Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Synthesis of benzo[4,5]imidazo[1,2-a]pyrimidines and 2,3-dihydroquinazolin-4(1*H*)-ones under metal-free and solvent-free conditions

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Section S1. Chemicals and instruments

1,4-butanesultone (99%), anthranilamide (99%), benzaldehyde (99%), 4-methylbenzaldehyde (98%), 1-methylimdazole (99%), ethyl acetoacetate (99%), benzaldehyde (99%), 4-methoxybenzaldehyde (98%), 4-fluorobenzaldehyde (98%), 4-chlorobenzaldehyde (97%), 4-nitrobenzaldehyde (98%), 3-chlorobenzaldehyde (97%), (97%), 4-methylbenzaldehyde (98%), 4-cyclohexanecarboxaldehyde (97%), 4- tertbutylbenzaldehyde (98%), 2-fluorobenzaldehyde (97%), 2-chlorobenzaldehyde (98%), 4-hydroxybenzaldehyde (98%) 2-nitrobenzaldehyde (98%), piperonal (99%), acetyl acetate (99%), 2-aminobenzimidazole (97%), sulfuric acid (H_2SO_4) were obtained from Sigma-Aldrich Chemical Company.

TLC plates (silica gel 60 F254), acetone, n-hexane, petroleum ether were obtained from Merck. Deuterated solvents, D_2O and DMSO-d_6, were purchased from Cambridge Isotope Laboratories (Andover, MA) and used without further purification.With Ag were obtained from Armar (Switzerland). Ethyl acetate (purity ≥ 99.5%), *n*-hexane, and chloroform (purity ≥ 99%), ethanol (purity ≥ 99.8%), acetone (purity ≥ 99%),), methanol (99%), diethyl ether (purity ≥ 99.5%), were obtained from Merck. All starting materials were used without further purification.

GC–MS spectra were performed on an Agilent GC System 7890 equipped with a mass selective detector Agilent 5973N and a capillary DB–5MS column (30 m x 250 μm x 0.25 μm). FT-IR spectra were analyzed from KBr pellets by a Bruker Vertex 70. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500. HRMS (ESI) data were performed on Bruker micrOTOF-QII MS at 80 eV.

Section S2. **Synthesis of [(4-SO_3H)BMIM]HSO_4 under solvent-free sonication**

The synthesis of the [(4-SO_3H)BMIM]HSO_4 was synthesized *via* one-pot two-step procedure according to the our previous literature:[1]

The first step: 1-Methylimidazole (1.5 mmol, 0.123 g) and 1,4-butane sultone (1.5 mmol, 0.204 g) were added into a 10 mL pressurized glass tube with

Teflon-coated septum. The reaction mixture was irradiated by ultrasound for 5 min at 80 ^{o}C (37 kHz)**.** After completion of the reaction, the zwitterion [4-(SO_3^-)BMIM]$^+$ was washed with diethyl ether (6 x 5 mL), and dried under vacuum at 80 ^{o}C for 30 min to give the pure product.

The second step: A mixture of [4-(SO_3^-)BMIM]$^+$ (1.5 mmol, 0.327 g) and sulfuric acid 98% (1.5 mmol, 0.147 g) was added into a 10 mL pressurized glass tube with Teflon-coated septum, which was irradiated by ultrasound for 60 min at 60 ^{o}C (37 kHz). The mixture reaction was washed with diethyl ether (10 x 3 mL). Then, the mixture [(4-SO_3H)BMIM]HSO_4 was dried under vacuum at 40 ^{o}C. The product was then characterized by ^{1}H and ^{13}C NMR, FT-IR, TGA, and HR-MS (ESI).

Table S1. Optimization of reaction condition for the first step.

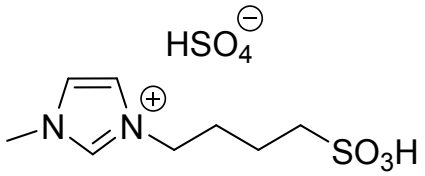
Entry	Time (min)	Temperature (^{o}C)	Isolated yield (%)
1	5	50	65
2	5	60	76
3	5	70	88
4	5	80	99
5	1	80	42
6	3	80	57

Table S2. Optimization of reaction conditions for the second step.

Entry	Time (min)	Temperature (^{o}C)	Isolated yield (%)
1	30	RT (30)	0
2	30	40	21
3	30	50	34
4	30	60	53
5	30	70	40
6	40	60	75
7	60	60	95
8	90	60	97

^{1}H NMR, ^{13}C NMR, IR, TGA, and HR-ESI-MS of 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate

1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate[1]



FT-IR (KBr, 4000 – 400 cm^{-1}) 3410, 1639, 1457, 1171, 1042, 752.

^{1}H NMR (500 MHz, D_2O) δ 8.59 (s, 1H), 7.35 (t, J = 1.7 Hz, 1H), 7.29 (t, J = 1.7 Hz, 1H), 4.10 (t, J = 7.0 Hz, 2H), 3.75 (s, 3H), 2.83 (t, J = 8.0, 2H), 1.82 (m, 2H), 1.60 (m, 2H).

^{13}C NMR (125 MHz, D_2O) δ 135.9, 123.6, 122.1, 50.0, 48.9, 35.7, 28.1, 20.9.

HRMS (ESI) *m/z* calcd for [M^+] $C_8H_{15}N_2O_3S^+$ 219.0798; found 219.0783.

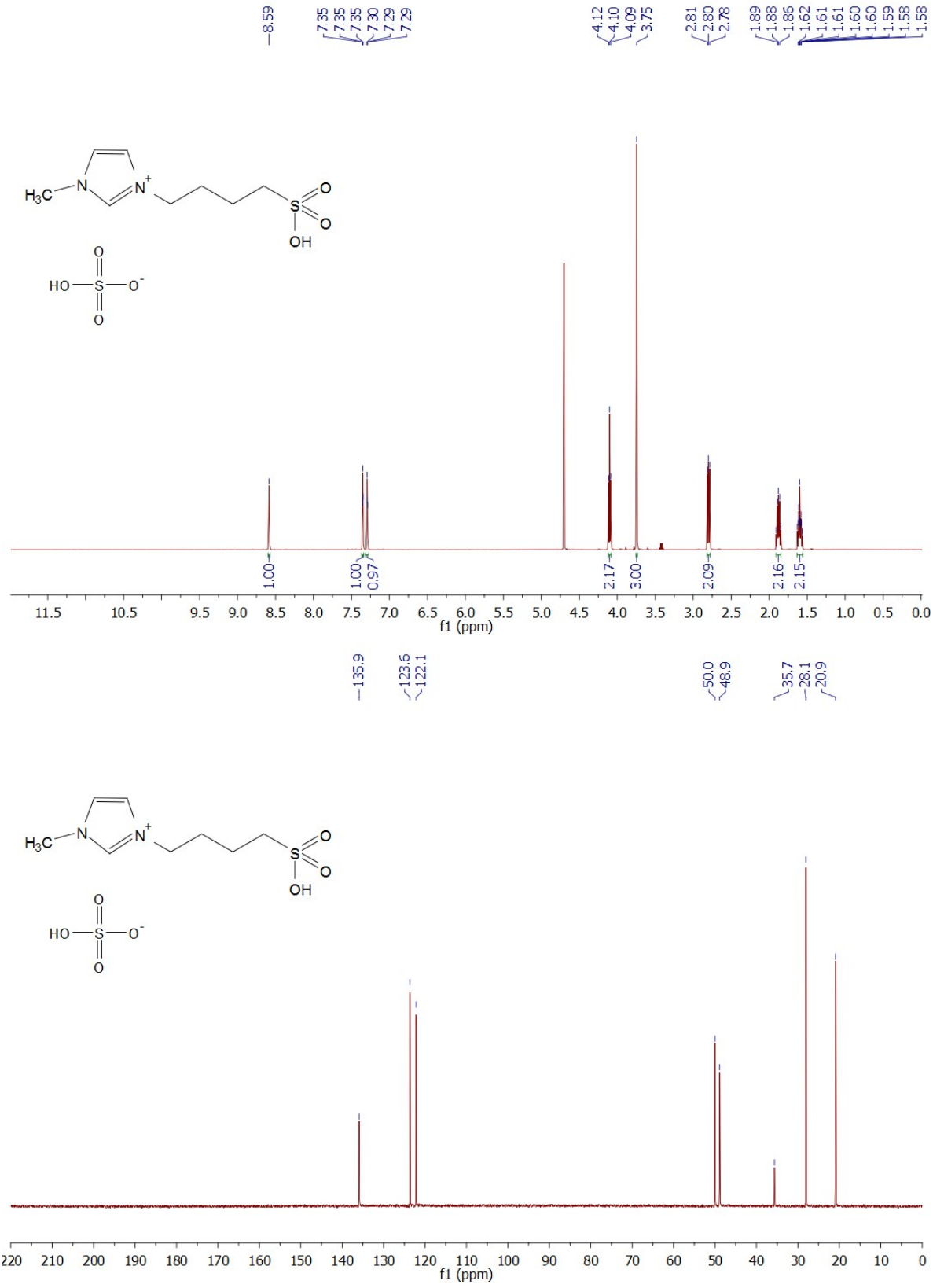


Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate

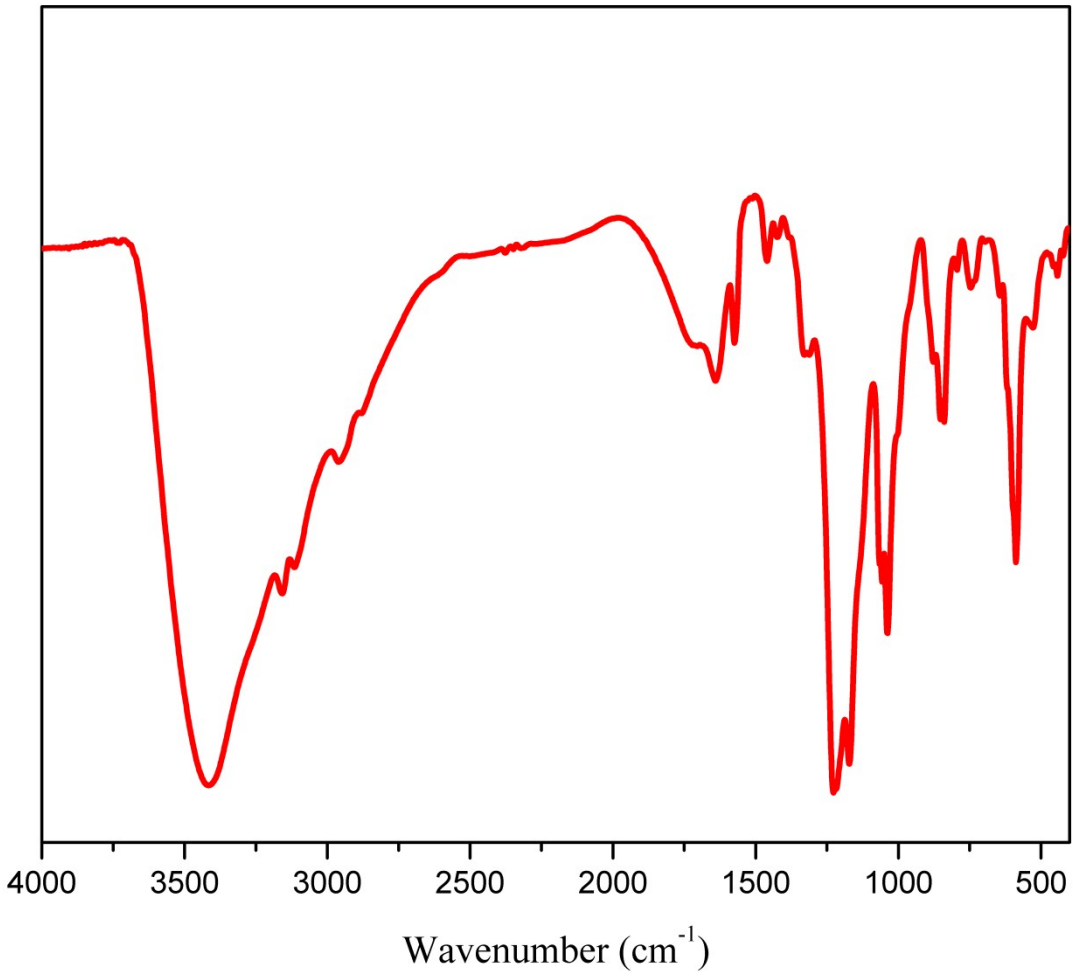


Figure 2. FT-IR spectrum of 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate

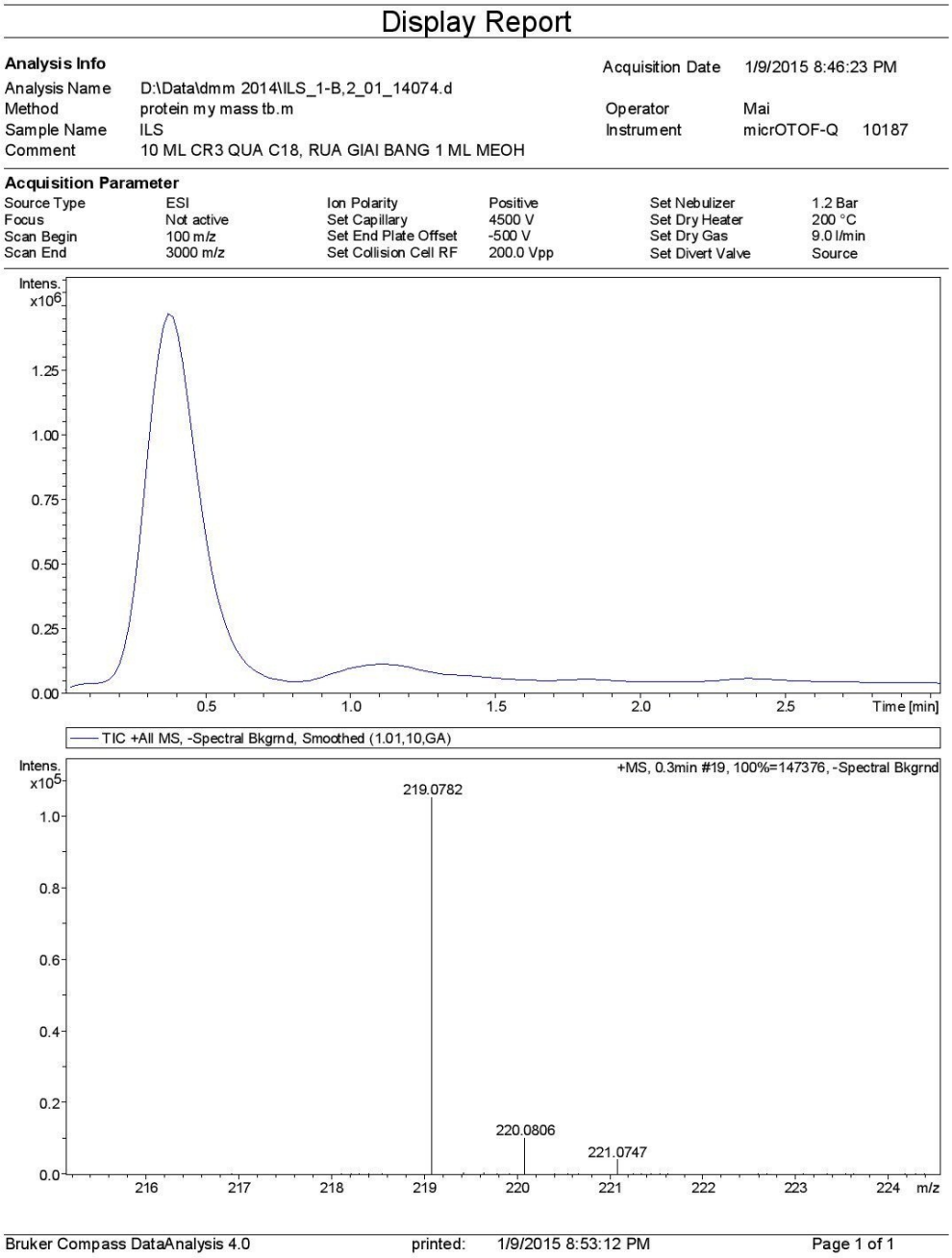


Figure 3. HR-ESI-MS 1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate.

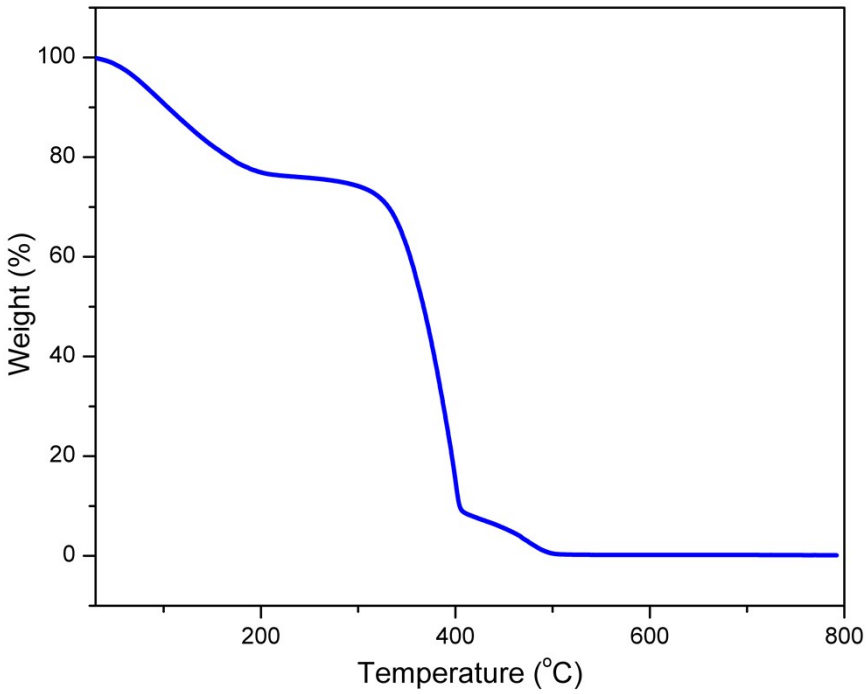


Figure 4. TGA of *1-(4-sulfobutyl)-3-methylimidazolium hydrogen sulfate*

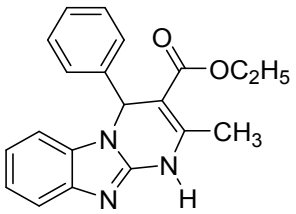
Section S3. General procedure and spectral data of benzo[4,5]imidazo[1,2-a]pyrimidines.

General procedure of benzo[4,5]imidazo[1,2-a]pyrimidines synthesis

A mixture of benzaldehyde (106 mg, 1 mmol), ethyl acetoacetate (130 mg, 1 mmol), 2-aminobenzimidazole (133 mg, 1 mmol) and [(4-SO_3H)BMIM]HSO_4 (31.6 mg, 0.1 mmol) was heated 100 ℃ and the process of reaction monitored by TLC. After completion of the conversion, the reaction mixture was quenched with cold ethanol (10 mL). The crude product was filtered and washed with petroleum ether (10 mL) and then purified by recrystallization from ethanol to obtain the desired product.

Spectral data of benzo[4,5]imidazo[1,2-a]pyrimidines synthesis

Ethyl 2-methyl-4-phenyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate [2, 3]

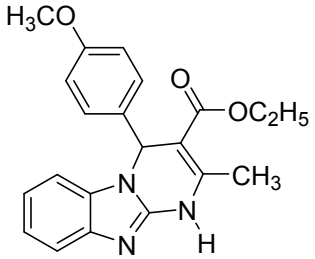


mp 287-288 °C

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.35 (m, 1H), 7.25 (m, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.41 (s, 1H), 4.07 – 3.96 (m, 1H), 2.45 (s, 1H), 2.07 (s, 1H), 1.13 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7, 146.9, 146.1, 142.7, 142.5, 132.0, 128.8, 128.2, 128.2, 127.5, 127.5, 122.2, 120.6, 117.2, 110.3, 98.4, 59.8, 56.4, 19.6, 14.5.

Ethyl 4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[2]

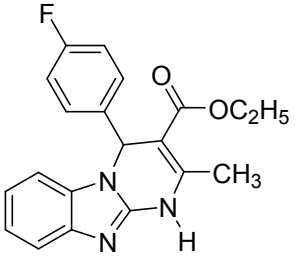


mp 269-270 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.25 (m, 3H), 7.06 – 7.01 (m, 1H), 6.98 – 6.90 (m, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.37 (s, 1H), 4.14 – 3.91 (m, 2H), 3.66 (s, 3H), 2.44 (s, 3H), 1.15 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7, 159.1, 146.6, 146.1, 142.8, 134.6, 132.0, 128.7, 128.7, 122.2, 120.6, 117.2, 114.1, 114.1, 110.3, 98.7, 59.8, 55.8, 55.4, 19.0, 14.6.

Ethyl 4-(4-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[3]

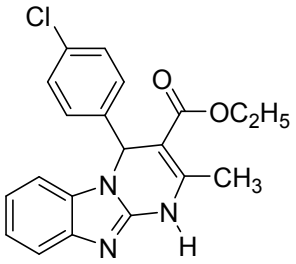


mp 283-284 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.40 (m, 2H), 7.34 (d, *J* = 8 Hz, 1H), 7.26 (d, *J* = 8 Hz, 1H), 7.11 – 7.01 (m, 2H), 6.95 (m, 1H), 6.45 (s, 1H), 4.12 – 3.90 (m, 1H), 2.45 (s, 3H), 1.14 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.6, 161.9 (d, *J* = 244.0 Hz), 147.1, 145.9, 142.7, 138.8, 131.9, 129.7, 129.6, 122.3, 120.7, 117.3, 115.7, 115.6, 110.3, 98.3, 59.9, 55.7, 19.1, 14.5.

Ethyl 4-(4-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[2]

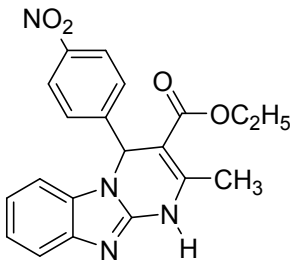


mp 286-287 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.19 (m, 4H), 7.10 – 7.03 (m, 1H), 7.00 – 6.93 (m, 1H), 6.46 (s, 1H), 4.21 – 3.76 (m, 2H), 2.46 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 147.5, 145.9, 144.9, 142.7, 133.3, 131.9, 130.9, 128.3, 127.6, 126.1, 122.4, 120.8, 117.4, 110.3, 97.8, 59.9, 55.8, 19.1, 14.5.

Ethyl 2-methyl-4-(4-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[3]

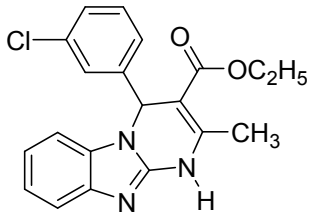


mp >350 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.60 (s, 1H), 4.02 (m, 2H), 2.47 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 165.4, 149.5, 147.4, 145.7, 132.3, 131.8, 129.0, 124.2, 124.1, 122.5, 120.9, 117.5, 110.2, 97.3, 60.0, 55.7, 19.2, 14.5.

Ethyl 4-(3-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[2]

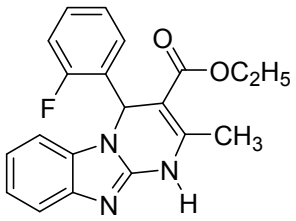


mp 269-270 °C

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.35 (dt, *J* = 11.3, 8.5 Hz, 5H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.98 – 6.92 (m, 1H), 6.44 (s, 1H), 4.25 – 3.67 (m, 2H), 2.45 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 165.6, 147.3, 145.9, 142.7, 141.4, 132.8, 131.9, 129.5, 129.5, 128.8, 128.8, 122.4, 120.7, 117.3, 110.3, 98.0, 59.9, 55.7, 19.1, 14.5.

Ethyl 4-(2-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[3]

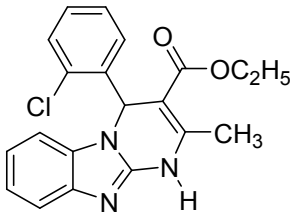


mp 288-289 °C

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.49 – 7.41 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.17 – 7.08 (m, 3H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.64 (s, 1H), 4.09 – 3.81 (m, 2H), 2.47 (s, 3H), 1.09 (t, *J* = 7.3 Hz, 3H.

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 159.9 (d, *J* = 246.7 Hz), 147.9, 145.8, 142.6, 132.0, 130.6 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 3.7 Hz), 128.9 (d, *J* = 12.6 Hz), 125.1 (d, *J* = 3.0 Hz), 122.4, 120.8, 117.4, 115.9 (d, *J* = 21.9 Hz), 109.3 (d, *J* = 1.8 Hz), 96.4, 59.8, 50.9 (d, *J* = 2.6 Hz), 19.1, 14.3.

***Ethyl 4-(2-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate*[2]**

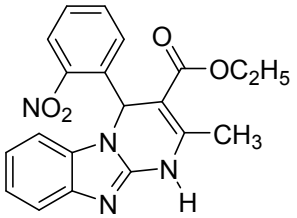


mp 290-291 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.30 – 7.18 (m, 3H), 7.06 – 7.02 (m, 1H), 6.95 (m, 1H), 6.75 (s, 1H), 4.10 – 3.88 (m, 2H), 2.46 (s, 3H), 1.08 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 147.8, 145.7, 142.2, 139.3, 132.2, 132.1, 131.0, 130.1, 130.0, 128.3, 122.4, 120.8, 117.4, 109.7, 96.8, 67.4, 59.8, 19.1, 14.5.

***Ethyl 2-methyl-4-(2-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate*[4]**

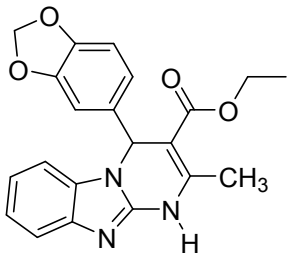


mp 286-288 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.91 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.43 (m, 3H), 7.26 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.11 (s, 1H), 7.10 – 7.07 (m, 1H), 7.00 – 6.95 (m, 1H), 4.03 – 3.97 (m, 1H), 3.94 – 3.88 (m, 1H), 2.42 (s, 3H), 1.05 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.4, 148.3, 147.8, 145.9, 137.3, 134.7, 134.7, 132.2, 129.7, 129.5, 124.5, 122.7, 121.3, 117.6, 110.0, 97.9, 60.1, 51.1, 19.4, 14.5.

Ethyl 4-(benzo[d][1,3]dioxol-5-yl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate[5]

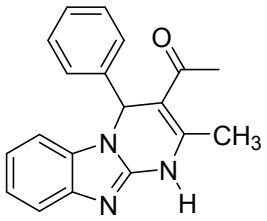


mp 245 - 247 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 5.92 (d, *J* = 6.5 Hz, 2H), 4.13 – 3.94 (m, 2H), 2.44 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7, 147.7, 147.1, 146.8, 146.0, 136.5, 132.0, 122.2, 121.1, 120.6, 117.2, 115.2, 110.5, 108.4, 107.8, 101.5, 98.5, 59.8, 56.1, 19.0, 14.6.

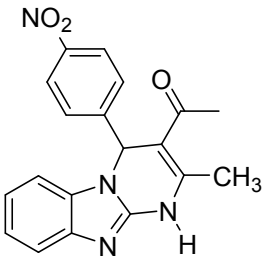
1-(2-methyl-4-phenyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[6]



mp 329-330 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.39 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (dd, *J* = 13.4, 6.0 Hz, 1H), 7.07 – 7.02 (t, *J* = 7.3 Hz 1H), 7.01 – 6.95 ((t, *J* = 7.3 H, 1H), 6.56 (s, 1H), 2.47 (s, 1H), 2.22 (s, 1H).

1-(2-methyl-4-(4-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[7]

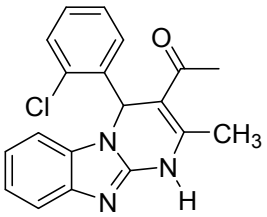


mp 304 - 305 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.12 (m, 2H), 7.66 (m, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.10 – 7.02 (m, 1H), 6.99 - 6.96 (m, 1H), 6.70 (s, 1H), 2.51 (s, 1H), 2.28 (s, 1H)

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.6, 149.1, 147.8, 147.4, 145.6, 142.5, 131.8, 128.9, 128.9, 124.2, 124.2, 122.7, 121.2, 117.5, 110.3, 109.0, 55.5, 31.4, 20.4

1-(4-(2-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[7]

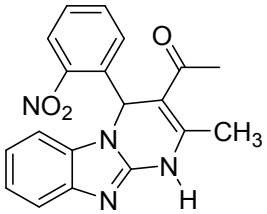


mp 291-292 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.35 (m, 2H), 7.28 - 7.25 (m, 2H), 7.21 (td, *J* = 7.7, 1.4 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.81 (s, 1H), 2.48 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.6, 146.6, 145.7, 142.4, 139.1, 132.2, 132.0, 131.1, 130.2, 130.1, 128.3, 122.5, 120.9, 117.4, 109.9, 108.8, 54.5, 31.4, 20.3.

***1-(2-methyl-4-(2-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one*[7]**

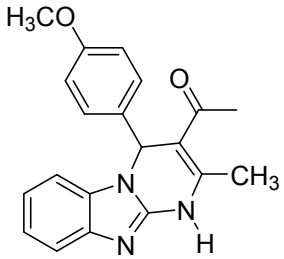


mp 305-306 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.51 - 7.47 (m, 2H), 7.45 – 7.35 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 2.49 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.2, 148.8, 147.4, 145.9, 142.6, 137.3, 134.1, 132.4, 129.2, 128.9, 124.1, 122.7, 121.3, 117.6, 110.7, 110.1, 51.2, 31.9, 31.1, 20.6.

1-(4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[2]

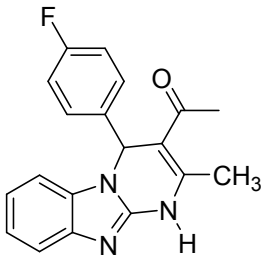


mp 276-278 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.04 (td, *J* = 7.5, 1.1 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.55 (s, 1H), 3.65 (s, 3H), 2.46 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.9, 159.2, 146.3, 145.9, 142.8, 134.2, 132.1, 128.9, 128.9, 122.2, 120.6, 117.3, 114.3, 114.3, 110.5, 109.2, 55.6, 55.5, 31.0, 20.1.

1-(4-(4-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[7]

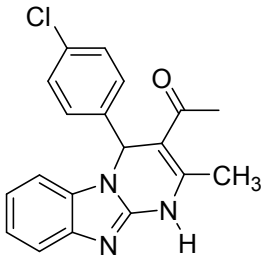


mp 319-322 °C

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.47 – 7.41 (m, 2H), 7.40 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.10 – 7.03 (m, 3H), 7.01 – 6.97 (m, 1H), 6.60 (s, 1H), 2.48 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.6, 161.9 (d, J = 244.2 Hz), 146.8, 145.9, 142.7, 138.5, 131.9, 129.7, 129.7, 122.3, 120.7, 117.4, 115.9, 115.7, 110.4, 109.2, 55.4, 31.2, 20.2.

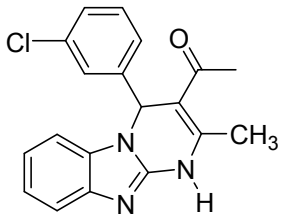
1-(4-(4-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[2]



^{1}H NMR (500 MHz, DMSO-d_6) δ 7.43 – 7.39 (m, 2H), 7.39 – 7.35 (m, 2H), 7.32 – 7.31 (m, 2H), 7.09 – 7.03 (m, 1H), 7.01 – 6.96 (m, 1H), 6.57 (s, 1H), 2.47 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.6, 147.0, 145.8, 142.6, 141.1, 132.9, 131.9, 129.5, 129.5, 129.0, 129.0, 122.4, 120.9, 117.4, 110.4, 109.1, 88.6, 55.4, 31.3, 20.2.

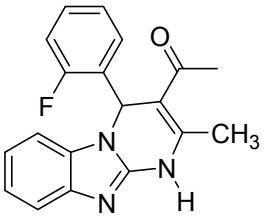
1-(4-(3-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[7]



^{1}H NMR (500 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.07 – 7.03 (m, 1H), 7.01 (m, 1H), 6.94 (s, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.53 (s, 1H), 5.93 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.7, 147.9, 147.3, 145.9, 142.8, 136.0, 132.1, 122.2, 121.2, 120.6, 117.3, 110.7, 109.1, 108.5, 108.0, 101.6, 55.9, 31.1, 20.2.

1-(4-(2-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one[7]



^{1}H NMR (500 MHz, DMSO-d_6) δ 10.89 (s, 1H), 7.48 (td, *J* = 7.8, 1.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.08 (m, 2H), 7.08 – 7.04 (m, 1H), 7.02 – 6.97 (m, 1H), 2.49 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6) δ 194.2, 145.8, 142.7, 132.0, 130.6 (d, *J* = 34.5 Hz), 130.4 (d, *J* = 15.5 Hz), 128.8, 128.7, 125.3 (d, *J* = 13.5 Hz), 122.4, 120.8, 117.5, 116.1 (d, *J* = 87.0 Hz), 109.5 (d, *J* = 13.5 Hz), 107.9, 51.0(d, *J* = 10.0 Hz), 31.2, 20.3.

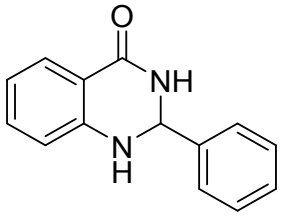
Section S4. General procedure and spectral data of 2,3-dihydroquinazolin-4(1*H*)-one

General procedure for 2,3-dihydroquinazolin-4(1*H*)-one

A mixture of anthranilamide (136 mg, 1 mmol), benzaldehyde (106 mg, 1 mmol), and [(4-SO_3H)BMIM]HSO_4 (31.6 mg, 0.1 mmol) was sonicated for 30 min at room temperature and the process of reaction monitored by TLC or GC-MS. After completion of the conversion, the reaction mixture was quenched with ethanol (10 mL). The crude product was filtered and washed with petroleum ether (2 x 5 mL) and then purified by recrystallization from ethanol to obtain the desired product.

Spectral data of 2,3-dihydroquinazolin-4(1*H*)-one

***2-phenyl-2,3-dihydroquinazolin-4(1H)-one*[8]**



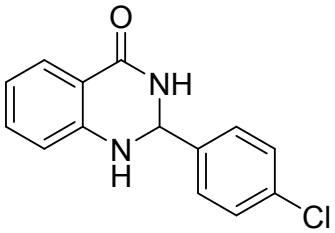
White solid; **mp** 219- 223 ^oC

FT-IR (KBr, 4000 – 400 cm^{-1}): 3462, 3306, 2900, 1659, 1615, 1509, 1483, 1443, 1387, 1298, 1247, 1159, 1028.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.28 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.40 - 7.33 (m, 3H), 7.24 (td, *J* = 7.5 Hz, *J*= 1.5 Hz, 1H), 7.10 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 5.75 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ 163.6, 147.8, 141.62, 133.3,128.3, 127.3, 126.8, 117.1, 114.9, 114.37, 66.5.

***2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1H)-one*[9]**



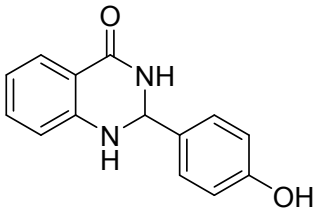
White solid; **mp** 199- 201 ^oC

FT-IR (KBr, 4000 – 400 cm^{-1}): 3447, 3305, 3188, 3062, 2950, 1914, 1659, 1607, 1481, 1431, 1381, 1288, 1161, 1089, 1010.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.32 (s, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 5.76 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ 163.3, 147.5, 140.5, 133.3, 132.8, 128.6, 128.1, 127.2, 117.1, 114.8, 114.3, 65.6.

***2-(4-hydroxyphenyl)-2,3-dihydroquinazolin-4(1H)-one*[11]**



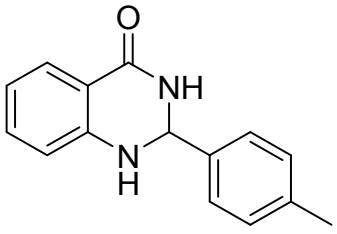
White solid; **mp** 212- 214 °C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3338, 3189, 2782, 2582, 1627, 1499, 1426, 1292, 1244, 1152, 1037.

^{1}H NMR (500 MHz, DMSO-d_6): δ 9.49 (s, 1H), 8.08 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.19 (m, 1H), 6.93 (s, 1H), 6.73 (m, 3H), 6.66 (t, *J* = 7.5 Hz, 1H), 5.63 (s, 1H).

^{13}C NMR (125 MHz, DMSO-d_6): δ 163.7, 157.7, 148.1, 133.2, 131.6, 128.3, 127.3, 117.0, 114.9, 114.4, 66.6.

***2-(p-tolyl)-2,3-dihydroquinazolin-4(1H)-one*[9]**



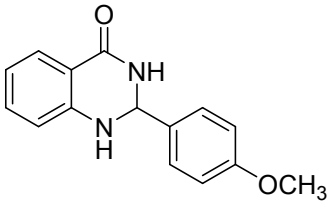
White solid; **mp** 233-234 °C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3443, 2900, 1661, 1510, 1438, 1384, 1294, 1160, 908.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.21 (s, 1H), 7.59 (s, 1H), 7.42 – 6.99 (m, 6H), 6.69 (s, *J* = 33.0 Hz, 2H), 5.69 (s, 1H), 2.28 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d_6): δ 164.1, 148.4, 139.2, 138.2, 133.7, 129.3, 127.8, 127.3, 117.5, 115.5, 114.8, 66.8, 21.2.

2-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1H)-one[9]



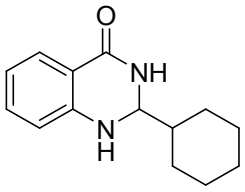
White solid; **mp**: 178- 179 °C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3426, 3298, 3180, 3025, 2925, 2831, 1657, 1610, 1505, 1434, 1383, 1298, 1247, 1167, 1118, 1028.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.18 (s, 1H), 7.60 (d, *J* = 7.0 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 6.7 Hz, 1H), 7.01 (s, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 6.7 Hz, 1H), 5.70 (s, 1H), 3.74 (s, 3H).

^{13} C NMR (125 MHz, DMSO-*d6*): δ 163.7, 159.4, 148.0, 133.5, 133.2, 128.2, 127.3, 117.1, 115.0 , 114.4, 113.6, 66.3, 55.2.

2- cyclohexyl-2,3- dihydroquinazolin-4(1H)-one[10]



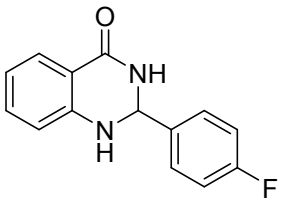
White solid ; **mp**: 202-205°C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3366, 3169. 3060, 2927, 2851, 1647, 1499, 1434, 1389, 1309, 1254, 1151, 1027.

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.88 (s, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 8 Hz, 1H), 6.60 (t, *J* = 7.0 Hz, 2H), 4.44 (s, 1H), 1.70-1.58 (m, 6H), 1.12 (d, *J* = 7 Hz, 5H).

^{13} C NMR (125 MHz, DMSO-d_6): δ 164.2, 148.8, 133.5, 127.7, 116.9, 115.3, 114.5, 69.0, 43.3, 27.5, 27.1, 26.4, 26.1, 26.0.

2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1H)-one[10]



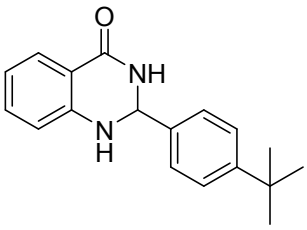
White solid ; **mp** 200-203 ^{o}C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3452, 3299, 3179, 3061, 2930, 1658, 1610, 1505, 1436, 1386, 1294, 1234, 1157.

^{1}H-NMR (500 MHz, DMSO-d_6): δ 8.27 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.53 (dd, *J* = 8.5, 6.0 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.10 (s, 1H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.68 (t, *J* = 7.5 Hz, 1H), 5.77 (s, 1H).

^{13} C NMR (125 MHz, DMSO-d_6): δ 164.0, 163.5 (d, *J*=242.6 Hz), 161.6 (d, *J*=242.6 Hz), 148.3, 138.3, 135.1, 133.8, 129.5 (d, *J*= 8.4 Hz), 127.8, 117.7, 115.6 (d, *J*=21.3 Hz), 115.4 (d, *J*=21.3 Hz), 114.9, 66.4.

***2-(4-tert-butryl)phenyl-2-3-dihydroquinazolin-4(1H)-one*[12]**



White solid; **mp** 181- 183 ^{o}C

FT-IR (KBr, 4000 – 400 cm^{-1}): 3271, 3192, 3068, 2959, 1915, 1655, 1612, 1515, 1442, 1387, 1295, 1158, 1021.

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.22 (s, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.42 (s, 4H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.06 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.67 (t, *J* = 7.2 Hz, 1H), 5.71 (s, 1H), 1.27 (s, 9H).

^{13} C NMR (125 MHz, DMSO-d_6): δ 164.1, 151.5, 148.4, 139.1, 133.7, 127.8, 127.2, 125.6, 117.5, 115.4, 114.8, 66.9, 34.8, 31.6.

Section S5. ^{1}H, ^{13}C NMR spectroscopy

NMR spectra of benzo[4,5]imidazo[1,2-a]pyrimidines

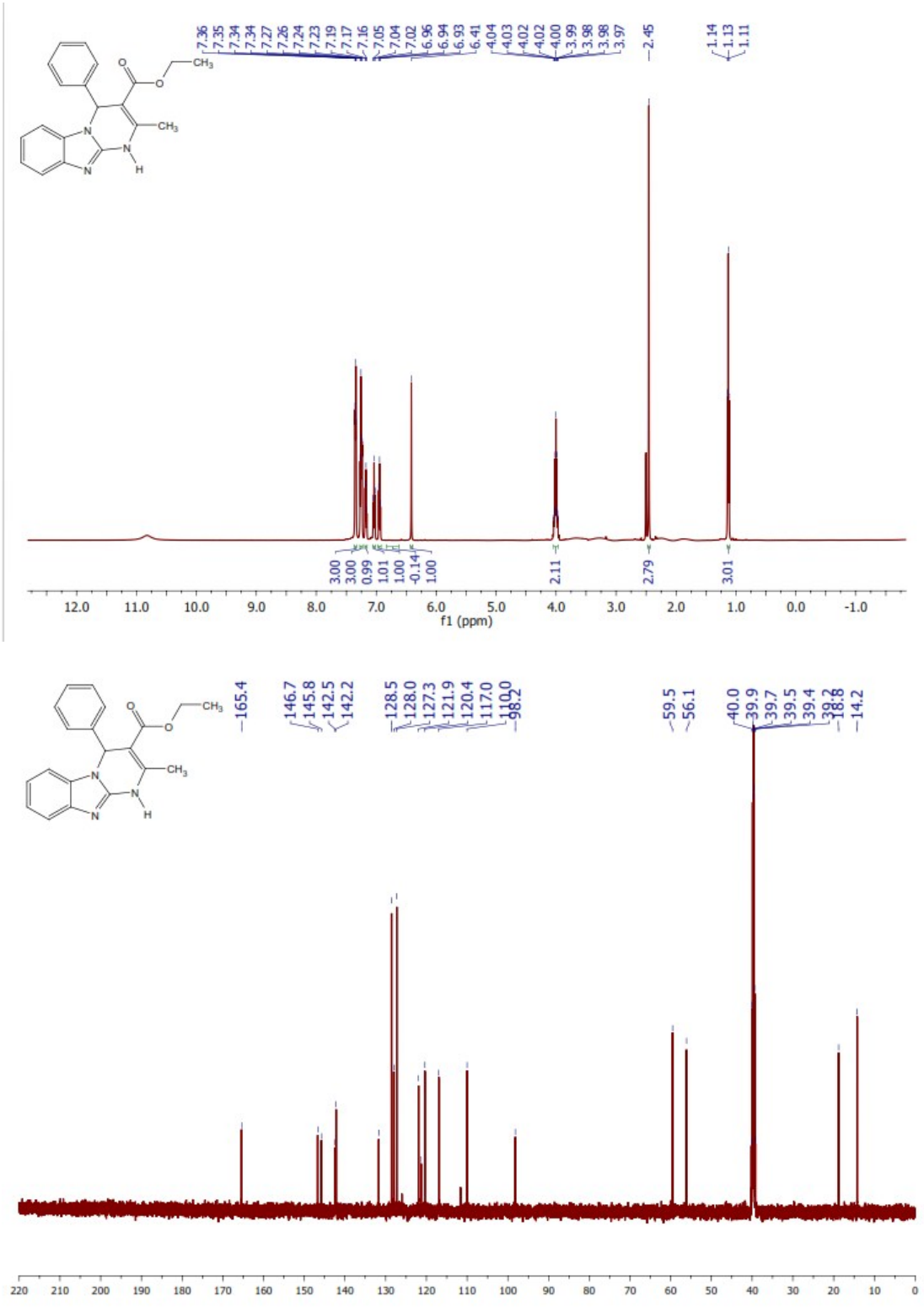


Figure 5. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 2-methyl-4-phenyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

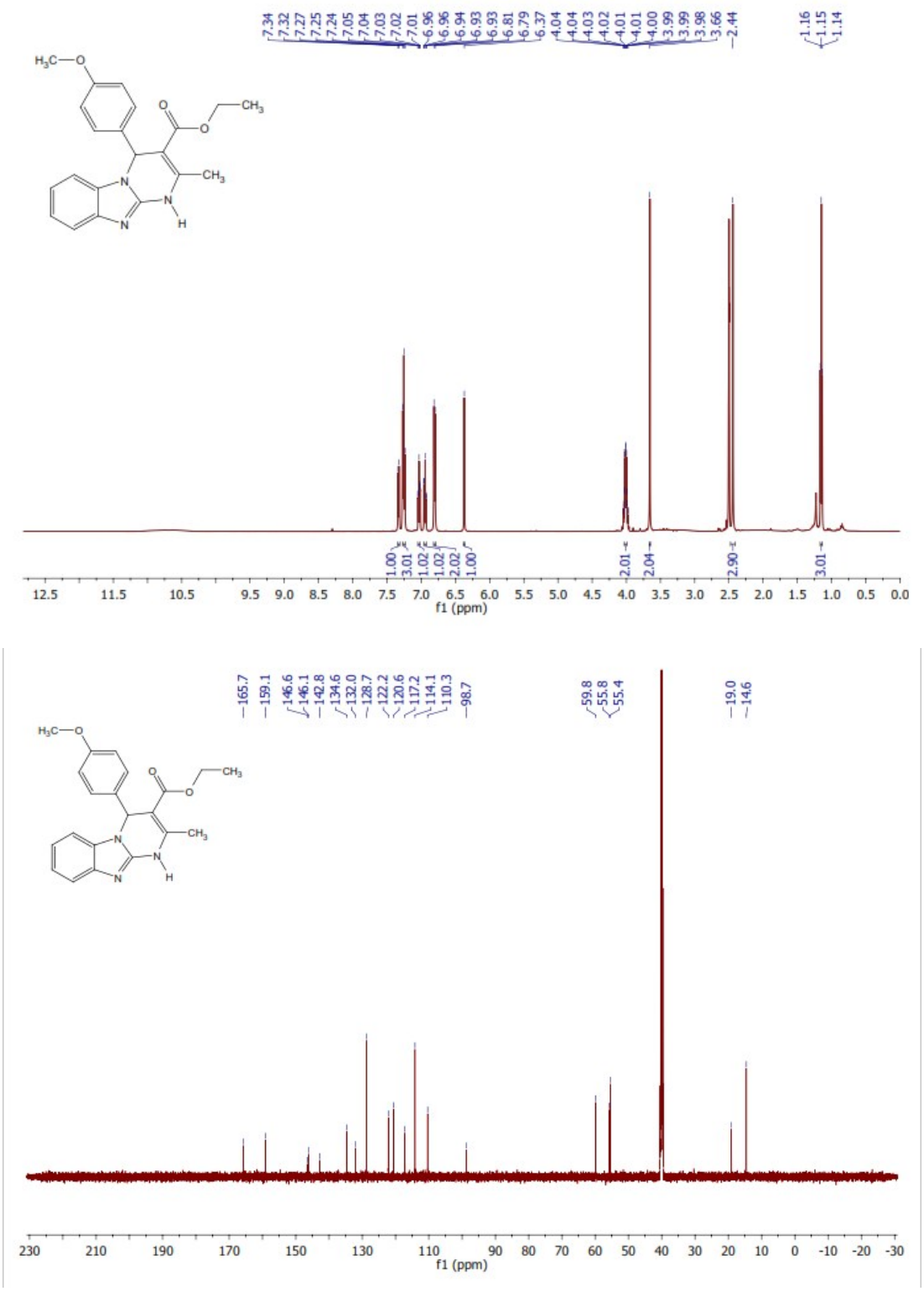


Figure 6. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

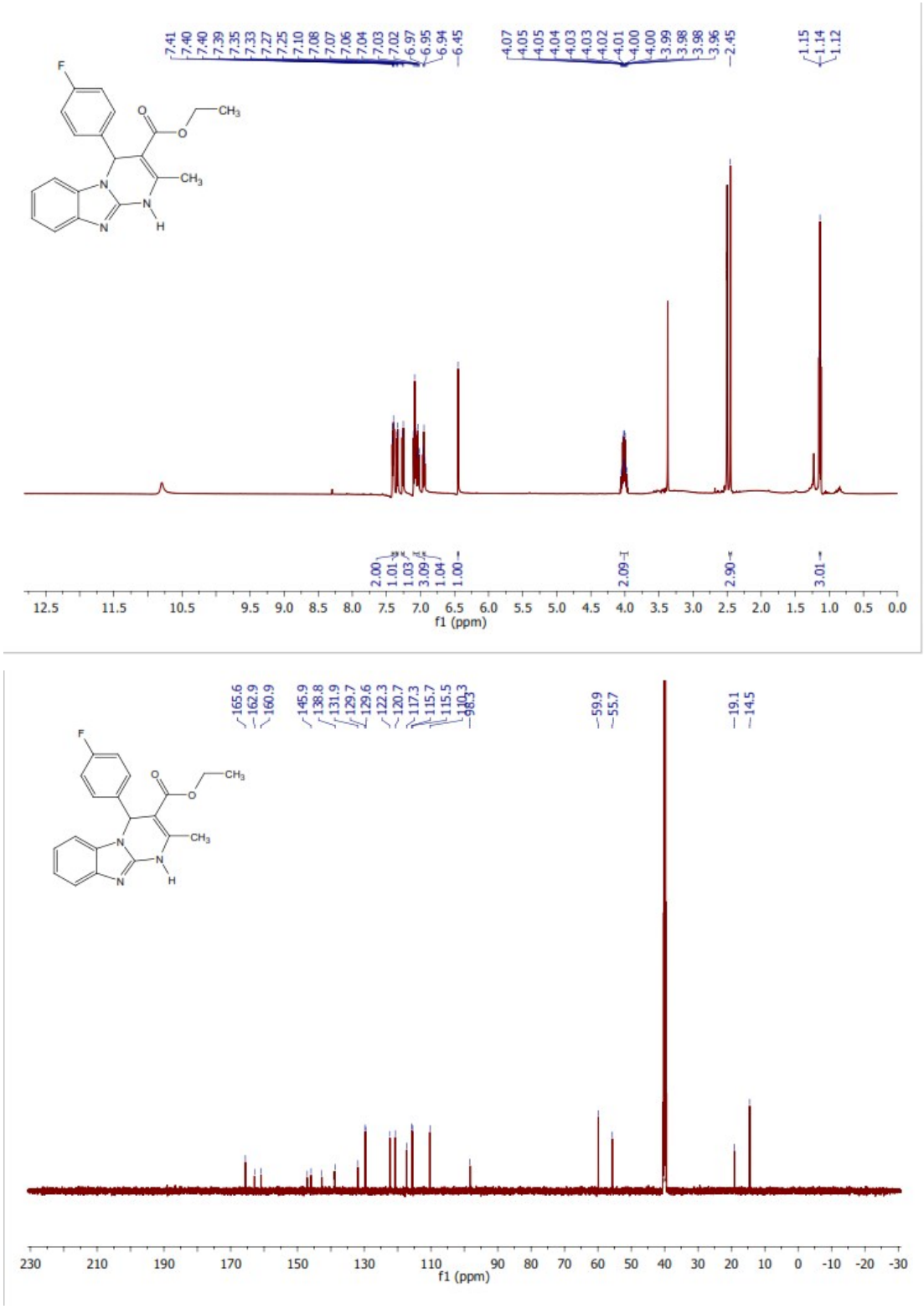


Figure 7. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(4-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

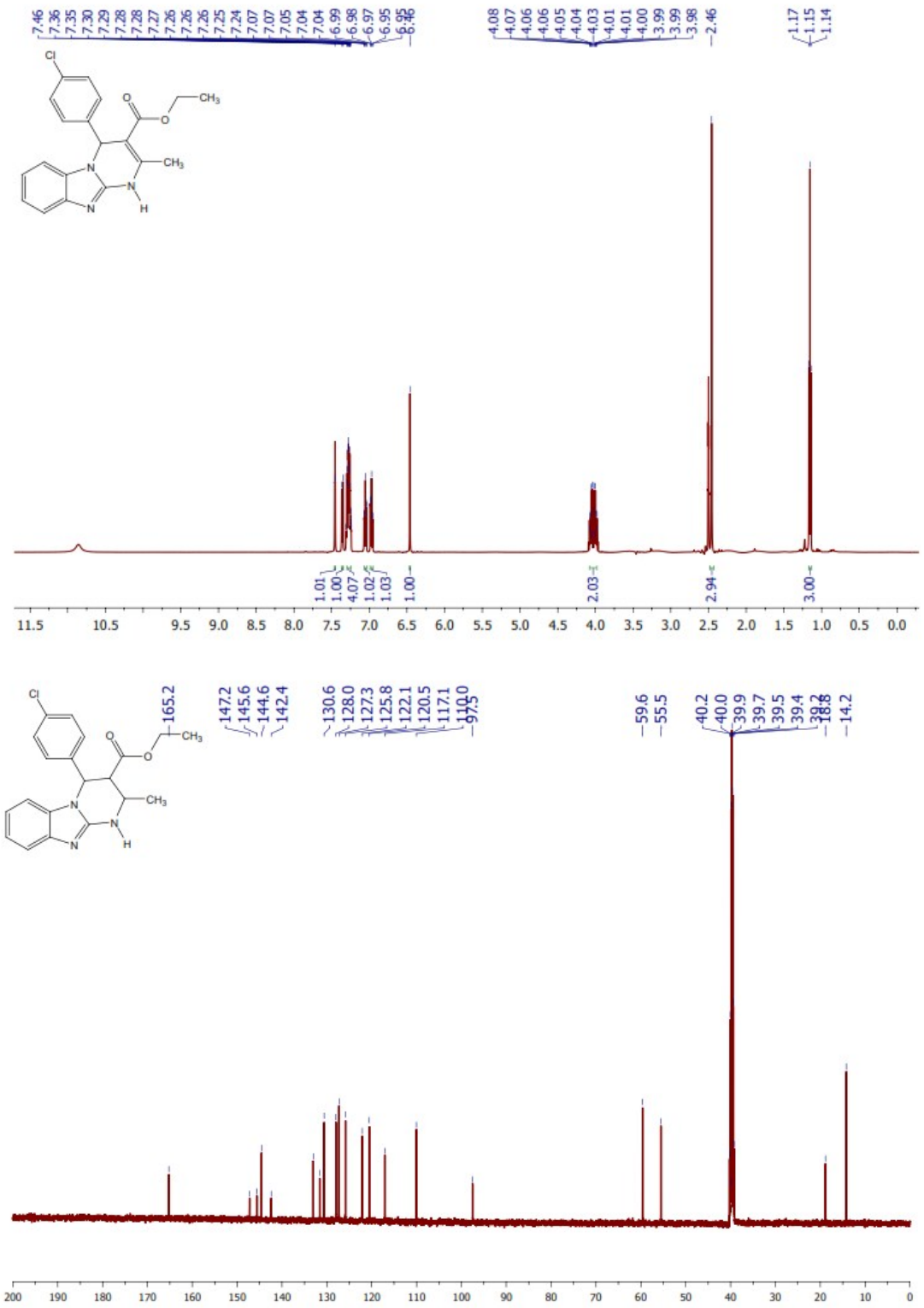


Figure 8. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(4-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

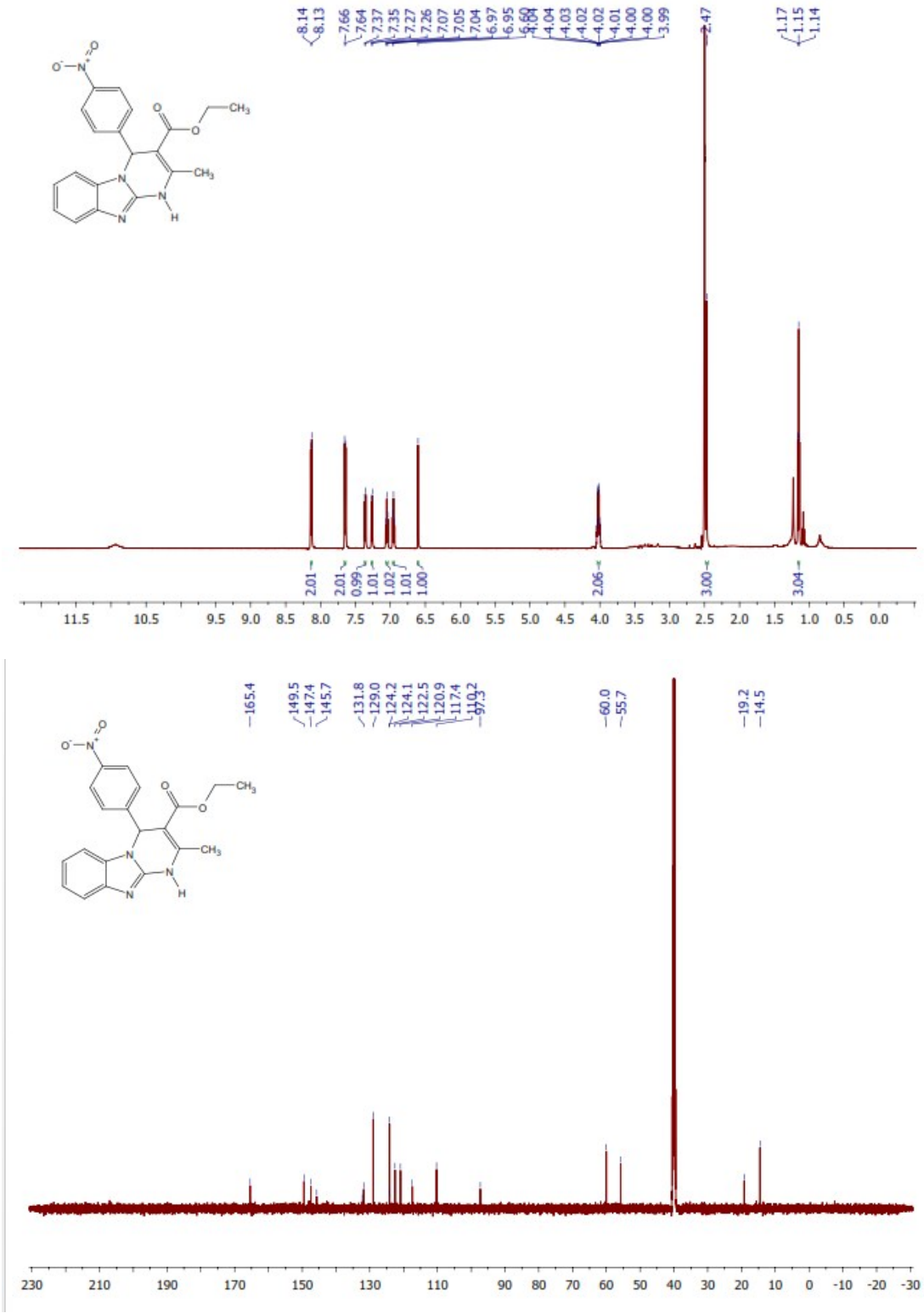


Figure 9. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 2-methyl-4-(4-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

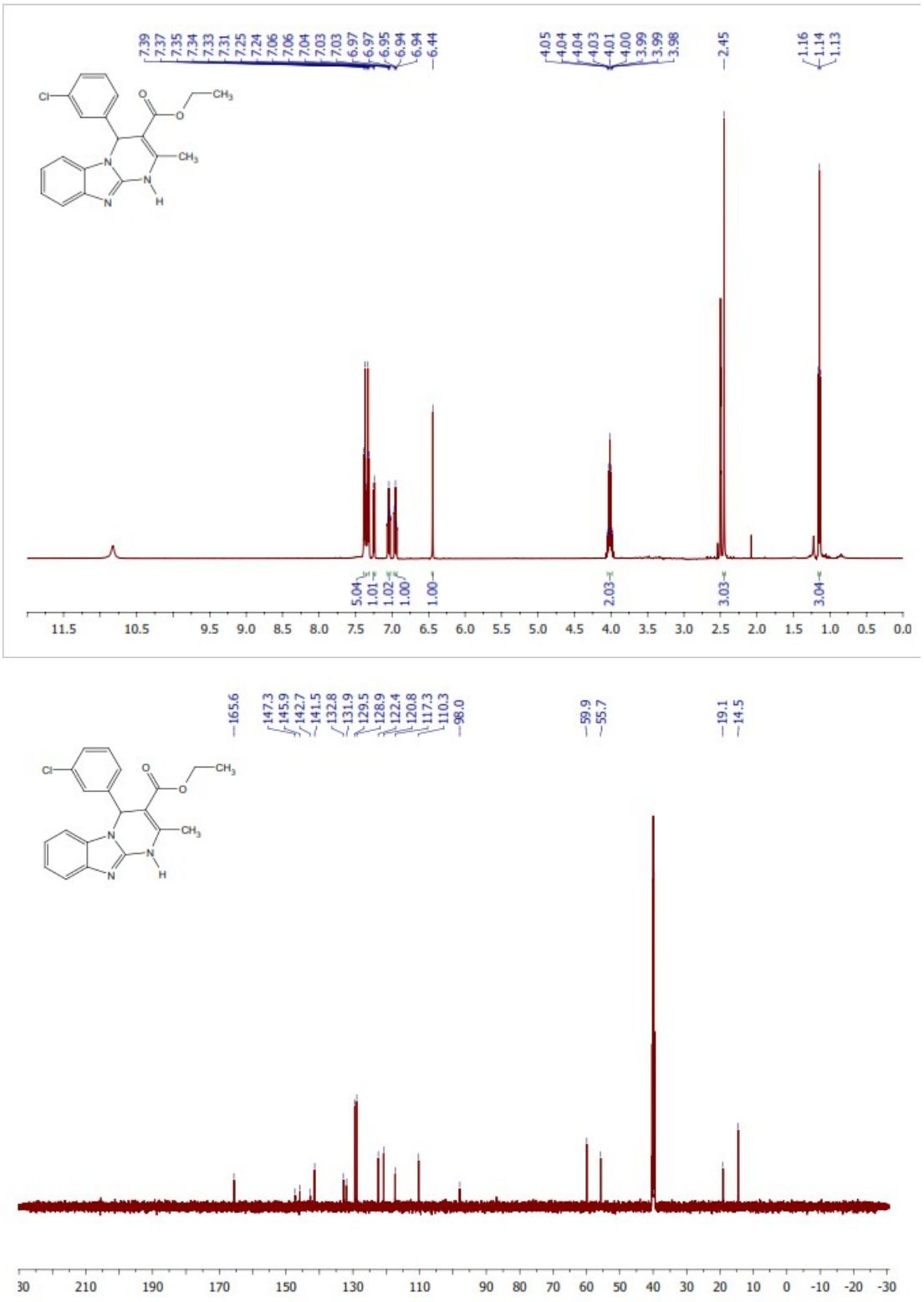


Figure 10. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(3-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

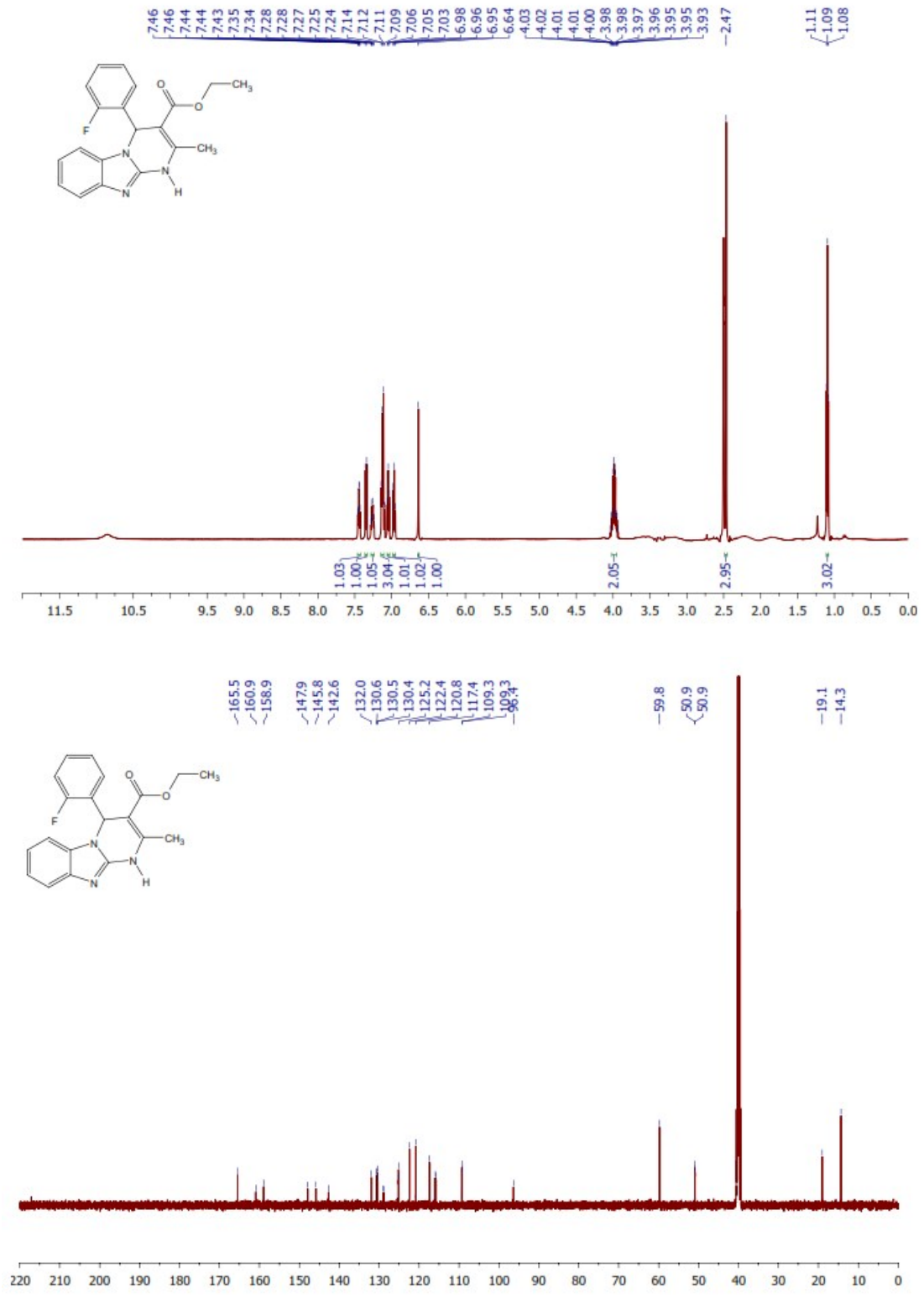


Figure 11. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(2-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

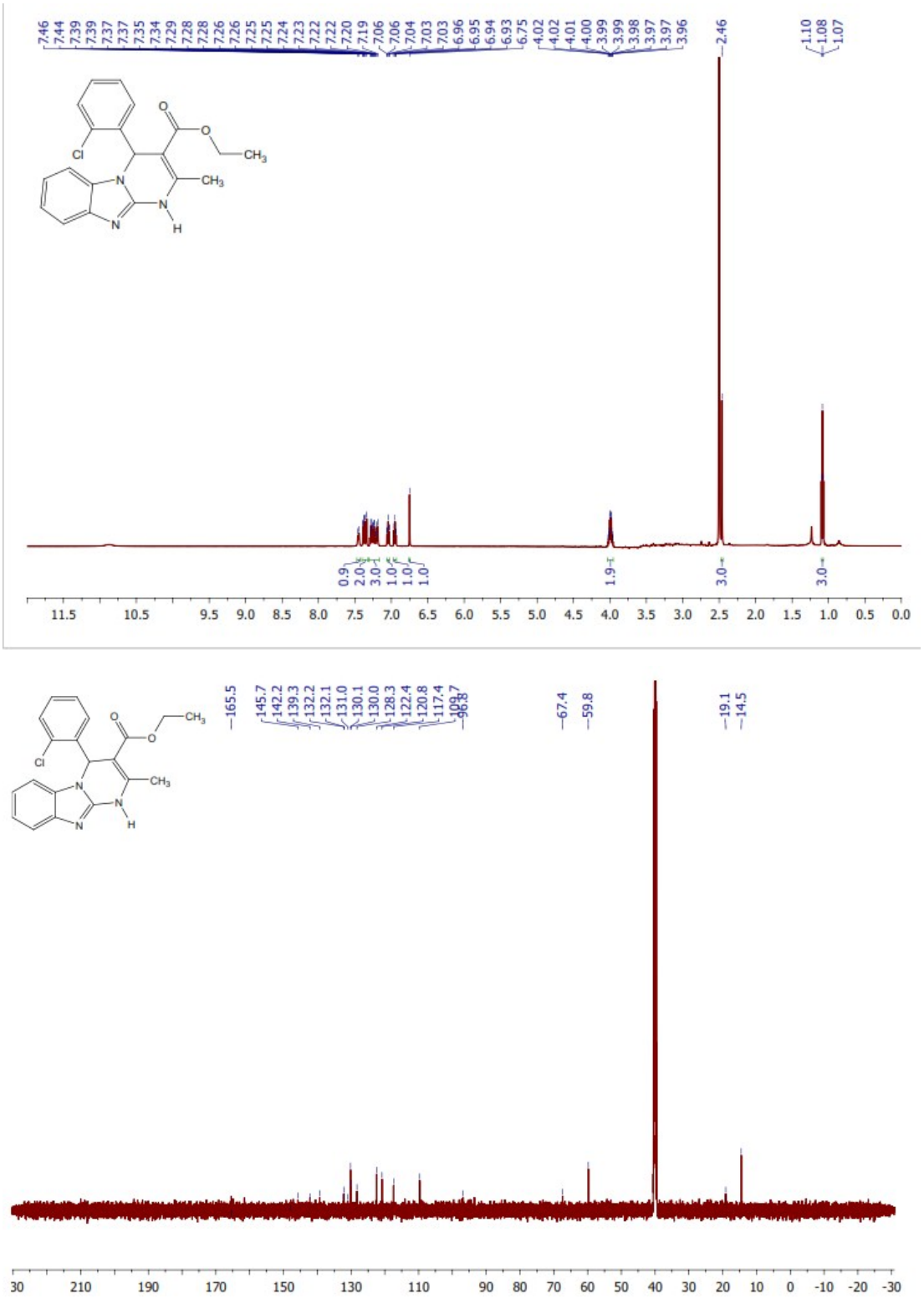


Figure 12. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(2-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

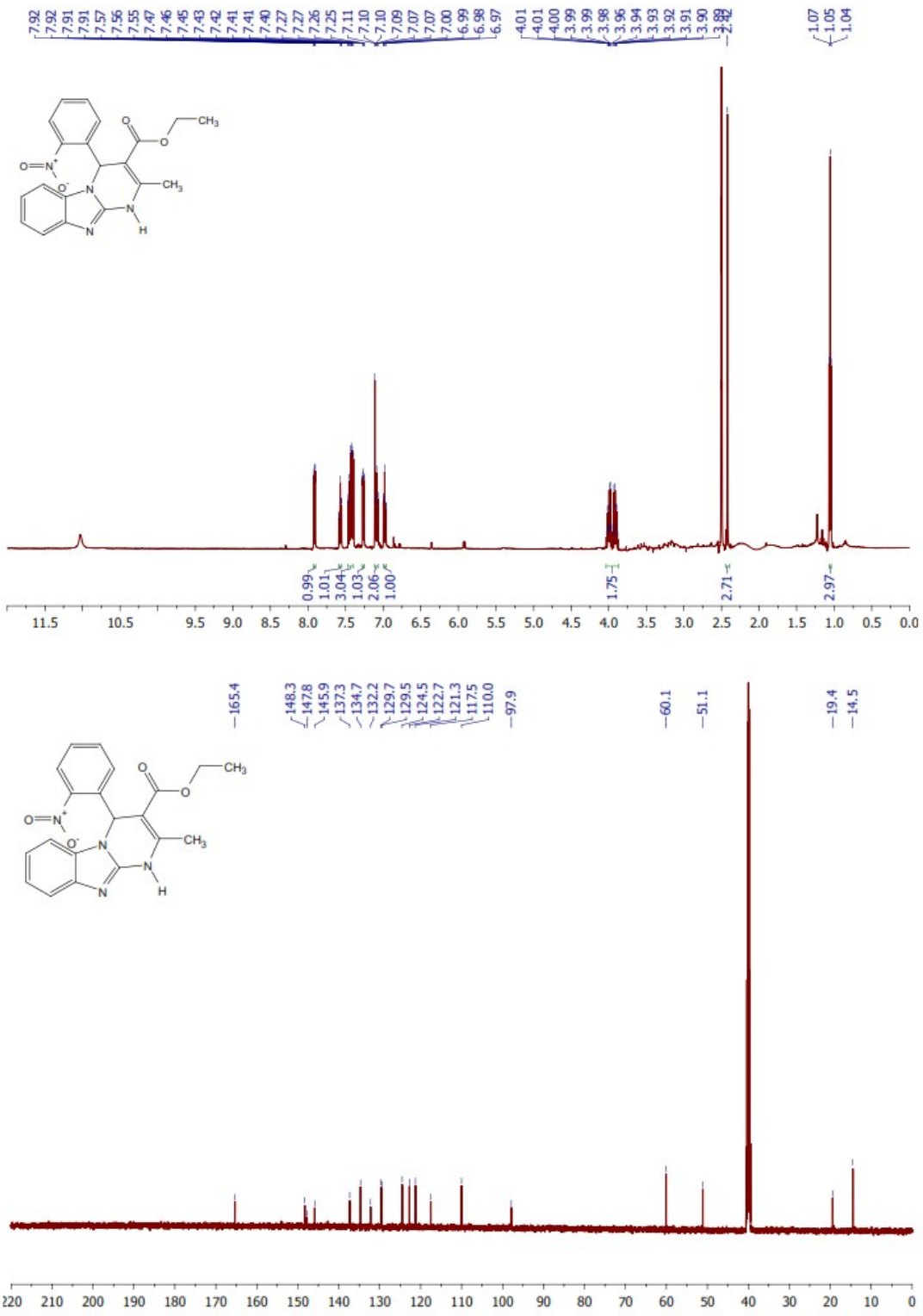


Figure 13. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 2-methyl-4-(2-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

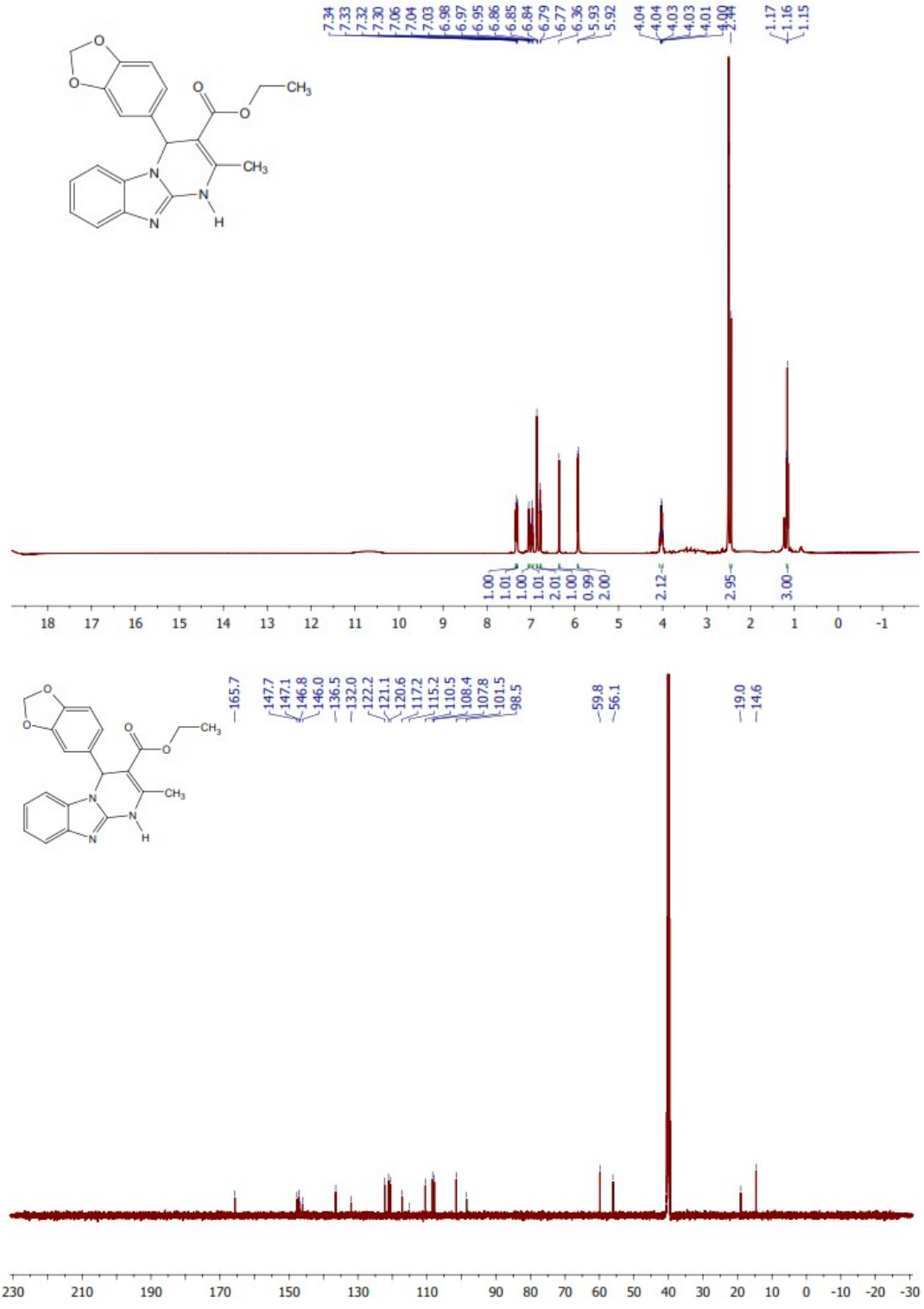


Figure 14. ^{1}H (top) and ^{13}C (bottom) NMR spetra of ethyl 4-(benzo[d][1,3]dioxol-5-yl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidine-3-carboxylate

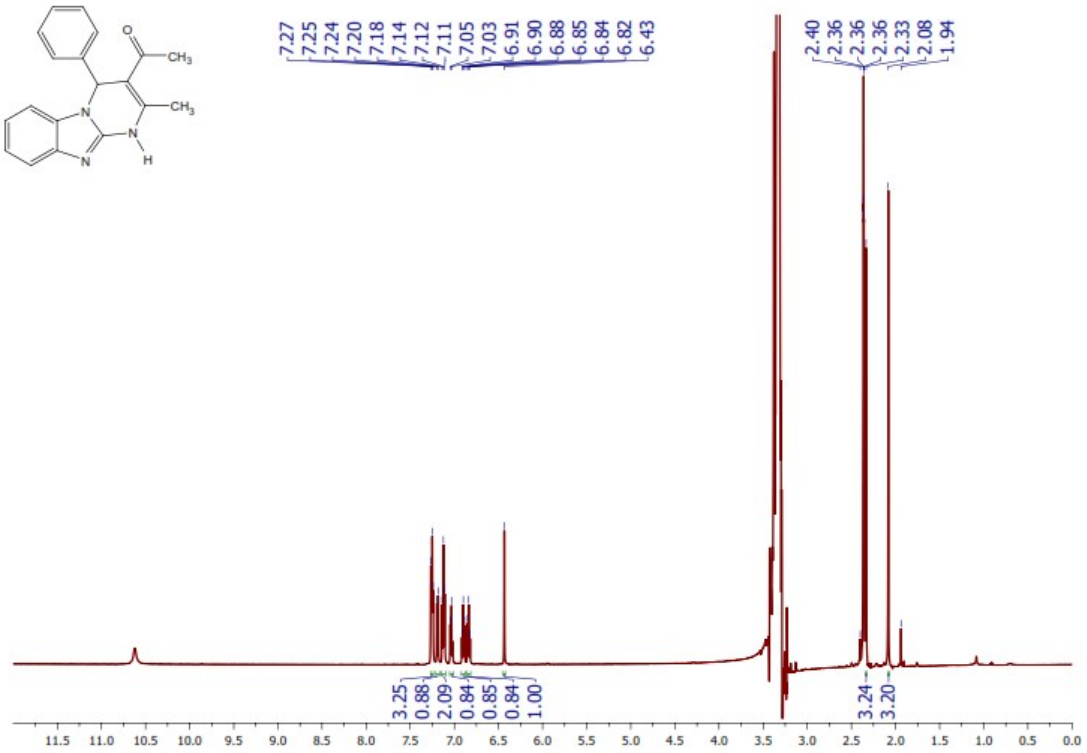


Figure 15. ^{1}H NMR spetru, of 1-(2-methyl-4-phenyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

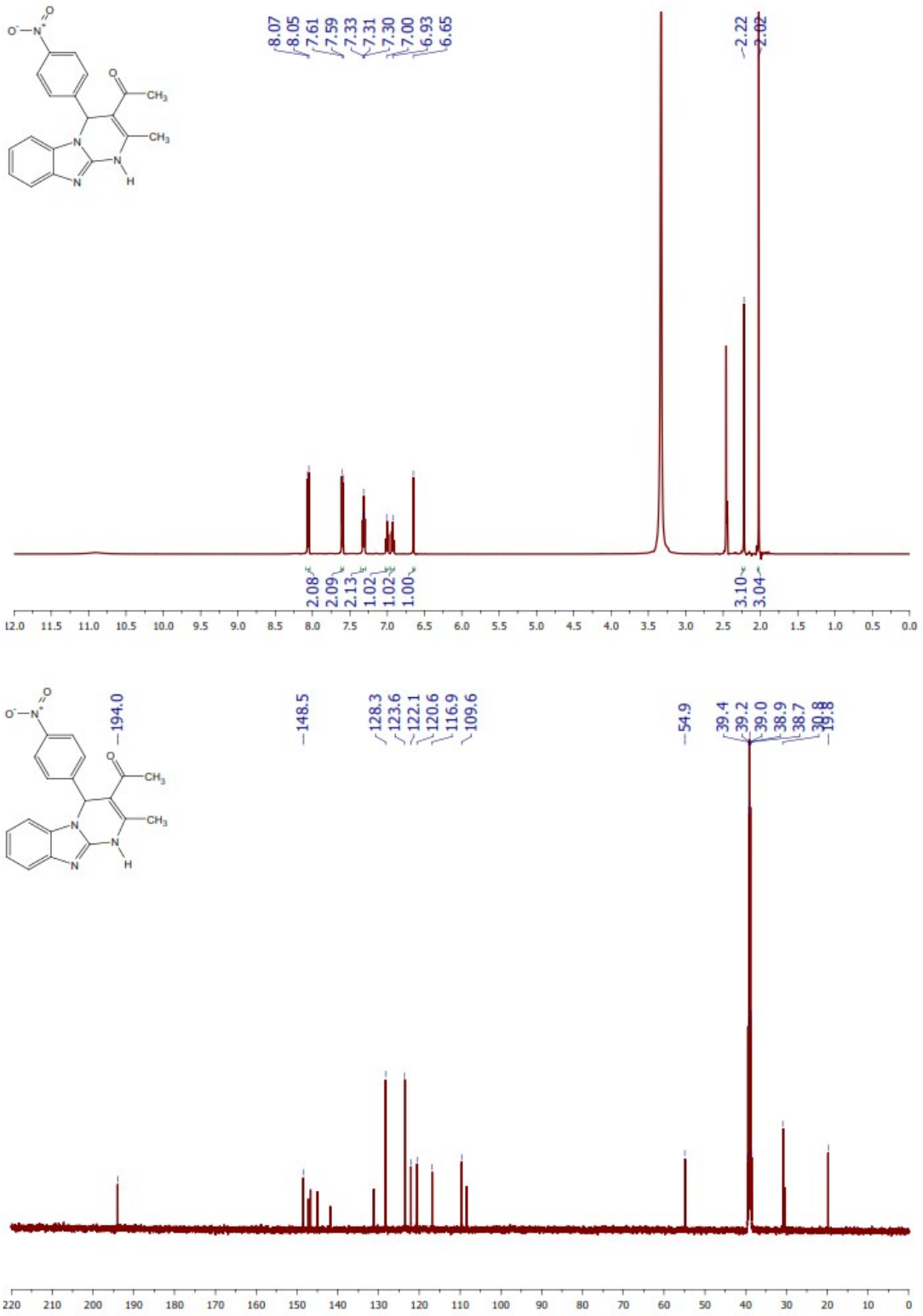


Figure 16. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(2-methyl-4-(4-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

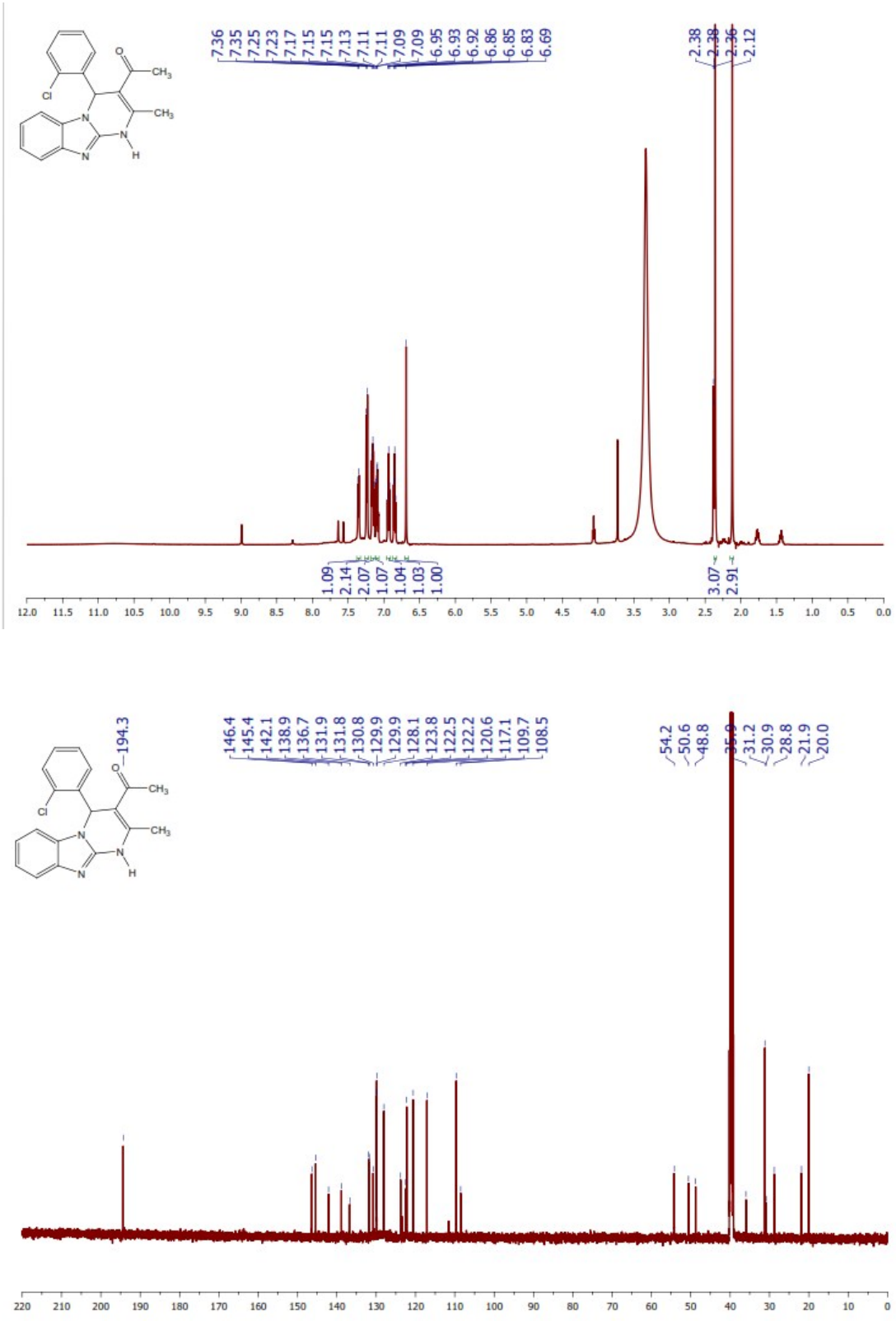


Figure 17. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(2-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

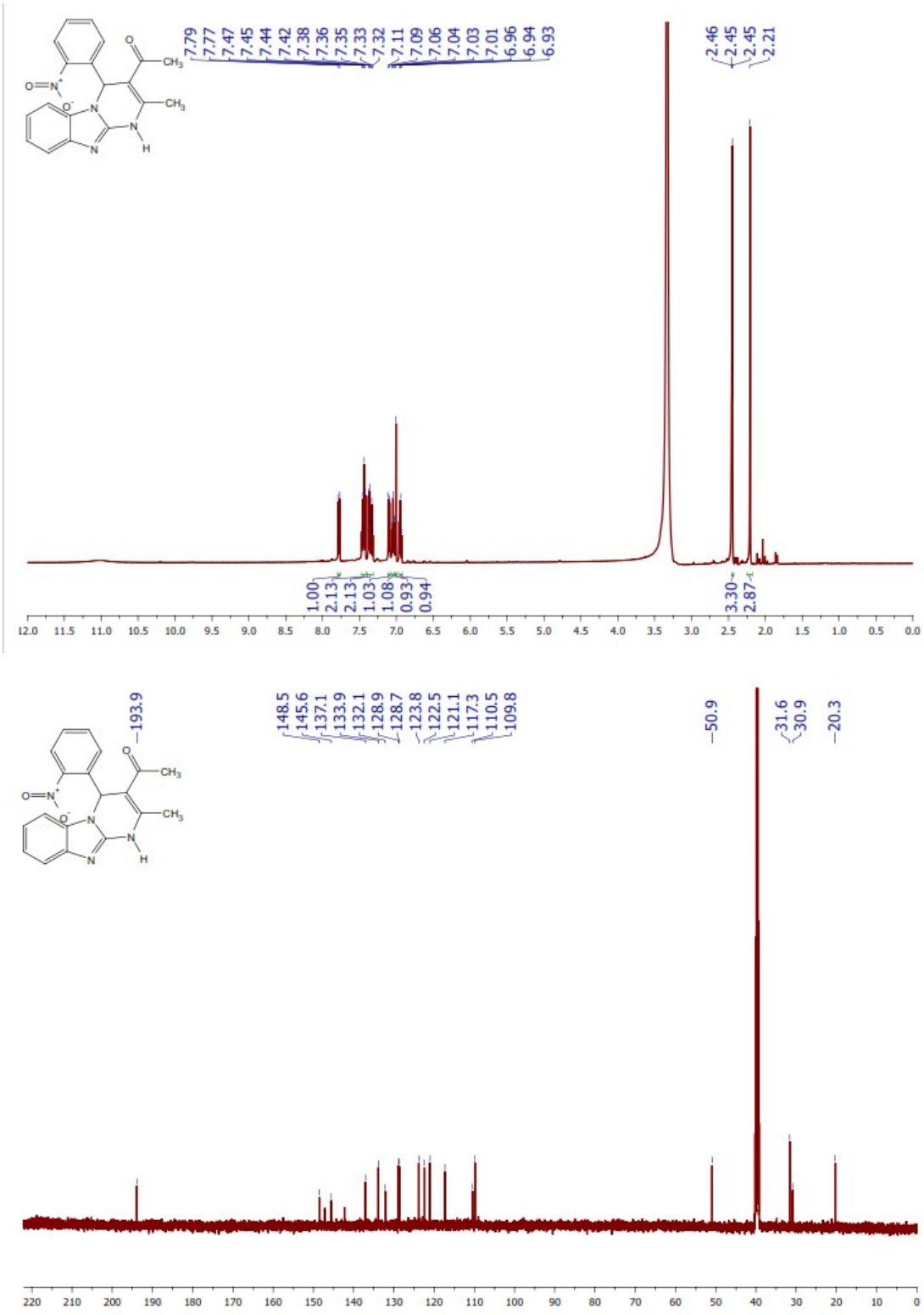


Figure 18. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(2-methyl-4-(2-nitrophenyl)-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

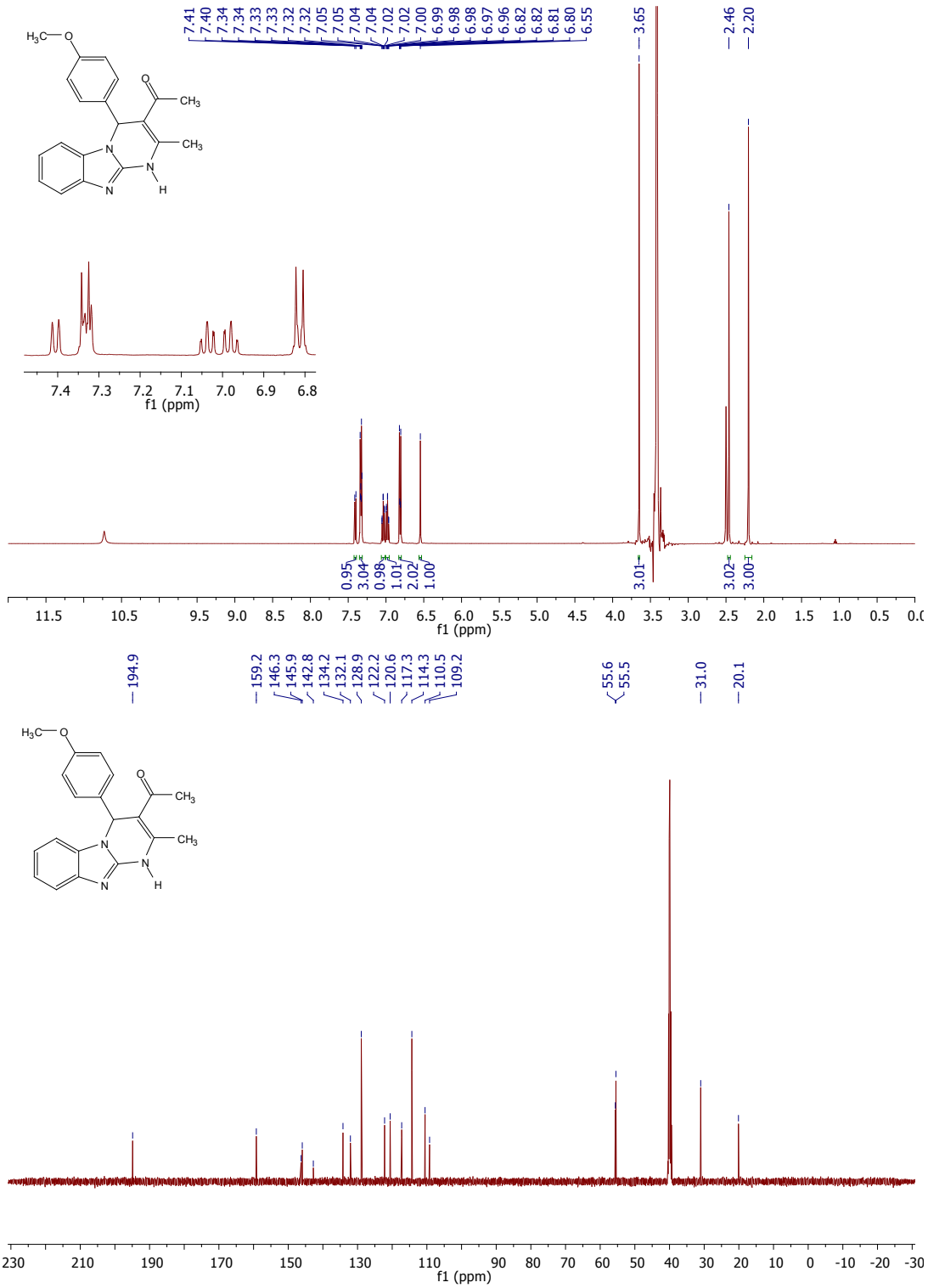


Figure 19. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(4-methoxyphenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

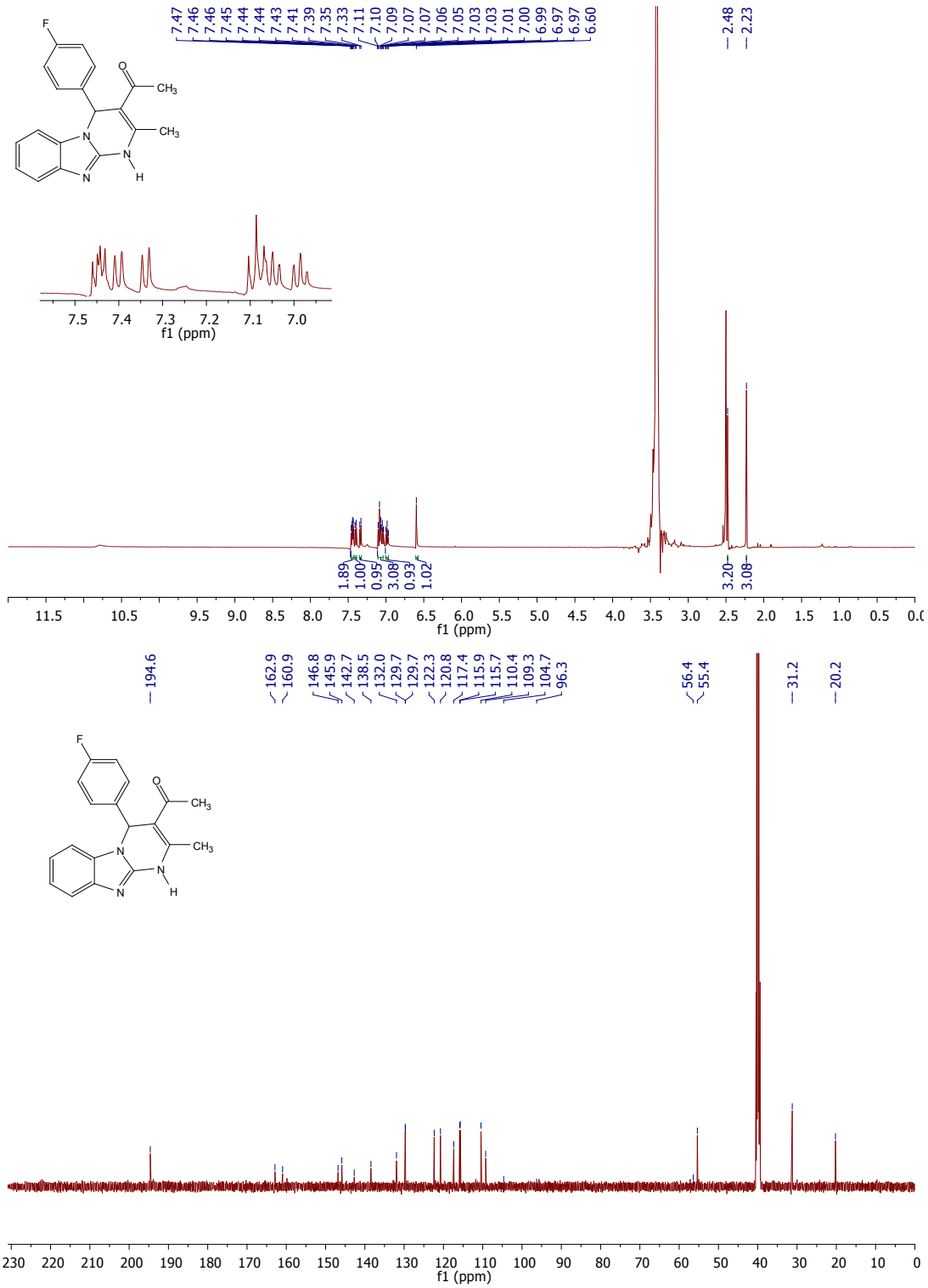


Figure 20. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(4-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

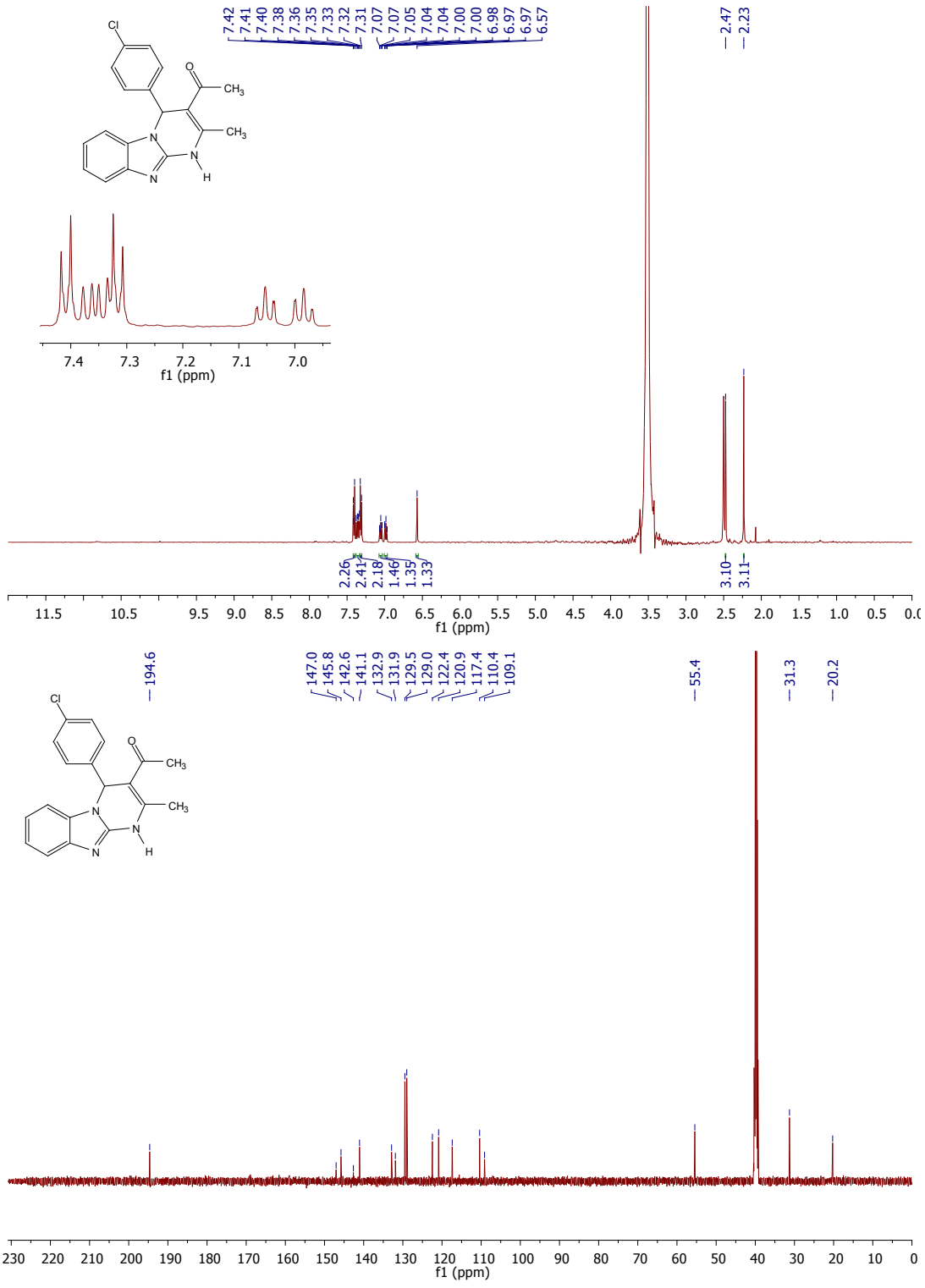


Figure 21. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(4-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

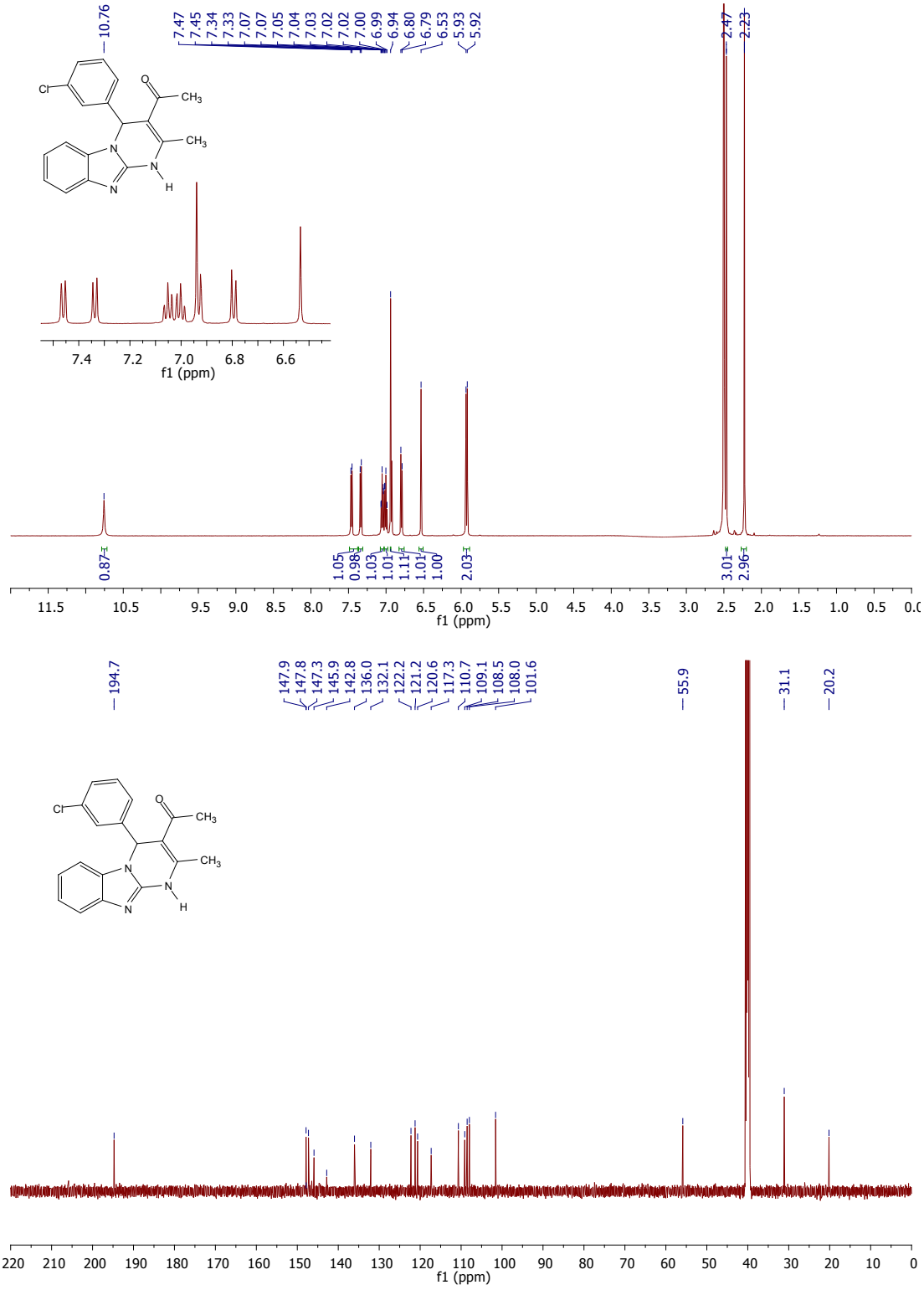


Figure 22. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(3-chlorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

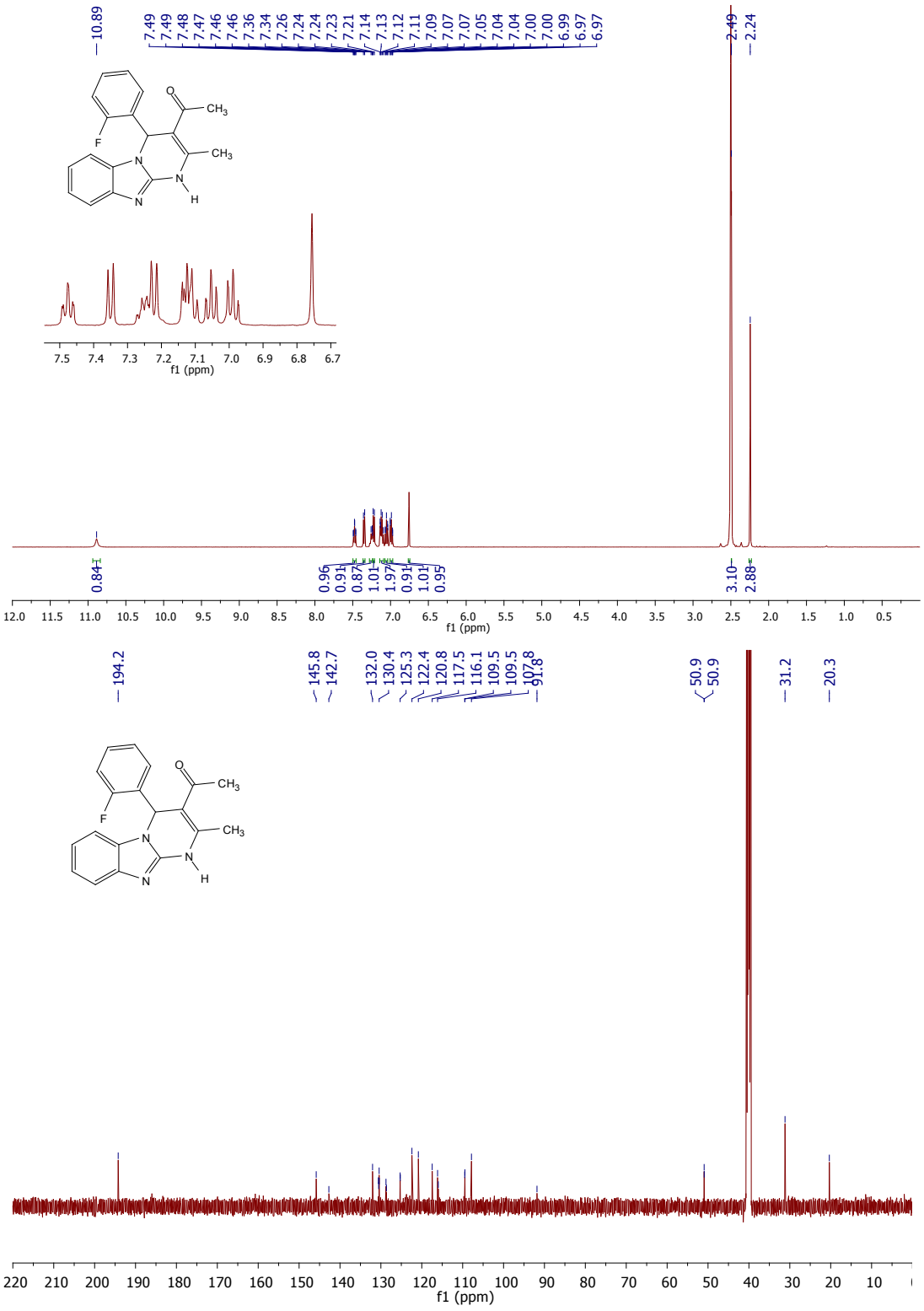


Figure 233. ^{1}H (top) and ^{13}C (bottom) NMR spetra of 1-(4-(2-fluorophenyl)-2-methyl-1,4-dihydrobenzo[4,5]imidazo[1,2-a]pyrimidin-3-yl)ethan-1-one

NMR Data of 2,3-dihydroquinazolin-4(1*H*)-one

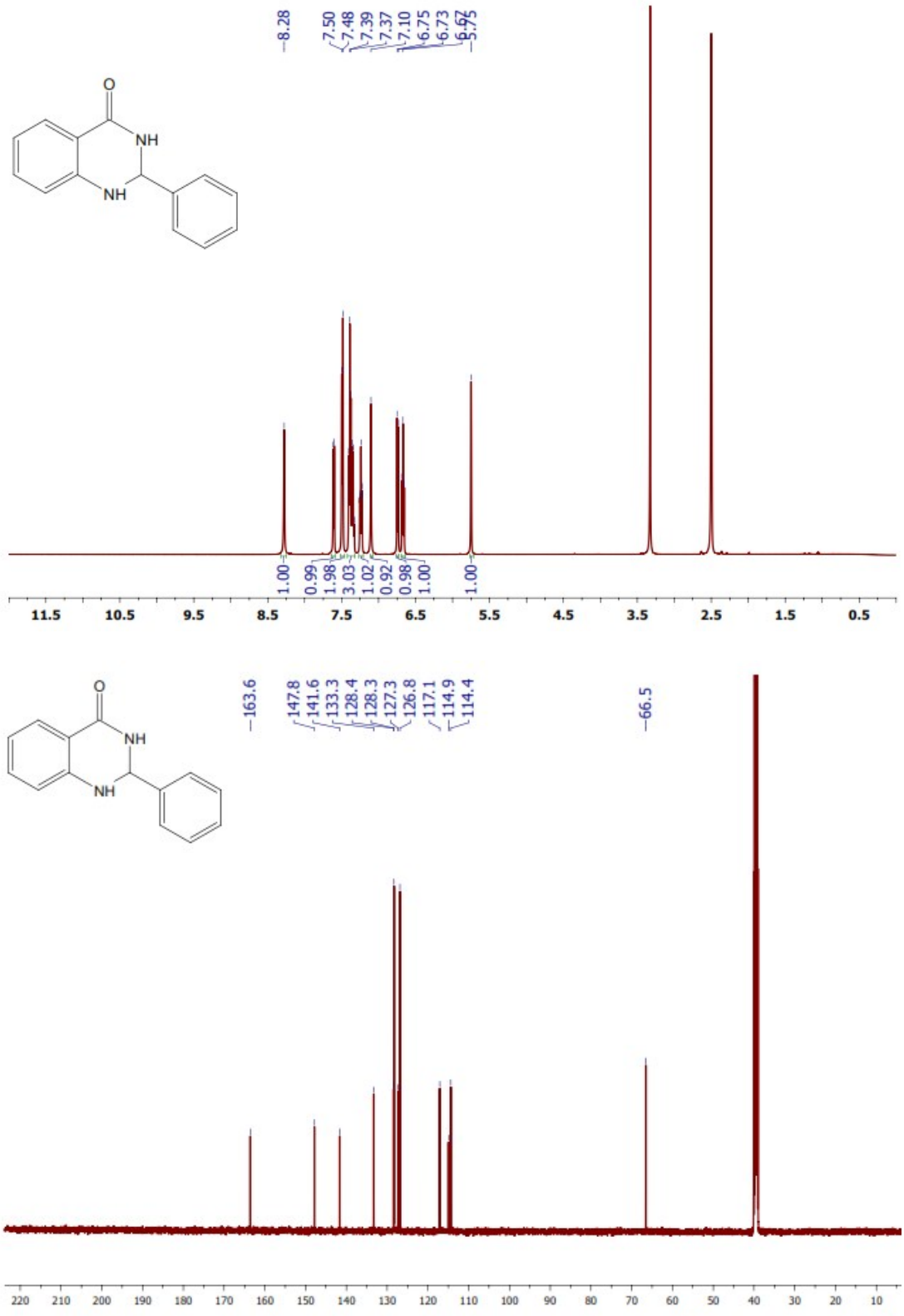


Fig. 24 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one

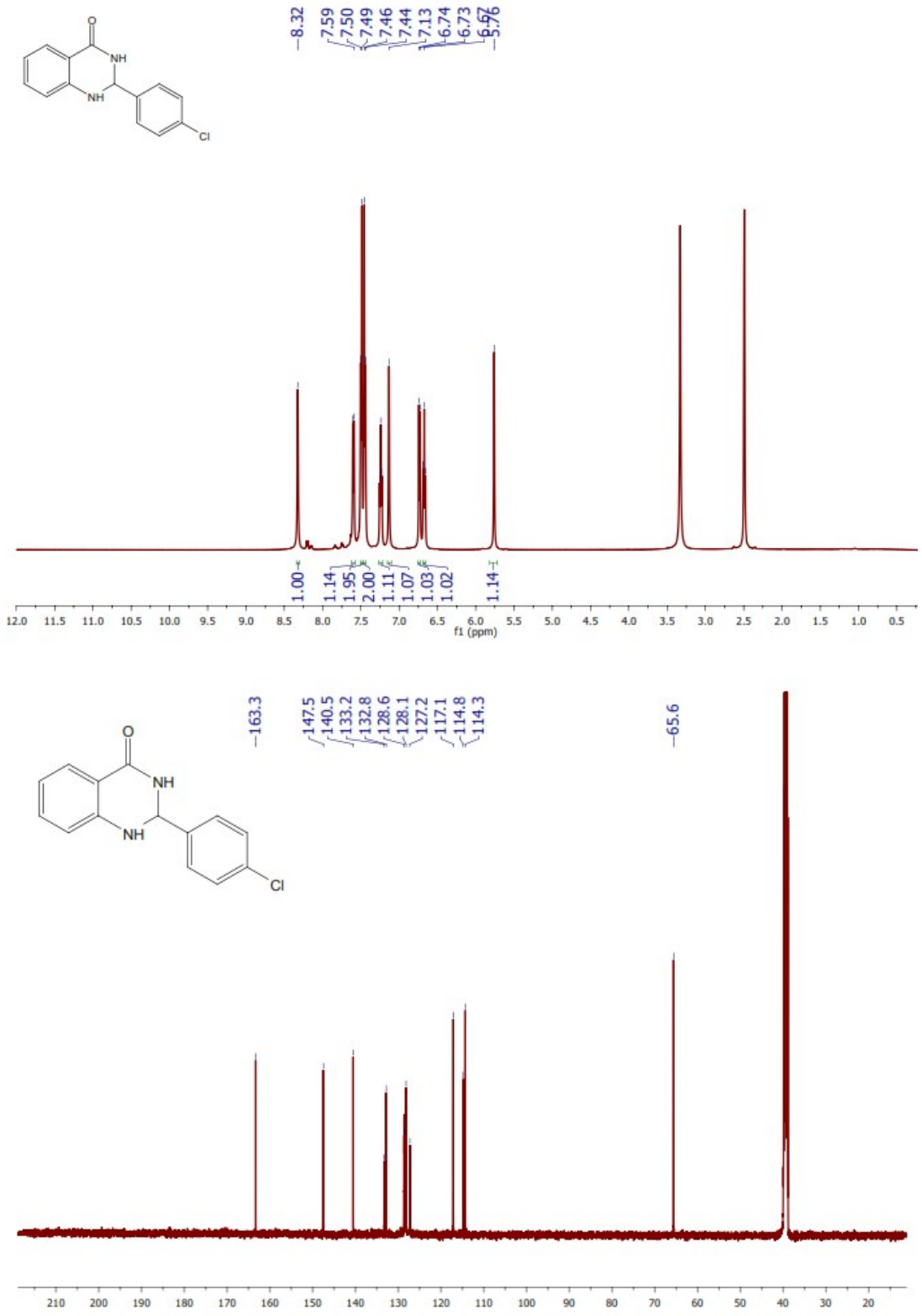


Fig. 25 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-chlorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one

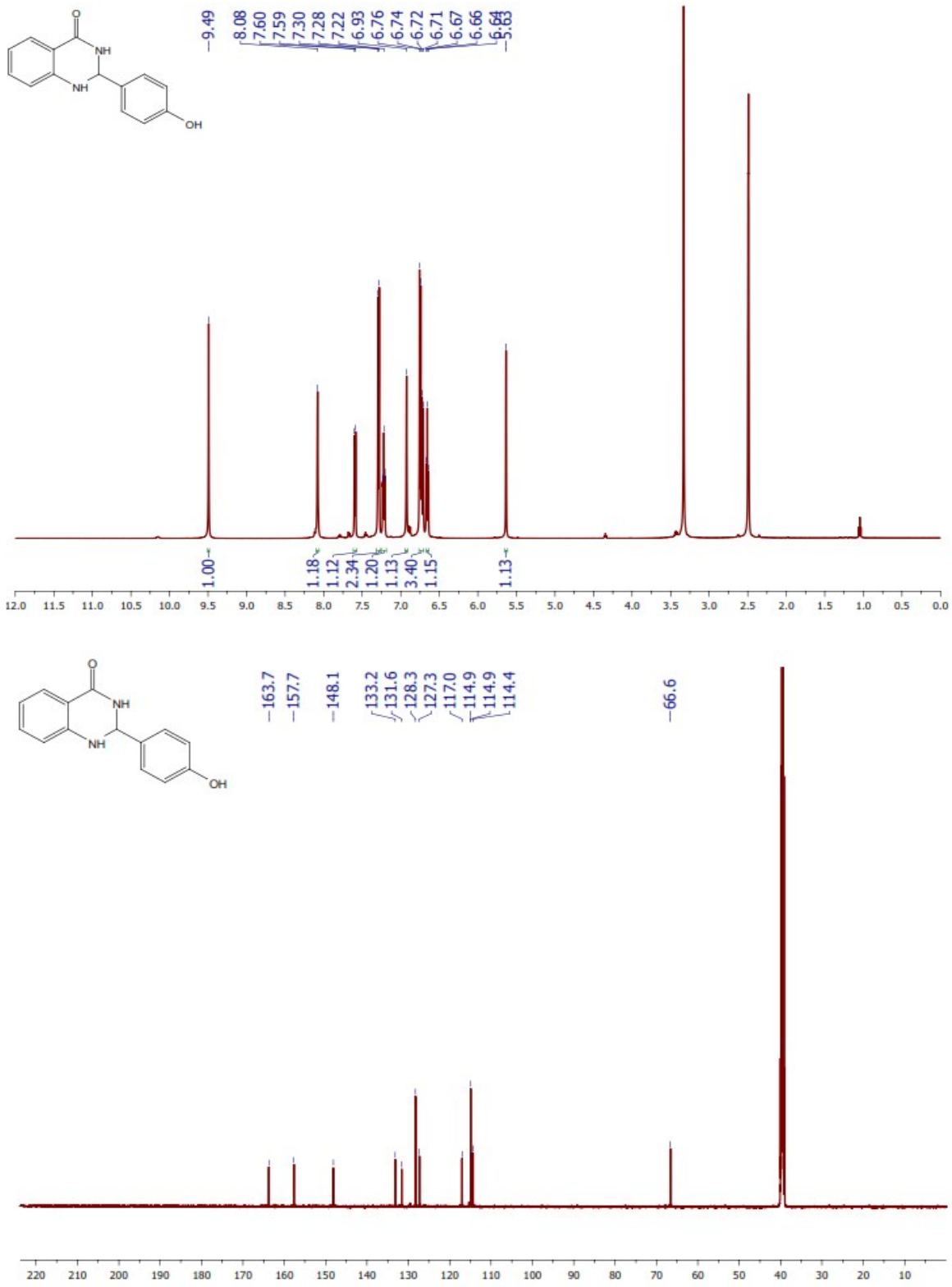


Fig. 26 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-hydroxyphenyl)-2,3-dihydroquinazolin-4(1*H*)-one

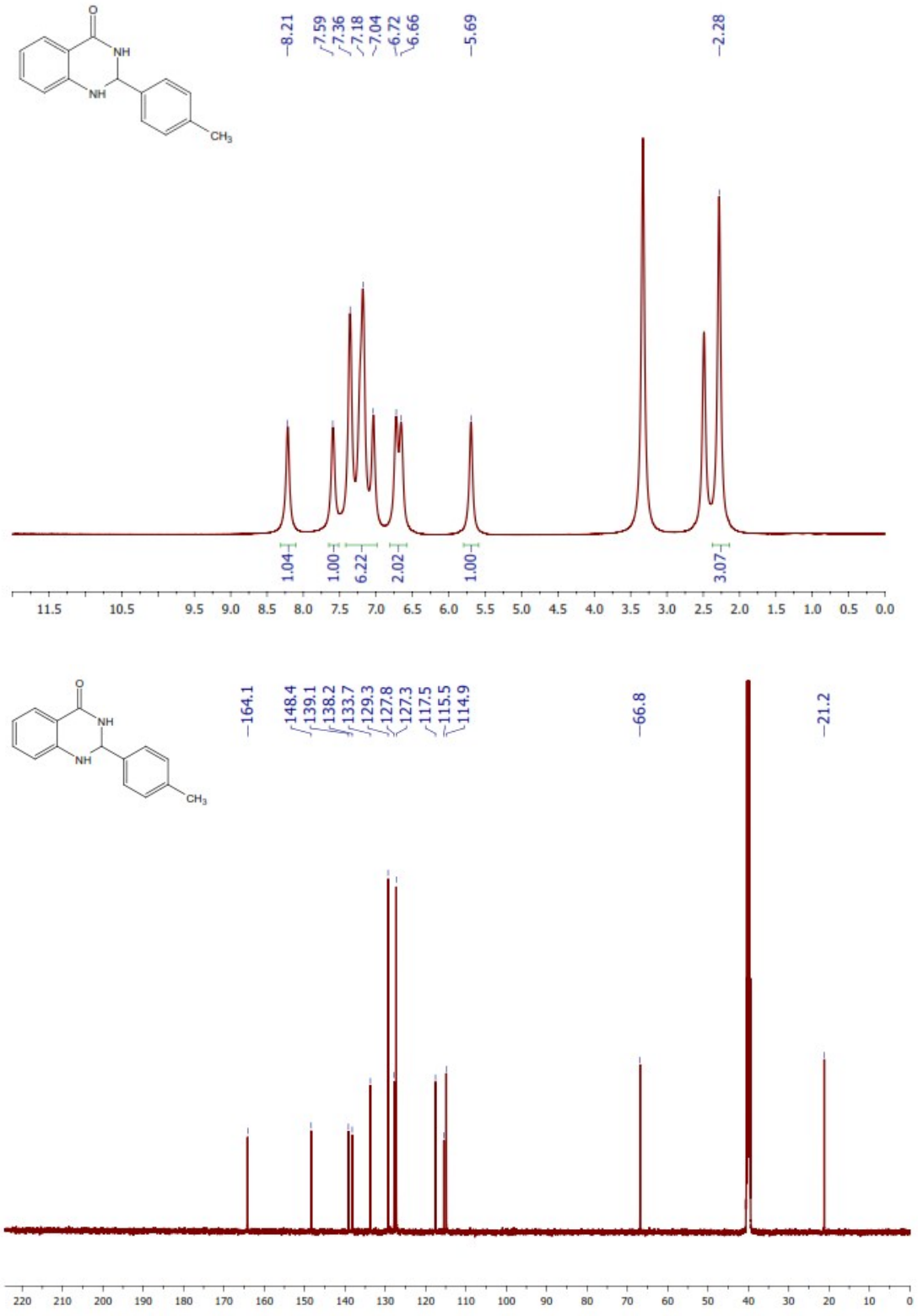


Fig. 27 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(p-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one

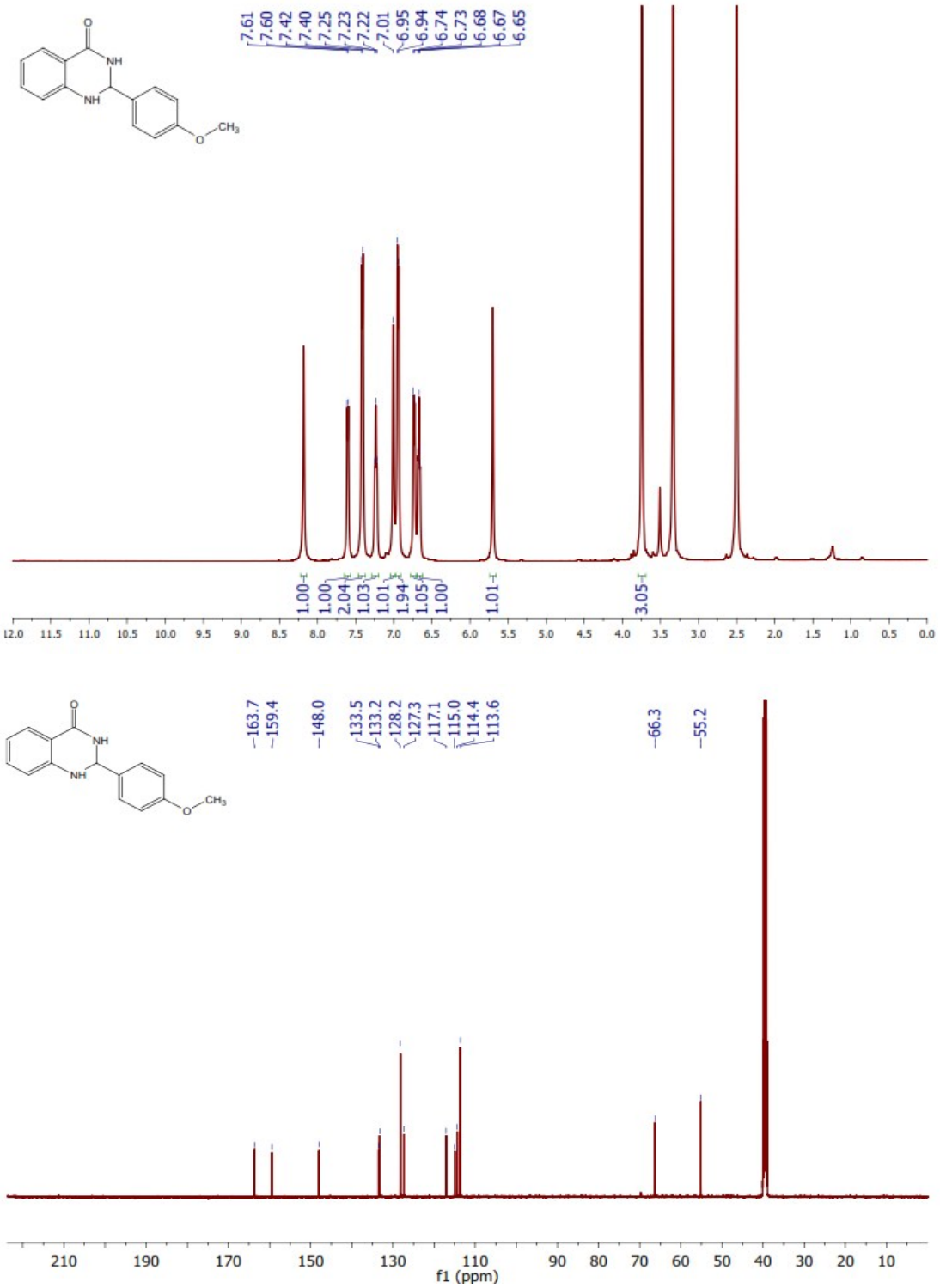


Fig. 28 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-methoxyphenyl)-2,3-dihydroquinazolin-4(1*H*)-one

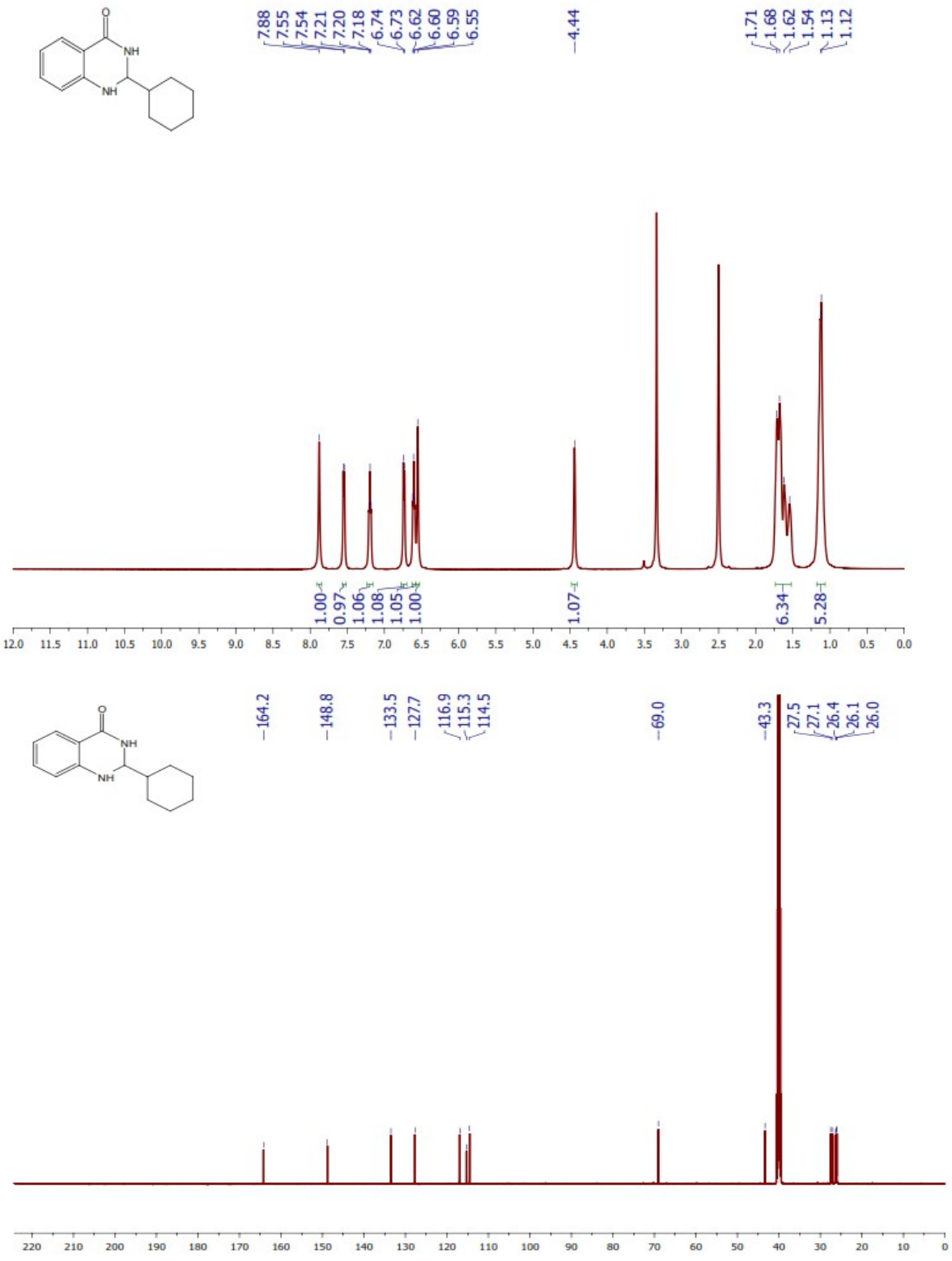


Fig. 29 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2- cyclohexyl-2,3-dihydroquinazolin-4(1*H*)-one

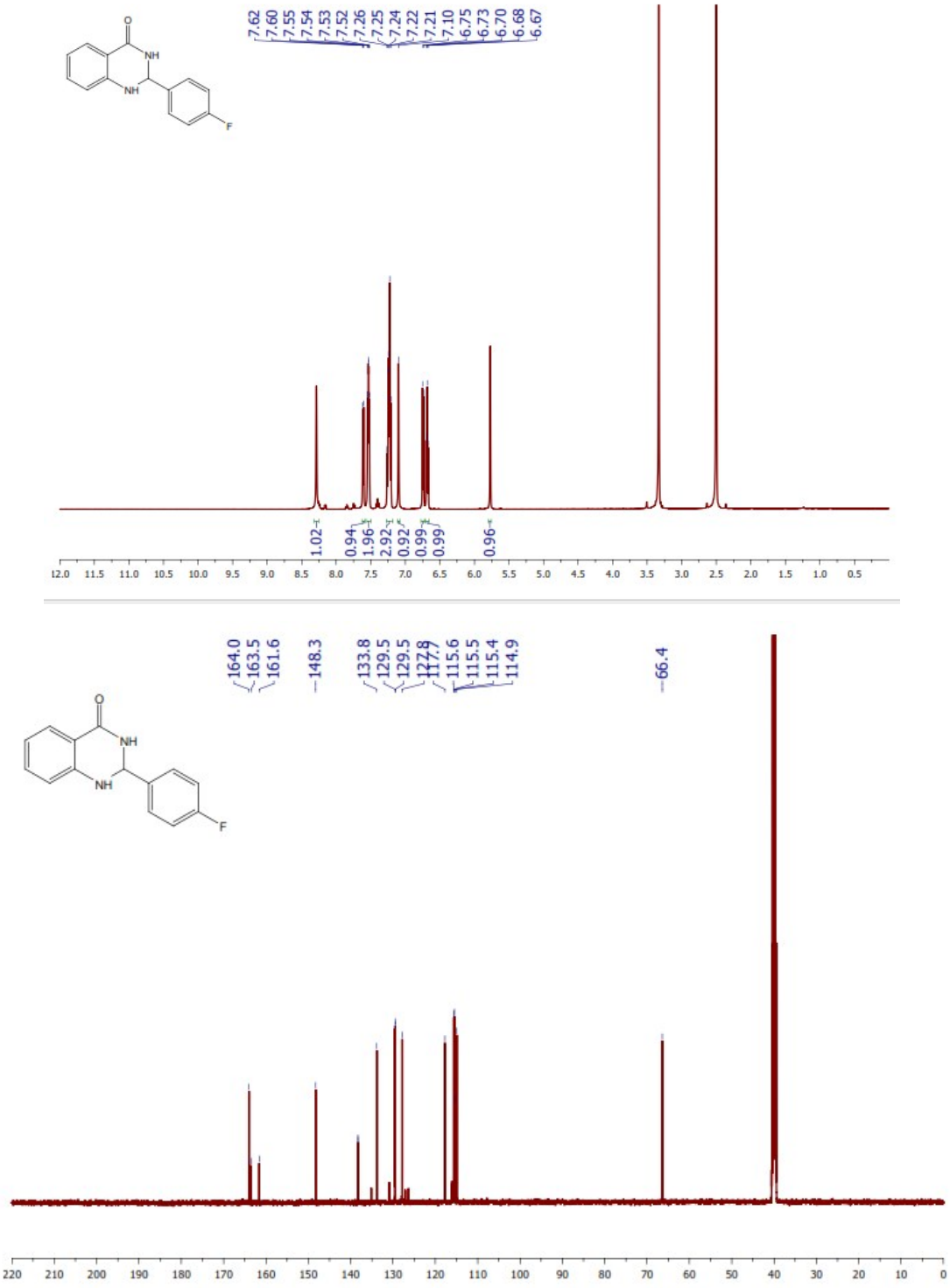


Fig. 30 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-fluorophenyl)-2,3-dihydroquinazolin-4(1*H*)-one

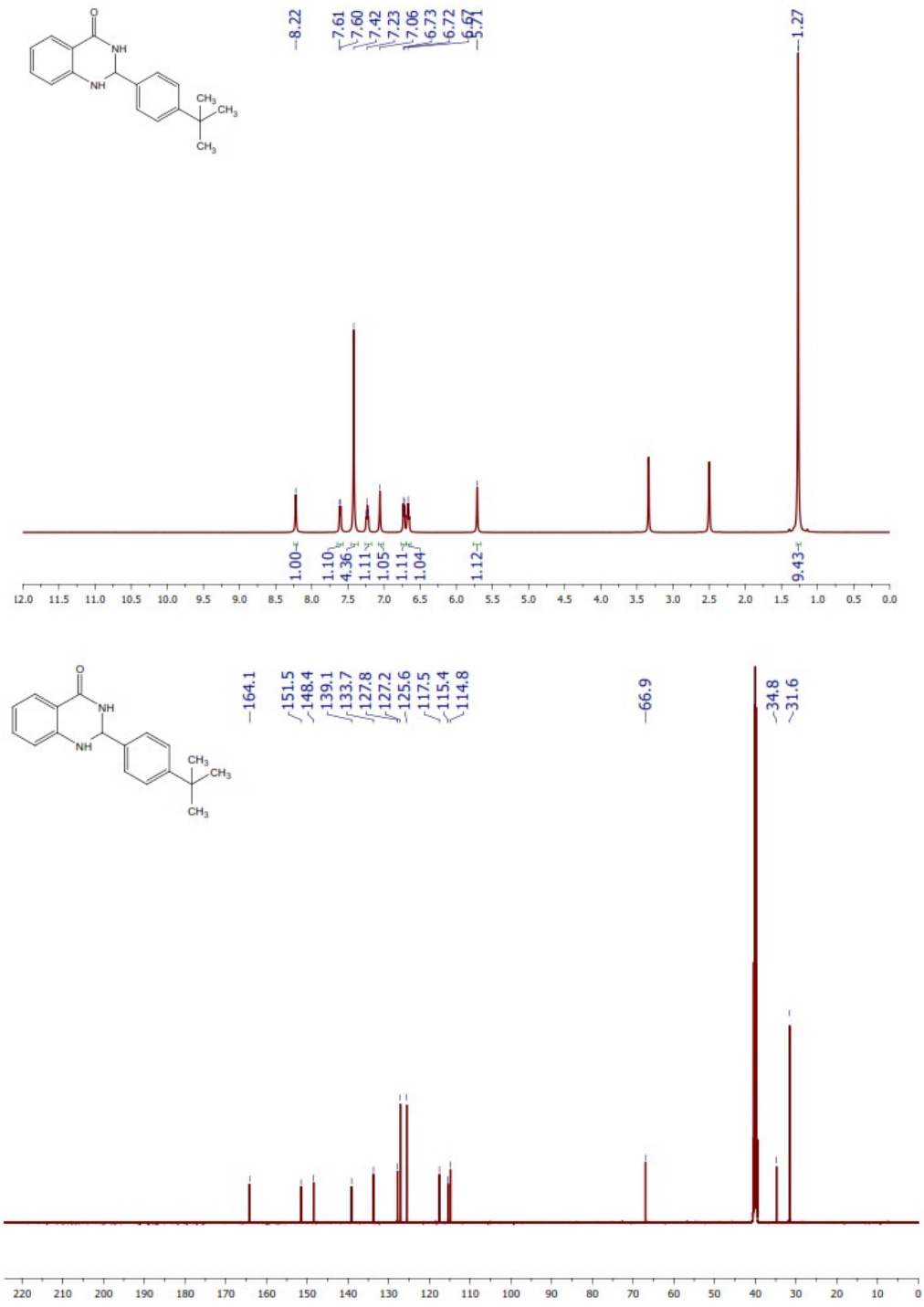


Fig. 31 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 2-(4-tert-butryl)phenyl-2-3-dihydroquinazolin-4(1*H*)-one

Section S6. References

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