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Supporting Information

Introduction of a novel nano sized *N*-Sulfonated Brönsted acidic catalyst for the promotion of the synthesis of polyhydroquinoline derivatives *via* Hantzsch condensation under solvent-free conditions

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Experimental

Material

Chemicals were purchased from Fluka, Merck, Aldrich and Southern Clay Products Chemical Companies. Yields refer to isolated products. Products were characterized by their physical constants, comparison with authentic samples and FT-IR and NMR spectroscopy. The purity determination of the substrate and reaction monitoring were accomplished by TLC on silics-gel polygram SILG/UV 254 plates.

Instrumentation

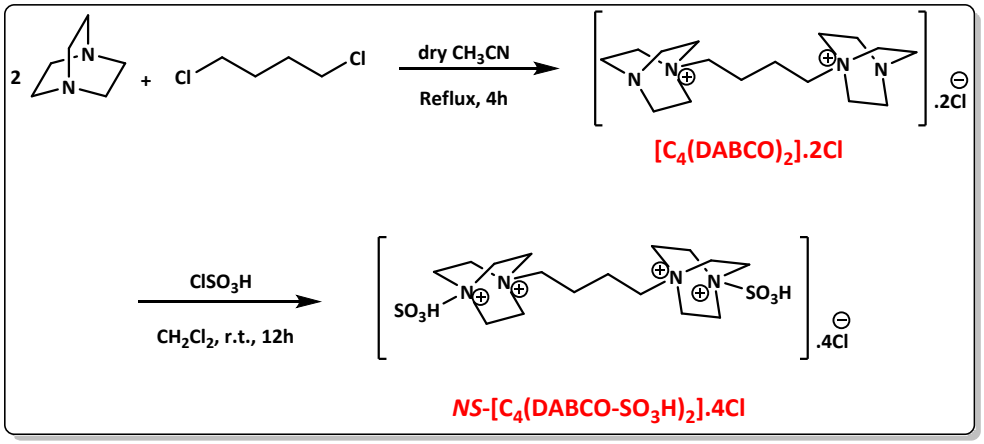
The FT-IR spectra were run on a VERTEX 70 Brucker company (Germany). Thermogravimetric analyses (TGA) were performed on TG/DTA6300 Sll-Nonotechnology Company (Japan). Samples were heated from 25 to 700 °C at ramp 10 °C/min under N_2 atmosphere. Scanning election microphotographs (SEM) were obtained on a SEM-Philips XL30. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Siemens D-500 X-ray diffractometer (Germany), using Ni-filtered Co-Kα radiation (λ=0.15418 nm). The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were run on a Bruker AVANCE^{III}-400 spectrometer in DMSO using TMS as an internal reference (δ in ppm). The surface morphologies were characterized by atomic force microscope (AFM, Ara nanoscope, Iran).

General procedure for the Synthesis of 1,1'-(butane-1,4-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) chloride ([C_4(DABCO)$_2$].2Cl):

1,4-Dichlorobutane (0.547 mL, 5.0 mmol) was added to a solution DABCO (1.121 g, 10.0 mmol) in dry CH_3CN (50 mL) and stirred for 4 hr under reflux conditions. After completion of the reaction the solvent was removed under vacuum. The white obtained solid was washed with diethyl ether. After drying at 50 °C 1,1'-(butane-1,4-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium)chloride ([C_4(DABCO)$_2$].2Cl) was obtained as a white solid in 98.7% yield (1.39 g).

General procedure for the Synthesis of nano sized 4,4'-(butane-1,4-diyl)bis(1-sulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium) chloride ([NS-C_4(DABCO-$SO_3H)_2$].4Cl):

Chlorosulfonic acid (0.66 mL, 10 mmol) was added drop wise to a solution of $C_4(DABCO)_2.2Cl$ (1.4 g, 5 mmol) in dry CH_2Cl_2 (25 mL) over a period of 30 min in an ice bath. After completion of the addition, the reaction mixture was stirred for 12h at room temperature. The residue was washed with dry diethyl ether (3 × 5 mL) and dried under vacuum to give nano sized 4,4'-(butane-1,4-diyl)bis(1-sulfo-1,4-diazabicyclo[2.2.2]octane-1,4-diium)chloride ([NS-C_4(DABCO-$SO_3H)_2$)].4Cl) as a white puffy solid in 98.7% yield (4.42 g).



Scheme 1. Synthesis of the NS-[C_4(DABCO-$SO_3H)_2$].4Cl.

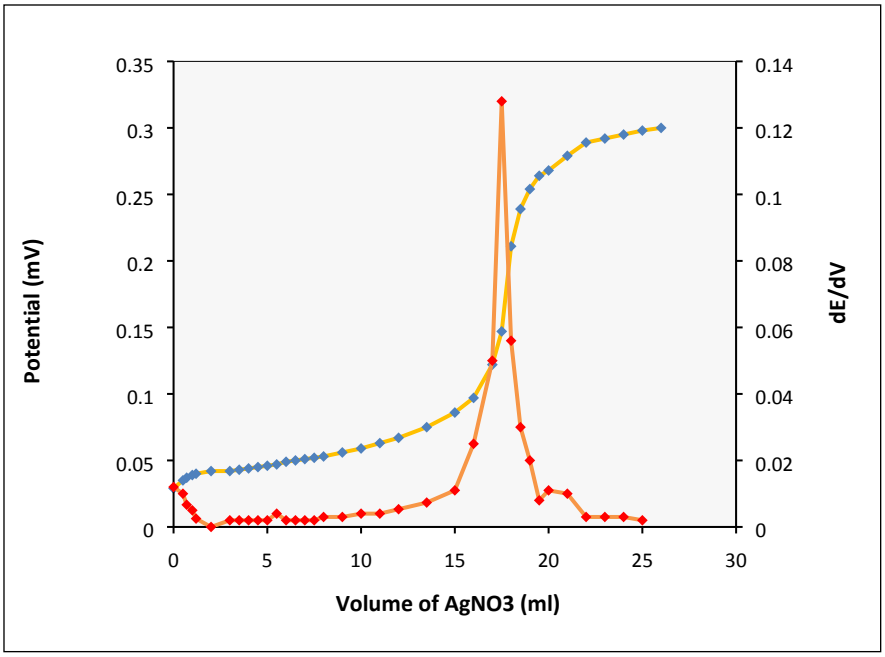


Fig. 1. Potentiometric titration and its first derivative curves of $[C_4(DABCO)_2].2Cl$ with $AgNO_3$.

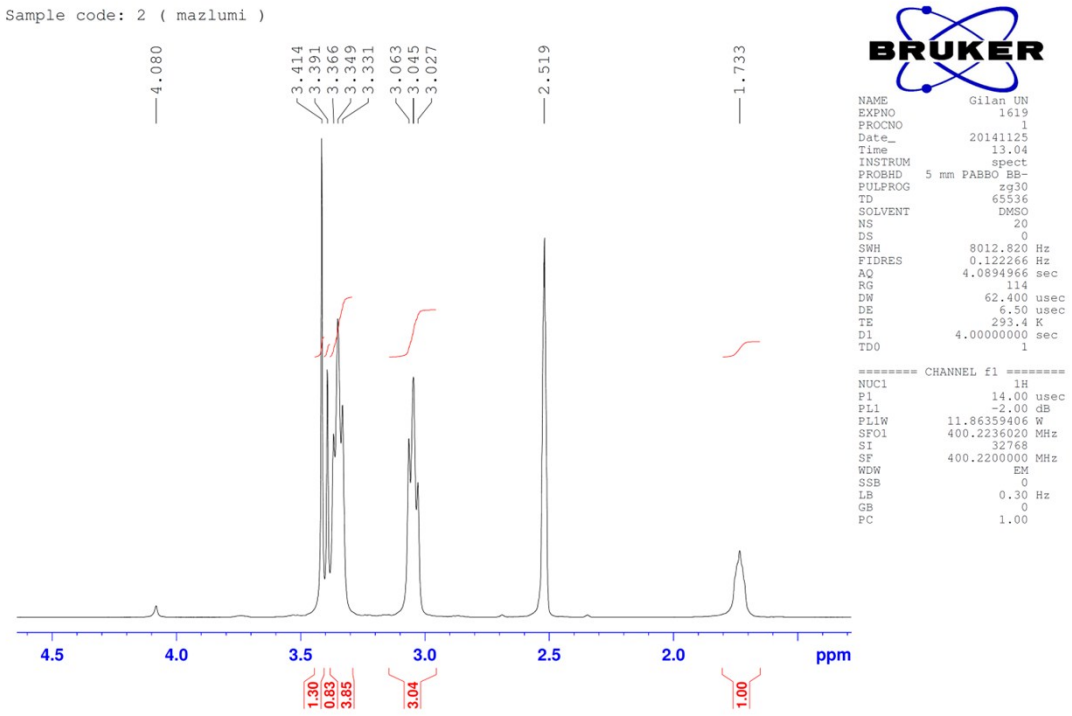


Fig. 2. ^1H NMR spectra of $[C_4(DABCO)_2].2Cl$.

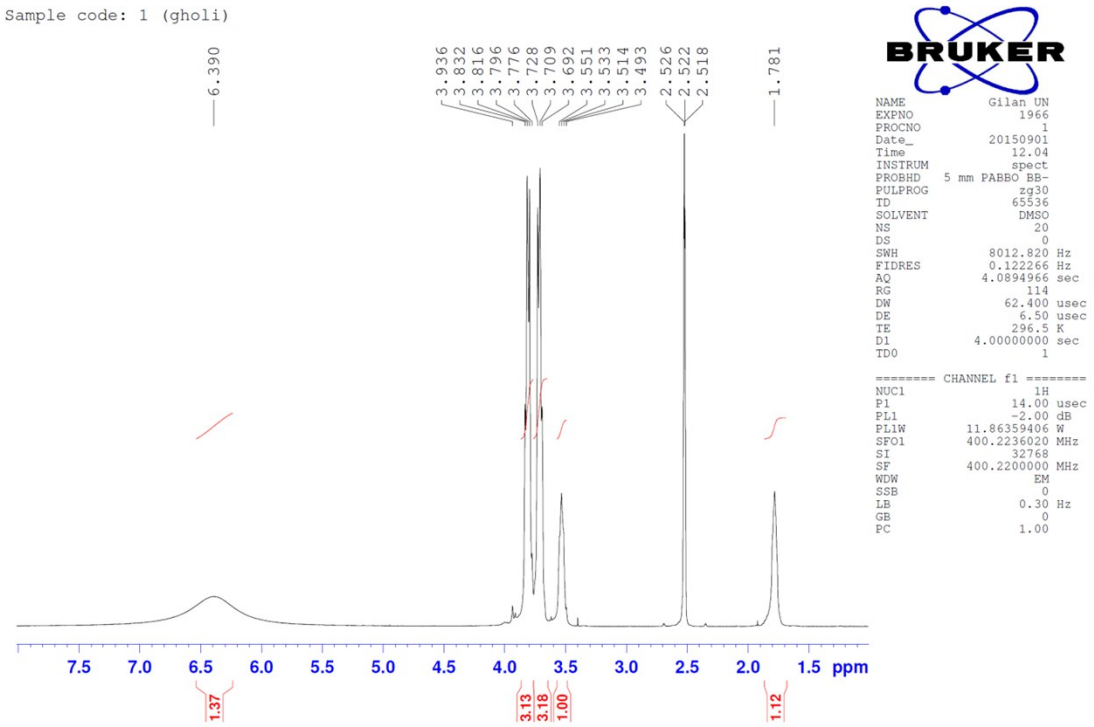


Fig. 3. ^{1}H NMR spectra of NS-[C_4(DABCO-$SO_3H)_2$].4Cl.

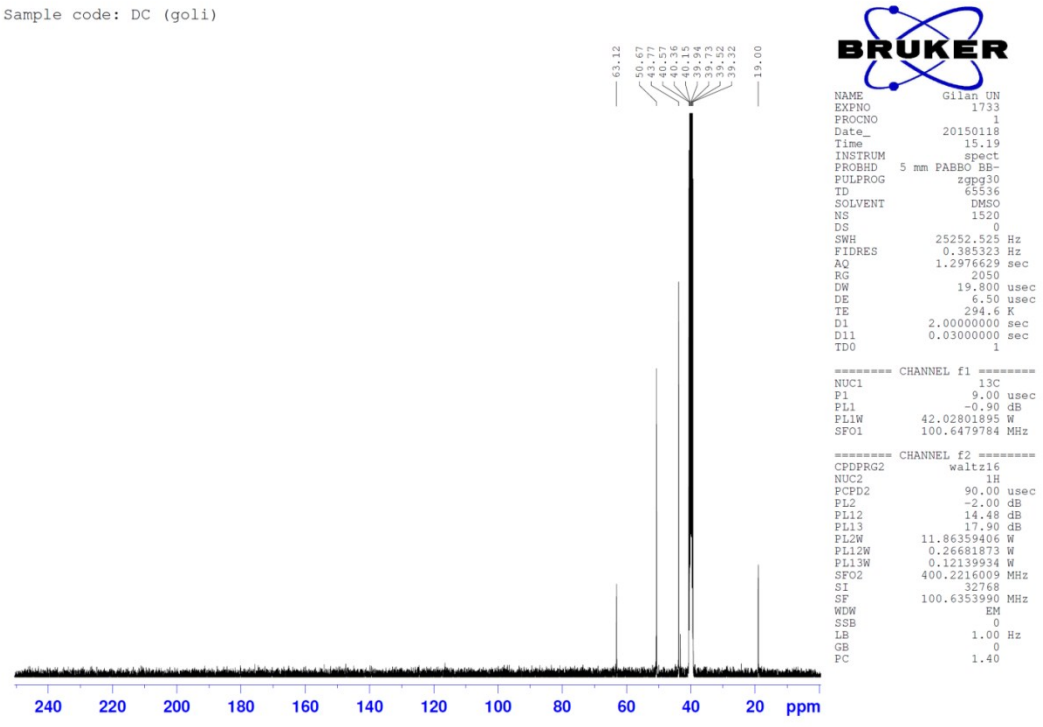


Fig. 4. ^{13}C NMR spectra of NS-[C_4(DABCO-$SO_3H)_2$].4Cl.

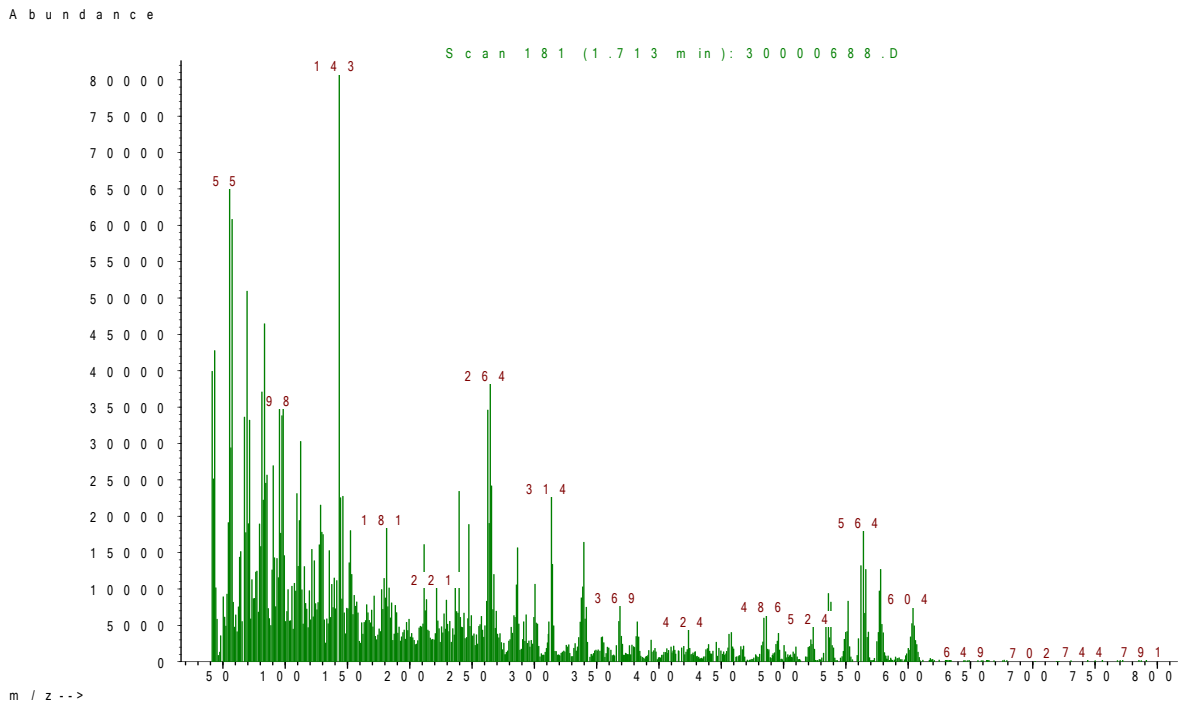


Fig. 5. Mass data of nano sized NS-[C_4(DABCO-$SO_3H)_2$].4Cl.

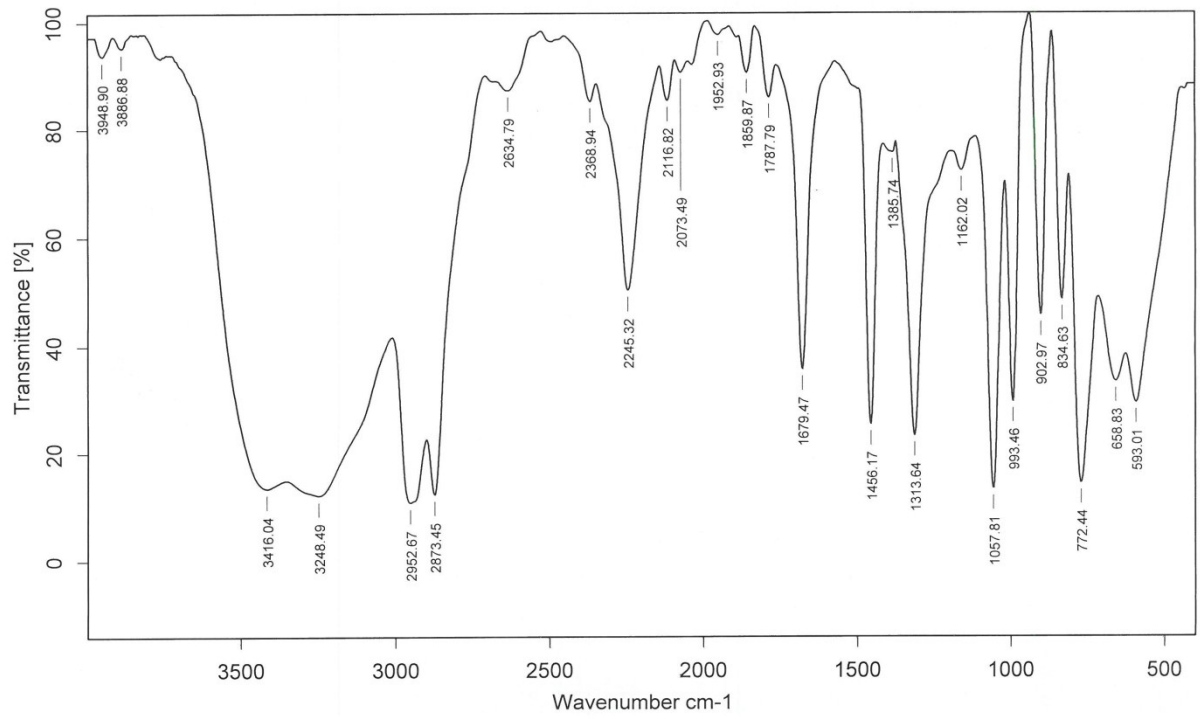


Fig. 6. FT-IR spectra of DABCO.

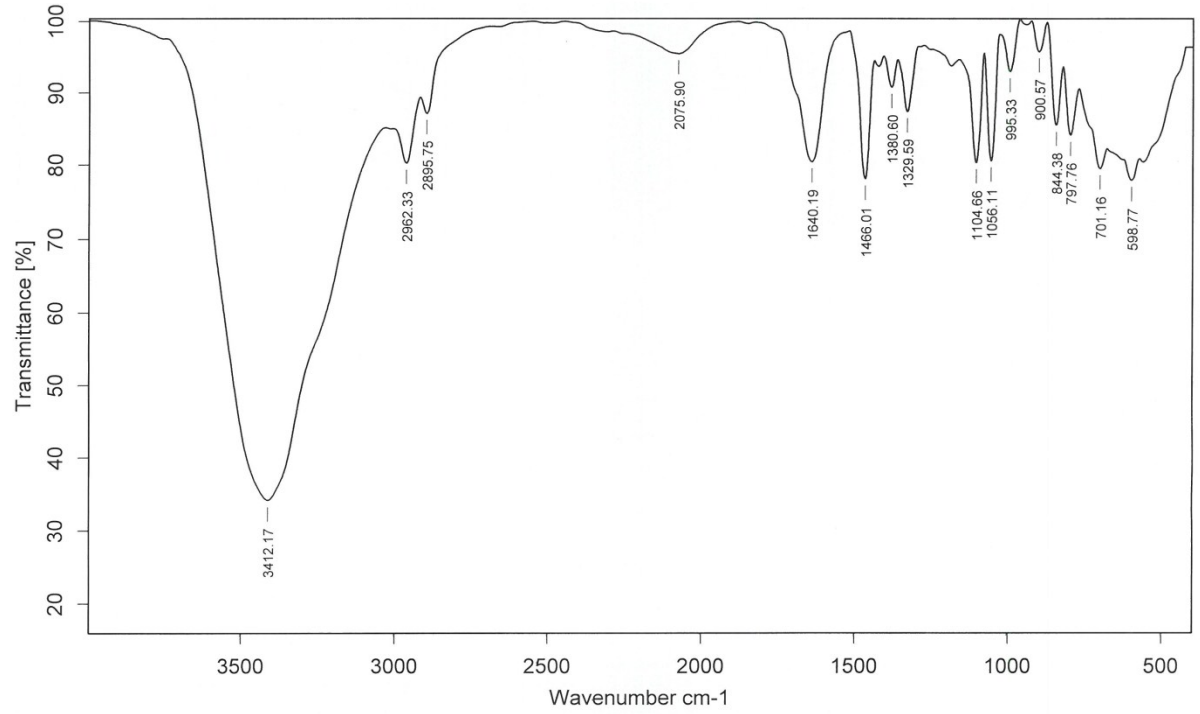


Fig. 7. FT-IR spectra of $[C_4(DABCO)_2].2Cl$.

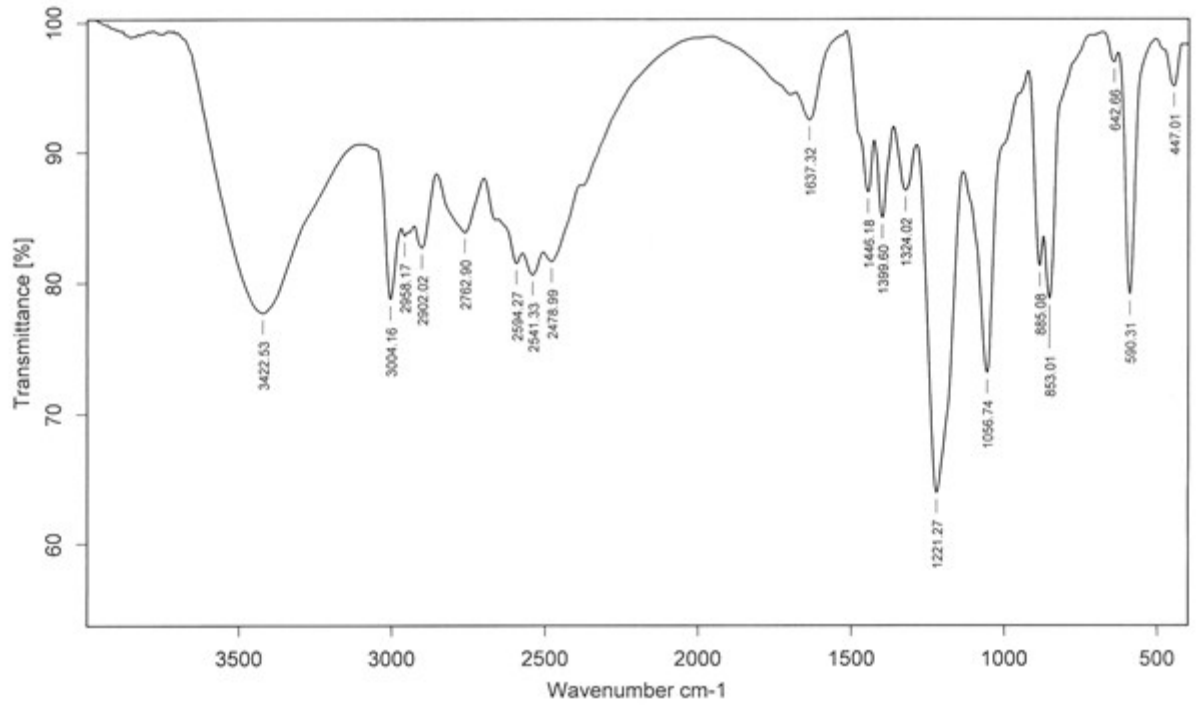


Fig. 8. FT-IR spectra of NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$ (c).

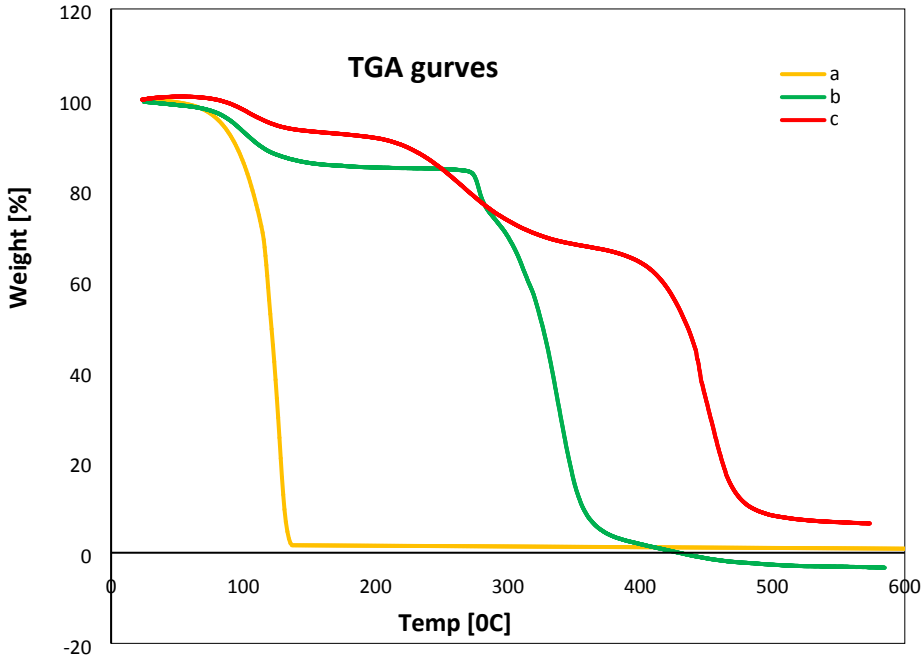


Fig. 9. TGA curves for DABCO, $[C_4(DABCO)_2].2Cl$ and NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$.

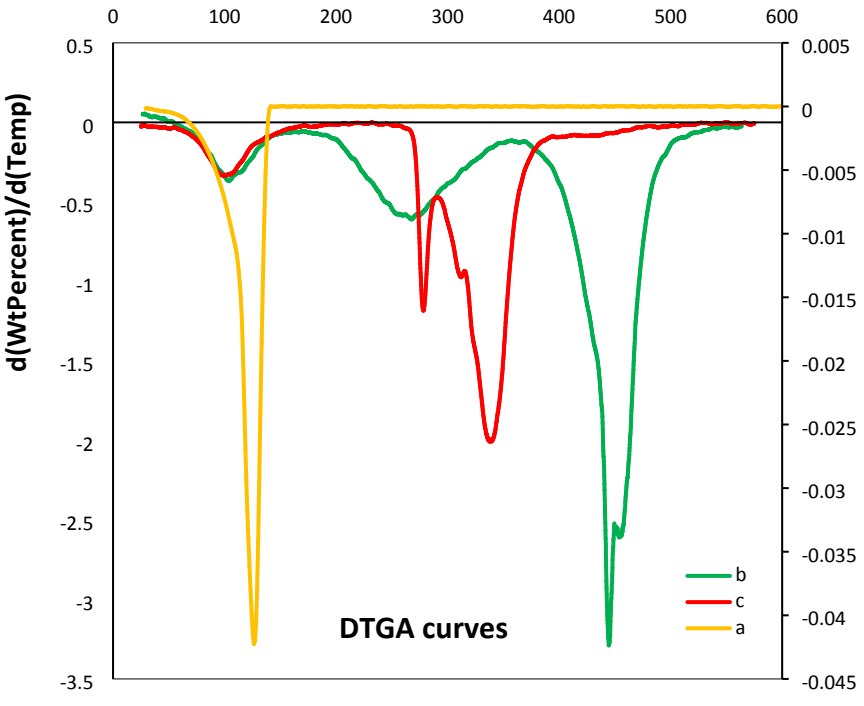


Fig. 10. DTGA curves for DABCO, $[C_4(DABCO)_2].2Cl$ and NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$.

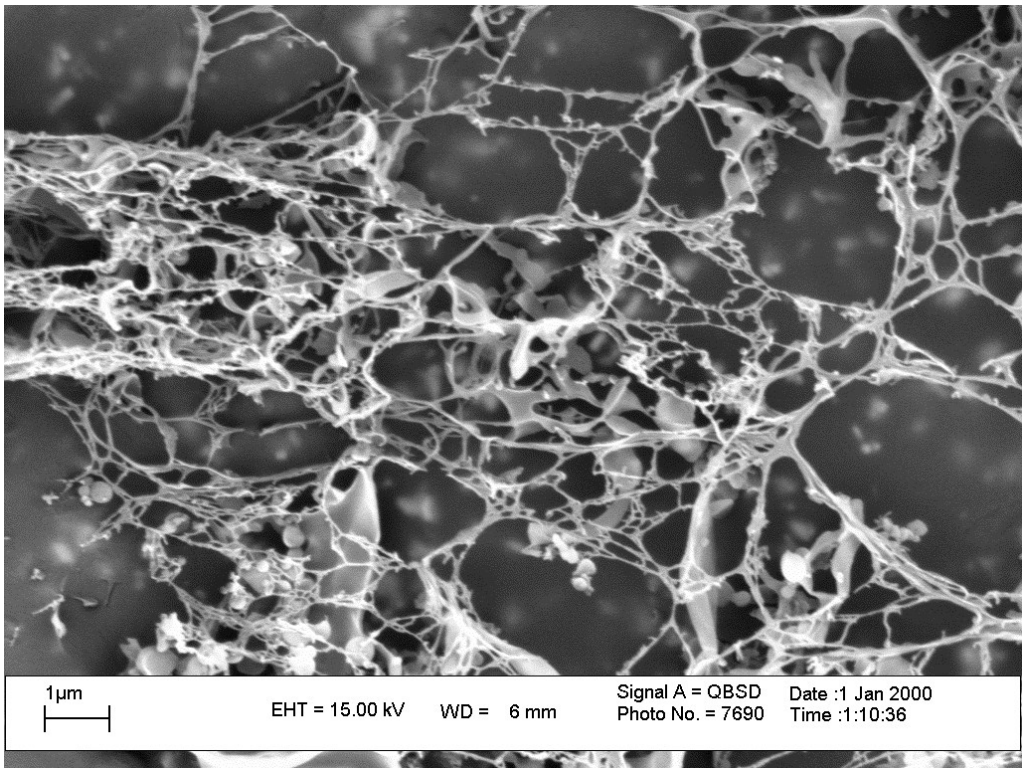


Fig. 11. SEM micrographs of DABCO.

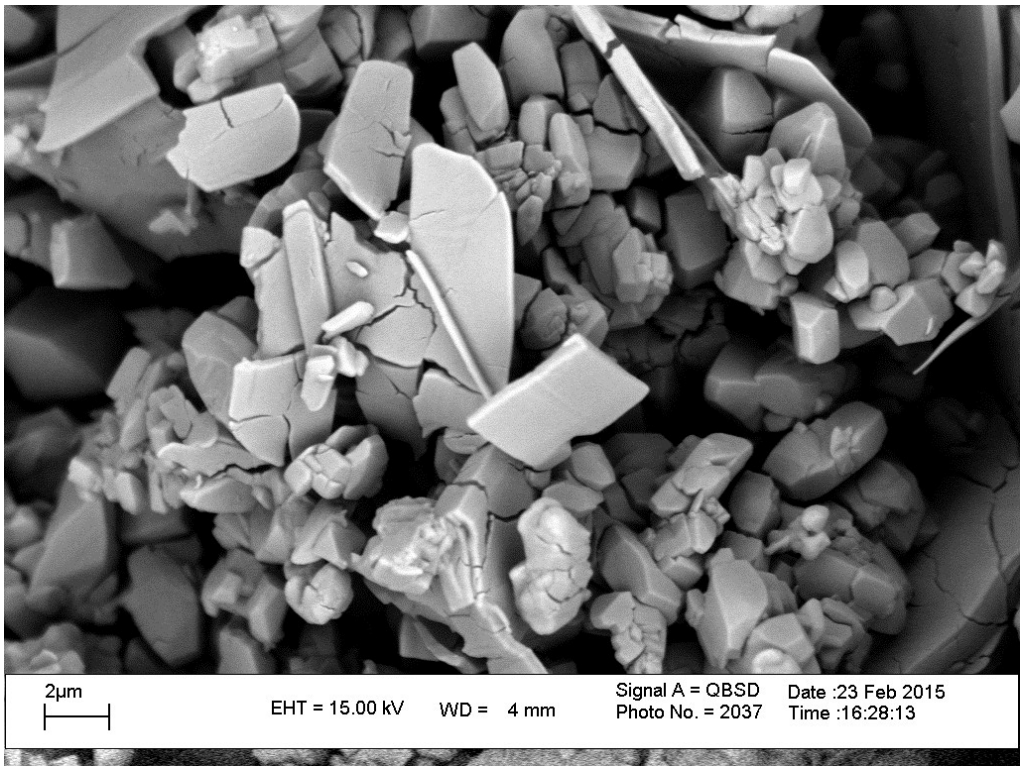


Fig. 12. SEM micrographs of $[C_4(DABCO)_2].2Cl$.

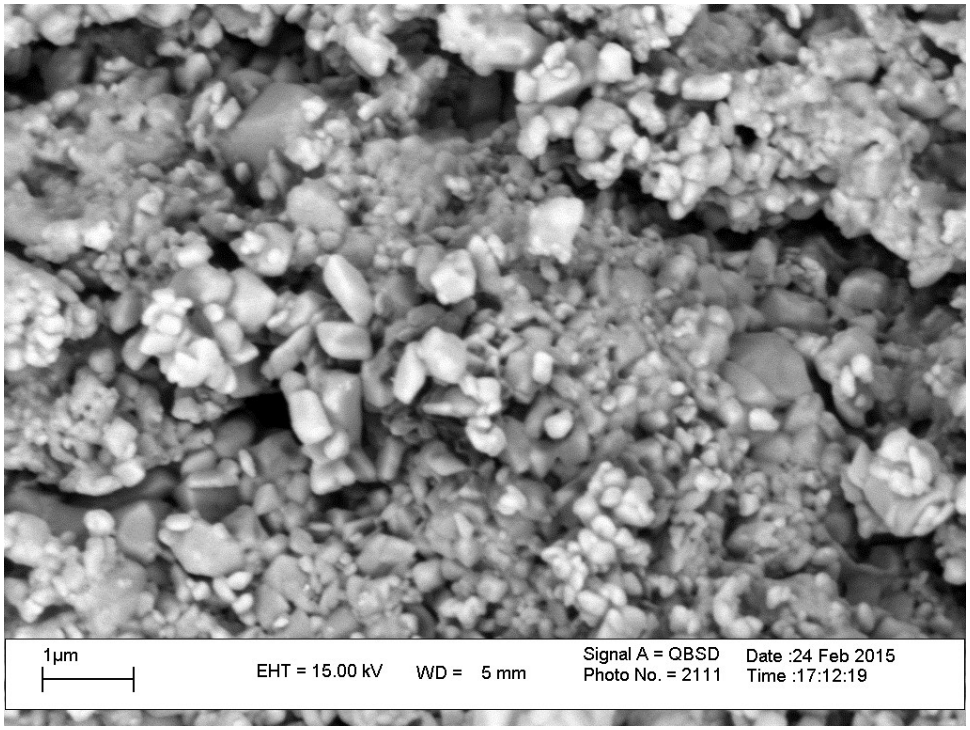


Fig. 13. SEM micrographs of NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$.

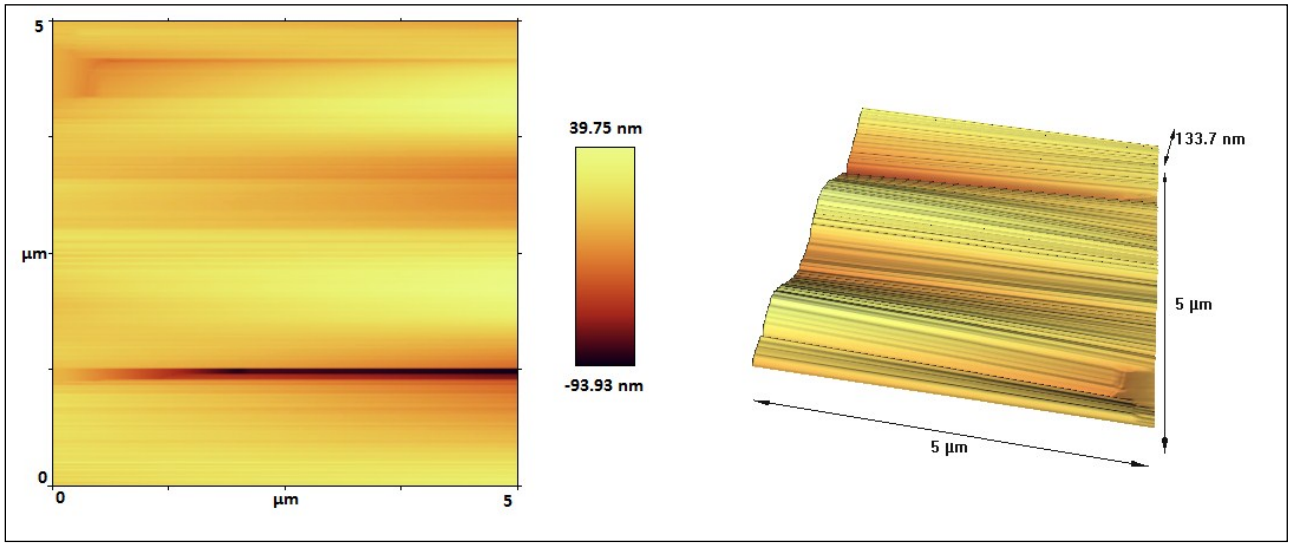


Fig. 14. Atomic force microscopy (AFM) images in two- and three dimensions for $[C_4(DABCO)_2].2Cl$.

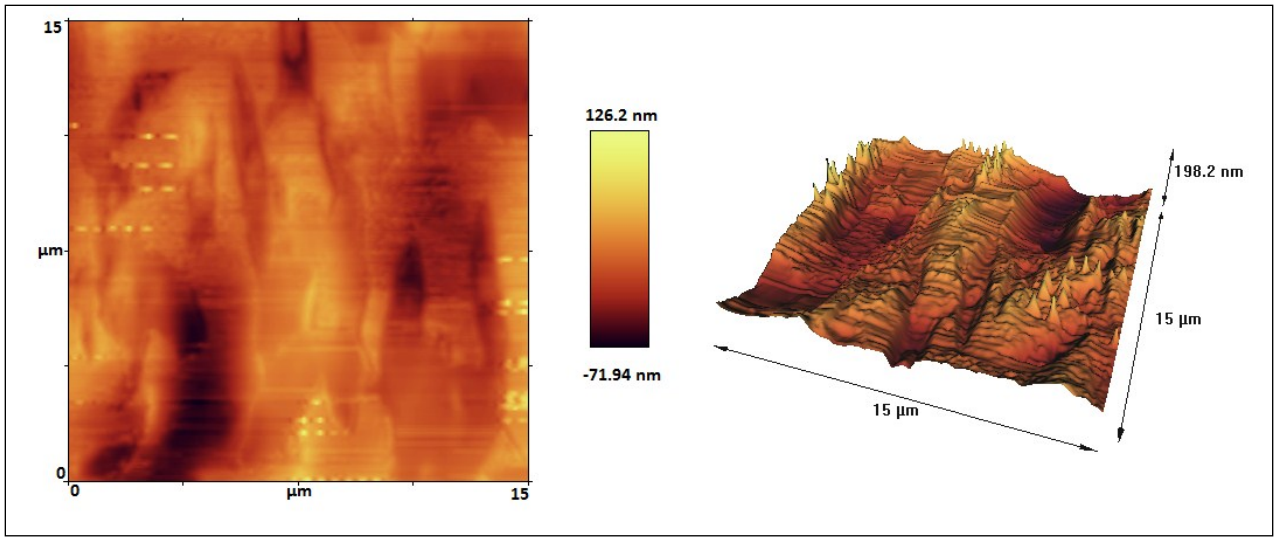


Fig. 15. Atomic force microscopy (AFM) images in two- and three dimensions for $[C_4(DABCO\text{-}SO_3H)_2].4Cl$.

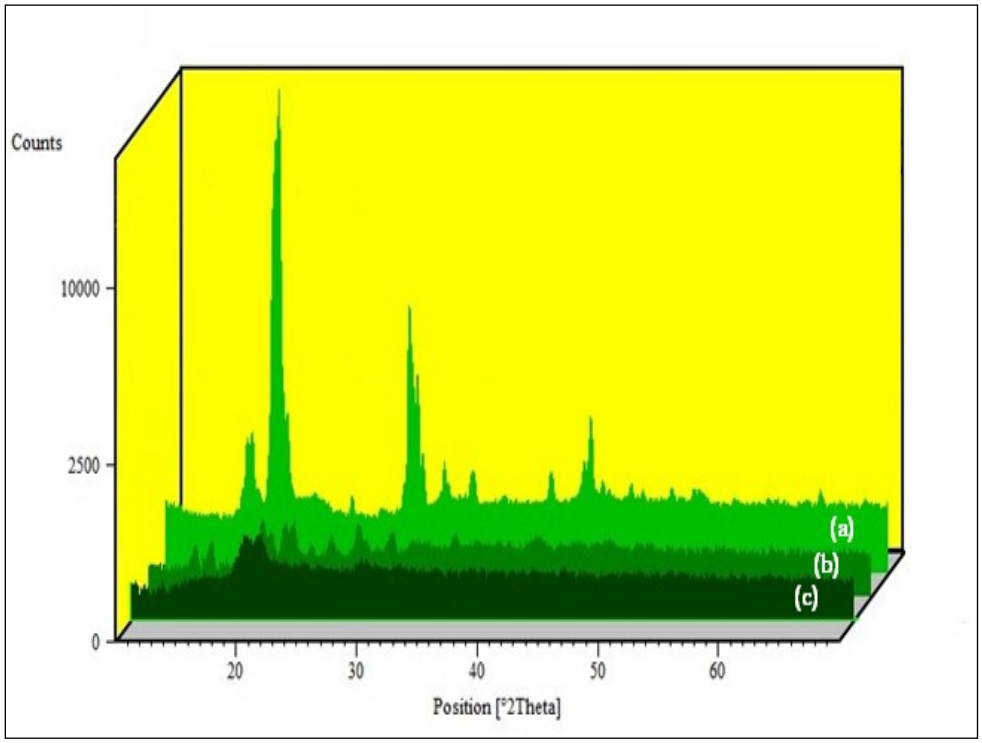


Fig. 16. XRD patterns of DABCO (a), $[C_4(DABCO)_2].2Cl$ (b) and NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$ (c).

Table 1. XRD data of DABCO (1), $[C_4(DABCO)_2].2Cl$ (2) and NS-$[C_4(DABCO\text{-}SO_3H)_2].4Cl$ (3).

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]
1	19.39	0.157	51.37
2	22.08	0.393	20.52
3	19.4	1.152	7

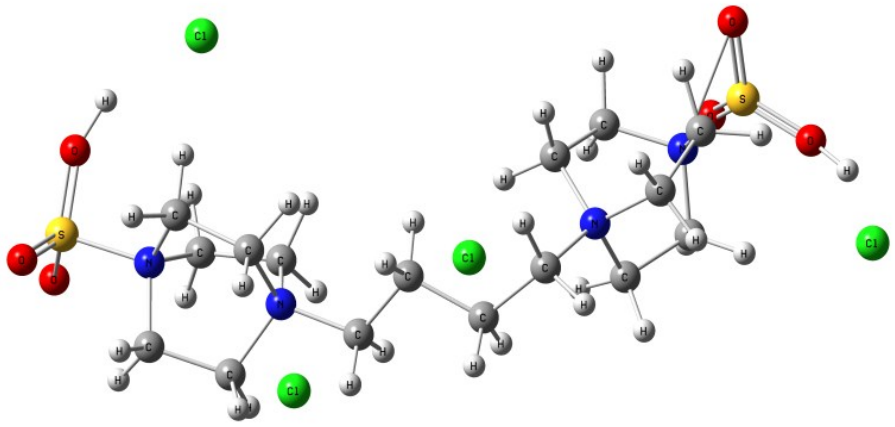


Fig. 17. The optimized geometry of NS-[C_4(DABCO-SO_3H)$_2$].4Cl.

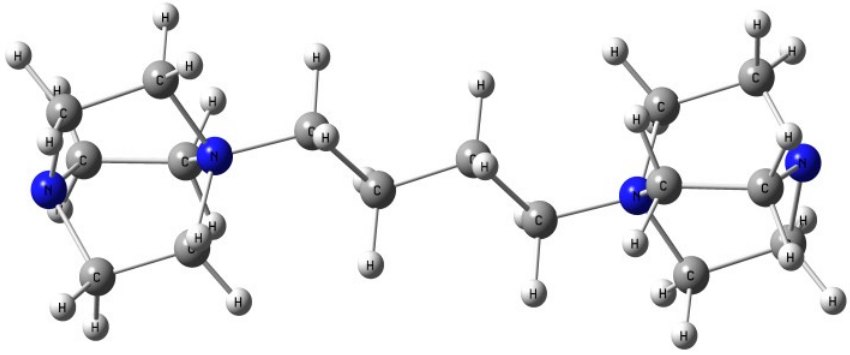


Fig. 18. The optimized geometry of [C_4(DABCO)$_2$].2Cl.

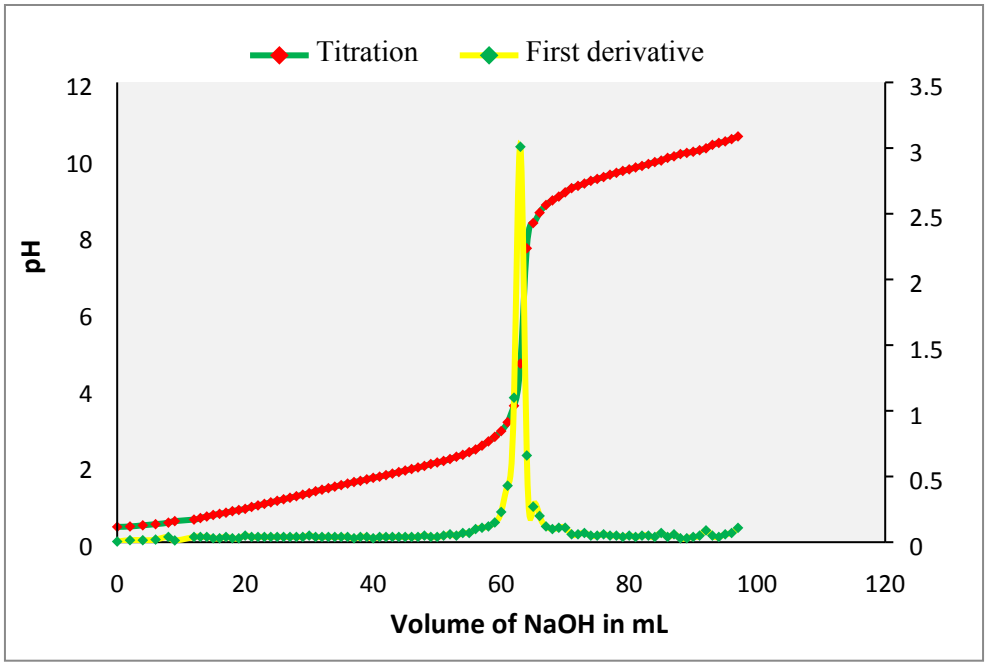


Fig. 19. Titration and its first derivative curves of NS-[C_4(DABCO-$SO_3H)_2$].4Cl by NaOH.

General procedure for the Synthesis of polyhydroquinolines:

In a round-bottomed flask a mixture of aldehyde (1 mmol), 1,3-cyclohexanedione and/or dimedone (1 mmol), ammonium acetate (1.5 mmol), a β-ketoester derivative (1 mmol) and [NS-C_4(DABCO-$SO_3H)_2$)].4Cl was stirred in the different conditions that the best result was obtained in the presence of 5 mol% [NS-C_4(DABCO-$SO_3H)_2$)].4Cl and 100 °C. After completion of the reaction, as monitored by TLC (eluent: EtOAc:*n*-hexane), water was added to separate the catalyst and the crude product was separated and recrystallized by EtOH.

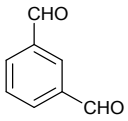
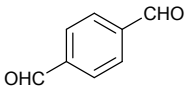
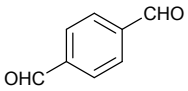
Table 2. Effect of the catalyst amount and temperature on the reaction between dimedone, 4-chlorobenzaldehyde, ethyl acetoacetate and ammonium acetate.

Entry	Catalyst amount (mol%)	Temp. (°C)	Time (min)	Conversion (%)[a]
1	2.5	25	60	60
2	2.5	80	45	75
3	2.5	100	40	80
4	5	25	40	80
5	5	80	30	100
6	**5**	**100**	**18**	**100**
7	10	100	20	100
8	-	100	6 h	20
9	DABCO (5)	100	6 h	23
10	$[C_4(DABCO)_2].2Cl$ (5)	100	6 h	60

[a] TLC or GC yields.

Table 3. Synthesis of polyhydroquinoline derivatives from dimedone, aryl aldehydes, β-ketoesters and ammonium acetate catalyzed by NS-[C_4(DABCO-$SO_3H)_2$].4Cl at 100 °C under solvent-free condition.

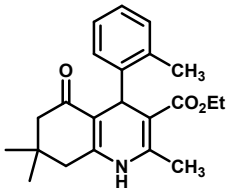
Entry	Aldehyde	R'	R''	Product	Time (min)	Yield (%)[a]	M.p. (°C)	
							Found	Reported [ref.]
1	C_6H_5–	CH_3	OEt	a	8	98	220-222	224-226 [42]
2	2-Cl-C_6H_4–	CH_3	OEt	b	10	95	202-204	207-209 [42]
3	2-OCH_3-C_6H_4–	CH_3	OEt	c	7	98	248-250	257-259 [42]
4	2-NO_2-C_6H_4–	CH_3	OEt	d	25	87	200-202	204-206 [42]
5	2-CH_3-C_6H_4–	CH_3	OEt	e	4	98	210-212	-
6	3-Br-C_6H_4–	CH_3	OEt	f	7	97	229-231	230-232 [43]
7	3-CH_3O-C_6H_4–	CH_3	OEt	g	8	97	198-200	201-203 [42]
8	3-NO_2-C_6H_4–	CH_3	OEt	h	22	90	170-172	173-175 [42]
9	4-Cl-C_6H_4–	CH_3	OEt	i	18	92	241-243	245-246 [42]
10	4-Br-C_6H_4–	CH_3	OEt	j	10	97	248-252	255-256 [43]
11	4-CH_3O-C_6H_4–	CH_3	OEt	k	15	95	254-256	258-260 [42]
12	4-NO_2-C_6H_4–	CH_3	OEt	l	27	87	238-240	242-244 [42]
13	4-OH-C_6H_4–	CH_3	OEt	m	4	98	227-229	228-230 [42]
14	4-CH_3-C_6H_4–	CH_3	OEt	n	2	98	259-261	256-258 [42]
15	4-CN-C_6H_4–	CH_3	OEt	o	15	90	140-142	140-142 [42]
16	4-CH_3S-C_6H_4–	CH_3	OEt	p	15	90	239-241	240-242 [44]
17	4-$(CH_3)_2N$-C_6H_4–	CH_3	OEt	q	50	88	231-233	233-235 [42]
18	4-Isopro-C_6H_4–	CH_3	OEt	r	40	85	179-181	182-184 [42]
19	C_6H_5–	H	OEt	s	10	95	250-252	240-242 [45]
20	4-Cl-C_6H_4–	H	OEt	t	5	98	243-246	234-236 [45]
21	4-Br-C_6H_4–	H	OEt	u	5	98	254-255	253-254 [45]
22	4-OH-C_6H_4–	H	OEt	v	3	98	244-246	222-224 [45]
23	4-CH_3O-C_6H_4–	H	OEt	w	5	98	194-195	192-193 [17]
24	4-CH_3-C_6H_4–	H	OEt	x	12	95	251-254	241-243 [45]
25	4-$(CH_3)_2N$-C_6H_4–	H	OEt	y	50	88	204-206	—
26	4-Cl-C_6H_4–	CH_3	OMe	z	20	89	220-221	220-221 [46]
27	4-CH_3O-C_6H_4–	CH_3	OMe	aa	5	98	248-252	249-251 [46]
28	4-CN-C_6H_4–	CH_3	OMe	bb	5	98	219-221	220-222 [46]
29	4-CH_3-C_6H_4–	CH_3	OMe	cc	3	98	267-269	274-276 [46]
30	4-$(CH_3)_2N$-C_6H_4–	CH_3	OMe	dd	40	93	258-259	257-258 [12]
31	Butyraldehyde	CH_3	OEt	ff	45	80	147-149	147-149 [42]
32	Isobutyraldehyde	CH_3	OEt	gg	40	80	160-162	161-163 [42]
33	Furan-2-carbaldehyde	H	OEt	hh	5	87	207-209	210-212 [19]

34	Furan-2-carbaldehyde	CH_3	OEt	ii	4	87	246-248	245-247 [42]
35		CH_3	OEt	ll	15	100	281-282	—
36		H	OEt	mm	5	85	293-294	—
37		CH_3	OEt	nn	7	98	305-307	294-296 [43]

[a] Isolated yields.

The spectral data of the new compounds are as follow:

Ethyl 2,7,7-trimethyl-5-oxo-4-(o-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (e): White solid., m.p. 210-212 °C., FT-IR (KBr, cm^{-1}) : 3302, 3070, 2962, 1698, 1606, 1481, 1377, 1275, 1212, 1065 cm^{-1}., ^1H NMR (DMSO-d6, 400 MHz): 0.8 (S, 3H, CH_3), 1(S, 3H, CH_3), 1.1 (t, *J*=7.2 Hz,3H, CH_3), 1.9 (d, *J*=16 Hz,1H, CH_2), 2.1 (d, *J*=16 Hz,1H, CH_2) ,2.27 (d,*J*=17.2 Hz,1H, CH_2), 2.29 (S, 3H), 2.43 (d, *J*=17.2 Hz,1H), 2.62 (S,3H), 3.9-4.00 (m, 2H, OCH_2), 4.93(S, 1H, CH), 6.91-6.96 (m, 2H, ArH), 7 (t, *J*=7.6 Hz,1H, ArH), 7.12(d, *J*=7.6 Hz,1H, ArH), 9.04 (NH,1H).



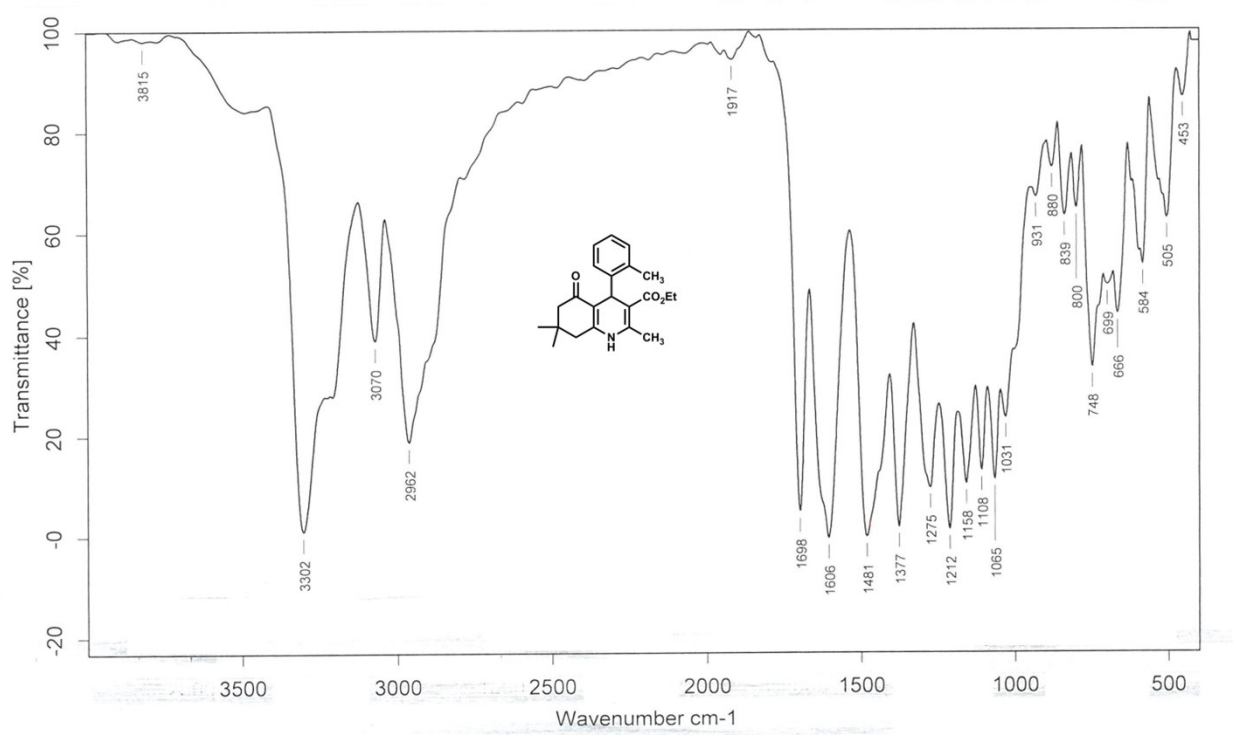


Fig. 20. FT-IR of ethyl 2,7,7-trimethyl-5-oxo-4-(o-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

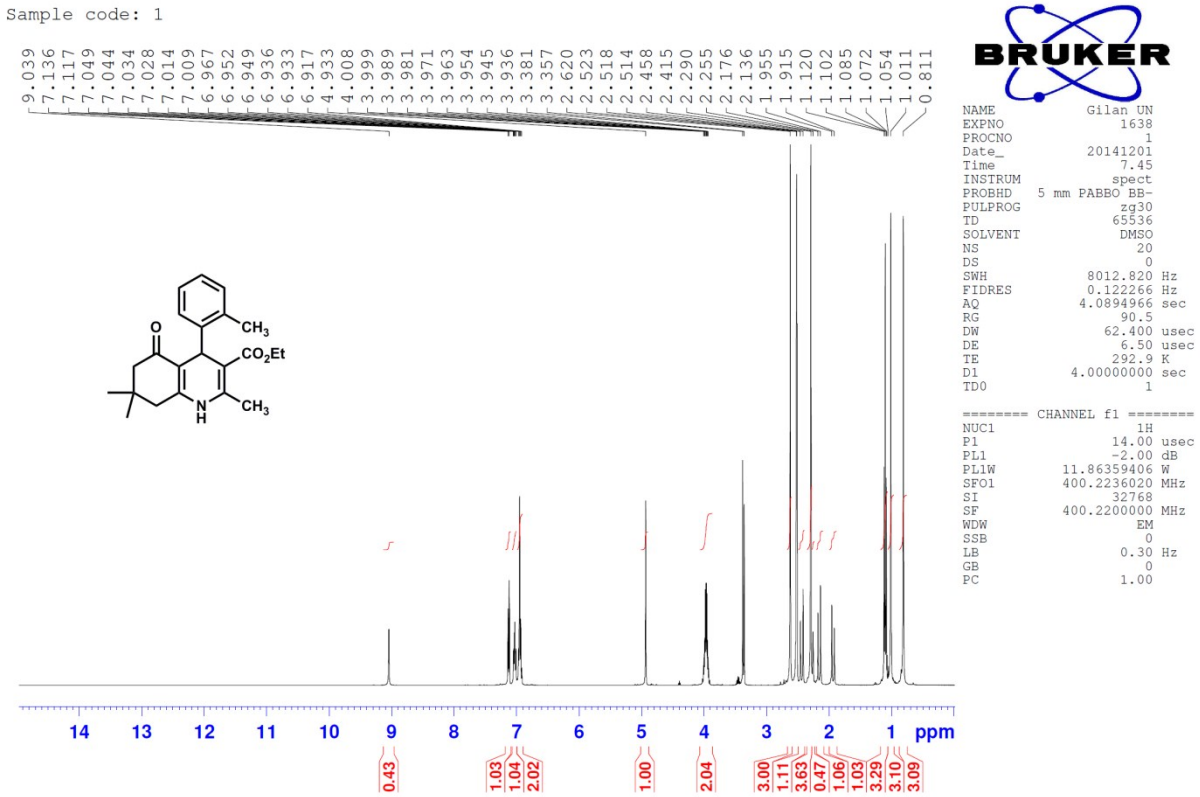
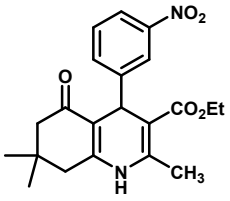


Fig. 21. H-NMR of ethyl 2,7,7-trimethyl-5-oxo-4-(o-tolyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (h): Pale yellow., m.p.= 170-172 °C., FT-IR (KBr, cm^{-1}): 3286, 3210, 3081, 2960, 1697, 1613, 1529, 1484, 1354, 1215, 1079, 686., ^1H NMR (400 MHz, $CDCl_3$) δ 0.949 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.22 (t, *J* =7.2 Hz, 3H, CH_3), 2.144-2.427 (m, 7H), 4.08 (q, *J* =7.2 Hz, 2H, OCH_2), 5.178 (s, 1H, CH), 6.696 (s, 1H, ArH), 7.398 (t, J= 8 Hz, 1H, ArH), 7.74 (d, *J* = 8 Hz, 1H, ArH), 8 (d, *J* = 8 Hz, 1H, ArH), 8.141 (s, 1H, NH).



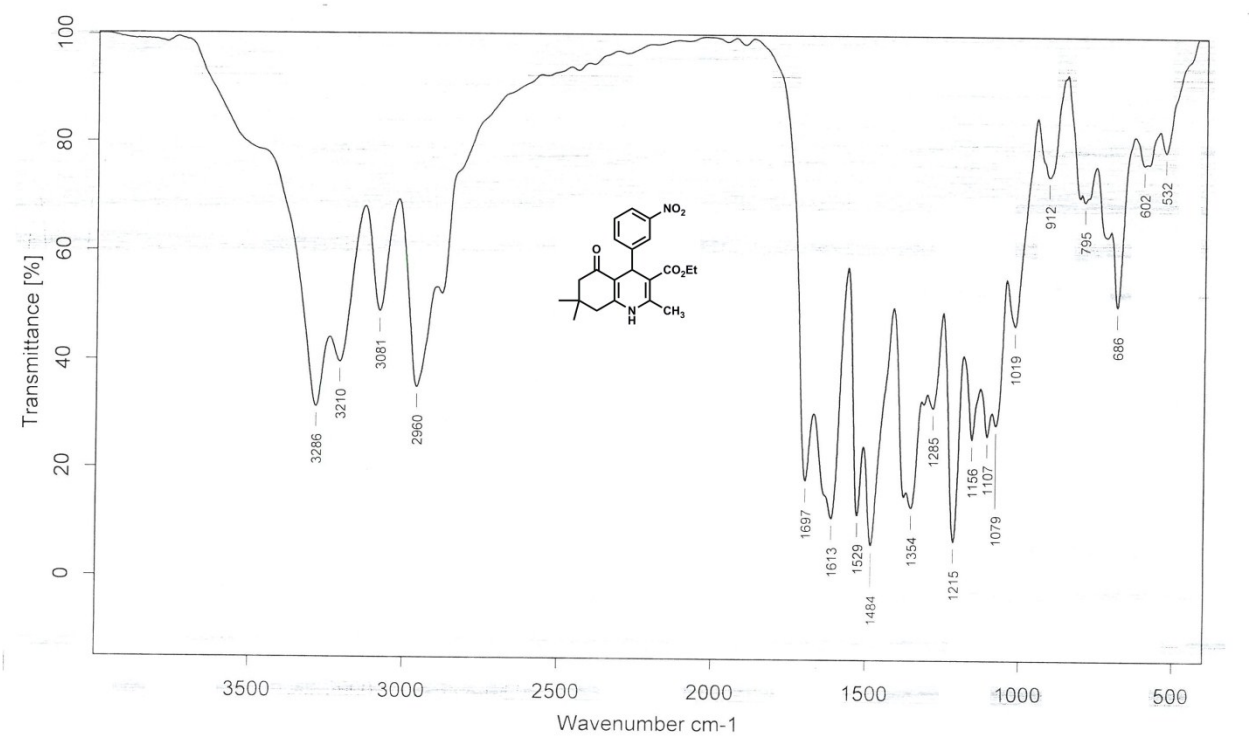


Fig. 22. FT-IR of ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

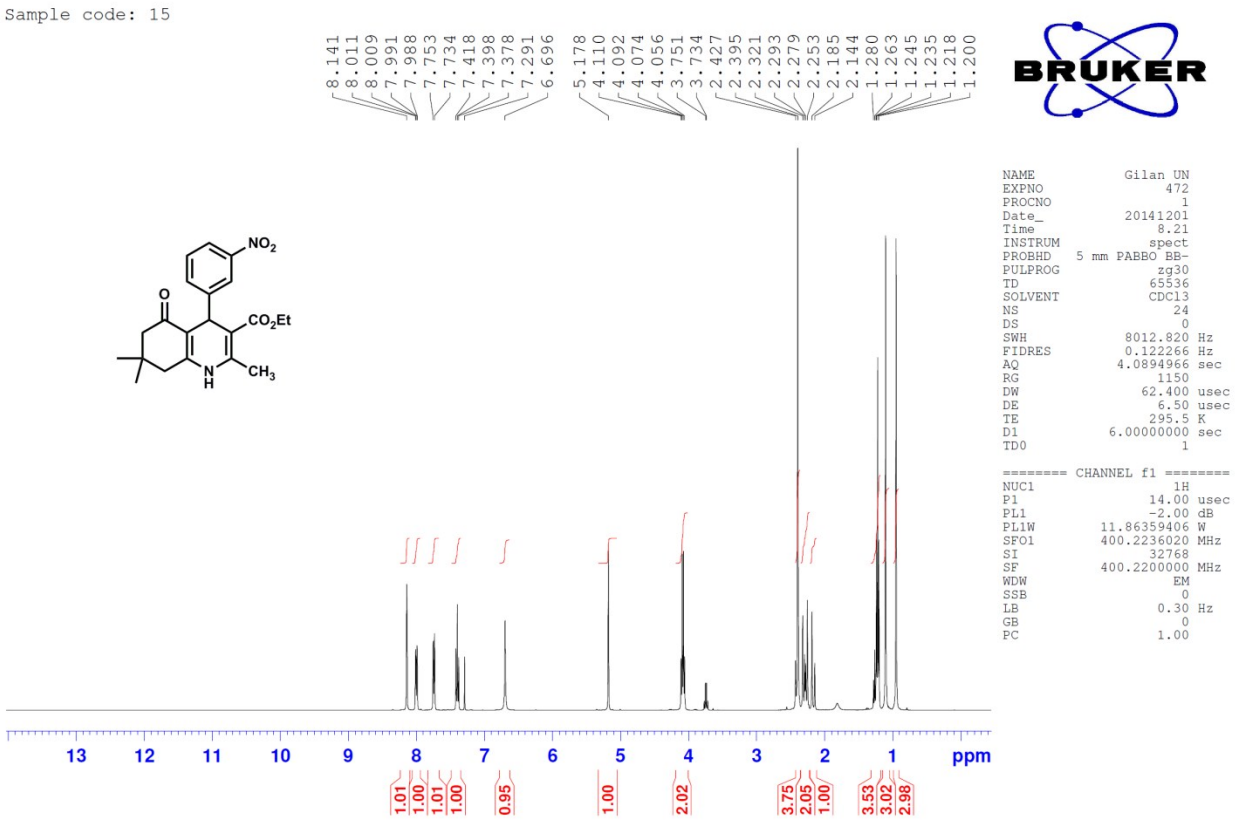


Fig. 23. ^{1}H NMR of ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (h).

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

White solid., m.p.= 241-243 °C., FT-IR (KBr, cm^{-1}): 3284, 3212, 3075, 2948, 1698, 1611, 1481, 1377, 1227, 1079, 828., ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.948 (s, 3H, CH_3), 1.086 (s, 3H, CH_3), 1.219 (t, *J*=7.2 Hz, 3H, CH_3), 2.143-2.345 (m, 4H, CH_2),2.386 (s, 3H), 4.08 (q, *J* = 7.2 Hz, 2H), 5.047 (s, 1H, CH), 6.5 (br, 1H, NH), 7.18 (d, J= 8.3 Hz, 2H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH).

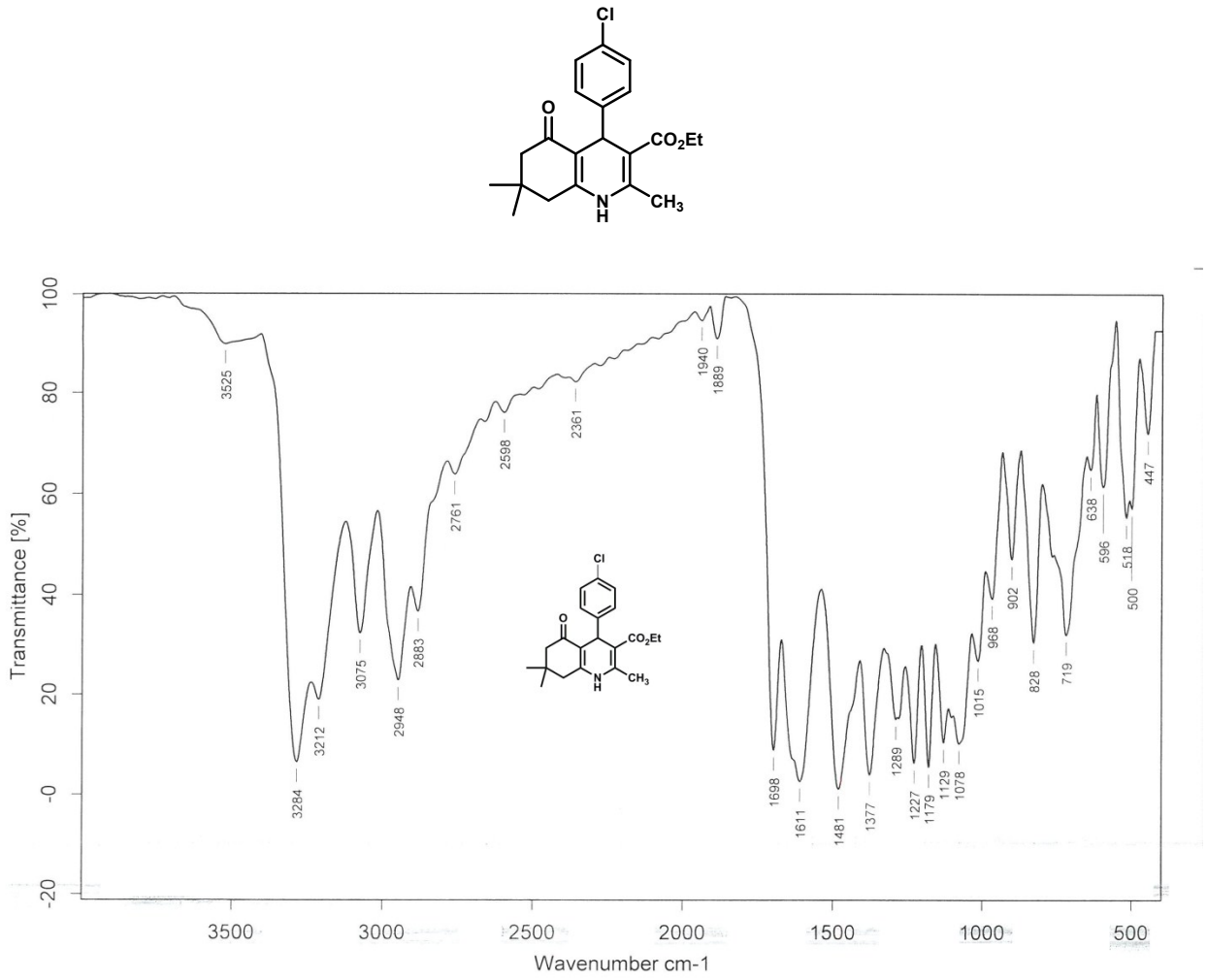


Fig. 24. FT-IR of ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

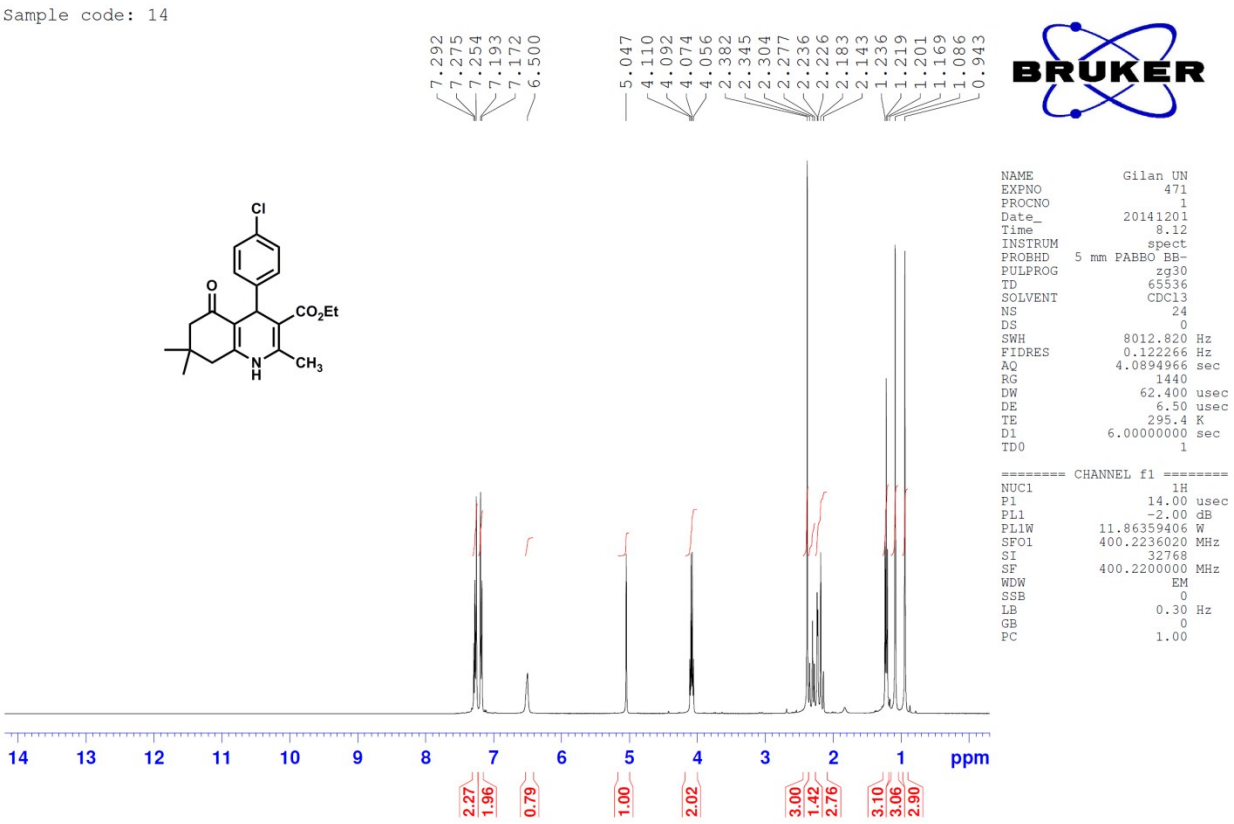


Fig. 25. ^{1}H NMR of ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (j):

White solid, m.p.= 248-252 °C., FT-IR (KBr, cm^{-1}): 3277, 3199, 3076, 2966, 1703, 1603, 1490, 1378, 1277, 1217, 1069, 842, 737, 529., ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.953 (s, 3H,CH_3), 1.099 (s, 3H, CH_3), 1.219 (t, *J* =7.2 Hz, 3H, CH_3), 2.152–2.399 (m, 7H), 4.08 (q, *J*= 7.2 Hz, 2H, OCH_2), 5.037 (s, 1H, CH), 6.01 (br, 1H, NH), 7.21 (d, *J* = 8.3 Hz, 2H, ArH), 7.34 (d, *J*= 8.5 Hz, 2H, ArH), 8.23 (s, 1H, NH).

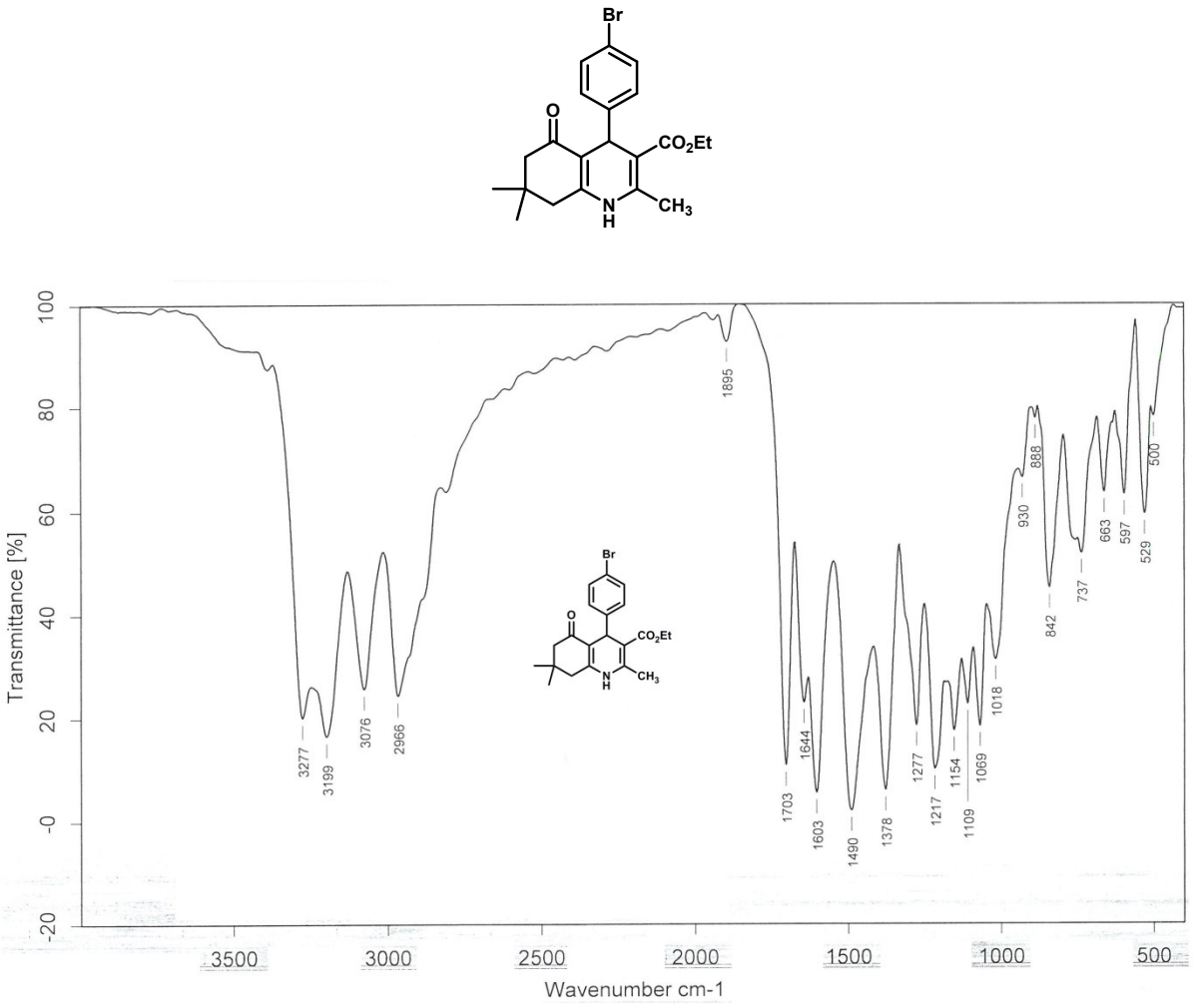


Fig. 26. FT-IR of ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

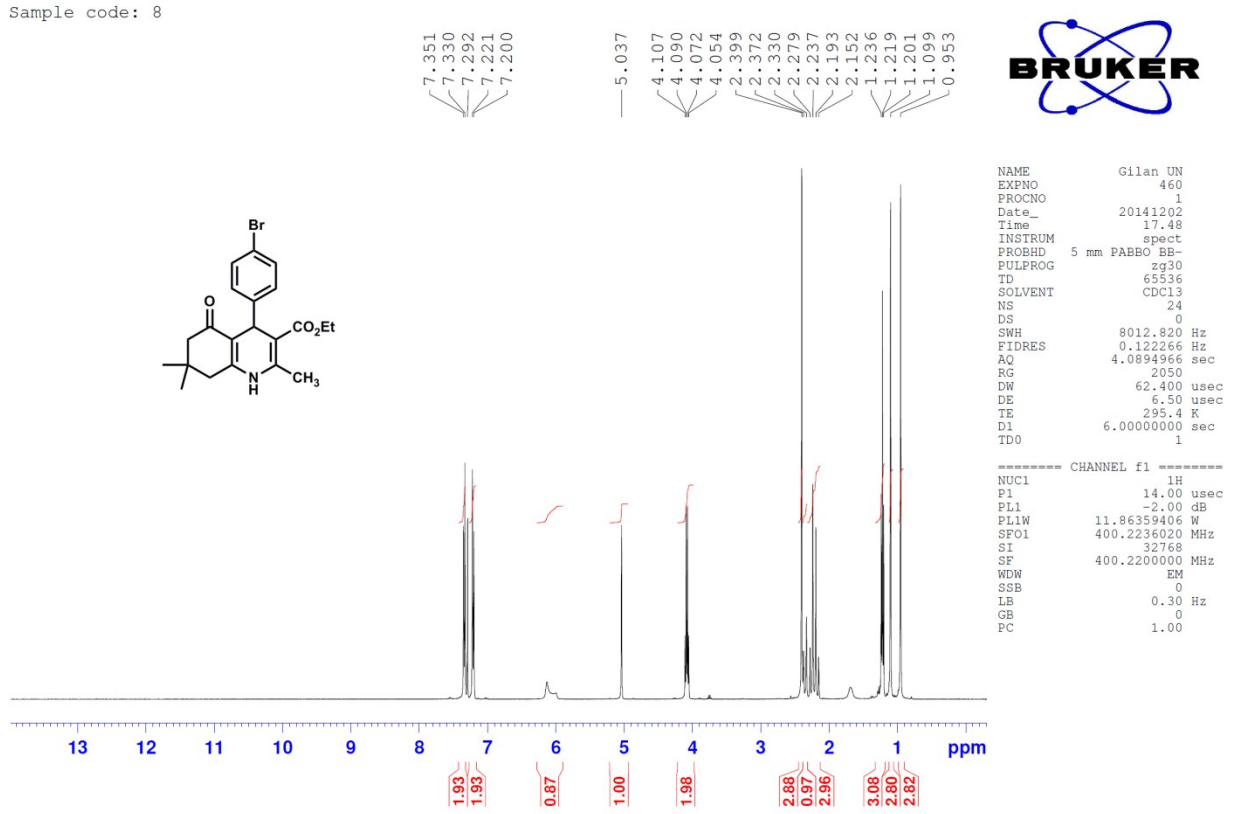


Fig. 27. ^{1}HNMR of ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (k): Pale yellow solid, m.p = 254-256 °C., FT-IR (KBr, cm^{-1}) 3278, 3201, 3077, 2959, 1702, 1604, 1498, 1379, 1272, 1223, 1108, 1071, 1030, 841, 760., ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.952 (s, 3H, CH_3), 1.073 (s, 3H, CH_3), 1.236 (t, 3H, *J*=7.4 Hz, CH_3), 2.178-2.269 (m, 4H), 2.362 (s, 3H), 3.744 (s, 3H), 4.085 (q, 2H, *J*=7.4 Hz, OCH_2), 5.17 (s, 1H, CH), 6.742-6.764 (d, 2H, *J*=8.8 Hz, ArH), 7.23 (d, 2H, *J*=8.8 Hz, ArH), 7.292 (s, 1H, NH).

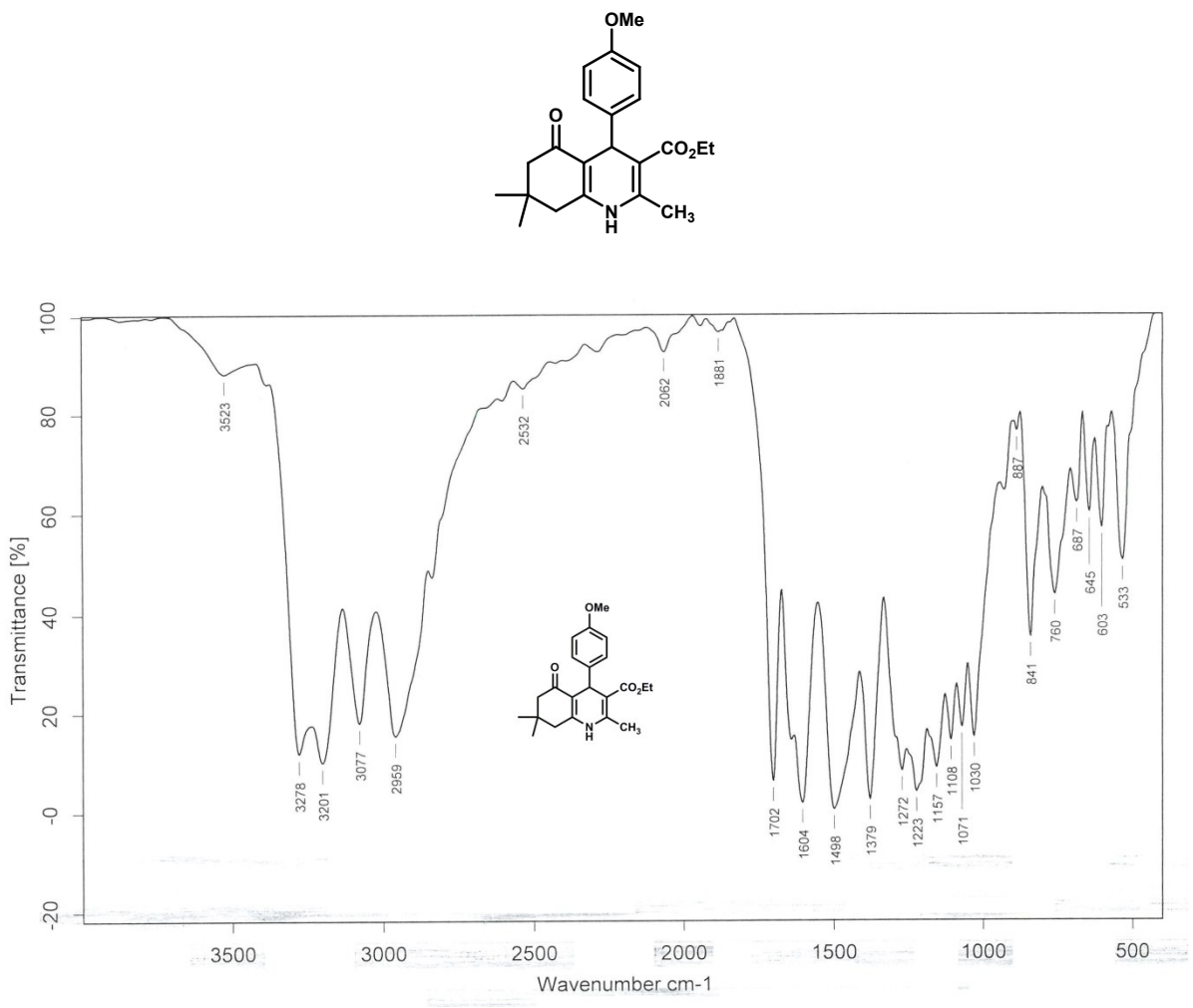


Fig. 28. FT-IR of ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

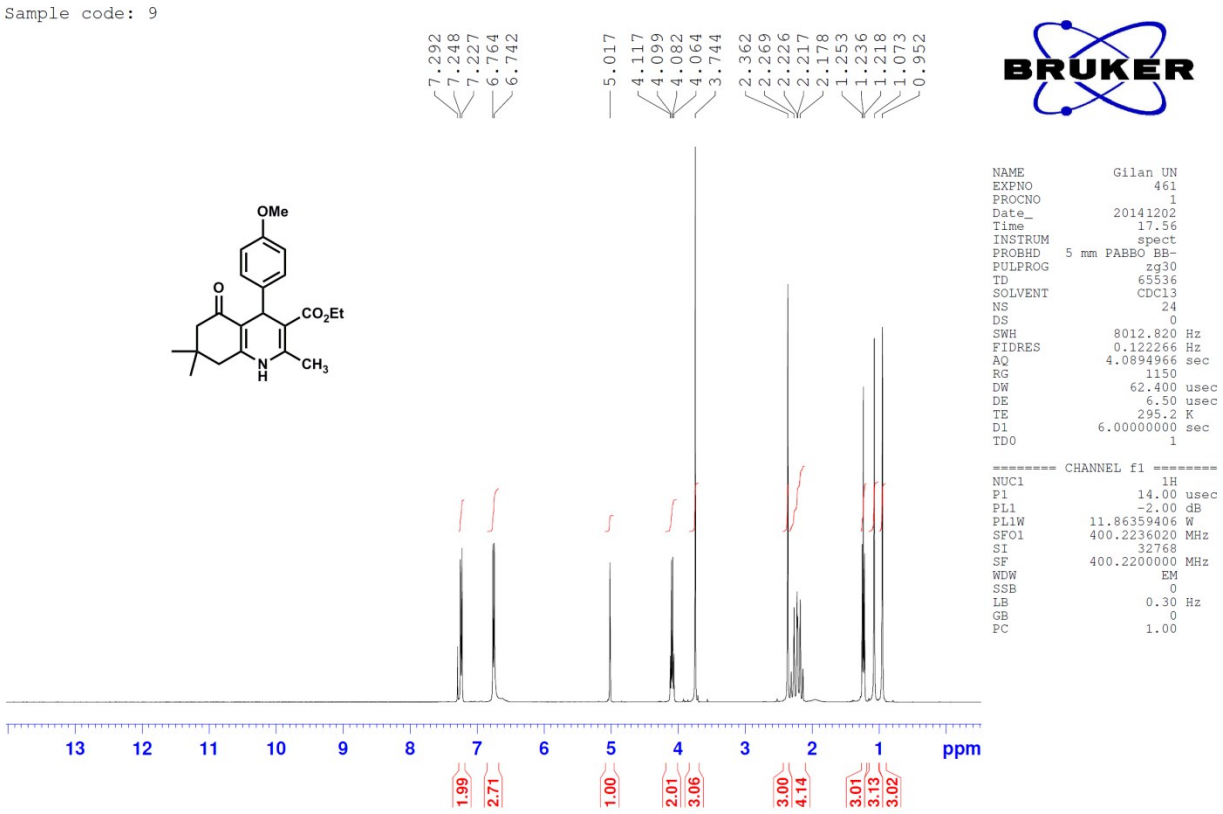


Fig. 29. ^{1}H NMR of of ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (l): Pale yellow solid, m.p = 238-240 °C., FT-IR (KBr, cm^{-1}) 3293, 3215, 3082, 2958, 1699, 1619, 1528, 1487, 1379, 1221, 1068, 698., ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.920 (s, 3H, CH_3), 1.092 (s, 3H, CH_3), 1.199 (t, 3H, *J*=7.3 Hz, CH_3), 2.15 (dd, 2H, CH_2), 2.26 (dd, 2H, CH_2), 2.402 (s, 6H, CH_3), 4.07 (q, 2H, *J*=7.4 Hz, OCH_2), 5.178 (s, 1H, CH), 6.718 (s, 1H, NH), 7.51 (d, 2H, *J*=9.4 Hz, ArH), 8.09 (d, 2H, *J*=9.4 Hz, ArH).

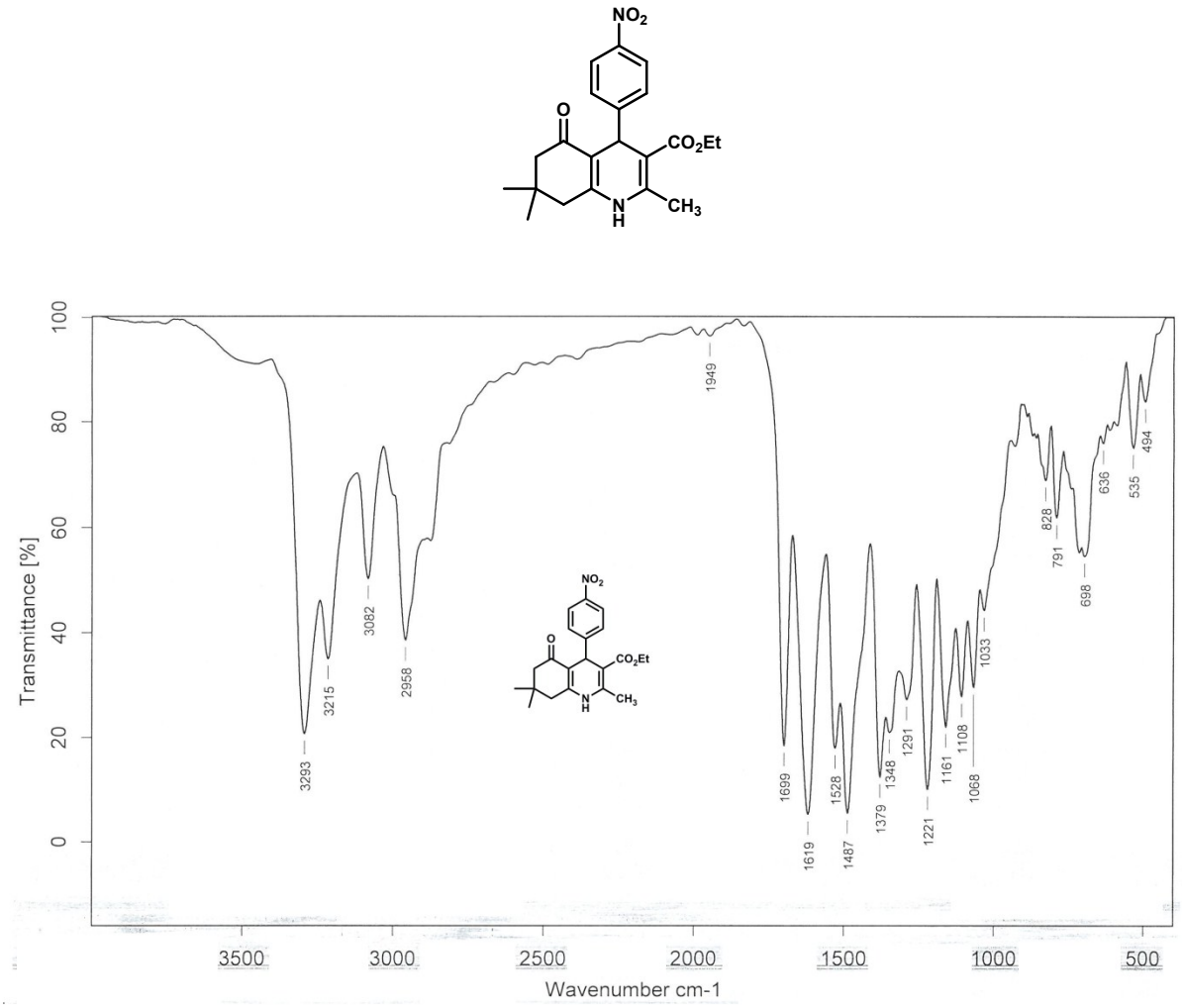


Fig. 30. FT-IR of ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

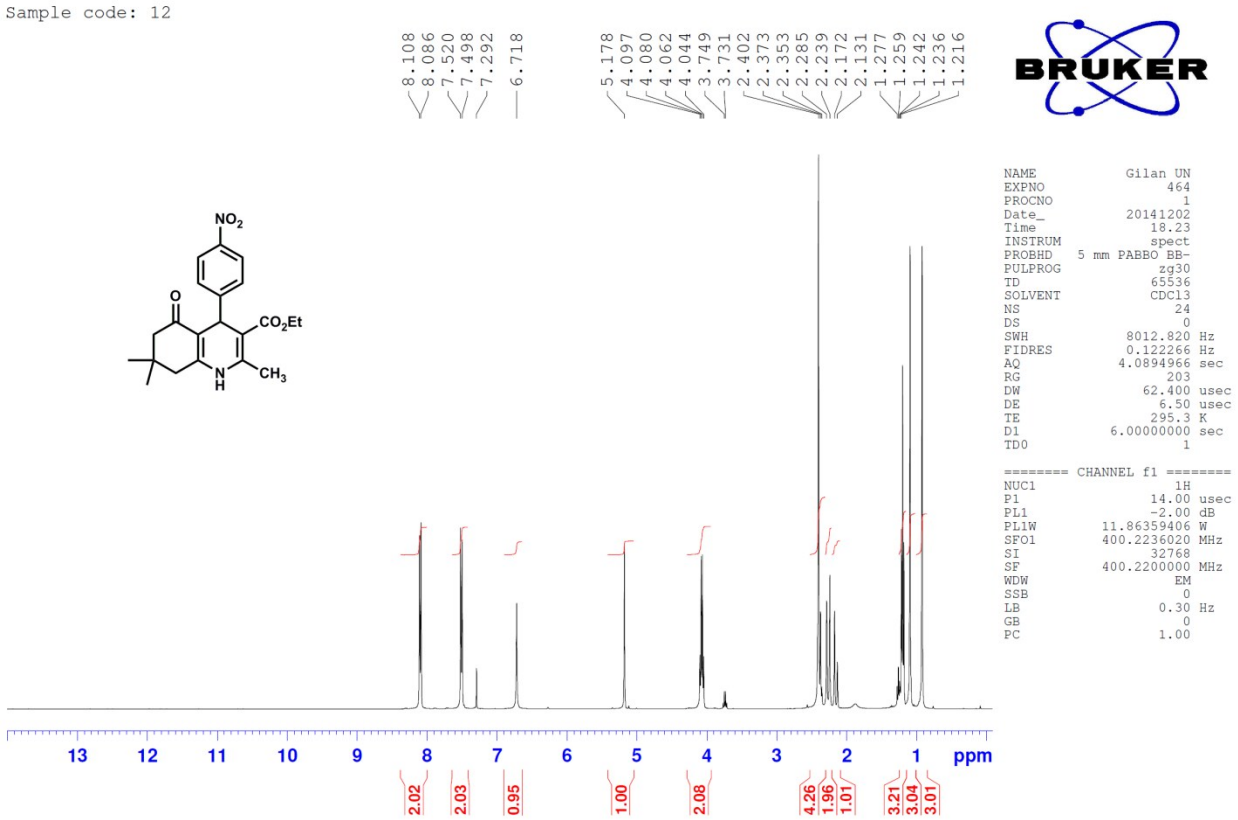


Fig. 31. ^{1}H NMR of ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-isopropylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (r):

White solid, m.p = 179-181 °C.; FT-IR (KBr, cm^{-1}) 3283, 3206, 3082, 2963, 1703, 1606, 1494, 1379, 1279, 1213, 843., ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.983 (s, 3H, CH_3), 1.091 (s, 3H, CH_3), 1.192-1.282 (m, 9H), 2.163 (m, 6H), 2.79 (m, 1H, CH), 4.08 (q, 2H, *J*=7.4 Hz, OCH_2), 5.048 (s, 1H, CH), 6.766 (s, 1H, NH), 7.06 (d, 2H, *J*=8 Hz, ArH), 7.22 (d, 2H, *J*=8 Hz, ArH).

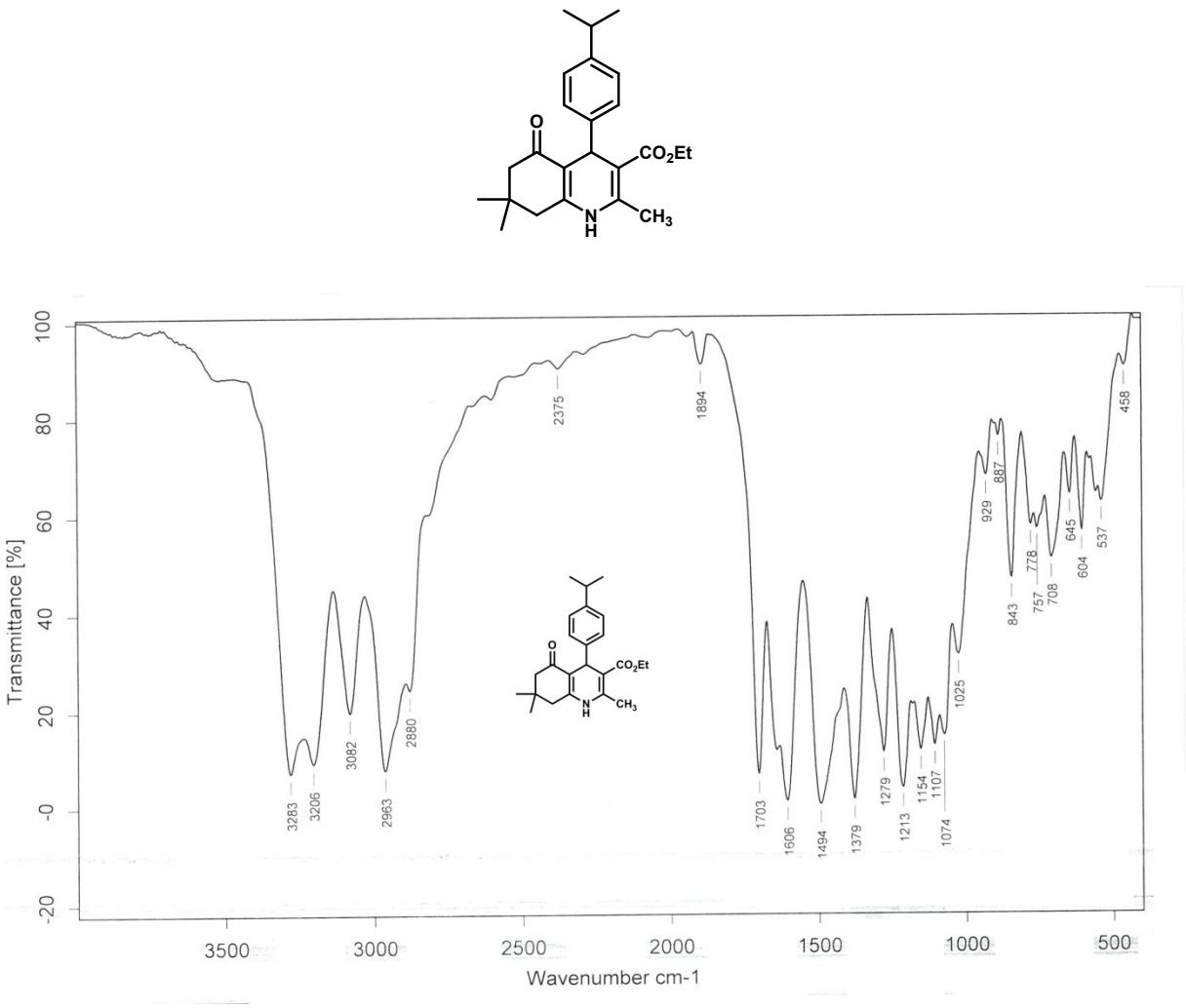


Fig. 32. FT-IR of ethyl 4-(4-isopropylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

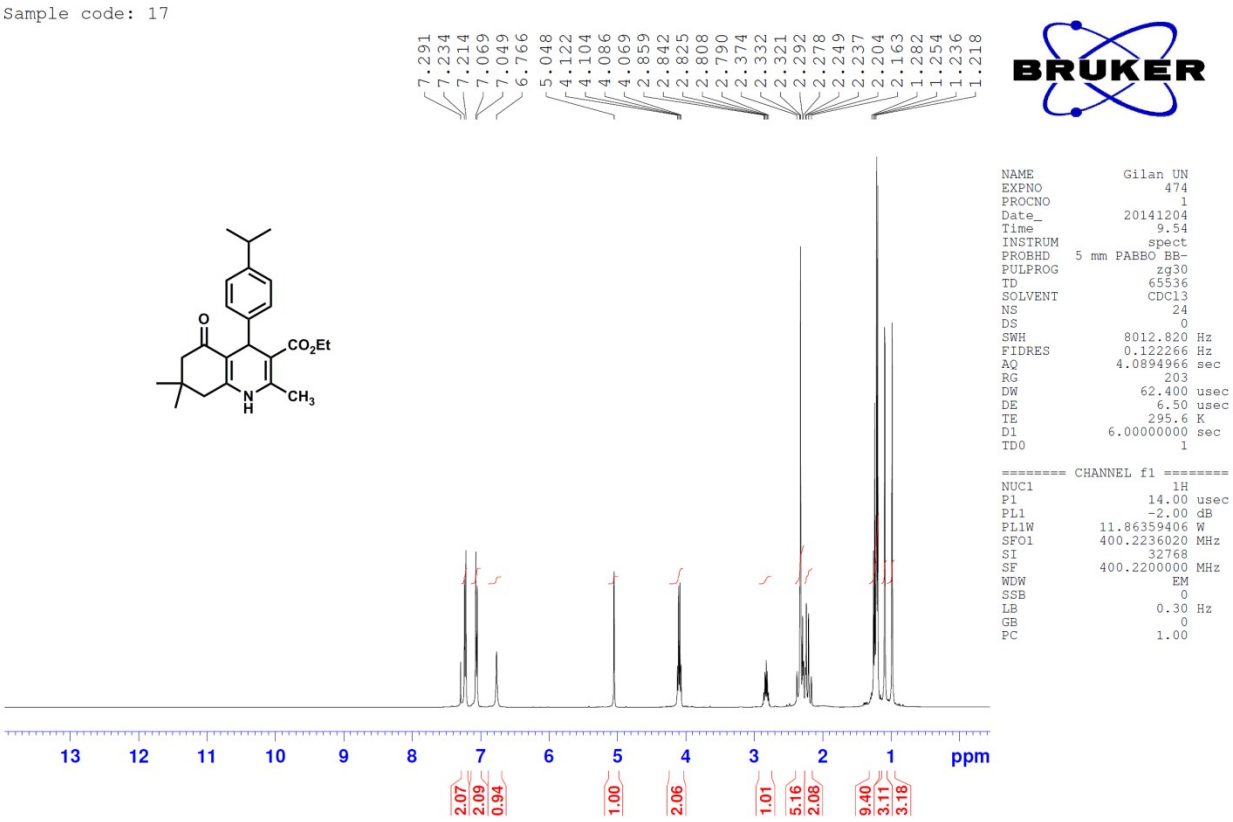


Fig. 33. ^{1}H NMR of ethyl 4-(4-isopropylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (t): White solid, m.p.= 243-246 °C., FT-IR (KBr, cm^{-1}): 3278, 3199, 3077, 2967, 1705, 1603, 1491, 1379, 1278, 1216, 1154, 1076, 843, 739., ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, *J* = 7.2 Hz, 3H), 1.644 (s, 1H), 1.944-2.053 (m, 2H), 2.330-2.482 (m, 7H), 4.08 (q, *J* = 7.2 Hz, 2H), 5.087 (s, 1H, CH), 6.013 (br, 1H, NH), 7.19 (d, *J* = 8 Hz, 2H, ArH), 7.24 (d, *J* = 8 Hz, 2H, ArH).

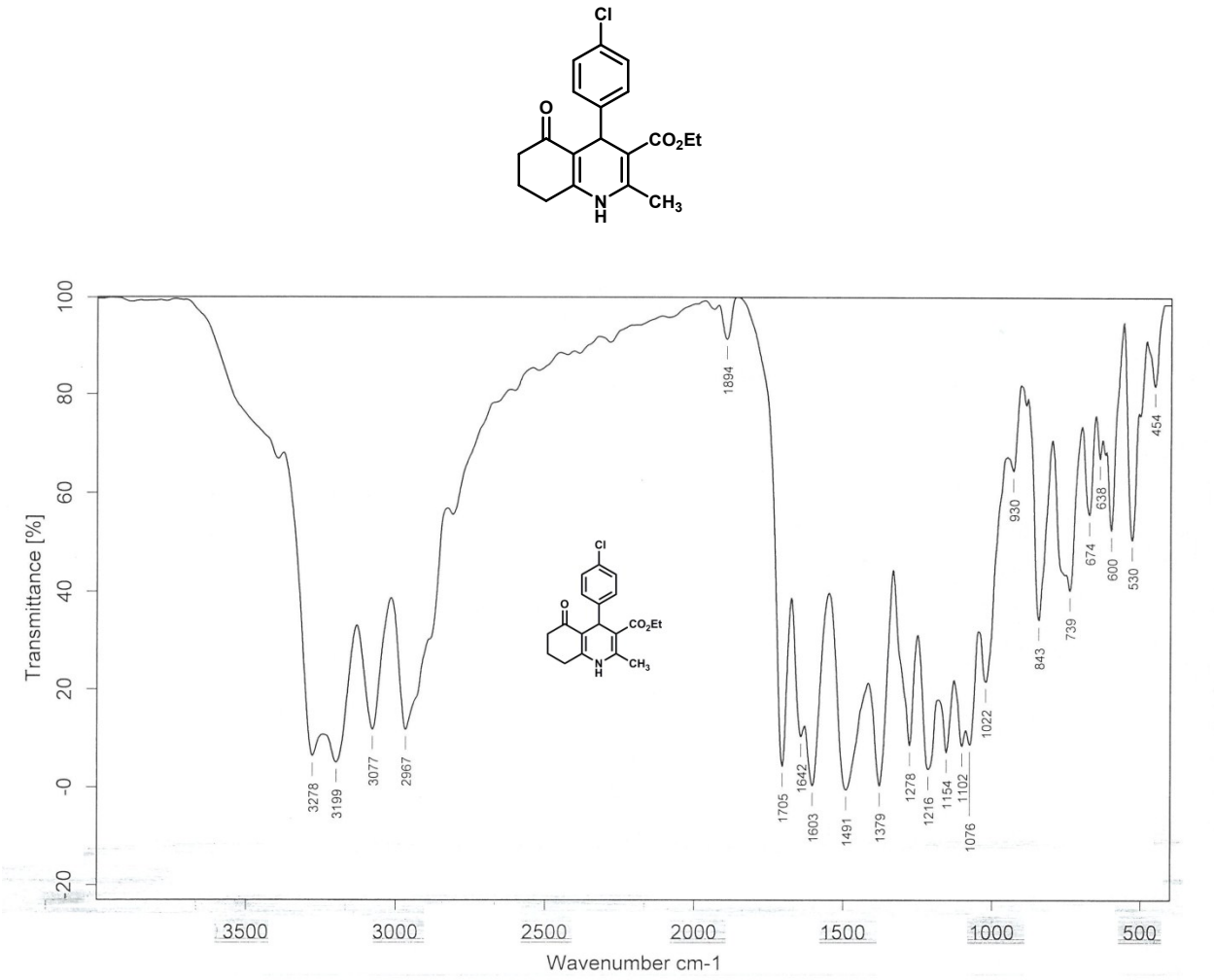


Fig. 34. FT-IR of ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

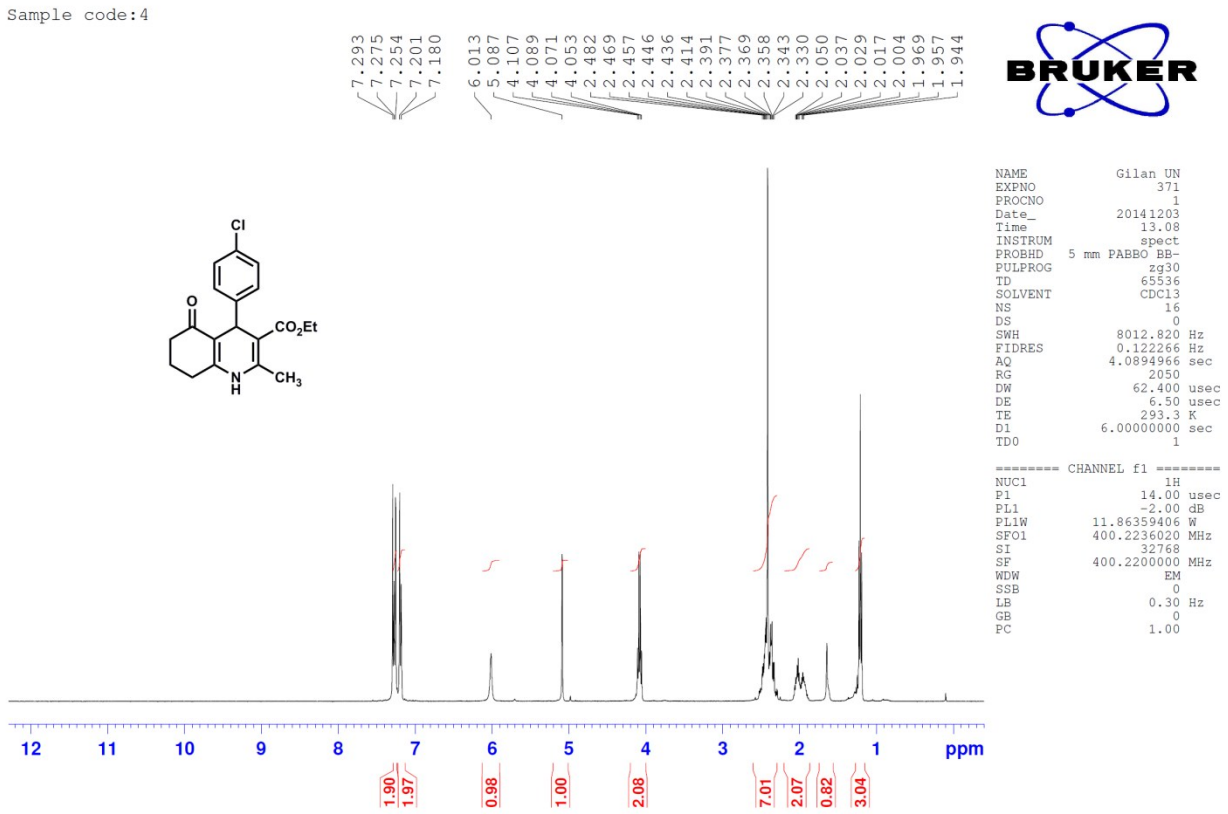


Fig. 35. ^{1}H NMR of ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Methyl 4-(4-bromophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (u): White solid, m.p.= 254-255 °C., FT-IR (KBr, cm^{-1}): 3338, 3248, 3094, 2948, 1699, 1648, 1485, 1309, 1214, 834., ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.924-2.042 (m, 2H), 2.3-2.38 (m, 2H), 2.393-2.454 (m, 5H), 3.634 (s, 3H, OCH_3), 5.085 (s, 1H, CH), 6.286 (s, 1H, NH), 7.19 (d, 2H, *J*=9.4 Hz, ArH), 7.34 (d, 2H, *J*=9.4 Hz, ArH)., ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.86, 167.70, 149.95, 146.03, 144.03, 131.11, 129.69, 119.90, 113.03, 105.23, 51.17, 36.99, 35.91, 27.41, 21.0, 19.46.

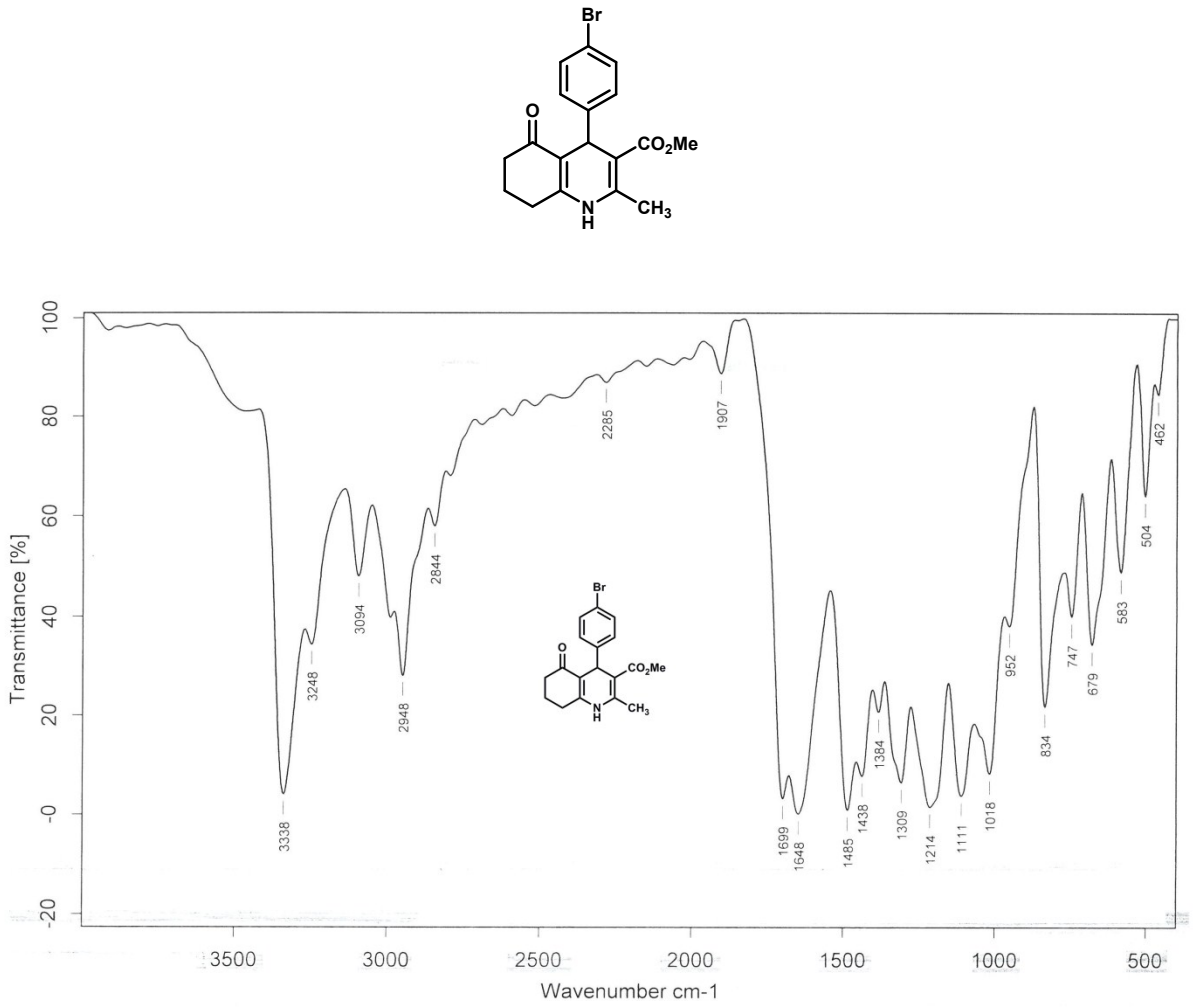


Fig. 36. FT-IR of methyl 4-(4-bromophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

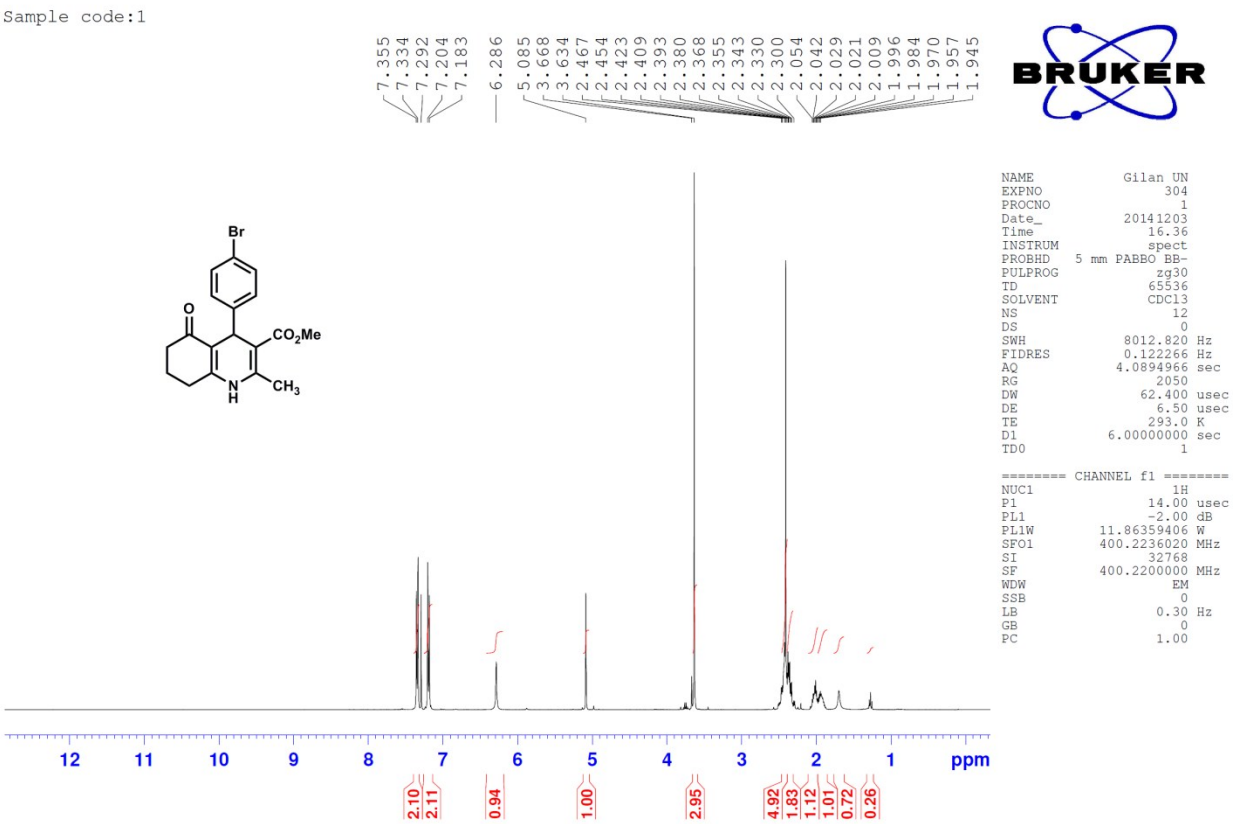
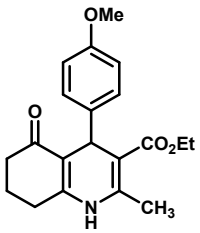


Fig. 37. ^{1}H NMR of methyl 4-(4-bromophenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-methoxyphenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (w): Pale yellow solid, m.p.= 194-195 °C., FT-IR (KBr, cm^{-1}): 3275, 3187, 3068, 2963, 1705, 1606, 1498, 1381, 1213, 1025, 843., ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.2 Hz, 3H), 1.91-2.02 (m, 2H), 2.29-2.42 (m, 7H), 3.75 (s, 3H), 4.08 (q, *J* = 7.2 Hz, 2H), 5.06 (s, 1H), 6.74-6.78 (m, 3H), 7.24 (d, *J* = 8.8 Hz, 2H, Ar–H).



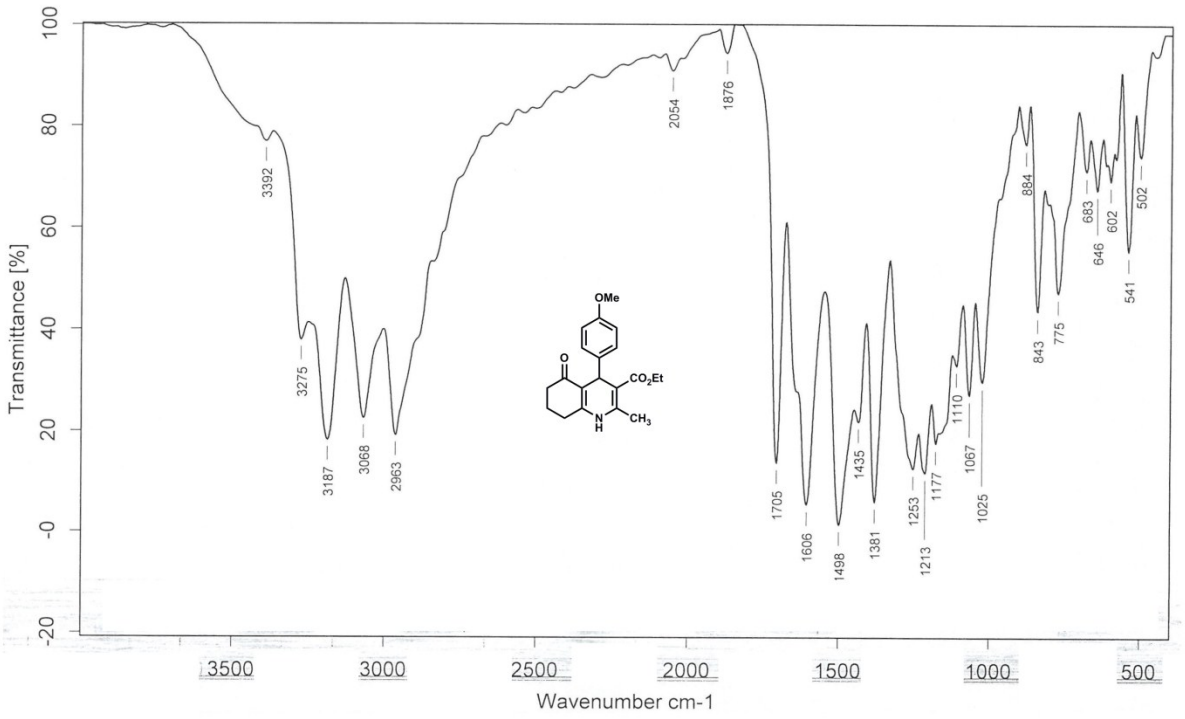


Fig. 38. FT-IR of ethyl 4-(4-methoxyphenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

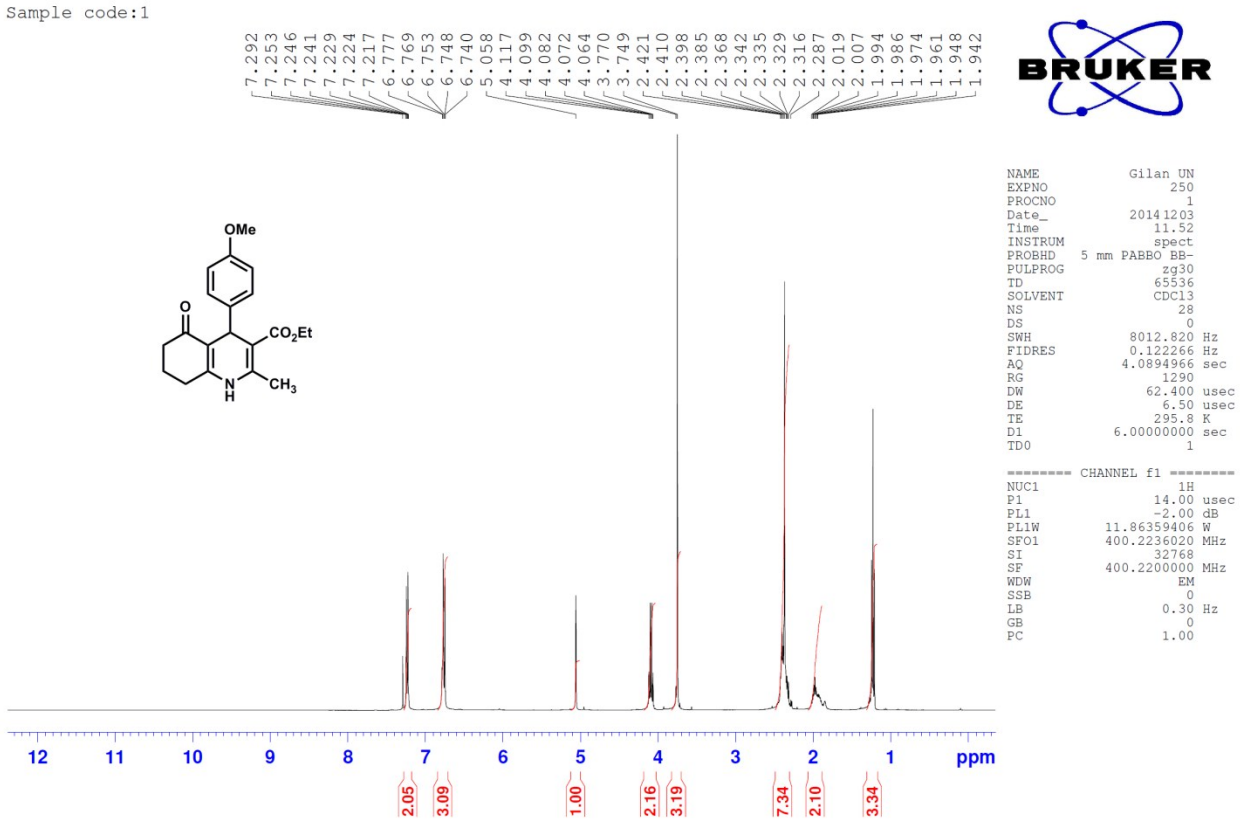
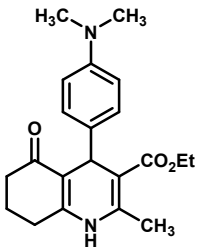


Fig. 39. ^{1}H NMR of ethyl 4-(4-methoxyphenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-(dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (y): Brown solid., m.p. = 204-206 °C., FT-IR (KBr, cm^{-1}): 3277, 3203, 3078, 2951, 1694, 1607, 1490, 1378, 1217, 772., ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.978 (s, 3H), 1.091 (s, 3H), 2.167-2.344 (m, 4H), 2.393 (s, 3H, OCH_3), 2.9 (s, 6H, NCH3), 4.966 (s, 1H, CH), 6.093 (br, 1H, NH), 6.64 (d, *J* = 8 Hz, 2H, ArH),7.18 (d, *J* = 8 Hz, 2H, ArH).



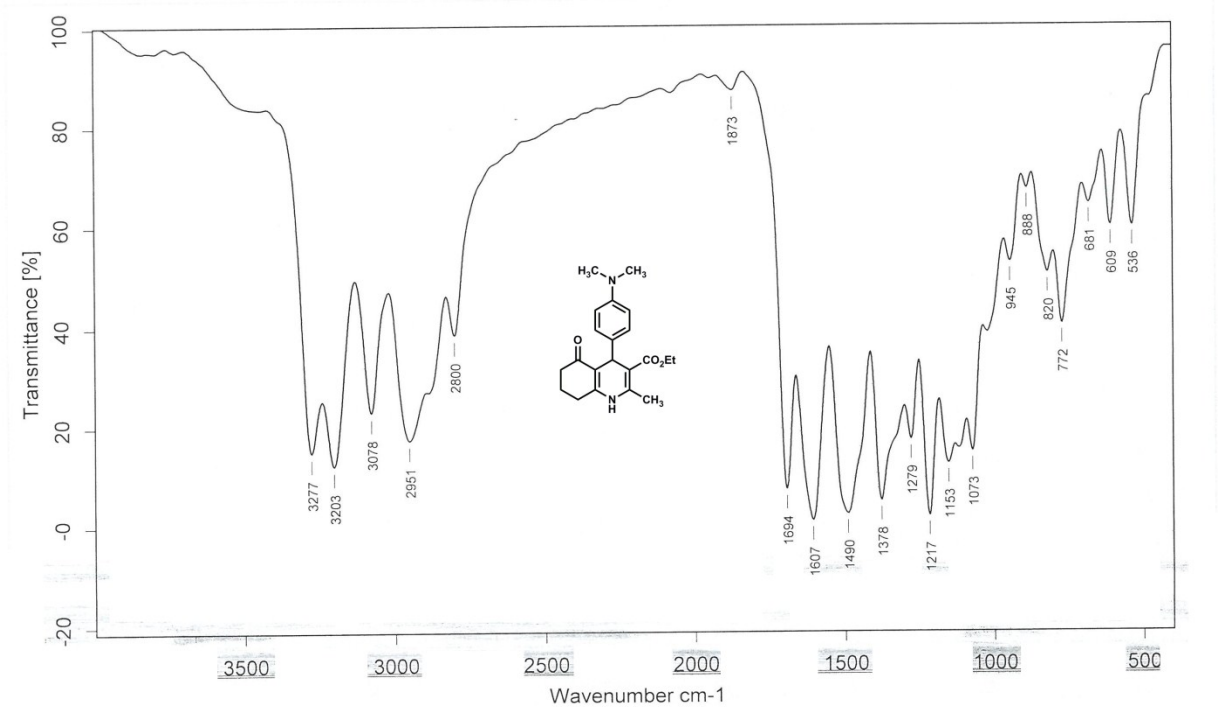


Fig. 40. FT-IR of ethyl 4-(4-(dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

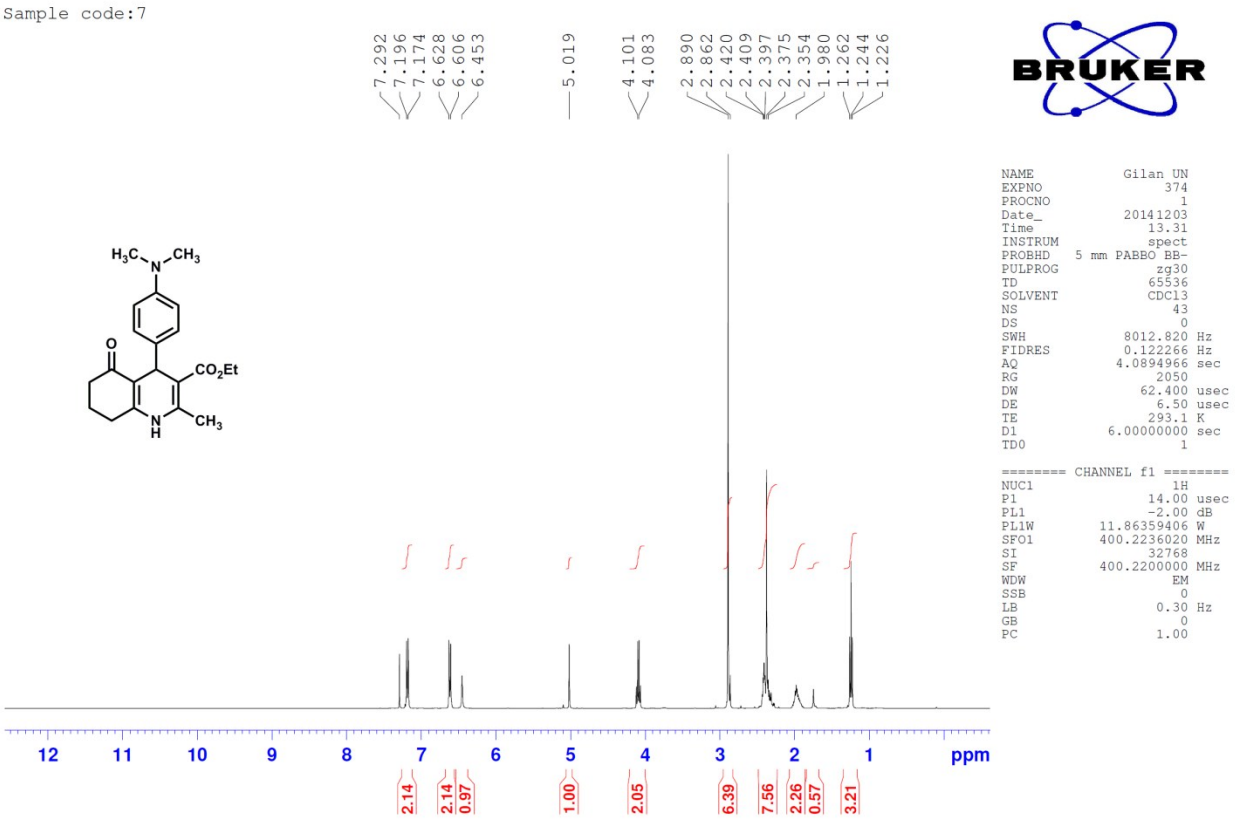
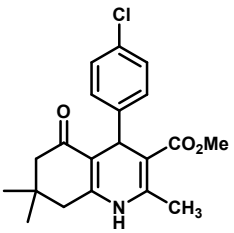


Fig. 41. ^{1}H NMR of ethyl 4-(4-(dimethylamino)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Methyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (z):

Yellow solid., m.p. = 220-221 °C., FT-IR (KBr, cm^{-1}): 3287, 3201, 3076, 2958, 1685, 1605, 1409, 1383, 1335, 1227, 1008, 841., ^{1}H NMR (400 MHz, DMSO-d6) δ 0.948 (s, 3H, CH_3), 1.102 (s, 3H, CH_3), 2.243-2.412 (m, 3H, CH_3), 3.636 (s, 3H, OCH_3), 5.062 (s, 1H, CH), 6.06 (br, 1H, NH), 7.18 (d, *J*= 8.6 Hz, 2H, ArH), 7.28 (d, *J* = 8.4 Hz, 2H, ArH).



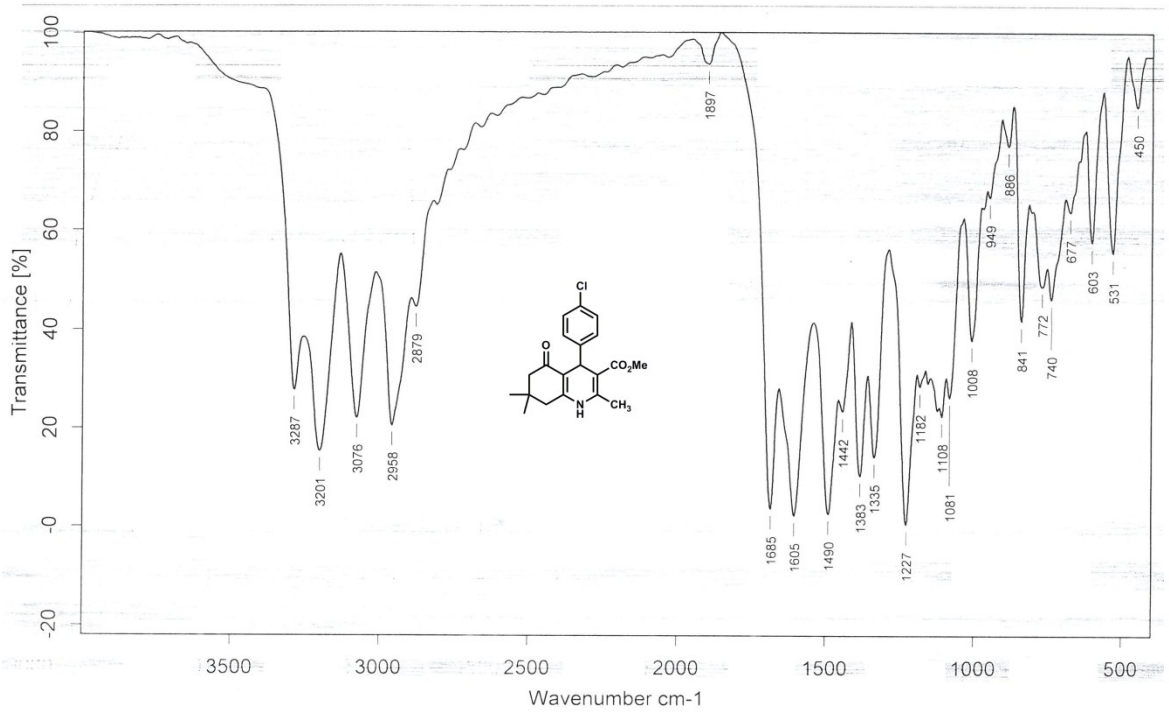


Fig. 42. FT-IR of methyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

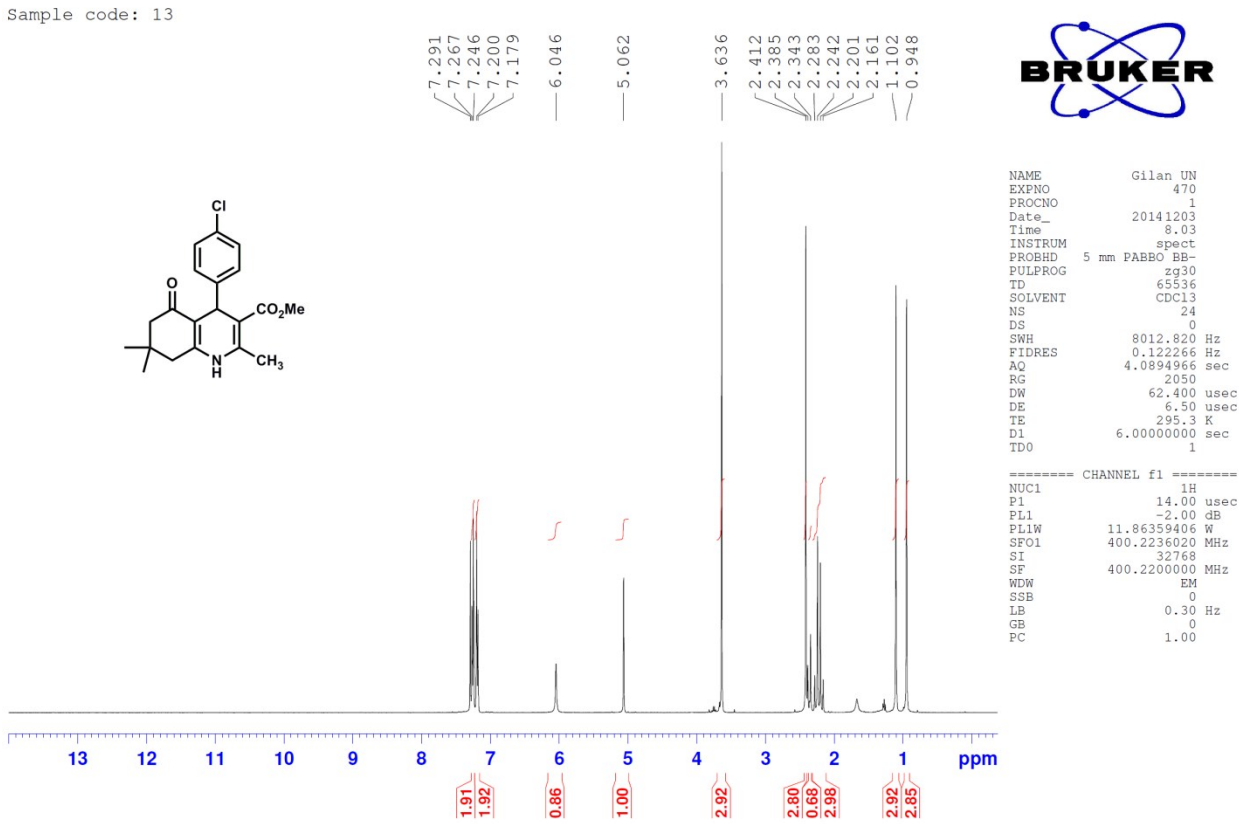


Fig. 43. ^{1}H NMR of methyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(4-(dimethylamino)phenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (dd):

Yellow solid, m.p. = 258-259 °C., FT-IR (KBr, cm^{-1}): 3297, 3208, 3072, 2961, 2776, 1699, 1608, 1485, 1377, 1213, 749., ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.2Hz, 3H), 1.98 (m, 2H), 2.35-2.42 (m, 7H), 2.89 (s, 6H), 4.09 (q, *J* = 7.2 Hz, 2H), 5.02 (s, 1H), 6.45 (s, 1H, NH), 6.62 (d, *J* = 8.8 Hz, 2H, Ar–H),7.18 (d, *J* = 8.8 Hz, 2H, Ar–H)., ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.08, 167.77, 149.83, 149.02, 143.05, 135.95, 128.6, 113.63, 112.36, 106.38, 59.77, 40.78, 37.14, 35.17, 27.37, 21.11, 19.34, 14.3.

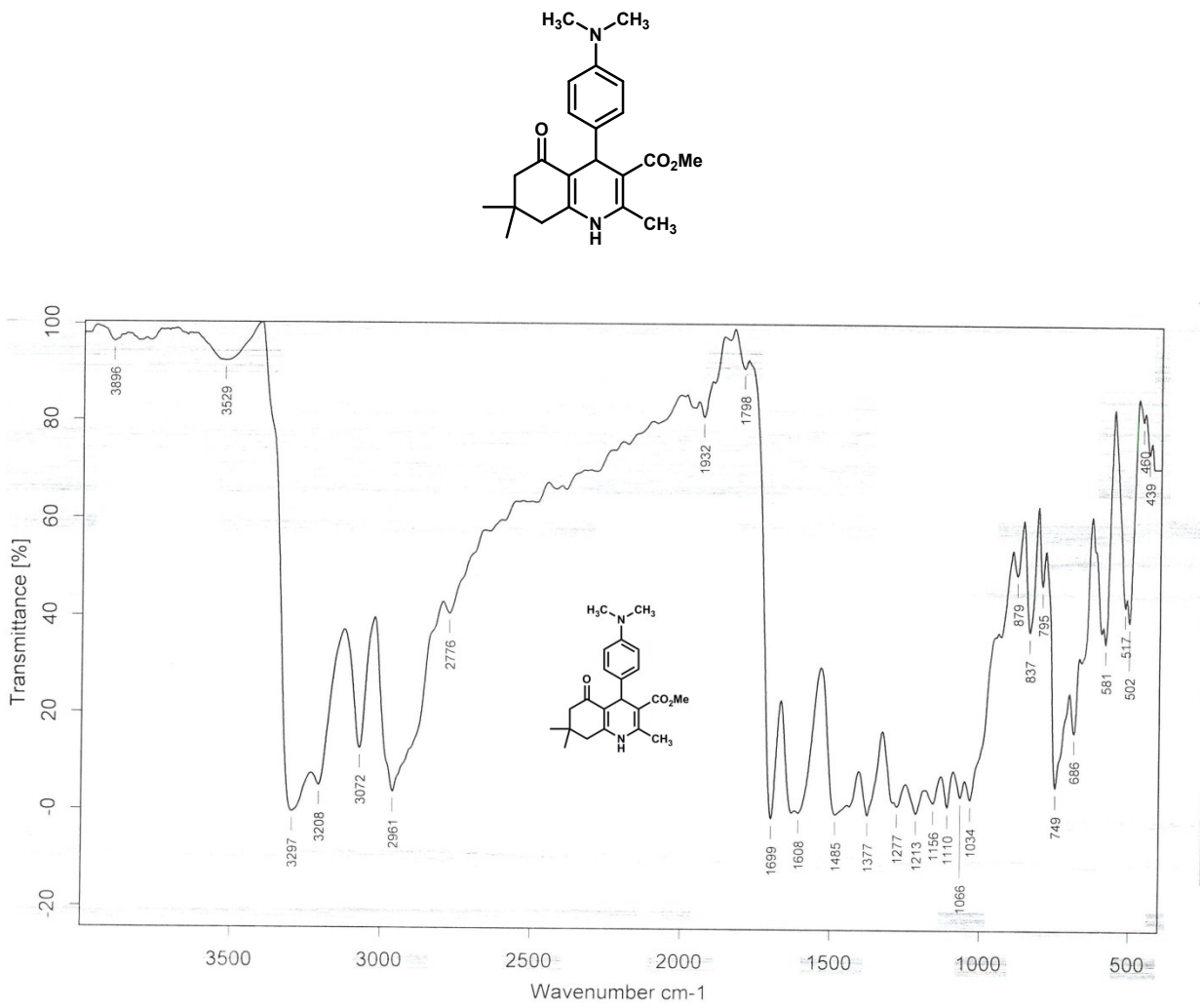


Fig. 44. FT-IR of ethyl 4-(4-(dimethylamino)phenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

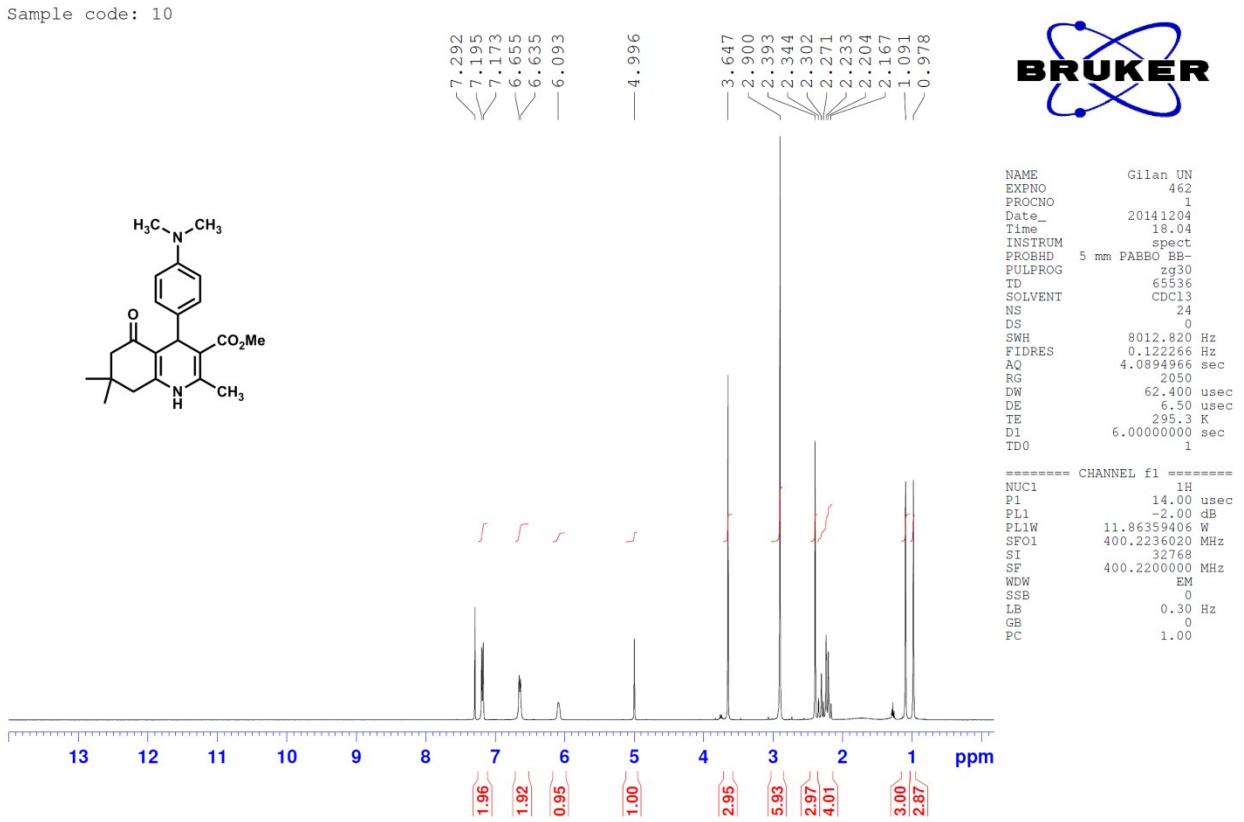
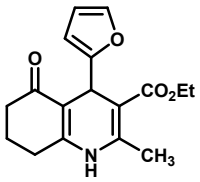


Fig. 45. ^{1}H NMR of ethyl 4-(4-(dimethylamino)phenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(furan-2-yl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (hh): brown solid, m.p = 207-209., FT-IR (KBr, cm^{-1}): 3302, 3070, 2962, 1696, 1606, 1481, 1377, 1275, 1212, 1158, 1108, 1065, 748., ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (t, 3H, *J*=7.2 Hz), 2.01-2.059 (m, 2H), 2.363-2.397 (m, 6H), 2.465-2.487 (m, 3H), 4.11-4.21 (m, 2H, OCH_2), 5.3 (s, 1H, CH), 6.01-6.018 (m, 1H, ArH), 6.14–6.23 (m, 2H, ArH), 7.22 (s, 1H, NH).



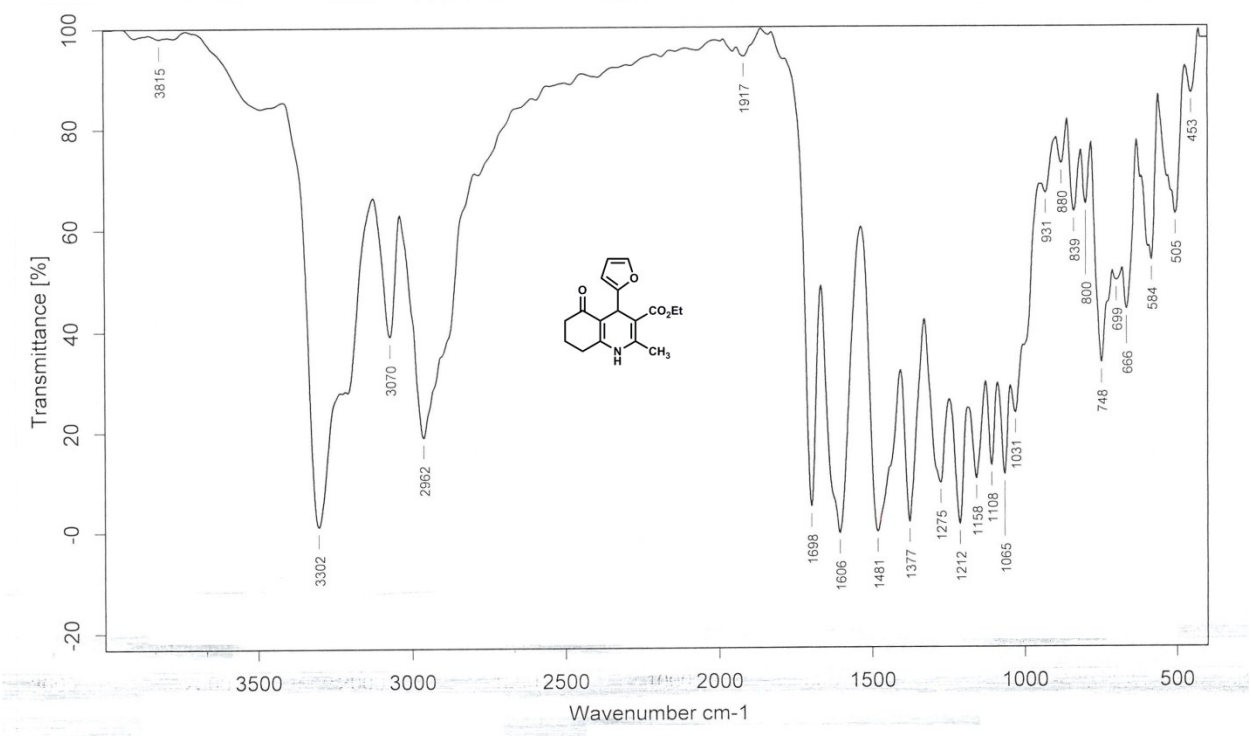


Fig. 46. FT-IR of ethyl 4-(furan-2-yl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

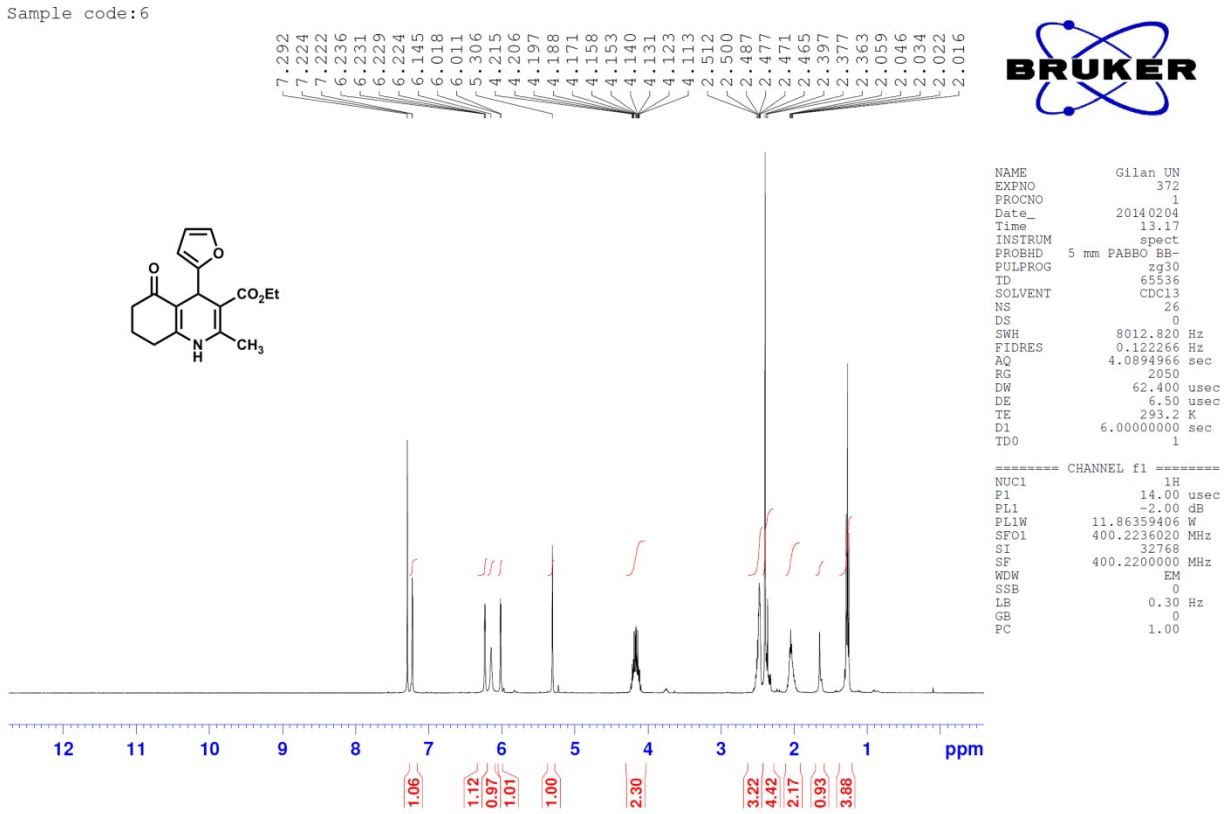
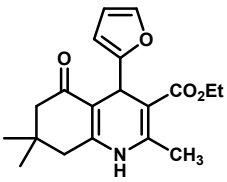


Fig. 47. ^{1}H NMR of ethyl 4-(furan-2-yl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Ethyl 4-(furan-2-yl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (ii): brown solid, m.p = 246-248 °C., FT-IR (KBr, cm^{-1}): 3286, 3211, 3078, 1690, 1614, 1485, 1378, 1285, 1220, 1155, 1079, 752., ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.047 (s, 3H, CH_3), 1.125 (s, 3H, CH_3), 1.28 (t, 3H, *J*=7.4 Hz, CH_3), 2.28 (m, 2H, CH_2), 2.32-2.41 (m, 5H), 4.17 (q, 2H, *J*=7.3 Hz, OCH_2), 5.27 (s, 1H, CH), 5.99-6.04 (m, 2H, ArH), 6.22 (m, 1H, ArH), 7.21 (s, 1H, NH).



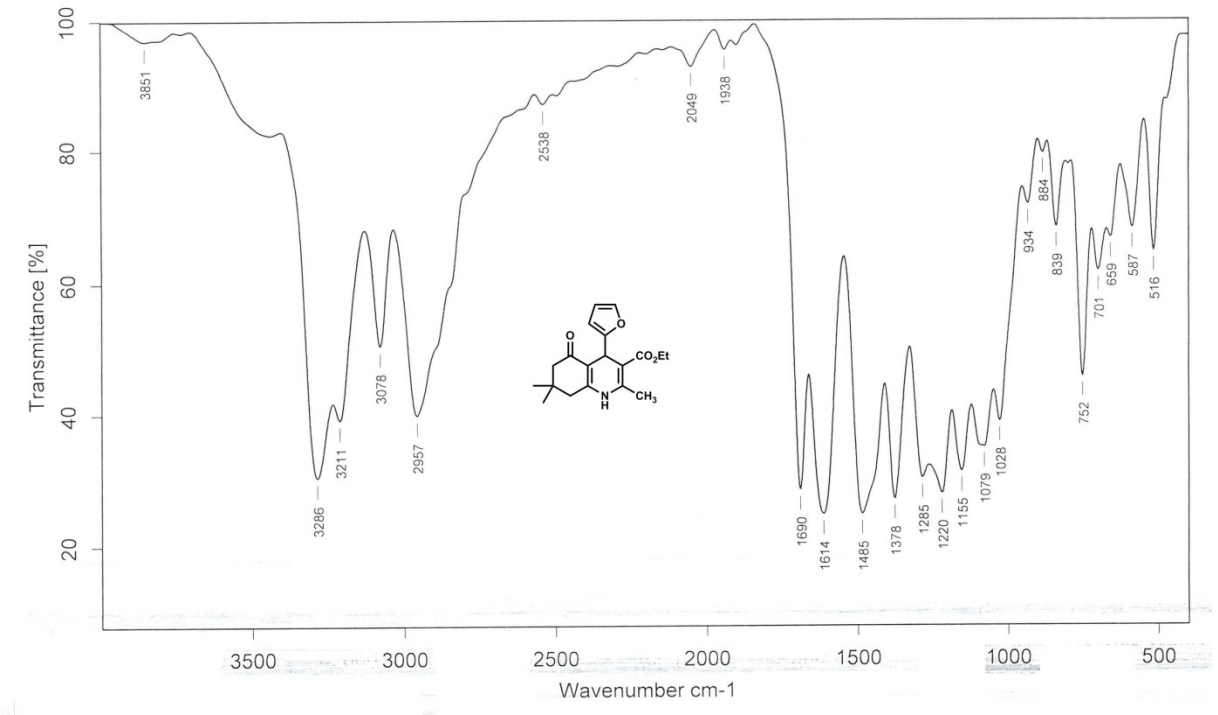


Fig. 48. FT-IR of ethyl 4-(furan-2-yl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

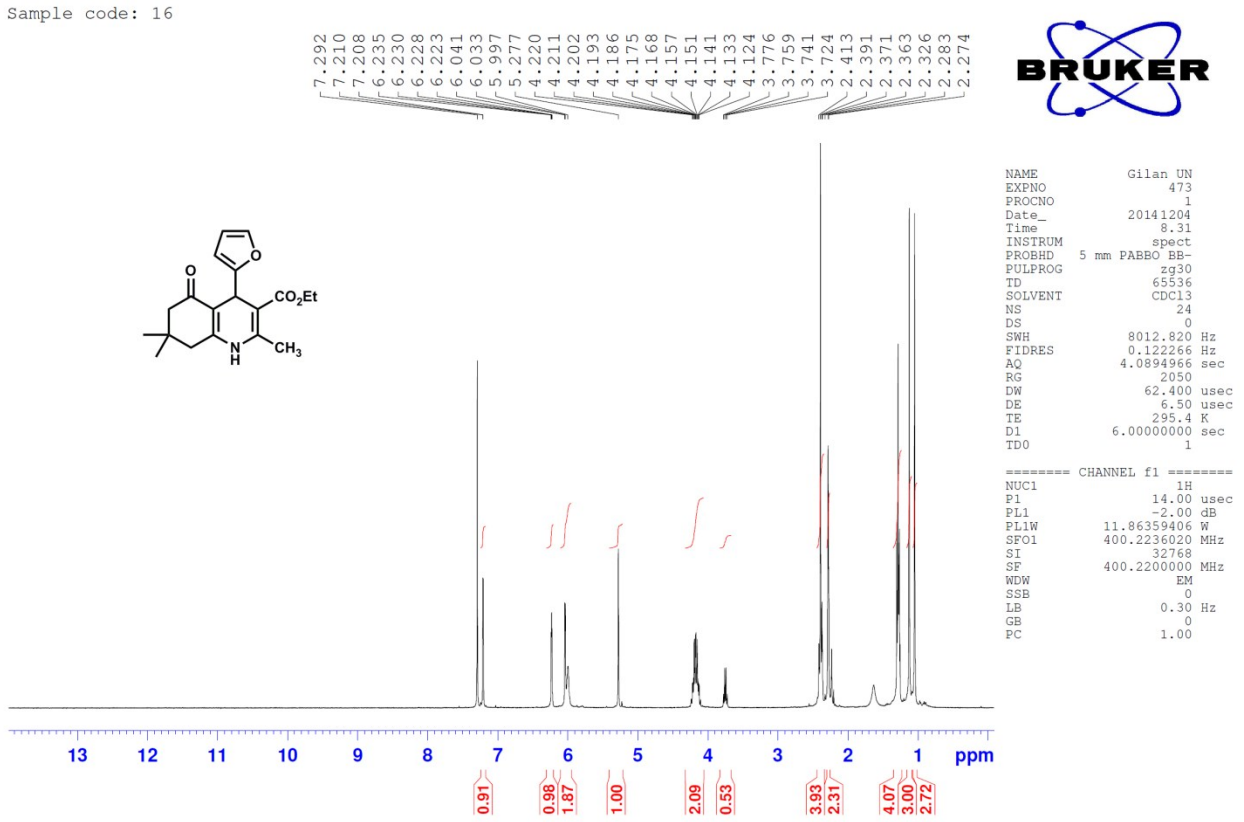


Fig. 49. ^{1}H NMR of ethyl 4-(furan-2-yl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate.

Diethyl 4,4'-(1,3-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate) (II): White solid, m.p. = 281-282 ^{o}C., FT-IR (KBr, cm^{-1}): 3295, 3214, 3079, 2959, 1692, 1614, 1489, 1379, 1218 cm^{-1}., ^{1}H NMR (DMSO, 400 MHz) δ 0.8 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 1.006 (s, 3H, CH_3), 1.015 (s, 3H, CH_3), 1.07 (t, *J*=7.2 Hz, 3H,CH_3), 1.17 (t, *J*=7.2 Hz, 3H, CH_3), 1.90-1.99 (m, 2H), 2.13-2.20 (m, 2H), 2.26-2.31 (8H, 2CH_3 and CH_2), 2.36-244 (m, 2H), 3.9-4.1 (m, 4H, 2CH_2), 4.77 (s, 1H, CH), 4.83(s, 1H, CH), 6.81-7 (m, 3H, ArH), 7 (s,1H, ArH), 9.00 (s, 1H, NH), 9.03(s, 1H, NH).

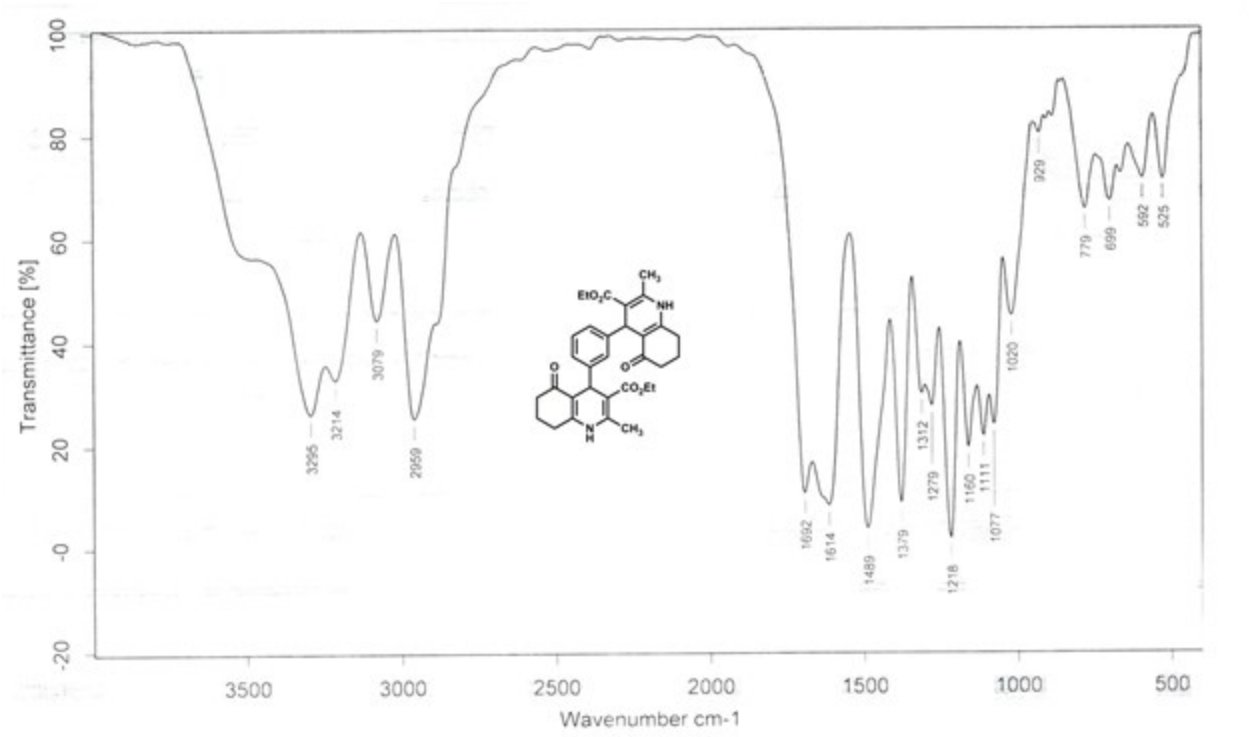


Fig. 50. FT-IR of diethyl 4,4'-(1,3-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate).

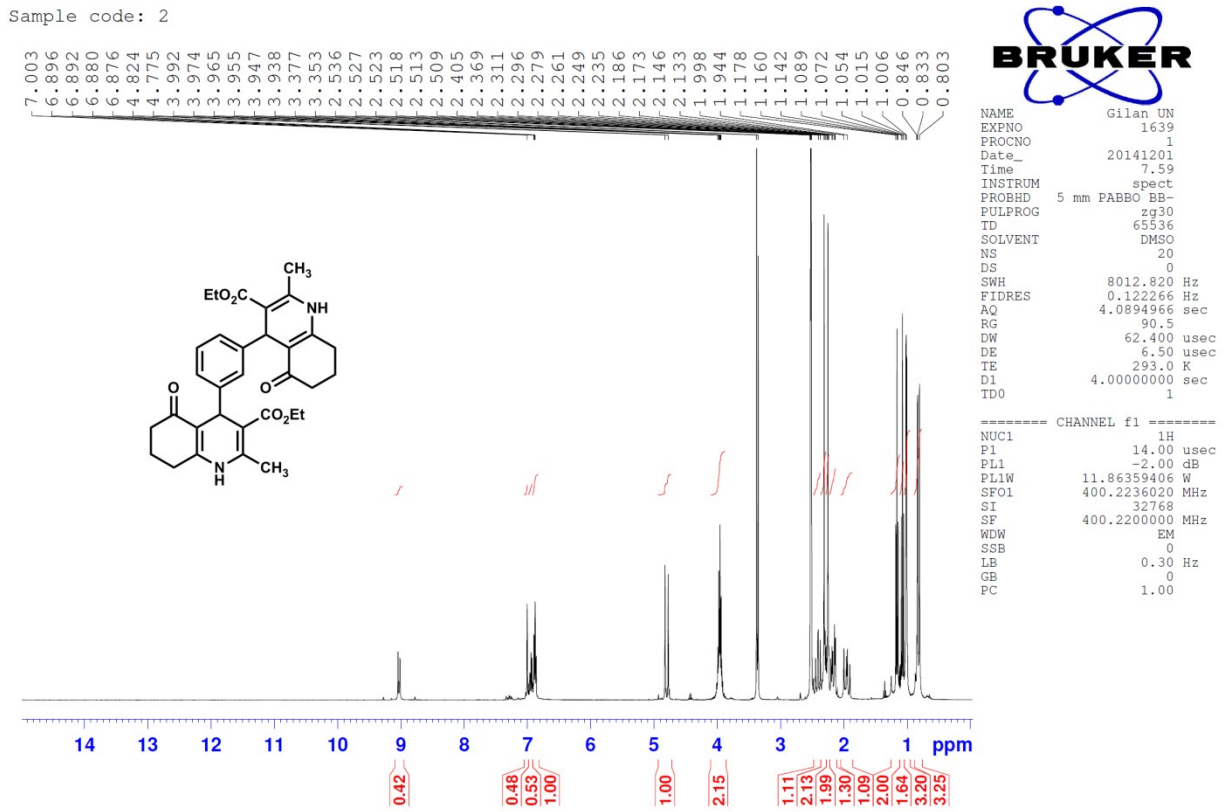


Fig. 51. ^{1}H NMR of diethyl 4,4'-(1,3-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate).

Diethyl 4,4'-(1,4-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate) (mm): White solid; m.p. 293-294 ^{o}C; FT-IR (KBr): ν = 3289, 3211, 3077, 2946, 1692, 1613, 1484, 1379, 1226, 1184 cm^{-1}., ^{1}H NMR (DMSO, 400 MHz): δ = 1.14 (t, 6H, 2CH_3), 1.79-1.81 (m, 4H, 2CH_2), 1.88-1.91 (m, 4H, 2CH_2), 2.17-2.21 (m, 4H, 2CH_2), 2.24 (s, 6H, 2CH_3), 3.9-4.02 (m, 4H, 2CH_2), 4.8 (s, 2H, CH), 6.95 (s, 4H, ArH), 9.15 (s, 1H, NH), 9.24 (s, 1H, NH).

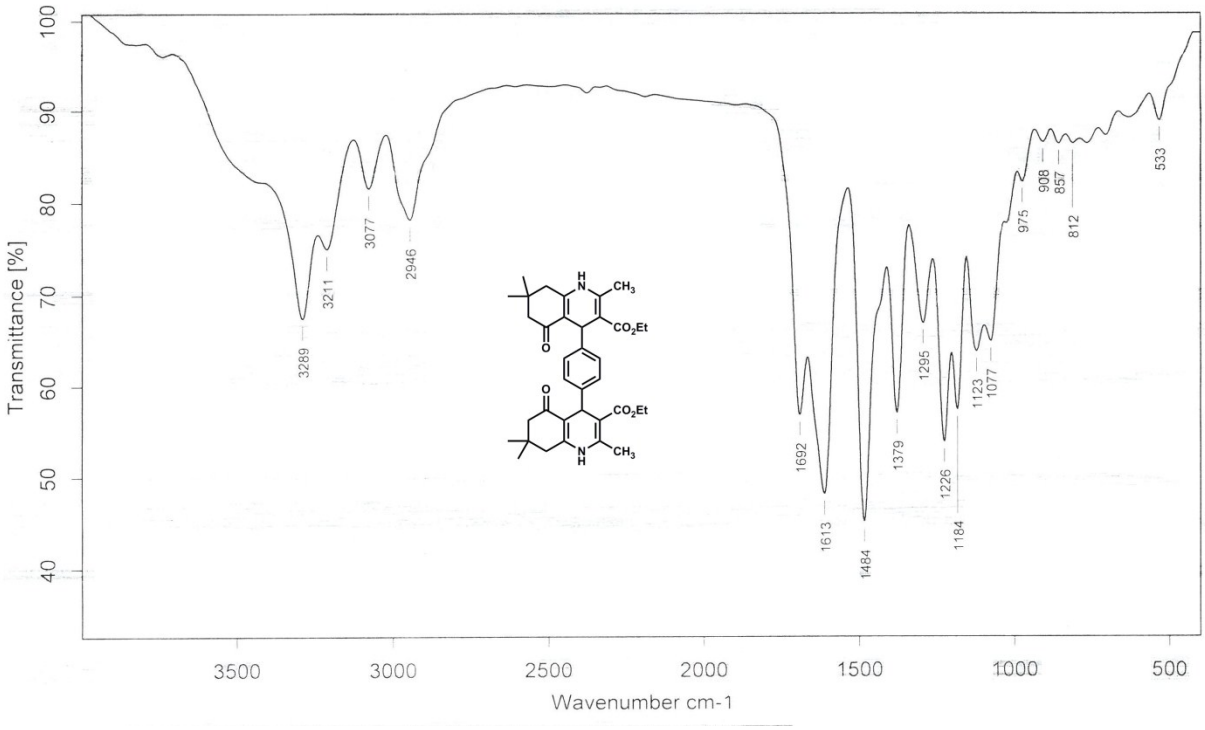


Fig. 52. FT-IR of diethyl 4,4'-(1,4-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate).

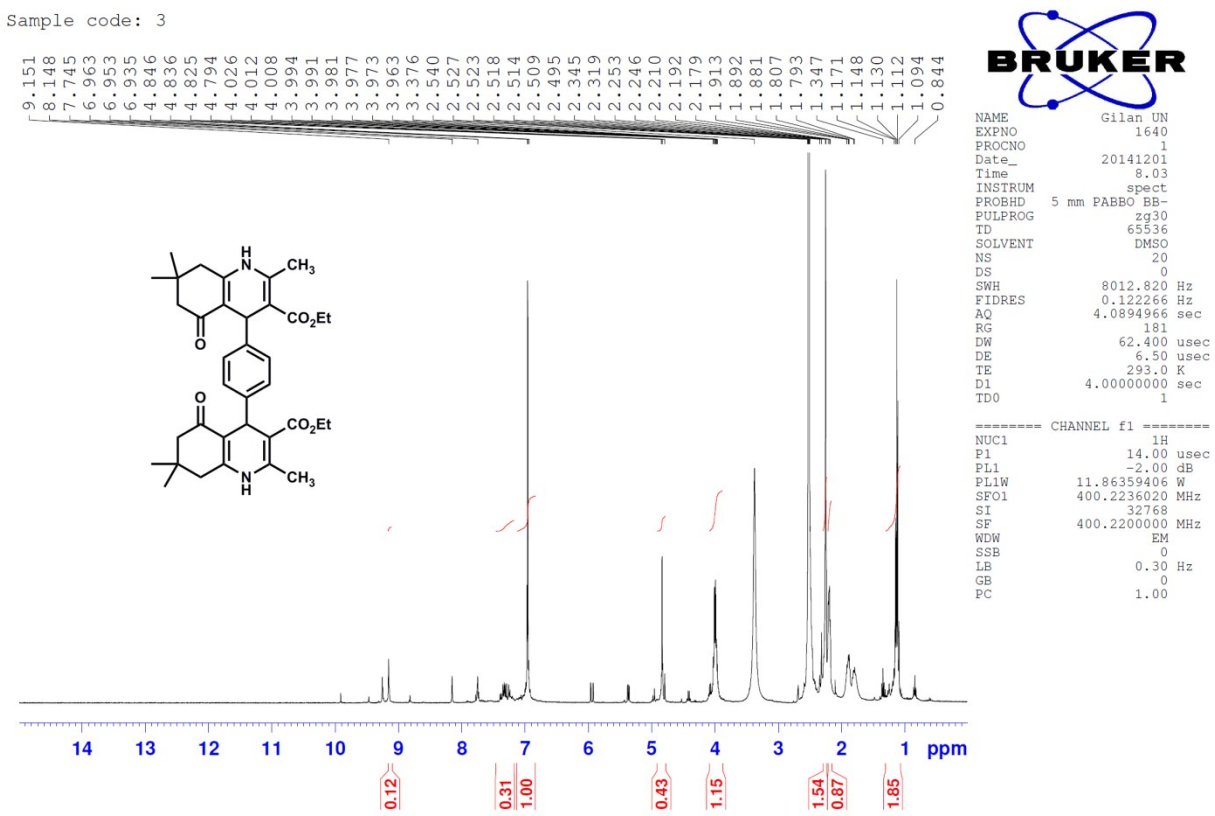


Fig. 53. ^{1}H NMR of diethyl 4,4'-(1,4-phenylene)bis(2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate).