**Supporting Information**

# Highly efficient modular metal-free synthesis of 3-substituted 2-quinolones

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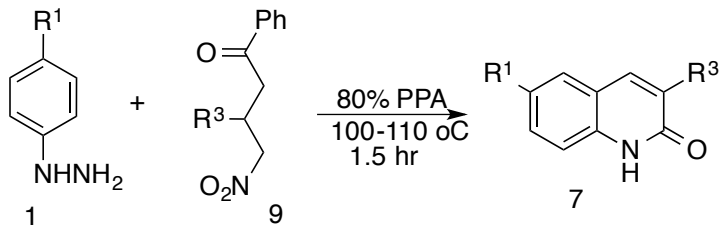
## Experimental Section:

Reagents, solvents and catalysts were purchased from commercial vendors and used as received. The reaction vessels (10 mL drum vials) were washed and oven-dried without special precautions. Since hot polyphosphoric acid notably deteriorates glass, it is not advised to reuse the vessel more than three times. Otherwise all the materials were handled and all the reactions were performed without special precautions in vessels open to the ambient atmosphere. The reaction progress was monitored by thin layer chromatography using pre-coated glass-supported TLC plates Silica gel 60 F254 (250 μm) (EMD Chemicals Inc.), visualized with UV light. Filtration of reaction mixtures was performed using a short pad of Silica gel (32-63 μm, 60 Å pore size). $^{1}$H and $^{13}$C NMR spectra were recorded on Bruker DRX-400 and Bruker DRX-500 spectrometers. Chemical shifts (δ) are reported in ppm relative to the TMS internal standard. Multiplet observed in NMR are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). IR spectra were recorded on Specord 75 IR in KBr. 4-Nitroketones starting materials were synthesized employing published procedures.[1]

[1] (a) Liang, Y.; Dong, D.; Lu, Y.; Wang, Y.; Pan, W.; Chai, Y.; Liu, Q. *Synthesis,* **2006**, 3301. (b) Liang, D.; Xin, X.; Duan, H.; Yin, Y.; Gao, H.; Lin, Y.; Xu, J. *Chem. Res. Chinese Universities,* **2008,** 36.

1. Synthesis of 2-Quinolones from arilhydrazine **1a-d**




**General procedure:** General procedure: The mixture of arylhydrazine **1** (1.0 mmol), 4-nitroketone **9** (1.0 mmol) and 80% PPA (2-3 g) was stirred at 100-110°C for 1.5 h. When TLC analysis indicated complete conversion, the mixture was cooled to room temperature, poured into cold water (50 ml) and neutralized by aqueous ammonia. Product **7** was extracted with chloroform (2 x 20 mL) and filered through a short pad of Silica gel. The solvent was removed in vacuum and the crude product was purified by recrystallization.

| entry | **1** | **$R^1$** | **9** | **$R^3$** | **7** | **Yield, %**[a] |
|---|---|---|---|---|---|---|
| 1 | **1a** | H | **9a** | Ph | **7aa** | 78 |
| 2 | **1a** | H | **9b** | 4-$MeOC_6H_5$ | **7ab** | 64 |
| 3 | **1a** | H | **9c** | 4-(*i*-Pr)$C_6H_5$ | **7ac** | 73 |
| 4 | **1a** | H | **9d** | 4-$FC_6H_5$ | **7ad** | 76 |
| 5 | **1a** | H | **9e** | 3-$BrC_6H_5$ | **7ae** | 76 |
| 6 | **1a** | H | **9f** | 3,4-$(MeO)_2C_6H_3$ | **7af** | 68 |
| 7 | **1a** | H | **9g** | *n*-Pr | **7ag** | 57 |
| 8 | **1a** | H | **9h** | H | **7ah** | 67 |
| 9 | **1b** | Me | **9a** | Ph | **7ba** | 79 |
| 10 | **1c** | MeO | **9a** | Ph | **7ca** | 71 |
| 11 | **1d** | Cl | **9a** | Ph | **7da** | 75 |

[a] Isolated yields of recrystallized products.

**3-Phenylquinolin-2(1H)-one (7aa)** White solid, mp 234-235°C[2] (dichloromethane/ethanol). $^1$H NMR ($CDCl_3$, 500 MHz) δ: 10.79 (bs, 1H), 7.92 (s, 1H), 7.79 (m, 2H), 7.61 (dd, J = 1.2 and 6.6 Hz, 1H), 7.52-7.47 (m, 3H), 7.43-7.39 (m 1H), 7.30-7.22 (m, 2H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) δ: 161.7, 139.1, 138.3, 137.0,132.2, 130.8, 129.4, 128.8, 128.6, 128.5, 122.5, 120.2, 115.4. The NMR spectral data are consistent with published results[3]. IR (KBr): 3456, 1647 cm $^{-1}$.

**3-(4-Methoxy-phenyl)quinolin-2(1H)-one (7ab):** White solid, mp 259-261°C (dichloromethane/ ethanol). $^1$H NMR ($CDCl_3$, 500 MHz) δ: 11.57 (bs, 1 H), 7.86 (s, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.27 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 8.3 Hz, 2H), 3.88 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) δ: 161.2, 159.0, 138.1, 136.3, 131.0, 129.9, 129.8, 128.5, 127.8, 121.8, 119.7, 114.6, 113.3, 55.1. The NMR spectral data are consistent with published results[4]. IR: 3480, 1661 cm$^{-1}$.

**3-(4-*i*-Propylphenyl)quinolin-2(1H)-one (7ac):** White solid, mp 220-221 °C (dichloromethane/ ethanol). $^1$H NMR ($CDCl_3$, 500 MHz) *δ* 11.46 (bs, 1H), 7.92 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50 (ddd, *J* = 1.1, 7.6 and 7.8, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.21 (dd, *J* = 7.8 and 8.6, 1H), 3.02-2.94 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 6H); $^{13}$C NMR ($CDCl_3$, 125 MHz) *δ:* 162.5, 148.5, 137.4, 137.3,133.0, 131.9, 129.6, 128.3, 127.2, 125.9, 122.1, 119.9, 114.9, 33.5, 23.4 (2C), IR: 3445, 1652 cm$^{-1}$. The NMR spectral data are consistent with published results[5]

**3-(4-Fluoro-phenyl)quinolin-2(1H)-one (7ad):** White solid, mp 246-248°C (dichloromethane/ethanol). $^1$H NMR (DMSO-$d_6$, 400 MHz) *δ* 11.97 (bs, 1H), 8.11 (s, 1H), 7.85-7.81 (m, 2H), 7.72 (d, *J* = 7.68 Hz, 1H), 7.50 (dd, *J* = 7.6 and 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.17-7.28 (m, 3H); $^{13}$C NMR (DMSO-

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[2] Katsuhiko, M. *Chem. Pharm. Bull.,* **1987,** 35, 2819.

[3] Pailer, M. *Monatsh. Chem.,***1965,** 96, 1695

[4] Manley, P.J.; Bilodeau, M.T. *Org. Lett.,* **2004,** 6, 2433

[5] Aksenov, A.V.; Smirnov, A.N.; Aksenov, N.A.; Aksenova, I.V.; Frolova, L.V.; Kornienko, A.; Magedov, I.V.; Rubin, M. *Chem. Commun.,* **2013,** 49, 9305.

$d_6$, 125 MHz) $\delta$: 163.1, 161.0, 160.6, 138.4, 137.6, 132.6, 130.8, 130.3, 128.1, 122.0 119.5, 114.9, 114.7. IR: 3588, 1651 $cm^{-1}$. The NMR spectral data are consistent with published results[5]

**3-(3-Bromo-phenyl)quinolin-2(1H)-one (7ae):** White solid, mp 211-212°C (dichloromethane/ethanol). $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 11.35 (bs, 1H), 7.96 (bs, 1 H), 7.92 (s, 1H), 7.75 (d, $J$ = 7.7 Hz, 1H), 7.62 (d, $J$ = 7.8 Hz, 1H), 7.55-7.51 (m, 2H), 7.36-7.33 (m, 2H), 7.24 (t, $J$ = 7.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$: 162.6, 139.0, 138.3, 138.2, 131.9, 131.3, 131.1, 130.9, 129.9, 128.2, 127.7, 123.0, 122.5, 120.3 115.6. IR: 3485, 1648 $cm^{-1}$. The NMR spectral data are consistent with published results[5]

**3-(3,4-dimethoxy)quinolin-2(1H)-one (7af):** White solid, mp 209-210°C (dichloromethane/ethanol). $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 11.87 (bs, 1H), 8.09 (s, 1H), 7.71 (d, $J$ = 7.5 Hz, 1H), 7.48 (ddd, $J$ = 0.9, 9.7 and 7.7 Hz, 1H), 7.42 (d, $J$ = 1.8 Hz, 1H), 7.38 (dd, $J$ = 1.9 and 8.3 Hz, 1H), 7.34 (d, $J$ = 8.2 Hz, 1H), 7.19 (t, $J$ = 7.4 Hz, 1H), 7.01 (d, $J$ = 8.4 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$: 161.1, 148.8, 148.1, 138.1, 136.5, 131.1, 129.8, 128.9, 127.9, 121.8, 121.3, 119.7, 114.6, 112.6, 111.3, 55.6, 55.5. IR: 3462, 1651 $cm^{-1}$ The NMR spectral data are consistent with published results[5]

**Quinolin-2(1H)-one (7ah):** White solid, mp 188-189°C[6] (hexane). $^1$H NMR ($CDCl_3$, 500 MHz) δ: 8.42 (d, J = 9 Hz, 1H), 8.14 (t, J = 8 Hz, 1H), 8.0 (bs, 1H), 7.36 (d, J = 8 Hz, 1H), 7.31 (d, J = 8 Hz, 1H), 7.14 (t, J = 8 Hz, 1H), 6.57 (d, J = 9 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 162.3, 139.5, 138.2, 128.8, 128.1, 124.2, 121.5, 119.1, 115.0.

**3-n-Propilquinolin-2(1H)-one (7ag):** White solid, mp 142-143 °C (hexane/ethyl acetate). $^1$H NMR ($CDCl_3$, 500 MHz,) δ: 12.77 (bs, 1H), 7.57 (s, 1H), 7.49-7.39 (m, 3H), 7.15 (ddd, J = 2 and 8,6 Hz, 1H), 2.67 (t, J = 7 Hz, 2H), 1.75 (sextet, J = 7 Hz, 2H), 1.04 (t, J = 7 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz)

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[6] Manimaran, T; Thiruvengadam, T.K; Ramakrishnan, V.T. *Syntesis*, **1975**, 739.

δ: 164.5, 137.4, 136.4, 133.7, 129.0, 126.7, 122.1, 120.1, 115.7, 32.3, 21.6, 14.0. The NMR spectral data are consistent with published results.[4] IR (KBr): 3455, 1655 cm-1.

**6-Methyl-3-phenylquinolin-2(1H)-one (7ba):** White solid, mp 218-219°C (ethanol); $^{1}$H NMR ($CDCl_3$/DMSO, 400 MHz) δ: 11.70 (s, 1H), 7.81 (s, 1H,), 7.76 (m, 2H), 7.45 (m, 2H), 7.36 (m, 2H), 7.28 (s, 2H), 2.41 (s, 3H); The NMR spectral data are consistent with published results[7]. IR: 3450, 1660 $cm^{-1}$.

**6-Methoxy-3-phenyl(1H)quinolin-2(1H)-one (7ca):** Pale yellow solid, mp 248-249°C[8] (chloroform/ethyl acetate); $^{1}$H NMR ($CDCl_3$, 400 MHz) δ: 10.89 (bs, 1H), 7.86 (s, 1H), 7.8 (s, 1H), 7.79 (s, 1H), 7.48 (m, 2H), 7.42 (m, 1H), 7.23 (d, $J$ = 9.0 Hz, 1H), 7.14(dd, $J$ = 2.7 and 6.1 Hz, 1H), 7.04 (d, $J$ = 2.7 Hz, 1H), 3.88 (s, 3H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) *δ:* 160.7, 154.3, 137.4, 136.6, 133.1, 132.0, 128.8, 128.0, 127.9, 120.3, 119.6, 116.1, 109.6, 55.6. The NMR spectral data are consistent with published results[4].

**6-Chloro-3-phenylquinolin-2(1H)-one (7da):** White solid, mp 249-250°C (hexane/ethyl acetate) (249-250°C); $^{1}$H NMR (DMSO-$d_6$, 400 MHz) δ: 12.06 (br s, 1H), 8.11 (s, 1H), 7.86 (d, $J$ = 2.0 Hz,1H), 7.77 (d, $J$ = 7.0 Hz, 2H), 7.56 (dd, $J$ = 2.0 and 9.0 Hz,1H), 7.50-7.42 (m, 3H), 7.38 (d, $J$ = 9.0 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz) *δ:* 160.7, 136.9, 136.4, 135.8, 132.7, 129.9, 128.6, 128.0, 127.9, 126.9, 125.6, 120.6, 116.5.The NMR spectral data are consistent with published results[9]. IR: 3455, 1650 $cm^{-1}$.

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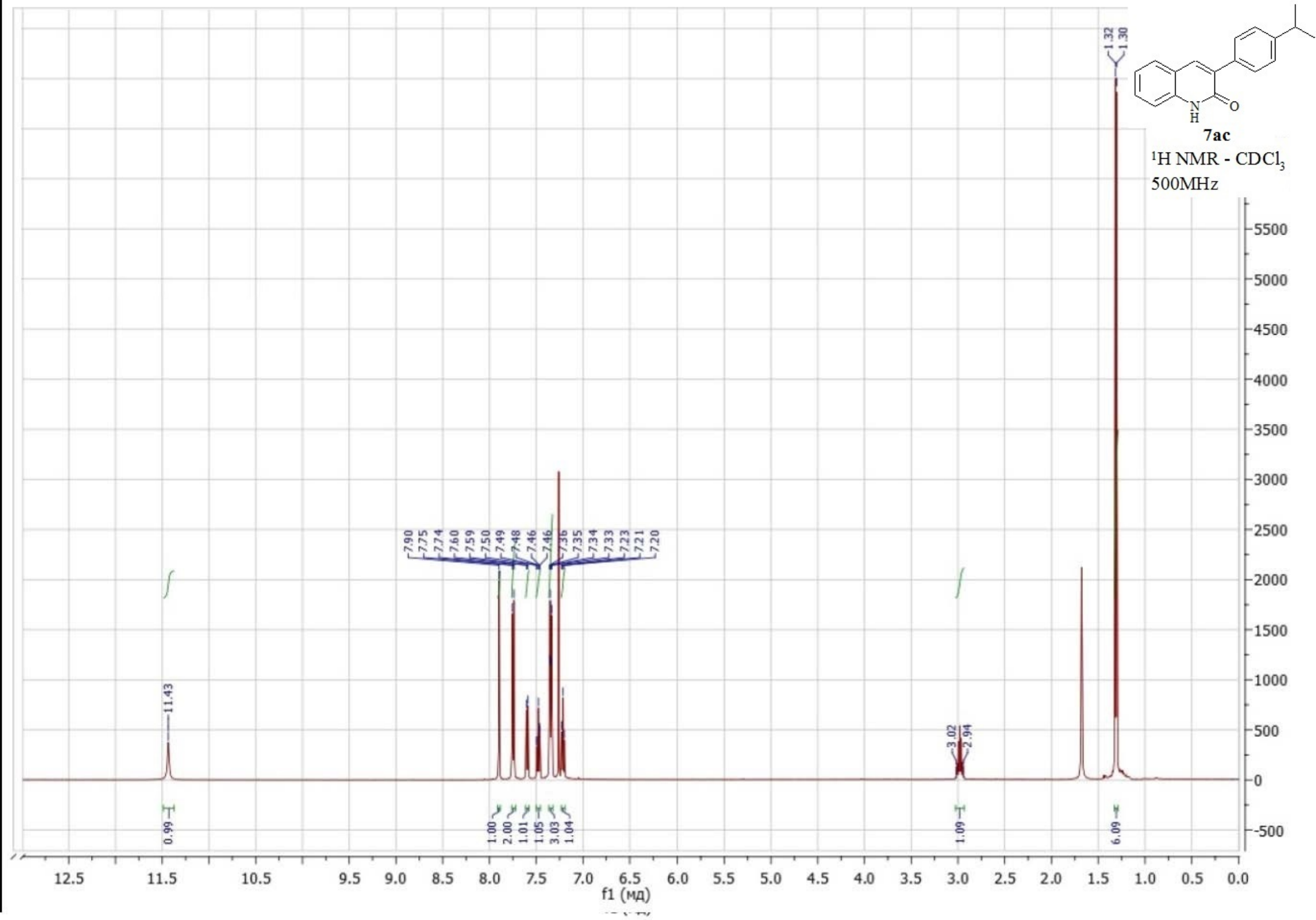
[7] Eicher, T.; Schneider, V. *Synthesis,* **1989,** 372.

[8] Fu, L. *Synthesis,* **2011,** 1547.

[9] Park, K.K.; Jung, J.Y. *Heteocycles,* **2005,** 65(9), 2095.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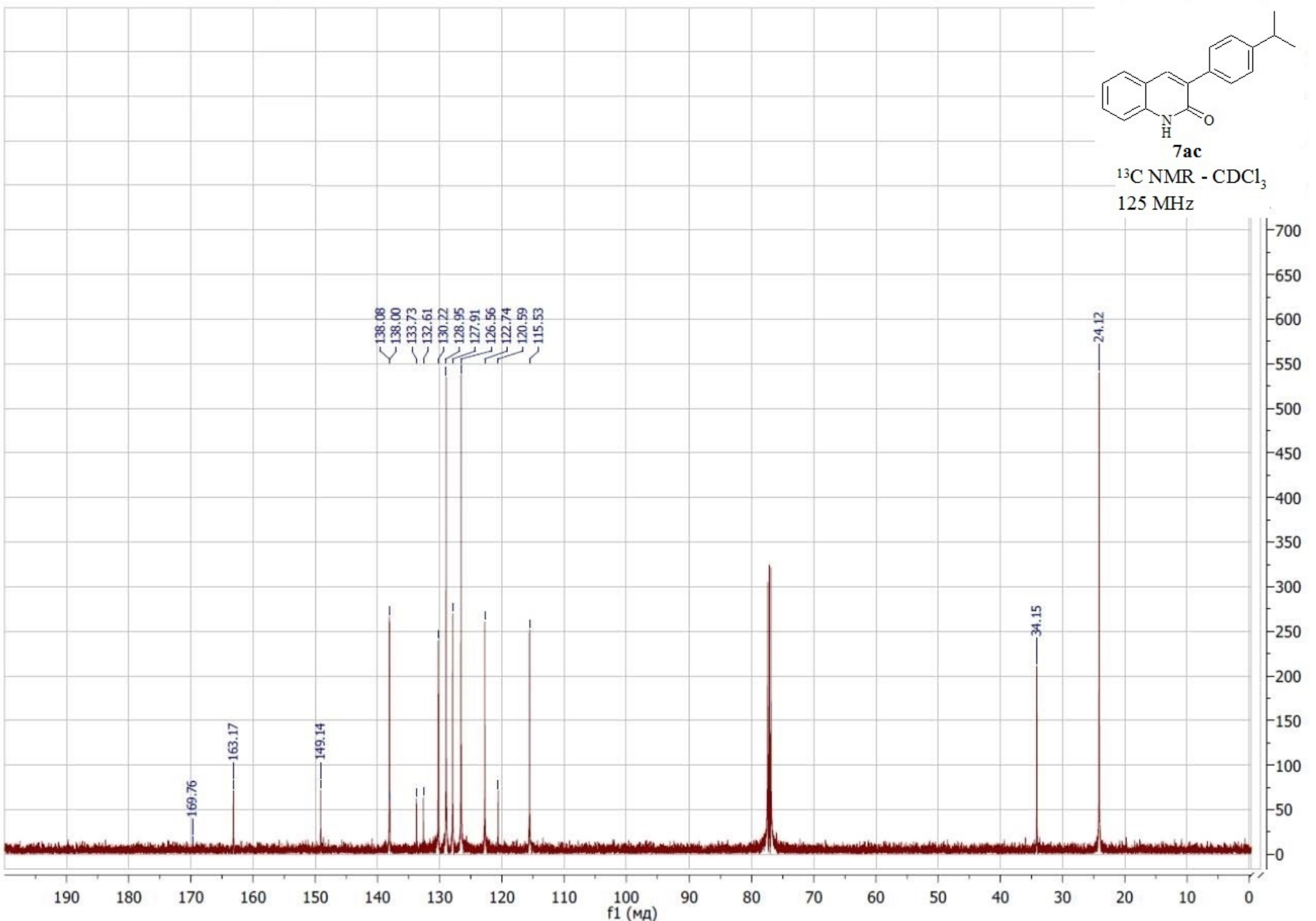
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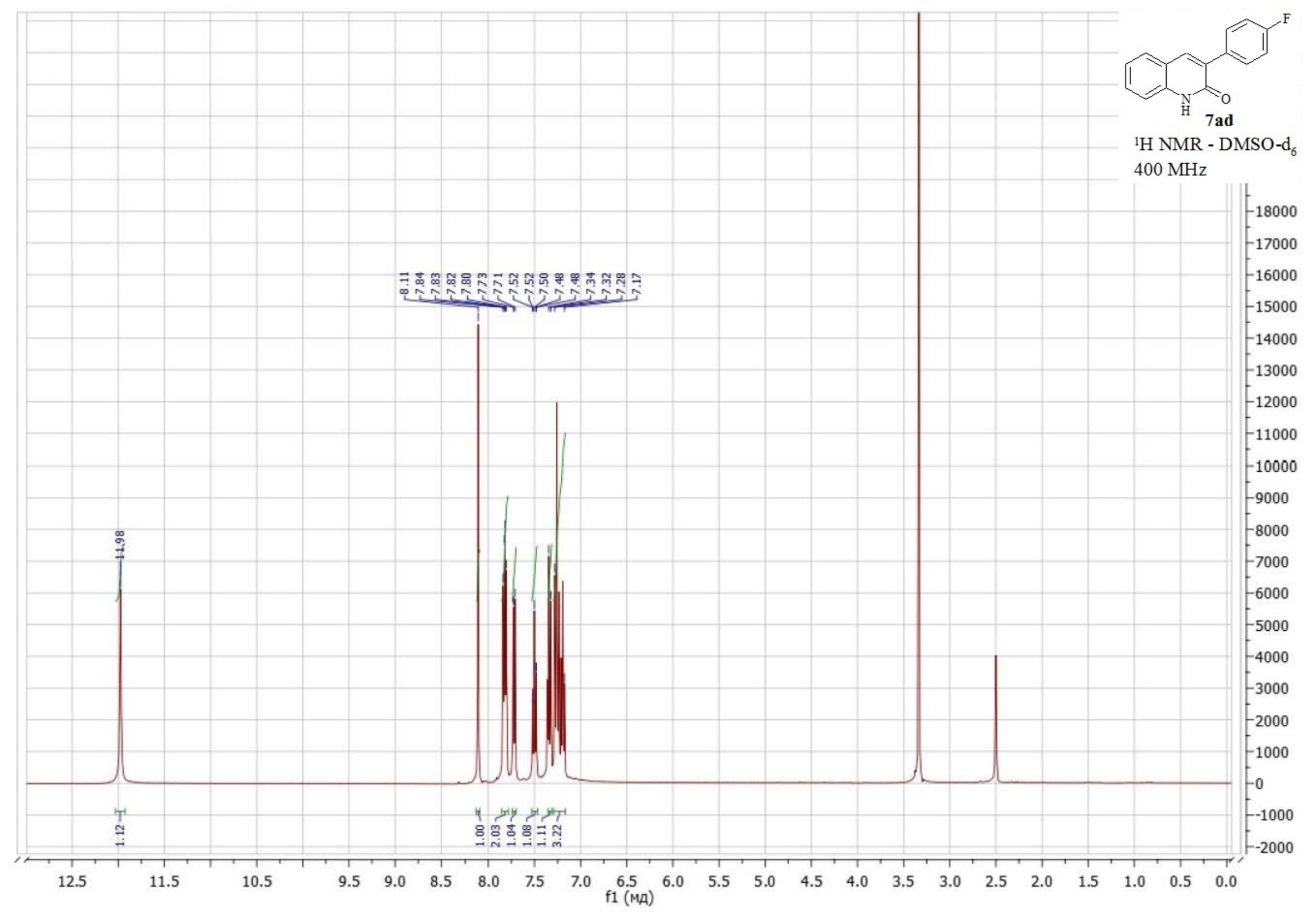
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7.71
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7.52
7.50
7.48
7.48
7.34
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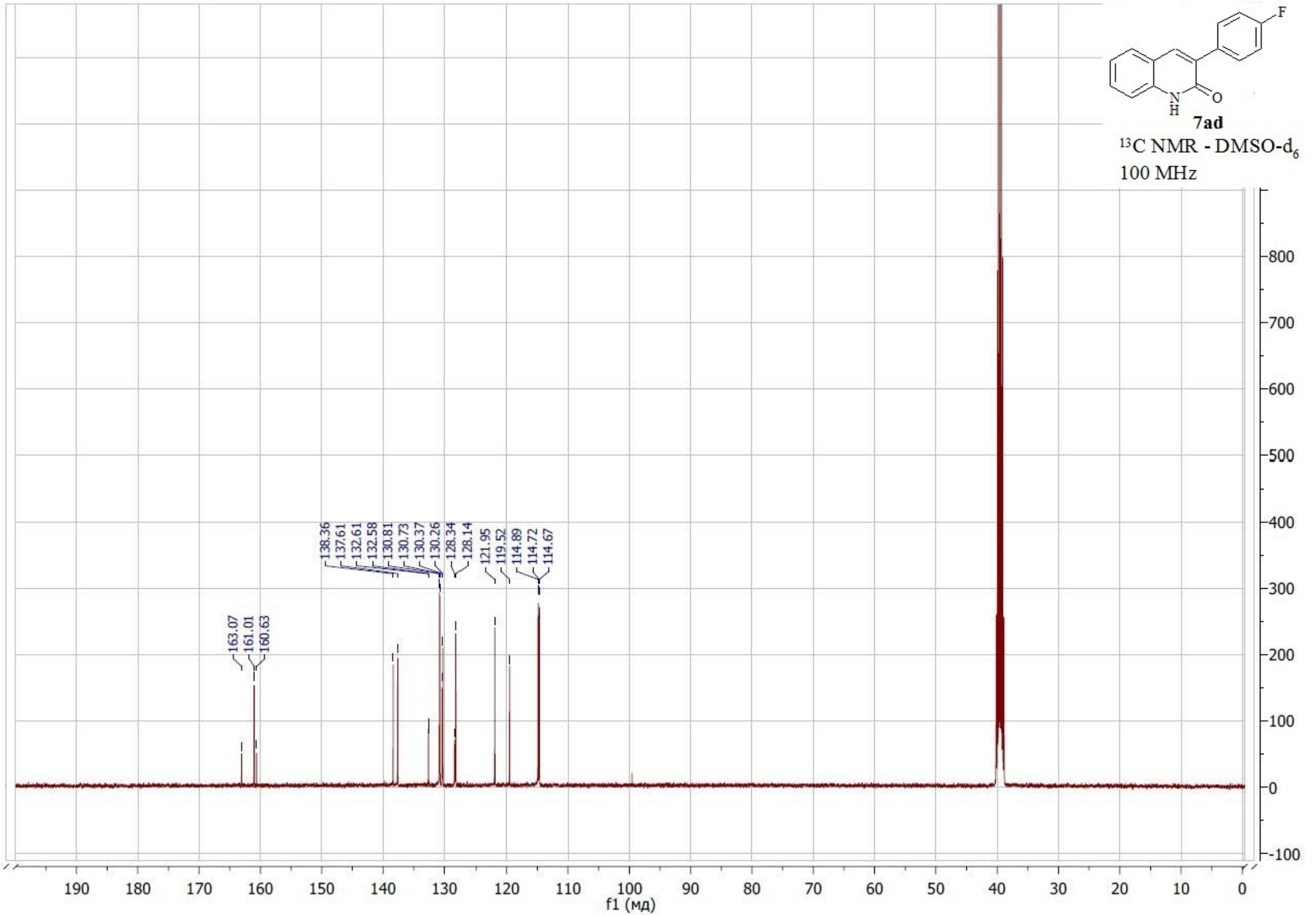
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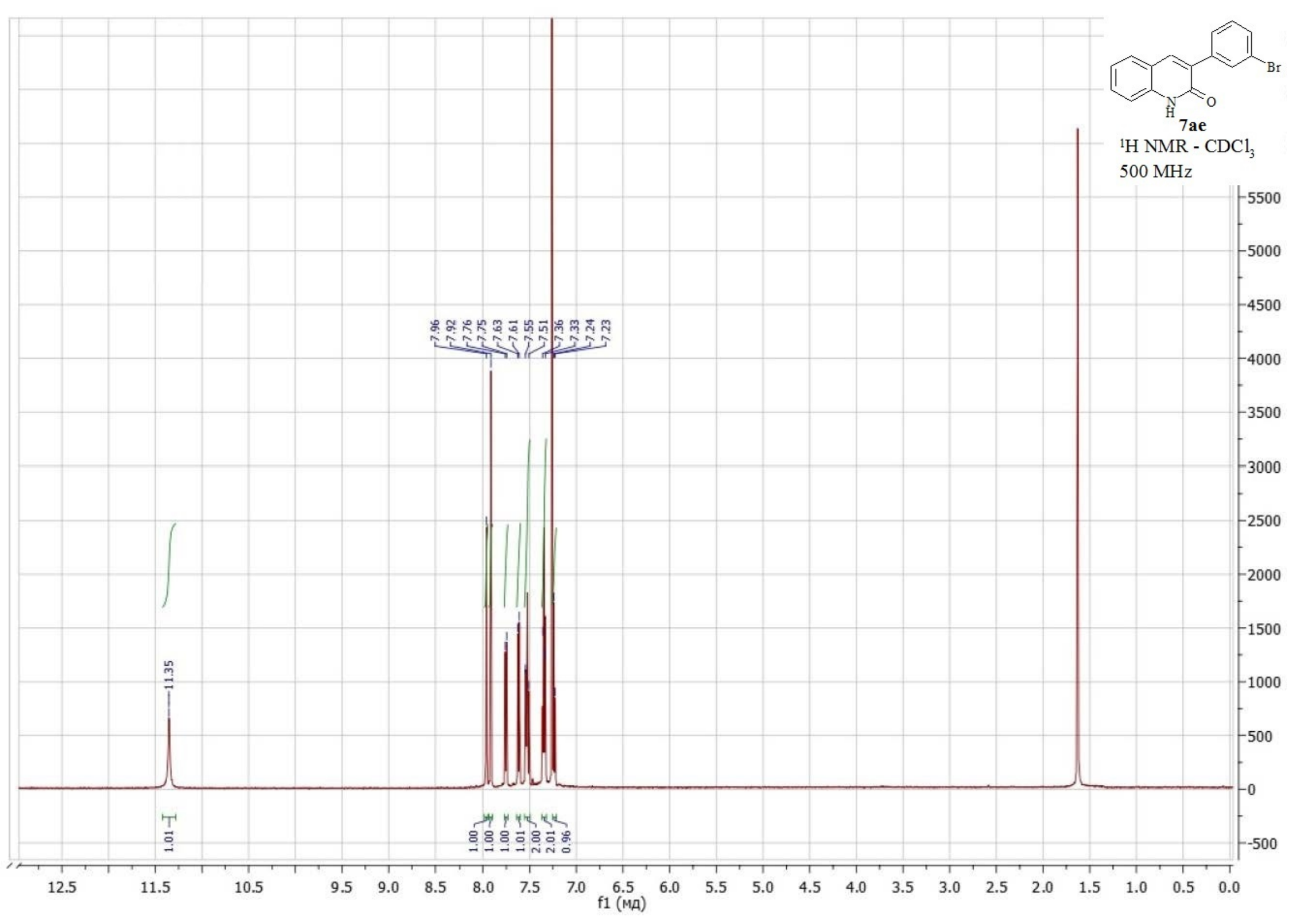
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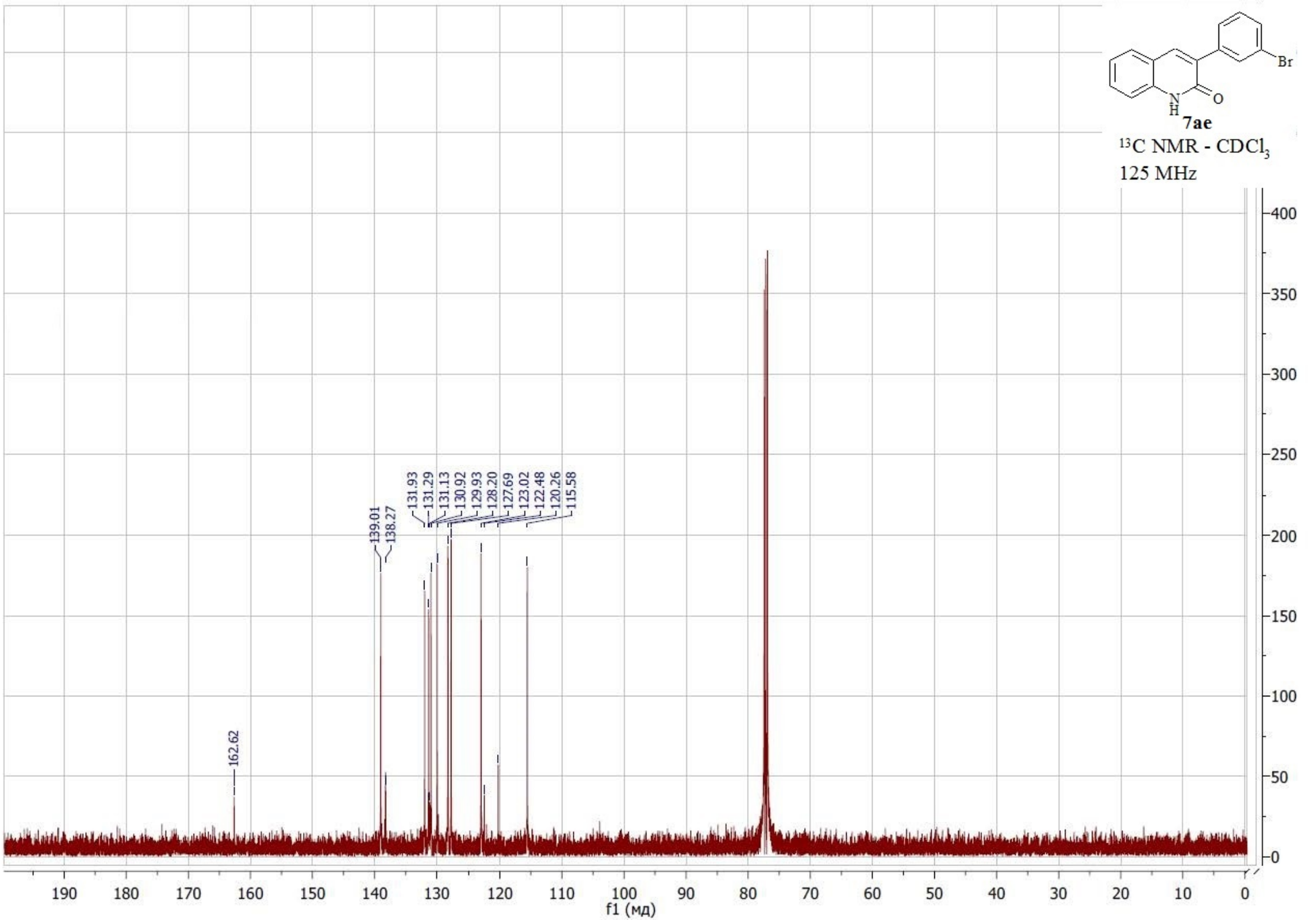
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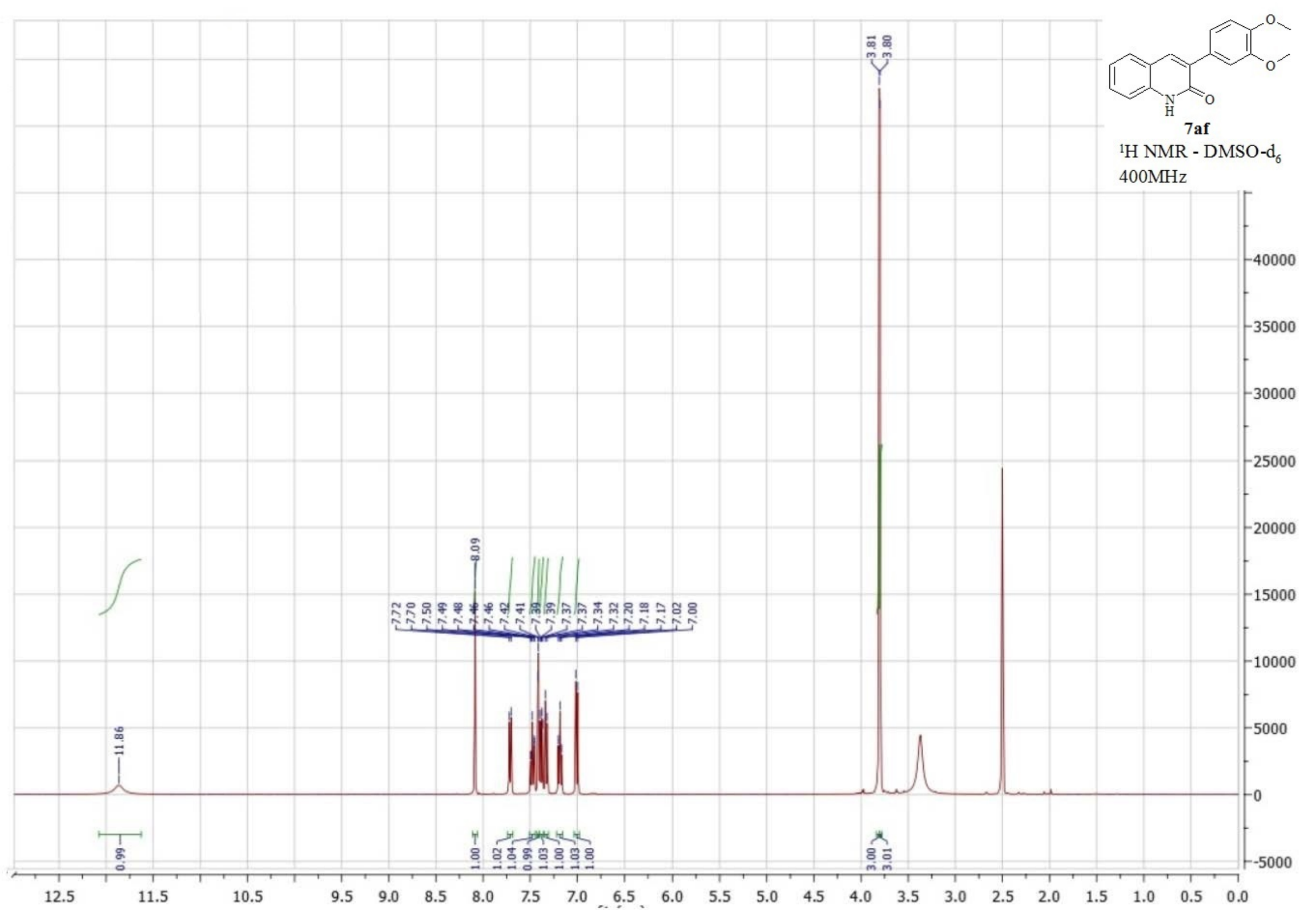
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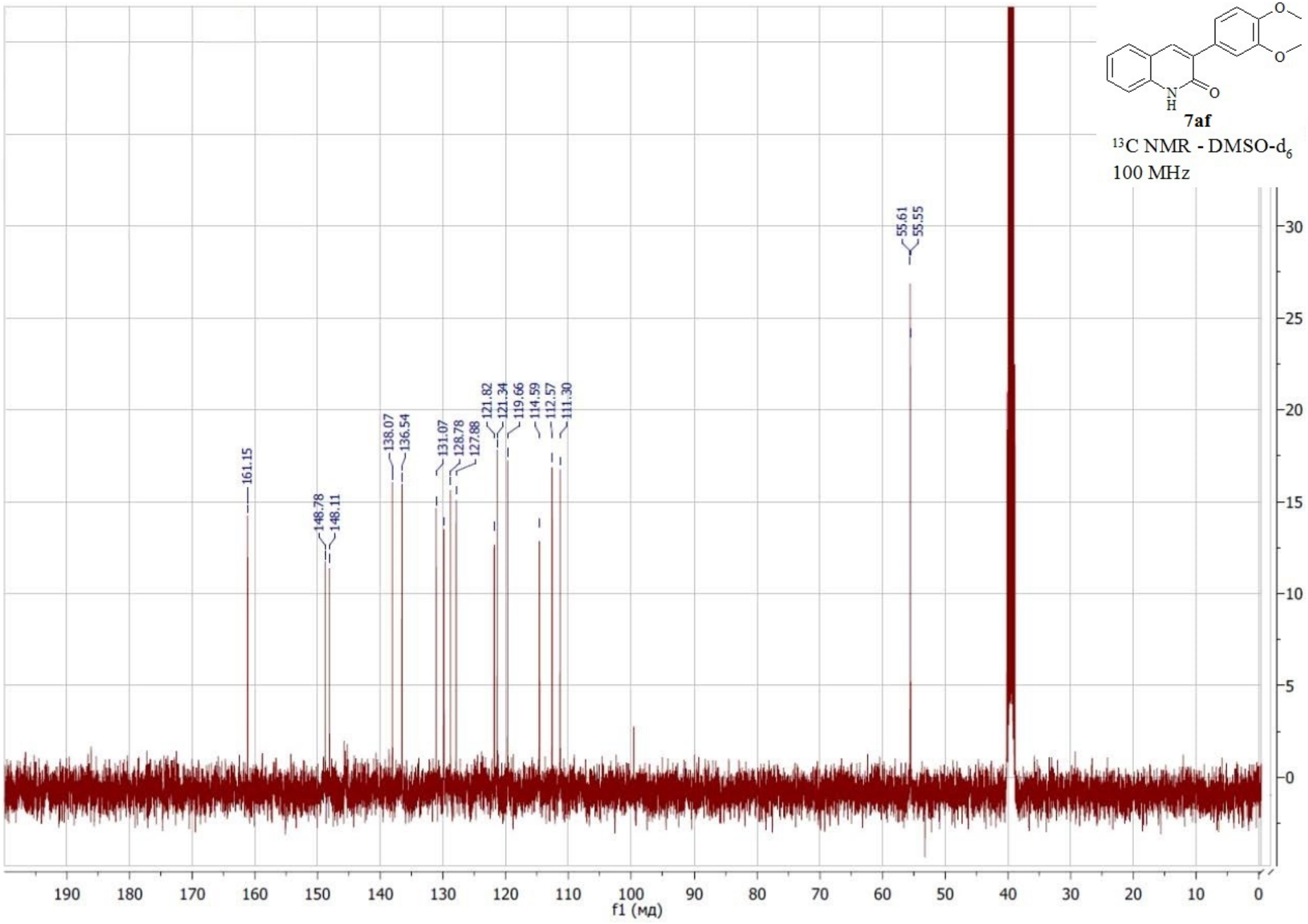
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55.61
55.55
f1 (мд)