Thermally reversible solidification of novel ionic liquid [im]HSO_4 by self-nucleated rapid crystallization: Investigations of ionic conductivity, thermal properties, and catalytic activity

Michał Bielejewski*[a], Mahdi Ghorbani[b]*, Mohammad Ali Zolfigol[c]*, Jadwiga Tritt-Goc[a], Soheila Noura[b], Mahdi Narimani[b] and Mohsen Oftadeh[b]

[a]*Institute of Molecular Physics, Polish Academy of Sciences, ul. M. Smoluchowskiego 17, 60-179 Poznan, Poland.*
[b]*Chemistry Department, Payame Noor University, Tehran, Iran.*
[c]*Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Po. Box: 6517838683, Iran.*

Electronic Supplementary Information (ESI)

*Corresponding Author:
Dr eng. Michal Bielejewski
Institute of Molecular Physics, PAS
60-179 Poznań, Poland
phone: +48 061 8695186
e-mail: bielejewski@ifmpan.poznan.pl

Mahdi Ghorbani
Chemistry Department, Payame Noor University, Tehran, Iran.
E-mail: ghorbanii.mahdi@gmail.com

Prof. Mohammad Ali Zolfigol
Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University
Hamedan, Iran
Phone: +988138282807, *Fax: +988138380709*

e-mail: zolfi@basu.ac.ir & mzolfigol@yahoo.com

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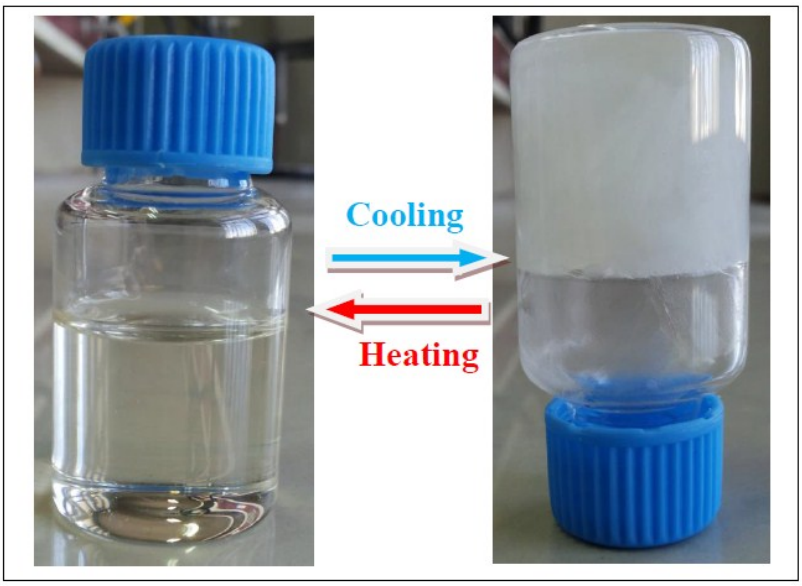


Figure S1. Images from nano crystal ionic liquid [im]HSO_4

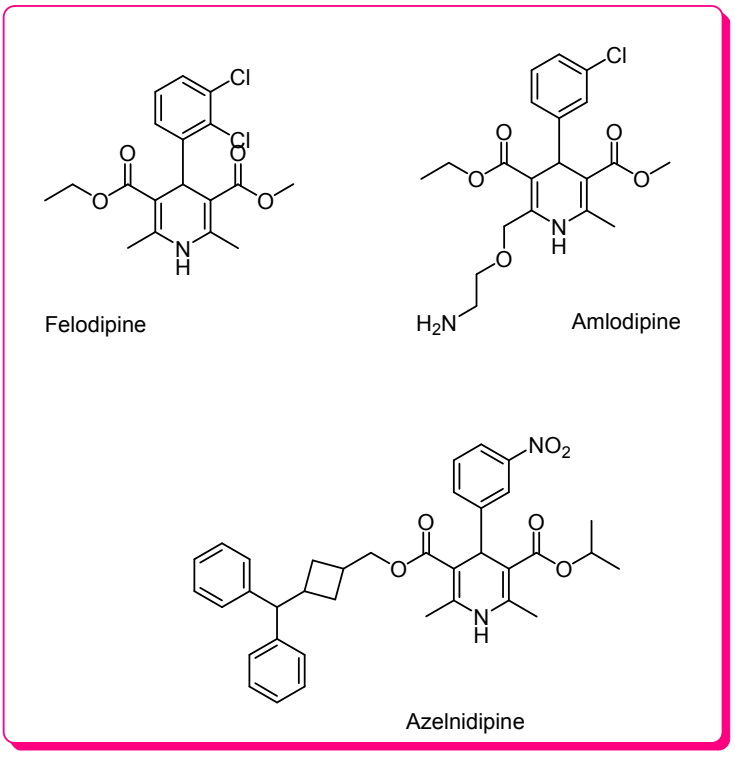


Figure S2. Typical dihydropyridine drugs

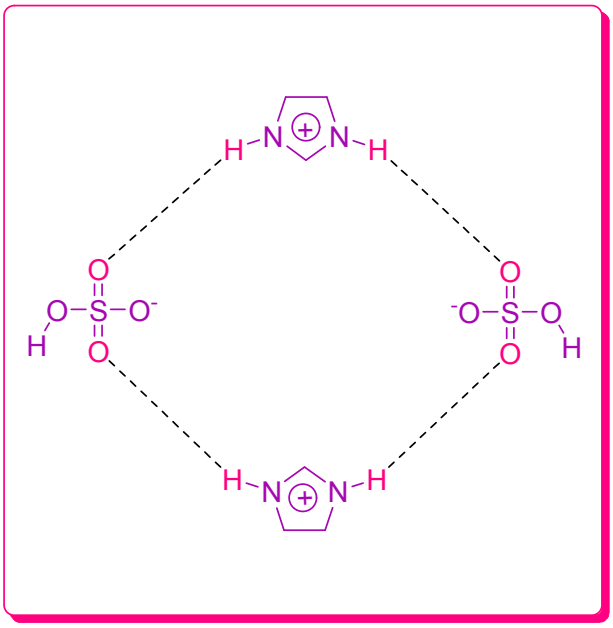


Figure S3. Molecular self-assembly of nano crystal ionic liquid [im]HSO_4 via hydrogen bonding

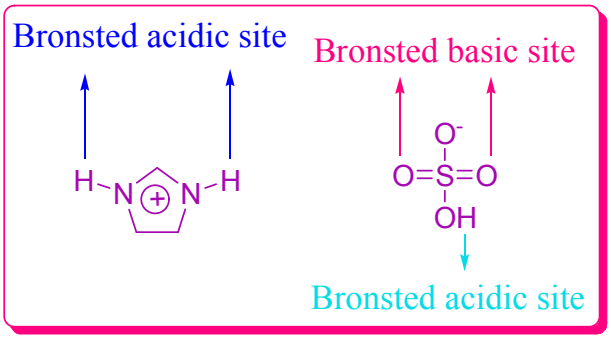


Figure S4. The structure of nano crystal ionic liquid [im]HSO_4

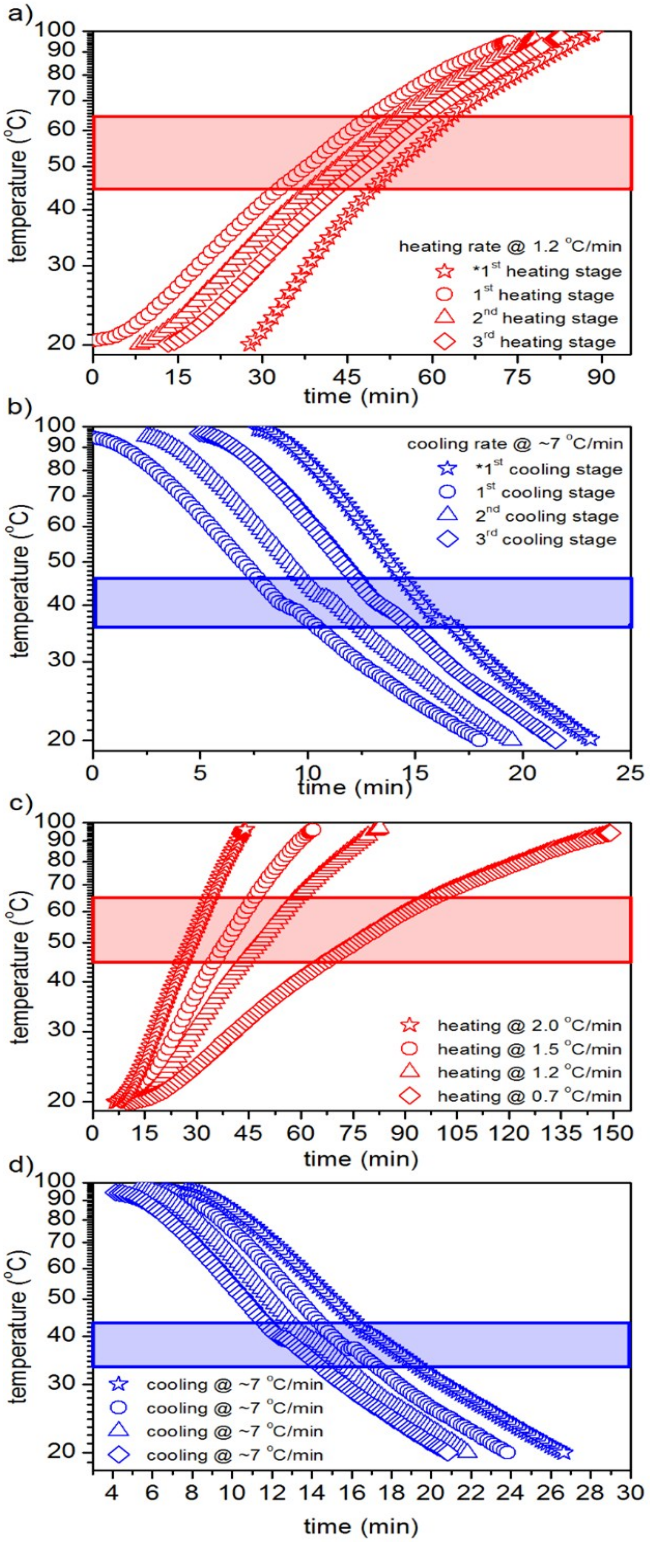


Figure S5. Temperature change of the [im]HSO_4 sample during TSC measurement for repeating heating cycles at 1.2°C/min (a) and cooling cycles at ~7°C/min (b) and for different heating rates during heating cycles (c) and corresponding cooling cycles (d). Red and blue rectangles denote the temperature region of observed anomalies in σ_{DC}.

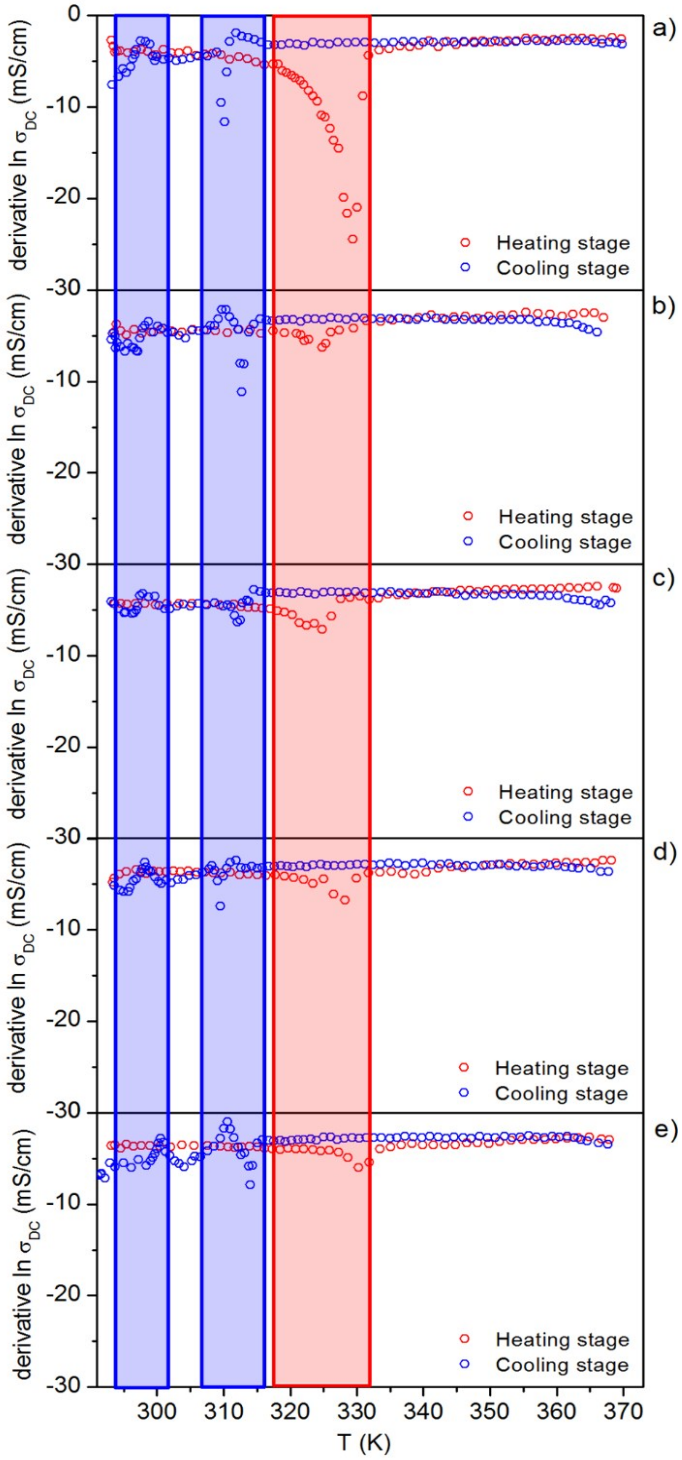


Figure S6. The derivative of the temperature dependence of the direct current conductivity σ_{DC} registered for [im]HSO_4 sample for heating and cooling cycles at 0.7°C/min heating rate 1st cycle (a), at 0.7°C/min heating rate 2nd cycle (b), at 1.2°C/min heating rate 1st(c), at 1.5°C/min heating rate 1st(d), at 2.0°C/min heating rate 1st(e).

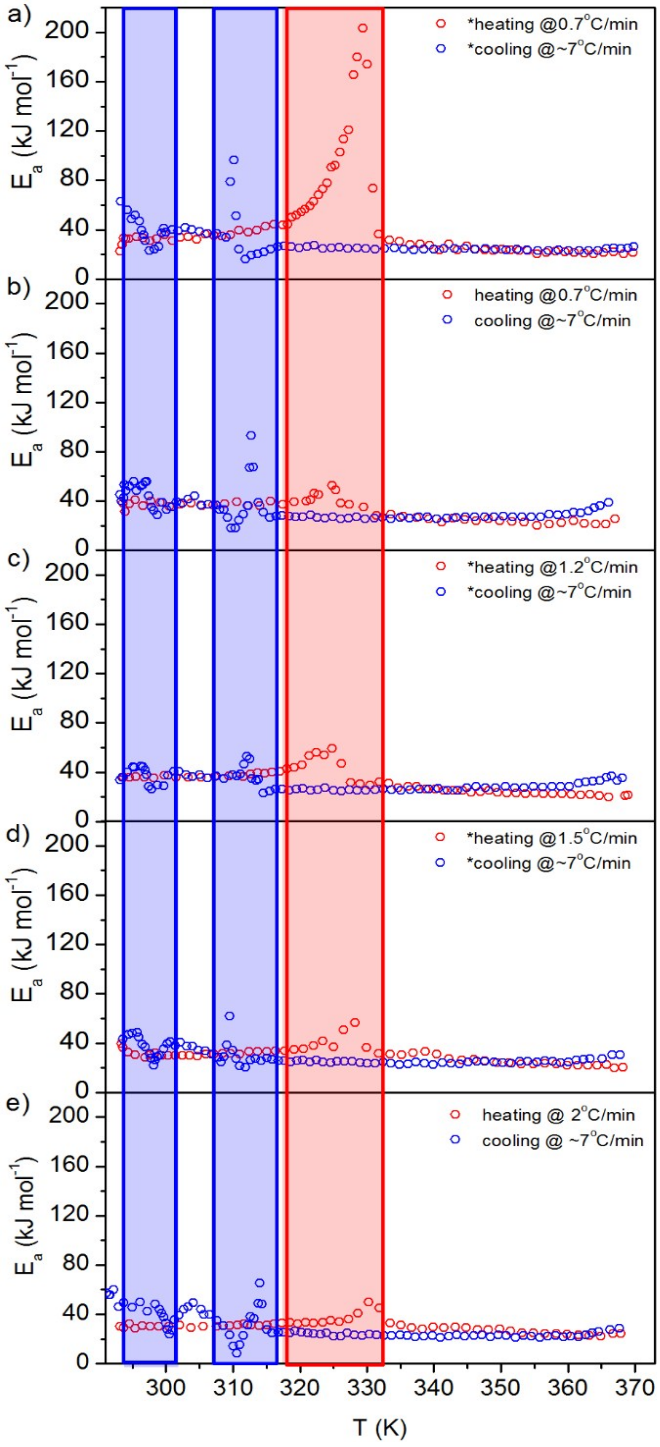


Figure S7. The temperature dependence of activation energy of the conduction process registered for IL1 sample for heating and cooling cycles at 0.7°C/min heating rate 1st cycle (a), at 0.7°C/min heating rate 2nd cycle (b), at 1.2°C/min heating rate 1st cycle (c), at 1.5°C/min heating rate 1st(d), at 2.0°C/min heating rate 1st(e).

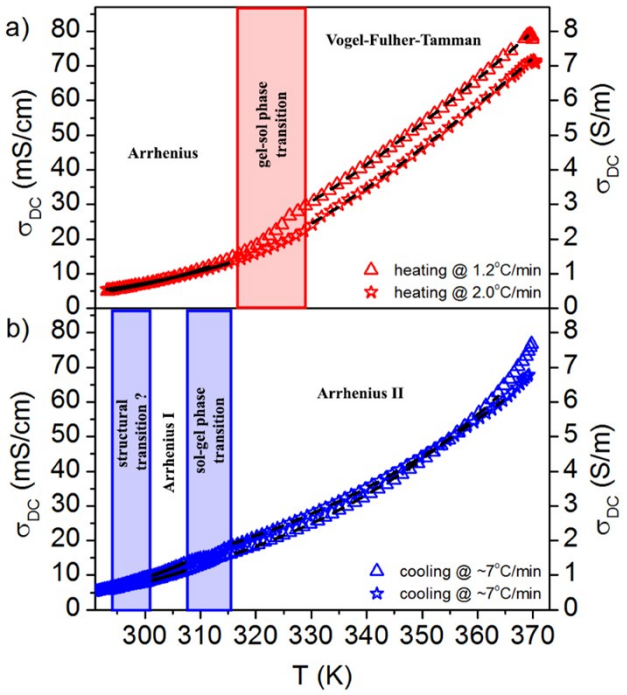


Figure S8. The temperature dependence of the direct current conductivity σ_{DC} registered for [im]HSO_4 sample at 0.7°C/min and 1.2°C/min heating rates (a) and corresponding cooling stages (b). The solid lines represents the best fits of Eq. (2) and dashed lines the best fits of Eq. (3) to the experimental data recorded in heating and cooling stages. The rectangles denote the regions where the anomalies were observed.

Table S1. The theoretical physical magnitudes extracted from the best fit of the Arrhenius-type and VFT-type equations (Eq. 2 and Eq. 3) to the experimental data during heating stage.

heating stage					
	Arrhenius		Vogel-Fulcher-Tamman		
heating rate	E_a (kJ/mol)	σ_∞ (mS/cm)	E_a (kJ/mol)	σ_∞ (mS/cm)	T_g (K)
0.7 °C/min	36.3	1.65E7	3.9	1387	207.2
1.2 °C/min	36.2	1.39E7	3.4	1153	218.2
1.5 °C/min	30.6	1.57E6	2.7	788	236.6
2.0 °C/min	30.3	1.40E6	2.8	887	236.9

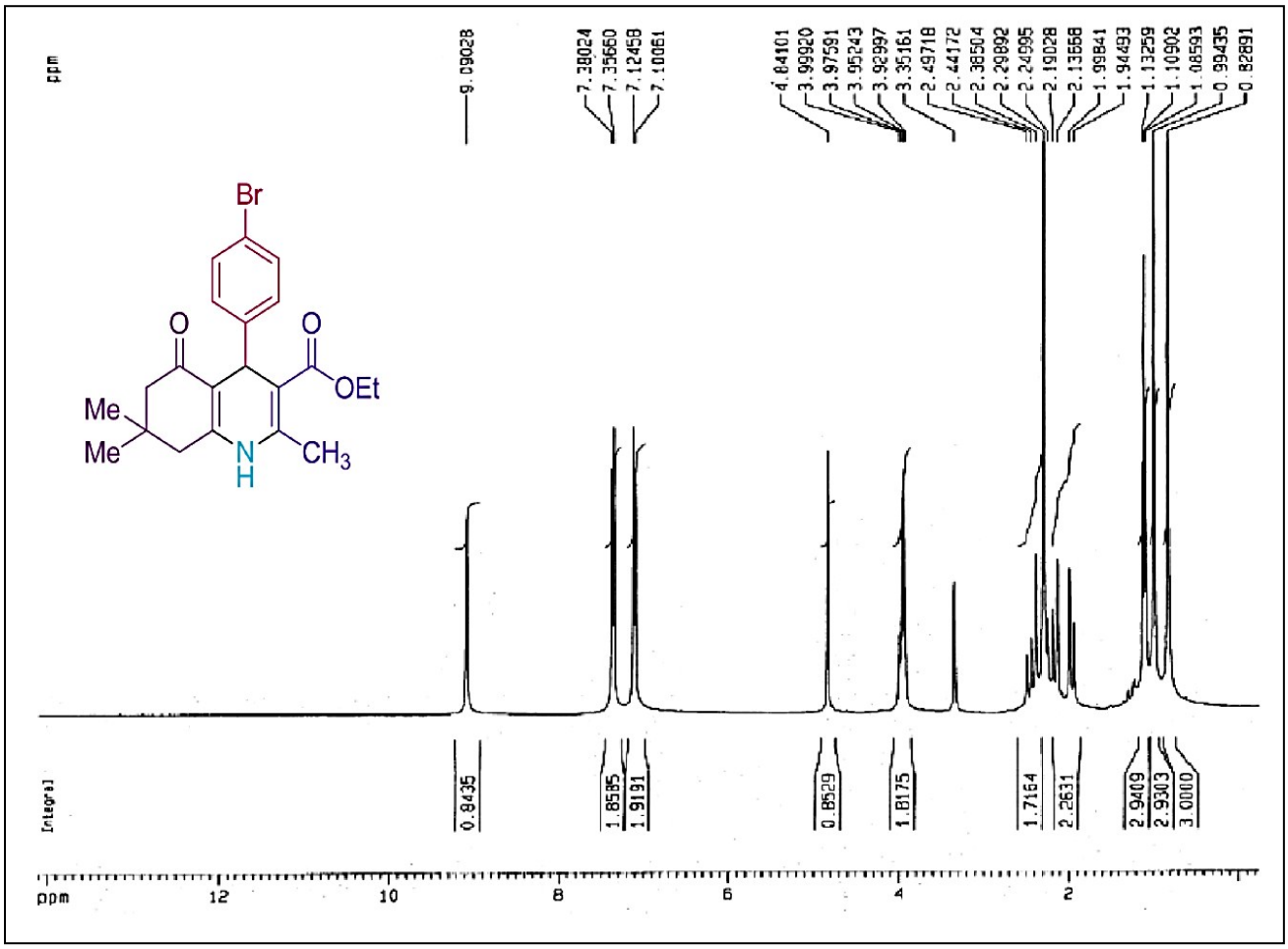
Table S2. The theoretical physical magnitudes extracted from the best fit of the Arrhenius-type equations (Eq. 2) to the experimental data during cooling stage.

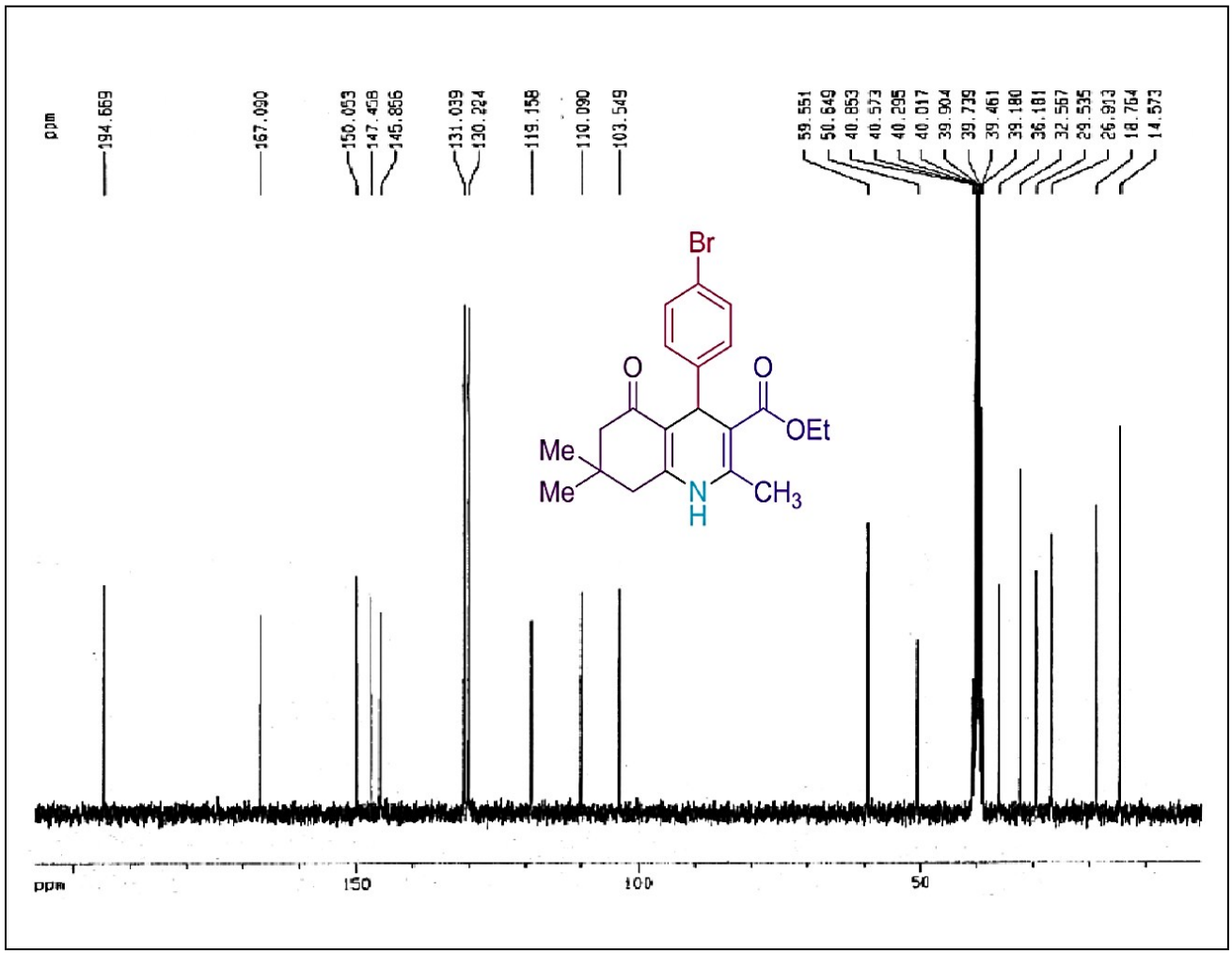
cooling stage				
	Arrhenius I		Arrhenius II	
cooling rate	E_a (kJ/mol)	σ_∞ (mS/cm)	E_a (kJ/mol)	σ_∞ (mS/cm)
~7 °C/min	37.9	3.38E7	26.6	4.22E5
~7 °C/min	37.1	2.30E7	26.8	4.43E5
~7 °C/min	36.4	2.01E7	24.4	1.89E5

~7 °C/min	41.7	1.66E8	22.6	1.04E5

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

White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.83 (s, 3H), 0.99 (s, 3H), 1.10 (t, J = 6.9 Hz, 3H), 1.96 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.1 Hz, 1H), 2.29 (s, 3H), 2.38-2.49 (m, 2H), 3.97 (q, J = 7.0 Hz, 2H), 4.84 (s, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 9.09 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.6, 18.8, 26.9, 29.5, 32.6, 36.2, 50.6, 59.5, 103.5, 110.1, 119.1, 130.2, 131.0, 145.8, 147.4, 150.0, 167.1, 194.7.

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Me
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CH3
ppm
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100
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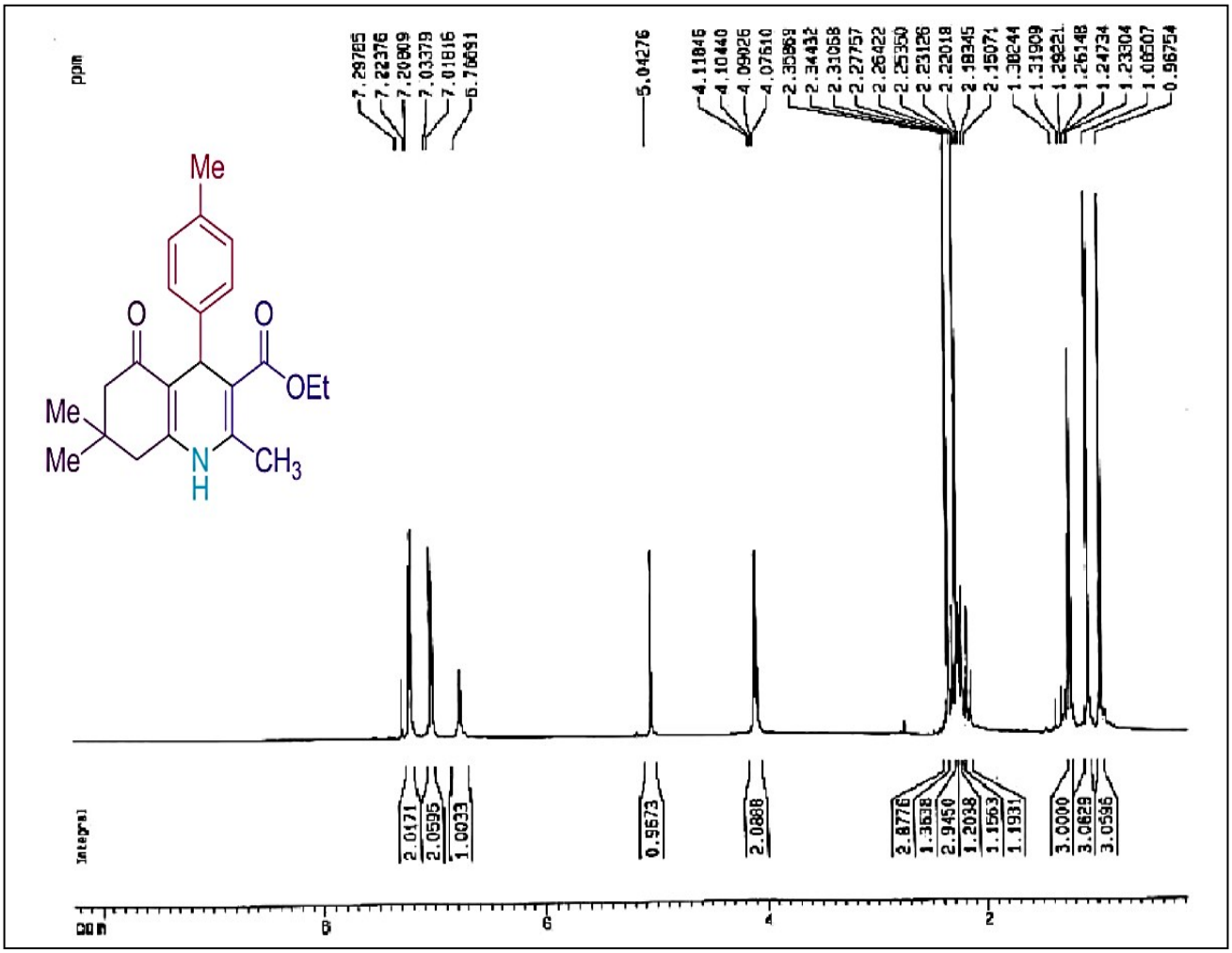
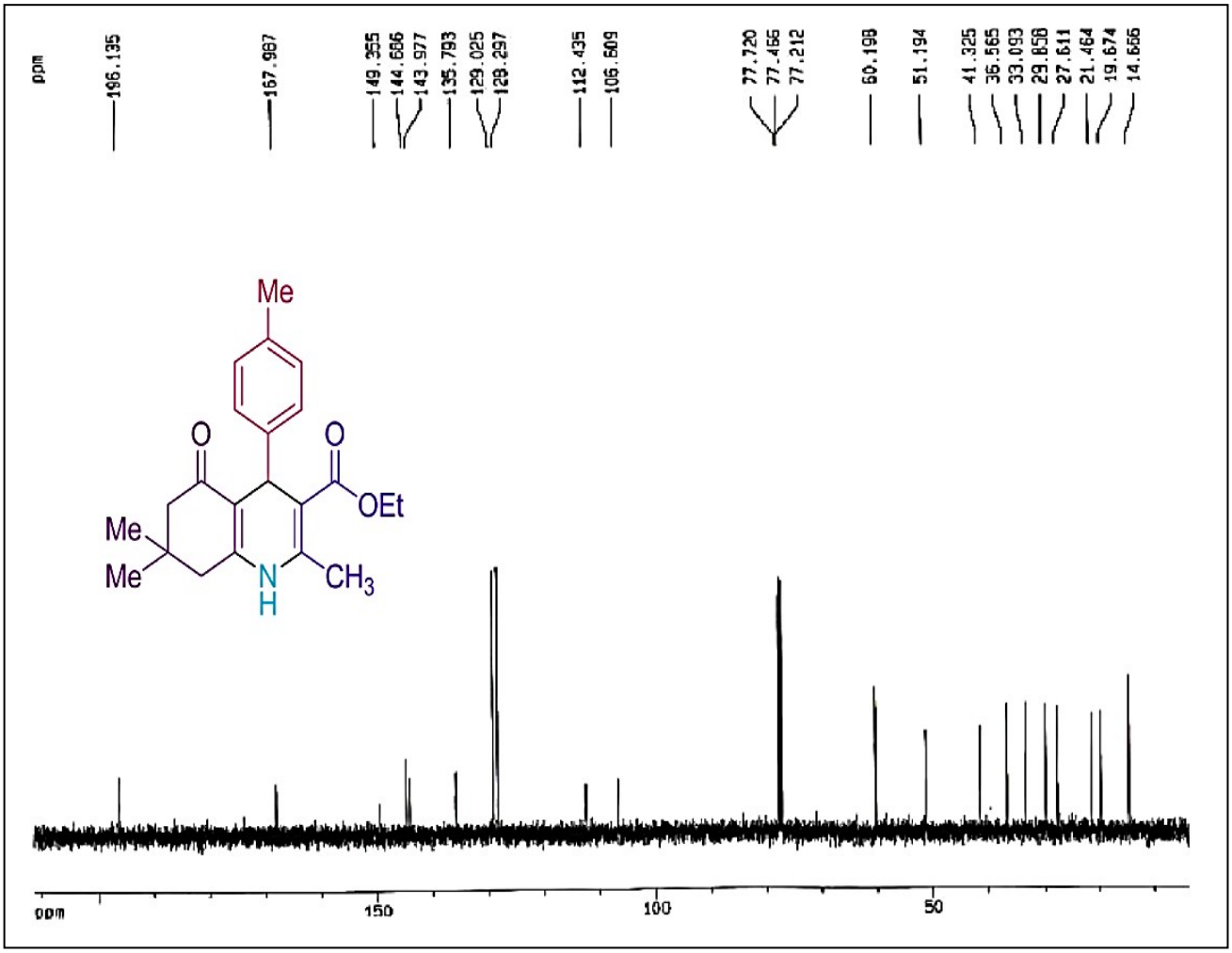
Ethyl 4-(p-tolyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylat

White solid, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.96 (s, 3H), 1.08 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 2.15-2.31 (m, 7H), 2.35 (s, 3H), 4.09 (q, J = 7.1 Hz, 2H), 5.04 (s, 1H), 6.76 (s, 1H), 7.02 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 14.7, 19.7, 21.5, 27.6, 29.8, 33.1, 36.6, 41.3, 51.2, 60.2, 106.6, 112.4, 128.3, 129.0, 135.8, 143.9, 144.7, 149.3, 167.9, 196.1.

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CH3
ppm
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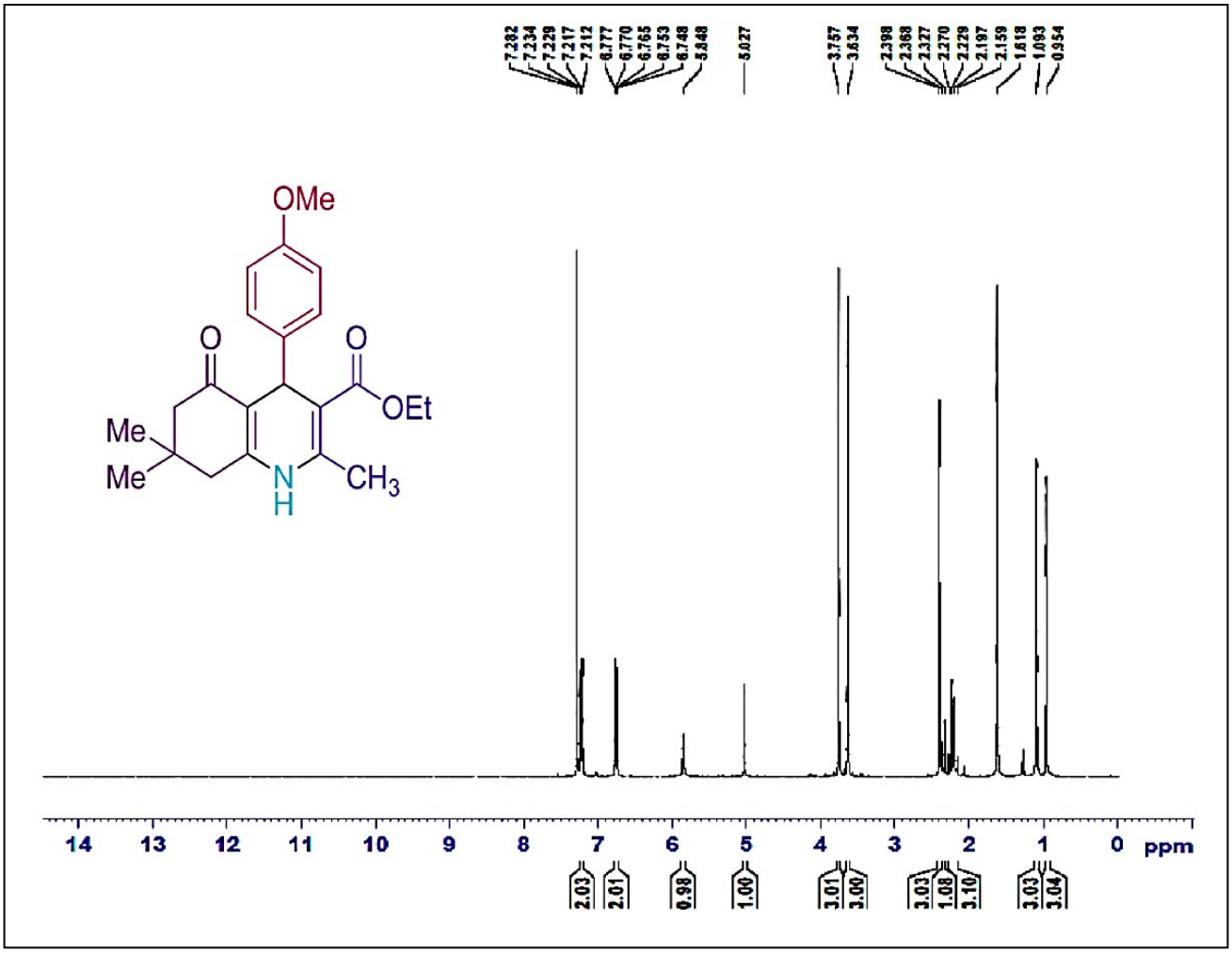
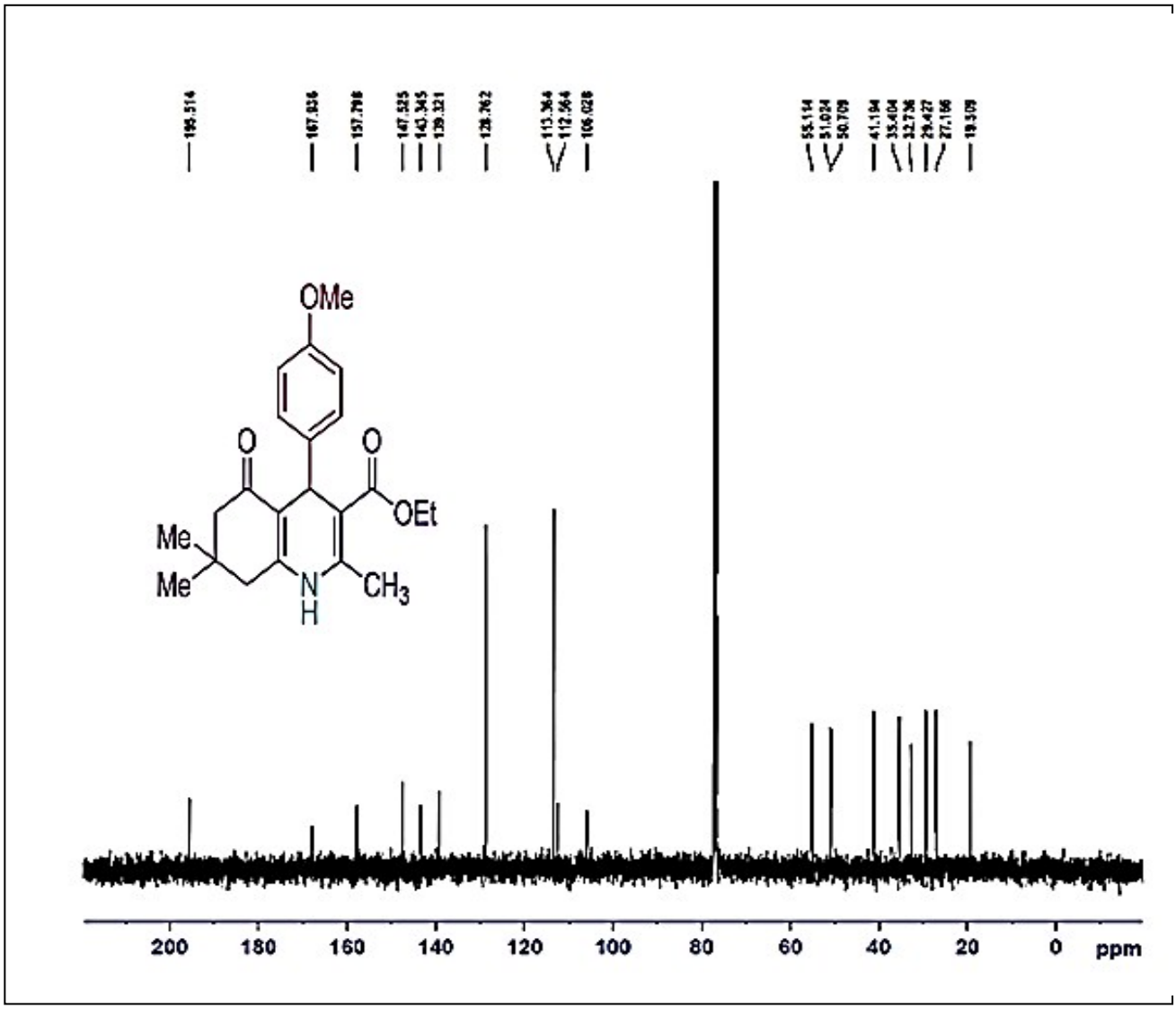
100
50

4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.85 (s, 3H), 1.00 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H), 1.96 (d, J = 16.0 Hz, 1H), 2.15 (d, J = 16.1 Hz, 1H), 2.27 (s, 3H), 2.37-2.49 (m, 2H), 3.66 (s, 3H), 3.97 (q, J = 7.0 Hz, 2H), 4.79 (s, 1H), 6.73 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 8.99 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 35.4, 50.6, 55.3, 59.4, 104.4, 110.7, 113.5, 128.8, 140.5, 145.1, 149.7, 157.7, 167.4, 194.

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Me
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H
CH3
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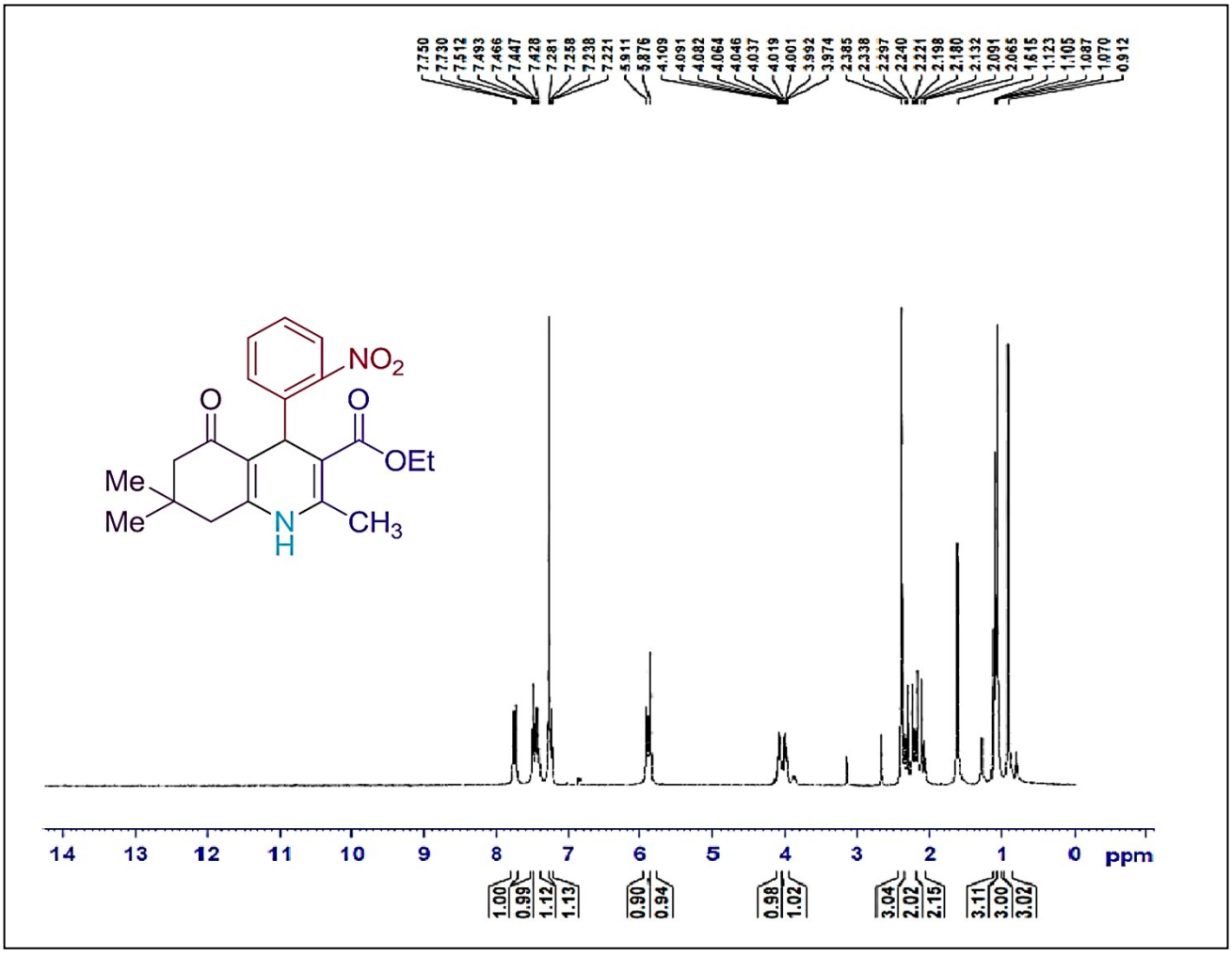
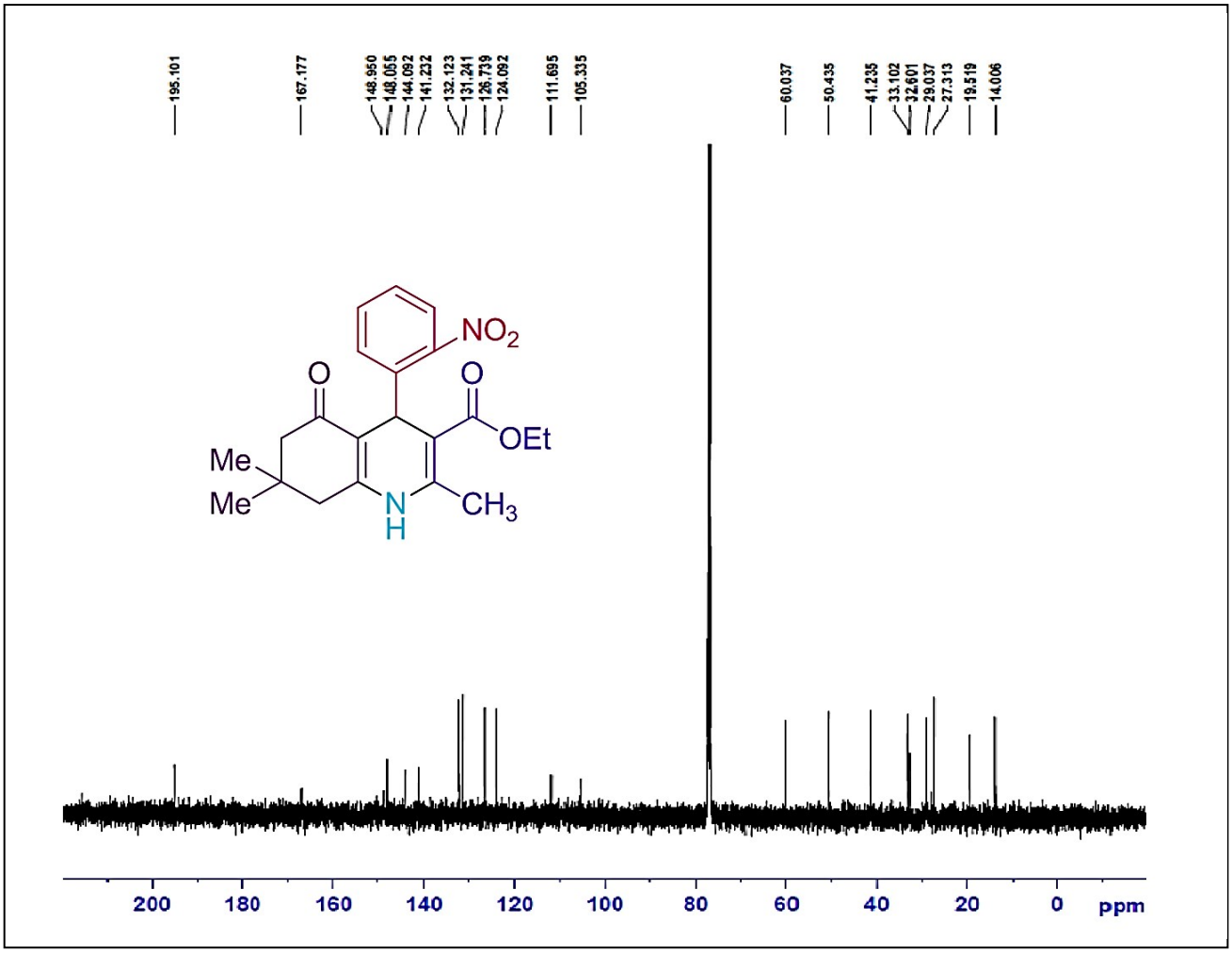
120
100
80
60
40
20
0
ppm

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

yellow solid, ^{1}H NMR: (400 MHz $CDCl_3$): δ (ppm) 0.91 (s, 3H), 1.09 (q, J =7.2, 3H), 1.61 (s, 3H), 2.07 (d, J =10.4, 1H), 2.18 (d, J =7.2, 1H), 2.30 (d, J=7.6, 1H), 2.29 (s, 1H), 2.38 (s, 3H), 3.97-4.10 (m, 2H), 5.87 (s, 1H), 5.91 (s, 1H), 7.23 (t, J = 8, 1H), 7.44 (t, J =7.6, 1H) 7.50 (d, J =7.6, 1H), 7.74 (d, J = 8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.0, 19.5, 27.3, 29.0, 32.6, 33.1, 41.2, 50.4, 60.0, 105.3, 111.6, 124.0, 126.7, 131.2, 132.1, 141.2, 144.0, 148.0, 148.9, 167.1, 195.1

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CH3
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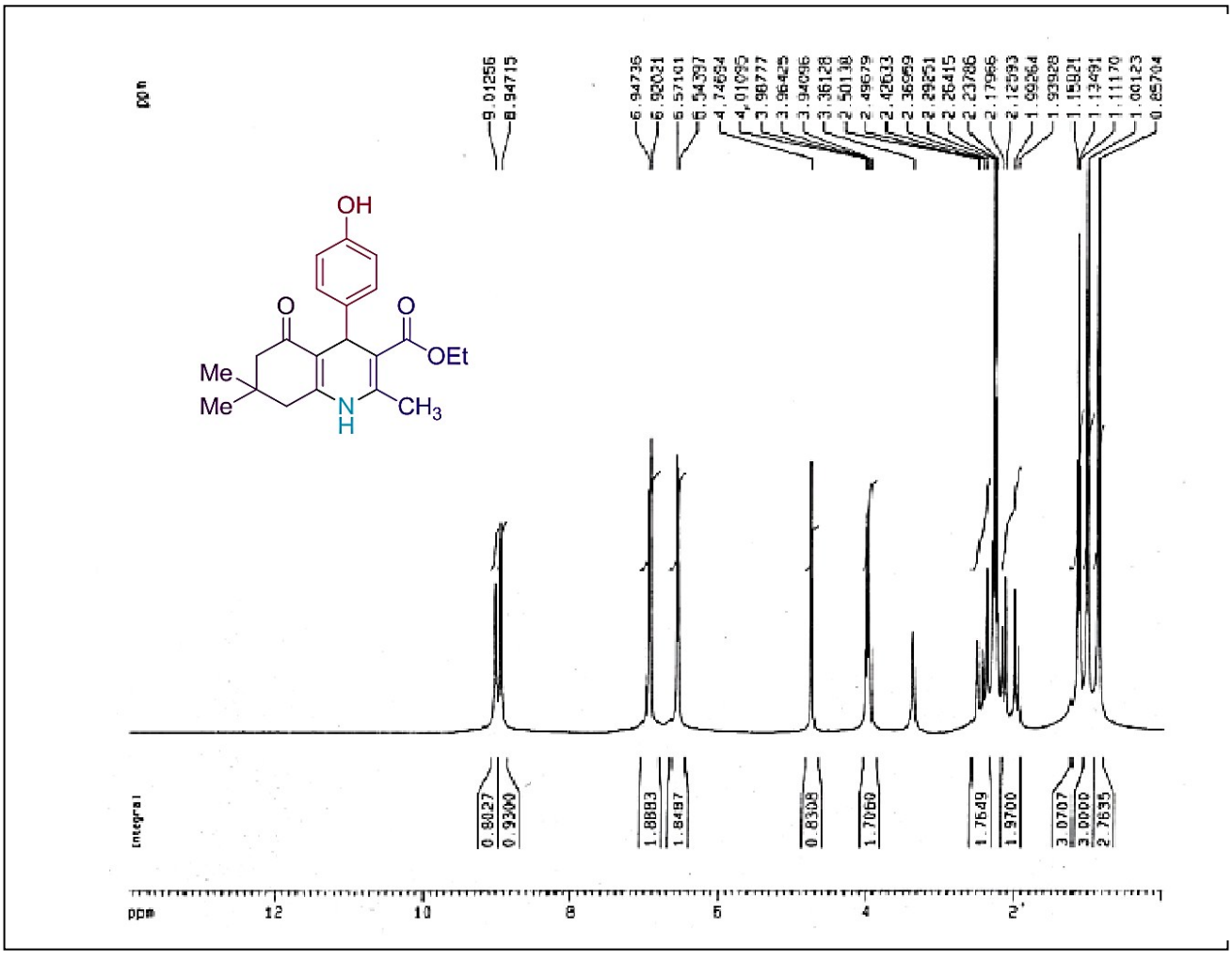
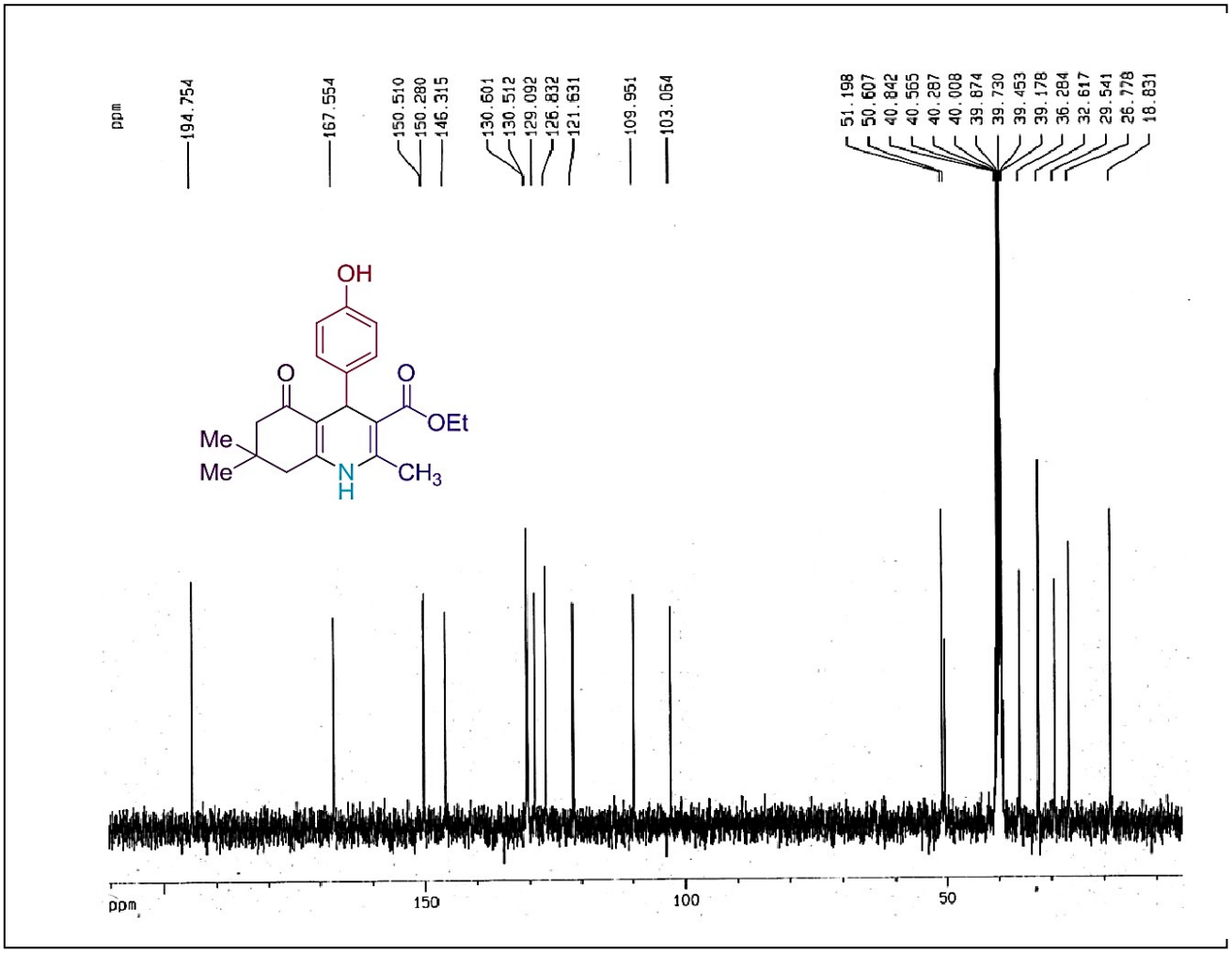
120
100
80
60
40
20
0
ppm

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

White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.86 (s, 3H), 1.00 (s, 3H), 1.14 (t, J = 7.0 Hz, 3H), 1.96 (d, J = 16.0 Hz, 1H), 2.15 (d, J = 16.1 Hz, 1H), 2.26 (s, 3H), 2.36-2.49 (m, 2H), 3.96 (q, J = 7.0 Hz, 2H), 4.74 (s, 1H), 6.56 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 8.94 (s, 1H), 9.01 (s, 1H); 13C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.6, 18.7, 26.9, 29.6, 32.6, 35.3, 50.8, 59.4, 104.6, 110.8, 114.9, 128.8, 138.9, 144.8, 149.6, 155.7, 167.5, 194.7.

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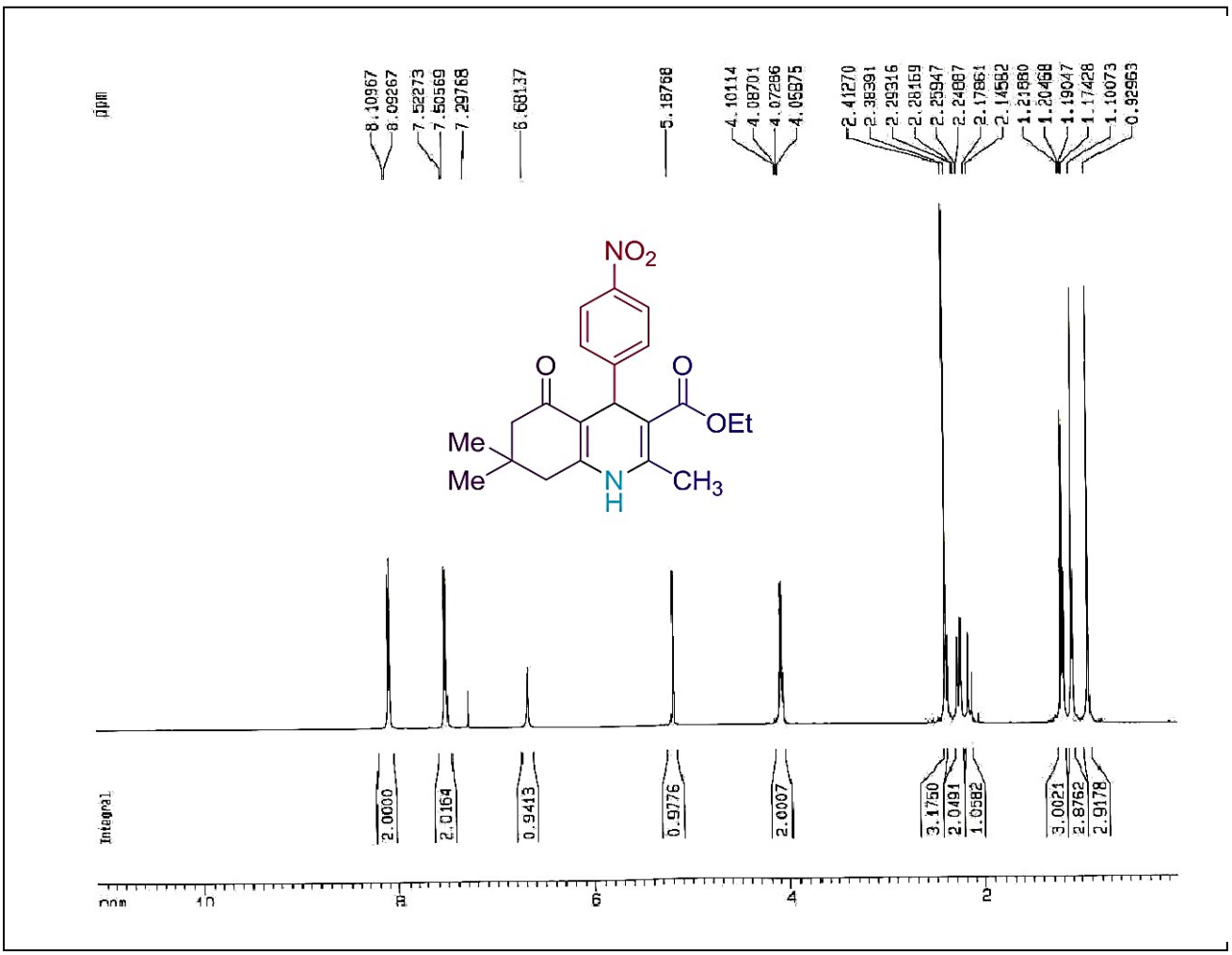
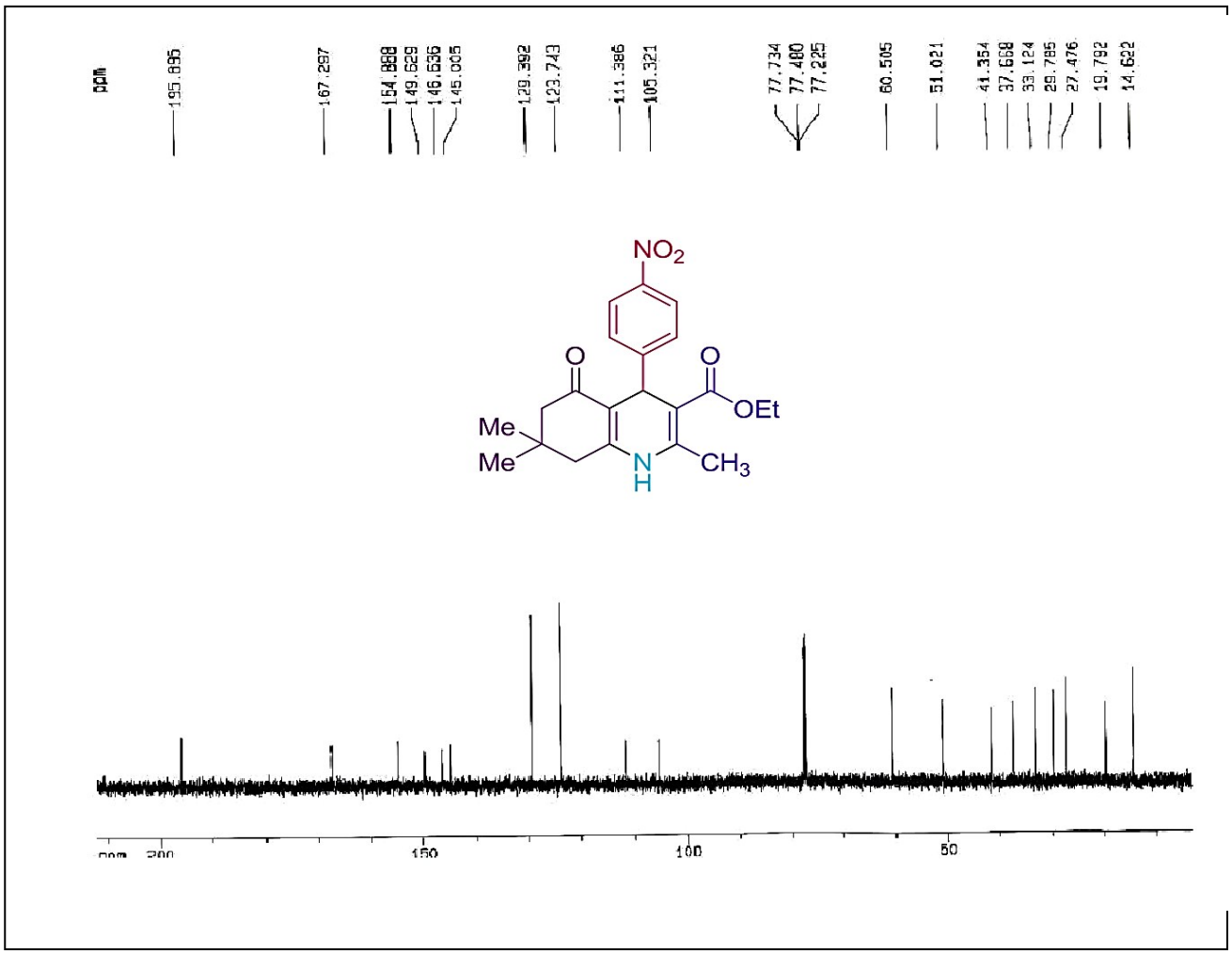
OH
O
O
OEt
Me
Me
N
H
CH3
ppm
150
100
50

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

White solid, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.92 (s, 3H), 1.10 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 2.16 (d, J = 16.4 Hz, 2H), 2.24-2.29 (Distorted AB system, 2H), 2.41 (s, 3H), 4.07 (q, J = 7.1 Hz, 2H), 5.18 (s, 1H), 6.68 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 8.09 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 14.6, 19.8, 27.5, 29.8, 33.1, 37.7, 41.3, 51.0, 60.5, 105.3, 111.4, 123.7, 129.4, 145.0, 146.6, 149.6, 154.9, 167.3, 195.9.

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29.795
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19.792
14.622
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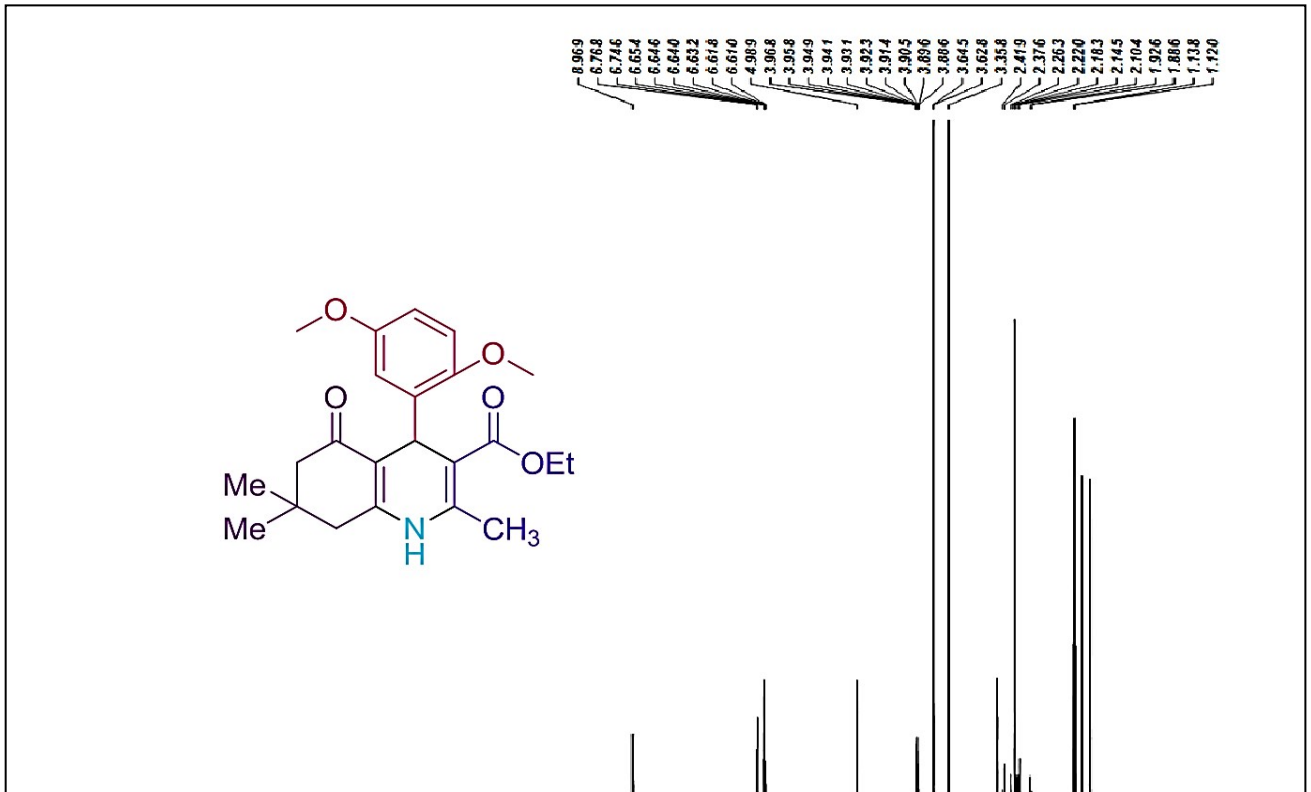
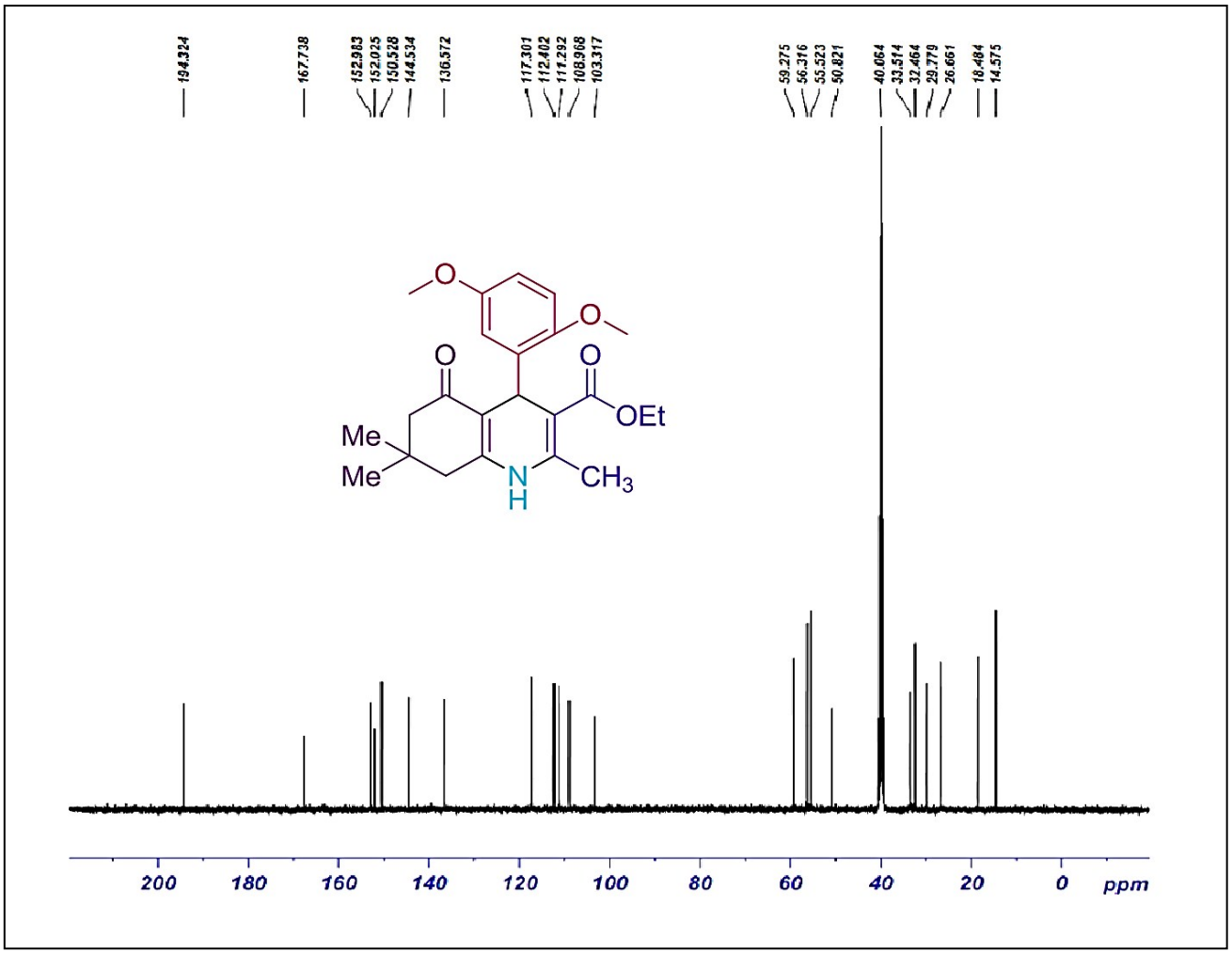
O
O
OEt
Me
Me
N
H
CH3
200
150
100
50

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

White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.86 (s, 3H, —CH3), 1.00 (s, 3H, —CH3), 10 1.14 (t, 3H, J = 7.2 Hz, —CH3), 1.93 (d, 1H, J = 8.0 Hz, —CH2), 2.14 (d, 1H, J = 8.2 Hz, —CH2), 2.18 (s, 3H, — CH3), 2.26 (d, 1H, J = 8.6 Hz, —CH2), 2.42 (d, 1H, J = 8.6 Hz, —CH2), 3.63 (s, 3H, —CH3), 3.64 (s, 3H, —CH3), 3.94 (q, 2H, J = 5.4 Hz, —CH2), 4.99 (s, 1H, —CH), 6.62 15 (d, 1H, J = 3.2 Hz, ArH), 6.65 (d, 1H, J = 2.4 Hz, ArH), 6.77 (s, 1H, ArH), 8.97 (s, 1H, —NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 14.6, 18.5, 26.7, 29.8, 32.5, 33.5, 40.1, 50.8, 55.5, 56.3, 59.3, 103.3, 109.0, 111.3, 112.4, 117.3, 136.6, 144.5, 150.5, 152.0, 153.0, 167.7, 194.3

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O
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OEt
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Me
N
H
CH3
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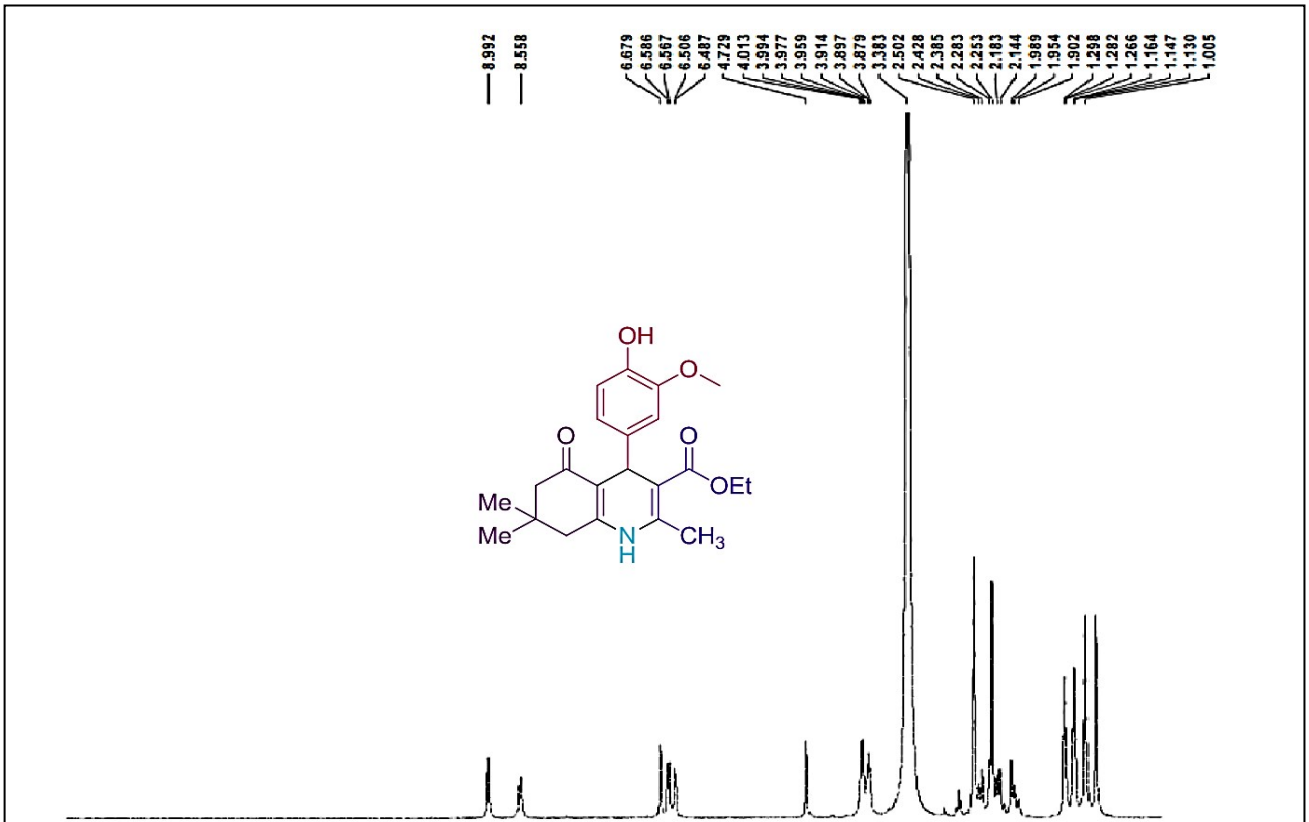
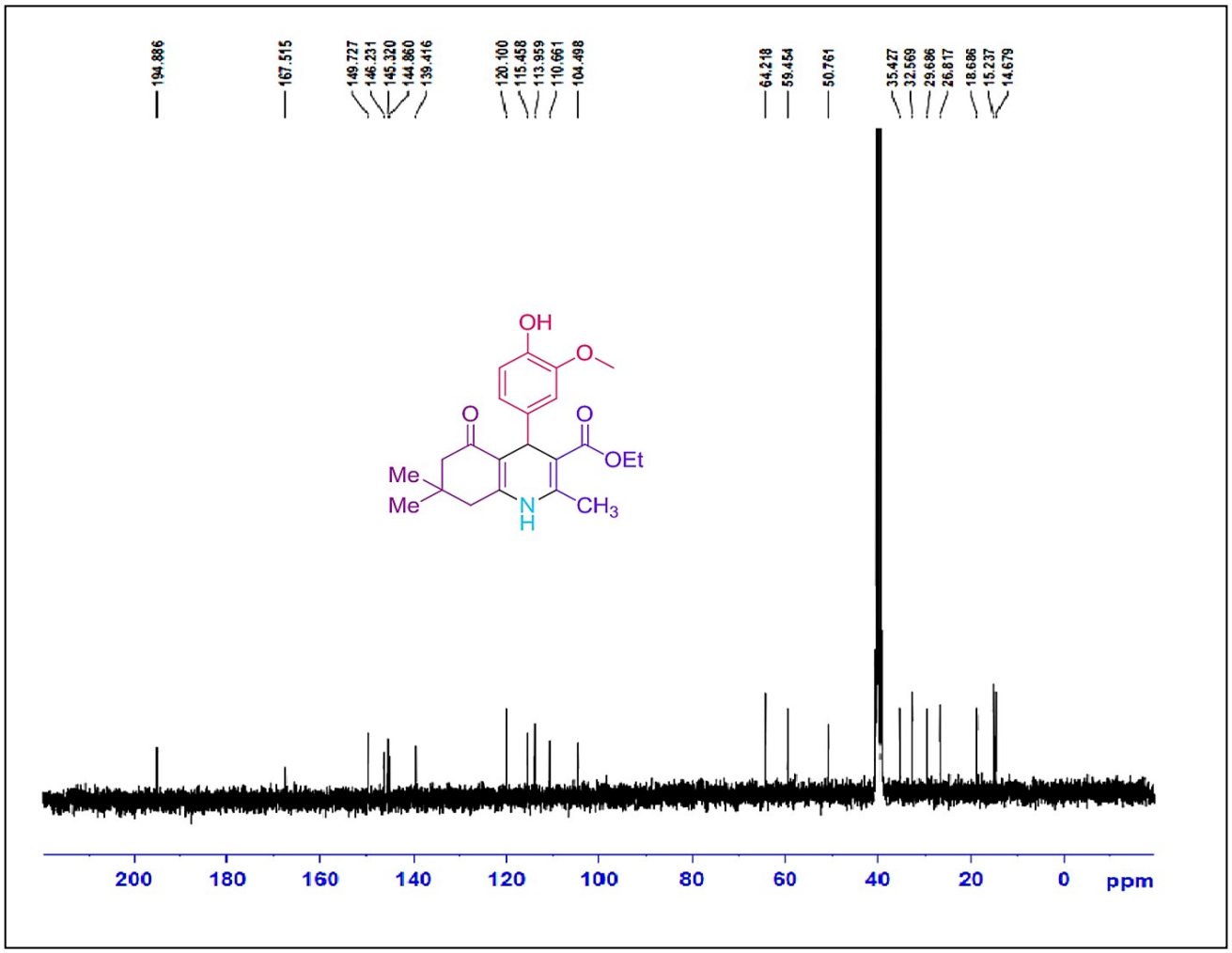
180
160
140
120
100
80
60
40
20
0
ppm

Ethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-Carboxylate.

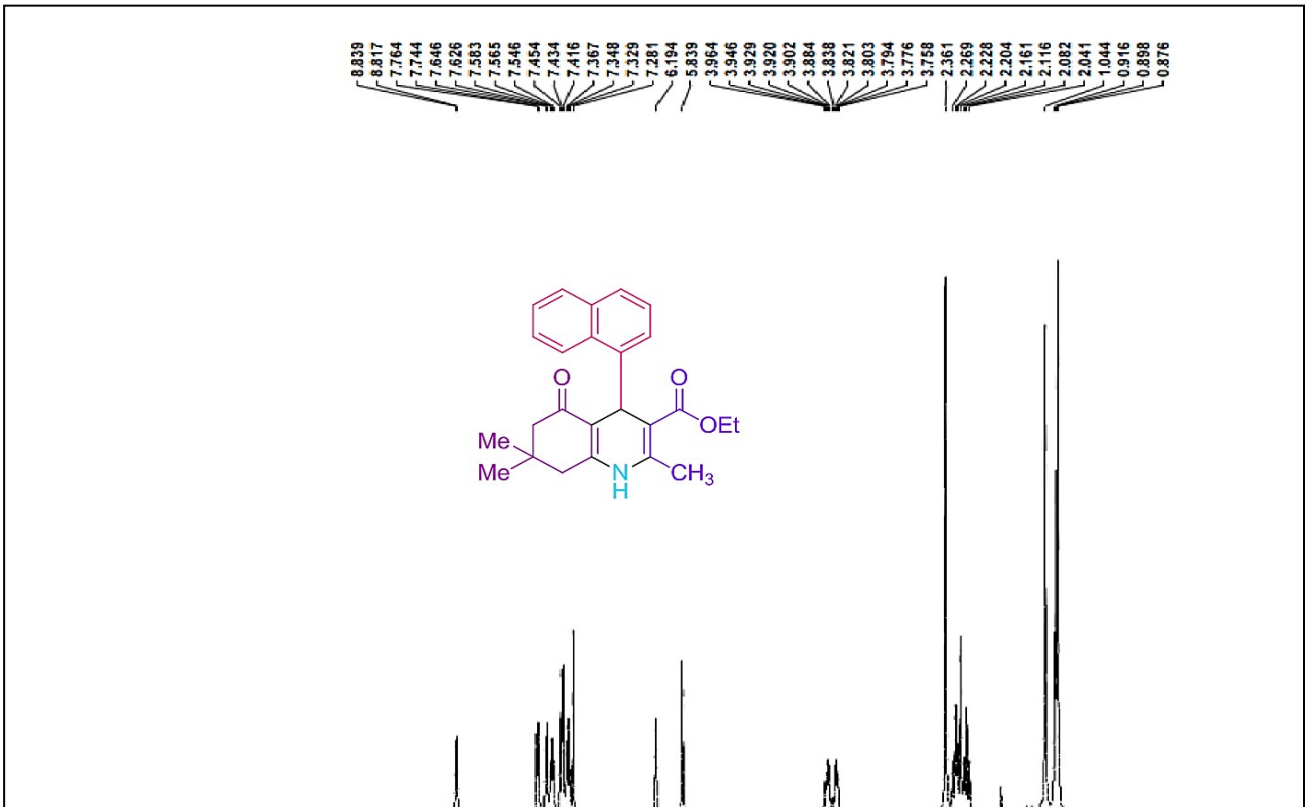
white solid, ^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) 1.00 (s, 3H), 1.14 (t, J = 6.8), 1.28 (t, J = 6.4), 1.90 (s, 3H), 1.97 (d, J =14, 1H), 2.16 (d, J =15.6, 1H), 2.26 (d, J =12, 1H), 2.38 (s, 3H), 2.42 (s, 1H), 3.89 (t, J =7.2, 2H), 3.98 (q, J =7.6, 2H), 4.72 (s, 1H), 5.57 (d, J =7.6, 1H), 6.49 (d, J =7.6, 1H), 6.67 (s, 1H), 8.55 (s, 1H), 8.99 (s, 1H); ^{13}C NMR (100MHz , DMSO-d_6): δ (ppm) 19.5, 27.1, 29.4, 32.7, 35.4, 41.1, 50.7, 51.0, 55.1, 106.0, 112.5, 113.3, 128.7, 139.3, 143.3, 147.5, 157.7, 167.9, 195.5

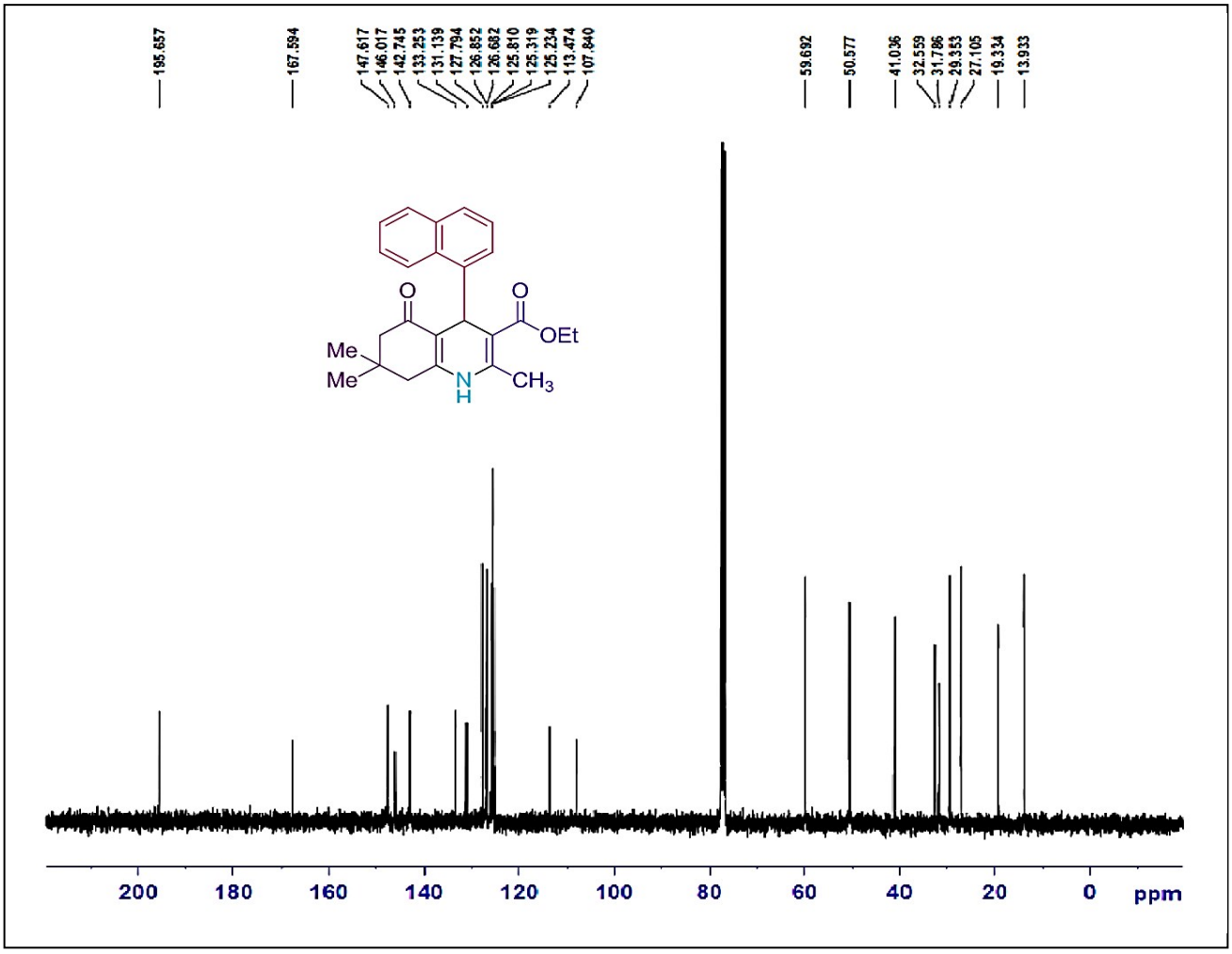



194.886
167.515
149.727
146.231
145.320
144.860
139.416
120.100
115.458
113.959
110.661
104.498
64.218
59.454
50.761
35.427
32.569
29.686
26.817
18.686
15.237
14.679
OH
O
O
O
OEt
Me
Me
N
H
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm

Ethyl 2,7,7-trimethyl-4-(naphthalen-1-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

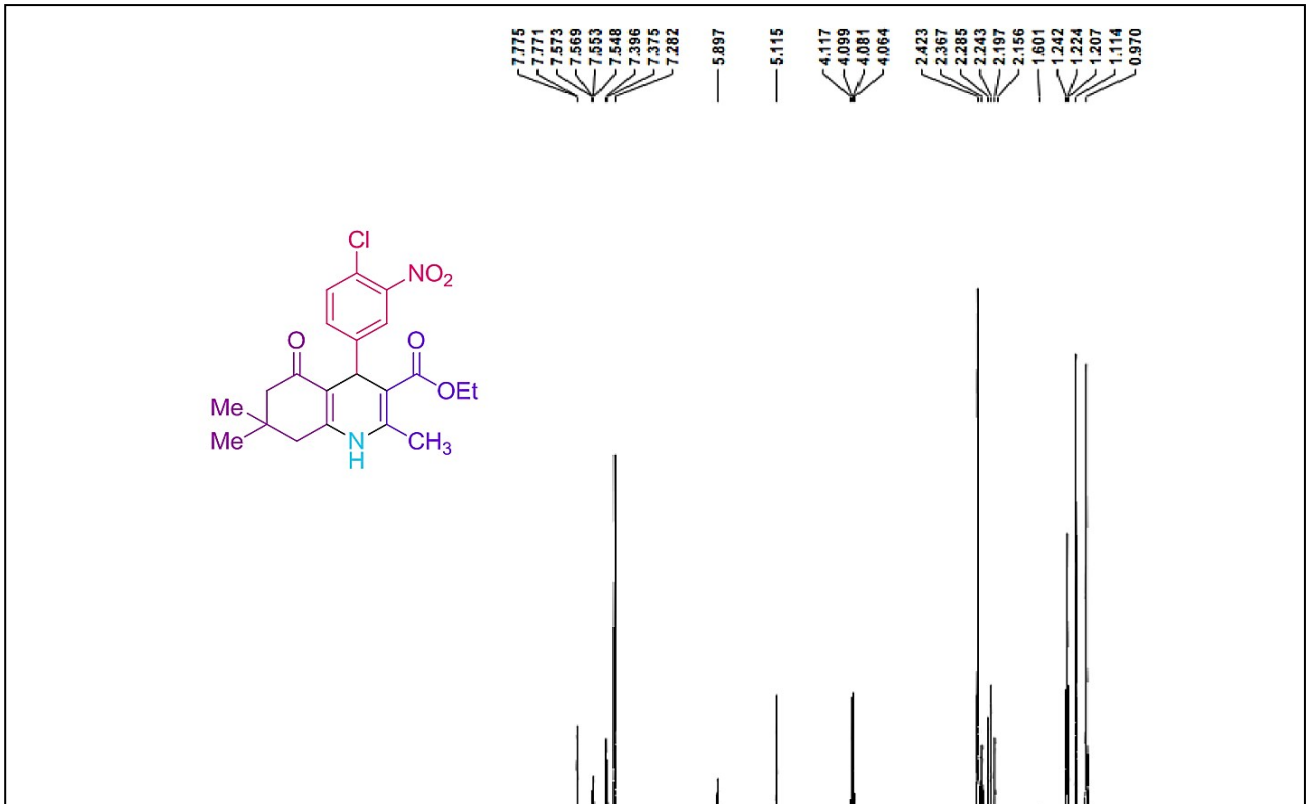
white solid, ^{1}H NMR: (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t J =8.8, 3H) 1.04 (s 3H) 2.04 (s 3H CH_3) 2.09 (d J =13.6, 1H) 2.16 (s 1H) 2.21 (d J =9.6, 1H) 2.26 (s 1H) 2.36 (s 3H) 3.75- 3.96 (m 2H) 5.83 (s 1H) 6.19 (s 1H) 7.28 (s 1H) 7.34 (t J =7.6, 1H) 7.434 (t J = 7.6 1H) 7.56 (t J = 7.6, 1H) 7.63 (d J = 8 1H) 7.75 (d J = 8, 1H) 8.82 (d J = 8.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 13.9 19.3 27.1 29.3 31.7 32.5 41.0 50.5 59.6 107.8 113.4 125.2 125.8 126.6 126.8 127.7 131.1 133.2 142.7 146.0 147.6 167.5 195.6

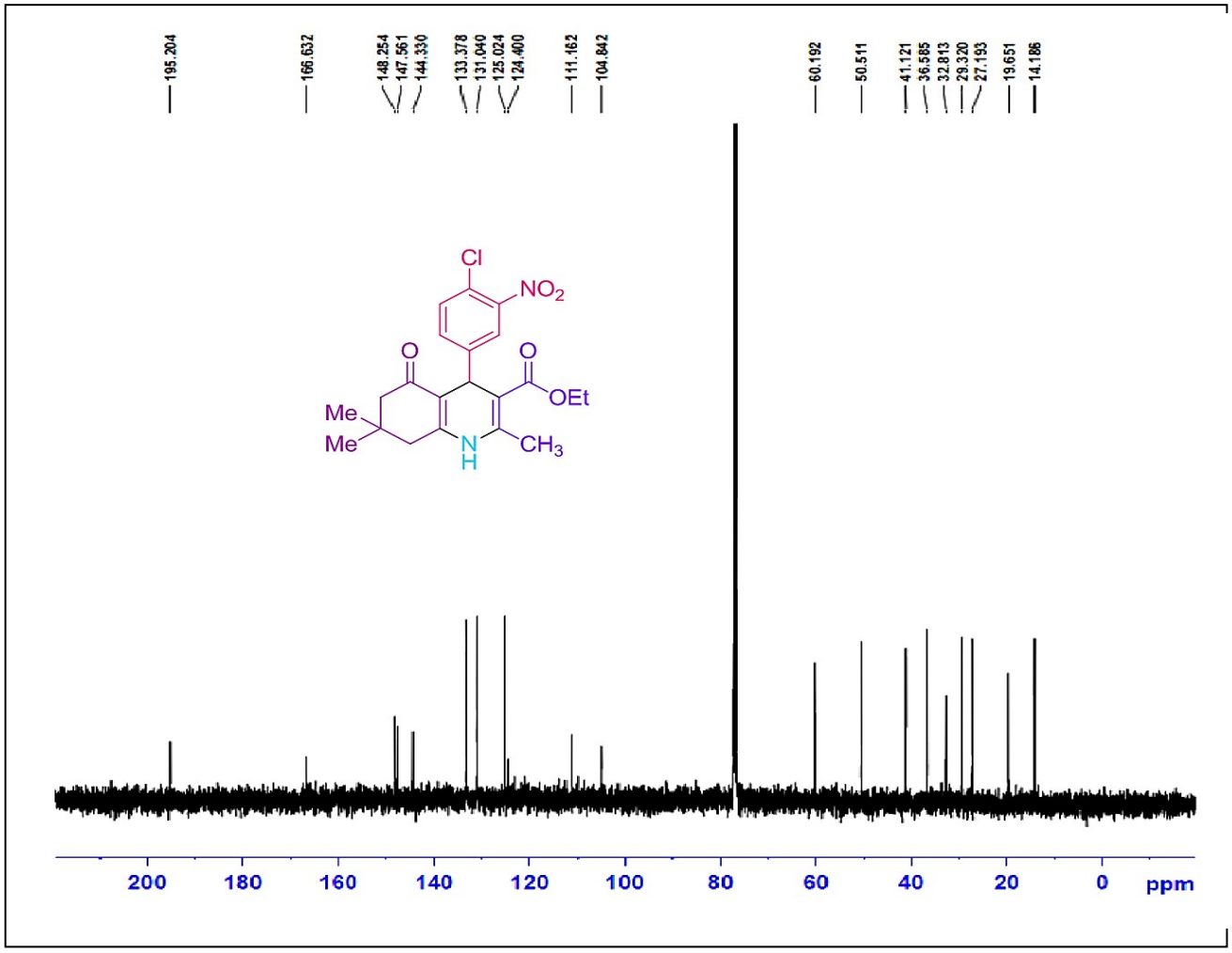



195.657
167.594
147.617
146.017
142.745
133.253
131.139
127.794
126.852
126.682
125.810
125.319
125.234
113.474
107.840
59.692
50.577
41.036
32.559
31.786
29.353
27.105
19.334
13.933
O
O
OEt
Me
Me
N
H
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm

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

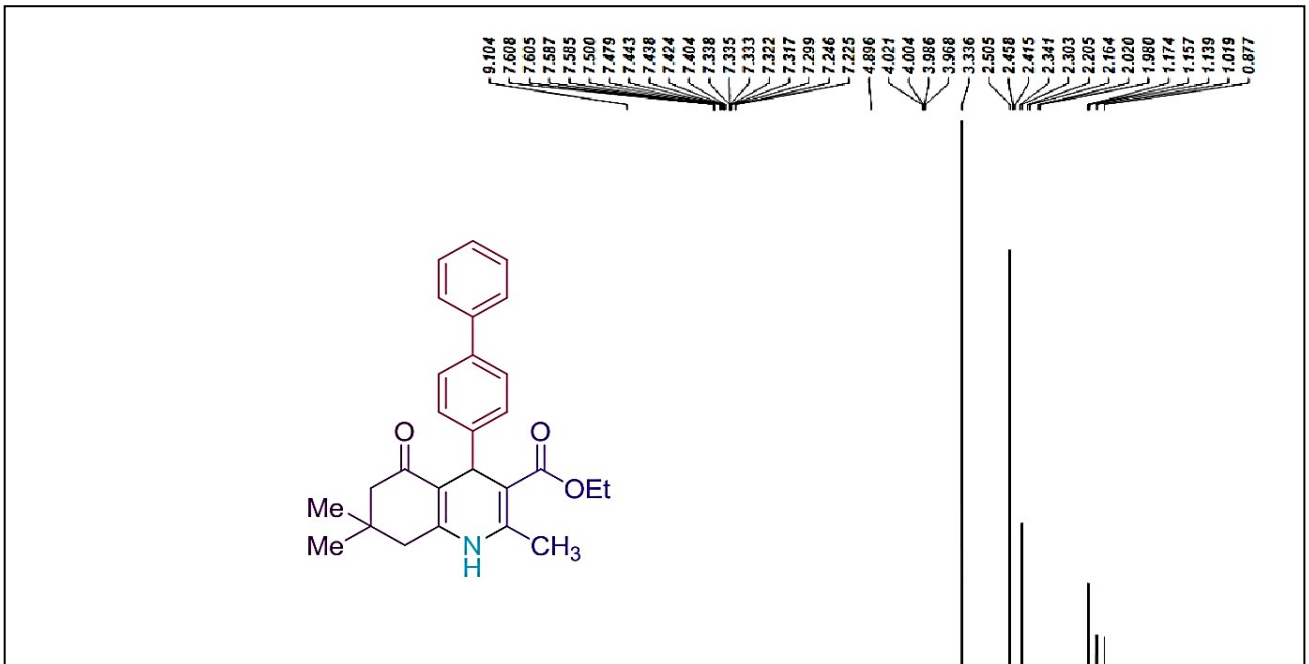
White solid, ^{1}H NMR: (400 MHz, $CDCl_3$): δ (ppm) 0.97 (s, 3H), 1.11 (s, 3H), 1.22 (t, J =7.2, 3H), 2.17 (d, J =16.4, 1H), 2.22 (d, J =16.8, 2H), 2.36 (s, 1H), 2.42 (s, 3H), 4.09 (q, J =7.2, 2H), 5.11 (s, 1H), 5.89 (s, 1H), 7.55 (d, J = 2, 1H), 7.57 (d, J =1.6, 1H), 7.77 (d, J = 1.6, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 14.1, 19.6, 27.1, 29.3, 32.8, 36.5, 41.1, 50.5, 60.1, 104.8, 111.1, 124.4, 125.0, 131.0, 133.3, 144.3, 147.5, 148.2, 166.6, 195.2.

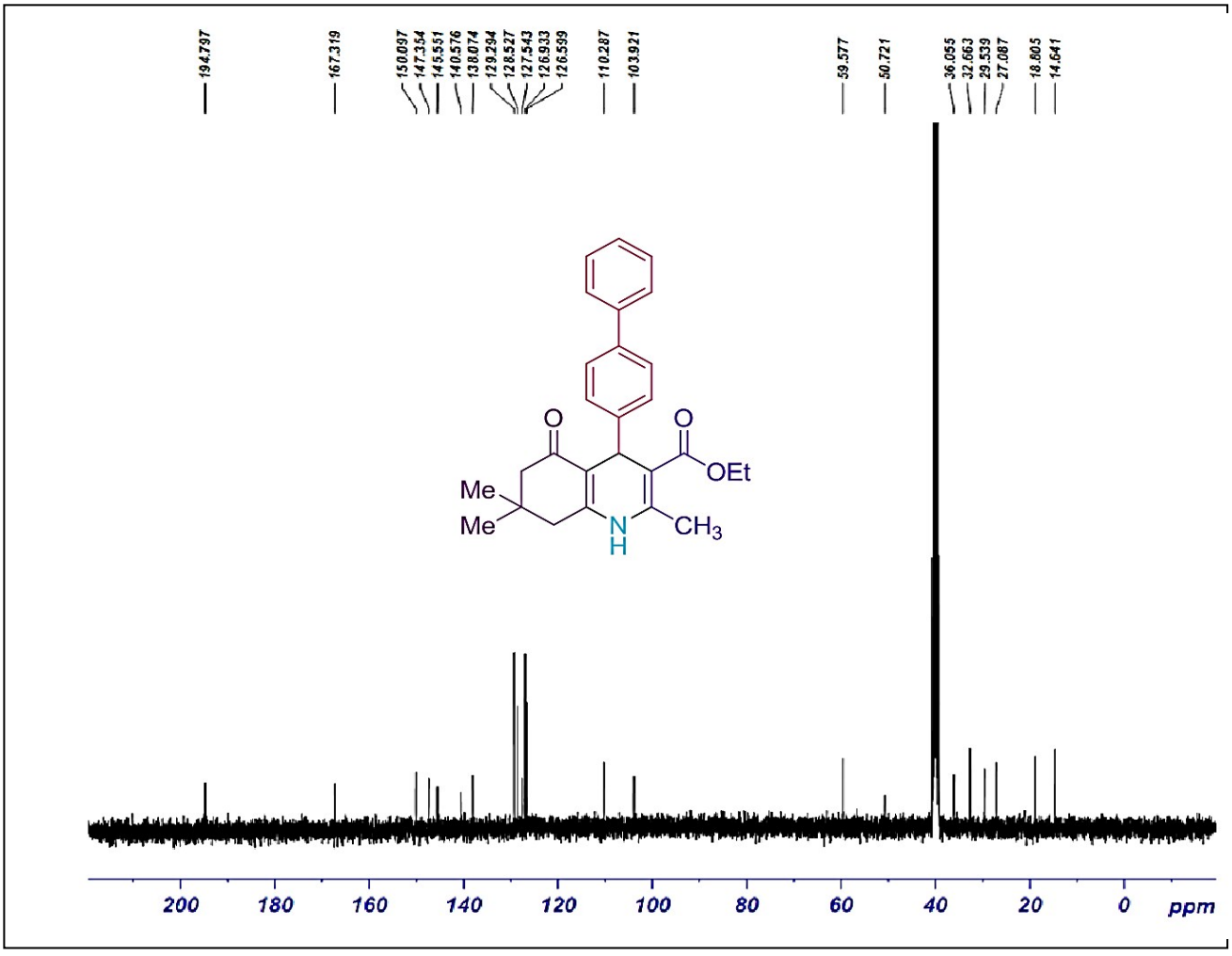



195.204
166.632
148.254
147.561
144.330
133.378
131.040
125.024
124.400
111.162
104.842
60.192
50.511
41.121
36.585
32.813
29.320
27.193
19.651
14.186
Cl
NO2
O
O
OEt
Me
Me
N
H
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm

Ethyl 4-(biphenyl-4-yl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8- hexahydroquinoline-3-carboxylate

White solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 0.87 (s, 3H, —CH3), 1.02 (s, 3H, —CH3), 1.17 (t, 3H, J = 7.0 Hz, —CH3), 2.02 (d, 1H, J = 8.8 Hz, —CH2), 2.20 (d,1H, J = 8.2 Hz, —CH2), 2.30 (s, 3H, —CH3), 2.34 (d, 1H, J = 7.6 Hz, —CH2), 2.46 (d, 1H, J = 8.6 Hz, —CH2), 4.02 (q, 2H, J = 7.2 Hz, —CH2), 4.90 (s, 1H, —CH), 7.25 (d, 100 2H, J = 8.4 Hz, ArH), 7.34 (t, 1H, J = 7.8 Hz, ArH), 7.42 (d, 2H, J = 8.0 Hz, ArH), 7.50 (d, 2H, J = 8.4 Hz, ArH), 7.61 (d, 2H, J = 9.2 Hz, ArH), 9.10 (s, 1H, —NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.6, 18.8, 27.1, 29.5, 32.7, 36.0, 50.7, 59.6, 103.9, 110.3, 126.6, 126.9, 127.5, 105128.5, 129.3, 138.1, 140.1, 145.5, 147.3, 150.1, 167.3, 194.8




194.797
167.319
150.097
147.354
145.551
140.576
138.074
129.294
128.527
127.543
126.933
126.599
110.287
103.921
59.577
50.721
36.055
32.663
29.539
27.087
18.805
14.641
O
O
OEt
Me
Me
N
H
CH3
200
180
160
140
120
100
80
60
40
20
0
ppm