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Supporting Information

TiO_2-Coated magnetic nanoparticles-supported sulfonic acid as a new, efficient, reusable and magnetically separable heterogeneous solid acid catalyst for multicomponent reactions

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Field emission scanning electron microscopy

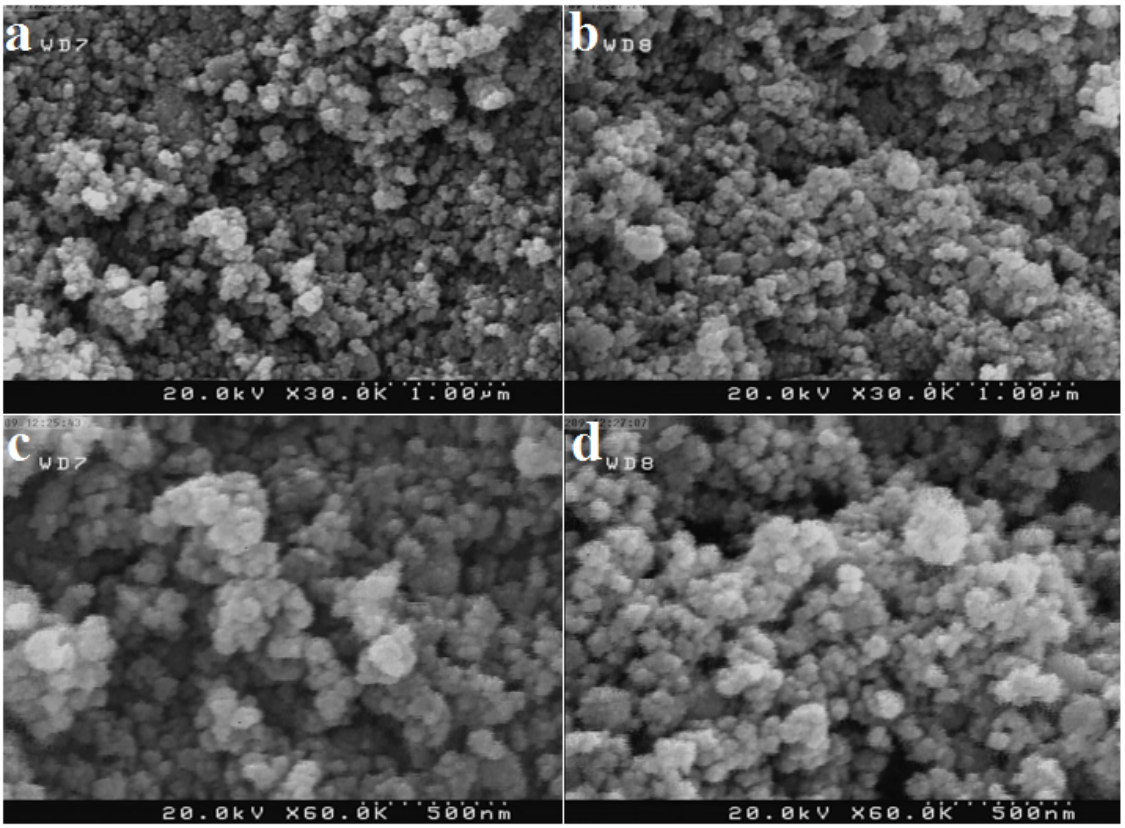


Fig.1. The FE-SEM image of nano-Fe_3O_4/TiO_2.

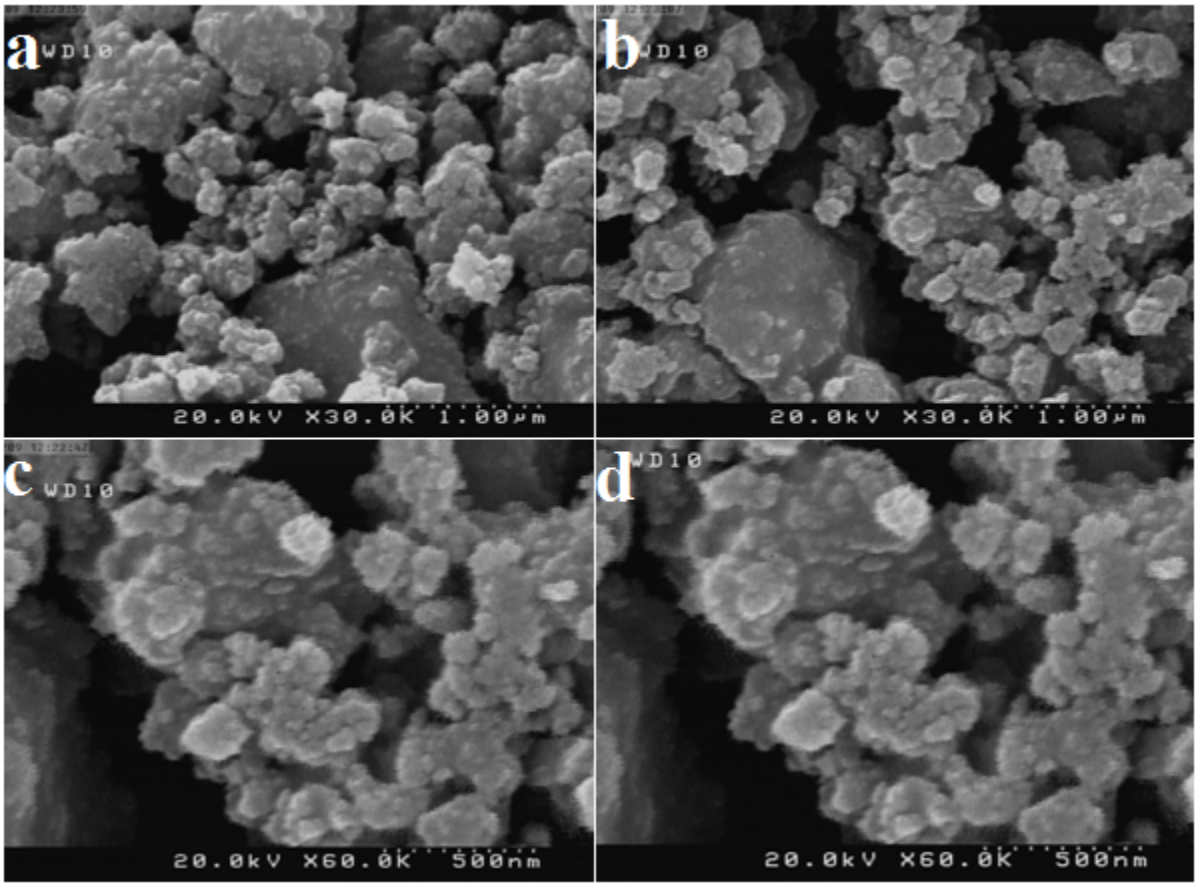


Fig.2. The FE-SEM image of nano-Fe_3O_4/TiO_2-SO_3H.

Vibration sample magnetometer

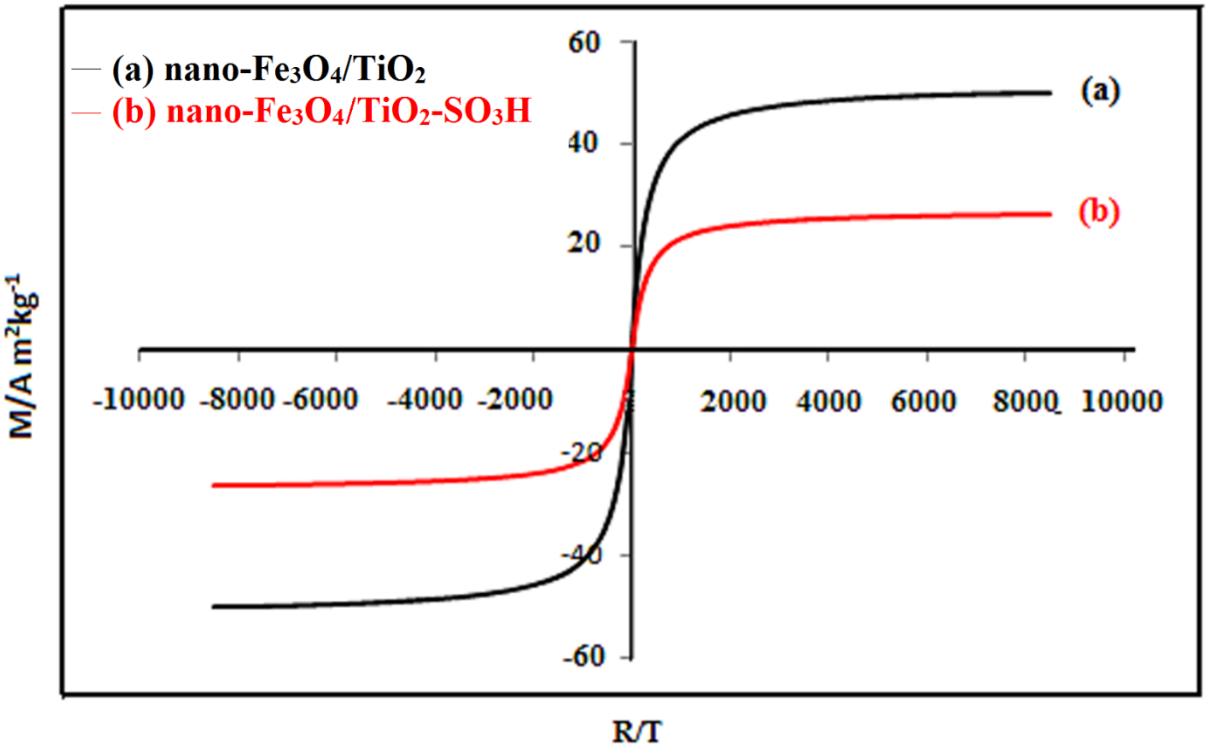


Fig.3. Room-temperature magnetization curves of (a) the nano-Fe_3O_4/TiO_2 and (b) nano-Fe_3O_4/TiO_2-SO_3H.

magnetic separation

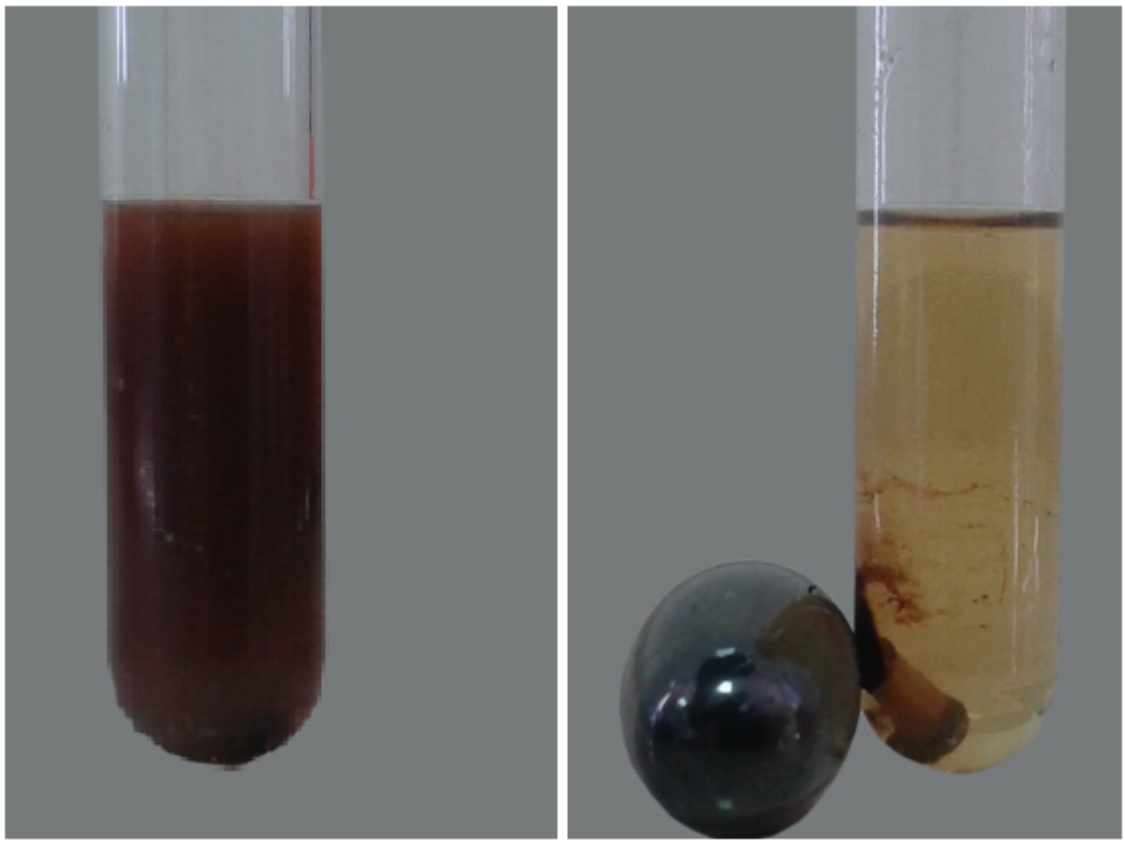


Fig.4. Photograph of aqueous suspension of nano-Fe_3O_4/TiO_2-SO_3H before (a) and after (b) magnetic capture.

Thermo gravimetric analysis

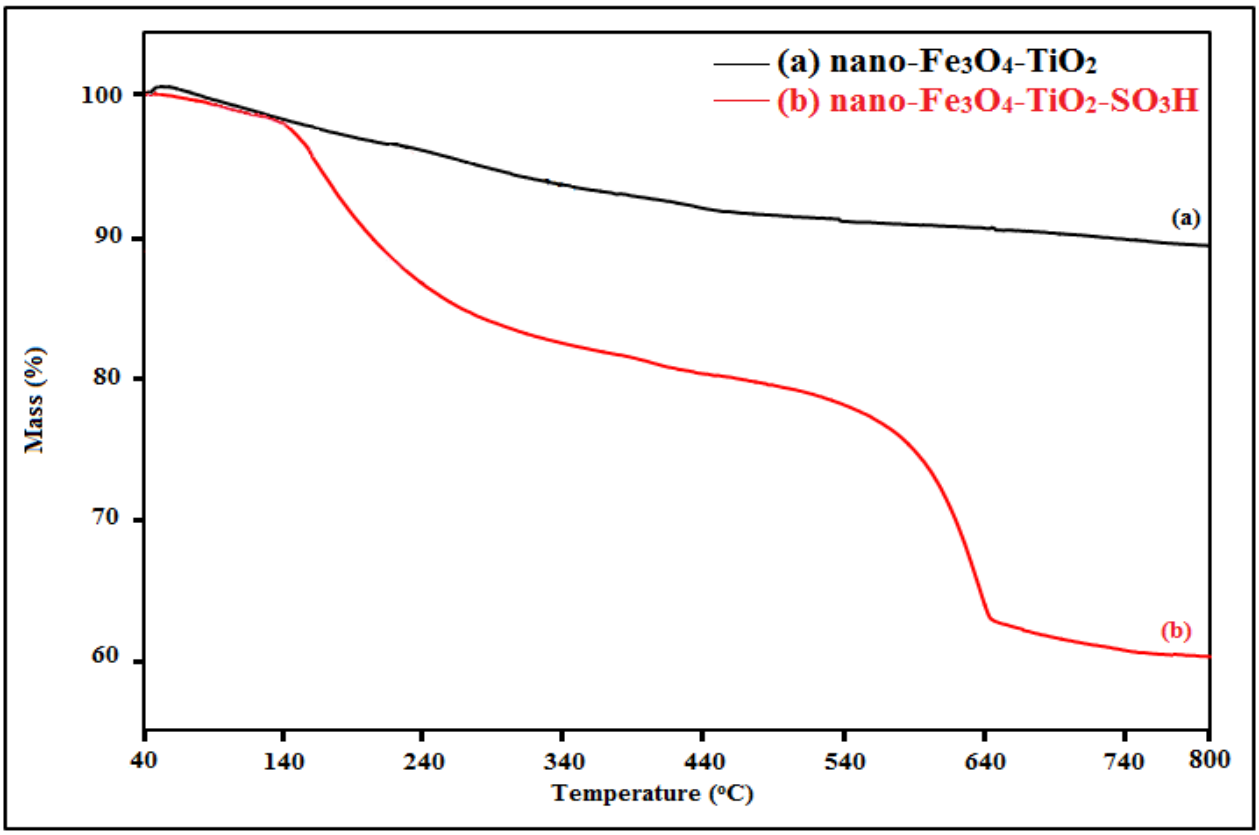


Fig.5. TGA cure of (a) the nano-Fe_3O_4/TiO_2 and (b) nano-Fe_3O_4/TiO_2-SO_3H.

Reusability of the n-FTSA

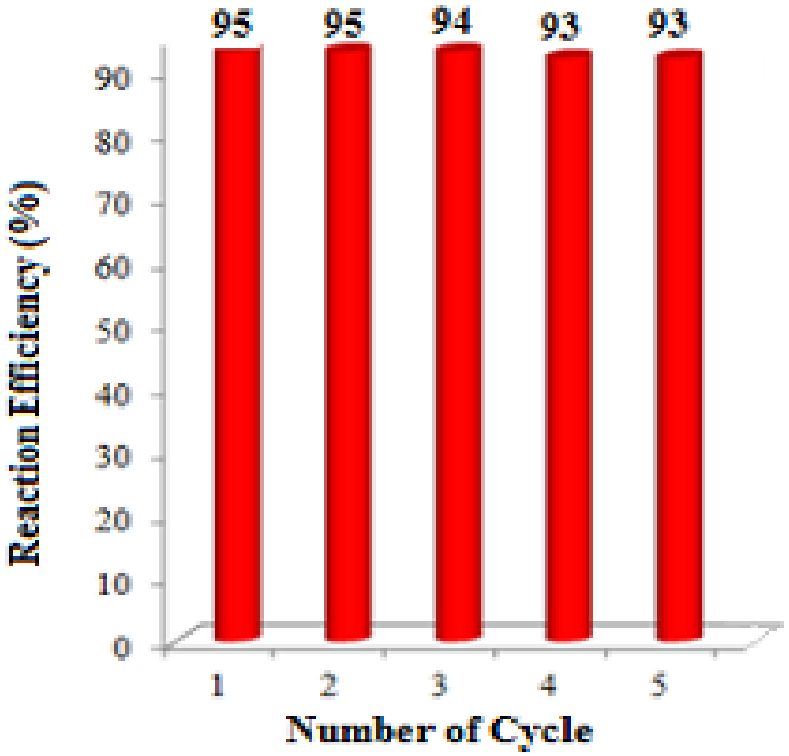
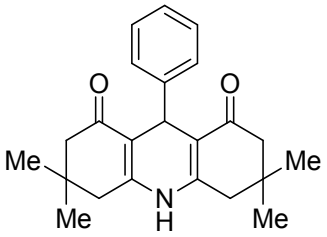


Fig.6. Reusability of n-FTSA for the synthesis of 1,8-dioxo-decahydroacridines, reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), NH_4OAc (2.5 mmol), reaction time: 50 min under solvent free conditions at 110 ºC.

Spectral data of some selected compound

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



M. P.: 190-191 °C; IR (KBr, Cm^{-1}) ν max: 3279, 3209, 3063, 2955, 2932, 1636, 1605, 1481, 1365, 1219, 1142. ^1H NMR (400 MHz, DMSO): δ 0.84 (s, 6H), 0.99 (s, 6H), 1.96 (d, J= 21.5 Hz, 2H), 2.15 (d, J= 21.5 Hz, 2H), 2.30 (d, J= 22.8 2H), 2.40-2.49 (m, 2H), 4.8 (s, 1H), 7.00-7.14 (m, 5H), 9.28 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 26.45, 29.13, 32.14, 32.86, 50.24, 111.47, 125.46, 127.56, 127.63, 147.15, 149.32, 194.36. Anal. Calc. for $C_{23}H_{27}NO_2$; C 79.05, H 7.79, N 4.01, O 9.16; Found: C 79.08, H 7.73, N 4.06, O 9.11.

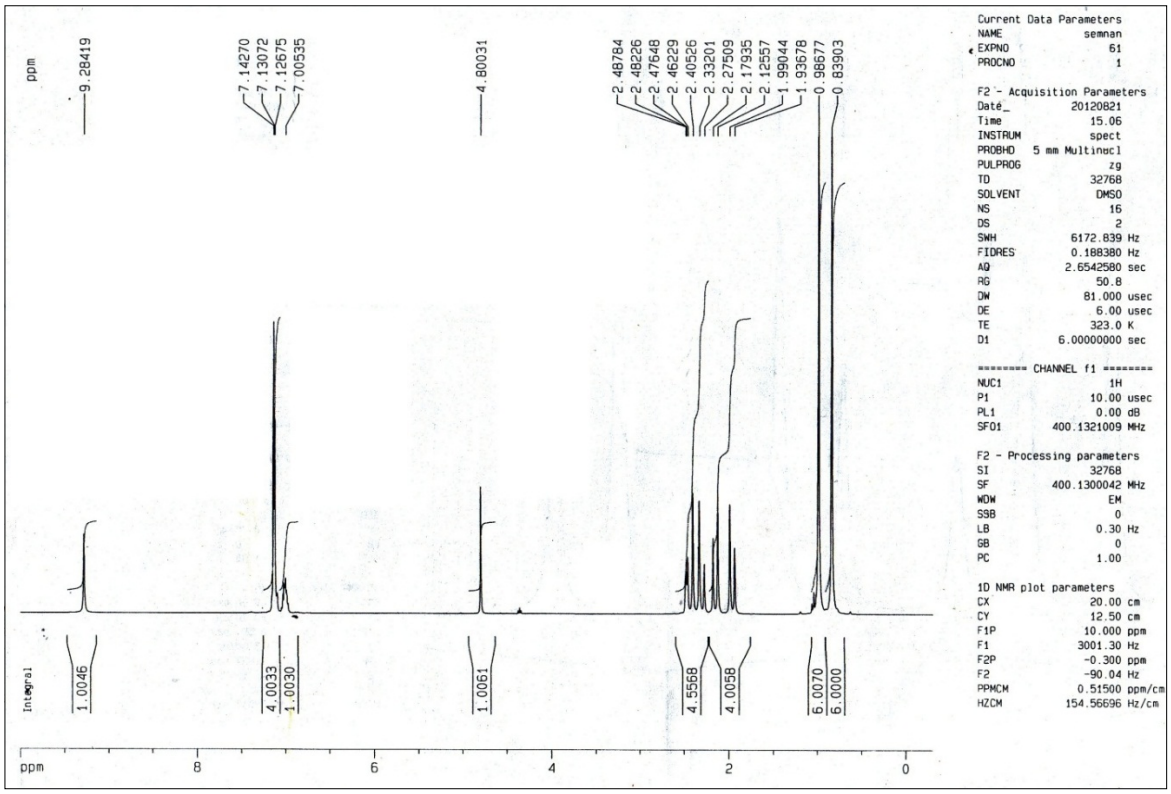


Fig.7. ^1H NMR of **(4a)**.

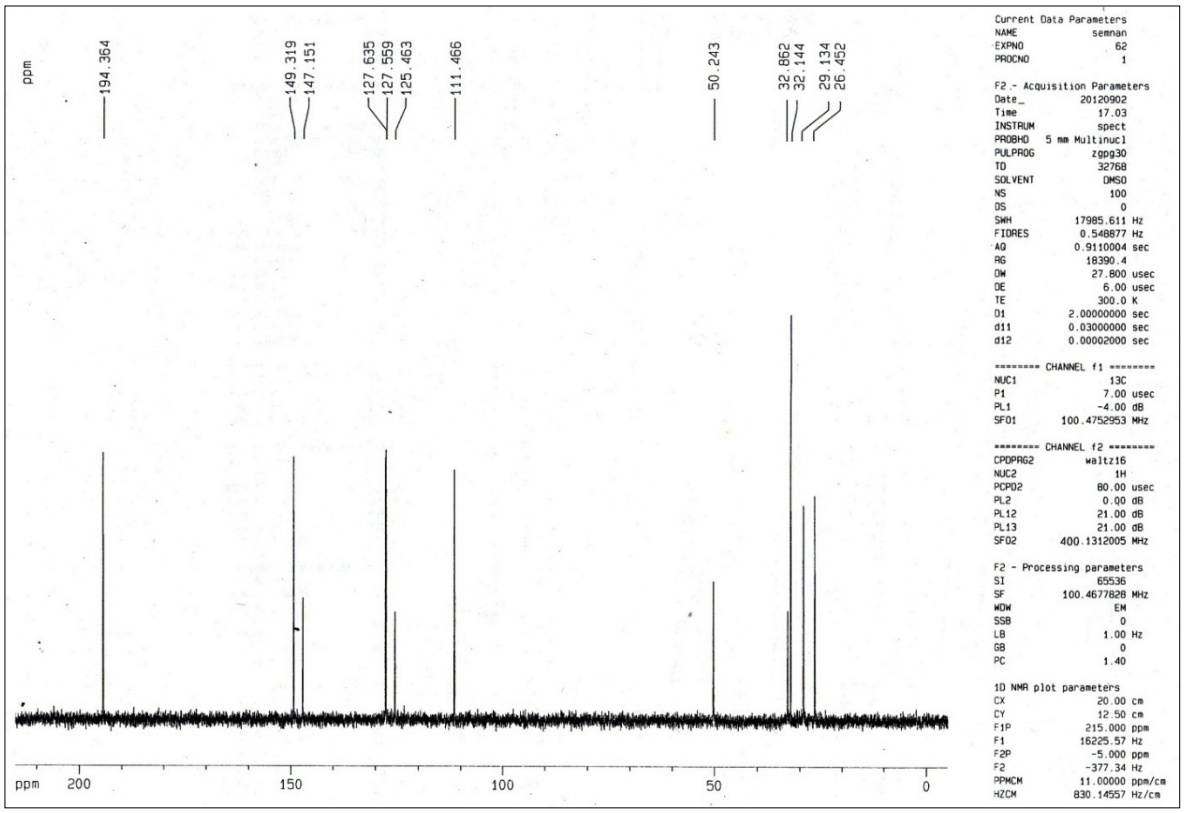
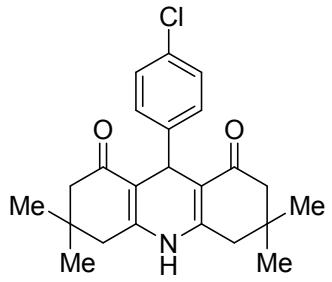


Fig. 8. ^{13}C NMR of **(4a)**.

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



M. P.: 299-302 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3288, 3205, 3068, 2956, 2869, 1643, 1608, 1475, 1363, 1223, 1171. ^{1}H NMR (500 MHz, DMSO): δ: 0.91 (s, 6H), 1.04 (s, 6H), 2.08-2.11 (d, J= 16, 2H), 2.26-2.29 (d, J= 16, 2H), 2.50-2.60 (dd, J= 14.65, 4H), 4.51 (s, 1H), 7.18-7.20 (d, J= 8.2 Hz, 2H), 7.28-7.29 (d, J= 8.2 Hz, 2H), 9.32 (s, 1H). Anal. Calc. for $C_{23}H_{26}ClNO_2$; C 71.96, H 6.83, N 3.65, O 8.33; Found: C 71.90, H 6.89, N 3.59, O 8.32.

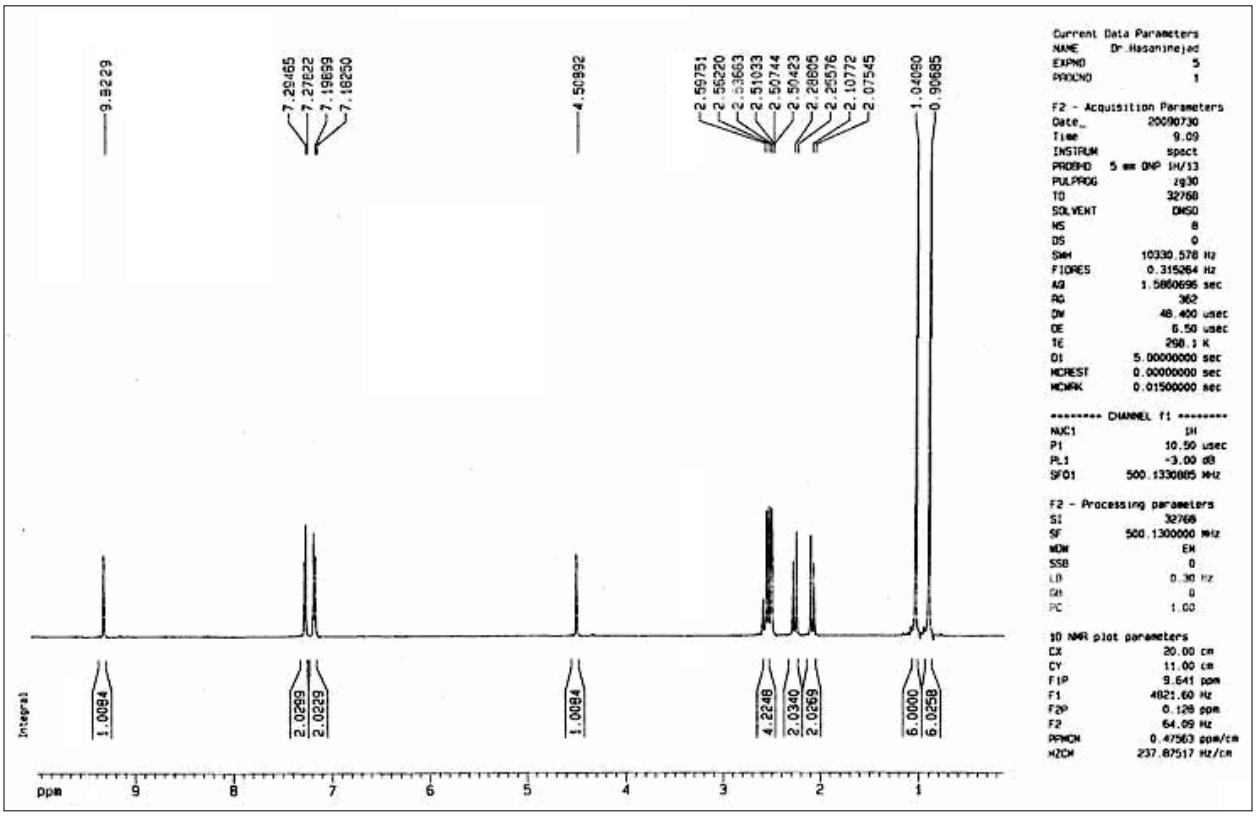
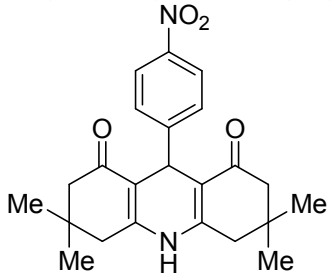


Fig. 9. ^{1}H NMR of **(4b)**.

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



M. P.: 284-286 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3384, 2958, 2908, 1643, 1602, 1514, 1447, 1364, 1221, 1171. ^{1}H NMR (500 MHz, DMSO) δ: 0.91 (s, 6H), 1.05 (s, 6H), 2.08-2.11 (d, J= 6.5 Hz, 2H), 2.27-2.30 (d, J= 6.5 Hz, 2H), 2.50-2.63 (m, 4H), 4.63 (s, 1H), 7.45-7.48 (m, 2H), 8.10-8.12 (m, 2H), 9.32 (s, 1H). Anal. Calc. for $C_{23}H_{26}N_2O_4$; C 70.03, H 6.64, N 7.10, O 16.22; Found: C 70.08, H 6.69, N 7.07, O 16.26.

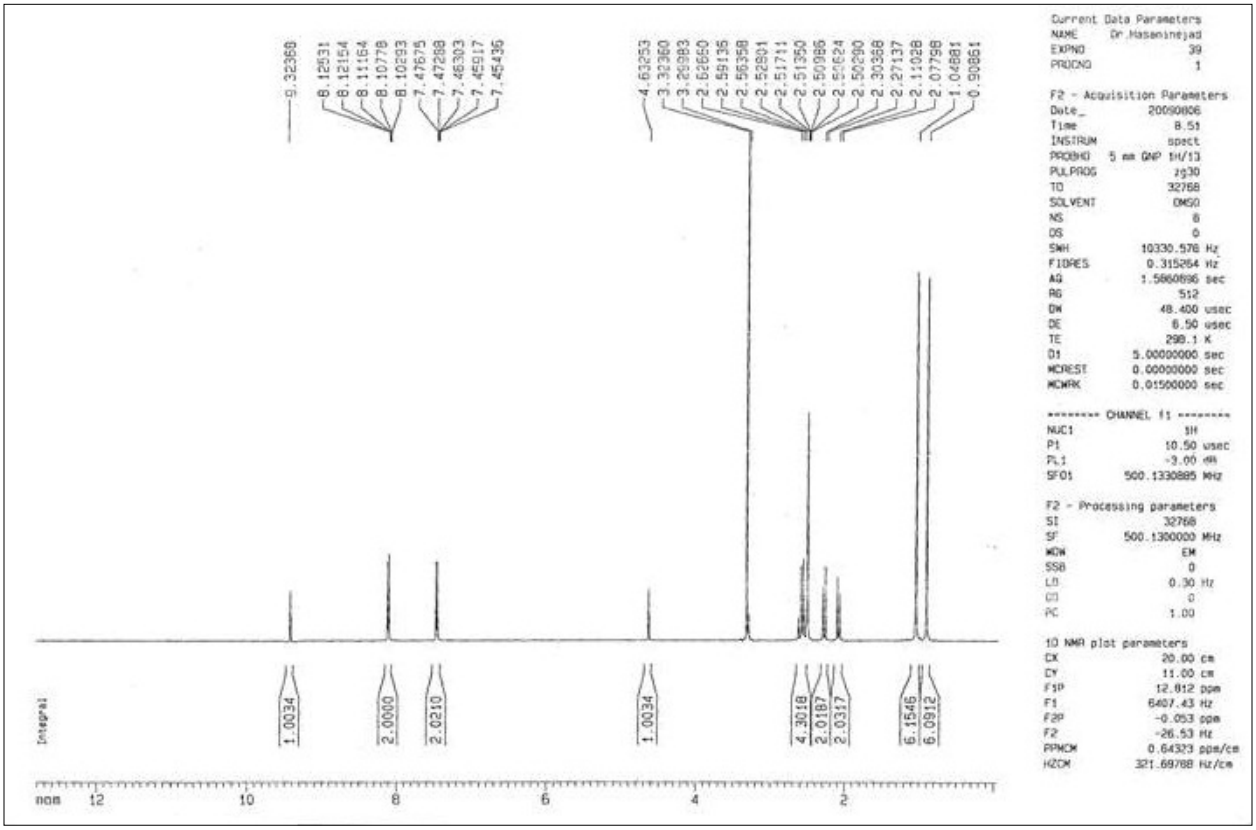
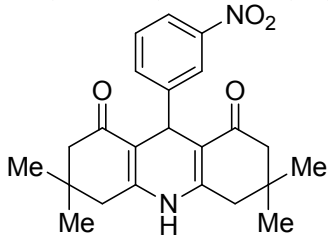


Fig. 10. ^{1}H NMR of **(4d)**.

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



M. P.: 299-301 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3282, 3193, 3070, 2957, 2930, 2889, 2870, 1649, 1612, 1577, 1434, 1364, 1225, 1171. ^{1}H NMR (500 MHz, DMSO): δ: 0.91 (s, 6H), 1.05 (s, 6H), 2.09-2.12 (d, J= 4.4 Hz, 2H), 2.27-2.30 (d, J= 6.4 Hz, 2H), 2.55-2.63 (dd, J= 7.2 Hz,4H), 4.64 (s, 1H), 7.55-7.58 (t, J= 3.1 Hz, 1H), 7.65-7.67 (d, J= 3 Hz, 1H), 7.99-8.02 (d, J= 5.1 Hz, 2H), 9.31 (s, 1H). Anal. Calc. for $C_{23}H_{26}N_2O_4$; C 70.03, H 6.64, N 7.10, O 16.22; Found: C 70.06, H 6.70, N 7.08, O 16.24.

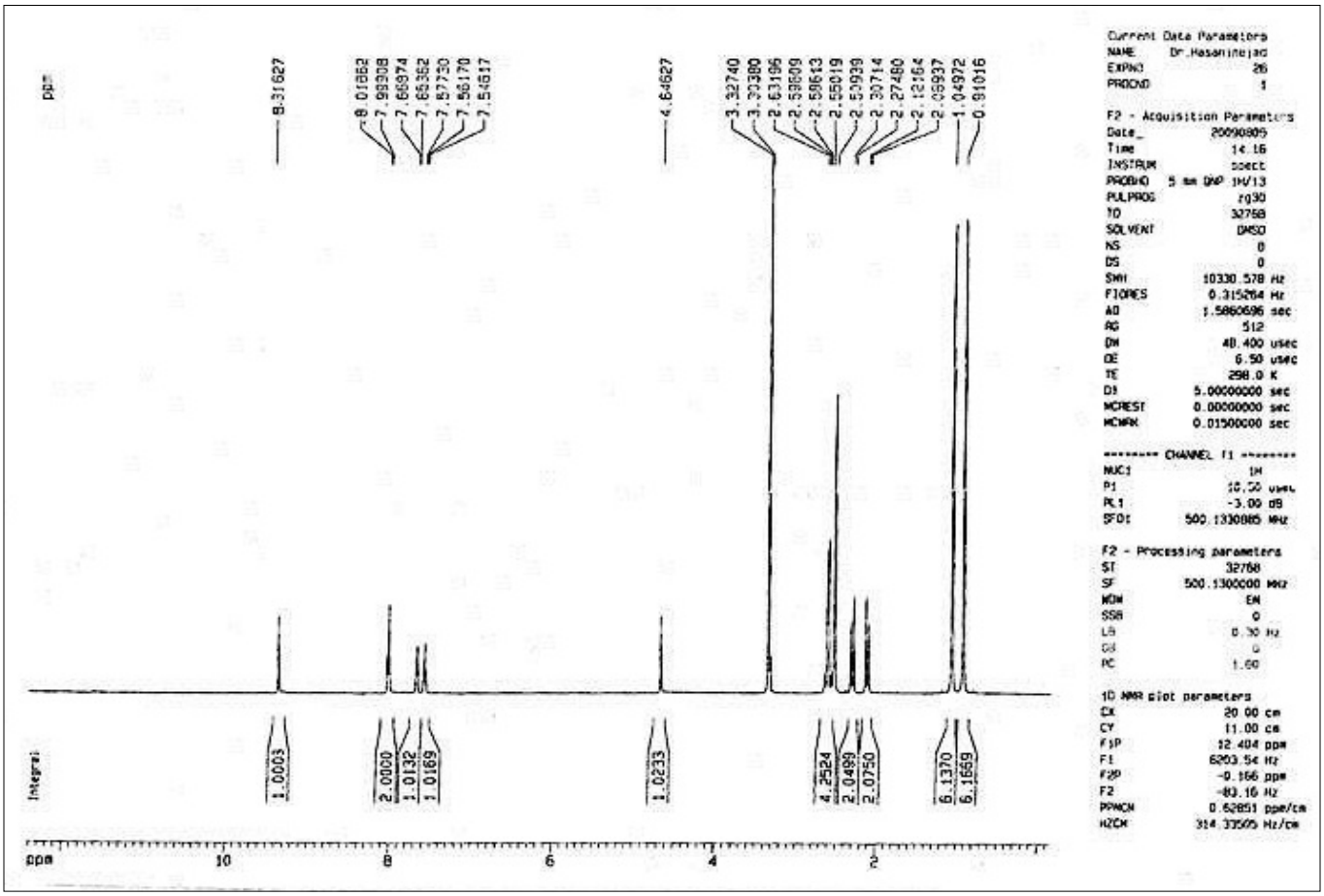
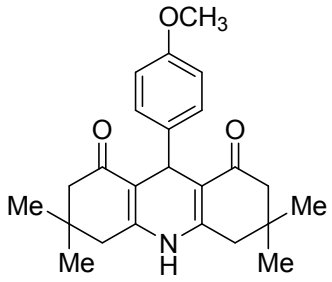


Fig. 11. ^{1}H NMR of **(4e)**.

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



M. P.: 300-301 °C; IR (KBr, Cm^{-1}) ν max: 3277, 3203, 3070, 2959, 2870, 1643, 1606, 1508, 1483, 1367, 1223, 1171. ^{1}H NMR (500 MHz, DMSO): δ 0.90 (s, 6H), 1.04 (s, 6H), 2.08 (d, J= 9.7 Hz, 2H), 2.26 (d, J= 9.9 Hz, 2H), 2.48-2.52 (m, 2H), 2.57 (d, J= 10.8 Hz, 2H), 3.68 (s, 3H), 4.7 (s, 1H), 6.77-6.78 (t, J= 4.1 2H), 7.06-7.08 (t. J= 5.12 Hz, 2H), 9.21 (s, 1H). Anal. Calc. for $C_{24}H_{29}NO_3$; C 75.96, H 7.70, N 3.69, O 12.65; Found: C 75.90, H 7.72, N 3.62, O 12.69.

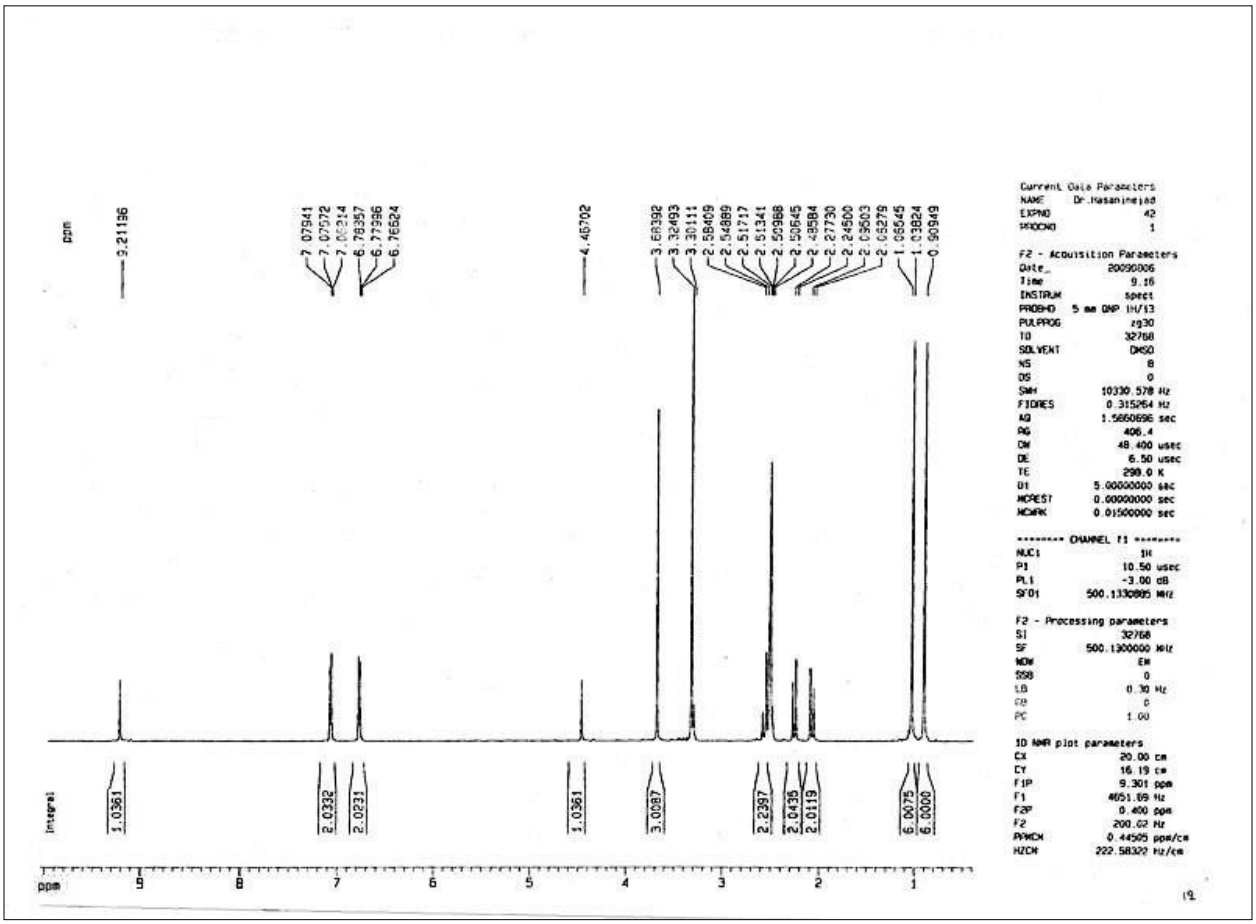
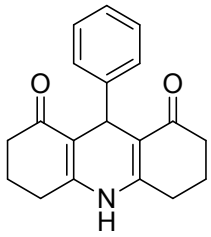


Fig. 12. ^{1}H NMR of **(4i)**.

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



M. P.: 278-280 °C; IR (KBr, Cm^{-1}) ν max: 3273, 3196, 3080, 1624, 1601, 1483, 1218, 1140. ^1H NMR (400 MHz, DMSO): δ 1.90-2.09 (m, 4H), 2.26-2.28 (m, 2H), 2.30-2.38 (m, 2H), 2.51-2.64 (m, 4H), 4.79 (s, 1H), 7.05-7.09 (t, J= 7.6, 2H), 7.11-7.12 (d, J= 8.4 Hz, 1H), 7.23-7.31 (dd, J= 8, 24.2, 2H), 9.17 (s, 1H). Anal. Calc. for $C_{19}H_{19}NO_2$; C 77.79, H 6.53, N 4.77, O 10.91; Found: C 77.73, H 6.59, N 4.71, O 10.92.

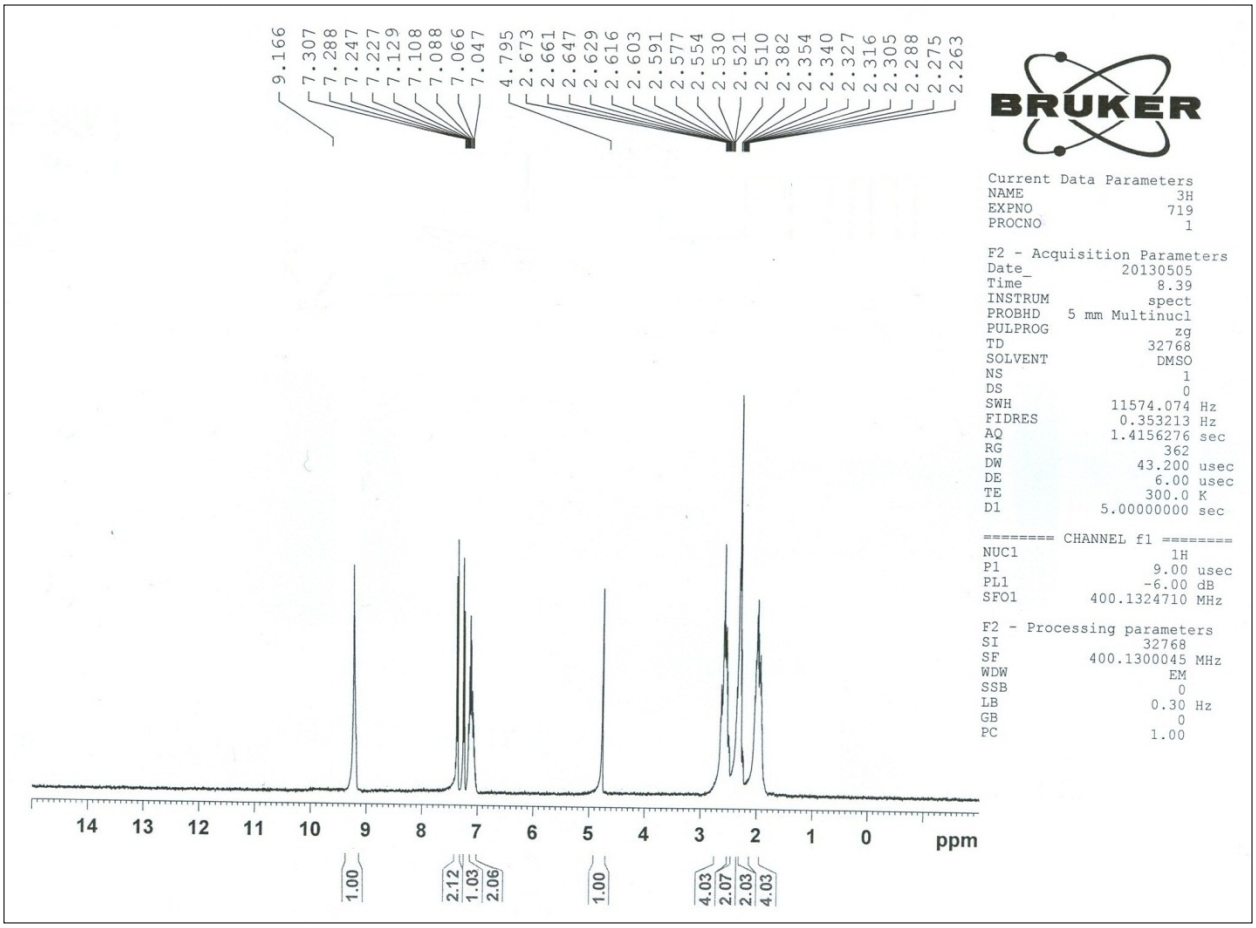


Fig. 13. ^1H NMR of **(5a)**.

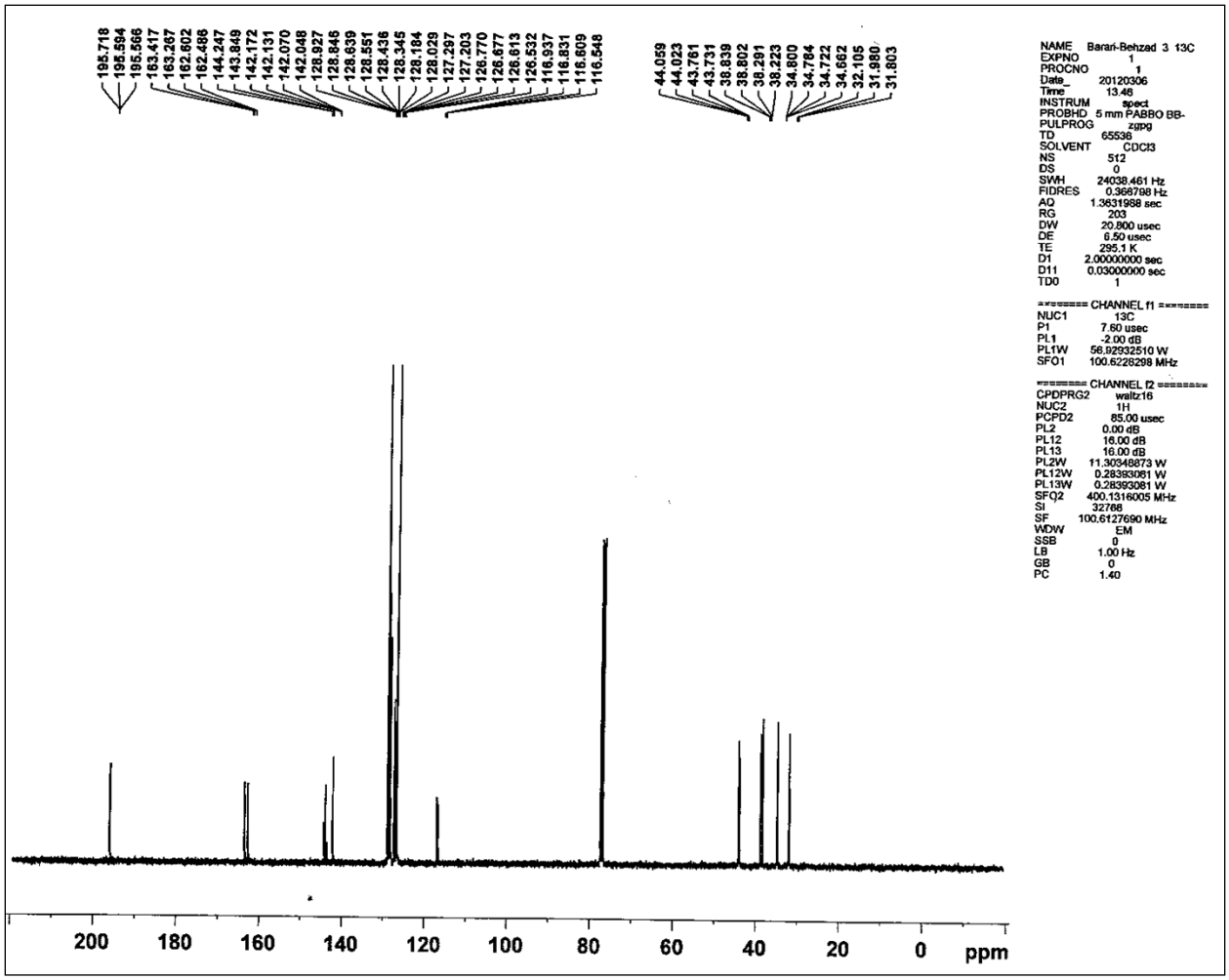
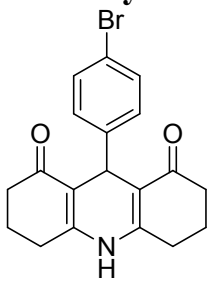


Fig. 14. ^{13}C NMR of **(5a)**.

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



M. P.: 310-312 °C; IR (KBr, Cm^{-1}) ν max: 3340, 3244, 2958, 2927, 1647, 1627, 1549, 1450, 1367, 1227, 1171. ^{1}H NMR (400 MHz, DMSO): δ 1.92-2.08 (m, 4H), 2.28-2.32 (m, 2H), 2.34-2.40 (m, 2H), 2.53-2.65 (m, 4H), 4.76 (s, 1H), 7.13-7.27 (m, 2H), 7.33-7.43 (dd, J= 30.6, 8.4 Hz, 2H), 9.38 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 20.10, 20.27, 27.13, 31.39, 36.76, 36.90, 112.08, 117.66, 127.83, 129.43, 146.47, 151.59, 171.19, 194.58. Anal. Calc. for $C_{19}H_{18}BrNO_2$; C 61.30, H 4.87, N 3.76, O 8.60; Found: C 61.33, H 4.81, N 3.71, O 8.69.

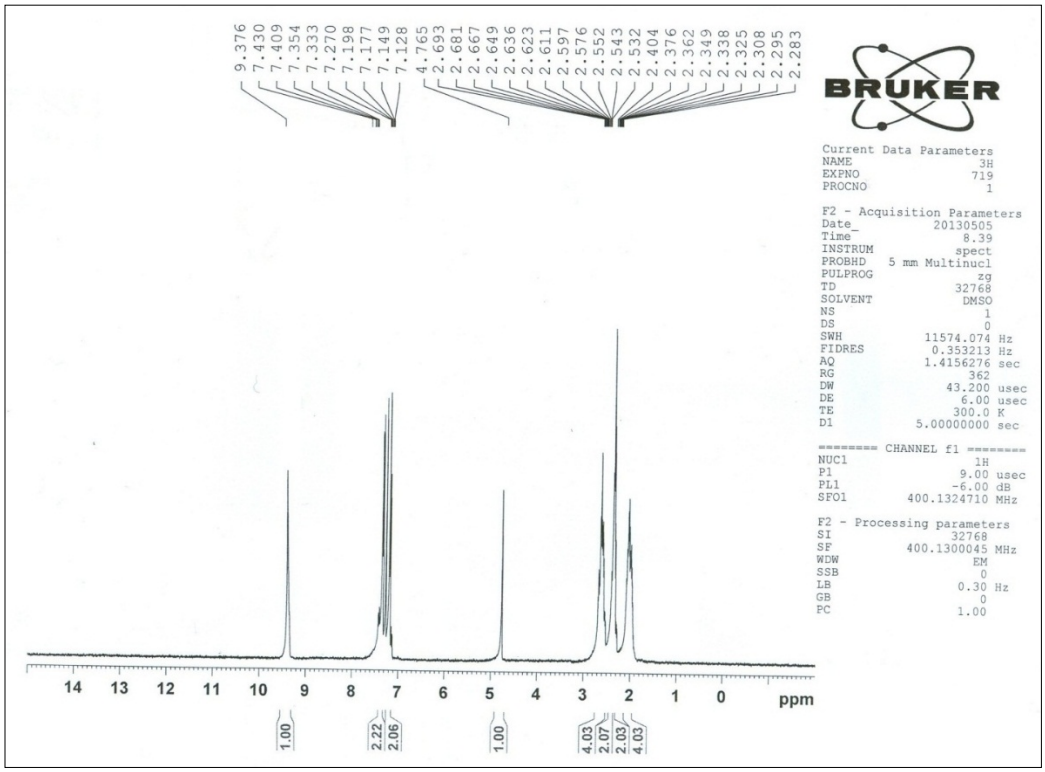


Fig. 15. ^{1}H NMR of **(5d)**.

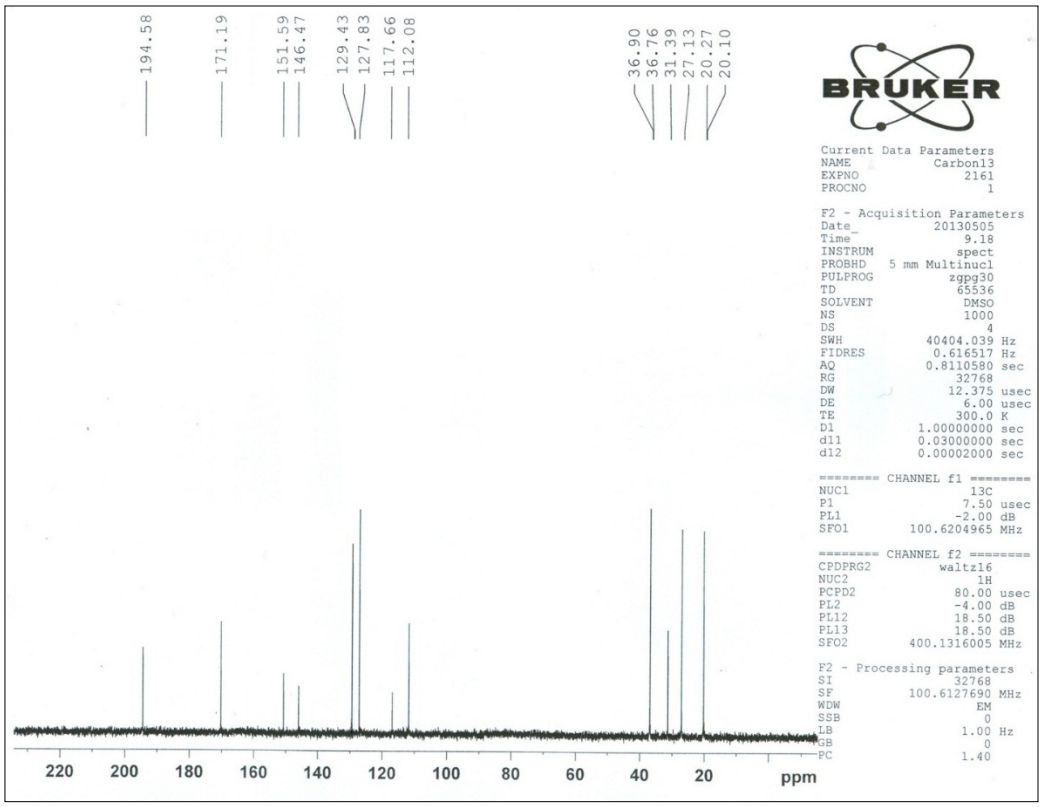
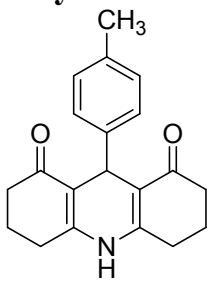


Fig. 16. ^{13}C NMR of **(5d)**.

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



M. P.: 254-256 °C; IR (KBr, Cm^{-1}) ν max: 3286, 3203, 3068, 2943, 2887, 1639, 1608, 1458, 1364, 1232, 1176. ^{1}H NMR (400 MHz, DMSO): δ 1.96-2.07 (m, 4H), 2.26 (s, 3H), 2.29-2.42 (m, 4H), 2.52-2.69 (m, 4H), 4.79 (s, 1H), 7.03-7.05 (d, J= 8 Hz, 2H), 7.12-7.21 (d, J= 7.6 Hz, 2H), 9.18 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 20.31, 21.06, 27.15, 31.22, 36.98, 55.14, 113.52, 117.03, 128.25, 128.84, 129.33, 135.86, 146.36, 150.53, 169.57, 194.52. Anal. Calc. for $C_{20}H_{21}NO_2$; C 78.15, H 6.89, N 4.56, O 10.41; Found: C 78.19, H 6.83, N 4.58, O 10.45.

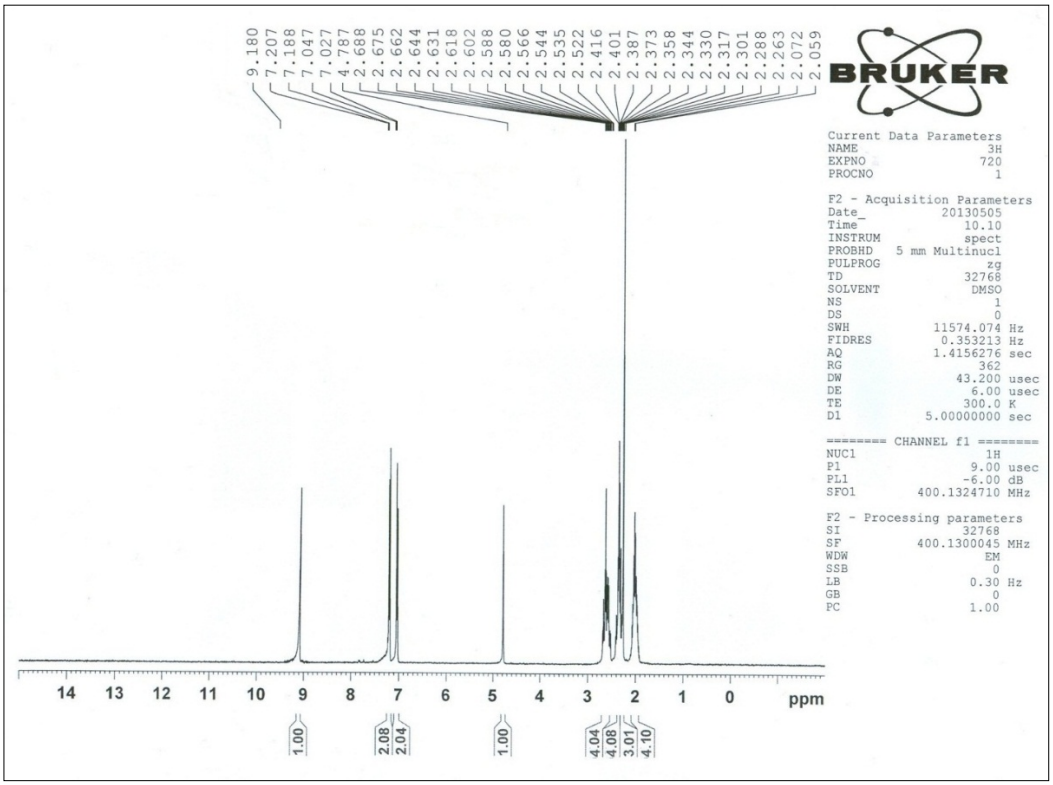


Fig. 17. ^{1}H NMR of **(5e)**.

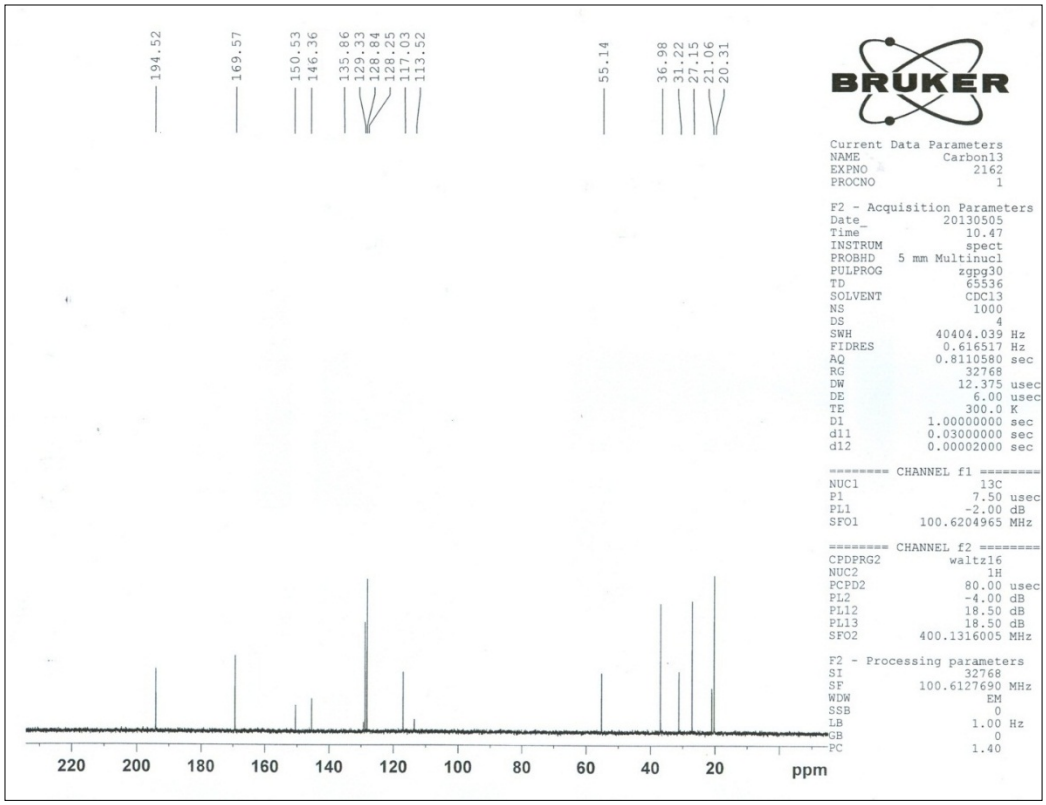
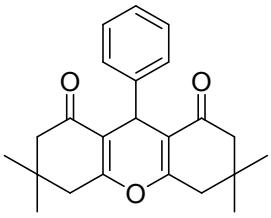


Fig. 18. ^{13}C NMR of **(5e)**.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-phenyl-2H-xanthene-1,8(5H,9H)-dione (6a)



M. P.: 203-204 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 2950, 1660, 1648, 1360, 1200, 1162, 1141, 998, 694. ^{1}H NMR (500 MHz, DMSO-*d*^{6}): δ: 0.90 (s, 6H), 1.04 (s, 6H), 2.07-2.10 (d, J= 6.4 Hz, 2H), 2.25-2.28 (d, J= 6.5 Hz, 2H), 2.51-2.60 (m, 3H), 4.53 (s, 1H), 7.09-7.12 (t, J= 2.8 Hz, 1H), 7.17-7.18 (d, J= 2.8 Hz,1H), 7.20-7.23 (t, J= 2.9 Hz, 3H). ^{13}C NMR (DMSO, 125 MHz), δ: 26.45, 29.13, 32.14, 32.88, 50.24, 111.47, 125.46, 127.56, 127.63, 147.15, 149.32, 194.36. Anal. Calcd for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48; O, 13.70; Found: C, 78.92; H, 7.59; O, 13.83.

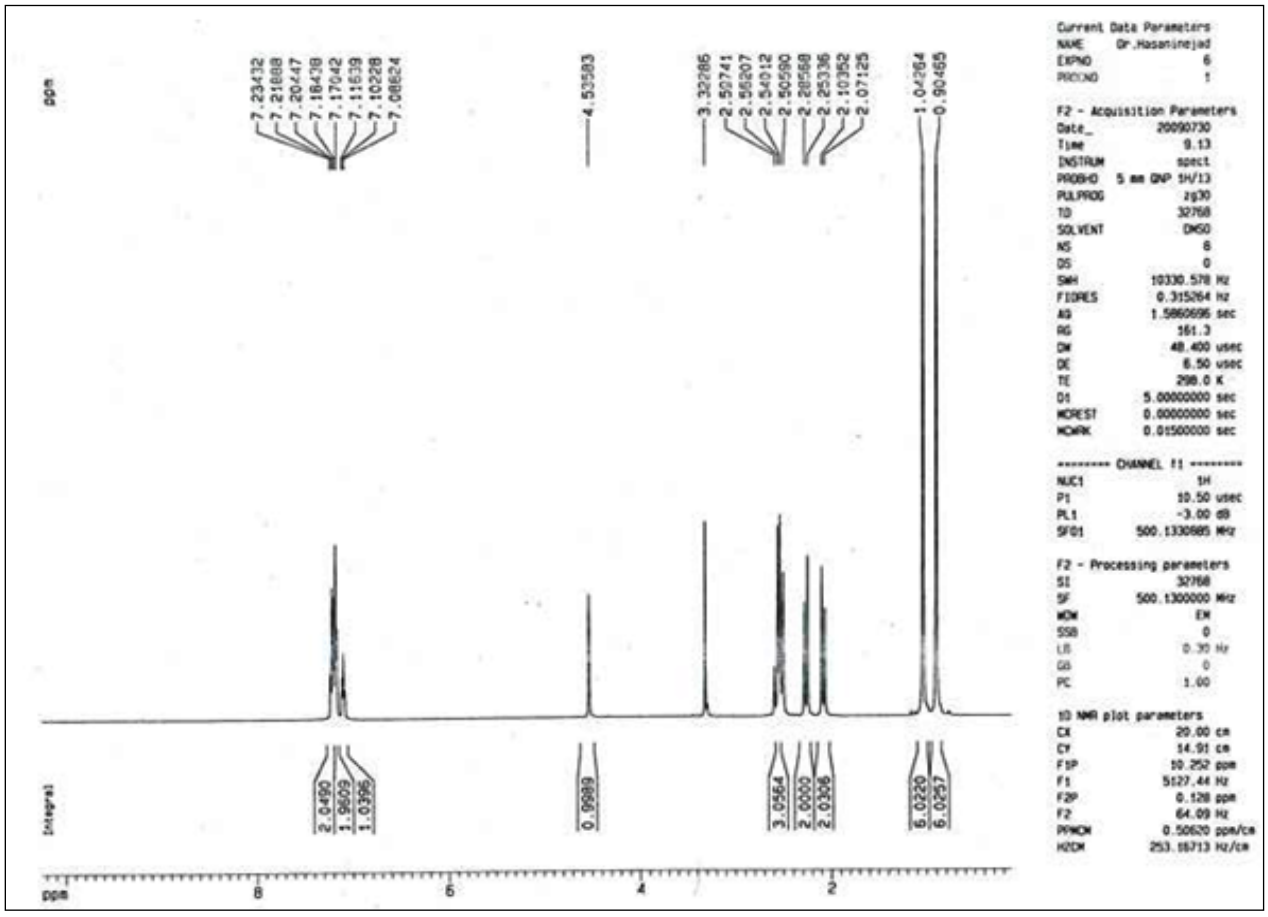


Fig. 19. ^{1}H NMR of **(6a)**.

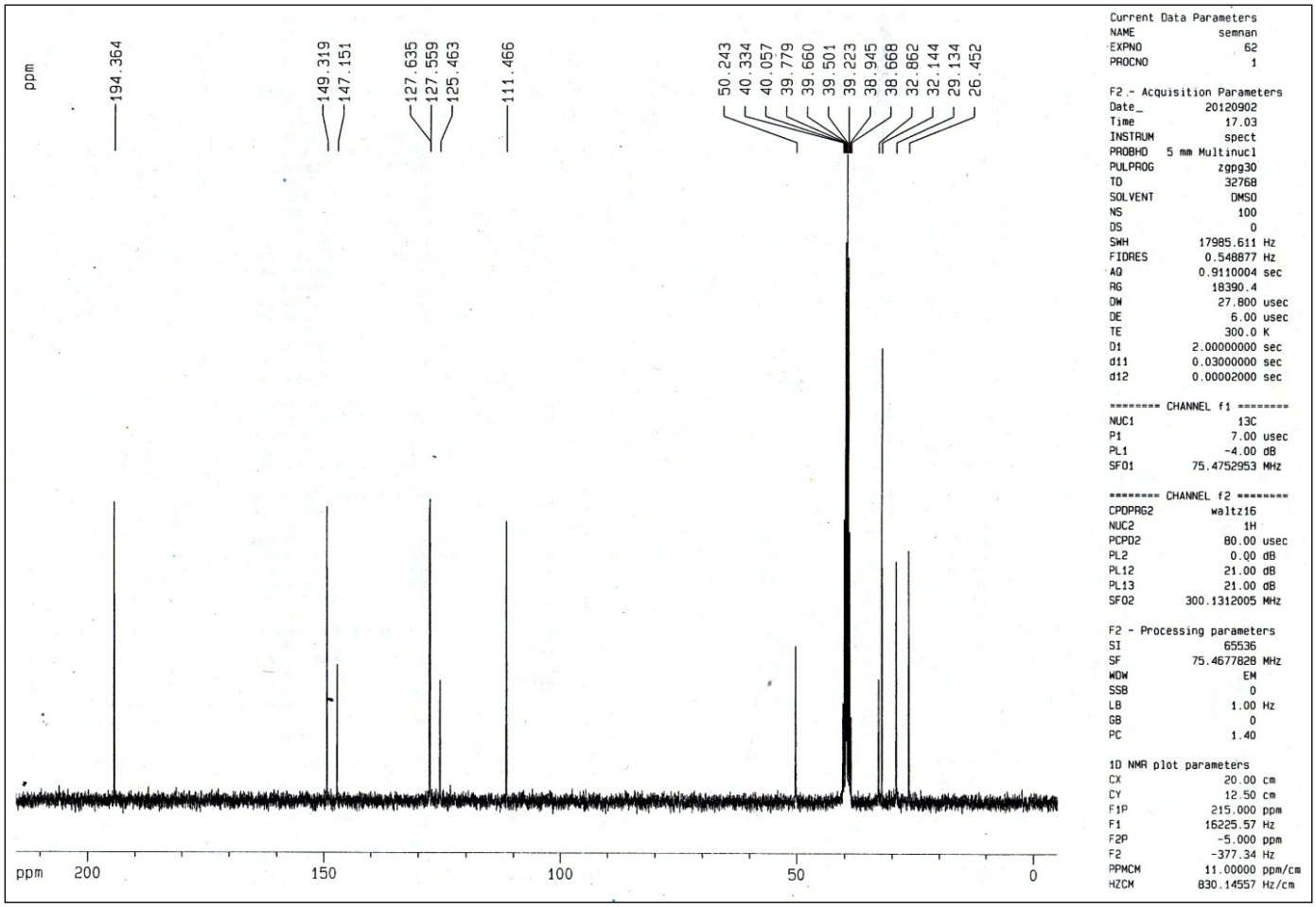
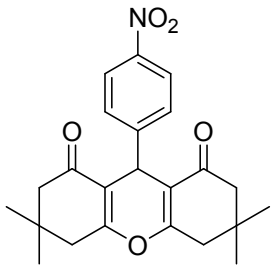


Fig. 20. ^{13}C NMR of **(6a)**.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(4-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione (6c)



M. P.: 222-224 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 2950, 1658, 1614, 1508, 1360, 1340, 1196, 1160, 1136. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.90 (s, 6H), 1.05 (s, 6H), 2.08-2.11 (d, J= 6.5 Hz, 2H), 2.27-2.30 (d, J= 6.5 Hz, 2H), 2.50-2.63 (m, 4H), 4.63 (s, 1H), 7.45-7.48 (m, 2H), 8.10-8.12 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 27.24, 29.57, 32.13, 32.74, 50.96, 56.69, 60.80, 106.33, 115.15, 136.86, 140.77, 153.26, 163.89, 197.11. Anal. Calcd for $C_{23}H_{25}NO_5$: C, 69.86; H, 6.37; N, 3.54; O, 20.23; Found: C, 69.91; H, 6.49; N, 3.68; O, 20.35.

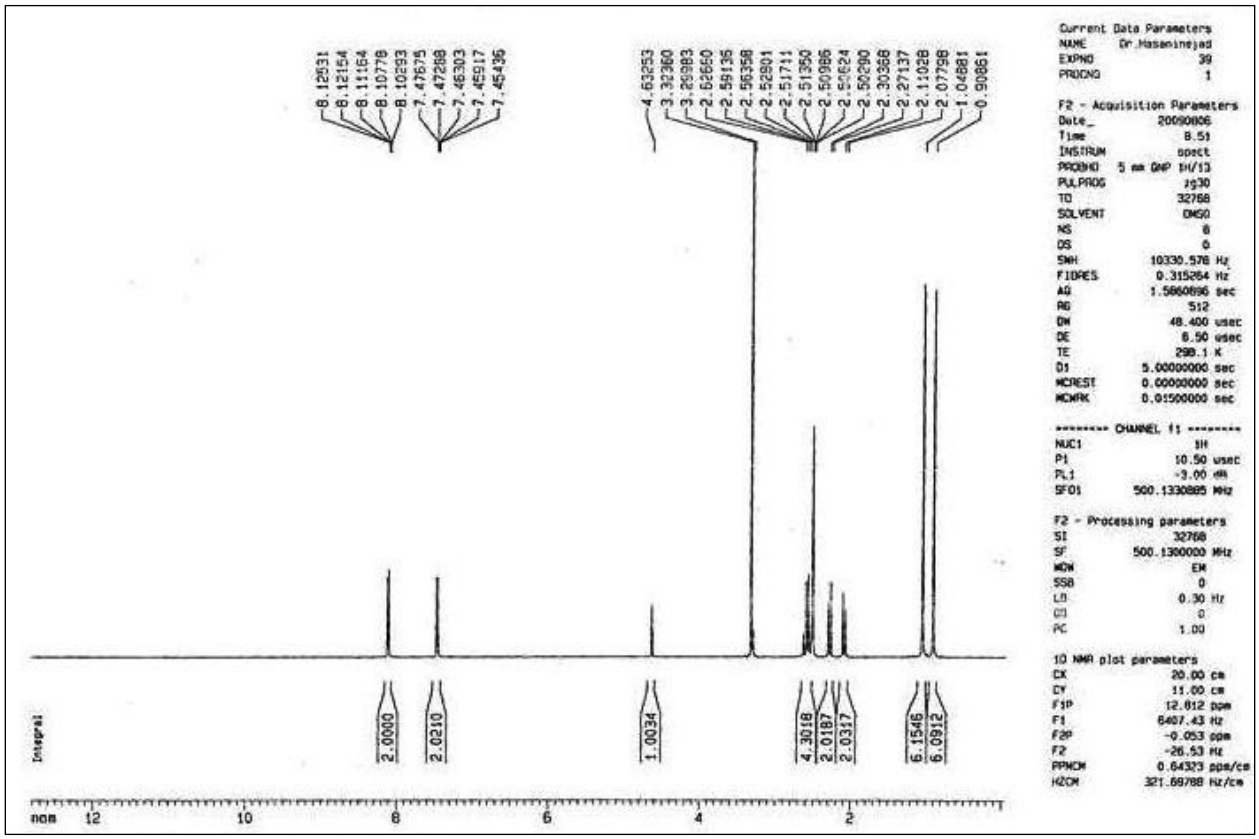


Fig. 21. ^{1}H NMR of **(6c)**.

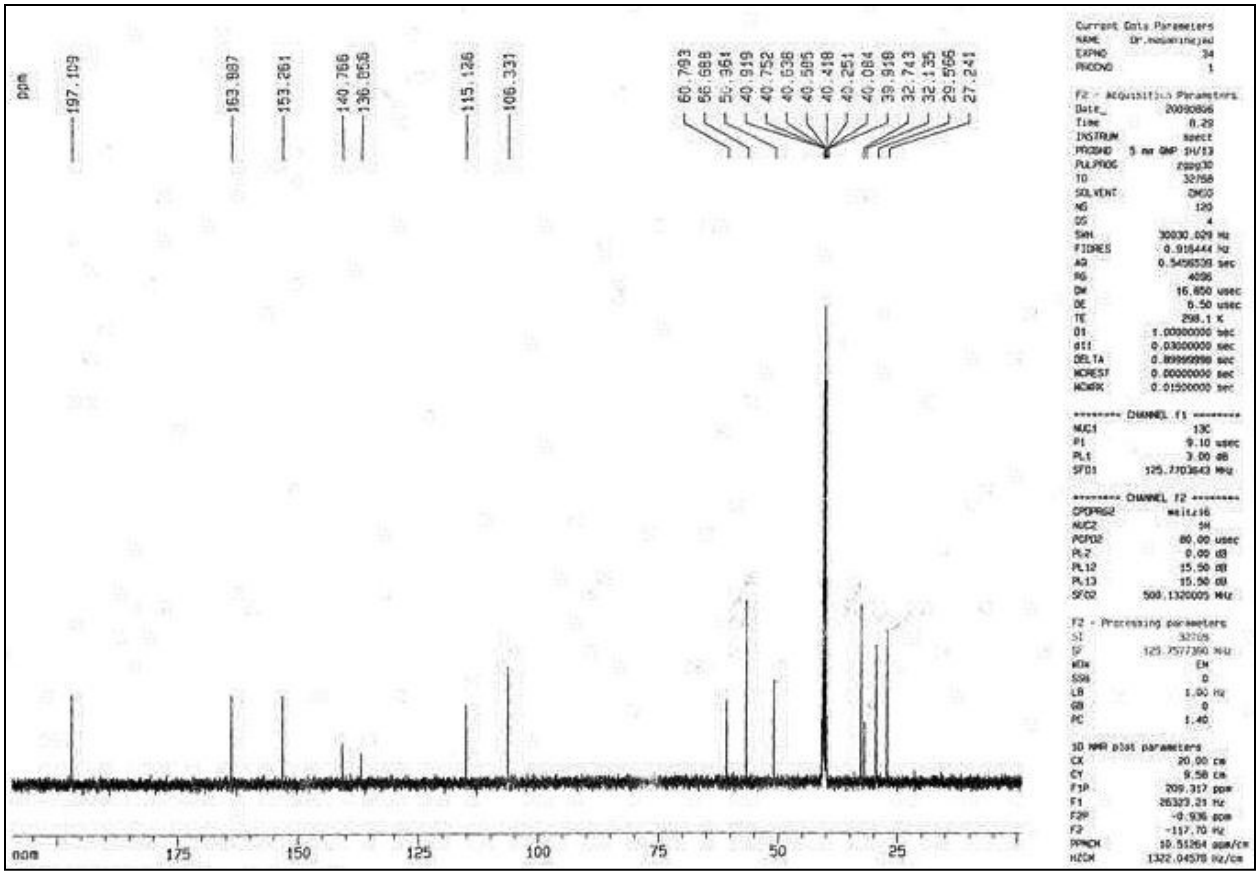
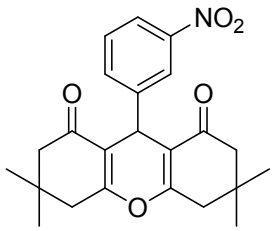


Fig. 22. ^{13}C NMR of **(6c)**.

3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-2H-xanthene-1,8(5H,9H)-dione (6d)



M. P.: 168-169 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 2950, 1659, 1619, 1520, 1360, 1200, 1180, 1000. ^1H NMR (500 MHz, $CDCl_3$): δ: 0.91 (s, 6H), 1.05 (s, 6H), 2.09-2.12 (d, J= 4.4 Hz, 2H), 2.27-2.30 (d, J= 6.4 Hz, 2H), 2.55-2.63 (dd, J= 7.2 Hz,4H), 4.64 (s, 1H), 7.55-7.58 (t, J= 3.1 Hz, 1H), 7.65-7.67 (d,J= 3 Hz, 1H), 7.99-8.02 (d, J= 5.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 27.24, 29.56, 32.03, 32.72, 50.02, 56.65, 60.77, 106.31, 115.13, 136.85, 140.75, 153.22, 163.89, 197.01. Anal. Calcd. for $C_{23}H_{25}NO_5$: C, 69.86; H, 6.37; N, 3.54; O, 20.23; Found: C, 69.91; H, 6.49; N, 3.68; O, 20.35.

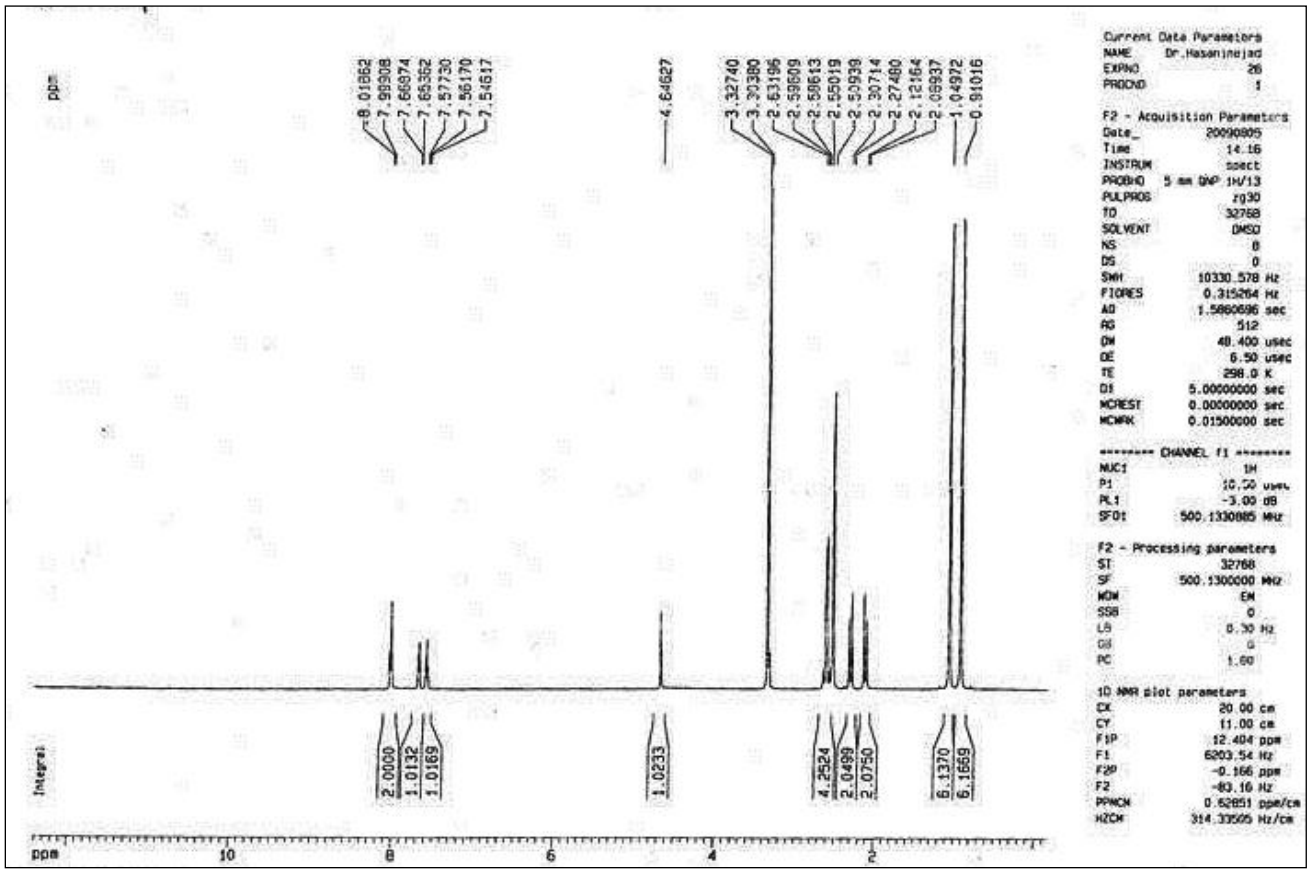


Fig.23. ^1H NMR of **(6d)**.

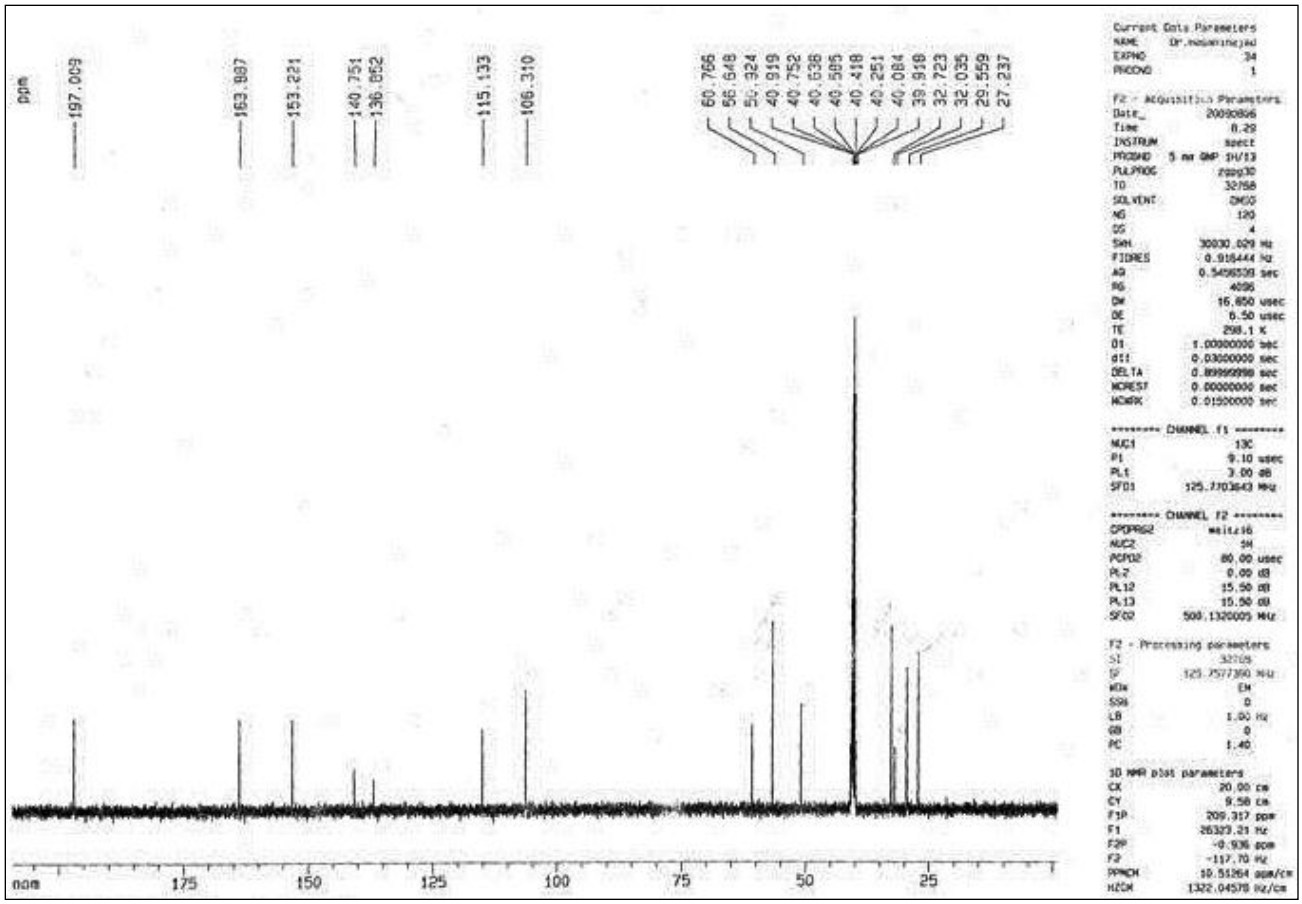
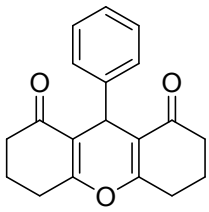


Fig. 24. ^{13}C NMR of **(6d)**.

9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7a)



M. P.: 213-215 °C; IR (KBr, Cm^{-1}) ν max: 3001, 1661, 1532, 1367, 1332, 1221, 1160, 1134, 1091, 841, 739. ^{1}H NMR (400 MHz, DMSO): δ 1.90-2.09 (m, 4H), 2.26-2.28 (m, 2H), 2.30-2.38 (m, 2H), 2.51-2.64 (m, 4H), 4.79 (s, 1H), 7.05-7.09 (t, J= 7.6, 2H), 7.11-7.12 (d, J= 8.4 Hz, 1H), 7.23-7.31 (dd, J= 8, 24.2, 2H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 20.42, 21.22, 27.19, 31.32, 37.08, 113.62, 117.13, 128.28, 128.93, 129.36, 135.97, 136.87, 141.76, 163.67, 196.62. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; O, 16.31; Found: C, 77.58; H, 6.19; O, 16.37.

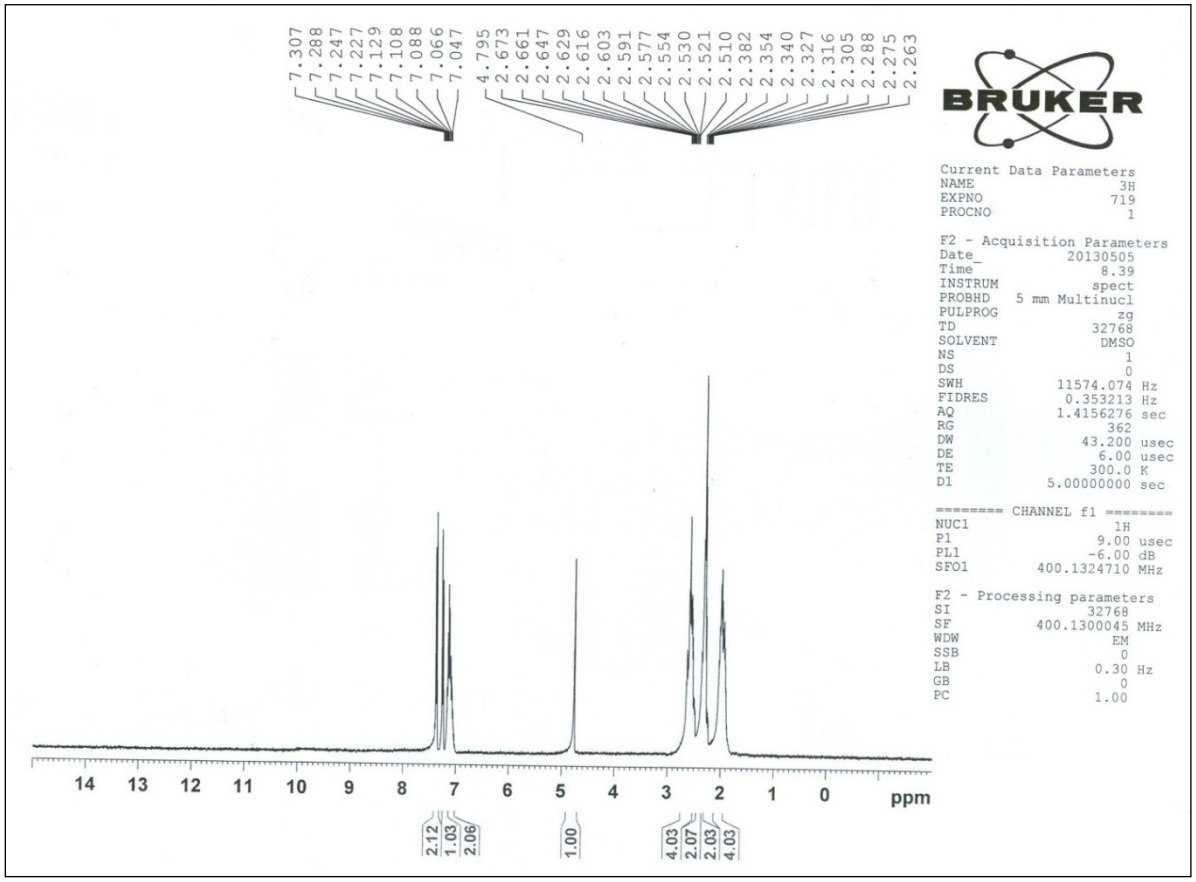


Fig. 25. ^{1}H NMR of **(7a).**

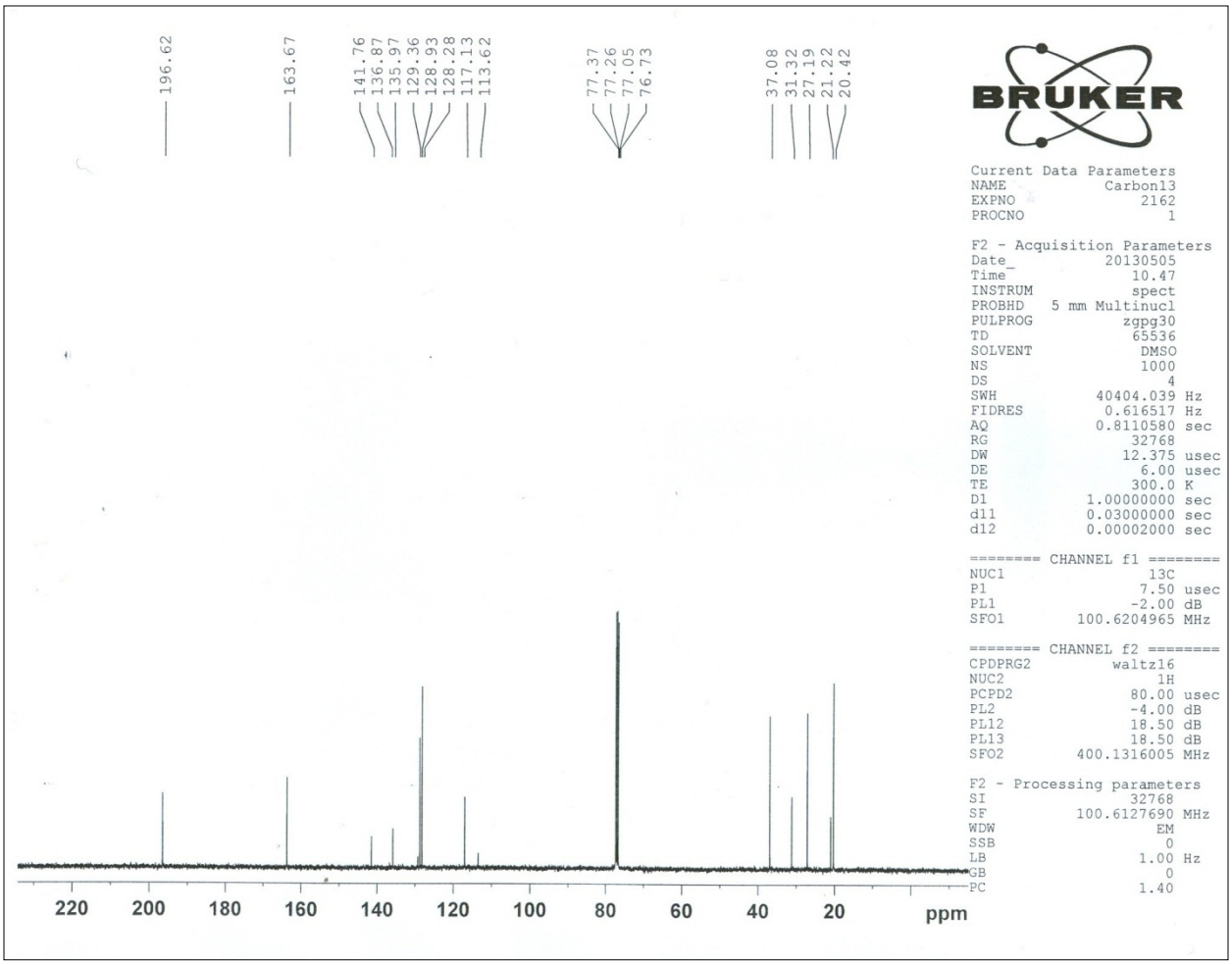
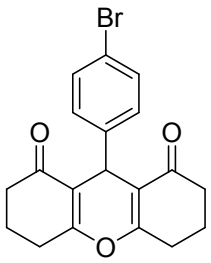


Fig. 26. ^{13}C NMR of **(7a).**

9-(4-bromophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7c)



M. P.: 222-225 °C; IR (KBr, Cm^{-1}) ν max: 2976, 1662, 1518, 1375, 1329, 1226, 1159, 1138, 1089, 829, 737. ^{1}H NMR (400 MHz, DMSO): δ 1.92-2.08 (m, 4H), 2.28-2.32 (m, 2H), 2.34-2.40 (m, 2H), 2.53-2.65 (m, 4H), 4.76 (s, 1H), 7.13-7.27 (m, 2H), 7.33-7.43 (dd, J= 30.6, 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 20.10, 20.27, 27.13, 31.39, 36.76, 36.90, 116.41, 120.28, 129.43, 130.21, 131.17, 131.66, 131.83, 133.08, 143.47, 158.49, 164.12, 196.51. Anal. Calcd for $C_{19}H_{17}BrO_3$: C, 61.14; H, 4.59; O, 12.86; Found: C, 61.19; H, 4.65; O, 12.93.

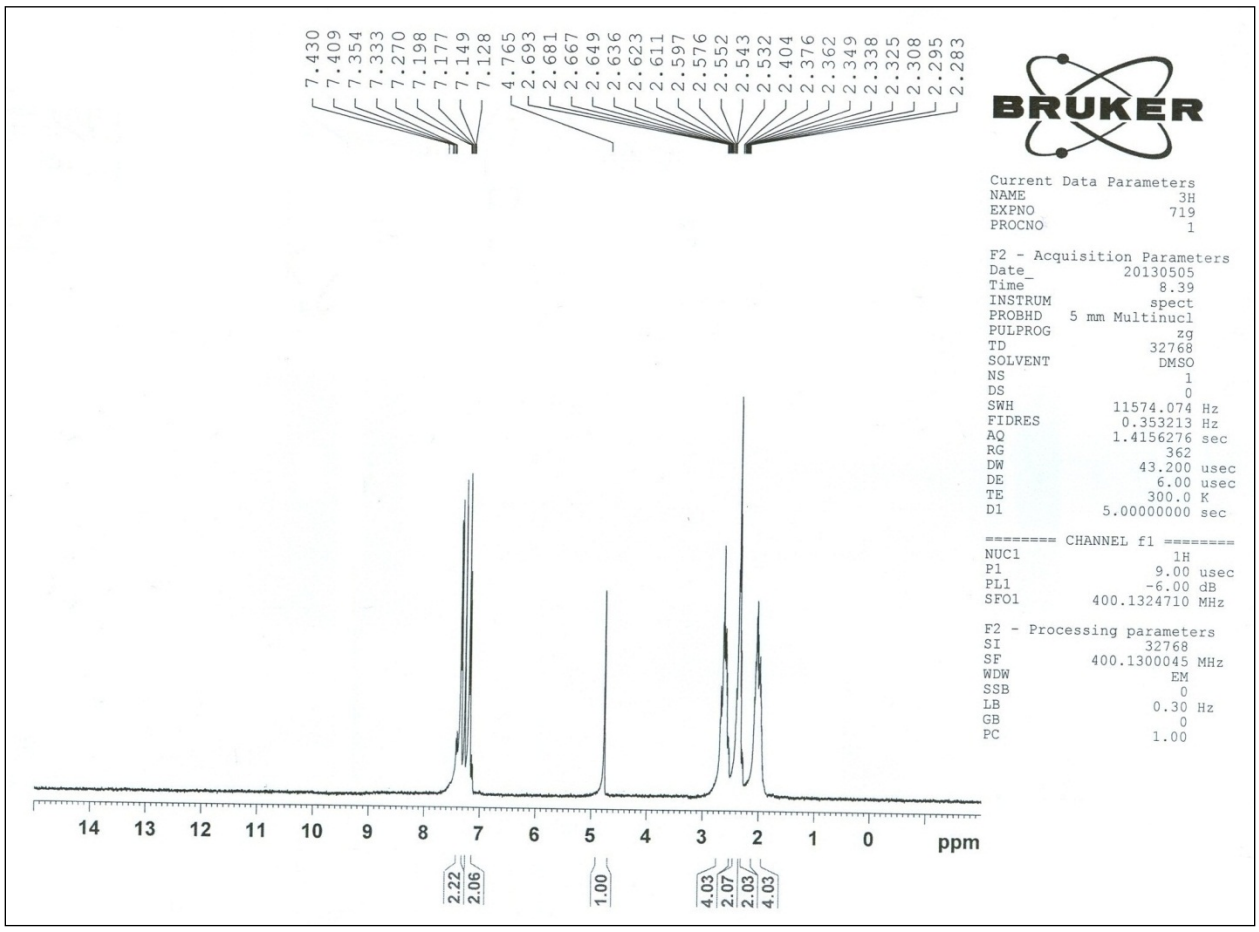


Fig. 27. ^{1}**H** NMR of **(7c)**.

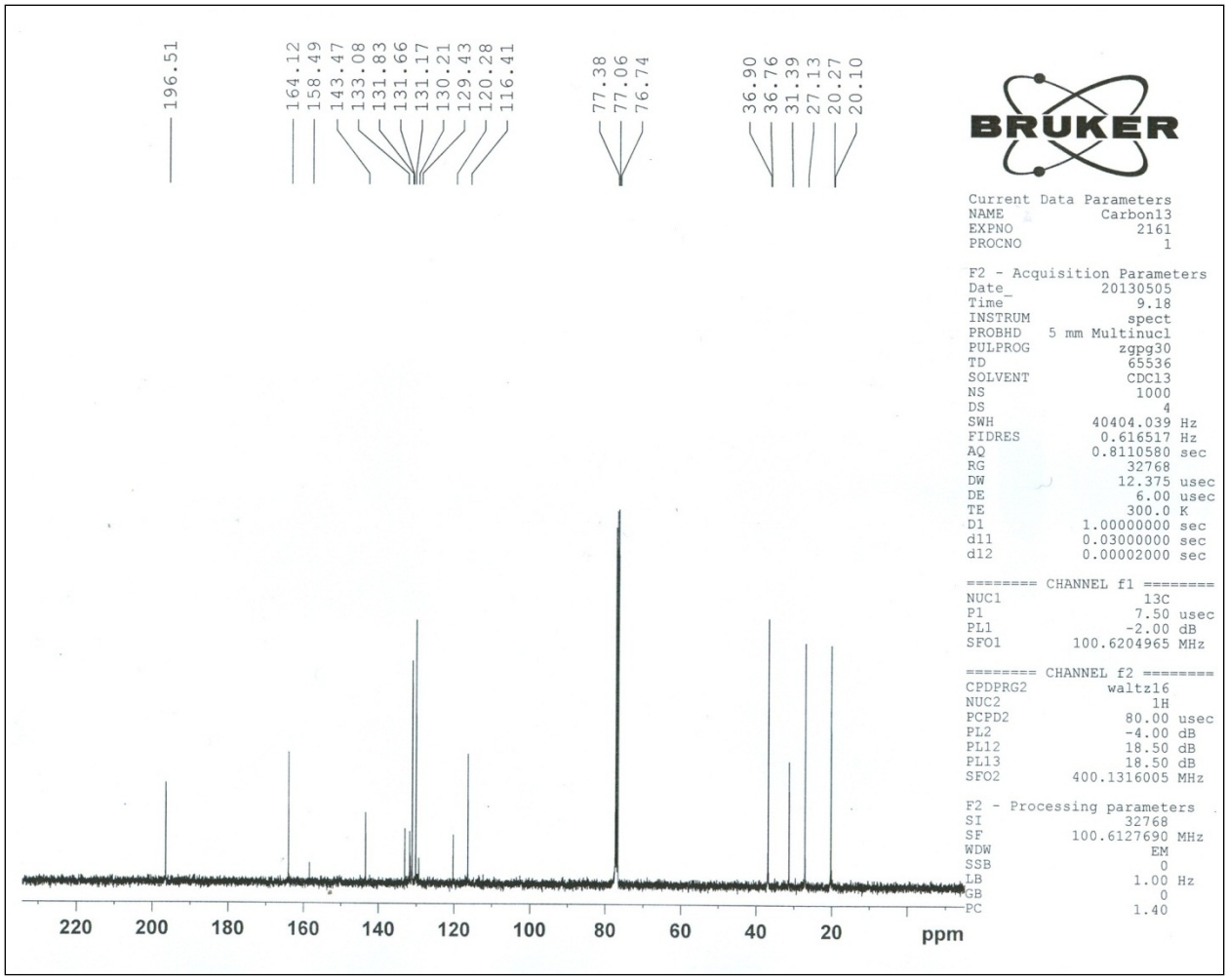
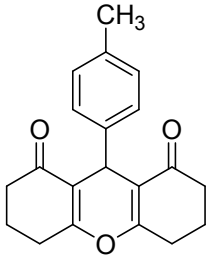


Fig. 28. ^{13}C NMR of **(7c).**

9-(p-tolyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (7d)



M. P.: 244-246 °C; IR (KBr, Cm^{-1}) ν max: 2973, 1667, 1531, 1362, 1328, 1224, 1158, 1132, 1081, 832, 739. ^{1}H NMR (400 MHz, DMSO): δ 1.96-2.07 (m, 4H), 2.26 (s, 3H), 2.29-2.42 (m, 4H), 2.52-2.69 (m, 4H), 4.79 (s, 1H), 7.03-7.05 (d, J= 8 Hz, 2H), 7.12-7.21 (d, J= 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d^6): δ 20.31, 21.06, 27.15, 31.22, 36.98, 55.14, 113.52, 117.03, 128.25, 128.84, 129.33, 135.86, 136.88, 141.53, 163.77, 196.52. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54; O, 15.57; Found: C, 77.97; H, 6.59; O, 15.64.

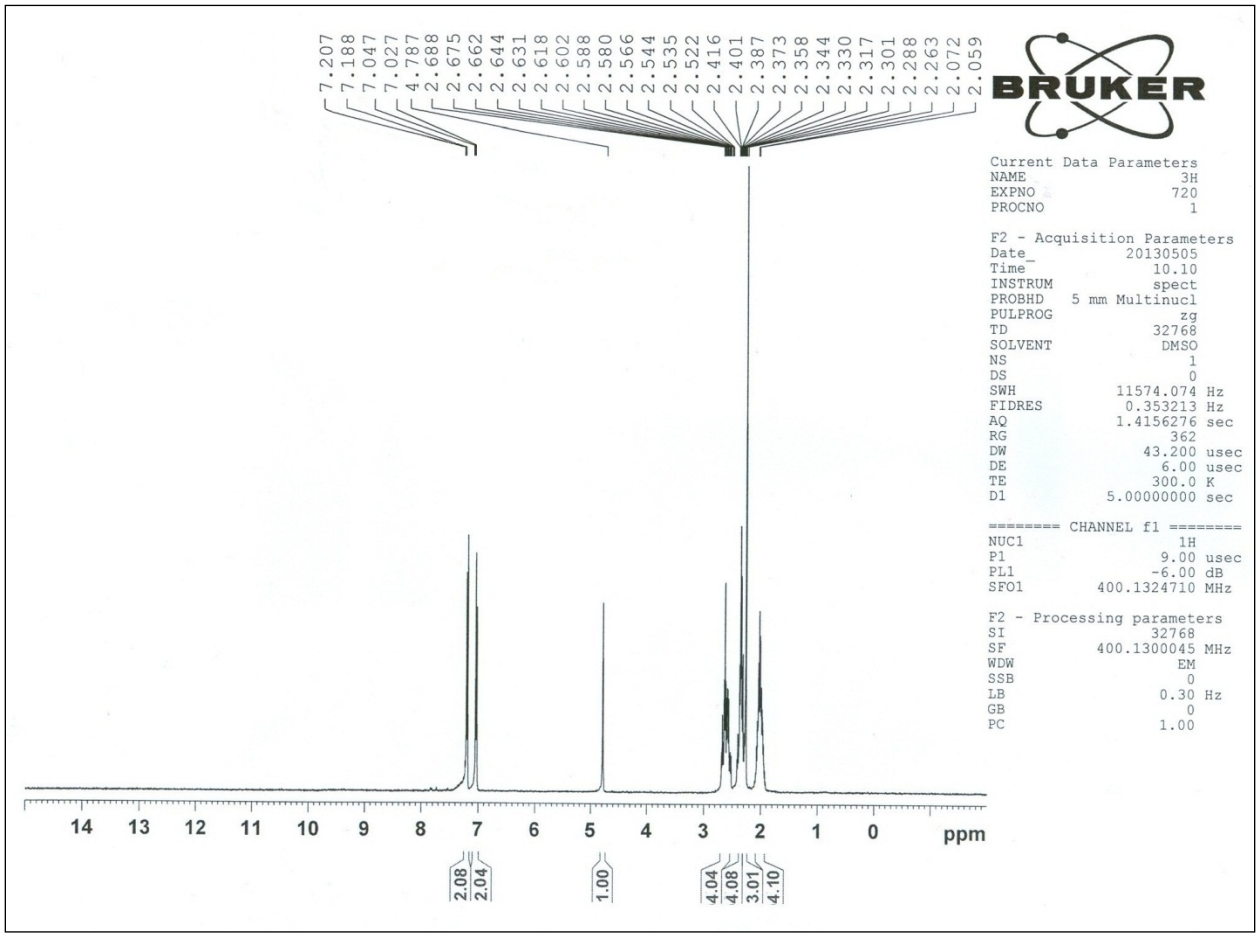


Fig. 29. ^{1}H NMR of **(7d)**.

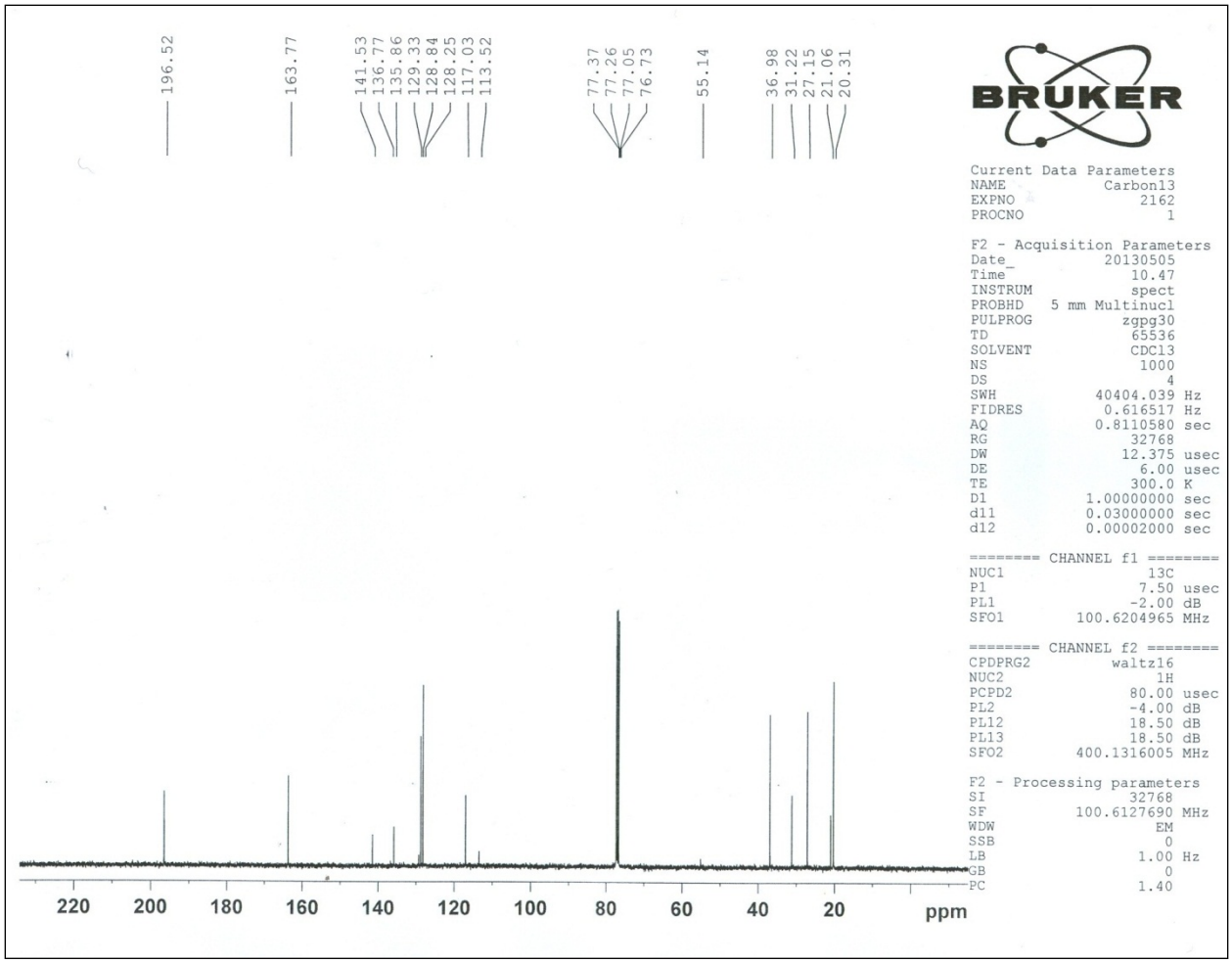
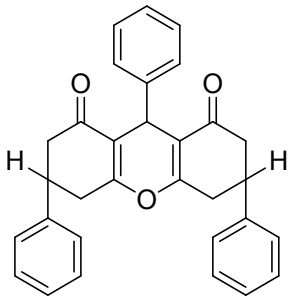


Fig 30. ^{13}C NMR of **(7d)**.

3,4,6,7-tetrahydro-3,6,9-triphenyl-2H-xanthene-1,8(5H,9H)-dione (8a)



M. P.: 196-198 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3031, 1667, 1365, 1188, 1134, 995, 694. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.57-2.75 (m, 4H), 2.80-3.01 (m, 4H), 3.30-3.55 (d, J= 3.9 Hz, 2H), 4.92-4.95 (d, J=3.5 Hz, 1H), 7.18-7.45 (m, Ar-H, 15H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.98, 34.74, 38.26, 38.82, 43.89, 116.73, 126.65, 127.25, 128.39, 128.89, 142.11, 143.859, 144.25, 162.94, 195.59. Anal. Calcd for $C_{31}H_{26}O_3$: C, 83.38; H, 5.87; O, 10.75; Found: C, 83.47; H, 5.95; O, 10.83.

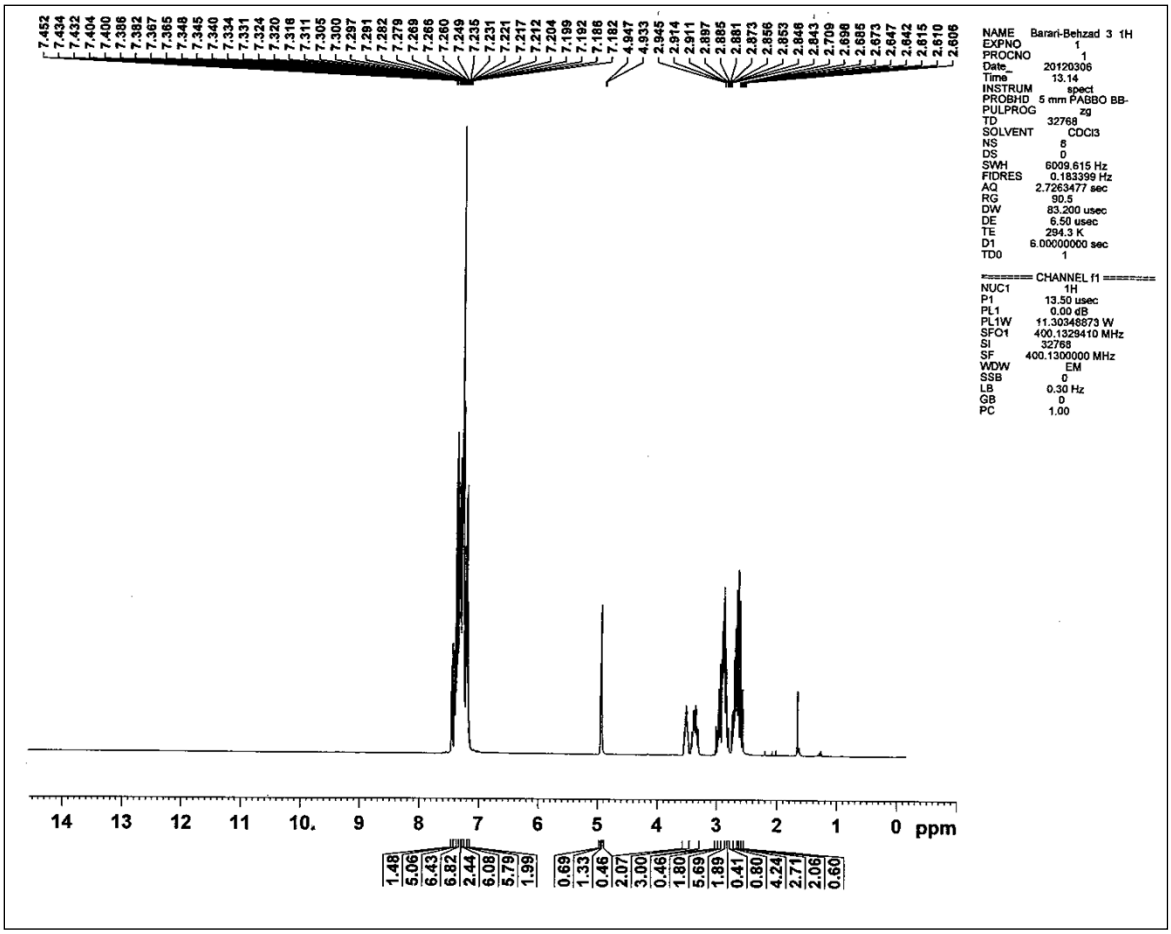
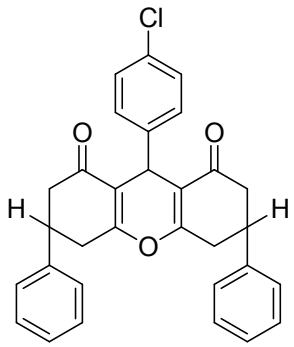


Fig. 31. ^{1}H NMR of **(8a)**.

9-(4-chlorophenyl)-3,4,6,7-tetrahydro-3,6-diphenyl-2H-xanthene-1,8(5H,9H)-dione (8b)



M. P.: 234-236 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3031, 1666, 1357, 1188, 1134, 995, 756, 694. ^1H NMR (400 MHz, $CDCl_3$) δ: 2.56-2.76 (m, 4H), 2.81-3.00 (m, 4H), 3.30-3.54 (d, J= 3.9 Hz, 2H), 4.88-4.89 (d, J=2.75 Hz, 1H), 7.17-7.40 (m, Ar-H, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.59, 34.69, 38.28, 38.61, 43.79, 116.33, 126.70, 127.31, 128.30, 128.91, 129.96, 132.29, 141.92, 142.36, 142.77, 195.61. Anal. Calcd. for $C_{31}H_{25}ClO_3$: C, 77.41; H, 5.24; Cl, 7.37; O, 9.98; Found: C, 77.50; H, 5.33;Cl, 7.45; O, 10.08.

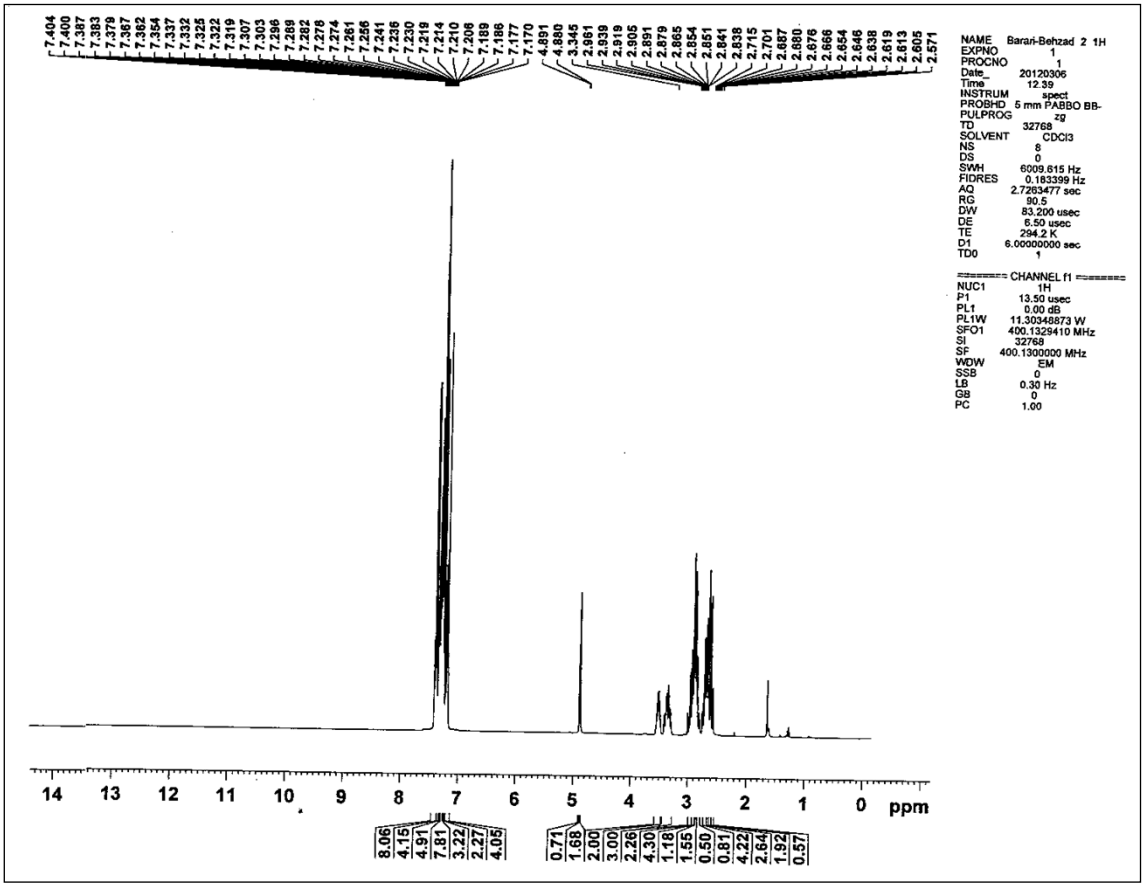


Fig. 32. ^1H NMR of (**8b**).

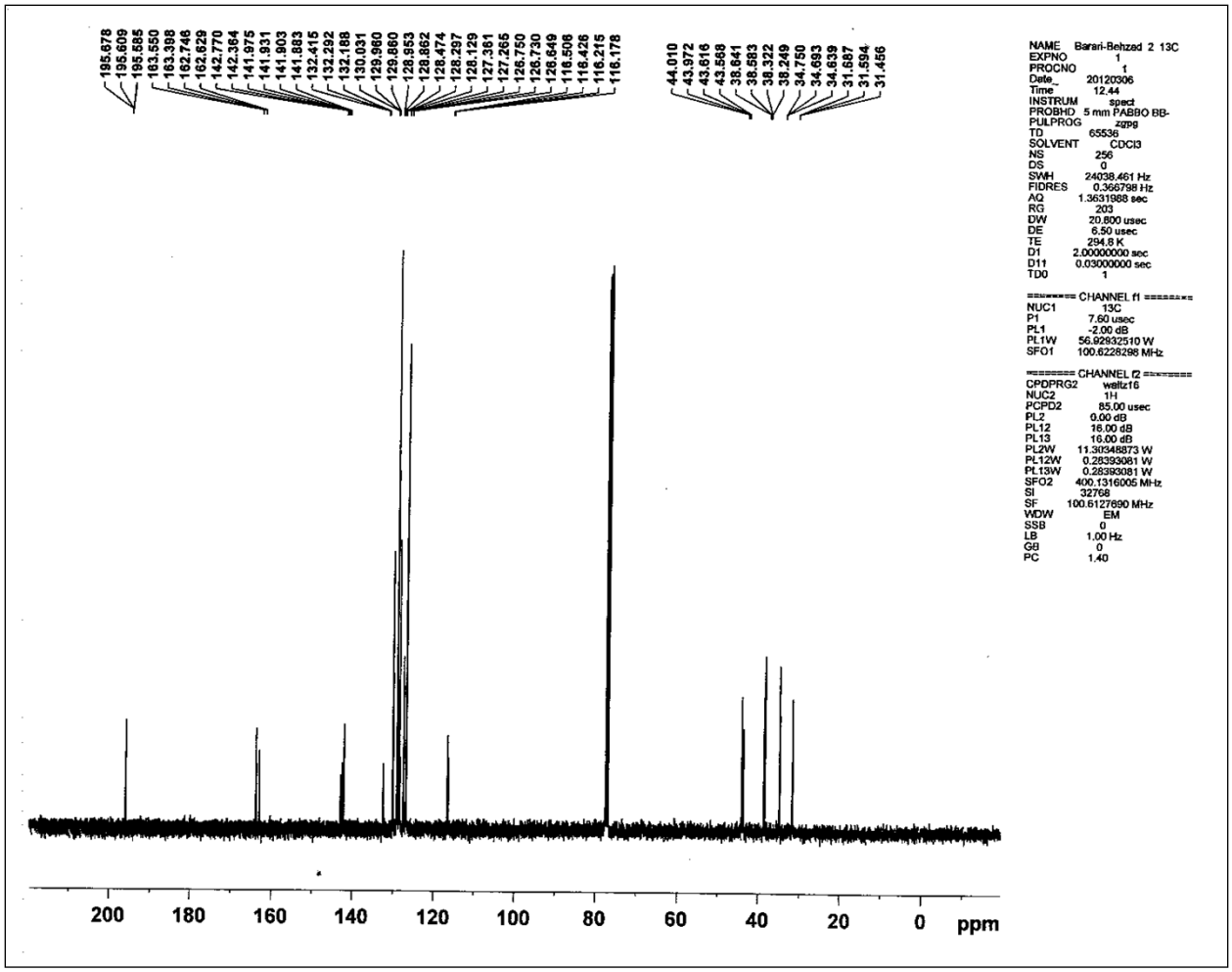
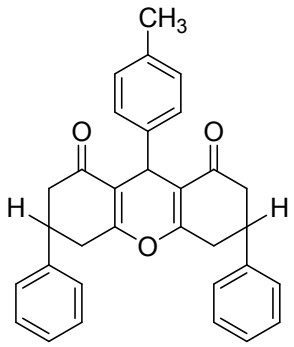


Fig. 33. ^{13}C NMR of **(8b)**.

9-(4-Methylphenyl)-3,4,6,7-tetrahydro-3,6-diphenyl-2H-xanthene-1,8(5H,9H)-dione (8c)



M. P.: 204-208 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 2939, 1666, 1504, 1358, 1242, 1180, 1134, 1033, 987, 764, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.56-2.73 (m, 4H), 2.79-2.95 (m, 4H), 3.30-3.53 (d, J= 3.2 Hz, 2H), 3.88 (s, 3H), 4.86-4.88 (d, J=3.2 Hz, 1H), 6.75-6.87 (m, Ar-H, 2H), 7.17-7.40 (m, Ar-H, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.03, 34.70, 38.29, 38.83, 43.91, 113.56, 116.85, 126.72, 127.12, 128.88, 129.51, 136.39, 142.12, 158.20, 163.14, 195.78. Anal. Calcd. for $C_{32}H_{28}O_3$: C, 83.45; H, 6.13; O, 10.42; Found: C, 83.52; H, 6.20; O, 10.51.

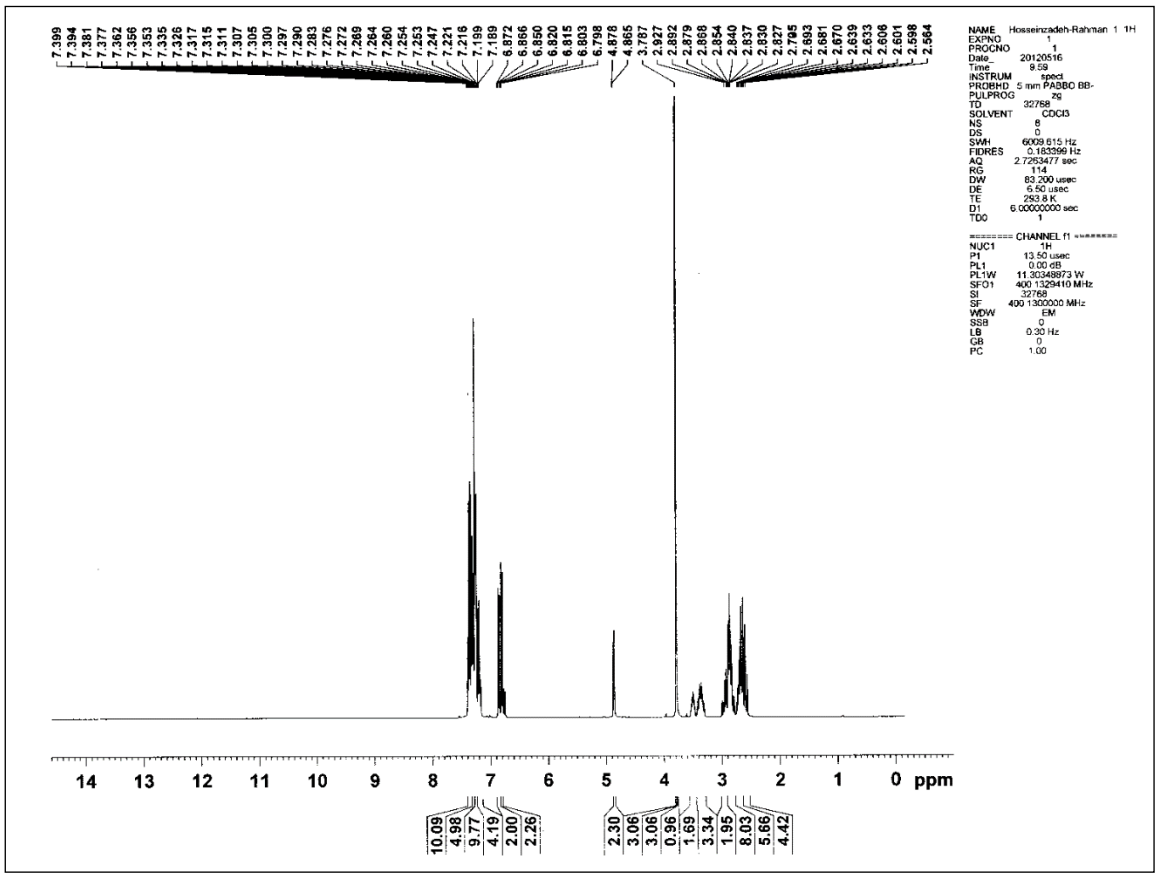


Fig. 34. ^{1}H NMR of **(8c)**.

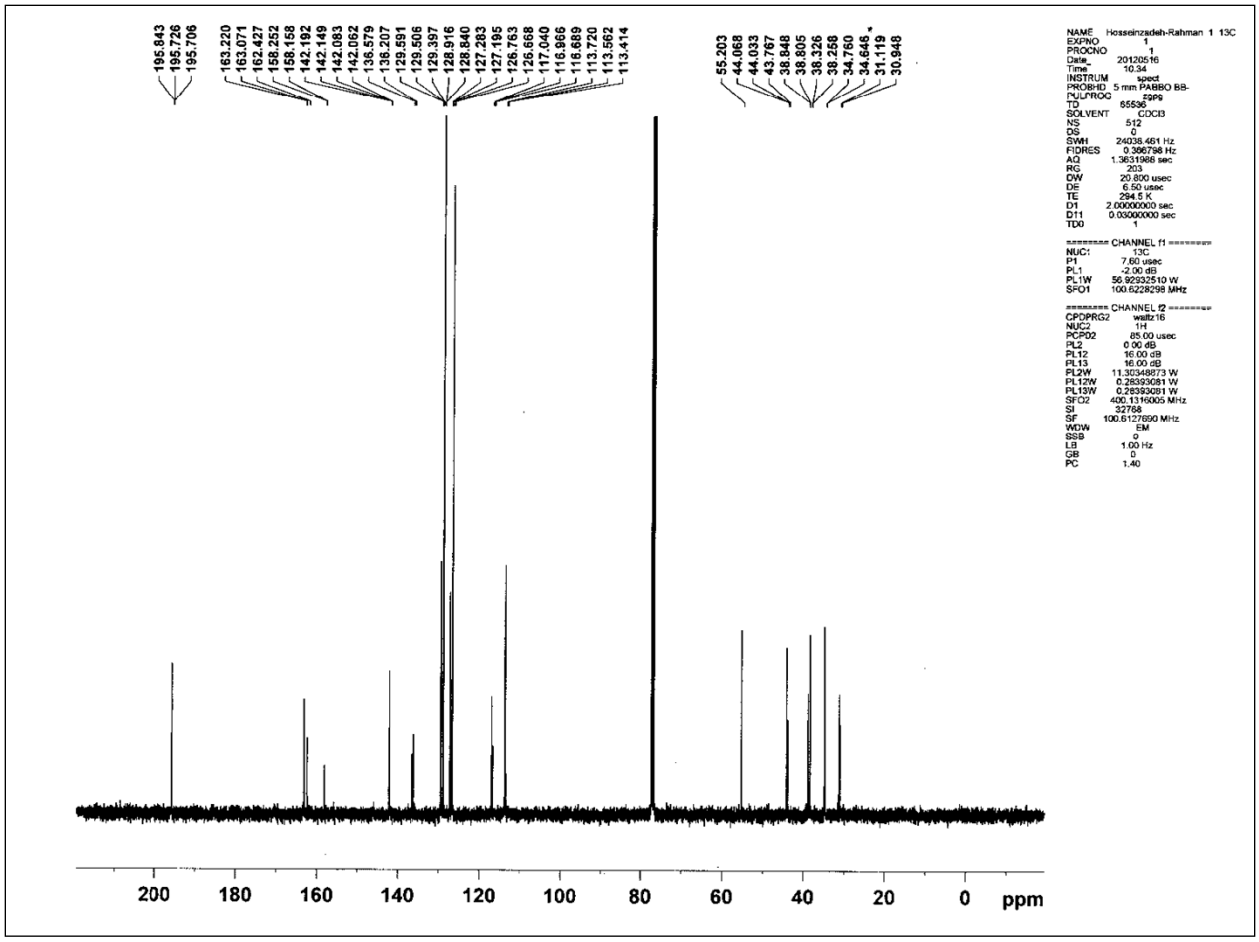
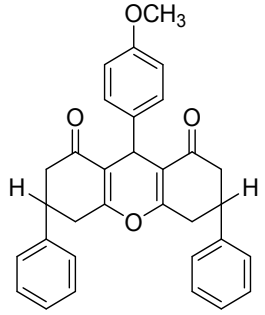


Fig. 35. ^{13}C NMR of **(8c)**.

9-(4-Methoxyphenyl)-3,4,6,7-tetrahydro-3,6-diphenyl-2H-xanthene-1,8(5H,9H)-dione (8d)



M. P.: 212-215 °C; FT-IR (KBr, Cm^{-1})ν_{max}: 3031, 1666, 1504, 1357, 1242, 1180, 1134, 987, 764, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.60-2.75 (m, 4H), 2.79-2.99 (m, 4H), 3.32-3.54 (d, J= 3.4 Hz, 2H), 3.79-3.80 (d, J=2.5 Hz, 3H), 4.87-4.88 (d, J=3 Hz, 1H), 6.80-6.88 (m, Ar-H, 4H), 7.19-7.40 (m, Ar-H, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.04, 34.71, 38.30, 38.81, 43.91, 113.64, 116.85, 126.72, 127.24, 128.88, 129.45, 136.40, 142.12, 158.21, 163.10, 195.77. Anal. Calcd for $C_{32}H_{28}O_4$: C, 80.65; H, 5.92; O, 13.43; Found: C, 80.74; H, 6.02; O, 13.56.

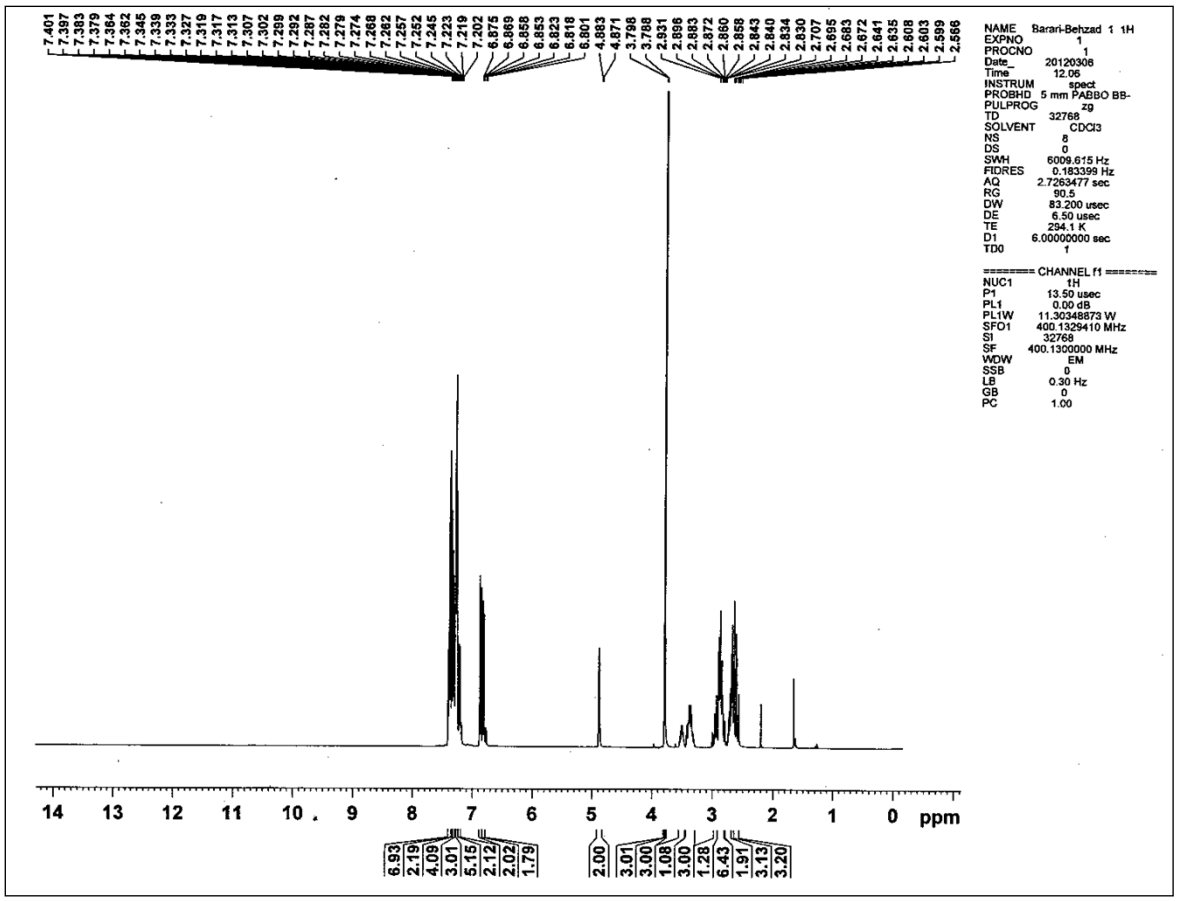


Fig. 36. ^{1}H NMR of (**8d**).

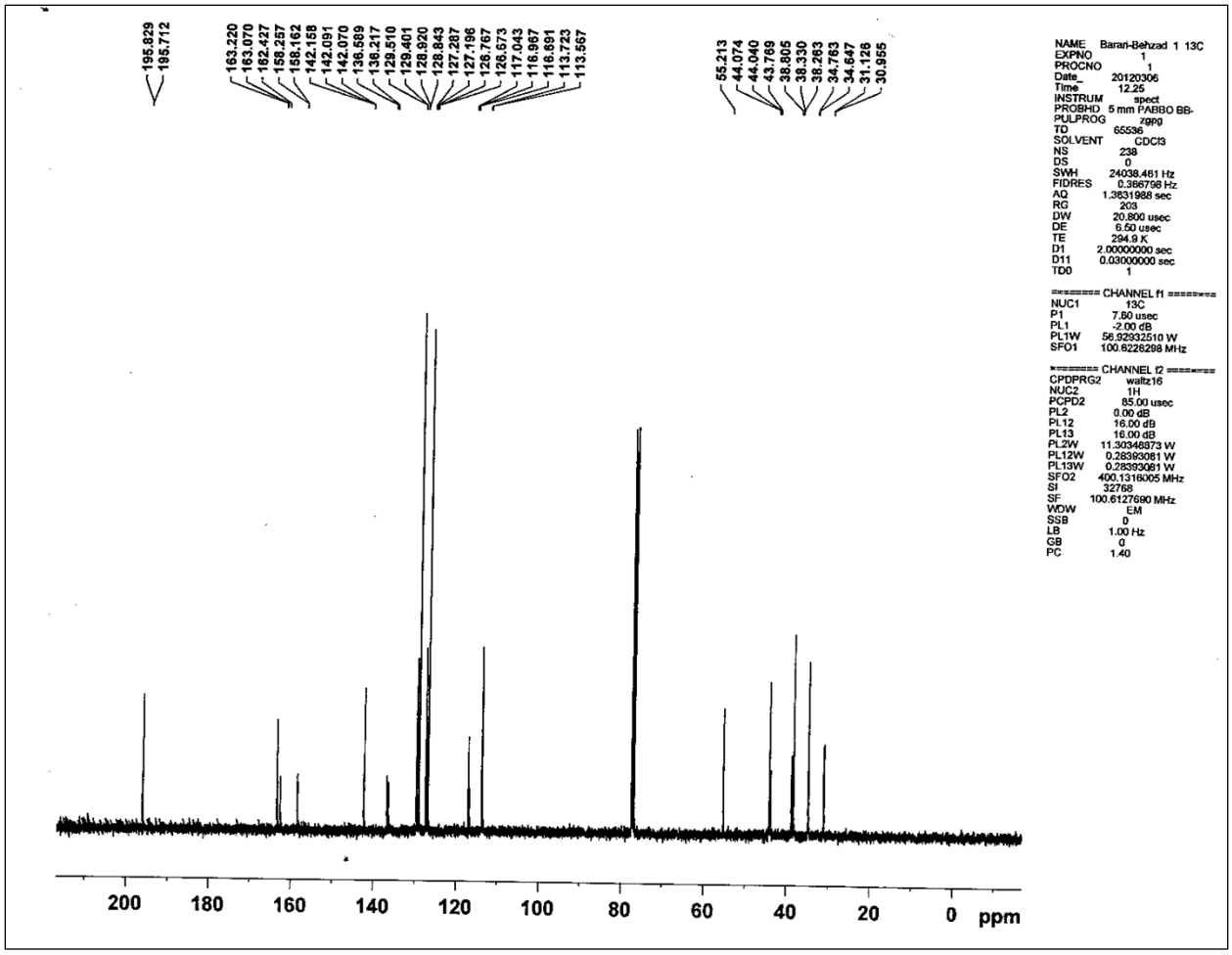
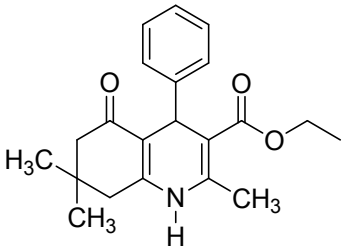


Fig. 37. ^{13}C NMR of (**8d**).

Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (10a)



M.p. 210-211 °C, FT-IR (KBr) 3275 (NH), 3080 (CH), 1700 (C=O) (acid), 1610 (C=O) (ketone), 1480 (OC_2H_5) (ester), 1225 (OCH_3) (ether) cm^{-1}; δH/ ppm (400 MHz, $CDCl_3$-*d*) 0.94 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.19-1.23 (t, J= 6.8 Hz, 3H, CH_3-CH_2-C=O), 2.14-2.35 (m, 4H,), 4.05-4.10 (q, J=7.2, 2H, -O-CH_2-CH_3), 5.05 (s, 1H, CH-Ph), 6.42 (s, 1H, NH), 7.09-7.13 (t, J= 7.2, 1H, CH (Ph)), 7.19-7.23 (t, J= 7.2, 2H, CH (Ph)), 7.28-7.33 (m, 2H, CH (Ph)); δC /ppm (100 MHz, $CDCl_3$) 195.67, 167.5, 148.5, 147.06, 143.4, 128.02, 127.88, 126.03, 112.08, 106.05, 50.73, 40.9, 36.6, 32.7, 29.45, 27.14, 19.34, 14.21.

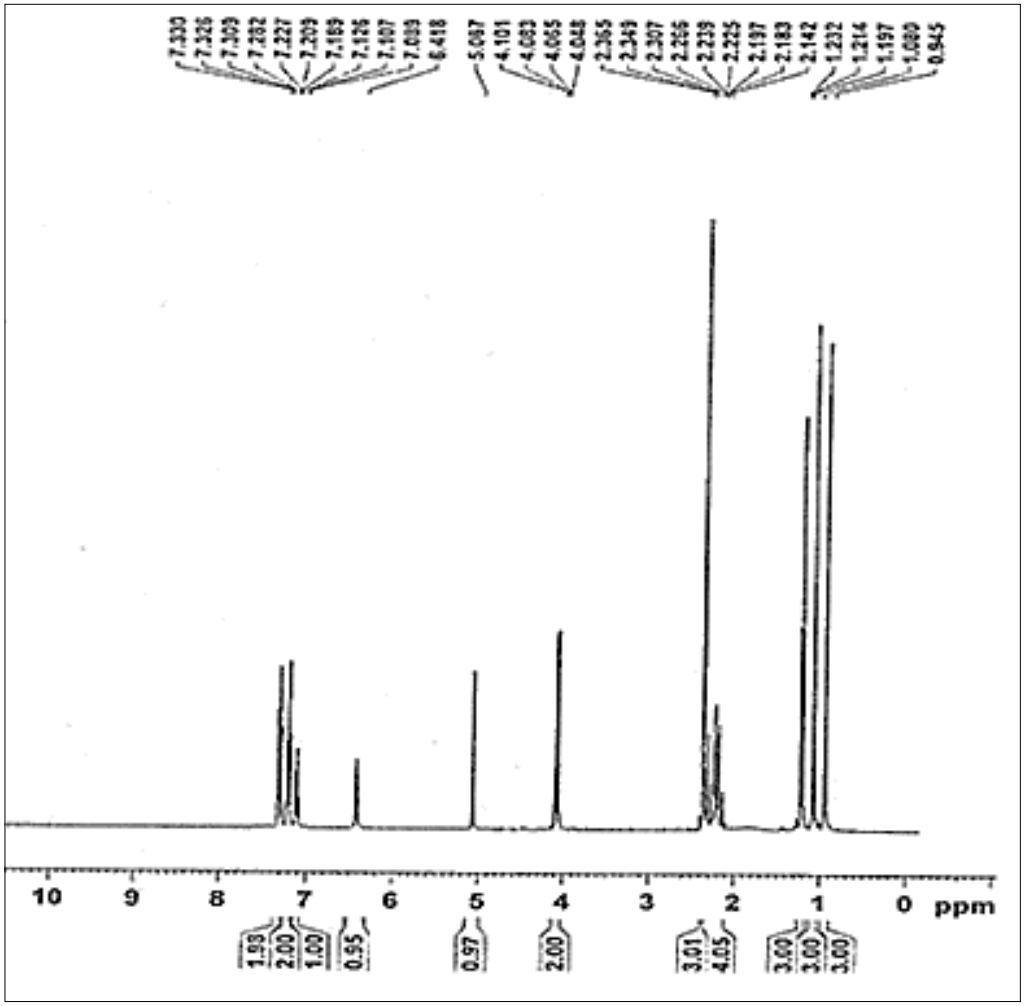


Fig. 38. ^{1}HNMR of **(10a)**.

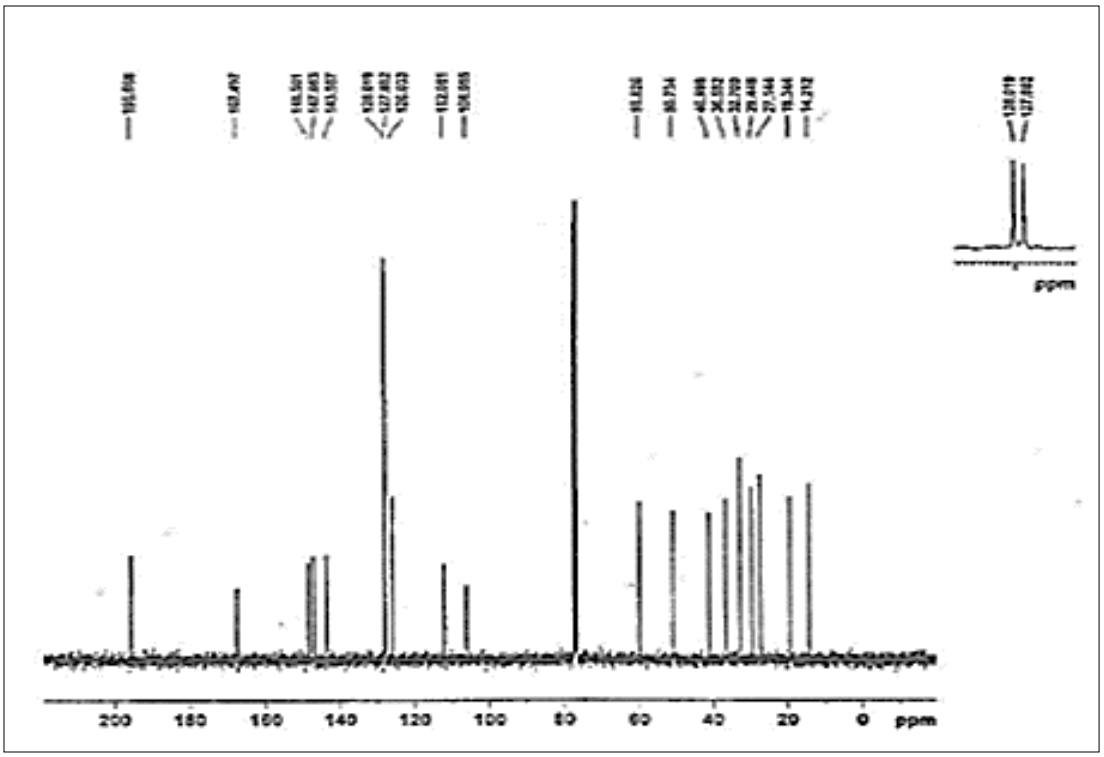
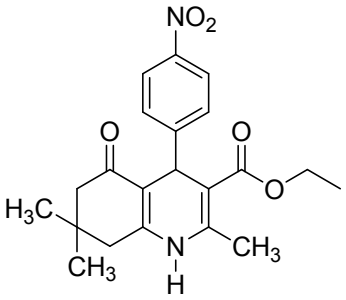


Fig. 39. ^{13}CNMR of **(10a)**.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (10b)



M.p. 207-209 °C, FT-IR (KBr) 3278 (NH), 3076 (CH), 1690 (C=O) (acid), 1615 (C=O) (ketone), 1482 (OC_2H_5) (ester), 1218 (OCH_3) (ether) cm^{-1}; δH/ ppm (400 MHz, $CDCl_3$-*d*) 0.77 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.04-1.09 (t, J= 9.6 Hz, 3H, CH_3-CH_2-C=O), 1.90-2.22 (m, 2H, C-CH_2-C=), 2.28 (s, 3H, CH_3), 2.38 (s, 1H), 2.43-2.46 (t, J= 2, 1H), 3.30 (s, 1H), 3.88-3.95 (q, J= 9.6, 2H, -O-CH_2-CH_3), 4.93 (s, 1H, CH-Ph), 7.36-7.39 (d, J= 11.6, 2H, CH (Ph)), 8.04-8.07 (d, J= 20.4, 2H, CH (Ph)), 9.19 (s, 1H, NH); δC /ppm (100 MHz, $CDCl_3$) 194.32, 166.48, 161.96, 155.07, 150.17, 146.24, 145.73, 128.84, 123.24, 109.11, 102.46, 59.33, 50.14, 36.71, 32.22, 29.08, 26.52, 18.42, 14.16.

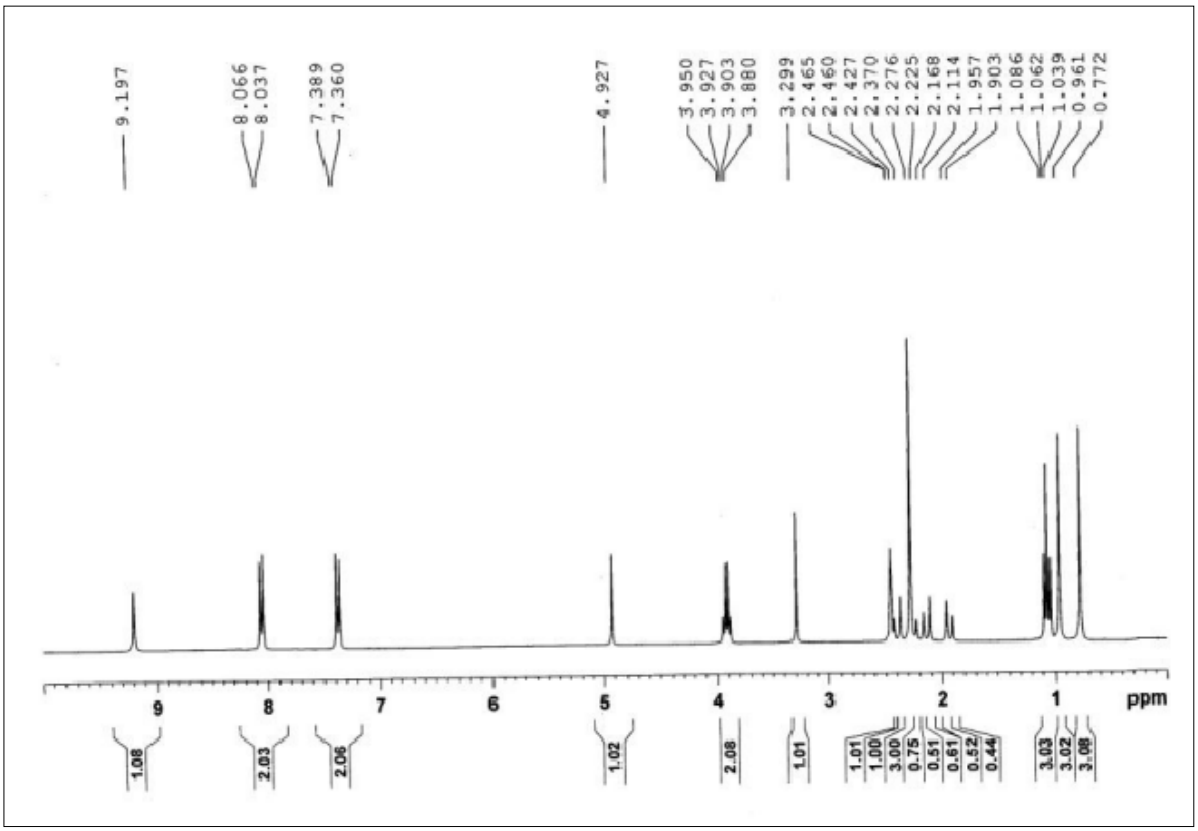


Fig. 40. ^{1}HNMR of **(10b)**.

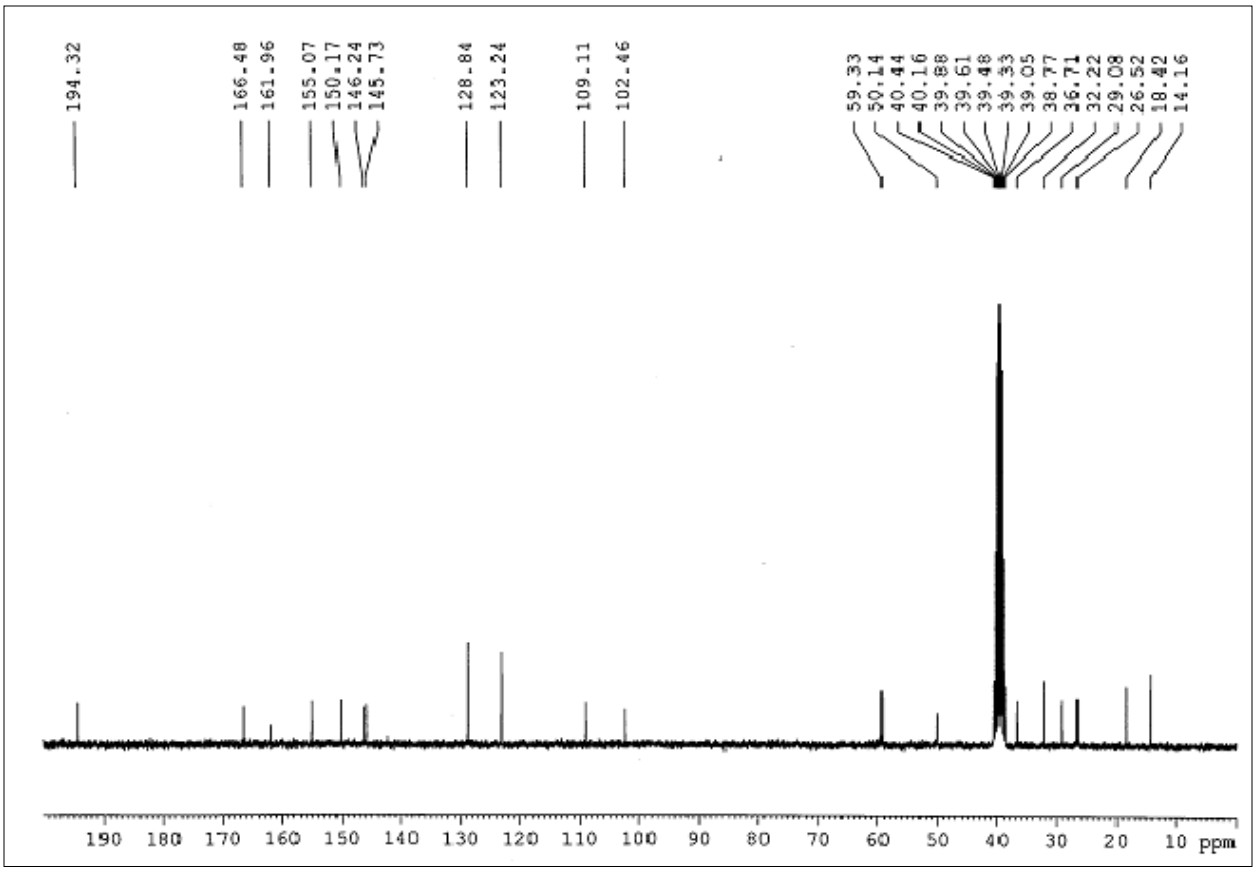
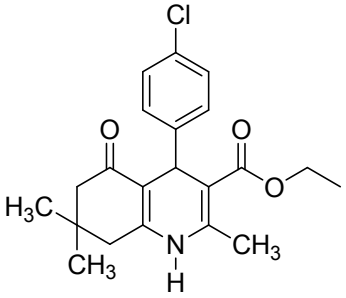


Fig. 41. ^{13}CNMR of **(10b)**.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (10d)



M.p. 243-245 °C, FT-IR (KBr) 3275 and 3196 (NH), 3080 and 2963 (CH), 1711 (C=O) (acid), 1605 (C=O) (ketone), 1480 (OC_2H_5) (ester), 1221 (OCH_3) (ether) cm^{-1}; δH/ ppm (400 MHz, $CDCl_3$-*d*) 0.94 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.19-1.22 (t, J= 7.2 Hz, 3H, CH_3-CH_2-C=O), 2.14-2.36 (m, 4H, C-CH_2-C=), 2.39 (s, 3H, N-C-CH_3), 4.04-4.09 (q, J= 7.2 Hz, 2H, -O-CH_2-CH_3), 5.04 (s, 1H, CH-Ph), 6.12 (s, 1H, NH), 7.16-7.28 (m, 4H, CH (Ph)); δC /ppm (100 MHz, $CDCl_3$) 195.49, 167.22, 148.12, 145.56, 143.62, 131.59, 129.45, 128.0, 111.90, 105.76, 59.92, 50.86, 41.08, 36.21, 32.72, 29.43, 27.11, 19.46, 14.21.

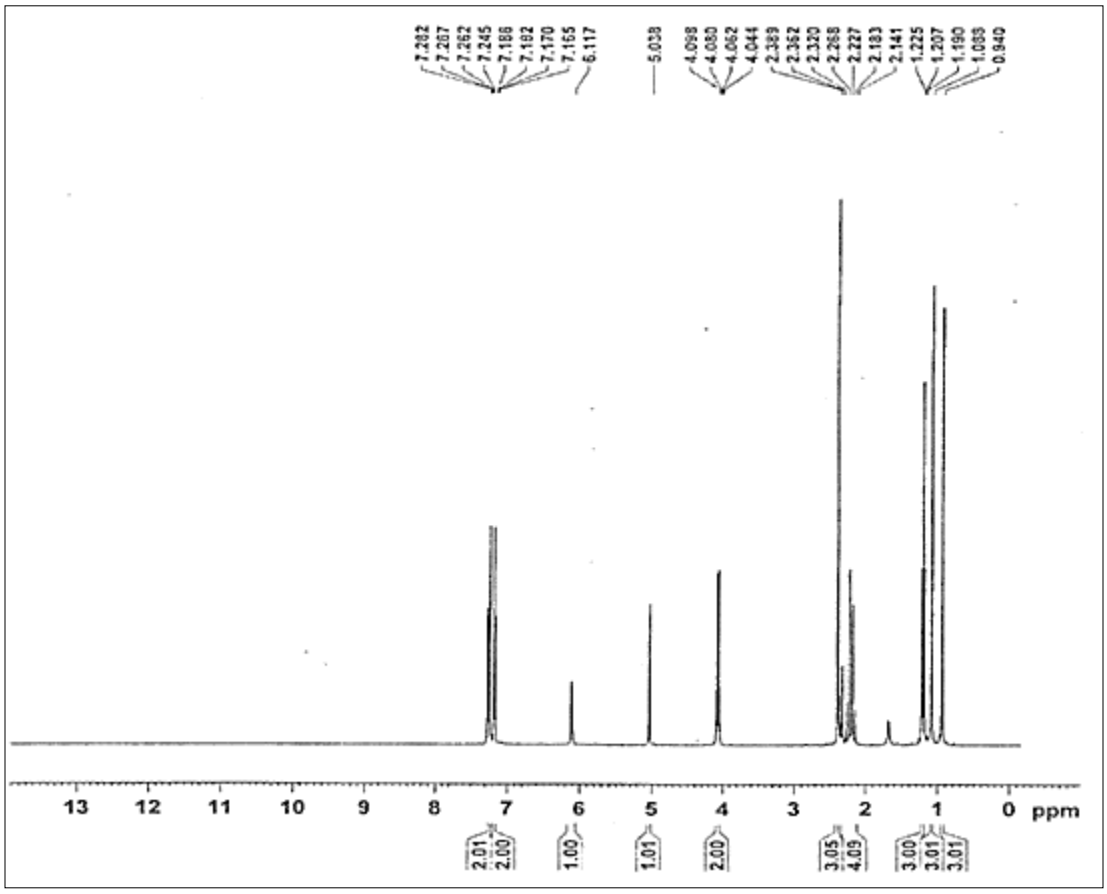


Fig. 42. ^{1}H NMR of **(10d)**.

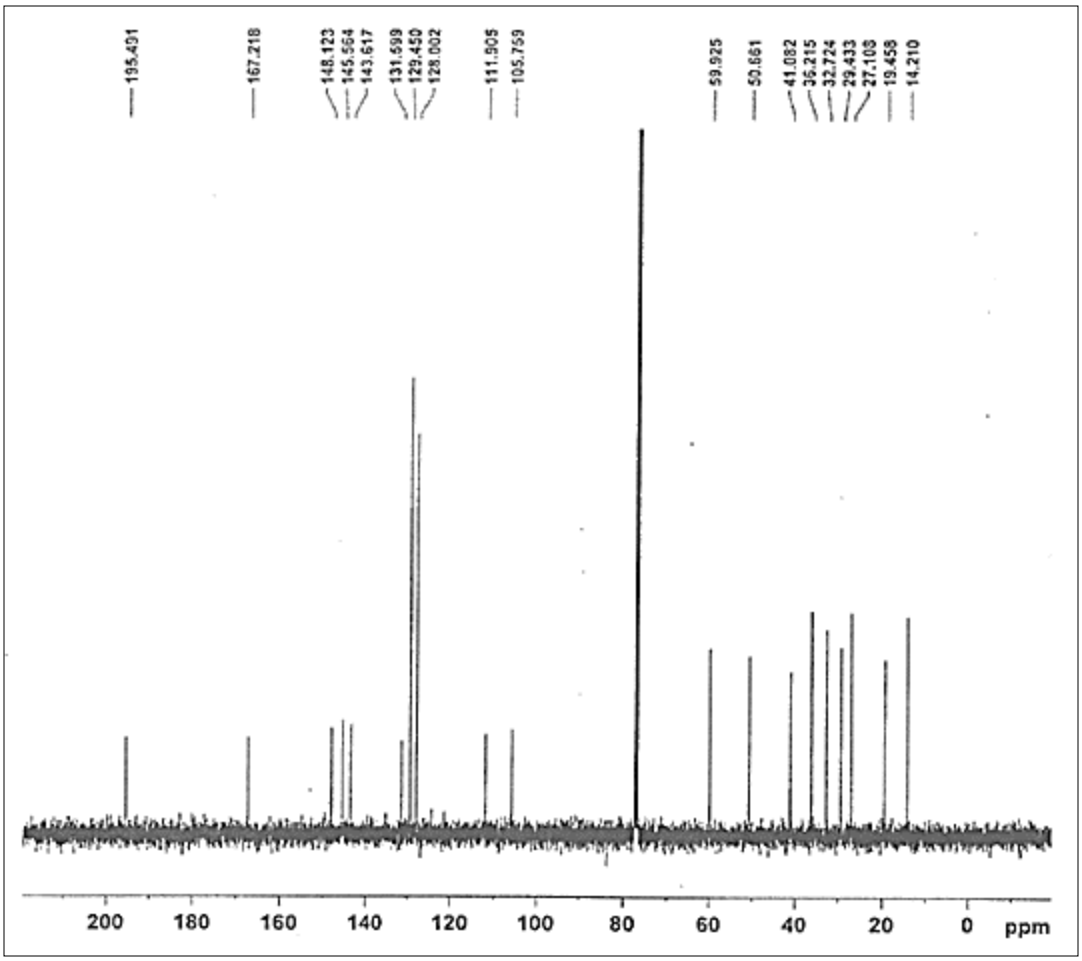
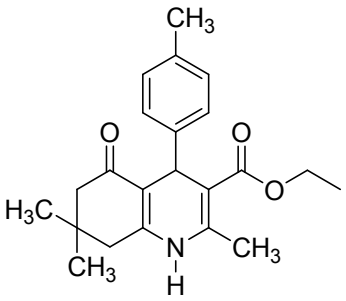


Fig. 43. ^{13}C NMR of **(10d)**.

Ethyl 2,7,7-trimethyl-5-oxo-4-(p-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (10g)



M.p. 283-284 °C, FT-IR (KBr) 3275 and 3207 (NH), 3085 and 2963 (CH), 1700 (C=O) (acid), 1610 (C=O) (ketone), 1494 (OC_2H_5) (ester), 1222 (OCH3) (ether) cm–1; δH/ ppm (400 MHz, $CDCl_3$-*d*) 0.96 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 1.21-1.25 (t, J= 7.2 Hz, 3H, CH_3-CH_2-C=O), 2.14-2.24 (m, 3H, C-CH_2-C=), 2.27 (s, 3H, N-C-CH_3), 2.29-2.33 (t, J= 7.6 Hz, 1H, C-CH_2-C=), 2.36 (s, 3H, H_3C-Ph), 4.05-4.10 (m, 2H, -O-CH_2-CH_3), 5.02 (s, 1H, CH-Ph), 6.18 (s, 1H, NH), 7.00-7.02 (d, J= 7.6 Hz, 2H, CH-Ar), 7.19-7.21 (d, J= 8 Hz, 2H, CH-Ar); δC /ppm (100 MHz, $CDCl_3$) 195.64, 167.53, 148.15, 144.15, 143.27, 135.40, 128.61, 127.88, 112.28, 106.25, 59.83, 50.73, 41.1, 36.07, 32.72, 29.42, 27.23, 21.05, 19.4, 14.22.

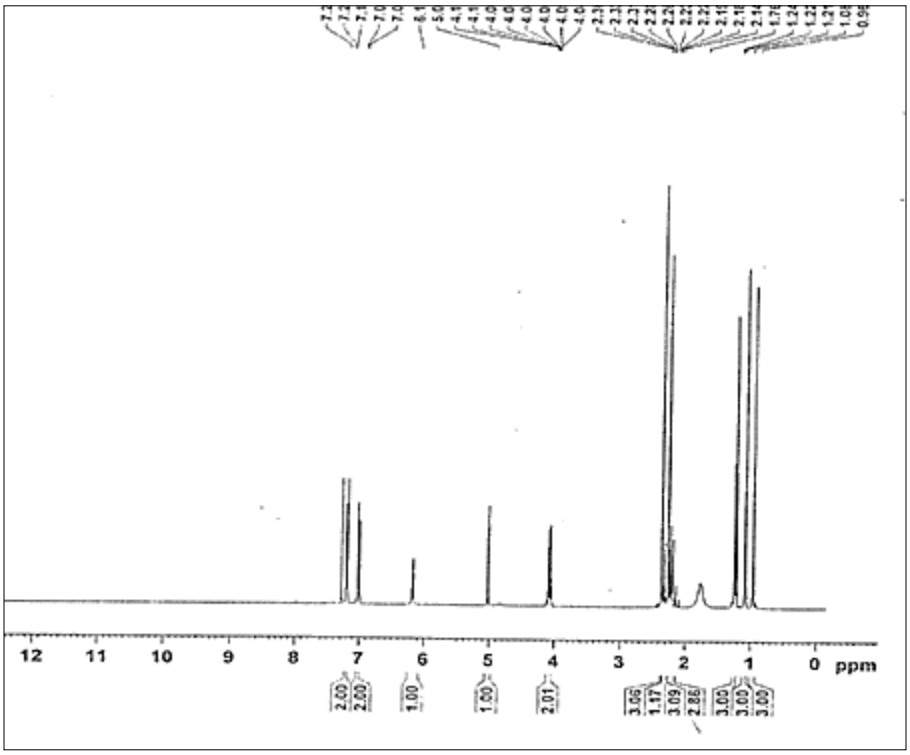


Fig. 44. ^{1}H NMR of **(10g)**.

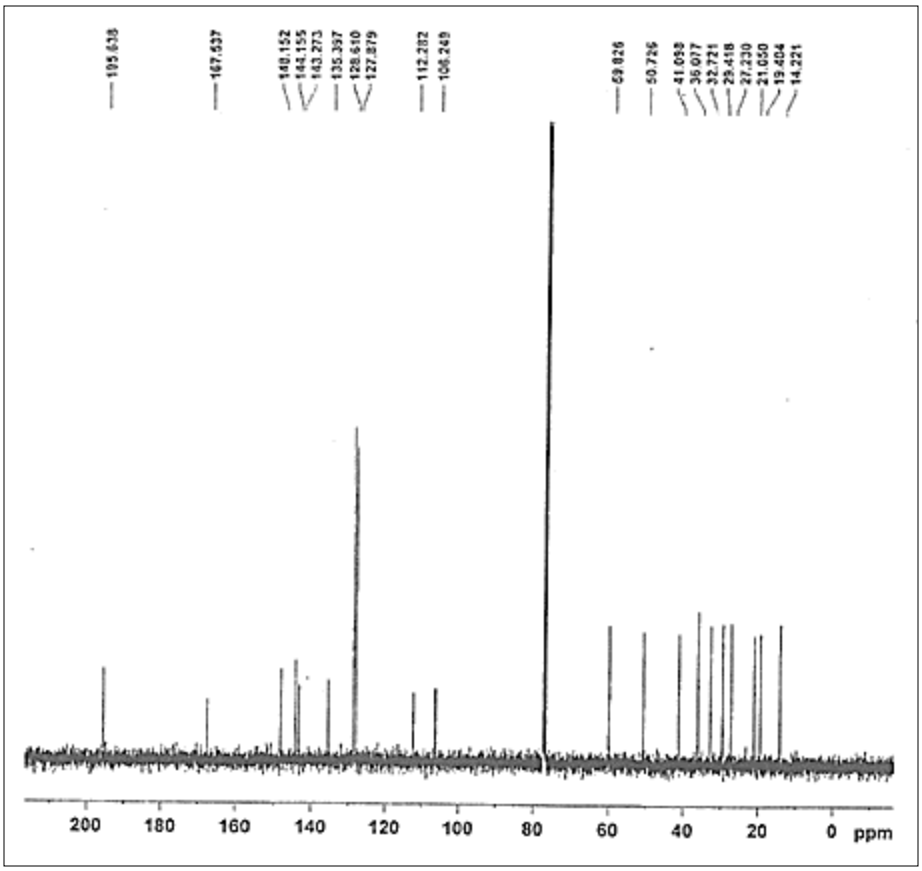
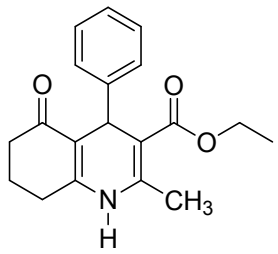


Fig. 45. ^{13}C NMR of **(10g)**.

Ethyl 2-methyl-5-oxo-4-phenyl-4,6,7,8-tetrahydro-1H-quinoline-3-carboxylate (11a)



M.p. 240-242 °C FT-IR (KBr) 3296 (NH), 1641 (C=O) (acid), 1608 (C=O) (ketone), 1488 (OC_2H_5) (ester) cm^{-1}; δH/ppm (300 MHz, $CDCl_3$-*d*) 1.17 (t, 3H, CH_3-CH_2-C=O), 1.59 (m, 2H, CH_2-CH_2-CH_2), 1.97 (m, 3H, CH_3-Ph), 2.30-2.46 (m, 4H, CH_2-CH_2), 4.05 (q, 2H, -O-CH_2-CH_3), 5.01 (s, 1H, CH-Ph), 5.94 (s, 1H, NH), 7.08-7.31 (m, 5H, CH (Ph)).

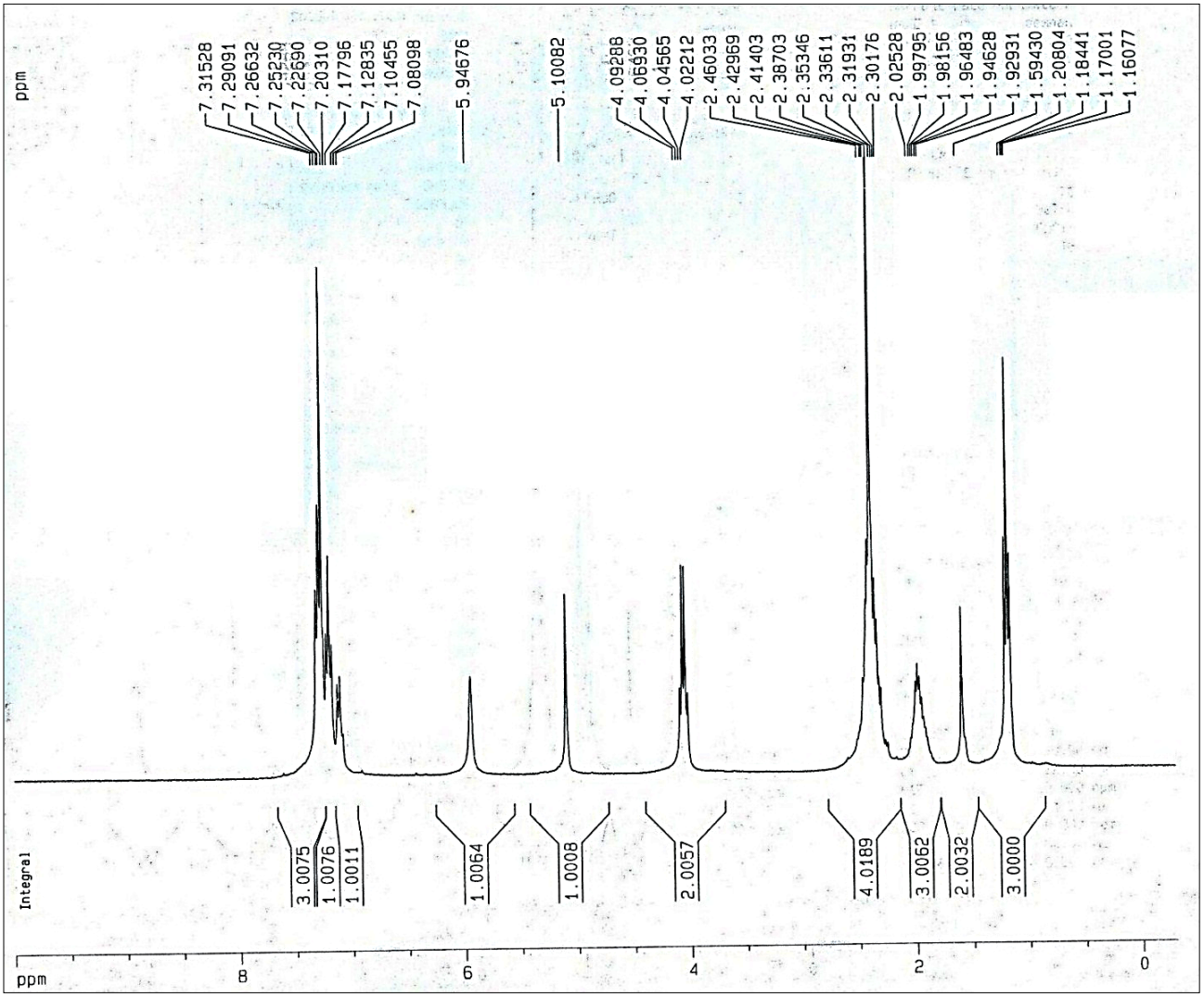
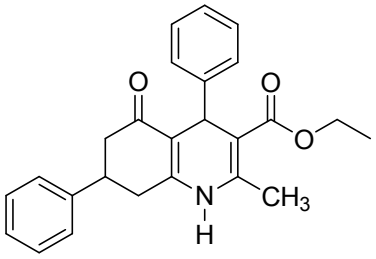


Fig. 46. ^{1}HNMR of **(11a)**.

Ethyl 2-methyl-5-oxo-4,7-diphenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (12a)



M.p. 213-215 °C, ν_{max} (KBr) 3276 (NH), 1701 (C=O) (acid), 1606 (C=O) (ketone), 1487 (OC_2H_5) (ester), cm^{-1}; δ_H (400 MHz, DMSO-d_6) 1.14 (t, 3H, CH_3-CH_2-O-C=O), 2.32 (s, 3H, CH_3), 2.35 (dd, 1H, 8 H), 2.5 (d, 1H, 8 H), 2.59 (m, 1H, 7 H), 2.68 (dd, 1H, 6 H), 2.79 (dd, 1H, 6 H), 3.17 (s, 1H, NH), 4.0 (q, 2H, -O-CH_2-CH_3), 4.98 (s, 1H, 4 H), 7.11 (m, 1H, 4'H), 7.19-7.24 (q, 5H, 2', 4', 6', 2", 6"H), 7.3-7.36 (m, 4H, 3', 5', 3", 5" H), 9.21 (s, 1H, NH) ppm; δ_C (100 MHz, DMSO-d_6) 194.4 (C-5), 167.3 (C=OOC_2H_5), 151.1 (C-2), 148.1 (C-1a), 145.3 (C-1"), 143.9 (C-1'), 128.9 (C-2' and C-6'), 128.3 (C-3' and C-5'), 127.9 (C-3" and C-5"),127.4 (C-2" and C-6"), 127 (C-4"), 126.2 (C-4'), 111.2 (C-5a), 104.2 (C-3), 59.5 (O-CH_2-CH_3), 44.4 (C-6), 38.8 (C-4), 36.2 (C-8), 34 (C-7), 18.7 (1C, CH_3), 14.6 (1C, CH_3-CH_2O).

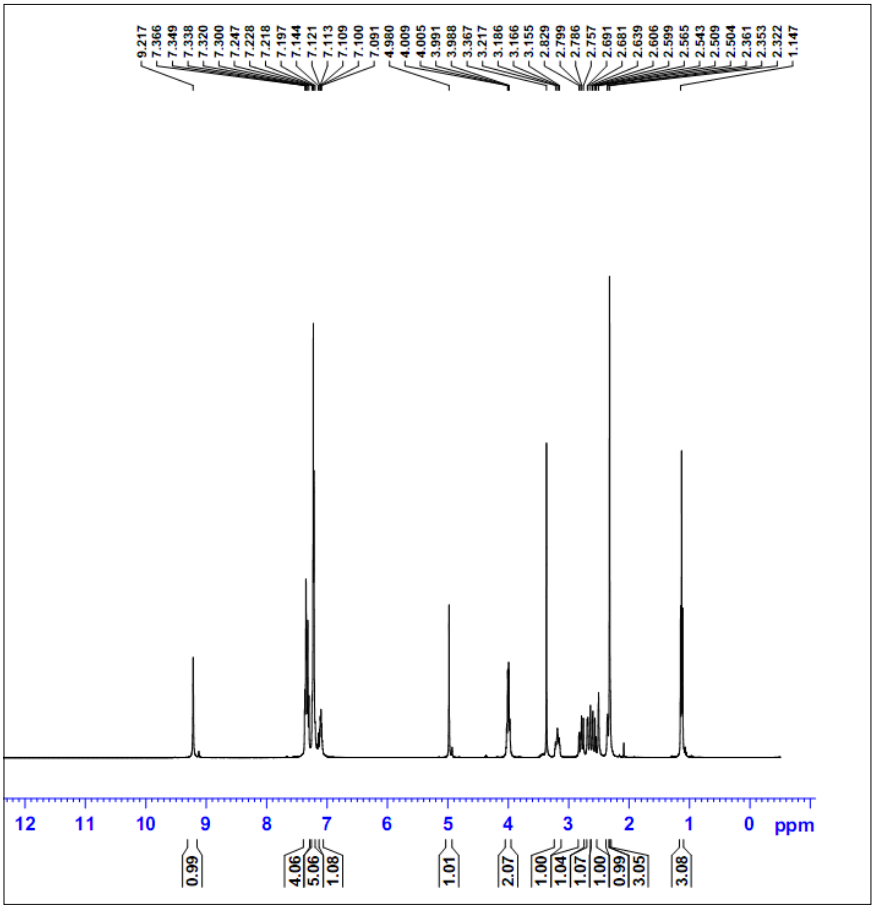


Fig. 47. ^{1}H NMR of **(12a)**.

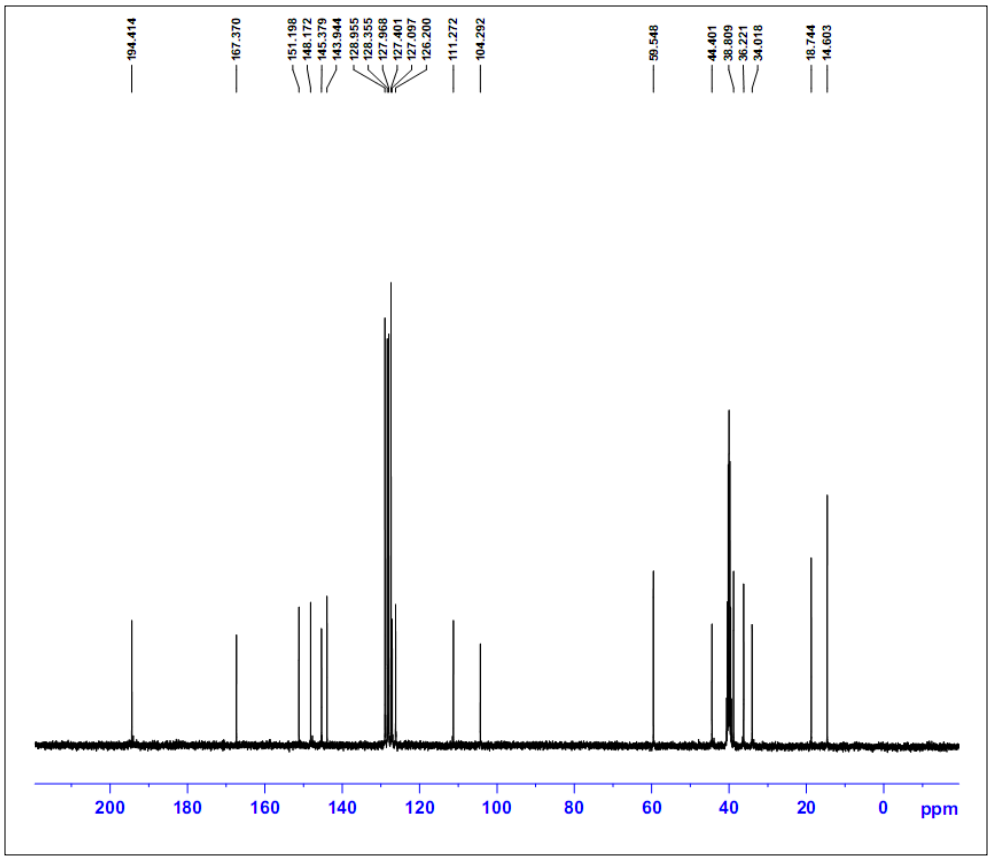
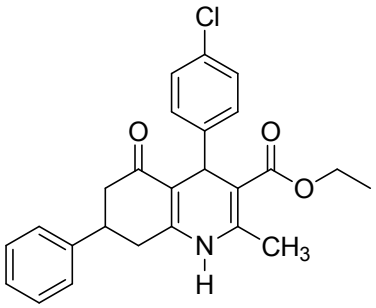


Fig. 48. ^{13}C NMR of **(12a)**.

Ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-7-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (12b)



M.p. 190-192 °C, ν_{max} (KBr) 3274 (NH), 1701(C=O) (acid), 1606 (C=O) (ketone), 1487 (OC_2H_5) (ester), 848 (C-Cl) cm^{-1}; δ_H (400 MHz, DMSO-d_6) 1.12 (t, 3H, CH_3-CH_2-O-C=O), 2.3 (t, 1H, 8 H), 2.31 (s, 3H, CH_3), 2.5 (t, 1H, 8 H), 2.54–2.59 (7, 1H, 8 H), 2.59-2.66 (m, 1H, 6 H), 2.74-2.82 (m, 1H, 6 H),), 3.17 (t, 1H,NH), 3.98 (q, 2H, -O-CH_2-CH_3),4.90 (d, 1H, 4 H), 7.22-7.28 (m, 5H, 2',6', 2", 4", 6" H), 7.31–7.33 (m, 4H, 3', 5', 3", 5" H), 9.21 (d, 1H, NH) ppm; δ_C (100 MHz, DMSO-d_6) 194.2 (C-5), 167.1 (C=OOC_2H_5), 151.3 (C-2), 150.8 (C-1a), 147.1 (C-1"), 145.7 (C-1'), 143.8 (C-4'), 130.7 (C-2' and C-6'), 129.8 (C-3' and C-5'), 128.8 (C-3" and C-5"), 128.1 (C-2" and C-6"), 127.1 (C-4"), 111.0 (C-5a), 103.6 (C-3), 44.3 (O-CH_2-CH_3), 43.7 (C-6), 38.8 (C-4), 36.0 (C-8), 33.7 (C-7), 18.7 (1C, CH_3), 14.5 (1C, CH_3-CH_2O).

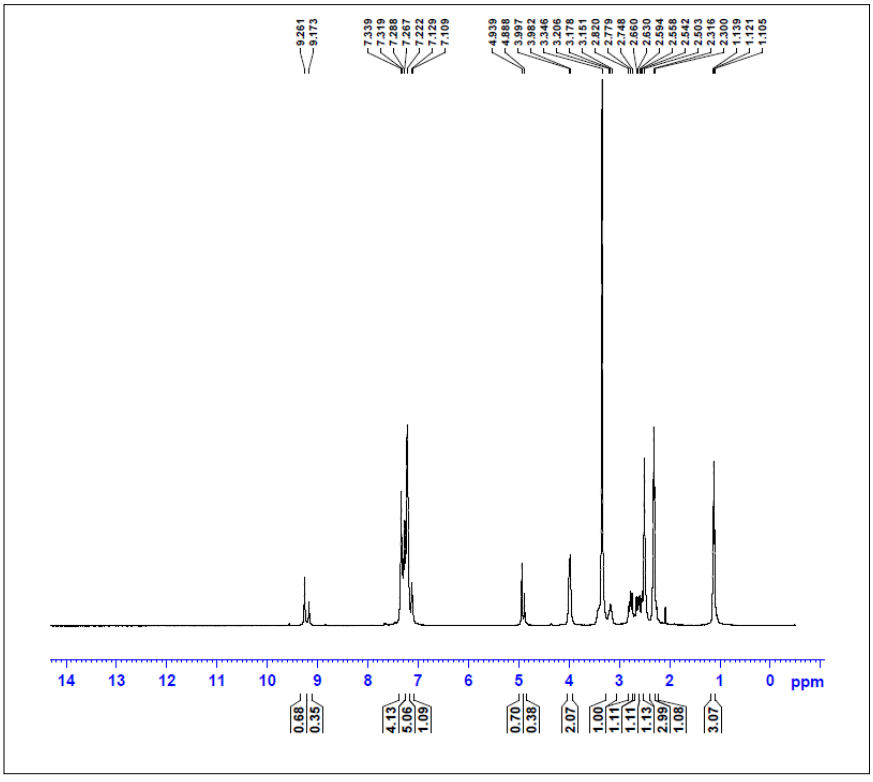


Fig. 49. ^{1}H NMR of **(12b)**.

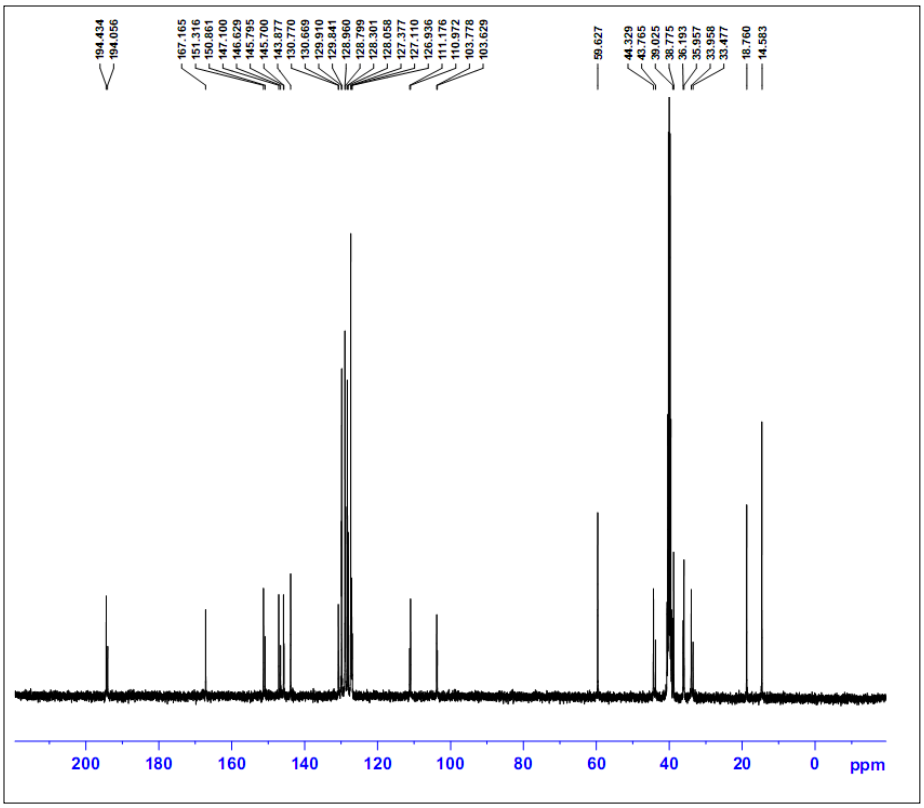
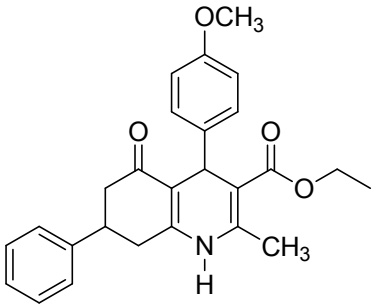


Fig. 50. ^{13}C NMR of **(12b)**.

Ethyl 4-(p-methoxyphenyl)-2-methyl-5-oxo-7-phenyl-4, 6, 7, 8-tetrahydro-1H-quinoline-3-carboxylate (12c)



M.p. 236-238 °C, FT-IR (KBr) 3280 (NH), 1689 (C=O) (acid), 1606 (C=O) (ketone), 1479 (OC_2H_5) (ester), 1222 (OCH_3) (ether) cm^{-1}; δH/ ppm (300 MHz, $CDCl_3$-*d*) 1.27 (m, 3H, CH_3-CH_2-C=O), 2.23-2.37 (m, 3H, CH_3-Ph), 2.38-2.52 (m, 5H, CH_2-CH-CH_2), 3.71 (s, 3H, CH_3-O-Ph), 4.07 (m, 2H, -O-CH_2-CH_3), 5.05 (m, 1H, CH-Ph), 6.71-7.12 (m, 4H, CH(p-OMe-Ph)), 6.96 (s, 1H, NH), 7.17-7.29 (m, 5H, CH (Ph)); δC /ppm (75 MHz, CDCl3) 195.2, 167.5, 157.8, 150, 149.5, 143.4, 142.6, 139.7, 139.3, 128.8, 127, 126.6, 113.2, 106.2, 59.8, 55.1, 39.5, 38.8, 35.8, 34.4, 19.1, 14.2.

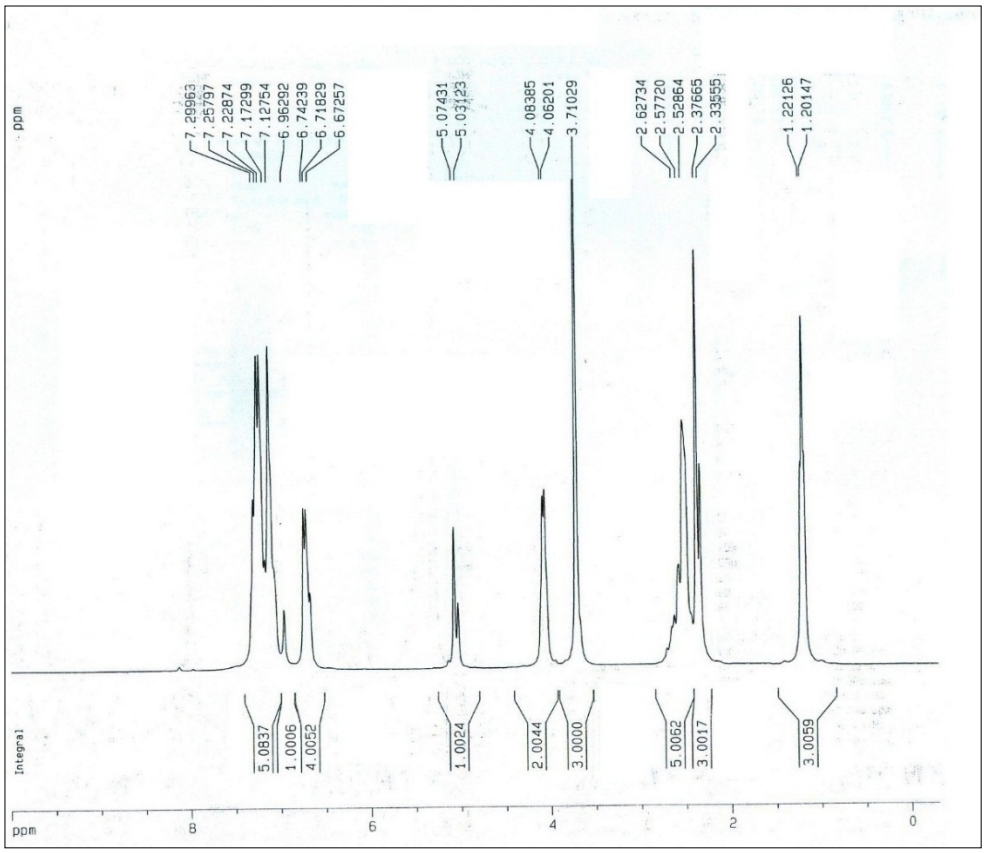


Fig. 51. ^{1}H NMR of **(12c)**.

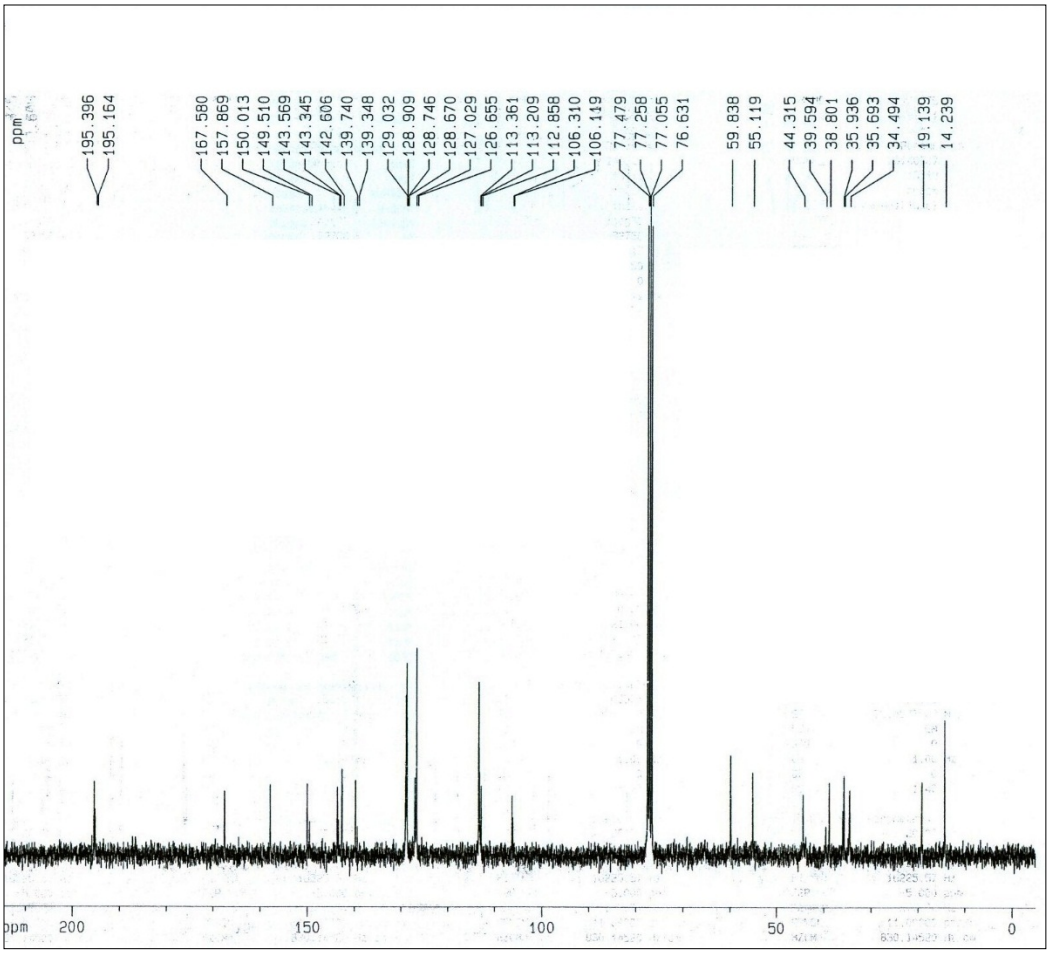


Fig. 52. ^{13}C NMR of **(12c)**.