Supplementary Information

Copper catalyzed arylsulfenylation of thiohydantoin using elemental sulfur and arylhalide: C-S coupling

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Received 29 April 2024; accepted (revised) 30 August 2024

Contents

1. Experimental Section:

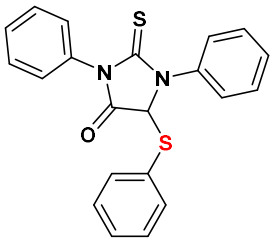
General information

All the basic chemicals, solvents were procured from university identified suppliers. Commercial reagents and solvents were used without further purification. The prepared compounds were characterized by ^{1}H NMR, ^{13}C NMR and mass spectral studies. Melting points were determined in open capillaries on a Veego electronic apparatus VMP-D (Veego Instrument Corporation, Mumbai, India) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectras were recorded on a 400 MHz FT NMR, Advance III Bruker model spectrometer using DMSO d6 as a solvent and TMS as internal standard. ESI mass spectra were recorded on a Bruker Daltonics MicroTof. NMR chemical shifts are reported as parts per million (ppm) downfield from TMS. The splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet.

General procedure for the synthesis of compound 3

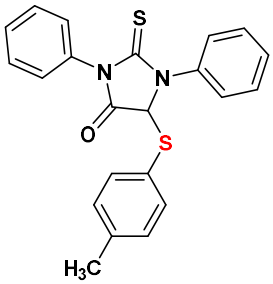
To a solution of 2-thiohydantoin[30] **1** (0.25 mmol) in DMF (1 ml), iodobenzene **2** (0.75 mmol), elemental sulfur (0.75 mmol) was added along with copper catalyst (0.2 equiv.) and base (1 mmol) in a reaction glass tube. The resulting mixture was stirred at 130 °C temperature for 24h in nitrogen atmosphere. The completion of reaction was confirmed by TLC. After the completion of reaction, it was poured into 10 ml sodium carbonate solution. The product was extracted with ethyl acetate (10 mL × 3) and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left the crude residue. Finally, the crude residue was purified by column chromatography to get the desired product **3**.

1) **1,3-Diphenyl-5-(phenylthio)-2-thioxoimidazolidin-4-one (3a)**



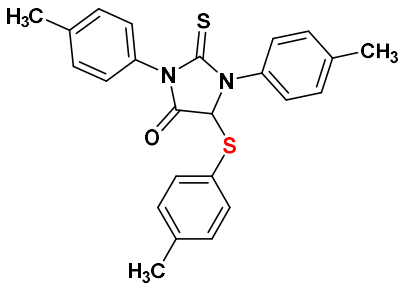
Yield: Trace. Light yellow solid; M.P: 240-242°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ:5.10(s, 1H), 6.85-6.87(m, 4H), 6.96-6.99(m, 2H), 7.01-7.34(m, 5H), 7.53-7.63(m, 4H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:83.95, 126.35, 128.60, 129.62, 129.83, 130.34, 132.63, 134.90, 141.29, 168.60, 178.34. Anal. Calcd. For $C_{21}H_{16}N_2OS_2$: C:67.00; H:4.28; N:7.44, Found: C:67.02; H:4.29; N:7.42, MS-EI (m/z) [M +H] +):376.4988. Found:376.4983.

2) **1,3-Diphenyl-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3b)**



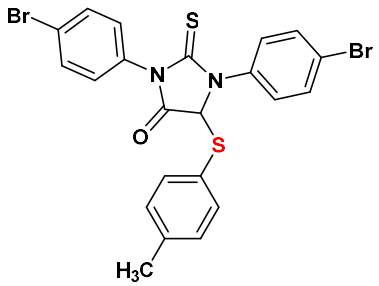
Yield: 50%. Yellow solid; M.P: 230-232°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.31(s, 3H), 4.99(s, 1H), 6.81(d, *J*=7.8Hz, 2H), 6.93(d, *J*=7.5Hz, 2H), 7.11-7.25(m, 4H), 7.53-7.66(m, 4H), 7.75-7.81(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.91, 83.36, 127.96, 128.58, 128.83, 129.52, 129.84, 130.54, 134.24, 141.54, 168.72, 178.42. Anal. Calcd. For $C_{22}H_{18}N_2OS_2$: C:67.66; H:4.65; N:7.17, Found: C:67.68; H:4.64; N:7.15, MS-EI (m/z) [M +H] +):390.5255. Found:390.5259.

3) 2-Thioxo-1,3-di-p-tolyl-5-(p-tolylthio)imidazolidin-4-one (3c)



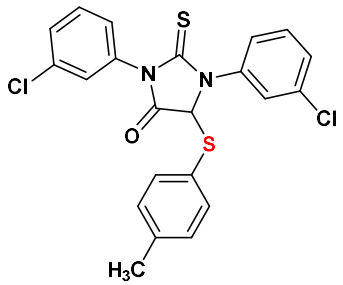
Yield: 75%. Yellow solid; M.P: 225-227°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.28(s, 6H), 2.33(s, 3H), 5.08(s, 1H), 6.83-6.89(m, 4H), 6.98-7.02(m, 4H), 7.25-7.38(m, 4H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.43, 21.90, 21.94, 83.44, 124.65, 126.48, 127.53, 128.55, 128.87, 130.41, 134.63, 137.57, 167.44, 176.93. Anal. Calcd. For $C_{24}H_{22}N_2OS_2$: C:68.87; H:5.30; N:6.69, Found: C:68.90; H:5.31; N:6.70, MS-EI (m/z) [M +H] +):418.5788. Found:418.5785.

4) 1,3-Bis(4-bromophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3d)



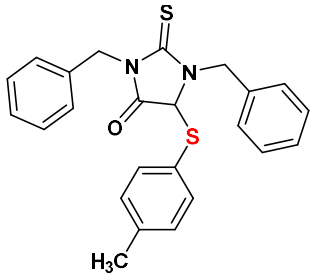
Yield: 56%. Dark yellow solid; M.P: 245-247°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.33(s, 3H), 5.06(s, 1H), 6.88(d, *J*=7.8Hz, 2H), 6.92(d, *J*=7.0Hz, 2H), 7.06-7.09(m, 2H), 7.11-7.13(m, 2H), 7.25-7.29(m, 2H), 7.81-7.89(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.56, 83.97, 121.83, 121.86, 128.41, 128.46, 129.13, 129.16, 131.86, 140.62, 140.68, 141.30, 141.32, 141.35, 141.39, 169.42, 179.66. Anal. Calcd. For $C_{22}H_{16}Br_2N_2OS_2$: C:48.19; H:2.94; N:5.11, Found: C:48.17; H:2.93; N:5.13, MS-EI (m/z) [M +H] +):548.3178. Found:548.3173.

5) 1,3-Bis(3-chlorophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3e)



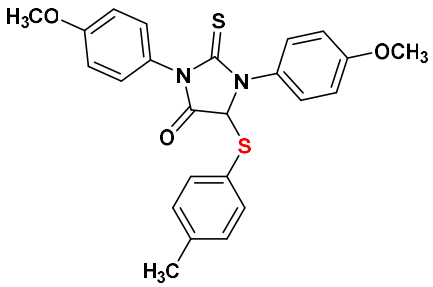
Yield: 52%. Dark yellow solid; M.P: 241-243°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ: 2.31(s, 3H), 5.09(s, 1H), 6.86(d, *J*=6.8Hz, 2H), 6.92(d, *J*=7.0Hz, 2H), 7.11(m, 2H), 7.33(m, 2H), 7.56(m, 2H), 7.82(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.71, 83.83, 128.66, 129.22, 129.76, 130.84, 131.41, 133.89, 134.17, 135.16, 140.95, 169.65, 179.45. Anal. Calcd. For $C_{22}H_{16}Cl_2N_2OS_2$: C:57.52; H:3.51; N:6.10, Found: C:57.54; H:3.52; N:6.13, MS-EI (m/z) [M +H] +):459.4158. Found:459.4161.

6) 1,3-Dibenzyl-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3f)



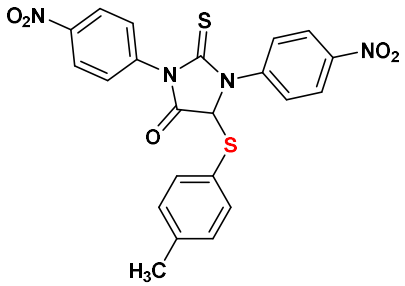
Yield: 63%. Yellow solid; M.P: 200-202°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.29(s, 3H), 4.74(s, 4H), 5.07(s, 1H), 6.83(d, *J*=7.2Hz, 2H), 6.90(d, *J*=6.8Hz, 2H), 6.98-7.20(m, 8H), 7.47-7.52(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.64, 55.83, 55.88, 84.13, 127.12, 127.15, 128.66, 128.69, 129.30, 129.33, 129.62, 129.64, 129.66, 129.67, 130.14, 130.16, 130.69, 132.60, 132.63, 133.92, 170.22, 176.34. Anal. Calcd. For $C_{24}H_{22}N_2OS_2$: C:68.87; H:5.30; N:6.89, Found: C:68.89; H:5.29; N:6.91, MS-EI (m/z) [M +H] +):418.5788. Found:418.5791.

7) 1,3-Bis(4-methoxyphenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3g)



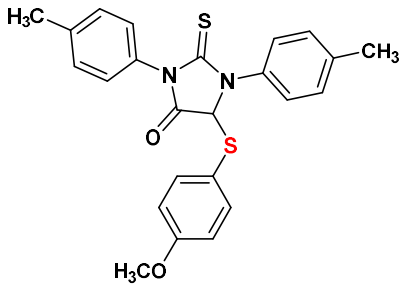
Yield: 79%. Light yellow solid; M.P: 215-217°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.32(s, 3H), 3.79(s, 6H), 5.07(s, 1H), 6.86(d, *J*=7.2Hz, 2H), 6.91(d, *J*=7.0Hz, 2H), 6.98-7.05(m, 4H), 7.62-7.78(m, 4H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.51, 56.11, 56.14, 83.82, 118.44, 118.47, 126.92, 126.98, 128.93, 128.95, 129.62, 129.69, 129.84, 130.76, 136.40, 136.47, 159.65, 169.49, 177.85. Anal. Calcd. For $C_{24}H_{22}N_2O_3S_2$: C:63.98; H:4.92; N:6.22, Found: C:63.96; H:4.93; N:6.24, MS-EI (m/z) [M +H] +):450.5770. Found:450.5776.

8) 1,3-Bis(4-nitrophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3h)



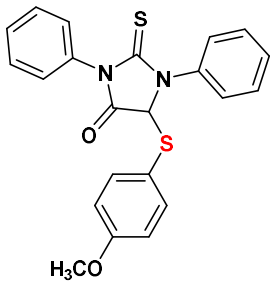
Yield: 43%. Orange solid; M.P: 249-251°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.34(s, 3H), 5.06(s, 1H), 6.86(d, *J*=7.4Hz, 2H), 6.92(d, *J*=7.6Hz, 2H), 7.33-7.51(m, 4H), 8.00-8.32(m, 4H). **^{13}C NMR** (100 MHz, DMSO-d6) δ: 21.96, 83.97, 124.98, 126.68, 128.89, 129.87, 134.30, 134.93, 134.99, 144.25, 144.30, 147,11, 147.17, 169.84, 178.17. Anal. Calcd. For $C_{22}H_{16}N_4O_5S_2$: C:54.99; H:3.36; N:11.66, Found: C:54.97; H:3.35; N:11.68, MS-EI (m/z) [M +H] +):480.5192. Found:480.5186.

9) 5-((4-Methoxyphenyl)thio)-2-thioxo-1,3-di-p-tolylimidazolidin-4-one (3i)



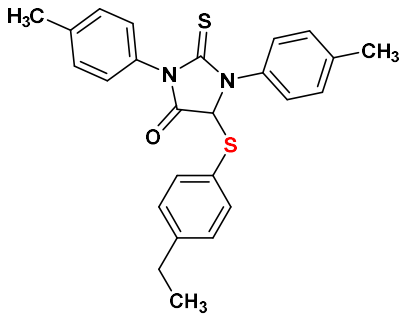
Yield: 76%. Yellow solid; M.P: 221-223°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.31(s, 6H), 3.79(s, 3H), 5.08(s, 1H), 6.85-6.89(m, 2H), 6.98-7.00(m, 2H), 7.04-7.08(m, 2H), 7.11-7.14(m, 2H), 7.20-7.22(m, 2H), 7.31-7.36(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:21.43, 55.83, 84.16, 118.82, 122.81, 126.84, 128.63, 128.66, 129.90, 129.97, 134.47, 136,67, 156.49, 170.16, 176.62. Anal. Calcd. For $C_{24}H_{22}N_2O_2S_2$: C:66.33; H:5.10; N:6.45, Found: C:66.35; H:5.09; N:6.48, MS-EI (m/z) [M +H] +):434.5780. Found:434.5773.

10) 5-((4-Methoxyphenyl)thio)-1,3-diphenyl-2-thioxoimidazolidin-4-one (3j)



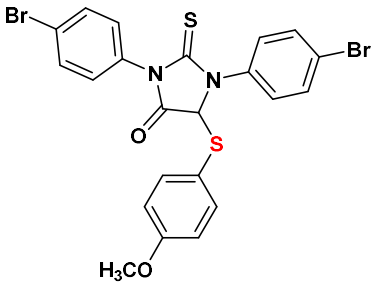
Yield: 66%. Yellow solid; M.P:230-232 °C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :3.78(s, 3H), 5.07(s, 1H), 6.87(d, *J*=6.0Hz, 2H), 6.94(d, *J*=6.4Hz, 2H), 6.99-7.01(m, 2H), 7.21-7.26(m, 2H), 7.31-7.34(m, 2H), 7.41-7.43(m, 2H), 7.49-7.52(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:55.93, 89.99, 119.17, 122.98, 126.74, 126.79, 129.80, 129.84, 130.13, 130.16, 132.43, 132.80, 159.89, 169.84, 176.86. Anal. Calcd. For $C_{22}H_{18}N_2O_2S_2$: C:65.00; H:4.46; N:6.89, Found: C:65.03; H:4.47; N:6.91, MS-EI (m/z) [M +H] +):406.5245. Found:406.5240.

11) 5-((4-Ethylphenyl)thio)-2-thioxo-1,3-di-p-tolylimidazolidin-4-one (3k)



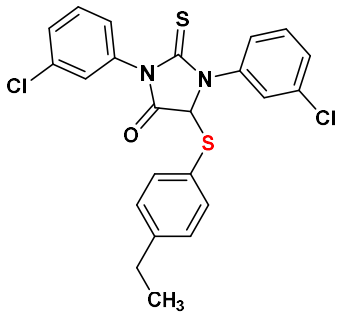
Yield: 75%. Dark yellow solid; M.P: 225-227°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :1.19(s, 3H), 2.33(s, 6H), 2.73(q, 2H), 5.06(s, 1H), 6.86(d, J=7.2hz, 2H), 6.91(d, J=7.0Hz, 2H), 6.99-7.05(m, 2H), 7.11-7.19(m, 2H), 7.25-7.29(m, 2H), 7.31-7.41(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:14.82, 21.64, 28.57, 83.95, 127.56, 127.73, 127.82, 128.79, 129.63, 134.24, 137.89, 139.86, 169.94, 177.19. Anal. Calcd. For $C_{25}H_{24}N_2OS_2$: C:69.41; H:5.59; N:6.48, Found: C:69.43; H:5.58; N:6.50, MS-EI (m/z) [M +H] +):432.6056. Found:432.6060.

12) 1,3-Bis(4-bromophenyl)-5-((4-methoxyphenyl)thio)-2-thioxoimidazolidin-4-one (3l)



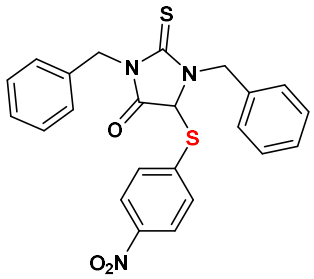
Yield: 51%. Dark yellow solid; M.P: 246-248°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :3.82(s, 3H), 5.08(s, 1H), 6.87(d, *J*=6.8Hz, 2H), 6.96(d, *J*=6.0Hz, 2H), 7.13-7.16(m, 2H), 7.29-7.32(m, 2H), 7.59-7.63(m, 2H), 7.79-7.81(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:55.88, 83.87, 118.87, 122.16, 122.81, 126.84, 131.46, 140.84, 141.61, 156.14, 170.24, 176.90. Anal. Calcd. For $C_{22}H_{16}Br_2N_2O_2S_2$: C:46.83; H:2.86; N:4.96, Found: C:46.85; H:2.87; N:4.94, MS-EI (m/z) [M +H] +):564.3168. Found:564.3165.

13) 1,3-Bis(3-chlorophenyl)-5-((4-ethylphenyl)thio)-2-thioxoimidazolidin-4-one (3m)



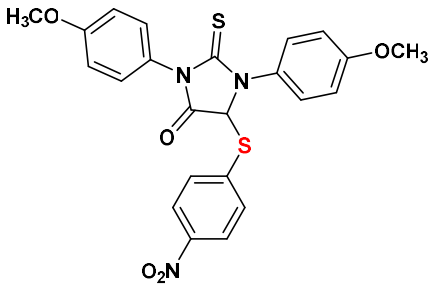
Yield: 69%. Yellow solid; M.P: 231-233°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :1.18(t, 3H), 2.73(q, 2H), 5.09(s, 1H), 6.86(d, *J*=6.8Hz, 2H) 6.94(d, *J*=6.0Hz, 2H), 7.11-7.14(m, 2H), 7.34-7.45(m, 4H), 7.86-7.91(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:14.66, 28.67, 83.81, 122.87, 127.33, 127.63, 128.82, 139.81, 139.95, 141.23, 141.67, 169.84, 177.17. Anal. Calcd. For $C_{23}H_{18}Cl_2N_2OS_2$: C:58.35; H:3.83; N:5.92, Found: C:58.33; H:3.84; N:5.94, MS-EI (m/z) [M +H] +):473.4425. Found:473.4431.

14) 1,3-Dibenzyl-5-((4-nitrophenyl)thio)-2-thioxoimidazolidin-4-one (3n)



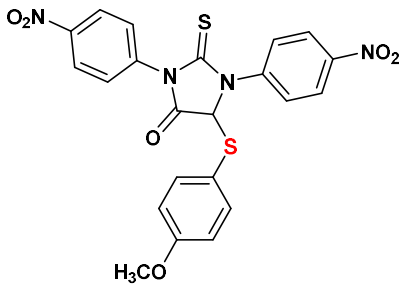
Yield: 65%. Dark yellow solid; M.P: 250-252°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :2.30(s, 4H), 4.73(s, 1H), 6.88-6.94(m, 4H), 7.20-7.23(m, 2H), 7.36-7.40(m, 2H), 7.50-7.53(m, 2H), 7.89(d, *J*=8.0Hz, 2H), 7.96(d, *J*=7.8Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:55.68, 83.95, 124.46, 126.86, 127.48, 129.63, 130.45, 132.87, 136.39, 144.66, 170.44, 177.84. Anal. Calcd. For $C_{23}H_{19}N_3O_3S_2$: C:61.45; H:4.26; N:9.35, Found: C:61.43; H:4.27; N:9.37, MS-EI (m/z) [M +H] +):449.5491. Found:449.5495.

15) 1,3-Bis(4-methoxyphenyl)-5-((4-nitrophe9nyl)thio)-2-thioxoimidazolidin-4-one (3o)



Yield: 54%. Dark yellow solid; M.P: 230-232°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :3.79(s, 6H), 5.11(s, 1H), 6.87-6.93(m, 2H), 6.96-7.01(m, 4H), 7.06-7.09(m, 2H), 7.98(d, *J*=8.0Hz, 2H), 7.91(d, *J*=7.8Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:56.36, 83.77, 118.61, 118.65, 124.64, 126.84, 134.64, 136.78, 139.47, 144.84, 159.48, 169.88, 177.85. Anal. Calcd. For $C_{23}H_{19}N_3O_5S_2$: C:57.37; H:3.98; N:8.73, Found: C:57.35; H:3.99; N:8.71, MS-EI (m/z) [M +H] +):481.5471. Found:481.5466.

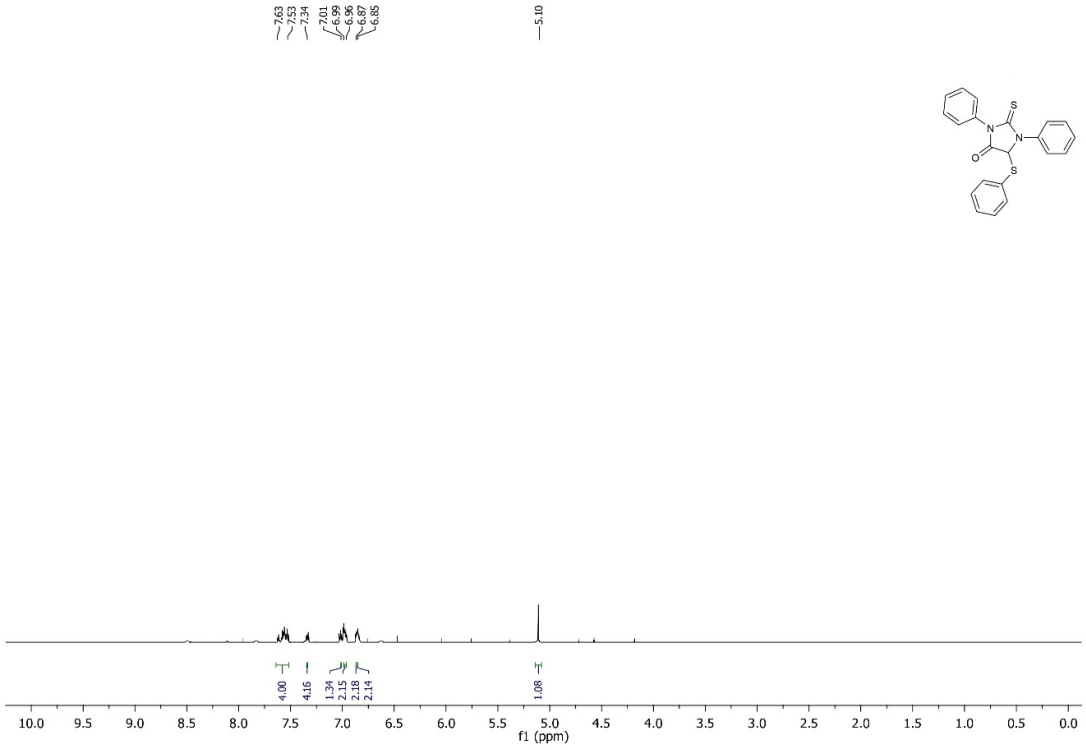
16) 5-((4-Methoxyphenyl)thio)-1,3-bis(4-nitrophenyl)-2-thioxoimidazolidin-4-one (3p)

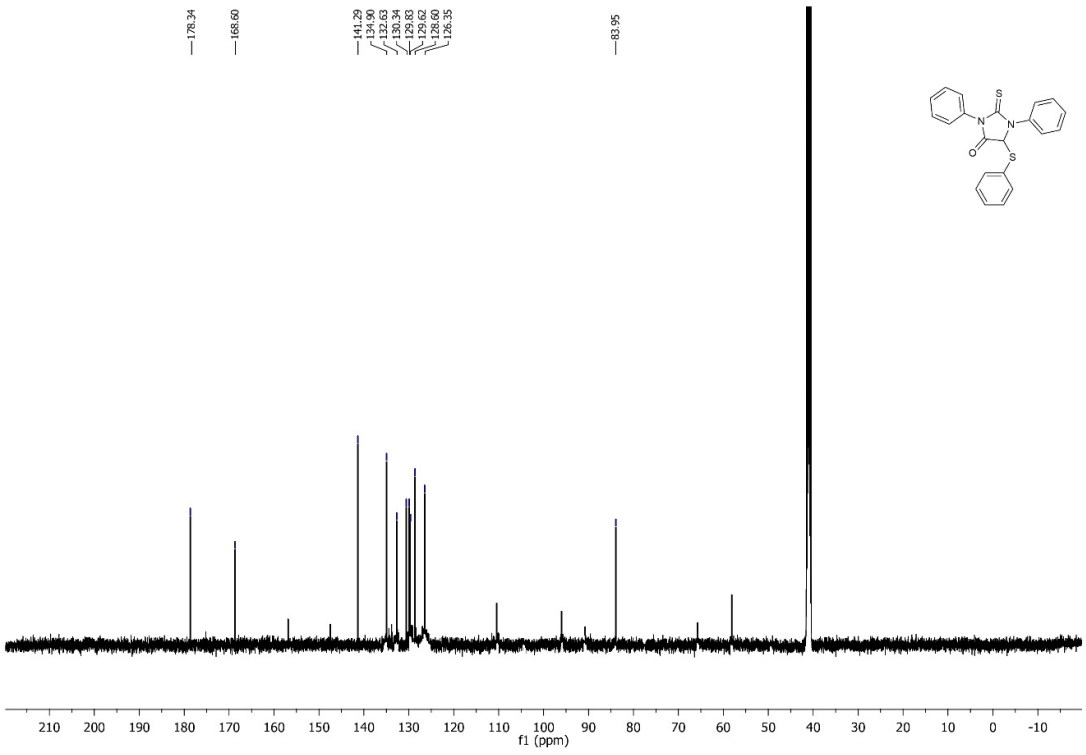


Yield: 61%. Dark yellow solid; M.P: 225-227°C; **^{1}H NMR** (400 MHz, DMSO-d6) δ :3.82(s, 3H), 5.06(s, 1H), 6.85(d, J=7.0Hz, 2H), 6.98(d, J=7.2Hz, 2H), 7.13-7.16(m, 2H), 7.36-7.40(m, 2H), 7.76-7.79(m, 2H), 8.21-8.24(m, 2H). **^{13}C NMR** (100 MHz, DMSO-d6) δ:55.91, 83.87, 118.87, 125.17, 126.68, 134.61, 136.40, 144.38, 147.37, 159.63, 169.65, 177.63. Anal. Calcd. For $C_{22}H_{16}N_4O_6S_2$: C:53.22; H:3.25; N:11.28, Found: C:53.20; H:3.26; N:11.30, MS-EI (m/z) [M +H] +):496.5182. Found:496.5187.

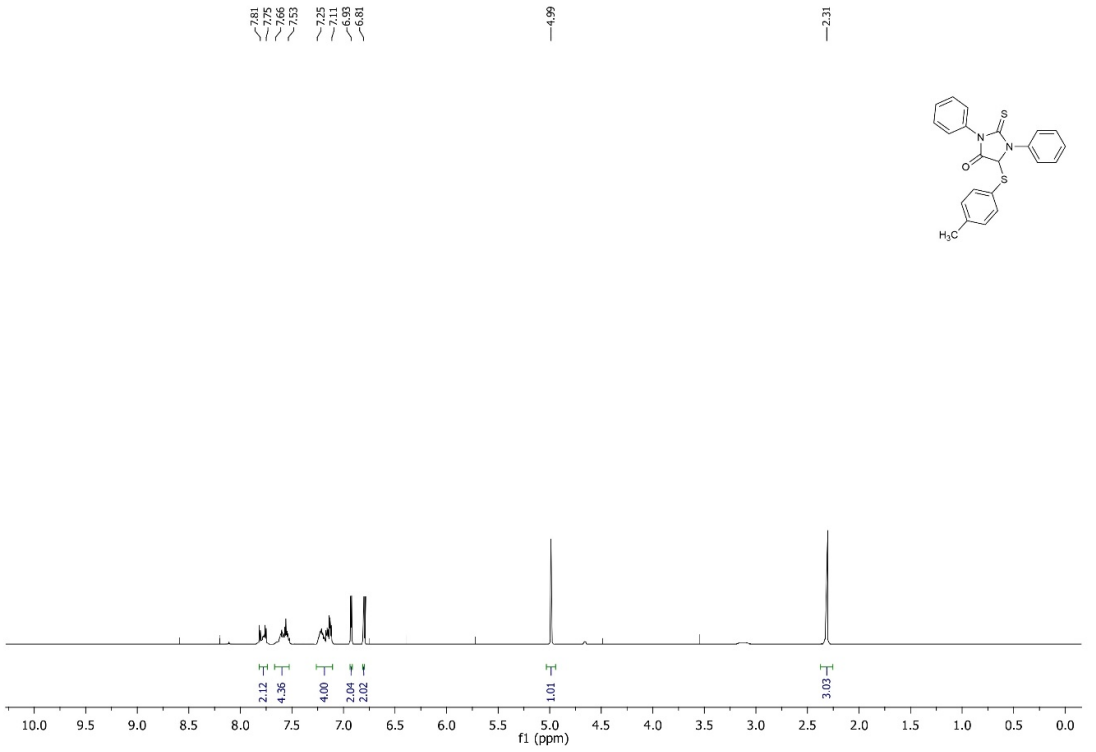
H NMR and ^{13}C NMR spectrum of……

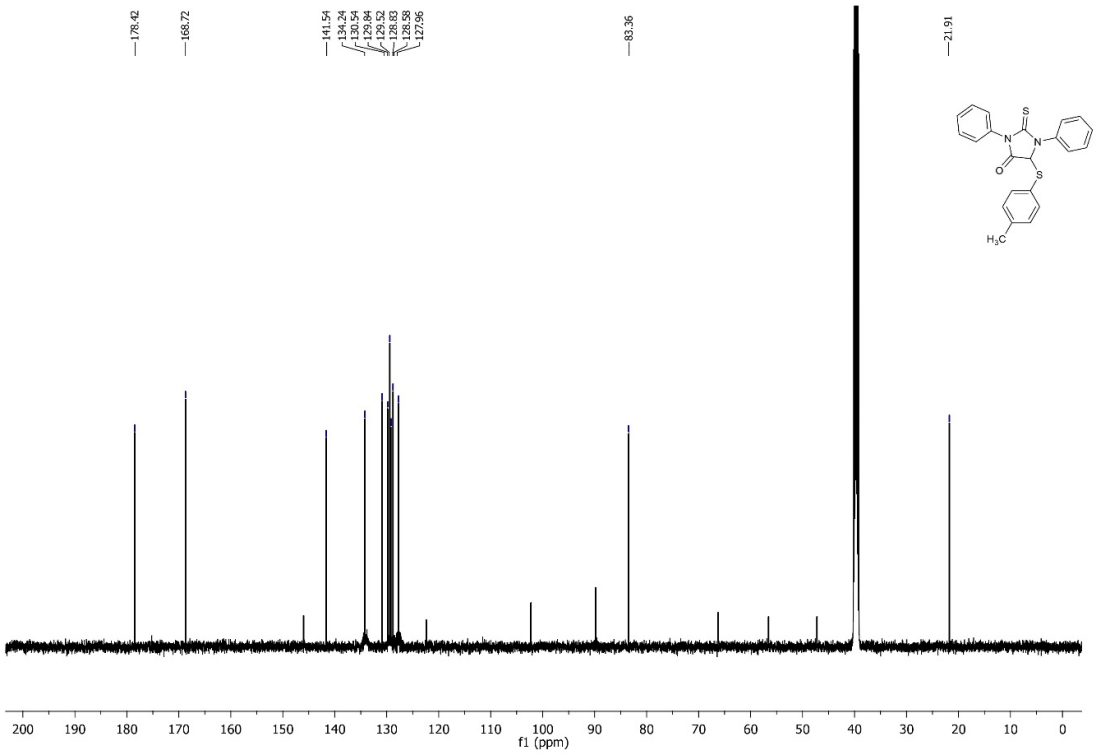
1) 1,3-Diphenyl-5-(phenylthio)-2-thioxoimidazolidin-4-one (3a)



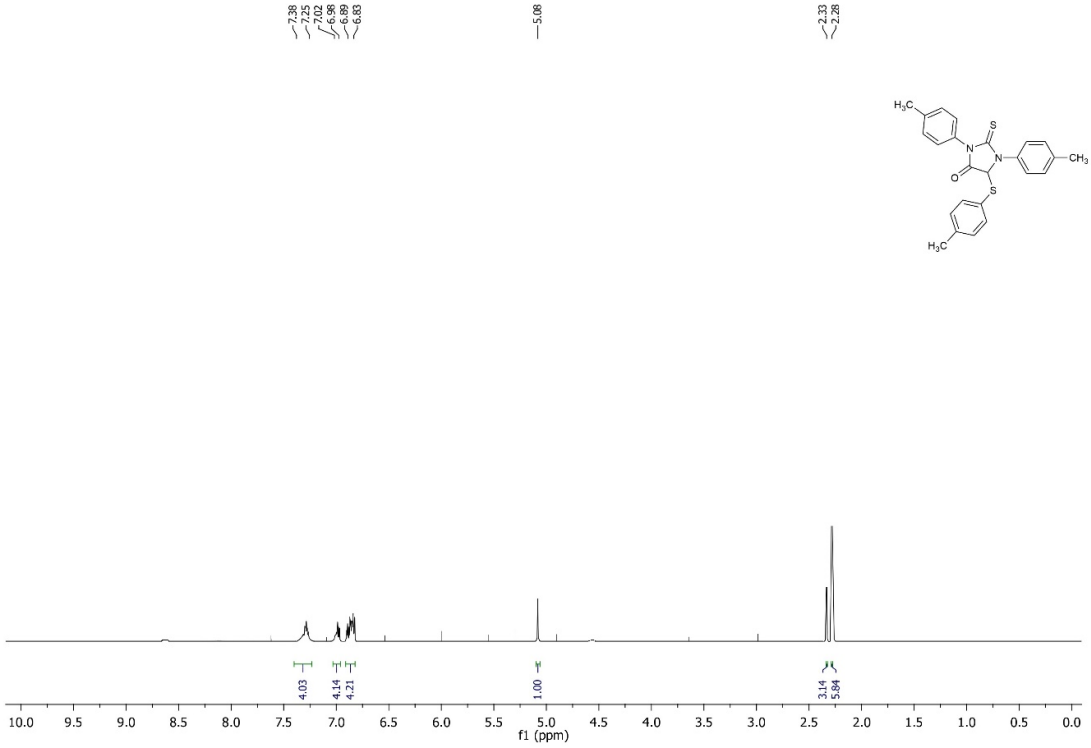


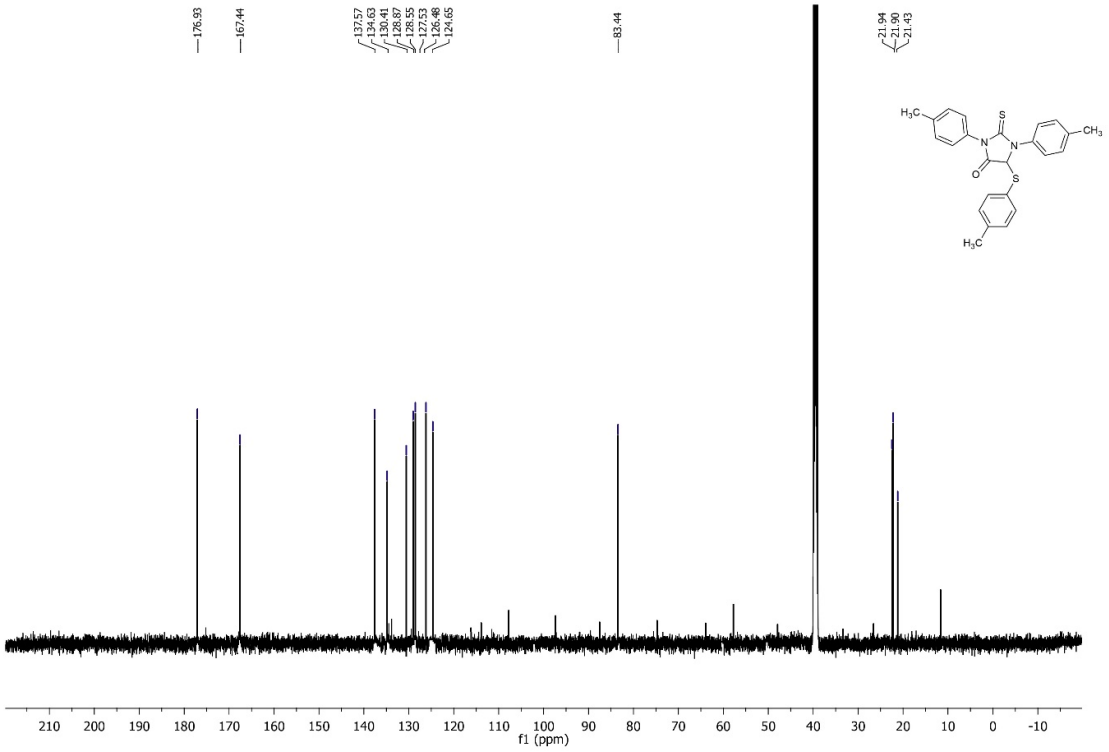
2) 1,3-Diphenyl-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3b)



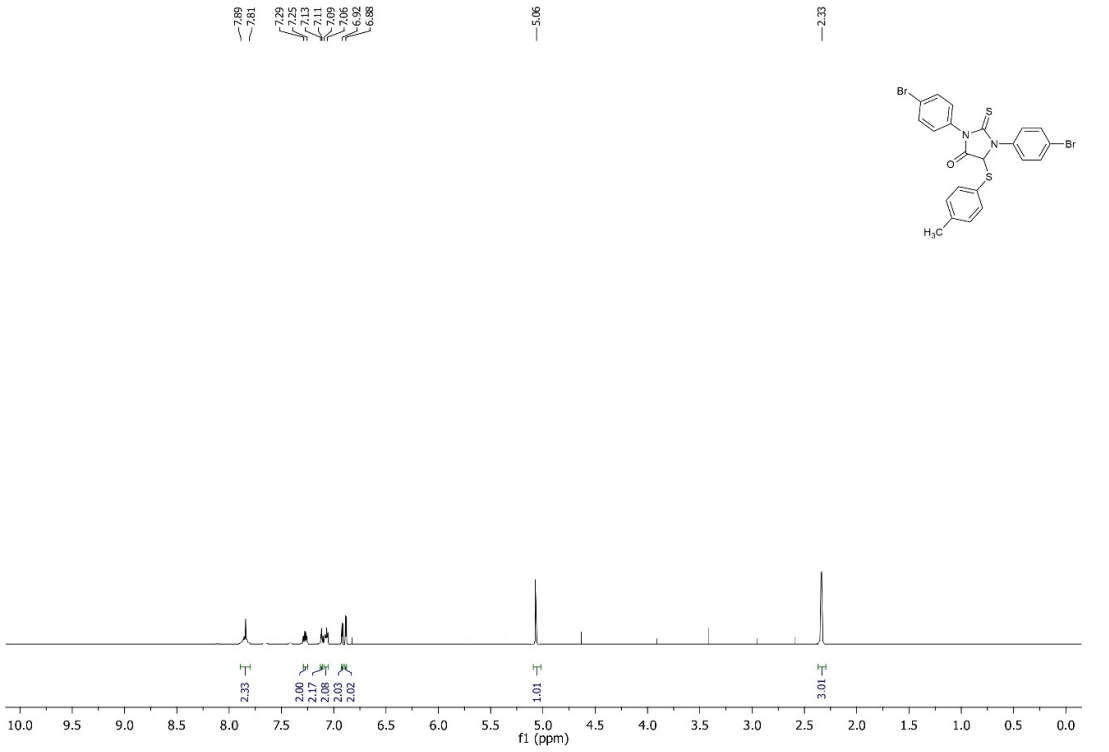


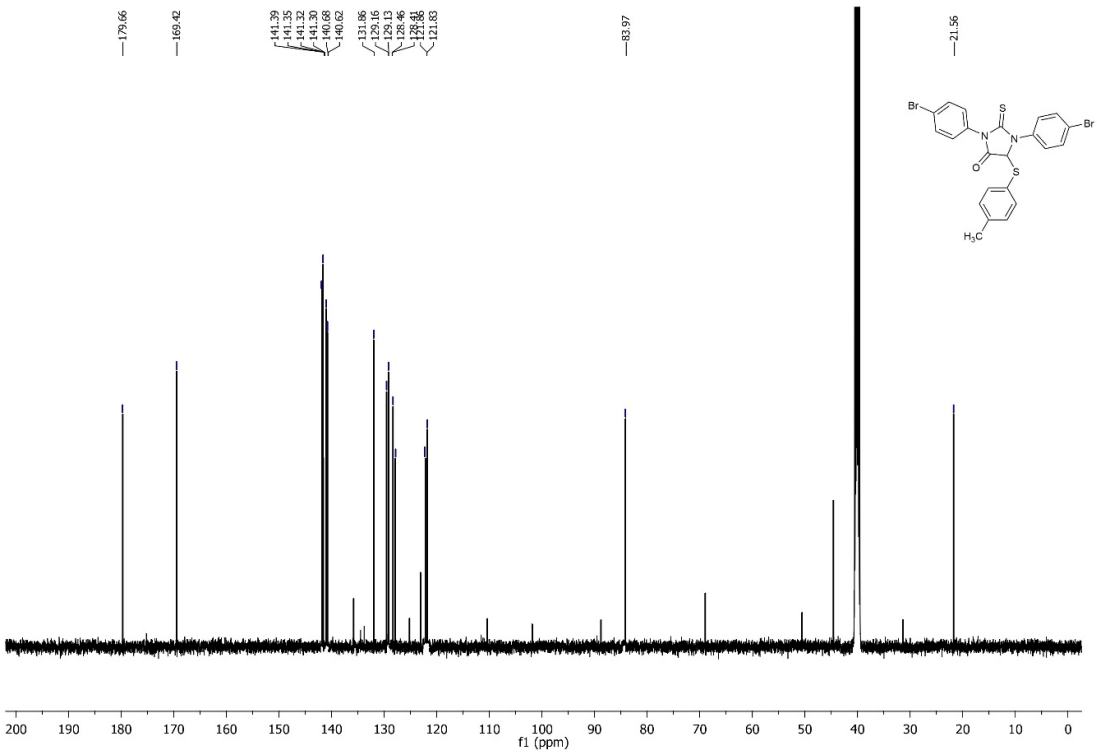
3) 2-Thioxo-1,3-di-p-tolyl-5-(p-tolylthio)imidazolidin-4-one (3c)



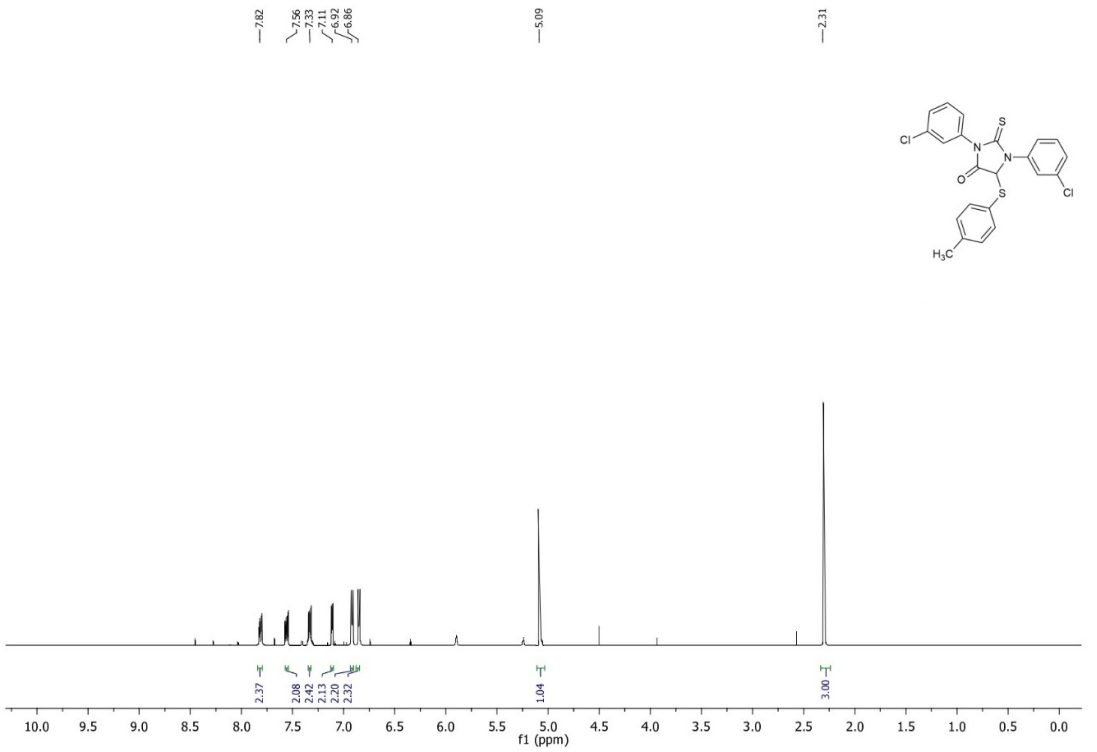


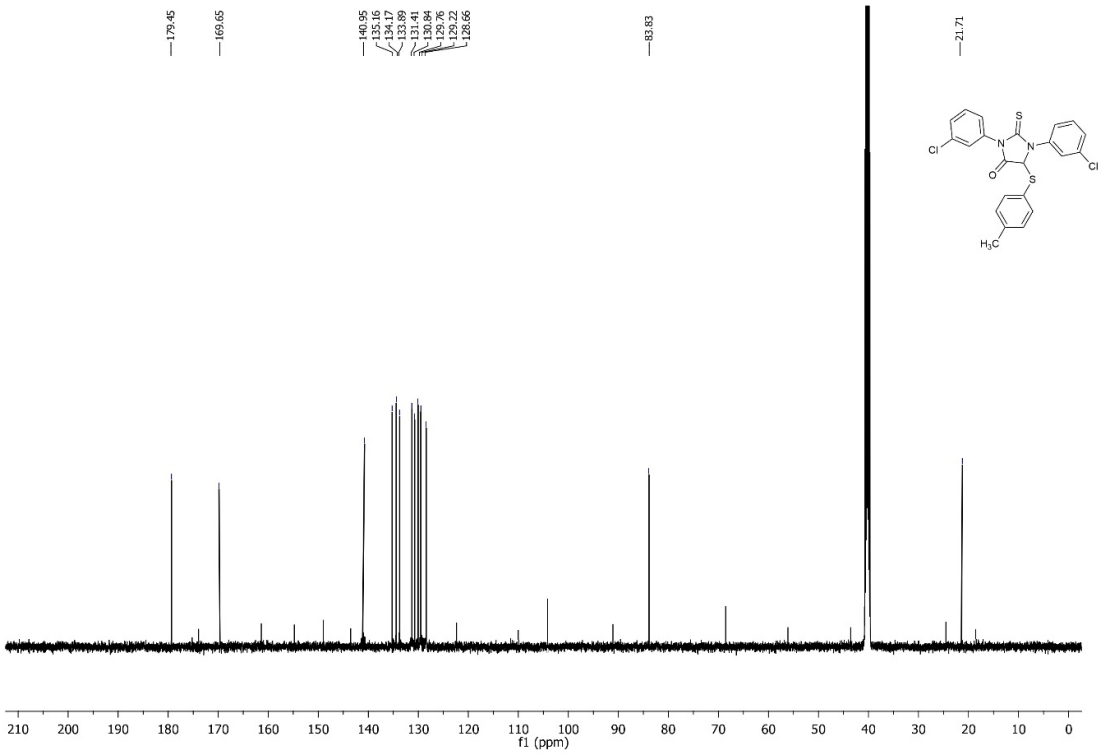
4) 1,3-Bis(4-bromophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3d)



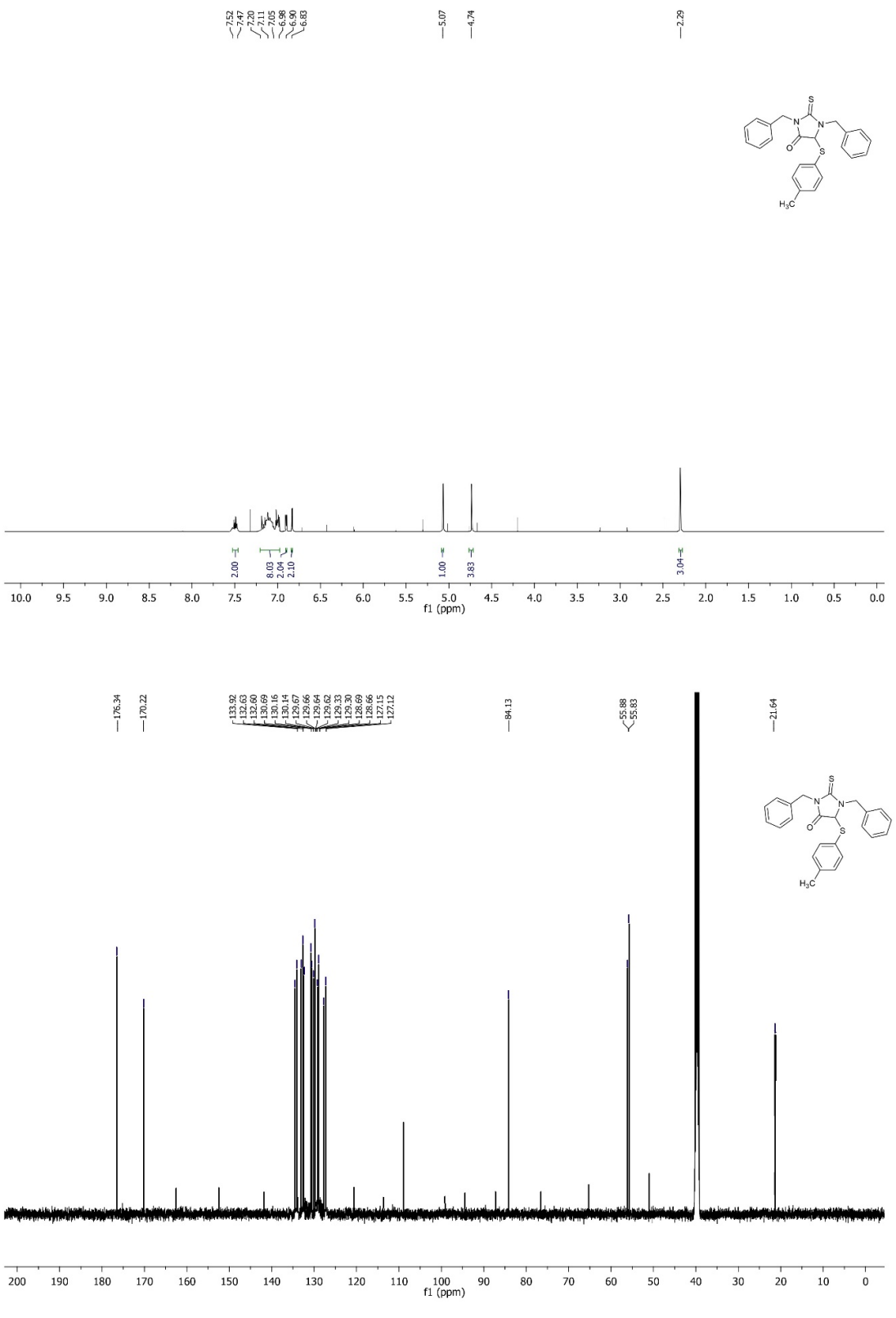


5) 1,3-Bis(3-chlorophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3e)

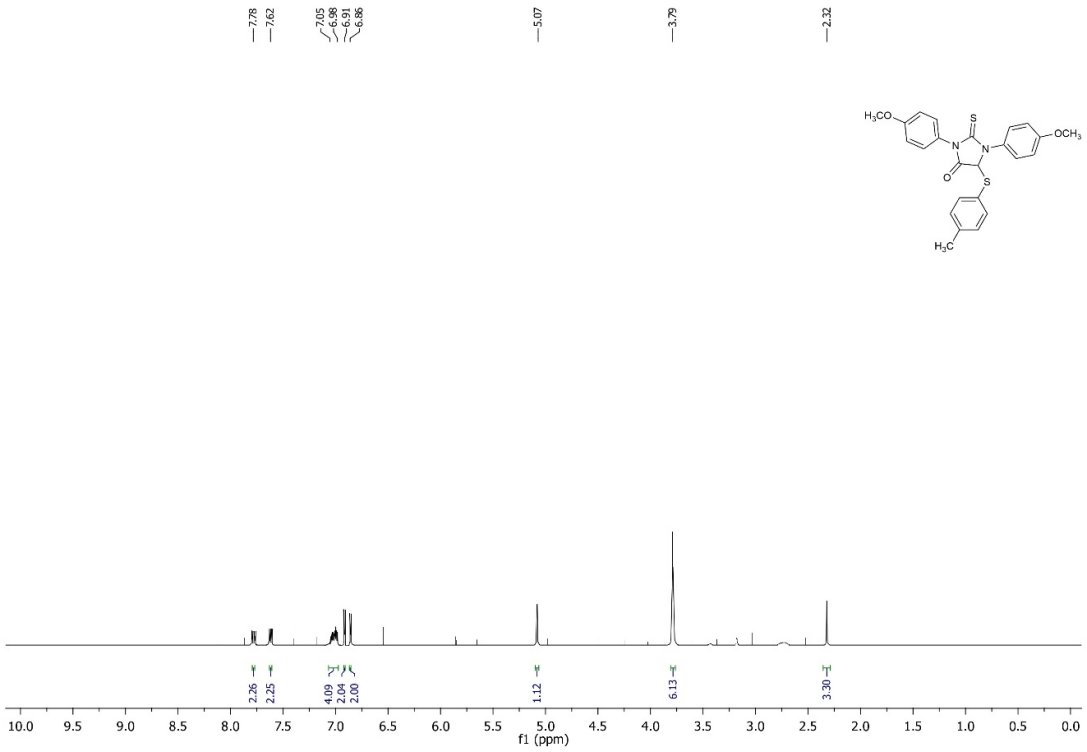


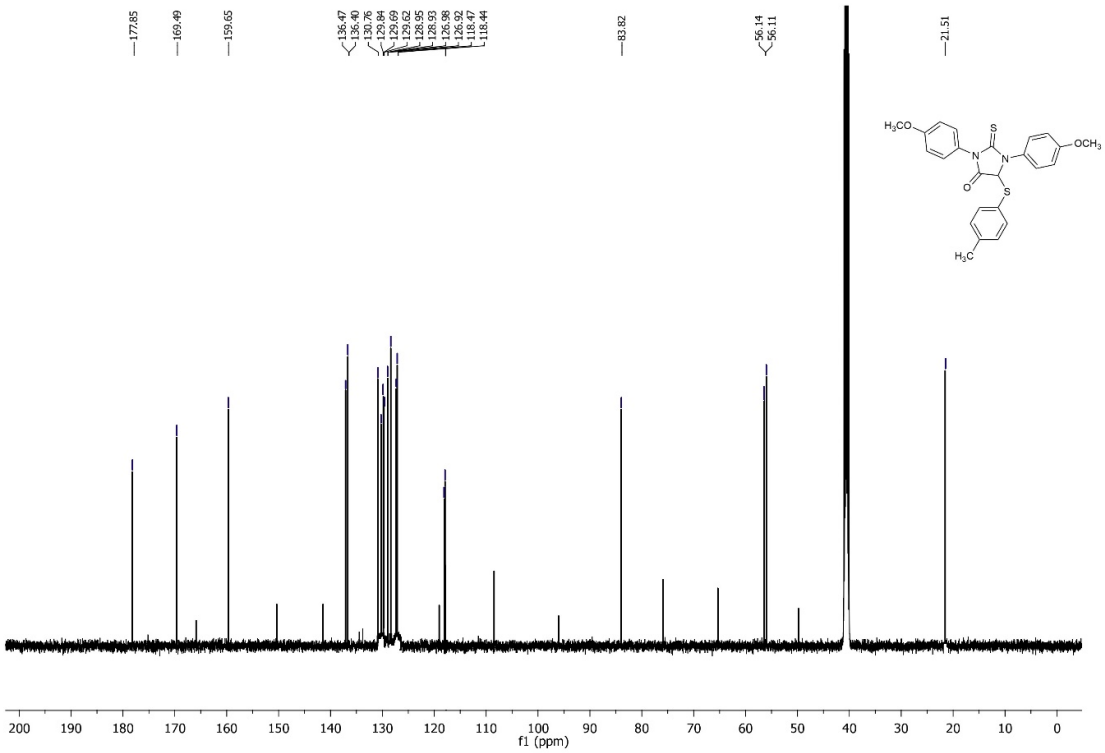


6) 1,3-Dibenzyl-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3f)

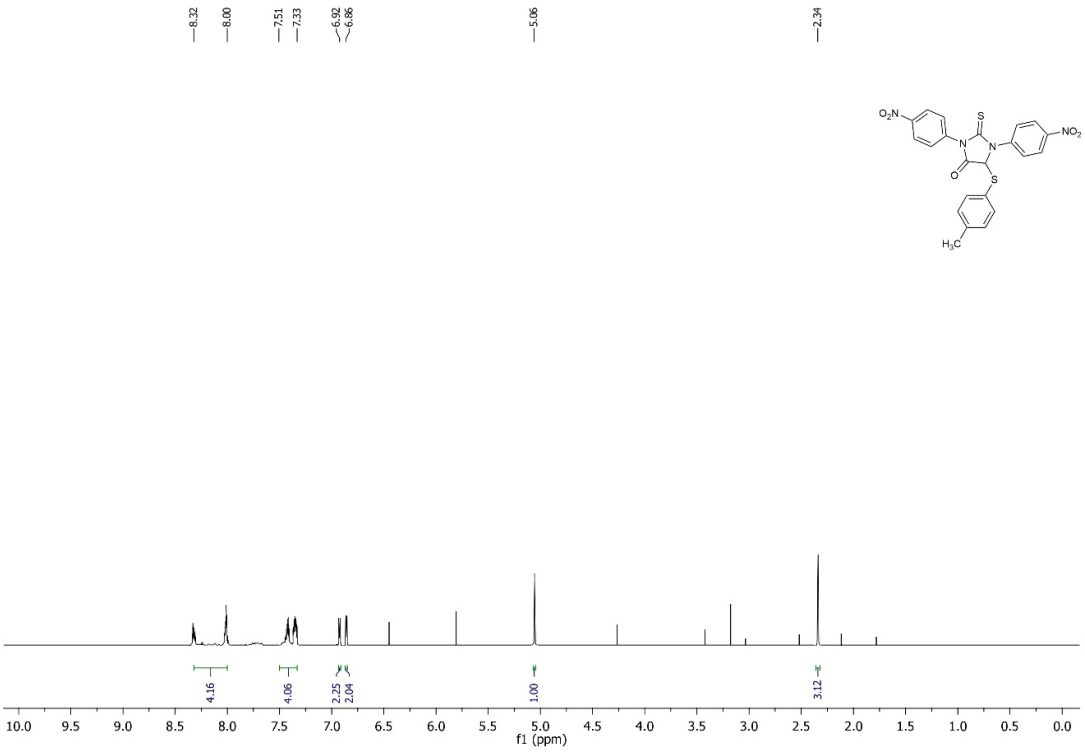


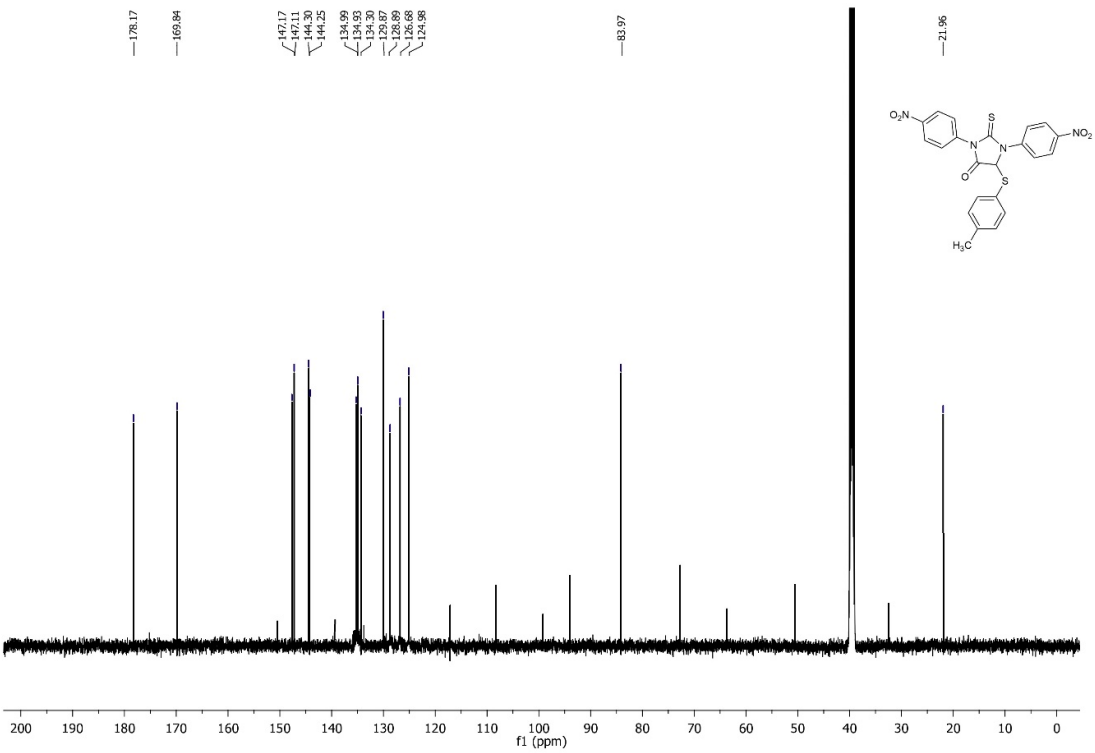
7) 1,3-Bis(4-methoxyphenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3g)



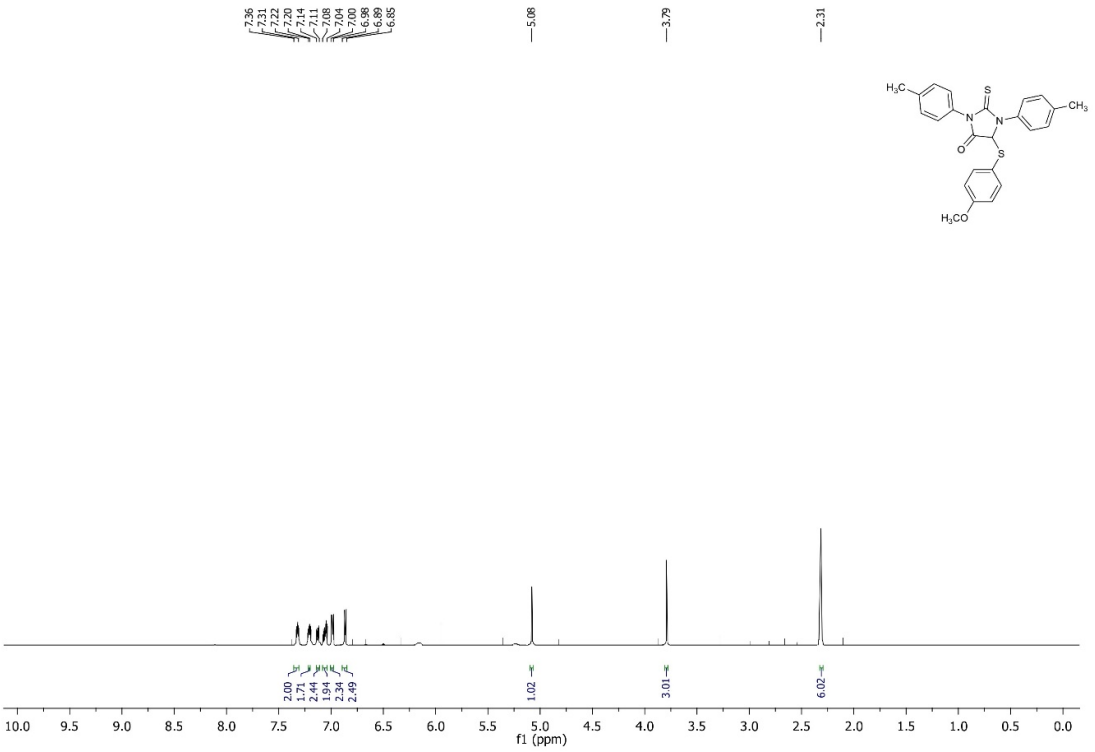


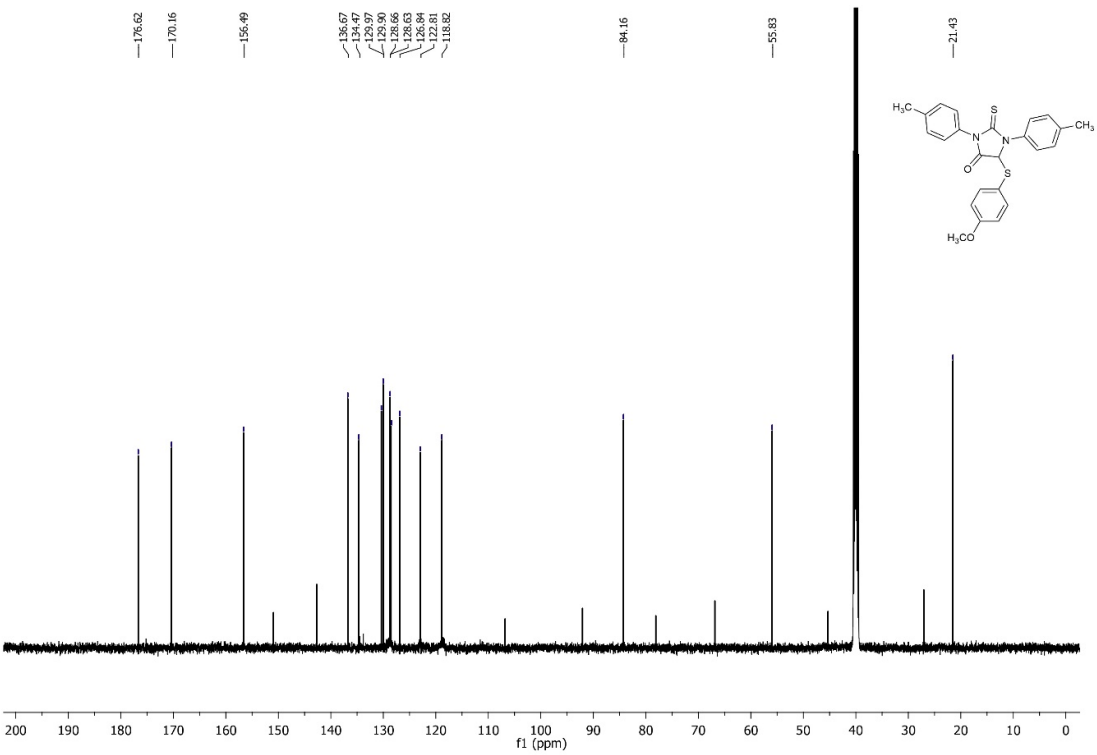
8) 1,3-Bis(4-nitrophenyl)-2-thioxo-5-(p-tolylthio)imidazolidin-4-one (3h)



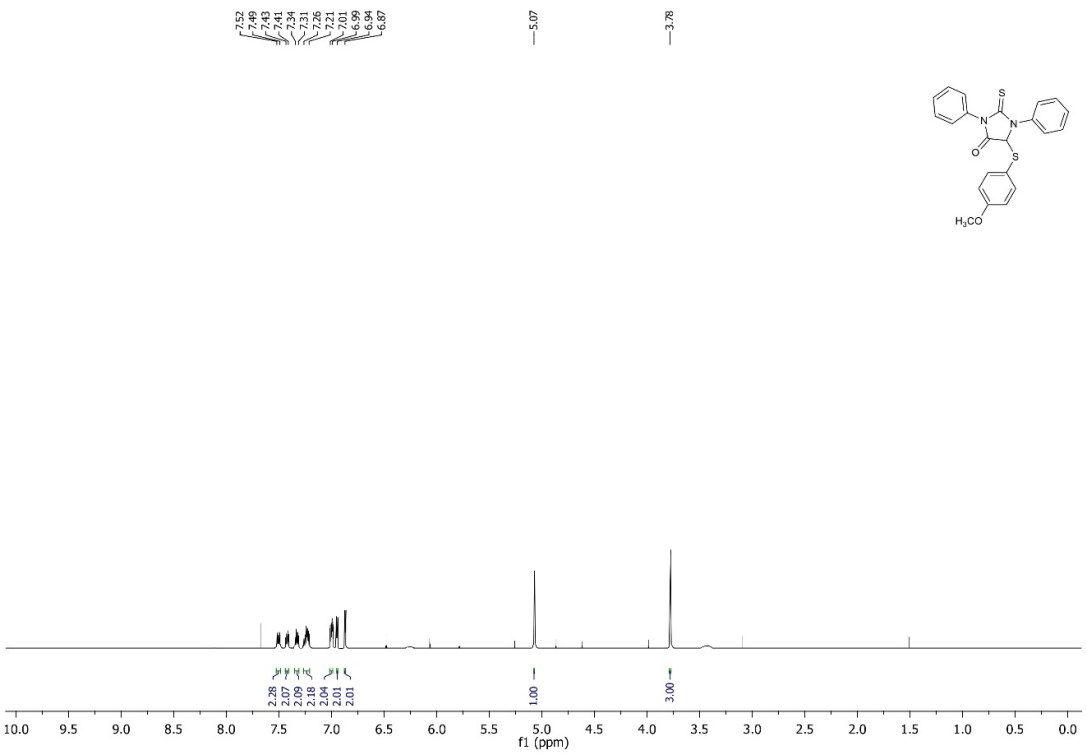


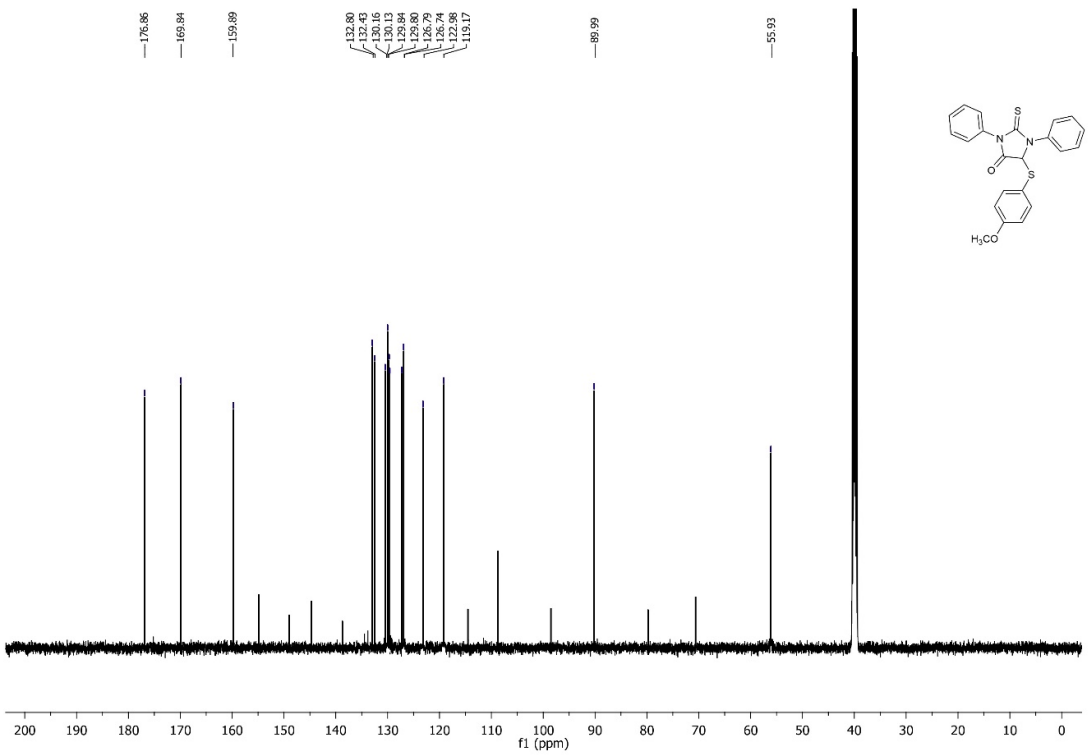
9) 5-((4-Methoxyphenyl)thio)-2-thioxo-1,3-di-p-tolylimidazolidin-4-one (3i)



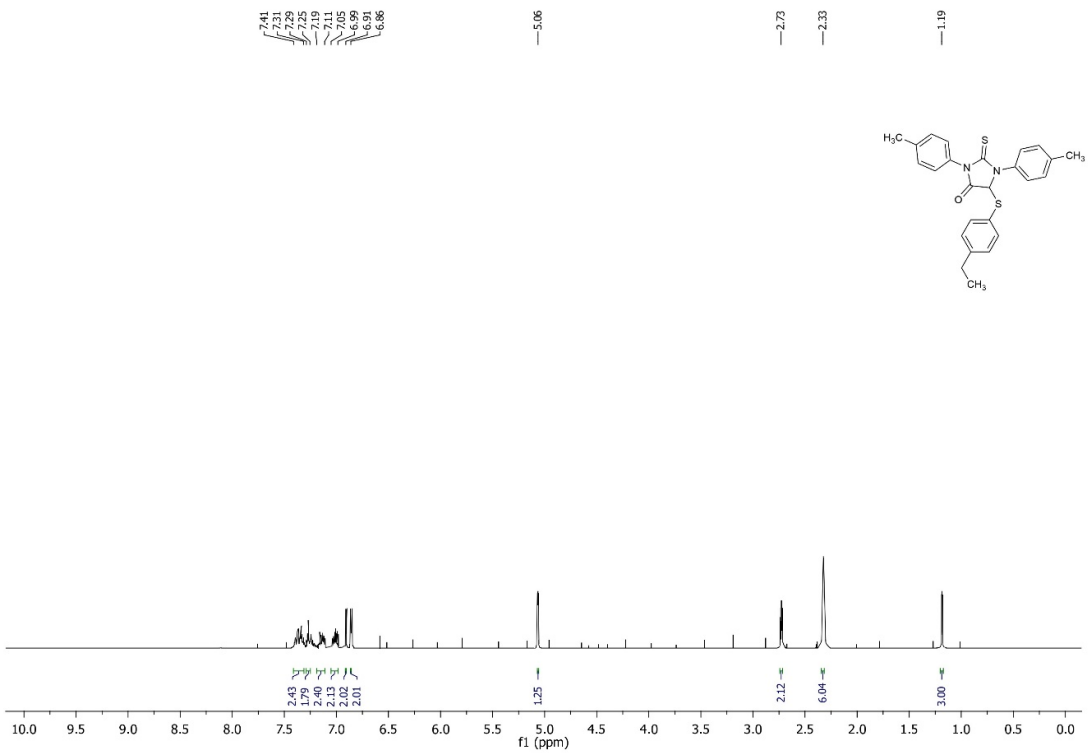


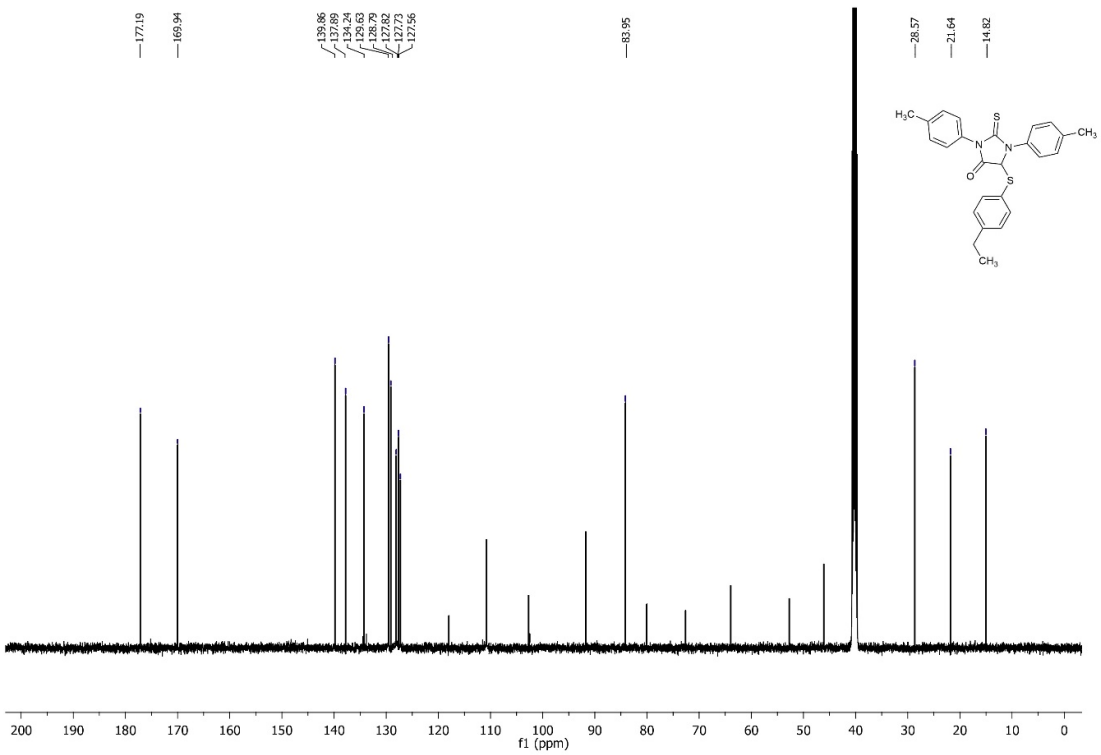
10) 5-((4-Methoxyphenyl)thio)-1,3-diphenyl-2-thioxoimidazolidin-4-one (3j)



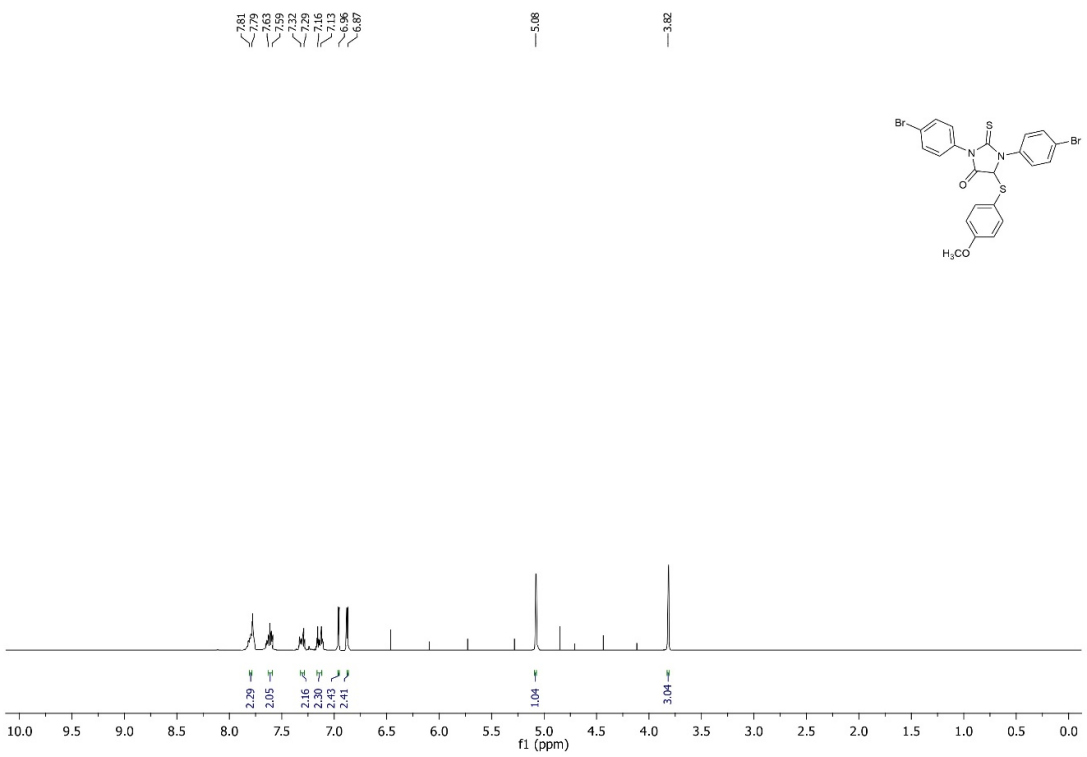


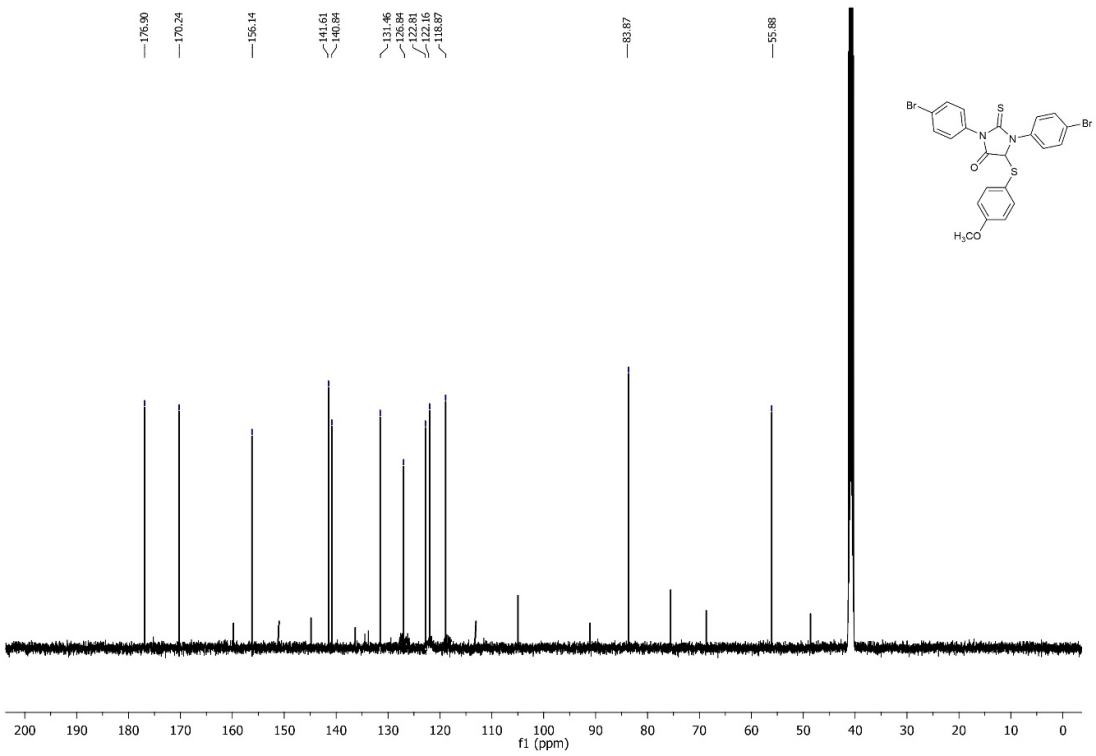
11) 5-((4-Ethylphenyl)thio)-2-thioxo-1,3-di-p-tolylimidazolidin-4-one (3k)



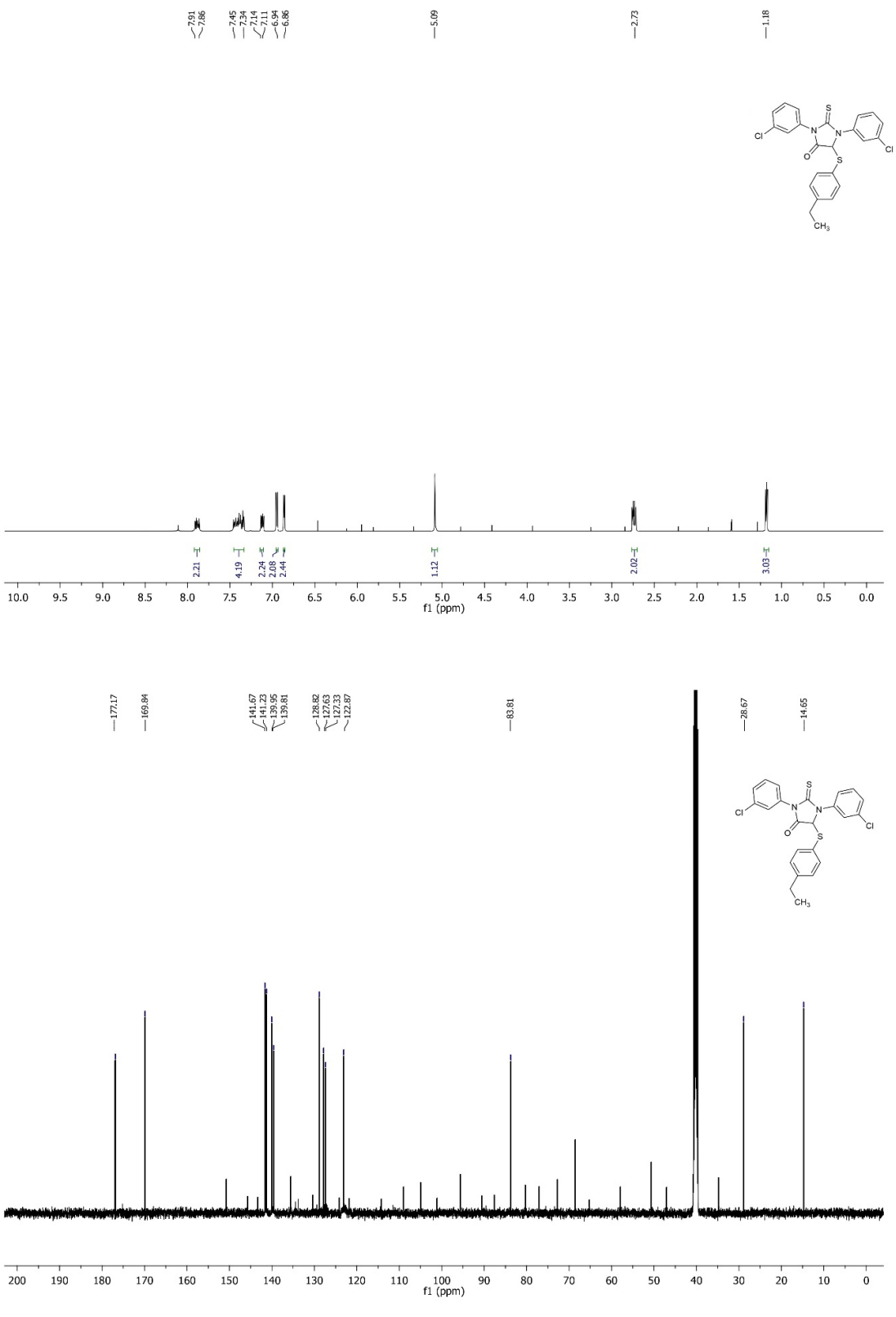


12) 1,3-Bis(4-bromophenyl)-5-((4-methoxyphenyl)thio)-2-thioxoimidazolidin-4-one (3l)

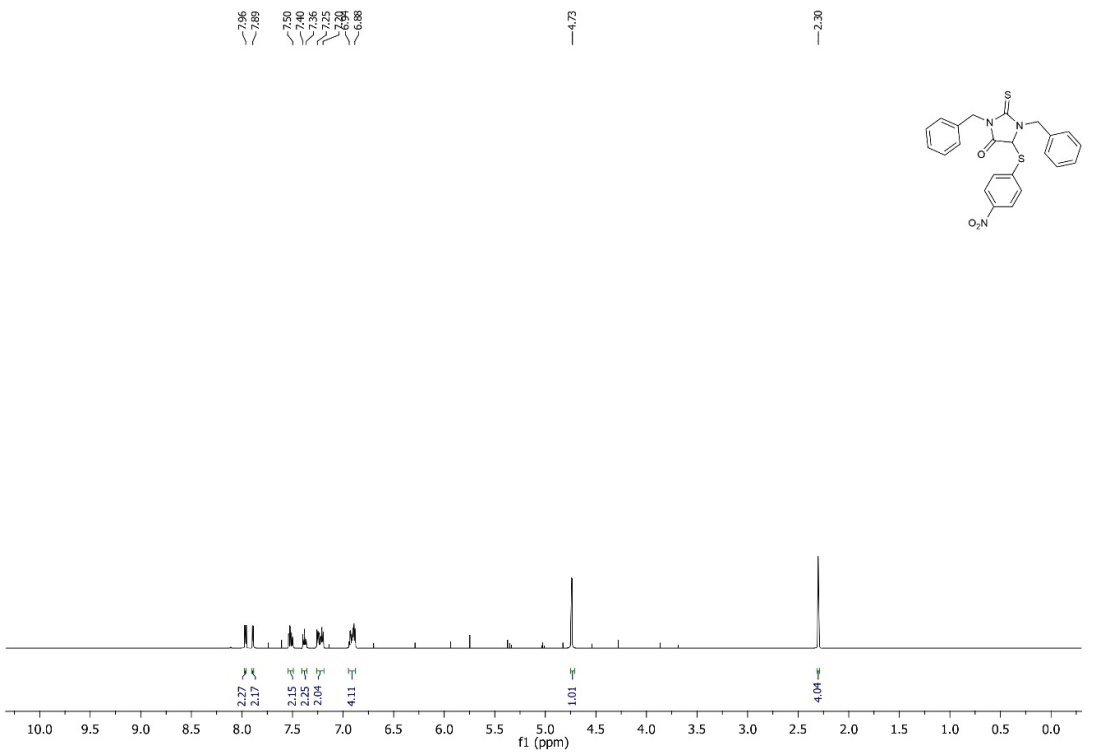


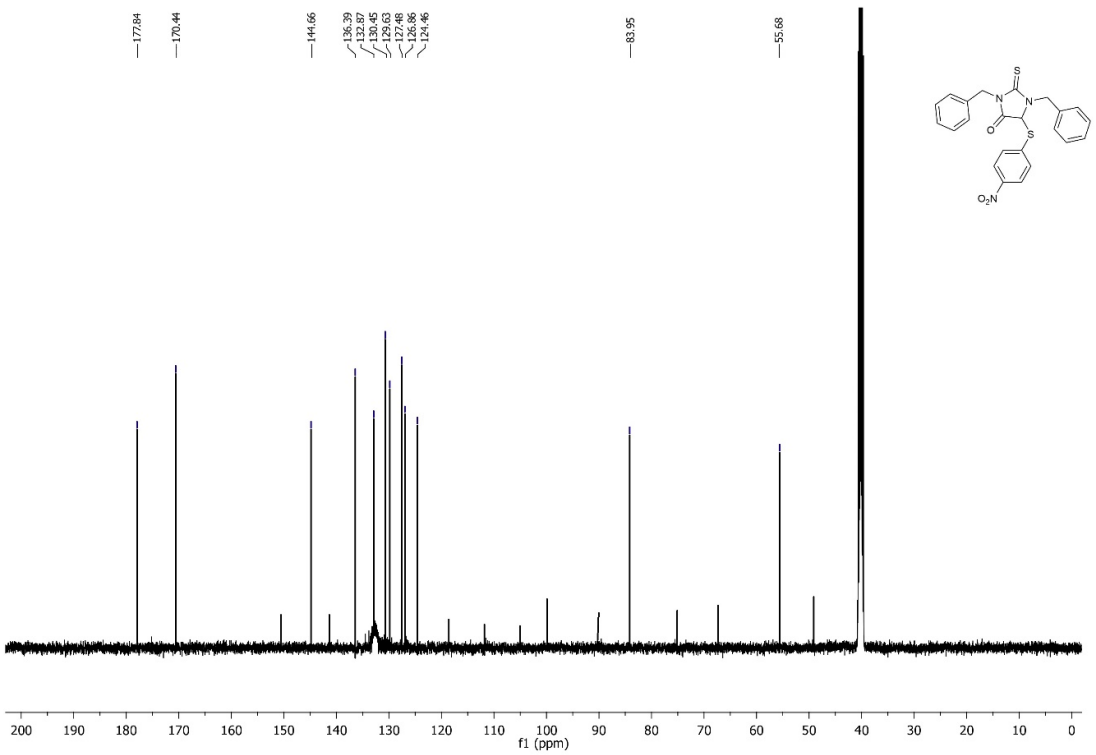


13) 1,3-Bis(3-chlorophenyl)-5-((4-ethylphenyl)thio)-2-thioxoimidazolidin-4-one (3m)

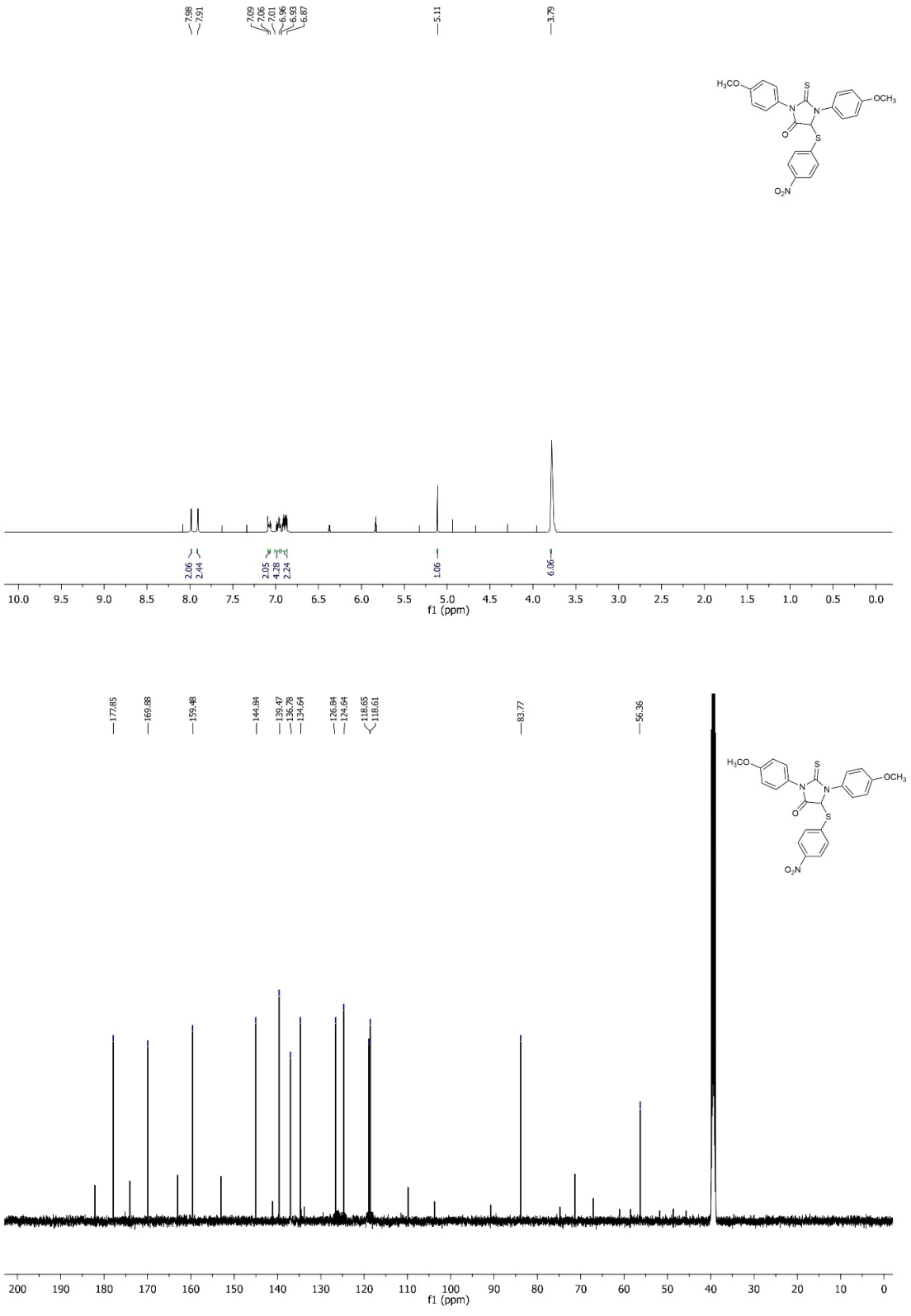


14) 1,3-Dibenzyl-5-((4-nitrophenyl)thio)-2-thioxoimidazolidin-4-one (3n)

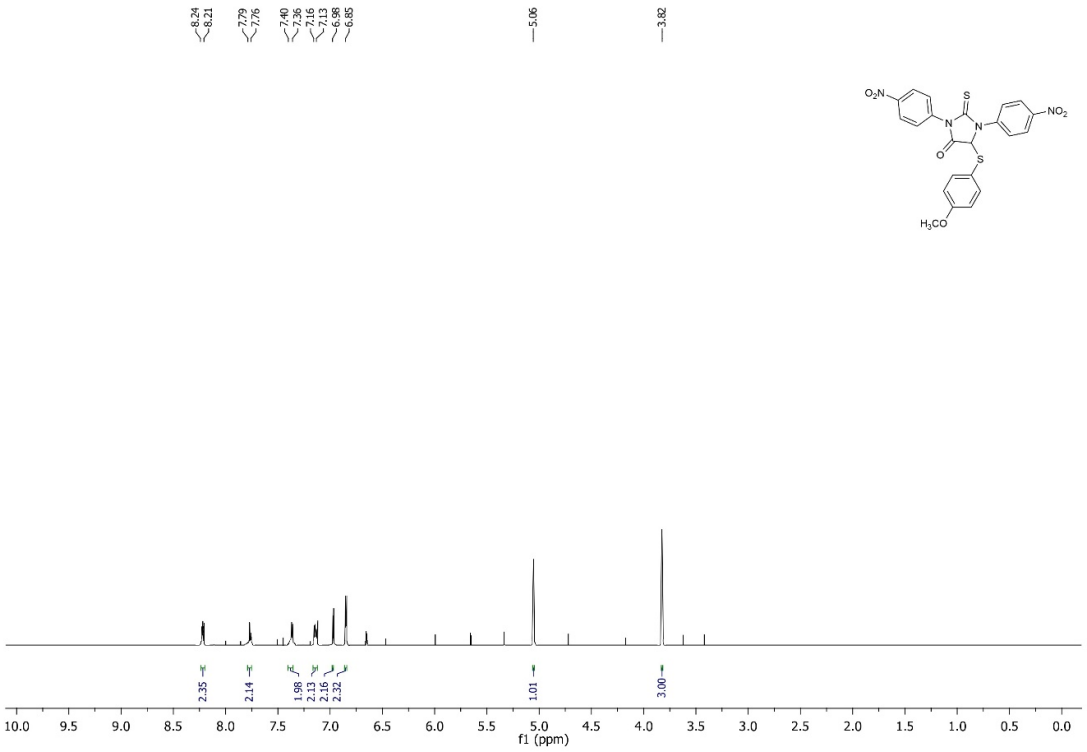




15) 1,3-Bis(4-methoxyphenyl)-5-((4-nitrophenyl)thio)-2-thioxoimidazolidin-4-one (3o)



16) 5-((4-Methoxyphenyl)thio)-1,3-bis(4-nitrophenyl)-2-thioxoimidazolidin-4-one (3p)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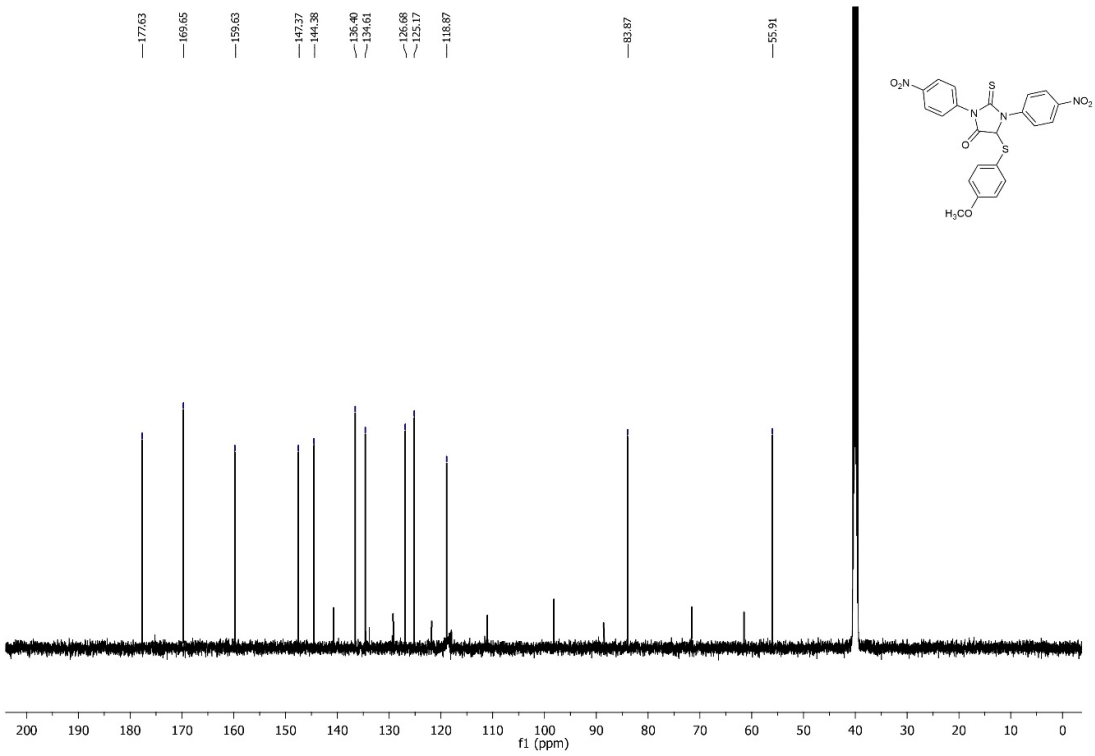
2.13
2.16
2.32
1.01
3.00
f1 (ppm)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f1 (ppm)