Supporting Information

Transition metal-free one-pot double C-H functionalization of quinolines by disubstituted electron-deficient acetylenes

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General Methods.

NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 MHz for ^{1}H and 100.62 MHz for ^{13}C) and AV-400 spectrometers (40.5 MHz for ^{15}N) in $CDCl_3$. The internal standards were HMDS (for ^{1}H nuclei δ 0.05 ppm) or the residual solvent signals (for ^{13}C nuclei δ 77.16 ppm), CH_3NO_2 (for ^{15}N nuclei δ 0.0 ppm). The signals in the ^{13}C NMR spectrum were assigned by the two-dimensional ^{1}H–^{13}C heteronuclear HSQC and HMBC techniques. IR spectra were recorded on a two-beam Bruker Vertex 70 spectrometer, in a microlyaer from chloroform. Mass spectrum of reaction mixture between quinolone **1a** and acetylene **2a** was recorded on a GCMS-QP5050A spectrometer made by Shimadzu Company. Chromatographic column parameters were as follows: SPB™-5, length 60 m, internal diameter 0.25 mm, thickness of stationary phase film 0.25 μm; injector temperature 250 °C, gas carrier – helium, flow rate 0.7 mL/min; detector temperature 250 °C; mass analyzer: quadrupole, electron ionization, electron energy: 70 eV, ion source temperature 200 °C; mass range 34-650 Da. Elemental analysis was carried out on a FLASH EA 1112 Series analyzer. Melting points were determined on a Kofler hot stage apparatus. Commercial samples of quinolines **1a-c** and cyanophenylacetylene **2g** were used. Quinolines **1d**,**e** were prepeared by methylation corresponding hydroxyl and mercapto quinolines.[1] Samples of aroyl(hetaroyl)arylacetylenes **2a-f** were obtained according to method.[2] Monitoring of the reaction was carried out using the method of IR spectroscopy to follow the drop of the C≡C bond intensity of acetylenes **2** at 2195-2264 cm^{-1} until it stopped changing or its complete disappearance. The products **3a-p, 4d** and **5g-i** were separated and purified by column chromatography. Column and thin-layer chromatography were carried out on silica gel (0.06-0.2 mm) with chloroform/toluene/ethanol (20:4:1) mixture as eluent.

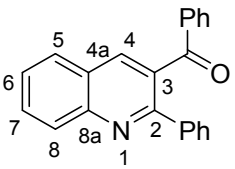
General Procedures.

Method A. A mixture of quinoline **1** (1 equiv), acetylene **2** (1 equiv), H_2O (55 equiv, 0.5 mL), KOH (20 mol%) and MeCN (1 mL) was stirred at 55-60 °C for 48 h. After that water layer was separated, organic layer was concentrated under the low pressure and the residue was passed through the chromatography column deliver to the target quinoline **3**.

Method B. A mixture of quinoline **1** (1.5 equiv), acetylene **2** (1 equiv), H_2O (5 equiv) and 20 mol% of KOH was stirred at rt for appropriate time. After that water layer was separated, organic residue was passed through the chromatography column deliver to the target quinoline **3**.

Method C. A mixture of quinoline **1** (1 equiv), acetylene **2** (1 equiv), H_2O (5 equiv) and 10 mol% of KOH was stirred at rt for appropriate time. After that water layer was separated, organic residue was passed through the chromatography column deliver to the target quinoline **3**.

Phenyl(2-phenylquinolin-3-yl)methanone (3a). **Method A:** from a mixture of quinoline (**1a**) (0.064 g, 0.500 mmol), acetylene **2a** (0.103 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3a** (0.069 g, 45%) was obtained as beige powder, mp 132-133 °C (ethanol).[3] Initial acetylene **2a** was recovered (0.013 g, conversion was 87%).



Analogously, from a mixture of quinoline **1b** (0.072 g, 0.500 mmol), acetylene **2a** (0.103 g, 0.500 mmol), H_2O (0.045 g, 2.500 mmol) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3a** (0.102 g, 66%) was obtained. Initial acetylene **2a** was recovered (0.014 g, conversion was 86%).

^{1}H, ^{13}C NMR and IR spectra are similar to the literature data.[2]

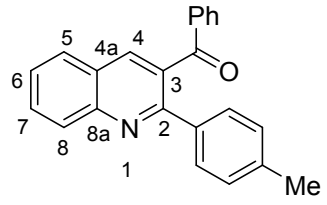
IR (microlayer): 1664 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.31 (s, 1H, H-4), 8.22 (m, 1H, H-8), 7.87 (m, 1H, H-5), 7.80 (m, 1H, H-7), 7.69 [m, 2H, H_o Ph from C(2)-Ph], 7.61 (m, 2H, H_o from Bz), 7.57 (m, 1H, H-6), 7.43 (m, 1H, H_p Ph from Bz), 7.31 (m, 2H, H_m Ph from Bz), 7.27 [m, 3H, $H_{m,p}$ from C(2)-Ph] ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 197.0 (C=O), 157.5 (C-2), 148.5 (C-8a), 139.9 [C_i from C(2)-Ph], 137.6 (C-4), 137.2 (C_i Ph from Bz), 133.4 (C_p Ph from Bz), 133.0 (C-3), 131.2 (C-7), 130.1

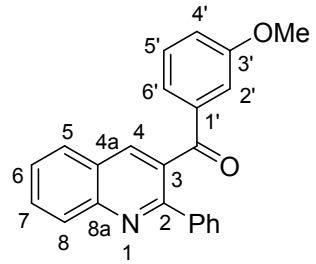
(C_o Ph from Bz), 129.8 (C-8), 129.4 [C_o from C(2)-Ph], 128.9 [C_p from C(2)-Ph], 128.5 [C_m from C(2)-Ph; C_m Ph from Bz], 128.2 (C-5), 127.4 (C-6), 125.9 (C-4a) ppm.
^{15}N NMR (40.55 MHz, $CDCl_3$): δ -70.7 (N-1) ppm.
$C_{22}H_{15}NO$ (309.36): calcd C 85.41, H 4.89, N 4.53; found C 85.46, H 4.58, N 5.21.

Phenyl(2-(*p*-tolyl)quinolin-3-yl)methanone (3b). **Method A**: from a mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2b** (0.110 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3b** (0.047 g, 29%) was obtained as a beige powder, mp 125-127 °C (ethanol). Initial acetylene **2b** was recovered (0.026 g, conversion was 76%).



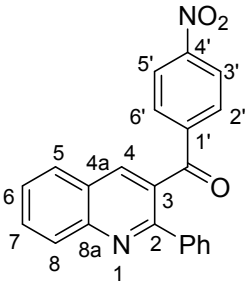
IR (microlayer): 1664 (C=O) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.27 (s, 1H, H-4), 8.21 (m, 1H, H-8), 7.85 (m, 1H, H-5), 7.79 (m, 1H, H-7), 7.72 (m, 2H, H_o Ph from Bz), 7.57 (m, 1H, H-6), 7.51 [m, 2H, H_o from C(2)-Ph], 7.46 (m, 1H, H_p Ph from Bz), 7.32 (m, 2H, H_m Ph from Bz), 7.07 [m, 2H, H_m from C(2)-Ph], 2.26 (s, 3H, Me) ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 197.1 (C=O), 157.6 (C-2), 148.5 (C-8a), 138.9 (C_i Ph from Bz), 137.5 (C-4), 137.1 [C_i from C(2)-Ph], 137.2 [C_p from C(2)-Ph], 133.4 (C_p Ph from Bz), 133.0 (C-3), 131.2 (C-7), 130.2 (C_o Ph from Bz; C-8), 129.3 [$C_{o,m}$ from C(2)-Ph], 128.5 [C_m Ph from Bz], 128.2 (C-5), 127.2 (C-6), 125.8 (C-4a), 21.3 (Me) ppm.
$C_{23}H_{17}NO$ (323.40): calcd C 85.42, H 5.30, N 4.33; found C 85.31, H 5.21, N 4.19.

(3-Methoxyphenyl)(2-phenylquinolin-3-yl)methanone (3c). **Method A**: from a mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2c** (0.118 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3c** (0.096 g, 56%) was obtained as a beige powder, mp 136-138 °C (ether).



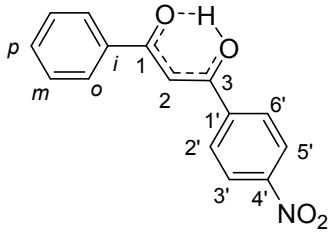
IR (microlayer): 1664 (C=O) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.29 (s, 1H, H-4), 8.22 (m, 1H, H-8), 7.86 (m, 1H, H-5), 7.78 (m, 1H, H-7), 7.60 [m, 2H, H_o from C(2)-Ph], 7.57 (m, 1H, H-6), 7.35-7.15 [m, 6H, H-2', H-5', H-6', $H_{m,p}$ from C(2)-Ph], 7.00 (m, 1H, H-4'), 3.74 (s, 3H, OMe) ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 196.7 (C=O), 159.7 (C-3'), 157.2 (C-2), 148.4 (C-8a), 139.9 [C_i from C(2)-Ph], 138.5 (C-1'), 137.6 (C-4), 133.0 (C-3), 131.3 (C-7), 129.8 (C-8), 129.5 (C-5'), 129.4 [C_o from C(2)-Ph], 128.9 [C_p from C(2)-Ph], 128.5 [C_m from C(2)-Ph], 128.2 (C-5), 127.4 (C-6), 125.8 (C-4a), 123.3 (C-6'), 120.2 (C-4'), 113.8 (C-2'), 55.2 (OMe) ppm.
$C_{23}H_{17}NO_2$ (339.39): calcd C 81.40, H 5.05, N 4.13; found C 81.77, H 5.34, N 3.79.

(4-Nitrophenyl)(2-phenylquinolin-3-yl)methanone (3d). **Method A**: from mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2d** (0.126 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3d** (0.033 g, 19%) was obtained as a light-brown powder, mp 184-186 °C (ether).



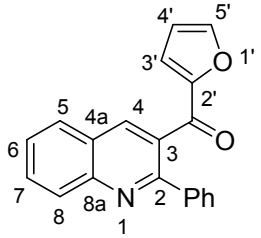
From mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2d** (0.126 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) (55-60 °C, 24 h) quinoline **3d** (0.043 g, 24%) was obtained.
IR (microlayer): 1665 (C=O) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.44 (s, 1H, H-4), 8.25 (m, 1H, H-8), 8.05 (m, 2H, H-3',5'), 7.94 (m, 1H, H-5), 7.86 (m, 1H, H-7), 7.72 (m, 2H, H-2',6'), 7.54 [m, 2H, H_o from C(2)-Ph], 7.64 (m, 1H, H-6), 7.24 [m, 3H, $H_{m,p}$ from C(2)-Ph] ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 195.6 (C=O), 157.1 (C-2), 150.1 (C-4'), 148.8 (C-8a), 141.9 (C-1'), 139.6 [C_i from C(2)-Ph], 138.6 (C-4), 131.8 (C-3), 131.9 (C-7), 130.6 (C-2',6'), 129.9

(C-8), 129.5 [C_o from C(2)-Ph], 129.4 [C_p from C(2)-Ph], 128.8 [C_m from C(2)-Ph], 123.5 (C-3',5'), 128.4 (C-5), 127.8 (C-6), 126.0 (C-4a) ppm.
$C_{22}H_{14}N_2O_3$ (354.37): calcd C 74.57, H 3.98, N 7.91; found C 74.87, H 3.93, N 7.52.



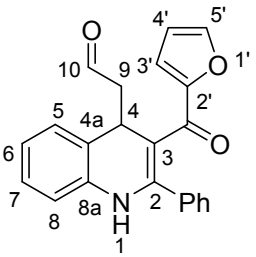
Also here **(*Z*)-3-hydroxy-1(3)-(4-nitrophenyl)-(3)1-phenylprop-2-en-1-one (4d)** (0.015 g, 11%) was isolated as a white powder, mp 160-162 (ether).[4]
^{1}H NMR and IR spectra are similar to the literature data.[4]
IR (microlayer): 1726, 1344, 1523 (NO_2), 1654 (C=O), 3371 (OH) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 16.65 (br. s, 1H, OH), 8.32 (m, 2H, H-3',5'), 8.12 (m, 2H, H-2',6'), 7.99 [m, 2H, H_o from C(1)-Ph], 7.60 [m, 1H, H_p from C(1)-Ph], 7.50 [m, 2H, H_m from C(1)-Ph], 6.88 (s, 1H, H-2) ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 186.9 (C-1), 180.8 (C-3), 149.0 (C-4'), 140.1 (C-1'), 134.3 [C_i from C(1)-Ph], 132.3 [C_p from C(1)-Ph], 128.0 (C-2',6'), 127.2 [C_m from C(1)-Ph], 126.6 [C_o from C(1)-Ph], 123.0 (C-3',5'), 93.4 (C-2) ppm.

2-Furyl(2-phenyl-3-quinolinyl)methanone (3e). **Method A**: from mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2e** (0.098 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3e** (0.033 g, 59%) was obtained as a light-beige powder, mp 120-121 °C (ethanol).



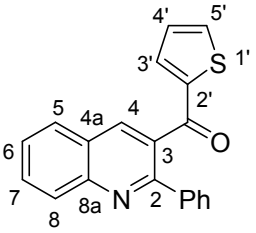
Method C: from a mixture of quinoline **1a** (0.129 g, 1.000 mmol), acetylene **2e** (0.196 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.006 g, 10 mol%) (rt, 240 h) quinoline **3e** (0.198 g, 66%) was obtained. Initial acetylene **2e** was recovered (0.010 g, conversion was 95%).
IR (microlayer): 1652 (C=O) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.33 (s, 1H, H-4), 8.18 (m, 1H, H-8), 7.82 (m, 1H, H-5), 7.73 (m, 1H, H-7), 7.65 [m, 2H, H_o from C(2)-Ph], 7.50 (m, 1H, H-6), 7.40 (m, 1H, H-5'), 7.26 [m, 3H, $H_{m,p}$ Ph from C(2)-Ph], 6.88 (m, 1H, H-3'), 6.29 (m, 1H, H-4') ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 183.6 (C=O), 157.0 (C-2), 152.3 (C-2'), 148.3 (C-8a), 147.3 (C-5'), 139.7 [C_i from C(2)-Ph], 137.6 (C-4), 131.8 (C-3), 131.2 (C-7), 129.5 (C-8), 129.0 [C_o from C(2)-Ph], 128.7 [C_p from C(2)-Ph], 128.3 [C_m from C(2)-Ph], 128.1 (C-5), 127.2 (C-6), 125.6 (C-4a), 120.5 (C-3'), 112.4 (C-4') ppm.
^{15}N NMR (40.55 MHz, $CDCl_3$): δ -70.7 (N-1) ppm.
$C_{20}H_{13}NO_2$ (299.32): calcd C 80.25, H 4.38, N 4.68; found C 80.60, H 4.20, N 4.70.
Method B: from a mixture of quinoline **1a** (0.097 g, 0.750 mmol), acetylene **2e** (0.098 g, 0.500 mmol), H_2O (0.045 g, 2.500 mmol) and KOH (0.006 g, 20 mol%) (rt, 144 h) quinoline **3e** (0.059 g, 39%) and 1,4-dihydroquinoline **5e** (11%, ^{1}H NMR) were obtained. Initial acetylene **2e** was recovered (0.016 g, conversion was 84%).

2-(3-(Furan-2-carbonyl)-2-phenyl-1,4-dihydroquinolin-4-yl)acetaldehyde (5e).



IR (microlayer): 1648, 1707 (C=O), 3274 (NH) cm^{-1}
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 9.82 (t, $^3J_{H9,H10}$ = 5.4 Hz, 1H, H-10), 7.37 (m, 2H, H_o from Ph), 7.30-7.20 (m, 3H, $H_{m,p}$ from Ph; 1H H-5; 1H H-7; 1H NH), 7.10 (t, $^3J_{H6,H7}$ = 7.7 Hz, $^3J_{H5,H6}$ = 7.7 Hz, 1H, H-6), 6.98 (d, $^3J_{H7,H8}$ = 8.2 Hz, 1H, H-8), 6.94 (m, 1H, H-5'), 6.56 (m, 1H, H-3'), 6.02 (m, 1H, H-4'), 4.42 (t, $^3J_{H4,H9}$ = 6.4 Hz, 1H, H-4), 2.76, 2.61 (2m, 2H, H-9) ppm.

(2-Phenylquinolin-3-yl)(thiophen-2-yl)methanone (3f). **Method A**: from mixture of quinoline **1a** (0.064 g, 0.500 mmol), acetylene **2f** (0.106 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3f** (0.093 g, 59%) was obtained as a brown powder, mp 130-132 °C (ethanol).



Method C: from a mixture of quinoline **1a** (0.129 g, 1.000 mmol), acetylene **2f** (0.212 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.006 g, 10 mol%) (rt, 240 h) quinoline **3f** (0.227 g, 72%) was obtained. Initial acetylene **2f** was recovered (0.011 g, conversion was 95%).

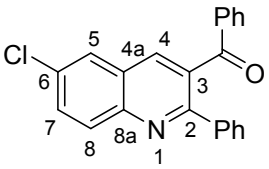
IR (microlayer): 1641 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.29 (s, 1H, H-4), 8.19 (m, 1H, H-8), 7.81 (m, 1H, H-5), 7.74 (m, 1H, H-7), 7.66 [m, 2H, H_o from C(2)-Ph], 7.55 (m, 1H, H-5'), 7.51 (m, 1H, H-6), 7.26 [m, 1H, H-3'; 3H, $H_{m,p}$ Ph from C(2)-Ph], 6.89 (m, 1H, H-4') ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 188.0 (C=O), 156.8 (C-2), 148.3 (C-8a), 144.3 (C-2'), 139.6 [C_i from C(2)-Ph], 137.1 (C-4), 135.3 (C-5'), 135.2 (C-3'), 132.6 (C-3), 131.1 (C-7), 129.6 (C-8), 129.2 [C_o from C(2)-Ph], 128.8 [C_p from C(2)-Ph], 128.3 [C_m from C(2)-Ph], 128.1 (C-5), 128.0 (C-4'), 127.3 (C-6), 125.6 (C-4a) ppm.

$C_{20}H_{13}NOS$ (315.39): calcd C 76.16, H 4.15, N 4.44, S 10.17; found C 75.89, H 4.03, N 4.71, S 9.90.

(6-Chloro-2-phenylquinolin-3-yl)(phenyl)methanone (3g). **Method A**: from a mixture of quinoline **1c** (0.082 g, 0.500 mmol), acetylene **2a** (0.103 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3g** (0.048 g, 28%) was obtained as a white powder, mp 161-163 °C (ethanol).[2b,d] Initial acetylene **2a** was recovered (0.019 g, conversion was 82%).



^{1}H, ^{13}C NMR and IR spectra are similar to the literature data.[2b,d]

IR (microlayer): 1666 (C=O) cm^{-1}.

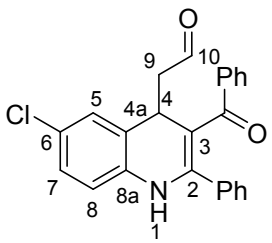
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.22 (s, 1H, H-4), 8.16 (m, 1H, H-8), 7.87 (d, $^4J_{H5,H7}$ = 2.0 Hz, 1H, H-5), 7.74 (dd, $^3J_{H7,H8}$ = 9.0 Hz, 1H, H-7), 7.69 (m, 2H, H_o Ph from Bz), 7.59 [m, 2H, H_o from C(2)-Ph], 7.47 (m, 1H, H_p Ph from Bz), 7.32 (m, 2H, H_m Ph from Bz), 7.26 [m, 3H, $H_{m,p}$ from C(2)-Ph] ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 196.7 (C=O from Bz), 157.8 (C-2), 146.8 (C-8a), 139.5 [C_i from C(2)-Ph], 136.9 (C_i Ph from Bz), 136.6 (C-4), 133.8 (C-6), 133.6 (C_p Ph from Bz), 133.2 (C-3), 132.2 (C-8), 131.4 (C-7), 130.1 [C_o from C(2)-Ph], 129.4 [C_m from C(2)-Ph], 129.2 [C_p from C(2)-Ph], 128.6 ($C_{o,m}$ Ph from Bz], 126.8 (C-5), 126.6 (C-4a) ppm.

$C_{22}H_{14}ClNO$ (343.81): calcd C 76.86, H 4.10, Cl 10.31, N 4.07; found C 76.63, H 3.96, Cl 10.26, N 4.29.

Method C: from a mixture of quinoline **1c** (0.163 g, 1.000 mmol), acetylene **2a** (0.206 g, 1.000 mmol), H_2O (0.045 g, 2.500 mmol) and KOH (0.006 g, 10 mol%) in MeCN (0.1 mL for homogenization of reaction mixture) (rt, 336 h) quinoline **3g** (0.037 g, 11%) and 1,4-dihydroquinoline **5g** (0.048 g, 12%) were obtained. Initial acetylene **2a** was recovered (0.048 g, conversion was 77%).

2-(3-Benzoyl-6-chloro-2-phenyl-1,4-dihydroquinolin-4-yl)acetaldehyde (5g). Yellow powder, mp 195-197 °C (acetone).

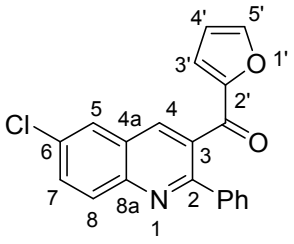


IR (microlayer): 1717 (C=O), 3271 (NH) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 9.83 (t, $^3J_{H\,9,H10}$ = 5.4 Hz, 1H, H-10), 7.26 [m, 2H, H_o from C(2)-Ph], 7.22 (d, $^4J_{H5,H7}$ = 1.5 Hz, 1H, H-5), 7.19 (dd, $^3J_{H7,H8}$ = 8.4 Hz, 1H, H-7), 7.15 (m, 2H, H_o Ph from Bz), 7.08 [m, 1H, H_p from C(2)-Ph], 7.02 [m, 1H, H_p Ph from Bz; 2H, H_m from C(2)-Ph], 7.27 (m, 2H, H_m Ph from Bz), 6.85 (d, $^3J_{H7,H8}$

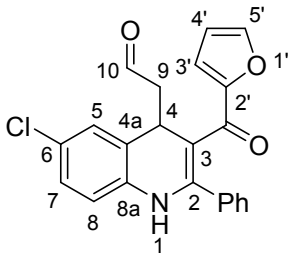
= 8.4 Hz, 1H, H-8), 6.18 (br. s, 1H, NH), 4.61 (t, $^3J_{H4,H9}$ = 6.4 Hz, 1H, H-4), 2.75, 2.63 (2m, 2H, H-9) ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 201.5 (C-10), 195.7 (C=O from Bz), 151.5 (C-8a), 140.8 (C_i Ph from Bz), 135.8 (C-2), 135.5 [C_i from C(2)-Ph], 130.4 [C_p from C(2)-Ph], 130.3 (C_p Ph from Bz), 129.8 (C_o Ph from Bz), 129.1 [C_m from C(2)-Ph], 129.1 (C-6), 128.5 (C_m Ph from Bz; C-5), 127.6 (C-7), 127.5 [C_o from C(2)-Ph], 127.2 (C-4a), 116.2 (C-8), 106.6 (C-3), 52.0 (C-9), 35.0 (C-4) ppm.
$C_{24}H_{18}ClNO_2$ (387.86): calcd C 74.32, H 4.68, Cl 9.14, N 3.61; found C 73.95, H 4.86, Cl 8.77, N 3.30.

(6-Chloro-2-phenylquinolin-3-yl)(furan-2-yl)methanone (3h). **Method A**: from a mixture of quinoline **1c** (0.082 g, 0.500 mmol), acetylene **2e** (0.098 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3h** (0.033 g, 20%) as a light-beige powder, mp 129-130 °C (ethanol) and 1,4-dihydroquinoline **5h** (6%, ^{1}H NMR) were obtained. Initial acetylene **2e** was recovered (0.033 g, conversion was 66%).



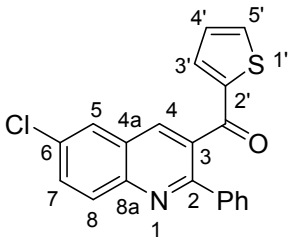
IR (microlayer): 1655 (C=O) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.32 (s, 1H, H-4), 8.15 (d, $^3J_{H7,H8}$ = 9.0 Hz, 1H, H-8), 7.89 (d, $^4J_{H5,H7}$ = 2.0 Hz, 1H, H-5), 7.74 (dd, $^3J_{H7,H8}$ = 9.0 Hz, $^4J_{H5,H7}$ = 2.0 Hz, 1H, H-7), 7.64 (m, 2H, H_o from Ph), 7.46 (d, $^3J_{H4',H5'}$ = 1.5 Hz, 1H, H-5'), 7.32 (m, 3H, $H_{m,p}$ from Ph), 6.95 (d, $^3J_{H3',H4'}$ = 3.6 Hz, 1H, H-3'), 6.40 (dd, $^3J_{H4',H5'}$ = 1.5 Hz, $^3J_{H3',H4'}$ = 3.6 Hz, 1H, H-4') ppm.
^{13}C NMR (100.62 MHz, $CDCl_3$): δ 183.6 (C=O), 157.6 (C-2), 152.4 (C-2'), 147.7 (C-5'), 146.9 (C-8a), 139.5 (C_i from Ph), 136.8 (C-4), 133.2 (C-6), 133.8 (C-3), 132.4 (C-8), 131.4 (C-7), 129.2 ($C_{o,p}$ from Ph), 128.8 (C_m from Ph), 126.8 (C-5), 126.5 (C-4a), 120.8 (C-3'), 112.7 (C-4') ppm.
$C_{20}H_{12}ClNO_2$ (333.77): calcd C 71.97, H 3.62, Cl 10.62, N 4.20; found C 71.68, H 3.63, Cl 10.81, N 4.06.
Method C: from a mixture of quinoline **1c** (0.163 g, 1.000 mmol), acetylene **2e** (0.196 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.006 g, 10 mol%) in MeCN (0.2 mL for homogenization of reaction mixture) (rt, 336 h) quinoline **3h** (0.035 g, 10%) and 1,4-dihydroquinoline **5h** (0.080 g, 21%) were obtained. Initial acetylene **2e** was recovered (0.101 g, conversion was 49%).

2-(6-Chloro-3-(furan-2-carbonyl)-2-phenyl-1,4-dihydroquinolin-4-yl)acetaldehyde (5h). Yellow powder, mp 148-150 °C (acetone).



IR (microlayer): 1716 (C=O), 3299 (NH) cm^{-1}.
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 9.84 (t, $^3J_{H9,H10}$ = 5.4 Hz, 1H, H-10), 7.34 [m, 2H, H_o from C(2)-Ph], 7.25-7.15 [m, 3H $H_{m,p}$ from C(2)-Ph; 2H H-5, H-7], 6.93 (m, 1H, H-5'), 6.86 (d, $^3J_{H7,H8}$ = 8.2 Hz, 1H, H-8), 6.85 (br. s, 1H, NH), 6.54 (m, 1H, H-3'), 6.01 (m, 1H, H-4'), 4.53 (t, $^3J_{H4,H9}$ = 6.4 Hz, 1H, H-4), 2.77, 2.68 (2m, 2H, H-9) ppm.
^{13}C NMR (100.62 MHz, DMSO-d_6): δ 201.8 (C-10), 180.9 (C=O), 152.8 (C-8a), 152.3 (C-2'), 144.6 (C-5'), 136.1 (C-2), 135.6 [C_i from C(2)-Ph], 129.8 [C_p from C(2)-Ph], 129.4 [C_o from C(2)-Ph], 127.9 [C_m from C(2)-Ph], 127.4 (C-5), 127.1 (C-6), 126.9 (C-7), 126.8 (C-4a), 117.5 (C-3'), 115.7 (C-8), 111.2 (C-4'), 103.5 (C-3), 51.7 (C-9), 33.8 (C-4) ppm.
$C_{22}H_{16}ClNO_3$ (377.82): calcd C 69.94, H 4.27, Cl 9.38, N 3.71; found C 69.56, H 4.13, Cl 9.76, N 3.36.

(6-Chloro-2-phenylquinolin-3-yl)(thiophen-2-yl)methanone (3i). **Method A**: from a mixture of quinoline **1c** (0.082 g, 0.500 mmol), acetylene **2f** (0.106 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3i** (0.054 g, 31%) as a



light-beige powder, mp 181-182 °C (ethanol), and 1,4-dihydroquinoline **5i** (4%, ^{1}H NMR) were obtained. Initial acetylene **2f** was recovered (0.049 g, conversion was 54%).

IR (microlayer): 1641 (C=O) cm^{-1}.

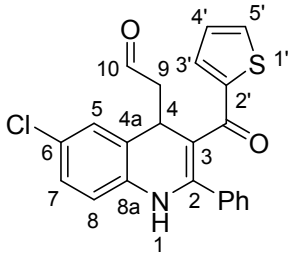
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.28 (s, 1H, H-4), 8.16 (d, $^3J_{H7,H8}$ = 9.0 Hz, 1H, H-8), 7.87 (d, $^4J_{H5,H7}$ = 2.0 Hz, 1H, H-5), 7.75 (dd, 1H, H-7), 7.67 (m, 2H, H_o from Ph), 7.65 (d, $^3J_{H3',H4'}$ = 5.0 Hz, 1H, H-3'), 7.35 (m, 3H, $H_{m,p}$ from Ph), 7.31 (d, 1H, H-5'), 6.99 (dd, $^3J_{H4',H5'}$ = 3.8 Hz, 1H, H-4') ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 188.5 (C=O), 157.3 (C-2), 146.9 (C-8a), 144.2 (C-2'), 139.4 (C_i from Ph), 136.3 (C-4), 135.7 (C-5'), 135.6 (C-3'), 133.6 (C-6), 133.3 (C-3), 132.3 (C-8), 131.4 (C-7), 129.3 ($C_{o,p}$ from Ph), 128.7 (C_m from Ph), 128.4 (C-4'), 126.8 (C-5), 126.4 (C-4a) ppm.

$C_{20}H_{12}ClNOS$ (349.83): calcd C 68.67, H 3.46, Cl 10.13, N 4.00, S 9.17; found: C 68.37, H 3.31, Cl 10.41, N 4.24, S 8.82.

Method C: from a mixture of quinoline **1c** (0.163 g, 1.000 mmol), acetylene **2f** (0.212 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.006 g, 10 mol%) in MeCN (0.2 mL for homogenization of reaction mixture) (rt, 336 h) quinoline **3i** (0.045 g, 52%) and 1,4-dihydroquinoline **5i** (0.044 g, 46%) were obtained. Initial acetylene **2f** was recovered (0.124 g, conversion was 42%).

2-(6-Chloro-2-phenyl-3-(thiophene-2-carbonyl)-1,4-dihydroquinolin-4-yl)acetaldehyde (5i).



Dark-yellow powder, mp 152-154 °C (ether).

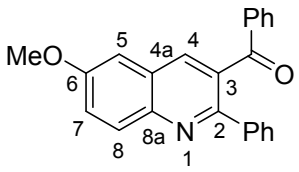
IR (microlayer): 1718 (C=O), 3288 (NH) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 9.80 (t, $^3J_{H9,H10}$ = 5.4 Hz, 1H, H-10), 7.29 [m, 2H, H_o from C(2)-Ph], 7.22 (d, $^4J_{H5,H7}$ = 1.5 Hz, 1H, H-5), 7.20-7.10 [m, 3H $H_{m,p}$ from C(2)-Ph; 2H, H-3', H-7], 7.00 (br. s, 1H, NH), 6.89 (d, $^3J_{H7,H8}$ = 8.4 Hz, 1H, H-8), 6.86 (m, 1H, H-5'), 6.50 (m, 1H, H-4'), 4.49 (t, $^3J_{H4,H9}$ = 6.4 Hz, 1H, H-4), 2.73, 2.65 (2m, 2H, H-9) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 201.6 (C-10), 187.4 (C=O), 149.9 (C-8a), 145.4 (C-2'), 136.0 (C-2), 135.6 [C_i from C(2)-Ph], 132.8 (C-3'), 131.5 (C-5'), 130.4 [C_p from C(2)-Ph], 129.4 [C_o from C(2)-Ph], 128.9 (C-6), 128.7 [C_m from C(2)-Ph], 128.3 (C-5), 127.6 (C-7), 126.9 (C-4a), 126.7 (C-4'), 116.4 (C-8), 106.6 (C-3), 51.8 (C-9), 35.4 (C-4) ppm.

$C_{22}H_{16}ClNO_2$ (393.89): calcd C 67.08, H 4.09, Cl 9.00, N 3.56, S 8.14; found C 67.47, H 4.46, Cl 8.67, N 3.30, S 8.17.

(6-Methoxy-2-phenylquinolin-3-yl)(phenyl)methanone (3j).



Method A: from a mixture of quinoline **1d** (0.080 g, 0.500 mmol), acetylene **2a** (0.103 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3j** (0.105 g, 62%) was obtained as a white powder, mp 157-159 °C (hexane). Initial acetylene **2a** was recovered (0.016 g, conversion was 84%).

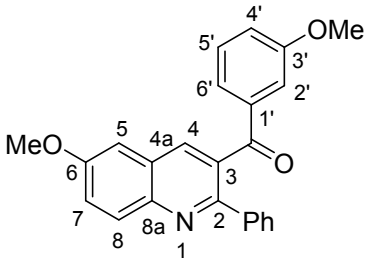
IR (microlayer): 1663 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.17 (s, 1H, H-4), 8.10 (d, $^3J_{H7,H8}$ = 9.2 Hz, 1H, H-8), 7.67 [m, 2H, H_o Ph from C(2)-Ph], 7.58 (m, 2H, H_o from Bz), 7.44 (dd, $^3J_{H7,H8}$ = 9.2 Hz, $^4J_{H5,H7}$ = 2.6 Hz, 1H, H-7), 7.40 (m, 1H, H_p Ph from Bz), 7.33-7.17 [m, 5H, $H_{p,m,m'}$ Ph from Bz and C(2)-Ph], 7.09 (d, $^4J_{H5,H7}$ = 2.6 Hz, 1H, H-5), 3.87 (s, 3H, OMe) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 197.2 (C=O), 158.4 (C-6), 155.0 (C-2), 144.6 (C-8a), 139.8 [C_i from C(2)-Ph], 137.1 (C_i from Bz), 136.3 (C-4), 133.3 (C_p from Bz), 133.0 (C-3), 131.1 (C-8), 130.0 [C_o from C(2)-Ph], 129.2 [C_m from C(2)-Ph], 128.6 [C_p from C(2)-Ph], 128.4 ($C_{o,m}$ from Bz), 126.9 (C-4a), 124.1 (C-7), 105.3 (C-5), 55.7 (OMe) ppm.

$C_{23}H_{17}NO_2$ (339.39): calcd C 81.40, H 5.05, N 4.13; found C 81.01, H 4.79, N 3.79.

(6-Methoxy-2-phenylquinolin-3-yl)(3-methoxyphenyl)methanone (3k).



Method A: from a mixture of quinoline **1d** (0.080 g, 0.500 mmol), acetylene **2c** (0.118 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 24 h) quinoline **3k** (0.083 g, 45%) was obtained as a white powder, mp 185-187 °C (MeCN). Initial acetylene **2c** was recovered (0.004 g, conversion was 97%).

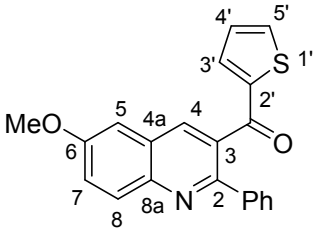
IR (microlayer): 1664 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.19 (s, 1H, H-4), 8.11 (d, $^3J_{H7,H8}$ = 9.2 Hz, 1H, H-8), 7.58 [m, 2H, H_o Ph from C(2)-Ph], 7.46 (dd, $^3J_{H7,H8}$ = 9.2 Hz, $^4J_{H5,H7}$ = 2.6 Hz, 1H, H-7), 7.32-7.17 [m, 3H, H-2', H-5', H-6'; 3H, $H_{m,p}$ from C(2)-Ph], 7.12 (d, $^4J_{H5,H7}$ = 2.6 Hz, 1H, H-5), 7.00 (m, 1H, H-4'), 3.92 (s, 3H, OMe), 3.75 (s, 3H, OMe') ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 197.1 (C=O), 159.7 (C-3'), 158.5 (C-6), 155.1 (C-2), 144.7 (C-8a), 139.9 [C_i from C(2)-Ph], 138.6 (C-1'), 136.3 (C-4), 133.2 (C-3), 131.2 (C-8), 129.5 (C-5'), 129.3 [C_o from C(2)-Ph], 128.7 [C_p from C(2)-Ph],128.5 [C_m from C(2)-Ph], 126.9 (C-4a), 124.2 (C-7), 123.3 (C-6'), 120.2 (C-4'), 113.8 (C-2'), 105.4 (C-5), 55.8 (OMe), 55.6 (OMe') ppm.

$C_{24}H_{19}NO_3$ (369.42): calcd C 78.03, H 5.18, N 3.79; found C 78.04, H 5.00, N 3.64.

(6-Methoxy-2-phenylquinolin-3-yl)(thiophen-2-yl)methanone (3l).



Method A: from a mixture of quinoline **1d** (0.080 g, 0.500 mmol), acetylene **2f** (0.106 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3l** (0.092 g, 53%) was obtained as a white powder, mp 188-190 °C (MeCN).

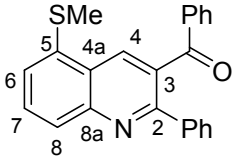
IR (microlayer): 1640 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.24 (s, 1H, H-4), 8.10 (d, $^3J_{H7,H8}$ = 9.2 Hz, 1H, H-8), 7.65 [m, 2H, H_o from C(2)-Ph], 7.60 (d, $^4J_{H4',H5'}$ = 4.8 Hz, 1H, H-5'), 7.45 (m, $^3J_{H7,H8}$ = 9.2 Hz, $^4J_{H5,H7}$ = 2.3 Hz, 1H, H-7), 7.35-7.25 [m, 1H, H-3'; 3H, $H_{m,p}$ Ph from C(2)-Ph], 7.12 (d, $^4J_{H5,H7}$ = 2.3 Hz, 1H, H-5), 6.95 (m, 1H, H-4'), 3.92 (s, 3H, OMe) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 189.2 (C=O), 158.5 (C-6), 154.6 (C-2), 144.7 (C-8a), 144.5 (C-2'), 139.8 [C_i from C(2)-Ph], 135.9 (C-4), 135.5 (C-5'), 135.3 (C-3'), 133.0 (C-3), 131.2 (C-8), 129.2 [C_o from C(2)-Ph], 128.7 [C_p from C(2)-Ph], 128.6 [C_m from C(2)-Ph], 128.2 (C-4'), 126.9 (C-4a), 124.2 (C-7), 105.3 (C-5), 55.8 (OMe) ppm.

$C_{21}H_{15}NO_2S$ (345.42): calcd C 73.02, H 4.38, N 4.06, S 9.28; found C 72.97, H 4.25, N 3.98, S 9.65.

(5-(Methylthio)-2-phenylquinolin-3-yl)(phenyl)methanone (3m).



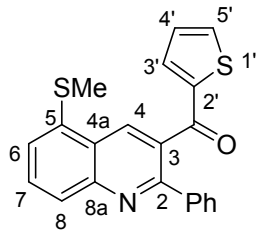
Method A: from a mixture of quinoline **1e** (0.088 g, 0.500 mmol), acetylene **2a** (0.103 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3m** (0.090 g, 51%) was obtained as a yellow oil (80% purity according 1H NMR). Initial acetylene **2a** was recovered (0.004 g, conversion was 96%).

IR (microlayer): 1663 (C=O) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.75 (s, 1H, H-4), 8.04 (d, $^3J_{H7,H8}$ = 8.4 Hz, 1H, H-8), 7.74 (t, $^3J_{H7,H8}$ = 8.4 Hz, $^3J_{H6,H7}$ = 8.4 Hz, 1H, H-7), 7.71 [m, 2H, H_o Ph from C(2)-Ph], 7.61 (m, 2H, H_o from Bz), 7.48 (d, $^3J_{H6,H7}$ = 8.4 Hz, 1H, H-6), 7.46 (m, 1H, H_p Ph from Bz), 7.35-7.25 [m, 2H, H_m Ph from Bz; 3H, $H_{m,p}$ from C(2)-Ph], 2.58 (s, 3H, SMe) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 196.8 (C=O), 157.6 (C-2), 148.6 (C-8a), 139.5 [C_i from C(2)-Ph], 137.3 (C-5), 137.0 (C_i Ph from Bz), 134.3 (C-4), 133.4 (C_p Ph from Bz), 132.5 (C-3), 130.9 (C-7), 130.1 [C_o from C(2)-Ph], 129.3 [C_m from C(2)-Ph], 129.0 [C_p from C(2)-Ph], 128.5 ($C_{o,m}$ Ph from Bz), 127.2 (C-8), 124.8 (C-6), 124.7 (C-4a), 16.5 (SMe) ppm.

(5-(Methylthio)-2-phenylquinolin-3-yl)(thiophen-2-yl)methanone (3n).



Method A: from a mixture of quinoline **1e** (0.088 g, 0.500 mmol), acetylene **2f** (0.106 g, 0.500 mmol), H_2O (0.5 mL) and KOH (0.006 g, 20 mol%) in MeCN (1 mL) (55-60 °C, 48 h) quinoline **3n** (0.068 g, 38%) was obtained as a white powder, mp 138-140 °C (acetone). Initial acetylene **2f** was recovered (0.026 g, conversion was 75%).

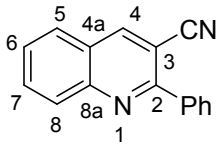
IR (microlayer): 1642 (C=O) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ 8.80 (s, 1H, H-4), 8.02 (d, $^3J_{H7,H8}$ = 8.4 Hz, 1H, H-8), 7.74 (t, $^3J_{H7,H8}$ = 8.4 Hz, $^3J_{H6,H7}$ = 8.4 Hz, 1H, H-7), 7.69 [m, 2H, H_o from C(2)-Ph], 7.65 (m, 1H, H-5'), 7.47 (d, $^3J_{H6,H7}$ = 8.4 Hz, 1H, H-6), 7.33 [m, 3H, $H_{m,p}$ from C(2)-Ph; 1H, H-3'], 6.99 (m, 1H, H-4'), 2.59 (s, 3H, SMe) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 188.8 (C=O), 157.3 (C-2), 148.8 (C-8a), 144.5 (C-2'), 139.5 [C_i from C(2)-Ph], 137.4(C-5), 135.6 (C-5'), 135.4 (C-3'), 134.1 (C-4), 132.4 (C-3), 131.0 (C-7), 129.3 [C_o from C(2)-Ph], 129.2 [C_p from C(2)-Ph], 128.7 [C_m from C(2)-Ph], 128.4 (C-4'), 127.3 (C-8), 125.1 (C-6), 124.8 (C-4a), 16.7 (SMe) ppm.

$C_{21}H_{15}NOS_2$ (361.48): calcd C 69.78, H 4.18, N 3.87, S 17.74; found C 70.19, H 4.07, N 3.55, S 17.48.

2-Phenylquinoline-3-carbonitrile (3o). From a mixture of quinoline **1a** (0.129 g, 1.000 mmol), acetylene **2g** (0.127 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.012 g, 20 mol%) in MeCN (0.5 mL for the homogenization of reaction mixture) (55-60 °C, 6 h) quinoline **3o** (0.042 g, 18%) was obtained as a white powder, mp 197-198 °C (ethanol).[2b,d]



^1H, ^{13}C NMR and IR spectra are similar to the literature data.[2b,d]

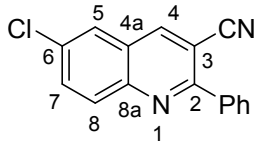
IR (microlayer): 1618 (C=C), 2219 (CN) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ 8.66 (s, 1H, H-4), 8.19 (m, 1H, H-8), 7.99 (m, 2H, H_o from Ph), 7.87 (m, 1H, H-7), 7.90 (m, 1H, H-5), 7.65 (m, 1H, H-6), 7.56 (m, 3H, $H_{m,p}$ from Ph) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 158.2 (C-2), 148.9 (C-8a), 144.3 (C-4), 137.8 (C_i from Ph), 133.1 (C_p from Ph), 130.2 (C-7), 130.1 (C-8), 129.3 (C_o from Ph), 128.9 (C_m from Ph), 128.2 (C-5), 127.9 (C-6), 125.2 (C-4a), 118.1 (CN), 105.8 (C-3) ppm.

$C_{16}H_{10}N_2$ (230.27): calcd C 83.46, H 4.38, N 12.17; found C 83.21, H 4.12, N 12.57.

6-Chloro-2-phenylquinoline-3-carbonitrile (3p). From a mixture of quinoline **1c** (0.163 g, 1.000 mmol), acetylene **2g** (0.127 g, 1.000 mmol), H_2O (0.090 g, 5.000 mmol) and KOH (0.012 g, 20 mol%) in MeCN (0.5 mL for the homogenization of reaction mixture) (55-60 °C, 16 h) quinoline **3p** (0.047 g, 18%) was obtained as a white powder, mp 197-198 °C (ethanol).[2b,d]



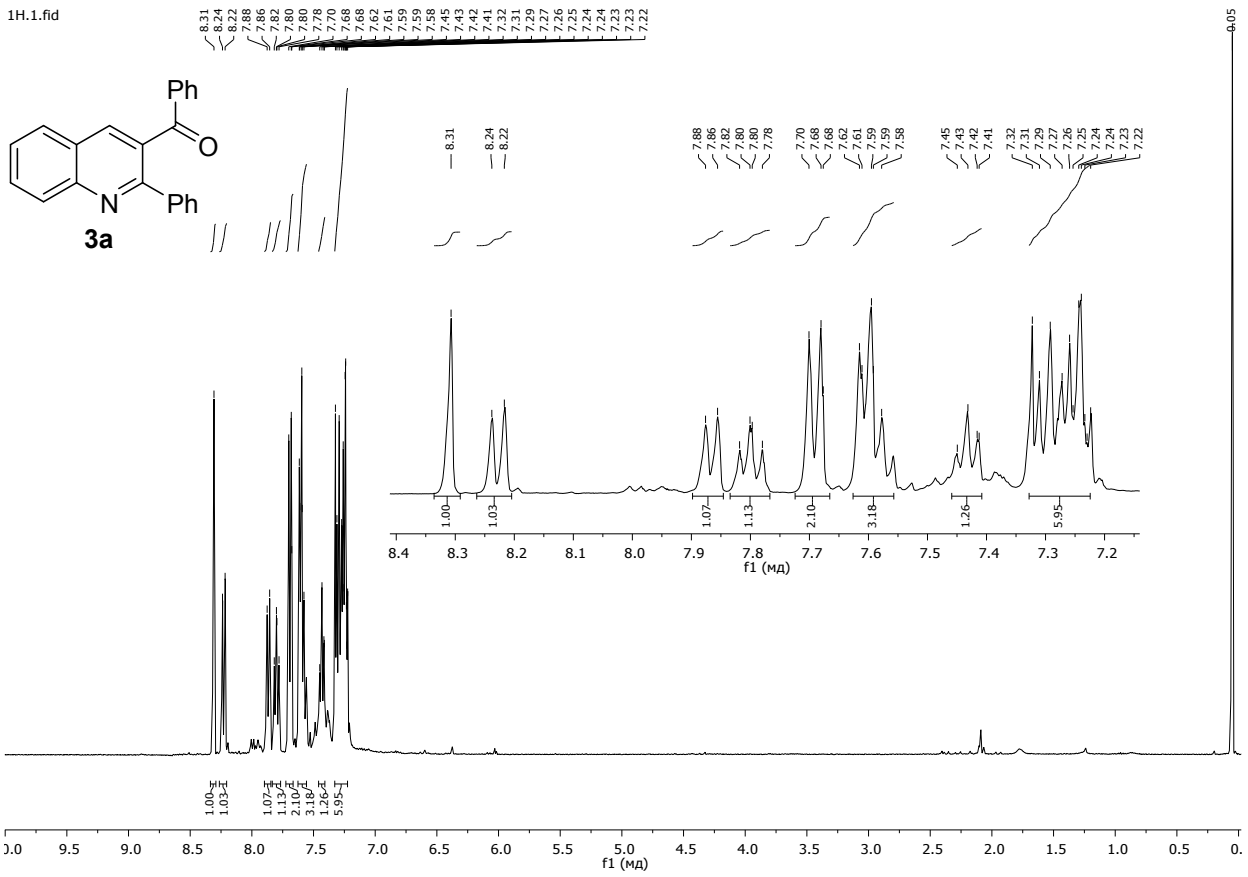
^1H, ^{13}C NMR and IR spectra are similar to the literature data.[2b,d]

IR (KBr): 1691 (C=C), 2217 (CN) cm^{-1}.

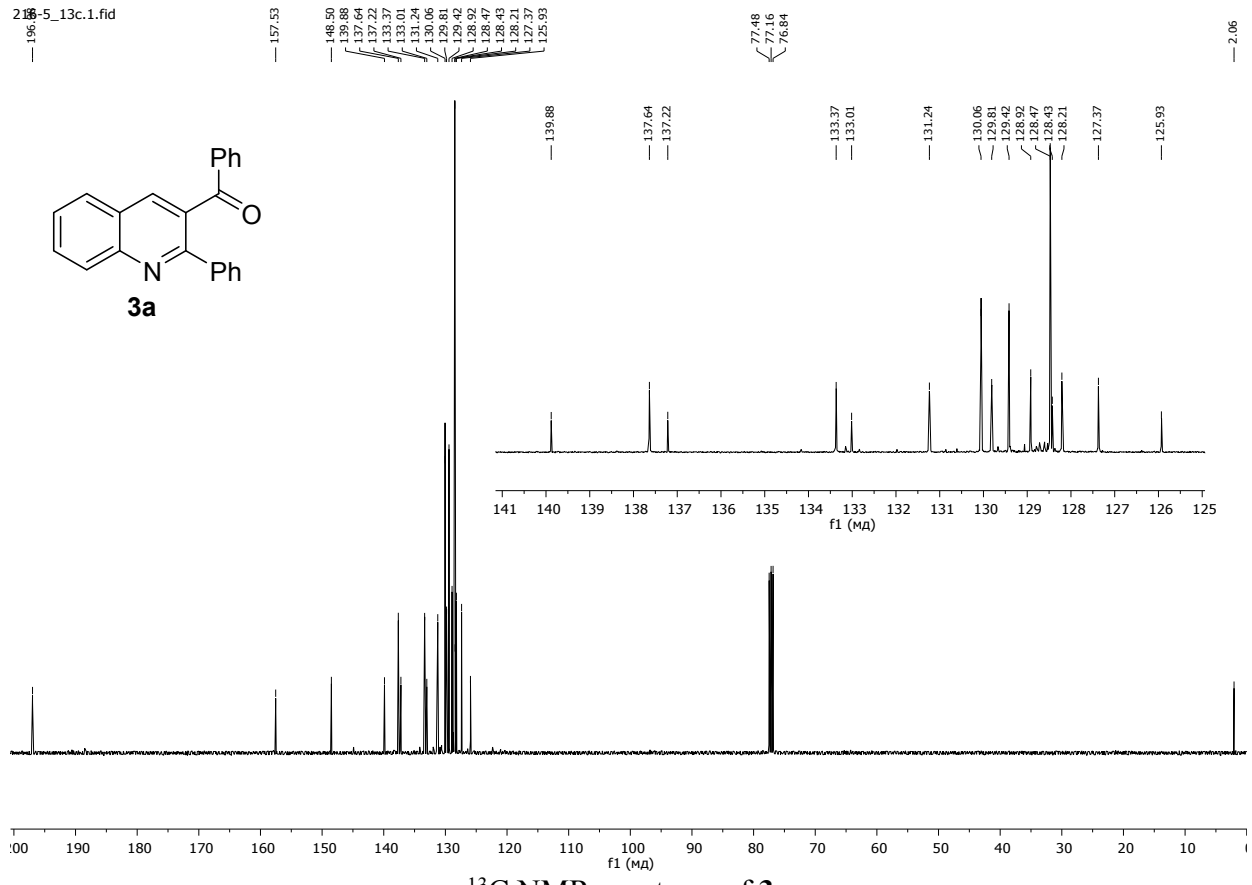
^1H NMR (400.13 MHz, $CDCl_3$): δ 8.54 (s, 1H, H-4), 8.12 (d, $^3J_{H7,H8}$ = 8.8 Hz, 1H, H-8), 7.97 (m, 2H, H_o from Ph), 7.79 (d, $^3J_{H7,H8}$ = 8.8 Hz, 1H, H-7), 7.86 (s, 1H, H-5), 7.54 (m, 3H, $H_{m,p}$ from Ph) ppm.

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 158.3 (C-2), 147.2 (C-8a), 143.2 (C-4), 137.4 (C_i from Ph), 134.2 (C-6), 134.0 (C_p from Ph), 130.5 (C-7), 131.7 (C-8), 129.3 (C_o from Ph), 128.9 (C_m from Ph), 126.4 (C-5), 125.7 (C-4a), 117.6 (CN), 106.8 (C-3) ppm.

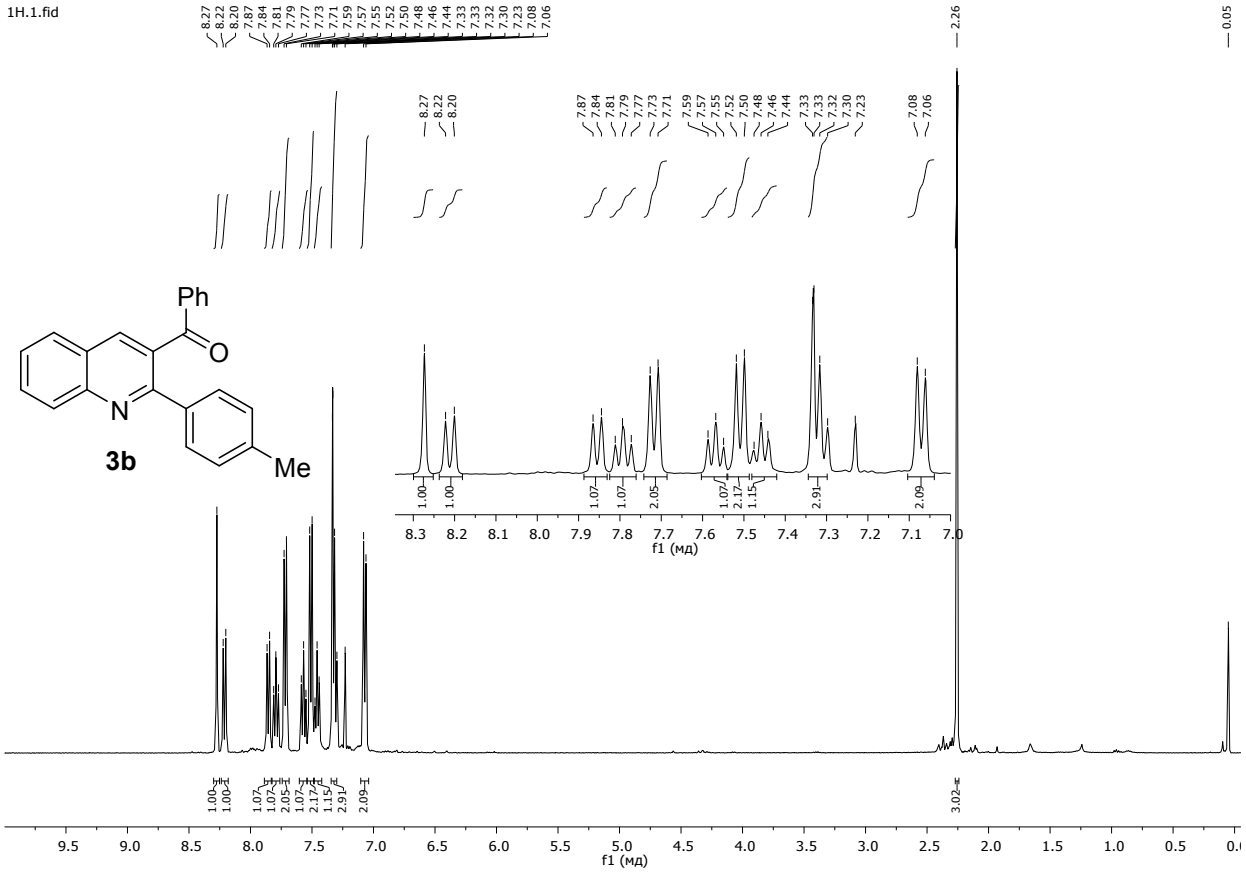
$C_{16}H_9ClN_2$ (264.71): calcd C 72.60, H 3.43, Cl 13.39, N, 10.58; found C 72.48, H 3.37, N 13.39, Cl 10.72.



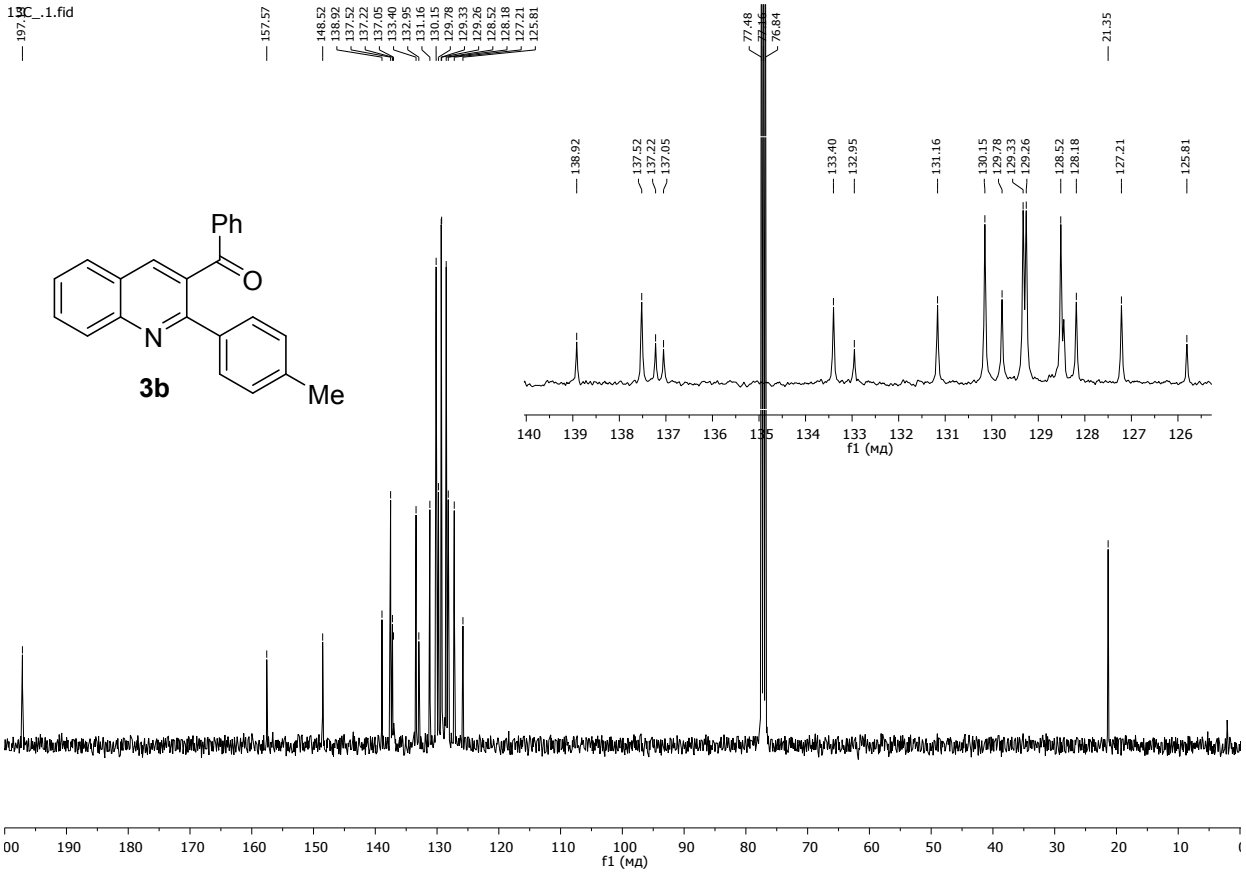
^{1}H NMR spectrum of **3a**



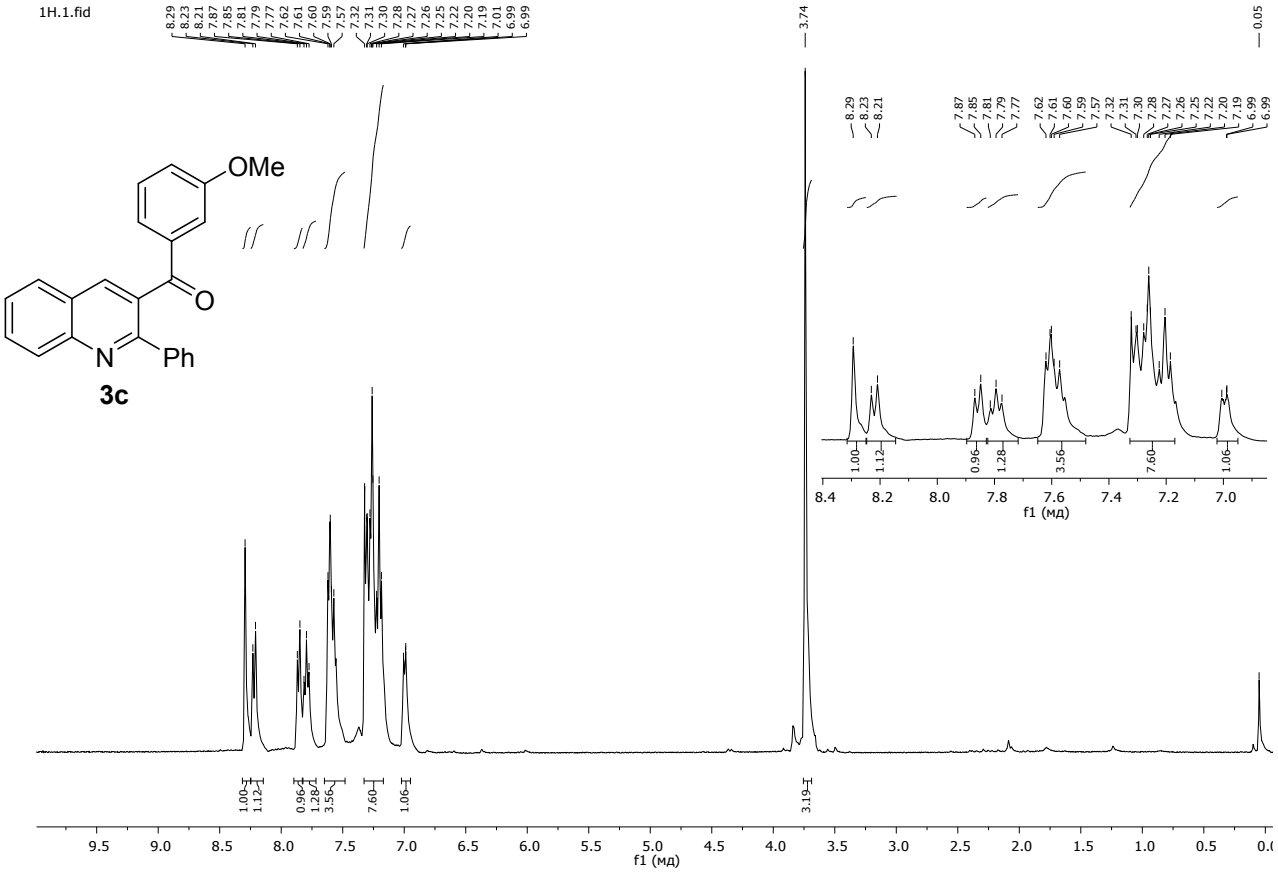
^{13}C NMR spectrum of **3a**



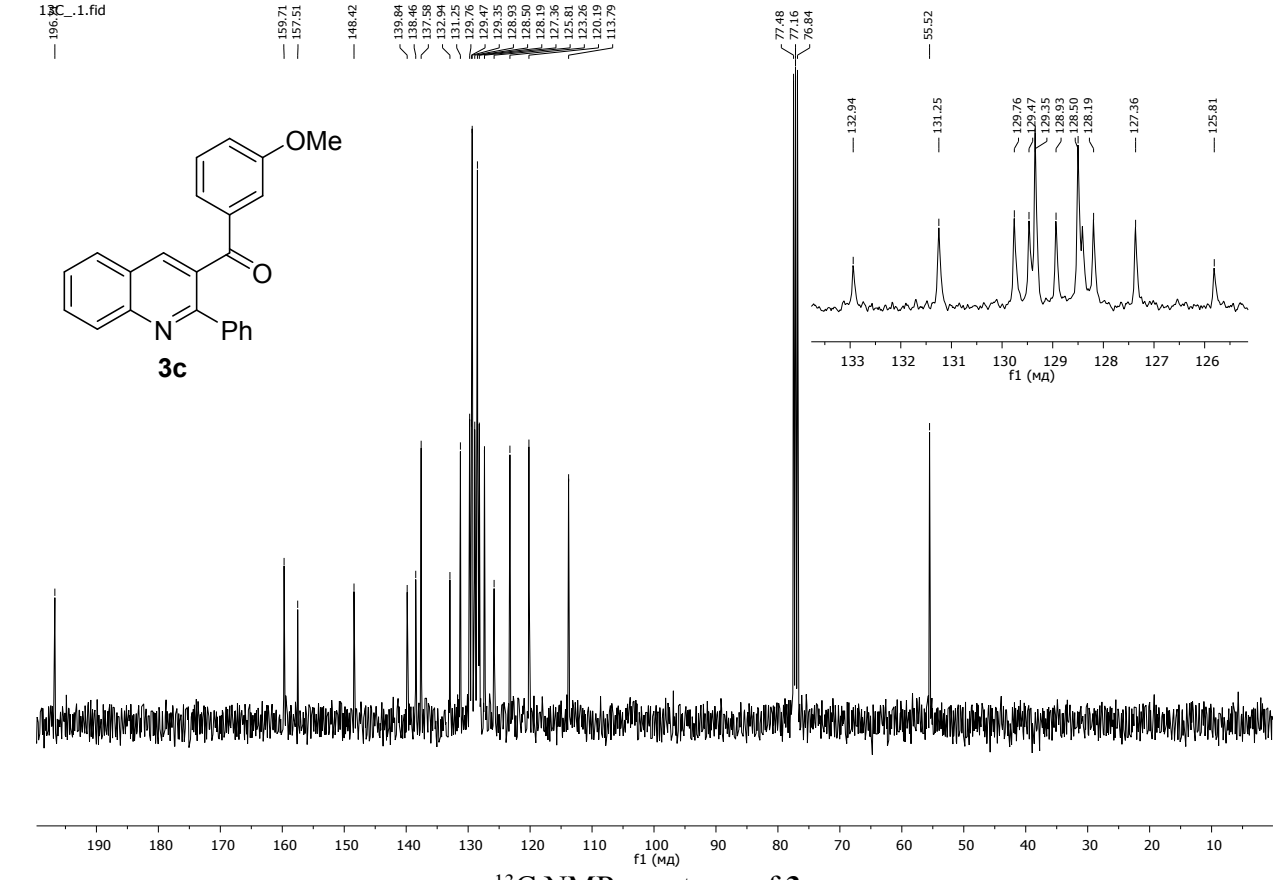
^{1}H NMR spectrum of **3b**



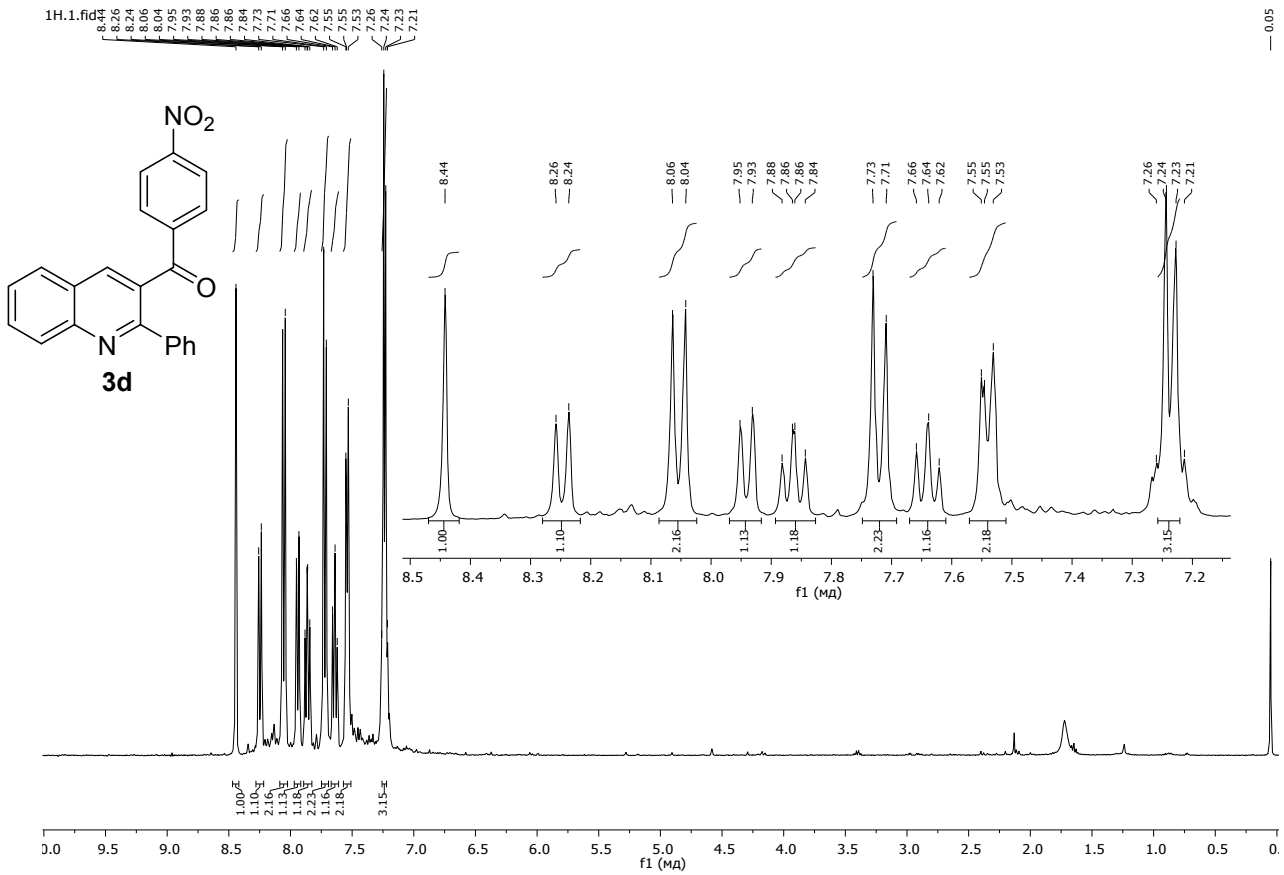
^{13}C NMR spectrum of **3b**



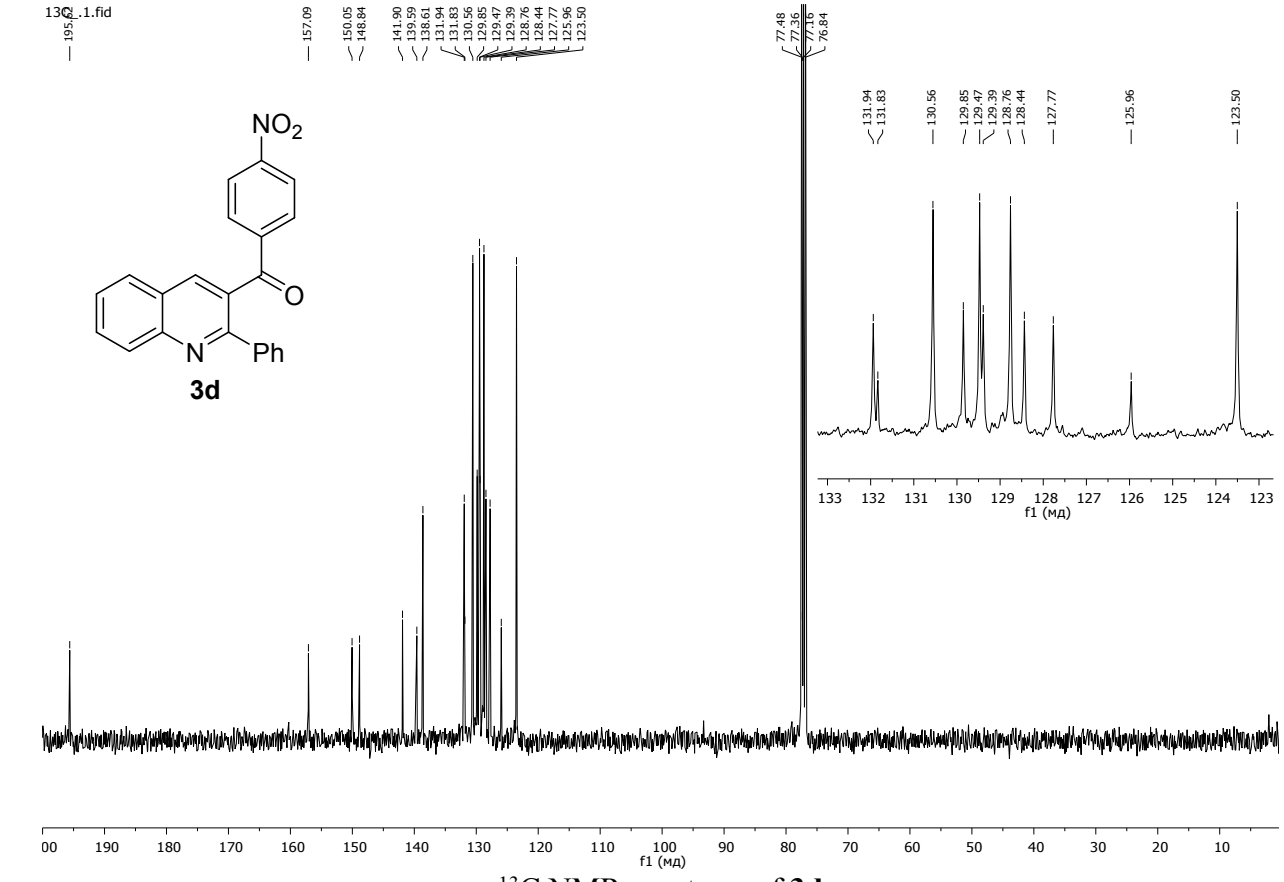
^{1}H NMR spectrum of **3c**



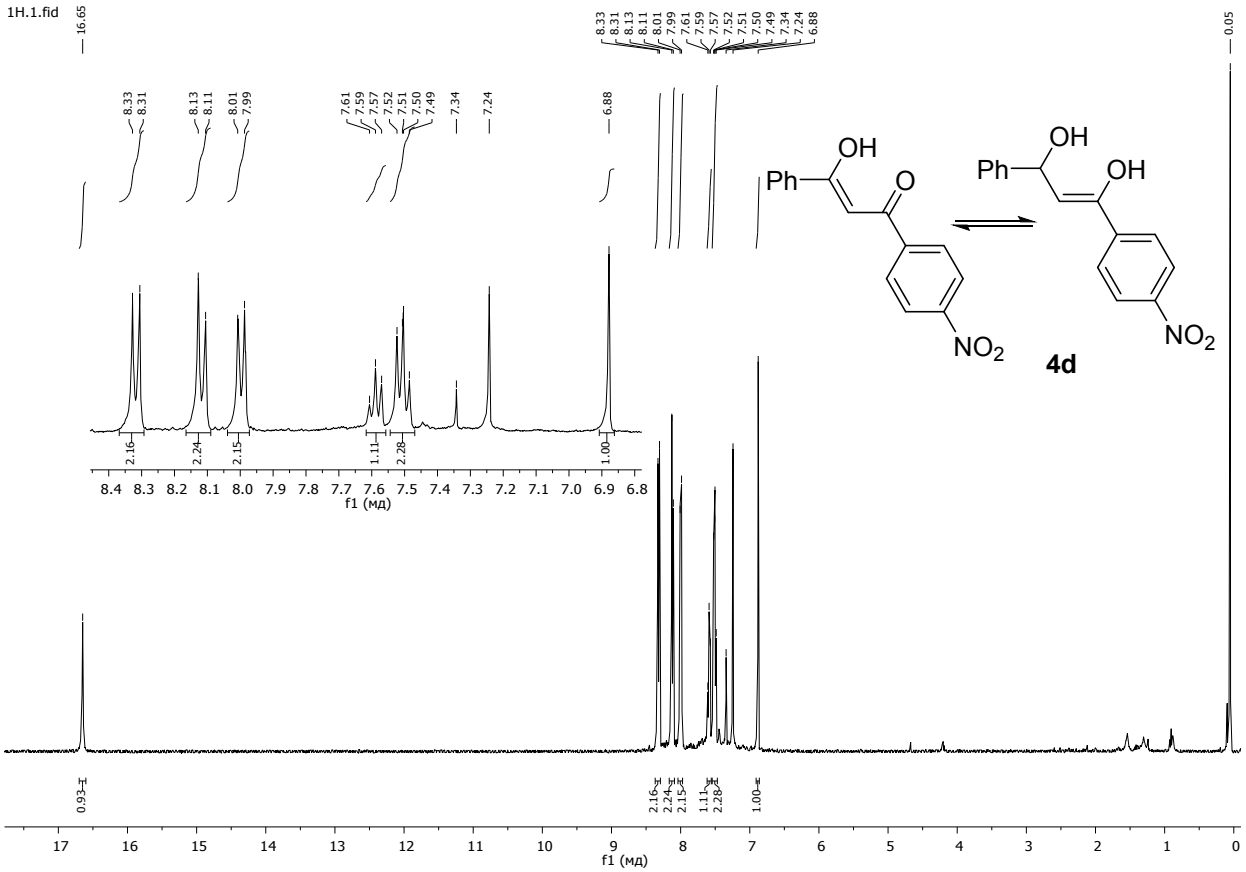
^{13}C NMR spectrum of **3c**



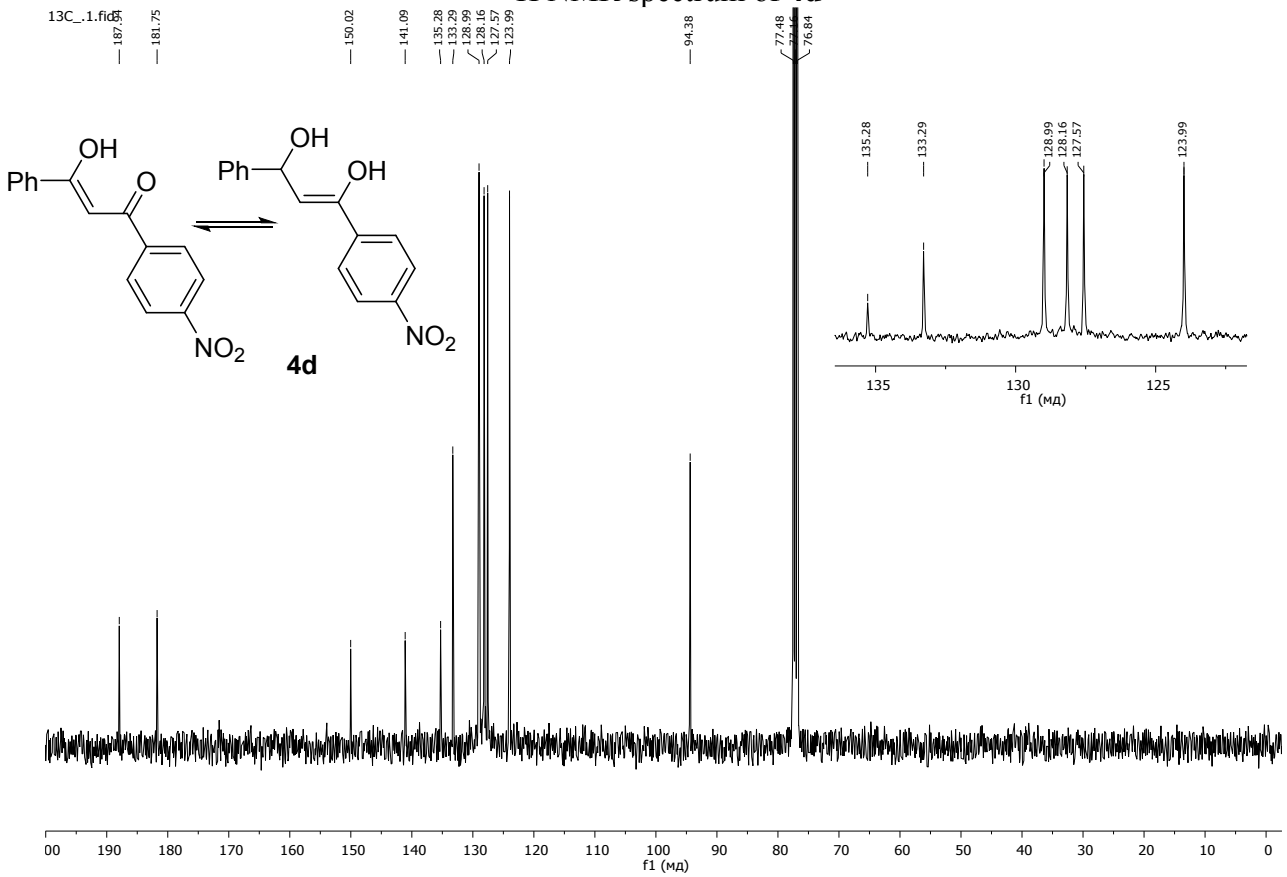
^{1}H NMR spectrum of **3d**



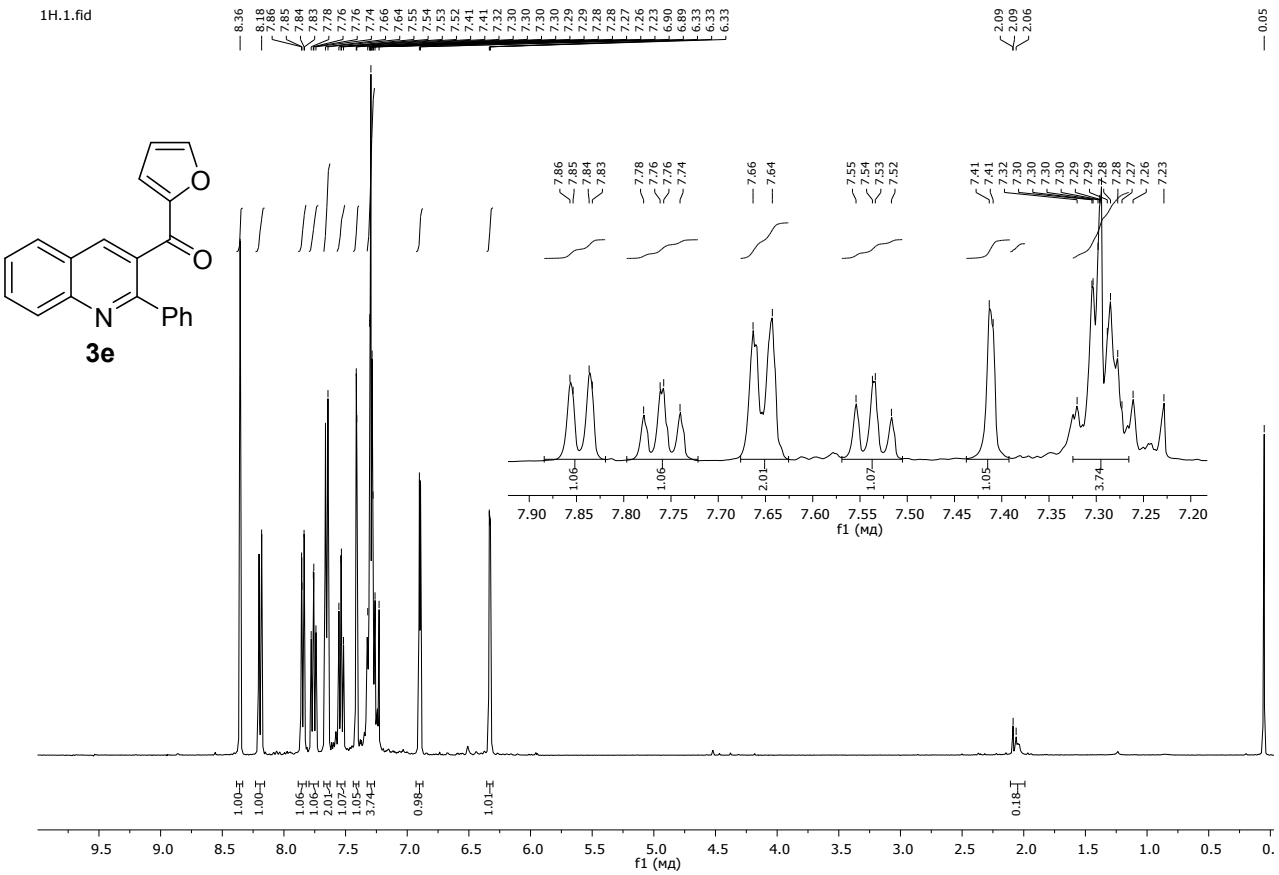
^{13}C NMR spectrum of **3d**



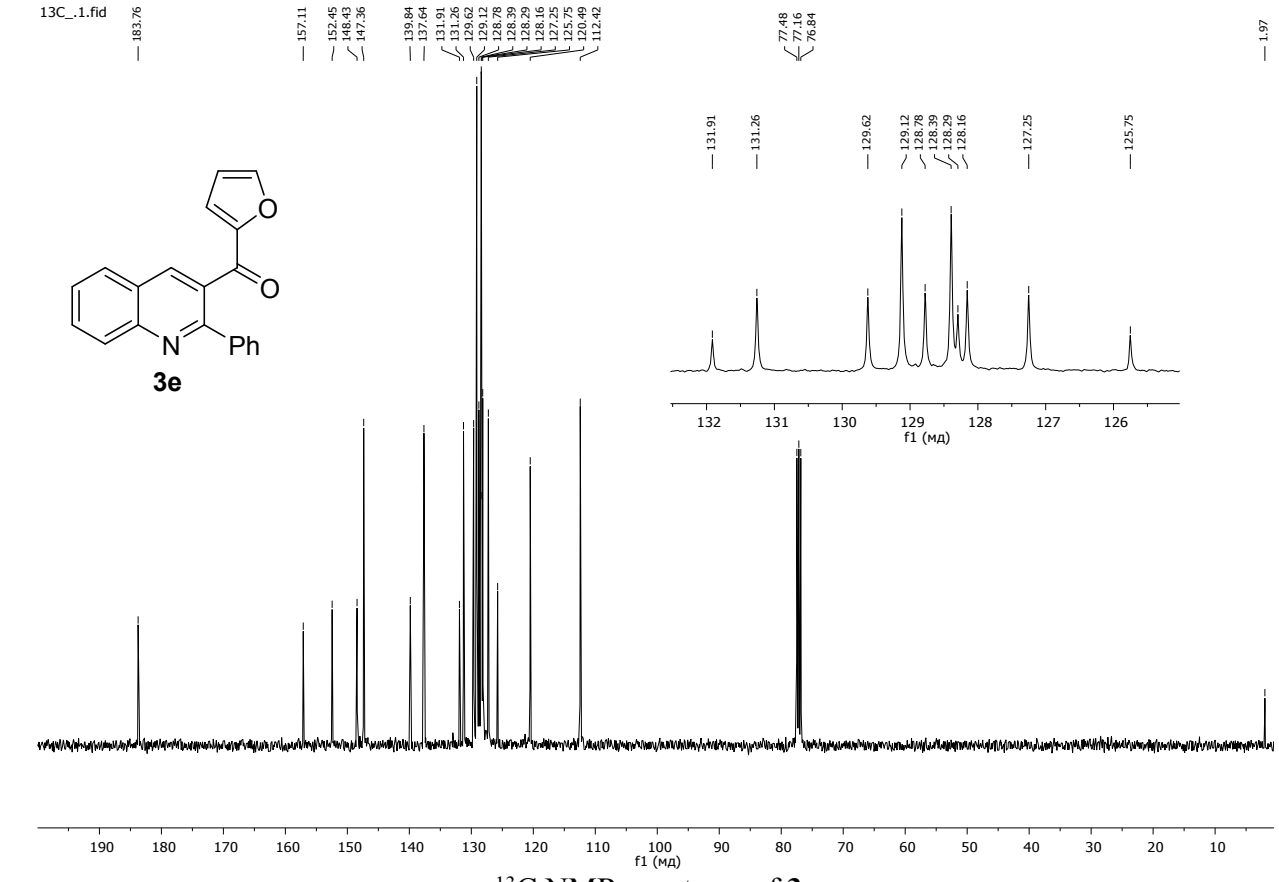
^{1}H NMR spectrum of **4d**



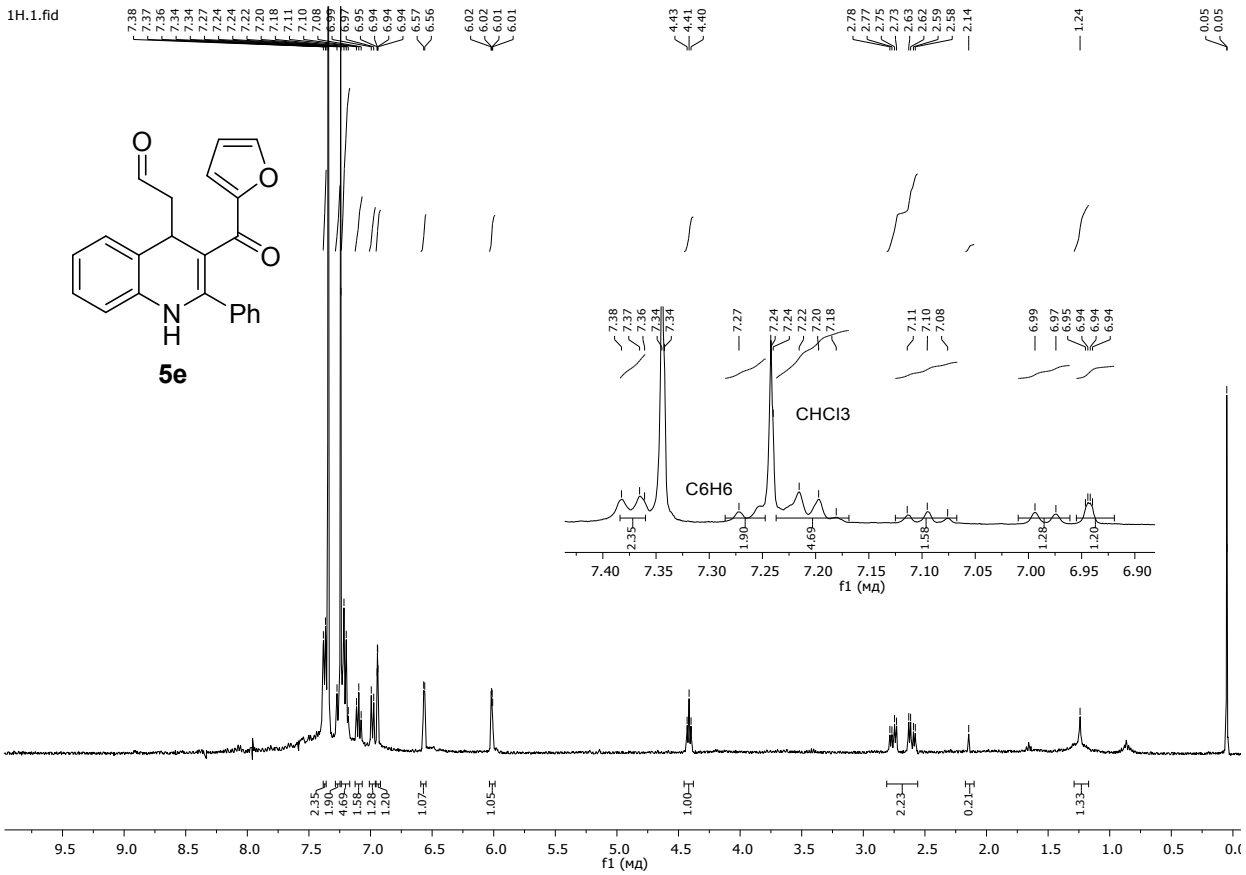
^{13}C NMR spectrum of **4d**



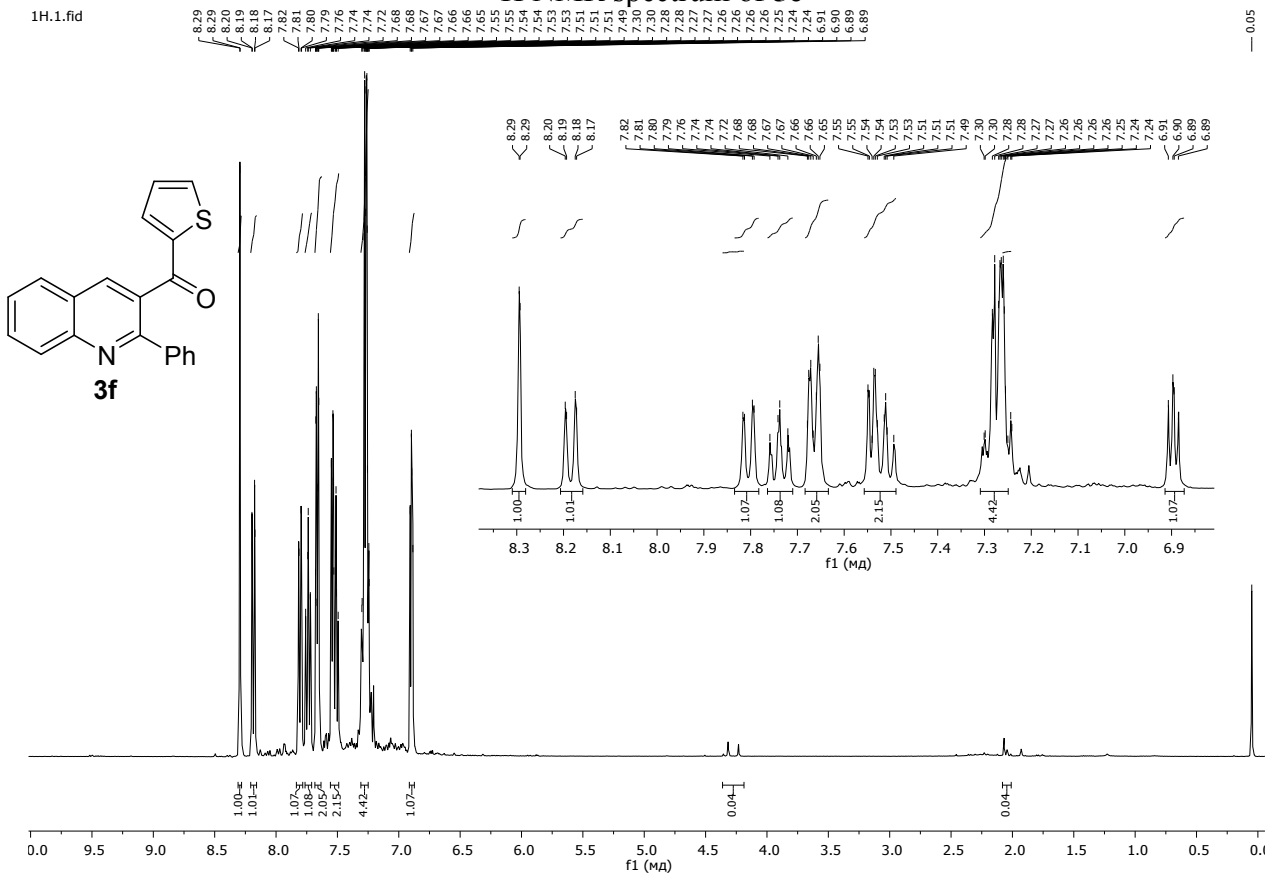
^{1}H NMR spectrum of **3e**



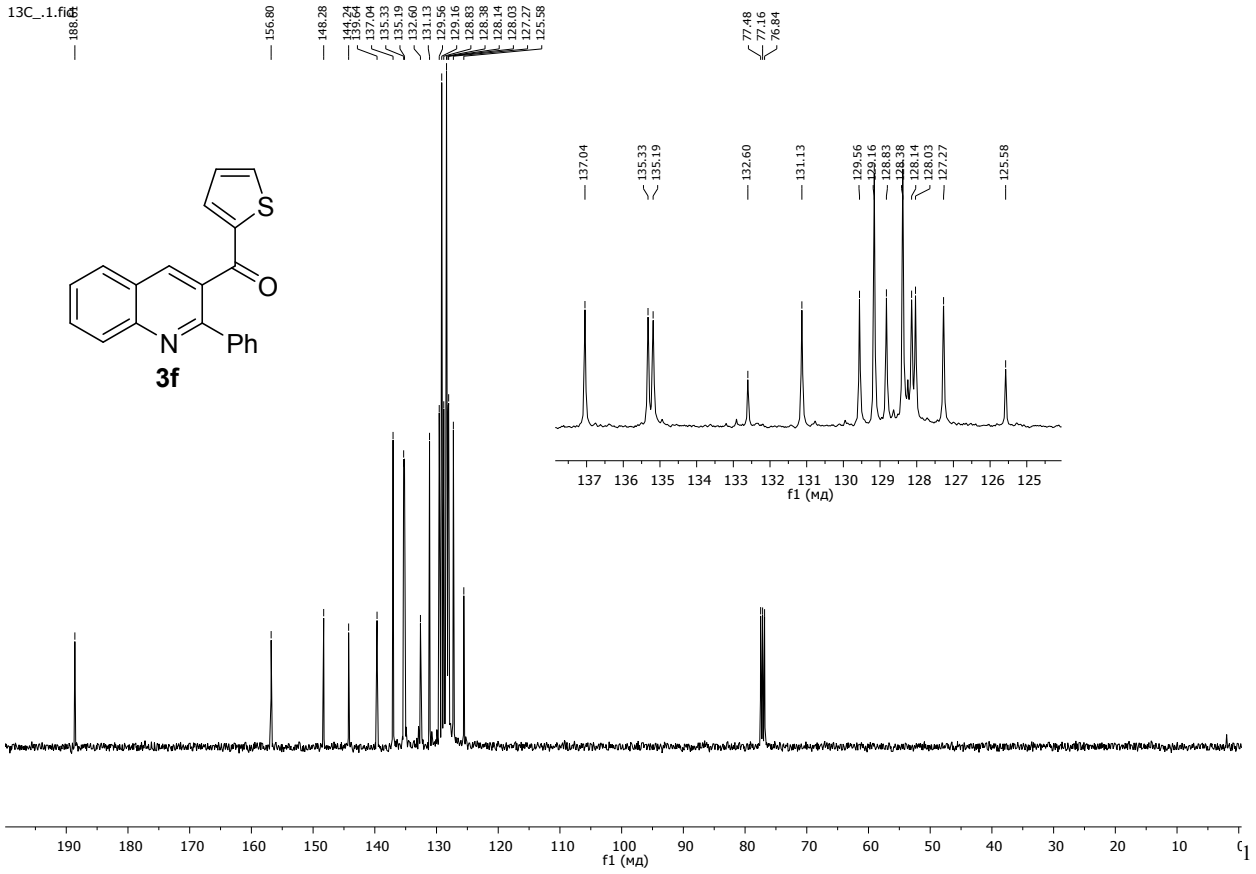
^{13}C NMR spectrum of **3e**



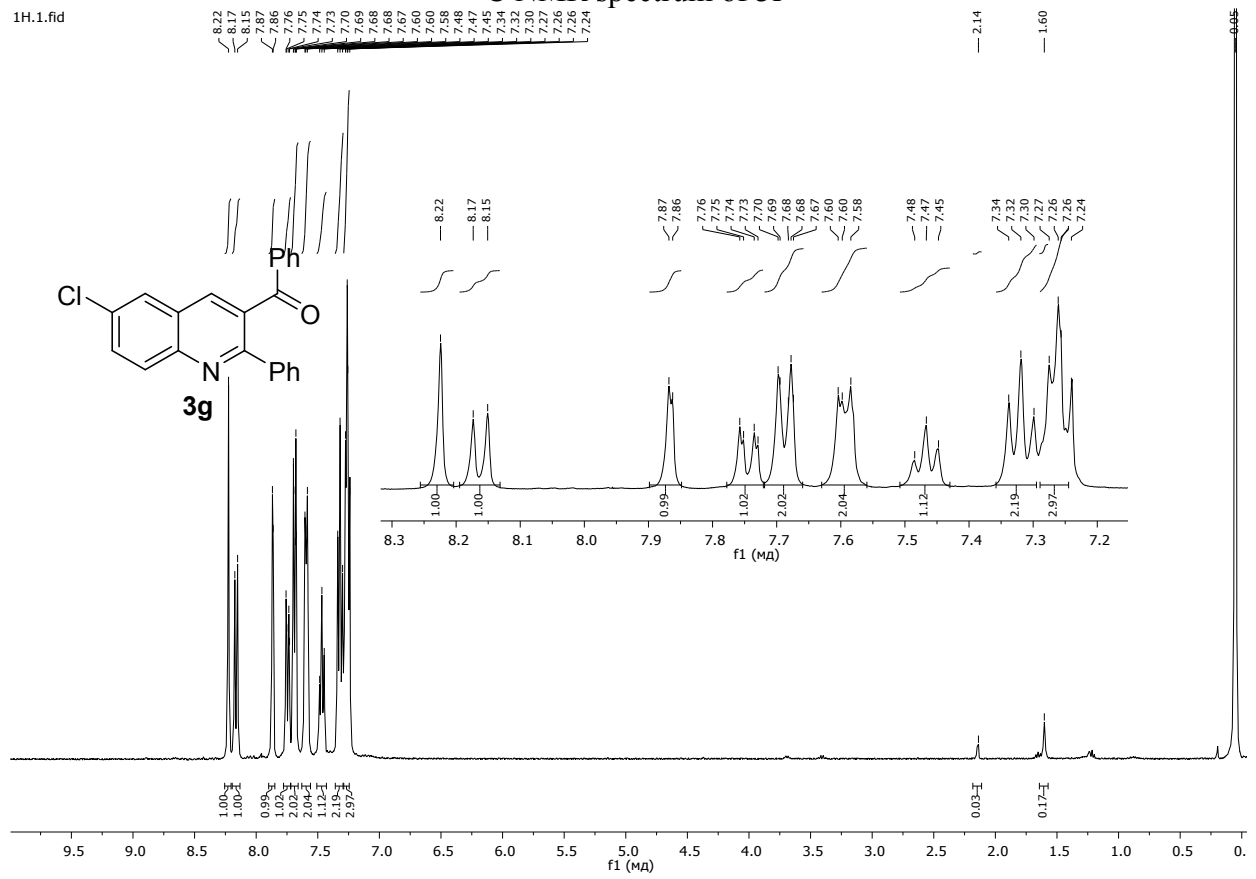
^{1}H NMR spectrum of **5e**



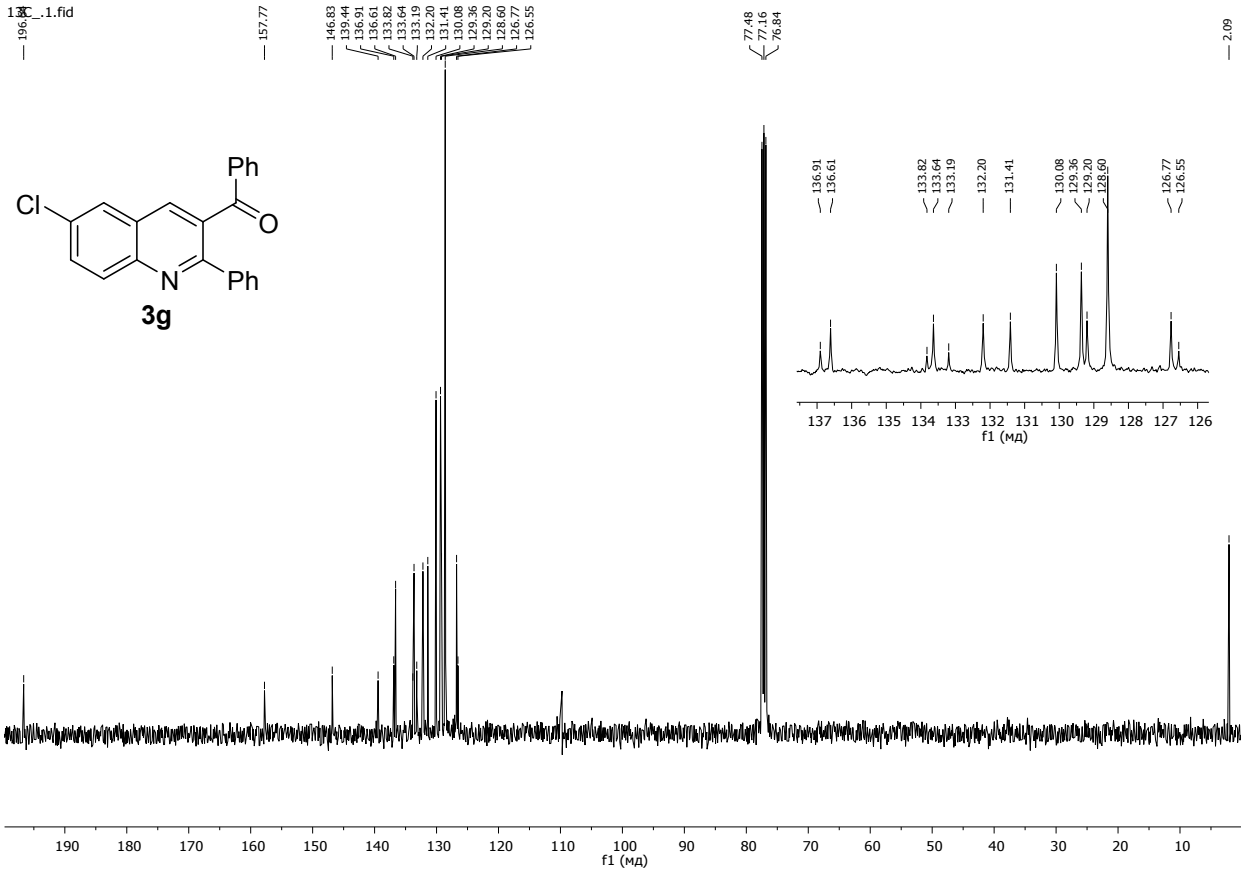
^{1}H NMR spectrum of **3f**



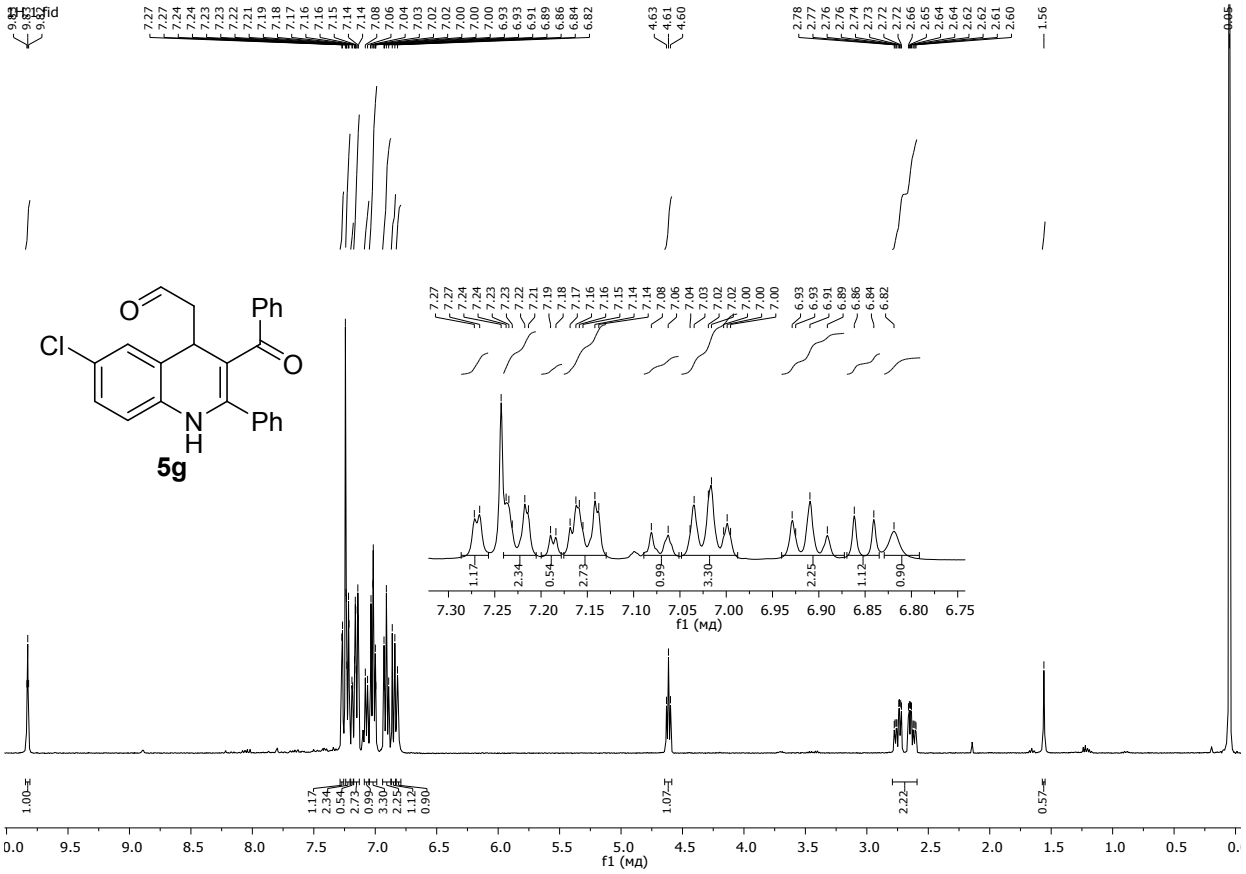
^{3}C NMR spectrum of **3f**



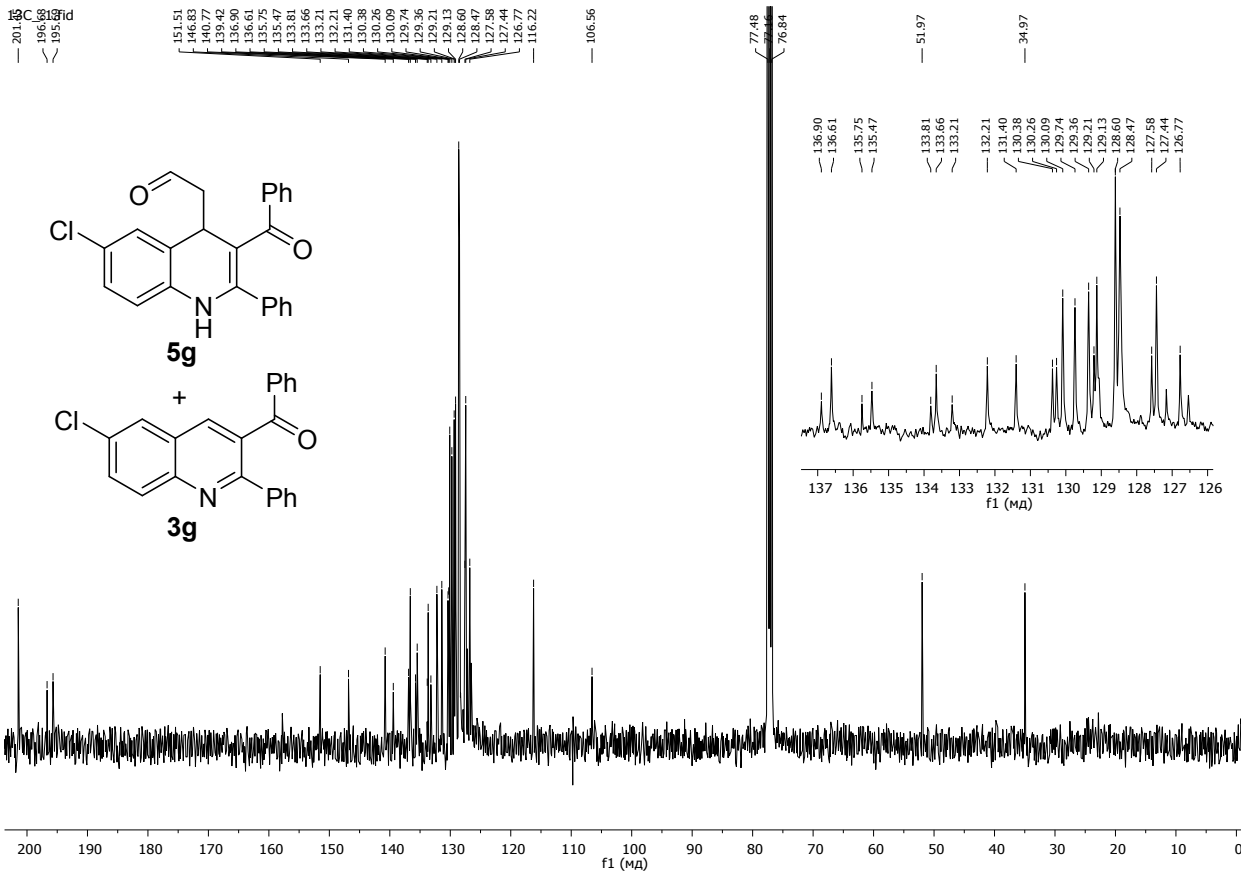
^{1}H NMR spectrum of **3g**



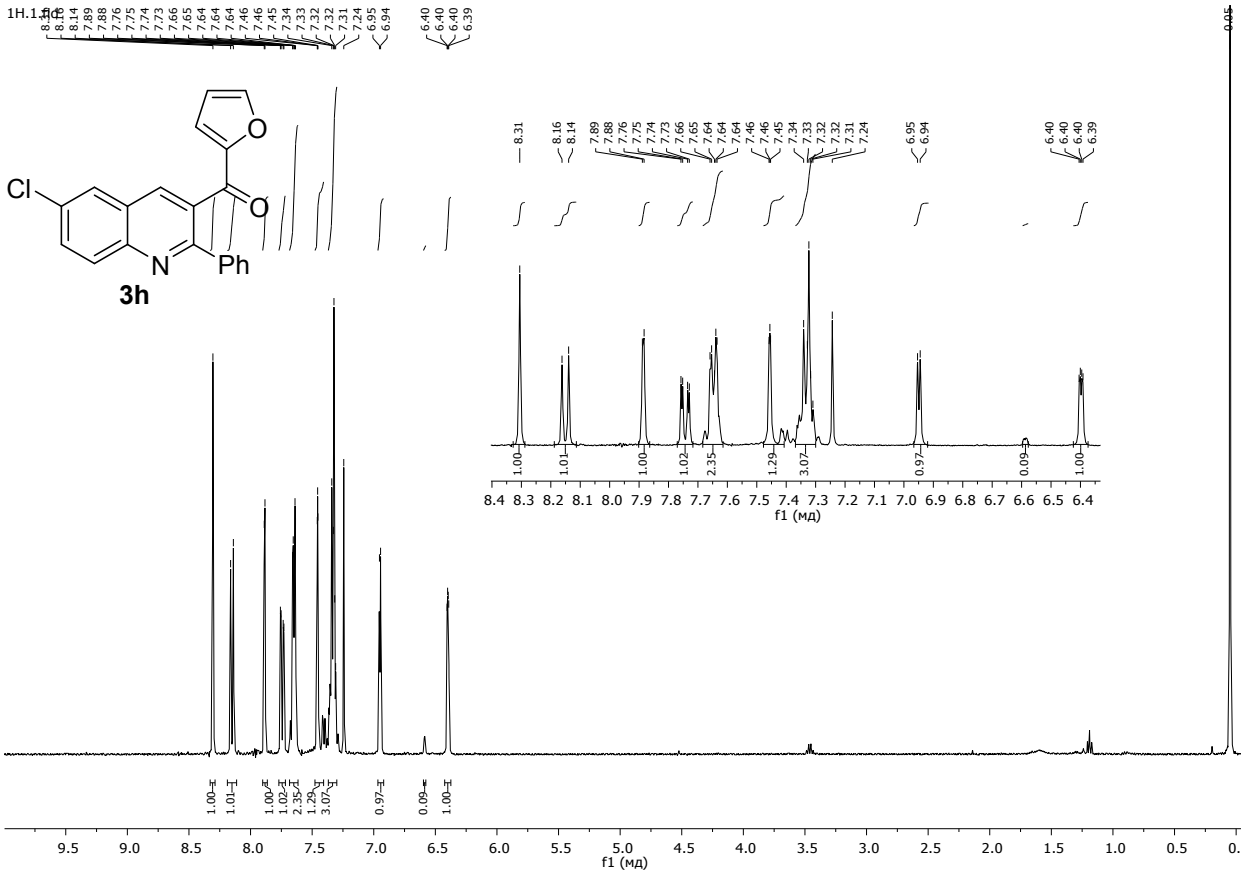
^{13}C NMR spectrum of **3g**



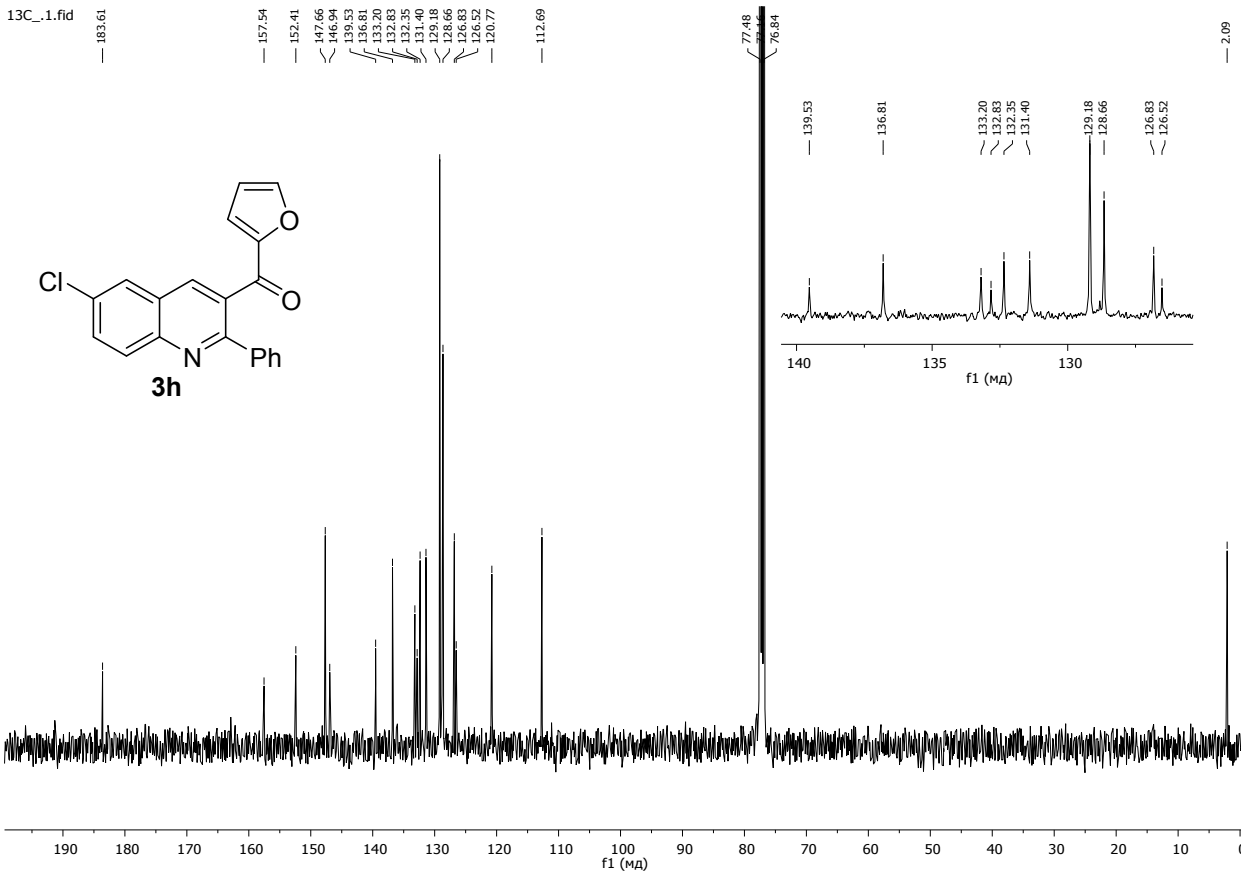
^{1}H NMR spectrum of **5g**



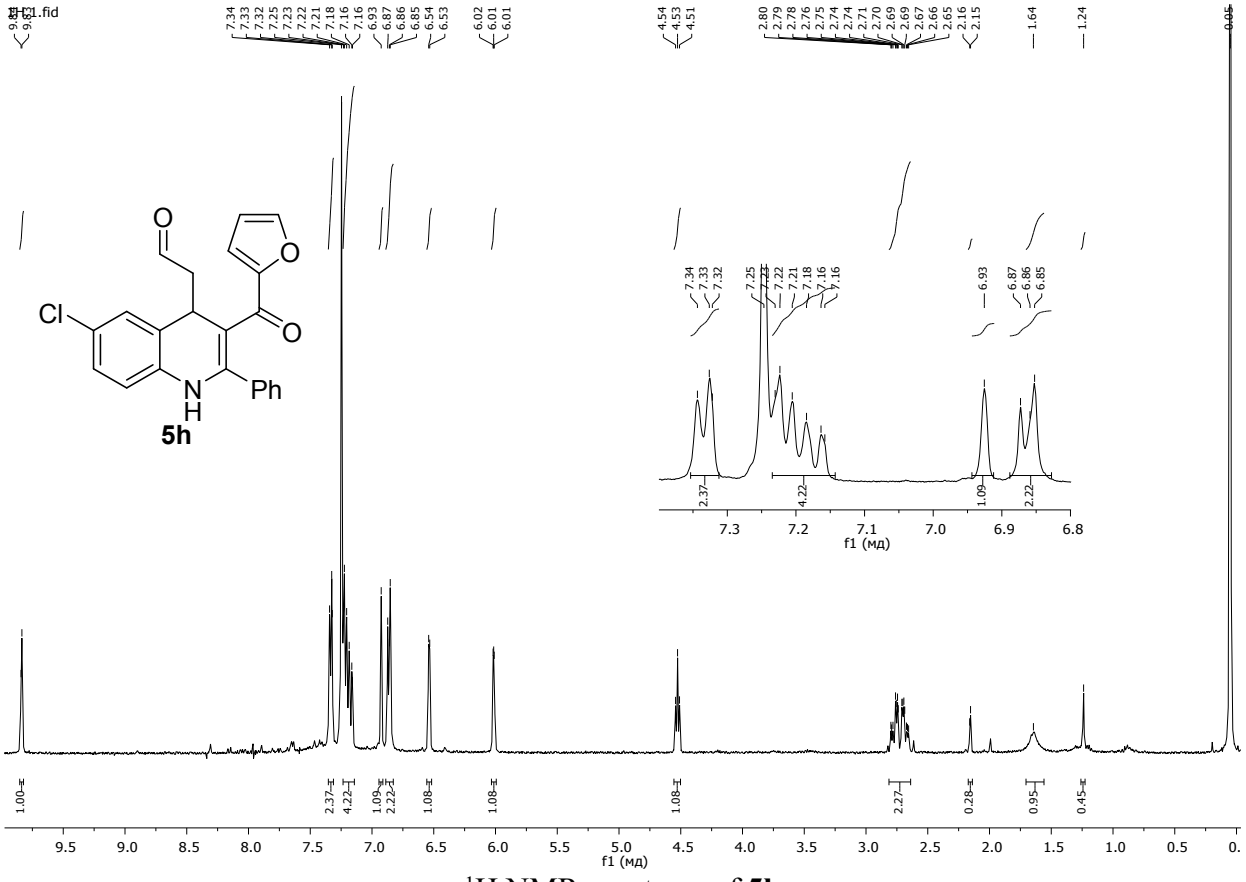
^{13}C NMR spectrum of mixture **5g** and **3g** (signals at 196.7, 157.8, 146.8, 139.4, 136.9, 136.6, 133.8, 133.7, 133.2, 132.2, 131.4, 130.1, 129.4, 129.2, 128.6, 126.8, 126.5 ppm are from **3g**)



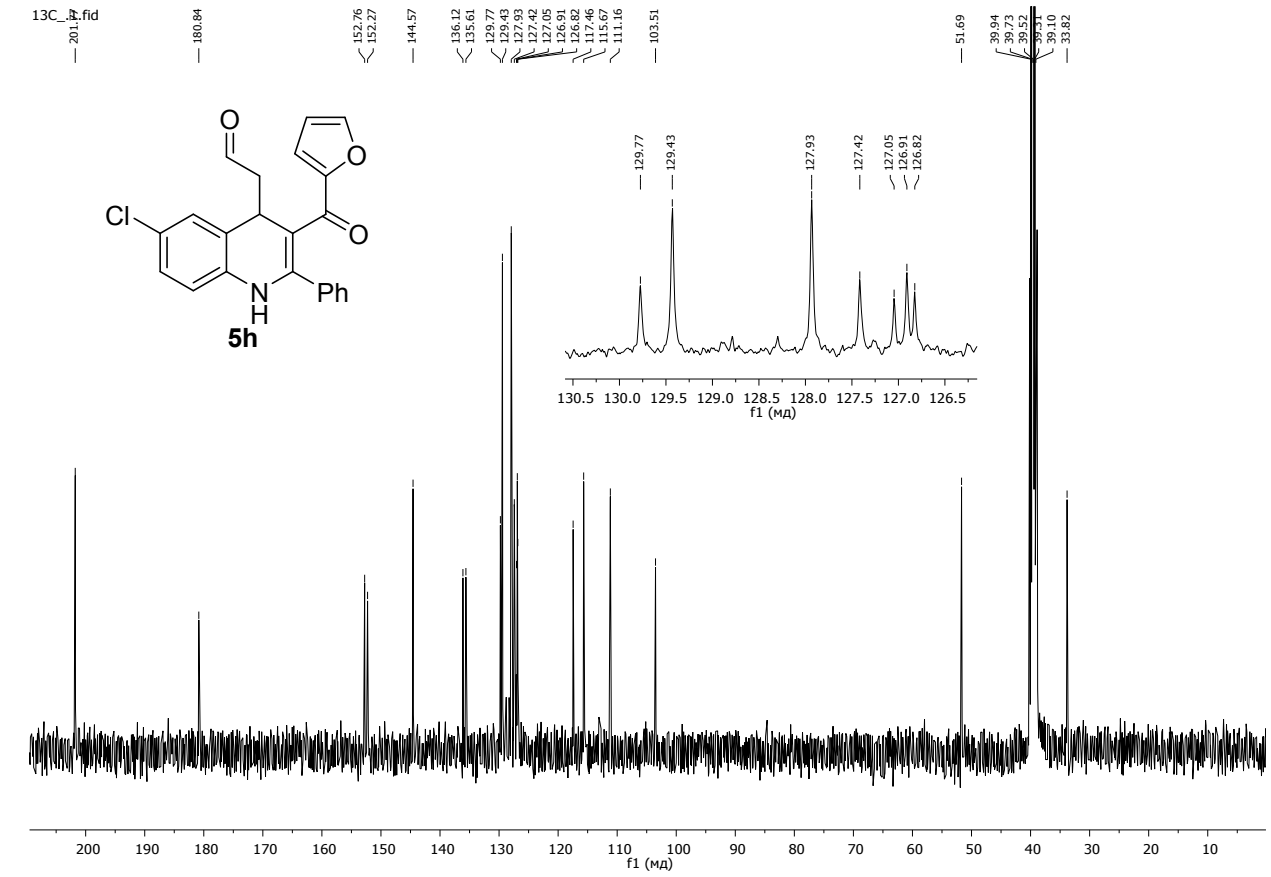
^{1}H NMR spectrum of **3h**



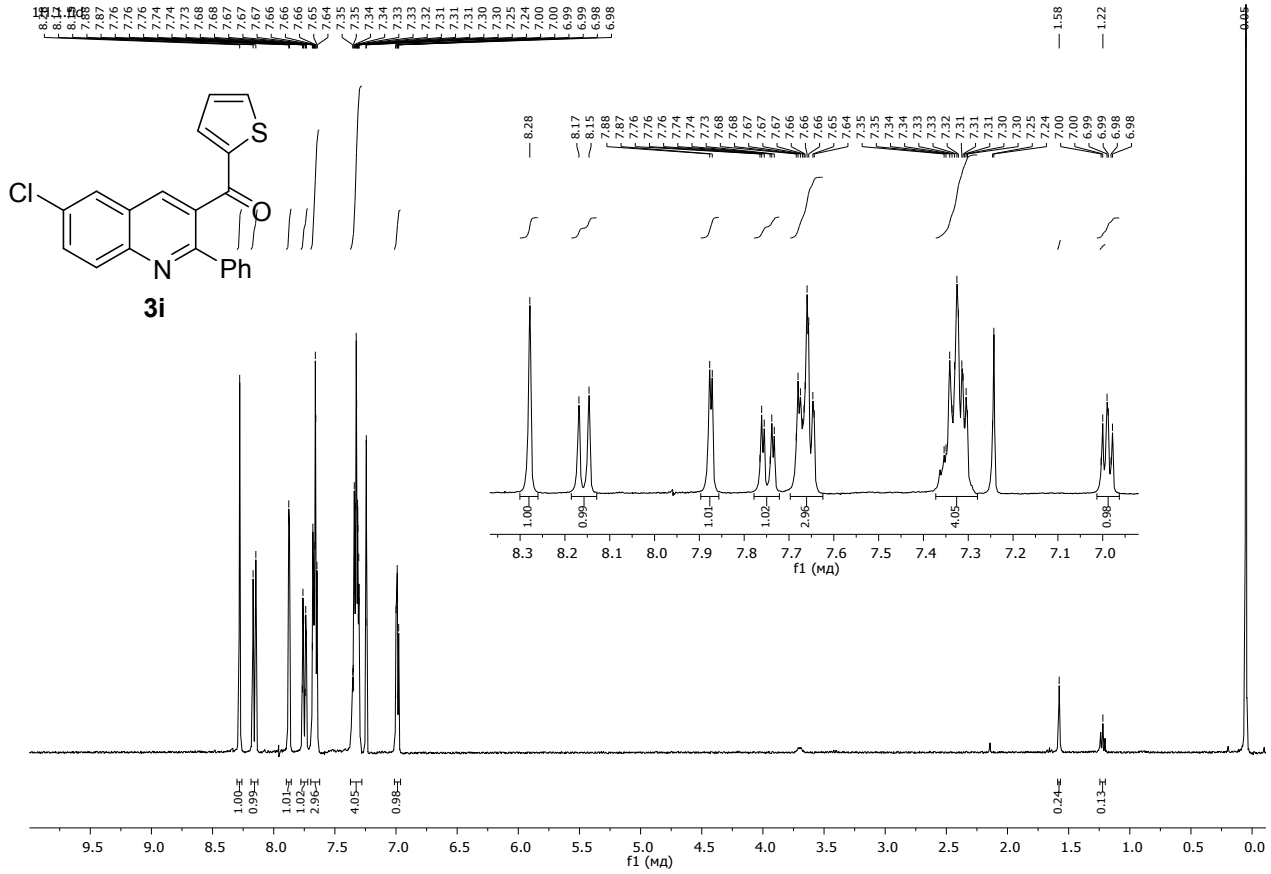
^{13}C NMR spectrum of **3h**



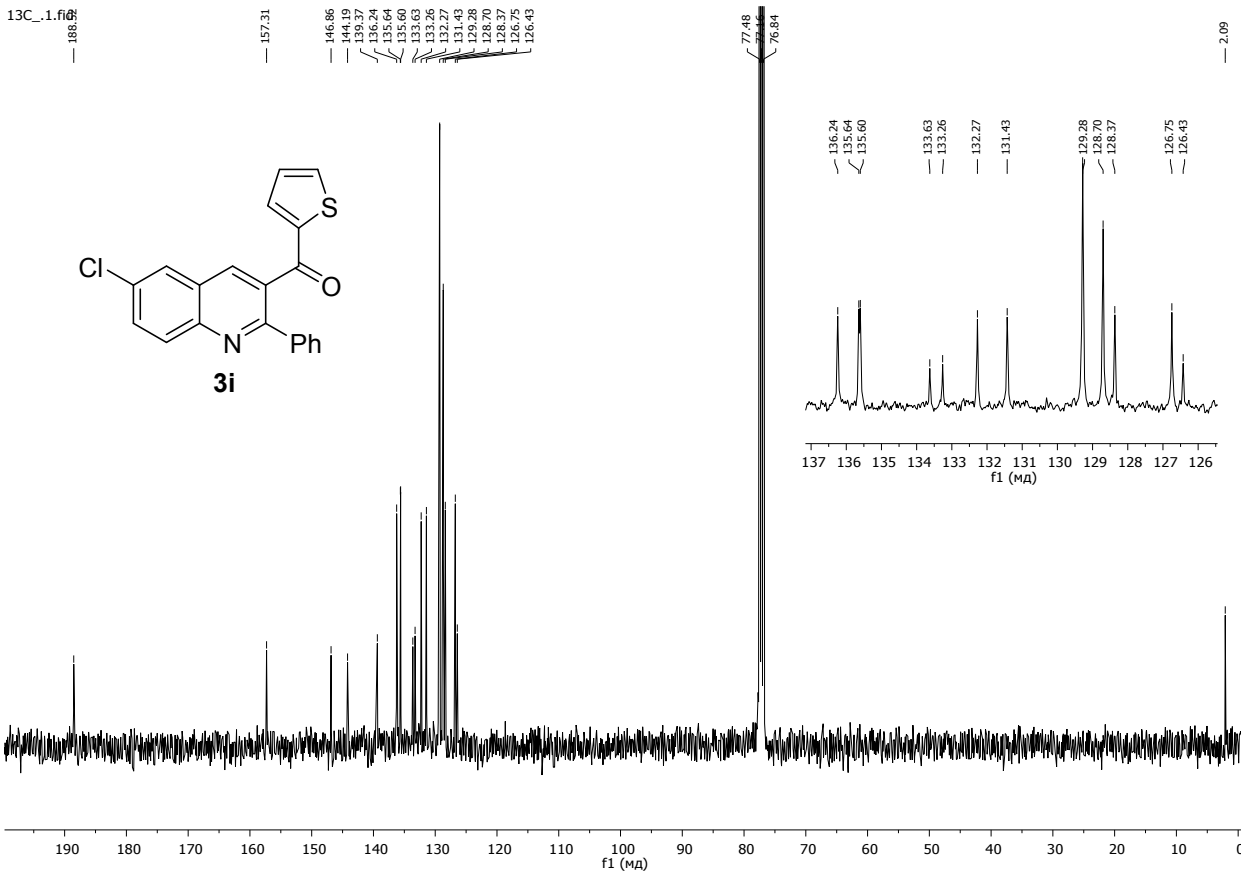
^{1}H NMR spectrum of **5h**



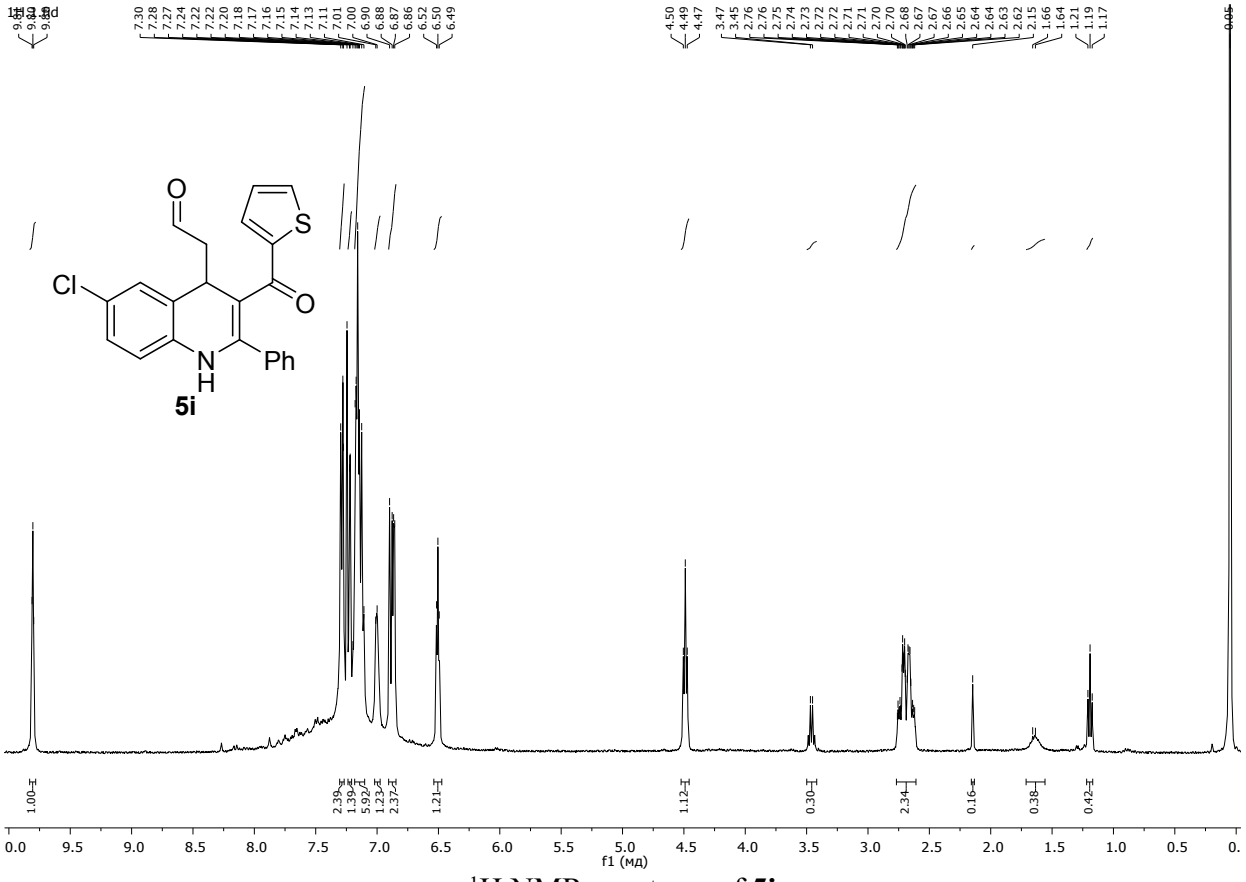
^{13}C NMR spectrum of **5h** (in DMSO-d6)



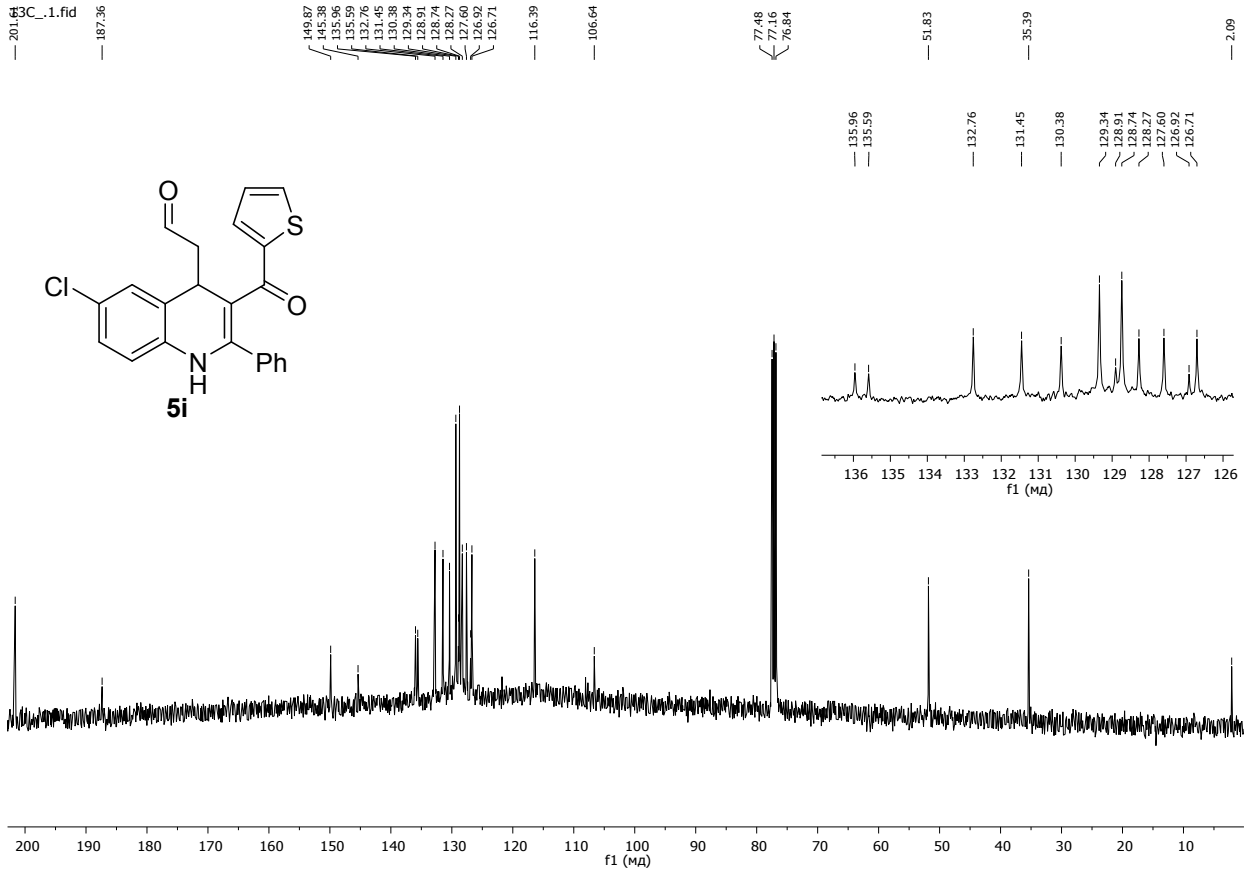
^{1}H NMR spectrum of **3i**



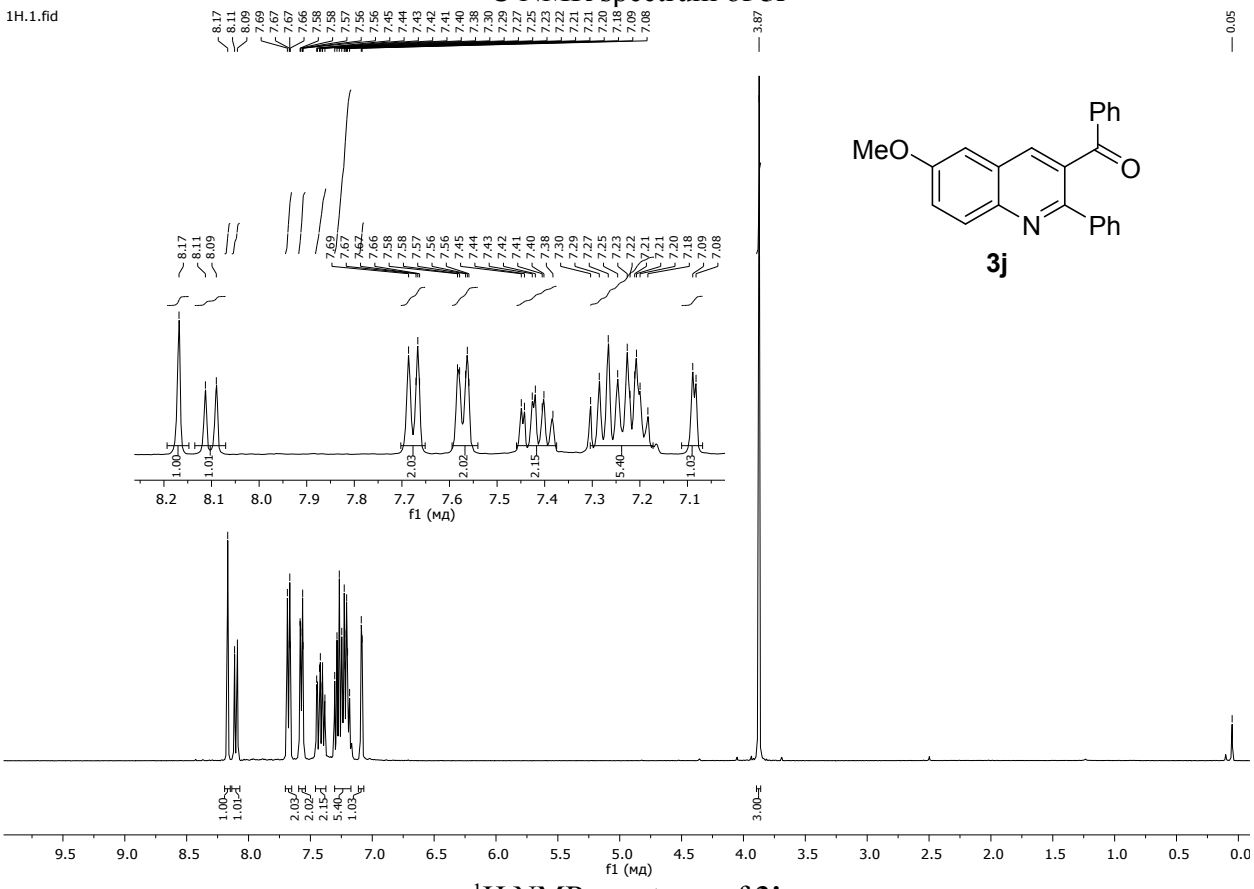
^{13}C NMR spectrum of **3i**



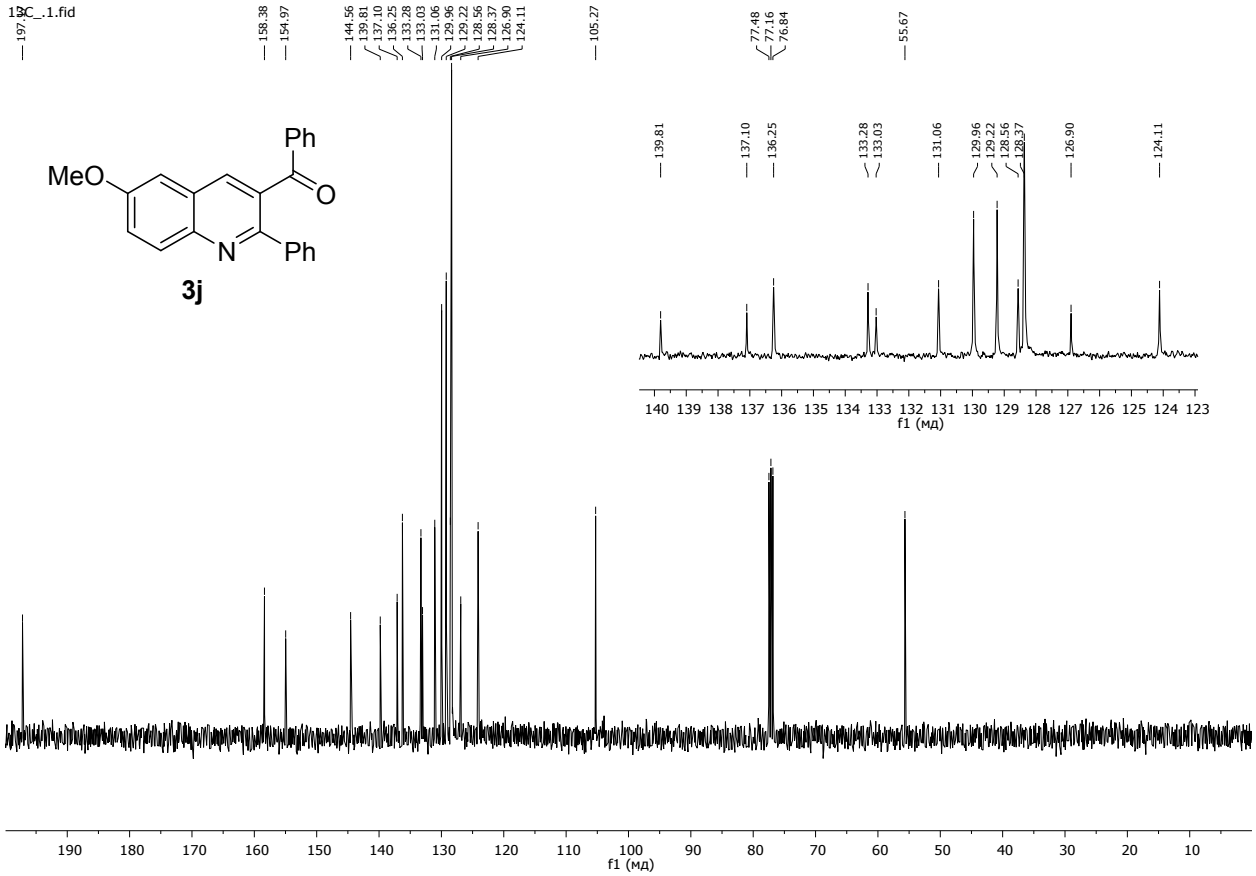
^{1}H NMR spectrum of **5i**



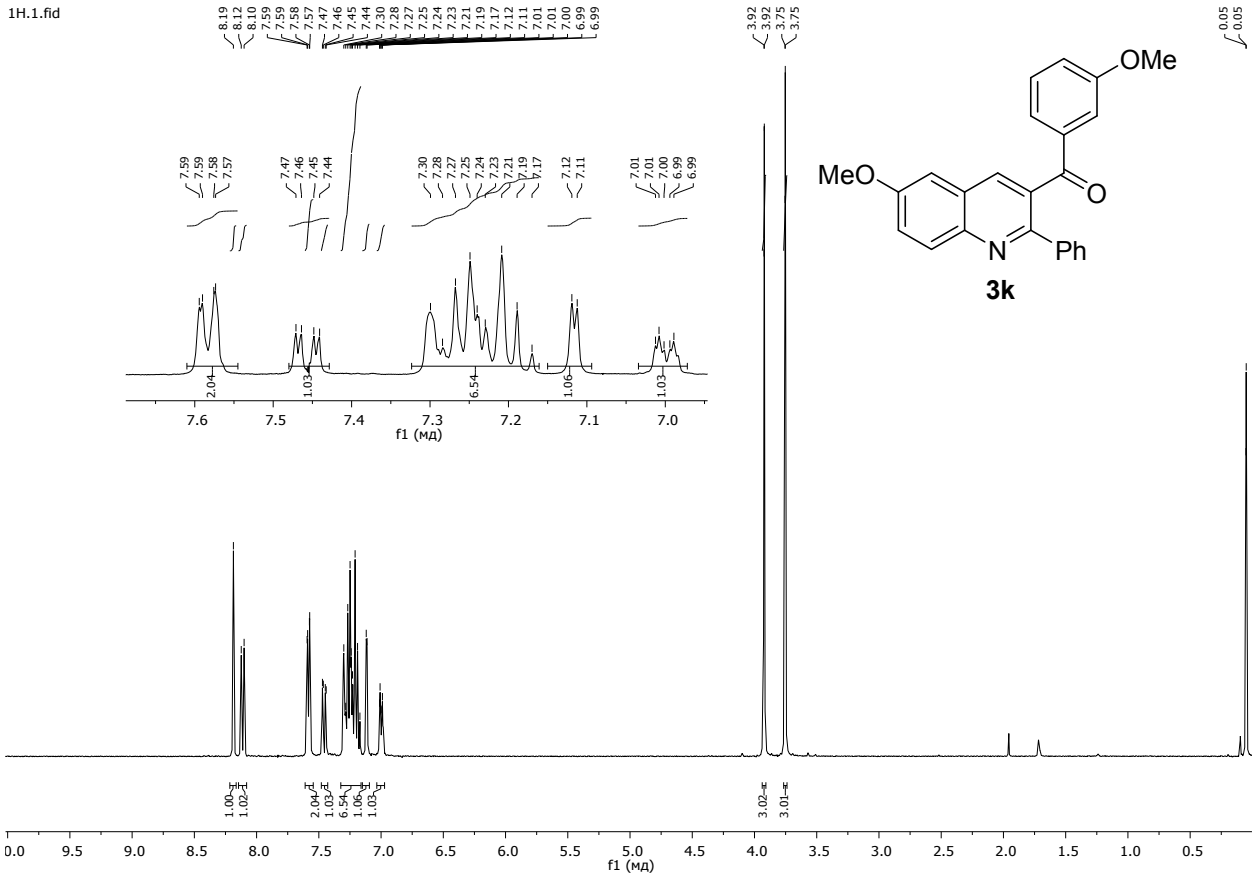
^{13}C NMR spectrum of **5i**



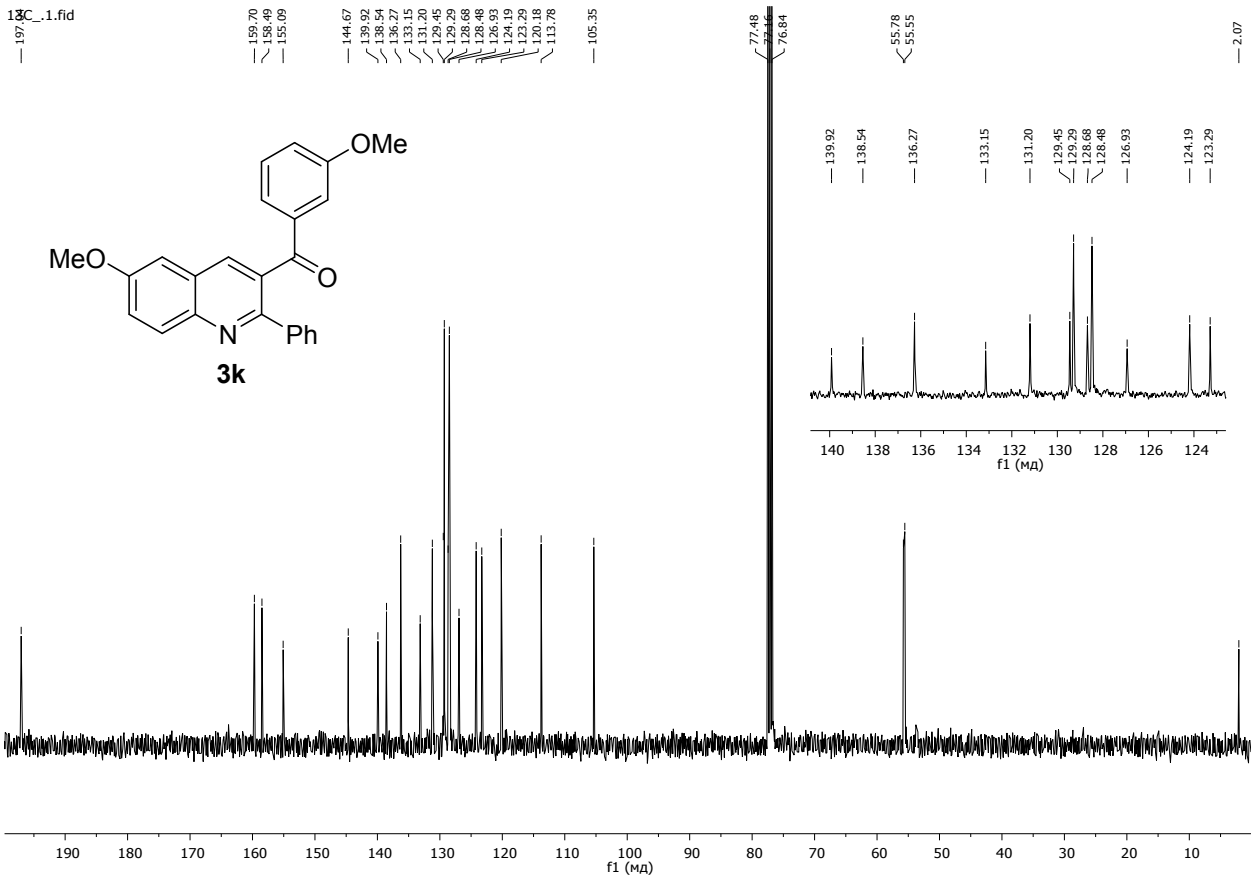
^{1}H NMR spectrum of **3j**



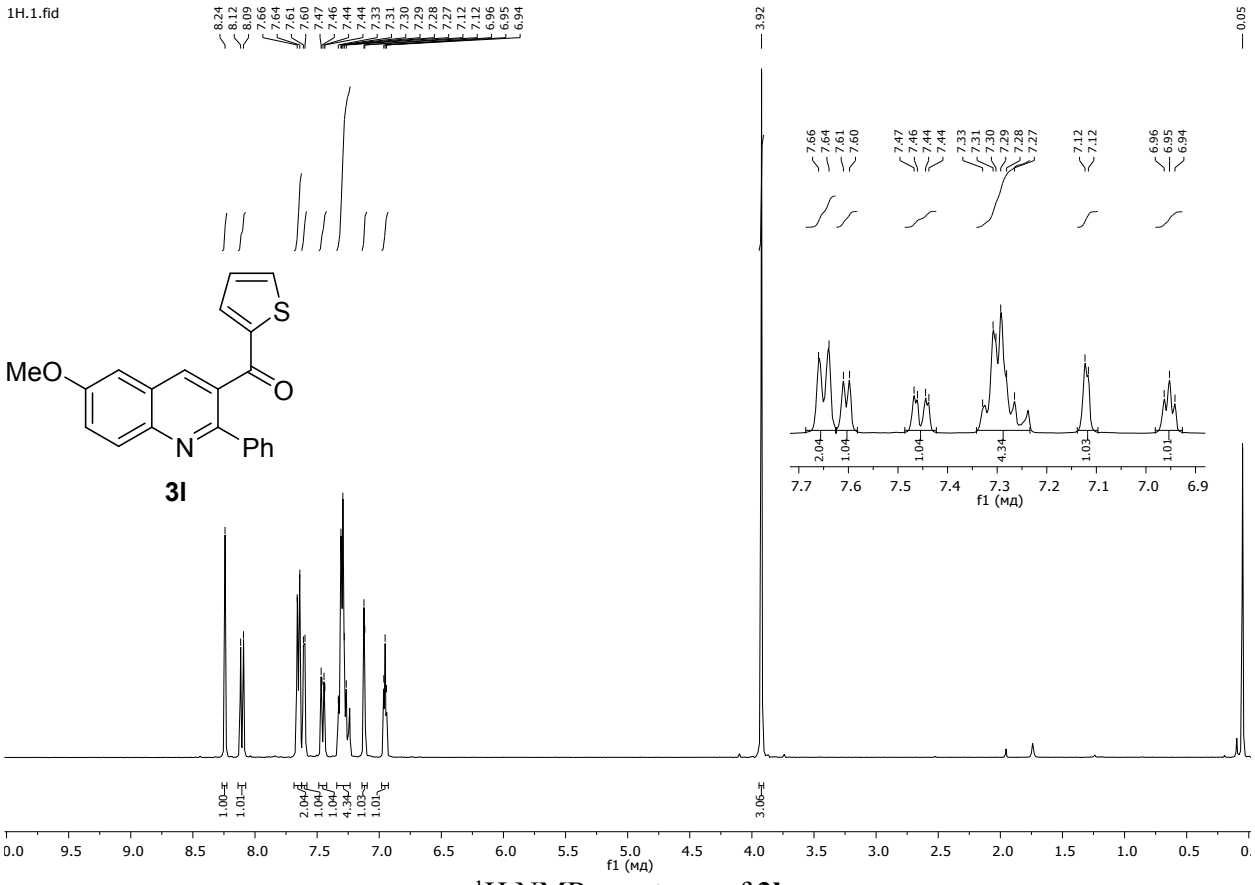
^{13}C NMR spectrum of **3j**



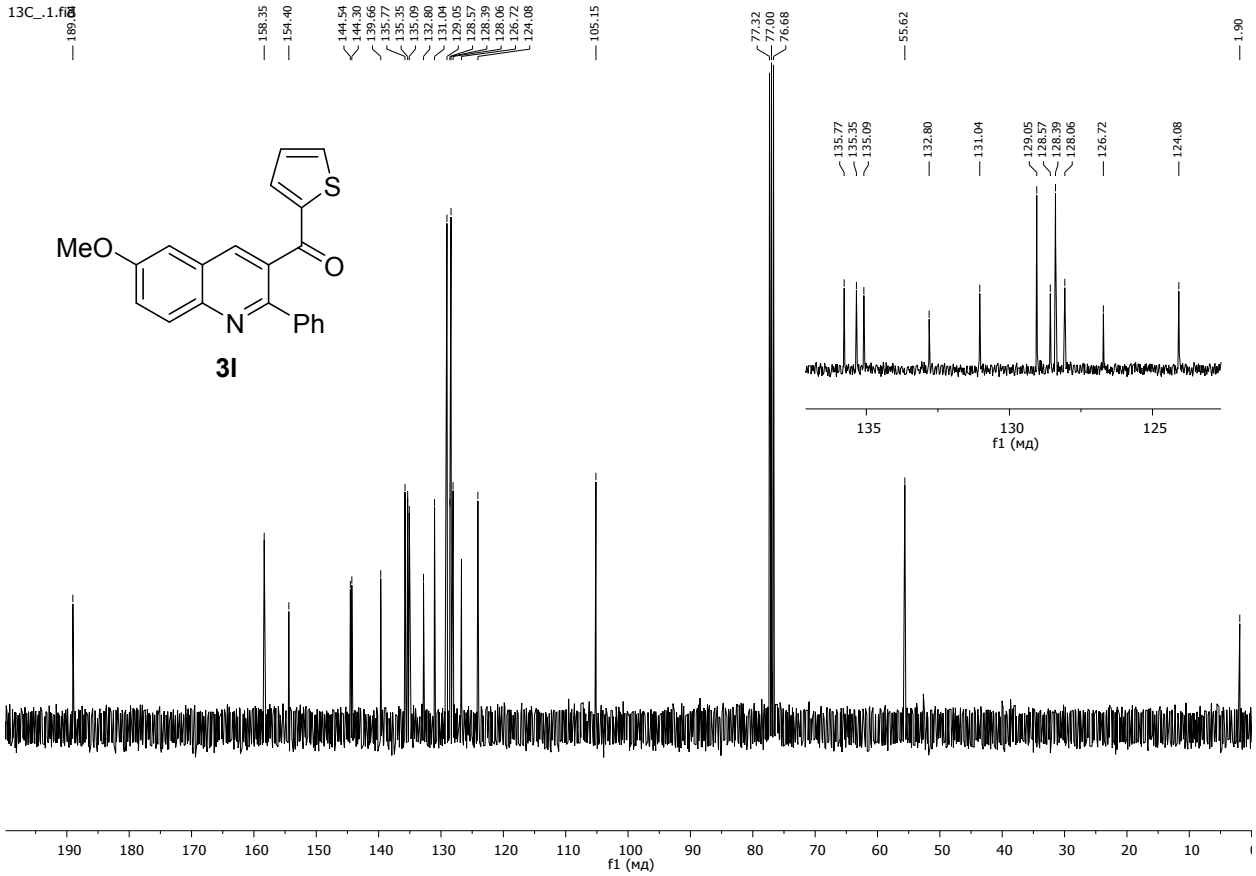
^{1}H NMR spectrum of **3k**



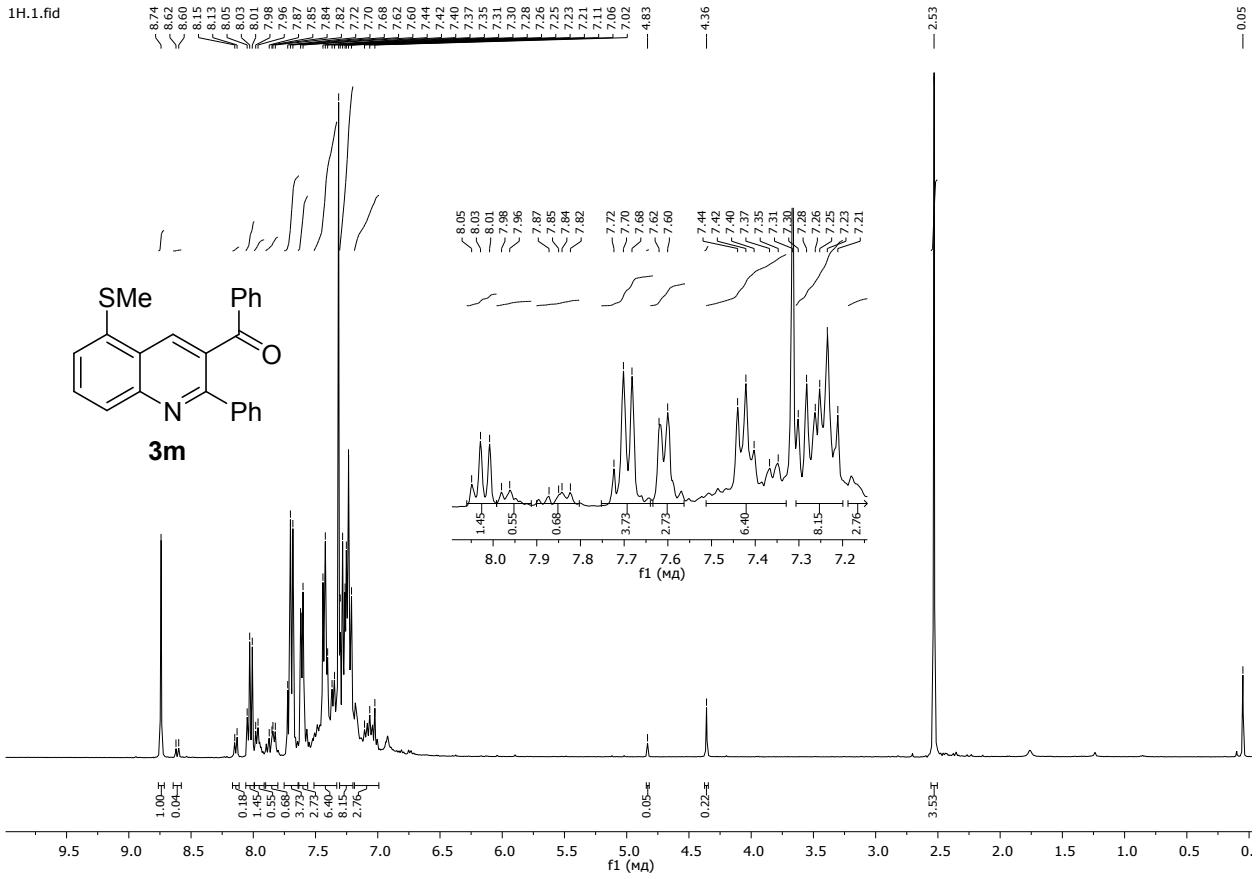
^{13}C NMR spectrum of **3k**



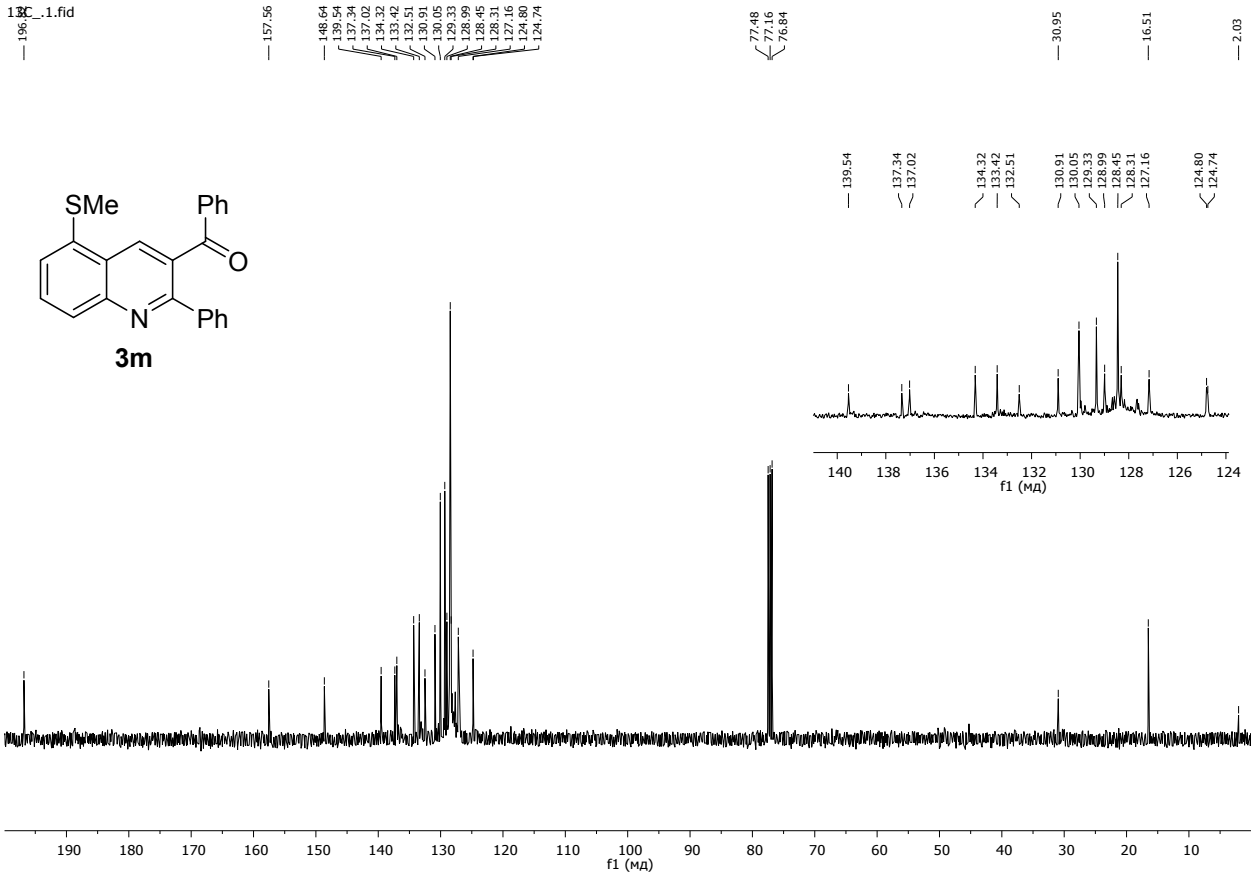
^{1}H NMR spectrum of **3l**



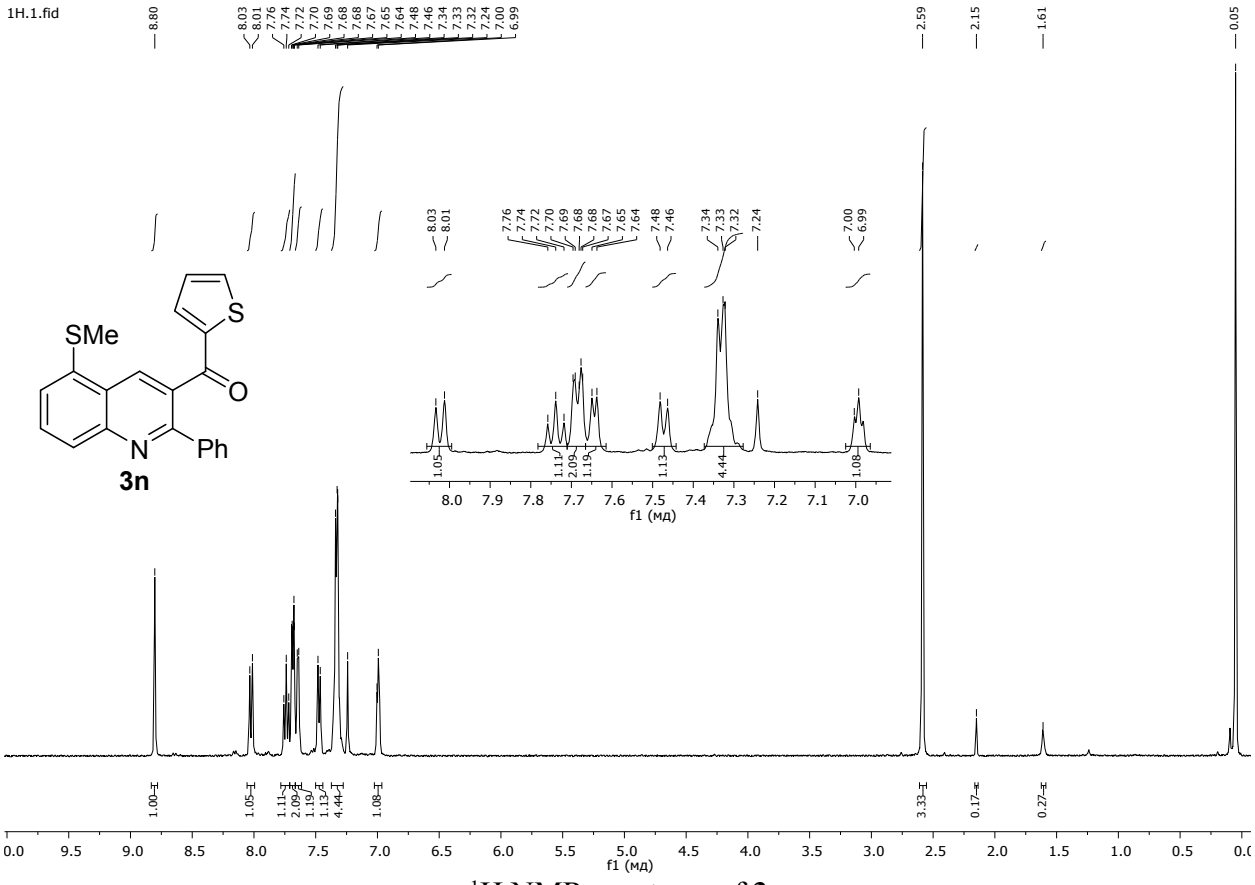
^{13}C NMR spectrum of **3l**



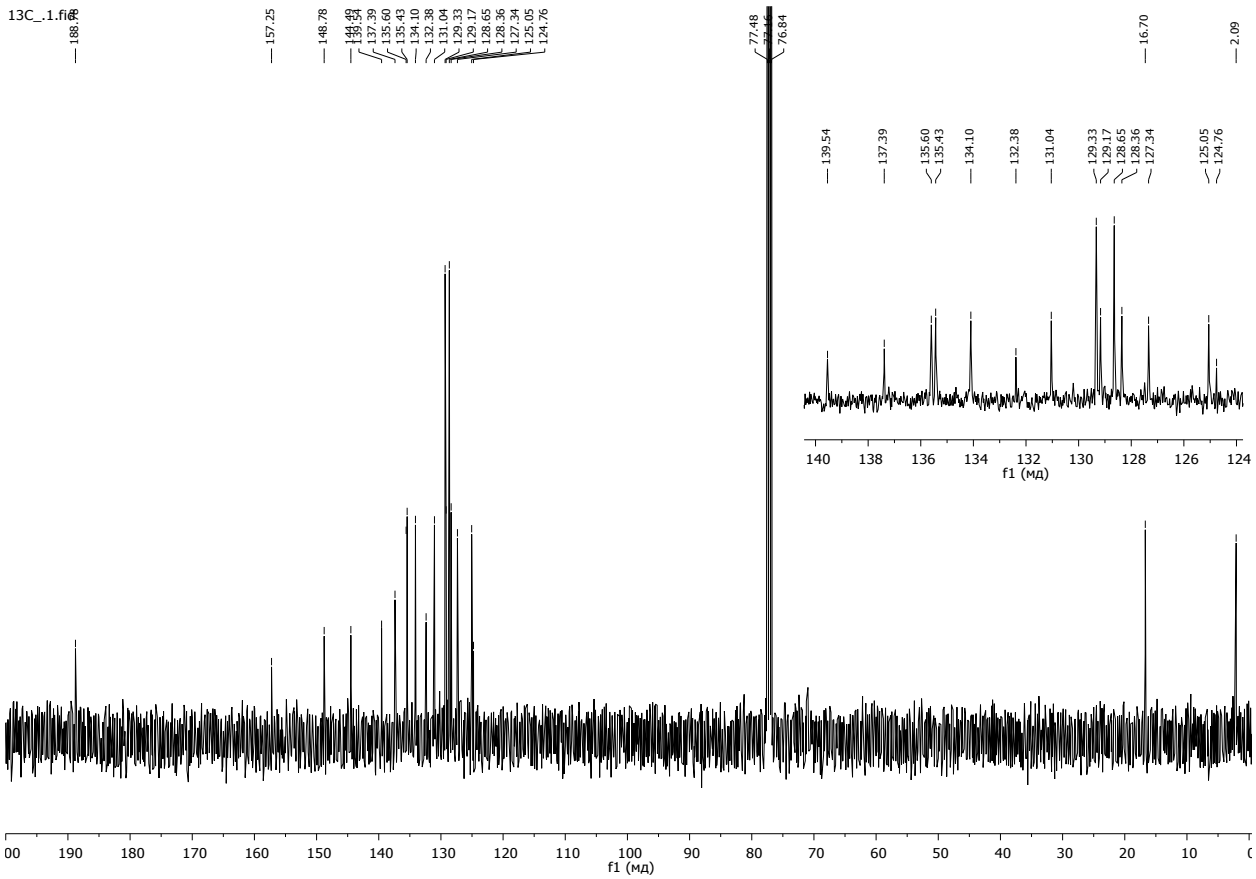
^{1}H NMR spectrum of **3m**



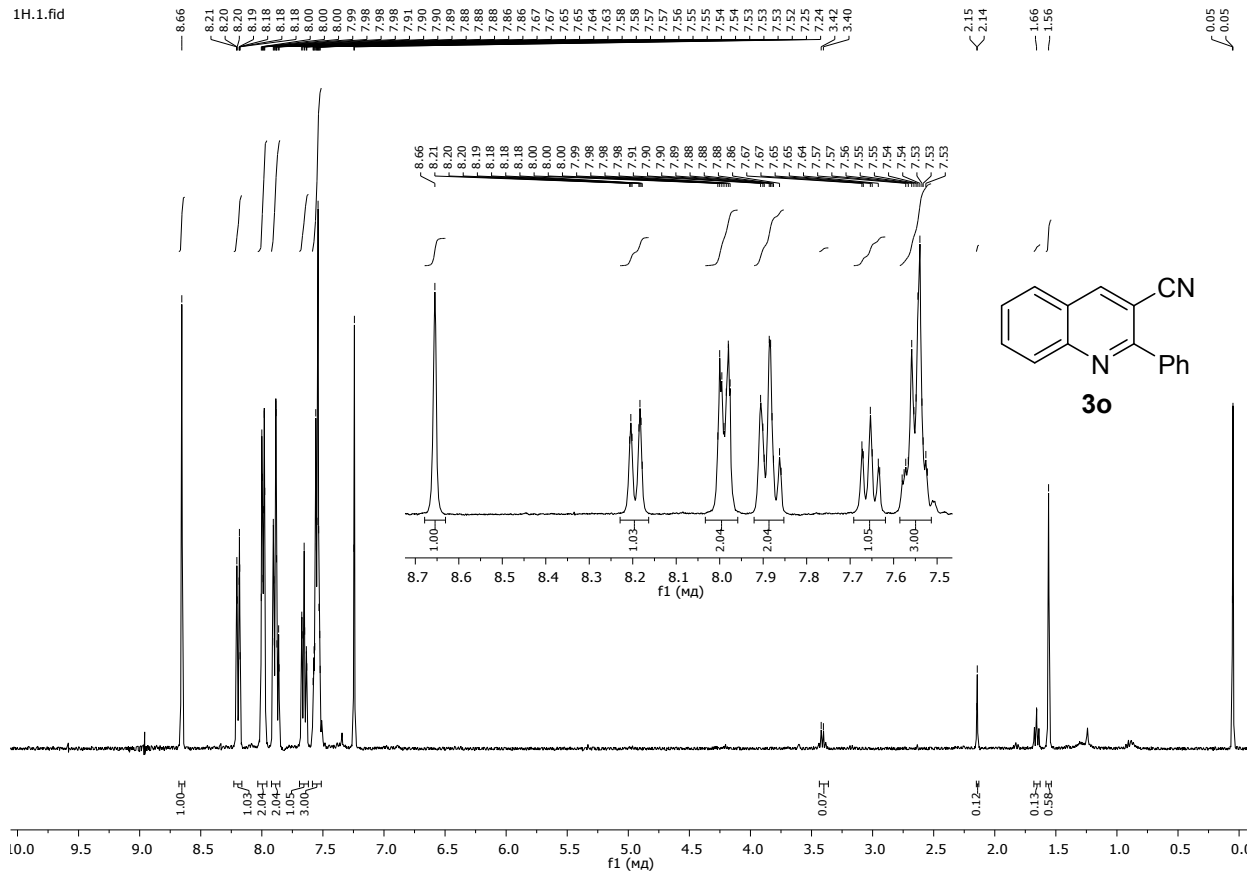
^{13}C NMR spectrum of **3m**



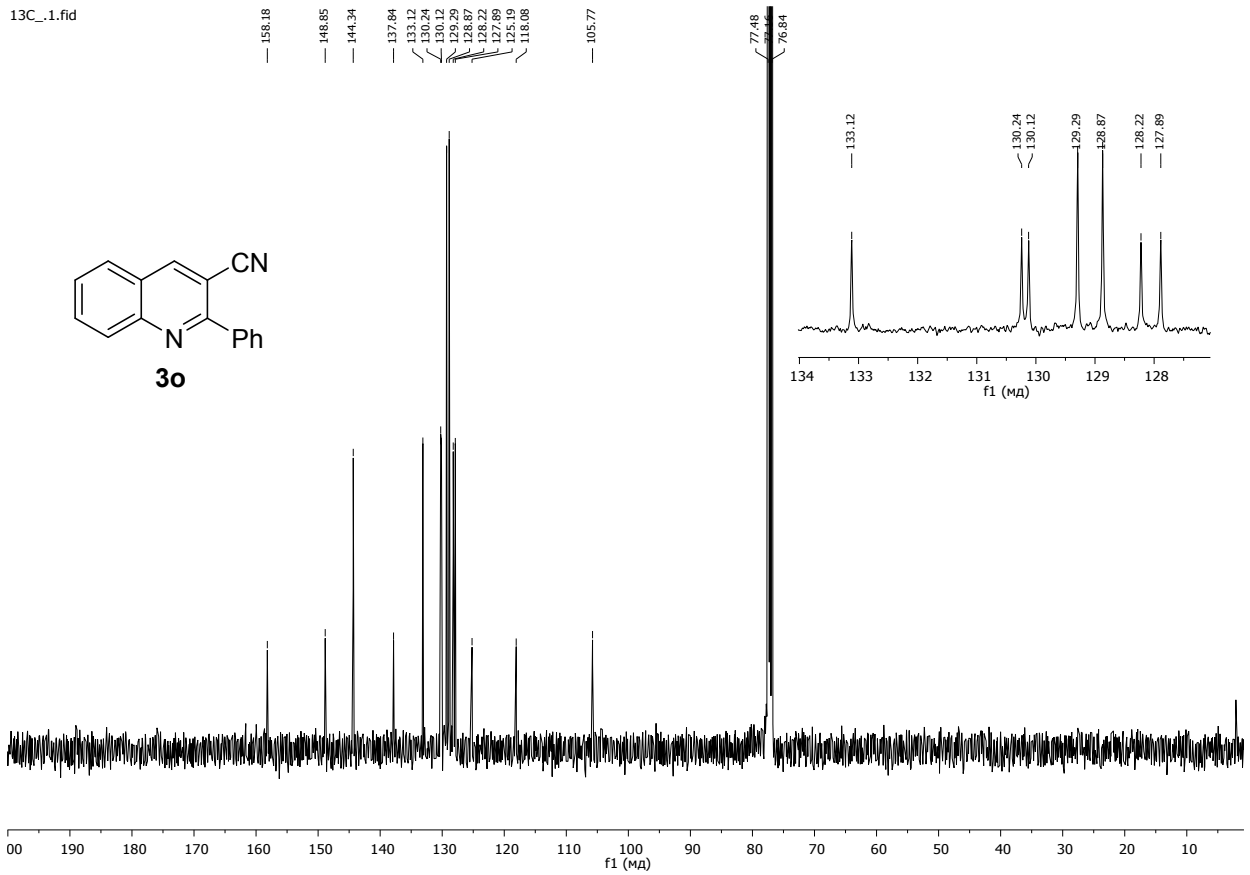
^{1}H NMR spectrum of **3n**



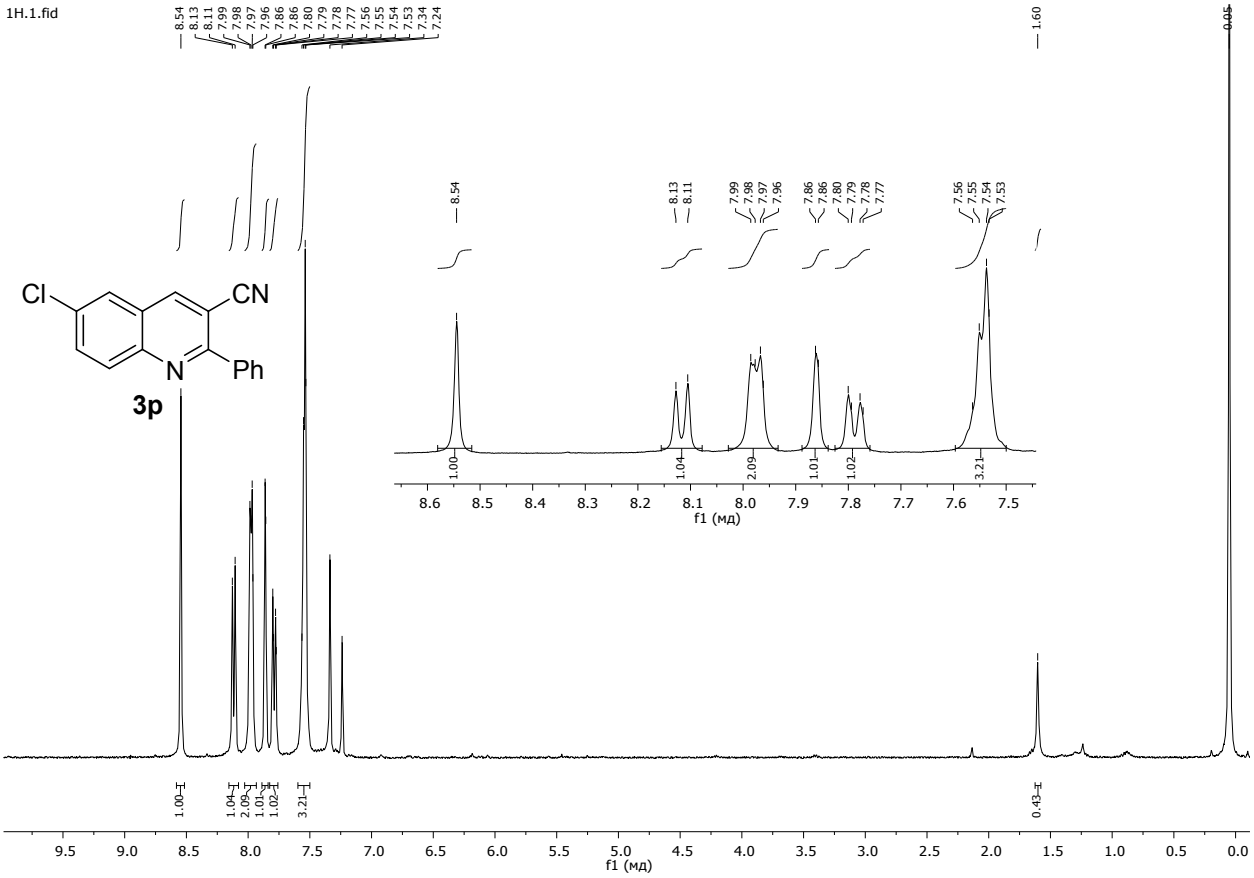
^{13}C NMR spectrum of **3n**



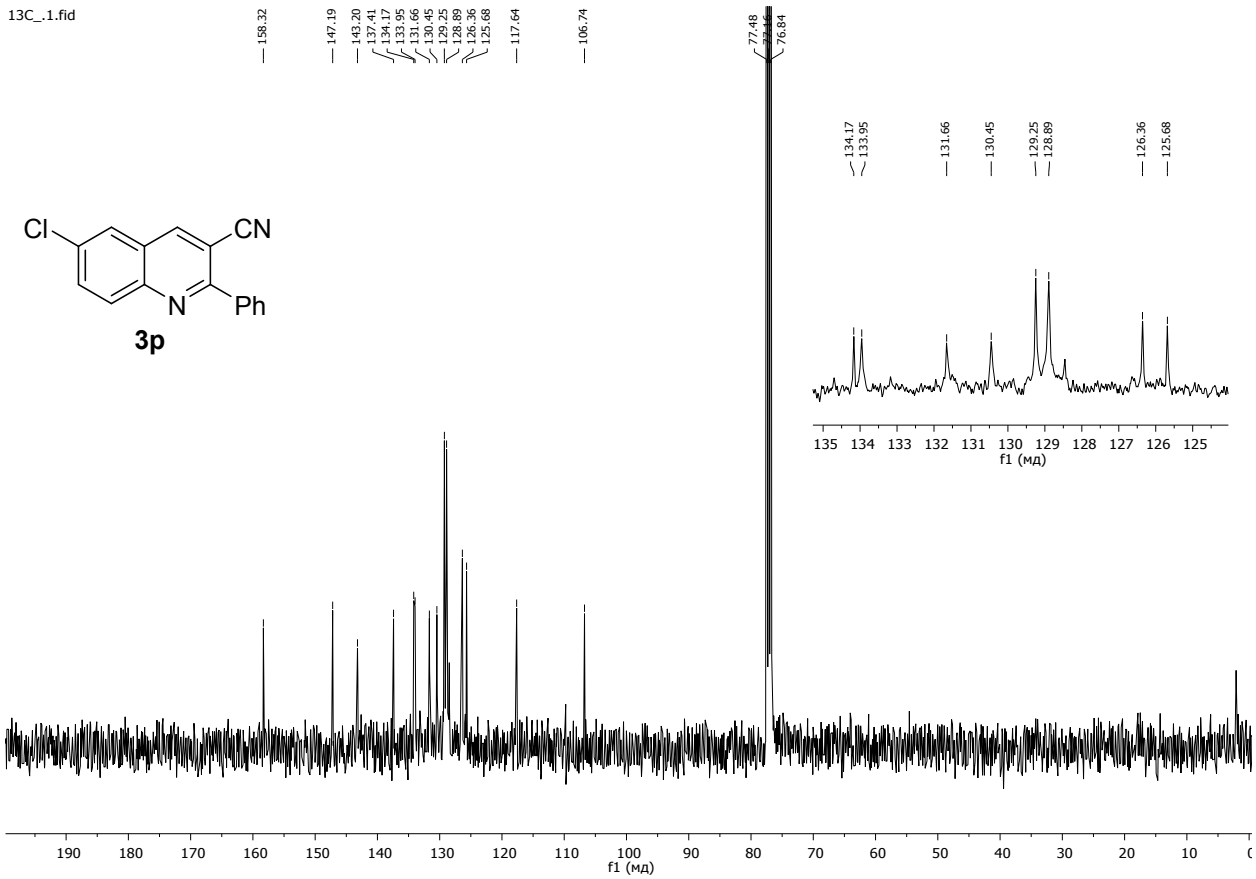
^{1}H NMR spectrum of **3o**



^{13}C NMR spectrum of **3o**



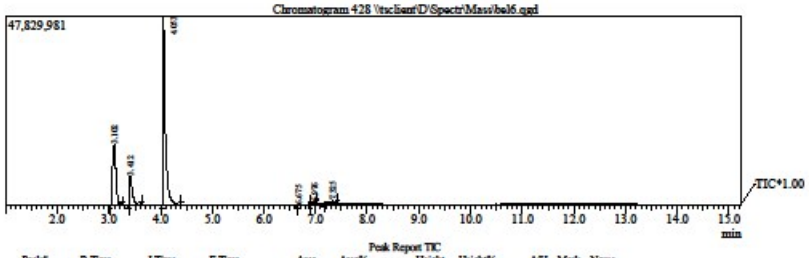
^{1}H NMR spectrum of **3p**



^{13}C NMR spectrum of **3p**

Detection of acetaldehyde by mass-spectroscopy (experiment with D_2O)

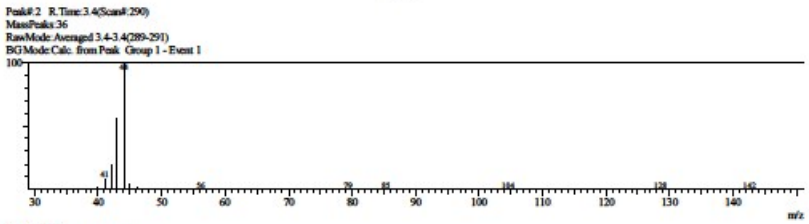
The reaction between quinoline **1a** (0.194 g, 1.500 mmol), acetylene **2a** (0.206 g, 1.000 mmol), D_2O (0.107 g, 5.000 mmol) and KOH (0.006 g, 10 mol%) (rt, 144 h) was carried out in a 10 mL tightly closed with rubber cap flask filled with argon. To get the gas analytical sampling, the reaction mixture was cooled in liquid nitrogen, evacuated, and heated. Detection of acetaldehyde in the gas phase was carried out in the Shumadzu Mass-spectrometer. After standard treatment of reaction mixture quinoline **3a** (0.059 g, 19%) was obtained.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	3.102	3.025	3.258	67846967	26.01	15563492	21.59	4.36		
2	3.412	3.383	3.633	27237188	10.44	7566024	10.50	3.60		
3	4.053	4.025	4.400	158576963	60.79	47739267	66.24	3.32		
4	6.675	6.642	6.900	1392947	0.53	152504	0.21	9.13		
5	6.976	6.900	7.025	1981143	0.76	483097	0.67	4.10		
6	7.325	7.167	7.417	3815694	1.46	570338	0.79	6.69		
				260850902	100.00	72074722	100.00			

Spectrum



Mass Table
Peak#:2 R.Time:3.4(Scan#:290)
MassPeaks:36
Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	34.20	621	0.02	13	47.90	1030	0.03	25	69.70	395	0.01
2	36.20	1220	0.04	14	51.15	647	0.02	26	71.30	276	0.01
3	37.20	271	0.01	15	52.90	759	0.02	27	75.40	291	0.01
4	39.05	997	0.03	16	53.90	274	0.01	28	78.15	39	0.00
5	40.00	61014	1.89	17	55.05	696	0.02	29	79.35	875	0.03
6	41.05	264721	8.21	18	56.15	1564	0.05	30	85.35	275	0.01
7	42.05	629710	19.54	19	57.25	565	0.02	31	101.70	280	0.01
8	43.05	1814374	56.30	20	57.60	571	0.02	32	104.50	755	0.02
9	44.05	3222715	100.00	21	60.25	28	0.00	33	110.50	329	0.01
10	45.05	147576	4.58	22	64.25	271	0.01	34	126.70	276	0.01
11	46.10	65999	2.05	23	67.45	542	0.02	35	128.50	307	0.01
12	47.10	24013	0.75	24	68.45	675	0.02	36	142.50	308	0.01

X-ray diffraction structural analysis data

The X-ray diffraction structural analysis was carried out on a Bruker D8 Venture monocrystal diffractometer with a Photon 100 detector using ω-2θ scanning. The reflection intensities were integrated using the Bruker SAINT monitoring program. X-ray absorption by the crystal was taken into account by analysis of the intensities of equivalent reflections. After averaging the intensities of equivalent reflections, only independent reflections were used. The search for a model was carried out using the SHELXS program[5] and direct methods, which gave the coordinates of all the non-hydrogen atoms. The structures obtained were refined by method of least squares using the SHELXL program.4 The complete information on the crystal structures of quinolines **3e,l** and 1,4-dihydroquinoline **5g** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1482718, 1838494 and 1482717, respectively).

The determination of the unit cell and the data collection for 2-furyl(2-phenyl-3-quinolinyl) methanone (**3e**) was performed at 100.0(2) K using the ω–φ scan technique. A specimen of $C_{20}H_{13}NO_2$, approximate dimensions 0.070 mm x 0.360 mm x 0.970 mm, clear, colorless, irregular crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *P2₁/c* space group yielded a total of 46541 reflections to a maximum θ angle of 27.53° (0.77 Å resolution), of which 3373 were independent (average redundancy 13.798, completeness = 99.9%, Rint = 5.89%, Rsig = 2.29%) and 2950 (87.46%) were greater than 2σ(F2). The final cell constants of **a** = 12.1150(9) Å, **b** = 16.3598(14) Å, **c** = 7.7826(6) Å, β=108.183(3)°, Z= 4, volume = 1465.5(2) Å^3, are based upon the refinement of the XYZ-centroids of 9941 reflections above 20 σ(I) with 4.979° < 2θ < 54.95°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.848. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9194 and 0.9939. The structure was solved and refined using the Bruker SHELXTL Software Package.[5] The H atoms were determined from a difference Fourier synthesis.

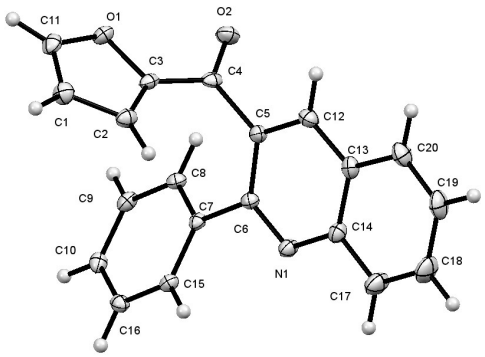


Figure 1. X-ray structure of 2-furyl(2-phenyl-3-quinolinyl)methanone **3e**. Thermal ellipsoids set at 50% probability.

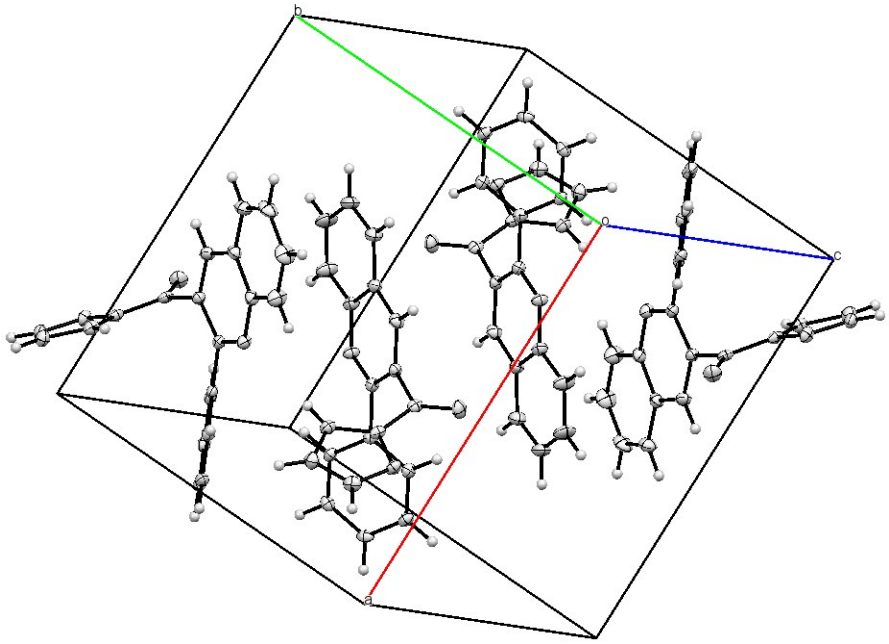


Figure 2. X-ray data on unit cell of 2-furyl(2-phenyl-3-quinolinyl) methanone (**3e**).

The final anisotropic full-matrix least-squares refinement on F2 with 208 variables converged at R1 = 3.98%, for the observed data and wR2 = 10.48% for all data. The goodness-of-fit was 1.061. The largest peak in the final difference electron density synthesis was 0.40 e-/Å3 and the largest hole was -0.230 e-/Å3 with an RMS deviation of 0.057 e-/Å3. On the basis of the final model, the calculated density was 1.357 g/cm3 and F(000), 624 e-. CCDC 1482718.

The determination of the unit cell and the data collection for (5-(methylthio)-2-phenylquinolin-3-yl)(thiophen-2-yl)methanone (**3l**) was performed on a Bruker D8 VENTURE PHOTON 100 CMOS diffractometer with MoK_α radiation ($\lambda = 0.71073$) at 297.0(2) K using the ω–φ scan technique. A specimen of $C_{21}H_{15}N_1O_2S_1$, approximate dimensions 0.51 mm x 0.56 mm x 0.79 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an orthorombic unit cell with *Pna2₁* space group yielded a total of 27881 reflections to a maximum θ angle of 26.12° (0.81 Å resolution), of which 3426 were independent (completeness = 99.8%, Rint = 3.40%, Rsig = 2.09%) and 3060 (89.3%) were greater than 2σ(F2). The final cell constants of **a** = 10.0386(7) Å, **b** = 16.6863(11) Å, **c** = 10.3764(7) Å, Z= 4, volume = 1738.1(2) $Å^3$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.9568. The structure was solved and refined using the Bruker SHELXTL Software Package.[5] The H atoms were determined from a difference Fourier synthesis.

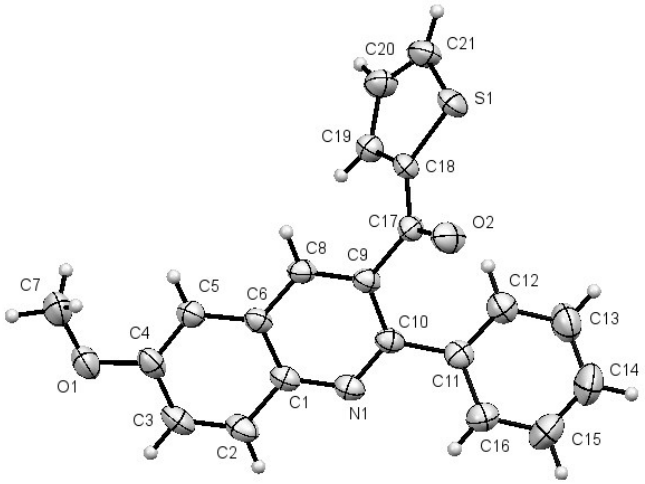


Figure 3. X-ray structure of (5-(methylthio)-2-phenylquinolin-3-yl)(thiophen-2-yl)methanone (**3l**). Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F2 with 227 variables converged at R1 = 3.06%, for the observed data and wR2 = 7.17% for all data. The goodness-of-fit was 1.093. The largest peak in the final difference electron density synthesis was 0.130 e-/Å^3 and the largest hole was -0.220 e-/Å^3 . On the basis of the final model, the calculated density was 1.320 g/cm^3 and F(000), 720 e-. CCDC 1838494.

The determination of the unit cell and the data collection for 2-(3-benzoyl-6-chloro-2-phenyl-1,4-dihydro-4-quinolinyl)acetaldehyde (**5g**) was performed at 296.15(2) K using the ω–φ scan technique. A specimen of $\underline{C_{24}H_{18}ClNO_2}$, approximate dimensions 0.103 mm x 0.121 mm x 0.430 mm, lustrous, clear, needle crystal was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using an monoclinic unit cell with *P2$_1$/n* space group yielded a total of 66778 reflections to a maximum θ angle of 26.1° (0.77 Å resolution), of which 3714 were independent (average redundancy 11.108, completeness = 99.7%, Rint = 10.04%, Rsig = 2.99%) and 2619 (87.46%) were greater than 2σ(F2). The final cell constants of **a** = 10.9587(3) Å, **b** = 7.7456(2) Å, **c** = 22.4121(7) Å, β=100.151(1)^o, Z= 4, volume = 1872.60(9) Å^3, are based upon the refinement of the XYZ-centroids of 8797 reflections above 20 σ(I) with 4.654° < 2θ < 56.75°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.896. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.968 and 0.977. The structure was solved and refined using the Bruker SHELXTL Software Package.[5] The H atoms were determined from a difference Fourier synthesis.

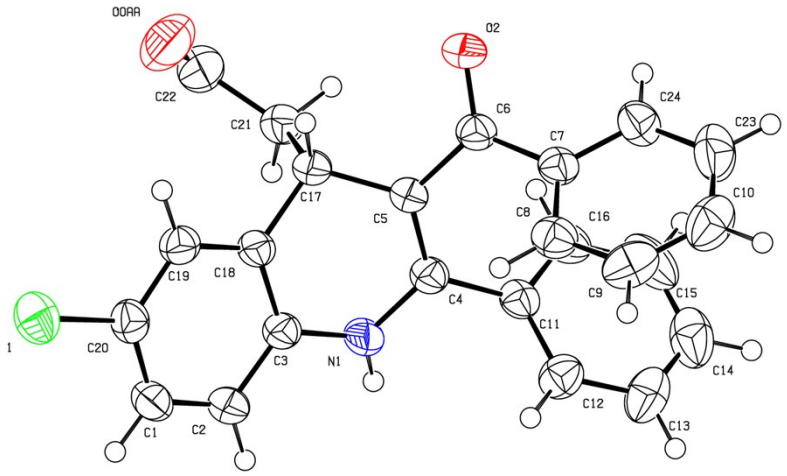


Figure 4. X-ray structure of 2-(3-benzoyl-6-chloro-2-phenyl-1,4-dihydro-4-quinolinyl) acetaldehyde (**5g**). Thermal ellipsoids set at 50% probability.

The final anisotropic full-matrix least-squares refinement on F2 with 254 variables converged at R1 = 4.32%, for the observed data and wR2 = 13.97% for all data. The goodness-of-fit was 1.112. The largest peak in the final difference electron density synthesis was 0.23 e-/Å3 and the largest hole was -0.210 e-/Å3 with an RMS deviation of 0.046 e-/Å3. On the basis of the final model, the calculated density was 1.372 g/cm3 and F(000), 804 e-. CCDC 1482717.

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