Supporting Information

Nano-ferrous ferric oxide (nano-Fe_3O_4): magnetite catalytic system for the one-pot four-component tandem Imine/enamine formation-Knoevenagel-Michael-Cyclocondensation reaction of dimedone, aldehydes, *β*-ketoesters and ammonium acetate under green media

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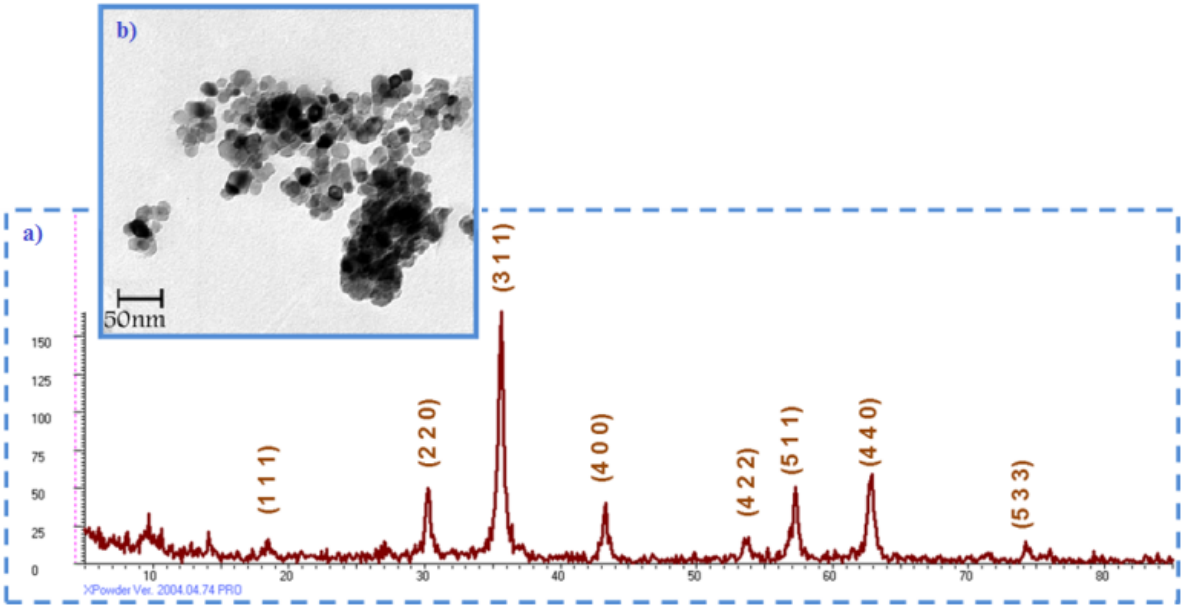


Fig S1. XRD pattern of the nano-Fe_3O_4 (a) and transmission electron microscopy (TEM) of the nano-Fe_3O_4 (b).

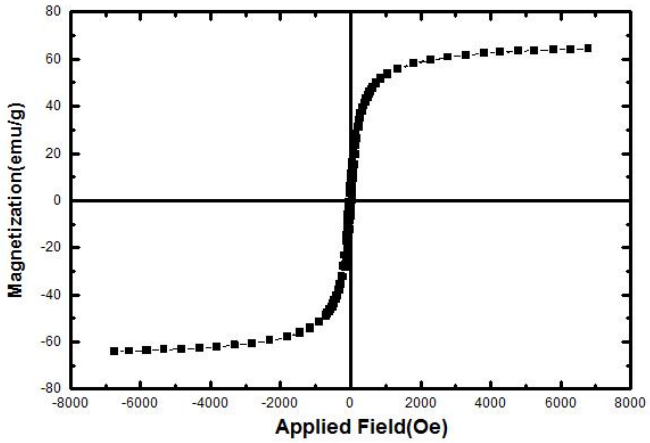


Fig S2. The vibrating sample magnetometer (VSM) of the nano-Fe_3O_4.

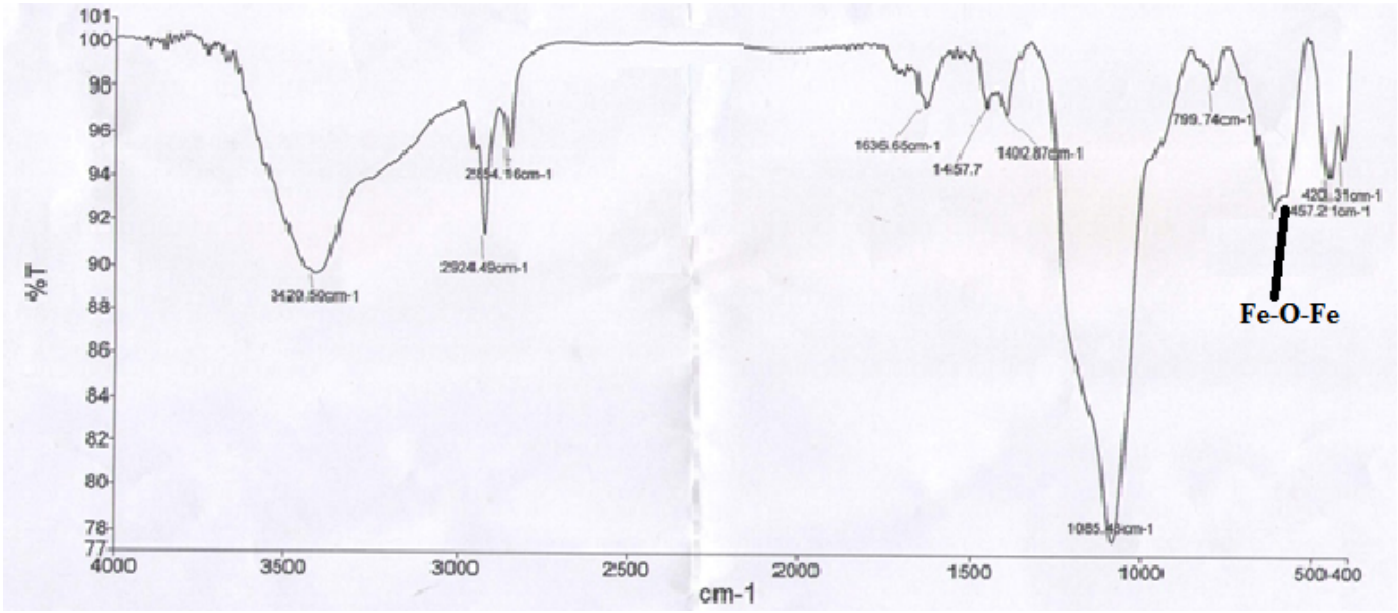


Fig S3. FT-IR spectrum of the nano-Fe_3O_4.

Central Composite Design

We have examined the catalytic activity of the catalyst to promote the synthesis of hexahydroquinolines. For this purpose, a mixture of dimedone, 4-nitrobenzaldehyde, ethyl acetoacetate and ammonium acetate using of nano-Fe_3O_4 under solvent-free condition was chosen as model reaction. Optimization of the reaction condition was investigated using the response surface method {Central Composite Design (CCD)} with five replicate at central point for developing a second order model with 19 runs (Table S1). In statistics, a central composite design is an experimental design, useful in response surface methodology, for building a second order (quadratic) model for the response variable without needing to use a complete three-level factorial experiment. Three variables that can effect on yield and time of the reaction are temperature (A with levels of the variables 35 to 65 ^{o}C), amount of catalyst (B with levels of the variables 2.8 to 8.2 mol%) and amount of ammonium acetate (C with levels of the variables 2.2 to 2.8 mmol). The levels of the variables and the corresponding response values of the CCD are shown in Table S2. Yield and time of the reaction were used as the dependent variables and were fitted to a quadratic polynomial model. After programming optimization (Table S3 and S4), two polynomial response surface models based on significant levels and actual values for time and yield were obtained (Fig. 1 and Fig. 2).

Table S1.Design Matrix

RUN	F1 (Temprature: oC)	F2 (Catalyst: mol%)	F3 (Ammonium acetate: mmol)	R1 (Time: min)	R2 (Yield: %)
1	64.86509	2.824284	2.797302	13	80
2	75	5.5	2.5	5.5	91
3	50	5.5	2.5	7	90
4	35.13491	2.824284	2.202698	15	76
5	35.13491	8.175716	2.202698	7	89
6	50	5.5	3	7	90
7	50	5.5	2.5	7.5	89
8	64.86509	2.824284	2.202698	13	79
9	50	5.5	2.5	7.5	89
10	64.86509	8.175716	2.202698	5.5	91
11	35.13491	2.824284	2.797302	15	76
12	64.86509	8.175716	2.797302	5	91
13	50	5.5	2.5	7.5	89
14	50	10	2.5	5	92
15	50	1	2.5	25	71
16	50	5.5	2.5	7.5	89
17	50	5.5	2	7	88
18	35.13491	8.175716	2.797302	7.5	89
19	50	5.5	2.5	7.5	89

Table S2

Levels of the experimental variables of the CCD.

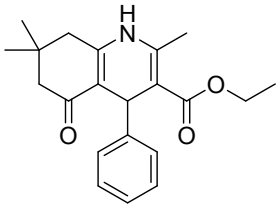
Variables	Units	Low Actual	High Actual
A	^{o}C	-7.5	7.5
B	g×1000	3.25	7.75
C	eq.	1.5	2.5

Table S3
Analysis of variance for the response surface quadratic model for time

Source	Sum ofSquares	df	MeanSquare	FValue	p-valueprob> F
Model	430.1705	3	143.3902	143.5109	< 0.0001
A-Temprature	11.08055	1	11.08055	11.08988	0.0046
B-Catalyst	305.9119	1	305.9119	306.1695	< 0.0001
B^2	105.2703	1	105.2703	105.3589	< 0.0001

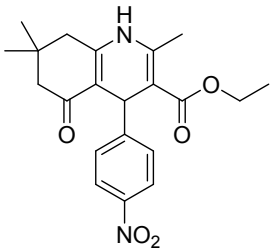
Table S4
Analysis of variance for the response surface quadratic model for yield

Source	Sum ofSquares	df	MeanSquare	FValue	p-value prob> F
Model	698.9412	4	174.7353	121.0036	< 0.0001
A-Temprature	31.47444	1	31.47444	21.79594	0.0004
B-Catalyst	520.5786	1	520.5786	360.4989	< 0.0001
A^2	11.66522	1	11.66522	8.078128	0.0130
B^2	127.6191	1	127.6191	88.37577	< 0.0001
Residual	20.21671	14	1.444051		



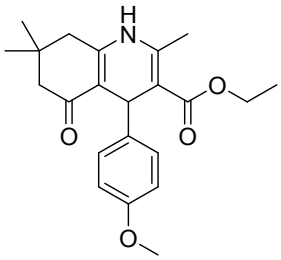
*Ethyl 2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**1**)*

White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.85 (s, 3H), 1.00 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H), 2.01-2.20 (m, 2H), 2.29 (s, 3H), 2.38-2.50 (m, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 4.82 (s, 1H), 7.05 (m, 1H), 7.18 (t, *J* = 6.7 Hz, 2H), 7.21 (t, *J* = 6.5 Hz, 2H), 9.12 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 14.5, 18.8, 26.8, 29.5, 32.6, 36.5, 50.6, 59.6, 103.4, 109.9, 113.5, 126.9, 128.8, 130.5, 146.0, 150.3, 167.0, 194.7.



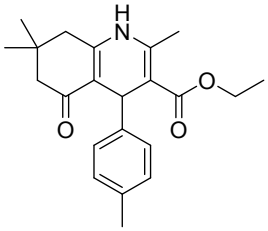
*Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**2**)*

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.



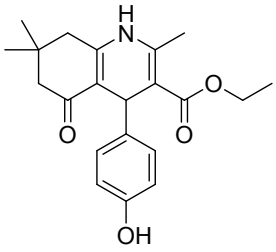
Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(3)***

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.



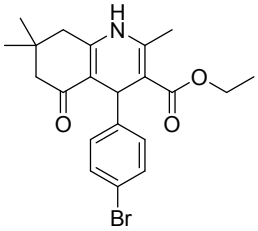
Ethyl 2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(4)***

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.



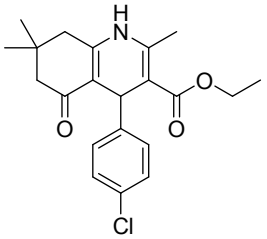
Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(5)***

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); ^{13}C 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.



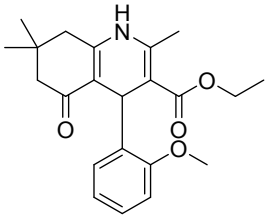
Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(6)***

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

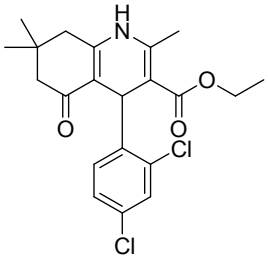
White solid, IR (KBr): (3274, 1707, 1605, 1489, 1382 cm^{-1}; ^{1}H NMR (400 MHZ, DMSO-d_6): δ 0.82 (s, 3H), 0.99 (s, 3H), 1.11 (t, *J* = 7.08Hz, 3H), 1.97 (d, *J* =16.08, 3H), 2.16 (d, *J* =16.12 Hz,1H), 2.43-2.50 (Distorted AB system, 2H), 3.96 (d, *J* =7.08 Hz, 2H), 4.83 (s, 1H), 7.15 (d, *J* =8.48, 2H), 7.24 (d, *J* =8.44, 2H), 9.01 (s, 1H).



*Ethyl 4-(2-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**9**)*

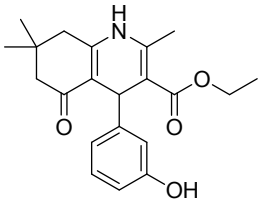
White solid, IR (KBr): 3285, 2957, 1689, 1611, 1488, 1381, 1216 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.83 (s, 3H), 0.99 (s, 3H), 1.10 (t, *J* =7.08 Hz, 3H), 1.89 (d, *J* =16.08 Hz, 1H), 2.11 (d, *J* =16.08 Hz, 1H), 2.18 (s, 3H), 2.40-2.50 (Distorted AB system, 2H), 3.68 (s, 3H), 3.91 (q, *J* =3.64 Hz, 2H), 5.04 (s, 1H), 6.75 (d, *J* =7.44 Hz, 1H), 6.82 (d, *J* =8.04 Hz, 1H), 7.03 (d, *J* =7.36 Hz, 1H), 7.09 (q, *J* =1.44 Hz, 1H), 8.93 (s, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): 14.05, 18.00,

26.15, 29.28, 31.95, 32.77, 50.36, 55.14, 58.72, 102.89, 108.64, 110.96, 119.44, 126.90, 130.46, 134.93, 144.08, 149.94, 157.10, 167.26, 193.79.



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

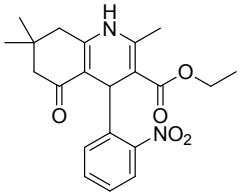
White solid, IR (KBr): (3285, 1706, 1609, 1493, 1381, 1214 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.83 (s, 3H), δ 0.92 (s, 3H), 1.07 (t, *J* =7.08 Hz, 3H), 1.91 (d, *J* =16.04 Hz, 1H), 2.14 (d, *J* =16.08 Hz, 1H), 2.22 (s, 3H), 2.49-2.50 (Distorted AB system, 2H), 3.95-3.91 (m, 2H), 5.14 (s, 1H), 7.31 (s, 2H), 7.34 (s, 1H), 9.12 (s, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): 14.07, 18.19, 26.37, 29.01, 31.94, 34.73, 50.14, 58.99, 102.69, 109.18, 126.83, 128.16, 130.70, 132.75, 132.82,144.19, 145.44, 149.85, 196.3.



*Ethyl 4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**11**):*

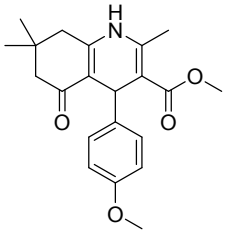
White solid, IR (KBr): (3408, 3289, 1675, 1606, 1485, 1220 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (s, 3H), 1.00 (s.3H). 1.13 (t, *J* =7.04 Hz, 3H), 2.00 (s, 1H), 2.15 (d, *J* =16.08 Hz, 1H), 2.26 (s, 3H), 2.38-2.50 (Distorted AB system, 2H), 3.97 (q, *J* =7.08 Hz, 2H), 4.78 (s,

1H), 6.46-6.43 (m, 1 H), 6.57 (d, *J* =7.24 Hz, 2H), 6.93 (t, *J* =7.96 Hz,1H), 9.01 (s,1H), 9.06 (s, 1H) ; ^{13}C NMR (22.5 MHz, DMSO-d_6): 14.8, 18.9, 27.4, 29.8, 32.8, 36.4, 40.4, 51.2, 59.7, 104.6, 110.8, 113.4, 115.4, 119.0, 129.3, 145.4, 150.2, 157.7, 167.8, 195.0.



*Ethyl 2,7,7-trimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **(14)**.*

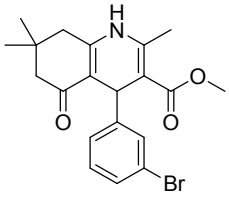
yellow solid, mp 205-207 C. IR (KBr): 3303, 2926, 2703, 1726, 1711, 1665, 1634, 1553, 1367, 1257 cm^{-1}. ^{1}H NMR: (400 MHz $CDCl_3$): δ (ppm) 0.91 (s, 3H), 1.09 (q, *J* =7.2, 3H), 1.61 (s, 3H), 2.07 (d, *J* =10.4, 1H), 2.18 (d, *J* =7.2, 1H), 2.30 (d, *J*=7.6, 1H), 2.29 (s, 1H), 2.38 (s, 3H), 3.97-4.10 (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; MS: m/z = 384 (M^+).



*Methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **(15)***

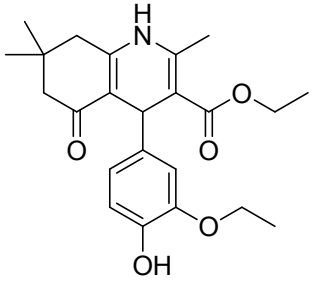
White solid, IR (KBr): 3348 3050 2928 2820 1725 1700 1680 1646 1446 1256 cm^{-1}. ^{1}H NMR: (400 MHz, $CDCl_3$): δ (ppm) 0.95 (s 3H) 1.09 (s 3H) 2.15 (s 3H) 2.21

(d J=12.8 1H) 2.27 (s 1H) 2.32 (s 1H) 2.38 (d J=12 1H) 3.63 (s 3H) 3.75 (s 3H) 5.02 (s 1H) 5.84 (s 1H) 6.77-6.74 (m 2H) 7.22 (dd J=4.8, J=2 1H) 7.28 (s 1H). ^{13}C NMR (100 MHz $CDCl_3$): 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.



*Methyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate **(16)***

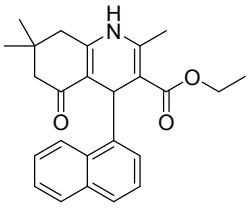
White solid, ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 0.83 (s, 3H), 1.00 (s, 3H), 1.99 (d, J = 16.0 Hz, 1H), 2.18 (d, J = 16.1 Hz, 1H), 2.30 (s, 3H), 2.39-2.49 (m, 2H), 3.53 (s, 3H), 4.85 (s, 1H), 7.14-7.16 (m, 2H), 7.25-7.27 (m, 2H), 9.15 (s, 1H); 13C NMR (75 MHz, DMSO-d_6): δ (ppm) 18.8, 26.8, 29.5, 32.6, 36.3, 103.1, 109.9, 121.6, 126.8, 129.1, 130.5, 130.6, 146.3, 150.3, 150.5, 167.5, 194.7.



*Ethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate. **(21)***

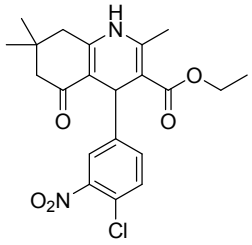
white solid, IR (KBr): 3563, 3326, 2956, 2892, 1735, 1703, 1668, 1645, 1626, 1603, 1326 cm^{-1}. ^{1}H NMR: (400 MHz, DMSO-d_6): δ (ppm) 1.00 (s, 3H), 1.14 (t, J = 6.8), 1.28 (t, J

= 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; MS: m/z 399 (M^+).



Ethyl 2,7,7-trimethyl-4-(naphthalen-1-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(23)***

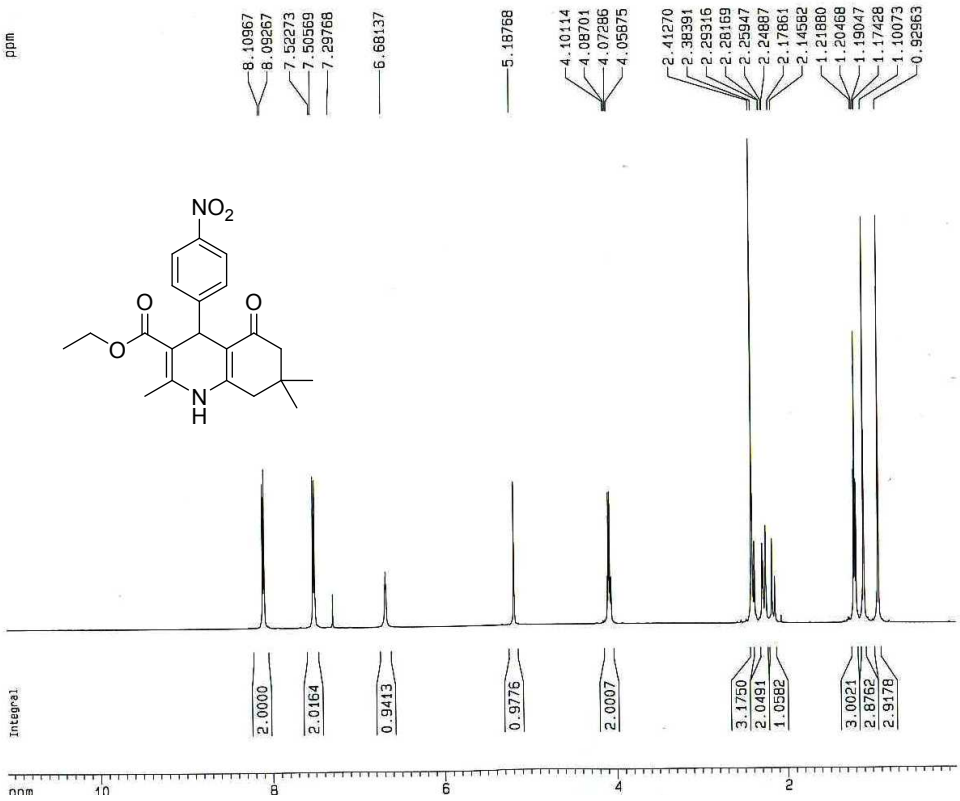
white solid, IR (KBr): 3402 2960 2901 1703 1675 1636 1381 1215 756 cm^{-1}. ^{1}H NMR: (400 MHz, $CDCl_3$): δ (ppm) 0.89 (t J =8.8, 3H) 1.04 (s 3H) 2.04 (s 3H CH_3) 2.09 (d J =13.6, 1H) 2.16 (s 1H) 2.21 (d J =9.6, 1H) 2.26 (s 1H) 2.36 (s 3H) 3.75-3.96 (m 2H) 5.83 (s 1H) 6.19 (s 1H) 7.28 (s 1H) 7.34 (t 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; MS: m/z 389 (M^+).

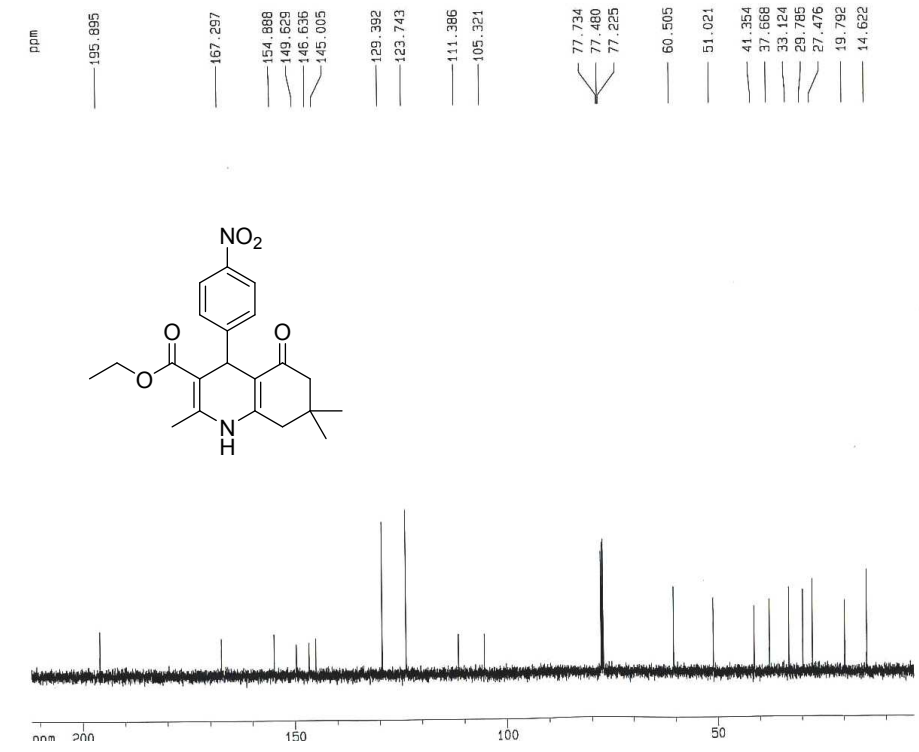


Ethyl 4-(4-chloro-3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate ***(24)***

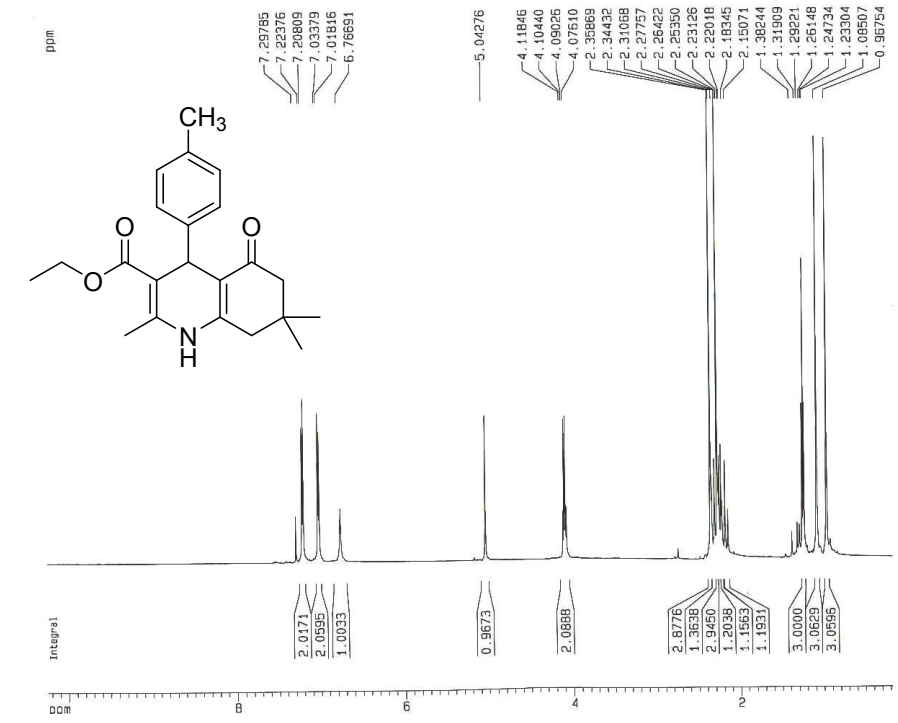
White solid, IR (KBr): 3397, 3100, 2906, 2823, 1725, 1706, 1635, 1641, 1436, 1578, 1326, 1241, 778 cm^{-1}; ^{1}H NMR: (400 MHz, $CDCl_3$): δ (ppm) 0.97 (s, 3H), 1.11 (s, 3H), 1.22 (t, *J* =7.2, 3H), 2.17 (d, *J* =16.4, 1H), 2.22 (d, *J* =16.8, 2H), 2.36 (s, 1H), 2.42 (s, 3H), 4.09 (q, *J* =7.2, 2H), 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.

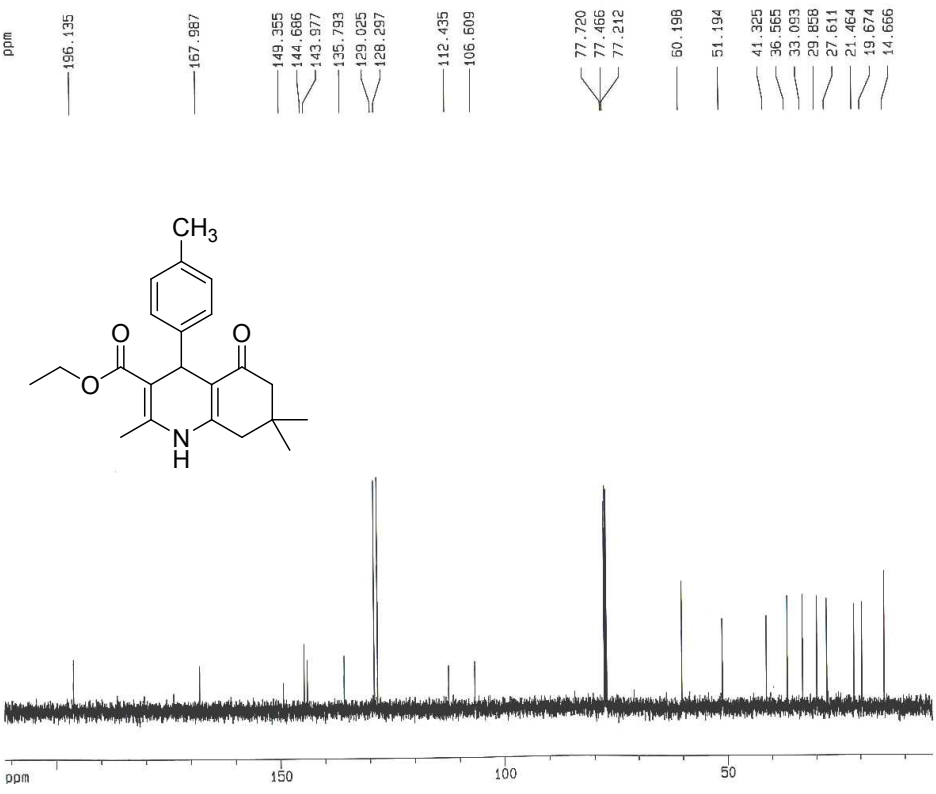
*Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**2**)*



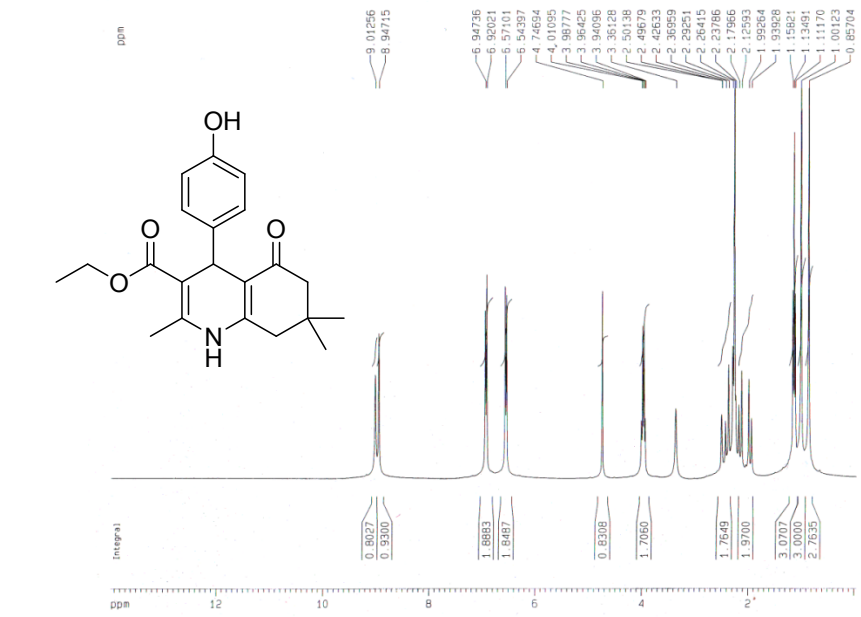


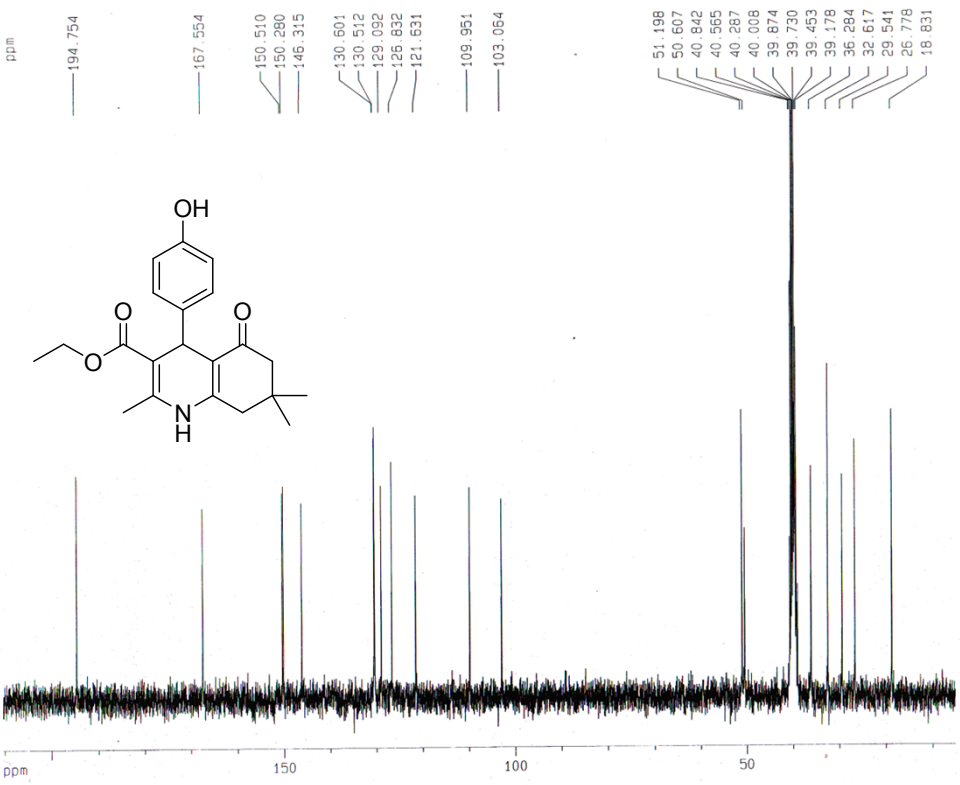
*Ethyl 2,7,7-trimethyl-5-oxo-4-p-tolyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**4**)*



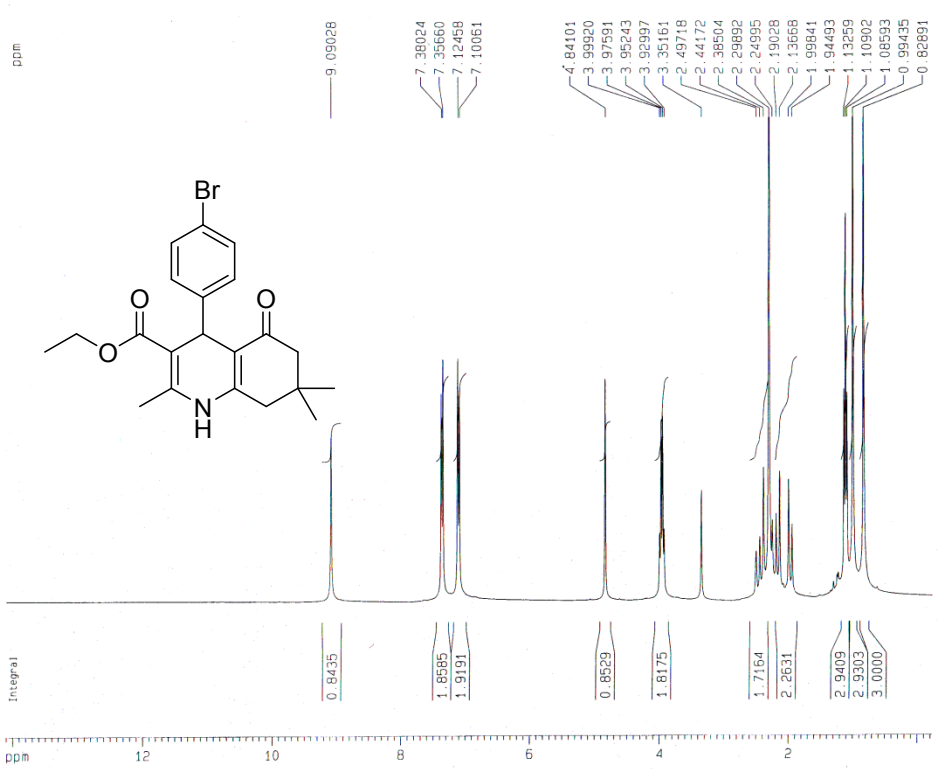


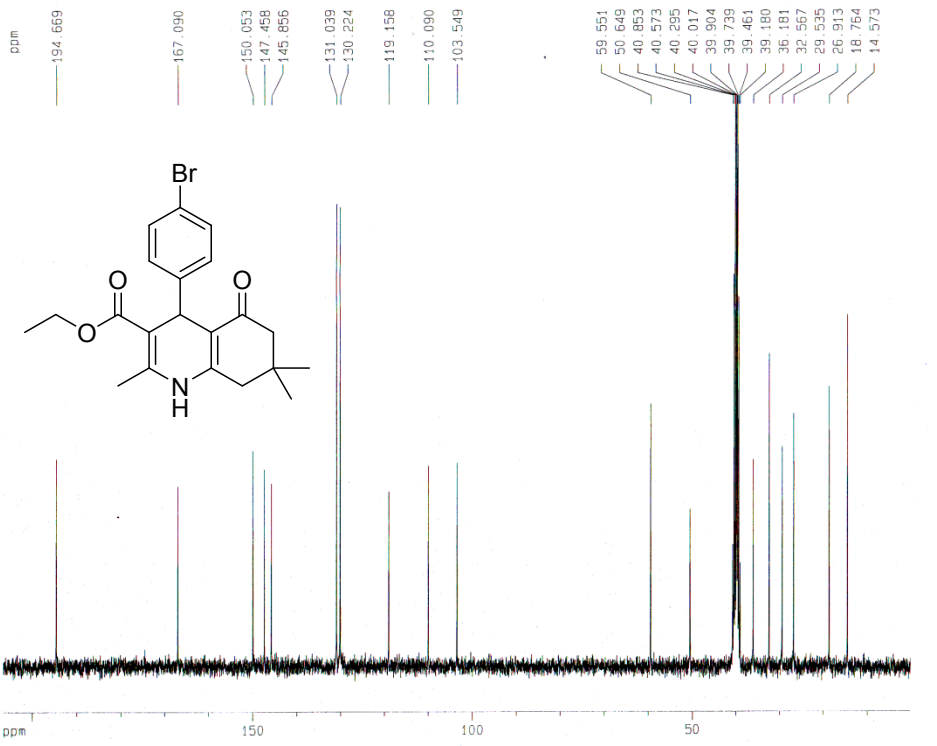
*Ethyl 4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**5**)*



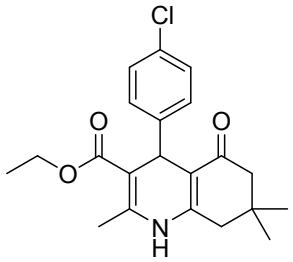


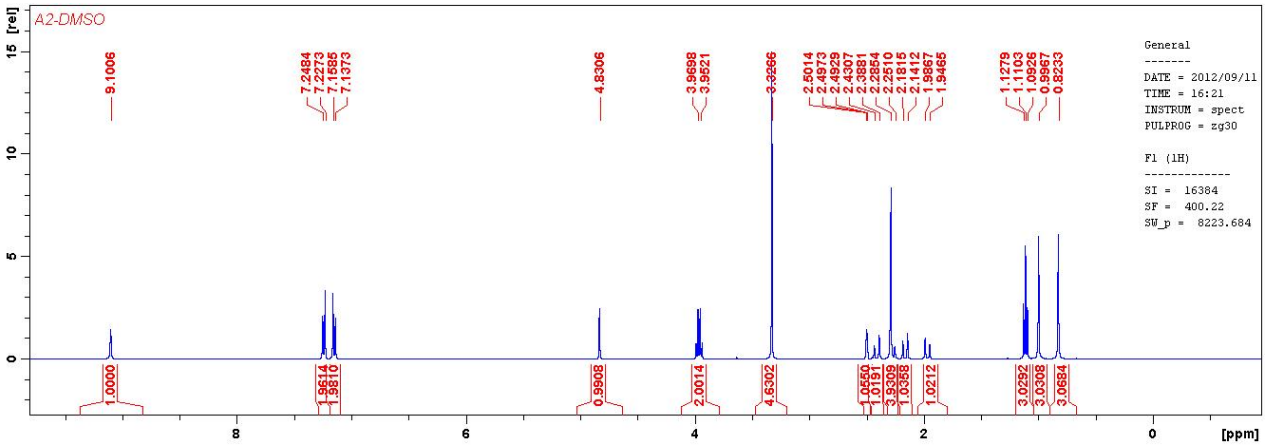
*Ethyl 4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**6**)*

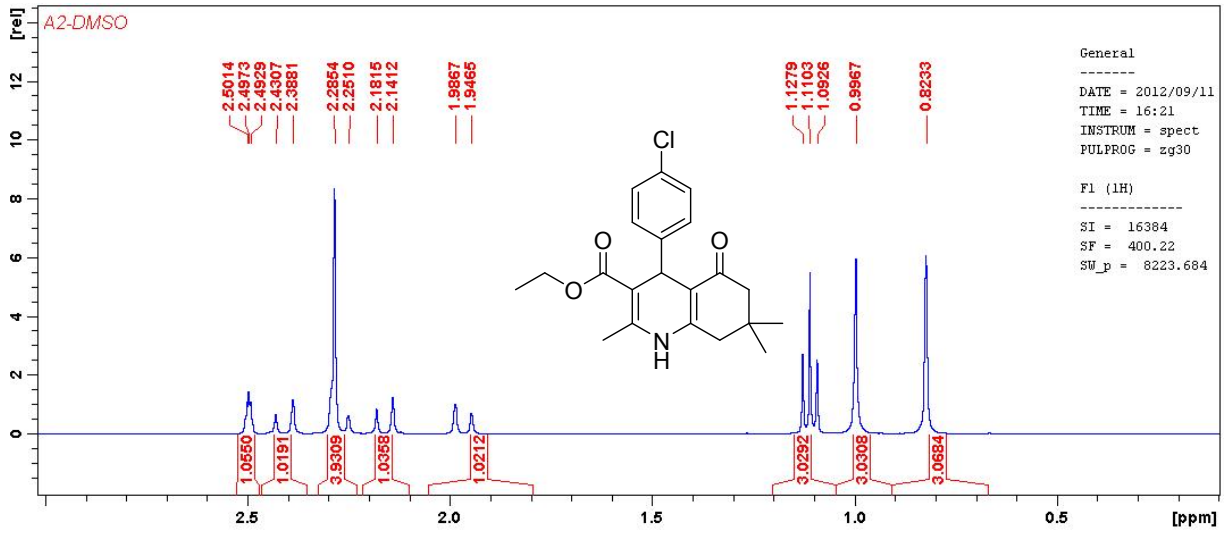




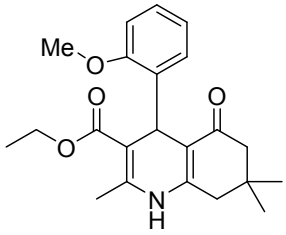
*Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**8**)*

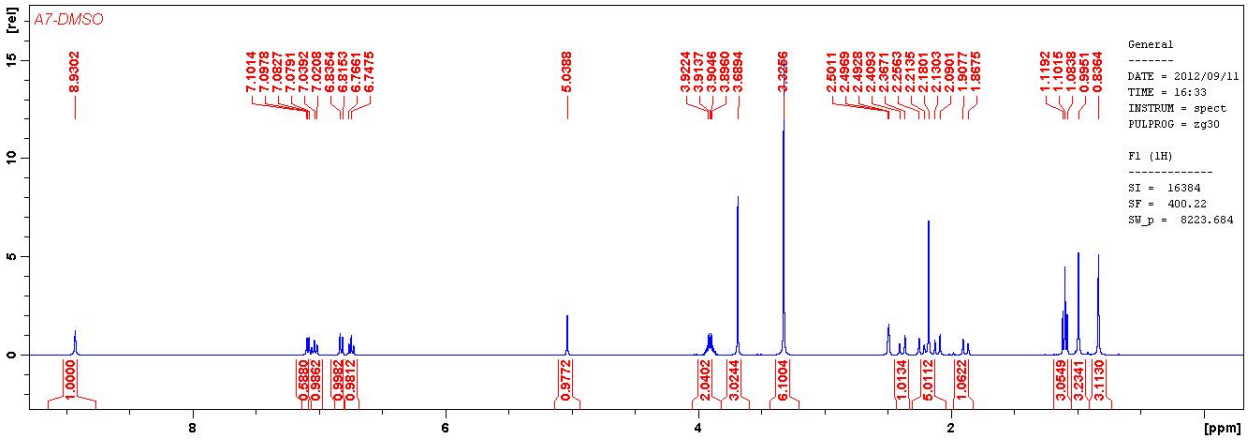


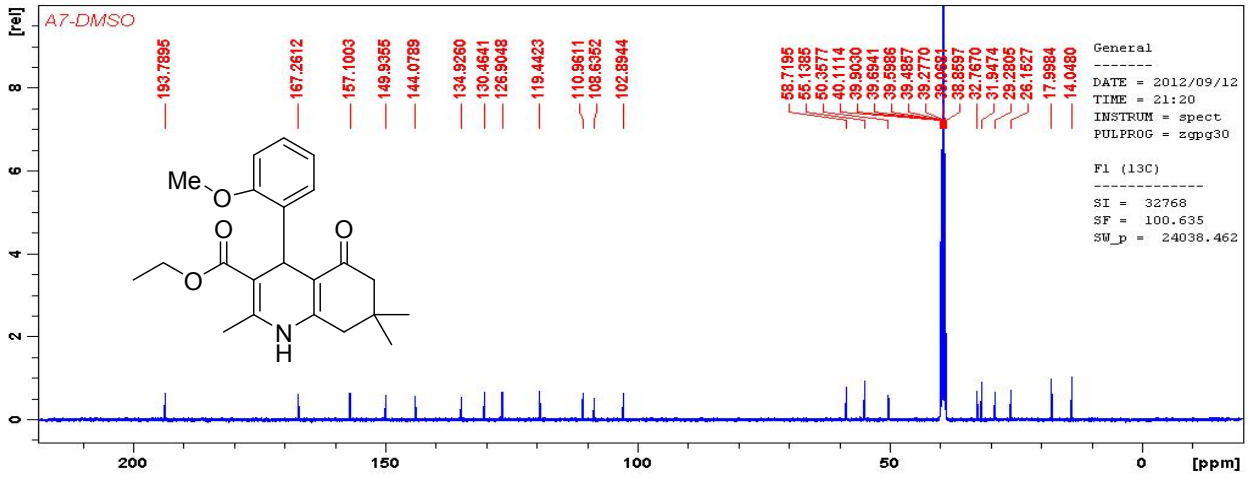




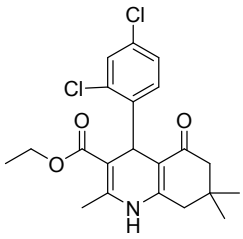
*Ethyl 4-(2-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**9**)*

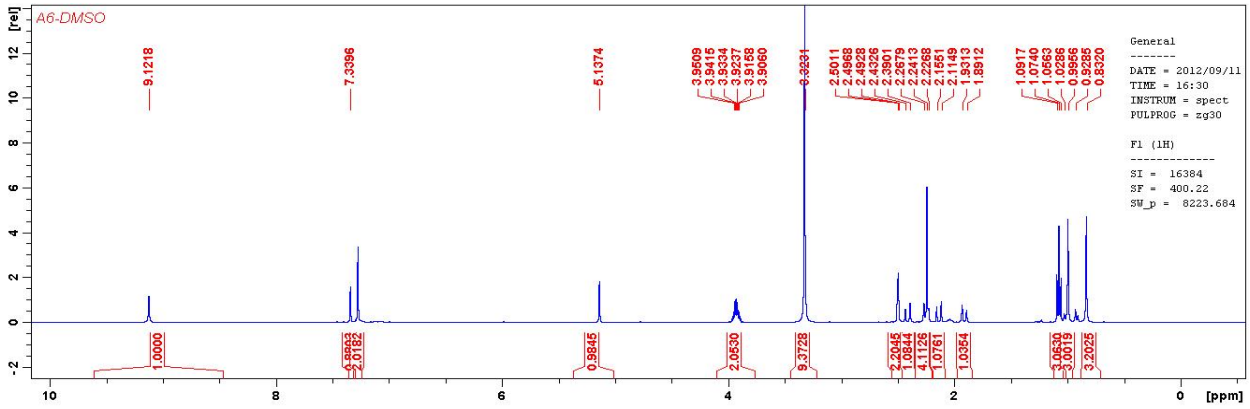


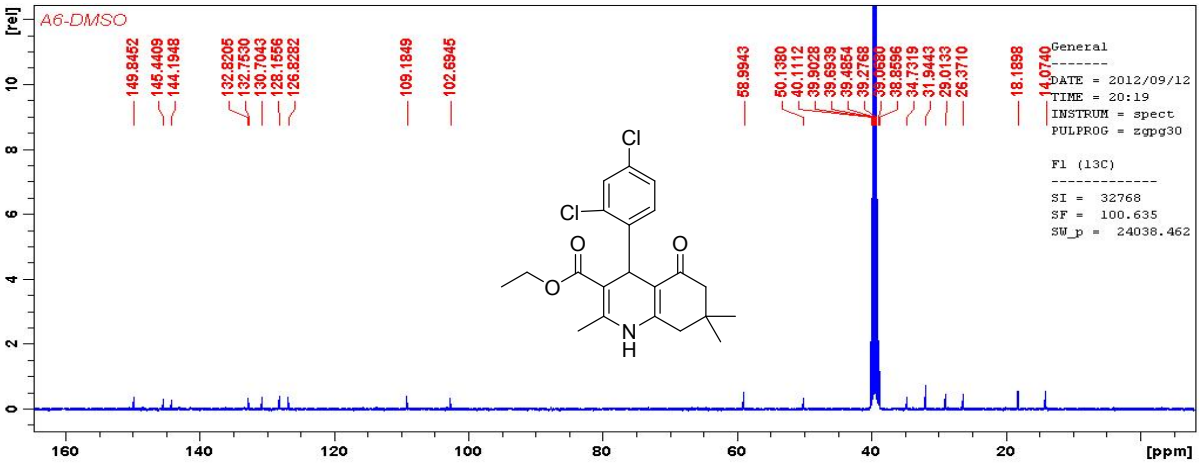




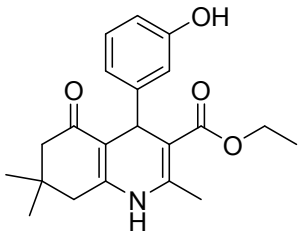
*Ethyl 4-(2,4-dichlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**10**)*

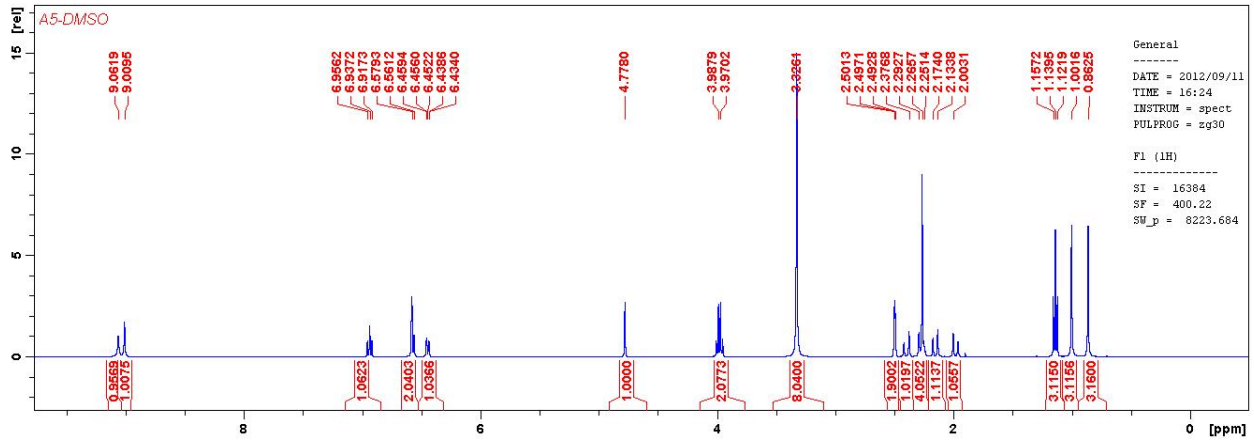


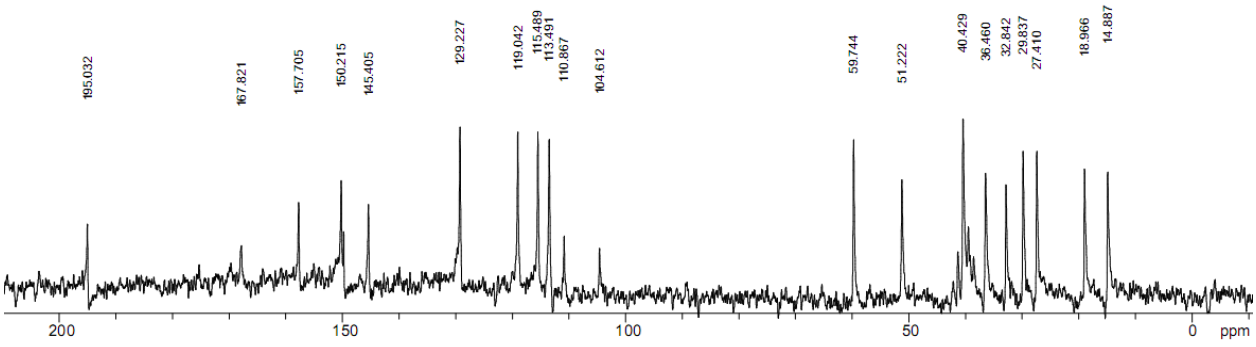




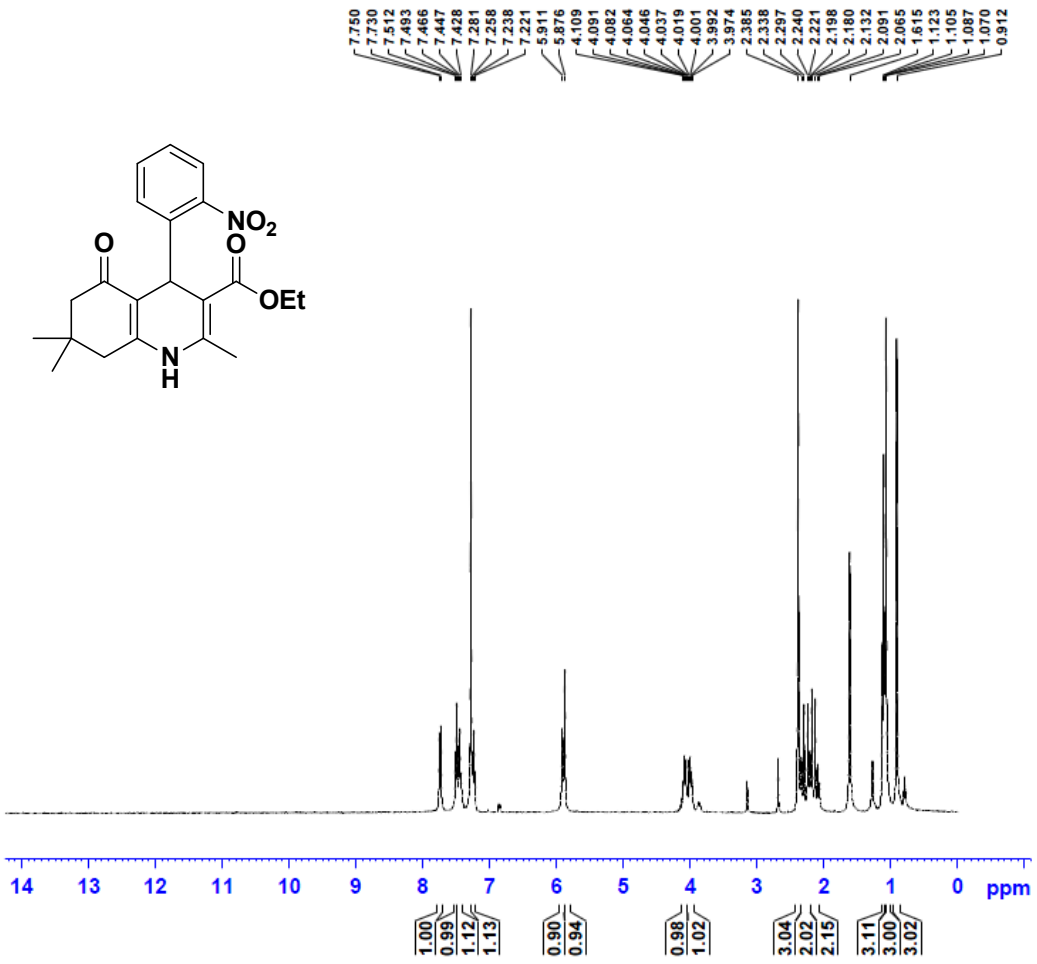
*Ethyl 4-(3-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**11**)*

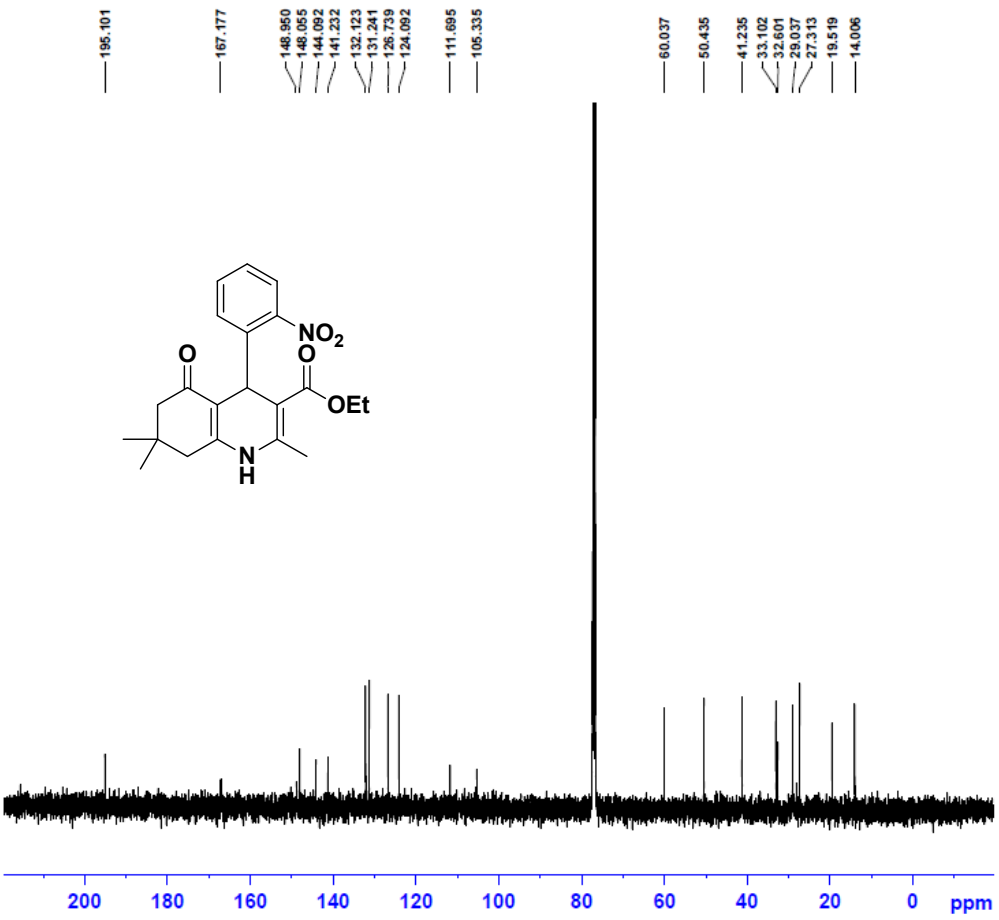






*Ethyl 2,7,7-trimethyl-4-(2-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**14**).*




195.101
167.177
148.950
148.055
144.092
141.232
132.123
131.241
126.739
124.092
111.695
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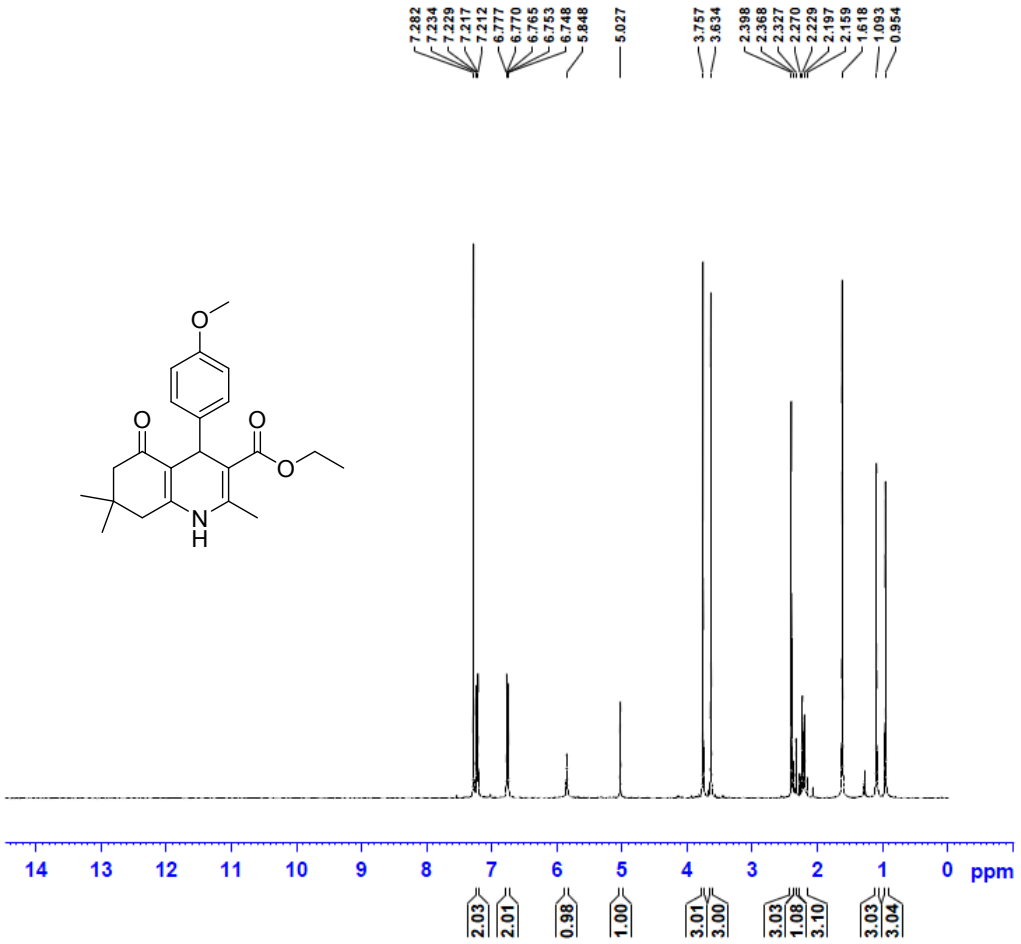
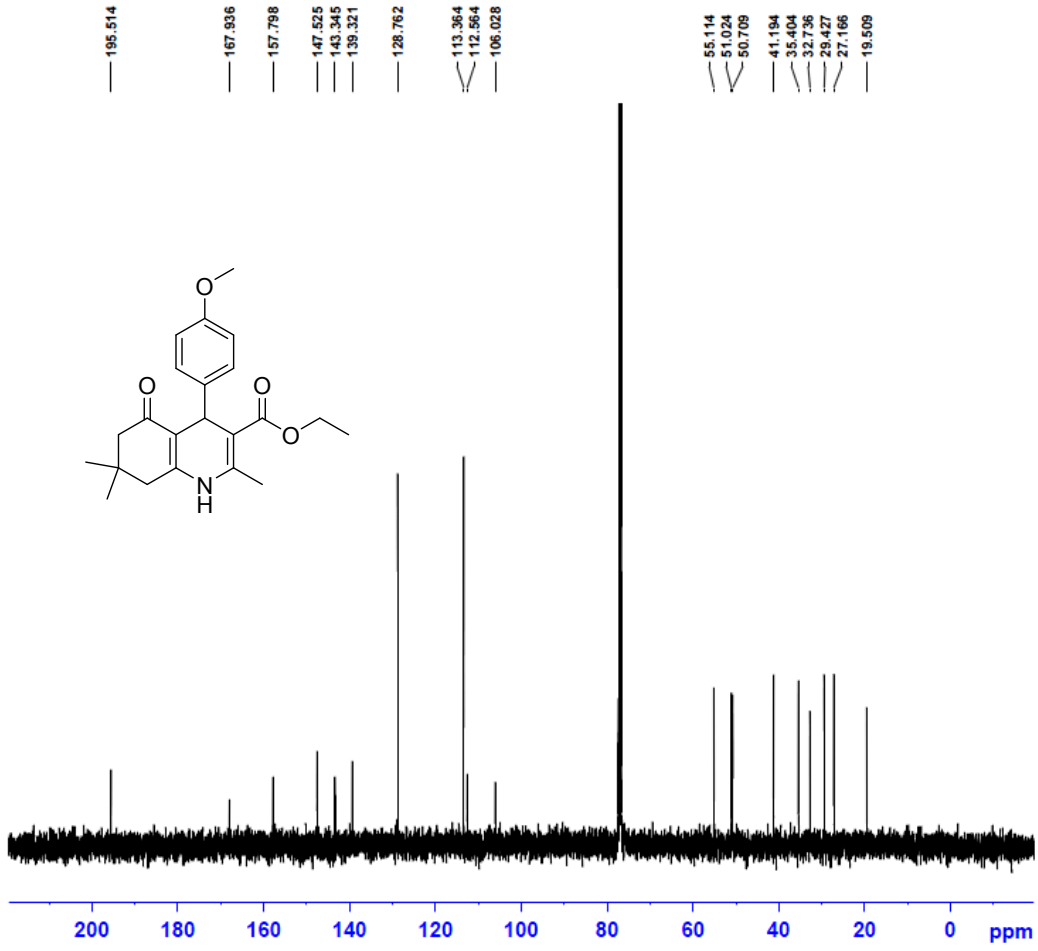
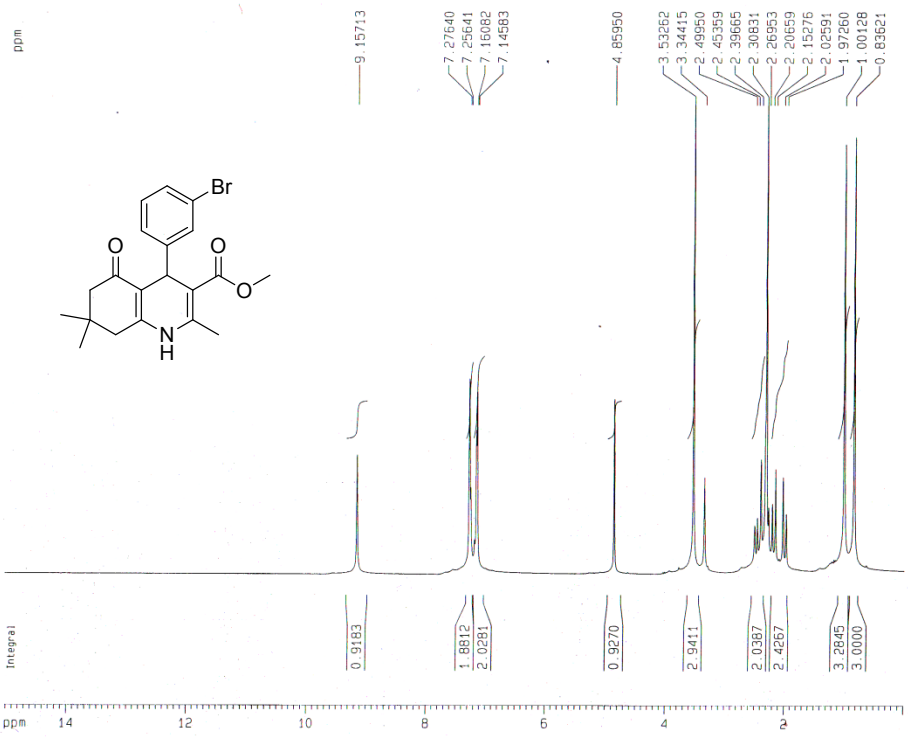
60.037
50.435
41.235
33.102
32.601
29.037
27.313
19.519
14.006
NO2
O
O
OEt
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm

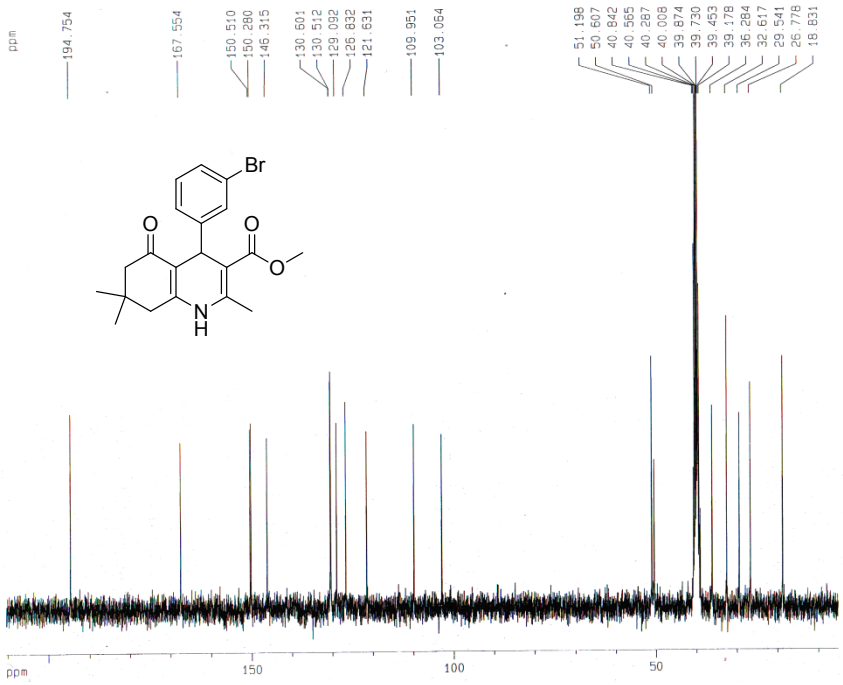
*Methyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**15**)*



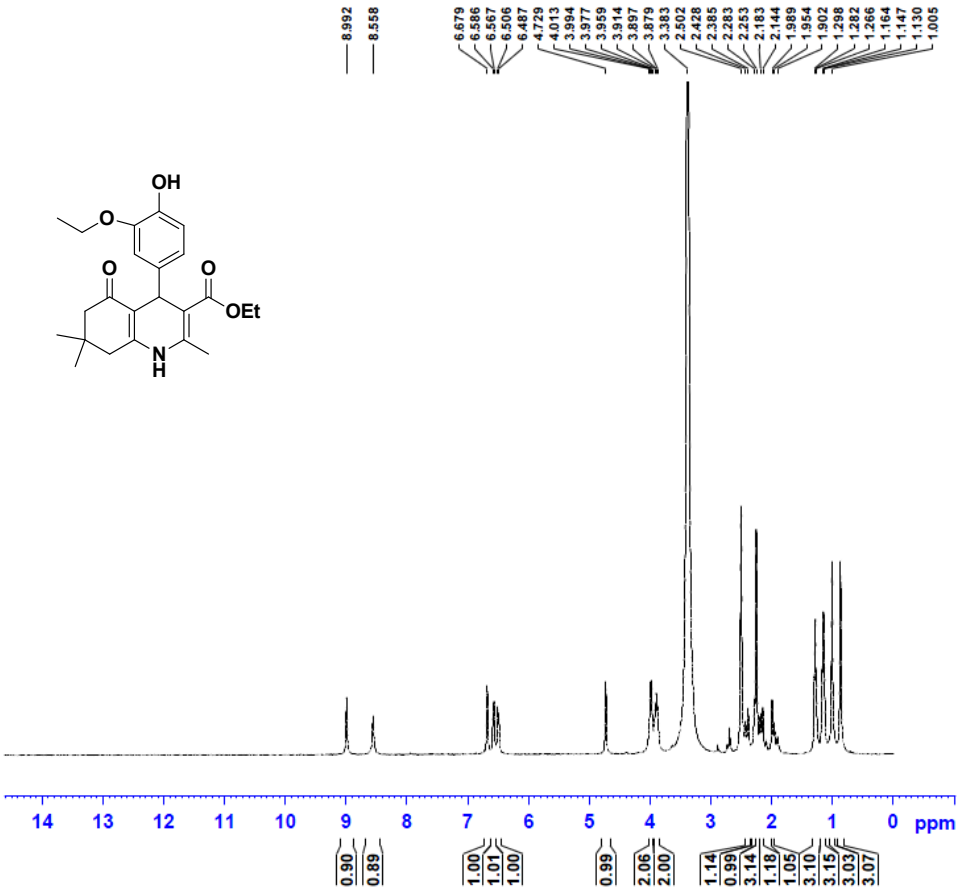

195.514
167.936
157.798
147.525
143.345
139.321
128.762
113.364
112.564
106.028
55.114
51.024
50.709
41.194
35.404
32.736
29.427
27.166
19.509
O
O
O
O
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm

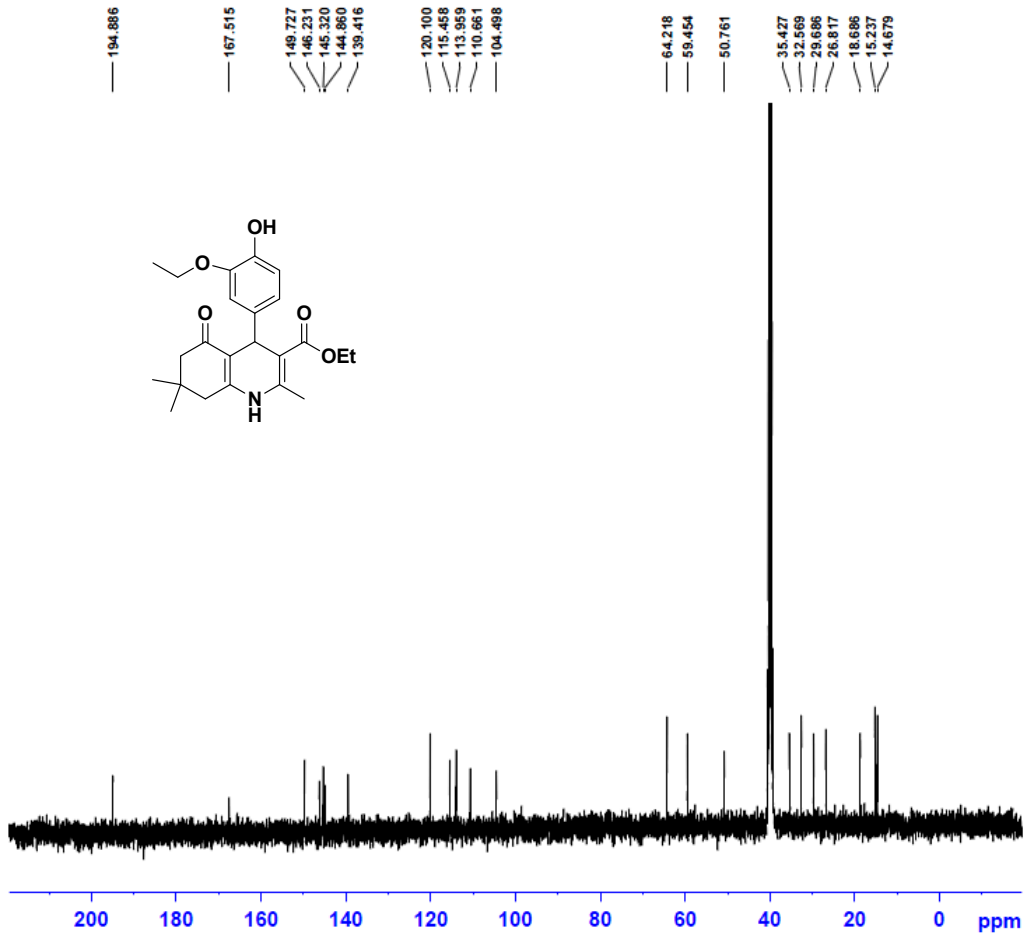
*Methyl 4-(3-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (**16**)*





Ethyl 4-(3-ethoxy-4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate. ***(21)***




194.886
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149.727
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144.860
139.416
120.100
115.458
113.959
110.861
104.498
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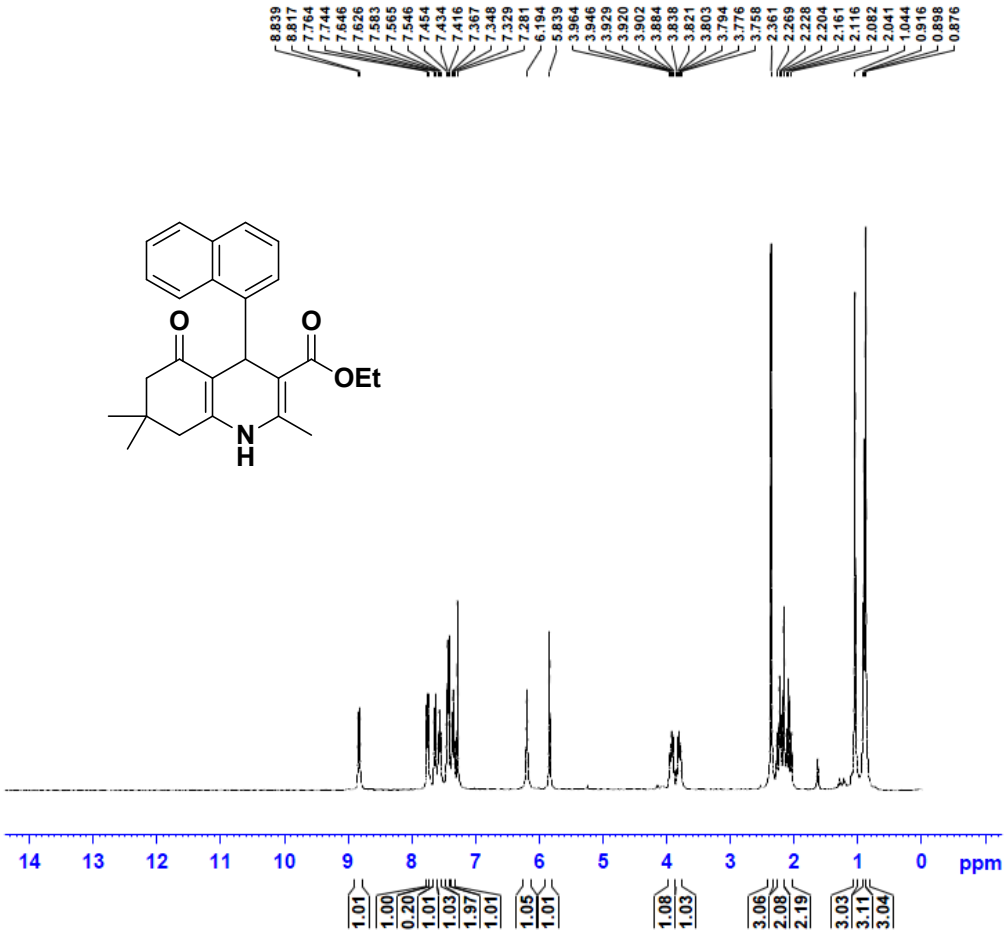
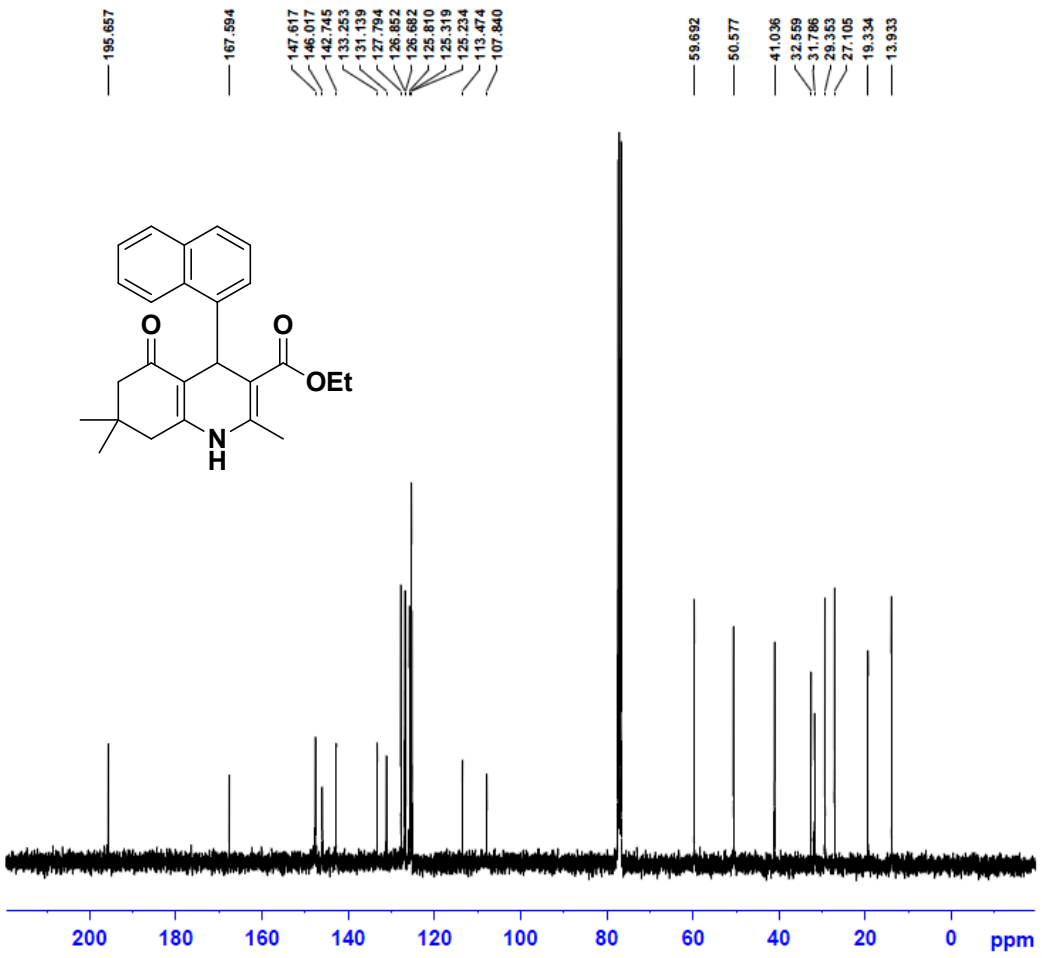
59.454
50.761
35.427
32.569
29.686
26.817
18.686
15.237
14.679
OH
O
O
O
OEt
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm

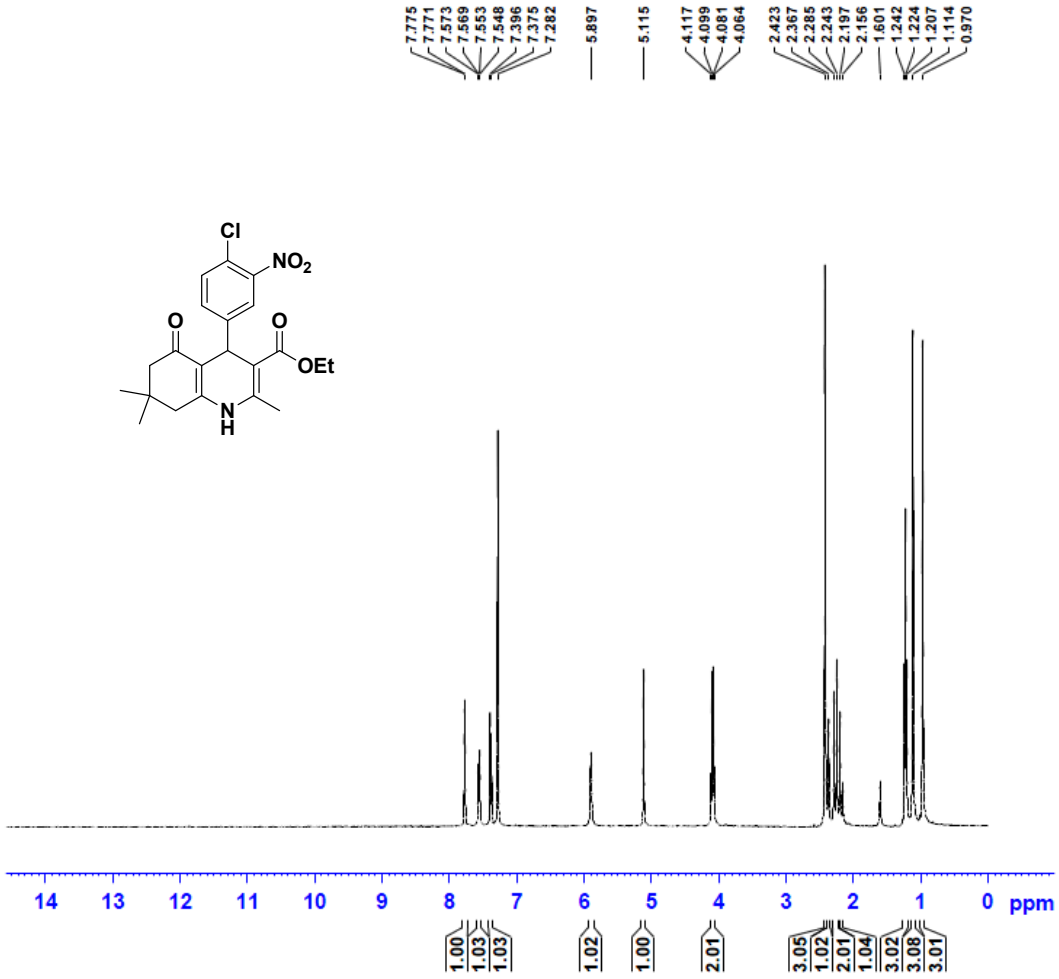
Ethyl 2,7,7-trimethyl-4-(naphthalen-1-yl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate

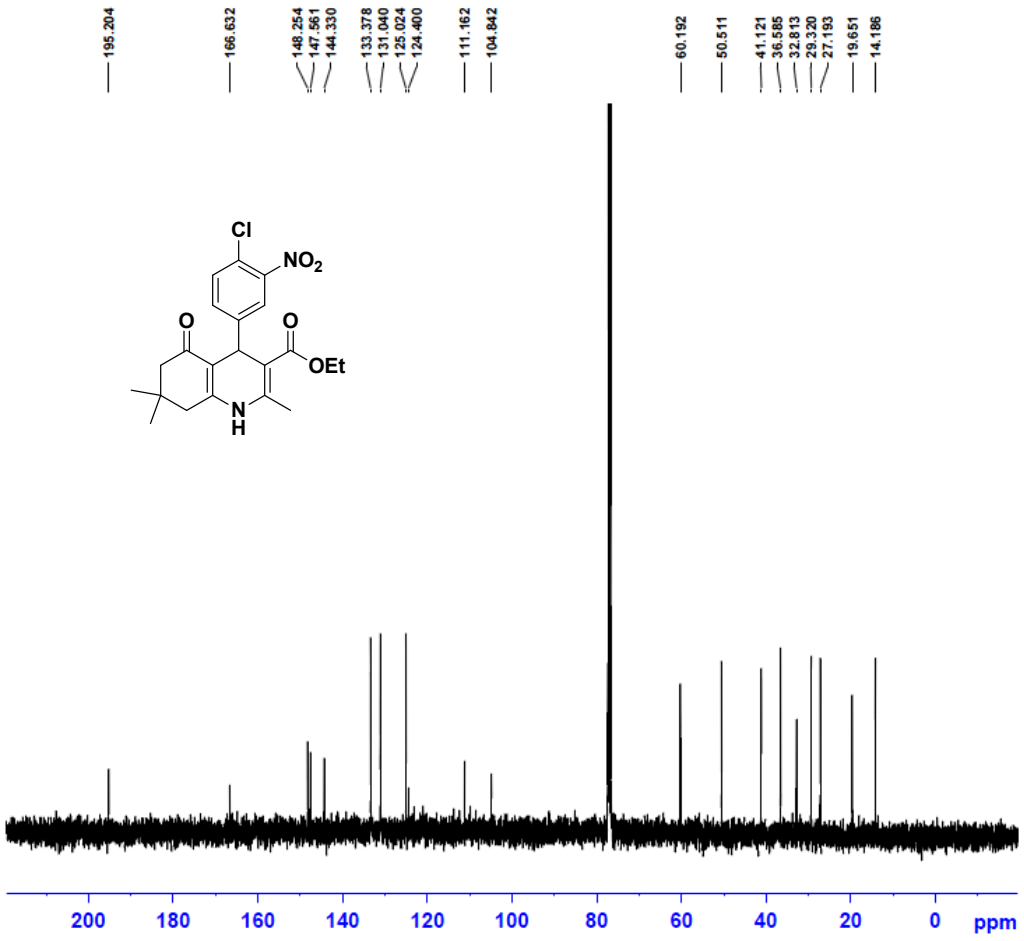
(23)




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
N
H
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 ***(24)***




195.204
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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
N
H
200
180
160
140
120
100
80
60
40
20
0
ppm