Supplementary information for

Cu(II)-catalyzed C-N coupling of 2-aminobenzothiazoles with boronic acids at room temperature

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1. General Remarks

Acetonitrile, DMSO, 1,10-Phenanthroline, copper(II) acetate, Cu(I) iodide, phenylboronic acid, 3-nitro, 3-fluoro, 4-chloro and 2-fluoro phenylboronic acids were acquired from Sigma-Aldrich. DME, DCE, 4-CF_3, 2-methyl and 4-fluoro phenylboronic acids were bought from Spectrochem. Potassium phosphate and 2-aminobenzothiazole were procured from Alfa aeser. 6-Methyl 2-aminobenzothiazole and 2-aminothiazole were obtained from TCI Co., Ltd. Hexane, ethyl acetate and silica gel (100–200 mesh) utilized in column chromatography were purchased from Merck Specialties Pvt. Ltd. We have utilized distilled solvents for all reactions and purification. Reactions were performed in an oven dried 50 mL round bottom flask under stirring at room temperature. The NMR spectra were noted with Bruker-400 MHz NMR spectrometer instrument [400 (^{1}H) and 100 (^{13}C) MHz]. The chemical shift values were defined in 'ppm' relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as internal standards. Coupling constants (*J*) were specified in Hertz (Hz). The HRMS and GC-MS were recorded on XEVO G2 Q-TOF (Waters) and Agilent mass spectrometers respectively. Thin layer

chromatography (using Merck Silica Gel 60/UV254) was performed through UV fluorescence and iodine chamber.

2. Procedure for the synthesis of 2-Aminobenzothiazole derivatives.

2-Aminobenzothiazole derivatives (0.50 mmol, 1 *equiv.*) and phenylboronic acid derivatives (0.60 mmol, 1.2 *equiv.*) were taken in an oven dried 50 ml round bottom flask with 3 mL of acetonitrile. To this 10 mol% of $Cu(OAc)_2$, 20 mol% of 1,10-phenanthroline and 1.5 equiv. of K_3PO_4 were added and stirred well for 24 h at room temperature. The reaction was then quenched by adding distilled water and extracted with ethyl acetate (3x15 mL). Ethyl acetate layer was washed with brine solution, separated and dried using anhydrous sodium sulphate. Organic layer was concentrated and the crude product was purified by column chromatography, employing hexane and ethyl acetate as the eluent.

3. Optimization Reactions

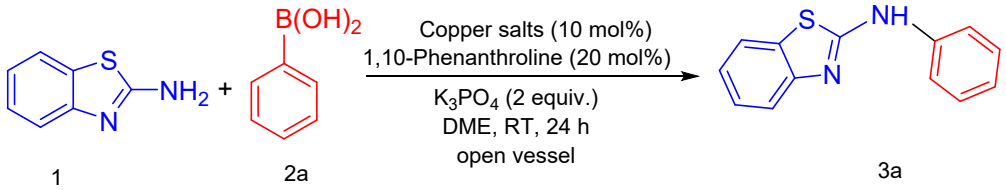
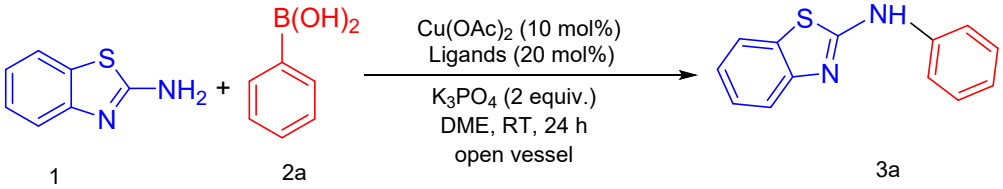


Table S1. Screening of various copper salts.

Entry	Copper Salts	Yield (%) of 3a [a,b]
1.	CuI	30
2.	CuBr	28
3.	$CuBr_2$	51
4.	$Cu(OAc)_2$	62
5.	$Cu(O_2C_5H_7)_2$	50
6.	-	nd

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronic acid (1.2 equiv.), Cu salts (10 mol%), 1,10-phenanthroline (20 mol%), K_3PO_4 (2 equiv.), DME (2 mL), reaction time: 24 h, temperature: RT, air. Open vessel. [b] Isolated yield. nd = not detected.

Table S2. Optimization of ligands.

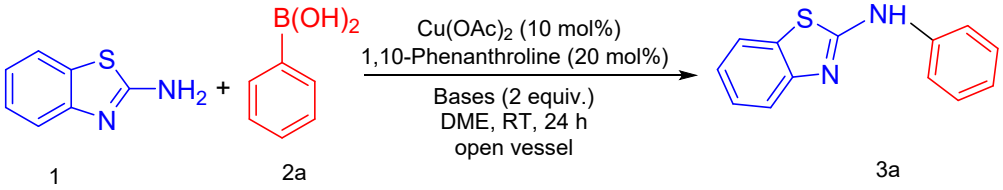


1 2a 3a

Entry	Ligands	Yield (%) of 3a [a,b]
1.	*L*-Proline	42
2.	DABCO	20
3.	DMEDA	55
4.	Triphenyl phosphine	30
5.	1,10-Phenanthroline	62
6.	2,2'-Bipyridine	60
7.	Ethylene diamine	46
8.	*Trans*-1,2-diaminocyclohexane	10
9.	*Trans*-1,2-cyclohexanediol	14
10.	1,1'-Bi-2-naphthol	42
11.	Ethylene glycol	37
12.	-	Traces[c]

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronicacid (1.2 equiv.), $Cu(OAc)_2$ (10 mol%), Ligands (20 mol%), K_3PO_4 (2 equiv.), DME (2 mL), reaction time: 24 h, temperature: RT, air. Open vessel. [b] Isolated yield. [c]Absence of ligands.

Table S3. Optimization of bases.



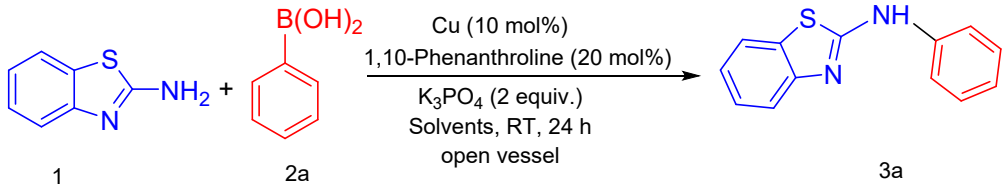
1 2a 3a

Entry	Bases	Yield (%) of 3a [a,b]
1	Potassium Carbonate	45
2	Potassium Phosphate	62
3	Potassium Hydroxide	51
4	Cyclohexylamine	36
5	Dicyclohexylamine	27
6	Cesium Carbonate	56

7	Sodium carbonate	39
8	Sodium Hydroxide	46
9.	Triethylamine	20
10	DBU	43
11	DABCO	41
12	Sodium Bicarbonate	19
13	Sodium *tert*-butoxide	17
14	Lithium *tert*-butoxide	23
15	Potassium *tert*-butoxide	19
16	Sodium Acetate	Traces
17	-	18[c]

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronicacid (1.2 equiv.), $Cu(OAc)_2$ (10 mol%), 1,10-Phenanthroline (20 mol%), bases (2 equiv.), DME (2 mL), reaction time: 24 h, temperature: RT, air. Open vessel. [b] Isolated yield. [c]Absence of bases.

Table S4. Optimization of solvents.



Entry	Solvents	Yield (%) of 3a [a,b]
1	DME	62
2	DCE	70
3	DCM	60
4	Acetonitrile	76
5	Chlorobenzene	66
6	Dichlorobenzene	70
7	1,4-Dioxane	45
8	Chloroform	45
9.	Toluene	38
10	DMF	41
11	THF	30
12	DMSO	40
13	NMP	38

14	Water	20[c]
15	Ethylene glycol	11
16	2-Propanol	15
17	^{t}BuOH	16
18	Ethanol	26
19	Methanol	20

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronicacid (1.2 equiv.), $Cu(OAc)_2$ (10 mol%), 1,10-Phenanthroline (20 mol%), K_3PO_4 (2 equiv.), solvents (2 mL), reaction time: 24 h, temperature: RT, air. Open vessel. [b] Isolated yield.[c] 1 equiv. of TBAB used.

Table S5. Optimization of time and temperature.

Entry	Time (h)	Temperature (^{0}C)	Yield (%) of 3a[a,b]
1.	24	RT	76
2.	24	45	35
3.	24	65	10
4.	18	RT	61
5.	30	RT	73

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronicacid (1.2 equiv.), $Cu(OAc)_2$ (10 mol%), 1,10-Phenanthroline (20 mol%), K_3PO_4 (2 equiv.), Acetonitrile (2 mL), reaction time: 18-30 h, temperature: RT-65 ^{o}C , air. Open vessel. [b] Isolated yield.

Table S6. Optimization of catalyst and ligand loading.

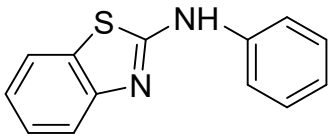
Entry	$Cu(OAc)_2$ (mol%)	1,10-Phenanthroline (mol%)	Yield (%) of 3a[a,b]
1.	5	10	68
2.	10	20	76
3.	15	30	60
4.	10	10	63
5.	10	20	75[c]
6.	10	20	36[d]
7.	10	20	77[e]
8.	10	20	19[f]

[a] Reaction conditions: 2-Aminobenzothiazole (1 equiv.), Phenylboronic acid (1.2 equiv.), $Cu(OAc)_2$ (5-15mol%), 1,10-Phenanthroline (10-30 mol%), K_3PO_4 (2 equiv.), Acetonitrile (2 mL), reaction time: 24 h,

temperature: RT, air. Open vessel. [b] Isolated yield. [c] 1.5 equiv. of K_3PO_4, [d] Excess of O_2, [e] 1.6 equiv. of Phenylboronic acid. [f]in N_2 atmosphere.

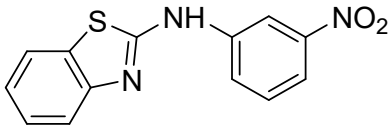
4. Compound Characterization Data

3a. *N*-Phenylbenzo[*d*]thiazol-2-amine



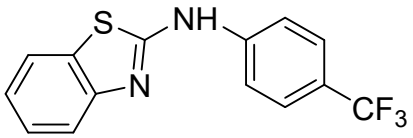
Chemical Formula: $C_{13}H_{10}N_2S$; Appearance: White spongy powder; Yield: 76%; MP: 158-161 °C (lit.[1]158-160 °C); **FT-IR** (neat): 3186, 3126, 2931, 1618, 1325, 1293, 1128 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.60 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.41 (t, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 2H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 164.2, 151.3, 139.6, 129.9, 129.5, 126.1, 124.3, 122.4, 120.8, 120.0, 119.4 ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_{10}N_2S$ ($[M + H]^+$): 227.0643, found: 227.0650.

3b. *N*-(3-Nitrophenyl)benzo[*d*]thiazol-2-amine



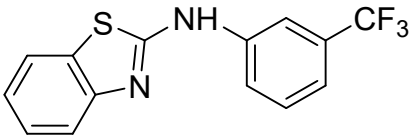
Chemical Formula: $C_{13}H_9N_3O_2S$; Appearance: Yellow powder; Yield: 72%; MP: 192-194 °C (lit.[2] 190-193 °C); **FT-IR** (neat): 3123, 3074, 2943, 1616, 1346, 1263, 1129 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 11.02 (brs, 1H), 8.87 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.68-7.62 (m, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 161.2, 151.6, 148.3, 141.6, 130.4, 130.0, 126.2, 123.6, 123.0, 121.3, 119.8, 116.4, 111.6 ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9N_3O_2S$ ($[M + H]^+$): 272.0494, found: 272.0484.

3c. *N*-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



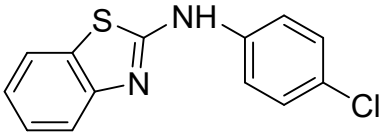
Chemical Formula: $C_{14}H_9F_3N_2S$; Appearance: White powder; Yield: 70%; MP: 187-190 °C (lit.[2] 189-191 °C); **FT-IR** (neat): 3135, 3036, 2905, 1611, 1316, 1221, 1181 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.70-7.62 (m, 6H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 162.1, 151.0, 142.7, 130.0, 126.7 (q, $^4J_{CF}$ = 3.6 Hz, 2C), 126.4, 125.5, 124.9, 123.2, 120.9, 120.0, 118.2 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_9F_3N_2S$ ($[M + H]^+$): 295.0517, found: 295.0512.

3d. *N*-(3-(Trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



Chemical Formula: $C_{14}H_9F_3N_2S$; Appearance: White powder; Yield: 51%; MP: 140-142 °C; **FT-IR** (neat): 3189, 3067, 2947, 1602, 1321, 1280, 1183 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.86 (brs, 1H), 8.29 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 161.3, 151.8, 141.3, 130.2, 130.1, 129.7 (q, $^2J_{CF}$ = 32 Hz, 1C), 126.1, 125.6 (q, $^1J_{CF}$ = 270 Hz, 1C), 122.8, 121.2, 119.7, 118.2, 117.8, 113.6 ppm; **GC-MS** (EI): m/z calculated for $C_{14}H_9F_3N_2S$ (M^+): 294.0, found: 294.1.

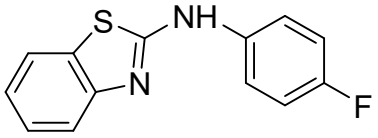
3e. *N*-(4-Chlorophenyl)benzo[*d*]thiazol-2-amine



Chemical Formula: $C_{13}H_9ClN_2S$; Appearance: White solid; Yield: 92%; MP: 206-208 °C (lit.[1] 208-209 °C); **FT-IR** (neat): 3174, 3066, 2919, 1615, 1324, 1265, 1130 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.66 (d, *J* = 7.6 Hz, 2H),7.51 (d, *J* = 8.8 Hz, 2H), 7.38-7.33 (m, 3H), 7.19 (t, *J* = 8.4 Hz, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 163.1, 151.7, 138.4, 130.2,

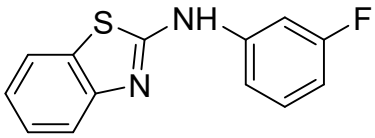
129.6, 129.0, 126.4, 122.9, 120.9, 120.0, 96.2 ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9ClN_2S$ ($[M + H]^+$): 261.0253, found: 261.0261.

3f. *N*-(4-Fluorophenyl)benzo[*d*]thiazol-2-amine



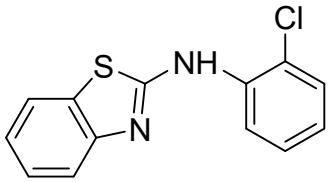
Chemical Formula: $C_{13}H_9FN_2S$; Appearance: White solid; Yield: 90%; MP: 214-217 ^oC (lit.[1] 216-217 ^oC); **FT-IR** (neat): 3193, 3054, 2906, 1621, 1327, 1272, 1128 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.51(brs, 1H), 7.80 (d, *J* = 8.0 Hz, 3H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.23-7.13 (m, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 161.7, 158.6 (d, $^1J_{CF}$ = 237.0 Hz, 1C), 152.1, 137.1, 130.0, 125.9, 122.4, 121.1, 119.4, 119.2, 115.7 (d, $^2J_{CF}$ = 22.2 Hz, 2C) ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9FN_2S$ ($[M + H]^+$): 245.0549, found: 245.0551.

3g. *N*-(3-Fluorophenyl)benzo[*d*]thiazol-2-amine



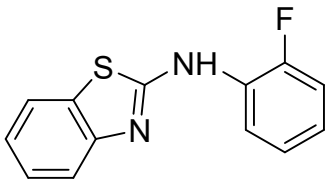
Chemical Formula: $C_{13}H_9FN_2S$; Appearance: White spongy solid; Yield: 87%; MP: 139-142 ^oC; **FT-IR** (neat): 3190, 3062, 2925, 2233, 1608, 1328, 1275, 1159 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.74 (brs, 1H), 7.93 (d, *J* = 12.0Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.43-7.32 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 8.4 Hz, 1H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 163.8 (d, $^1J_{CF}$ = 239.7 Hz, 1C), 161.3, 151.9, 142.3 (d, $^3J_{CF}$ = 11.2 Hz, 1C), 130.7 (d, $^3J_{CF}$ = 9.6 Hz, 1C), 130.0, 126.1, 122.7, 121.2, 119.6, 113.6, 108.4 (d, $^2J_{CF}$ = 21.1 Hz, 1C), 104.7 (d, $^2J_{CF}$ = 26.6 Hz, 1C) ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9FN_2S$ ($[M + H]^+$): 245.0549, found: 245.0547.

3h. *N*-(2-Chlorophenyl)benzo[*d*]thiazol-2-amine



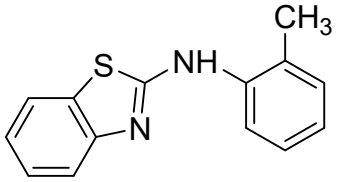
Chemical Formula: $C_{13}H_9ClN_2S$; Appearance: White powder; Yield: 40%; MP: 121-124 °C, (lit.[2] 123-126 °C); **FT-IR** (neat): 3101, 3063, 2239, 1575, 1287, 1110, 1031 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.61-7.53 (m, 2H), 7.40 (d, *J* = 7.6Hz, 2H), 7.19-7.07 (m, 3H), 6.92 (brs, 1H), 6.55 (d, *J* = 7.2 Hz, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 140.3, 138.1, 134.4, 132.5, 131.7, 130.0, 127.8, 127.4, 126.9, 124.5, 115.9, 115.5, 109.9 ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9ClN_2S$ ($[M + H]^+$): 261.0253, found: 261.0246.

3i. *N*-(2-Fluorophenyl)benzo[*d*]thiazol-2-amine



Chemical Formula: $C_{13}H_9FN_2S$; Appearance: White crystals; Yield: 30%; MP: 122-124 °C; **FT-IR** (neat): 3196, 3060, 2915, 1616, 1318,1285, 1124, 1066 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.31 (t, *J*= 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.23-7.05 (m, 4H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 162.4, 153.9 (d, $^1J_{CF}$ = 242.2 Hz, 1C), 151.2, 130.1, 128.2 (d, $^3J_{CF}$ = 9.6 Hz, 1C), 126.4, 124.9 (d, $^4J_{CF}$ = 3.4 Hz, 1C), 124.0 (d, $^3J_{CF}$ = 7.2 Hz, 1C), 123. 2, 121.0, 120.5, 120.1, 115.5 (d, $^2J_{CF}$ = 18.7 Hz, 1C) ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9FN_2S$ ($[M + H]^+$): 245.0549, found: 245.0543.

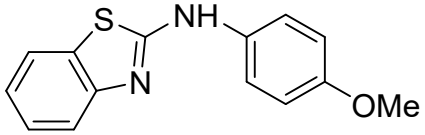
3j. *N*-(*o*-Tolyl)benzo[*d*]thiazol-2-amine



Chemical Formula: $C_{14}H_{12}N_2S$; Appearance: White crystals; Yield: 49%; MP: 118-120 °C; **FT-IR** (neat): 3065, 2917, 2849, 2236, 1642, 1377, 1287, 1127, 1055 cm^{-1}; **^{1}H NMR**

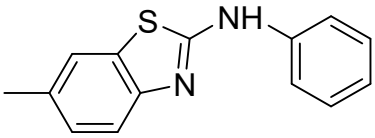
($CDCl_3$, 400 MHz) δ 7.53-7.48 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.15-7.08 (m, 2H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.87 (brs, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 139.7, 137.4, 135.7, 134.0, 131.7, 130.7, 127.1, 126.4, 125.9, 124.4, 117.0, 115.3, 110.1, 20.2 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{12}N_2S$ ($[M + H]^+$): 241.0799, found: 241.0794.

3k. *N*-(4-Methoxyphenyl)benzo[*d*]thiazol-2-amine



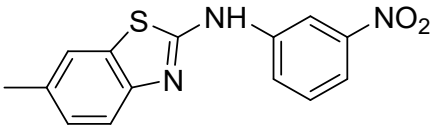
Chemical Formula: $C_{14}H_{12}N_2OS$; Appearance: White solid with purple shade; Yield: 45%; MP: 152-155 °C (lit.[1] 153-155 °C); **FT-IR** (neat): 3179, 3026, 2833, 1617, 1313, 1265, 1166, 1035 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.66 (brs, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 3H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.7, 157.5, 151.7, 133.1, 129.7, 126.1, 124.4, 121.9, 120.9, 118.8, 114.9, 55.6 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{12}N_2OS$ ($[M + H]^+$): 257.0749, found: 257.0745.

6a. 6-Methyl-*N*-phenylbenzo[*d*]thiazol-2-amine



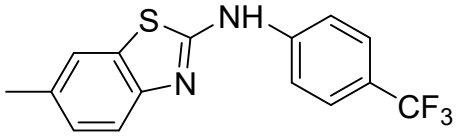
Chemical Formula: $C_{14}H_{12}N_2S$; Appearance: White solid; Yield: 67%; MP: 163-166 °C (lit.[1] 165-167 °C); **FT-IR** (neat): 3190, 3053, 2938, 1620, 1301, 1268, 1134, 1029 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.16 (brs, 1H), 7.50-7.38 (m, 6H), 7.18-7.13 (m, 2H), 2.42 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 164.3, 149.2, 140.1, 132.2, 129.9, 129.6, 127.4, 124.2, 120.9, 120.2, 118.9, 21.4 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{12}N_2S$ ($[M + H]^+$): 241.0799, found: 241.0790.

6b. 6-Methyl-*N*-(3-nitrophenyl)benzo[*d*]thiazol-2-amine



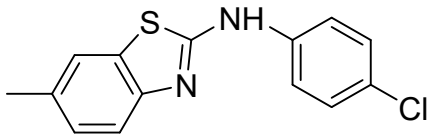
Chemical Formula: $C_{14}H_{11}N_3O_2S$; Appearance: Yellow powder; Yield: 65%; MP: 194-196 °C (lit.[2] 195-197 °C); **FT-IR** (neat): 3185, 3086, 2919, 1619, 1330, 1279, 1134, 1091 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.98 (brs, 1H), 8.85 (t, *J* = 2.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 2H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 2.36 (s, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 160.3, 149.5, 148.3, 141.7, 132.2, 130.2, 130.1, 127.2, 123.5, 121.1, 119.4, 116.1, 111.5, 20.9 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{11}N_3O_2S$ ($[M + H]^+$): 286.0650, found: 286.0655.

6c. 6-Methyl-*N*-(4-(trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



Chemical Formula: $C_{15}H_{11}F_3N_2S$; Appearance: White crystals; Yield: 62%; MP: 198-200 °C; **FT-IR** (neat): 3181, 3041, 2921, 1609, 1320, 1203, 1159, 1012 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.83 (brs, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.61 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 160.3, 149.7, 144.0, 132.2, 130.2, 126.0 (q, $^1J_{CF}$ = 270 Hz, 1C), 127.2, 126.3 (q, $^4J_{CF}$ = 4 Hz, 2C), 121.8 (q, $^2J_{CF}$ = 32 Hz, 1C), 121.0, 119.4, 117.3, 20.9 ppm; **HRMS** (QToF): m/z calculated for $C_{15}H_{11}F_3N_2S$ ($[M + H]^+$): 309.0673, found: 309.0695.

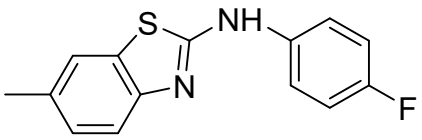
6d. *N*-(4-Chlorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



Chemical Formula: $C_{14}H_{11}ClN_2S$; Appearance: White solid; Yield: 89%; MP: 172-174 °C; **FT-IR** (neat): 3177, 3075, 2904, 1619, 1301, 1248, 1174, 1014 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.55 (brs, 1H), 7.83-7.80 (m, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H) ppm; **^{13}C NMR** (DMSO-

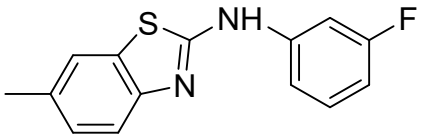
d_6, 100 MHz) δ 160.5, 149.8, 139.6, 131.8, 130.1, 128.8, 127.1, 125.2, 121.0, 119.0, 20.9 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{11}ClN_2S$ ($[M + H]^+$): 275.0410, found: 275.0408.

6e. *N*-(4-Fluorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



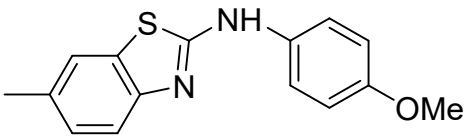
Chemical Formula: $C_{14}H_{11}FN_2S$; Appearance: White solid; Yield: 86%; MP: 175-177 °C; **FT-IR** (neat): 3201, 3044, 2914, 2849, 1621, 1328, 1285, 1133, 1056 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.44 (brs, 1H), 7.82-7,79 (m, 2H), 7.56 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.19 (t, J = 8.8 Hz, 2H), 7.12 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 160.9, 158.5 (d, $^1J_{CF}$ = 236.9 Hz, 1C), 149.9, 137.3, 131.6, 130.1, 127.0, 120.9, 119.3 (d, $^3J_{CF}$ = 7.6 Hz, 2C), 118.9, 115.6 (d, $^2J_{CF}$ = 22.2 Hz, 2C), 20.90 ppm; **HRMS** (QToF): m/z calculated for $C_{13}H_9FN_2S$ ($[M + H]^+$): 259.0705, found: 259.0704.

6f. *N*-(3-Fluorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



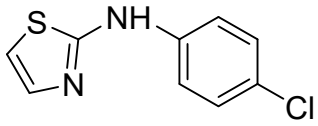
Chemical Formula: $C_{14}H_{11}FN_2S$; Appearance: White spongy solid; Yield: 80%; MP: 168-170 °C; **FT-IR** (neat): 3192, 3064, 2921, 1620, 1336, 1237, 1166, 1003 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.66 (brs, 1H), 7.94 (d, J = 11.6 Hz, 1H), 7.58 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.42-7.33 (m, 2H), 7.14 (d, J = 8.4 Hz, 1H), 6.81 (t, J = 8.4 Hz, 1H) 2.34 (s, 3H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 163.7 (d, $^1J_{CF}$ = 239.5 Hz, 1C), 160.5, 149.8, 142.4 (d, $^3J_{CF}$ = 11.4 Hz, 1C), 131.9, 130.5 (d, $^3J_{CF}$ = 9.6 Hz, 1C), 130.0, 127.1, 120.9, 119.2, 113.4, 108.2 (d, $^2J_{CF}$ = 21.1 Hz, 1C), 104.5 (d, $^2J_{CF}$ = 26.7 Hz, 1C), 20.8 ppm; **HRMS** (QToF): m/z calculated for $C_{14}H_{11}FN_2S$ ($[M + H]^+$): 259.07052, found: 259.07046.

6g. *N*-(4-Methoxyphenyl)-6-methylbenzo[*d*]thiazol-2-amine



Chemical Formula: $C_{15}H_{14}N_2OS$; Appearance: White crystals; Yield: 41%; MP: 168-170 °C (lit.[2] 167-170 °C); **FT-IR** (neat): 3070, 2904, 1679, 1324, 1267, 1164, 1031 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40-7.35 (m, 4H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.78 (brs, 1H), 3.84 (s, 3H), 2.39 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 166.4, 157.2, 149.6, 133.2, 131.8, 129.9, 127.3, 124.0, 120.9, 118.6, 114.8, 55.6, 21.3 ppm; **HRMS** (QToF): m/z calculated for $C_{15}H_{14}N_2OS$ ($[M + H]^+$): 271.0905, found: 271.0908.

8a. *N*-(4-Chlorophenyl)thiazol-2-amine



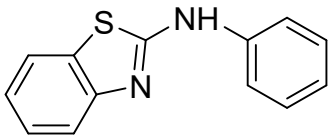
Chemical Formula: $C_9H_7ClN_2S$; Appearance: Off-white crystals; Yield: 28%; MP: 155-159 °C; **FT-IR** (neat): 3187, 3124, 2917, 1612, 1303, 1206, 1182, 1060 cm^{-1}; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 10.34 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 3.6 Hz, 1H) ppm; **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 163.5, 140.2, 138.8, 128.7, 124.3, 118.2, 108.9 ppm; **GC-MS** (EI): m/z calculated for $C_9H_7ClN_2S$ (M^+): 210, found: 209.9.

5. References

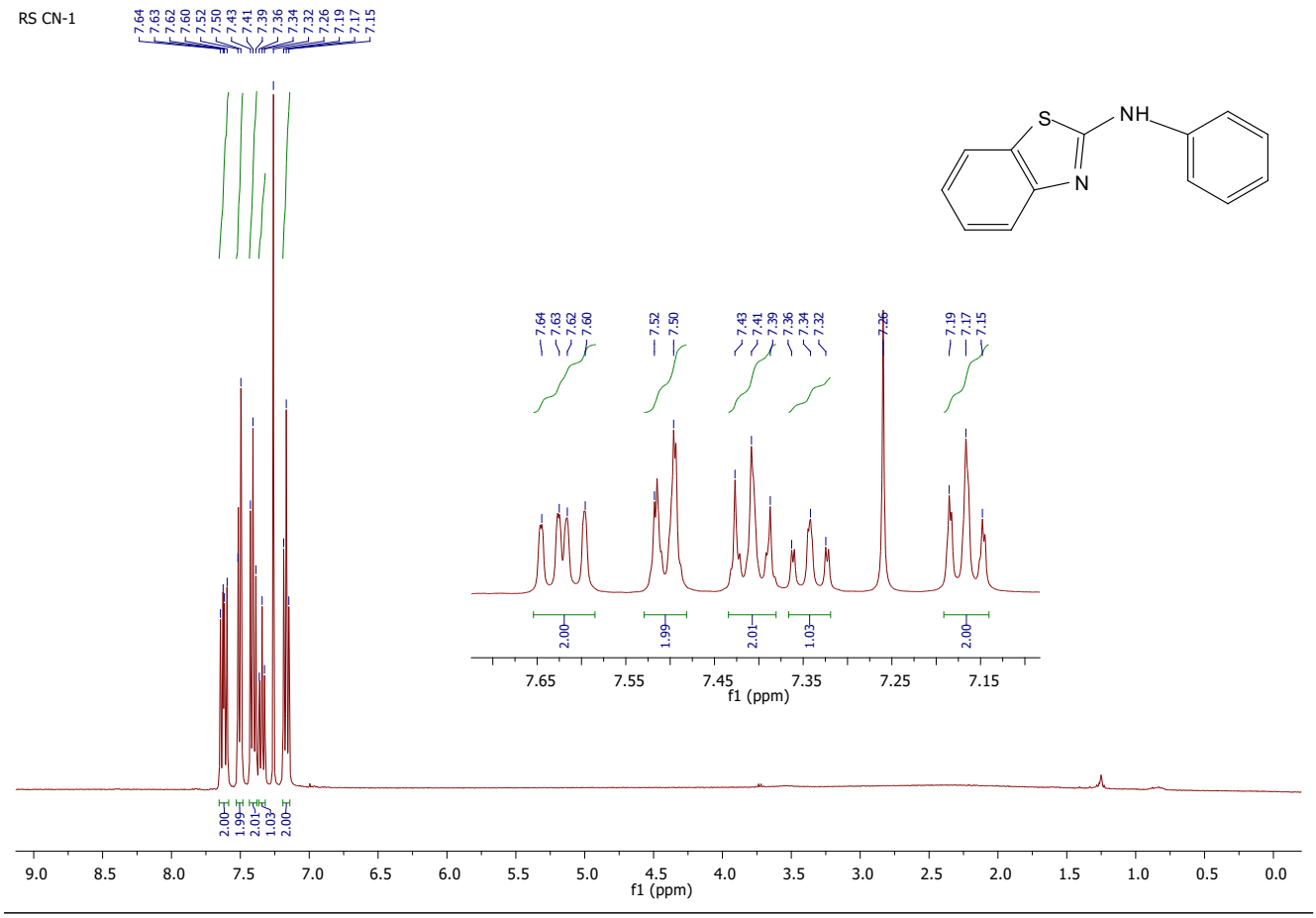
1. Q. Ding, B. Cao, X. Liu, Z. Zong, Y. Peng, *Green Chem*. **2010**, *12*, 1607.
2. N. Khatun, L. Jamir, M. Ganesh, B. K. Patel, *RSC Adv.* **2012**, *2*, 11557.

6. ^{1}H and ^{13}C NMR Spectra of Compounds

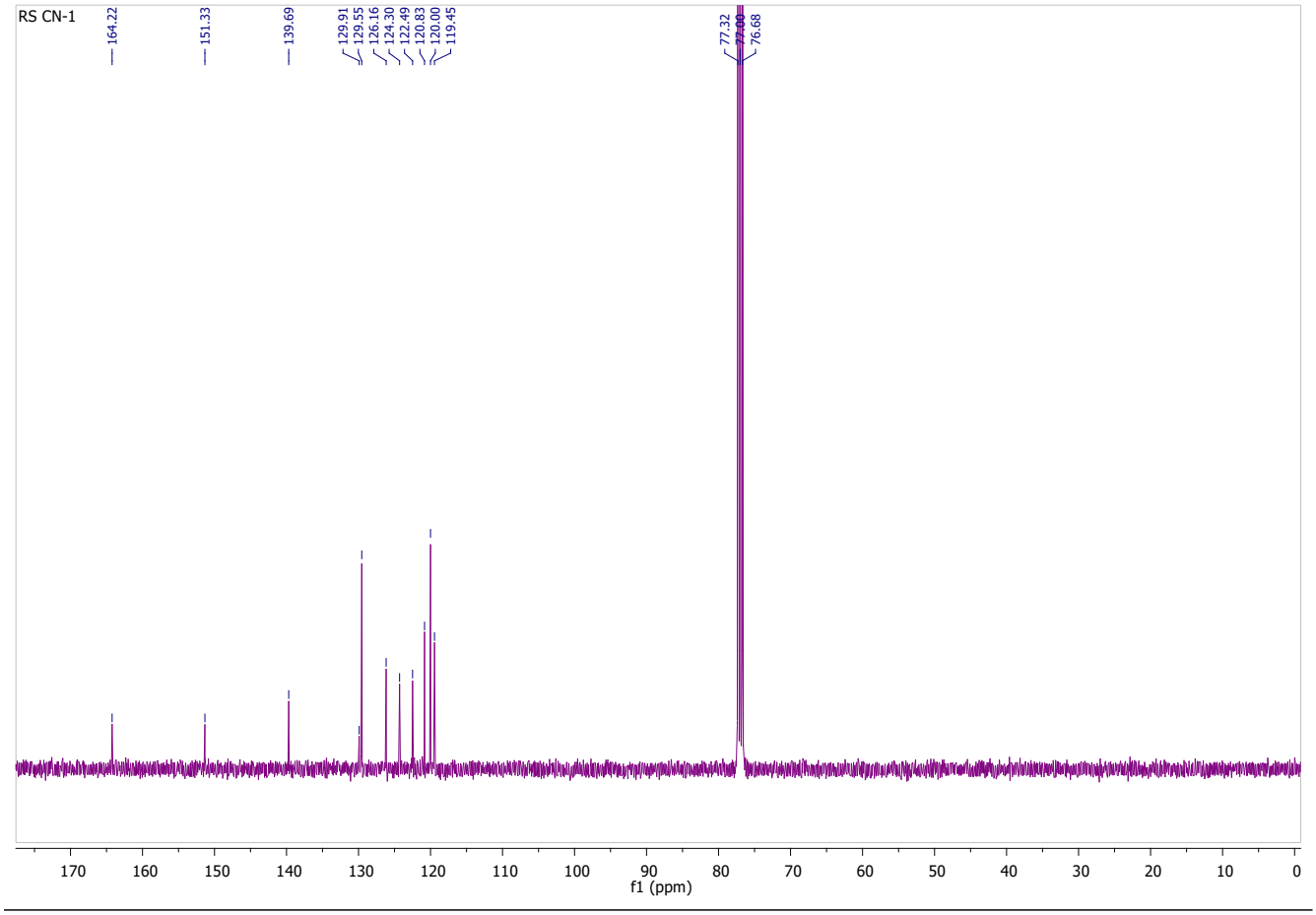
3a. *N*-Phenylbenzo[*d*]thiazol-2-amine



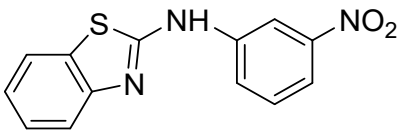
^{1}H NMR of 3a:



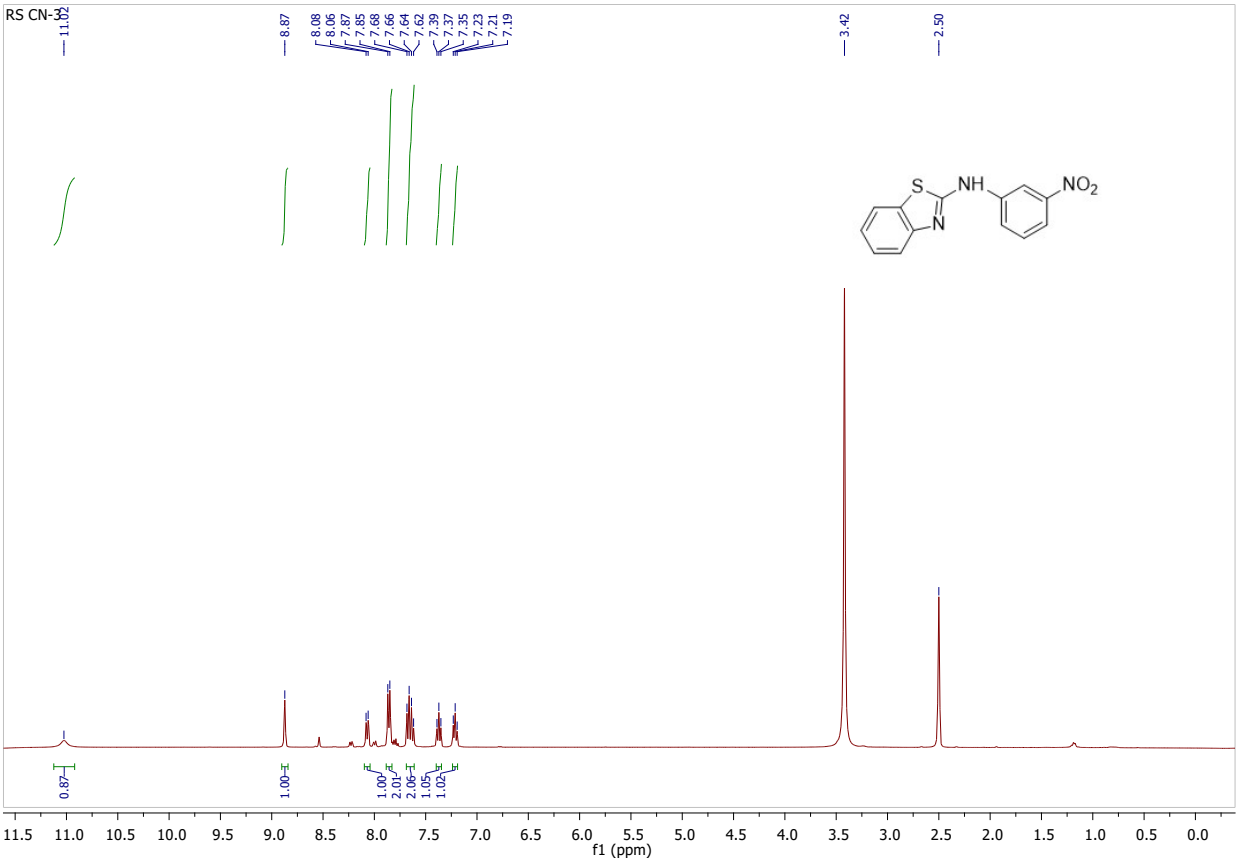
^{13}C NMR of 3a:



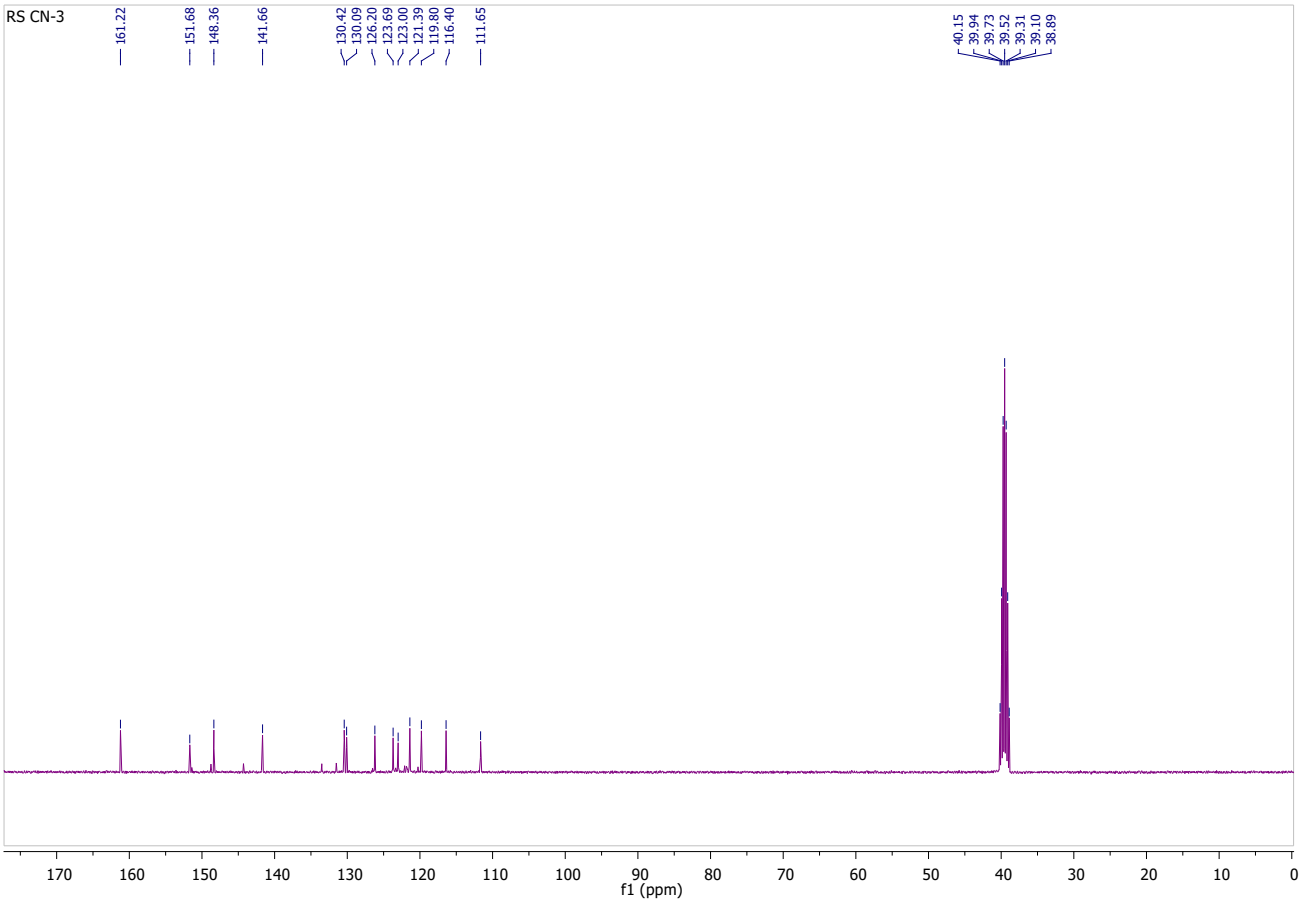
3b. *N*-(3-Nitrophenyl)benzo[*d*]thiazol-2-amine



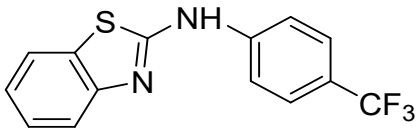
^{1}H NMR of 3b:


RS CN-32
11.02
8.87
8.08
8.06
7.87
7.85
7.68
7.66
7.64
7.62
7.39
7.37
7.35
7.23
7.21
7.19
3.42
2.50
S
NH
N
NO2
0.87
1.00
1.00
2.01
2.06
1.05
1.02
11.5 11.0 10.5 10.0 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 0.0
f1 (ppm)

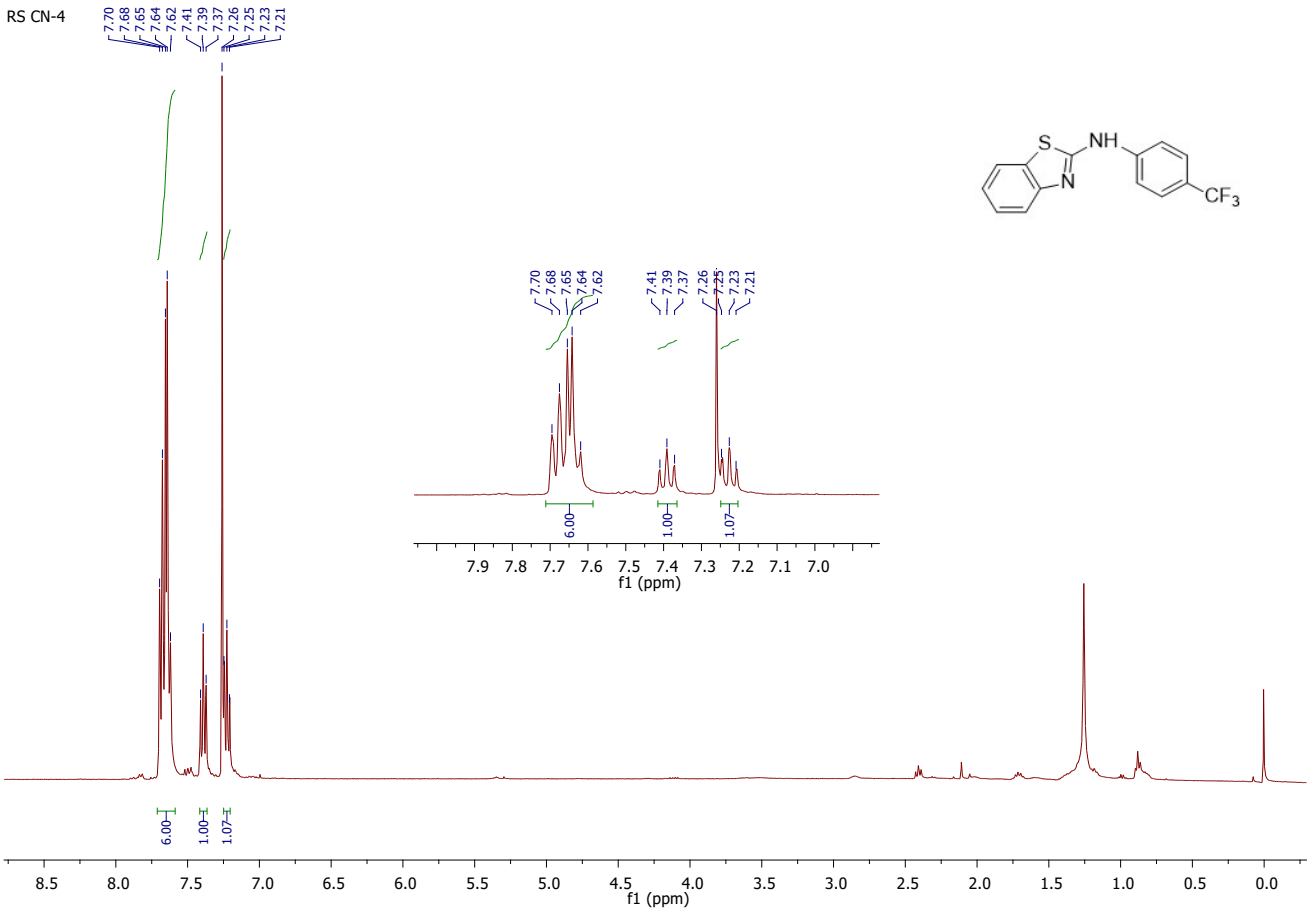
^{13}C NMR of 3b:



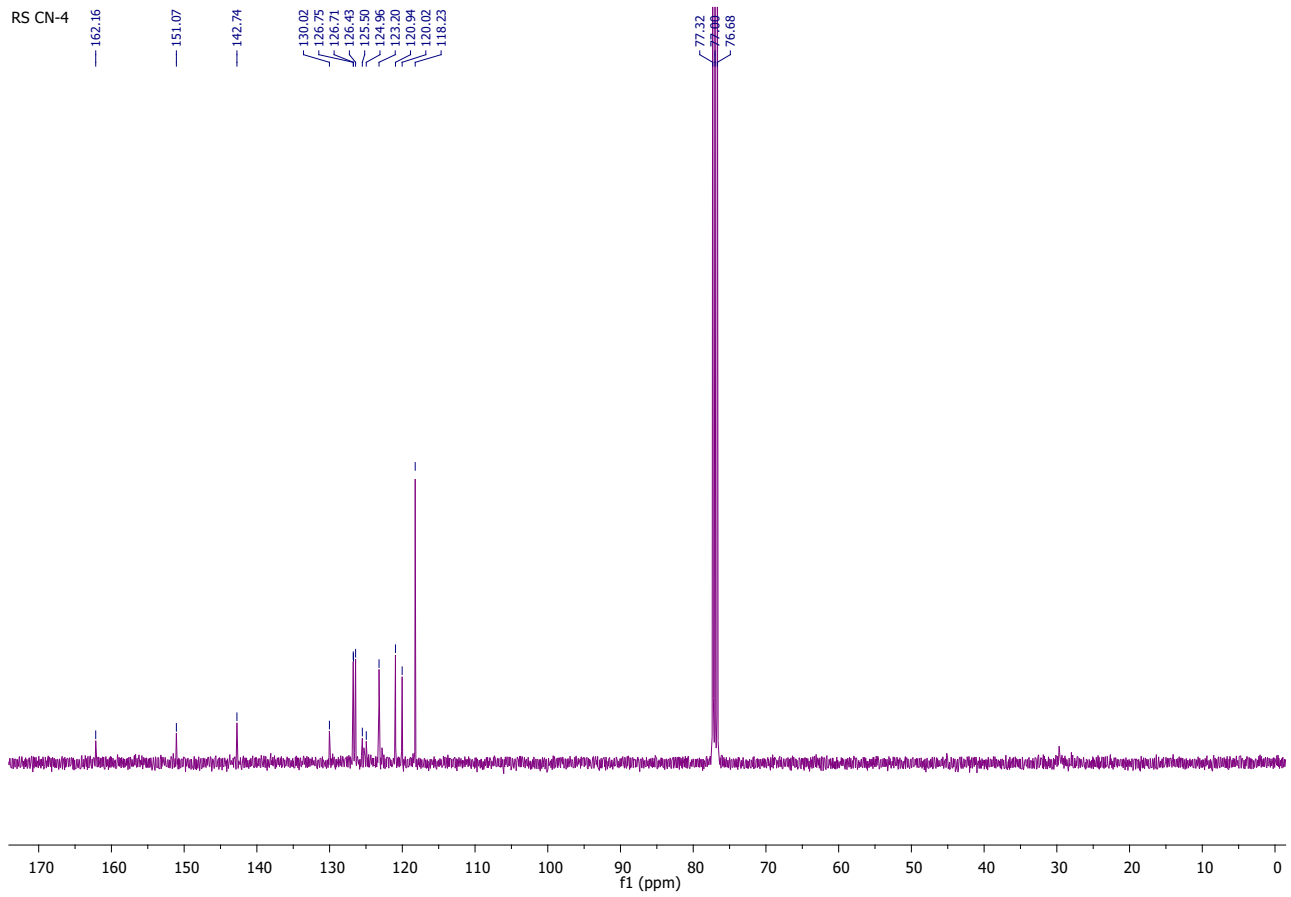
3c. *N*-(4-(Trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



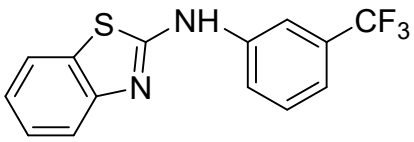
^{1}H NMR of 3c:


RS CN-4
7.70
7.68
7.65
7.64
7.62
7.41
7.39
7.37
7.26
7.25
7.23
7.21
S
NH
N
CF3
6.00
1.00
1.07
f1 (ppm)

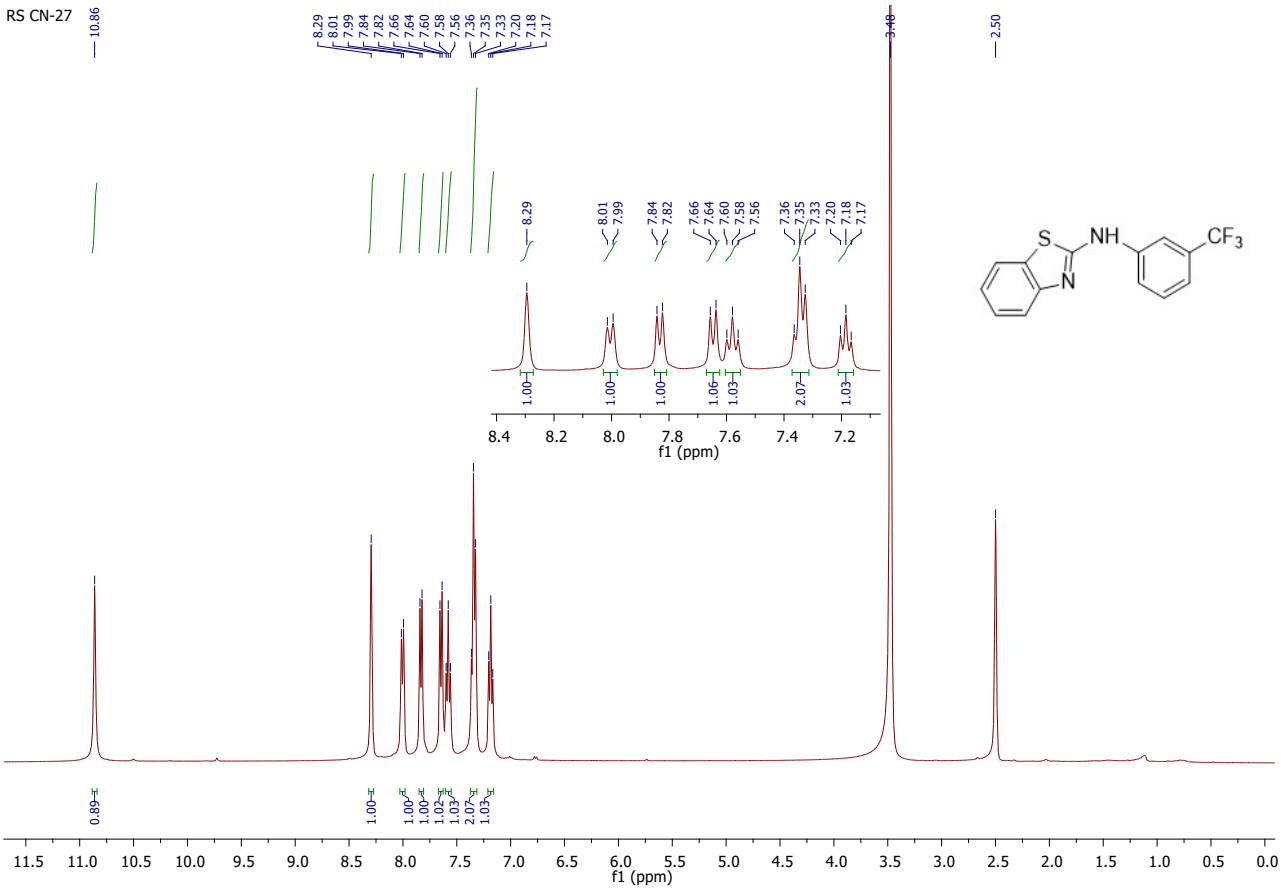
^{13}C NMR of 3c:



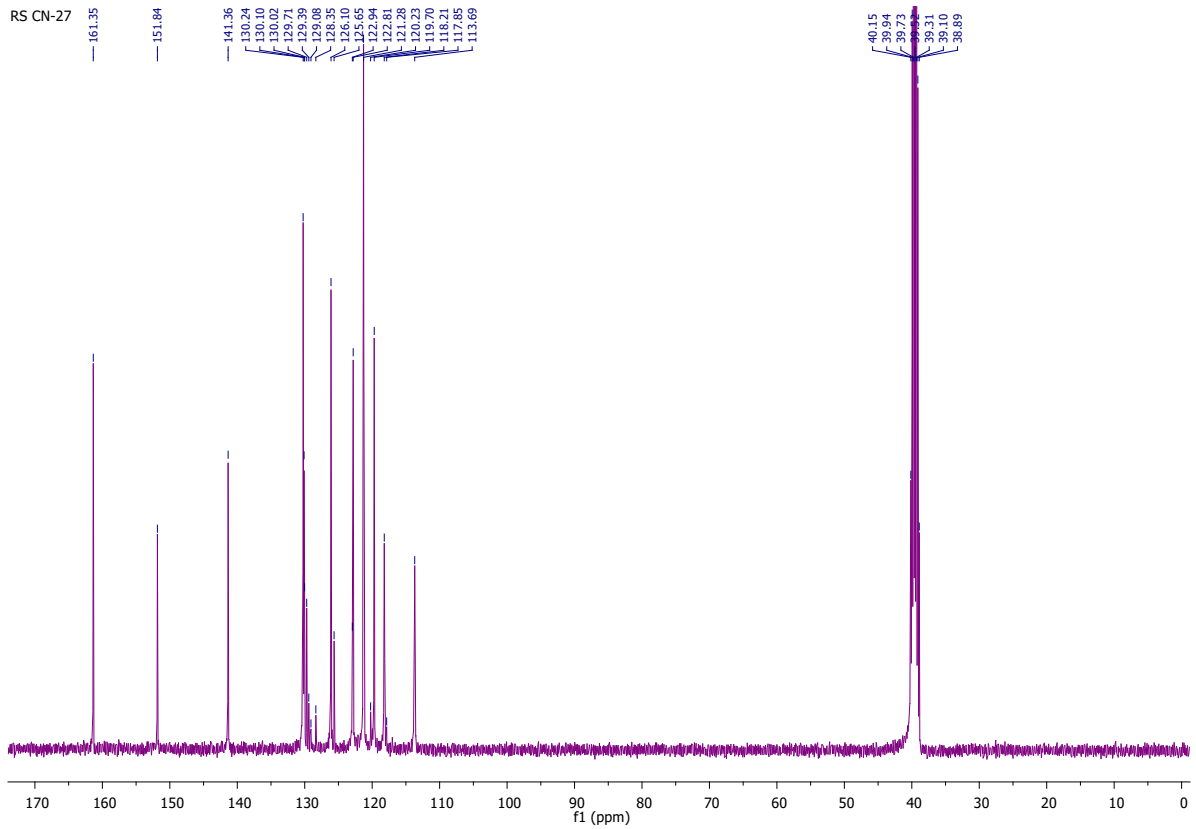
3d. *N*-(3-(Trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



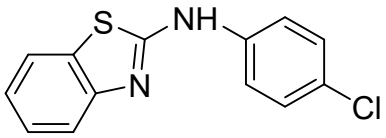
^{1}H NMR of 3d:


RS CN-27
10.86
8.29
8.01
7.99
7.84
7.82
7.66
7.64
7.60
7.58
7.56
7.36
7.35
7.33
7.20
7.18
7.17
3.48
2.50
S
NH
CF3
N
f1 (ppm)
f1 (ppm)

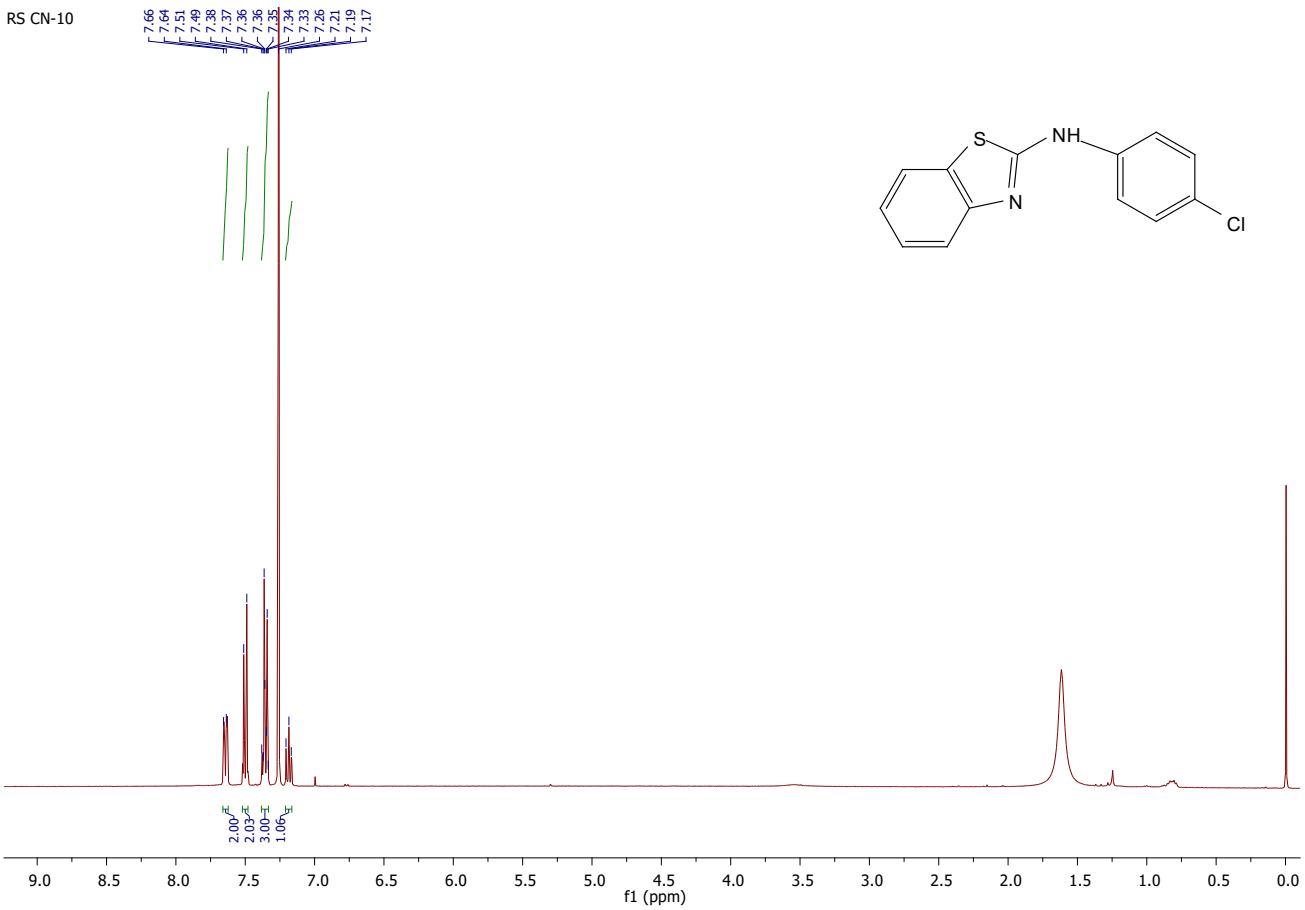
^{13}C NMR of 3d:



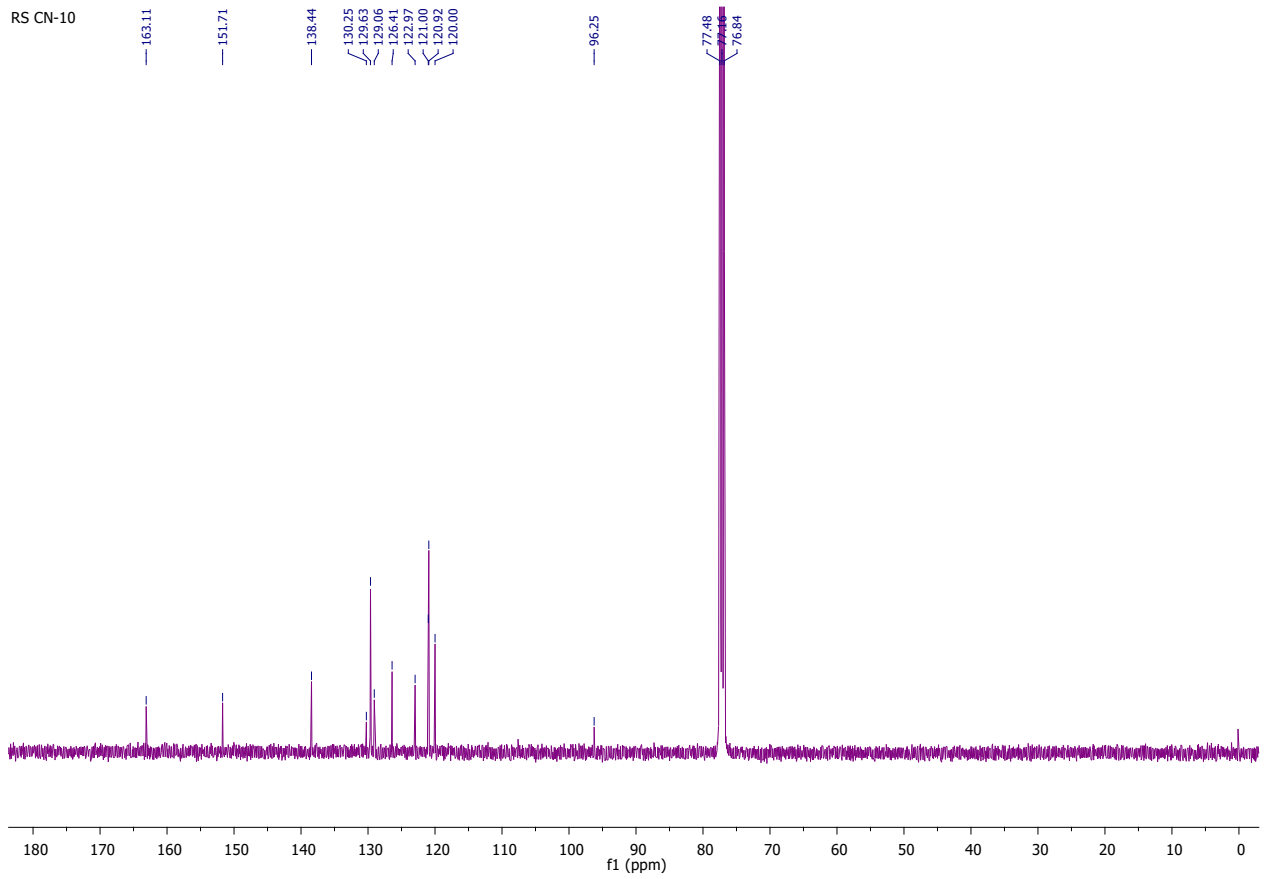
3e. *N*-(4-Chlorophenyl)benzo[*d*]thiazol-2-amine



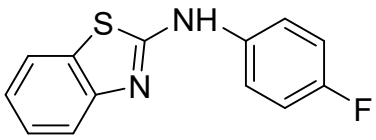
^{1}H NMR of 3e:


RS CN-10
7.66
7.64
7.51
7.49
7.38
7.37
7.36
7.36
7.35
7.34
7.33
7.26
7.21
7.19
7.17
S
NH
N
Cl
2.00
2.03
3.00
1.06
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
0.0
f1 (ppm)

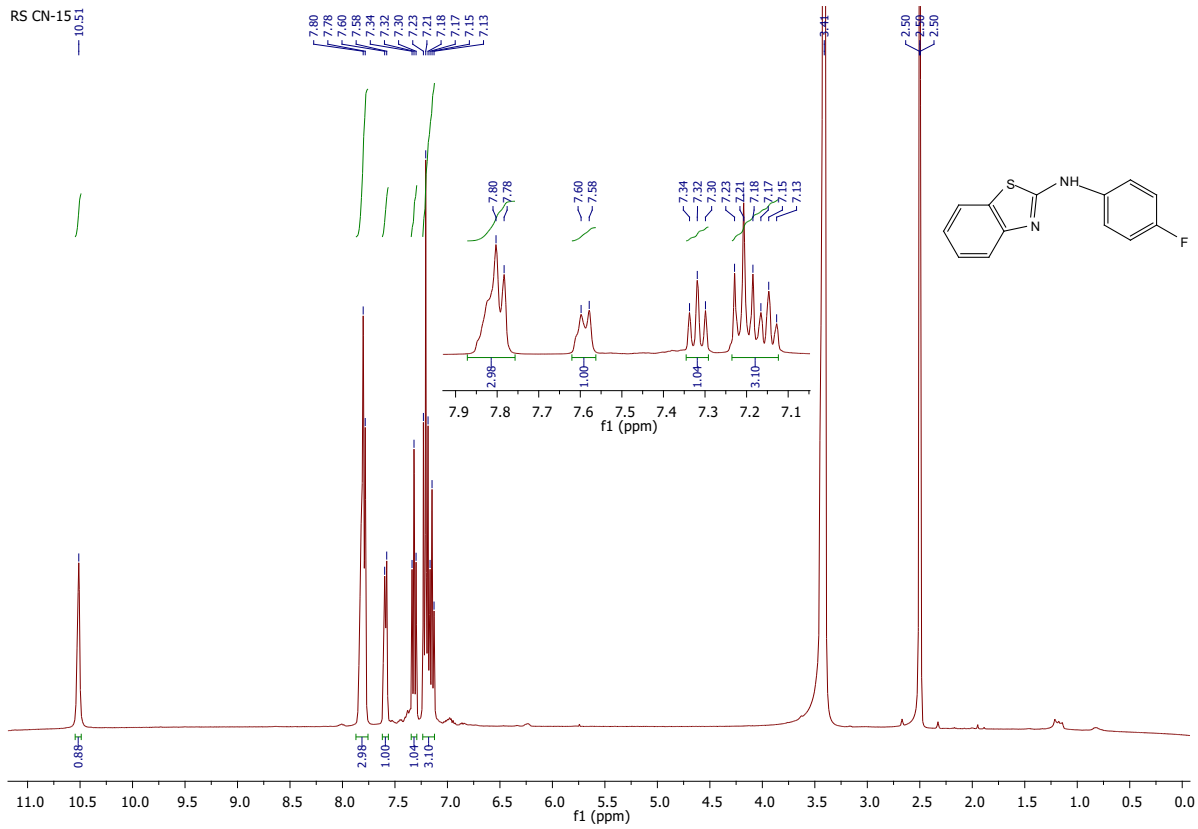
^{13}C NMR of 3e:



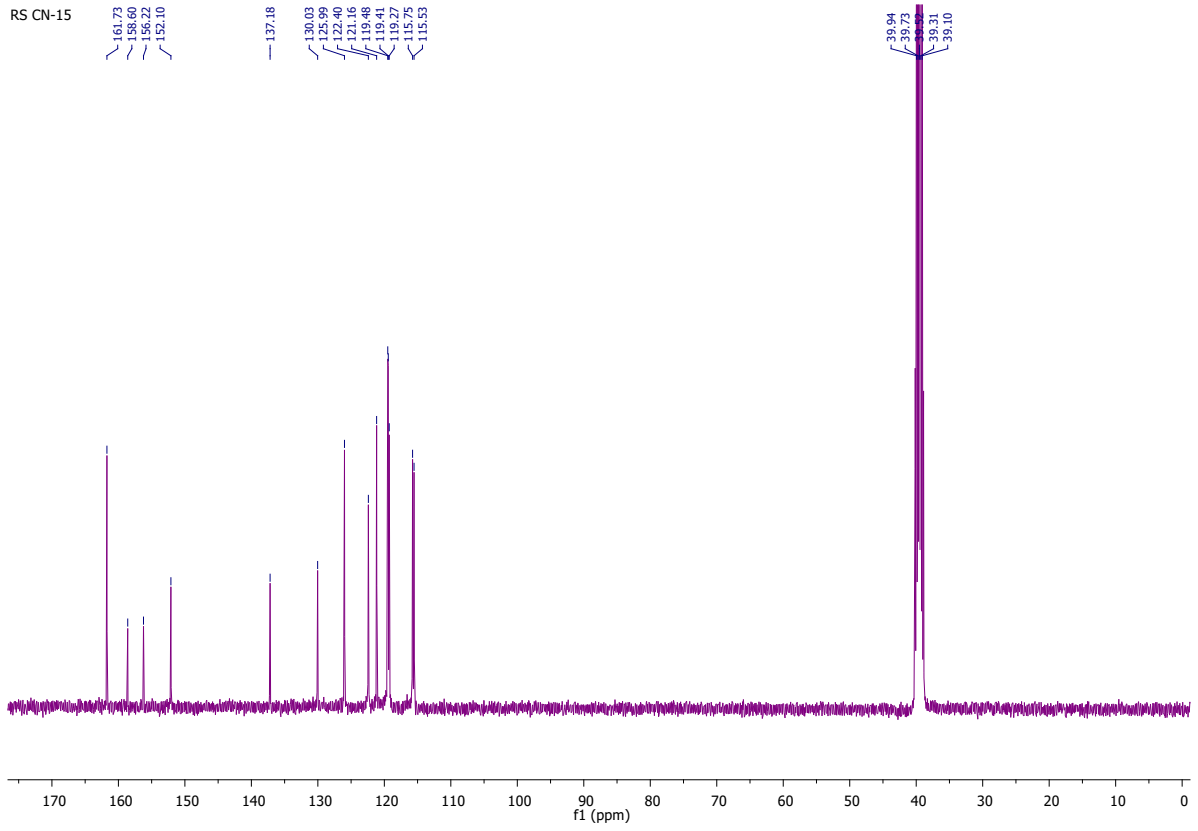
3f. *N*-(4-Fluorophenyl)benzo[*d*]thiazol-2-amine



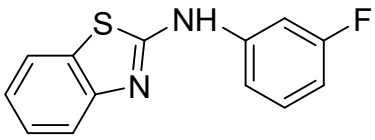
^{1}H NMR of 3f:


RS CN-15
10.51
7.80
7.78
7.60
7.58
7.34
7.32
7.30
7.23
7.21
7.18
7.17
7.15
7.13
3.41
2.50
2.50
2.50
S
NH
N
F
0.88
2.98
1.00
1.04
3.10
f1 (ppm)

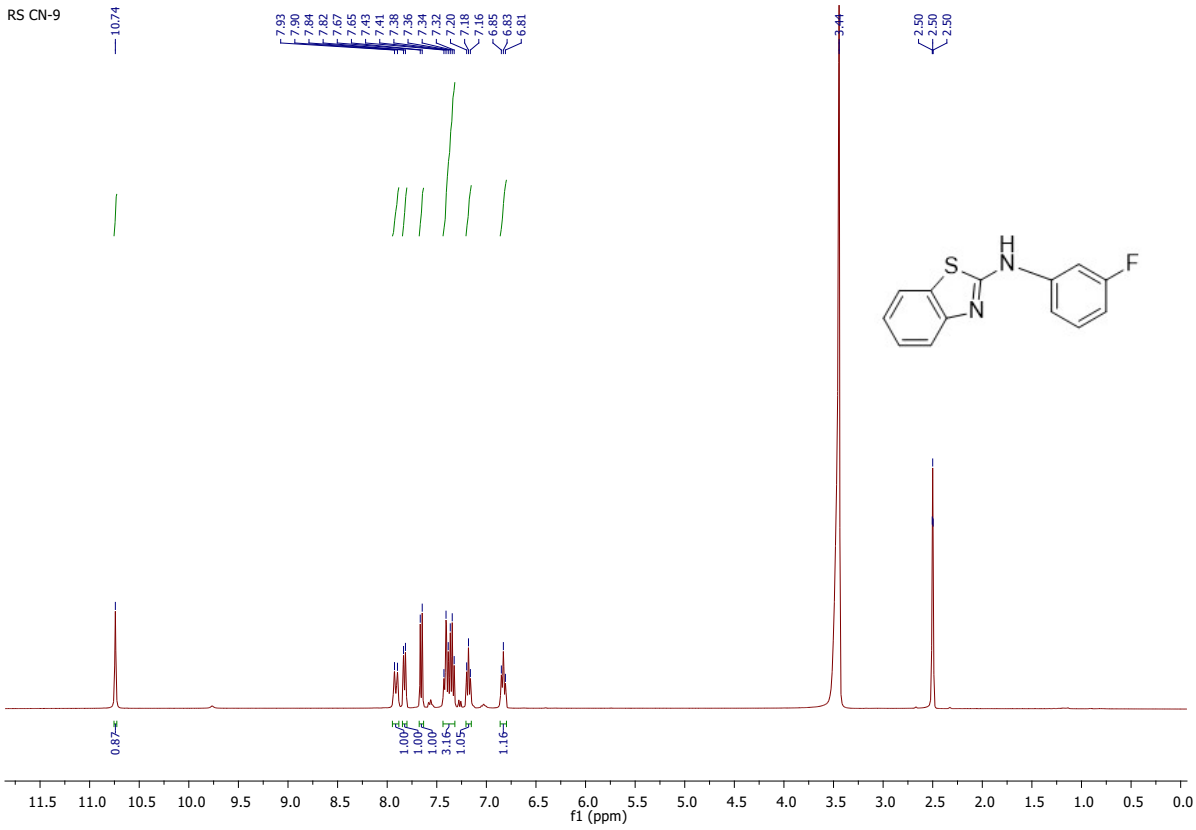
^{13}C NMR of 3f:


RS CN-15
161.73
158.60
156.22
152.10
137.18
130.03
125.99
122.40
121.16
119.48
119.41
119.27
115.75
115.53
39.94
39.73
39.52
39.31
39.10
f1 (ppm)

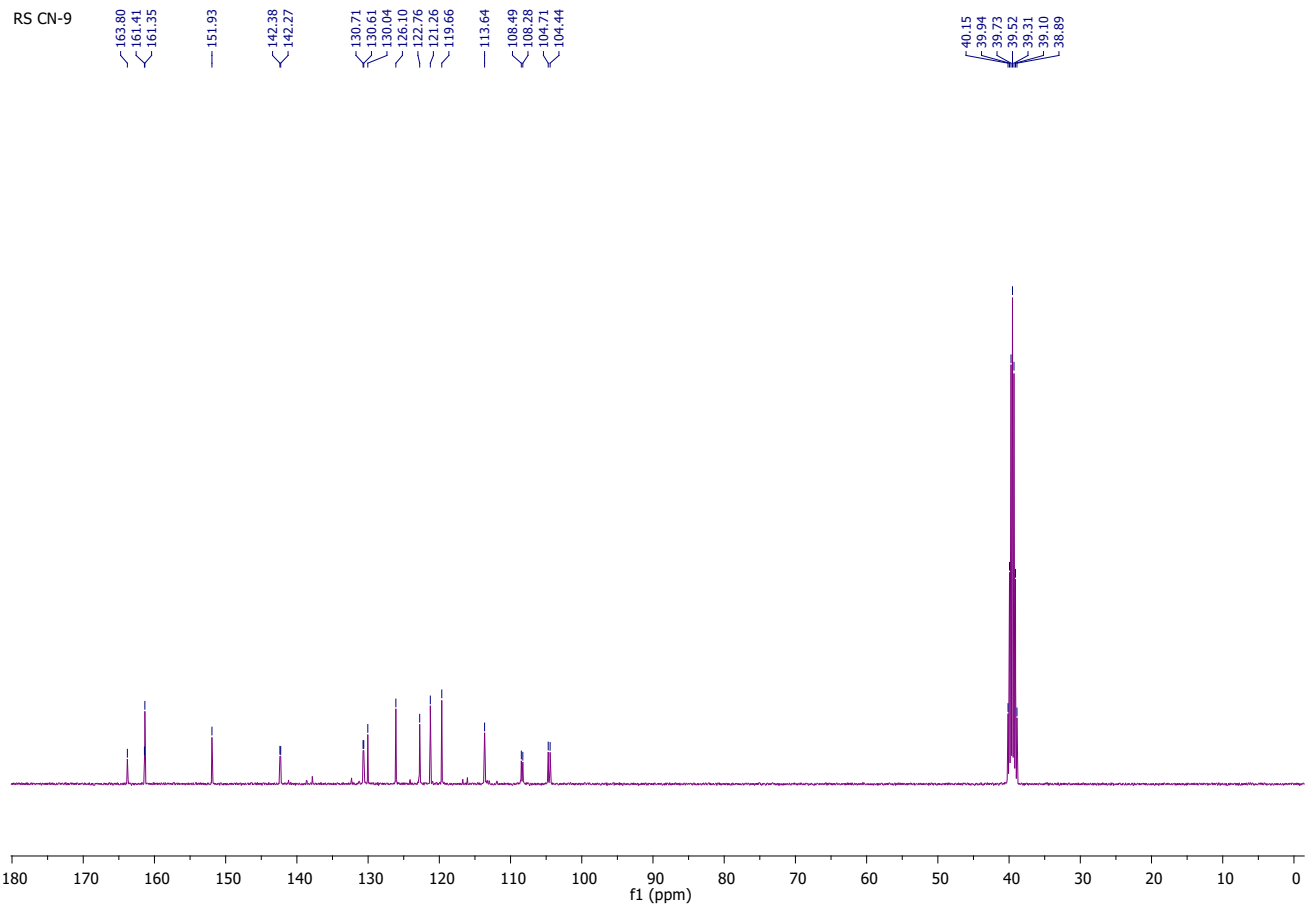
3g. *N*-(3-Fluorophenyl)benzo[*d*]thiazol-2-amine



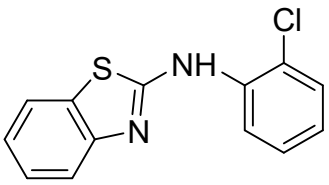
^{1}H NMR of 3g:



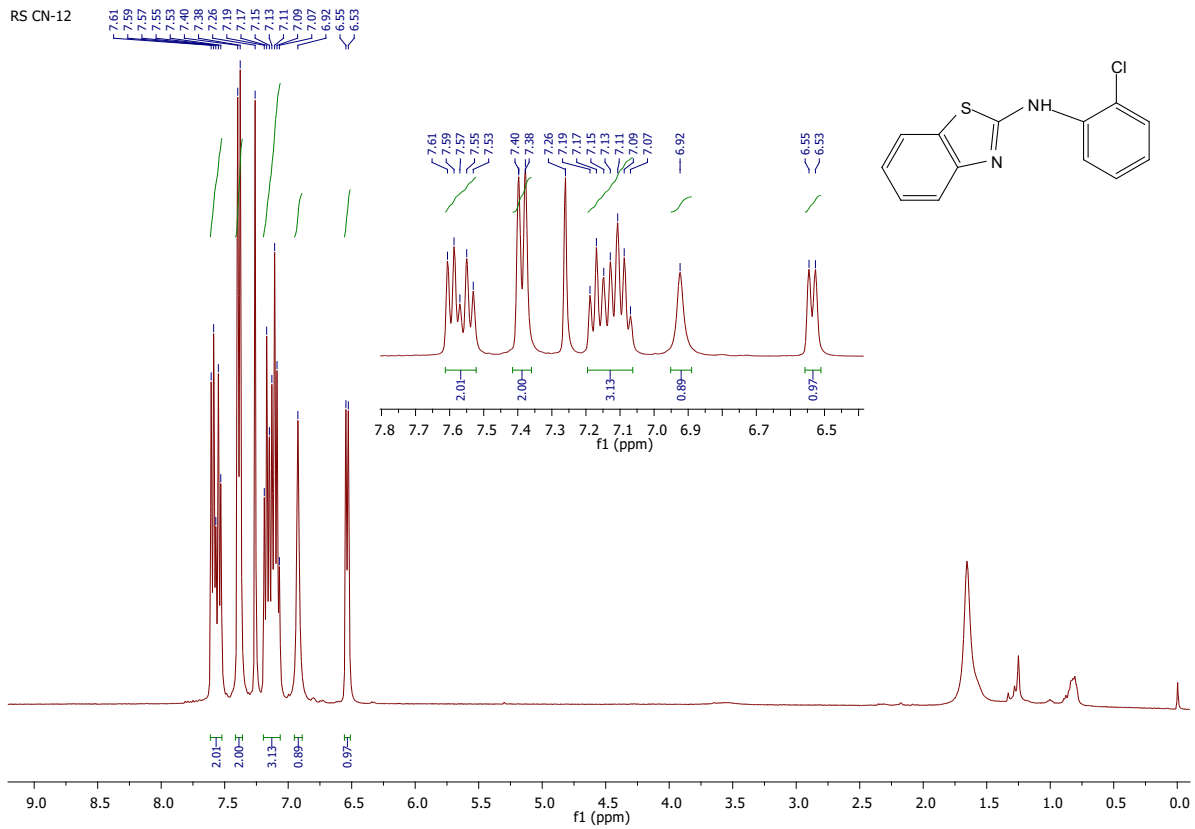
^{13}C NMR of 3g:



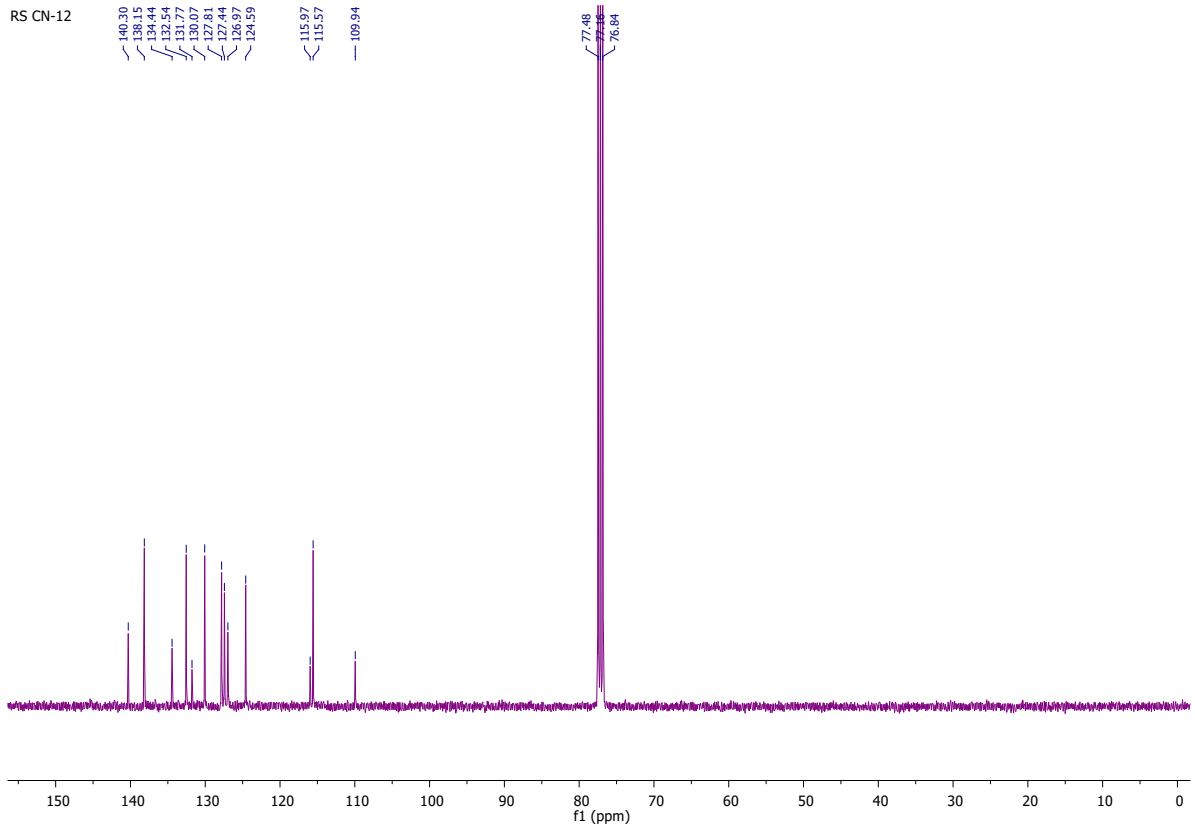
3h. *N*-(2-Chlorophenyl)benzo[*d*]thiazol-2-amine



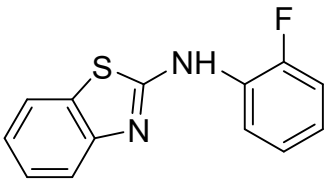
^{1}H NMR of 3h:


RS CN-12
7.61
7.59
7.57
7.55
7.53
7.40
7.38
7.26
7.19
7.17
7.15
7.13
7.11
7.09
7.07
6.92
6.55
6.53
2.01
2.00
3.13
0.89
0.97
f1 (ppm)
Cl
NH
S
N

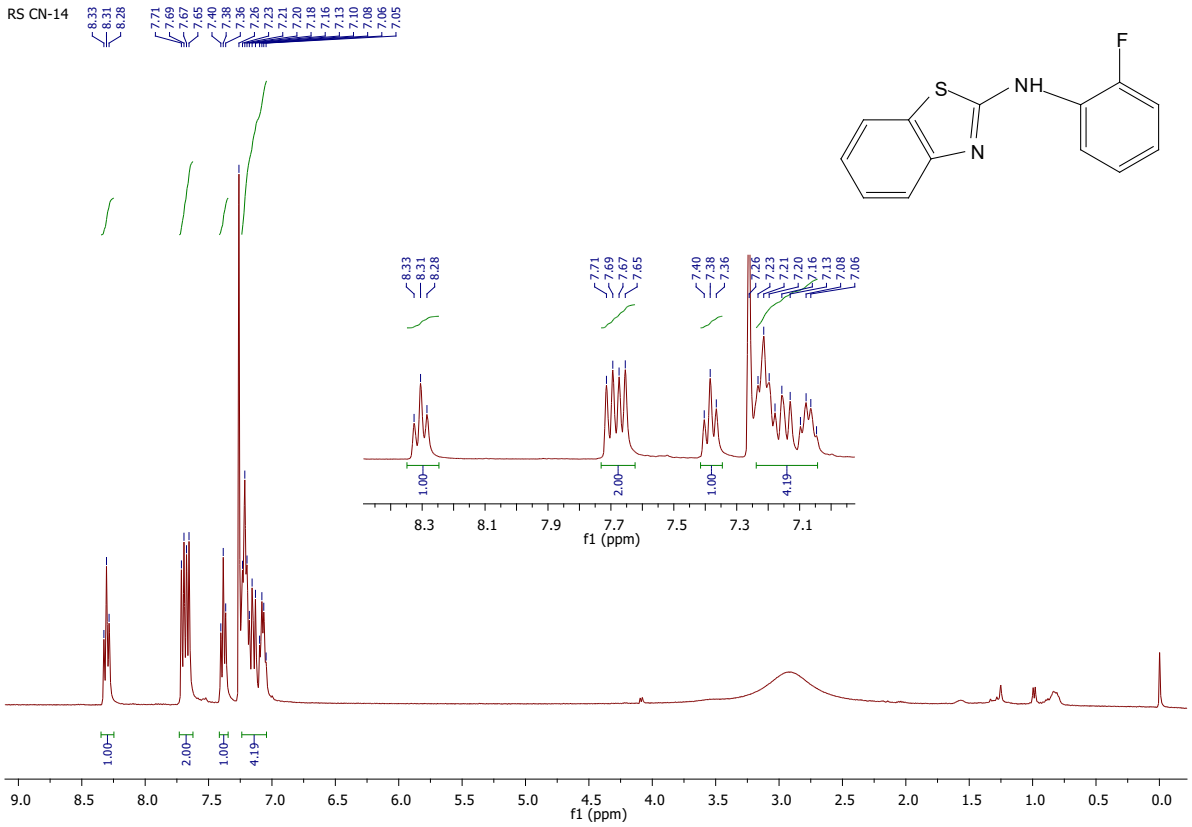
^{13}C NMR of 3h:


RS CN-12
140.30
138.15
134.44
132.54
131.77
130.07
127.81
127.44
126.97
124.59
115.97
115.57
109.94
77.48
77.16
76.84
f1 (ppm)

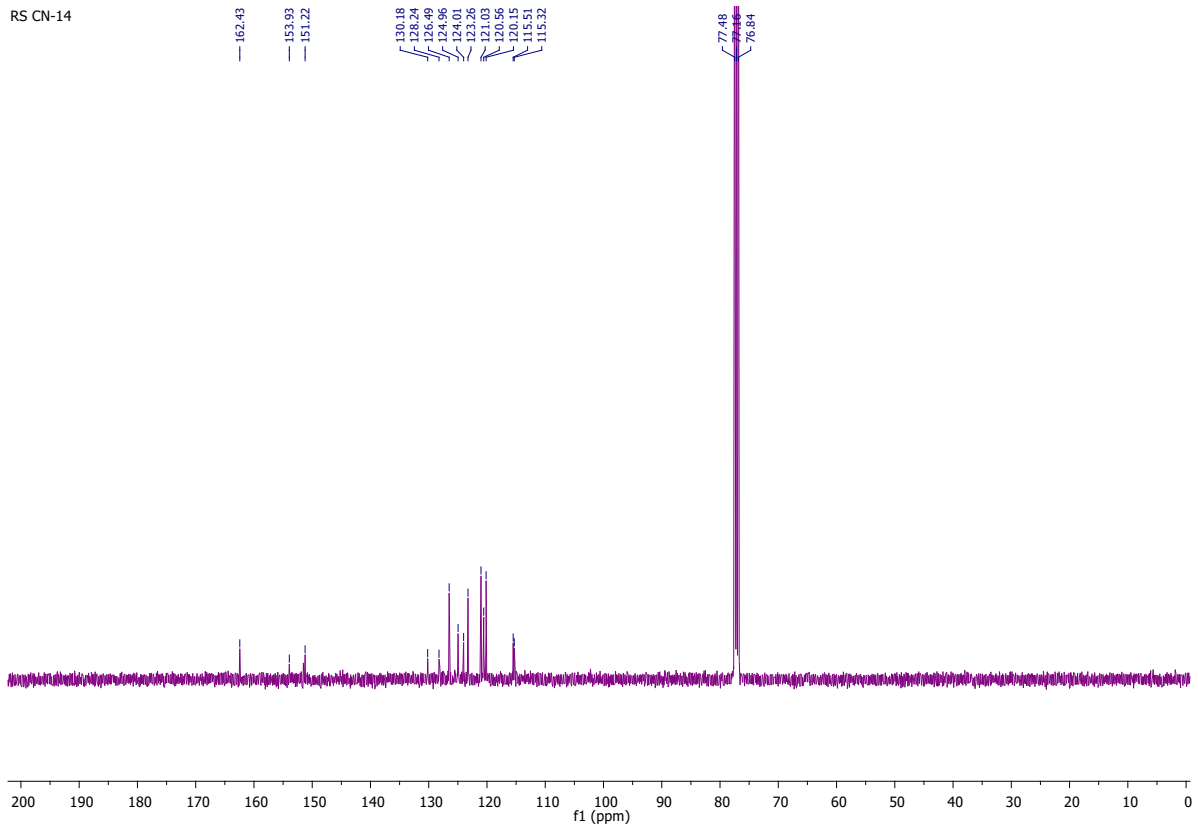
3i. *N*-(2-Fluorophenyl)benzo[*d*]thiazol-2-amine



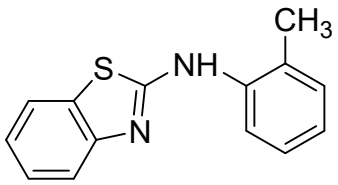
^{1}H NMR of 3i:



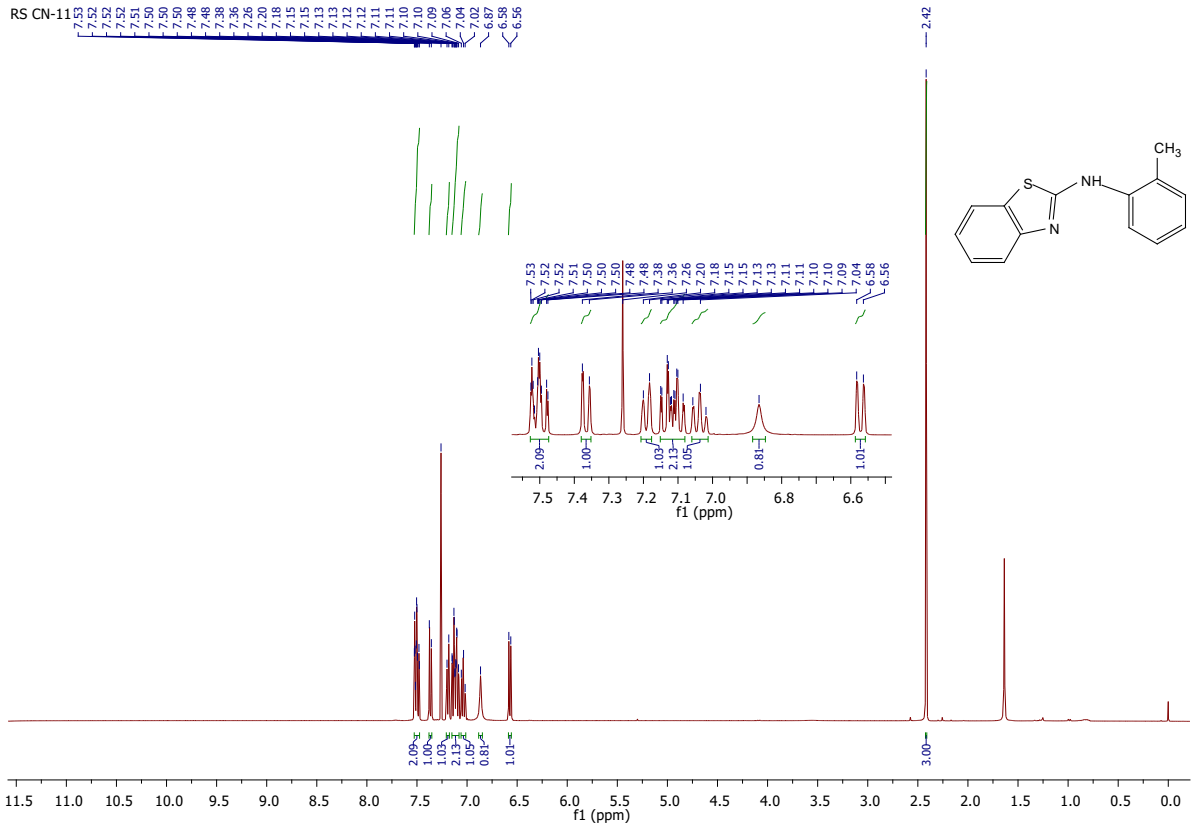
^{13}C NMR of 3i:



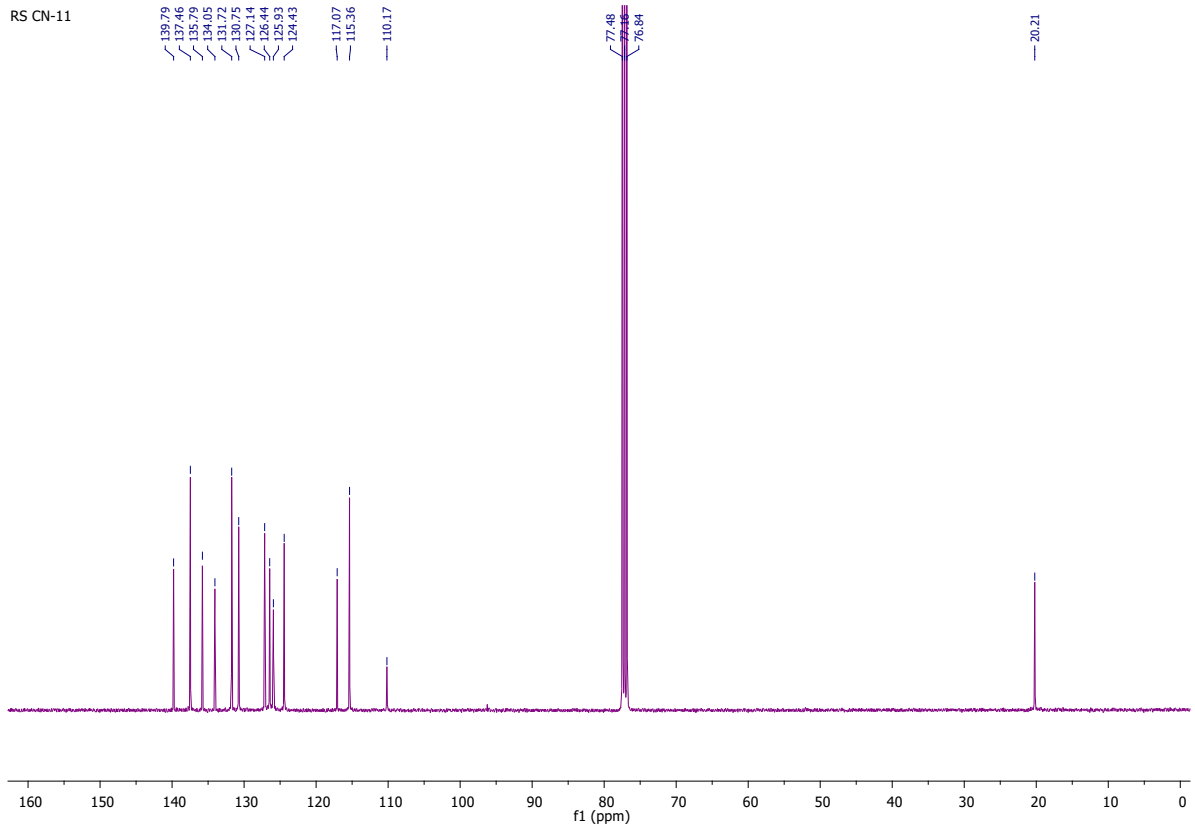
3j. *N*-(*o*-Tolyl)benzo[*d*]thiazol-2-amine



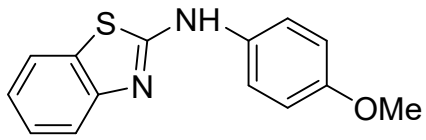
^{1}H NMR of 3j:



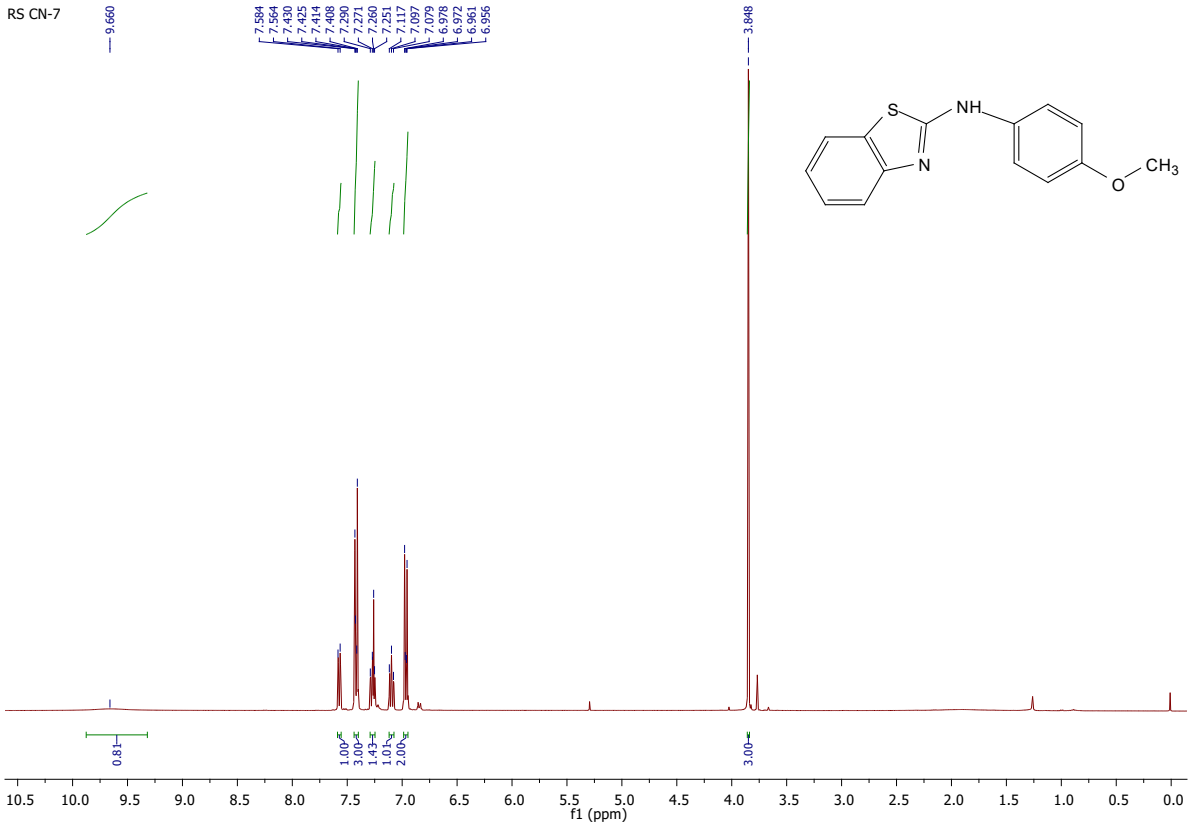
^{13}C NMR of 3j:



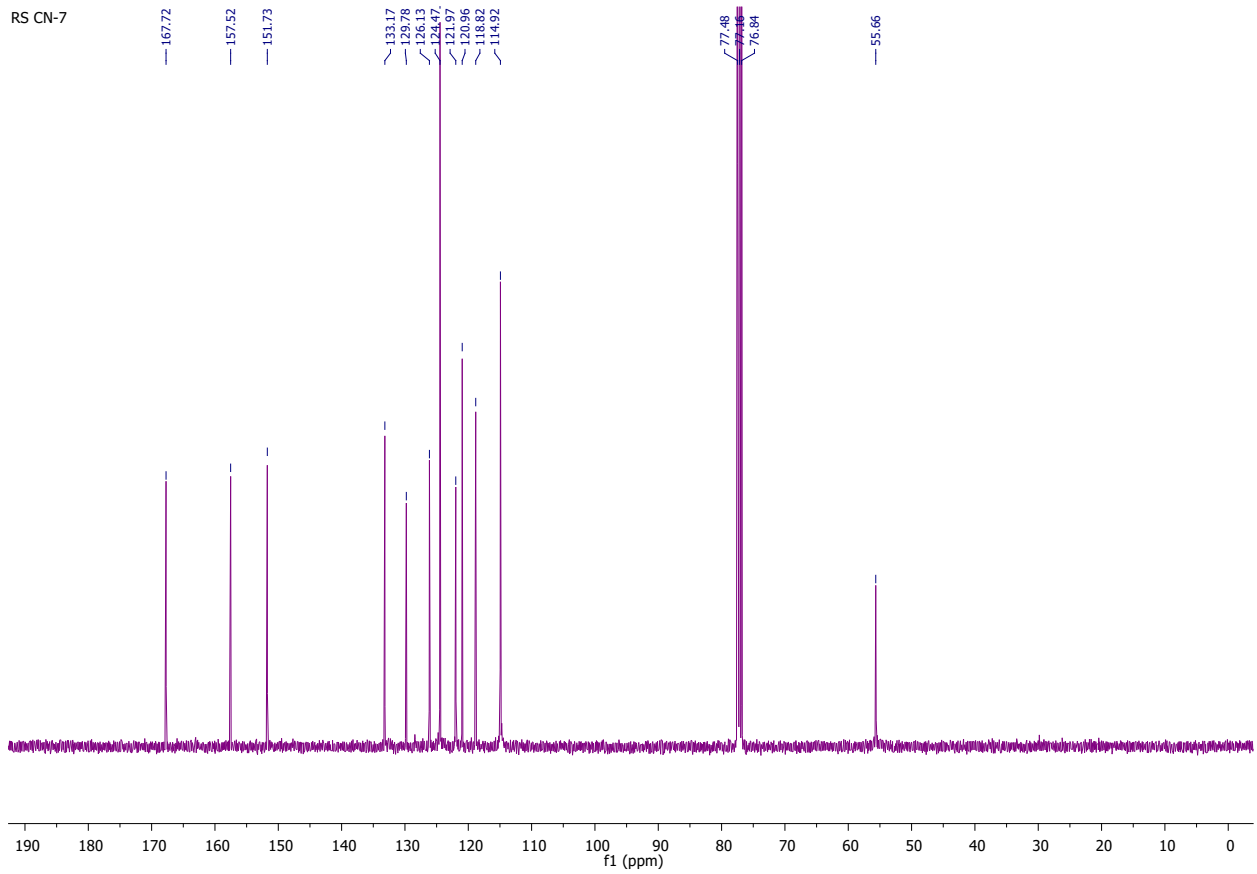
3k. *N*-(4-Methoxyphenyl)benzo[*d*]thiazol-2-amine



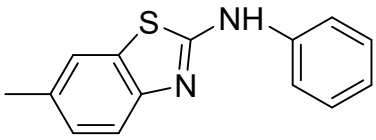
^{1}H NMR of 3k:



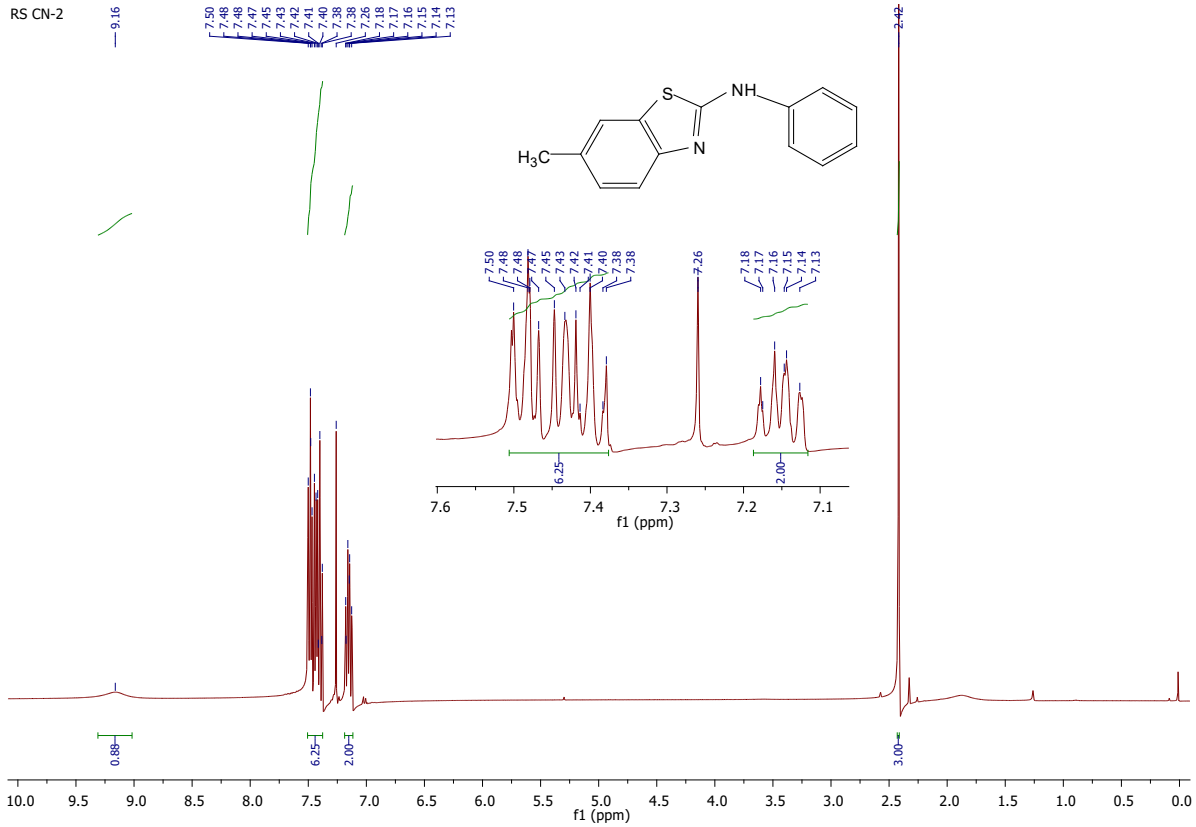
^{13}C NMR of 3k:



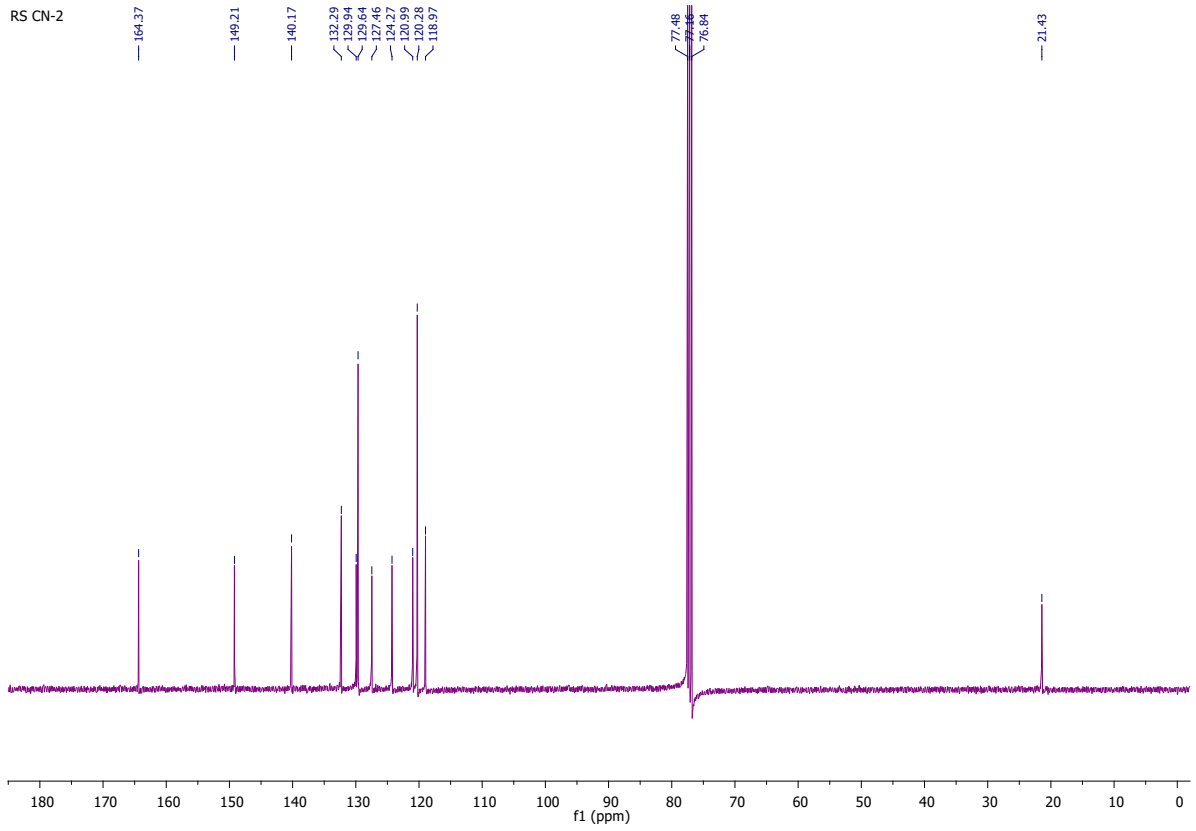
6a. 6-Methyl-*N*-phenylbenzo[*d*]thiazol-2-amine



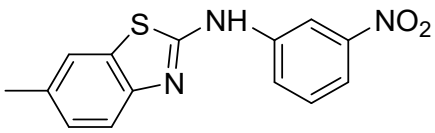
^{1}H NMR of 6a:


RS CN-2
9.16
7.50
7.48
7.48
7.47
7.45
7.43
7.42
7.41
7.40
7.38
7.38
7.26
7.18
7.17
7.16
7.15
7.14
7.13
2.42
S
NH
N
H_3C
6.25
2.00
0.88
6.25
2.00
3.00
f1 (ppm)

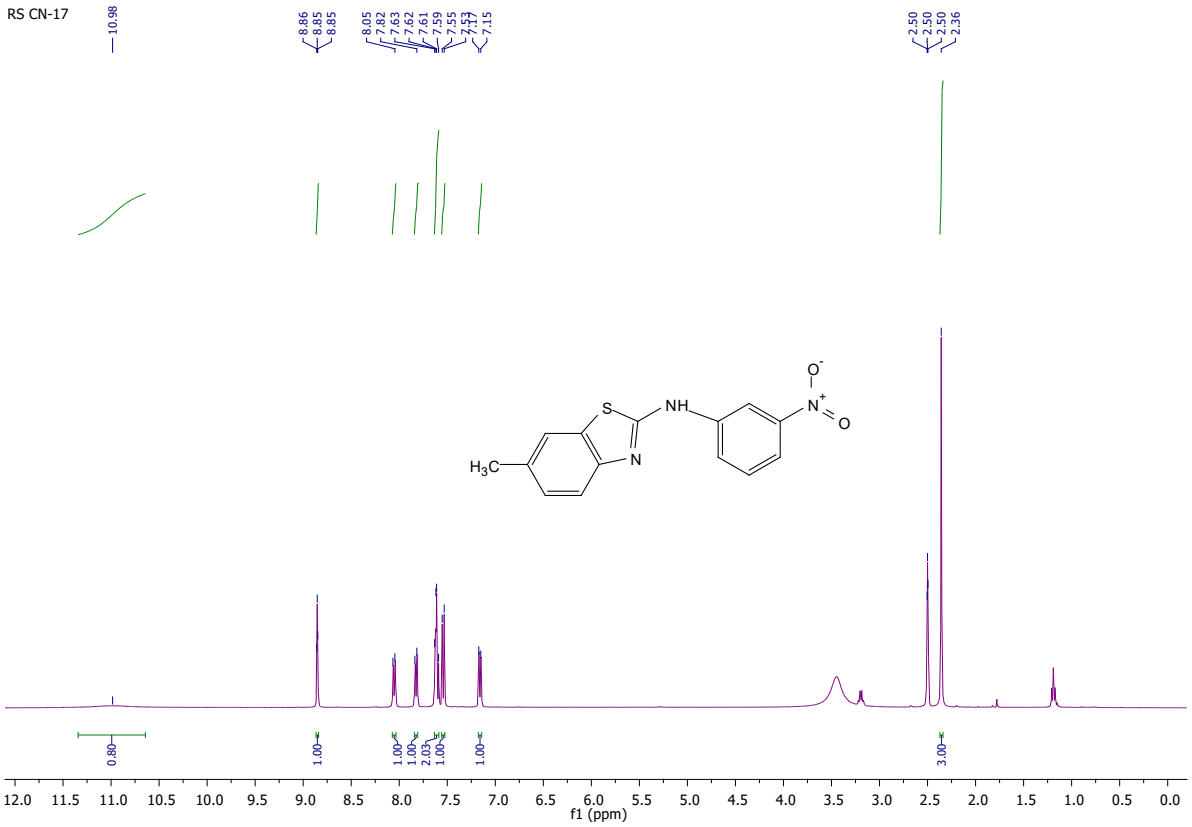
^{13}C NMR of 6a:


RS CN-2
164.37
149.21
140.17
132.29
129.94
129.64
127.46
124.27
120.99
120.28
118.97
77.48
77.16
76.84
21.43
f1 (ppm)

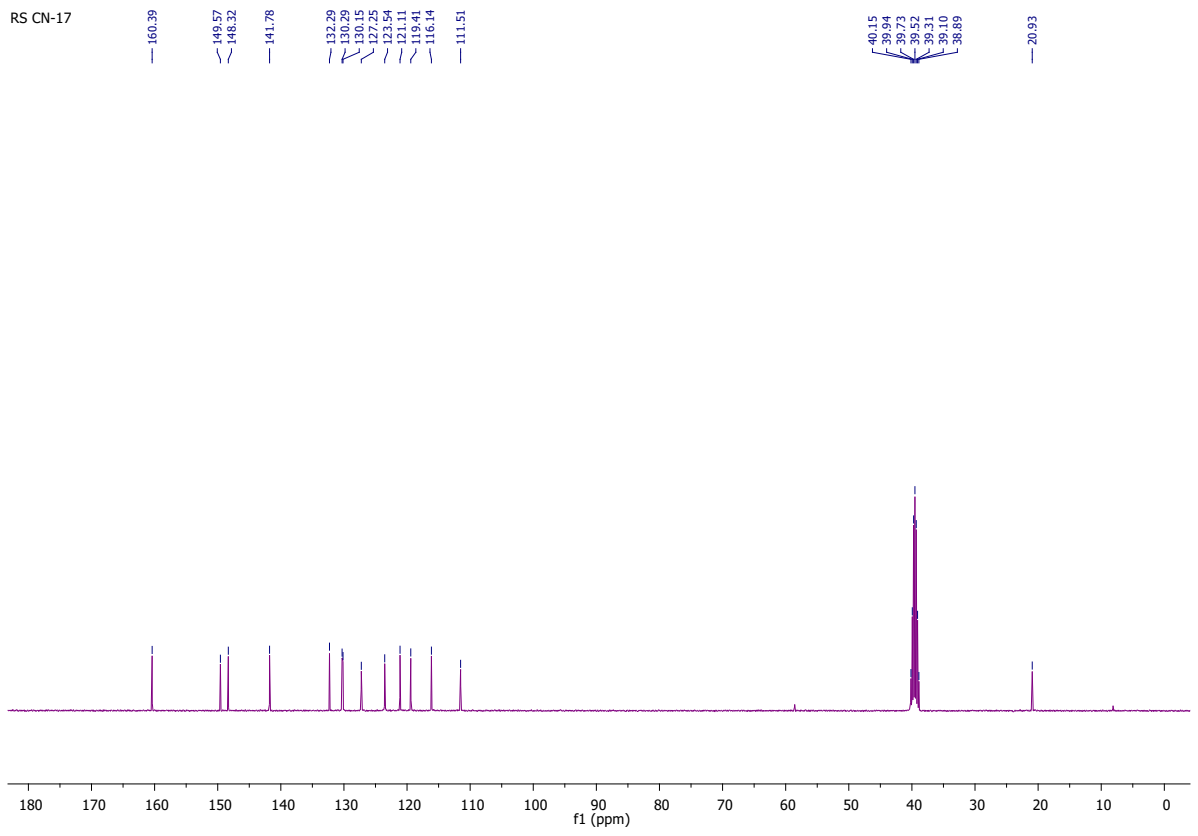
6b. 6-Methyl-*N*-(3-nitrophenyl)benzo[*d*]thiazol-2-amine



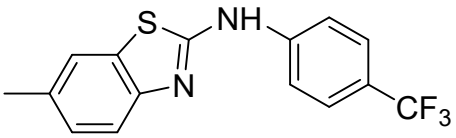
^{1}H NMR of 6b:



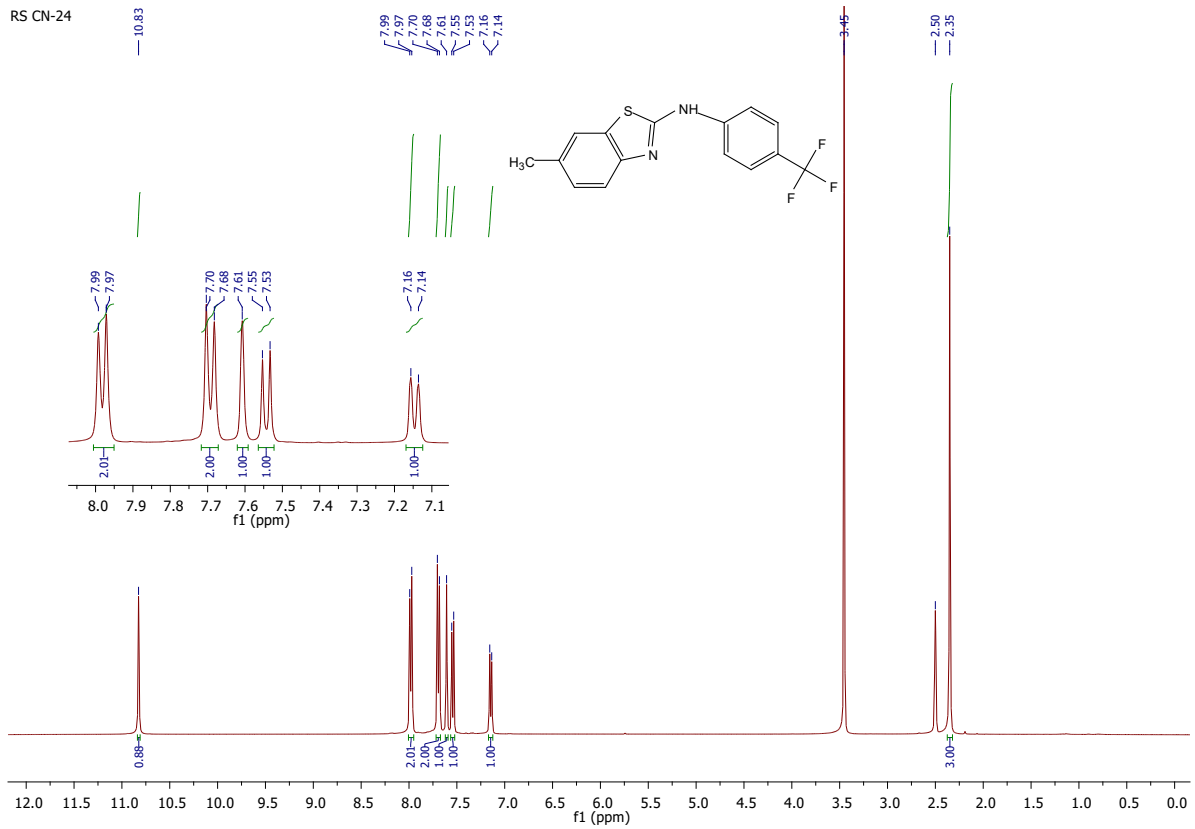
^{13}C NMR of 6b:



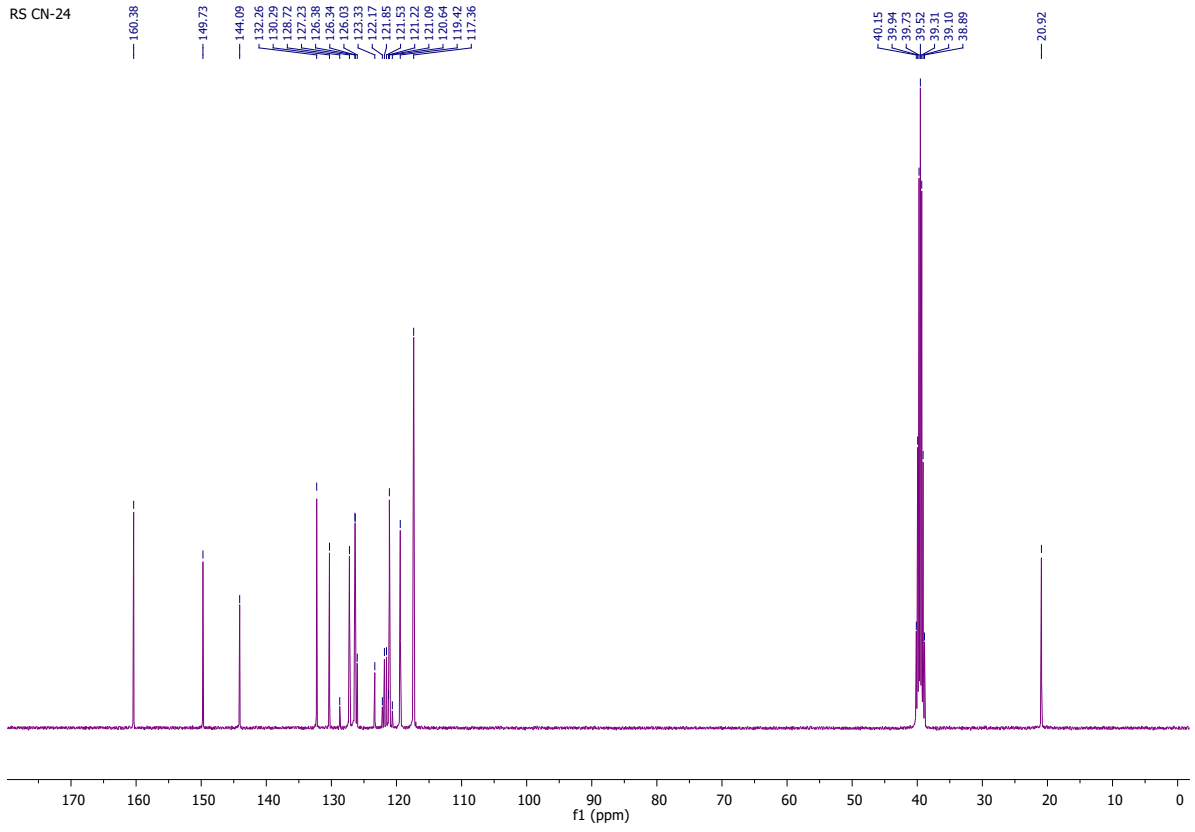
6c. 6-Methyl-*N*-(4-(trifluoromethyl)phenyl)benzo[*d*]thiazol-2-amine



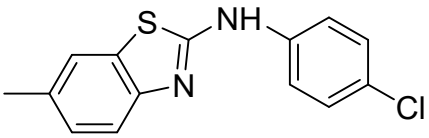
^{1}H NMR of 6c:


RS CN-24
10.83
7.99
7.97
7.70
7.68
7.61
7.55
7.53
7.16
7.14
3.45
2.50
2.35
S
NH
N
H3C
F
F
F
f1 (ppm)

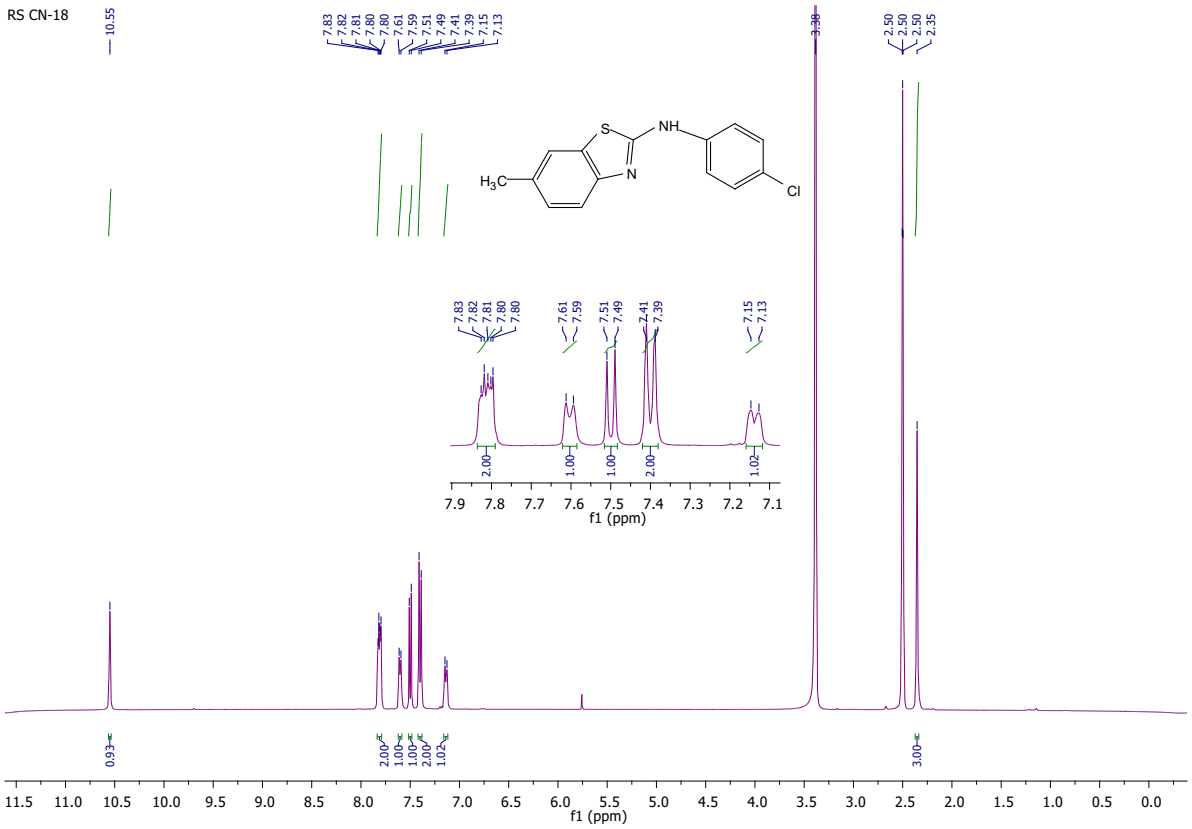
^{13}C NMR of 6c:


RS CN-24
160.38
149.73
144.09
132.26
130.29
128.72
127.23
126.38
126.34
126.03
123.33
122.17
121.85
121.53
121.22
121.09
120.64
119.42
117.36
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.92
f1 (ppm)

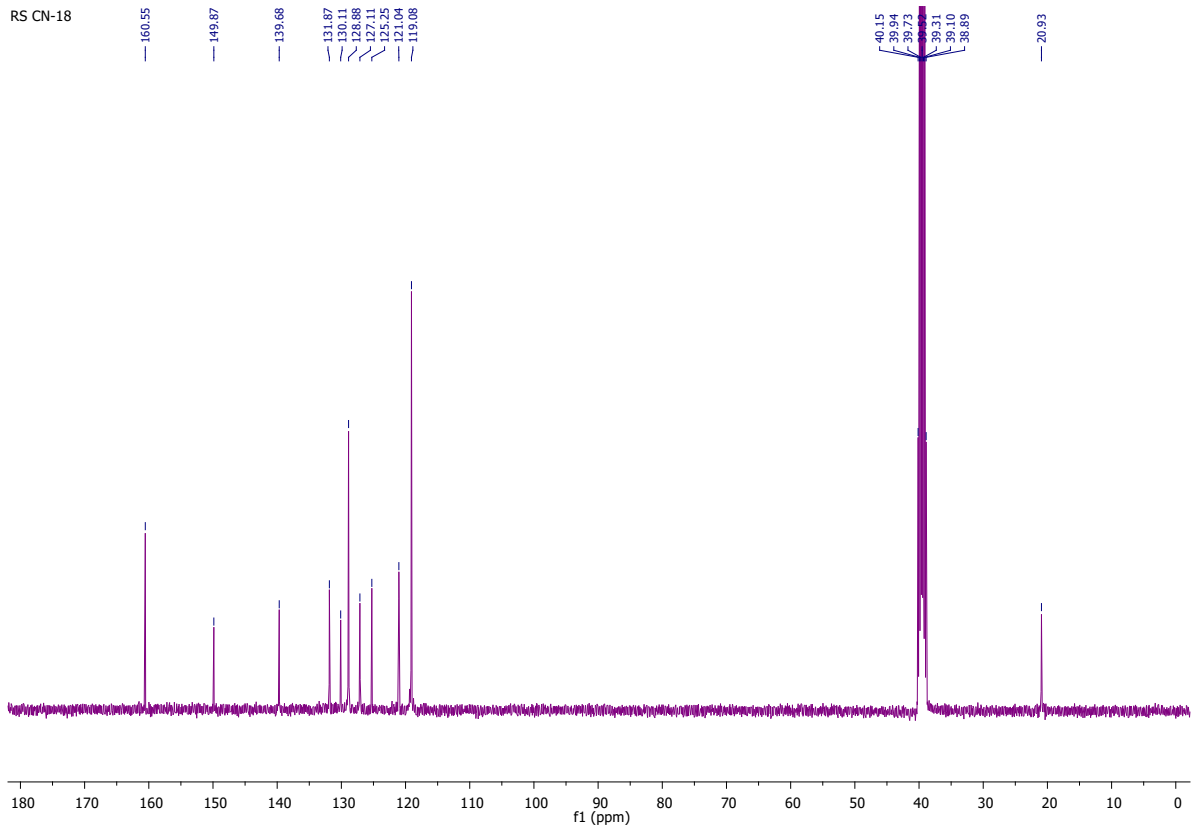
6d. *N*-(4-Chlorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



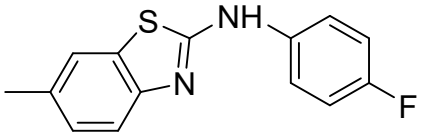
^{1}H NMR of 6d:



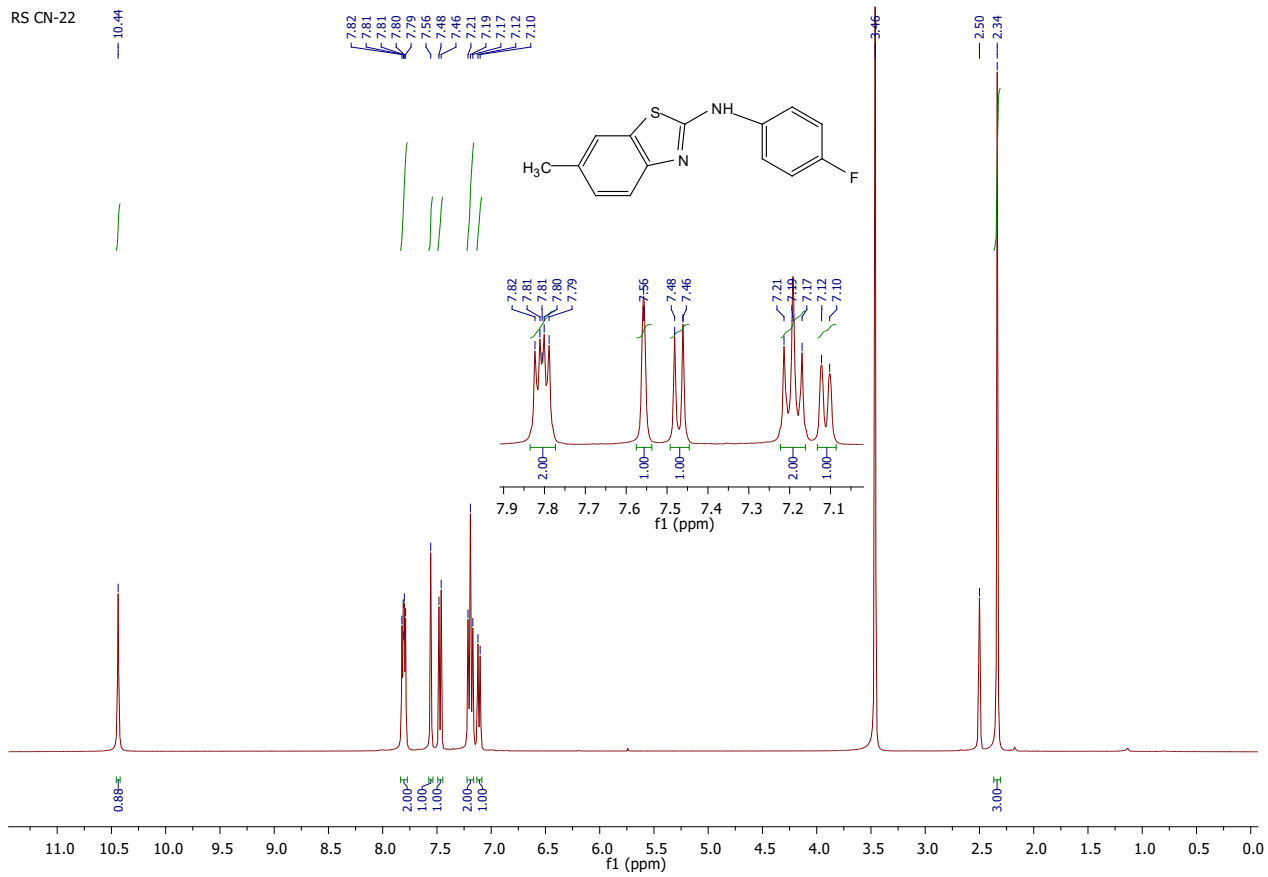
^{13}C NMR of 6d:



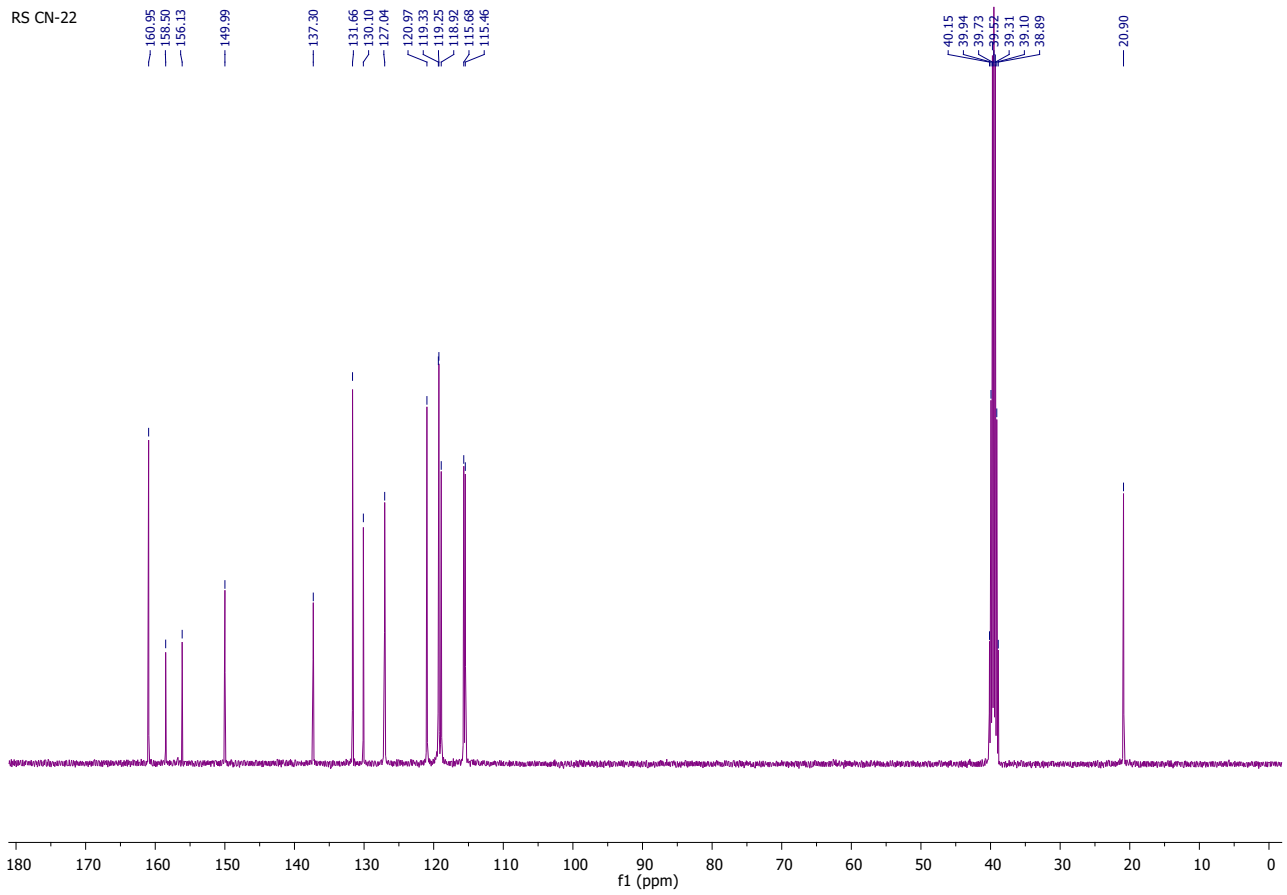
6e. *N*-(4-Fluorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



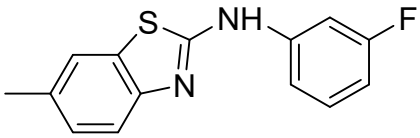
^{1}H NMR of 6e:


RS CN-22
10.44
7.82
7.81
7.81
7.80
7.79
7.56
7.48
7.46
7.21
7.19
7.17
7.12
7.10
3.46
2.50
2.34
S
NH
N
H3C
F
0.88
2.00
1.00
1.00
2.00
1.00
3.00
f1 (ppm)

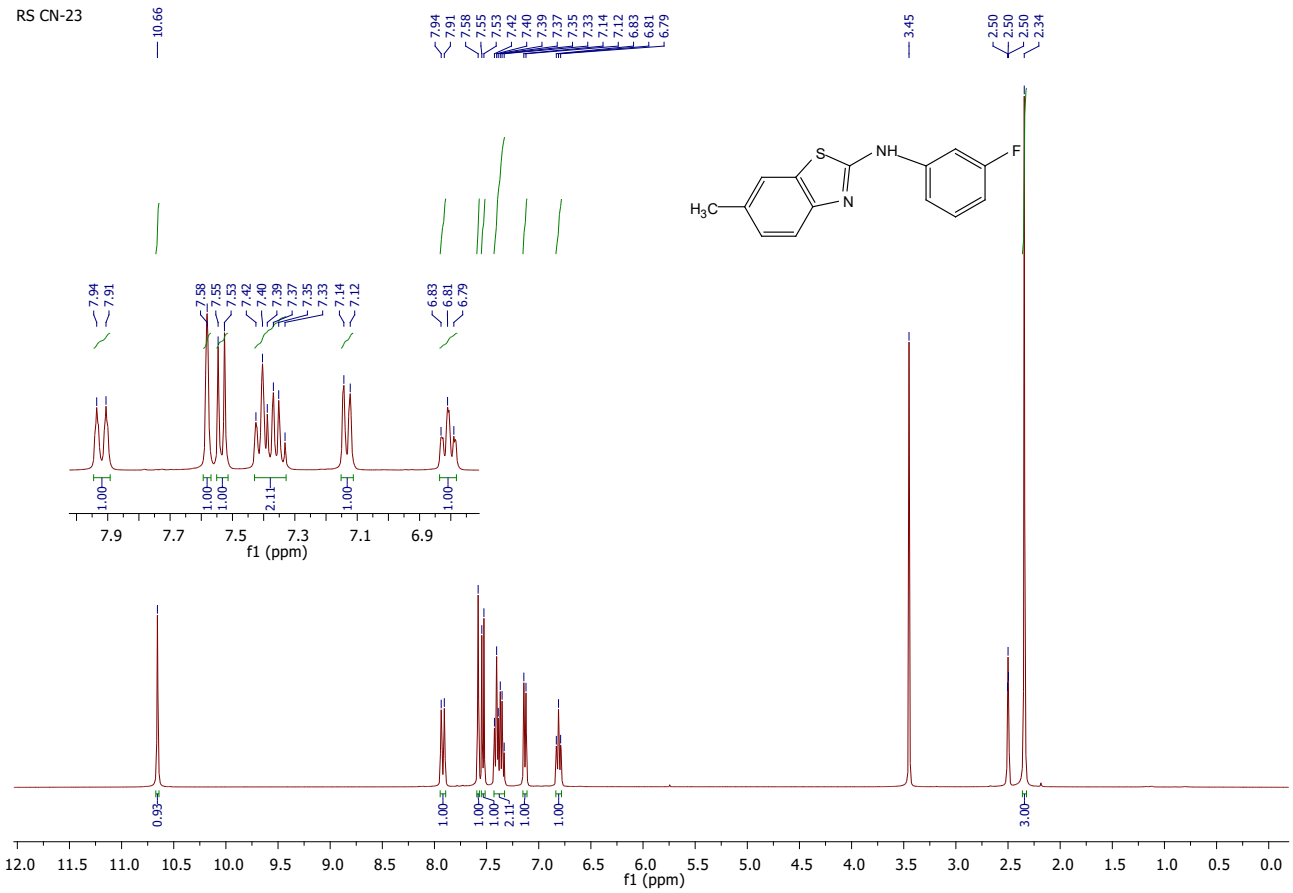
^{13}C NMR of 6e:



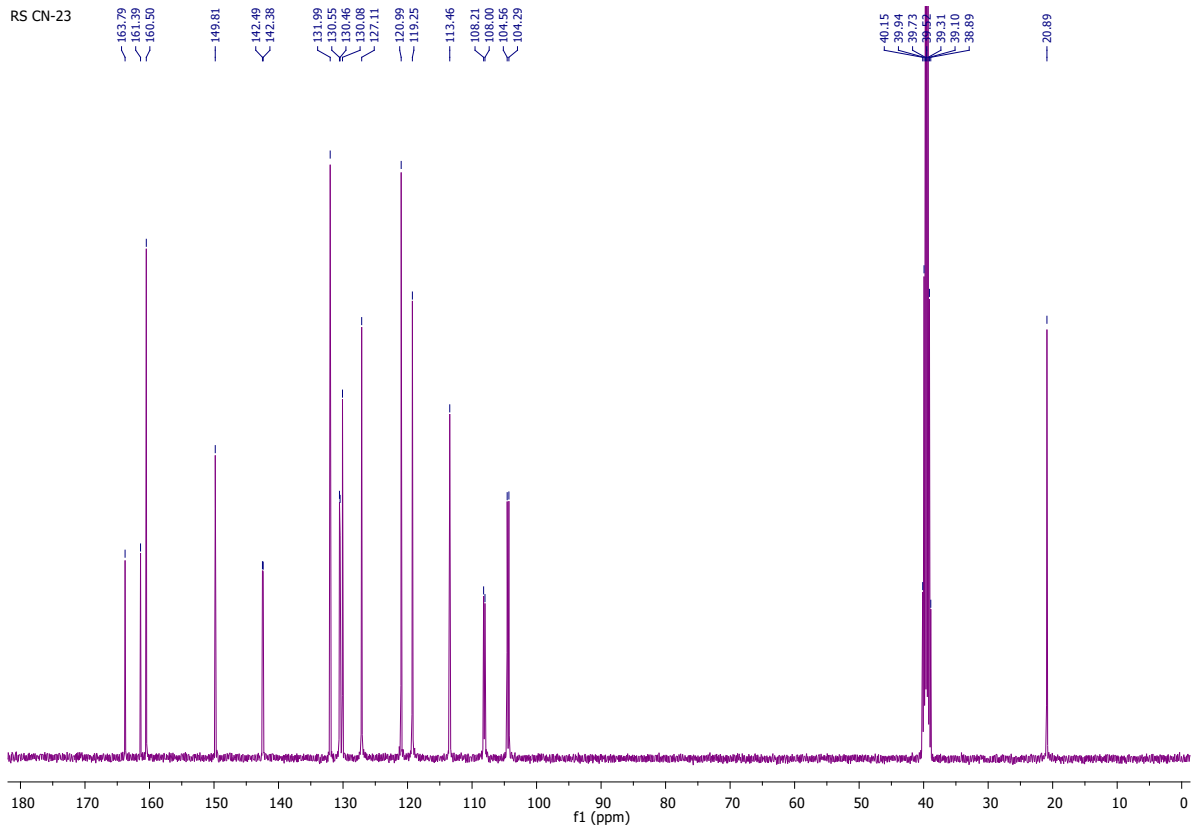
6f. *N*-(3-Fluorophenyl)-6-methylbenzo[*d*]thiazol-2-amine



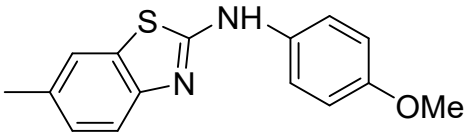
^{1}H NMR of 6f:


RS CN-23
10.66
7.94
7.91
7.58
7.55
7.53
7.42
7.40
7.39
7.37
7.35
7.33
7.14
7.12
6.83
6.81
6.79
3.45
2.50
2.50
2.50
2.34
S
NH
F
N
H3C
f1 (ppm)
f1 (ppm)

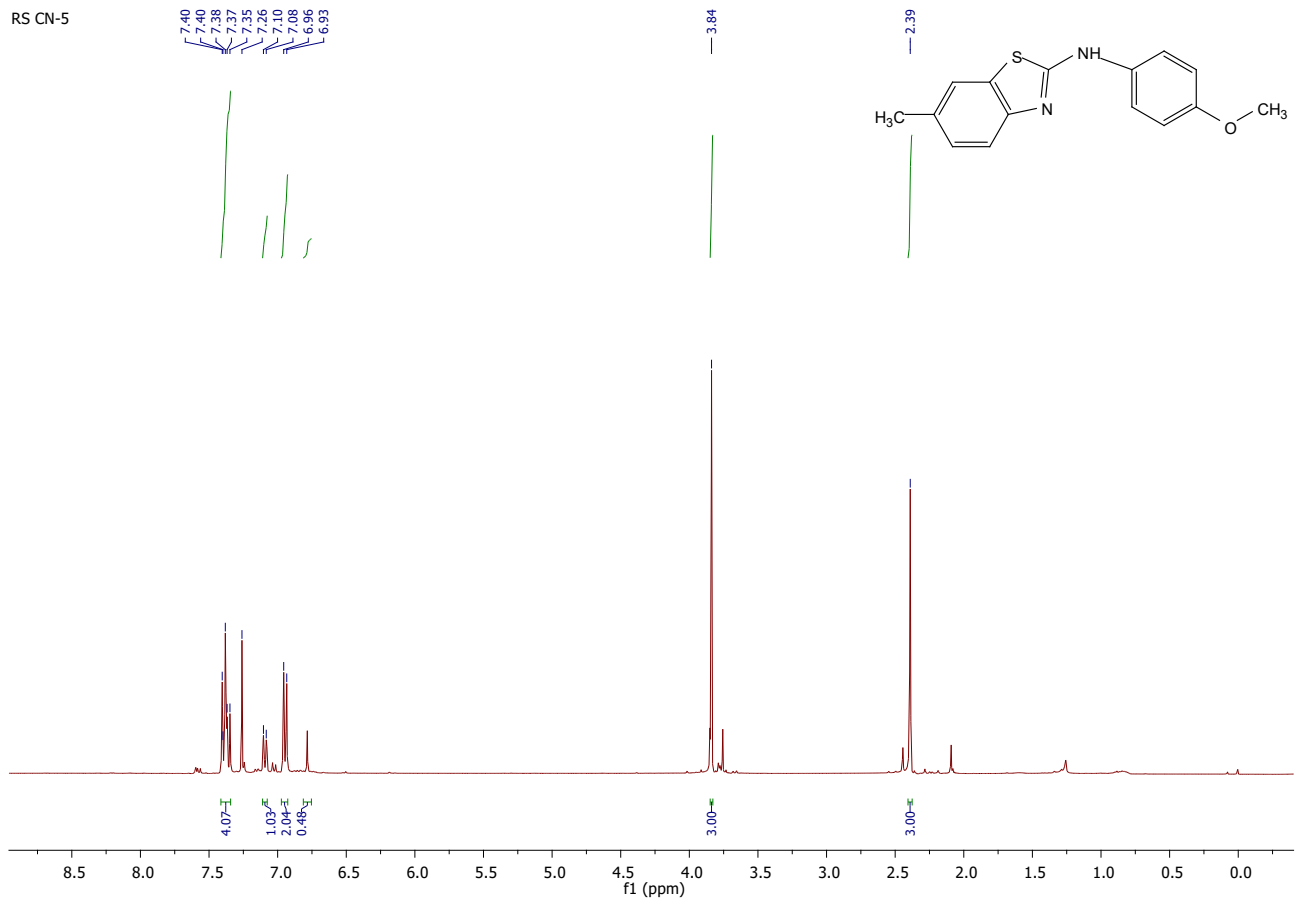
^{13}C NMR of 6f:



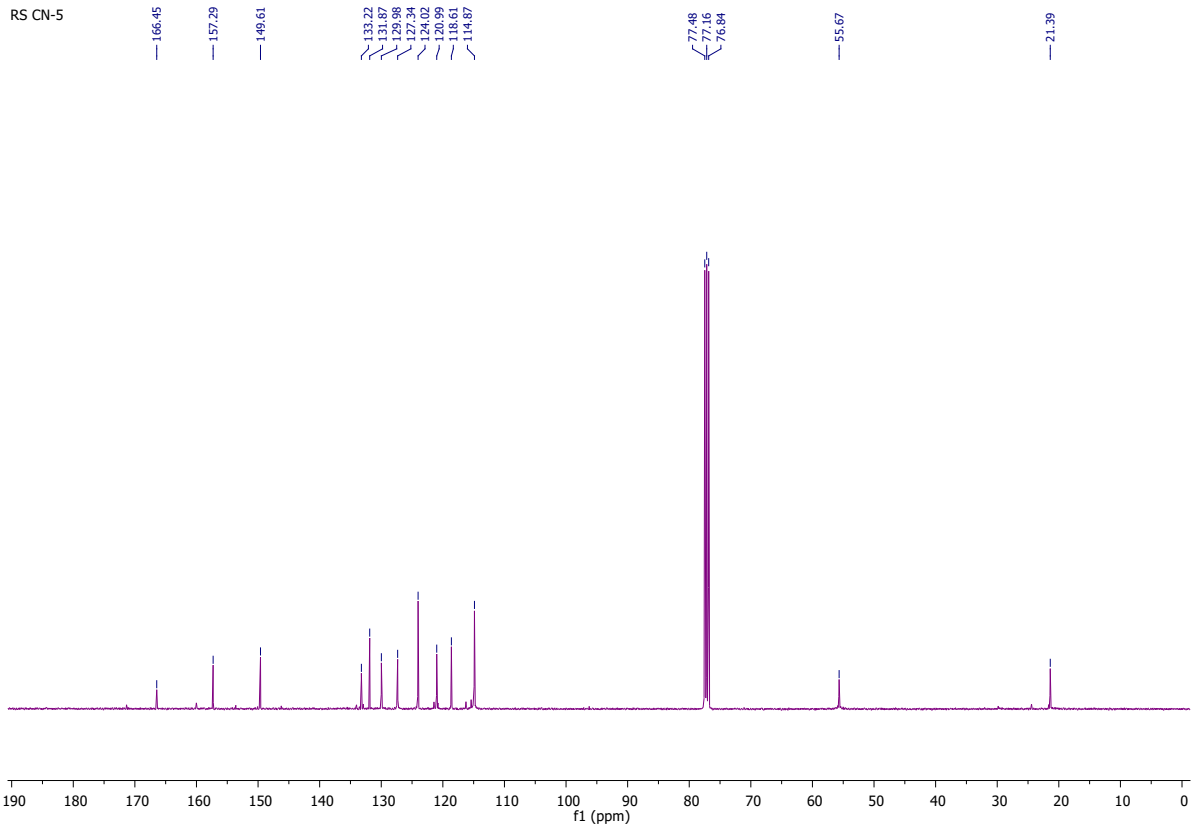
6g. *N*-(4-Methoxyphenyl)-6-methylbenzo[*d*]thiazol-2-amine



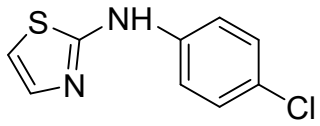
^{1}H NMR of 6g:


RS CN-5
7.40
7.40
7.38
7.37
7.35
7.26
7.10
7.08
6.96
6.93
3.84
2.39
S
NH
N
H3C
O
CH3
4.07
1.03
2.04
0.48
3.00
3.00
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
0.0
f1 (ppm)

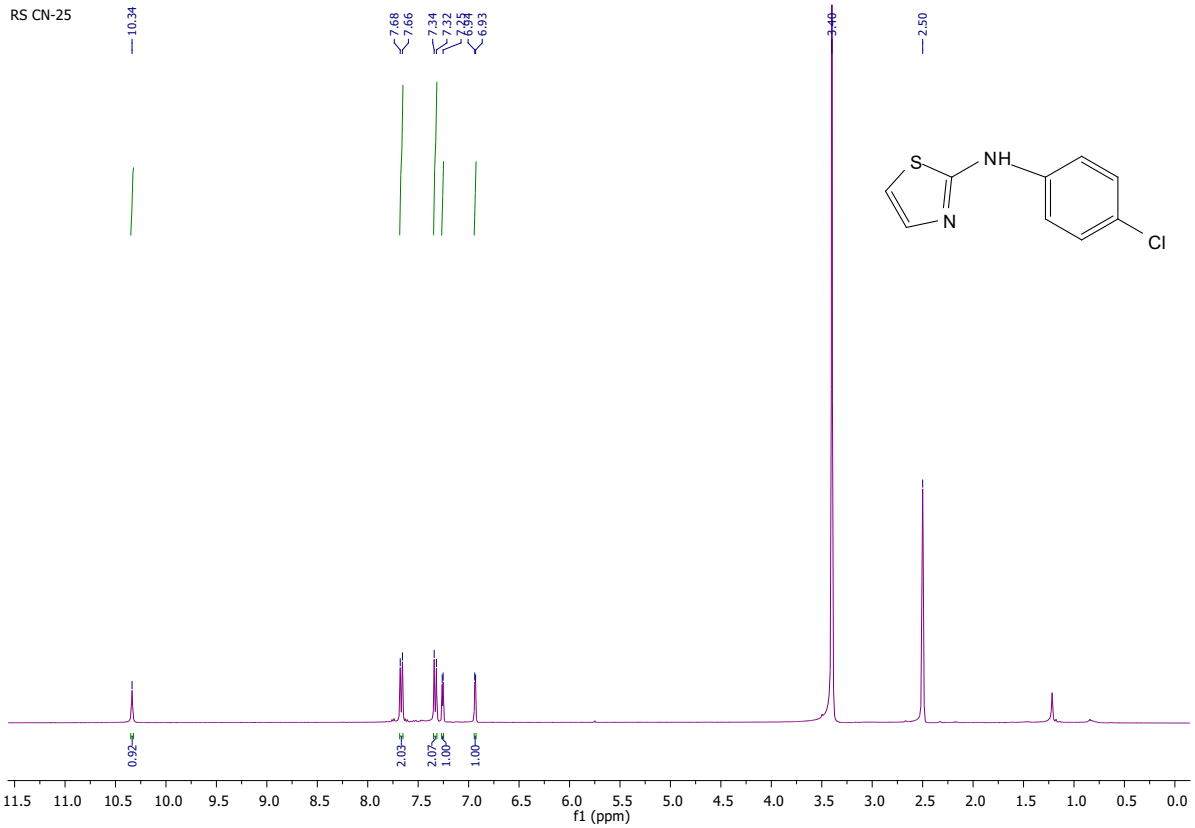
^{13}C NMR of 6g:


RS CN-5
166.45
157.29
149.61
133.22
131.87
129.98
127.34
124.02
120.99
118.61
114.87
77.48
77.16
76.84
55.67
21.39
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

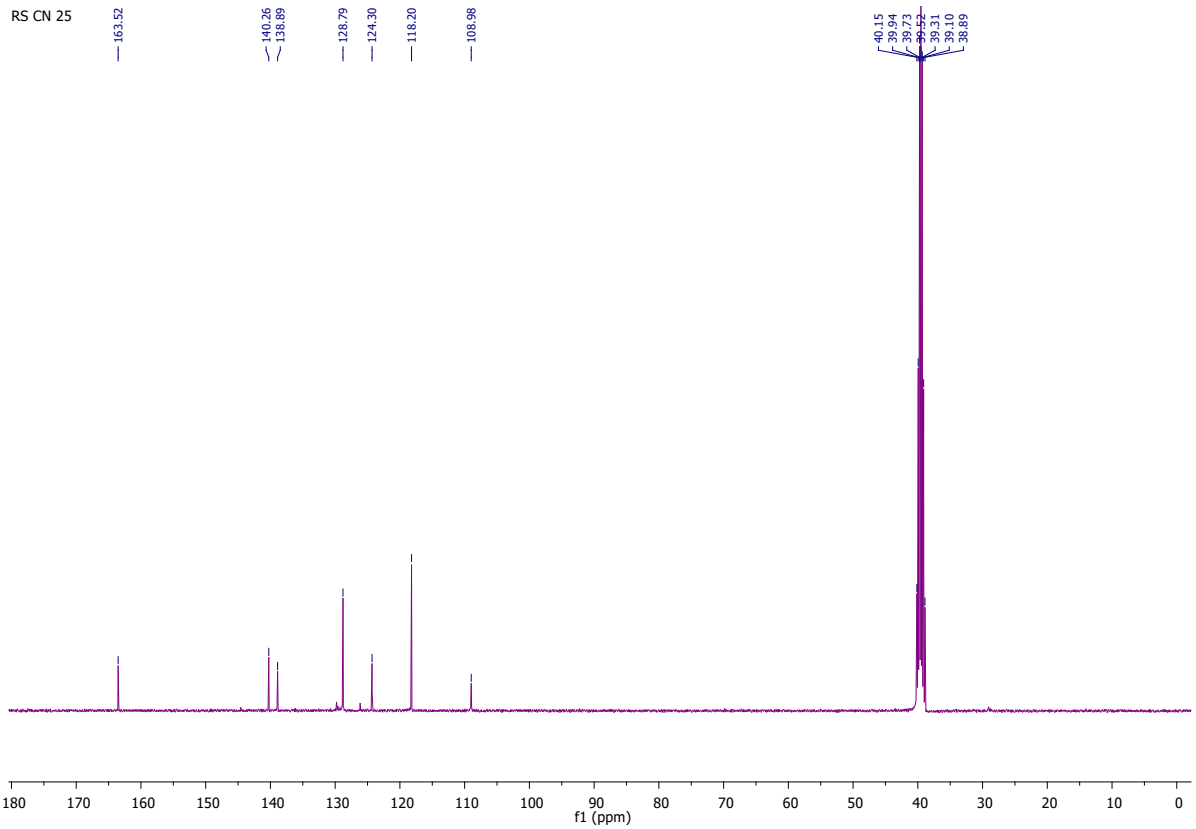
8a. *N*-(4-Chlorophenyl)thiazol-2-amine



^{1}H NMR of 8a:



^{13}C NMR of 8a:


RS CN 25
163.52
140.26
138.89
128.79
124.30
118.20
108.98
40.15
39.94
39.73
39.52
39.31
39.10
38.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)