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Multimolecular self-organization of acetylene and arylamines into 1-aryl-3-ethyl-4-vinylpyrroles in the KOBu^t/DMSO system

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The IR spectra were recorded on a Bruker IFS25 spectrophotometer. The NMR spectra were recorded on a Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C, and 40.5 MHz for ^{15}N) in $CDCl_3$. The assignment of signals was made using COSY, NOESY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments. The MS spectra were measured on a Shimadzu GCMS-QP5050A spectrometer. HR-MS spectrum was measured on a HR-TOF-ESI-MS Agilent 6210.

The reaction of arylamines **1a-d** *with acetylene in the KOBu^t/DMSO system (typical procedure).* A mixture of arylamine **1a-d** (10 mmol) and KOBu^t (10 mmol, 1.12 g) in DMSO (50 ml) was placed into a 0.25 dm^3 steel Parr reactor equipped with mechanical stirrer and manometer. The reactor was fed with acetylene under pressure from commercially available acetylene cylinder (initial pressure at ambient temperature was ~12 atm) and then decompressed to atmospheric pressure to remove air. The reactor was fed with acetylene again and heated (80 °C) for 1 h. The mixture after cooling to room temperature was diluted with H_2O (100 ml) and extracted with Et_2O (7×25 ml). The combined organic extracts were washed with H_2O (3×20 ml) and dried over K_2CO_3. Ether was evaporated, and the crude product **2a-d** was eluted with *n*-hexane from the SiO_2-packed column.

3-Ethyl-1-phenyl-4-vinyl-1H-pyrrole **2a** was prepared from **1a** (10 mmol, 0.93 g), yellow oil, yield 0.31 g (20%, based on aniline **1a** consumed). Unreacted aniline **1a** (0.19 g, 80% conversion) was also recovered upon column chromatography. ^{1}H NMR, δ: 7.41-7.36 (m, 4H, H^o, H^m), 7.24-7.20 (m, 1H, H^p), 7.17 (d, ^4J 2.2 Hz, 1H, H^5), 6.85 (m, 1H, H^2), 6.66 (dd, ^3J 17.7 Hz, ^3J 11.3 Hz, 1H, C*H*=CH$_2$), 5.45 (dd, ^3J 17.7 Hz, ^2J 1.6 Hz, 1H, CH=C*H*$_2$), 5.05 (dd, ^3J 11.3 Hz, ^2J 1.6 Hz, 1H, CH=C*H*$_2$), 2.63 (q, ^3J 7.4 Hz, 2H, CH$_2$), 11.27 (t, ^3J 7.4 Hz, 3H, Me). ^{13}C NMR, δ: 140.0 (C^i), 129.4 (C^m), 129.2 (C^p), 129.1 (H*C*=CH$_2$), 129.9 (C^3), 123.3 (C^4), 119.8 (C^o), 116.9 (C^5), 116.7 (C^2), 110.4 (HC=*C*H$_2$), 19.1 (CH$_2$), 14.3 (Me). IR (film, ν/cm^{-1}): 2964, 2927, 2873, 1599, 1520, 1512, 1371, 1225, 1061, 889, 757, 694. HRMS (ESI) calculated for $C_{14}H_{16}N$ [M+H]$^+$: 198.1277, found: 198.1288.

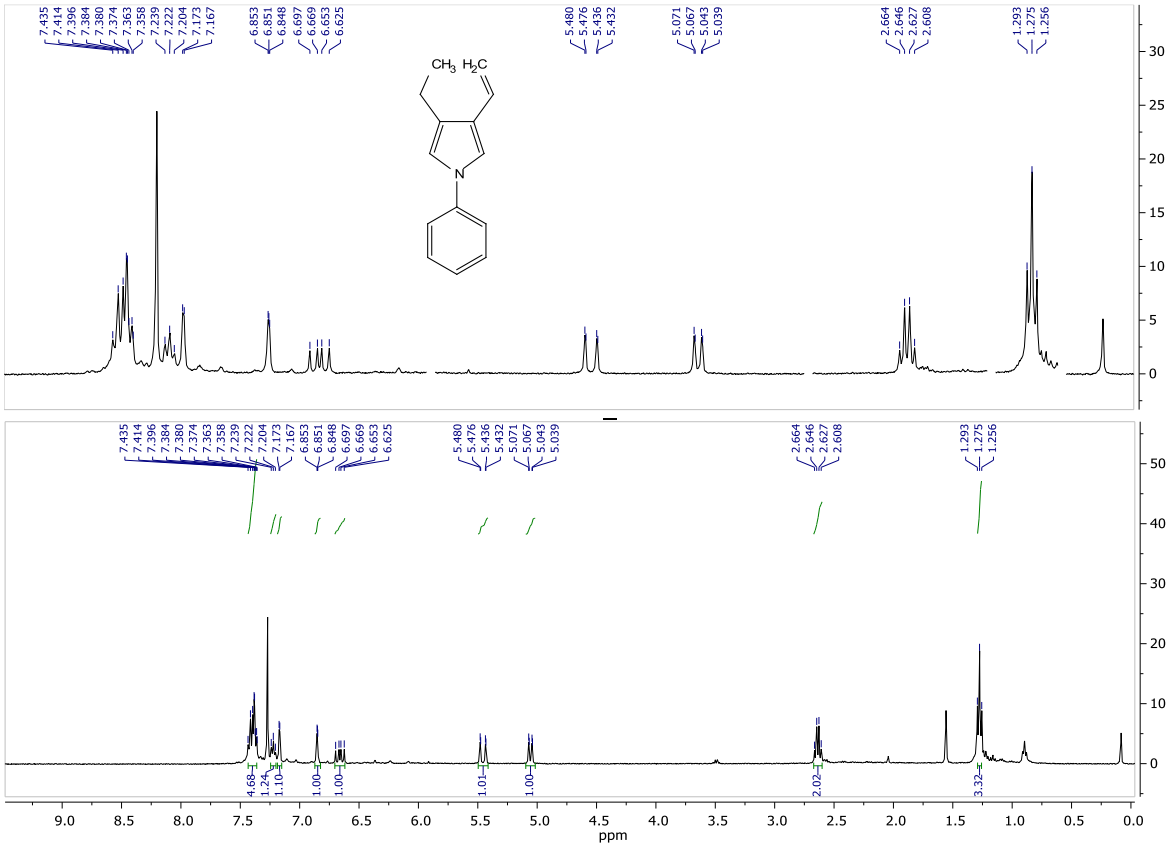
3-Ethyl-1-(3-fluorophenyl)-4-vinyl-1H-pyrrole **2b** was prepared from **1b** (10 mmol, 1.11 g), yellow oil, yield 0.17 g (17%, based on amine **1b** consumed). Unreacted amine **1b** (0.60 g, 46% conversion) was recovered upon column chromatography. ^{1}H NMR δ: 7.40-7.34 (m, 1H, H$^5{}_{Ar}$), 7.18-7.17 (m, 1H, H$^6{}_{Ar}$), 7.15 (d, ^4J 2.0 Hz, 1H, H^5), 7.13-7.05 (m, 2H, H$^2{}_{Ar}$), 6.94-6.89 (m, 1H, H$^4{}_{Ar}$), 6.84-6.83 (m, 1H, H^2), 6.65 (dd, ^3J 17.9 Hz, ^3J 11.3 Hz, 1H, C*H*=CH$_2$), 5.47 (dd, ^3J 17.9 Hz, ^2J 1.5 Hz, 1H, CH=C*H*$_2$), 5.08 (dd, ^3J 11.3 Hz, ^2J 1.5 Hz, 1H, CH=C*H*$_2$), 2.62 (q, ^3J 7.5 Hz, 2H, CH$_2$), 1.27 (t, ^3J 7.5 Hz, 3H, Me). ^{13}C NMR, δ: 163.5 (d, $^1J_{CF}$ 246.7 Hz, C$^3{}_{Ar}$), 142.0 (d, ^3J 9.9

Hz, C^{1}_{Ar}), 130.9 (d, ^{3}J 9.5 Hz, C^{5}_{Ar}), 129.2 (H*C*=CH_2), 127.6 (C^3), 124.1 (C^4), 116.9 (C^5), 116.7 (C^2), 115.1 (d, ^{4}J 3.0 Hz, C^{6}_{Ar}), 112.1 (HC=*C*H_2), 112.0 (d, ^{2}J 21.1 Hz, C^{4}_{Ar}), 107.1 (d, ^{2}J 25.1 Hz, C^{2}_{Ar}), 19.2 (CH_2), 14.4 (Me). ^{15}N NMR, δ: -213.4. IR (film, ν/cm^{-1}): 2967, 2929, 2876, 1709, 1609, 1521, 1496, 1459, 1379, 1258, 1170, 1057, 856, 779, 685. MS (EI), *m/z* (%): 215.1 $[M]^{+\bullet}$. Calc. for $C_{14}H_{14}FN$, *m/z*: 215.2.

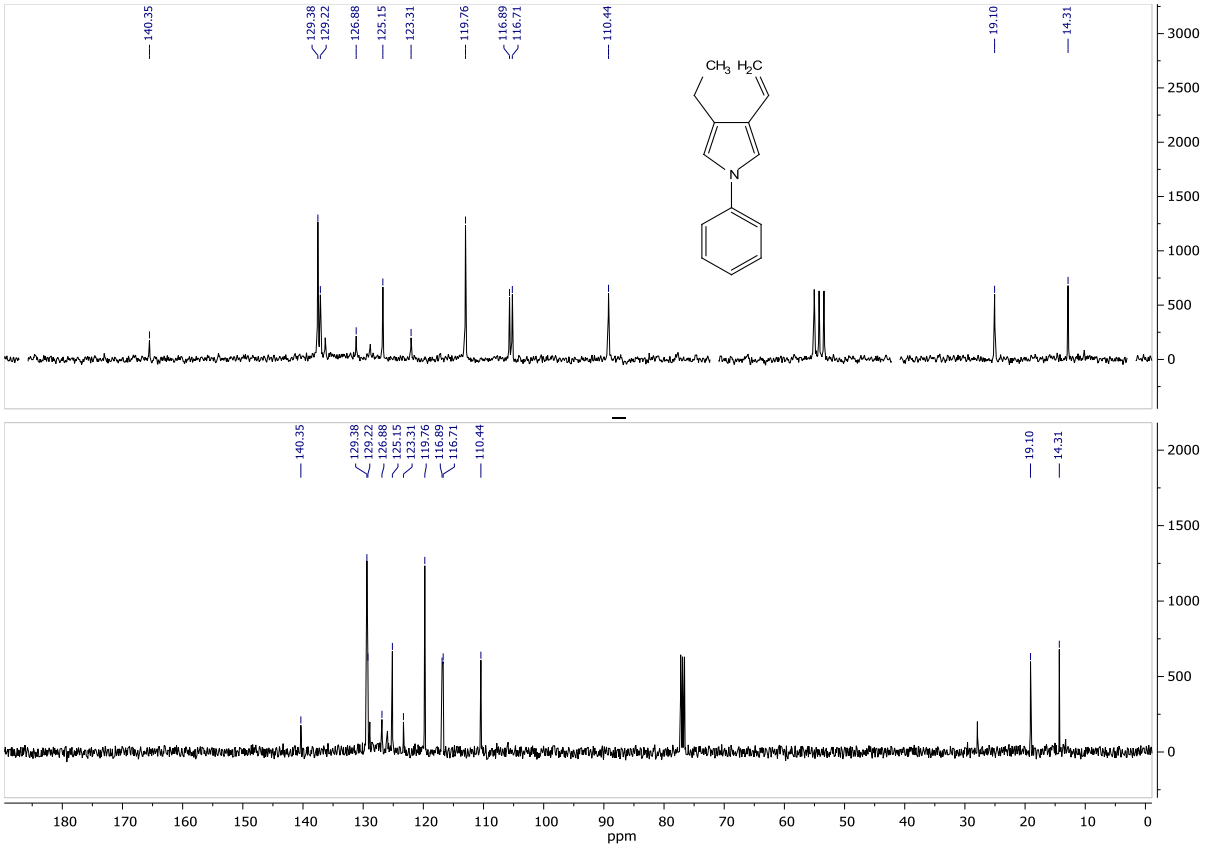
1-(4-Chlorophenyl)-3-ethyl-4-vinyl-1H-pyrrole **2c** was prepared from **1c** (10 mmol, 1.28 g), yellow oil, yield 0.21 g (14%, based on amine **1c** consumed). Unreacted amine **1c** (0.45 g, 65% conversion) was recovered upon column chromatography. ^{1}H NMR, δ: 7.39-7.37 (d, ^{3}J 8.0 Hz, 2H, H^m), 7.31-7.29 (d, ^{3}J 8.0 Hz, 2H, H^o), 7.12 (d, ^{4}J 2.6 Hz, 1H, H^5), 6.80 (m, 1H, H^2), 6.64 (dd, ^{3}J 17.7 Hz, ^{3}J 11.3 Hz, 1H, C*H*=CH_2), 5.46 (dd, ^{3}J 17.7 Hz, ^{2}J 1.6 Hz, 1H, CH=C*H*$_2$), 5.07 (dd, ^{3}J 11.3 Hz, ^{2}J 1.6 Hz, 1H, CH=C*H*$_2$), 2.63 (q, ^{3}J 7.5 Hz, 2H, CH_2), 1.27 (t, ^{3}J 7.5 Hz, 3H, Me). ^{13}C NMR, δ: 139.1 (C^i), 130.7 (C^p), 129.7 (C^m), 129.2 (H*C*=CH_2), 127.5 (C^4), 123.9 (C^3), 121.0 (C^o), 116.9 (C^5), 116.8 (C^2), 111.1 (HC=*C*H_2), 19.2 (CH_2), 14.5 (Me). ^{15}N NMR, δ: -214.9. IR (film, ν/cm^{-1}): 2965, 2927, 2874, 1707, 1629, 1596, 1520, 1498, 1375, 1227, 1095, 1058, 1009, 890, 826, 783. MS (EI), *m/z* (%): 231.1 $[M]^{+\bullet}$. Calc. for $C_{14}H_{14}ClN$, *m/z*: 231.2.

1-(4-Bromophenyl)-3-ethyl-4-vinyl-1H-pyrrole **2d** was prepared from **1d** (10 mmol, 1.72 g), yellow oil, yield 0.18 g (16%, based on amine **1d** consumed). Unreacted amine **1d** (1.00 g, 42 % conversion) was recovered upon column chromatography. ^{1}H NMR, δ: 7.52 (d, ^{3}J 8.8 Hz, 2H, H^m), 7.25 (d, ^{3}J 8.8 Hz, 2H, H^o), 7.12 (d, ^{4}J 2.5 Hz, 1H, H^5), 6.81-6.80 (m, 1H, H^2), 6.64 (dd, ^{3}J 17.8 Hz, ^{3}J 11.2 Hz, 1H, C*H*=CH_2), 5.46 (dd, ^{3}J 17.8 Hz, ^{2}J 1.7 Hz, 1H, CH=C*H*$_2$), 5.08 (dd, ^{3}J 11.2 Hz, ^{2}J 1.7 Hz, 1H, CH=C*H*$_2$), 2.63 (q, ^{3}J 7.5 Hz, 2H, CH_2), 1.27 (t, ^{3}J 7.2 Hz, 3H, Me). ^{13}C NMR, δ: 139.6 (C^i), 132.6 (C^m), 129.2 (H*C*=CH_2), 127.6 (C^4), 124.0 (C^3), 121.3 (C^o), 118.3 (C^p), 116.8 (C^5), 116.7 (C^2), 111.1 (HC=*C*H_2), 19.2 (CH_2), 14.4 (Me). IR (film, ν/cm^{-1}): 2966, 2928, 2913, 1524, 1499, 1376, 1229, 1174, 1065, 889, 824, 783, 690. MS (EI), *m/z* (%): 275.0 $[M]^{+\bullet}$. Calc. for $C_{14}H_{14}BrN$, *m/z*: 275.2.

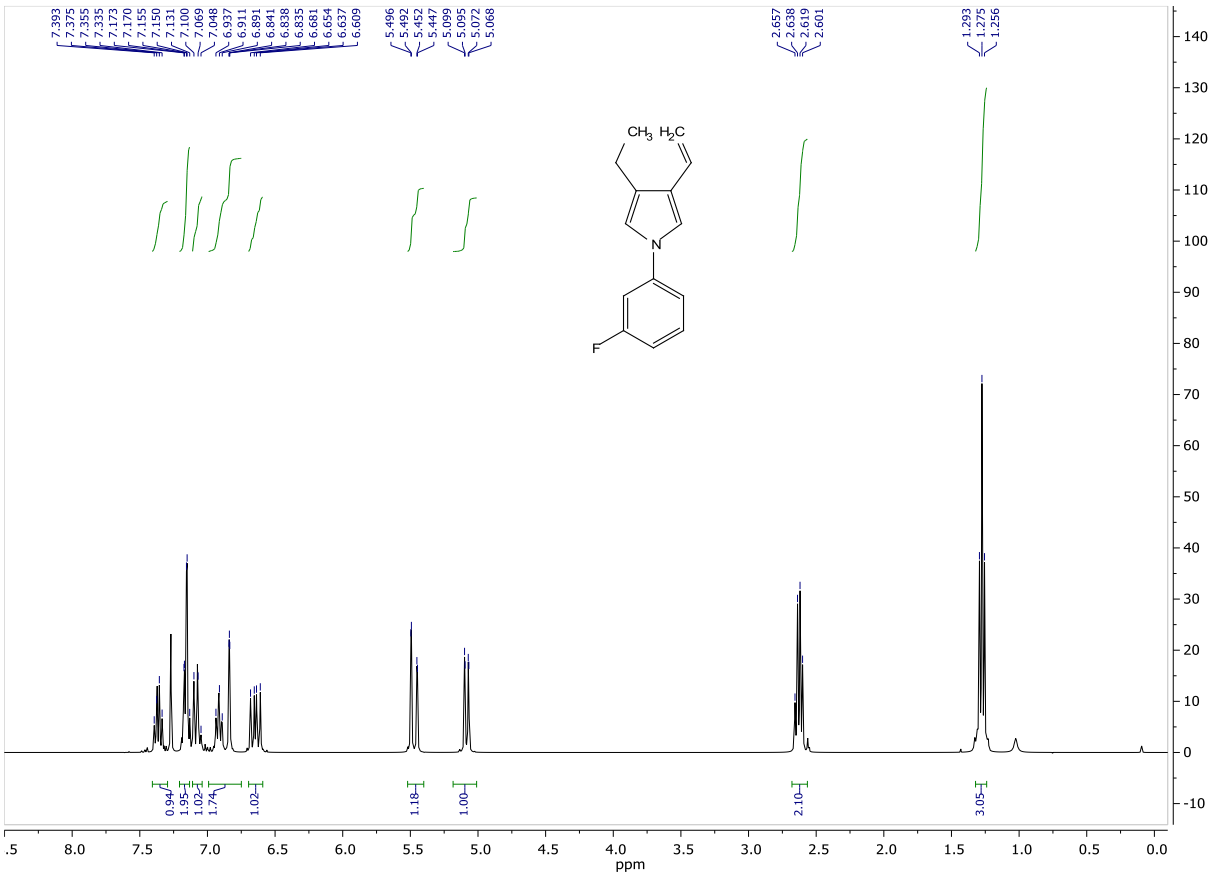
NMR Spectra



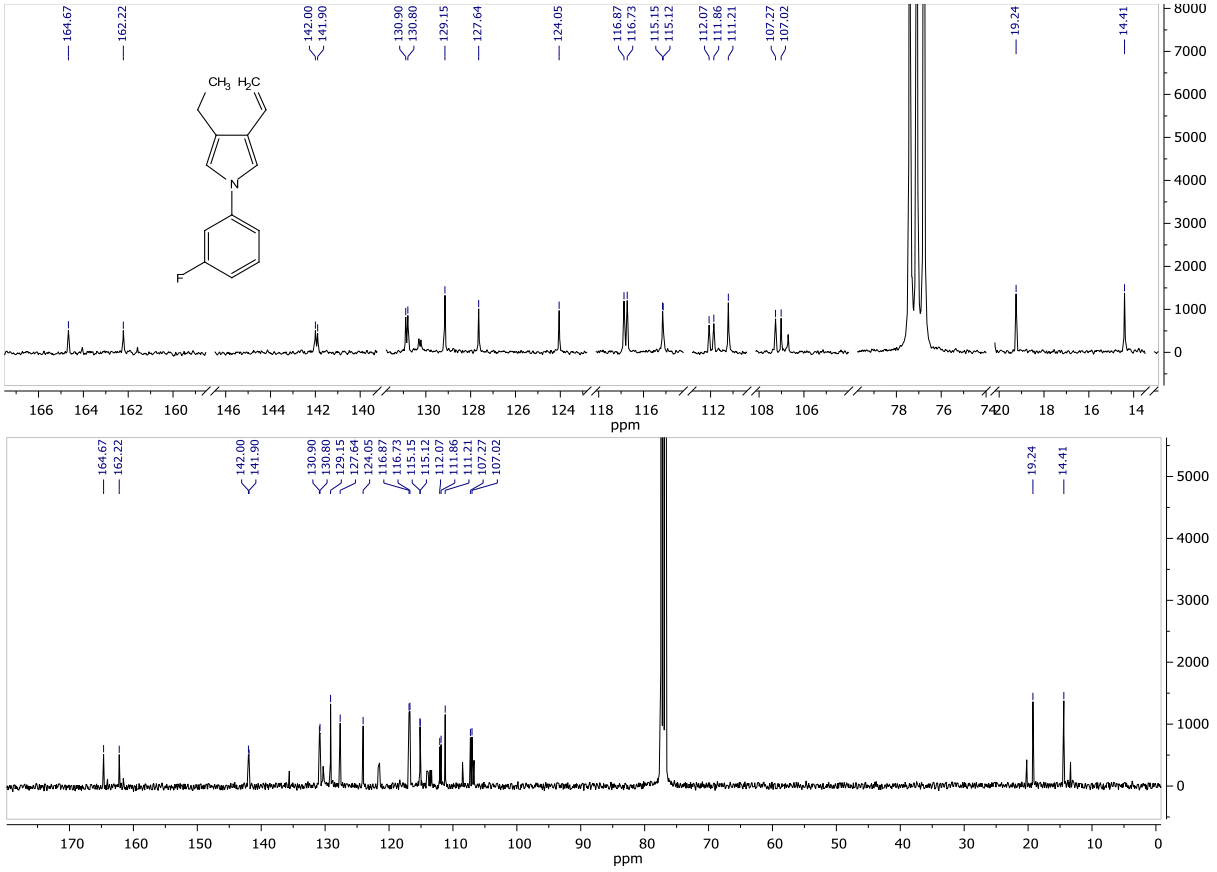
^{1}H NMR spectrum of **2a**



^{13}C NMR spectrum of **2a**



^{1}H NMR spectrum of **2b**



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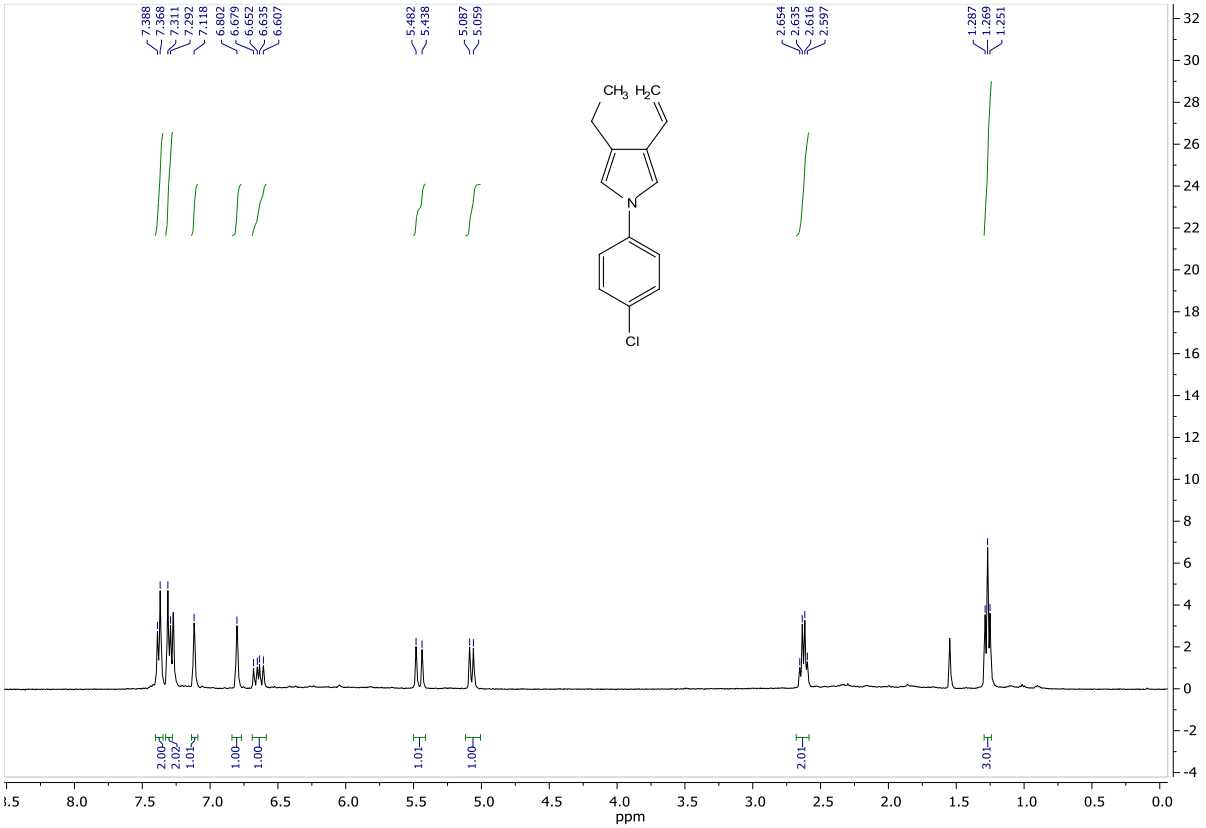

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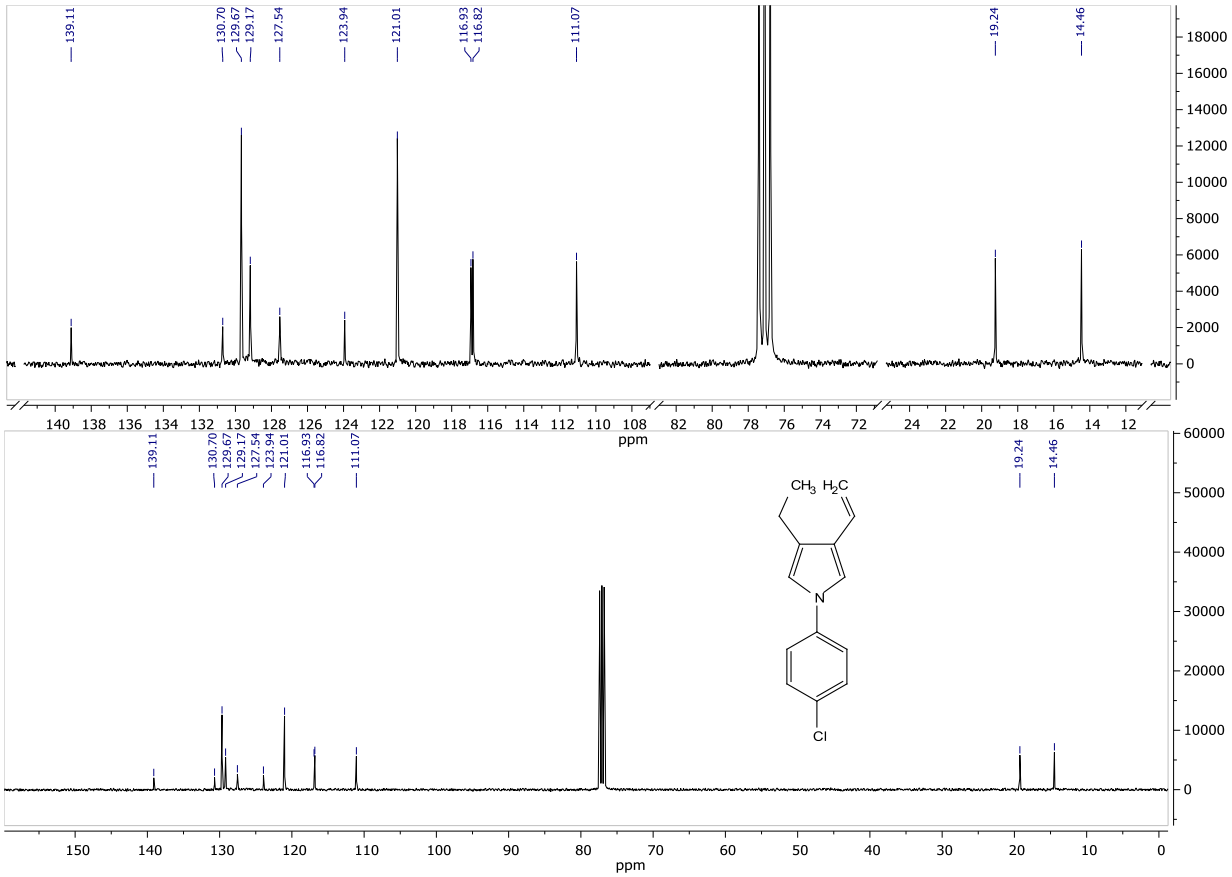

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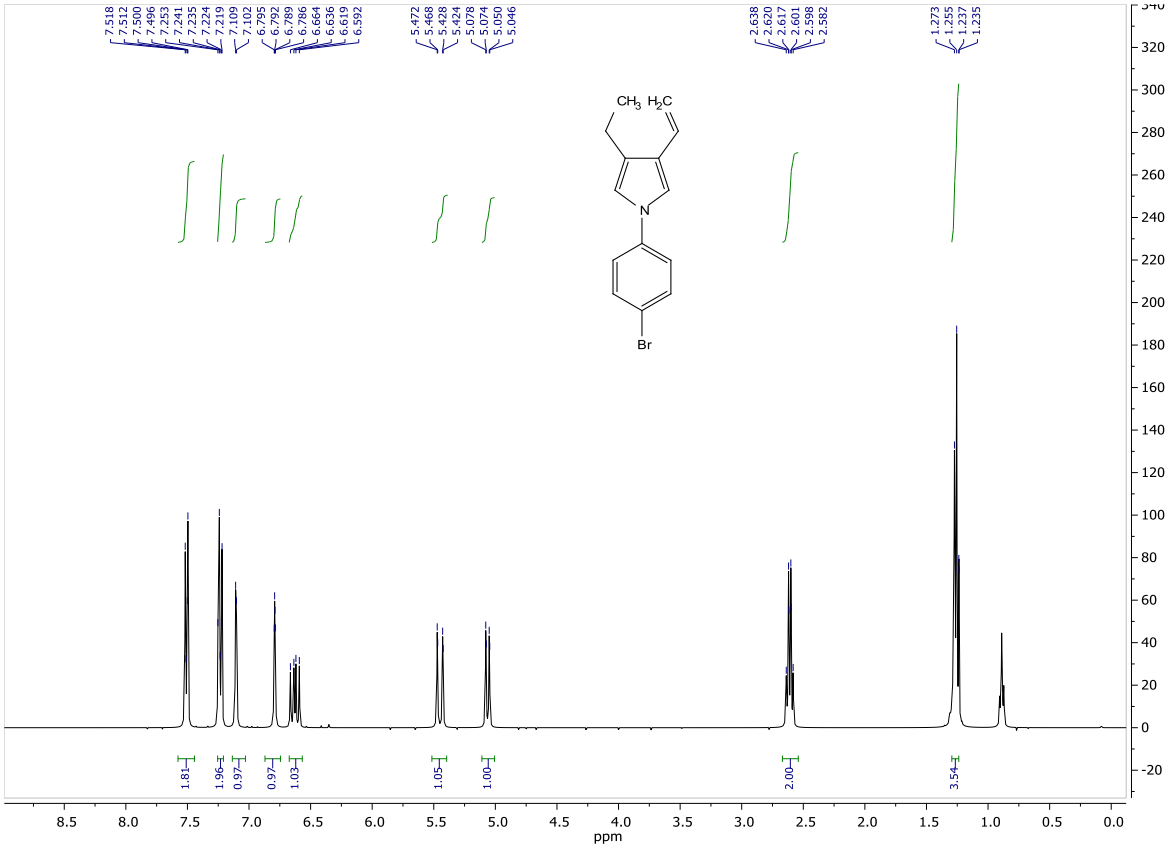
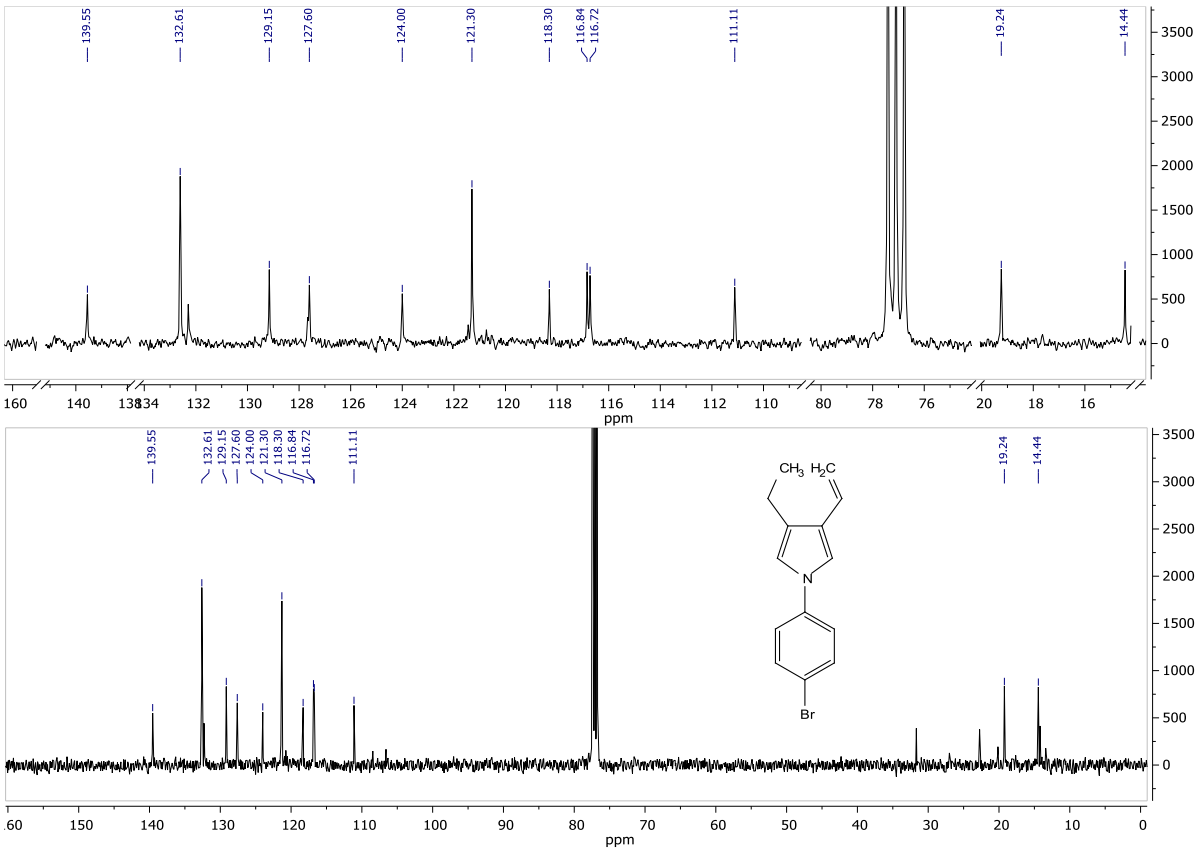


^{1}H NMR spectrum of **2d**



^{13}C NMR spectrum of **2d**