Supplementary Information for

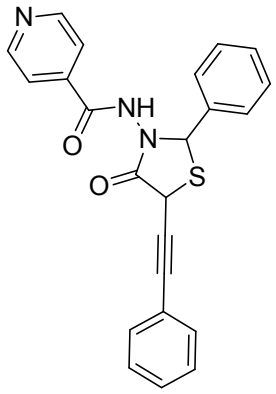
An efficient Alkynylation of 4-Thiazolidinone with terminal alkyne under C-H functionalisation

Mohammed Umar M. Shaikh, Sulochana S. Mudaliar and Kishor H. Chikhalia*
Department of Chemistry, School of Science,
Gujarat University, Ahmedabad 380009, Gujarat, India
Chikhalia_kh@yahoo.com, Tel. No : 079-

1. **Characterization of coupling yield…….....2**

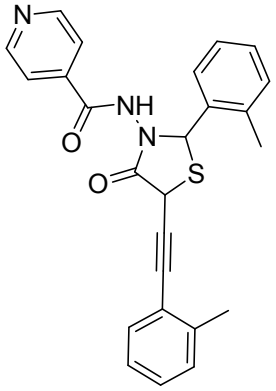
2. **^{1}H and ^{13}C NMR Spectra..…….....11**

1. Characterisation of the product:



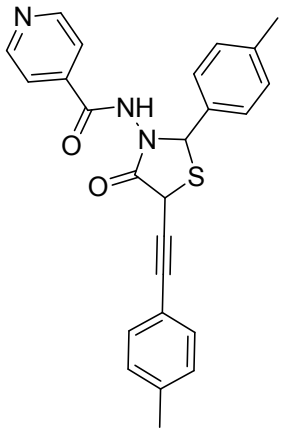
Compound 3a

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 4.52 (s, 1H), 6.20 (s, 1H), 7.17 (d, J = 0.8 Hz, 2H), 7.24 (dd, J=1.2 Hz, 1H), 7.26 (dd, 1.0 Hz, 1H), 7.28 (d, J = 1.2, 2H), 7.31 (d, J = 1.2 Hz, 2H), 7.42 (d, J = 1.0 Hz, 2H), 7.70 (d, J = 2.2 Hz, 2H), 8.33 (d, J = 2.4 Hz, 2H), 8.87 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 68.17, 70.12, 83.47, 97.42, 123.48, 123.80, 126.70, 127.74, 128.53, 128.59, 128.93, 131.08, 139.20, 139.96, 151.38, 160.65, 181.93. **Anal. Calcd.** For $C_{24}H_{19}N_3O_2S$: C: 75.57; H: 5.02; N: 11.02. ***Found:*** *C: 75.51; H: 5.06; N: 11.00.* ***M.P.*** *235-240 °C.*



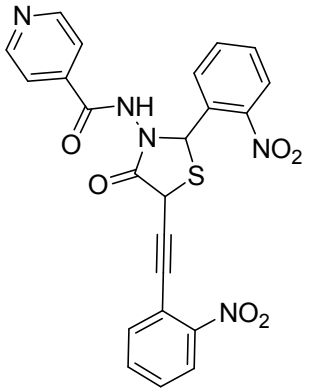
Compound 3b

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.32 (s, 3H), 2.39 (s, 3H), 4.52 (s, 1H), 6.49 (s, 1H), 7.09 (dd, J = 0.4 Hz, 1H), 7.12 (dd, J = 0.4 Hz, 1H), 7.13 (d, J= 1 Hz, 1H), 7.15 (d, J= 1.0 Hz, 1H), 7.17 (d, J= 1.0 Hz, 1H), 7.19 (dd, J= 0.6 Hz, 1H), 7.22 (dd, J= 0.8 Hz, 1H), 7.37 (d, J= 0.8 Hz, 1H), 7.62 (d, J= 2.8 Hz, 2H), 8.41 (d, J= 2.8 Hz, 2H), 8.87 (s, 1H, s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 20.91, 19.96, 67.48, 70.12, 91.24, 97.42, 123.52, 124.66, 126.79, 128.17, 128.43, 129.27, 131.83, 132.97, 139.28, 139.44, 140.04, 151.86, 160.87, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_3O_2S$: C: 70.24; H: 4.95; N: 9.83. ***Found:*** *C: 70.21; H: 4.96; N: 9.81.* ***M.P.*** *257-262 °C.*



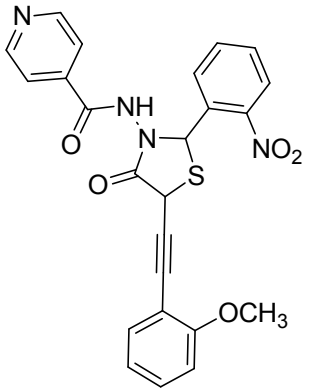
Compound 3c

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.34 (s, 3H), 2.35 (s, 3H), 4.52 (s, 1H), 6.67 (s, 1H), 7.09 (d, J= 3.0 Hz, 2H), 7.19 (d, J= 2.8 Hz, 2H), 7.21 (d, J= 3.2 Hz, 2H), 7.45 (d, J= 3.2 Hz, 2H), 7.61 (d, J= 3.2 Hz, 2H), 8.13 (d, J= 3.0 Hz, 2H), 8.86 (s, 1H, s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 21.31, 71.49, 69.74, 89.11, 97.42, 123.52, 125.91, 126.80, 128.14, 128.89, 129.58, 130.02, 136.90, 138.44, 139.28, 142.49, 151.86, 160.87, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_3O_2S$: C: 70.24; H: 4.95; N: 9.83. ***Found:*** *C: 70.26; H: 4.94; N: 9.85.* ***M.P.*** *257-262 °C.*



Compound 3d

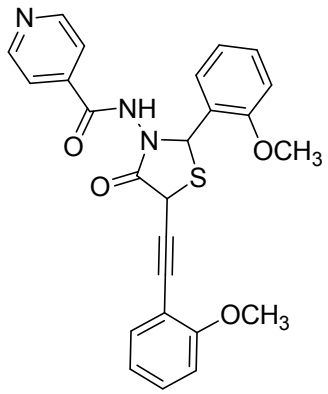
^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 4.52 (s, 1H), 6.70 (s, 1H), 6.90 (dd, J= 0.6 Hz, 1H), 7.41 (d, J= 0.8 Hz, 1H), 7.47 (dd, J= 0.6 Hz, 1H), 7.55 (d, J= 0.6 Hz, 1H), 7.58 (dd, J= 0.8 Hz, 1H), 7.61 (dd, J= 0.8 Hz, 1H), 7.70 (d, J= 1.0 Hz, 1H), 7.72 (d, J= 1.0 Hz, 1H), 7.96 (d, J= 3.2 Hz, 2H), 8.17 (d, J= 3.0Hz, 2H), 8.90 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 66.71, 70.69, 86.17, 97.42, 122.06, 122.80, 123.48, 124.29, 126.76, 128.13, 129.72, 132.59, 133.47, 134.42, 137.61, 139.20, 149.50, 149.84, 151.38, 160.65, 181.93. **Anal. Calcd.** For $C_{25}H_{15}N_5O_6S$: C: 56.44; H: 3.09; N: 14.31. ***Found:*** *C: 56.45; H: 3.10; N: 14.29.* ***M.P.*** *250-255°C.*



Compound 3e

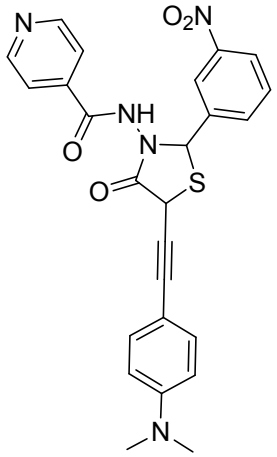
^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 3.80 (s, 3H), 4.52 (s, 1H), 6.41 (s, 1H), 6.95 (dd, J= 0.6 Hz, 1H), 7.00 (d, J= 1.0 Hz, 1H), 7.12 (d, J= 0.6 Hz, 1H), 7.26 (dd, J= 0.8 Hz, 1H), 7.36

(d, J= 2.8 Hz, 1H), 7.44 (dd, J= 0.6 Hz, 1H), 7.46 (dd, J= 0.8 Hz, 1H), 7.60 (d, J= 3.0 Hz, 1H), 7.79 (d, J= 3.0 Hz, 2H), 8.19 (d, J= 3.2 Hz, 2H), 8.89 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 56.79, 67.79, 74.85, 87.87, 97.42, 112.48, 117.05, 120.04, 123.52, 124.32, 126.80, 128.14, 130.79, 131.38, 133.48, 138.40. 139.28, 148.78, 151.86, 158.31, 160.87, 181.05. **Anal. Calcd.** For $C_{24}H_{18}N_4O_5S$: C: 60.75; H: 3.80; N: 11.82. ***Found:*** *C: 60.73; H: 3.78; N: 11.80.* ***M.P.*** *260-265 °C.*



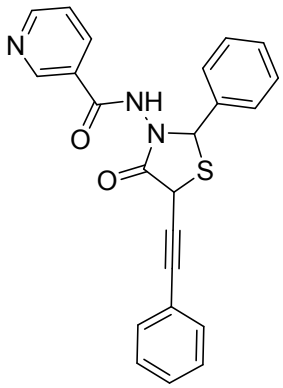
Compound 3f

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 3.72 (s, 3H), 3.74 (s, 3H), 4.52 (s, 1H), 6.47 (s, 1H), 6.82 (dd, J= 0.8 Hz, 1H), 6.88 (d, J= 0.6 Hz, 1H), 6.89 (dd, J= 0.4 Hz, 1H), 6.97 (d, J= 0.8 Hz, 1H), 7.20 (dd, J= 0.6 Hz, 1H), 7.27 (dd, J= 0.8 Hz, 1H), 7.28 (d, J= 0.4 Hz, 1H), 7.47 (d, J= 1.0 Hz, 1H), 7.75 (d, 2.6 Hz, 2H), 8.77 (d, J= 2.8 Hz, 2H), 8.89 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 56.79, 63.99, 74.85, 87.87, 97.42, 112.48, 113.79, 117.05, 120.04, 121.51, 123.52, 126.16, 129.40, 129.75, 130.79, 131.38, 139.28, 151.86, 154.13, 158.31, 160.87, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_3O_4S$: C: 65.34; H: 4.61; N: 9.14. ***Found:*** *C: 65.35; H: 4.58; N: 9.18.* ***M.P.*** *260-265 °C.*



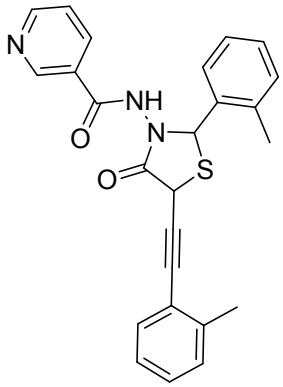
Compound 3g

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.90 (s, 6H), 4.52 (s, 1H), 6.40 (s, 1H), 6.73 (d, J= 3.0 Hz, 2H), 6.93 (d, J= 3.2 Hz, 2H), 7.36 (m, 1H), 7.42 (d, J= 0.8 Hz, 1H), 7.58 (d, J= 0.6 Hz, 1H), 7.61 (dd, J= 0.8 Hz, 1H), 7.75 (d, J= 3.2 Hz, 2H), 8.31 (d, J= 2.8 Hz, 2H), 8.92 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 41.91, 69.44, 71.49, 89.11, 96.42, 111.05, 113.04, 119.79, 119.88, 123.52, 131.01, 132.10, 139.28, 142.44, 149.44, 151.86, 160.87, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_5O_4S$: C: 61.59; H: 4.34; N: 14.36. ***Found:*** *C: 61.63; H: 4.37; N: 14.37.* ***M.P.*** *276-280 °C.*



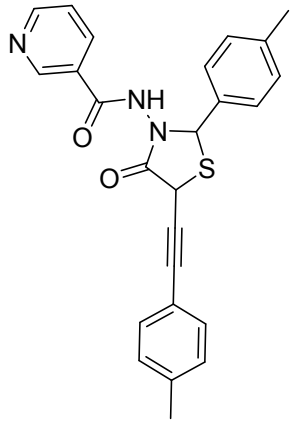
Compound 3h

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 4.52 (s, 1H), 6.18 (s, 1H), 6.93 (dd, J= 0.8 Hz, 1H), 7.00 (d, J= 0.8 Hz, 2H), 7.24 (d, J= 1.0 Hz, 2H), 7.31 (d, J= 0.6 Hz, 2H), 7.32 (d, J= 1.0 Hz, 2H), 7.51 (dd, J= 0.6 Hz, 1H), 7.55 (dd, J= 0.8 Hz, 1H), 7.61 (dd, 0.6 Hz, 1H), 8.17 (dd, J= 0.6 Hz, 1H), 8.74 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 69.74, 71.49, 89.11, 97.42, 122.77, 123.02, 126.74, 127.76, 128.55, 128.60, 128.94, 131.12, 131.85, 137.84, 139.88, 149.72, 150.89, 160.04, 181.05. **Anal. Calcd.** For $C_{25}H_{17}N_3O_2S$: C: 69.15; H: 4.29; N: 10.52. ***Found:*** *C: 69.13; H: 4.27; N: 10.53.* ***M.P.*** *240-245 °C.*



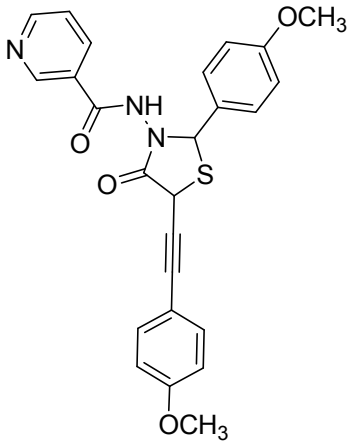
Compound 3i

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.25 (s, 3H), 2.40 (s, 3H), 4.52 (s, 1H), 6.39 (s, 1H), 7.09 (dd, J= 0.4 Hz, 1H), 7.11 (d, J= 0.8 Hz, 1H), 7.12 (d, J= 0.6 Hz, 1H), 7.15 (d, J= 0.8 Hz, 1H), 7.17 (dd, J= 0.8 Hz, 1H), 7.19 (d, J= 1.0 Hz, 1H), 7.21 (d, J= 0.6 Hz, 1H), 7.29 (d, J= 1.0 Hz, 1H), 7.36 (dd, J= 2.4 Hz, 1H), 7.47 (d, J= 2.4 Hz, 1H), 8.07 (m, 1H), 8.71 (s, 1H), 8.89 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 19.46, 20.91, 67.88, 70.12, 91.24, 97.42, 122.77, 123.52, 124.66, 126.79, 128.17, 128.43, 129.27, 131.85, 132.97, 137.84, 139.44, 140.04, 149.72, 150.89, 164.04, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_3O_2S$: C: 70.24; H: 4.95; N: 9.83. ***Found:*** *C: 70.22; H: 4.99; N: 9.84.* ***M.P.*** *255-260 °C.*



Compound 3j

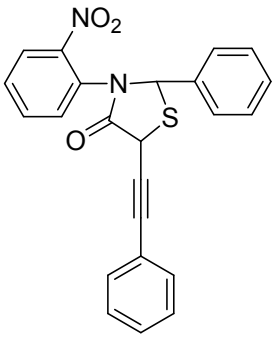
^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.20 (s, 3H), 2.34 (s, 3H), 4.52 (s, 1H), 6.30 (s, 1H), 7.10 (d, J= 2.8 Hz, 2H), 7.12 (d, J= 2.8 Hz, 2H), 7.19 (d, J= 3.0 Hz, 2H), 7.33 (d, J= 2.8 Hz, 2H), 7.39 (dd, 0.8 Hz, 1H), 7.48 (d, J= 3.0 Hz, 1H), 8.08 (d, J= 3.0, 1H), 8.71 (s, 1H), 8.88 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 21.31, 69.74, 71.49, 89.11, 97.42, 117.43, 122.77, 125.91, 128.89, 129.58, 130.02, 131.85, 136.90, 137.85, 138.44, 142.49, 149.72, 150.89, 160.04, 181.05. **Anal. Calcd.** For $C_{25}H_{21}N_3O_2S$: C: 70.24; H: 4.95; N: 9.83. ***Found:*** *C: 70.28; H: 4.97; N: 9.86.* ***M.P.*** *255-260 °C.*



Compound 3k

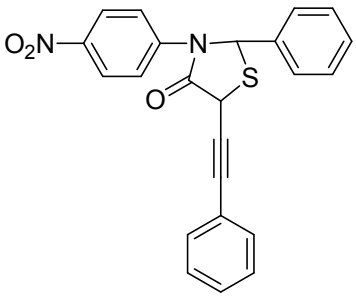
^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 3.77 (s, 3H), 3.83 (s, 3H), 4.52 (s, 1H), 6.37 (s, 1H), 6.89 (d, J= 3.2 Hz, 2H), 6.91 (d, J= 3.2 Hz, 2H), 7.27 (d, J= 2.8 Hz, 2H), 7.48 (d, J= 3.0 Hz,

2H), 7.43 (dd, J= 2.8 Hz, 1H), 8.11 (d, J= 0.4 Hz, 1H), 8.17 (d, J= 3.0 Hz, 1H), 8.34 (s, 1H), 8.68 (s, 1H, D_2O exchangeable). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 56.04, 69.74, 71.49, 89.11, 97.42, 114.07, 114.68, 114.87, 122.77, 126.88, 131.49, 131.85, 134.84, 137.84, 149.72, 150.89, 159.89, 162.00, 164.04, 181.04. **Anal. Calcd.** For $C_{25}H_{21}N_3O_2S$: C: 65.34; H: 4.61; N: 9.14. ***Found:*** *C: 65.31; H: 4.60; N: 9.11.* ***M.P.*** *265-270 °C.*



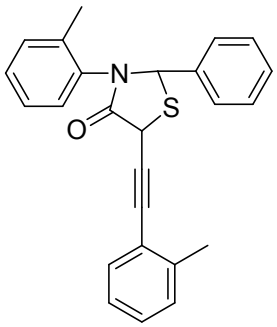
Compound 3l

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 4.68 (s, 1H), 6.60 (s, 1H), 7.21 (d, J= 2.6 Hz, 2H), 7.24 (dd, J= 2.8 Hz, 1H), 7.26 (dd, J= 2.4 Hz, 1H), 7.28 (d, J= 1.8 Hz, 2H), 7.30 (d, J= 2.4 Hz, 2H), 7.33 (dd, J= 2.6 Hz, 1H), 7.46 (d, J= 2.4 Hz, 2H), 7.48 (dd, J= 2.2 Hz, 1H), 7.64 (dd, J= 2.2 Hz, 1H), 8.14 (dd, J= 2.4 Hz, 1H). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 67.08, 68.17, 83.47, 96.12, 123.80, 125.93, 126.55, 127.20, 127.95, 128.53, 128.59, 128.96, 129.20, 131.08, 132.28, 135.36, 139.63, 142.19, 175.37. **Anal. Calcd.** For $C_{23}H_{16}N_2O_3S$: C: 68.98; H: 4.03; N: 7.00. ***Found:*** *C: 68.95; H: 3.99; N: 7.02.* ***M.P.*** *180 °C.*



Compound 3m

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 4.60 (s, 1H), 6.45 (s, 1H), 7.18 (dd, J= 2.6 Hz, 1H), 7.20 (d, J= 3.0 Hz, 2H), 7.23 (dd, J= 3.2 Hz, 1H), 7.25 (d, J= 2.6 Hz, 2H), 7.29 (d, J= 2.8 Hz, 2H), 7.34 (d, J= 2.8 Hz, 2H), 7.41 (d, J= 3.0 Hz, 2H), 8.10 (d, J= 2.8 Hz, 2H). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 66.83, 68.11, 83.40, 96.12, 121.78, 123.80, 126.47, 127.20, 128.53, 128.59, 128.96, 129.20, 131.08, 139.63, 143.47, 144.57, 176.28. **Anal. Calcd.** For $C_{23}H_{16}N_2O_3S$: C: 68.98; H: 4.03; N: 7.00. ***Found:*** *C: 69.00; H: 4.01; N: 6.99.* ***M.P.*** *173 °C.*

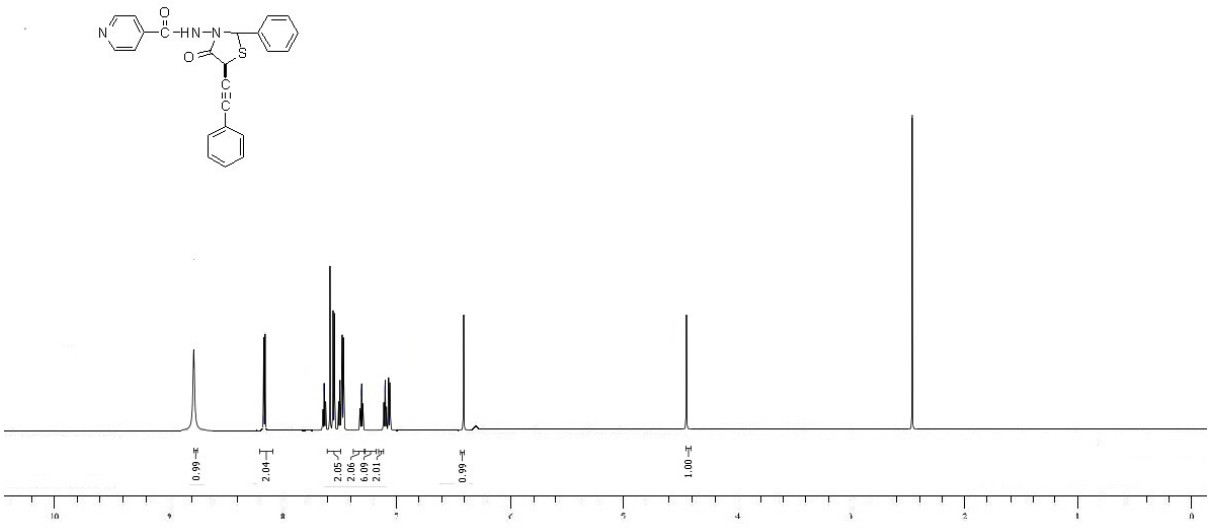


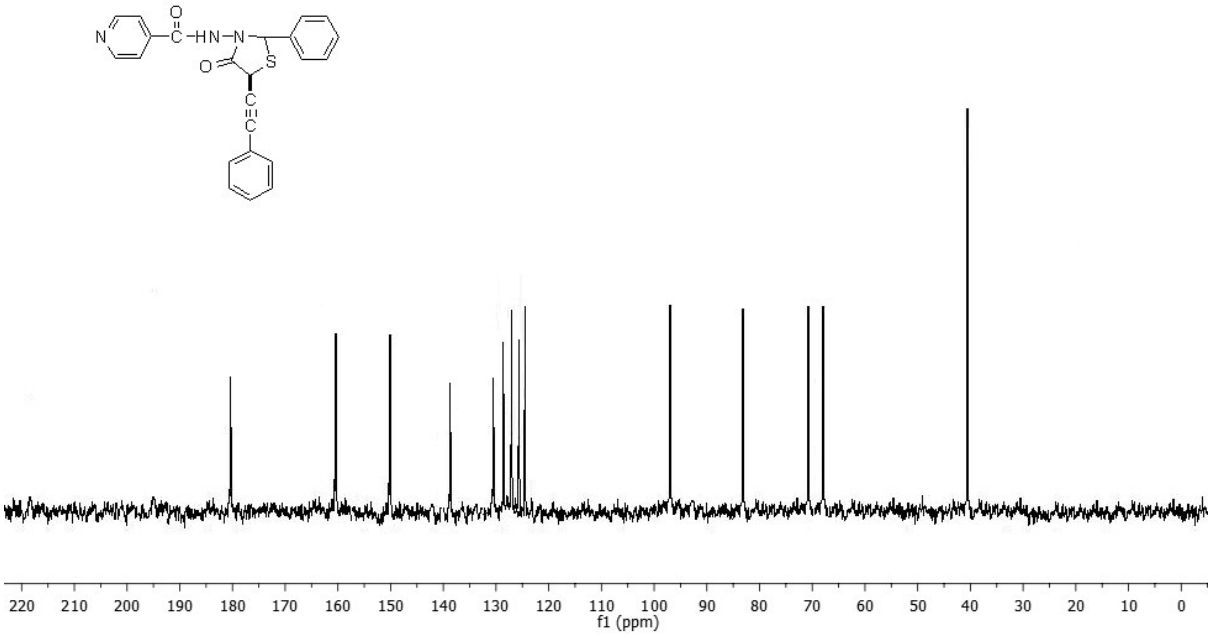
Compound 3n

^{1}H NMR (200 MHz, DMSO-d_6) δ ppm: 2.41 (s, 3H), 2.45(s, 3H), 4.68 (s, 1H), 6.85 (s, 1H), 7.08 (dd, J= 0.8 Hz, 1H), 7.11 (dd, J= 0.6 Hz, 1H), 7.13 (dd, J= 0.6 Hz, 1H), 7.17 (dd, J= 0.8 Hz, 1H), 7.20 (dd, J= 0.6 Hz, 1H), 7.22 (dd, J= 0.8 Hz, 1H), 7.24 (dd, J= 0.8 Hz, 1H), 7.26 (dd, J= 0.8 Hz, 1H), 7.33 (d, J= 2.8 Hz, 2H), 7.35 (dd, J= 0.8 Hz, 1H), 7.39 (d, J= 2.8 Hz, 2H). **^{13}C NMR** (300 MHZ, DMSO-d_6) δ ppm: 19.12, 20.08, 67.08, 68.17, 83.47, 96.12, 123.80, 125.93, 126.55, 127.20, 127.95, 128.53, 128.59, 128.96, 129.20, 131.08, 132.28, 135.36, 139.63, 142.19, 175.37. **Anal. Calcd.** For $C_{25}H_{21}NOS$: C: 78.30; H: 5.52; N: 3.65. ***Found:*** *C: 78.33; H: 5.50; N: 3.66.* ***M.P.*** *170 °C.*

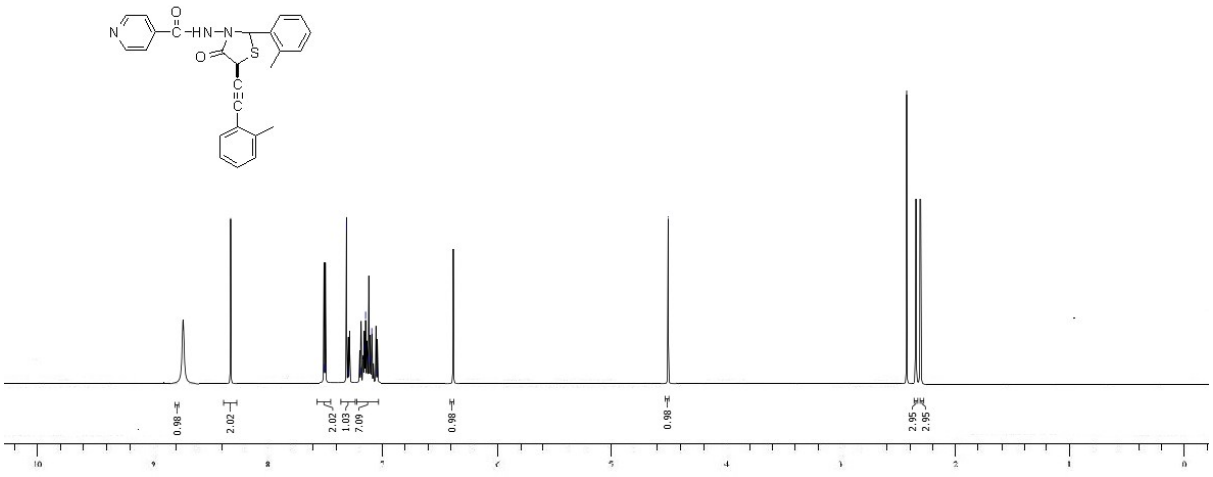
2. ^{1}H NMR and ^{13}C NMR spectra :

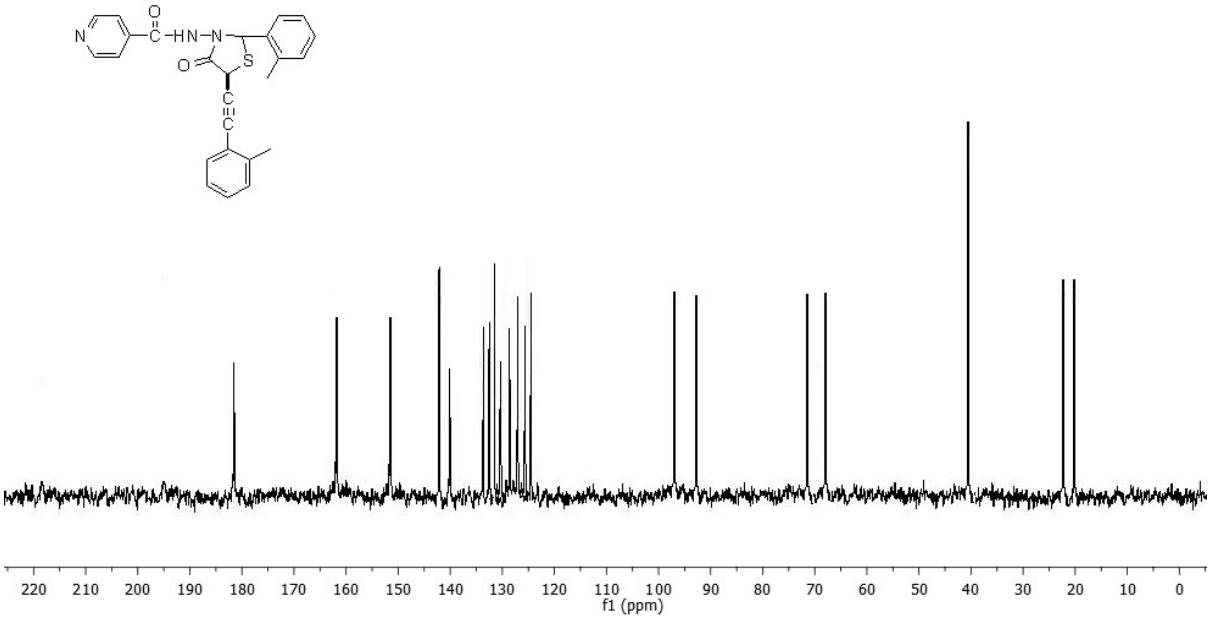
Compound 3a



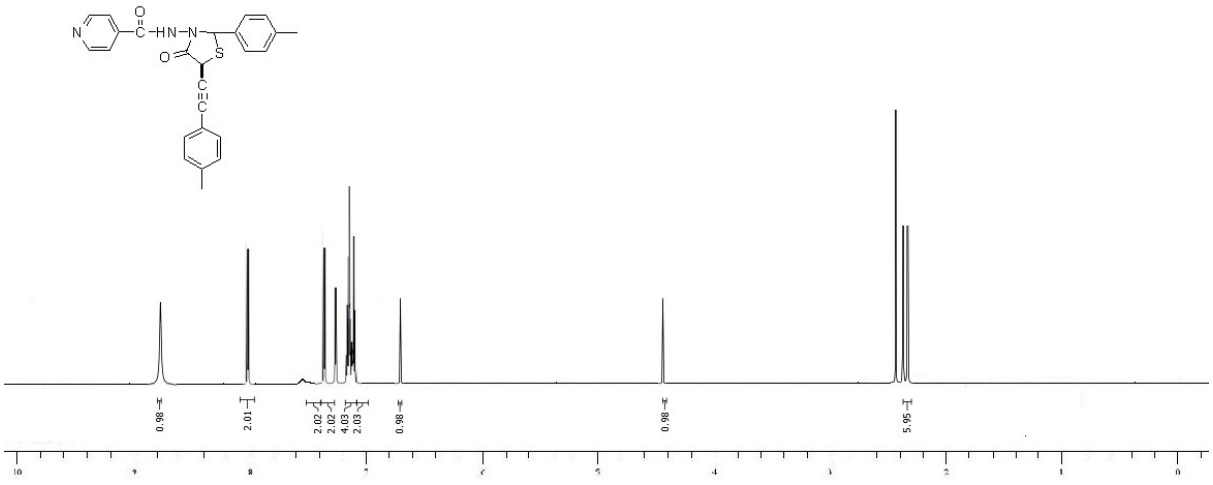


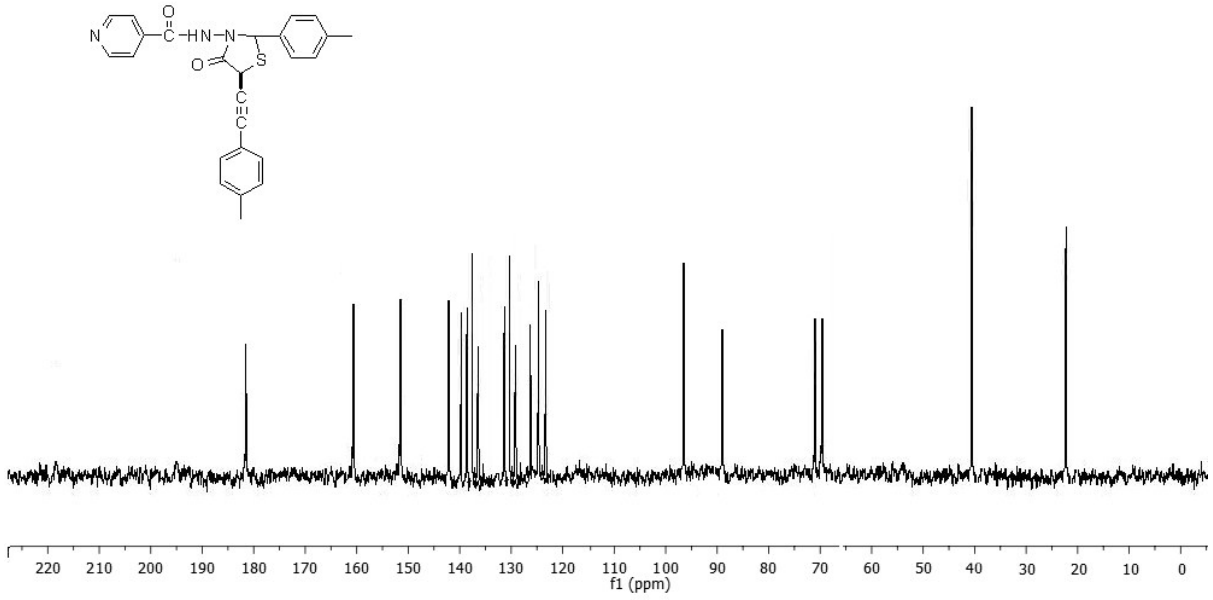
Compound 3b


0.98
2.02
2.02
1.03
7.09
0.98
0.98
2.95
2.95

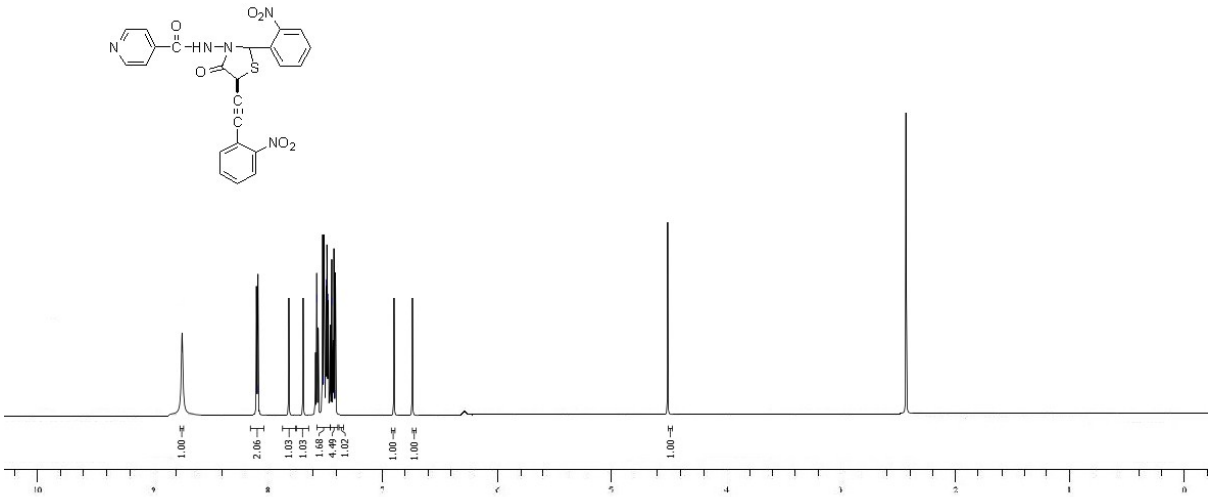

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

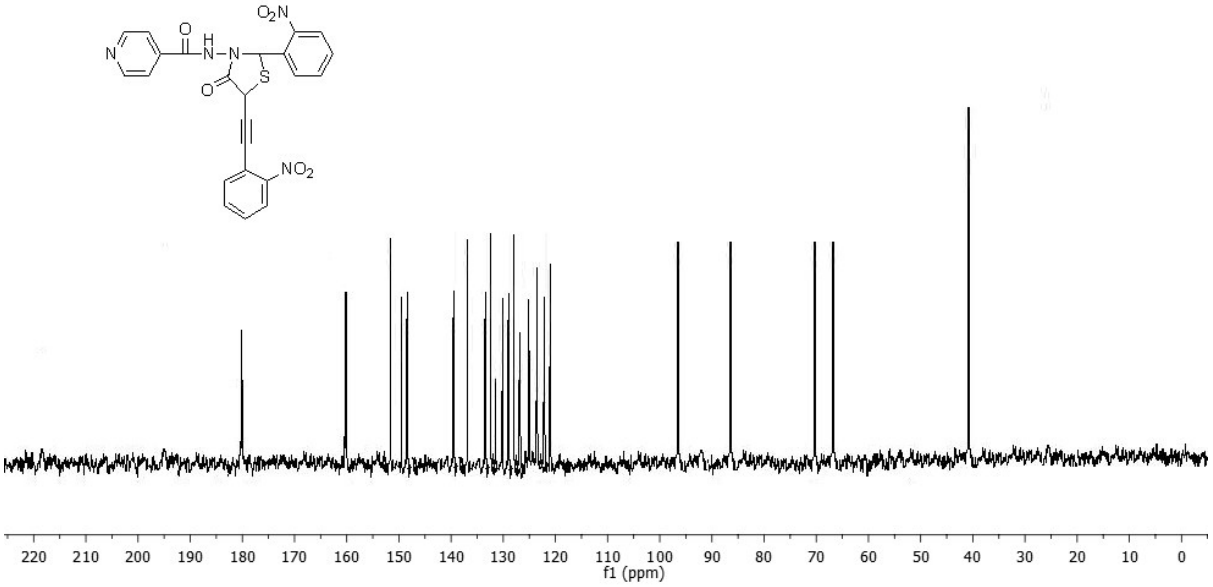
Compound 3c


0.98
2.01
2.02
2.02
4.03
2.03
0.98
0.98
5.95

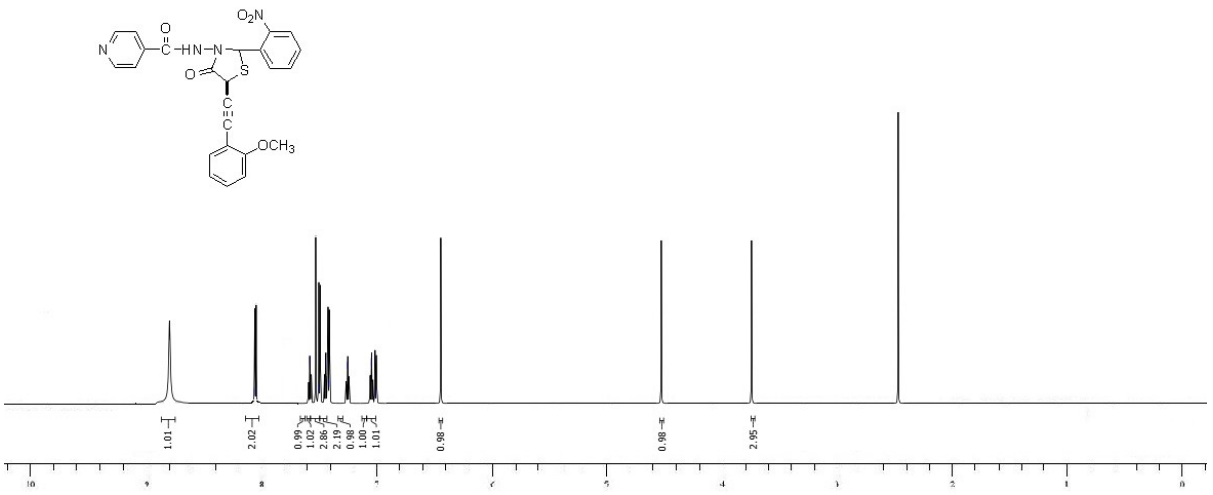

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

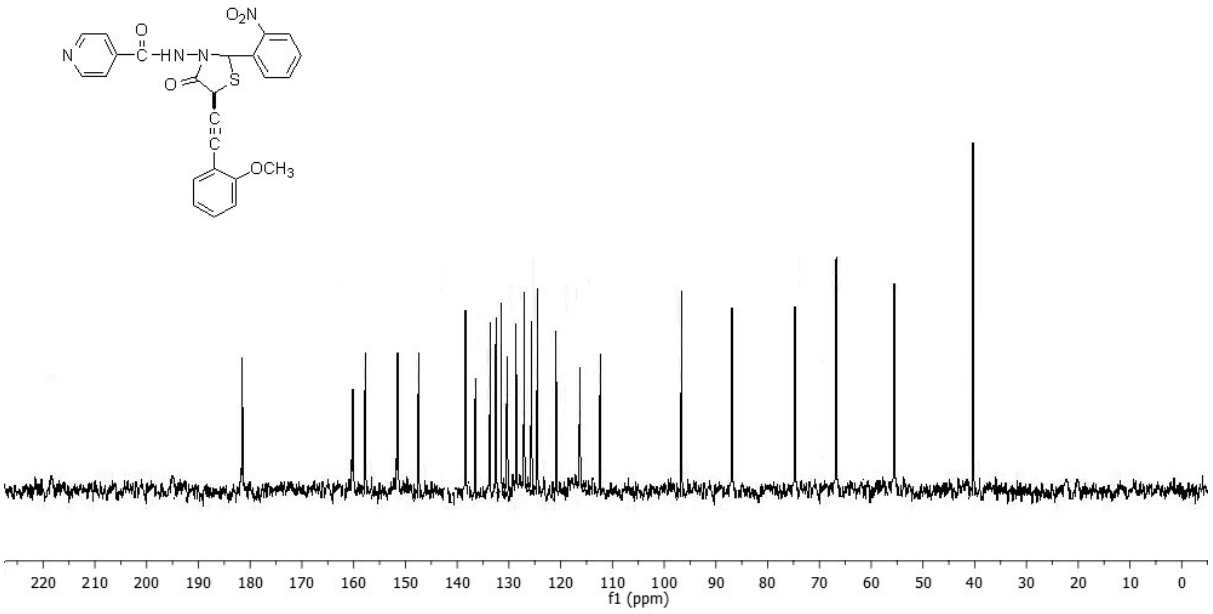
Compound 3d



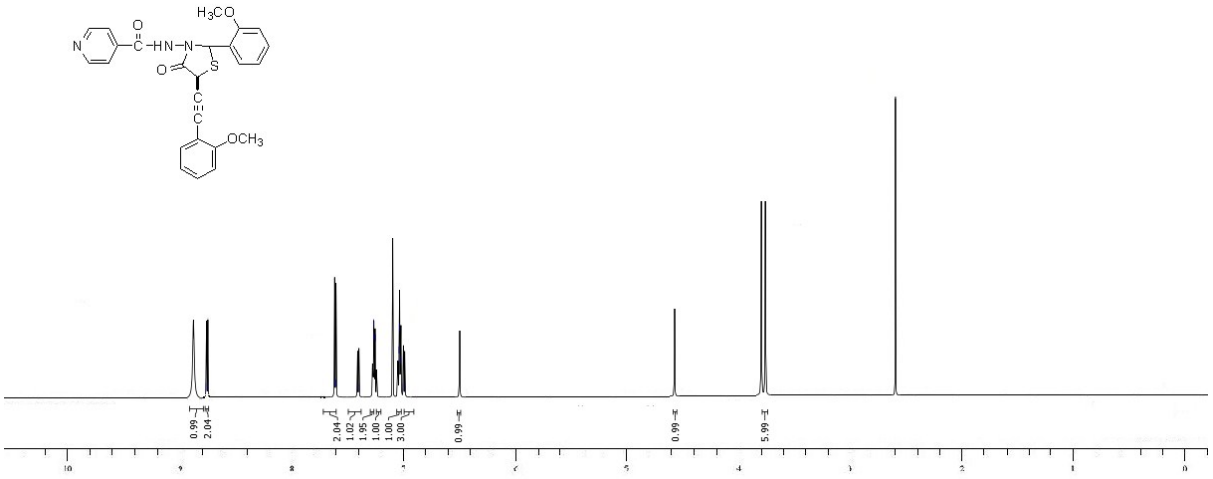

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

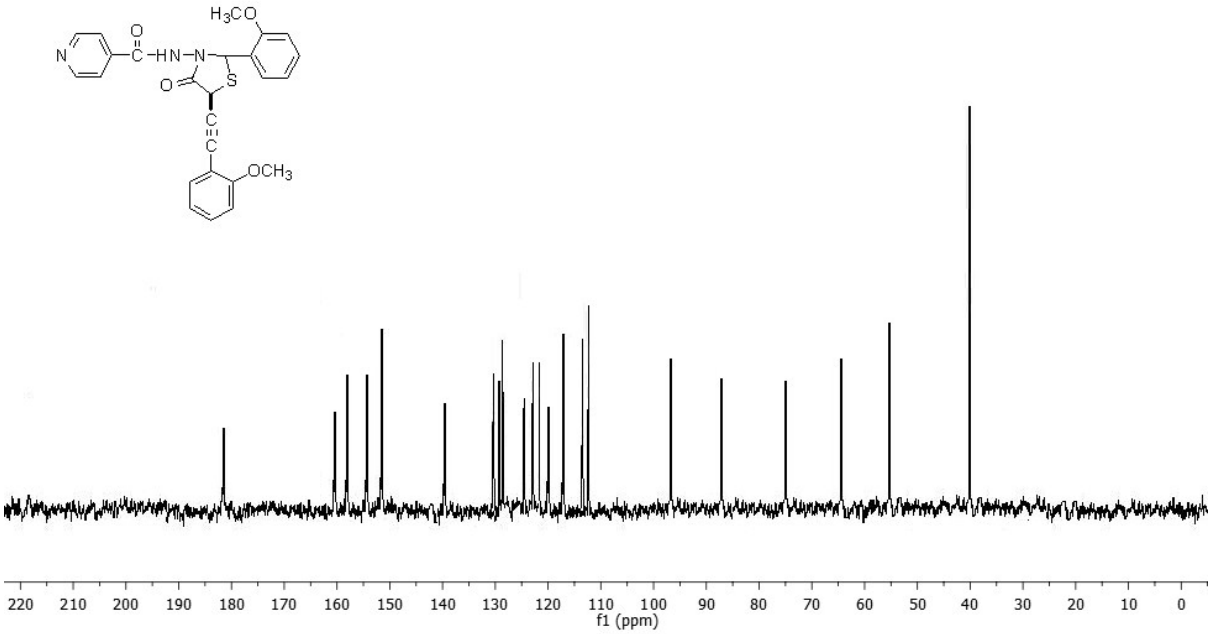
Compound 3e


O2N
O
N
C
HN
N
O
S
C
C
OCH3
1.01
2.02
0.99
1.02
2.86
2.19
0.98
1.00
1.01
0.98
0.98
2.95

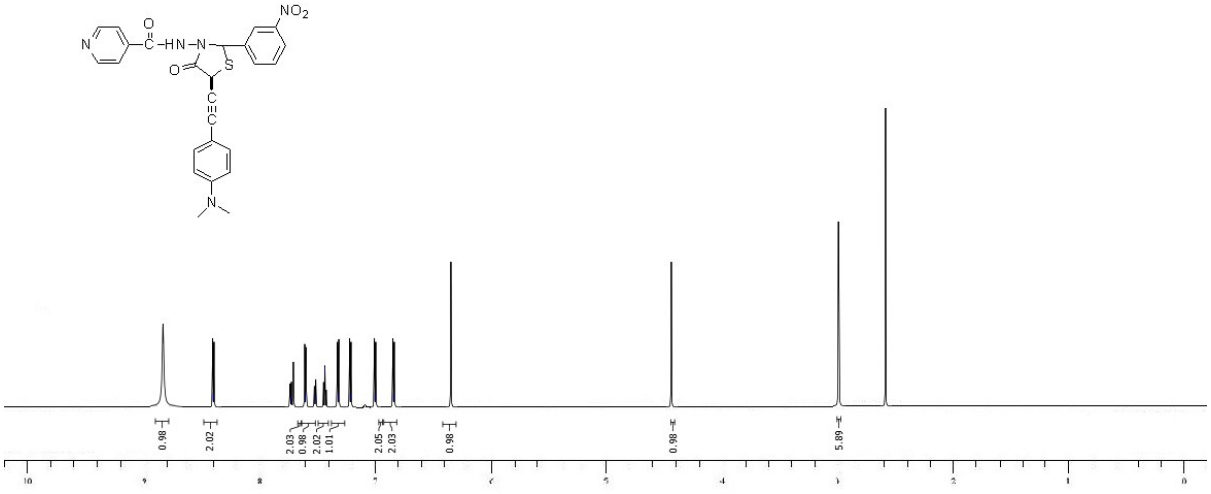

O2N
O
N
C
HN
N
O
S
C
C
OCH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

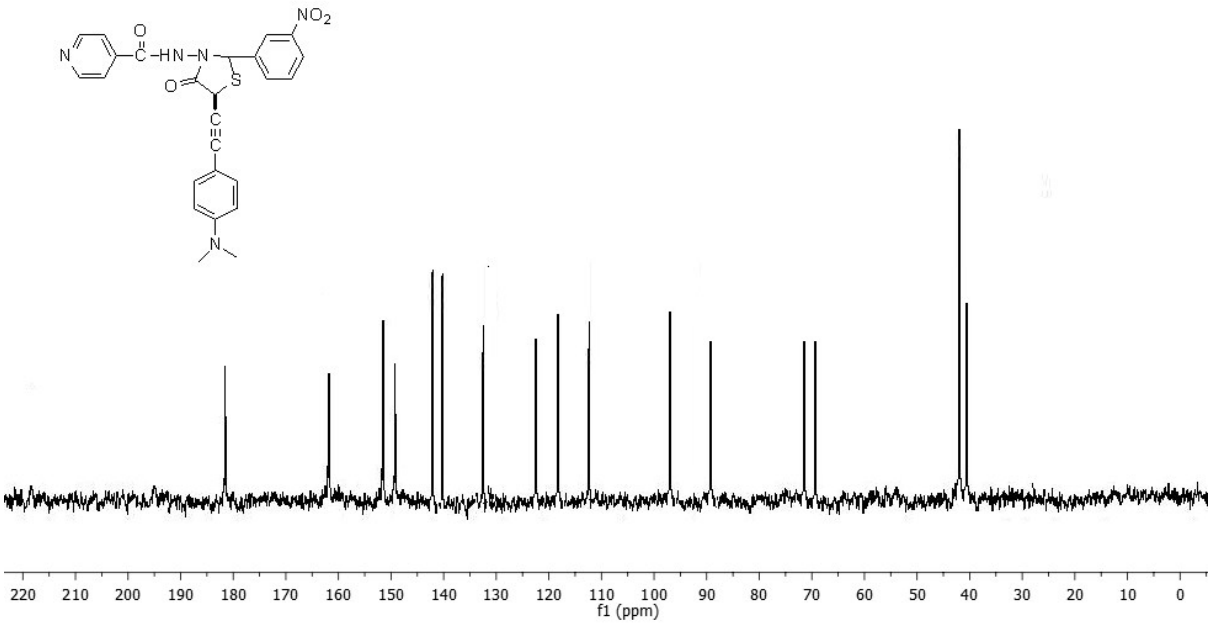
Compound 3f


H3CO
O
N
C
HN
N
O
S
C
C
OCH3
0.99
2.04
2.04
1.02
1.95
1.00
1.00
3.00
0.99
0.99
5.99

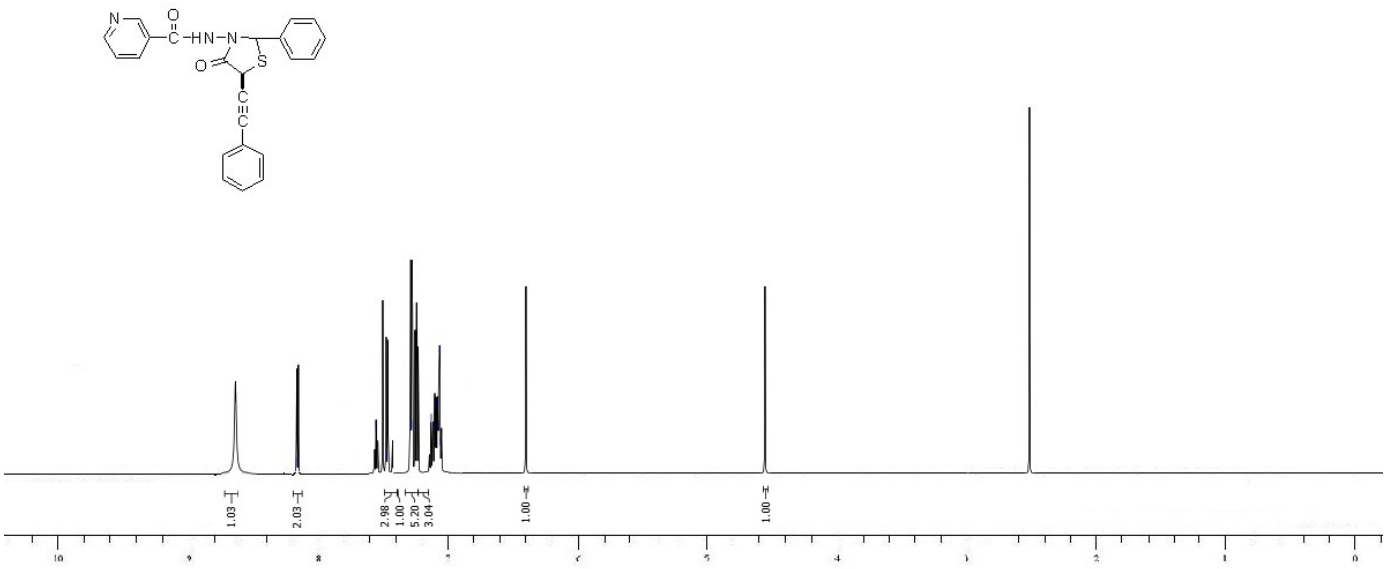

H3CO
O
N
C
HN
N
O
S
C
C
OCH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

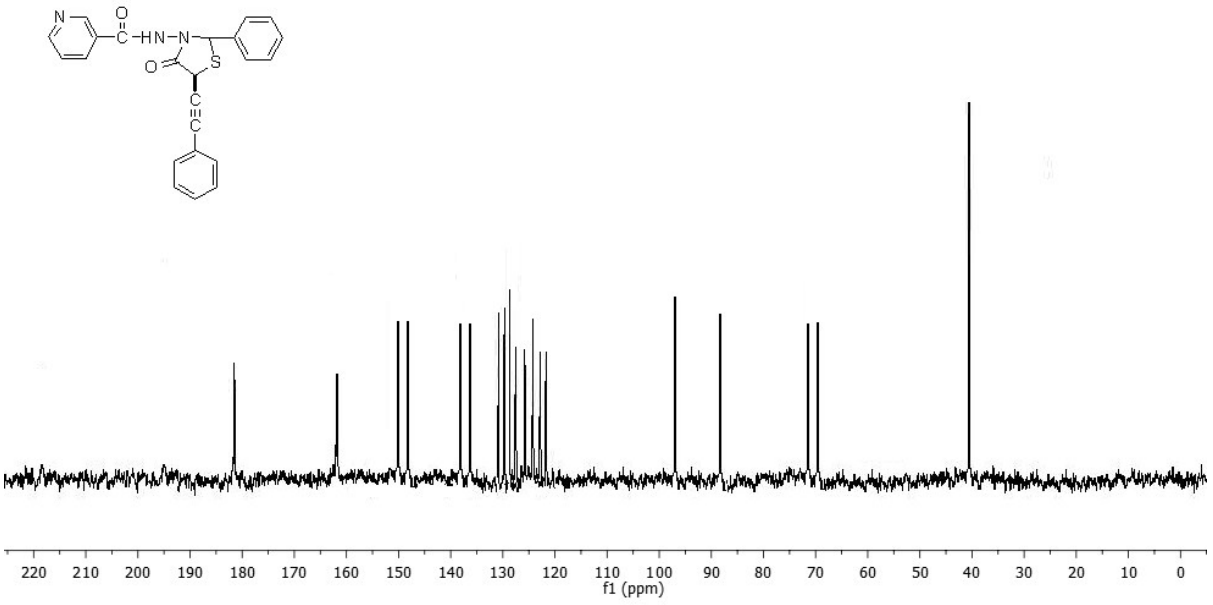
Compound 3g


NO2
O
HN
N
S
O
N
0.98
2.02
2.03
0.98
2.02
1.01
2.05
2.03
0.98
0.98
5.89

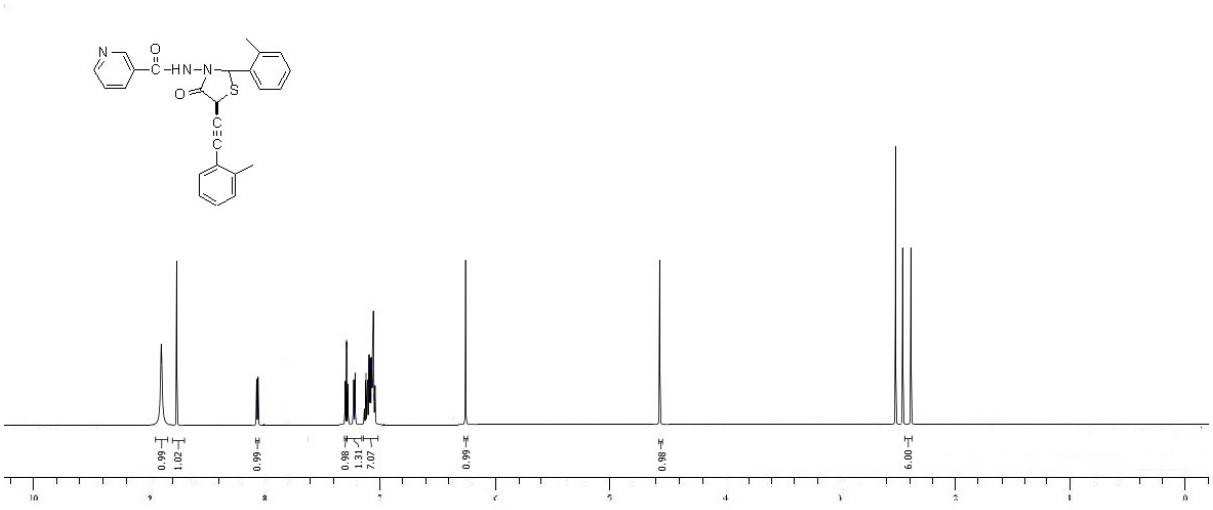

NO2
O
HN
N
S
O
N
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

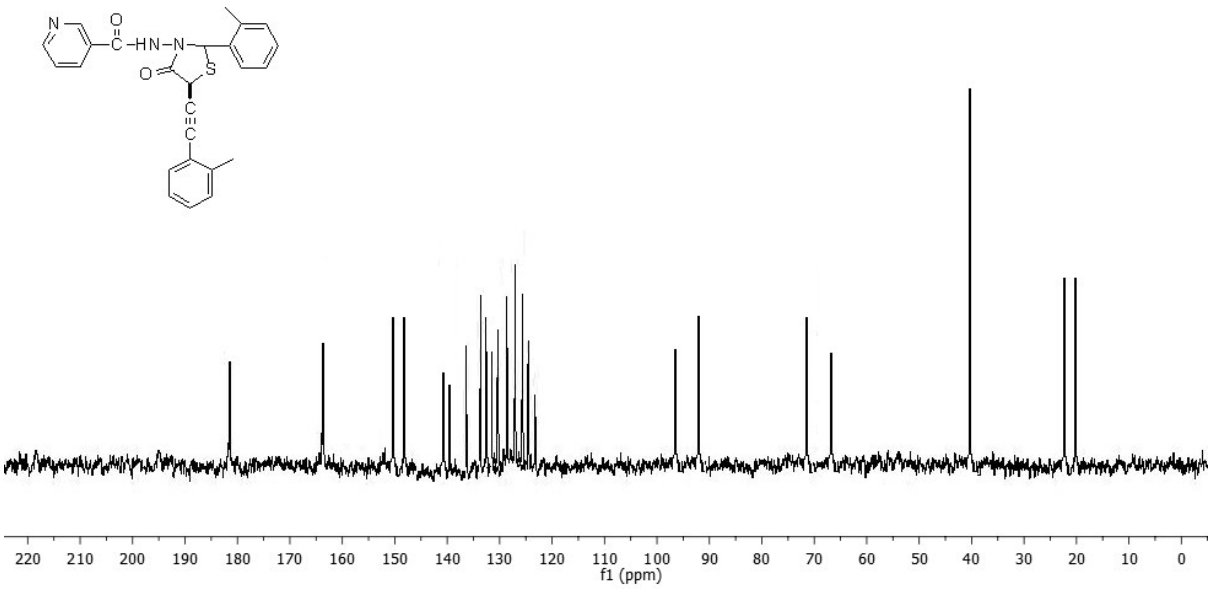
Compound 3h


1.03
2.03
2.98
1.00
5.20
3.04
1.00
1.00

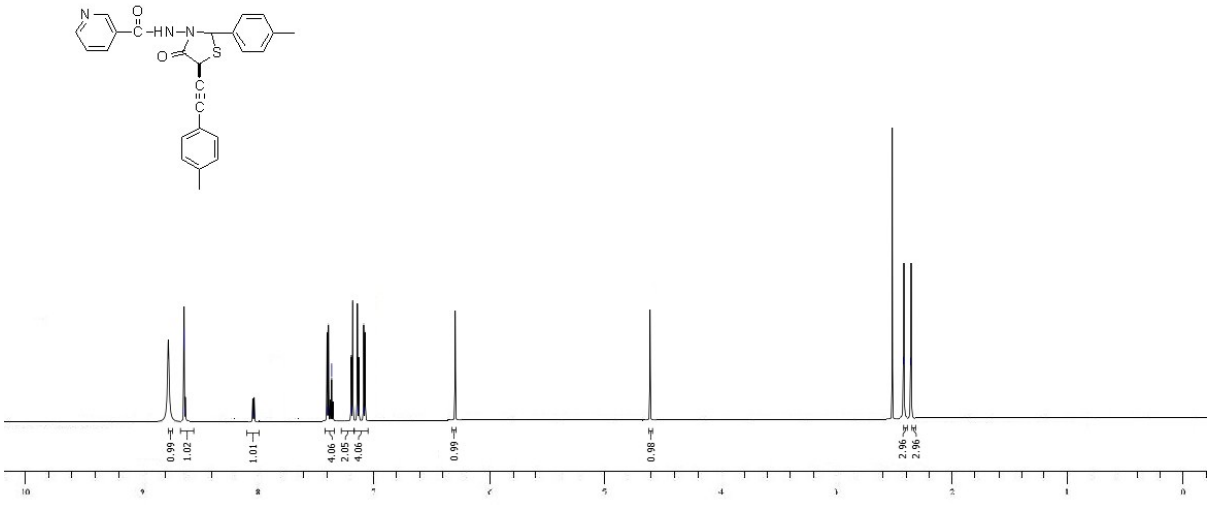

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

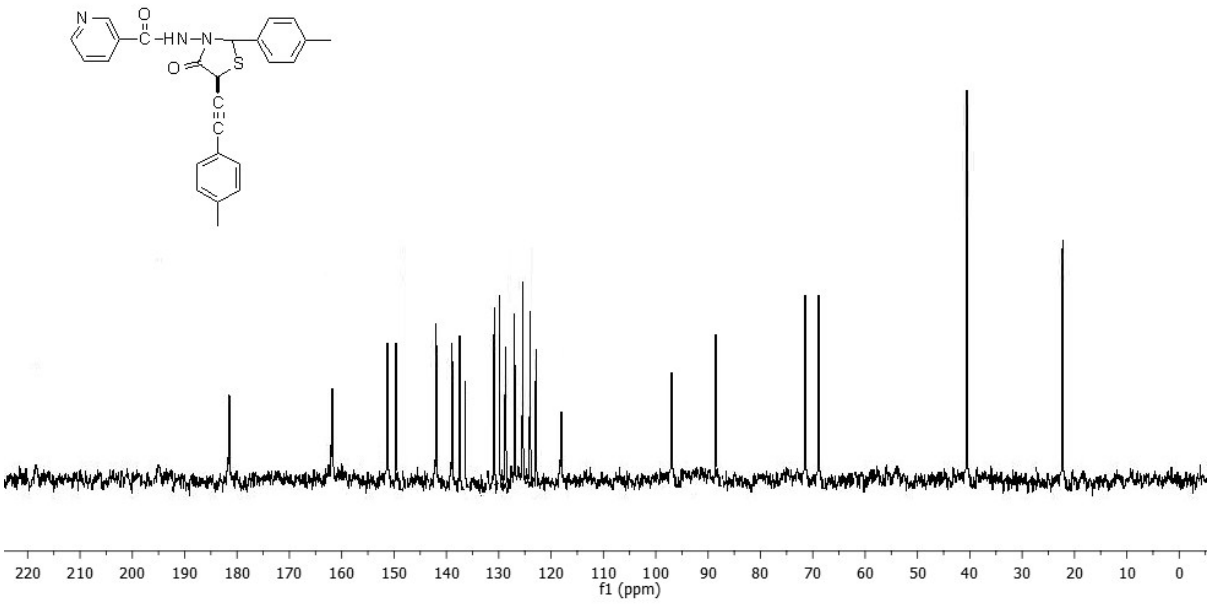
Compound 3i


0.99
1.02
0.99
0.98
1.31
7.07
0.99
0.98
6.00

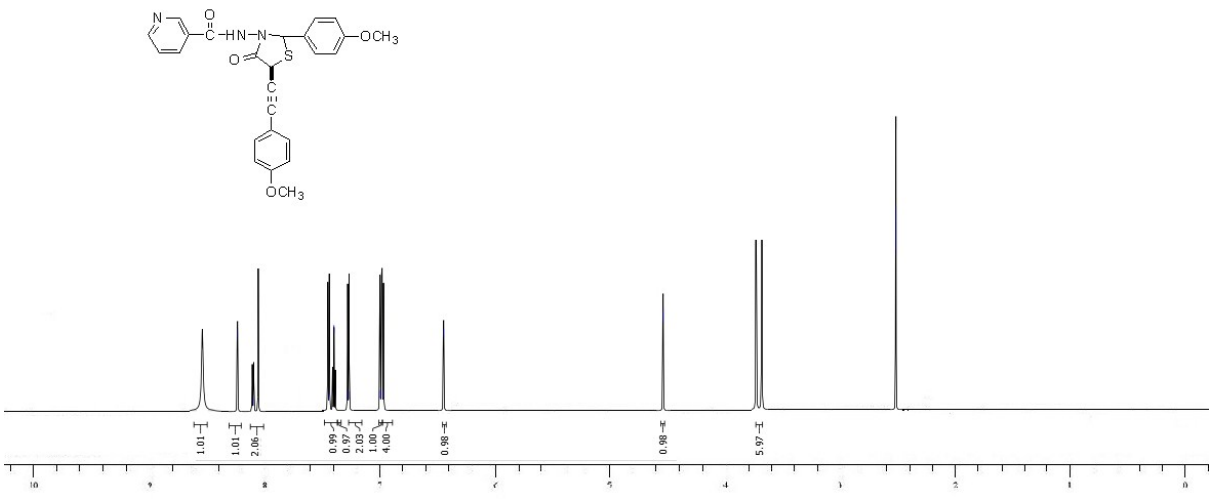

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

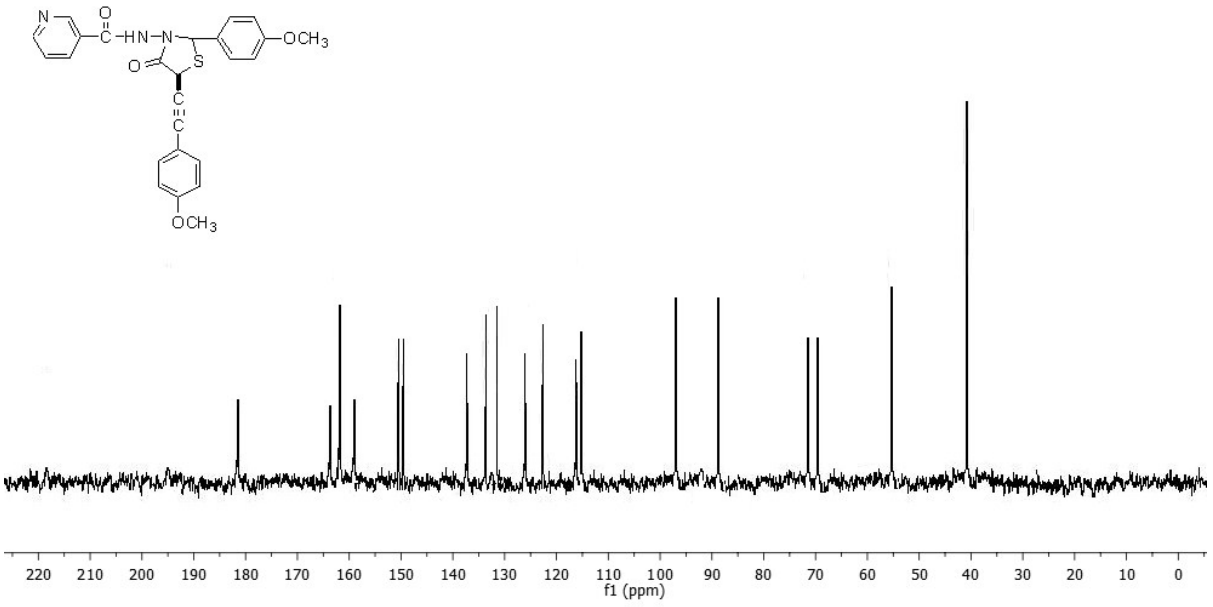
Compound 3j


0.99
1.02
1.01
4.06
2.05
4.06
0.99
0.98
2.96
2.96

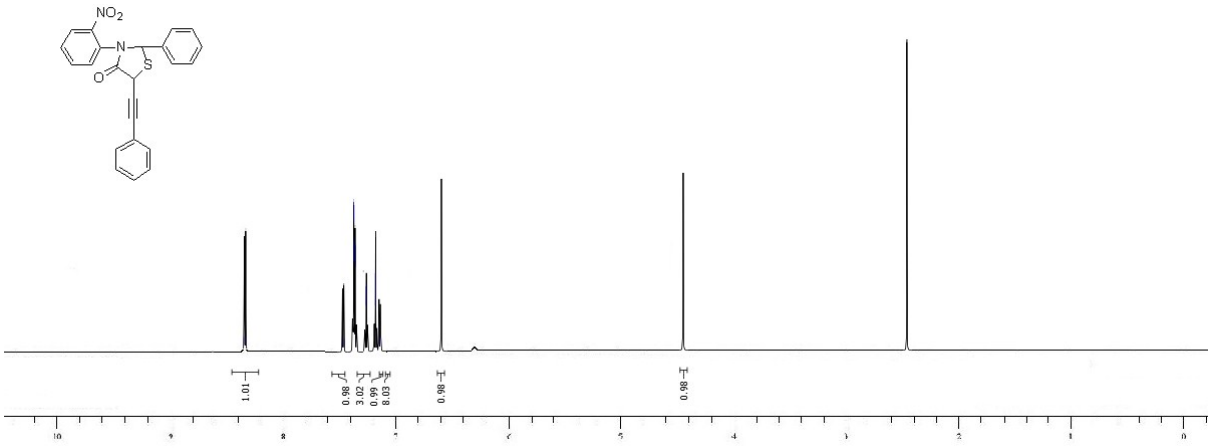

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

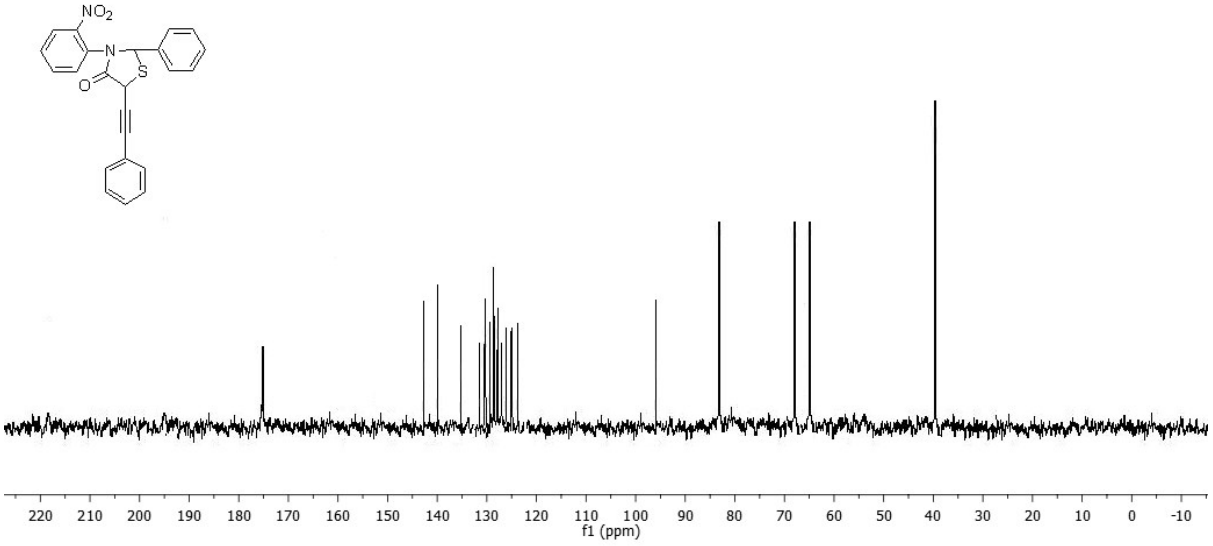
Compound 3k


N
O
HN
N
S
O
OCH3
OCH3
1.01
1.01
2.06
0.99
0.97
2.03
1.00
4.00
0.98
0.98
5.97

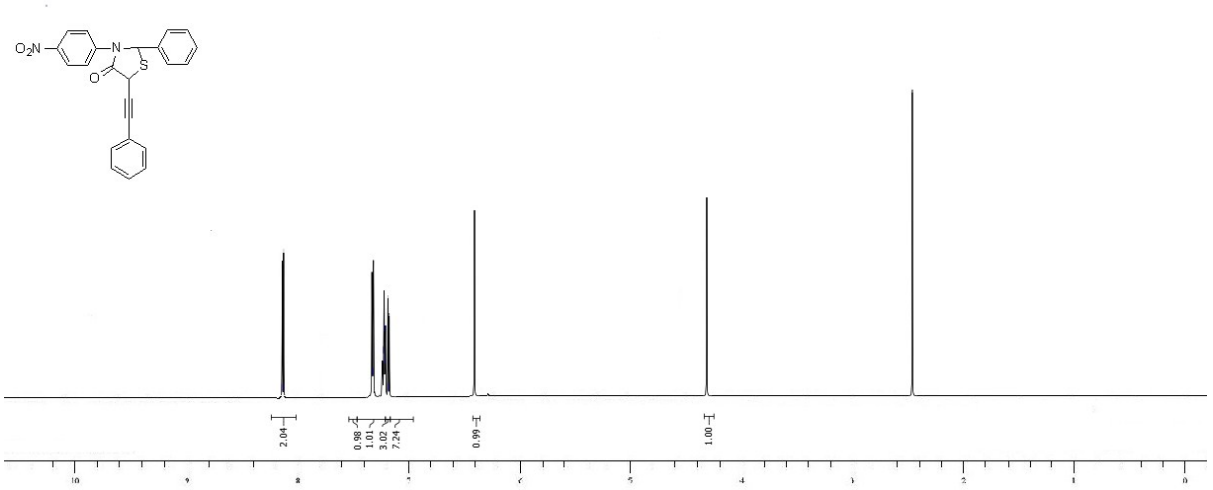

N
O
HN
N
S
O
OCH3
OCH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

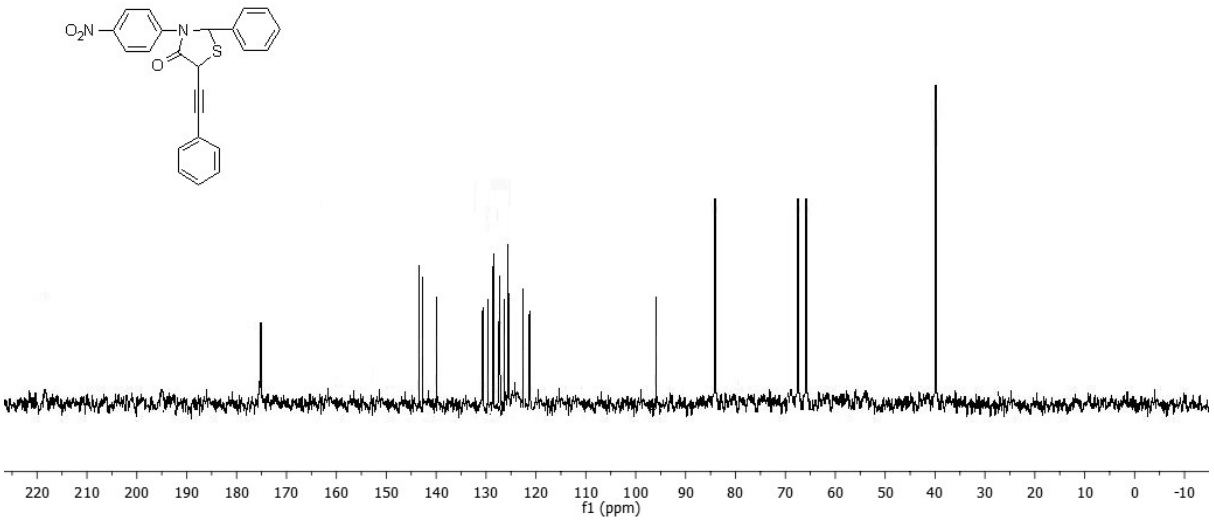
Compound 3l



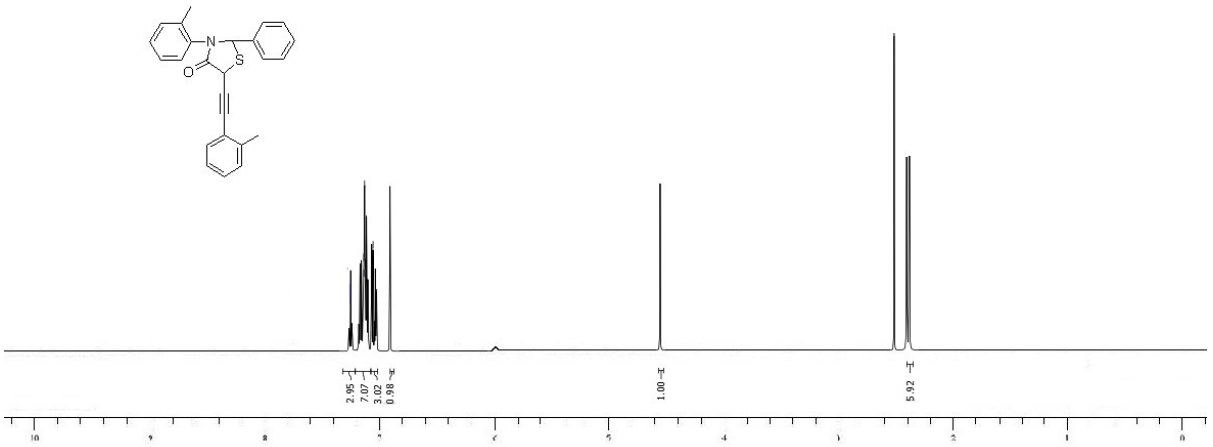


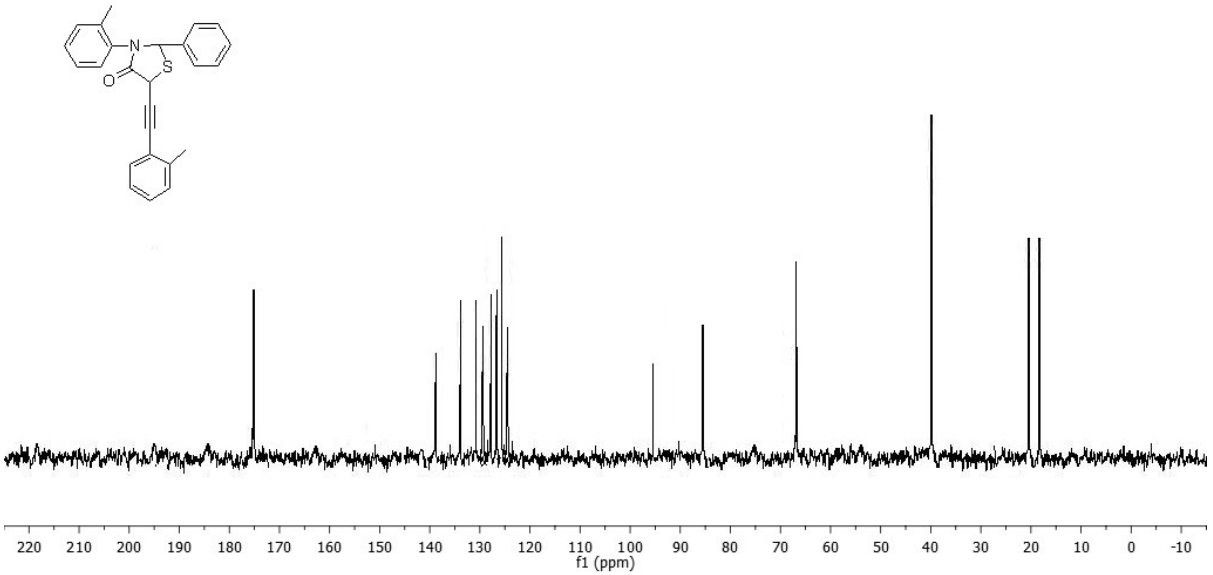
Compound 3m


O2N
N
S
O
2.04
0.98
1.01
3.02
7.24
0.99
1.00


O2N
N
S
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Compound 3n


2.95
7.07
3.02
0.98
1.00
5.92


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)