Electronic Supplementary Material (ESI) for RSC Advances.

Novel ionic liquid [2-Eim] HSO_4 as a dual catalytic-solvent system for preparation of hexahydroquinolines under green condition

M. Ghorbani*, [a], S. Noura[a], M. Oftadeh[a], E. gholami[a], M. A. Zolfigol[b]

[a]Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran

[b]Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

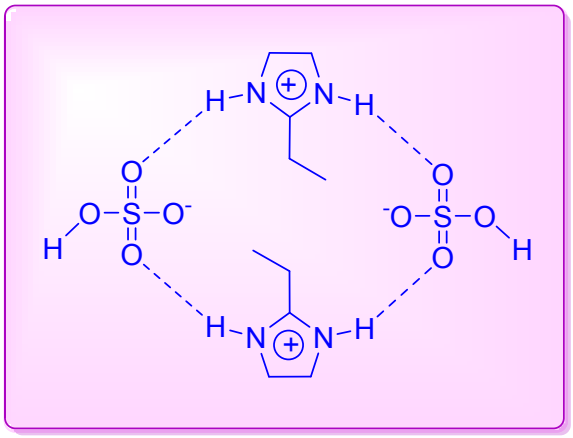


Fig. S1. Molecular self-assembly of [2-Eim] HSO_4 via hydrogen bonding.

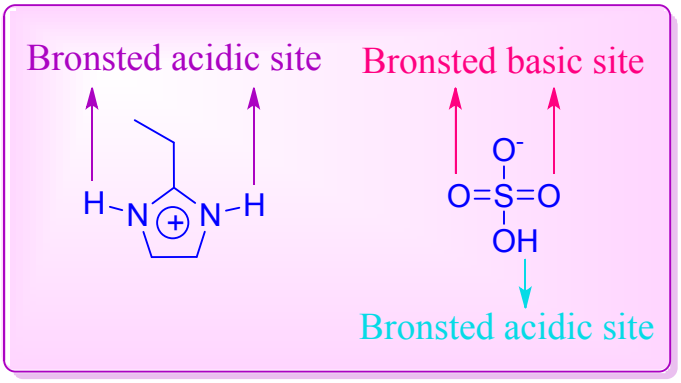


Fig. S2. The structure of [2-Eim] HSO_4

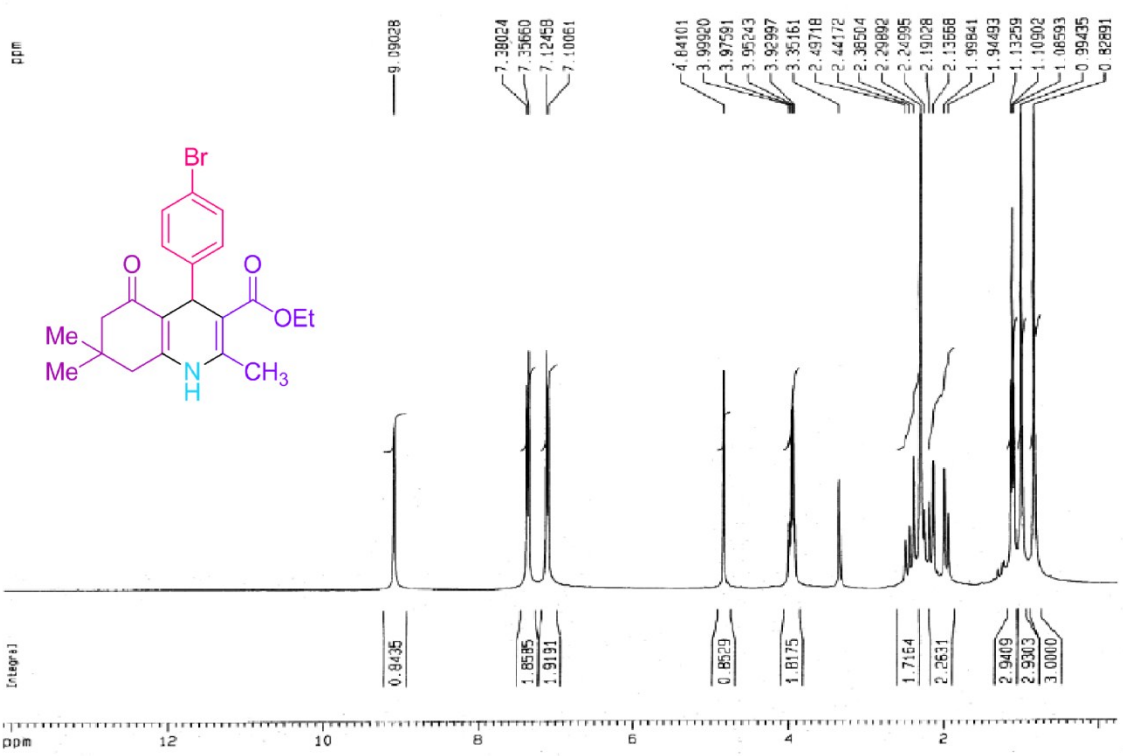
Table S2 ANOVA for the response surface quadratic model for time					
Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob>F
Model	428.42	3	142.81	196.83	<0.0001
A-Catalyst	373.99	1	373.99	515.46	<0.0001
B-Ammonium acetate	9.37	1	9.37	12.91	0.0071
A^2	45.07	1	45.07	62.11	<0.0001

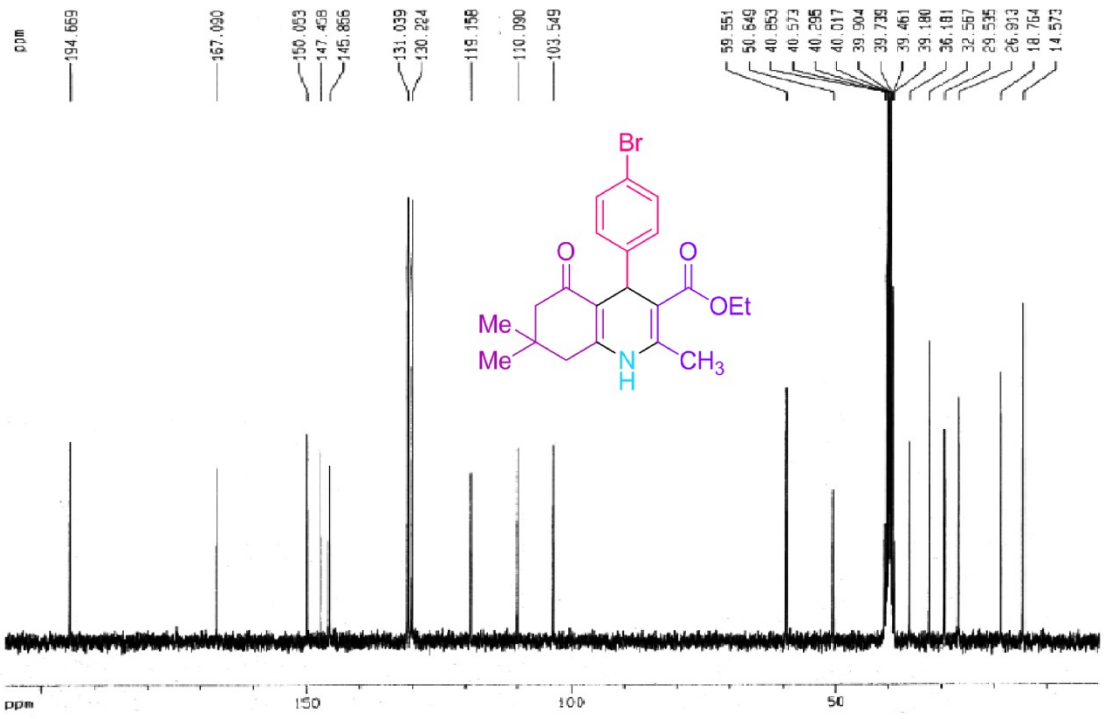
Table S1. Design Matrix					
Std	Run	Factor 1 (A: Catalyst: mol%)	Factor 2 (Ammonium acetate: mmol)	Response 1 (Time: min)	Response 2 (Yield: %)
1	9	3.6	10	18	74
2	7	11.5	10	5	94
3	3	3.6	10.6	16	75
4	10	11.5	10.6	4	94
5	2	1.96386	10.3	24	67
6	1	13.1361	10.3	3	95
7	12	7.55	9.87574	11	87
8	6	7.55	10.7243	7	93
9	11	7.55	10.3	8	93
10	4	7.55	10.3	8	93
11	8	7.55	10.3	7.5	93
12	5	7.55	10.3	8	93

Table S3 ANOVA for the response surface quadratic model for Yield					
Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob>F
Model	1040.49	4	260.12	174.69	<0.0001
A-Catalyst	772.21	1	772.21	518.59	<0.0001
B-Ammonium acetate	11.25	1	11.25	7.55	0.0286
A^2	255.02	1	255.02	171.27	<0.0001
B^2	21.03	1	21.03	14.12	0.0071
Residual	10.42	7	1.49		

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

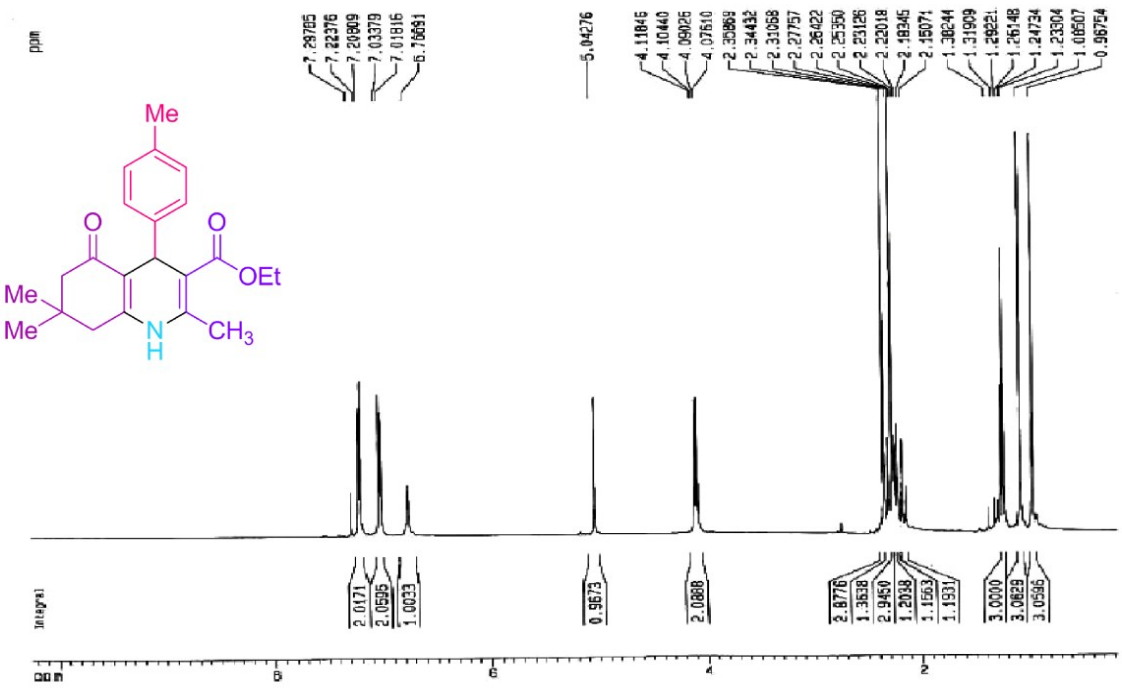
White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.83 (s, 3H), 0.99 (s, 3H), 1.10 (t, J = 6.9 Hz, 3H), 1.96 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.1 Hz, 1H), 2.29 (s, 3H), 2.38-2.49 (m, 2H), 3.97 (q, J = 7.0 Hz, 2H), 4.84 (s, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 9.09 (s, 1H); ^{13}C 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.





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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N
H
CH3
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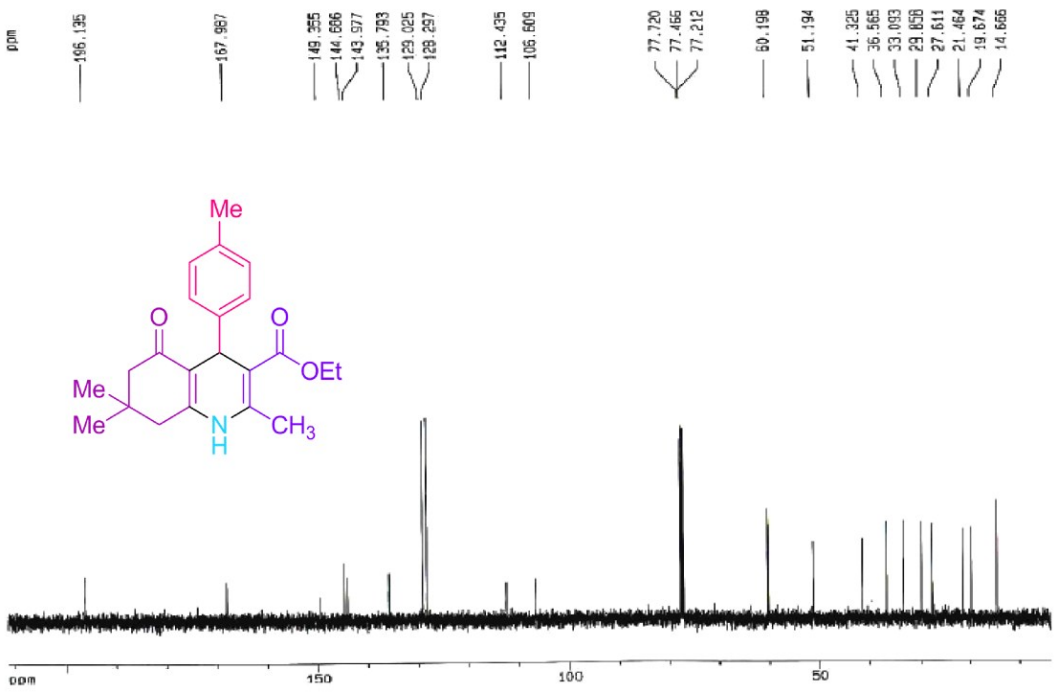
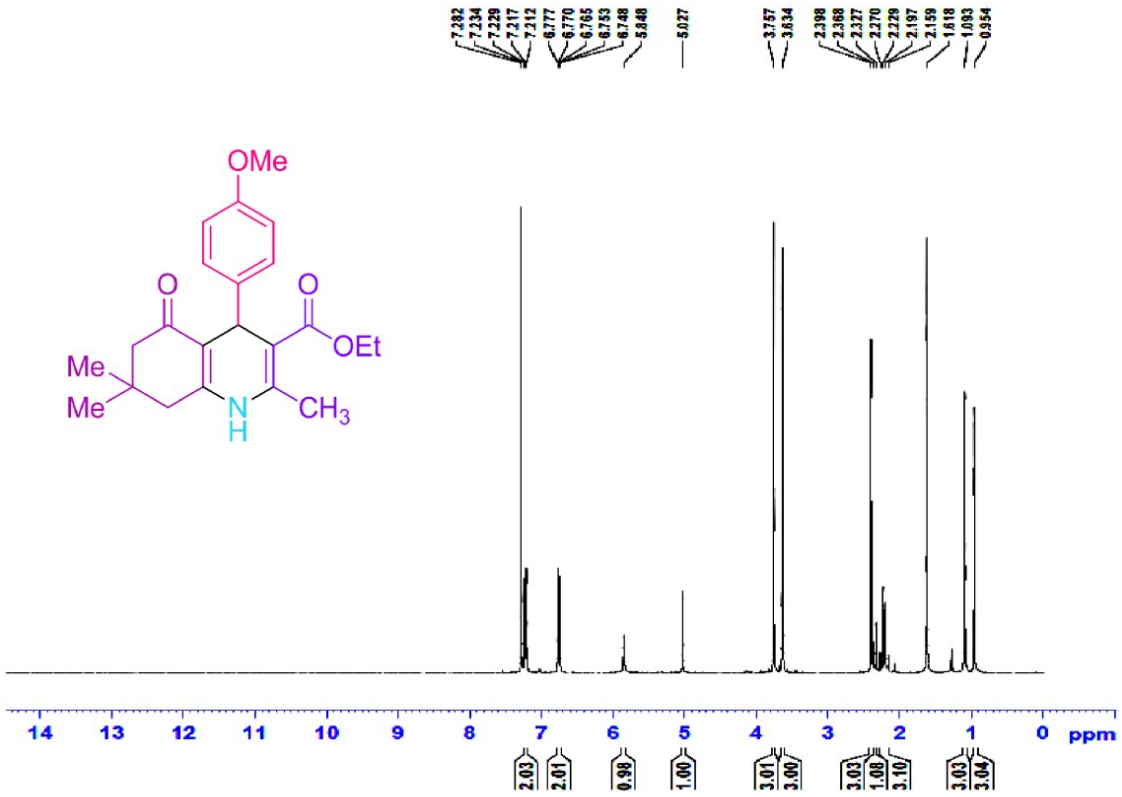
4
2



Ethyl 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, 194.7.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CH3
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10
9
8
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2
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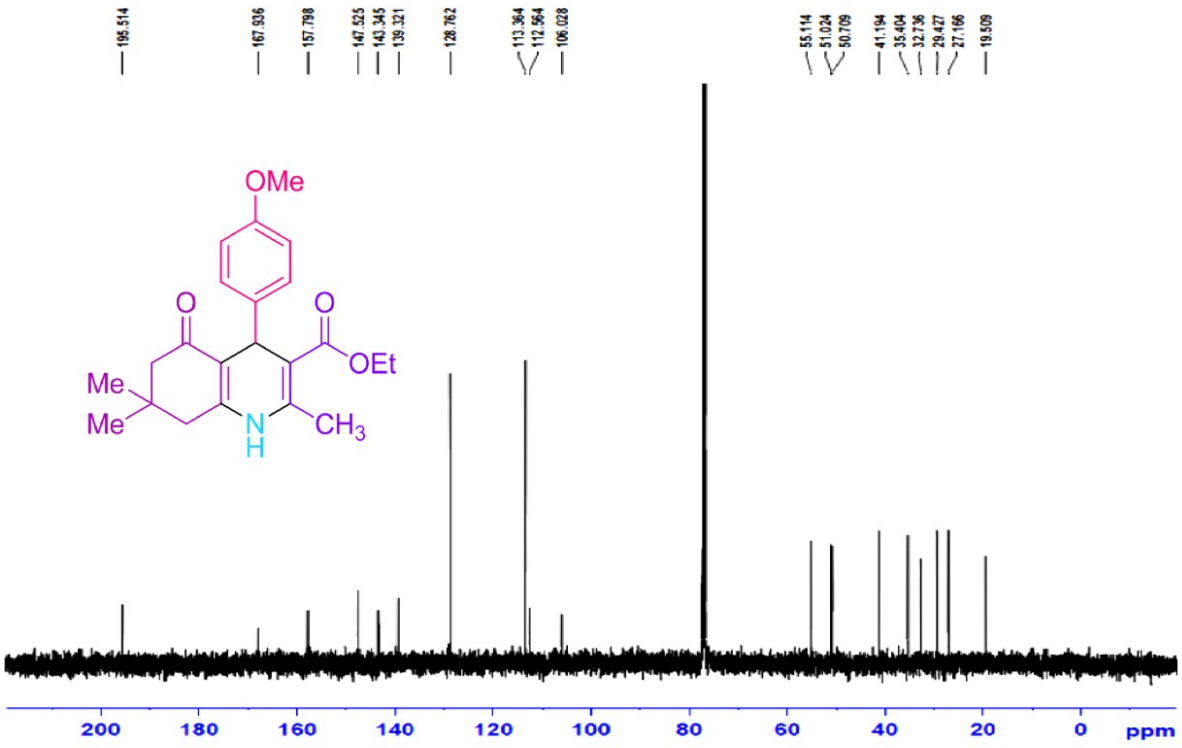
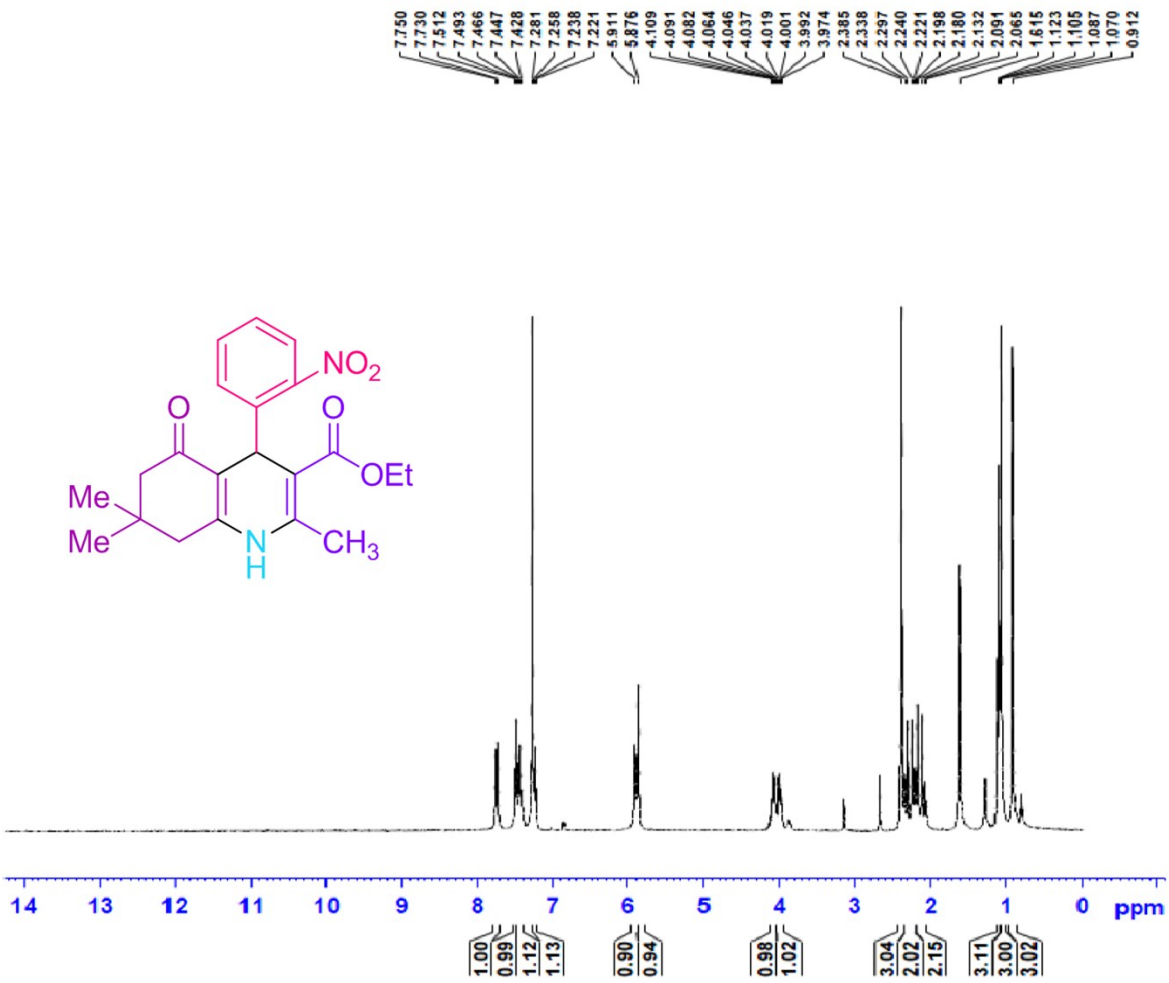
3.03
3.04



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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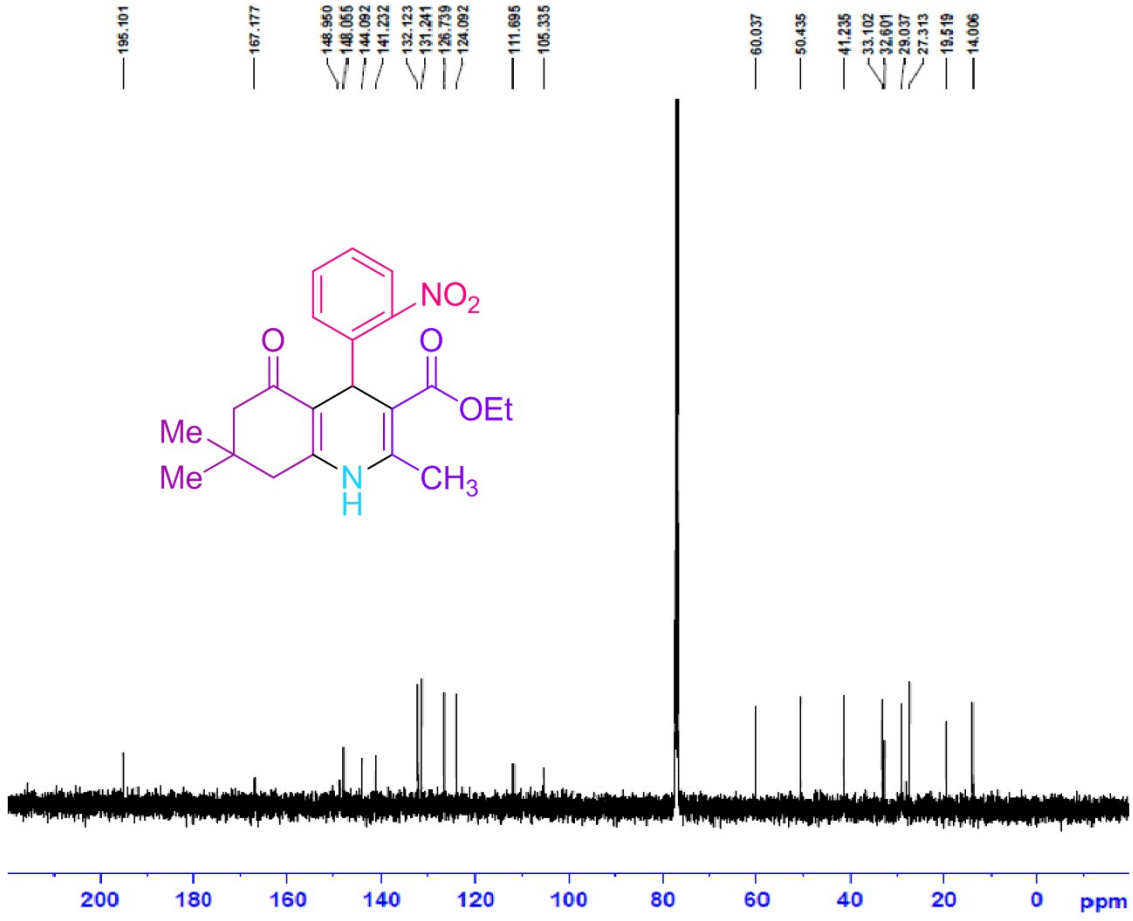
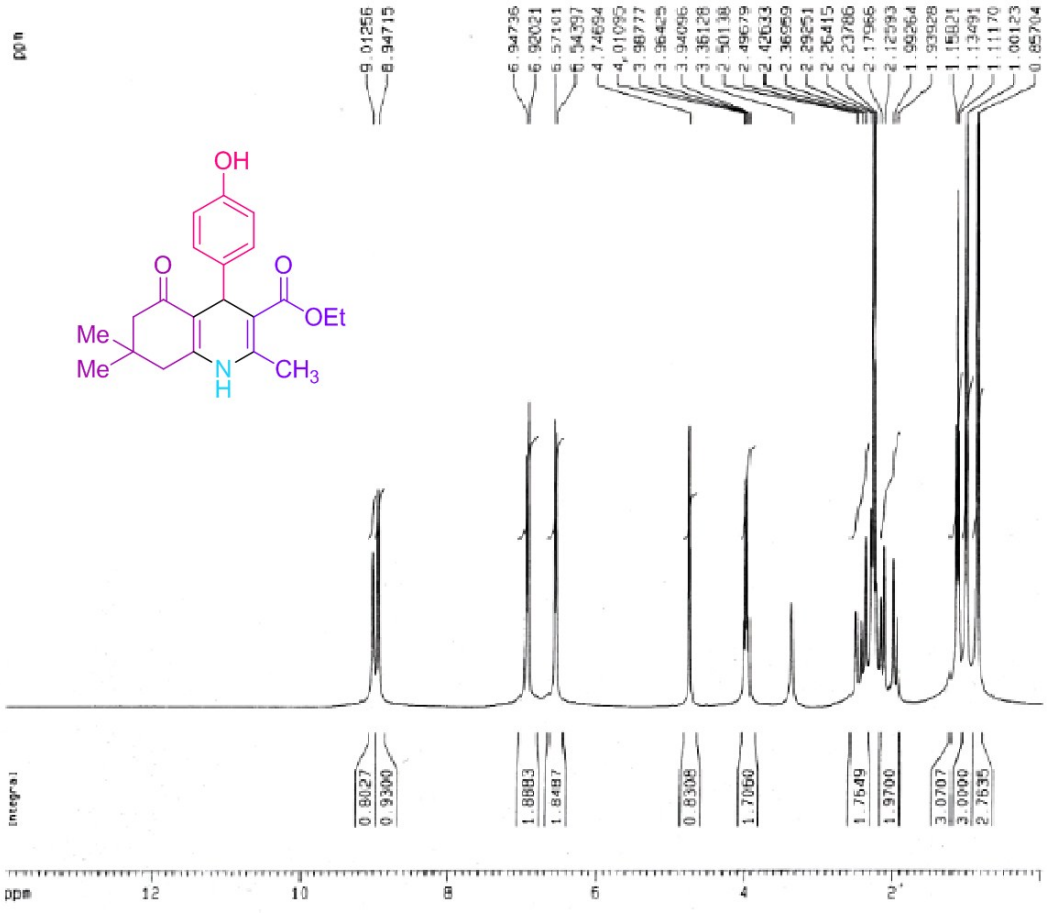


Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

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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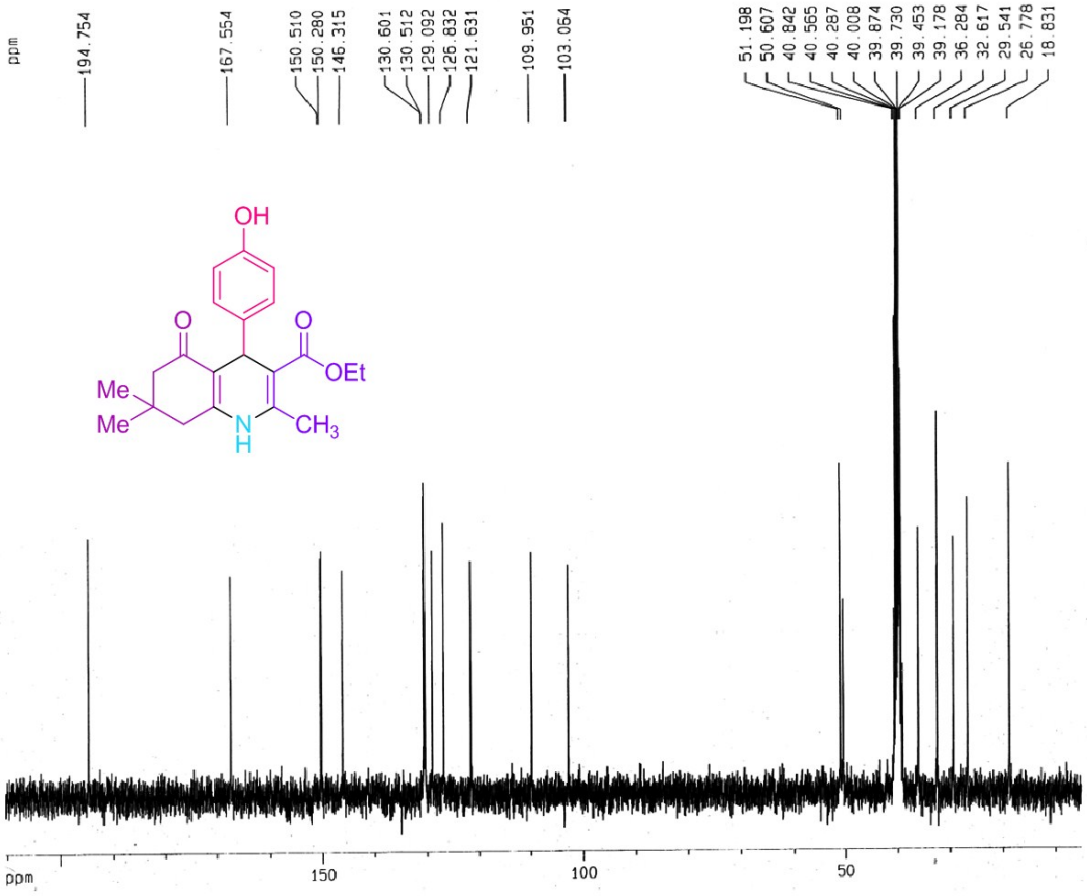
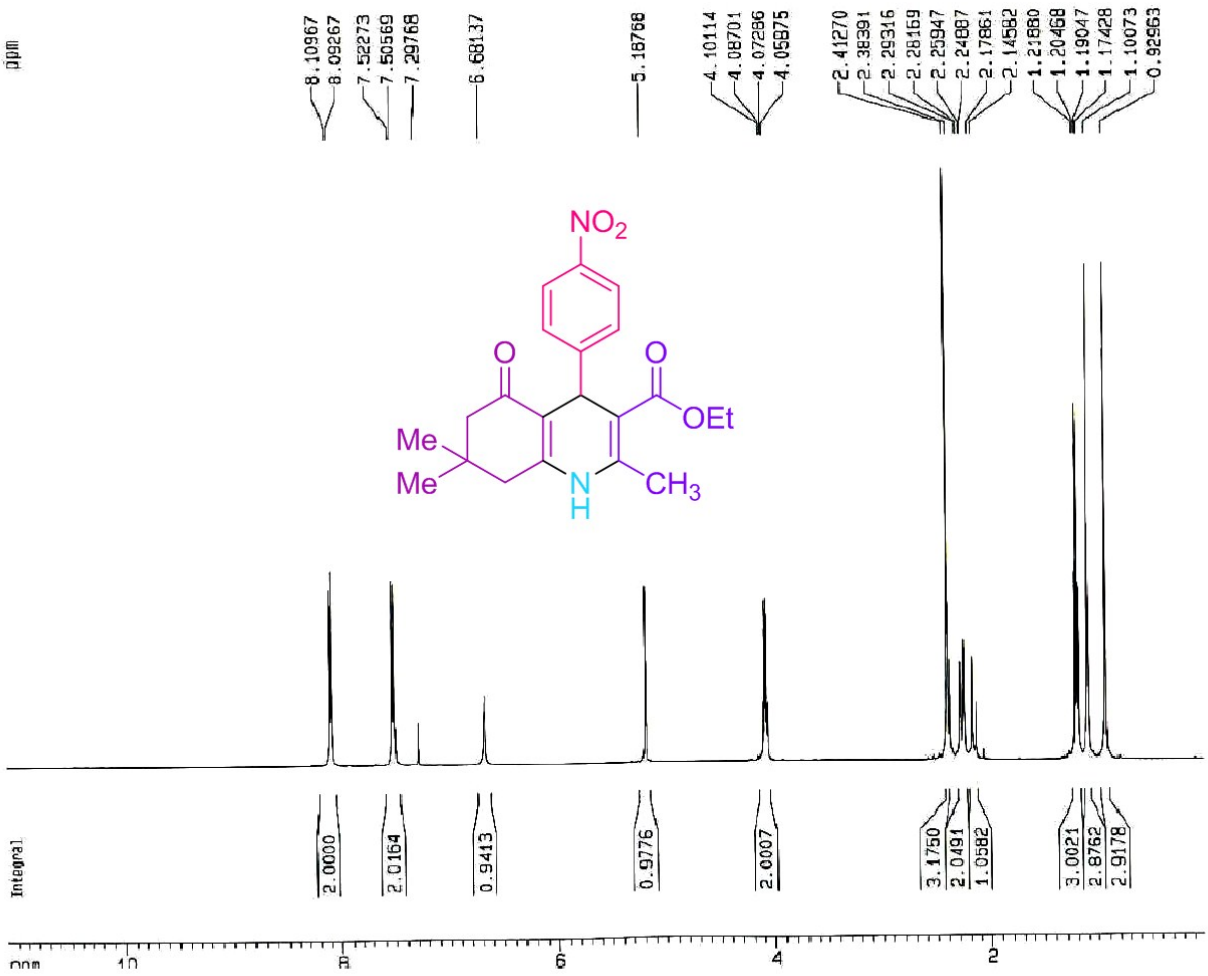


Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

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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H
CH3
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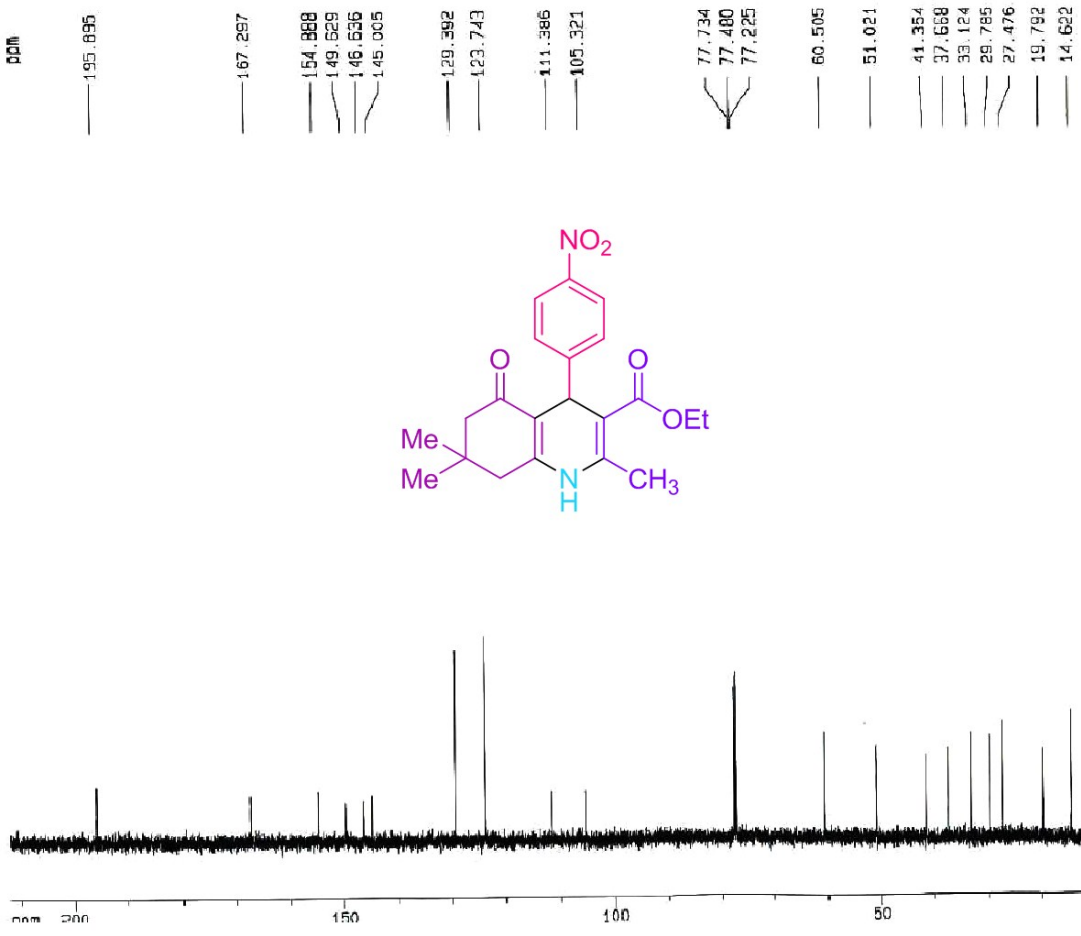
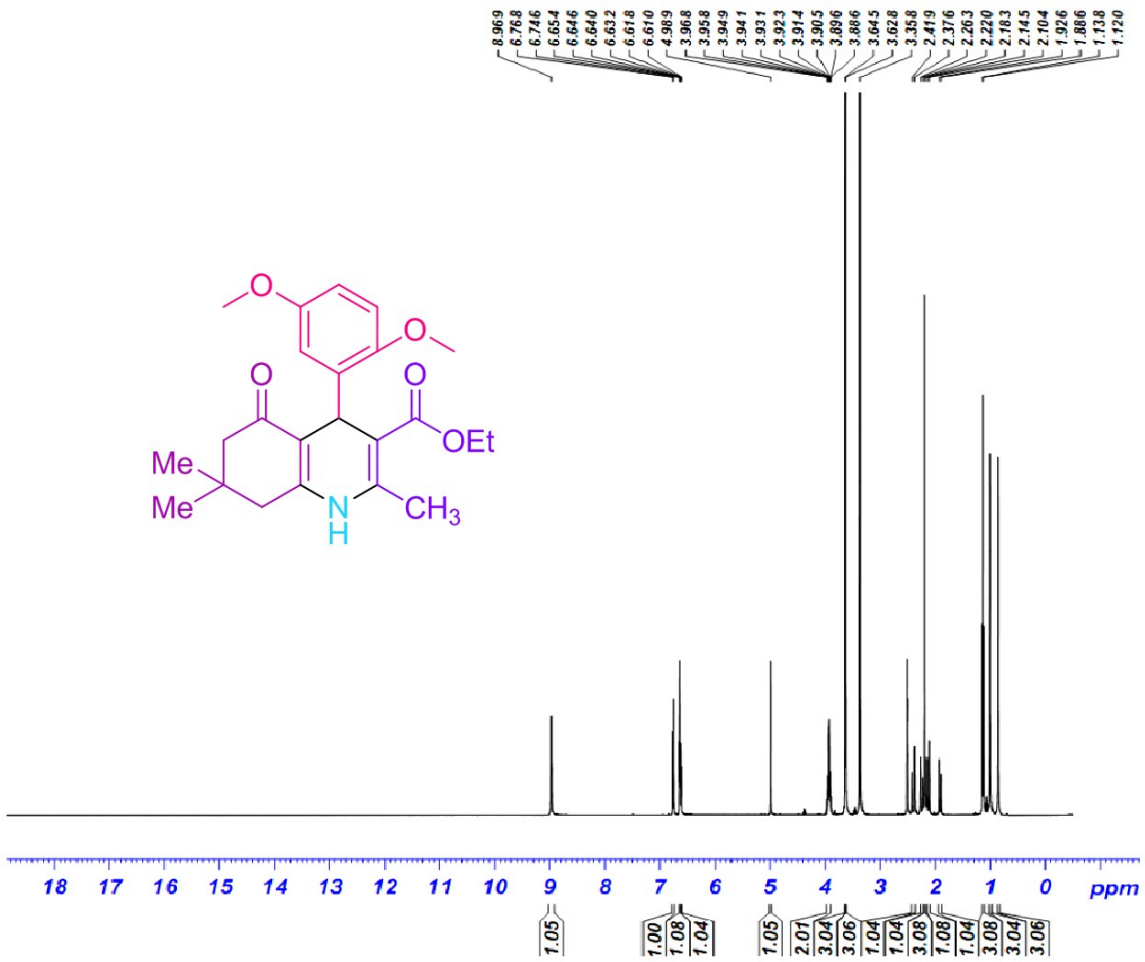


Ethyl 4-(2,5-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo- 1,4,5,6,7,8-hexahydroquinoline-3 carboxylate

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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1.04
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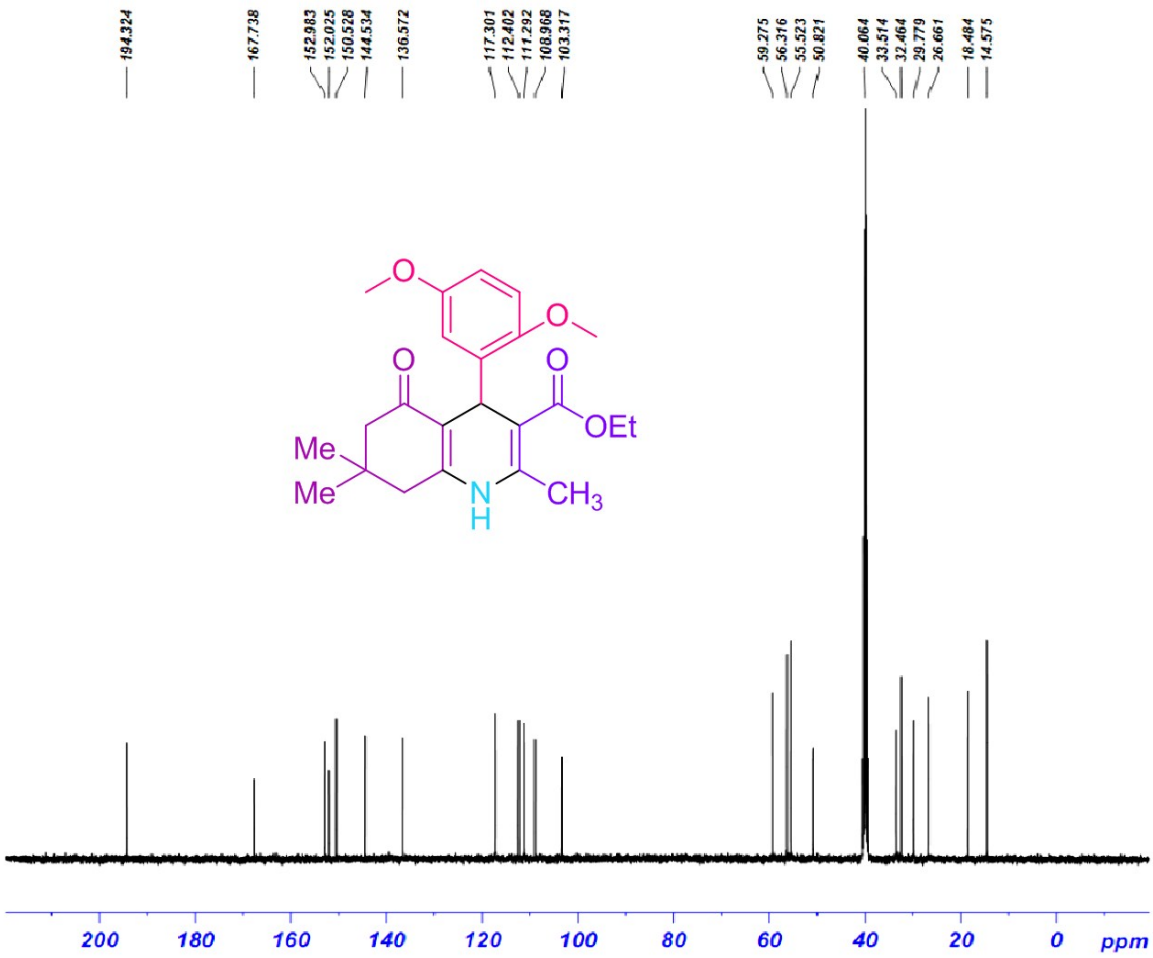
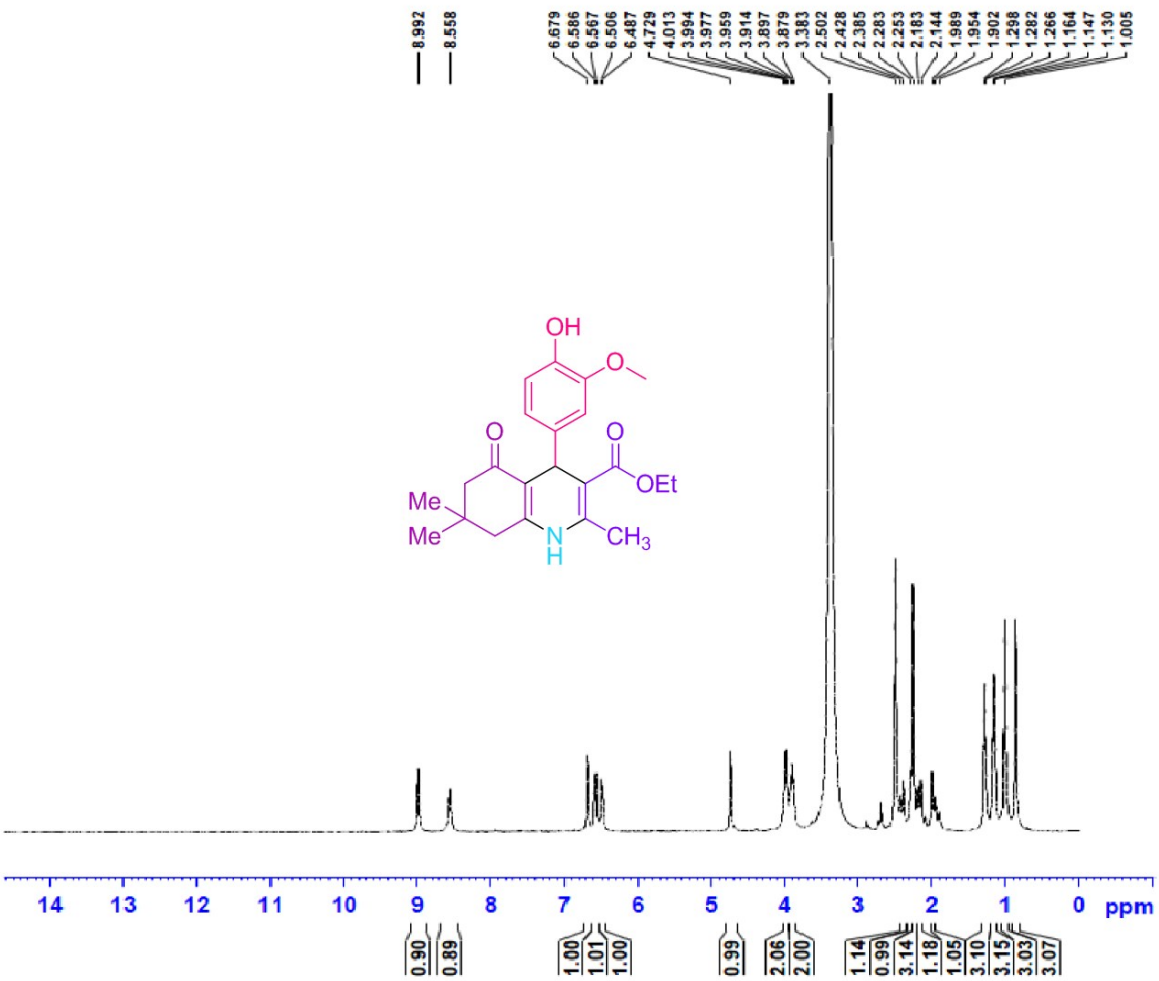


Ethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-Carboxylate.

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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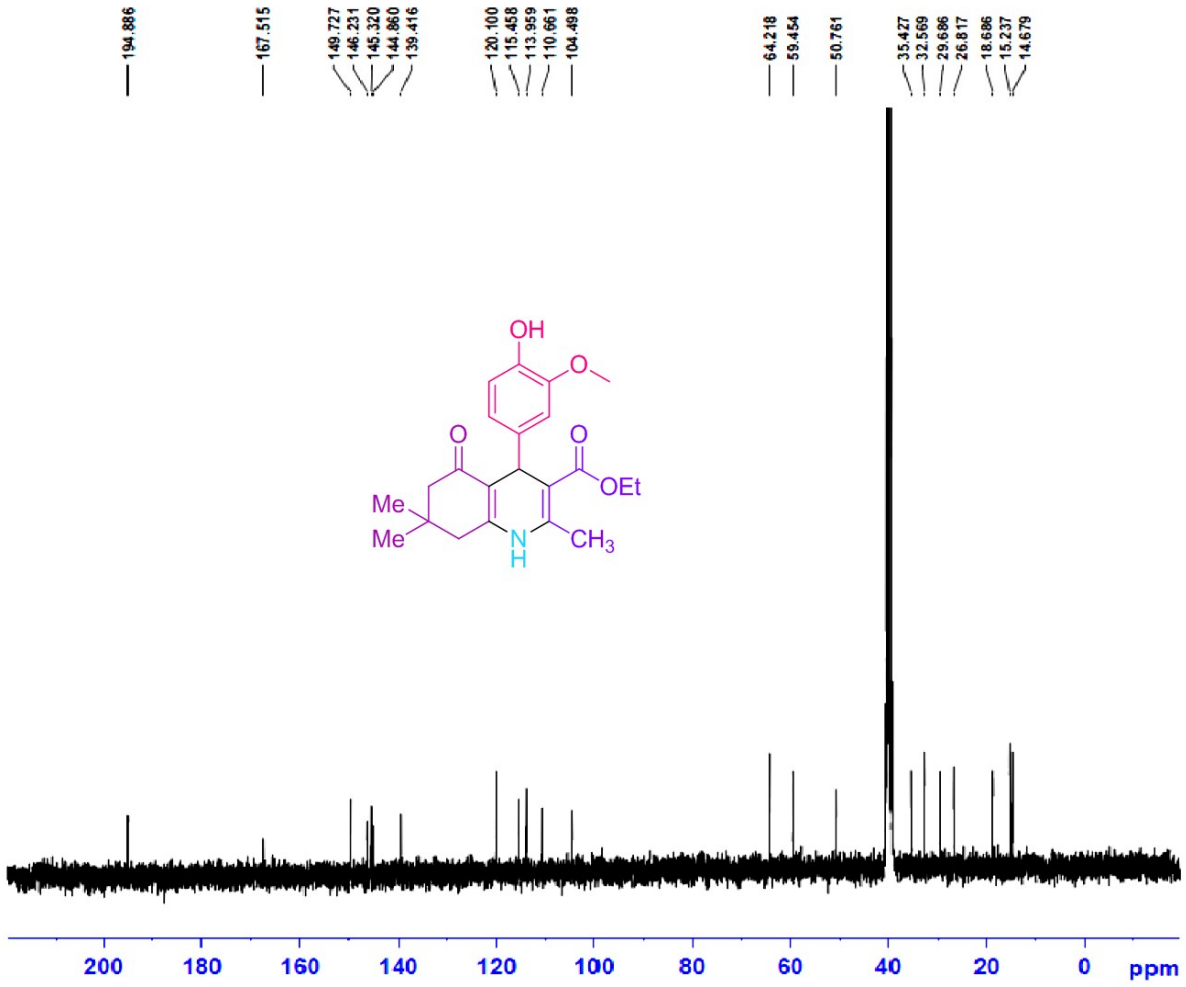
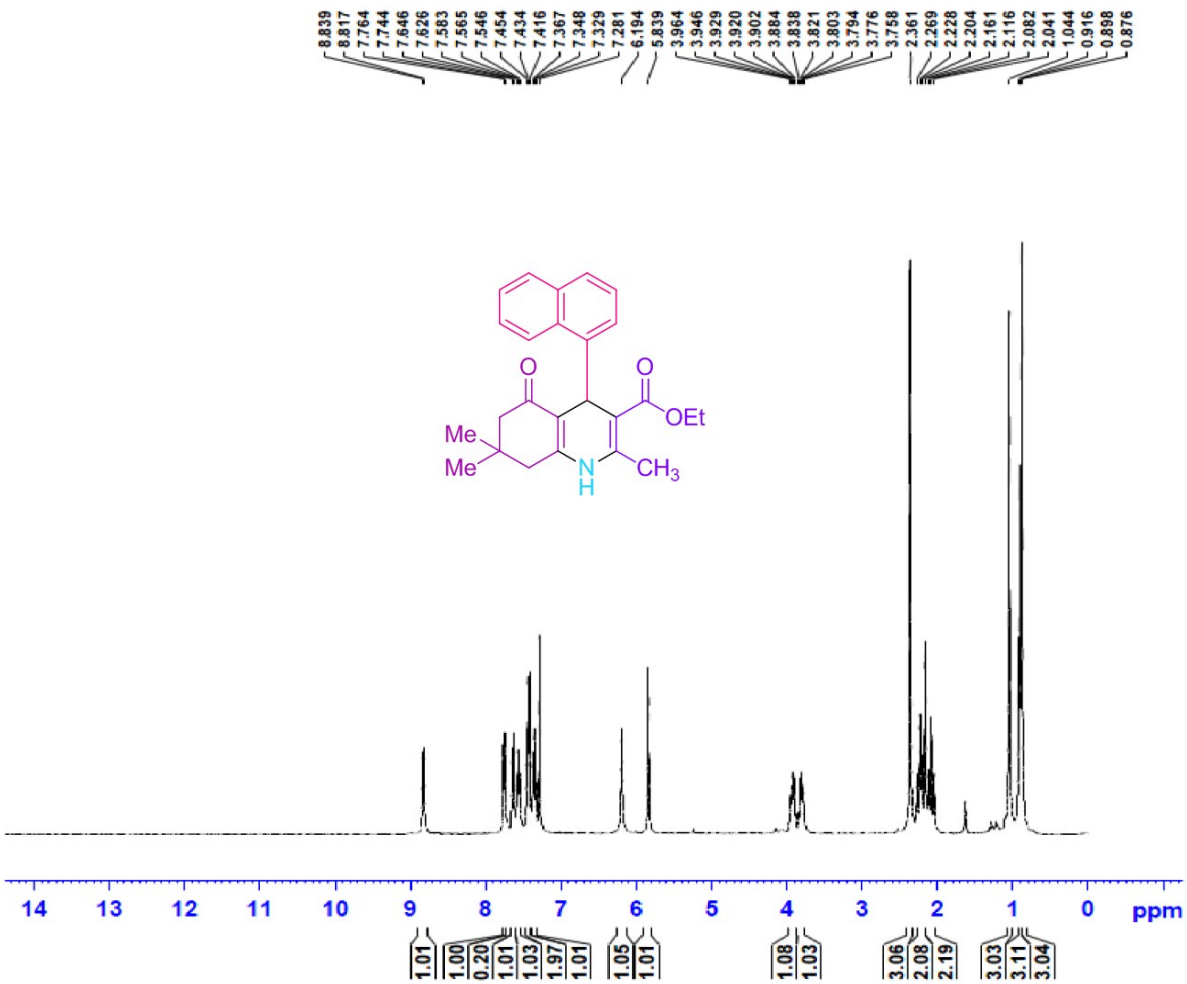


Ethyl 2,7,7-trimethyl-4-(naphthalen-1-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

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;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7.764
7.744
7.646
7.626
7.583
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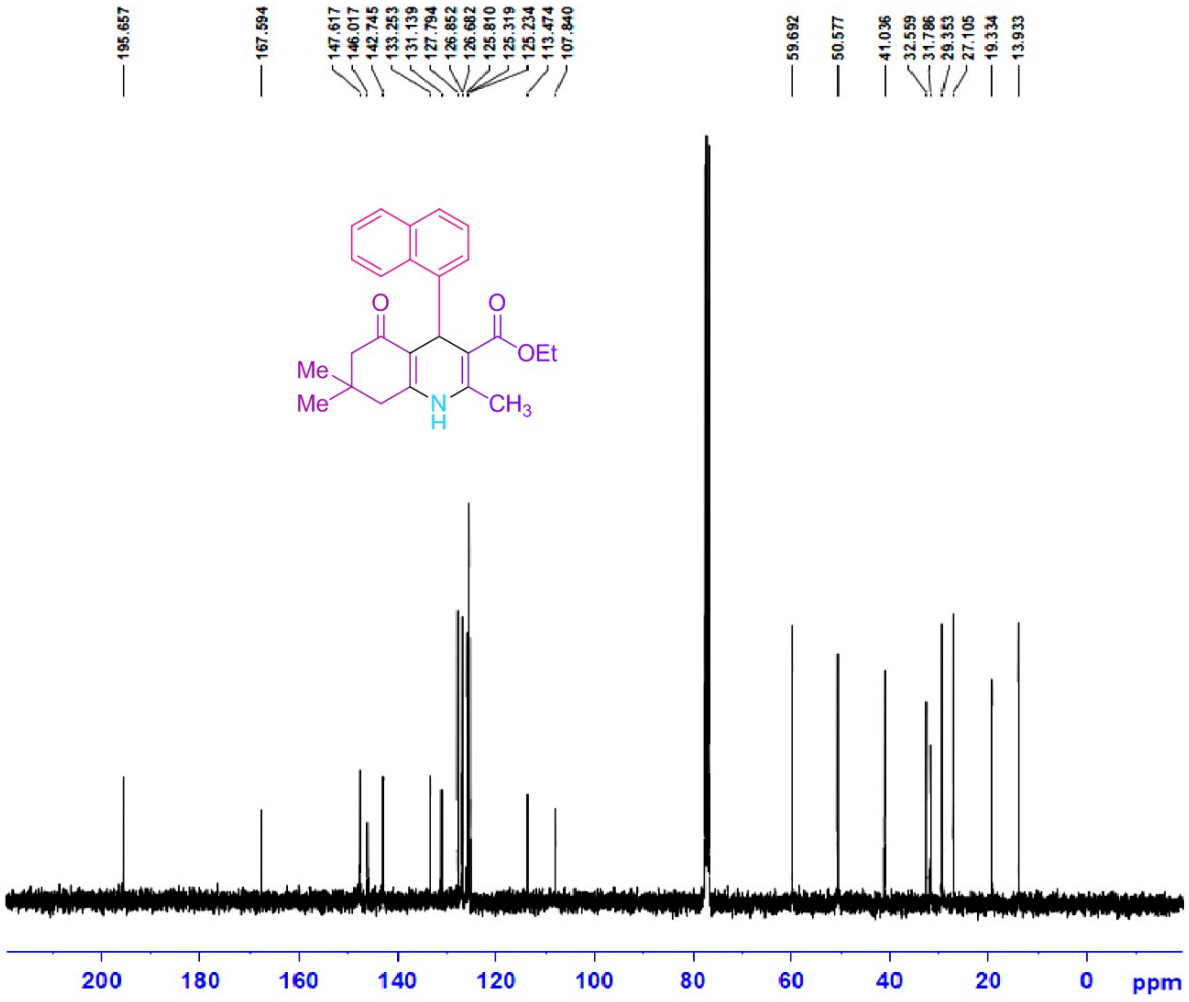
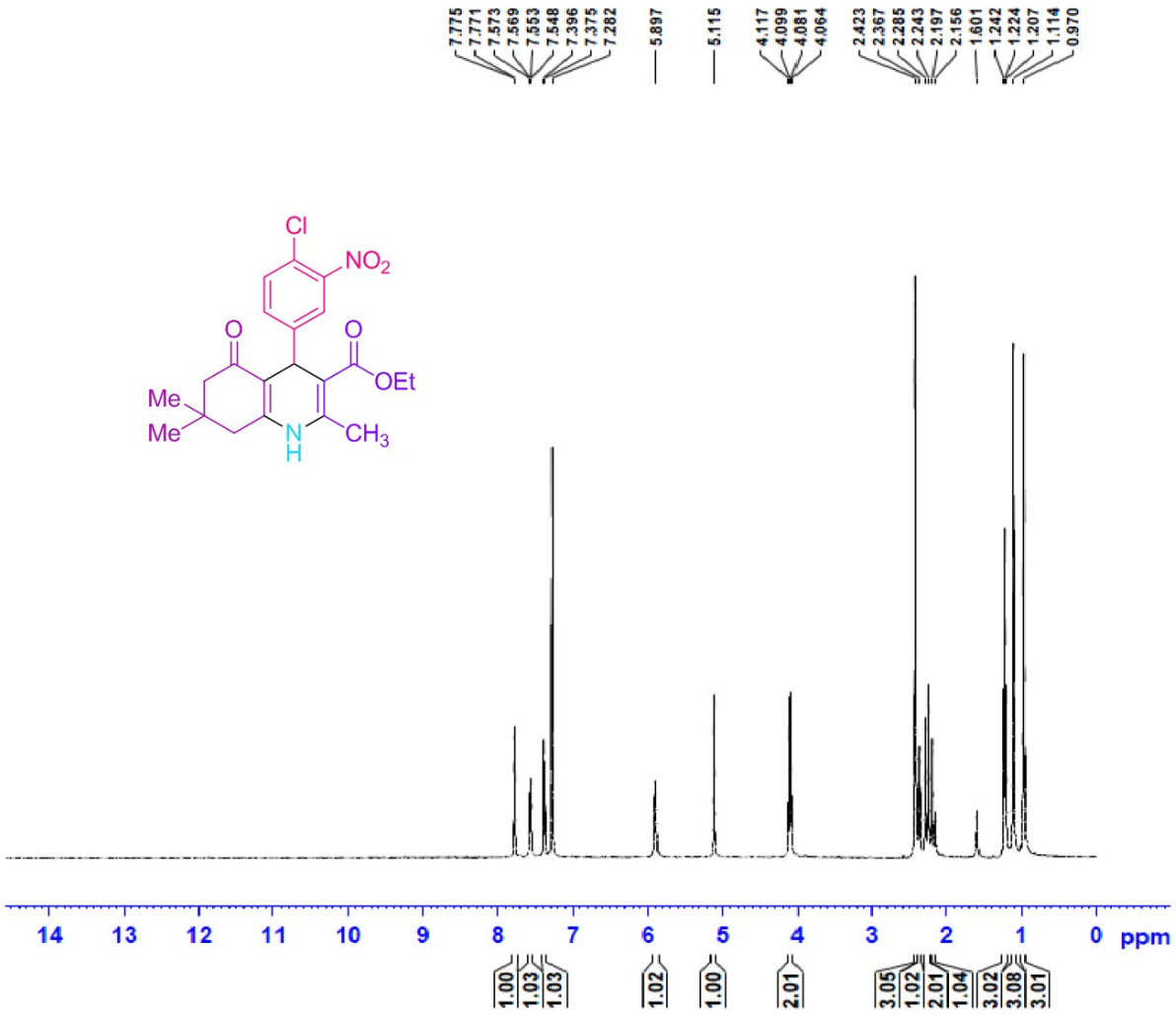
7.454
7.434
7.416
7.367
7.348
7.329
7.281
6.194
5.839
3.964
3.946
3.929
3.920
3.902
3.884
3.838
3.821
3.803
3.794
3.776
3.758
2.361
2.269
2.228
2.204
2.161
2.116
2.082
2.041
1.044
0.916
0.898
0.876
O
O
OEt
Me
Me
N
H
CH3
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
0.20
1.01
1.03
1.97
1.01
1.05
1.01
1.08
1.03
3.06
2.08
2.19
3.03
3.11
3.04



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.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4.099
4.081
4.064
2.423
2.367
2.285
2.243
2.197
2.156
1.601
1.242
1.224
1.207
1.114
0.970
Cl
NO2
O
O
OEt
Me
Me
N
H
CH3
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
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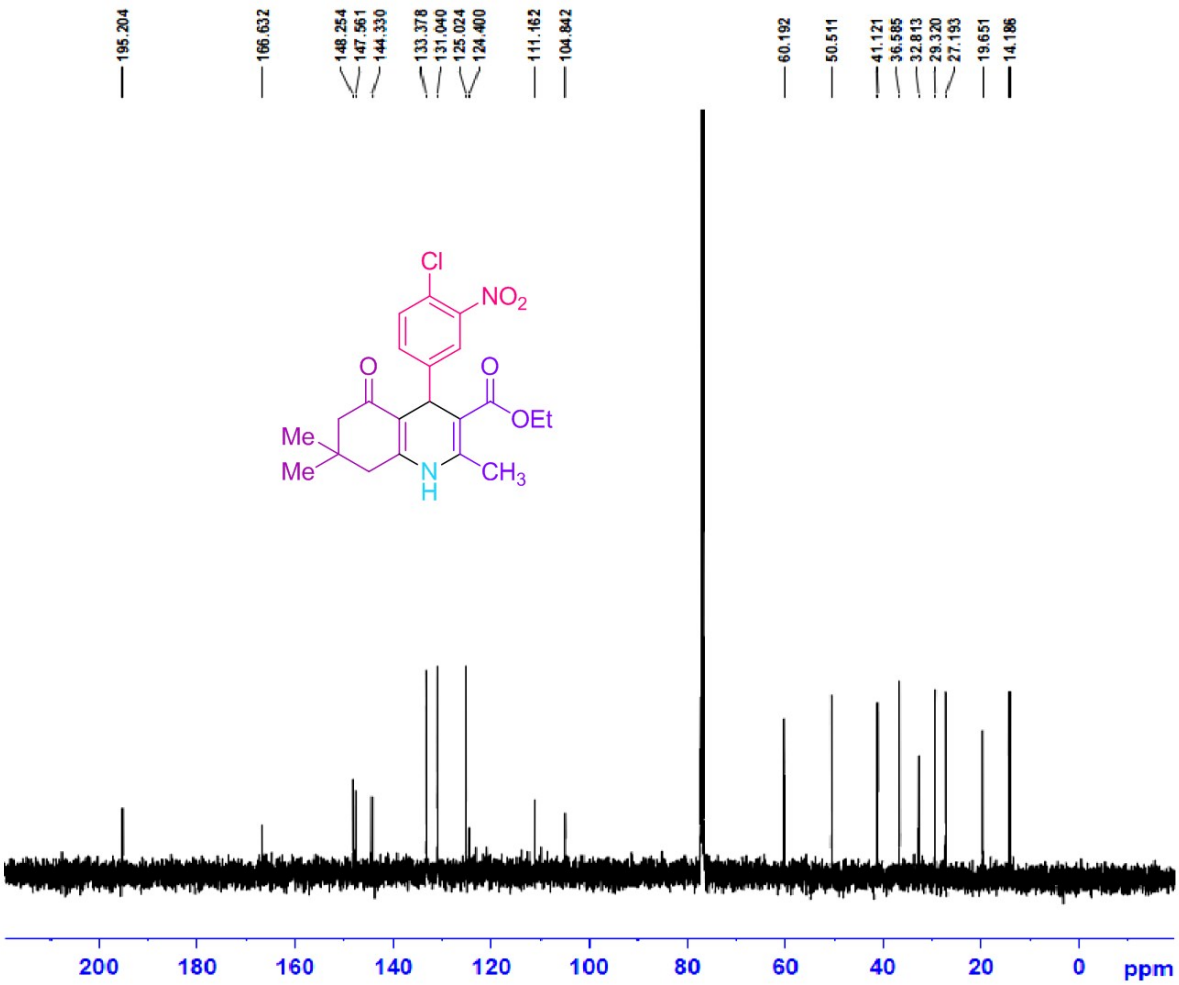
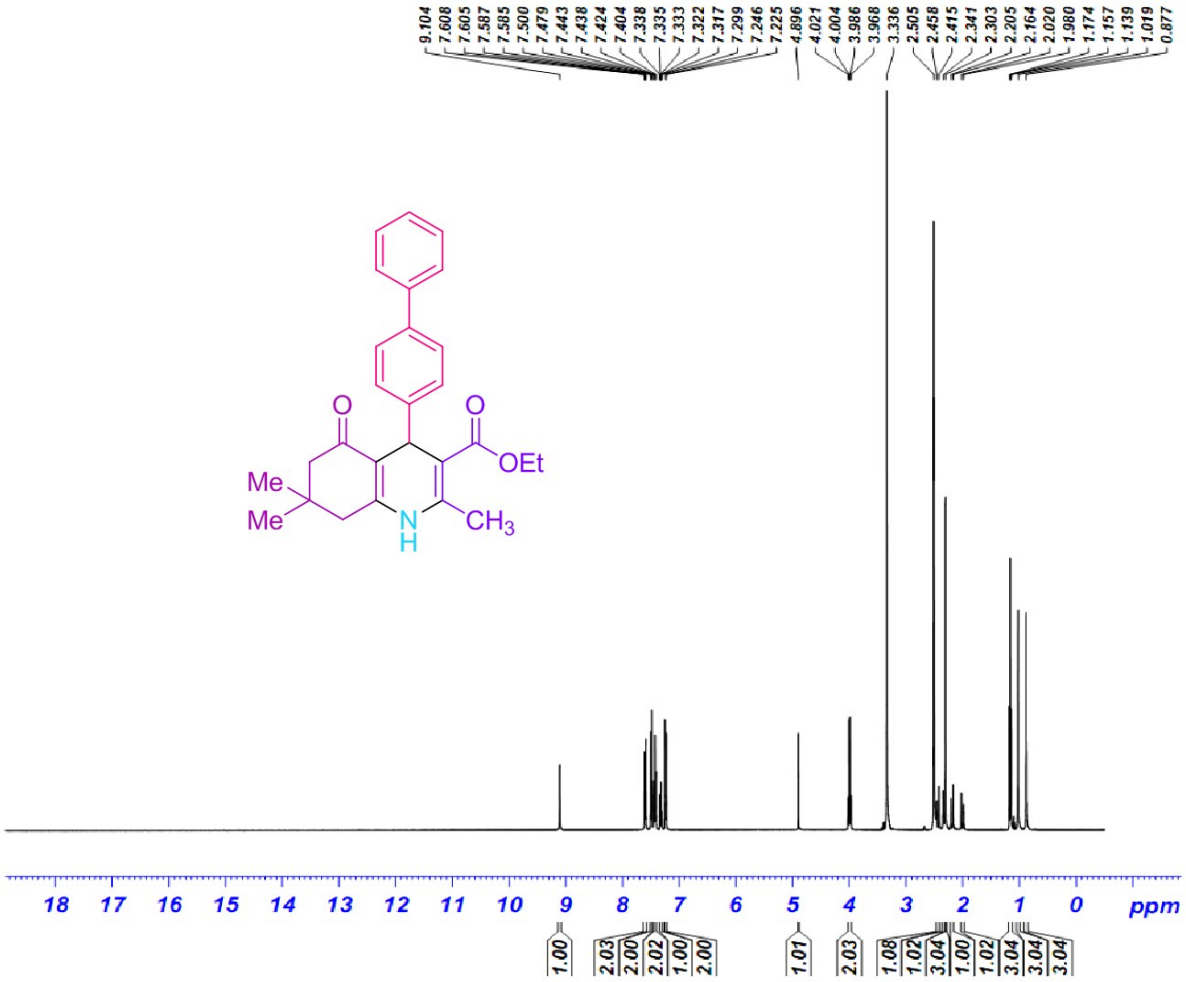
1.03
1.02
1.00
2.01
3.05
1.02
2.01
1.04
3.02
3.08
3.01



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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7.587
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7.338
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7.322
7.317
7.299
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7.225
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3.968
3.336
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2.458
2.415
2.341
2.303
2.205
2.164
2.020
1.980
1.174
1.157
1.139
1.019
0.877
O
O
OEt
Me
Me
N
H
CH3
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
2.03
2.00
2.02
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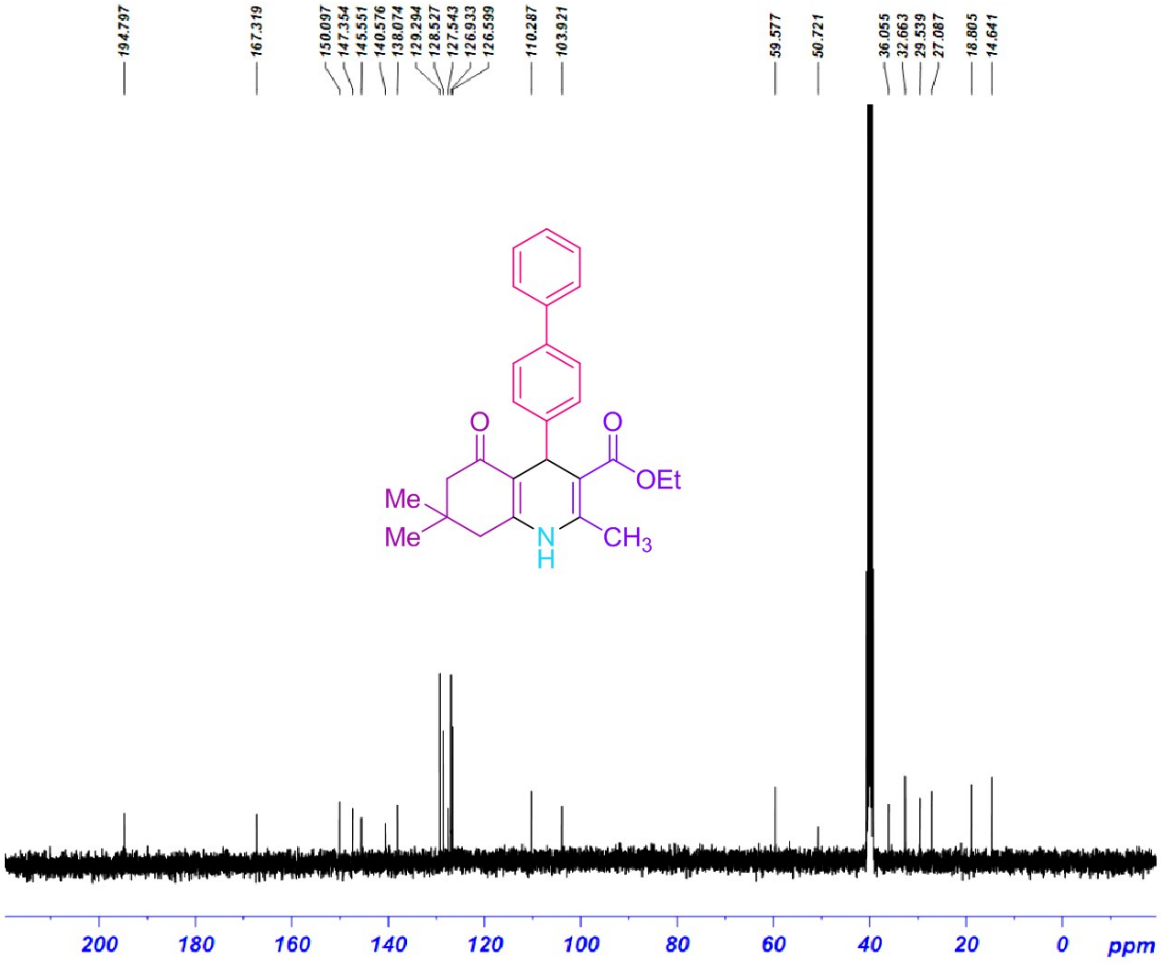
3.04
1.00
1.02
3.04
3.04
3.04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103.921
59.577
50.721
36.055
32.663
29.539
27.087
18.805
14.641
O
O
OEt
Me
Me
N
H
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200
180
160
140
120
100
80
60
40
20
0
ppm