Supporting Information

Table of Contents

Experimental Section

1 Materials and methods:

Melting points are taken on a precision melting point apparatus (DBK) instrument and are uncorrected. IR spectra are obtained in potassium bromide (KBr) disks on a Bruker IR Spectrometer and H^1 NMR spectra were obtained on deuteriodimethylsulfoxide (DMSO-*d6*) as well as $CDCl_3$ on a 400 MHz spectrometer. GC (VARIAN CP-3800 GC, HP-5 capillary column, FID detector), Mass spectra were recorded on a MicroMass spectrometer by Waters. All starting materials purchased from commercial source. Substrate (2s to 2w) was synthesised following reported process. [1] Raw materials procured from spectrochem.

2 General procedure for synthesis of compounds 3a-3ao*.*

4 mmol of carboxylic acid in toluene (5 vol) was added with sodium borohydride (2.5 mmol) in portions at 0-5°C. To the mixture was added EnCat Ni 2.5%. Gradually raise the temperature to 25-30°C. To the mixture was added 1 mmol secondary amine. Raise the temperature to 80°C. To the reaction mixture was added 1.5 mmol of sodiumborohydride in portions. The progress of the reaction was monitored by TLC. After the completion of reaction, reaction mixture was quenched with 1N HCl to pH 7 to 8 and separated organic solution washed with water. Solvent was distilled out under reduce pressure at 50°C. The product was isolated by crystallisation in isopropyl alcohol and conc. Hydrochloric acid followed by filtration and drying to yield (90-99%) solid hydrochloride salt as product.

3 Characterisation Data.

4-(benzo[d]thiazol-2-yl(methyl)amino)-2-fluoro-N-methylbenzamide (3x); White solid, m.p 235°C- 238°C. IR (cm^{-1}) 3065, 2850, 1605, 1578, 1556, 1375, 1350; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.10(3H, s, N-CH_3), 3.19 (3H, s, N-CH_3); 6.80 (1H, brs, CON-H), 7.29-7.46(4H, m, Ar-H), 7.77-7.79(1H, d, Ar-H), 7.85-7.87 (1H, d, Ar-CH), 8.27-8.31(1H, t, Ar-CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 316.3702,

Anal. Calcd for $C_{16}H_{14}F_1N_3OS$: C, 60.94; H, 4.47; N, 13.32, Found: C, 60.94, ; H, 4.47; N, 13.32.

5-(benzo[d]thiazol-2-yl(ethyl)amino)-3-(trifluoromethyl)picolinonitrile (3y); White solid, m.p 223-228°C. IR (cm^{-1}) 3076, 2938, 2230,1350, 1185; ^1H NMR (400 MHz, DMSO) δ: 0.89 (3H, t,CH_3), 3.05 (2H, q, CH_2), 7.01-7.64 (5H, m, Ar-CH), 8.31(1H, s, CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 349.3510, Anal. Calcd for $C_{16}H_{11}F_3N_4S$: C, 55.17; H, 3.18; N, 16.08, Found: C, 55.16; H, 3.19; N, 16.06.

N-ethyl-N-(2-nitro-4-(trifluoromethyl)phenyl)benzo[d]thiazol-2-amine (3z); White solid, m.p 255-269°C. IR (cm^{-1}) 3105, 2963, 2230, 1555, 1375, 1320, 1565; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.06 (3H, t, CH_3), 3.06 (2H, q, CH_2), 7.55-7.64 (2H, m, Ar-CH), 7.86 -7.91(2H, m, Ar-CH), 8.1 (2H, m, Ar-CH), 8.46 (1H, s, Ar-CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 368.3511, Anal. Calcd for $C_{16}H_{12}F_3N_3O_2S$: C, 52.314; H, 3.29; N, 11.44, Found: C, 52.31; H, 3.29; N, 11.44.

4-((6-chlorobenzo[d]thiazol-2-yl)(ethyl)amino)-2-(trifluoromethyl)benzonitrile (3ab); white solid, m.p 255-259°C. IR (cm^{-1}) 3105, 2970, 2230, 1382,1570,1500, ^1H NMR (400 MHz, $CDCl_3$) δ: 1.06(3H, t, CH3), 3.06(2H, q, CH_2), 7.43-7.45(1H, t, Ar-CH), 7.67-7.69(1H, d, Ar-CH), 7.81-7.86(2H,m, Ar-H), 7.91(1H,s, Ar-H), 8.07(1H, d, Ar-H), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 382.80, Anal. Calcd for $C_{17}H_{11}ClF_3N_3S$: C, 53.48; H, 2.90; N, 11.01 Found: C, 53.48; H, 2.90; N, 11.01.

4-(benzo[d]thiazol-2-yl(propyl)amino)-2-(trifluoromethyl)benzonitrile (3ac); White solid, m.p 244-248°C. IR (cm^{-1}) 3050, 2235, 1570, 1460,1399, 1240 ; ^1H NMR (400 MHz, DMSO) δ: 0.89(3H, t, CH_3), 1.49(2H, m, CH_2), 3.01 (2H, t, CH_2), 7.26 (1H, t, Ar-CH); 7.4 (1H, t, Ar-CH); 7.72(1H, d, Ar-CH); 7.91(1H, d, Ar-CH); 8.12(1H, d, Ar-CH); 8.21(1H, d, Ar-CH); 8.40(1H, s, Ar-CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 361.3801, Anal. Calcd for $C_{18}H_{14}F_3N_3S$: C, 59.82; H, 3.90; N, 11.63 Found: C, 59.82; H, 3.90; N, 11.63.

4-(benzo[d]thiazol-2-yl(ethyl)amino)-2-fluoro-N-methylbenzamide (3ad); White solid, m.p 237-242°C. IR (cm^{-1}) 3096, 1555,1440, 1399; ^1H NMR (400 MHz,

$CDCl_3$) δ: 1.06 (3H, d, CH_3), 3.06 (2H, q), 3.3 (3H, s, N-CH_3); 6.80 (1H, brs, CON-H), 7.29-7.46(4H, m, Ar-H), 7.77-7.79(1H, d, Ar-H), 7.85-7.87 (1H, d, Ar-CH), 8.27-8.31(1H, t, Ar-CH). HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 330.4010, Anal. Calcd for $C_{17}H_{16}F_1N_3OS$: C, 61.99; H, 4.90; N, 12.76. Found: C, 61.98; H, 4.90; N, 12.76.

5-(benzo[d]thiazol-2-yl(propyl)amino)-3-(trifluoromethyl)picolinonitrile (3ae); yellow solid, m.p 244-248°C. IR (cm^{-1}) 3050, 2230, 1570, 1460,1399; ^1H NMR (400 MHz, DMSO) δ: 0.89(3H, t, CH_3), 1.49(2H, m, CH_2), 3.15 (2H, t, CH_2), 7.01-7.64 (5H, m, Ar-CH), 8.31(1H, s, CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 321.02, Anal. Calcd for $C_{17}H_{13}F_3N_4S$: C, 56.35; H, 3.62; N, 15.46, Found: C, 56.35; H, 3.62; N, 15.46.

N-(2-nitro-4-(trifluoromethyl)phenyl)-N-propylbenzo[d]thiazol-2-amine (3af); White solid, m.p 252-257°C. IR (cm^{-1}) 3050, 570, 1464,1370,1272;; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.89(3H, t, CH_3), 1.47(2H, m, CH_2), 3.02 (2H, t, CH_2), 7.55-7.64 (2H, m, Ar-CH), 7.86 -7.91(2H, m, Ar-CH), 8.1 (2H, m, Ar-CH), 8.46 (1H, s, Ar-CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 382.3701, Anal. Calcd for $C_{17}H_{14}F_3N_3O_2S$: C, 53.54; H, 3.70; N, 11.02, Found: C, 53.54; H, 3.70; N, 11.02.

4-(benzo[d]thiazol-2-yl(isopentyl)amino)-2-(trifluoromethyl)benzonitrile (3ag); White solid, m.p 238-242°C. IR (cm^{-1}) 3165, 2895, 2230, 1556, 1440,1265; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.91(6H, d, $2CH_3$), 1.26(1H, m, CH), 1.54(2H, q, CH_2), 3.25 (2H, d, CH_2), 7.55(2H, m, Ar-CH); 7.86(2H, m, Ar-CH); 8.10(2H, m, Ar-CH); 8.46(1H, s, Ar-CH); 8.12(1H, d, Ar-CH); 8.21(1H, d, Ar-CH). Mass $(EI)^+$: 390.4410, Anal. Calcd for $C_{20}H_{18}F_3N_3S$: C, 61.68; H, 4.66; N, 10.79, Found: C, 61.68; H, 4.66; N, 10.79.

N-isobutyl-N-(2-nitro-4-(trifluoromethyl)phenyl)benzo[d]thiazol-2-amine (3ah); White solid, m.p 261-265°C. IR (cm^{-1}) 3045, 2230, 1562,1485, 1355, 1265; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.91(6H, d, $2CH_3$), 1.26 (1H, m, CH), 3.20 (2H, d, CH_2), 7.55-7.64 (2H, m, Ar-CH), 7.86 -7.91(2H, m, Ar-CH), 8.1 (2H, m, Ar-CH), 8.46 (1H, s, Ar-CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 396.4011, Anal. Calcd for $C_{18}H_{16}F_3N_3O_2S$: C, 54.68; H, 4.08; N, 10.63, Found: C, 54.68; H, 4.08; N, 10.63.

4-((6-chlorobenzo[d]thiazol-2-yl)(isobutyl)amino)-2-(trifluoromethyl)benzonitrile (3ai); White solid, m.p 237-241°C. IR (cm^{-1}) 3085, 2855, 2230, 2801; IR (KBr): v (cm^{-1}) 3449, 3245, 2957, 2166, 1625, 1276, 1148; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.91(6H, d, $2CH_3$), 1.26(1H, m, CH), 3.20 (2H, d, CH_2), 7.43-7.45(1H, t, Ar-CH), 7.67-7.69(1H, d, Ar-CH), 7.81-7.86(2H,m, Ar-H), 7.91(1H,s, Ar-H), 8.07(1H, d, Ar-H). HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 410.8601, Anal. Calcd for $C_{19}H_{15}ClF_3N_3S$: C, 55.68; H, 3.69; N, 10.25, Found: C, 55.68; H, 3.68; N, 10.25.

4-(benzo[d]thiazol-2-yl(isobutyl)amino)-2-(trifluoromethyl)benzonitrile (3aj); White solid, m.p 233-238°C. IR (cm^{-1}) 3051, 2285, 2230, 1521,1245; ^1H NMR (400 MHz, DMSO) δ: : 0.91(6H, d, $2CH_3$), 1.28(1H, m, CH), 3.22 (2H, d, CH_2), 7.26 (1H, t, Ar-CH); 7.4 (1H, t, Ar-CH); 7.72(1H, d, Ar-CH); 7.91(1H, d, Ar-CH); 8.12(1H, d, Ar-CH); 8.21(1H, d, Ar-CH); 8.40(1H, s, Ar-CH). HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 376.3511, Anal. Calcd for $C_{19}H_{16}F_3N_3S$: C, 60.79; H, 4.30; N, 11.19, Found: C, 60.79; H, 4.30; N, 11.19.

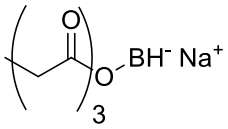
4-((6-chlorobenzo[d]thiazol-2-yl)(propyl)amino)-2-(trifluoromethyl)benzonitrile (3ak); White solid; m.p 24-245°C, IR (cm^{-1}) 3015, 2230, 1605, 1345, 1247; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.89(3H, t, CH_3), 1.47(2H, m, CH_2), 3.02 (2H, t, CH_2), 7.43-7.45(1H, t, Ar-CH), 7.67-7.69(1H, d, Ar-CH), 7.81-7.86(2H,m, Ar-H), 7.91(1H,s, Ar-H), 8.07(1H, d, Ar-H), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 396.8311, Anal. Calcd for $C_{18}H_{13}ClF_3N_3S$: C, 54.62; H, 3.31; N, 10.62, Found: C, 54.62; H, 3.31; N, 10.62.

5-(benzo[d]thiazol-2-yl(isobutyl)amino)-3-(trifluoromethyl)picolinonitrile (3al); White solid, m.p 252-255°C. IR (cm^{-1}) 3015, 2885, 2230,1565,1276 ; ^1H NMR (400 MHz, DMSO) δ: 0.91(6H, d, $2CH_3$), 1.26(1H, m, CH), 3.05 (2H, d, CH_2), 7.01-7.64 (5H, m, Ar-CH), 8.31(1H, s, CH), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 377.4101, Anal. Calcd for $C_{18}H_{15}F_3N_4S$: C, 57.44; H, 4.02; N, 14.88 Found: C, 57.44; H, 4.02; N, 14.87.

5-hexyl-10,11-dihydro-5H-dibenzo[b,f]azepine (3i); Yellow oil, IR (cm^{-1}) 3031, 2879, 2806, 1348, 1214; ^{1}H NMR (400 MHz, CDCl3) δ: 7.35-7.33 (dd, 2H, Ar), 7.12- 6.88(m, 6H, Ar), 3.81(t, 2H), 2.87 (s, 4H), 1.67-1.55 (m, 2H), 1.42- 1.32 (m, 2H), 1.31- 1.14(m, 4H), 0.89 (t, 3H). HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 280.2011.

10-(3-chloropropyl)-10H-benzo[b]pyrido[2,3-e][1,4]thiazine (3r); ^{1}H NMR (400 MHz, DMSO) 7.20- 7.169(m, 4H), 7.36 (1H, dd, Ar-H), 7.84 (1H, dd, Ar-H), 8.28 (1H, dd, Ar-H), 3.89 (2H, t, $\underline{CH_2}$-Cl), 3.64 (2H, t, $\underline{CH_2}$-N), 1.91 (2H, m, $\underline{CH_2}$-CH_2-N), HRMS (ESI) for $C_{17}H_{12}F_3N_3S$ $[M+H]^+$: 277.8039, Anal. Calcd for $C_{14}H_{13}ClN_2S$: C, 60.7510; H, 4.73; N, 10.12 Found: C, 60.72, 4.02; N, 14.85.

Sodium tri(propionyloxy) borohydride.



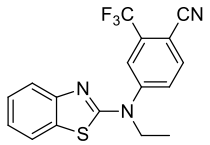
Colorless solid. IR (cm^{-1}) 3449, 2981, 2942, 2884, 2463, 1701, 1669, 1635 cm-1; FAB-HR-MS calcd for $C_9H_{16}BO_6$ $[M]^-$ 231.1042, found 231.1042.

4 References

[1] S. A. I. Quadri, T. C. Das, M. Farooqui, *ChemistrySelect* **2017**, 2, 1802.

5 Copies of H^1 NMR spectra of compounds 3w to 3al, 3i and 3r

4-(benzo[d]thiazol-2-yl(ethyl)amino)-2-(trifluoromethyl)benzonitrile (3w)



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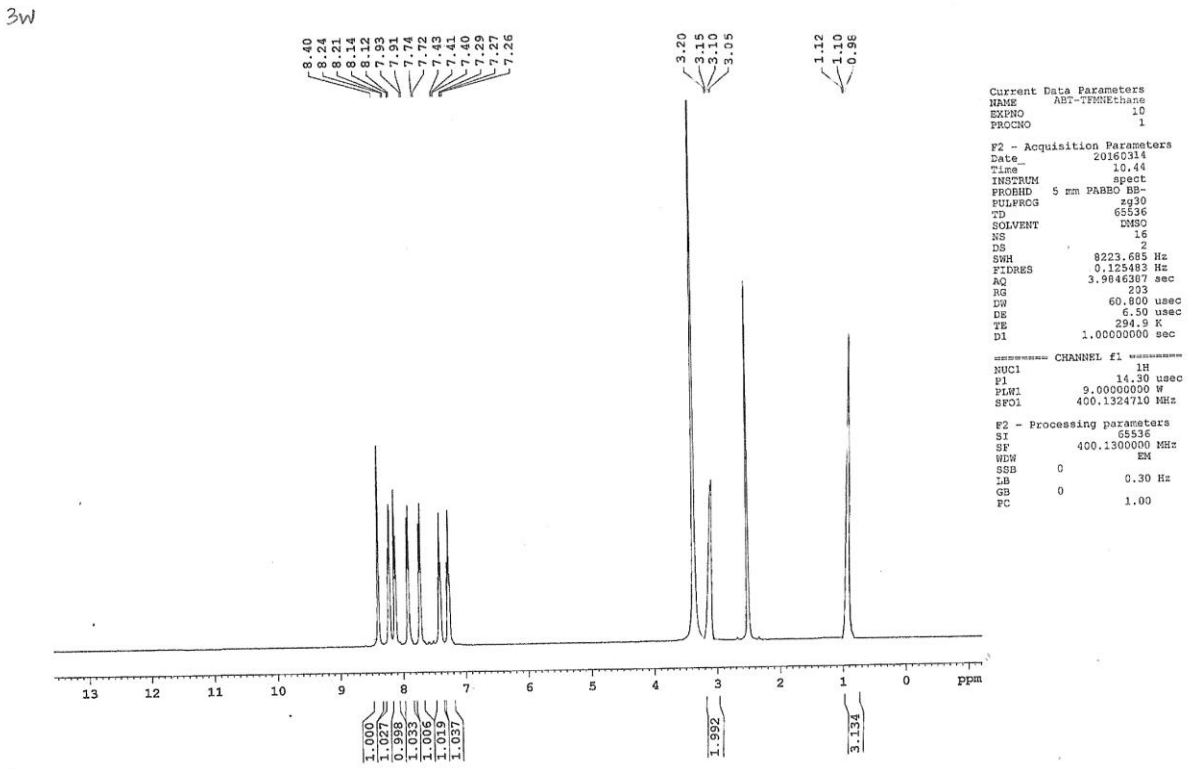
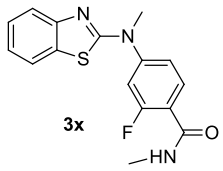


4-(benzo[d]thiazol-2-yl(methyl)amino)-2-fluoro-N-methylbenzamide (3x)



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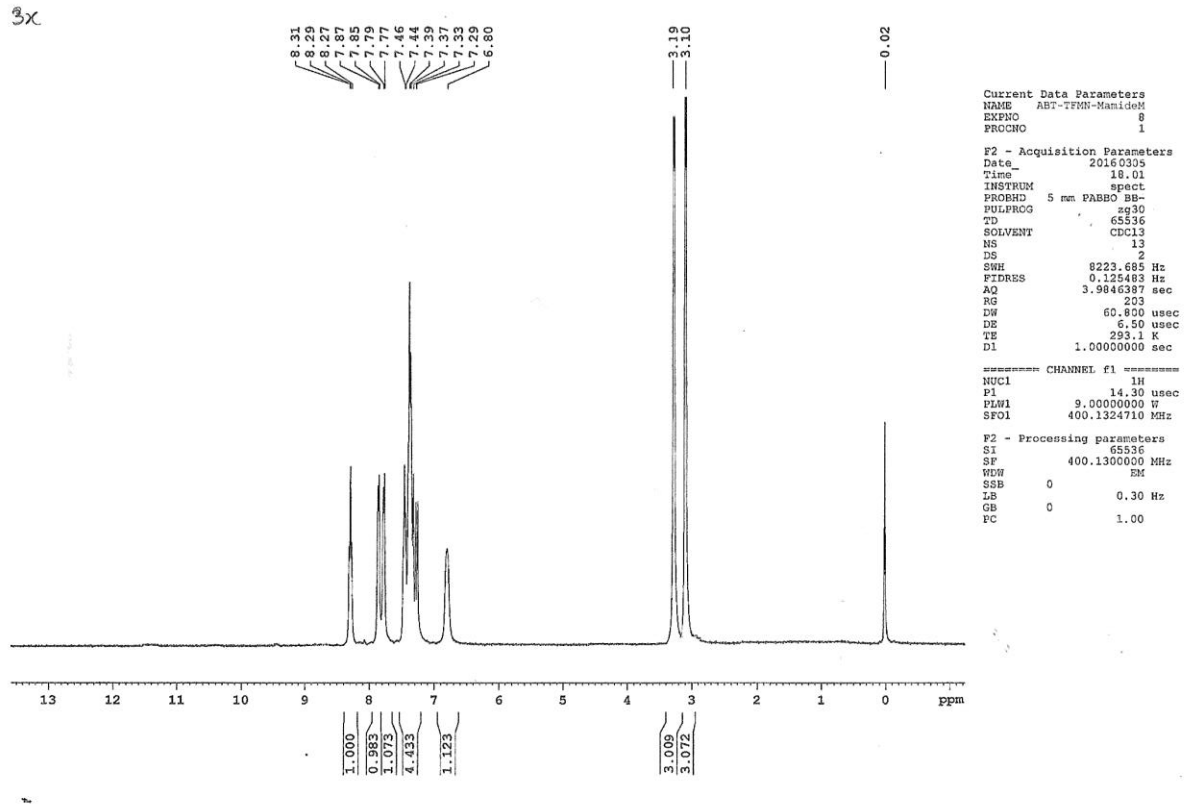


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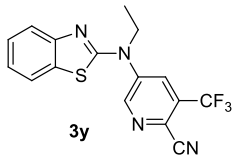
5-(benzo[d]thiazol-2-yl(ethyl)amino)-3-(trifluoromethyl)picolinonitrile (3y);



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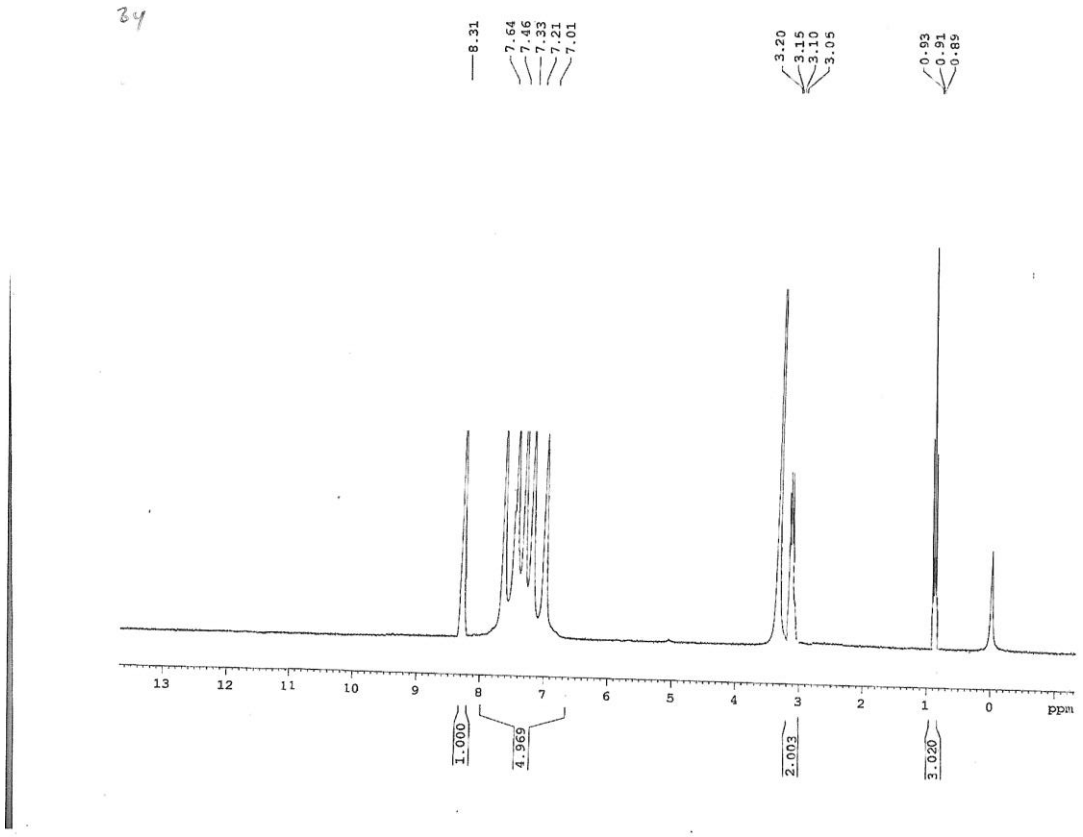


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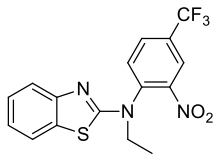

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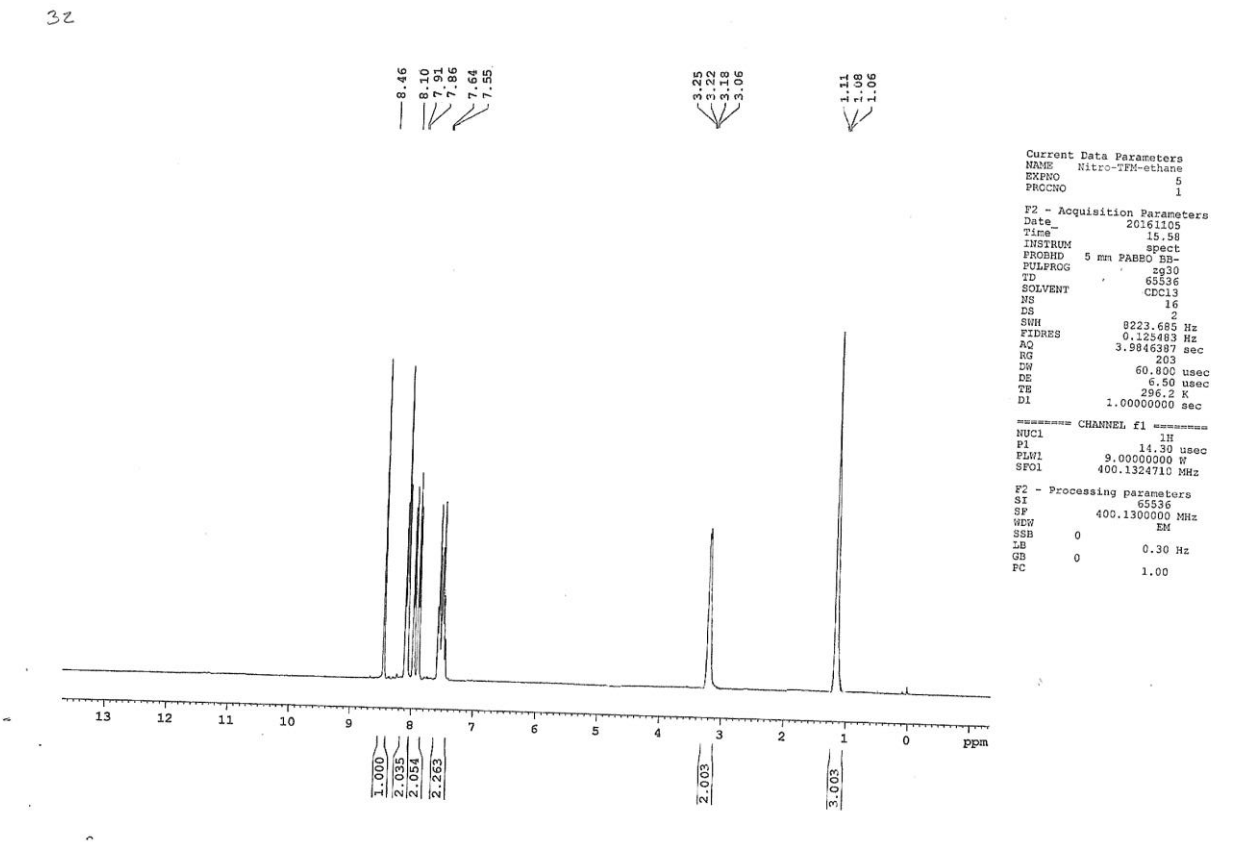


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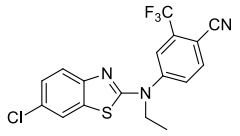

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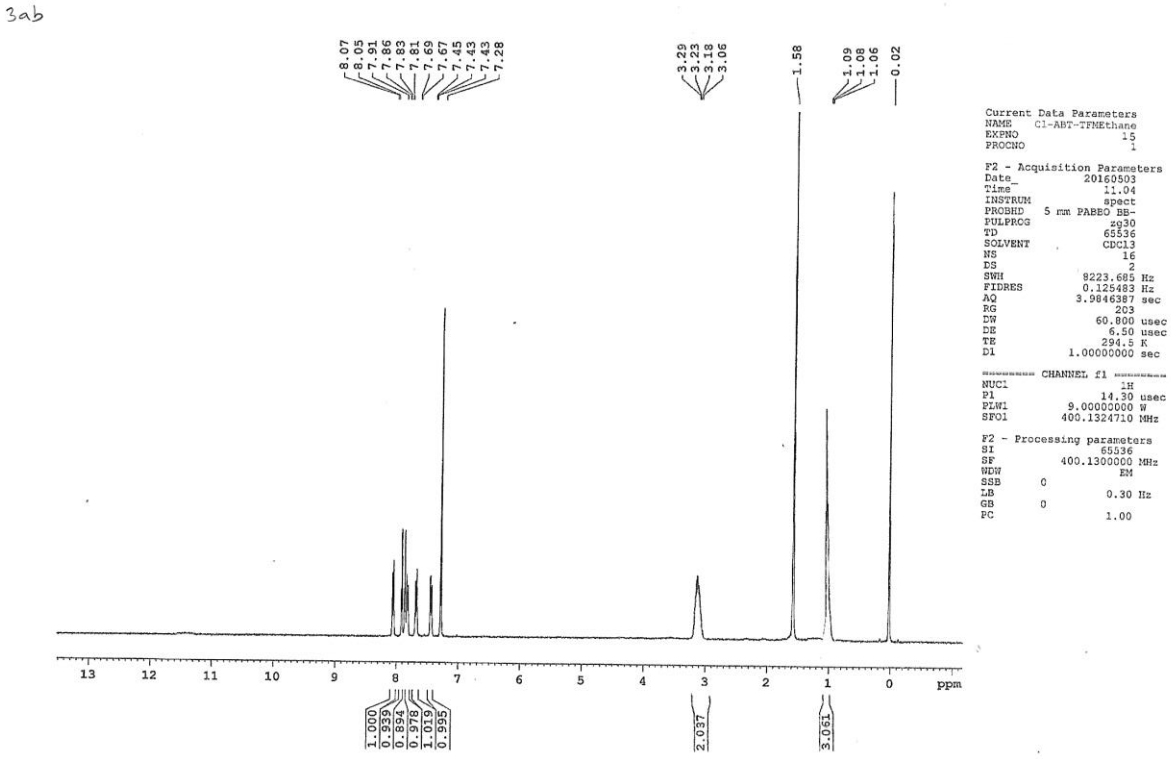
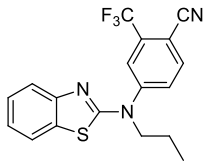


4-(benzo[d]thiazol-2-yl(propyl)amino)-2-(trifluoromethyl)benzonitrile (3ac);



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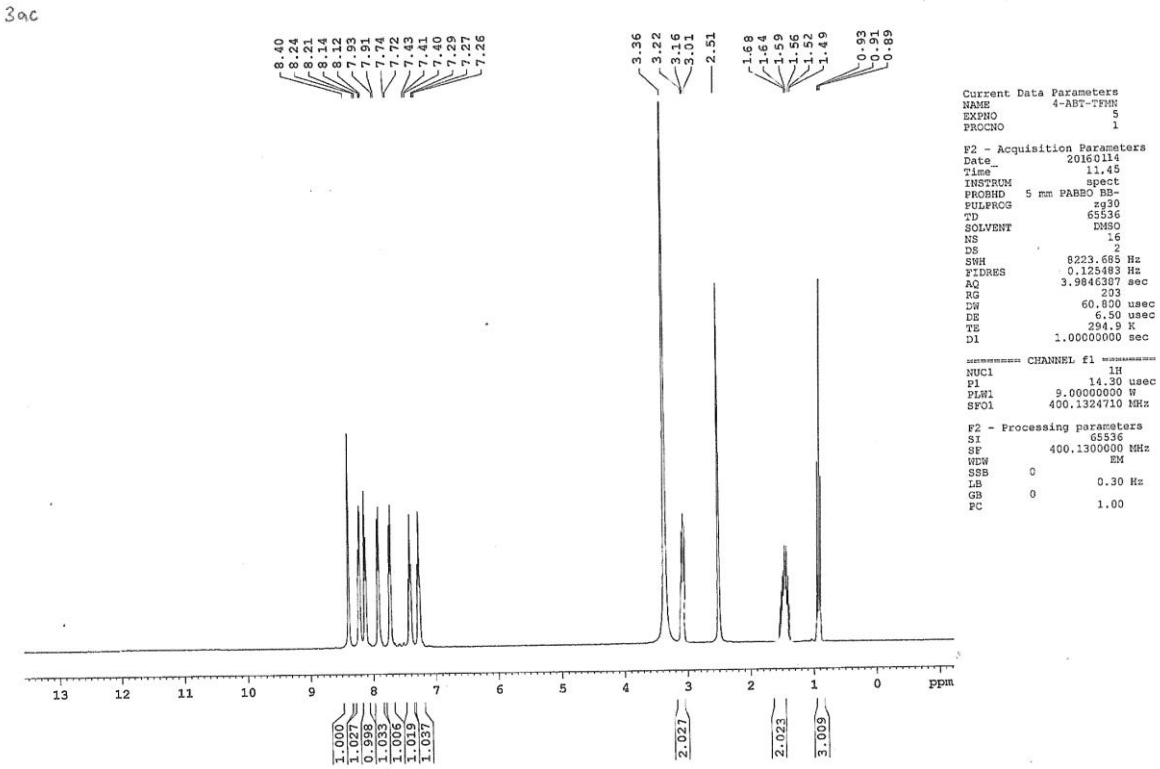
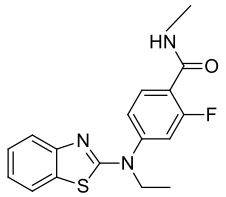
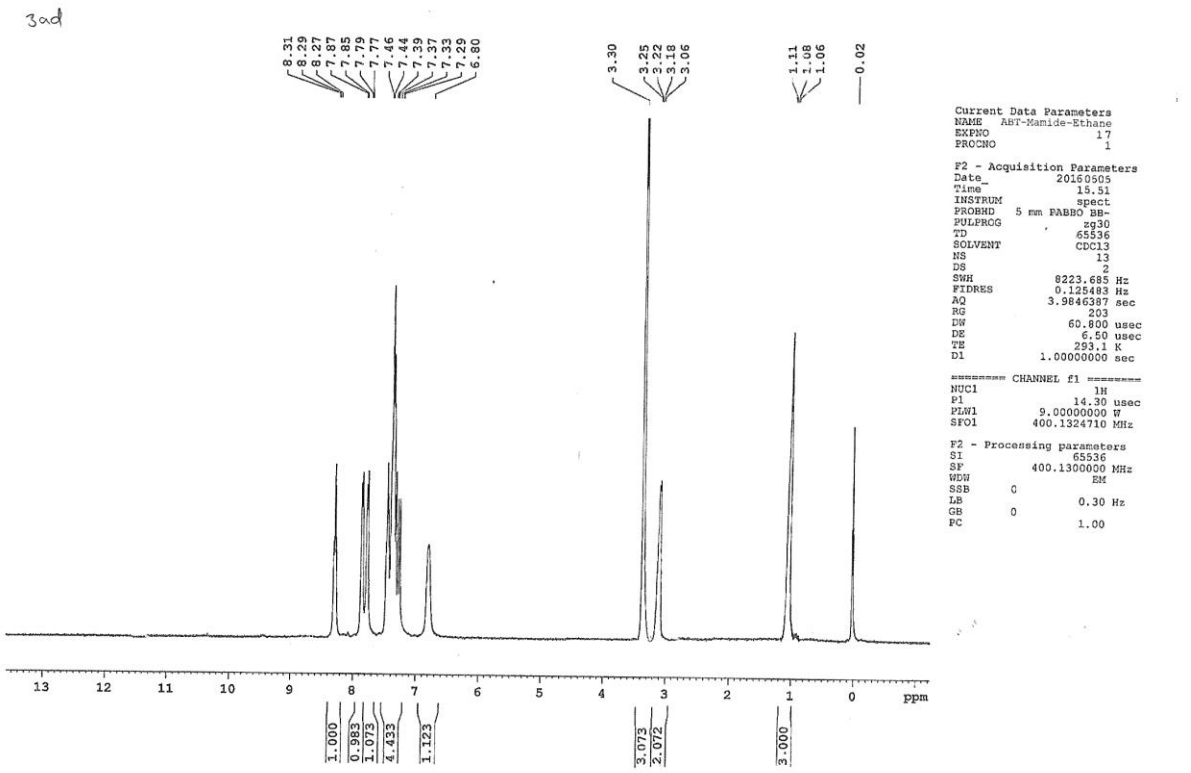


4-(benzo[d]thiazol-2-yl(ethyl)amino)-2-fluoro-N-methylbenzamide (3ad);



3ad

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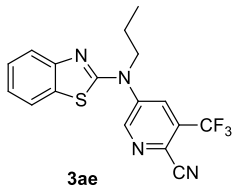
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    13
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ              3.9846387 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                293.1 K
D1             1.00000000 sec

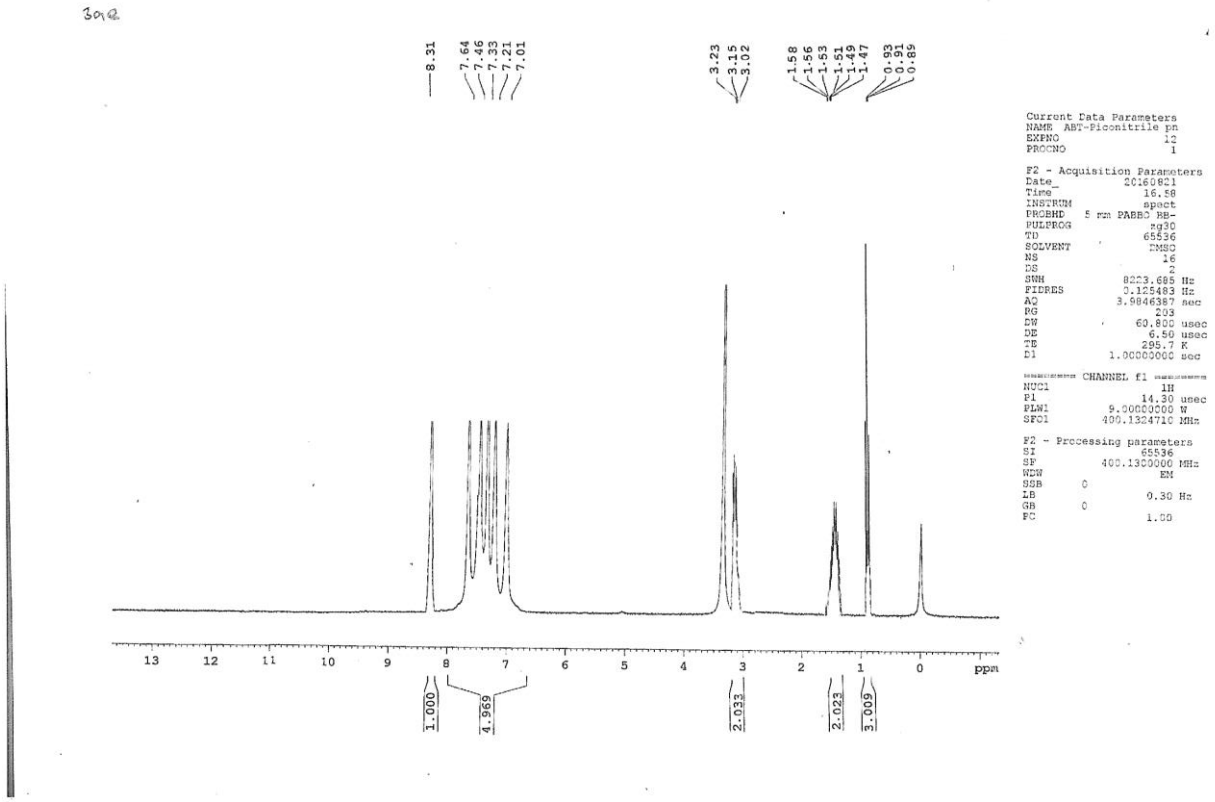
========== CHANNEL f1 =========
NUC1                  1H
P1                 14.30 usec
PLW1        9.00000000 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF          400.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

5-(benzo[d]thiazol-2-yl(propyl)amino)-3-(trifluoromethyl)picolinonitrile (3ae);



3ae



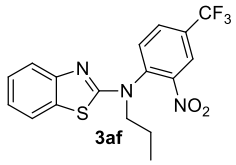

```
Current Data Parameters
NAME  ABT-Piconitrile pn
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160621
Time              16.58
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   203
DW                60.800 usec
DE                 6.50 usec
TE                295.7 K
D1              1.00000000 sec

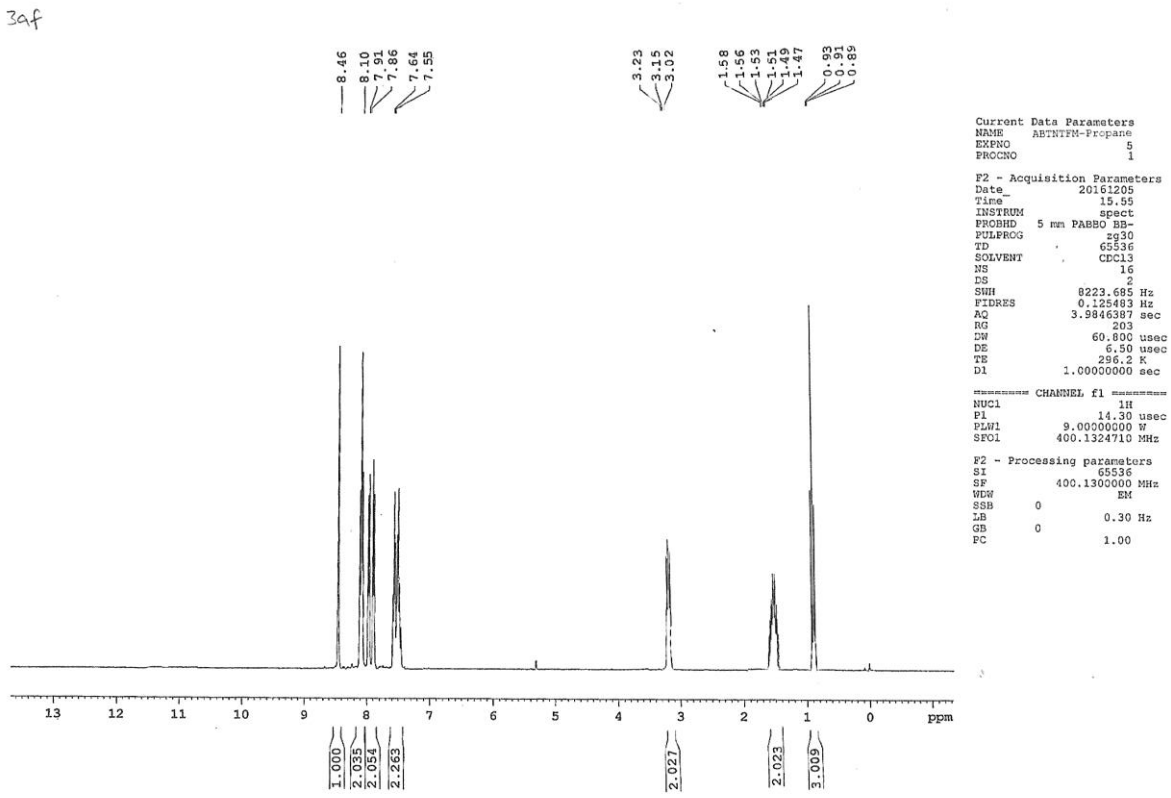
======== CHANNEL f1 ========
NUC1                1H
P1                14.30 usec
PLW1         9.00000000 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

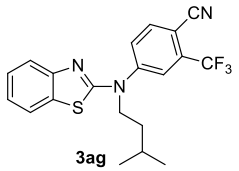
N-(2-nitro-4-(trifluoromethyl)phenyl)-N-propylbenzo[d]thiazol-2-amine (3af);



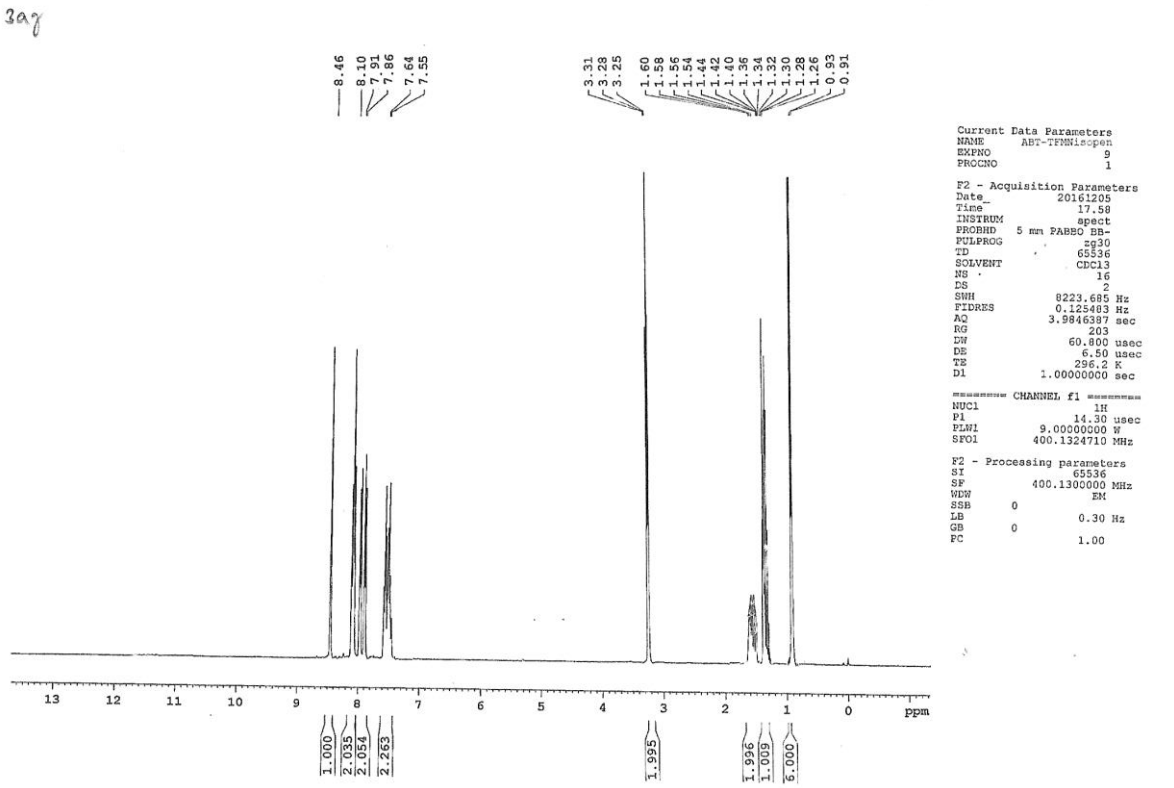
3af



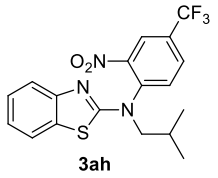
4-(benzo[d]thiazol-2-yl(isopentyl)amino)-2-(trifluoromethyl)benzonitrile (3ag);



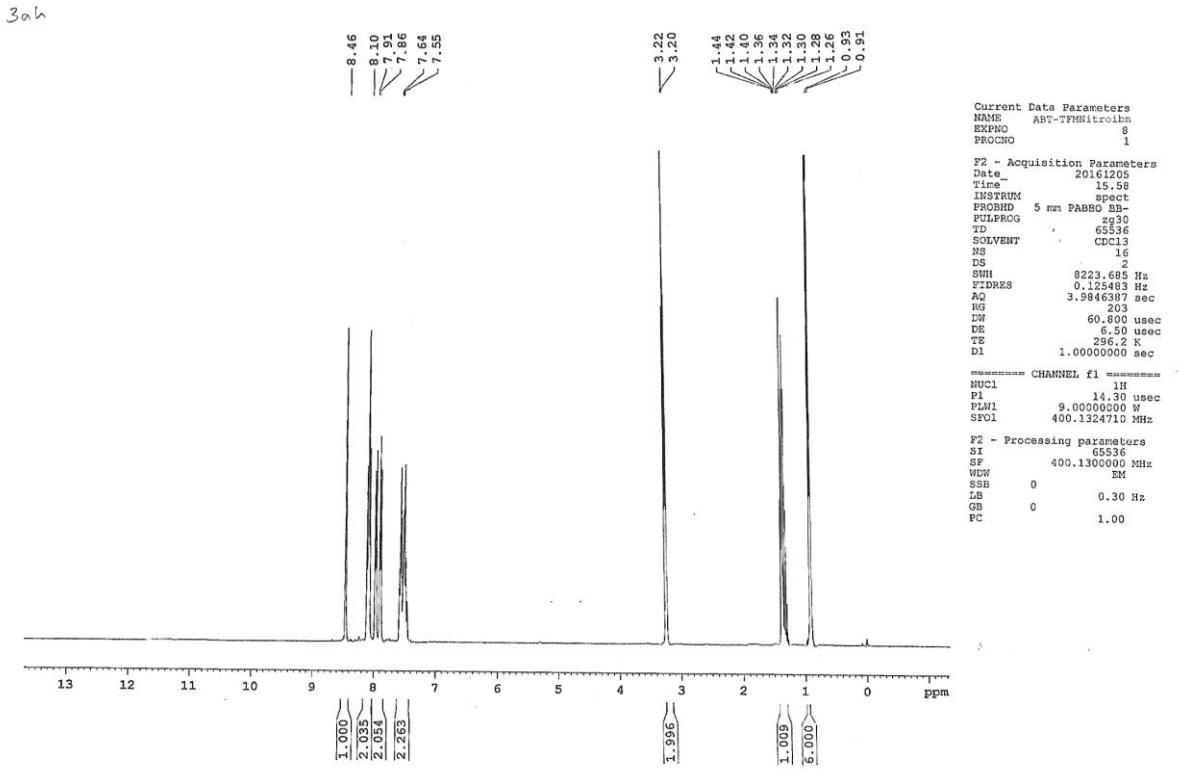
3ag



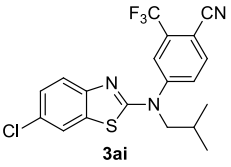
N-isobutyl-N-(2-nitro-4-(trifluoromethyl)phenyl)benzo[d]thiazol-2-amine (3ah);



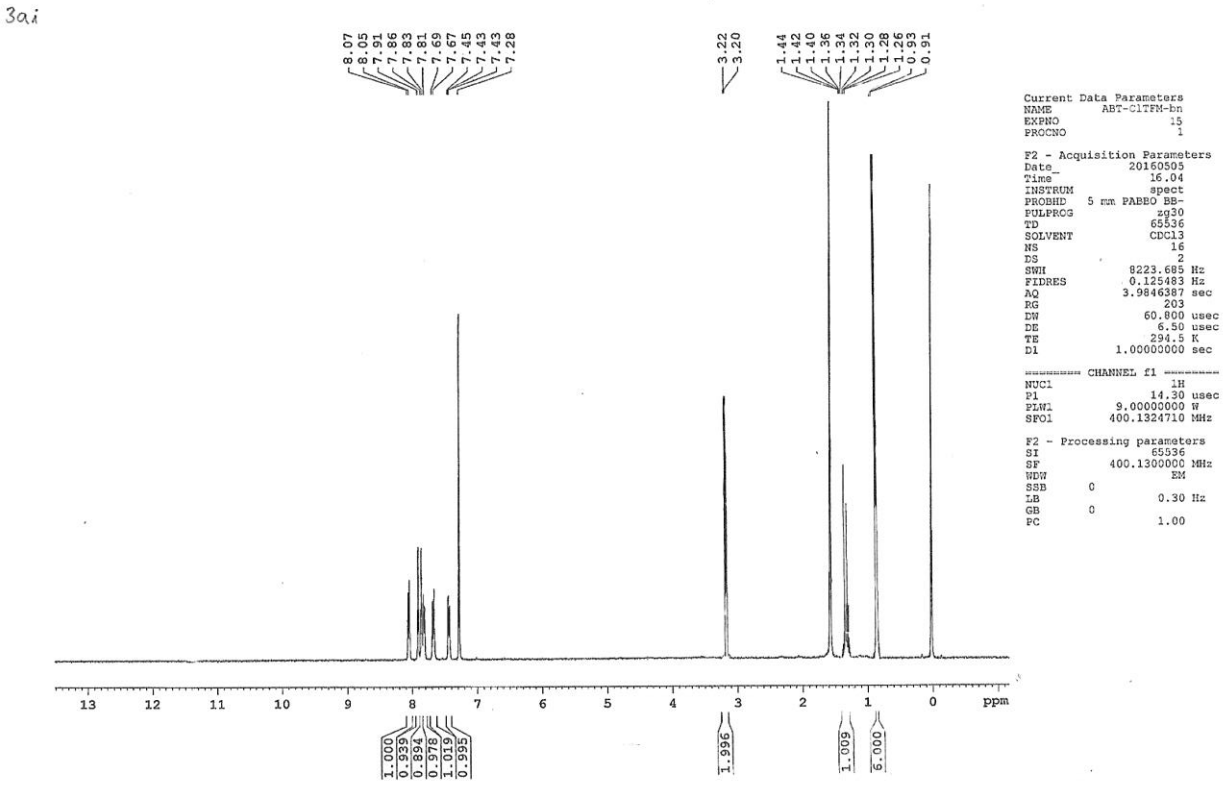
3ah



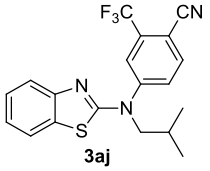
4-((6-chlorobenzo[d]thiazol-2-yl)(isobutyl)amino)-2-(trifluoromethyl)benzonitrile (3ai);



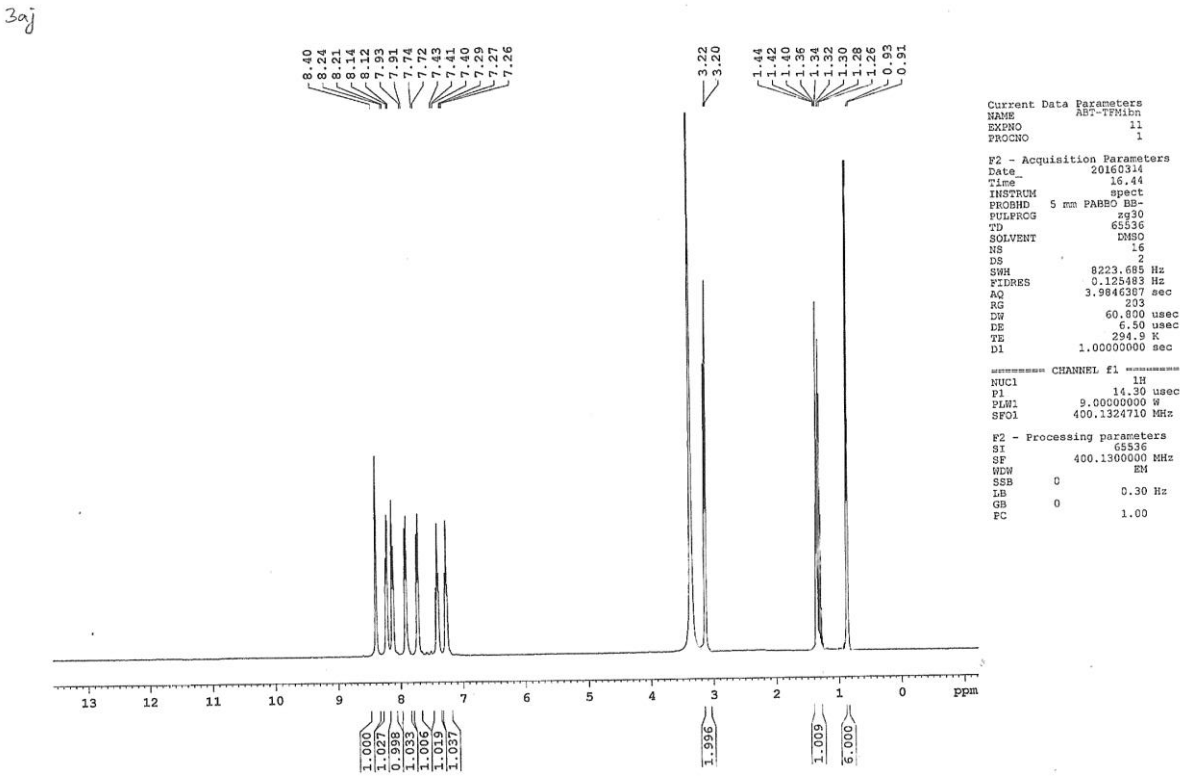
3ai



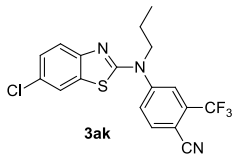
4-(benzo[d]thiazol-2-yl(isobutyl)amino)-2-(trifluoromethyl)benzonitrile (3aj);

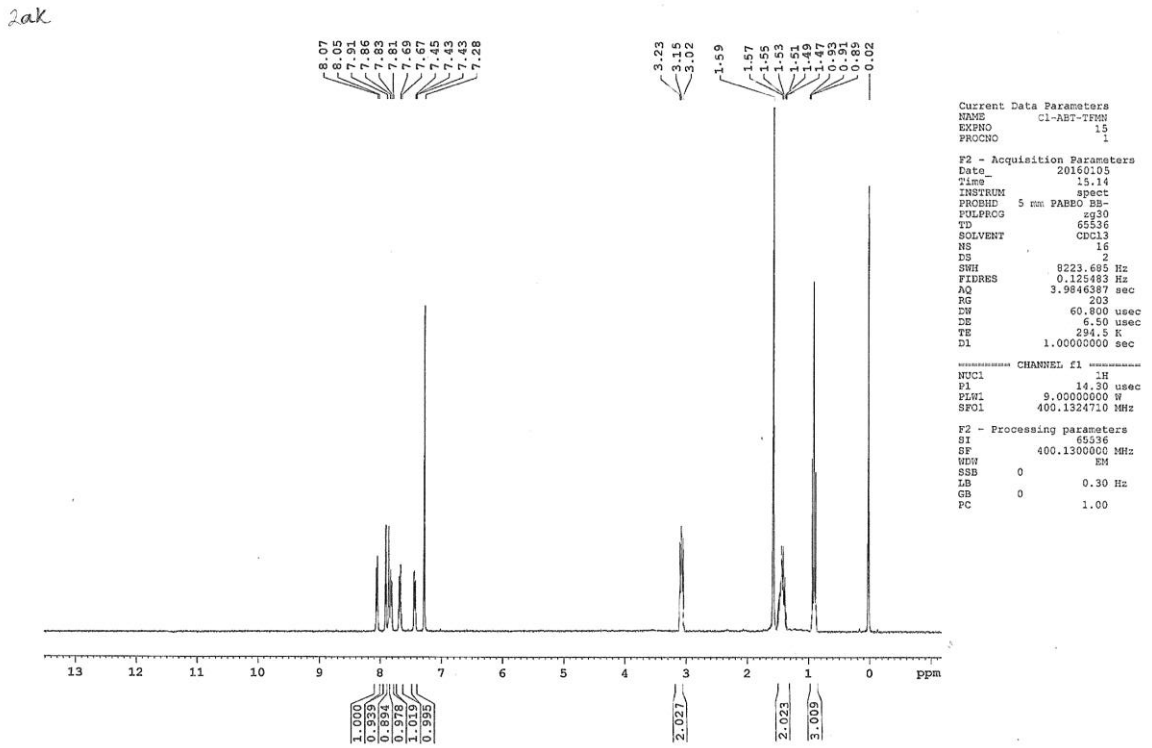


3aj

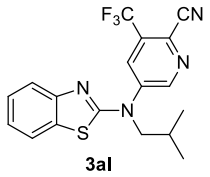


4-((6-chlorobenzo[d]thiazol-2-yl)(propyl)amino)-2-(trifluoromethyl)benzonitrile (3ak);

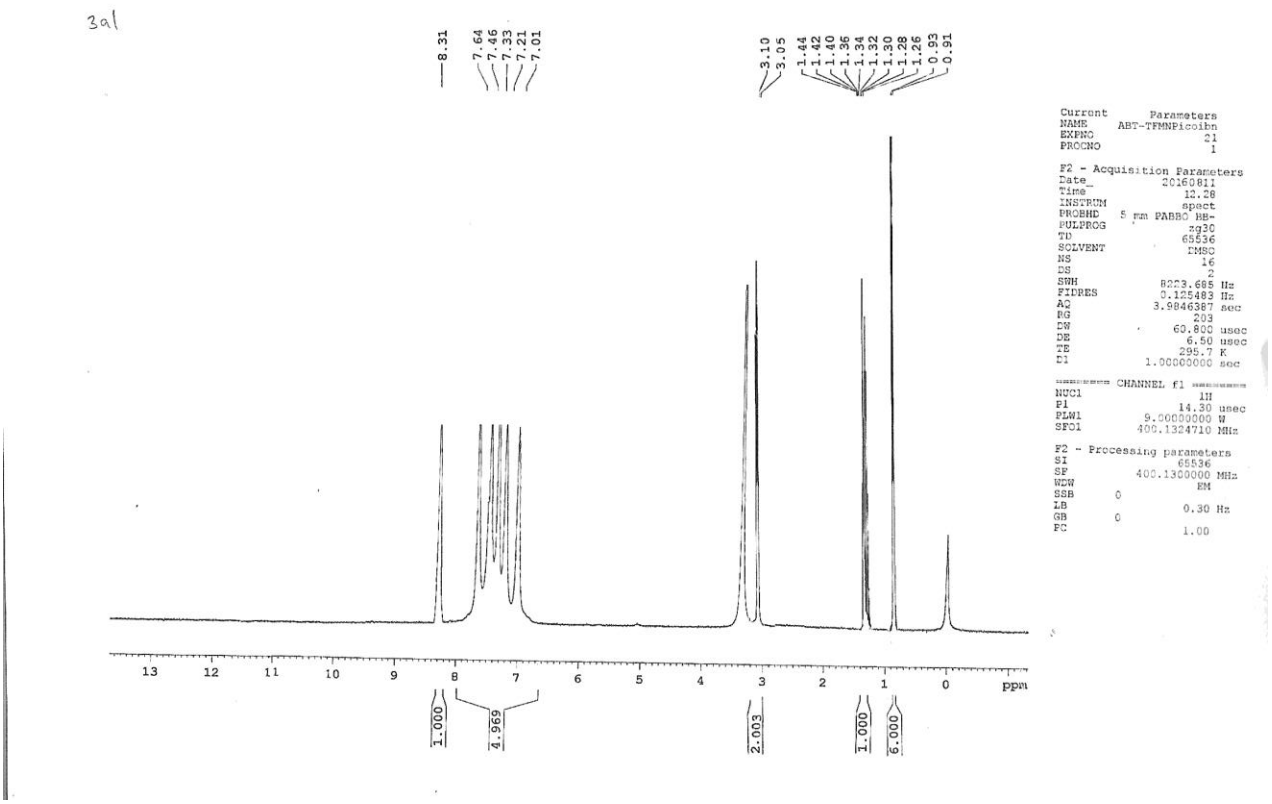




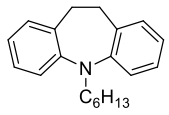
5-(benzo[d]thiazol-2-yl(isobutyl)amino)-3-(trifluoromethyl)picolinonitrile (3al);



3al

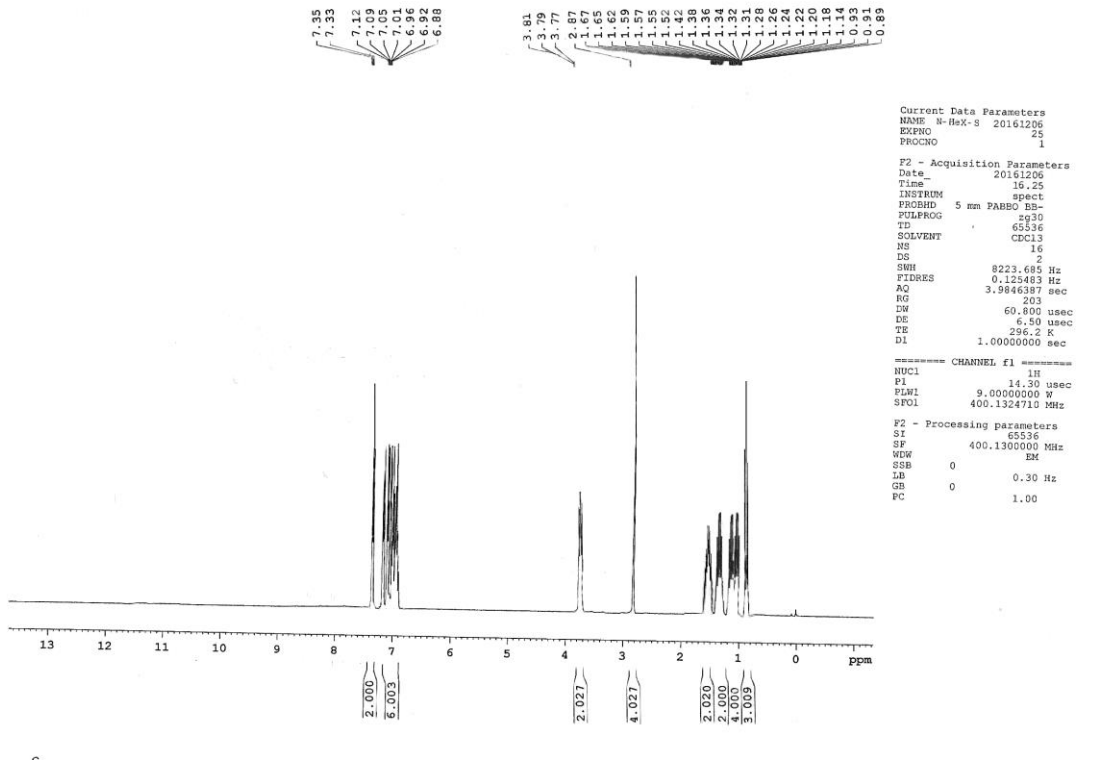


5-hexyl-10,11-dihydro-5H-dibenzo[b,f]azepine

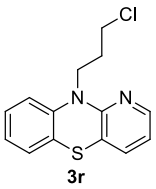


3i

3i



10-(3-chloropropyl)-10H-benzo[b]pyrido[2,3-e][1,4]thiazine



3r

3r