material 9a were determined by the integration of two baseline separated signals.