Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

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 (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 parantheses following the chemical shift value. IR spectra were recorded in substance on NaCl or KBr plates. Wavenumbers ($\tilde{\upsilon}$) are given in cm^{-1}. The peak intensities are defined as strong (s), medium (m) or weak (w). Mass spectra were obtained at 70eV.

B Experimental procedures, analytical data and copies of NMR-spectra

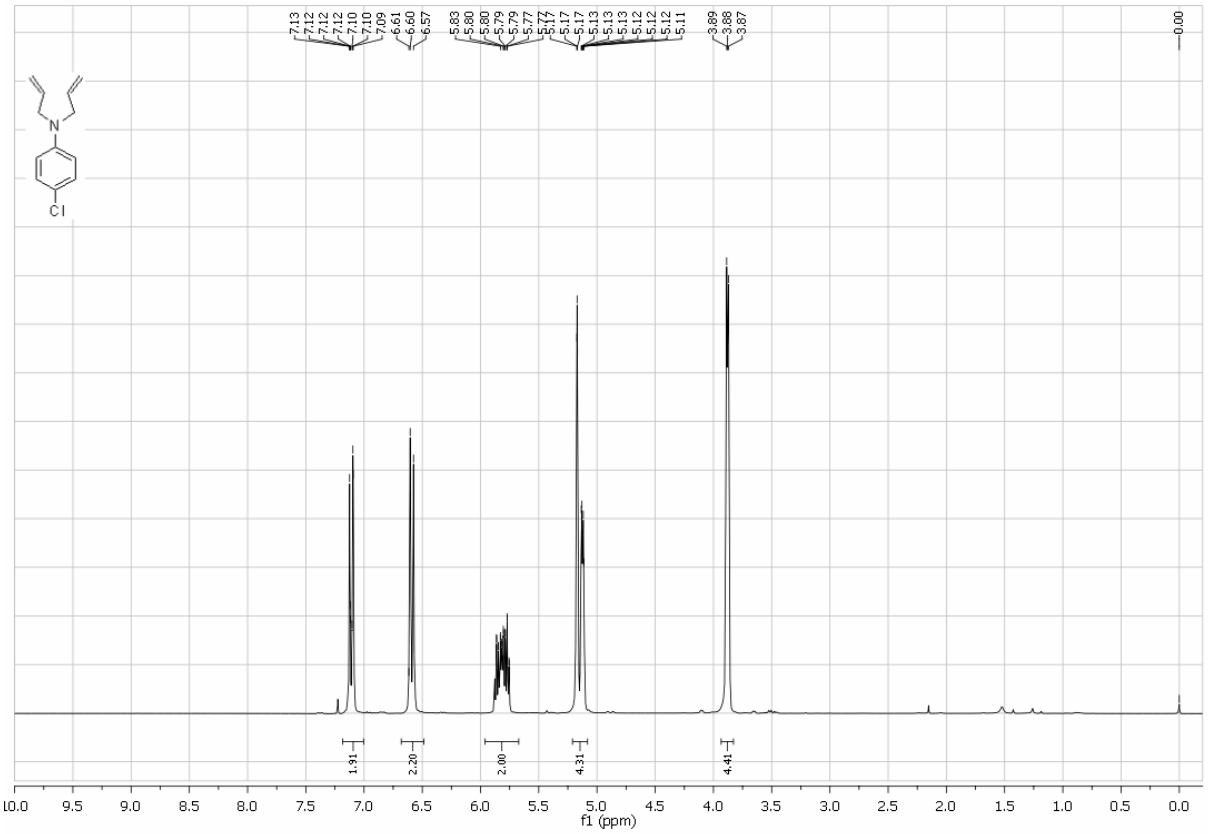
*B1 General procedure for the Synthesis of N-aryl diallylanilines **2** from anilines **1***

The appropriate Aniline **1** (20 mmol) was dissolved in a mixture of ethanol (64 mL) and water (16 mL). Then 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 over $MgSO_4$, filtered and all volatiles were removed in vacuo. The residue was purified by column chromatography.

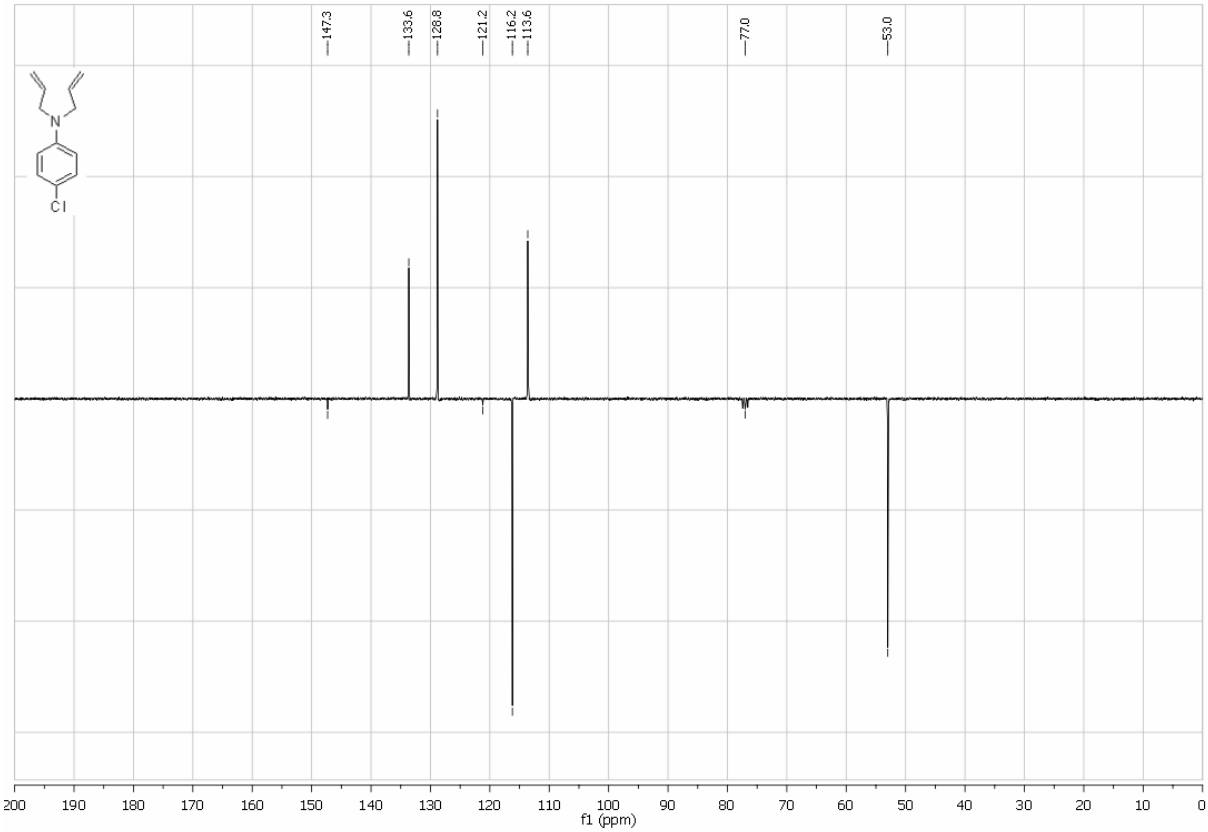
***N*,*N*-Diallyl-4-chloroaniline (2a)**

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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 2a



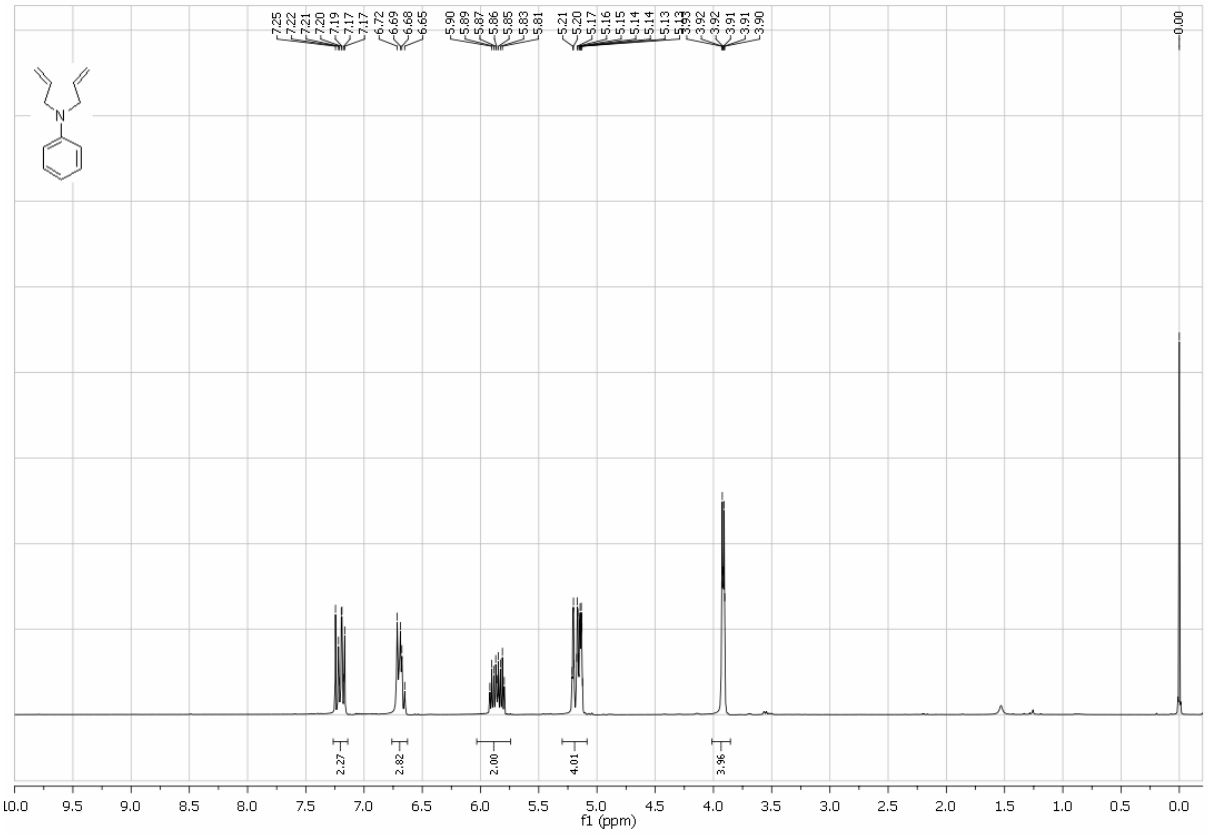
^{13}C NMR spectrum of 2a



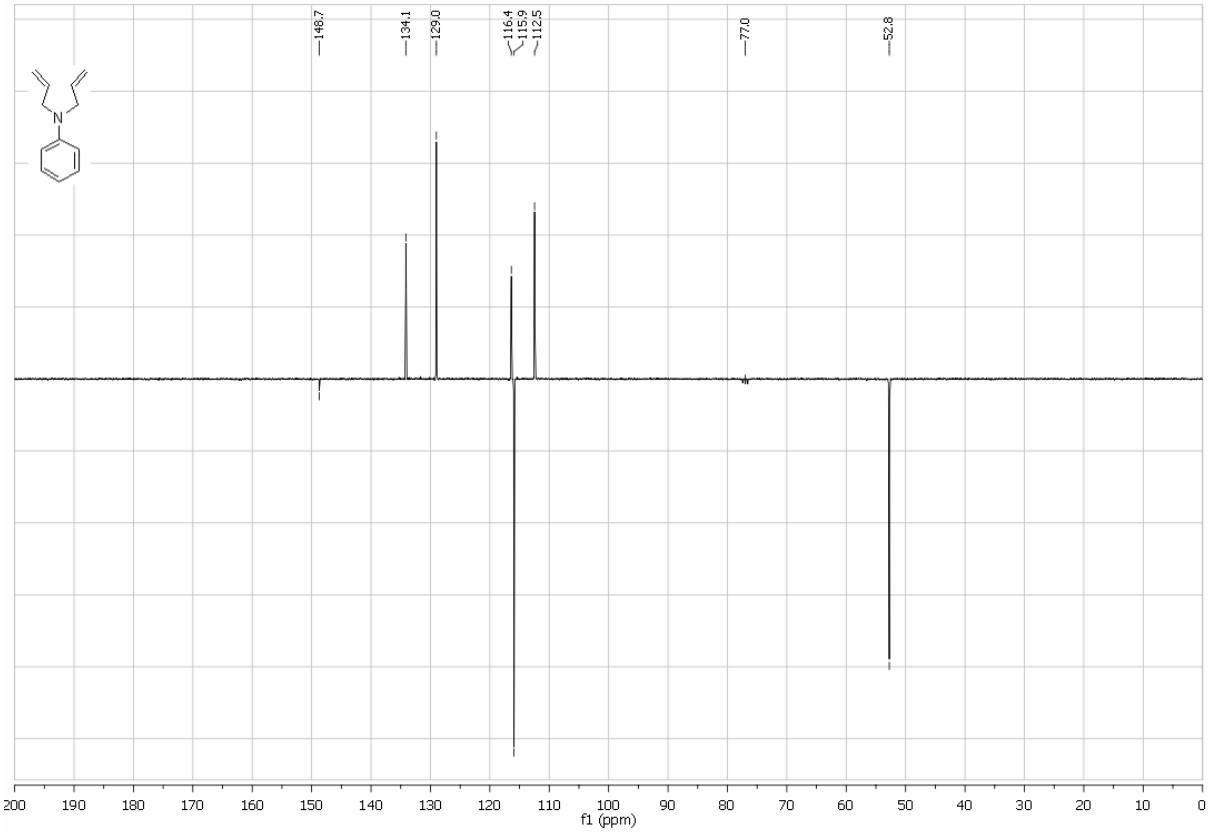
***N*,*N*-Diallylaniline (2b)**

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: $\tilde{\upsilon}$ = 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



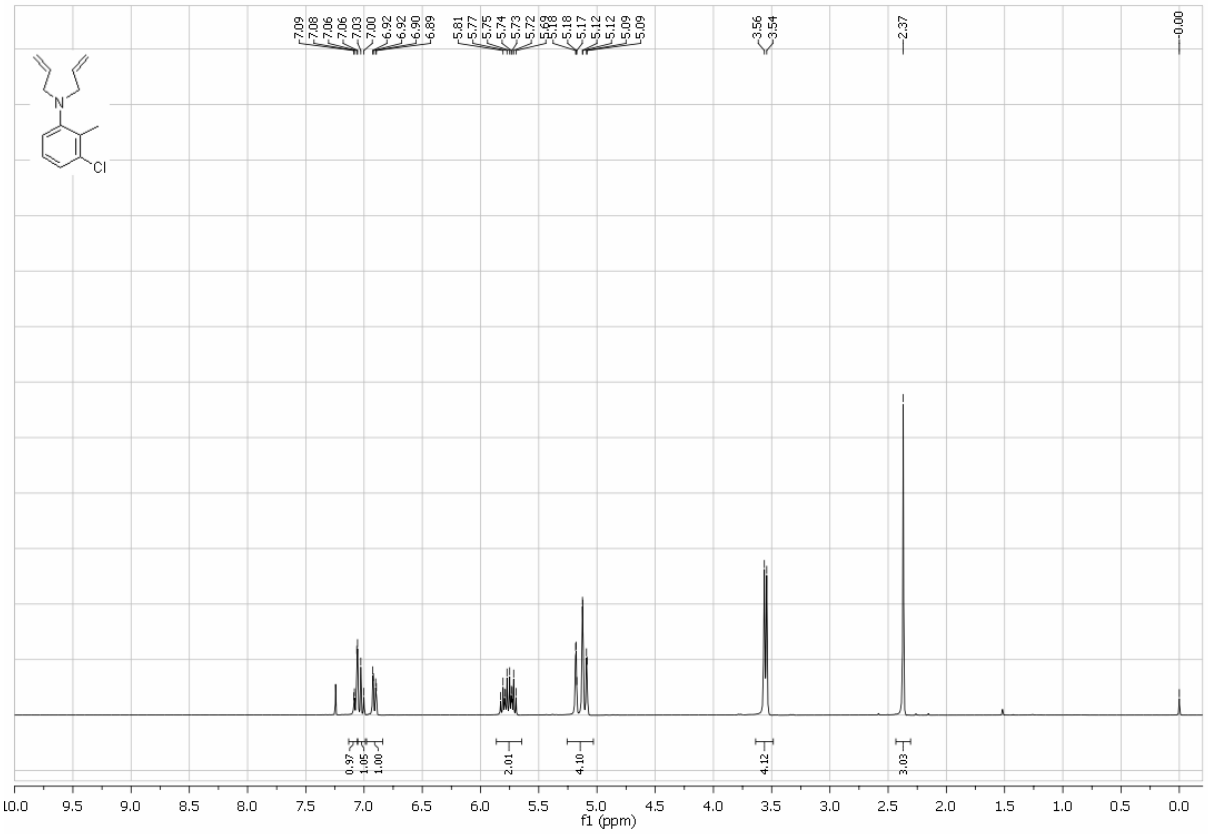
^{13}C NMR spectrum of 2b



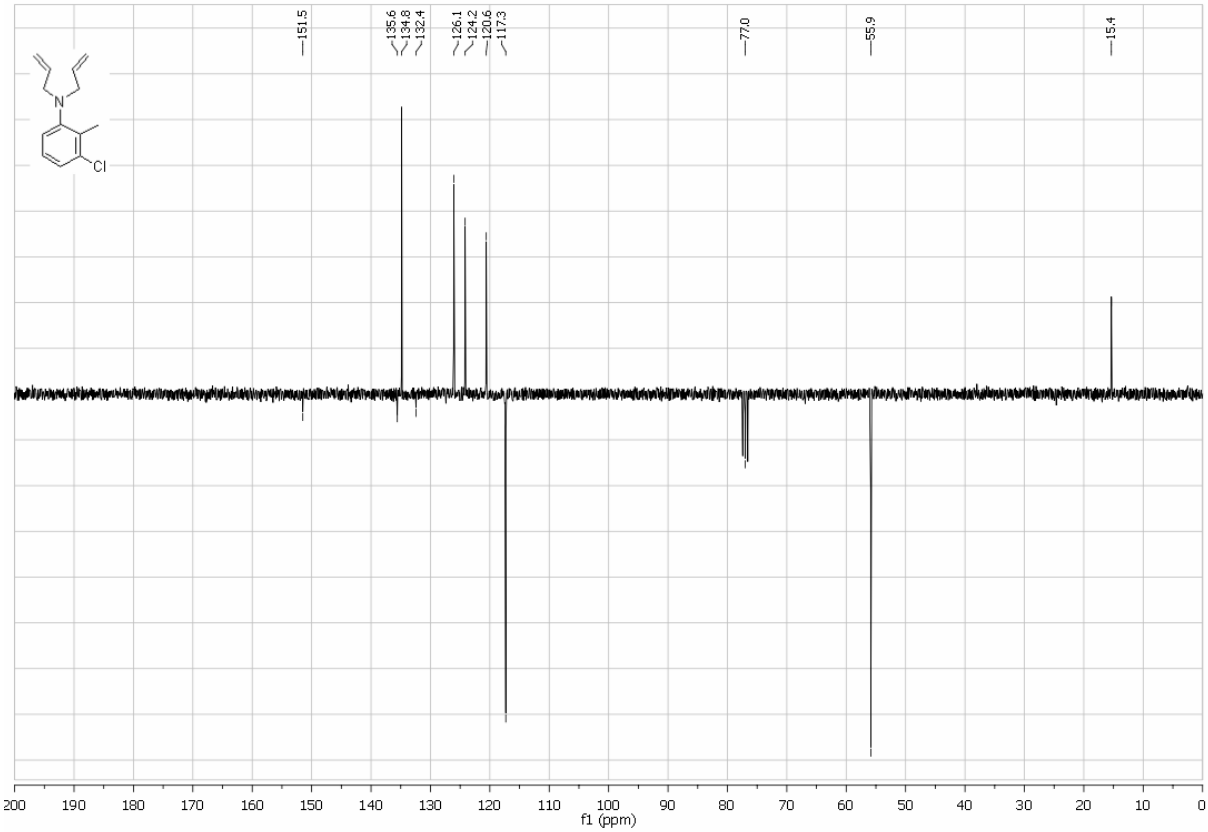
***N*,*N*-Diallyl-3-chloro-2-methylaniline (2c)**

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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



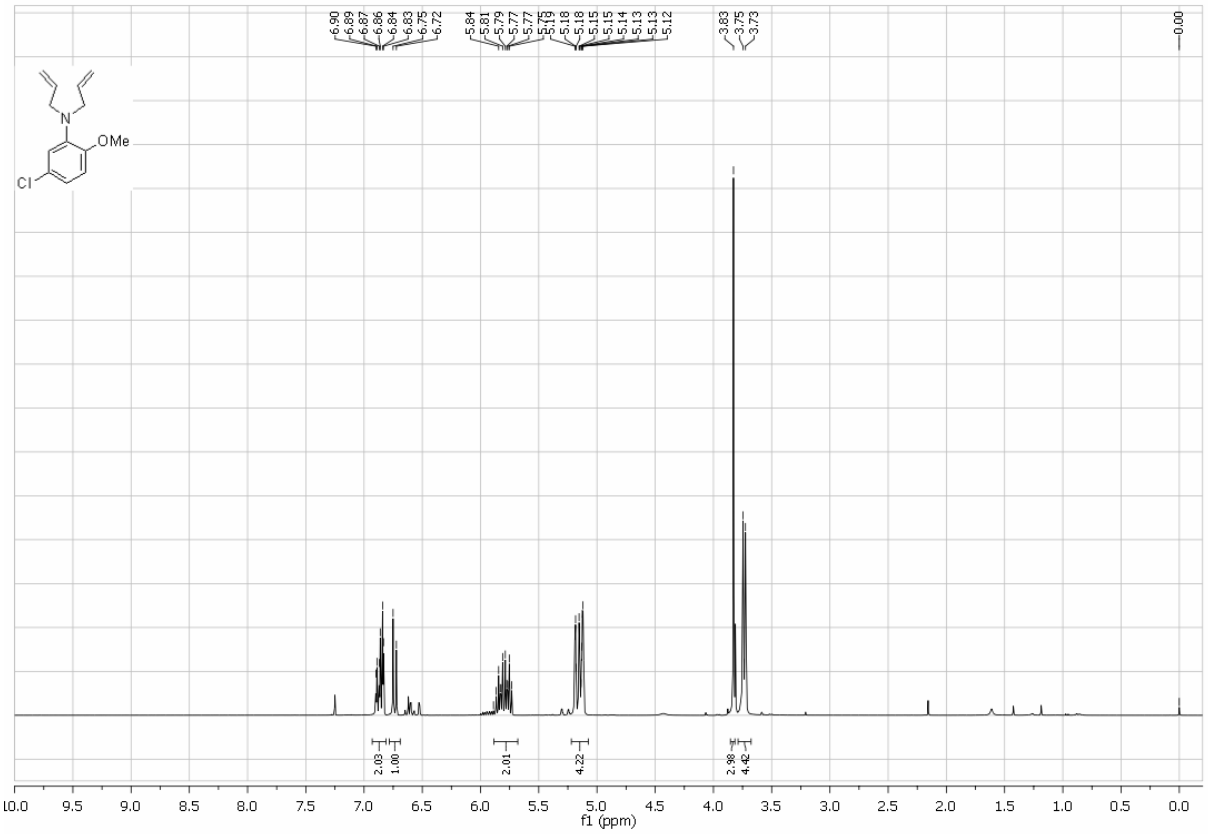
^{13}C NMR spectrum of 2c



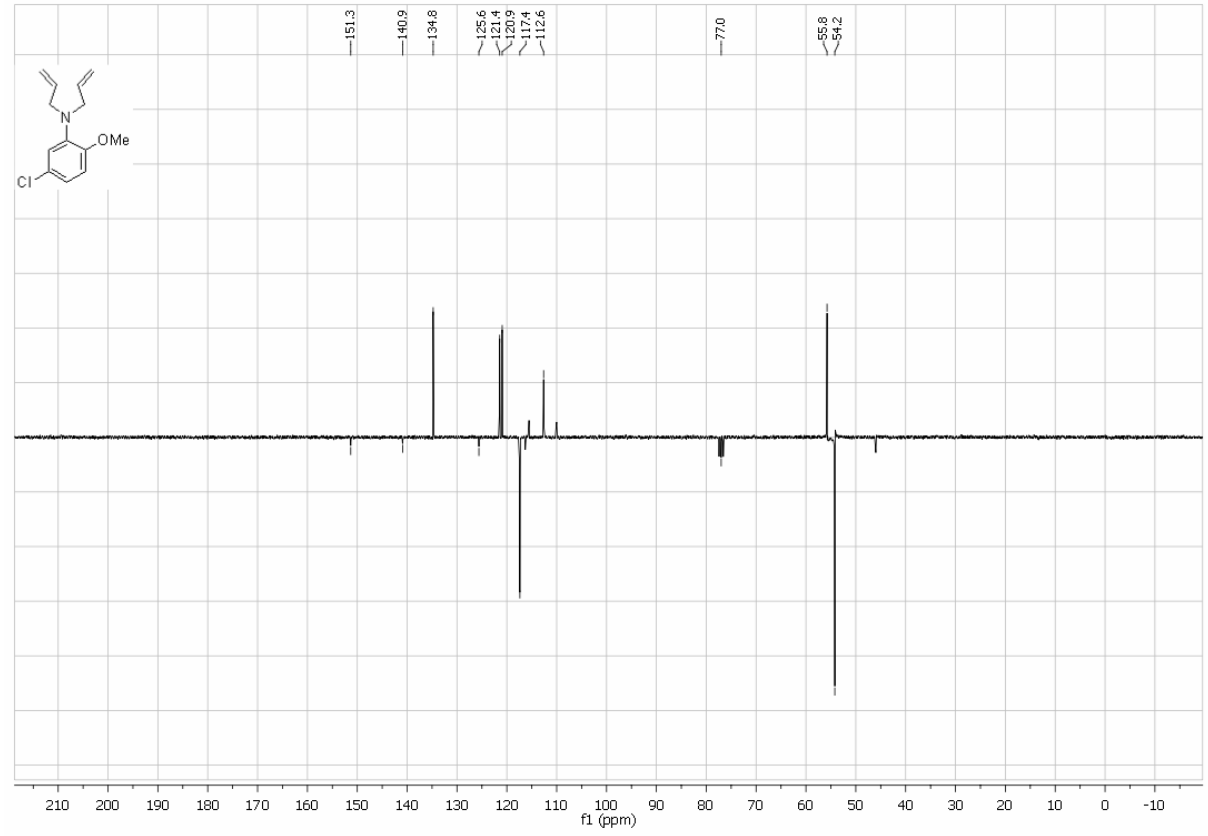
***N*,*N*-Diallyl-5-chloro-2-methoxyaniline (2d)**

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 2d



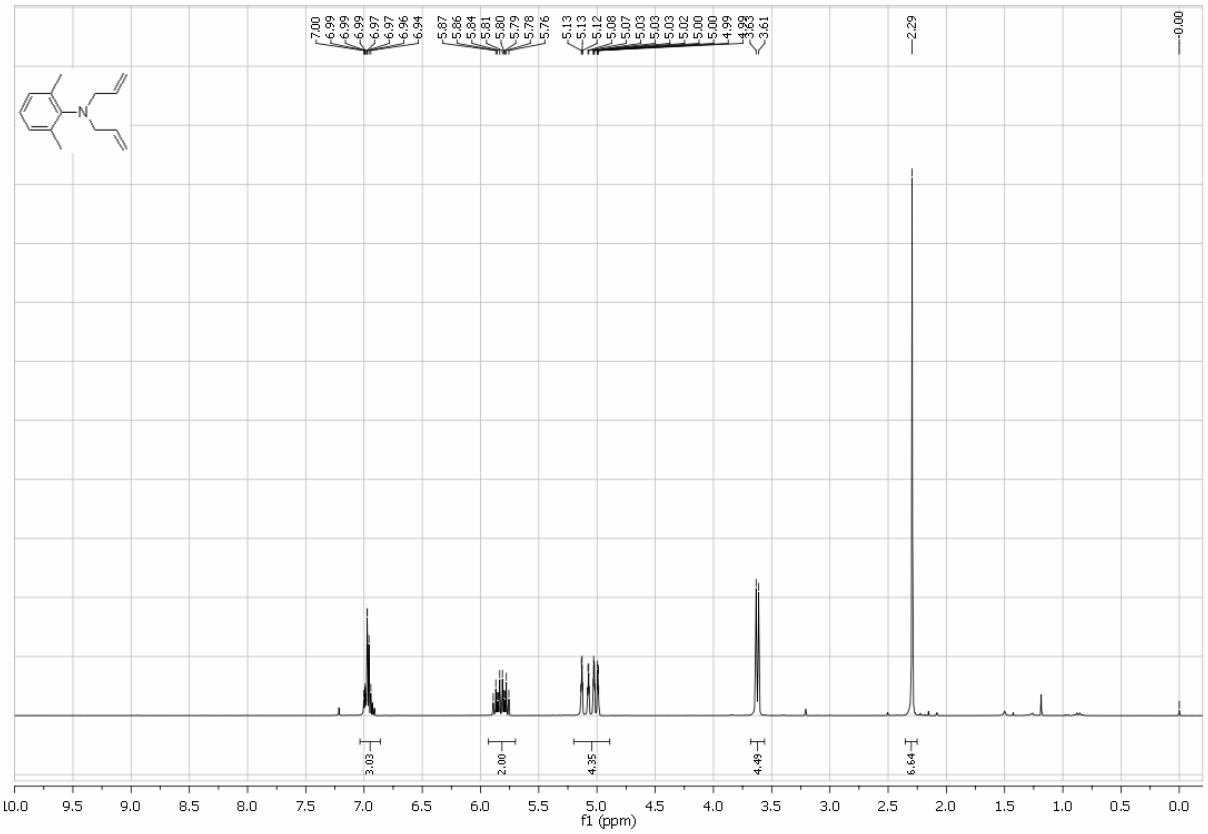
^{13}C NMR spectrum of 2d



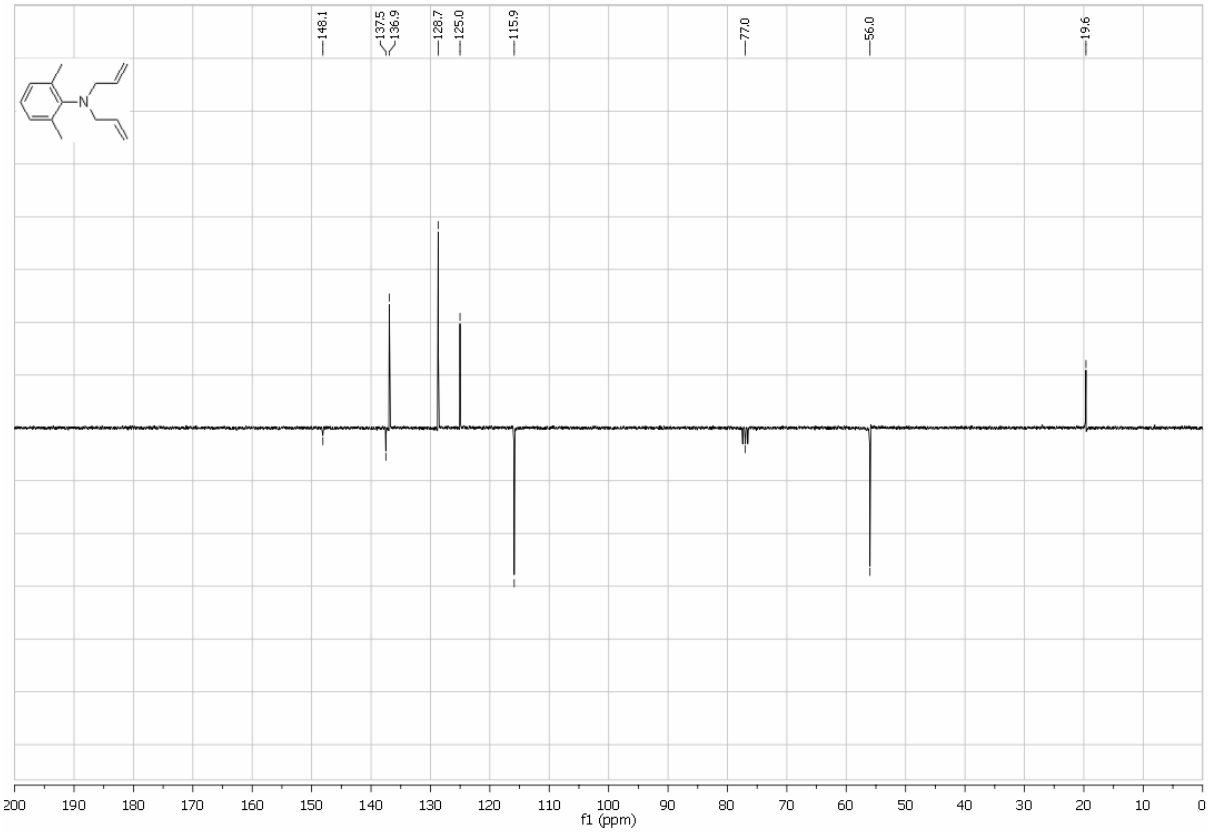
***N*,*N*-Diallyl-2,6-dimethylaniline (2e)**

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: $\tilde{\upsilon}$ = 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



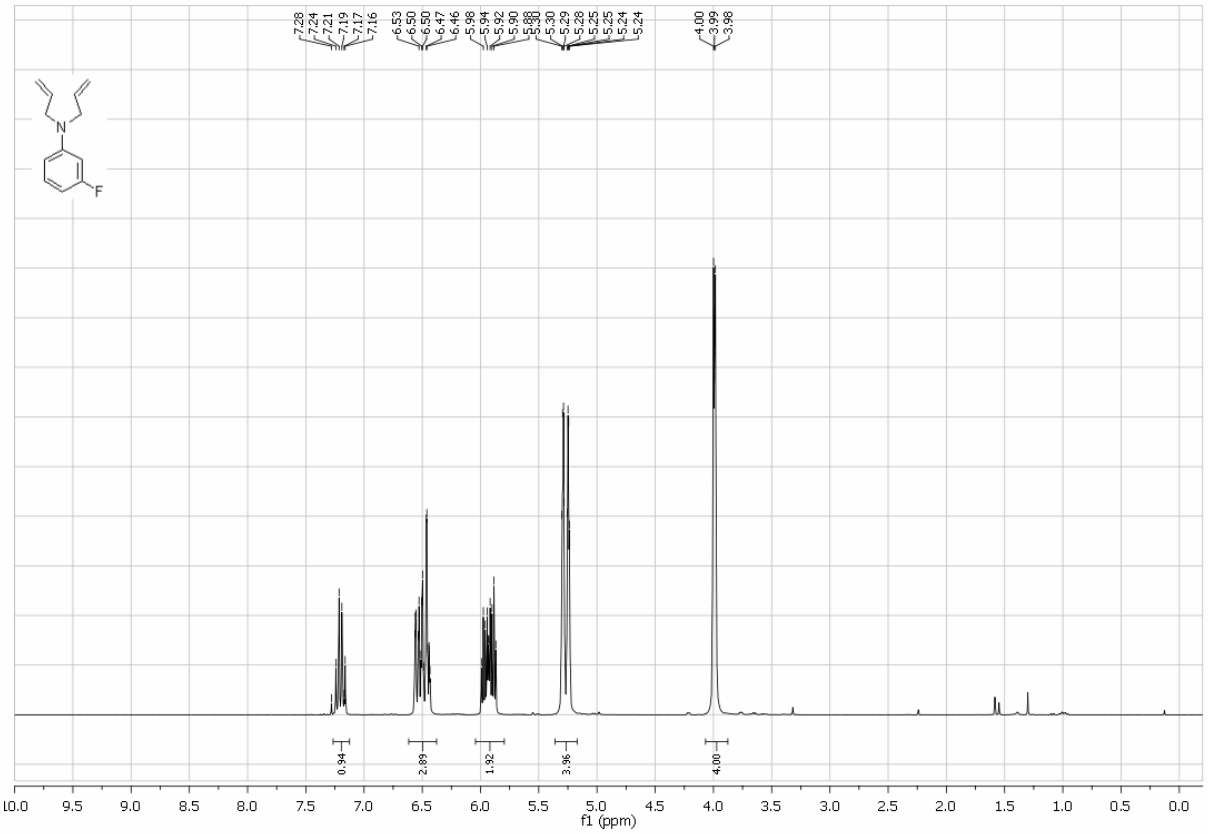
^{13}C NMR spectrum of 2e



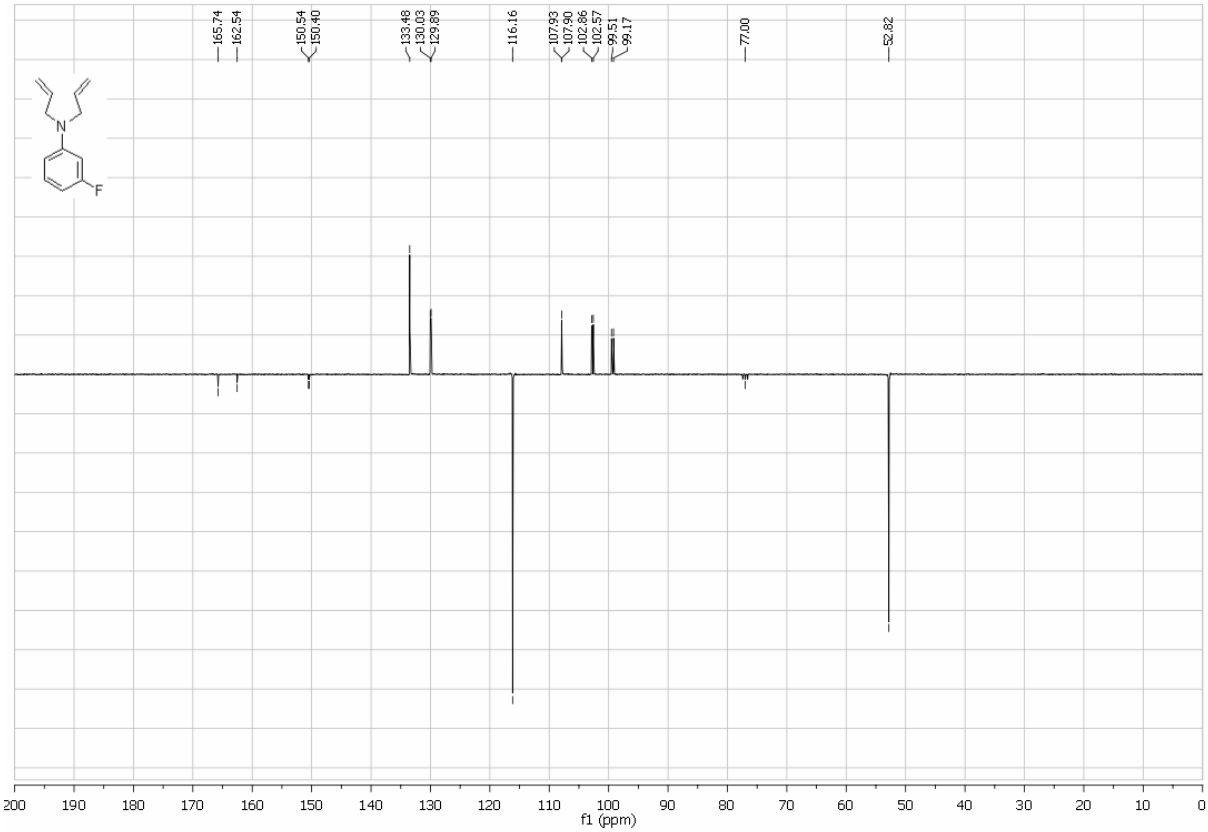
***N*,*N*-Diallyl-3-fluoroaniline (2f)**

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, $CDCl_3$) 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, ^{1}J = 242.6), 150.5 (0, d, ^{3}J = 10.7), 133.5 (1, 2C), 130.0 (1, d, ^{3}J = 10.4), 116.2 (2, 2C), 107.9 (1, d, ^{4}J = 2.0), 102.7 (1, d, ^{2}J = 21.7), 99.3 (1, d, ^{2}J = 26.1) 52.8 (2, 2C); IR: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 2f



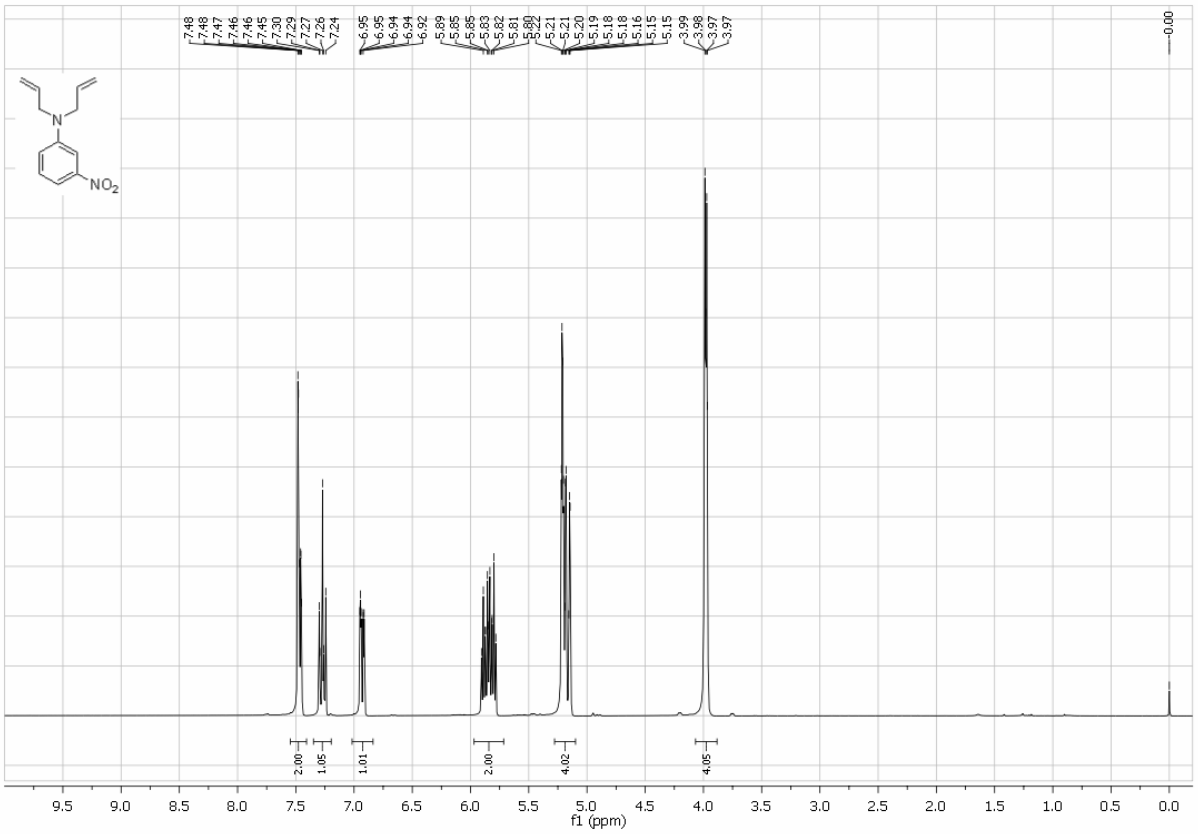
^{13}C NMR spectrum of 2f



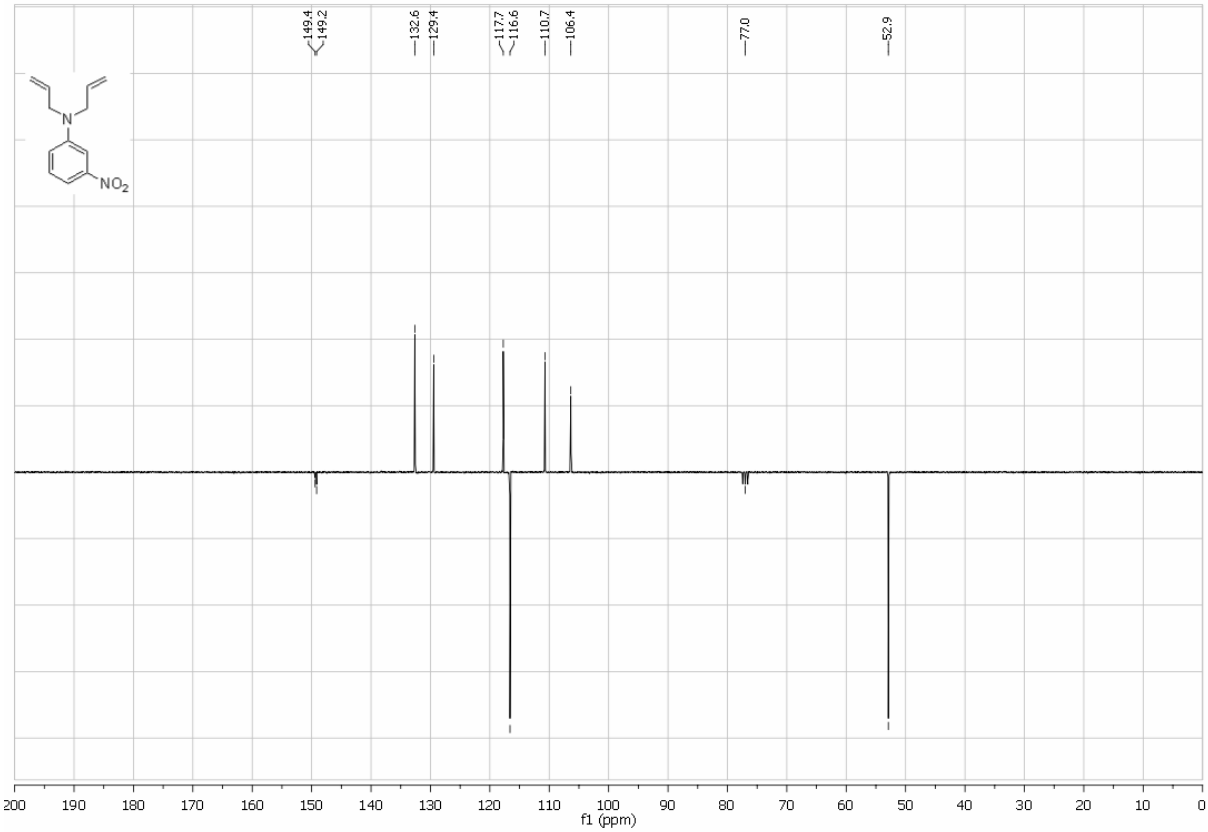
_N,N_-Diallyl-3-nitroaniline (2g) and _N_-allyl-3-nitroaniline (3g)

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 a 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: $\tilde{\upsilon}$ = 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 (***2g***)*: 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).

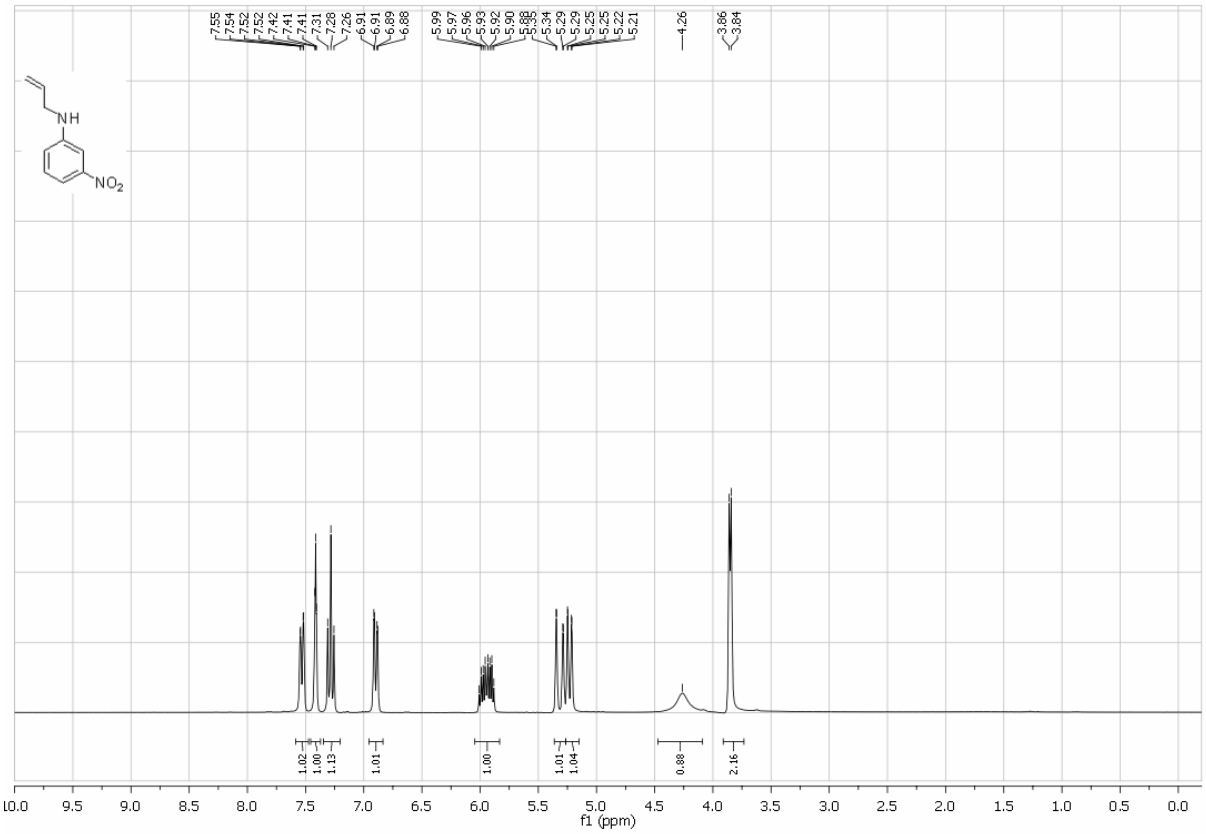
^{1}H NMR spectrum of 2g



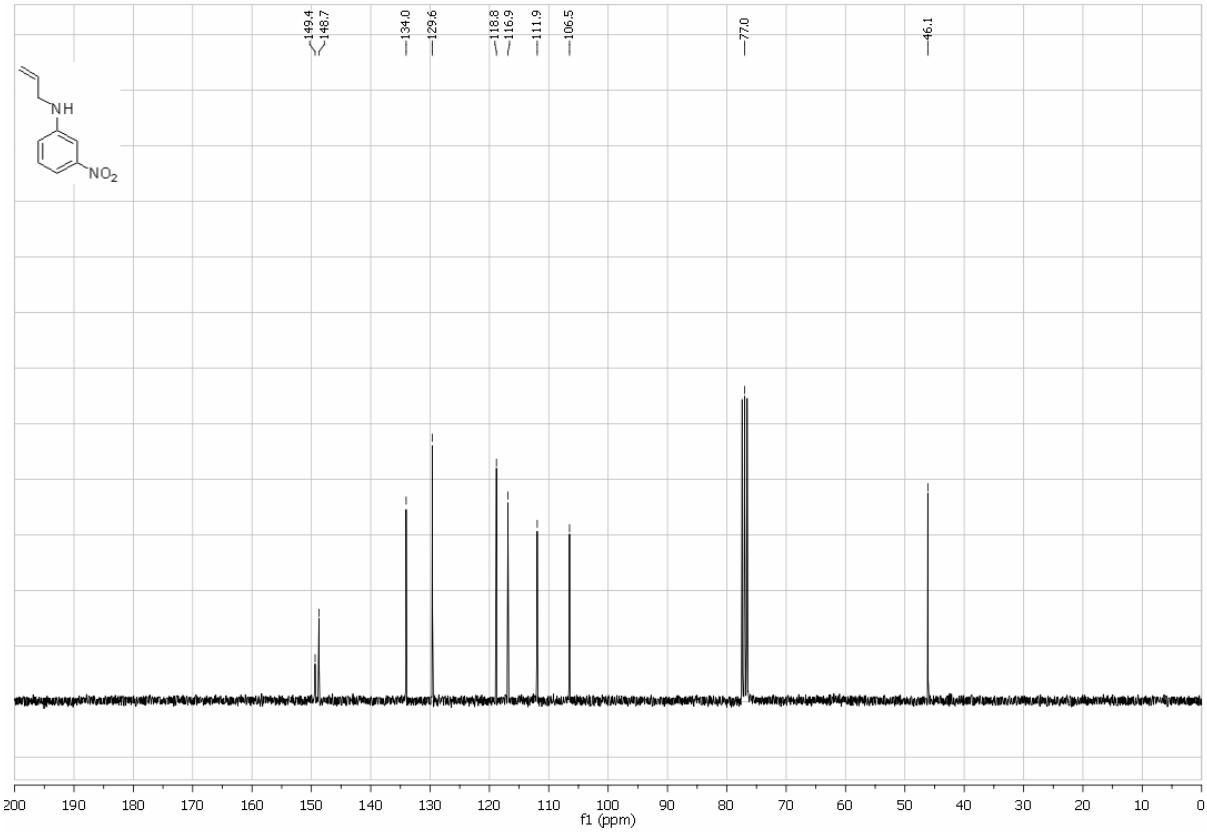
^{13}C NMR spectrum of 2g



^{1}H NMR spectrum of 3g



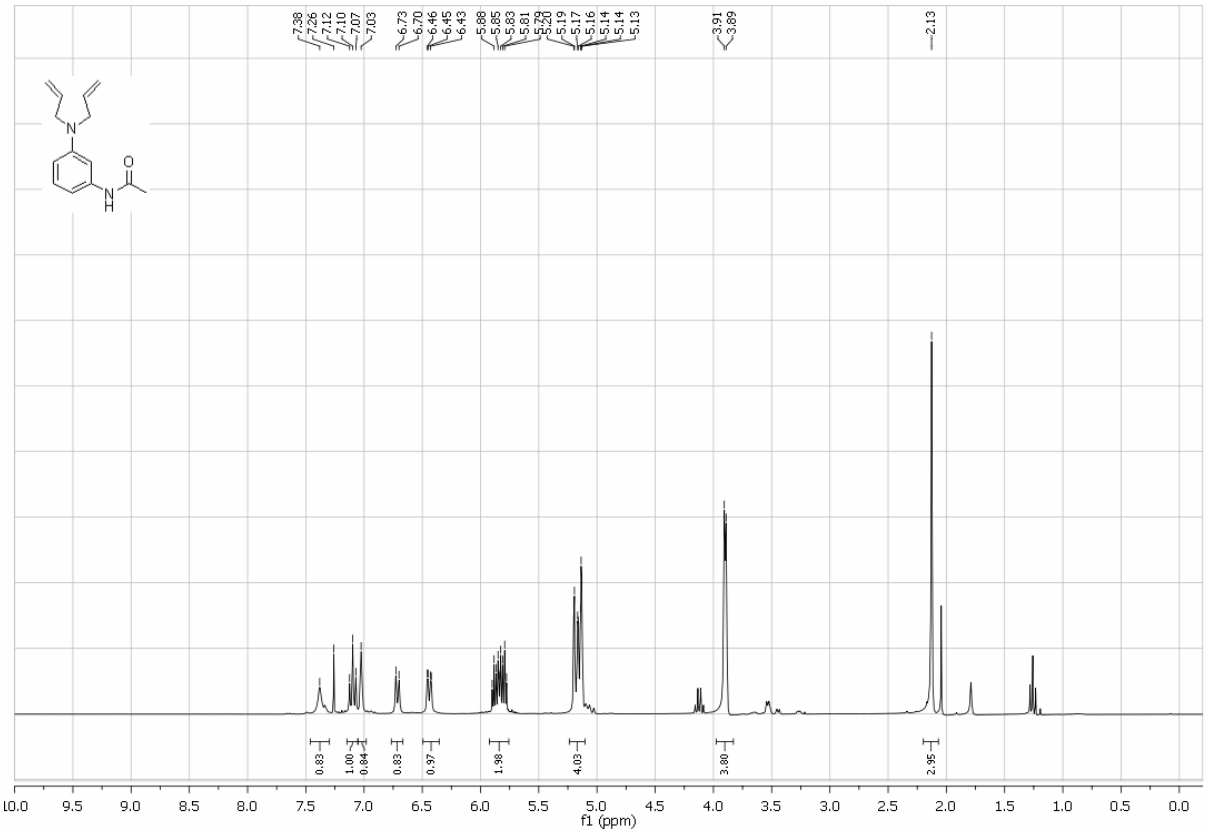
^{13}C NMR spectrum of 3g



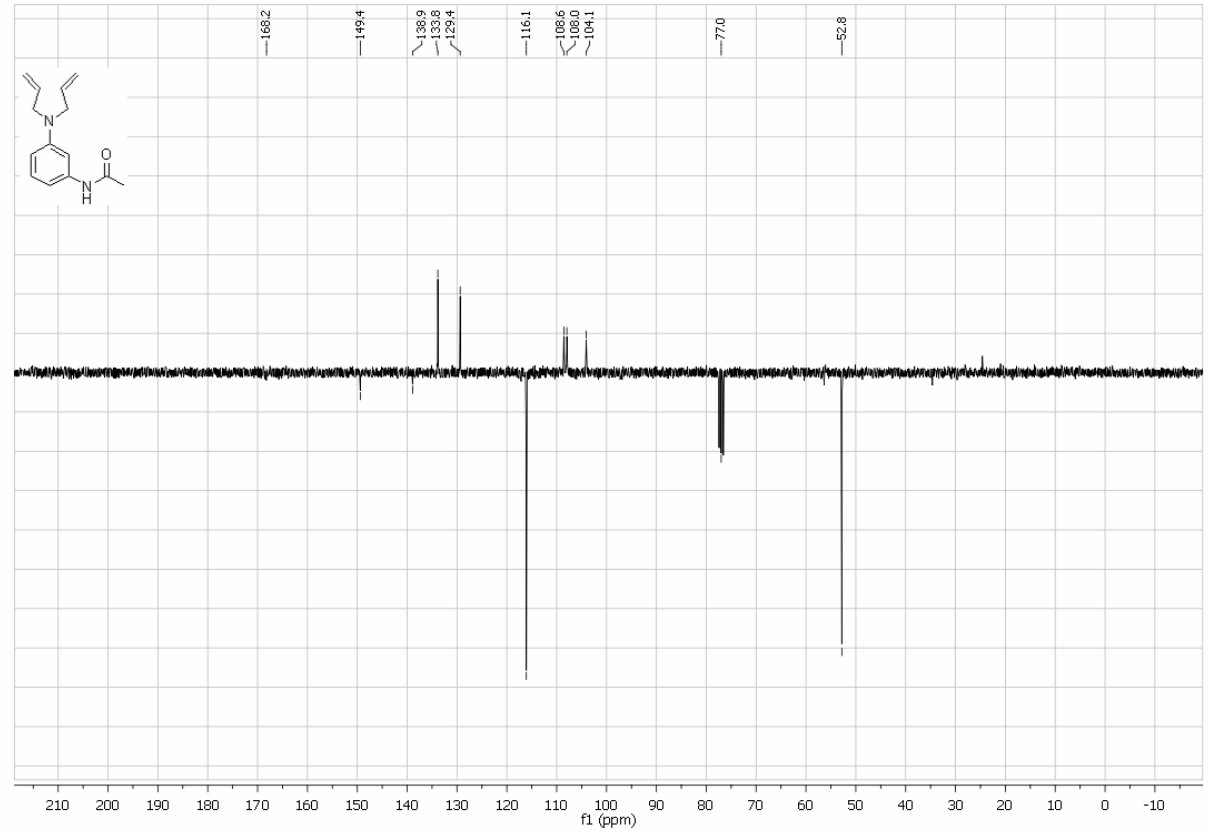
_N_-(3-(Diallylamino)phenyl)acetamide (2h)

Following the general procedure, **2h** was obtained from **1h** (3.00 g, 20.0mmol) 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 2h



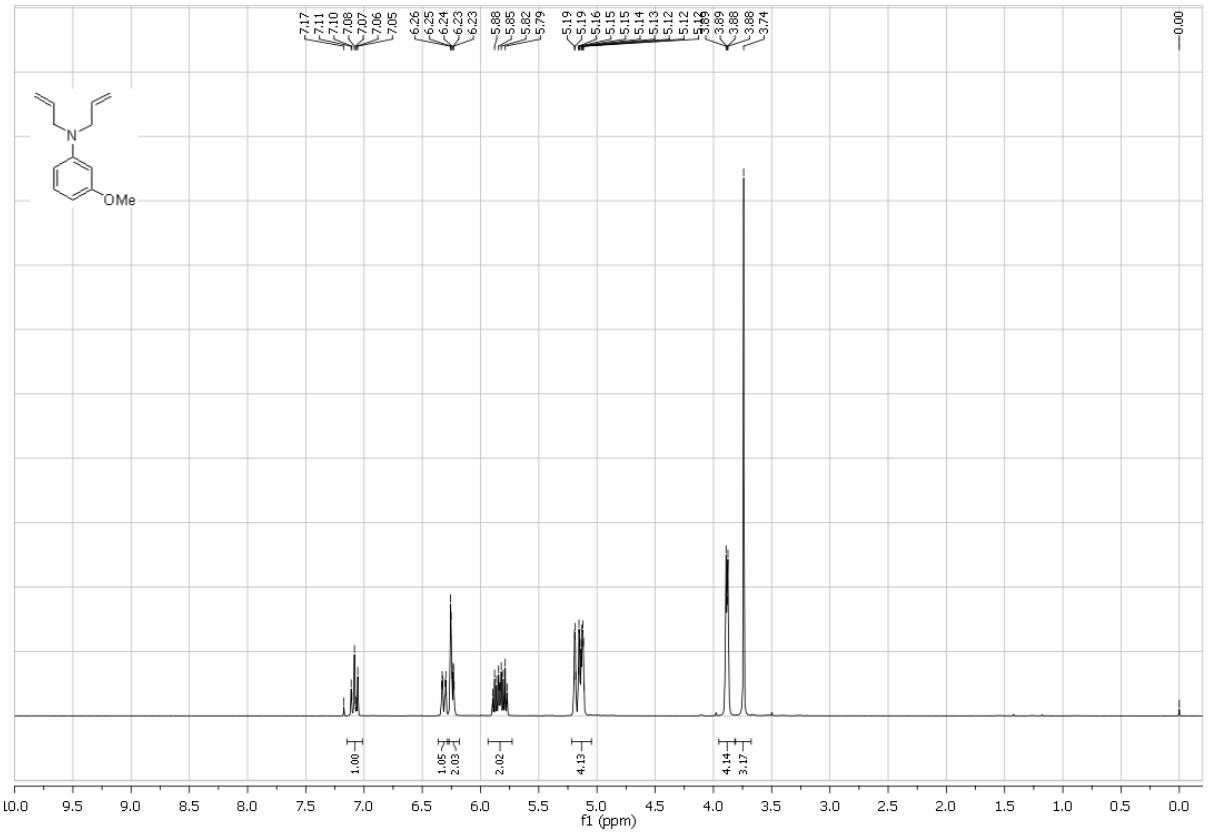
^{13}C NMR spectrum of 2h



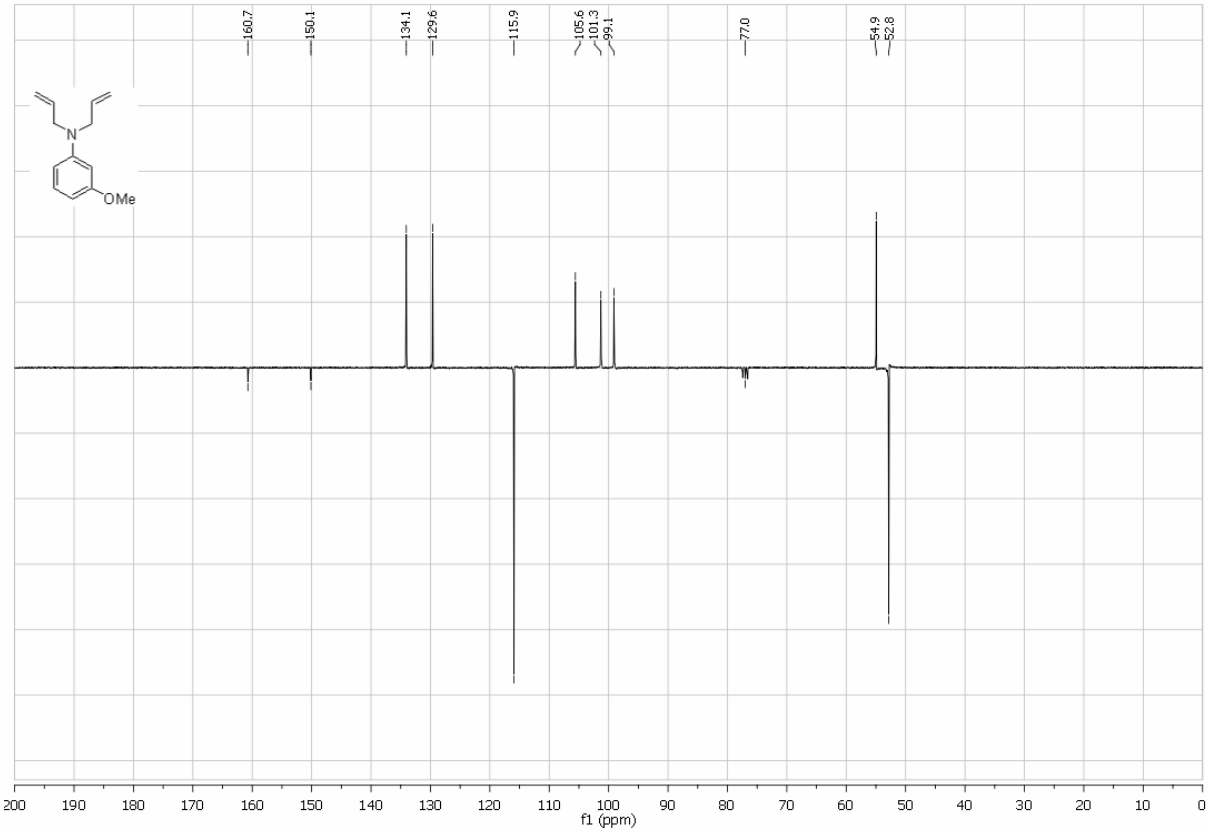
_N,N_-Diallyl-3-methoxyaniline (2i)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 2i



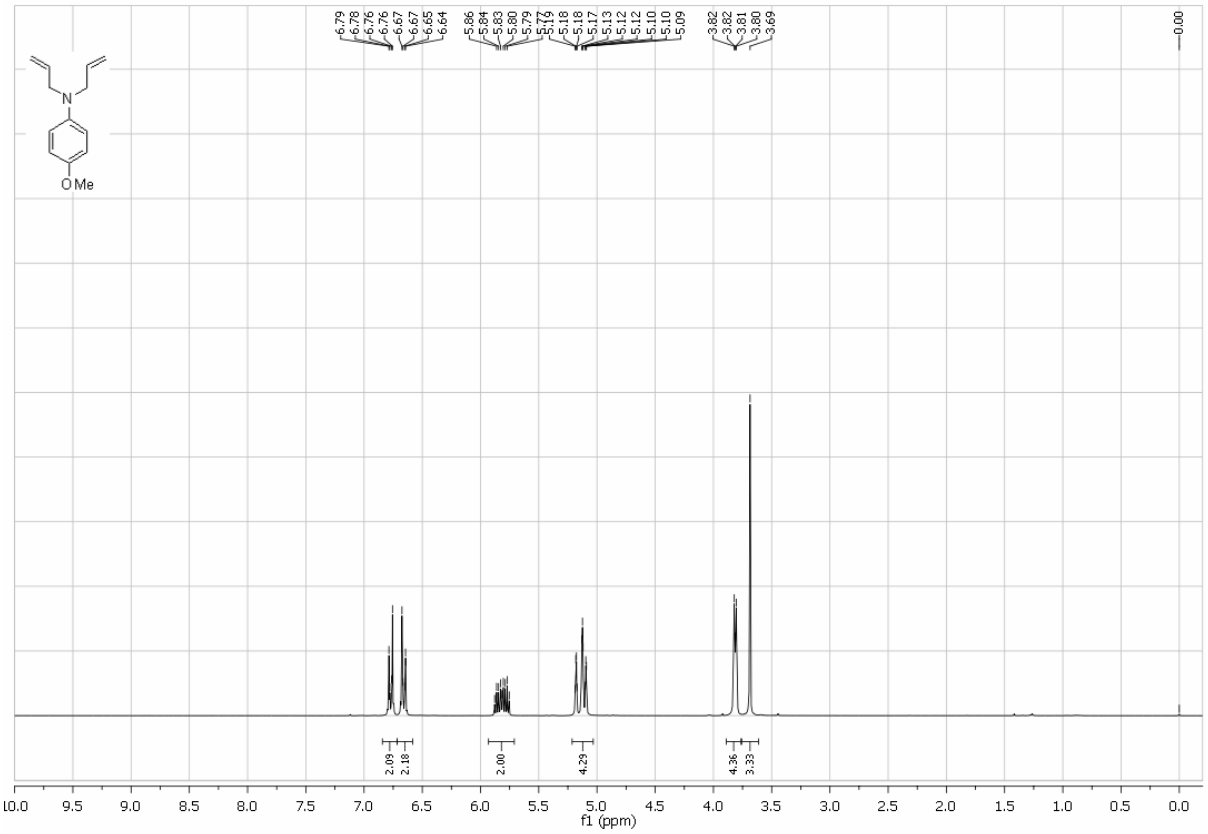
^{13}C NMR spectrum of 2i



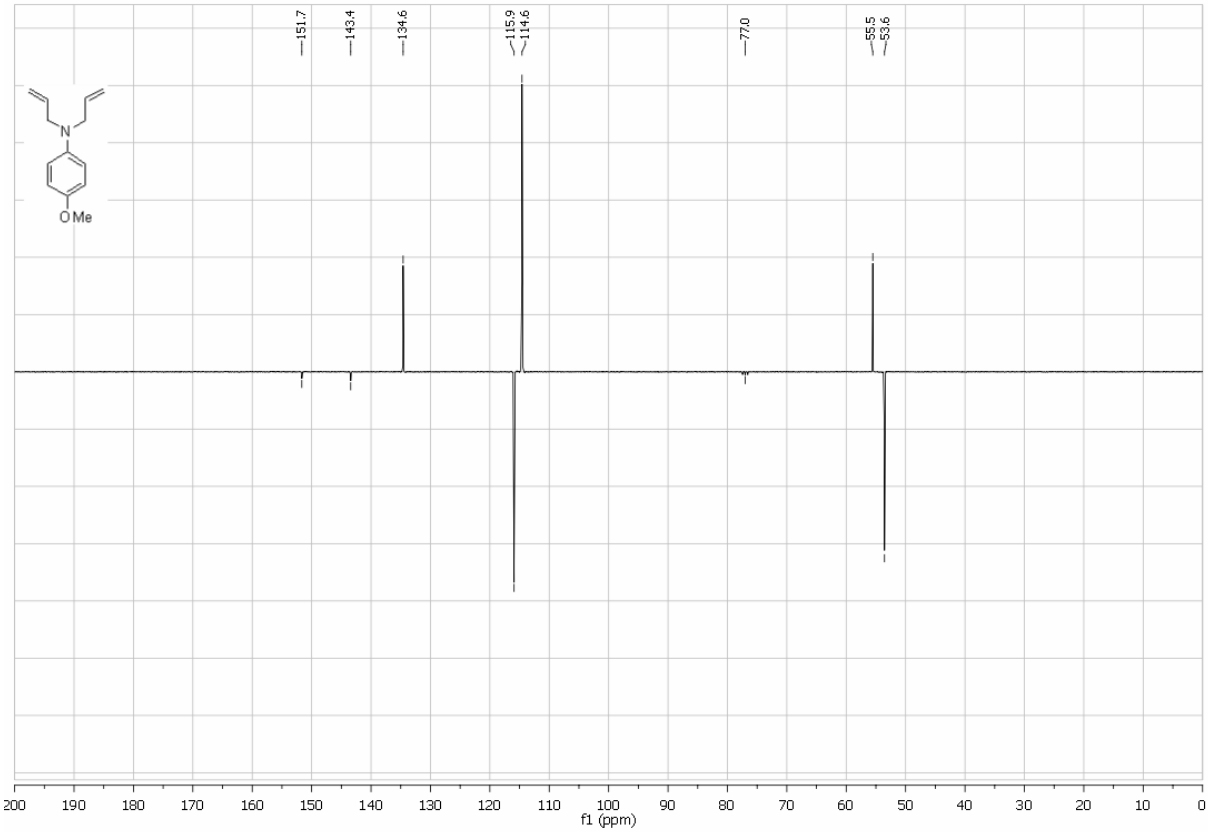
***N*,*N*-Diallyl-4-methoxyaniline (2j)**

Following the general procedure, **2j** was obtained from **1j** (2.46 g, 20mmol) 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: $\tilde{\upsilon}$ = 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



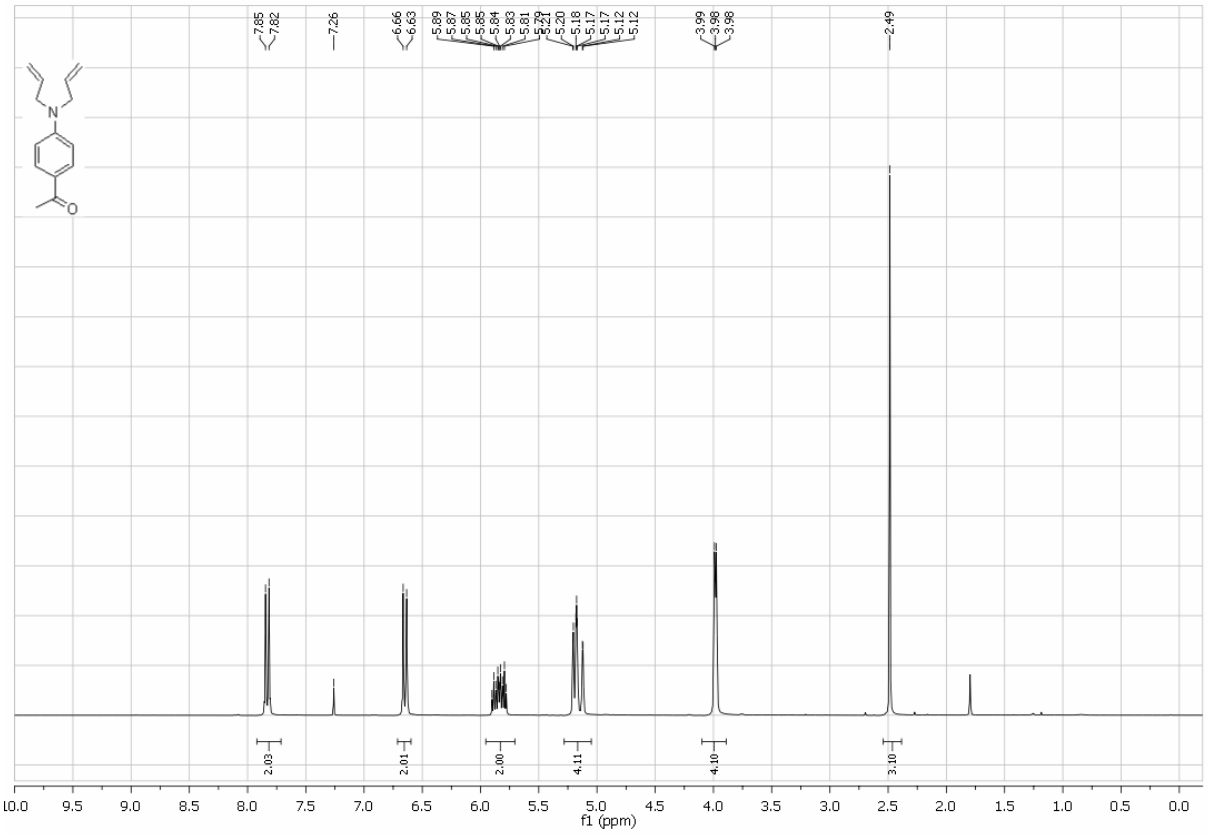
^{13}C NMR spectrum of 2j



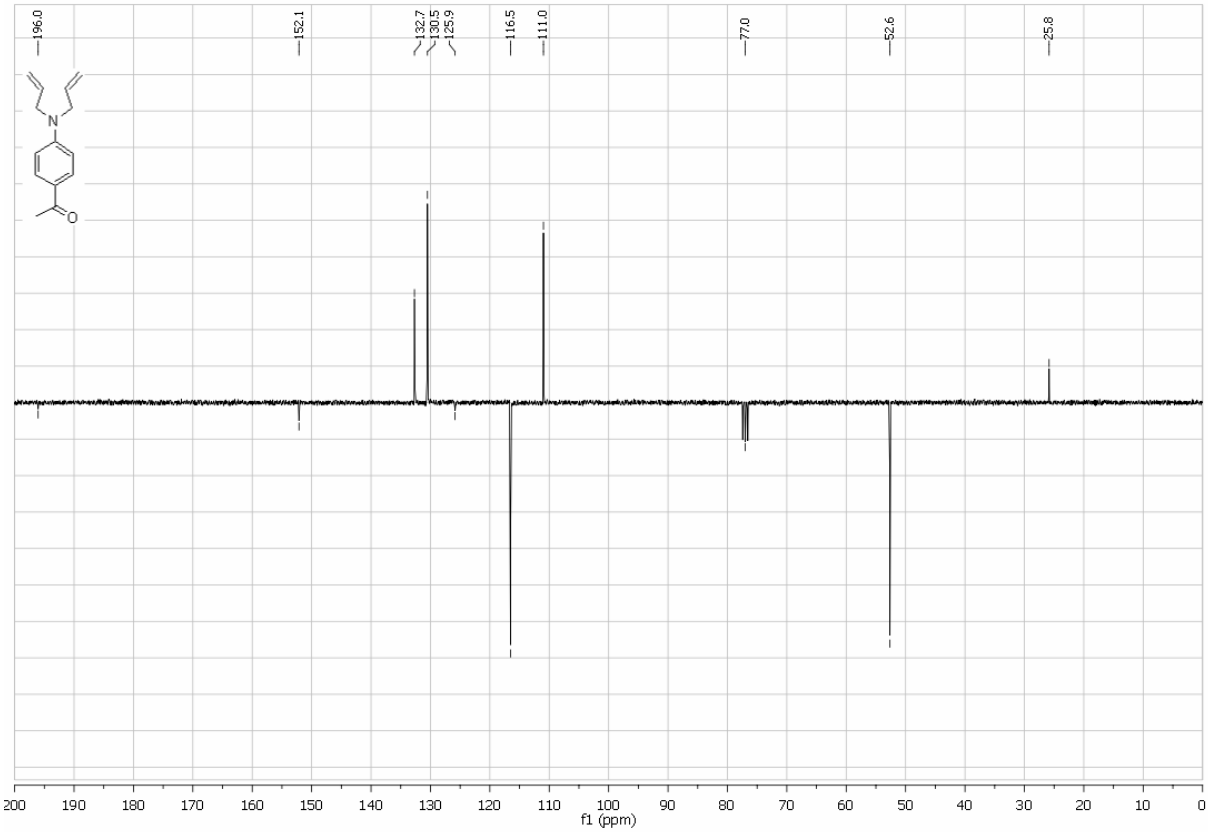
1-(4-(Diallylamino)phenyl)ethanone (2k)

Following the general procedure, **2k** was obtained from **1k** (2.70 g, 20.0mmol) 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: $\tilde{\upsilon}$ = 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



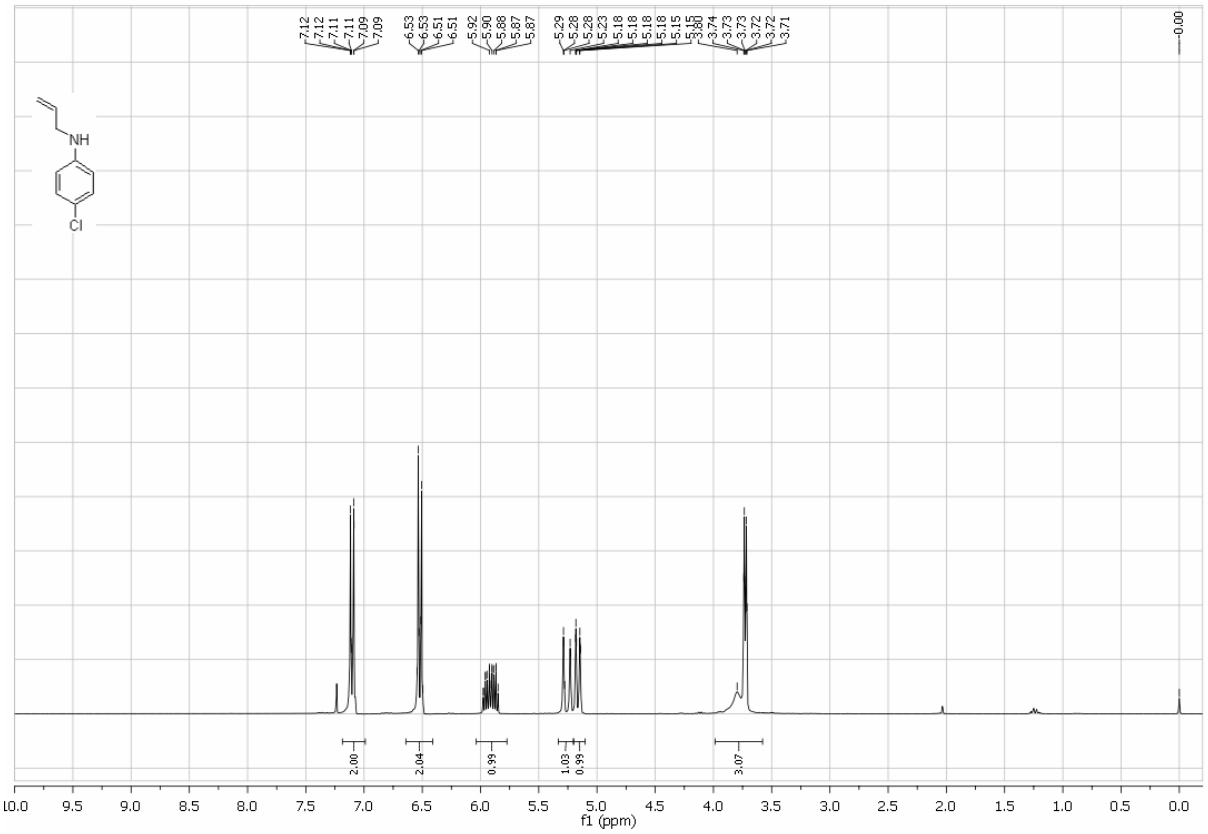
^{13}C NMR spectrum of 2k



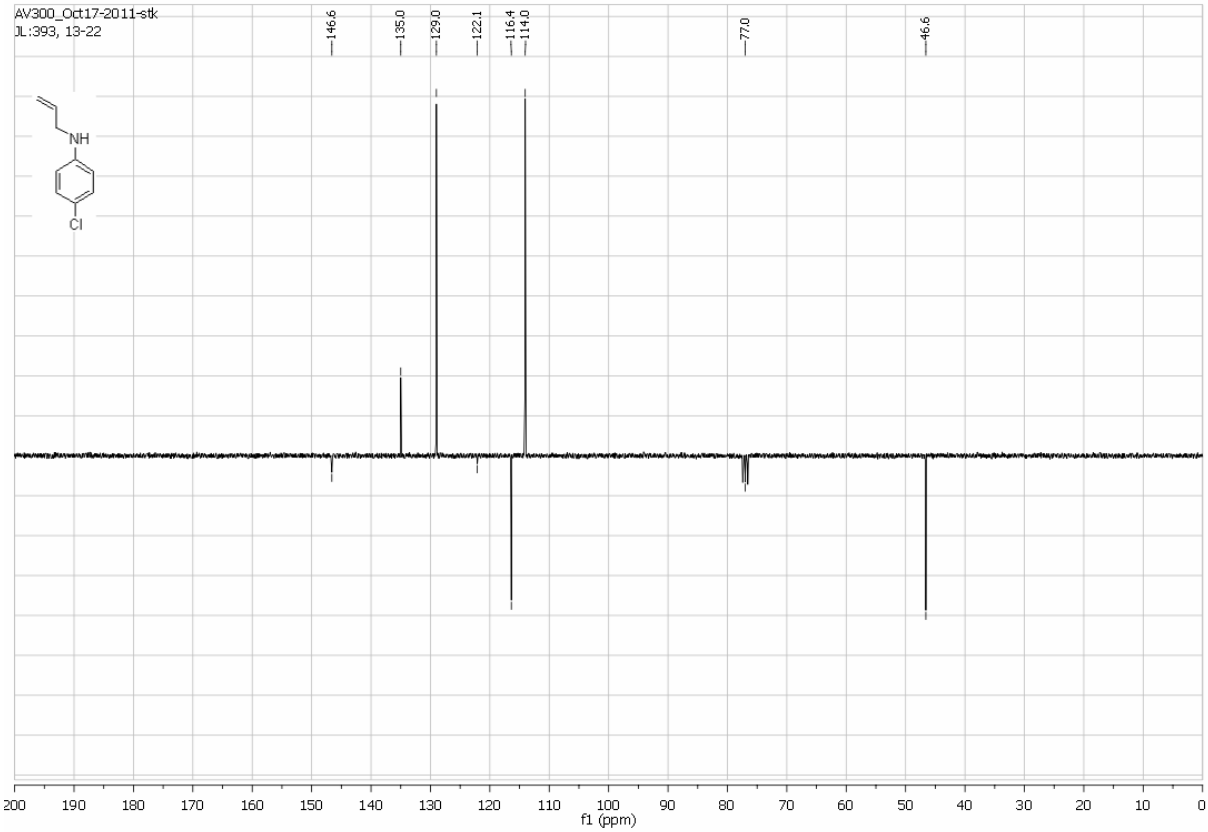
_N_-Allyl-4-chloroaniline (3a)

Aniline **1a** (2.54 g, 20 mmol) was dissolved in a mixture of Ethanol (64 mL) and water (16 mL). Then 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% d. Th.). 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 3a



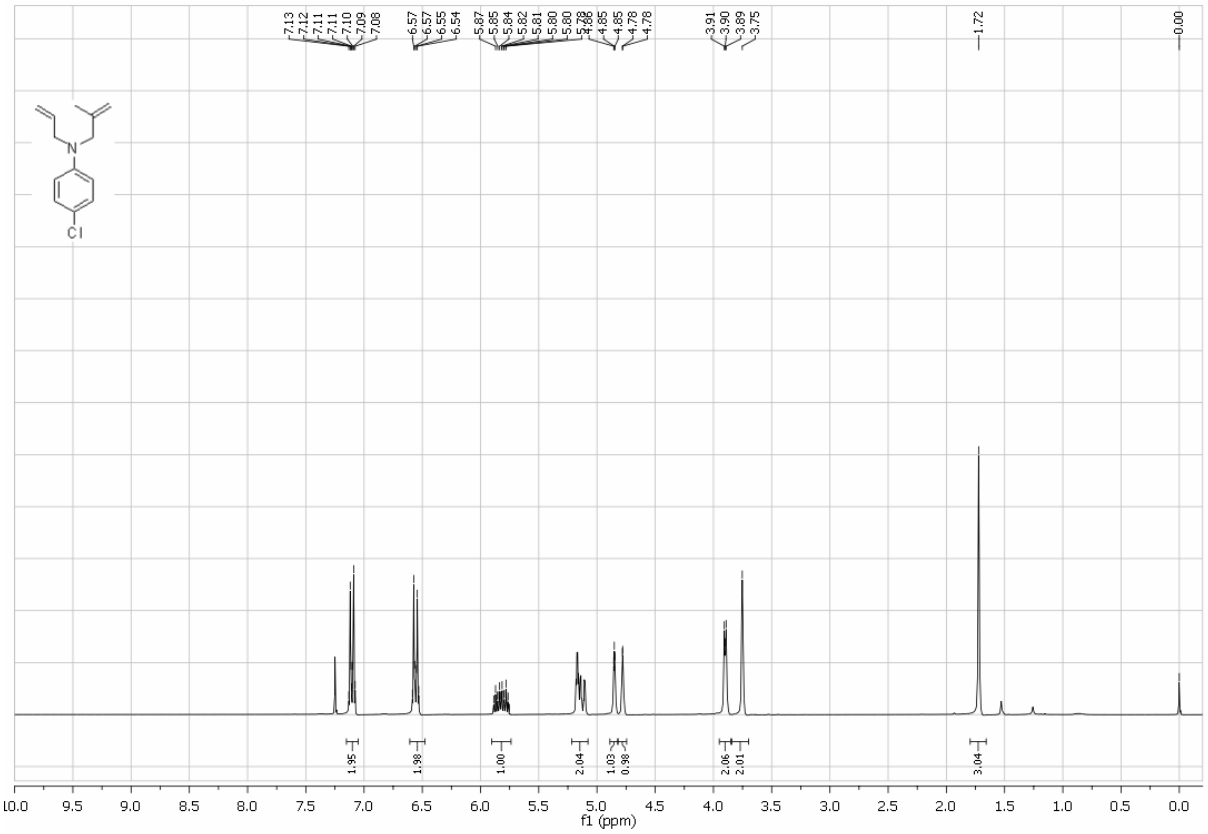
^{13}C NMR spectrum of 3a



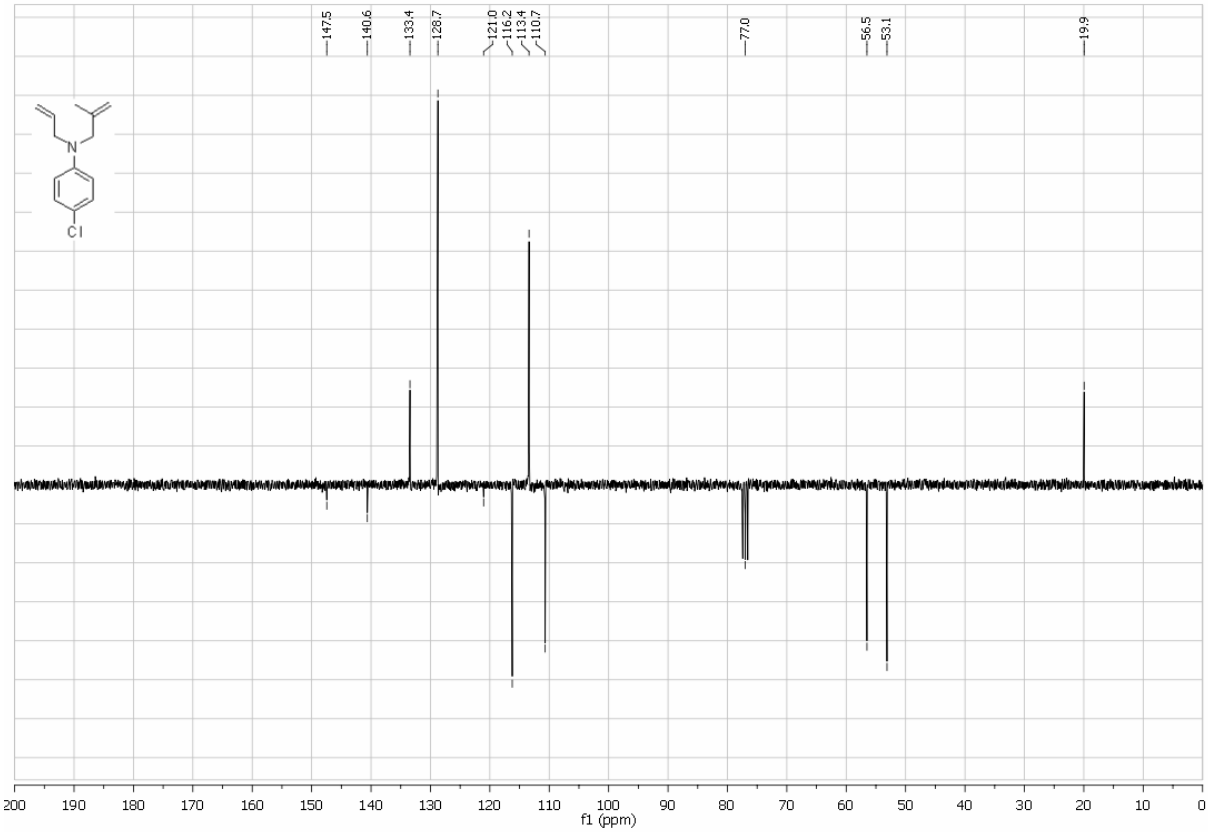
***N*-Allyl-4-chloro-*N*-(2-methylallyl)aniline (4a)**

Aniline **3a** (835 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K_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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 4a



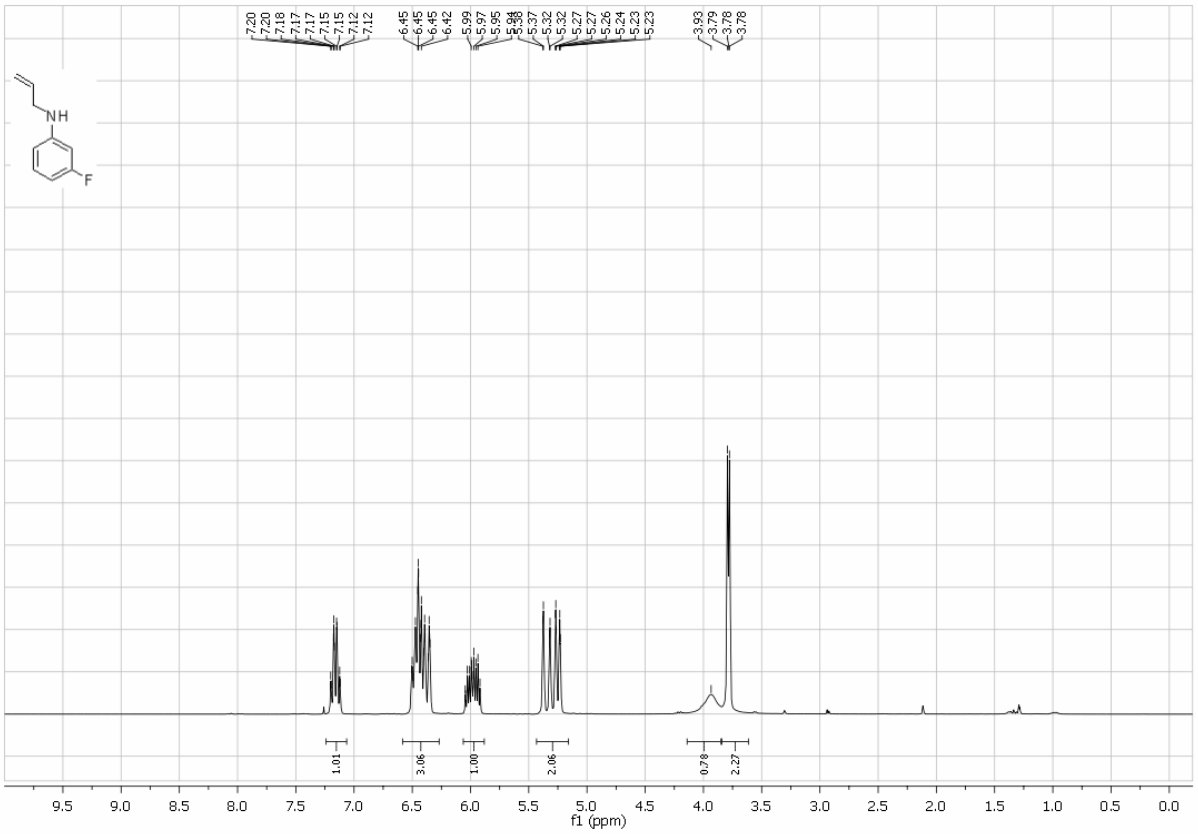
^{13}C NMR spectrum of 4a



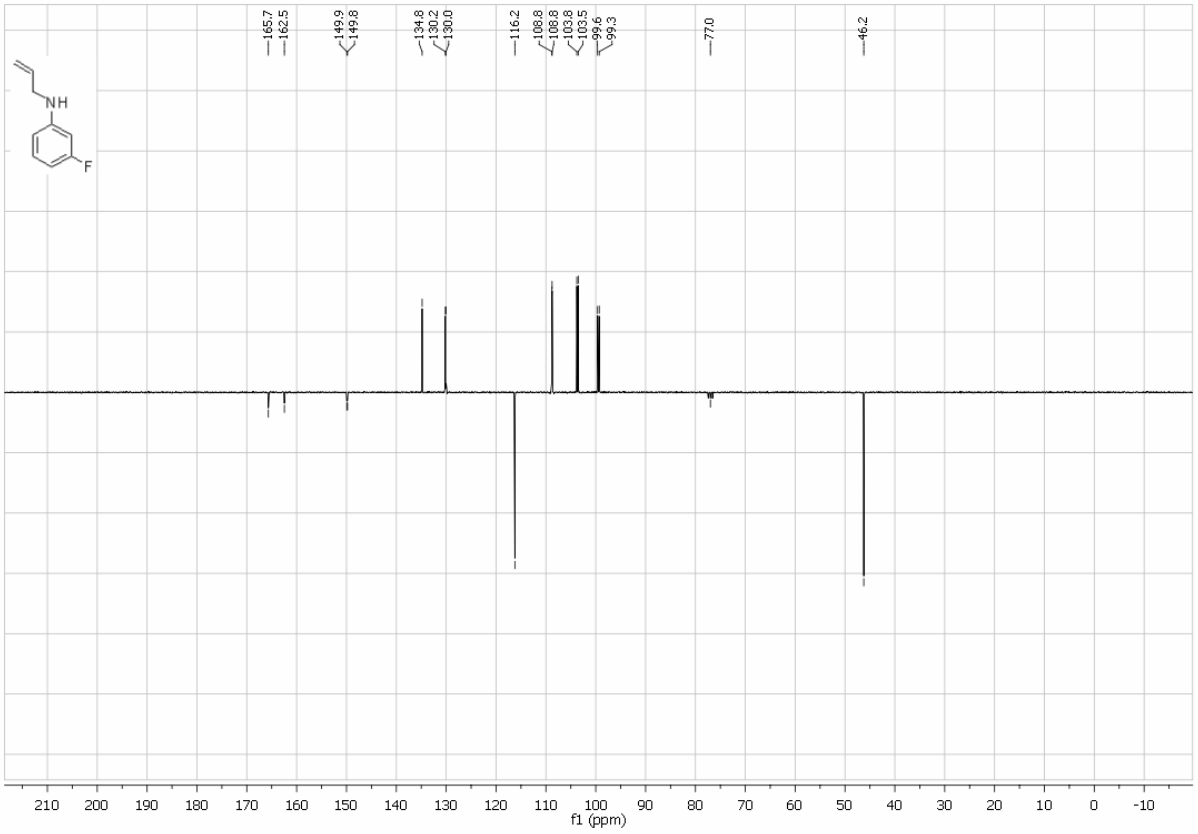
_N_-Allyl-3-fluoroaniline (3f)

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% d. Th.). 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 3f



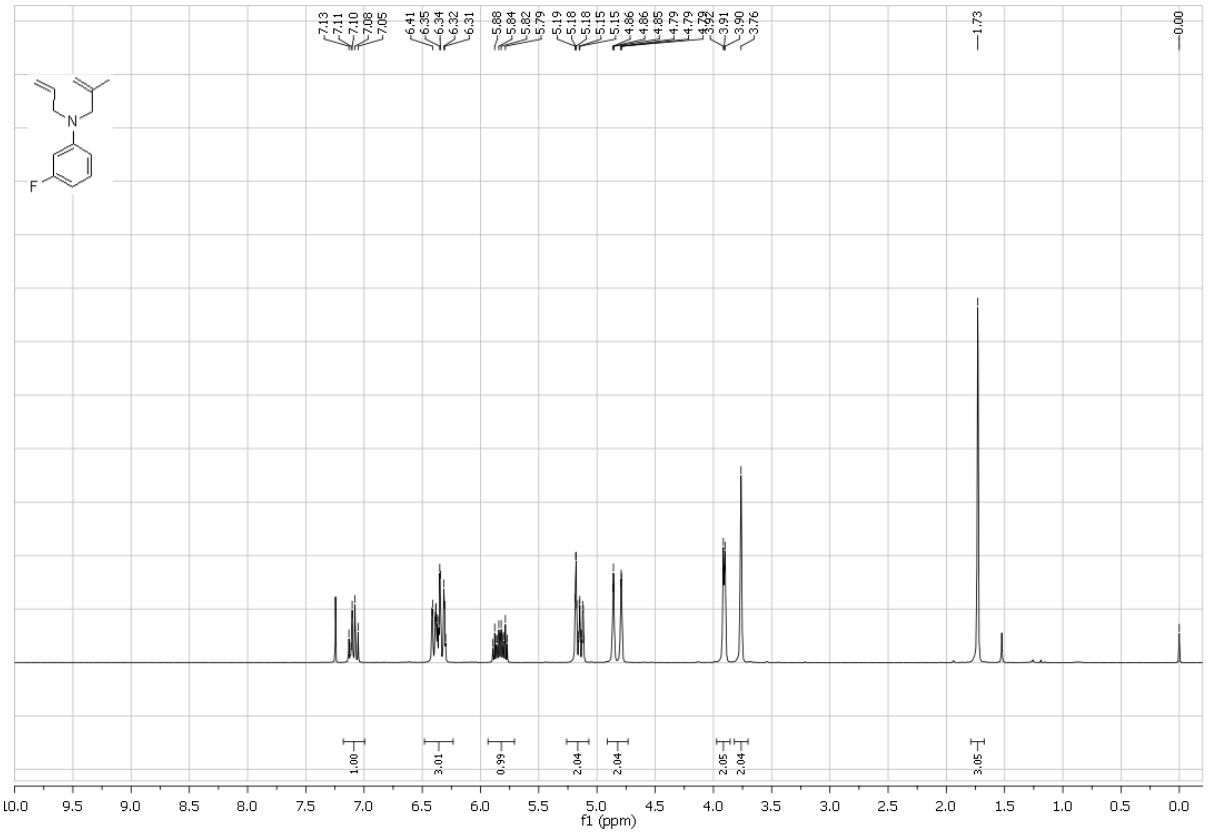
^{13}C NMR spectrum of 3f



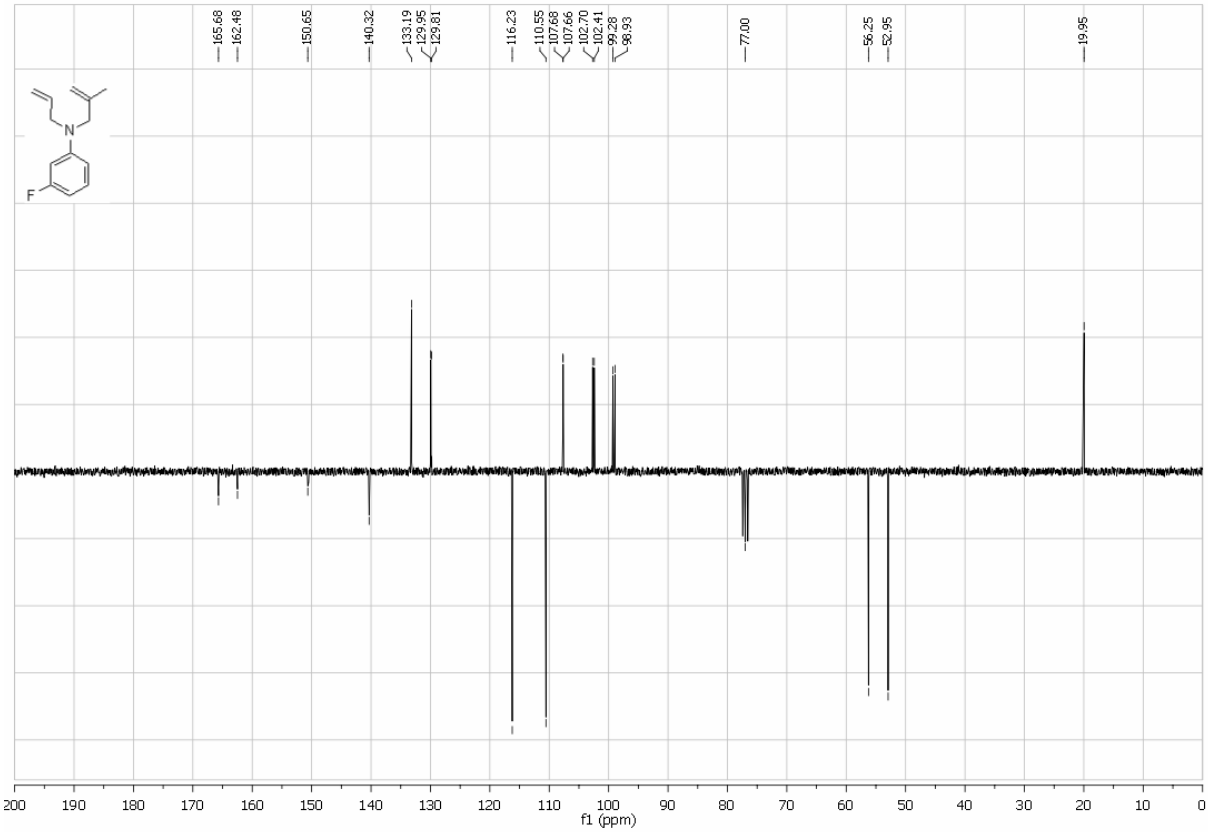
_N_-Allyl-3-fluoro-_N_-(2-methylallyl)aniline (4f)

Aniline **3f** (756 mg, 5.0 mmol) was dissolved in acetonitrile (25 mL). Then K_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).

^{1}H NMR spectrum of 4f



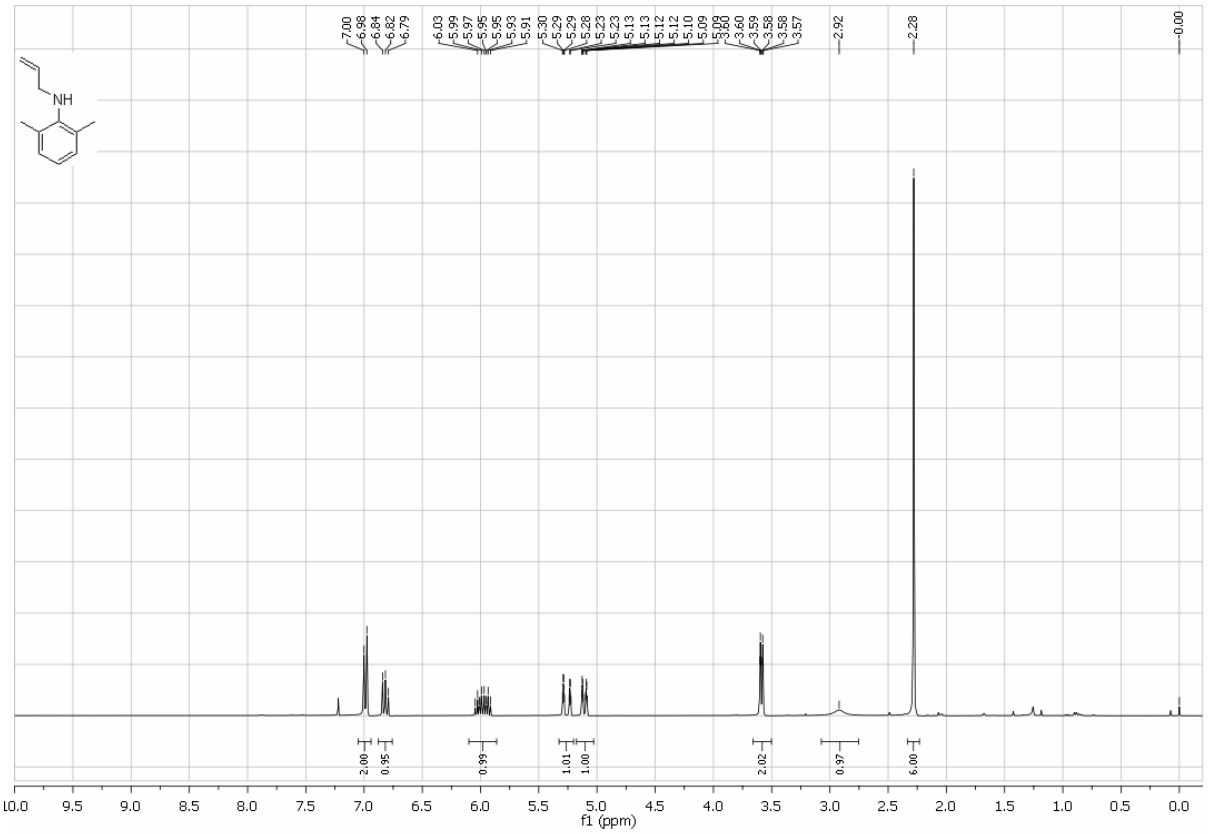
^{13}C NMR spectrum of 4f



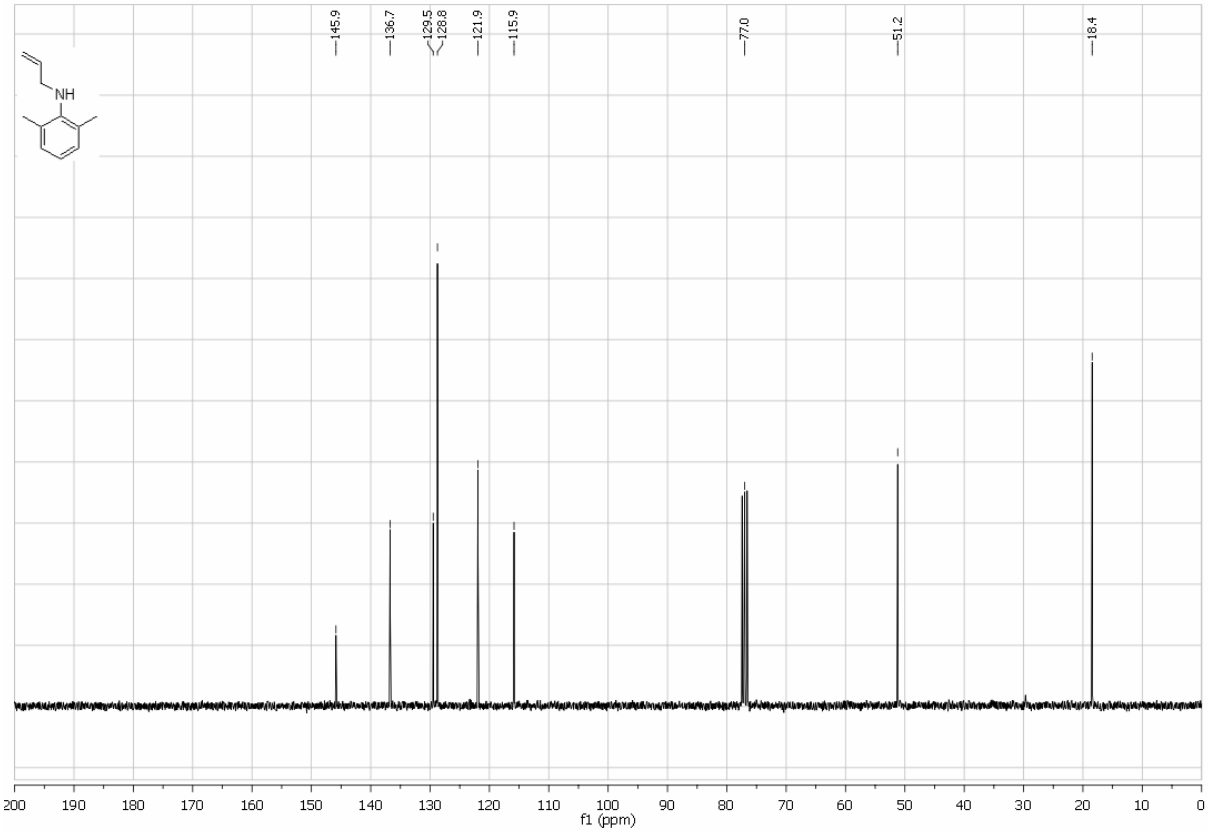
_N_-Allyl-2,6-dimethylaniline (3e)

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, $CDCl_3$) 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}H NMR spectrum of 3e



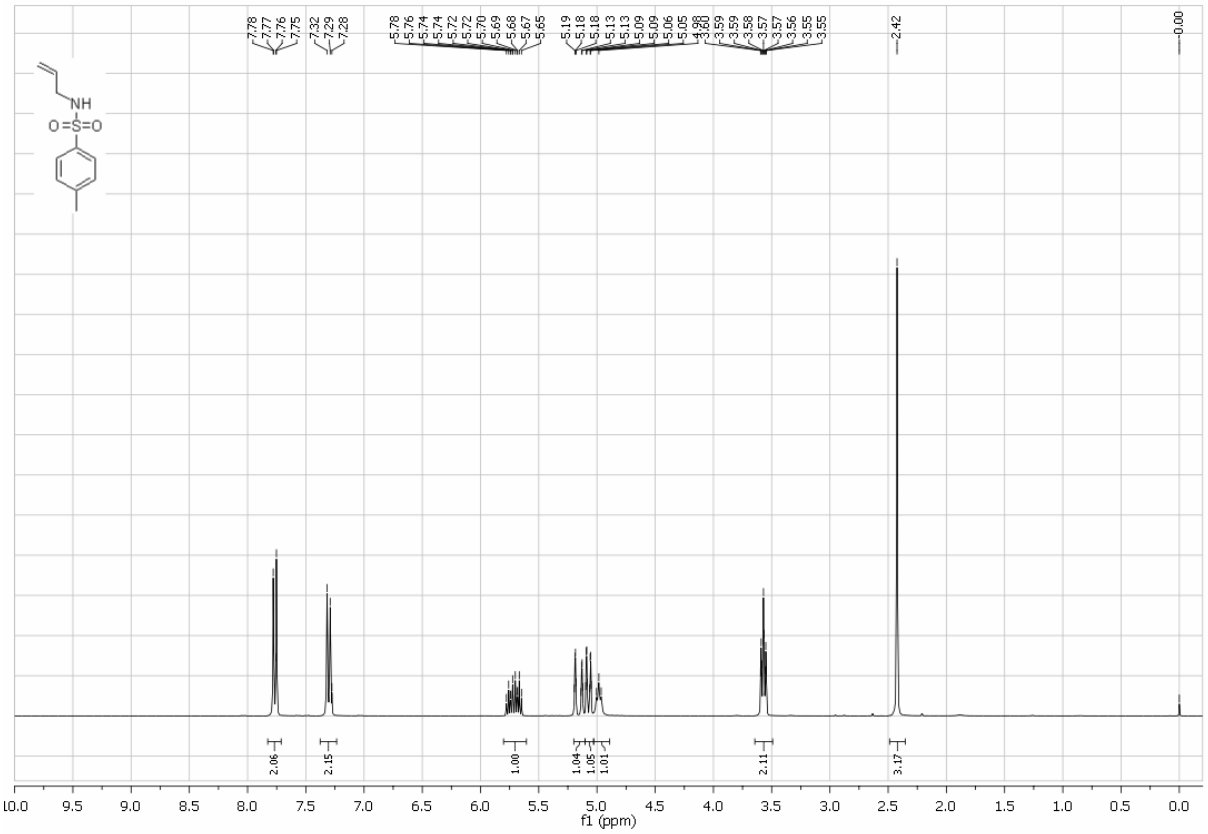
^{13}C NMR spectrum of 3e



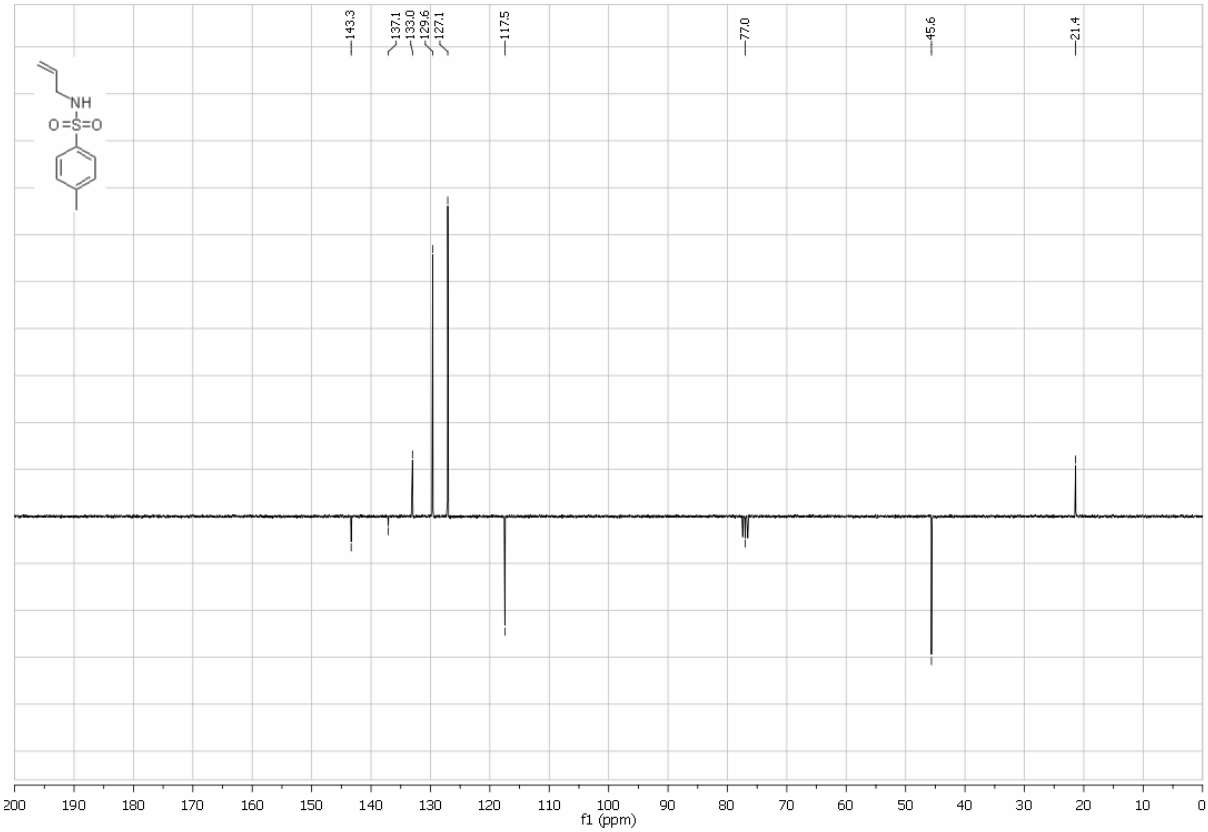
_N_-Allyl-4-methylbenzenesulfonamide (7)

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 $MgSO_4$, 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).

^{1}H NMR spectrum of 7



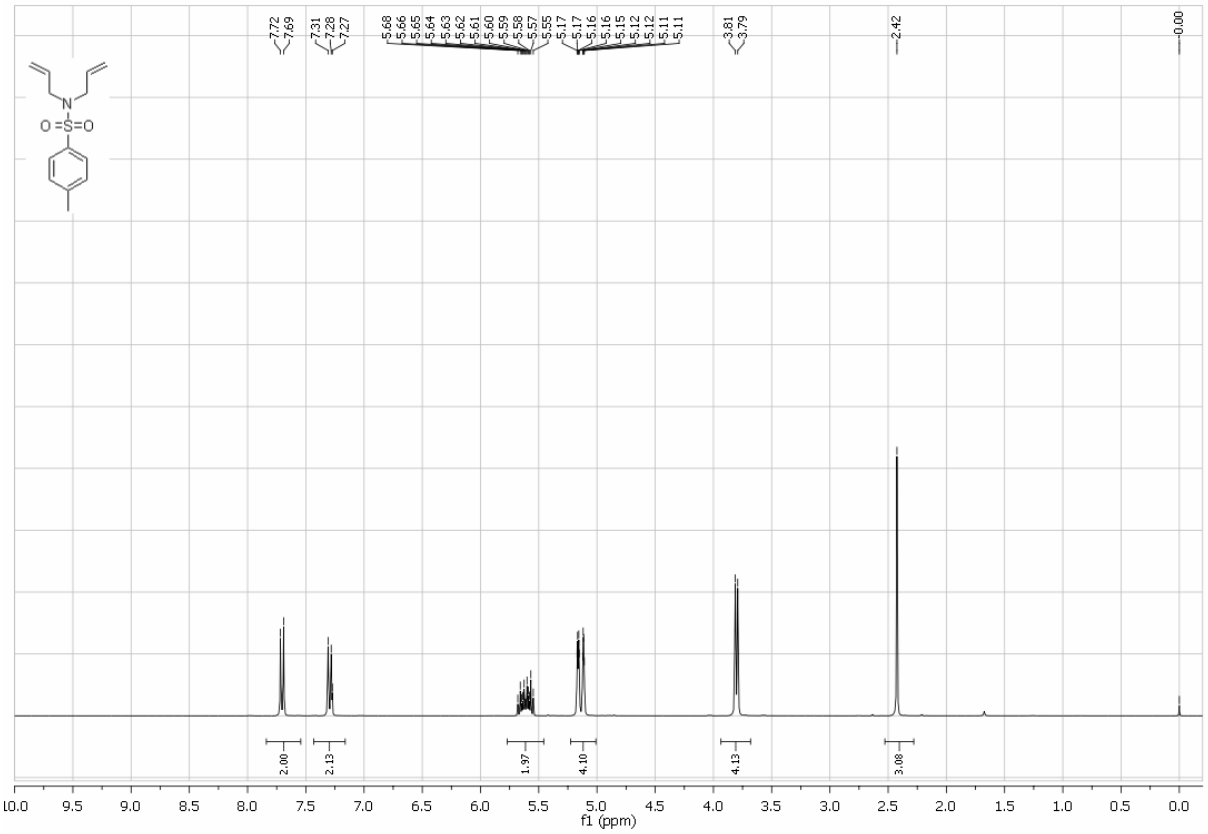
^{13}C NMR spectrum of 7



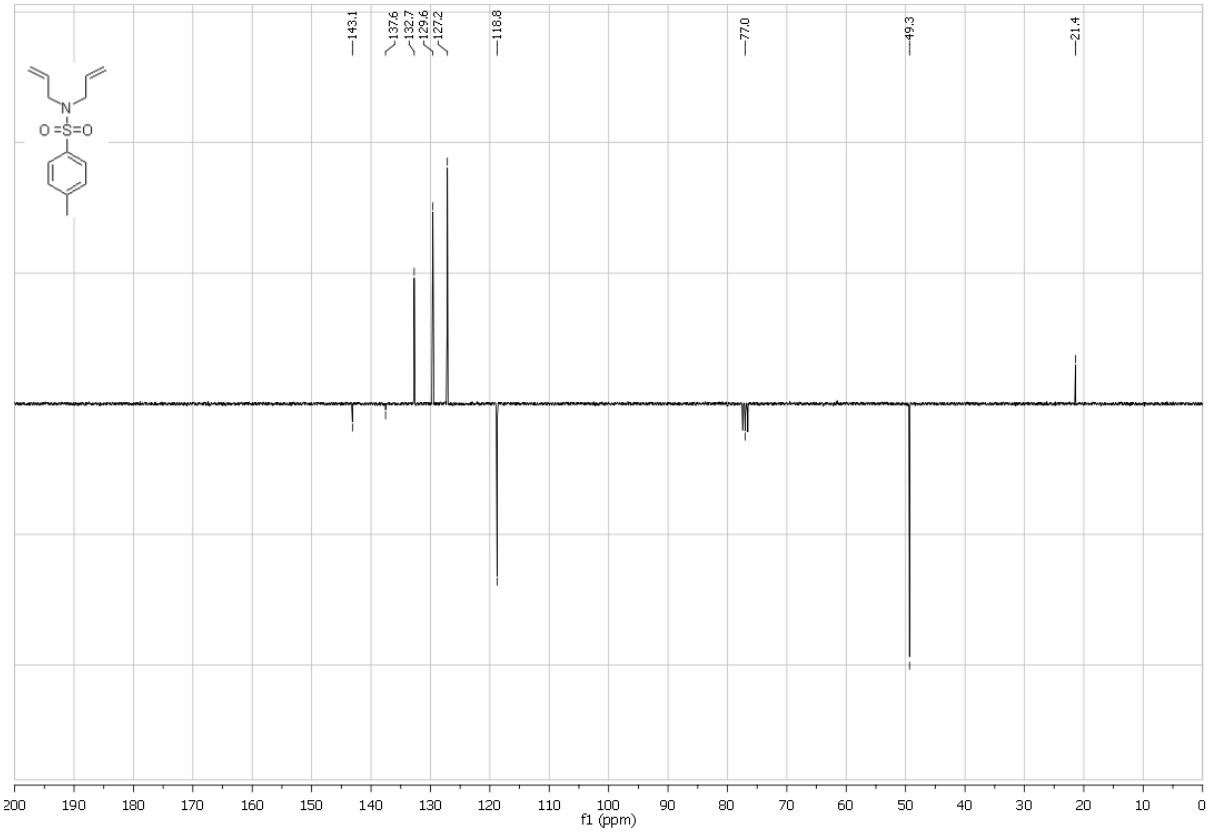
***N*,*N*-Diallyl-4-methylbenzenesulfonamide (8a)**

p-Toluenesulfonamide (**5**) (6.34 g, 36.4 mmol) was dissolved in acetonitrile (200 mL). Then 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).

^{1}H NMR spectrum of 8a



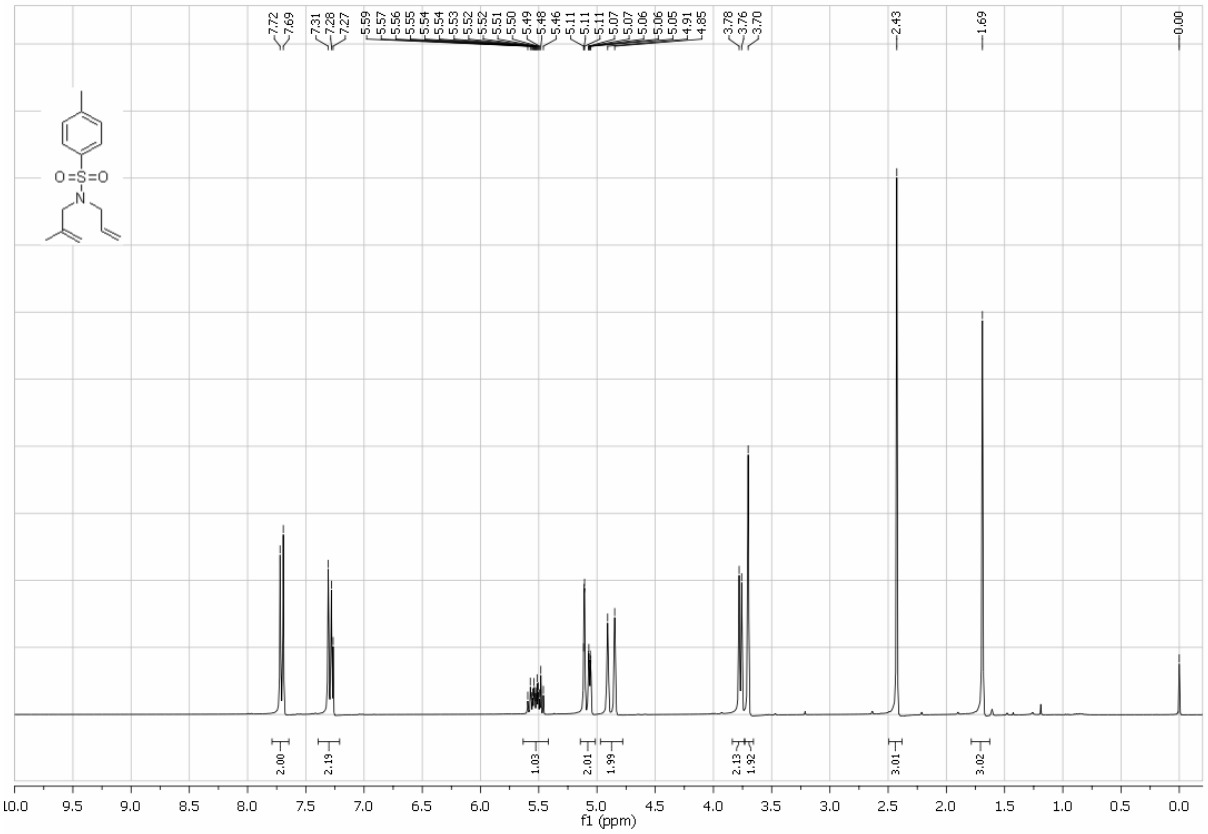
^{13}C NMR spectrum of 8a



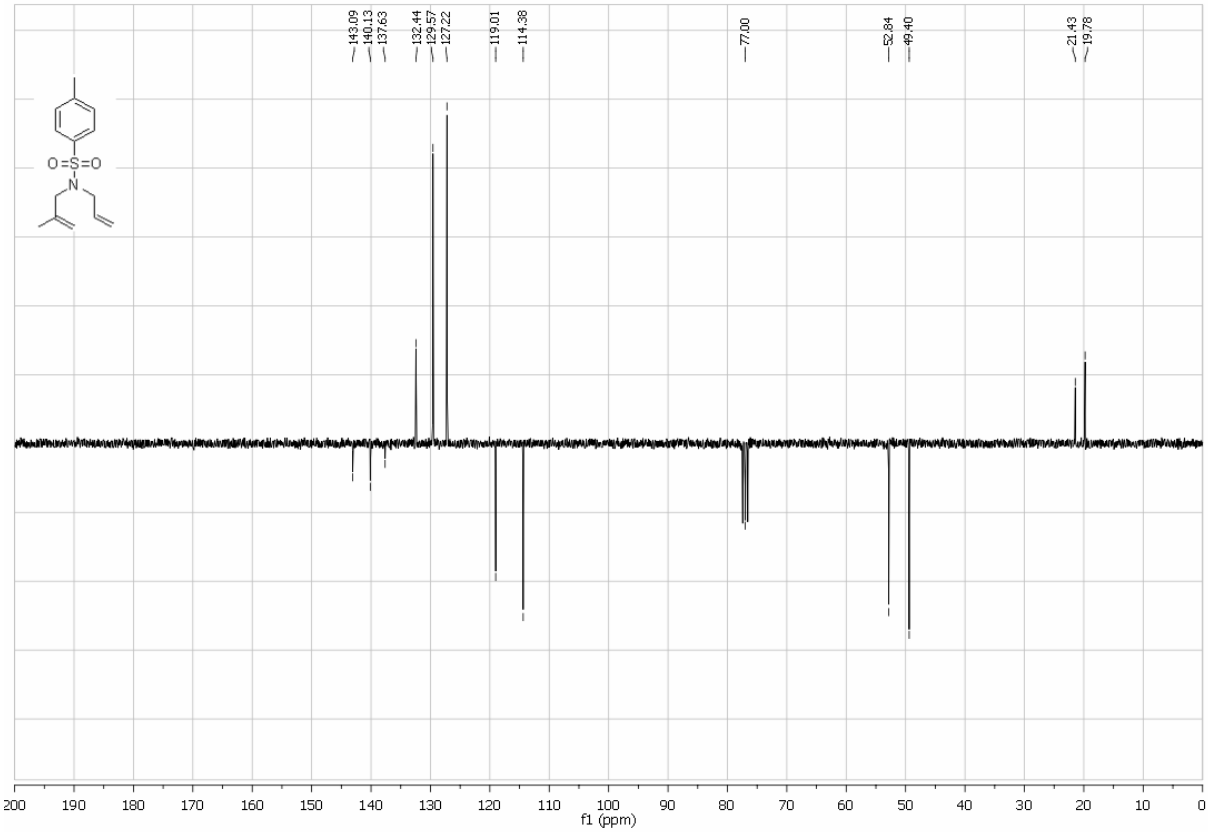
_N_-Allyl-4-methyl-_N_-(2-methylallyl)benzenesulfonamide (8b)

Amine **7** (1.27 g, 6.0 mmol) was dissolved in acetonitrile (33 mL). Then K_2CO_3 (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}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.

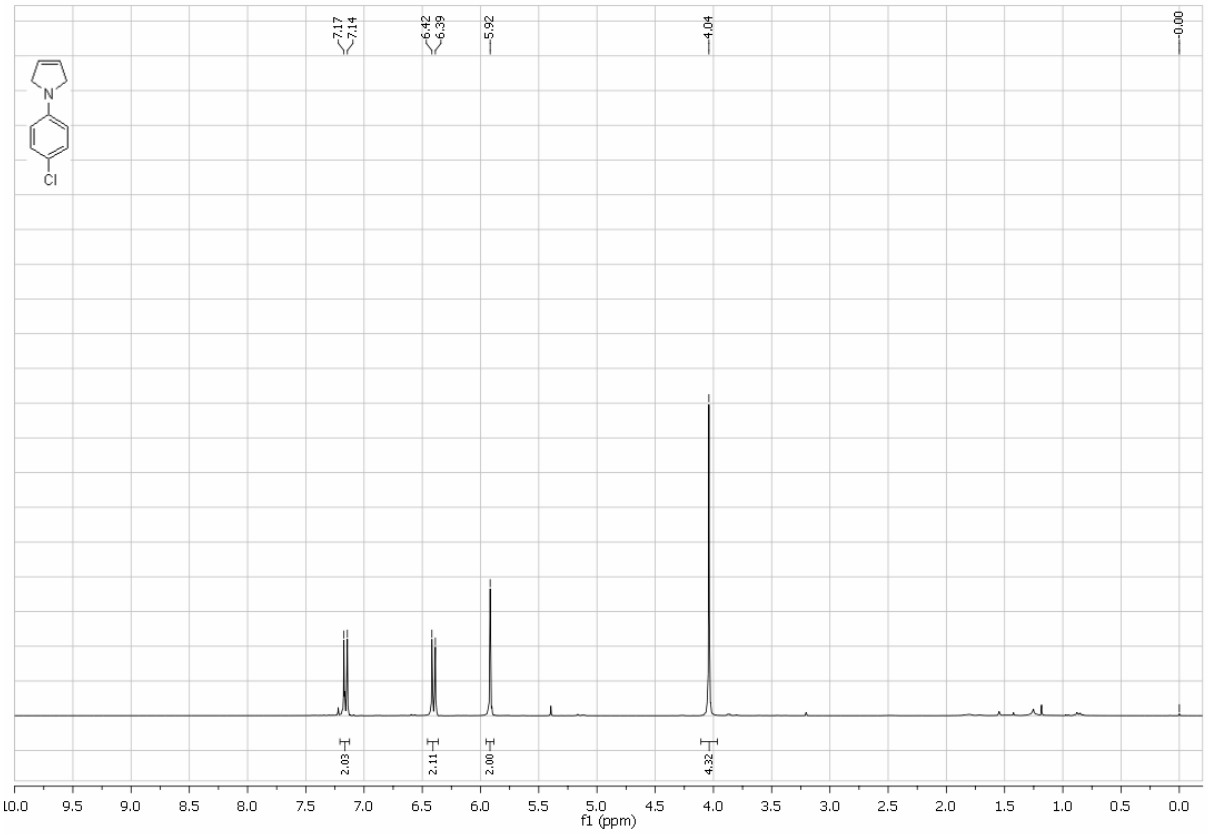
*B3 General procedure for the synthesis of disubstituted pyrrols **10l** and **10m** via RCM-aromatization*

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 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.

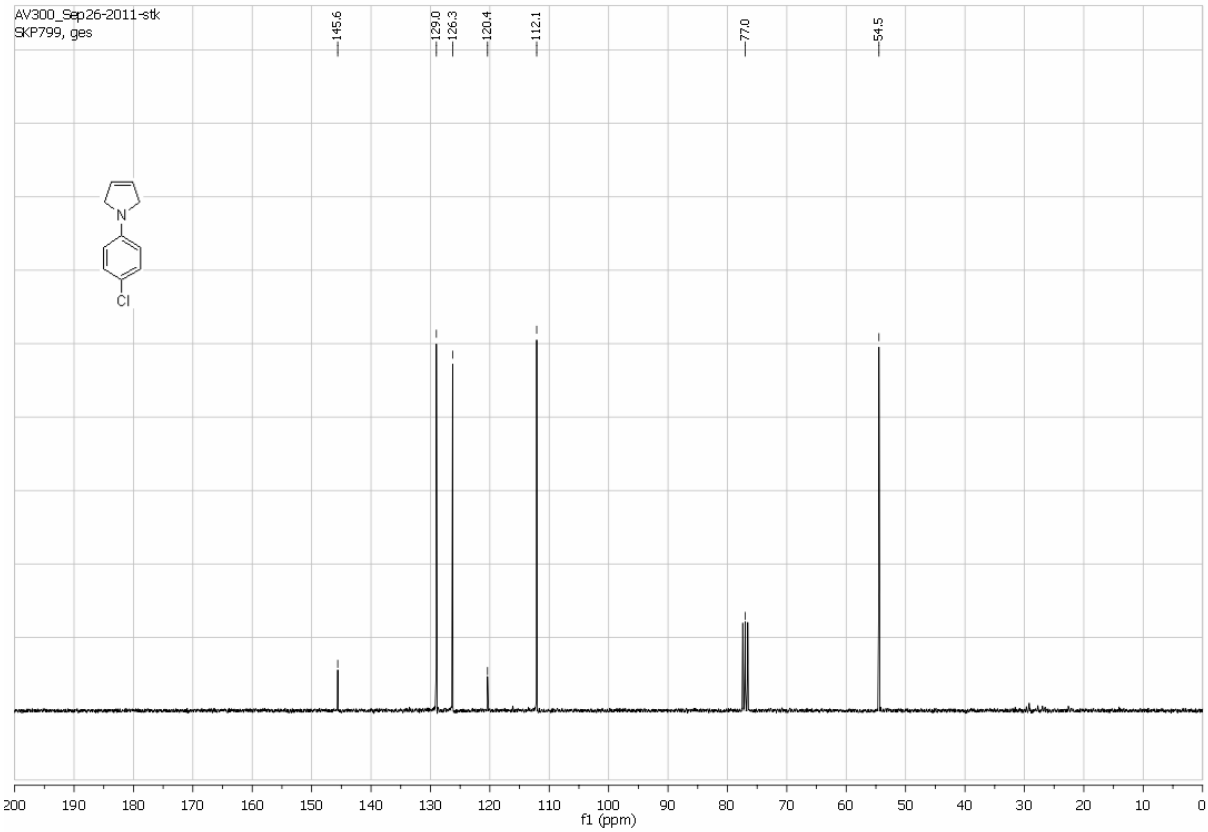
1-(4-Chlorophenyl)-2,5-dihydro-1*H*-pyrrole (9a)

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: $\tilde{\upsilon}$ = 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



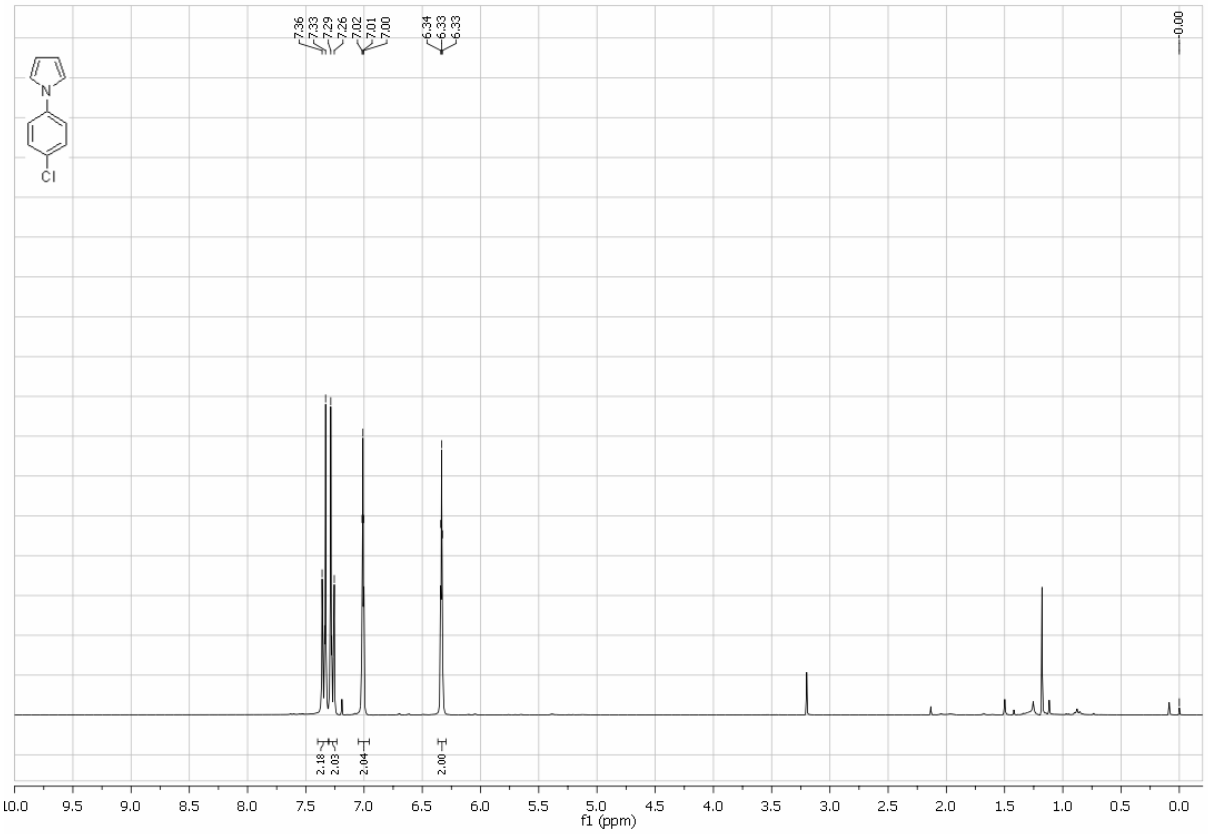
^{13}C NMR spectrum of 9a



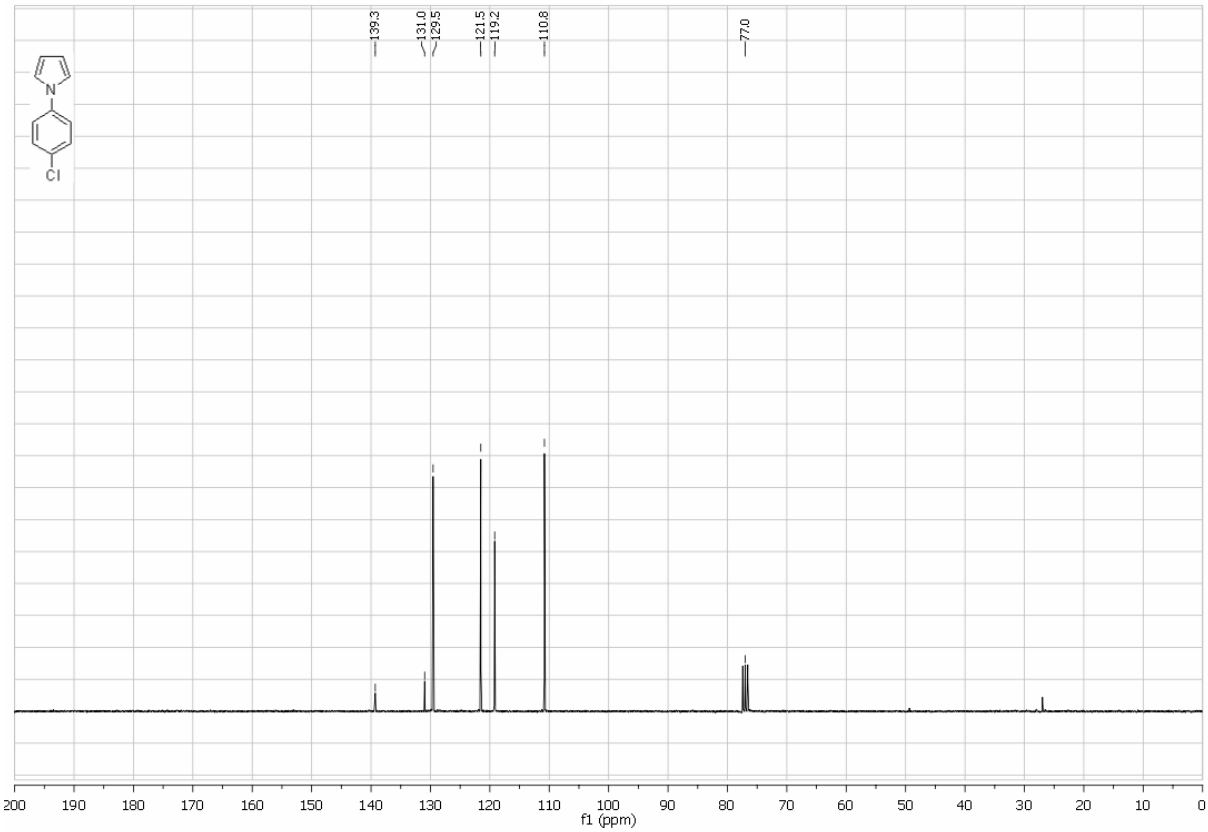
1-(4-Chlorophenyl)-1*H*-pyrrole (10a)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10a



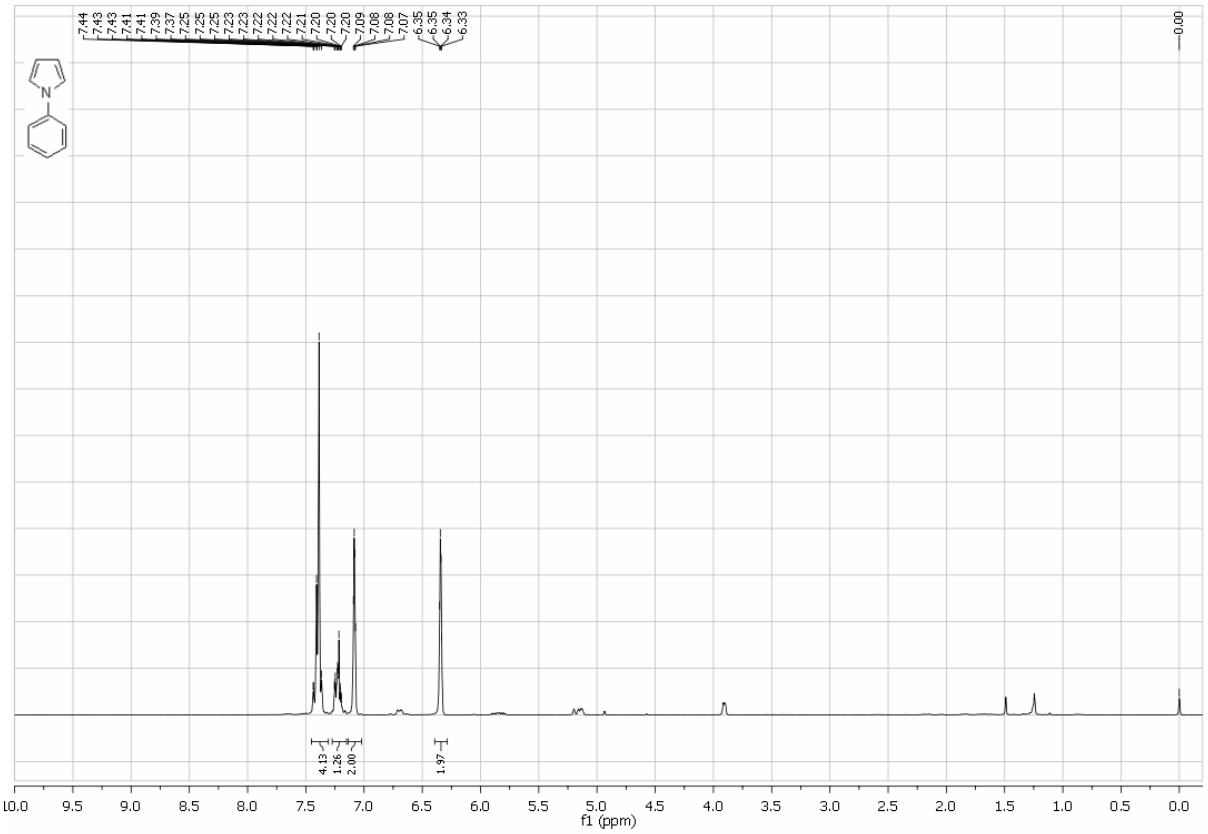
^{13}C NMR spectrum of 10a



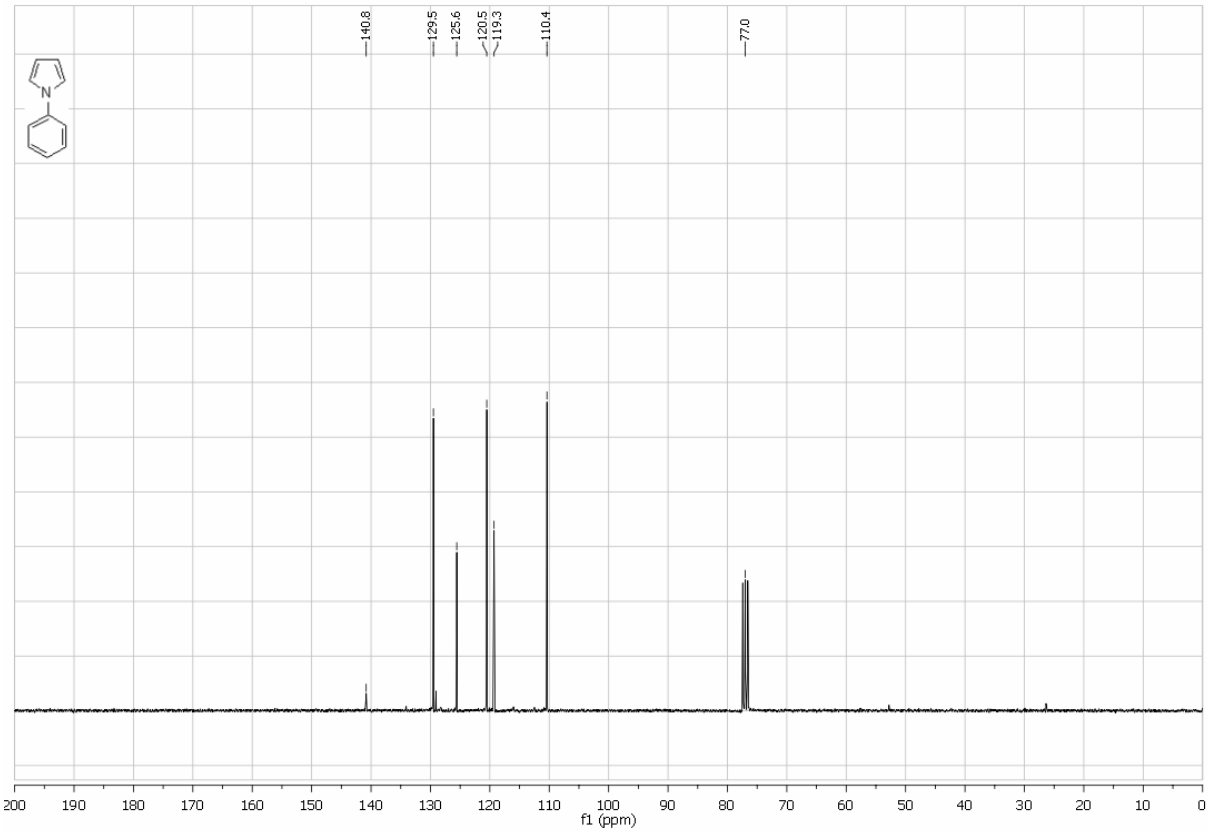
1-Phenyl-1*H*-pyrrole (10b)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10b



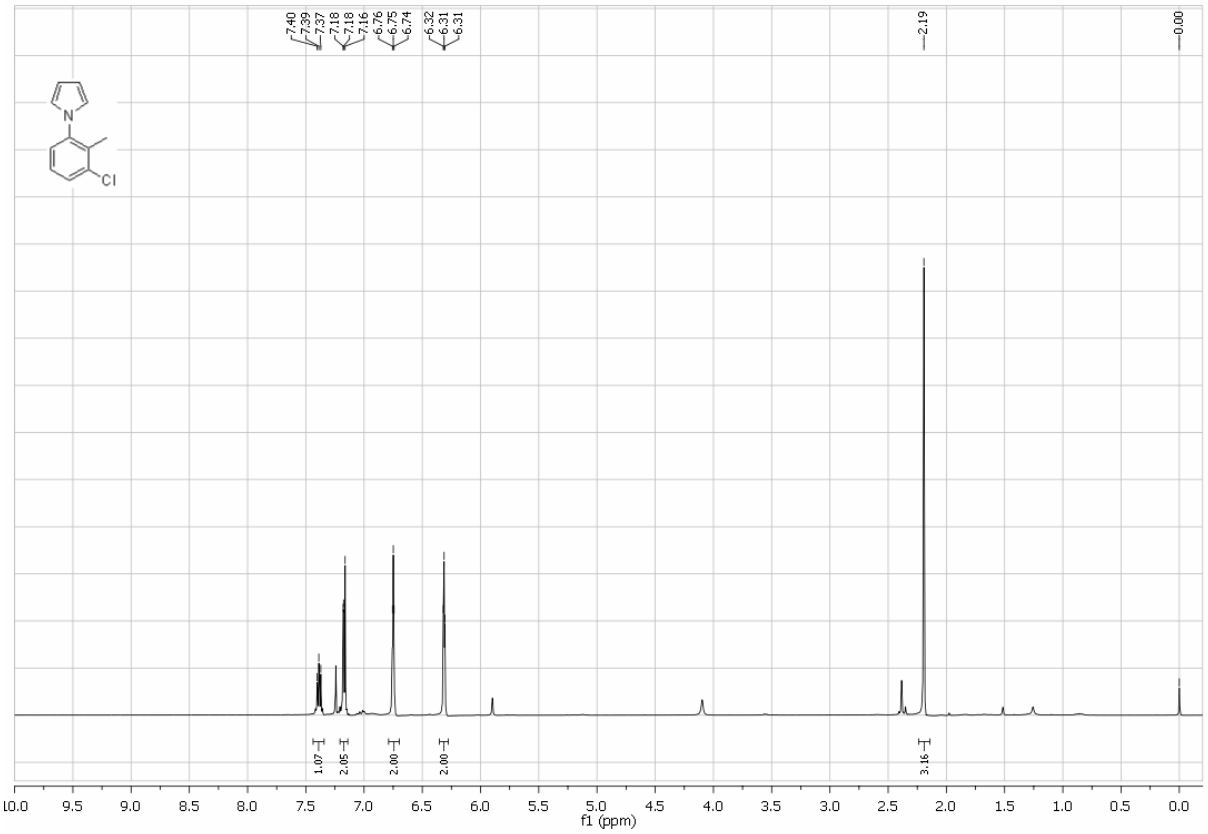
^{13}C NMR spectrum of 10b



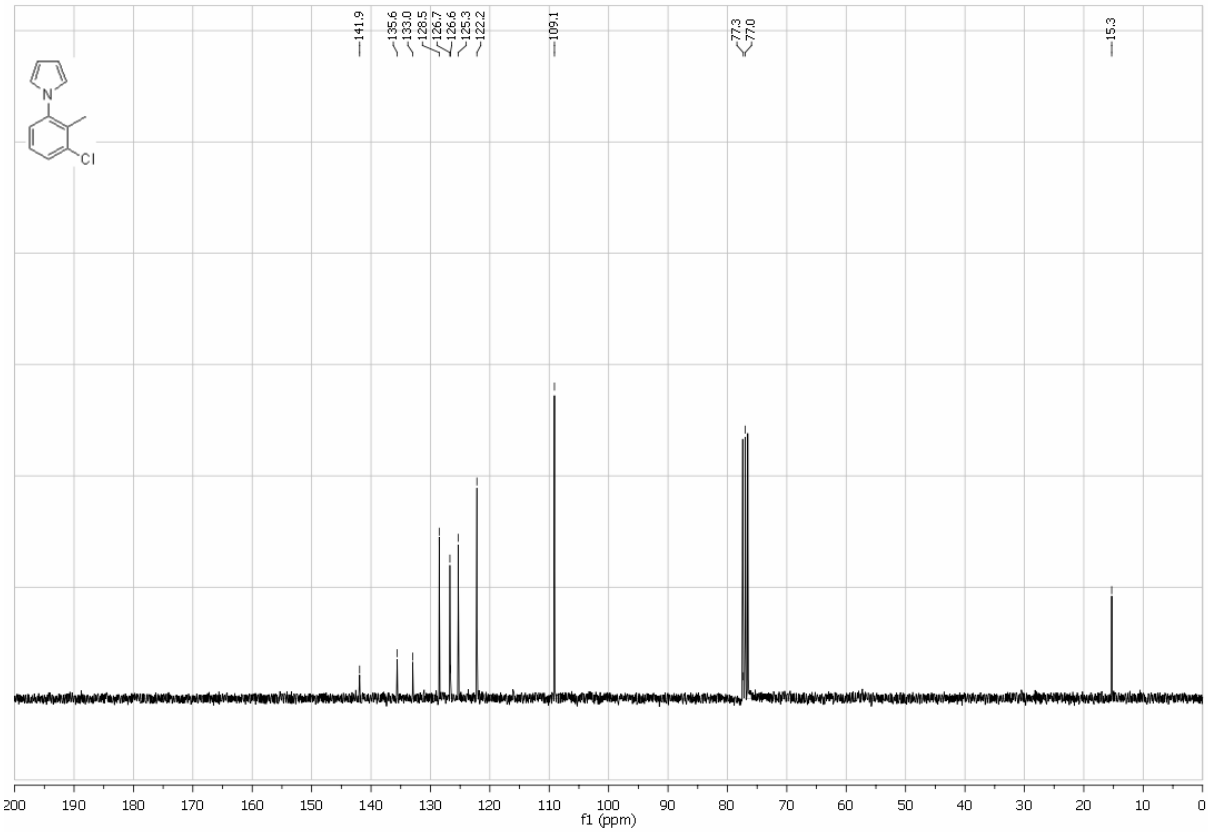
1-(3-Chloro-2-methylphenyl)-1*H*-pyrrole (10c)

Following the general procedure B2, **10c** was obtained from **2c** (221mg, 1.0mmol) 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: $\tilde{\upsilon}$ = 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



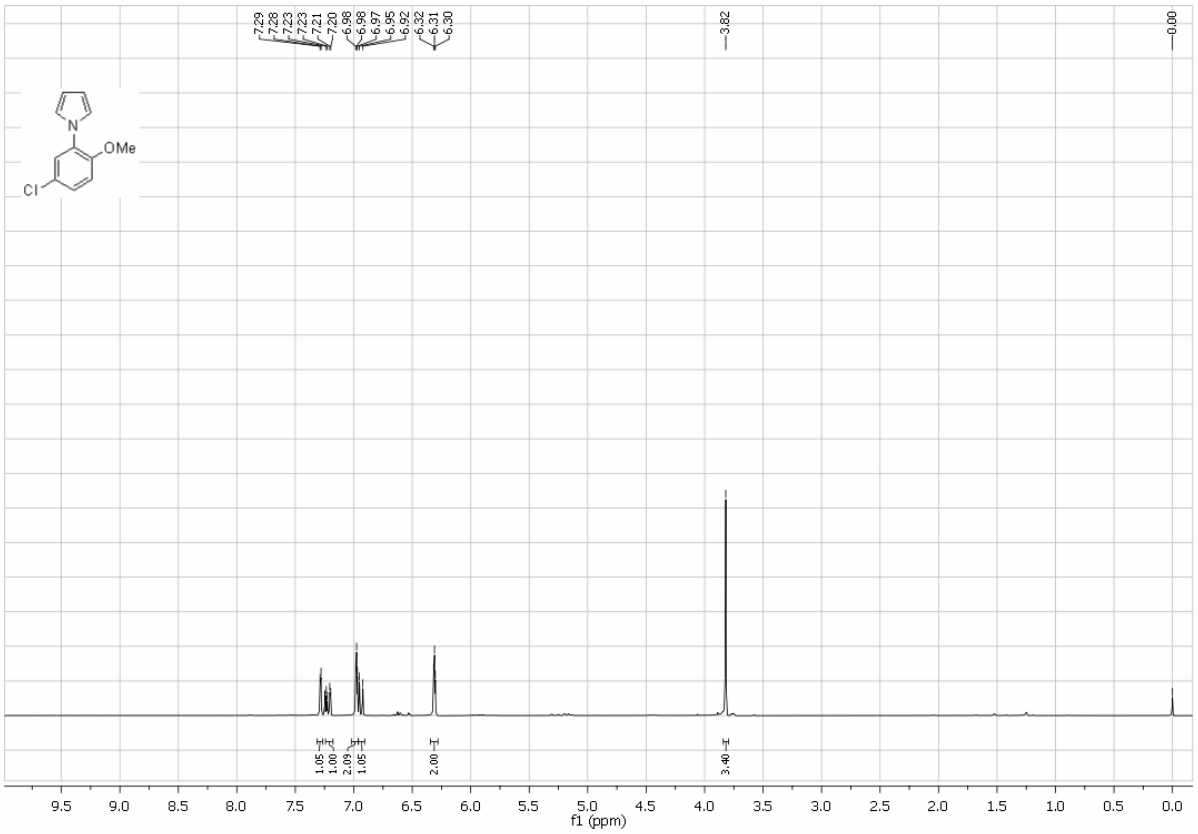
^{13}C NMR spectrum of 10c



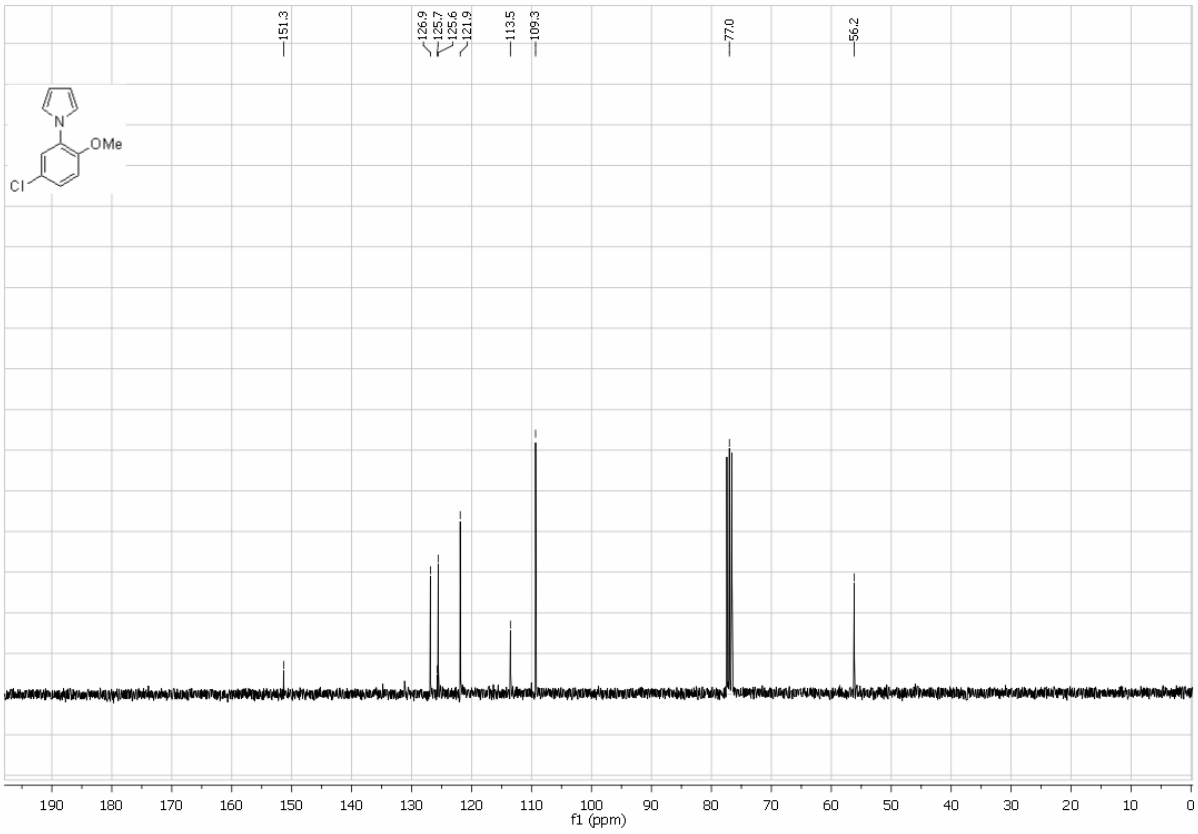
1-(5-Chloro-2-methoxyphenyl)-1*H*-pyrrole (10d)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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



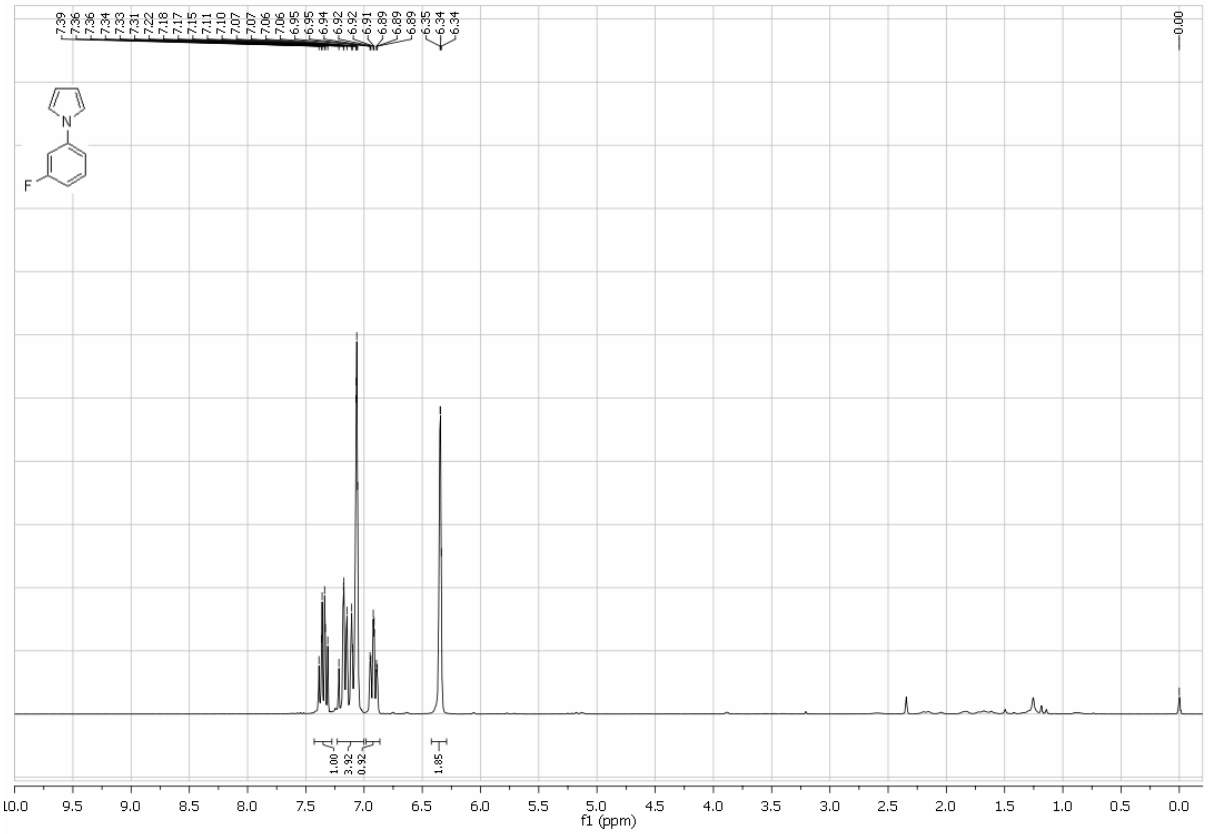
^{13}C NMR spectrum of 10d



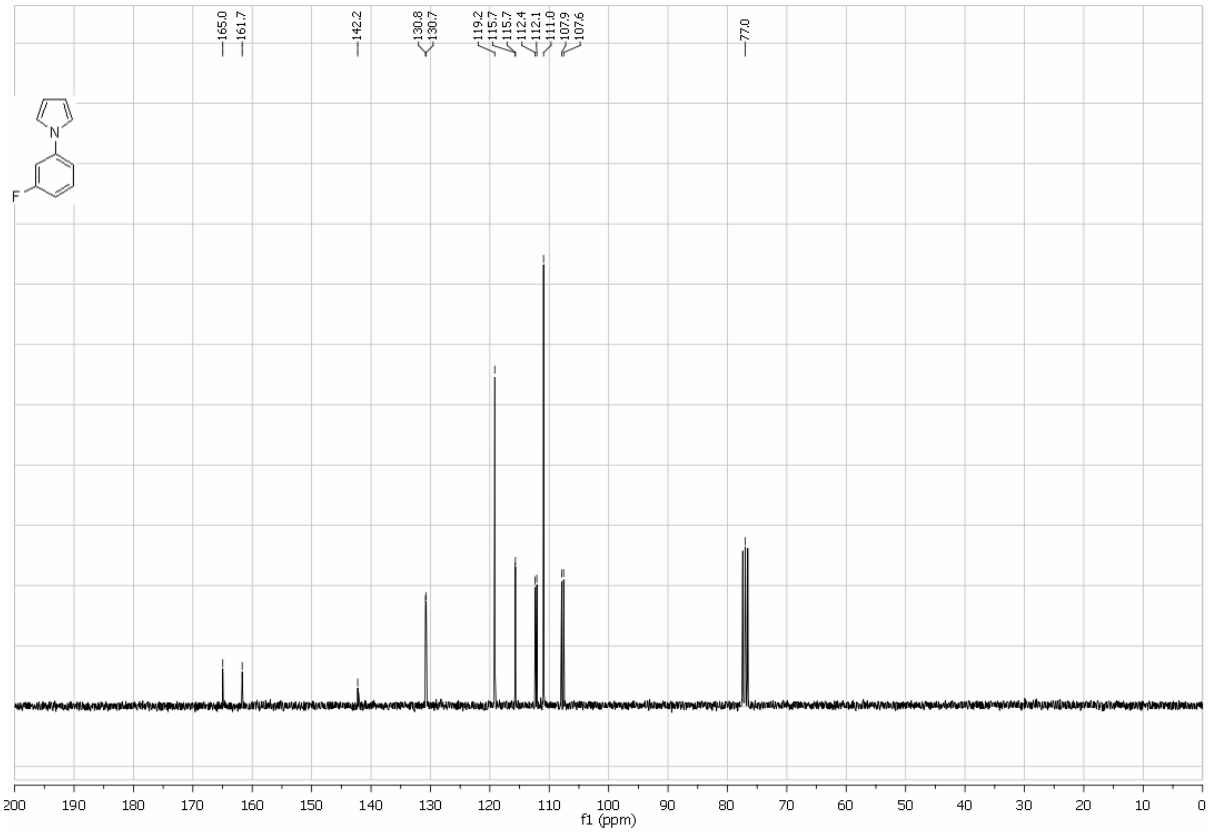
1-(3-Fluorophenyl)-1*H*-pyrrole (10f)

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, $CDCl_3$) 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, ^{1}J = 246.6), 142.2 (1, d, ^{3}J = 9.8), 130.8 (1, d, ^{3}J = 9.3), 119.2 (1, 2C), 115.7 (1, d, ^{4}J = 2.9), 112.3 (d, ^{2}J = 21.2), 111.0 (1, 2C), 107.8 (1, d, ^{2}J = 25.1); IR: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10f



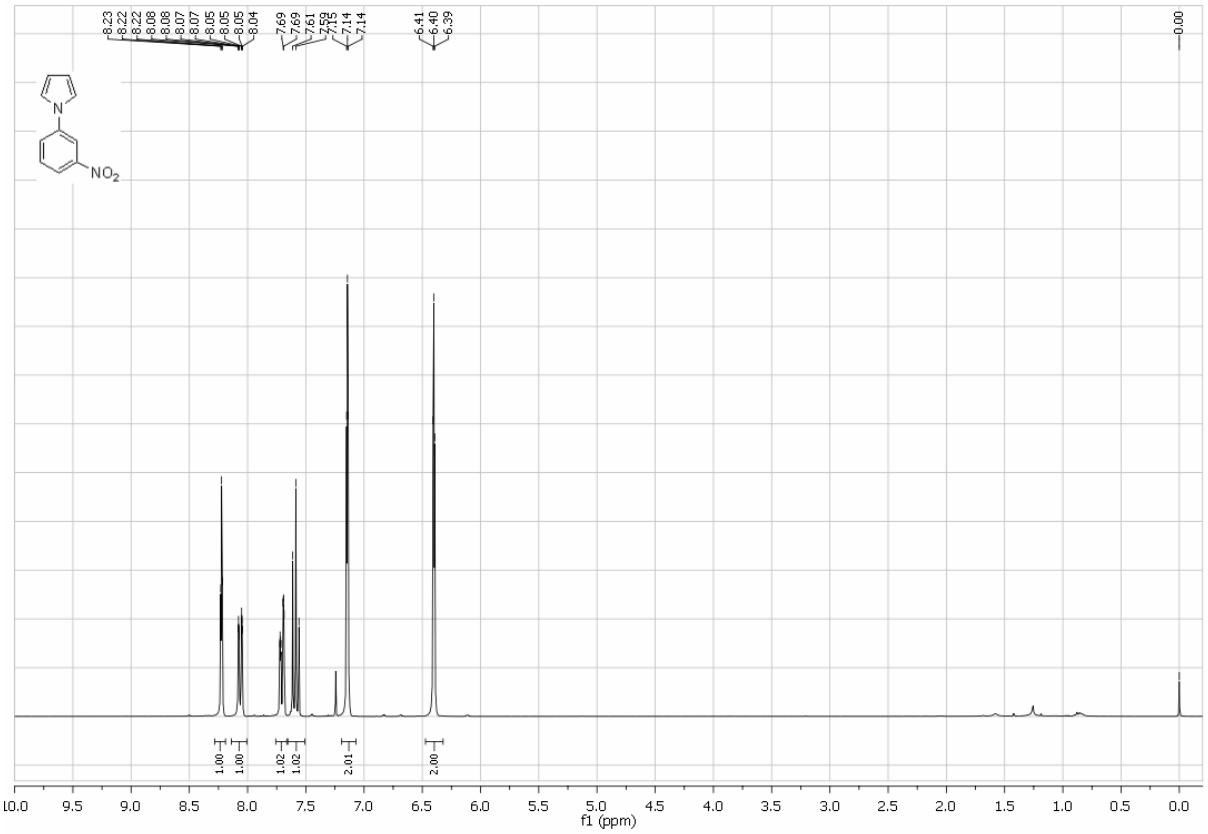
^{13}C NMR spectrum of 10f



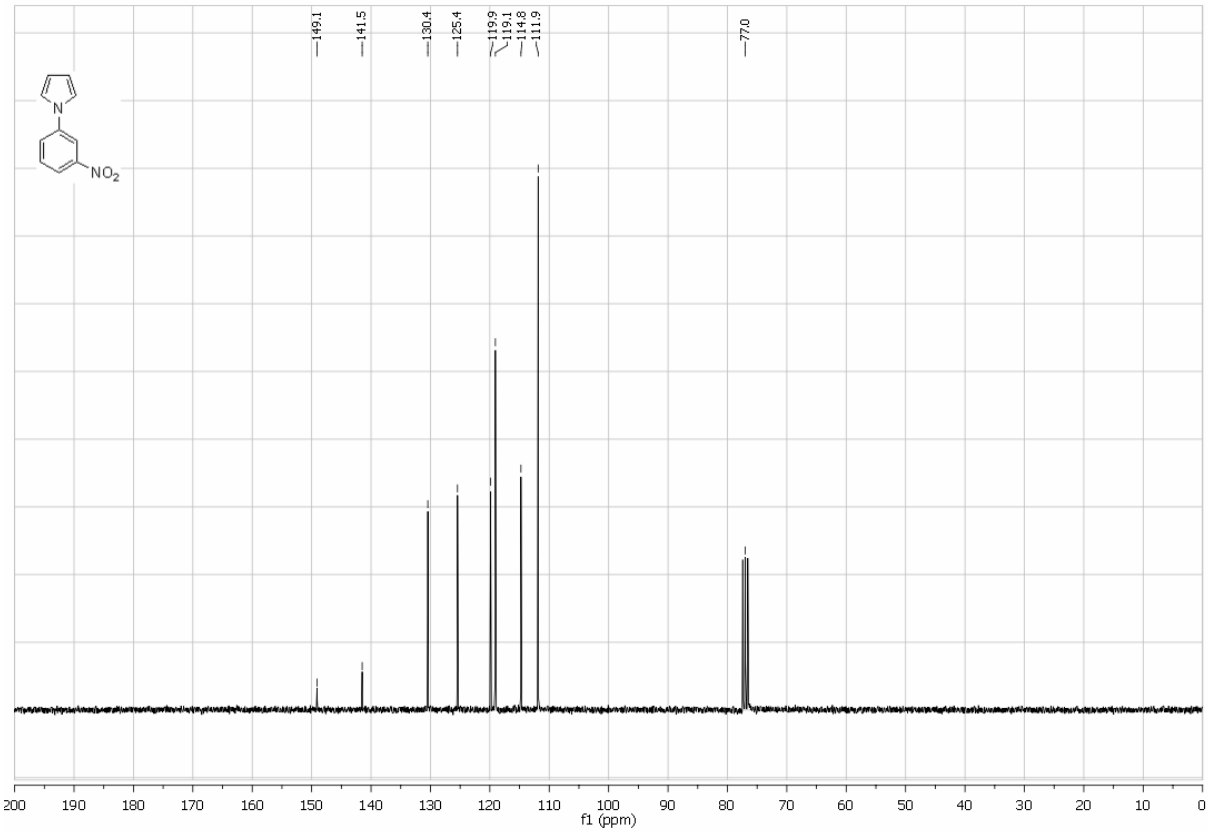
1-(3-Nitrophenyl)-1*H*-pyrrole (10g)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 10g



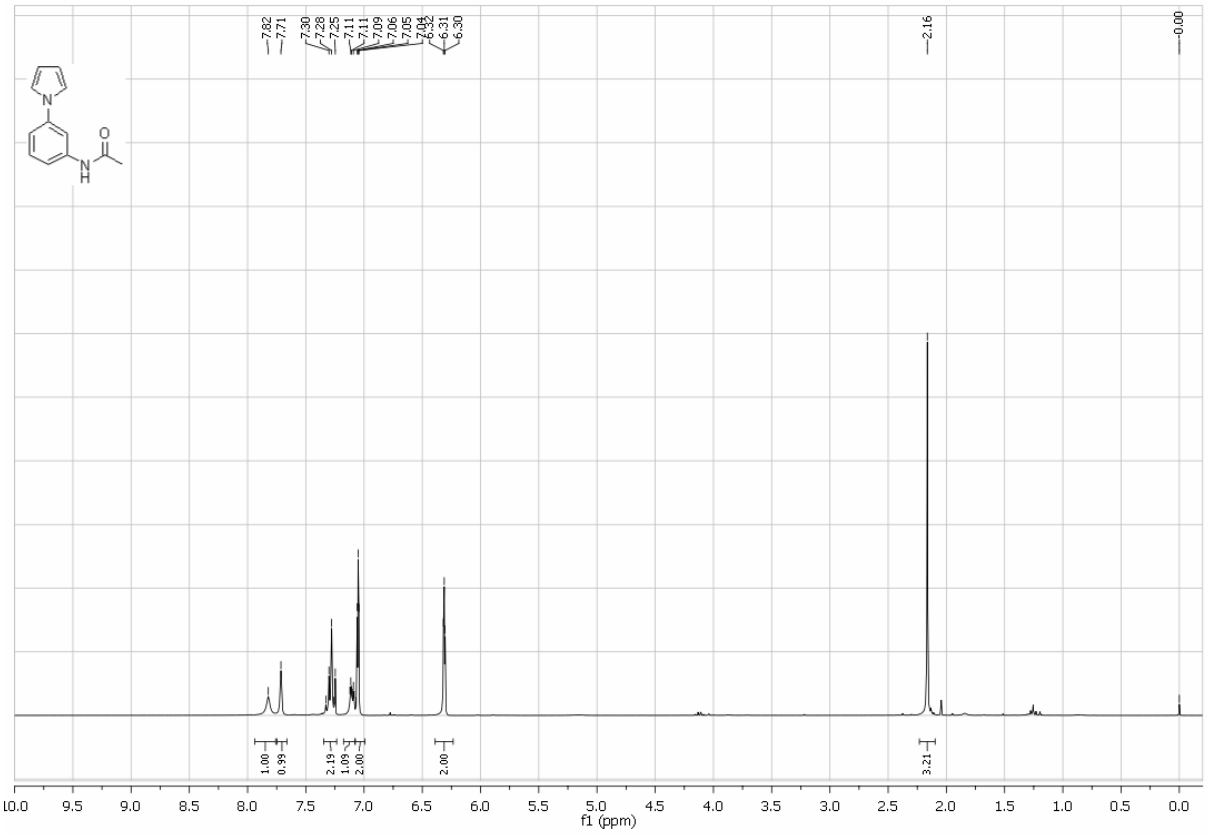
^{13}C NMR spectrum of 10g



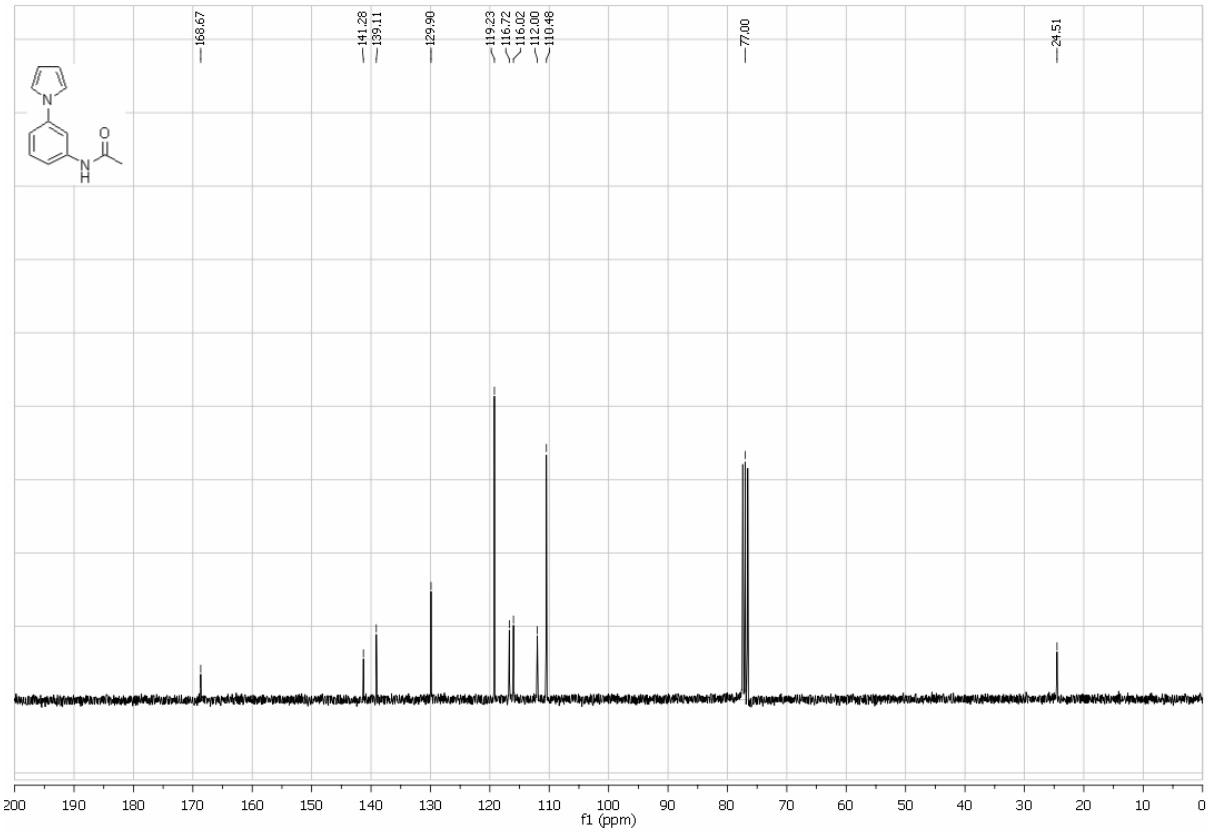
_N_-(3-(1_H_-pyrrol-1-yl)phenyl)acetamide (10h)

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 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: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10h



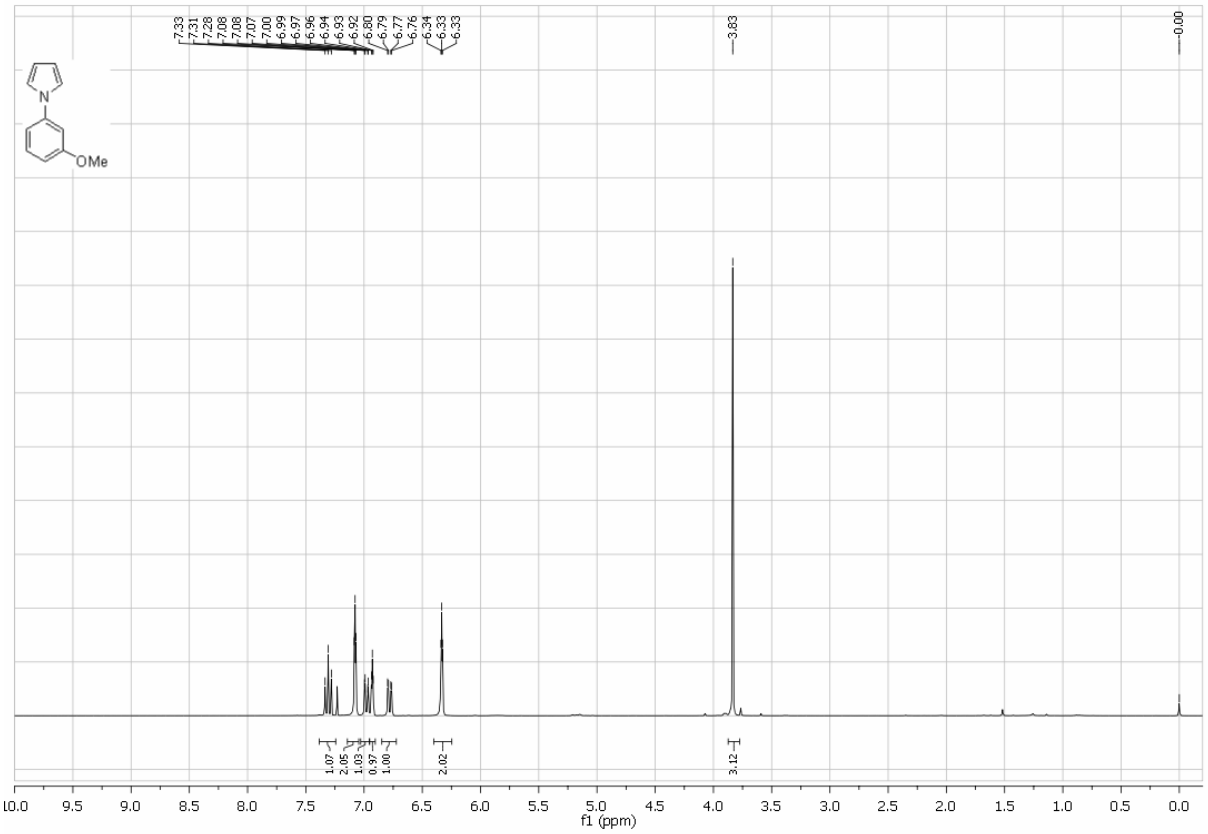
^{13}C NMR spectrum of 10h



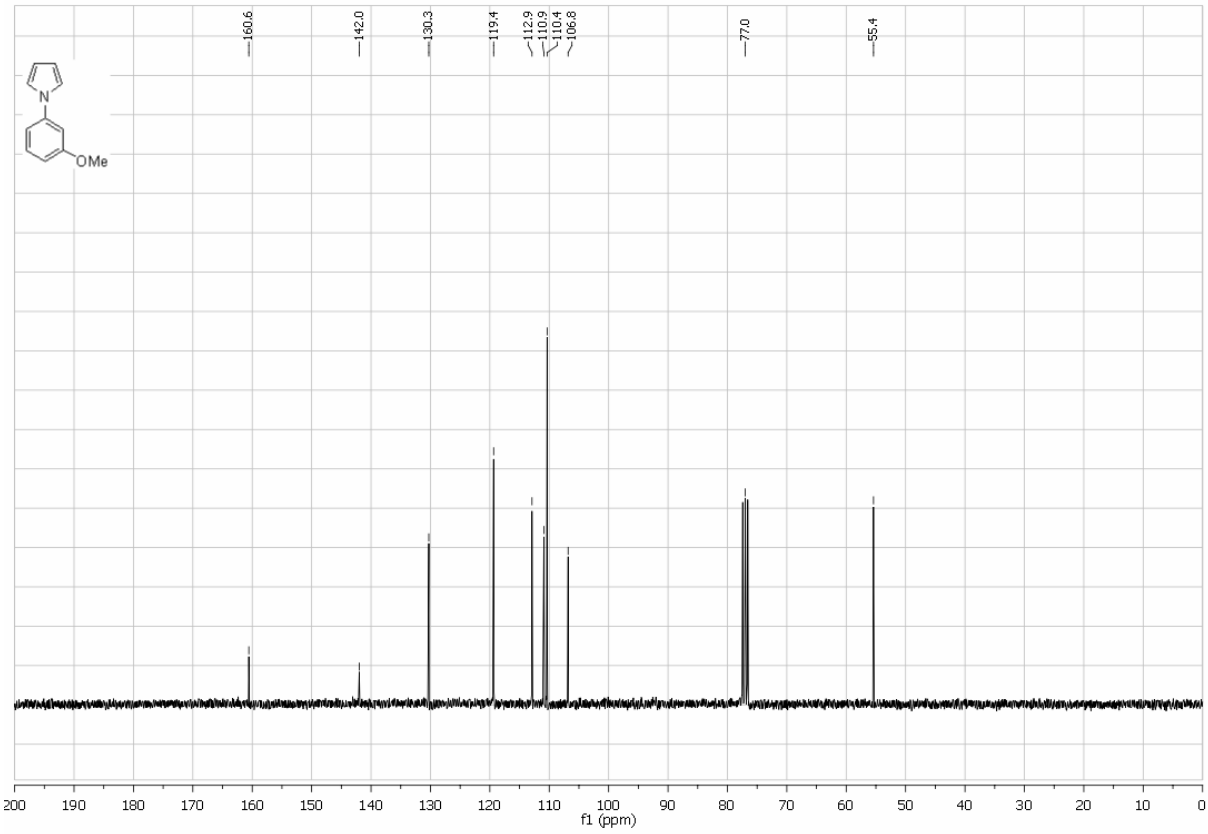
1-(3-Methoxyphenyl)-1*H*-pyrrole (10i)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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



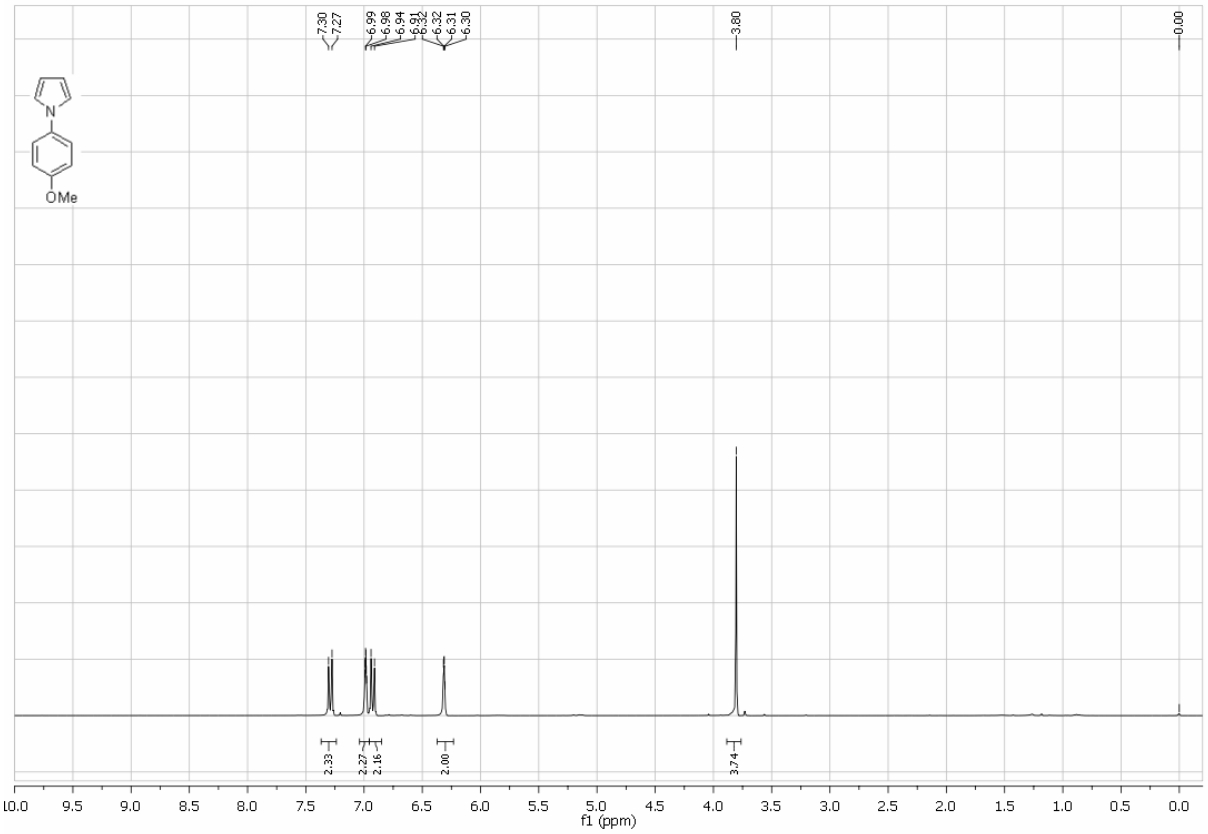
^{13}C NMR spectrum of 10i



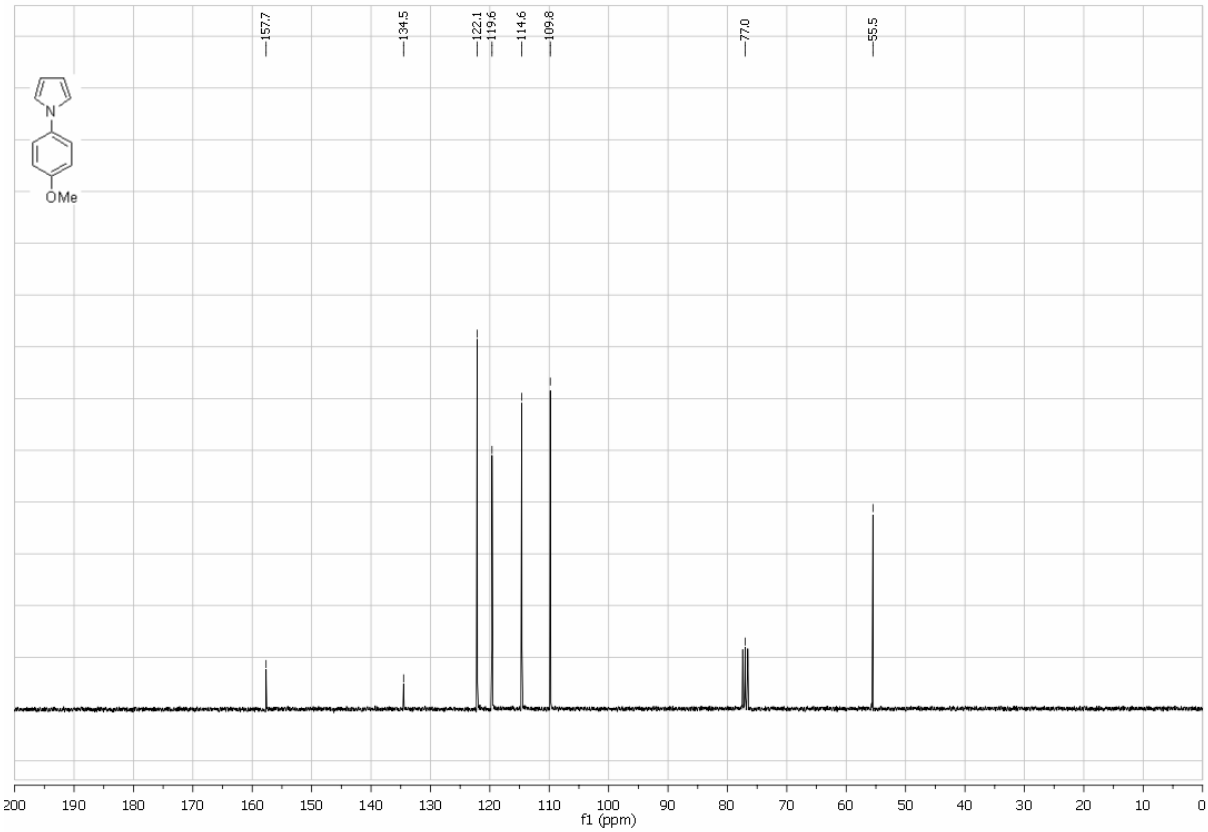
1-(4-Methoxyphenyl)-1*H*-pyrrole (10j)

Following the general procedure B2, **10j** was obtained from **2j** (203mg, 1.0mmol) as a colorless solid (150 mg, 87%). Mp: 110 – 111 °C; ^{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: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10j



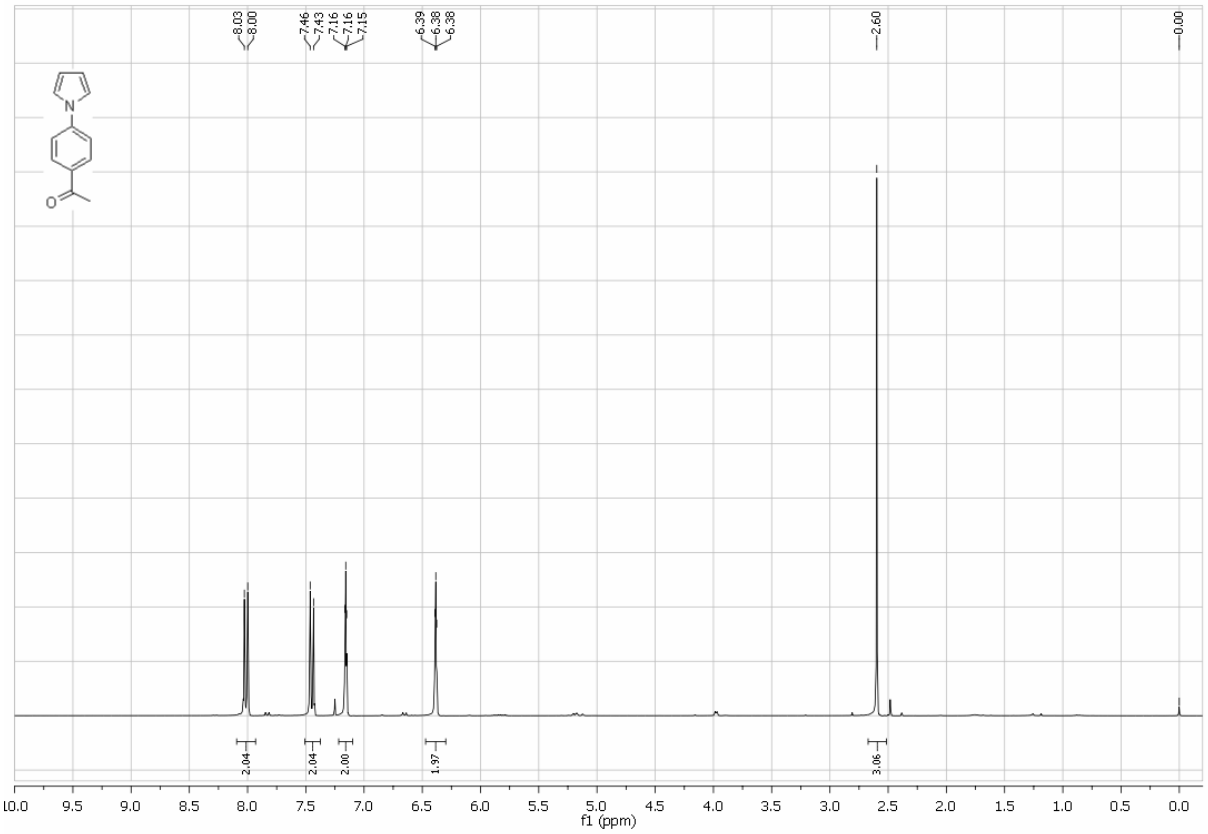
^{13}C NMR spectrum of 10j



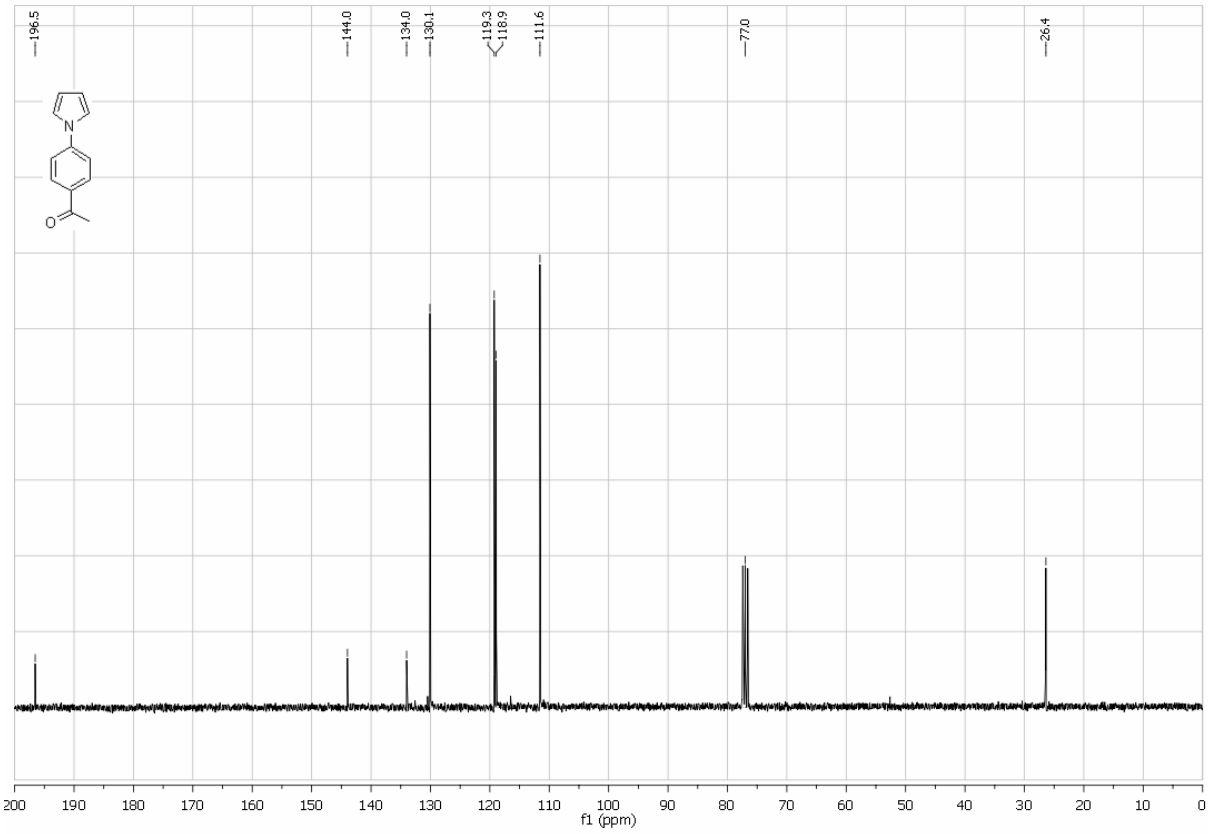
1-(4-(1*H*-Pyrrol-1-yl)phenyl)ethanone (10k)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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



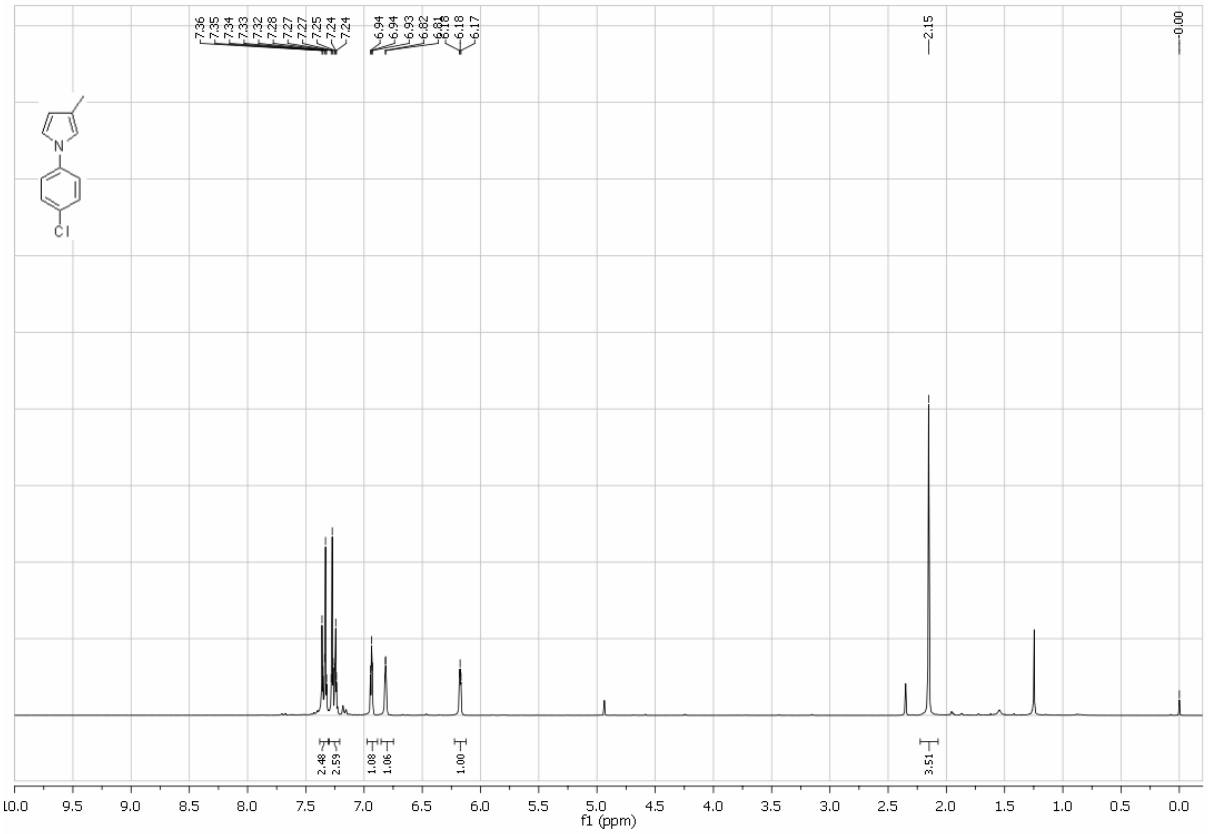
^{13}C NMR spectrum of 10k



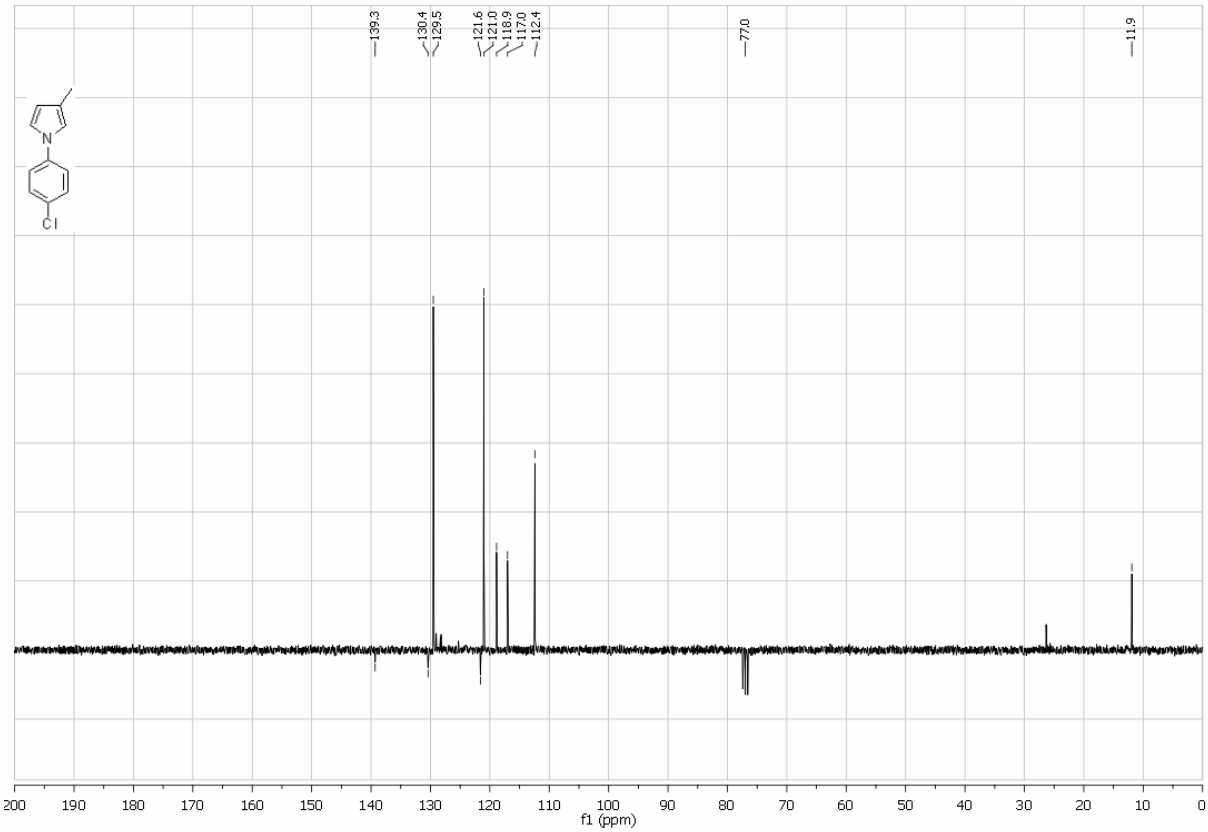
1-(4-Chlorophenyl)-3-methyl-1*H*-pyrrole (10l)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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



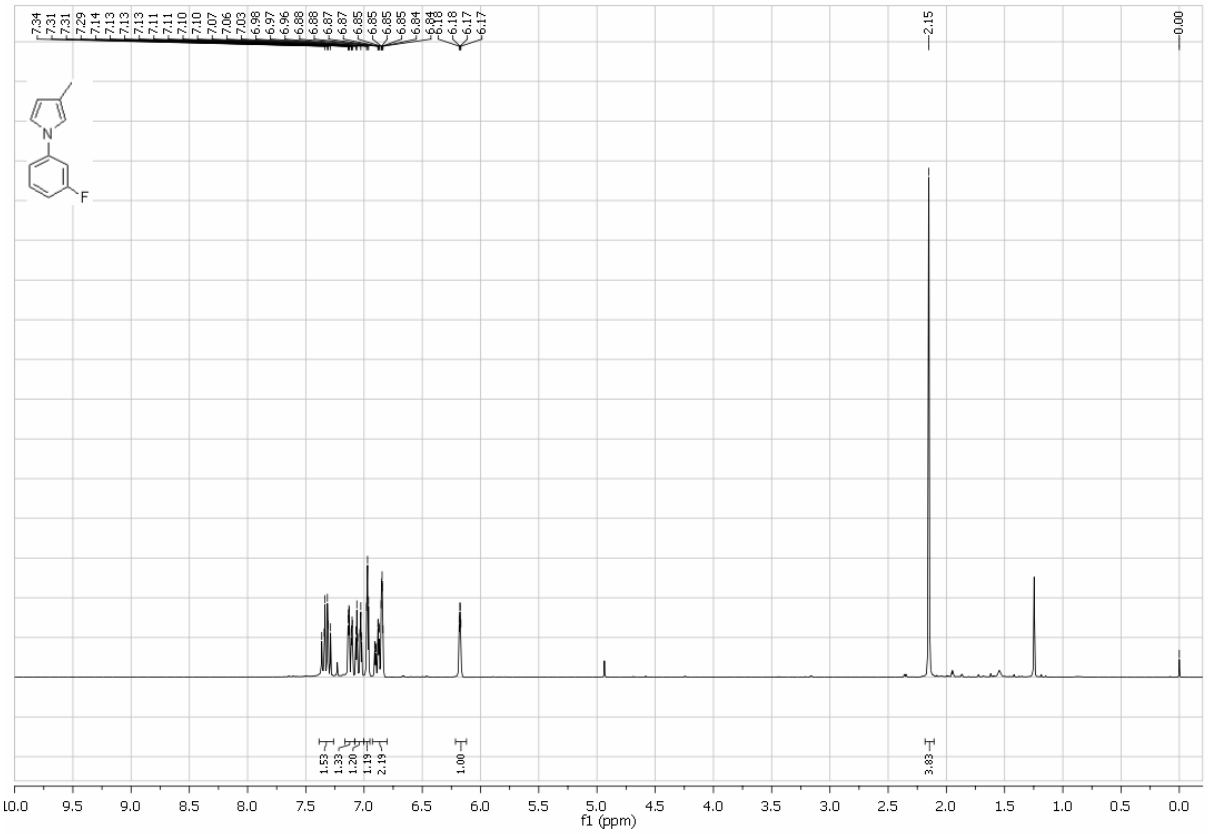
^{13}C NMR spectrum of 10l



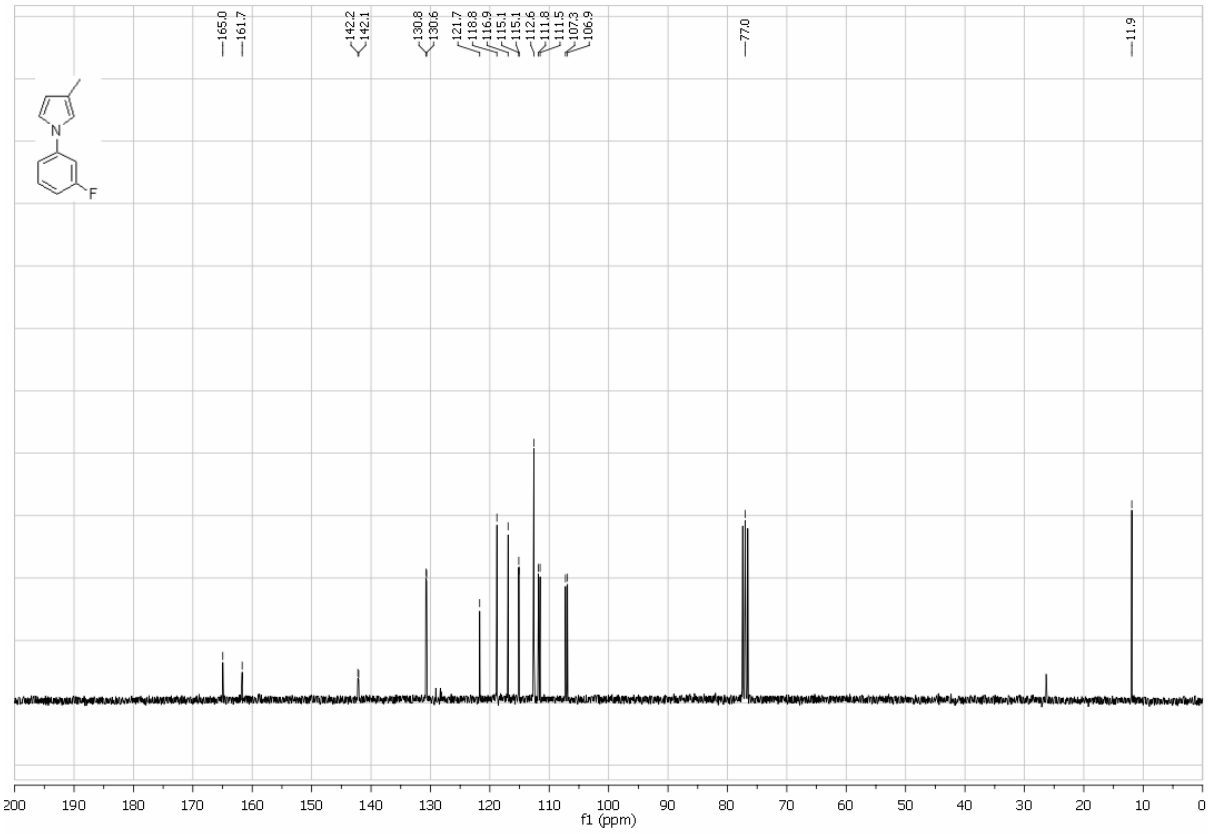
1-(3-Fluorophenyl)-3-methyl-1*H*-pyrrole (10m)

Following the general procedure B3, **10m** was obtained from **4f** (154mg, 0.75mmol) as a colorless solid (121 mg, 92%). Mp: 57 – 59 °C; ^{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, ^{1}J = 246.2), 142.2 (0, d, ^{3}J = 10.2), 130.7 (1, d, ^{3}J = 9.4), 121.7 (0), 118.8 (1), 116.9 (1), 115.1 (1, d, ^{4}J = 2.9), 112.6 (1), 111.7 (1, d, 2*J* = 21.2), 107.1 (1, d, ^{2}J = 25.0), 11.9 (3); IR: $\tilde{\upsilon}$ = 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}H NMR spectrum of 10m



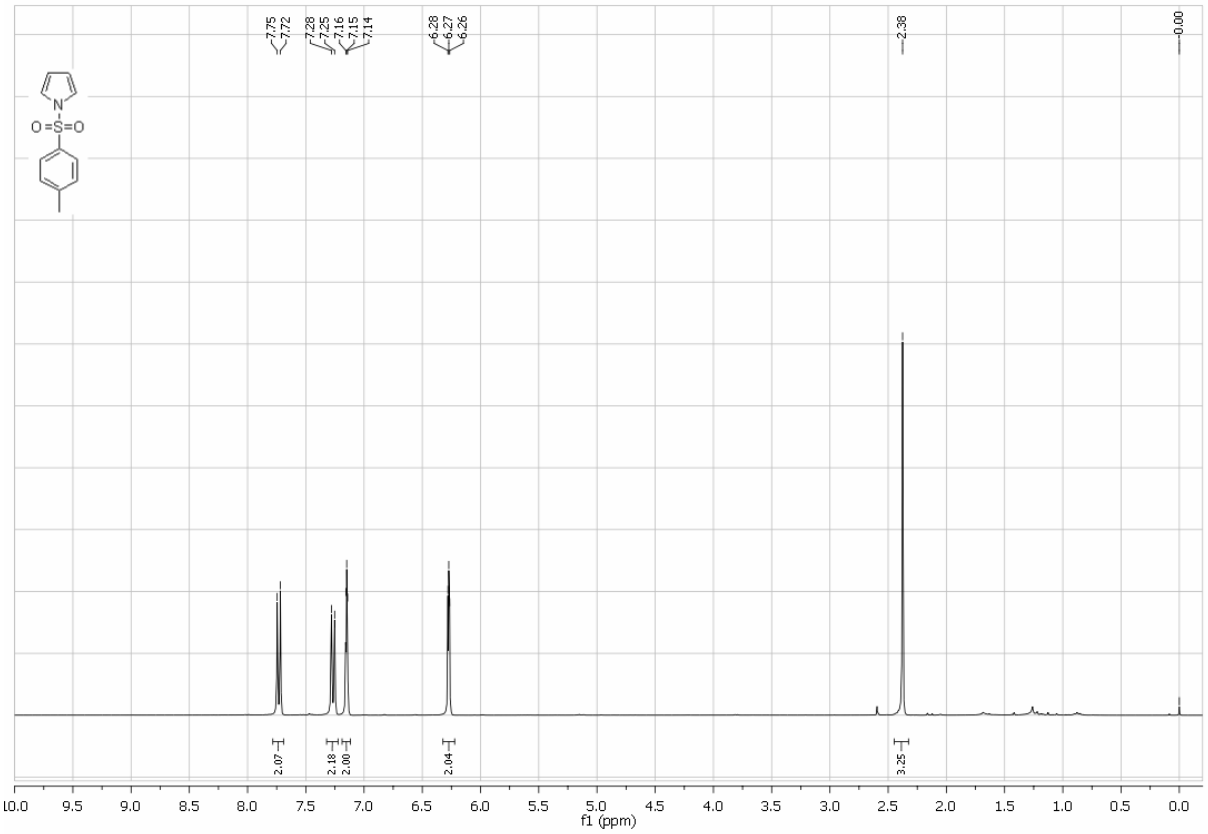
^{13}C NMR spectrum of 10m



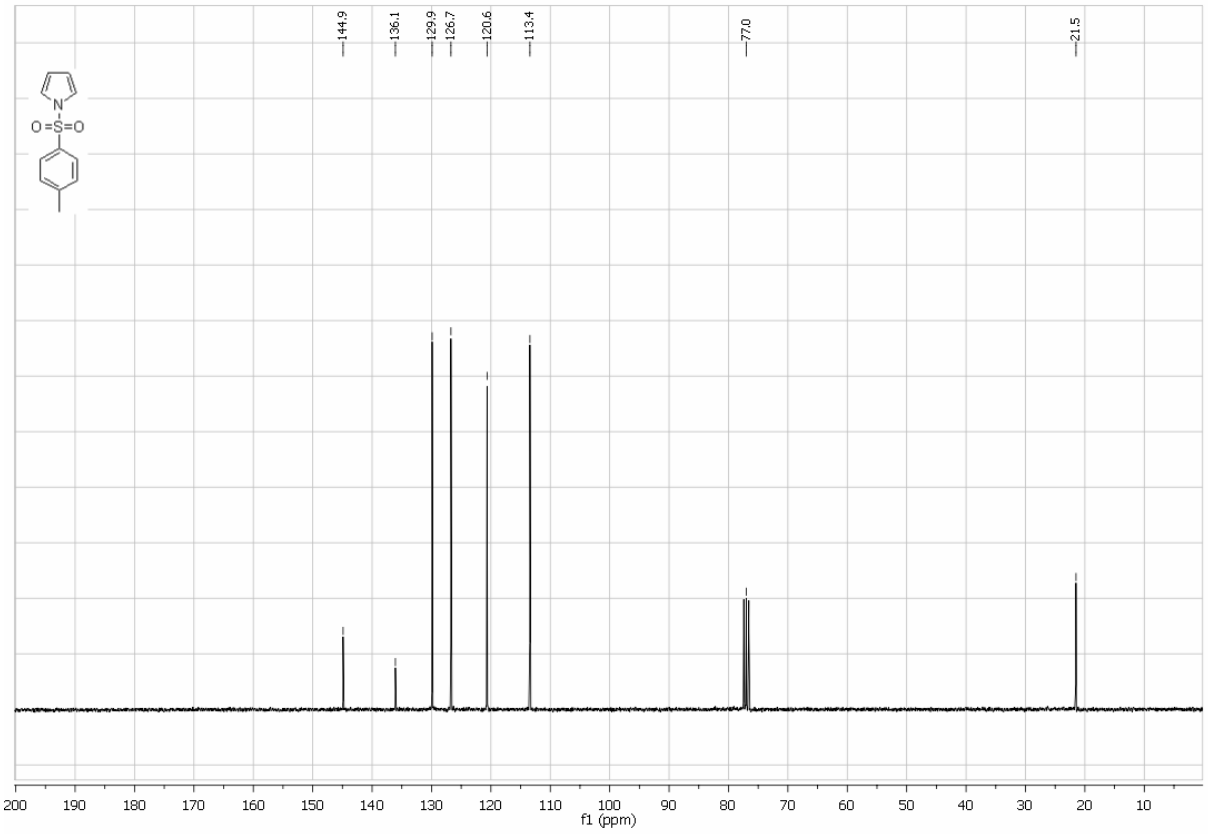
1-Tosyl-1*H*-pyrrole (12a)

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 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: $\tilde{\upsilon}$ = 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).

^{1}H NMR spectrum of 12a



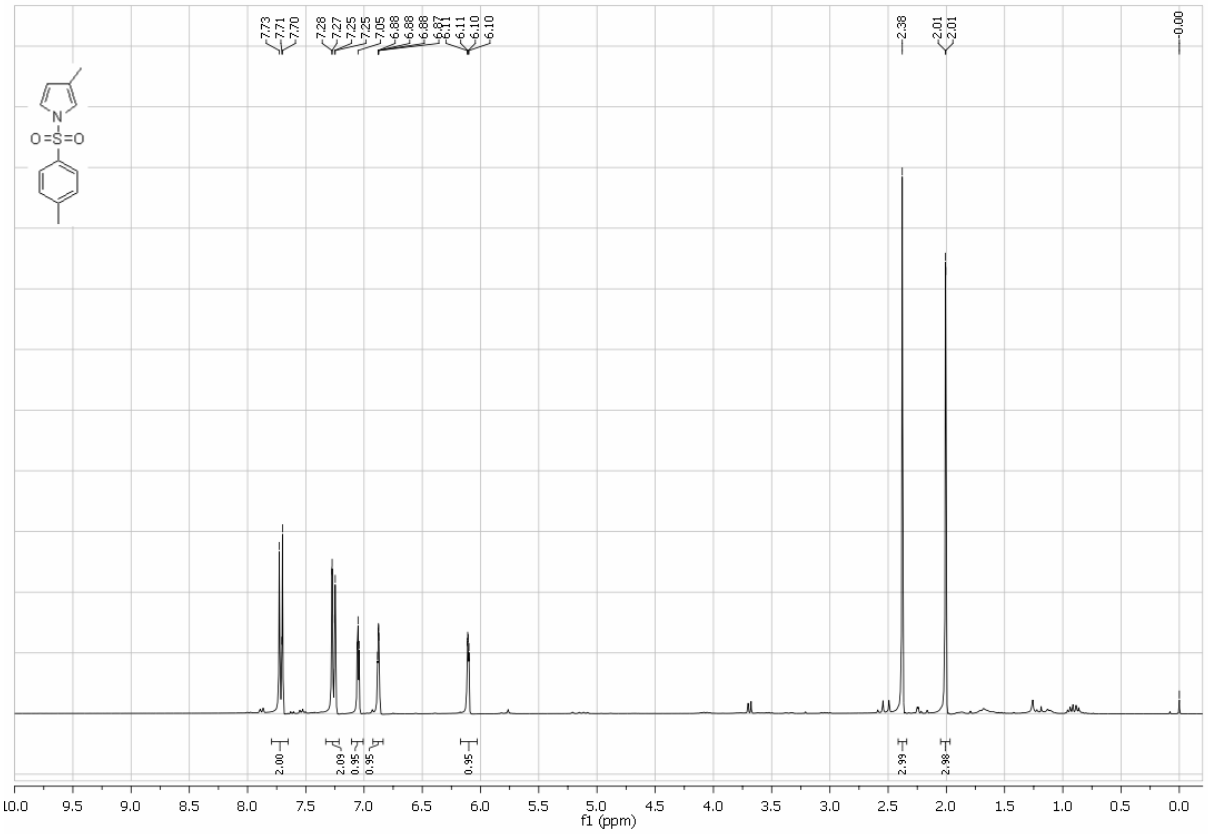
^{13}C NMR spectrum of 12a



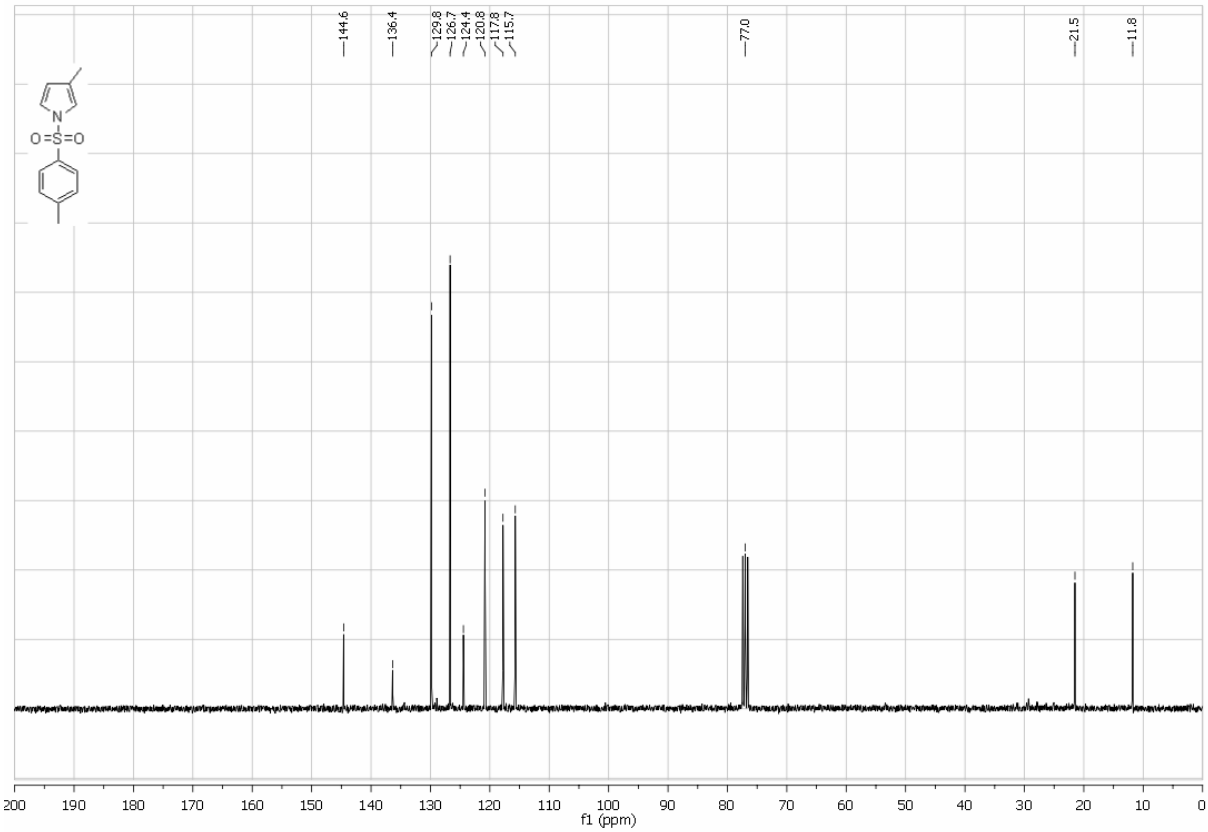
3-Methyl-1-tosyl-1H-pyrrole (12b) and 3-Methyl-1-tosyl-2,5-dihydro-1H-pyrrole (11b)

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-1*H*-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; ^{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: $\tilde{\upsilon}$ = 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).

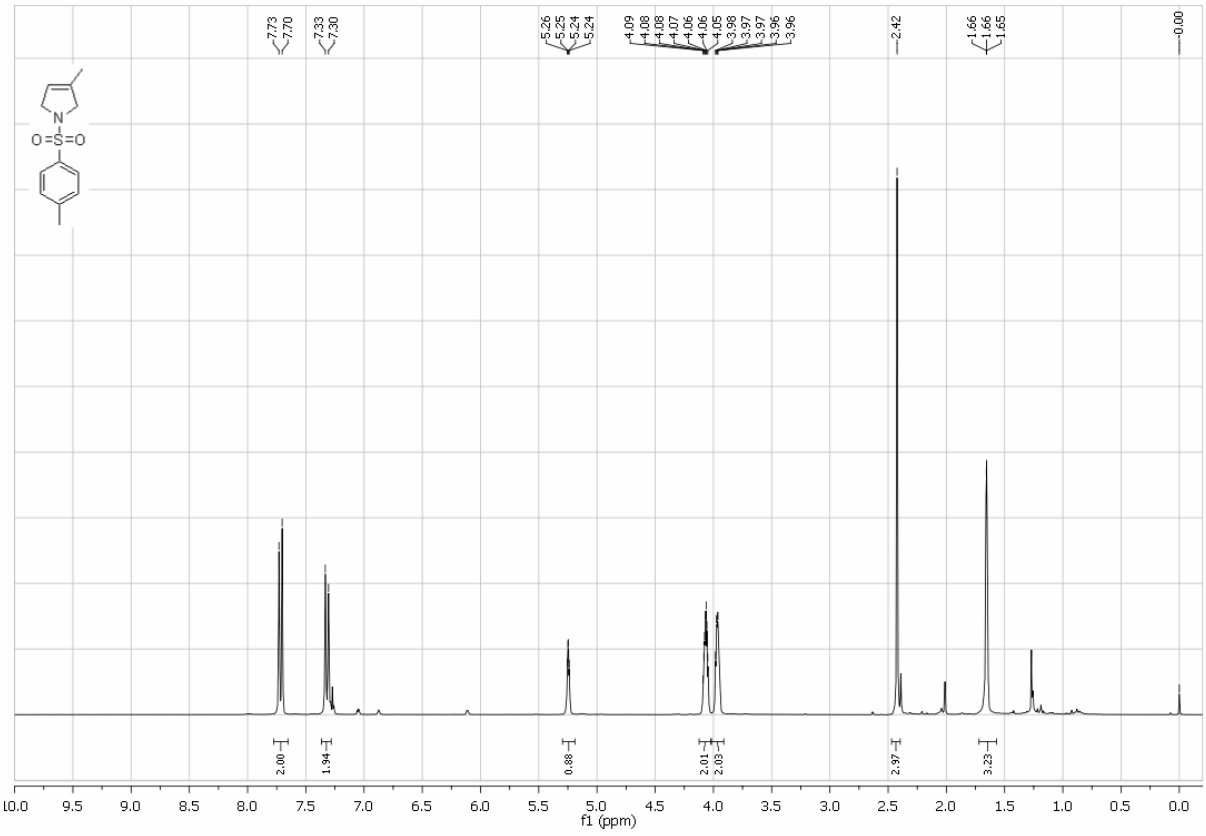
^{1}H NMR spectrum of 12b



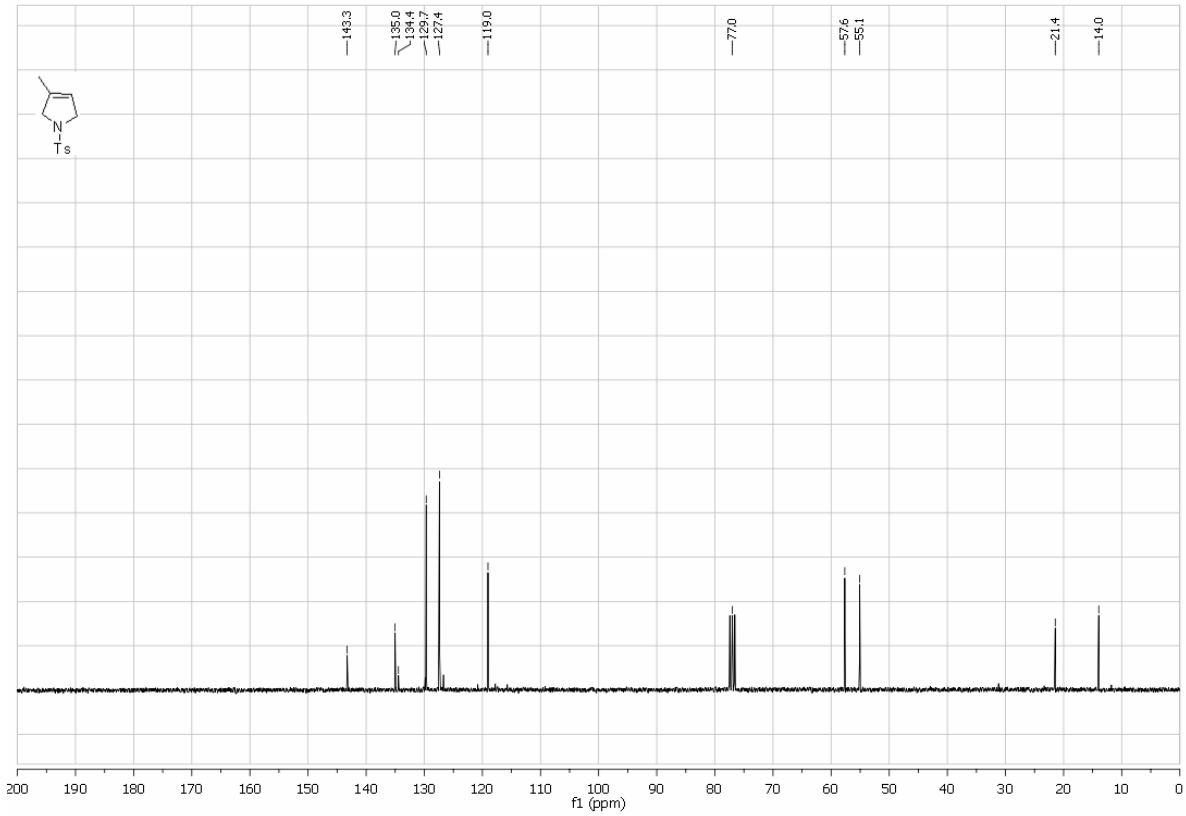
^{13}C NMR spectrum of 12b



^{1}H NMR spectrum of 11b



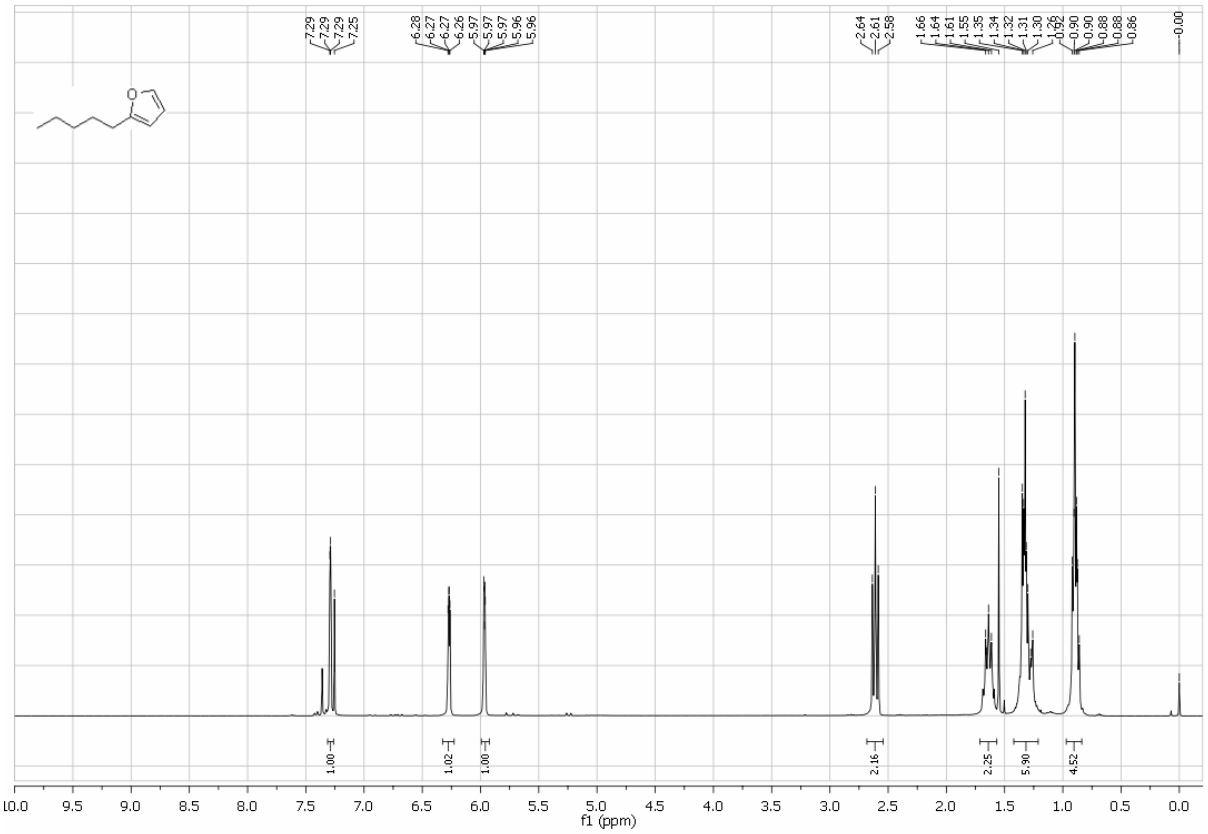
^{13}C NMR spectrum of 11b



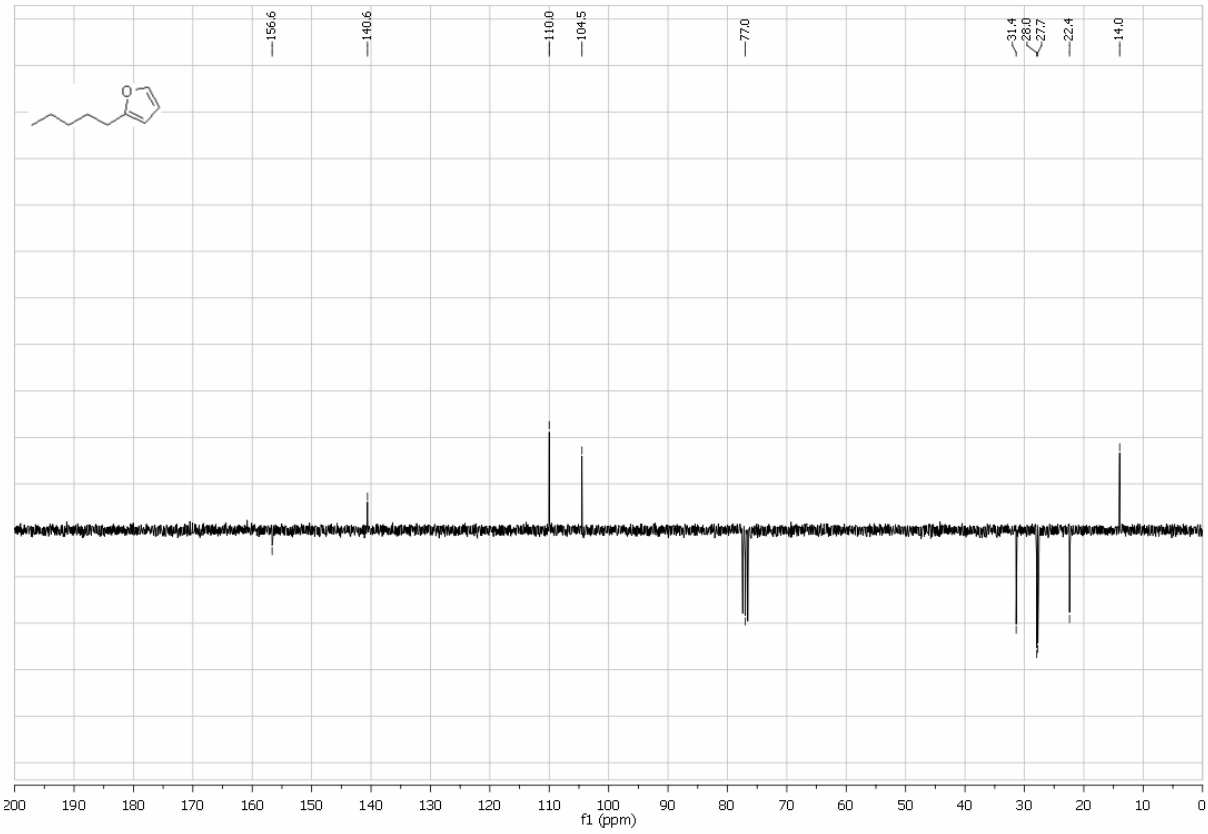
2-Pentylfuran (14a)

Following the general procedure B2, **14a** was obtained from **13a** (168mg, 1.0mmol) 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: $\tilde{\upsilon}$ = 2957 (s), 2927 (s), 2858 (m), 1797 (w), 1720 (w), 1467 (w).

^{1}H NMR spectrum of 14a



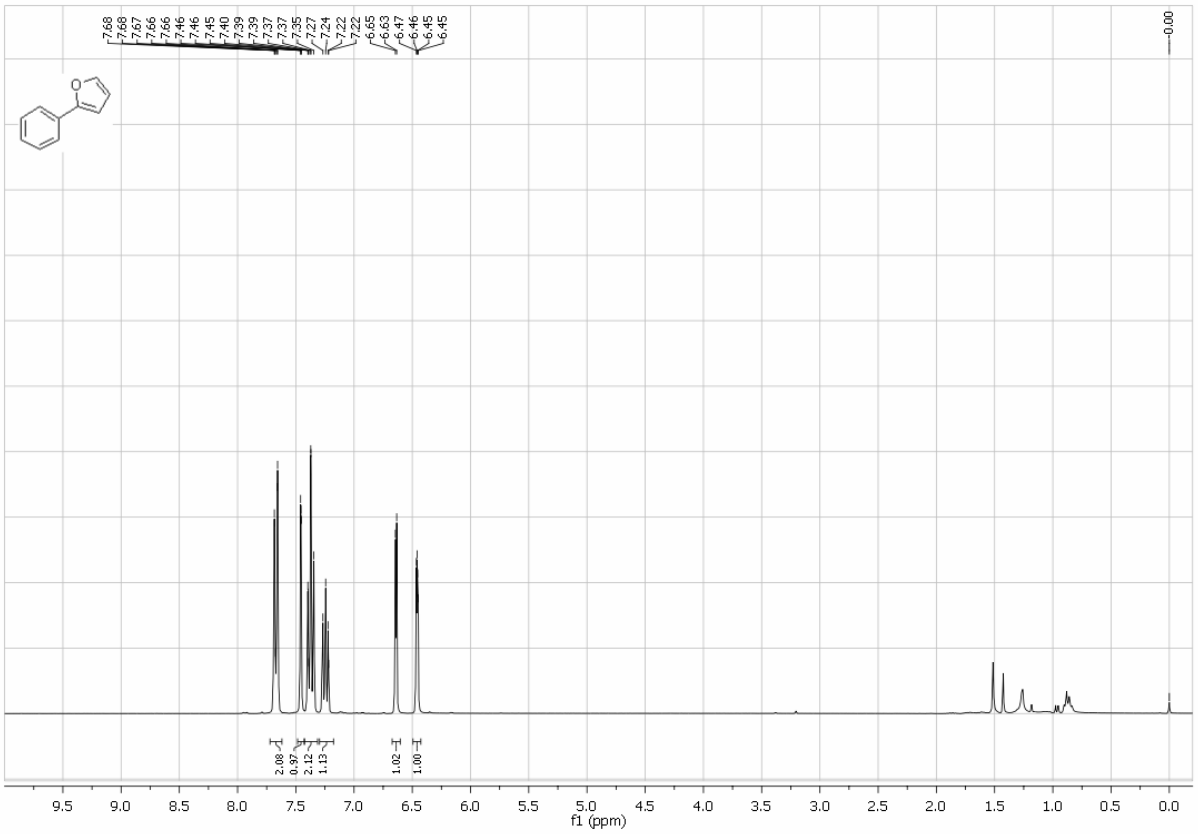
^{13}C NMR spectrum of 14a



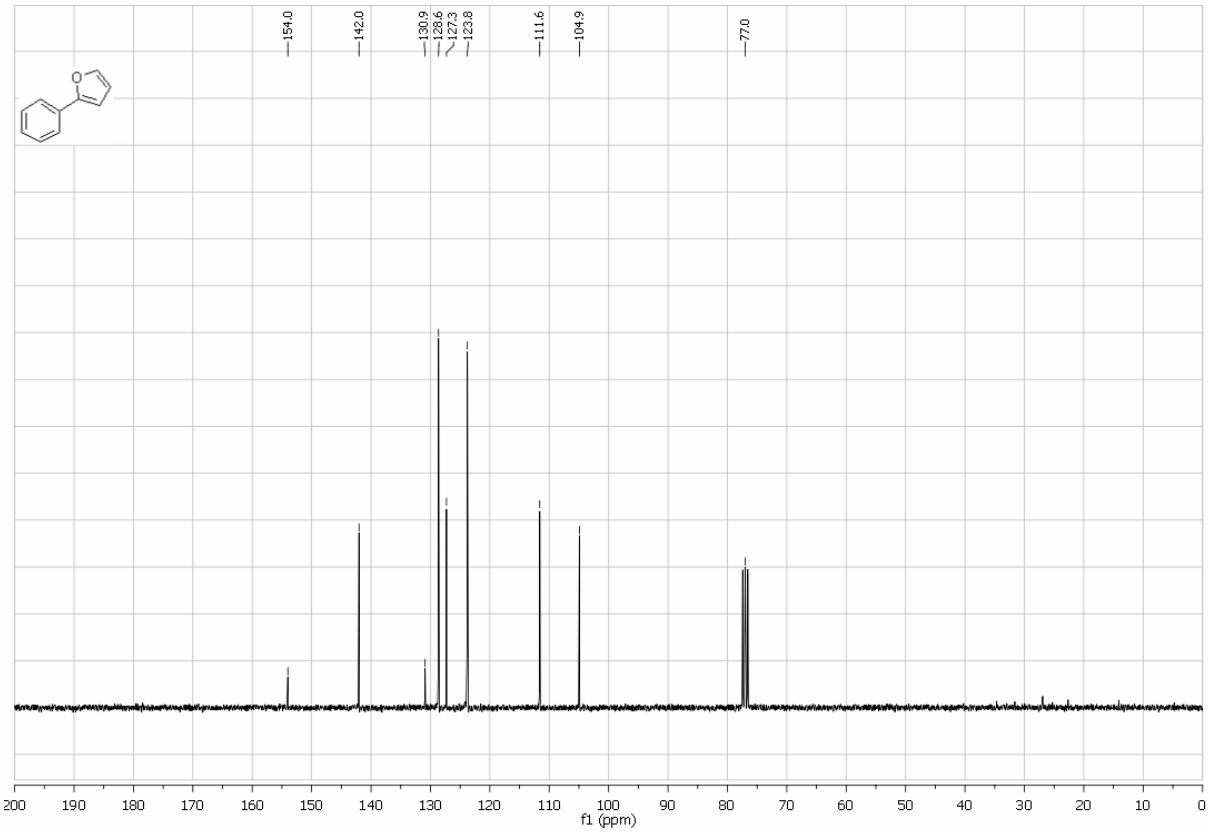
2-Phenylfuran (14b)

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, $CDCl_3$) 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).

^{1}H NMR spectrum of 14b



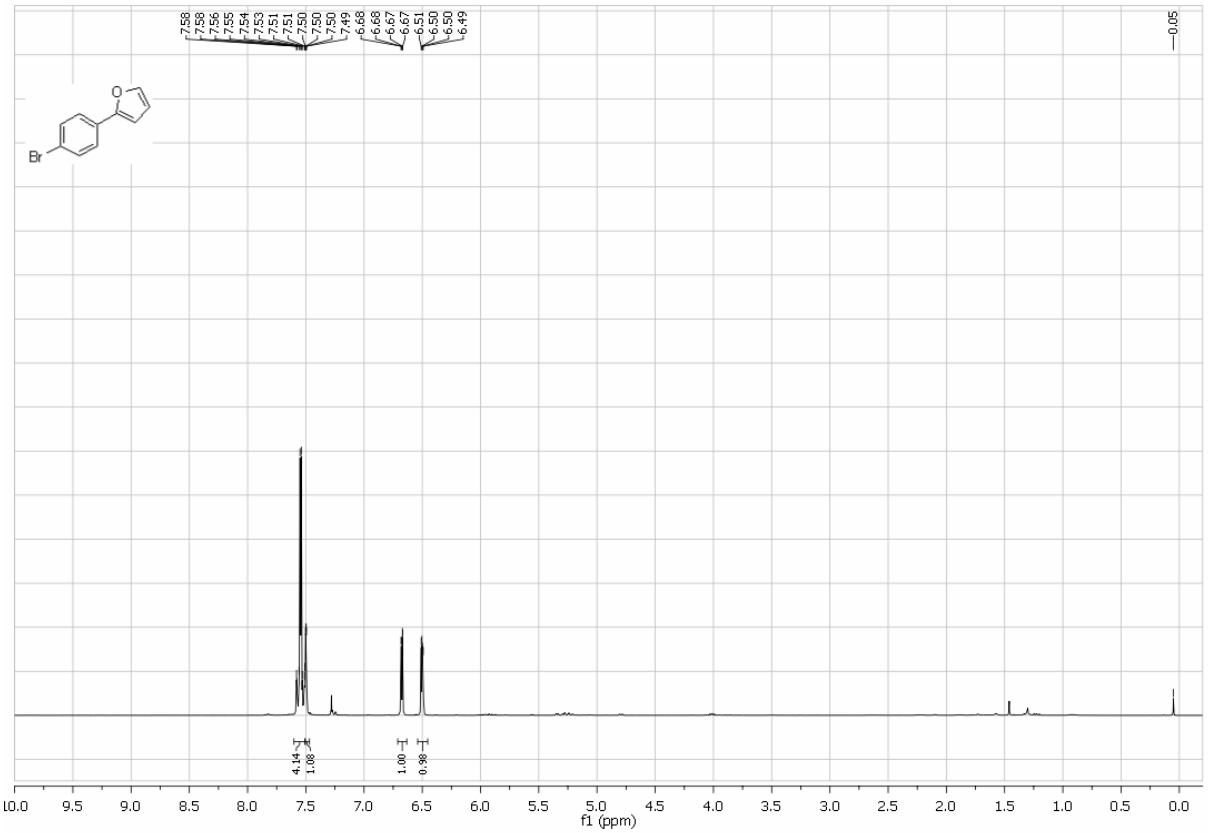
^{13}C NMR spectrum of 14b



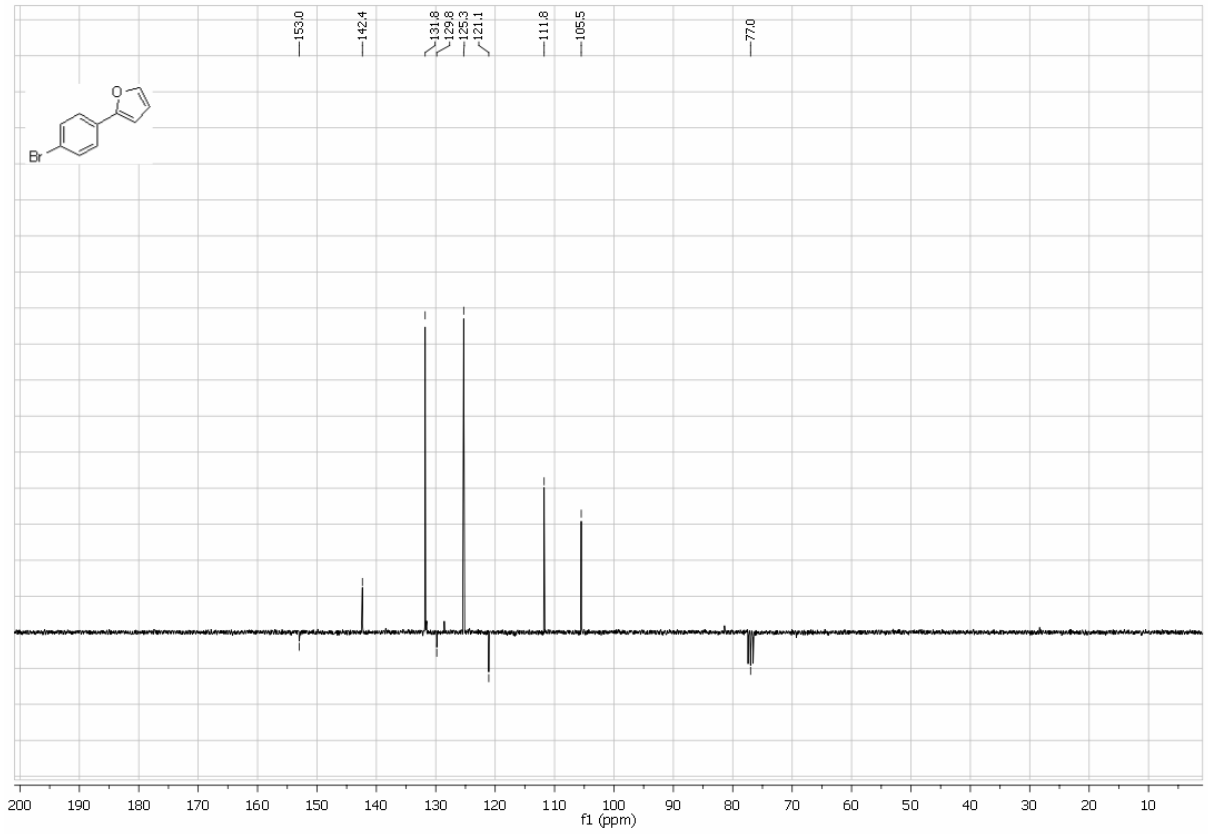
2-(4-Bromophenyl)furan (14c)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 2927 (w), 1729 (w), 1495 (m), 1469 (m), 1405 (w), 1220 (w), 1157 (m), 1072 (w), 1009 (s).

^{1}H NMR spectrum of 14c



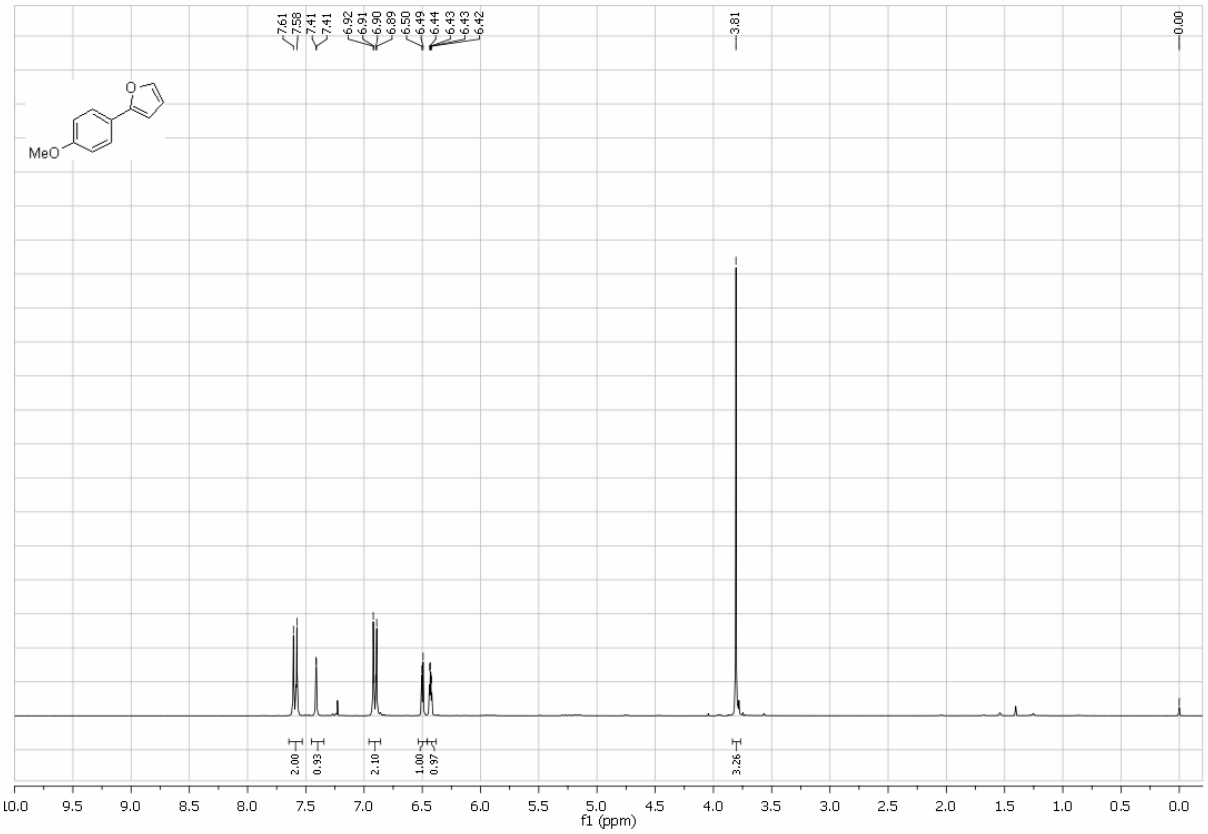
^{13}C NMR spectrum of 14c



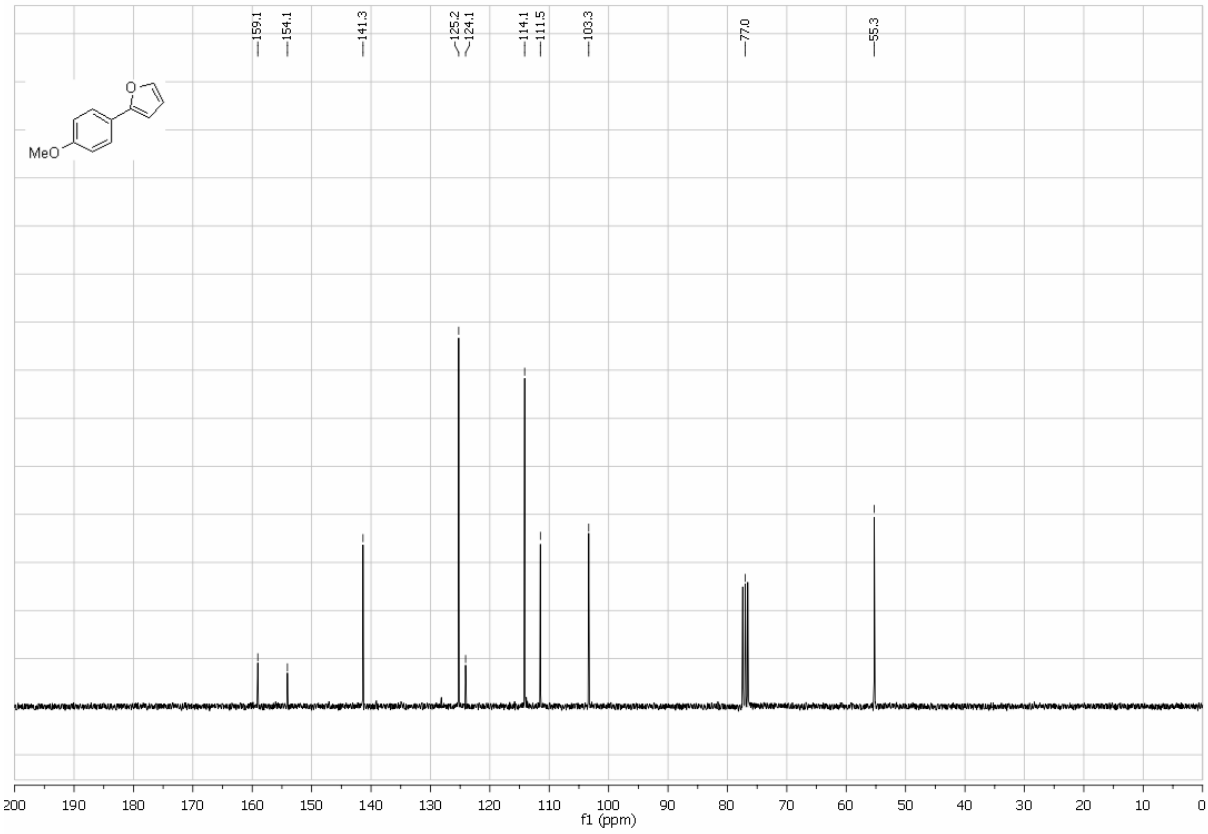
2-(4-Methoxyphenyl)furan (14d)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 3004 (w), 2958 (w), 2837 (w), 1613 (w), 1513 (s), 1484 (w), 1297 (m), 1247 (s).

^{1}H NMR spectrum of 14d



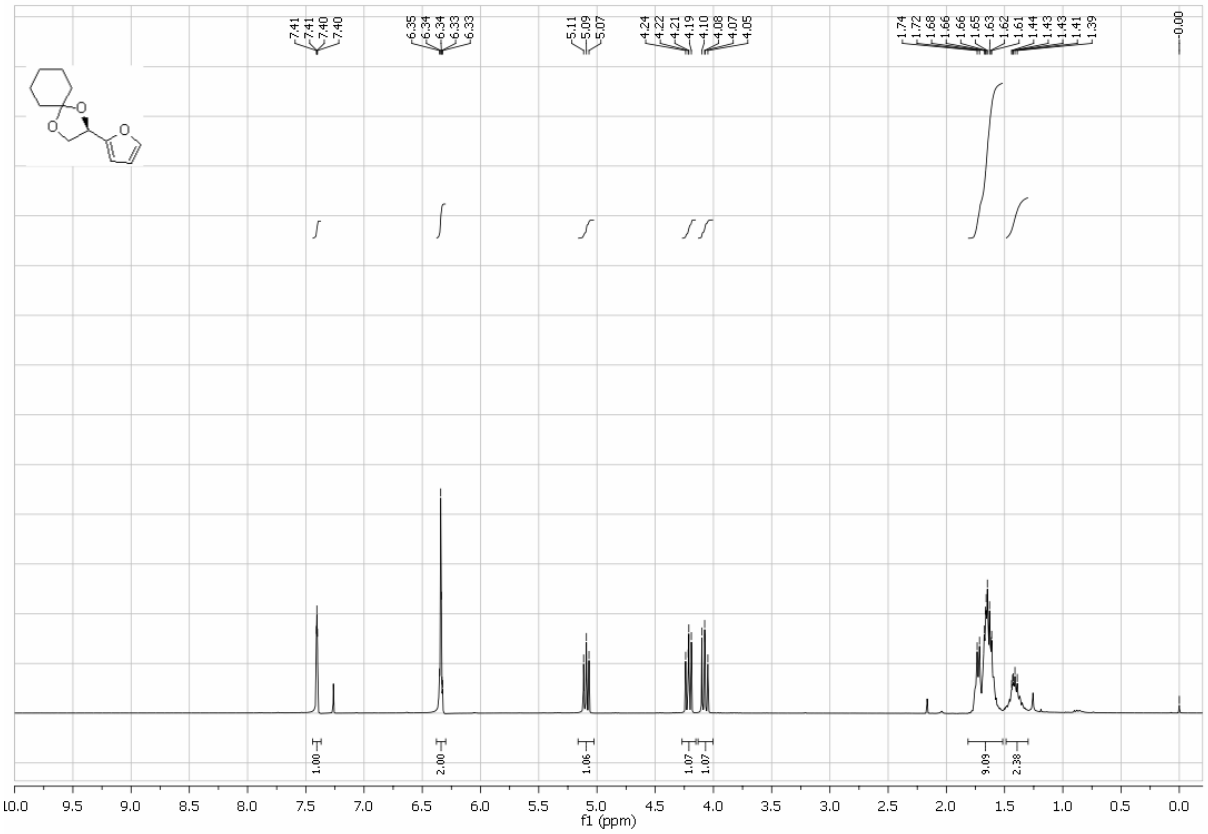
^{13}C NMR spectrum of 14d



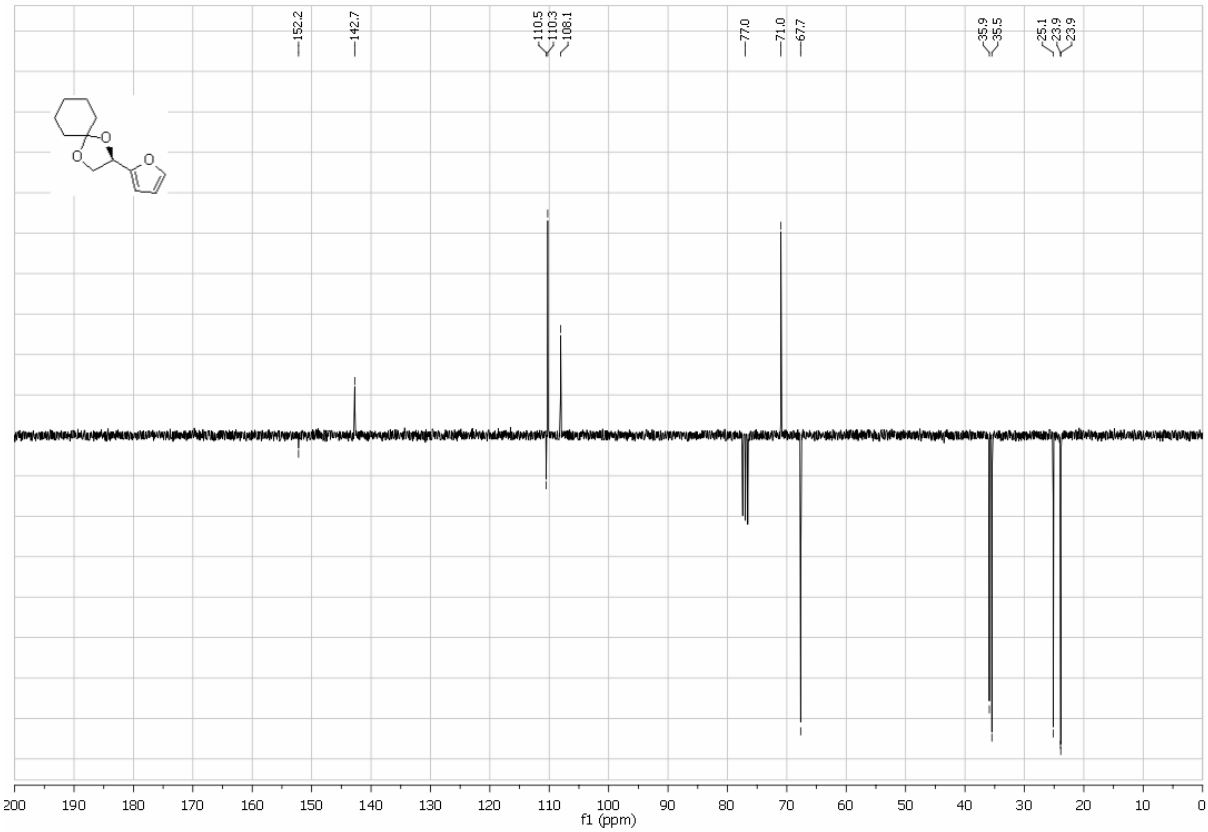
(*R*)-2-(Furan-2-yl)-1,4-dioxaspiro[4.5]decane (14e)

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, $CDCl_3$) 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: $\tilde{\upsilon}$ = 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 ^{t}BuOOH (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 ^{t}BuOOH (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.