

Electronic Supporting Information for

SnCl₄-functionalized nano-Fe₃O₄ encapsulated-silica particles as a novel heterogeneous solid acid for synthesis of 1,4-dihydropyridine derivatives

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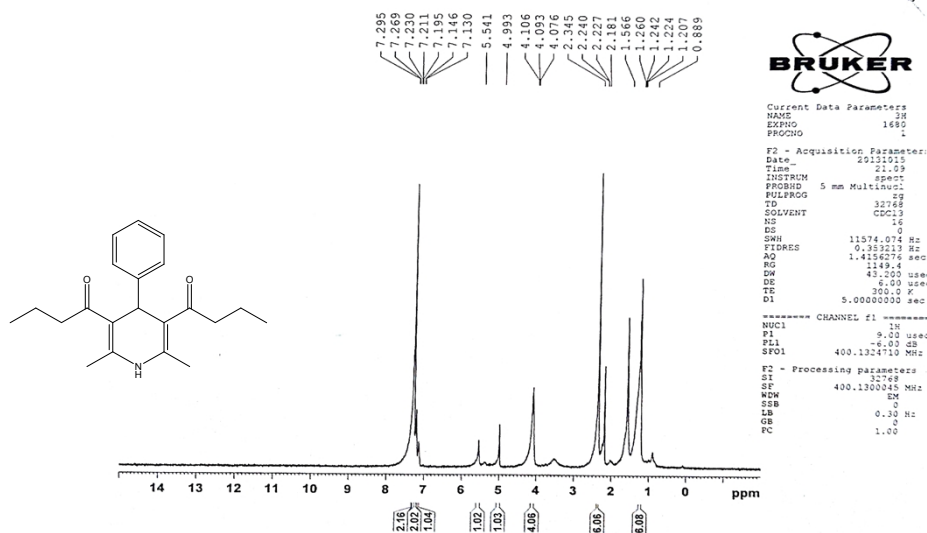
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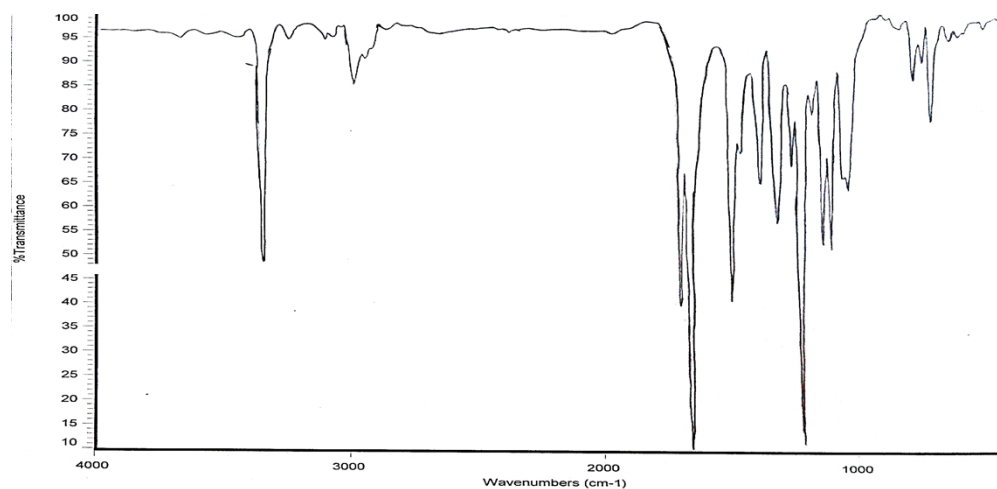
Spectroscopic data for 1,4-dihydropyridines

➤ 2,6-Dimethyl-4-phenyl-1,4-dihydropyridine-3,5-diethylcarboxylate (compound 4a)

Yellowish solid, IR (KBr, cm^{-1}): 3342 (NH), 1689 (C=O, ester), 1487 (C=C, aromatic), 1212 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.28 (d, $J = 7$ Hz, 2H, Ar-H), 7.21 (t, $J = 6.9$ Hz, 2H, Ar-H), 7.13 (d, $J = 6.9$ Hz, 1H, Ar-H), 5.54 (s, 1H, NH), 4.99 (s, 1H, CH), 4.09 (q, $J = 6.8$ Hz, 4H, 2 OCH₂), 2.34 (s, 6H, 2CH₃), 1.22 (t, $J = 6.8$ Hz, 6H, 2CH₃CH₂).

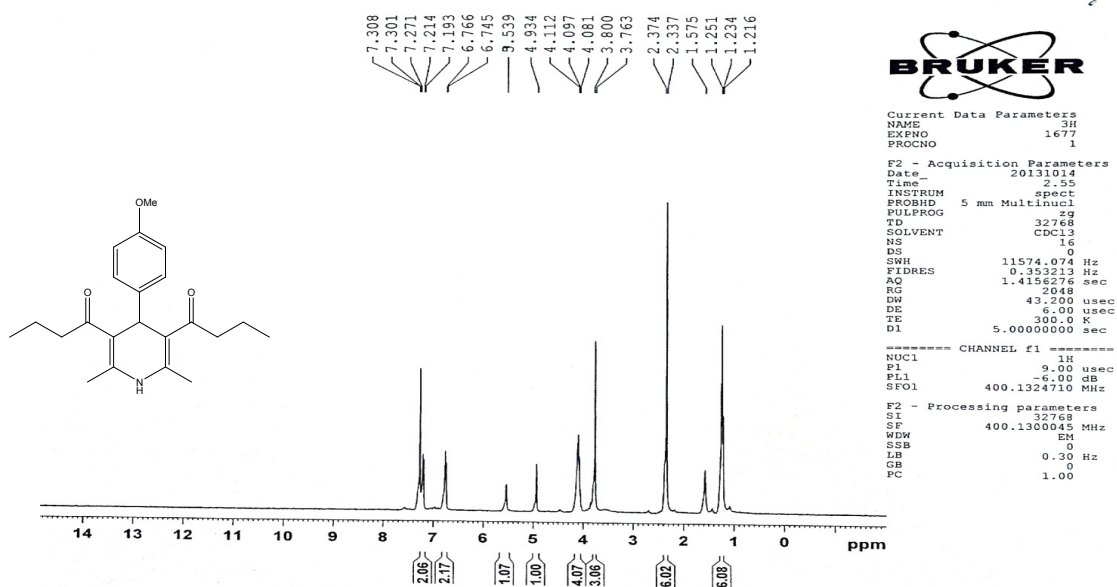


^1H NMR spectrum of compound 4a

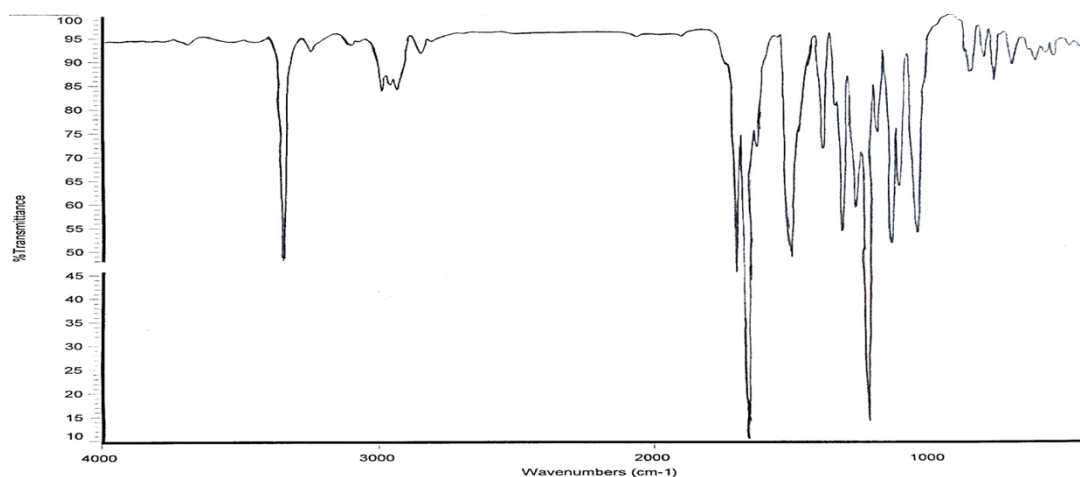


FT-IR spectrum of compound 4a

- 2,6-Dimethyl-4-(4-methoxyphenyl)-1,4-dihydropyridine-3,5-diethylcarboxylate (compound **4b**) Yellow solid, IR (KBr, cm^{-1}): 3343 (NH), 1689 (C=O, ester), 1489 (C=C, aromatic), 1211 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.20 (d, $J = 7.9$ Hz, 2H, Ar-H), 6.75 (d, $J = 7.9$ Hz, 2H, Ar-H), 5.54 (s, 1H, NH), 4.93 (s, 1H, CH), 4.10 (q, $J = 7.4$ Hz, 4H, 2 OCH_2), 3.76 (s, 3H, OCH_3), 2.33 (s, 6H, 2 CH_3), 1.23 (t, $J = 7.4$ Hz, 6H, 2 CH_2CH_3).

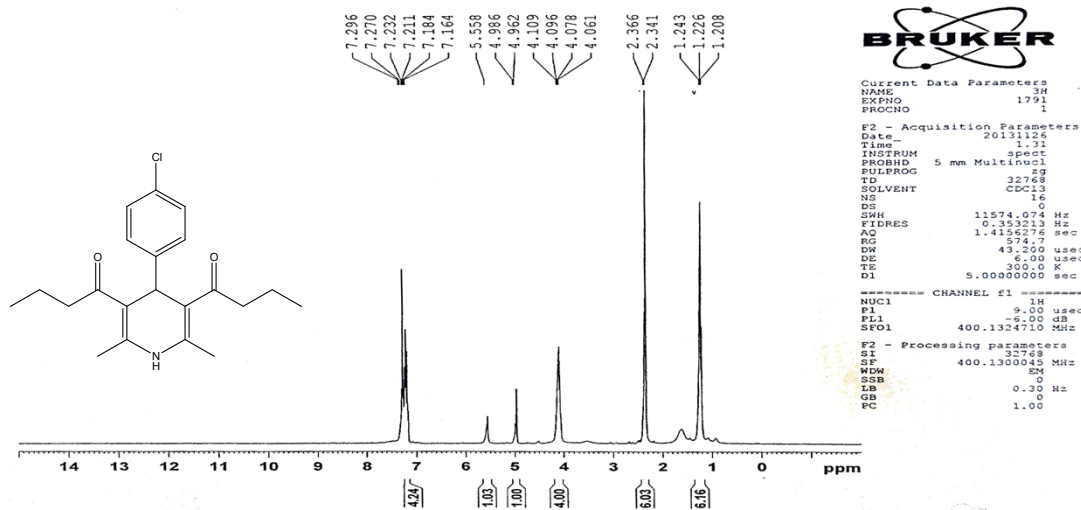


^1H NMR spectrum of compound **4b**

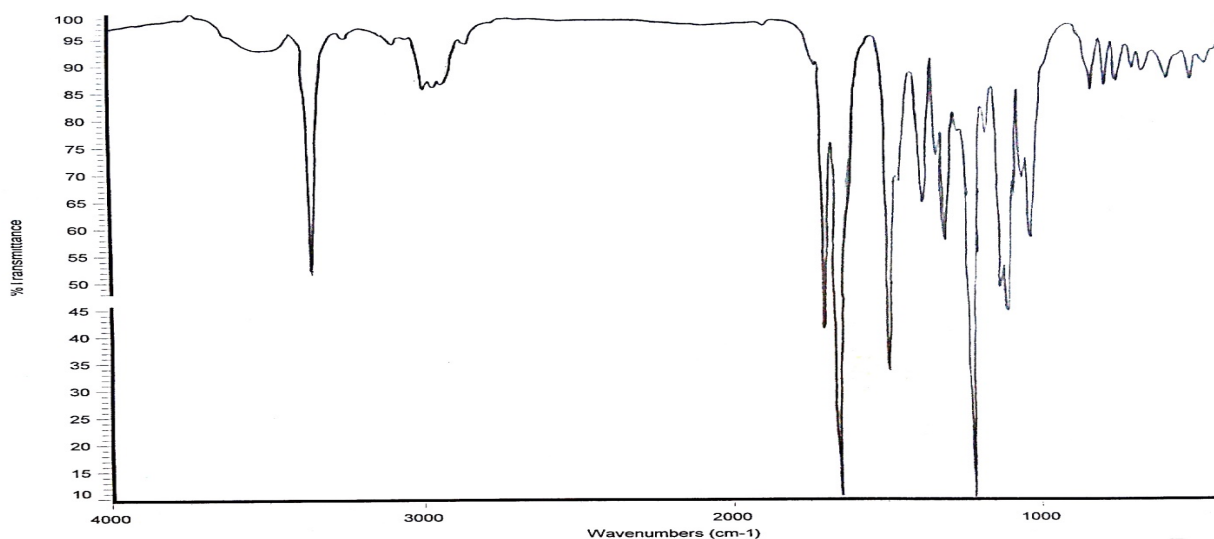


FT-IR spectrum of compound **4b**

- 2,6-Dimethyl-4-(4-chlorophenyl)-1,4-dihydropyridine-3,5-diethylcarboxylate (compound **4c**) Yellowish solid, IR (KBr, cm^{-1}): 3356 (NH), 1695 (C=O, ester), 1486 (C=C aromatic), 1214 (C-O), 1117 (C-Cl). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.22 (d, $J = 8$ Hz, 2H, Ar-H), 7.17 (d, $J = 8$ Hz, 2H, Ar-H), 5.55 (s, 1H, NH), 4.96 (s, 1H, CH), 4.08 (q, $J = 7.2$ Hz, 4H, 2 OCH₂), 2.34 (s, 6H, 2CH₃), 1.22 (t, $J = 7.2$ Hz, 6H, 2CH₃CH₂).

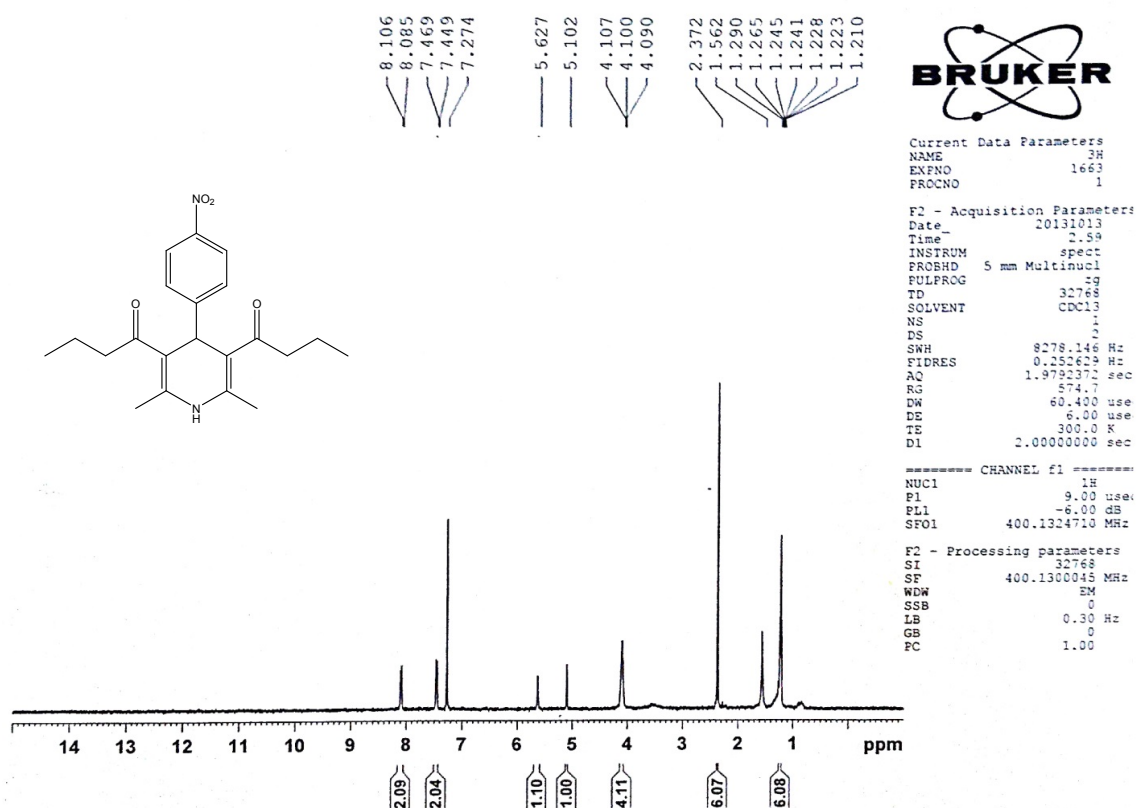


^1H NMR spectrum of compound **4c**

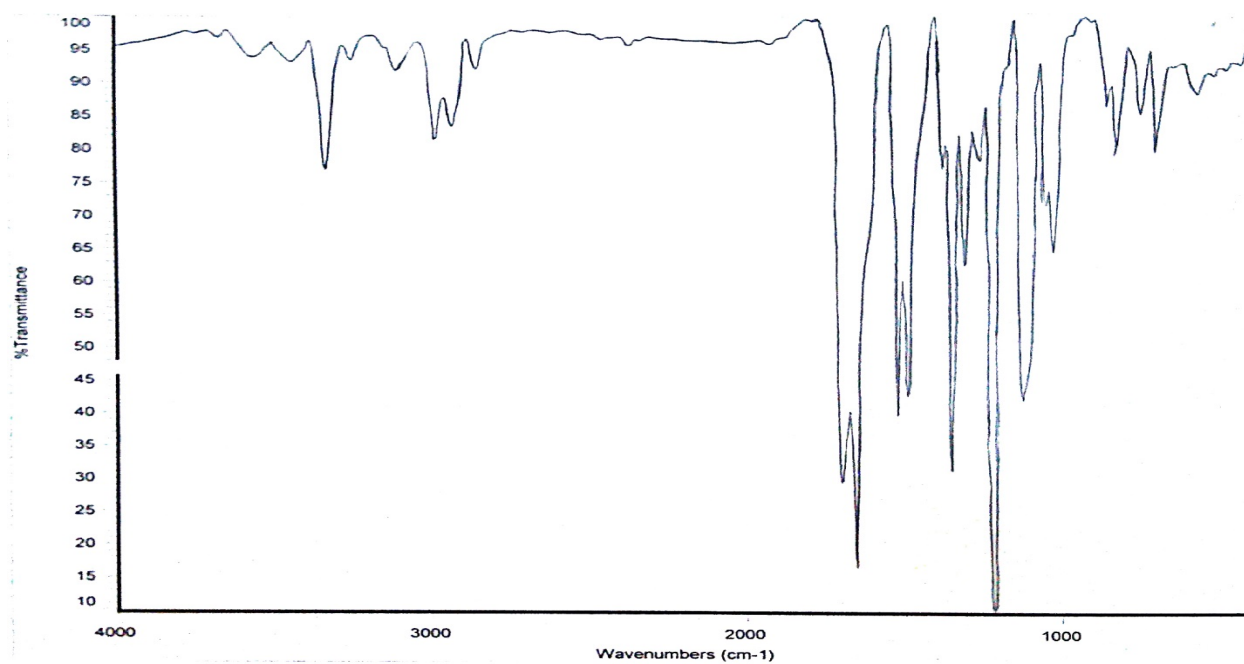


FT-IR spectrum of compound 4c

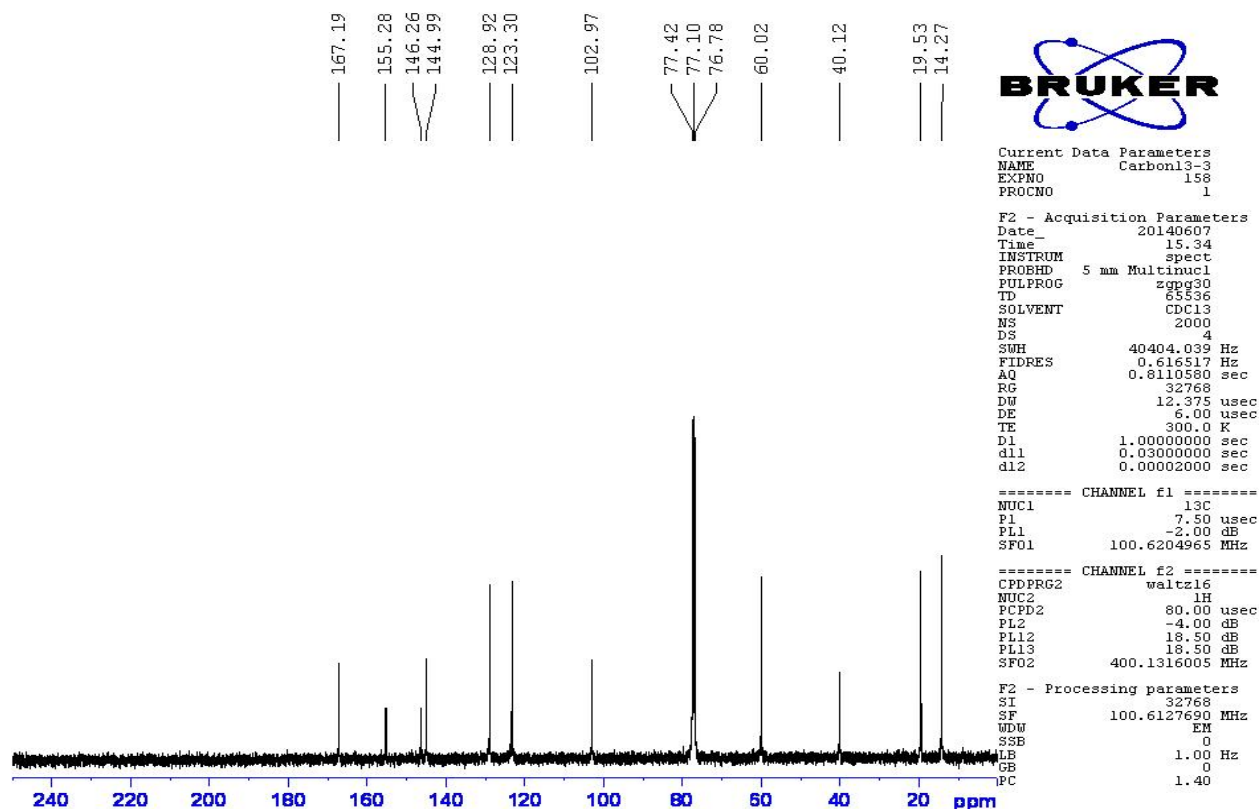
- 2,6-Dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-diethylcarboxylate (compound **4d**) White solid, IR (KBr, cm^{-1}): 3327 (NH), 1696 (C=O, ester), 1517 (NO_2), 1486 (C=C, aromatic), 1345 (NO_2), 1213 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 8.09 (d, $J = 7.9$ Hz, 2H, Ar-H), 7.45 (d, $J = 7.9$ Hz, 2H, Ar-H), 5.63 (s, 1H, NH), 5.10 (s, 1H, CH), 4.08 (q, $J = 7.4$ Hz, 4H, 2 OCH_2), 2.37 (s, 6H, 2 CH_3), 1.24 (t, $J = 7.4$ Hz, 6H, 2 CH_3CH_2). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 167.19, 155.28, 146.26, 144.99, 128.92, 123.30, 102.992, 60.02, 40.12, 19.53, 14.27.



^1H NMR spectrum of compound 4d

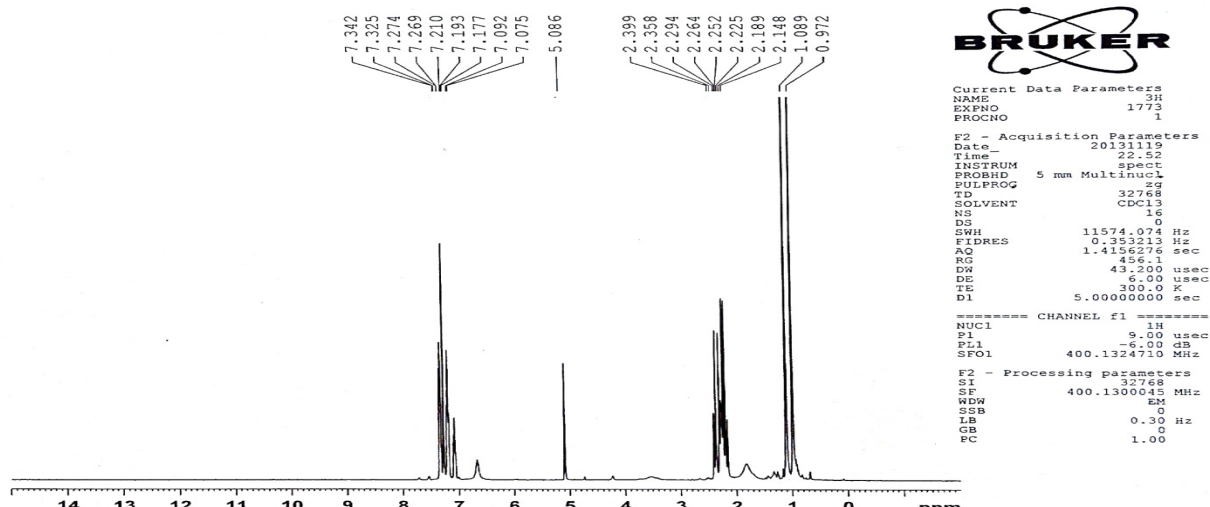


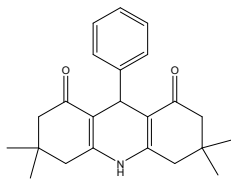
FT-IR spectrum of compound 4d



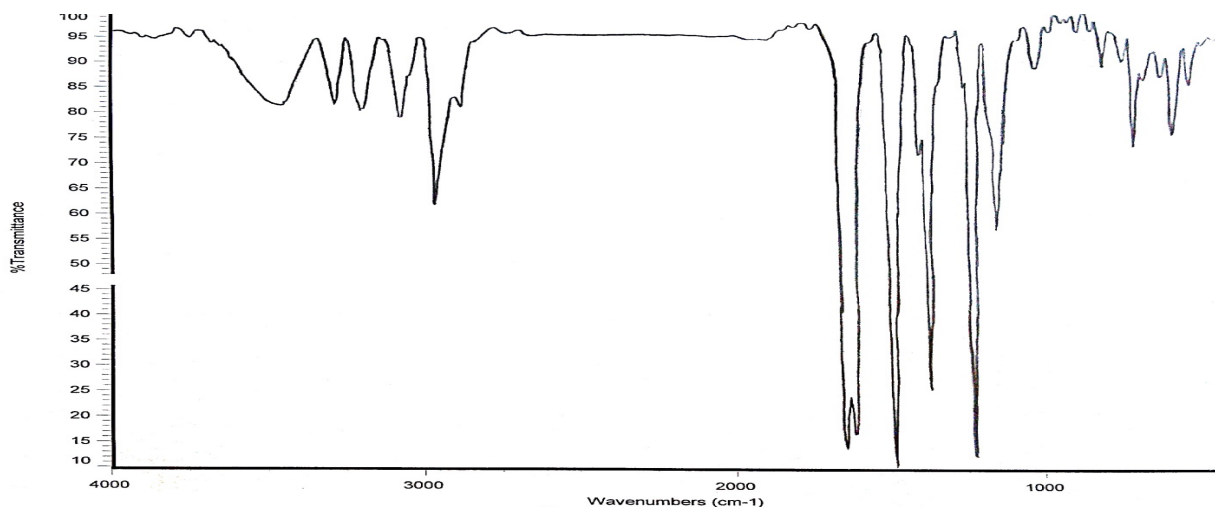
¹³C NMR spectrum of compound 4d

- 3,3,6,6-Tetramethyl-9-4-phenyl-3,4,6,7-tetrahydroacridine 1,8(2H,5H,9H,10H)-dione (compound **4e**) Yellowish solid, IR (KBr, cm⁻¹): 3279(NH), 1641 (C=O, dimedone), 1484 (C=C, aromatic). ¹H NMR (CDCl₃, 400 MHz) δ: 7.33 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.19 (t, *J* = 7.5 Hz, 2H, Ar-H), 7.07 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.68 (s, 1H, NH), 5.08 (s, 1H, CH), 2.14–2.39 (m, 8H, 4 CH₂), 1.08 (s, 6H, 2 CH₃), 0.97 (s, 6H, 2 CH₃).



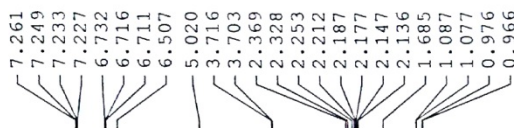


¹H NMR spectrum of compound 4e



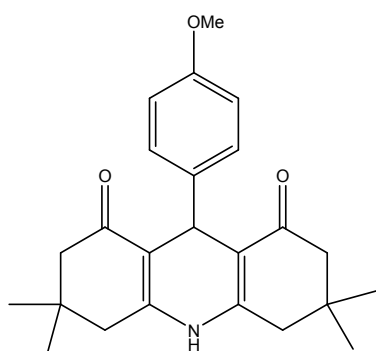
FT-IR spectrum of compound 4e

- 3,3,6,6-Tetramethyl-9-(4-methoxyphenyl)-3,4,6,7-tetrahydroacridine-1,8(2H,5H,9H,10H)-dione (compound **4f**) Yellow solid, IR (KBr, cm⁻¹) 3279 (NH), 1640 (C=O, dimedone), 1482 (C=C, aromatic), 1224 (C-O). ¹H NMR (CDCl₃, 400 MHz) δ: 7.23 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.72 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.51 (s, 1H, NH), 5.02 (s, 1H, CH), 3.70 (s, 3H, OCH₃), 2.14- 2.37 (m, 8H, 4 CH₂), 1.08 (s, 6H, 2 CH₃), 0.96 (s, 6H, 2 CH₃). ¹³C-NMR (CDCl₃, 100 MHz) δ: 196.37, 157.62, 149.90, 139.30, 128.92, 113.27, 113.09, 54.97, 50.96, 40.36, 32.76, 29.61, 27.05.

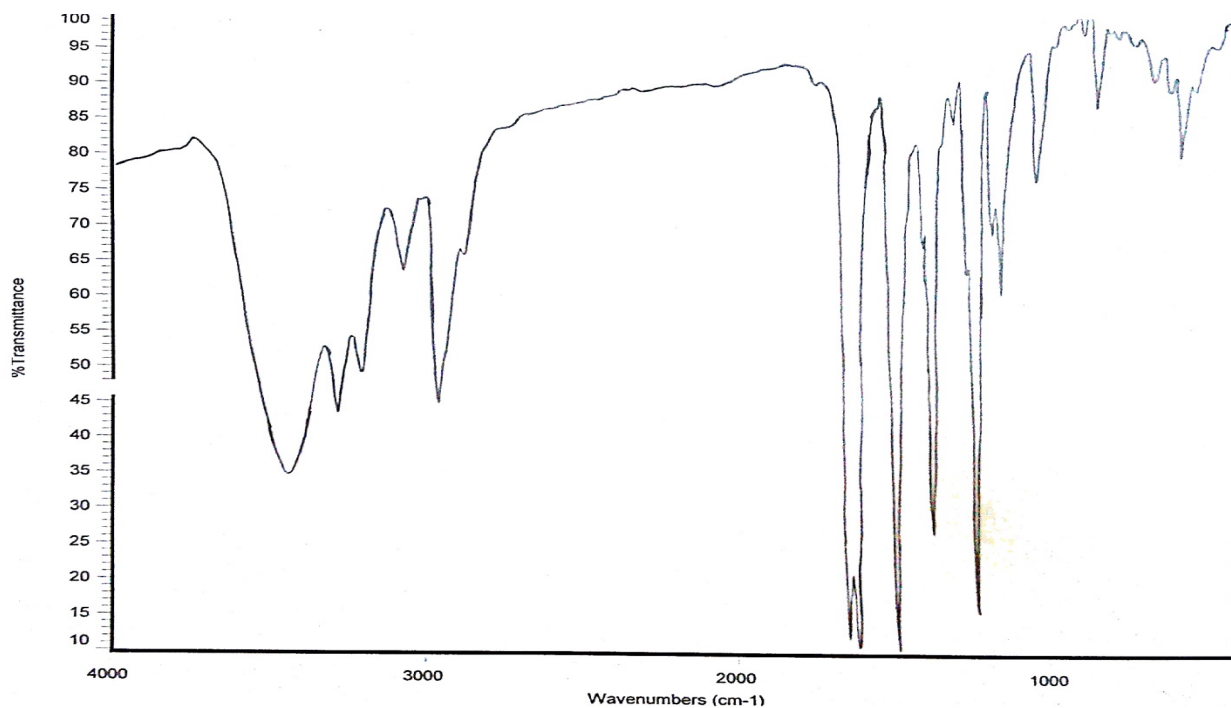


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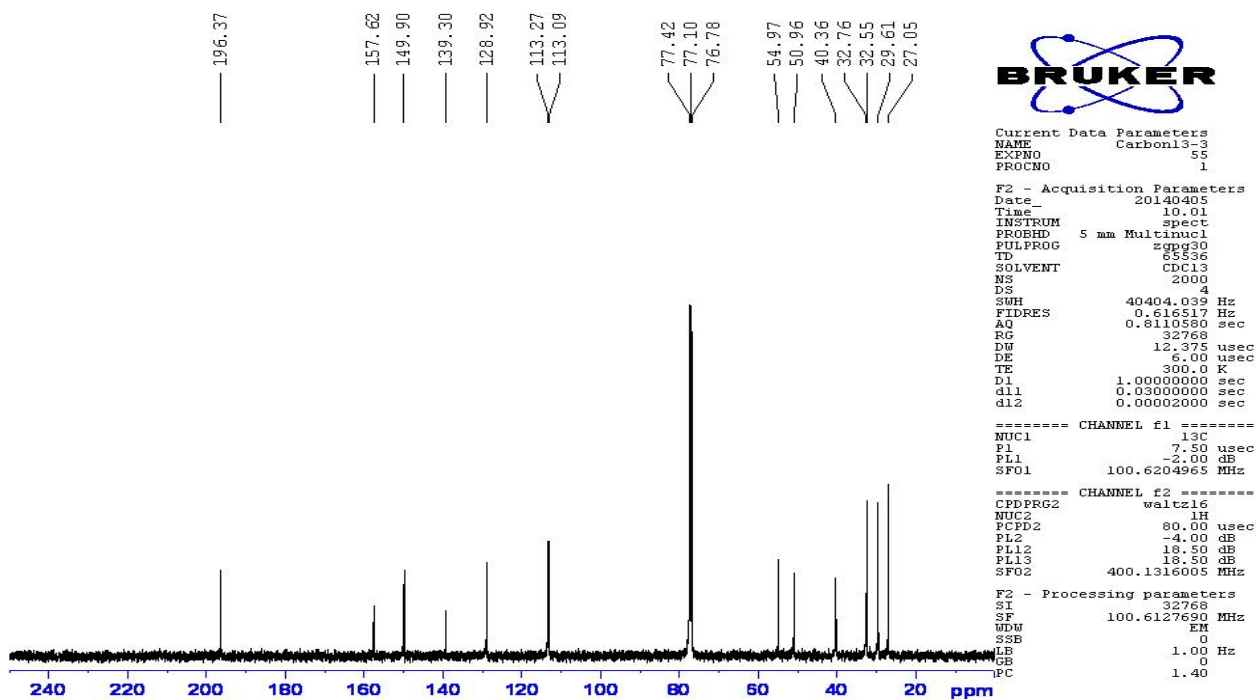
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¹H NMR spectrum of compound 4f

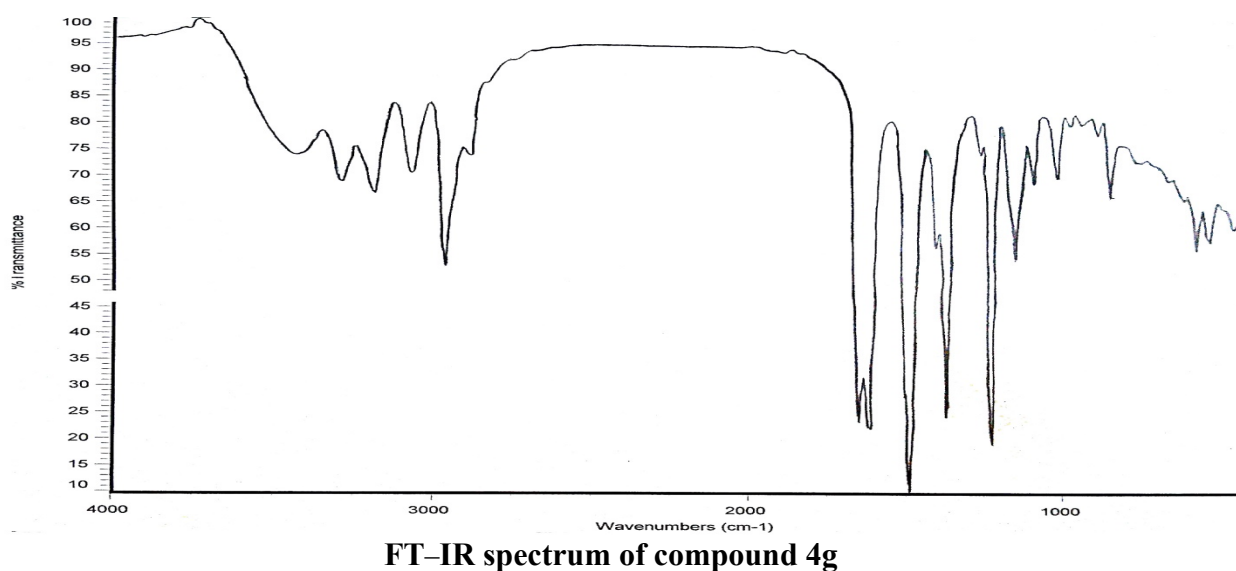
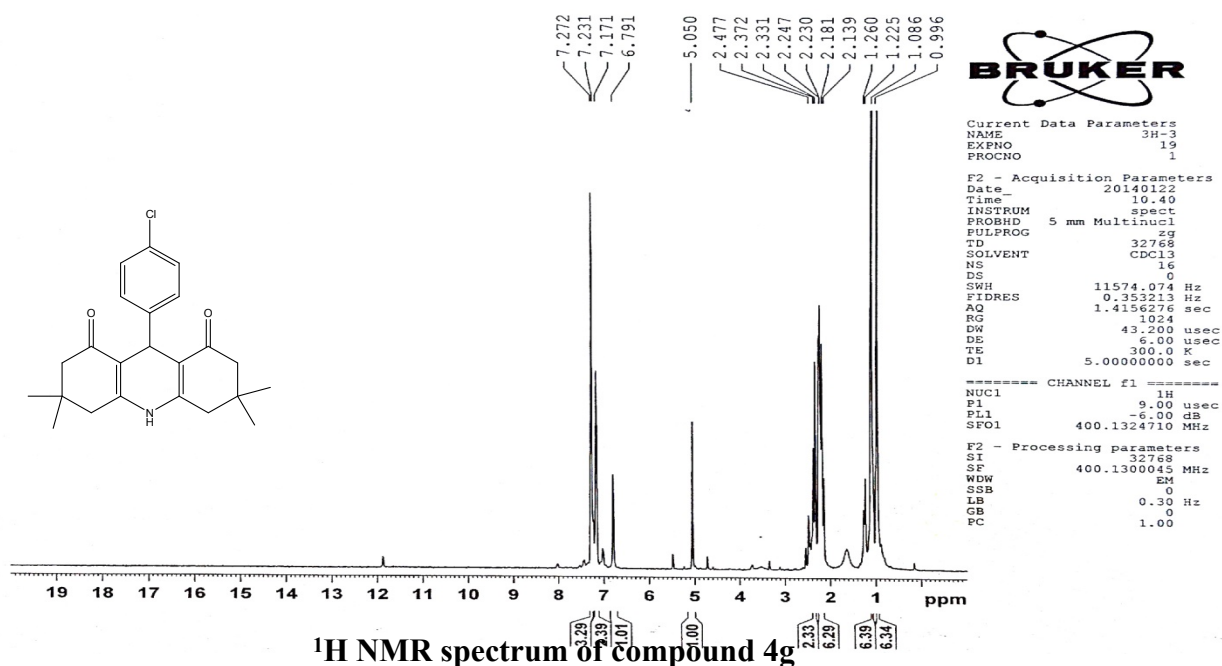


FT-IR spectrum of compound 4f

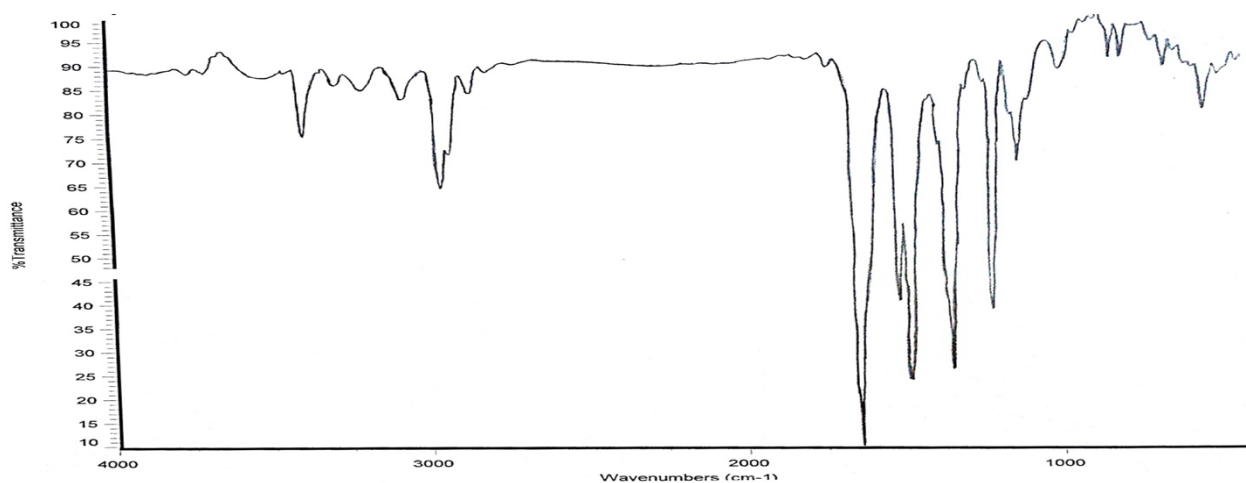
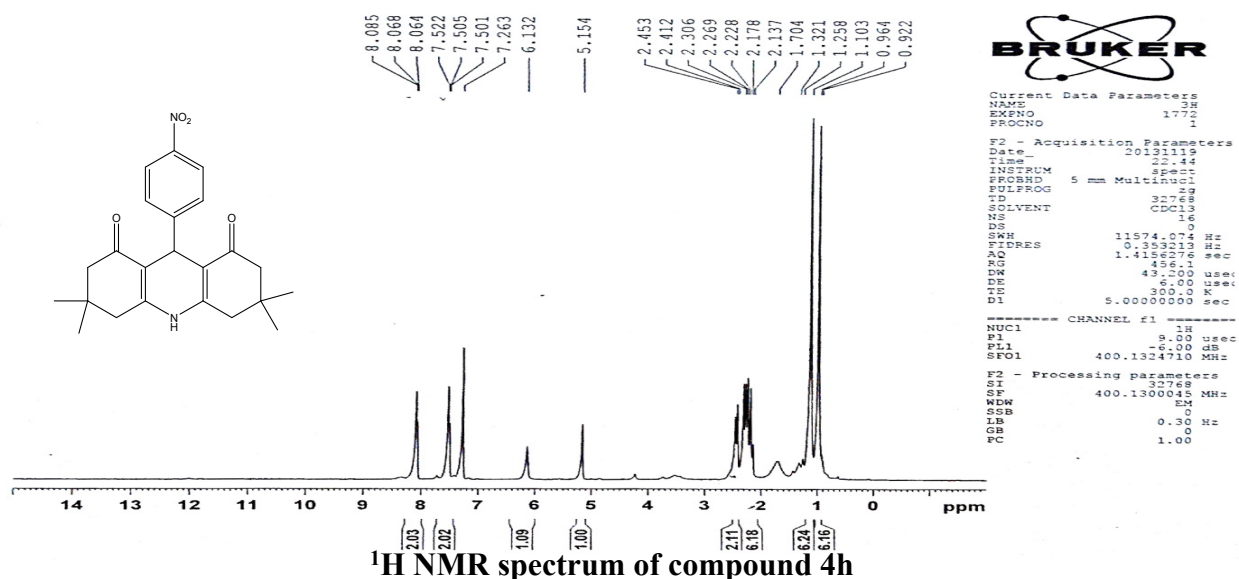


¹³C NMR spectrum of compound 4f

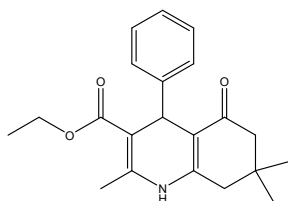
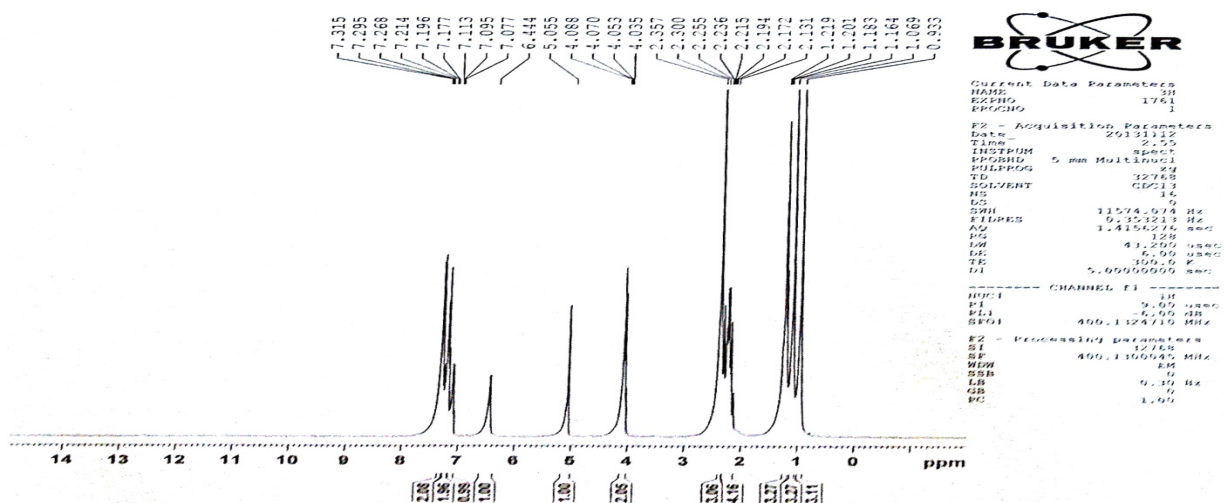
- 3,3,6,6-Tetramethyl-9-(4-chlorophenyl)- 3,4,6,7-tetrahydroacridine-1,8(2H,5H,9H,10H)-dione (compound **4g**) Yellow solid, IR (KBr, cm^{-1}) 3279 (NH) , 1644 (C=O, dimedone), 1486 (C=C, aromatic), 1145 (C-Cl). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.27 (d, $J = 8$ Hz, 2H, Ar-H), 7.17 (d, $J = 8$ Hz, 2H, Ar-H), 6.79 (s, 1H, NH), 5.05 (s, 1H, CH), 2.13- 2.37 (m, 8H, 4 CH_2), 1.08 (s, 6H, 2 CH_3), 0.96 (s, 6H, 2 CH_3).



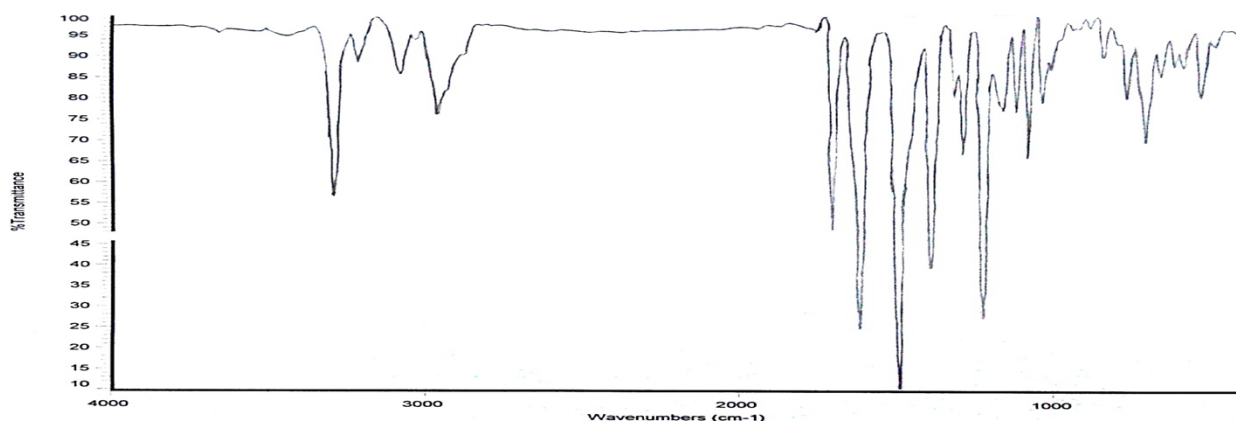
- 3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-3,4,6,7-tetrahydroacridine-1,8(2H,5H,9H,10H)-dione (compound **4h**) Yellow-orange solid, IR (KBr, cm^{-1}) 3384 (NH), 1643 (C=O, dimedone), 1514 (NO_2), 1481 (C=C, aromatic), 1344 (NO_2). ^1H NMR (CDCl_3 , 400 MHz) δ : 8.07 (d, $J = 8.3$ Hz, 2H, Ar-H), 7.51 (d, $J = 8.3$ Hz, 2H, Ar-H), 6.13 (s, 1H, NH), 5.15 (s, 1H, CH), 2.14- 2.45 (m, 8H, 4 CH_2), 1.10 (s, 6H, 2 CH_3), 0.96 (s, 6H, 2 CH_3).



- 2,7,7-Trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (compound **4i**) Yellowish solid, IR (KBr, cm^{-1}): 3289 (NH), 1698 (C=O, ester), 1640 (C=O, dimedone), 1485 (C=C, aromatic). 1215 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.30 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.19 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.09 (t, $J = 7.2$ Hz, 1H, Ar-H), 6.44 (s, 1H, NH), 5.05 (s, 1H, CH), 4.06 (q, $J = 7.2$ Hz, 2H, OCH_2), 2.35 (s, 3H, Ar-H), 2.13–2.30 (m, 4H, 2 CH_2), 1.18 (t, $J = 7.2$ Hz, 3H, CH_3CH_2), 1.07 (s, 3H, CH_3), 0.93 (s, 3H, CH_3).

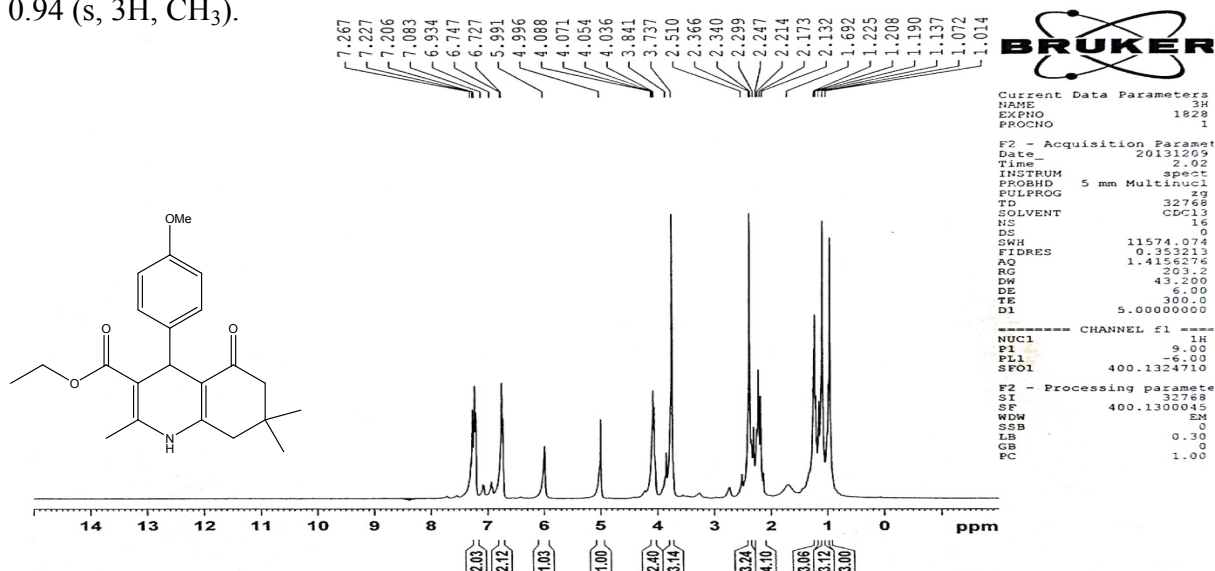


^1H NMR spectrum of compound **4i**

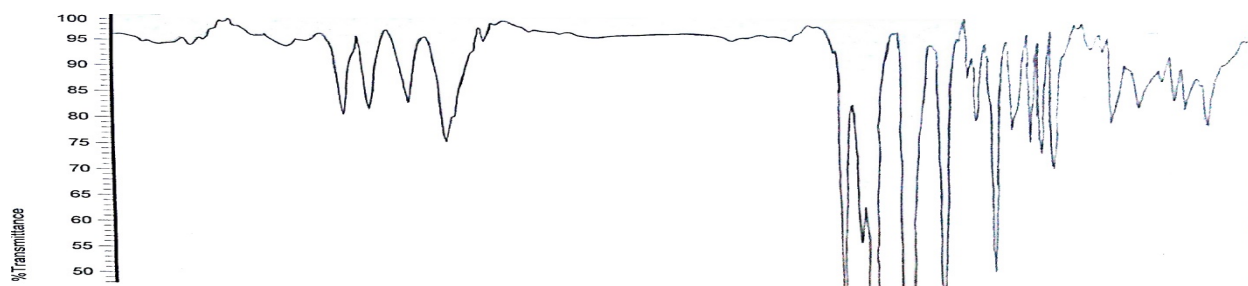


FT-IR spectrum of compound 4i

- 2,7,7-Trimethyl-5-oxo-4-(4-methoxyphenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (compound **4j**) Yellow solid, IR (KBr, cm^{-1}): 3279 (NH), 1700 (C=O, ester), 1645 (C=O, dimedone), 1497 (C=C, aromatic), 1217 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.73 (d, $J=8$ Hz, 2H, Ar-H), 7.10 (d, $J=8$ Hz, 2H, Ar-H), 5.99 (s, 1H, NH), 4.99 (s, 1H, CH), 4.06 (q, $J=6.8$ Hz, 2H, OCH_2), 3.73 (s, 3H, OCH_3), 2.36 (s, 3H, CH_3), 2.13–2.34 (m, 4H, 2 CH_2), 1.20 (t, $J=6.8$ Hz, 3H, CH_3CH_2), 1.07 (s, 3H, CH_3), 0.94 (s, 3H, CH_3).

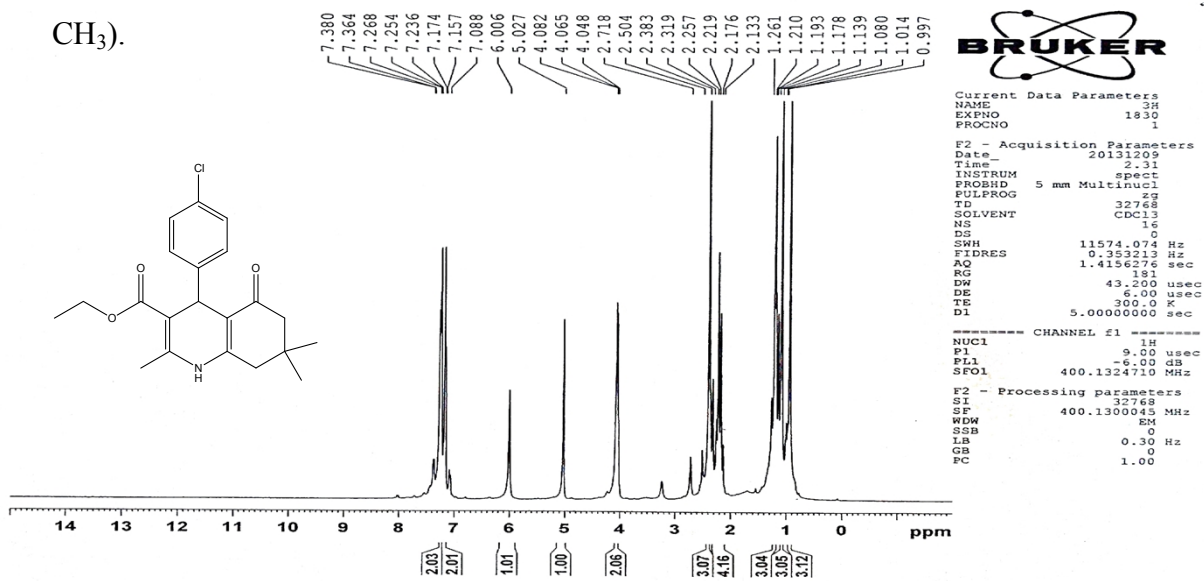


^1H NMR spectrum of compound 4j

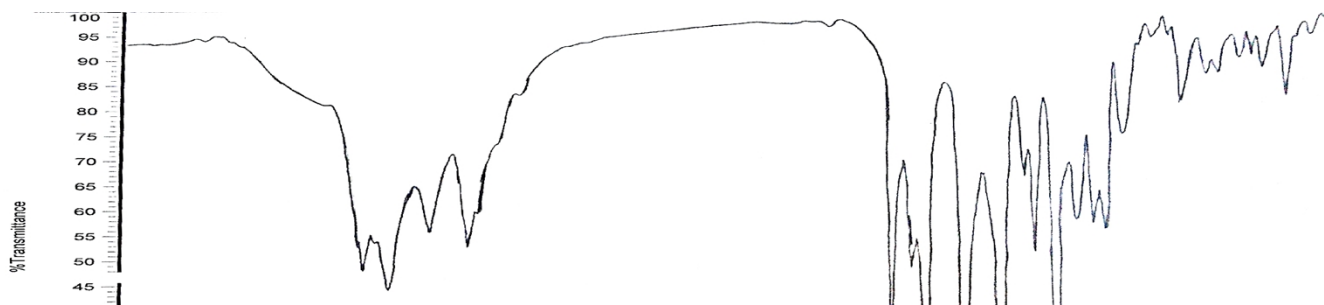


FT-IR spectrum of compound 4j

- 2,7,7-Trimethyl-5-oxo-4-(4-chlorophenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (compound **4k**) Yellow solid, IR (KBr, cm^{-1}): 3276 (NH), 1703 (C=O, ester), 1645 (C=O, dimedone), 1490 (C=C, aromatic), 1217 (C-O), 1158 (C-Cl). ^1H NMR (CDCl_3 , 400 MHz) δ : 7.26 (d, $J=6.9$ Hz, 2H, Ar-H), 7.16 (d, $J=6.9$ Hz, 2H, Ar-H), 6.00 (s, 1H, NH), 5.02 (s, 1H, CH), 4.06 (q, $J=6.8$ Hz, 2H, OCH_2), 2.38 (s, 3H, CH_3), 2.13–2.31 (m, 4H, 2 CH_2), 1.19 (t, $J=6.8$ Hz, 3H, CH_3CH_2), 1.08 (s, 3H, CH_3), 0.93 (s, 3H, CH_3).

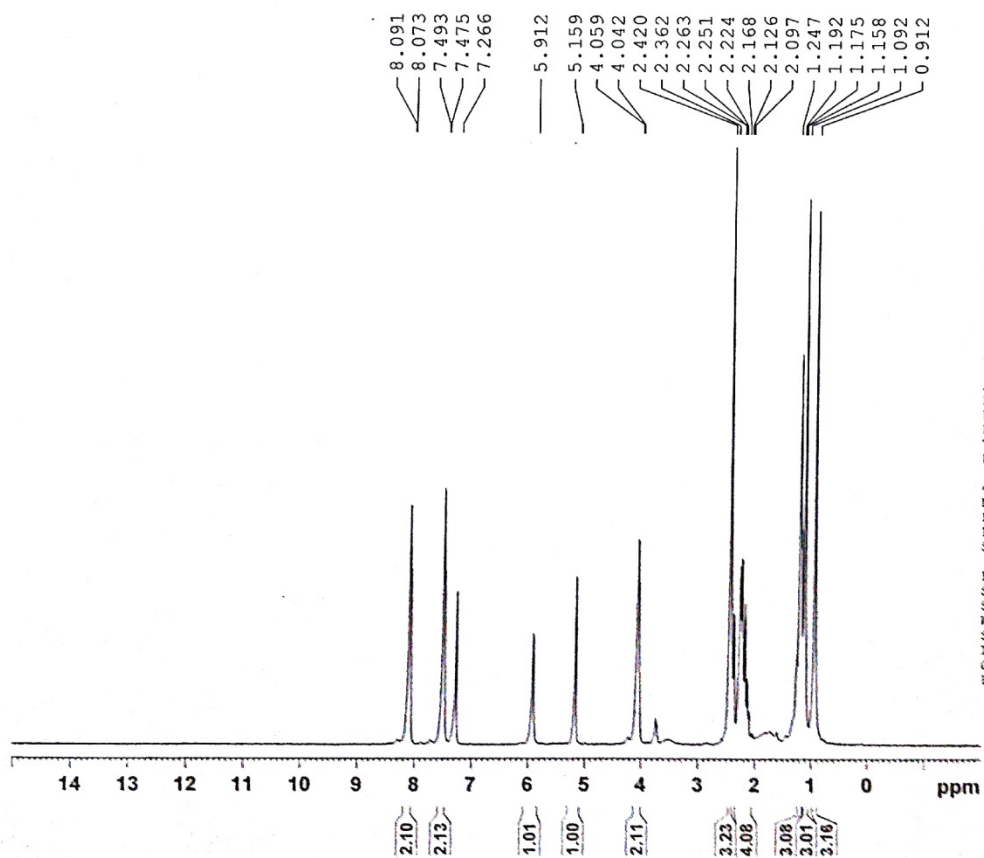


^1H NMR spectrum of compound 4k



FT-IR spectrum of compound 4k

- 2,7,7-Trimethyl-5-oxo-4-(4-nitrophenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (compound **4l**) Yellow solid, IR (KBr, cm^{-1}): 3279 (NH), 1702 (C=O, ester), 1647 (C=O, dimedone), 1517 (NO_2), 1490 (C=C, aromatic), 1344 (NO_2), 1218 (C-O). ^1H NMR (CDCl_3 , 400 MHz) δ : 8.08 (d, $J=7.9$ Hz, 2H, Ar-H), 7.48 (d, $J=7.9$ Hz, 2H, Ar-H), 5.91 (s, 1H, NH), 5.15 (s, 1H, CH), 4.05 (q, $J=7.1$ Hz, 2H, OCH_2), 2.42 (s, 3H, CH_3), 2.10–2.36 (m, 4H, 2 CH_2), 1.17 (t, $J=7.1$ Hz, 3H, CH_3CH_2), 1.09 (s, 3H, CH_3), 0.91 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 195.84, 167.03, 154.72, 150.16, 146.11, 145.10, 128.97, 123.28, 110.55, 104.59, 58.22, 50.64, 40.60, 37.30, 32.62, 29.37, 26.98, 19.16, 14.21

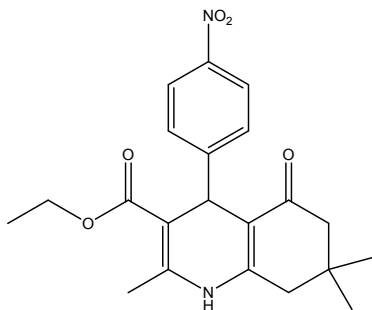


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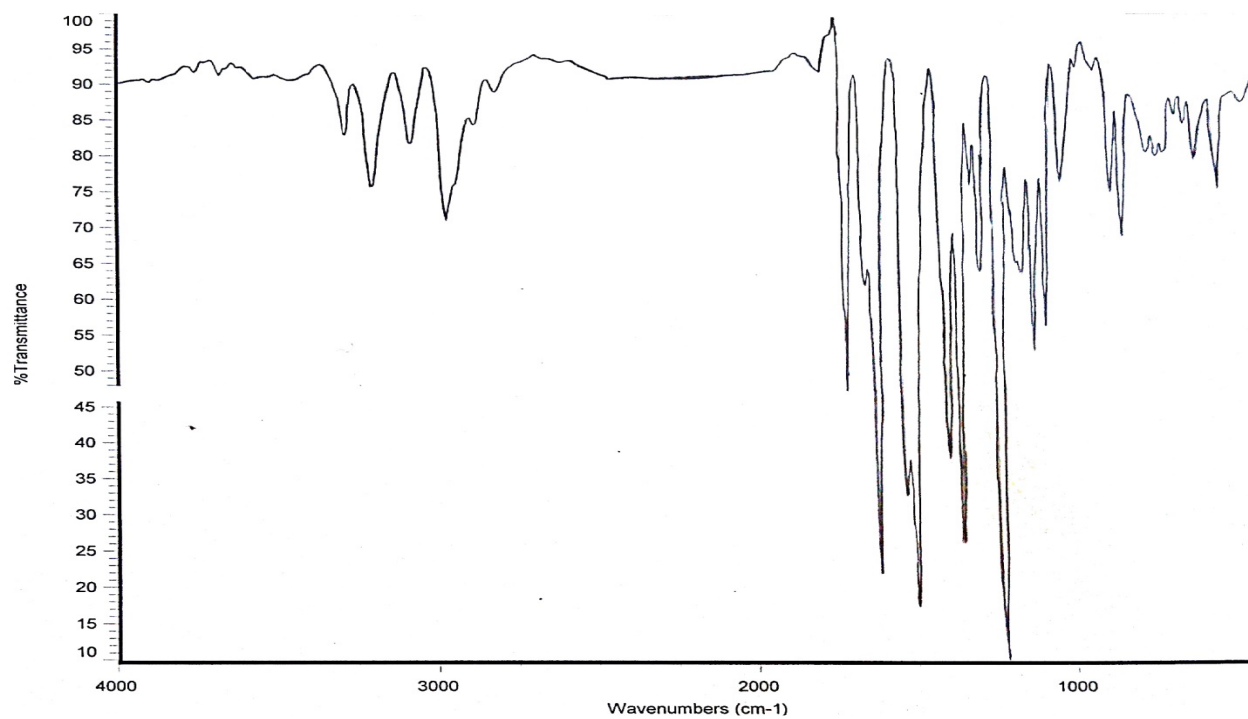
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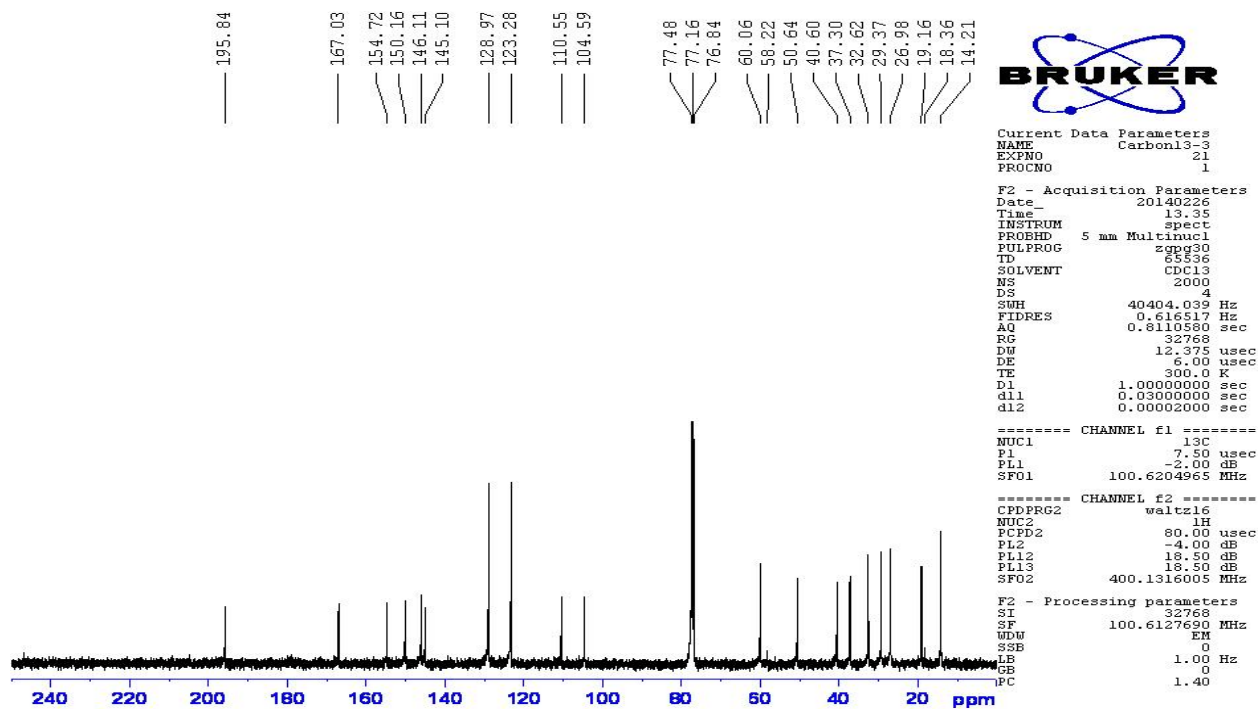
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^1H NMR spectrum of compound 4l



FT-IR spectrum of compound 4l



¹³C NMR spectrum of compound 4l