

Supplementary Information for

Pt NPs@GO as Highly Efficient and Reusable Catalyst for One-Pot Synthesis of Acridinedione Derivatives

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Materials and Instrumentation

PtCl₄ (99 % Alfa Aesar), tetrahydrofuran (THF) (99.5 %, Merck) and ethanol (99.9 %) were purchased from Merck, octylamine (Sigma Aldrich) were used as received from suppliers. THF was distilled over sodium under argon atmosphere and stored under inert atmosphere. De-ionized water was filtered by Millipore water purification system (18 MΩ) analytical grade. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by washing with distilled water before drying in an oven.

The chemicals used in the synthesis of acridinedione derivatives were obtained from Merck and Aldrich Chemical Company. All chemicals and solvents used for the synthesis were of spectroscopic reagent grade.

Transmission electron microscopy (TEM) images were obtained on a JEOL 200 kV TEM instrument. Sample preparation for TEM analysis involves placement of a drop of 0.5 mg/mL ethanol solution of the prepared catalysts with a carbon support on a carbon covered 400-mesh copper grid; the solvent is then allowed to evaporate. Excess solution was removed with an adsorbent paper and the sample was dried under vacuum at room temperature before analysis. More than 300 particles were calculated to get the integrated information about the overall distribution of Pt-based catalyst sample.

Thermo Scientific spectrometer was used for X-ray Photoelectron Spectroscopy (XPS) measurements and the X-ray source was Kα lines of Mg (1253.6 eV, 10 mA). Samples

were prepared by depositing the catalyst on Cu double-sided tape (3M Inc.). C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line.

A Panalytical Empirian diffractometer with Ultima+theta–theta high resolution goniometer, having an X-ray generator (Cu K α radiation, λ = 1.54056 Å) and operating condition of 45 kV and 40 mA, were employed in XRD analysis.

An MFP-3D (Asylum Research) was used to carry out tapping-mode atomic force microscopy (AFM) imaging. Samples were directly deposited on a 75 mm 25 mm glass slide (VWR International) and imaged using rectangular silicon tips (Olympus AC240TS) with a nominal spring constant of 2 N m⁻¹. Both topographic and height images were recorded during AFM analysis. Height analysis was performed using Igor Pro software.

Melting points were measured on a Bibby Scientific Stuart Digital, Advanced, and SMP30. Fourier Transform Infrared (FT–IR) spectra were recorded on Bruker Optics, ALPHA FT–IR spectrometer. The ¹H-NMR and ¹³C-NMR spectra were obtained in DMSO-*d*₆ with Bruker DPX-300 as solvents with tetramethylsilane as the internal reference. The mass analyses were performed on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/HRMS at the advanced technology research centre of Dumlupınar University (ILTEM).

Characterization of Pt NPs@GO

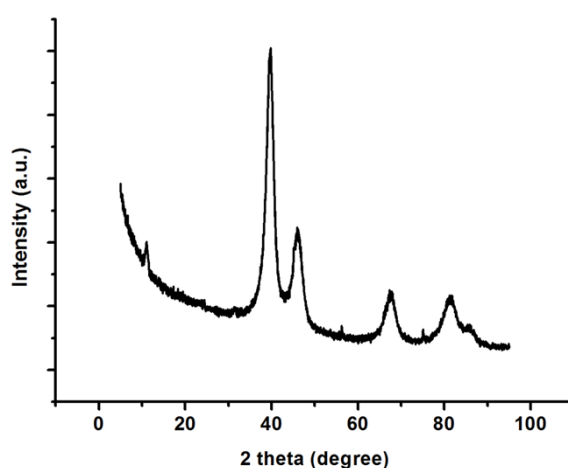


Fig. S1. XRD of catalyst Pt NPs@GO

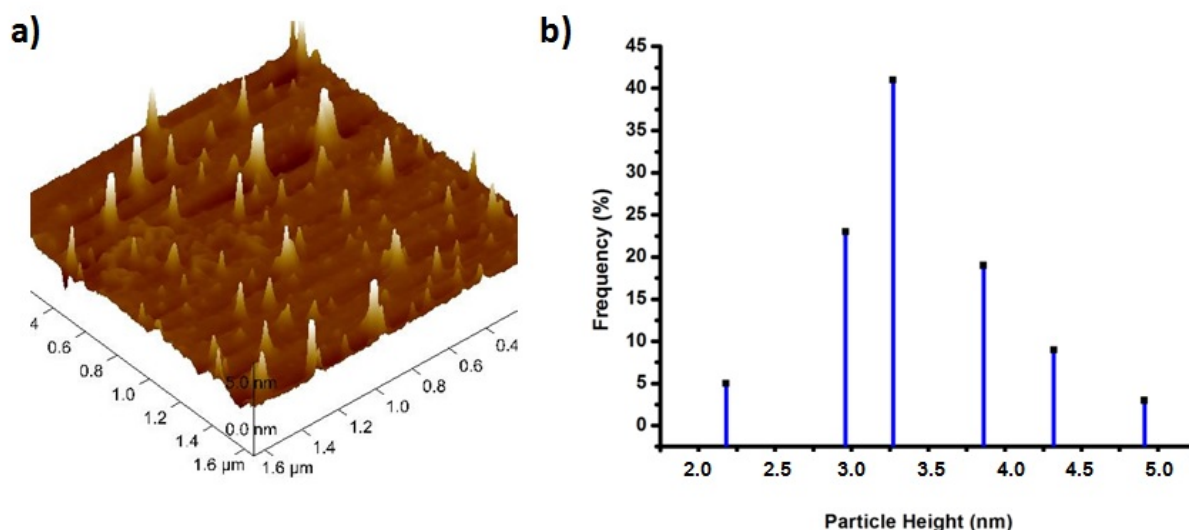


Fig. S2. AFM image of Pt NPs@GO catalyst (a). Histogram of height of particles obtained from AFM data (b).

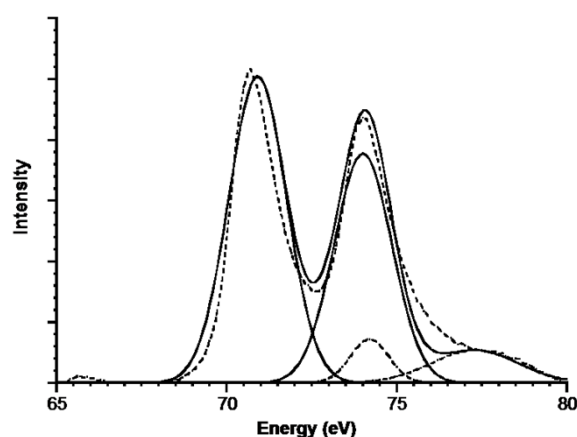


Fig. S3. Pt 4f electron spectra of Pt NPs@GO

The preparation of Graphene Oxide

Graphene oxide (GO) was synthesized from graphite powder using modified Hummer's method. In brief, 1 g of graphite and 0.5 g of sodium nitrate were mixed together followed by the addition of 23 ml of conc. sulphuric acid under constant stirring. After 1 h, 3 g of KMnO_4 was added gradually to the above solution while keeping the temperature less than 20°C to prevent overheating and explosion. The mixture was stirred at 35°C for 12 h and the resulting solution was diluted by adding 500 ml of water under vigorous stirring. To ensure the completion of reaction with KMnO_4 , the suspension was further treated with 30% H_2O_2 solution (5 ml). The resulting mixture was washed with HCl and H_2O respectively, followed by filtration and drying, graphene oxide sheets were thus obtained.

Characterization of acridinedione derivatives

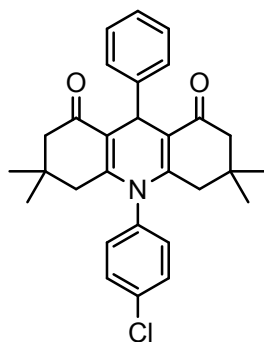
Whereas the infrared (IR) spectra of all the 1,8-dioxoacridine **4a-j** aromatic C–H stretching bands are observed between 3061-3006 cm^{-1} , the aliphatic C–H stretching bands were observed between 2959-2952 cm^{-1} . Besides, in the IR spectra of all **4a-j** compounds, the carbonyl groups showed sharp peaks in the region between 1653 and 1632 cm^{-1} .

The ^1H -NMR spectra of the compounds **4a-j** belonging to protons of the methyl groups showed singlet peaks in position 3 and 6 approximate between 0.70-0.90 ppm. The methoxy protons of compound **4g** were observed 3.70 ppm. The signals for the -CH protons were observed at 4.95–5.15 ppm and the signals for the aromatic protons were observed in the range between 6.61-8.14 ppm.

The signals observed in ^{13}C -NMR (APT) spectrums of all the acridinedione **4a-j** molecules are determined to be in line with the recommended molecule structures.

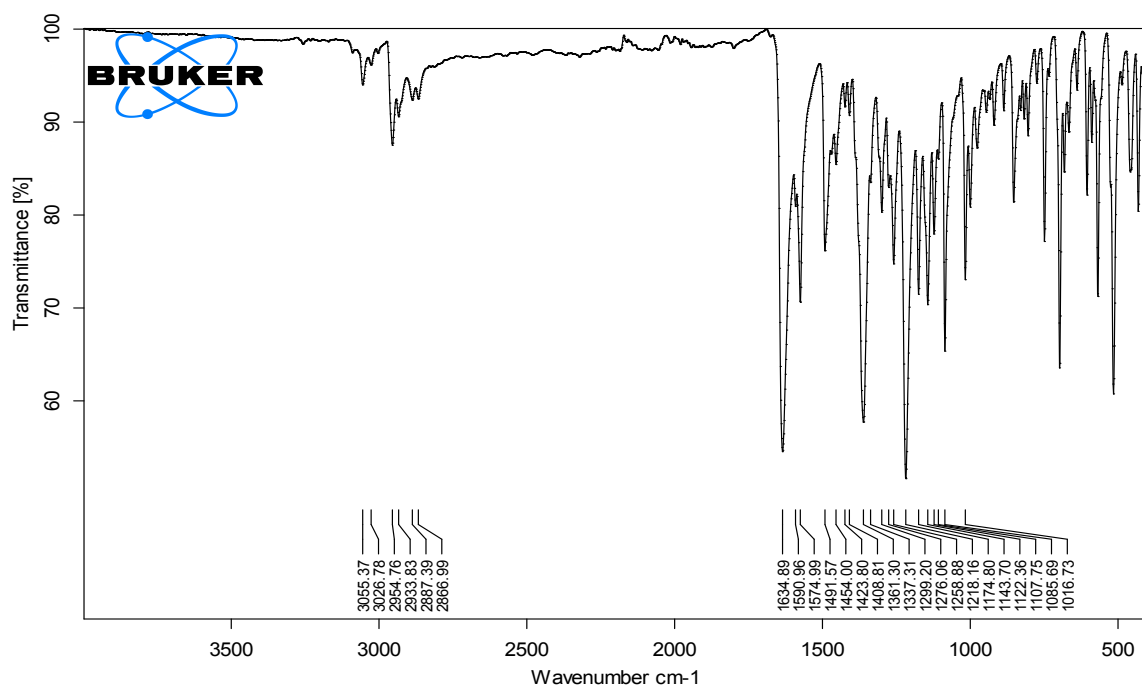
Further, when their high resolution mass spectra (HRMS) are examined, the observed molecule ion peaks are in compliance with the recommended structures.

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4a)

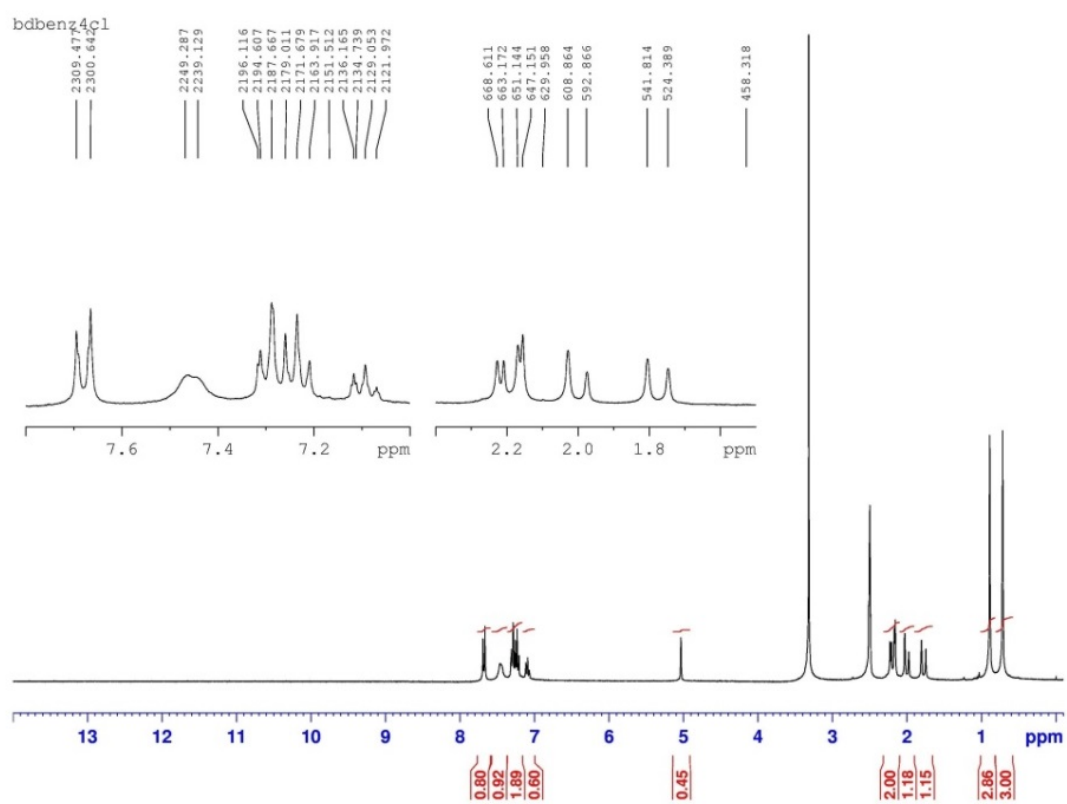


As yellow crystals, (0.422 g, 92 %), mp. (300-302 °C) [49] (ethanol). ^1H -NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 0.72 (s, 6H, 2x- CH_3), 0.88 (s, 6H, 2x- CH_3), 1.78 (d, 2H, J = 17.43 Hz, - CH_2), 2.00 (d, 2H, J = 16.00 Hz, - CH_2), 2.16-2.22 (m, 4H, - CH_2), 5.05 (s, 1H, -CH), 7.07-7.12 (m, 1H, Ar-H), 7.21-7.32 (m, 4H, Ar-H), 7.48 (d, 2H, J = 5.44 Hz, 10.58, Ar-H), 7.68 (d, 2H, J = 8.84 Hz, Ar-H); ^{13}C -NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm): 26.50, 29.72, 32.33, 32.44, 41.35, 50.03, 113.55, 126.26, 127.97, 128.38, 130.56, 134.37, 137.79, 146.57, 150.58, 195.54; IR (cm^{-1}): 3026 w (Ar-H), 2954 s (-CH), 1634 s (C=O), 1590 s (C=C); HRMS (QTOF-ESI): m/z $\text{C}_{29}\text{H}_{30}\text{ClNO}_2$: 459.1965; found: 460.2061 ($[\text{M}+\text{H}]^+$).

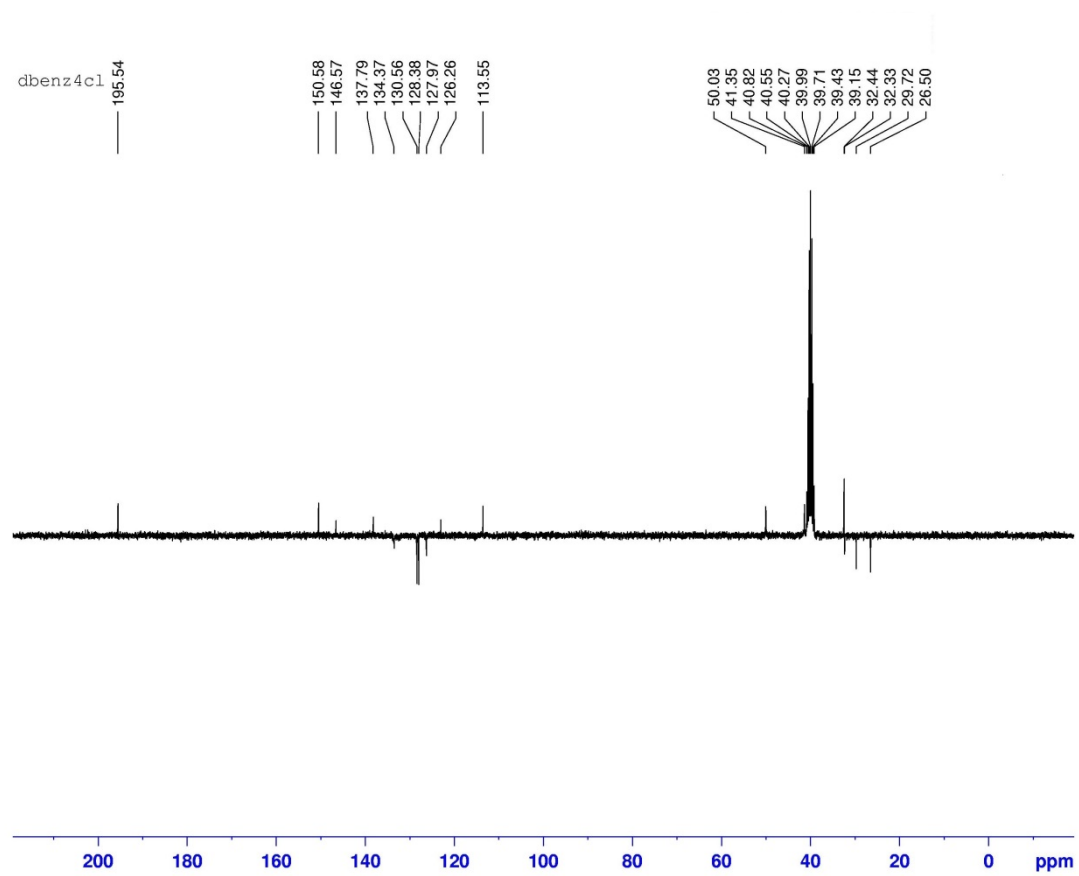
a)



b)



c)



d)

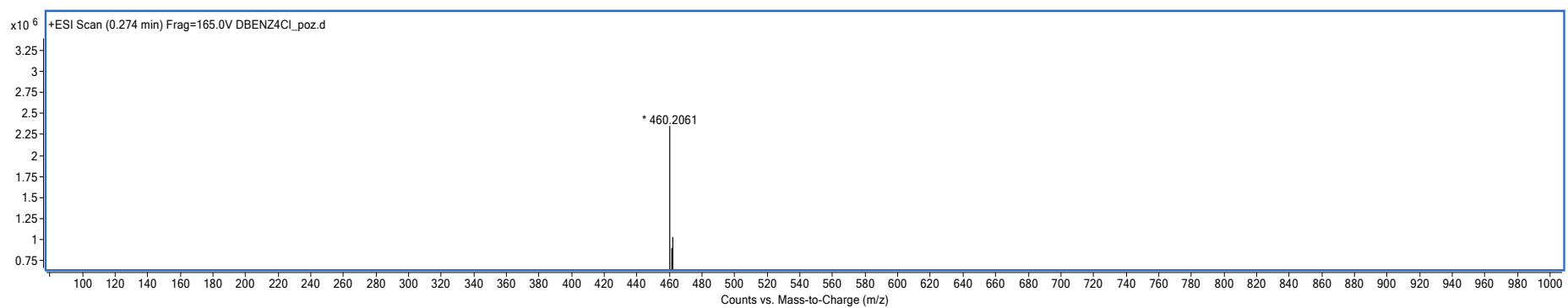
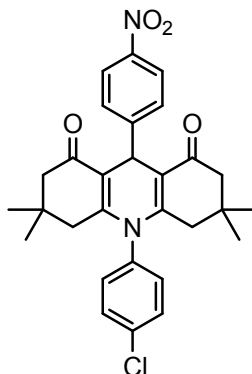


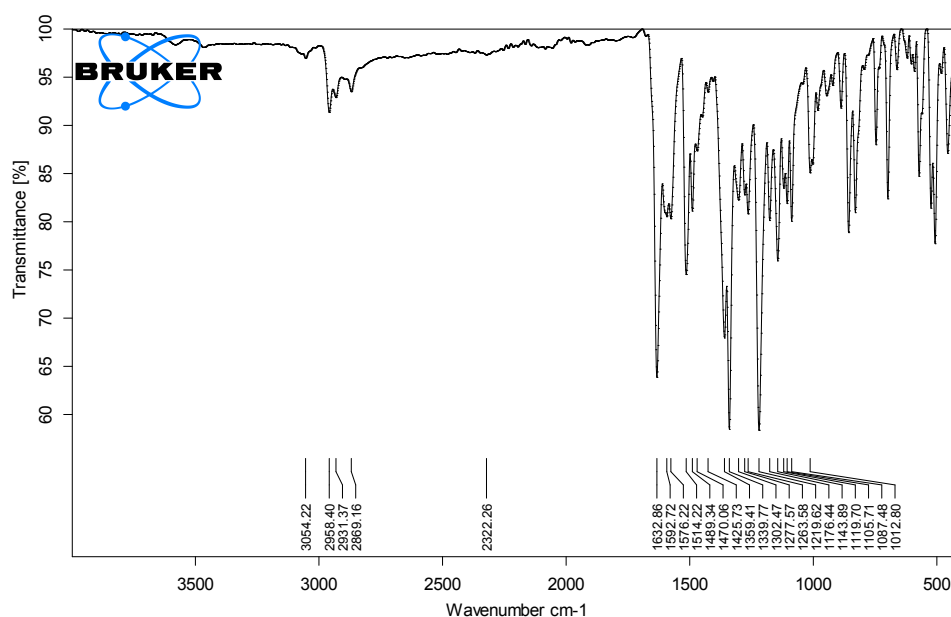
Fig. S4. a) FT-IR, **b)** ^1H NMR, **c)** ^{13}C NMR (APT), **d)** Q-TOF LC/HRMS of **4a**

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,6,7,9,10 hexahydroacridine-1,8(2H,5H)-dione (4b)

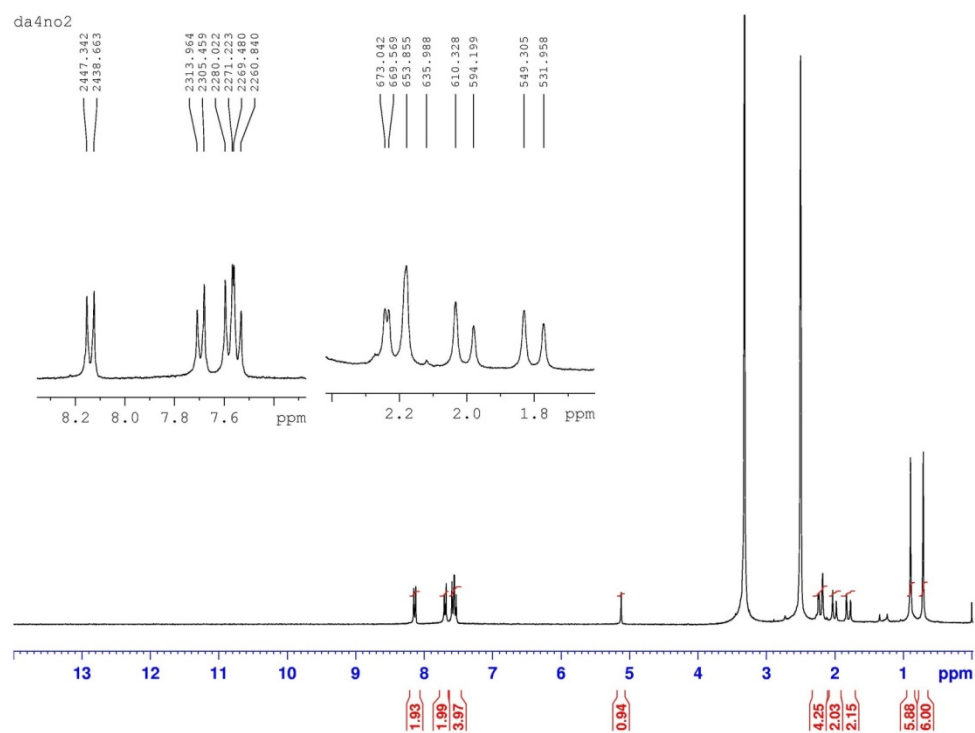


As yellow crystals, (0.478 g, 91 %), mp. (315-317 °C) [50] (ethanol). $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ (ppm): 0.70 (s, 6H, 2x- CH_3), 0.90 (s, 6H, 2x- CH_3), 1.80 (d, 2H, $J = 17.35$ Hz, - CH_2), 2.01 (d, 2H, $J = 16.13$ Hz, - CH_2), 2.18-2.24 (m, 4H, - CH_2), 5.10 (s, 1H, -CH), 7.54-7.60 (m, 4H, Ar-H), 7.70 (d, 2H, $J = 8.51$ Hz, Ar-H), 8.14 (d, 2H, $J = 8.68$ Hz, Ar-H); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 26.57, 29.61, 32.47, 33.35, 41.39, 49.86, 112.51, 119.43, 123.76, 129.43, 134.55, 137.55, 146.16, 151.32, 154.01, 195.53; IR (cm^{-1}): 3054 w (Ar-H), 2958 w (-CH), 1632 s (C=O), 1592 w (C=C); HRMS (QTOF-ESI): m/z calcd. For $\text{C}_{29}\text{H}_{29}\text{ClN}_2\text{O}_4$: 504.1816; found: 527.1729 ($[\text{M}+\text{Na}]^+$).

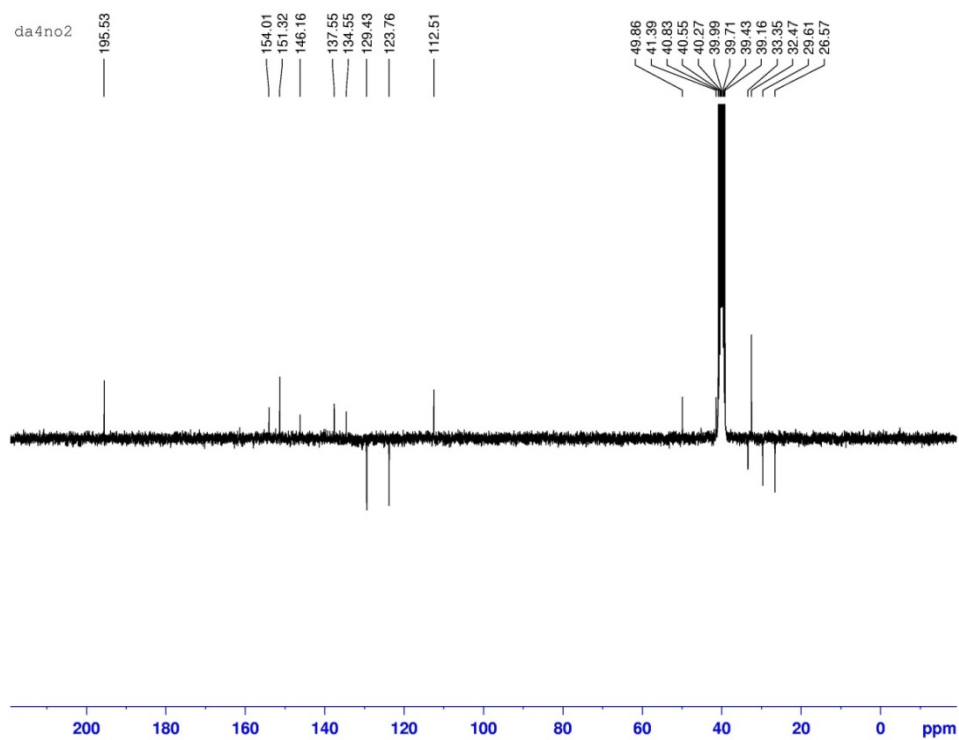
a)



c)



c)



d)

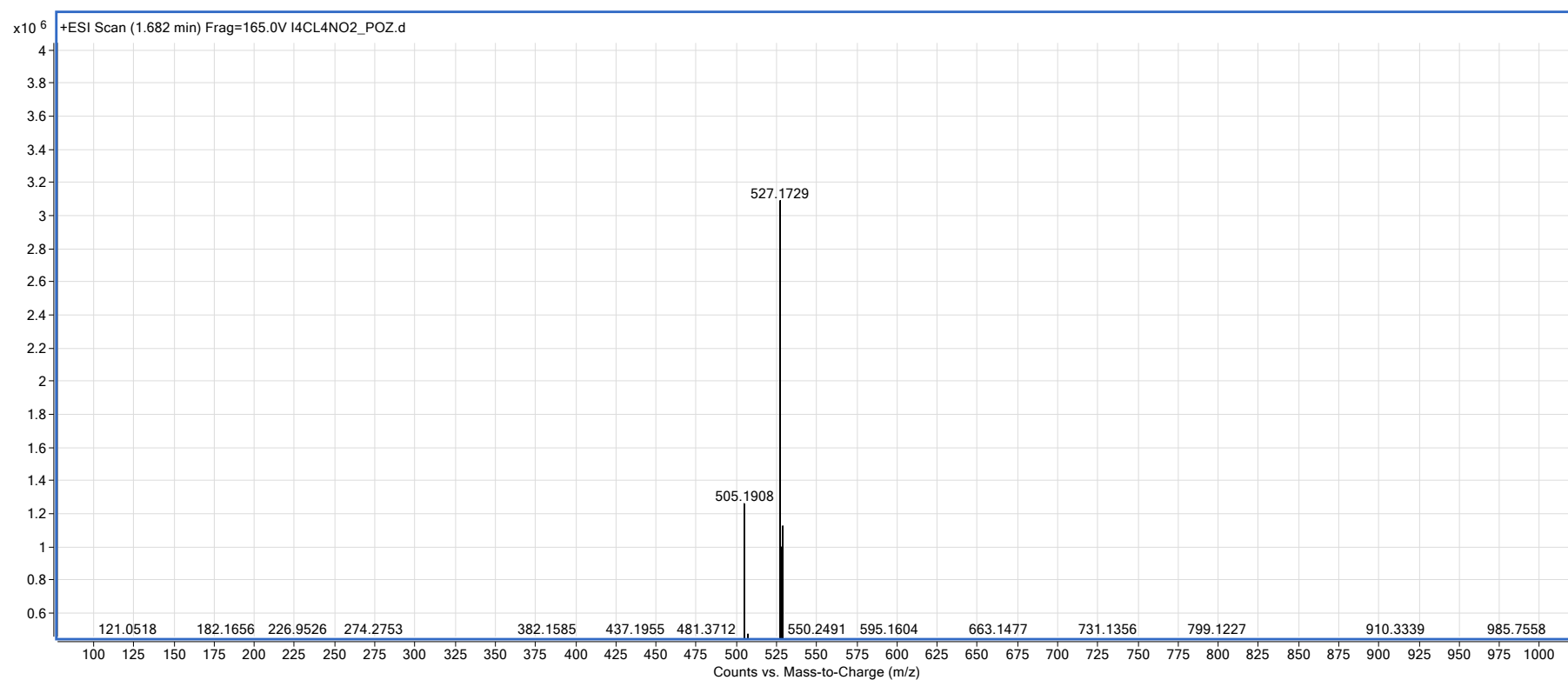
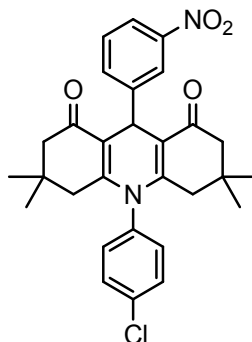


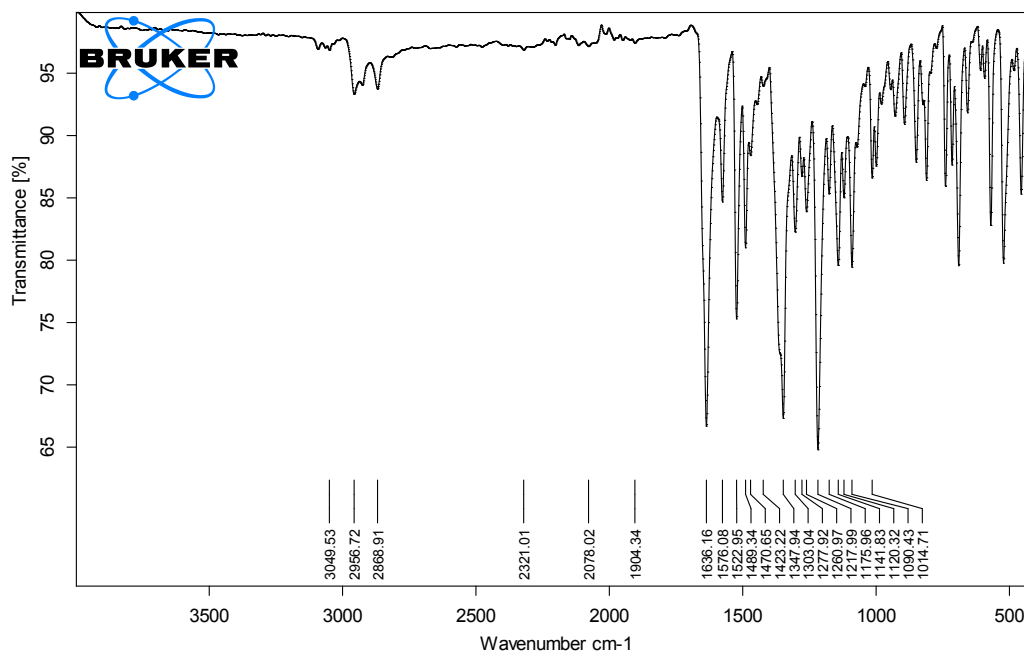
Fig. S5. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of **4b**

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,6,7,9,10 hexahydroacridine-1,8(2H,5H)-dione (4c)

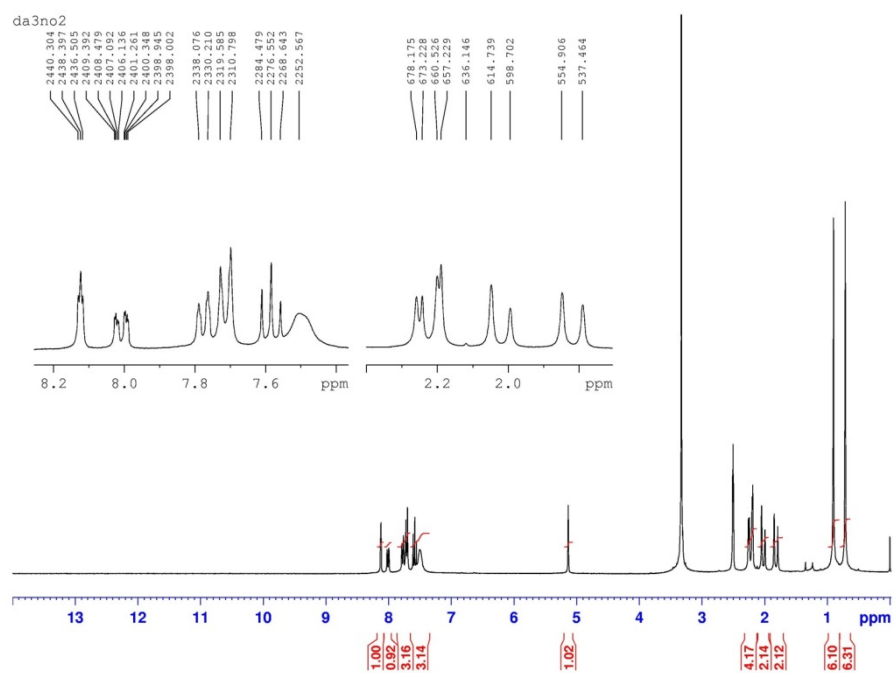


As yellow crystals, (0.464 g, 92 %), mp. (285-287 °C) [51] (ethanol). ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 0.72 (s, 6H, 2x-CH₃), 0.88 (s, 6H, 2x-CH₃), 1.82 (d, 2H, *J*= 17.44 Hz, -CH₂), 2.02 (d, 2H, *J*= 16.04 Hz, -CH₂), 2.20 (d, 2H, *J*= 3.30 Hz, -CH₂), 2.25 (d, 2H, *J*= 4.95 Hz, -CH₂), 5.15 (s, 1H, -CH), 7.51-7.61 (m, 3H, Ar-H), 7.72 (d, 2H, *J*= 8.79 Hz, Ar-H), 7.78 (d, 1H, *J*= 7.87 Hz, Ar-H), 7.99-8.03 (m, 1H, Ar-H), 8.12-8.13 (m, 1H, Ar-H)); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ (ppm): 26.47, 29.62, 32.52, 32.92, 41.34, 49.84, 112.72, 121.50, 122.56, 130.21, 130.65, 134.58, 134.75, 137.52, 147.88, 148.60, 151.39, 195.63; IR (cm⁻¹): 3049 w (Ar-H), 2956 w (-CH), 1636 s (C=O), 1576 s (C=C); HRMS (QTOF-ESI): *m/z* calcd. For C₂₉H₂₉ClN₂O₄: 504.1816; found: 527.1655 ([M+Na]⁺).

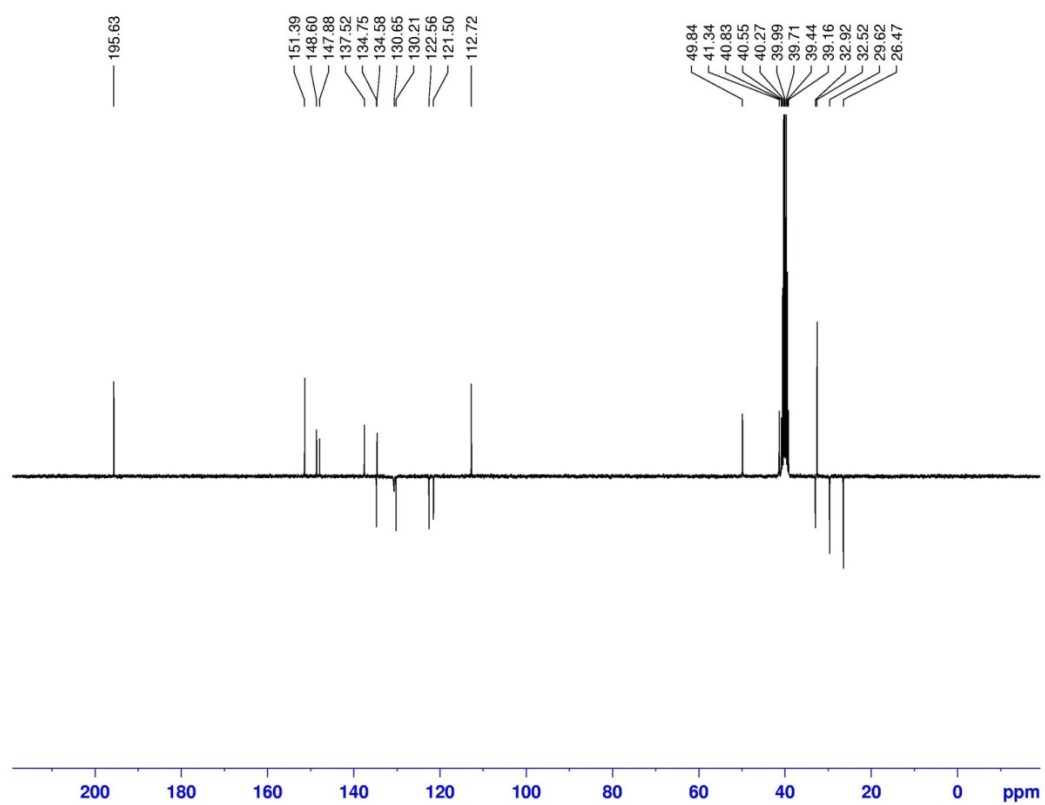
a)



b)



c)



d)

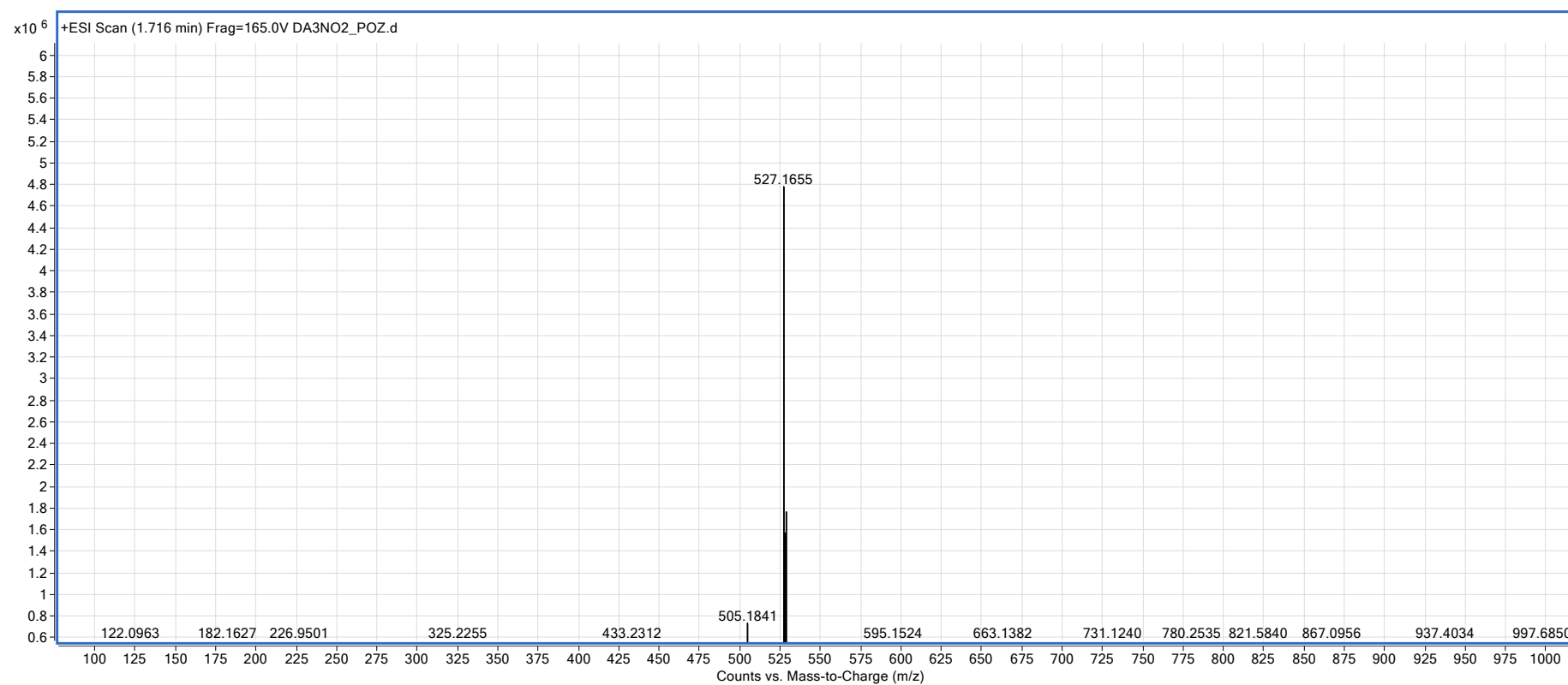
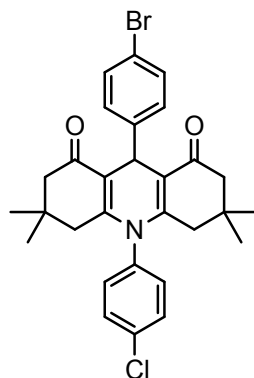


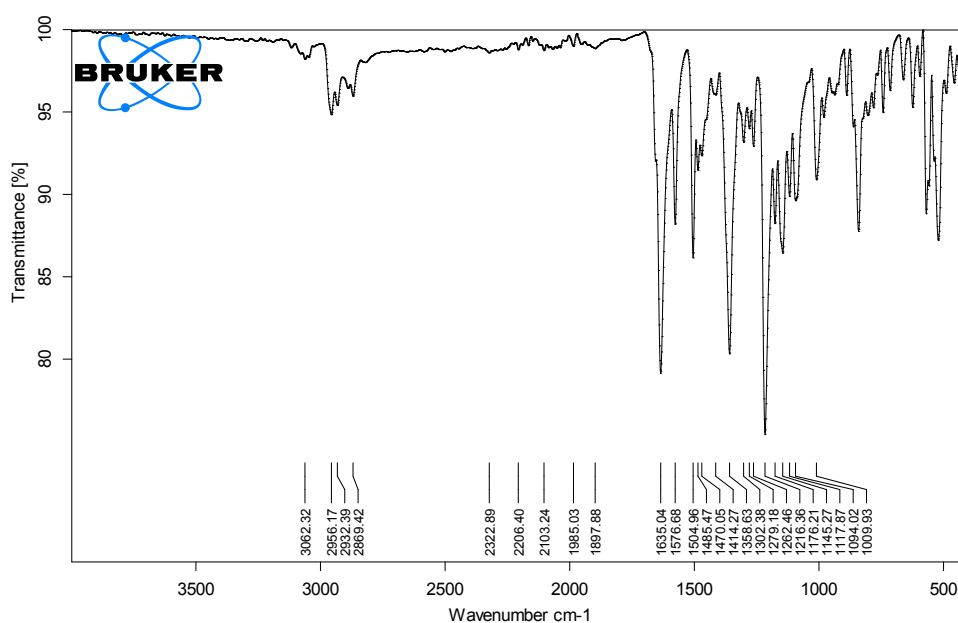
Fig. S6. a) FT-IR, **b)** ^1H NMR, **c)** ^{13}C NMR (APT), **d)** Q-TOF LC/HRMS of **4c**

**9-(4-Bromophenyl)-10-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10
hexahydroacridine-1,8(2H,5H)-dione (4d)**

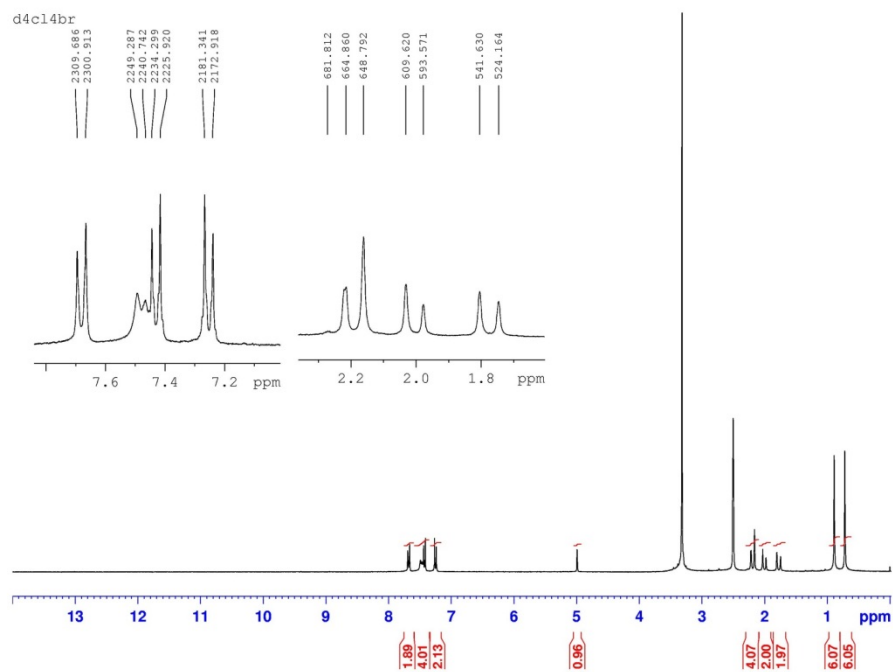


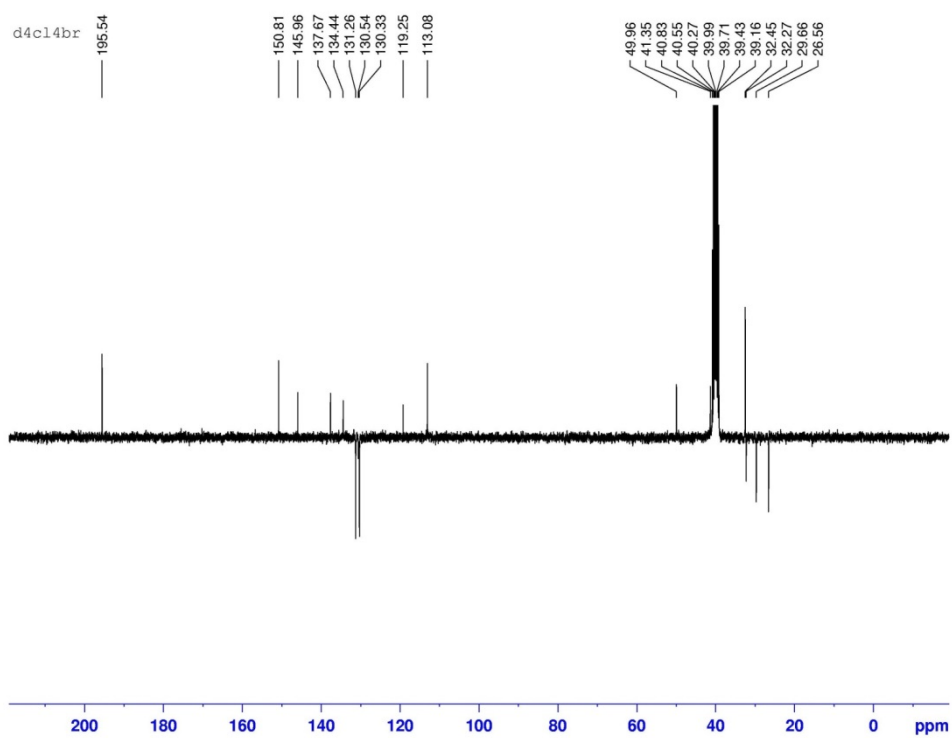
As yellow crystals, (0.504 g, 94 %), mp. (304-305 °C) [50] (ethanol). ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 0.70 (s, 6H, 2x-CH₃), 0.90 (s, 6H, 2x-CH₃), 1.78 (d, 2H, *J*= 17.47 Hz, -CH₂), 2.01 (d, 2H, *J*= 16.05 Hz, -CH₂), 2.16-2.19 (m, 4H, -CH₂), 5.00 (s, 1H, -CH), 7.26 (d, 2H, *J*= 8.42 Hz, Ar-H), 7.42-7.50 (m, 4H, Ar-H), 7.68 (d, 2H, *J*= 8.77 Hz, Ar-H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ (ppm): 26.56, 29.66, 32.27, 32.45, 41.35, 49.96, 113.08, 119.25, 130.33, 130.54, 131.26, 134.44, 137.67, 145.96, 150.81, 195.54; IR (cm⁻¹): 3062 w (Ar-H), 2956 w (-CH), 1635 s (C=O), 1576 s (C=C); HRMS (QTOF-ESI): *m/z* calcd. For C₂₉H₂₉BrClNO₂: 537.1070; found: 538.1123 ([M+H]⁺).

a)



c)





d)

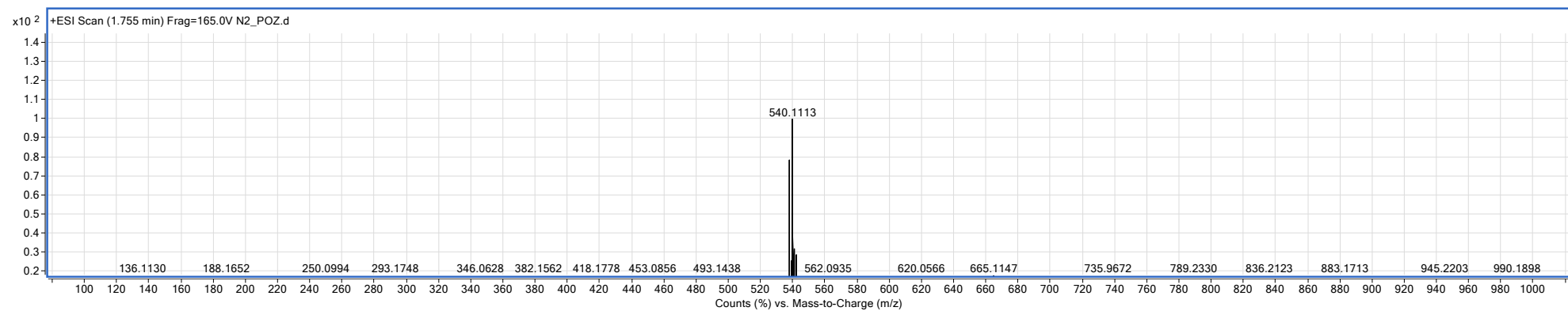
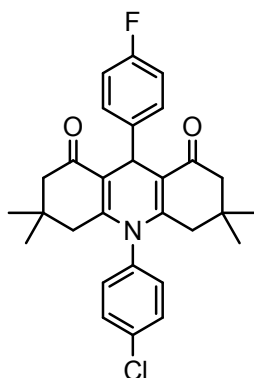


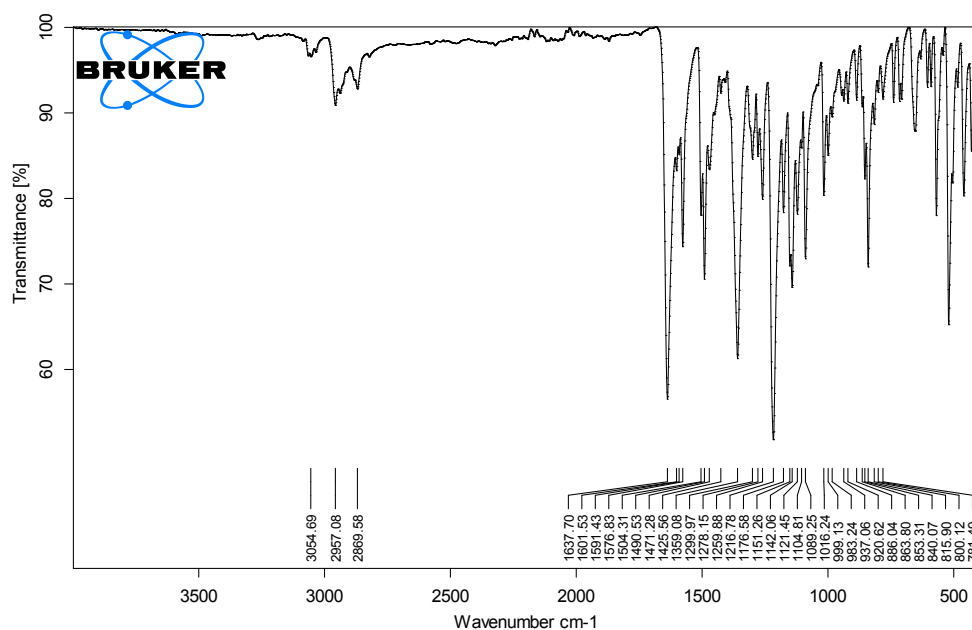
Fig. S7. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of **4d**

10-(4-Chlorophenyl)-9-(4-fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8 (2H,5H)-dione (4e)

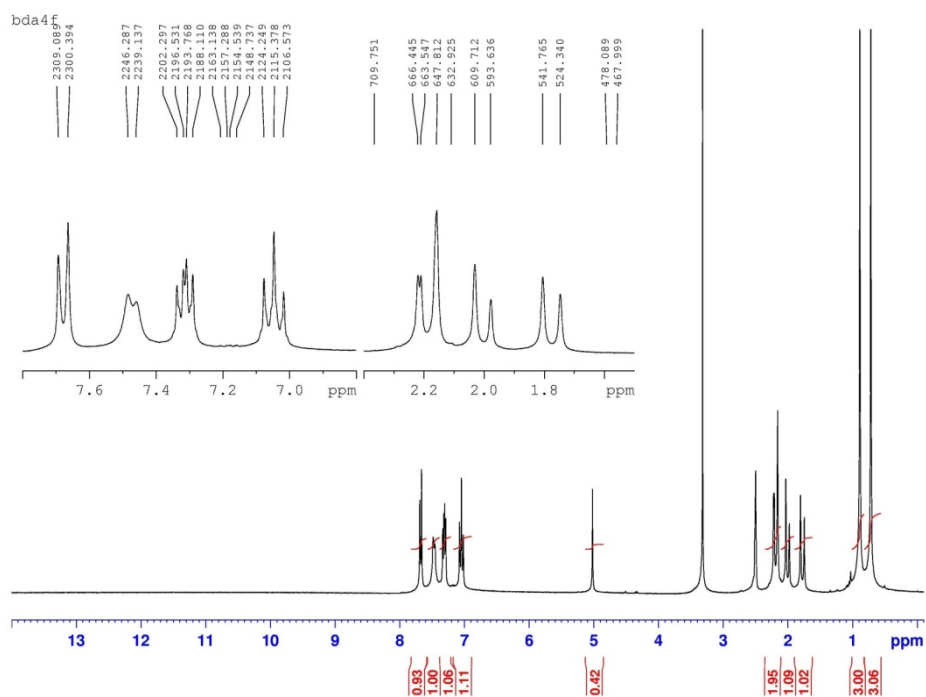


As yellow crystals, (0.434 g, 91 %), mp. (280-282 °C) [52] (ethanol). $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ (ppm): 0.70 (s, 6H, 2x- CH_3), 0.90 (s, 6H, 2x- CH_3), 1.78 (d, 2H, $J = 17.43$ Hz, - CH_2), 2.01 (d, 2H, $J = 16.08$ Hz, - CH_2), 2.16-2.22 (m, 4H, - CH_2), 5.05 (s, 1H, -CH), 7.05 (t, 2H, $J = 8.84$ Hz, Ar-H), 7.29-7.34 (m, 2H, Ar-H), 7.48 (d, 2H, $J = 7.15$ Hz, Ar-H), 7.68 (d, 2H, $J = 8.70$ Hz, Ar-H); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 26.52, 29.68, 31.84, 32.45, 41.35, 49.98, 113.42, 114.86, 129.79, 130.53, 134.42, 137.72, 142.80, 150.64, 159.29, 195.55; IR (cm^{-1}): 3054 w (Ar-H), 2957 s (-CH), 1637 s (C=O), 1576 s (C=C); HRMS (QTOF-ESI): m/z calcd. For $\text{C}_{29}\text{H}_{29}\text{ClFNO}_2$: 477.1871; found: 478.1956 ($[\text{M}+\text{H}]^+$).

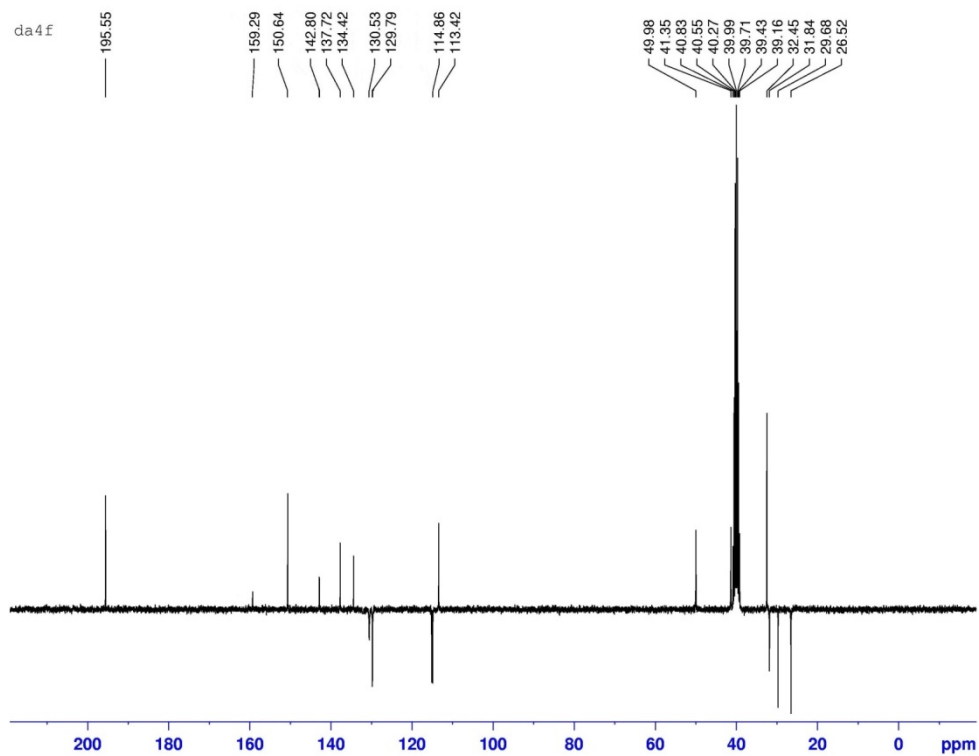
a)



b)



c)



d)

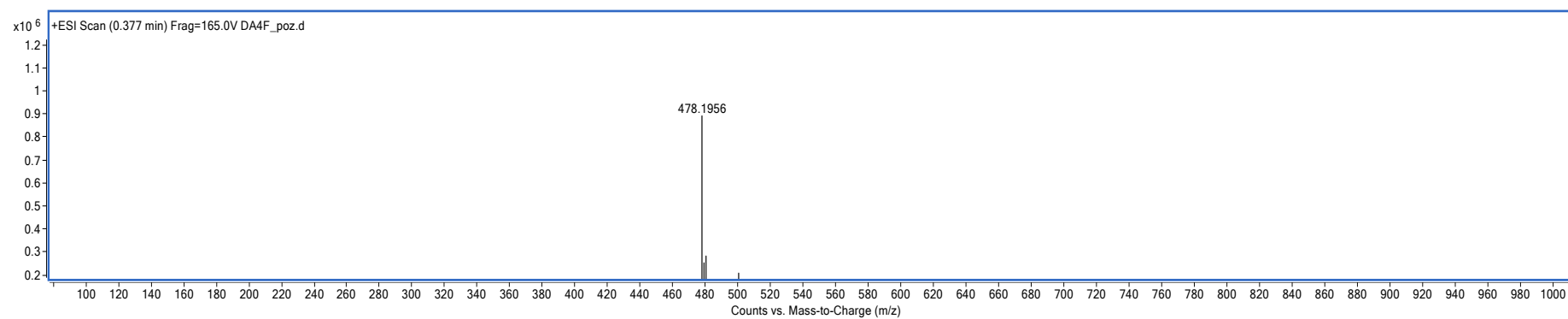
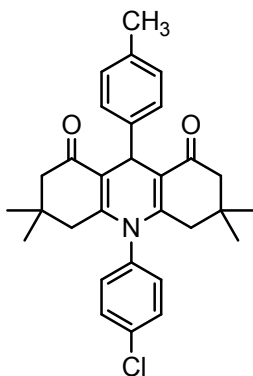


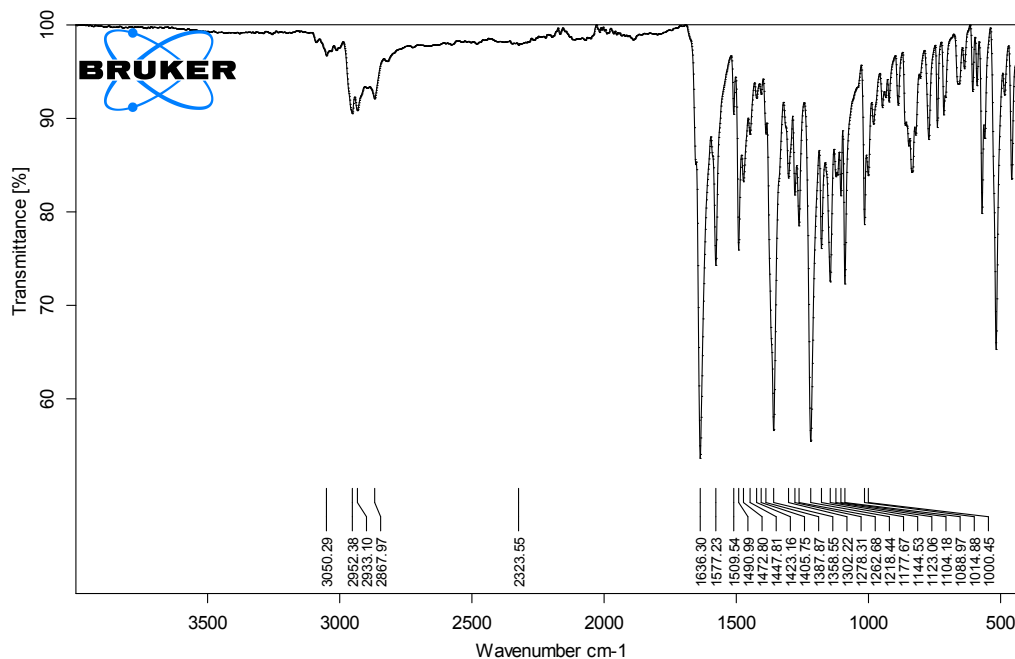
Fig. S8. a) FT-IR, **b)** ^1H NMR, **c)** ^{13}C NMR (APT), **d)** Q-TOF LC/HRMS of **4e**

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4f)



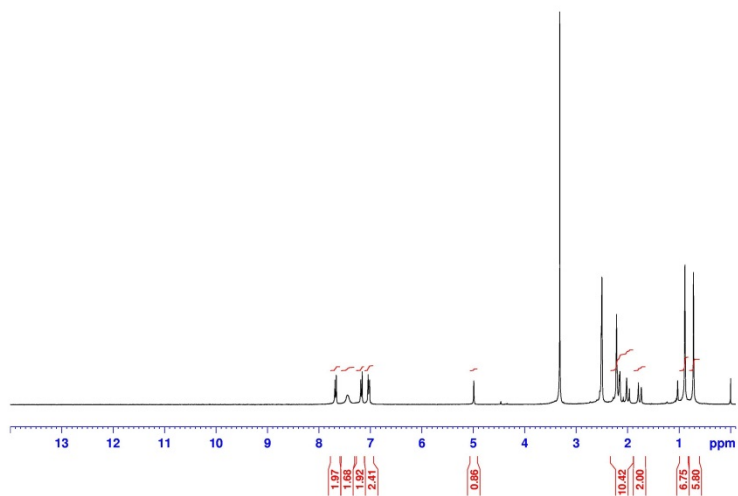
As yellow crystals, (0.435 g, 91 %), mp. (262-265 °C) [51] (ethanol). ^1H -NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm): 0.75 (s, 6H, 2x- CH_3), 0.80 (s, 6H, 2x- CH_3), 1.76 (d, 2H, $J = 17.29$ Hz, - CH_2), 1.97-2.22 (m, 9H, - CH_2 and - CH_3), 5.00 (s, 1H, -CH), 7.04 (d, 2H, $J = 8.05$ Hz, Ar-H), 7.18 (d, 2H, $J = 8.00$ Hz, Ar-H), 7.35-7.55 (m, 2H, Ar-H), 7.68 (d, 2H, $J = 8.82$ Hz, Ar-H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm): 26.53, 29.15, 31.83, 32.32, 32.43, 41.33, 50.05, 113.69, 127.87, 128.40, 128.96, 134.34, 135.10, 137.83, 143.69, 150.43, 195.54; IR (cm^{-1}): 3050 w (Ar-H), 2952 w (-CH), 1636 s ($\text{C}=\text{O}$), 1577 s ($\text{C}=\text{C}$); HRMS (QTOF-ESI): m/z calcd. For $\text{C}_{30}\text{H}_{32}\text{ClNO}_2$: 473.2122; found: 474.2215 ($[\text{M}+\text{H}]^+$).

a)

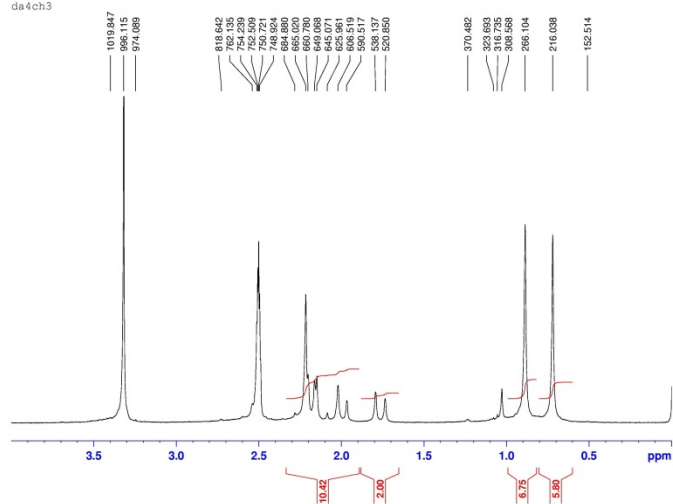


b)

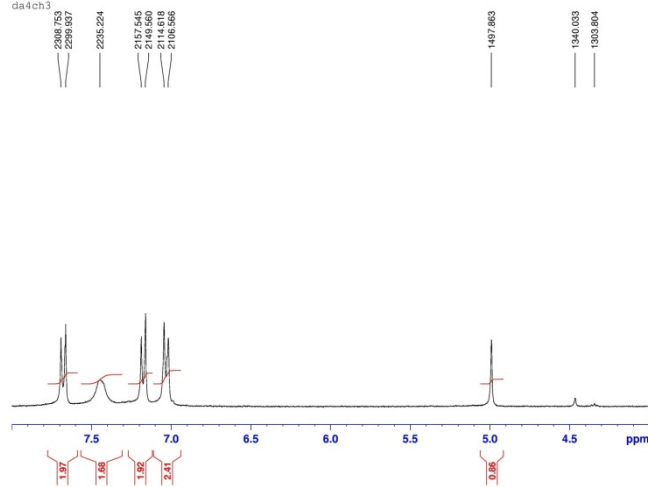
da4ch3



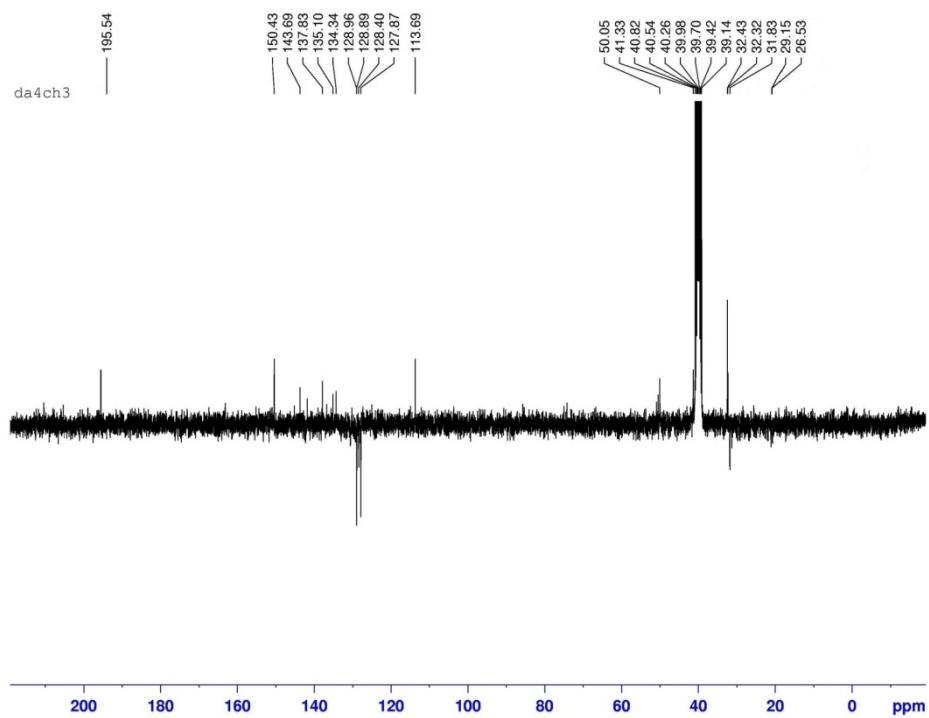
da4ch3



da4ch3



c)



d)

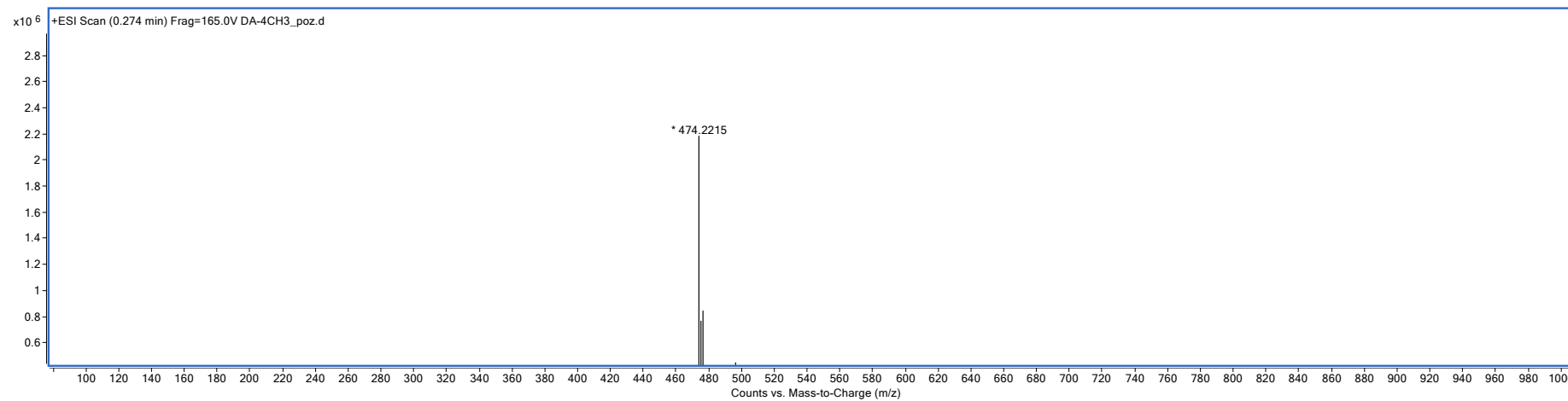
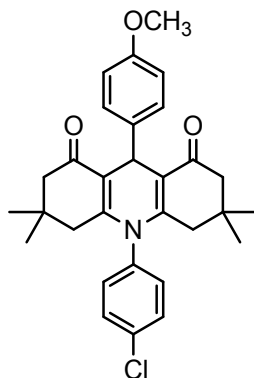


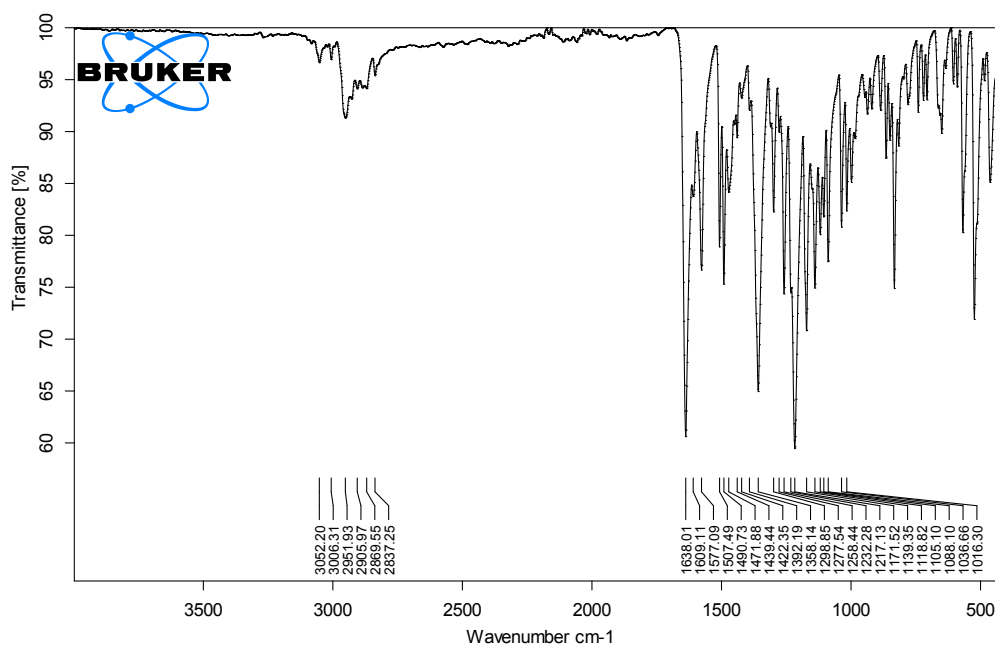
Fig. S9. a) FT-IR, **b)** ^1H NMR, **c)** ^{13}C NMR (APT), **d)** Q-TOF LC/HRMS of **4f**

10-(4-Chlorophenyl)-9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4g)



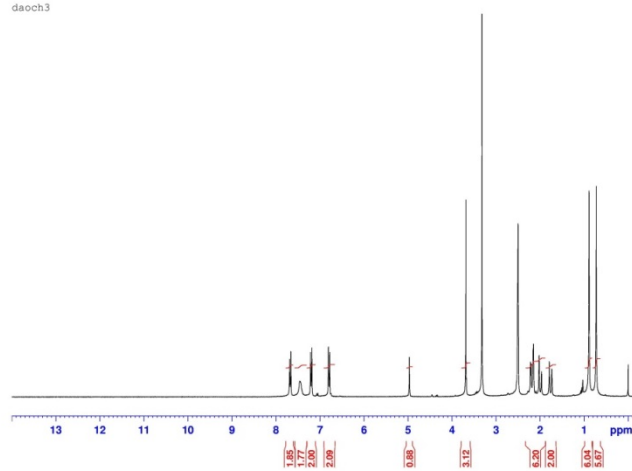
As yellow crystals, (0.440 g, 91 %), mp. (255-257 °C) [53] (ethanol). $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ (ppm): 0.75 (s, 6H, 2x- CH_3), 0.85 (s, 6H, 2x- CH_3), 1.76 (d, 2H, $J = 17.40$ Hz, - CH_2), 1.97-2.22 (m, 6H, - CH_2), 3.70 (s, 1H, - OCH_3), 4.95 (s, 1H, -CH), 6.80 (d, 2H, $J = 8.62$ Hz, Ar-H), 7.20 (d, 2H, $J = 8.61$ Hz, Ar-H), 7.40-7.55 (m, 2H, Ar-H), 7.68 (d, 2H, $J = 8.78$ Hz, Ar-H); $^{13}\text{C NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 26.56, 29.73, 31.39, 32.44, 50.07, 55.31, 113.71, 113.83, 128.93, 130.56, 134.34, 137.85, 138.92, 150.28, 157.76, 195.55; IR (cm^{-1}): 3006 w (Ar-H), 2951 w (-CH), 1638 s (C=O), 1577 s (C=C); HRMS (QTOF-ESI): m/z calcd. For $\text{C}_{30}\text{H}_{32}\text{ClNO}_3$: 489.2071; found: 490.2160 ($[\text{M}+\text{H}]^+$).

a)

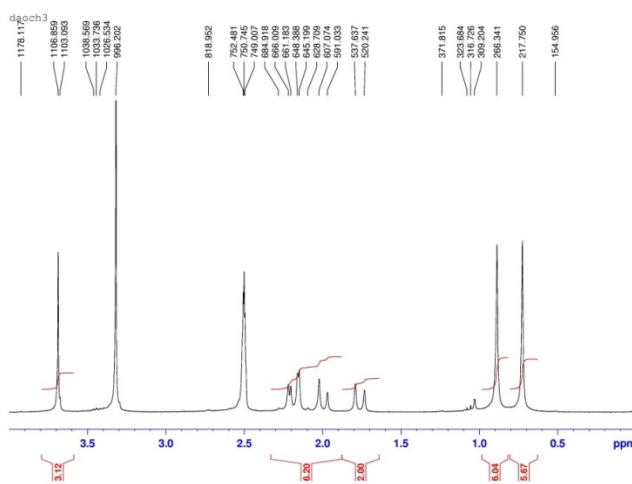


b)

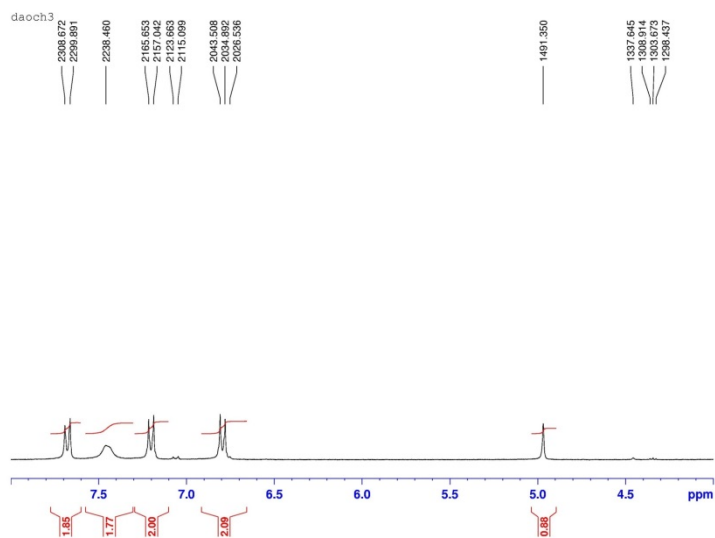
daoeh3



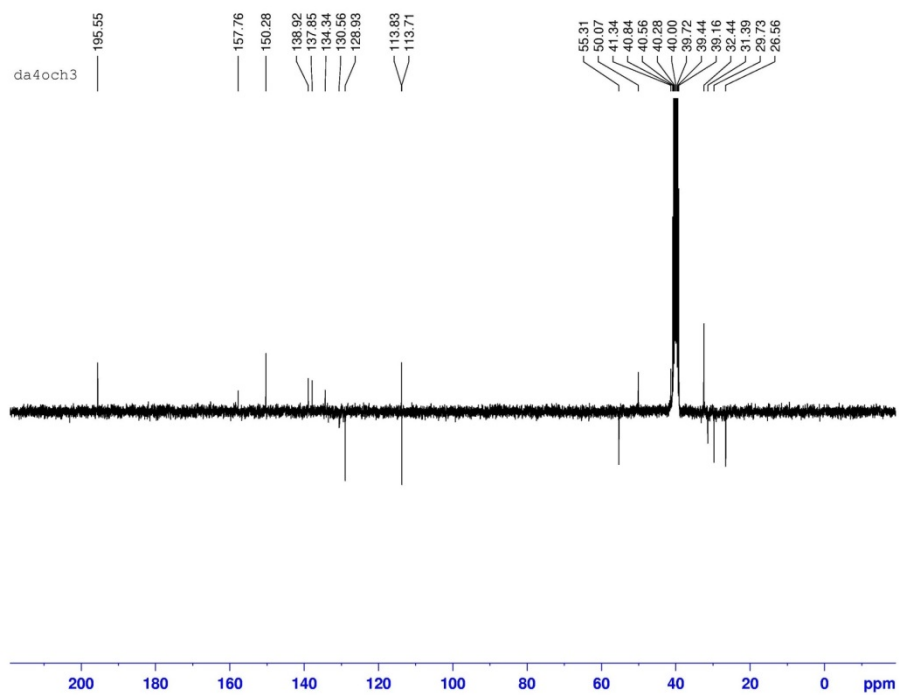
daoeh3



daoeh3



c)



d)

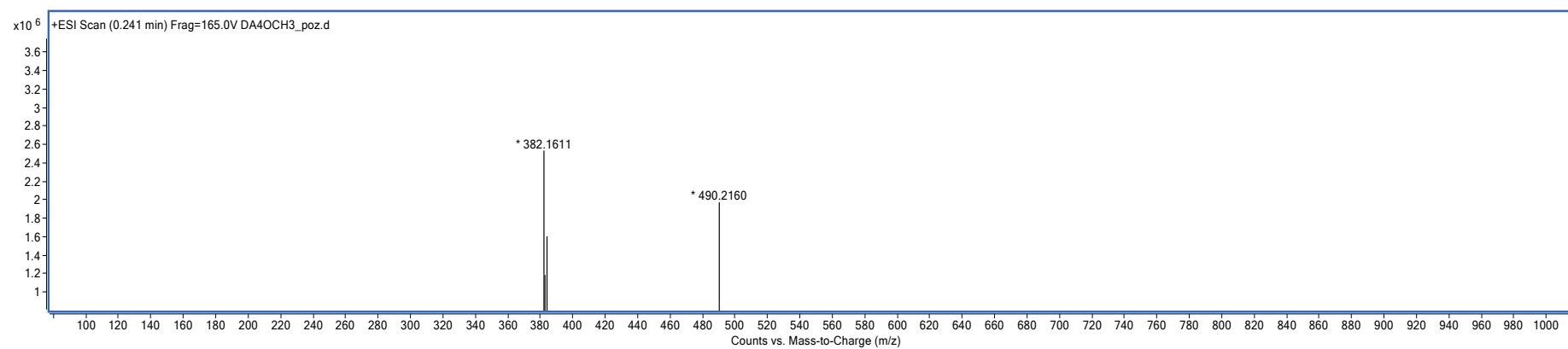
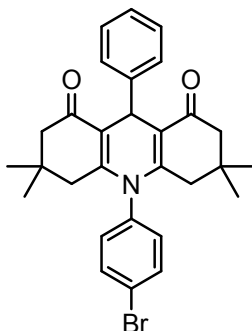


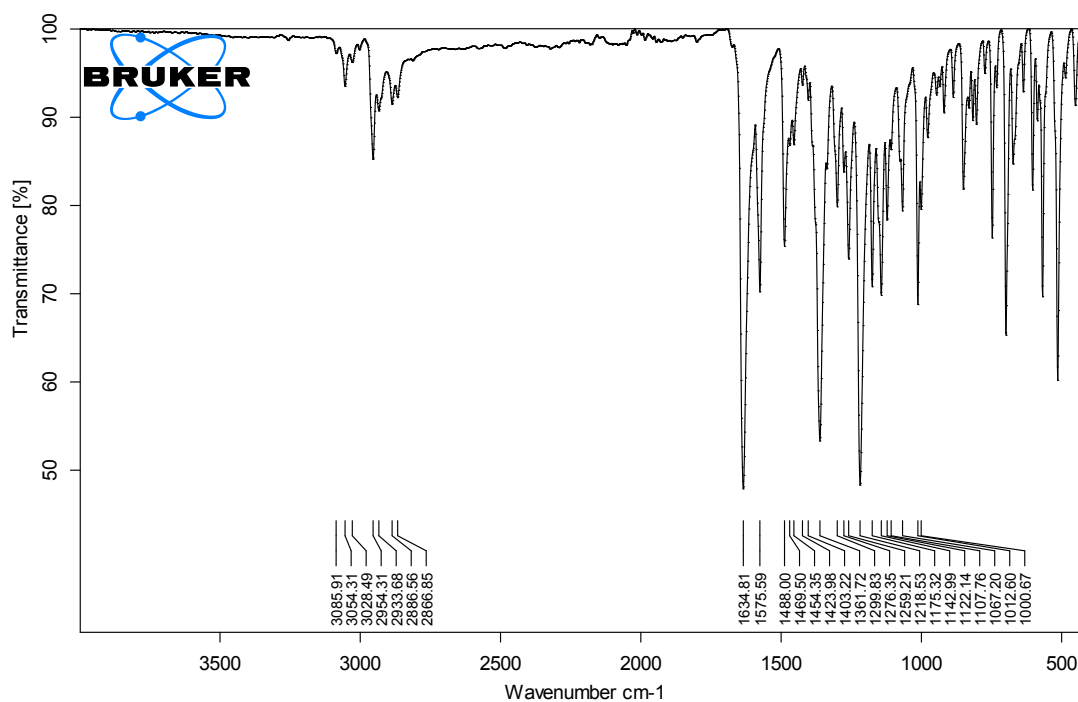
Fig. S10. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of **4g**

10-(4-Bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4h)

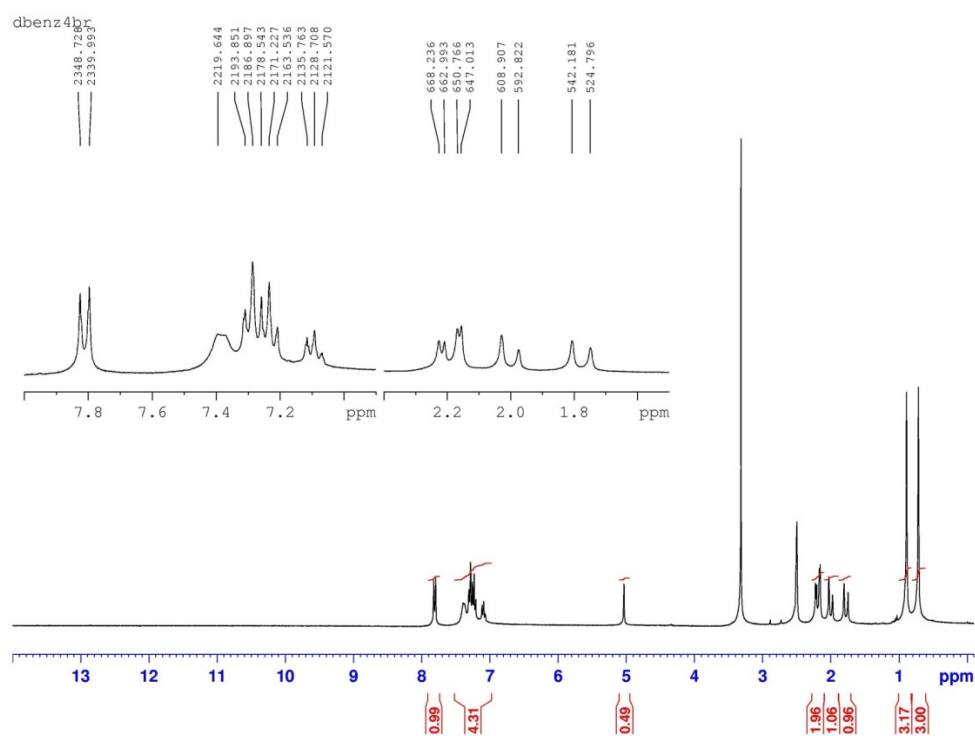


As yellow crystals, (0.472 g, 94 %), mp. (303-305 °C) [54] (ethanol). $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$) δ (ppm): 0.70 (s, 6H, 2x- CH_3), 0.90 (s, 6H, 2x- CH_3), 1.78 (d, 2H, $J = 17.39$ Hz, - CH_2), 2.00 (d, 2H, $J = 16.90$ Hz, - CH_2), 2.16-2.23 (m, 4H, - CH_2), 5.05 (s, 1H, -CH), 7.07-7.40 (m, 7H, Ar-H), 7.81 (d, 2H, $J = 8.74$ Hz, Ar-H); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$) δ (ppm): 26.50, 29.71, 32.32, 32.45, 41.35, 50.03, 113.54, 123.01, 126.27, 127.97, 128.37, 133.54, 138.22, 146.57, 150.51, 195.54; IR (cm^{-1}): 3028 s (Ar-H), 2954 s (-CH), 1634 s (C=O), 1575 s (C=C); HRMS (QTOF-ESI): m/z calcd. For $\text{C}_{29}\text{H}_{30}\text{BrNO}_2$: 503.1460; found: 504.1529 ($[\text{M}+\text{H}]^+$).

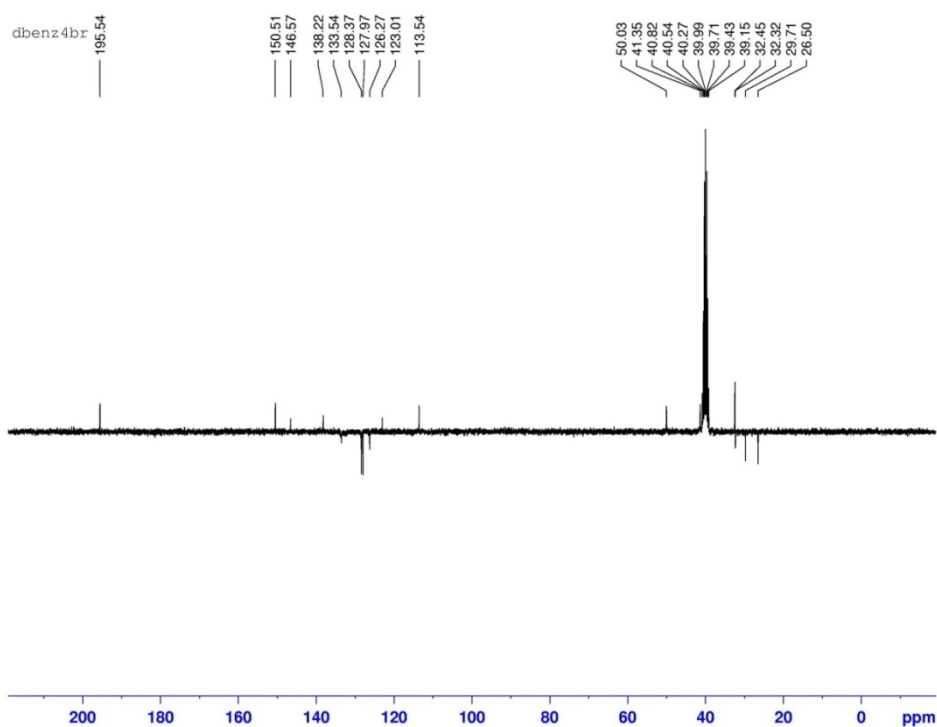
a)



b)



c)



d)

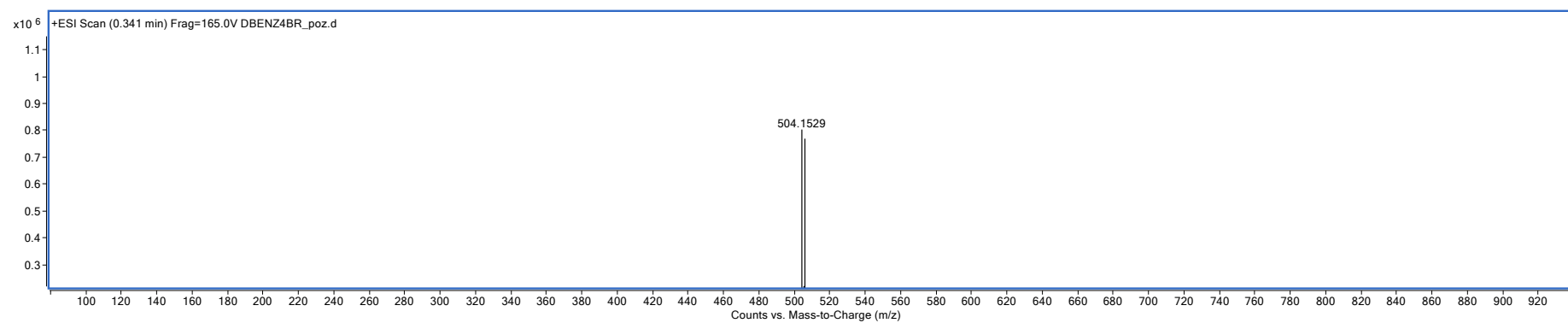
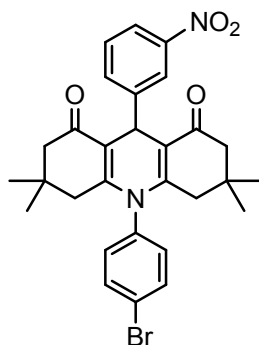
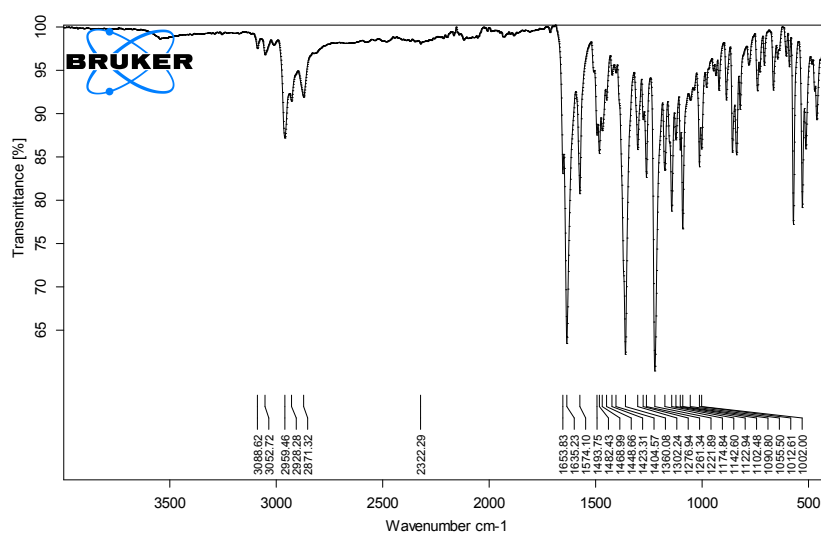


Fig. S11. a) FT-IR, **b)** ¹H NMR, **c)** ¹³C NMR (APT), **d)** Q-TOF LC/HRMS of **4h**

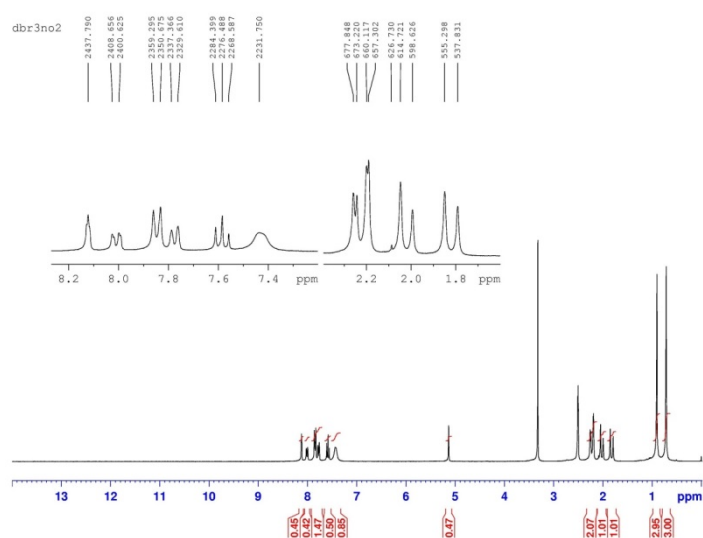
10-(4-bromophenyl)-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4i)



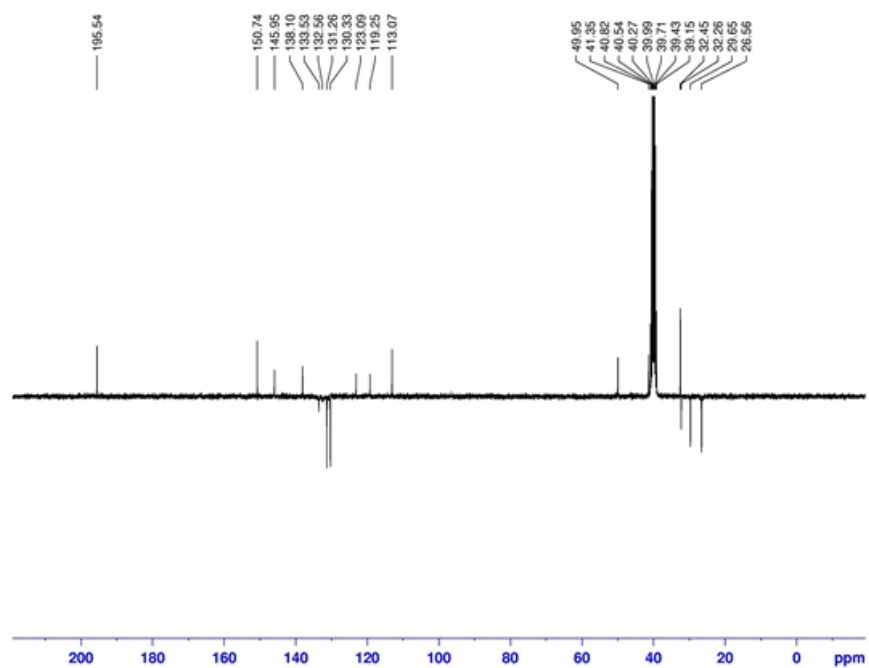
a)



b)



c)



d)

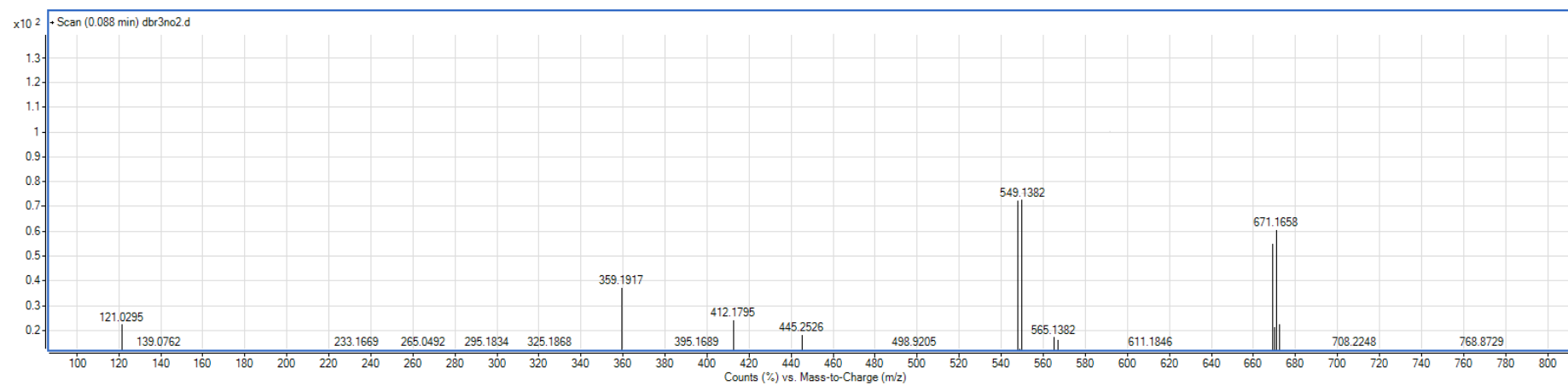
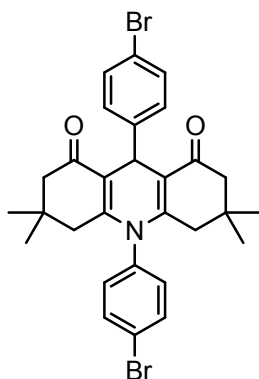
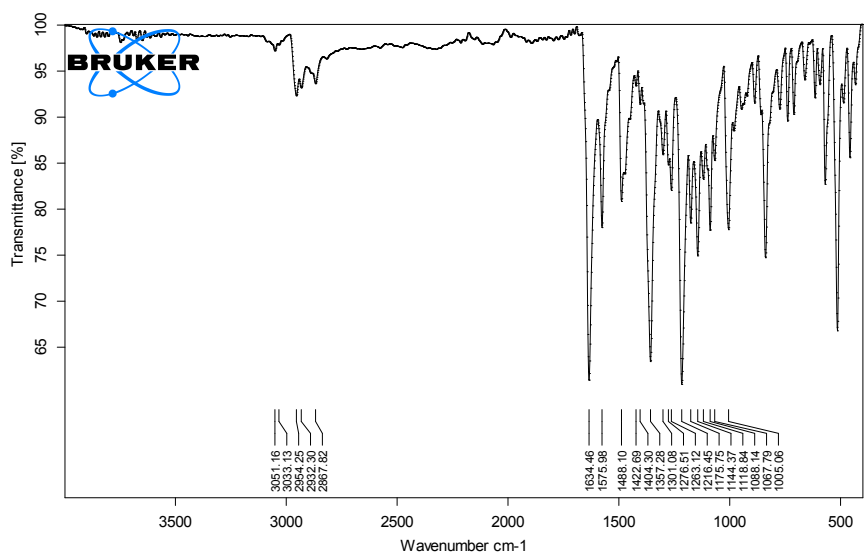


Fig. S12. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of 4i

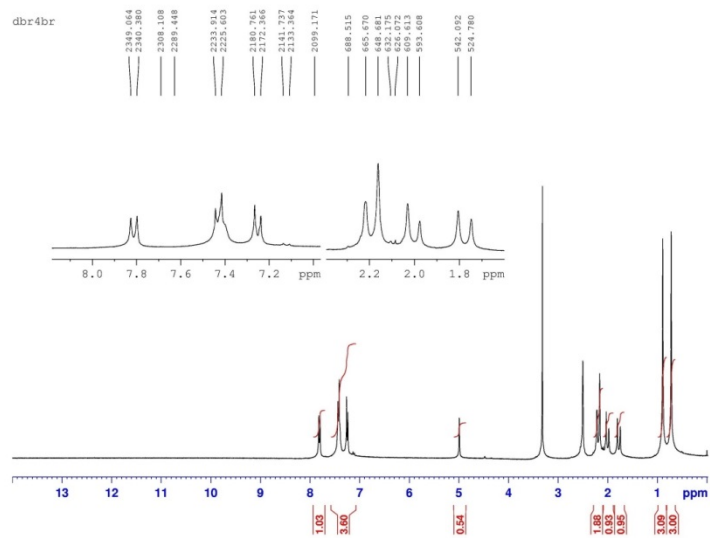
9,10-bis(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4j)



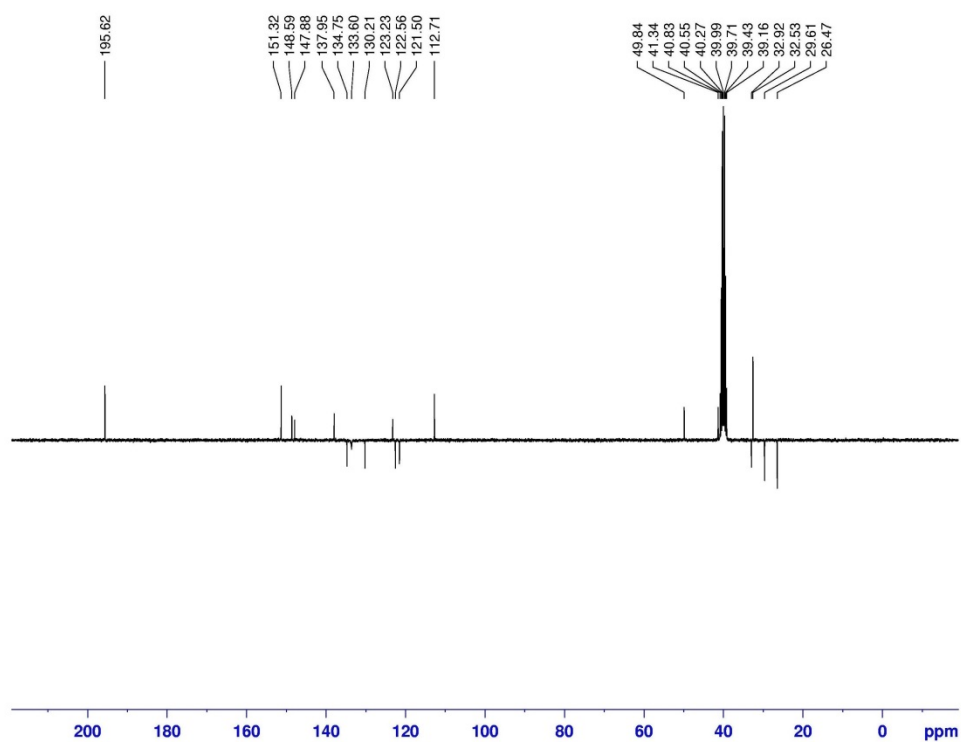
a)



b)



c)



d)

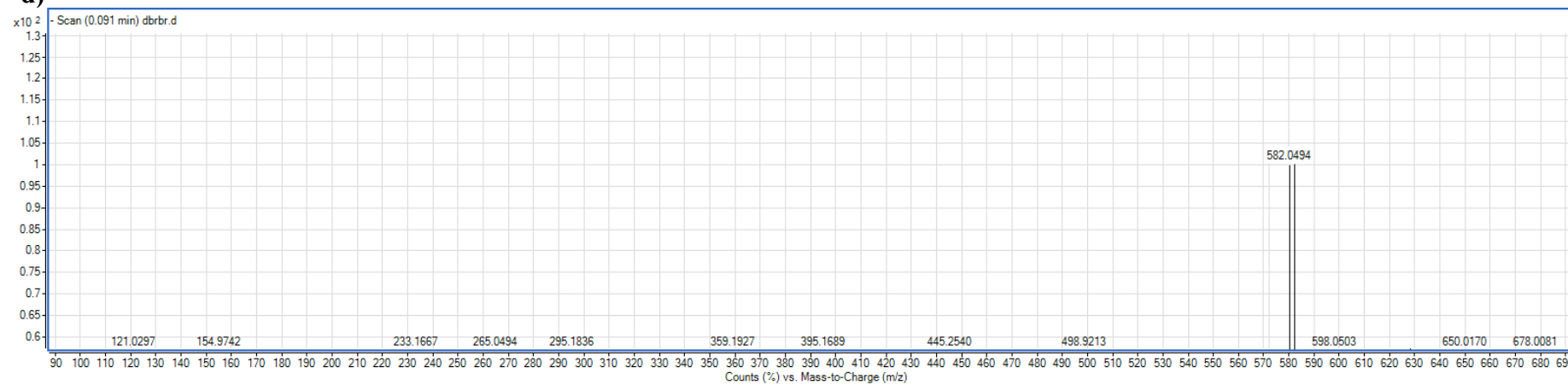


Fig. S13. a) FT-IR, **b)** ^1H NMR, **c)** ^{13}C NMR (APT), **d)** Q-TOF LC/HRMS of **4j**

