Electronic Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Material

Zn^{II} doped and immobilized on functionalized magnetic hydrotalcite (Fe_3O_4/HT-SMTU-Zn^{II}): a novel, green and magnetically recyclable bifunctional nanocatalyst for one-pot multi-component synthesis of acridinediones under solvent-free conditions

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Experimental

General

All chemical reagents and solvents were purchased from Merck and Sigma-Aldrich chemical companies and were used as received without further purification. The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates or GLC on a shimadzu model GC-17A instrument.

The FT-IR spectra were recorded on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The NMR spectra were obtained in Brucker Avance 300 MHz instruments in DMSO-d_6. Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in *m/z* (rel %). Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 Series instrument. All yields refer to isolated products after purification by thin layer chromatography or recrystallization.

3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4a). Yellow solid; isolated yield: 95%; mp 252-254 °C (from EtOH) (lit.,[1] 254-256 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.65-7.43 (4H, m, Ph), 7.63 (2H, d, *J* = 6 Hz, Ph), 7.26 (2H, t, *J* = 8 Hz, Ph), 7.11 (2H, t, *J* = 8 Hz, Ph), 5.10 (1H, s, CH), 2.26-2.10 (4H, m, $2CH_2$), 2.02 (2H, d, *J* = 15.9 Hz, CH_2), 1.78 (2H, d, *J* = 15.9 Hz, CH_2), 0.88 (6H, s, $2CH_3$), 0.72 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 150.7, 146.7, 138.9, 130.5, 129.8, 128.3, 128.0, 126.2, 113.4, 50.0, 41.45, 32.4, 29.8, 26.5; MS, *m/z* (%): 426 (60%, M^+), 348 (100%, M^+- C_6H_5), 328 (30%, M^+- $C_6H_{10}O$).

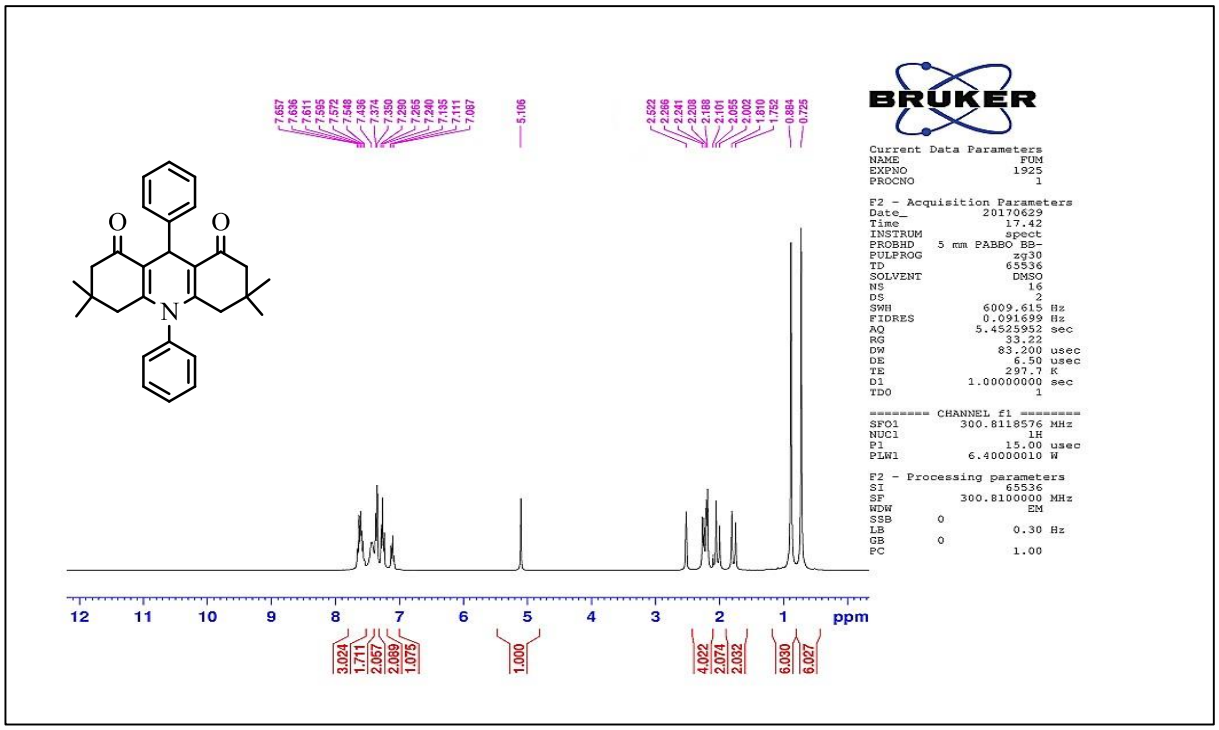


Figure 1: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4a**).

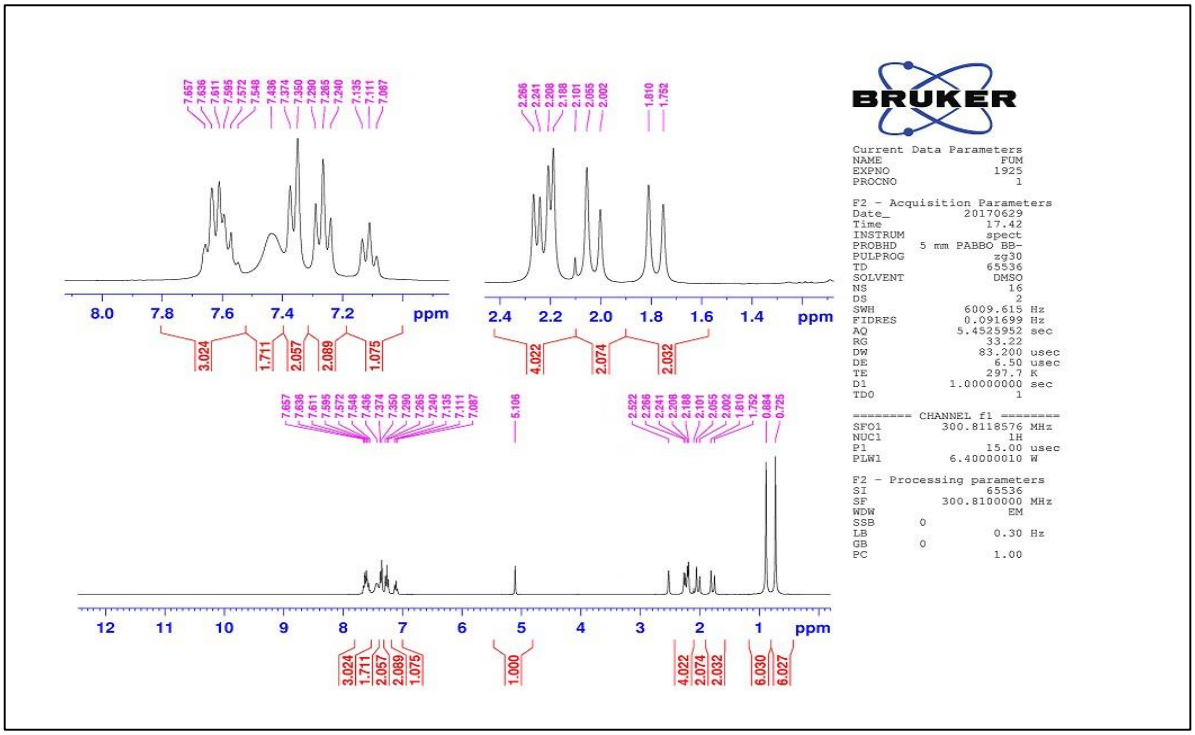


Figure 2: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4a**) expanded.

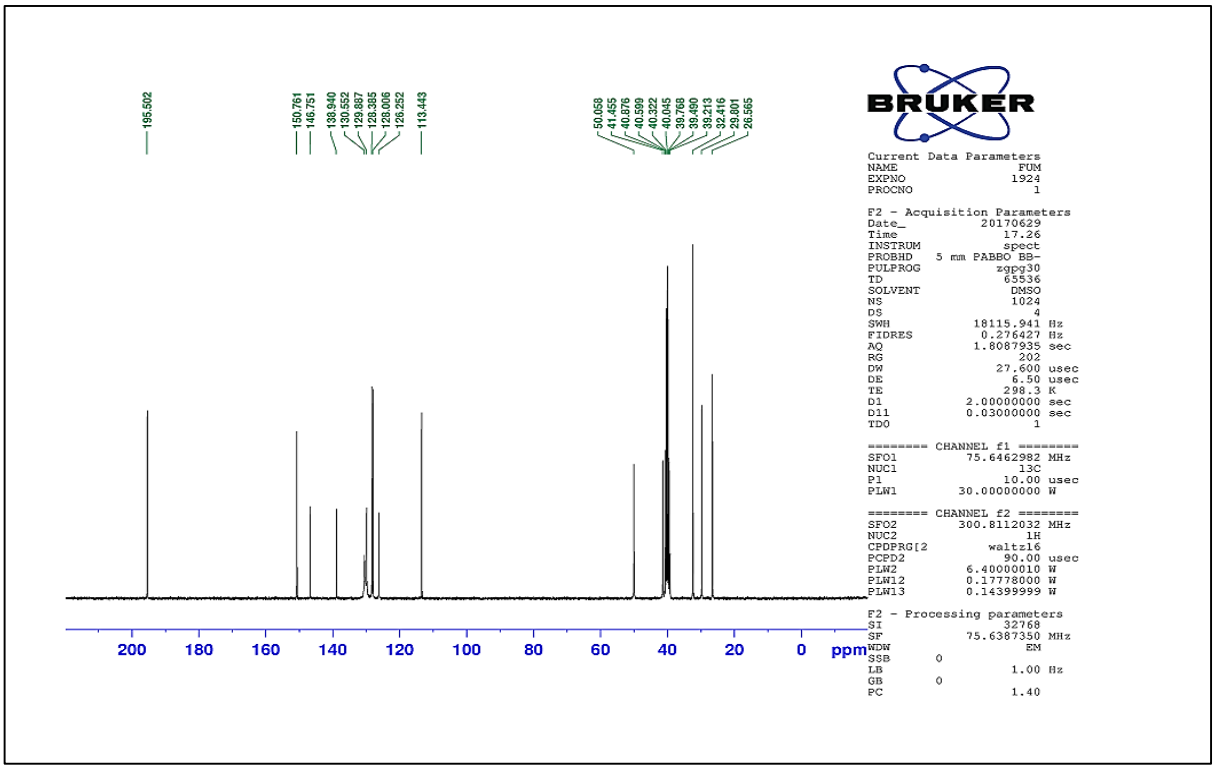


Figure 3:^{13}CNMR (75MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4a**).

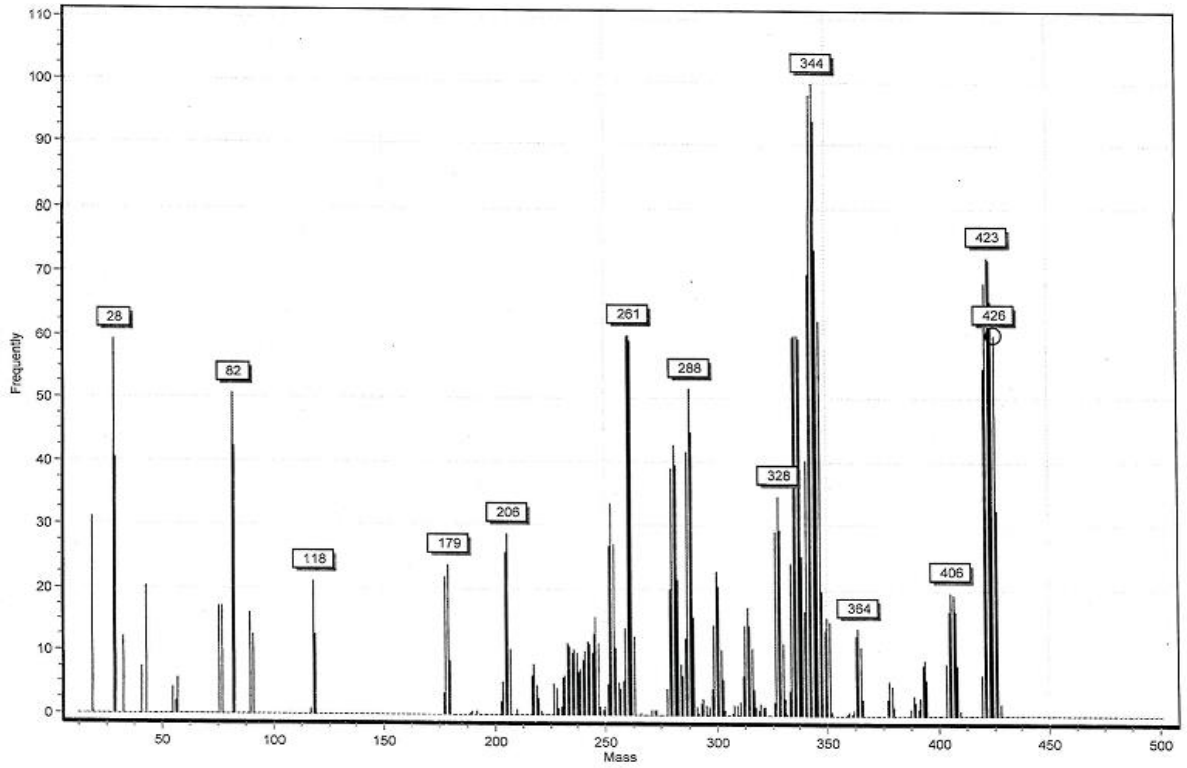


Figure 4: Mass spectrum of 3,3,6,6-tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4a**).

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine 1,8(2*H*,5*H*)-dione (4b). Yellow solid; isolated yield: 95%; mp 216-218 °C (from EtOH) (lit.,[1] 218-220 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.65-7.40 (5H, m, Ph), 7.22 (2H, d, J = 8.7 Hz, Ph), 8.81 (2H, d, J = 8.7 Hz, Ph), 4.99 (1H, s, CH), 3.70 (3H, s, CH_3), 2.24-2.16 (4H, m, $2CH_2$), 1.87 (4H, dd, J = 17.4 Hz, J = 15.9 Hz, $2CH_2$), 0.88 (6H, s, $2CH_3$), 0.72 (6H, s, $2CH_3$); ^{13}CNMR (75 MHz, DMSO-d_6): δ 195.5, 157.7, 150.4, 139.0, 138.9, 130.5, 129.8, 128.9, 128.2, 113.7, 113.6, 55.3, 50.0, 41.4, 32.4, 31.4, 29.7, 26.5; MS, *m/z* (%): 455 (98%, M^+), 344 (100%, M^+- C_7H_7O).

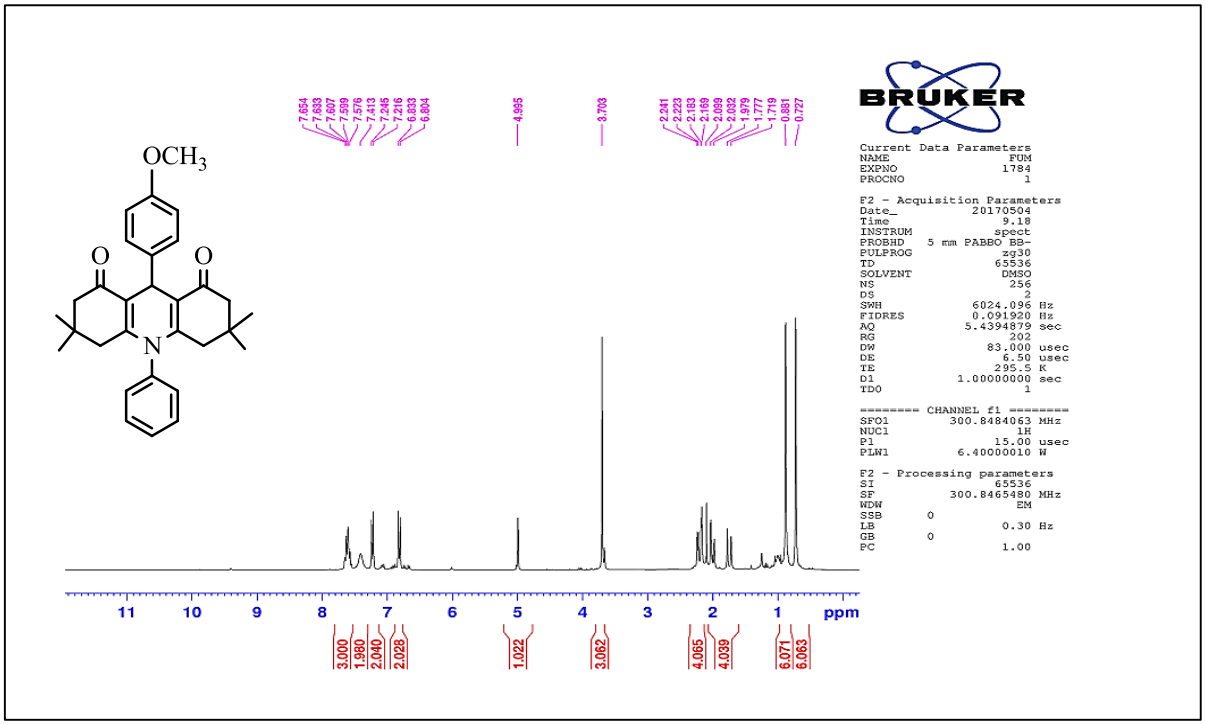


Figure 5: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4b**).

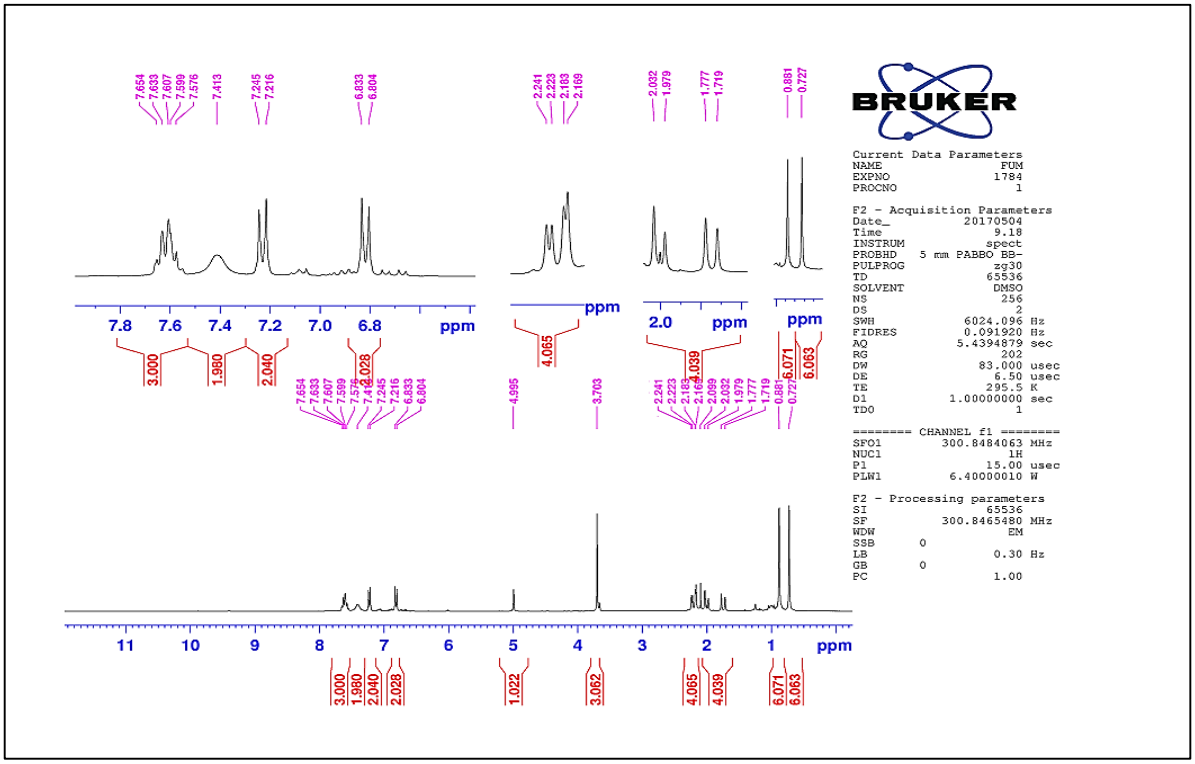


Figure 6: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4b**) expanded.

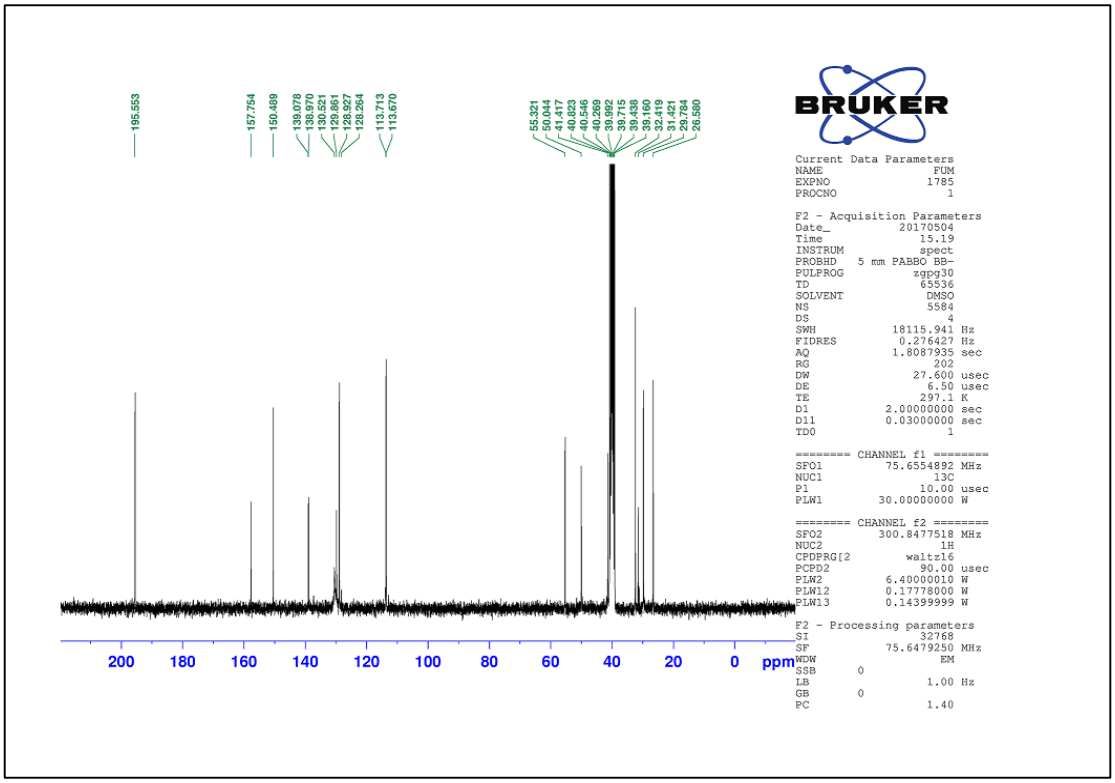


Figure 7: ^{13}CNMR (75 MHz, DMSO-d_6) spectrum of 9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4b**).

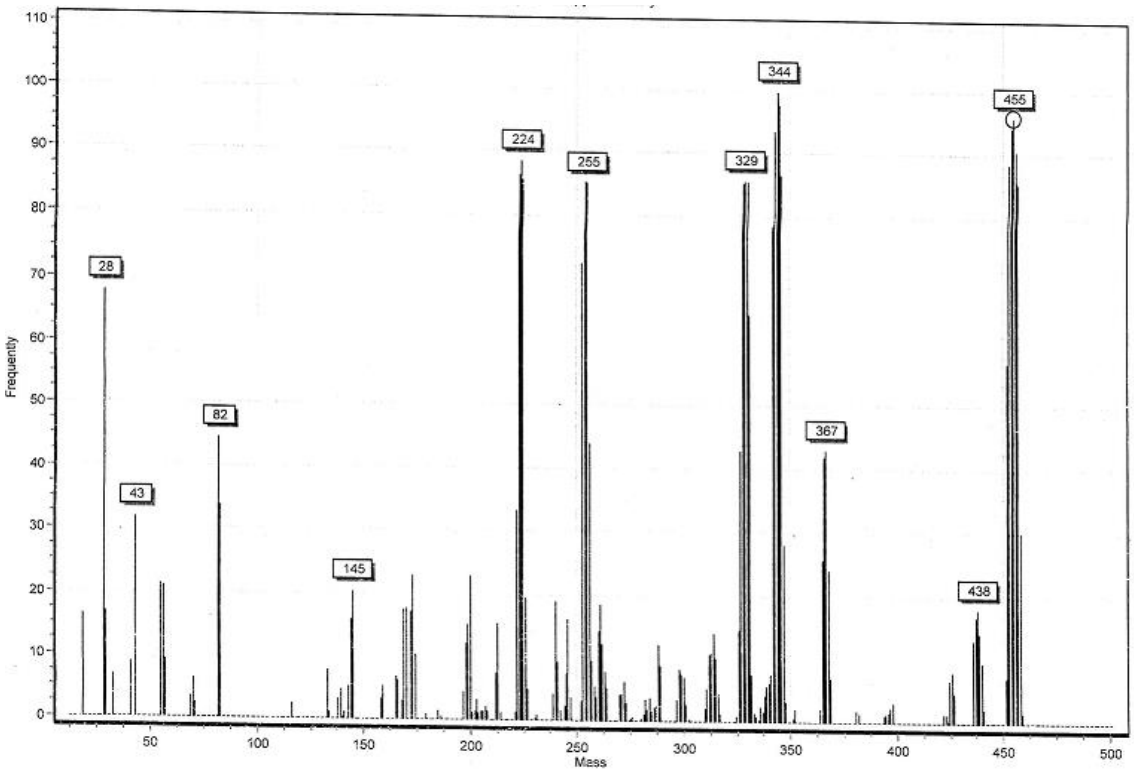


Figure 8: Mass spectrum of 9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4b**).

3,3,6,6-tetramethyl-10-phenyl-9-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4c). Yellow solid; isolated yield: 90%; mp 259-261°C (from EtOH) (lit.,[2] 260-262 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.65-7.42 (5H, m, $2CH_2$), 7.23 (2H, d, J = 6 Hz, Ph), 7.06 (2H, d, J = 6 Hz, Ph), 5.05 (1H, s, CH), 3.37 (3H, s, CH_3), 2.25-2.17 (4H, m, $2CH_2$), 2.01 (2H, d, J = 15.9 Hz, CH_2), 1.76 (2H, d, J = 15.9 Hz, CH_2), 0.88 (6H, s, $2CH_3$), 0.72 (6H, s, $2CH_3$); ^{13}CNMR (75 MHz, DMSO-d_6): δ 195.4, 150.6, 143.8, 138.9, 135.0, 130.5, 129.9, 128.8, 127.9, 113.5, 50.0, 41.4, 32.4, 31.9, 29.8, 26.5, 21.1; MS, *m/z* (%): 440 (82%, M^+), 345 (100%, M^+- C_7H_7), 91 (54%, C_7H_7).

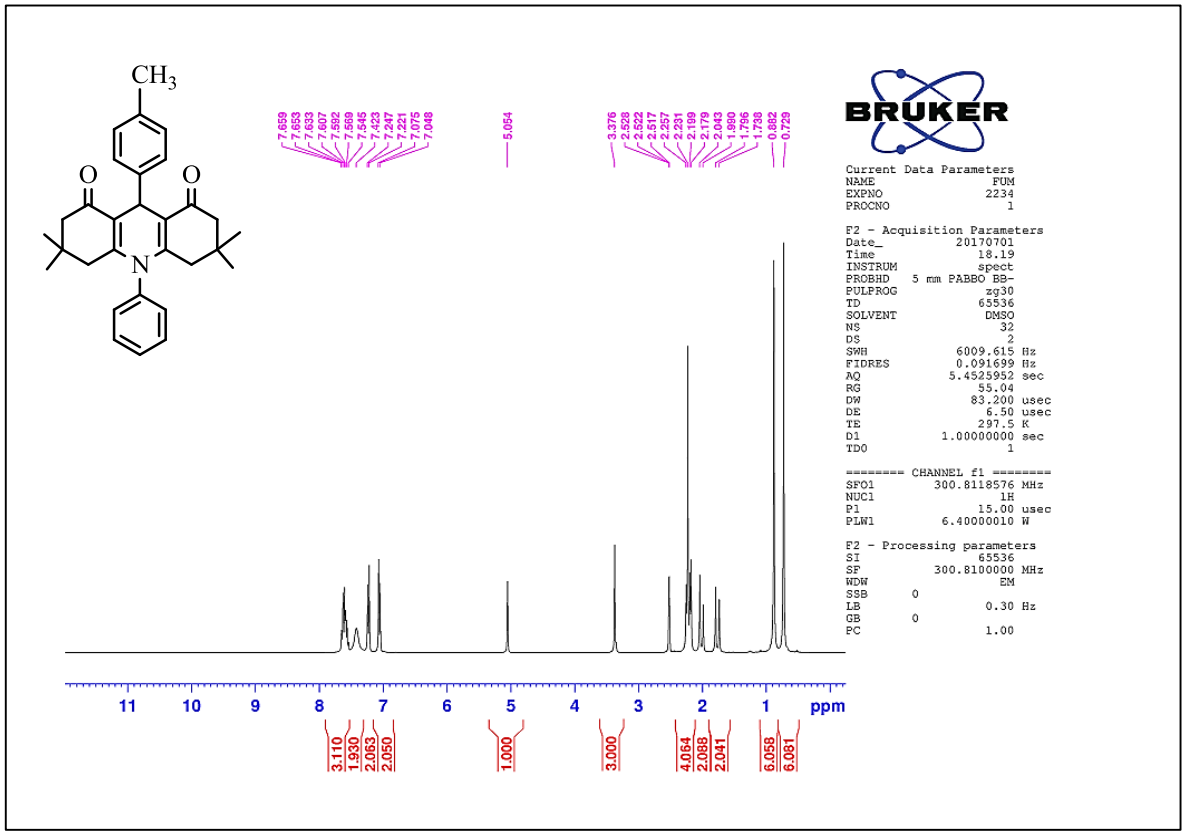


Figure 9: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4c**).

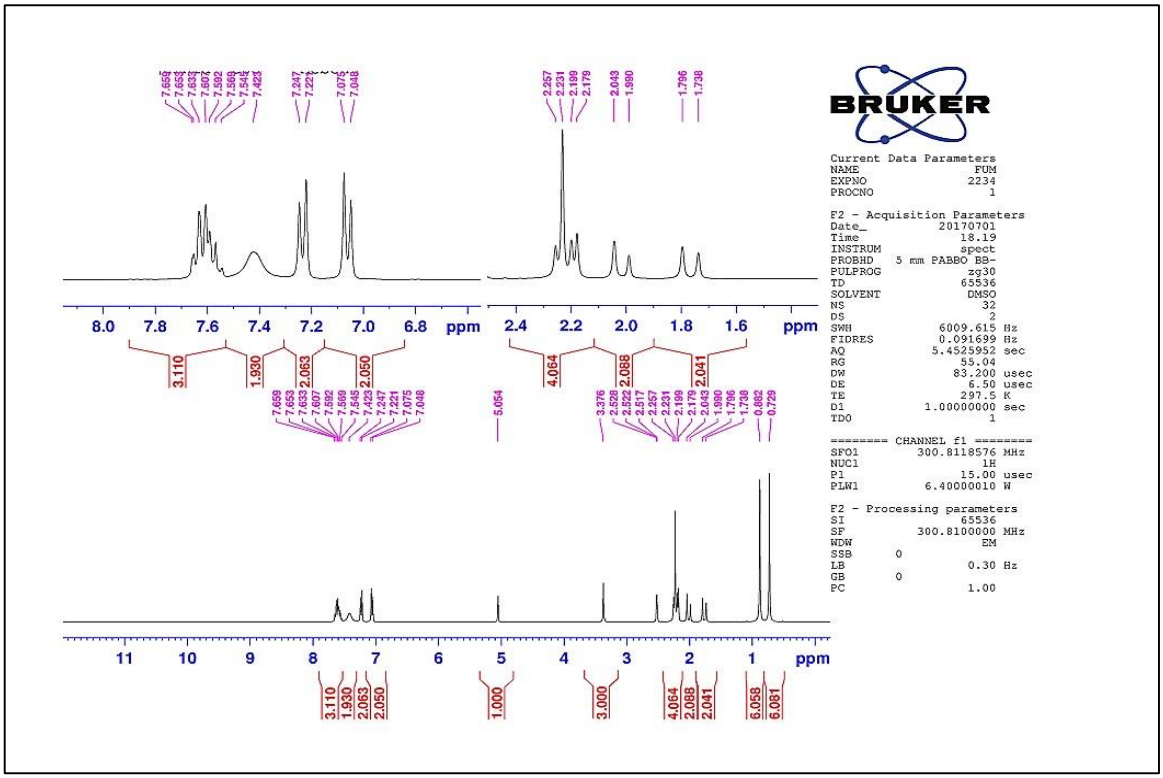


Figure 10: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4c**) expanded.

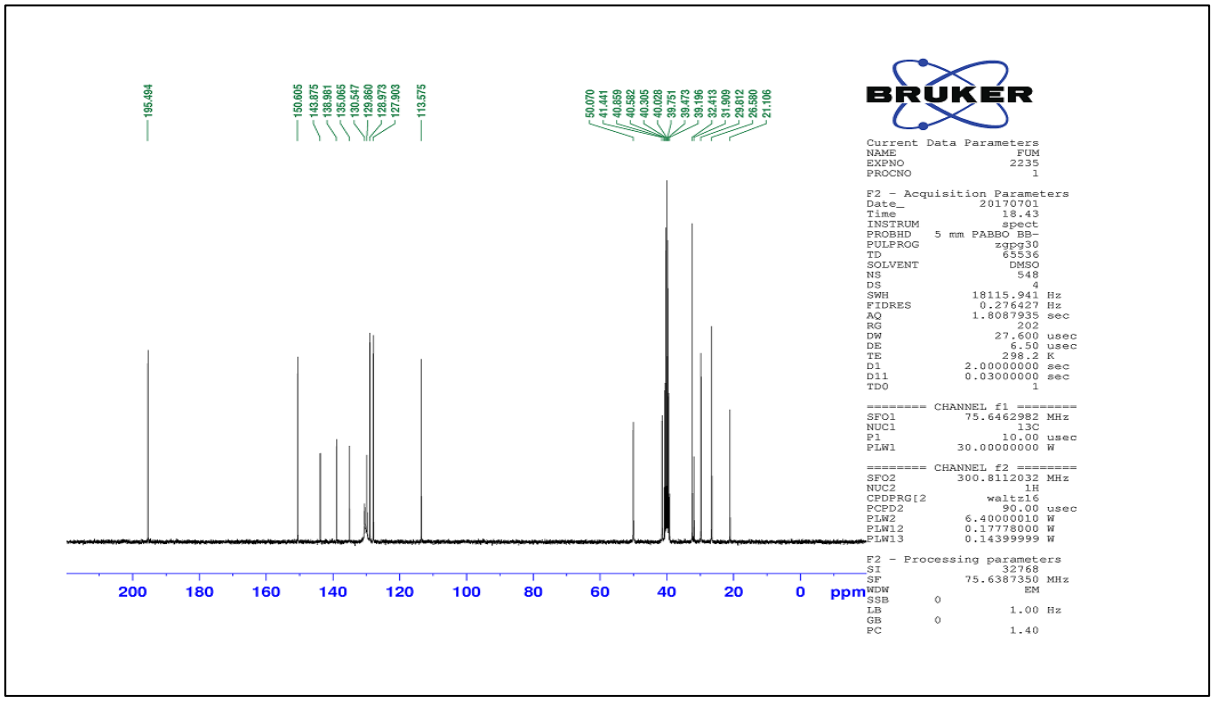


Figure 11: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4c**).

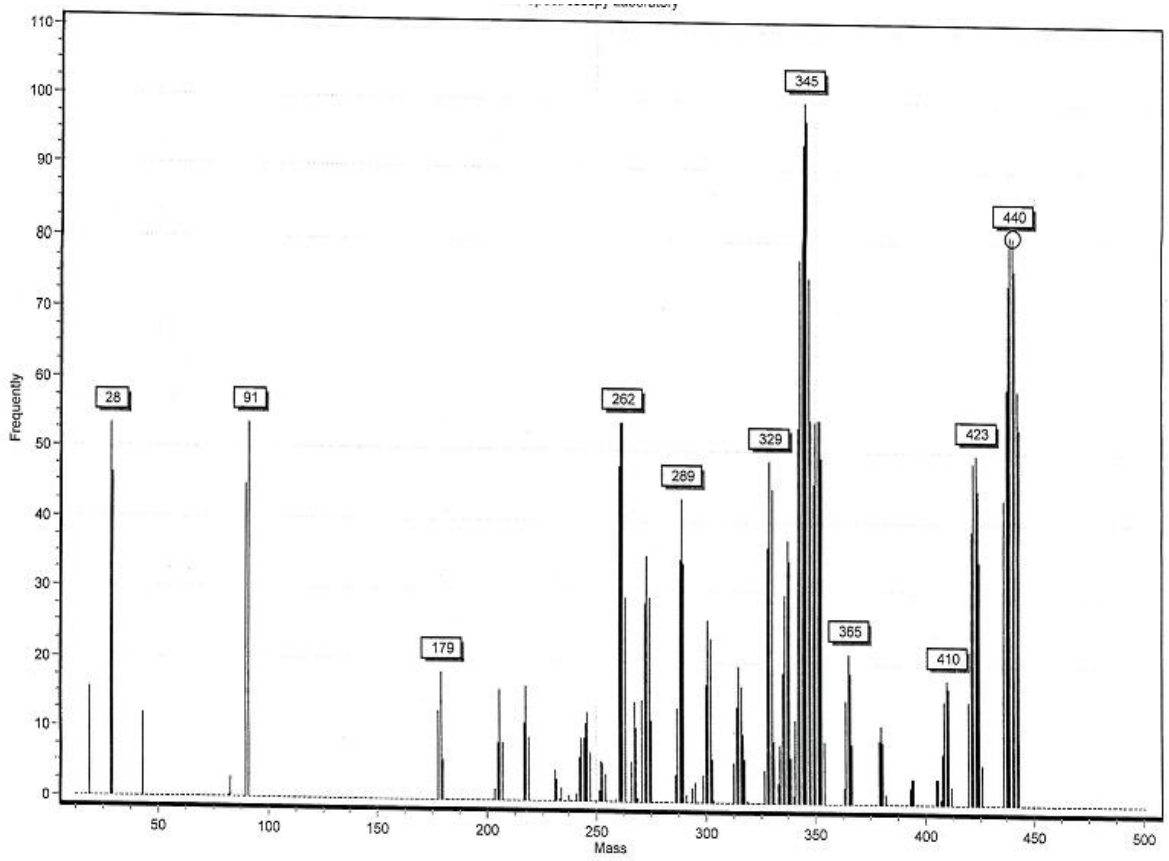


Figure 12: Mass spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4c**).

9-(4-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4d). Yellow solid; isolated yield: 95%; mp 253-255 °C (from EtOH) (lit.,[2] 254-256 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.67-7.58 (3H, m, Ph), 7.47-7.44 (4H, m, Ph), 7.28 (2H, d, *J* = 8.4 Hz, Ph), 5.03 (1H, s, CH), 2.56-2.19 (4H, m, 2CH_2), 2.02 (2H, d, *J* = 18 Hz, CH_2), 1.82 (2H, d, *J* = 18 Hz, CH_2), 0.89 (6H, s, 2CH_3), 0.73 (6H, s, 2CH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 151.0, 146.1, 138.8, 131.2, 130.5, 130.3, 129.9, 119.2, 112.9, 49.4, 41.4, 32.43, 32.31, 29.7, 26.6; MS, *m/z* (%): 505 (47%, M^++2), 503 (52%, M^+), 344 (71%, M^+-C_6H_4Br).

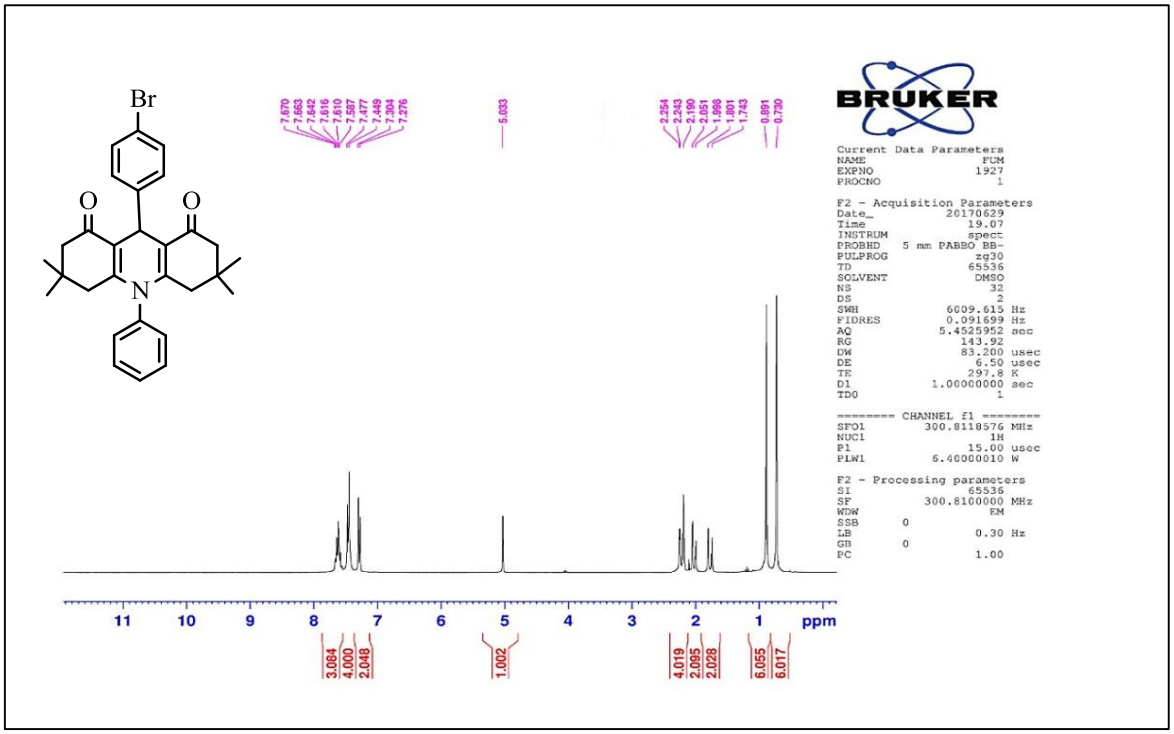


Figure 13: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4d**).

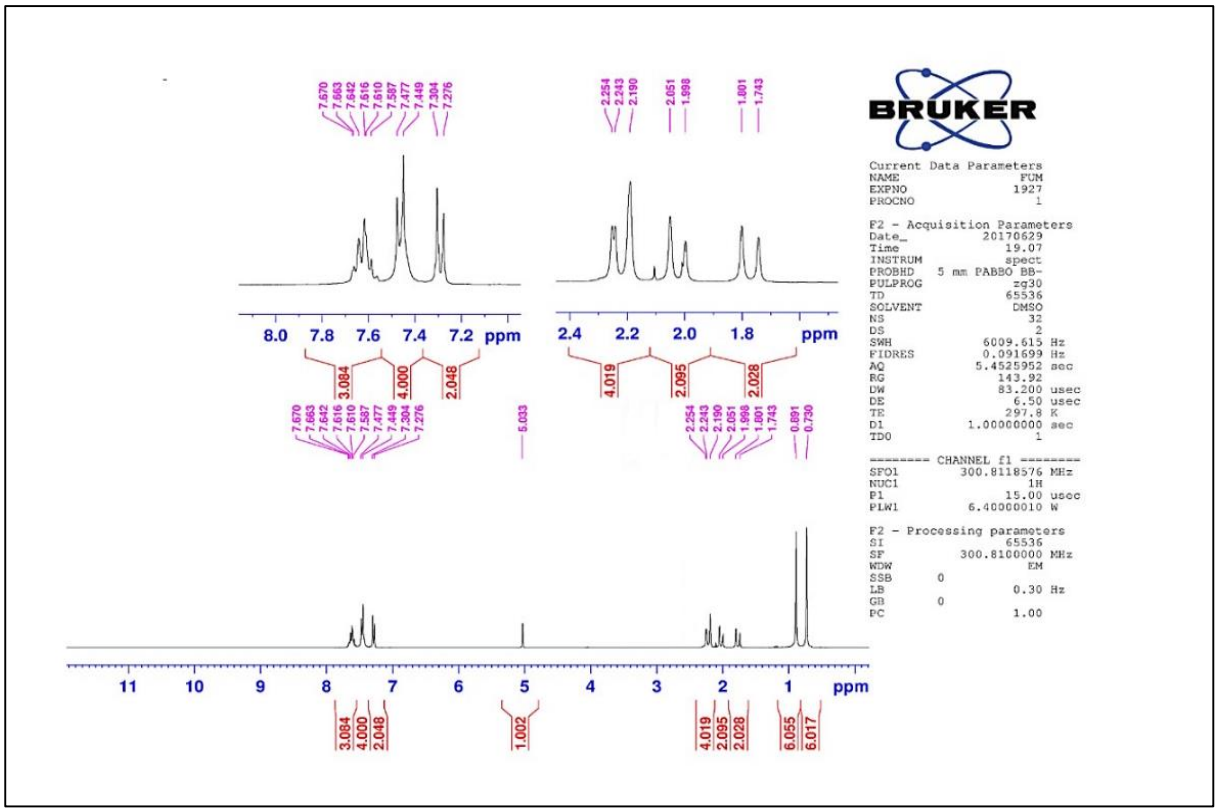


Figure 14: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4d**) expanded.

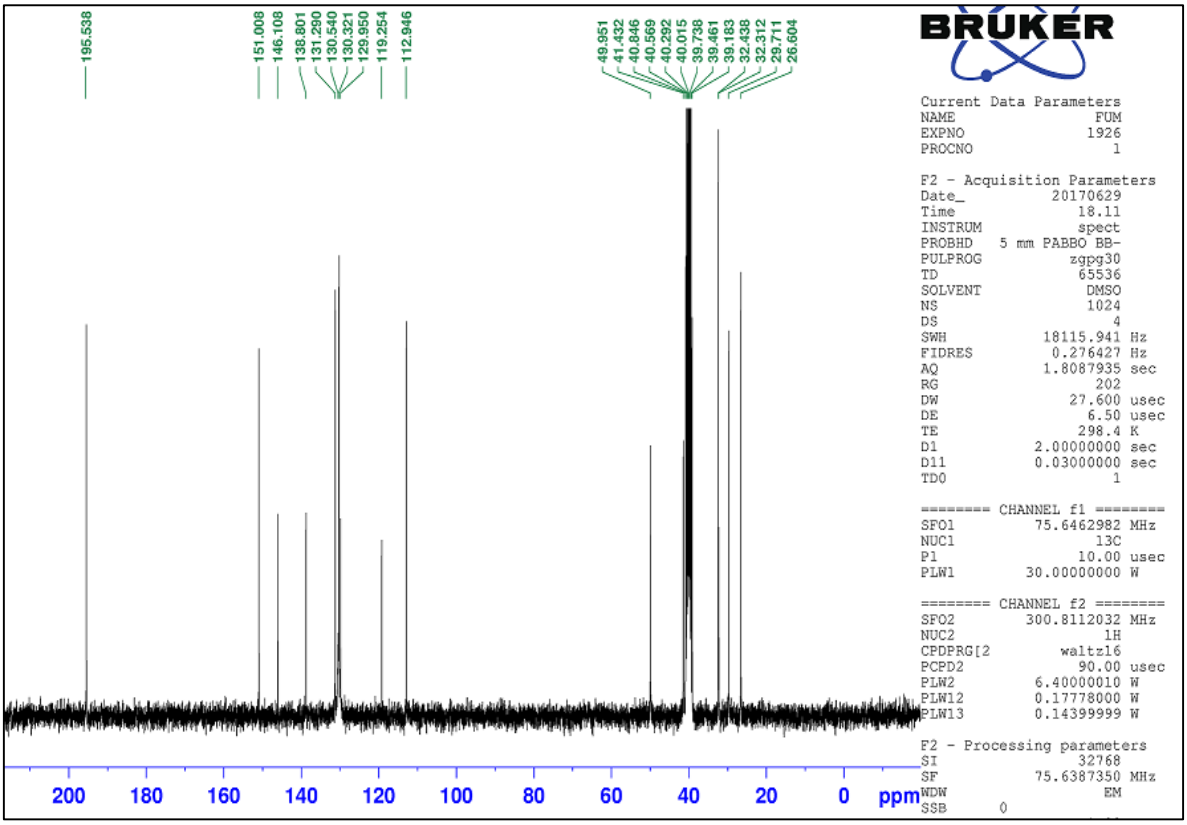


Figure 15: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4d**).

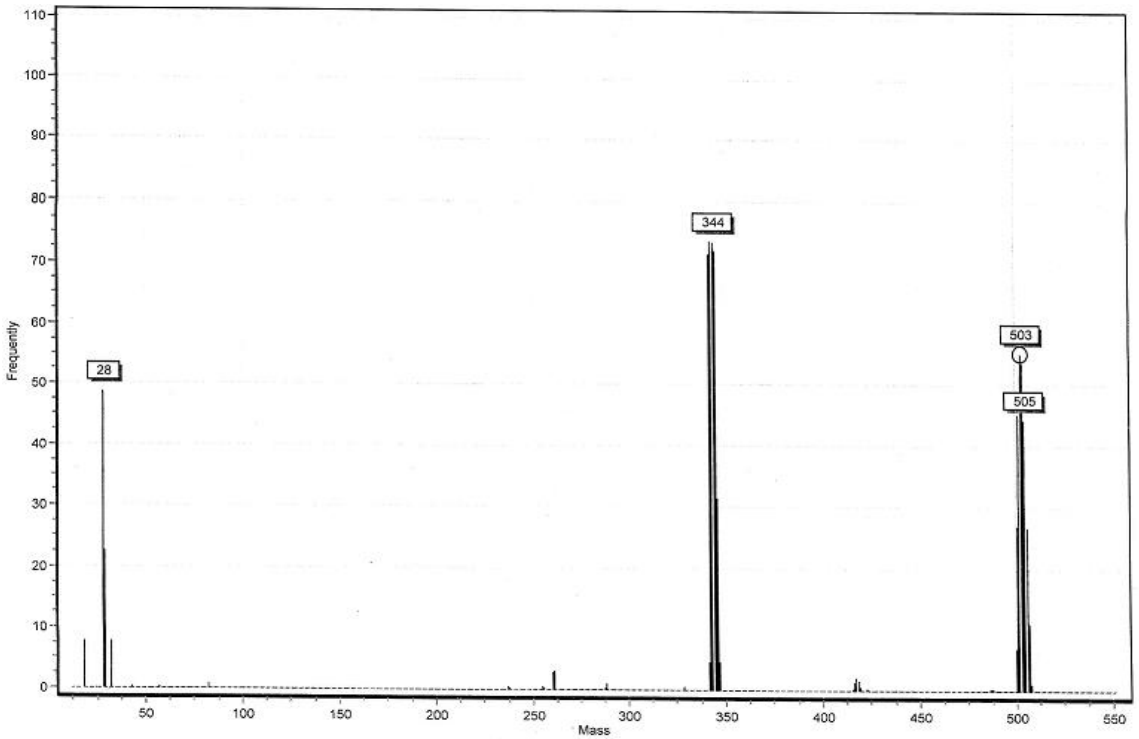


Figure 16: Mass spectrum of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4d**).

9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4e). Yellow solid; isolated yield: 90%; mp 250-252 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3175, 3059, 2955, 2879, 2810, 1647, 1609, 1489, 1145, 1011; ^{1}HNMR (300 MHz, DMSO-d_6): δ 7.67-7.58 (2H, m, Ph), 7.48 (1H, d, J = 1.5 Hz, Ph), 7.41-7.24 (6H, m, Ph), 5.04 (1H, s, CH), 2.26-2.19 (4H, m, $2CH_2$), 2.07-1.76 (4H, m, $2CH_2$), 0.89 (6H, s, $2CH_3$), 0.73 (6H, s, $2CH_3$); ^{13}CNMR (75 MHz, DMSO-d_6): δ 195.5, 151.1, 149.2, 138.7, 131.1, 130.8, 129.9, 129.1, 126.7, 121.5, 112.8, 49.9, 41.4, 32.4, 29.7, 26.5; MS, *m/z* (%): 504 (65%, M^+), 344 (100%, M^+- C_6H_4Br); Elemental analysis: Found: C, 69.08; H, 5.93; N, 2.79. Calc. for $C_{29}H_{30}BrNO_2$: C, 69.05; H, 5.99; N, 2.78%.

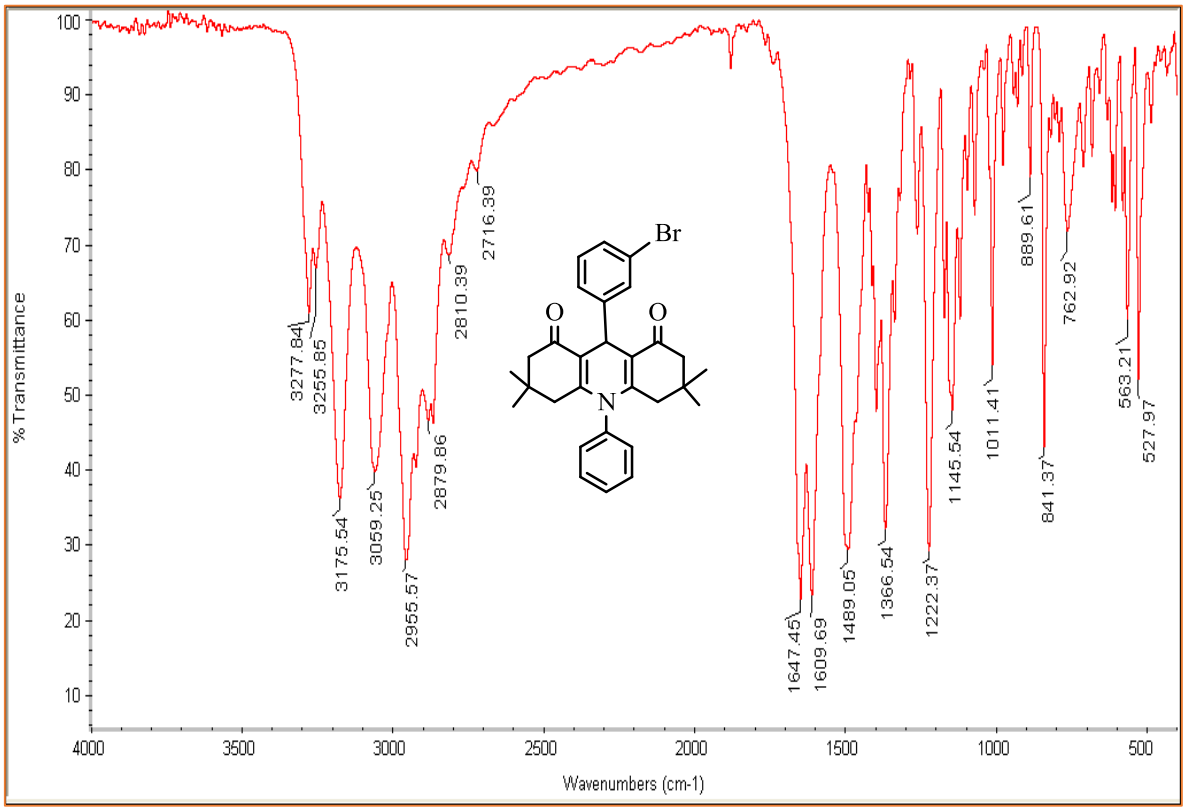


Figure 17: FT-IR (KBr) spectrum of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**).

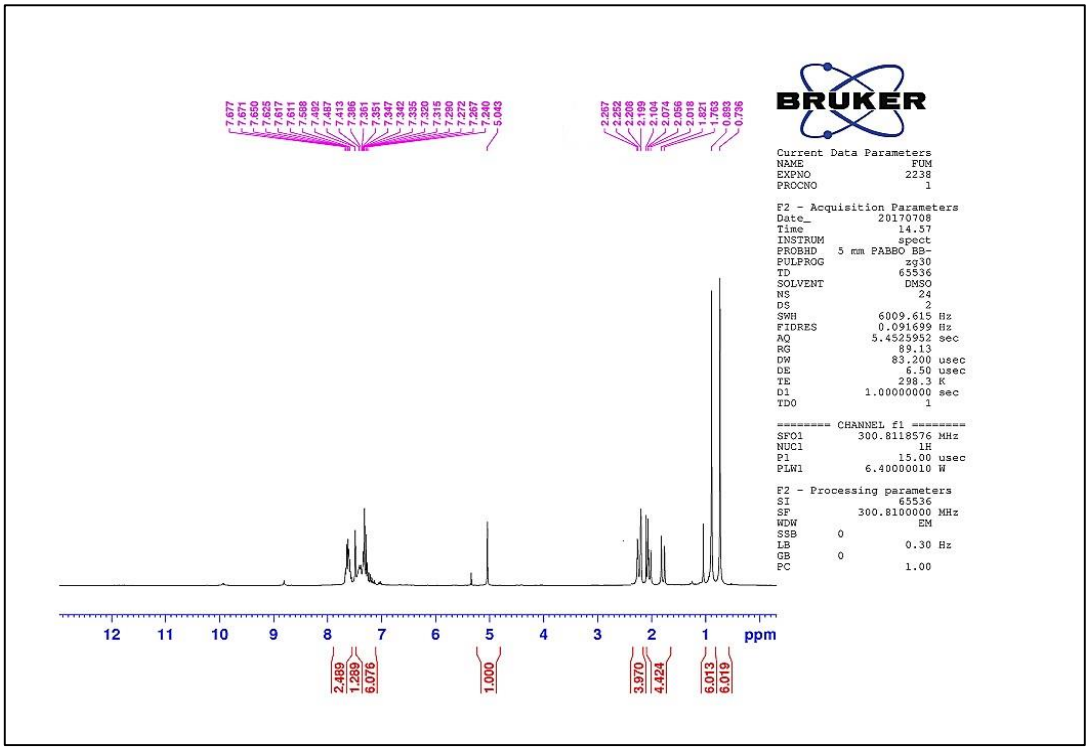


Figure 18: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**).

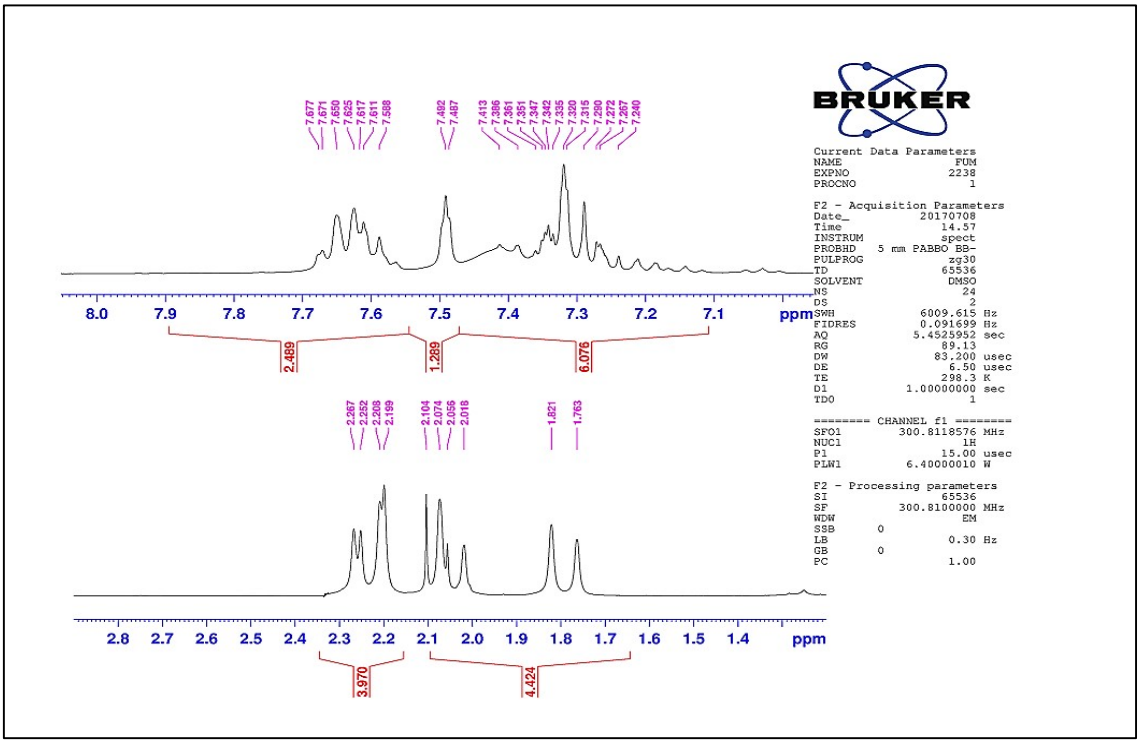


Figure 19: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**) expanded.

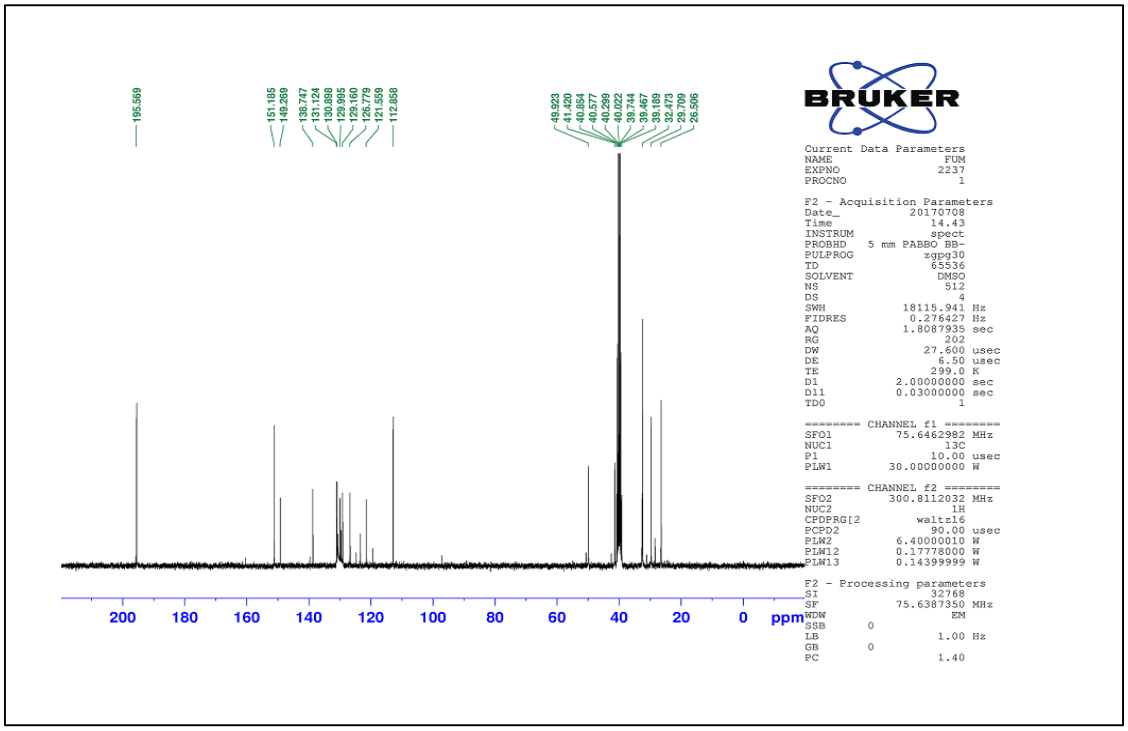


Figure 20: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**).

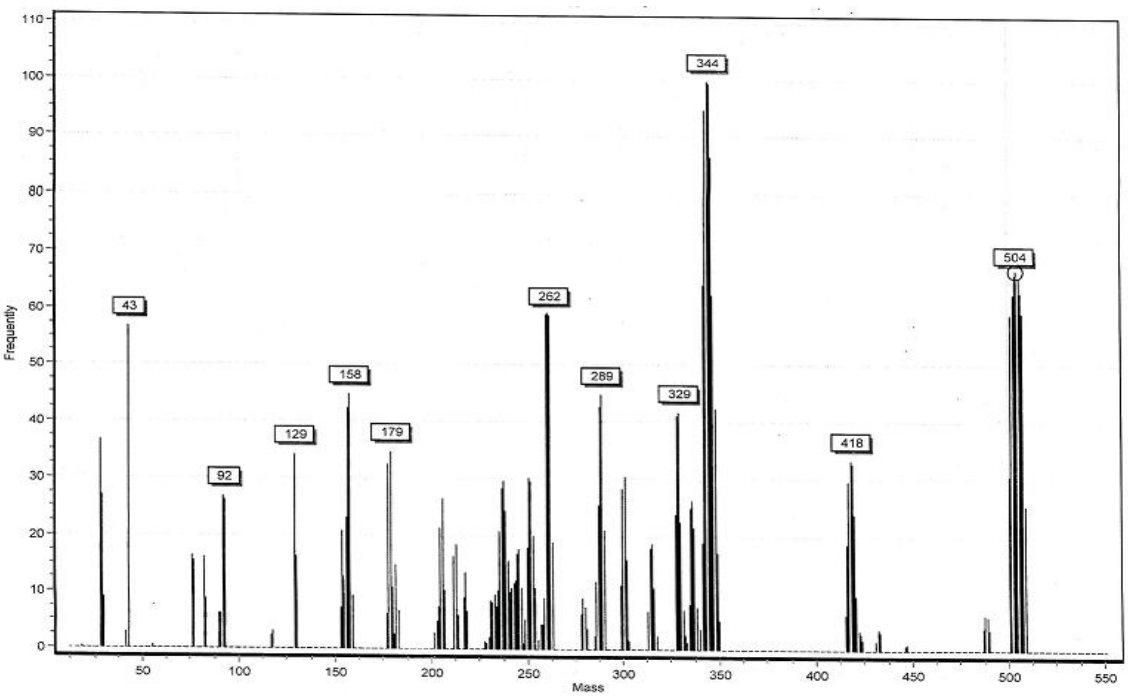
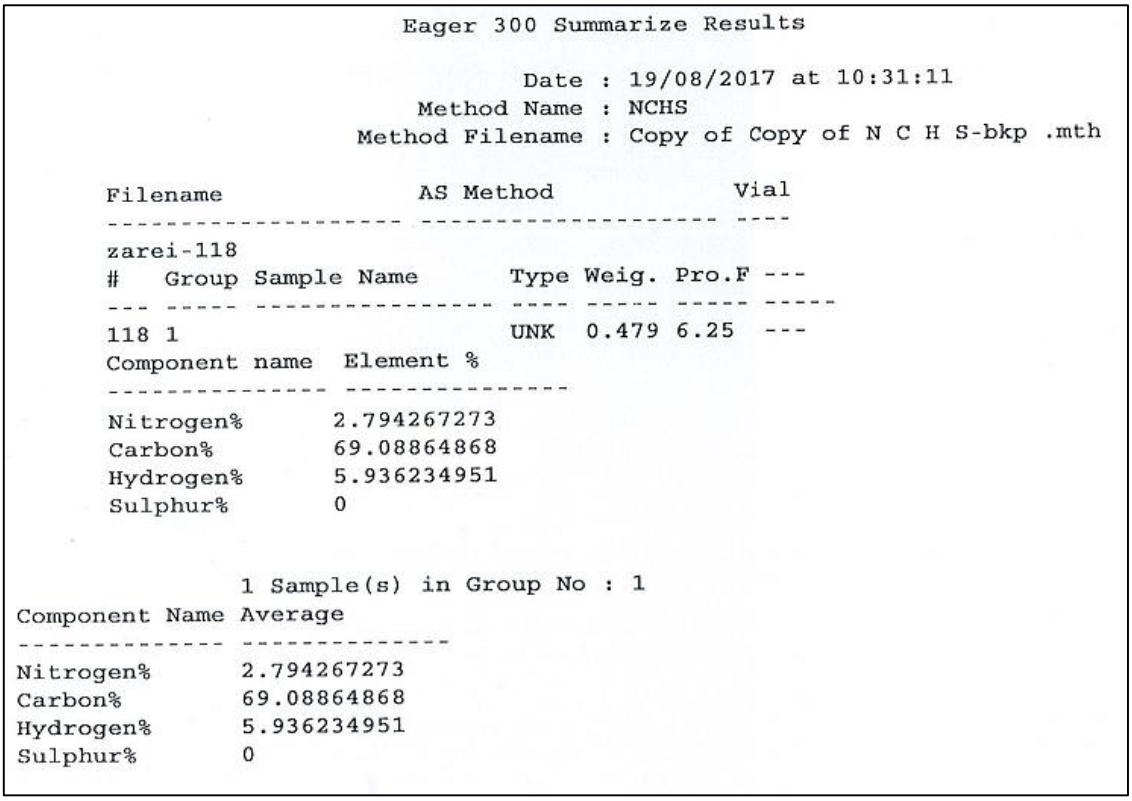


Figure 21: Mass spectrum of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**).



Eager 300 Summarize Results

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zarei-118		

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Component name	Element %
Nitrogen%	2.794267273
Carbon%	69.08864868
Hydrogen%	5.936234951
Sulphur%	0

1 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	2.794267273
Carbon%	69.08864868
Hydrogen%	5.936234951
Sulphur%	0

Figure 22: CHN analysis of 9-(3-bromophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4e**).

4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (4f). Yellow solid; isolated yield: 95%; mp 210-213 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3060, 3031, 2954, 2870, 2834, 2229, 1645, 1577, 1508, 1033; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.73 (2H, d, *J* = 8.1 Hz, Ph), 7.67-7.58 (3H, m, Ph), 7.54 (2H, d, *J* = 8.1 Hz, Ph), 7.48-7.46 (2H, m, Ph), 5.12 (1H, s, CH), 2.26-2.00 (4H, m, $2CH_2$), 2.05-1.76 (4H, m, $2CH_2$), 0.88 (6H, s, $2CH_3$), 0.71 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 152.0, 151.4, 138.6, 132.4, 130.5, 130.0, 129.2, 119.4, 112.4, 109.1, 49.8, 41.4, 33.4, 32.4, 29.6, 26.6; MS, *m/z* (%): 450 (88%, M^+), 344 (100%, M^+- C_7H_4N); Elemental analysis: Found: C, 79.92; H, 6.72; N, 6.21. Calc. for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22%.

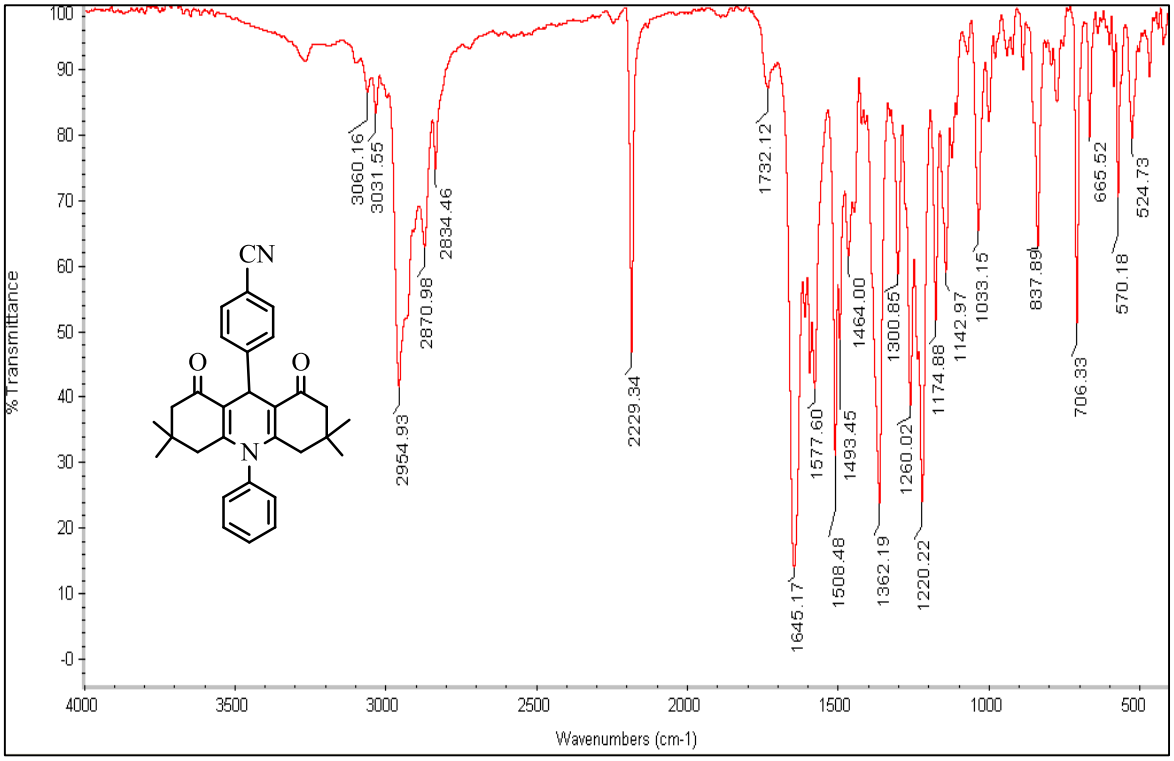

Figure 23: FT-IR (KBr) spectrum of 4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**).

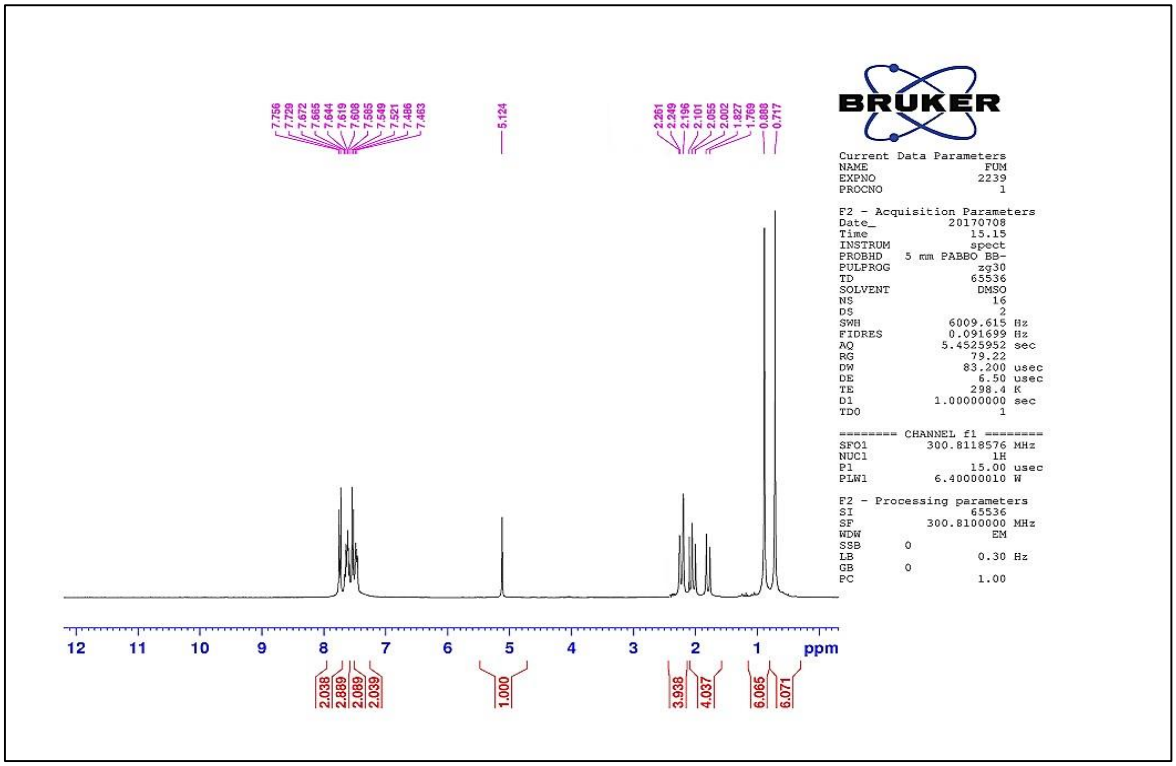

Figure 24: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**).

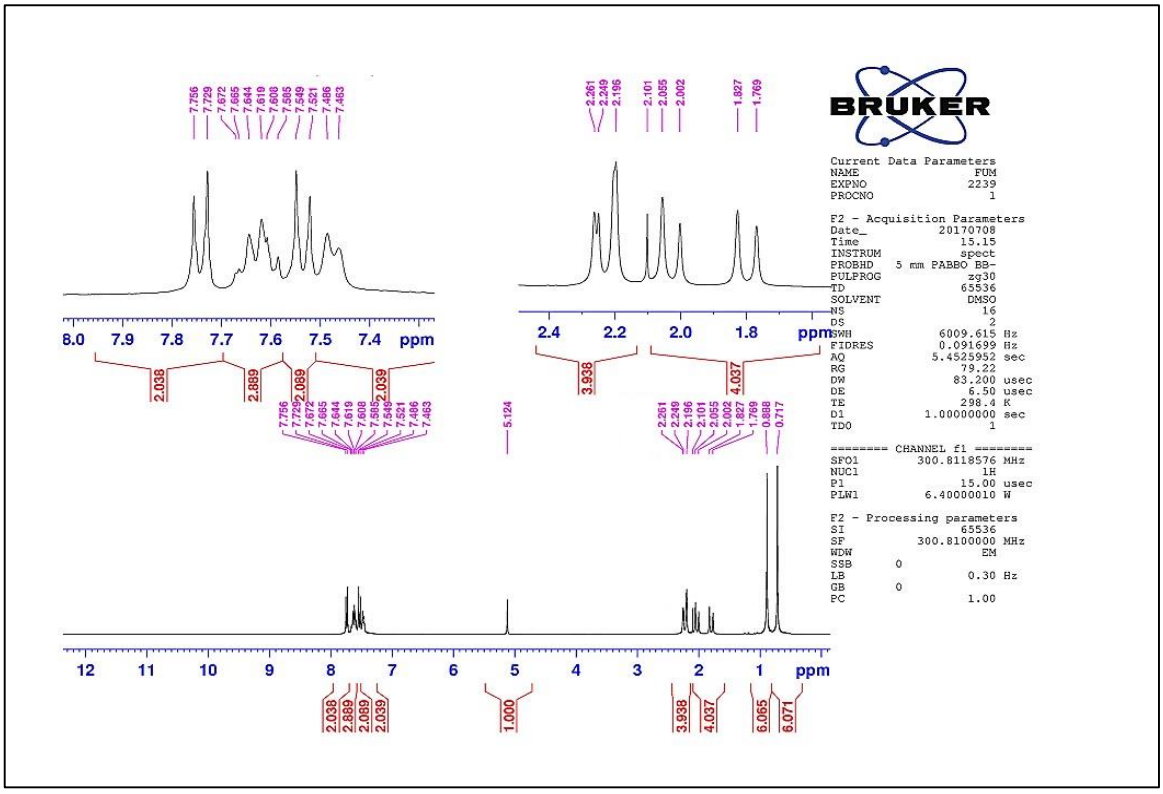

Figure 25: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**) expanded.

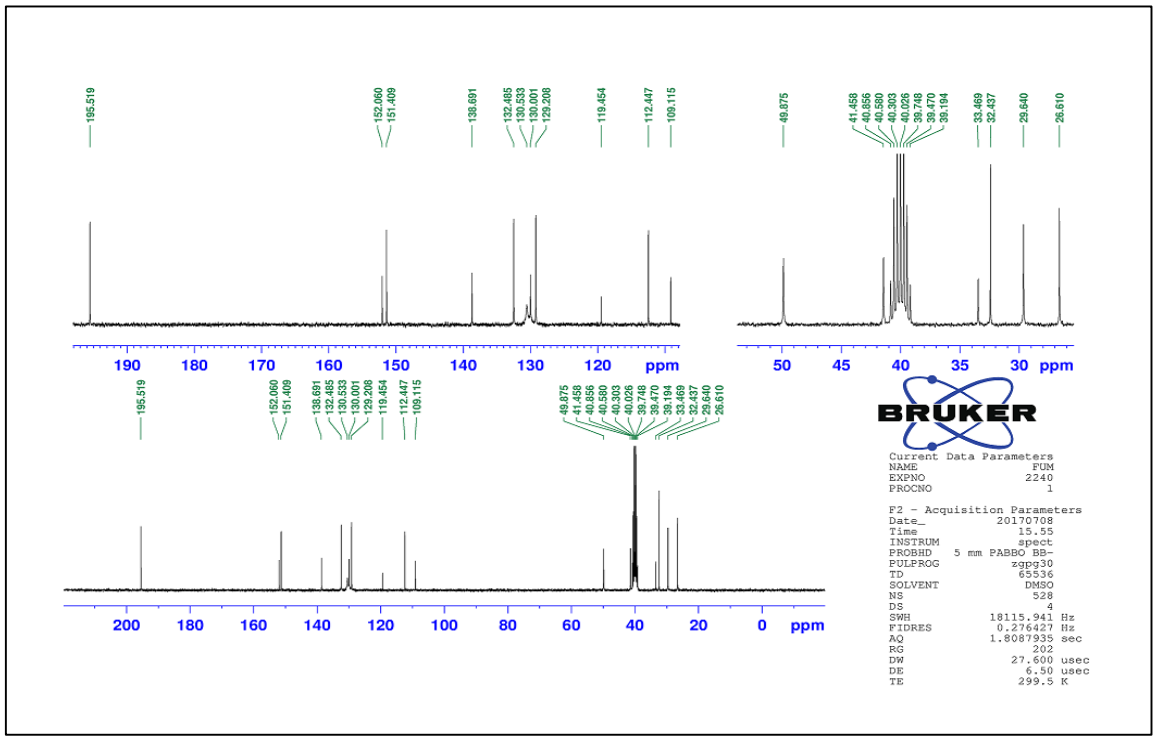

Figure 26: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**).

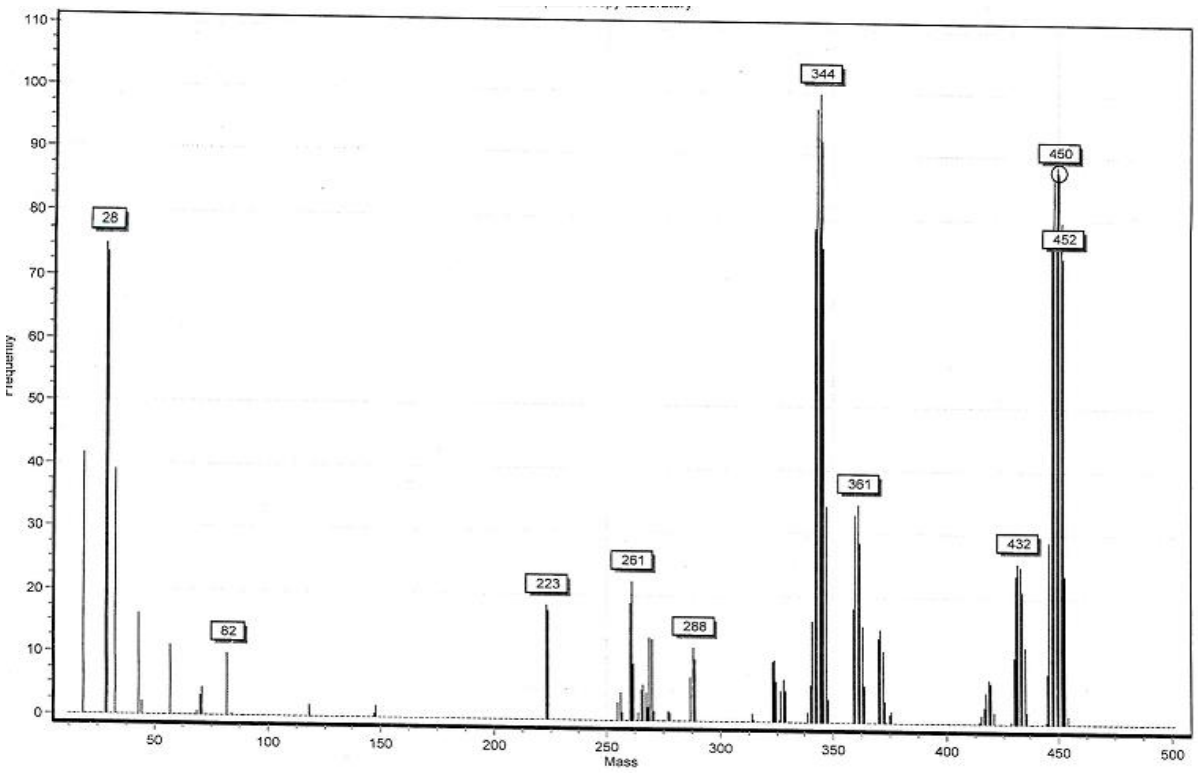

Figure 27: Mass spectrum of 4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**).

Eager 300 Summarize Results

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Carbon%	79.92004211
Hydrogen%	6.727438927
Sulphur%	0

1 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	6.214727211
Carbon%	79.92004211
Hydrogen%	6.727438927
Sulphur%	0

Figure 28: CHN analysis of 4-(3,3,6,6-tetramethyl-1,8-dioxo-10-phenyl-1,2,3,4,5,6,7,8,9,10-decahydroacridin-9-yl)benzonitrile (**4f**).

3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4g). Yellow solid; isolated yield: 85%; mp 205-207 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3060, 3028, 2954, 2929, 2868, 1641, 1573, 1512; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.46 (2H, d, *J* = 6 Hz, Pyridine), 7.64-7.59 (3H, m, Ph), 7.47-7.45 (2H, m, Ph), 7.30 (2H, d, *J* = 6 Hz, Pyridine), 5.04 (1H, s, CH), 2.26-2.20 (4H, m, $2CH_2$), 2.04 (2H, d, *J* = 15 Hz, CH_2), 1.78 (2H, d, *J* = 15 Hz, CH_2), 0.89 (6H, s, $2CH_3$), 0.73 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 154.5, 151.5, 149.9, 138.6, 130.0, 123.3, 112.0, 49.8, 41.4, 32.5, 32.4, 29.6, 26.6; MS, *m/z* (%): 426 (64%, M^+), 344 (100%, M^+- C_4H_4N); Elemental analysis: Found: C, 78.54; H, 7.05; N, 6.54. Calc. for $C_{28}H_{30}N_2O_2$: C, 78.84; H, 7.09; N, 6.57%.

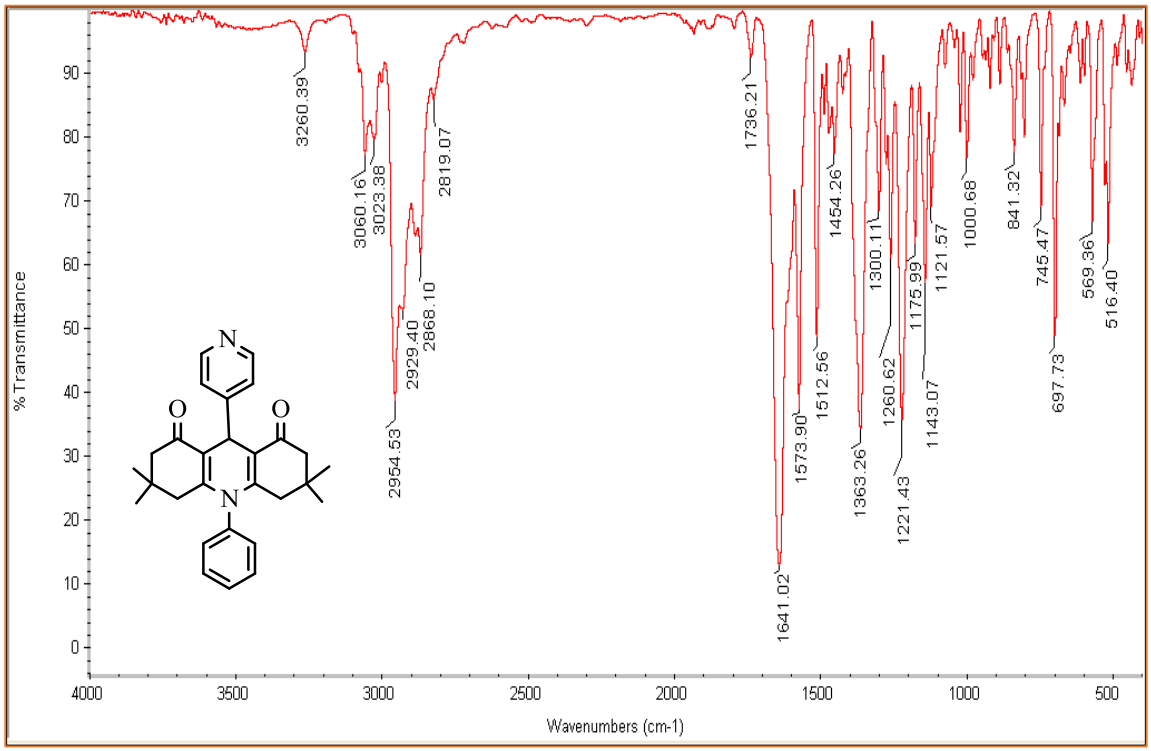


Figure 29: FT-IR (KBr) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**).

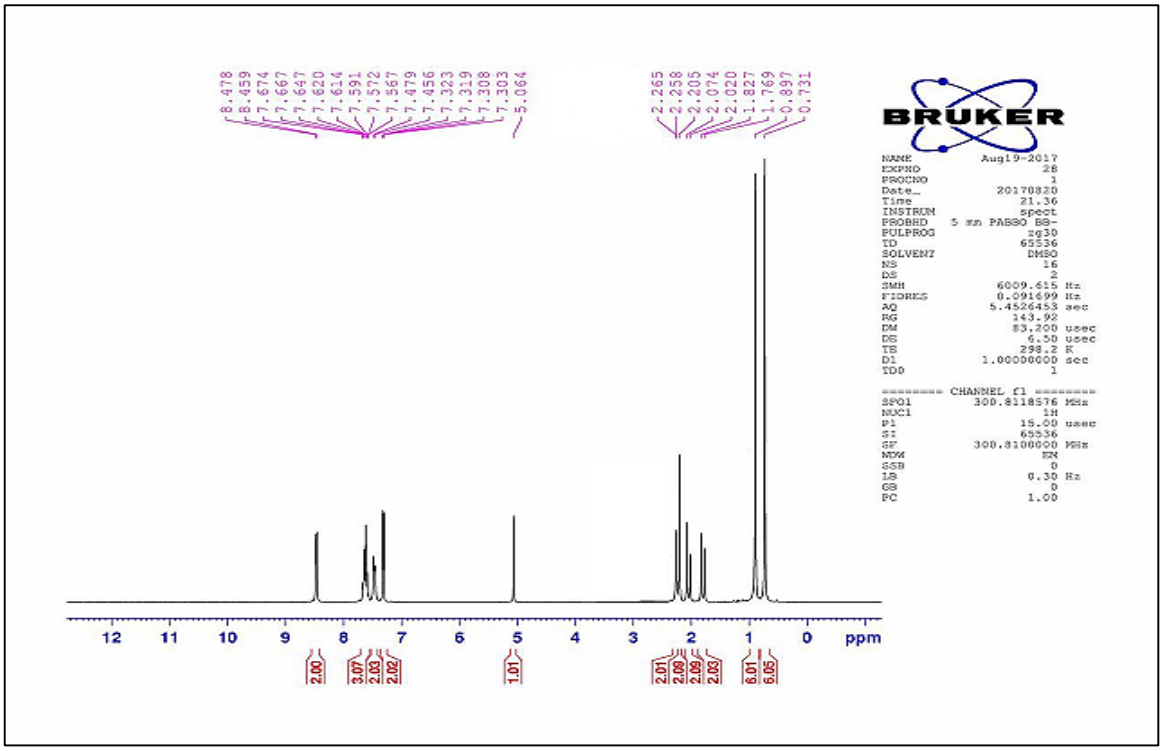


Figure 30: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**).

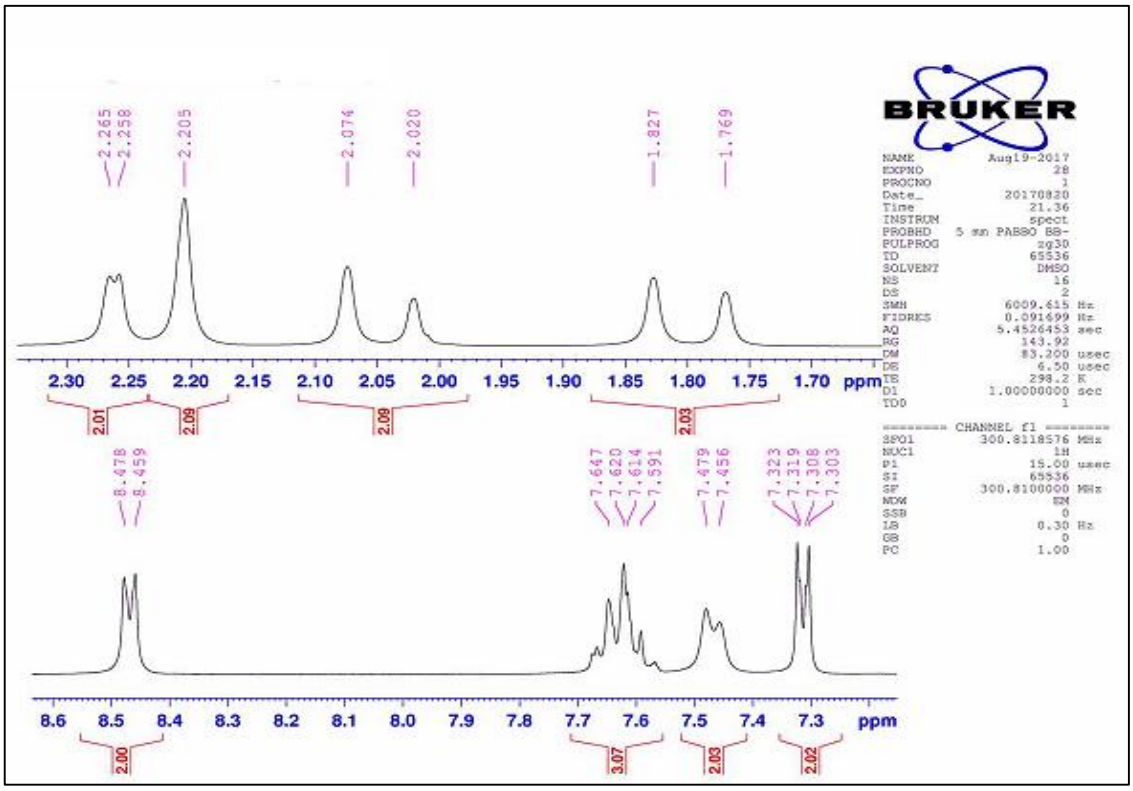


Figure 31: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**) expanded.

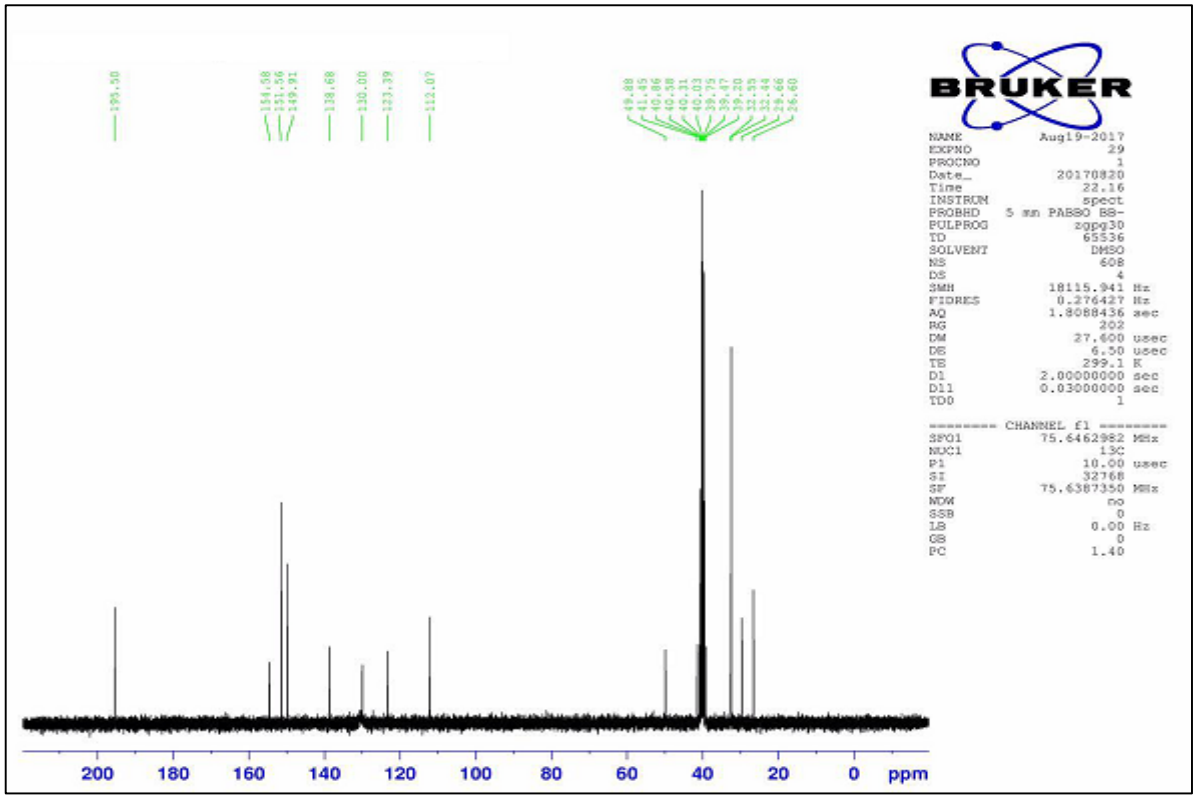


Figure 32: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**).

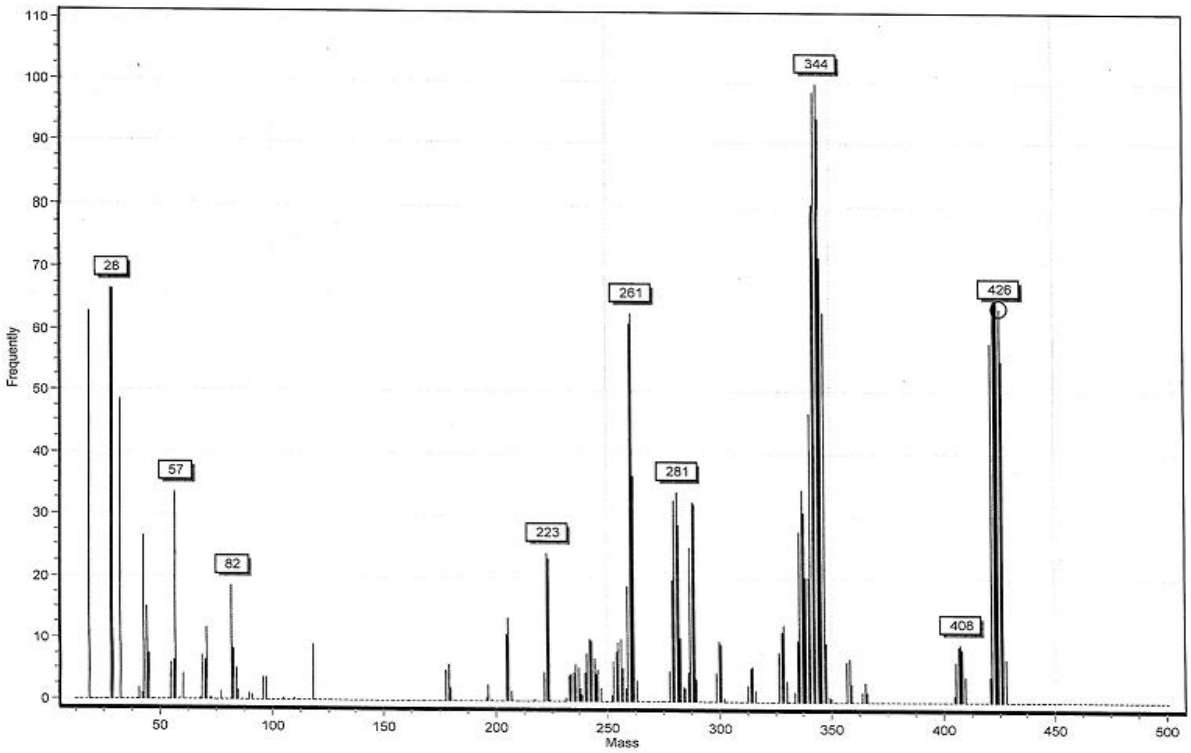
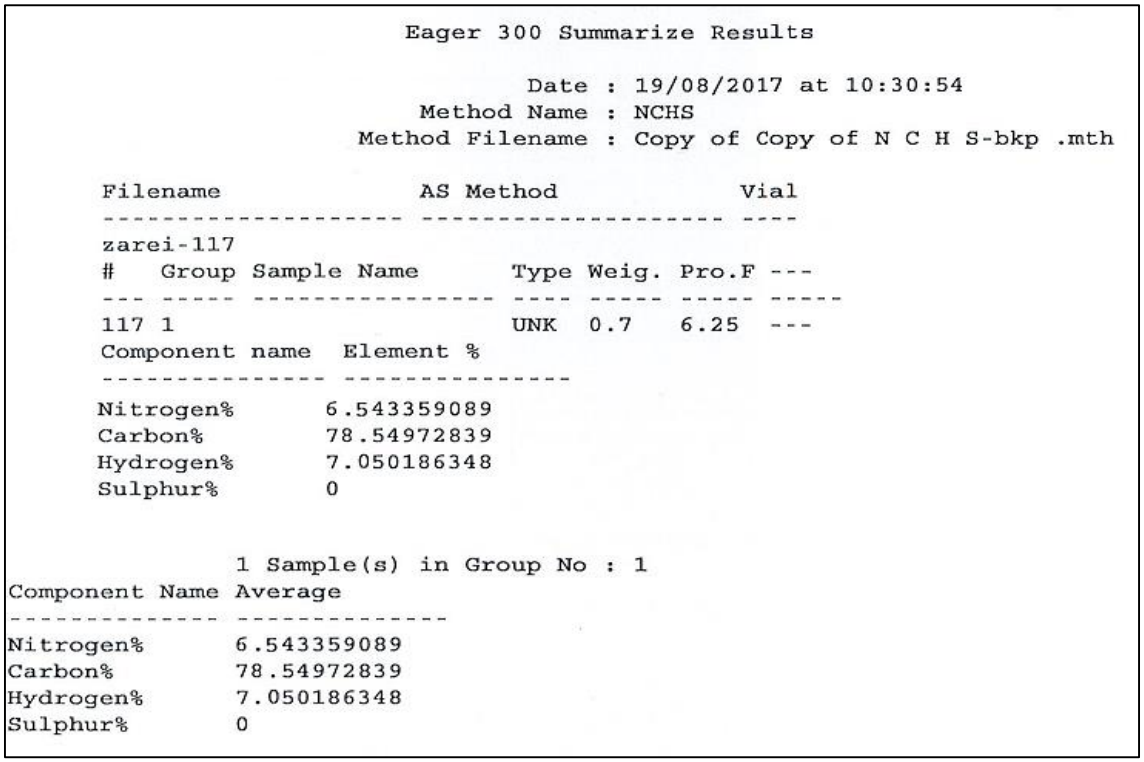


Figure 33: Mass spectrum of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**).



Eager 300 Summarize Results

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Hydrogen%	7.050186348
Sulphur%	0

1 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	6.543359089
Carbon%	78.54972839
Hydrogen%	7.050186348
Sulphur%	0

Figure 34: CHN analysis of 3,3,6,6-tetramethyl-10-phenyl-9-(pyridin-4-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4g**).

10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4h). Yellow solid; isolated yield: 90%; mp 213-215 °C (from EtOH) (lit.,[2] 215-216 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.39-7.28 (3H, m, Ph), 7.26-7.08 (6H, m, Ph), 5.07 (1H, s, CH), 3.87 (3H, s, OCH_3), 2.53-2.18 (4H, m, $2CH_2$), 2.04-1.80 (4H, m, $2CH_2$), 0.90 (6H, s, $2CH_3$), 0.73 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 159.7, 151.3, 146.7, 131.4, 128.3, 127.9, 126.2, 115.4, 113.3, 60.2, 55.9, 50.0, 32.3, 32.3, 29.8, 26.5; MS, *m/z* (%): 545(68%, M^+), 374 (73%, M^+- C_6H_5), 43 (100%, $COCH_2$).

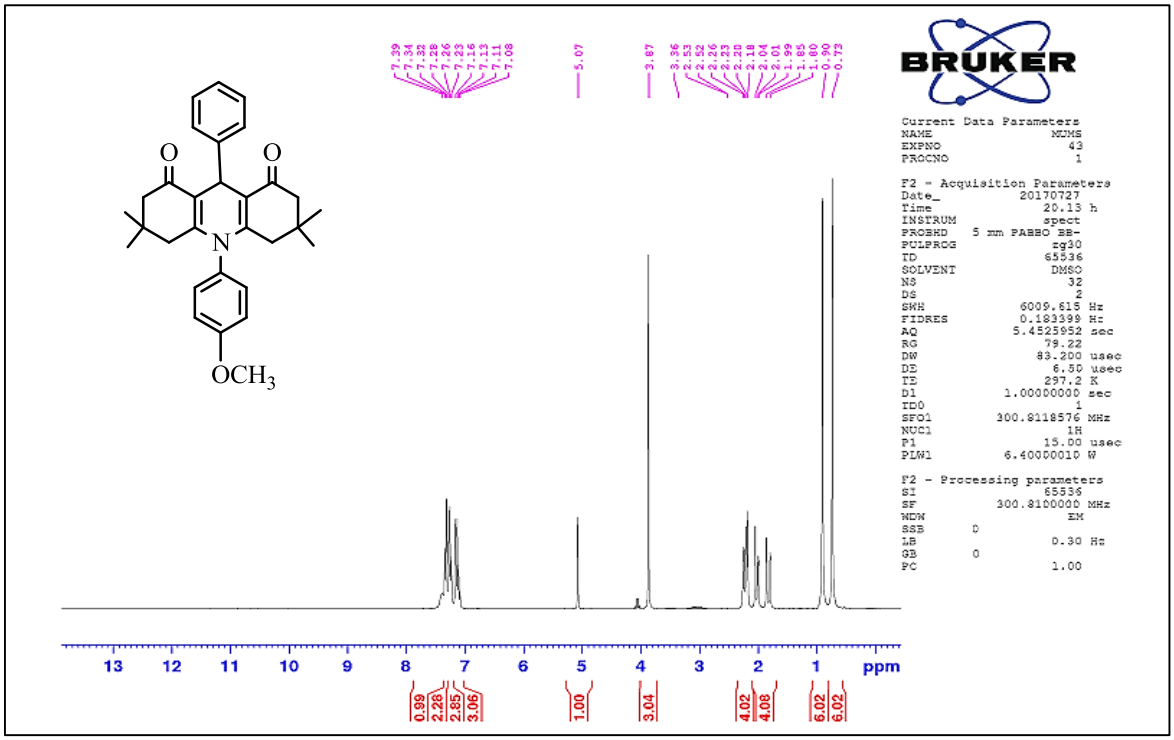

Figure 35: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4h**).

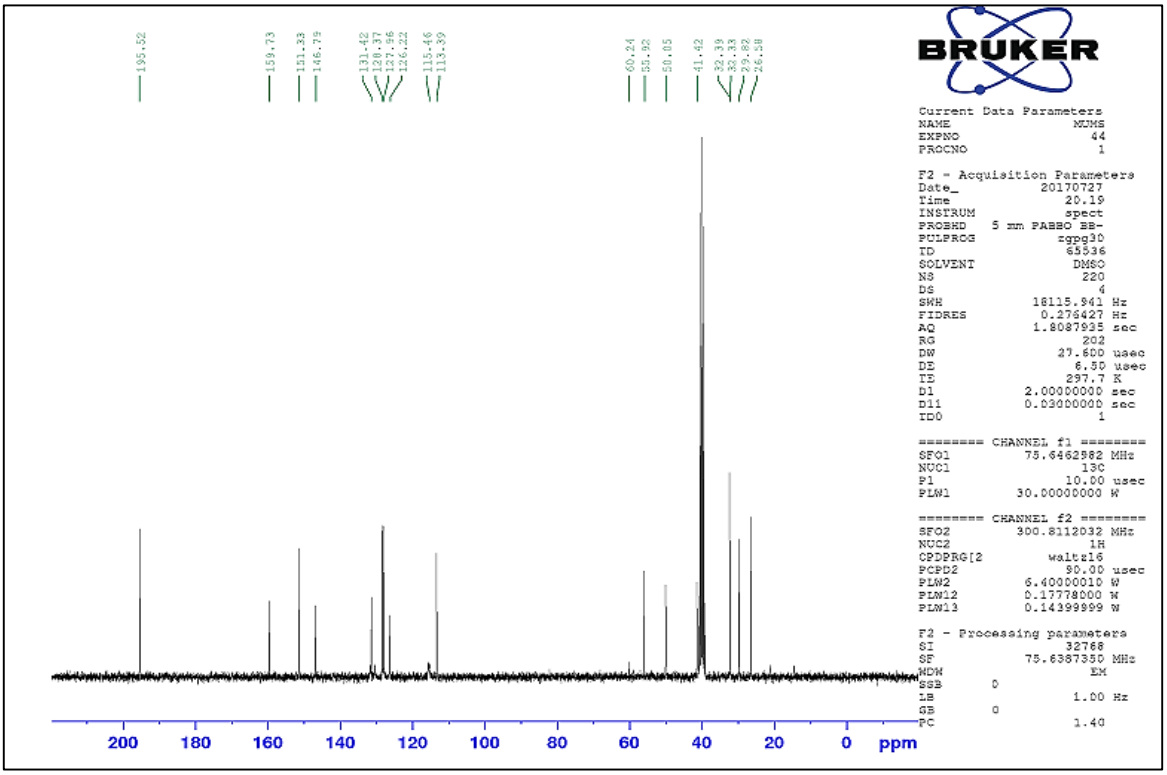

Figure 36: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4h**).

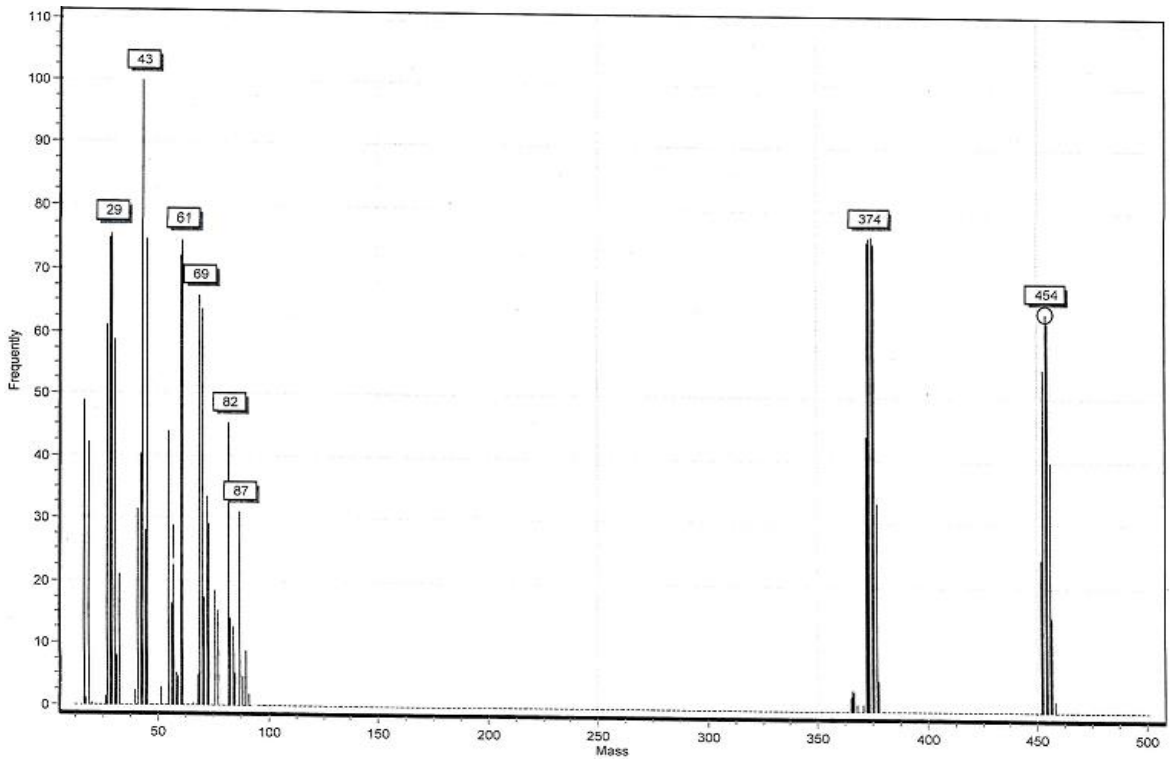

Figure 37: Mass spectrum of 10-(4-methoxyphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4h**).

10(3,4dimethylphenyl)3,3,6,6tetramethyl9phenyl3,4,6,7,9,10hexahydroacridine1,8(2*H*,5*H*)-dione (4i). Yellow solid; isolated yield: 90%; mp 251-253 °C (from EtOH); IR (KBr): ν_{max}/cm^{-1} 3084, 3031, 2960, 2937, 2872, 2822, 1641, 1575, 1176, 1141, 998; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.38-7.33 (3H, m, Ph), 7.28-7.23 (2H, m, Ph), 7.12-7.08 (3H, m, Ph), 5.08 (1H, s, CH), 6.05 (6H, s, $2CH_3$), 2.26-2.17 (4H, m, $2CH_2$), 2.0 (2H, d, J = 15 Hz, $2CH_2$), 1.82 (2H, d, J = 15 Hz, $2CH_2$), 0.89 (6H, s, $2CH_3$), 0.73 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.4, 151.0, 146.8, 138.1, 136.5, 128.3, 128.0, 126.2, 113.3, 50.0, 41.3, 32.4, 32.3, 29.7, 26.6, 19.9, 18.6; MS, *m/z* (%): 454 (28%, M^+), 374 (100%, M^+- C_6H_5), 346 (25%, M^+- C_8H_9), 77 (14%, C_6H_5); Elemental analysis: Found: C, 82.09; H, 7.22; N, 3.76. Calc. for $C_{31}H_{35}NO_2$: C, 82.08; H, 7.78; N, 3.09%.

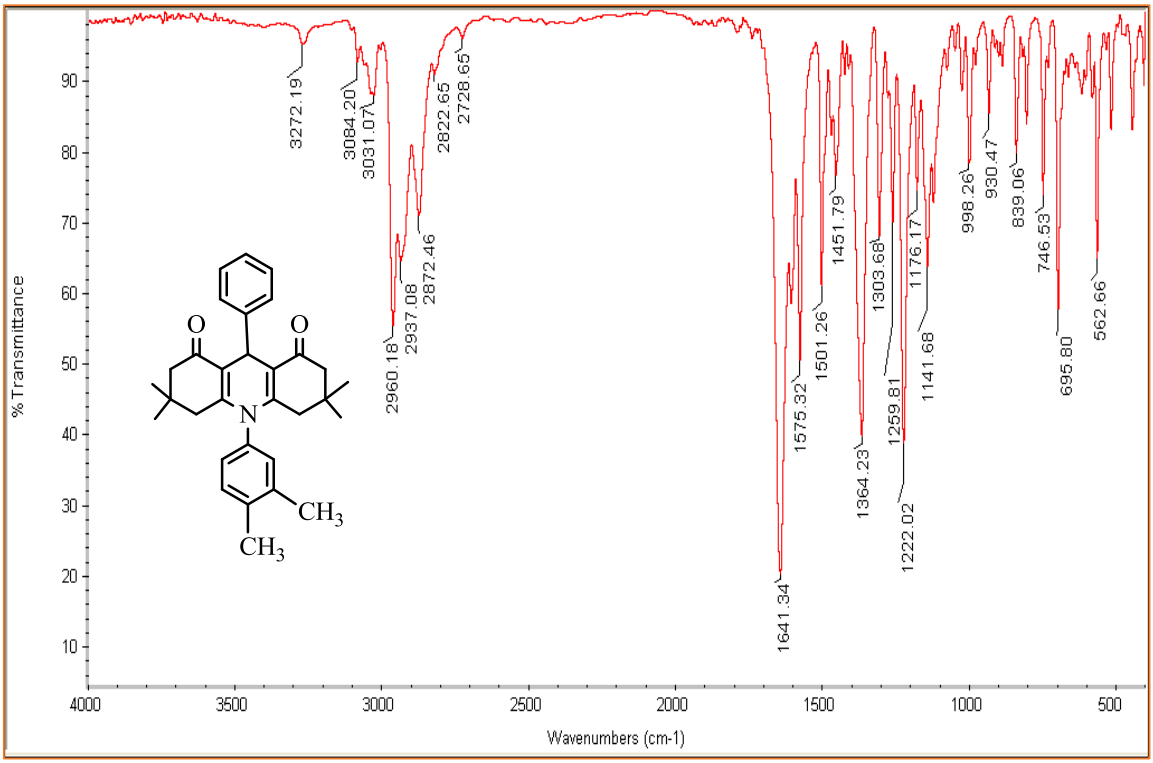

Figure 38: FT-IR (KBr) spectrum of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**).

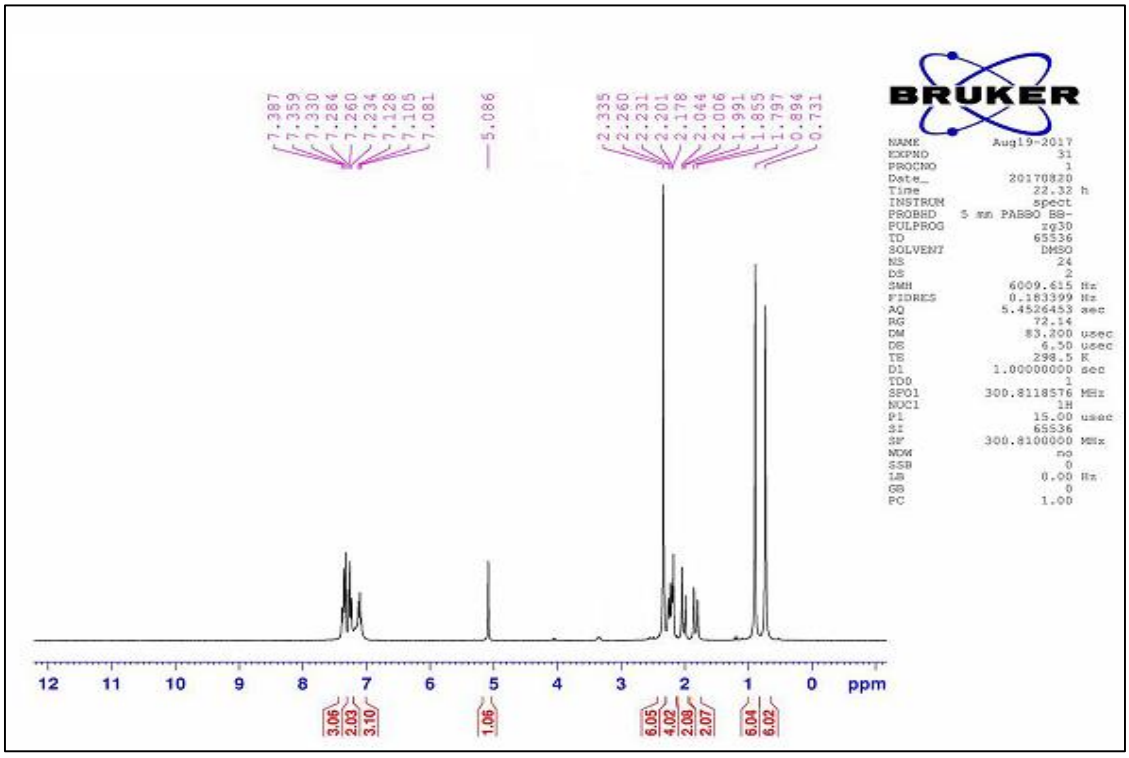

Figure 39: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**).

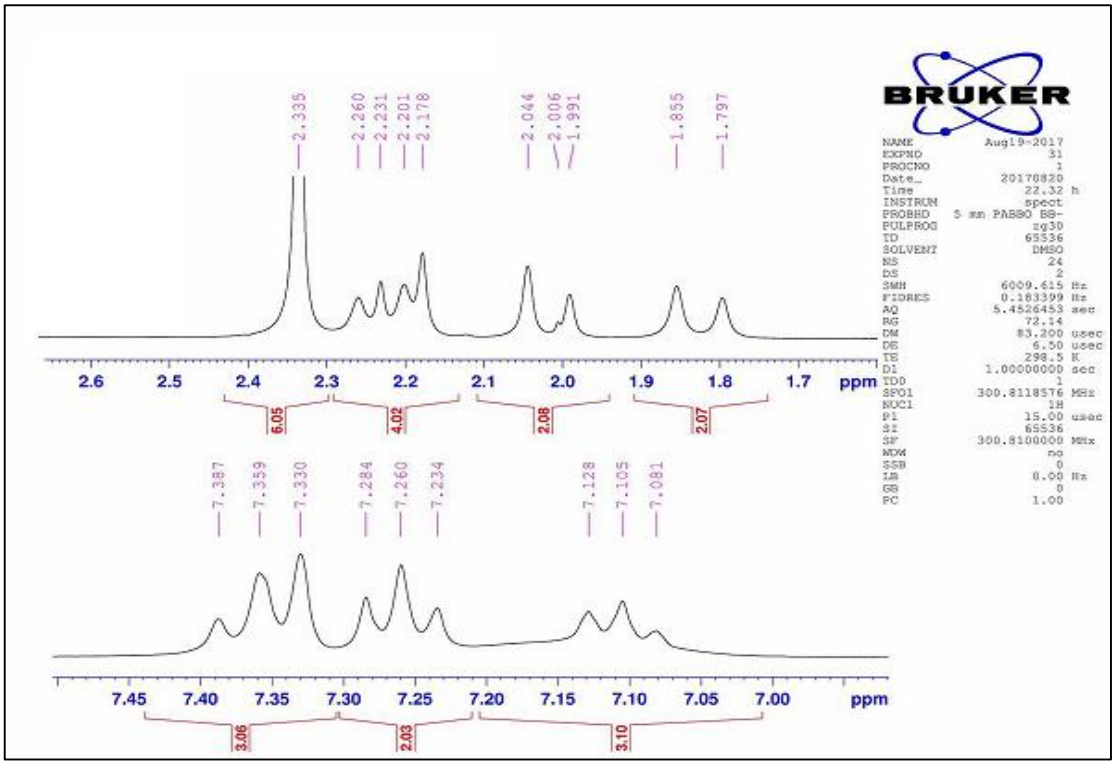

Figure 40: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**) expanded.

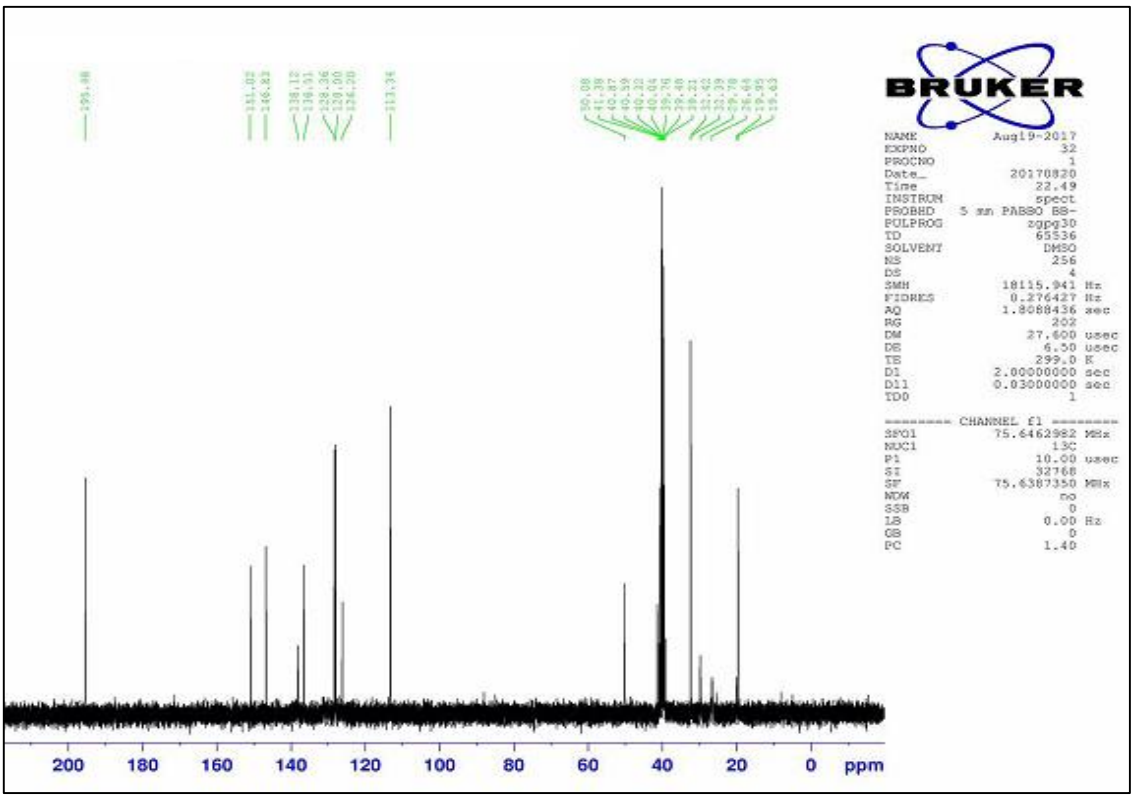

Figure 41: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**).

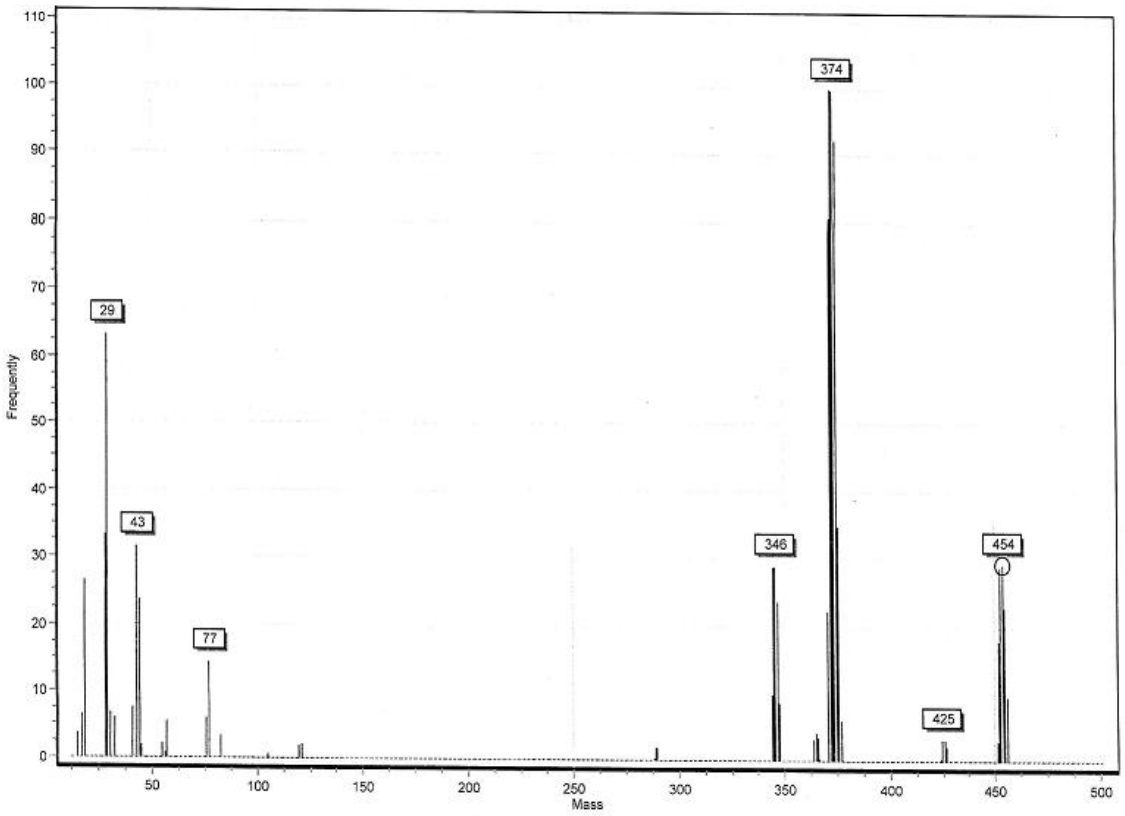

Figure 42: Mass spectrum of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**).

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                        Eager 300 Summarize Results

                                    Date : 19/08/2017 at 10:31:24
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      Component name  Element %
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      Carbon%         82.09004211
      Hydrogen%       7.227438927
      Sulphur%        0


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Component Name  Average
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Nitrogen%       3.764727211
Carbon%         82.09004211
Hydrogen%       7.227438927
Sulphur%        0
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Figure 43: CHN analysis of 10-(3,4-dimethylphenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4i**).

3,3,6,6-tetramethyl-9-phenyl-10-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4j). Yellow solid; isolated yield: 92%; mp 259-261 °C (from EtOH) (lit., [1] 260-262 °C); MS, *m/z* (%): 440 (70%, M^+), 43 (46%, $COCH_2$).

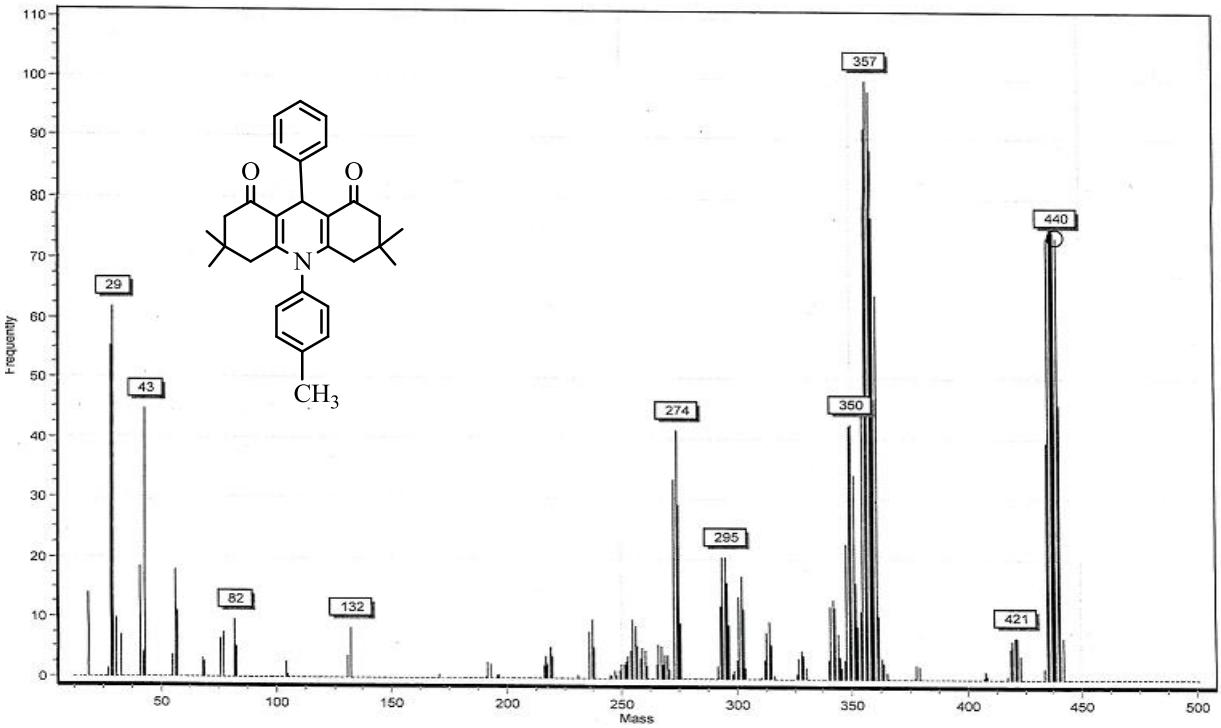


Figure 44: Mass spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*p*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4j**).

3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4k). Yellow solid; isolated yield: 95%; mp 262-264 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3064, 3031, 2958, 2869, 2819, 1641, 1577, 1143, 1122; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.53-7.48 (1H, m, Ph), 7.40-7.33 (3H, m, Ph), 7.28-7.23 (3H, m, Ph), 7.13-7.08 (2H, m, Ph), 5.08 (1H, s, CH), 2.43 (3H, s, CH_3), 2.26-2.18 (4H, m, $2CH_2$), 2.0 (2H, d, *J* = 15 Hz, $2CH_2$), 1.82 (2H, d, *J* = 15 Hz, $2CH_2$), 0.89 (6H, s, $2CH_3$), 0.73 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 150.8, 146.8, 138.8, 130.5, 128.3, 128.0, 126.2, 113.3, 50.0, 41.3,

32.4, 29.7, 26.6, 21.3; MS, *m/z* (%): 440 (68%, M^+), 43 (52%, $COCH_2$); Elemental analysis: Found: C, 81.92; H, 7.57; N, 3.18. Calc. for $C_{30}H_{33}NO_2$: C, 81.97; H, 7.57; N, 3.19%.

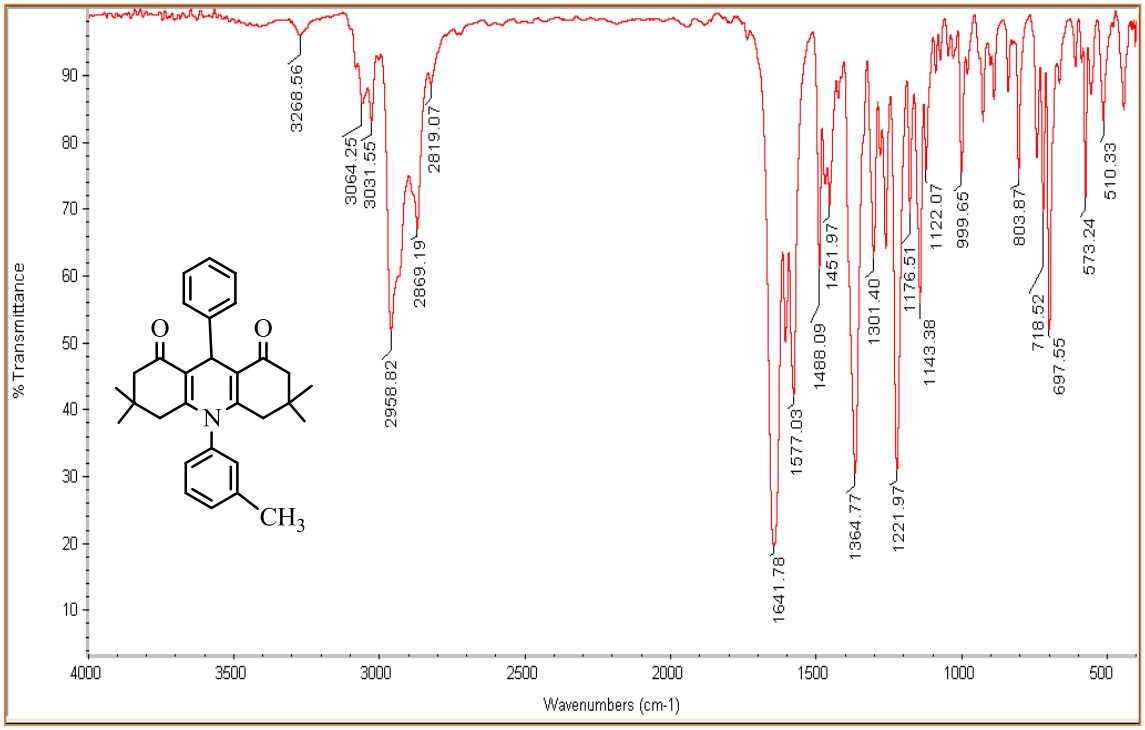


Figure 45: FT-IR (KBr) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**).

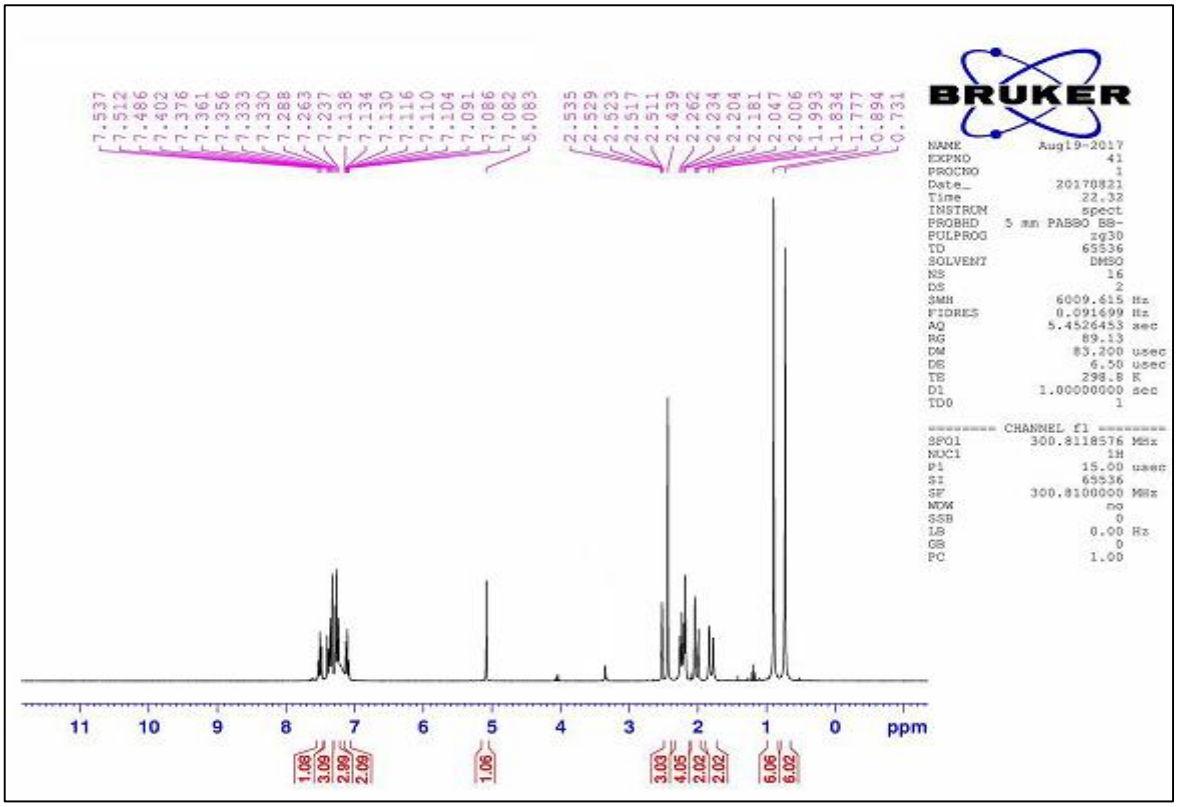


Figure 46: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**).

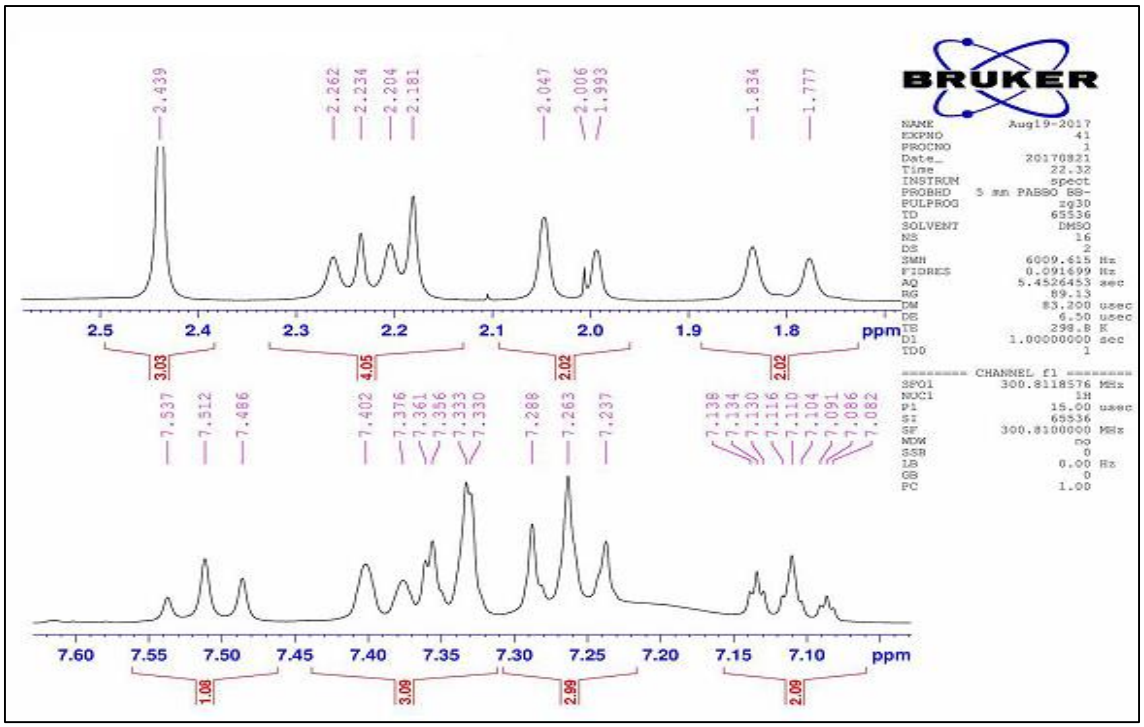


Figure 47: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**) expanded.

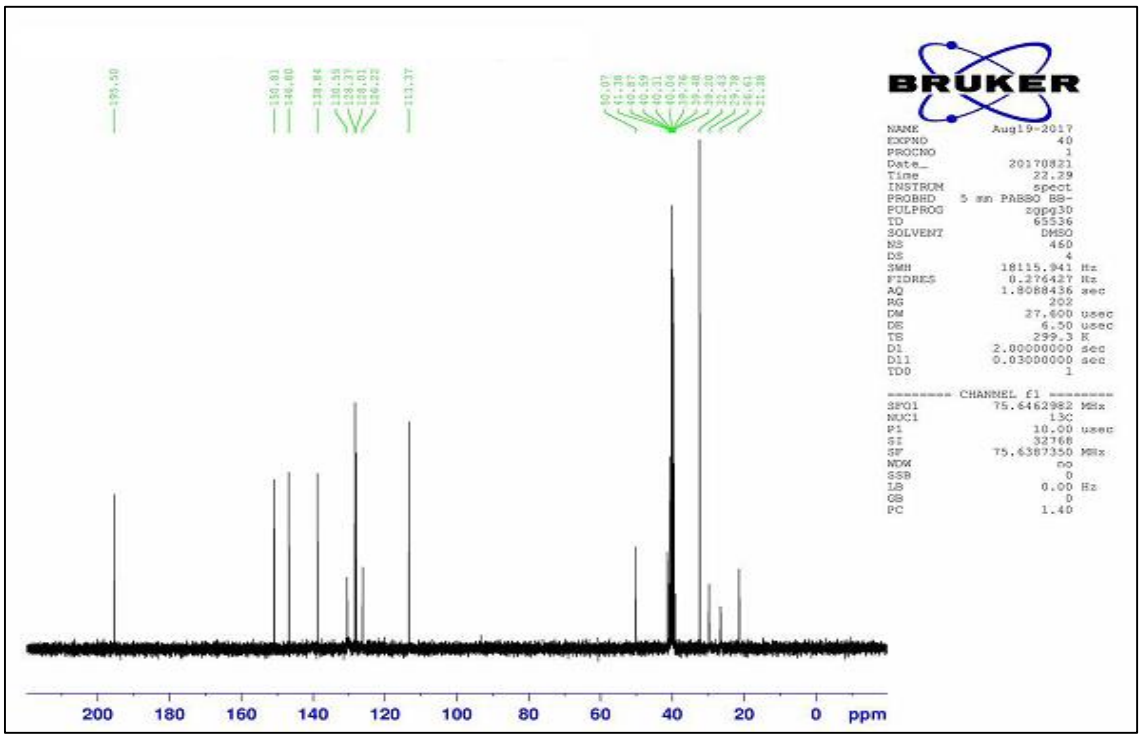


Figure 48: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**).

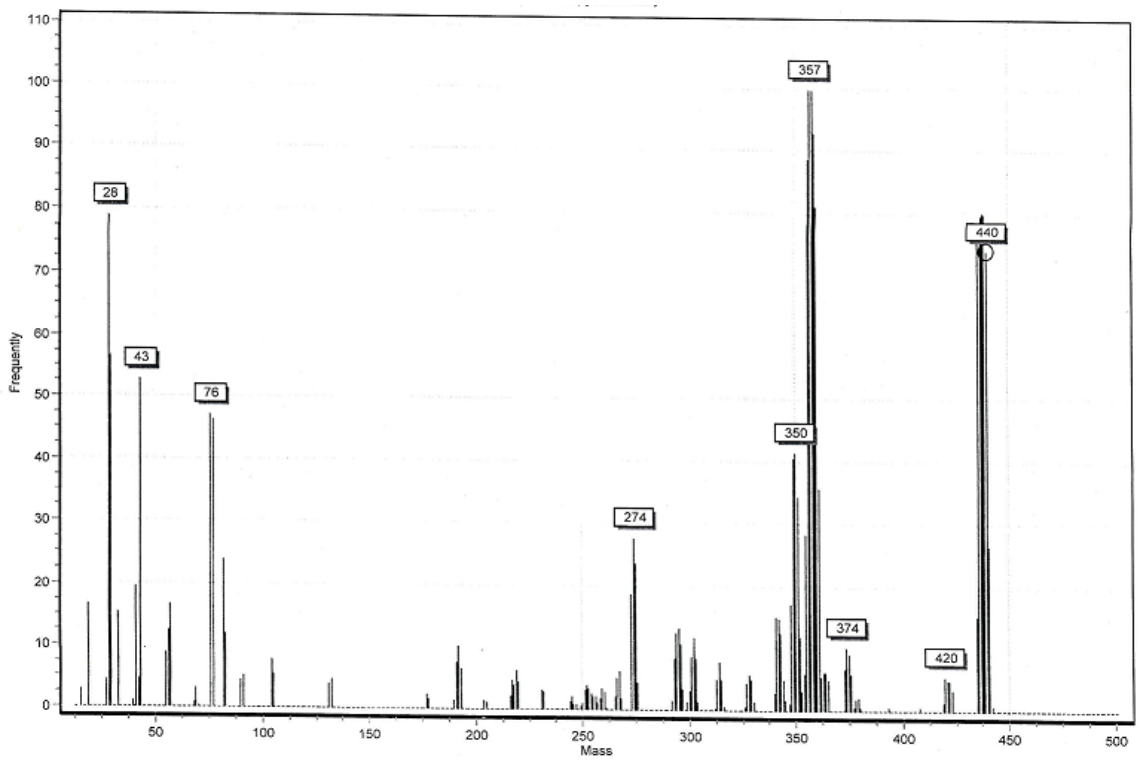
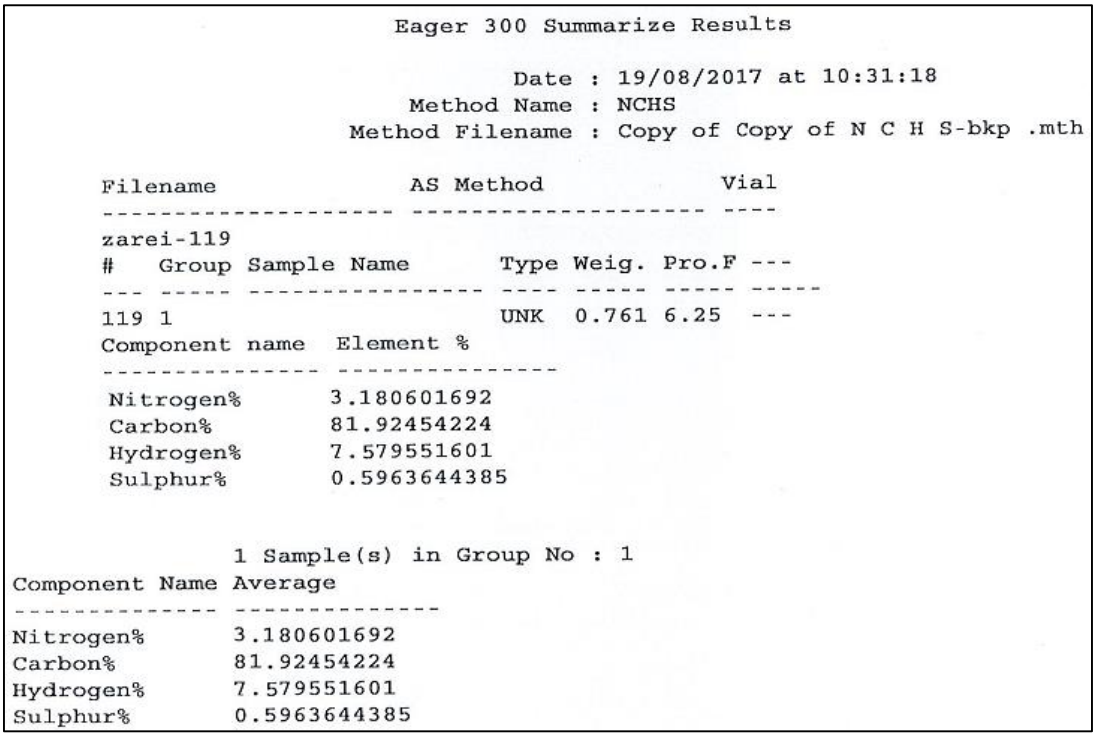


Figure 49: Mass spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**).



Eager 300 Summarize Results

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Hydrogen%	7.579551601
Sulphur%	0.5963644385

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Component Name	Average
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Carbon%	81.92454224
Hydrogen%	7.579551601
Sulphur%	0.5963644385

Figure 50: CHN analysis of 3,3,6,6-tetramethyl-9-phenyl-10-(*m*-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4k**).

10-(4-chlorophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4l). Yellow solid; isolated yield: 90%; mp 301-303 °C (from EtOH) (lit.,[3] 303-305 °C); FT-IR (KBr): ν_{max}/cm^{-1} 3092, 3056, 2955, 2937, 2888, 2868, 1640, 1576; MS, *m/z* (%): 459 (82%, M^+), 379 (100%, M^+- C_6H_5), 344 (25%, M^+- C_6H_4Cl).

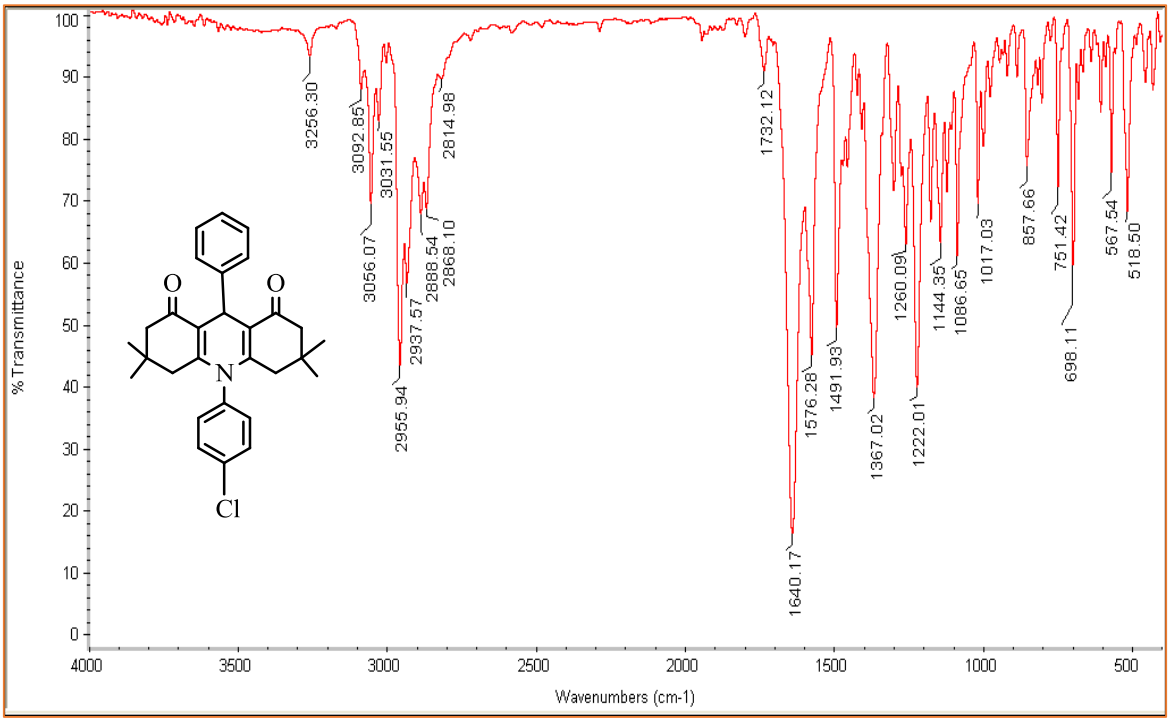

Figure 51: FT-IR (KBr) spectrum of 10-(4-chlorophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4l**).

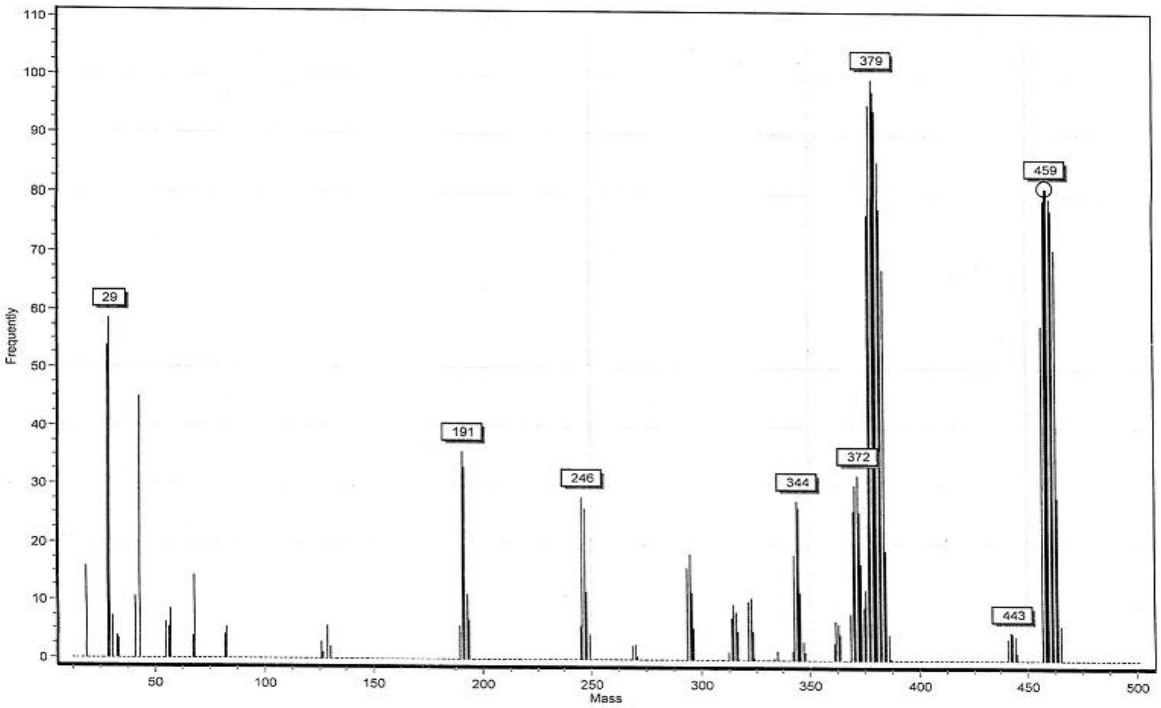

Figure 52: Mass spectrum of 10-(4-chlorophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4l**).

10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4m). Yellow solid; isolated yield:75%; mp 269-271 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3060, 2956, 2934, 2887, 1639, 1576, 1144, 1087; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.97 (1H, d, *J* = 6 Hz, Ph), 7.66-7.51 (5H, m, Ph), 7.24 (2H, t, *J* = 8 Hz, ph), 7.08 (1H, t, *J* = 8 Hz, Ph), 5.0 (1H, s, CH), 2.24-2.16 (4H, m, $2CH_2$), 1.99 (2H, d, *J* = 18 Hz, CH_2), 1.50 (2H, d, *J* = 18 Hz, CH_2), 0.88 (6H, s, $2CH_3$), 0.78 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.4, 149.7, 146.7, 137.6, 134.0, 132.7, 132.0, 129.8, 129.0, 127.9, 126.0, 124.7, 113.5. 49.9, 41.6, 33.5, 32.2, 30.2, 26.0; MS, *m/z* (%): 504 (83%, M^+), 426 (100%, M^+- C_6H_5); Elemental analysis: Found: C, 69.02; H, 5.67; N, 2.78. Calc. for $C_{29}H_{30}BrNO_2$: C, 69.05; H, 5.99; N, 2.78%.

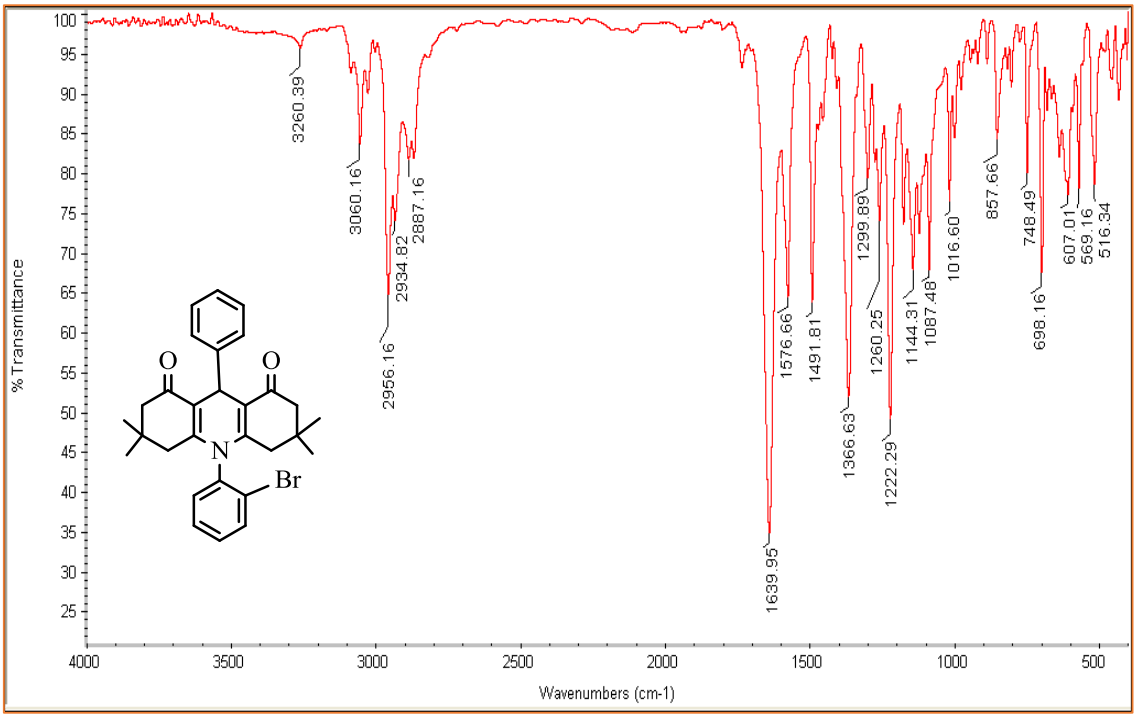

Figure 53: FT-IR (KBr) spectrum of 10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4m**).

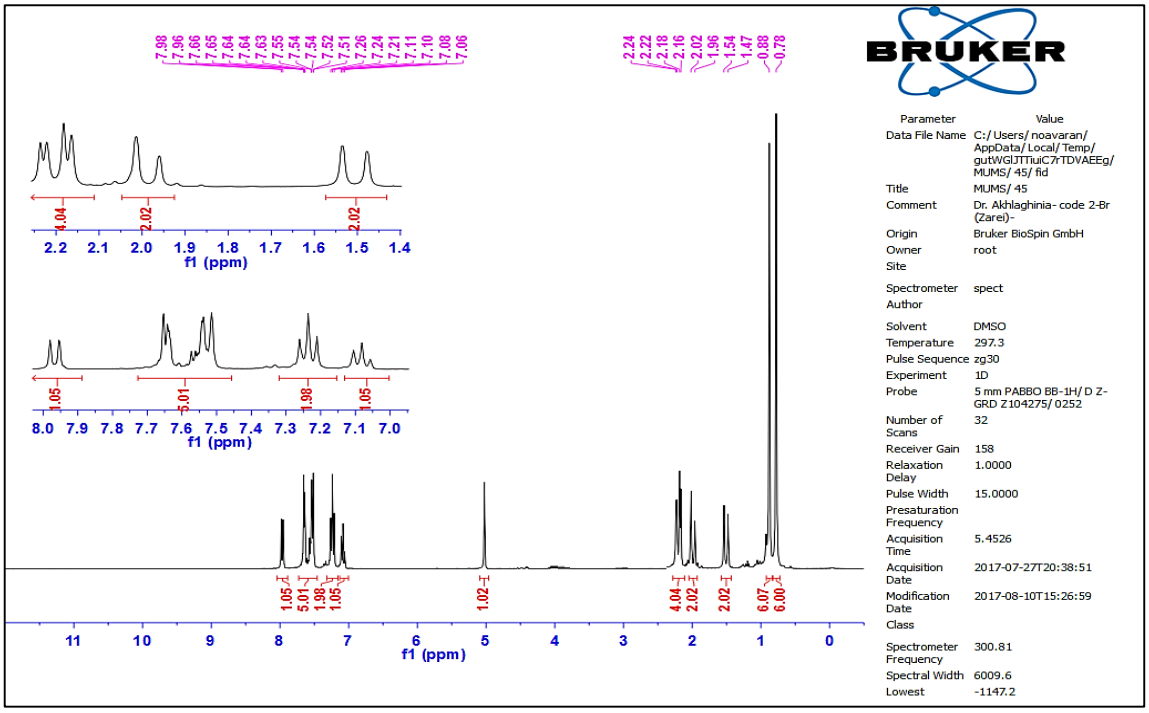

Figure 54: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4m**).

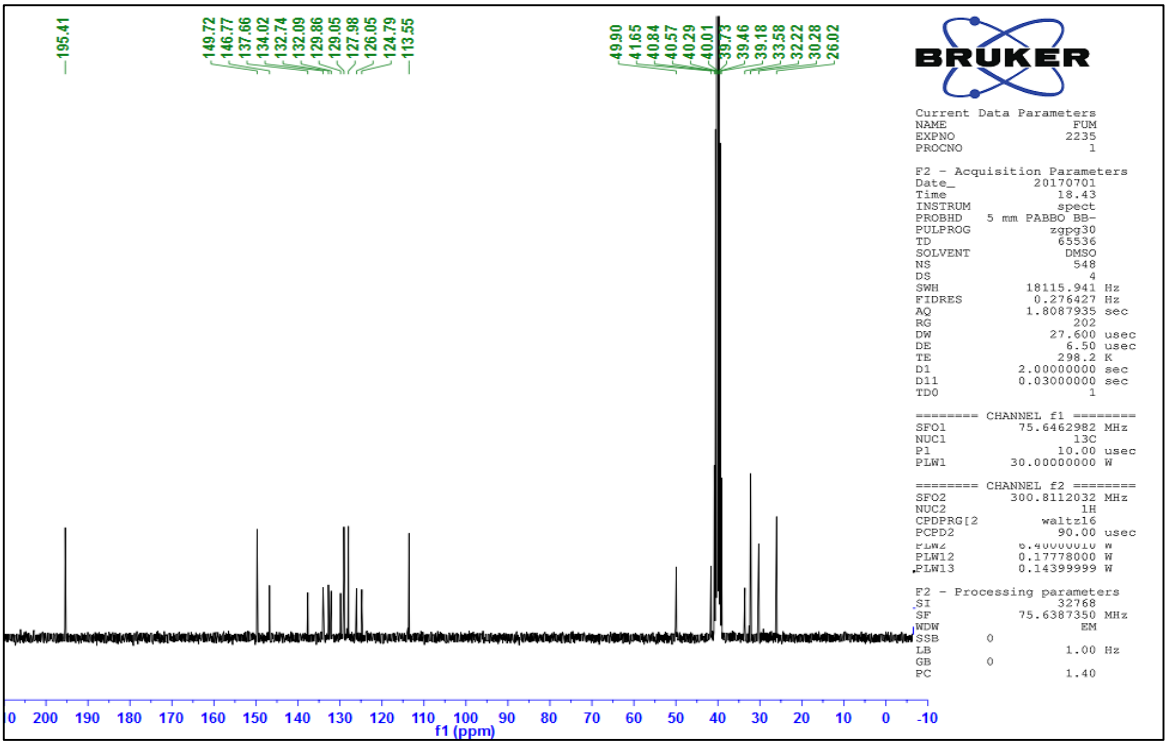

Figure 55: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4m**).

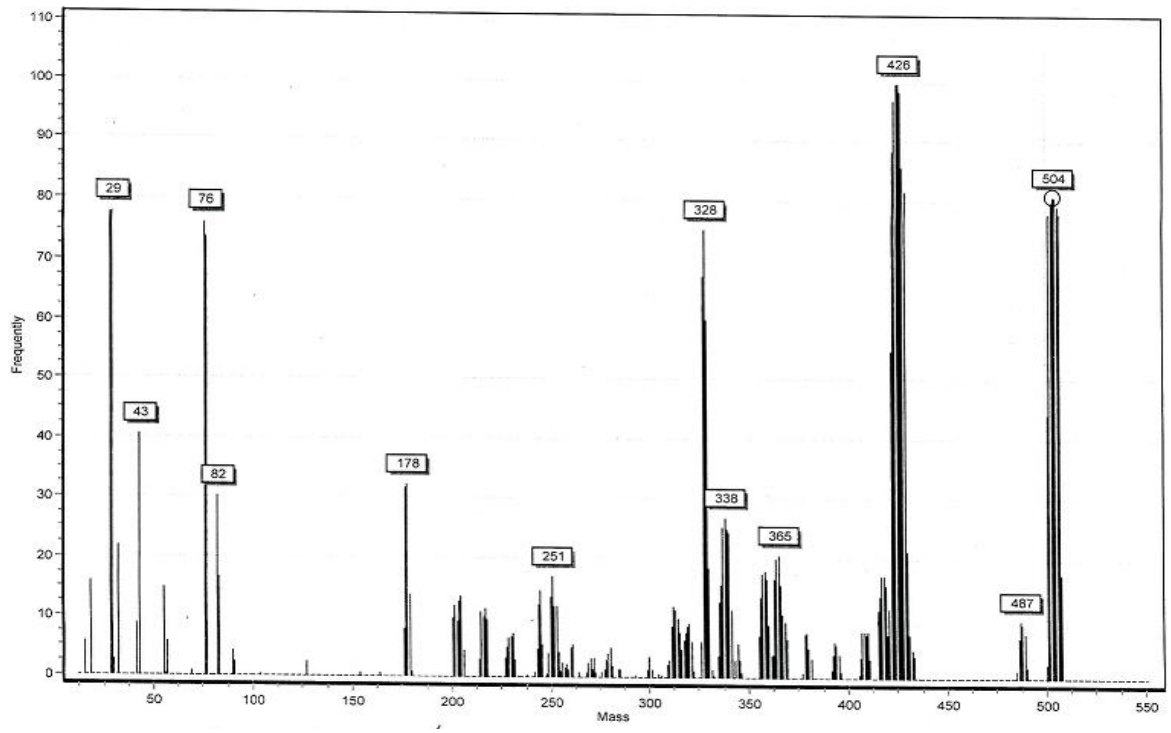

Figure 56: Mass spectrum of 10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4m**).

Eager 300 Summarize Results

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Carbon%	69.02454224
Hydrogen%	5.679551601
Sulphur%	0.5963644385

1 Sample(s) in Group No : 1

Component Name	Average
Nitrogen%	2.780601692
Carbon%	69.02454224
Hydrogen%	5.679551601
Sulphur%	0.5963644385

Figure 57: CHN analysis of 10-(2-bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4m**).

3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4n). Yellow solid; isolated yield: 30%; mp 255-257 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3051, 3026, 2957, 2869, 1641, 1583, 1178, 1144, 1122; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.76 (1H, s, Pyridine), 8.13 (1H, td, J = 7.8 Hz, J = 1.8 Hz, Pyridine), 7.66-7.62 (2H, m, Pyridine), 7.40-7.37 (2H, m, Ph), 7.27-7.22 (2H, m, Ph), 7.10 (1H, t, J = 6 Hz, Ph), 5.04 (1H, s, CH), 2.25-2.18 (4H, m, $2CH_2$), 1.99 (2H, d, J = 18 Hz, CH_2), 1.70 (2H, d, J = 18 Hz, CH_2), 0.88 (6H, s, $2CH_3$), 0.72 (6H, s, $2CH_3$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 195.5, 151.8, 150.6, 149.9, 146.7, 140.1, 128.2, 128.2, 126.2, 125.5, 125.4, 113.5, 50.0, 40.8, 32.6, 32.5, 29.6, 21.6; MS, *m/z* (%): 426 (47%, M^+), 345 (82%, M^+ - C_6H_5), 44 (100%, $COCH_2$); Elemental analysis: Found: C, 78.20; H, 7.08; N, 6.51. Calc. for $C_{28}H_{30}N_2O_2$: C, 78.84; H, 7.09; N, 6.57%.

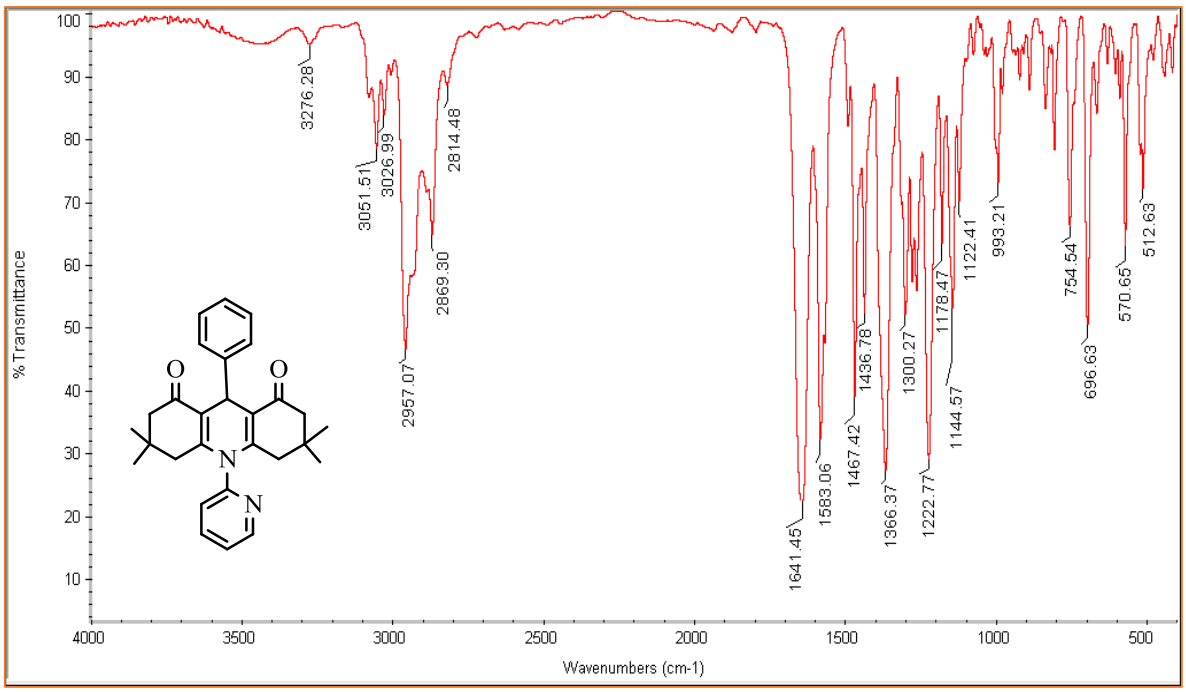


Figure 58: FT-IR (KBr) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**).

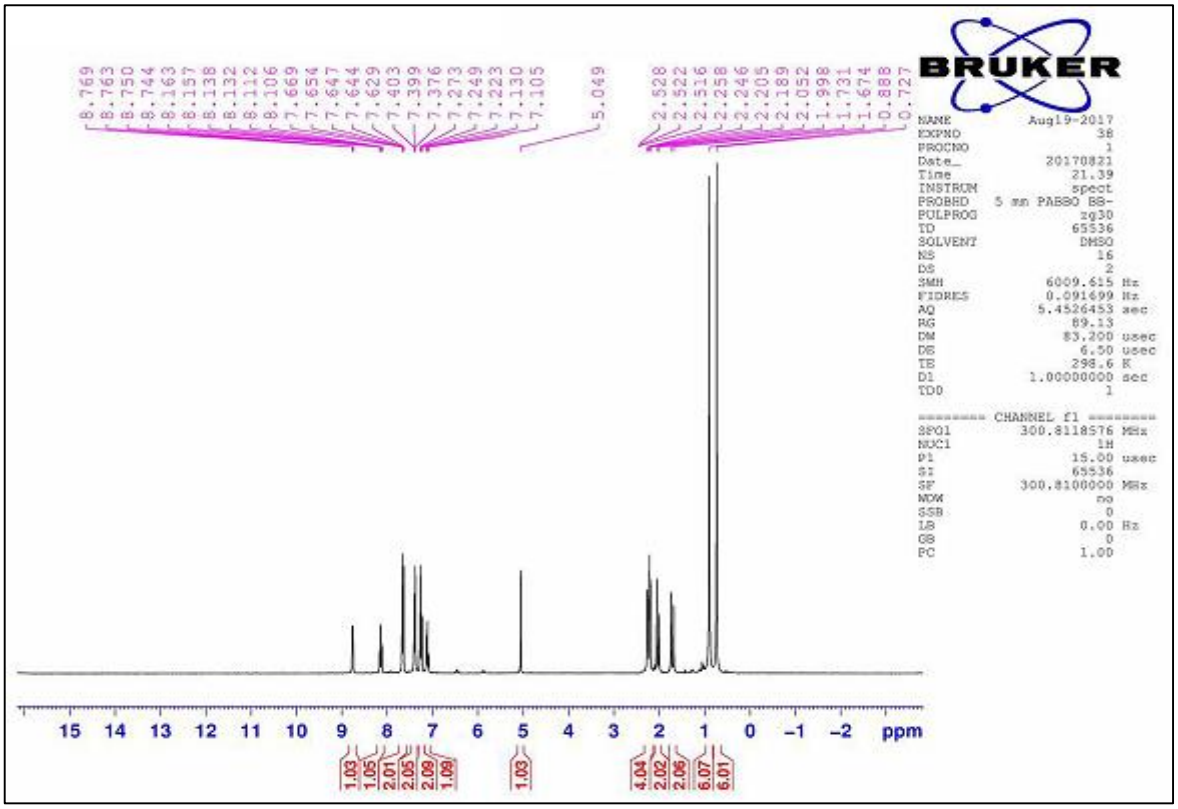


Figure 59: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**).

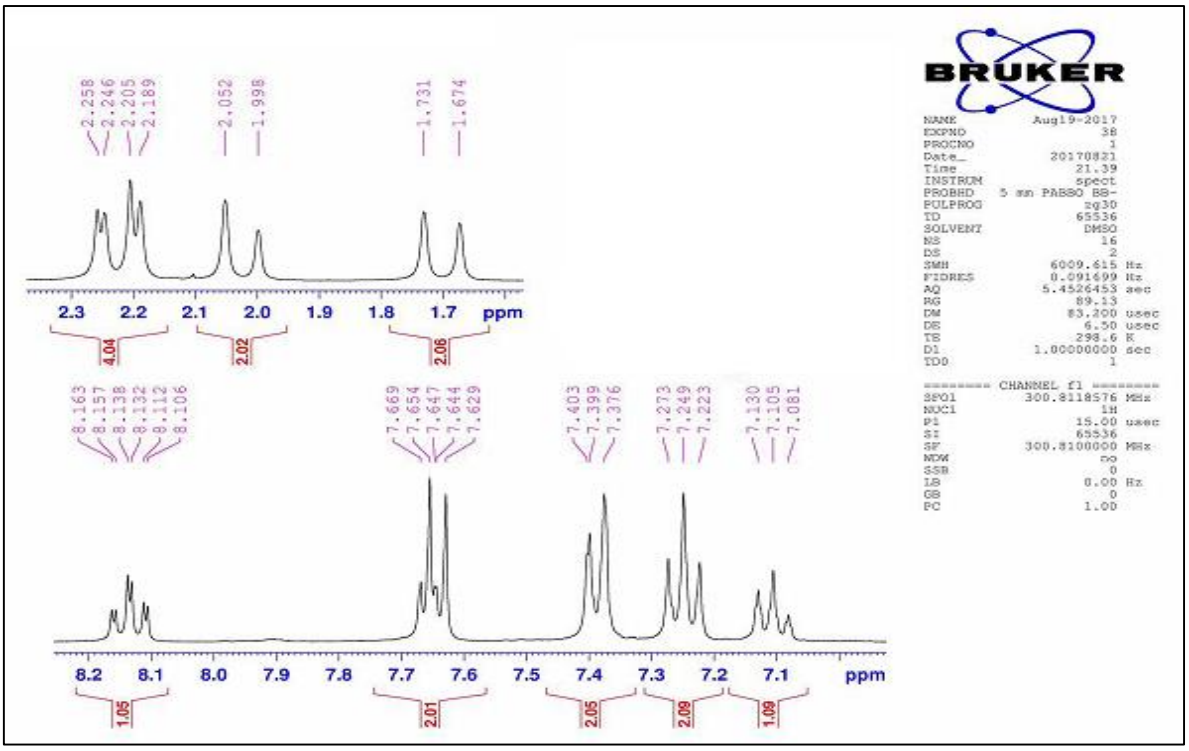


Figure 60: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**) expanded.

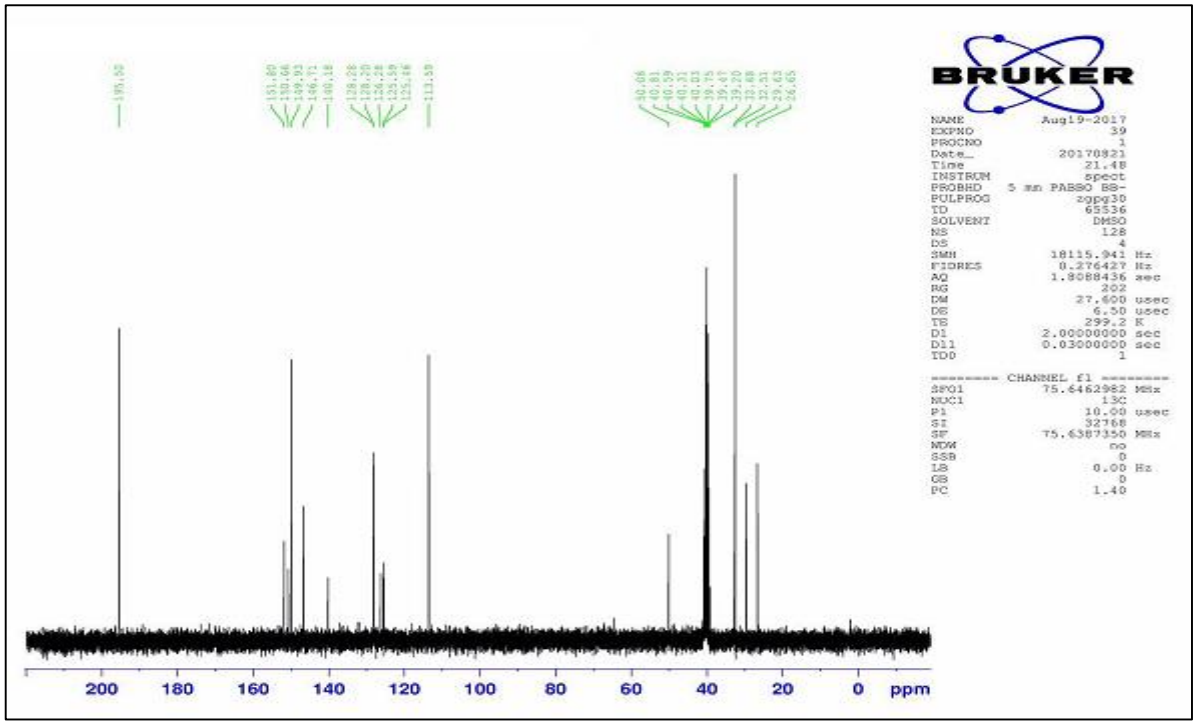


Figure 61: ^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**).

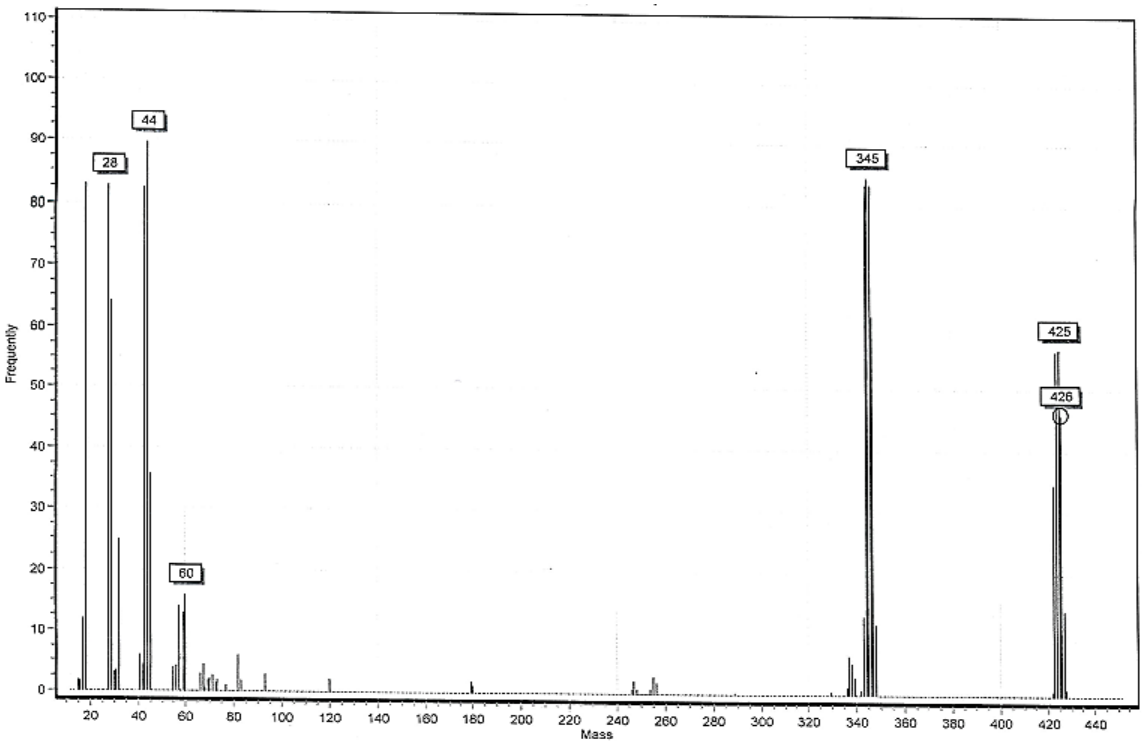
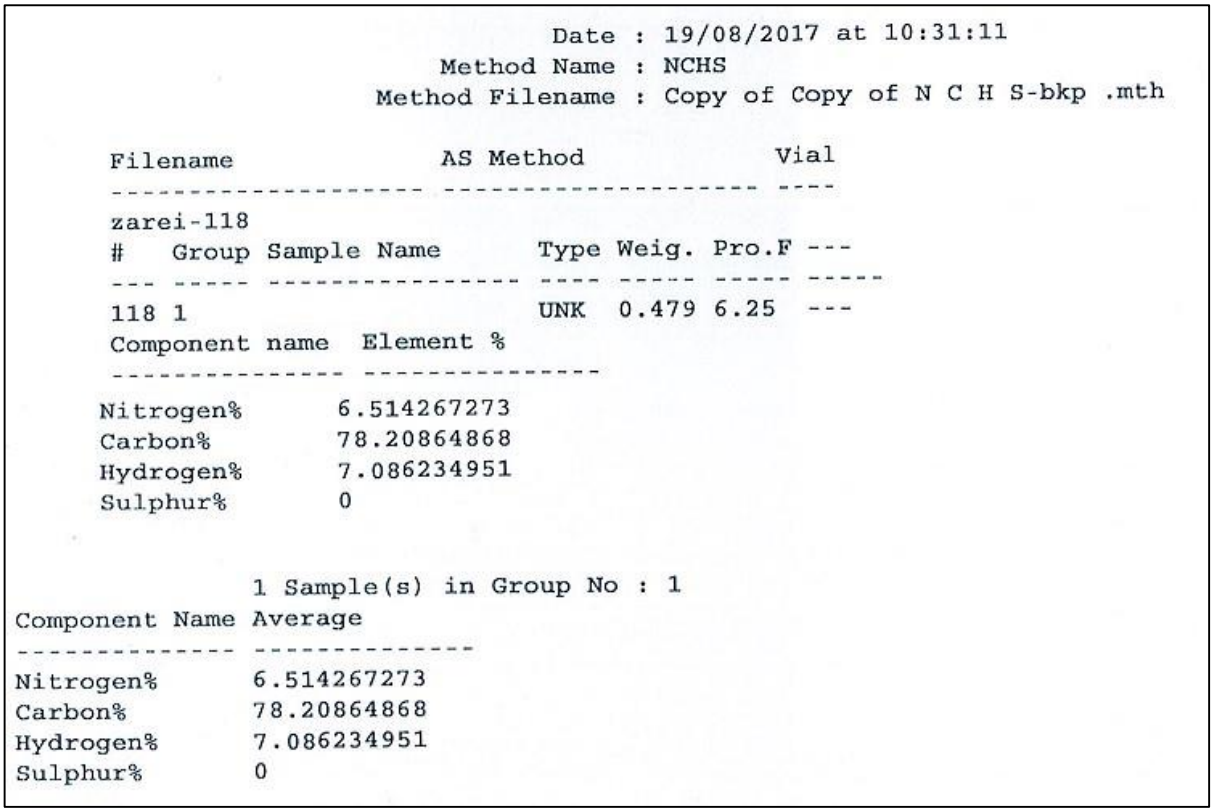


Figure 62: Mass spectrum of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**).



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      Component name  Element %
      --------------- ---------------
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     Carbon%         78.20864868
     Hydrogen%       7.086234951
     Sulphur%        0


                1 Sample(s) in Group No : 1
Component Name Average
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Nitrogen%      6.514267273
Carbon%        78.20864868
Hydrogen%      7.086234951
Sulphur%       0
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Figure 63: CHN analysis of 3,3,6,6-tetramethyl-9-phenyl-10-(pyridin-2-yl)-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4n**).

3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4o).

Yellow solid; isolated yield: 95%; mp 276-278 °C (from EtOH) (lit., [1] 277-279 °C); ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.32 (1H, s, NH), 7.18-7.17 (5H, m, Ph), 4.84 (1H, s, CH), 2.53-2.37(4H, m, $2CH_2$), 2.32-1.84 (4H, m, $2CH_2$), 1.03 (6H, s, $2CH_3$), 0.88 (6H, s, $2CH_3$); MS, *m/z* (%): 349 (M^+, 6%), 269 (M^+- C_6H_5, 100), 77 (C_6H_5, 34).

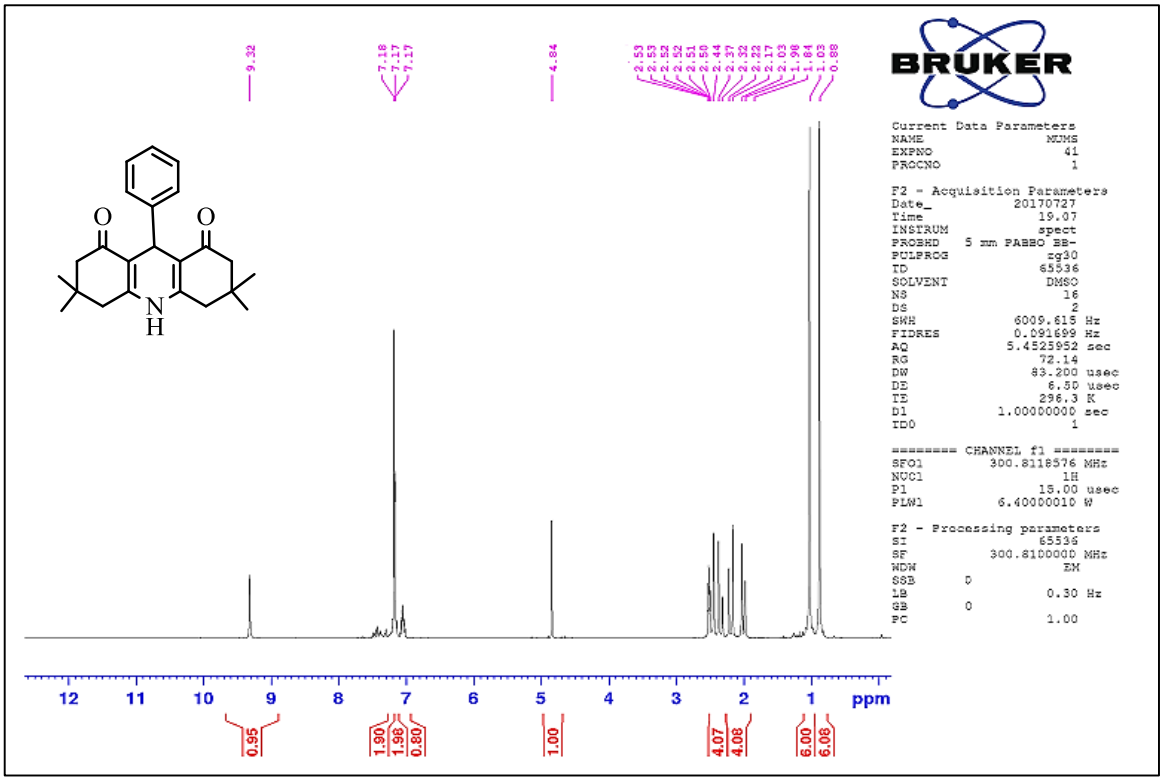

Figure 64: ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4o**).

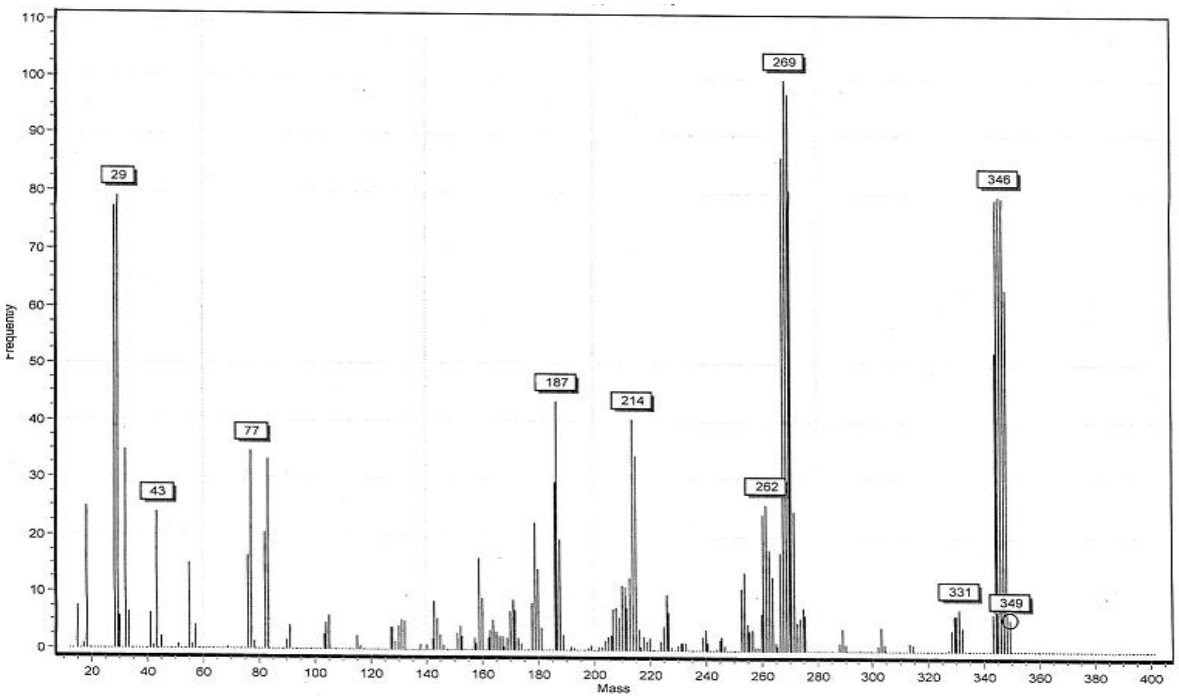

Figure 65: Mass spectrum of 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4o**).

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4p). Yellow solid; isolated yield: 95%; mp 277-280 °C (from EtOH) (lit., [1] 278-280 °C); MS, *m/z* (%): 380 (60%, M^+), 269 (100%, M^+- C_6H_5), 77 (60%, C_6H_5).

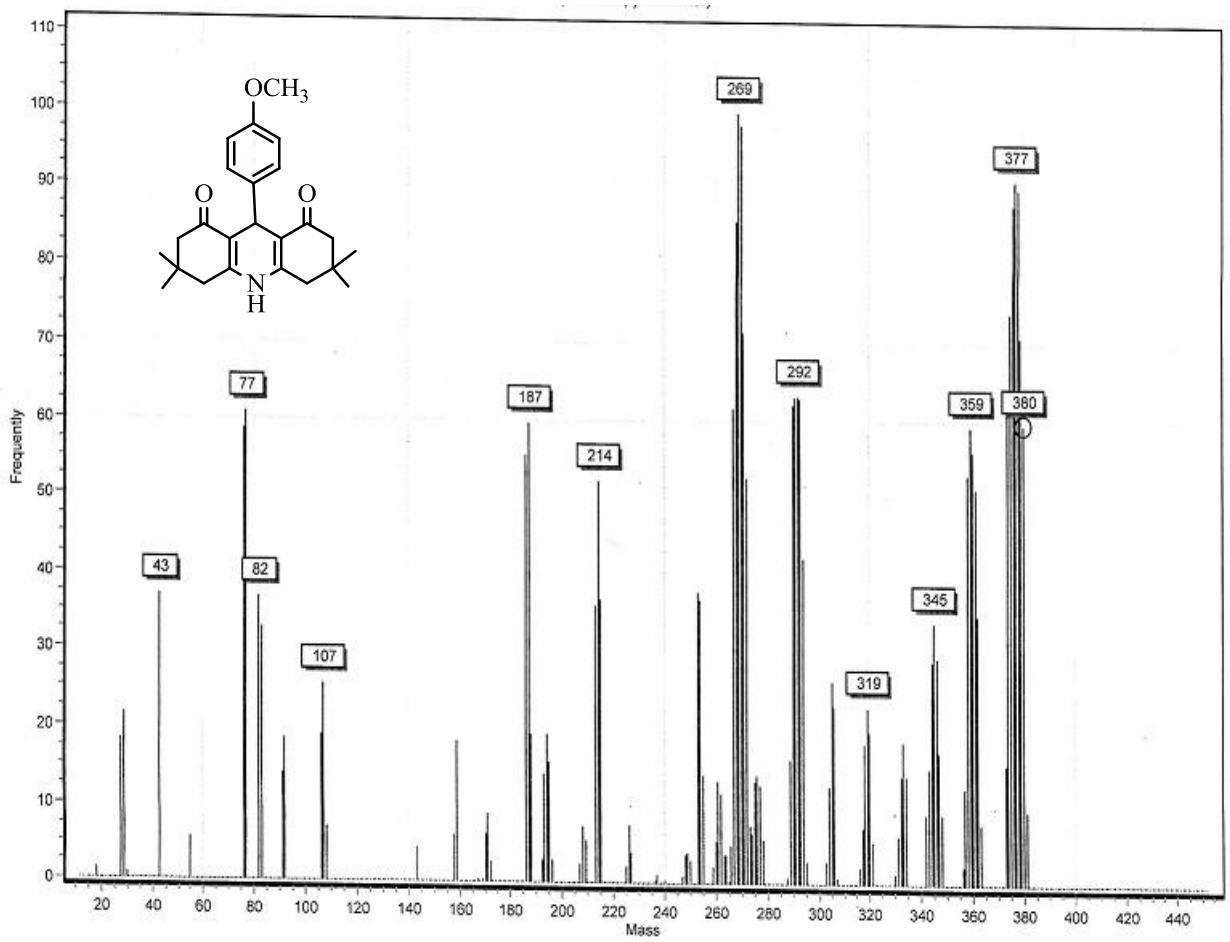

Figure 66: Mass spectrum of 9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4p**).

9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4q). Yellow solid; isolated yield: 95%; mp 315-317 °C (from EtOH) (lit., [1] 317-320 °C); MS, *m/z* (%): 383 (51%, M^+), 268 (100%, M^+- C_6H_5).

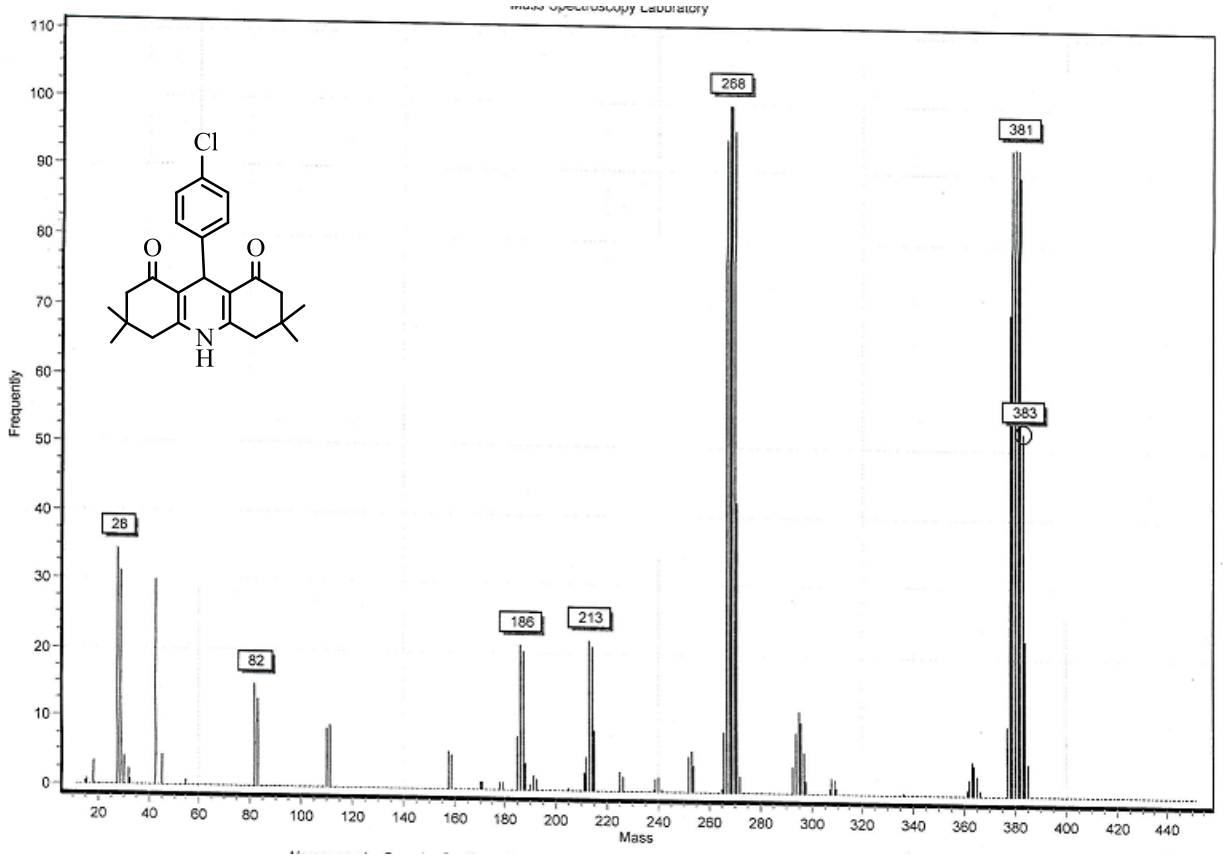

Figure 67: Mass spectrum of 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4q**).

9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (4r). Yellow solid; isolated yield: 95%; mp 239-241 °C (from EtOH) (lit., [4] 240-242 °C); MS, *m/z* (%): 429 (54%, M^++ 2), 427 (98%, M^+).

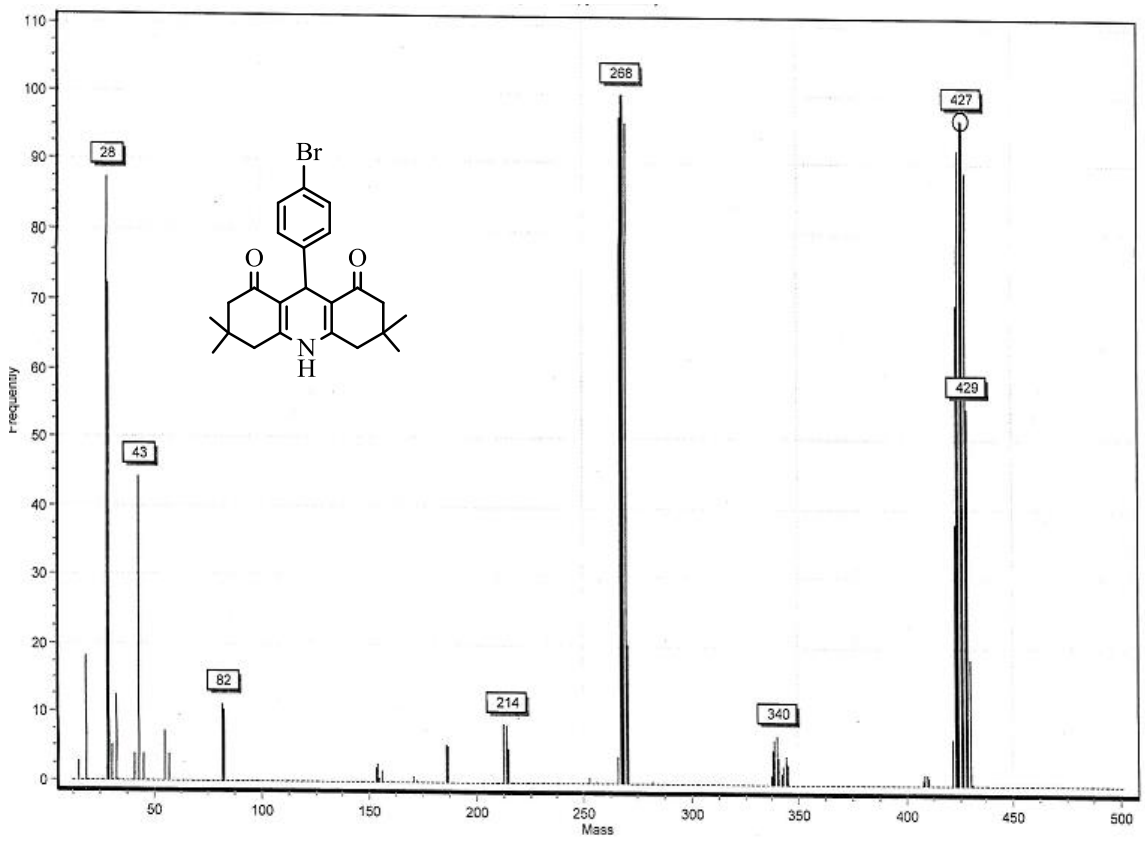

Figure 68: Mass spectrum of 9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2*H*,5*H*)-dione (**4r**).

2,2'-((4-methoxyphenyl)methylene)bis(5,5-dimethylcyclohexane-1,3dione)(Intermediate III). Yellow solid; isolated yield: 95%; mp 219-220 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3060, 3002, 2957, 2872, 2839, 1665, 1596, 1510; MS, *m/z* (%): 398 (8%, M^+), 292 (40%, M^+-C_7H_7O).

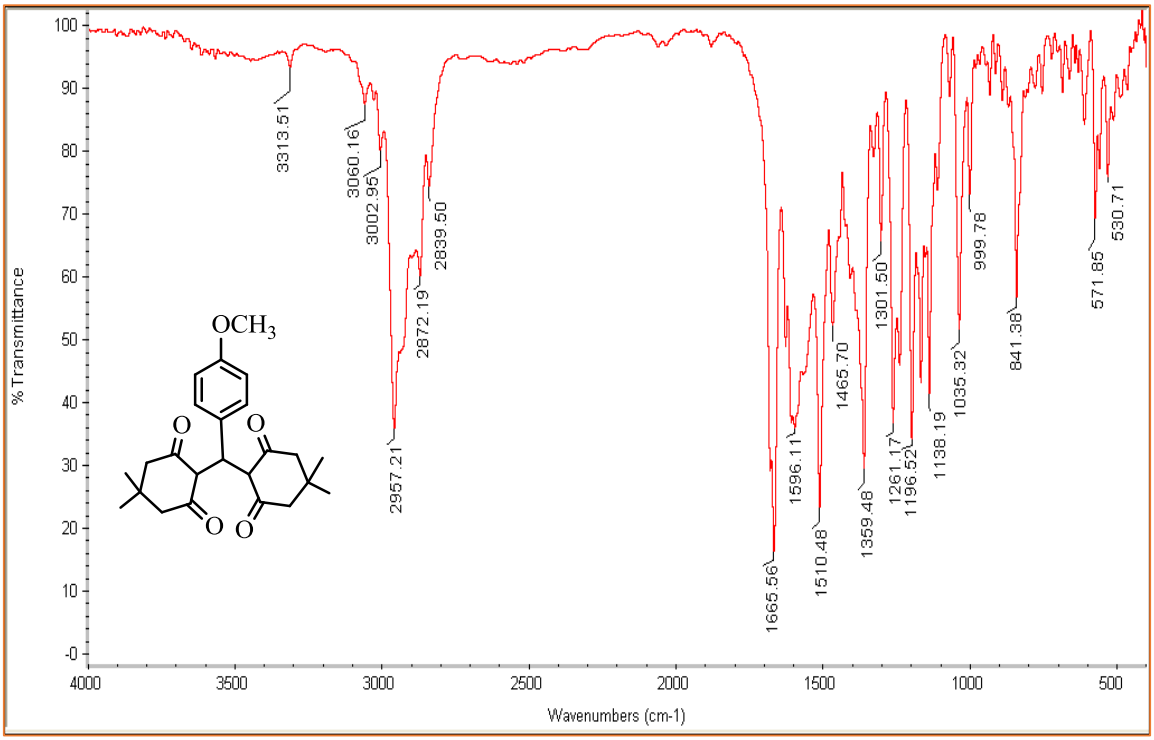

Figure 69: FT-IR (KBr) spectrum of 2,2'-((4-methoxyphenyl)methylene)bis(5,5-(dimethylcyclohexane-1,3-dione) (**Intermediate III**).

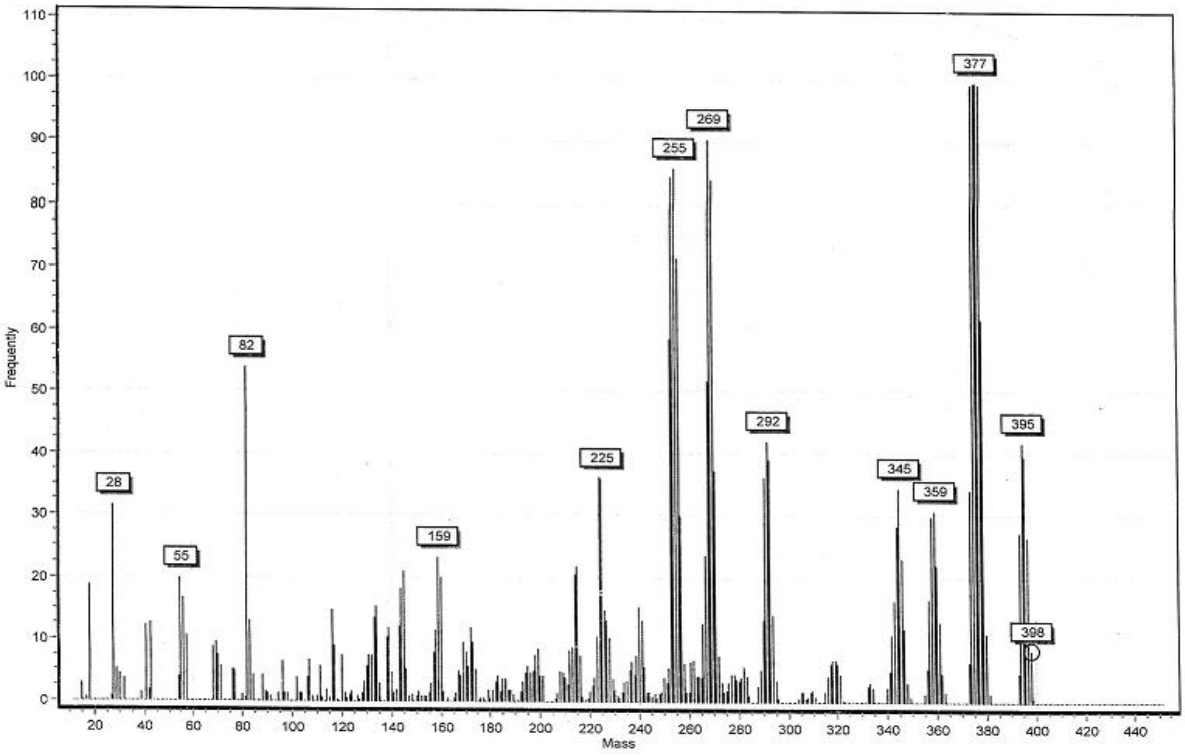

Figure 70: Mass spectrum of 2,2'-((4-methoxyphenyl)methylene)bis(5,5-(dimethylcyclohexane-1,3-dione) (**Intermediate III**).

2-(4-methoxybenzylidene)-5,5-dimethylcyclohexane-1,3-dione (Knoevenagel product II).

Yellow solid; isolated yield: 95%; mp 196-198 °C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 2955, 2925, 2868, 2835, 1561, 1508; MS, *m/z* (%): 258 (4%, M^+), 224 (84%, M^+- OCH_3).

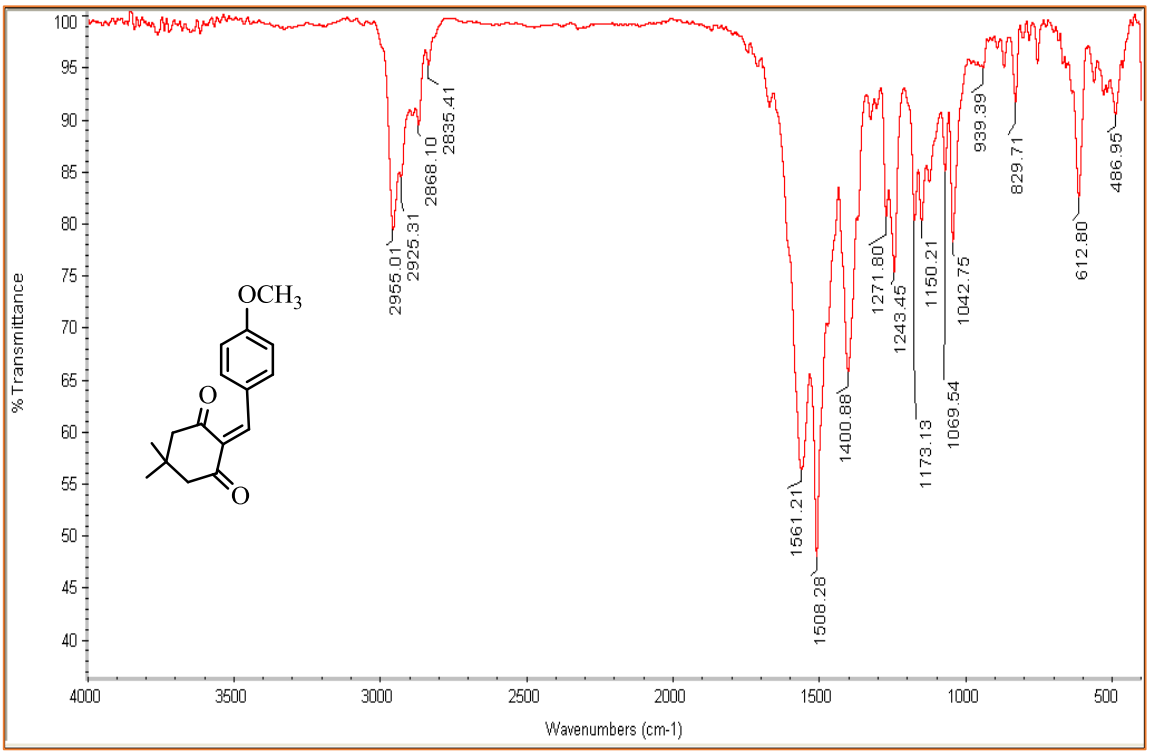

Figure 71: FT-IR (KBr) spectrum of 2-(4-methoxybenzylidene)-5,5-dimethylcyclohexane-1,3-dione (**Knoevenagel product II**).

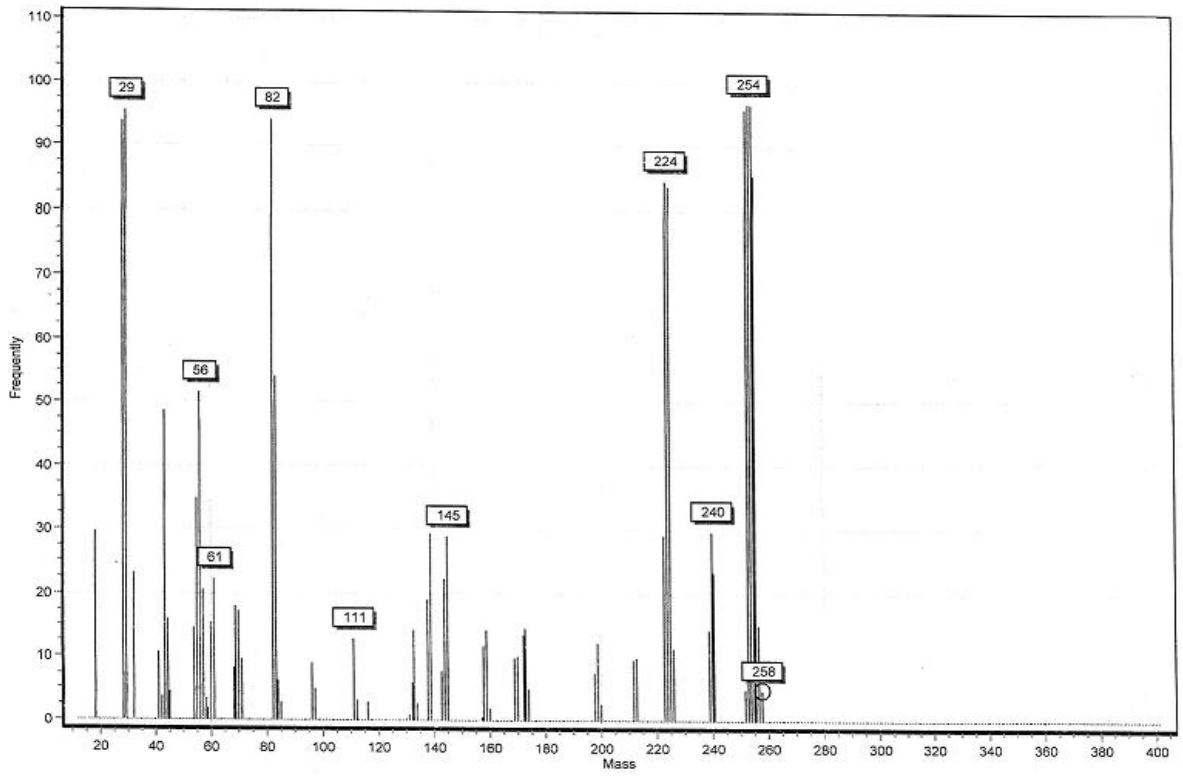

Figure 72: Mass spectrum of 2-(4-methoxybenzylidene)-5,5-dimethylcyclohexane-1,3-dione (**Knoevenagel product II**).

References

[1] G. M. Ziarani, A. Badiei, M. Hassanzadeh and S. Mousavi, *Arab. J. Chem*., 2014, **7**, 335.

[2] M. A. Ghasemzadeh, J. Safaei-Ghomi and H. Molaei, *C. R. Chimie*., 2012, **15**, 969.

[3] B. Aday, H. Pamuk, M. Kaya and F. Sen, *J. Nanosci. Nanotechnol*., 2016, **16**, 6498.

[4] A. Khojastehnezhad, M. Rahimizadeh, H. Eshghi, F. Moeinpour and M. Bakavoli, *Chinese. J. Catal*., 2014, **35**, 376.