Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

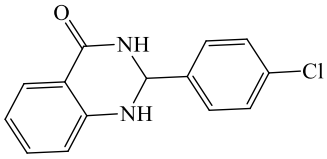
The First Report on the Preparation of Boehmite Silica Sulfuric Acid and Its Application in Some Multicomponent Organic Reactions

Arash Ghorbani-Choghamarani,* Bahman Tahmasbi

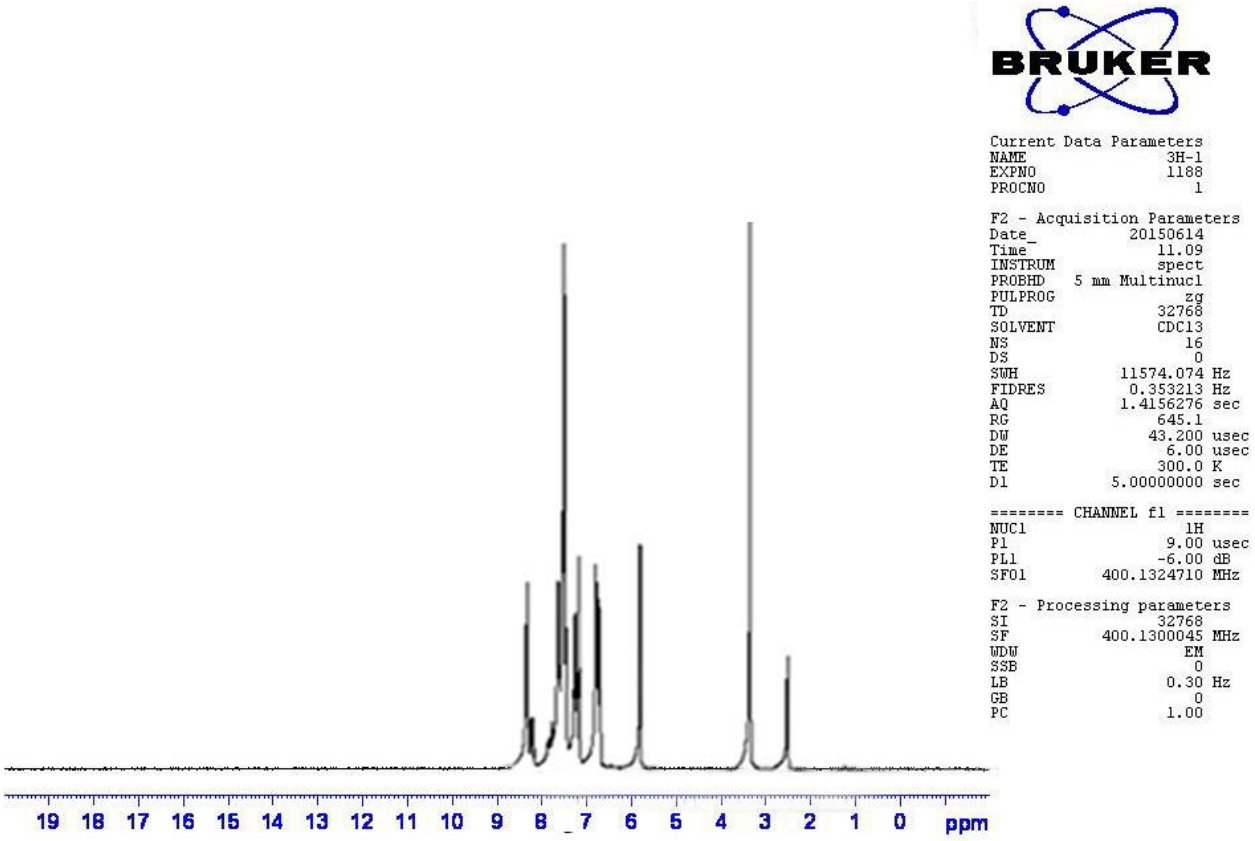
Department of Chemistry, Faculty of Science, Ilam University, Ilam, Iran

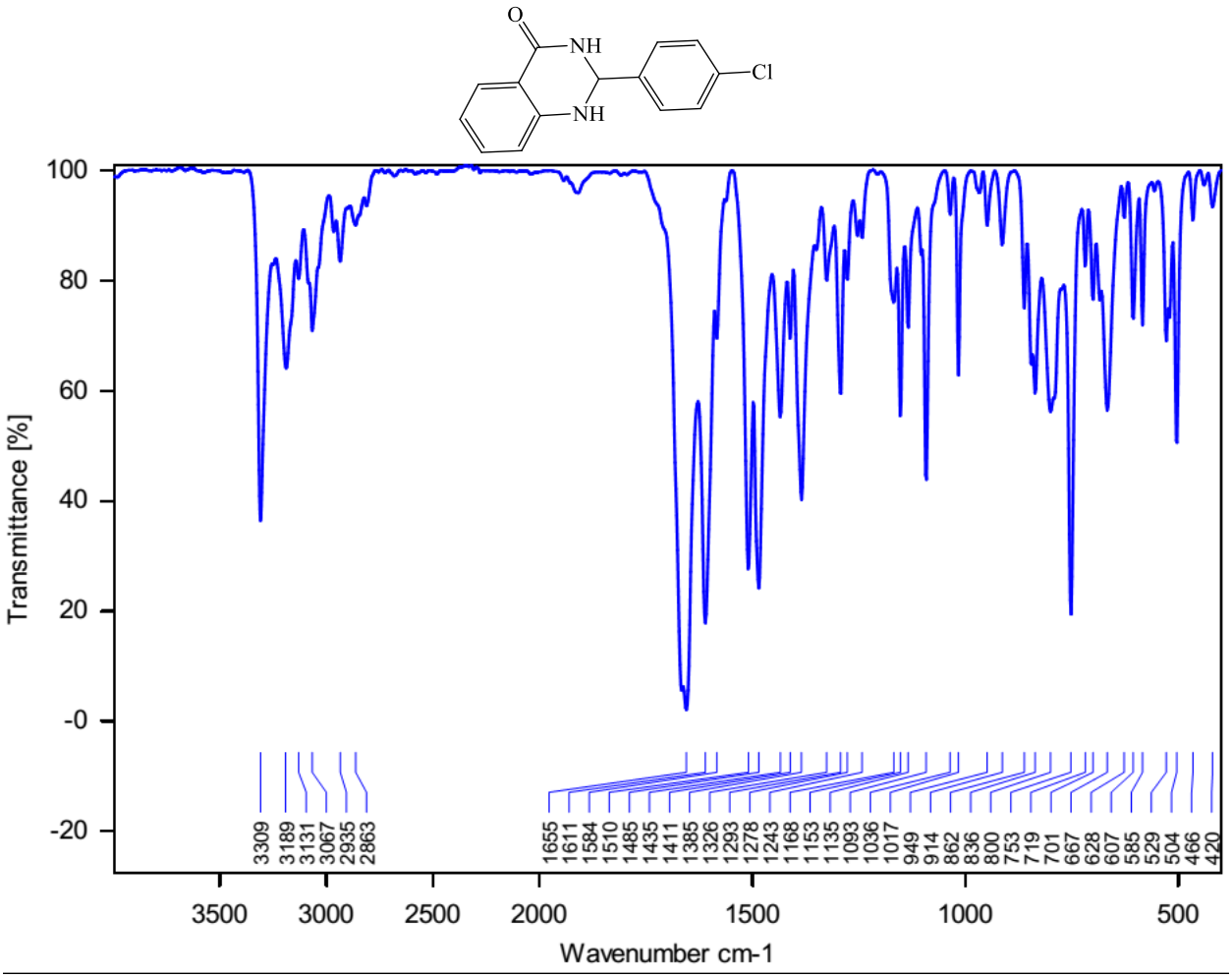
E-mail address: arashghch58@yahoo.com or a.ghorbani@mail.ilam.ac.ir

Abstract. Boehmite silica sulfuric acid (Boehmite-SSA) has been prepared for the first time *via* efficient sequential synthetic procedure. Initially, boehmite nanoparticles was prepared, coated by silica, then reacted with chlorosulfunic acid to obtain Boehmite-SSA. A simple, inexpensive, environmentally friendly and efficient procedure for the synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1*H*)-one derivatives using this compound as an efficient and novel nanocatalyst. Boehmite-SSA is stable, heterogeneous, cost-effective, easy to handle, recoverable catalyst and can be reused for several consecutive runs without significant loss of catalytic activity. Its structure was characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).



2-(4-chlorophenyl)-2,3-dihydoquinazolin-4(1*H*)-one (entry 1, table 3): Mp: 202-204 °C. IR (KBr) cm^{-1}: 3309, 1655, 1611, 1435. 1H NMR (400 MHz, DMSO-d6): δH= 8.29 (s, 1H), 7.61-7.43 (m, 5H), 7.26-7.20 (t, J=7.5, 1H), 7.12 (s, 1H), 6.75-6.63 (m, 2H), 5.75 (s, 1H) ppm.




O
NH
NH
Cl
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80
60
40
20
-0
-20
Transmittance [%]
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3189
3131
3067
2935
2863
1655
1611
1584
1510
1485
1435
1411
1385
1326
1293
1278
1243
1168
1153
1135
1093
1036
1017
949
914
862
836
800
753
719
701
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504
466
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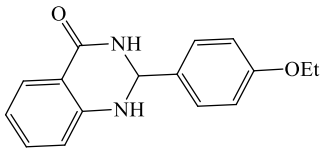
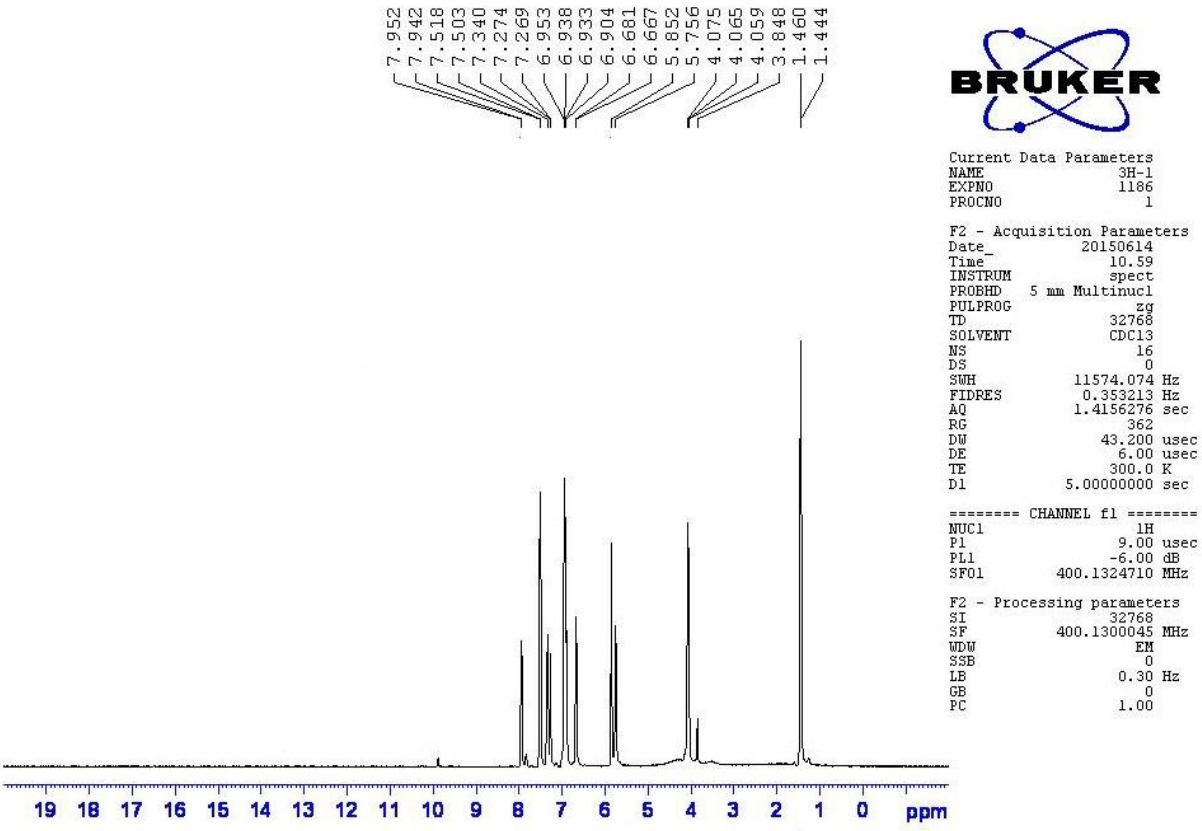
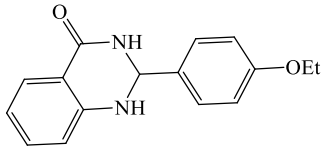
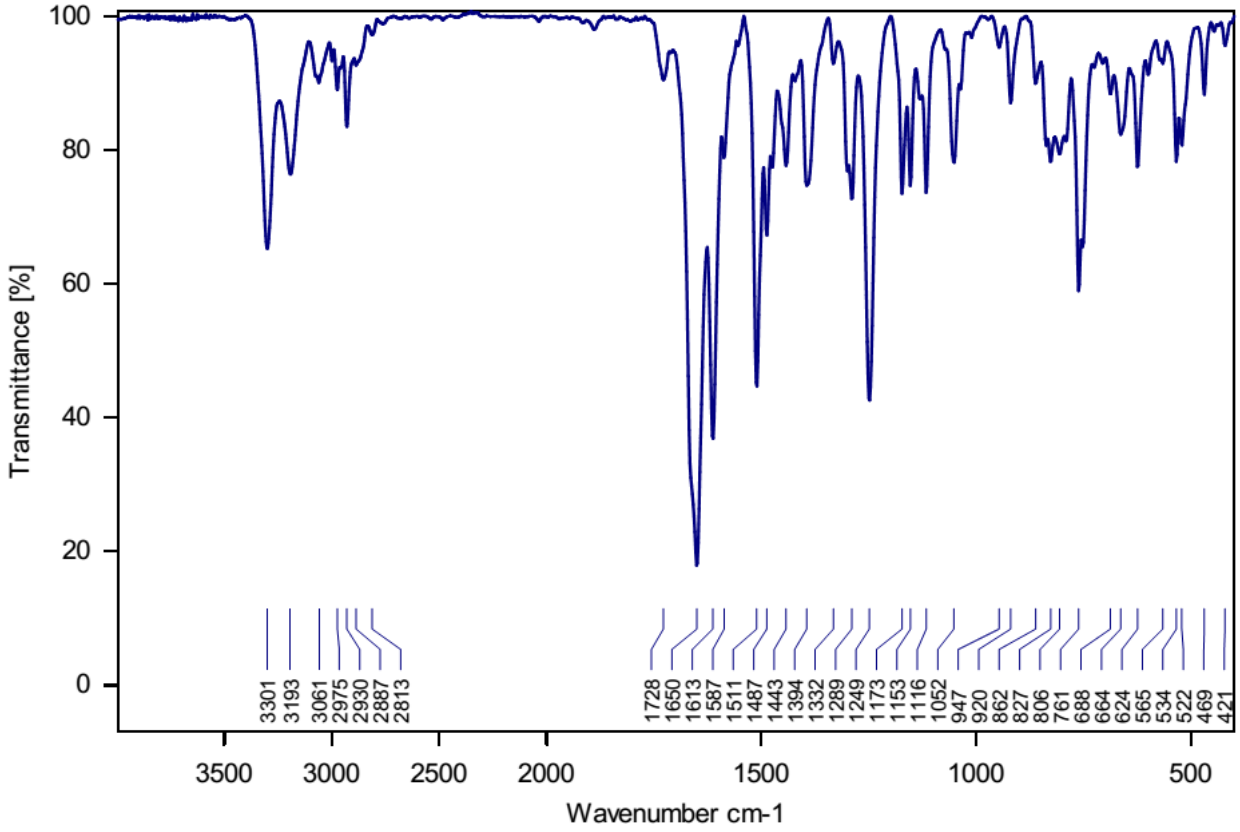
3000
2500
2000
1500
1000
500
Wavenumber cm-1



2-(4-ethoxyphenyl)-2,3-dihydoquinazolin-4(1*H*)-one (entry 3, table 3): Mp: 168-170 °C. IR (KBr) cm^{-1}: 3301, 1650, 1613, 1443. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 7.95-7.94 (b, 1H), 7.52-7.50 (m, 2H), 7.34 (s, 1H), 7.26 (s, 1H), 6.95-6.90 (m, 3H), 6.68-6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.07-4.05 (q, *J*=4, 2H), 1.46-1.44 (s, 3H) ppm.




O
NH
NH
OEt


Transmittance [%]
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40
20
0
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3301
3193
3061
2975
2930
2887
2813
1728
1650
1613
1587
1511
1487
1443
1394
1332
1289
1249
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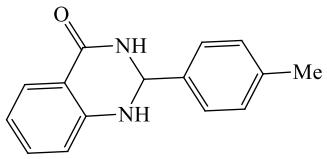
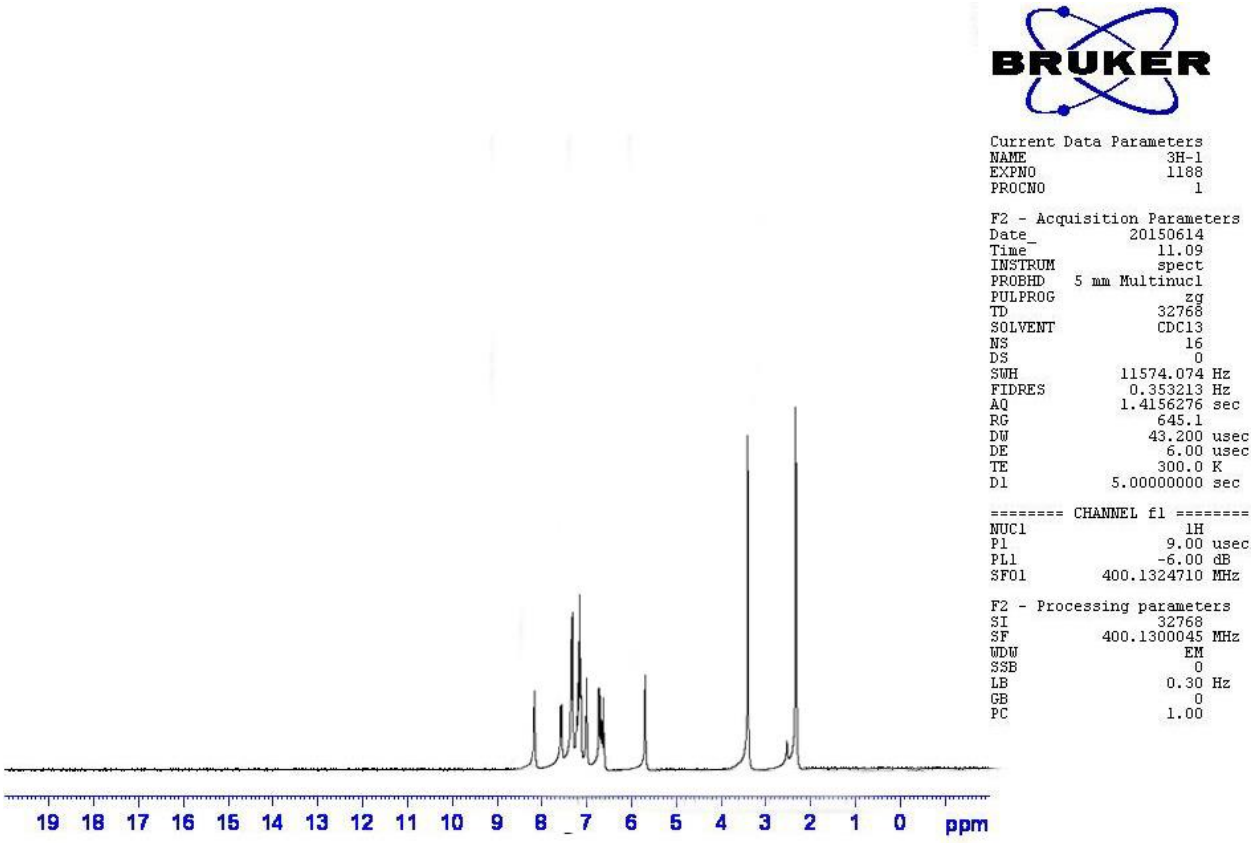
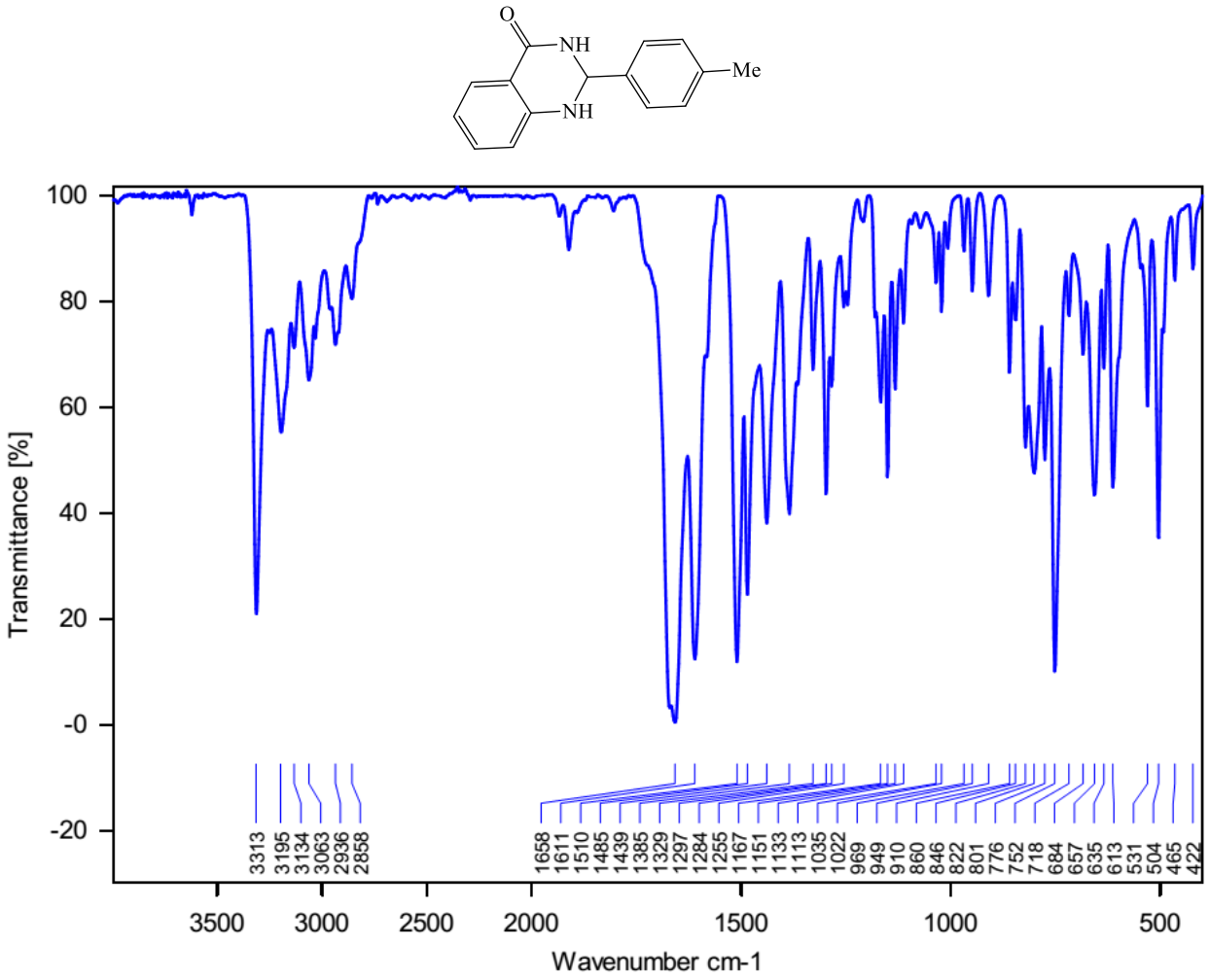
761
688
664
624
565
534
522
469
421



2-(4-methylphenyl)-2,3-dihydroquinazolin-4(1*H*)-one (entry 6, table 3): Mp: 230-232 °C. IR (KBr) cm^{-1}: 3313, 1658, 1611, 1439. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H= 8.21 (s, 1H), 7.62-7.59 (d, *J*=7.5, 1H), 7.38-7.35 (d, *J*=7.5, 2H), 7.26-7.14 (m, 3H), 7.03 (s, 1H), 6.75-6.64 (m, 2H), 5.71 (s, 1H), 2.49-2.42 (s, 3H) ppm.




O
NH
NH
Me
Transmittance [%]
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40
20
-0
-20
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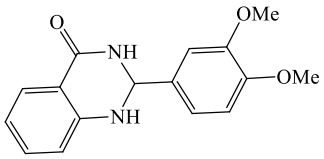
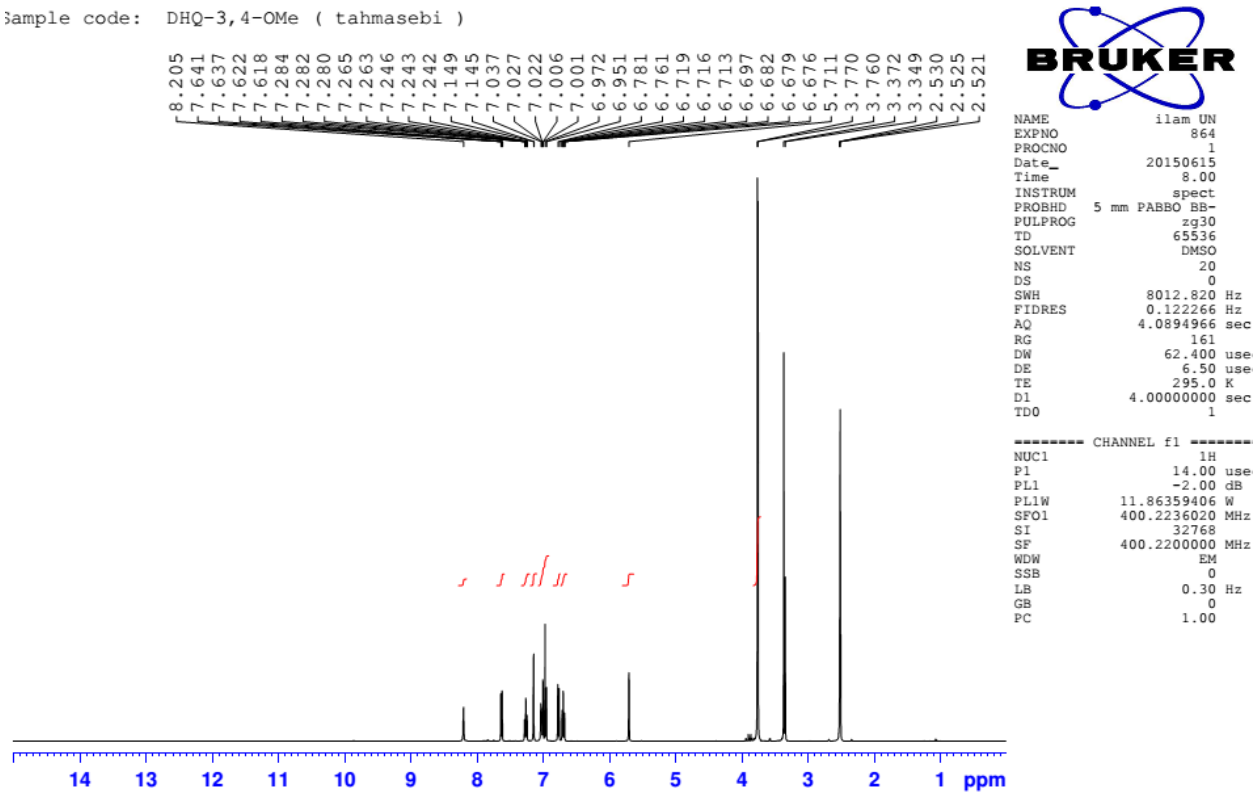
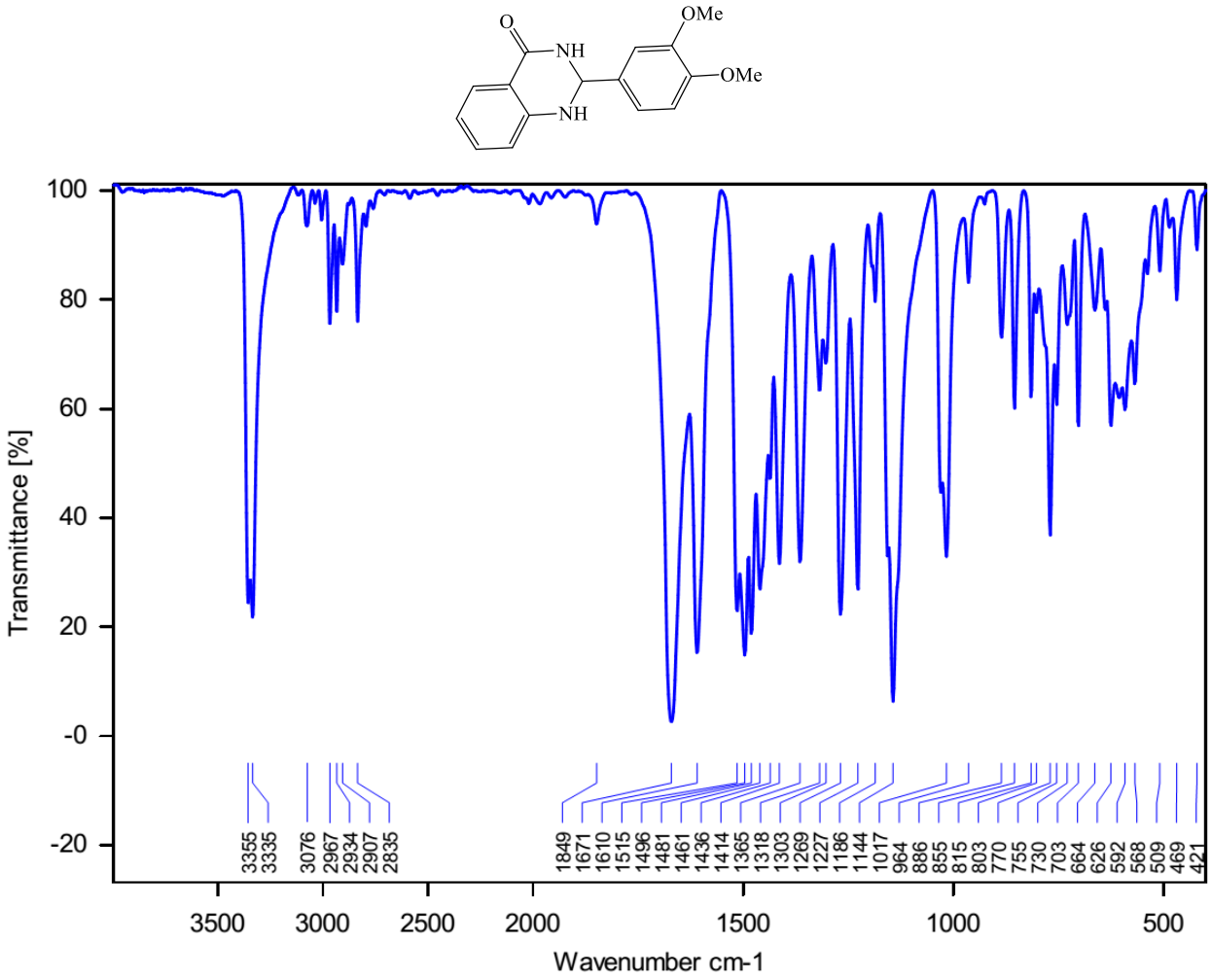
3134
3063
2936
2858
1658
1611
1510
1485
1439
1385
1329
1297
1284
1255
1167
1151
1133
1113
1035
1022
969
949
910
860
846
822
801
776
752
718
684
657
635
613
531
504
465
422
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



2-(3,4-dimethoxyphenyl)-2,3-dihydoquinazolin-4(1*H*)-one (entry 7, table 3): Mp: 211-214 °C. IR (KBr) cm^{-1}: 3335, 1671, 1610, 1436. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H= 8.21 (s, 1H), 7.64-7.62 (d, *J*=7.6, 1H), 7.28-7.24 (t, *J*=0.8, 1H), 7.15 (d, *J*=1.6, 1H), 7.04-6.97 (m, 2H), 6.95 (s, 1H), 6.78-6.76 (d, *J*=8, 1H), 6.72-6.67 (t, *J*=1.2, 1H), 5.71 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm.




O
NH
NH
OMe
OMe
Transmittance [%]
100
80
60
40
20
-0
-20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3355
3335
3076
2967
2934
2907
2835
1849
1671
1610
1515
1496
1481
1461
1436
1414
1365
1318
1303
1269
1227
1186
1144
1017
964
886
855
815
803
770
755
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703
664
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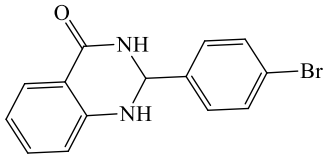
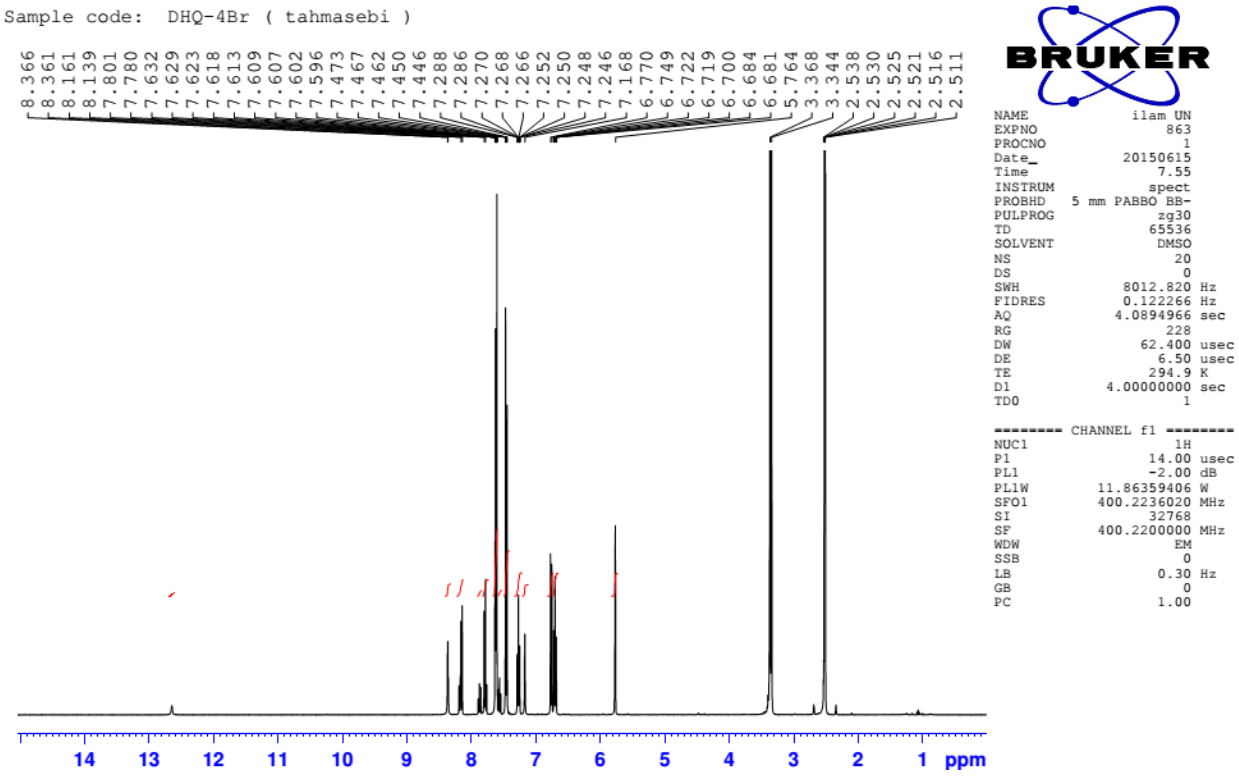
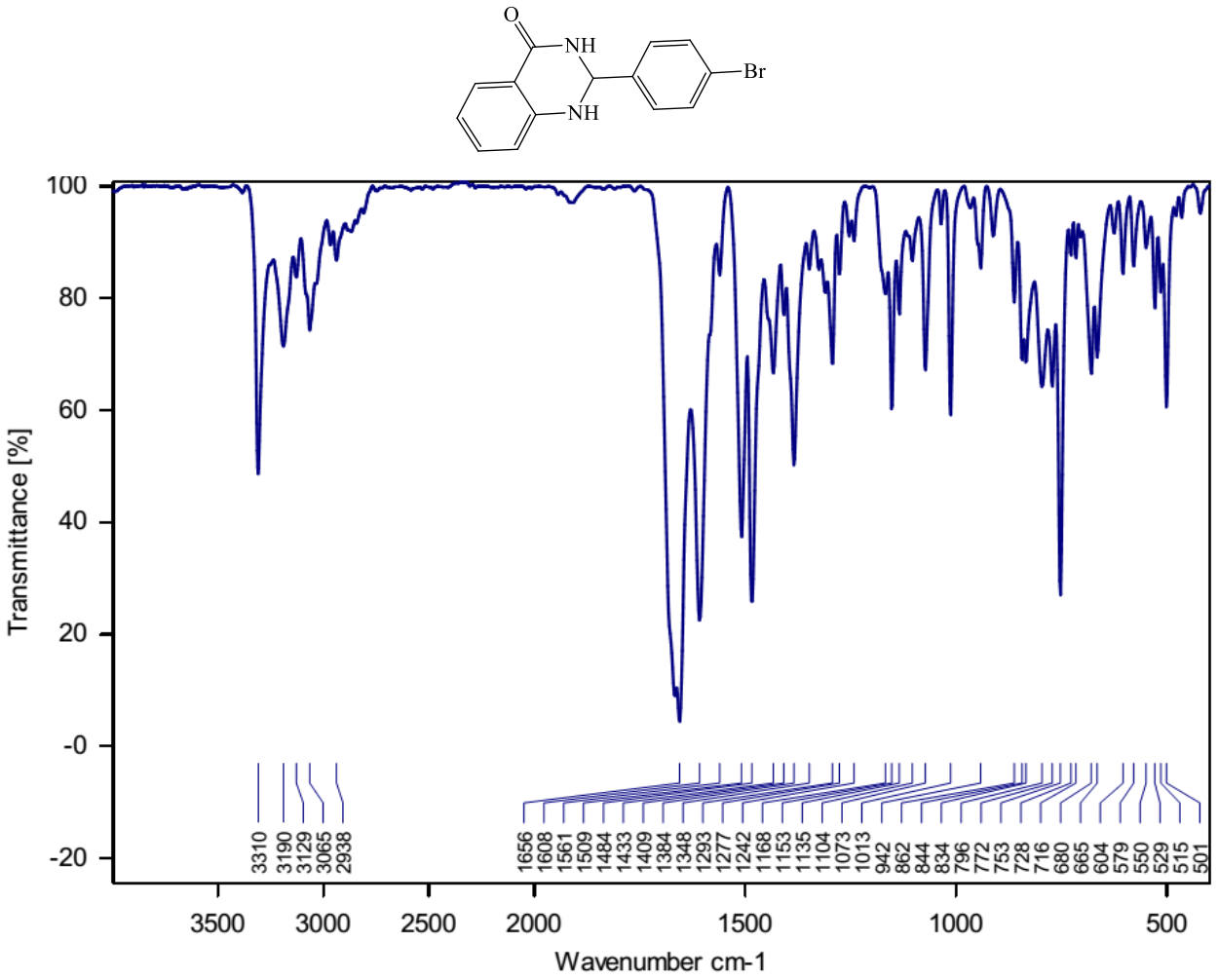
592
568
509
469
421



2-(4-bromophenyl)-2,3-dihydoquinazolin-4(1*H*)-one (entry 8, table 3): Mp: 196-198 °C. IR (KBr) cm^{-1}: 3310, 1656, 1608, 1433. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 8.17-8.14 (m, 1H), 7.80-7.78 (m, 1H), 7.63-7.59 (m, 3H), 7.47-7.44 (m, 2H), 7.30-7.24 (m, 1H), 6.77-6.72 (d, *J*=19.2, 1H), 6.71-6.68 (m, 1H), 5.76 (s, 1H) ppm.




O
NH
NH
Br
Transmittance [%]
100
80
60
40
20
-0
-20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3310
3190
3129
3065
2938
1656
1608
1561
1509
1484
1433
1409
1384
1348
1293
1277
1242
1168
1153
1135
1104
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550
529
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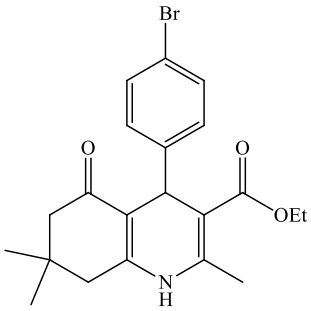
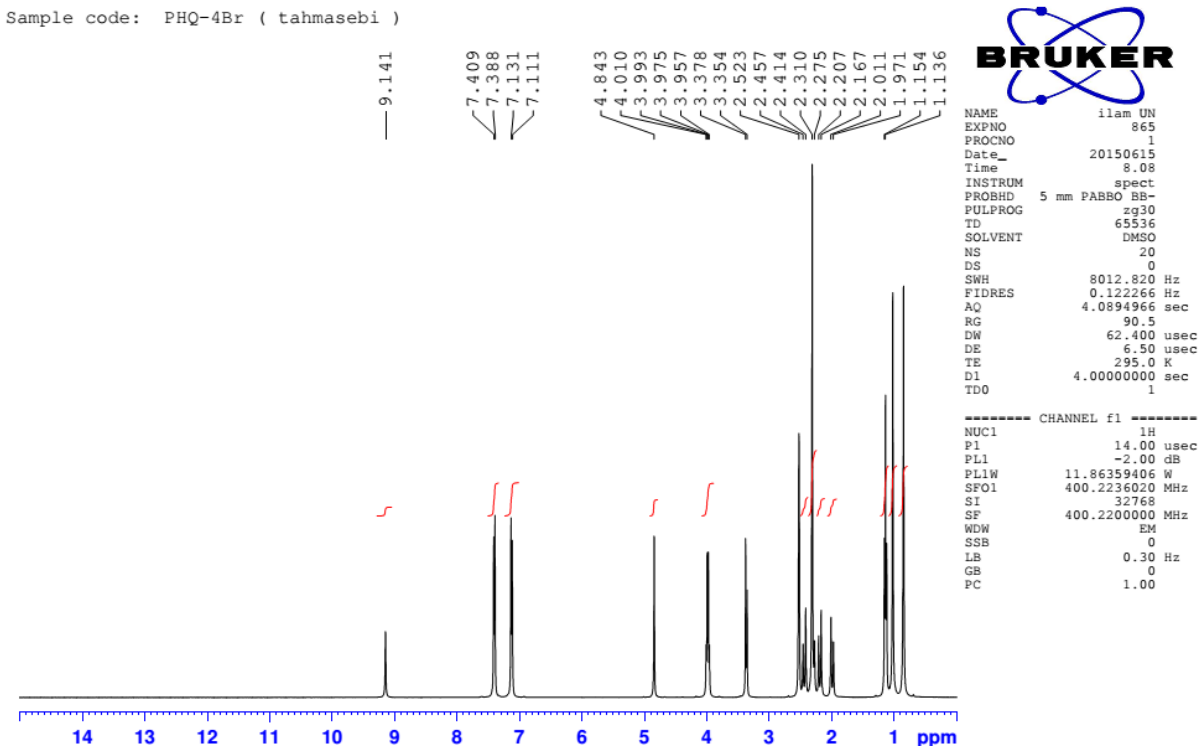
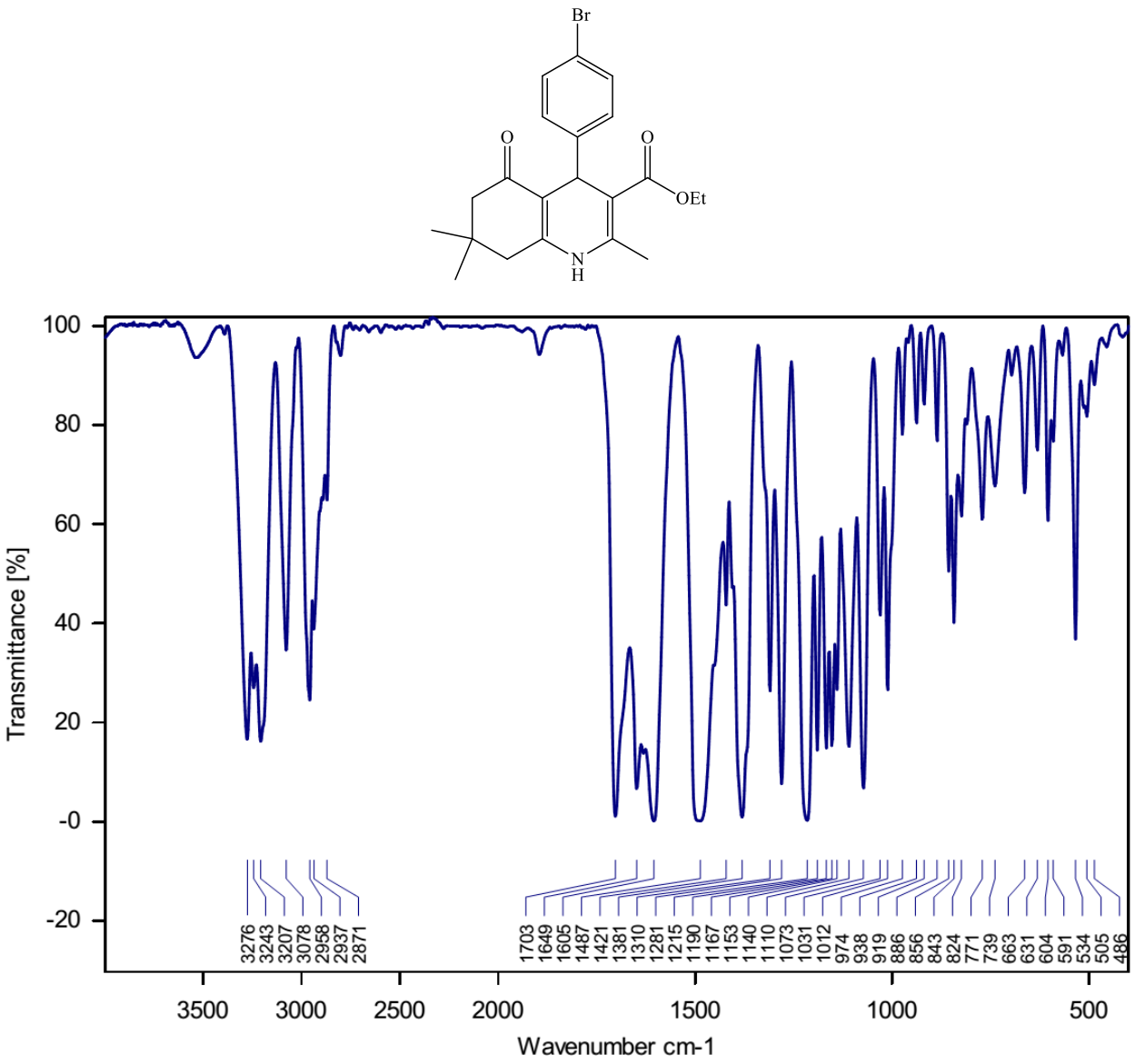
501



Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, table 5): Mp: 251-253 °C. IR (KBr) cm^{-1}: 3276, 3243, 3207, 1703, 1649, 1421. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.14 (s, 1H), 7.41-7.39 (d, *J*=8.4, 2H), 7.13-7.11 (d, *J*=8, 2H), 4.84 (s, 1H), 4.01-3.96 (q, *J*=6.8, 2H), 2.52-2.46 (d, *J*=26.4 1H), 2.31-2.27 (m, 4H), 2.21-2.17 (d, *J*=16, 1H), 2.01-1.97 (d, *J*=16, 1H), 1.15-1.12 (t, *J*=7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.




Br
O
O
OEt
N
H
Transmittance [%]
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40
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-20
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3243
3207
3078
2958
2937
2871
1703
1649
1605
1487
1421
1381
1310
1281
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1190
1167
1153
1140
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1073
1031
1012
974
938
919
886
856
843
824
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739
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631
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505
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3000
2500
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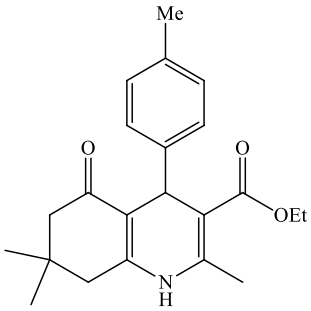
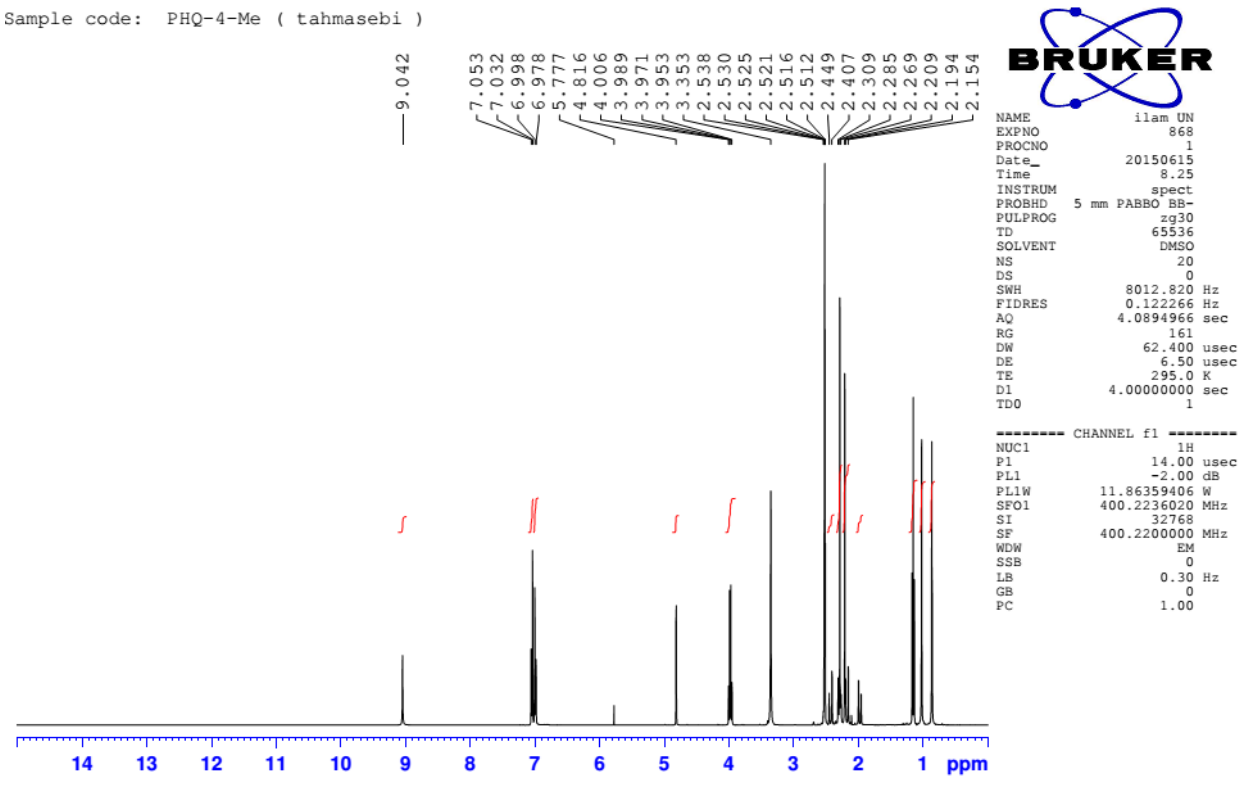
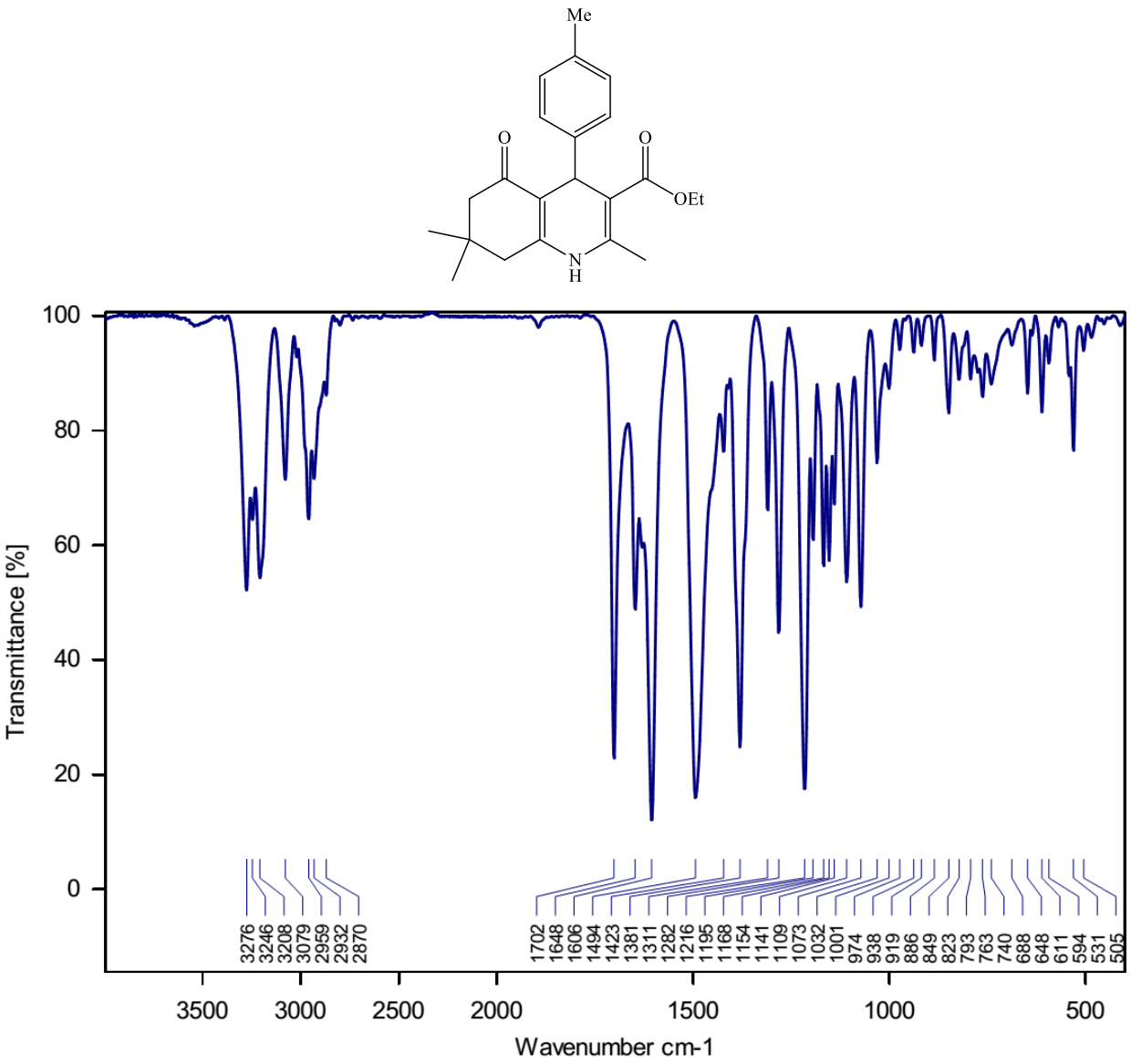
1500
1000
500
Wavenumber cm-1



Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 4, table 5): Mp: 250-253 °C. IR (KBr) cm^{-1}: 3276, 3276, 3246, 3208, 1702, 1648, 1423. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H= 9.04 (s, 1H), 7.05-7.03 (d, *J*=8, 2H), 7.00-6.98 (d, *J*=8, 2H), 4.82 (s, 1H), 4.00-3.95 (q, *J*=7.2, 2H), 2.45-2.41 (d, *J*=16, 1H), 2.31-2.27 (m, 4H), 2.21-2.15 (m, 4H), 2.10-1.96 (d, *J*=16, 1H), 1.17-1.13 (t, *J*=6.8, 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm.




Me
O
O
OEt
N
H
100
80
60
40
20
0
Transmittance [%]
3276
3246
3208
3079
2959
2932
2870
1702
1648
1606
1494
1423
1381
1311
1282
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1195
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1109
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1032
1001
974
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919
886
849
823
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688
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611
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531
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2500
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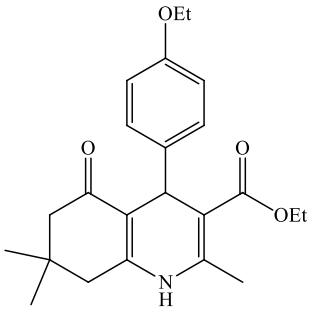
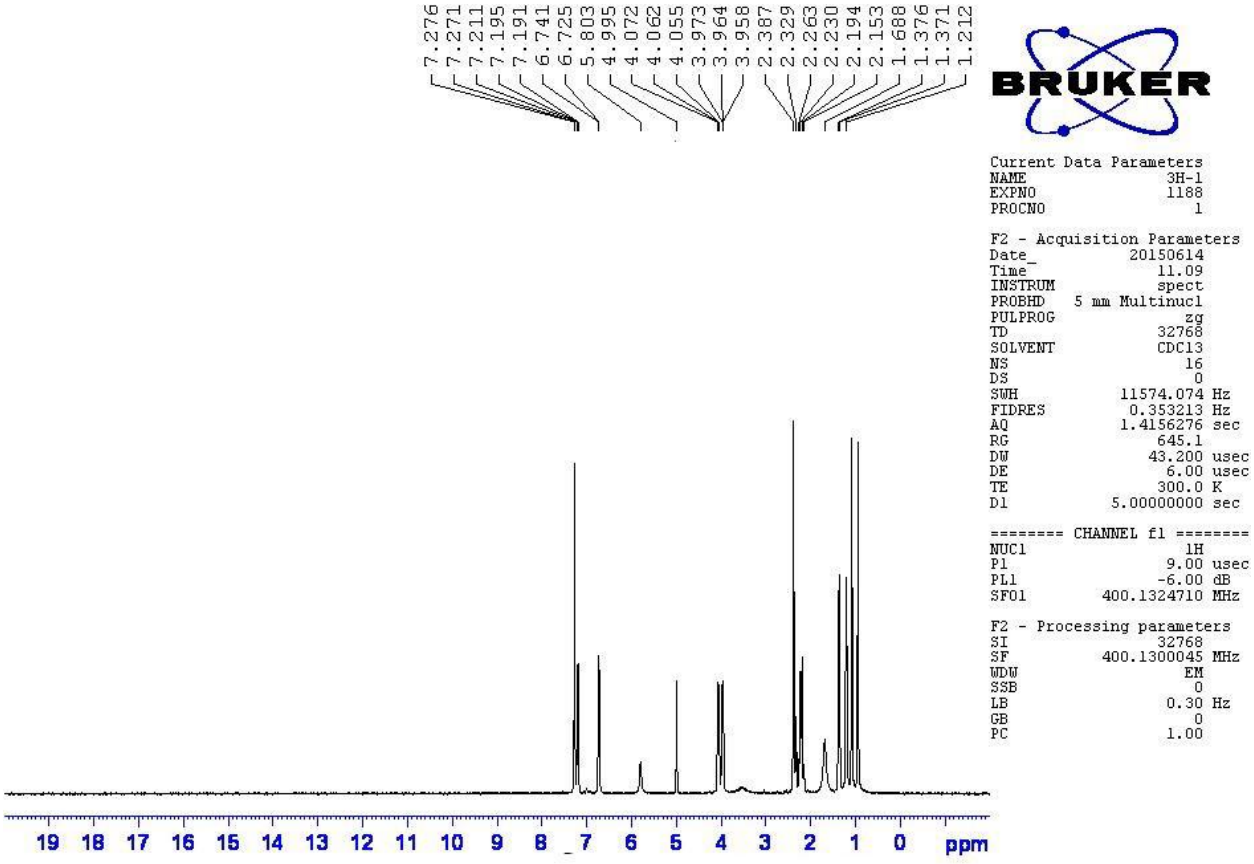
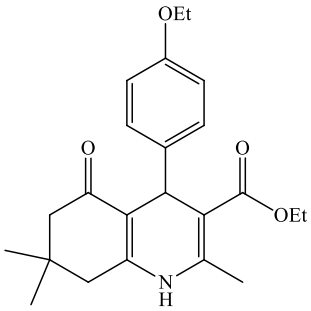
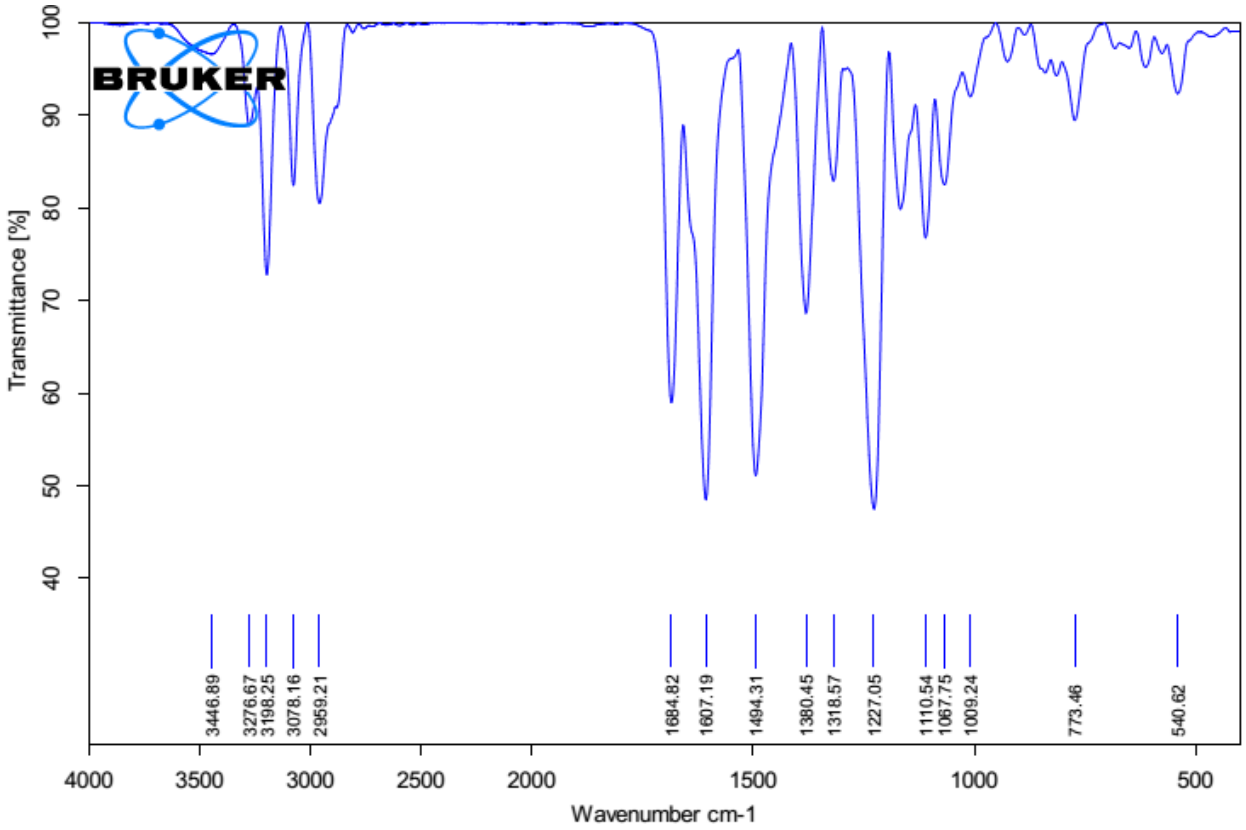
1500
1000
500
Wavenumber cm-1



Ethyl-4-(4-ethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3 carboxylate (entry 5, table 5): Mp: 172-174 °C. IR (KBr) cm^{-1}: 3446, 3276, 3198, 1684, 1607, 1494. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 7.28-7.19 (m, 2H), 6.74-6.72 (d, *J*=8, 2H), 5.80 (s, 1H), 4.99 (s, 1H), 4.07-4.05 (t, *J*=4, 2H), 3.97-3.96 (t, *J*=3.6 ,2H), 2.39-2.15 (m, 7H), 1.38-1.37 (m, 3H), 1.21-1.20 (m, 3H), 1.07 (s, 3H), 0.95 (s, 3H) ppm.




OEt
O
O
OEt
N
H


BRUKER
Transmittance [%]
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80
70
60
50
40
3446.89
3276.67
3198.25
3078.16
2959.21
1684.82
1607.19
1494.31
1380.45
1318.57
1227.05
1110.54
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540.62
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3500
3000
2500
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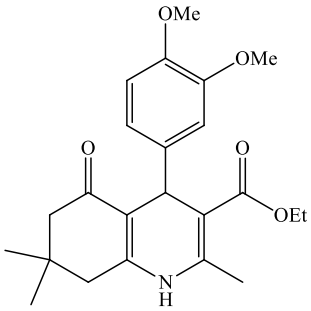
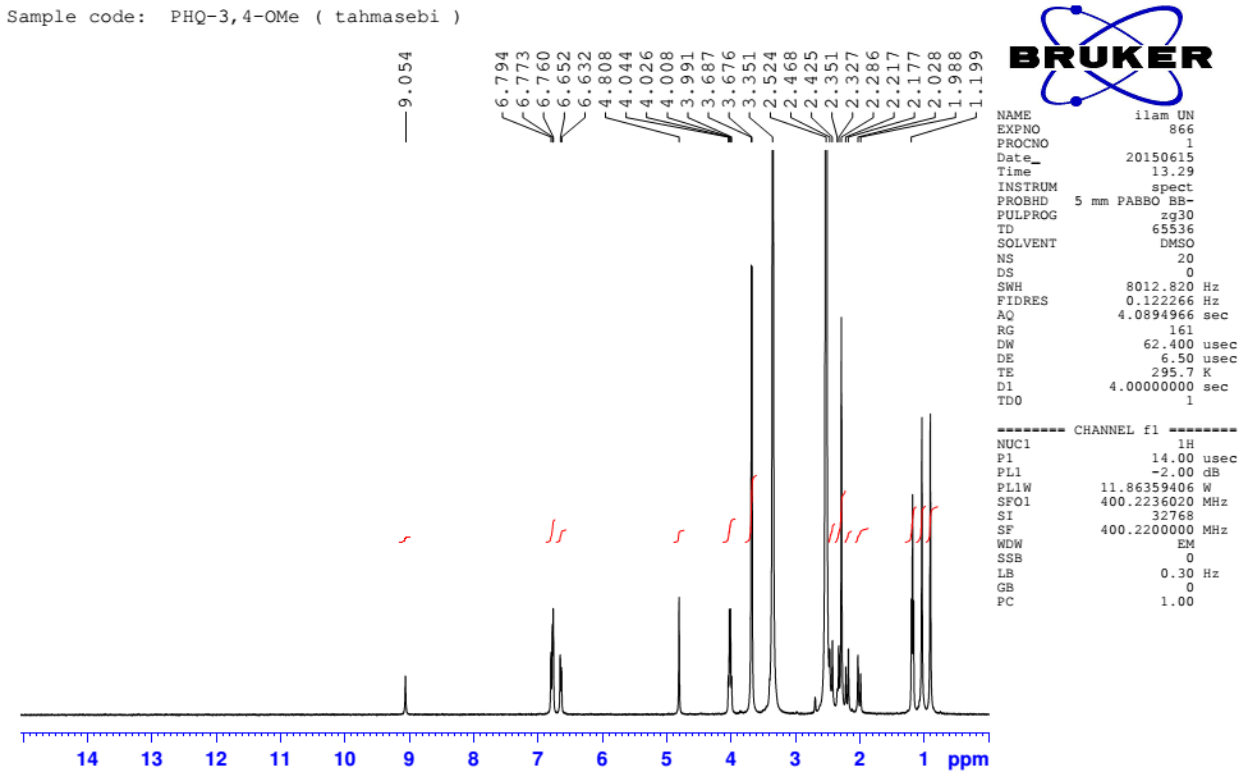
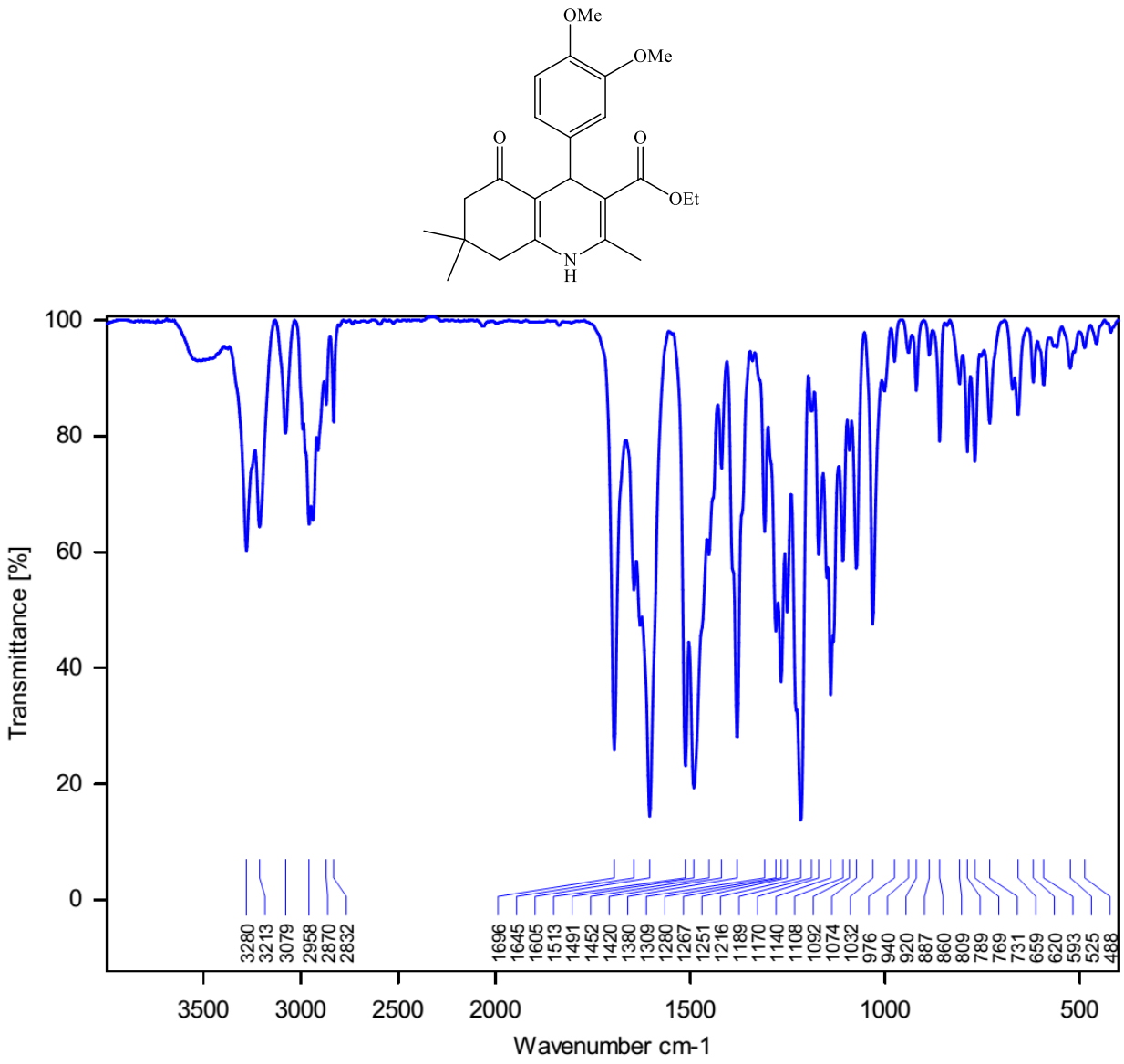
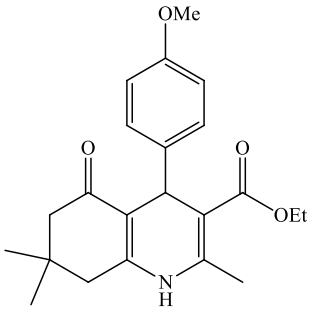
1500
1000
500
Wavenumber cm-1



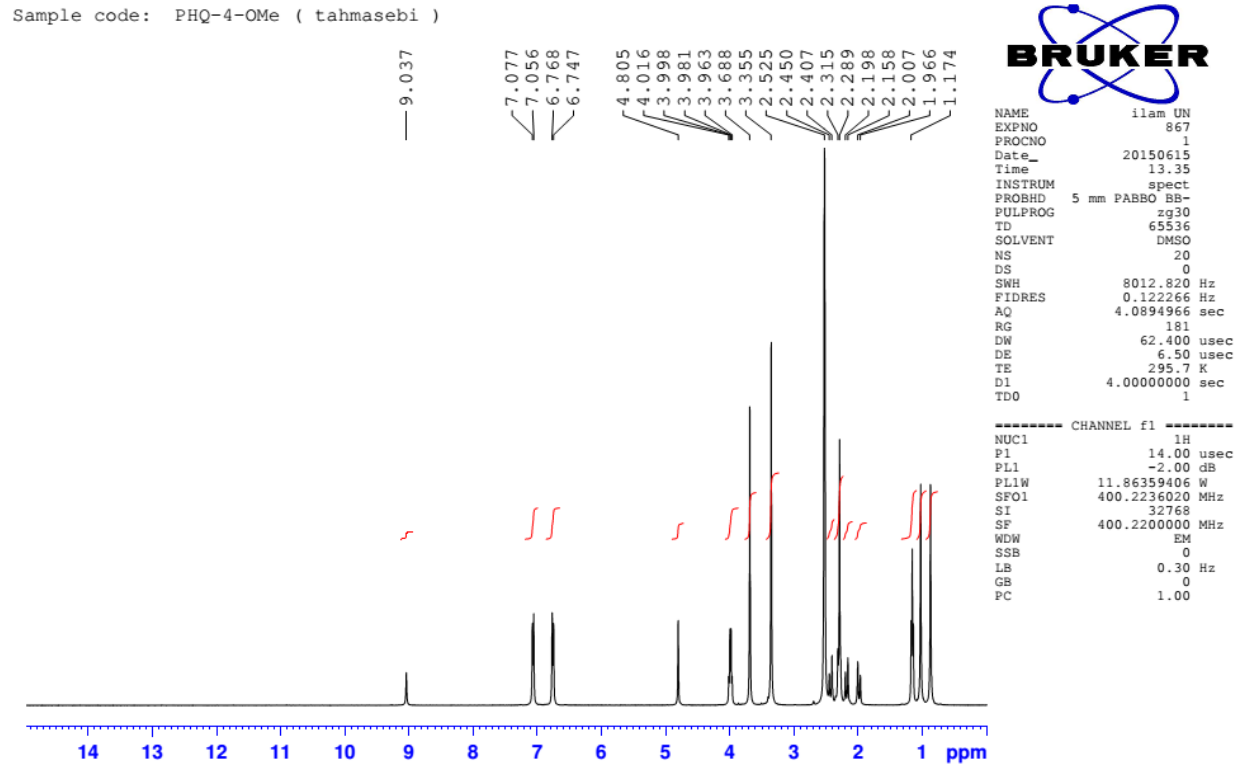
Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, table 5): Mp: 204-206 °C. IR (KBr) cm^{-1}: 3280, 3213, 1696, 1645, 1452. ^1H NMR (400 MHz, DMSO-d_6): δ_H= 9.05 (s, 1H), 6.79-6.76 (m, 2H), 6.65-6.63 (d, *J*=8, 1H), 4.80 (s, 1H), 4.04-3.99 (q, *J*=7.2, 2H), 3.69-3.68 (d, *J*=4.4, 5H), 2.47-2.42 (d, *J*=17.2, 2H), 2.35-2.27 (m, 4H), 2.22-2.18 (d, *J*=16, 1H), 2.03-1.99 (d, *J*=16, 1H), 1.20-1.16 (t, *J*=6.8, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.

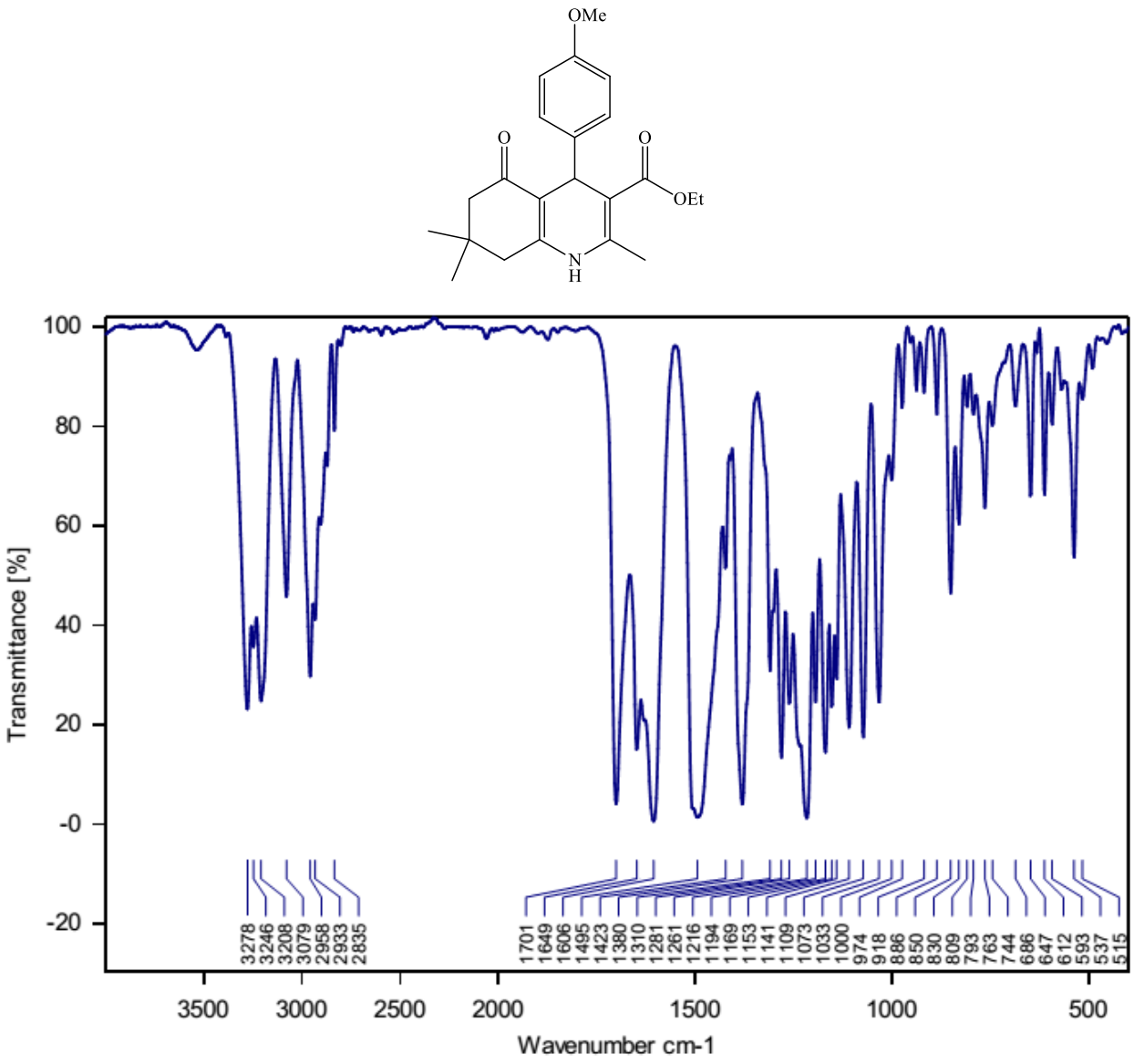



OMe
OMe
O
O
OEt
N
H
100
80
60
40
20
0
Transmittance [%]
3280
3213
3079
2958
2870
2832
1696
1645
1605
1513
1491
1452
1420
1380
1309
1280
1267
1251
1216
1189
1170
1140
1108
1092
1074
1032
976
940
920
887
860
809
789
769
731
659
620
593
525
488
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 8, table 5): Mp: 248-250 °C. IR (KBr) cm^{-1}: 3278, 3246, 3208, 1701, 1649, 1423. 1^{H} NMR (400 MHz, DMSO-d_6): δ_H= 9.04 (s, 1H), 7.08-7.06 (d, *J*=8.4, 2H), 6.77-6.75 (d, *J*=8.4, 2H), 4.80 (s, 1H), 4.02-3.96 (q, *J*=7.2, 2H), 3.69 (s, 3H), 2.52-2.45 (d, *J*=29.2, 1H), 2.31-2.29 (m, 4H), 2.20-2.16 (d, *J*=16, 1H), 2.01-1.97 (d, *J*=16.4, 1H), 1.17-1.14 (t, *J*=7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm




OMe
O
O
OEt
N
H
100
80
60
40
20
-0
-20
Transmittance [%]
3278
3246
3208
3079
2958
2933
2835
1701
1649
1606
1495
1423
1380
1310
1281
1261
1216
1194
1169
1153
1141
1109
1073
1033
1000
974
918
886
850
830
809
793
763
744
686
647
612
593
537
515
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1