Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 109–111

Superbase-promoted multi-molecular acetylene/arylamine self-organization to 1-arylpyrroles

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The IR spectra were recorded on a Bruker IFS25 spectrophotometer. The NMR spectra were recorded on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C) in $CDCl_3$. The assignment of signals was made using COSY, NOESY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC experiments.

2,5-Dimethyl-1-(o-tolyl)-1H-pyrrole **2b** was prepared from **1b** (10 mmol, 1.07 g), yellow oil, yield 0.22 g (12%). ^{1}H NMR, δ: 7.38-7.37, 7.33-7.32, 7.23-7.21 (m, 4H, H_{Ar}), 5.97 (s, 2H, H3, H4), 1.99 (s, 3H, Me), 1.98, 1.97 (s, 6H, Me). Lit. [S1], δ: 7.33-7.32 (m, 2H), 7.29-7.27 (m, 1H), 7.16 (d, 1H, *J* 7.3 Hz), 5.91 (s, 2H), 1.93 (s, 3H), 1.91 (s, 6H). ^{13}C NMR, δ: 138.2, 137.3, 130.7, 128.9, 128.5, 128.4 (C_{Ar}), 126.7 (C2, C5), 105.3 (C3, C4), 17.2 (Me), 12.6 (Me). Lit. [S1], δ: 138.1, 137.1, 130.6, 128.8, 128.3, 128.2, 126.6, 105.2, 17.0, 12.5. Found (%): C, 84.31; H, 8.28; N, 7.41. Calc. for $C_{13}H_{15}N$ (%): C, 84.28; H, 8.16; N, 7.56.

2,5-Dimethyl-1-(m-tolyl)-1H-pyrrole **2c** was prepared from **1c** (10 mmol, 1.07 g), yellow oil, yield 0.70 g (47%, based on aniline **1c** consumed). Aniline **1c** (0.20 g, 81% conversion) was recovered upon column chromatography. ^{1}H NMR, δ: 7.32-7.28 (m, 1H), 7.17-7.15 (m, 1H), 6.99-6.97 (m, 2H) [H_{Ar}], 5.93 (s, 2H, H3, H4), 2.44 (s, 3H, Me), 2.07 (s, 6H, Me). Lit. [S1], δ: 7.33 (t, 1H, *J* 8.0 Hz), 7.19 (d, 1H, *J* 8.0 Hz), 7.01 (m, 2H), 5.89 (s, 2H), 2.39 (s, 3H), 2.02 (s, 6H). ^{13}C NMR, δ: 138.9, 128.8, 128.73, 128.72, 128.3 (C_{Ar}), 125.2 (C2, C5), 105.5 (C3, C4), 21.3 (C_m-*Me*), 13.0 (Me). Lit. [S1], δ: 138.94, 138.9, 128.8, 128.74,128.73, 128.3, 125.2, 105.5, 21.3, 12.9. IR (film, ν/cm^{-1}): 2964, 2924, 2873, 1667, 1494, 1451, 1396, 1327, 1173, 1088, 1041, 787, 758, 701. Found (%): C, 84.21; H, 8.18; N, 7.61. Calc. for $C_{13}H_{15}N$ (%): C, 84.28; H, 8.16; N, 7.56.

1-(4-Methoxyphenyl)-2,5-dimethyl-1H-pyrrole **2d** was prepared from **1d** (10 mmol, 1.23 g), yellow oil, yield 0.49 g (24%). %). ^{1}H NMR, δ: 7.14 (d, *J* 8.4 Hz, 2H, H_o), 6.98 (d, *J* 8.4 Hz, 2H, H_m), 5.89 (s, 2H, H3, H4), 3.87 (s, 3H, OMe), 2.01 (s, 6H, Me). Lit. [S1], δ: 7.12 (d, 2H, *J* 8.5 Hz), 6.96 (d, 2H, *J* 8.5 Hz), 5.88 (s, 2H), 3.86 (s, 3H), 2.01 (s, 6H). ^{13}C NMR, δ: 158.9 (C_p), 131.8 (C_i), 129.2 (C_o), 129.0 (C2, C5), 114.2 (C_m), 105.3 (C3, C4), 55.4 (OMe), 13.0 (Me). Lit. [S1], δ: 158.8, 131.7, 129.2, 128.9, 114.1, 105.2, 55.4, 12.9. IR (film, ν/cm^{-1}): 2960, 2925, 1670, 1635, 1513, 1449, 1377, 1292, 1246, 1174, 1036, 834, 754. Found (%): C, 77.63; H, 7.58; N, 6.70. Calc. for $C_{13}H_{15}NO$ (%): C, 77.58; H, 7.51; N, 6.96.

1-(3-Fluorophenyl)-2,5-dimethyl-1H-pyrrole **2e** was prepared from **1e** (10 mmol, 1.11 g), brown oil, yield 0.38 g (25%, based on aniline **1e** consumed). Aniline **1e** (0.20 g, 82% conversion) was recovered upon column chromatography. ^{1}H NMR, δ: 7.47-7.41, 7.16-7.11, 7.04-7.02, 6.98-6.96

(m, 4H, H_{Ar}), 5.92 (s, 2H, 3H, 4H), 2.06 (s, 6H, Me). Lit. [S1], *δ*: 7.45-7.39 (m, 1H), 7.12-7.10 (m, 1H), 7.01 (d, 1H, *J* 7.8 Hz), 6.95 (dt, 1H, *J* 9.0, 1.8 Hz), 5.90 (s, 2H), 2.04 (s, 6H). ^{13}C NMR, *δ*: 162.8 (d, *J* 247.4 Hz, C_3), 130.2 (d, *J* 9.0 Hz, C_5), 128.8 (C2, C5), 128.1 (d, *J* 6.7 Hz, C_1), 124.2 (d, *J* 2.7 Hz, C_6), 115.8 (d, *J* 22.0 Hz), 114.8 (d, *J* 20.8 Hz) [C_2, C_4], 106.2 (C3, C4), 13.0 (Me). Lit. [S1], *δ*: 162.7 (d, *J* 247.9 Hz), 140.5 (d, *J* 9.5 Hz), 130.1 (d, *J* 9.1 Hz), 128.7, 124.1 (d, *J* 3.3 Hz), 115.7 (d, *J* 21.9 Hz), 114.8 (d, *J* 20.7 Hz), 106.1, 12.9. IR (film, *ν*/cm^{-1}): 2962, 2924, 1605, 1491, 1452, 1402, 1241, 1179, 1152, 1036, 871, 783, 765. Found (%): C, 76.26; H, 6.47; F, 9.84; N, 7.43. Calc. for $C_{12}H_{12}FN$ (%): C, 76.17; H, 6.39; F, 10.04; N, 7.40.

1-(4-Fluorophenyl)-2,5-dimethyl-1H-pyrrole **2f** was prepared from **1f** (10 mmol, 1.11 g), yellow oil, yield 0.43 g (28%, based on aniline **1f** consumed). Aniline **1f** (0.21 g, 81% conversion) was recovered upon column chromatography. ^{1}H NMR, *δ*: 7.22-7.18 (m, 4H, H_{Ar}), 5.95 (s, 2H, H3, H4), 2.06 (s, 6H, Me). Lit. [S1], *δ*: 7.20-7.11 (m, 4H), 5.89 (s, 2H), 2.01 (s, 6H). ^{13}C NMR, *δ*: 161.8 (d, *J* 247.2 Hz, C-F), 135.0 (d, *J* 2.7 Hz, C_i), 129.8 (d, *J* 8.5 Hz, C_o), 128.8 (C2, C5), 115.9 (d, *J* 22.7 Hz, C_m), 105.7 (C3, C4), 12.9 (Me). Lit. [S1], *δ*: 161.8 (d, *J* 247.0 Hz),134.9 (d, *J* 3.3 Hz), 129.8 (d, *J* 8.7 Hz), 128.8, 115.9 (d, *J* 22.3 Hz), 105.7, 12.9. IR (film, *ν*/cm^{-1}): 2964, 2925, 2866, 1644, 1511, 1446, 1406, 1225, 1157, 1094, 1036, 1000, 841, 758. Found (%): C, 76.14; H, 6.41; F, 9.89; N, 7.56. Calc. for $C_{12}H_{12}FN$ (%): C, 76.17; H, 6.39; F, 10.04; N, 7.40.

1-(2-Chlorophenyl)-2,5-dimethyl-1H-pyrrole **2g** was prepared from **1g** (10 mmol, 1.28 g), yellow oil, yield 0.25 g (12%). ^{1}H NMR, *δ*: 7.57-7.54 (m, 1H), 7.41-7.38 (m, 2H), 7.32-7.30 (m, 1H) [H_{Ar}], 5.95 (s, 2H, H3, H4), 1.98 (s, 6H, Me). Lit. [S2], *δ*: 7.54–7.52 (m, 1H), 7.40–7.23 (m, 3H), 5.93 (s, 2H), 1.95 (s, 6H). ^{13}C NMR, *δ*: 136.8, 134.0, 130.6, 130.2, 129.5, 127.5 (6C, C_{Ar}), 128.6 (C2, C5), 105.7 (C3, C4), 12.4 (Me).

1-(4-Chlorophenyl)-2,5-dimethyl-1H-pyrrole **2h** was prepared from **1h** (10 mmol, 1.28 g), yellow oil, yield 0.63 g (31%). ^{1}H NMR, *δ*: 7.45 (d, *J* 8.5 Hz, 2H, H_o), 7.17 (d, *J* 8.5 Hz, 2H, H_m), 5.92 (s, 2H, H3, H4), 2.04 (s, 6H, Me). Lit. [S1], *δ*: 7.42 (d, 2H, *J* 8.5 Hz), 7.14 (d, 2H, *J* 8.5 Hz), 5.89 (s, 2H), 2.02 (s, 6H). ^{13}C NMR, *δ*: 134.4 (C_p), 130.3, 130.1 (C_m, C_o), 129.5 (C_i), 128.1 (C2, C5), 106.9 (C3, C4), 13.8 (Me). Lit. [S1], *δ*: 137.5, 133.5, 129.5, 129.3, 128.7, 106.0, 12.9. IR (film, ν/cm^{-1}): 2965, 2925, 2863, 1634, 1595, 1495, 1402, 1324, 1173, 1093, 1006, 834, 757. Found (%): C, 70.28; H, 5.62; Cl, 17.31; N, 6.79. Calc. for $C_{12}H_{12}ClN$ (%): C, 70.07; H, 5.88; Cl, 17.24; N, 6.81.

1-(2-Bromophenyl)-2,5-dimethyl-1H-pyrrole **2i** was prepared from **1i** (10 mmol, 1.72 g), yellow oil, yield 0.33 g (13%). ^{1}H NMR, *δ*: 7.73-7.71 (m, 1H), 7.44-7.40 (m, 1H), 7.31-7.29 (m, 2H) [H_{Ar}], 5.94 (s, 2H, H3, H4), 1.97 (s, 6H, Me). Lit. [S3], *δ*: 7.72 (d, *J* 8.0 Hz, 1H), 7.46-7.40 (m, 1H), 7.34-7.28 (m, 2H), 5.94 (s, 2H), 1.97 (s, 6H). ^{13}C NMR, *δ*: 138.5, 133.3, 130.5, 129.8, 128.5, 124.4 (6C, C_{Ar}), 128.2 (C2, C5), 105.6 (C3, C4), 12.6 (Me). Lit. [S3], *δ*: 138.5, 133.3, 130.5, 129.8, 128.4, 128.1, 124.1, 105.6, 12.5. IR (film, ν/cm^{-1}): 3062, 2922, 1640, 1593, 1484, 1439, 1400, 1321, 1190, 1024, 955, 756. Found (%): C, 57.72; H, 4.92; Br, 31.95; N, 5.41. Calc. for $C_{12}H_{12}BrN$ (%): C, 57.62; H, 4.84; Br, 31.94; N, 5.60.

1-(4-Bromophenyl)-2,5-dimethyl-1H-pyrrole **2j** was prepared from **1j** (10 mmol, 1.72 g), yellow oil, yield 0.53 g (21%). ^{1}H NMR, *δ*: 7.58 (d, *J* 8.4 Hz, 2H, H_o), 7.08 (d, *J* 8.4 Hz, 2H, H_m), 5.89 (s, 2H, H3, H4), 2.02. (s, 6H, Me). Lit. [S1], *δ*: 7.58 (d, 2H, *J* 8.6 Hz), 7.09 (d, 2H, *J* 8.6 Hz), 5.89 (s,

2H), 2.02 (s, 6H). ^{13}C NMR, δ: 138.0 (C_i), 132.3 (C_m), 129.8 (C_j), 128.6 (C2, C5), 121.5 (C_i), 106.1 (C3, C4), 12.9 (Me). Lit. [S1], δ: 137.9, 132.3, 129.8, 128.6, 121.5, 106.0, 12.9. IR (film, ν/cm^{-1}): 3350, 3035, 2917, 1624, 1497, 1430, 1408, 1280, 1173, 1025, 950, 883, 756, 694. Found (%): C, 57.70; H, 4.86; Br, 31.87; N, 5.57. Calc. for $C_{12}H_{12}BrN$ (%): C 57.62; H, 4.84; Br, 31.94; N, 5.60.

2,5-Dimethyl-1-(naphthalen-1-yl)-1H-pyrrole **2k** was prepared from **1k** (5 mmol, 0.72 g), yellow oil, yield 0.30 g (40%, based on 1-aminonaphtalene **1k** consumed). 1-Aminonaphtalene **1k** (0.23 g, 68% conversion) was also recovered upon column chromatography. ^{1}H NMR, δ: 7.94 (d, *J* 8.3 Hz, 2H), 7.57-7.51 (m, 2H), 7.48-7.42 (m, 2H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.02 (s, 2H, H3, H4), 1.91(s, 6H, Me). Lit. [S1], 7.92 (d, 2H, *J* 8.0 Hz), 7.57-7.49 (m, 2H), 7.44-7.42 (m, 2H), 7.13 (d, 1H, *J* 8.3 Hz), 6.01 (s, 2H), 1.89 (s, 6H). ^{13}C NMR, δ: 135.8, 134.2, 131.9, 129.8, 128.5 (C2, C5), 128.0, 127.2, 126.5, 126.2, 125.3, 123.3, 105.4 (C3, C4), 12.5 (Me). Lit. [S1], 135.7, 134.2, 131.9, 129.8, 128.5, 128.0, 127.2, 126.5, 126.2, 125.4, 123.3, 105.4, 12.5. IR (film, *v*/cm^{-1}): 3052, 2958, 2924, 2860, 1648, 1591, 1515, 1461, 1412, 1023, 964, 801, 774. Found (%): C, 86.87; H, 6.87; N, 6.26. Calc. for $C_{16}H_{15}N$ (%): C, 86.84; H, 6.83; N, 6.33.

4-(2,5-Dimethyl-1H-pyrrol-1-yl)pyridine **2l** was prepared from **1l** (10 mmol, 0.94 g), yellow oil, yield 0.18 g (10%). ^{1}H NMR, δ: 8.75-8.73 (m, 2H), 7.19-7.18 (m, 2H) [H_{Pyr}], 5.96 (s, 2H, H3, H4), 2.11 (s, 6H, Me). Lit. [S4], δ: 8.85 (d, 2H, *J* 5.8 Hz), 7.29–7.23 (dd, 2H, *J* 9.45, *J* 5.85 Hz), 6.45 (d, 1H, *J* 8.95 Hz), 2.35(d, 3H, *J* 9.25 Hz), 2.06 (d, 3H, *J* 9.15 Hz). ^{13}C NMR, δ: 150.6 (C_2, C_6), 146.1 (C_4), 127.9 (C2, C5), 122.4 (C_3, C_5), 107.0 (C3, C4), 12.7 (Me). IR (film, *v*/cm^{-1}): 3377, 3035, 2966, 2924, 2747, 1947, 1707, 1647, 1589, 1498, 1404, 1330, 1218, 1039, 993, 834, 776, 710. Found (%): C, 76.68; H, 6.97; N, 16.35. Calc. for $C_{11}H_{12}N_2$ (%): C, 76.71; H, 7.02; N, 16.27.

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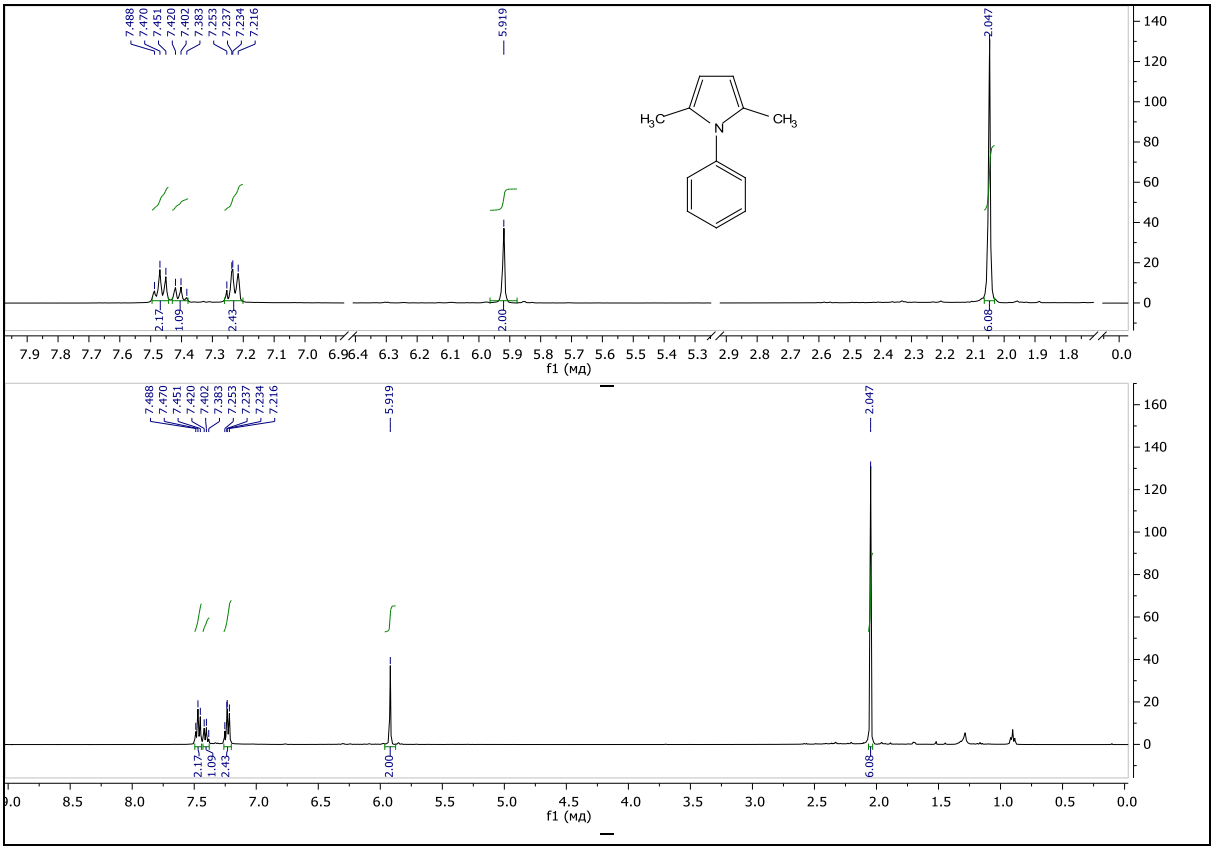
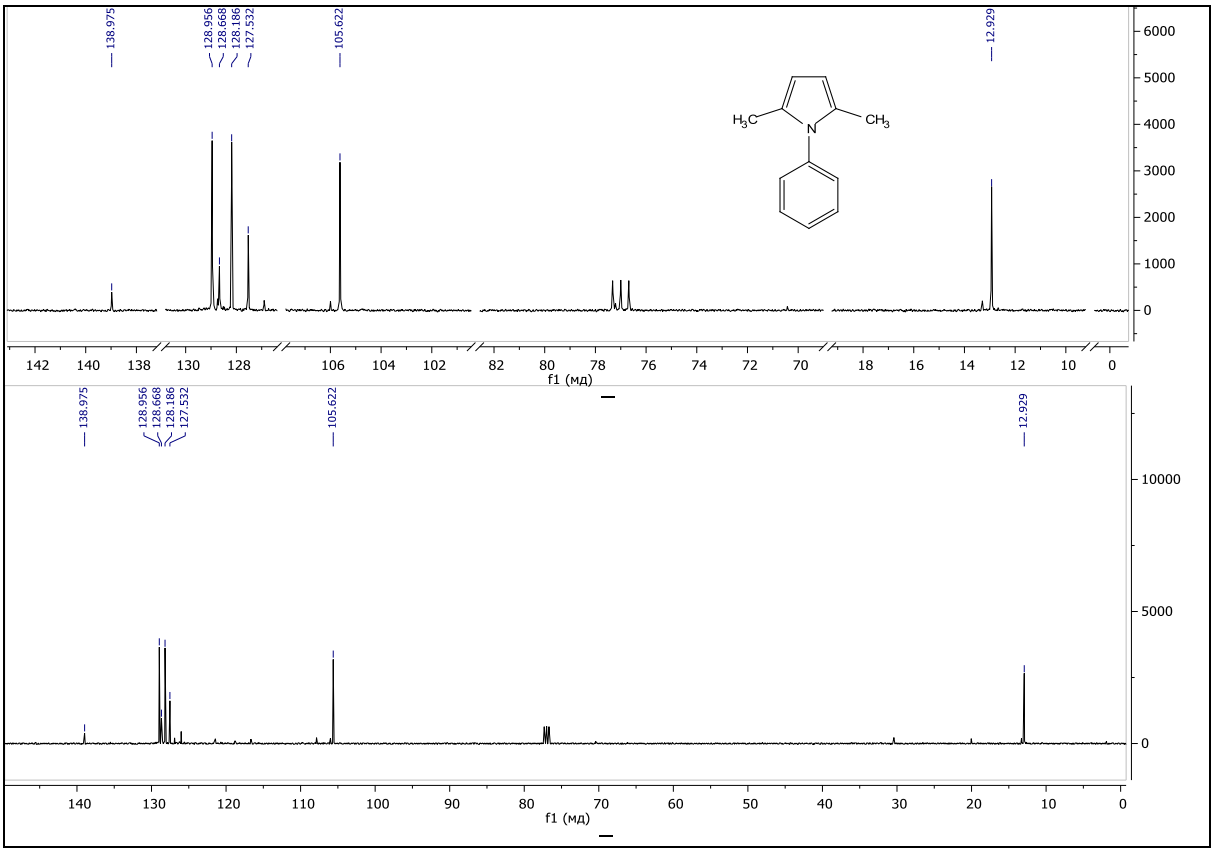
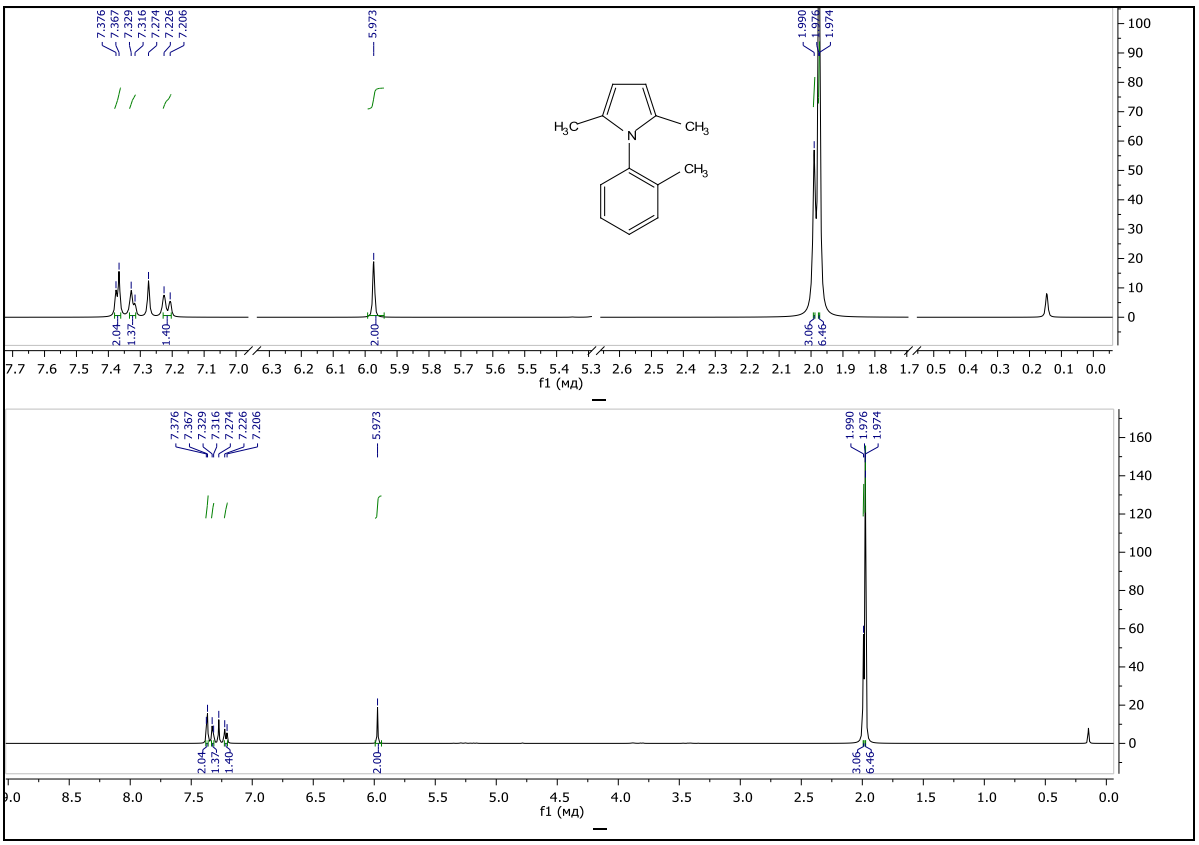
NMR Spectra



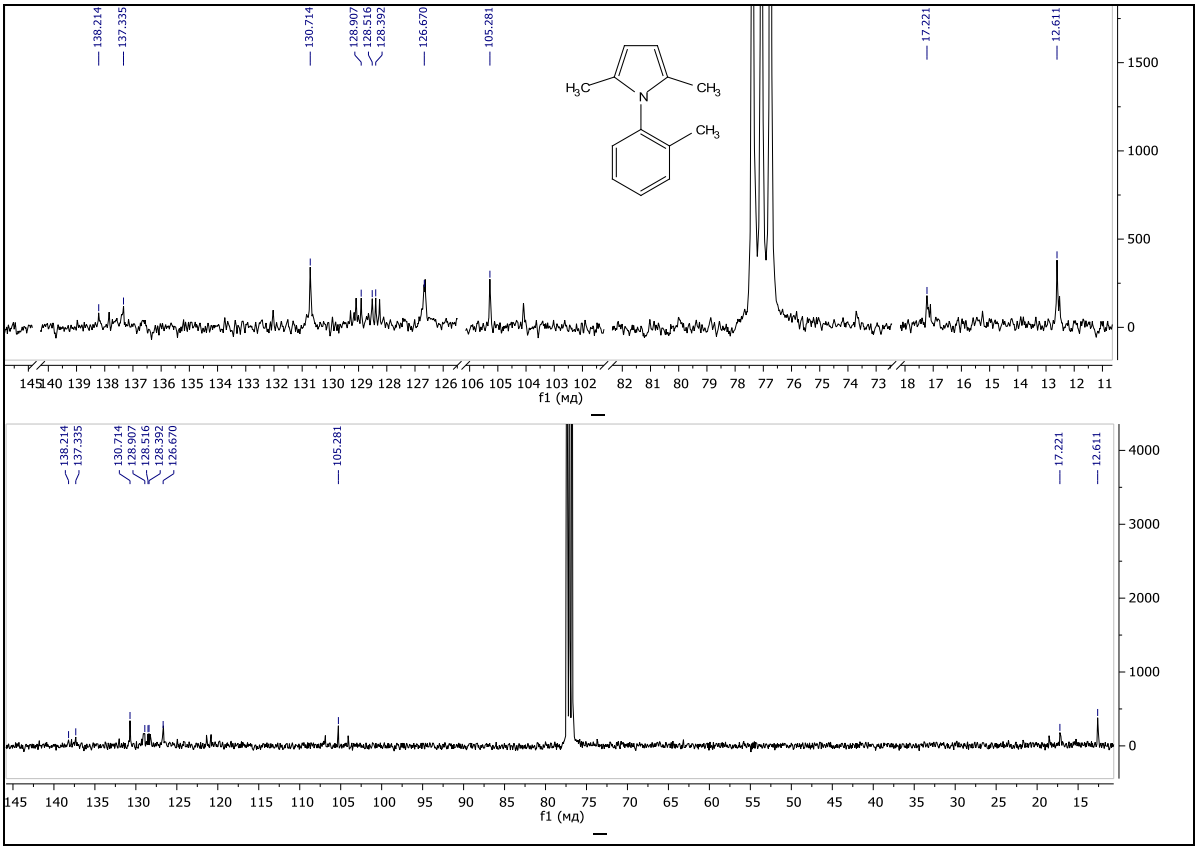
^{1}H NMR Spectrum of **2a**



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



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



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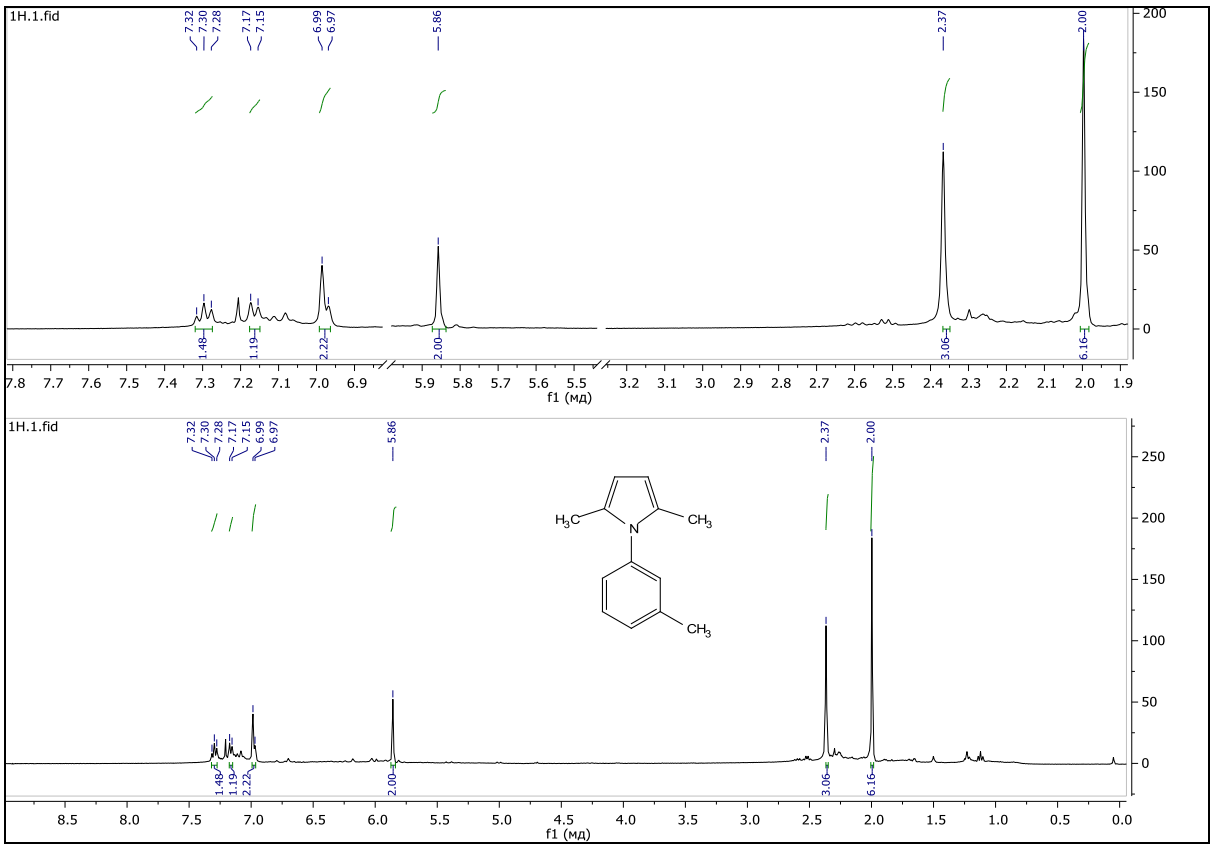

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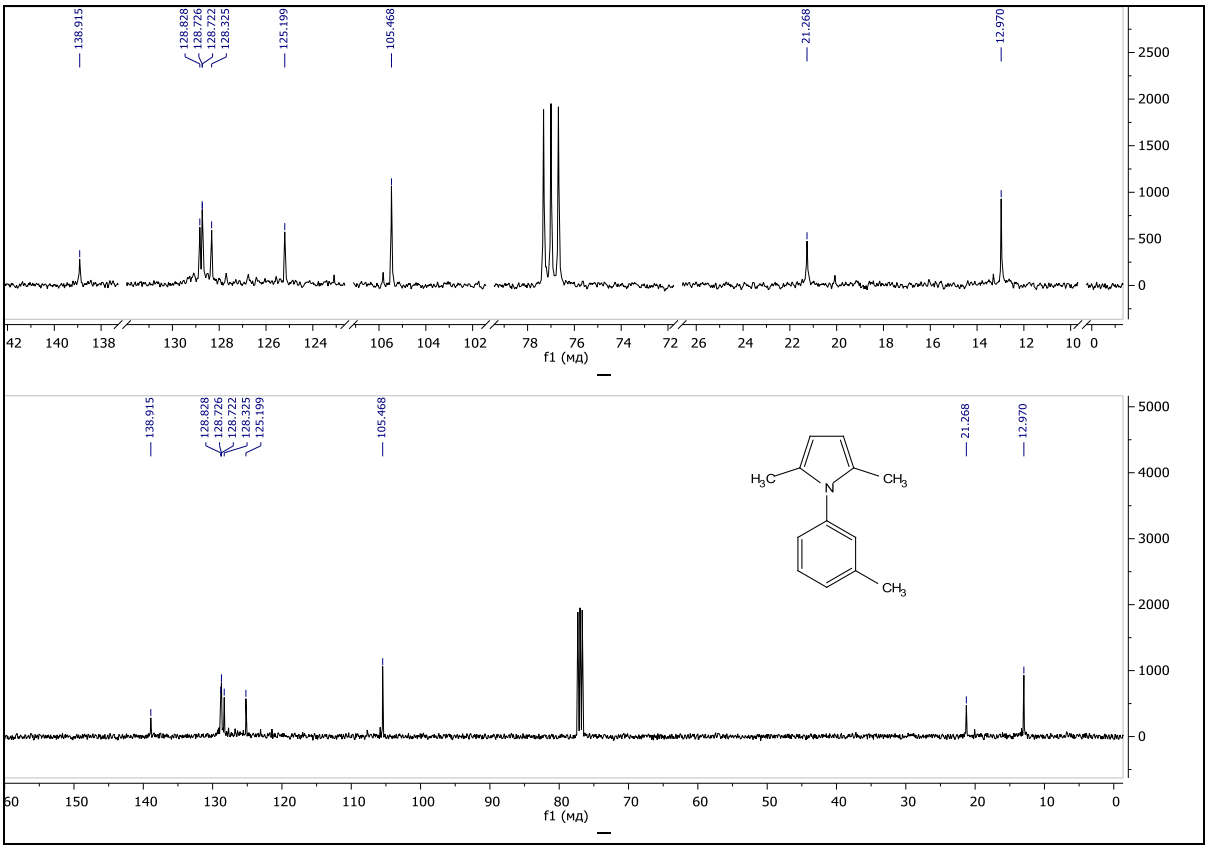
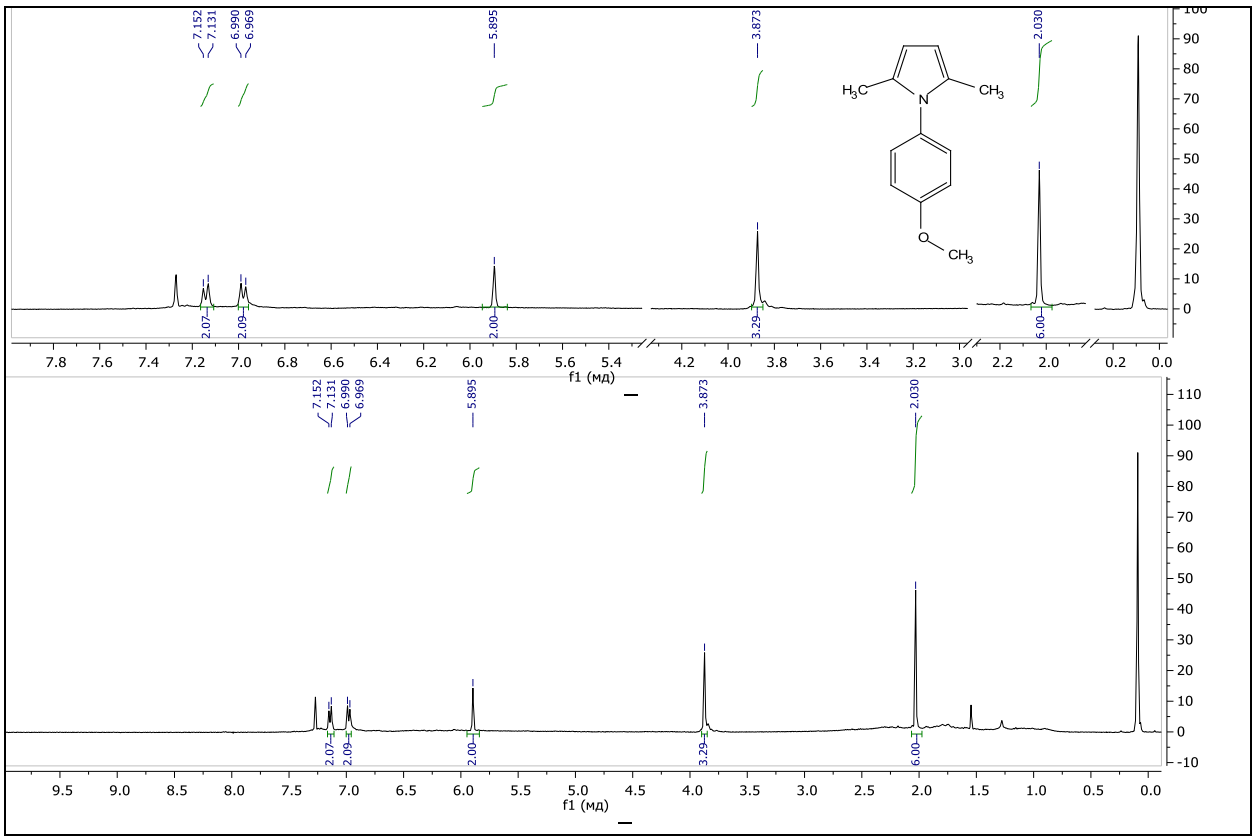
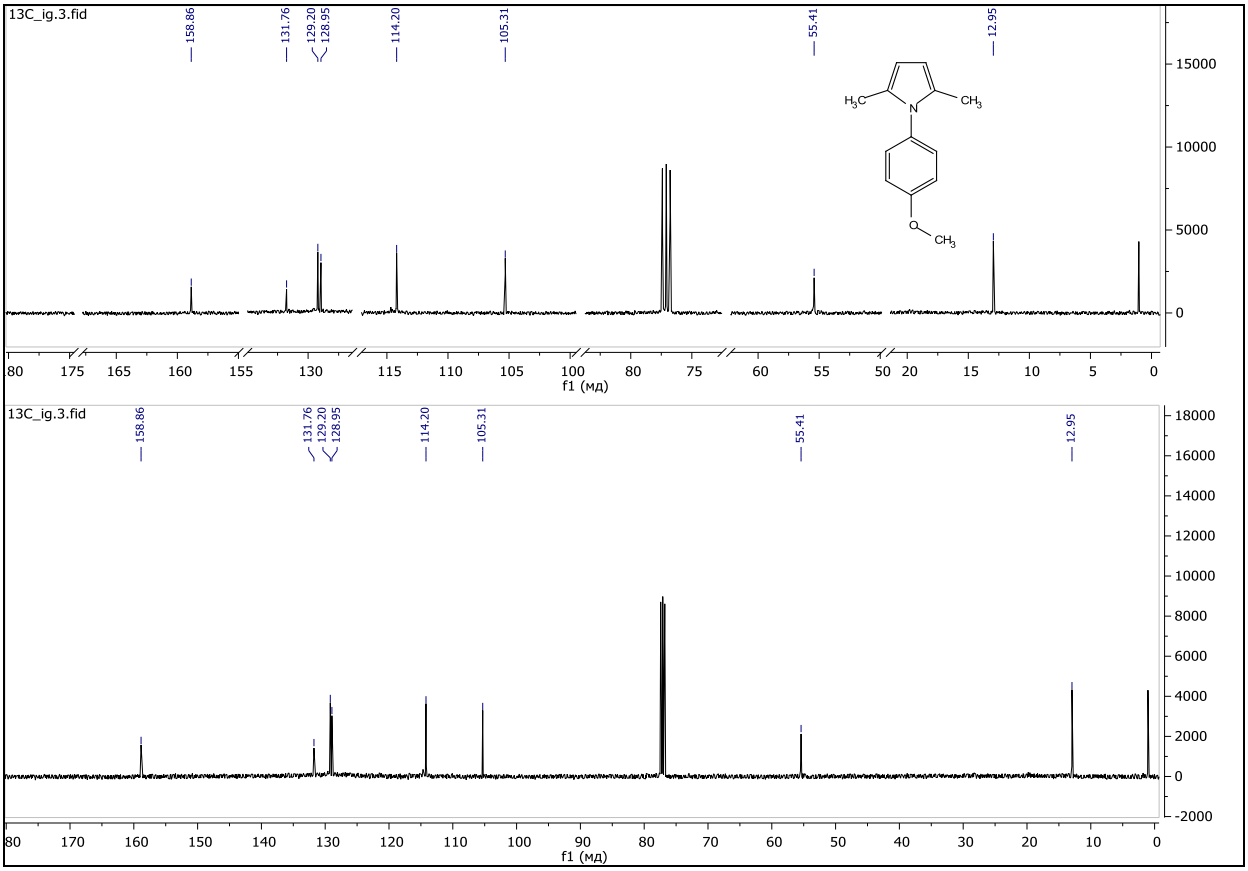


^{13}C NMR Spectrum of **2c**



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



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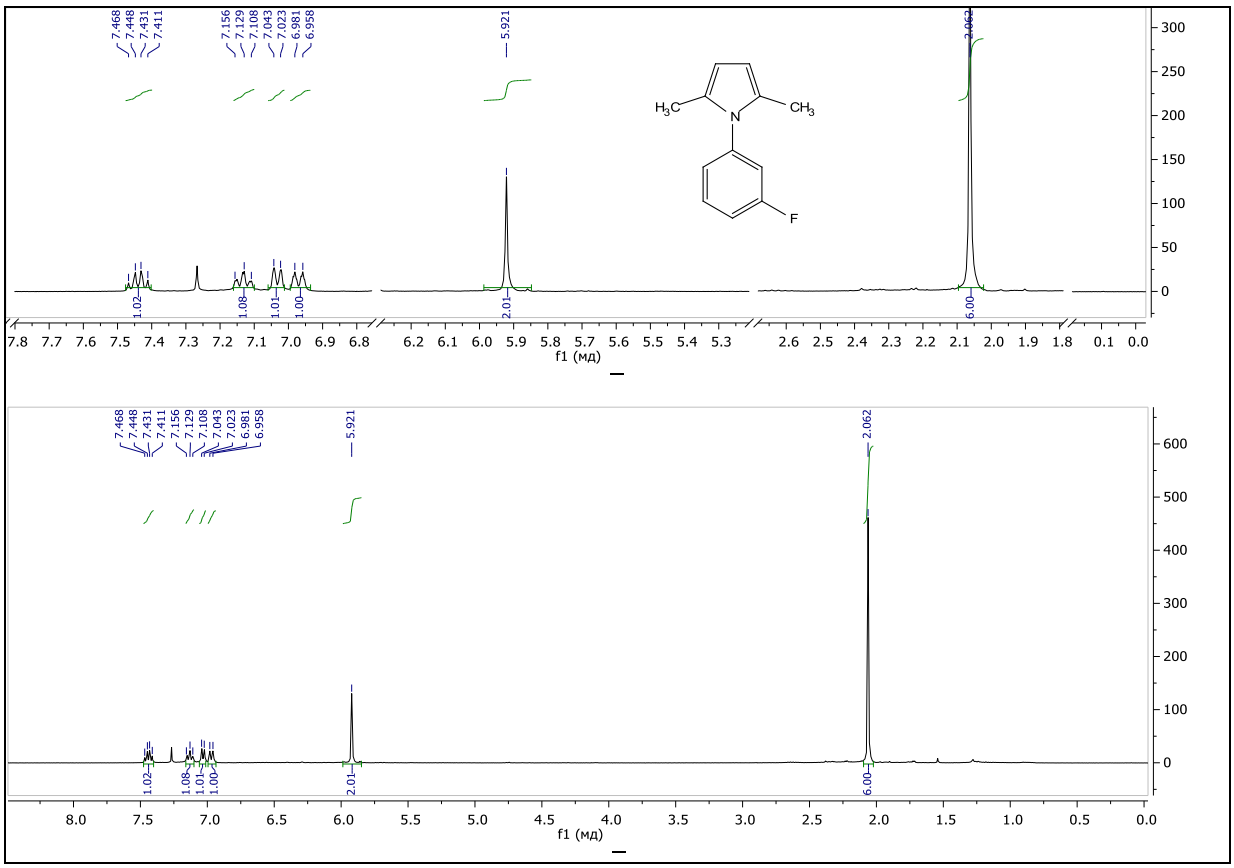
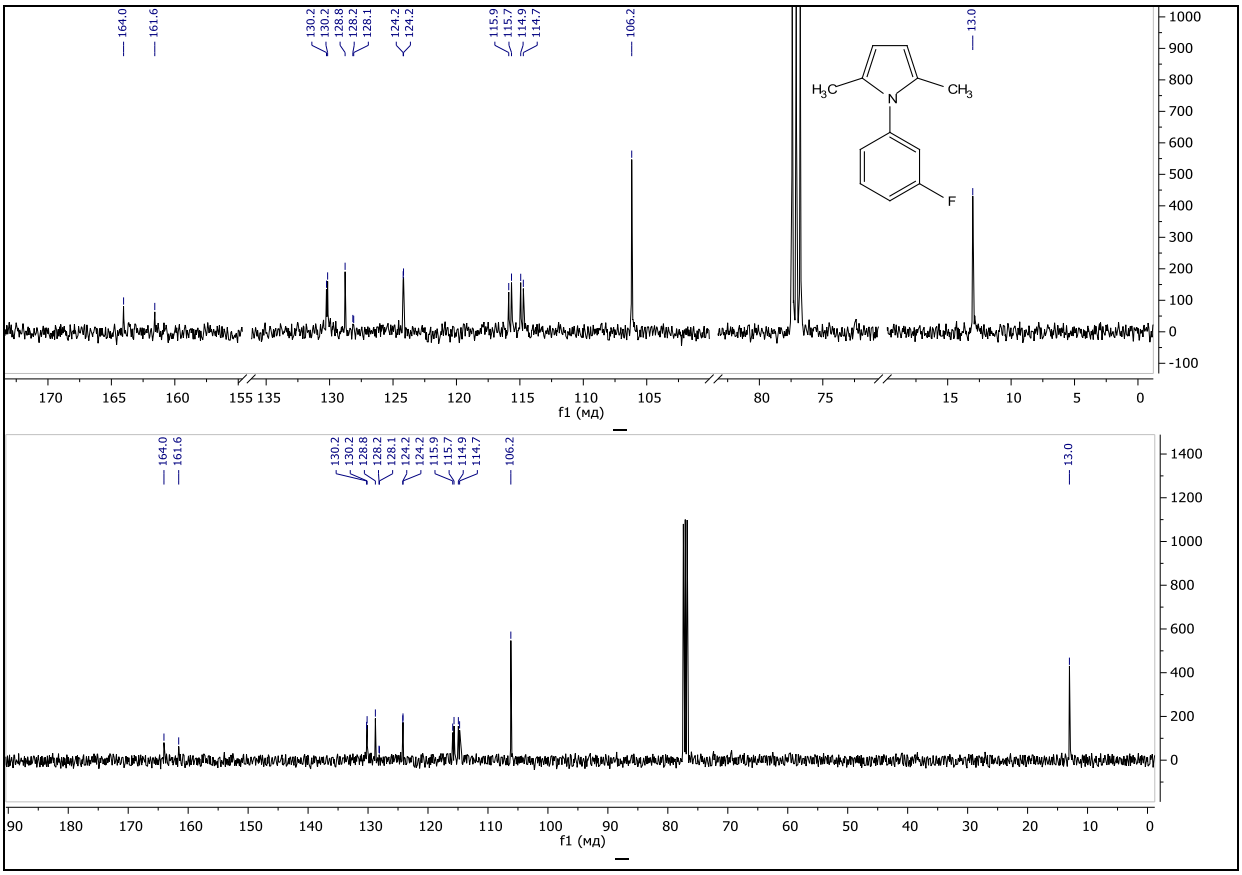
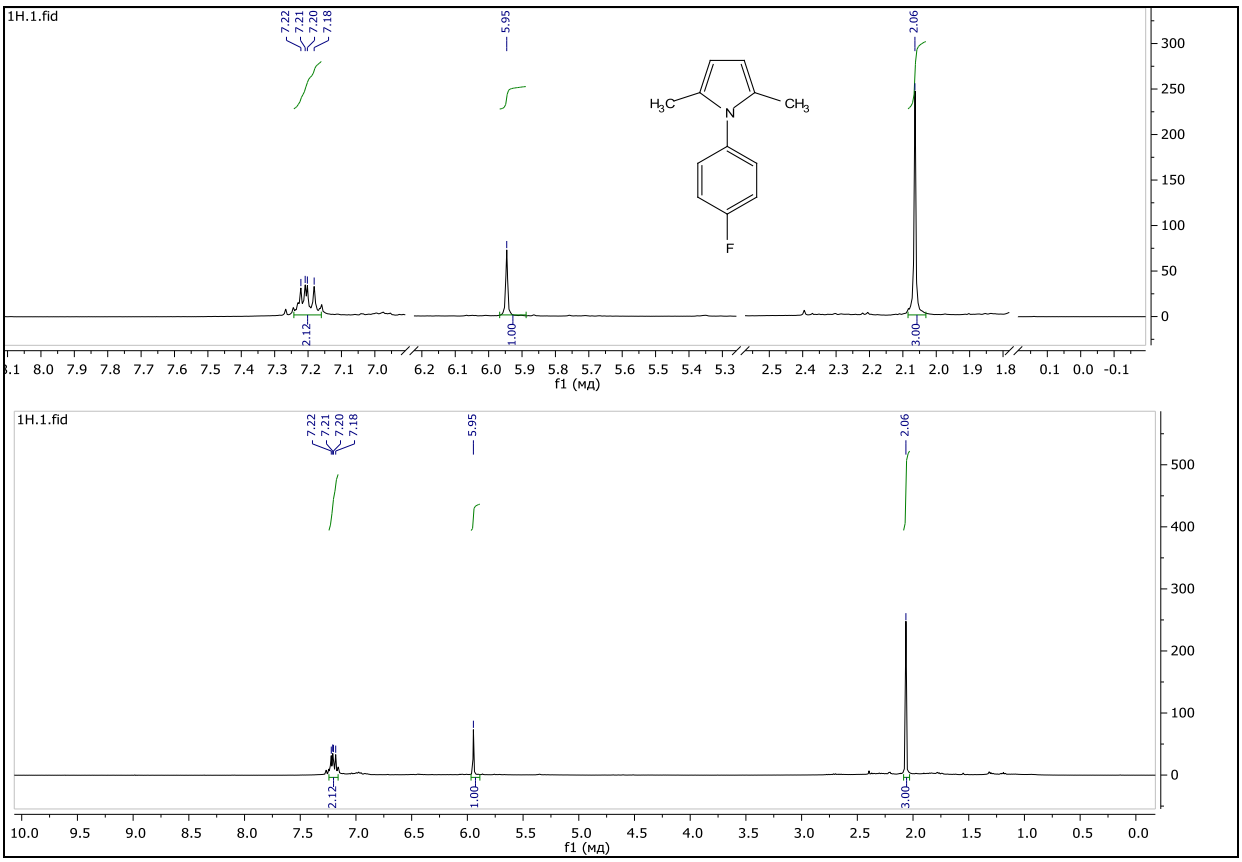


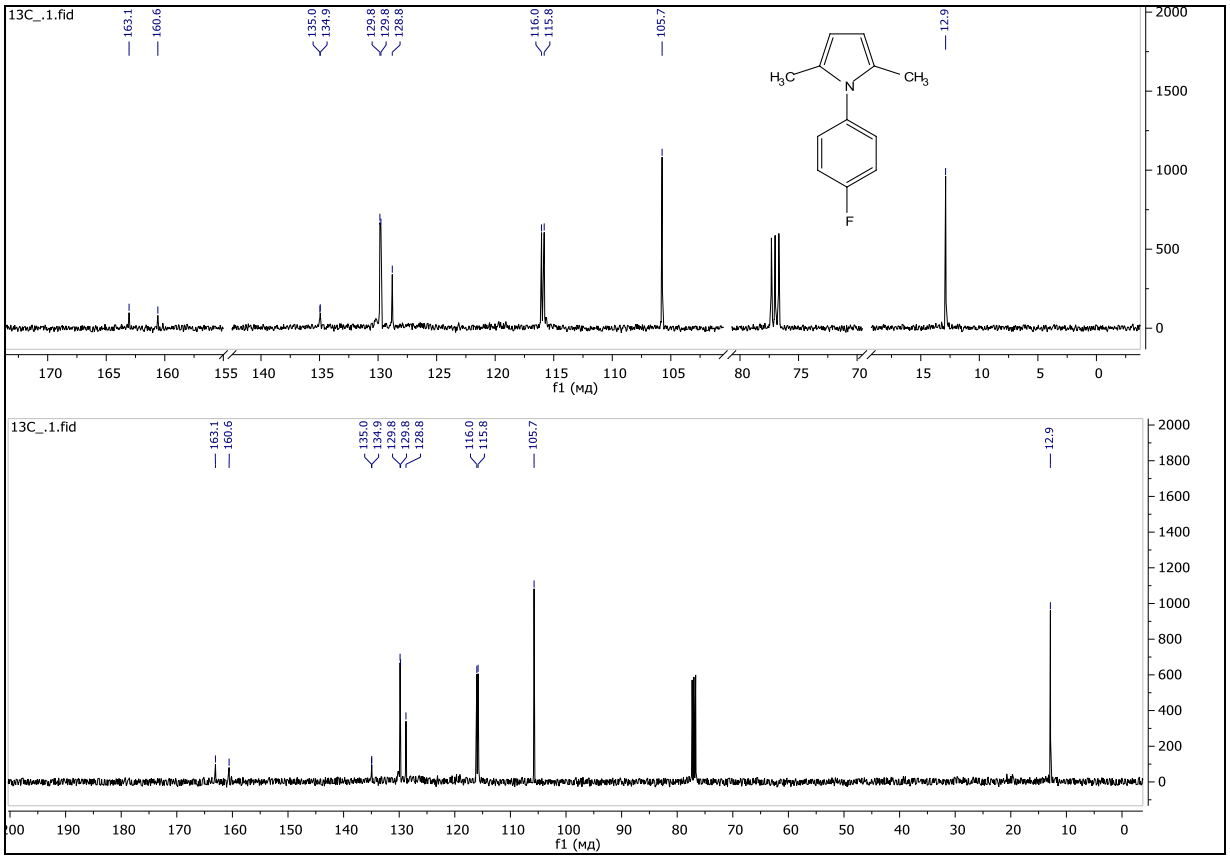
^{1}H NMR Spectrum of **2e**



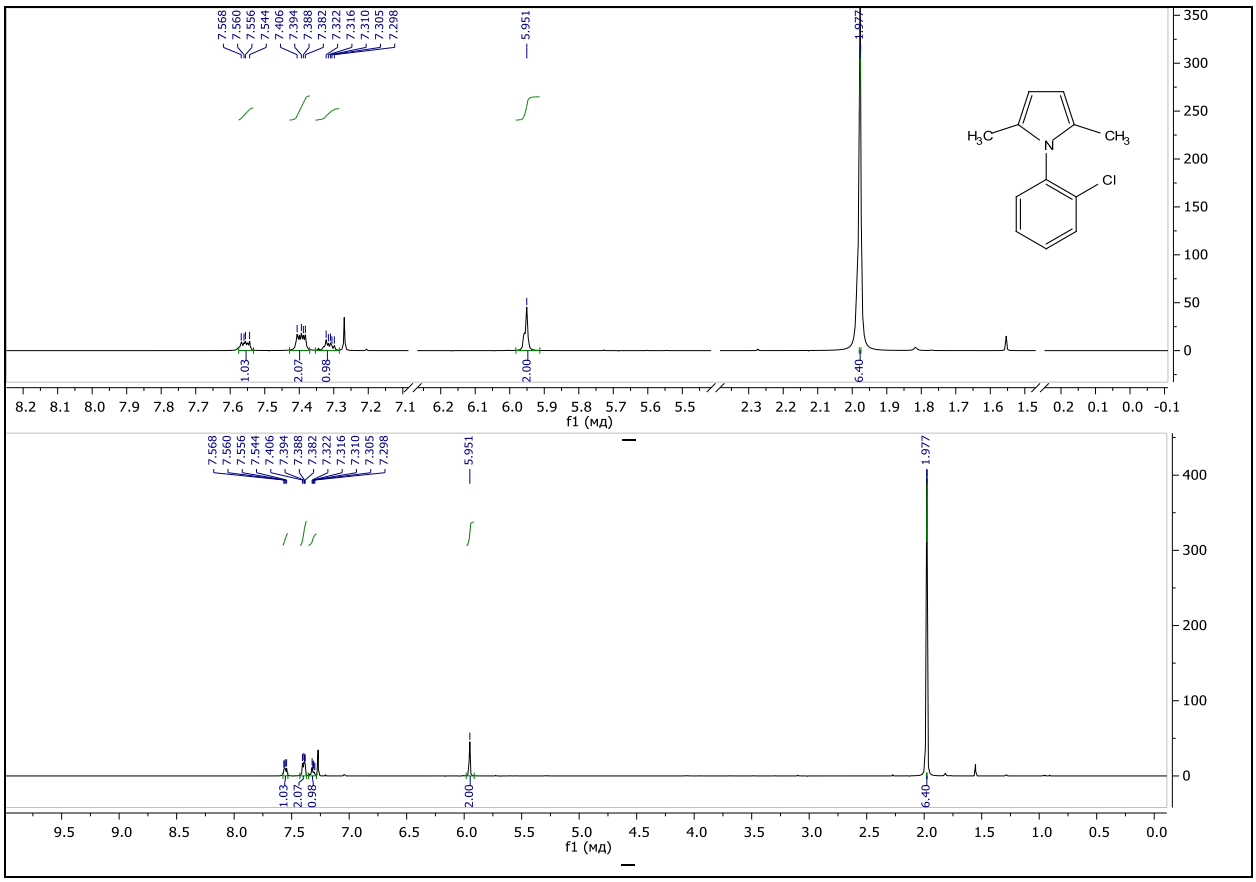
^{13}C NMR Spectrum of **2e**



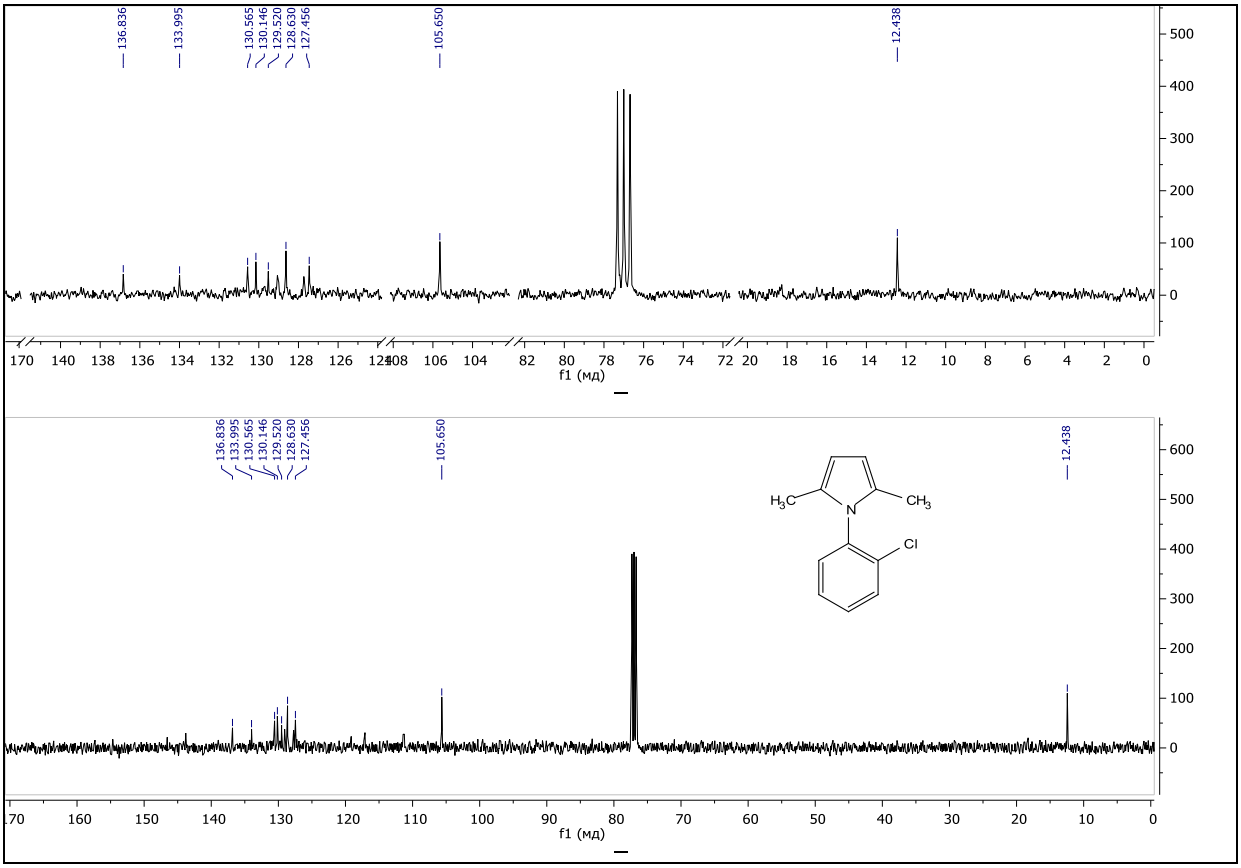
^{1}H NMR Spectrum of **2f**



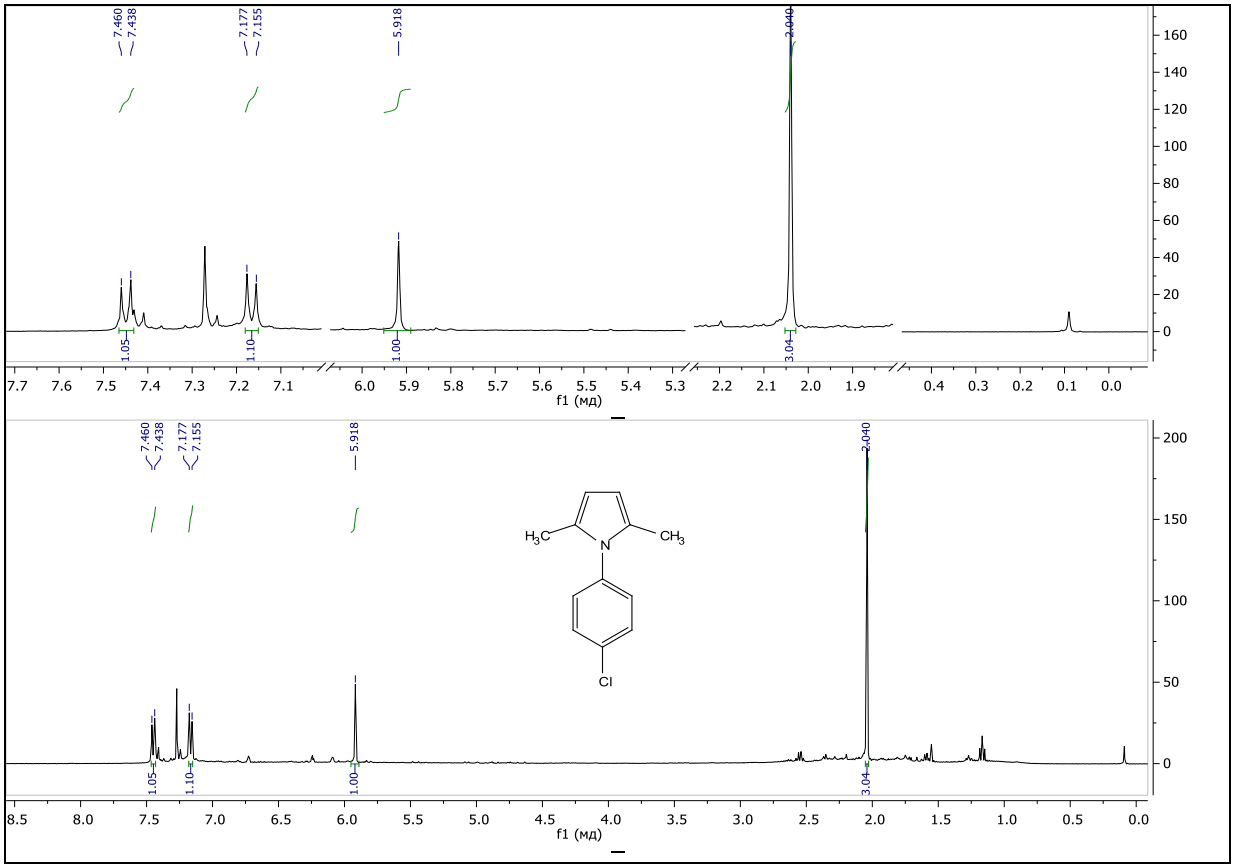
^{13}C NMR Spectrum of **2f**



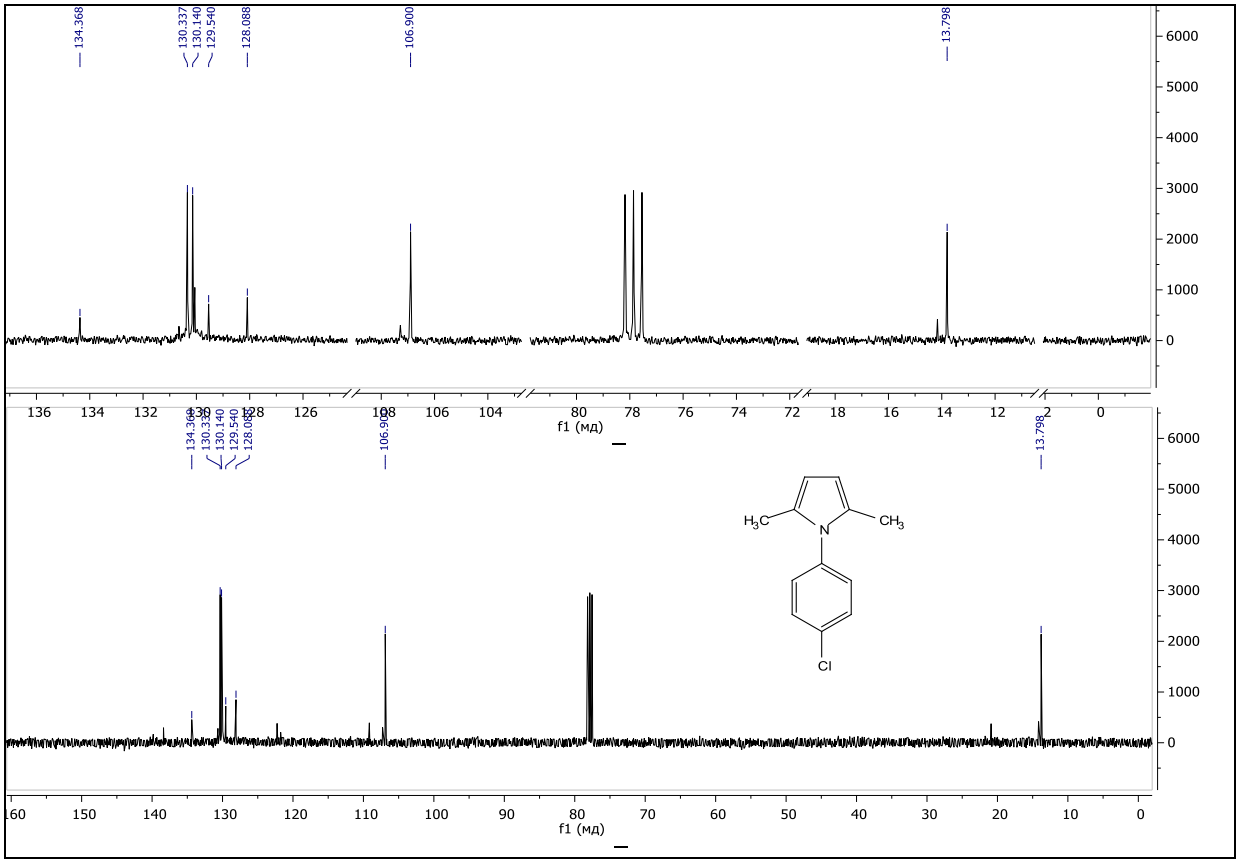
^{1}H NMR Spectrum of **2g**



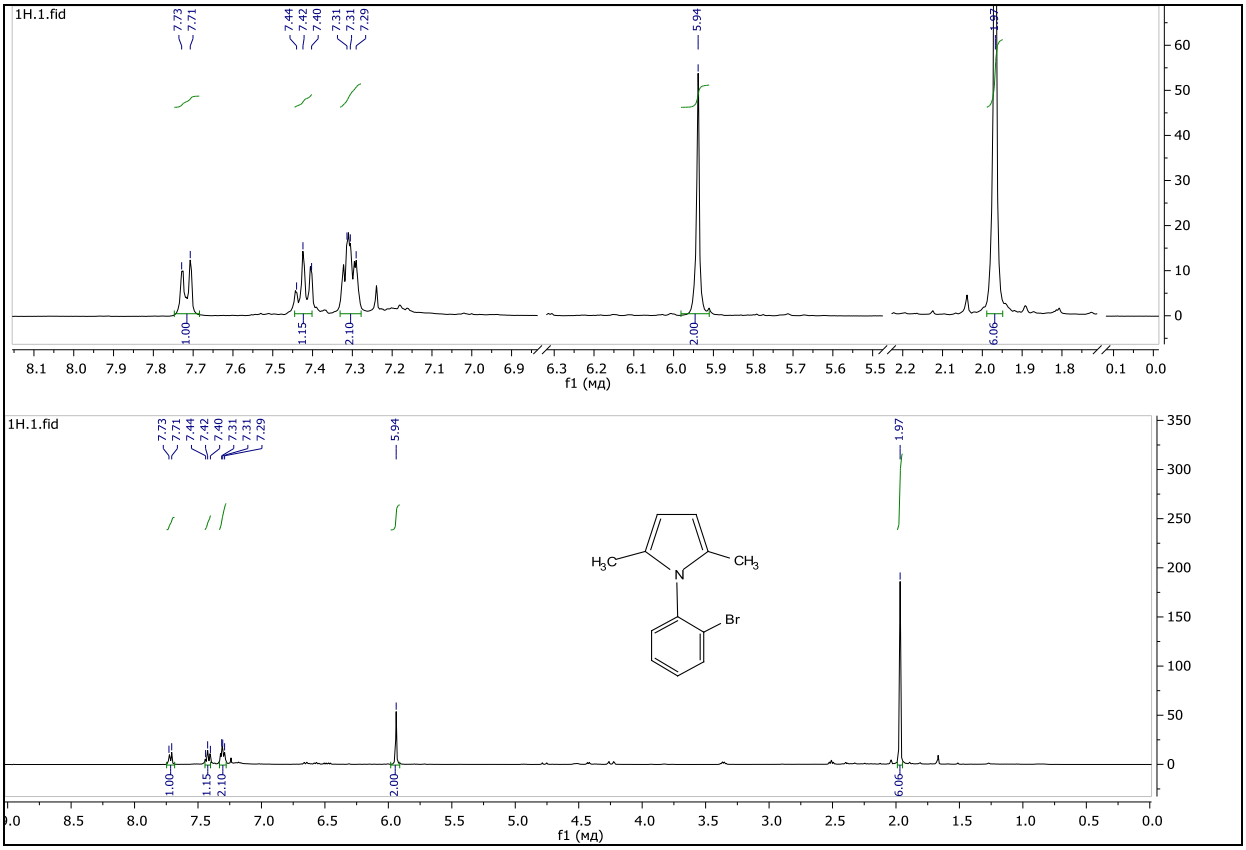
^{13}C NMR Spectrum of **2g**



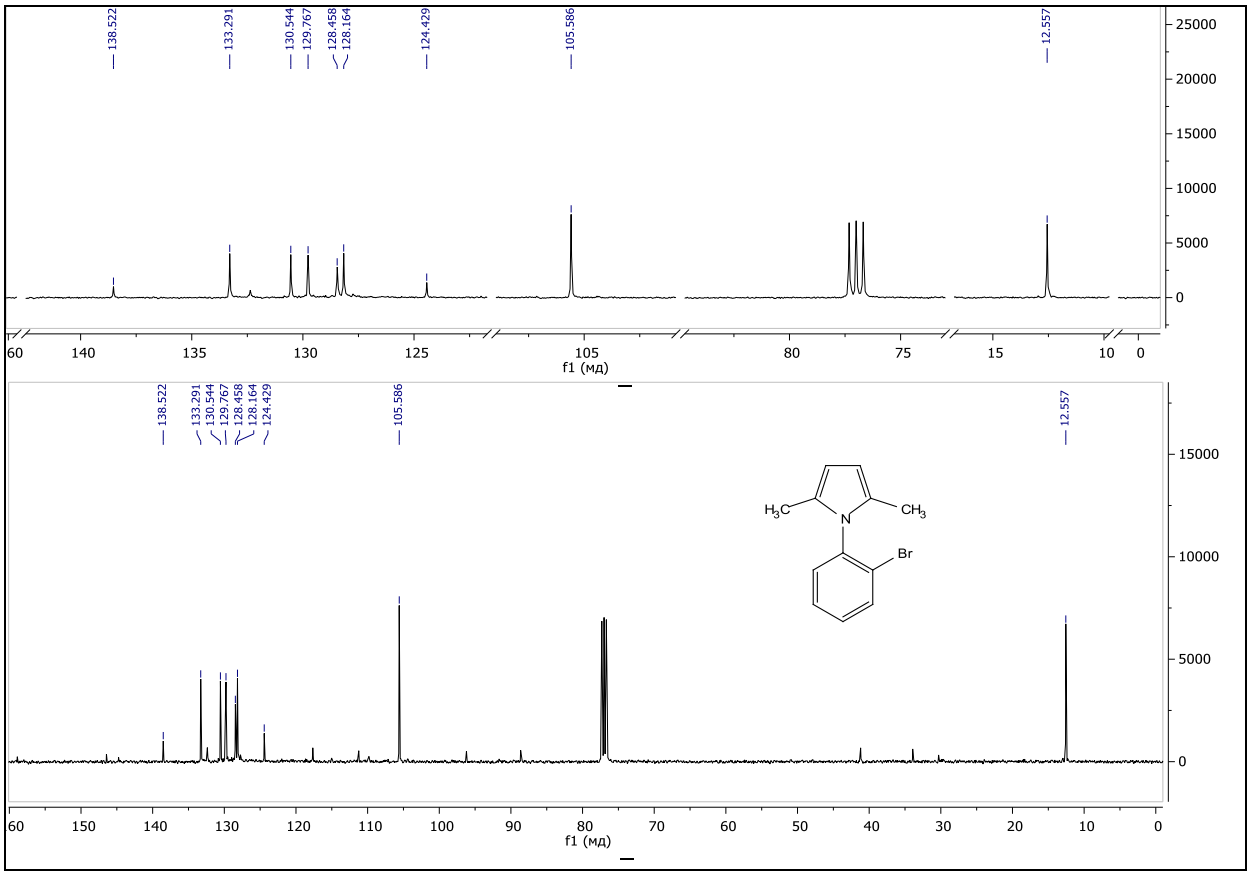
^{1}H NMR Spectrum of **2h**



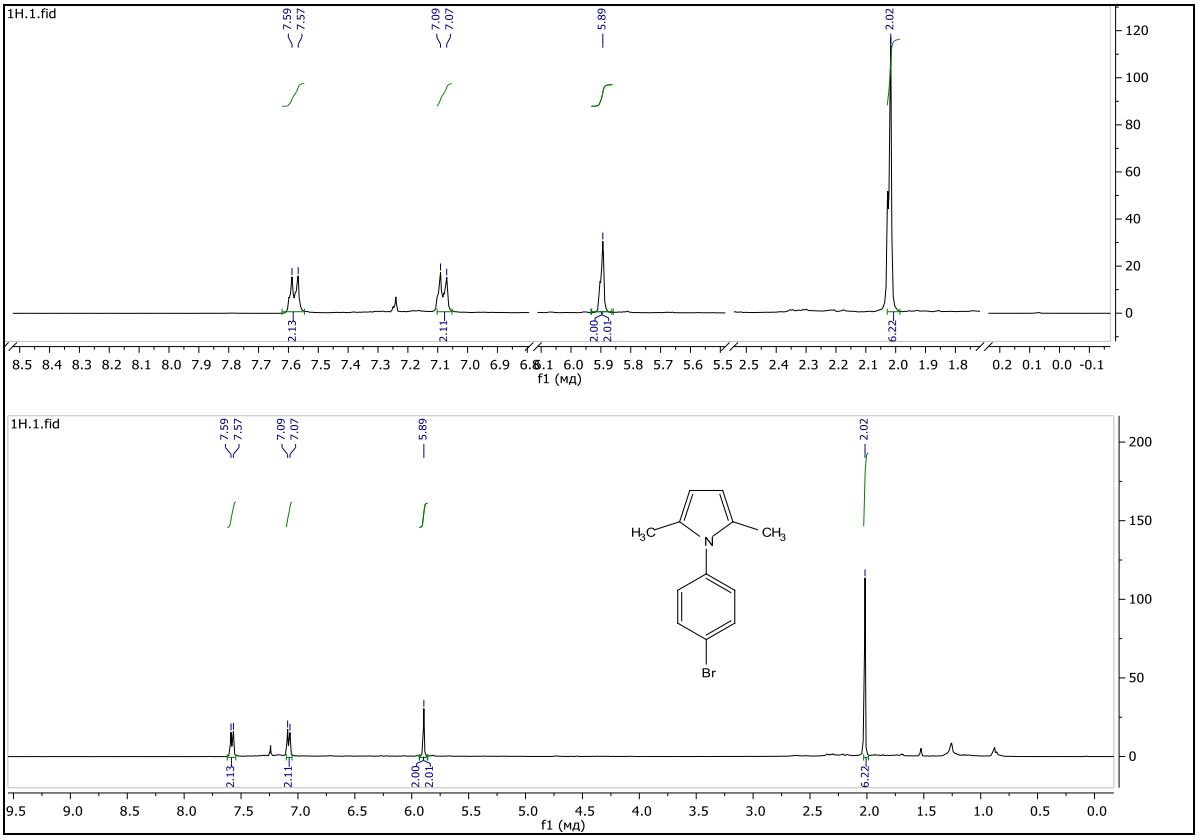
^{13}C NMR Spectrum of **2h**



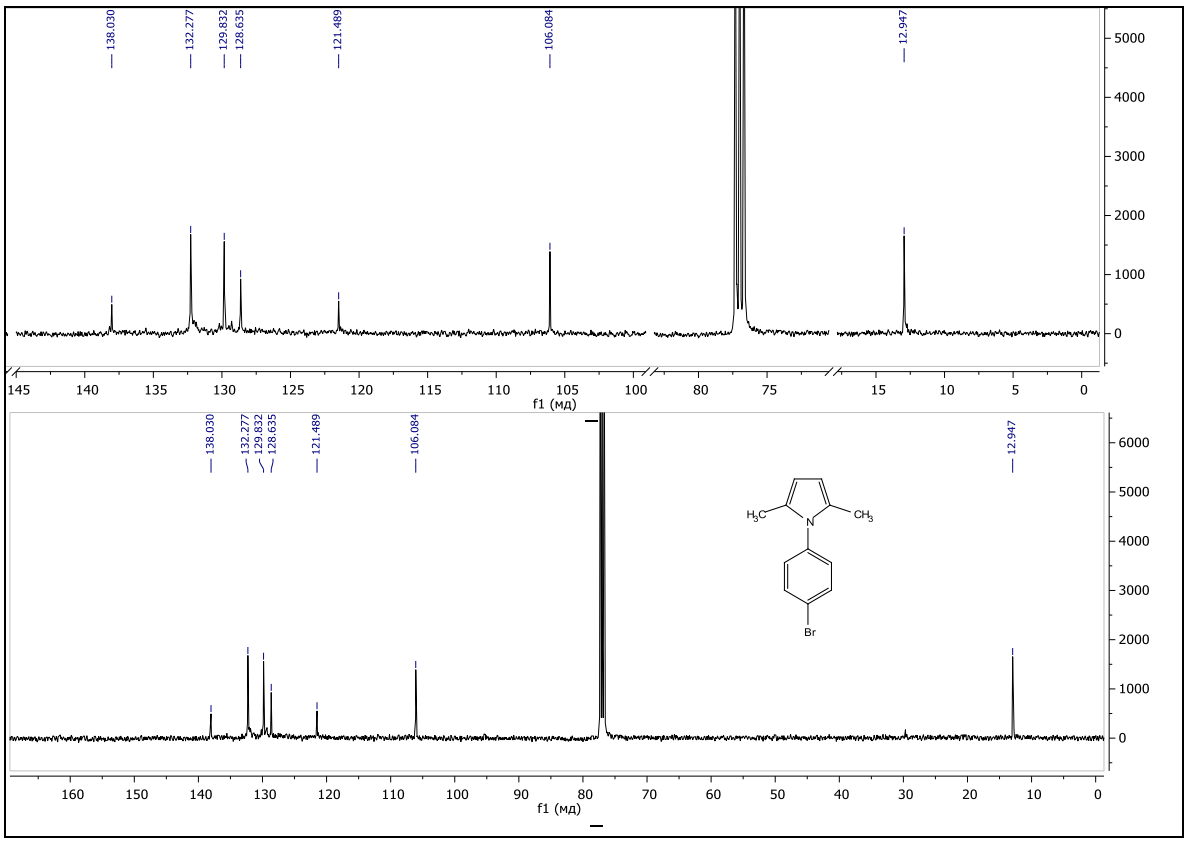
^{1}H NMR Spectrum of **2i**



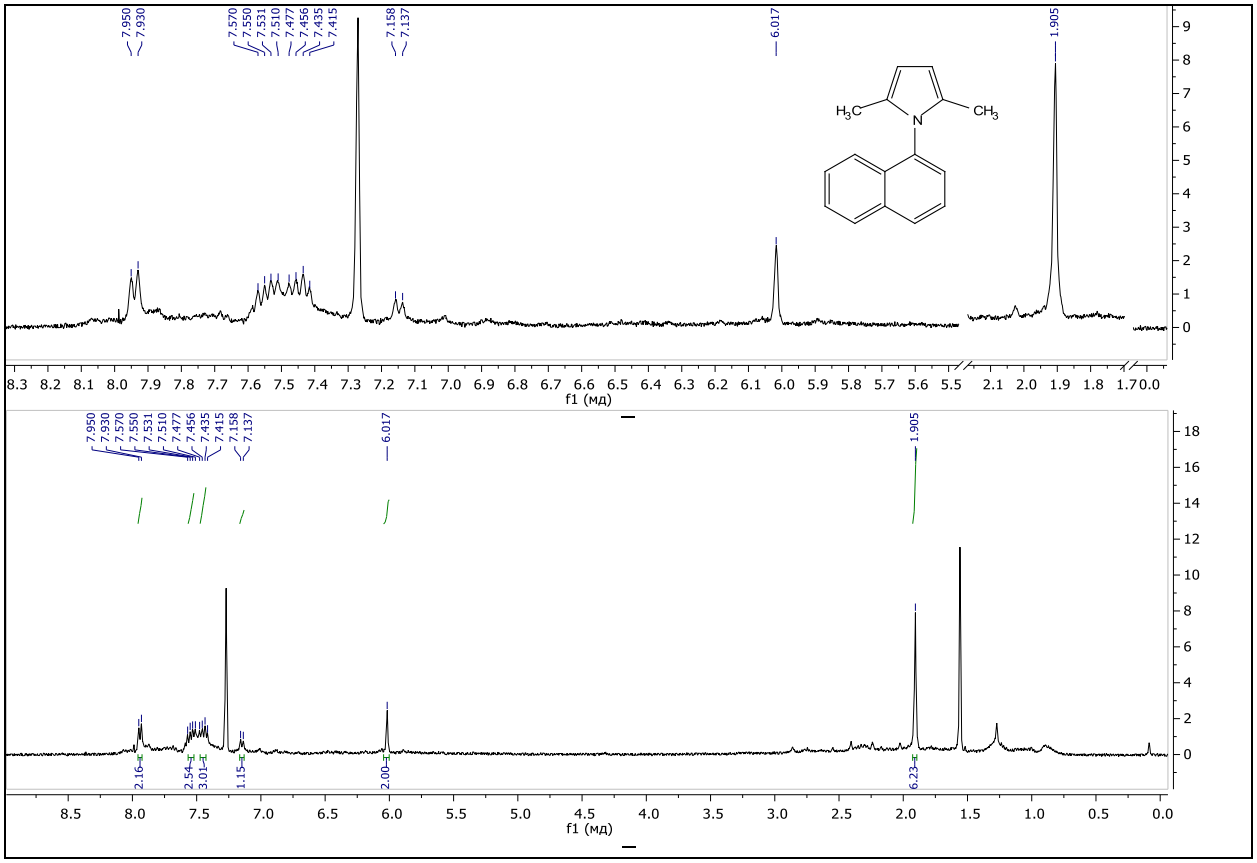
^{13}C NMR Spectrum of **2i**



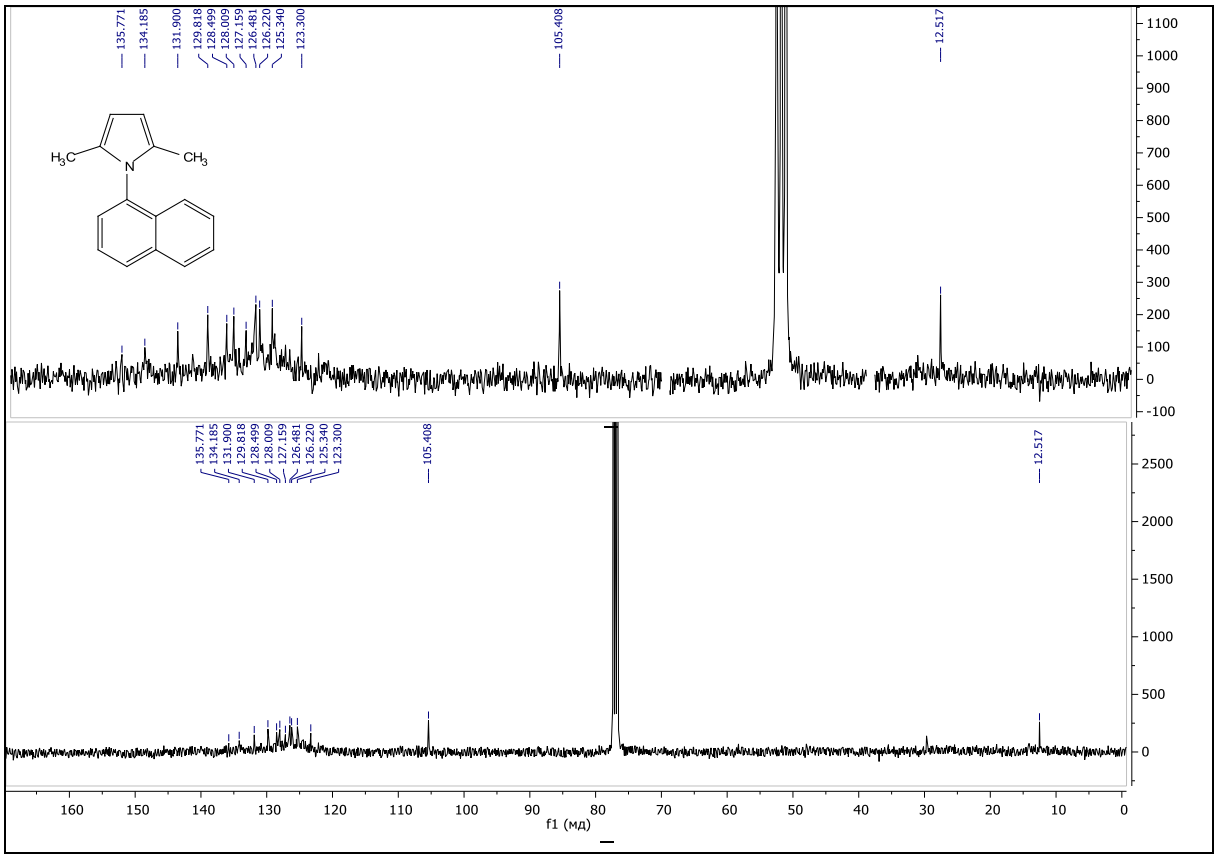
^{1}H NMR Spectrum of **2j**



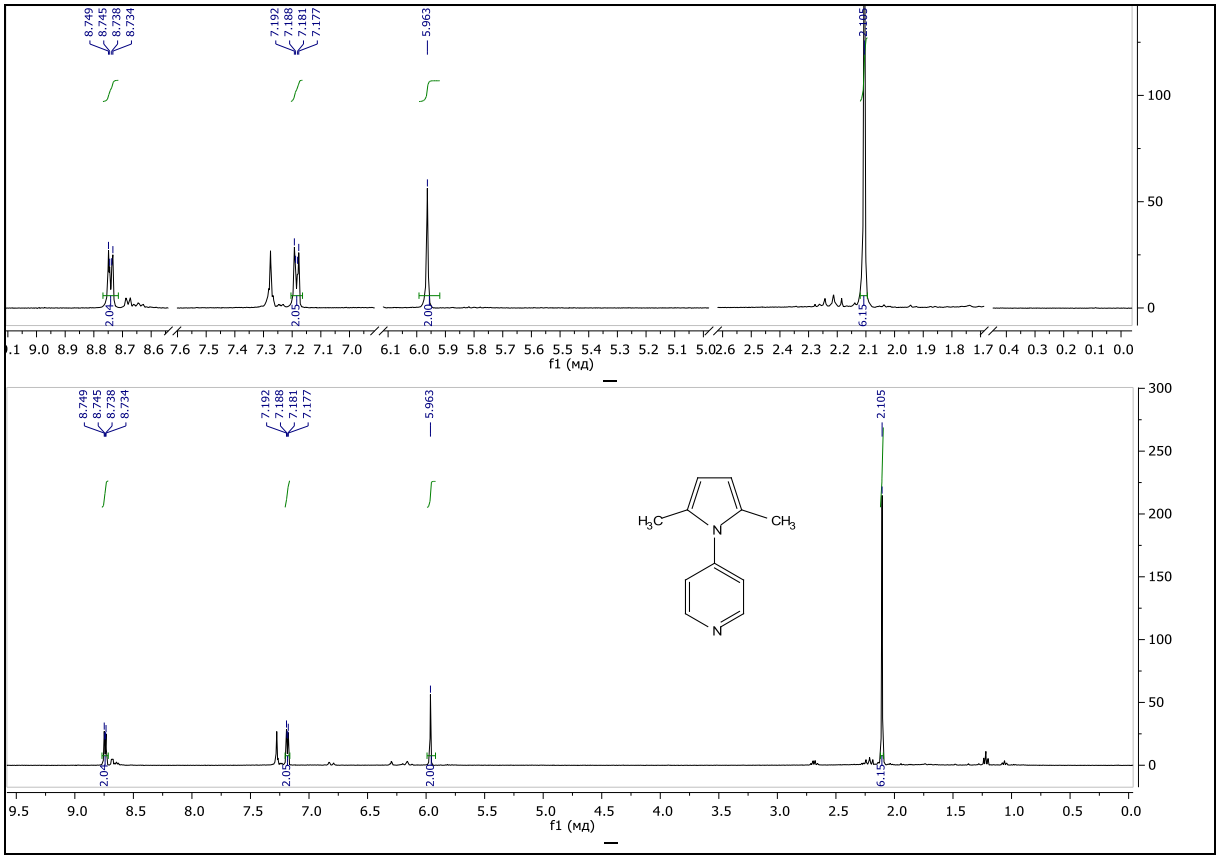
^{13}C NMR Spectrum of **2j**



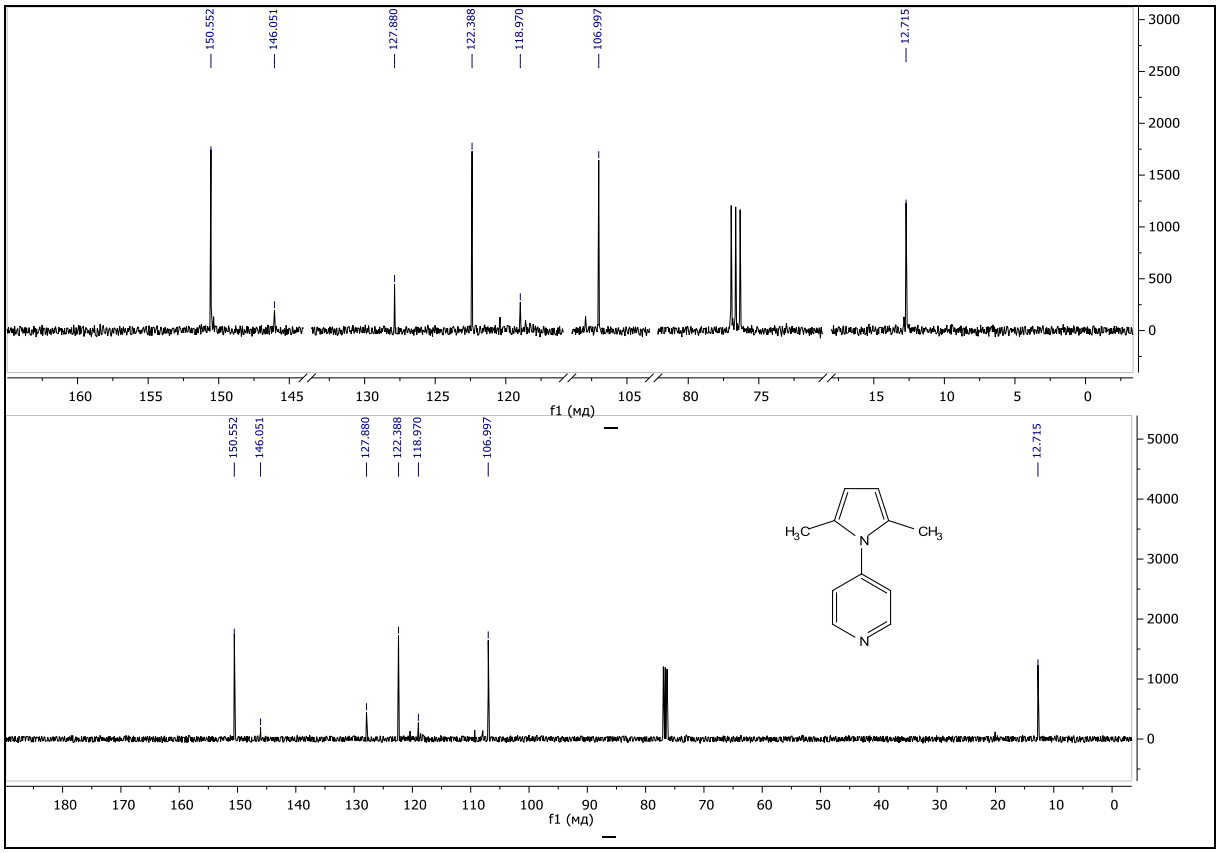
^{1}H NMR Spectrum of **2k**



^{13}C NMR Spectrum of **2k**



^{1}H NMR Spectrum of **2l**



^{13}C NMR Spectrum of **2l**

Identification of the vinylacetylene ***G*** *in the volatile products from the reaction of aniline with acetylene by GLC-MS*