Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

for

A straightforward metal-free synthesis of 2-substituted thiazolines in air

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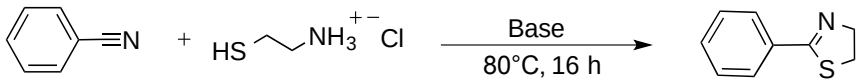
1 General considerations

All reactions were carried out in air. All reagents were purchased and used as received. ^{1}H, ^{13}C-{^{1}H} and ^{19}F-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded at 298K on a Brucker Avance 400 Ultrashield or on a Brucker Avance 500 Ultrashield spectrometer using the residual solvent peak for ^{13}C-{^{1}H} NMR ($CDCl_3$: δ_C = 77.16 ppm) and TMS as reference for ^{1}H NMR. Gas chromatography (GC) analyses were performed on an Agilent 7890A apparatus equipped with a flame ionization detector and a (5%-phenyl)-methylpolysiloxane column (30 m, 320 μm, film: 0.25 μm). IR measurements were performed on a ReactIR A15 system (Mettler Toledo Autochem) with a DiComp AgX FiberConduit probe (9.5 mm). Mass spectroscopy was performed by the EPSRC National Mass Spectrometry Service Centre at Swansea University, UK.

2 Optimisation of reaction conditions

Table S1. Optimisation of reaction conditions

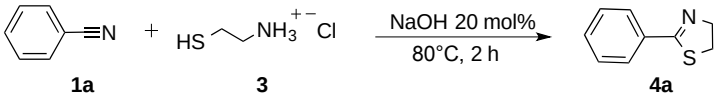


1a **3** **4a**

Entry	**3** (mmol)	Base (Loading)	Time (h)	Conversion (%)
1	1	NaOH (30 mol%)	16	> 99
2	1	NaOH (20 mol%)	16	> 99
3	1	NaOH (10 mol%)	16	> 99
4	1	CsOH (10 mol%)	16	> 99
5	1	KOH (10 mol%)	16	> 99
6	1	NaOH (5 mol%)	16	91
7	0.75	NaOH (20 mol%)	16	> 99
8	0.75	NaOH (20 mol%)	**2**	**> 99** (**98**)[c]
9	0.75	NaOH (20 mol%)	1	94

[a] Reaction conditions: **1** (0.5 mmol), **3** (0.75-1 mmol), base-catalyst, 80 ºC, 1-16h. [b] Conversion determined by GC, based on benzonitrile, average of 2 reactions. [c] Isolated yield.

Table S2. Comparison of sources of NaOH[a]



1a **3** **4a**

Entry	Base	Conversion[b] (%)
1	NaOH batch1	> 99
2	NaOH batch2	> 99
3	NaOH batch3	> 99
4	NaOH semiconductor grade	> 99

[a] Reaction conditions: 1 (0.5 mmol), 3 (0.75 mmol), NaOH (20 mol%), 80 ºC, 2h.
[b] Conversion determined by GC, based on benzonitrile, average of 2 reactions.

3 In Situ FTIR Spectroscopy

Figure S1 IR spectra of benzonitrile, **1a**

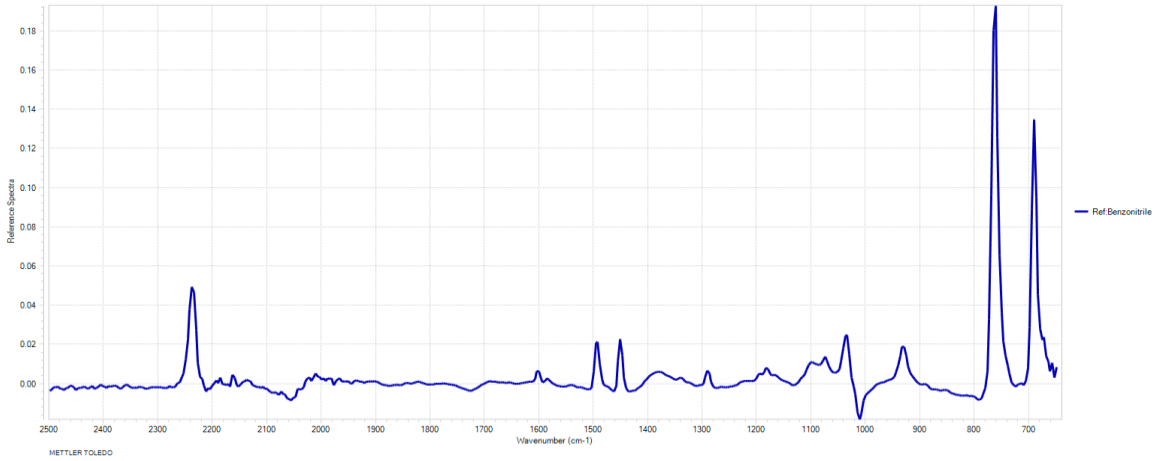
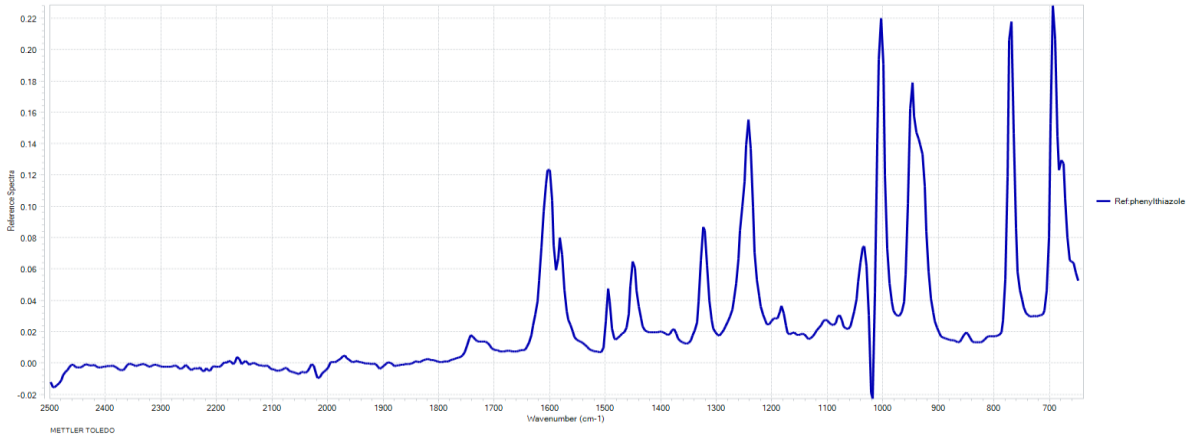
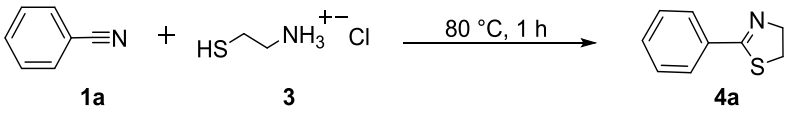


Figure S2 IR spectra of 2-Phenyl-4,5-dihydrothiazole, **4a**



Reaction between benzonitrile and cysteamine hydrochloride without base



1a **3** **4a**

PROCEDURE: In air, a 5 mL round bottom flask was charged with benzonitrile (19.4 mmol, 2.0 g) and cysteamine hydrochloride (29.1 mmol, 3.3 g). The mixture was heated at 80°C until cysteamine hydrochloride was completely melted. The probe was submerged in the reaction mixture and the IR measurements were started. The reaction was stirred (350 rpm) at 80°C for 1h under solvent-free conditions.

Figure S3 3D plot of *in situ* IR measurements of the reaction between **1a** and **3** without base.

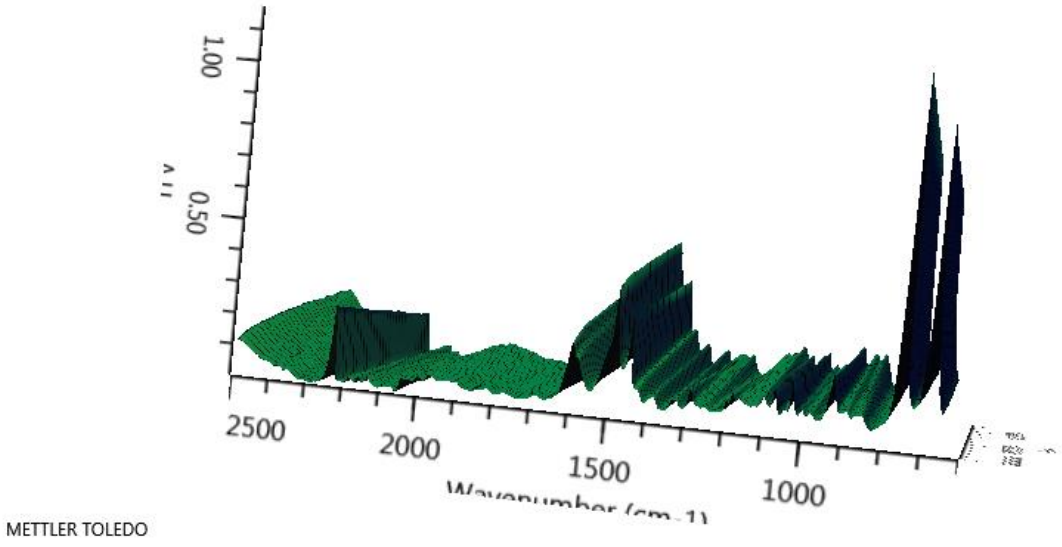
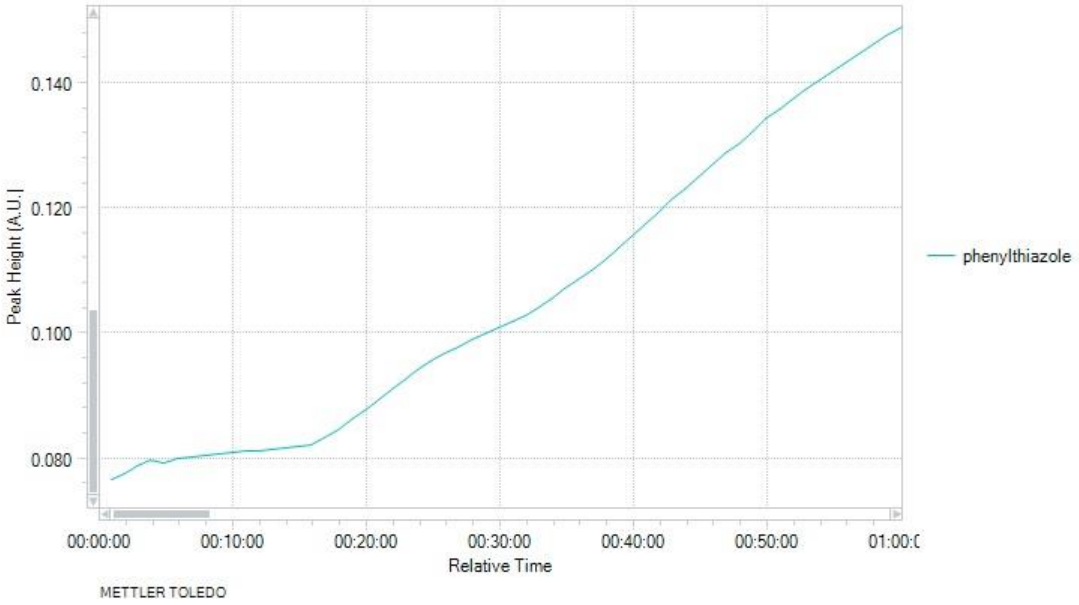
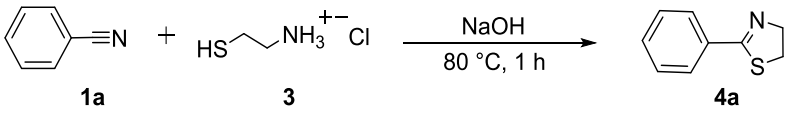


Figure S4 IR plot of the reaction between **1a** and **3** without base.



Reaction between benzonitrile and cysteamine hydrochloride in the presence of NaOH



1a **3** **4a**

PROCEDURE: In air, a 5 mL round bottom flask was charged with benzonitrile (19.4 mmol, 2.0 g) and cysteamine hydrochloride (29.1 mmol, 3.3 g). The mixture was heated at 80 °C until cysteamine hydrochloride was completely melted. The probe was submerged inside of the reaction mixture and the IR measurements were started. After 5 minutes 20 mol % of NaOH (2 mmol, 80 mg) were added. The reaction was stirred (350 rpm) at 80 °C for 1h under solvent-free conditions.

Figure S5 3D plot of *in situ* IR measurements of the reaction between **1a** and **3** in the presence of NaOH.

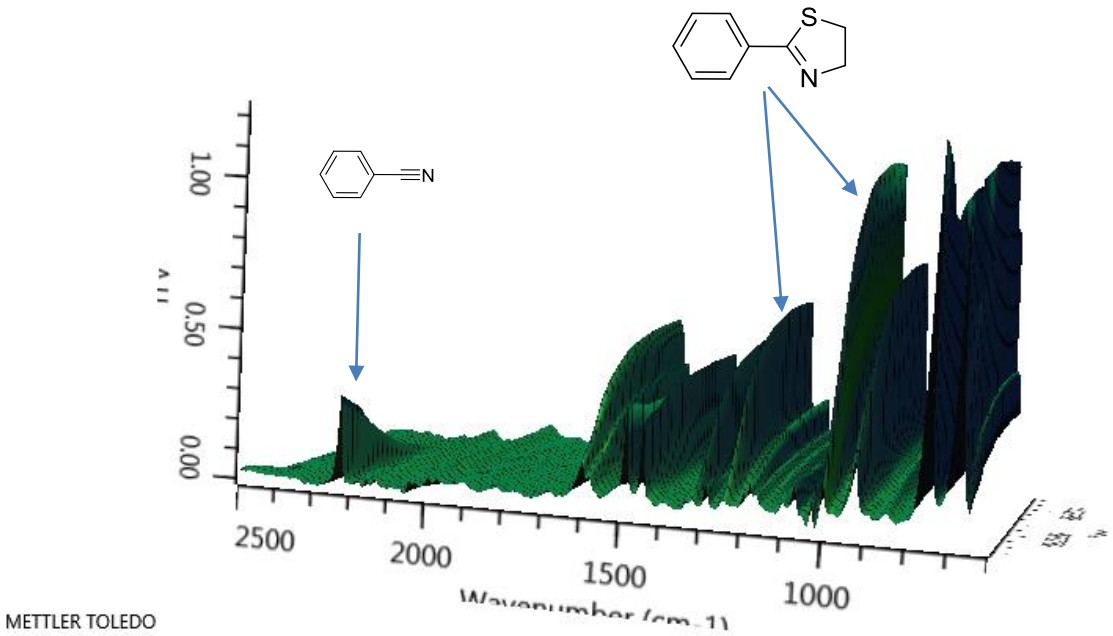
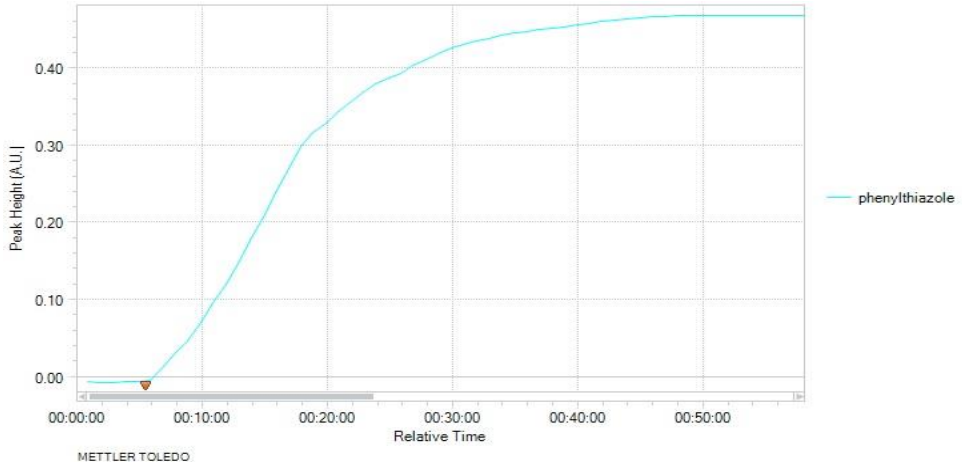


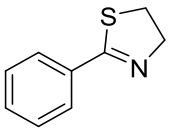
Figure S6 IR plot of the reaction between **1a** and **3** in the presence of NaOH.



4 Synthesis and characterisation of thiazolines

In air, a vial was charged with the nitrile (1 mmol), cysteamine hydrochloride (1.5 mmol) and NaOH (0.2 mmol). The reaction was stirred at 80 °C for the appropriate time under solvent-free conditions. The crude product was dissolved in ethyl acetate (2 mL) and water (10 mL) was added. The aqueous layer was then extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and dried under vacuum to give the desired compound. The conversion was determined by GC analysis or by ^{1}H NMR.

2-Phenyl-4,5-dihydrothiazole, **4a**[1]

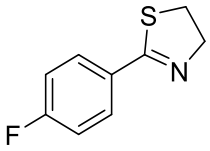


The general procedure yielded to the title compound as a yellow oil (153 mg, 98%).

^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.85-7.82 (m, 2H, $C_{Ar}H$), 7.47-7.38 (m, 3H, $C_{Ar}H$) 4.45 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.40 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K): δ (ppm) = 168.6 (s, C^{IV}), 133.5 (s, C^{IV}), 131.3 (s, C_{Ar}H), 128.7 (s, C_{Ar}H), 128.6 (s, C_{Ar}H), 65.5 (s, CH_2), 33.9 (s, CH_2).

2-(4-Fluorophenyl)-4,5-dihydrothiazole, **4b**[2]



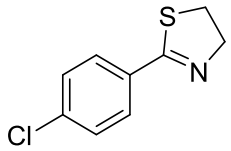
The general procedure yielded to the title compound as a colourless oil (168 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.84-7.79 (m, 2H, $C_{Ar}H$), 7.10-7.04 (m, 2H, $C_{Ar}H$), 4.41 (t, $^3J_{HH}$ = 8.3 Hz, 2H, CH_2), 3.38 (t, $^3J_{HH}$ = 8.3 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.1 (s, C^{IV}), 164.5 (d, $^1J_{CF}$= 251.5 Hz, C^{IV}), 130.5 (d, $^4J_{CF}$= 8.7 Hz, C_{Ar}H), 129.7 (d, $^5J_{CF}$= 3.6 Hz, C^{IV}), 115.6 (d, $^3J_{CF}$= 22.2 Hz, C_{Ar}H), 65.3 (s, CH_2), 34.0 (s, CH_2).

^{19}F-{^{1}H} NMR (376 MHz, 298K): δ (ppm) = -108.73 (s, CF).

2-(4-Chlorophenyl)-4,5-dihydrothiazole, **4c**[1]



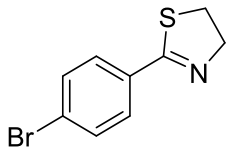
The general procedure yielded to the title compound as a colourless solid (179 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.78-7.75 (m, 2H, $C_{Ar}H$), 7.39-7.37 (m, 2H, $C_{Ar}H$), 4.47-4.43 (m, 2H, CH_2), 3.45-3.40 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.6 (s, C^{IV}), 137.5 (s, C^{IV}), 132.0 (s, C^{IV}), 129.9 (s, $C_{Ar}H$), 129.0 (s, $C_{Ar}H$), 65.6 (s, CH_2), 34.2 (s, CH_2).

Melting point: 53 °C

2-(4-Bromophenyl)-4,5-dihydrothiazole, **4d**[3]



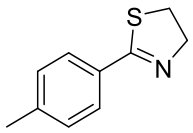
The general procedure yielded to the title compound as a colourless solid (228 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.71-7.69 (m, 2H, $C_{Ar}H$), 7.56-7.53 (m, 2H, $C_{Ar}H$), 4.44 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.45-3.41 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.7 (s, C^{IV}), 132.5 (s, C^{IV}), 132.0 (s, $C_{Ar}H$), 130.1 (s, $C_{Ar}H$), 126.0 (s, C^{IV}), 65.6 (s, CH_2), 34.3 (s, CH_2).

Melting point: 91 °C

2-*p*-Tolyl-4,5-dihydrothiazole, **4e**[1]



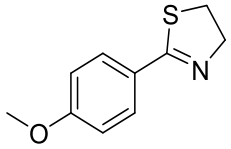
The general procedure yielded to the title compound as a colourless solid (158 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.74-7.71 (m, 2H, $C_{Ar}H$), 7.21-7.19 (m, 2H, $C_{Ar}H$), 4.43 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2), 3.38 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2), 2.37 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 168.6 (s, C^{IV}), 141.7 (s, C^{IV}), 130.9 (s, C^{IV}), 129.4 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 65.4 (s, CH_2), 33.9 (s, CH_2), 21.7 (s, CH_3).

Melting point: 42 °C

2-(4-Methoxyphenyl)-4,5-dihydrothiazole, **4f**[3]



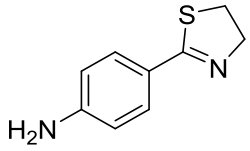
The general procedure yielded to the title compound as a yellow solid (188 mg, 97%).

^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.79-7.76 (m, 2H, $C_{Ar}H$), 6.90-6.88 (m, 2H, $C_{Ar}H$), 4.39 (t, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_2), 3.80 (s, 3H, OCH_3), 3.35 (t, $^{3}J_{HH}$ = 8.2 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K): δ (ppm) = 167.7 (s, C^{IV}), 162.0 (s, C^{IV}), 130.1 (s, $C_{Ar}H$), 126.2 (s, C^{IV}), 113.9 (s, $C_{Ar}H$), 65.2 (s, CH_2), 55.5 (s, OCH_3), 33.8 (s, CH_2).

Melting point: 53 °C

4-(4,5-Dihydrothiazol-2-yl)aniline, **4g**[4]

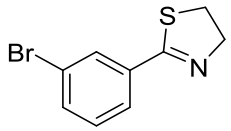


The general procedure yielded to the title compound as a pale yellow oil (166 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.65-7.63 (m, 2H, $C_{Ar}H$), 6.64-6.61 (m, 2H, $C_{Ar}H$), 4.40-4.36 (m, 2H, CH_2), 3.98 (s, 2H, NH_2), 3.36-3.32 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 168.2 (s, C^{IV}), 149.6 (s, C^{IV}), 130.3 (s, $C_{Ar}H$), 123.7 (s, C^{IV}), 114.5 (s, $C_{Ar}H$), 65.1 (s, CH_2), 33.7 (s, CH_2).

2-(3-Bromophenyl)-4,5-dihydrothiazole, **4h**[5]



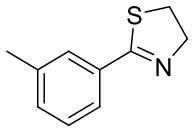
The general procedure yielded to the title compound as a pale brown solid (226 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.00 (d, $^{5}J_{HH}$ = 1.9 Hz, 1H, $C_{Ar}H$), 7.72 (dt, $^{3}J_{HH}$ = 7.8 Hz, $^{5}J_{HH}$ = 1.4 Hz, 1H, $C_{Ar}H$), 7.57 (dq, $^{3}J_{HH}$ = 7.8 Hz, $^{5}J_{HH}$ = 1.2 Hz, 1H, $C_{Ar}H$), 7.26 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, $C_{Ar}H$), 4.44 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.42 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.2 (s, C^{IV}), 135.4 (s, C^{IV}), 134.2 (s, $C_{Ar}H$), 131.4 (s, $C_{Ar}H$), 130.2 (s, $C_{Ar}H$), 127.3 (s, $C_{Ar}H$), 122.8(s, C^{IV}), 65.5 (s, CH_2), 34.2 (s, CH_2).

Melting point: 45 °C

2-*m*-Tolyl-4,5-dihydrothiazole, **4i**[6]

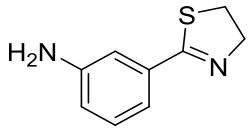


The general procedure yielded to the title compound as a colourless oil (150 mg, 85%).

^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.67 (s, 1H, $C_{Ar}H$), 7.62 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H, $C_{Ar}H$), 7.30-7.24 (m, 2H, $C_{Ar}H$), 4.43 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.38 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3).

^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K): δ (ppm) = 168.8 (s, C^{IV}), 138.5 (s, C^{IV}), 133.4 (s, C^{IV}), 132.1 (s, $C_{Ar}H$), 129.0 (s, $C_{Ar}H$), 128.6 (s, $C_{Ar}H$), 125.9 (s, $C_{Ar}H$), 65.4 (s, CH_2), 33.8 (s, CH_2), 21.5 (s, CH_3).

3-(4,5-Dihydrothiazol-2-yl)aniline, **4j**[1]



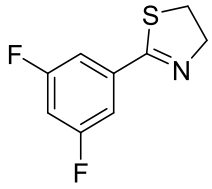
The general procedure yielded to the title compound as a brown solid (176 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.20-7.13 (m, 3H, $C_{Ar}H$), 6.74-6.71 (m, 1H, $C_{Ar}H$), 4.40 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.79 (s, 2H, NH_2), 3.35 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 168.8 (s, C^{IV}), 146.8 (s, C^{IV}), 134.3 (s, C^{IV}), 129.5 (s, $C_{Ar}H$), 118.9 (s, $C_{Ar}H$), 117.9 (s, $C_{Ar}H$), 114.4 (s, $C_{Ar}H$), 65.2 (s, CH_2), 33.7 (s, CH_2).

Melting point: 66 °C

2-(3,5-Difluorophenyl)-4,5-dihydrothiazole, **4k**



The general procedure yielded to the title compound as a colourless solid (194 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.38-7.33 (m, 2H, $C_{Ar}H$), 6.93-6.88 (m, 1H, $C_{Ar}H$), 4.46 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2), 3.45 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2).

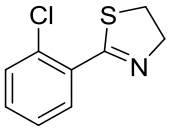
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 166.5 (m, C^{IV}), 163.0 (dd, $^{1}J_{CF}$= 249.9 Hz, $^{3}J_{CF}$= 14.2 Hz, C^{IV}), 136.5 (t, $^{3}J_{CF}$= 10.2 Hz, C^{IV}), 111.6 (dd, $^{2}J_{CF}$= 19.7 Hz, $^{4}J_{CF}$= 7.9 Hz, $C_{Ar}H$), 106.6 (t, $^{2}J_{CF}$= 25.6 Hz, $C_{Ar}H$), 65.5 (s, CH_2), 34.4 (s, CH_2).

^{19}F-{^{1}H} NMR (376 MHz, 298K): δ (ppm) = -109.01 (s, CF).

HRMS calcd. for $C_9H_8F_2NS$ $(M+H)^+$ 200.0340 **found** 200.0342.

Melting point: 43 °C

2-(2-Chlorophenyl)-4,5-dihydrothiazole, **4l**[1]

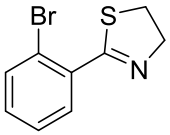


The general procedure yielded to the title compound as a light yellow oil (180 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.60 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HH}$ = 1.8 Hz, 1H, $C_{Ar}H$), 7.42 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{5}J_{HH}$ = 1.2 Hz, 1H, $C_{Ar}H$), 7.32 (td, $^{3}J_{HH}$ = 7.4 Hz, $^{5}J_{HH}$ 1.8 Hz, 1H, $C_{Ar}H$), 7.27 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HH}$ = 1.4 Hz,1H, $C_{Ar}H$), 4.46 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2), 3.44 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K): δ (ppm) = 166.2 (s, C^{IV}), 133.1 (s, C^{IV}), 132.5 (s, C^{IV}), 131.1 (s, $C_{Ar}H$), 130.8 (s, $C_{Ar}H$), 130.6 (s, $C_{Ar}H$), 126.8 (s, $C_{Ar}H$), 65.3 (s, CH_2), 34.9 (s, CH_2).

2-(2-Bromophenyl)-4,5-dihydrothiazole, **4m**



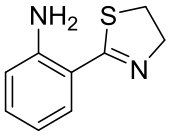
The general procedure yielded to the title compound as a colourless oil (234 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.60 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{5}J_{HH}$ = 1.1 Hz, 1H, $C_{Ar}H$), 7.52 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HH}$ = 1.8 Hz, 1H, $C_{Ar}H$), 7.31 (td, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HH}$ = 1.2 Hz, 1H, $C_{Ar}H$), 7.22 (td, $^{3}J_{HH}$ = 8.0 Hz, $^{5}J_{HH}$ = 1.8 Hz, 1H, $C_{Ar}H$), 4.46 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2), 3.45 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.2 (s, C^{IV}), 135.2 (s, C^{IV}), 133.7 (s, $C_{Ar}H$), 131.1 (s, $C_{Ar}H$), 130.5 (s, $C_{Ar}H$), 127.3 (s, $C_{Ar}H$), 121.2 (s, C^{IV}), 65.4 (s, CH_2), 35.1 (s, CH_2).

HRMS calcd. for C_9H_9BrNS $(M+H)^+$ 241.9634 **found** 241.9631.

2-(4,5-Dihydrothiazol-2-yl)aniline, **4n**[1]

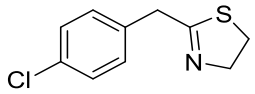


The general procedure yielded to the title compound as a pale yellow oil (176 mg, 99%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.47 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, $C_{Ar}H$), 7.16 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, $C_{Ar}H$), 6.68-6.64 (m, 2H, $C_{Ar}H$), 6.17 (s, 2H, NH_2), 4.49-4.45 (m, 2H, CH_2), 3.26-3.22 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 169.6 (s, C^{IV}), 147.8 (s, C^{IV}), 132.8 (s, $C_{Ar}H$), 131.7 (s, $C_{Ar}H$), 116.5 (s, $C_{Ar}H$), 116.2 (s, $C_{Ar}H$), 115.2 (s, C^{IV}), 65.5 (s, CH_2), 32.1 (s, CH_2).

2-(4-Chlorobenzyl)-4,5-dihydrothiazole, **4o**[1]

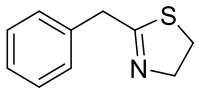


The general procedure yielded to the title compound as a yellow oil (194 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.28 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, $C_{Ar}H$), 7.21 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, $C_{Ar}H$), 4.23 (t, $^{3}J_{HH}$ = 8.4 HZ, 2H, CH_2), 3.77 (s, 2H, CH_2), 3.26 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 170.1 (s, C^{IV}), 134.8 (s, C^{IV}), 133.3 (s, C^{IV}), 130.7 (s, $C_{Ar}H$), 129.0 (s, $C_{Ar}H$), 64.9 (s, CH_2), 40.3 (s, CH_2), 34.5 (s, CH_2).

2-Benzyl-4,5-dihydrothiazole, **4p**[1]

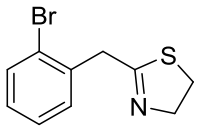


The general procedure yielded to the title compound as a yellow oil (172 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.30-7.19 (m, 5H, $C_{Ar}H$), 4.19-4.14 (m, 2H, CH_2), 3.78 (s, 2H, CH_2), 3.18-3.13 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 170.1 (s, C^{IV}), 136.1 (s, C^{IV}), 129.1 (s, $C_{Ar}H$), 128.5 (s, $C_{Ar}H$), 127.0 (s, $C_{Ar}H$), 64.6 (s, CH_2), 40.7 (s, CH_2), 34.1 (s, CH_2).

2-(2-Bromobenzyl)-4,5-dihydrothiazole, **4q**



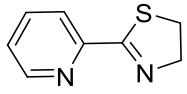
The general procedure yielded to the title compound as a colourless oil (232 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.54 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, $C_{Ar}H$), 7.32-7.30 (m, 1H, $C_{Ar}H$), 7.26-7.23 (m, 1H, $C_{Ar}H$), 7.12-7.08 (m, 1H, $C_{Ar}H$), 4.21 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2), 3.95 (s, 2H, CH_2), 3.24 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 169.0 (s, C^{IV}), 136.2 (s, C^{IV}), 133.0 (s, $C_{Ar}H$), 131.3 (s, $C_{Ar}H$), 128.9 (s, $C_{Ar}H$), 127.7 (s, $C_{Ar}H$), 125.0 (s, C^{IV}), 64.8 (s, CH_2), 40.8 (s, CH_2), 34.2 (s, CH_2).

HRMS calcd. for $C_{10}H_{11}BrNS$ $(M+H)^+$ 255.9790 **found** 255.9790.

2-(Pyridin-2-yl)-4,5-dihydrothiazole, **4r**[1]



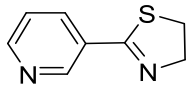
The general procedure yielded to the title compound as a colourless solid (159 mg, 97%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.66 (s, 1H, $C_{Ar}H$), 8.08-8.05 (m, 1H, $C_{Ar}H$), 7.79-7.73 (m, 1H, $C_{Ar}H$), 7.48-7.33 (m, 1H, $C_{Ar}H$), 4.57-4.51 (m, 2H, CH_2), 3.41-3.34 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 171.1 (s, C^{IV}), 151.3 (s, C^{IV}), 149.4 (s, C_{Ar}H), 136.7 (s, C_{Ar}H), 125.5 (s, C_{Ar}H), 121.6 (s, C_{Ar}H), 65.9 (s, CH_2), 32.7 (s, CH_2).

Melting point: 92 °C

2-(Pyridin-3-yl)-4,5-dihydrothiazole, **4s**[1]

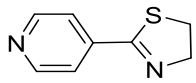


The general procedure yielded to the title compound as a yellow oil (158 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 9.04 (d, $^{5}J_{HH}$ 1.6 Hz, 1H, $C_{Ar}H$), 8.68 (dd, $^{3}J_{HH}$ = 4.8 Hz, $^{5}J_{HH}$ = 1.6 Hz, 1H,$C_{Ar}H$), 8.10 (dt, $^{3}J_{HH}$ = 8.0 Hz, $^{5}J_{HH}$ = 1.9 Hz, 1H, $C_{Ar}H$), 7.35 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{5}J_{HH}$ = 4.8 Hz, 1H, $C_{Ar}H$), 4.46 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 3.45 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 165.6 (s, C^{IV}), 151.8 (s, C_{Ar}H), 149.4 (s, C_{Ar}H), 135.4 (s, C_{Ar}H), 129.1 (s, C^{IV}), 123.3 (s, C_{Ar}H), 65.2 (s, CH_2), 33.9 (s, CH_2).

2-(Pyridin-4-yl)-4,5-dihydrothiazole, **4t**[1]



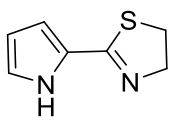
The general procedure yielded to the title compound as a colourless solid (157 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 8.70 (dd, $^{3}J_{HH}$ = 4.5 Hz, $^{5}J_{HH}$ = 1.7 Hz, 2H, $C_{Ar}H$), 7.67 (dd, $^{3}J_{HH}$ = 4.5 Hz, $^{5}J_{HH}$ = 1.7 Hz, 2H, $C_{Ar}H$), 4.50 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2), 3.47 (t, $^{3}J_{HH}$ = 8.5 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 167.2 (s, C^{IV}), 150.6 (s, C_{Ar}H), 140.3 (s, C^{IV}), 122.3 (s, C_{Ar}H), 65.7 (s, CH_2), 34.2 (s, CH_2).

Melting point: 73 °C

2-(1*H*-Pyrrol-2-yl)-4,5-dihydrothiazole, **4u**[7]



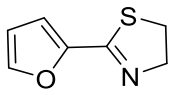
The general procedure yielded to the title compound as a colourless solid (300 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 10.54 (s, 1H, N*H*), 6.90 (s, 1H, $C_{Ar}H$), 6.64 (d, $^{3}J_{HH}$ = 2.9 Hz, 1H, $C_{Ar}H$), 6.23 (t, $^{3}J_{HH}$ = 2.9 Hz, 1H, $C_{Ar}H$), 4.35 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, CH_2), 3.38 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 161.5 (s, C^{IV}), 126.0 (s, C^{IV}), 122.6 (s, C_{Ar}H), 115.0 (s, C_{Ar}H), 110.0 (s, C_{Ar}H), 64.1 (s, CH_2), 33.7 (s, CH_2).

Melting point: 94 °C

2-(2-Furanyl)-4,5-dihydrothiazole, **4v**[6]

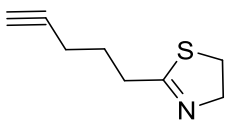


The general procedure yielded to the title compound as a yellow oil (291 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 7.52-7.51 (m, 1H, $C_{Ar}H$), 6.88 (d, $^{3}J_{HH}$ = 3.5 Hz, 1H, $C_{Ar}H$), 6.46 (dd, $^{3}J_{HH}$ = 3.5 Hz, $^{5}J_{HH}$ 1.8 Hz, 1H, $C_{Ar}H$), 4.37 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2), 3.34 (t, $^{3}J_{HH}$ = 8.3 Hz, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 157.2 (s, C^{IV}), 147.6 (s, C^{IV}), 144.4 (s, $C_{Ar}H$), 113.2 ($C_{Ar}H$), 111.4 ($C_{Ar}H$), 64.5 (s, CH_2), 33.1 (s, CH_2).

2-(Pent-4-yn-1-yl)-4,5-dihydrothiazole, **4w**



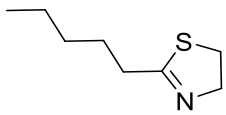
The general procedure yielded to the title compound as a colourless oil (132 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 4.24-4.19 (m, 2H, CH_2), 3.31-3.21 (m, 2H, CH_2), 2.65-2.61 (m, 2H, CH_2), 2.31-2.27 (m, 2H, CH_2), 2.00-1.93 (m, 1H, CH), 1.93-1.86 (m, 2H, CH_2).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 170.8 (s, C^{IV}), 83.6 (s, CH), 69.3 (s, C^{IV}), 64.8 (s, CH_2), 34.0 (s, CH_2), 33.2 (s, CH_2), 26.3 (s, CH_2), 18.1 (s, CH_2).

HRMS calcd. for $C_8H_{12}NS$ $(M+H)^+$ 154.0685 **found** 154.0683.

2-Pentyl-4,5-dihydrothiazole, **4x**[8]



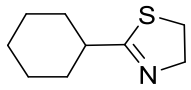
The general procedure yielded after flash chromatography (SiO_2, penthane/ ethyl acetate 7:3) to the title compound as a colourless oil (85 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 4.21 (tt, $^{3}J_{HH}$ = 8.4 Hz, $^{5}J_{HH}$ = 1.4 Hz, 2H, CH_2), 3.27 (t, $^{3}J_{HH}$ = 8.4 Hz, 2H, CH_2), 2.52-2.48 (m, 2H, CH_2), 1.69-1.61 (m, 2H, CH_2), 1.36-1.31 (m, 4H, CH_2), 0.92-0.88 (m, 3H, CH_3).

^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 172.0 (s, C^{IV}), 64.8 (s, CH_2), 34.6 (s, CH_2), 34.0 (s, CH_2), 31.6 (s, CH_2), 27.5 (s, CH_2), 22.6 (s, CH_2), 14.2 (s, CH_3).

HRMS calcd. for $C_8H_{16}NS$ $(M+H)^+$ 158.0998 **found** 158.0997.

2-Cyclohexyl-4,5-dihydrothiazole, **4y**[8]



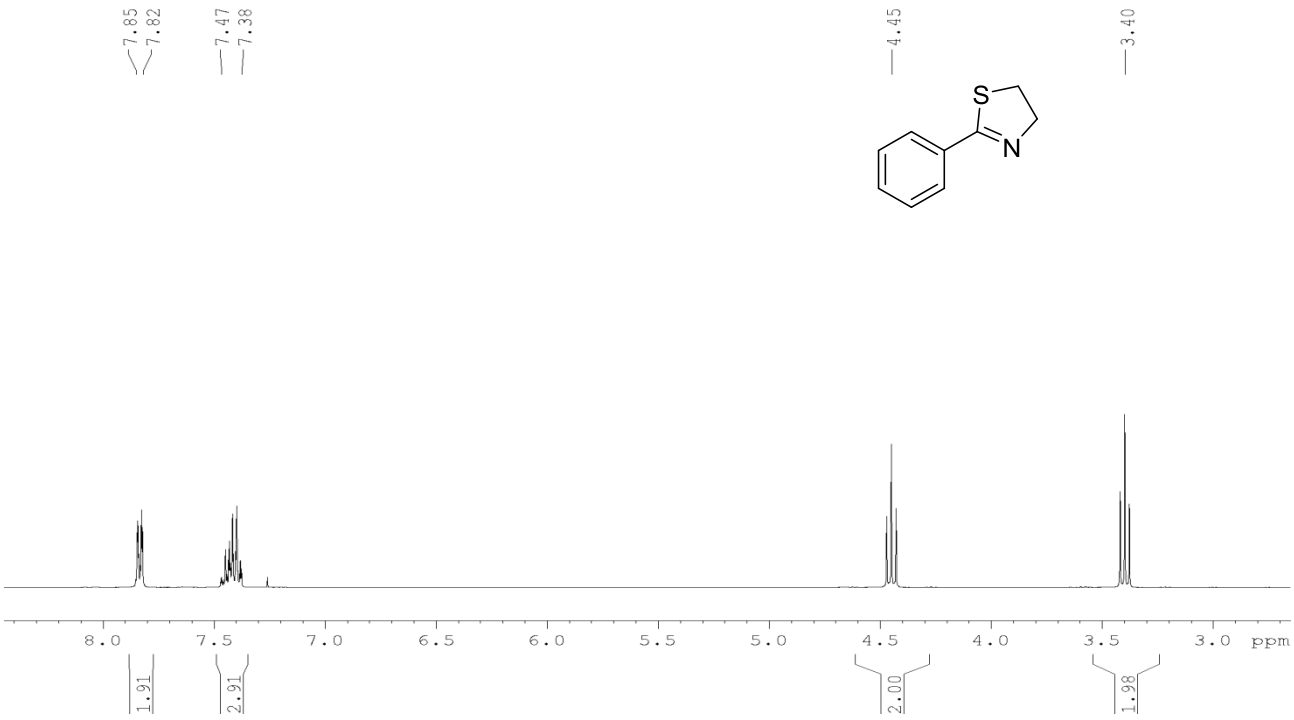
The general procedure yielded after flash chromatography (SiO_2, penthane/ ethyl acetate 8:2) to the title compound as a colourless oil (77 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS): δ (ppm) = 4.20 (td, $^3J_{HH}$ = 8.4 Hz, $^5J_{HH}$ = 1.1 Hz, 2H, CH_2), 3.22 (t, $^3J_{HH}$ = 8.4 Hz, 2H, CH_2), 2.53-2.46 (m, 1H, C*H*), 1.97-1.93 (m, 2H, CH_2), 1.81-1.76 (m, 2H, CH_2), 1.70-1.65 (m, 1H, CH_2), 1.57-1.16 (m, 5H, CH_2).

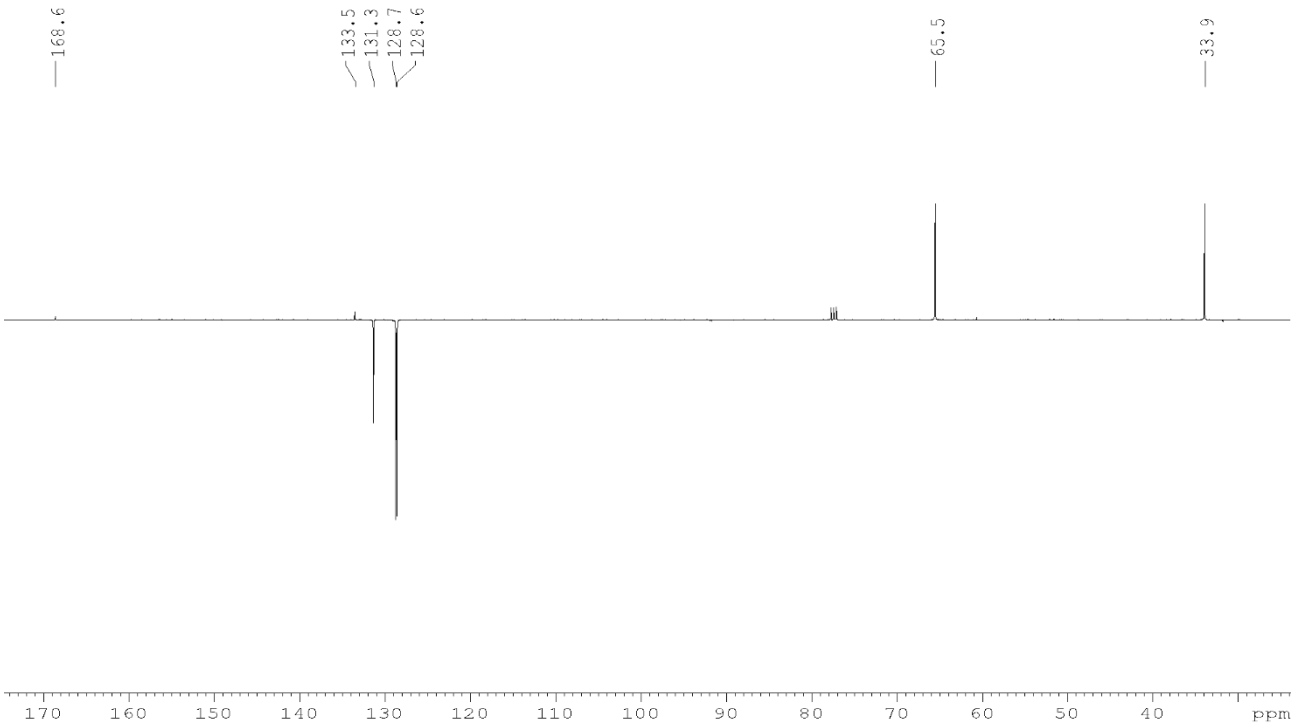
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K): δ (ppm) = 176.7 (s, C^{IV}), 64.7 (s, *C*H_2), 43.6 (s, *C*H), 33.3 (s, *C*H_2), 31.8 (s, *C*H_2), 26.2 (s, *C*H_2).

5 NMR spectra

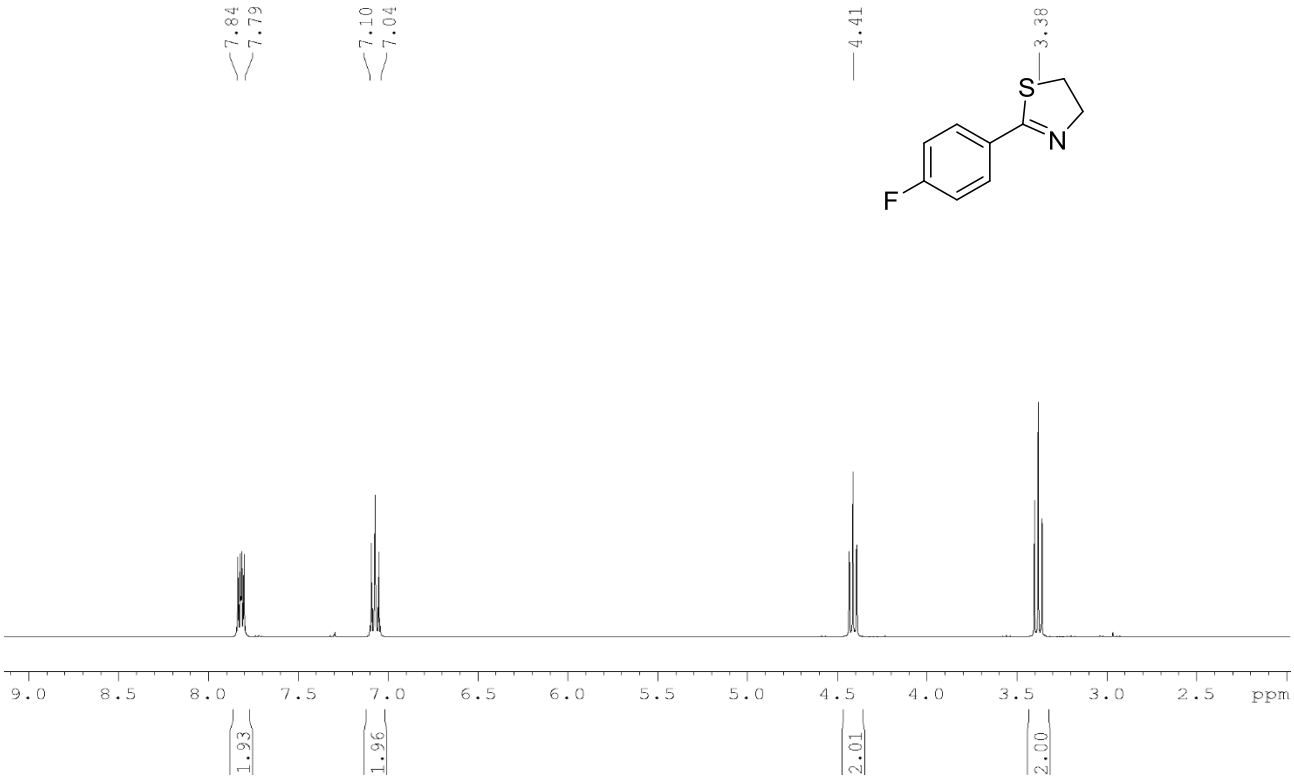
^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS) of 2-phenyl-4,5-dihydrothiazole, **4a**



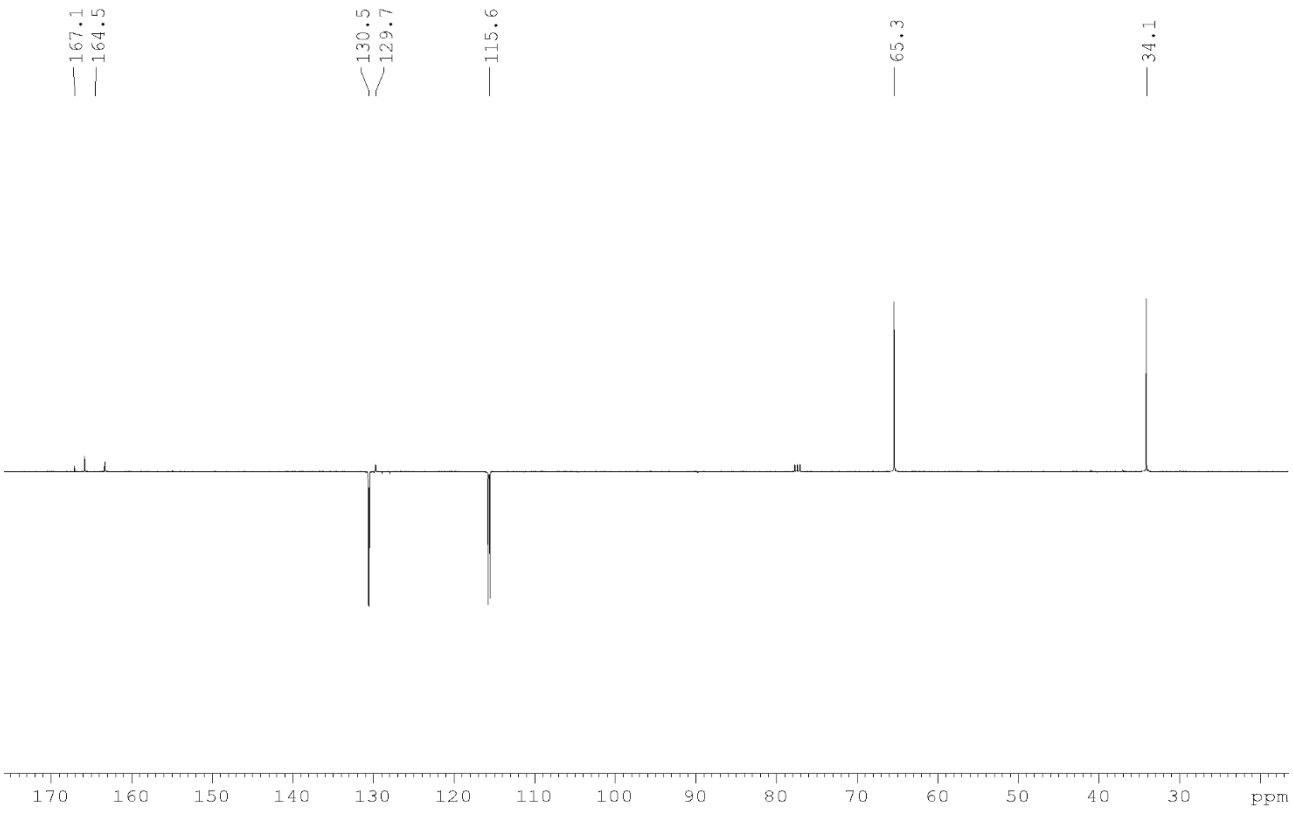
^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K) of 2-phenyl-4,5-dihydrothiazole, **4a**



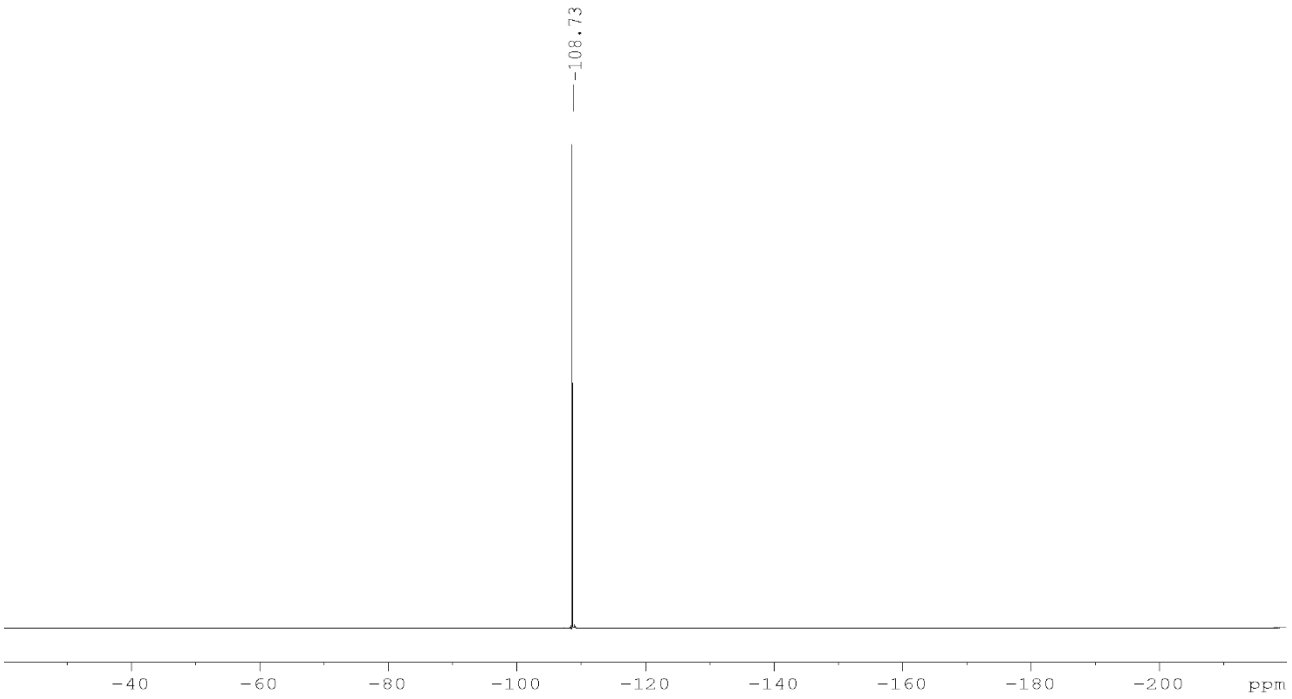
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(4-fluorophenyl)-4,5-dihydrothiazole, **4b**



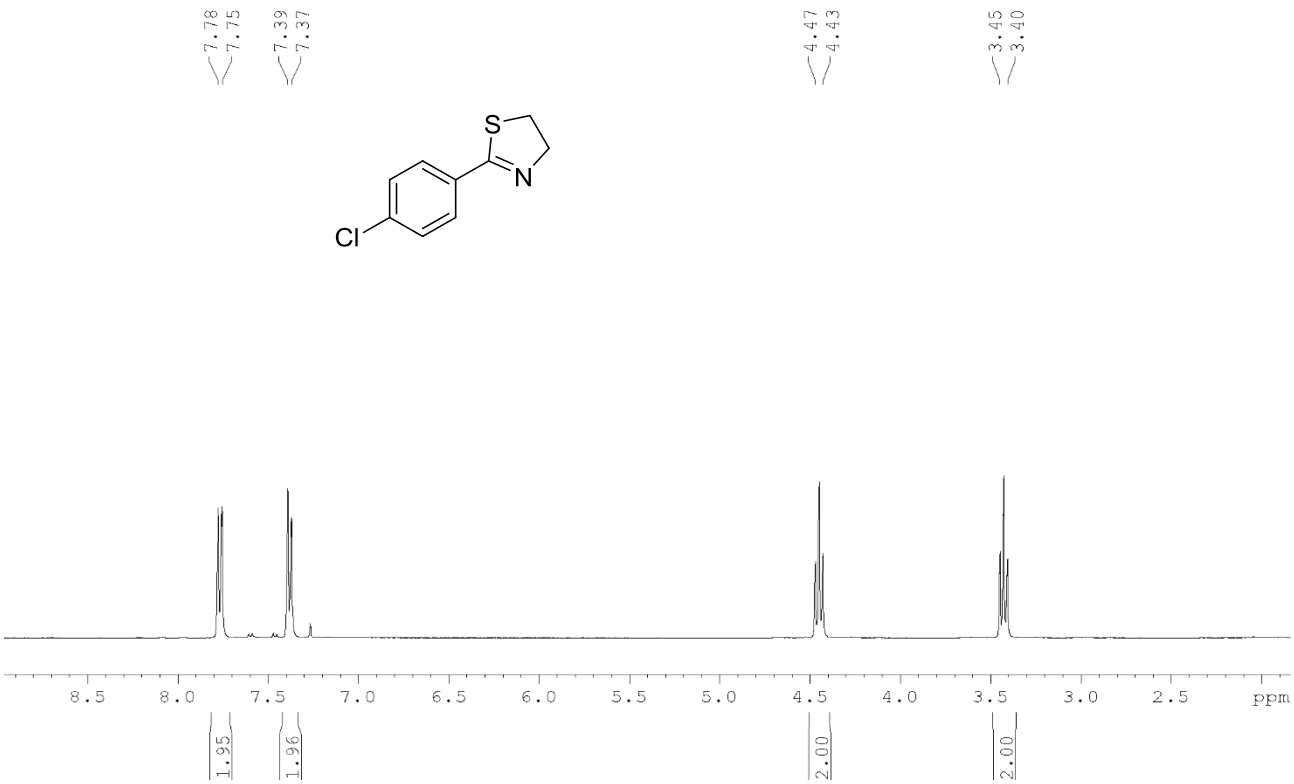
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(4-fluorophenyl)-4,5-dihydrothiazole, **4b**



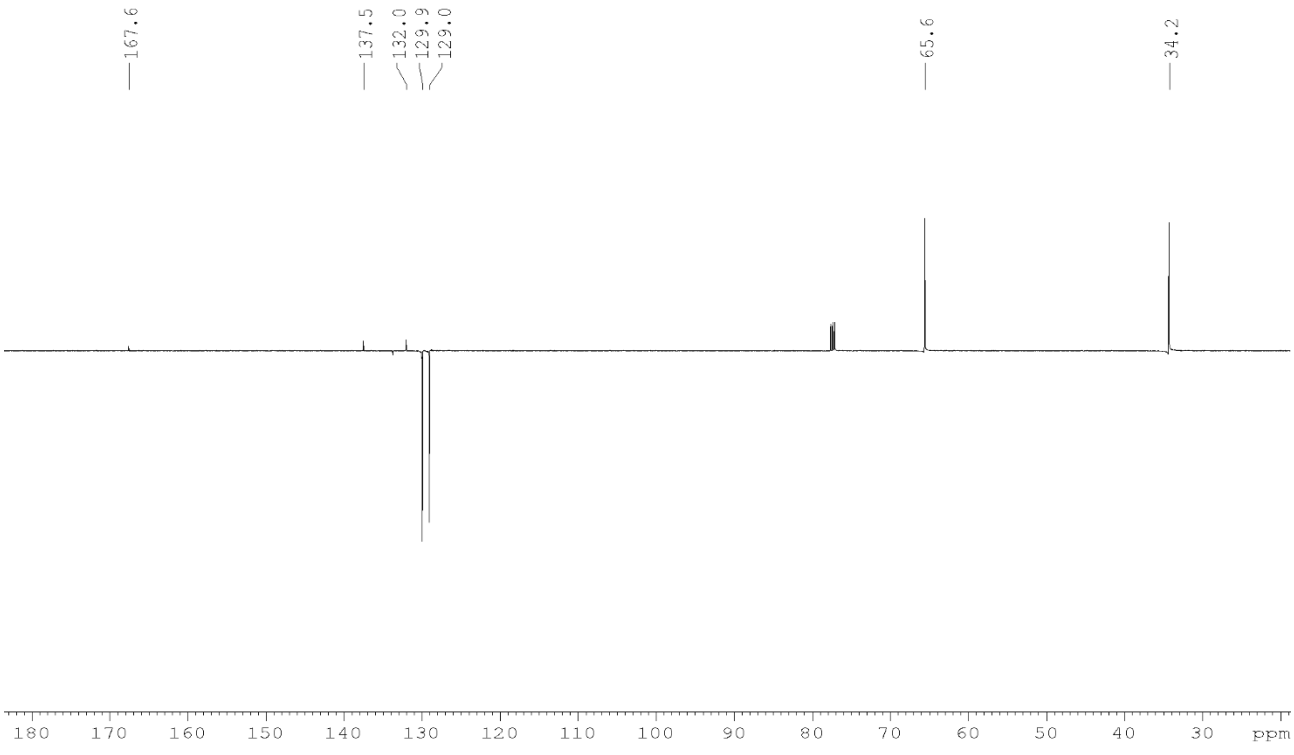
^{19}F-{^{1}H} NMR (376 MHz, 298K) of 2-(4-fluorophenyl)-4,5-dihydrothiazole, **4b**



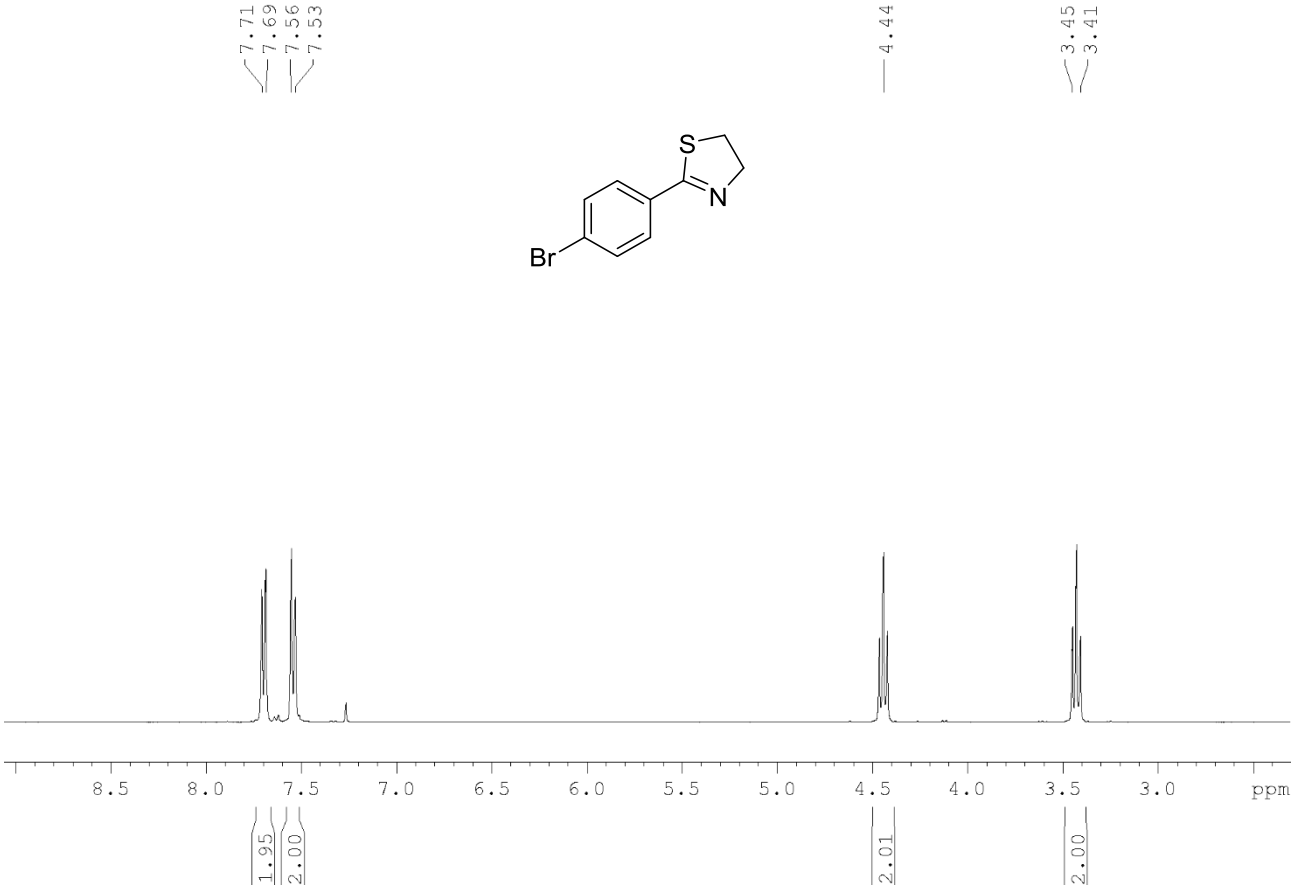
^{1}H NMR (400 MHz, CDCl3, 298K, TMS) of 2-(4-chlorophenyl)-4,5-dihydrothiazole, **4c**



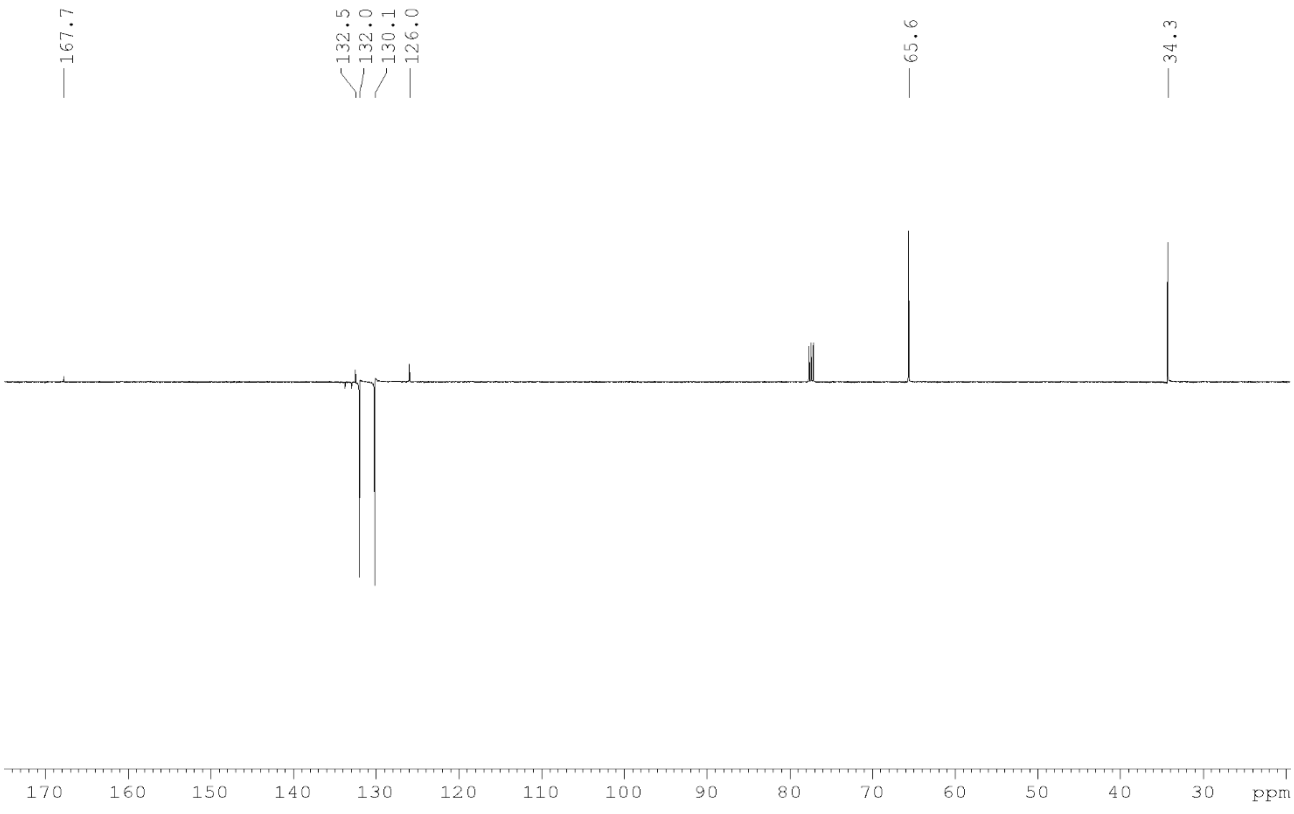
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(4-chlorophenyl)-4,5-dihydrothiazole, **4c**



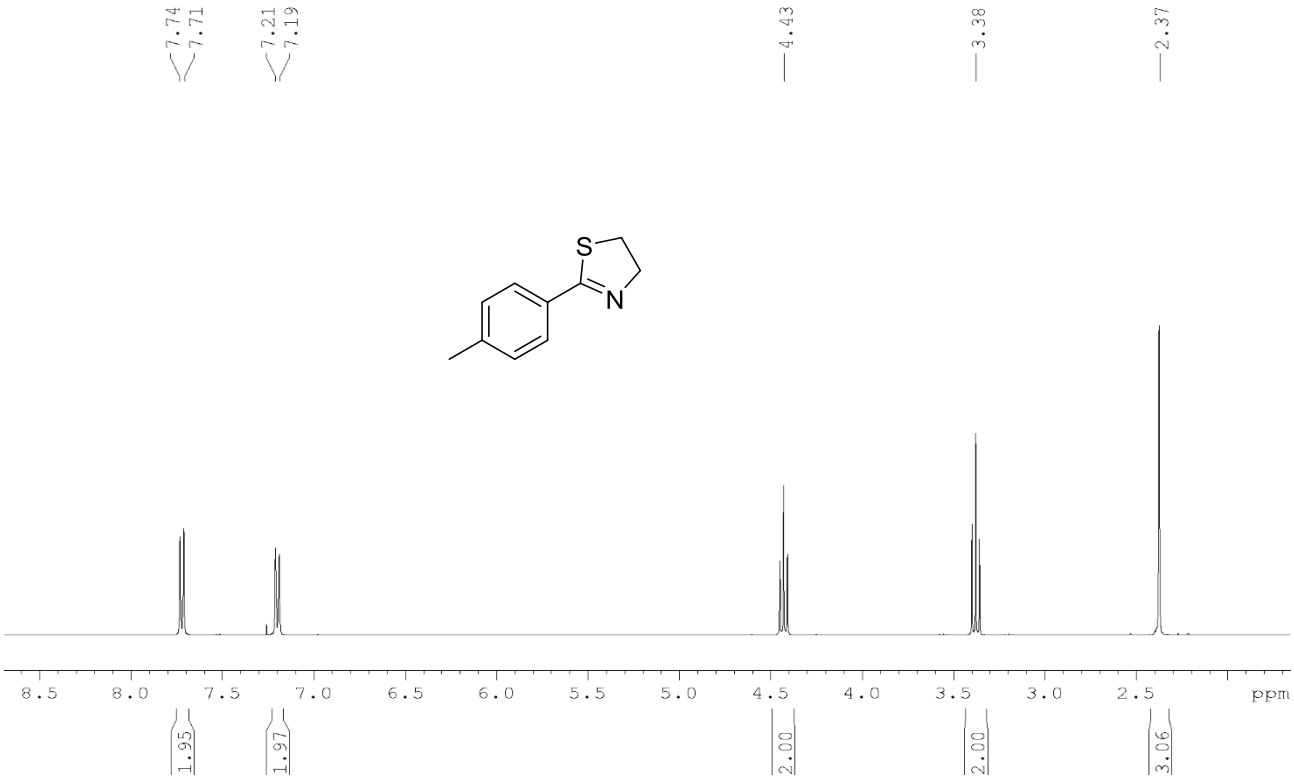
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(4-bromophenyl)-4,5-dihydrothiazole, **4d**



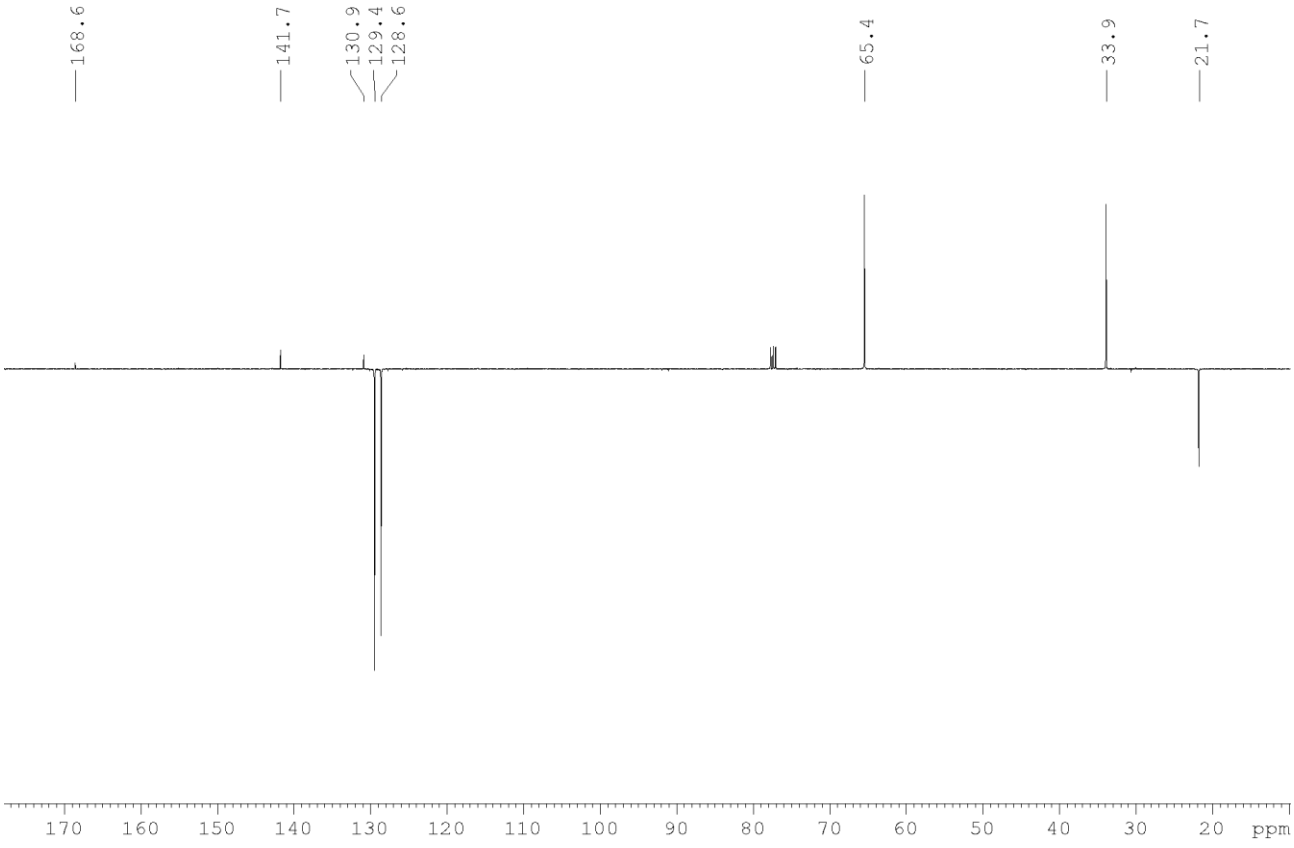
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(4-bromophenyl)-4,5-dihydrothiazole, **4d**



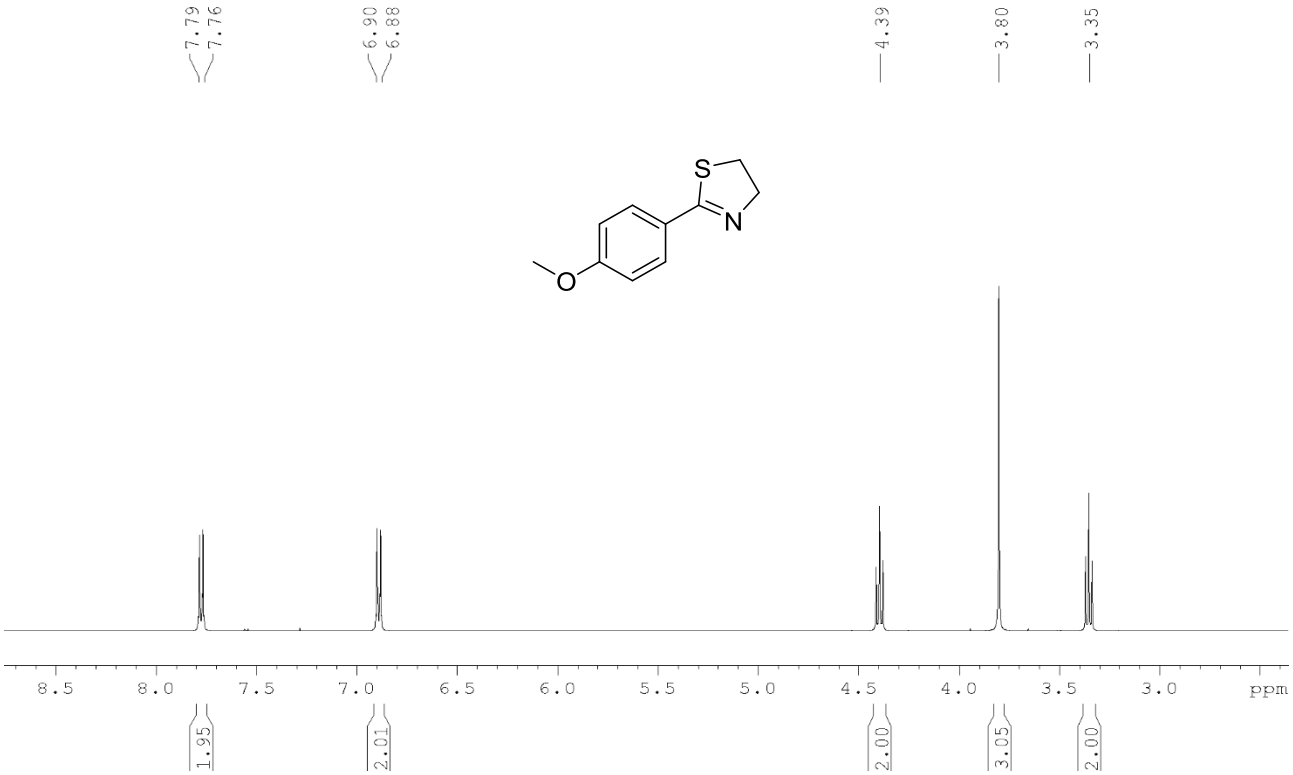
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-*p*-tolyl-4,5-dihydrothiazole, **4e**



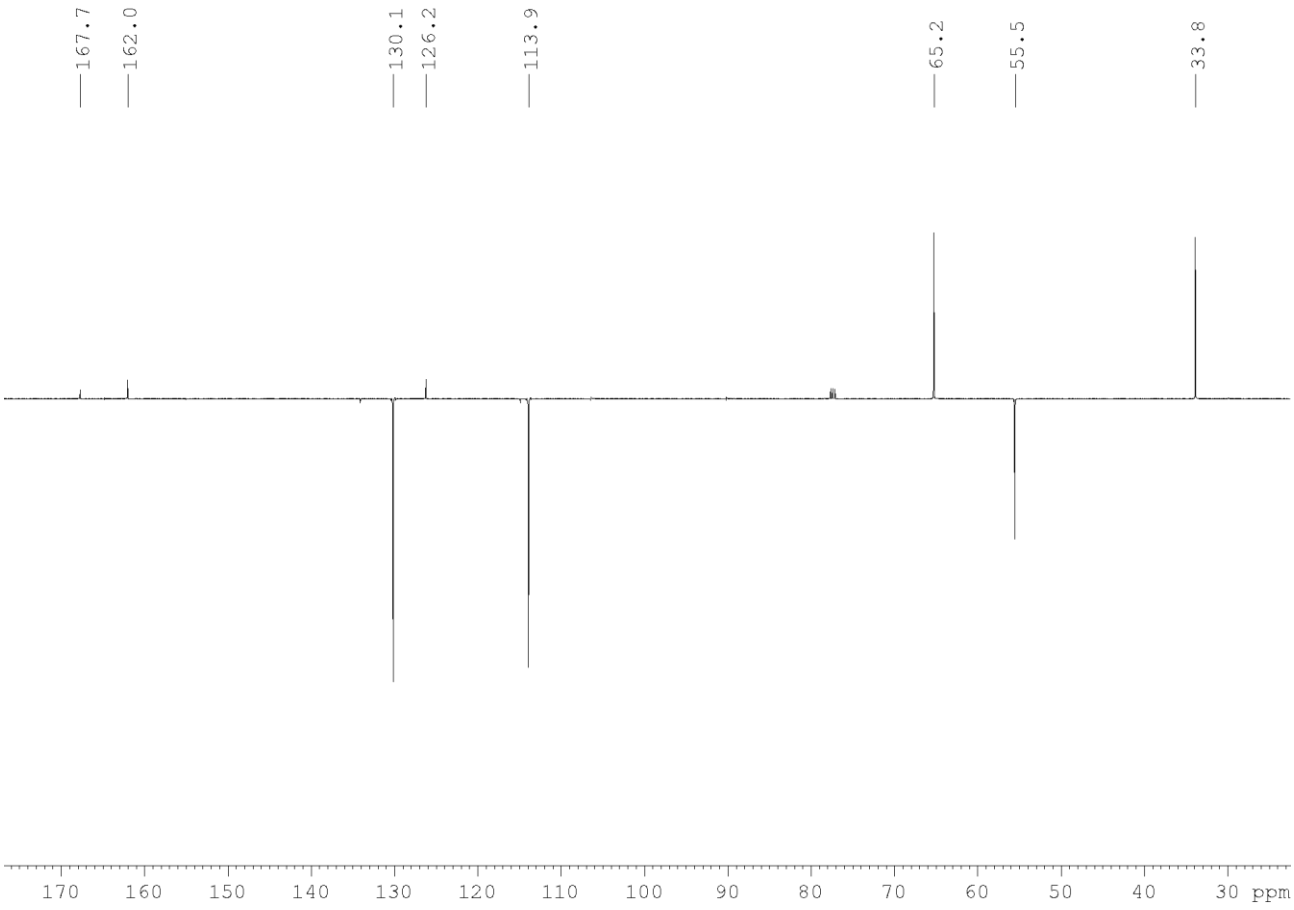
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-*p*-tolyl-4,5-dihydrothiazole, **4e**



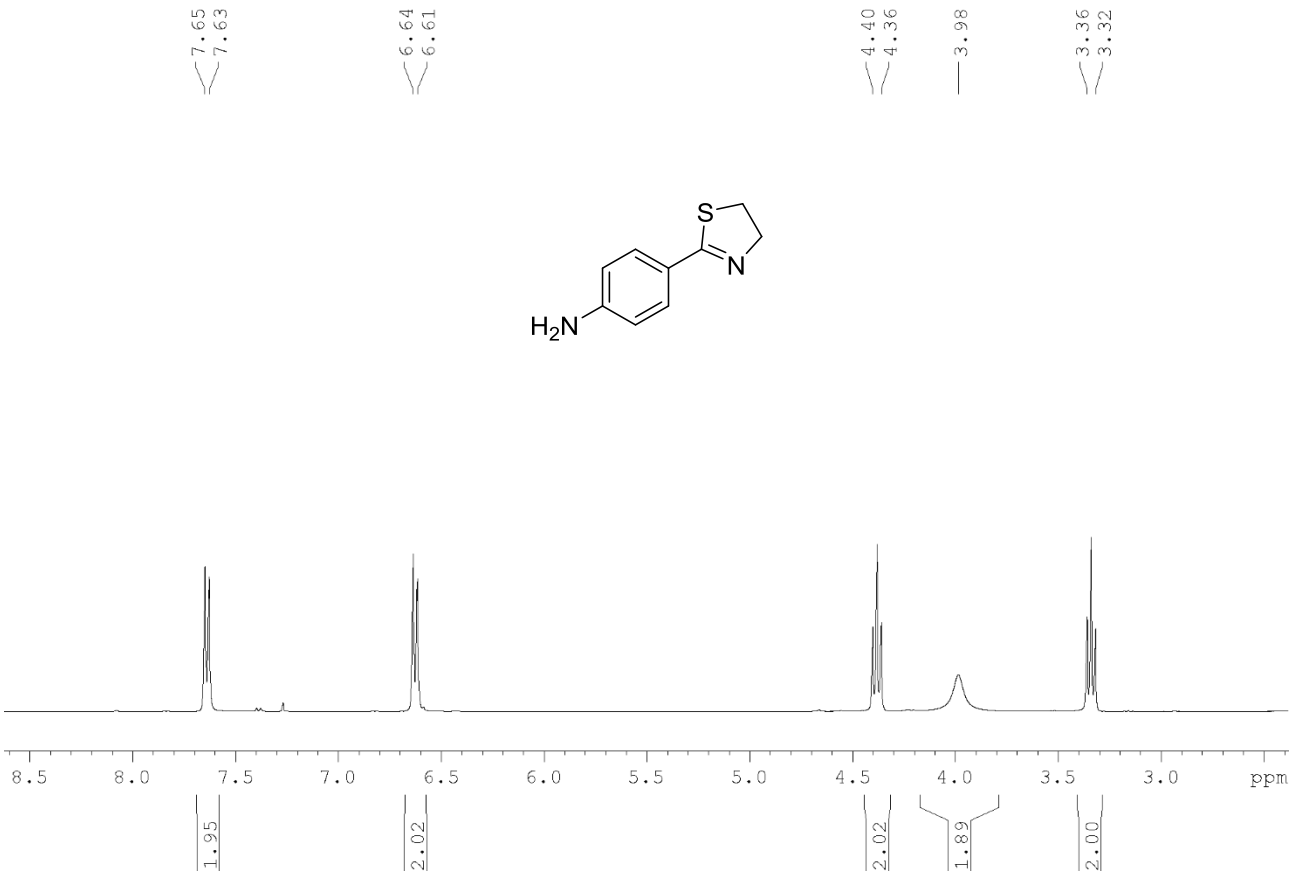
^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS) of 2-(4-methoxyphenyl)-4,5-dihydrothiazole, **4f**



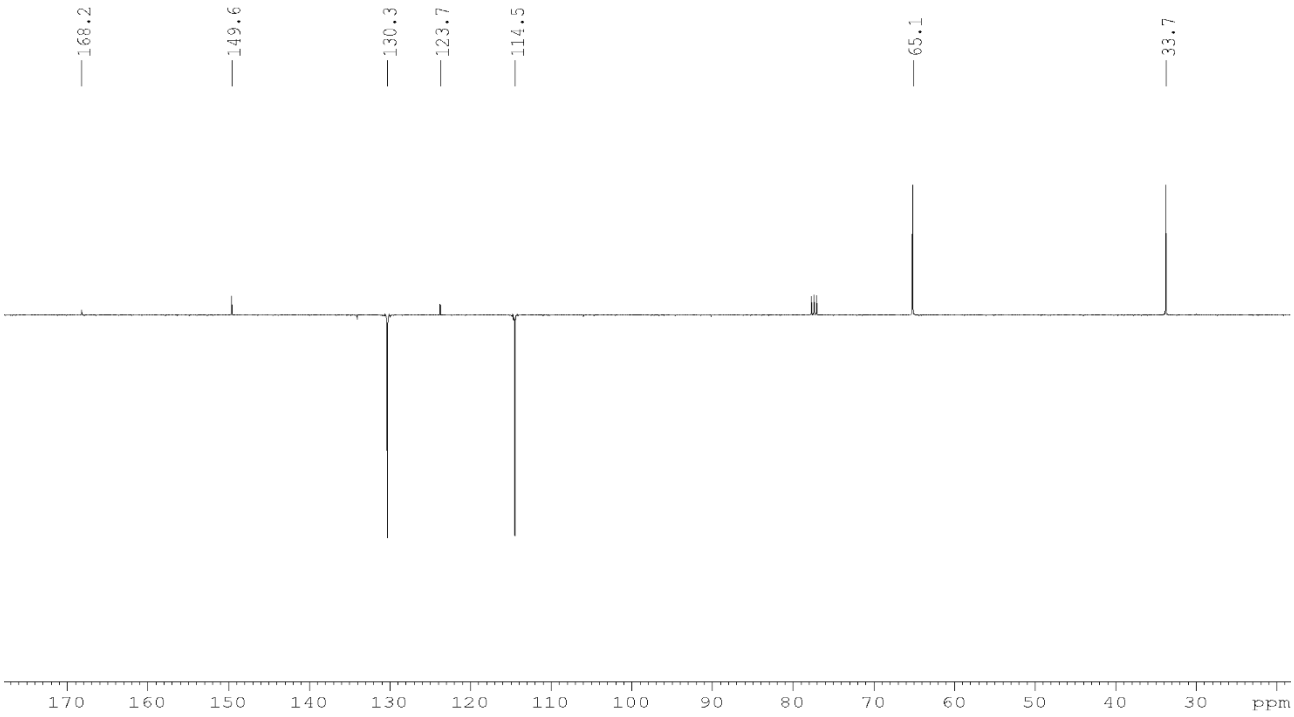
^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K) of 2-(4-methoxyphenyl)-4,5-dihydrothiazole, **4f**



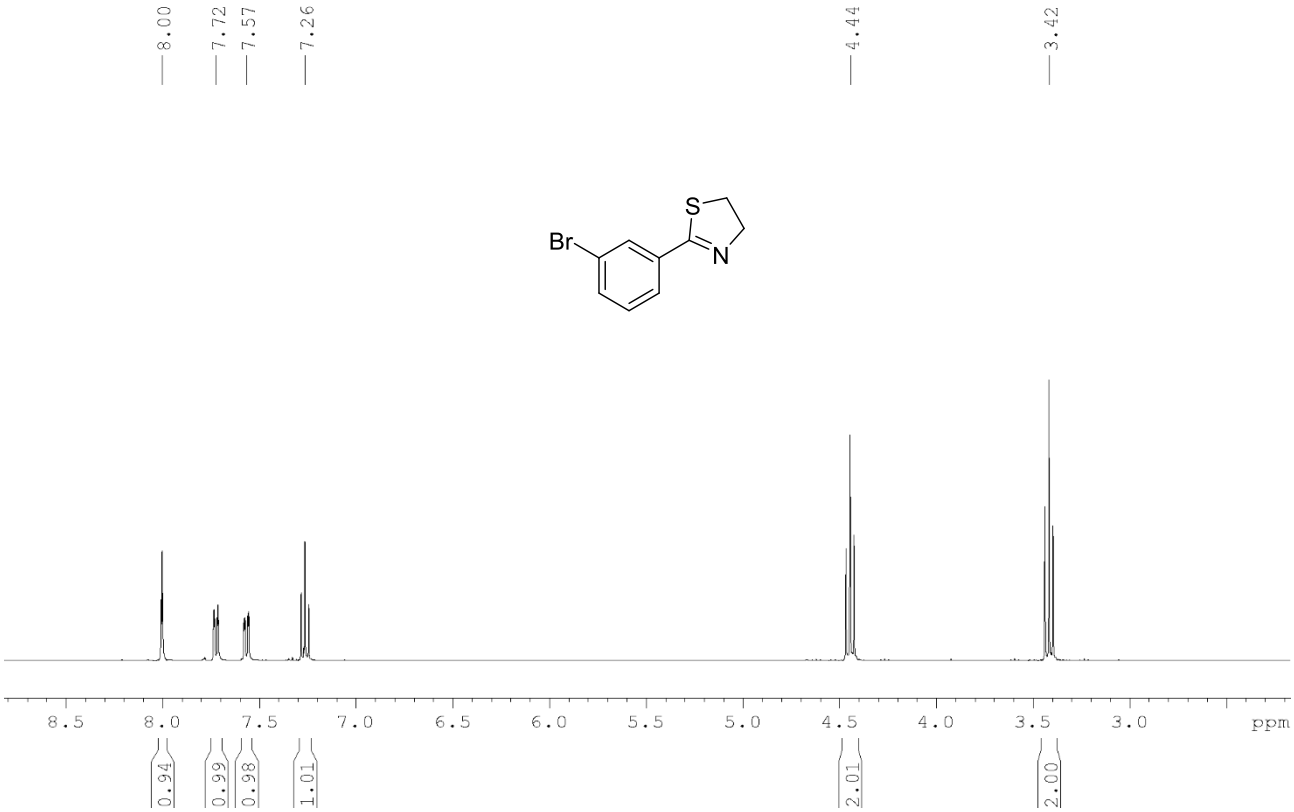
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 4-(4,5-dihydrothiazol-2-yl)aniline, **4g**



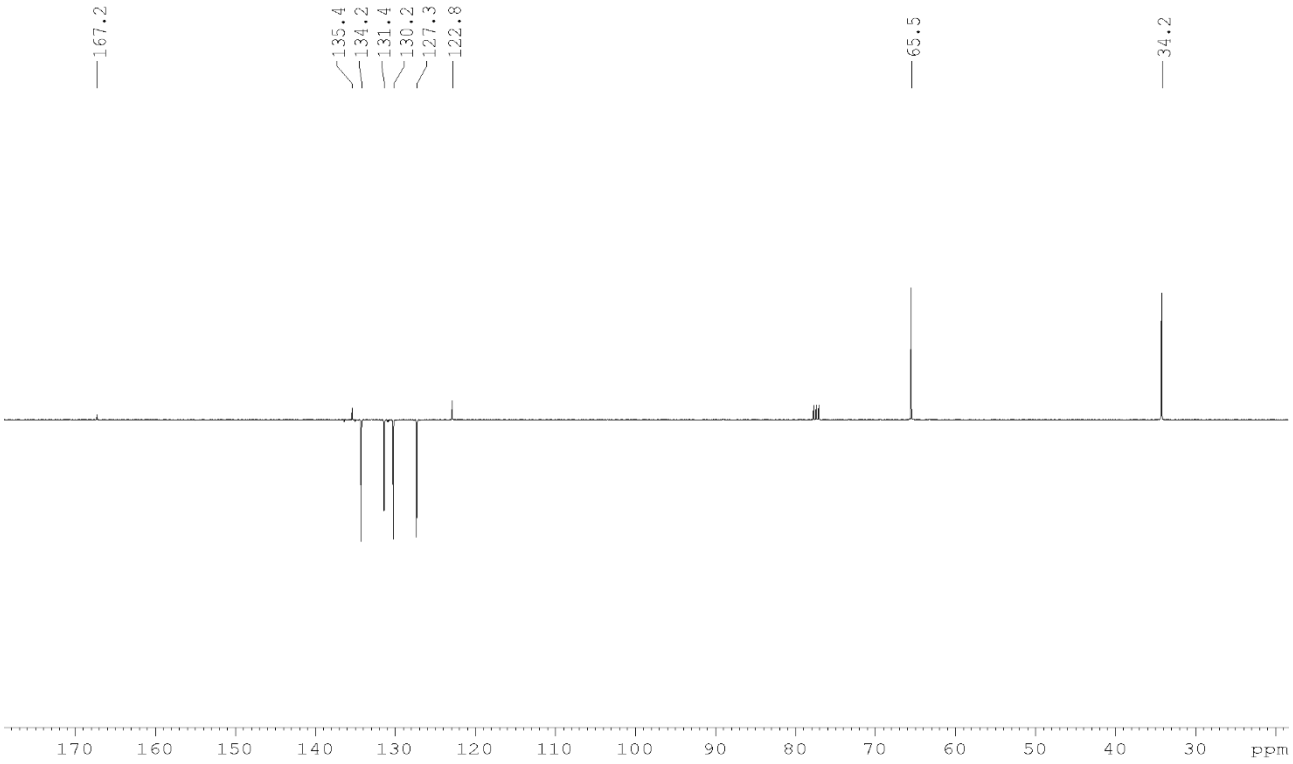
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 4-(4,5-dihydrothiazol-2-yl)aniline, **4g**



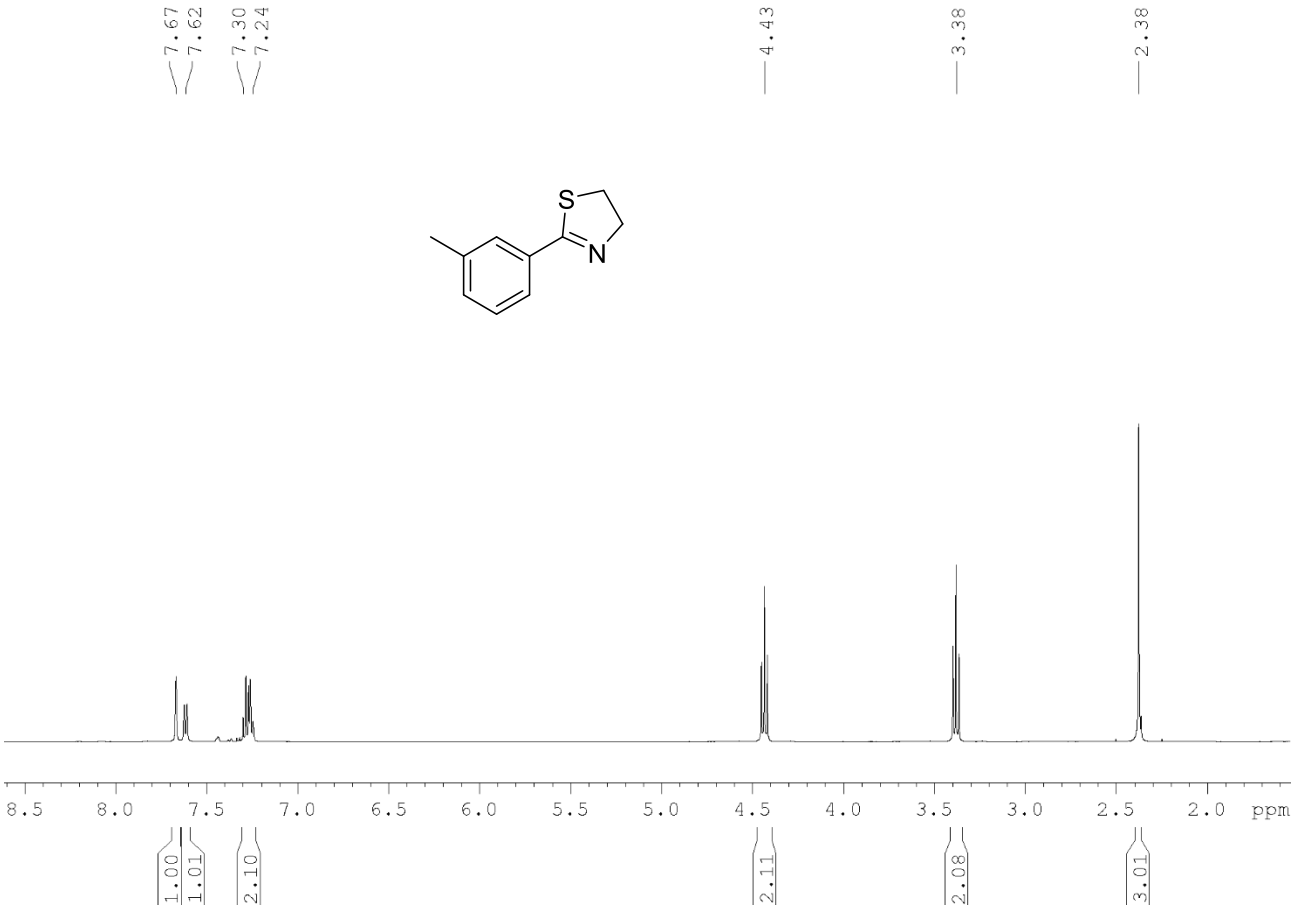
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(3-bromophenyl)-4,5-dihydrothiazole, **4h**



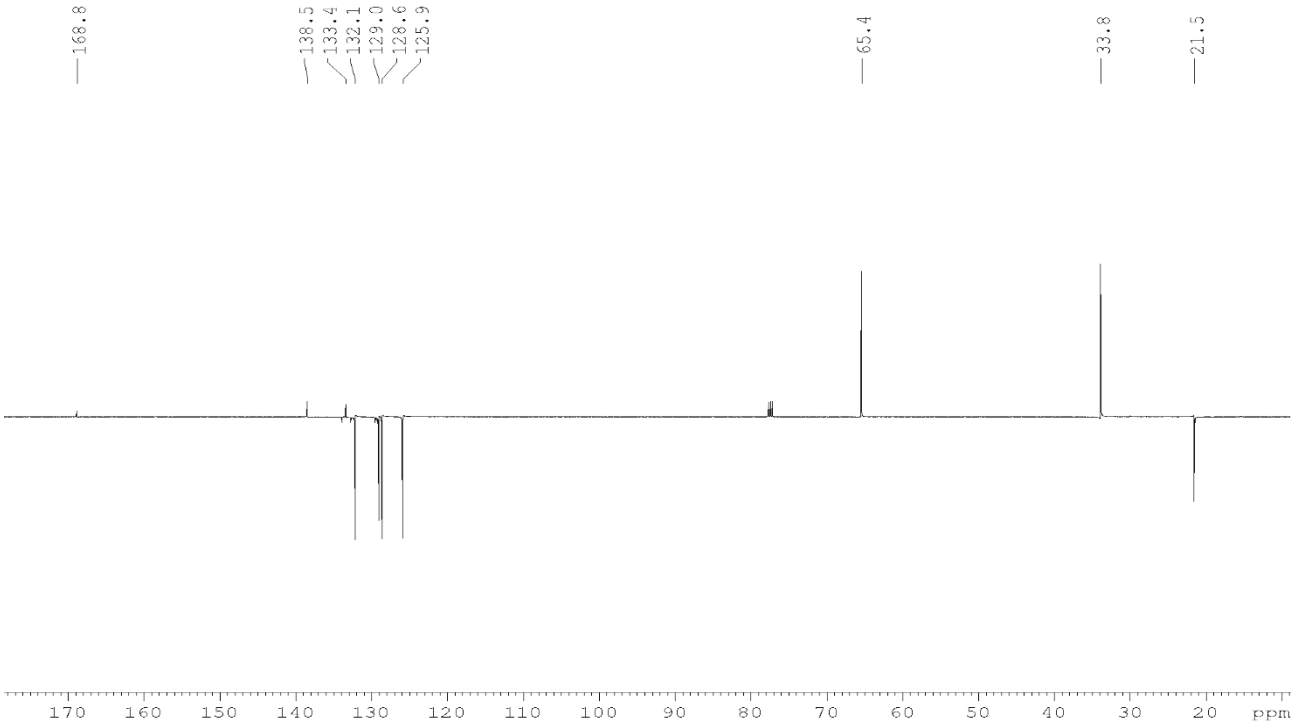
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(3-bromophenyl)-4,5-dihydrothiazole, **4h**



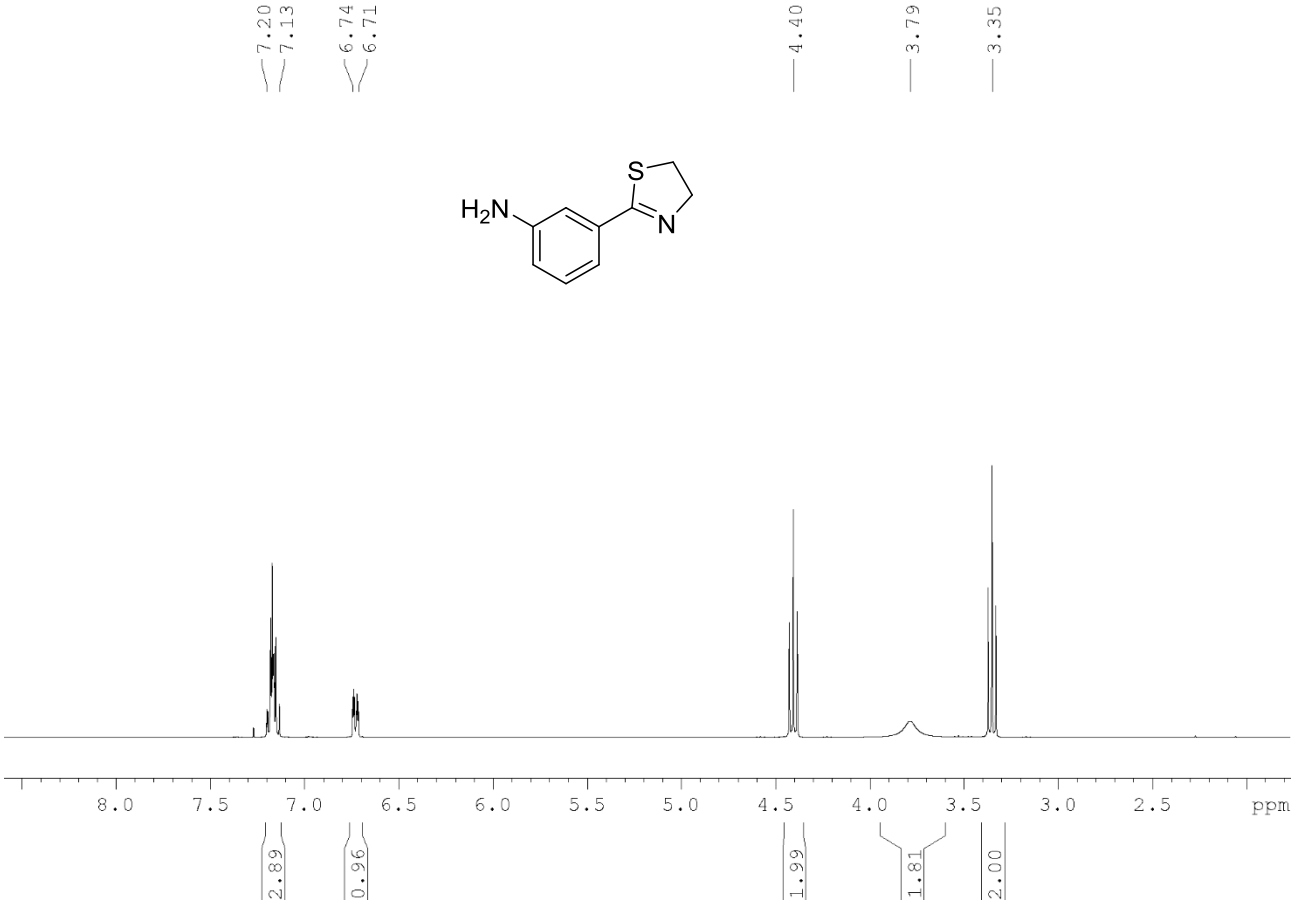
^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS) of 2-*m*-tolyl-4,5-dihydrothiazole, **4i**



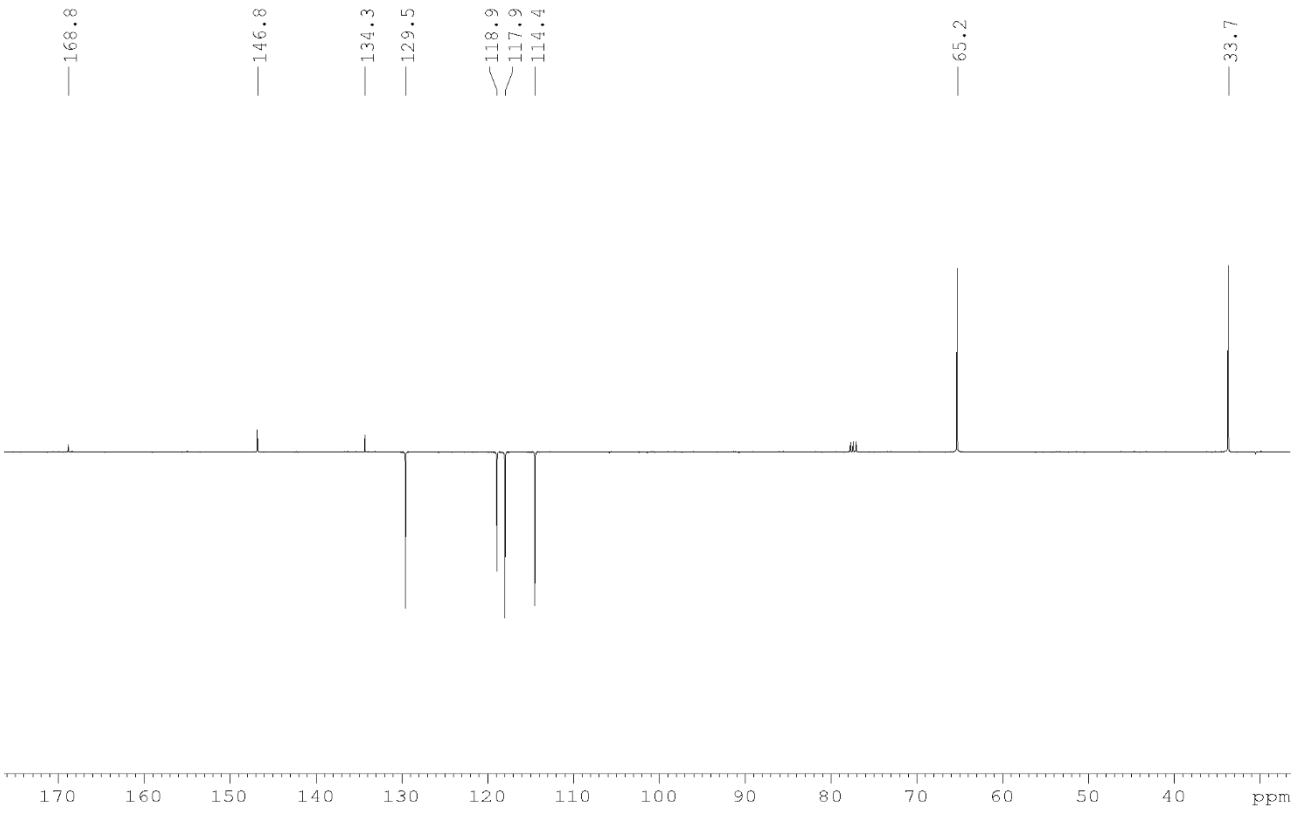
^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K) of 2-*m*-tolyl-4,5-dihydrothiazole, **4i**



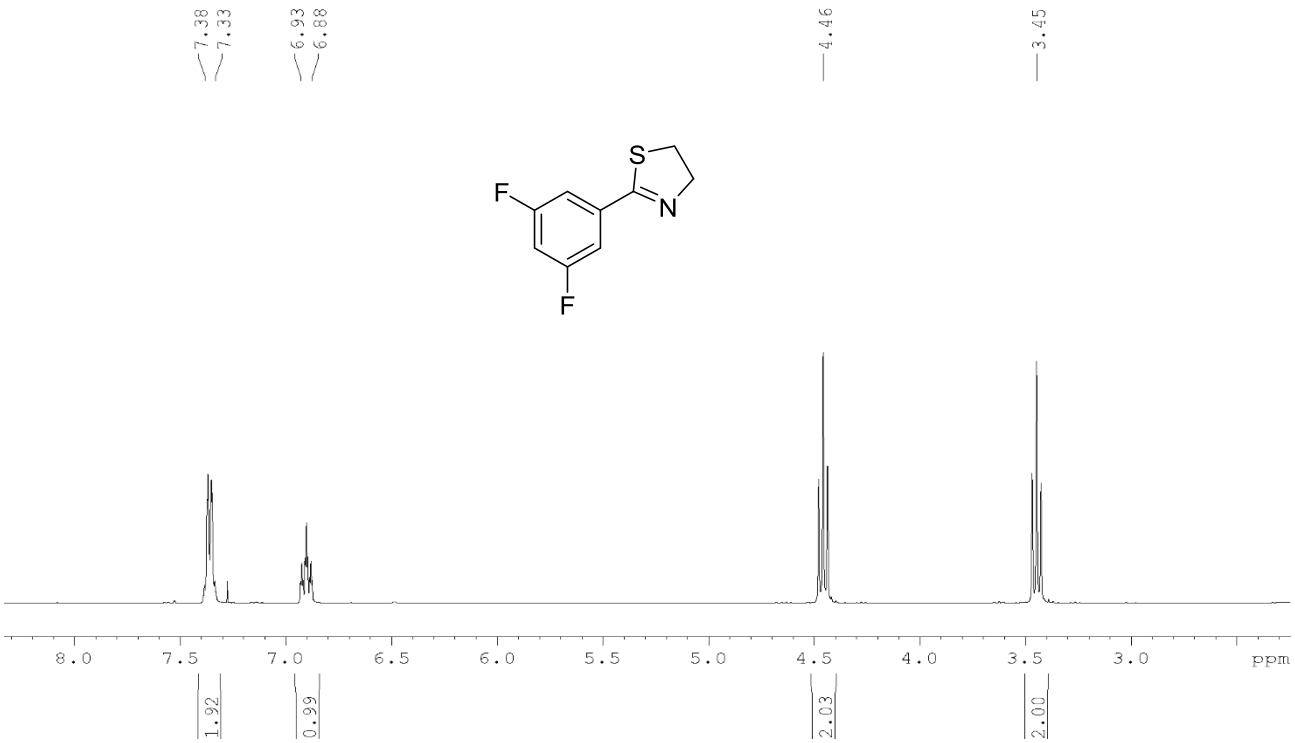
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 3-(4,5-dihydrothiazol-2-yl)aniline, **4j**



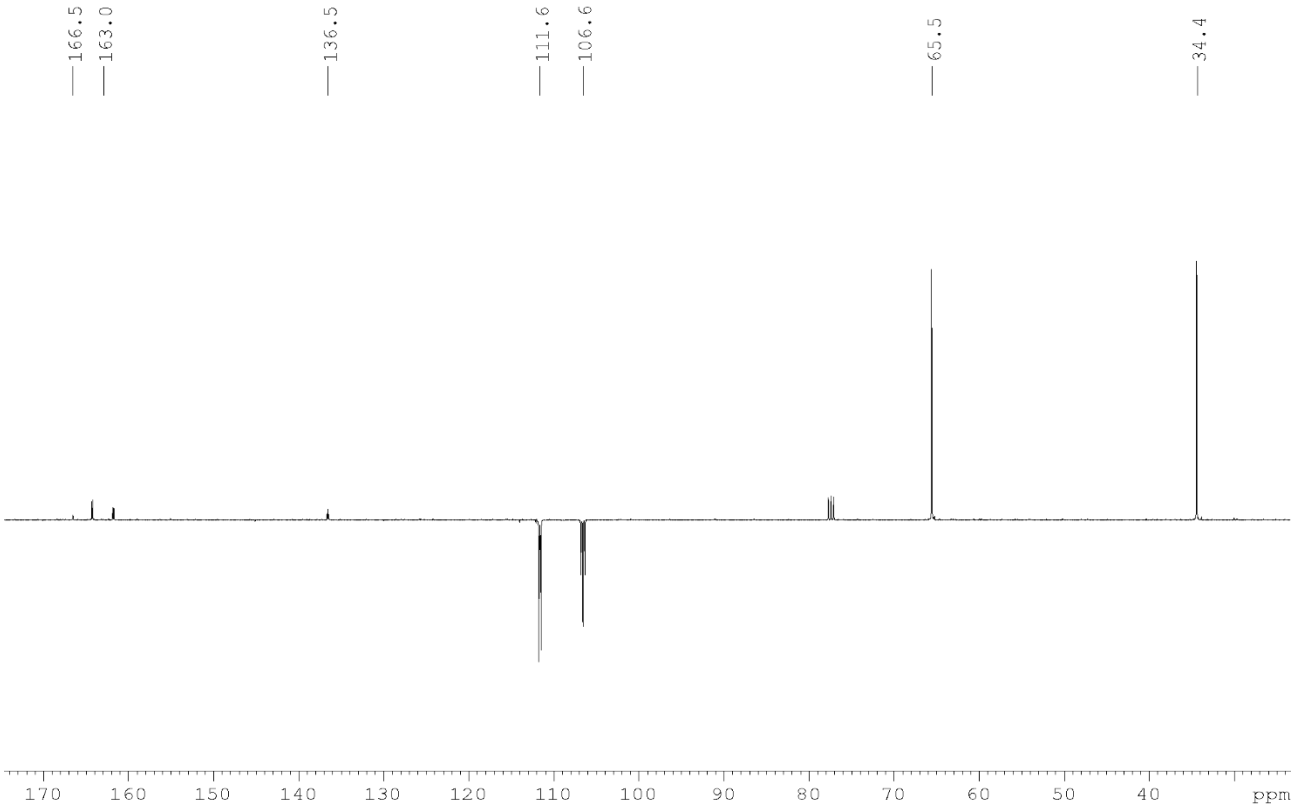
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 3-(4,5-dihydrothiazol-2-yl)aniline, **4j**



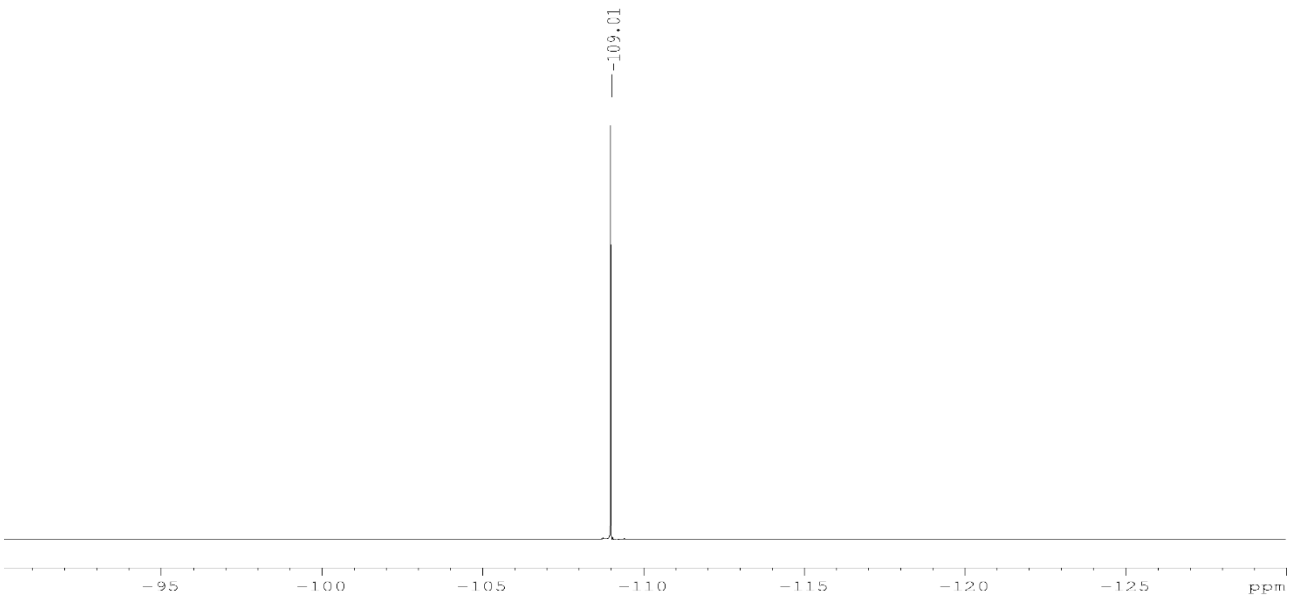
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(3,5-difluorophenyl)-4,5-dihydrothiazole, **4k**



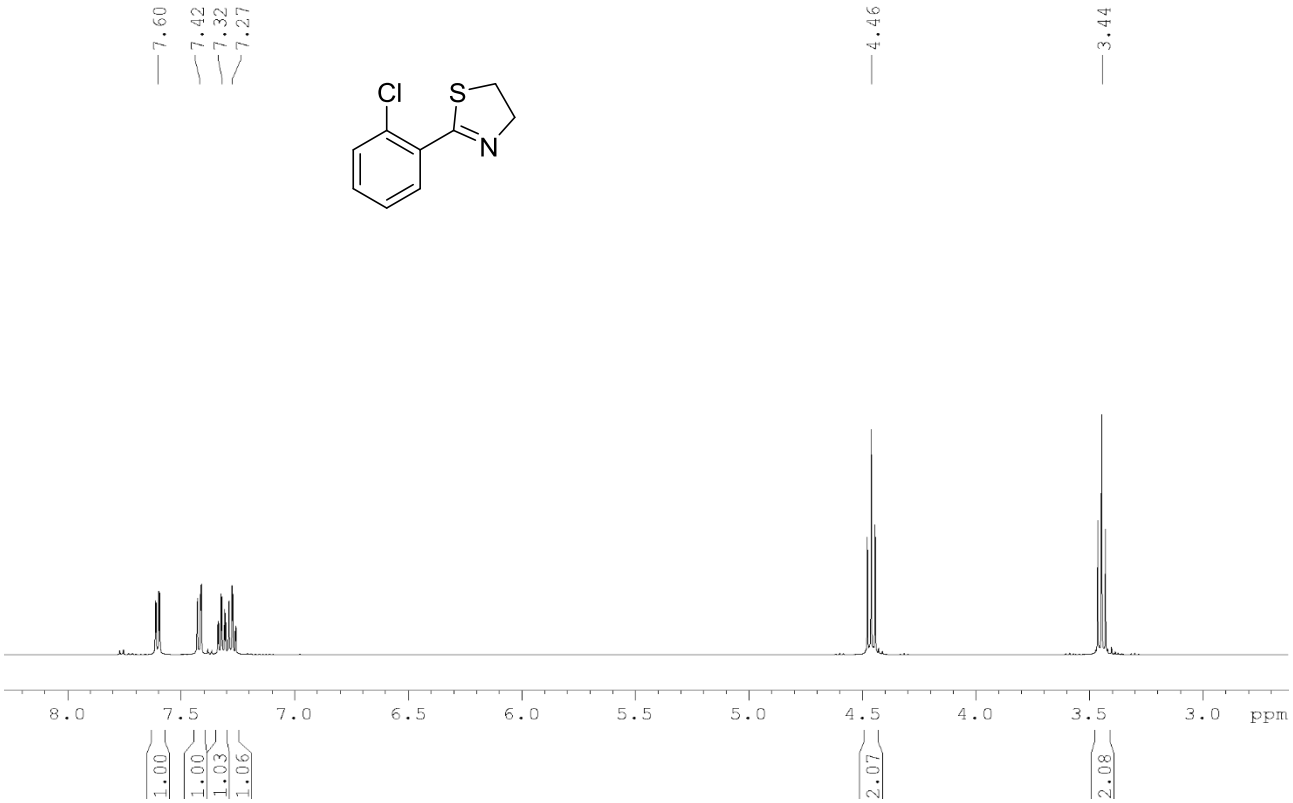
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(3,5-difluorophenyl)-4,5-dihydrothiazole, **4k**



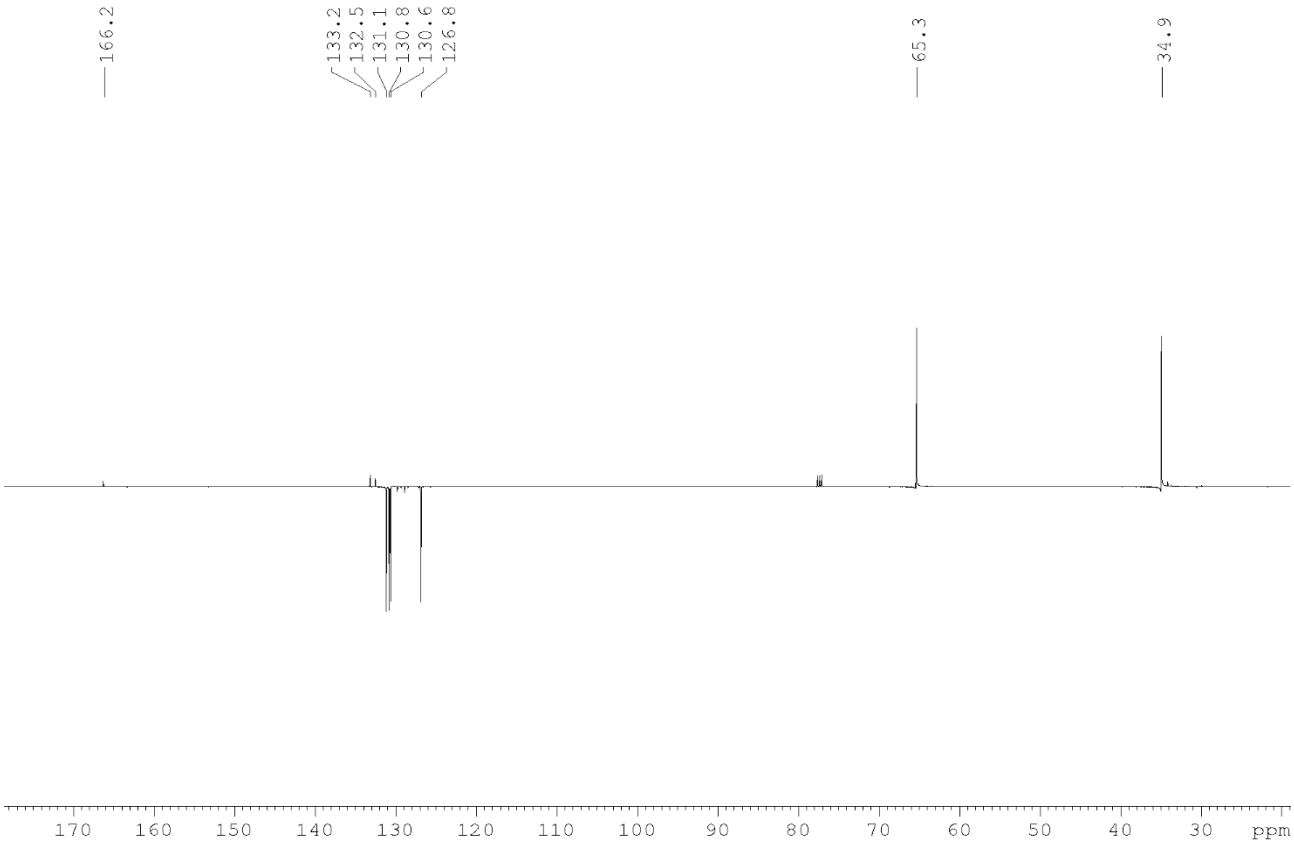
^{19}F-{^{1}H} NMR (376 MHz, 298K) of 2-(3,5-difluorophenyl)-4,5-dihydrothiazole, **4k**



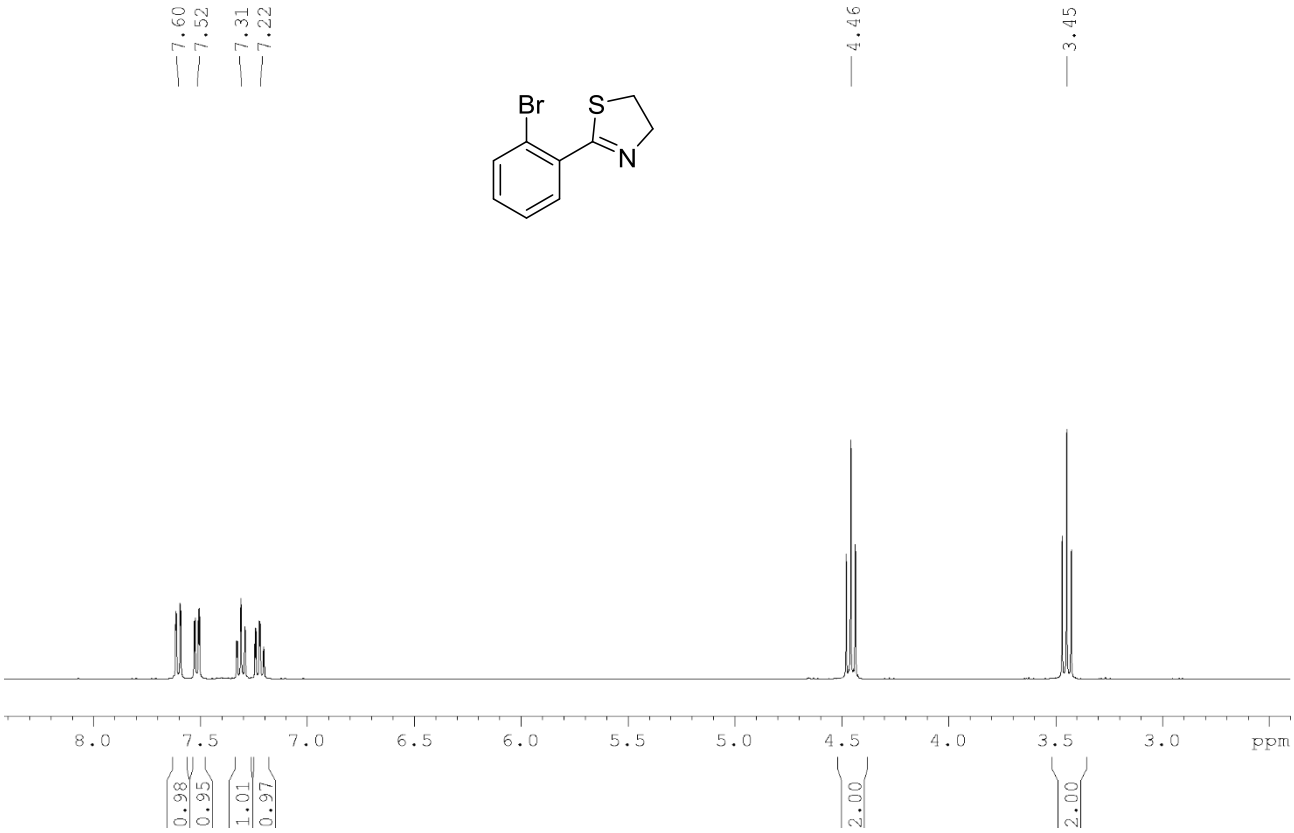
^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS) of 2-(2-chlorophenyl)-4,5-dihydrothiazole, **4l**



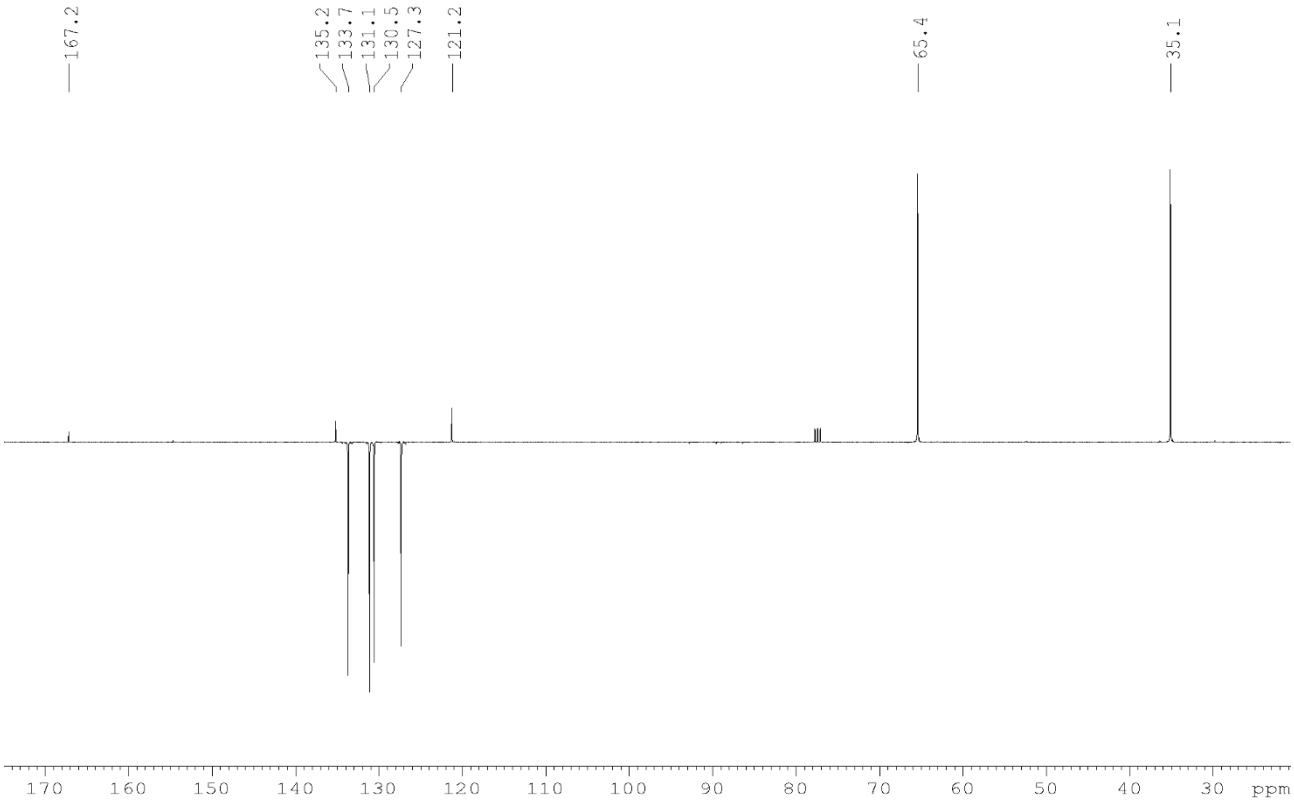
^{13}C-{^{1}H} NMR (125.7 MHz, $CDCl_3$, 298K) of 2-(2-chlorophenyl)-4,5-dihydrothiazole, **4l**



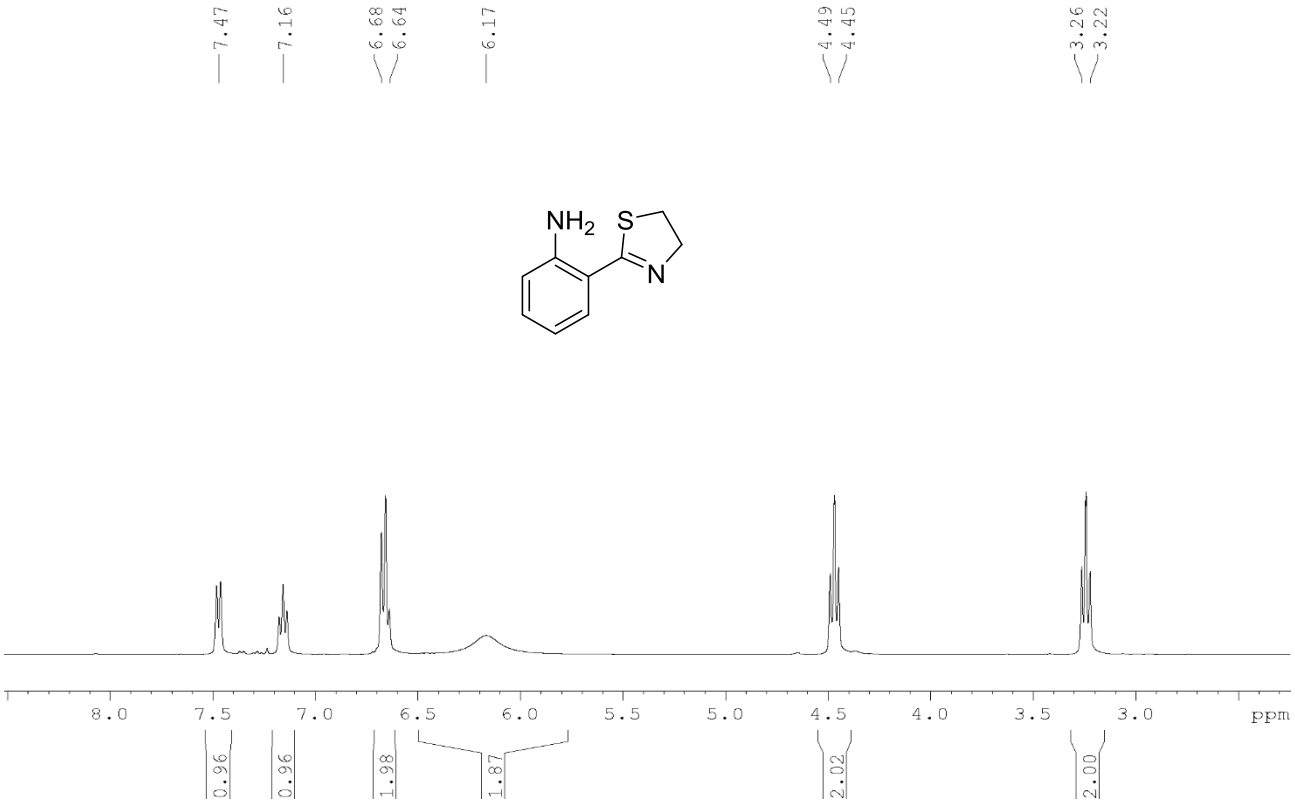
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(2-bromophenyl)-4,5-dihydrothiazole, **4m**



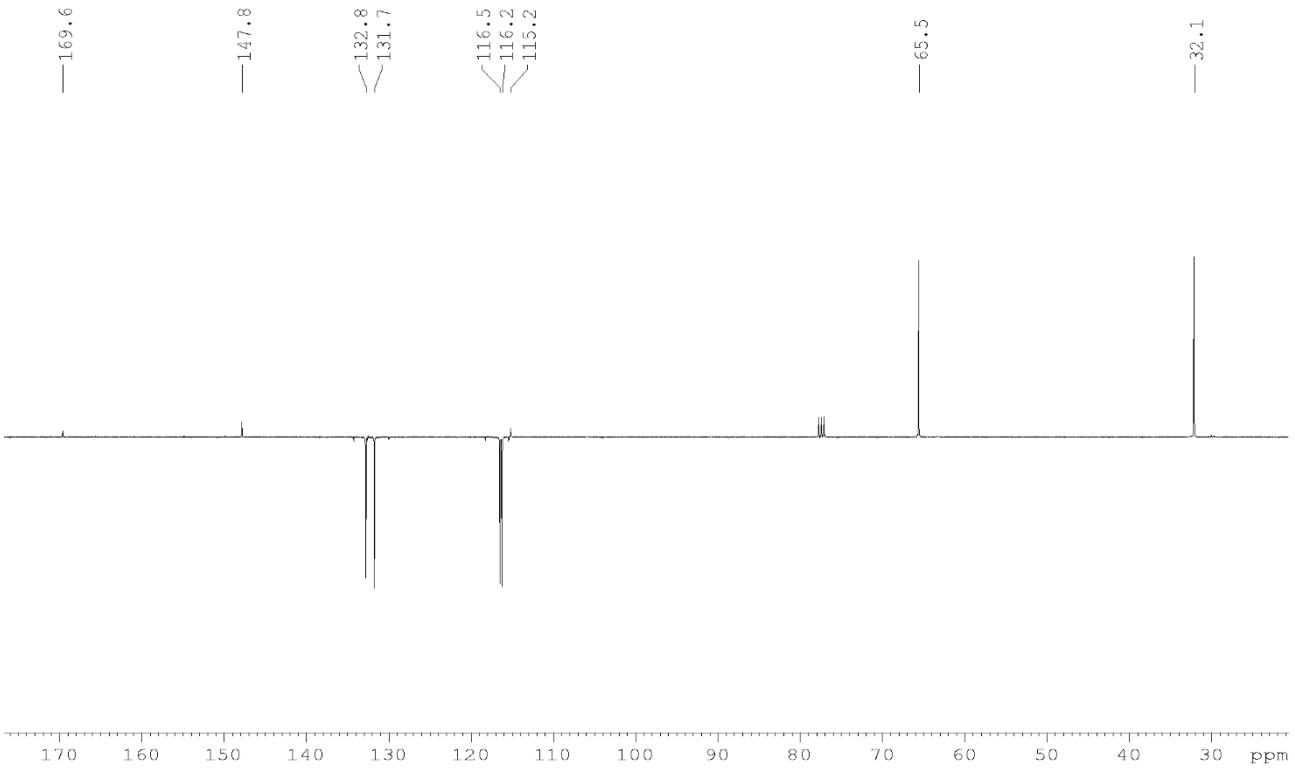
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(2-bromophenyl)-4,5-dihydrothiazole, **4m**



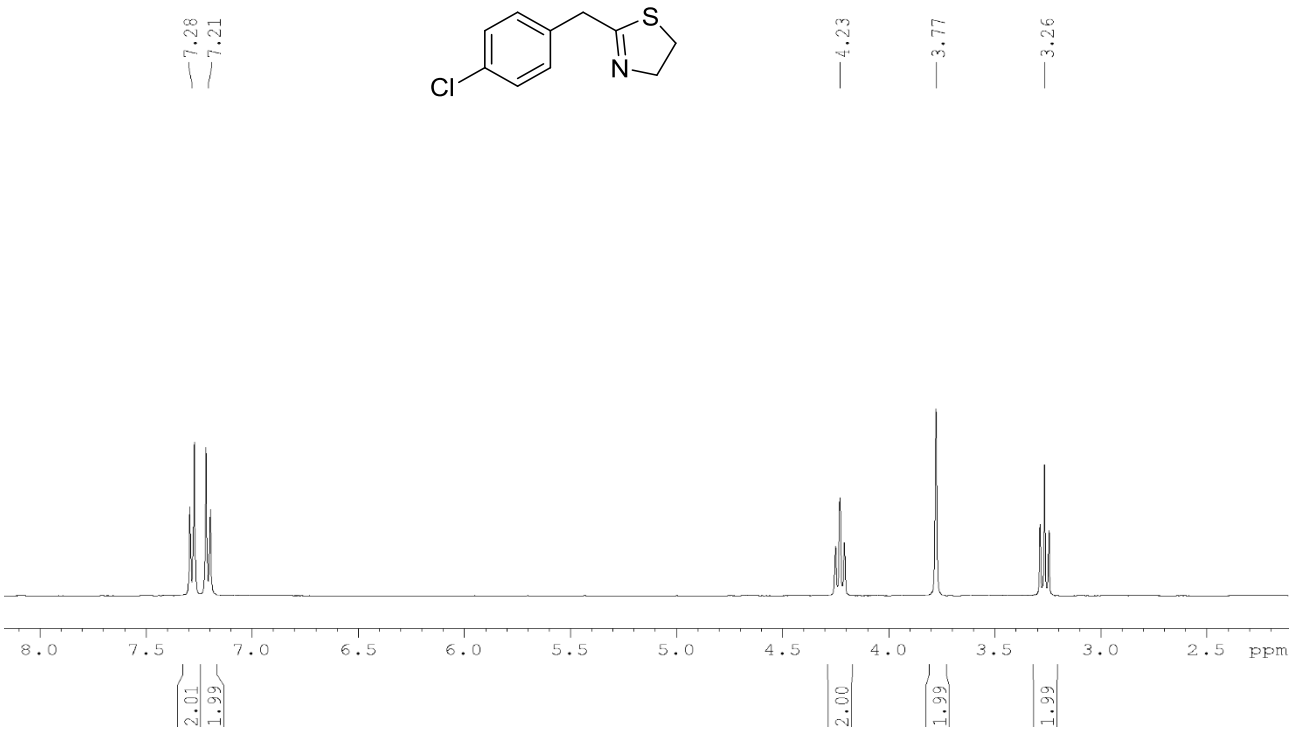
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(4,5-dihydrothiazol-2-yl)aniline, **4n**



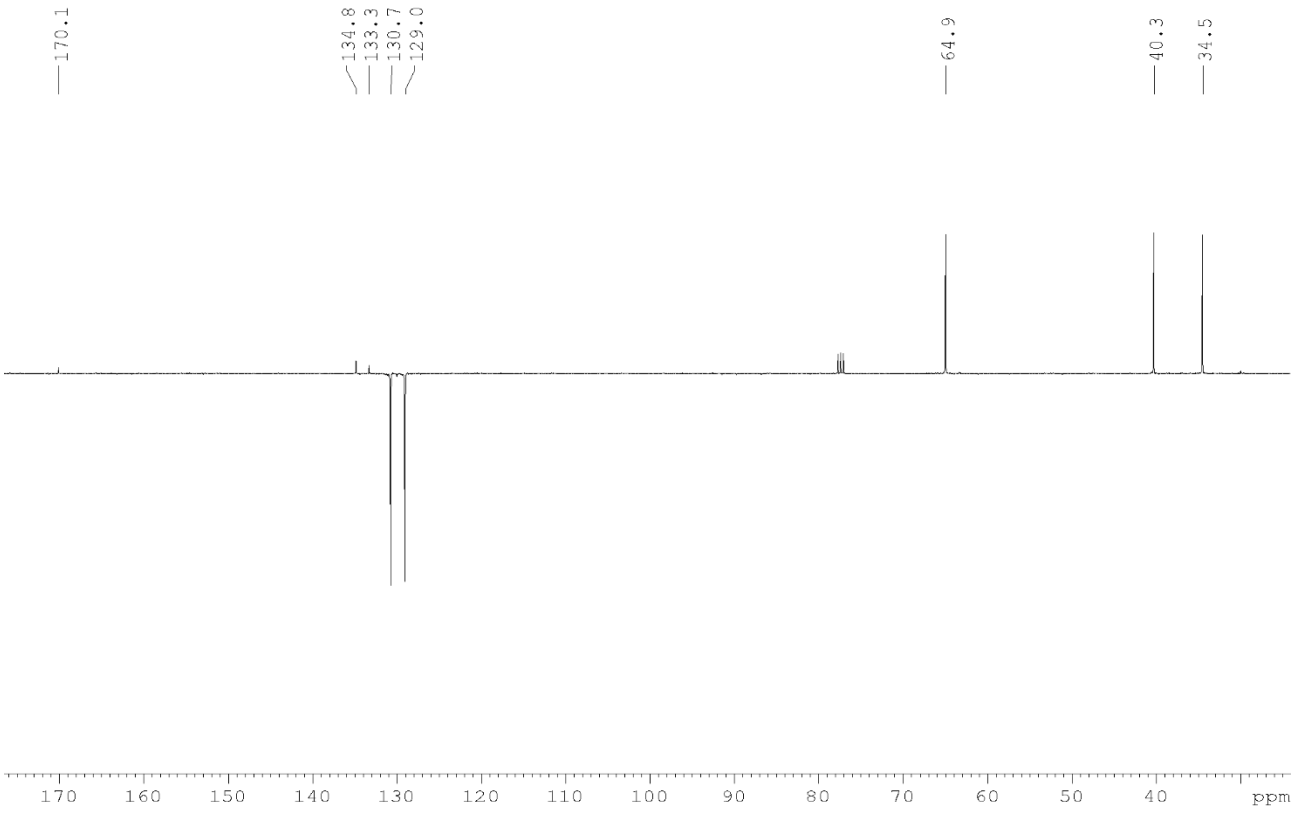
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(4,5-dihydrothiazol-2-yl)aniline, **4n**



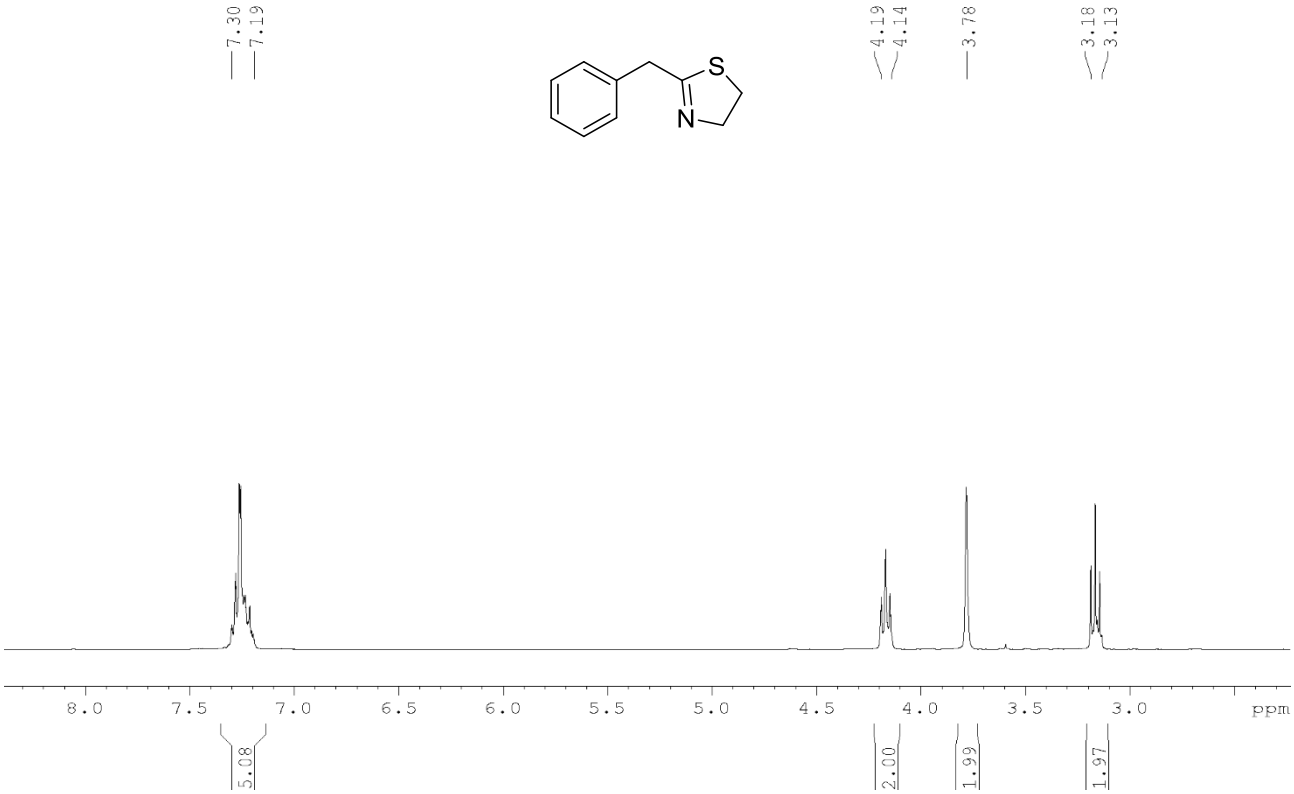
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(4-chlorobenzyl)-4,5-dihydrothiazole, **4o**



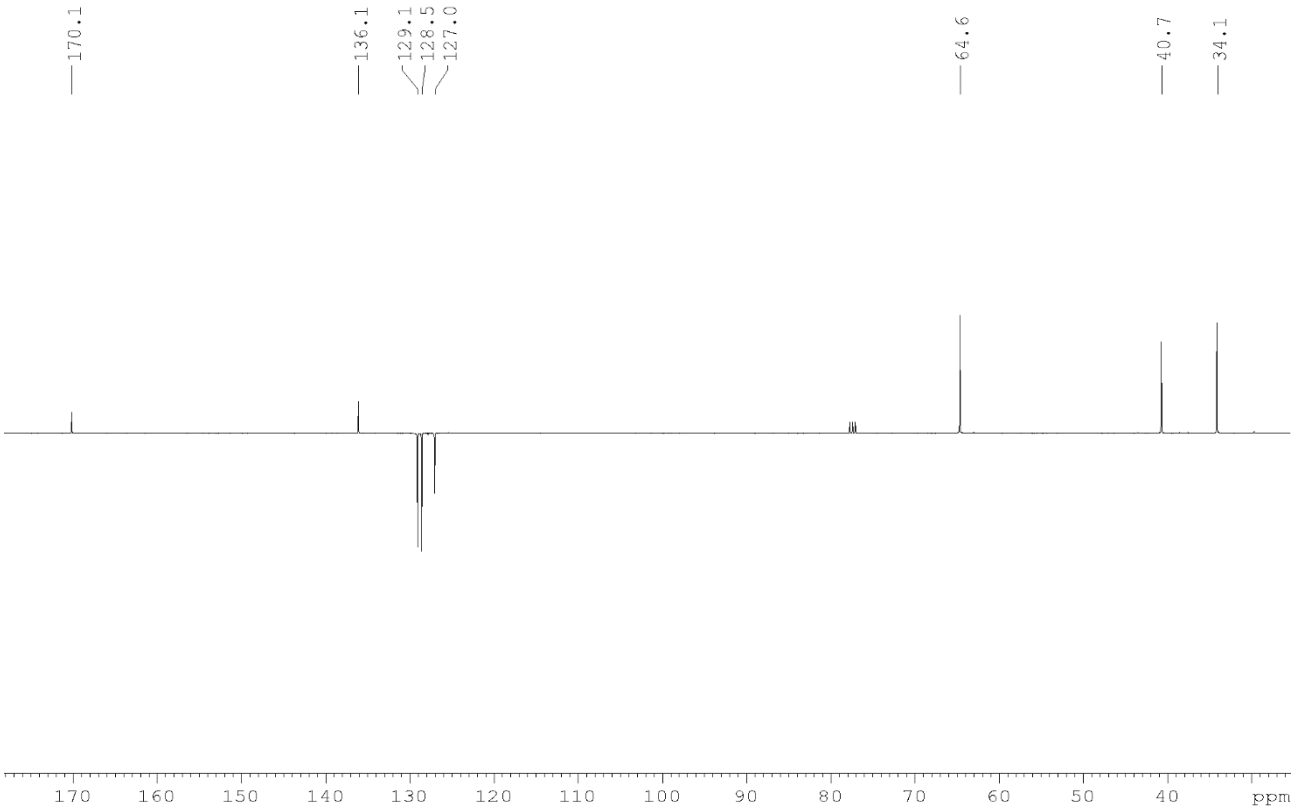
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(4-chlorobenzyl)-4,5-dihydrothiazole, **4o**



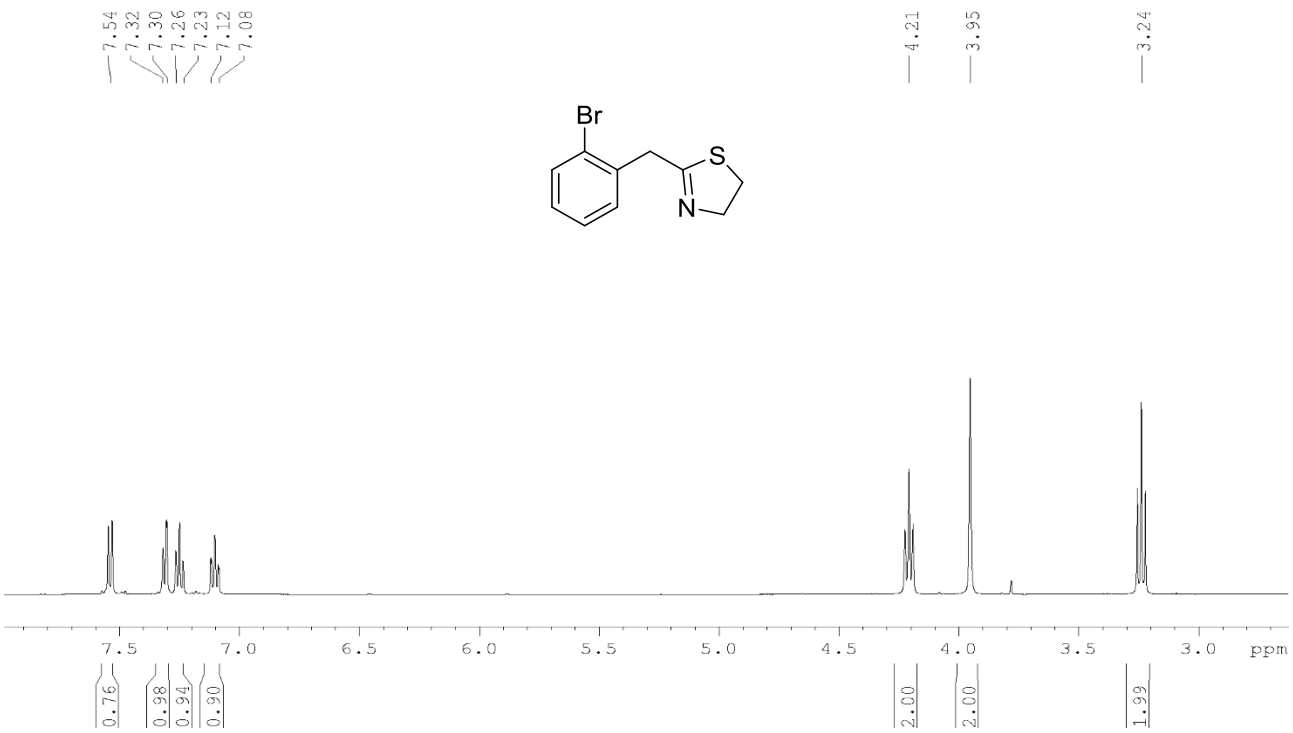
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-benzyl-4,5-dihydrothiazole, **4p**



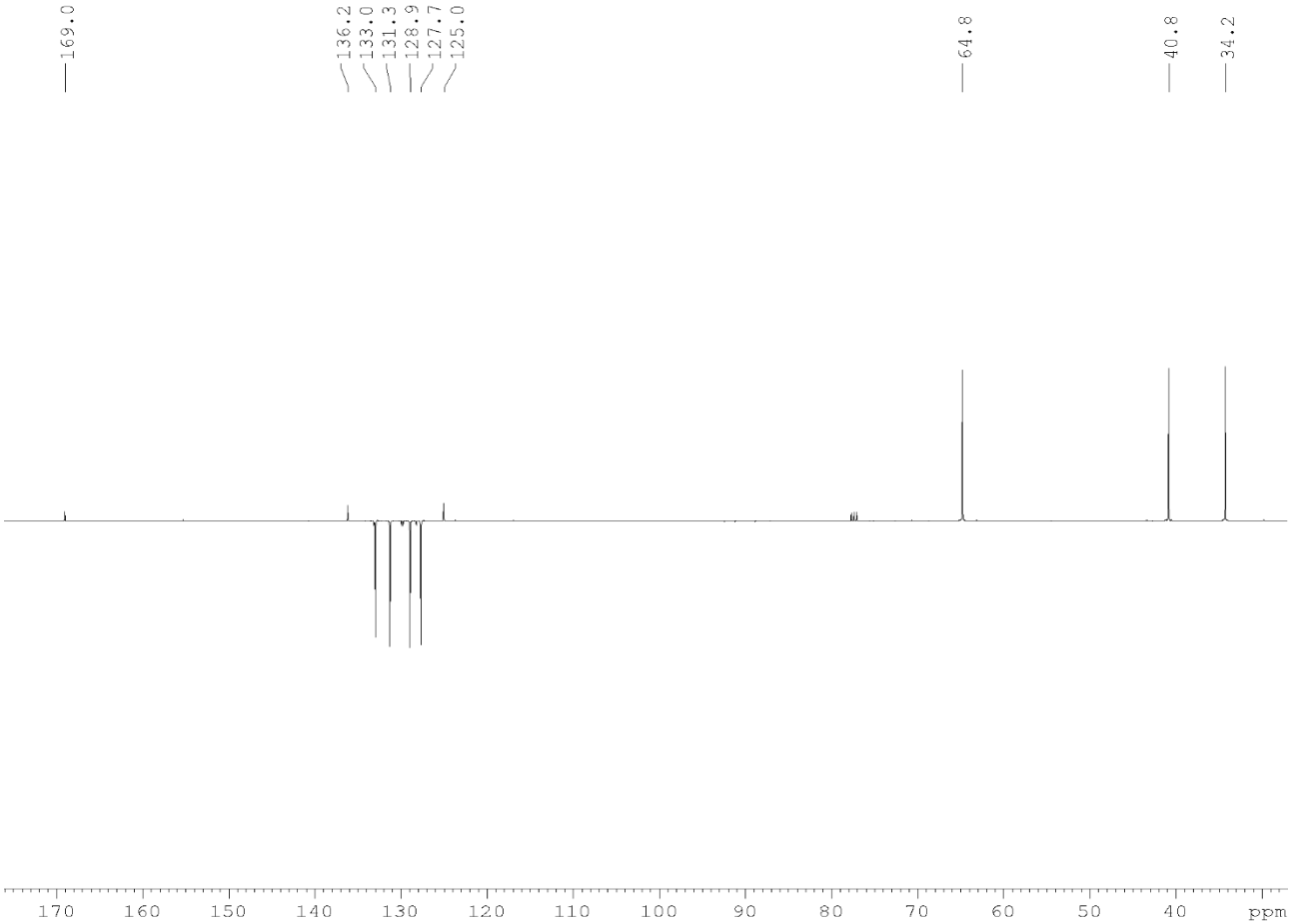
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-benzyl-4,5-dihydrothiazole, **4p**



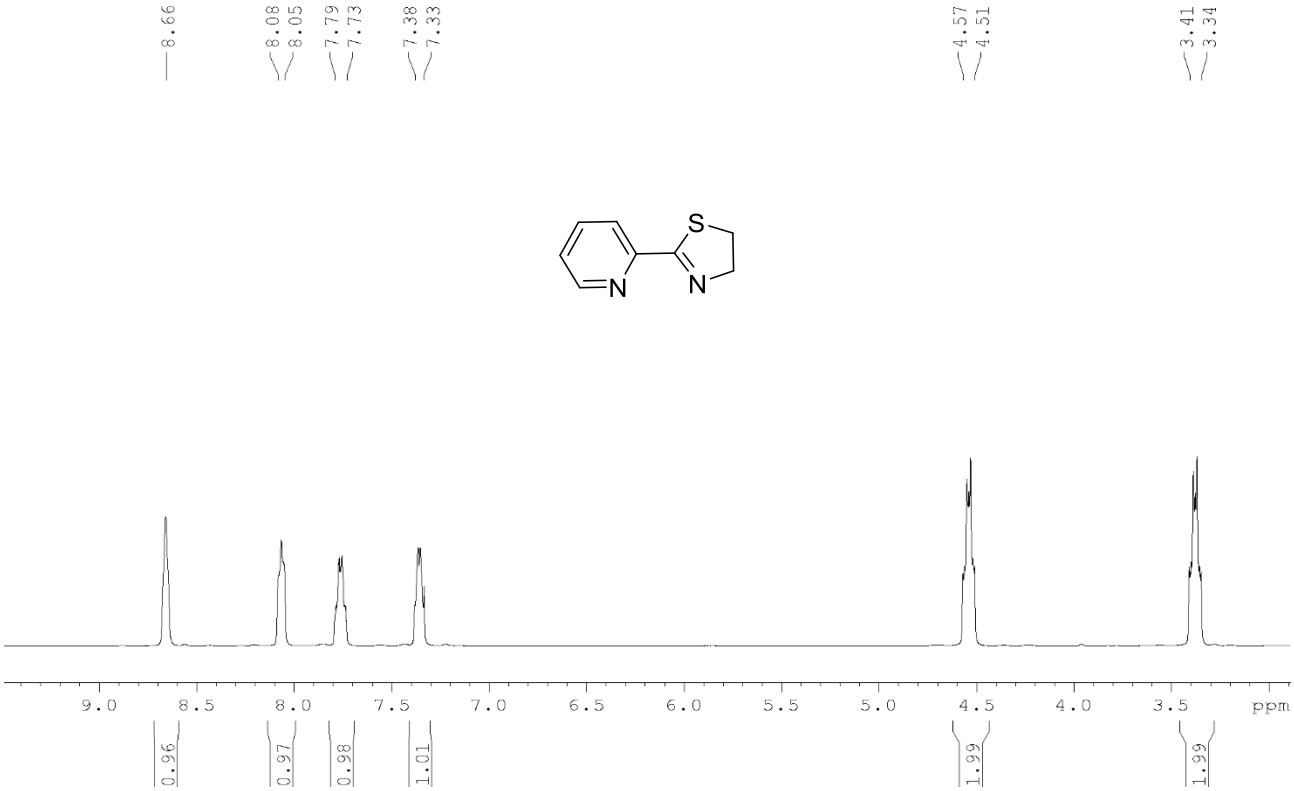
^{1}H NMR (500 MHz, $CDCl_3$, 298K, TMS) of 2-(2-bromobenzyl)-4,5-dihydrothiazole, **4q**



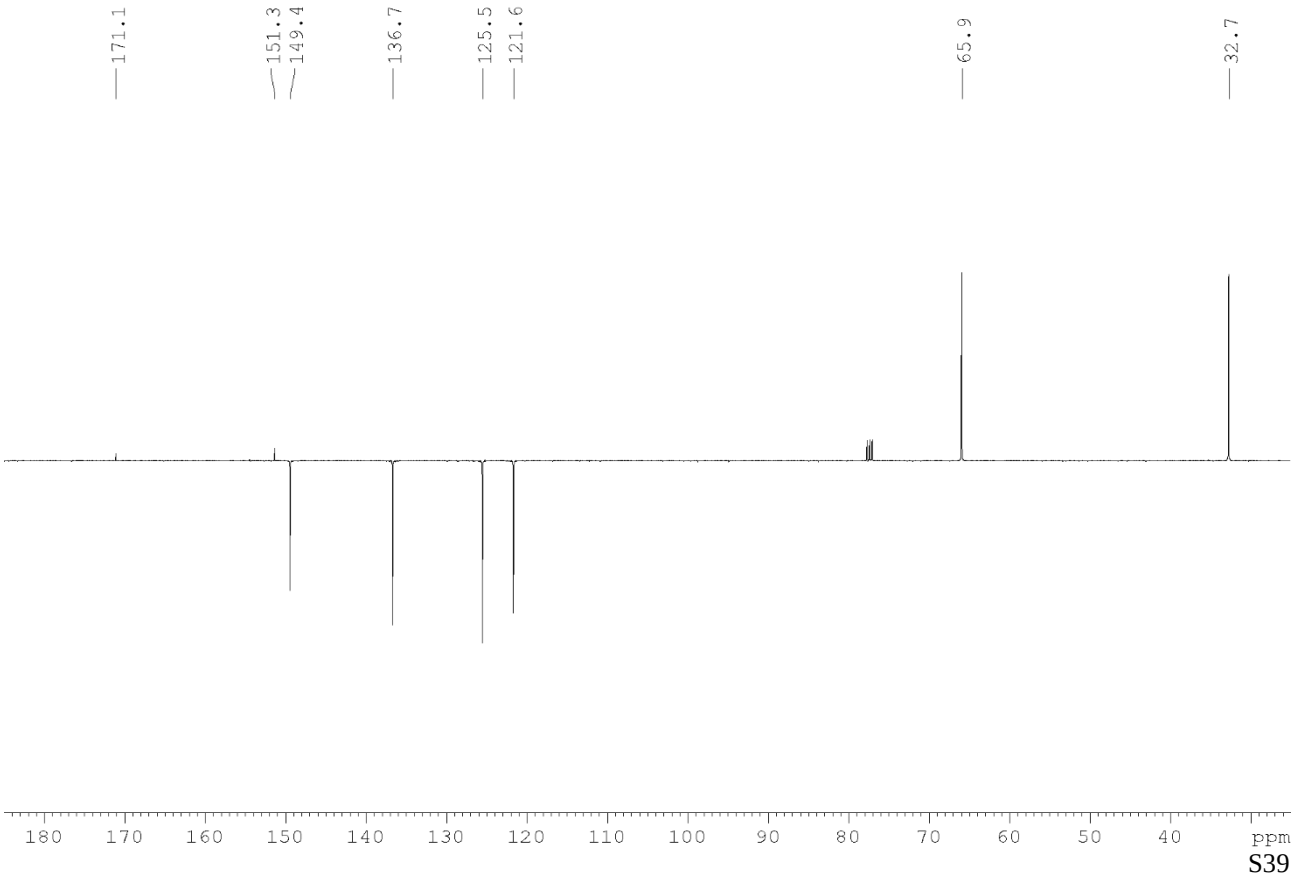
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(2-bromobenzyl)-4,5-dihydrothiazole, **4q**



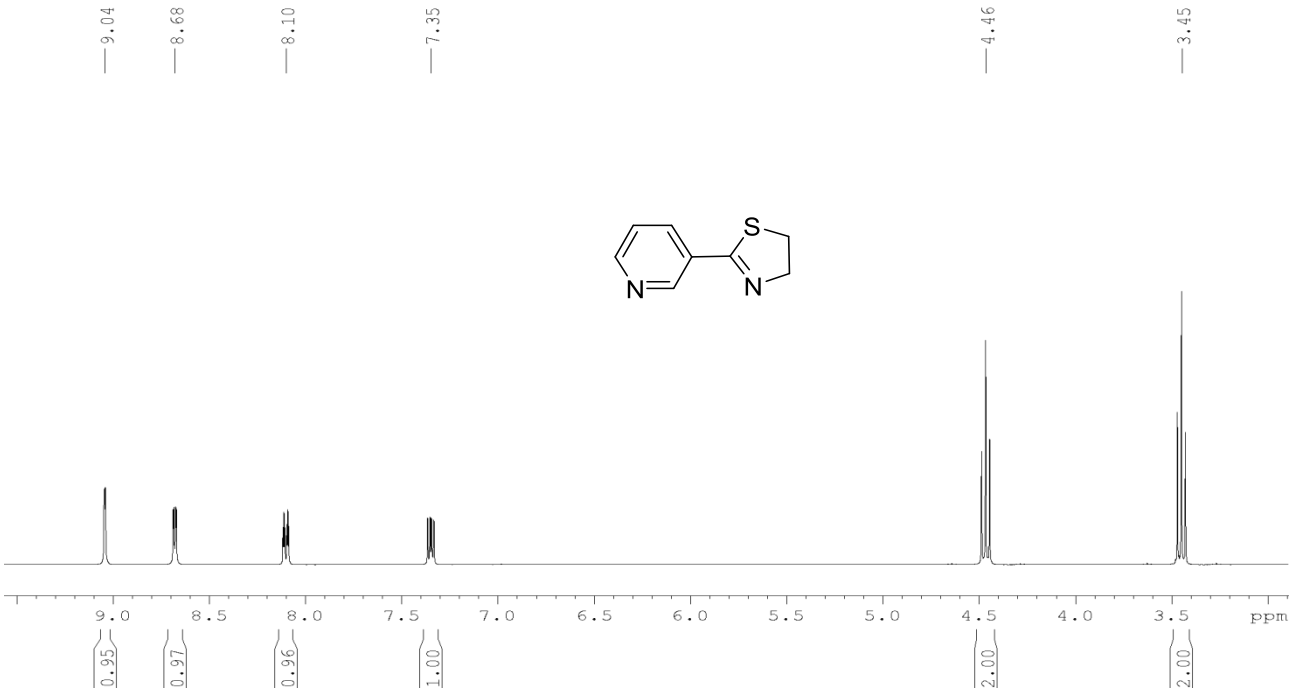
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(pyridin-2-yl)-4,5-dihydrothiazole, **4r**



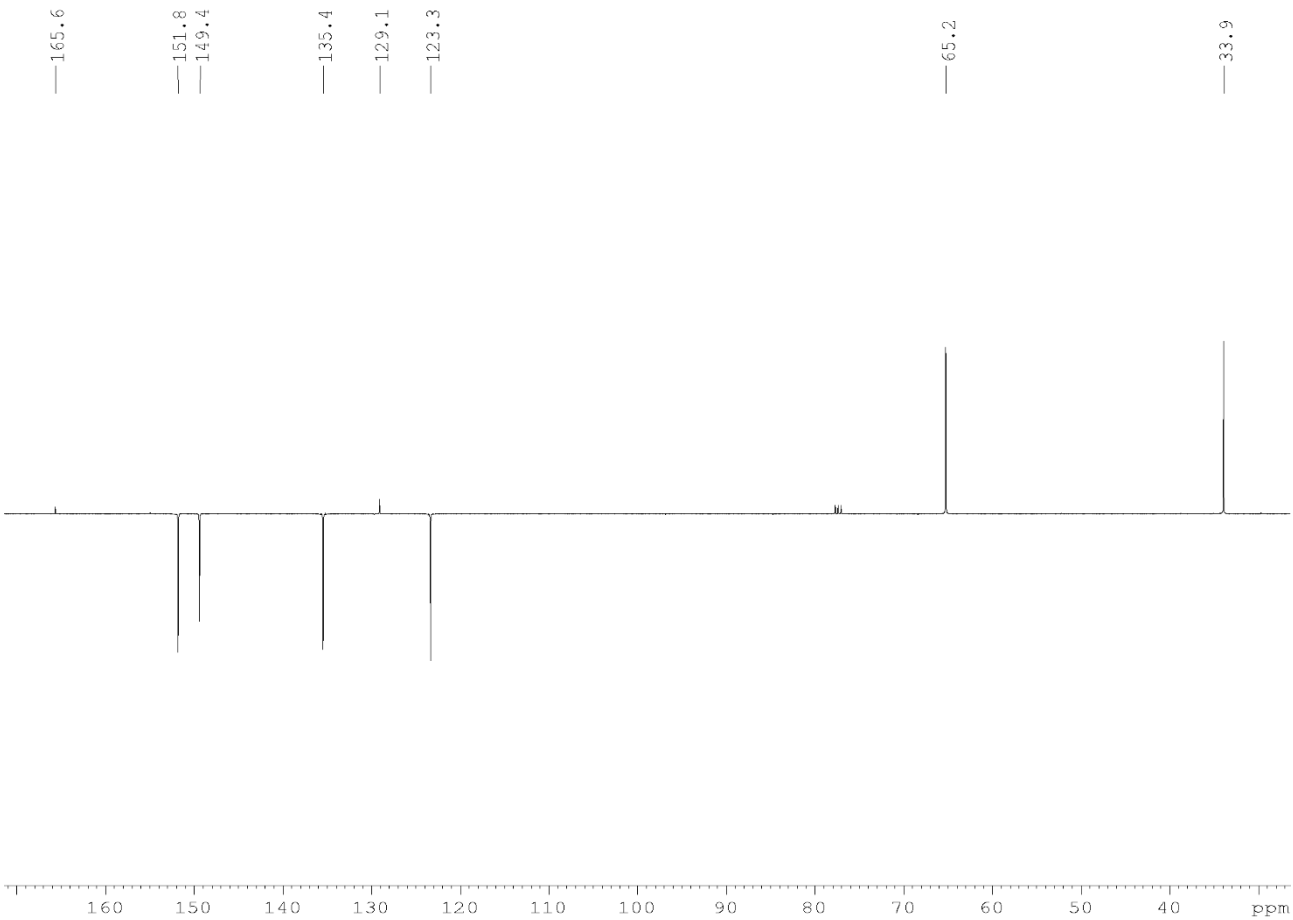
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(pyridin-2-yl)-4,5-dihydrothiazole, **4r**



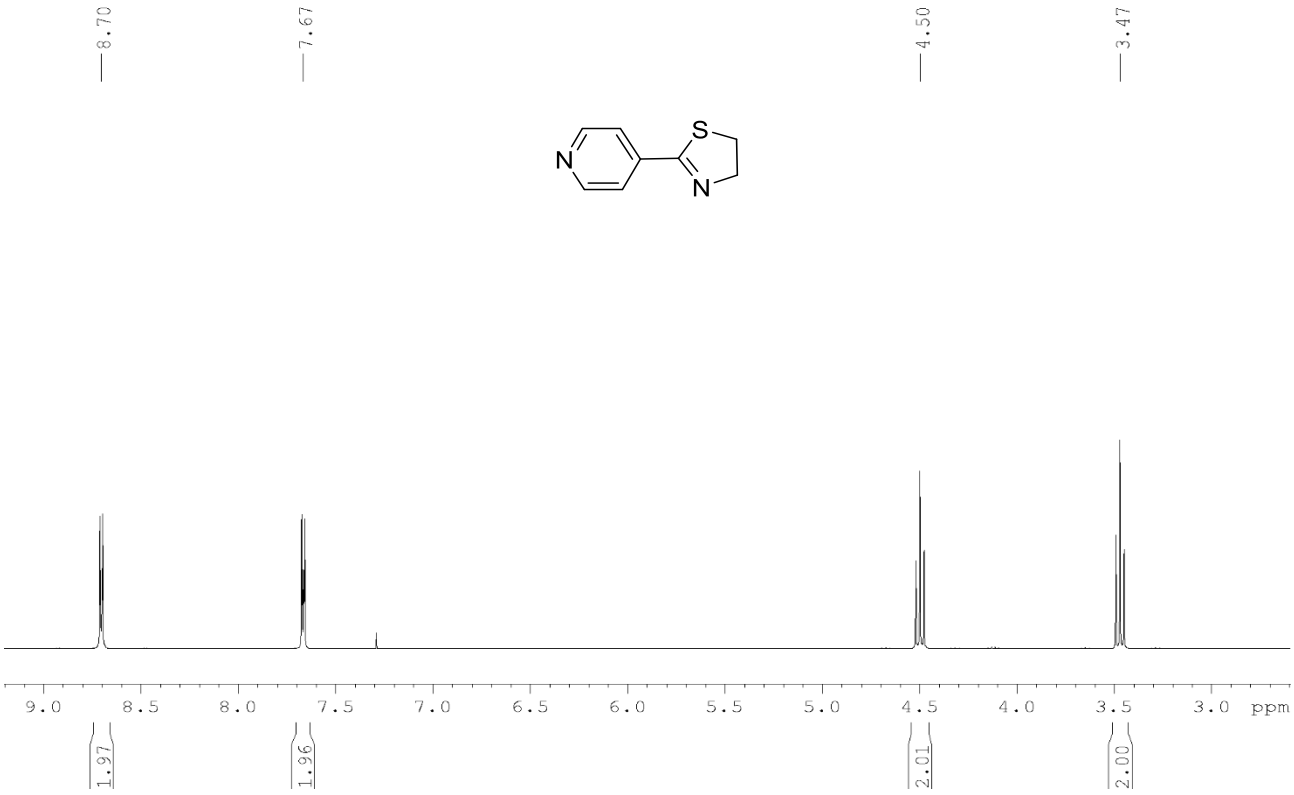
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(pyridin-3-yl)-4,5-dihydrothiazole, **4s**



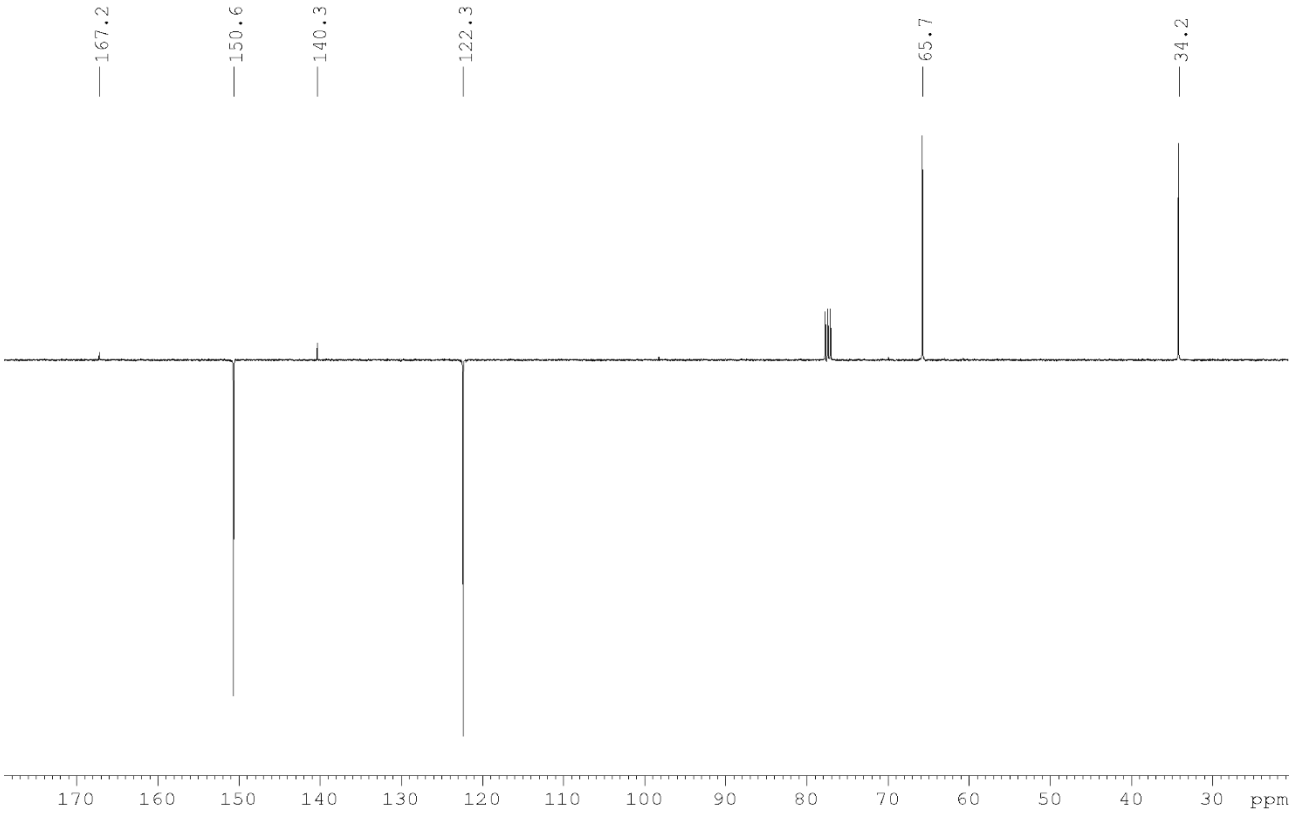
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(pyridin-3-yl)-4,5-dihydrothiazole, **4s**



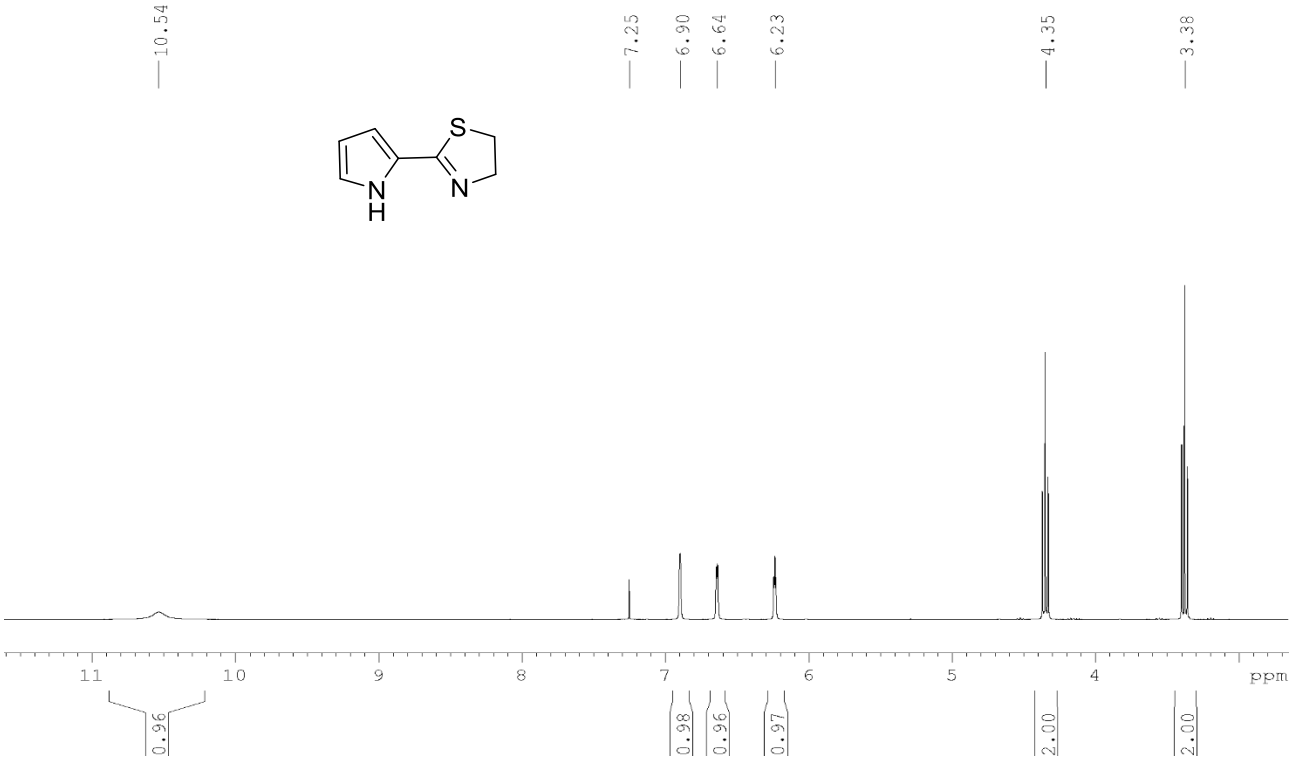
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(pyridin-4-yl)-4,5-dihydrothiazole, **4t**



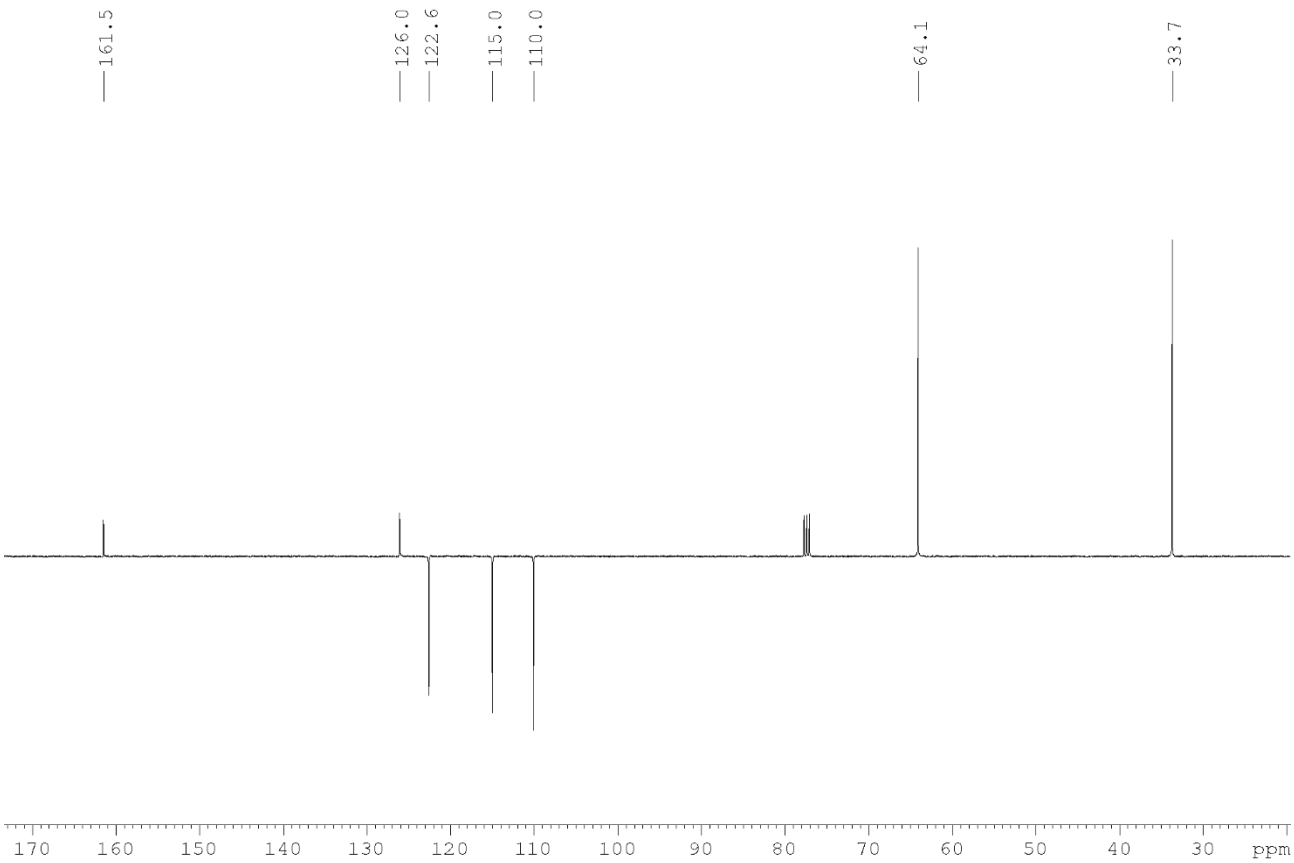
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(pyridin-4-yl)-4,5-dihydrothiazole, **4t**



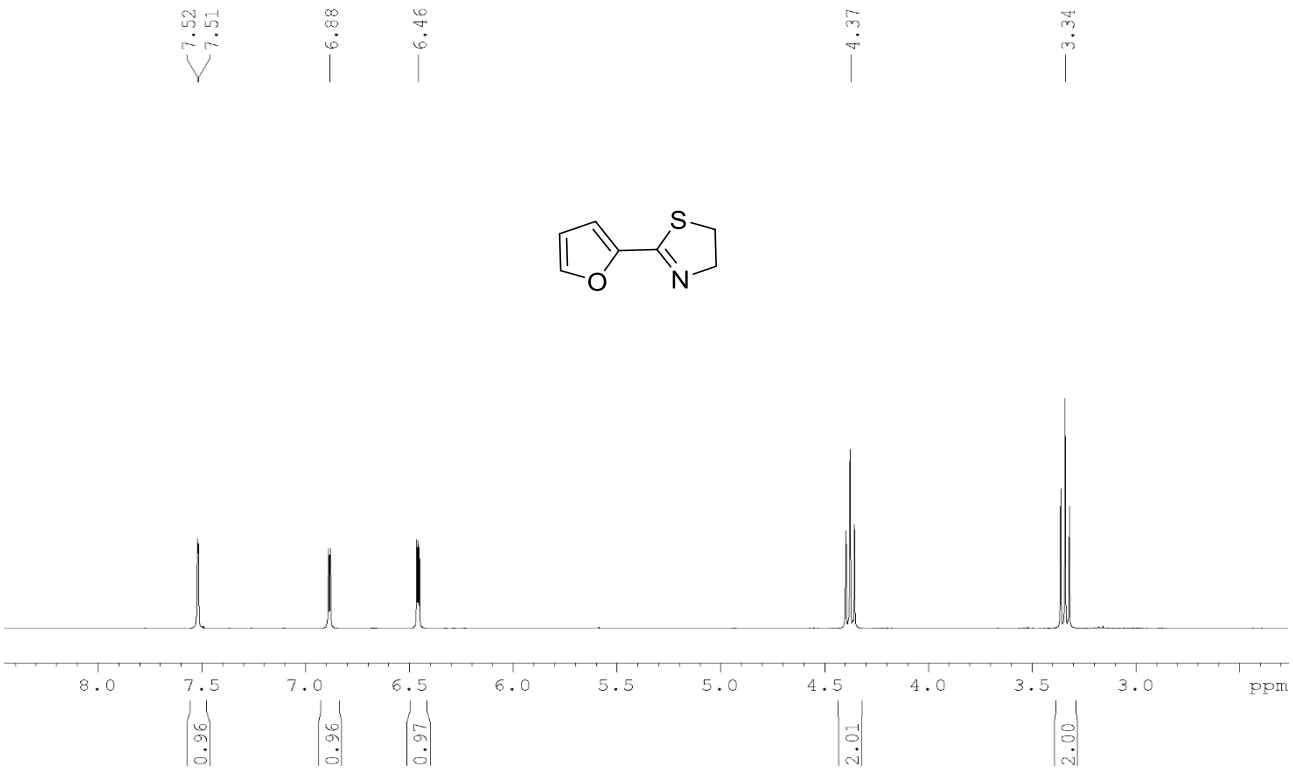
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(1*H*-pyrrol-2-yl)-4,5-dihydrothiazole, **4u**



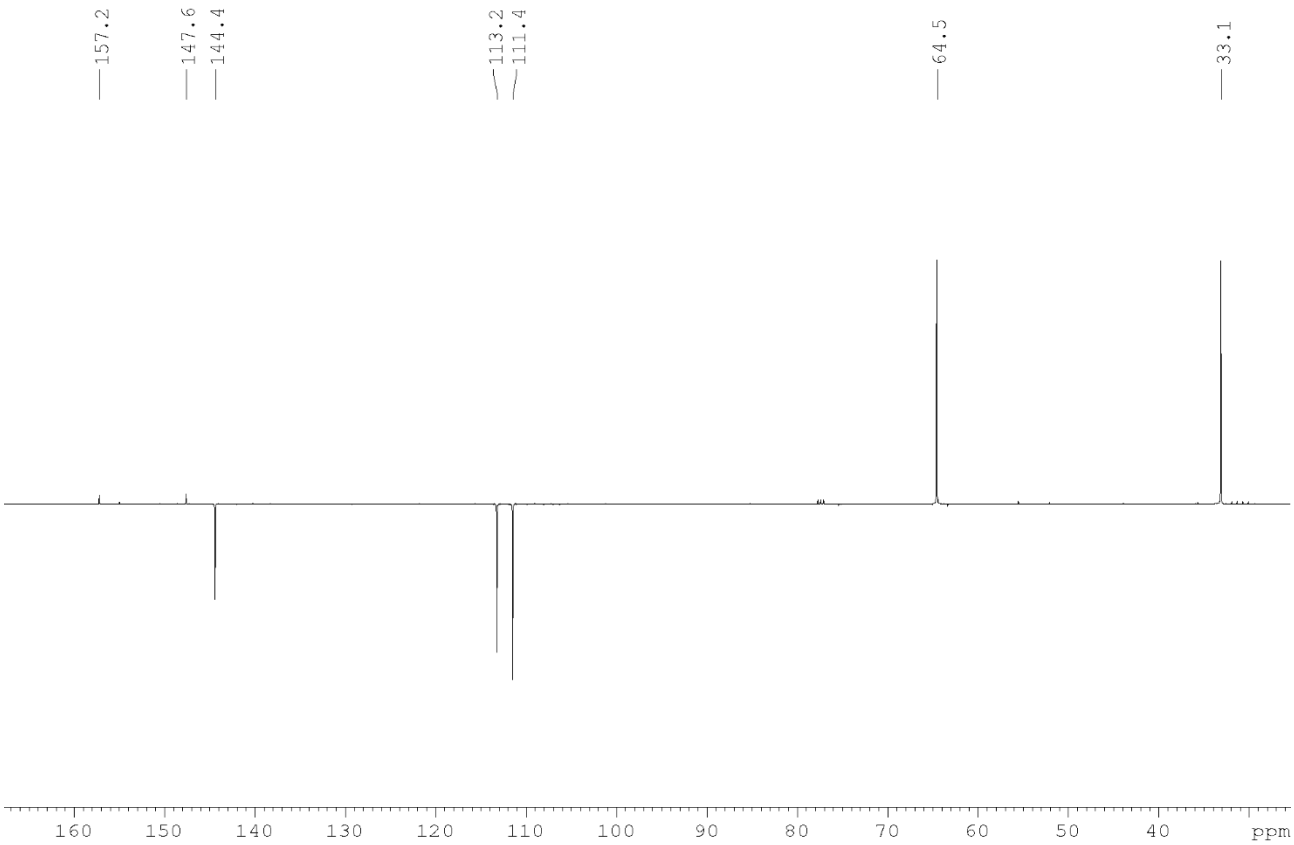
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(1*H*-pyrrol-2-yl)-4,5-dihydrothiazole, **4u**



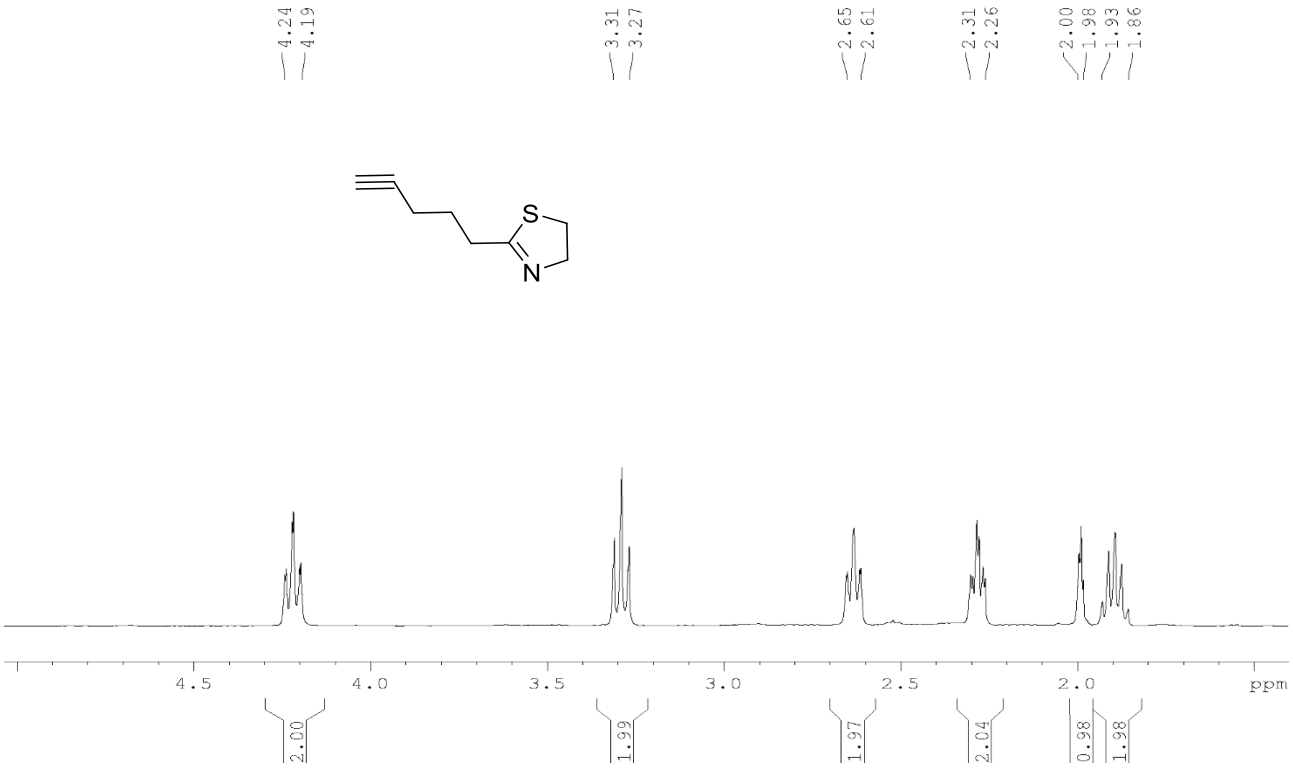
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(2-furanyl)-4,5-dihydrothiazole, **4v**



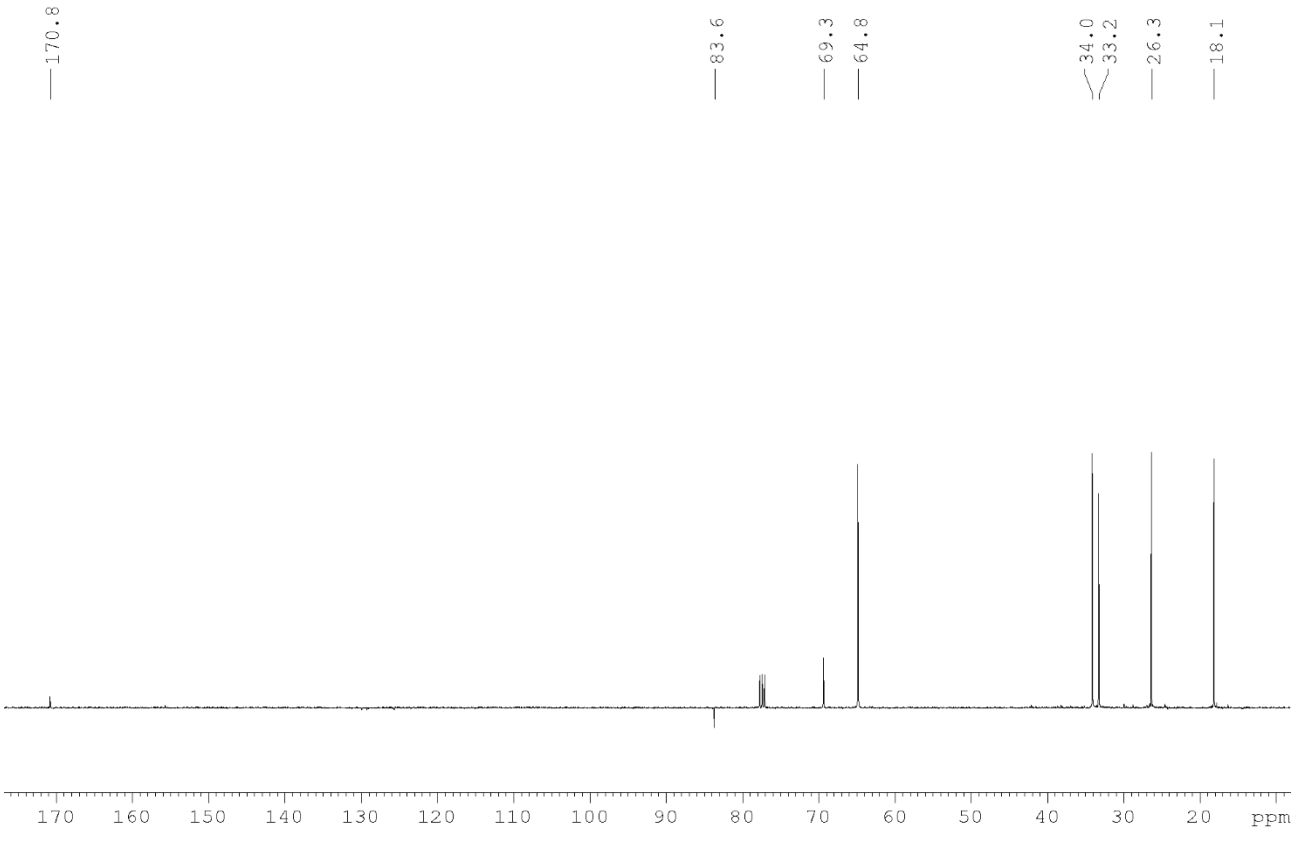
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(2-furanyl)-4,5-dihydrothiazole, **4v**



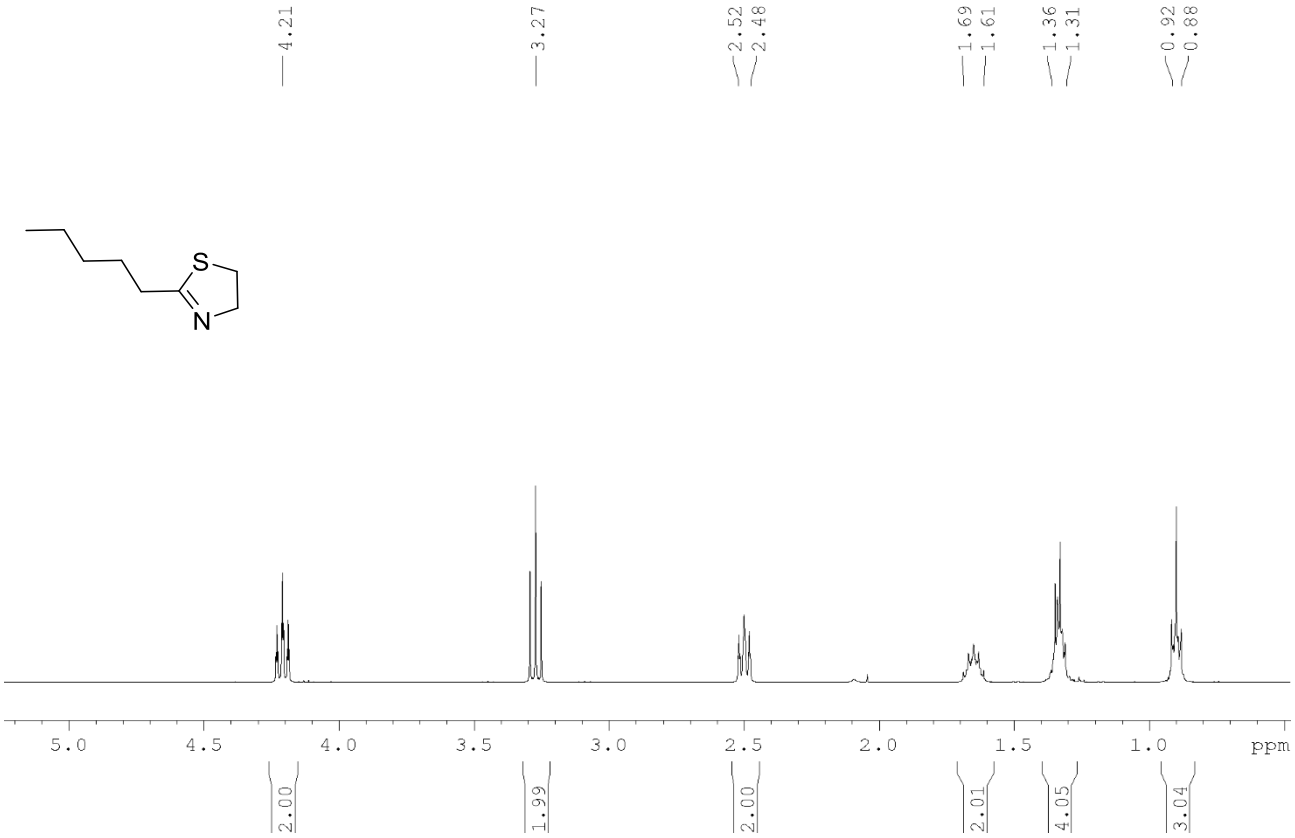
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-(pent-4-yn-1-yl)-4,5-dihydrothiazole, **4w**



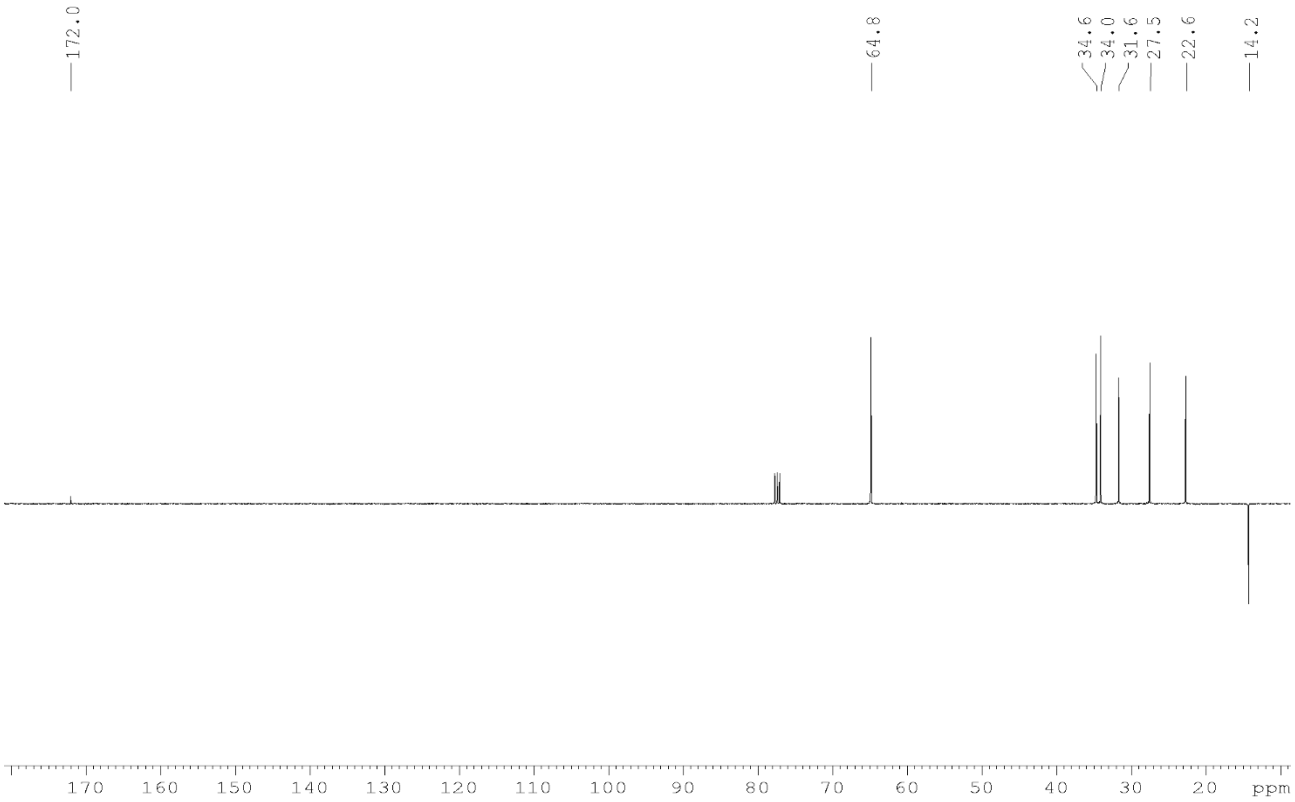
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-(pent-4-yn-1-yl)-4,5-dihydrothiazole, **4w**



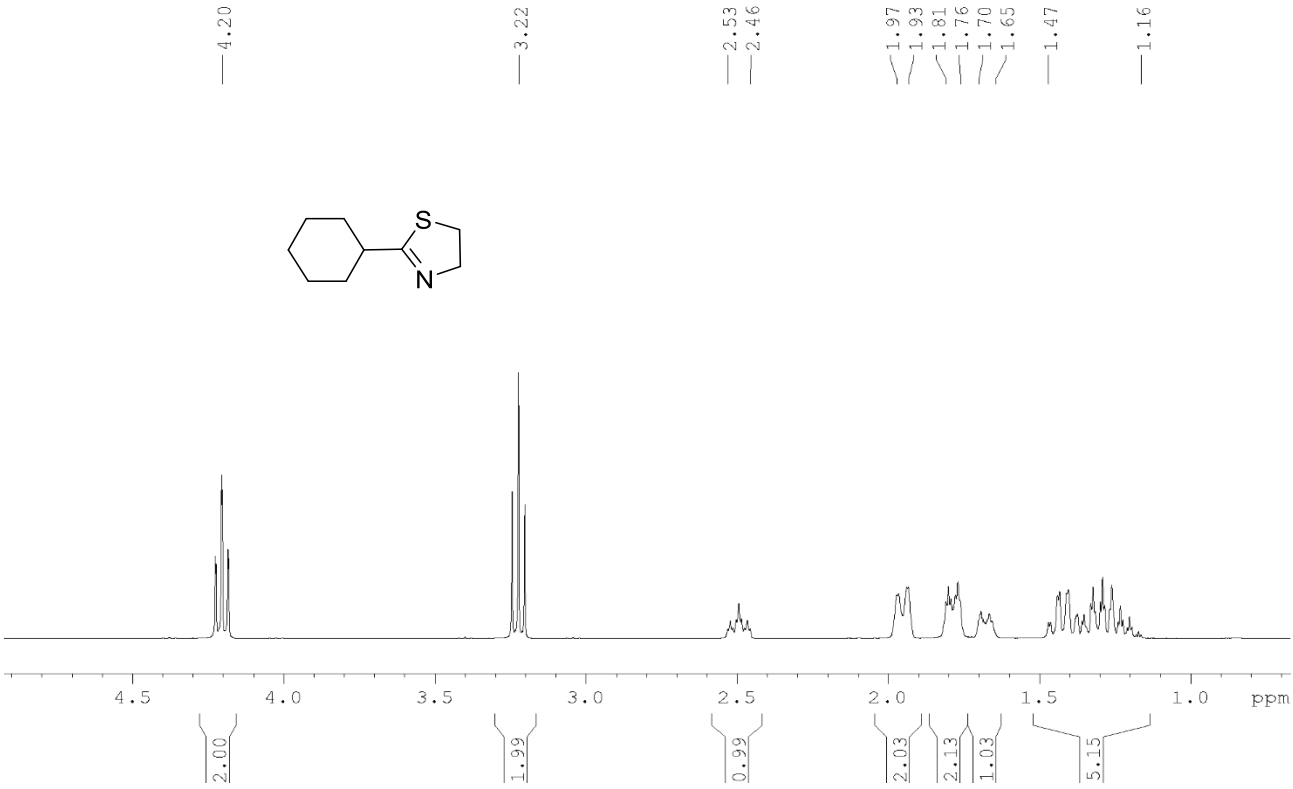
^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-pentyl-4,5-dihydrothiazole, **4x**



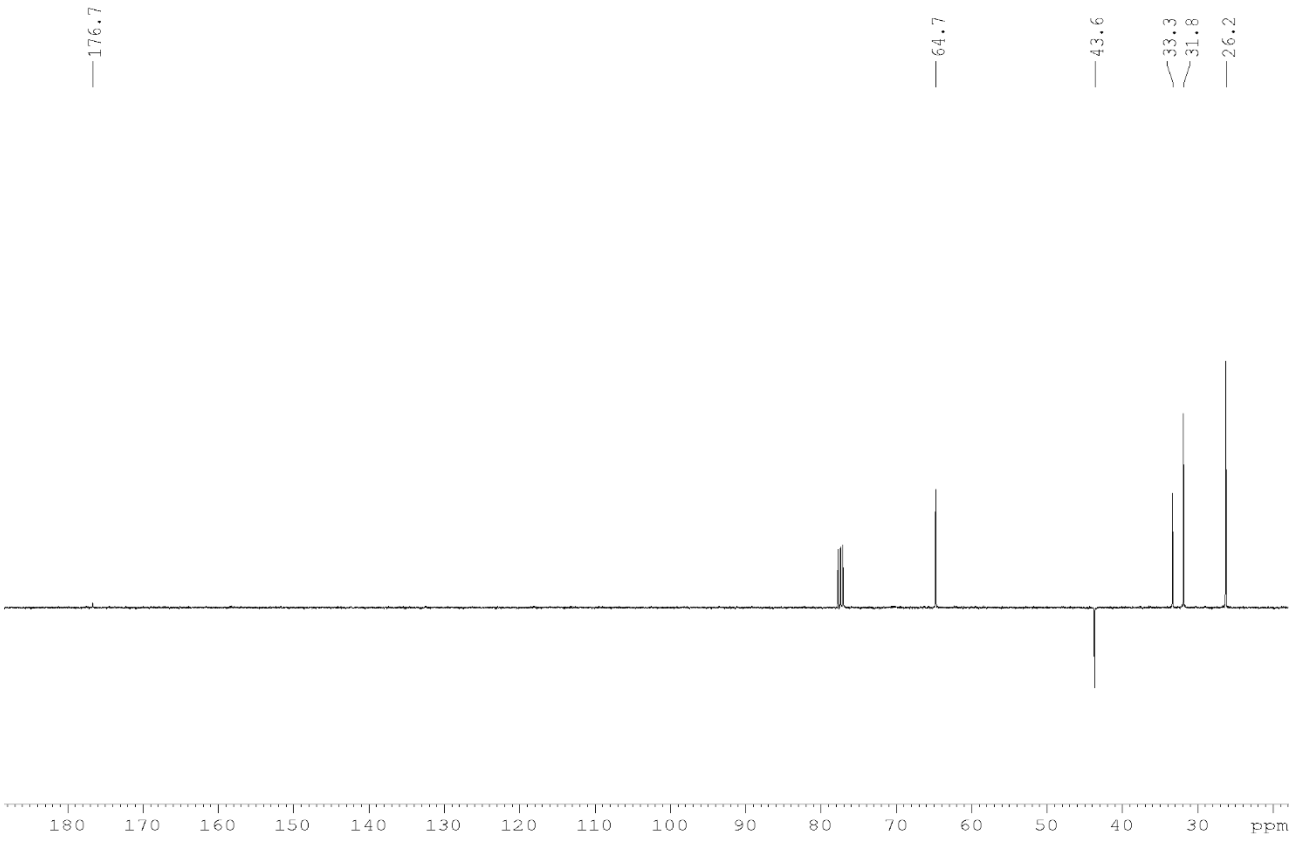
^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-pentyl-4,5-dihydrothiazole, **4x**



^{1}H NMR (400 MHz, $CDCl_3$, 298K, TMS) of 2-cyclohexyl-4,5-dihydrothiazole, **4y**



^{13}C-{^{1}H} NMR (75 MHz, $CDCl_3$, 298K) of 2-cyclohexyl-4,5-dihydrothiazole, **4y**



6 References

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