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Supporting Information For:

A Hydrazine Functionalized UiO-66(Hf) Metal-Organic Framework for the Synthesis of Quinolines by Friedländer Condensation

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Materials and characterization techniques:

A previously reported procedure was employed for synthesizing $H_2BDC\text{-}N_2H_3$ linker.[1] All the chemicals used in this work were commercially available and they were used without any further purification. Also, benzaldehyde and malononitrile were purchased from Sigma Aldrich and used as received without further treatments. XRPD (X-ray powder diffraction) patterns were recorded with a Bruker D2 Phaser X-ray diffractometer (30 kV, 10 mA) using Cu-*K*α (λ = 1.5406 Å) radiation. Fourier transform infrared spectroscopy was performed from KBr pellets in the range of 400-4000 cm^{-1} on a Perkin Elmer Spectrum Two FT-IR spectrometer. The following indications were used to indicate the corresponding absorption bands: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh) and broad (br). Thermogravimetric analyses (TGA) were carried out using a SDT Q600 thermogravimetric analyzer in the temperature range 25-700 °C under argon atmosphere at a heating rate of 10 °C min^1. The EDX experiments were carried out with a Hitachi S3400N SEM-EDX equipment. The surface morphology of material **1′** was analyzed via Field Emission - Scanning Electron Microscopy (FE-SEM) with a Zeiss (Sigma 300) scanning electron microscope. A Quantachrome Quadrasorb evo Automated Surface Area & Pore Size Analyzer was used for nitrogen sorption experiment at -196 °C. The compound was heated at 120 °C for 24 h before the sorption experiment. For catalytic investigations, the conversion and selectivity were determined with the help of Agilent 7820A gas chromatograph using nitrogen as carrier gas. The products were confirmed by analyzing the reaction mixture with Agilent 5890 GC-MS.

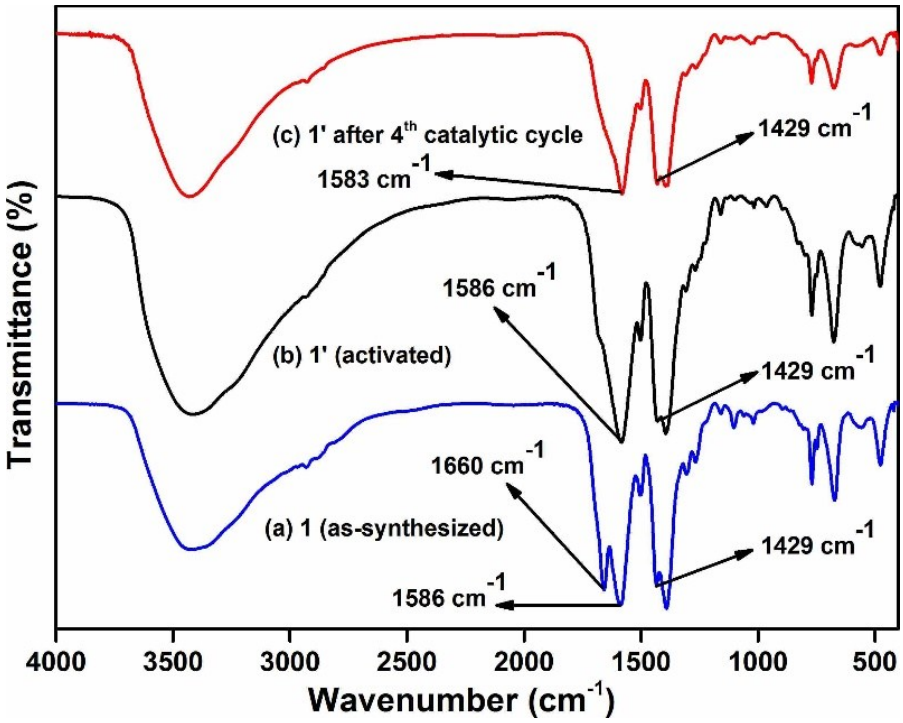

Figure S1. FT-IR spectra of (a) as-synthesized **1**, (b) activated **1′** and (c) **1′** after 4th catalytic cycle.

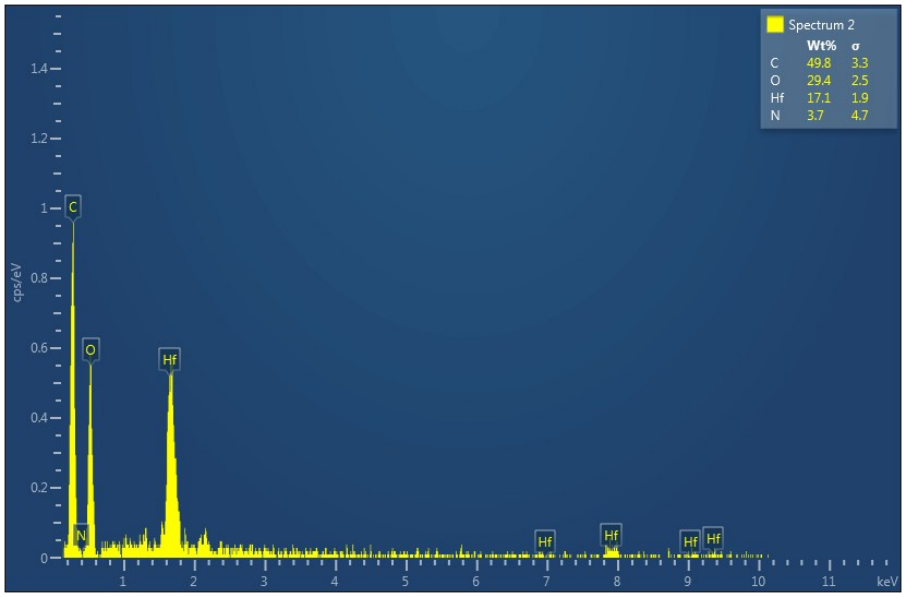

Figure S2. EDX spectrum of **1′** before catalysis.

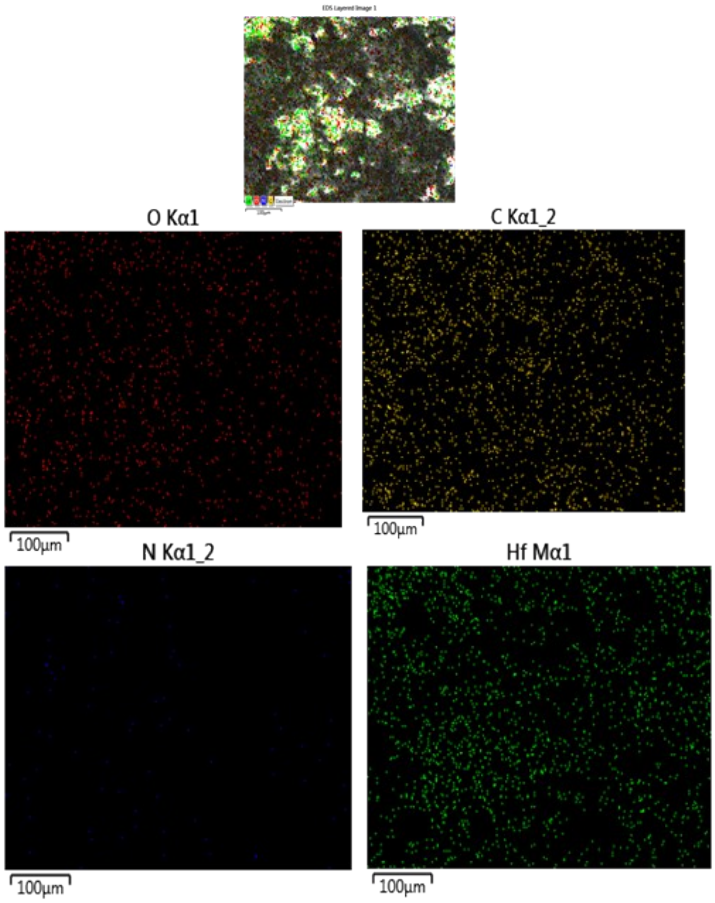

Figure S3. EDX elemental mapping of **1′** before catalysis.

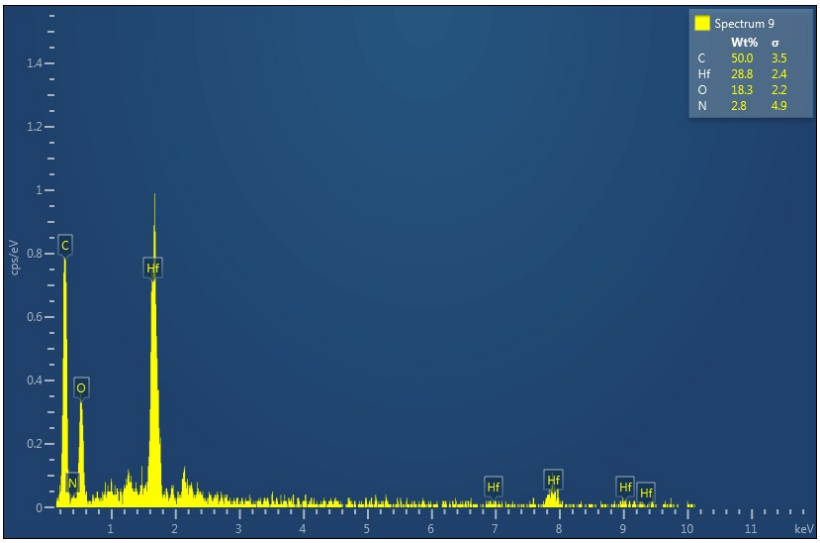

Figure S4. EDX spectrum of **1′** after 4th cycle of catalysis.

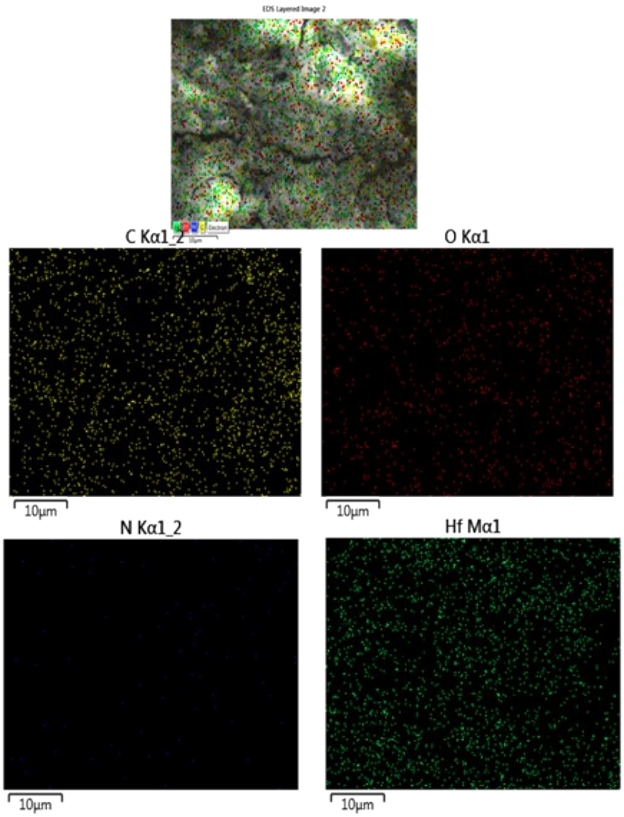

Figure S5. EDX elemental mapping of **1′** after 4th cycle of catalysis.

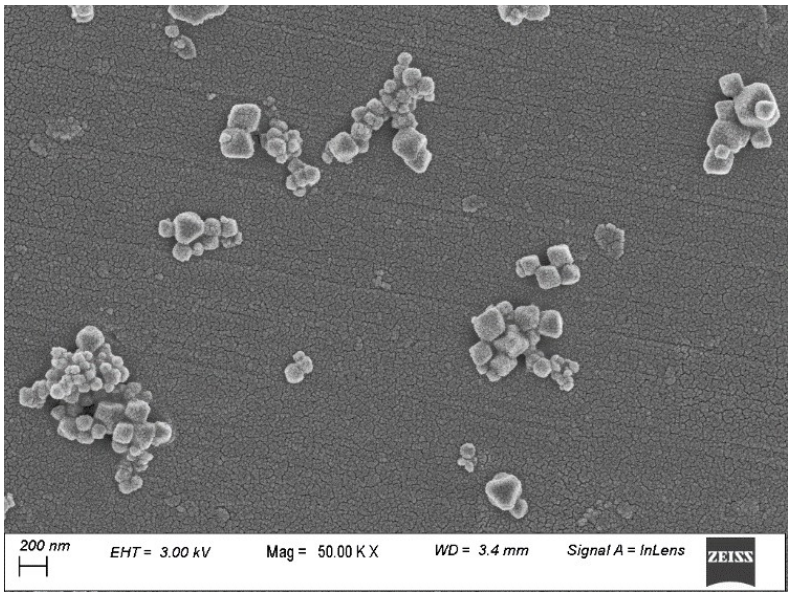

Figure S6. FE-SEM images of **1′** before catalysis.

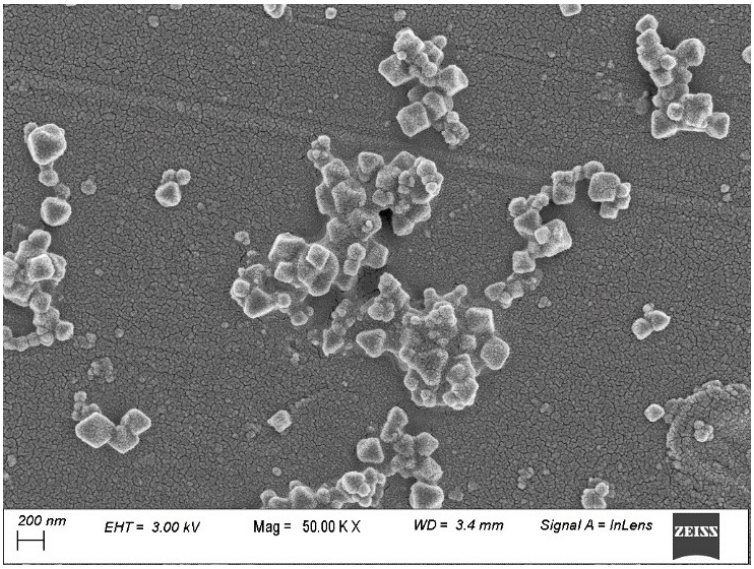

Figure S7. FE-SEM images of **1′** after 4th cycle of catalysis.

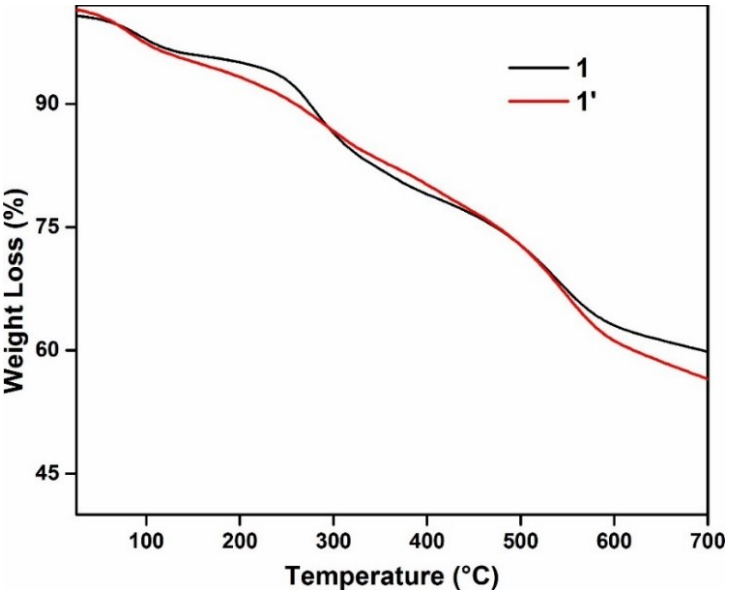

Figure S8. TG curves of as-synthesized **1** (black) and thermally activated **1′** (red) recorded under argon atmosphere in the temperature range of 25-700 °C with a heating rate of 10 °C min^{-1}.

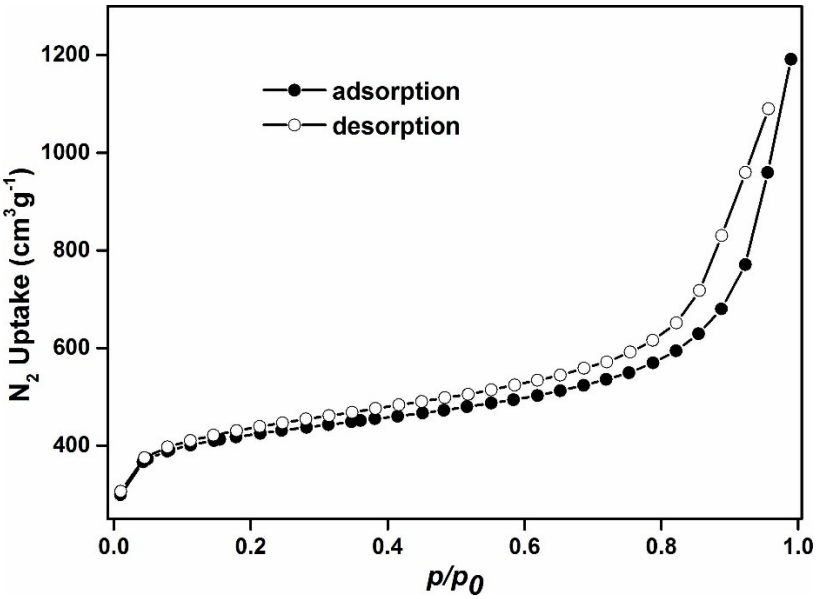

Figure S9. N_2 adsorption (solid circles) and desorption (empty circles) isotherms of **1′** measured at –196 °C.

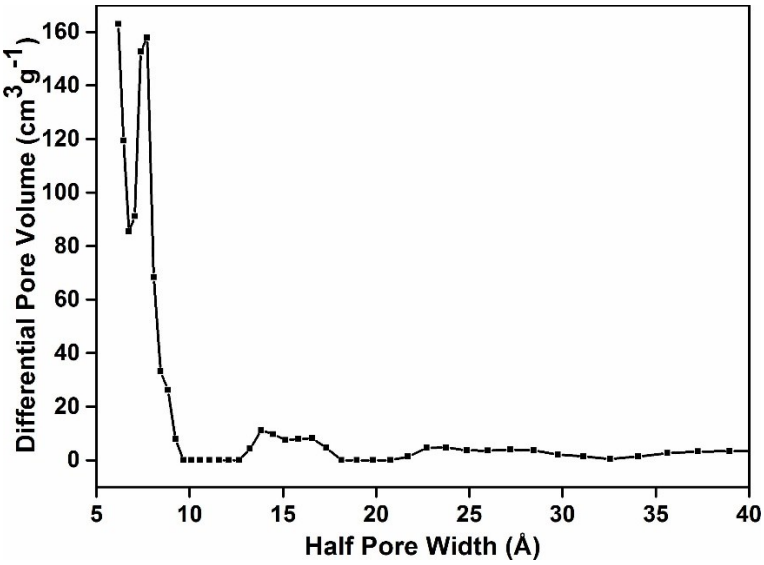

Figure S10. Density functional theory pore-size distribution curve of **1′** obtained from N_2 sorption isotherms measured at –196 °C.

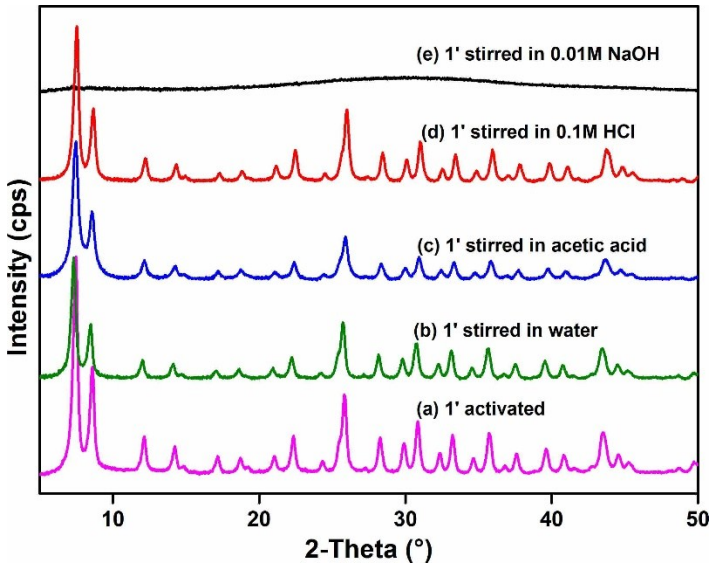

Figure S11. XRPD patterns of **1′** after stirring in different solvents: (a) fresh **1′**, (b) **1′** after stirring in water, (c) **1′** after stirring in acetic acid, (d) **1′** after stirring in 0.1 (M) HCl and (e) **1′** after stirring in 0.01 (M) NaOH.

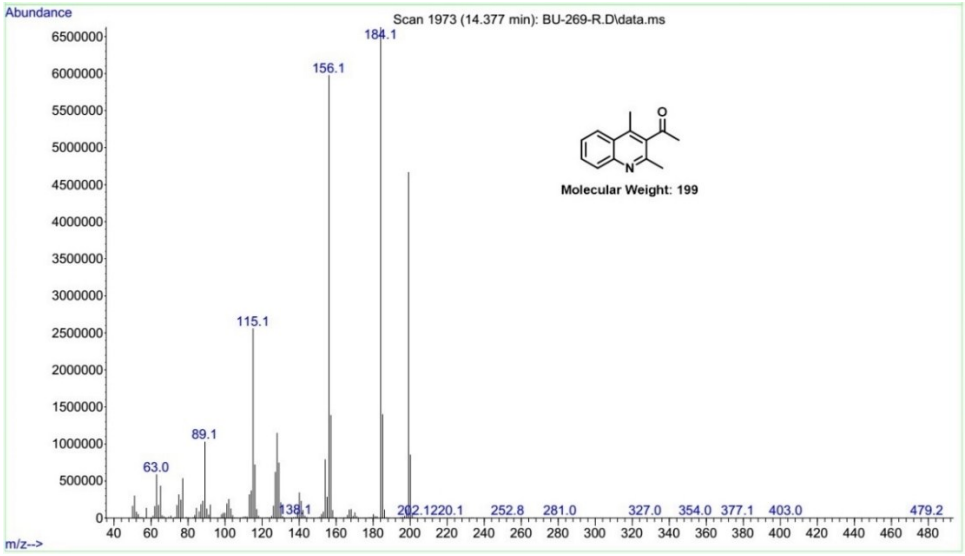

Figure 12. GC-MS trace of 1-(2,4-dimethylquinolin-3-yl)ethan-1-one.

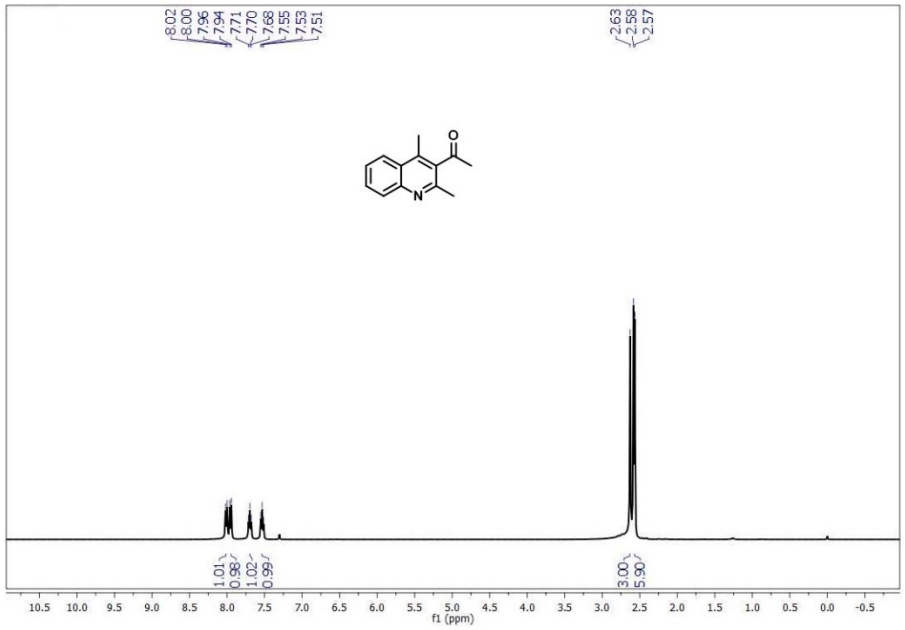

Figure 13. ^{1}H-NMR spectrum of 1-(2,4-dimethylquinolin-3-yl)ethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 2.63 (s, 3H), 2.57 (d, *J* = 7.0 Hz, 6H).

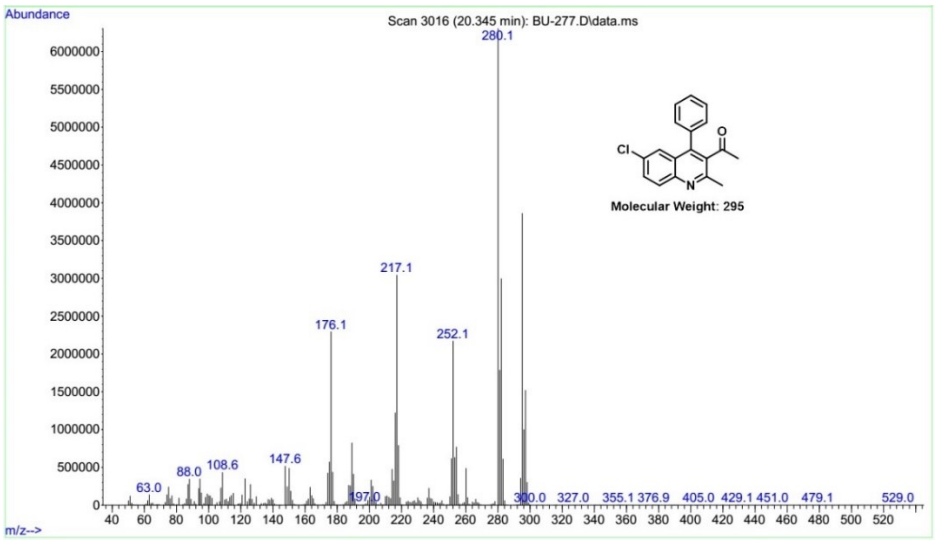

Figure 14. GC-MS trace of 1-(6-chloro-2-methyl-4-phenylquinolin-3-yl)ethan-1-one.

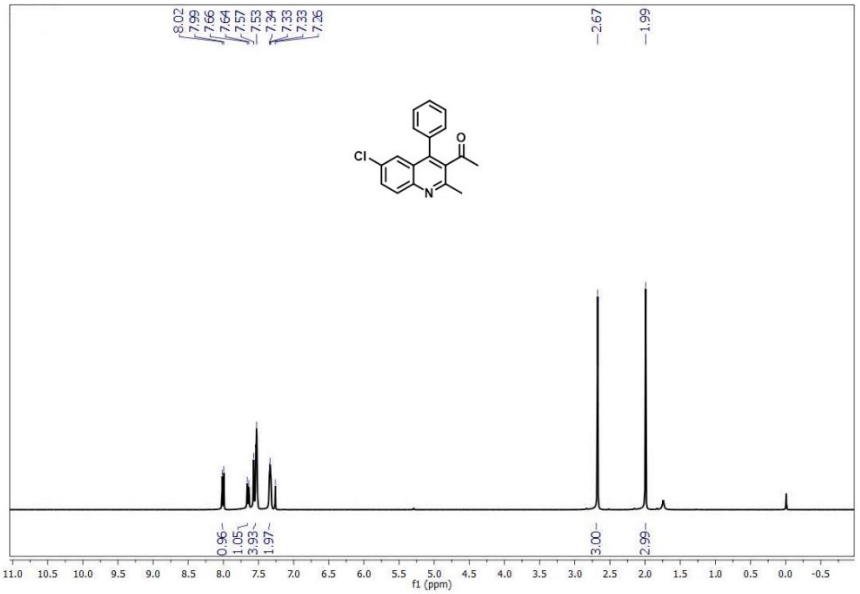

Figure 15. ^{1}H-NMR spectrum of 1-(6-chloro-2-methyl-4-phenylquinolin-3-yl)ethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.9 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 16.7 Hz, 4H), 7.40 – 7.29 (m, 2H), 2.67 (s, 3H), 1.99 (s, 3H).

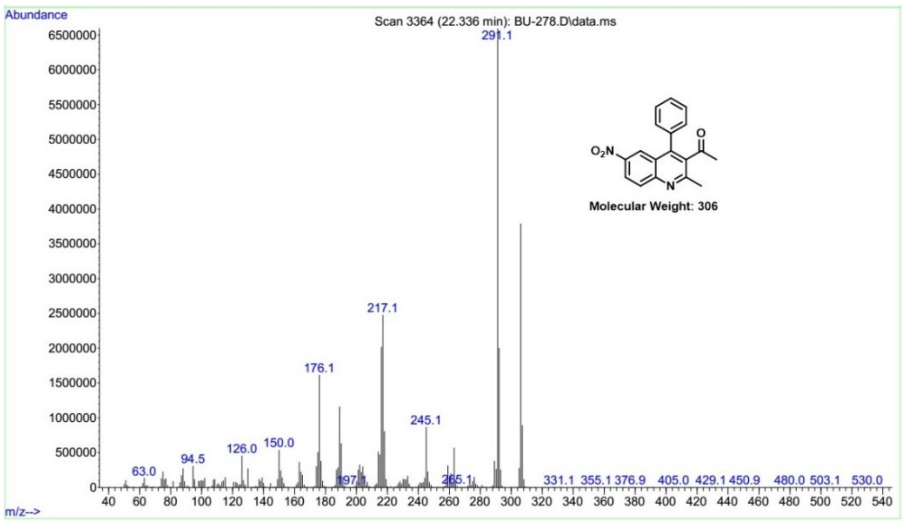

Figure 16. GC-MS trace of 1-(2-methyl-6-nitro-4-phenylquinolin-3-yl)ethan-1-one.

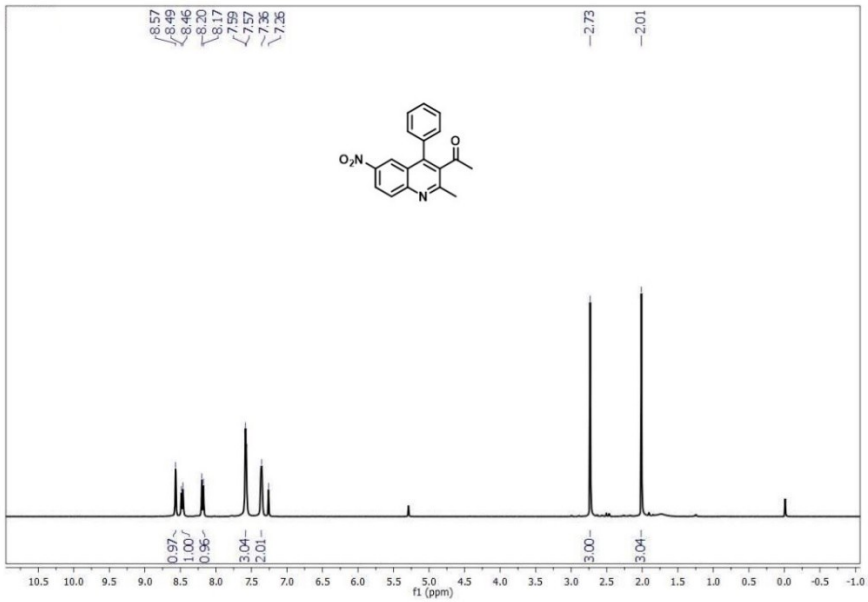

Figure 17. ^{1}H-NMR spectrum of 1-(2-methyl-6-nitro-4-phenylquinolin-3-yl)ethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.19 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 4.8 Hz, 3H), 7.36 (s, 2H), 2.73 (s, 3H), 2.01 (s, 3H).

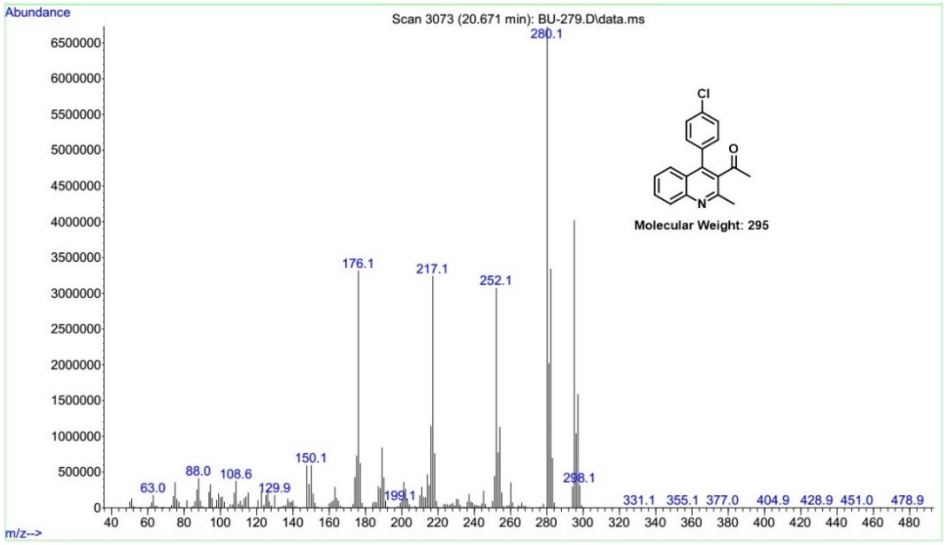

Figure 18. GC-MS trace of 1-(4-(4-chlorophenyl)-2-methylquinolin-3-yl)ethan-1-one.

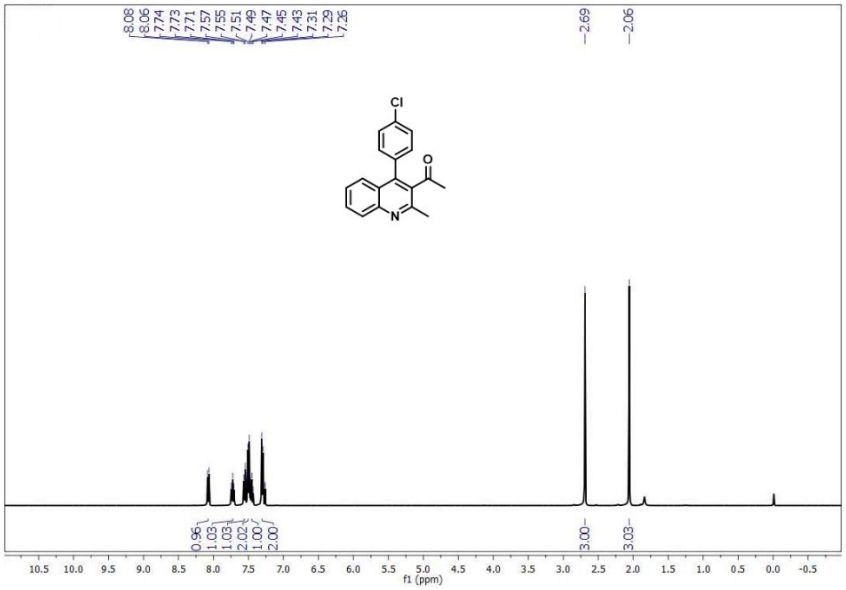

Figure 19. ^{1}H-NMR spectrum of 1-(4-(4-chlorophenyl)-2-methylquinolin-3-yl)ethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.69 (s, 3H), 2.06 (s, 3H).

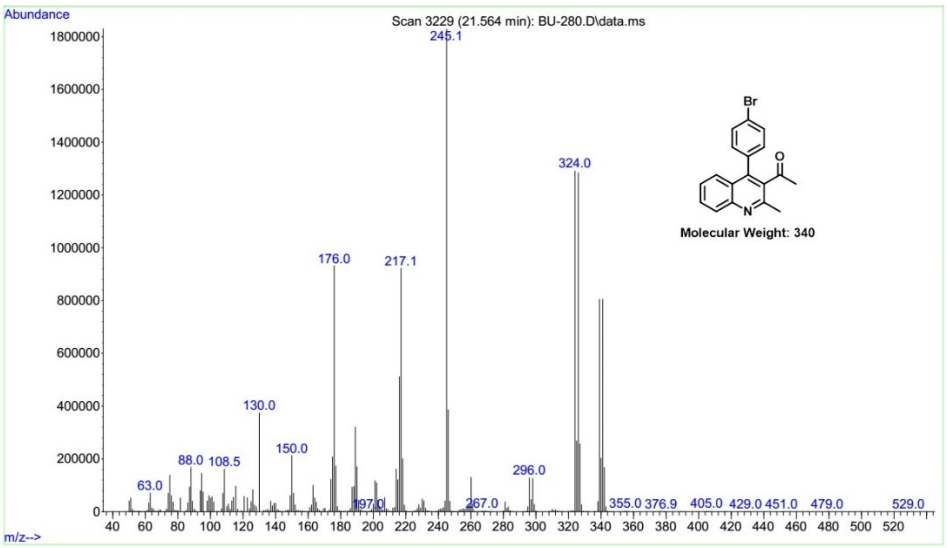

Figure 20. GC-MS trace of 1-(4-(4-bromophenyl)-2-methylquinolin-3-yl)ethan-1-one.

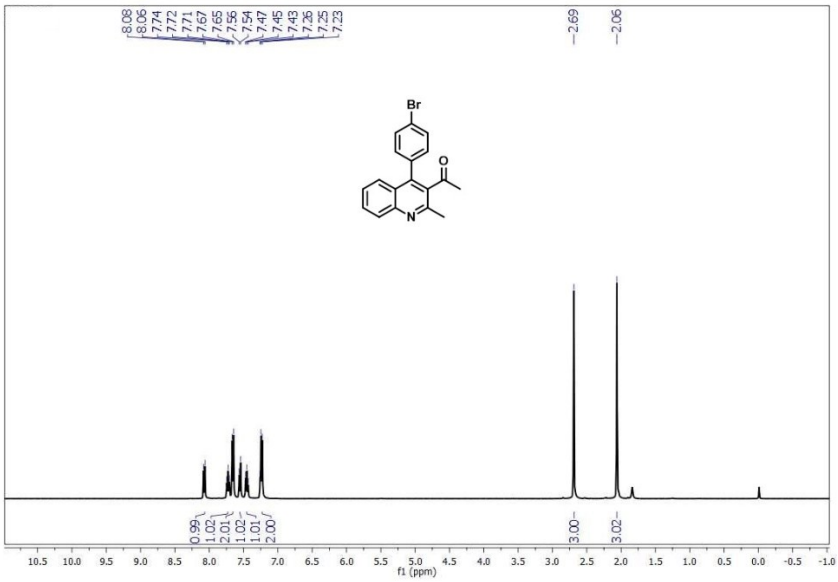

Figure 21. ^{1}H-NMR spectrum of 1-(4-(4-bromophenyl)-2-methylquinolin-3-yl)ethan-1-one.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.69 (s, 3H), 2.06 (s, 3H).

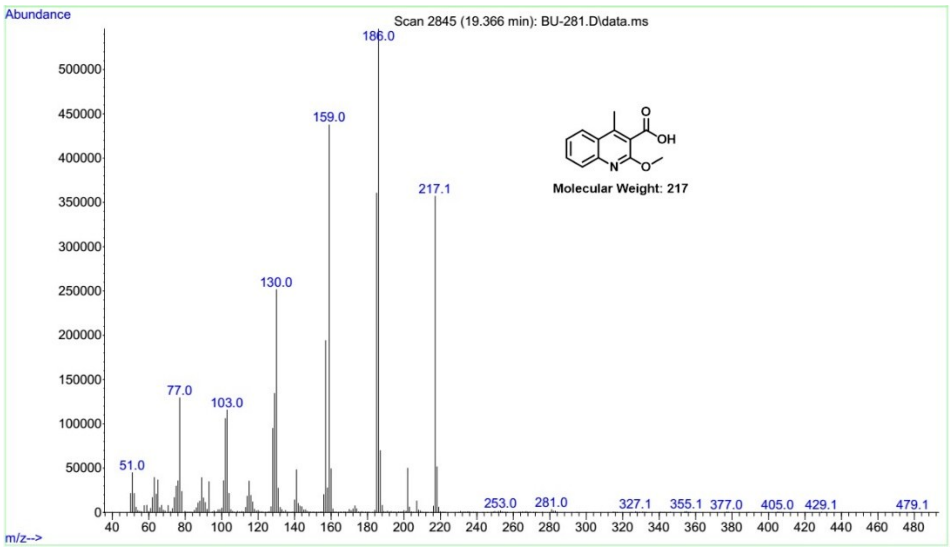

Figure 22. GC-MS trace of 2-methoxy-4-methylquinoline-3-carboxylic acid.

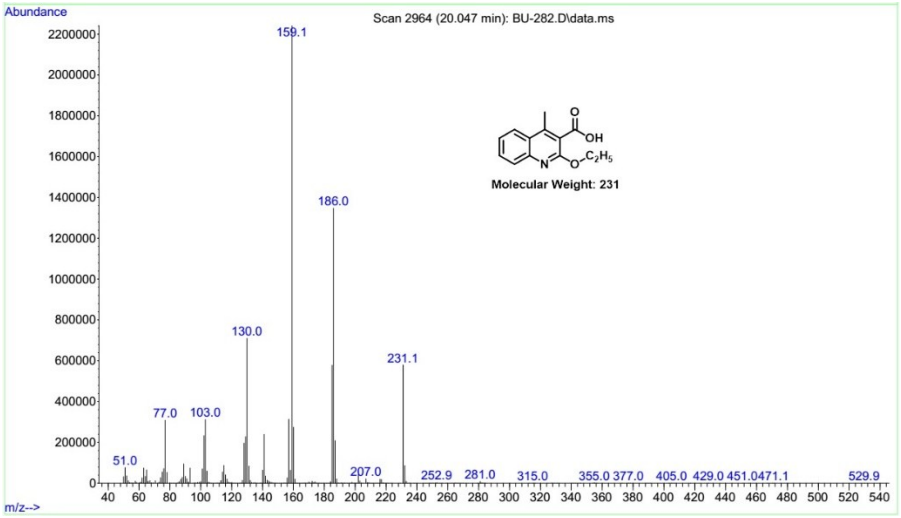

Figure 23. ^{1}H-NMR spectrum of 2-ethoxy-4-methylquinoline-3-carboxylic acid.

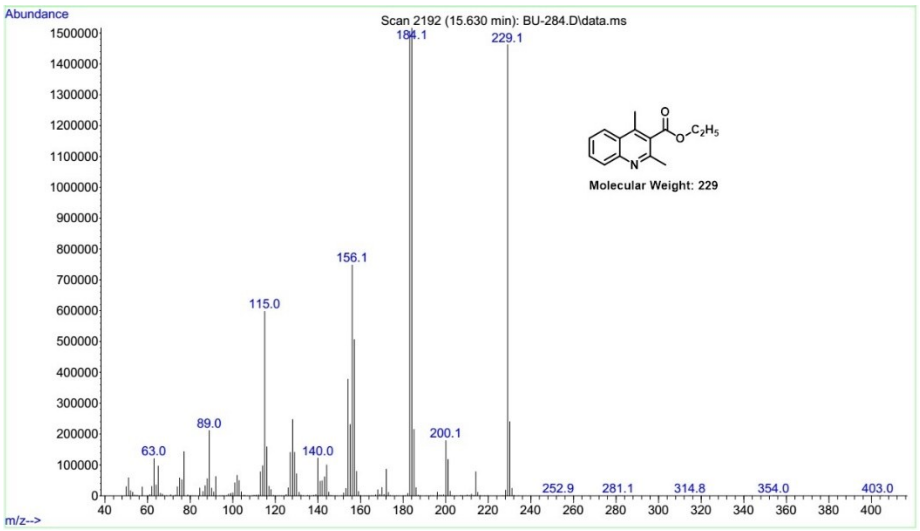

Figure 24. GC-MS trace of ethyl 2,4-dimethylquinoline-3-carboxylate.

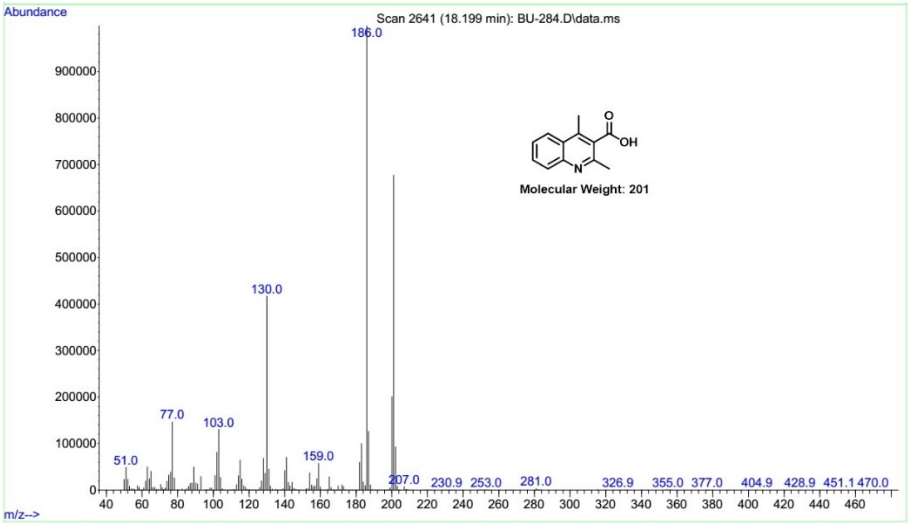

Figure 25. GC-MS trace of 2,4-dimethylquinoline-3-carboxylic acid.

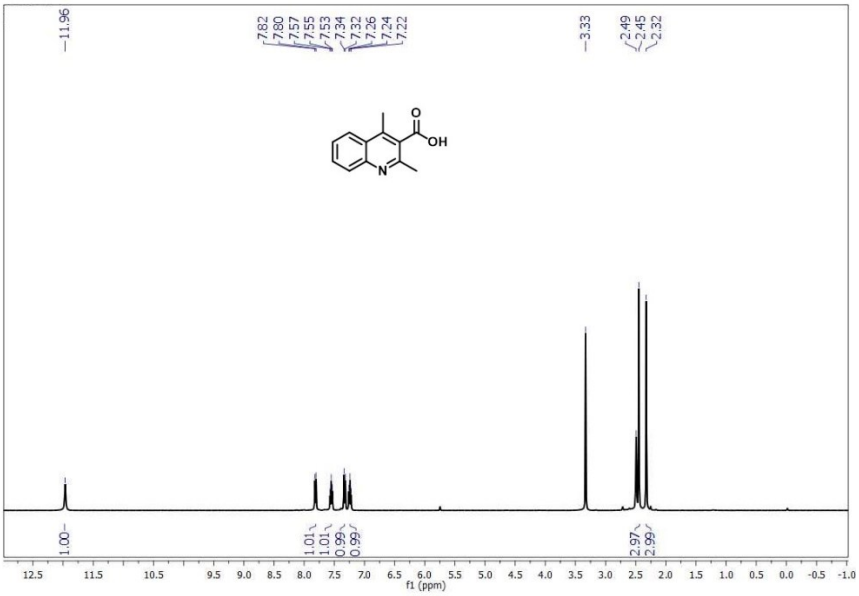

Figure 26. [1]H-NMR spectrum of 2,4-dimethylquinoline-3-carboxylic acid.
[1]H NMR (400 MHz, DMSO): δ = 11.96 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H).

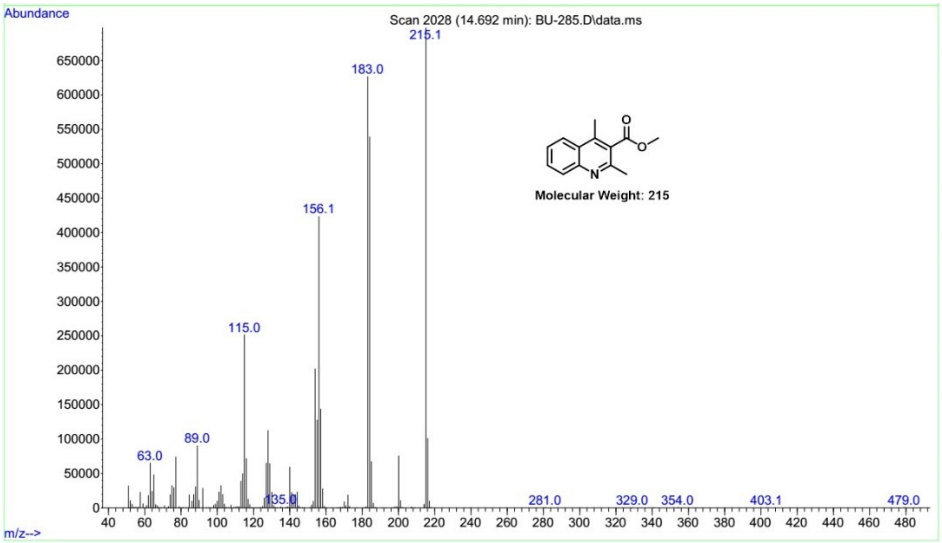

Figure 27. GC-MS trace of methyl 2,4-dimethylquinoline-3-carboxylate.

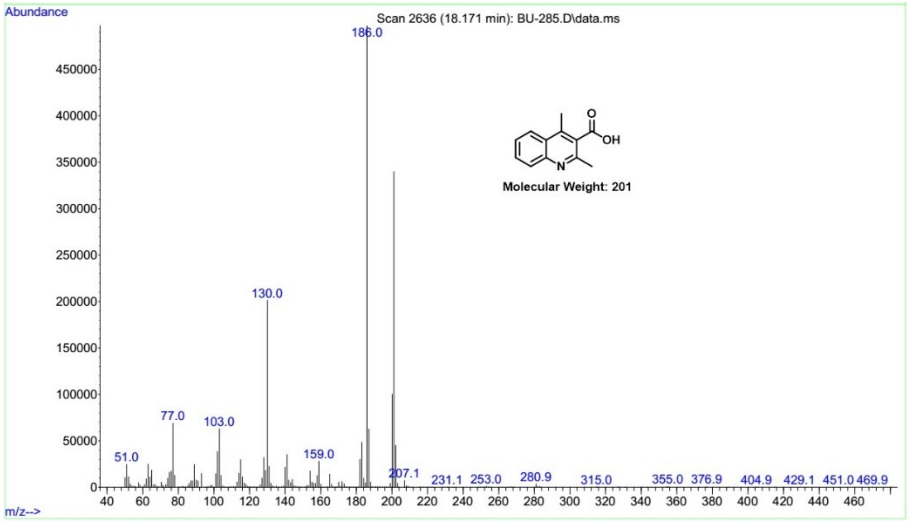

Figure 28. GC-MS trace of 2,4-dimethylquinoline-3-carboxylic acid.

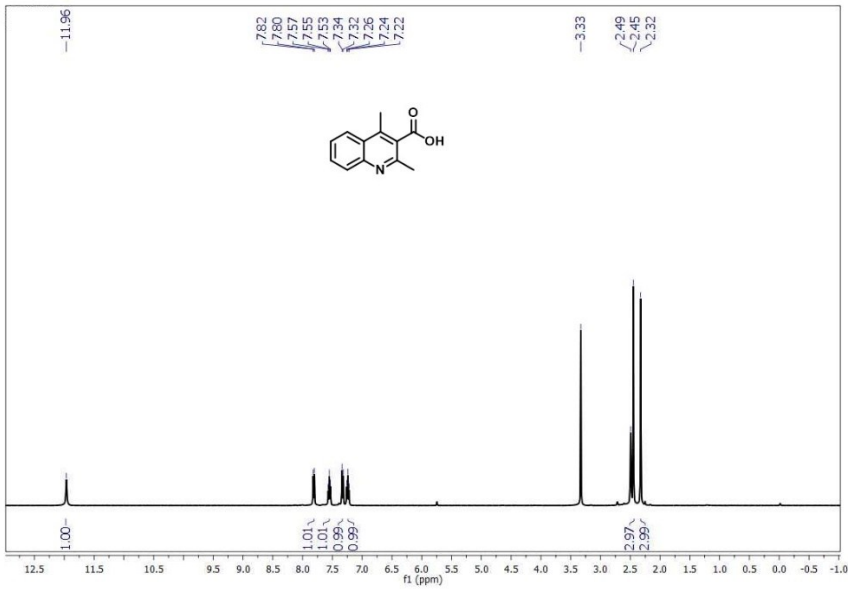

Figure 29. ^{1}H-NMR spectrum of 2,4-dimethylquinoline-3-carboxylic acid.
^{1}H NMR (400 MHz, DMSO): δ = 11.97 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H).

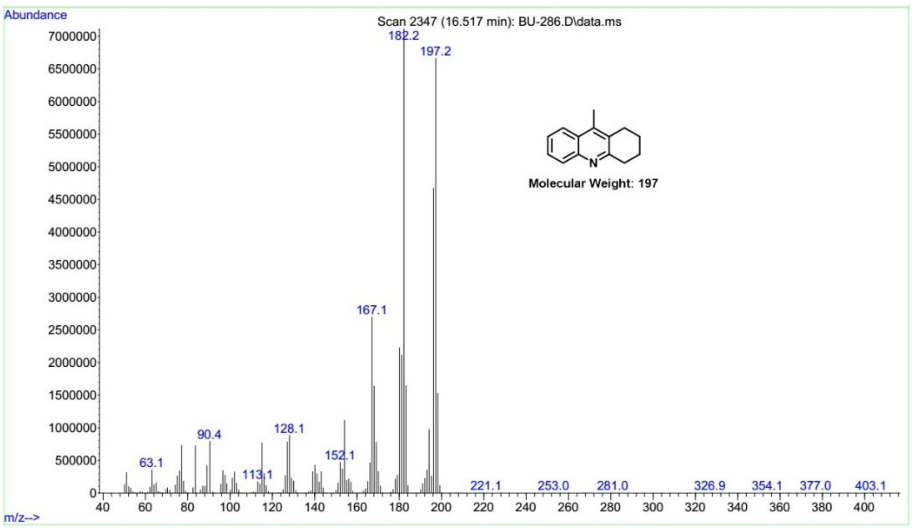

Figure 30. GC-MS trace of 9-methyl-1,2,3,4-tetrahydroacridine.

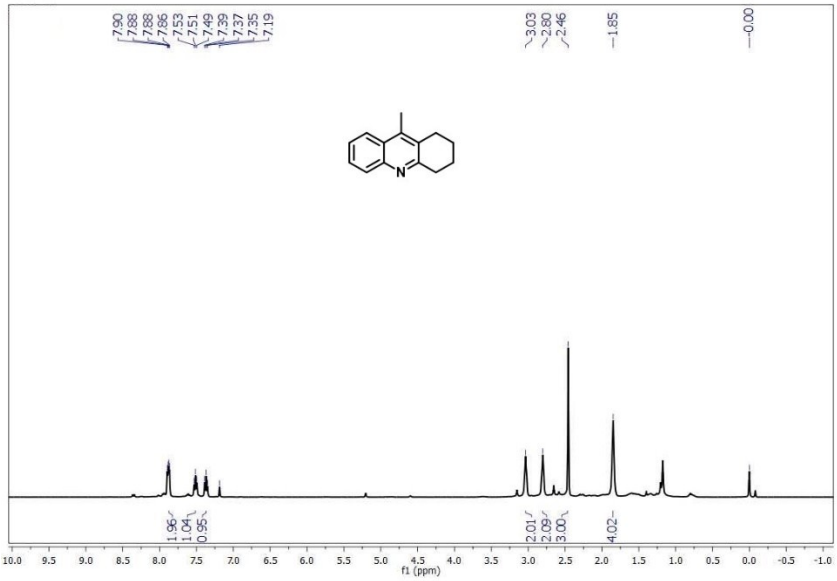

Figure 31. ^{1}H-NMR spectrum of 9-methyl-1,2,3,4-tetrahydroacridine.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (dd, *J* = 8.0, 4.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 3.03 (s, 2H), 2.80 (s, 2H), 2.46 (s, 3H), 1.85 (s, 4H).

References:

1. A. Das, N. Anbu, A. Dhakshinamoorthy and S. Biswas, *Microporous Mesoporous Mater.*, 2019, **284**, 459-467.