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

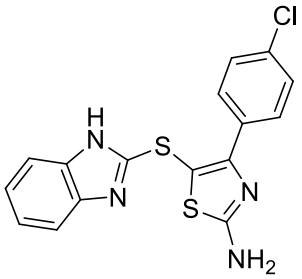
Metal free, Selective thiolation of C(sp2)-H bond Functionalization via *in situ*-generated NHTS for Synthesis of Novel Sulfenylated 2-aminothiazole and Imidazothiazole

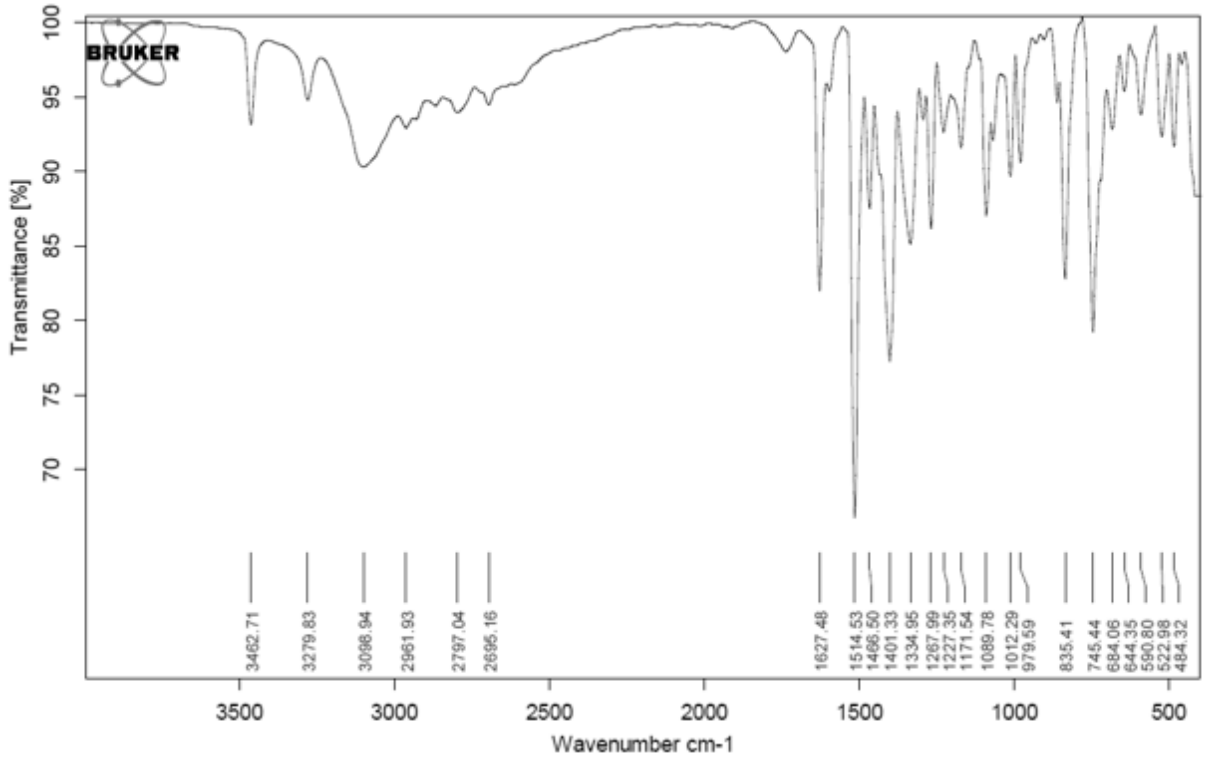
1. **a)** ***General procedure for the synthesis of 5-((1H-benzo[d]imidazol-2-yl)thio)-4-(4-chlorophenyl)thiazol-2-amine (5a).***

NCS (1.5 mmol) was taken in round bottom flask containing CH_3OH. To this same pot 1H-benzo[d]imidazole-2-thiol **(2a)** (**Scheme 2**) (2 mmol) was added slowly with constant stirring, and reaction mass was stirred at room temperature up to 5 minutes. As TLC indicate the formation of (NHTS). Furthermore to the same pot 4-(4-chlorophenyl)thiazol-2-amine (2 mmol) was added with small proportions at a time and stirring was continued for another 20 minutes, as TLC indicate the completion of reaction. The reaction mass was poured on ice cold water, solid product separated out was filtered, dried and washed with aqueous ethanol. No further purification like column chromatography was needed.

(b) Spectral data of ***5-((1H-benzo[d]imidazol-2-yl)thio)-4-(4-chlorophenyl)thiazol-2-amine (5a)*** pale yellow solid, mp 99-100 ºC. FT-IR: 3462 (-NH_2), 1171 (C-S-C) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 12.54 (s, 1H), 7.87 (m, 2H), 7.72 (m, 2H), 7.48 (m, 4H), 7.16 (m 2H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 171.06, 156.28, 150.20, 133.53, 133.20, 130.82, 128.60, 122.27, 114.77, 99.44, HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{11}ClN_4S_2$: 358.0114, found 359.0183.

IR


Cl
H
N
S
N
S
N
NH2


BRUKER
Transmittance [%]
100
95
90
85
80
75
70
3462.71
3279.83
3088.94
2961.93
2797.04
2696.16
1627.48
1514.53
1466.50
1401.33
1334.95
1267.99
1227.35
1171.54
1089.78
1012.29
979.59
835.41
745.44
684.06
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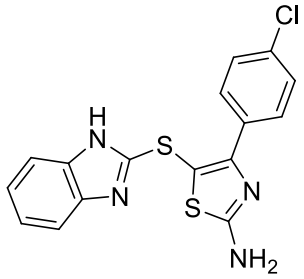
590.80
522.98
484.32
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

^{1}H NMR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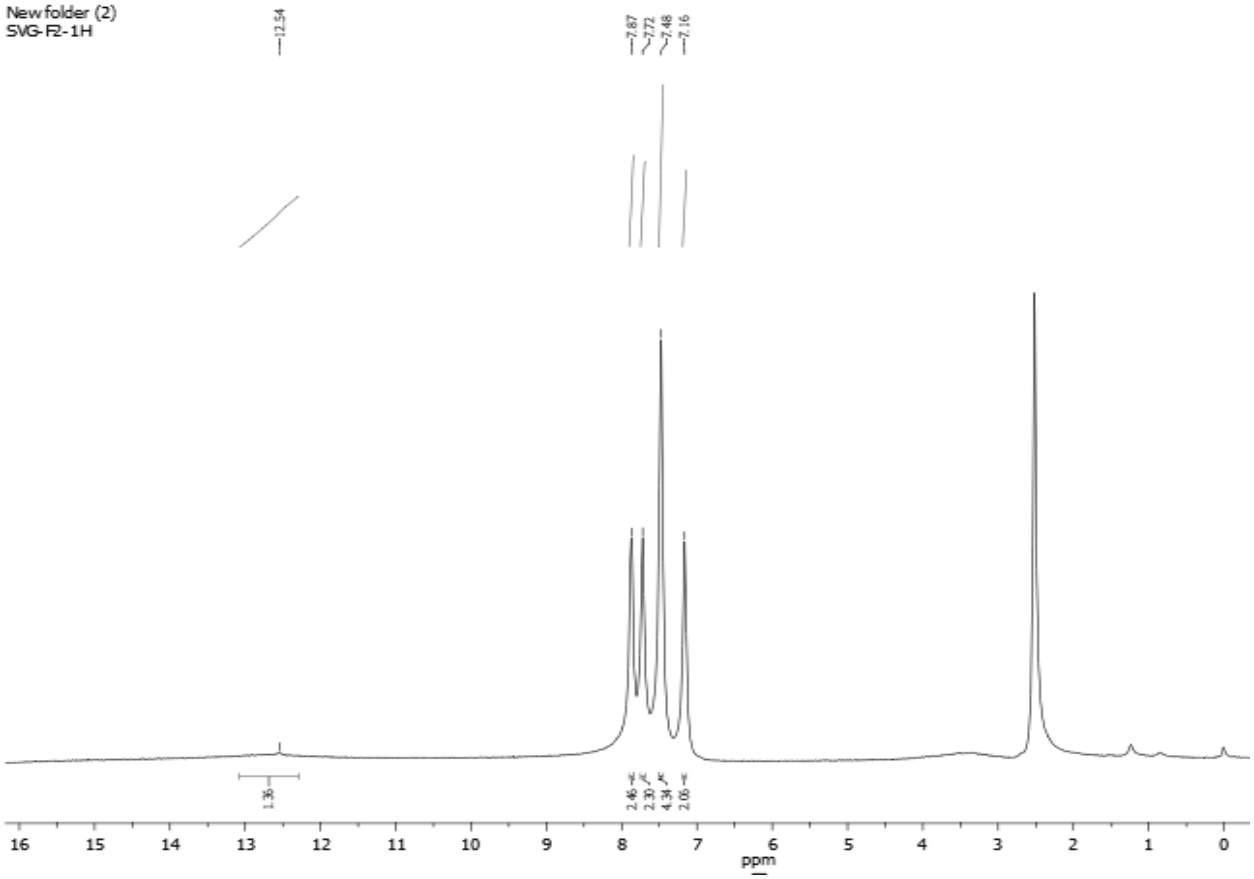
H
N
S
N
S
N
NH2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7.16
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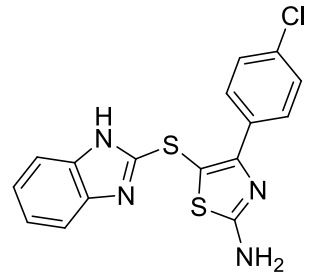
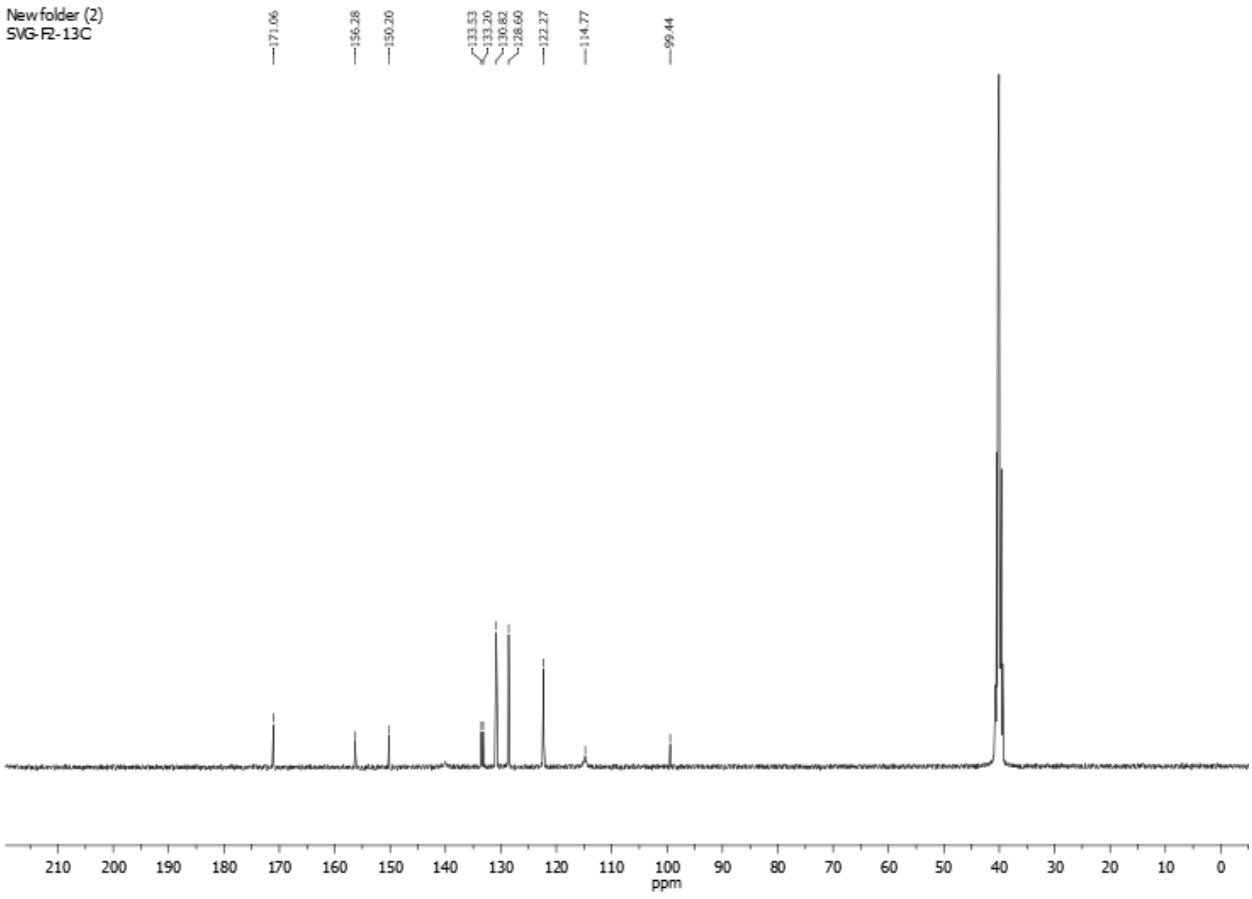
2.46
2.30
4.34
2.06
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{13}C NMR


Cl
H
N
S
N
S
N
NH2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156.28
150.20
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133.20
130.82
128.60
122.27
114.77
99.44
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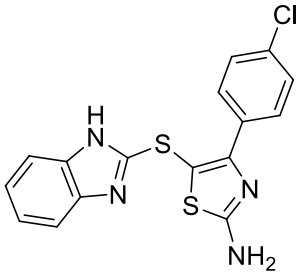
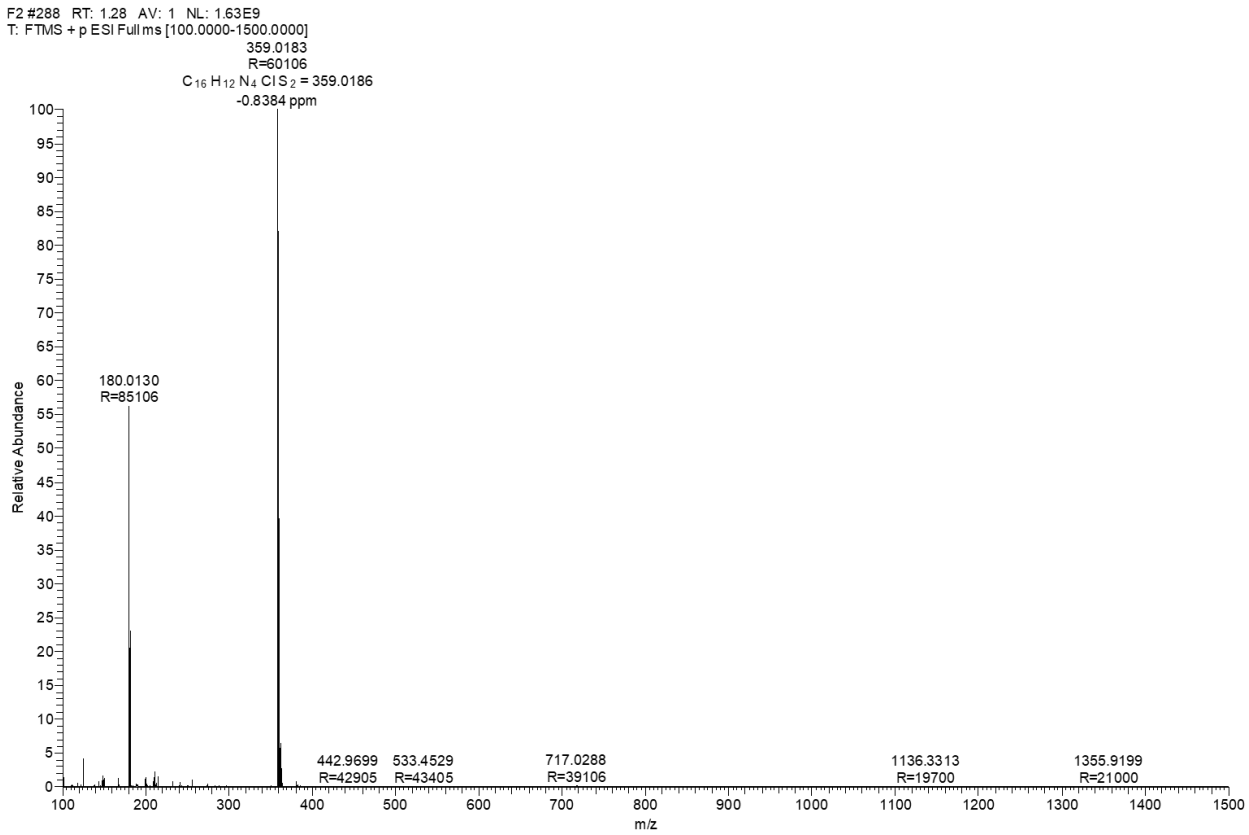
ppm

HRMS



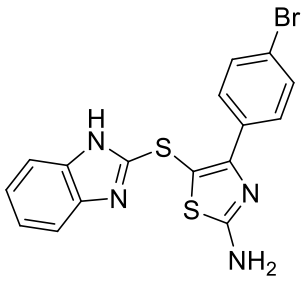
Calculated for $C_{16}H_{11}ClN_4S_2$: 358.0114, found 359.0183.

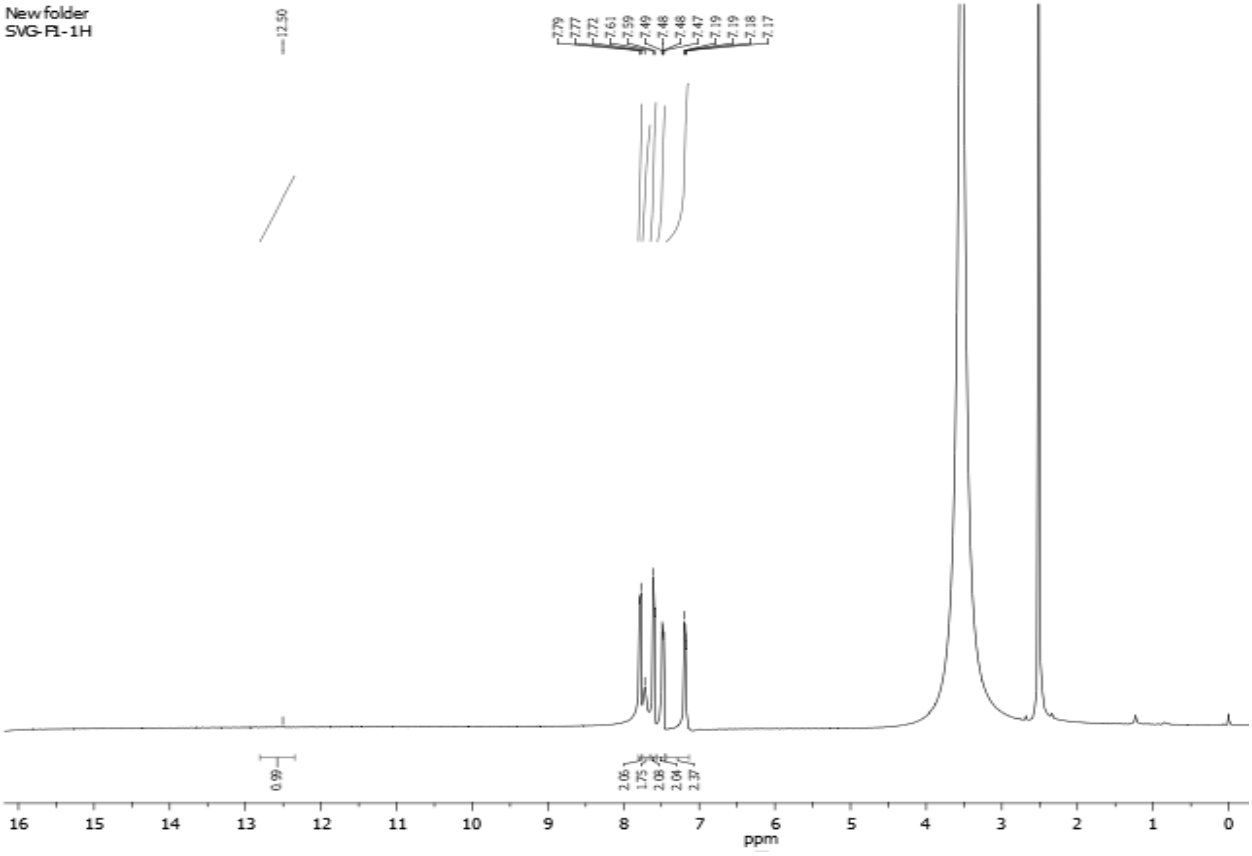


(c) Spectral data of *5-((1H-benzo[d]imidazol-2-yl)thio)-4-(4-bromophenyl)thiazol-2-amine (5b)* White solid, mp 110-111 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 12.50 (s, 1H), 7.79-7.61 (m, 2H), 7.59 (m, 2H), 7.49-7.48 (m, 2H), 7.47 (m 2H), 7.19-7.17 (m 2H). ^{13}C-NMR (400 MHz, DMSO-d_6,) δ 171.20, 156.57, 150.30, 133.42, 131.54, 131.11, 122.62,

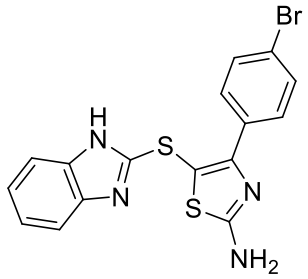
122.31, 114.69, 98.93. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{11}BrN_4S_2$: 401.9609, found 404.9672.

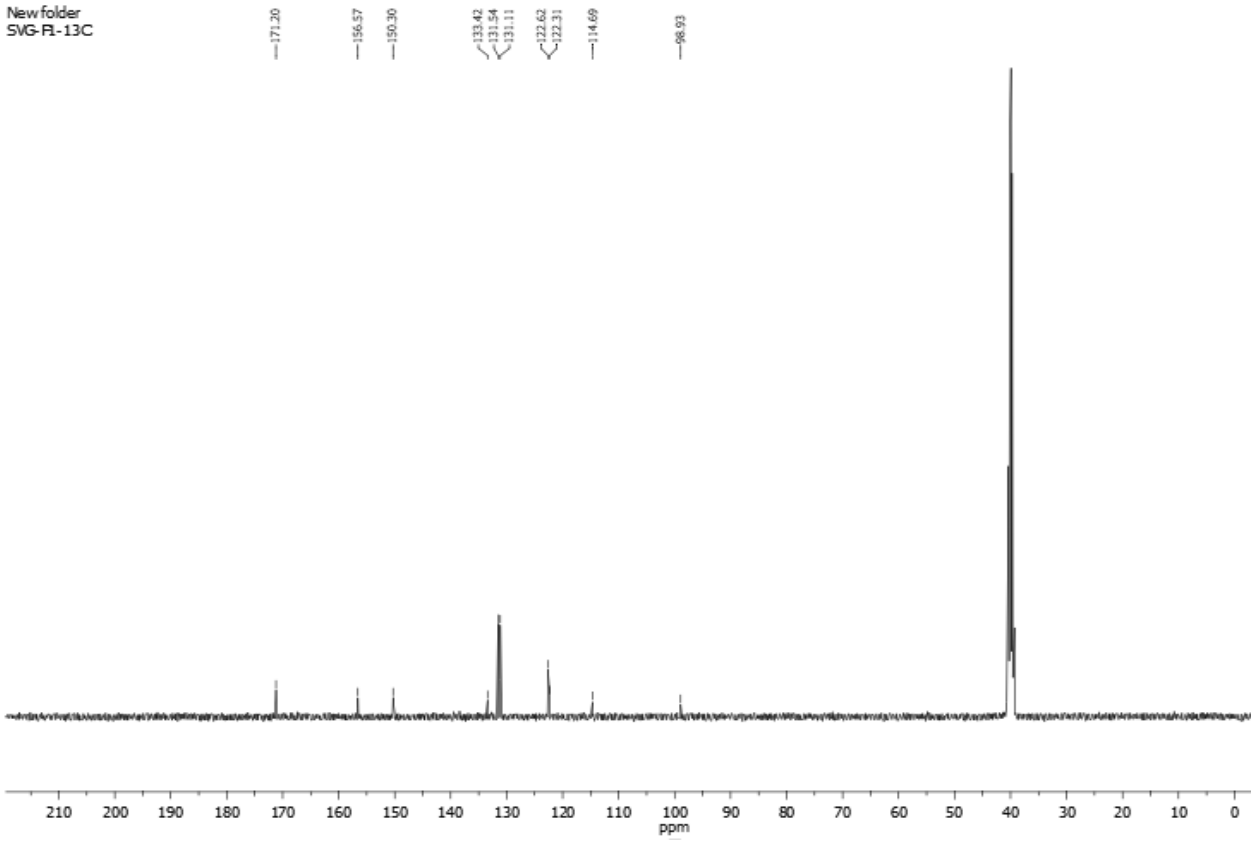
^{1}H NMR





^{13}C NMR


Br
H
N
S
N
N
S
NH2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SVG-FI-13C
171.20
156.57
150.30
133.42
131.54
131.11
122.62
122.31
114.69
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200
190
180
170
160
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140
130
120
110
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90
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50
40
30
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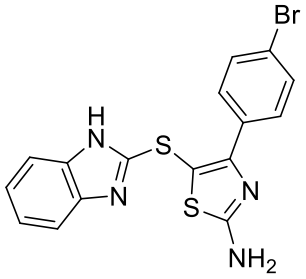
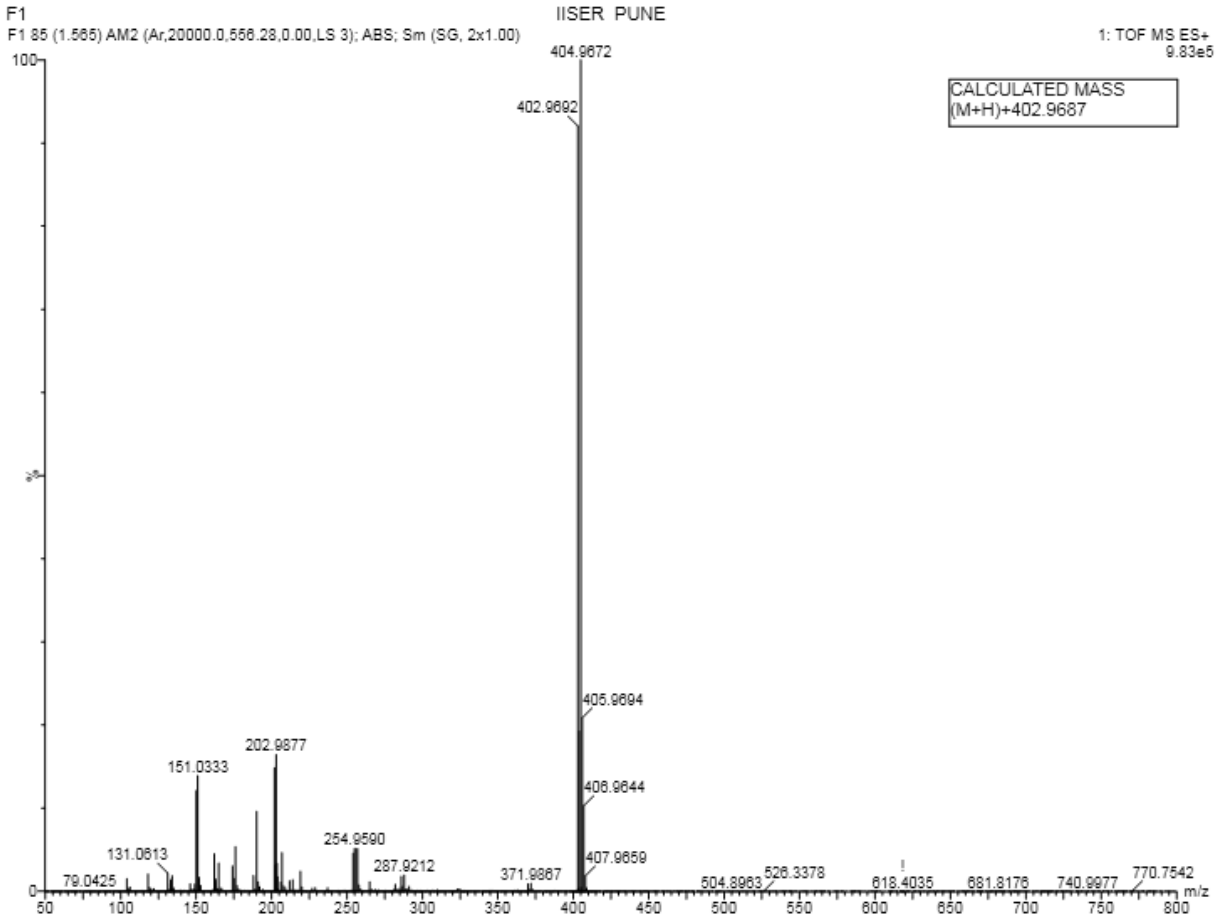
10
0
ppm

HRMS



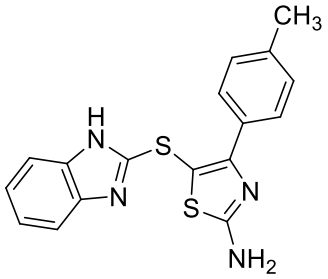
Calculated for $C_{16}H_{11}BrN_4S_2$: 401.9609, found 404.9672.

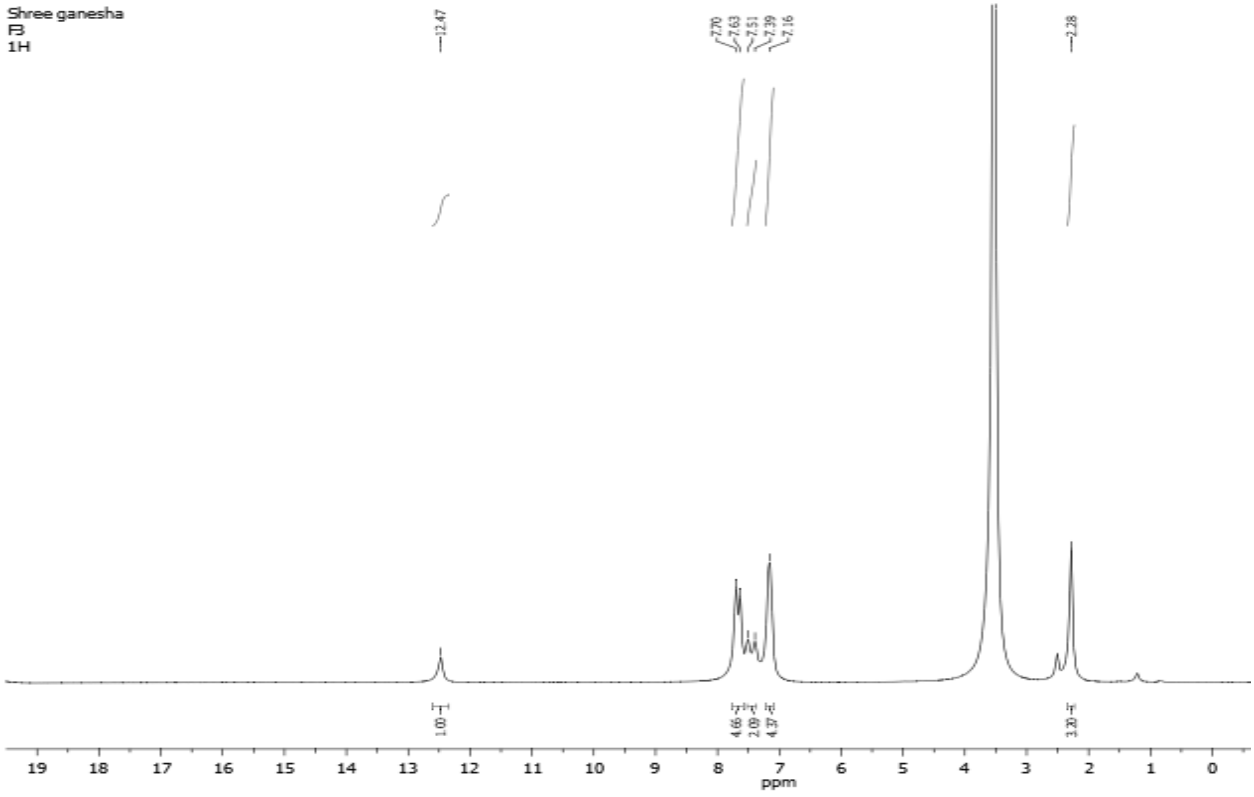


(d) Spectral data of 5-((1H-benzo[d]imidazol-2-yl)thio)-4-(p-tolyl)thiazol-2-amine ***(5c)*** White solid, mp 100-101 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 12.47 (s, 1H), (m,

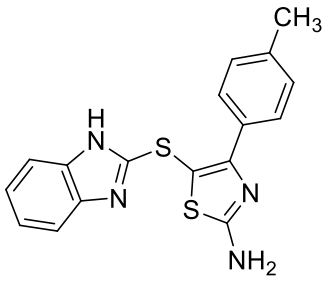
2H), 7.70-7.63 (m, 4H), 7.51-7.39 (m, 2H), 7.16 (m 4H), 2.28 (s 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 170.88, 157.74, 150.65, 138.36, 131.55, 129.09, 122.35, 122.00, 118.11, 111.32, 98.03, 21.30. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{17}H_{14}N_4S_2$: 338.0660, found 339.0730.

^{1}H NMR





^{13}C NMR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H
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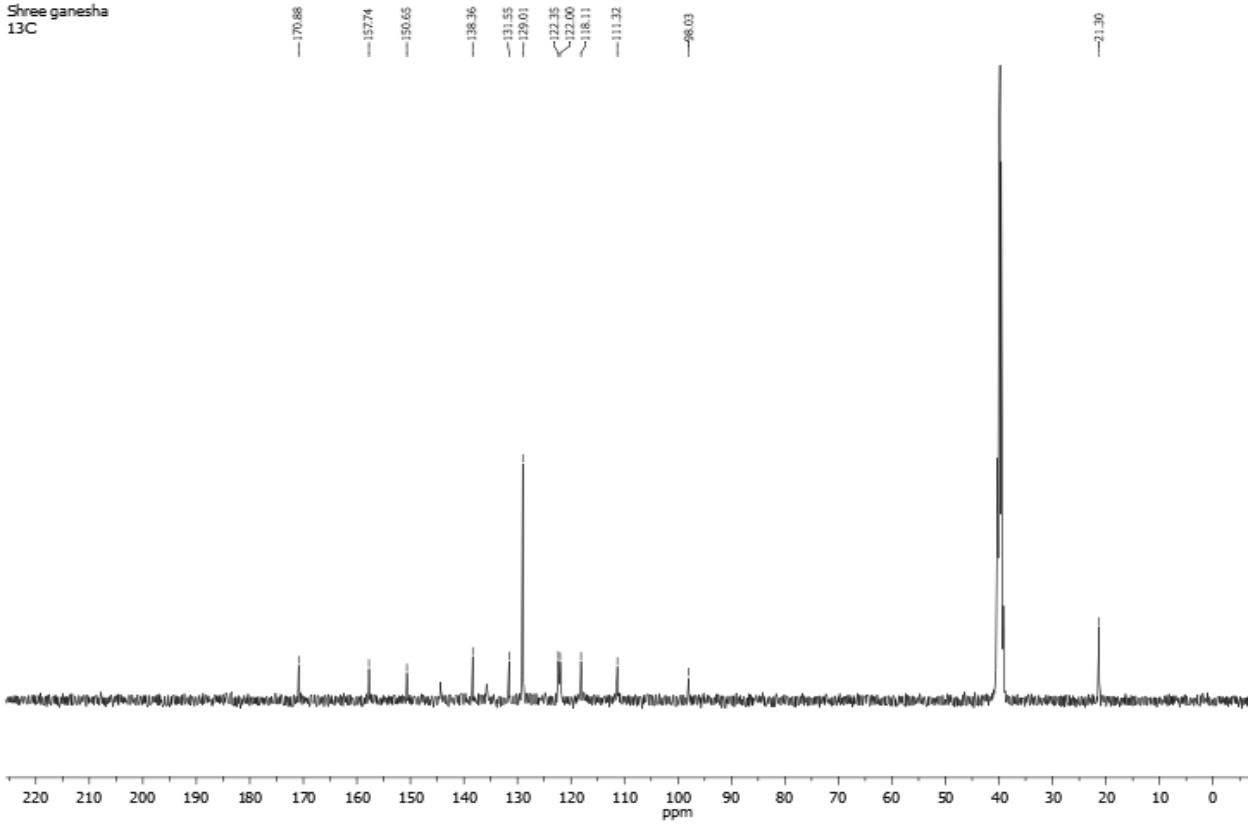
S
N
S
N
NH2


Shree ganesha
13C
170.88
157.74
150.65
138.36
131.55
129.01
122.35
122.00
118.11
111.32
98.03
21.30
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200
190
180
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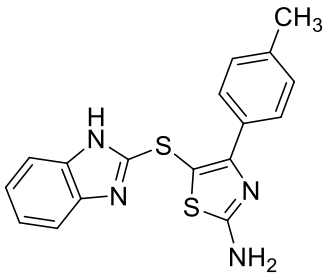
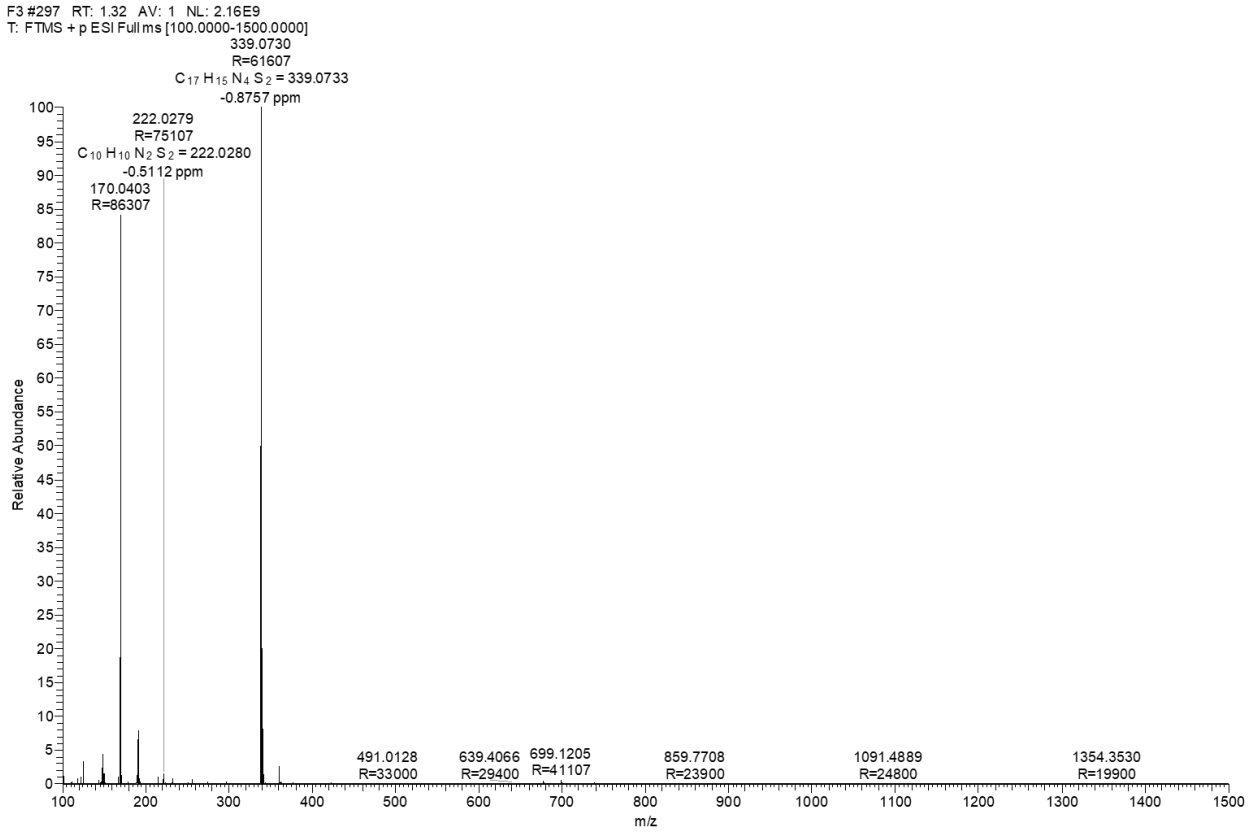
20
10
0
ppm

HRMS



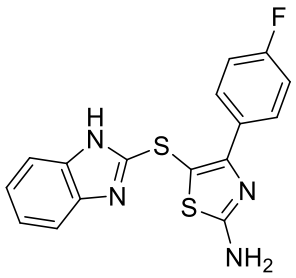
Calculated for $C_{17}H_{14}N_4S_2$: 338.0660, found 339.0730.

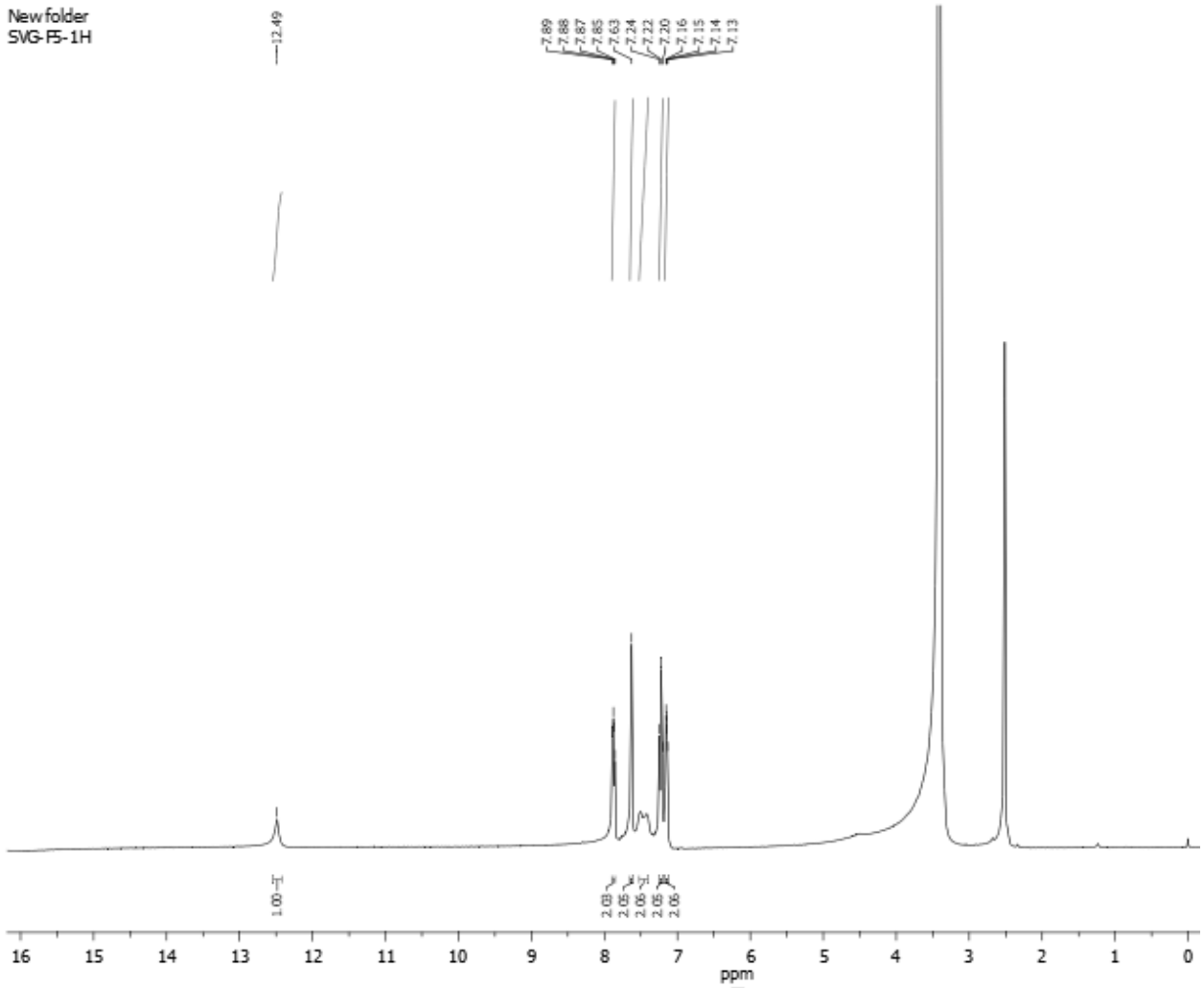


(e) Spectral data of 5-((1H-benzo[d]imidazol-2-yl)thio)-4-(4-fluorophenyl)thiazol-2-amine *(5d)* White solid, mp 112-113 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 12.49 (s, 1H), 7.89-7.85 (m, 2H), 7.63 (m, 2H), 7.24-7.20 (m, 2H), 7.16-7.15 (m 2H), 7.14-7.13 (m 2H). ^{13}C-NMR (400 MHz, DMSO-d_6,) δ 170.95, 163.67, 161.23, 156.57, 150.29, 144.45, 135.84, 131.27, 131.19, 130.88, 130.85, 122.38, 122.01, 118.20, 115.51, 115.30, 111.37,

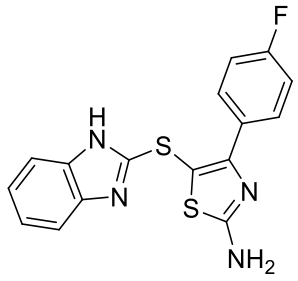
98.84. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{11}FN_4S_2$: 342.0409, found 343.0470.

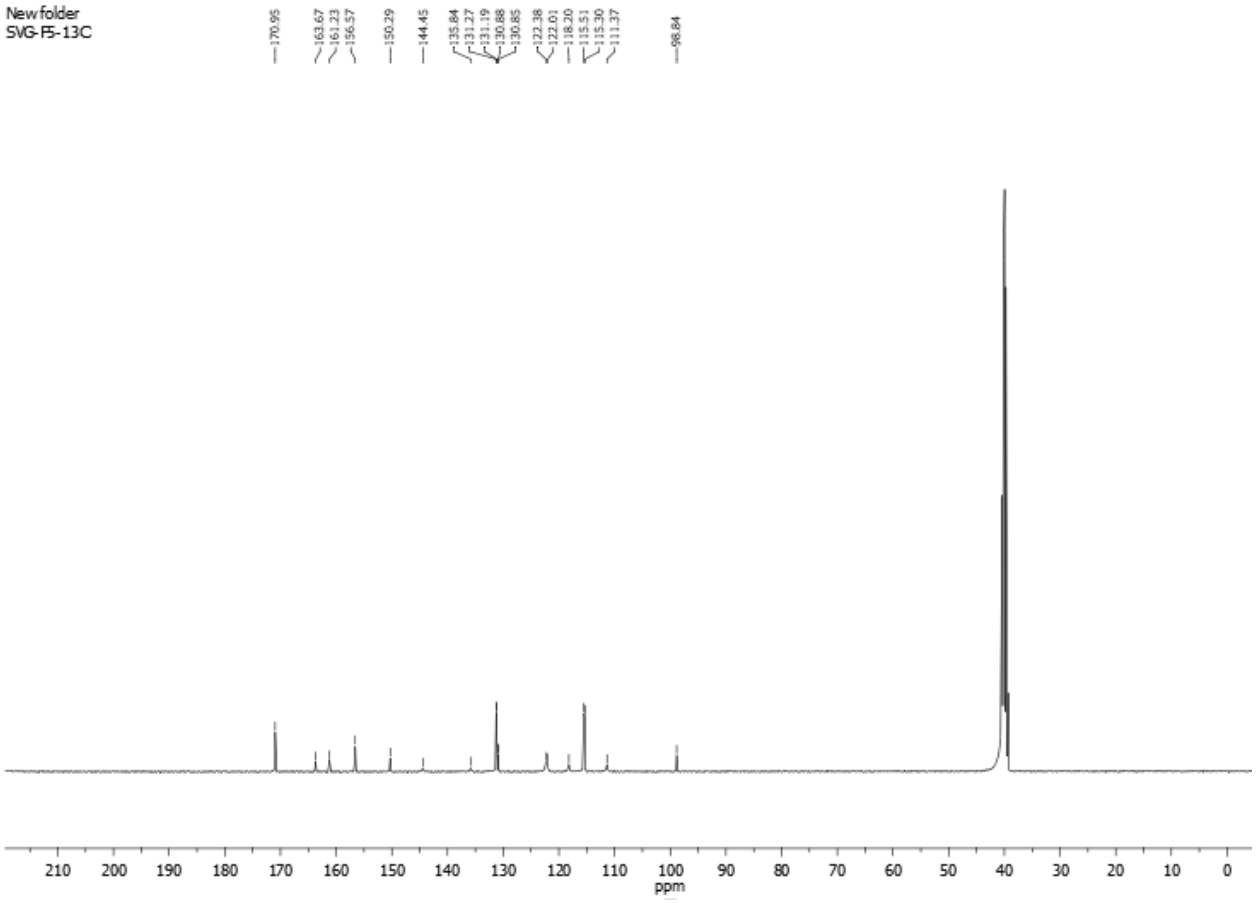
^{1}H NMR





^{13}C NMR


F
H
N
S
N
S
N
NH2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122.38
122.01
118.20
115.51
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111.37
98.84
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190
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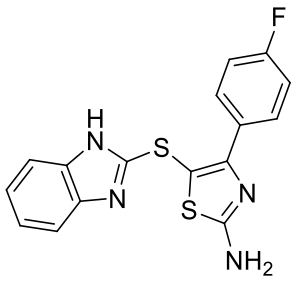
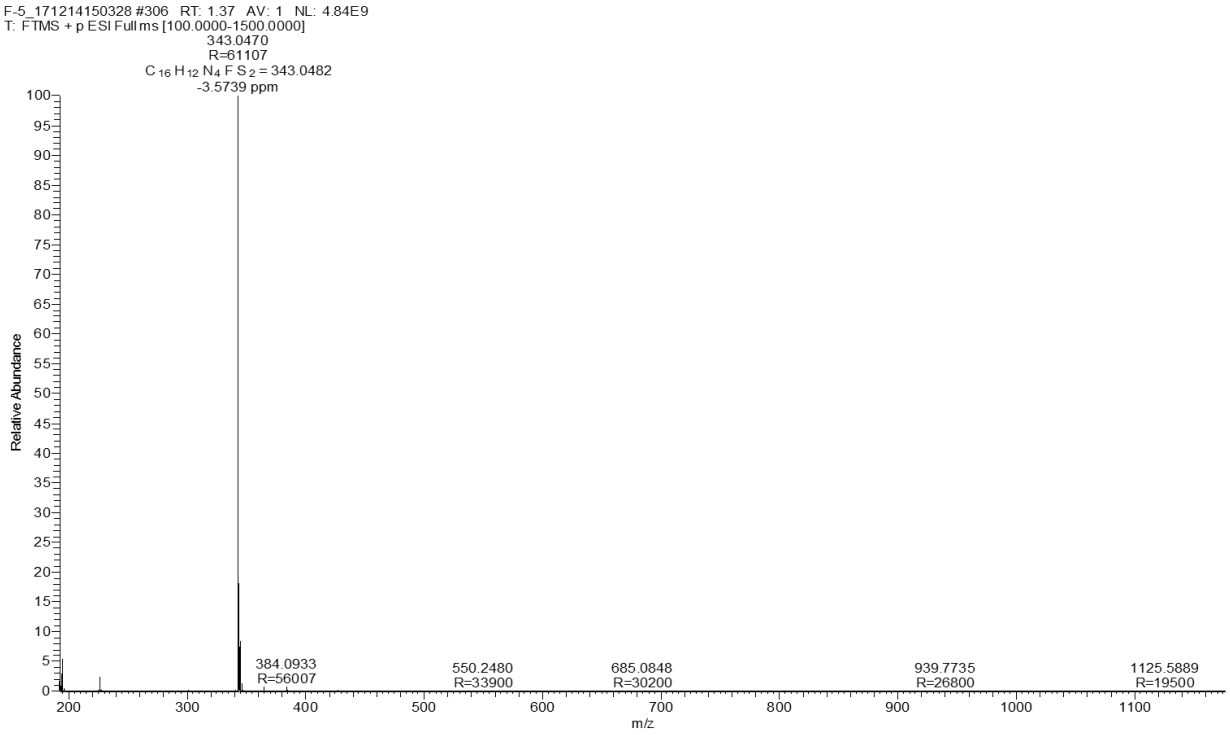
ppm

HRMS



Calculated for $C_{16}H_{11}FN_4S_2$: 342.0409, found 343.0470.



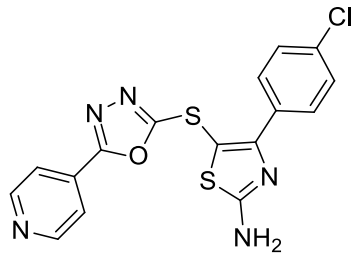
2. a) ***General procedure for the synthesis of 4-(4-chlorophenyl)-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)thiazol-2-amine (5e).***

NCS (1.5 mmol) was taken in round bottom flask containing CH_3OH. To this same pot 5-(pyridin-4-yl)-1,3,4-oxadiazole-2-thiol **(2c)** (**Scheme 2**) (2 mmol) was added slowly with constant stirring, and reaction mass was stirred at room temperature up to 5 minutes.

As TLC indicate the formation of (NHTS). Furthermore to the same pot 4-(4-chlorophenyl)thiazol-2-amine (2 mmol) was added with small proportions at a time and stirring was continued for another 20 minutes, as TLC indicate the completion of reaction. The reaction mass was poured on ice cold water, solid product separated out was filtered, dried and washed with aqueous ethanol. No further purification like column chromatography was needed.

b) Spectral data of 4-(4-chlorophenyl)-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)thiazol-2-amine *(5e)* White solid, mp 115-116 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 8.81 (s, 2H), 7.83 (m, 6H), 7.49-7.48 (m, 2H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 171.63, 164.63, 157.71, 151.43, 133.92, 132.62, 130.97, 130.50, 128.76, 120.48, 95.35. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{10}ClN_5OS_2$: 387.0015, found 388.0096.

^{1}H NMR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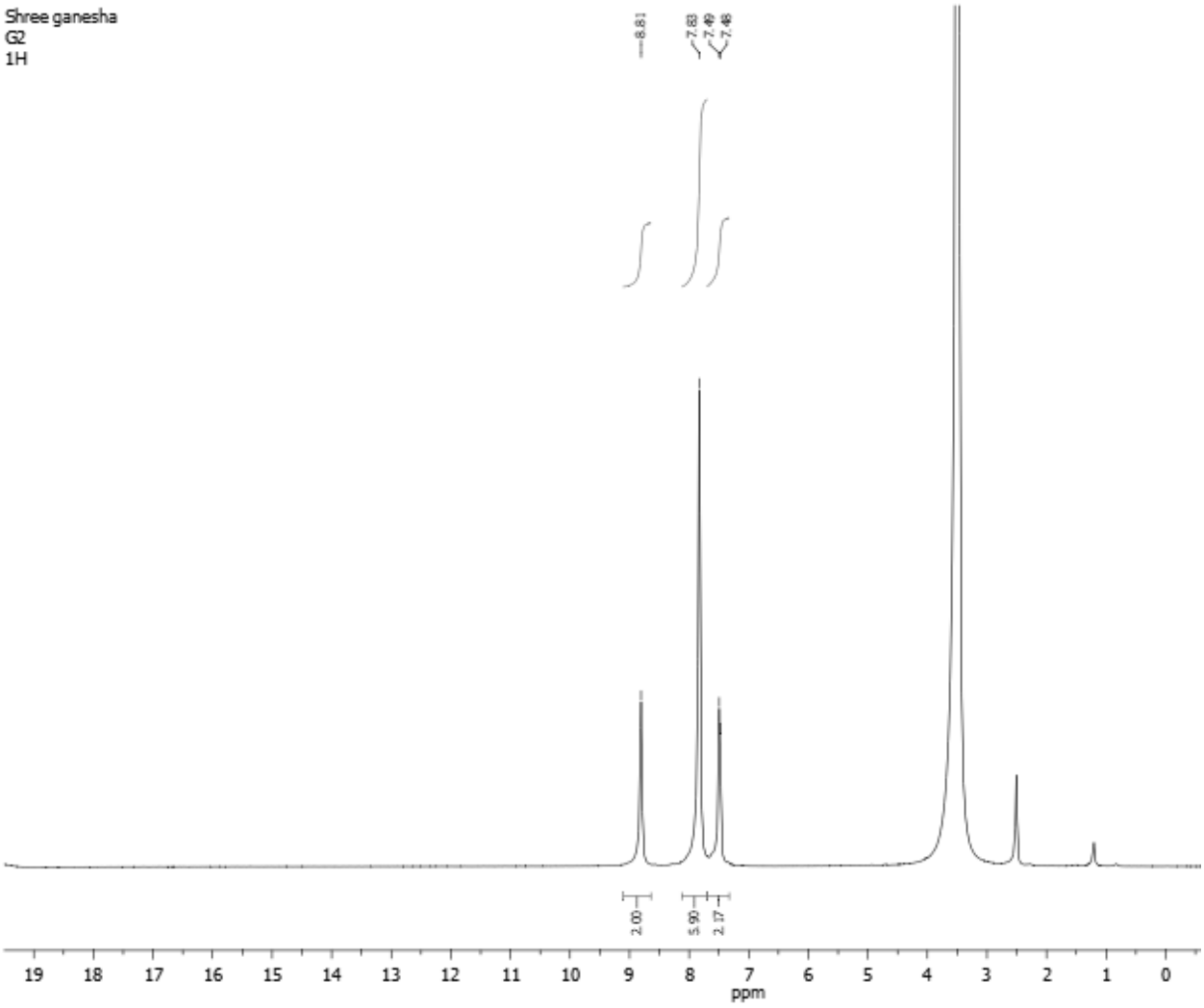
N
N
O
S
S
N
NH2
N


Shree ganesha
G2
1H
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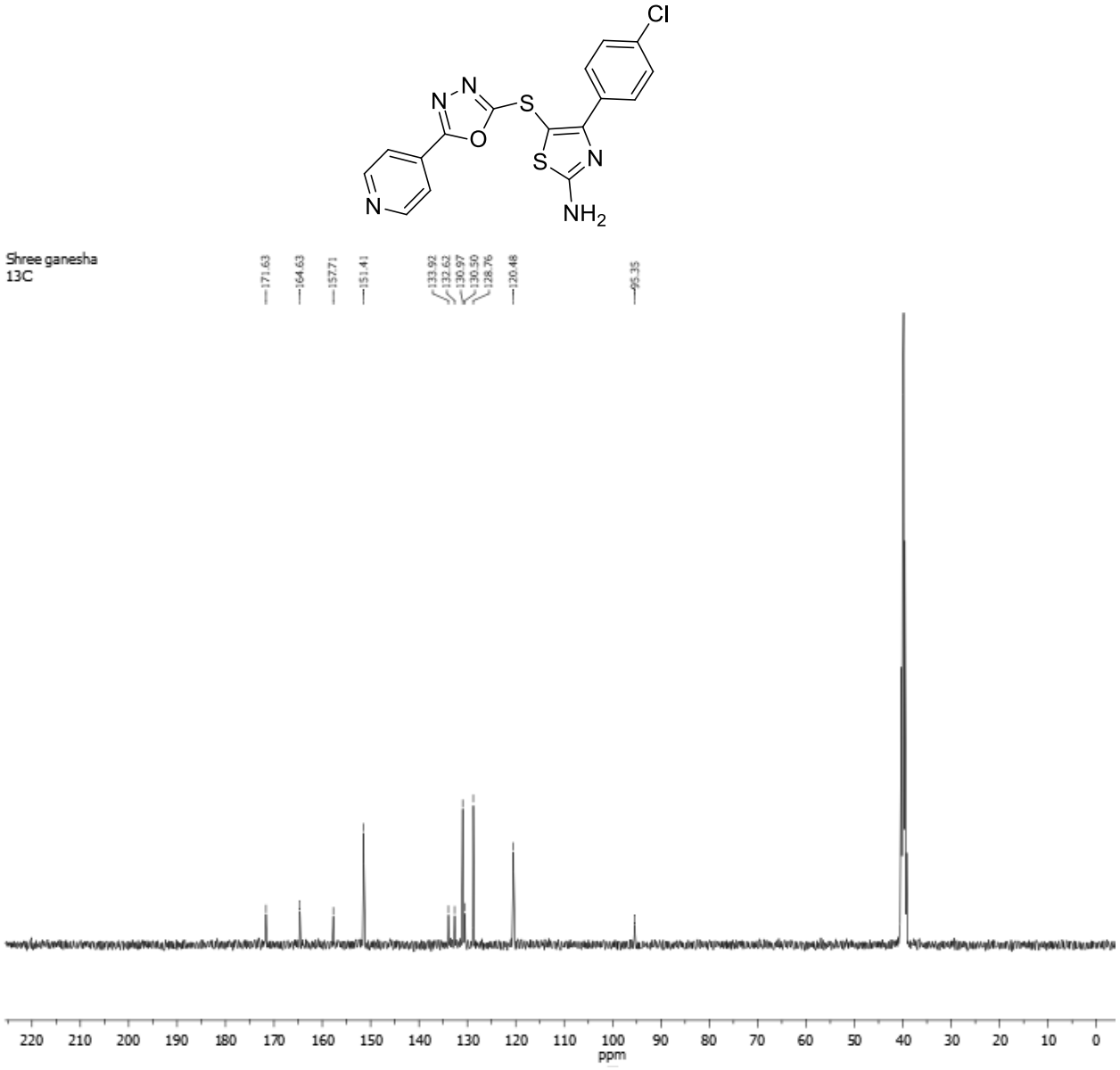
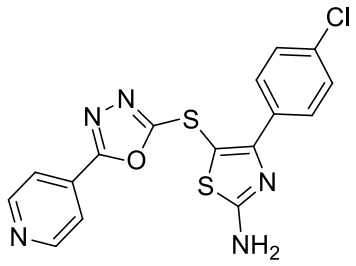
7.83
7.49
7.48
2.00
5.90
2.17
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

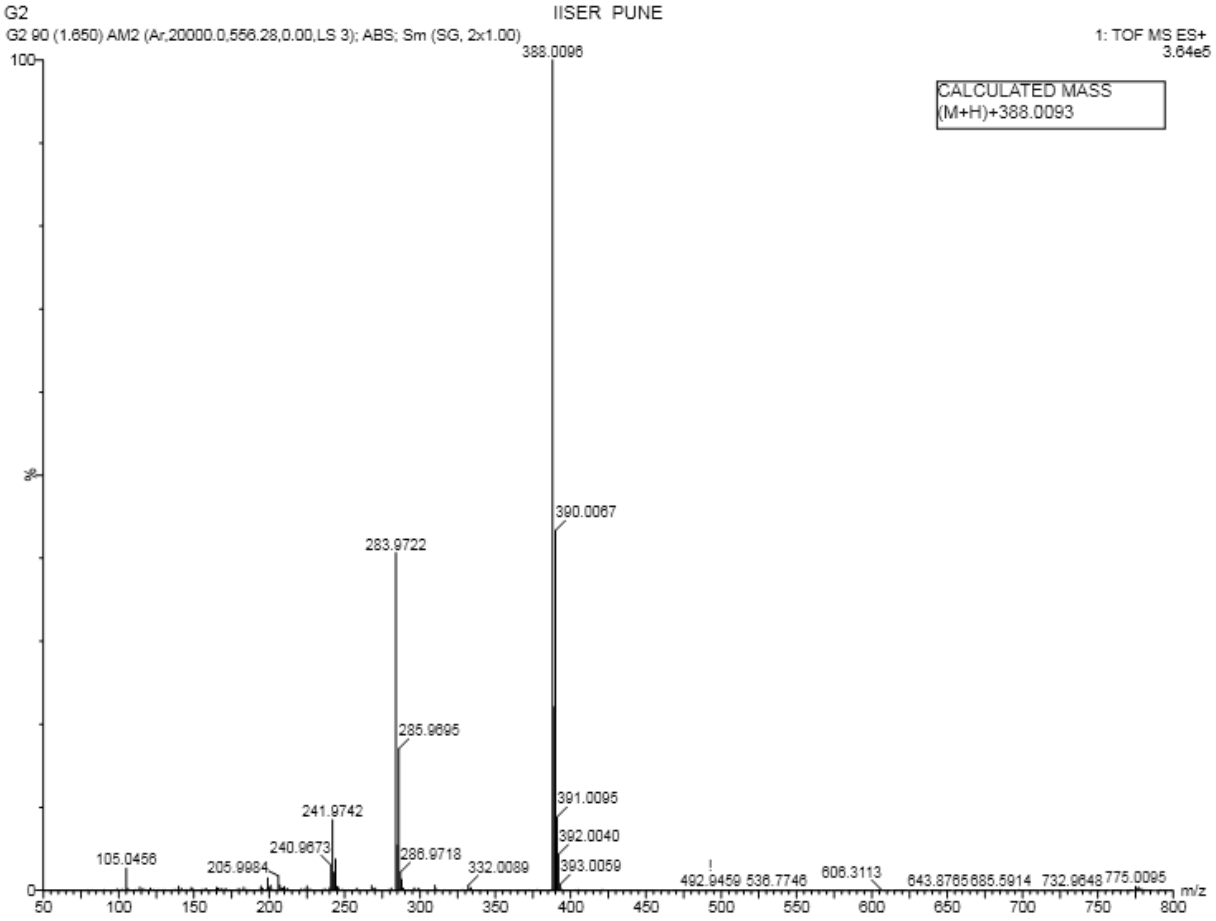
^{13}C NMR


Cl
N
N
S
O
S
N
N
NH2
Shree ganesha
13C
171.63
164.63
157.71
151.41
133.92
132.62
130.97
130.50
128.76
120.48
95.35
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



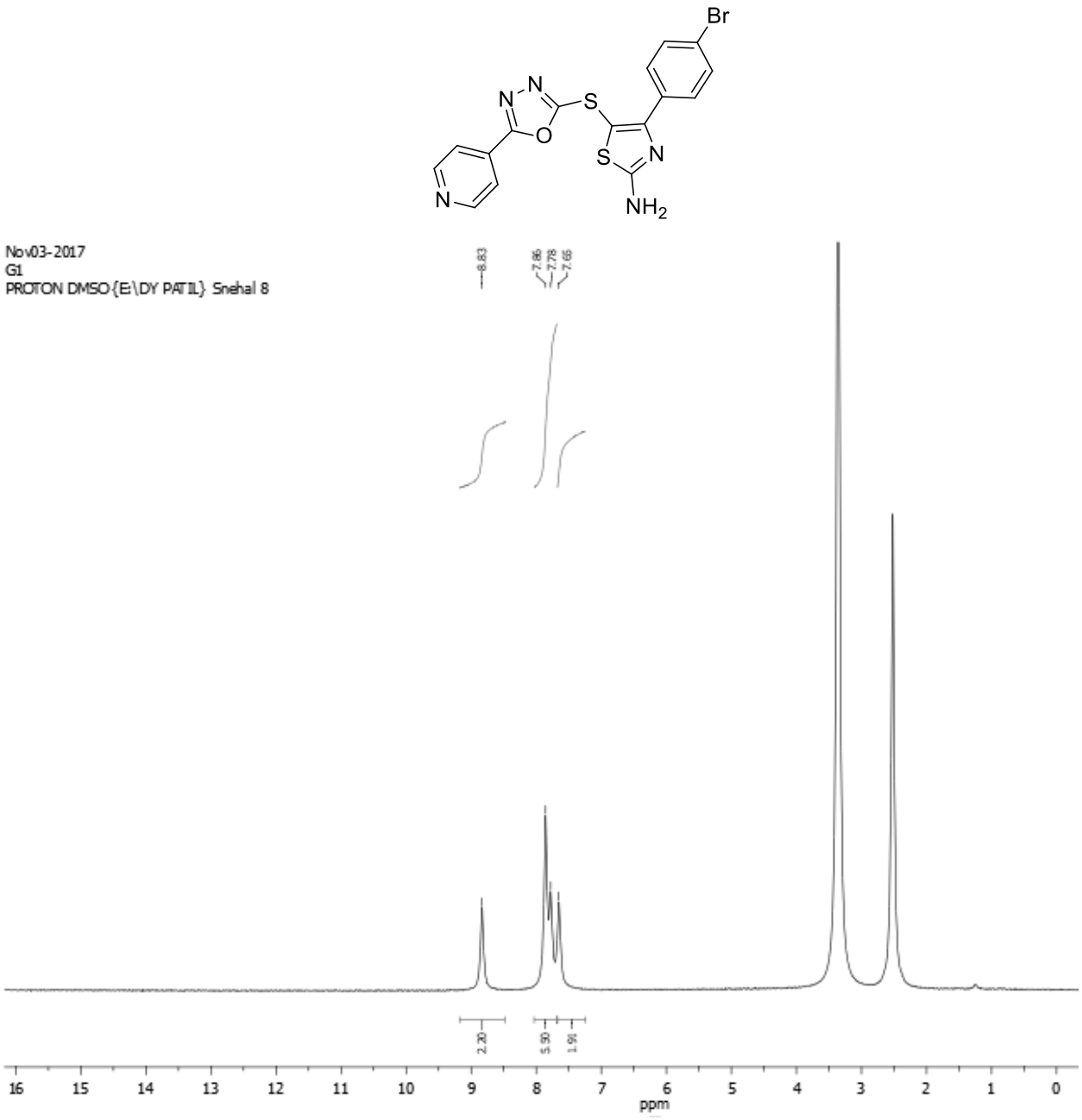
Calculated for $C_{16}H_{10}ClN_5OS_2$: 387.0015, found 388.0096.



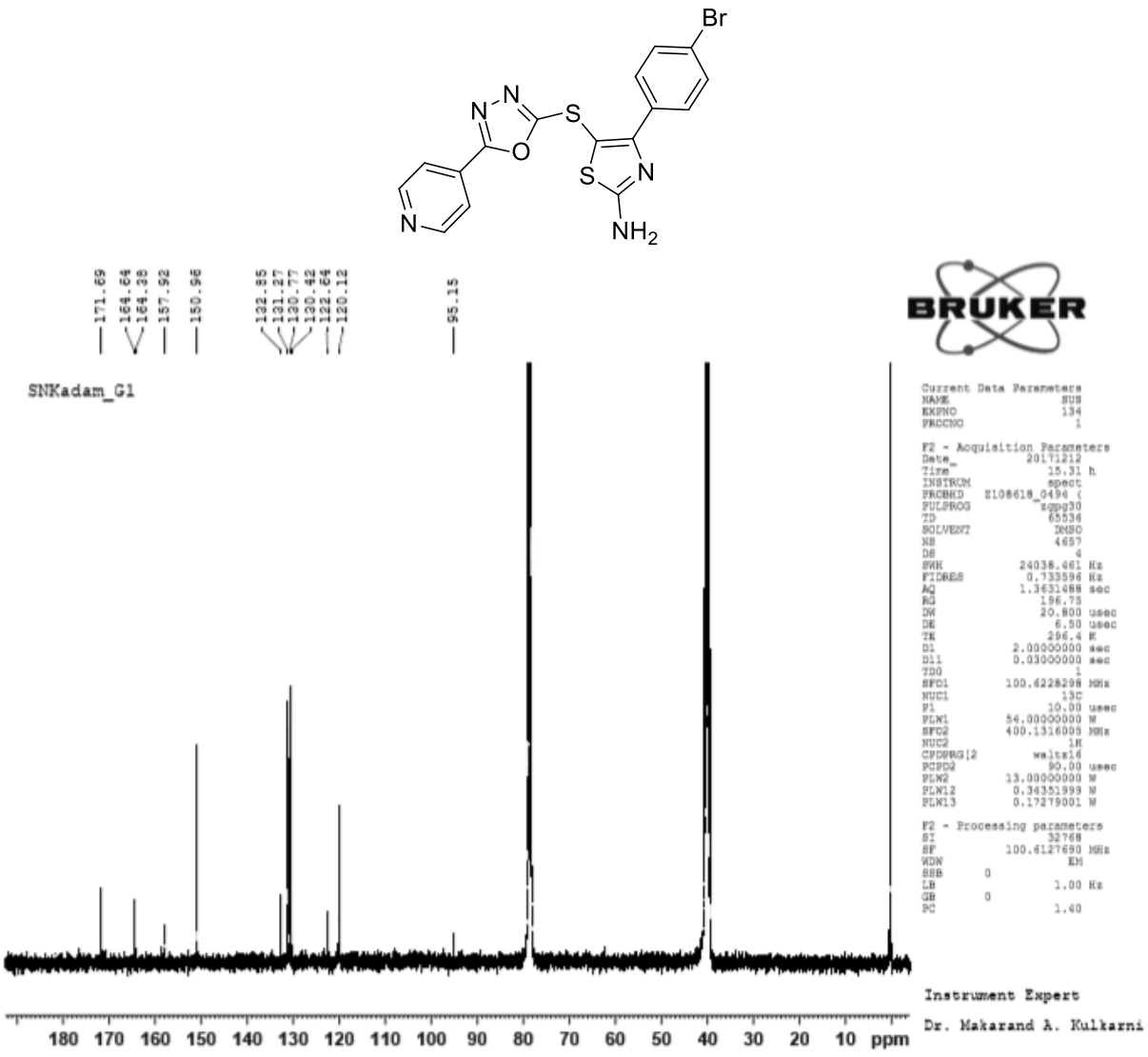
(c) Spectral data of *5-((1H-benzo[d]imidazol-2-yl)thio)-4-(4-bromophenyl)thiazol-2-amine (5f)* White solid, mp 120-121 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 8.83 (s, 2H), 7.86-7.78 (m, 6H), 7.66 (m, 2H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 171.69, 164.64,

164.33, 157.92, 150.98, 132.88, 131.27, 130.77, 130.42, 122.64, 120.12, 98.15. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{10}BrN_5OS_2$: 430.9510, found 433.9542.

^{1}H NMR



^{13}C NMR


Br
N
N
O
S
S
N
NH2
N
171.69
164.64
164.38
157.92
150.96
132.85
131.27
130.77
130.42
122.64
120.12
95.15
BRUKER
SNKadam_G1
Current Data Parameters
NAME SUS
EXPNO 134
PROCNO 1
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PULPROG zgpg30
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SOLVENT DMSO
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RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 296.4 K
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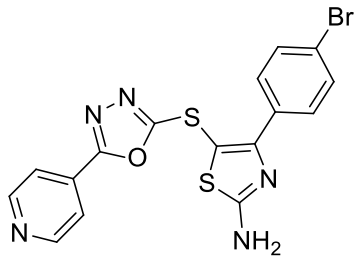
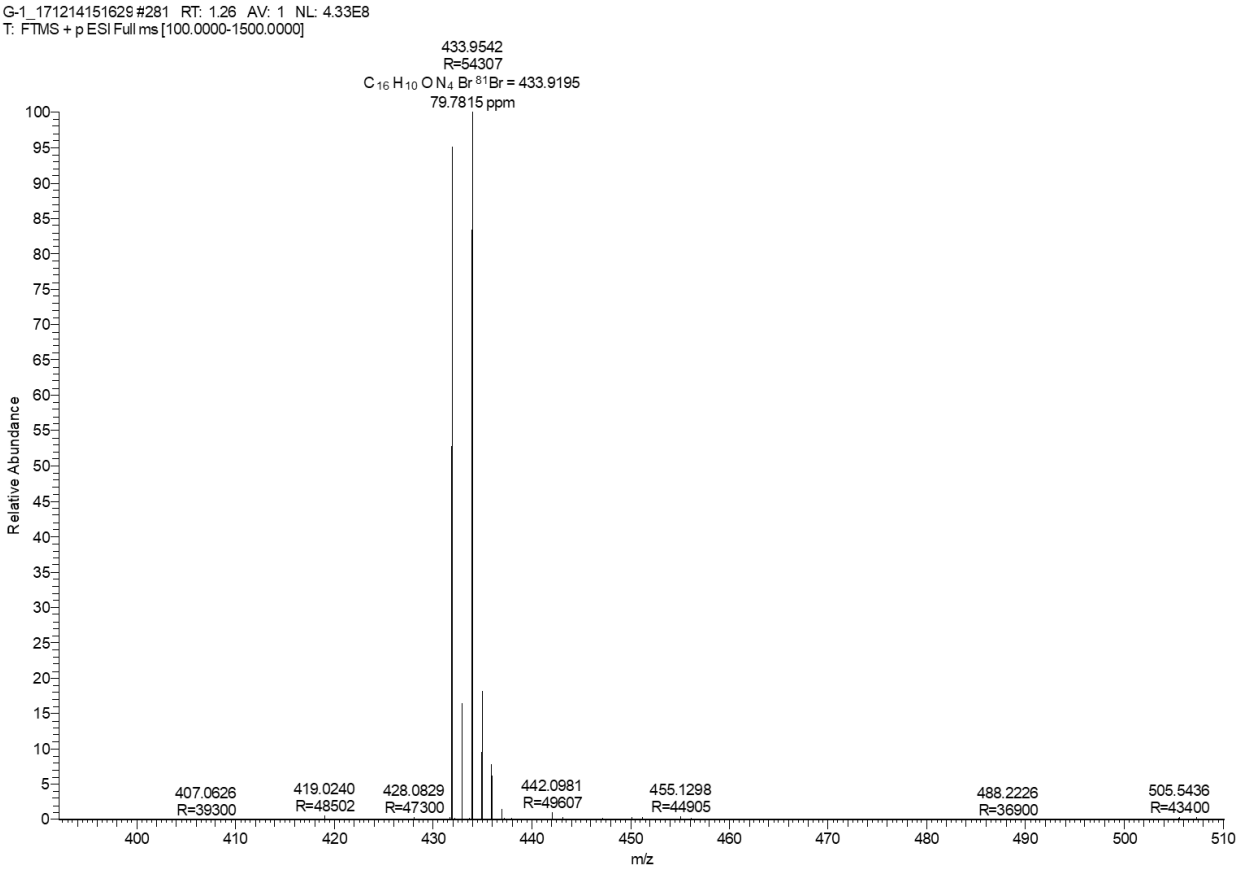
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.34351999 W
PLW13 0.17279001 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

HRMS



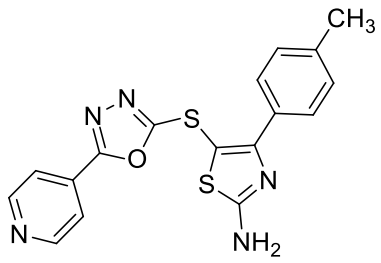
Calculated for $C_{16}H_{10}BrN_5OS_2$: 430.9510, found 433.9542.

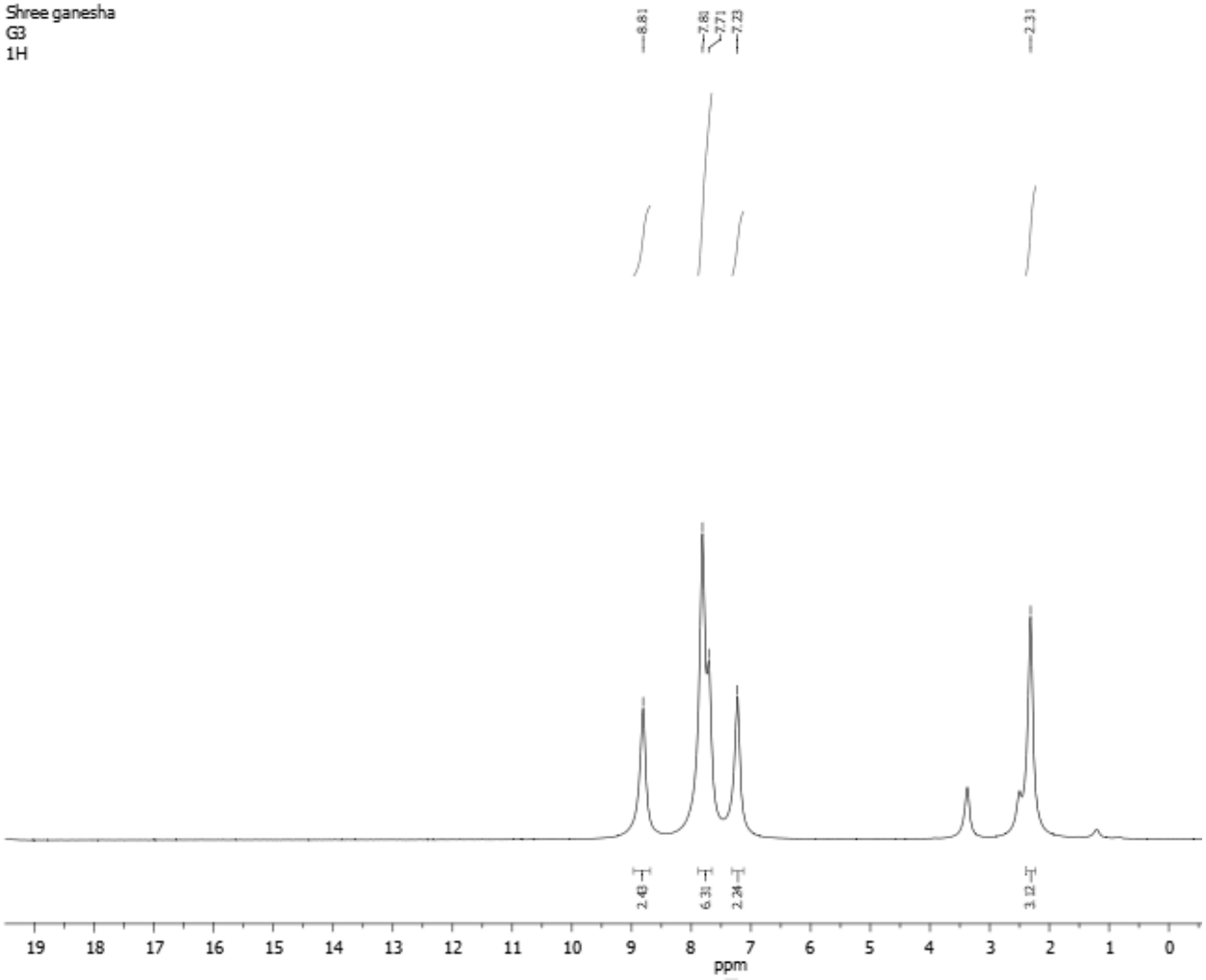


(d) Spectral data of 5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)-4-(p-tolyl)thiazol-2-amine *(5g)* White solid, mp 118-119 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 8.81 (s, 2H), 7.81-7.71 (m, 6H), 7.23 (m, 2H), 2.31 (s, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 171.48,

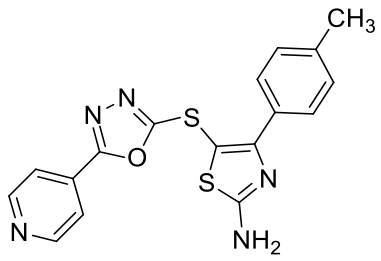
164.82, 164.56, 159.21, 151.41, 138.74, 131.12, 130.49, 129.21, 120.43, 93.91, 21.35. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{17}H_{13}N_5OS_2$: 367.0562, found 368.0643.

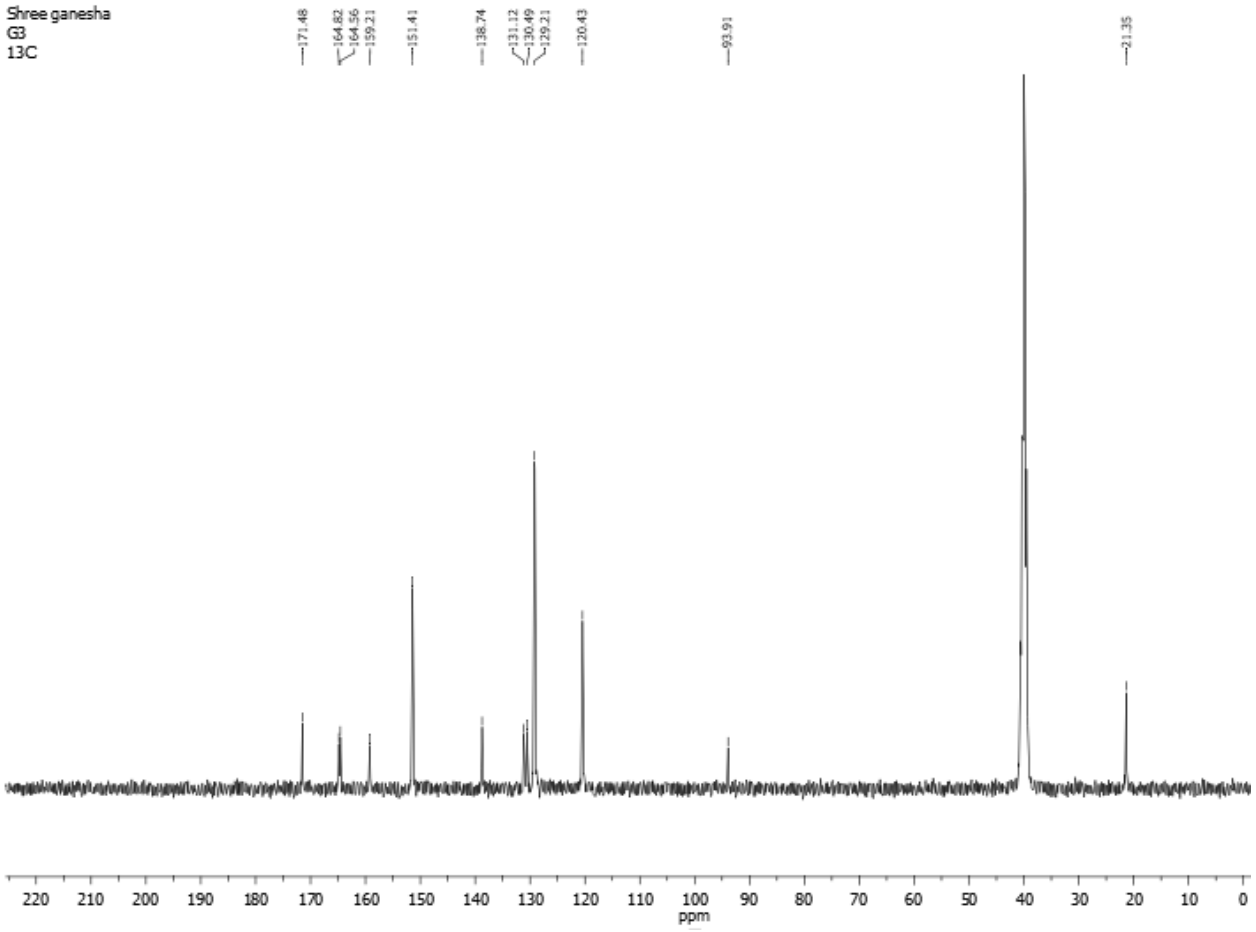
^{1}H NMR



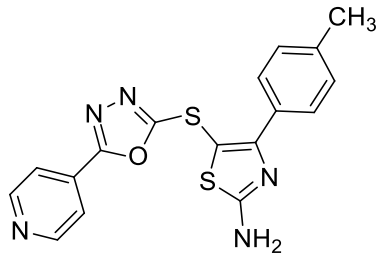


^{13}C NMR

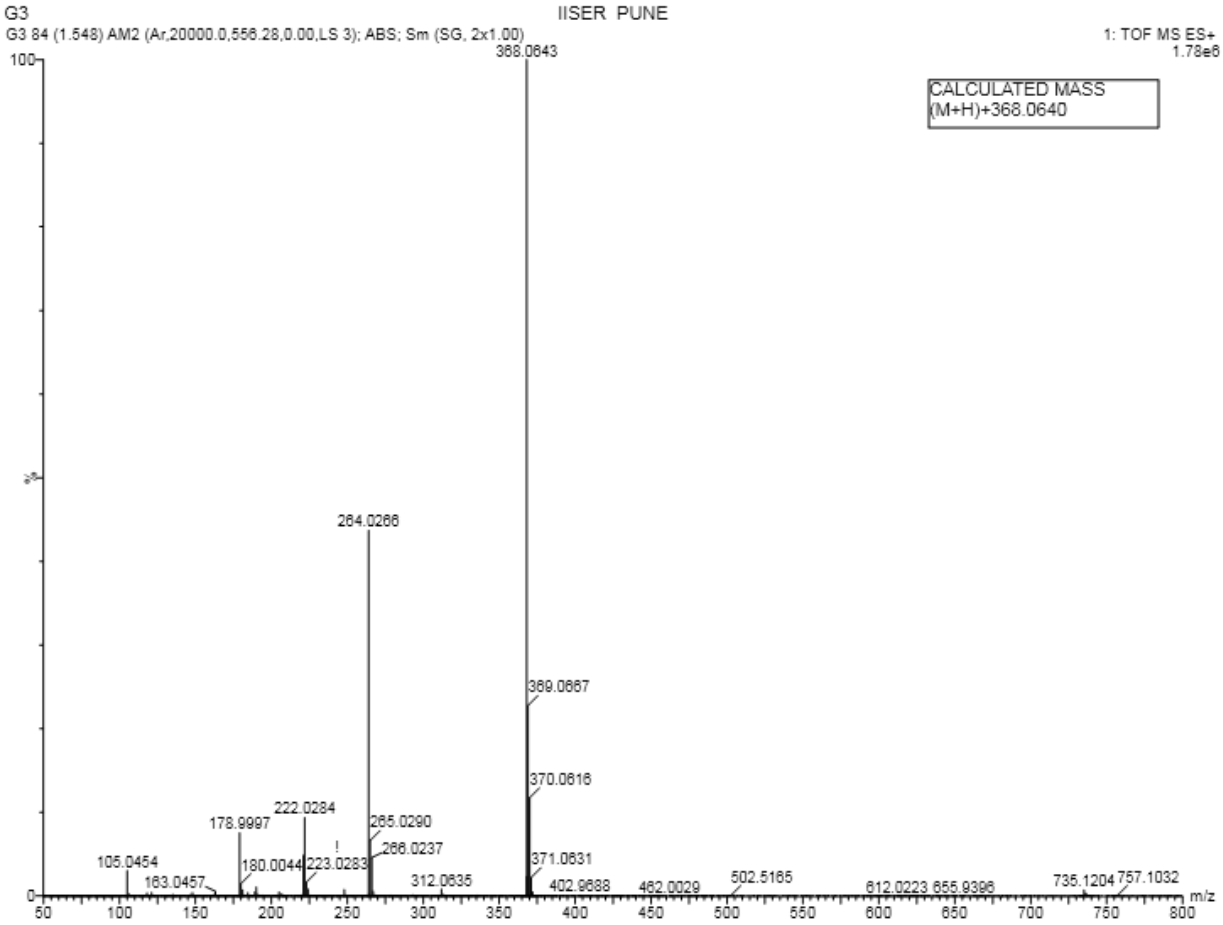

CH3
N
N
O
S
S
N
N
NH2


Shree ganesha
G3
13C
171.48
164.82
164.56
159.21
151.41
138.74
131.12
130.49
129.21
120.43
93.91
21.35
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



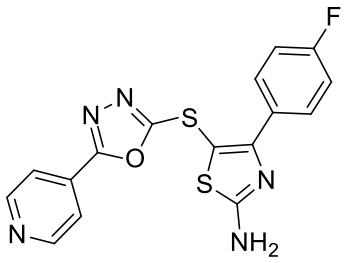
Calculated for $C_{17}H_{13}N_5OS_2$: 367.0562, found 368.0643.

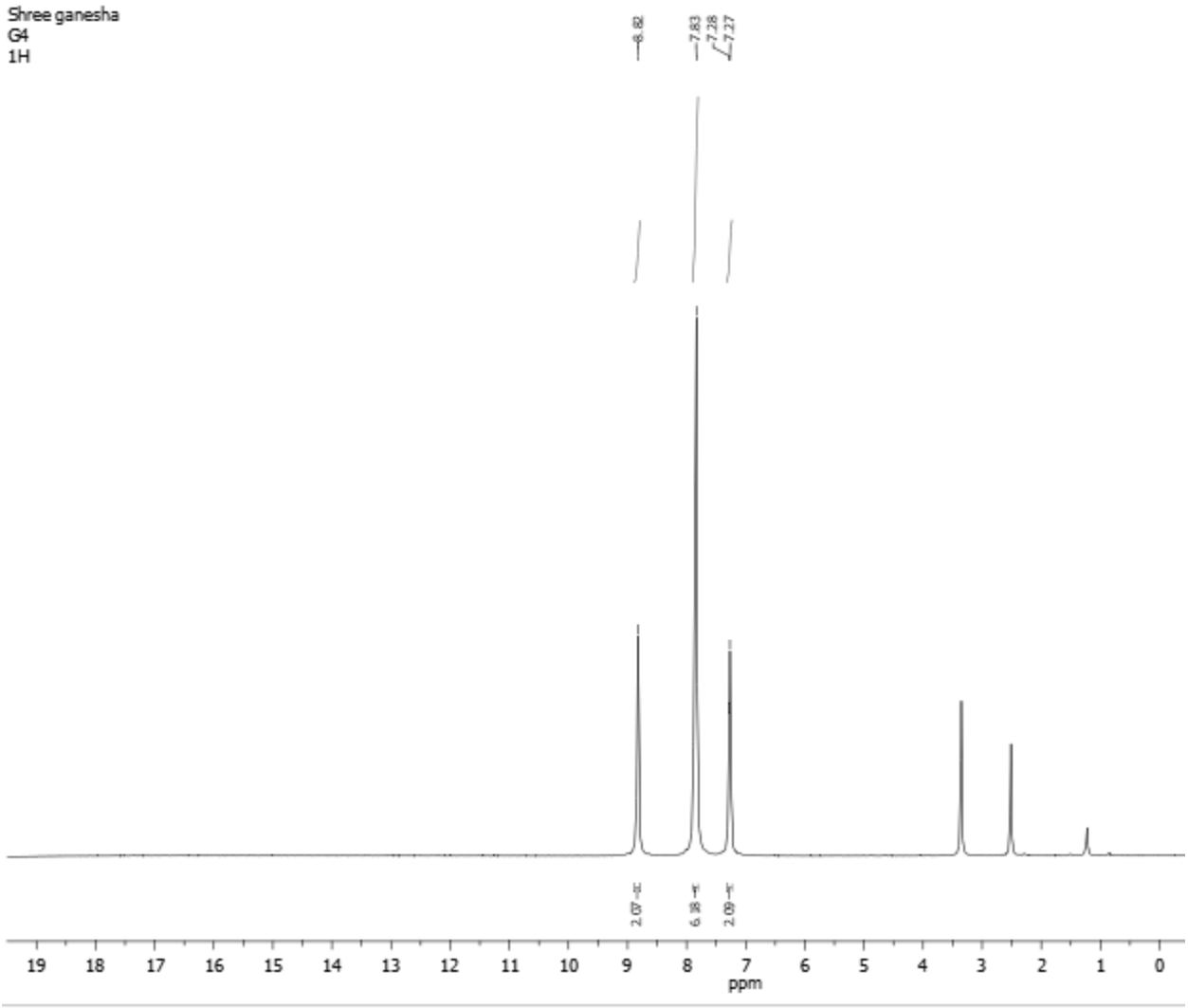


(e) Spectral data of 4-(4-fluorophenyl)-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)thiazol-2-amine *(5h)* White solid, mp 115-116 ºC. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$,) δ 8.82 (s, 2H), 7.83 (m, 6H), 7.28-7.27 (m, 2H). ^{13}C-NMR (400 MHz, DMSO-*d*$_6$) δ

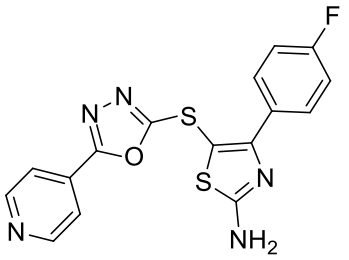
171.57,164.67, 163.88, 158.44, 131.48, 130.52, 130.35, 120.47, 115.73, 115.52, 94.54. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{10}FN_5OS_2$: 371.0311, found 372.0392.

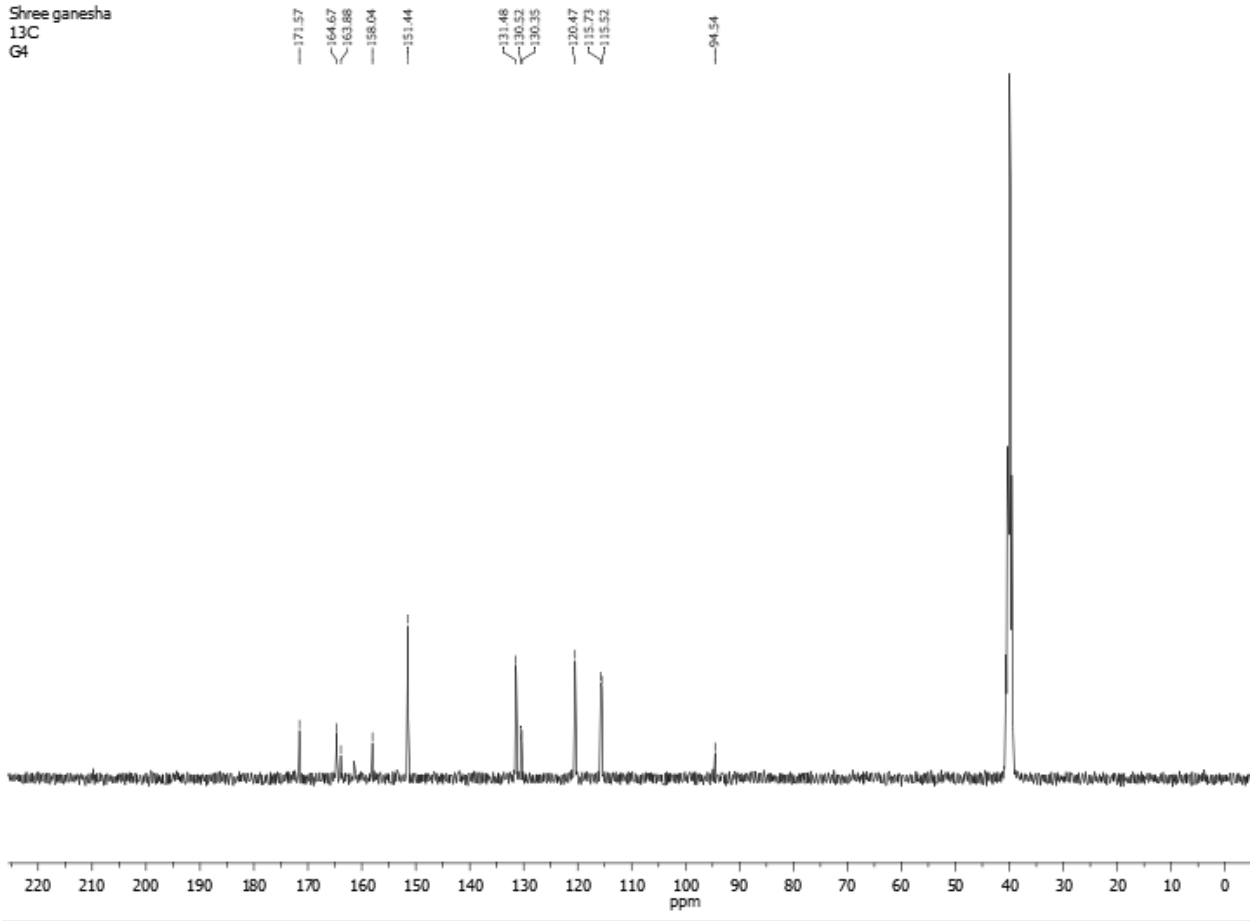
^{1}H NMR



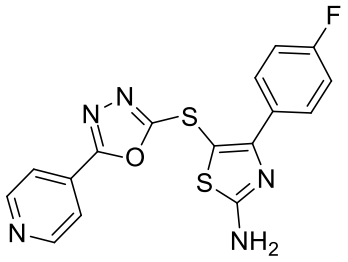


^{13}C NMR

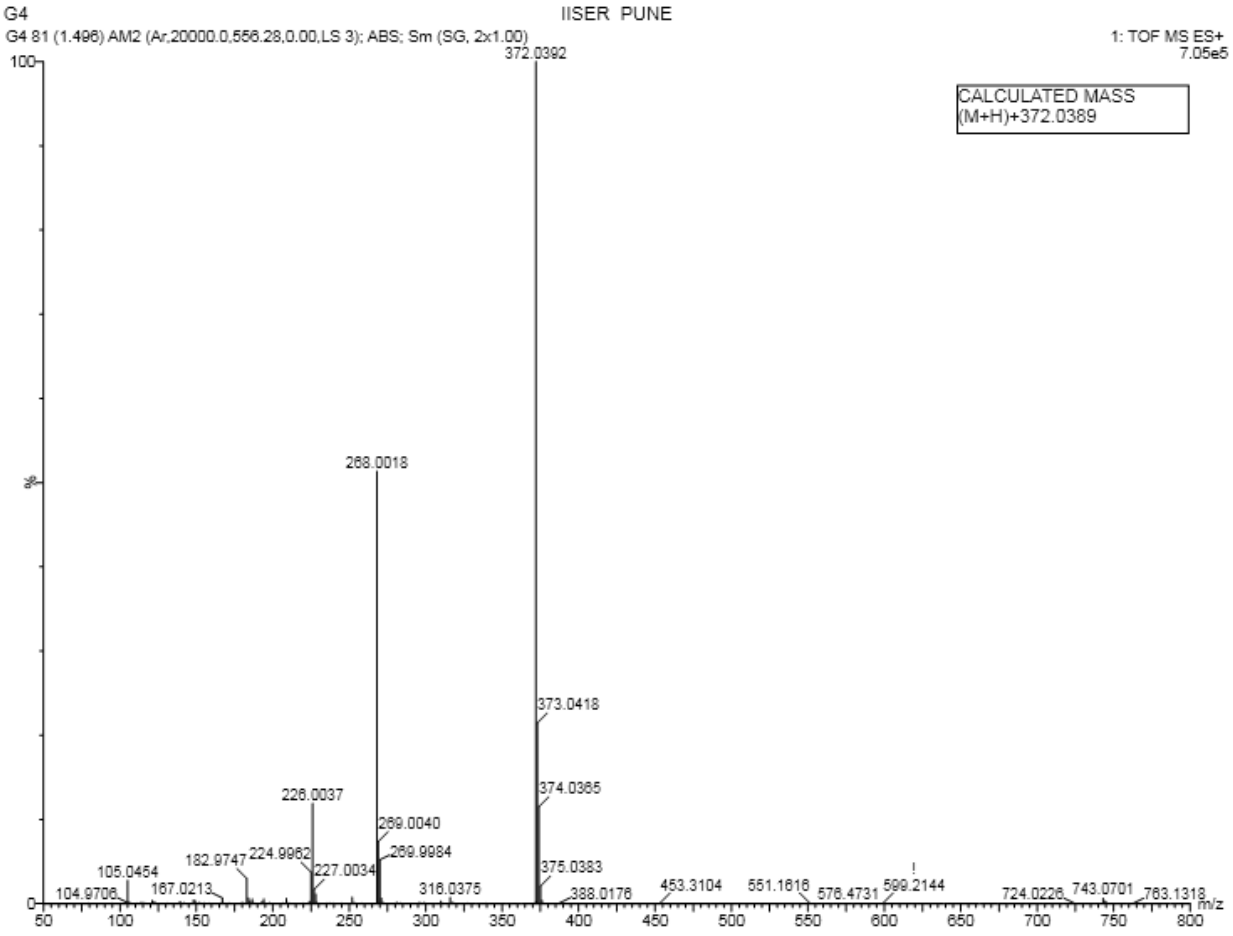

F
N
N
O
S
S
N
N
NH2


Shree ganesha
13C
G4
171.57
164.67
163.88
158.04
151.44
131.48
130.52
130.35
120.47
115.73
115.52
94.54
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



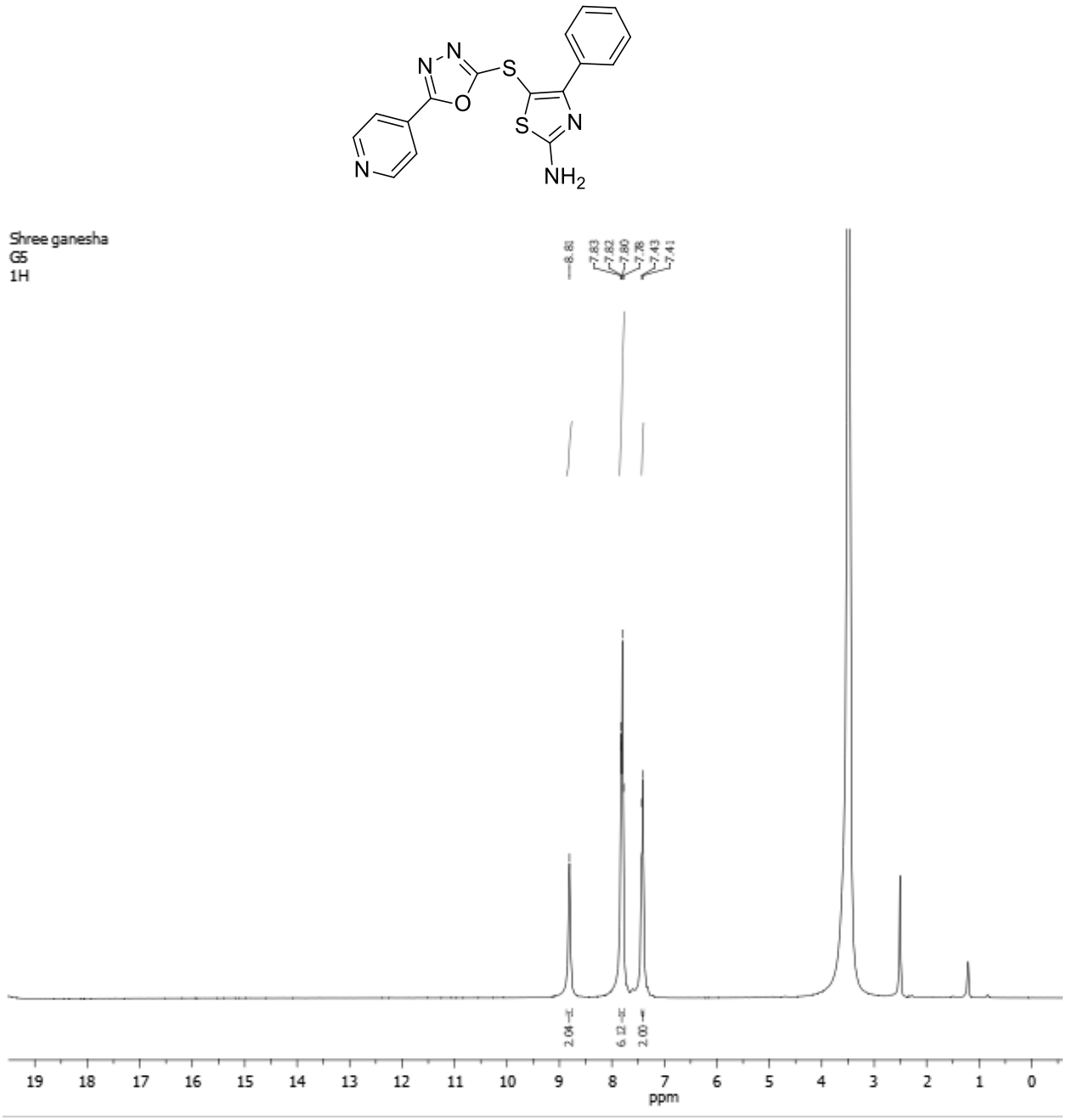
Calculated for $C_{16}H_{10}FN_5OS_2$: 371.0311, found 372.0392.



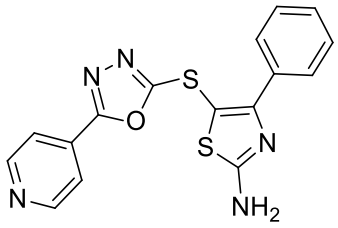
(f) Spectral data of 4-phenyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)thiazol-2-amine *(5i)* White solid, mp 110-112 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 8.81 (s, 2H), 7.83-7.78 (m, 6H), 7.43-7.41 (m, 2H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 171.57, 164.80,

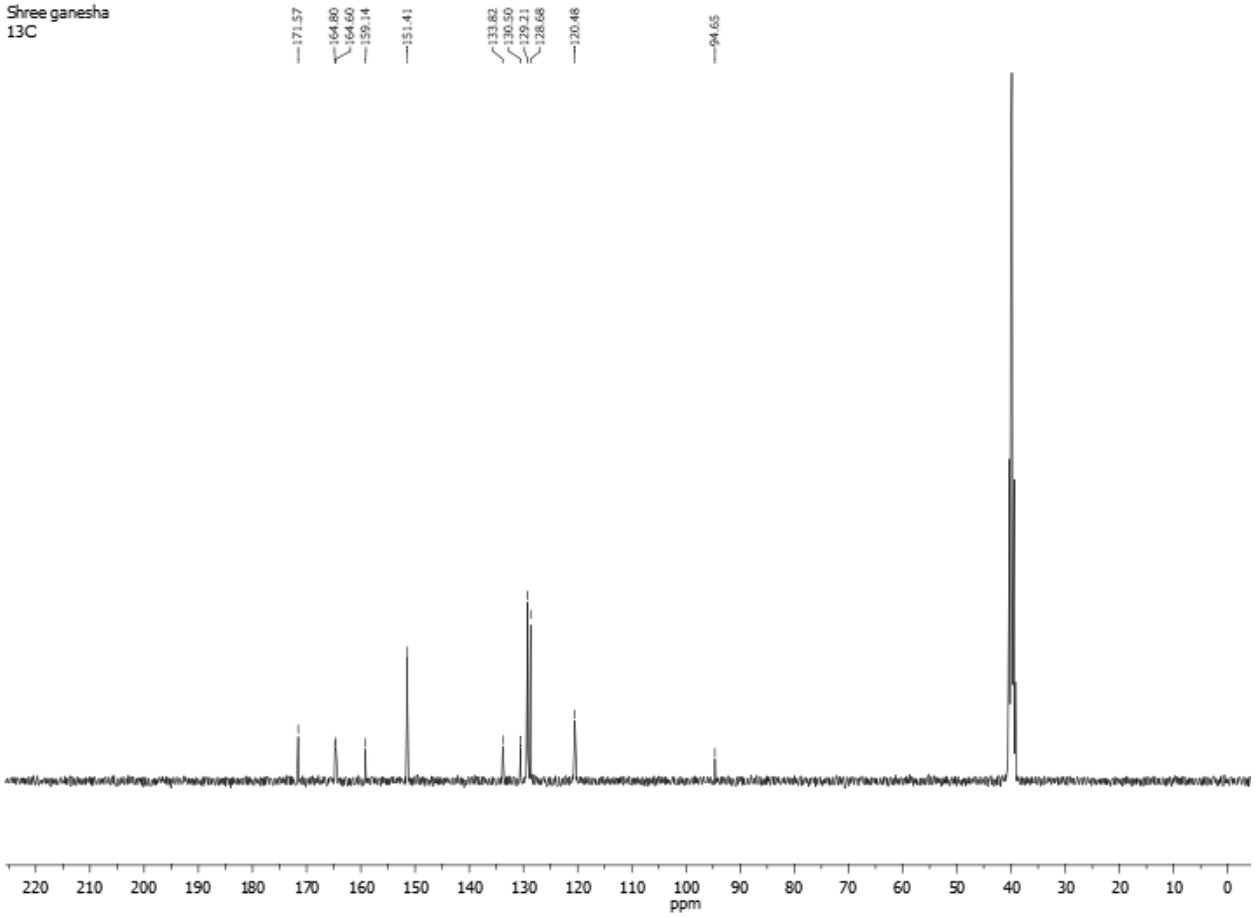
164.60, 159.14, 133.82, 130.50, 129.21, 128.68, 120.48, 94.65. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{16}H_{11}N_5OS_2$: 353.0405, found 354.0485.

^{1}H NMR

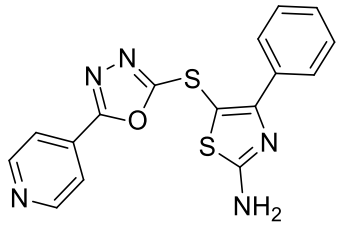


^{13}C NMR

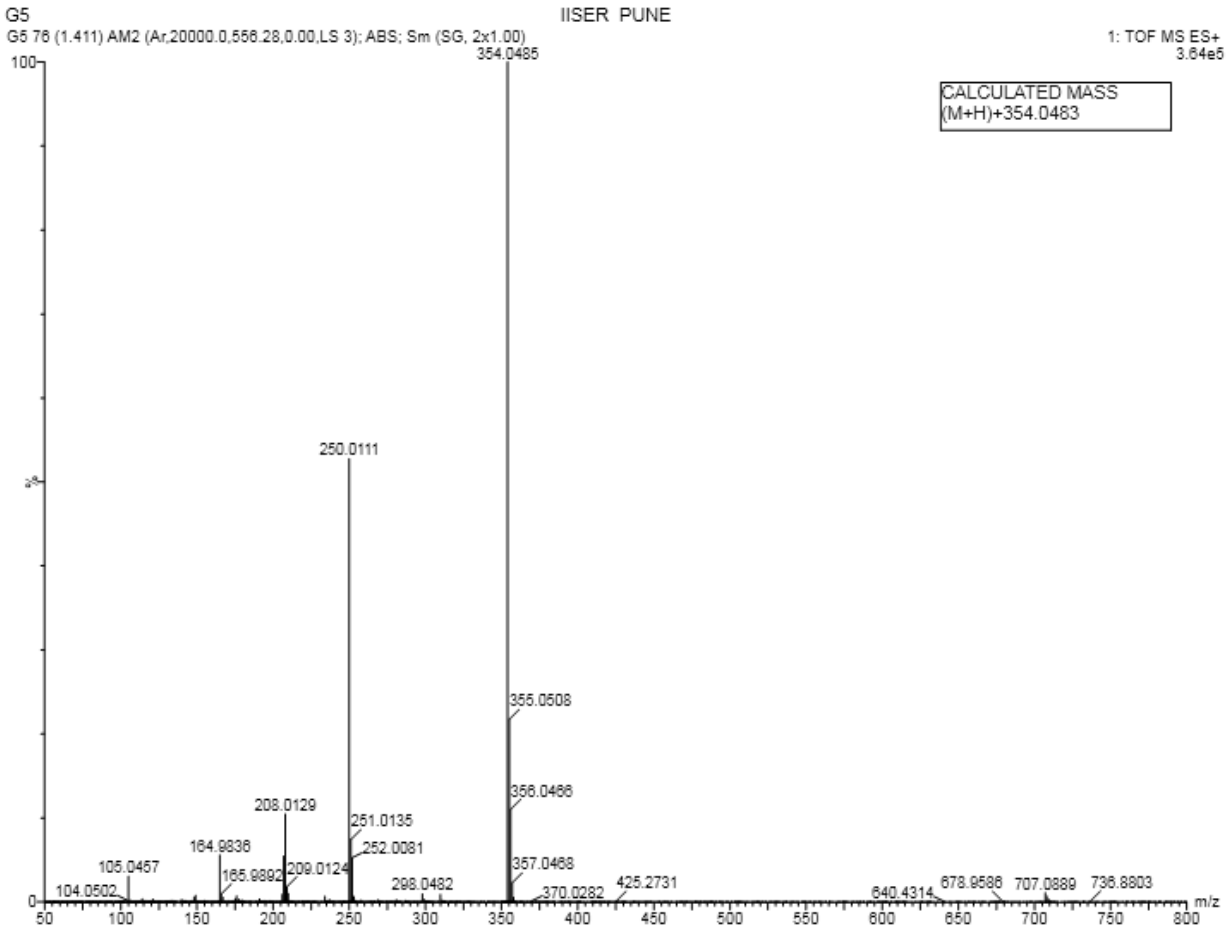

N
N
O
S
S
N
N
NH2


Shree ganesha
13C
171.57
164.80
164.60
159.14
151.41
133.82
130.50
129.21
128.68
120.48
94.65
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



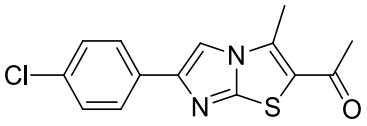
Calculated for $C_{16}H_{11}N_5OS_2$: 353.0405, found 354.0485.

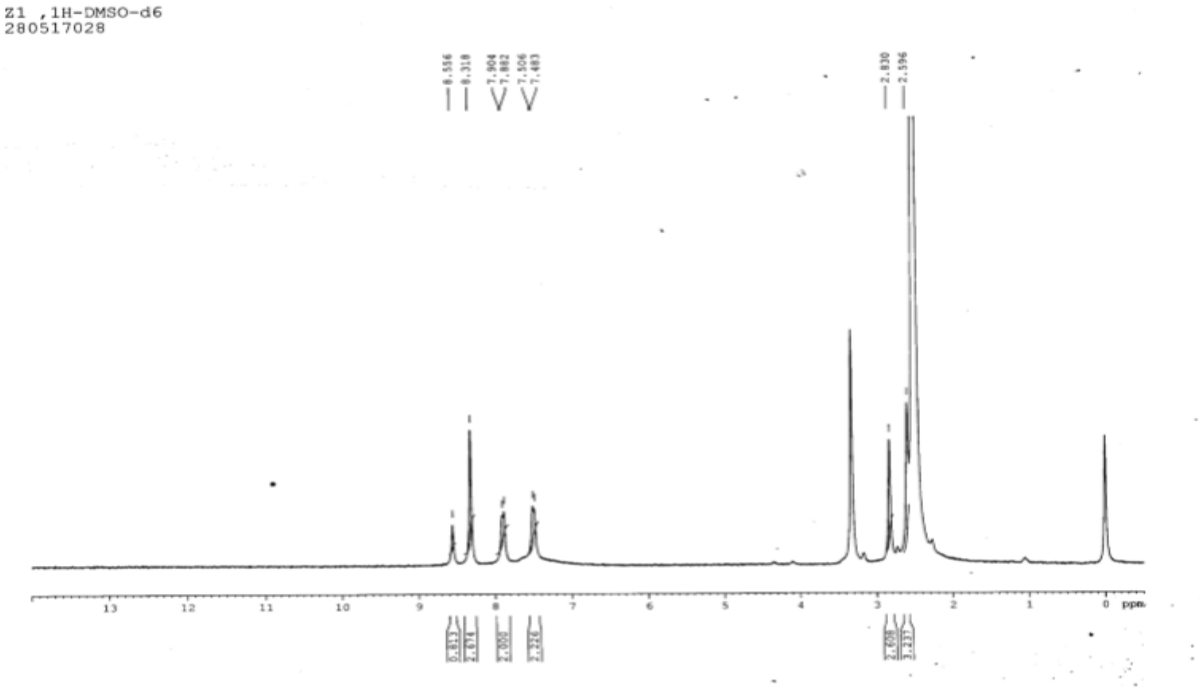


3. Spectral data of *1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethenone*

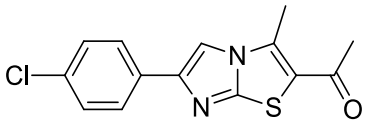
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 (s, 1H, =C-H), 7.89-7.87 (dd, 2H, Ar-H), 7.80-7.47 (dd, 2H, Ar-H), 2.81 (s, 3H, -CH_3), 2.58 (s, 3H, -CH_3). ^{13}C NMR (100 MHZ, DMSO-d_6): δ 190.77, 147.82, 147.25, 135.02, 132.87, 132.46, 128.84, 126.79, 125.24, 108.42, 29.73, 14.04.

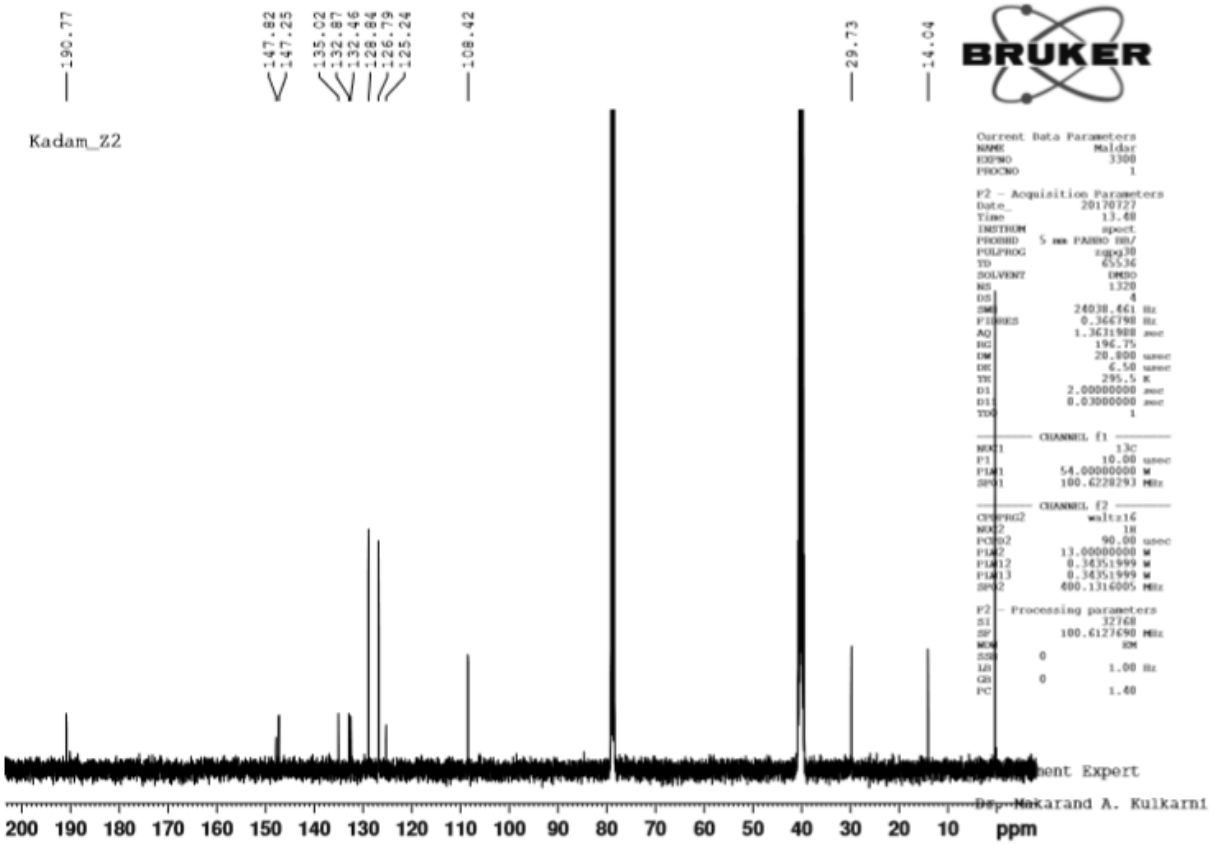
^{1}H NMR





^{13}C NMR





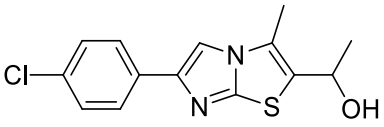
4. a) General procedure for the synthesis of 1-(6-(4-chlorophenyl)-3- methylimidazo[2,1 b]thiazol-2-yl)ethanol (6a).

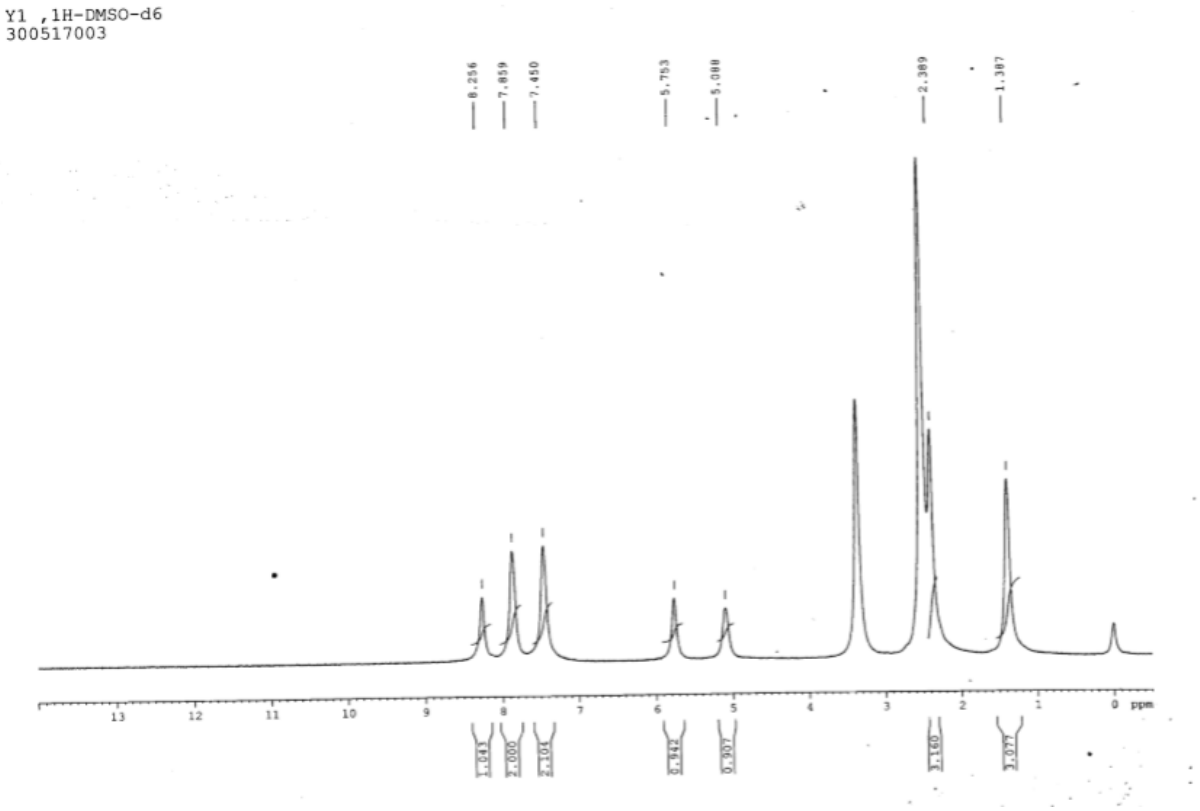
For the synthesis of 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (**6a**), 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethenone, (1mmol), was stirred in CH_3OH at room temperature for 1-2 hours in presence of $NaBH_4$ (1.5mmol) as reducing agent. After completion of reaction (monitored by TLC), the

reaction mass was poured in ice cold water and neutralized with dilute HCl. The solid separated was filtered, dried and washed with cold methanol to furnish product as white amorphous solid.

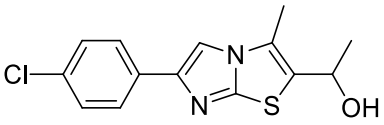
b) Spectral data of *1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (6a)*. white solid, mp 100-101 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.25 (s, 1H =C-H), 7.85 (s, 2H, Ar-H), 7.45 (s, 2H, Ar-H), 5.75 (s, 1H, >C-H), 5.08 (s, 1H, -OH), 2.38 (s, 3H, -CH_3), 1.38 (s, 3H, -CH_3). ^{13}C NMR (100 MHZ, DMSO-d_6): δ 147.69, 144.75, 133.43, 131.96, 131.35, 128.72, 126.42, 122.07, 107.33, 62.47, 25.15, 11.61. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{14}H_{13}ClN_2OS$: 292.0437, found 293.0522.

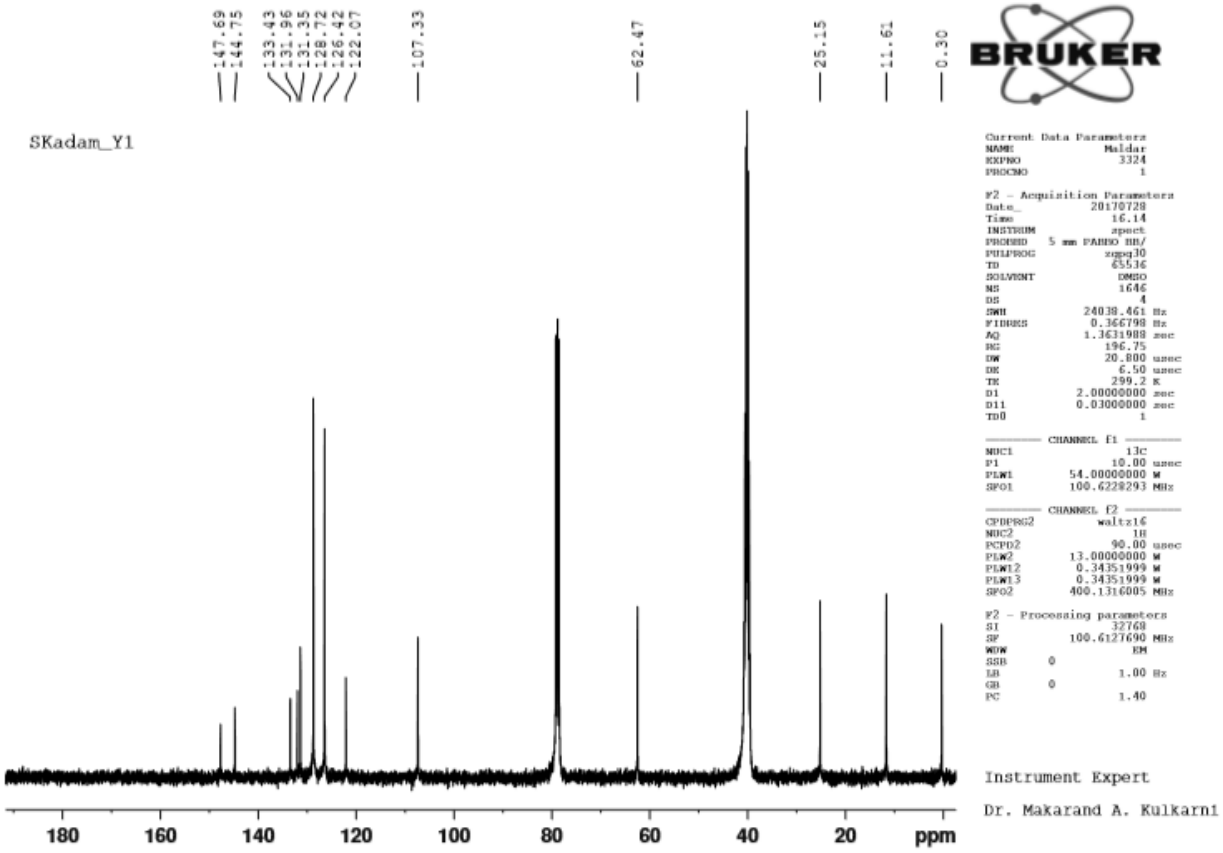
^{1}H NMR


Cl
N
N
S
OH

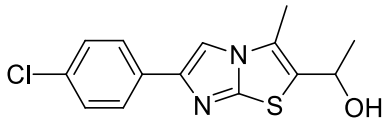

Y1 ,1H-DMSO-d6
300517003
8.256
7.859
7.450
5.753
5.088
2.389
1.387
13
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.041
2.000
2.104
0.842
0.907
3.160
3.077

^{13}C NMR

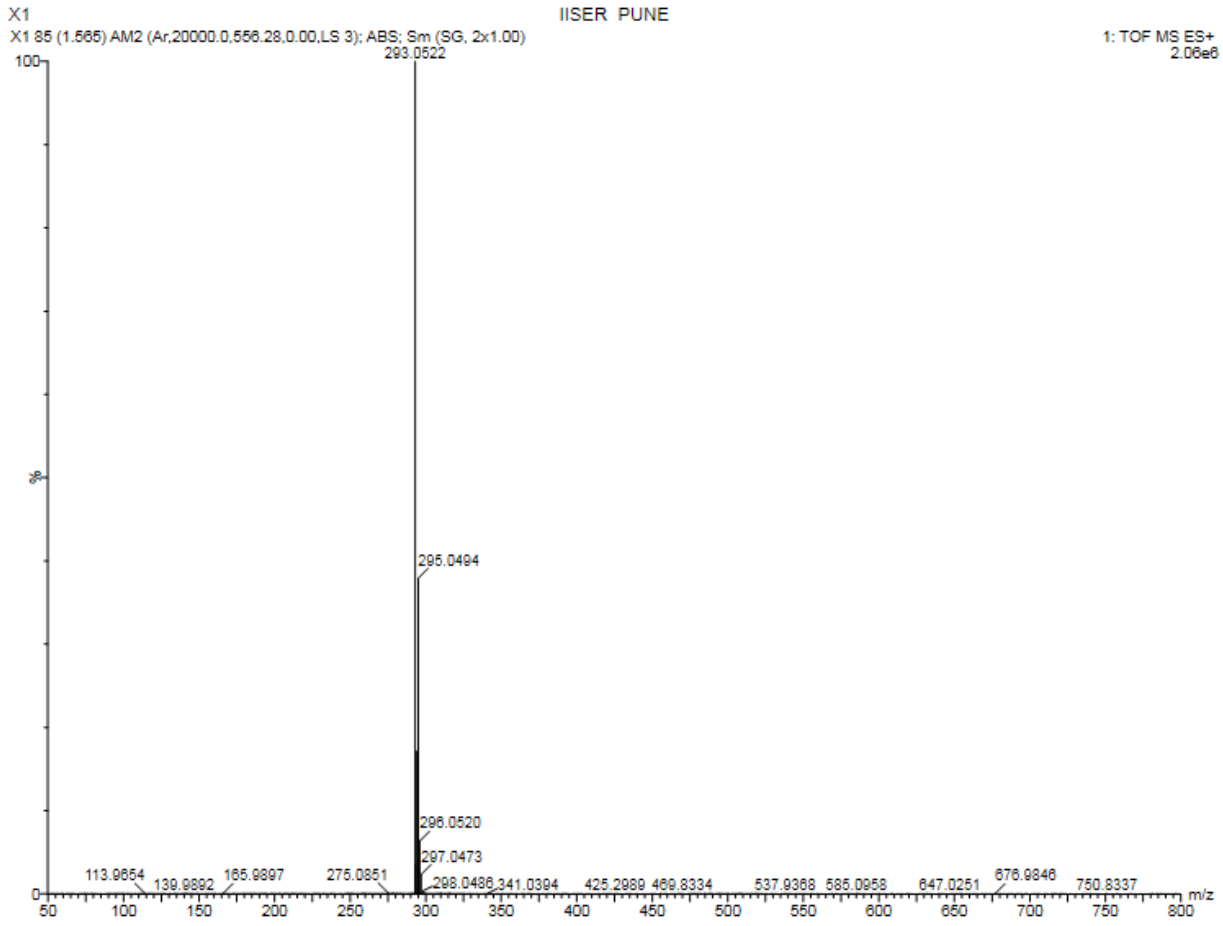

Cl
N
N
S
OH


147.69
144.75
133.43
131.96
131.35
128.72
126.42
122.07
107.33
62.47
25.15
11.61
0.30
BRUKER
SKadam_Y1
Current Data Parameters
NAME Maldar
EXPNO 3324
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170728
Time 16.14
INSTRUM zpoct
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1646
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 299.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13c
P1 10.00 usec
PLW1 54.00000000 W
SFO1 100.6228293 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.34351999 W
PLW13 0.34351999 W
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
180
160
140
120
100
80
60
40
20
ppm

HRMS



Calculated for $C_{14}H_{13}ClN_2OS$: 292.0437, found 293.0522.



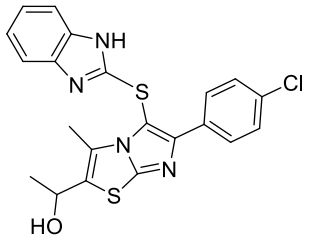
5. a) ***General procedure for the synthesis of 1-(5-((1H-benzo[d]imidazol-2-yl)thio)-6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (7a).***

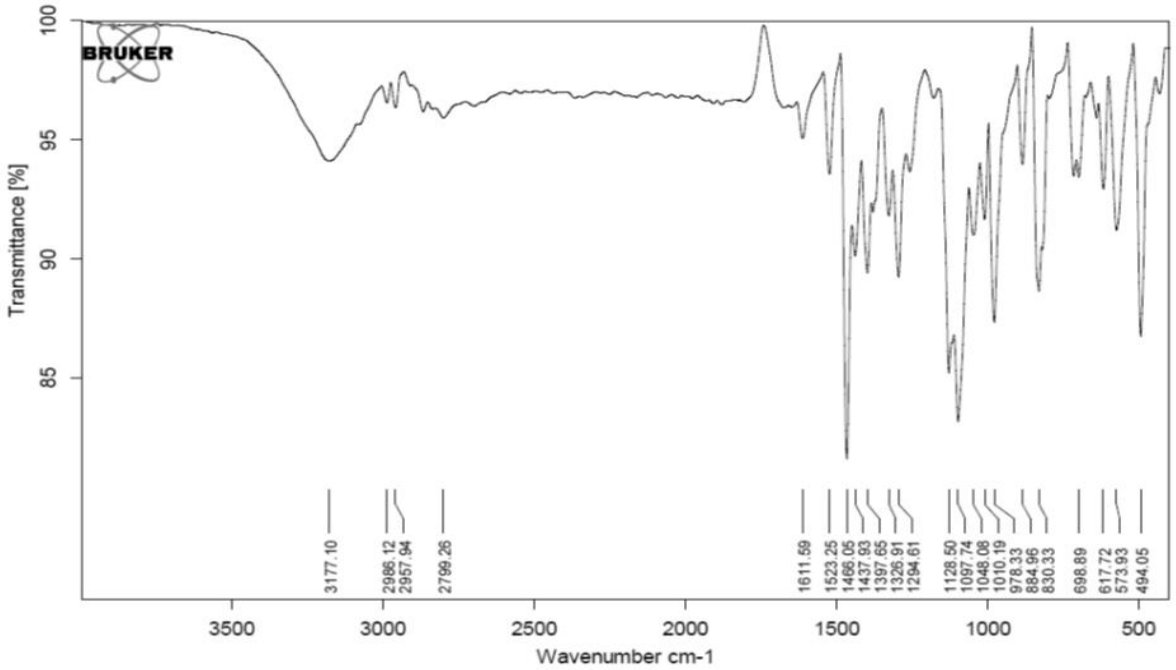
NCS (1.5 mmol) was taken in round bottom flask containing CH_3OH. To this same pot 1H-benzo[d]imidazole-2-thiol **(2a)** (**Scheme 2**) (2 mmol) was added slowly with constant stirring, and reaction mass was stirred at room temperature up to 5 minutes. As TLC indicate the formation of (NHTS). Furthermore to the same pot 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (2 mmol), was added with small proportions at a time and stirring was continued for another 20 minutes, as TLC indicate the completion of reaction. The reaction mass was poured on ice cold water, solid

product separated out was filtered, dried and washed with aqueous ethanol. No further purification like column chromatography was needed.

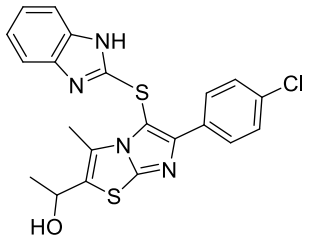
b) Spectral data of *1-(5-((1H-benzo[d]imidazol-2-yl)thio)-6-(4-chlorophenyl)-3 methylimidazo[2,1-b]thiazol-2-yl)ethanol (7a).* white solid, mp 111-113 ºC. FT-IR: 3177 (-OH), 1128 (C-S-C) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 12.63 (s, 1H), 7.93 (dd, 2H), 7.48 (m, 3H), 7.37 (s, 1H), 7.93 (dd, 2H), 5.86 (d, 1H), 5.07 (q, 1H), 2.46 (s, 3H), 1.37 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 152.12, 151.64, 149.92, 144.40, 135.71, 133.56, 133.02, 132.31, 129.55, 128.45, 124.86, 122.18, 121.79, 118.09, 111.04, 103.89, 62.24, 25.13, 12.13. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{17}ClN_4OS_2$: 440.0532, found 441.7851.

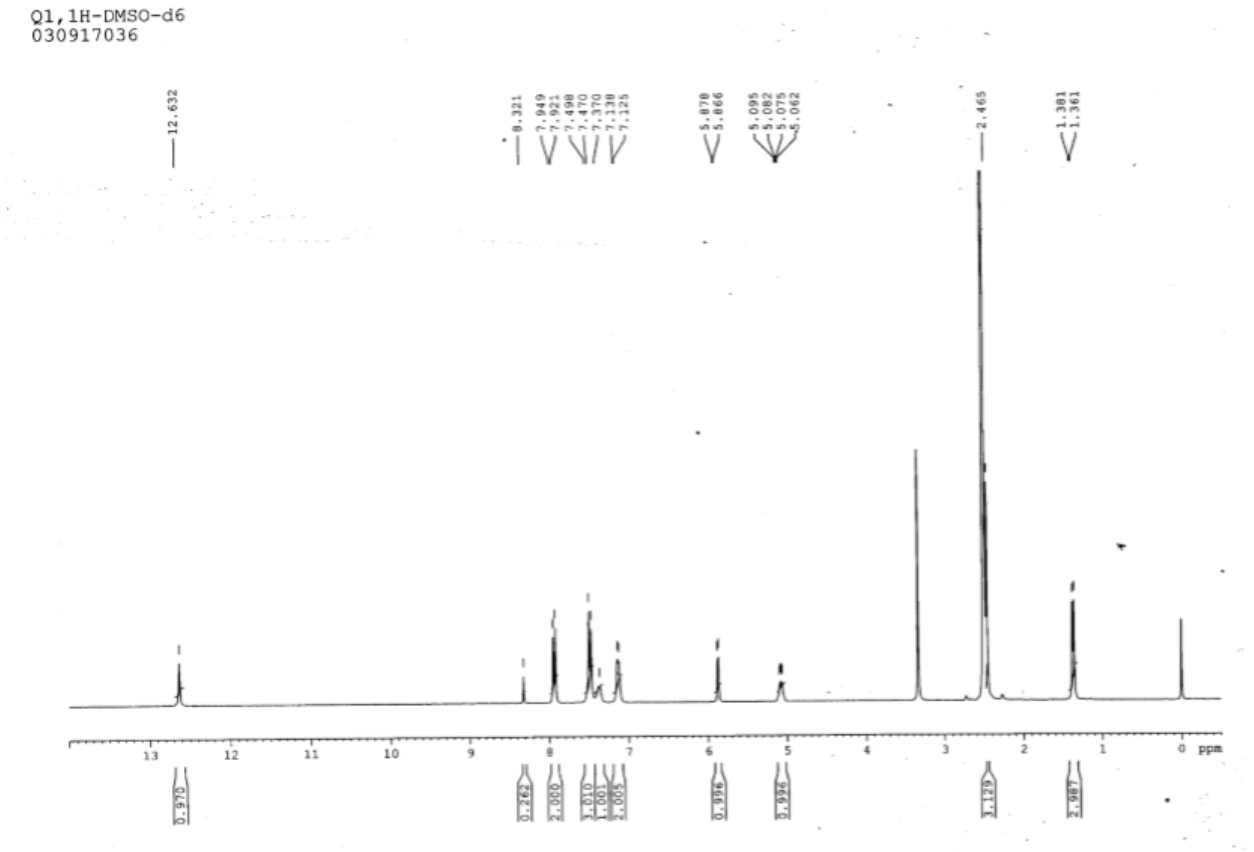
IR Spectra





^{1}H NMR


NH
N
S
Cl
N
N
S
HO


Q1,1H-DMSO-d6
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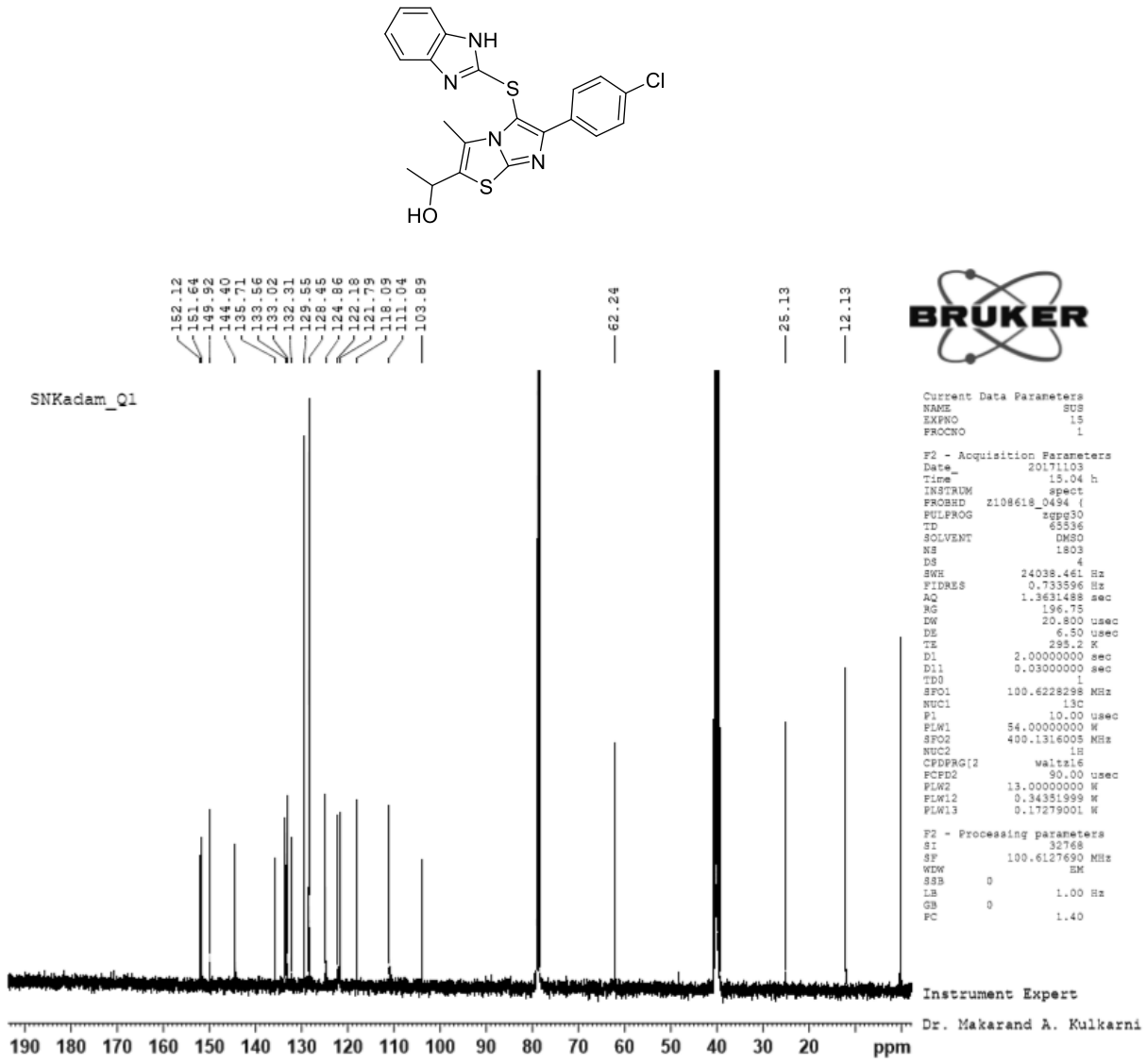
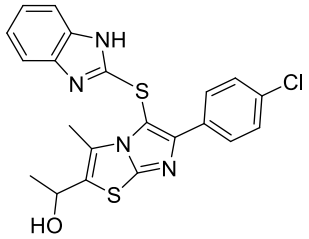
8.321
7.949
7.921
7.498
7.470
7.370
7.338
7.125
5.878
5.866
5.095
5.082
5.075
5.062
2.465
1.381
1.361
ppm
0.970
0.262
2.000
1.010
1.001
2.005
0.994
0.996
3.129
2.987

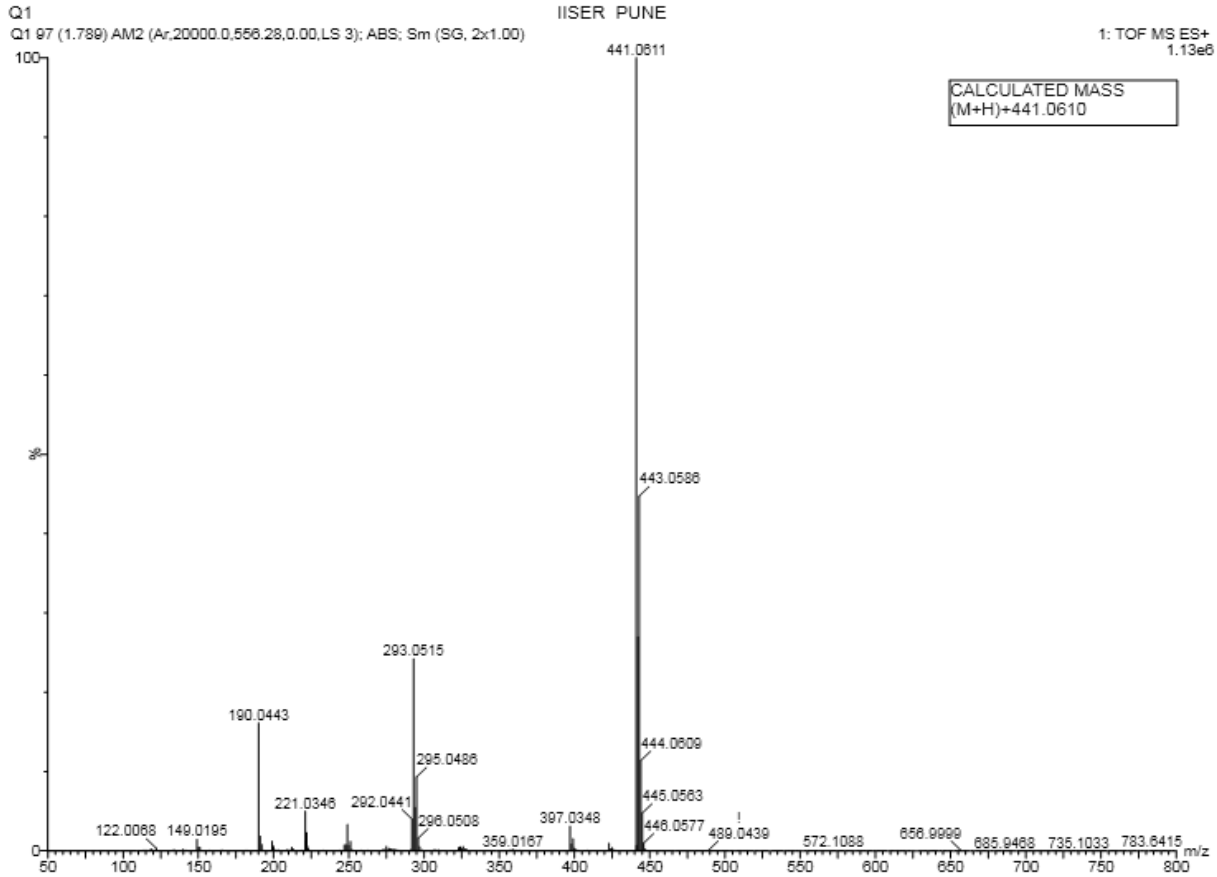
^{13}C NMR


NH
N
S
Cl
N
N
S
HO
152.12
151.64
149.92
144.40
135.71
133.56
133.02
132.31
129.55
128.45
124.86
122.18
121.79
118.09
111.04
103.89
62.24
25.13
12.13
BRUKER
SNKadam_Q1
Current Data Parameters
NAME SUS
EXPNO 15
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171103
Time 15.04 h
INSTRUM spect
PROBHD Z108618_0494 (
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1803
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.34351999 W
PLW13 0.17279001 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

HRMS



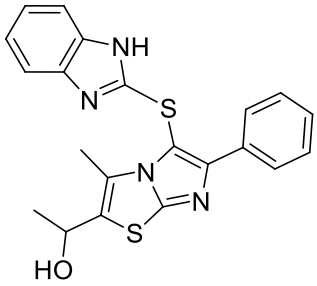
Calculated for $C_{21}H_{17}ClN_4OS_2$: 440.0532, found 441.7851.

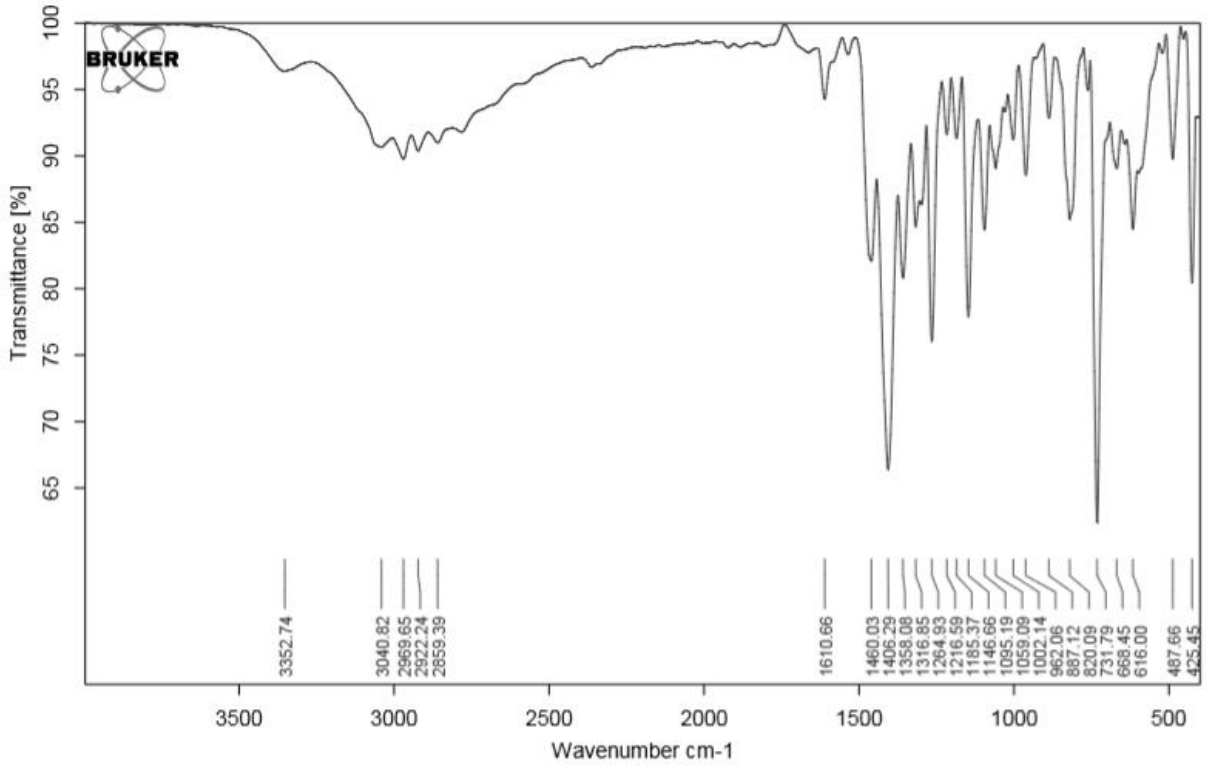


(c) Spectral data of *1-(5-((1H-benzo[d]imidazol-2-yl)thio)-3-methyl-6-phenylimidazo[2,1-b]thiazol-2-yl)ethanol (7b).* White solid, mp 115-117 ºC. FT-IR: 3040 (-OH), 1146 (C-S-C) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.60 (s, 1H), 7.89 (dd, 2H), 7.40 (m, 5H), 7.13 (m, 2H), 5.87 (s, 1H), 5.08 (m, 1H), 2.47 (s, 3H), 1.37(d, 3H). ^{13}C-NMR

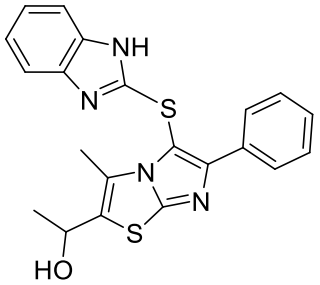
(400 MHz, DMSO-d_6) δ 153.02, 152.11, 150.38, 133.57, 132.68, 128.32, 128.20, 128.16, 124.91, 121.93, 103.43, 62.28, 25.08, 12.13. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{18}N_4OS_2$: 406.0922, found 407.0988.

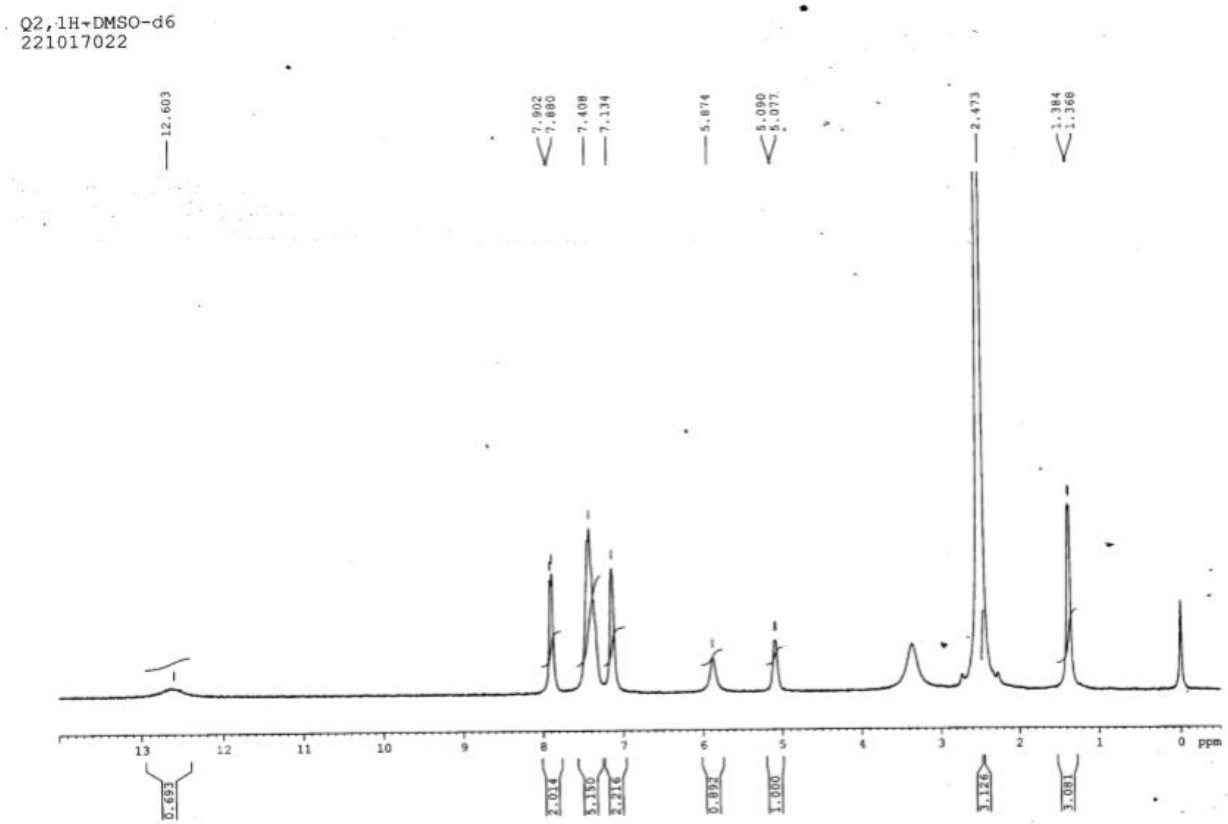
IR





^{1}H NMR


NH
N
S
N
N
S
HO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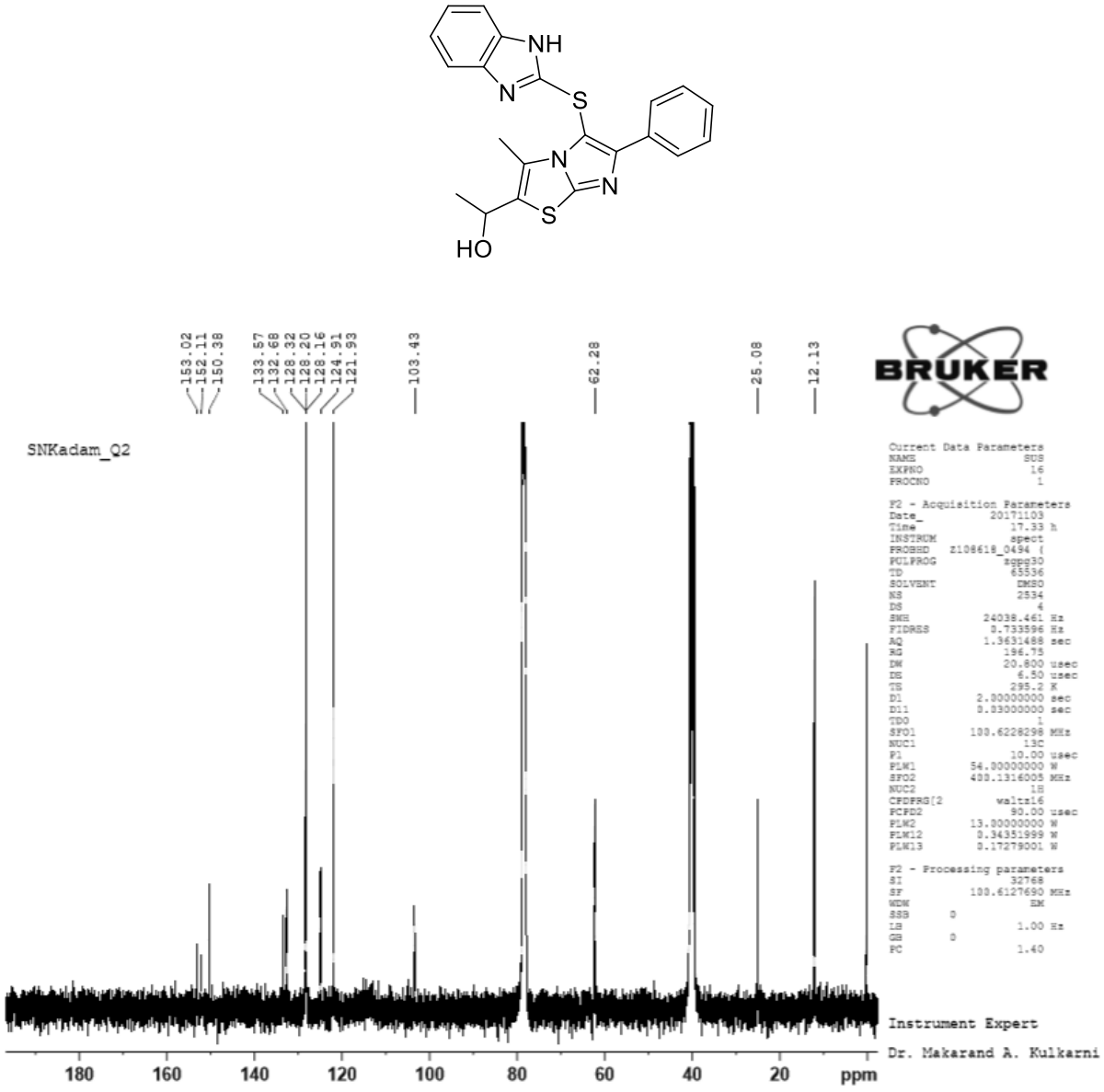
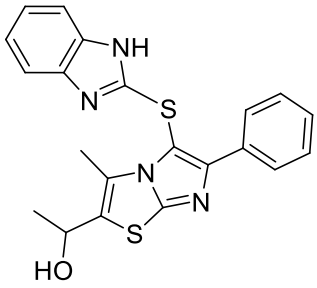
7.902
7.880
7.408
7.134
5.874
5.090
5.077
2.473
1.384
1.368
13
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.693
2.014
2.150
2.216
0.892
1.000
3.126
3.081

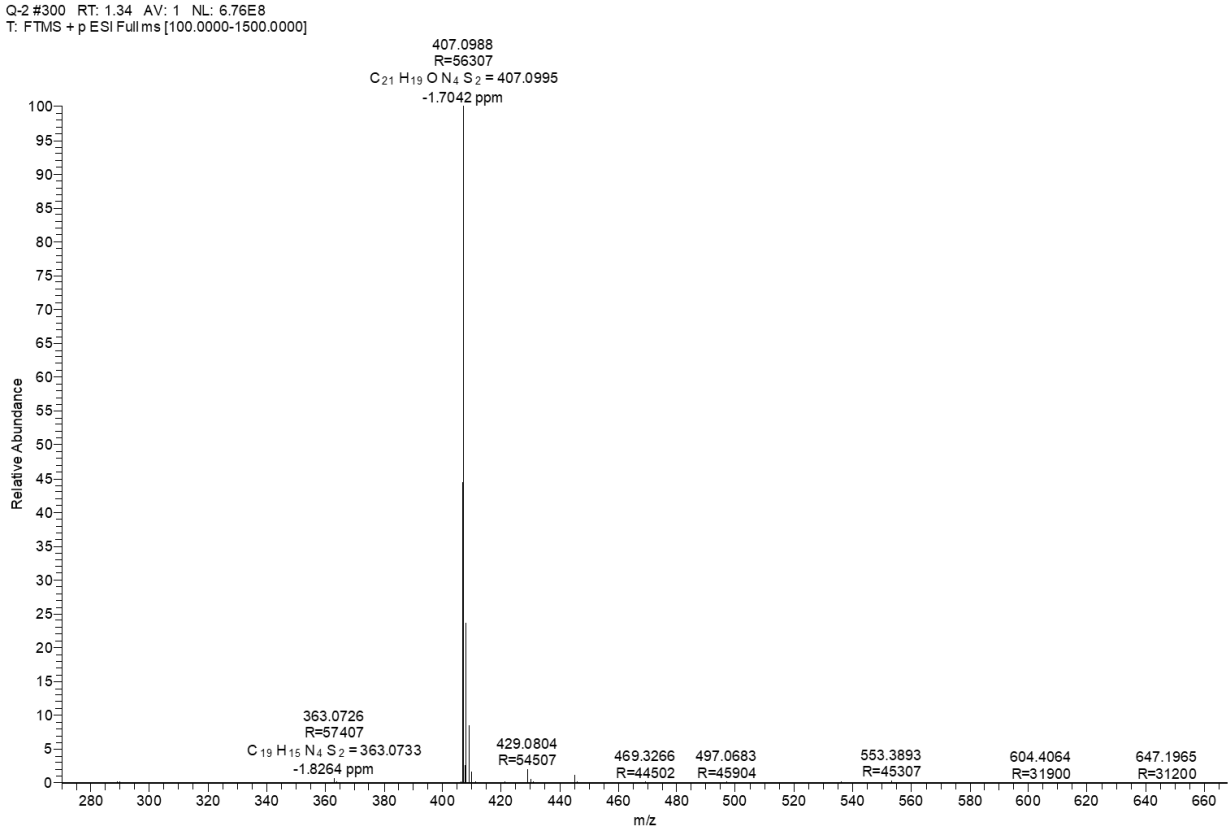
^{13}C NMR


NH
N
S
N
N
S
HO
153.02
152.11
150.38
133.57
132.68
128.32
128.20
128.16
124.91
121.93
103.43
62.28
25.08
12.13
BRUKER
SNKadam_Q2
Current Data Parameters
NAME SUS
EXPNO 16
PROCNO 1
F2 - Acquisition Parameters
Date_ 20171103
Time 17.33 h
INSTRUM spect
PROBHD Z108618_0494 (
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2534
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.34351999 W
PLW13 0.17279001 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
180
160
140
120
100
80
60
40
20
ppm

HRMS



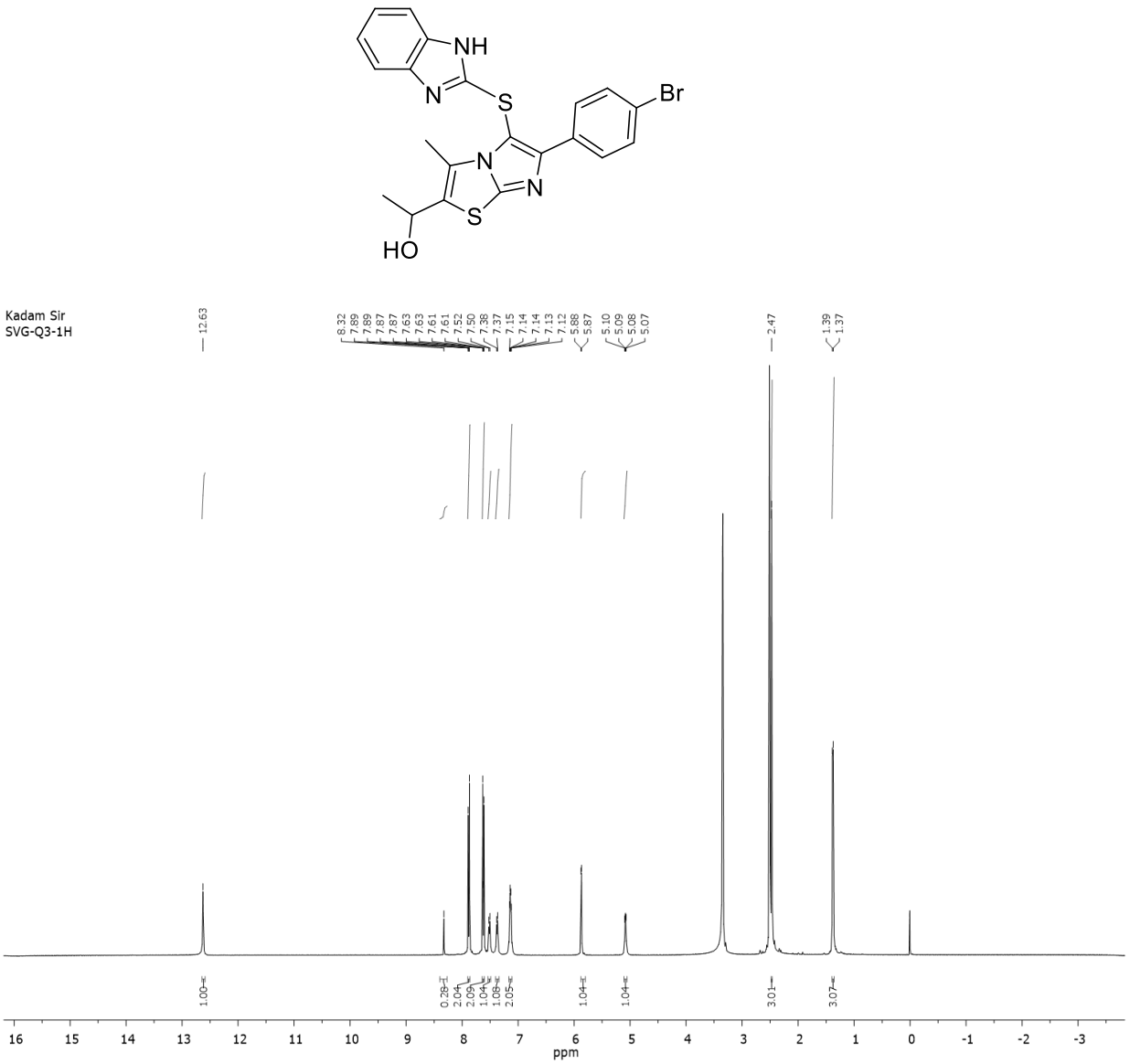
Calculated for $C_{21}H_{18}N_4OS_2$: 406.0922, found 407.0988.



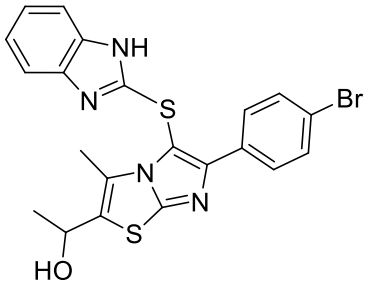
(d) Spectral data of *1-(5-((1H-benzo[d]imidazol-2-yl)thio)-6-(4-bromophenyl)-3-methylimidazo[2,1 b]thiazol-2-yl)ethanol (7c)*. White solid, mp 120-121 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.63 (s, 1H), 7.89-7.87 (dd, 2H), 7.63-7.61(dd, 2H), 7.52-7.50 (m, 1H), 7.38-7.37 (m, 1H), 7.15-7.12 (m, 2H), 5.88-5.87 (dd, 1H), 5.10-5.07 (q, 1H), 2.47 (s, 3H), 1.39-1.37 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 151.74, 151.32, 149.94, 133.38, 132.99, 131.80, 130.11,

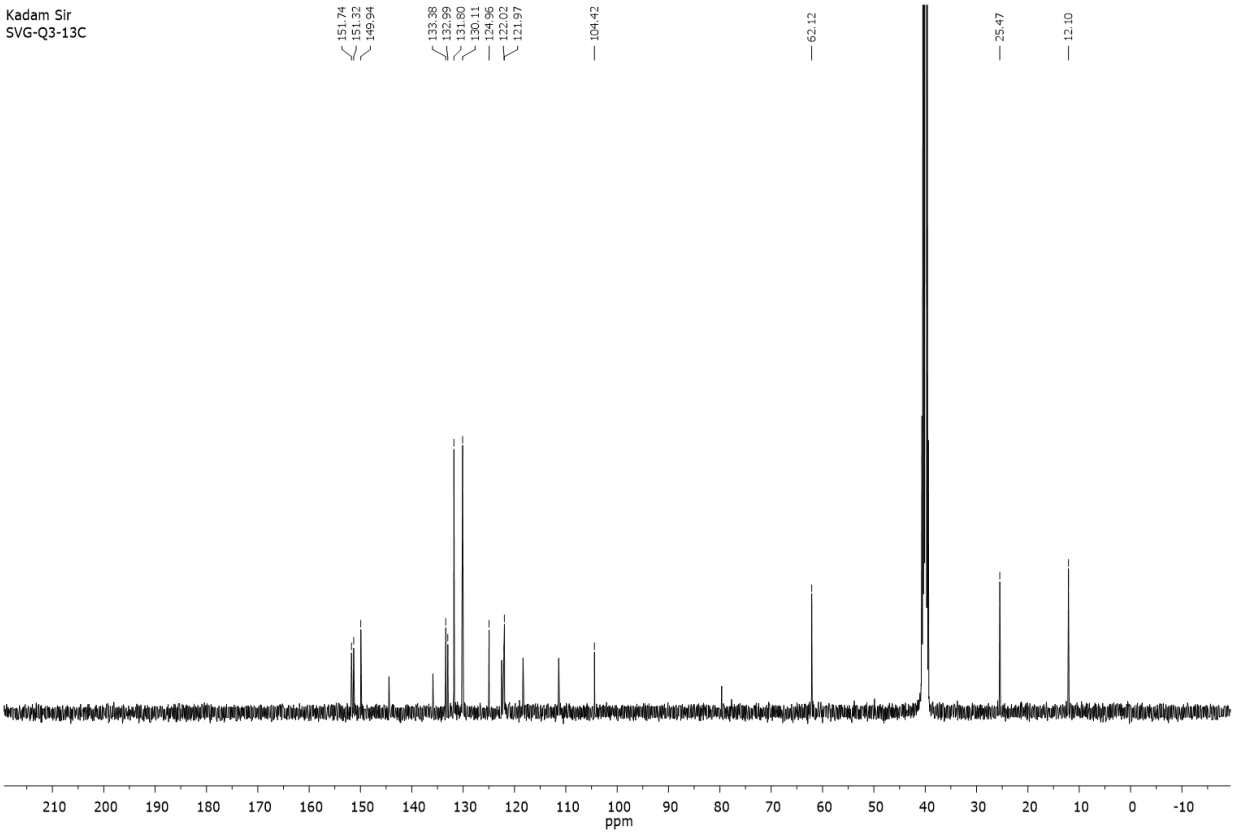
124.96, 122.02, 121.97, 104.42, 62.12, 25.47, 12.10. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{17}BrN_4OS_2$: 484.0027, found 485.0103.

^{1}H NMR

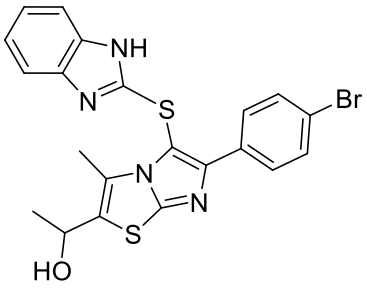


^{13}C NMR

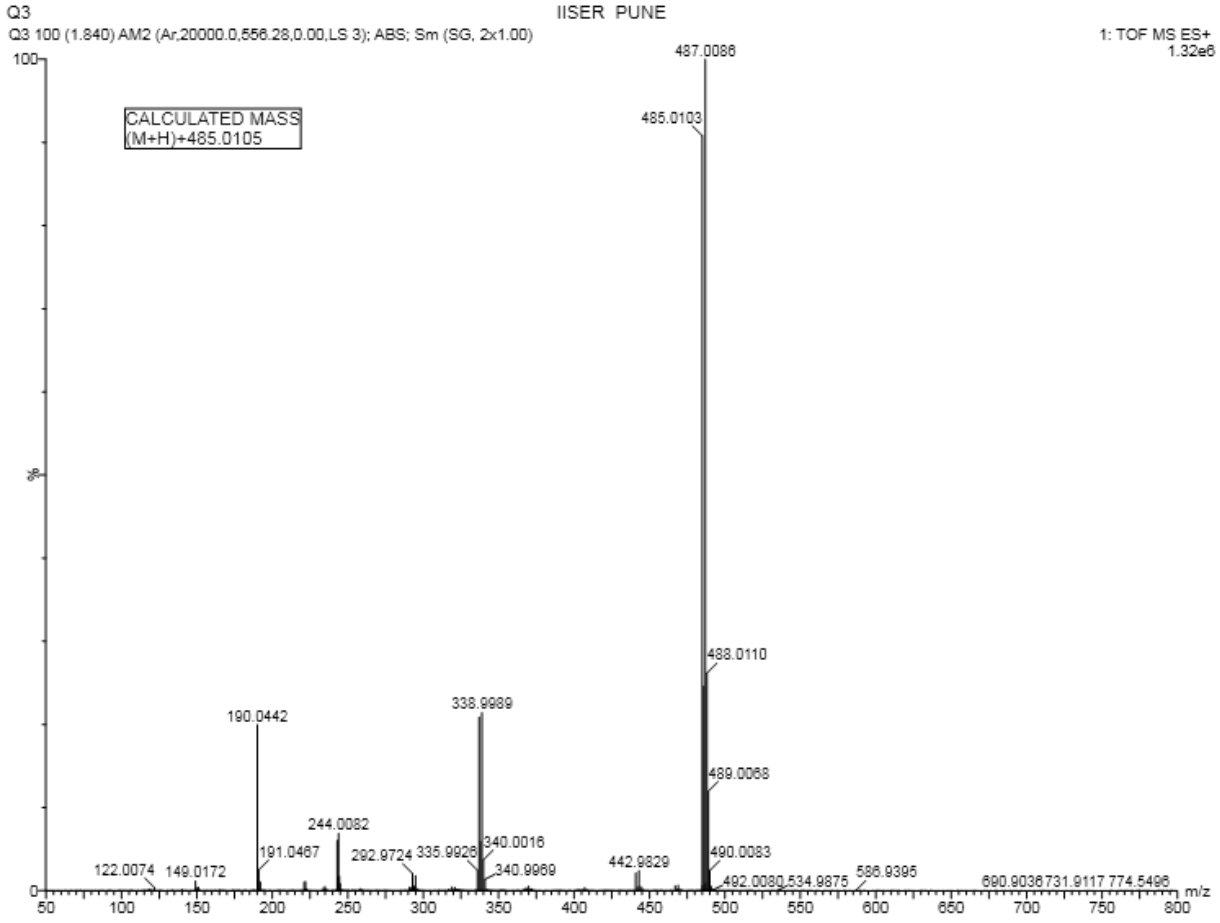

NH
N
S
Br
N
N
S
HO


Kadam Sir
SVG-Q3-13C
151.74
151.32
149.94
133.38
132.99
131.80
130.11
124.96
122.02
121.97
104.42
62.12
25.47
12.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

HRMS



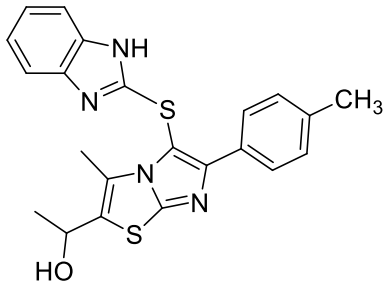
Calculated for $C_{21}H_{17}BrN_4OS_2$: 484.0027, found 485.0103.

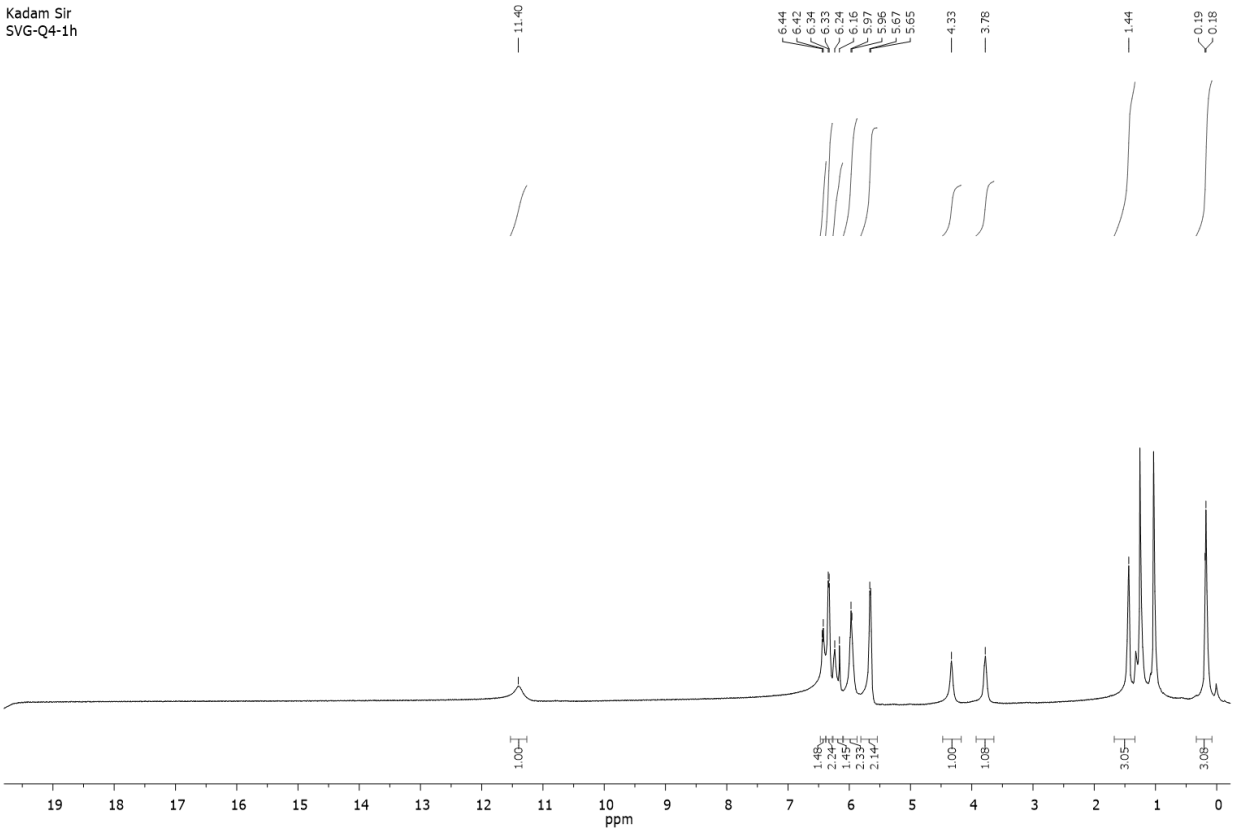


(e) Spectral data of *1-(5-((1H-benzo[d]imidazol-2-yl)thio)-3-methyl-6-(p-tolyl)imidazo[2,1-b]thiazol-2*

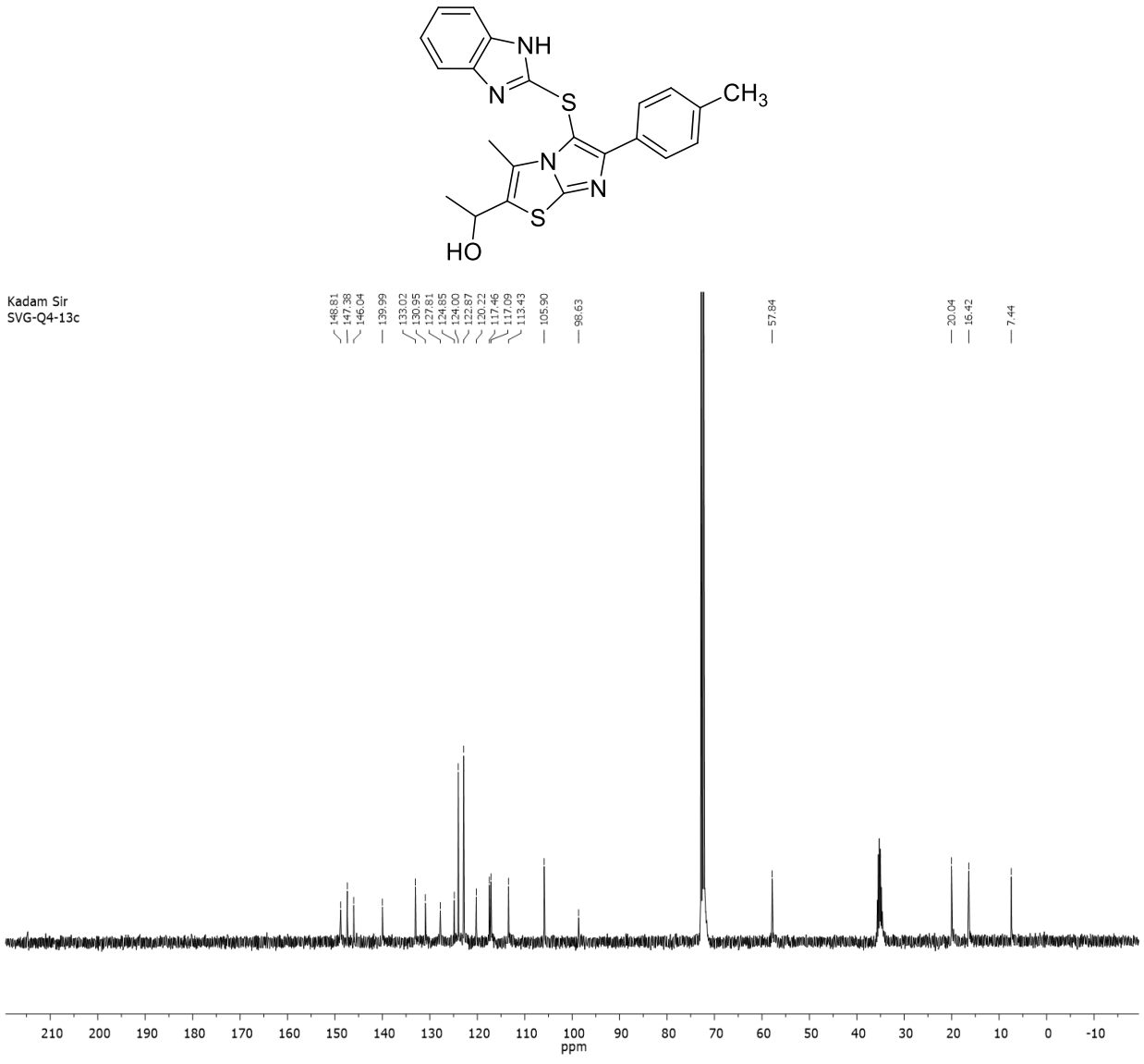
yl)ethanol (7d). White solid, mp 119-120 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 11.40 (s, 1H), 6.44-6.42 (m, 1H), 6.34-6.33 (m, 2H), 6.24-6.16 (m, 1H), 5.97-5.96 (m, 2H), 5.67-5.65 (m, 2H), 4.33 (s, 1H), 3.78 (s, 1H), 1.44 (s, 3H), 0.19-0.18 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 148.81, 147.38, 146.04, 139.99, 133.02, 130.95, 127.81, 124.85, 124.00, 122.87, 120.22, 117.09, 117.43, 105.90, 98.63, 57.84, 20.04, 16.42, 7.44. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{22}H_{20}N_4OS_2$: 420.1079, found 421.1155.

^{1}H NMR

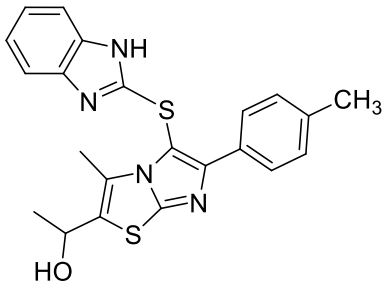




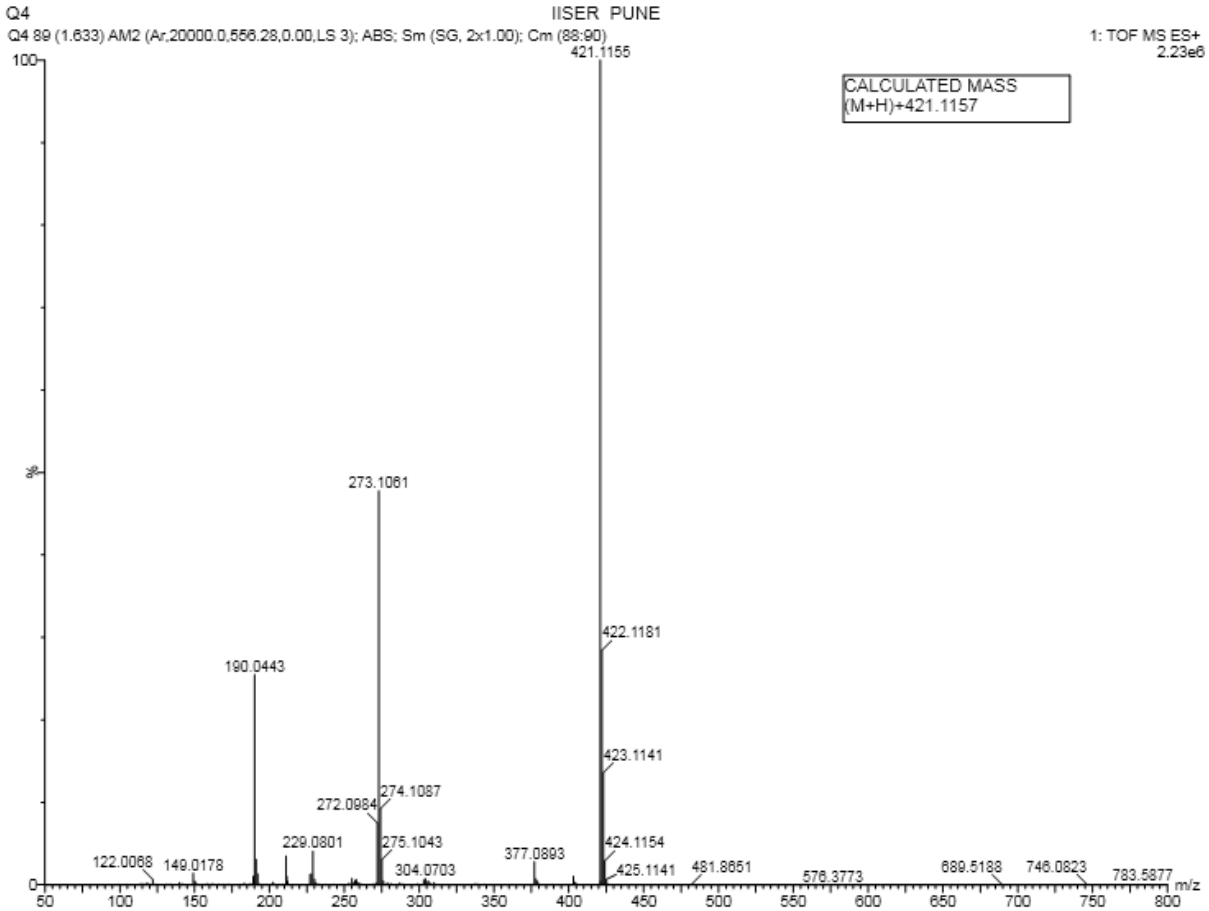
^{13}C NMR


NH
N
S
CH3
N
N
S
HO
Kadam Sir
SVG-Q4-13c
148.81
147.38
146.04
139.99
133.02
130.95
127.81
124.65
124.00
122.87
120.22
117.46
117.09
113.43
105.90
98.63
57.84
20.04
16.42
7.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

HRMS

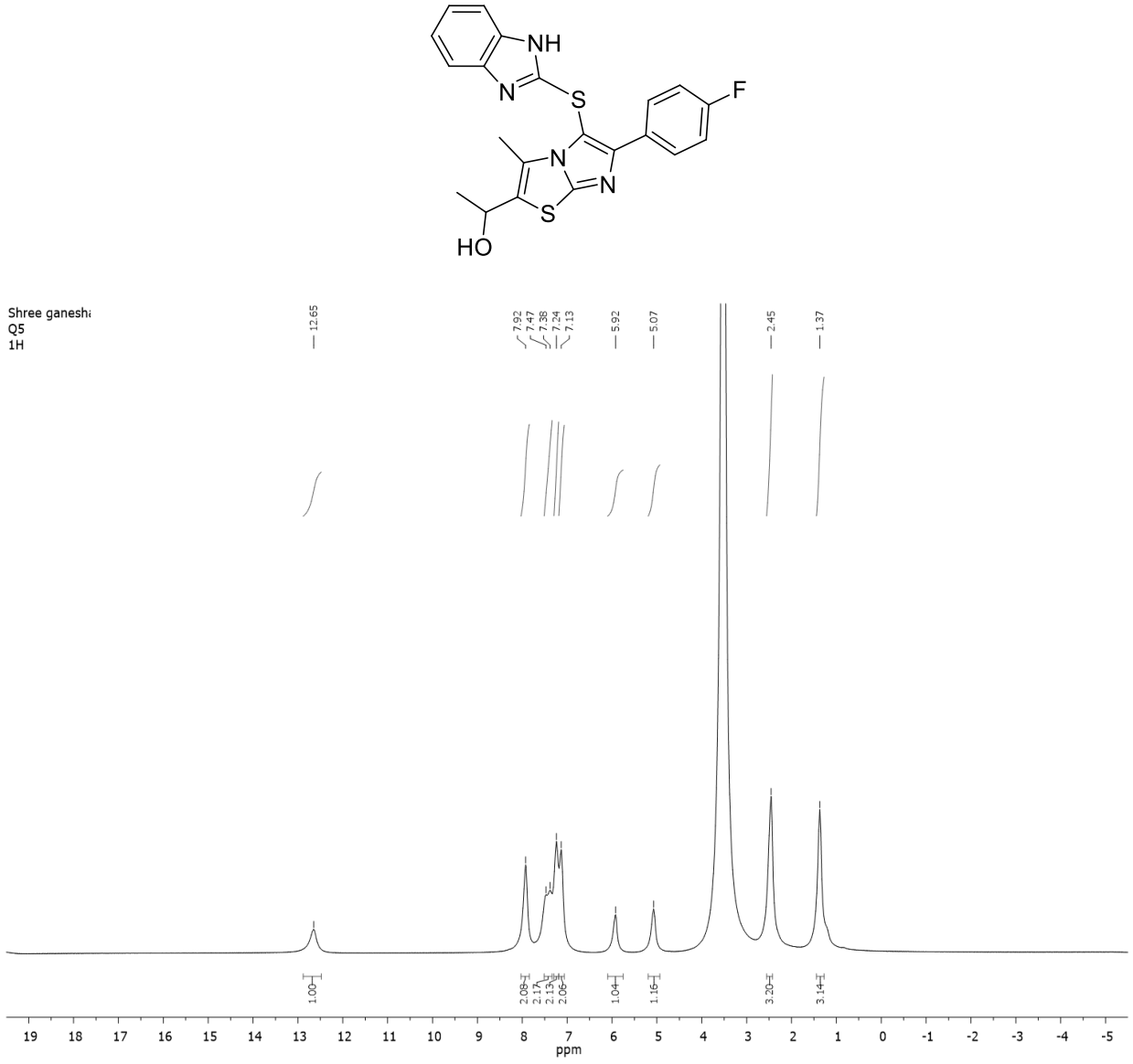


Calculated for $C_{22}H_{20}N_4OS_2$: 420.1079, found 421.1155.

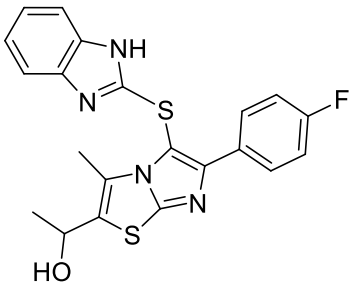


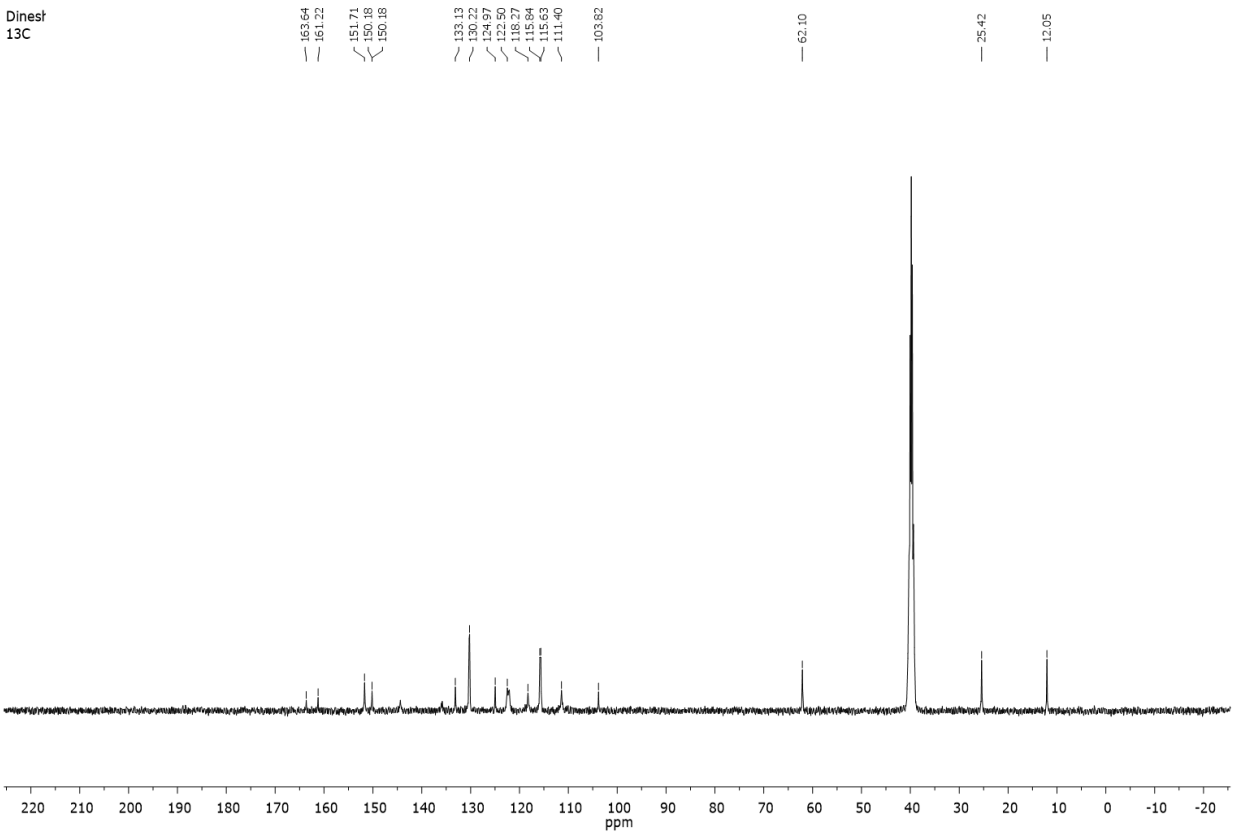
(f) Spectral data of *1-(5-((1H-benzo[d]imidazol-2-yl)thio)-6-(4-fluorophenyl)-3-methylimidazo[2,1 b]thiazol-2-yl)ethanol (7e).* White solid, mp 112-113 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 12.65 (s, 1H), 7.92 (m, 2H), 7.47-7.38 (m, 2H), 7.24 (m, 2H), 7.13 (m, 2H), 5.92 (m, 1H), 5.07 (s, 1H), 2.45 (s, 3H), 1.37 (s, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 163.64, 161.22, 151.71, 150.18, 150.18, 133.13, 130.22, 124.97, 122.50, 118.27, 115.84, 115.63, 111.40, 103.82, 62.10, 25.42, 12.05. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{17}FN_4OS_2$: 424.0828, found 425.0907.

^{1}H NMR

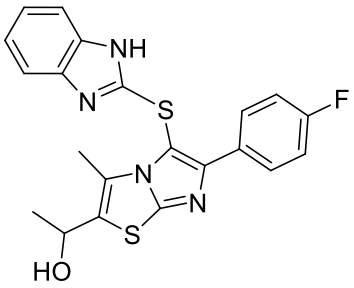


^{13}C NMR

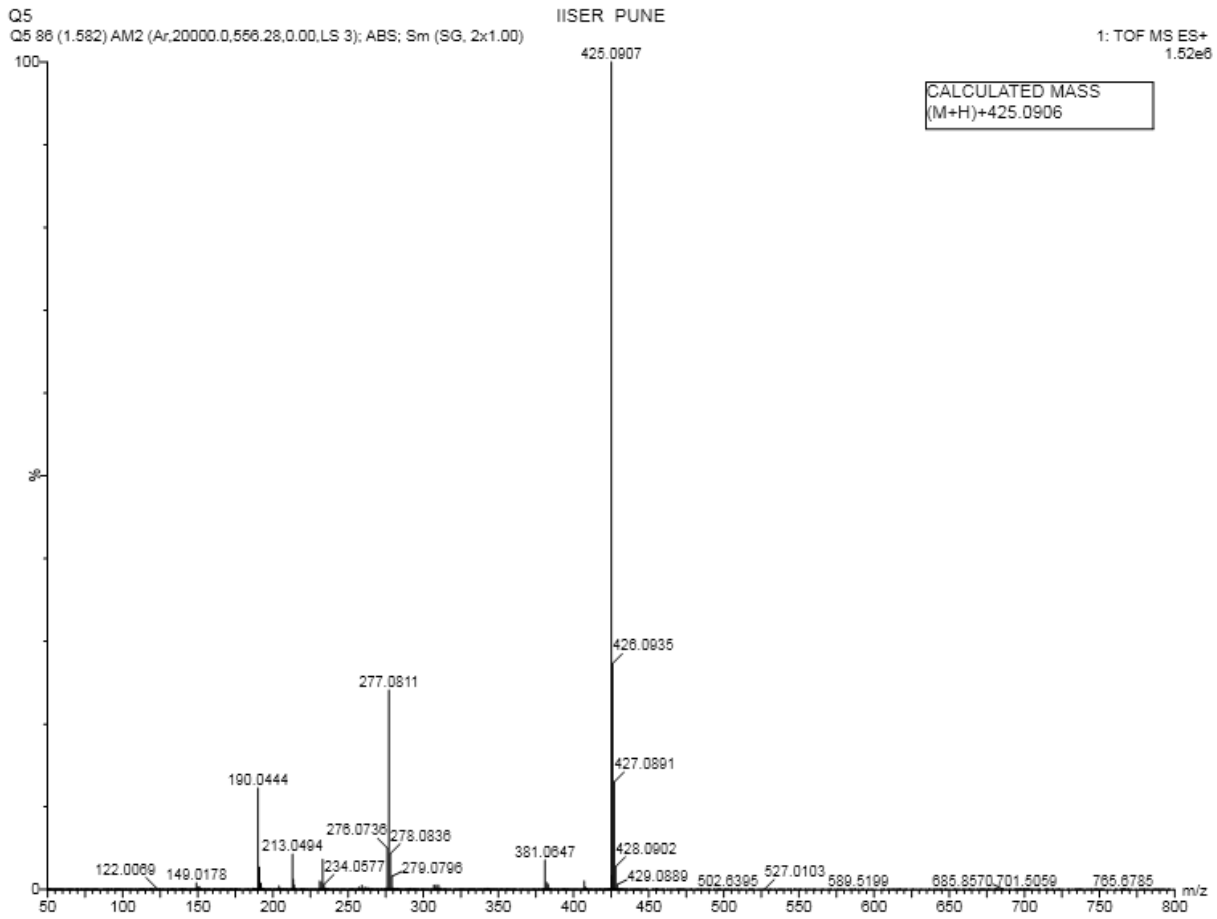

NH
N
S
F
N
N
S
HO


Dinest
13C
163.64
161.22
151.71
150.18
150.18
133.13
130.22
124.97
122.50
118.27
115.84
115.63
111.40
103.82
62.10
25.42
12.05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
ppm

HRMS



Calculated for $C_{21}H_{17}FN_4OS_2$: 424.0828, found 425.0907

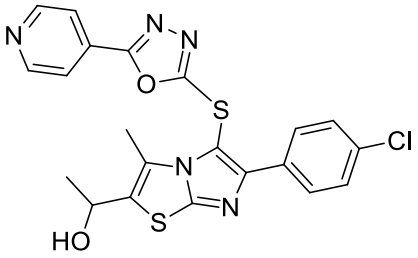


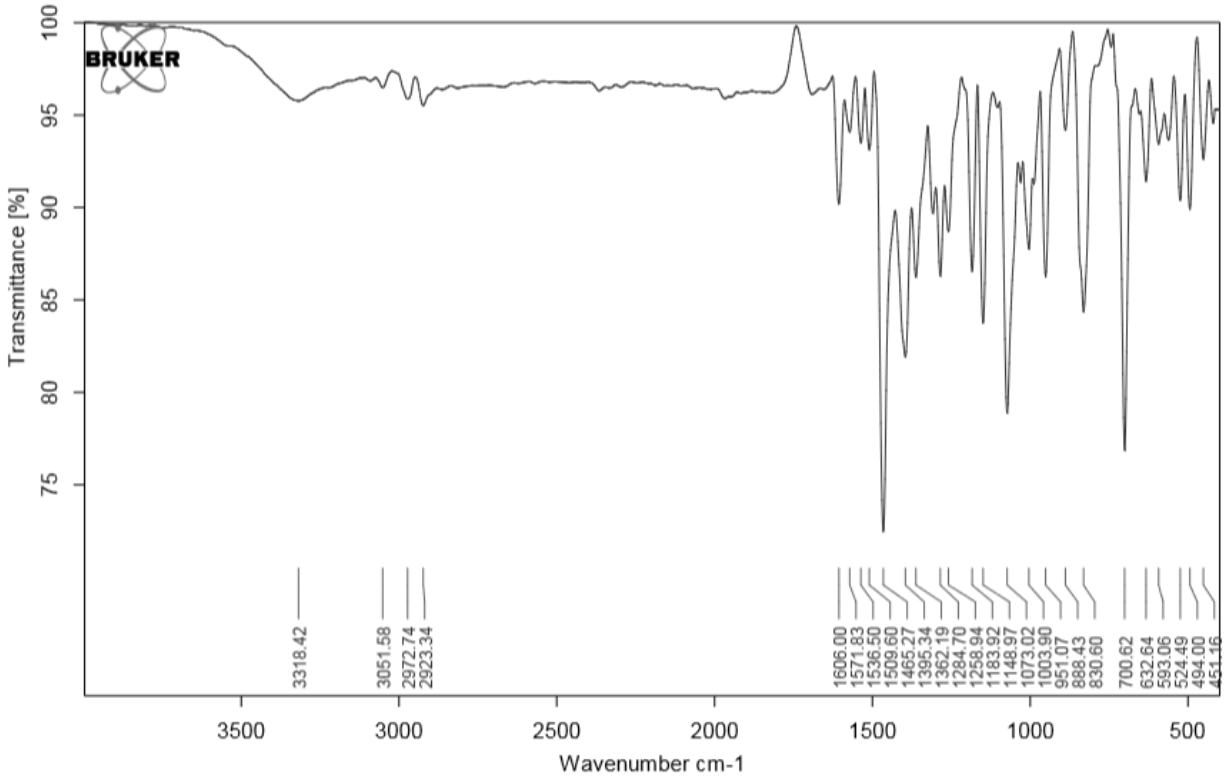
6. a) ***General procedure for the synthesis of 1-(6-(4-chlorophenyl)-3-methyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)imidazo[2,1-b]thiazol-2-yl)ethanol (7f).***

NCS (1.5 mmol) was taken in round bottom flask containing CH_3OH. To this same pot 5-(pyridin-4-yl)-1,3,4-oxadiazole-2-thiol **(2c)** (**Scheme 2**) (2 mmol) was added slowly with constant stirring, and reaction mass was stirred at room temperature up to 5 minutes. As TLC indicate the formation of (NHTS). Furthermore to the same pot 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (2 mmol) was added with small proportions at a time and stirring was continued for another 20 minutes, as TLC indicate the completion of reaction. The reaction mass was poured on ice cold water, solid product separated out was filtered, dried and washed with aqueous ethanol. No further purification like column chromatography was needed.

(b) Spectral data of 1-(6-(4-chlorophenyl)-3-methyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)imidazo[2,1-b]thiazol-2-yl)ethanol *(7f).* White solid, mp 117-118 ºC. FT-IR: 3318 (-OH) cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.82-8.80 (m, 2H), 7.99-7.97 (m, 2H), 7.82-7.81 (m, 2H), 7.54-7.52 (m, 2H), 5.94-5.93 (d, 1H) (Exchangeable with D_2O), 5.15-5.13 (q, 1H), 2.63-2.54 (s, 3H), 2.51 (s, 3H), 1.41-1.39 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 164.64, 164.02, 153.51,153.07, 150.77, 134.69, 133.07,131.12, 130.25, 129.58, 128.65, 125.03, 120.12, 99.75, 63.01, 24.69, 12.17. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{16}ClN_5O_2S_2$: 469.0434, found 470.0507.

IR


N
N
N
O
S
Cl
N
S
N
HO


BRUKER
Transmittance [%]
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90
85
80
75
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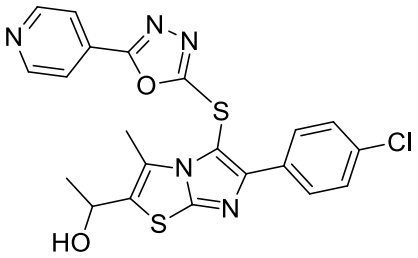
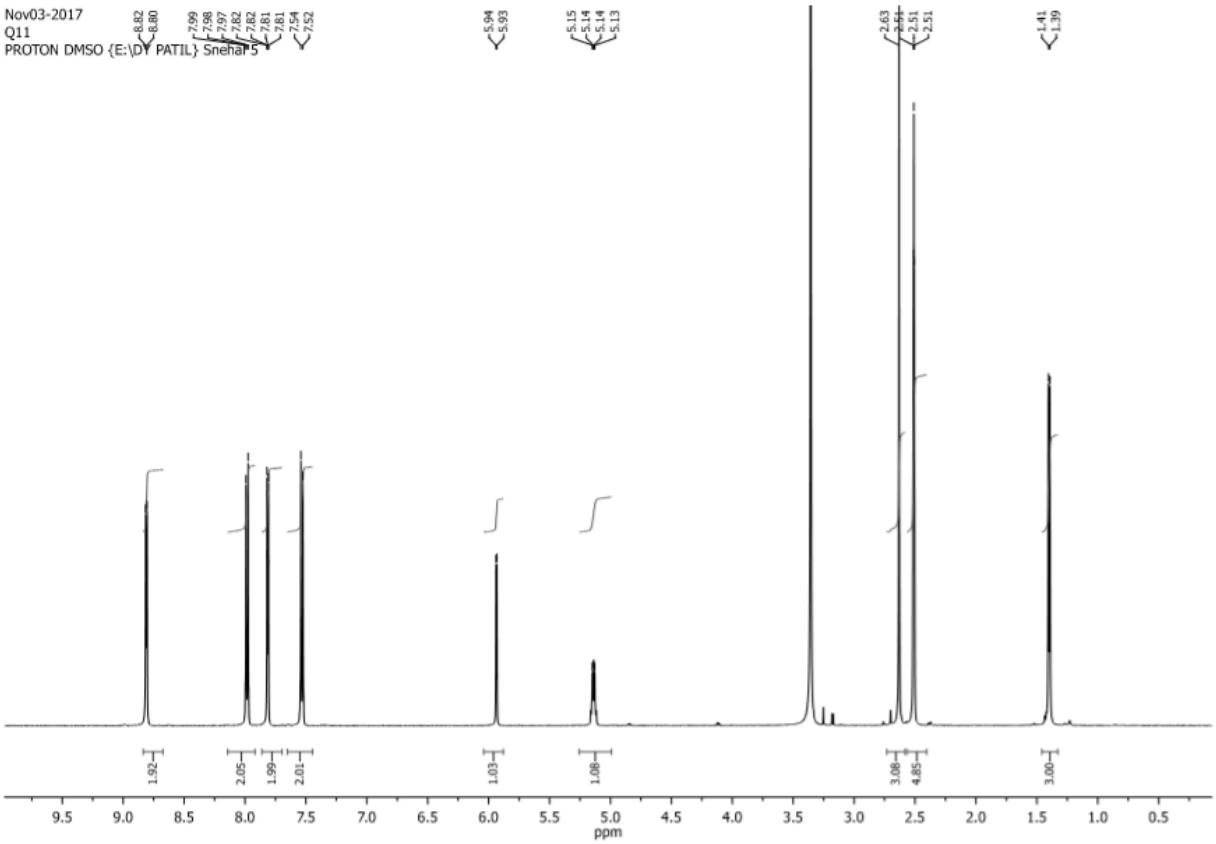
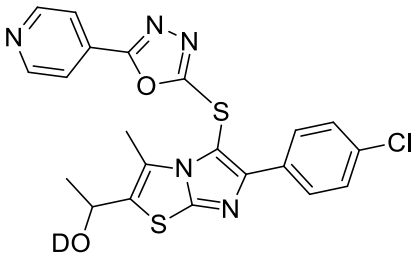
3051.58
2972.74
2923.34
1606.00
1571.83
1536.50
1509.60
1465.27
1395.34
1362.19
1284.70
1258.94
1183.92
1148.97
1073.02
1003.90
951.07
888.43
830.60
700.62
632.64
593.06
524.49
494.00
451.16
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

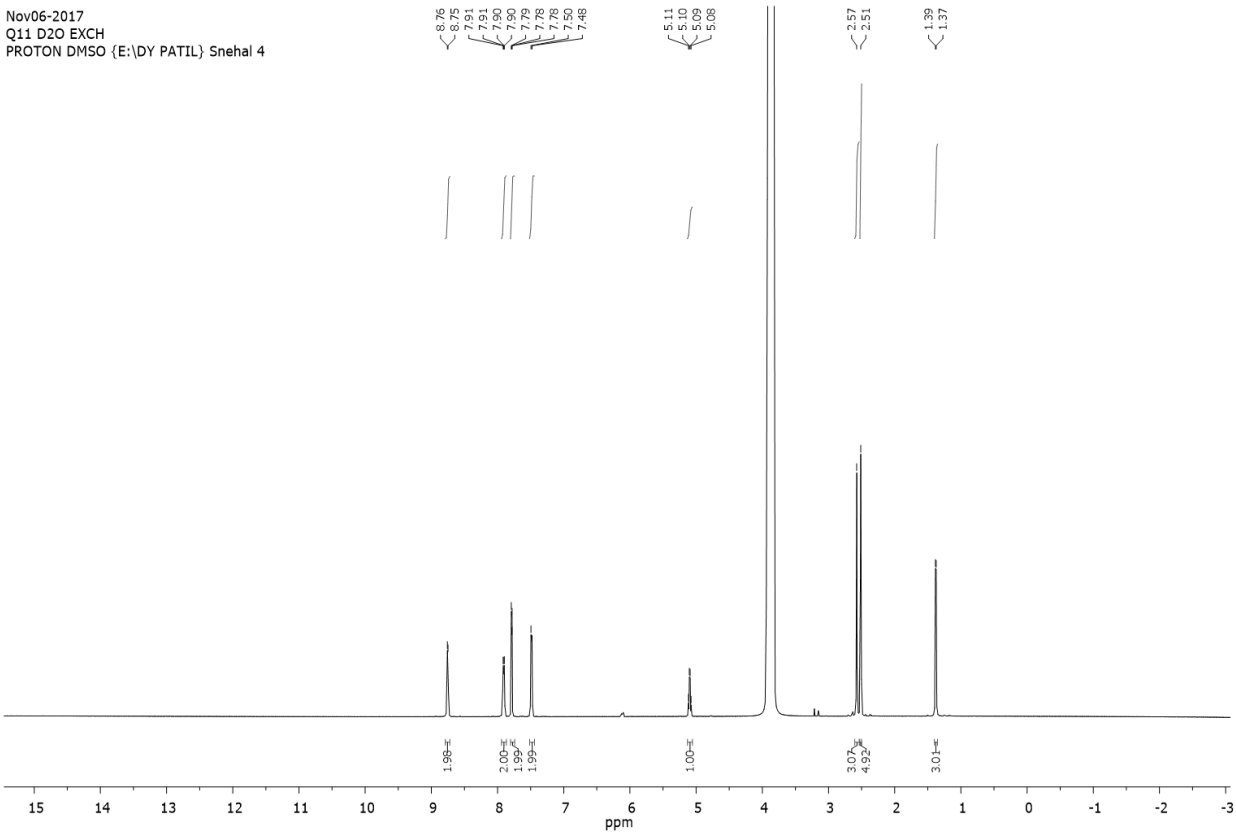
^{1}H NMR


N
N
N
O
S
Cl
N
S
N
HO

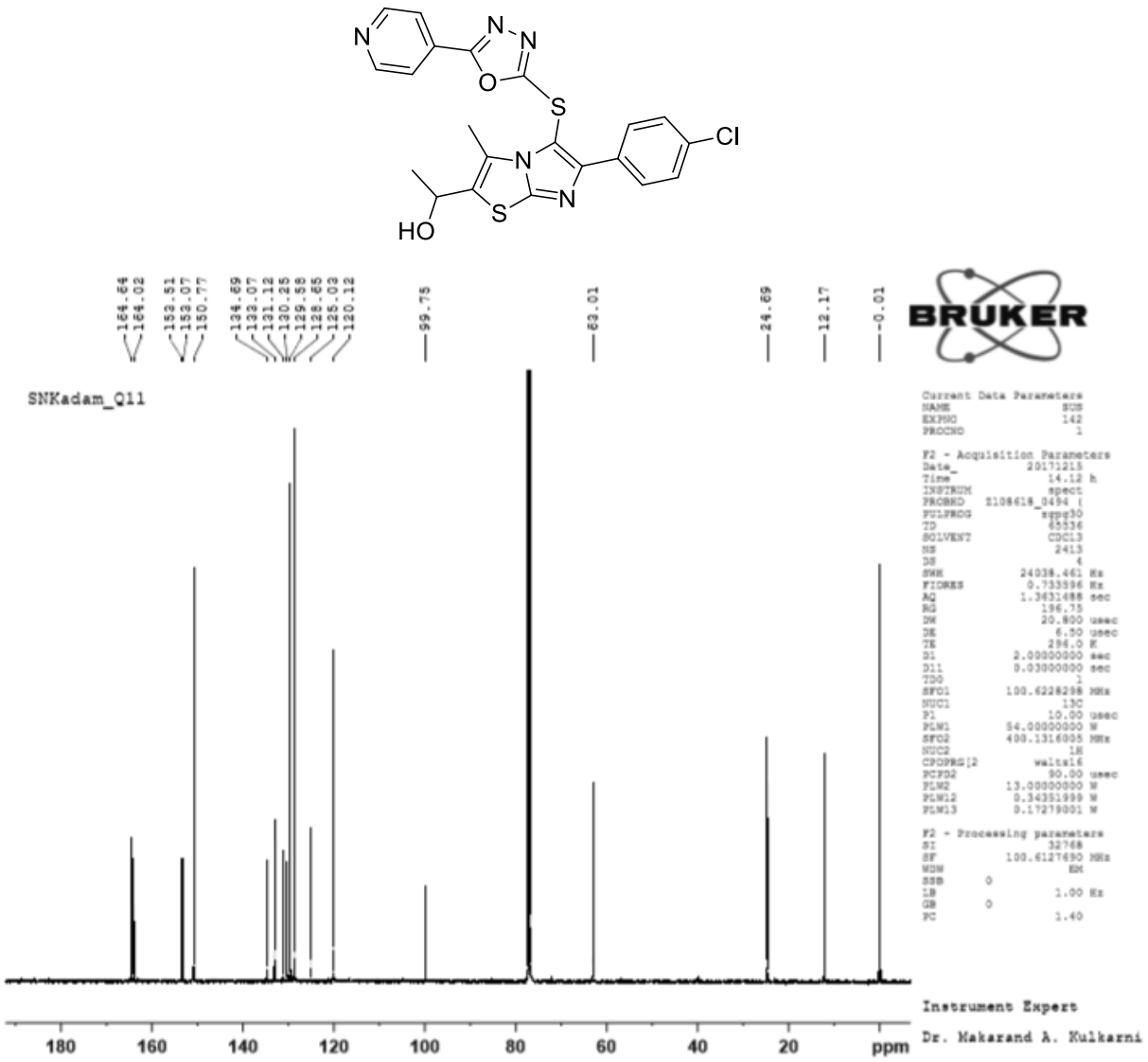

Nov03-2017
Q11
PROTON DMSO {E:\DY PATIL} Snehal 5
8.82
8.80
7.99
7.98
7.97
7.82
7.82
7.81
7.81
7.54
7.52
5.94
5.93
5.15
5.14
5.14
5.13
2.63
2.64
2.51
2.51
1.41
1.39
1.92
2.05
1.99
2.01
1.03
1.08
3.08
4.85
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H NMR (D_2O Exchange)





^{13}C NMR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N
N
O
S
Cl
N
HO
S
N
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164.02
153.51
153.07
150.77
134.69
133.07
131.12
130.25
129.58
128.65
125.03
120.12
99.75
63.01
24.69
12.17
-0.01
BRUKER
SNKadam_Q11
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PROCNO 1
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DE 6.50 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
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PLW13 0.17279001 W
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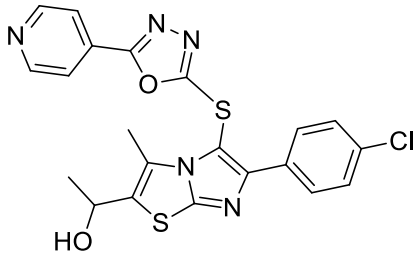
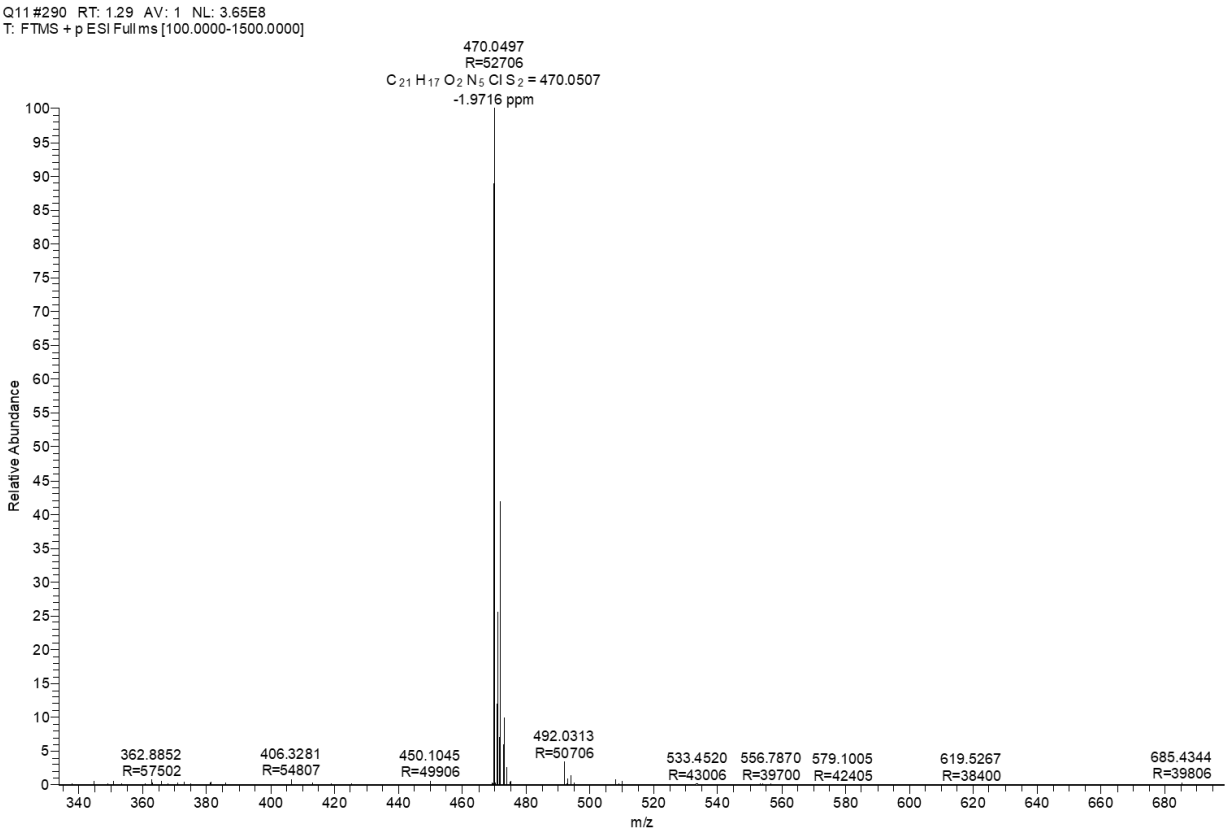
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
180
160
140
120
100
80
60
40
20
ppm

HRMS

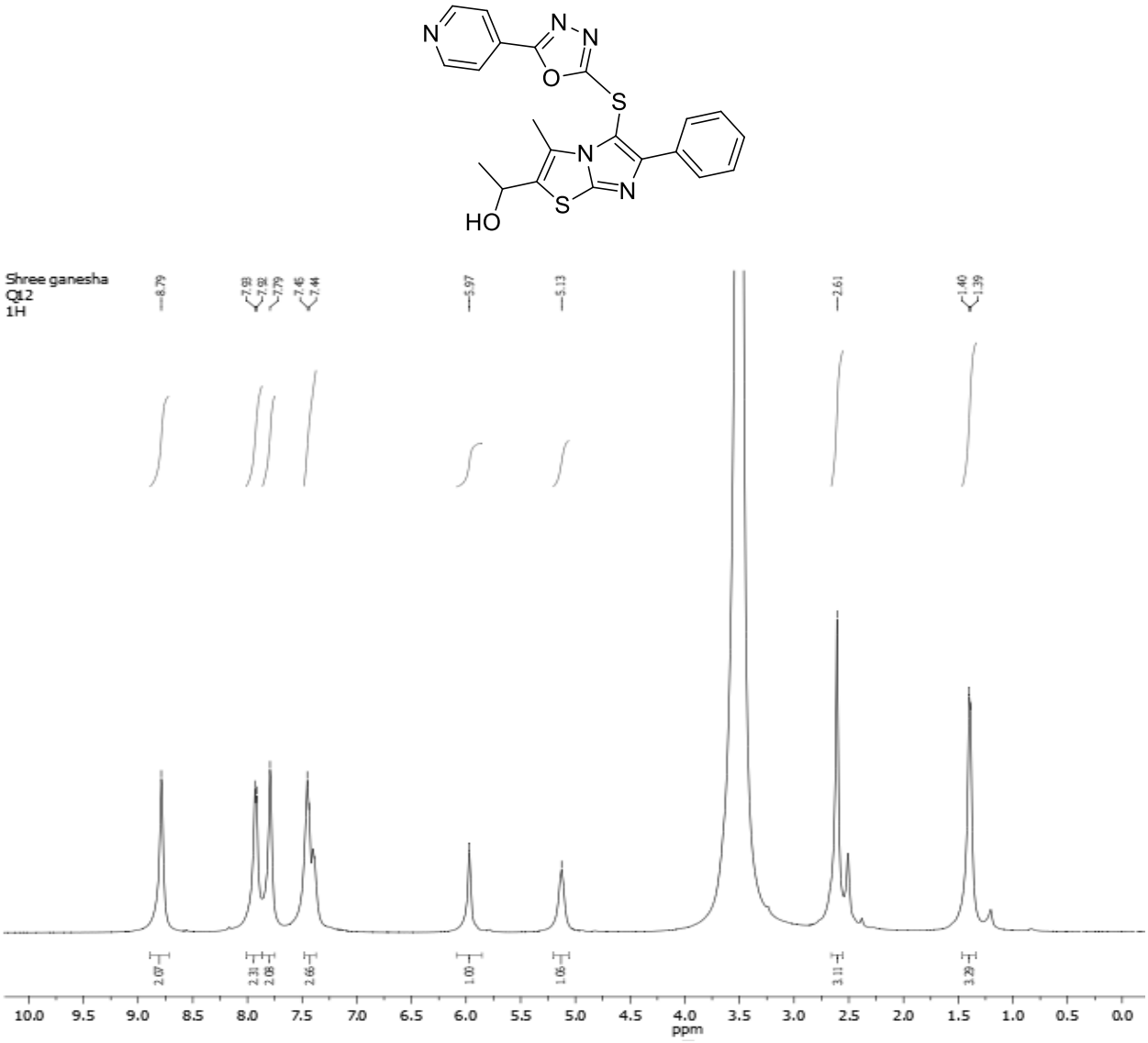


Calculated for $C_{21}H_{16}ClN_5O_2S_2$: 469.0434, found 470.0507.

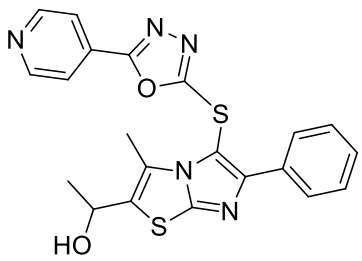


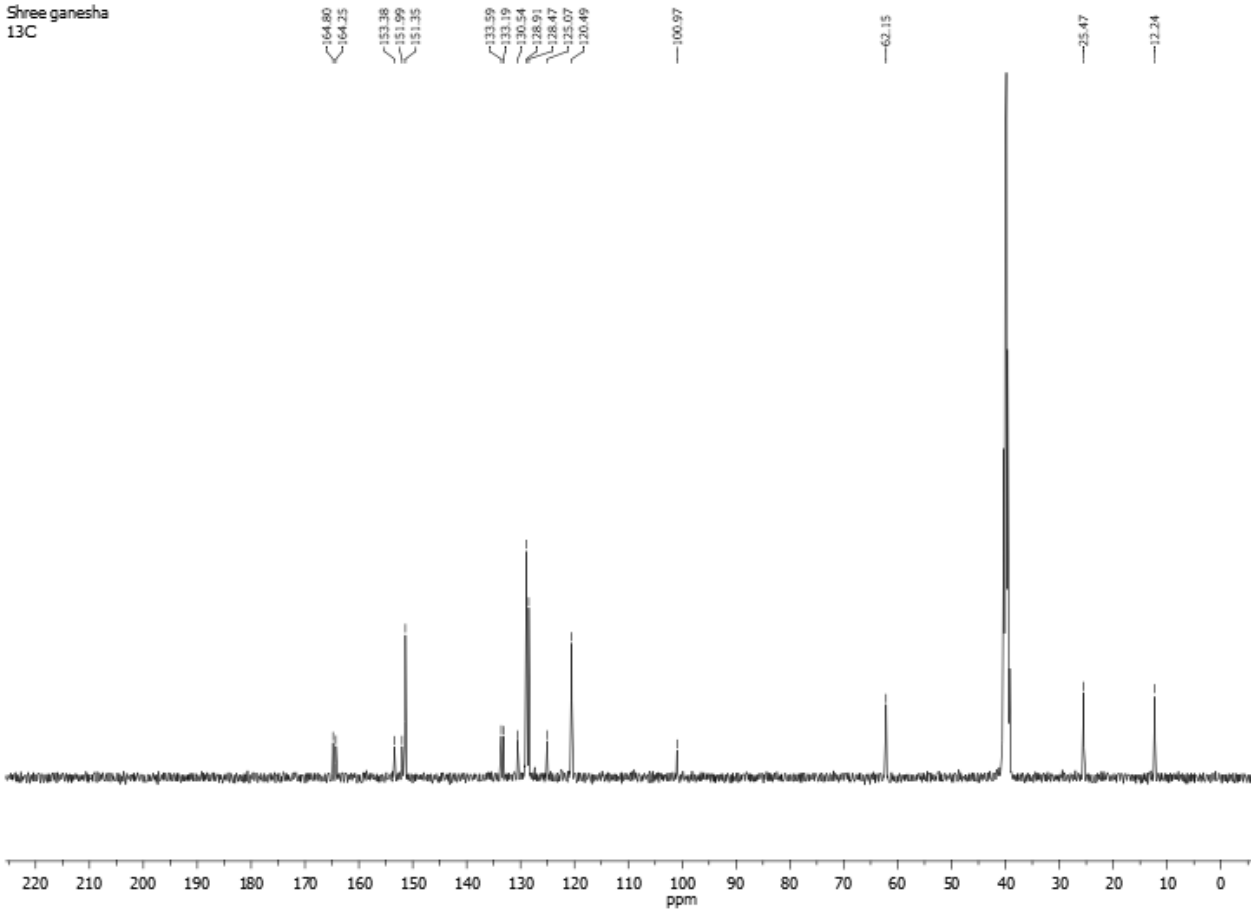
(c) Spectral data of *1-(3-methyl-6-phenyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)imidazo[2,1-b]thiazol-2-yl)ethanol (7g).* White solid, mp 120-121 ºC. ^{1}H-NMR (400 MHz, DMSO-*d*$_6$) δ 8.79 (s, 2H), 7.93-7.92 (m, 2H), 7.79 (m, 2H), 7.45-7.44 (m, 2H), 5.97 (s, 1H), 5.13 (s, 1H), 2.61 (s, 3H), 1.40-1.39 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-*d*$_6$) δ 164.80, 164.25, 153.38, 151.99, 151.35, 133.59, 133.19, 130.54, 128.91, 128.47, 125.07, 120.49, 100.97, 62.15, 25.47, 12.24. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{17}N_5O_2S_2$: 435.0824, found 436.0896.

^{1}H NMR

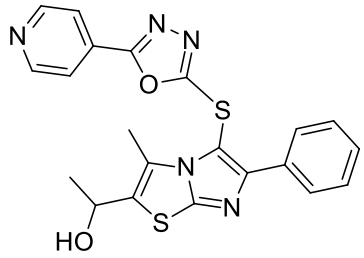


^{13}C NMR

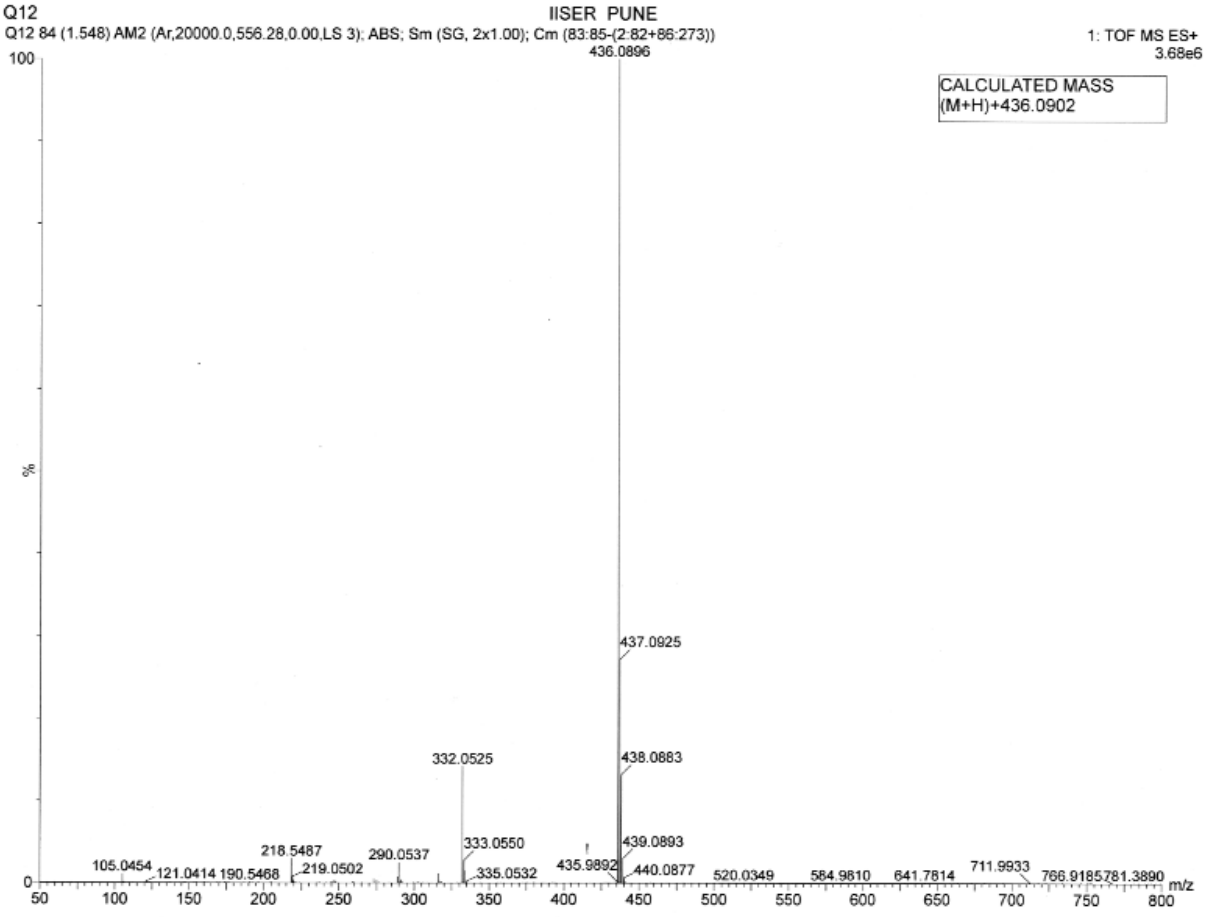

N
N
N
O
S
N
S
N
HO


Shree ganesha
13C
164.80
164.25
153.38
151.99
151.35
133.59
133.19
130.54
128.91
128.47
125.07
120.49
100.97
62.15
25.47
12.24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



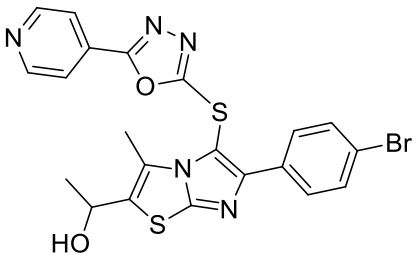
Calculated for $C_{21}H_{17}N_5O_2S_2$: 435.0824, found 436.0896.

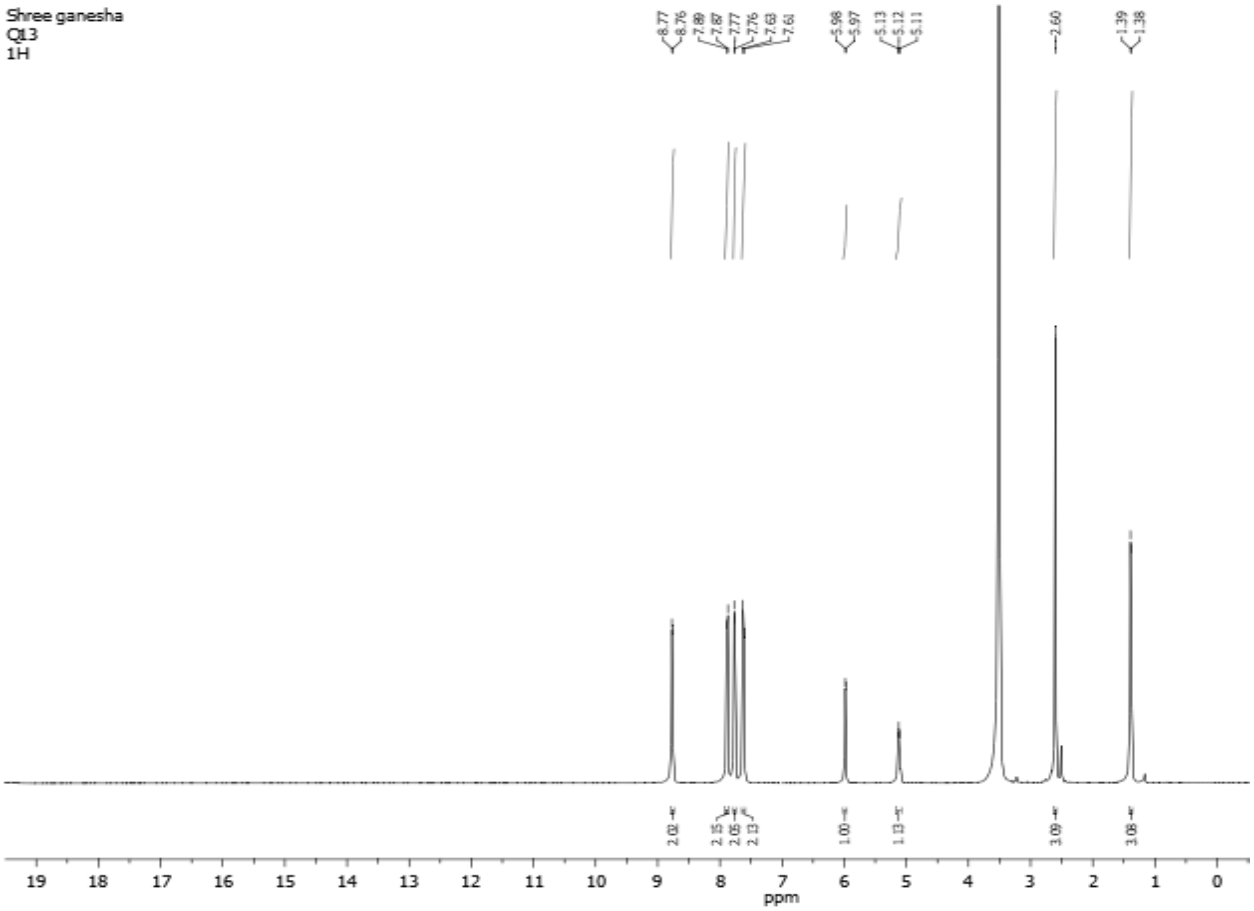


(d) Spectral data of *1-(6-(4-bromophenyl)-3-methyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)imidazo[2,1-b]thiazol-2-yl)ethanol (7h).* White solid, mp 117-118 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.77-8.76 (d, 2H), 7.89-7.87 (d, 2H), 7.77-7.67 (d, 2H),

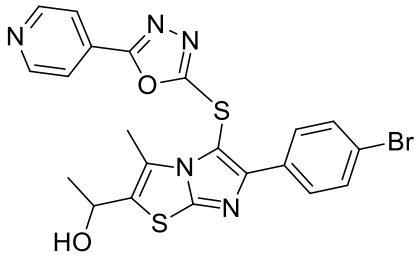
7.63-7.62 (d, 2H), 5.98-5.97 (d, 1H), 5.13-5.11 (m, 1H), 2.60 (s, 3H), 1.39-1.38 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 148.65, 141.73, 133.28, 132.55, 132.42, 128.91, 123.79, 90.77, 62.17, 25.39, 13.03. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{16}BrN_5O_2S_2$: 512.9929, found 515.9980.

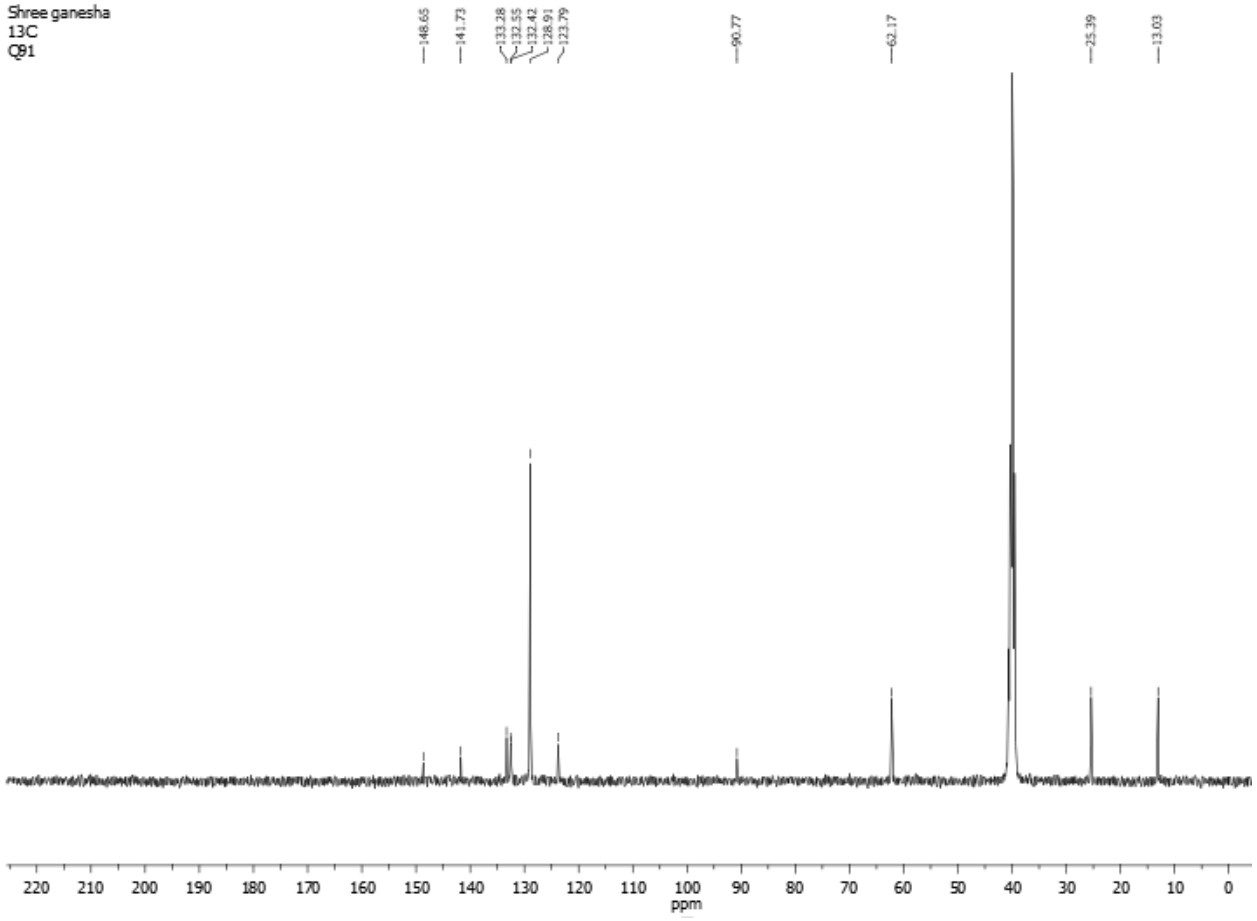
^{1}H NMR



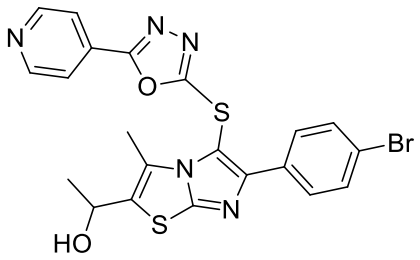


^{13}C NMR

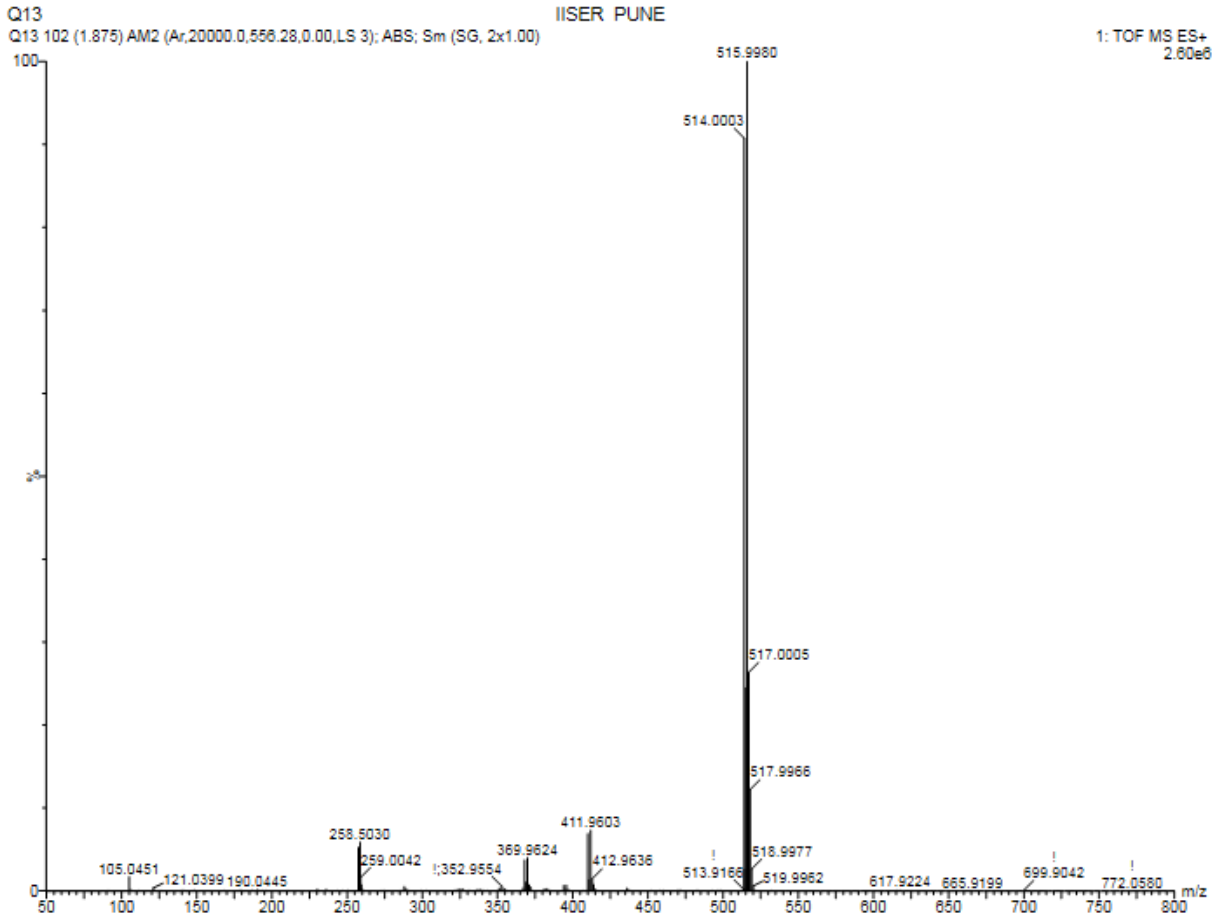

N
N
N
O
S
Br
N
S
N
HO


Shree ganesha
13C
Q81
148.65
141.73
133.28
132.55
132.42
128.91
123.79
90.77
62.17
25.39
13.03
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



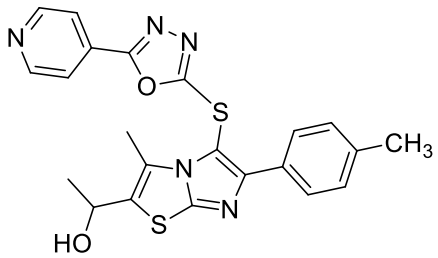
Calculated for $C_{21}H_{16}BrN_5O_2S_2$: 512.9929, found 515.9980.

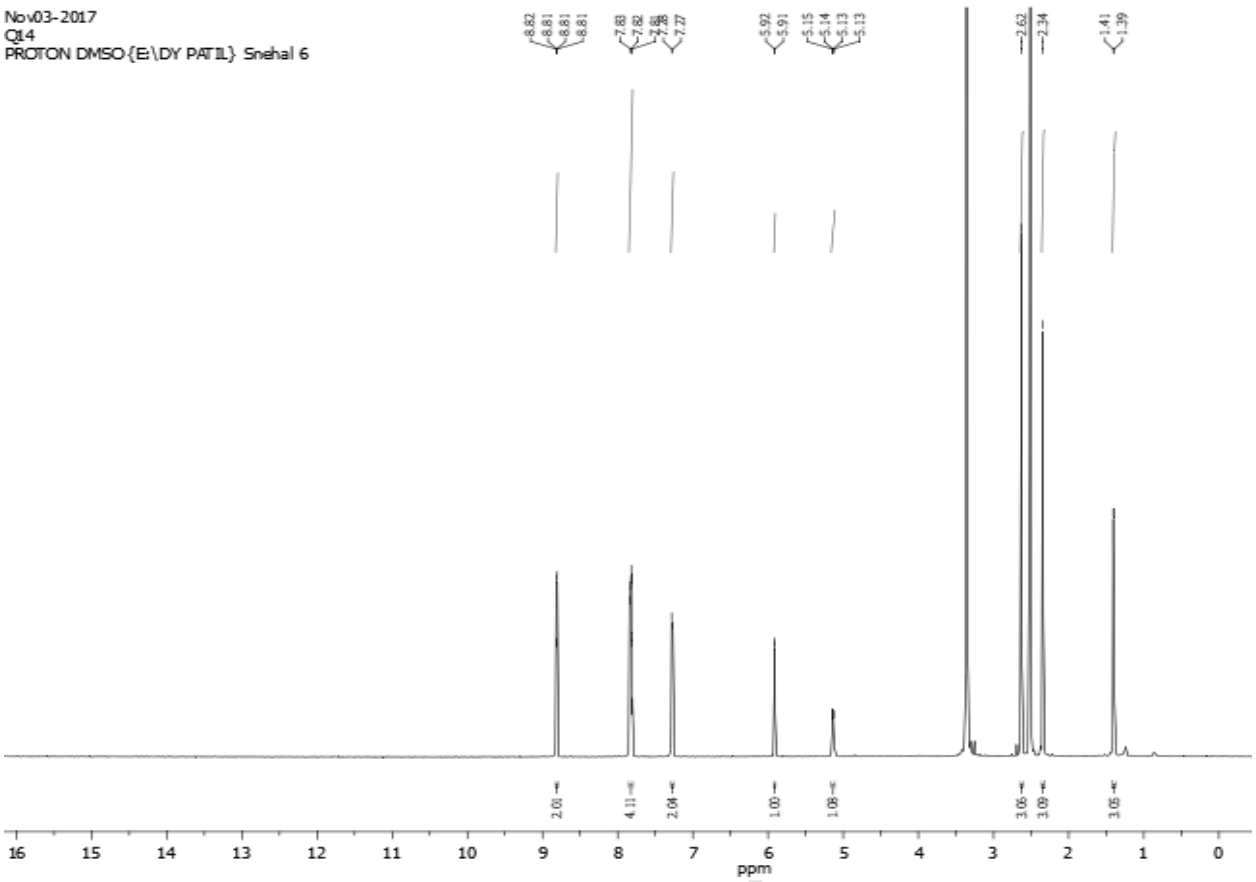


(e) Spectral data of *1-(3-methyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)-6-(p-tolyl)imidazo[2,1-b]thiazol-2-yl)ethanol (7i).* White solid, mp 115-116 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.82-8.81 (d, 2H), 7.84-7.81 (m, 4H), 7.28-7.27 (d, 2H), 5.92-5.91(d,

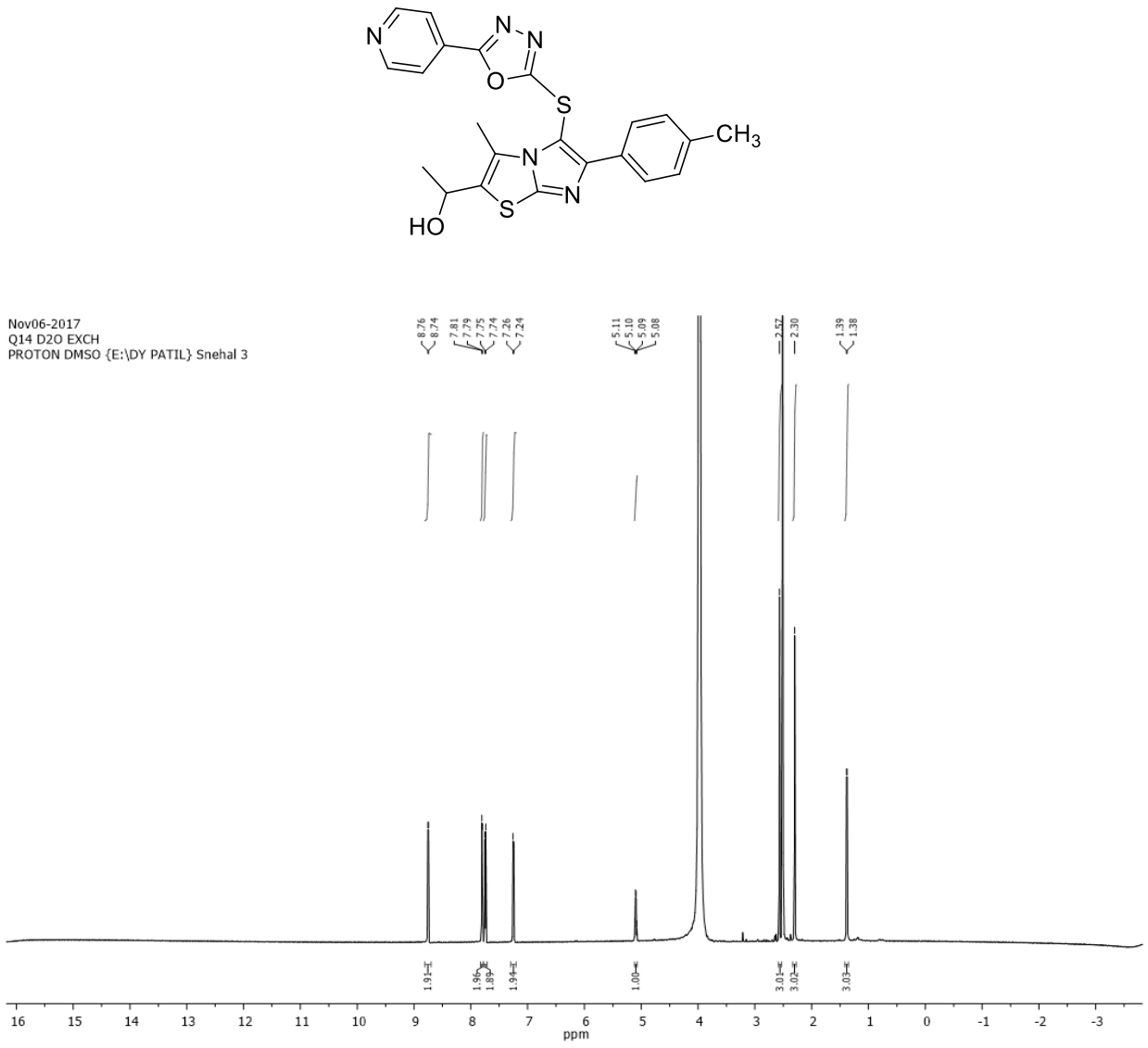
1H), (Exchangeable with D_2O), 5.15-5.13 (q, 1H), 2.62 (s, 3H), 2.34 (s, 3H), 1.41-1.39 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-*d*$_6$) δ 164.55, 164.36, 155.06, 152.93, 150.79, 138.72, 132.28, 130.32, 129.79, 129.17, 128.25, 125.26, 120.11, 99.20, 63.15, 24.65, 21.35, 12.20. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{22}H_{19}N_5O_2S_2$: 449.0980, found 450.1044.

^{1}H NMR

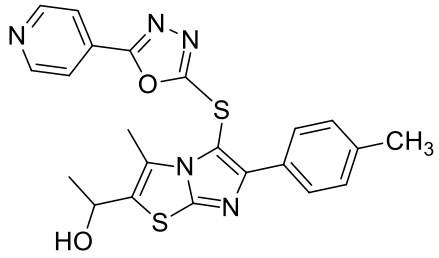


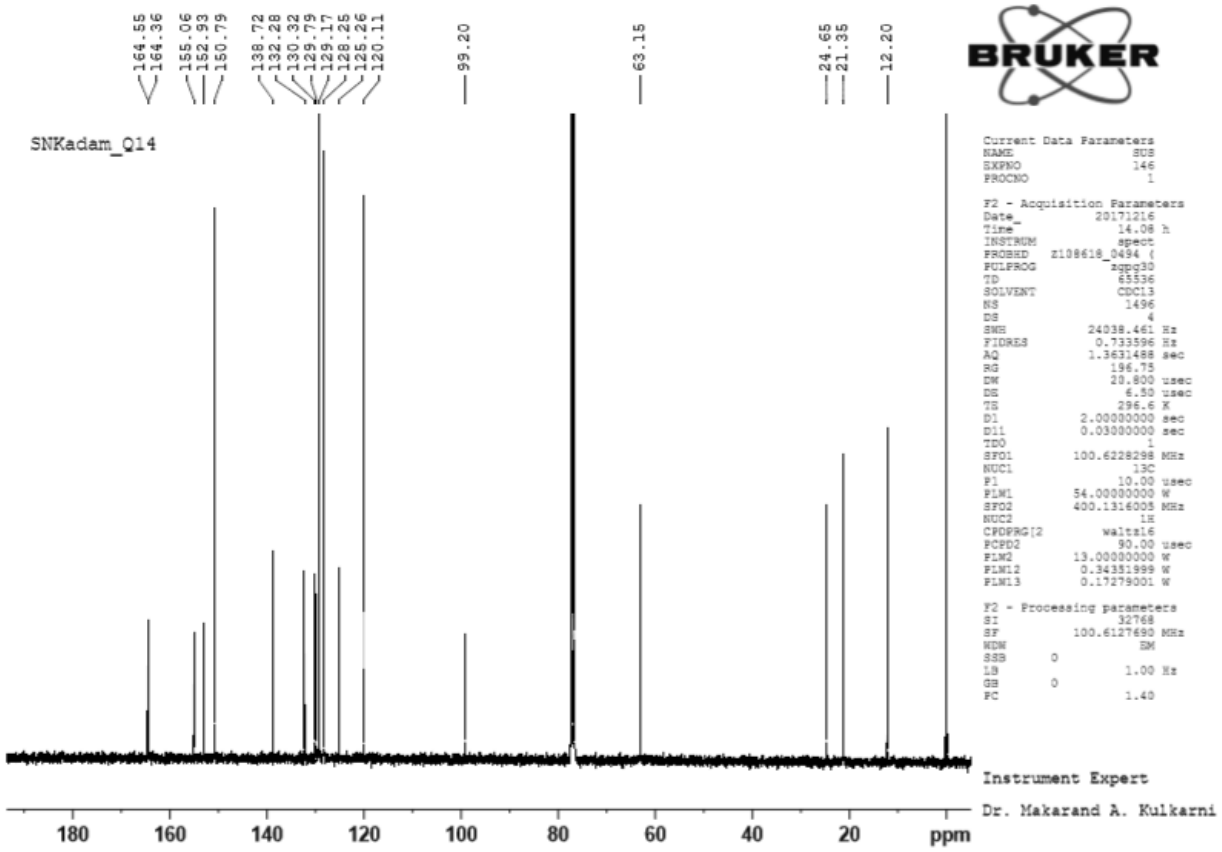


^{1}H NMR (D_2O Exchange)



^{13}C NMR


N
N
N
O
S
N
S
N
HO
CH3


164.55
164.36
155.06
152.93
150.79
138.72
132.28
130.32
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129.17
128.25
125.26
120.11
99.20
63.15
24.65
21.35
12.20
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SNKadam_Q14
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NS 1496
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FIDRES 0.733596 Hz
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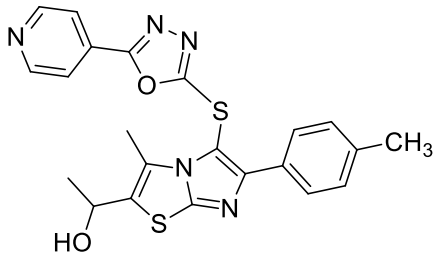
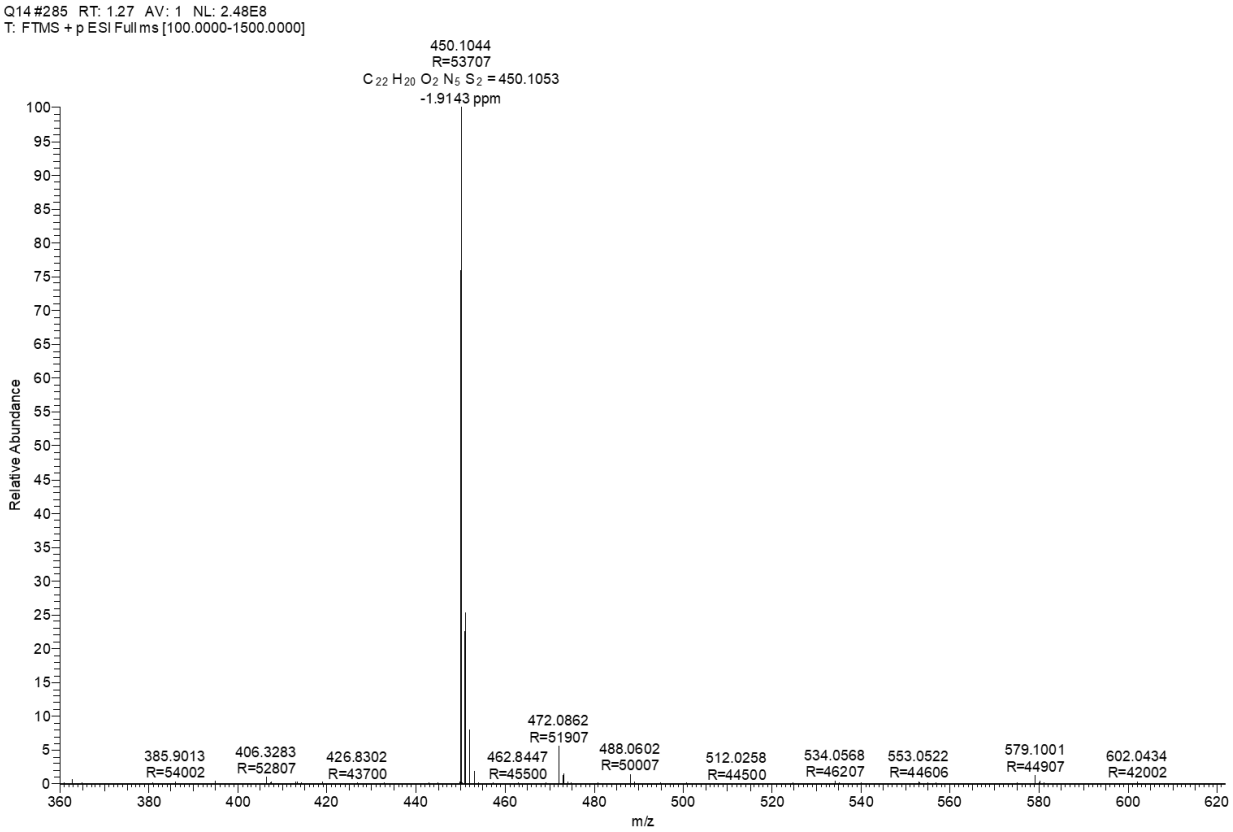
RG 196.75
DW 20.800 usec
DE 6.50 usec
TE 296.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 13.00000000 W
PLW12 0.34351999 W
PLW13 0.17279001 W
F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Instrument Expert
Dr. Makarand A. Kulkarni
180
160
140
120
100
80
60
40
20
ppm

HRMS



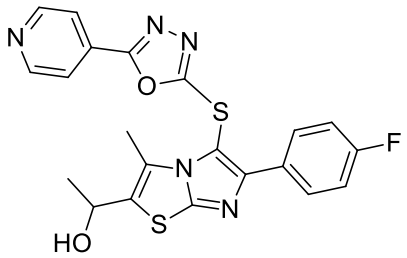
Calculated for $C_{22}H_{19}N_5O_2S_2$: 449.0980, found 450.1044.

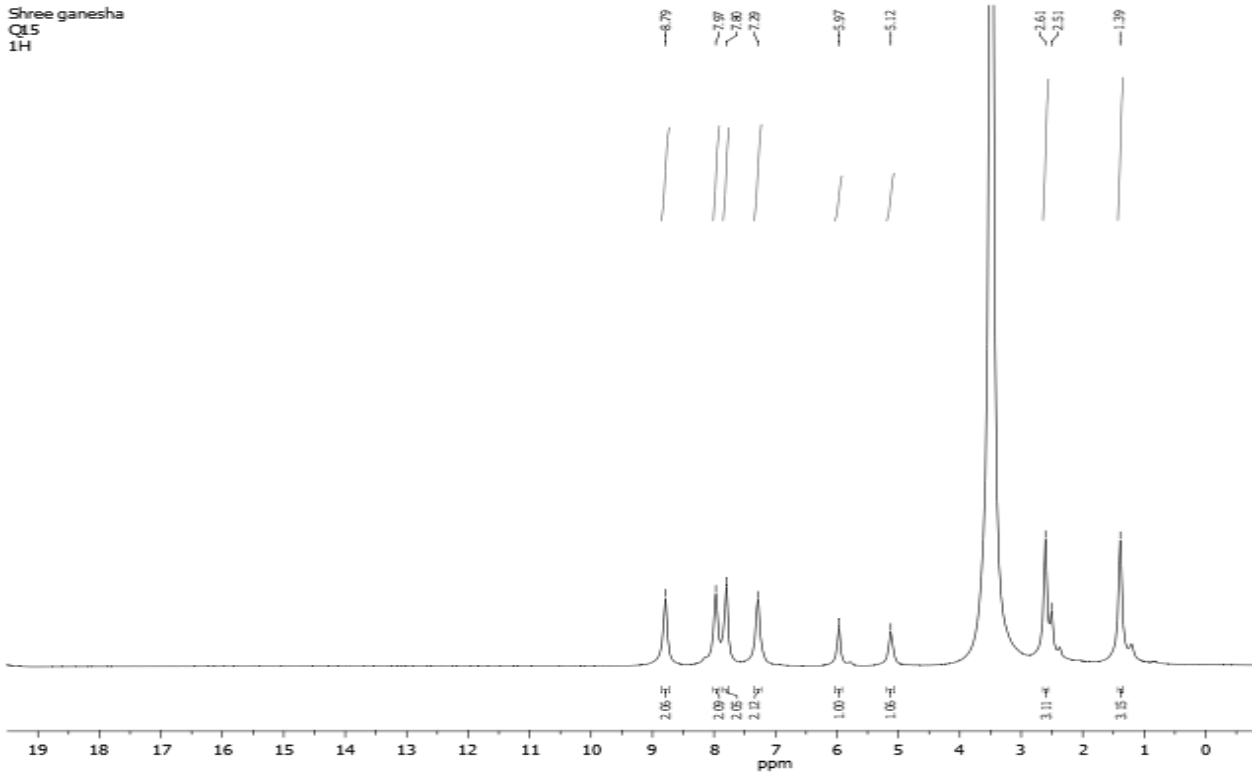


(f) Spectral data of *1-(6-(4-fluorophenyl)-3-methyl-5-((5-(pyridin-4-yl)-1,3,4-oxadiazol-2-yl)thio)imidazo[2,1-b]thiazol-2-yl)ethanol (7j).* White solid, mp 111-112 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.79 (s, 2H), 7.97 (d, 2H), 7.80 (d, 2H), 7.29 (d, 1H), 5.97 (s, 1H),

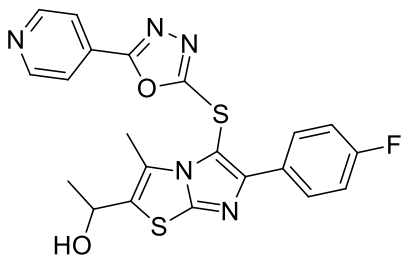
5.12 (s, 1H), 2.61-2.51 (d, 3H), 1.39 (d, 3H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 164.83, 164.12, 152.42, 151.97, 151.36, 133.66, 130.62, 130.55, 129.70, 125.06, 120.50, 115.97, 115.76, 100.96, 62.14, 25.46, 12.23. HRMS (ESI-TOF) m/z: [M+1] Calculated for $C_{21}H_{16}FN_5O_2S_2$: 453.0729, found 454.0800.

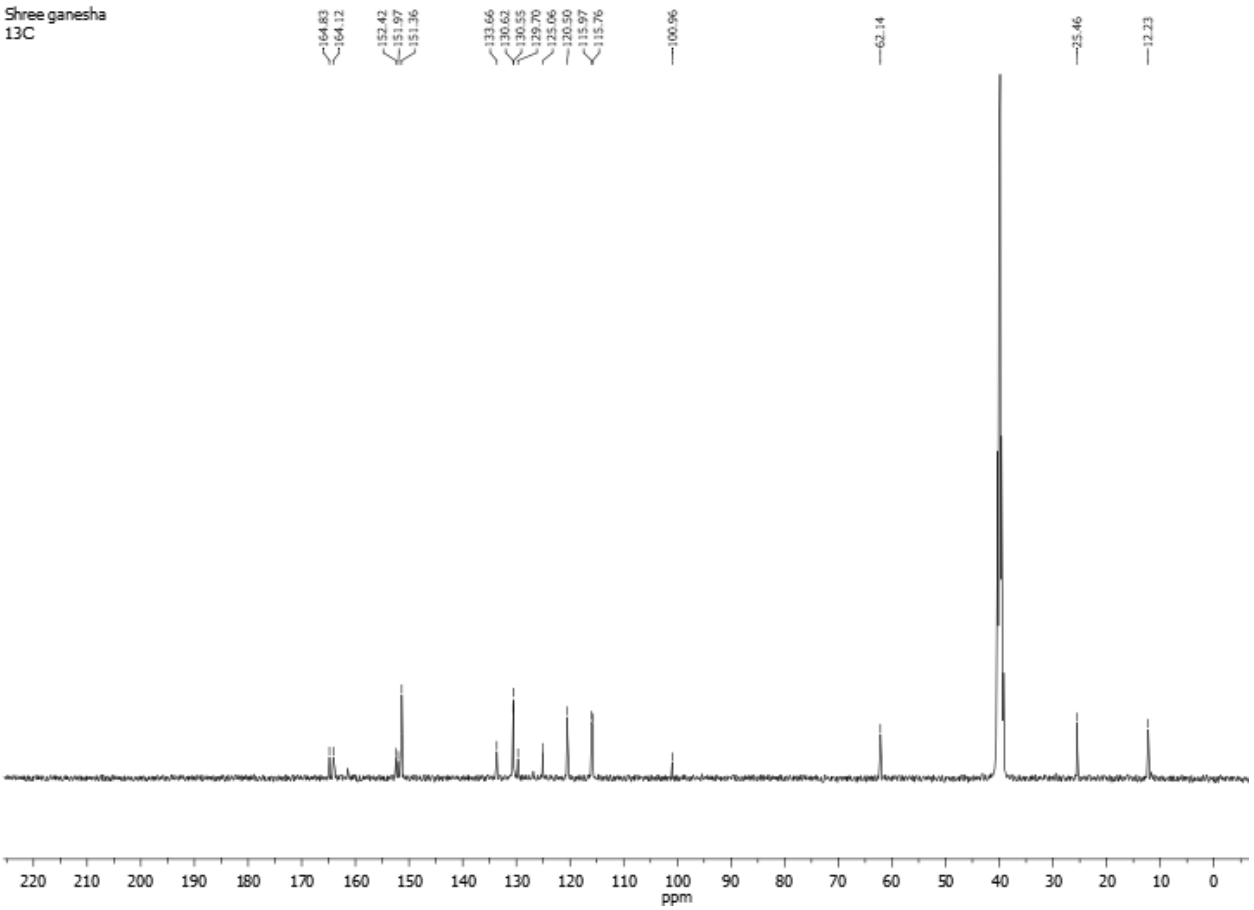
^{1}H NMR



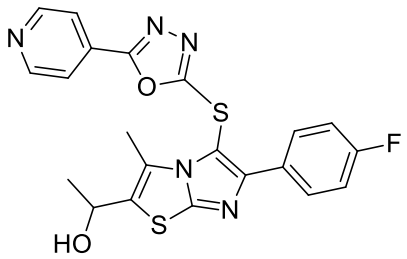


^{13}C NMR

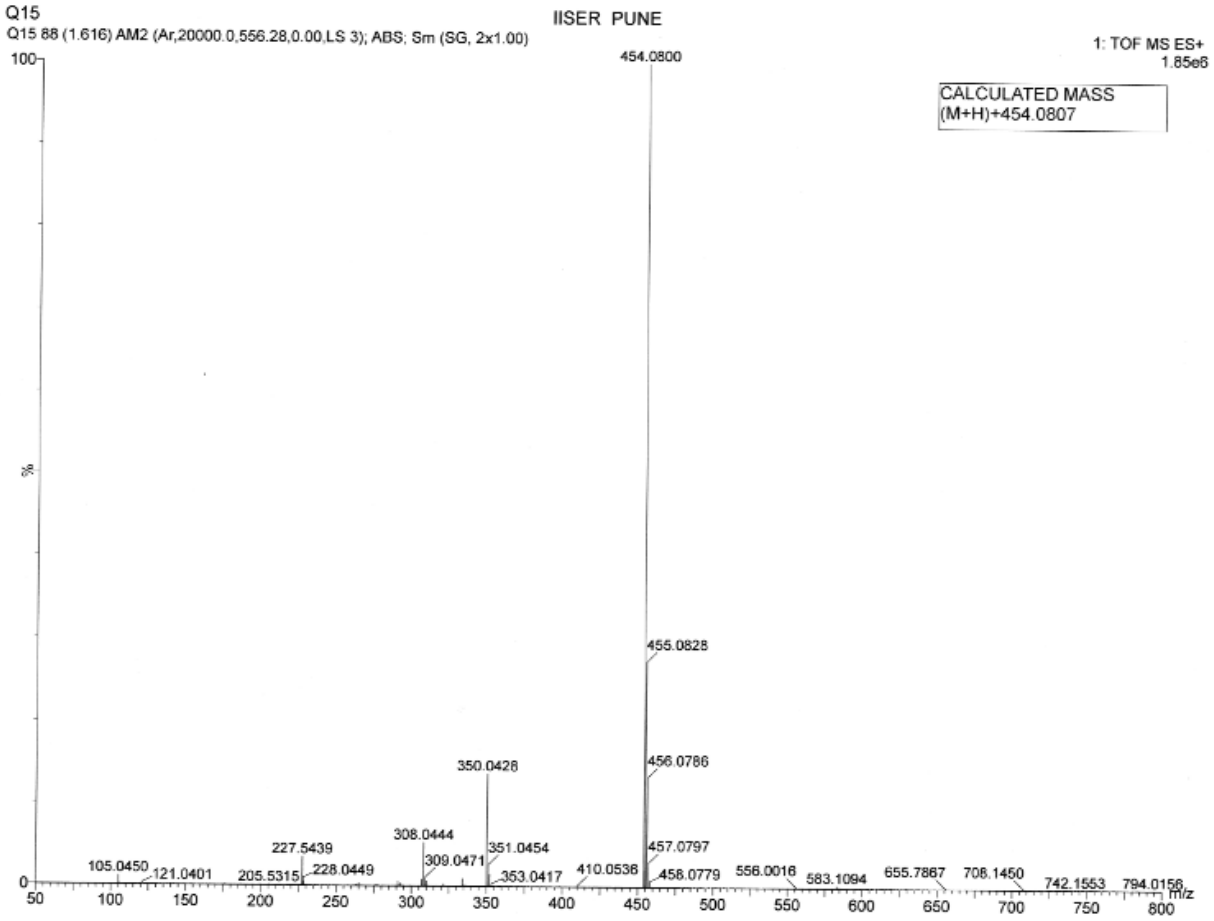

N
N
N
O
S
F
N
S
N
HO


Shree ganesha
13C
164.83
164.12
152.42
151.97
151.36
133.66
130.62
130.55
129.70
125.06
120.50
115.97
115.76
100.96
62.14
25.46
12.23
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

HRMS



Calculated for $C_{21}H_{16}FN_5O_2S_2$: 453.0729, found 454.0800

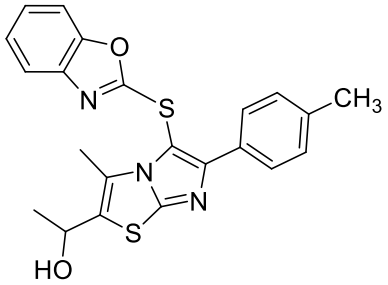


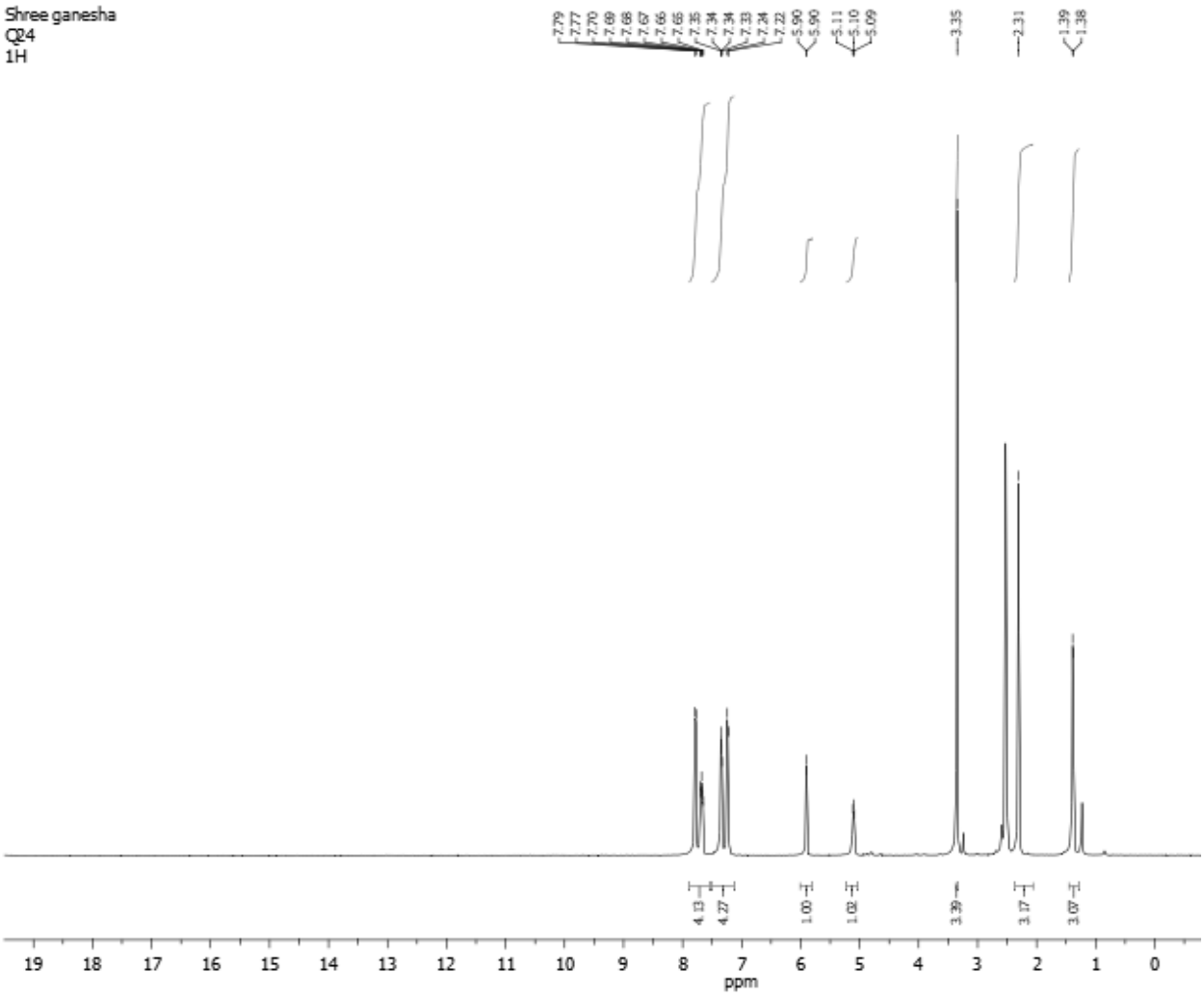
7. a) ***General procedure for the synthesis of 1-(5-(benzo[d]oxazol-2-ylthio)-3-methyl-6-(p-tolyl)imidazo[2,1-b]thiazol-2-yl)ethanol (7k).***

NCS (1.5 mmol) was taken in round bottom flask containing CH_3OH. To this same pot benzo[d]oxazole-2-thiol **(2c)** (**Scheme 2**) (2 mmol) was added slowly with constant stirring, and reaction mass was stirred at room temperature up to 5 minutes. As TLC indicate the formation of (NHTS). Furthermore to the same pot 1-(6-(4-chlorophenyl)-3-methylimidazo[2,1-b]thiazol-2-yl)ethanol (2 mmol) was added with small proportions at a time and stirring was continued for another 20 minutes, as TLC indicate the completion of reaction. The reaction mass was poured on ice cold water, solid product separated out was filtered, dried and washed with aqueous ethanol. No further purification like column chromatography was needed.

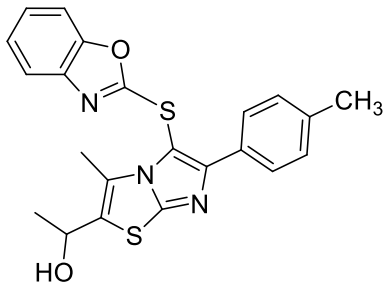
b) Spectral data of ***1-(5-(benzo[d]oxazol-2-ylthio)-3-methyl-6-(p-tolyl)imidazo[2,1-b]thiazol-2-yl)ethanol (7k).*** white solid, mp 115-116 ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 7.79-7.65 (m, 4H), 7.35-7.22 (m, 4H), 5.90 (s, 1H), 5.11-5.09 (m, 1H), 3.35 (s, 3H), 2.32 (s, 3H), 1.39-1.38 (m, 3H), 1.37. ^{13}C-NMR (400 MHz, DMSO-d_6) δ 163.03, 153.19, 152.05, 151.77, 141.61, 138.28, 133.47, 130.54, 129.49, 128.18, 125.40, 124.85, 119.44, 111.15, 101.52, 62.09, 25.47, 21.30, 12.17.

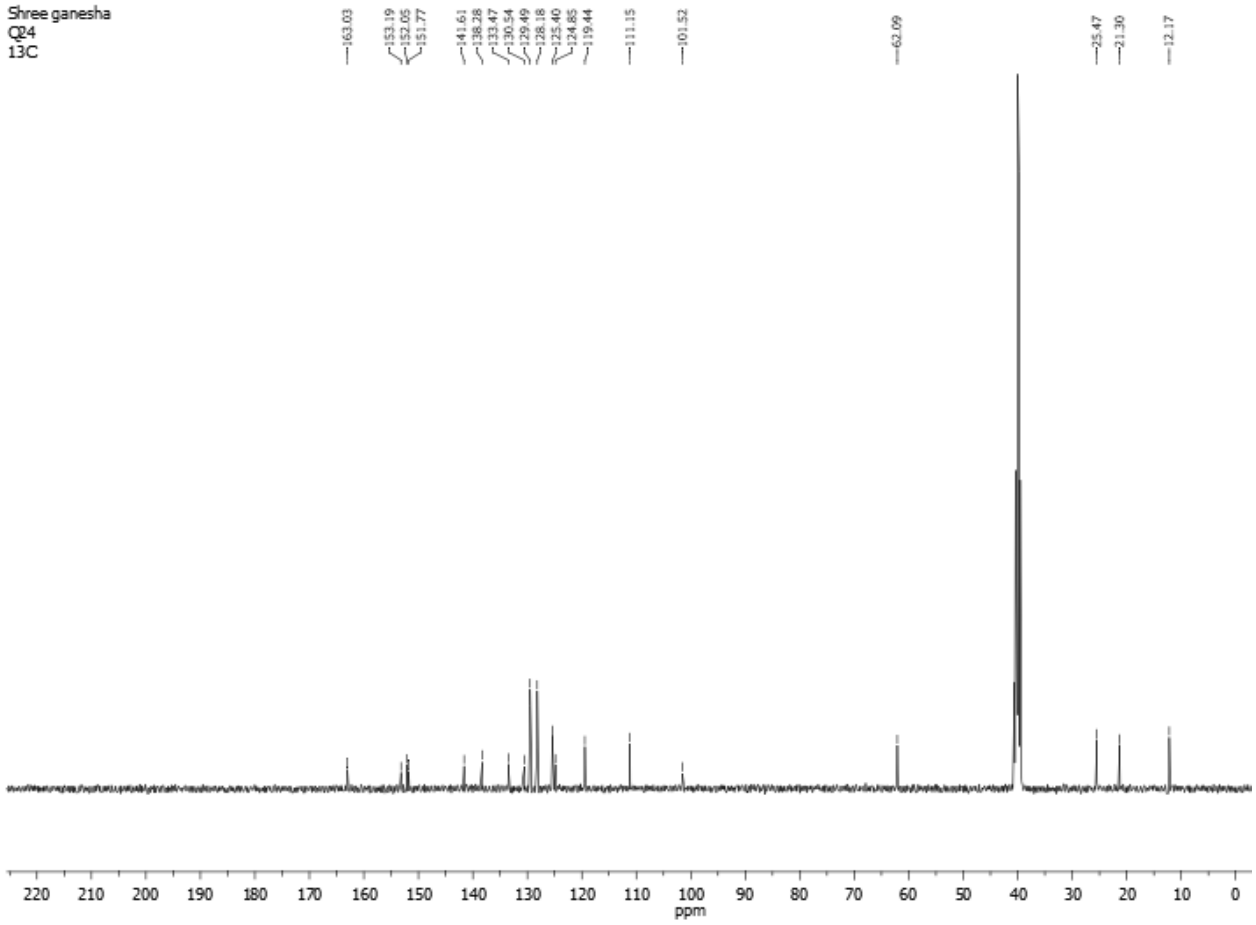
^{1}H NMR


O
N
S
CH3
N
N
S
HO


Shree ganesha
Q24
1H
7.79
7.77
7.70
7.69
7.68
7.67
7.66
7.65
7.35
7.34
7.34
7.33
7.24
7.22
5.90
5.90
5.11
5.10
5.09
3.35
2.31
1.39
1.38
4.13
4.27
1.00
1.02
3.39
3.17
3.07
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

^{13}C NMR

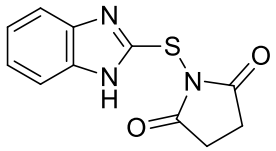

O
N
S
CH3
N
N
S
HO

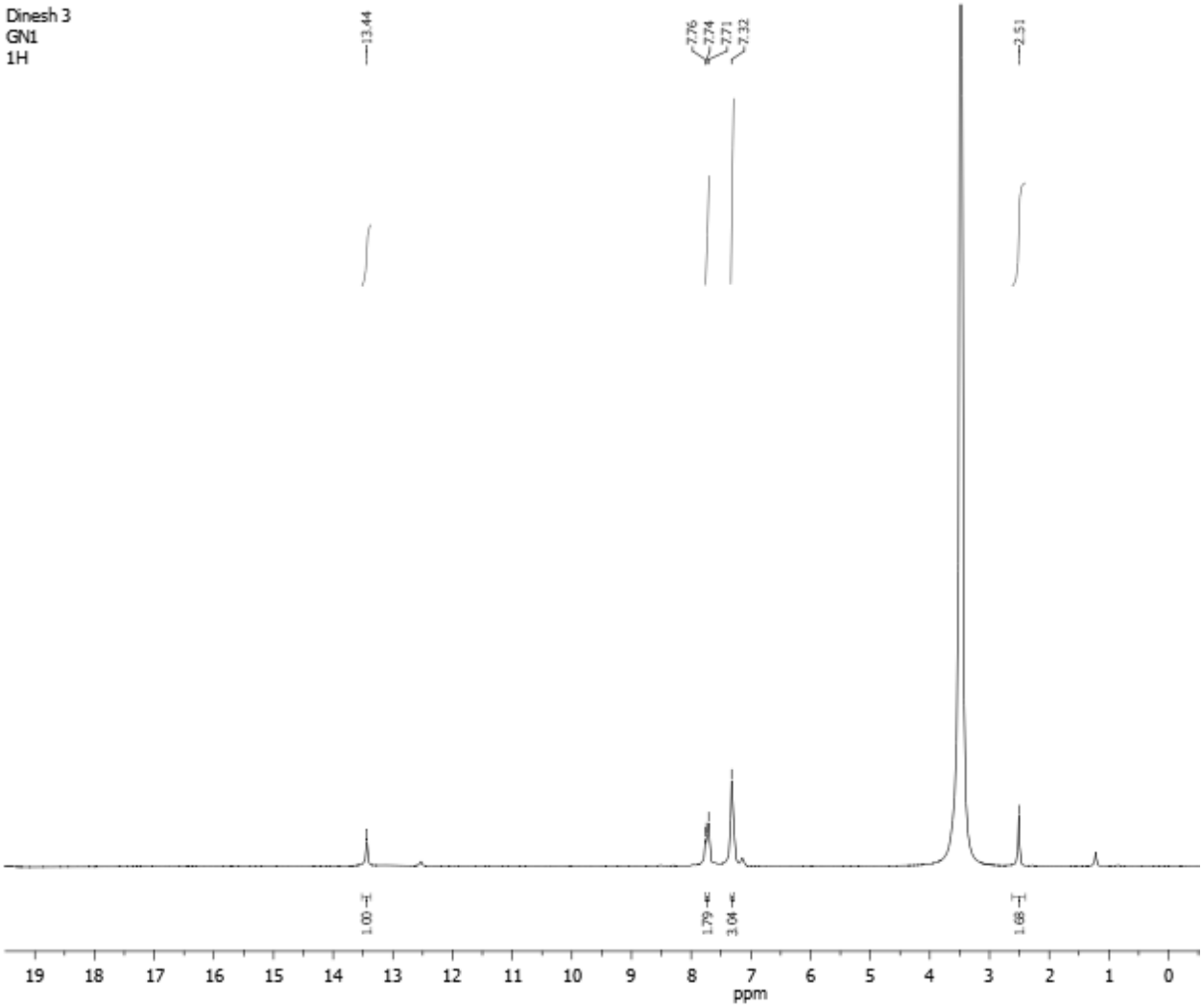

Shree ganesha
Q24
13C
163.03
153.19
152.05
151.77
141.61
138.28
133.47
130.54
129.49
128.18
125.40
124.85
119.44
111.15
101.52
62.09
25.47
21.30
12.17
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

8. a) ***General procedure for the synthesis of 1-((1H-benzo[d]imidazol-2-yl)thio)pyrrolidine-2,5-dione (NHTS) (3a)***

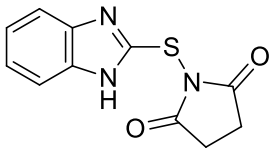
White solid, mp 60-61ºC. ^{1}H-NMR (400 MHz, DMSO-d_6,) δ 13.44 (s, 1H), 7.76-7.32 (m, 4H), 2.51 (m, 4H). ^{13}C-NMR (400 MHz, DMSO-d_6) δ 169.01, 142.68, 132.54, 131.60, 125.05, 123.36, 123.07, 112.61, 110.57.

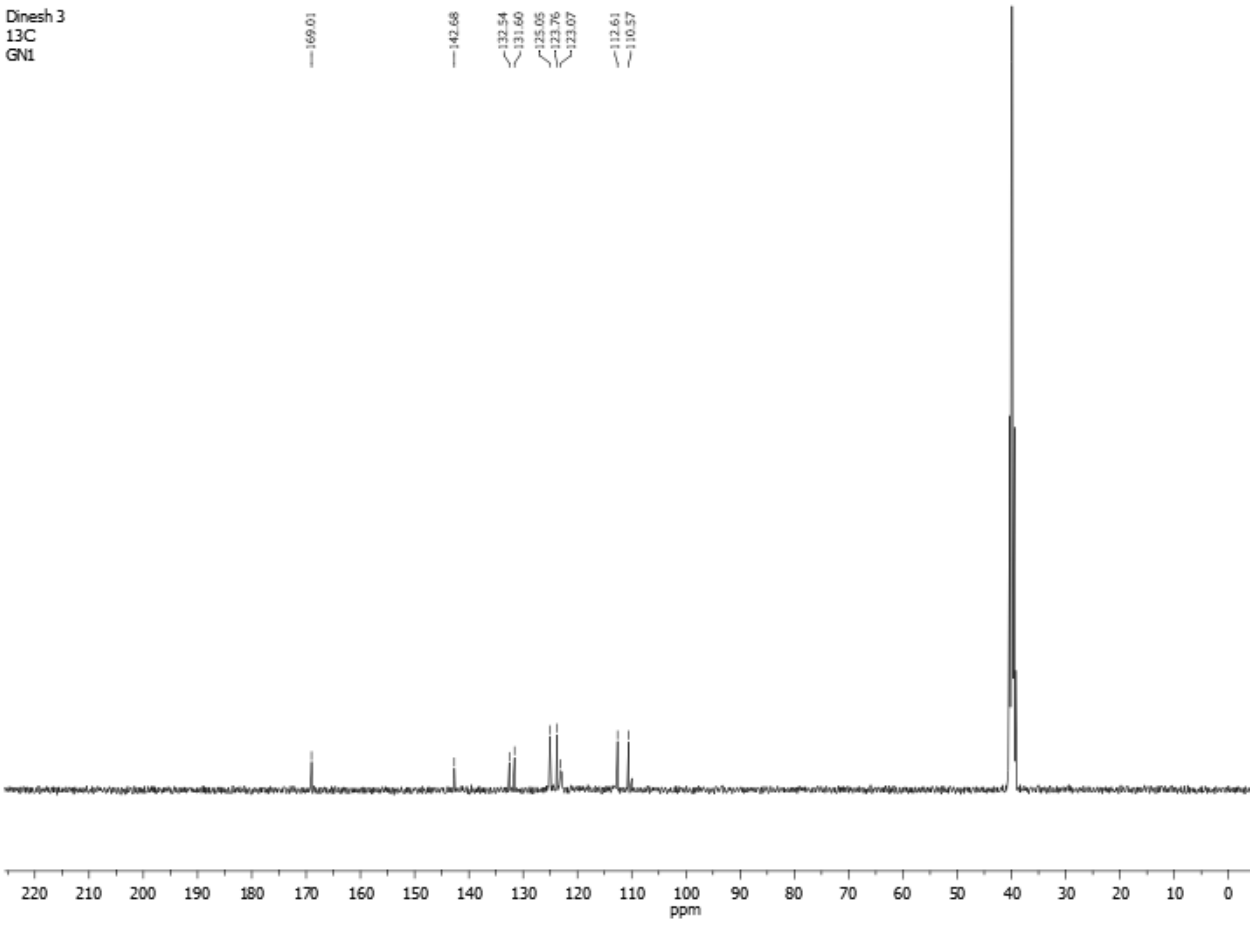
^{1}H NMR





^{13}C NMR



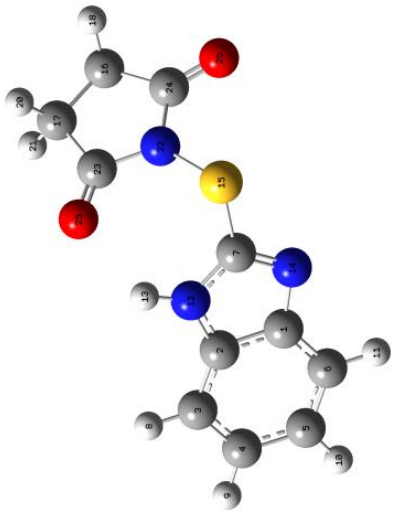


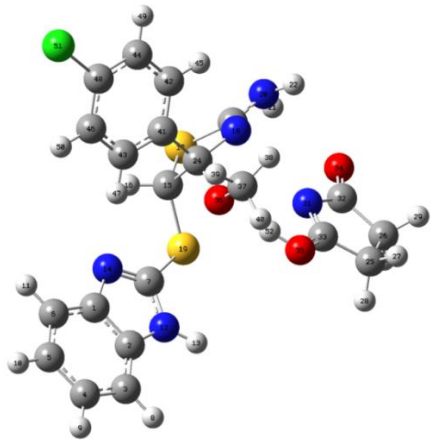
Computational details:

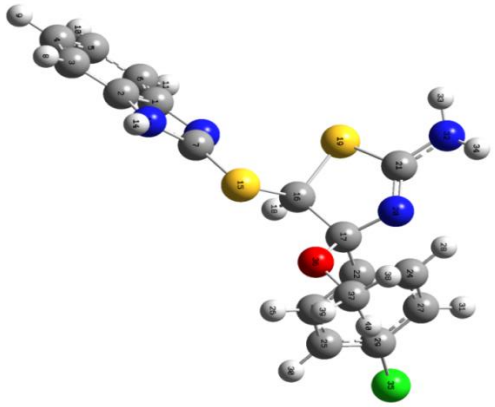
The geometries of all molecules including NHTS, intermediates found in this study and product 7a have been fully optimized at B3LYP/6-31+G(d,p) level without symmetry constraints by using Gaussian 16 software[1]. The second order harmonic frequencies have been calculated and found with all positive values

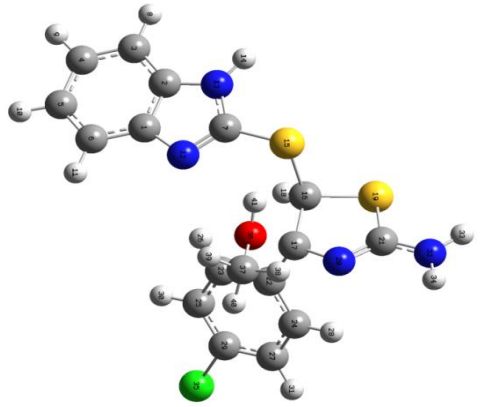
to ensure them minima on their respective potential energy surfaces. The optimized geometries have been visualized and IR frequencies have been analyzed by using Gaussview 6 software[2].

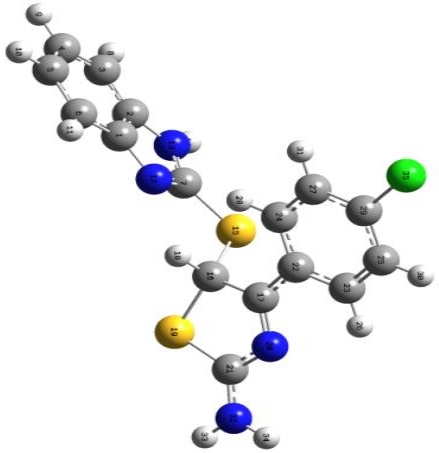
Table S1: The geometrical parameters of all the structures obtained at B3LYP/6-31+G(d,p) level.

Molecule	Structure of molecule	Total Energy (a.u.)	Label	Bond length (A)	Label	Bond Angle (°)	Label	Frequency(cm^{-1})	Intensity(KM/Mole)
NHTS		-1137.55035798	(S15-N22)	1.746	(C7-S15-N22)	101.4	(S15-N22)	645.81	33.2
			(S15-C7)	1.768			(S15-C7)	605.88	7.1
			(N22-C23)	1.400	(C23-N22-C24)	113.2	(N22-C23)	1170.77	90.5
			(N22-C24)	1.422			(N22-C24)	1170.77	90.5
			(C7-N12)	1.379	(N12-C7-N14)	113.7	(C7-N12)	1387.21	50.3
			(C7-N13) (N12-H13)	1.314 1.015			(C7-N13) (N12-H13)	1458.38 3581.65	15.7 207.9

Intermediate-1					
					
-2568.3853944					
(O35-H52)	(C24-N18)	(C15-H16)	(C15-C24)	(C24-O36)	(C15-S19)
0.994	1.442	1.088	1.598	1.444	1.852
(H52-O35-C33)	(C15-C24-N18)	(S19-C15-H16)	(S19-C15-C24)	(C24-O36-C37)	(S19-C15-S17)
111.8	109.9	106.1	117.5	115.3	107.3
(O35-H52) str.	(C24-N18) Str.	(C15-H16) bend.	(C15-C24) Str.	(C24-O36) str.	(C15-S19)
3331.73	1054.71	1294.97	1085.26	1054.71	749.74
1191.8	46.6	111.9	163.0	46.6	8.6

Intermediate-2					
					
-2207.70598969					
(C17-N20)	(C16-H18)	(C16-S19)	(C16-C17)	(C17-O36)	(S15-C16)
1.449	1.086	1.832	1.586	1.421	1.851
(C16-C17-N20)	(S15-C16-H18)	(C17-C16-S19)	(S15-C16-C17)	(C17-O36-C37)	(S15-C16-S19)
109.4	106.9	105.3	110.8	116.1	114.0
(C17-N20) str.	(C16-H18) bend.	(C16-S19) str.	(C16-C17) str.	(C37-O36) Str.	(S15-C16) Str.
1062.28	1263.55	768.84	1126.98	1126.98	768.84
41.3	57.6	62.5	236.3	236.3	62.5

Intermediate-3						
						
-2208.05602881						
(O36-H41)	(C17-N20)	(C16-H18)	(C16-S19)	(C16-C17)	(C17-O36)	(S15-C16)
1.000	1.408	1.088	1.827	1.590	1.575	1.876
(H41-O36-C17)	(C16-C17-N20)	(S15-C16-H18)	(C17-C16-S19)	(S15-C16-C17)	(C17-O36-C37)	(S15-C16-S19)
107.5	110.9	107.5	103.0	115.2	118.6	109.8
				(O36-H41) str.	(C16-H18) rock.	(S15-C16) Str.
				3210.41 3214.19	1301.68	828.38
				338.6 254.4	223.6	54.7

Intermediate-4				
				
-2092.34875162				
(C17-C22)	(C16-H18)	(C17-N20)	(C16-S19)	(C16-C17)
1.440	1.100	1.321	1.847	1.526
(C16-C17-C22)	(H18-C16-S19)	(C16-C17-N20)	(C17-C16-S19)	(C17-C16-S15)
122.9	109.6	116.0	104.7	113.5
(C17-C22)	(C16-H18) Str.	(C17-N20) Str.	(C16-S19) Str.	(C16-C17) Str.
1326.97	3016.38	1511.16	760.44	1084.30
442.9	203.1	238.0	36.4	41.5

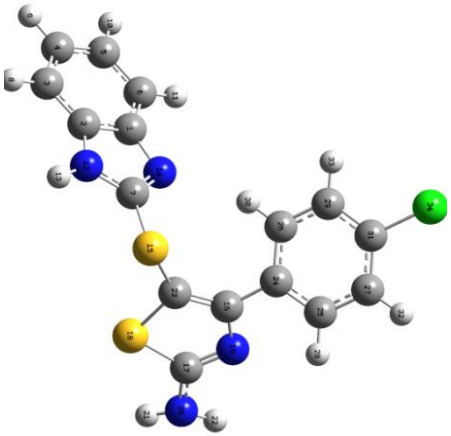
7a					
					
-2091.97347810					
(C16-C24)		(C16-N19)	(C23-S18)	(C23-C16)	
1.479		1.382	1.771	1.381	
(C24-C16-N19)	(C23-C16-C24)	(C23-C16-N19)	(C16-C23-S18)	(S15-C23-S18)	(S15-C23-C16)
117.7	127.1	115.2	109.5	120.3	129.5
(C16-C24) str.		(C16-N19) str.	(C23-S18) Str.	(C23-C16) str.	
1194.26		1361.38	848.52	1502.29	
7.0		114.8	44.1	109.0	

Table S2: Optimized Geometry Cartesian Coordinates of all structures obtained at B3LYP/6 31+G(d,p) level

Sr.no	Molecule	Cartesian coordinates				
1	NHTS	6	0	2.480005	-0.796902	0.083736
		6	0	2.268837	0.583005	-0.174774
		6	0	3.253065	1.548802	0.066242
		6	0	4.467599	1.089749	0.568384
		6	0	4.695081	-0.281834	0.827268
		6	0	3.712748	-1.236691	0.590832
		6	0	0.482817	-0.629654	-0.654193
		1	0	3.084862	2.602385	-0.133689
		1	0	5.262468	1.803220	0.764416
		1	0	5.659523	-0.590377	1.219130
		1	0	3.878500	-2.290610	0.788743
		7	0	0.982976	0.655483	-0.668649
		1	0	0.441592	1.467442	-0.946071
		7	0	1.339945	-1.524649	-0.218560
		16	0	-1.106959	-1.020671	-1.321996
		6	0	-3.885672	0.277147	1.338205
		6	0	-3.423747	1.607597	0.723396
		1	0	-4.945541	0.061288	1.178650
		1	0	-3.701397	0.212370	2.414772
		1	0	-4.206464	2.114393	0.150145
		1	0	-3.044956	2.326446	1.455096
		7	0	-2.161976	-0.149644	-0.236675
		6	0	-2.298788	1.243981	-0.232812
		6	0	-3.060740	-0.803605	0.649954
		8	0	-1.608187	2.015722	-0.872838
		8	0	-3.140699	-1.997436	0.799151
2	Intermediate-1	6	0	2.639122	2.941632	-0.619426
		6	0	1.808376	3.942119	-0.059675
		6	0	2.317033	5.113031	0.504182

		6	0	3.704884	5.260882	0.497262
		6	0	4.546858	4.276284	-0.059026
		6	0	4.029467	3.110618	-0.621714
		6	0	0.626964	2.234036	-0.855601
		1	0	1.671116	5.875208	0.929552
		1	0	4.144683	6.155446	0.927627
		1	0	5.621164	4.433656	-0.049369
		1	0	4.674926	2.354737	-1.057458
		7	0	0.518490	3.457137	-0.227346
		1	0	-0.335310	3.860098	0.128356
		7	0	1.867320	1.893733	-1.113583
		6	0	-0.225945	-0.395148	-1.276824
		1	0	0.754544	-0.373955	-1.748792
		16	0	-1.381145	-1.386122	-2.282146
		7	0	-1.328049	-1.976620	0.299819
		16	0	-0.840907	1.352110	-1.290676
		7	0	-3.119675	-2.921362	-0.886422
		1	0	-3.862950	-2.528588	-1.457499
		1	0	-3.463898	-3.234867	0.013851
		6	0	-2.002568	-2.144959	-0.773898
		6	0	-0.162127	-1.144653	0.132538
		6	0	-5.028597	1.538246	1.701421
		6	0	-6.099733	0.868658	0.826915
		1	0	-5.137758	1.334856	2.772012
		1	0	-4.968955	2.625444	1.585190
		1	0	-6.851539	0.314293	1.395128
		1	0	-6.633418	1.570128	0.178859
		7	0	-3.911845	0.017473	0.222407
		6	0	-5.286539	-0.107612	-0.044478
		6	0	-3.770220	0.886829	1.173511
		8	0	-5.752175	-0.896715	-0.846916
		8	0	-2.612884	1.228036	1.701315
		8	0	-0.195097	-0.114086	1.142151
		6	0	0.028607	-0.565058	2.489541

		1	0	-0.665376	-1.370961	2.746772
		1	0	1.060059	-0.902923	2.622692
		1	0	-0.154177	0.302847	3.125789
		6	0	1.140632	-1.952928	0.223513
		6	0	1.119139	-3.336914	0.425731
		6	0	2.380216	-1.303663	0.114008
		6	0	2.306471	-4.068318	0.517941
		1	0	0.166812	-3.846449	0.516776
		6	0	3.572569	-2.020541	0.208958
		1	0	2.418701	-0.231616	-0.057713
		6	0	3.524699	-3.401203	0.410600
		1	0	2.283075	-5.141606	0.671884
		1	0	4.528059	-1.514731	0.122690
		17	0	5.026029	-4.310932	0.528323
		1	0	-1.857688	0.730576	1.287907
3	Intermediate-2	6	0	-3.871203	1.120315	0.339541
		6	0	-4.703471	0.446281	-0.585786
		6	0	-6.065387	0.721323	-0.711109
		6	0	-6.586430	1.706748	0.130078
		6	0	-5.772253	2.387591	1.057194
		6	0	-4.411428	2.105431	1.174407
		6	0	-2.599874	-0.271542	-0.688927
		1	0	-6.695457	0.199263	-1.425035
		1	0	-7.642041	1.953206	0.066848
		1	0	-6.217016	3.147967	1.692138
		1	0	-3.780478	2.627590	1.886402
		7	0	-2.564665	0.648108	0.246735
		7	0	-3.856754	-0.445473	-1.232772
		1	0	-4.107324	-1.108975	-1.950079
		16	0	-1.245678	-1.229139	-1.290332
		6	0	0.011974	-0.656816	-0.059392
		6	0	1.442944	-1.252629	-0.396299
		1	0	0.000484	0.430546	-0.078184
		16	0	-0.336047	-1.181136	1.661472

		7	0	1.708095	-2.386124	0.465877
		6	0	0.936481	-2.432672	1.486273
		6	0	2.505860	-0.149642	-0.231034
		6	0	2.564465	0.887132	-1.174301
		6	0	3.404920	-0.137495	0.838736
		6	0	3.498806	1.915009	-1.055590
		1	0	1.880218	0.882383	-2.017674
		6	0	4.346730	0.886983	0.973571
		1	0	3.380893	-0.938148	1.569048
		6	0	4.384379	1.905380	0.024031
		1	0	3.541542	2.712483	-1.789429
		1	0	5.042813	0.890689	1.805259
		7	0	1.071515	-3.339403	2.501517
		1	0	0.253739	-3.568526	3.047547
		1	0	1.708609	-4.103746	2.319937
		17	0	5.568146	3.197429	0.182741
		8	0	1.371572	-1.660450	-1.755580
		6	0	2.495477	-2.390224	-2.254378
		1	0	2.627541	-3.326510	-1.705225
		1	0	2.268358	-2.597033	-3.301846
		1	0	3.415389	-1.796278	-2.191491
4	Intermediate-3	6	0	-3.448421	0.705781	-0.391885
		6	0	-4.238897	-0.072563	0.489314
		6	0	-5.486644	0.353421	0.956735
		6	0	-5.920057	1.598242	0.512613
		6	0	-5.143378	2.388567	-0.366547
		6	0	-3.906065	1.958948	-0.828873
		6	0	-2.344718	-1.094154	-0.031451
		1	0	-6.088273	-0.248760	1.629665
		1	0	-6.881600	1.973225	0.848179
		1	0	-5.529778	3.350649	-0.687005
		1	0	-3.312167	2.559080	-1.510148
		7	0	-2.274134	0.030681	-0.704056
		7	0	-3.495684	-1.221268	0.711104

		1	0	-3.745131	-2.007354	1.294686
		16	0	-1.133274	-2.388682	-0.064532
		6	0	0.371374	-1.503094	0.621970
		6	0	1.417616	-1.002129	-0.465125
		1	0	0.014860	-0.674650	1.231134
		16	0	1.356384	-2.656651	1.639966
		7	0	2.399559	-1.981655	-0.704932
		6	0	2.507173	-2.826236	0.270969
		6	0	1.929068	0.397784	-0.208516
		6	0	1.028992	1.474330	-0.118116
		6	0	3.299301	0.627626	-0.033008
		6	0	1.493924	2.758629	0.148426
		1	0	-0.034208	1.314782	-0.278809
		6	0	3.771670	1.911780	0.240620
		1	0	4.000585	-0.195019	-0.112653
		6	0	2.865521	2.969659	0.331627
		1	0	0.803460	3.592101	0.213878
		1	0	4.831999	2.090051	0.380159
		7	0	3.449882	-3.776489	0.340607
		1	0	3.437182	-4.490574	1.052789
		1	0	4.130599	-3.848756	-0.403237
		17	0	3.447991	4.577534	0.672965
		8	0	0.574220	-0.860929	-1.787593
		6	0	1.286576	-0.823286	-3.077068
		1	0	1.818694	-1.760637	-3.226037
		1	0	0.515397	-0.648712	-3.825908
		1	0	1.970127	0.020957	-3.017594
		1	0	-0.166664	-1.530419	-1.744885
5	Intermediate-4	6	0	3.282211	0.555601	-0.567702
		6	0	3.981057	0.373940	0.646964
		6	0	5.291943	0.814319	0.834585
		6	0	5.892152	1.451168	-0.250369
		6	0	5.208290	1.640098	-1.469975
		6	0	3.900275	1.197670	-1.647669

		6	0	1.937003	-0.468168	0.753614
		1	0	5.822331	0.671332	1.770450
		1	0	6.911711	1.810121	-0.153923
		1	0	5.717171	2.142214	-2.286430
		1	0	3.372922	1.340629	-2.584921
		7	0	1.995487	0.022759	-0.457743
		7	0	3.083289	-0.294456	1.480531
		1	0	3.265346	-0.637742	2.412842
		16	0	0.505471	-1.252955	1.462191
		6	0	-0.345589	-1.656356	-0.119323
		6	0	-1.811598	-1.233950	-0.146203
		1	0	0.243947	-1.143663	-0.893463
		16	0	-0.374365	-3.467668	-0.479658
		7	0	-2.693227	-2.211244	-0.258985
		6	0	-2.117685	-3.419426	-0.417536
		6	0	-2.229641	0.141756	-0.072655
		6	0	-3.605842	0.440457	0.099137
		6	0	-1.306000	1.208237	-0.207282
		6	0	-4.042185	1.752320	0.151341
		1	0	-4.316539	-0.371398	0.199937
		6	0	-1.743476	2.523037	-0.170043
		1	0	-0.249646	1.017161	-0.369037
		6	0	-3.107471	2.791995	0.015525
		1	0	-5.091806	1.983260	0.293316
		1	0	-1.041376	3.340787	-0.285994
		7	0	-2.872834	-4.498962	-0.546475
		1	0	-2.484273	-5.424630	-0.666697
		1	0	-3.880752	-4.393038	-0.533846
		17	0	-3.650377	4.434827	0.074205
6	7a	6	0	3.123438	-1.036023	-0.574974
		6	0	3.961771	-0.791791	0.540400
		6	0	5.301140	-1.186006	0.574936
		6	0	5.789759	-1.840613	-0.555635
		6	0	4.968142	-2.093408	-1.674537

		6	0	3.632831	-1.697657	-1.700149
		6	0	1.904659	-0.014744	0.860287
		1	0	5.936160	-0.994886	1.434705
		1	0	6.826313	-2.163423	-0.574141
		1	0	5.389557	-2.608875	-2.532284
		1	0	2.996642	-1.890453	-2.557856
		7	0	3.147541	-0.131068	1.448707
		1	0	3.418979	0.273868	2.332216
		7	0	1.843164	-0.549008	-0.333204
		16	0	0.573412	0.733082	1.779122
		6	0	-1.453461	1.435487	-0.083808
		6	0	-1.183484	3.539670	-0.762972
		16	0	0.251389	3.352408	0.231040
		7	0	-1.959301	2.490284	-0.819327
		7	0	-1.480353	4.722987	-1.387647
		1	0	-0.725022	5.358608	-1.597473
		1	0	-2.196746	4.653471	-2.098815
		6	0	-0.264516	1.692144	0.570587
		6	0	-2.230611	0.177753	-0.060171
		6	0	-3.633179	0.239965	0.000160
		6	0	-1.610181	-1.080079	-0.130434
		6	0	-4.402085	-0.922063	0.025348
		1	0	-4.120570	1.208725	0.028167
		6	0	-2.371867	-2.249400	-0.111379
		1	0	-0.532987	-1.147058	-0.241080
		6	0	-3.760632	-2.160662	-0.025644
		1	0	-5.483896	-0.869318	0.081295
		1	0	-1.890264	-3.219035	-0.175887
		17	0	-4.723687	-3.633957	0.001574

Table S3: First three vibrational frequencies obtained at B3LYP/6-31+G(d,p) level

Sr.no	Molecule	Frequencies (cm^{-1})	IR Intensity (KM/Mole)
1	**NHTS**	32.8585	1.0604
		38.4795	1.8192
		65.4810	1.6805
2	Intermediate-1	8.7058	0.2000
		19.6068	0.9536
		22.8512	0.3580
3	Intermediate-2	14.1242	0.7230
		21.1133	0.8494
		29.3789	0.5813
4	Intermediate-3	11.4077	1.7622
		21.6816	0.9774
		35.5339	1.3702
5	Intermediate-4	16.8384	0.2711
		27.6926	1.3219
		43.6896	3.0171
6	**7a**	16.6459	2.0015
		23.9034	0.6560
		37.6693	1.1543

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