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Supporting Information

Tribromide ion immobilized on magnetic nanoparticle as new, efficient and reusable nanocatalyst in multicomponent reactions

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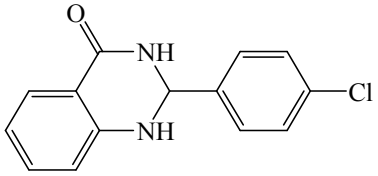
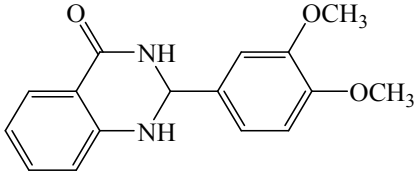
The synthesis of 2,3 dihydroquinazolin-4(1H)-ones derivatives and compounds characterization data

A stirred mixture of 4-chlorobenzaldehyde (1 mmol, 0.140 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.245 g (0.9496 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 95%.



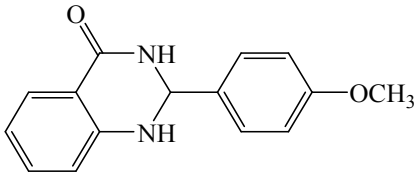
2-(4-Chlorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 1, Table 2) (1a). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H: 8.29 (s, 1H), 7.60–7.41 (m, 5H), 7.25–7.20 (t, J =7.5, 1H), 7.12 (s, 1H), 6.75–6.63 (m, 2H), 5.75 (s, 1H) ppm.

A stirred mixture of 3,4-dimethoxybenzaldehyde (1 mmol, 0.166 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.281 g (0.9894 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 99%.



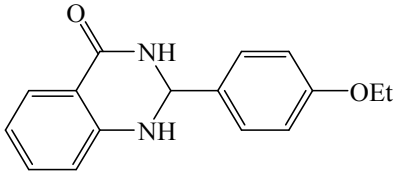
2-(3,4-Dimethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 2, Table 2) (1b). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.21 (s, 1H), 7.64–7.61 (d, J = 1.6, 1H), 7.29–7.25 (t, J = 8, 1H), 7.15- 7.14 (d, J = 1.6, 1H), 7.03–6.97 (m, 2H), 6.95 (s, 1H), 6.78–6.76 (d, J = 8, 1H), 6.72–6.68 (t, J= 1.2, 1H), 5.71 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm.

A stirred mixture of 4-methoxybenzaldehyde (1 mmol, 0.136 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.1778 g (0.7 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 70%.



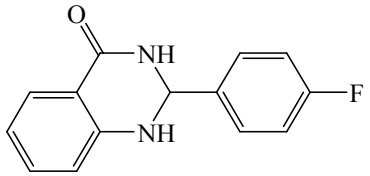
2-(4-Methoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 3, Table 2) (1c). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.22 (s, 1H), 7.66–7.63 (m, 1H), 7.46–7.44 (d, J = 8.8, 2H), 7.29- 7.24 (m, 1H), 7.04 (s, 1H), 6.99-6.69 (d, J=1.2, 2H), 6.78–6.76 (d, J = 8, 1H), 6.70–6.68 (t, J= 7.2, 1H), 5.74 (s, 1H), 3.77 (s, 3H) ppm.

A stirred mixture of 4-ethoxybenzaldehyde (1 mmol, 0.150 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.247 g (0.9216 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 92%.



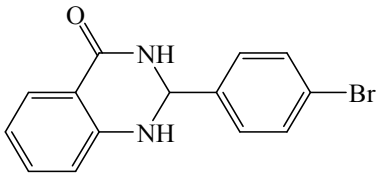
2-(4-Ethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 4, Table 2) (1d). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 7.95–7.94 (b, 1H), 7.51–7.50 (m, 2H), 7.34 (s, 1H), 7.27 (s, 1H), 6.94–6.90 (m, 3H), 6.68–6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.08–4.06 (q, J ¼ 4, 2H), 1.46– 1.44 (s, 3H) ppm.

A stirred mixture of 4-fluorobenzaldehyde (1 mmol, 0.124 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.23 g (0.95 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 95%.



2-(4-Fluorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 5, Table 2) (1e). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.32 (s, 1H), 7.65–7.63 (m, 1H), 7.59–7.54 (m, 2H), 7.30- 7.23 (m, 3H), 7.13 (s, 1H), 6.79-6.77 (d, J=0.8, 1H), 6.69-6.67 (t, J=8, 1H) 5.80 (s, 1H) ppm.

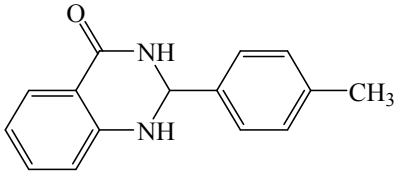
A stirred mixture of 4-bromobenzaldehyde (1 mmol, 0.185 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.248 g (0.8184 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 82%.



2-(4-Bromophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 6, Table 2) (1f). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.17–8.14 (m, 1H), 7.79–7.77 (m, 1H), 7.63–7.59 (m, 3H), 7.48–7.45 (m, 2H), 7.29–7.23 (m, 1H), 6.77–6.72 (d, J = 19.2, 1H), 6.70–6.67 (m, 1H), 5.76 (s, 1H) ppm.

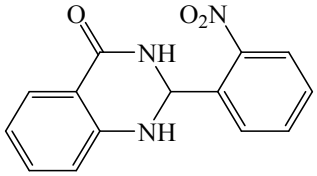
A stirred mixture of 4-methylbenzaldehyde (1 mmol, 0.1202 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed

by evaporation. Finally, 0.2286 g (0.9596 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 96%.



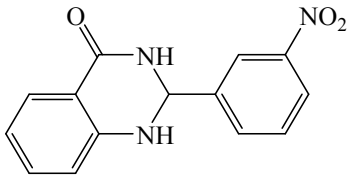
2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 7, Table 2) (1g). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.21 (s, 1H), 7.63–7.60 (d, J = 7.5, 1H), 7.38–7.35 (d, J = 7.5, 2H), 7.25–7.13 (m, 3H), 7.03 (s, 1H), 6.74–6.63 (m, 2H), 5.71 (s, 1H), 2.49–2.42 (s, 3H) ppm.

A stirred mixture of 2-nitrobenzaldehyde (1 mmol, 0.151 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.215 g (0.7992 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 80%.



2-(2-Nitrophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 8, Table 2) (1h). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H :8.25 (s, 1H), 8.10–8.08 (d, J = 8, 1H), 7.90–7.87 (d, J = 8, 1H), 7.83–7.79 (t, J = 0.8, 1H), 7.69–7.63 (m, 2H), 7.30–7.26 (m, 1H), 7.04 (s, 1H), 6.81 (d, J = 1.2, 1H), 6.77–6.72 (m, 1H), 6.36 (m, 1H) ppm.

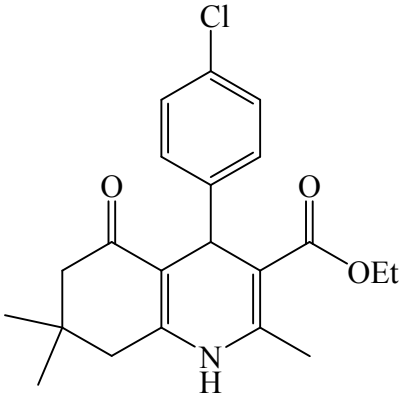
A stirred mixture of 3-nitrobenzaldehyde (1 mmol, 0.151 g), 2-aminobenzamide (1.05 mmol, 0.1429 g) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, 0.266 g (0.9888 mmol) of corresponding pure product was obtained by recrystallization by EtOH. The yield of the product was obtained 99%.



2-(3-Nitrrophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 9, Table 2) (1i). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.57 (s, 1H), 8.40–8.39 (t, J=1.6, 1H), 8.24–8.21 (m, 2H), 7.98- 7.96 (d, J=7.6, 1H), 7.74-7.70 (t, J=8, 1H), 7.66-7.64 (m, 1H), 7.38 (s, 1H), 7.32-7.28 (m, 1H), 6.83-6.81 (d, J=8, 1H), 6.74-6.70 (m, 1H), 5.98 (s, 1H) ppm.

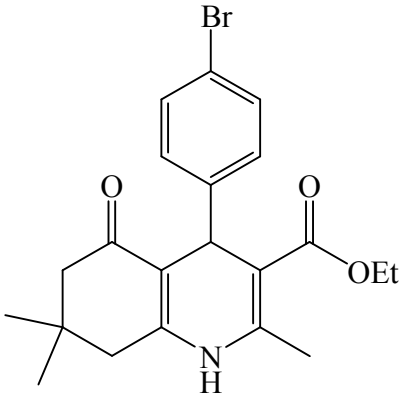
The synthesis of polyhydroquinoline derivatives and compounds characterization data

A mixture of 4-chlorobenzaldehyde (1 mmol, 0.140 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.343 g (0.9183 mmol) pure product was obtained in yield of 92%.



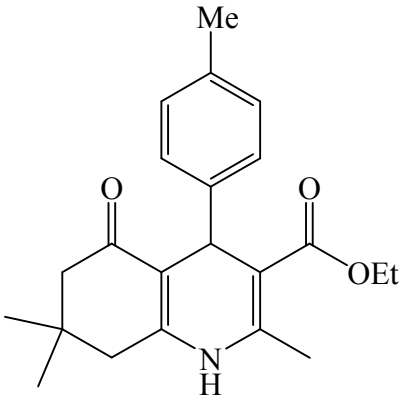
Ethyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8- hexahydroquinoline-3-carboxylate (entry 1, Table 4) (2a). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.13 (s, 1H), 7.25–7.28 (m, 2H), 7.17–7.19 (m, 2H), 4.86 (s, 1H), 4.01–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (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.

A mixture of 4-bromobenzaldehyde (1 mmol, 0.185 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.372 g (0.8899 mmol) pure product was obtained in yield of 89%.



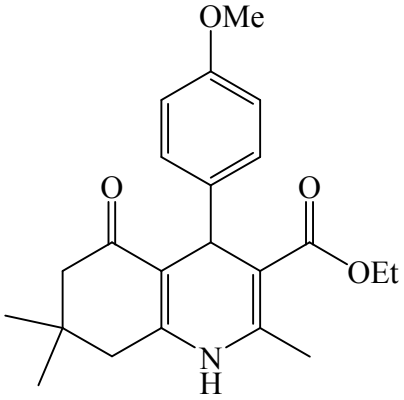
Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, Table 4) (2b). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.14 (s, 1H), 7.41–7.39 (d, J = 8.4, 2H), 7.13–7.11 (d, J = 8.4, 2H), 4.84 (s, 1H), 4.01–3.95 (q, J = 6.8, 2H), 2.52–2.46 (d, J = 26.4, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.01–1.97 (d, J = 16, 1H), 1.15–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

A mixture of 4-methylbenzaldehyde (1 mmol, 0.1202 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.3037 g (0.8598 mmol) pure product was obtained in yield of 86%.



Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 3, Table 4) (2c). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.04 (s, 1H), 7.05–7.03 (d, J = 8, 2H), 7.00–6.97 (d, J = 8, 2H), 4.81 (s, 1H), 4.01–3.95 (q, J = 6.8, 2H), 2.44–2.40 (d, J = 16, 1H), 2.30–2.26 (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.

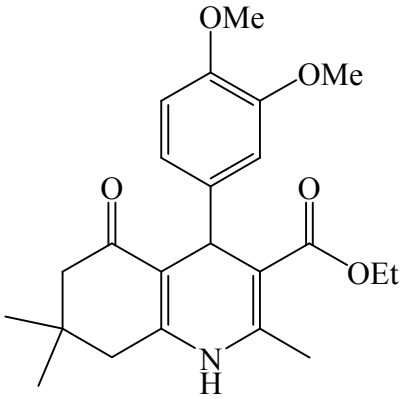
A mixture of 4-methoxybenzaldehyde (1 mmol, 0.136 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.303 g (0.8211 mmol) pure product was obtained in yield of 82%.



Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, Table 4) (2d). ^{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), 4.81 (s, 1H), 4.01–3.96 (q, J = 7.2, 2H), 3.68 (s,

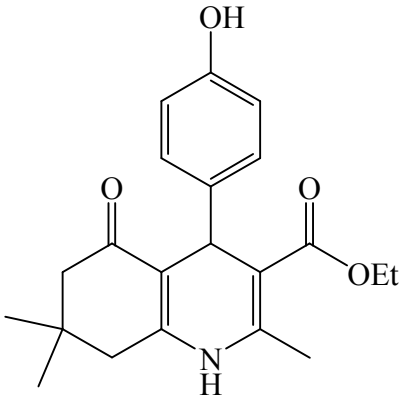
3H), 2.45–2.41 (d, J = 29.2, 1H), 2.31–2.29 (m, 4H), 2.20–2.16 (d, J = 16, 1H), 2.01–1.97 (d, J = 16.4, 1H), 1.17–1.14 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

A mixture of 3,4-dimethoxybenzaldehyde (1 mmol,0.166 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.36 g (0.9022 mmol) pure product was obtained in yield of 90%.



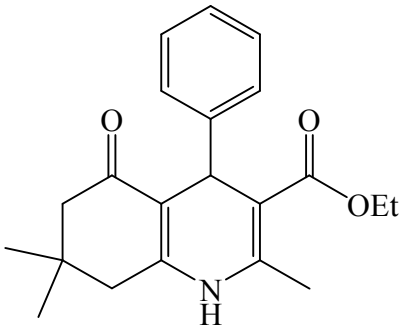
Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8- hexahydroquinoline-3-carboxylate (entry 6, Table 4) (2e). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.05 (s, 1H), 6.79–6.76 (m, 2H), 6.65–6.63 (d, J = 8, 1H), 4.81(s, 1H), 4.04–3.99 (q, J = 7.2, 2H), 3.69–3.68 (d, J = 4.4, 5H), 2.47–2.42 (d, J = 17.2, 2H), 2.35–2.29 (m, 4H), 2.22–2.18 (d, J = 16, 1H), 2.03–1.99 (d, J = 16, 1H), 1.20–1.16 (t, J = 7.2, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.

A mixture of 4-hydroxybenzaldehyde (1 mmol, 0.1221 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.284 g (0.7997 mmol) pure product was obtained in yield of 80%.



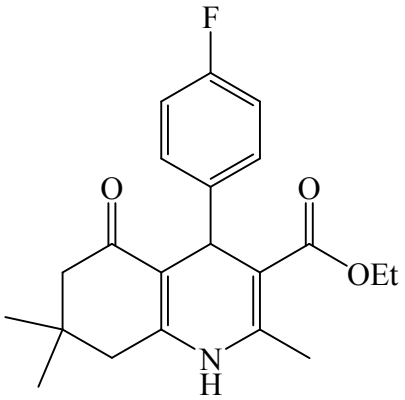
Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 7, Table 4) (2f). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.05 (s, 1H), 8.99 (s,1H), 6.95–6.93 (d, j=8.8, 2H), 6.58-6.55 (m, 2H), 4.75 (s, 1H), 4.02–3.98 (m, 2H), 2.44–2.40 (d, J = 16.8, 1H), 2.30–2.26 (m, 4H), 2.19–2.15 (d, J = 16, 1H), 2.00–1.96 (d, J = 16, 1H), 1.17–1.14 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

A mixture of benzaldehyde (1 mmol, 0.106 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.255 g (0.7522 mmol) pure product was obtained in yield of 75%.



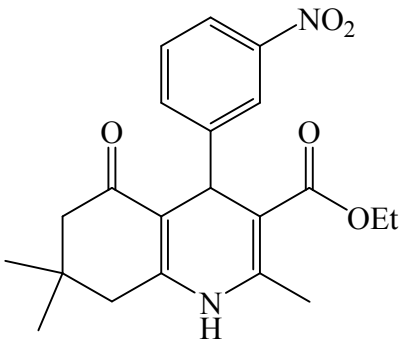
Ethyl-4-(phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8 hexahydroquinoline-3-carboxylate (entry 8, Table 4) (2g). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.08 (s, 1H), 7.22–7.17 (m, 4H), 7.10–7.06 (m, 1H), 4.88 (s, 1H), 4.02–3.97 (q, J = 7.2, 2H), 2.46–2.42(d, J = 17.2 1H), 2.33–2.29 (t, J=8.8, 4H), 2.21–2.17 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.16–1.13 (t, J = 7.2, 3H), 1.03 (s, 3H), 0.86 (s, 3H) ppm.

A mixture of 4-fluorobenzaldehyde (1 mmol, 0.124 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.31 g (0.8683 mmol) pure product was obtained in yield of 87%.



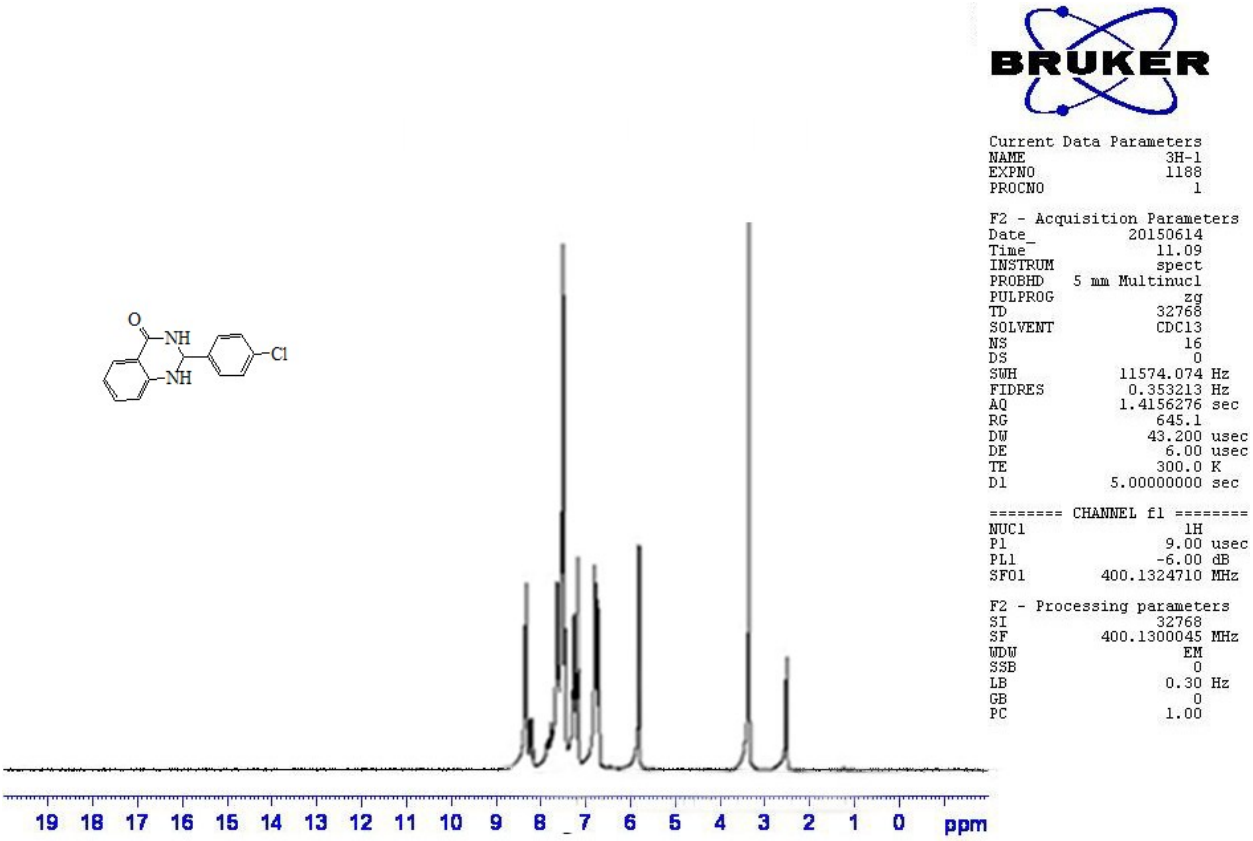
Ethyl-4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 9, Table 4) (2h). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.11 (s, 1H), 7.20–7.17 (m, 2H), 7.04–7.00 (t, J = 8.8, 2H), 4.87 (s, 1H), 4.02–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.32–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.15–1.12 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.

A mixture of 3-nitrobenzaldehyde (1 mmol, 0.151 g), dimedon (1 mmol, 0.140 g), ethylacetoacetate (1 mmol, 0.130 g), ammonium acetate (1.2 mmol, 0.092 g) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and product was recrystallized in ethanol, which the 0.33 g (0.8593 mmol) pure product was obtained in yield of 86%.

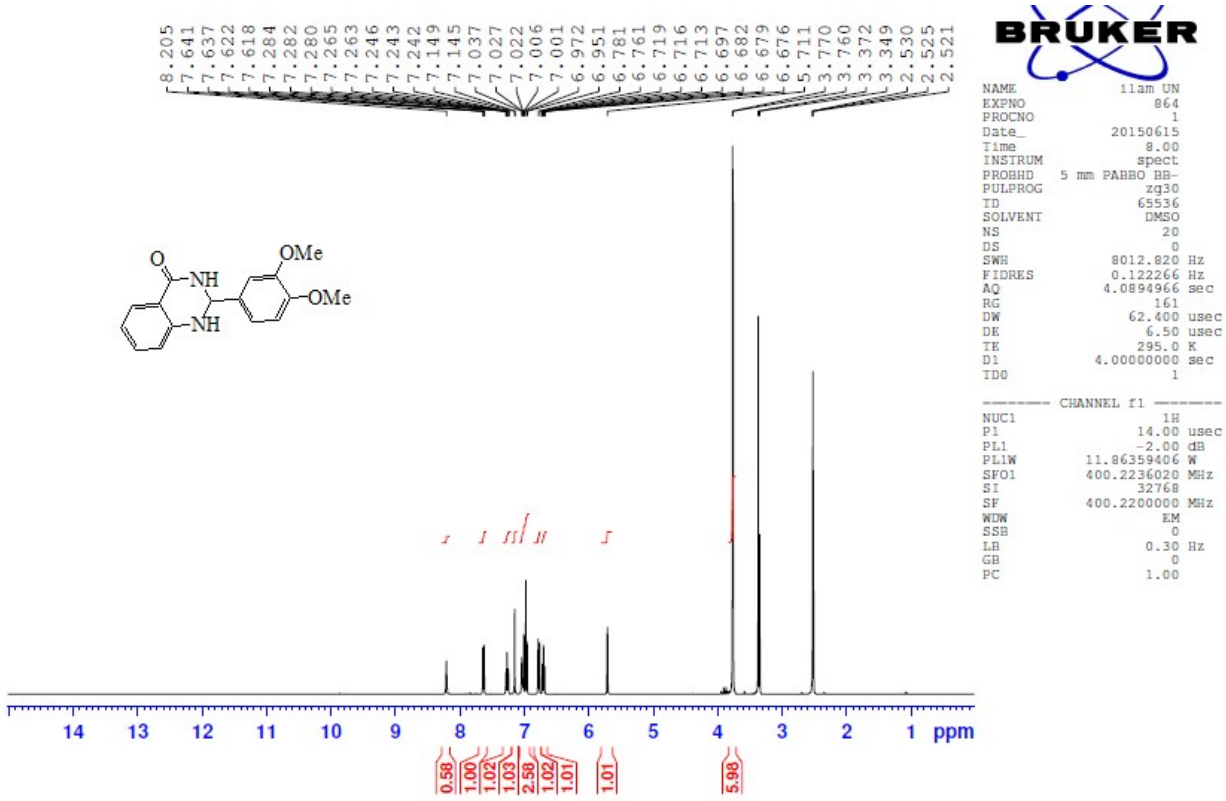


Ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8- hexahydroquinoline-3-carboxylate (entry 10, Table 4) (2i). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.25 (s, 1H), 8.12–8.10 (d, J = 8.4, 2H), 7.45–7.43 (d, J = 8.4, 2H), 4.99 (s, 1H), 4.01–3.95 (q, J = 7.2, 2H), 2.48–2.44 (d, J = 17.2, 1H), 2.34–2.30(d,J=16.8, 4H), 2.22–2.18 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.14–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

^{1}H NMR 1a



^{1}H NMR 1b



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FIDRES	0.122266 Hz
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RG	161
DW	62.400 usec
DE	6.50 usec
TE	295.0 K
D1	4.00000000 sec
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SFO1	400.2236020 MHz
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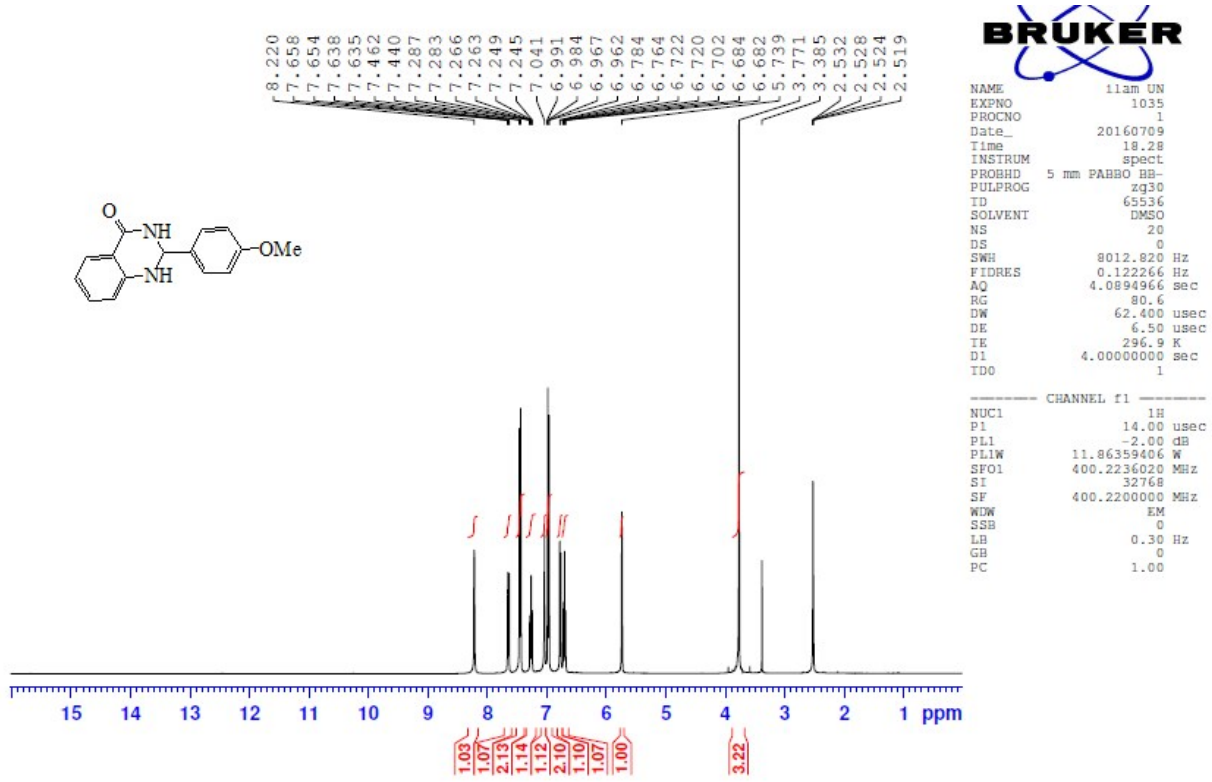
PC	1.00

^{1}H NMR 1c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7.041
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6.984
6.967
6.962
6.784
6.764
6.722
6.720
6.702
6.684
6.682
5.739
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3.385
2.532
2.528
2.524
2.519
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NH
NH
OMe
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1.07
2.13
1.14
1.12
2.10
1.10
1.07
1.00
3.22
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PROCNO 1
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Time 18.28
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PULPROG zg30
TD 65536
SOLVENT DMSO
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
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DE 6.50 usec
TE 296.9 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
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PL1 -2.00 dB
PL1W 11.86359406 W
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SI 32768
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WDW EM
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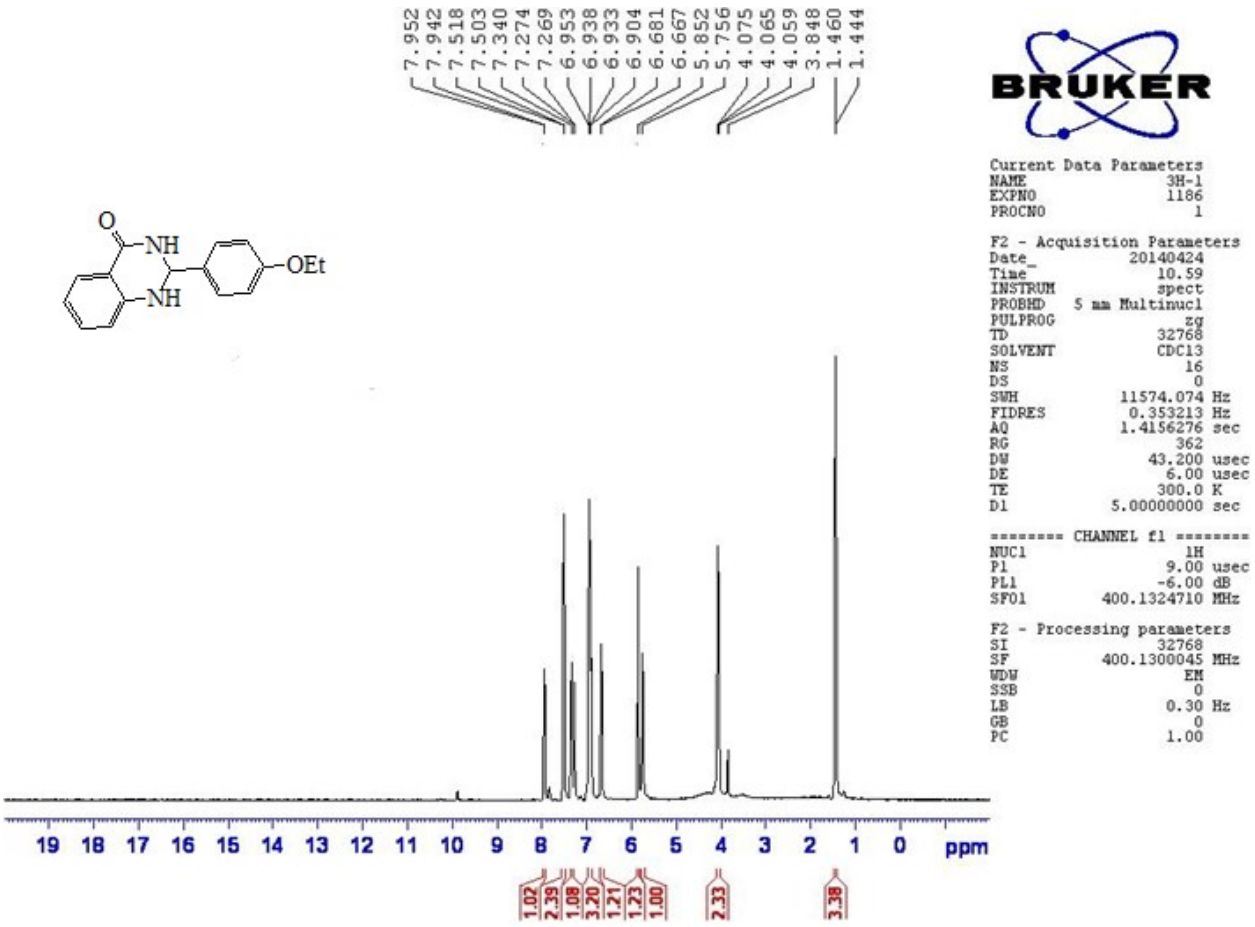
PC 1.00

[1]H NMR 1d



BRUKER

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EXPNO 1186
PROCNO 1

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TD 32768
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FIDRES 0.353213 Hz
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RG 362
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TE 300.0 K
D1 5.00000000 sec

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PL1 -6.00 dB
SFO1 400.1324710 MHz

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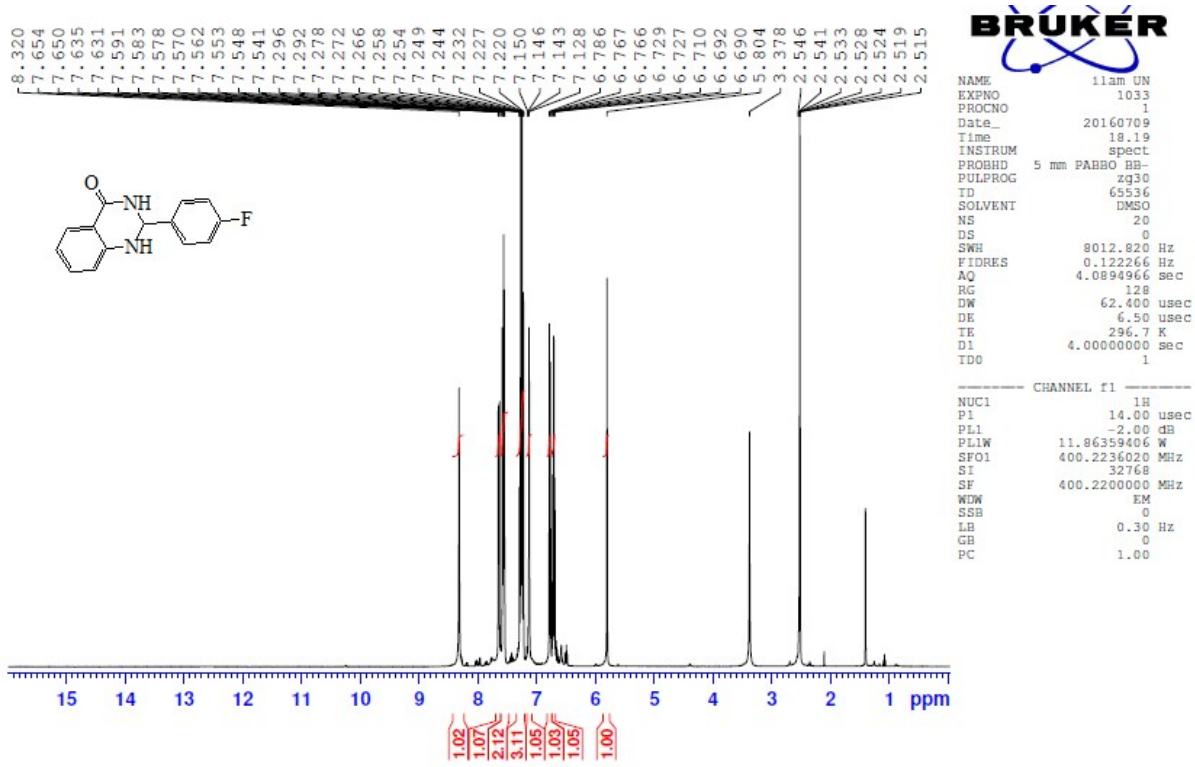
PC 1.00

[1]H NMR 1e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7.296
7.292
7.278
7.272
7.266
7.258
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7.249
7.244
7.232
7.227
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7.150
7.146
7.143
7.128
6.786
6.767
6.766
6.729
6.727
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6.690
5.804
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2.546
2.541
2.533
2.528
2.524
2.519
2.515
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NH
F
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1.07
2.12
3.11
1.05
1.03
1.05
1.00
BRUKER
NAME 11am UN
EXPNO 1033
PROCNO 1
Date_ 20160709
Time 18.19
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PULPROG zg30
TD 65536
SOLVENT DMSO
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
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RG 128
DW 62.400 usec
DE 6.50 usec
TE 296.7 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
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PL1 -2.00 dB
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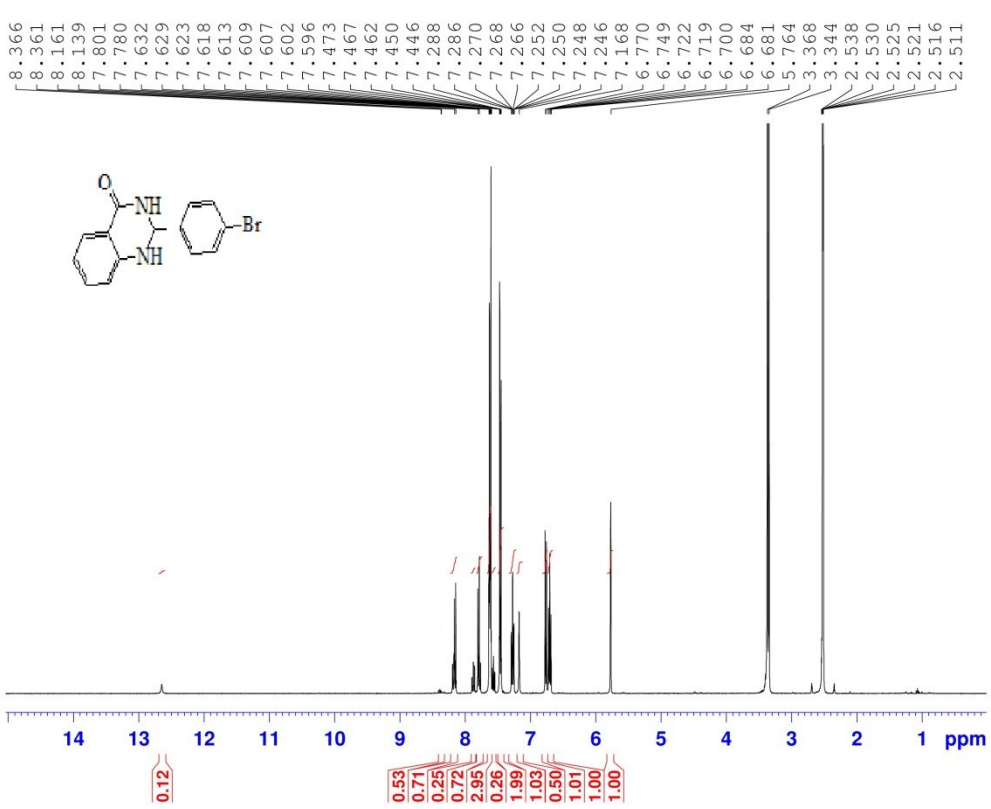
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR 1f



BRUKER

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PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	20
DS	0
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	228
DW	62.400 usec
DE	6.50 usec
TE	294.9 K
D1	4.00000000 sec
TD0	1
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PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
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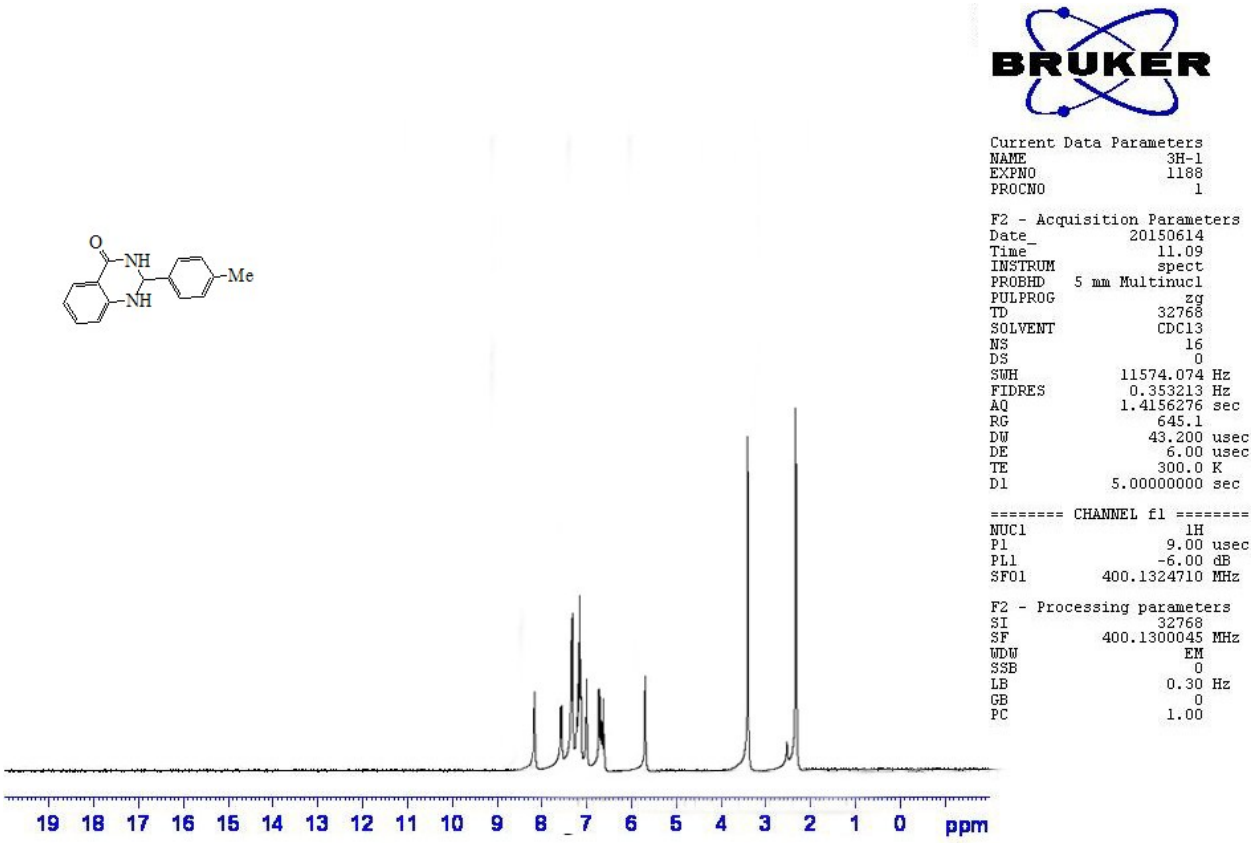
PC	1.00

^{1}H NMR 1g

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EXPNO                 1188
PROCNO                   1

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TD                   32768
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SWH              11574.074 Hz
FIDRES           0.353213 Hz
AQ               1.4156276 sec
RG                   645.1
DW                  43.200 usec
DE                   6.00 usec
TE                  300.0 K
D1              5.00000000 sec

======== CHANNEL f1 ========
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P1                   9.00 usec
PL1                 -6.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
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WDW                     EM
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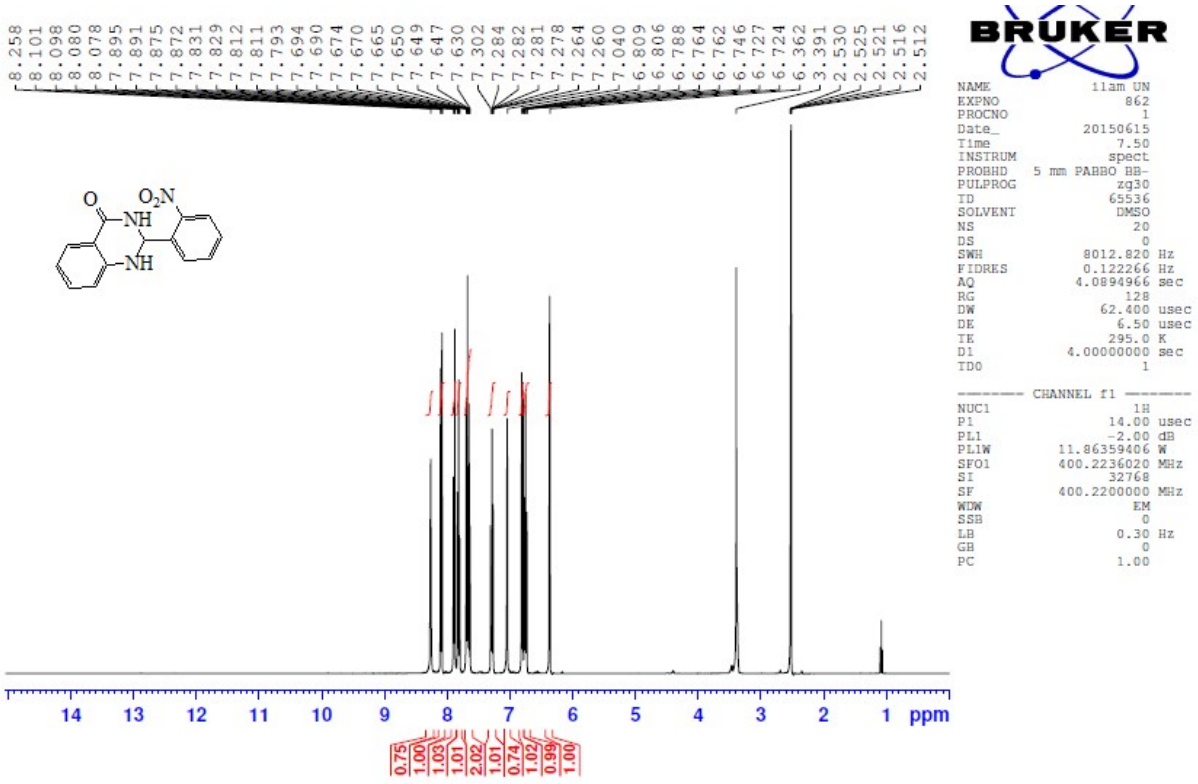
^{1}H NMR 1h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7.812
7.811
7.793
7.694
7.690
7.674
7.670
7.665
7.650
7.649
7.647
7.630
7.302
7.284
7.282
7.281
7.278
7.264
7.260
7.040
6.809
6.806
6.788
6.764
6.762
6.746
6.727
6.724
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2.525
2.521
2.516
2.512
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O2N
NH
NH
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NAME 11am UN
EXPNO 862
PROCNO 1
Date_ 20150615
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PULPROG zg30
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SOLVENT DMSO
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FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 128
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
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PL1 -2.00 dB
PL1W 11.86359406 W
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SF 400.2200000 MHz
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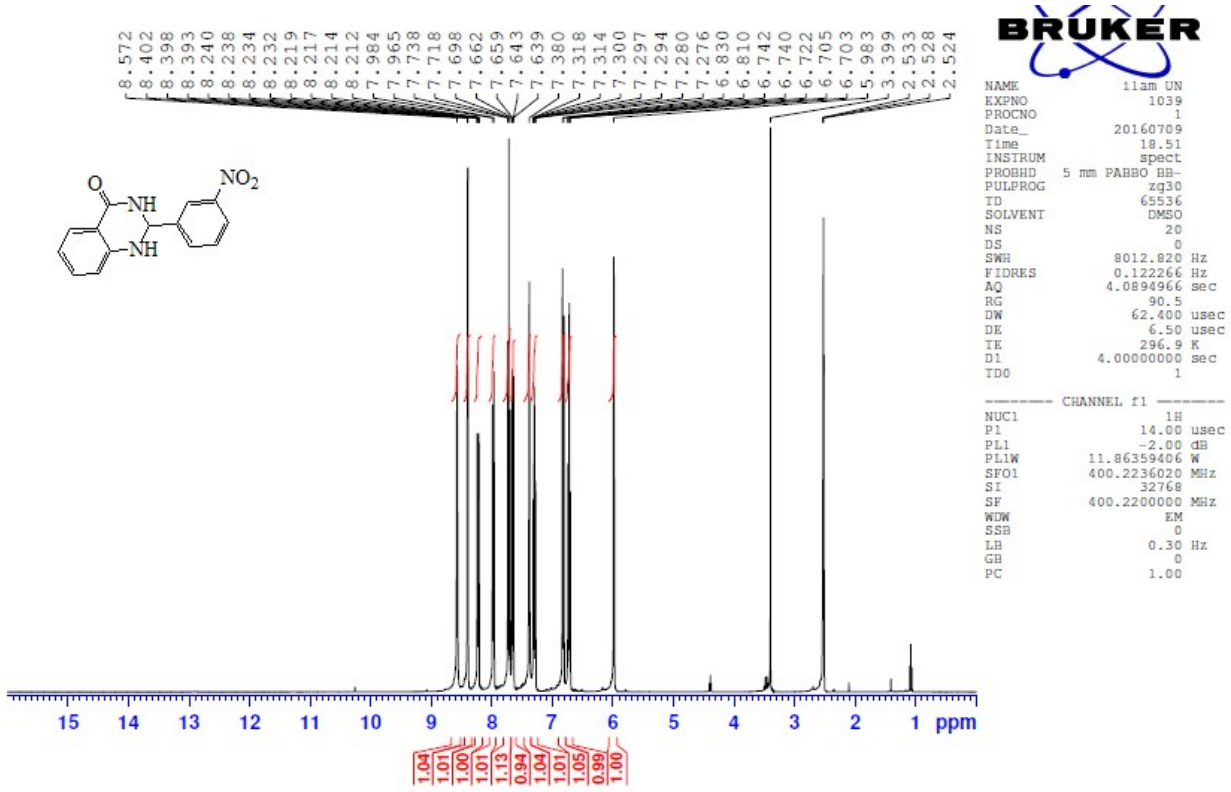
PC 1.00

^{1}H NMR 1i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8.232
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8.217
8.214
8.212
7.984
7.965
7.738
7.718
7.698
7.662
7.659
7.643
7.639
7.380
7.318
7.314
7.300
7.297
7.294
7.280
7.276
6.830
6.810
6.742
6.740
6.722
6.705
6.703
5.983
3.399
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2.528
2.524
O
NH
NH
NO2
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EXPNO 1039
PROCNO 1
Date_ 20160709
Time 18.51
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PULPROG zg30
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SOLVENT DMSO
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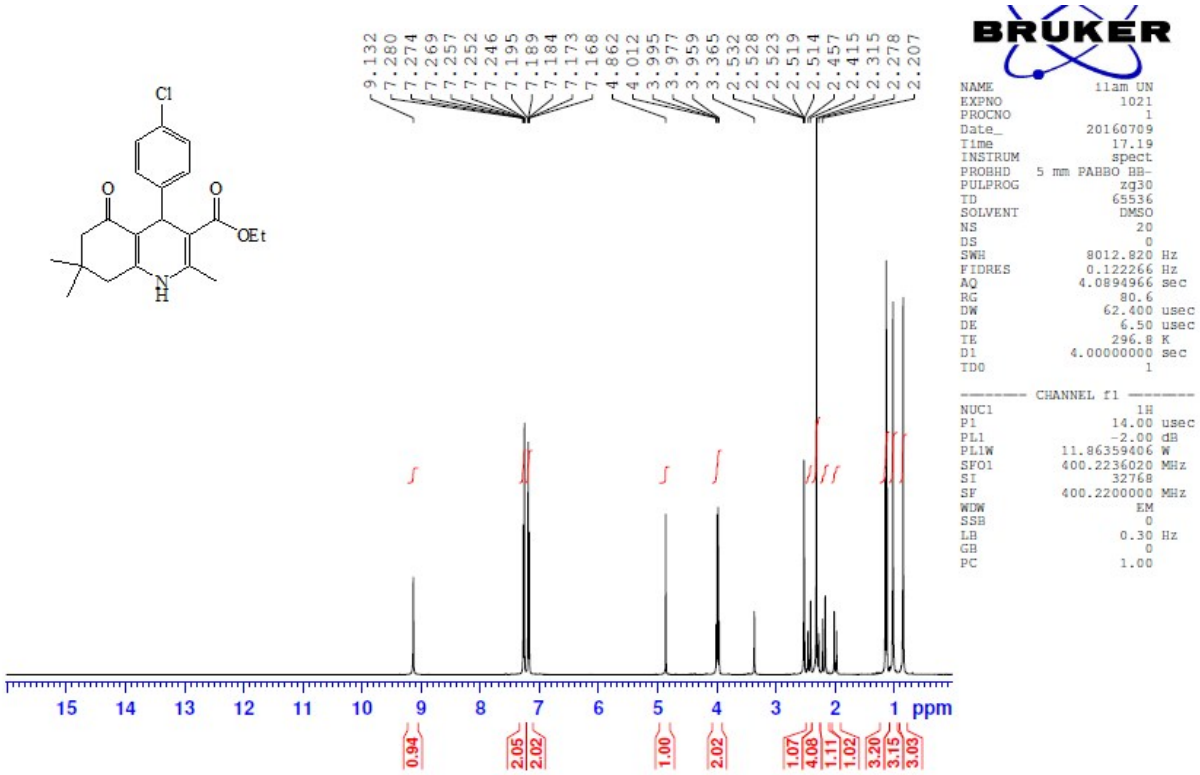
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 296.9 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR **2a**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4.012
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3.977
3.959
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2.528
2.523
2.519
2.514
2.457
2.415
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2.278
2.207
Cl
O
O
OEt
N
H
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0.94
2.05
2.02
1.00
2.02
1.07
4.08
1.11
1.02
3.20
3.15
3.03
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PROCNO 1
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PULPROG zg30
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SOLVENT DMSO
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 296.8 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
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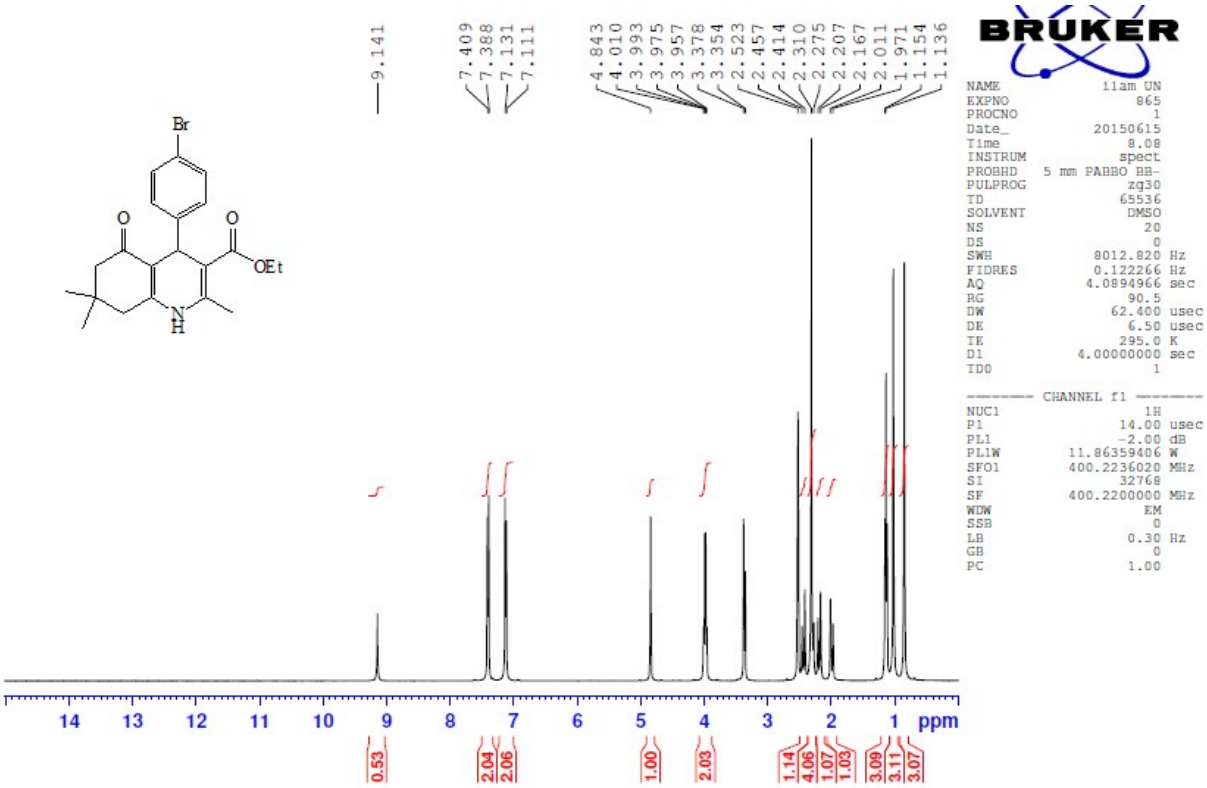
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR **2b**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7.131
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2.523
2.457
2.414
2.310
2.275
2.207
2.167
2.011
1.971
1.154
1.136
Br
O
O
OEt
N
H
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2.04
2.06
1.00
2.03
1.14
4.06
1.07
1.03
3.09
3.11
3.07
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TD 65536
SOLVENT DMSO
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
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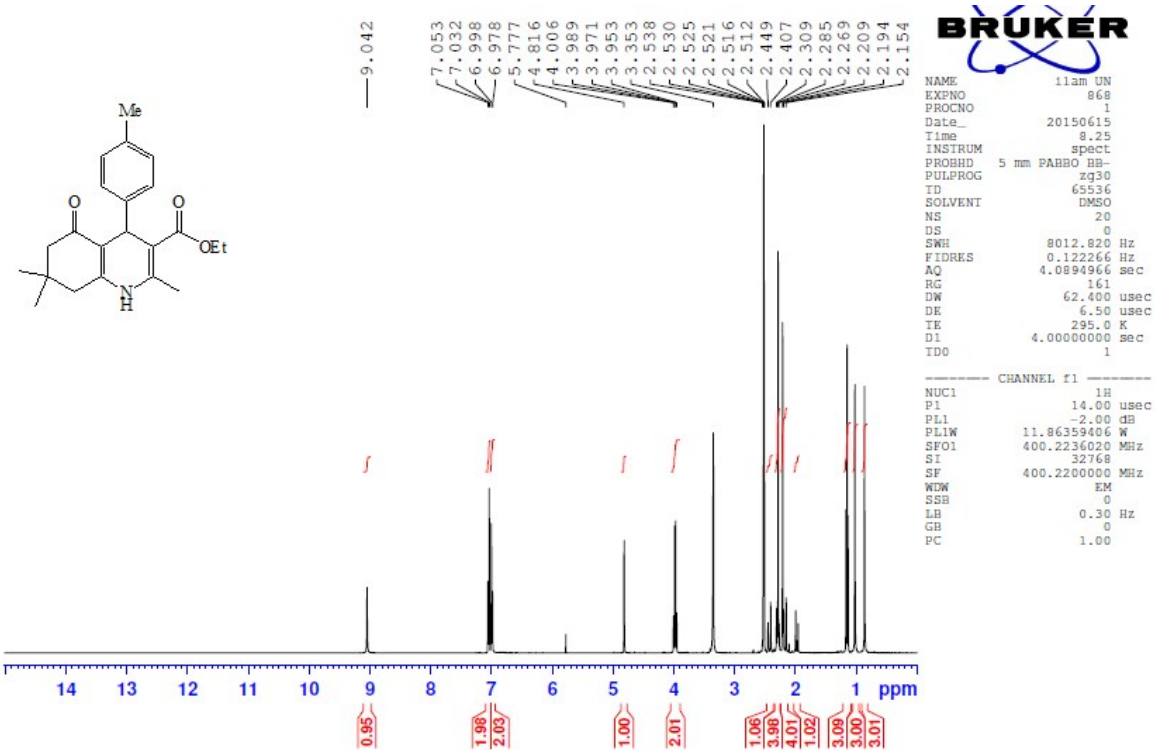
GB 0
PC 1.00

^{1}H NMR **2c**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3.971
3.953
3.353
2.538
2.530
2.525
2.521
2.516
2.512
2.449
2.407
2.309
2.285
2.269
2.209
2.194
2.154
Me
O
O
OEt
N
H
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
1.96
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1.00
2.01
1.06
3.98
4.01
1.02
3.09
3.00
3.01
BRUKER
NAME 11am UN
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PROCNO 1
Date_ 20150615
Time 8.25
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
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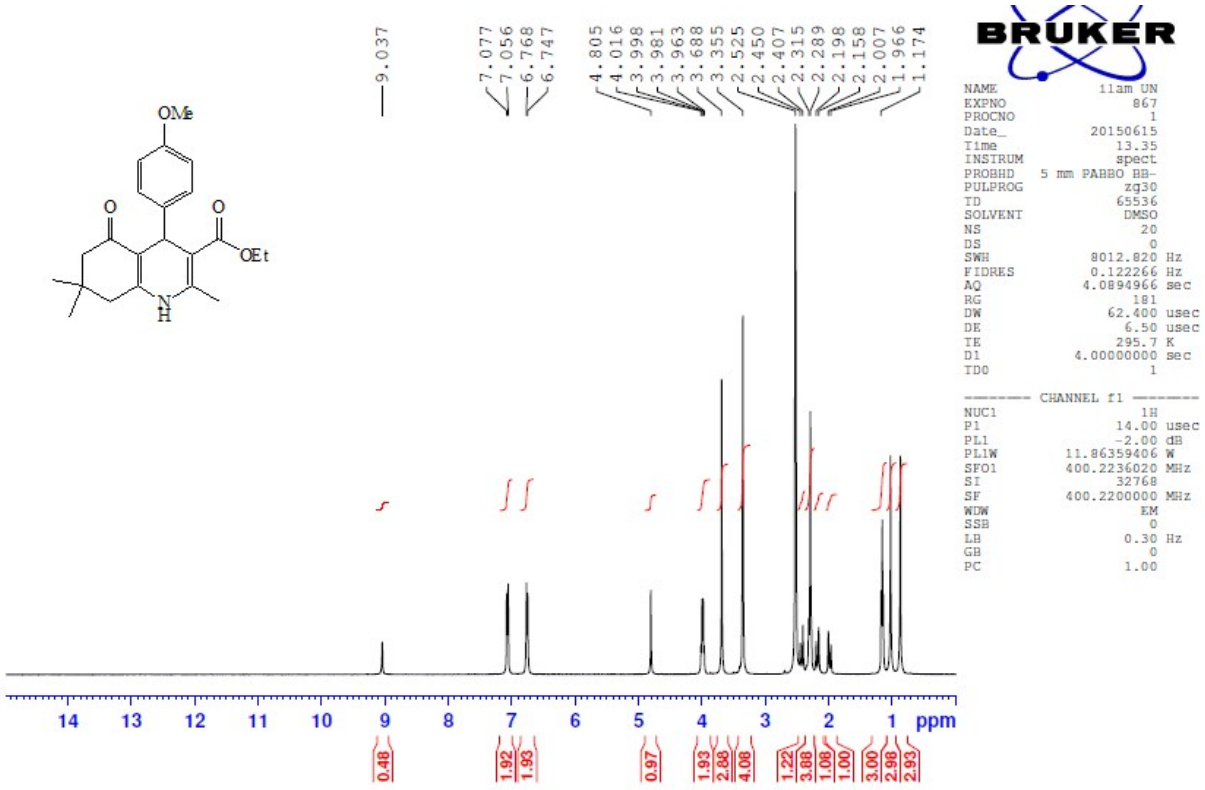
^{1}H NMR **2d**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1.174
OMe
O
O
OEt
N
H
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1.93
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1.22
3.68
1.06
1.00
3.00
2.96
2.93
BRUKER
NAME 11am UN
EXPNO 867
PROCNO 1
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Time 13.35
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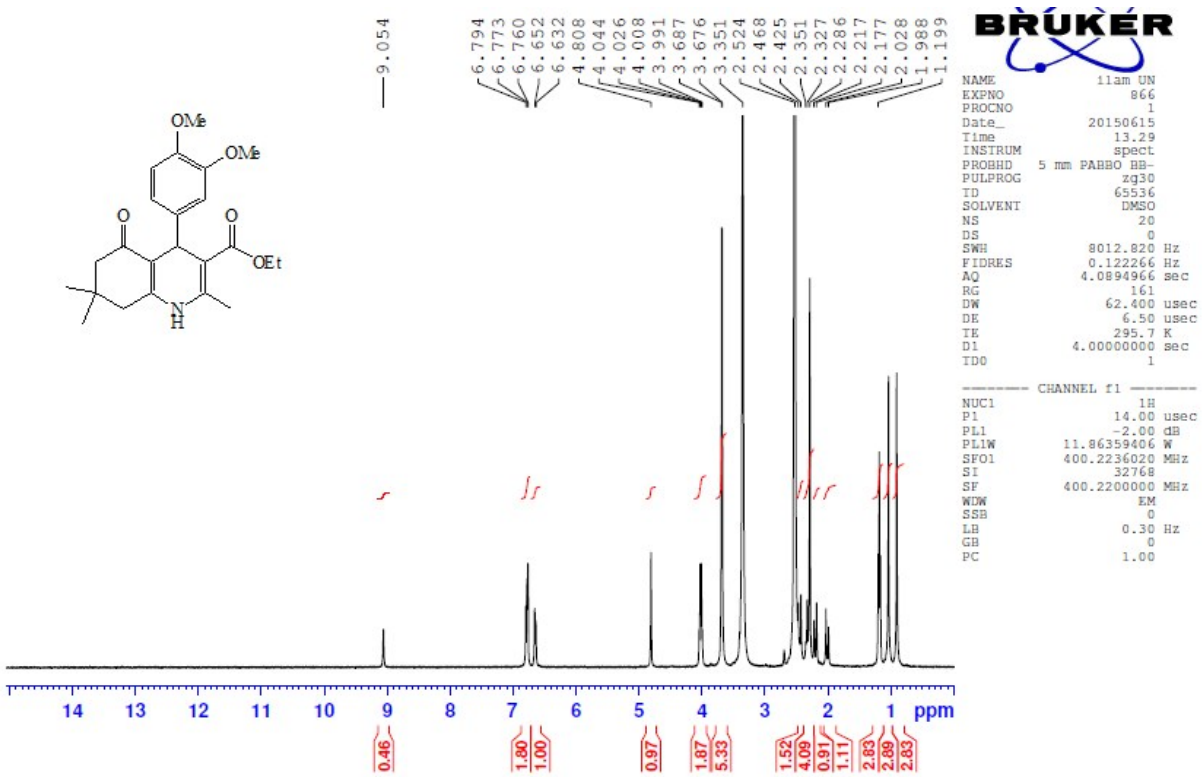
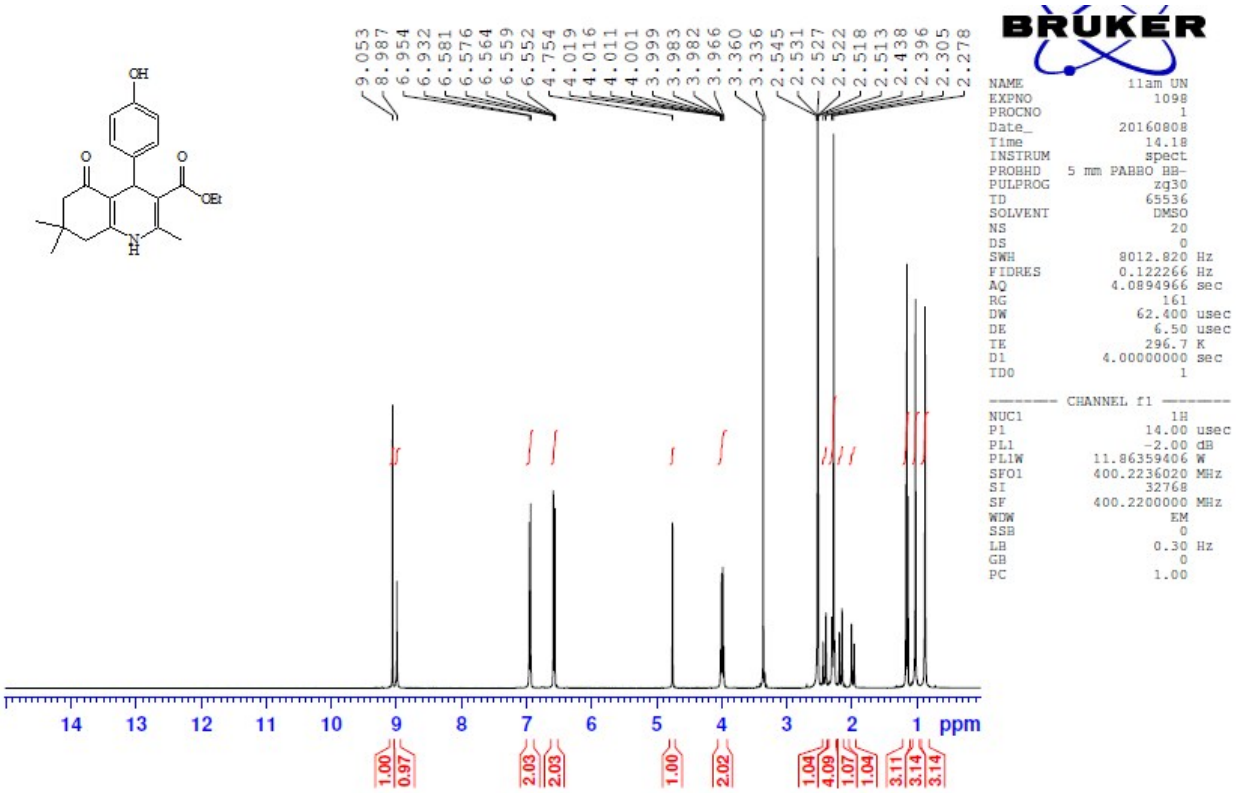
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 181
DW 62.400 usec
DE 6.50 usec
TE 295.7 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR **2e**


9.054
6.794
6.773
6.760
6.652
6.632
4.808
4.044
4.026
4.008
3.991
3.687
3.676
3.351
2.524
2.468
2.425
2.351
2.327
2.286
2.217
2.177
2.028
1.988
1.199
OMe
OMe
O
O
OEt
N
H
BRUKER
NAME 11am UN
EXPNO 866
PROCNO 1
Date_ 20150615
Time 13.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 161
DW 62.400 usec
DE 6.50 usec
TE 295.7 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.46
1.80
1.00
0.97
1.87
5.33
1.52
4.09
0.91
1.11
2.83
2.89
2.83

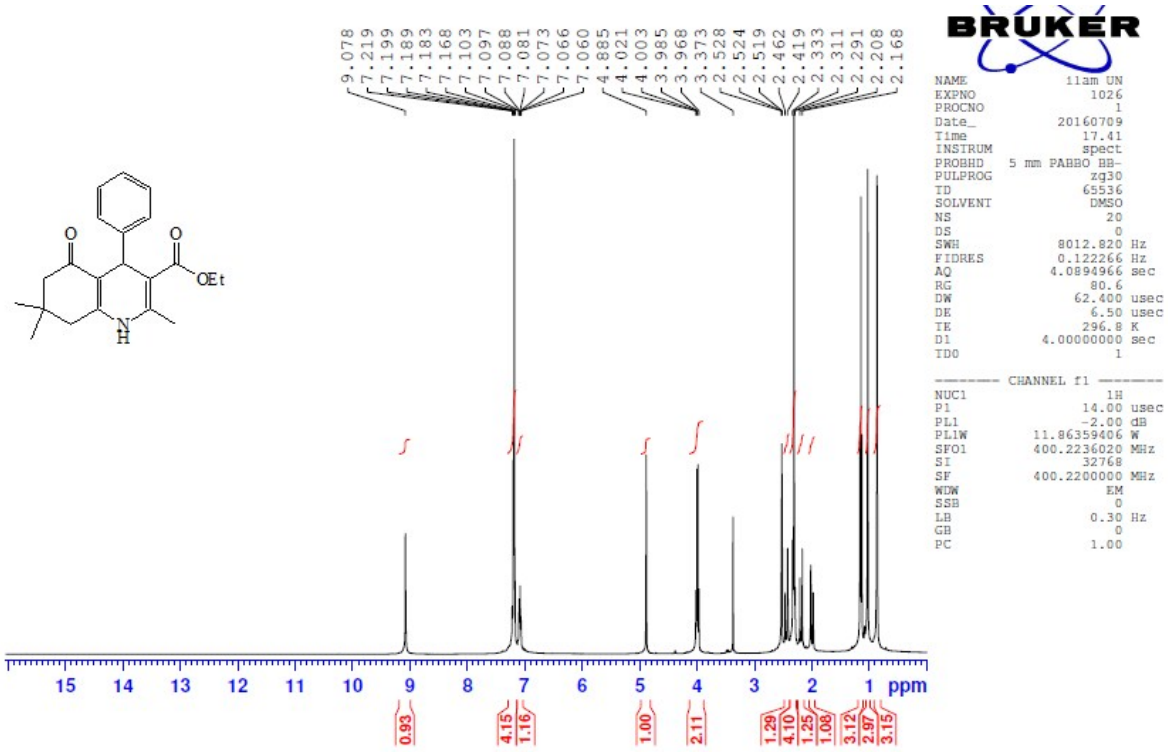
^{1}H NMR **2f**



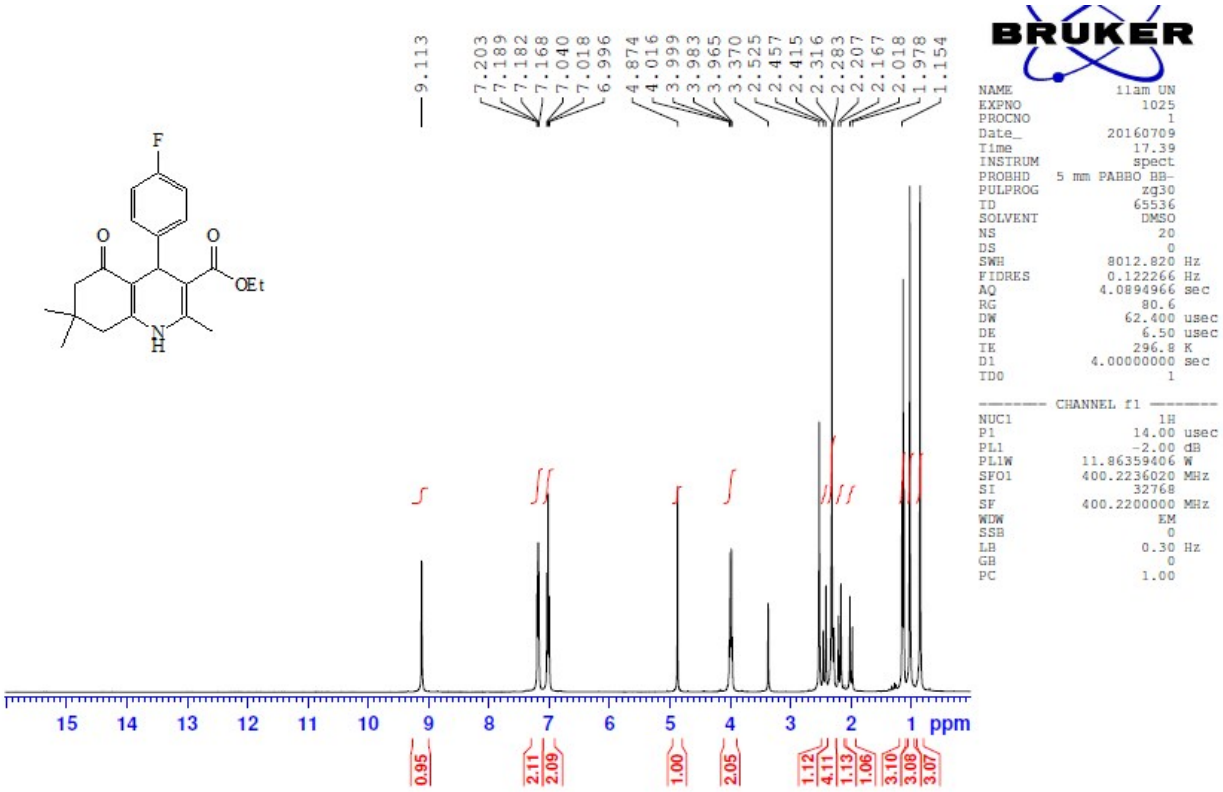
BRUKER

NAME	11am UN
EXPNO	1098
PROCNO	1
Date_	20160808
Time	14.18
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	20
DS	0
SWH	8012.820 Hz
FIDRES	0.122266 Hz
AQ	4.0894966 sec
RG	161
DW	62.400 usec
DE	6.50 usec
TE	296.7 K
D1	4.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.00 usec
PL1	-2.00 dB
PL1W	11.86359406 W
SFO1	400.2236020 MHz
SI	32768
SF	400.2200000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

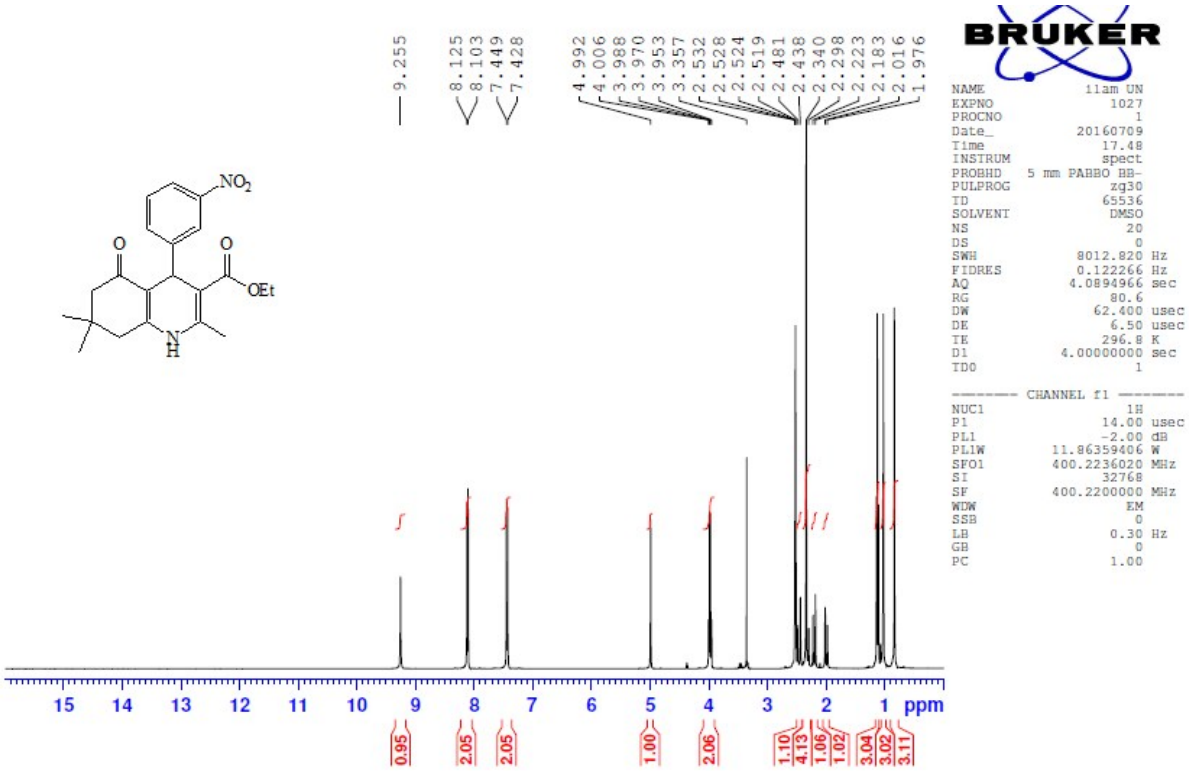
^{1}H NMR **2g**


9.078
7.219
7.199
7.189
7.183
7.168
7.103
7.097
7.088
7.081
7.073
7.066
7.060
4.885
4.021
4.003
3.985
3.968
3.373
2.528
2.524
2.519
2.462
2.419
2.333
2.311
2.291
2.208
2.168
O
O
OEt
N
H
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.93
4.15
1.16
1.00
2.11
1.29
4.10
1.25
1.08
3.12
2.97
3.15
BRUKER
NAME 11am UN
EXPNO 1026
PROCNO 1
Date_ 20160709
Time 17.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 296.8 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR **2h**


9.113
7.203
7.189
7.182
7.168
7.040
7.018
6.996
4.874
4.016
3.999
3.983
3.965
3.370
2.525
2.457
2.415
2.316
2.283
2.207
2.167
2.018
1.978
1.154
F
O
O
OEt
N
H
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
2.11
2.09
1.00
2.05
1.12
4.11
1.13
1.06
3.10
3.08
3.07
BRUKER
NAME 11am UN
EXPNO 1025
PROCNO 1
Date_ 20160709
Time 17.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 296.8 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR **2i**


9.255
8.125
8.103
7.449
7.428
4.992
4.006
3.988
3.970
3.953
3.357
2.532
2.528
2.524
2.519
2.481
2.438
2.340
2.298
2.223
2.183
2.016
1.976
NO2
O
O
OEt
N
H
BRUKER
NAME 11am UN
EXPNO 1027
PROCNO 1
Date_ 20160709
Time 17.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 80.6
DW 62.400 usec
DE 6.50 usec
TE 296.8 K
D1 4.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.95
2.05
2.05
1.00
2.06
1.10
4.13
1.06
1.02
3.04
3.02
3.11