Supporting information

Rapid, room-temperature self-organization of polyarylated 1*H*-pyrroles from acetylenes and nitriles in the KOBu^t/DMSO system

Elena Yu. Schmidt[a], Inna V. Tatarinova[a], Natal'ya A. Lobanova[a], Igor A. Ushakov[a], Irina Yu. Bagryanskaya[b] and Boris A. Trofimov[a]*

[a]*A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky Str., 664033 Irkutsk, Russia*

[b]*N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia*

E-mail: boris_trofimov@irioch.irk.ru

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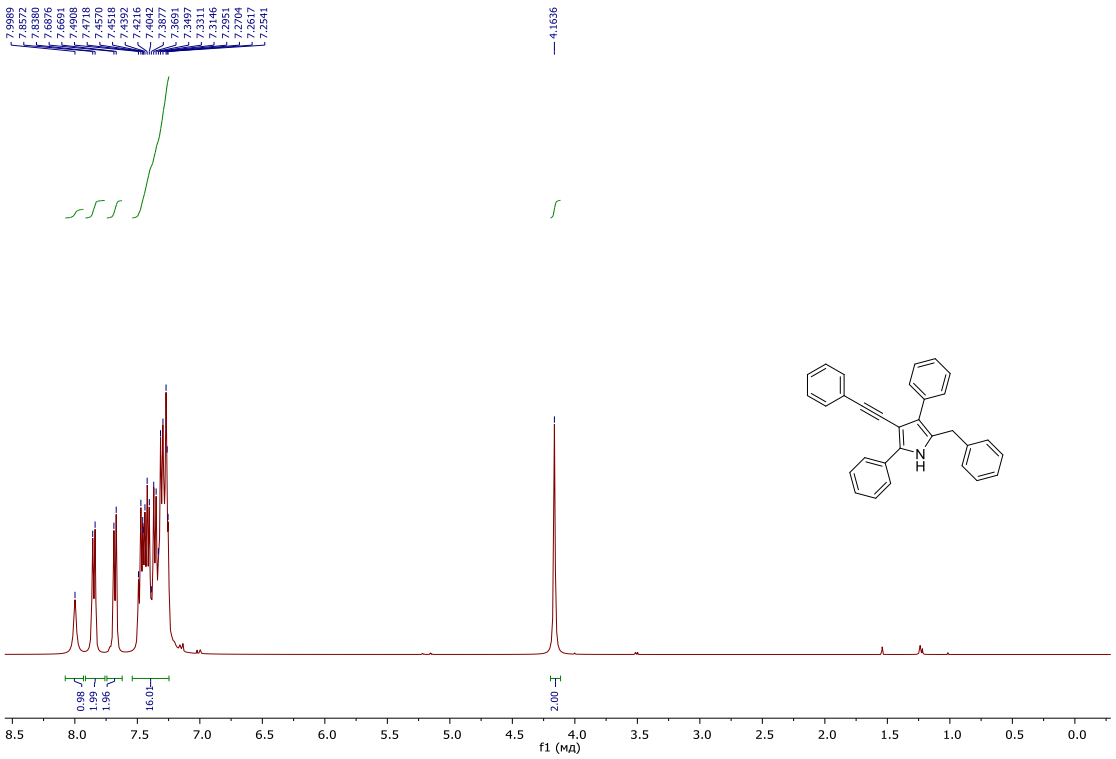
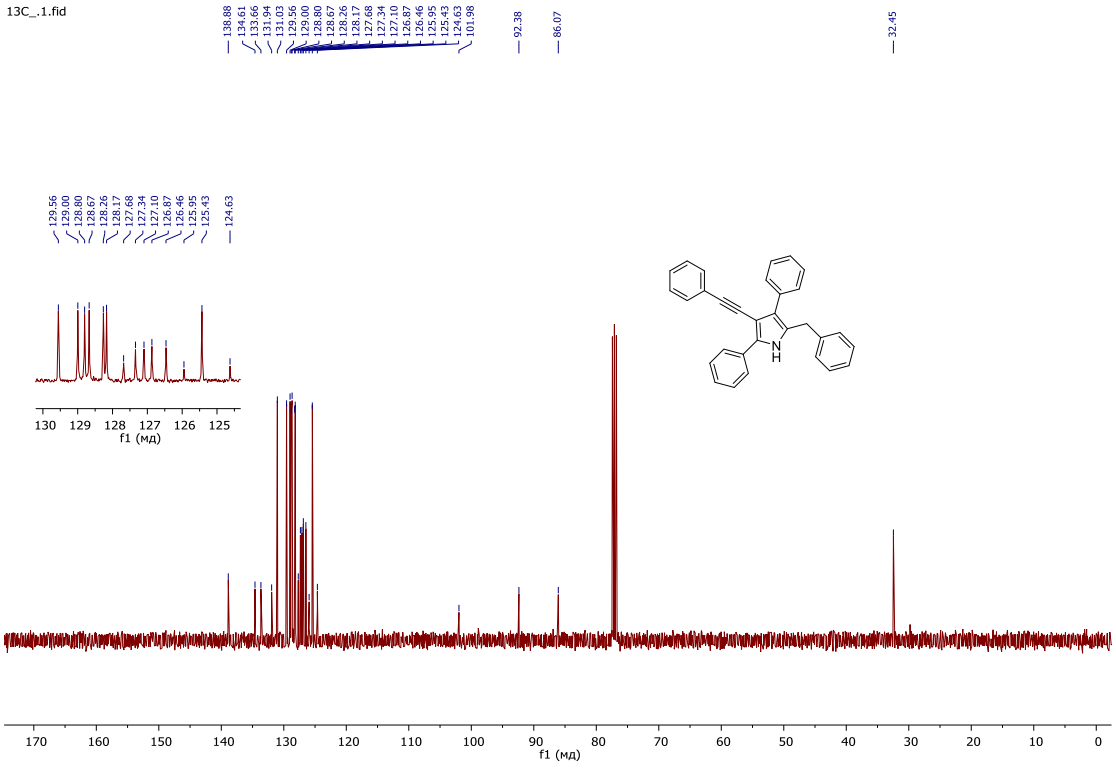
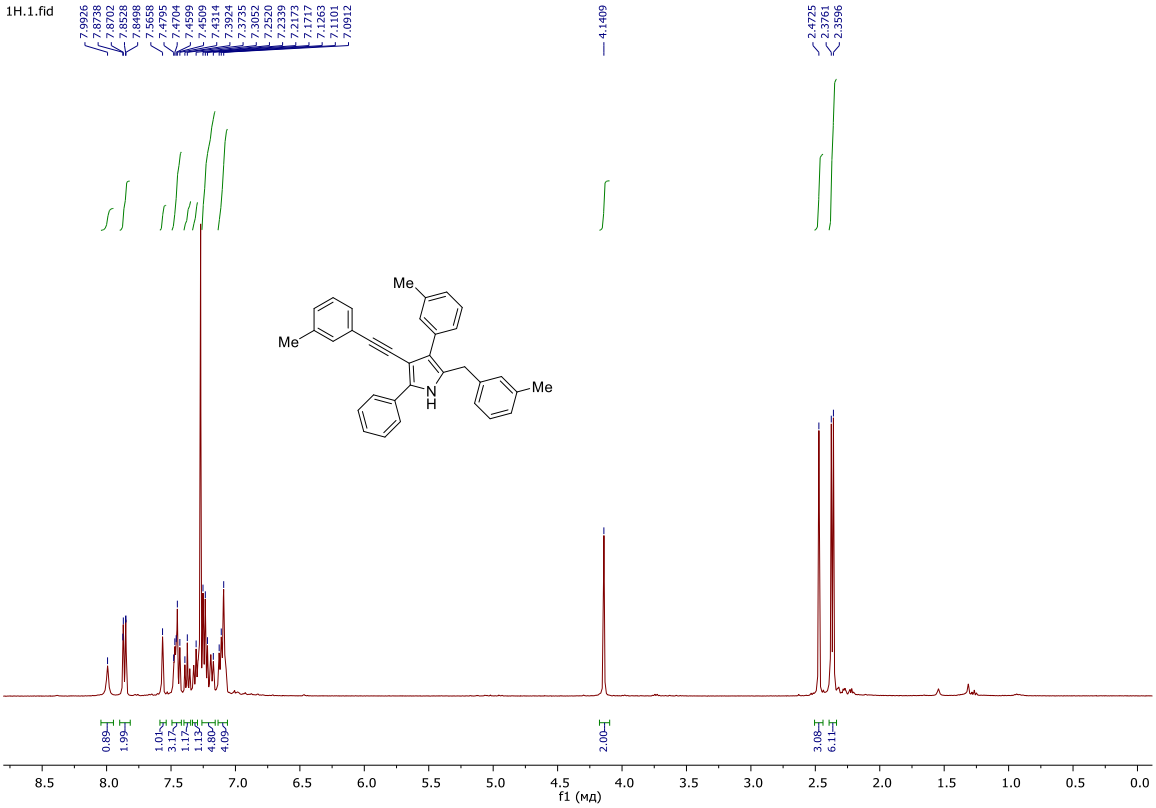
1. NMR spectra



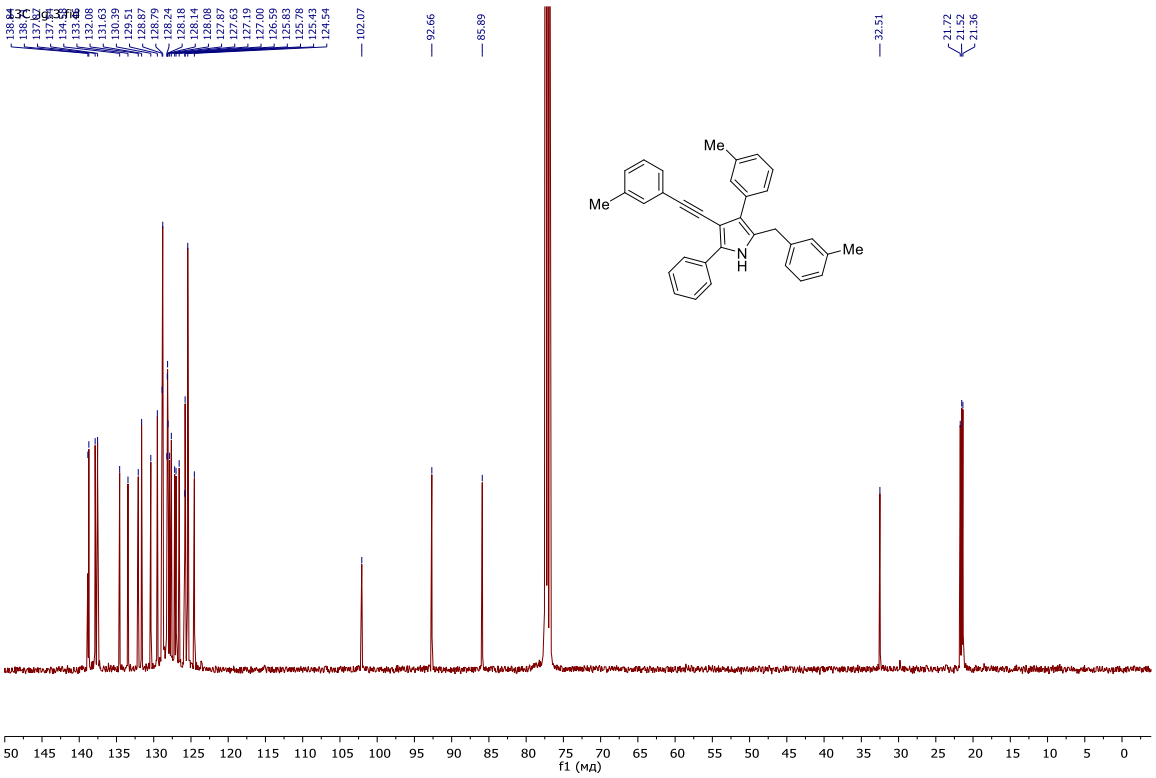
^{1}H NMR Spectrum of **3aa** (400.1 MHz, $CDCl_3$)



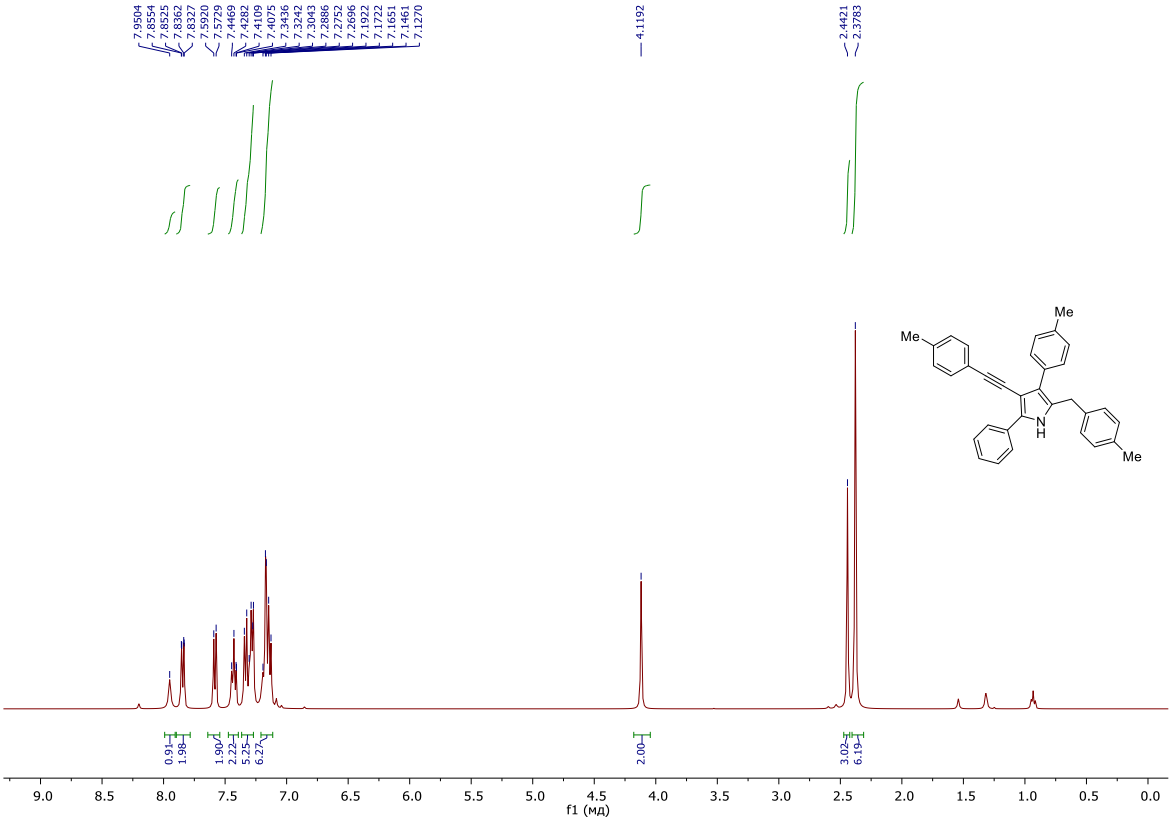
^{13}C NMR Spectrum of **3aa** (100.6 MHz, $CDCl_3$)



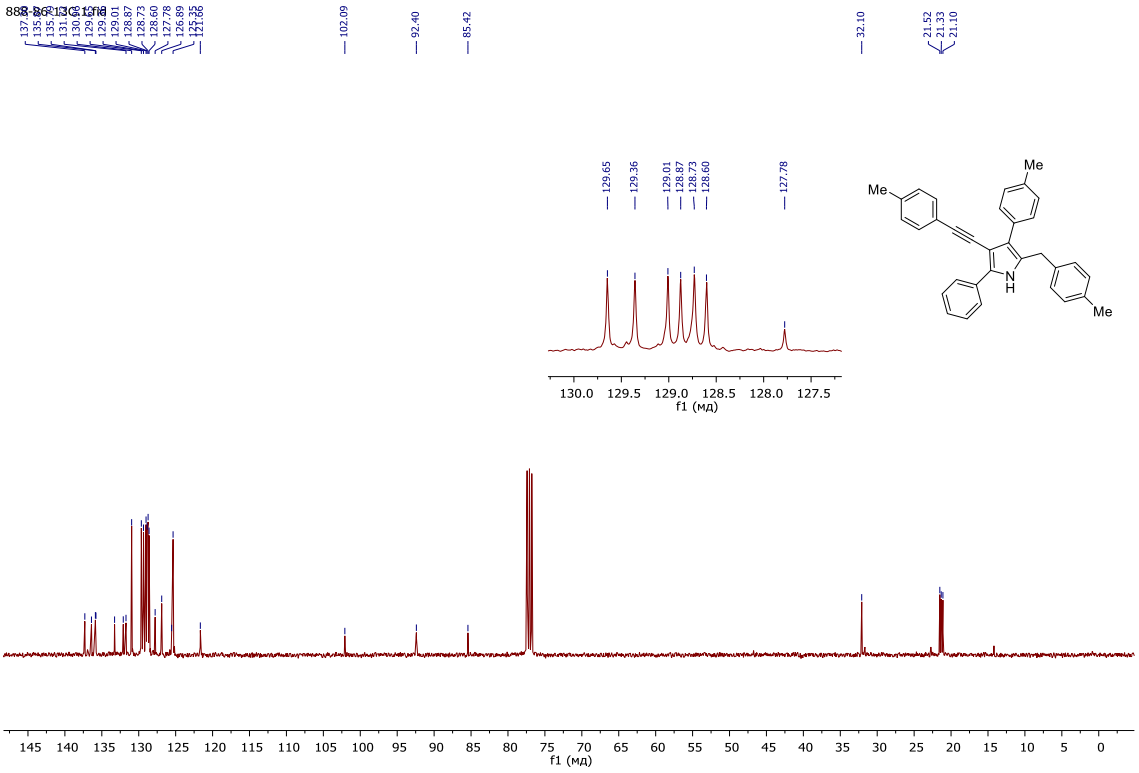
^{1}H NMR Spectrum of **3ba** (400.1 MHz, $CDCl_3$)



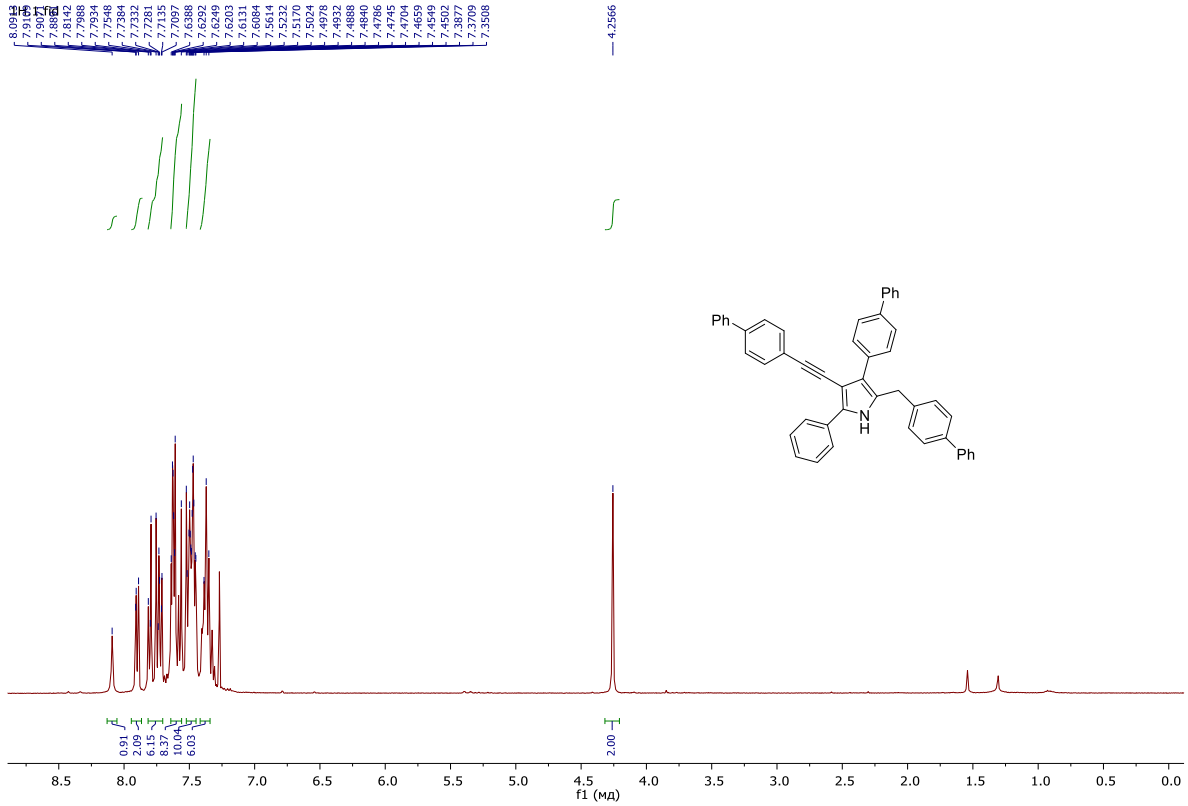
^{13}C NMR Spectrum of **3ba** (100.6 MHz, $CDCl_3$)



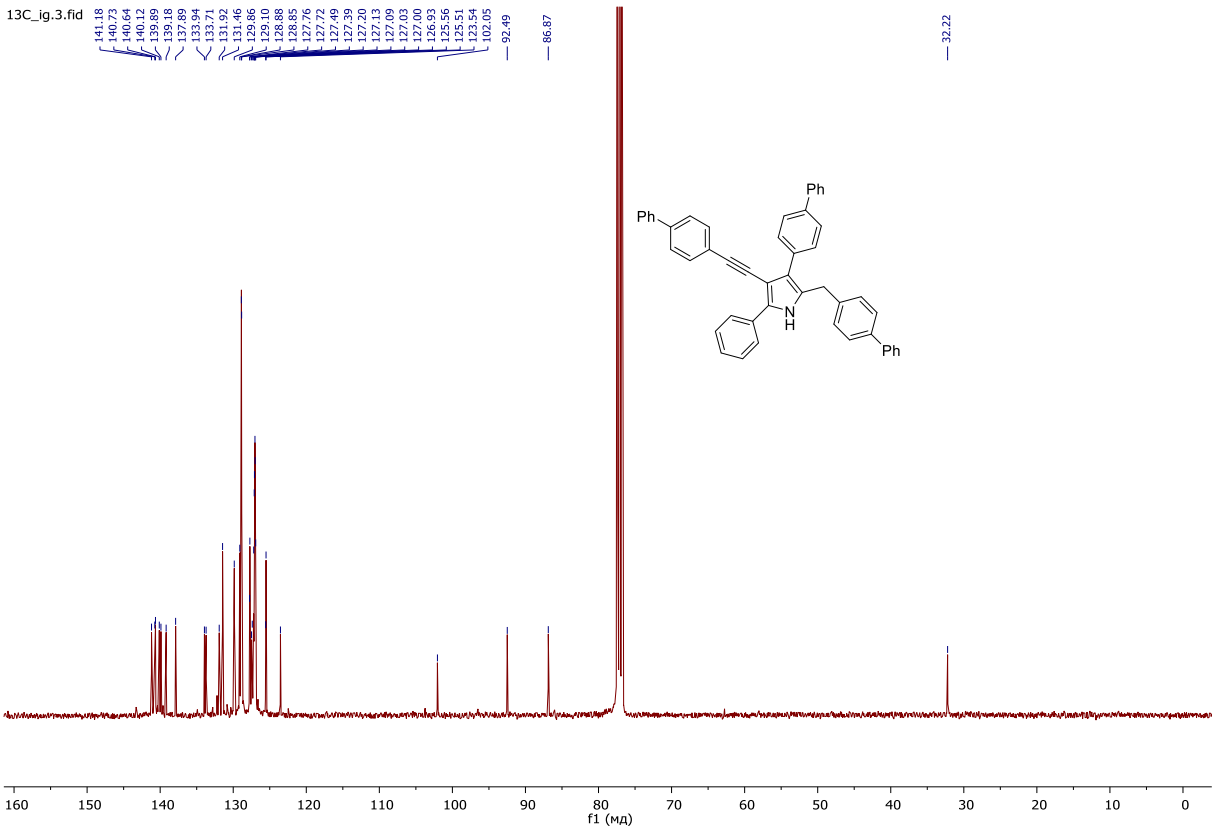
^{1}H NMR Spectrum of **3ca** (400.1 MHz, $CDCl_3$)



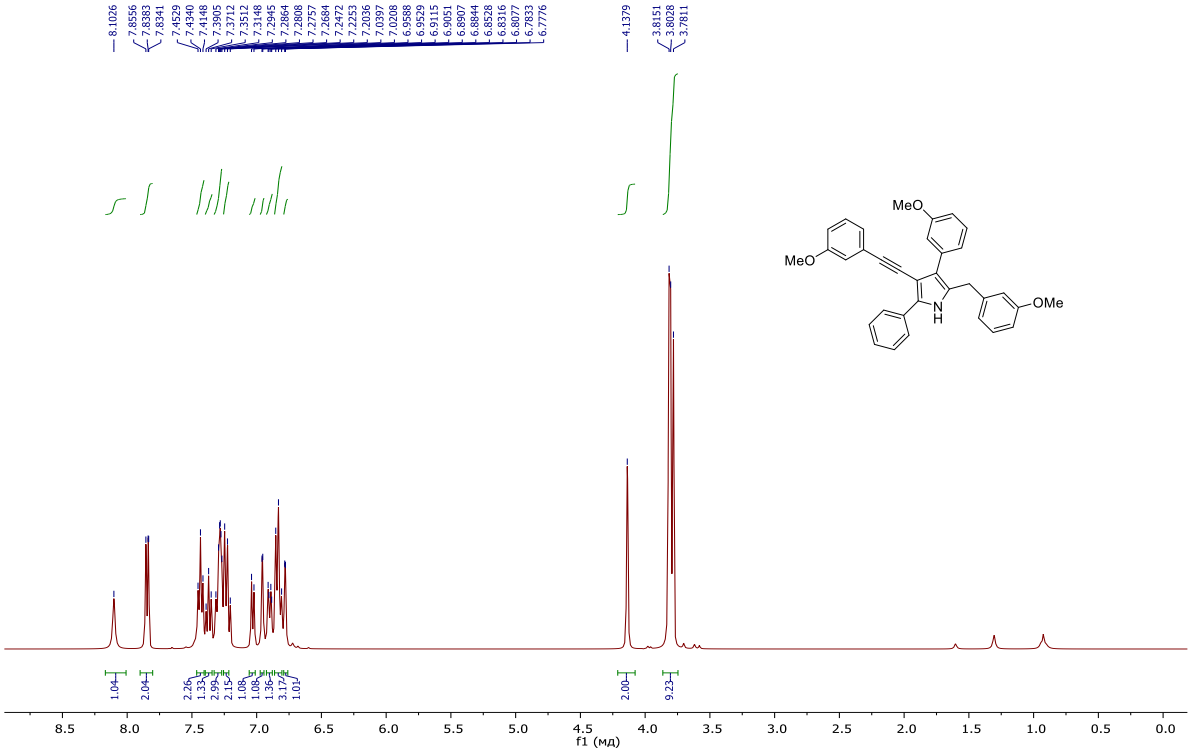
^{13}C NMR Spectrum of **3ca** (100.6 MHz, $CDCl_3$)



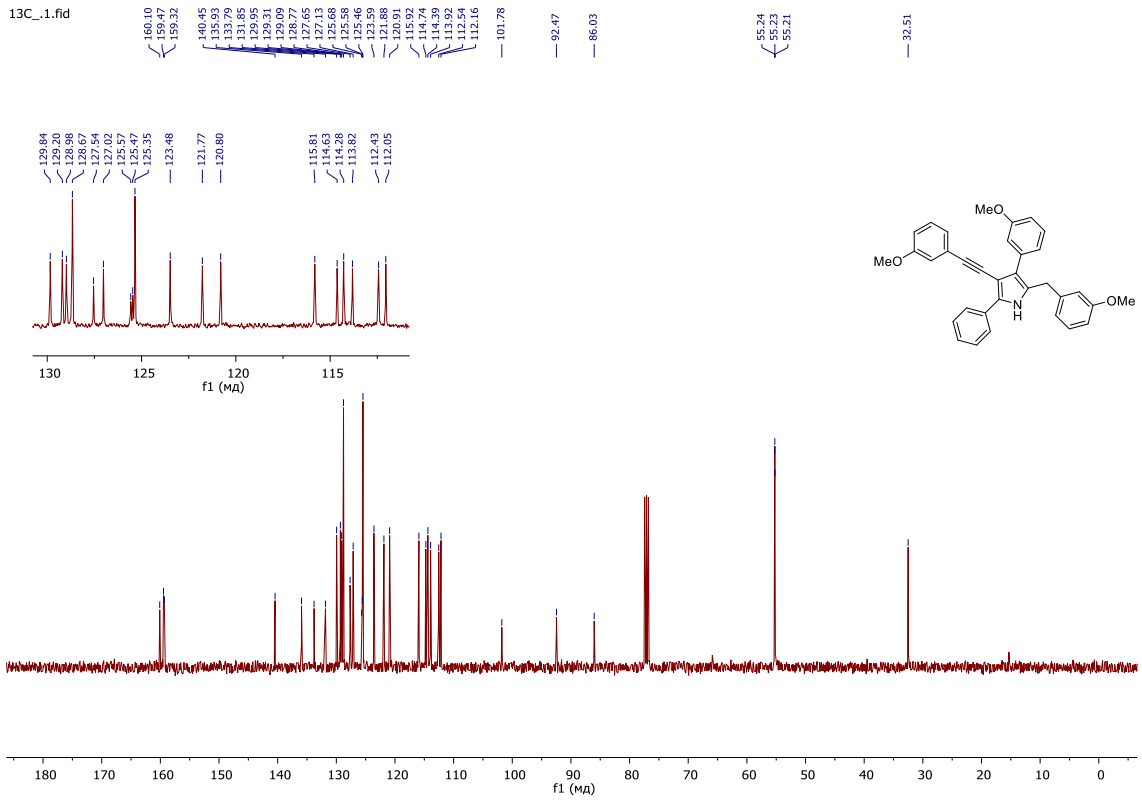
^{1}H NMR Spectrum of **3da** (400.1 MHz, $CDCl_3$)



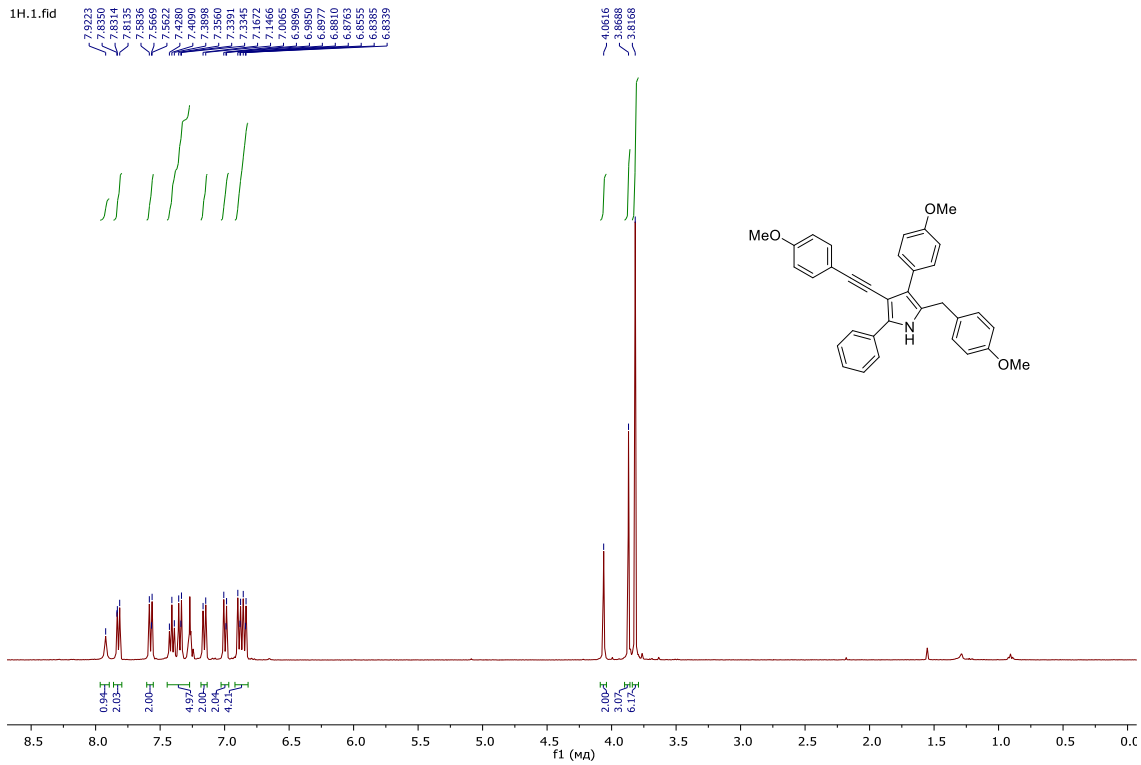
^{13}C NMR Spectrum of **3da** (100.6 MHz, $CDCl_3$)



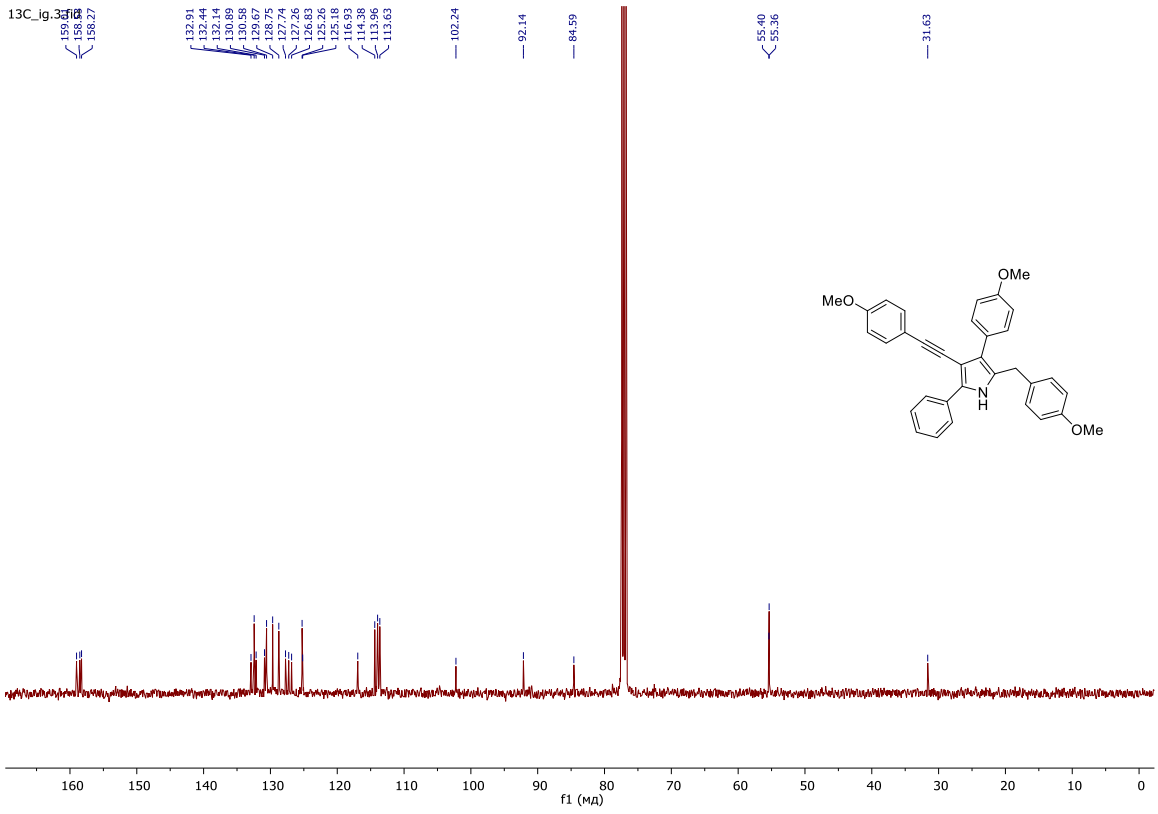
^{1}H NMR Spectrum of **3ea** (400.1 MHz, $CDCl_3$)



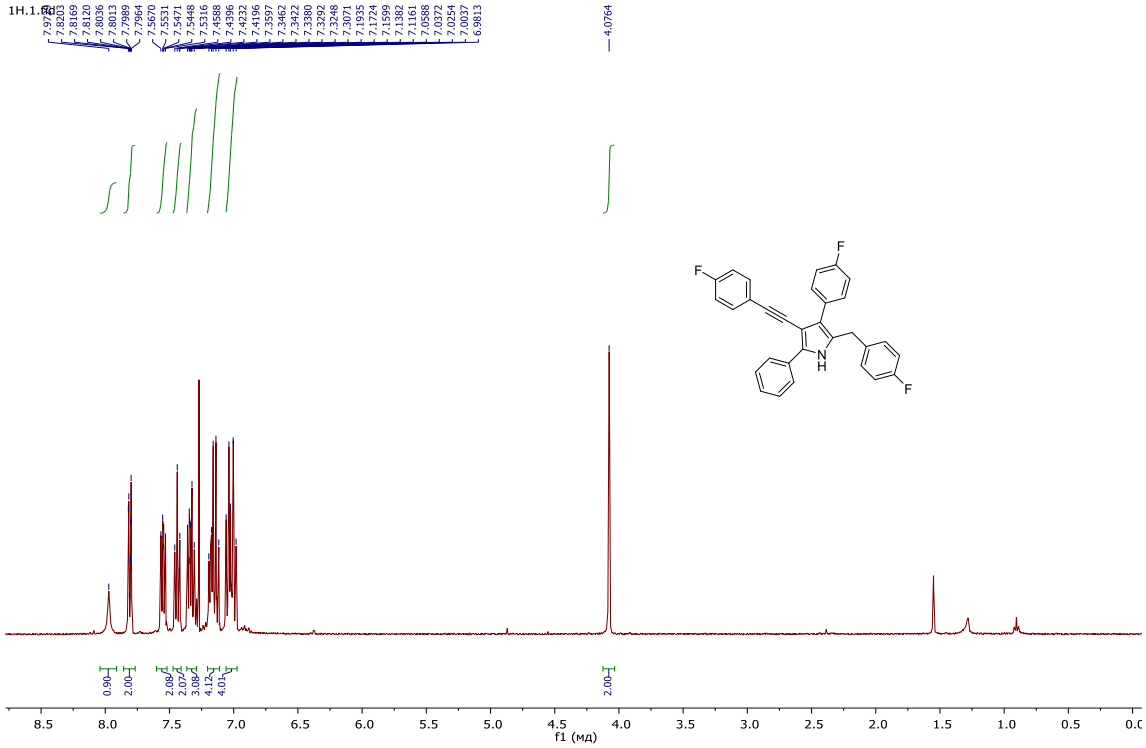
^{13}C NMR Spectrum of **3ea** (100.6 MHz, $CDCl_3$)



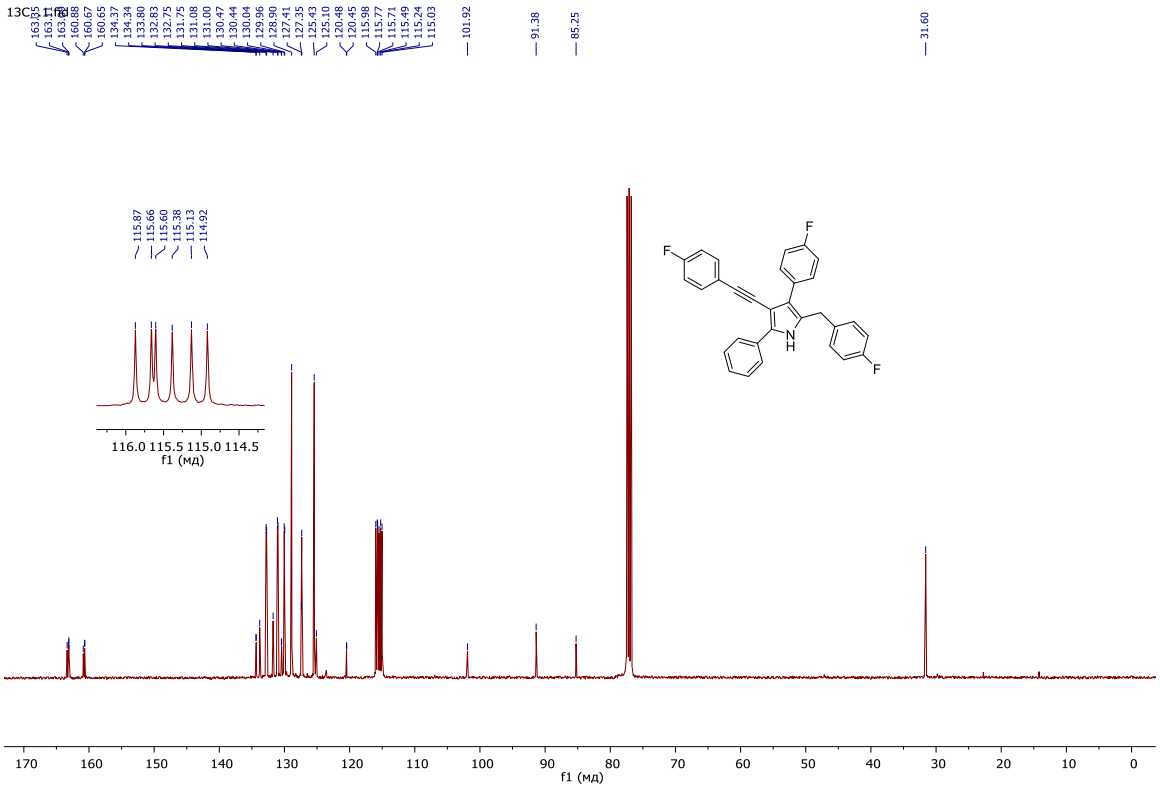
^{1}H NMR Spectrum of **3fa** (400.1 MHz, $CDCl_3$)



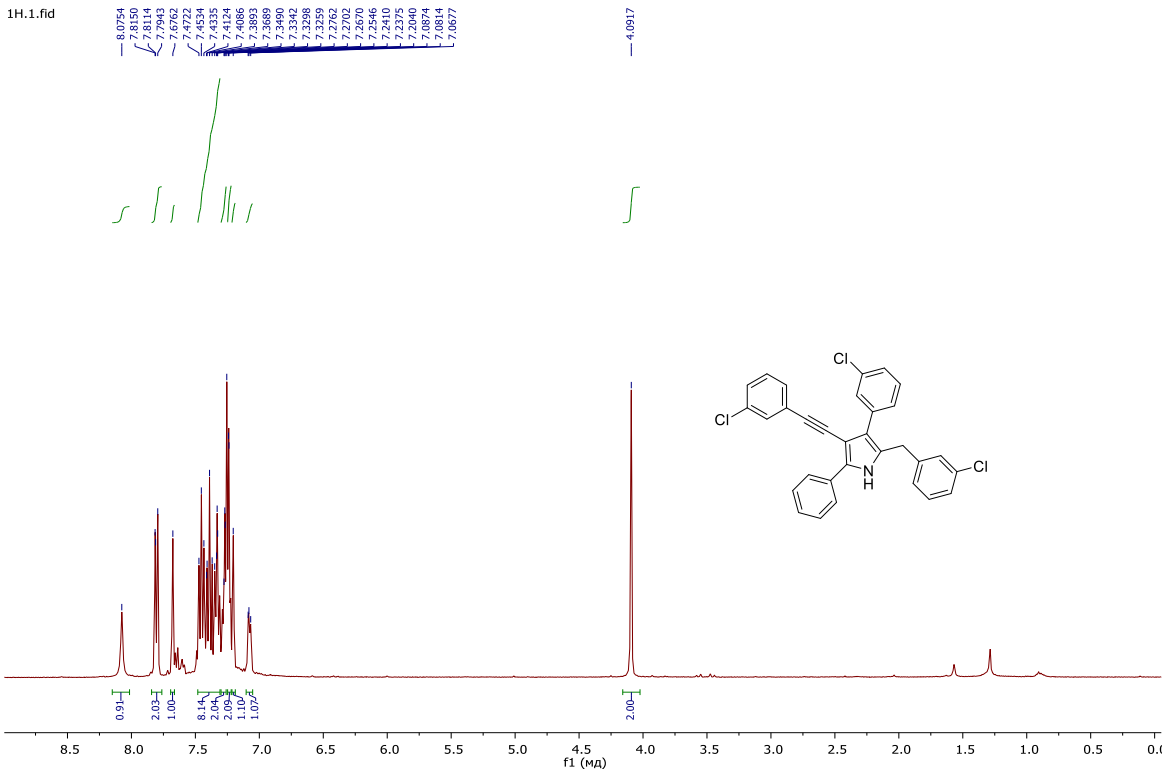
^{13}C NMR Spectrum of **3fa** (100.6 MHz, $CDCl_3$)



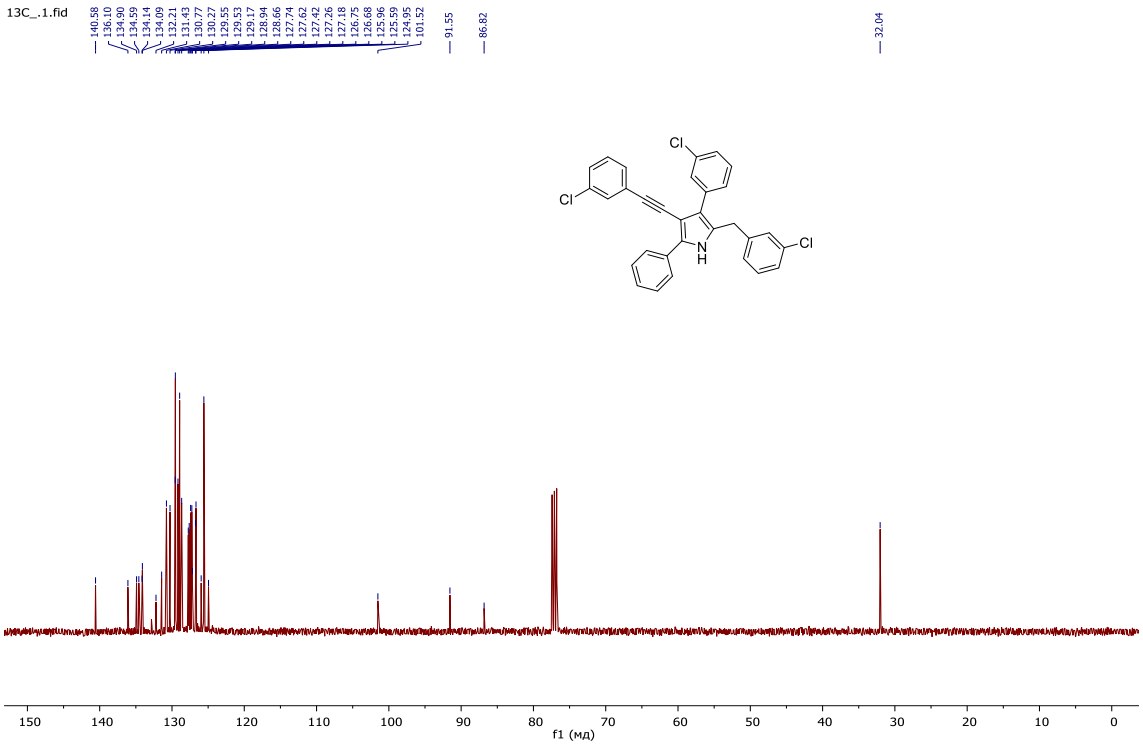
^{1}H NMR Spectrum of **3ga** (400.1 MHz, $CDCl_3$)



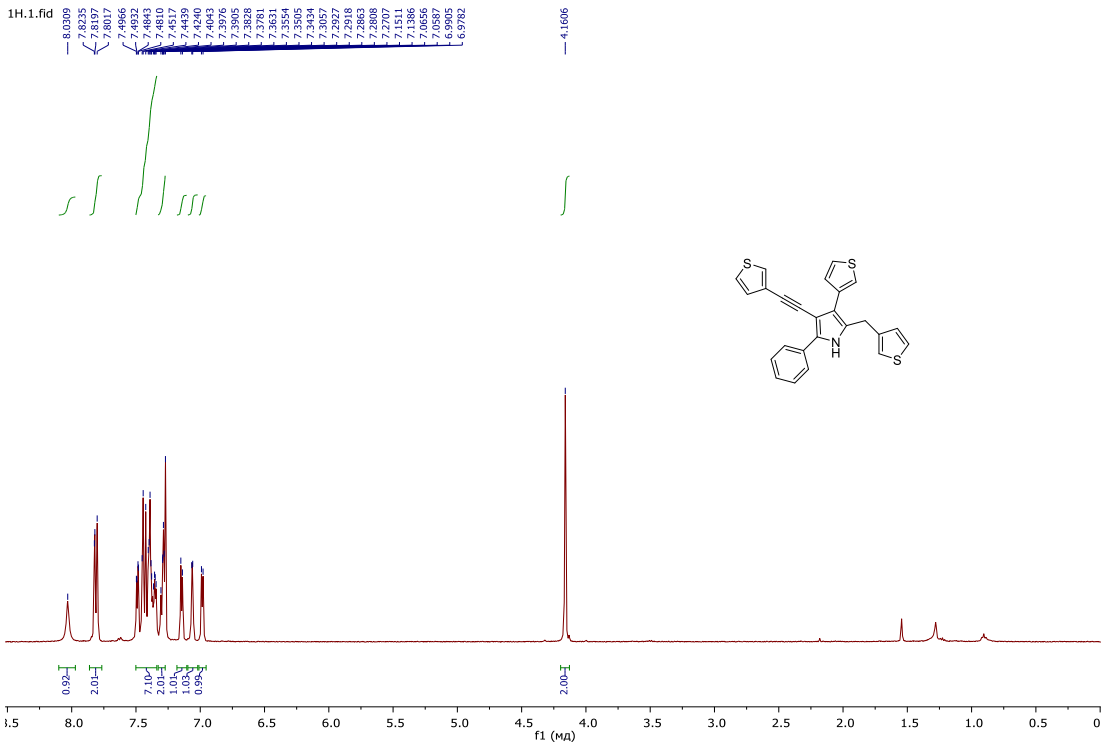
^{13}C NMR Spectrum of **3ga** (100.6 MHz, $CDCl_3$)



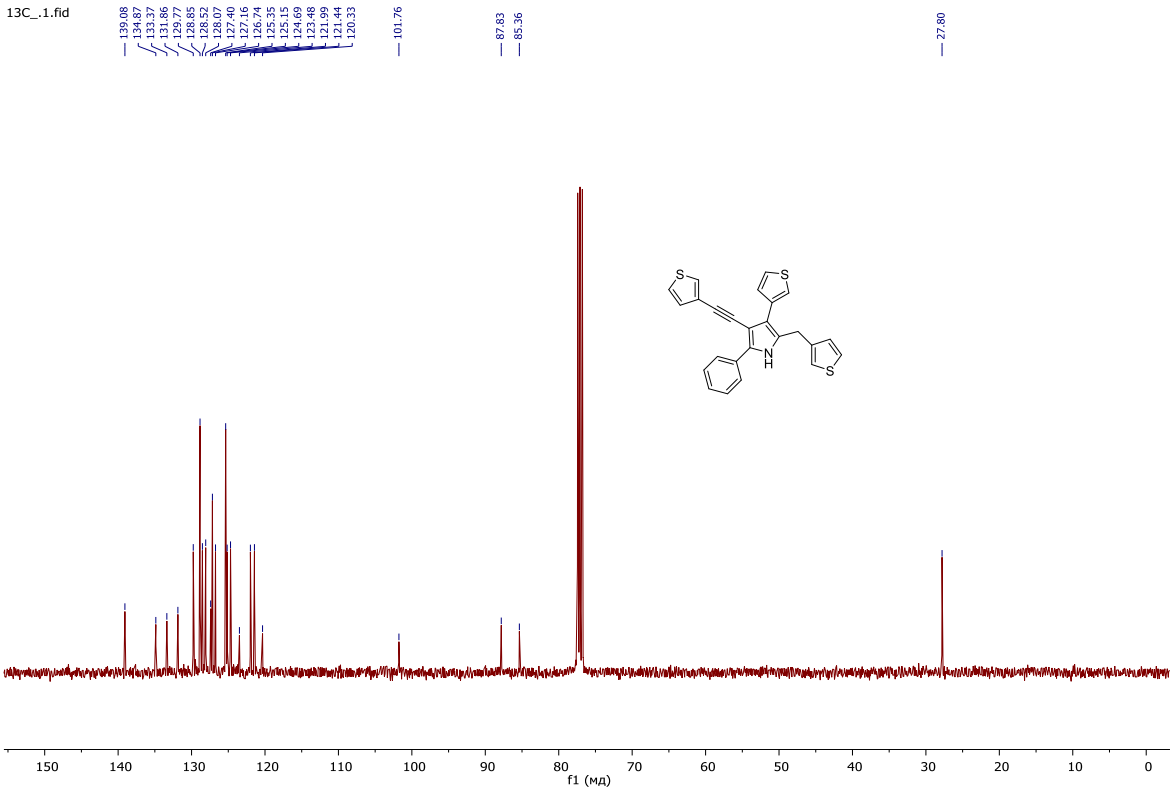
^{1}H NMR Spectrum of **3ha** (400.1 MHz, $CDCl_3$)



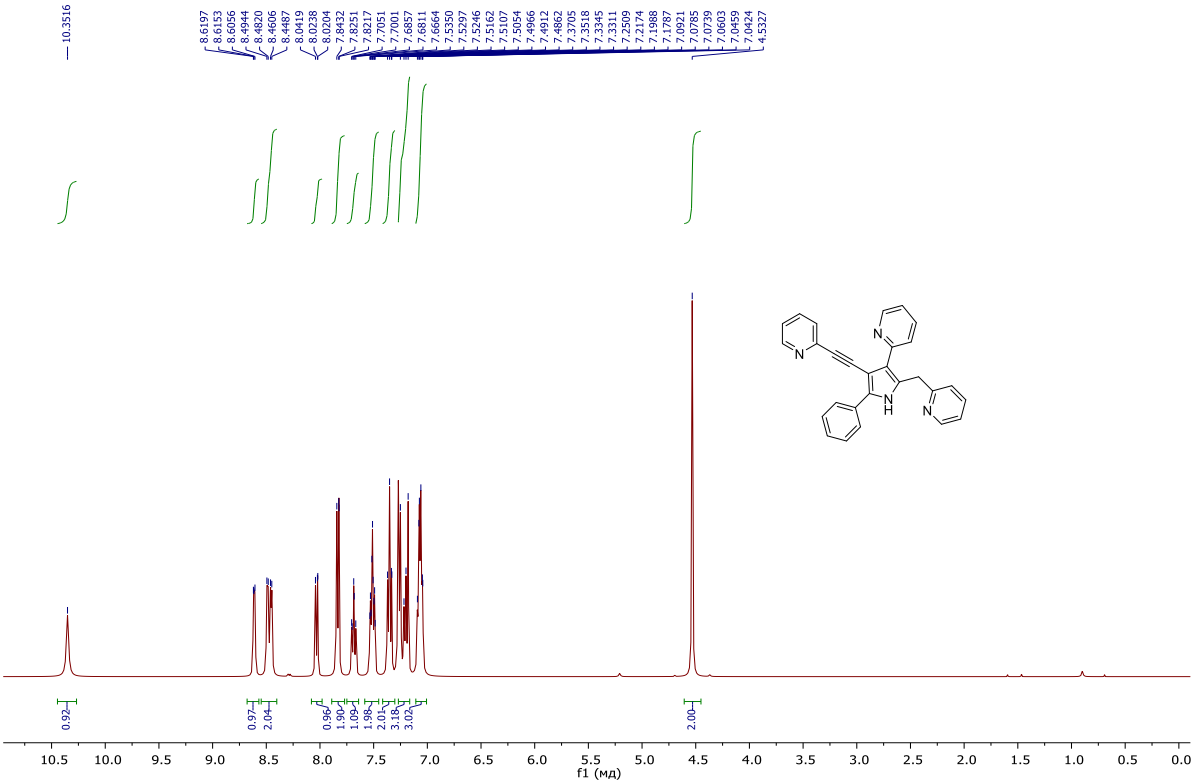
^{13}C NMR Spectrum of **3ha** (100.6 MHz, $CDCl_3$)



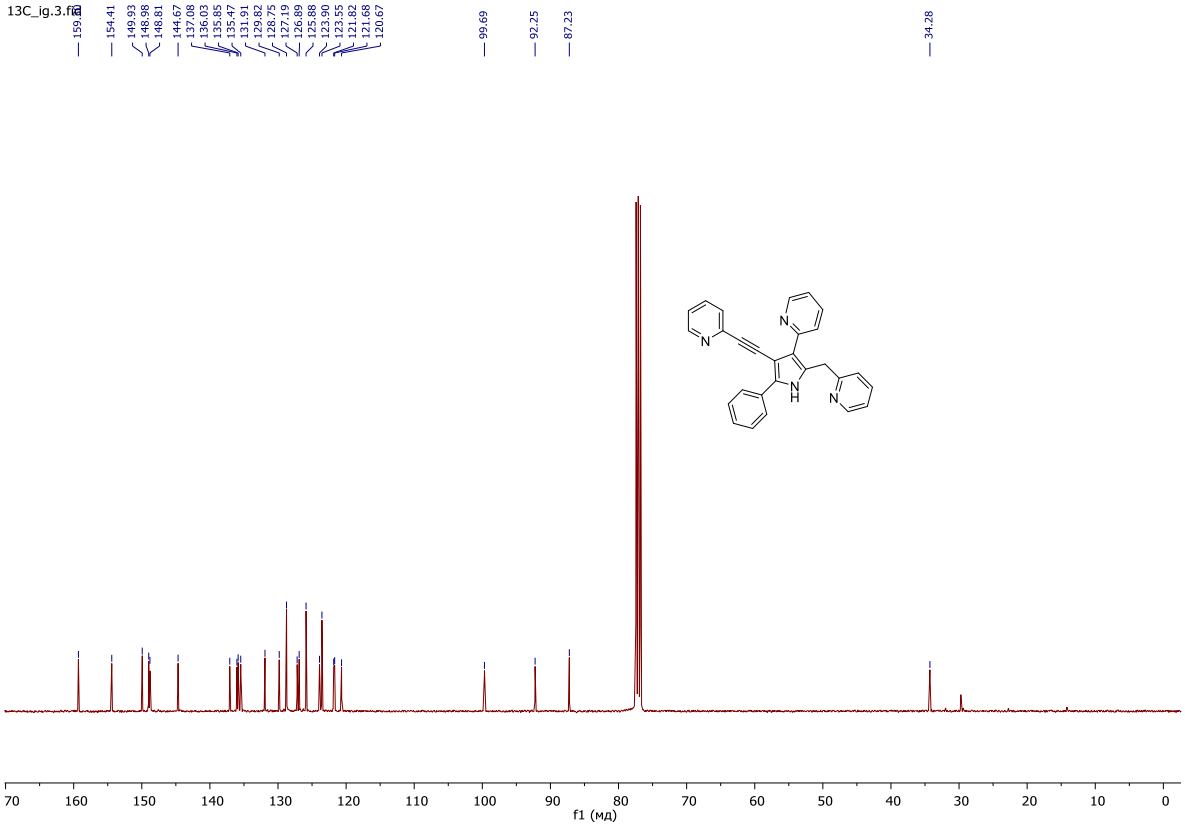
^{1}H NMR Spectrum of **3ia** (400.1 MHz, $CDCl_3$)



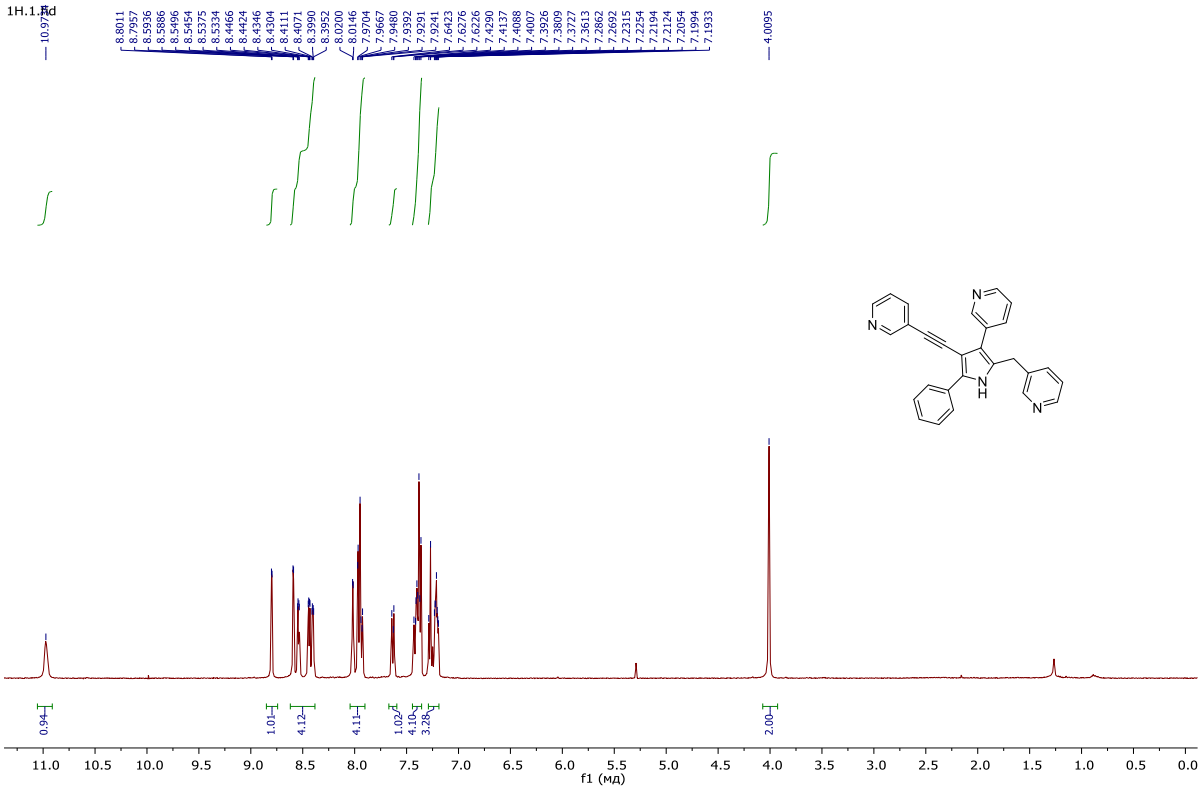
^{13}C NMR Spectrum of **3ia** (100.6 MHz, $CDCl_3$)



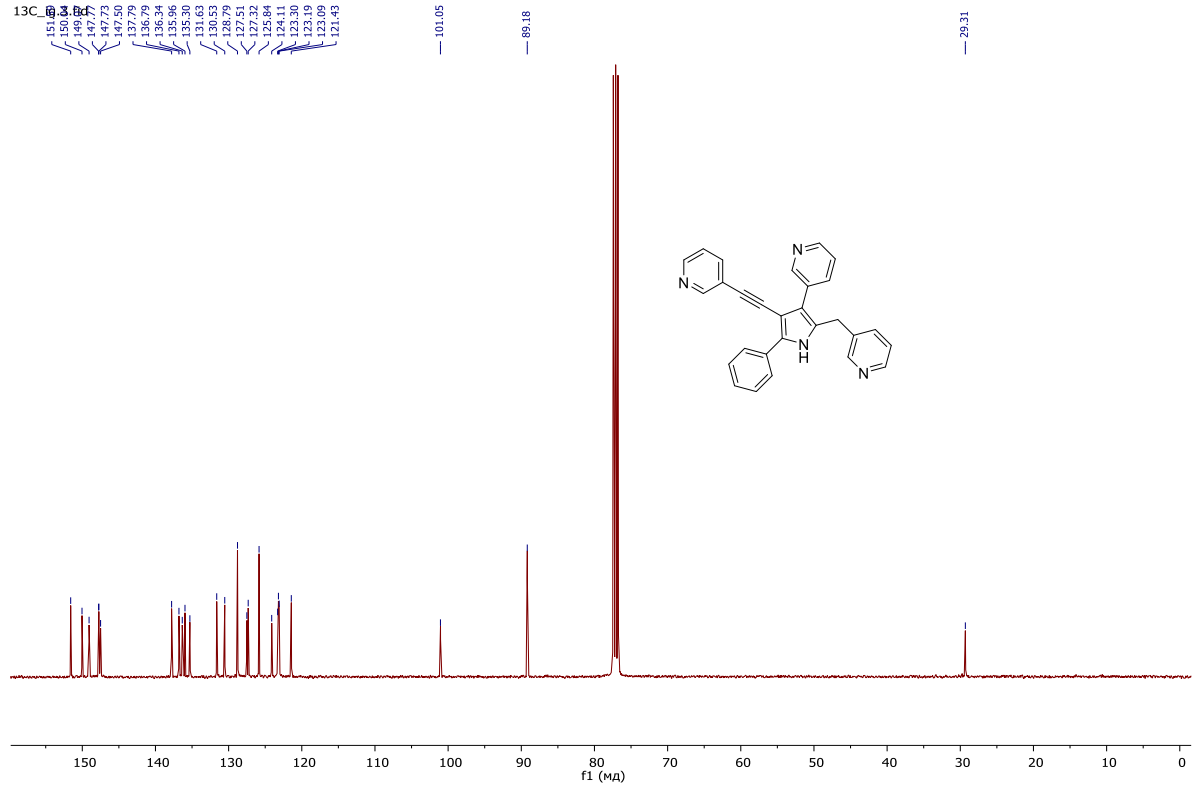
^{1}H NMR Spectrum of **3ja** (400.1 MHz, $CDCl_3$)



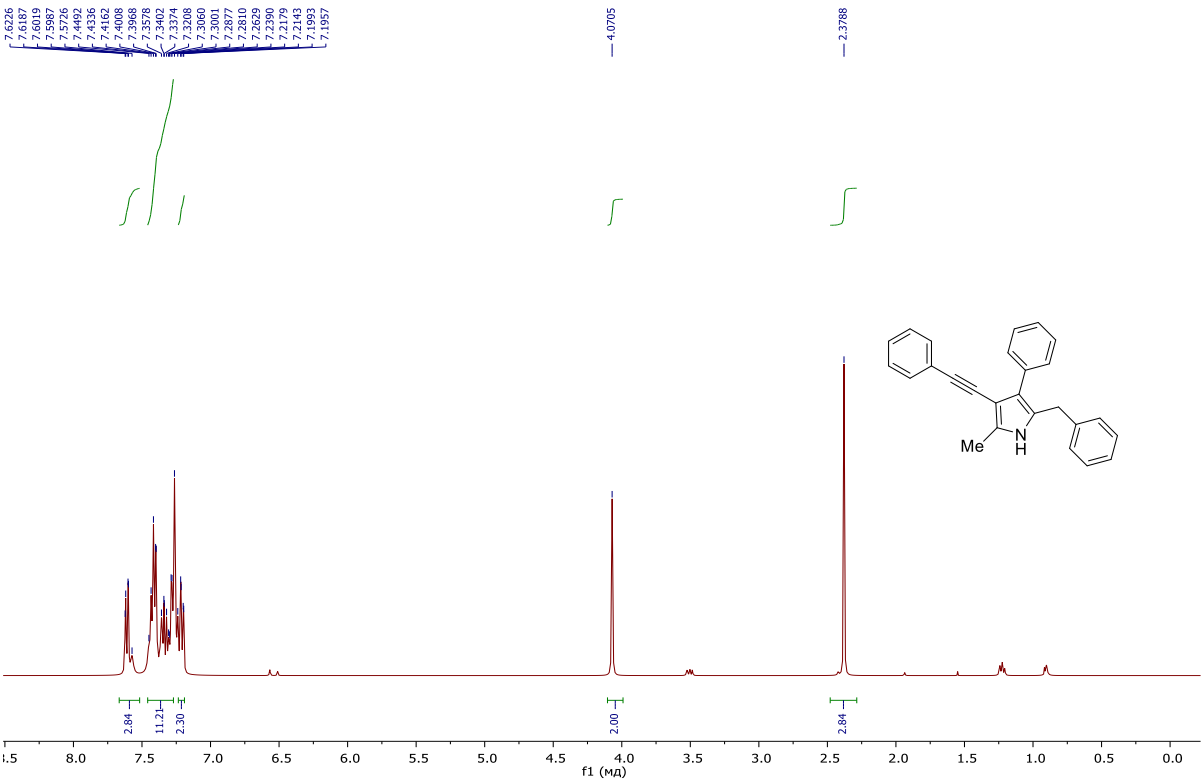
^{13}C NMR Spectrum of **3ja** (100.6 MHz, $CDCl_3$)



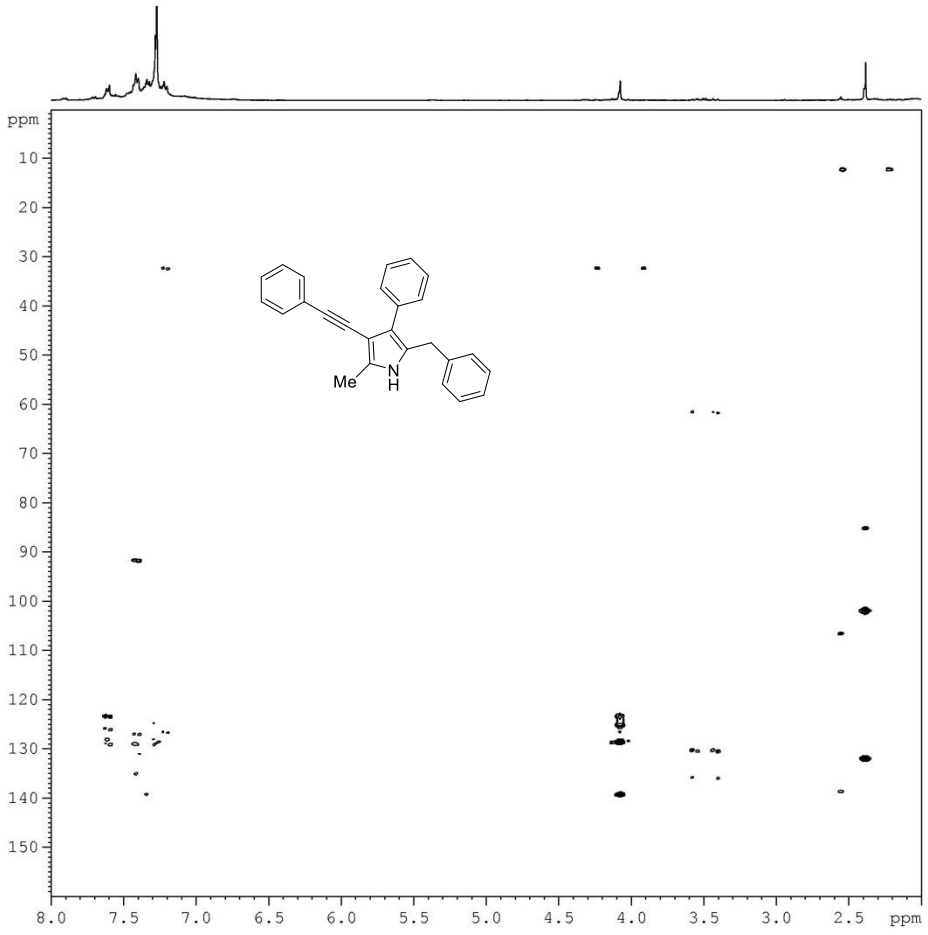
^{1}H NMR Spectrum of **3ka** (400.1 MHz, $CDCl_3$)



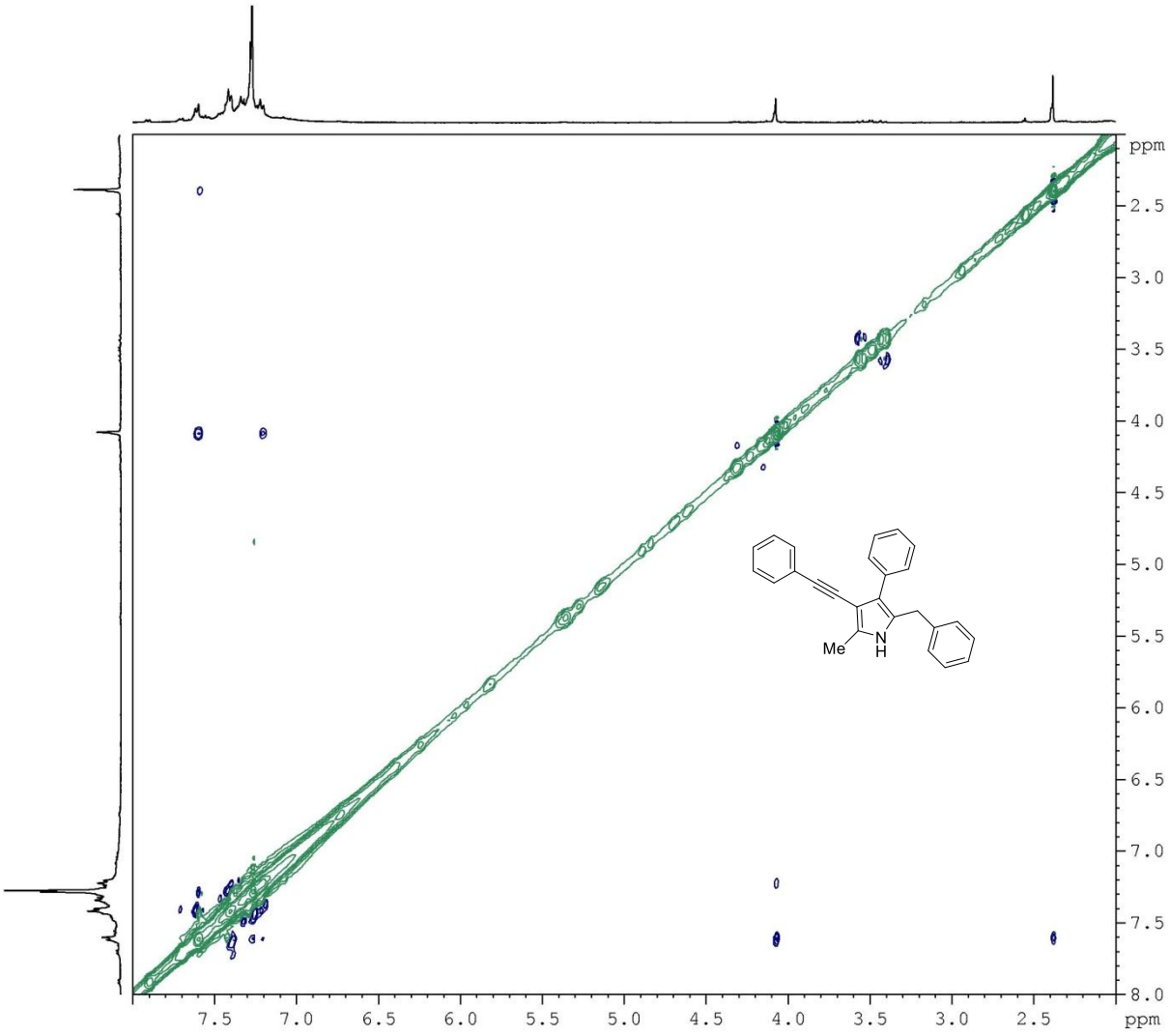
^{13}C NMR Spectrum of **3ka** (100.6 MHz, $CDCl_3$)



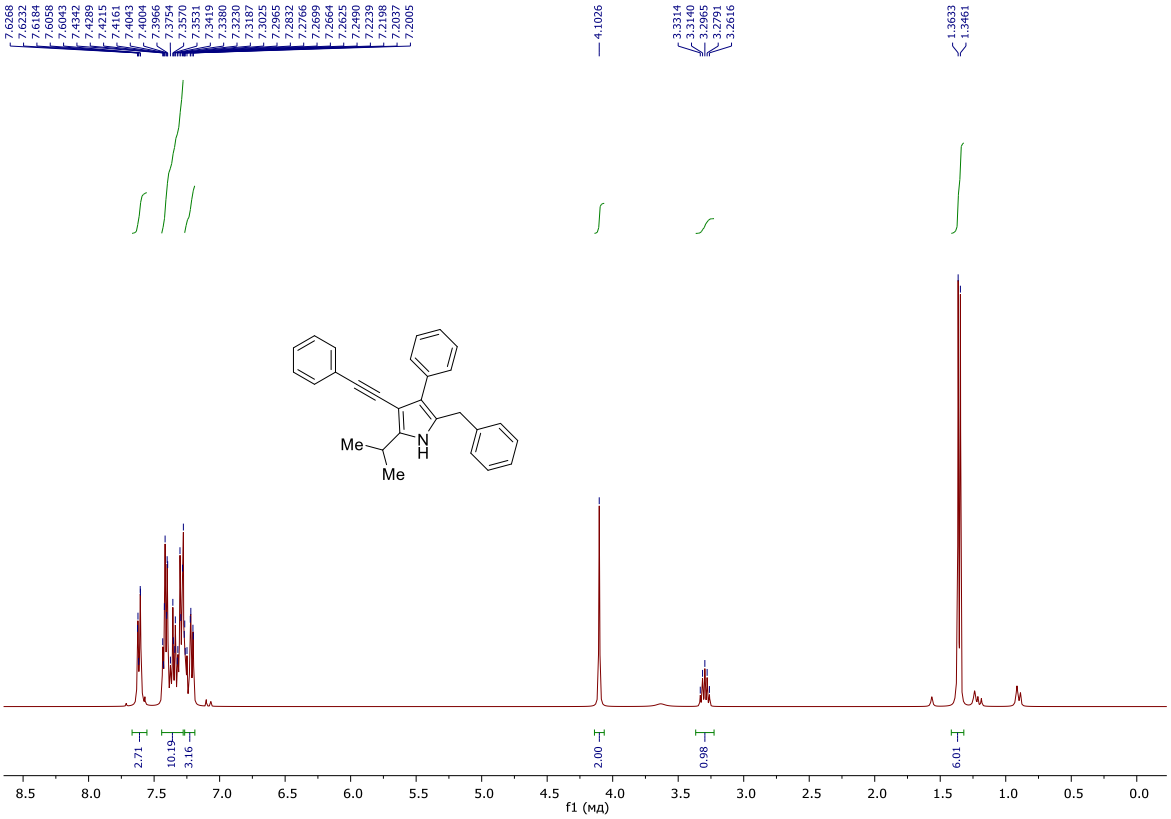
^{1}H NMR Spectrum of **3ab** (400.1 MHz, $CDCl_3$)



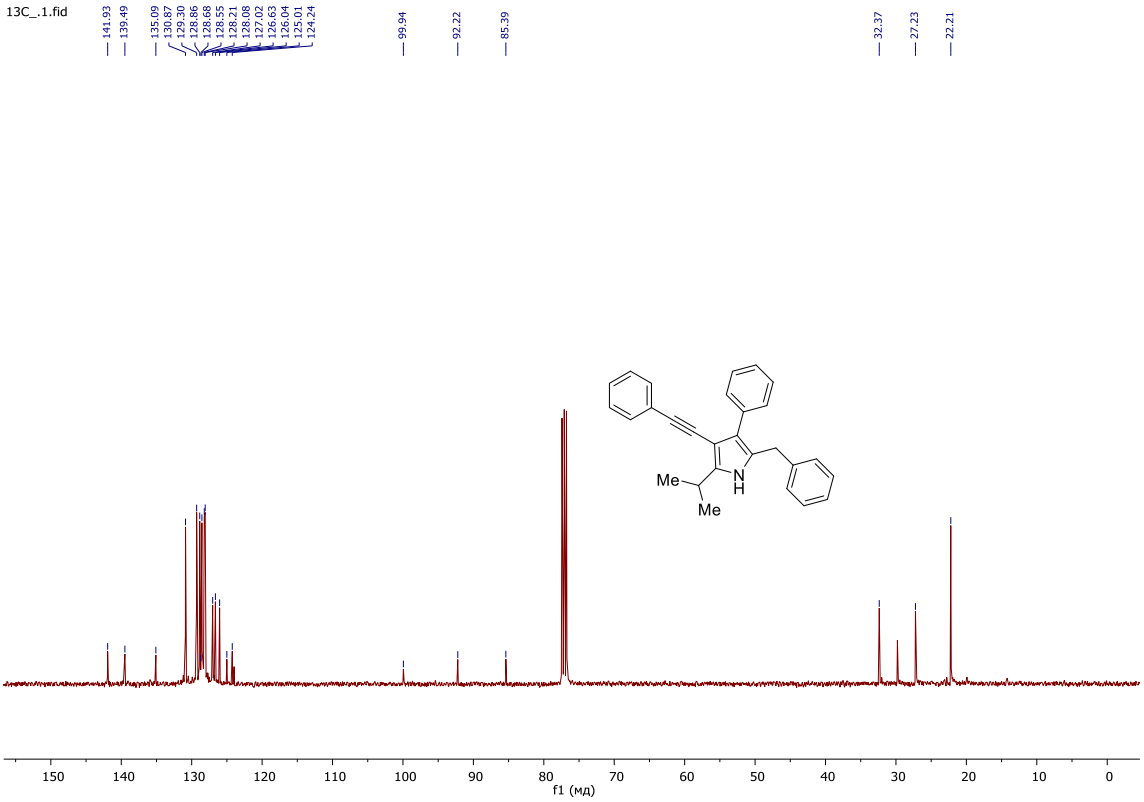
2D ^{1}H-^{13}C HMBC Spectrum of **3ab**



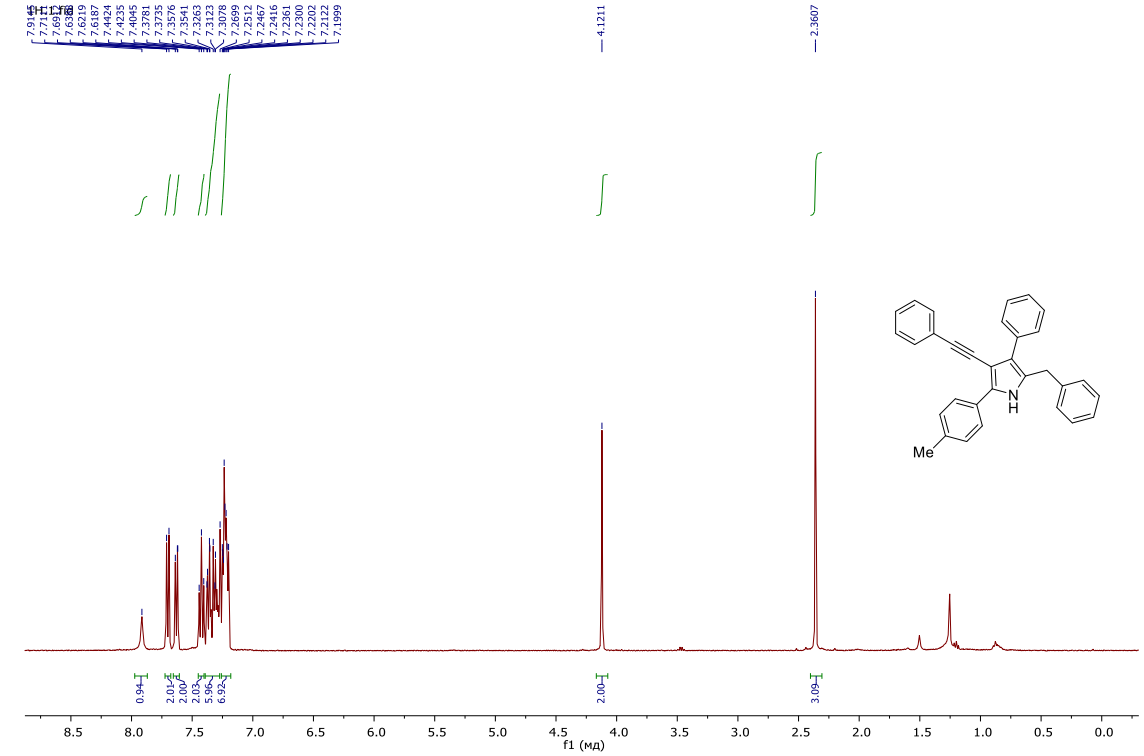
2D NOESY Spectrum of **3ab**



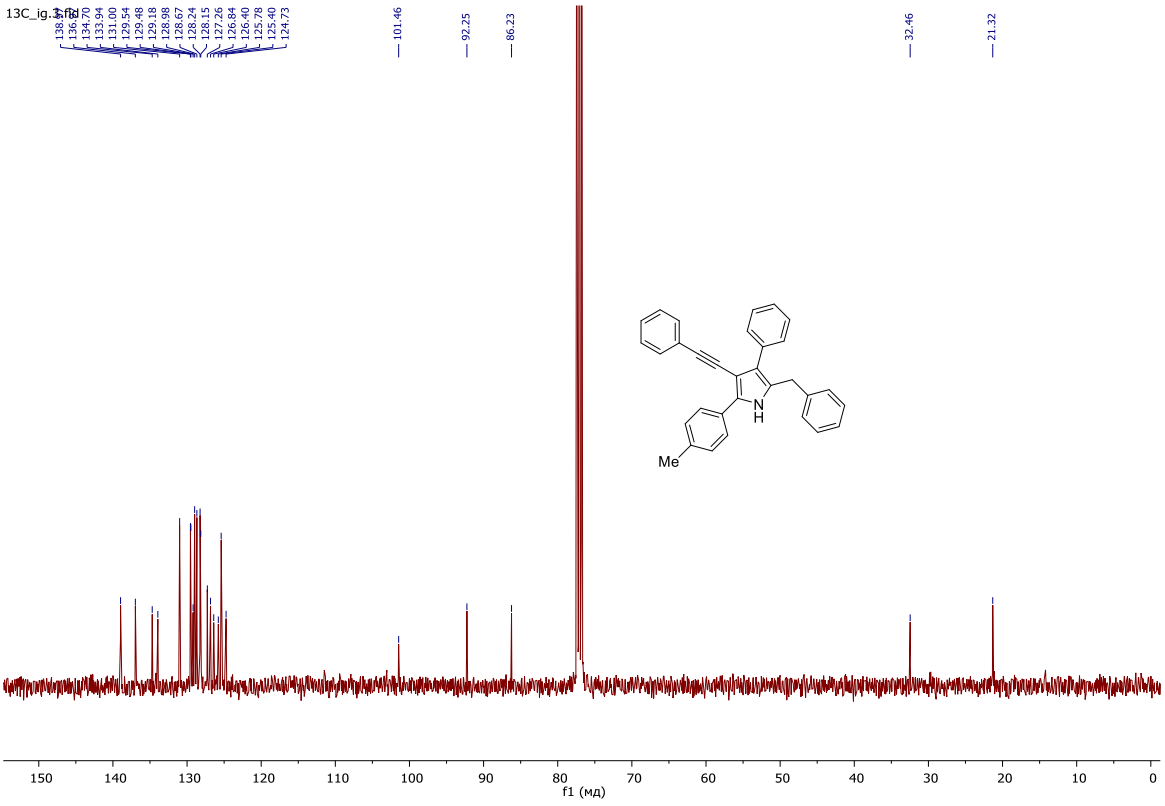
^{1}H NMR Spectrum of **3ac** (400.1 MHz, $CDCl_3$)



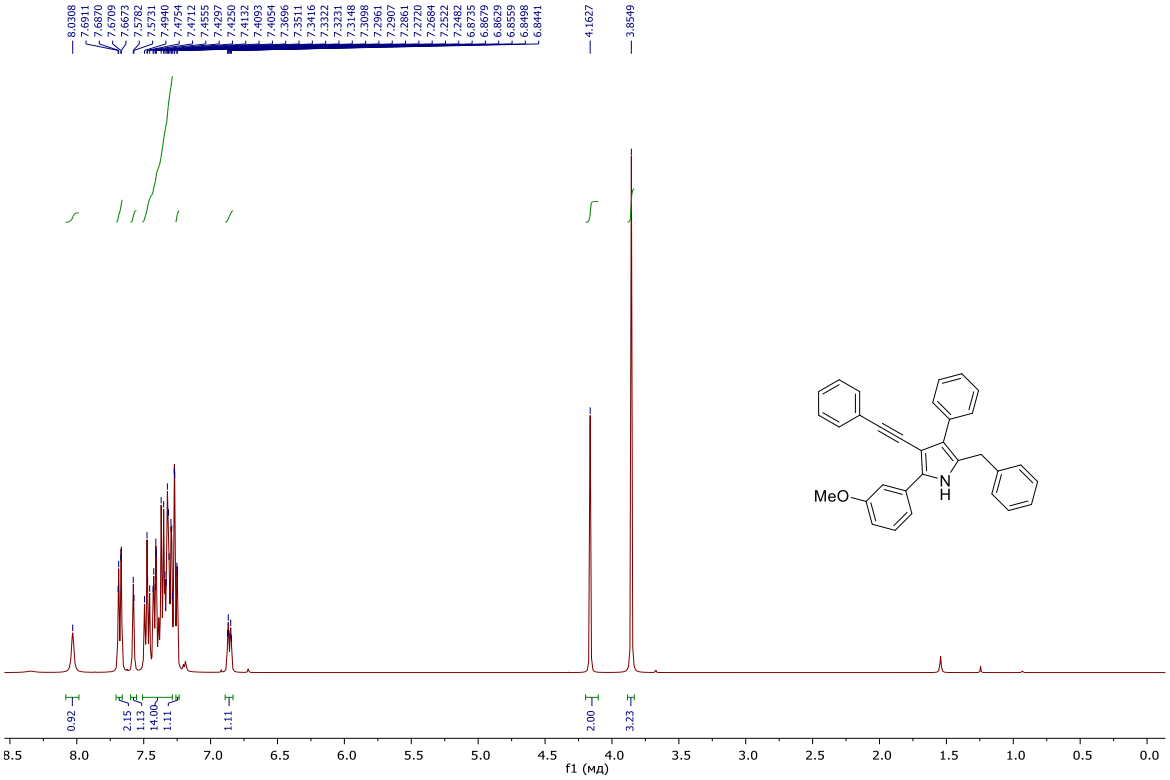
^{13}C NMR Spectrum of **3ac** (100.6 MHz, $CDCl_3$)



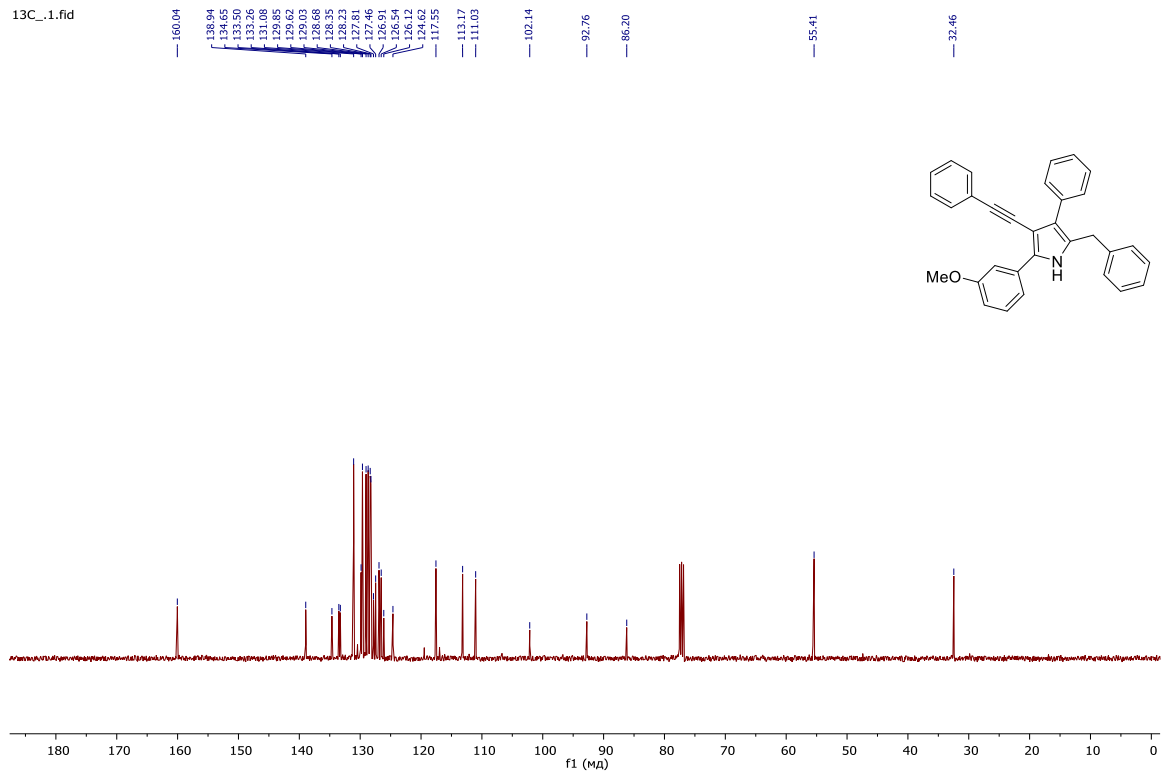
^{1}H NMR Spectrum of **3ae** (400.1 MHz, $CDCl_3$)



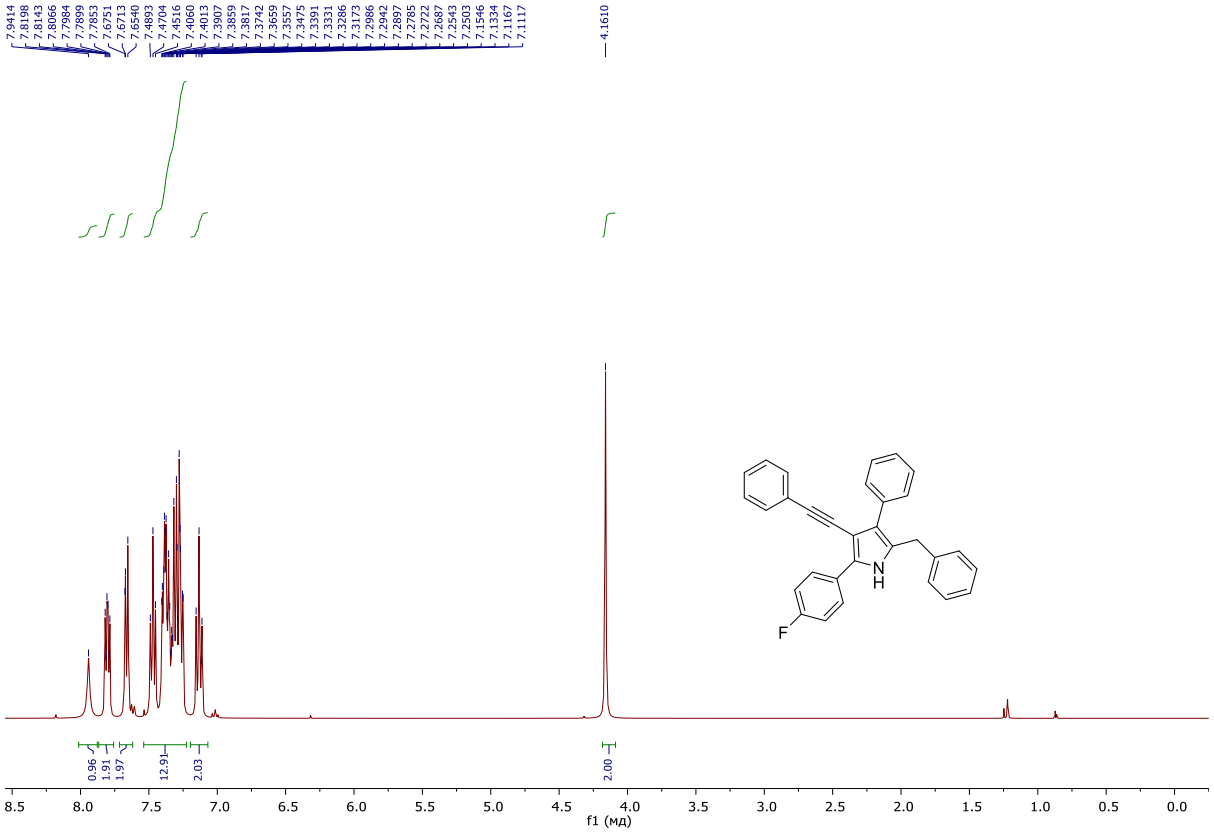
^{13}C NMR Spectrum of **3ae** (100.6 MHz, $CDCl_3$)



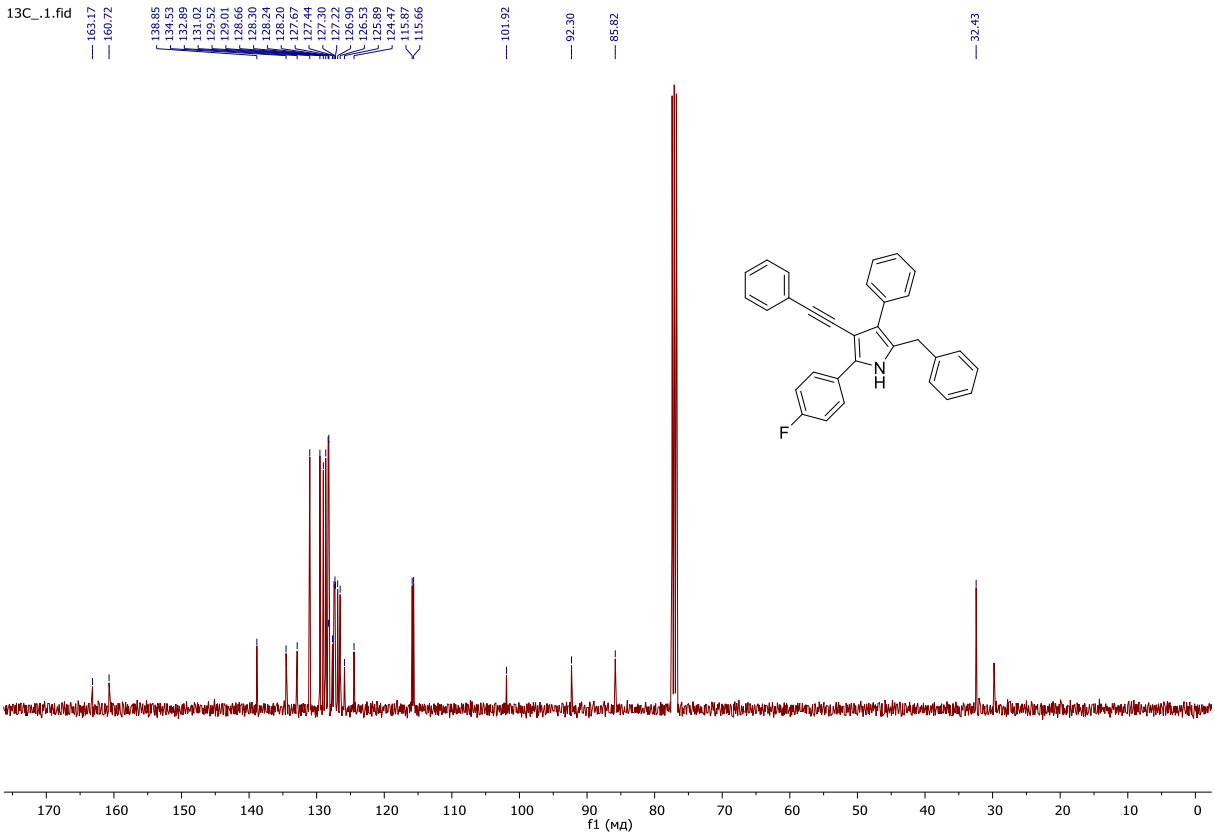
^{1}H NMR Spectrum of **3af** (400.1 MHz, $CDCl_3$)



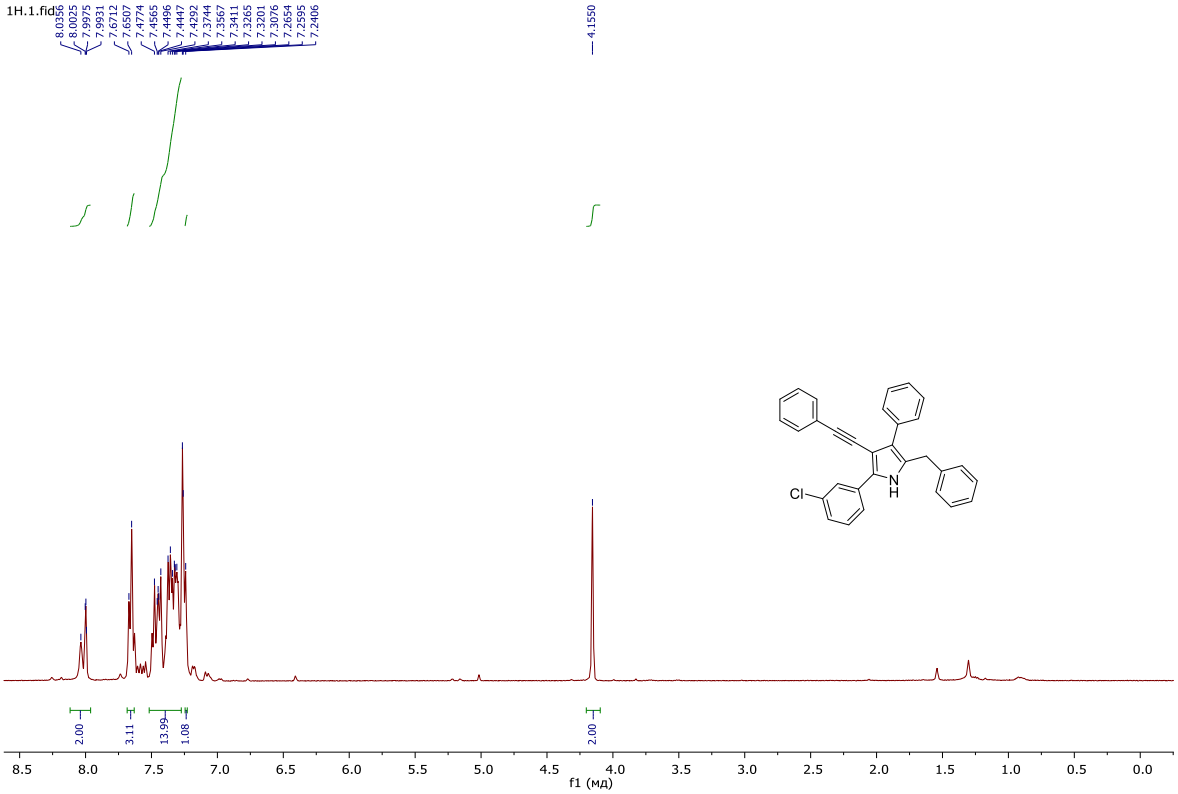
^{13}C NMR Spectrum of **3af** (100.6 MHz, $CDCl_3$)



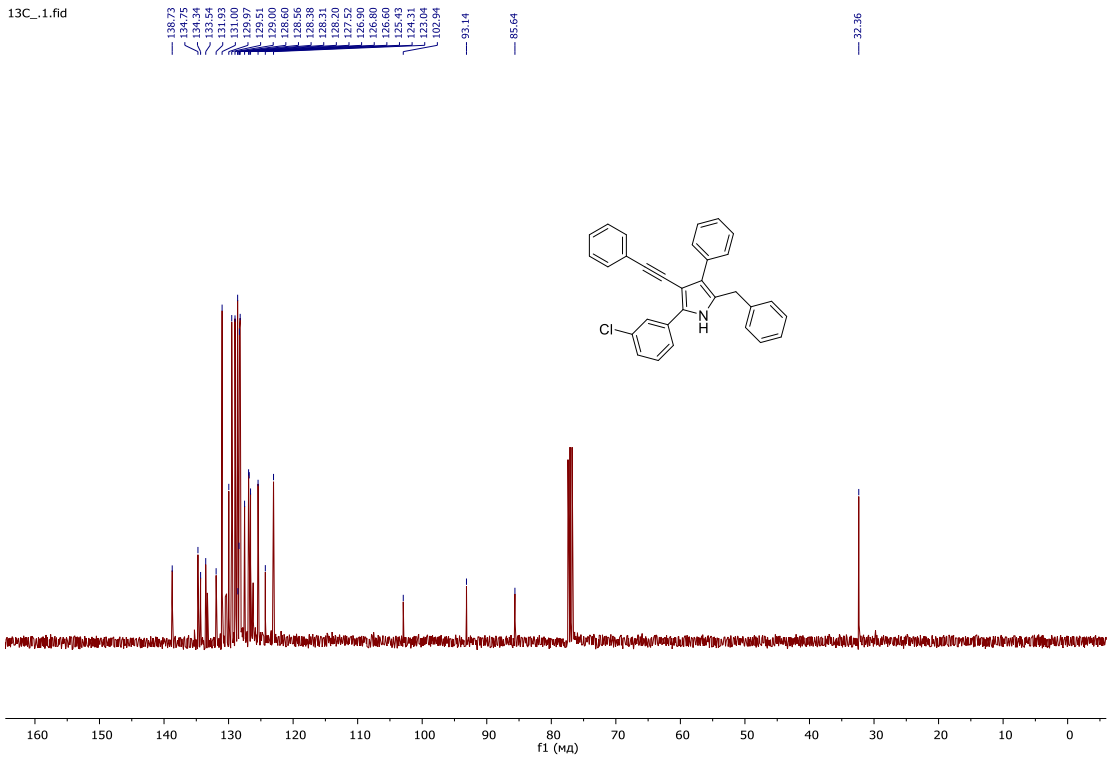
^{1}H NMR Spectrum of **3ag** (400.1 MHz, $CDCl_3$)



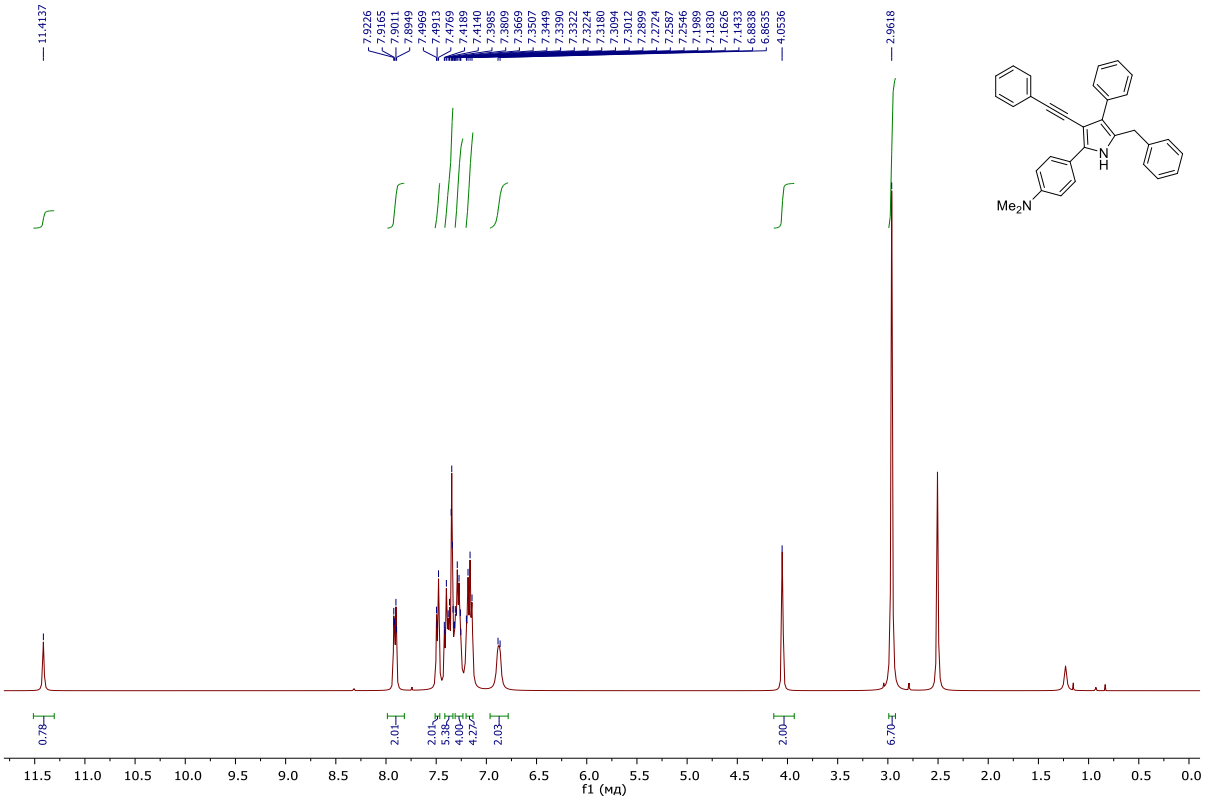
^{13}C NMR Spectrum of **3ag** (100.6 MHz, $CDCl_3$)



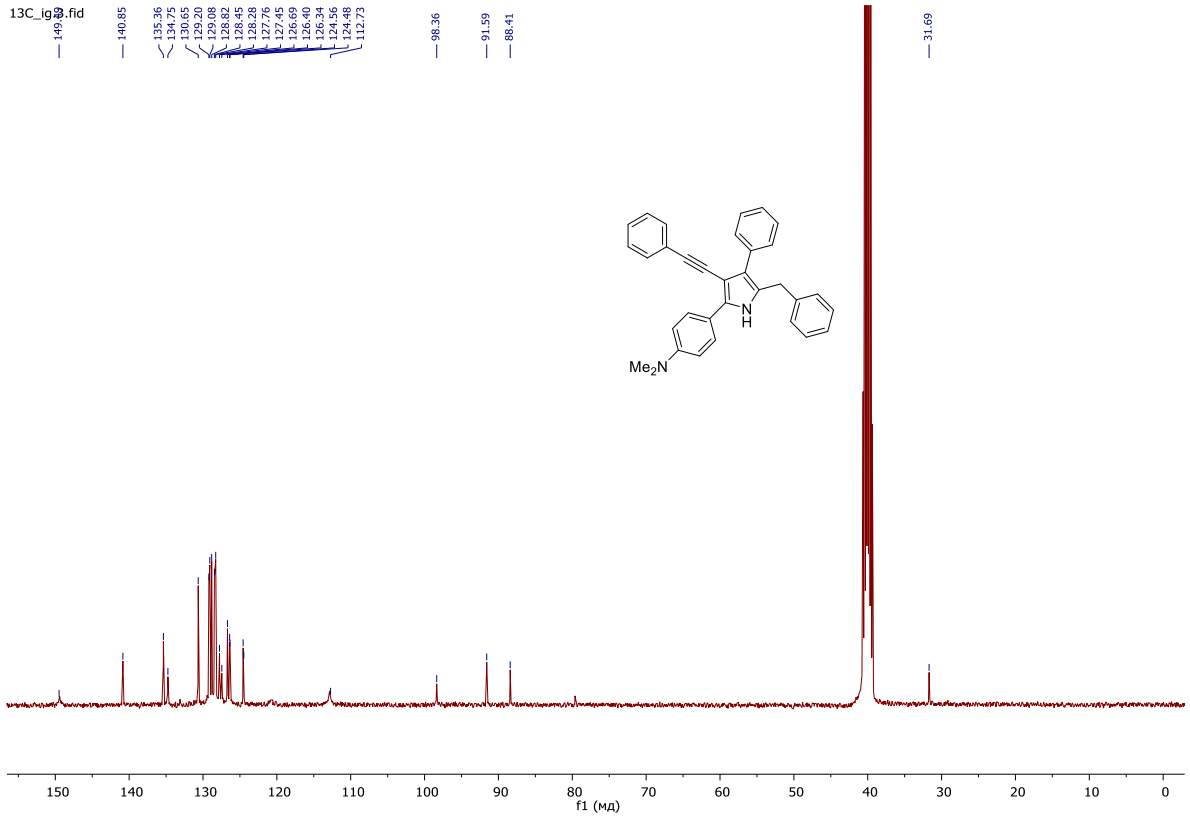
^{1}H NMR Spectrum of **3ah** (400.1 MHz, $CDCl_3$)



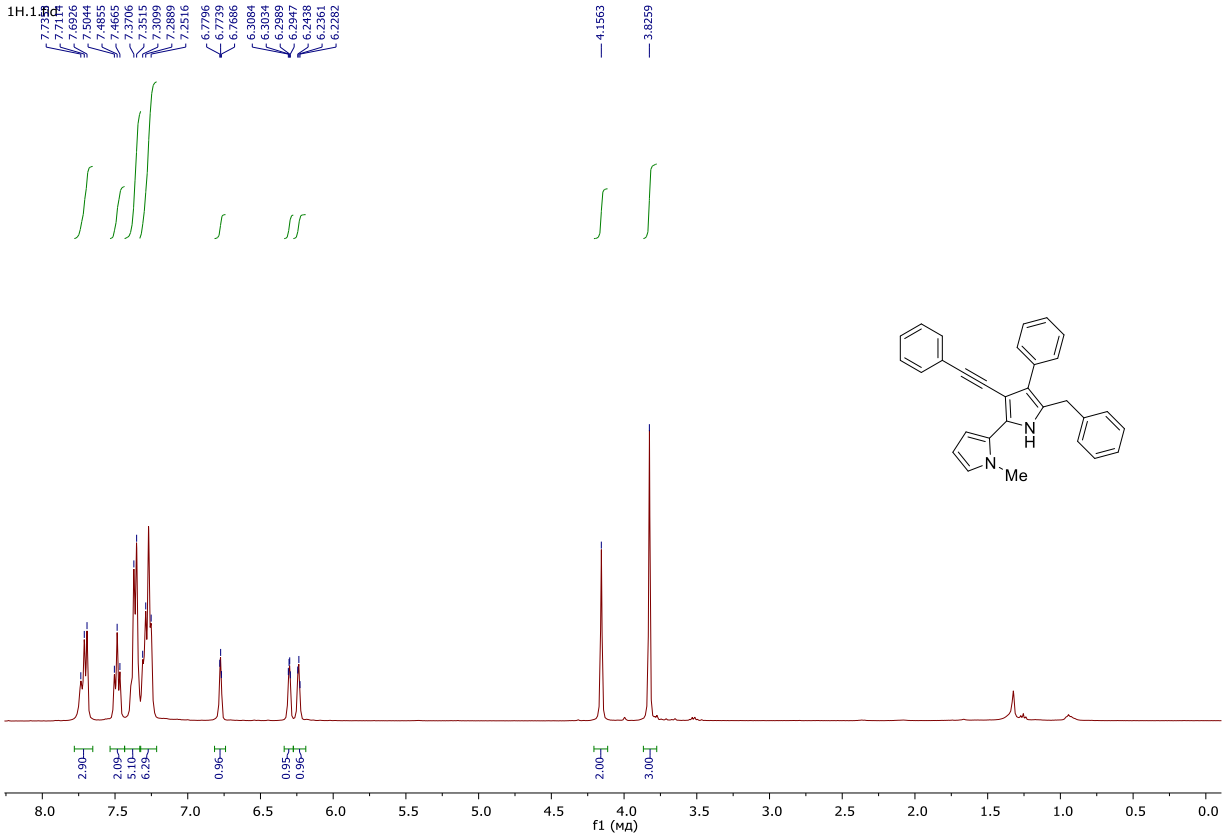
^{13}C NMR Spectrum of **3ah** (100.6 MHz, $CDCl_3$)



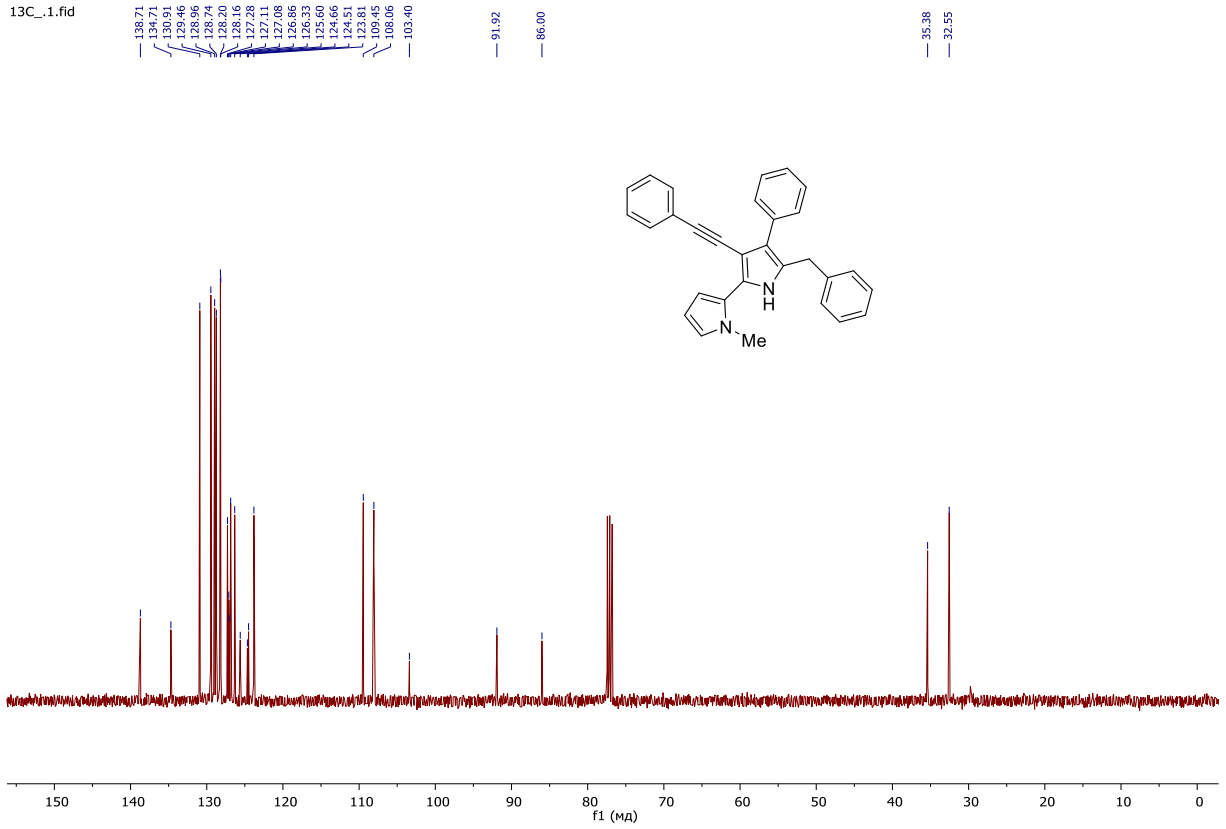
^{1}H NMR Spectrum of **3ai** (400.1 MHz, DMSO-D_6)



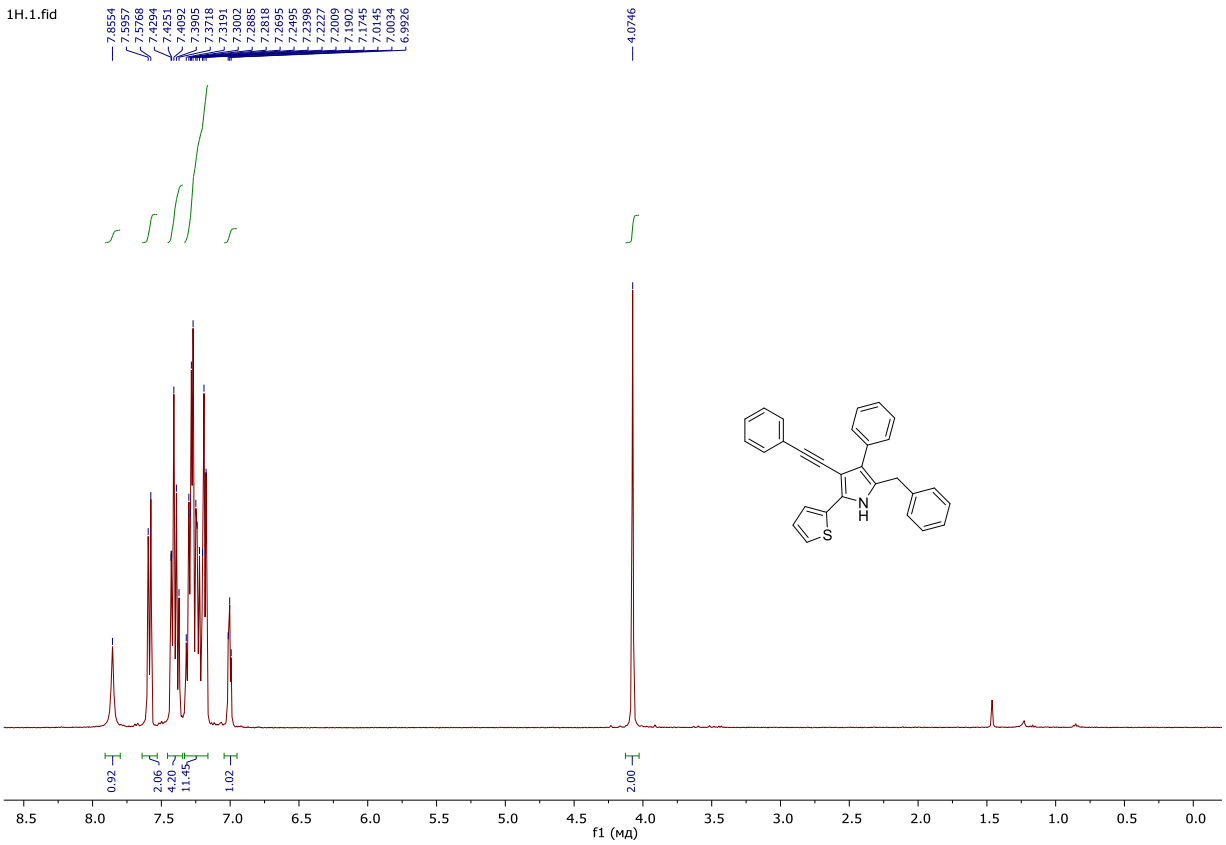
^{13}C NMR Spectrum of **3ai** (100.6 MHz, DMSO-D_6)



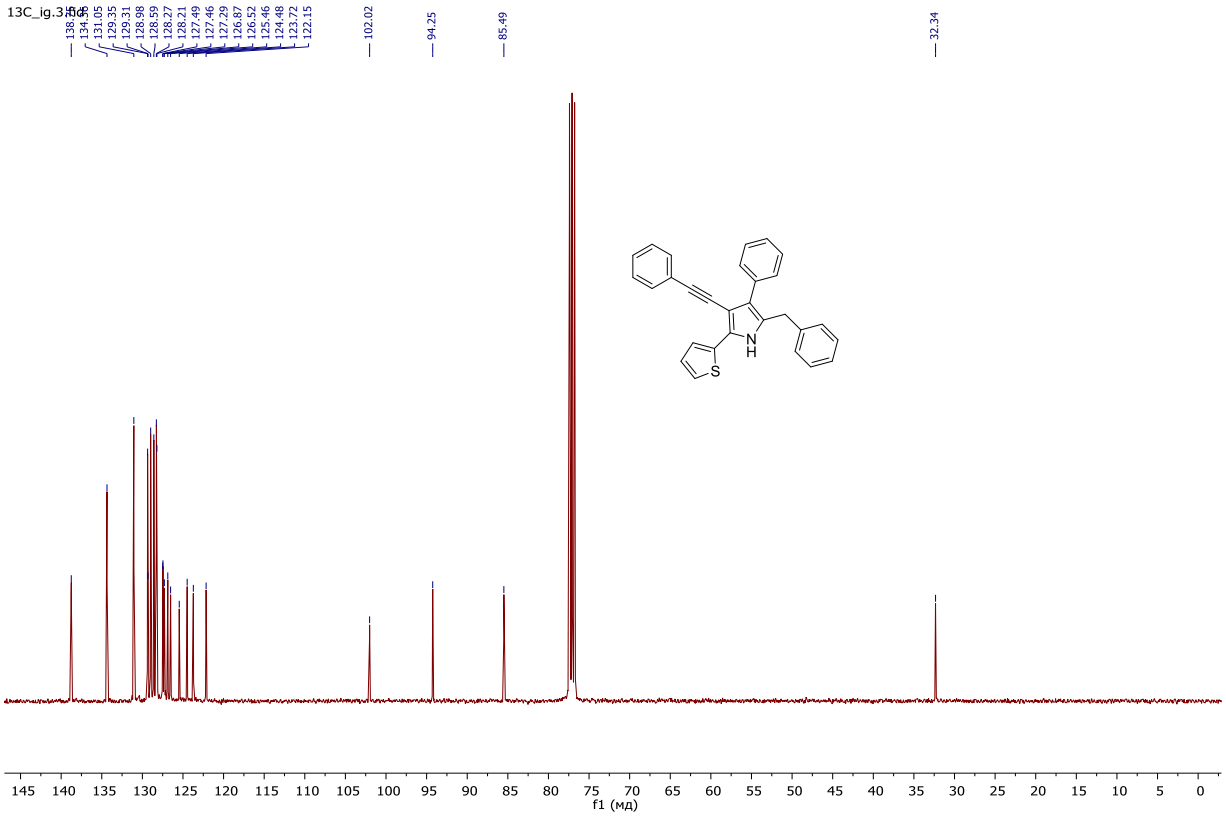
^{1}H NMR Spectrum of **3ak** (400.1 MHz, $CDCl_3$)



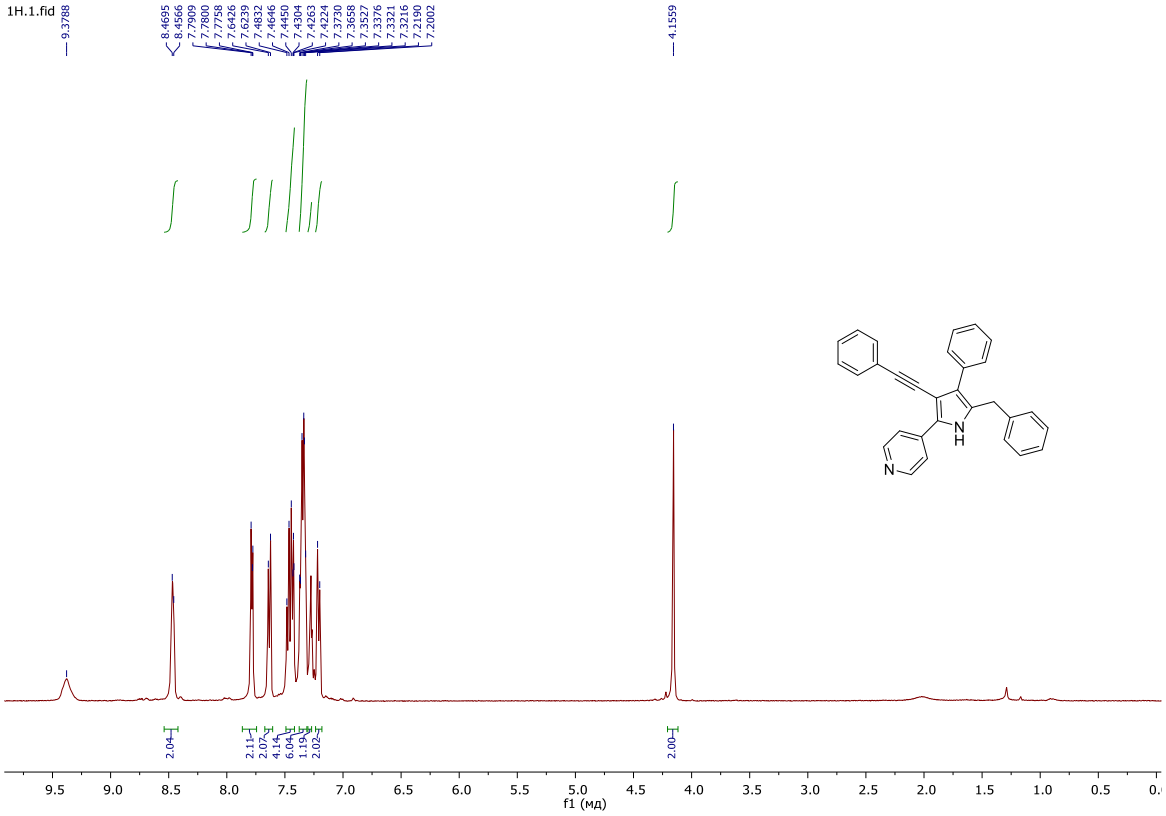
^{13}C NMR Spectrum of **3ak** (100.6 MHz, $CDCl_3$)



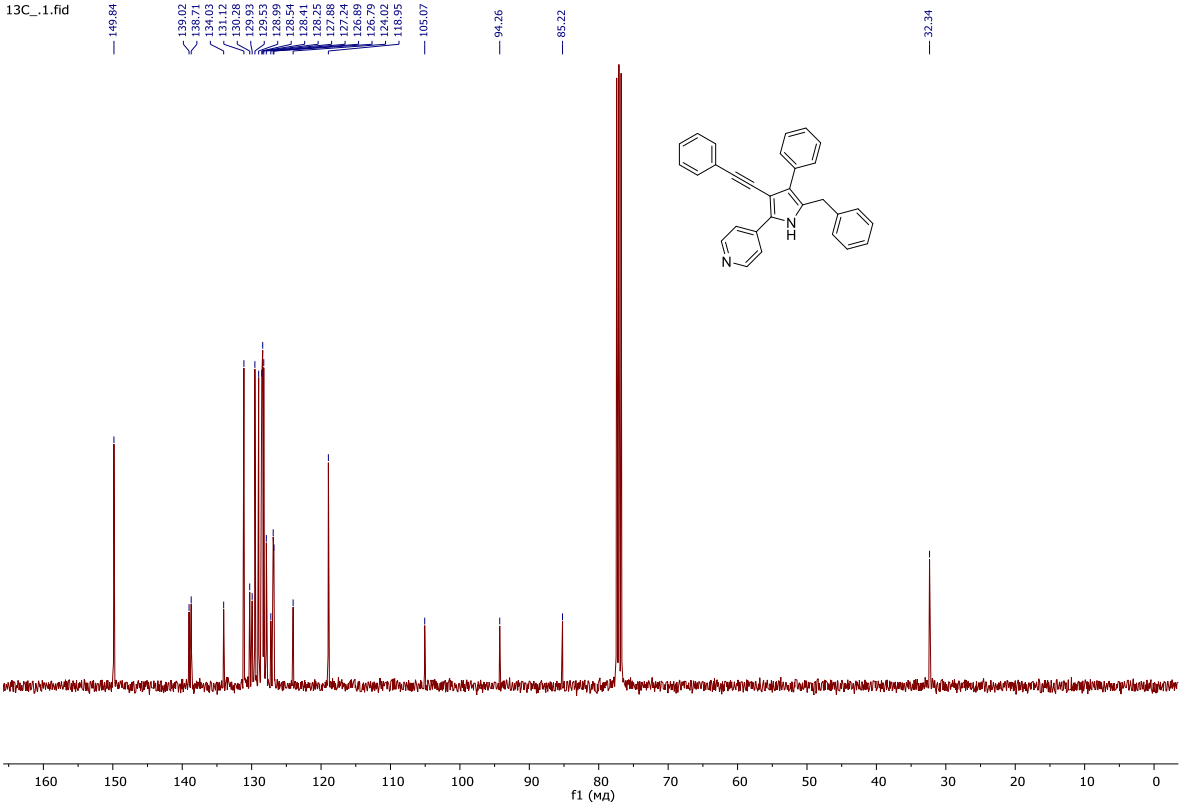
^{1}H NMR Spectrum of **3al** (400.1 MHz, $CDCl_3$)



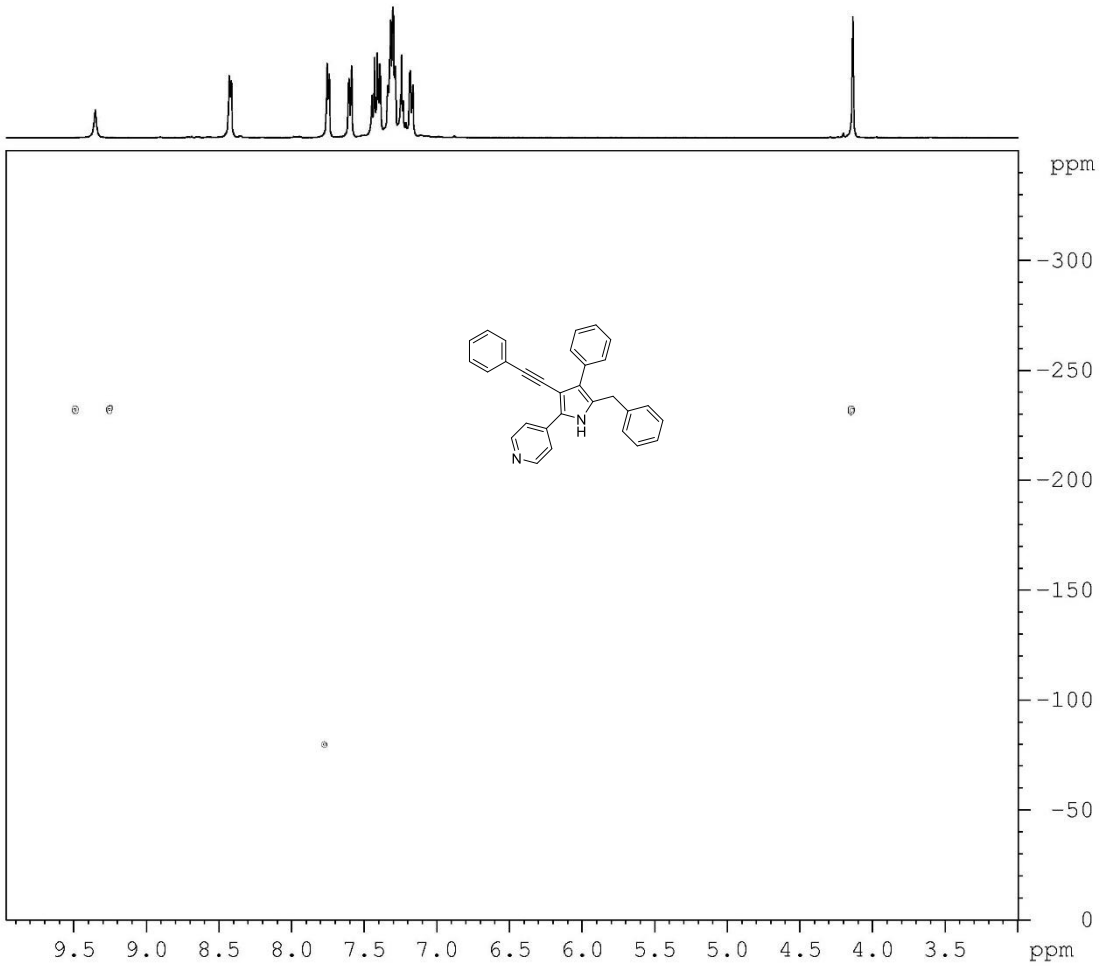
^{13}C NMR Spectrum of **3al** (100.6 MHz, $CDCl_3$)



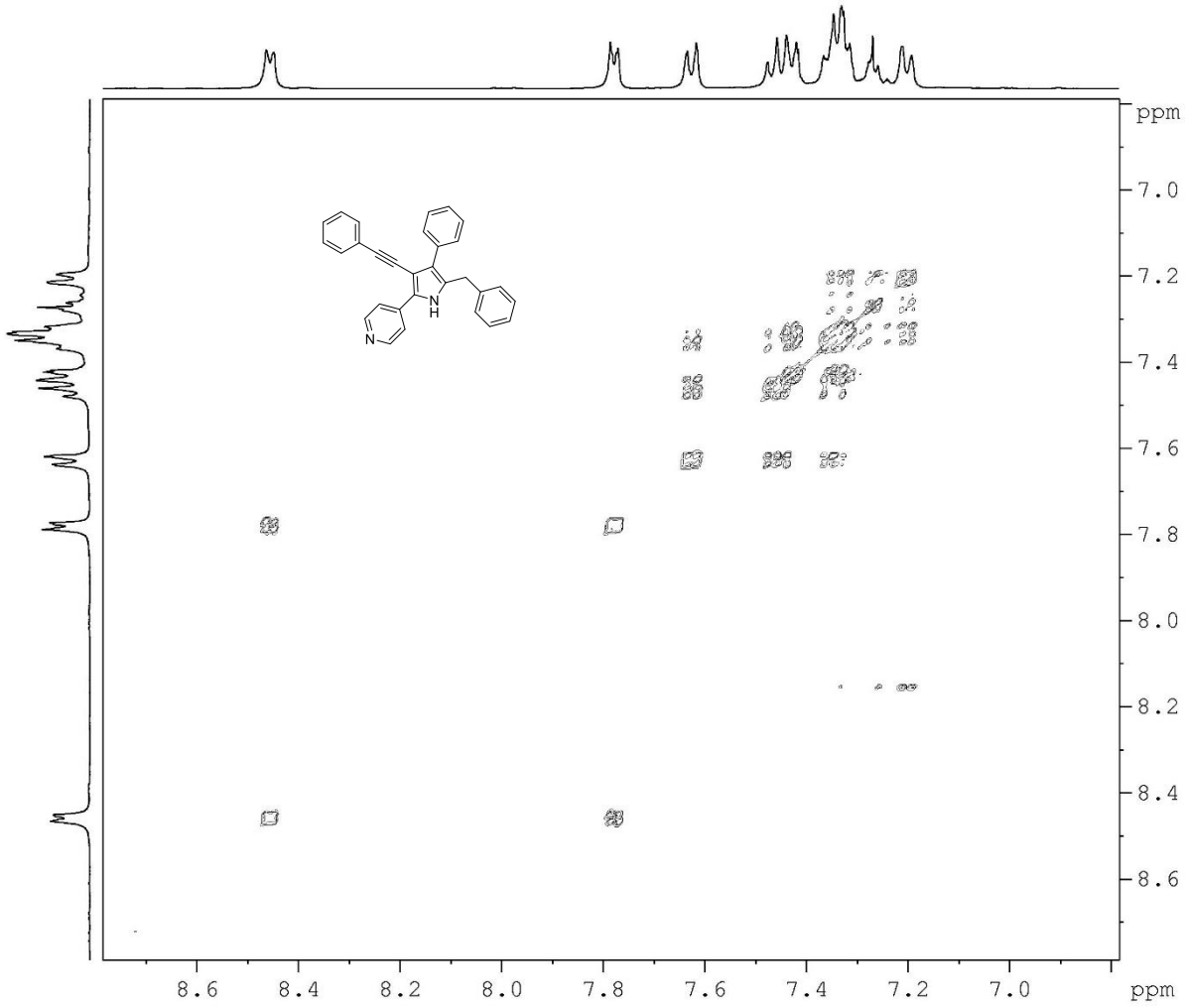
^{1}H NMR Spectrum of **3am** (400.1 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3am** (100.6 MHz, $CDCl_3$)



2D ^{1}H-^{15}N HMBC Spectrum of **3am**



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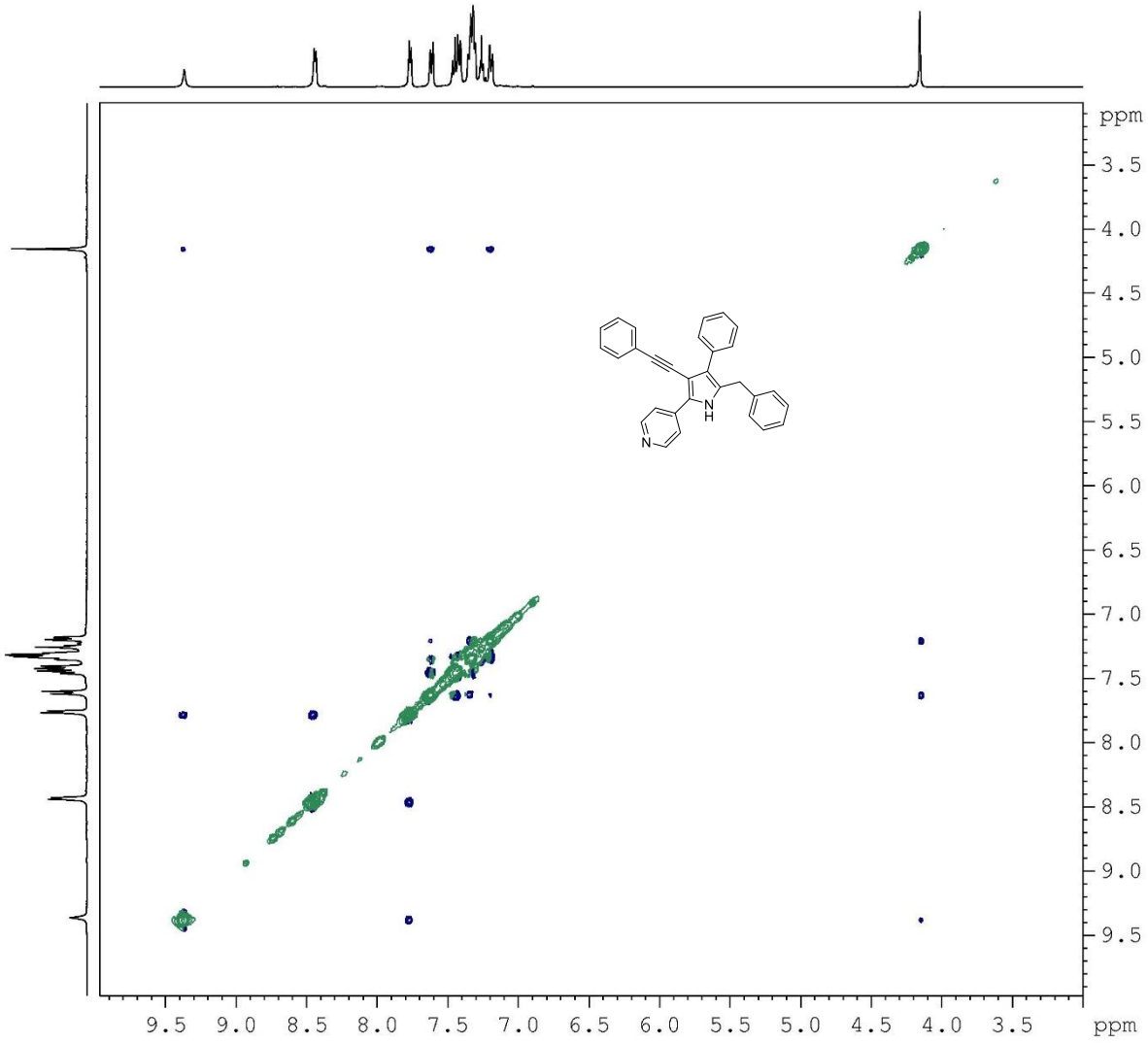
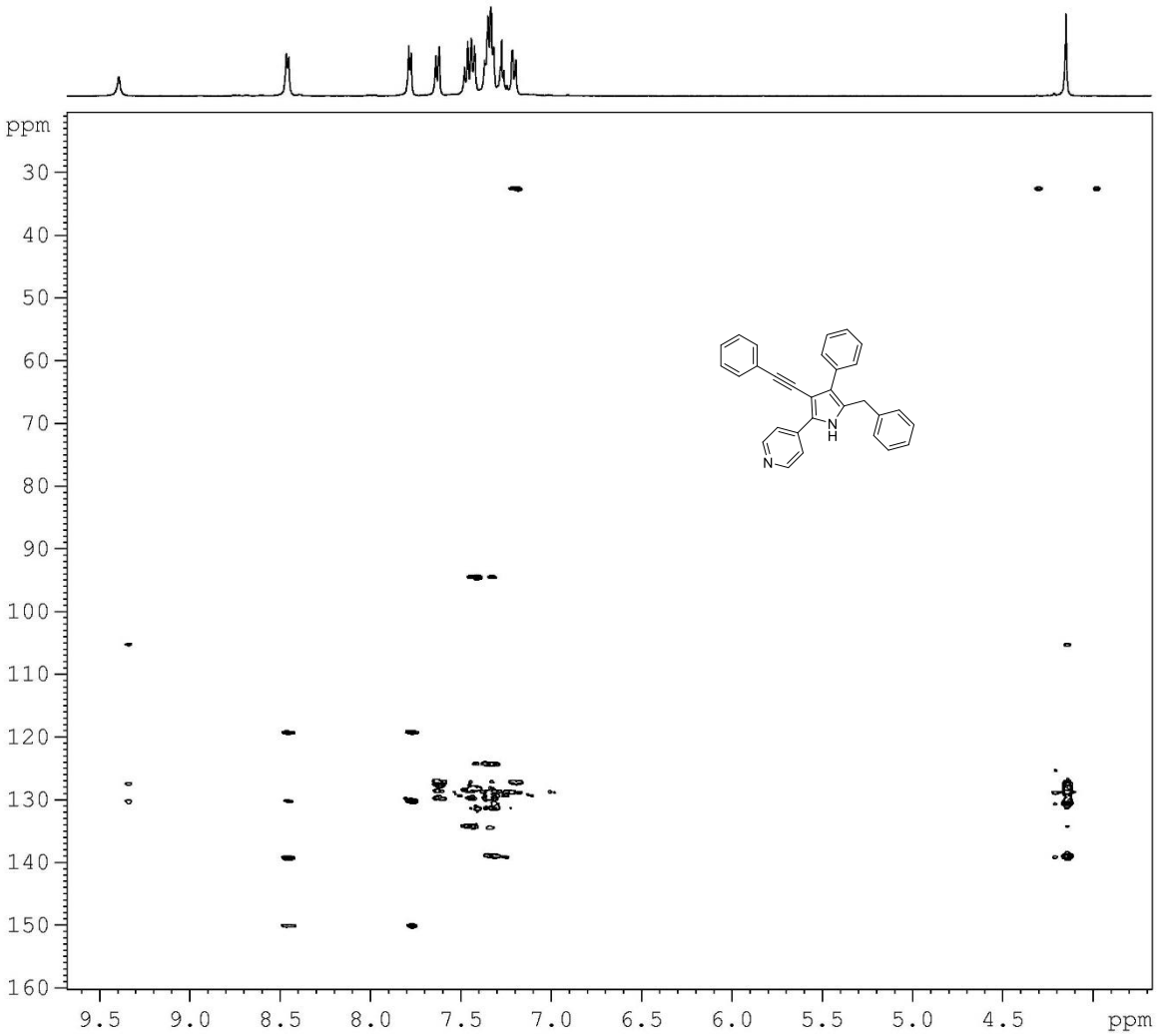
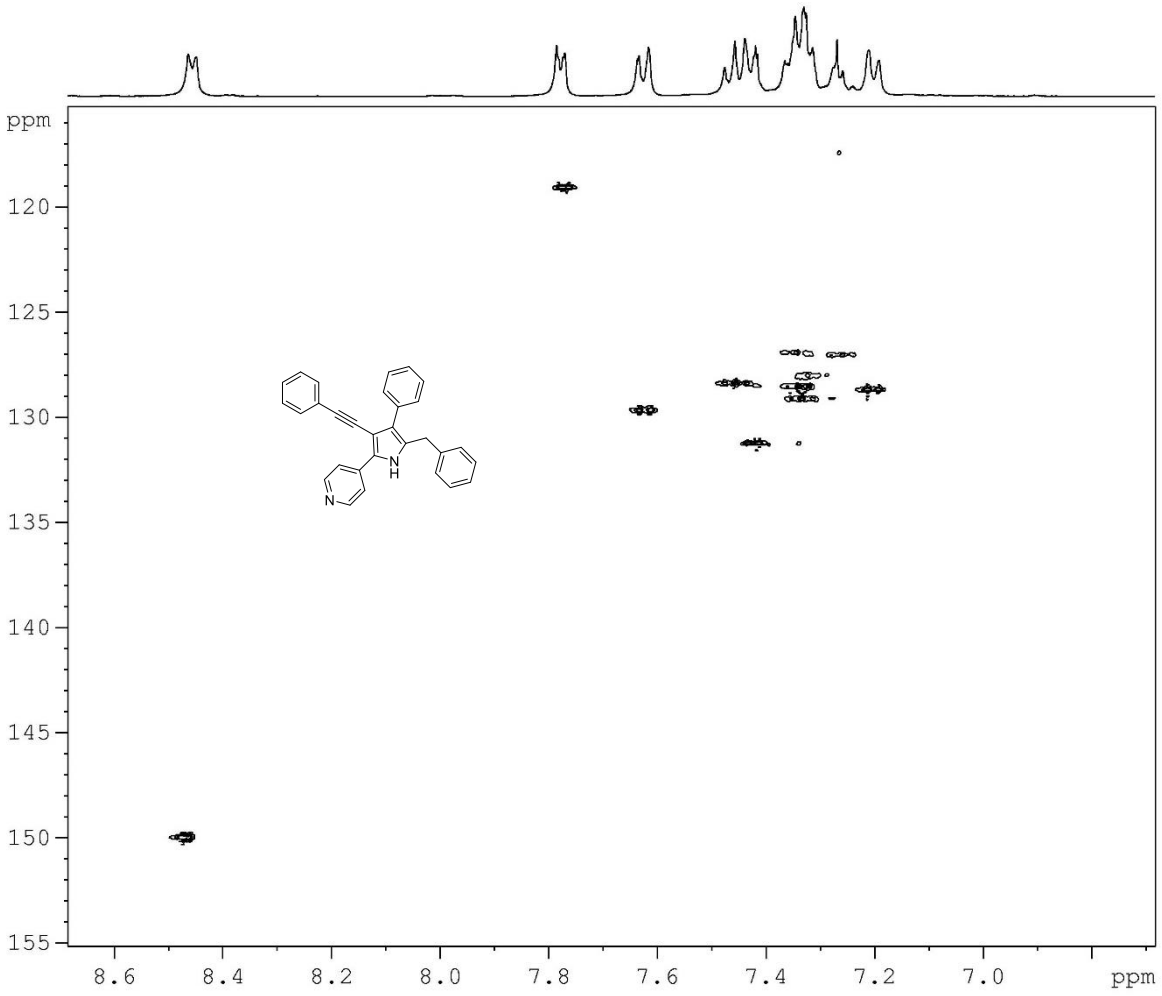


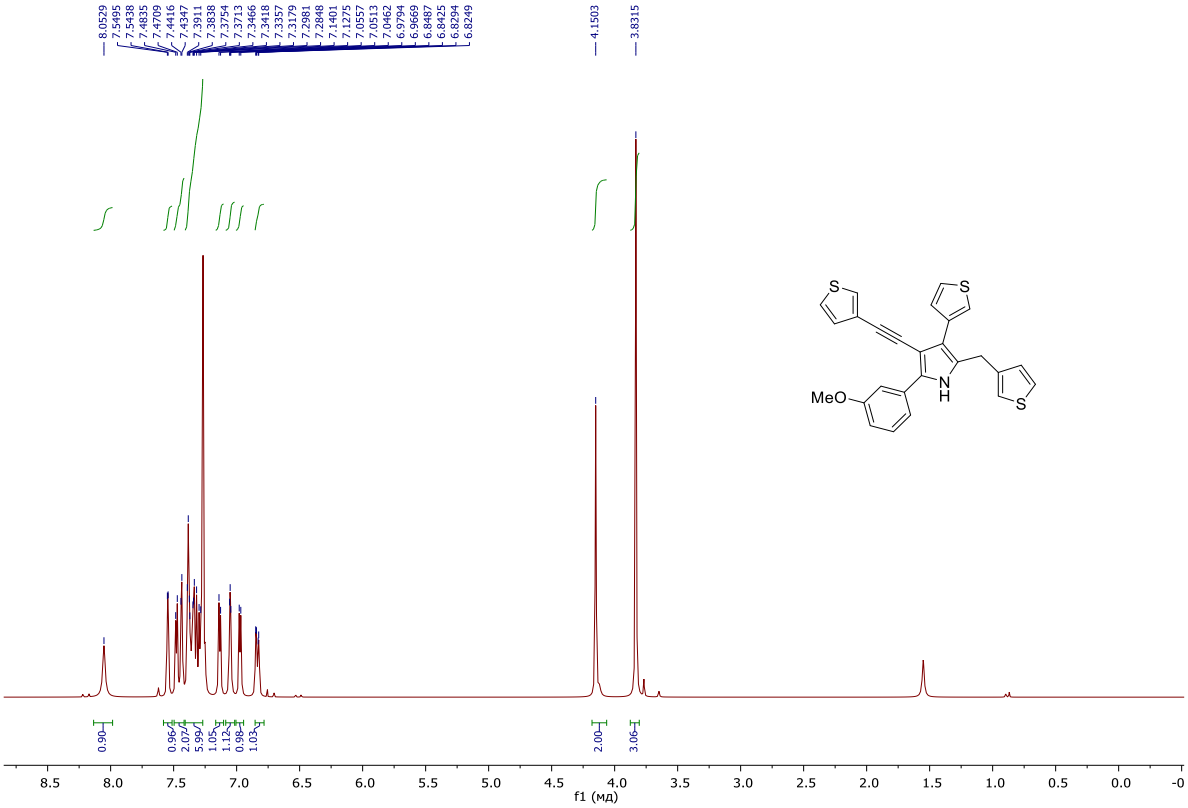
2D NOESY Spectrum of **3am**



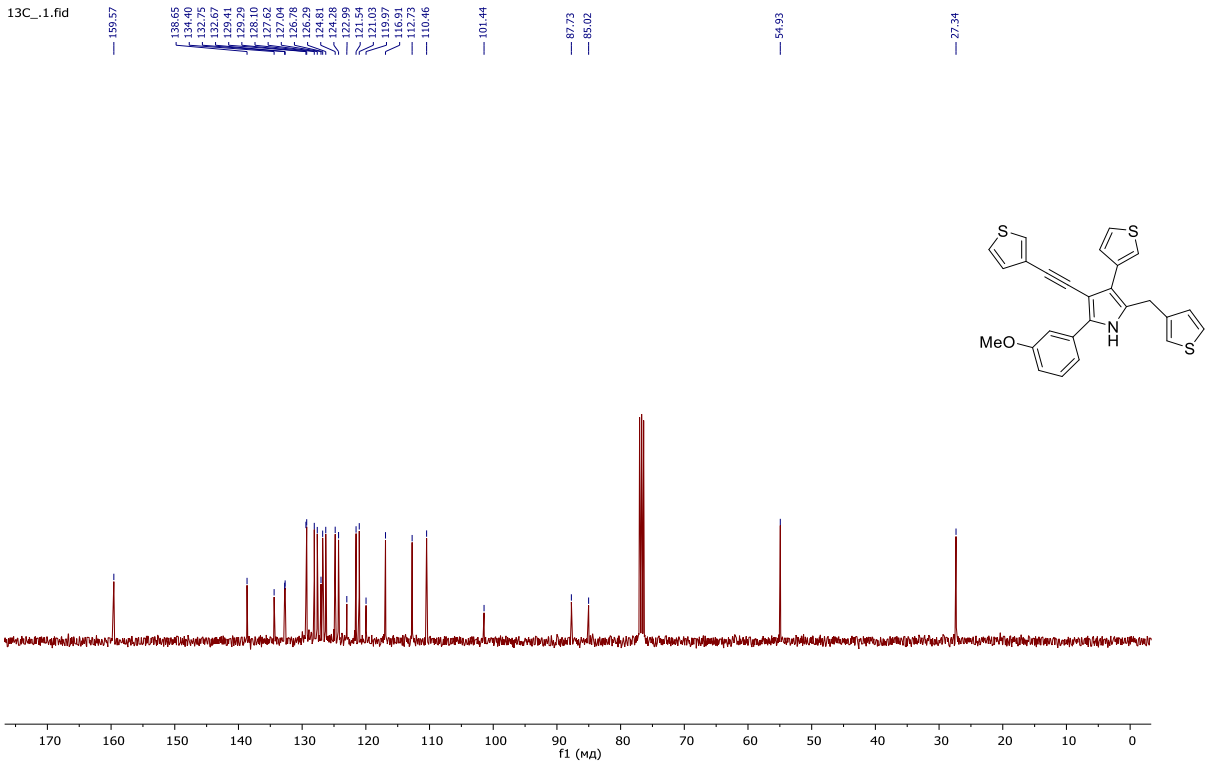
2D ^{1}H-^{13}C HMBC Spectrum of **3am**



2D ^{1}H-^{13}C HSQC Spectrum of **3am**



^{1}H NMR Spectrum of **3if** (400.1 MHz, $CDCl_3$)



^{13}C NMR Spectrum of **3if** (100.6 MHz, $CDCl_3$)

2. X-ray diffraction analysis

The structures was solved by direct methods using the SHELXT-2014/5 and refined by full-matrix least-squares method against all F2 in anisotropic approximation using the SHELXL-2018/3[1]. The hydrogen atoms positions were calculated with the riding model. The hydrogen atom position for NH-groups was located from difference Fourier map. Absorption corrections were applied using the empirical multiscan method with the SADABS program[2]. Compound **3al** is monoclinic, space group $P2_1$, *a* = 9.1310(4), b = 8.5709(3), c = 13.8389(5) Å, β = 91.507(2)°, V = 1082.67(7) $Å^3$, Z = 2, $C_{29}H_{21}NS$, formula weight 415.53, crystal density Dc = 1.275 г/см3, μ = 0.166 mm-1, F(0 0 0) = 436, yellow crystal size 0.90 x 0.15 x 0.06 mm^3, independent reflections 4956 (Rint = 0.0423), wR_2 = 0.0756, goodness of fit S = 1.02 for all reflections and R = 0.0330 for 4183 I > 2σ, absolute structure parameter (Flack parameter) is equal to 0.06(3), difference electron density max is 0.11 and min is -0.12 e-/ $Å^3$. The thiophene cycle is disordered by two positions with 0.767 : 0.233(4) occupation ratio. CCDC 2260734 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif. Molecular structures of compound **3al** is illustrated in Figure 1.

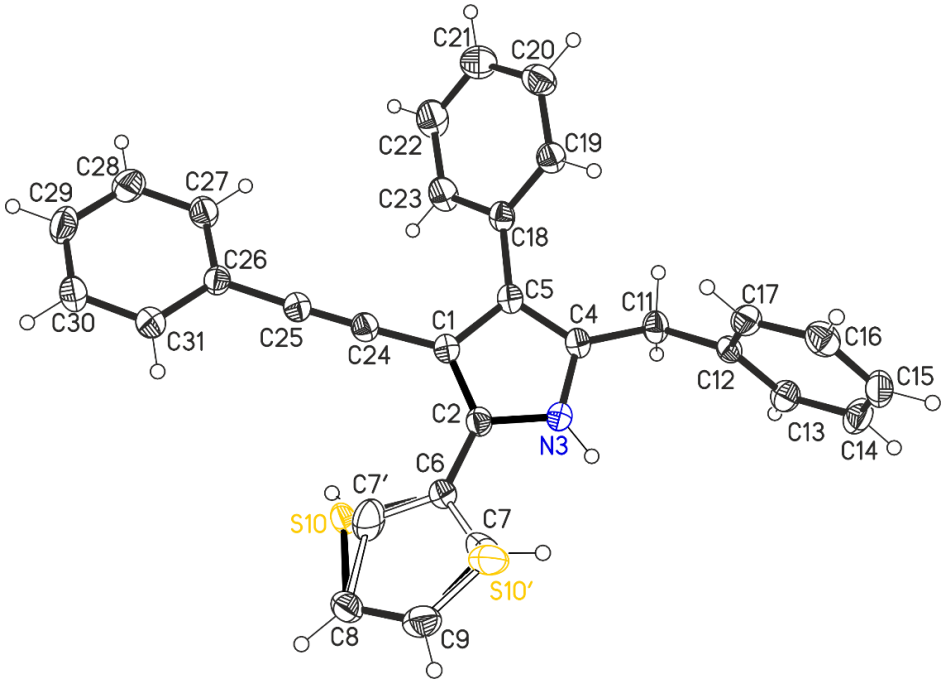


Figure 1. Molecular structures and atomic numbering for **3al** (30% thermal ellipsoids are shown).

The obtained crystal structures were analyzed for the geometrical parameters and short contacts between non-bonded atoms using PLATON[3] and MERCURY programs[4]. The

geometric parameters for all compounds agreed within 3σ of the corresponding mean statistical values[5].

According to the of X-ray diffraction data the all cycles are perfectly planar in the crystal. The dihedral angle between 1H-pyrrole cycle and thiophene cycle is equal to 28.2(2)°, the dihedral angle between 1H-pyrrole cycle and phenyl cycle C18 – C 23 is equal to 48.8(1)°, the dihedral angle between phenyl cycle C18 – C 23 and phenyl cycle C12 – C 17 is equal to 58.3(1)°. The shortened S10...H7a 2.82 Å contact lead to formation of 1D chains. Note, that normal S...H contact is 2.92 Å[6]. Additionally to the S...H, the C-H…π interaction H-atoms of the C7-H7a and C8-H8a bonds of one molecule with thiophene and phenyl cycles of another are observed, the H-atoms-to-plane distances are from 2.81 to 2.97 Å.

3. References

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