# Supplementary Information

# Domino Reaction of 3-Chlorochromones with Aminoheterocycles. Synthesis of Pyrazolopyridines and Benzofuropyridines and their Optical and Phosphatase Inhibitory Effects

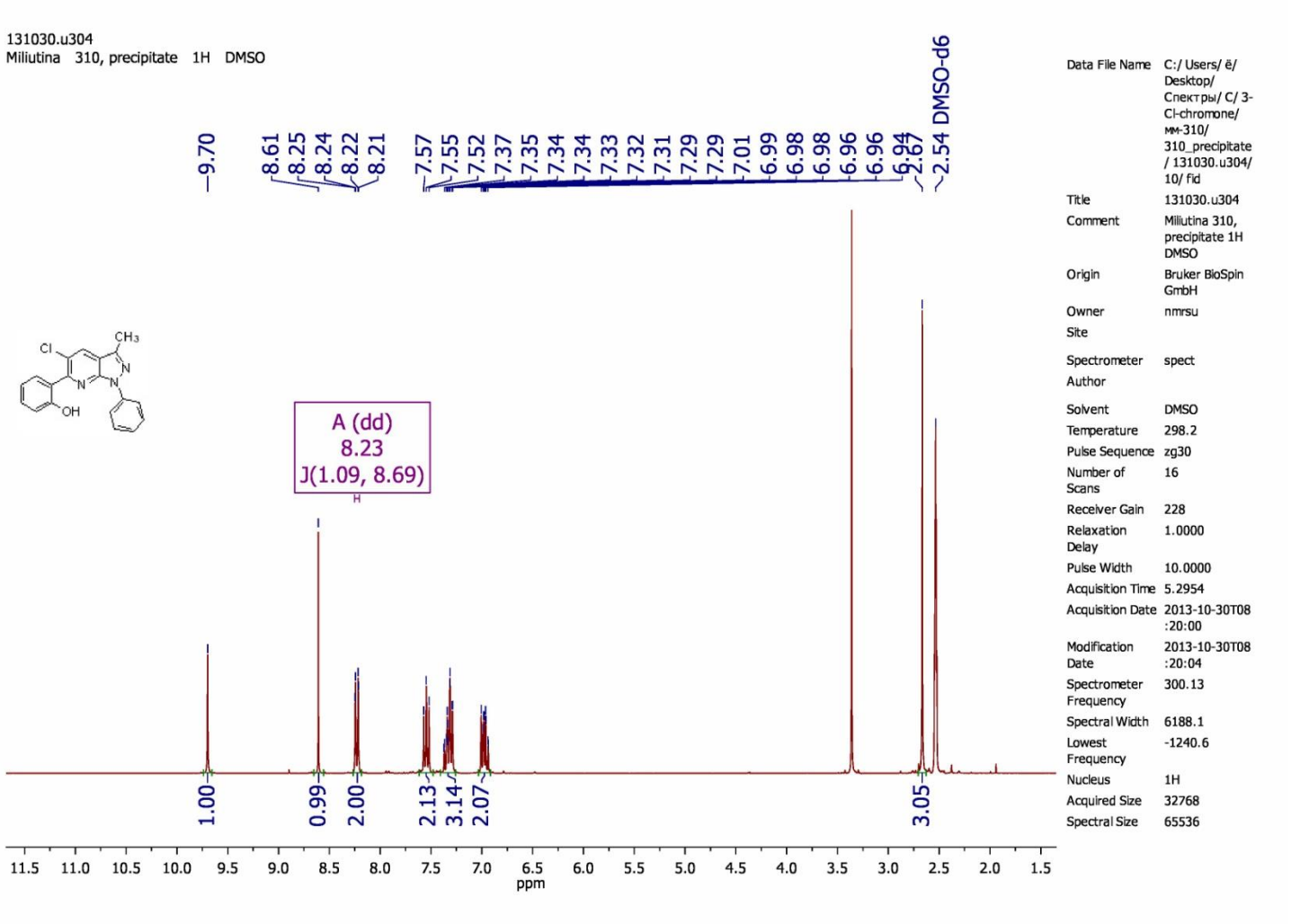
Mariia Miliutina,[a] Julia Janke,[a] Sidra Hassan,[b] Jamshed Iqbal,[b] Joanna Lecka,[c,d] Jean Sévigny,[c,d] Alexander Villinger,[a] Aleksej Friedrich,[e] Stefan Lochbrunner,[e] Peter Langer[a,f]*

[a] *Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany; peter.langer@uni-rostock.de*
[b] *Centre for Advanced Drug Research, COMSATS Institute of Information Technology, Abbottabad, Pakistan*
[c] *Département de microbiologie-infectiologie et d'immunologie, Faculté de Médecine, Université Laval, Québec, QC, G1V 0A6, Canada*
[d] *Centre de Recherche du CHU de Québec – Université Laval, Québec, QC, G1V 4G2, Canada*
[e] *Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany*
[f] *Leibniz Institut für Katalyse an der Universität Rostock e.V., Albert-Einstein-Str. 29a, 18059 Rostock, Germany*

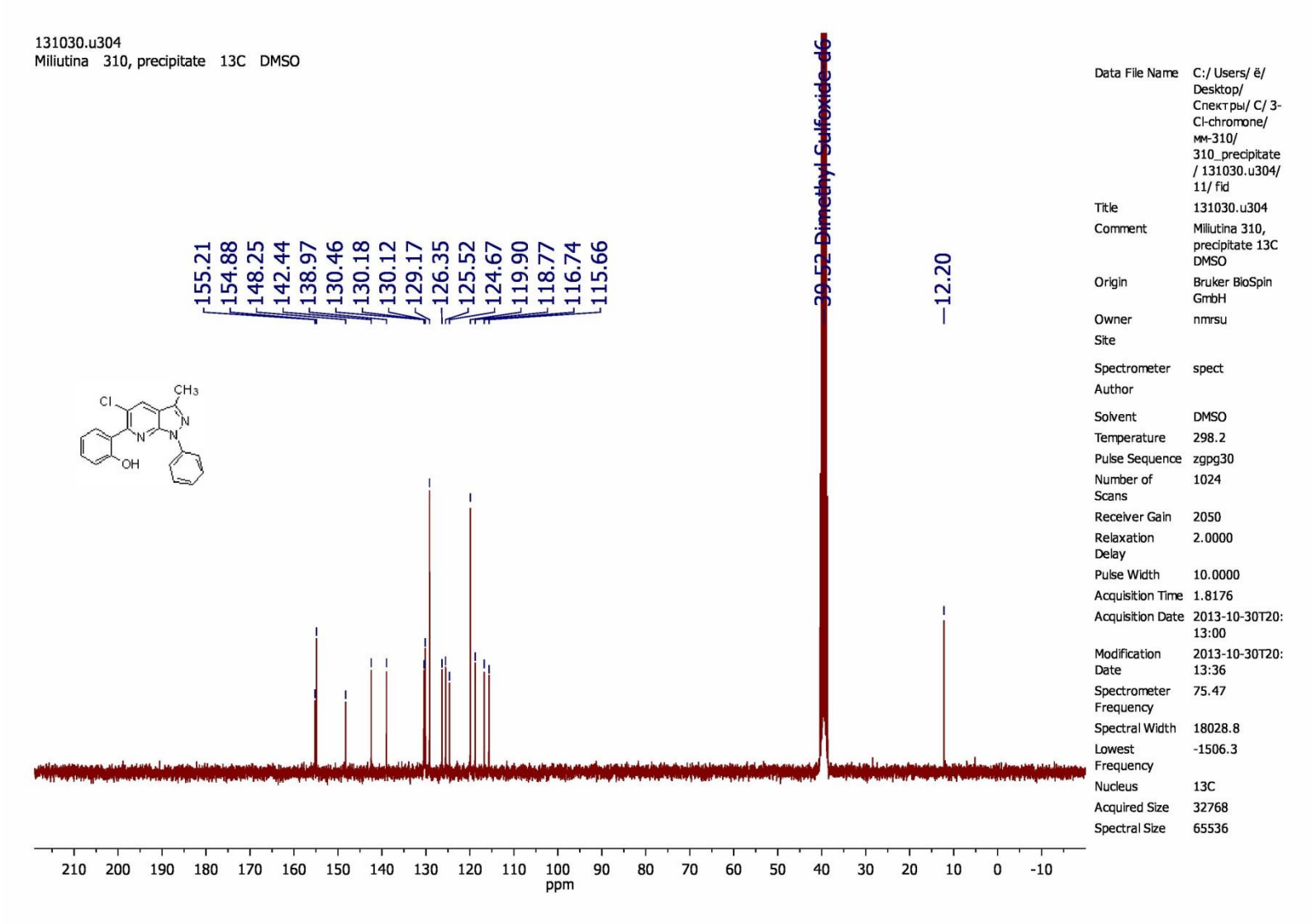
## Content

## 1H and 13C NMR spectra of products 3.

**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3a).**



**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3a).**



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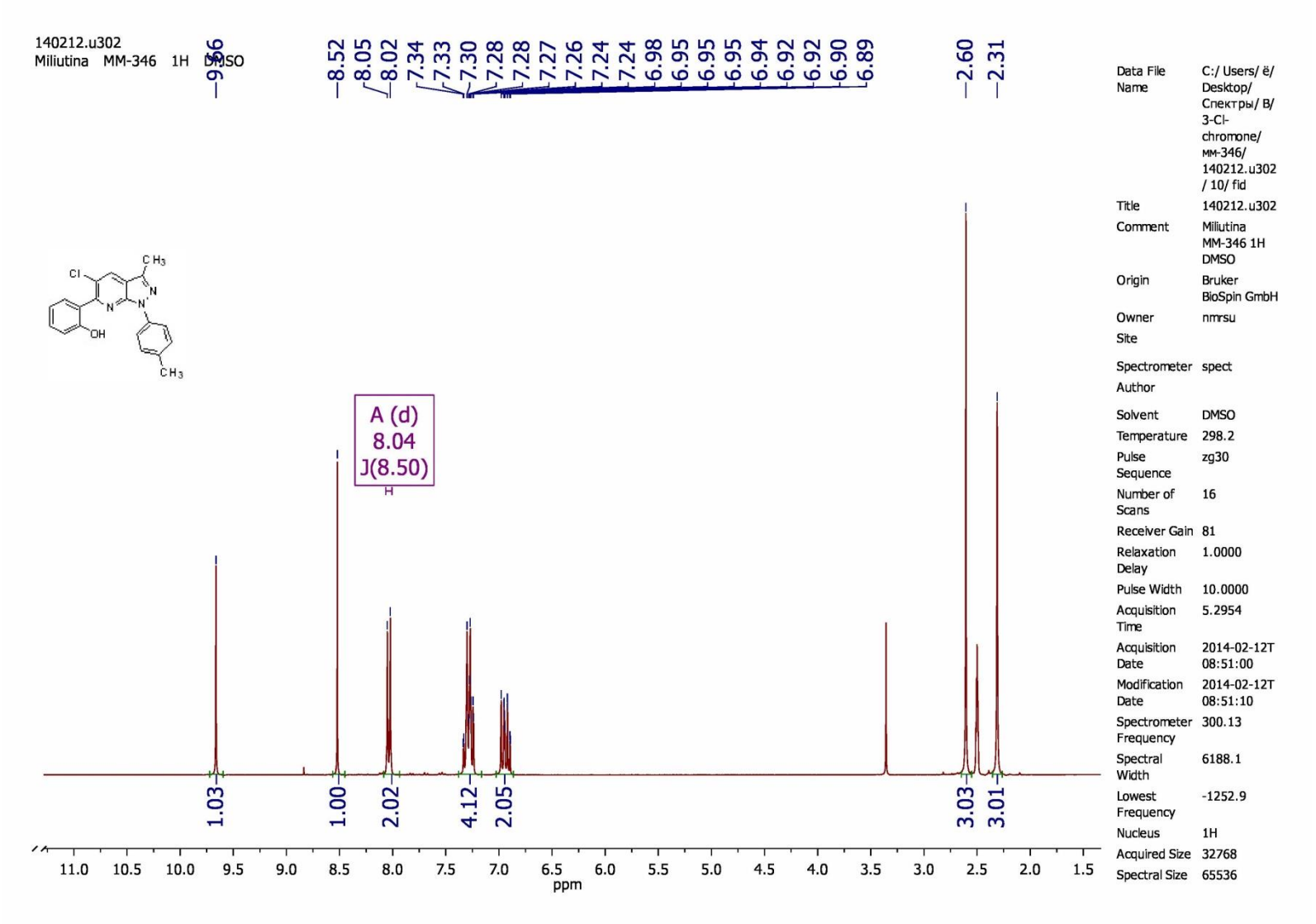
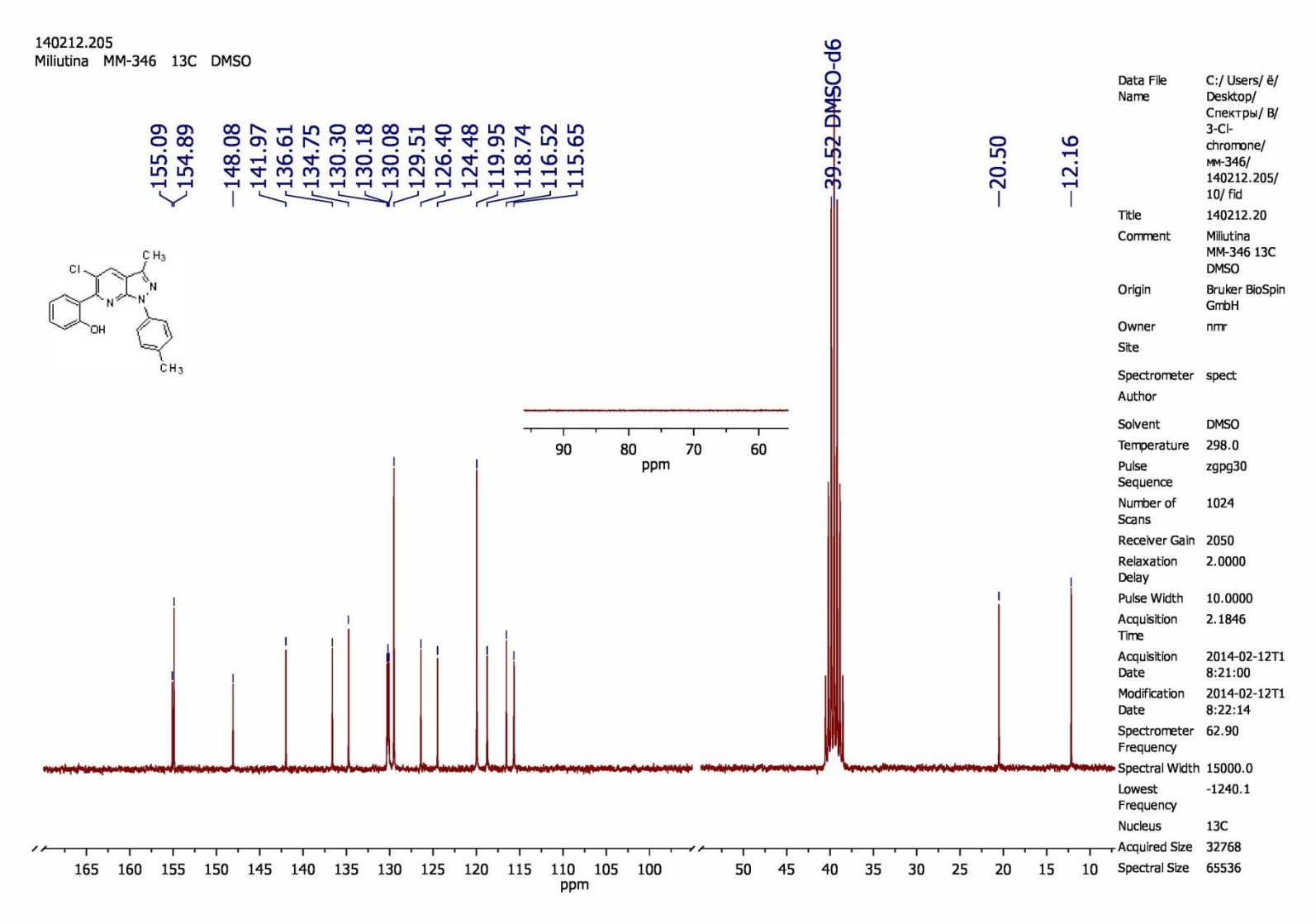
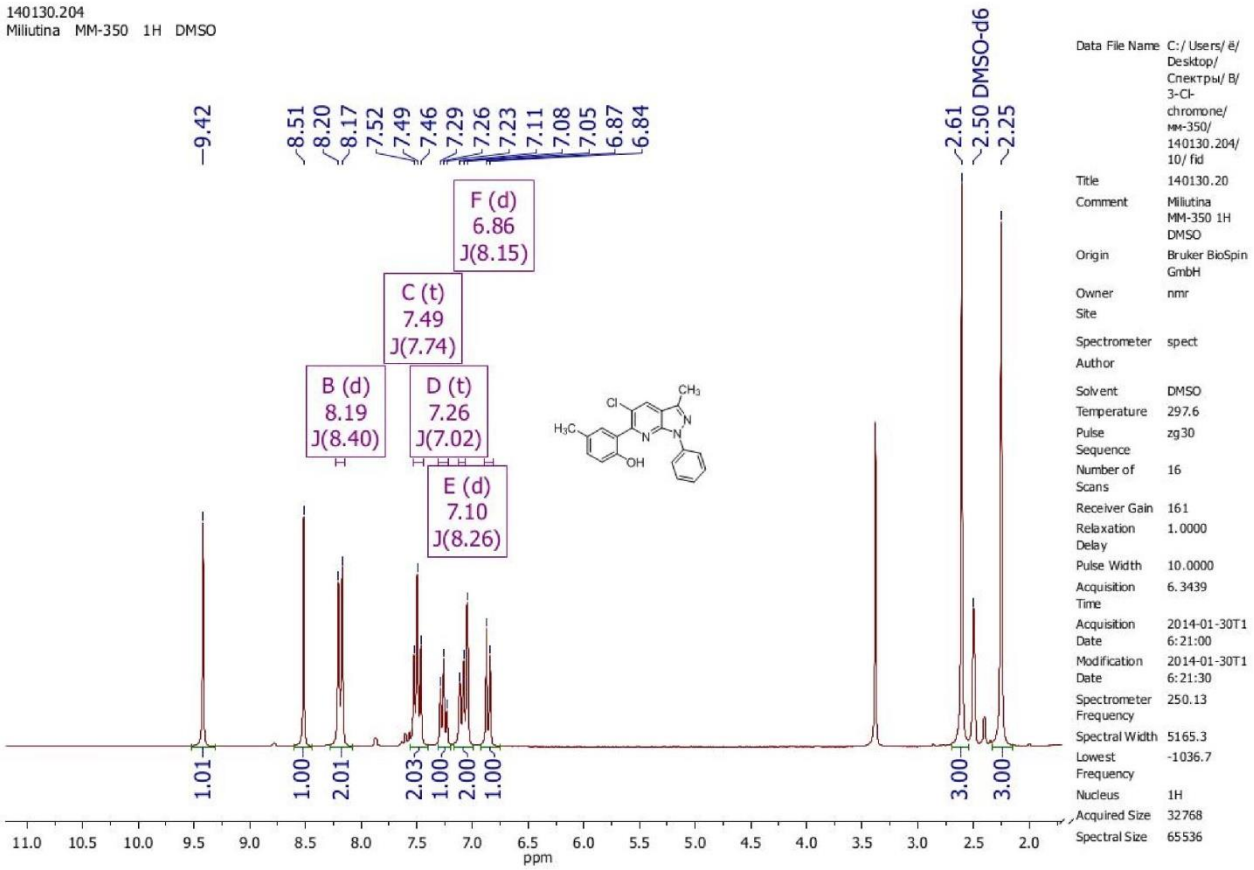


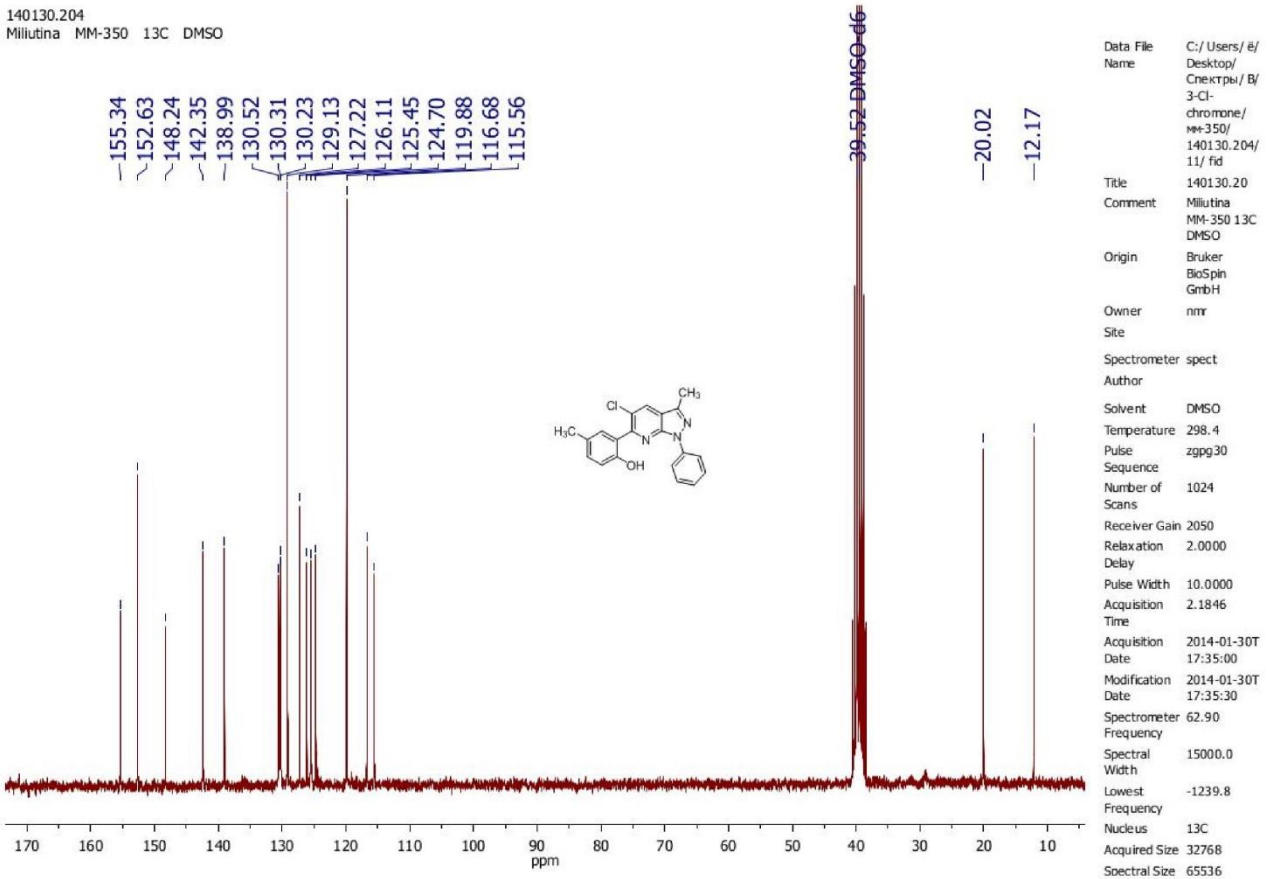
**2-(5-Chloro-3-methyl-1-*p*-tolyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3b).**



**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-4-methylphenol (3c).**



**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-4-methylphenol (3c).**

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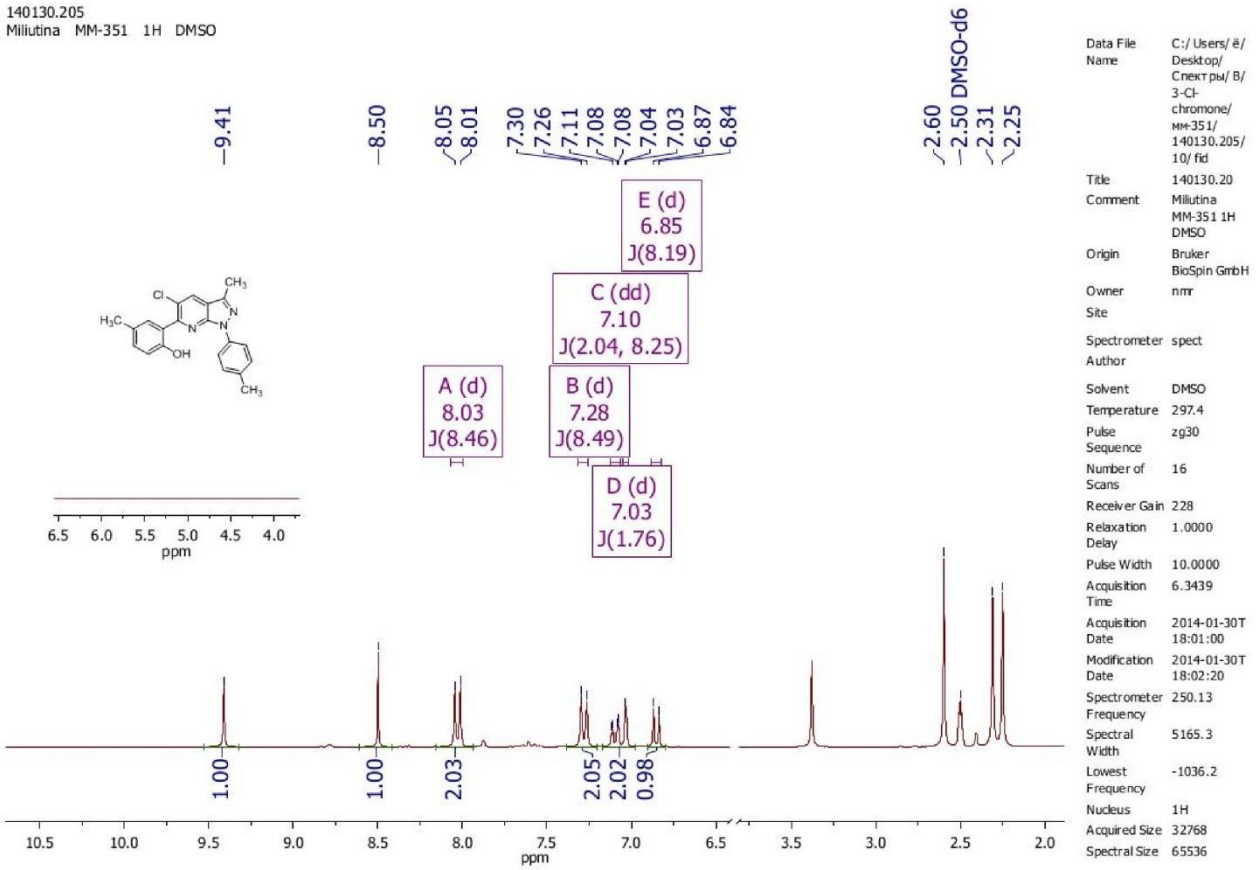
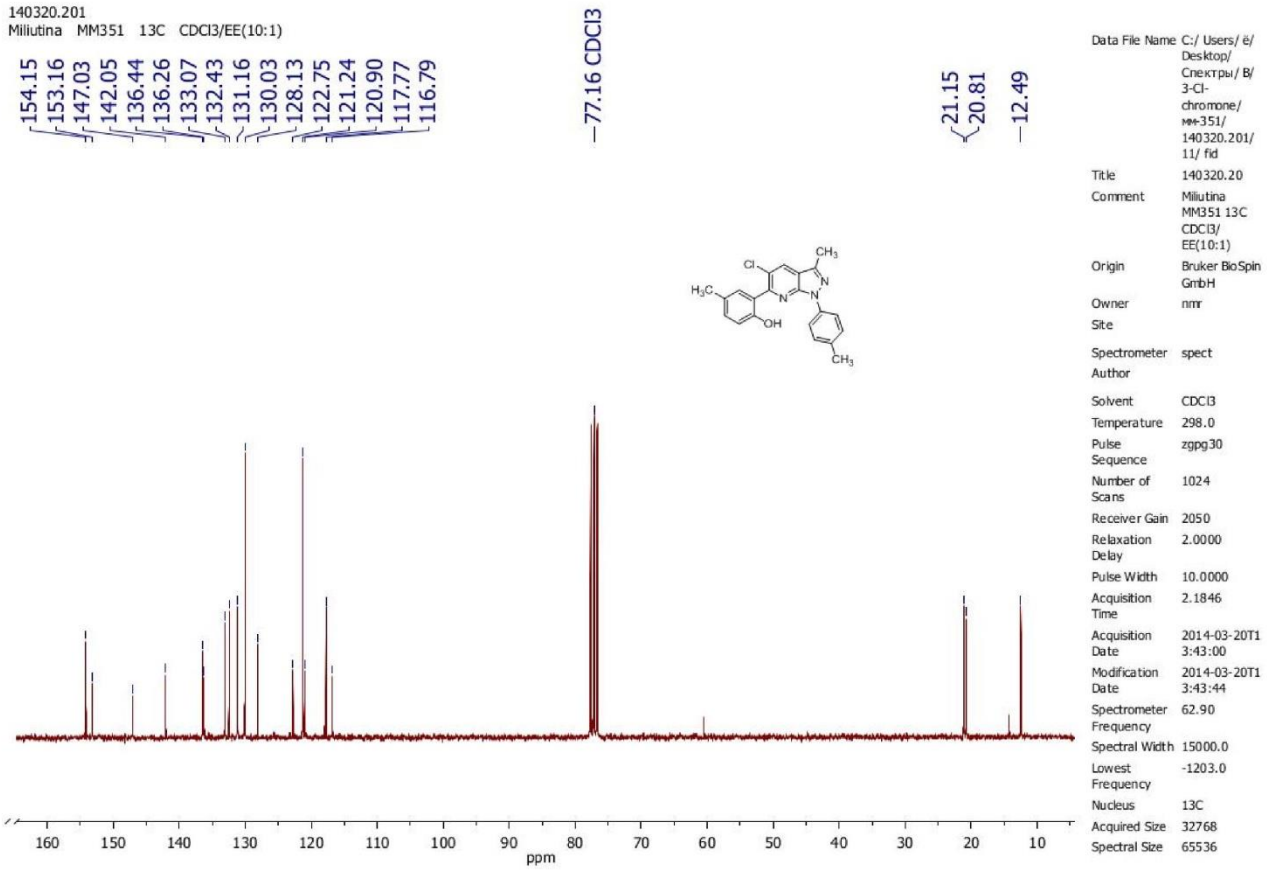
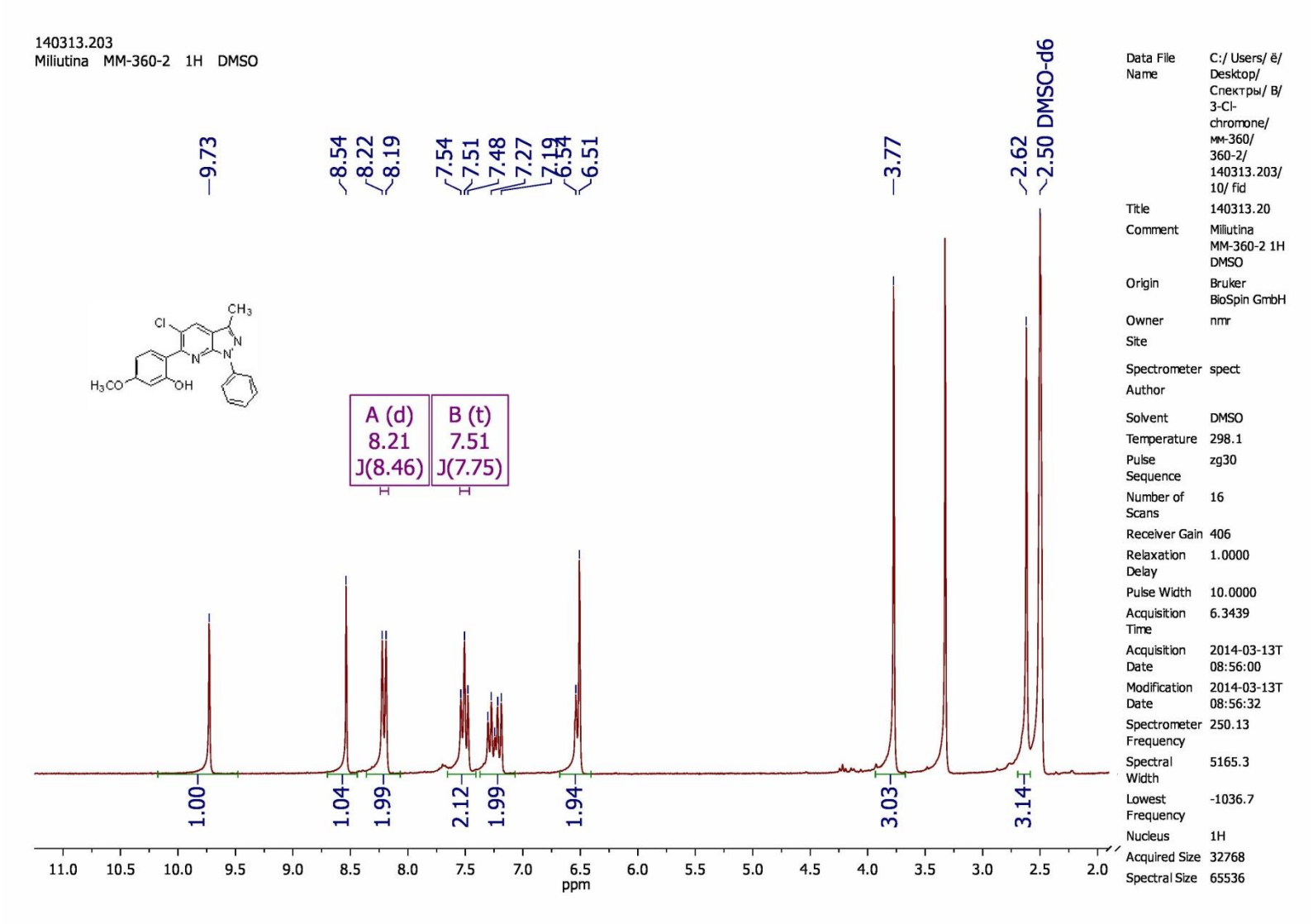


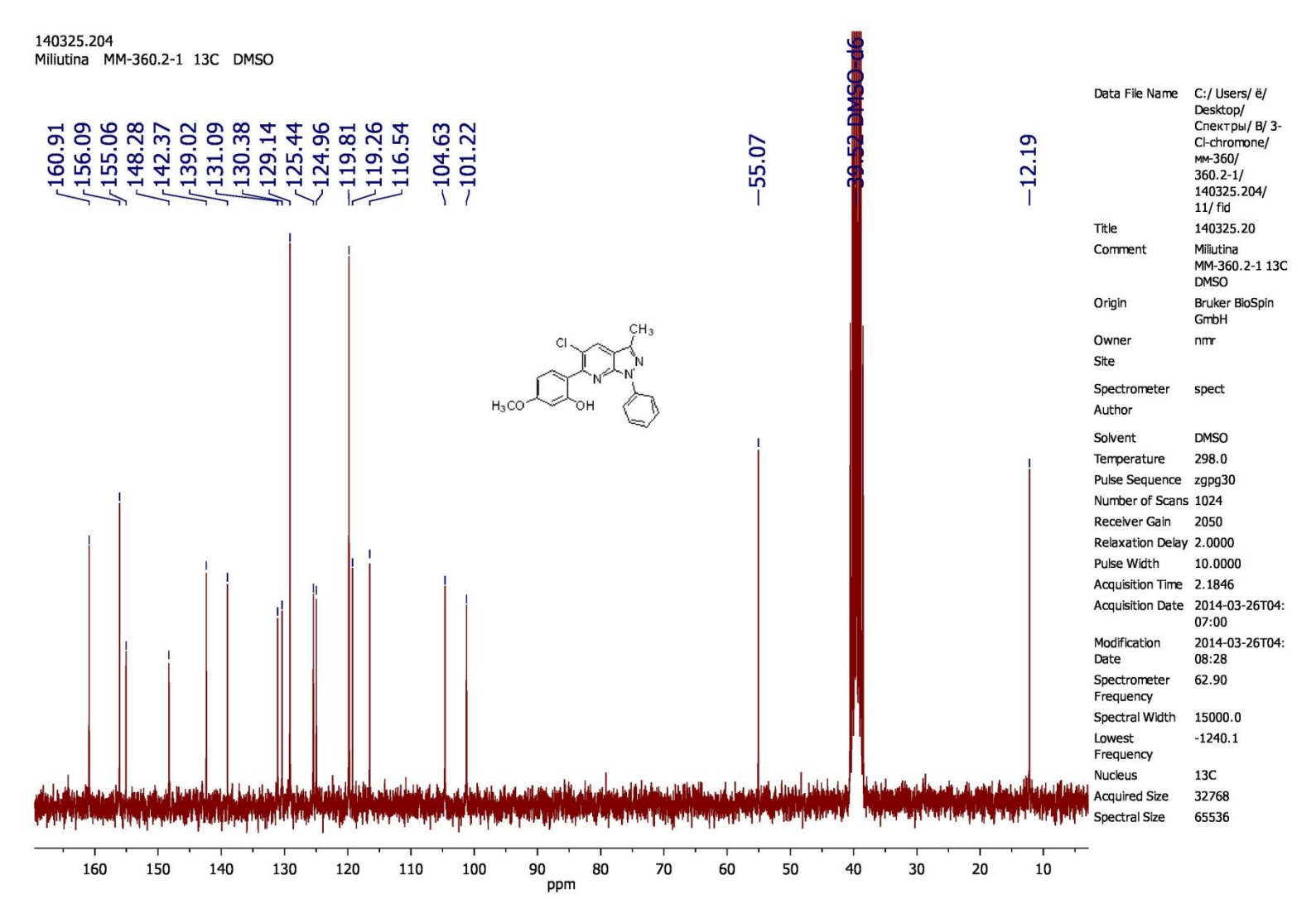
**2-(5-Chloro-3-methyl-1-*p*-tolyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-4-methylphenol (3d).**



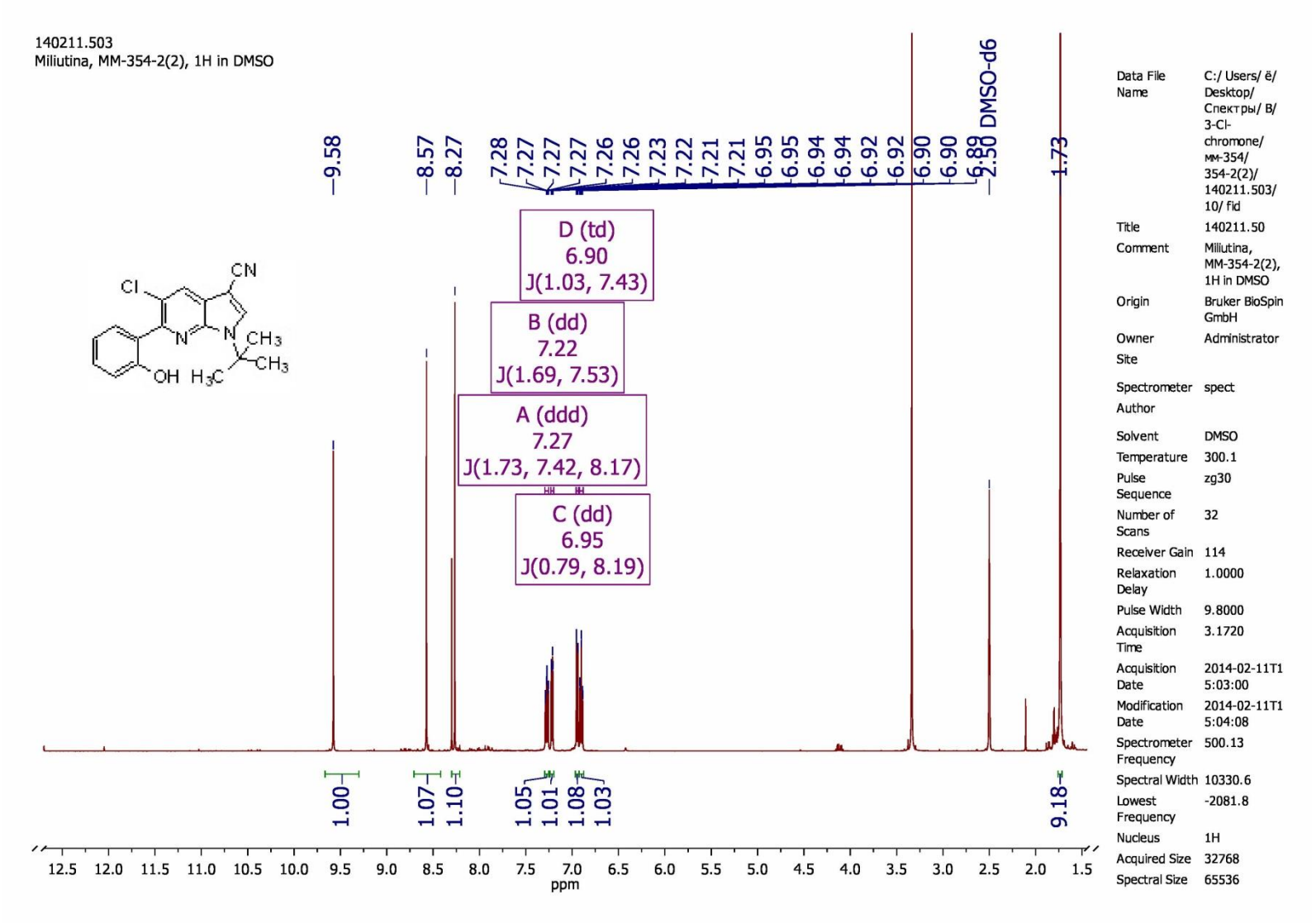
**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-5-methoxyphenol (3e).**



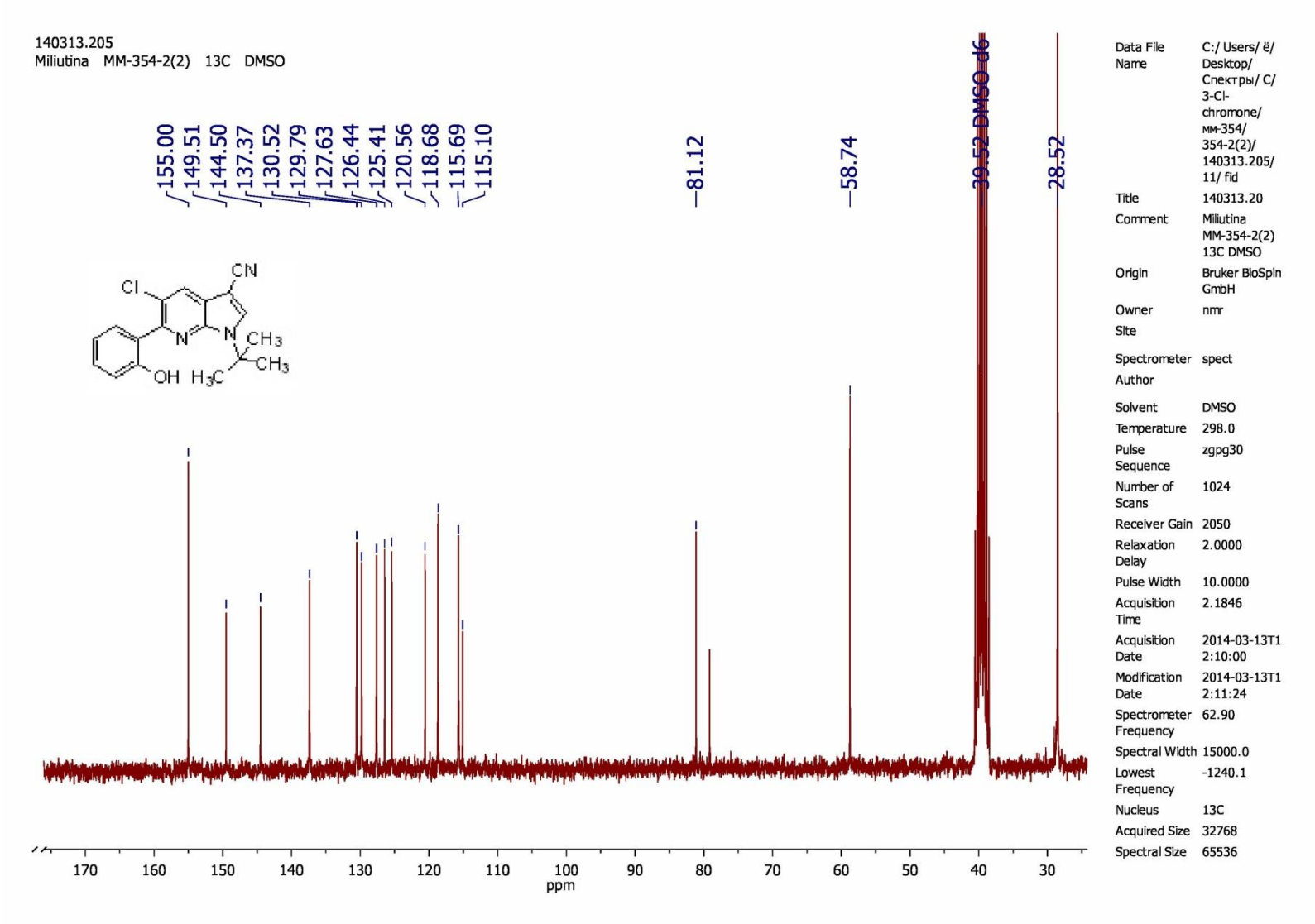
**2-(5-Chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-5-methoxyphenol (3e).**



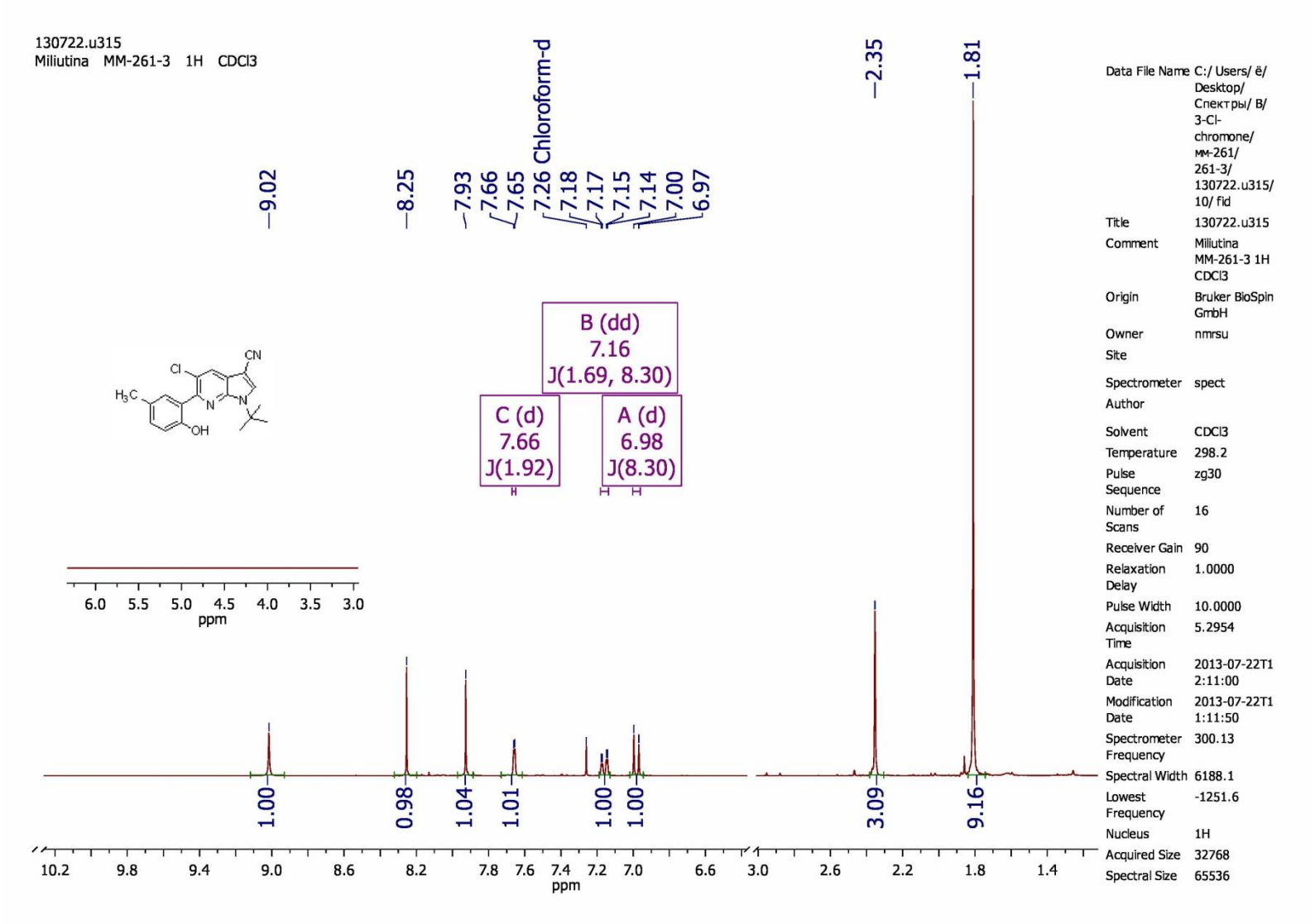
**1-*tert*-Butyl-5-chloro-6-(2-hydroxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonitrile (3g).**



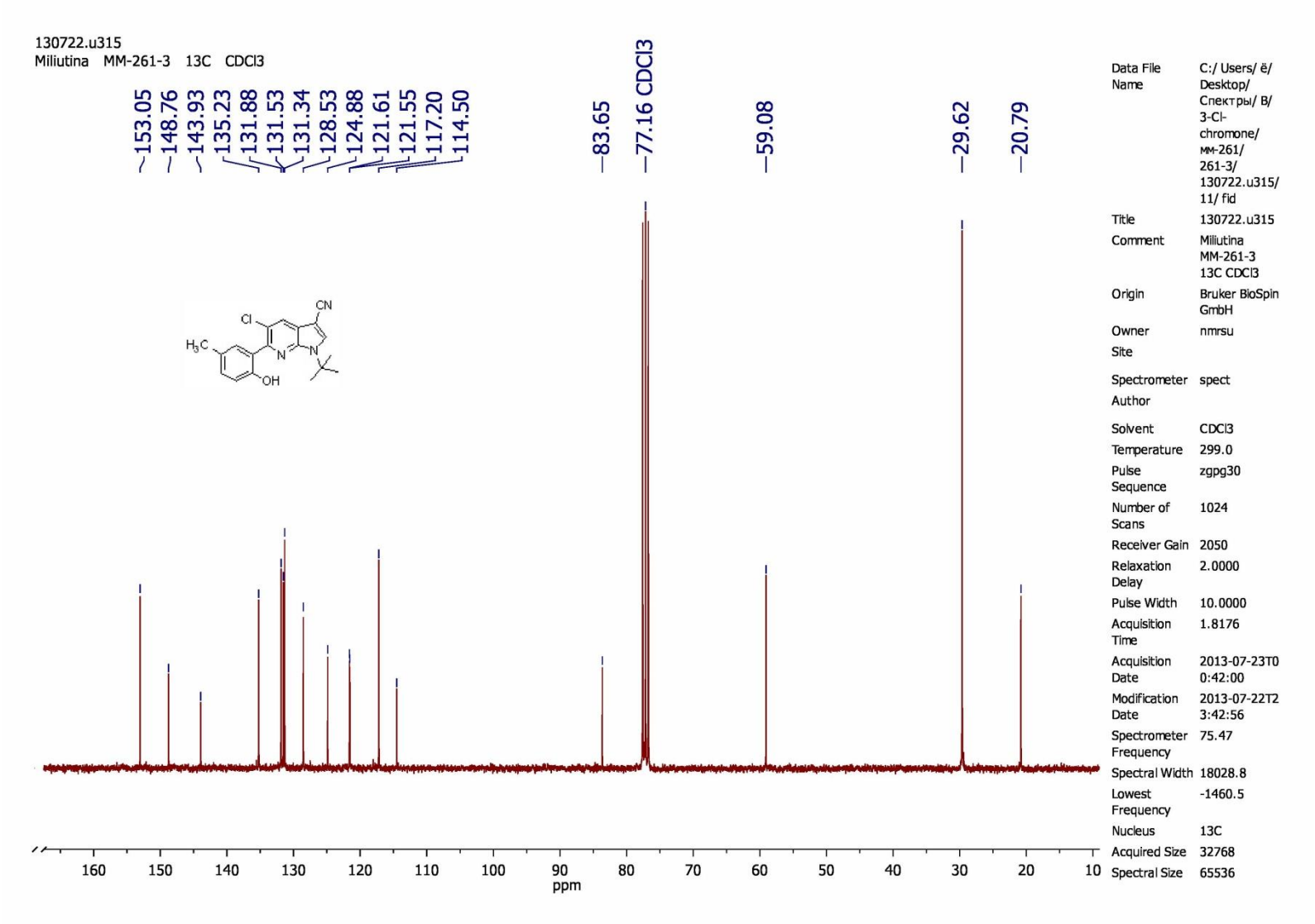
**1-*tert*-Butyl-5-chloro-6-(2-hydroxyphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonitrile (3g).**



**1-*tert*-Butyl-5-chloro-6-(2-hydroxy-5-methylphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonitrile (3h).**



**1-*tert*-Butyl-5-chloro-6-(2-hydroxy-5-methylphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine-3-carbonitrile (3h).**



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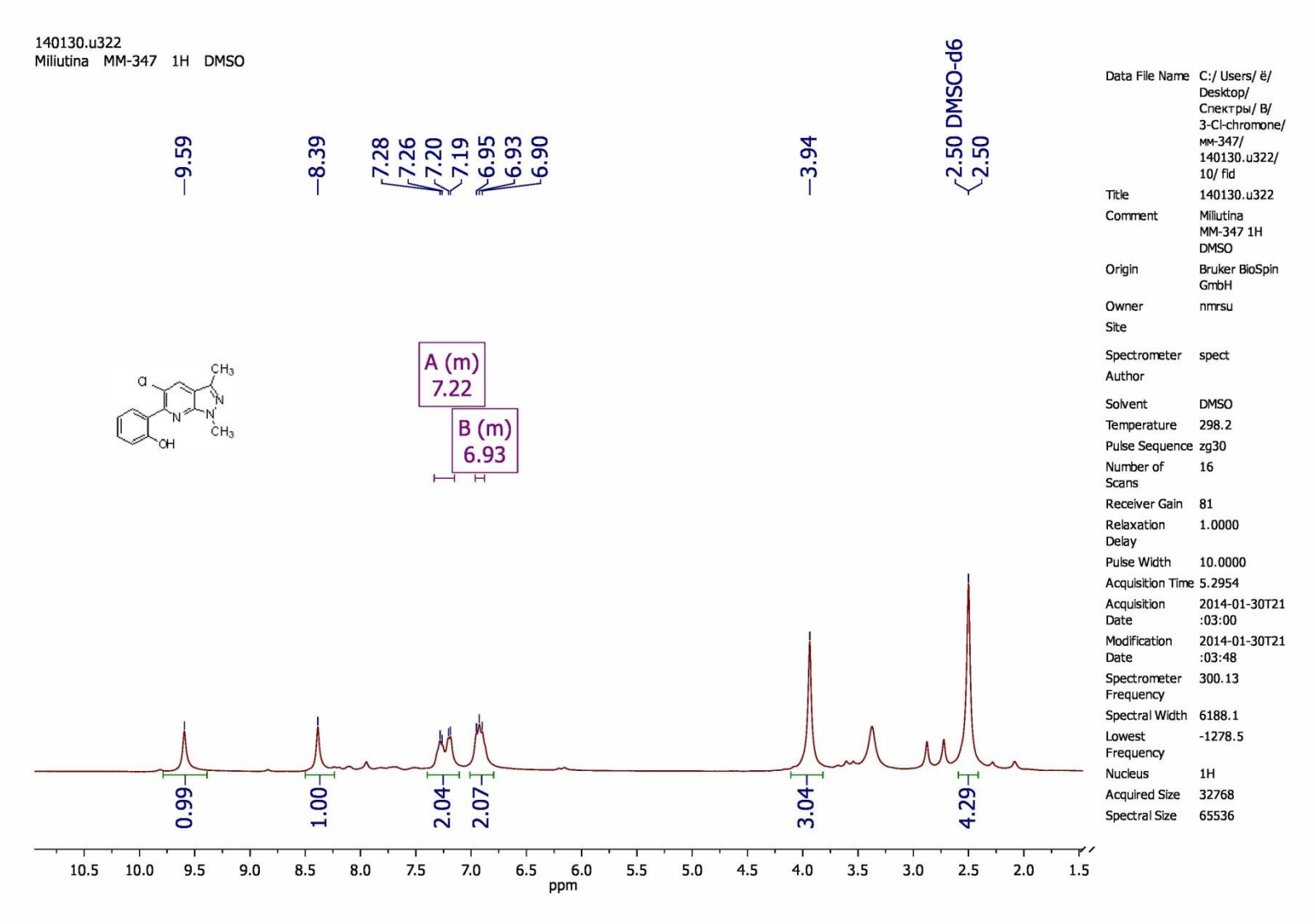
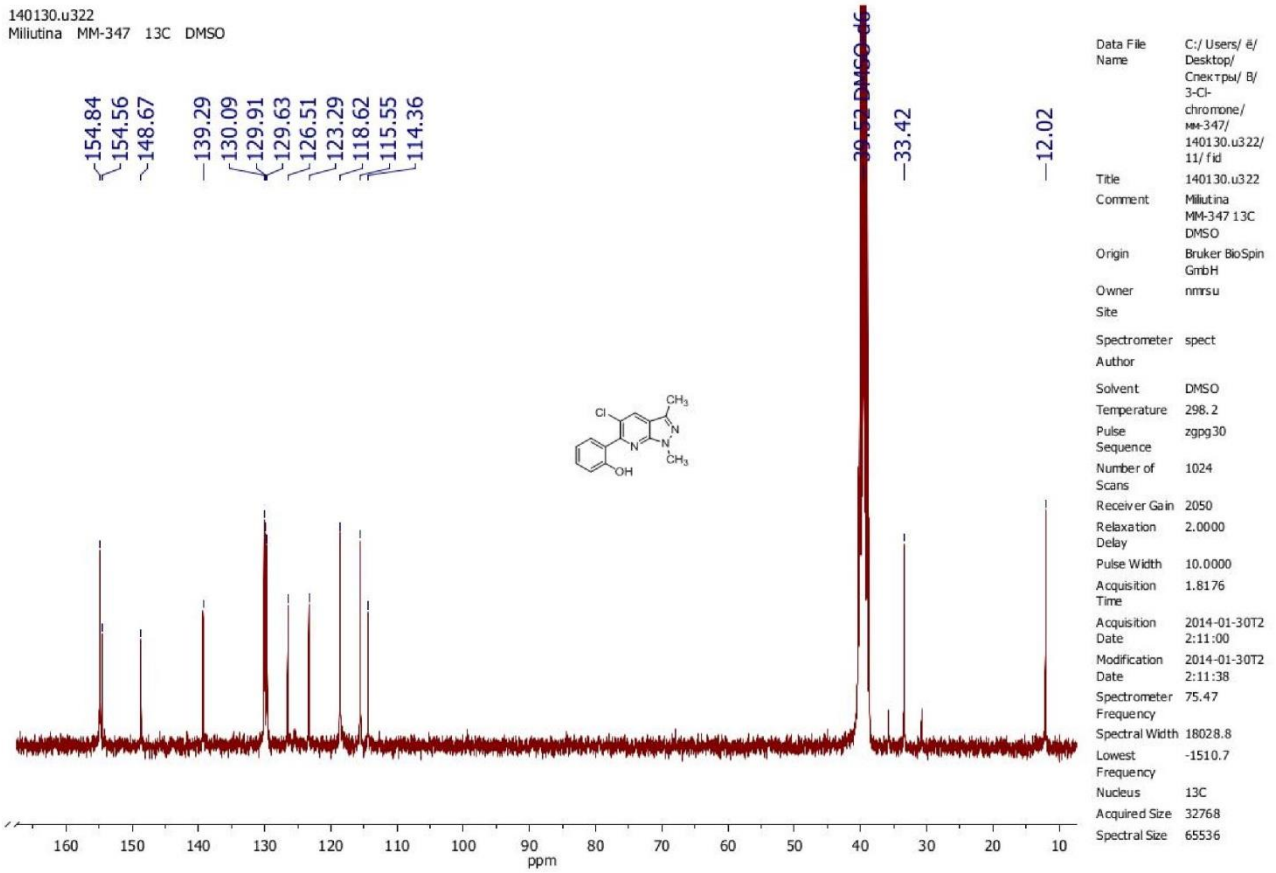
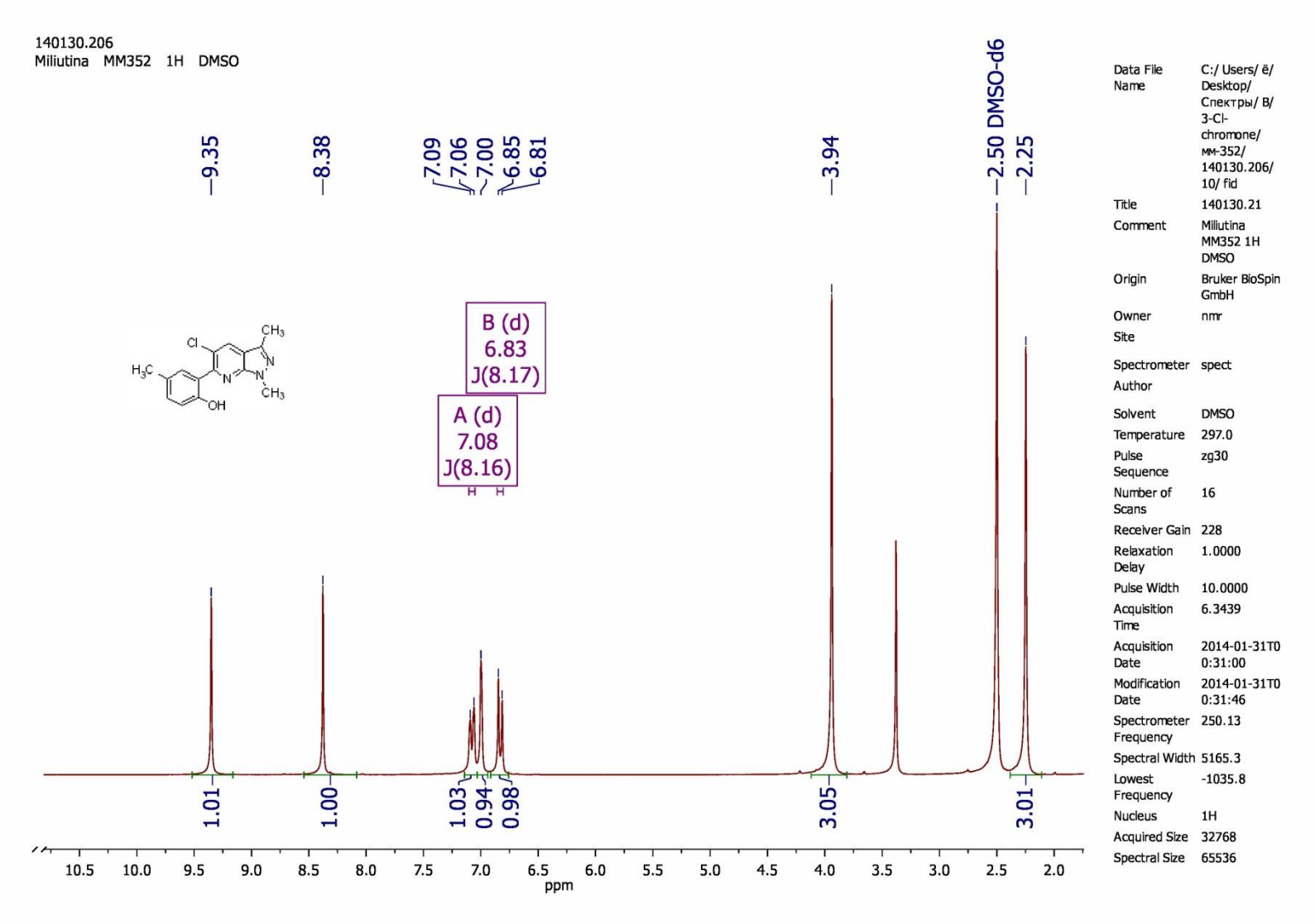


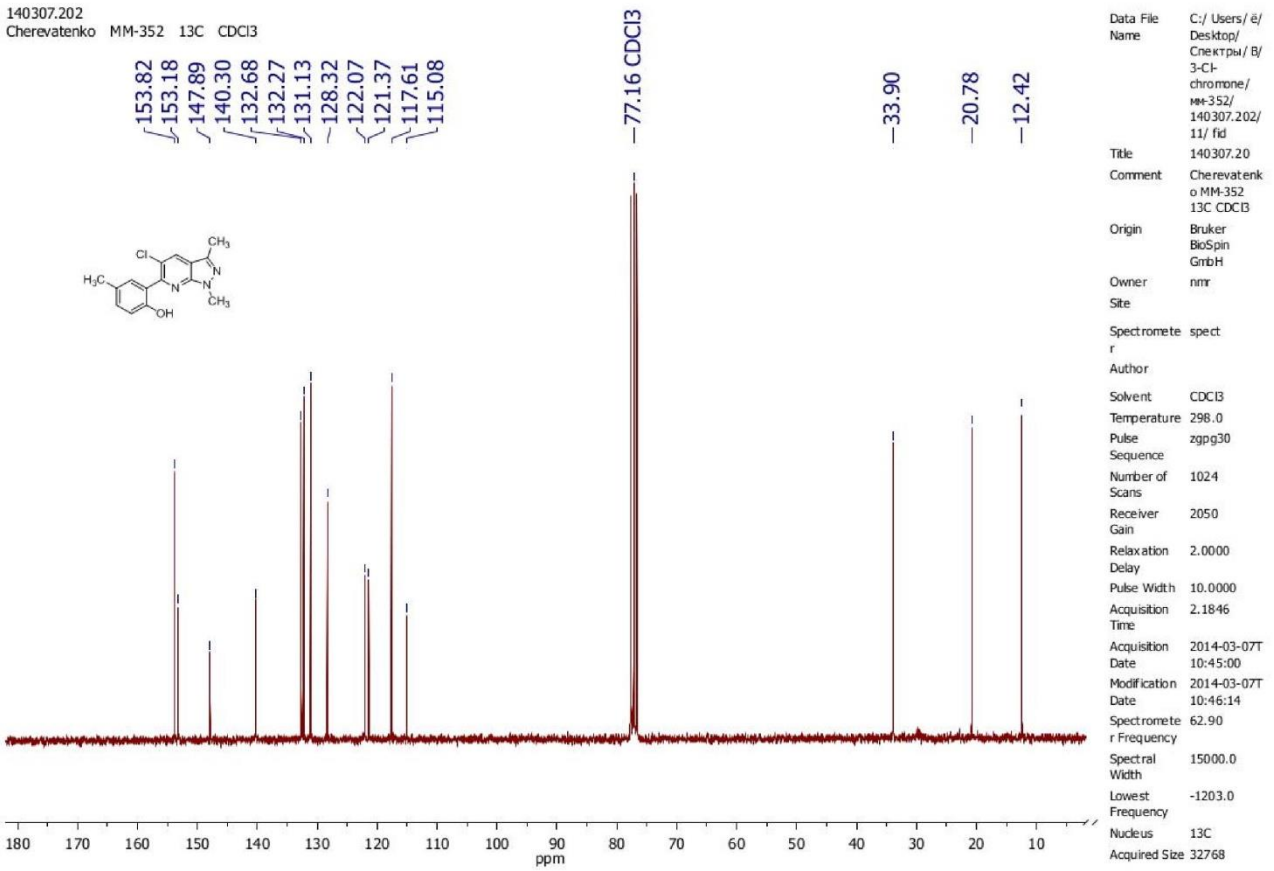
**2-(5-Chloro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3i).**



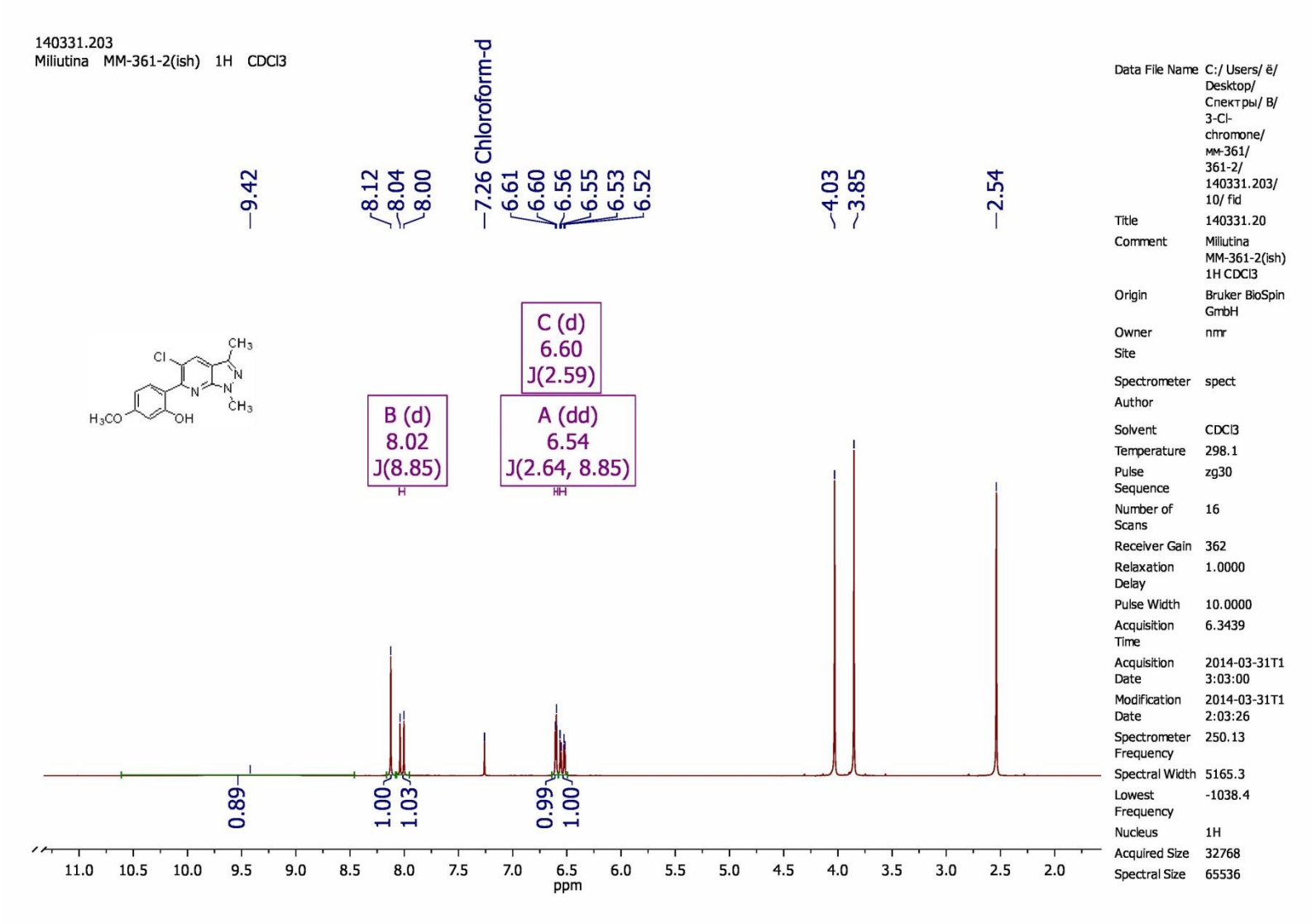
**2-(5-Chloro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-4-methylphenol (3j).**



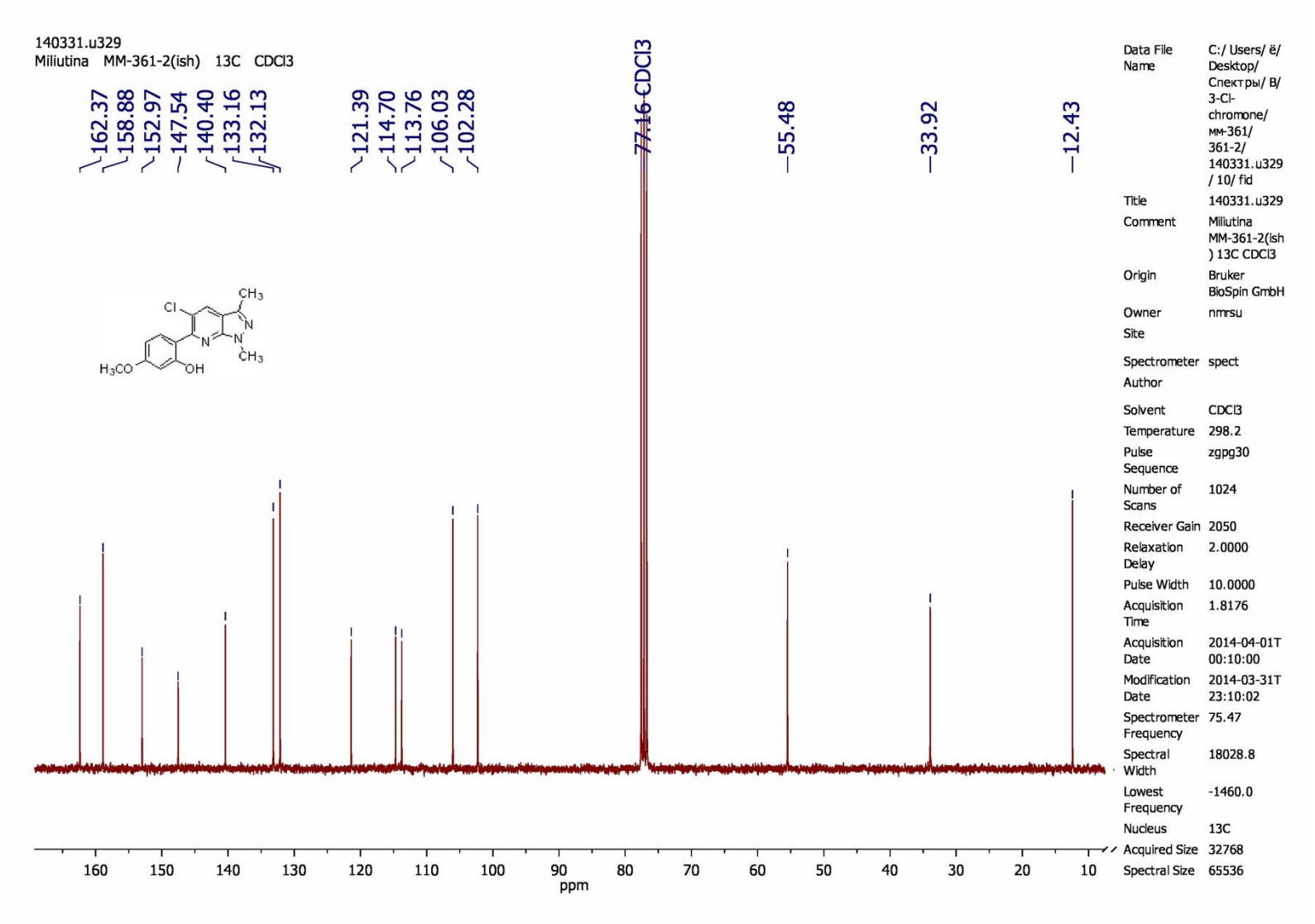
**2-(5-Chloro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-4-methylphenol (3j).**



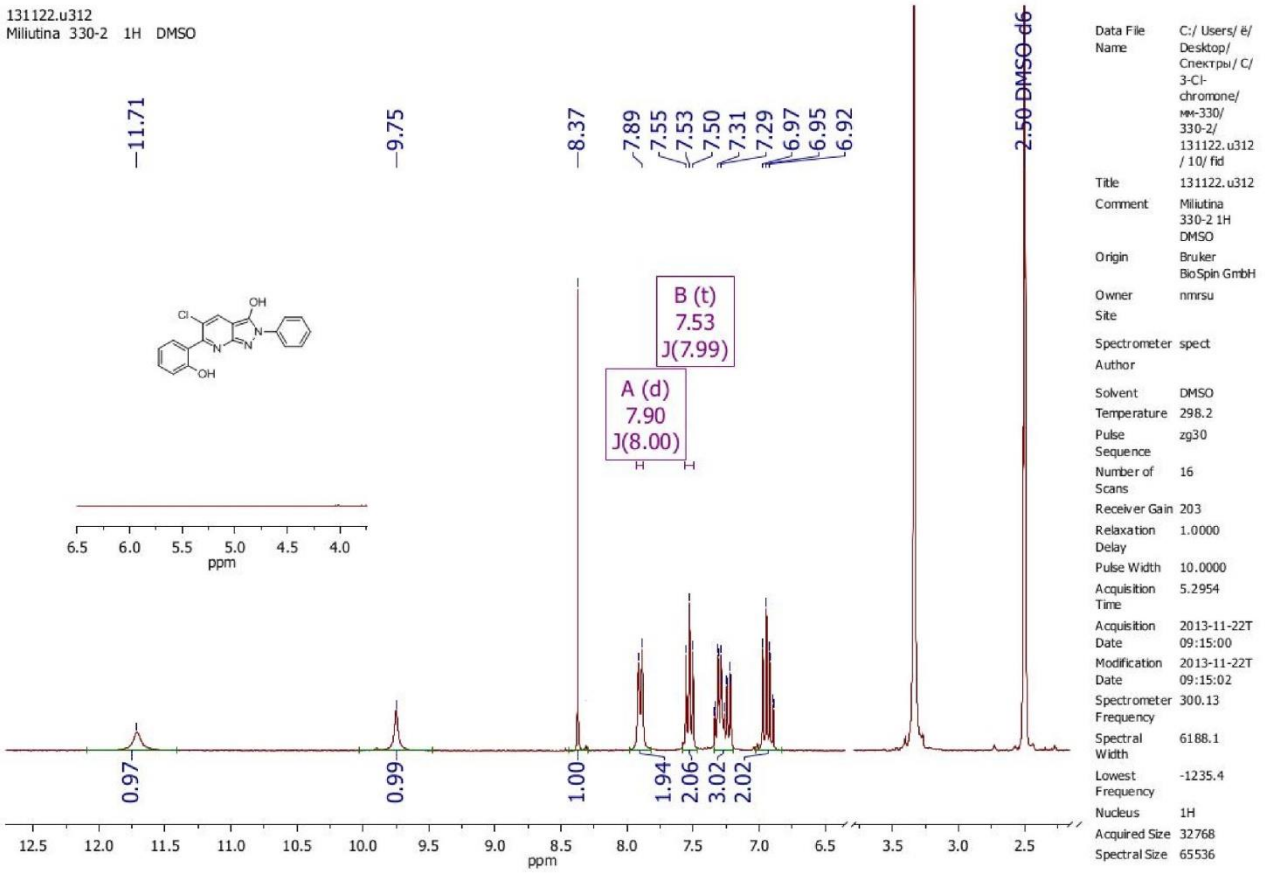
**2-(5-Chloro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-5-methoxyphenol (3k).**



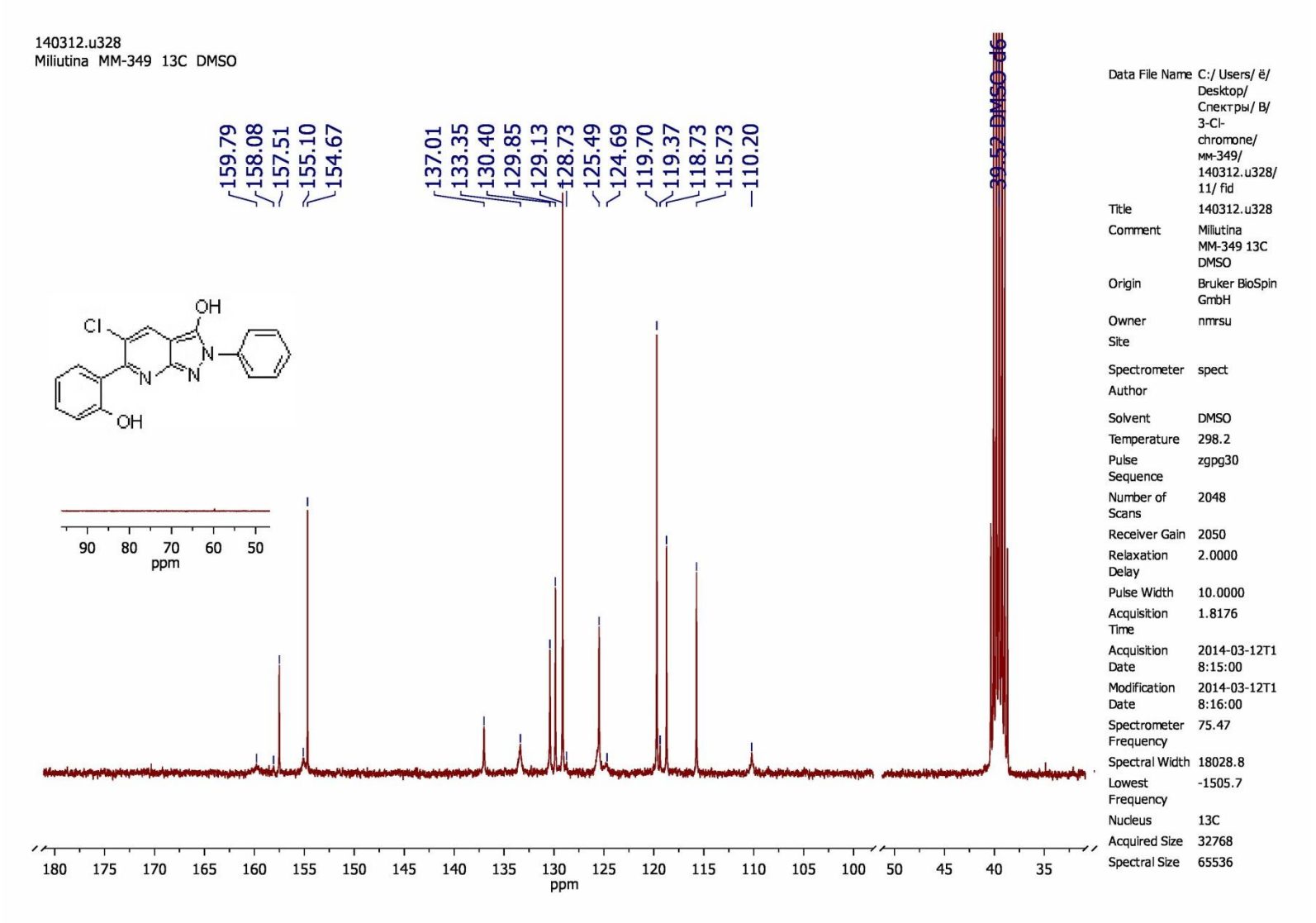
**2-(5-Chloro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)-5-methoxyphenol (3k).**



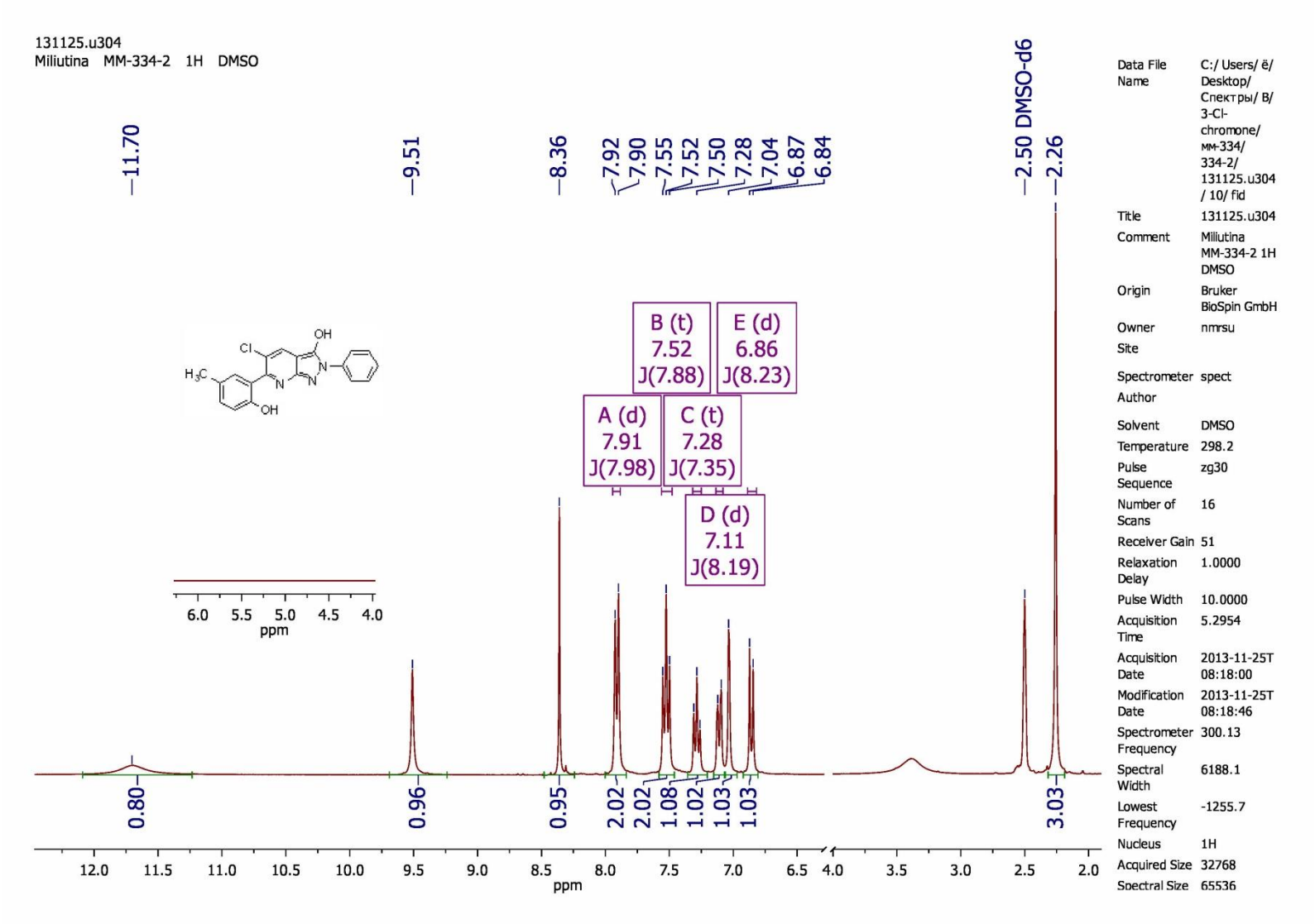
**5-Chloro-6-(2-hydroxyphenyl)-2-phenyl-2*H*-pyrazolo[3,4-*b*]pyridin-3-ol (3l).**



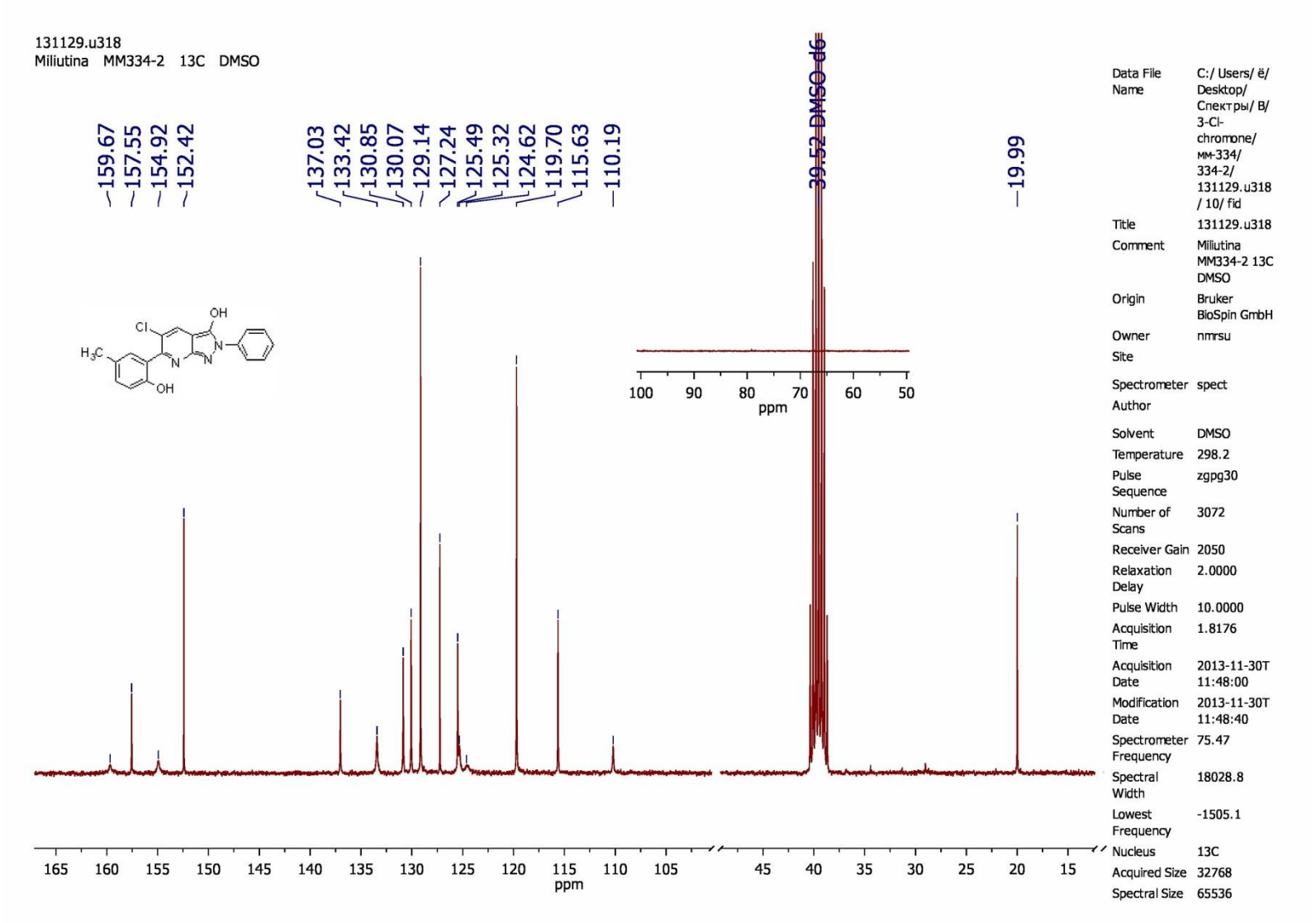
**5-Chloro-6-(2-hydroxyphenyl)-2-phenyl-2*H*-pyrazolo[3,4-*b*]pyridin-3-ol (3l).**



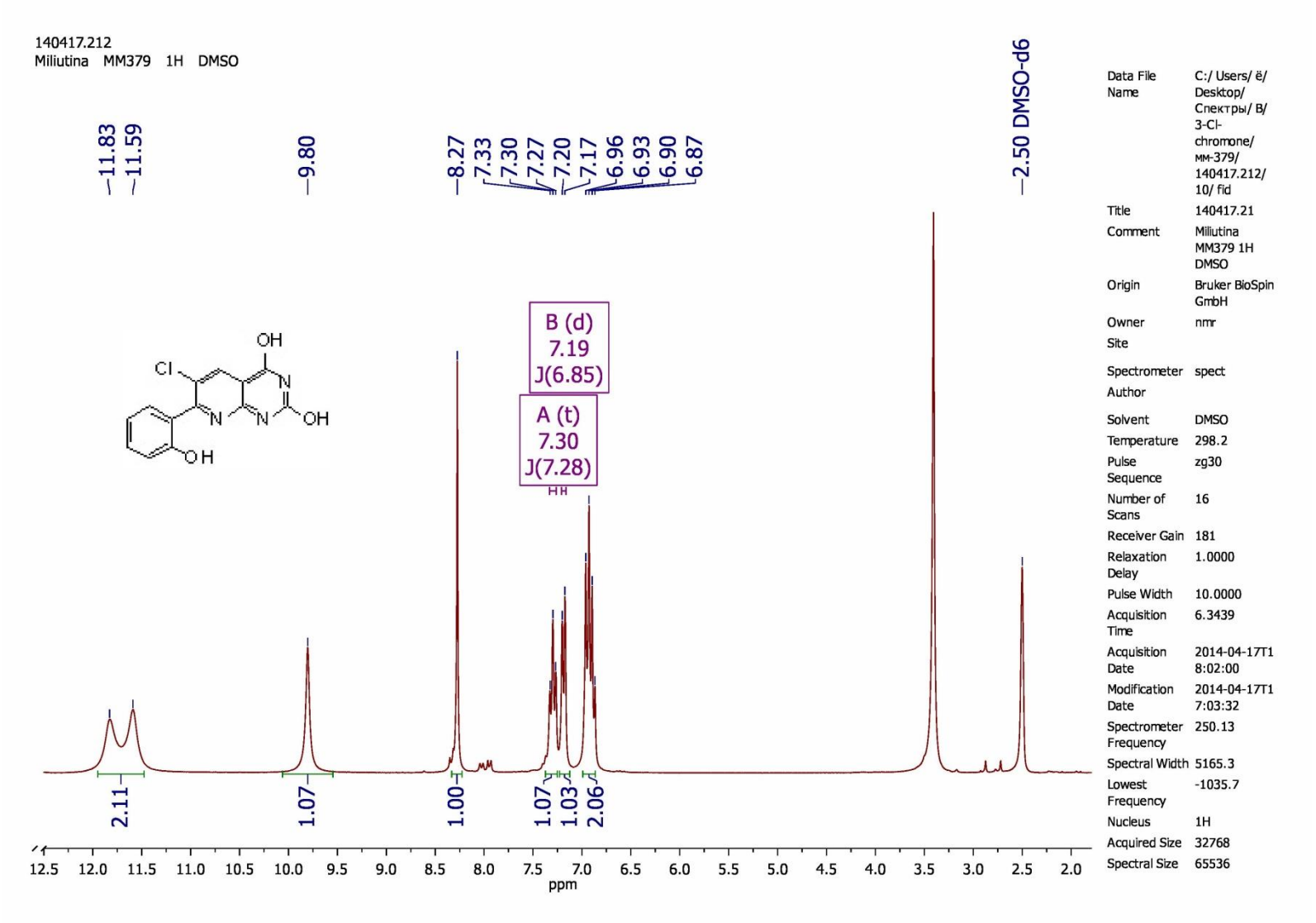
**5-Chloro-6-(2-hydroxy-5-methylphenyl)-2-phenyl-2*H*-pyrazolo[3,4-*b*]pyridin-3-ol (3m).**



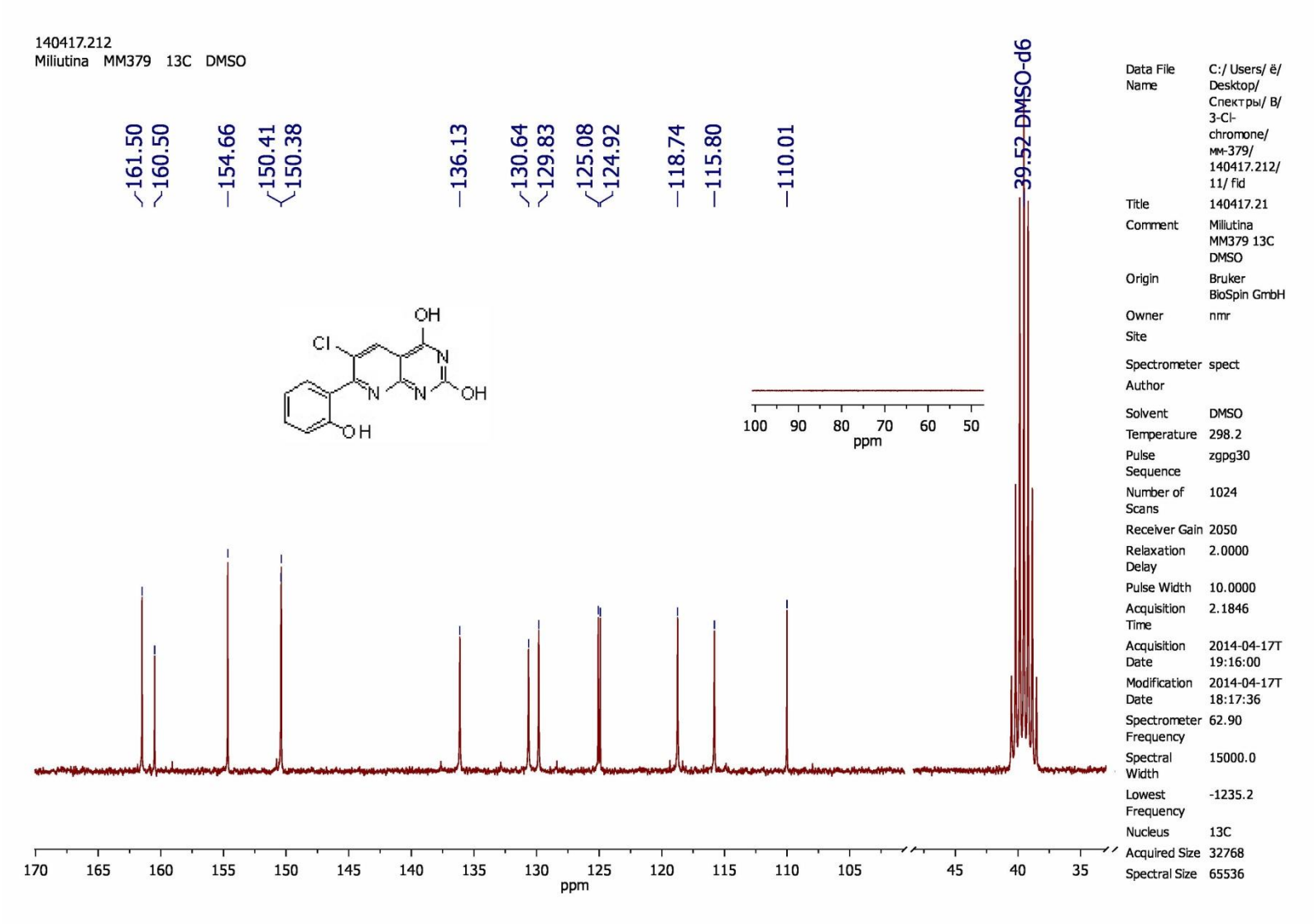
**5-Chloro-6-(2-hydroxy-5-methylphenyl)-2-phenyl-2*H*-pyrazolo[3,4-*b*]pyridin-3-ol (3m).**



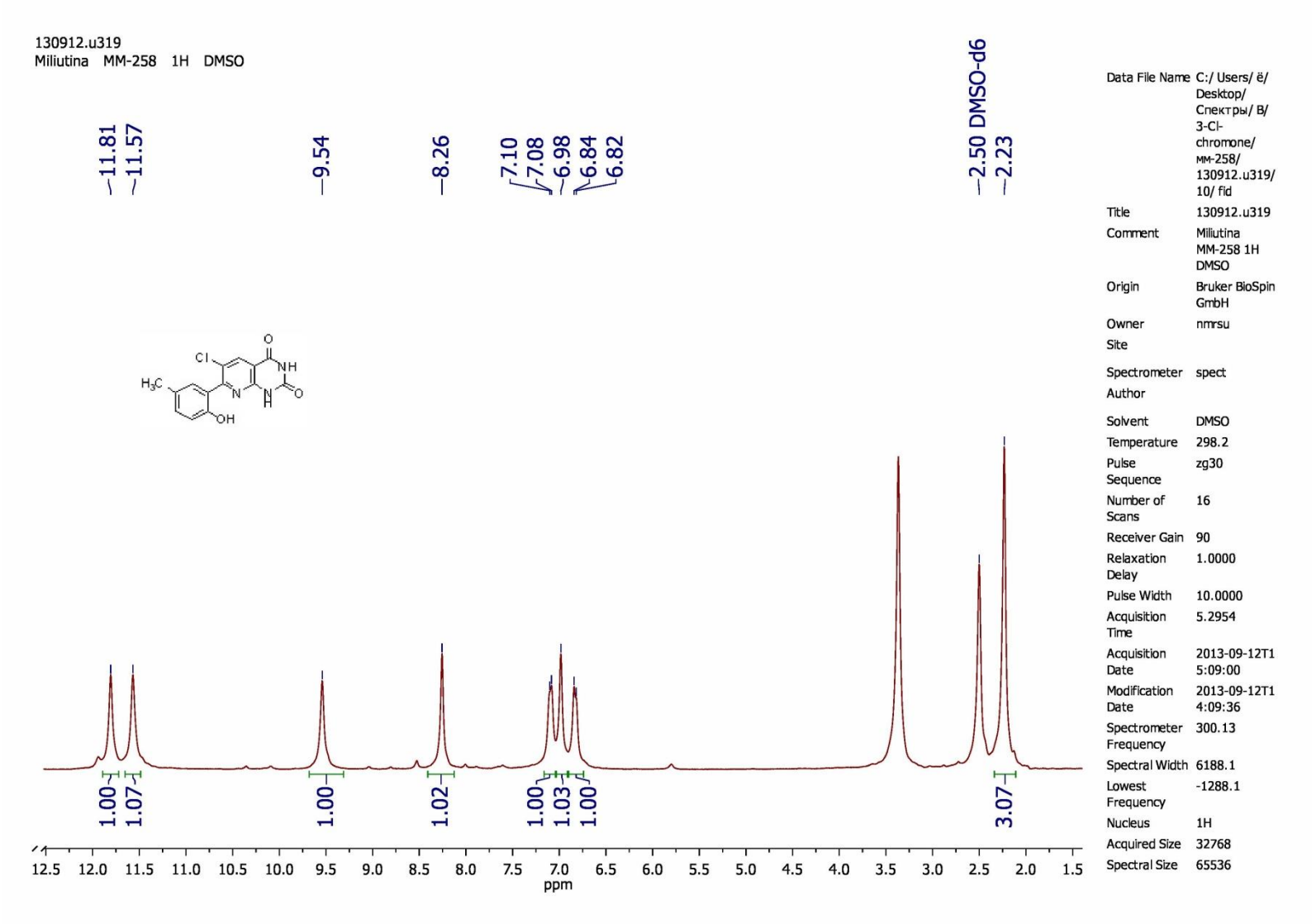
**6-Chloro-7-(2-hydroxyphenyl)pyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3n).**



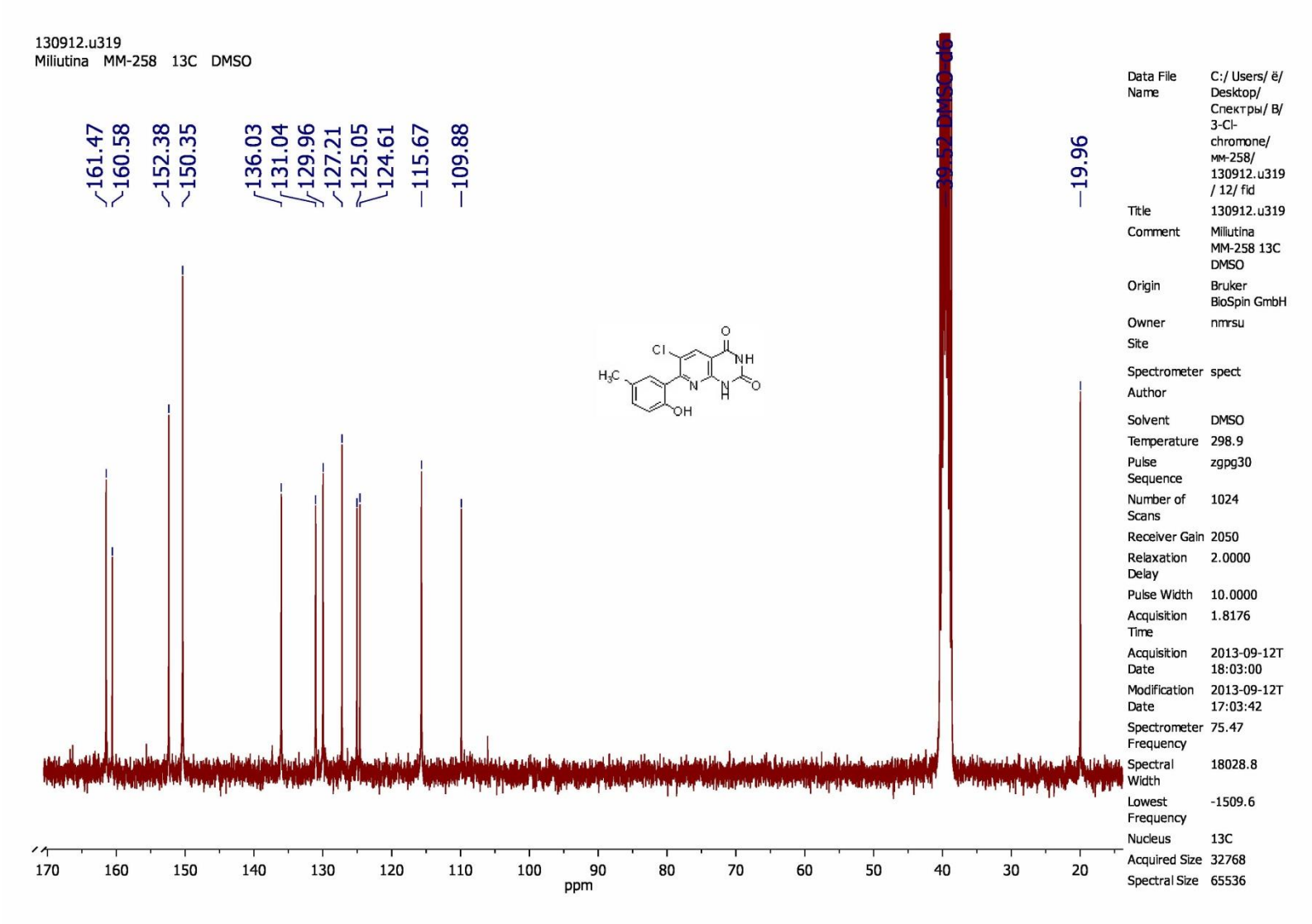
**6-Chloro-7-(2-hydroxyphenyl)pyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3n).**



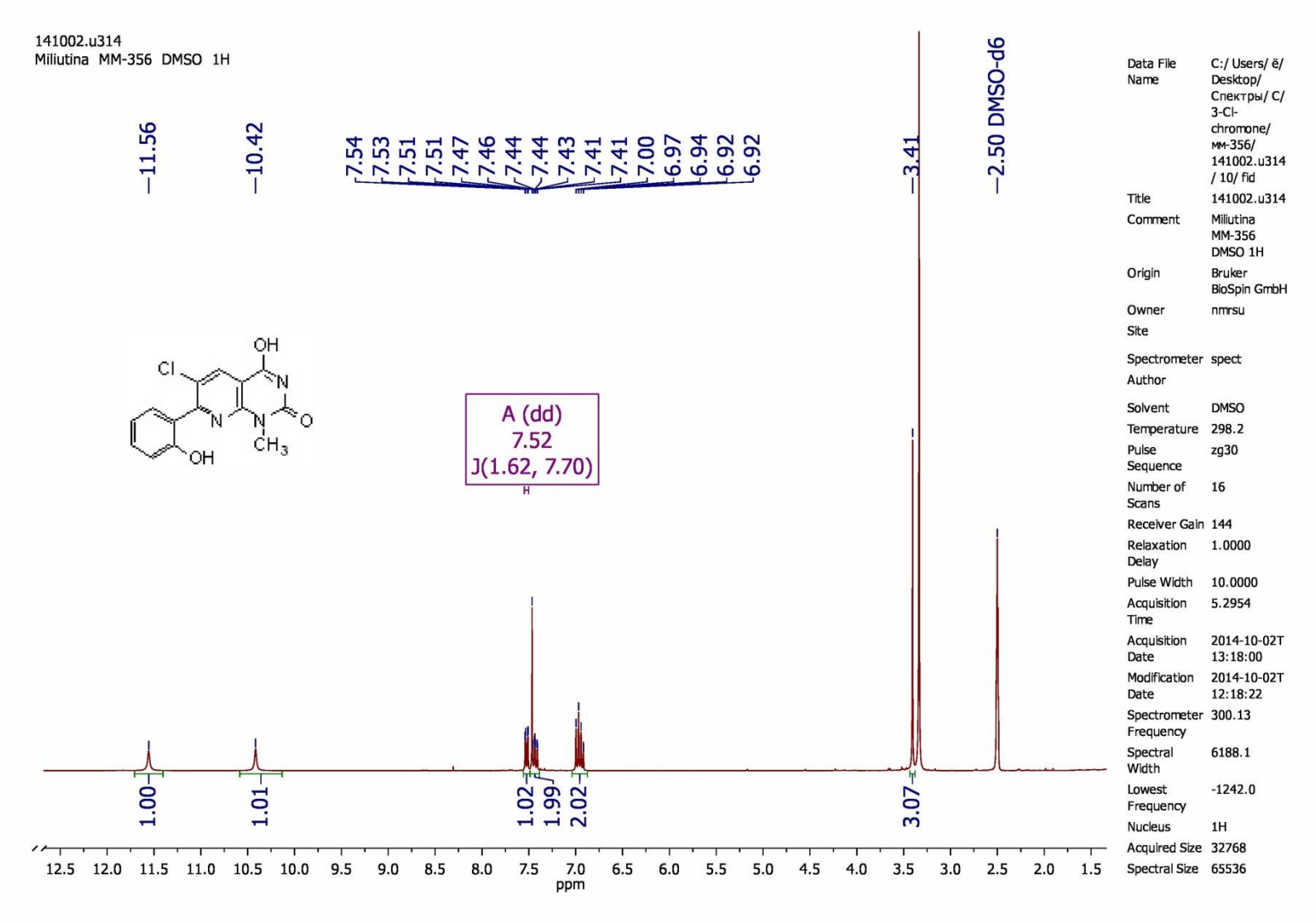
**6-Chloro-7-(2-hydroxy-5-methylphenyl)pyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3o).**



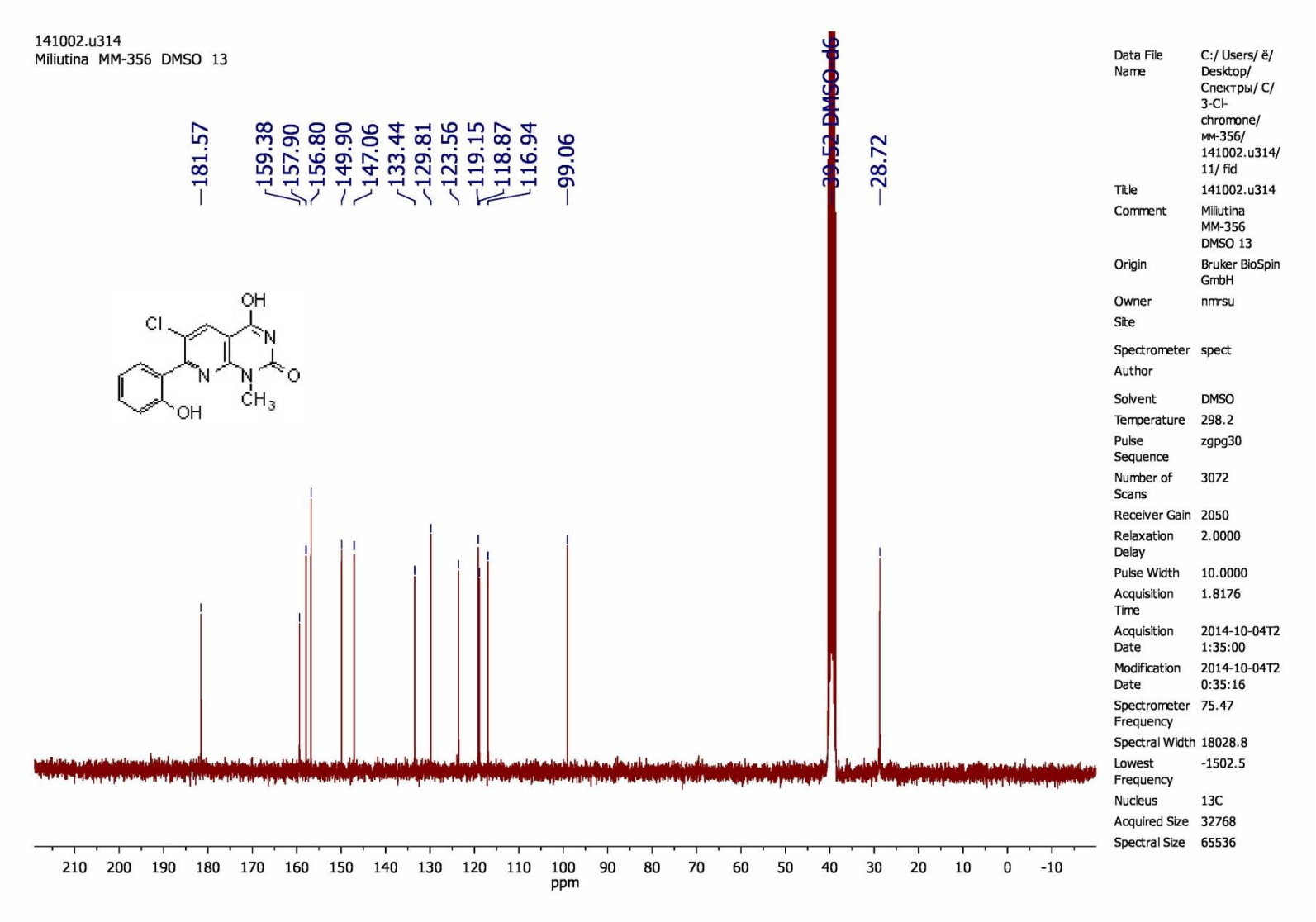
**6-Chloro-7-(2-hydroxy-5-methylphenyl)pyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3o).**



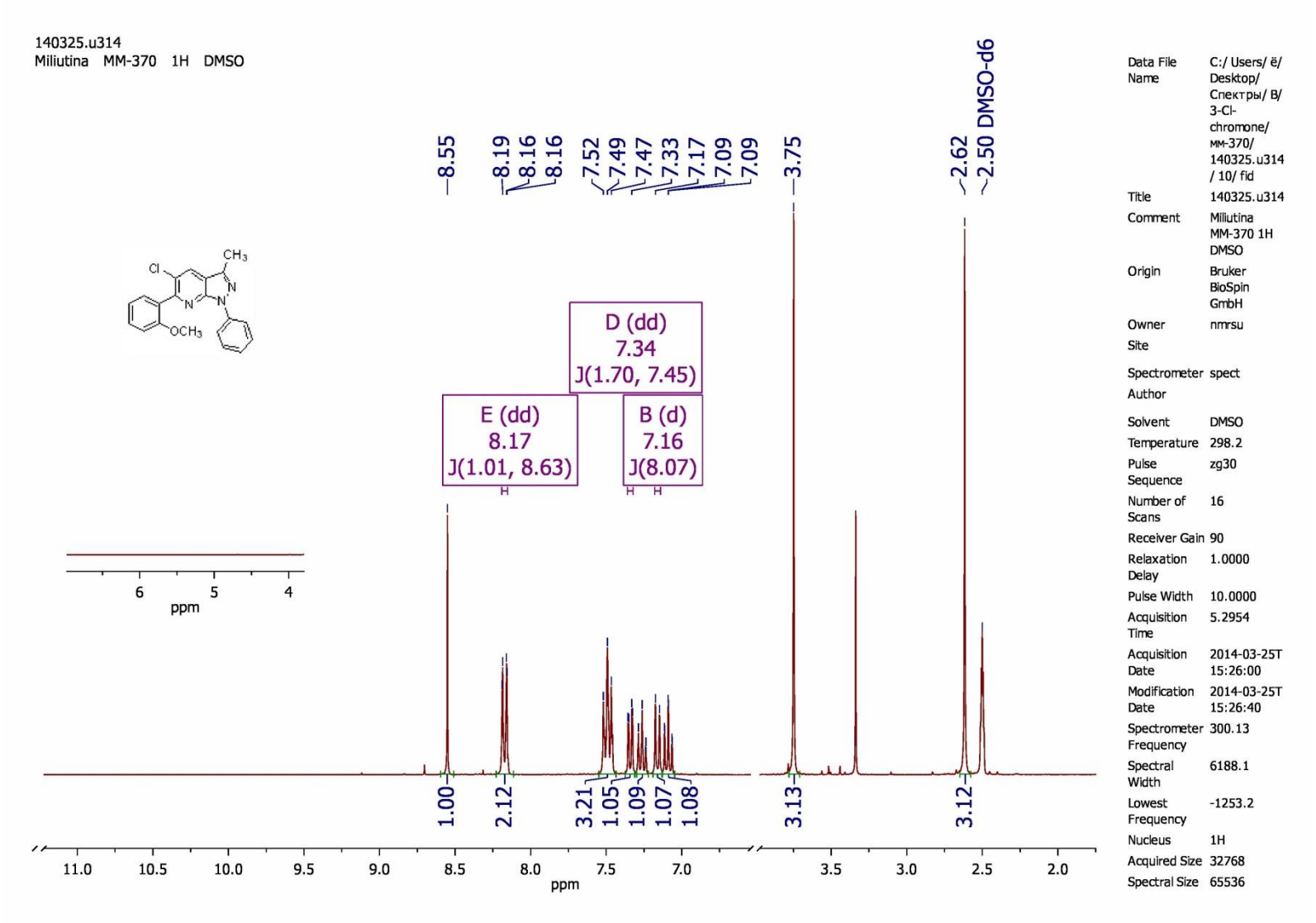
**6-Chloro-7-(2-hydroxyphenyl)-1-methylpyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3p).**



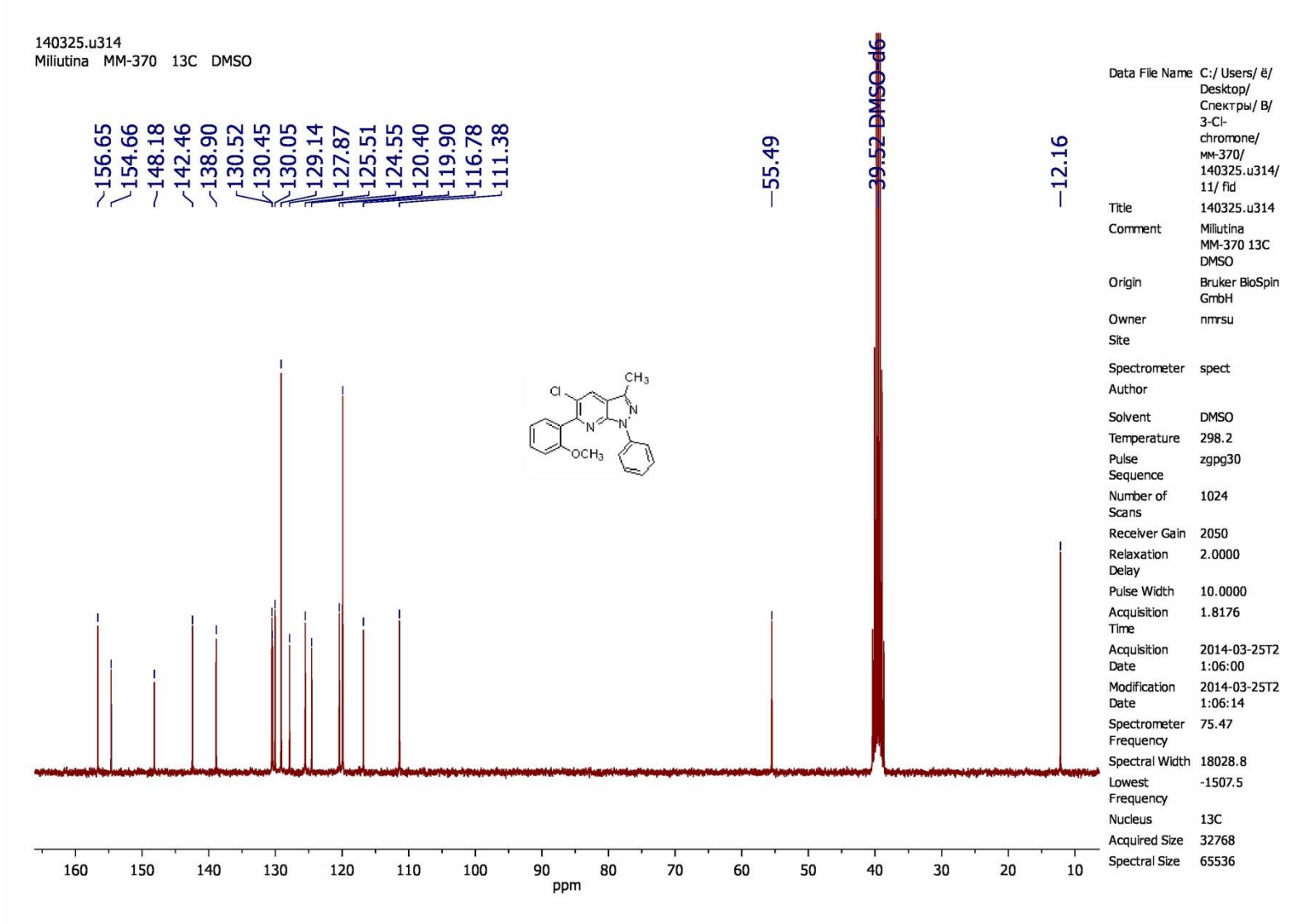
**6-Chloro-7-(2-hydroxyphenyl)-1-methylpyrido[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (3p).**



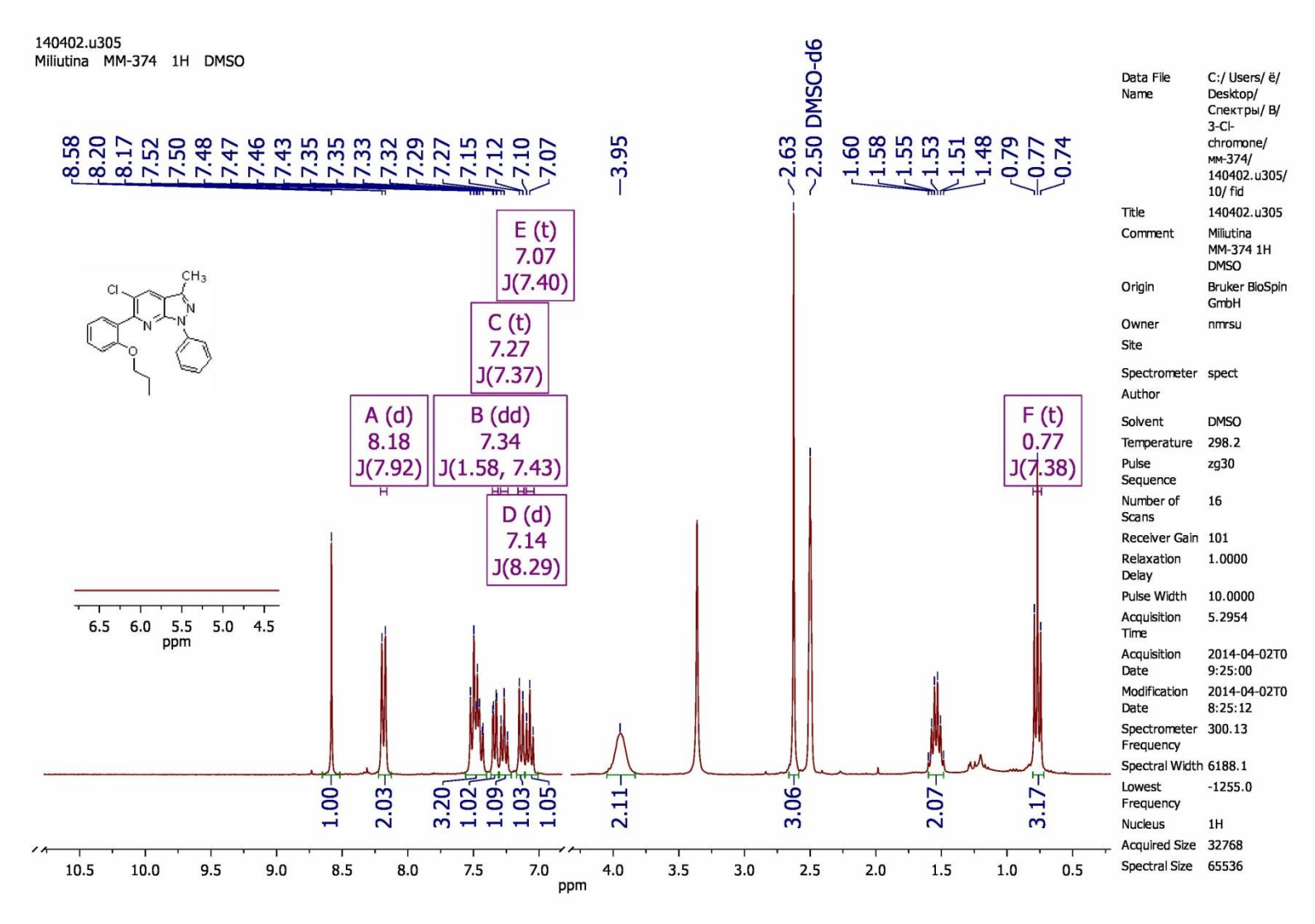
**5-Chloro-6-(2-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (3q).**



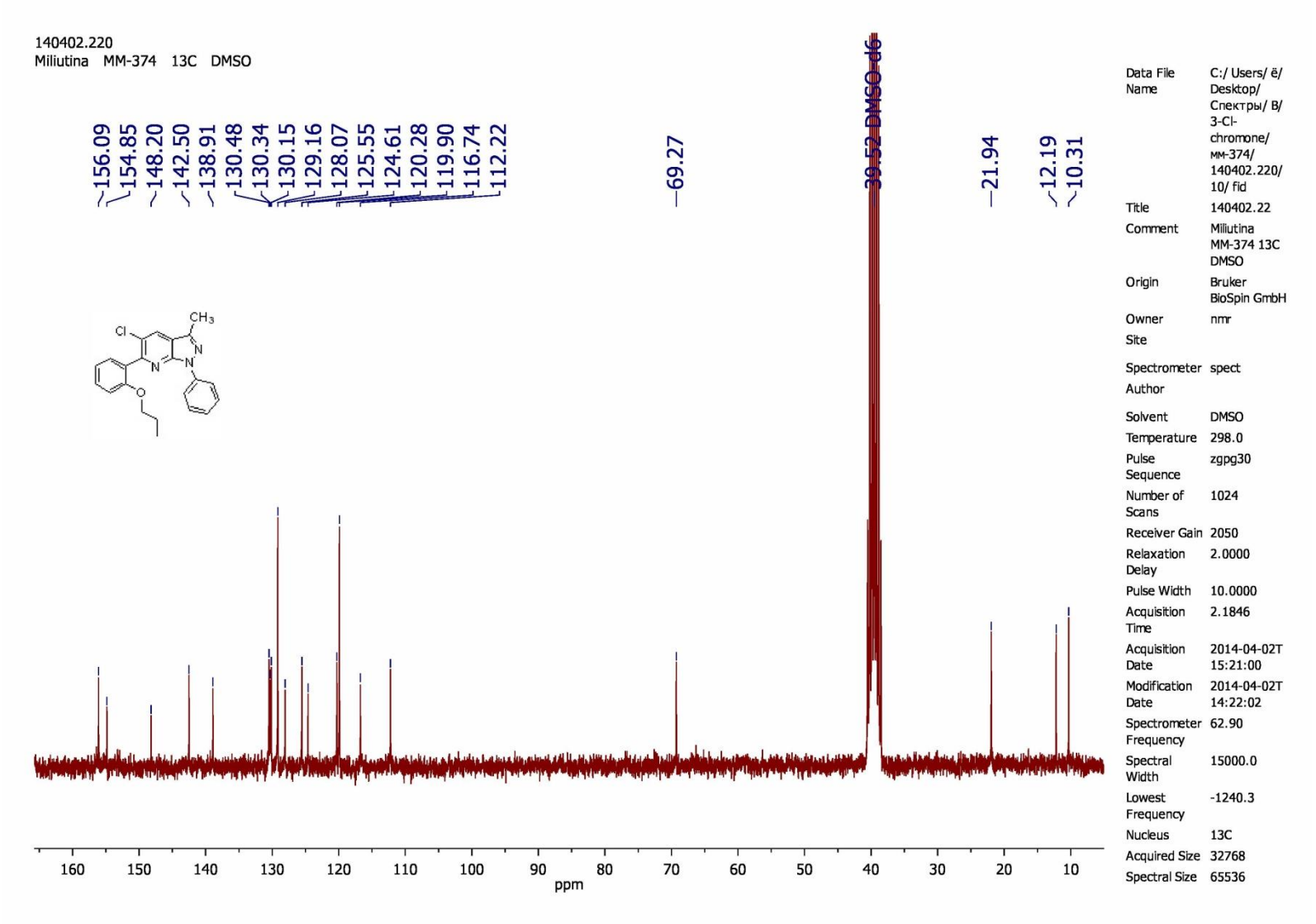
**5-Chloro-6-(2-methoxyphenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (3q).**



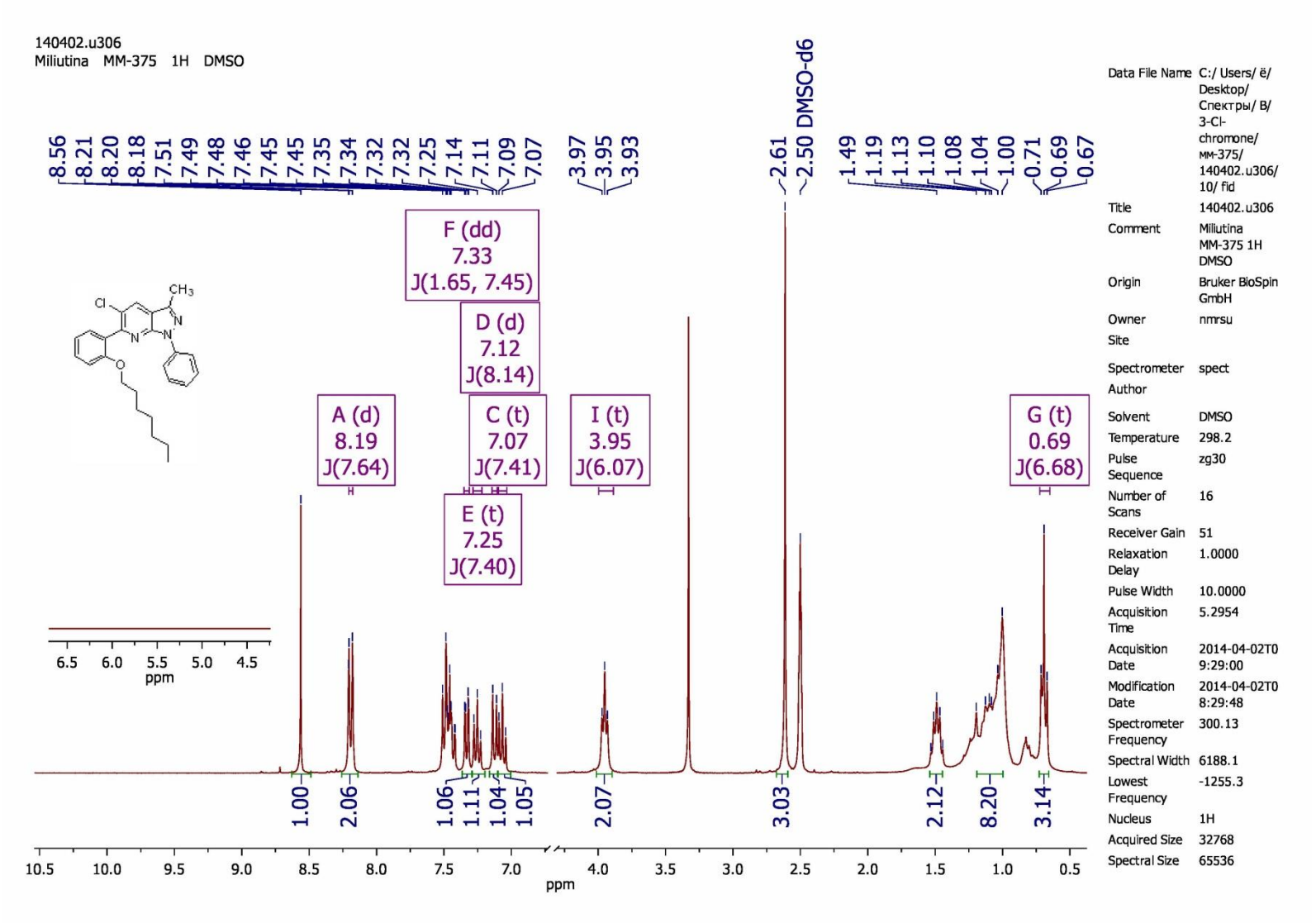
**5-Chloro-3-methyl-1-phenyl-6-(2-propoxyphenyl)-1*H*-pyrazolo[3,4-*b*]pyridine (3r).**



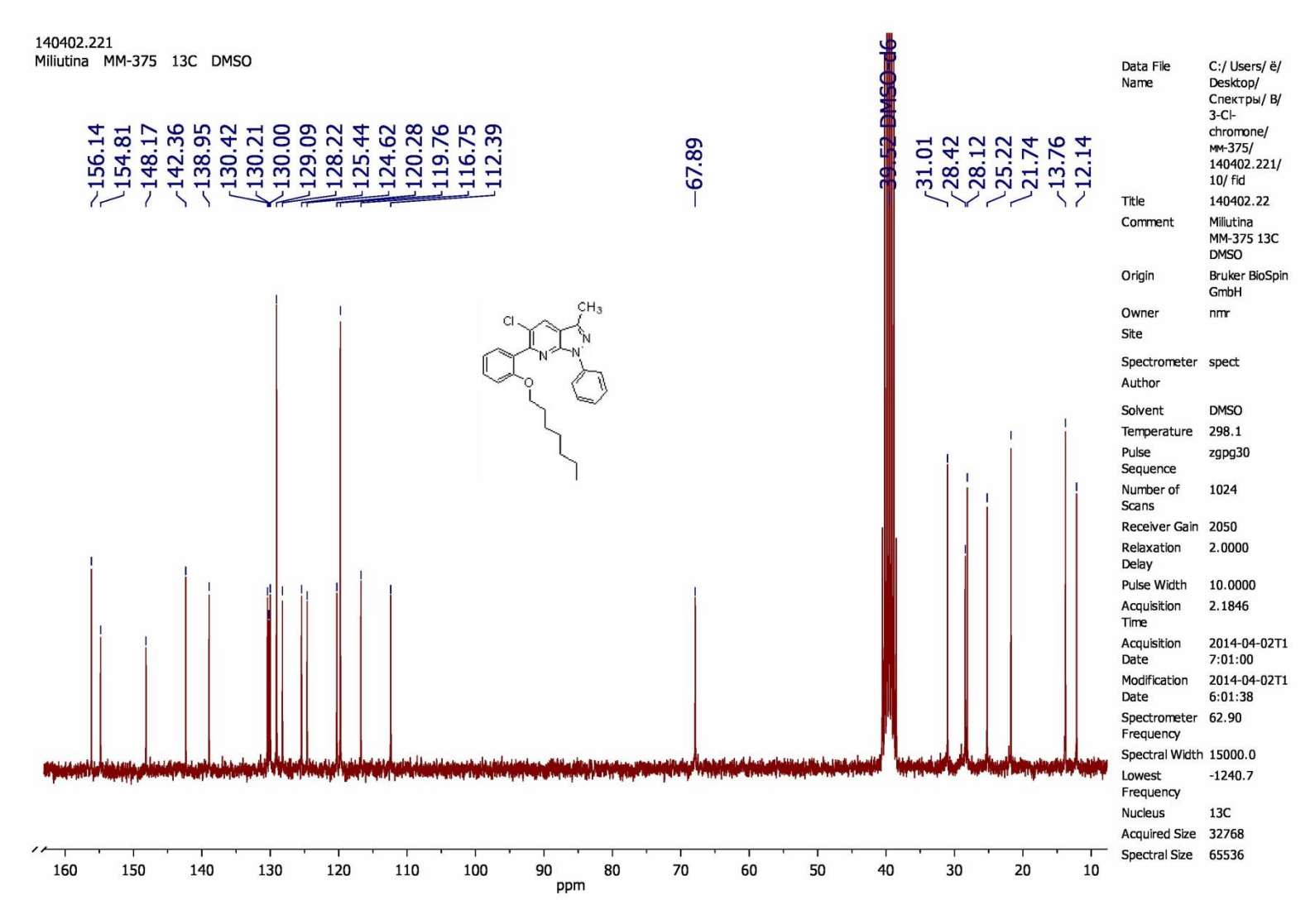
**5-Chloro-3-methyl-1-phenyl-6-(2-propoxyphenyl)-1*H*-pyrazolo[3,4-*b*]pyridine (3r).**



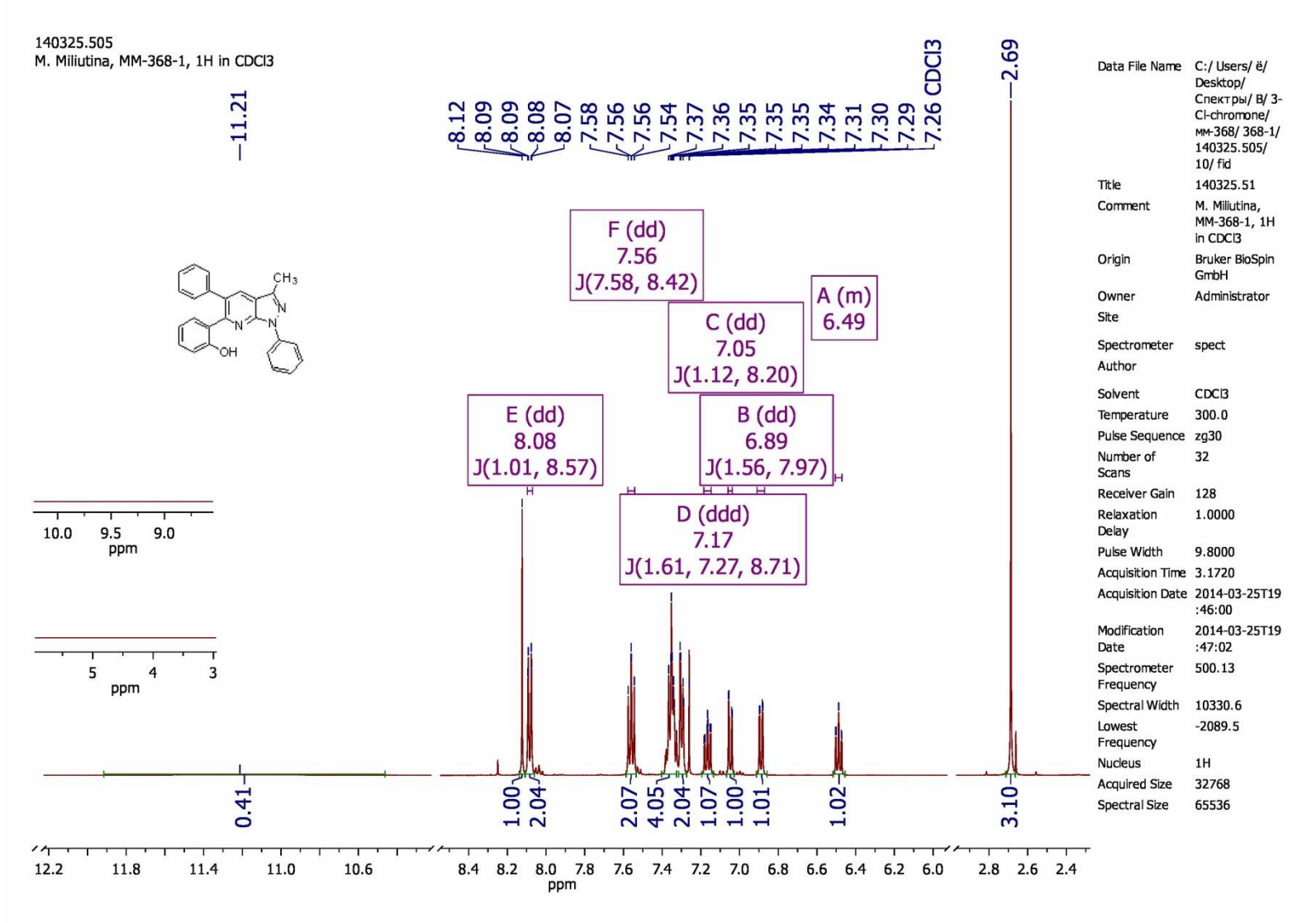
**5-Chloro-6-(2-(heptyloxy)phenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (3s).**



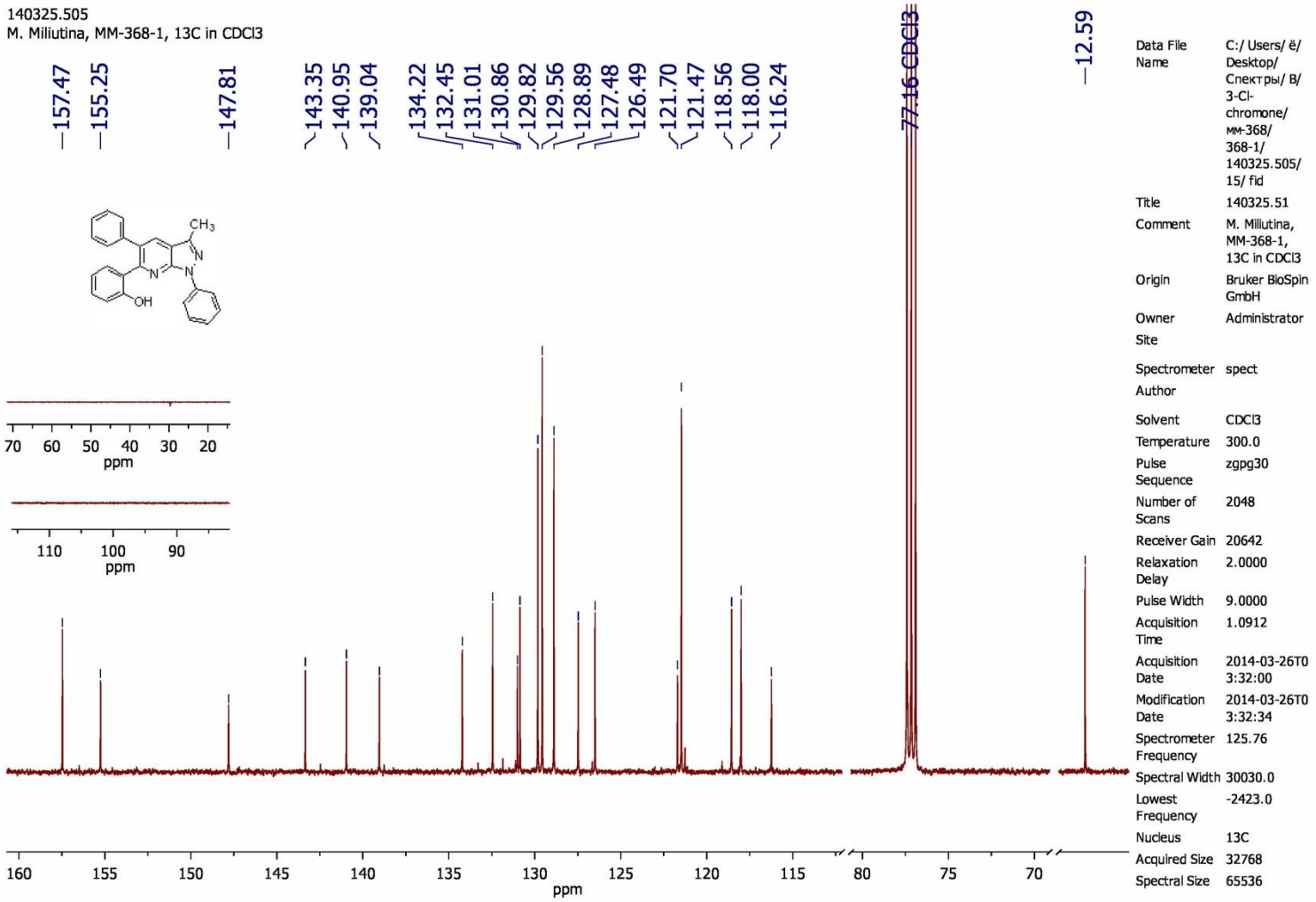
**5-Chloro-6-(2-(heptyloxy)phenyl)-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (3s).**



**2-(3-Methyl-1,5-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3t).**

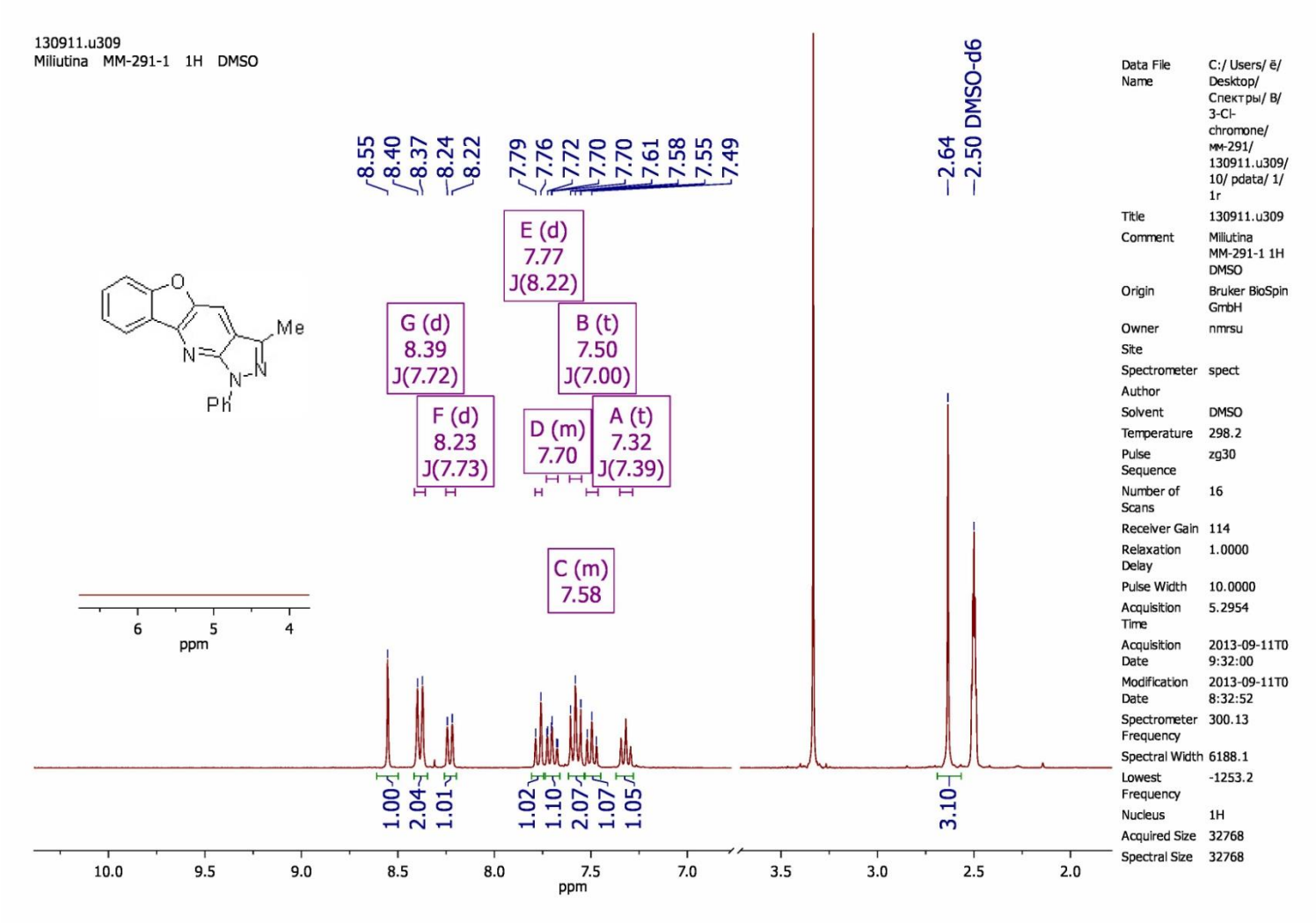


**2-(3-Methyl-1,5-diphenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-yl)phenol (3t).**

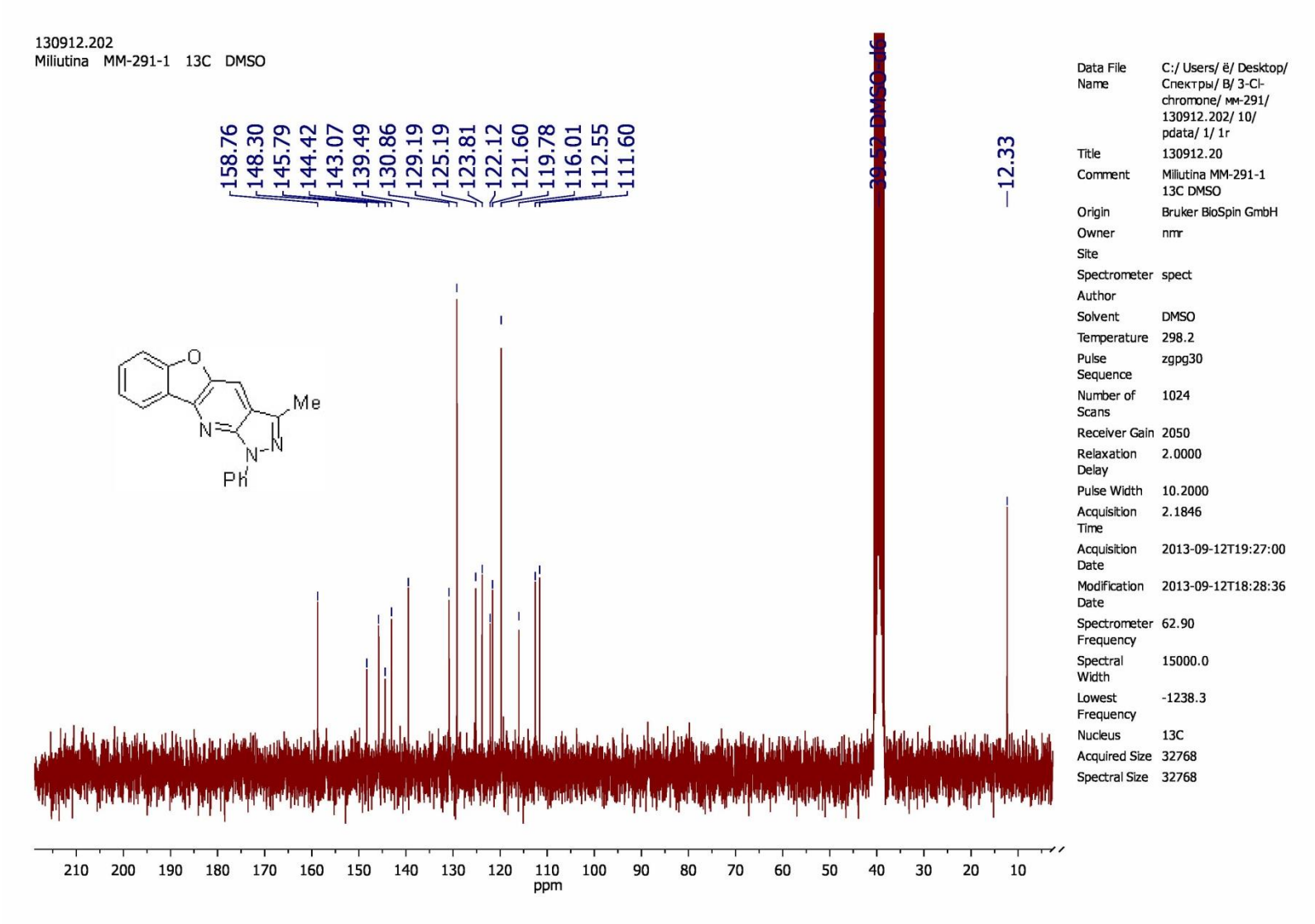


## 1H and 13C NMR spectra of products 4.

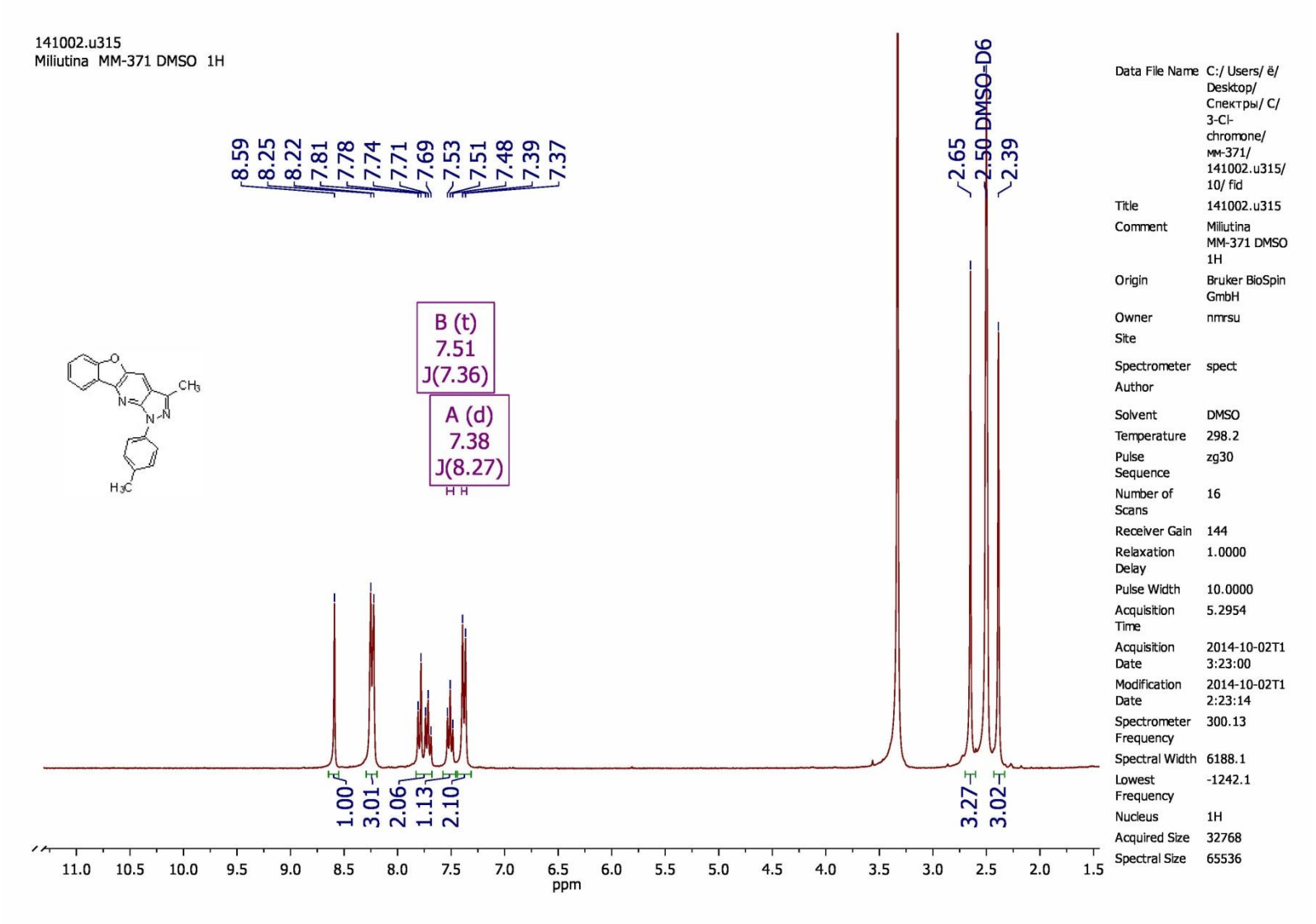
**3-Methyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4a).**



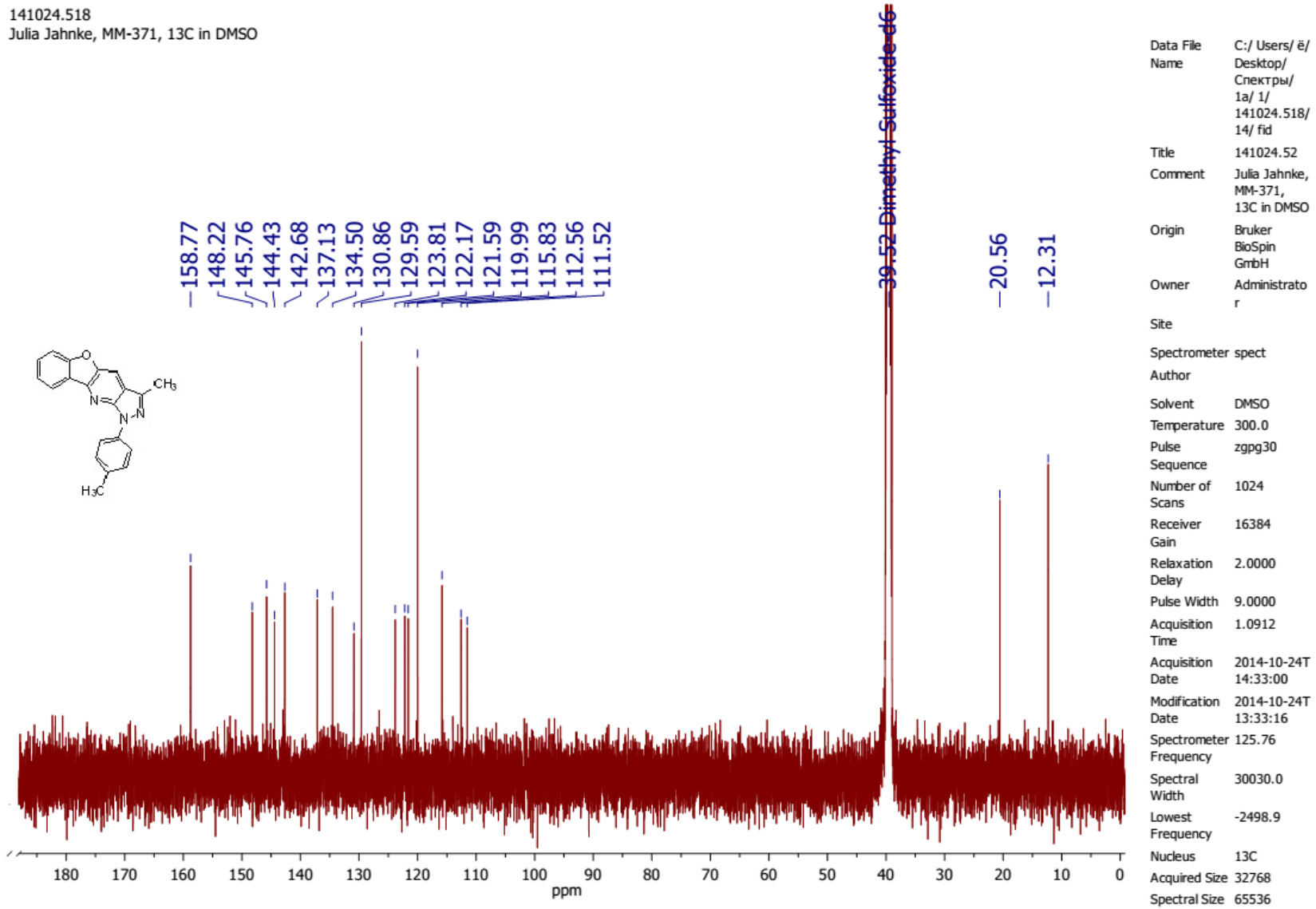
**3-Methyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4a).**



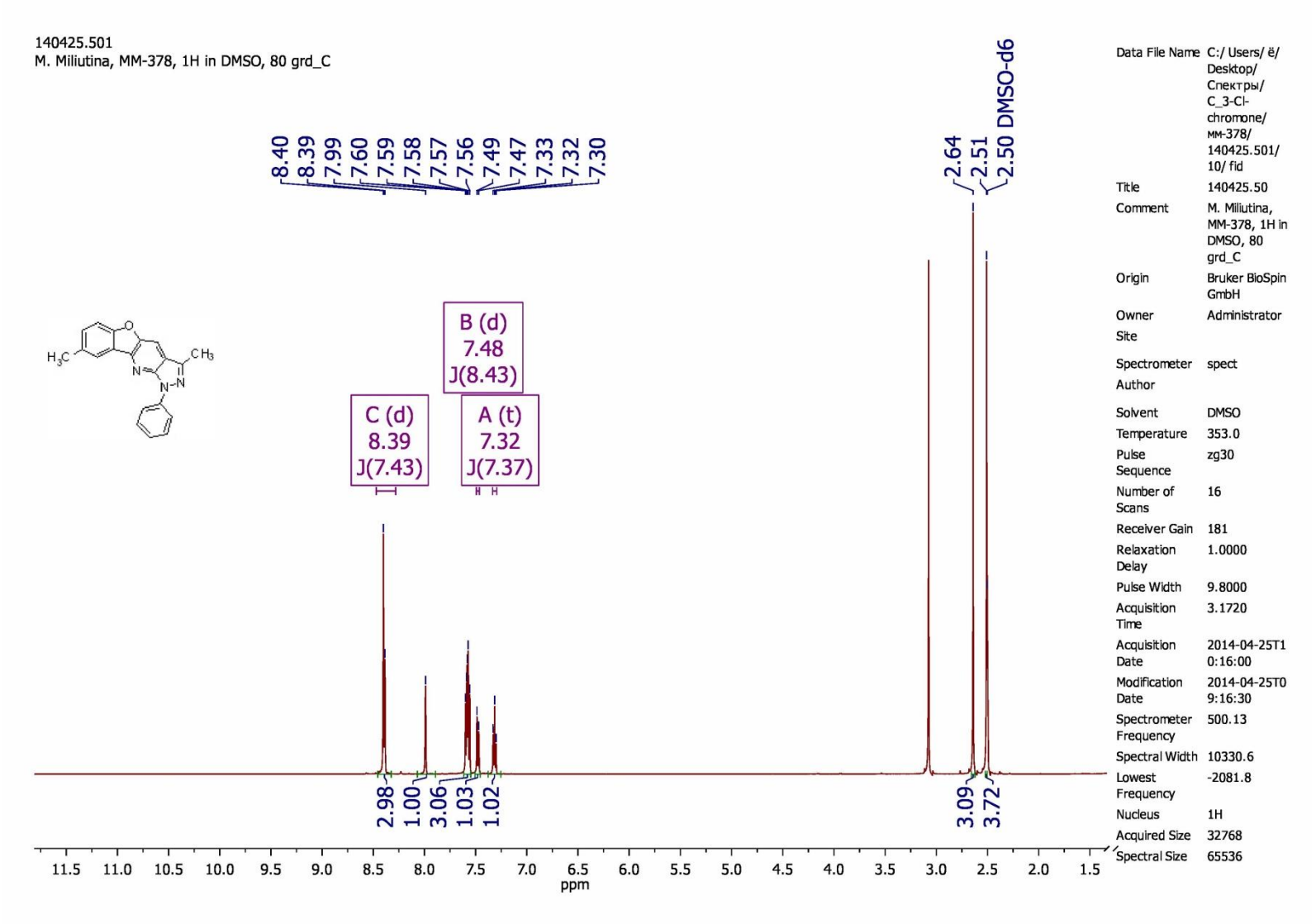
**3-Methyl-1-*p*-tolyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4b).**



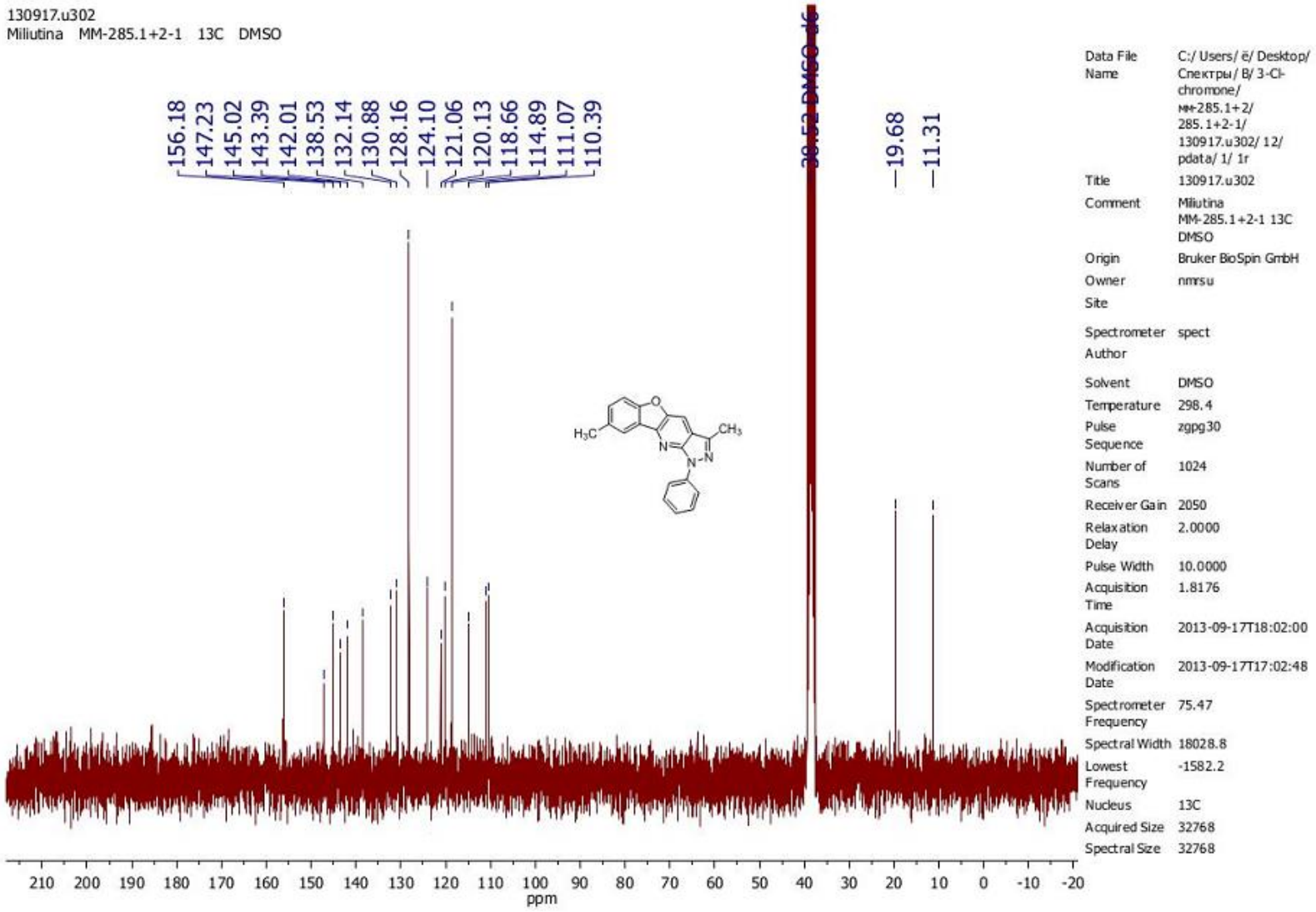
**3-Methyl-1-*p*-tolyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4b).**



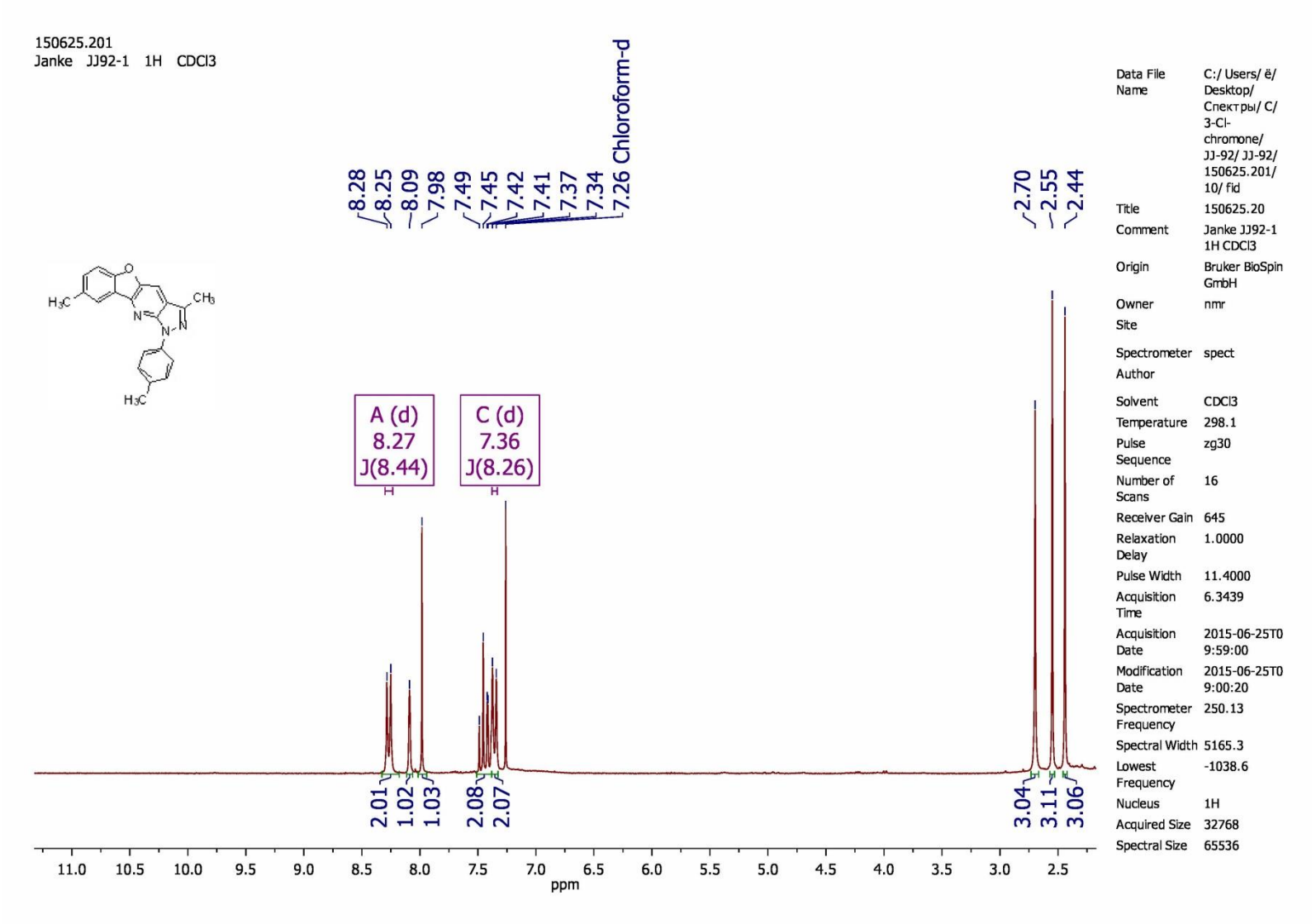
**3,8-Dimethyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4c).**



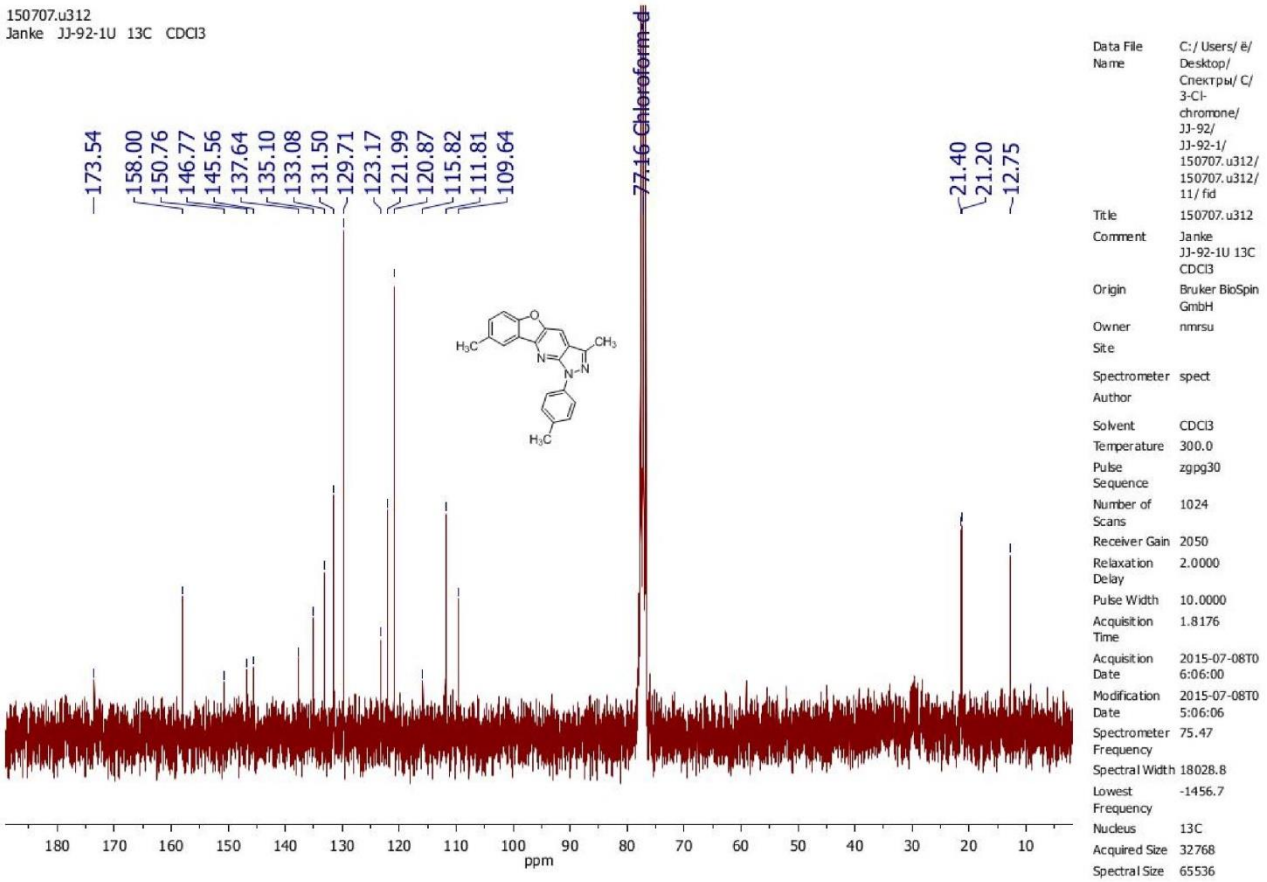
**3,8-Dimethyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4c).**



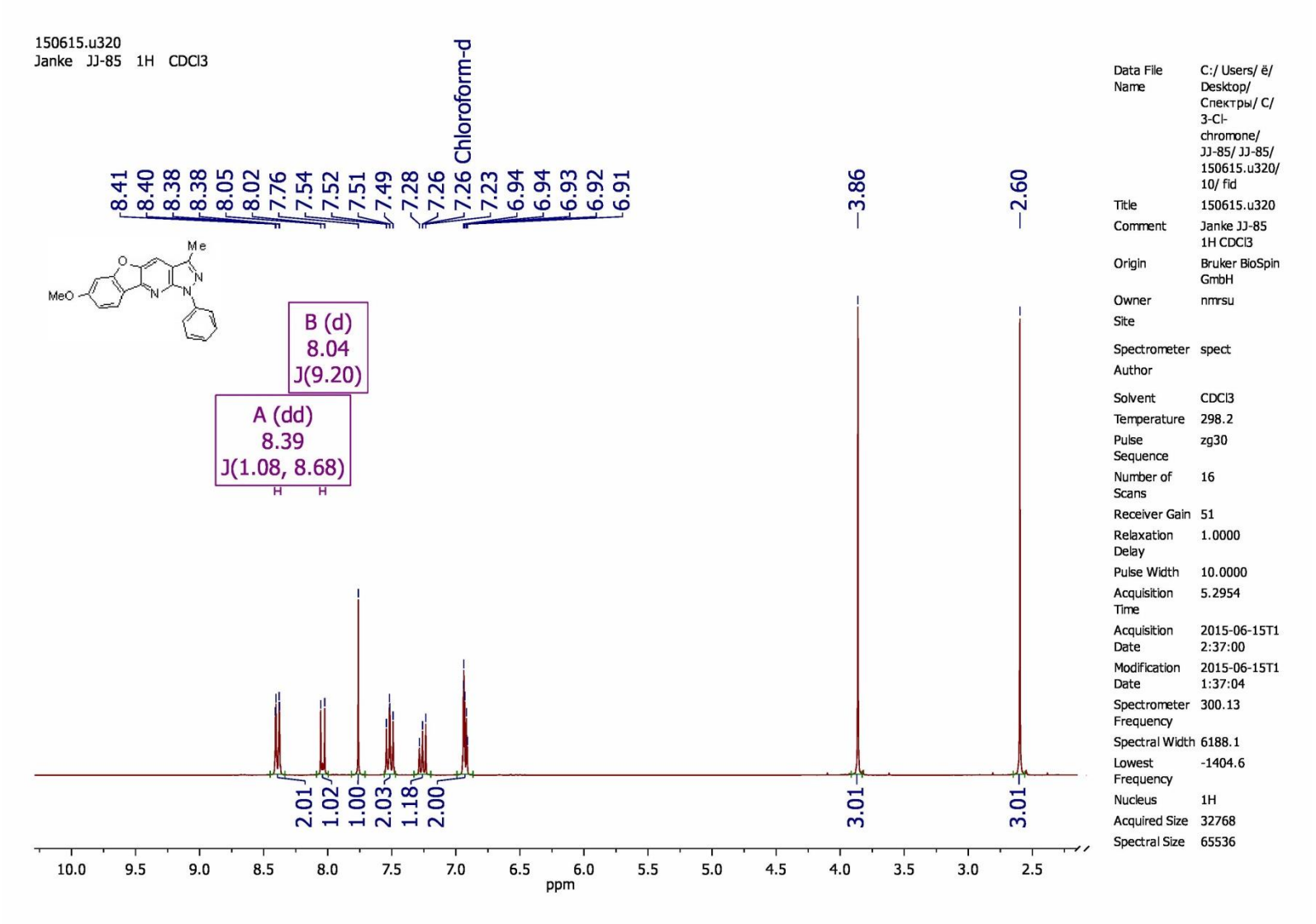
**3,8-Dimethyl-1-*p*-tolyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4d).**



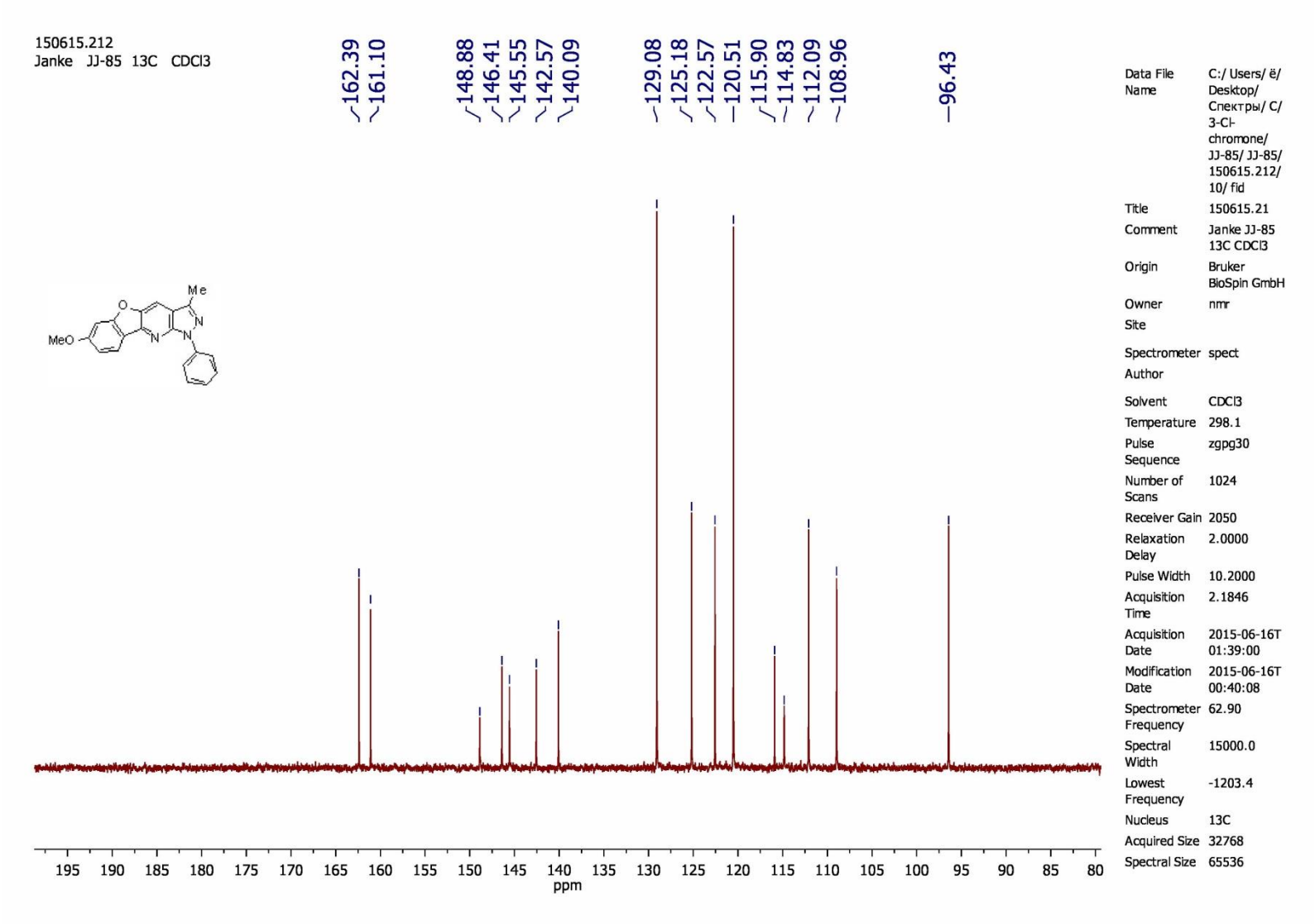
**3,8-Dimethyl-1-*p*-tolyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4d).**



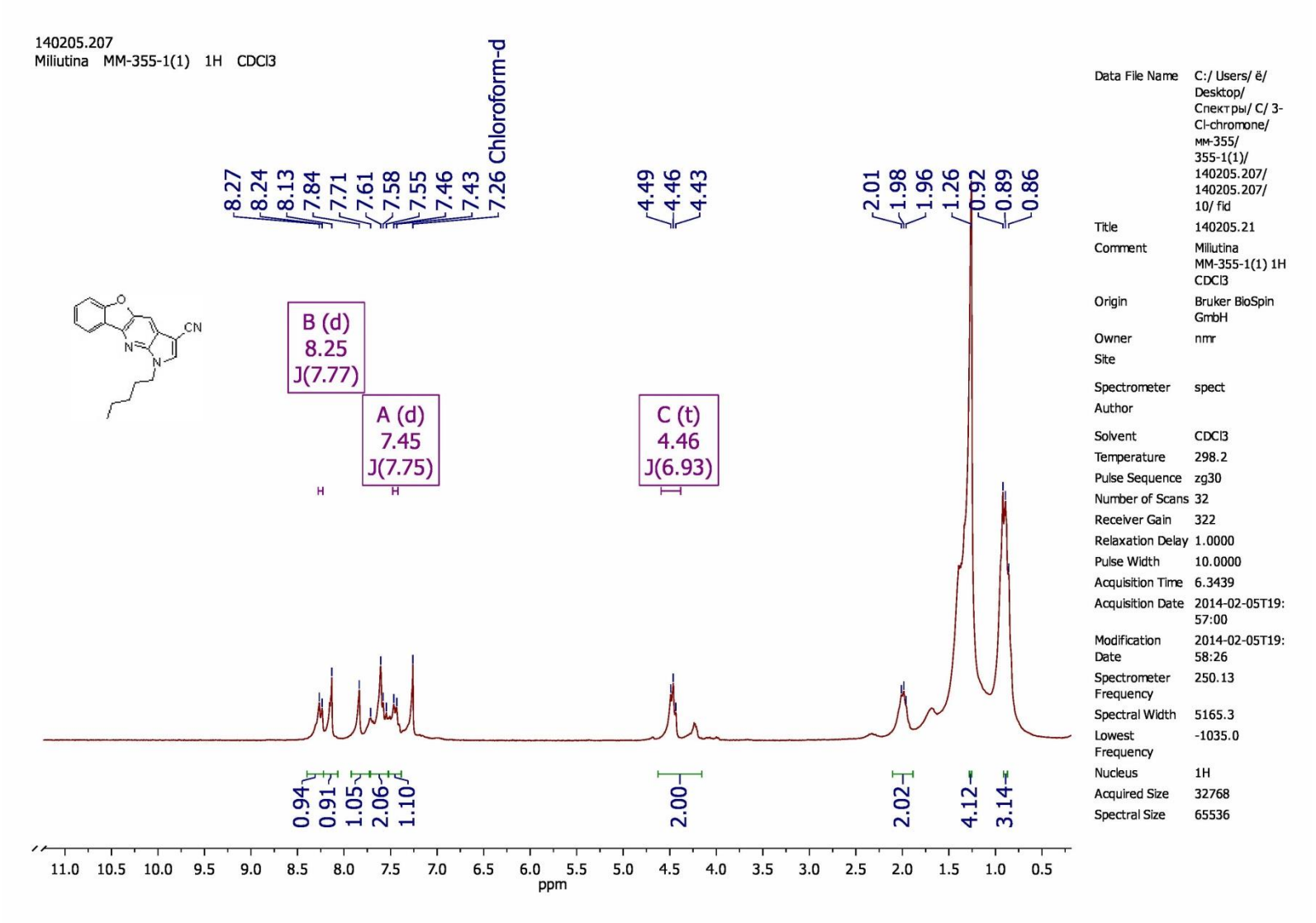
**7-Methoxy-3-methyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4e).**



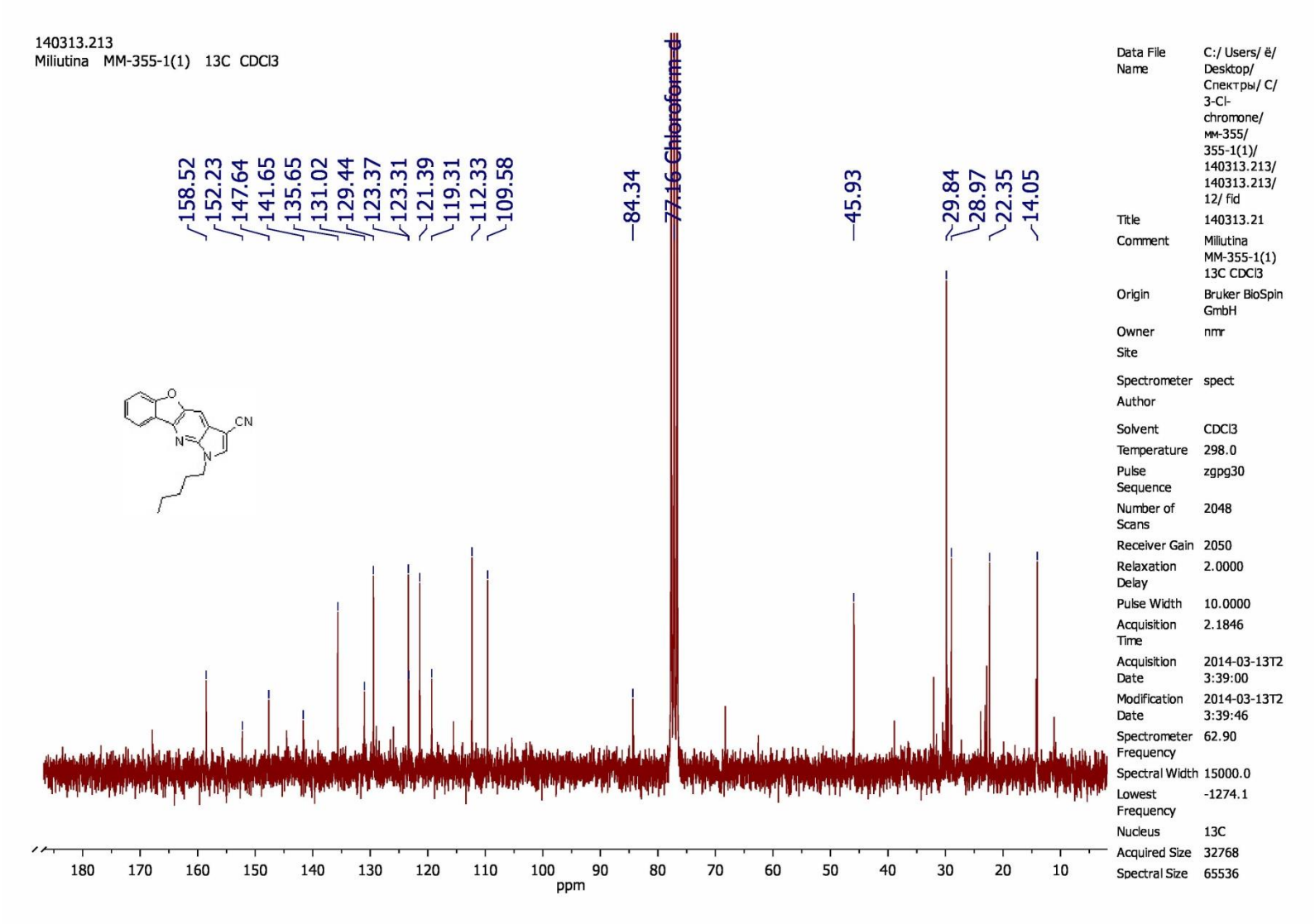
**7-Methoxy-3-methyl-1-phenyl-1*H*-benzofuro[3,2-*b*]pyrazolo[4,3-*e*]pyridine (4e).**



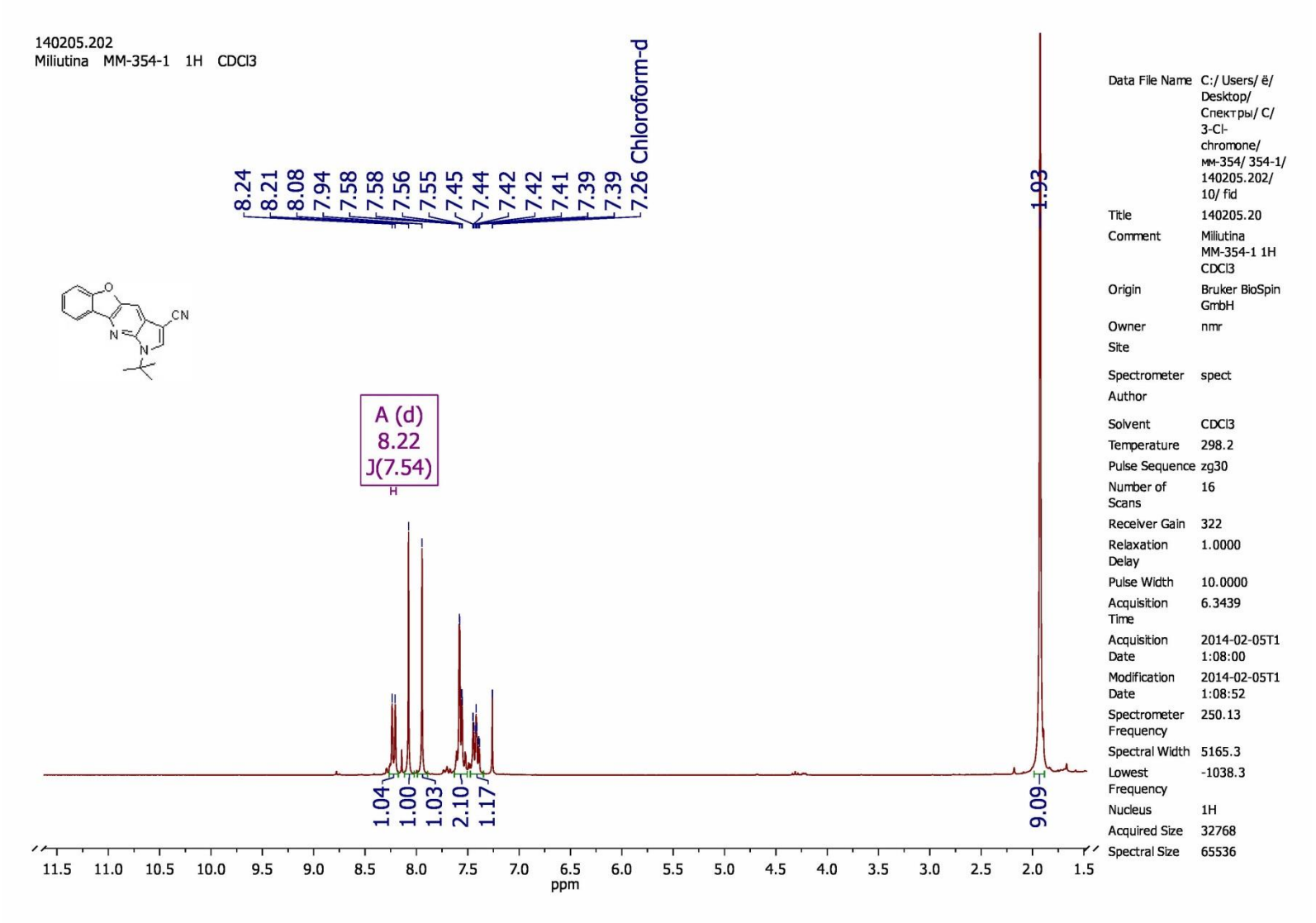
**1-Pentyl-1*H*-benzofuro[3,2-*b*]pyrrolo[3,2-*e*]pyridine-3-carbonitrile (4f).**



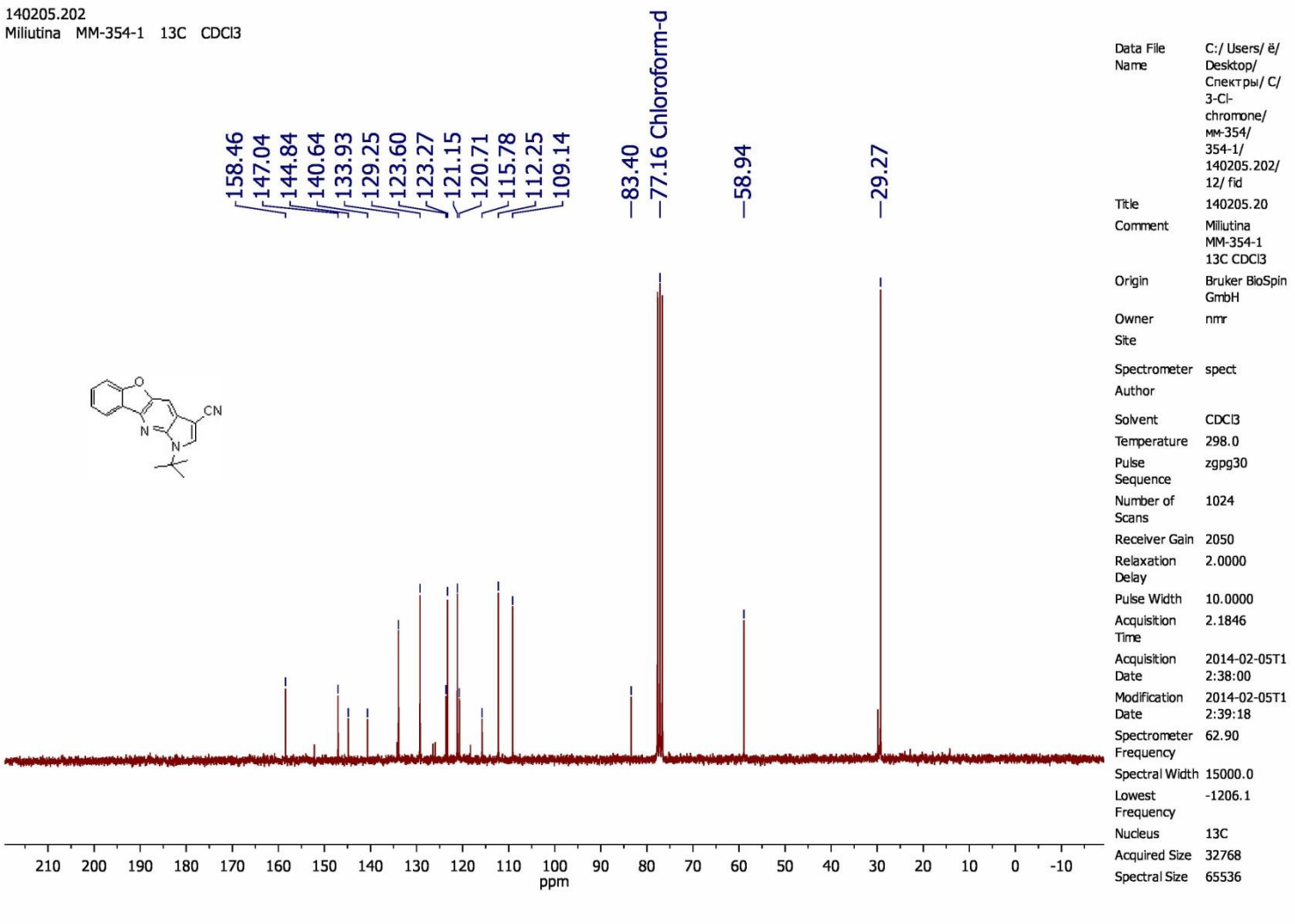
**1-Pentyl-1*H*-benzofuro[3,2-*b*]pyrrolo[3,2-*e*]pyridine-3-carbonitrile (4f).**



**1-*tert*-Butyl-1*H*-benzofuro[3,2-*b*]pyrrolo[3,2-*e*]pyridine-3-carbonitrile (4g).**

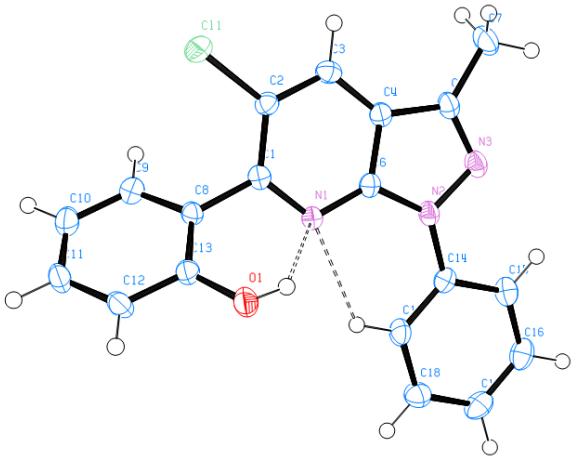


**1-*tert*-Butyl-1*H*-benzofuro[3,2-*b*]pyrrolo[3,2-*e*]pyridine-3-carbonitrile (4g).**

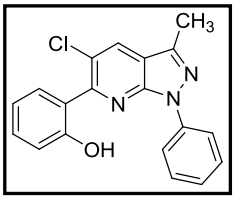


## X-Ray structures of compounds 3a, 3m, 3o and 4c.

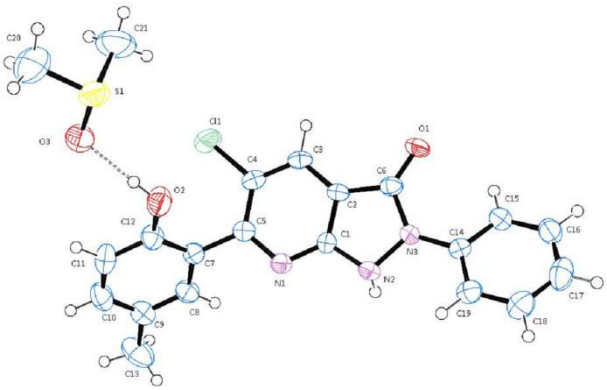
**X-Ray structure of compound 3a.**



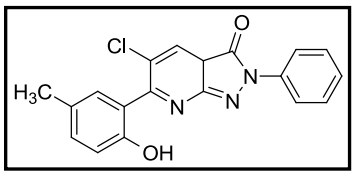
| | | |
|---|---|---|
| Identification Code | is_mm251 | |
| Empirical formula | C19 H14 Cl N3 O | |
| Formula weight | 335.78 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group (H.-M.) | $P\,2_1/c$ | |
| Space group (Hall) | -P 2ybc | |
| Unit cell dimensions | a = 12.6542(8) Å | α = 90.00° |
| | b = 6.7364(4) Å | β = 103.364(3)° |
| | c = 18.7735(12) Å | γ = 90.00° |
| Volume | 1556.99(17) Å$^3$ | |
| Z | 4 | |
| Calculated density | 1.432 Mg/m$^3$ | |
| Absorption coefficient | 0.256 mm$^{-1}$ | |
| F(000) | 696 | |
| Crystal size | 0.99 x 0.04 x 0.03 mm$^3$ | |
| Θ range for data collection | 3.07 to 27.50° | |
| Index ranges | -16 ≤ h ≤ 16, -8 ≤ k ≤ 5, -24 ≤ l ≤ 24 | |
| Reflections collected | 16946 | |
| Independent reflections | 3568 [R(int) = 0.0960] | |
| Completeness to Θ = 28.00° | 99,7% | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.9924 and 0.7857 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2134 / 0 / 222 | |
| Goodness-of-fit on F^2 | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0623, wR2 = 0.1084 | |
| R indices (all data) | R1 = 0.1236, wR2 = 0.1338 | |
| Largest diff. peak and hole | 0.320 and -0.291 e.Å$^{-3}$ | |



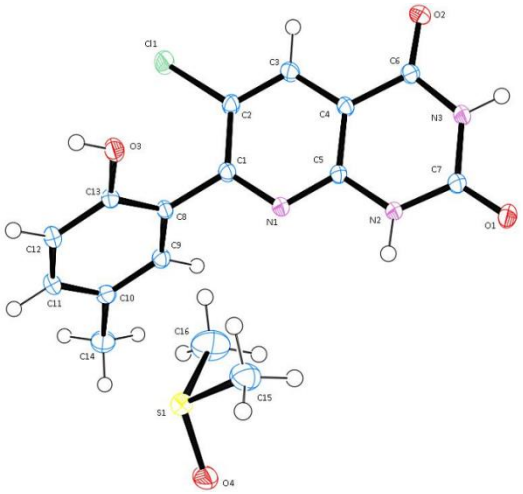
**X-Ray structure of compound 3m.**



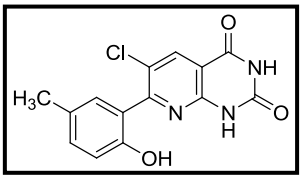
| | | |
|---|---|---|
| Identification Code | is_mm353 | |
| Empirical formula | C21 H20 Cl N3 O3 S | |
| Formula weight | 429.91 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group (H.-M.) | $P\,2_1/c$ | |
| Space group (Hall) | -P 2ybc | |
| Unit cell dimensions | a = 20.255(10) Å | α = 90° |
| | b = 7.228(4) Å | β = 107.35(3)° |
| | c = 14.842(8) Å | γ = 90° |
| Volume | 2074(2) Å$^3$ | |
| Z | 4 | |
| Calculated density | 1.377 Mg/m$^3$ | |
| Absorption coefficient | 0.313 mm$^{-1}$ | |
| F(000) | 896 | |
| Crystal size | 0.480 x 0.150 x 0.010 mm$^3$ | |
| Θ range for data collection | 2.876 to 22.362° | |
| Index ranges | -19 ≤ h ≤ 21, -7 ≤ k ≤ 5, -15 ≤ l ≤ 15 | |
| Reflections collected | 14125 | |
| Independent reflections | 2637 [R(int) = 0.0854] | |
| Completeness to Θ = 28.00° | 98,9% | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.7448 and 0.6520 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 1575 / 6 / 282 | |
| Goodness-of-fit on F^2 | 1.030 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0491, wR2 = 0.0970 | |
| R indices (all data) | R1 = 0.1086, wR2 = 0.1205 | |
| Largest diff. peak and hole | 0.217 and -0.326 e.Å$^{-3}$ | |



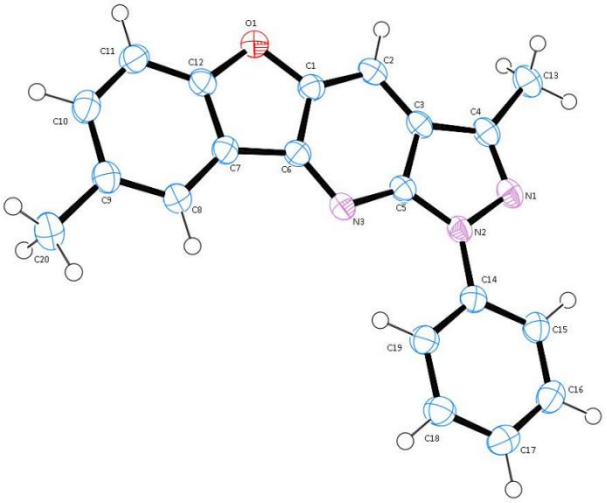
**X-Ray structure of compound 3o.**




| | | |
|---|---|---|
| Identification Code | is_mm258 | |
| Empirical formula | C16 H16 Cl N3 O4 S | |
| Formula weight | 381.83 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | triclinic | |
| Space group (H.-M.) | $P\bar{1}$ | |
| Space group (Hall) | -P 1 | |
| Unit cell dimensions | a = 7.2883(2) Å | α = 78.2630(10)° |
| | b = 7.8141(2) Å | β = 86.7750(10)° |
| | c = 15.5616(3) Å | γ = 76.9220(10)° |
| Volume | 845.17(4) Å$^3$ | |
| Z | 2 | |
| Calculated density | 1.500 Mg/m$^3$ | |
| Absorption coefficient | 0.377 mm$^{-1}$ | |
| F(000) | 396 | |
| Crystal size | 0.290 x 0.230 x 0.060 mm$^3$ | |
| Θ range for data collection | 2.674 to 32.500° | |
| Index ranges | -10 ≤ h ≤ 11, -11 ≤ k ≤ 11, -23 ≤ l ≤ 23 | |
| Reflections collected | 27106 | |
| Independent reflections | 6050 [R(int) = 0.0233] | |
| Completeness to Θ = 28.00° | 99,0% | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.7464 and 0.6974 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4834 / 0 / 241 | |
| Goodness-of-fit on F^2 | 1.039 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0390, wR2 = 0.0941 | |
| R indices (all data) | R1 = 0.0550, wR2 = 0.1038 | |
| Largest diff. peak and hole | 0.531 and -0.351 e.Å$^{-3}$ | |



**X-Ray structure of compound 4c.**




| | | |
|---|---|---|
| Identification Code | ah_mm378 | |
| Empirical formula | C20 H15 N3 O | |
| Formula weight | 313.35 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group (H.-M.) | *C* 2/*c* | |
| Space group (Hall) | -C 2yc | |
| Unit cell dimensions | a = 32.653(2) Å | α = 90° |
| | b = 4.8634(4) Å | β = 119.984(4)° |
| | c = 21.7870(16) Å | γ = 90° |
| Volume | 2996.8(4) Å$^3$ | |
| Z | 8 | |
| Calculated density | 1.389 Mg/m$^3$ | |
| Absorption coefficient | 0.088 mm$^{-1}$ | |
| F(000) | 1312 | |
| Crystal size | 0.890 x 0.070 x 0.040 mm$^3$ | |
| Θ range for data collection | 2.597 to 28.998° | |
| Index ranges | -44 ≤ h ≤ 44, -4 ≤ k ≤ 6, -29 ≤ l ≤ 29 | |
| Reflections collected | 20234 | |
| Independent reflections | 3999 [R(int) = 0.0559] | |
| Completeness to Θ = 28.00° | 99,9% | |
| Absorption correction | Multi-scan | |
| Max. and min. transmission | 0.7462 and 0.6353 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 2728 / 0 / 219 | |
| Goodness-of-fit on F^2 | 1.019 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0462, wR2 = 0.1076 | |
| R indices (all data) | R1 = 0.0757, wR2 = 0.1274 | |
| Largest diff. peak and hole | 0.229 and -0.233 e.Å$^{-3}$ | |