ESI

Ruthenium Catalyzed Intramolecular C-S coupling Reactions: Synthetic Scope and Mechanistic Insight

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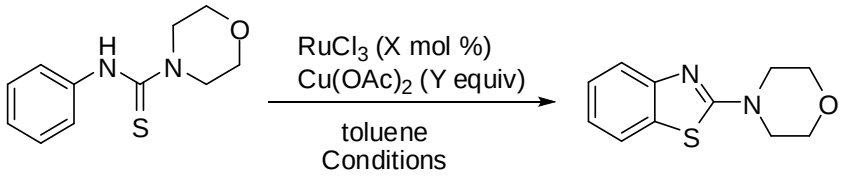
1. General Considerations

All the reactions were carried out under argon atmosphere using standard Schlenk techniques. Anhydrous DCE was purchased from Sigma-Aldrich. N-arylthioureas 8 were readily prepared by reacting corresponding arylthiocyanates and amines[1]. All other reagents were purchased from Sigma Aldrich or Spectrochem and used as such without purification. Analytical TLC were performed using 2.5 ×5 cm plate coated with 0.25 mm thickness of silica gel (60F-254 Merck) and visualization was accomplished with UV light or I_2/ $KMnO_4$ staining. ^1H and ^{13}C NMR spectra were obtained from Bruker's Ascend 500 MHz spectrophotometer operating at 500.3 MHz for ^1H and 125.8 MHz for ^{13}C experiments. The chemical shifts are reported in ppm scale with respect to $CDCl_3$ (7.269 ppm) for ^1H and (77.00 ppm) for ^{13}C NMR as internal standard.The abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, brs = broad singlet & br = broad signal. Melting Points were recorded on Buchi M-655 Melting point apparatus and are uncorrected. Kinetic studies were performed on HPLC system LC-2010CHT (M/s Shimadzu Co Ltd Tokya Japan) using C-18 RP HPLC column (C18G, 250 x 4.6 mm, 5 µm, Spinco Biotech Pvt Ltd, Mumbai, India). The mobile phase consisted of water and acetonitrile in 40:60 v/v ratio at a flow rate of 1.0 mL/ min at the scanning wavelength of 254 nm. High resolution mass spectra (ESI-HRMS) were measured with a Waters GCT Premier-CAB155 instrument and accurate masses were reported for the molecular ion (M^+). All the computational analysis has been carried out using Gaussian 09 program suit.

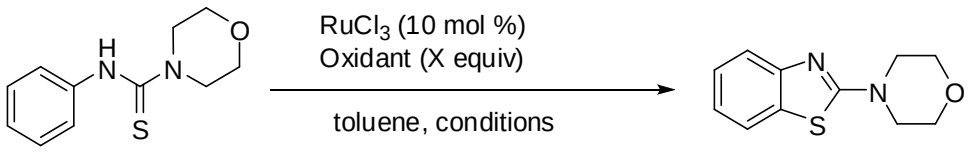
2. Detailed Results of Screening

2.1 *Table S1:* Initial Screening



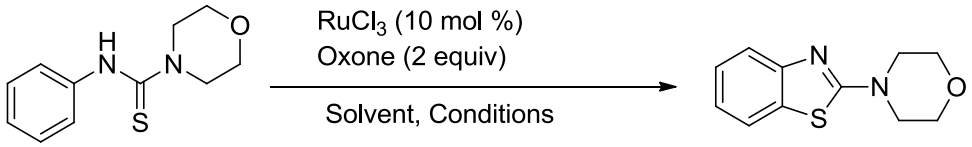
S.No.	X	Y	Conditions	Isolated yield (%)
1.	**10**	**1**	**110 °C, 24 h**	**61**
2.	10	2	110 °C, 24 h	54
3.	10	1	110°C, 36 h	68
4.	10	1	70 °C, 36 h	43
5.	10	1	90 °C, 36 h	48
6.	10	0	110 °C, 36 h	18
7.	0	1	110 °C, 36 h	10

2.2 *Table S2:* Oxidant effect



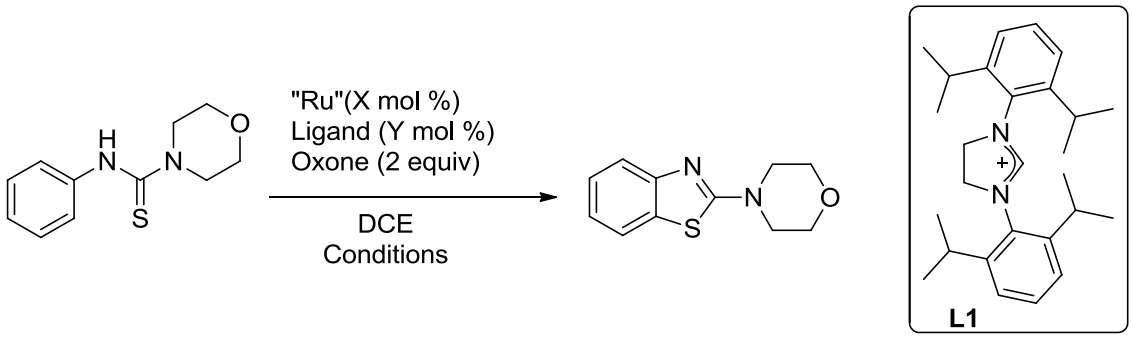
S.No.	Oxidant	X	Conditions	Isolated yield (%)
1.	$K_2S_2O_8$	1	110 ^oC, 24 h	59
2.	$NH_4S_2O_8$	1	110 ^oC, 24 h	63
3.	DDQ	1	110 ^oC, 48 h	28
4.	BQ	1	110 ^oC, 48 h	35
5.	$Cu(OAc)_2$	1	110 ^oC, 24 h	61
6.	AgOAc	1	110 ^oC, 48 h	25
7.	CuI	1	110 ^oC, 24 h	69
8.	**Oxone**	**2**	110 ^oC, 24 h	**80**
9.	Oxone	1	110 ^oC, 24 h	67
10.	Oxone	3	110 ^oC, 24 h	81
11.	^{t}BuOOH	1	110 ^oC, 48 h	0
12.	-	-	110 ^oC, 48 h	18

2.3 *Table S3:* Solvent effect



S.No.	Solvent	Conditions	Isolated yield (%)
1	toluene	110^{o}C, 24 h	80
2	THF	80^{o}C, 48 h	75
3	dioxane	110^{o}C, 48 h	38
4	DCM	50^{o}C, 48 h	27
5	**DCE**	**100^{o}C, 6 h**	**89**
6	xylene	110^{o}C, 48 h	65
7	DMF	110^{o}C, 48 h	12
8	DMSO	110^{o}C, 48 h	57
9	H_2O	110^{o}C, 48 h	35
10	CH_3COOH	120^{o}C, 48 h	15
11	CH_3CN	90^{o}C, 48 h	20
12	EtOH	85^{o}C, 48 h	40

2.4 *Table S4:* Ruthenium source and ligand effect



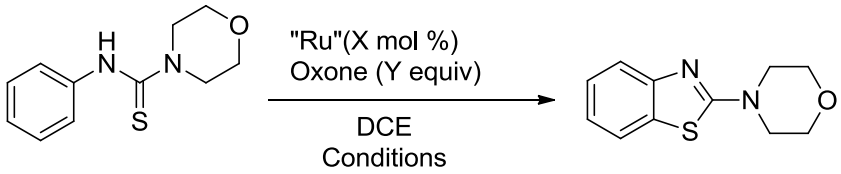
S.No.	"Ru" Catalyst	X	Ligand	Y	Conditions	Isolated

						Yield (%)
1.	$RuCl_3$	10	-	-	100 °C, 24 h	89
2.	$[RuCp^*Cl_2]_2$	10	-	-	100 °C, 48 h	37
3.	$RuCl_3$	10	PPh_3	20	100 °C, 48 h	80
4.	$RuCl_3$	10	Xantphos	20	100 °C, 48 h	78
5.	$RuCl_3$	10	dppf	20	100 °C, 48 h	65
6.	$RuCl_3$	10	**L1**[b]	30	120 °C, 24 h	77
7.	$RuCl_3$	10	2,2'-bipyridine	30	100 °C, 48 h	54
8.	$[RuCl_2(p\text{-cymene})]_2$[b]	10	PPh_3	20	100 °C, 48 h	78
9.	$[RuCl_2(p\text{-cymene})]_2$[b]	10	Xantphos	20	100 °C, 48 h	70
10.	$[RuCl_2(p\text{-cymene})]_2$[b]	10	dppf	20	100 °C, 48 h	65
11.	$[RuCl_2(p\text{-cymene})]_2$[b]	10	**L1**[c]	30	120 °C, 24 h	72
12.	$[RuCl_2(p\text{-cymene})]_2$	10	2,2'-bipyridine	30	100 °C, 48 h	64
13.	$[RuCl_2(p\text{-cymene})]_2$[b]	10	-	-	100 °C, 6 h	82

[a]*NHCwas generated by reacting L1 with Cs_2CO_3 as reported earlier;*[2] [b]*$AgSbF_6$ used to activate the catalyst.*

Protocol for generation of Ru-NHC complex[1]: [a]*N*-phenylmorpholine-4-carbothioamide (1.00 mmol) were added to a solution of $[RuCl_2(p\text{-cymene})]_2$ (0.10 mmol), **L1** (0.30 mmol) and Cs_2CO_3 (3.00 mmol) in *N*-Methylpyrrolidone(NMP) (2 mL). The resulting mixture was stirred at 120 °C for 24 h.

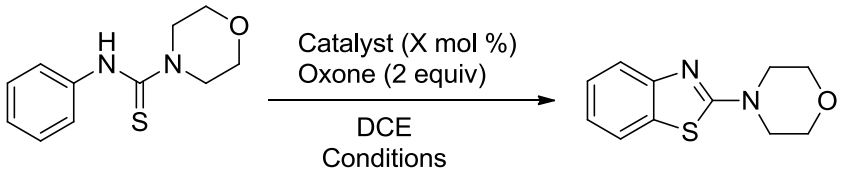
2.5 *Table S5:* Final optimization with $RuCl_3$ and $[RuCl_2(p\text{-cymene})]_2$



S.No.	Catalyst	X	Y	Conditions	Yield (%)
1.	$RuCl_3$	10	2	100 °C, 6 h	89
2.	**$RuCl_3$**	**5**	**2**	**100 °C, 6 h**	**87**
3.	$RuCl_3$	2.5	2	100 °C, 6 h	80
4.	$RuCl_3$	1	2	100 °C, 6 h	50
5.	$RuCl_3$	5	3	100 °C, 24 h	89
6.	$RuCl_3$	5	1	100 °C, 24 h	67
7.	$RuCl_3$	5	2	60°C, 24 h	45
8.	$RuCl_3$	5	2	80°C, 24 h	70
9.	-	-	2	100 °C, 24 h	15
10.	$RuCl_3$	5	0	100 °C, 24 h	12
11.	**$[RuCl_2(p\text{-cymene})]_2$**[a]	**5**	**2**	**100 °C, 6 h**	**80**
12.	$[RuCl_2(p\text{-cymene})]_2$[a]	10	2	100 °C, 6 h	82
13.	$[RuCl_2(p\text{-cymene})]_2$[a]	5	2	60°C, 24 h	48
14.	$[RuCl_2(p\text{-cymene})]_2$[a]	5	2	80°C, 24 h	64
15.	-	-	2	100 °C, 6 h	15
16.	$[RuCl_2(p\text{-cymene})]_2$[b]	5	0	100 °C, 6 h	20

[a]*$AgSbF_6$ used to activate the catalyst.*

2.6 *Table S6:* Screening of Catalyst



S.No.	Catalyst	X	Conditions	Isolated Yield (%)
1.	$PdCl_2$	5	80 ^oC, 6 h	91
2.	$Pd(OAc)_2$	5	80 ^oC, 6 h	92
3.	$[RuCl_2(p\text{-cymene})]_2$	5	100 ^oC, 6 h	80
4.	$RhCl_3$	10	100 ^oC, 24 h	0
5.	$[RhCp^*Cl_2]_2$	10	100 ^oC, 24 h	0
6.	$FeCl_3$	10	100 ^oC, 24 h	12
7.	$NiCl_2$	10	100 ^oC, 24 h	0
8.	AuCl	10	100 ^oC, 24 h	0

3. General procedure for the synthesis of compounds 9a-v:

A schlenk tube equipped with a stir-bar was charged with thiourea. Then DCE was added to the reaction tube via a syringe. The reaction tube was purged with argon. Then after 5-10 min, Oxone and $RuCl_3$ was added to the reaction mixture followed by purging of argon gas. Subsequently, argon was replaced by air and the reaction mixture was stirred at 110 ^oC for 4-10 h. On the completion of the reaction on TLC, the reaction mixture was passed through celite bed and concentrated under reduced pressure and then purified by silica gel chromatography (EtOAc:petroleum ether) to yield the desired product. The specific reaction condition and characterization data for each reaction are given below.

9a: 4-(Benzo[d]thiazol-2-yl)morpholine

N-Phenylmorpholine-4-carbothioamide (0.05g, 0.224mmol), Oxone (0.138g, 0.448mmol), $RuCl_3$ (0.0023g, 0.012mmol), DCE (3mL). Product: golden brown solid, yield: 0.044 g (87%); m.p.:118-119 °C [lit.[3] 119-120 °C]. ^1H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.62 (dd, 1H, aromatic C-*H*, *J* = 0.5, 8 Hz), 7.58 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.32(dt, 1H, aromatic C-*H*, *J* = 1.0, 8.5 Hz), 7.12 (dt, 1H, aromatic C-*H*, *J* = 1.0, 8.0 Hz), 3.84 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz), 3.63 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 169.05, 152.49, 130.58, 126.13, 121.72, 120.81, 119.33, 66.26, 48.51. HRMS (EI) calcd for $C_{11}H_{12}N_2OS$ (M^+) 220.0670, found 220.0679.

9b: 4-(6-Ethylbenzo[d]thiazol-2-yl)morpholine

N-(4-Ethylphenyl)morpholine-4-carbothioamide (0.05 g, 0.199 mmol), Oxone (0.061 g, 0.398 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: brown solid, yield: 0.035 g (71%); m.p.: 100-102 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.49 (d, 1H, aromatic C-*H*, *J* = 8.5 Hz), 7.46 (d, 1H, aromatic C-*H*, *J* = 1.5 Hz), 7.16 (dd, 1H, aromatic C-*H*, *J* = 1.5, 8 Hz), 3.84 (t, 4H, sp^3 C-*H*, *J* = 4.7 Hz), 3.61 (t, 4H, sp^3 C-*H*, *J* = 4.7 Hz), 2.70 (q, 2H, sp^3 C-H, *J*= 7.5 Hz), 1.26 (t, 3H., sp^3 C-*H*, *J*= 7.5 Hz),^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 168.63, 150.44, 138.11, 130.63, 126.25, 119.70, 119.03, 66.28, 48.53, 28.73, 16.02. HRMS (EI) calcd for $C_{13}H_{16}N_2OS$ (M^+) 248.0983, found 248.0987.

9c: 4-(6-Methoxybenzo[d]thiazol-2-yl)morpholine

N-(4-Methoxyphenyl)morpholine-4-carbothioamide (0.05g, 0.198mmol), Oxone (0.122g, 0.396mmol), $RuCl_3$ (0.002g, 0.01mmol), DCE (3mL). Product: brick brown solid, yield: 0.042 g(85%);m.p.: 137-138 °C [lit.[3] 137-138 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.48 (dd, 1H, aromatic C-*H*, *J* = 3.5, 9 Hz), 7.16 (t, 1H, aromatic C-*H*, *J* = 3 Hz), 6.92 (dd, 1H, aromatic C-*H*, *J* = 2.5, 8.8 Hz), 3.85-3.83 (m, 4H, sp^3 C-*H*), 3.83 (s, 3H, O*C*H_3), 3.58 (t, 4H, sp^3 C-*H*, *J* = 4.75 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 167.70, 155.22, 146.64, 131.59, 119.79, 113.79, 105.22, 66.28, 55.85, 48.53. HRMS (EI) calcd for $C_{12}H_{14}N_2O_2S$ (M^+) 250.0776, found 250.0767.

9d: 4-(6-Nitrobenzo[d]thiazol-2-yl)morpholine

N-(4-Nitrophenyl)morpholine-4-carbothioamide (0.05 g, 0.187 mmol), Oxone (0.115 g, 0.374 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: yellowsolid,yield: 0.039 g (79%); m.p.: decompose >200 °C [lit.[3] decompose >200 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.51 (d, 1H, aromatic C-*H*, *J* = 2.4 Hz), 8.20 (dd, 1H, aromatic C-*H*, *J* = 2.5, 9 Hz), 7.51 (d, 1H, aromatic C-*H*, *J* = 9 Hz), 3.86 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz), 3.71 (t, 4H, sp^3 C-*H*, *J* = 4.8 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 172.03, 157.87, 141.88, 130.76, 122.65, 118.39, 117.37, 66.15, 48.59. HRMS (EI) calcd for $C_{11}H_{11}N_3O_3S$ (M^+) 265.0521, found 265.0526.

9e: 4-(6-Fluorobenzo[d]thiazol-2-yl)morpholine

N-(4-Fluorophenyl)morpholine-4-carbothioamide (0.05 g, 0.208mmol), Oxone (0.128 g, 0.416 mmol), $RuCl_3$ (0.002 g, 0.01 mmol), DCE (3 mL). Product: brick brown solid, yield: 0.037 g (75%); m.p.: 146-147 °C [lit.[3] 146-147.5 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.49 (dd, 1H, aromatic C-*H*, *J* = 4.5, 8.5 Hz), 7.34 (dd, 1H, aromatic C-*H*, *J* = 2.5, 8 Hz), 7.04 (ddd, 1H, aromatic C-*H*, *J* = 2.5, 9 Hz), 3.84 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.60 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 168.64, 158.26 ($J_{C\text{-}F}$ = 239 Hz), 148.92, 131.23, 119.78 ($J_{C\text{-}F}$ = 8.5 Hz), 113.84 ($J_{C\text{-}F}$ = 23.5 Hz), 107.55 ($J_{C\text{-}F}$ = 27 Hz), 66.23, 48.48. HRMS (EI) calcd for $C_{11}H_{11}FN_2OS$ (M^+) 238.0576, found 238.0573.

9f: 4-(6-Chlorobenzo[d]thiazol-2-yl)morpholine

N-(4-Chlorophenyl)morpholine-4-carbothioamide (0.05 g, 0.194 mmol), Oxone (0.119 g, 0.388 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: brick red solid, yield: 0.036 g (73%); m.p.: 142-144 °C [lit.[4] 144-145 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.58 (d, 1H, aromatic C-*H*, *J* = 2 Hz), 7.46 (d, 1H, aromatic C-*H*, *J* = 9 Hz), 7.26 (dd, 1H, aromatic C-*H*, *J* = 2.5, 9 Hz), 3.84 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.62 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 169.06, 151.08, 131.77, 126.82, 126.60, 120.60, 119.96, 66.20, 48.49. HRMS (EI) calcd for $C_{11}H_{11}ClN_2OS$ (M^+) 254.0281, found 254.0280.

9g: 4-(6-Bromobenzo[d]thiazol-2-yl)morpholine

N-(4-Bromophenyl)morpholine-4-carbothioamide (0.05 g, 0.167 mmol), Oxone (0.103 g, 0.334 mmol), $RuCl_3$ (0.0017 g, 0.008 mmol), DCE (3 mL). Product: brown solid, yield: 0.033 g (67%); m.p.: 165-166 °C [lit.[4] 165-167 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.72 (d, 1H, aromatic C-*H*, *J* = 1.35 Hz), 7.41 (t, 2H, aromatic C-*H*, *J* = 1.73 Hz), 3.84 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz), 3.62 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 169.06, 151.49, 132.22, 129.37, 123.29, 120.41, 114.02, 66.20, 48.47. HRMS (EI) calcd for $C_{11}H_{11}BrN_2OS$ (M^+) 297.9775, found 297.9772.

9h: Methyl 2-morpholinobenzo[d]thiazole-6-carboxylate

Ethyl 4-(morpholine-4-carbothioamido)benzoate (0.05 g, 0.178 mmol), Oxone (0.109 g, 0.356 mmol), $RuCl_3$ (0.002 g, 0.009 mmol), DCE (3 mL). Product: off-white solid, yield: 0.044 g (80%); m.p.: 118-119 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.33 (d, 1H, aromatic C-*H*, *J* = 1.5 Hz), 8.02 (dd, 1H, aromatic C-*H*, *J* = 1.7, 8.5 Hz), 7.55 (d, 1H, aromatic C-*H*, *J* = 8.5 Hz), 4.38 (q, 2H, sp^3 C-*H*, *J* = 7.1 Hz), 3.85 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz), 3.68 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz), 1.41 (t, 3H, sp^3 C-*H*, *J* = 7.1 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 171.01, 166.46, 156.28, 130.44, 128.01, 123.67, 122.81, 118.52, 66.21, 60.88, 48.49, 14.42. HRMS (EI) calcd for $C_{13}H_{14}N_2O_3S$ (M^+) 278.0725, found 278.0722.

9i: 4-(5-Methoxybenzo[d]thiazol-2-yl)morpholine

N-(3-Methoxyphenyl)morpholine-4-carbothioamide (0.05 g, 0.198 mmol), Oxone (0.122 g, 0.396 mmol), $RuCl_3$ (0.002 g, 0.01 mmol), DCE (3 mL). Product: pale yellow solid, yield: 0.045 g (91%); m.p.: 120-122 °C[lit.[3] 125-126 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.46 (d, 1H, aromatic C-*H*, *J* = 8.5 Hz), 7.14 (d, 1H, aromatic C-*H*, *J* = 2.5 Hz), 6.74 (dd, 1H, aromatic C-*H*, *J* = 2.5, 9 Hz), 3.83 (t, 7H, sp^3 C-*H*, *J* = 5 Hz), 3.61 (t, 4H, sp^3 C-*H*, *J* = 4.7 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 170.35, 159.07, 153.69, 121.99, 121.03, 110.40, 103.43, 66.24, 55.54, 48.42. HRMS (EI) calcd for $C_{12}H_{14}N_2O_2S$ (M^+) 250.0776, found 250.0780.

9j: 4-(5-Nitrobenzo[d]thiazol-2-yl)morpholine

N-(3-Nitrophenyl)morpholine-4-carbothioamide (0.05 g, 0.187 mmol), Oxone (0.115 g, 0.374 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: yellowish orange solid, yield: 0.038 g (77%); m.p.: 172-175 °C [lit.[4] 172-174 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.36 (d, 1H, aromatic C-*H*, *J* = 2 Hz), 7.97 (dd, 1H, aromatic C-*H*, *J* = 2, 8.5 Hz), 7.70 (d, 1H, aromatic C-*H*, *J* = 9 Hz), 3.86 (t, 4H, sp^3 C-*H*, *J* = 4.92 Hz), 3.68 (t, 4H, sp^3 C-*H*, *J* = 4.9 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 170.28, 152.98, 147.00, 137.82, 120.78, 116.37, 114.05, 66.17, 48.52. HRMS (EI) calcd for $C_{11}H_{11}N_3O_3S$ (M^+) 265.0521, found 265.0519.

9k: 4-(7-Nitrobenzo[d]thiazol-2-yl)morpholine

N-(3-Nitrophenyl)morpholine-4-carbothioamide (0.05 g, 0.187 mmol), Oxone (0.115 g, 0.374 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: orange solid, yield: 0.038 g (77%); m.p.: 178-180 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.06 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.82 (d, 1H, aromatic C-*H*, *J* = 7.5 Hz), 7.46 (t, 1H, aromatic C-*H*, *J* = 8 Hz), 3.87 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.72 (t, 4H, sp^3 C-*H*, *J* = 4.7 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 171.27, 155.03, 142.16, 126.82, 126.21, 124.85, 117.33, 66.20, 48.33. HRMS (EI) calcd for $C_{11}H_{11}N_3O_3S$ (M^+) 265.0521, found 265.0517.

A mixture of 9l: 4-(5-chlorobenzo[d]thiazol-2-yl)morpholine and 9m: 4-(7-chlorobenzo[d]thiazol-2-yl)morpholine

N-(3-Chlorophenyl)morpholine-4-carbothioamide (0.05 g, 0.194 mmol), Oxone (0.119 g, 0.388 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: creamish brown solid, yield: 0.034 g (69%); m.p.: 112-113 °C [lit.[3] 112-113 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.54 (d, 1H, aromatic C-*H*, *J* = 2 Hz), 7.50 (d, 1H, aromatic C-*H*, *J* = 8.5 Hz), 7.45 (dd, 1H, aromatic C-*H*, *J* = 1, 8Hz), 7.25 (t, 1H, aromatic C-*H*, *J* = 8 Hz), 7.10-7.06 (m, 2H, aromatic C-*H*), 3.85-3.82 (m, 8H, sp^3 C-*H*), 3.65-3.61 (m, 8H, sp^3 C-*H*). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 170.04, 168.81, 153.59, 153.32, 131.99, 130.58, 128.79, 127.07, 126.00, 121.80, 121.39, 119.26, 117.40, 66.20, 48.44. HRMS (EI) calcd for $C_{11}H_{11}ClN_2OS$ (M^+) 254.0281, found 254.0284.

9n: 4-(4-Chlorobenzo[d]thiazol-2-yl)morpholine

N-(2-Chlorophenyl)morpholine-4-carbothioamide (0.05 g, 0.194 mmol), Oxone (0.119 g, 0.388 mmol), $RuCl_3$ (0.0018 g, 0.009 mmol), DCE (3 mL). Product: yellowish brown solid, yield: 0.032g (64%); m.p.: 101-102 °C [lit.[3] 101-102 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.50 (dd, 1H, aromatic C-*H*, *J* = 1, 8 Hz), 7.33 (d, 1H, aromatic C-*H*, J = 1, 7.5 Hz), 7.02 (t, 1H, aromatic C-*H*, *J* = 8 Hz), 3.85 (t, 4H, sp^3 C-*H*, *J* = 4.7 Hz), 3.67 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 168.96, 149.58, 147.52, 131.73, 126.40, 122.00, 119.25, 66.25, 48.45. HRMS (EI) calcd for $C_{11}H_{11}ClN_2OS$ (M^+) 254.0281, found 254.0280.

9o:4-(4-Bromobenzo[d]thiazol-2-yl)morpholine

N-(2-Bromophenyl)morpholine-4-carbothioamide (0.05 g, 0.166 mmol), Oxone (0.102 g, 0.332 mmol), $RuCl_3$ (0.0016 g, 0.008 mmol), DCE (3 mL). Product: red solid, yield: 0.039 g (78%); m.p.: 81-85 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.54 (d, 1H, aromatic C-*H*, *J* = 7 Hz), 7.50 (d, 1H, aromatic C-*H*, *J* = 7.5 Hz), 6.95 (t, 1H, aromatic C-*H*, *J* = 8 Hz), 3.85 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.66 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 168.61, 150.82, 131.10, 129.47, 122.39, 119.90, 112,43, 66.26, 48.41. HRMS (EI) calcd for $C_{11}H_{11}BrN_2OS$ (M^+) 297.9775, found 297.9779.

9p: 4-(4-iodobenzo[d]thiazol-2-yl)morpholine

N-(2-Iodophenyl)morpholine-4-carbothioamide (0.05 g, 0.143 mmol), Oxone (0.088 g, 0.286 mmol), $RuCl_3$ (0.0014 g, 0.007 mmol), DCE (3 mL). Product: off-white oil, yield: 0.027 g (55%); ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.72 (dd, 1H, aromatic C-*H*, *J* = 1, 8 Hz), 7.56 (dd, 1H, aromatic C-*H*, *J* = 1, 7.5 Hz), 6.81 (t, 1H, aromatic C-*H*, *J* = 7.7Hz), 3.85 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.66 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$):167.72, 153.53, 135.59, 129.01, 122.92, 120.78, 85.85, 66.26, 48.39. HRMS (EI) calcd for $C_{11}H_{11}IN_2OS$ (M^+) 345.9637, found 345.9639.

9q: *N*-Phenylbenzo[d]thiazol-2-amine

1,3-Diphenylthiourea (0.05 g, 0.219 mmol), Oxone (0.135 g, 0.438 mmol), $RuCl_3$ (0.0021 g, 0.010 mmol), DCE (3 mL). Product: cream solid, yield: 0.041 g (82%); m.p.: 158-159°C [lit.[5] 157-159 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.82 (bs, 1H, N-*H*), 7.64 (dd, 1H, aromatic C-*H*, *J* = 0.5, 7.5 Hz), 7.59 (d, 2H, aromatic C-*H*, *J* = 8 Hz), 7.52 (dd, 2H, aromatic C-*H*, *J* = 1, 8.5 Hz), 7.42 (t, 2H, aromatic C-*H*, *J* = 8 Hz), 7.34 (dt, 1H, aromatic C-*H*, *J* = 1, 8 Hz), 7.17 (m, 2H, aromatic C-*H*). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$):164.71, 151.43, 139.87, 129.92, 129.61, 126.18, 124.41, 122.44, 120.89, 120.28, 119.40. HRMS (EI) calcd for $C_{13}H_{10}N_2S$ (M^+) 226.0565, found 226.0560.

9r: *N*-(4-Chloro-3-fluorophenyl)-5-methoxybenzo[d]thiazol-2-amine

1-(4-Chloro-3-fluorophenyl)-3-(4-methoxyphenyl)thiourea (0.05 g, 0.160 mmol), Oxone (0.098 g, 0.320 mmol), $RuCl_3$ (0.0016 g, 0.008 mmol), DCE (3 mL). Product: off white solid, yield: 0.038 g (76%); m.p.: 186-189 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$ + 30 μL of DMSO-d_6), 9.72 (brs, 1H, N-H), 7.89-7.87 (m, 1H, aromatic C-*H*), 7.47-7.45 (m, 1H, aromatic C-*H*), 7.34 (d, 1H, aromatic C-*H*, *J* = 8.6 Hz), 7.10 (d, 1H, aromatic C-*H*, *J* = 2.4 Hz), 6.96 (t, 1H, aromatic C-*H*, *J* = 8.8 Hz), 6.66-6.64 (m, 1H, aromatic C-*H*, *J* = 2.5, 8.6 Hz), 3.73 (s, 3H, OCH_3). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$+ 30 μL DMSO-d_6): (125 MHz, $CDCl_3$): 163.10, 158.77, 154.19, 153.34, 152.25, 137.60, 121.65, 120.69, 119.93, 117.85, 117.80, 116.49, 116.32, 111.02, 103.97, 55.49.

9s: 2-(4-(2-Fluorophenyl)piperazin-1-yl)benzo[d]thiazole

4-(2-Fluorophenyl)-N-phenylpiperidine-1-carbothioamide (0.05 g, 0.158 mmol), Oxone (0.097 g, 0.317 mmol), $RuCl_3$ (0.0016 g, 0.007 mmol), DCE (3 mL). Product: brown solid, yield: 0.037 g (74%); m.p.: 130-132 °C [lit.[6] 106-107 °C]. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.63 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.59 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.32 (dt, 1H, aromatic C-*H*, *J* = 1, 8 Hz), 7.12-7.06 (m, 3H, aromatic C-*H*), 7.02-6.97 (m, 2H, aromatic C-*H*), 3.83 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.23 (t, 4H, sp^3 C-*H*, *J* = 5 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$):`168.78, 154.84 (J_{C-F} = 258.75 Hz), 139.64 (J_{C-F} = 7.4 Hz), 130.76, 126.10, 124.60 (J_{C-F} = 2.5 Hz), 123.27 (J_{C-F} = 7.5 Hz), 121.61, 120.77, 119.28 (J_{C-F} = 5 Hz), 116.32 (J_{C-F} = 20 Hz), 50.13 (J_{C-F} = 2.5 Hz), 48.56. HRMS (EI) calcd for $C_{17}H_{16}FN_3S$ (M^+) 313.1049, found 313.1039.

9t: 2-(4-(4-Fluorophenyl)piperazin-1-yl)benzo[d]thiazole

4-(4-Fluorophenyl)-N-phenylpiperidine-1-carbothioamide (0.05 g, 0.158 mmol), Oxone (0.097 g, 0.317 mmol), $RuCl_3$ (0.0016 g, 0.007 mmol), DCE (3 mL). Product: light pink solid, yield: 0.039 g (79%); m.p.: 98-100 °C . ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.61 (d, 1H, aromatic C-*H*, *J* = 7.5 Hz), 7.32 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.03-6.99 (m, 2H, aromatic C-*H*), 6.96-6.92 (m, 3H, aromatic C-*H*), 3.83 (t, 4H, sp^3 C-*H*, *J* = 5 Hz), 3.23 (t, 4H, sp^3 C-*H*, *J* = 5.3 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$):`168.28, 157.79 (J_{C-F} = 237.5 Hz), 150.95, 147.54, 131.33, 129.48, 122.37, 119.94, 118.94 (J_{C-F} = 7.5 Hz), 115.82 (J_{C-F} = 22.5 Hz), 112.35, 50.21, 48.31. HRMS (EI) calcd for $C_{17}H_{16}FN_3S$ (M^+) 313.1049, found 313.1043.

9u: 5-Methoxy-N-phenylbenzo[d]thiazol-2-amine

1-(3-Methoxyphenyl)-3-phenylthiourea (0.05 g, 0.193 mmol), Oxone (0.119 g, 0.386 mmol), $RuCl_3$ (0.002 g, 0.010 mmol), DCE (3 mL). Product: off white solid, yield: 0.045 g (90%); m.p.: 177-178.3 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.76 (dd, 3H, aromatic C-*H*, *J* = 7.5, 8.5 Hz), 7.43-7.40 (m, 2H, aromatic C-*H*, *J* = 6.5 Hz), 7.18-7.14 (m, 2H, aromatic C-*H*), 6.81 (dd, 1H, aromatic C-*H*, *J* = 2.5, 8.5 Hz), 3.82 (s, 3H, sp^3 C-*H*, *J* = 4.7 Hz).^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 166.04, 159.08, 152.62, 139.87, 129.56, 124.39, 121.33, 121.10, 120.35, 111.17, 103.46, 55.52. HRMS (EI) calcd for $C_{14}H_{12}N_2OS$ (M^+) 256.0670, found 256.0675.

9v: 5-Methoxy-N-(3-nitrophenyl)benzo[d]thiazol-2-amine

1-(3-Methoxyphenyl)-3-(3-nitrophenyl)thiourea (0.05 g, 0.164 mmol), Oxone (0.101 g, 0.328 mmol), $RuCl_3$ (0.0017 g, 0.008 mmol), DCE (3 mL). Product: yellow solid, yield: 0.037 g (74 %); m.p.: 156-159 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.54 (t, 1H, aromatic C-*H*, *J* = 1.7 Hz), 7.94 (dd, 1H, aromatic C-*H*, *J* = 2, 8 Hz), 7.89 (dd, 1H, aromatic C-*H*, *J* = 2, 8.5 Hz), 7.56-7.51 (m, 3H, aromatic C-*H*), 7.25 (d, 1H, aromatic C-*H*, *J* = 2 Hz), 6.87 (dd, 1H, aromatic C-*H*, *J* = 2, 8.5 Hz), 3.82 (s, 3H, sp^3 C-*H*, *J* = 4.7 Hz).^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 163.25, 159.30, 152.22, 148.97, 141.08, 139.33, 130.18, 124.33, 121.27, 117.86, 113.30, 112.32, 104.08, 55.64. HRMS (EI) calcd for $C_{14}H_{11}N_3O_3S$ (M^+) 303.0521, found 303.0525.

Synthesis of 2-(2,3-diphenyl-1H-indol-1-yl)benzo[d]thiazole (16): A schlenk tube equipped with a stir-bar was charged with **9q** (0.05 g, 0.22 mmol), diphenylacetylene (0.039 g, 0.22 mmol). Then 3 ml of DCE was added to the reaction tube via syringe. The reaction tube was purged with argon. Then after 5-10 min, $[Ru(p\text{-cymene})Cl_2]_2$ (0.007 g, 0.01 mmol), $AgSbF_6$ (0.076 g, 0.22 mmol), $Cu(OAc)_2$ (0.04 g, 0.22 mmol) were added to the reaction mixture The mixture was stirred at 120 ^oC for 12 hrs. On the completion of the reaction on TLC, the reaction mixture was passed through Celite bed and concentrated under reduced pressure and then purified by silica gel chromatography (EtOAc: hexane) to furnish the desired product **16** as light yellow solid, 0.075 g ; (84%); m.p.: 98-102 °C.^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 8.43 (d, 1H, aromatic C-*H*, *J* = 8.5 Hz), 8.07 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 7.74 (d, 1H, aromatic C-*H*, *J* = 7.5 Hz), 7.66 (d, 1H, aromatic C-*H*, *J* = 7.5 Hz), 7.50 (dt, 1H, aromatic C-*H*, *J* = 1.5, 8.5 Hz), 7.43 (dt, 1H, aromatic C-*H*, *J* = 1, 8.5 Hz), 7.38- 7.31 (m, 12H, aromatic C-*H*). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 158.78, 149.94, 137.57, 135.72, 134.50, 133.56, 131.90, 130.41, 130.10, 128.85, 128.78, 128.50, 128.36, 126.72, 126.27, 124.76, 124.64, 123.01, 122.78, 121.14, 120.86, 119.79, 113.63.

4. Analytical Data of the compounds

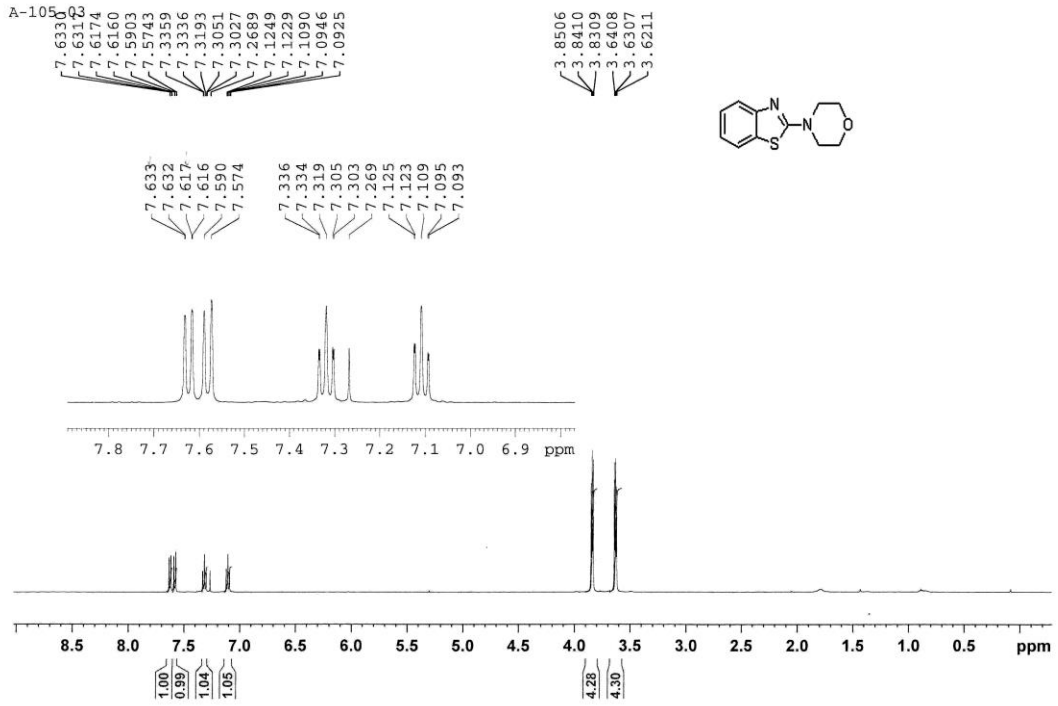


Figure S1: ^{1}H NMR spectra of 4-(benzo[d]thiazol-2-yl)morpholine (**9a**).

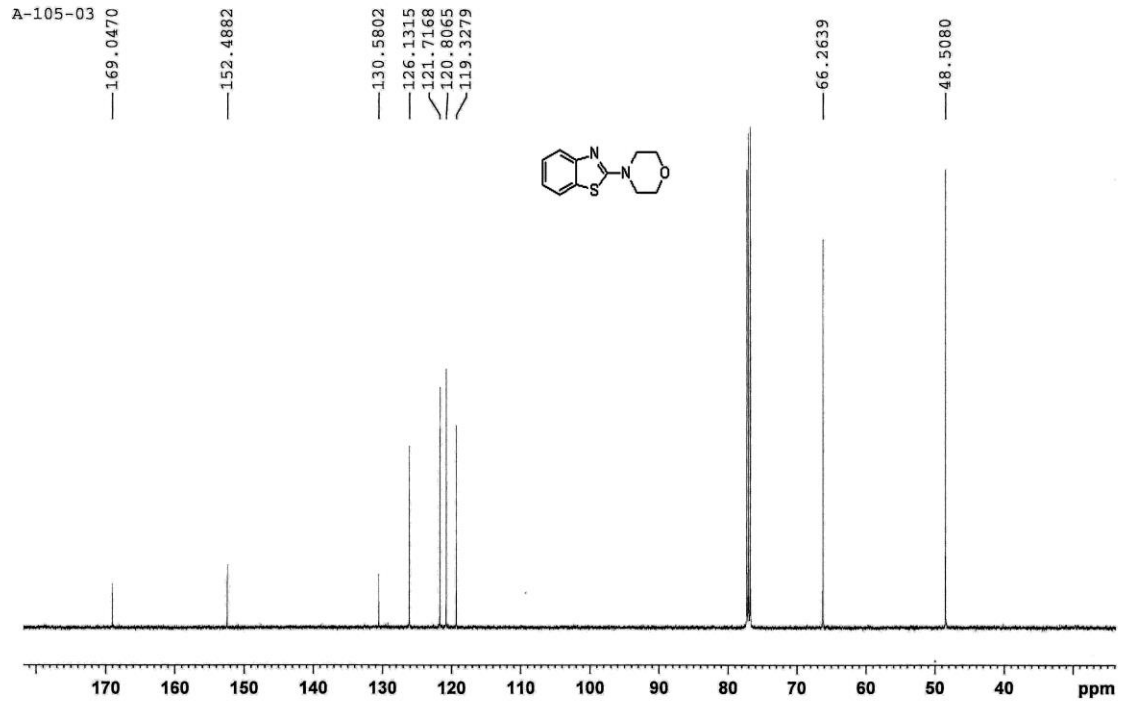


Figure S2: ^{13}C NMR spectra of4-(benzo[d]thiazol-2-yl)morpholine (**9a**).

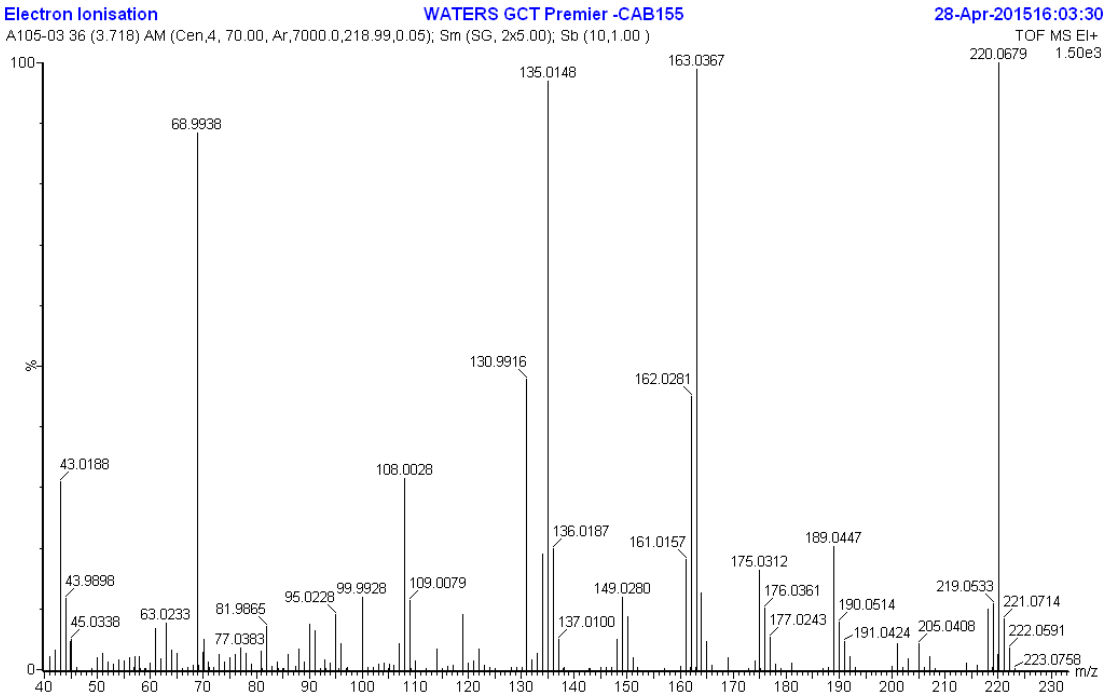


Figure S3: HRMS-EI spectra of 4-(benzo[d]thiazol-2-yl)morpholine (**9a**).

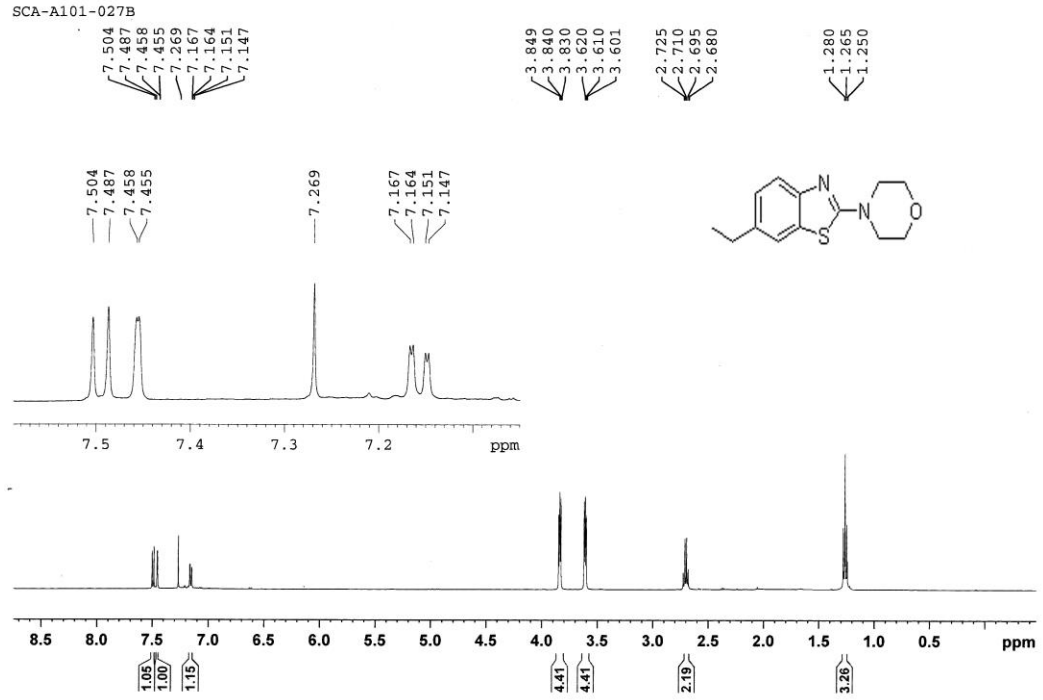


Figure S4: ^{1}H NMR spectra of 4-(6-ethylbenzo[d]thiazol-2-yl)morpholine (**9b**).

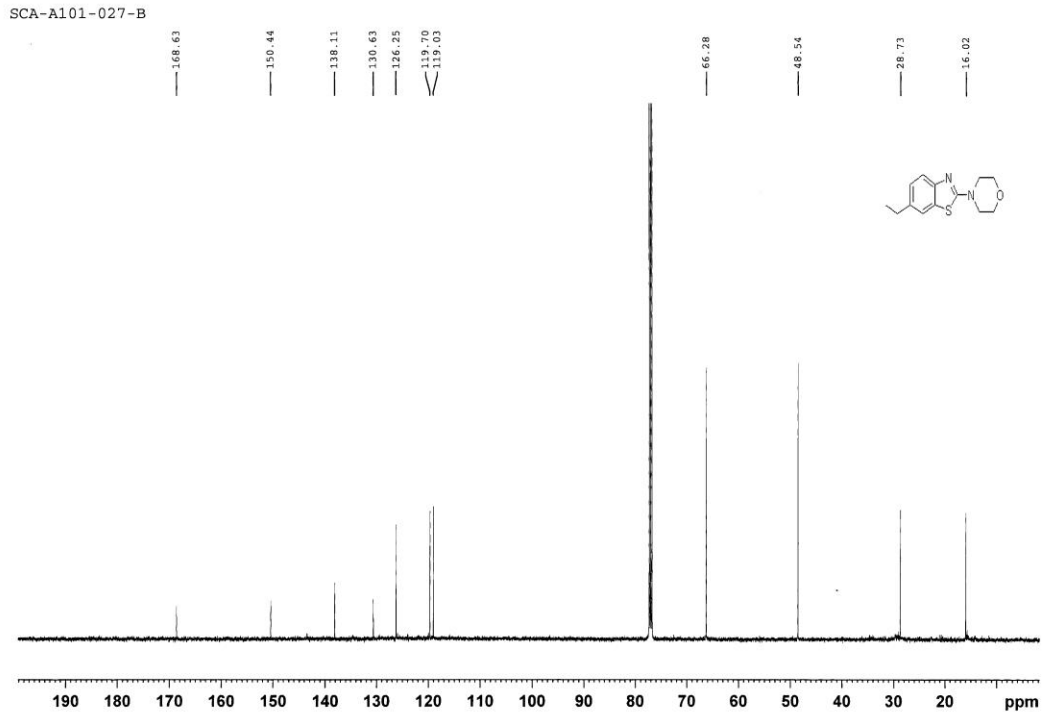


Figure S5: ^{13}C NMR spectra of 4-(6-ethylbenzo[d]thiazol-2-yl)morpholine (**9b**).

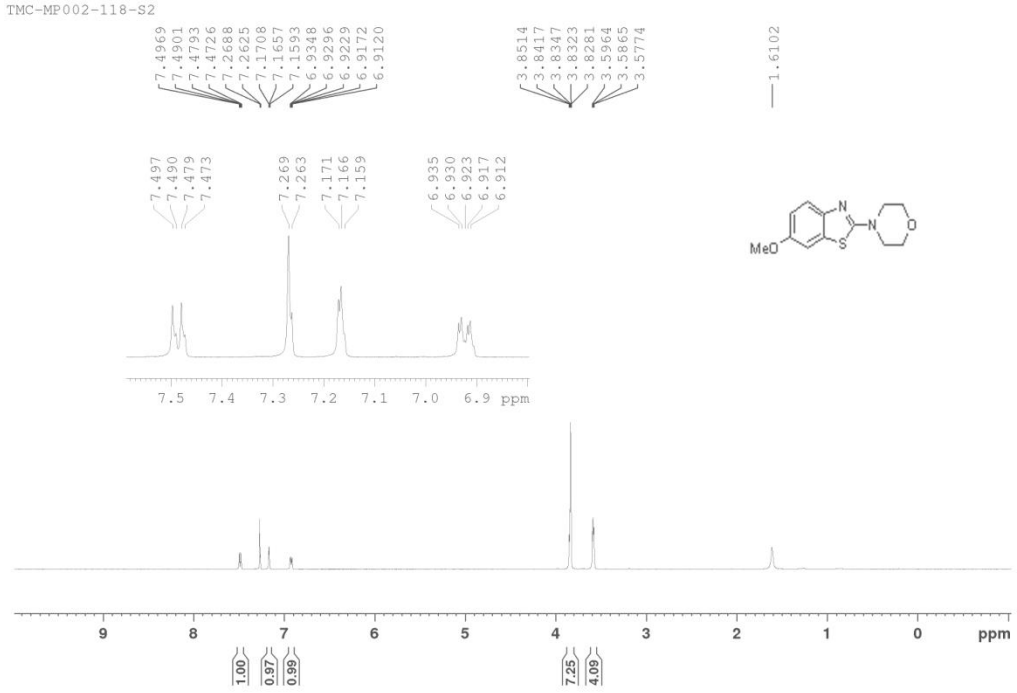


Figure S6: ^{1}H NMR spectra of4-(6-methoxybenzo[d]thiazol-2-yl)morpholine (**9c**).

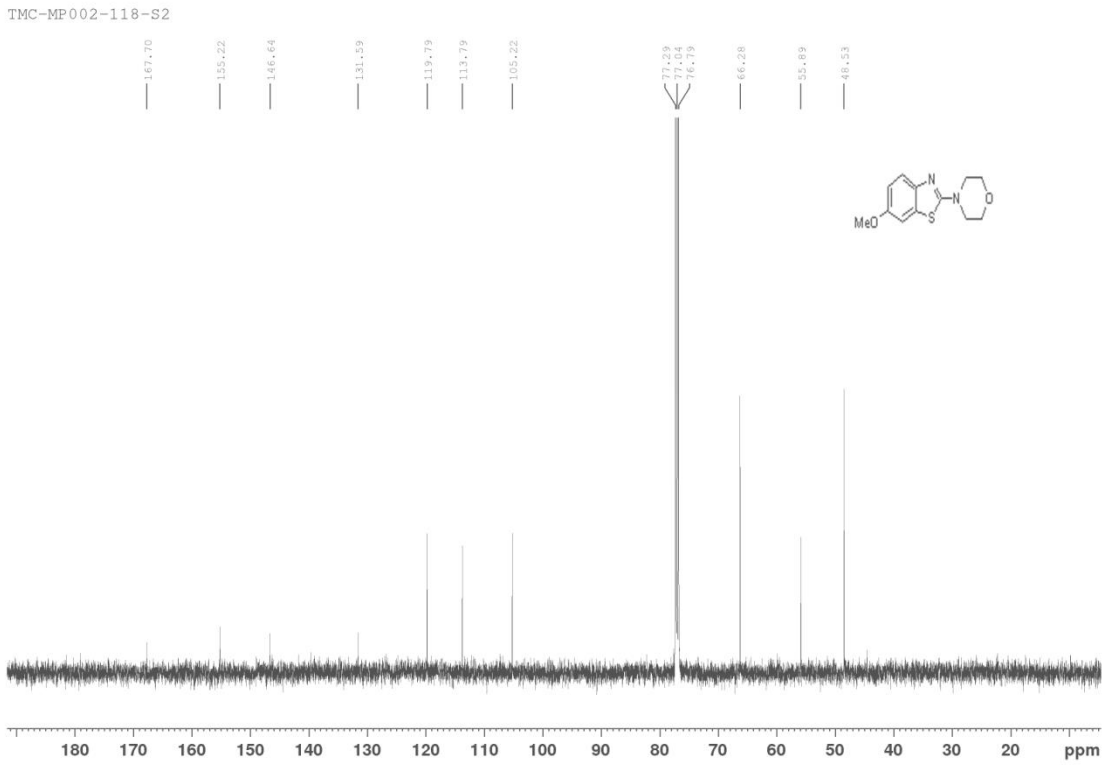


Figure S7: ^{13}C NMR spectra of 4-(6-methoxybenzo[d]thiazol-2-yl)morpholine (**9c**).

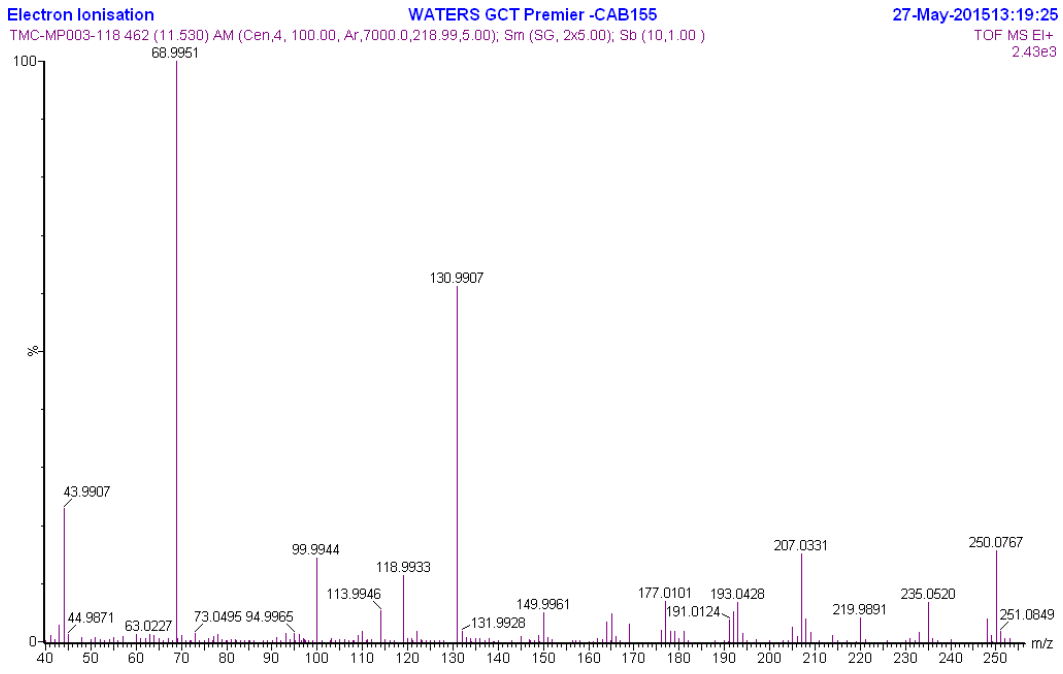


Figure S8: HRMS-EI spectra of 4-(6-methoxybenzo[d]thiazol-2-yl)morpholine (**9c**).

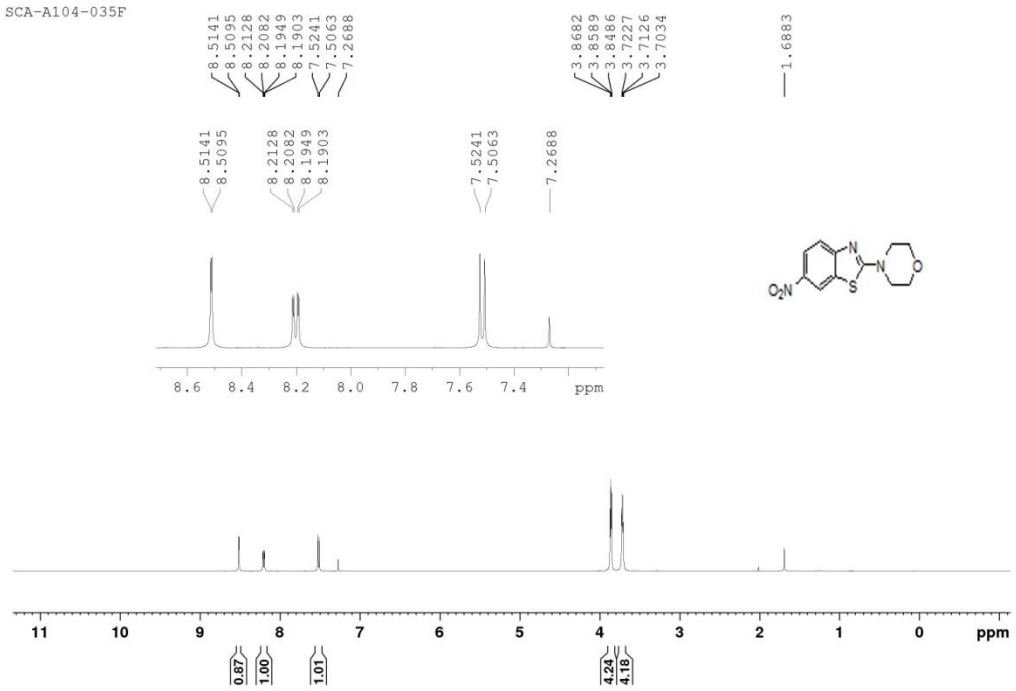


Figure S9: ^{1}H NMR spectra of4-(6-nitrobenzo[d]thiazol-2-yl)morpholine (**9d**).

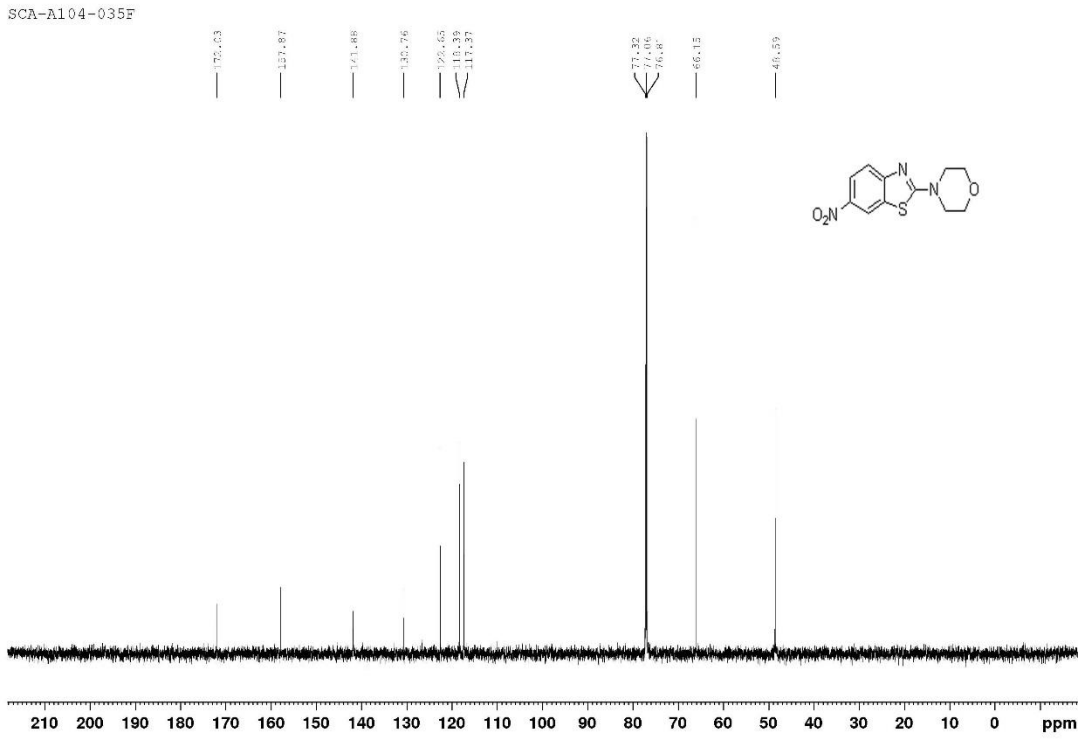


Figure S10: ^{13}C NMR spectra of4-(6-nitrobenzo[d]thiazol-2-yl)morpholine (**9d**).

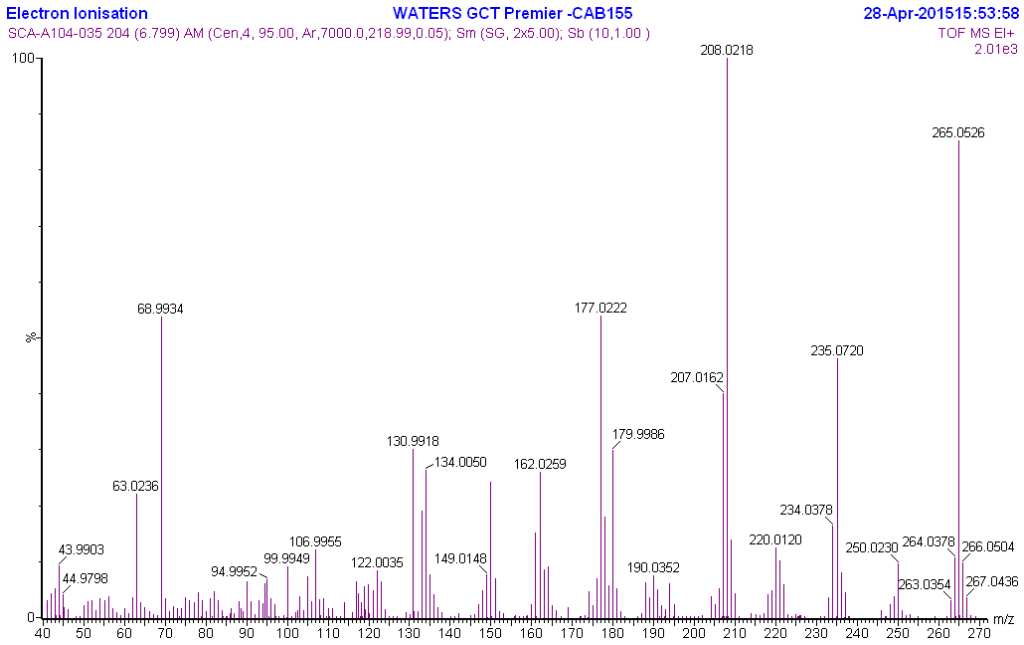


Figure S11: HRMS-EI spectra of 4-(6-nitrobenzo[d]thiazol-2-yl)morpholine (**9d**).

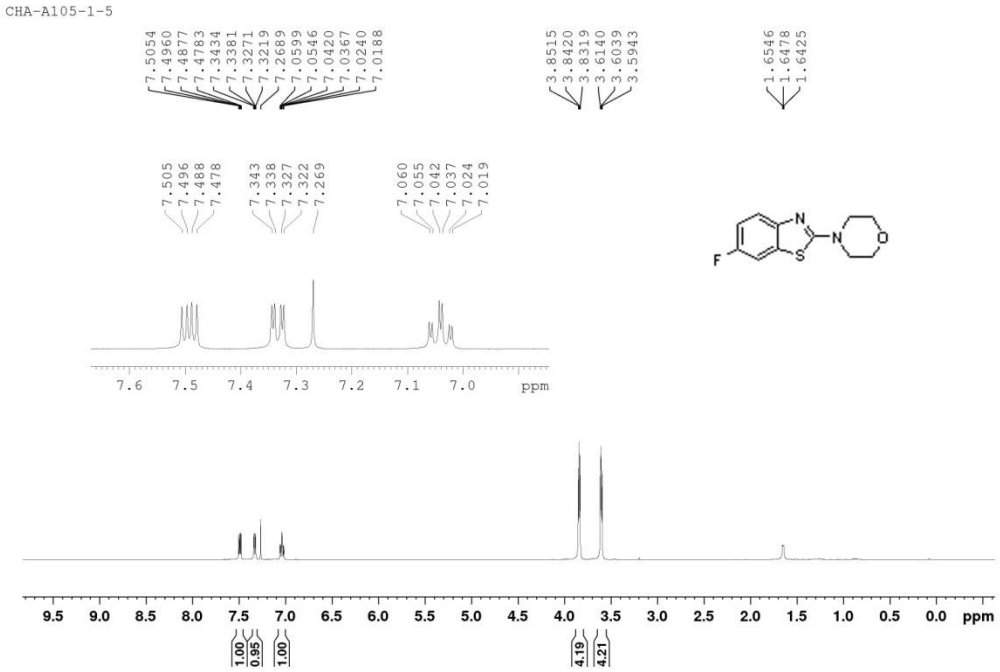


Figure S12: ^{1}H NMR spectra of 4-(6-fluorobenzo[d]thiazol-2-yl)morpholine (**9e**).

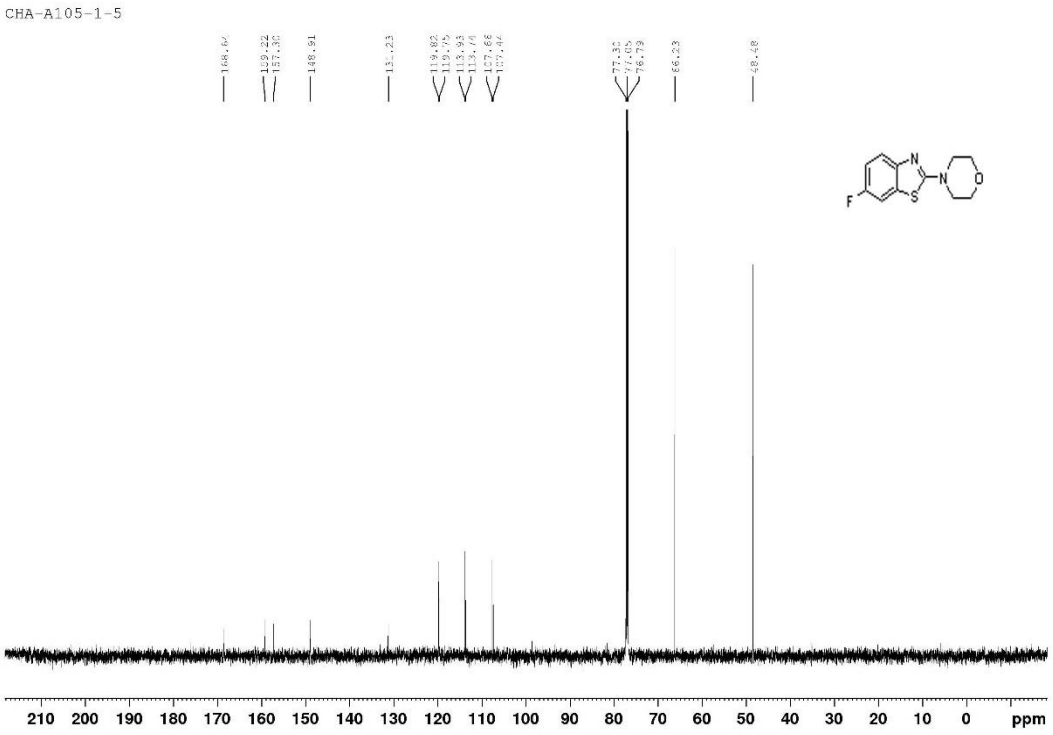


Figure S13: ^{13}C NMR spectra of 4-(6-fluorobenzo[d]thiazol-2-yl)morpholine (**9e**).

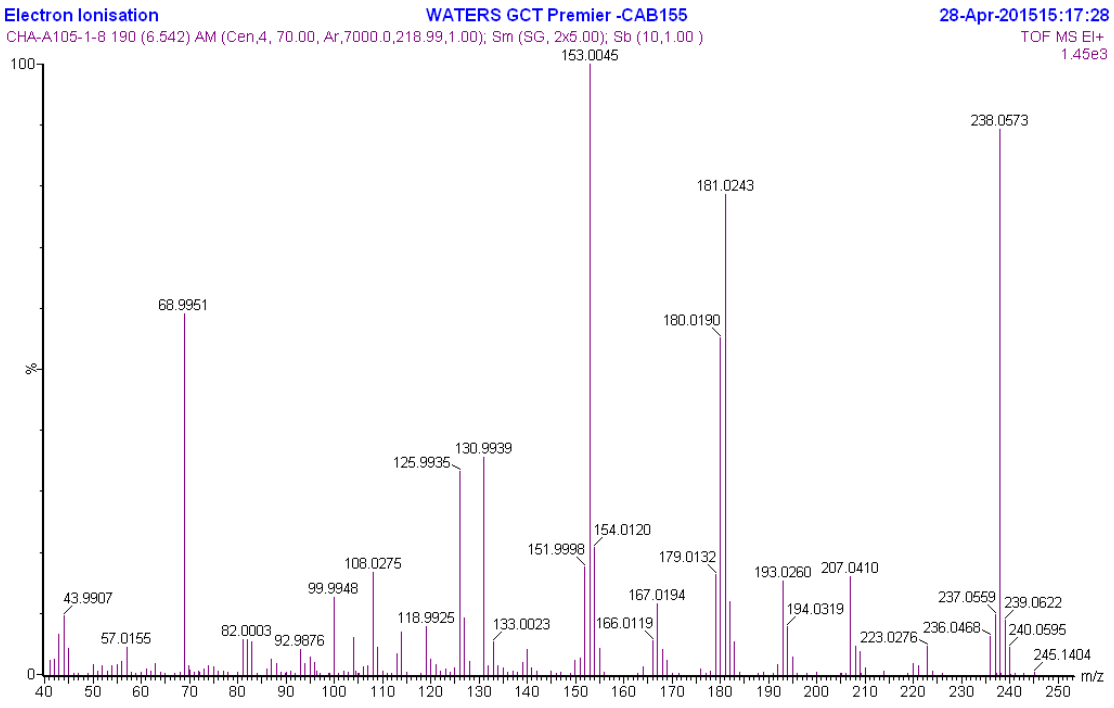


Figure S14: HRMS spectra of 4-(6-fluorobenzo[d]thiazol-2-yl)morpholine (9e).

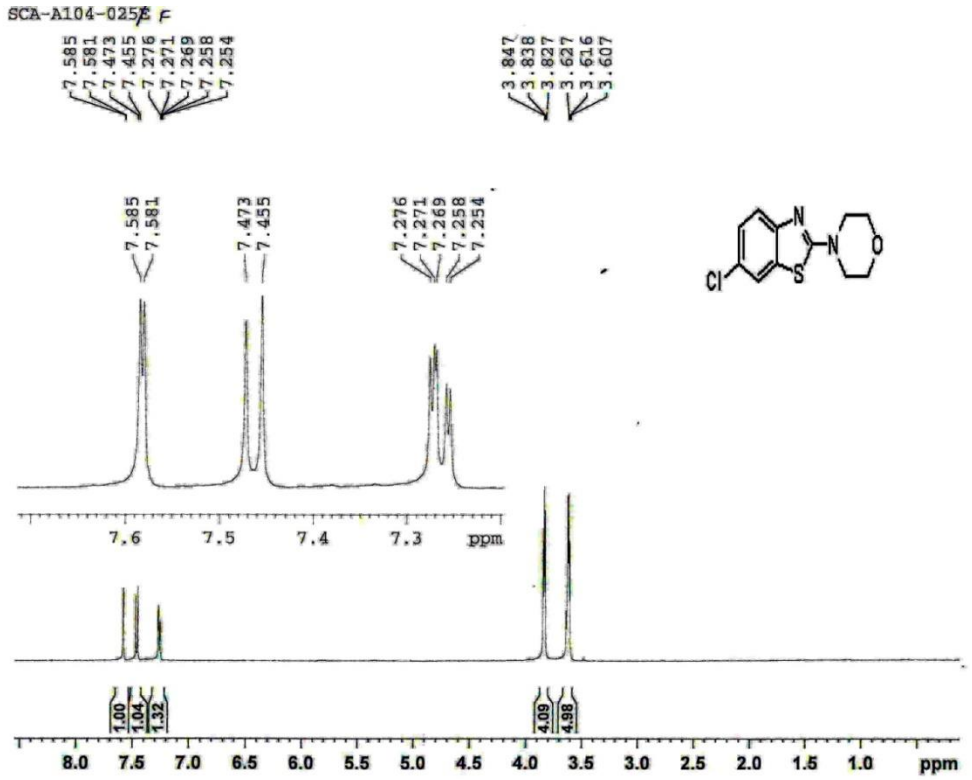


Figure S15: [1]H NMR spectra of 4-(6-chlorobenzo[d]thiazol-2-yl)morpholine (**9f**).

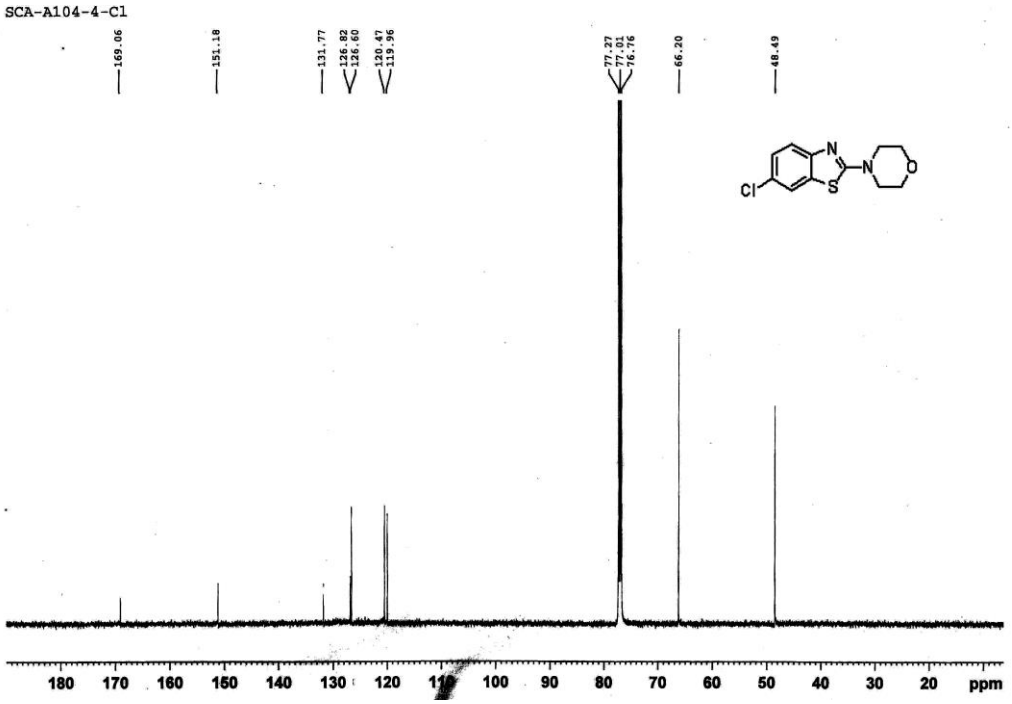


Figure S16: [13] NMR spectra of 4-(6-chlorobenzo[d]thiazol-2-yl)morpholine (**9f**).

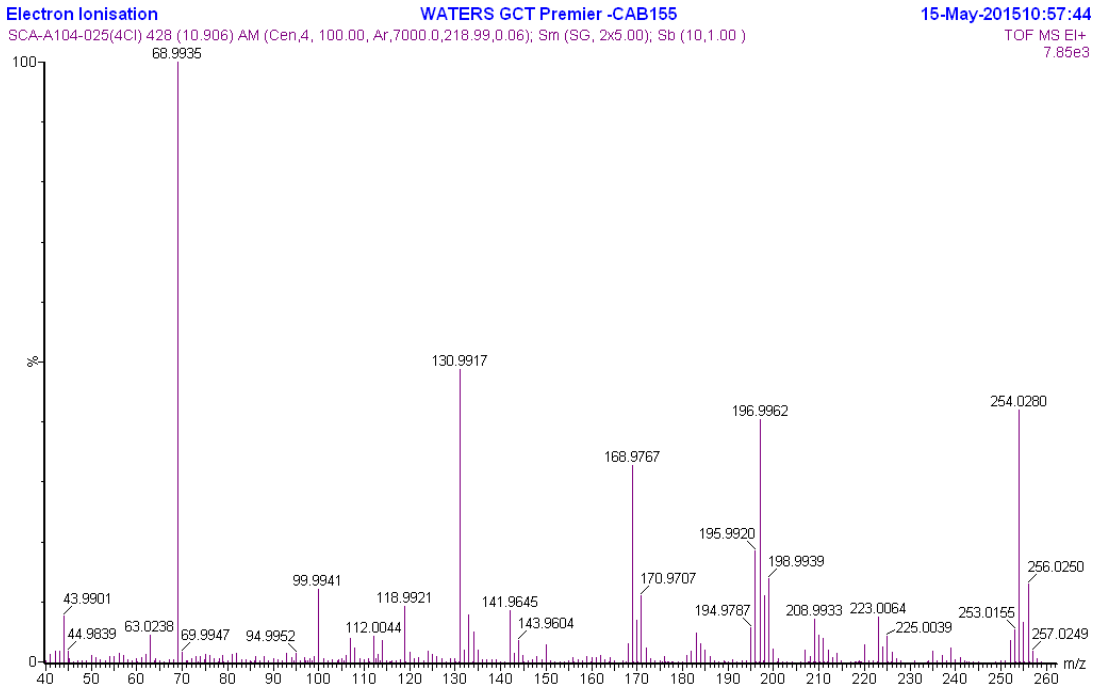


Figure S17: HRMS-EI spectra of 4-(6-chlorobenzo[d]thiazol-2-yl)morpholine(**9f**).

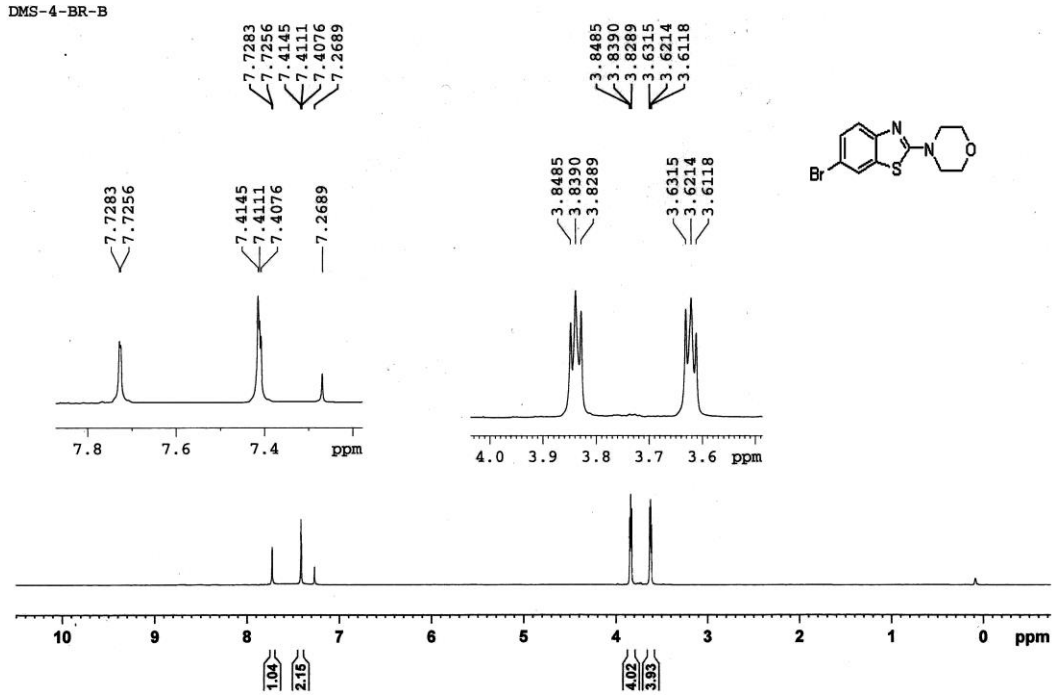


Figure S18: ^{1}H NMR spectra of 4-(6-bromobenzo[d]thiazol-2-yl)morpholine (**9g**).

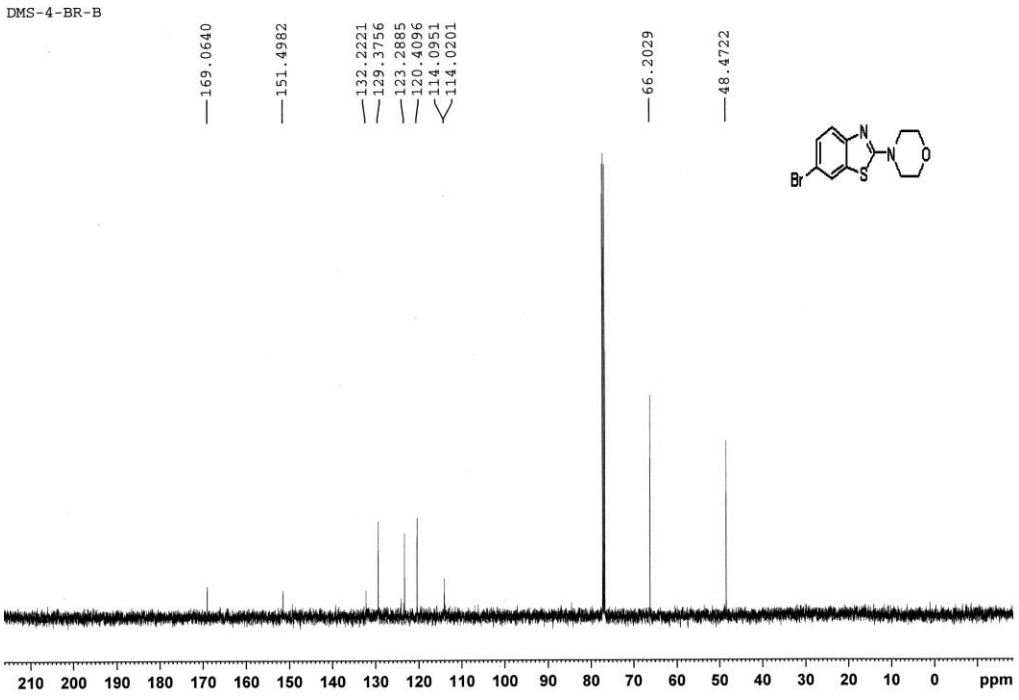


Figure S19: ^{13}C NMR spectra of 4-(6-bromobenzo[d]thiazol-2-yl)morpholine (**9g**).

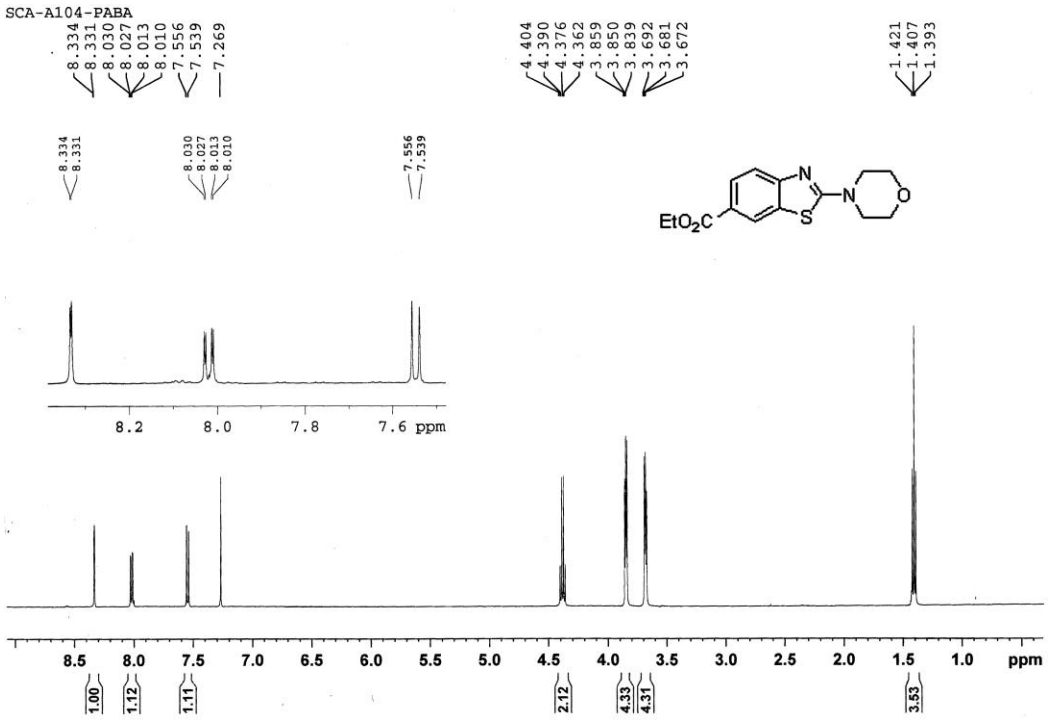


Figure S20: ^{1}H NMR spectra of methyl-2-morpholinobenzo[d]thiazole-6-carboxylate (**9h**).

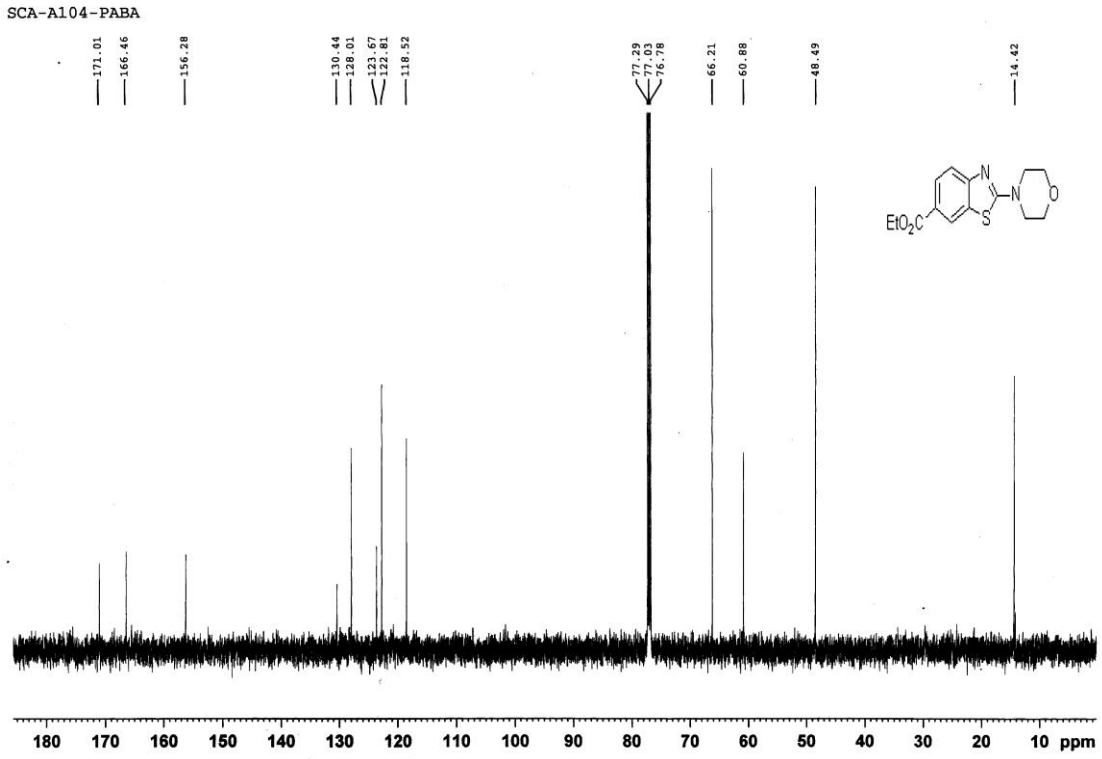


Figure S21: ^{13}C NMR spectra of methyl2-morpholinobenzo[d]thiazole-6-carboxylate (**9h**).

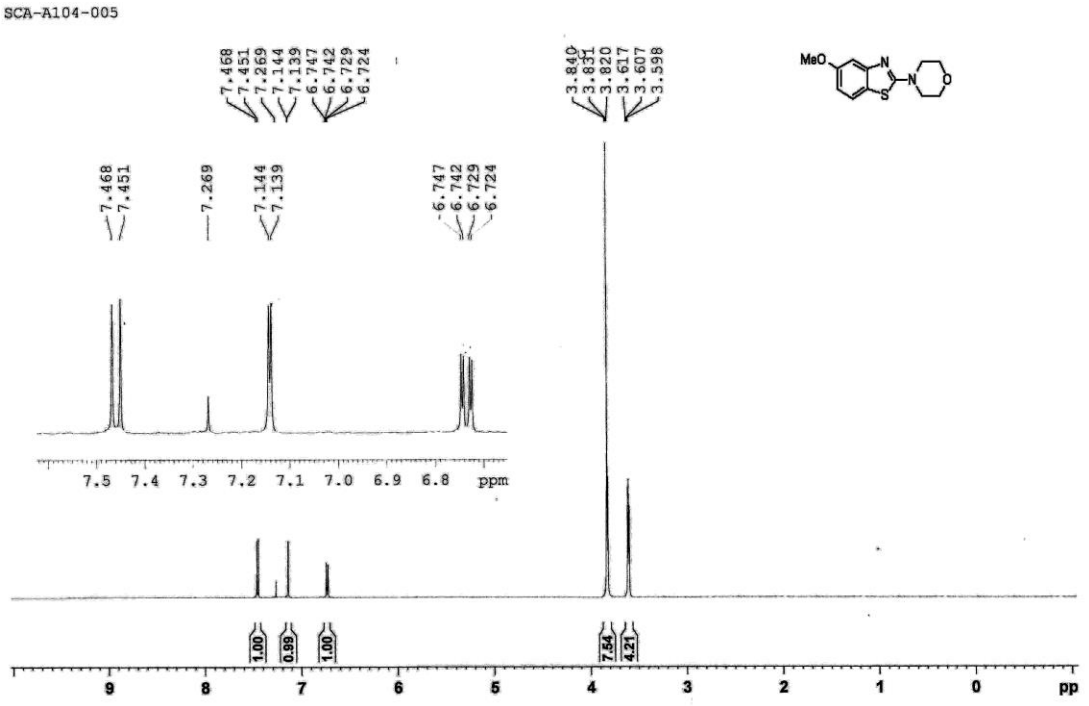


Figure S22: ^{1}H NMR spectra of4-(5-methoxybenzo[d]thiazol-2-yl)morpholine (**9i**).

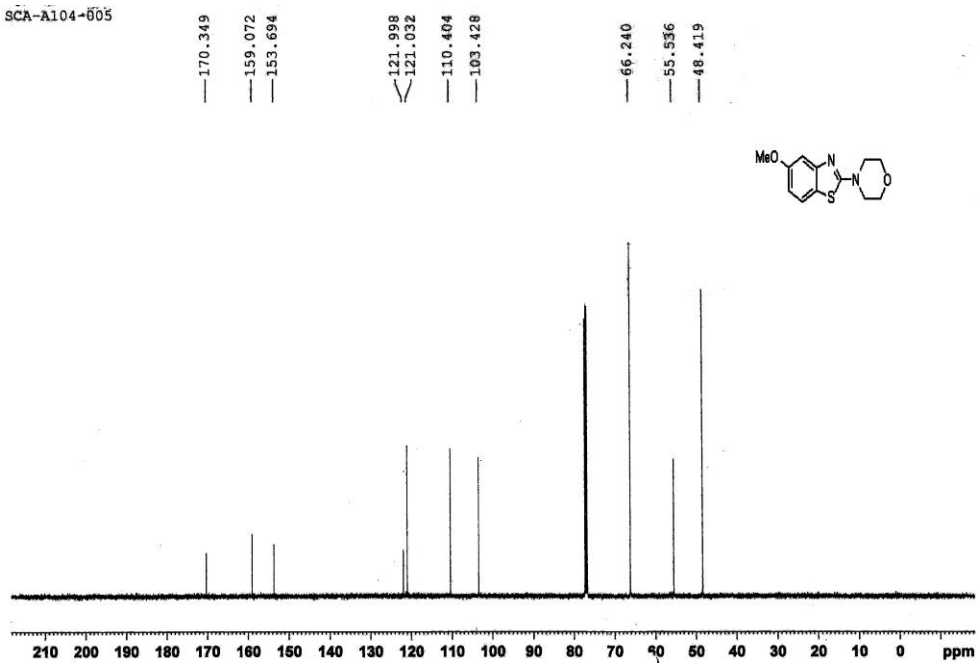


Figure S23: ^{13}C NMR spectra of4-(5-methoxybenzo[d]thiazol-2-yl)morpholine (**9i**).

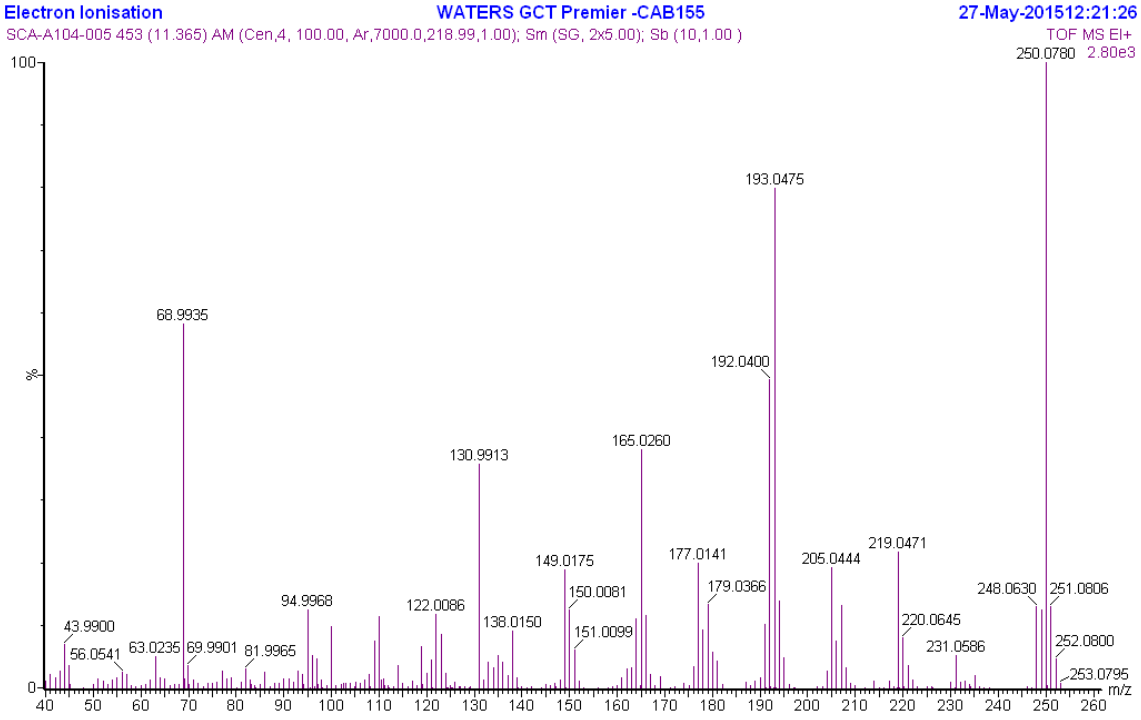


Figure S24: HRMS-EI spectra of 4-(5-methoxybenzo[d]thiazol-2-yl)morpholine (**9i**).

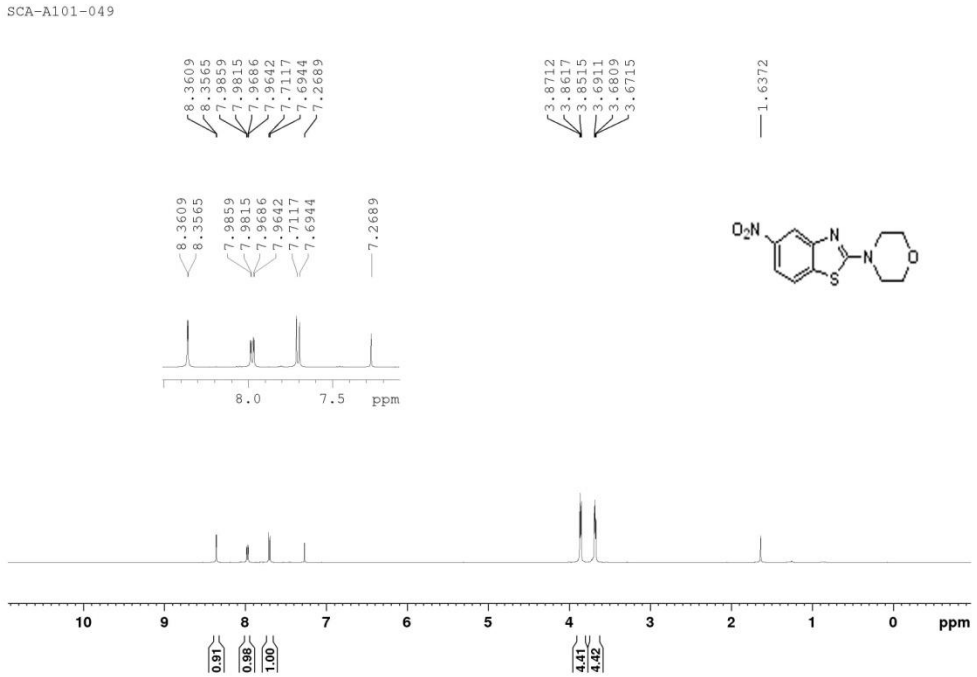


Figure S25: ^{1}H NMR spectra of4-(5-nitrobenzo[d]thiazol-2-yl)morpholine (**9j**).

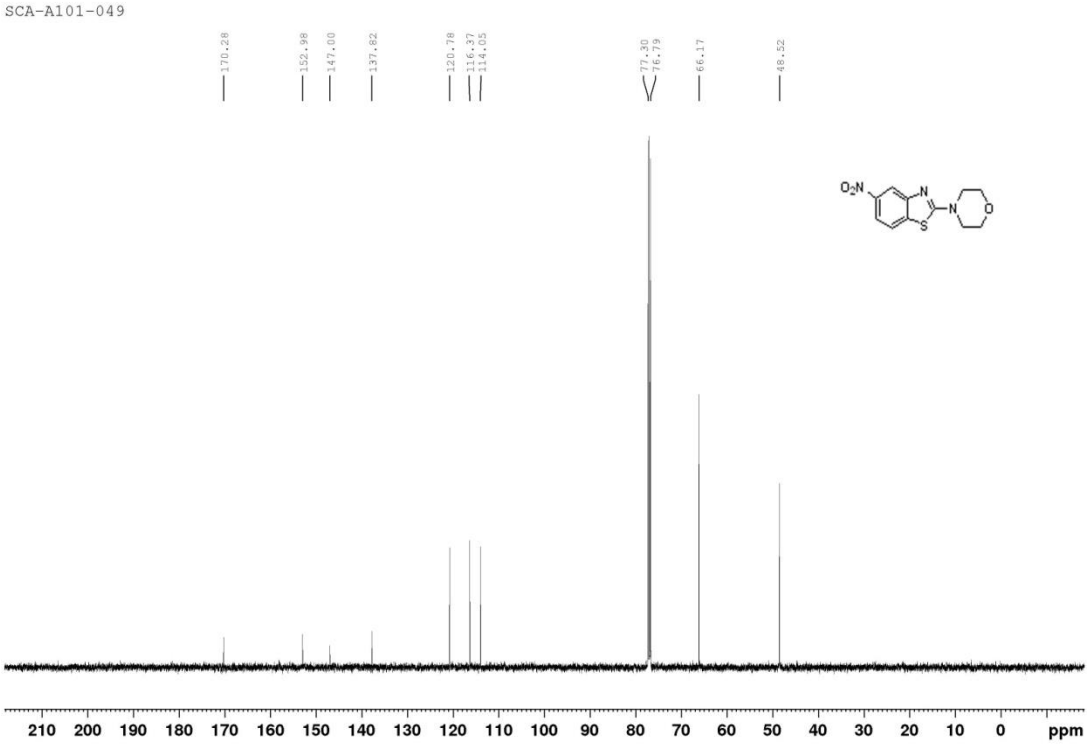


Figure S26: ^{13}C NMR spectra of4-(5-nitrobenzo[d]thiazol-2-yl)morpholine(**9j**).

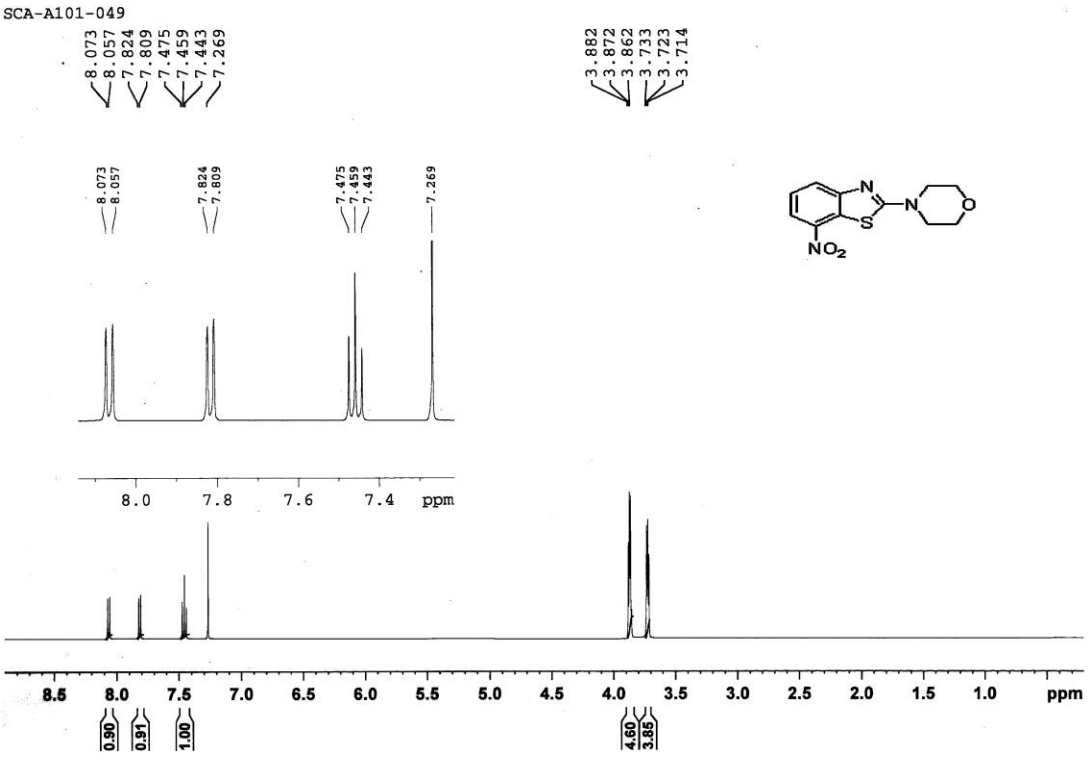


Figure S27: ^{1}H NMR spectra of 4-(7-nitrobenzo[d]thiazol-2-yl)morpholine (**9k**).

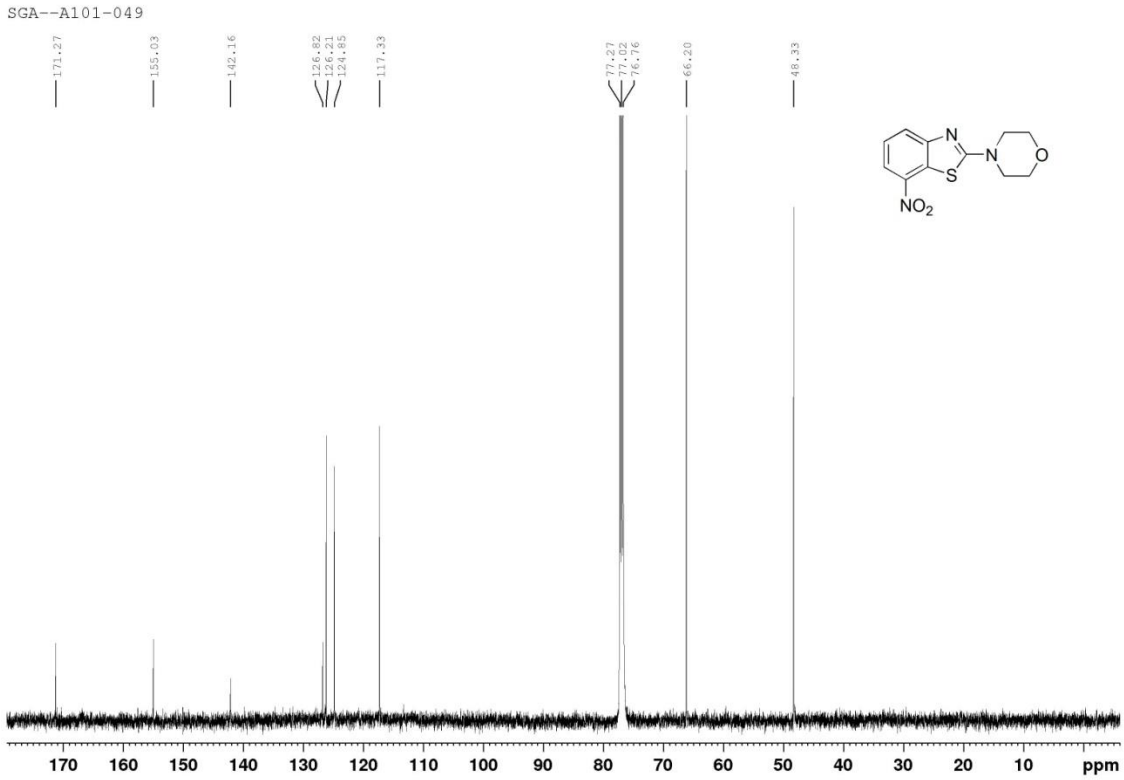


Figure S28: ^{13}C NMR spectra of 4-(7-nitrobenzo[d]thiazol-2-yl)morpholine (**9k**).

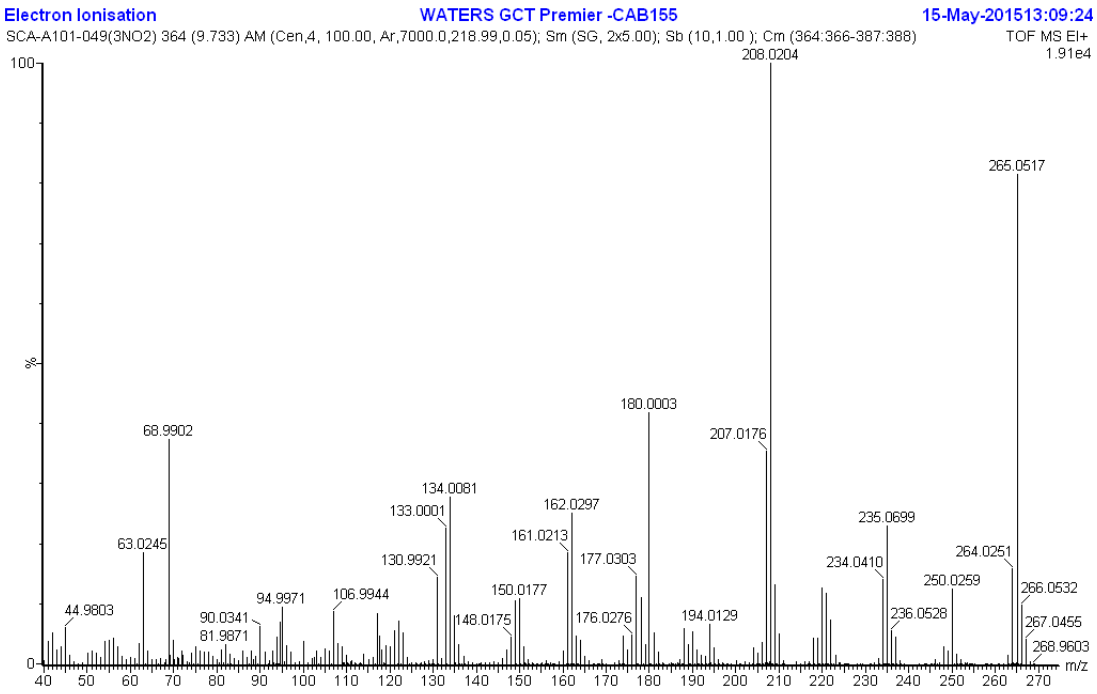


Figure S29: HRMS-EI spectra of 4-(7-nitrobenzo[d]thiazol-2-yl)morpholine (**9k**).

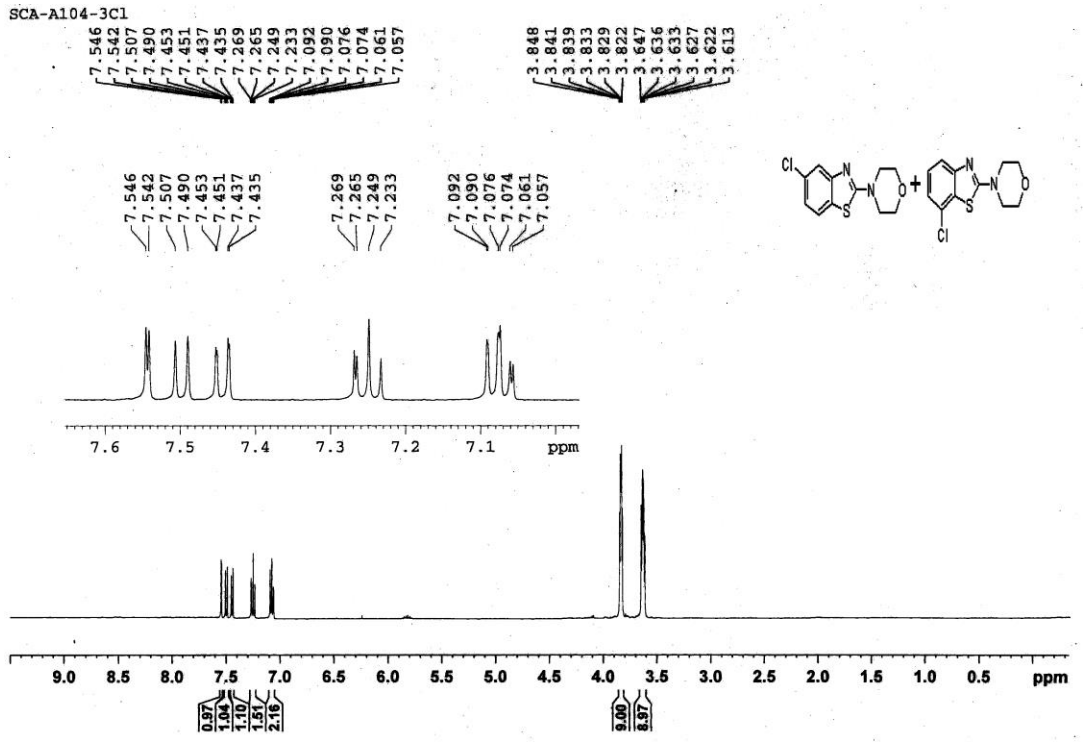


Figure S30: [1]H NMR spectra ofmixture of 4-(5-chlorobenzo[d]thiazol-2-yl)morpholine (**9l**) and 4-(7-chlorobenzo[d]thiazol-2-yl)morpholine (**9m**).

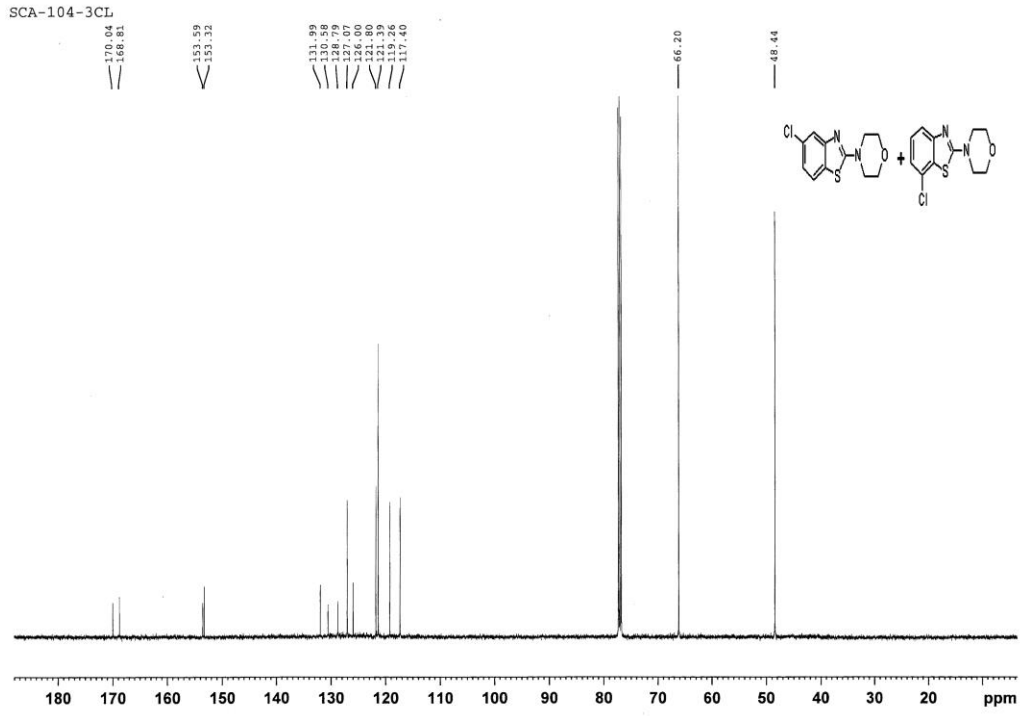


Figure 31: ^{13}C NMR spectra of mixture of 4-(5-chlorobenzo[d]thiazol-2-yl)morpholine (**9l**) and 4-(7-chlorobenzo[d]thiazol-2-yl)morpholine (**9m**).

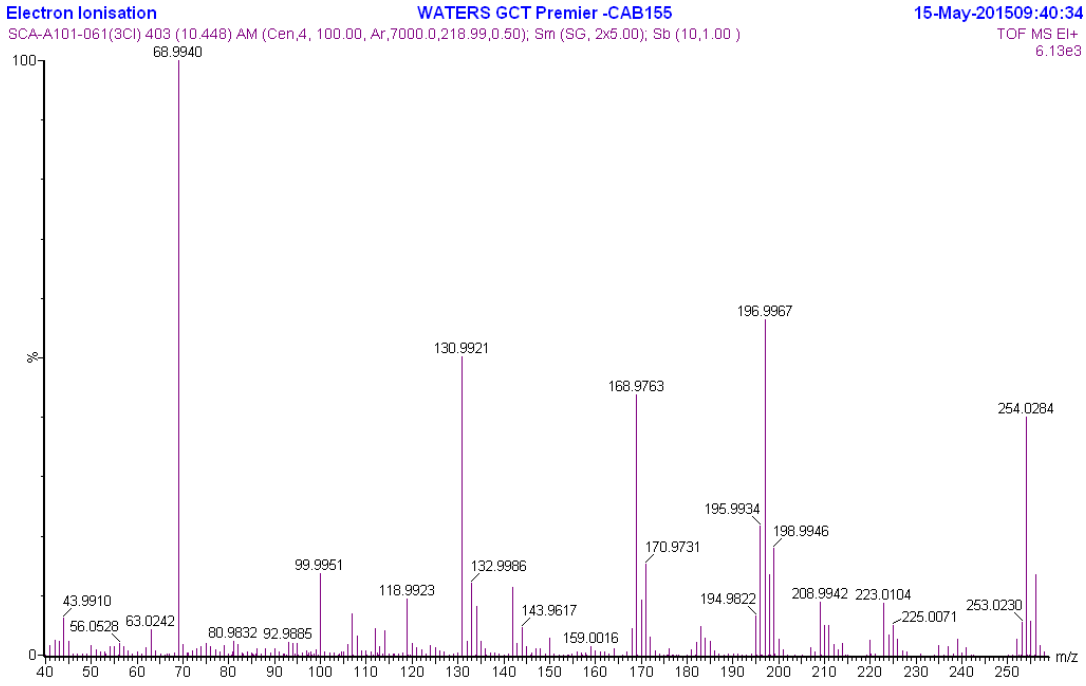


Figure S32: HRMS-EI spectra of mixture of 4-(5-chlorobenzo[d]thiazol-2-yl)morpholine (**9l**) and 4-(7-chlorobenzo[d]thiazol-2-yl)morpholine (**9m**).

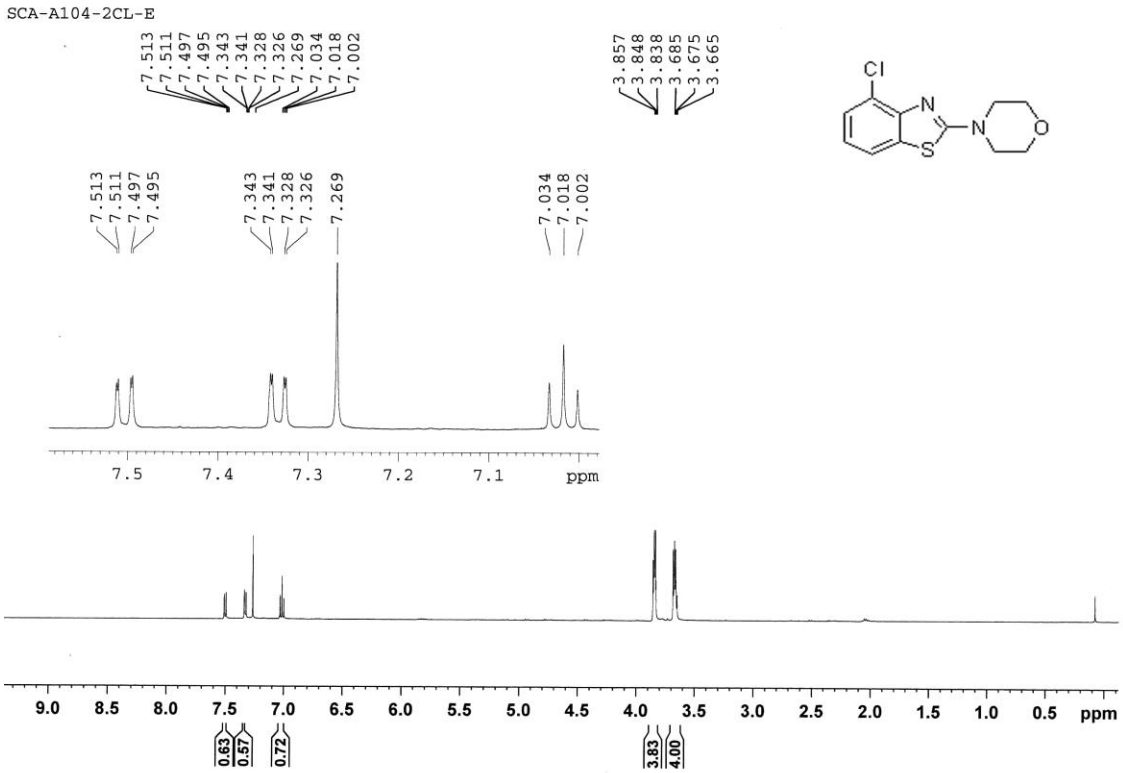


Figure S33: ^{1}H NMR spectra of 4-(4-chlorobenzo[d]thiazol-2-yl)morpholine (**9n**).

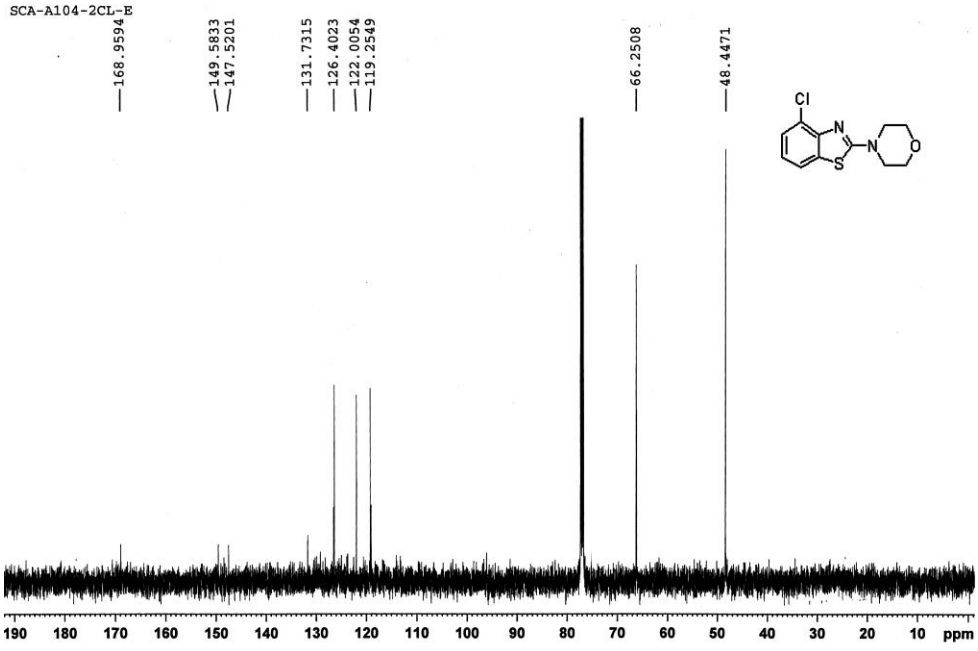


Figure 34: ^{13}C NMR spectra of 4-(4-chlorobenzo[d]thiazol-2-yl)morpholine (**9n**).

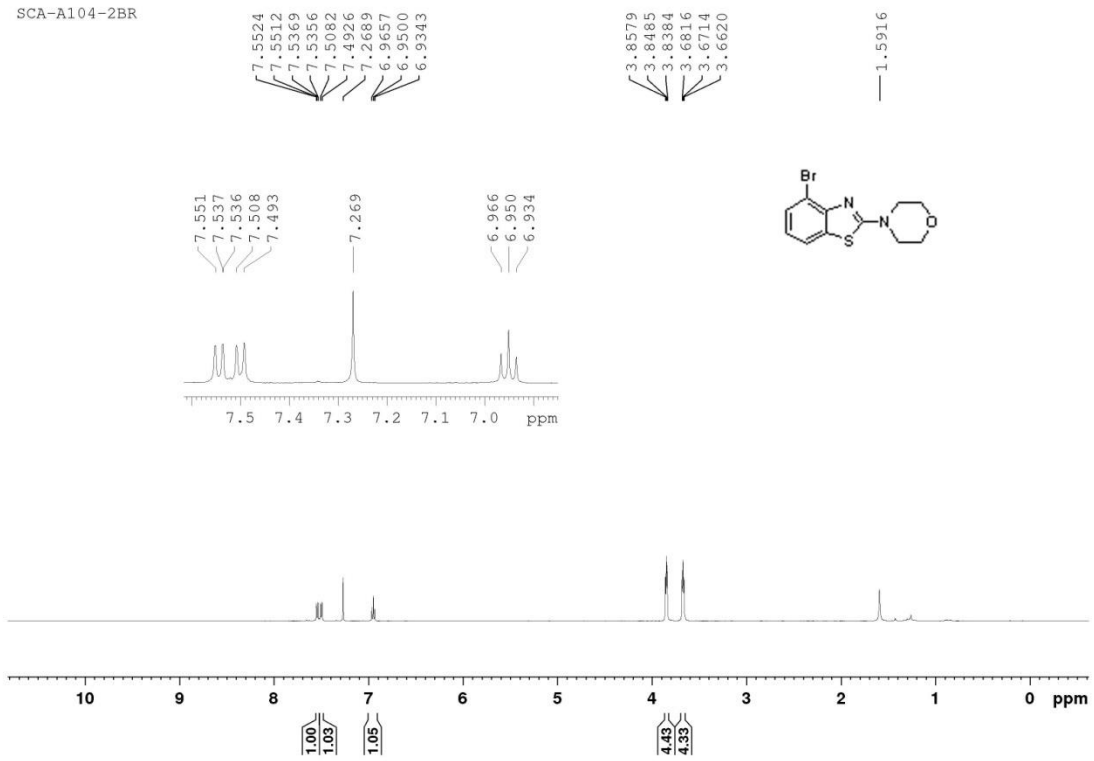


Figure 35: ^{1}H NMR spectra of 4-(4-bromobenzo[d]thiazol-2-yl)morpholine (**9o**).

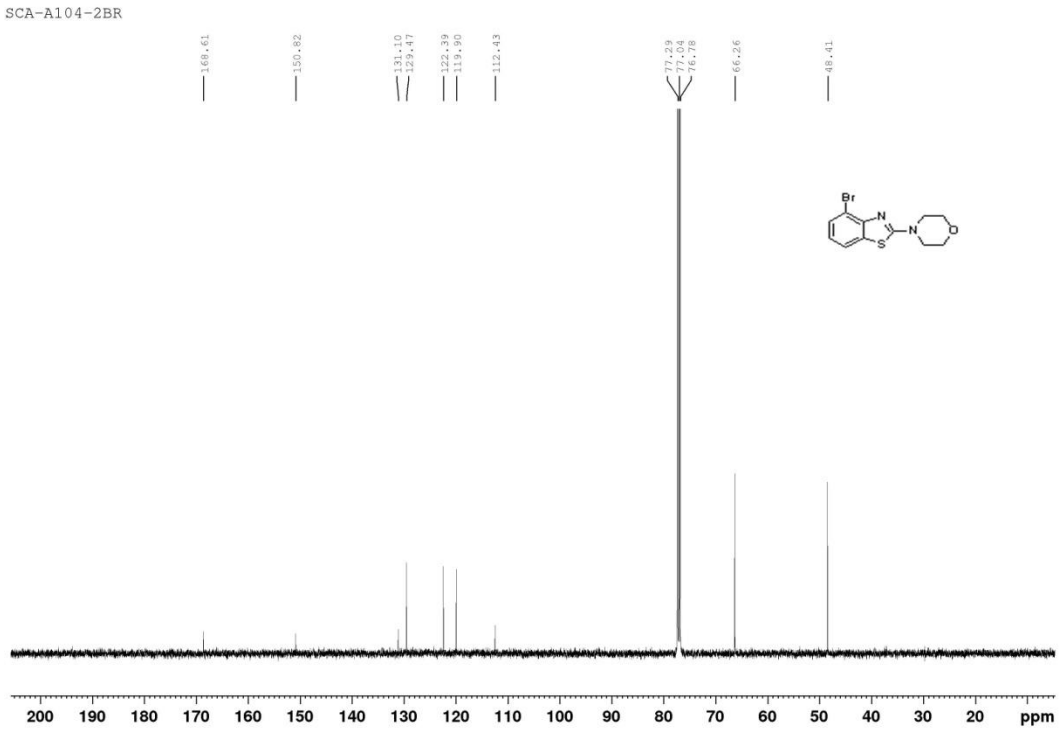


Figure 36: ^{13}C NMR spectra of4-(4-bromobenzo[d]thiazol-2-yl)morpholine (**9o**).

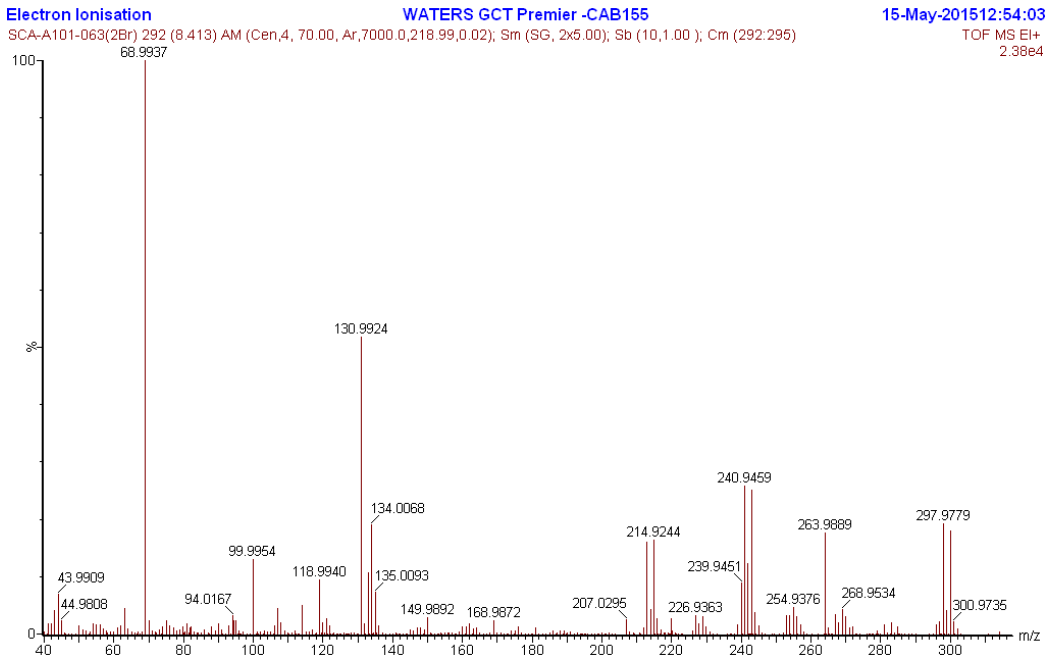


Figure 37: HRMS-EI spectra of 4-(4-bromobenzo[d]thiazol-2-yl)morpholine (**9o**).

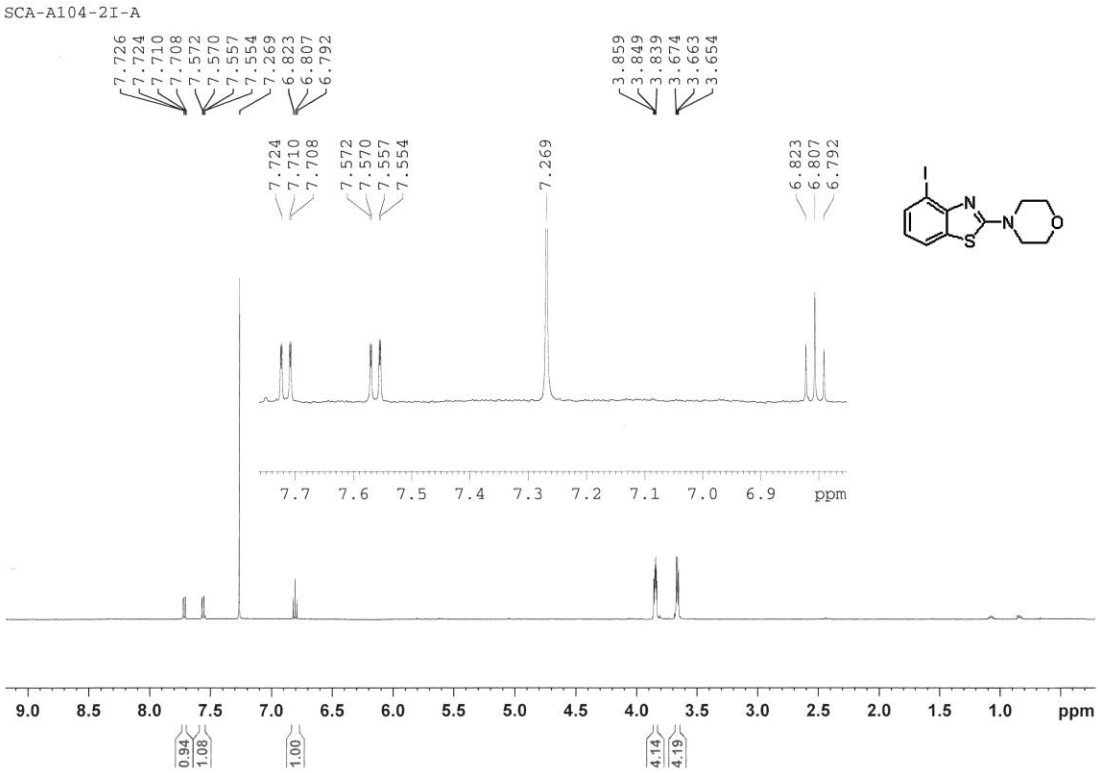


Figure 38: ^{1}H NMR spectra of 4-(4-iodobenzo[d]thiazol-2-yl)morpholine (**9p**).

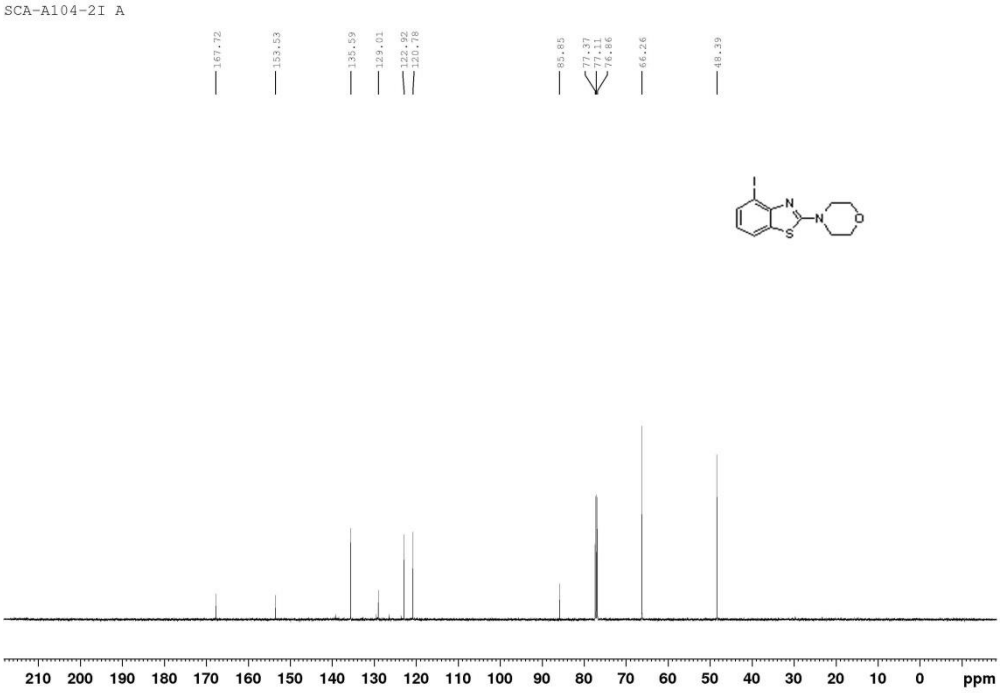


Figure 39: ^{13}C NMR spectra of 4-(4-iodobenzo[d]thiazol-2-yl)morpholine (**9p**).

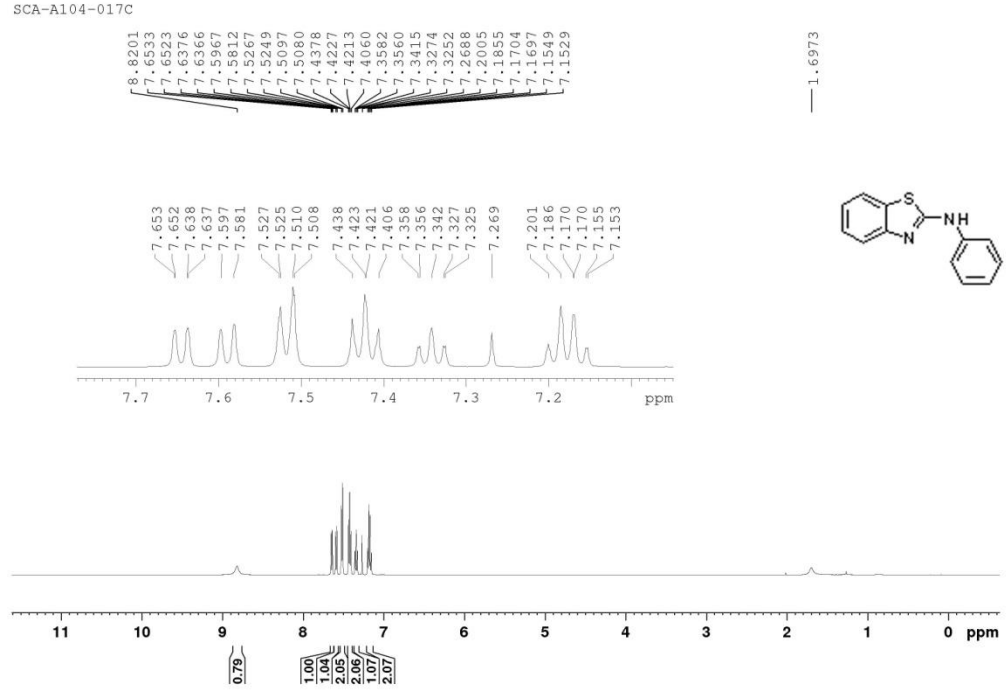


Figure 40: ^{1}H NMR spectra of *N*-phenylbenzo[d]thiazol-2-amine (**9q**).

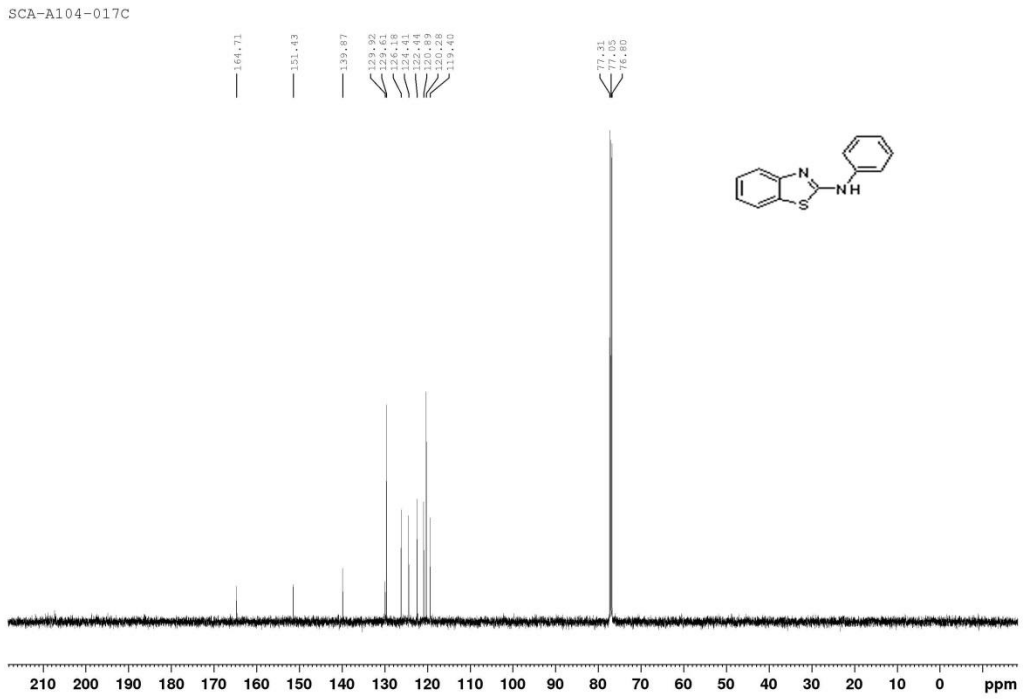


Figure 41: ^{13}C NMR spectra of *N*-phenylbenzo[d]thiazol-2-amine (**9q**).

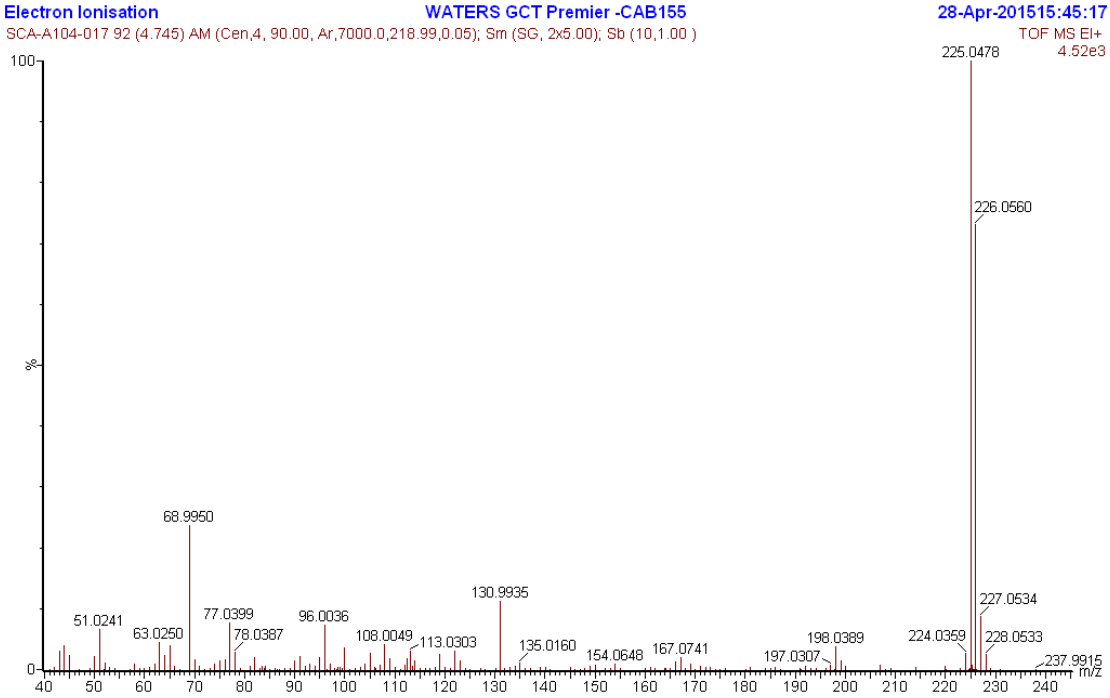


Figure 42: HRMS-EI spectra of *N*-phenylbenzo[d]thiazol-2-amine (**9q**).

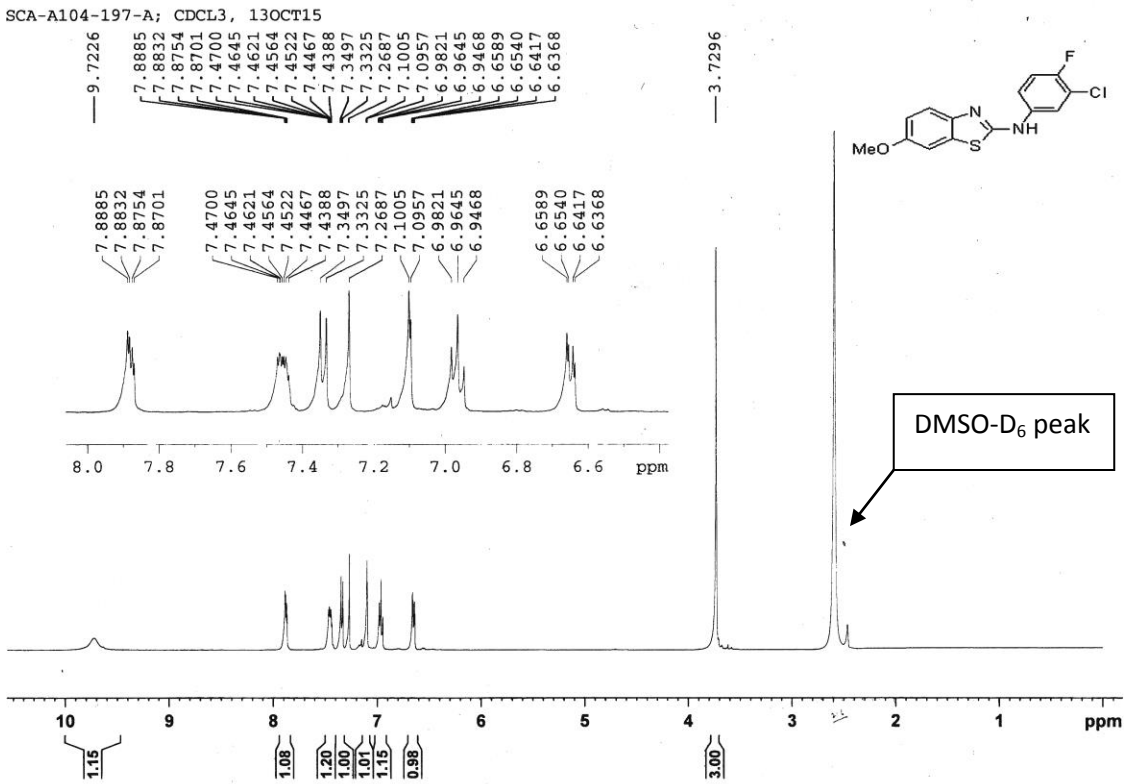


Figure 43: ^{1}H NMR spectra of*N*-(4-chloro-3-fluorophenyl)-5-methoxybenzo[d]thiazol-2-amine (**9r**).

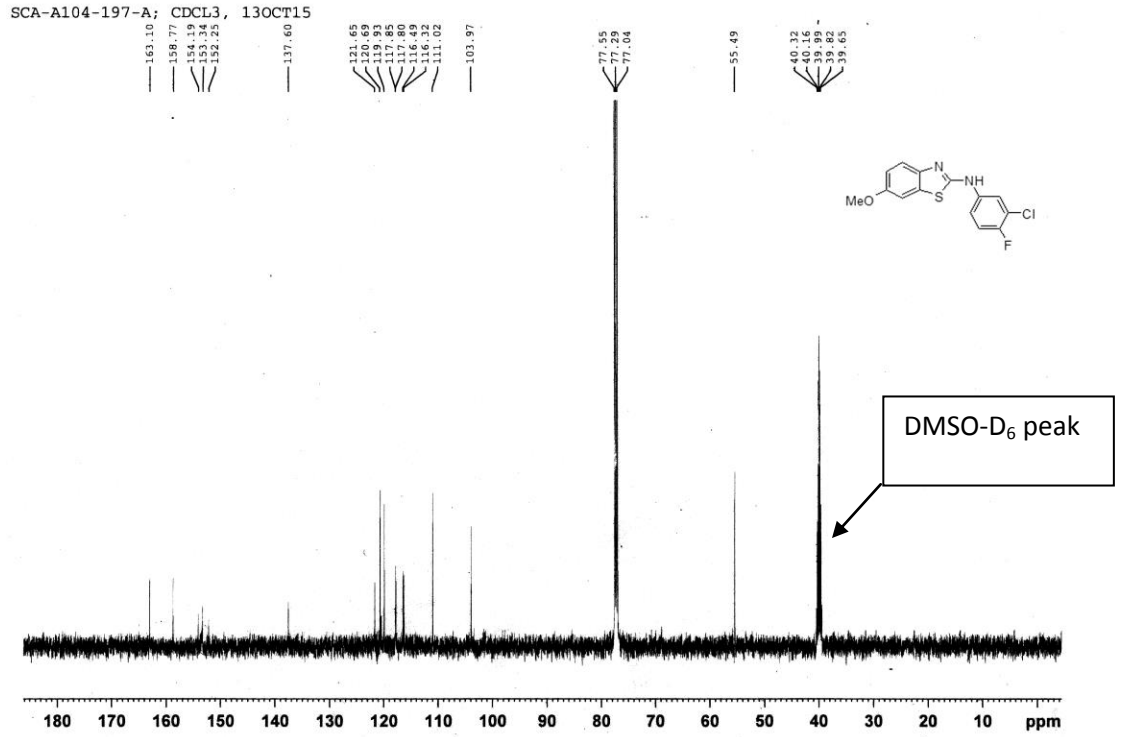


Figure 44: ^{13}C NMR spectra of of*N*-(4-chloro-3-fluorophenyl)-5-methoxybenzo[d]thiazol-2-amine (**9r**).

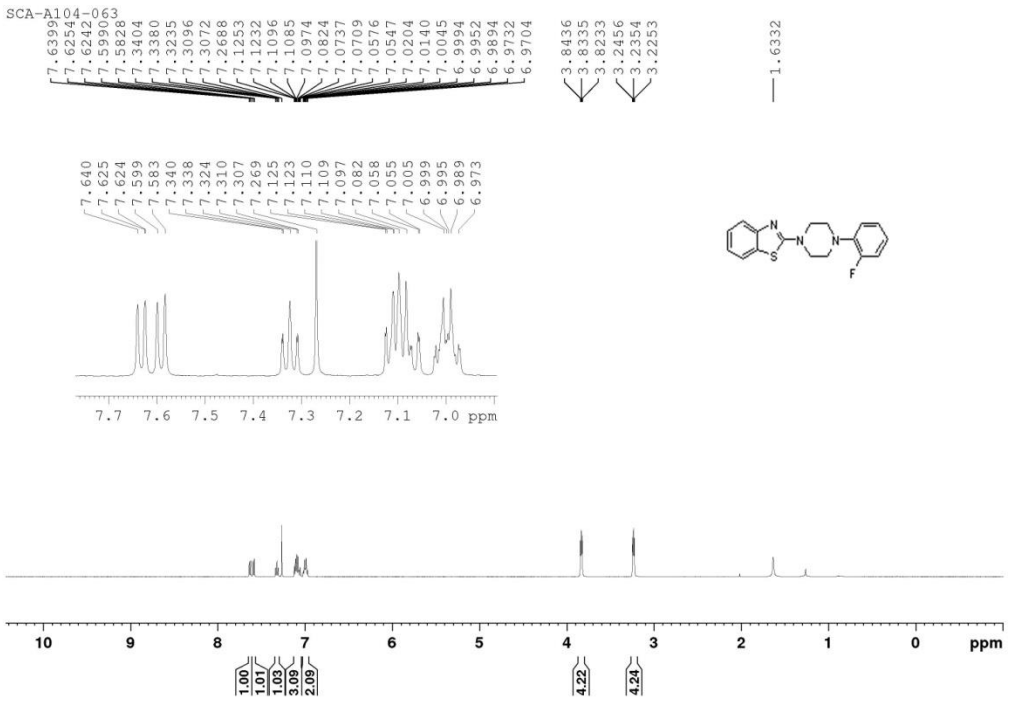


Figure S45: [1]H NMR spectra of 2-(4-(2-fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**9s**).

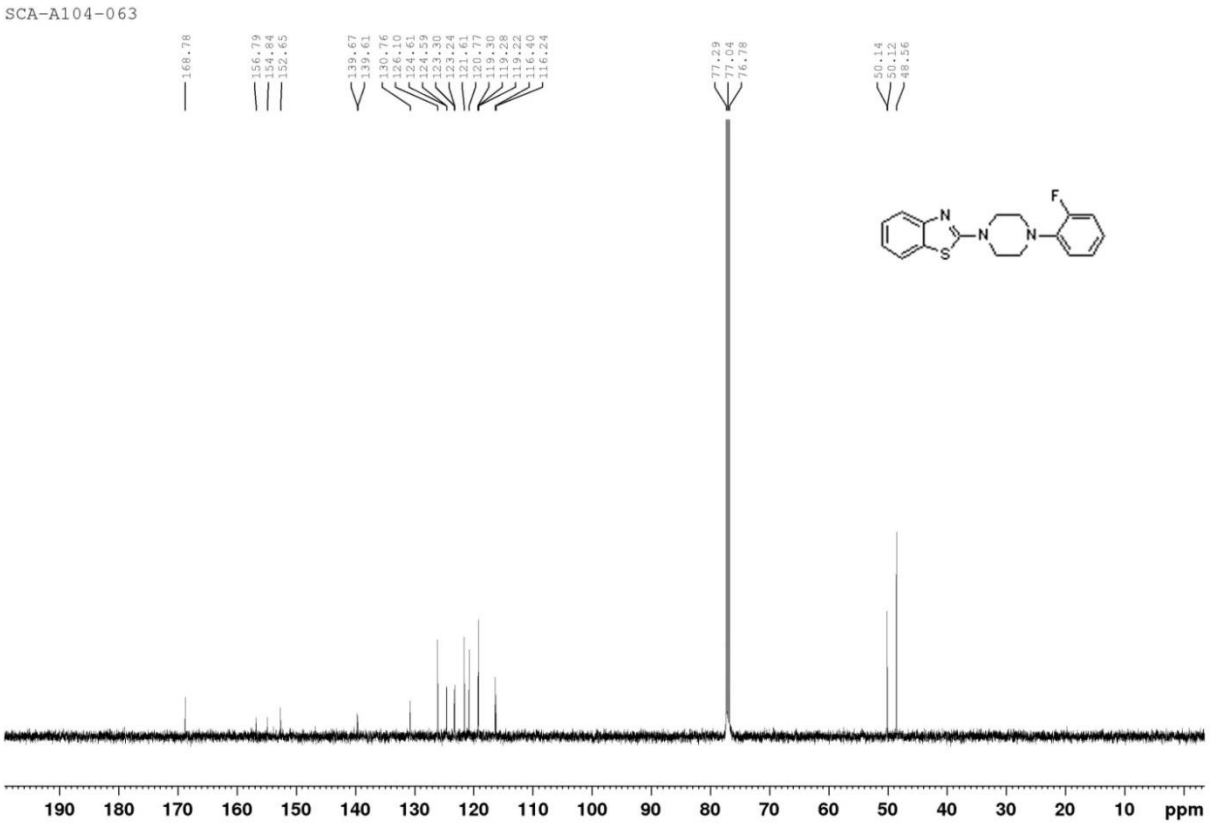


Figure S46: [13]C NMR spectra of 2-(4-(2-fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**9s**).

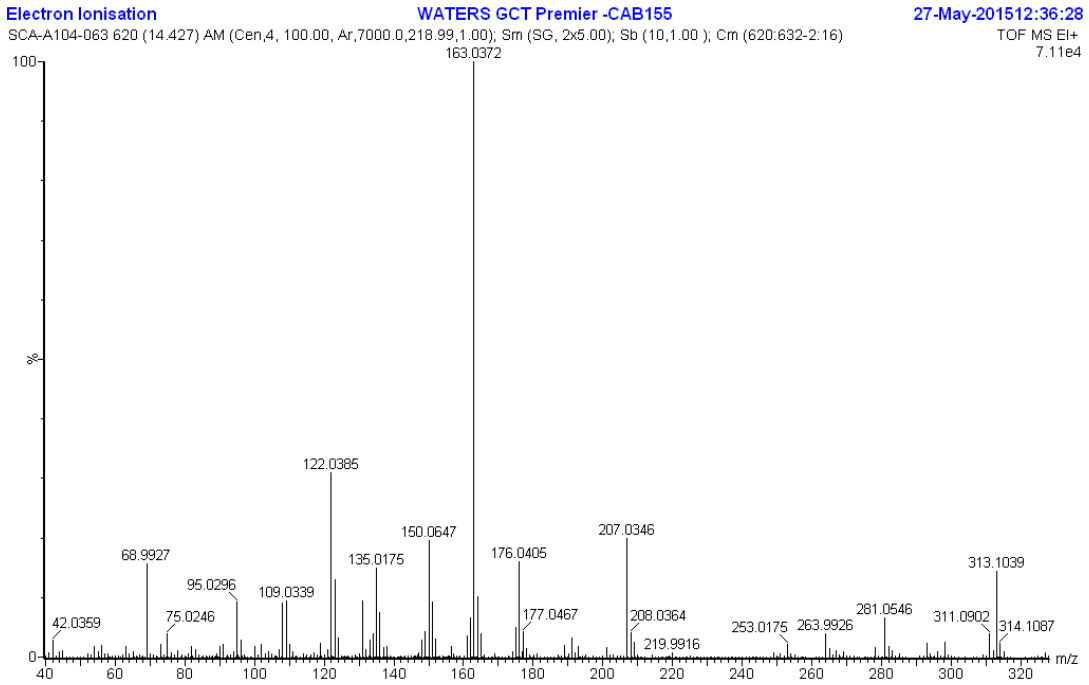


Figure S47: HRMS-EI spectra of 2-(4-(2-fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**9s**).

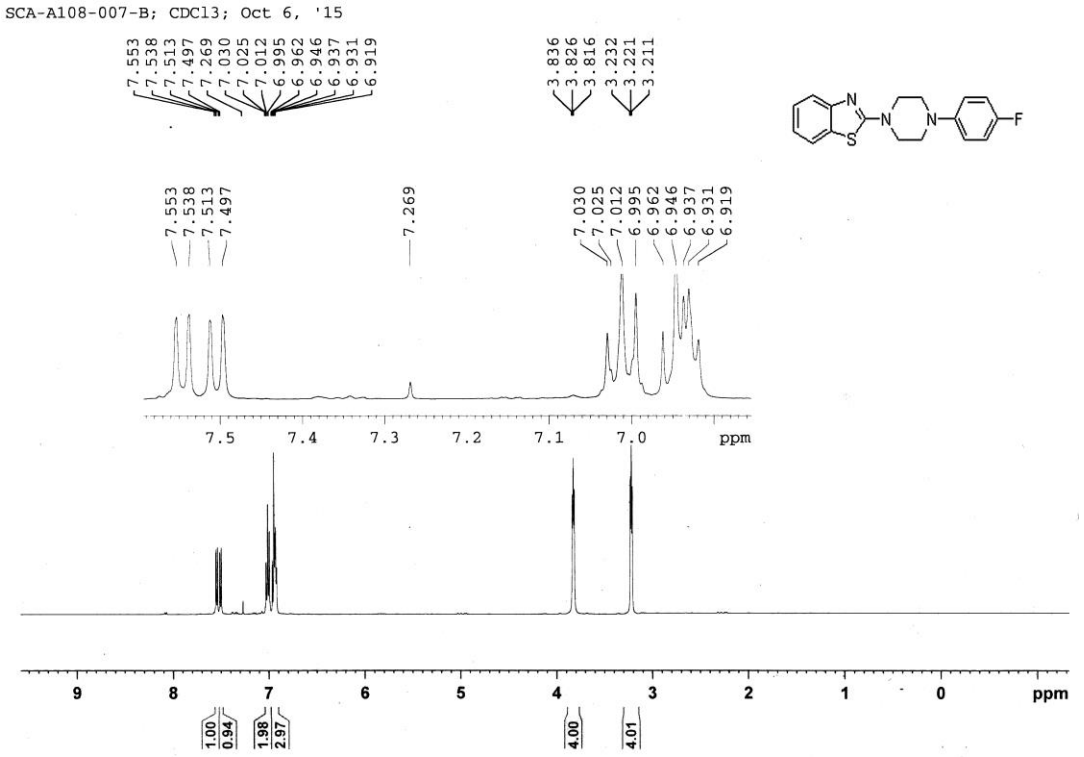


Figure S48: ^{1}H NMR spectra of 2-(4-(4-fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**9t**).

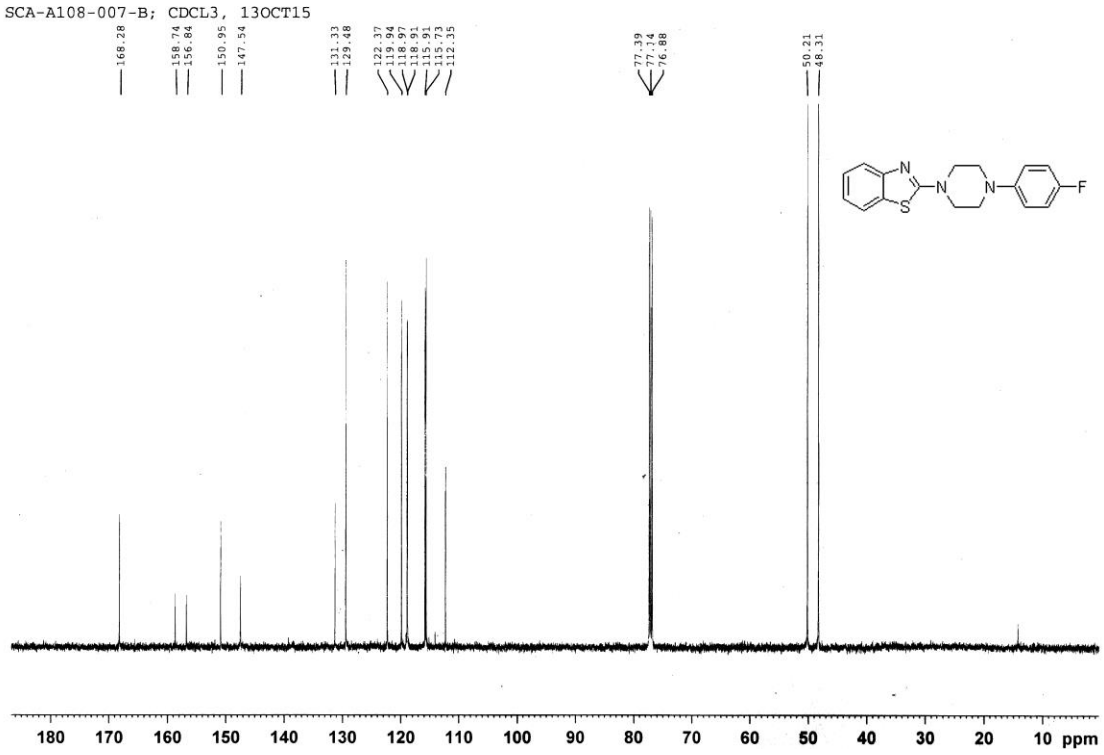


Figure S49: ^{13}C NMR spectra of 2-(4-(4-fluorophenyl)piperazin-1-yl)benzo[d]thiazole (**9t**).

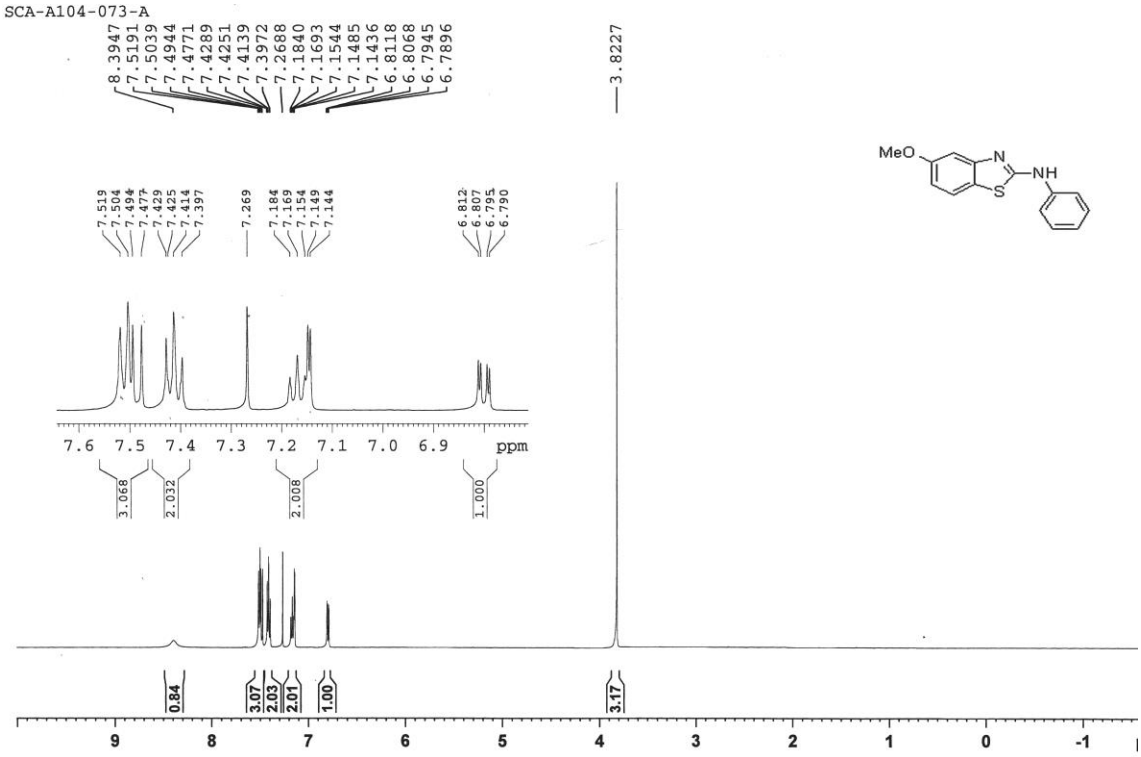


Figure S50:^{1}H NMR spectra of 5-methoxy-N-phenylbenzo[d]thiazol-2-amine (**9u**).

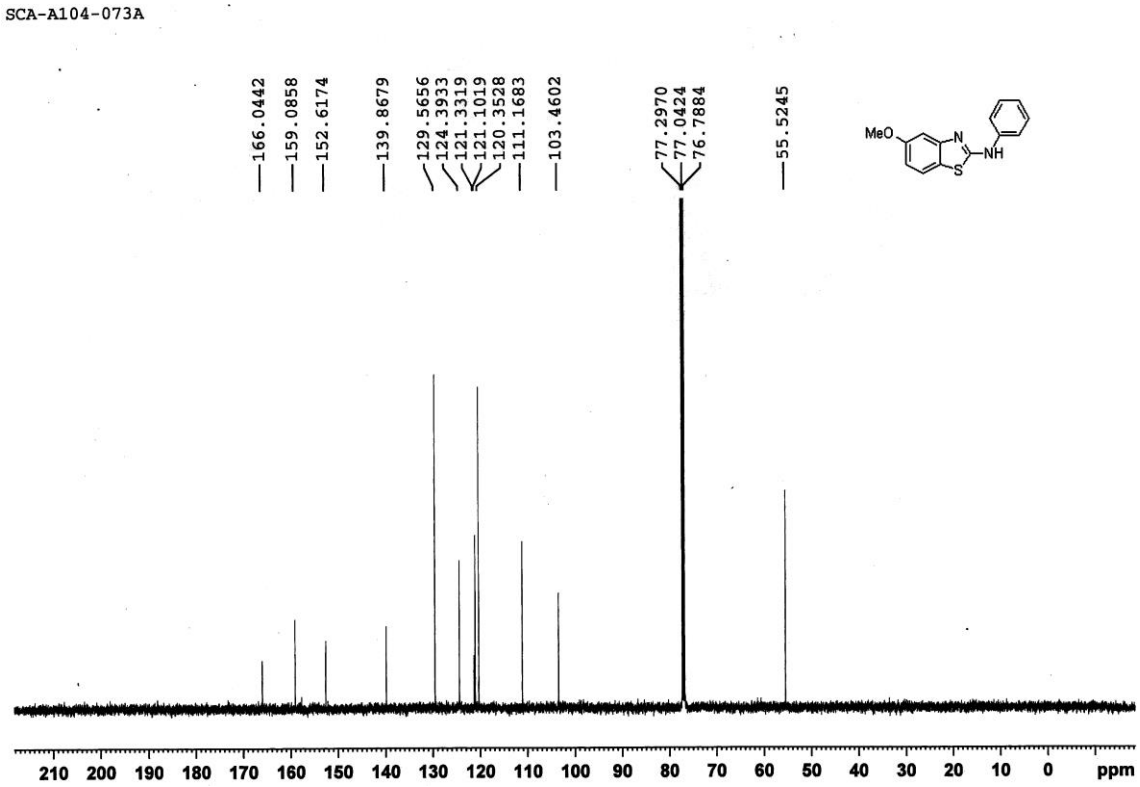


Figure S51: ^{13}C NMR spectra of 5-methoxy-N-phenylbenzo[d]thiazol-2-amine (**9u**).

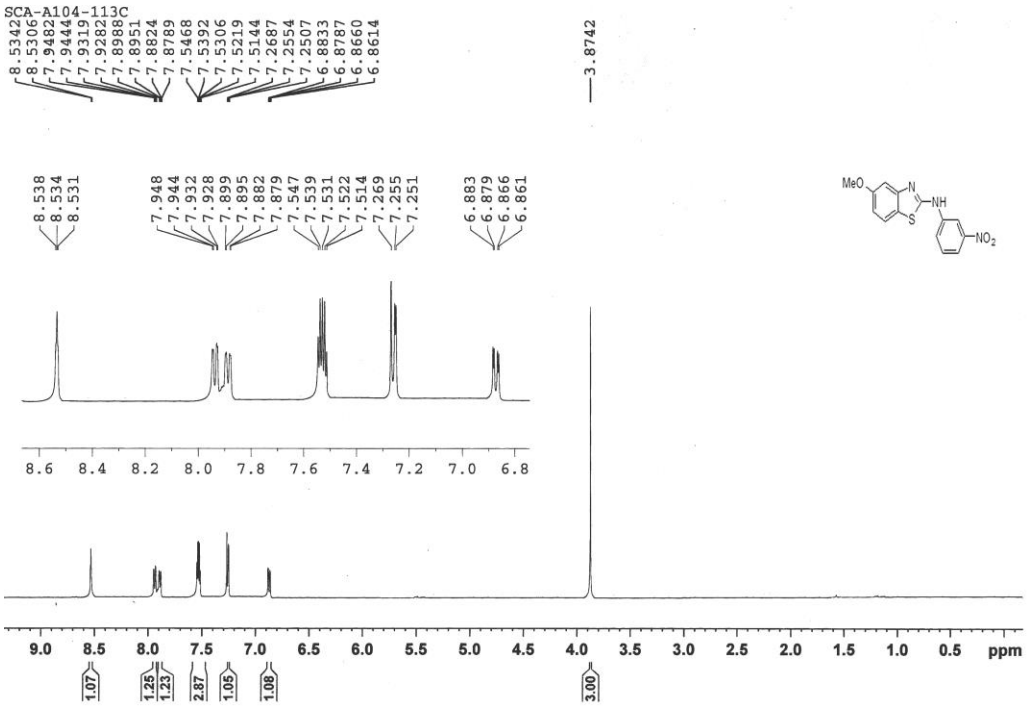


Figure S52: ^{1}H NMR spectra of 5-methoxy-N-(3-nitrophenyl)benzo[d]thiazol-2-amine (**9v**).

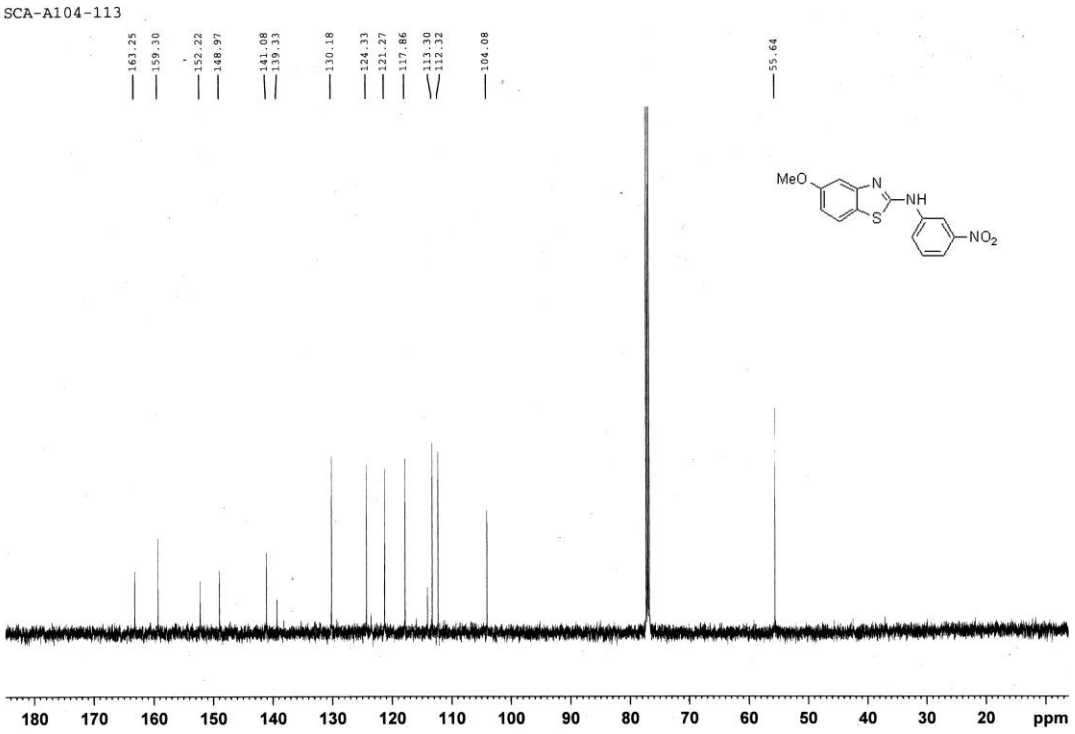


Figure S53: ^{13}C NMR spectra of 5-methoxy-N-(3-nitrophenyl)benzo[d]thiazol-2-amine (**9v**).

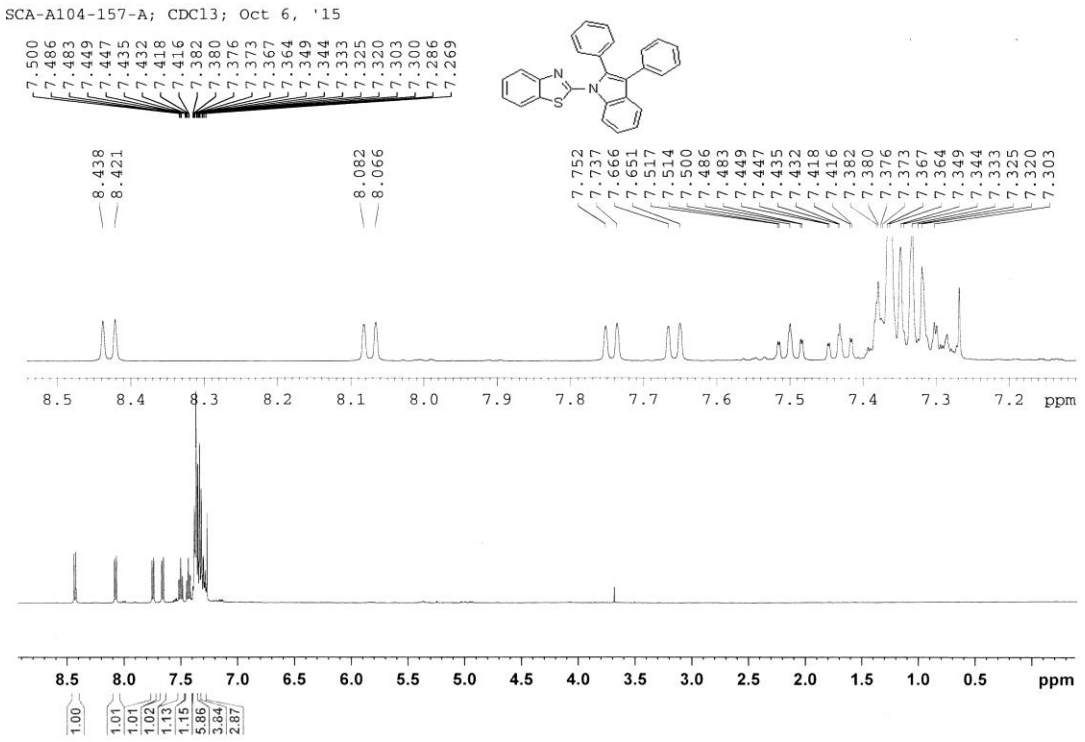


Figure S54: ^{1}H NMR spectra of 2-(2,3-diphenyl-1H-indol-1-yl)benzo[d]thiazole (**16**).

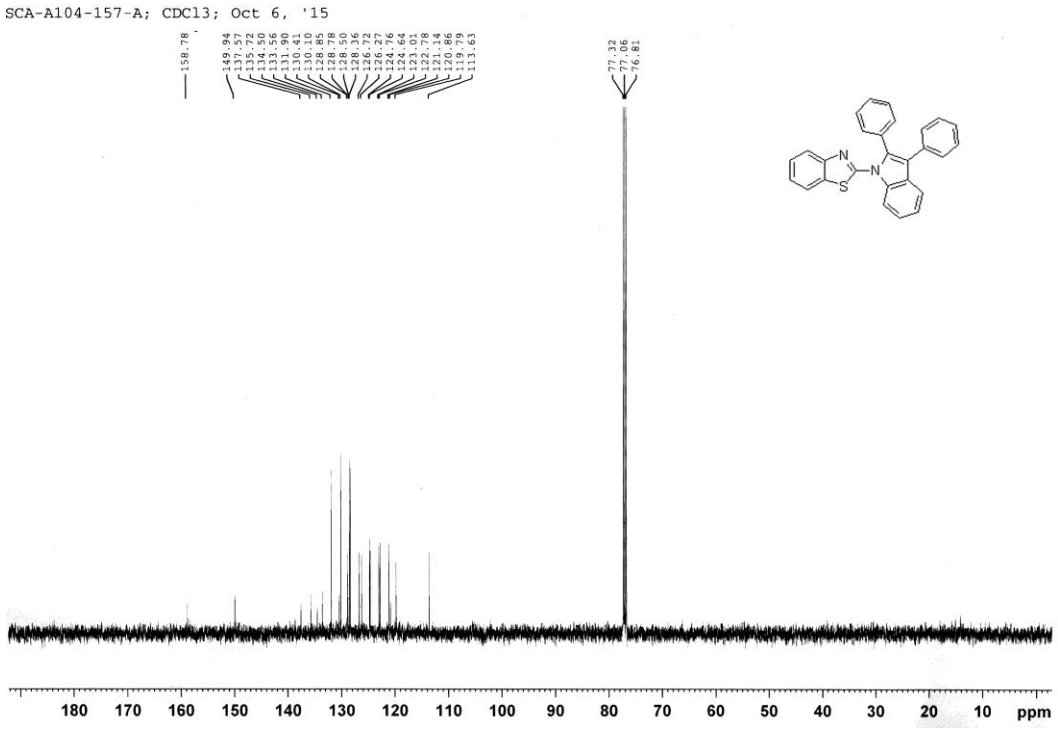
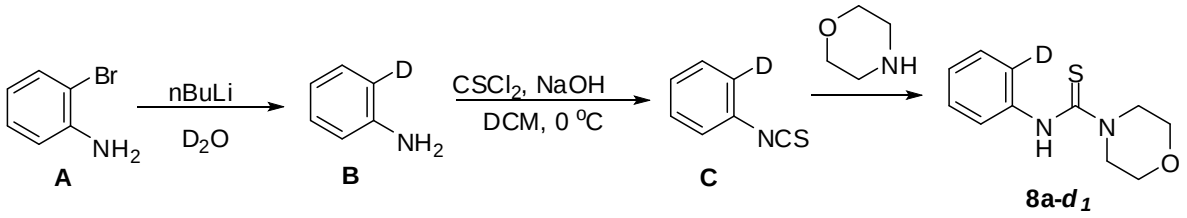


Figure S55: ^{13}C NMR spectra of 2-(2,3-diphenyl-1H-indol-1-yl)benzo[d]thiazole (**16**).

5. Kinetic Isotopic Effect Experiment: Preparation of *N*-2-deutriumphenylmorpholinse-4-carbothioamide



5.1. Preparation of 2-deuterium aniline (B): 2-Bromoaniline (1.5gm) was dissolved in dry diethylether (9 ml) and washed with deuterium oxide (3 x 5 ml) to replace most of the amine protons by deuterium. The ethereal layer is dried over Na_2SO_4, filtered and concentrated to get 1 gm (5.81 mmol) of yellow liquid, which was dissolved in 5 mL of anhydrous THF and transferred to the reaction flask via a syringe, the flask was evacuated and replaced by argon (thrice) and then ^{n}BuLi (18.4 mL, 29 mmol, 1.6 M) was added to the mixture at -78 ^{o}C. After stirring at -78 ^{o}C for 1 h, the mixture was warmed to rt and stirred for 1 h. Then, D_2O (0.29 mol) was added to the reaction mixture at -78 ^{o}C, stirred for 30 min, warmed to rt and kept at rt for 1 h. Finally the reaction mixture was quenched with water and extracted with ethyl acetate (100 mL x 2). The organic layers were combined, dried over Na_2SO_4 and concentrated *in vacuo*, and purified by silica gel chromatography (EtOAc: petroleum ether = 20: 80) to obtain the desired compound **6;** yield: 0.50 g (91.4%). The product so obtained was used in the subsequent reaction.

5.2. Preparationof2-deutriumphenylisothiocyanate (C) : A schlenk tube equipped with a stir-bar was charged with pure compound **6** (0.5 g, 5.31 mmol) and dissolved it in 15 mL DCM. The reaction tube was purged with argon. Then the reaction mixture was cooled to 0 ^{o}C and added thiophosgene (1.4 mL, 14.97 mmol) via syringe dropwise. Subsequently, crushed NaOH was added and the reaction mixture was stirred for 1 hr. On completion of reaction on TLC, the reaction mixture was extracted with DCM (20 mL x 2). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure to obtain the crude **7**.

5.3. Preparation of *N*-2-deutriumphenylmorpholine-4-carbothioamide 8a-*d*$_1$: A 10 mL round bottom flask was charged with crude **7** (0.2 gm, 1.468 mmol) and morpholine (0.116 gm, 1.334 mmol) under neat reactions at rt. The reaction stirred for 1 h to obtained gummy solid. The reaction mixture was purified by silica gel chromatography (EtOAc: petroleum ether = 20: 80) to obtain the desired compound **8a-*d*$_1$**. Product: white solid, yield: 0.380 g (75%, 95% deuterium incorporation); m.p.: 118.5 °C. ^{1}H NMR (δ ppm): (500 MHz, $CDCl_3$), 7.35 (m, 2H, aromatic C-*H*, *J* = Hz), 7.31 (bsr, 1H, N-*H*), 7.17 (t, 1H, aromatic C-*H*, *J* = 7.5 Hz), 7.13 (d, 1H, aromatic C-*H*, *J* = 8 Hz), 3.82 (t, 4H, sp^3 C-*H*, *J* = 4.8 Hz), 3.73 (t, 4H, sp^3 C-*H*, *J* = 4.82 Hz). ^{13}C NMR (δ ppm): (125 MHz, $CDCl_3$): 183.81, 139.74, 129.30, 129.20, 125.42, 122.92, 66.14, 49.75.

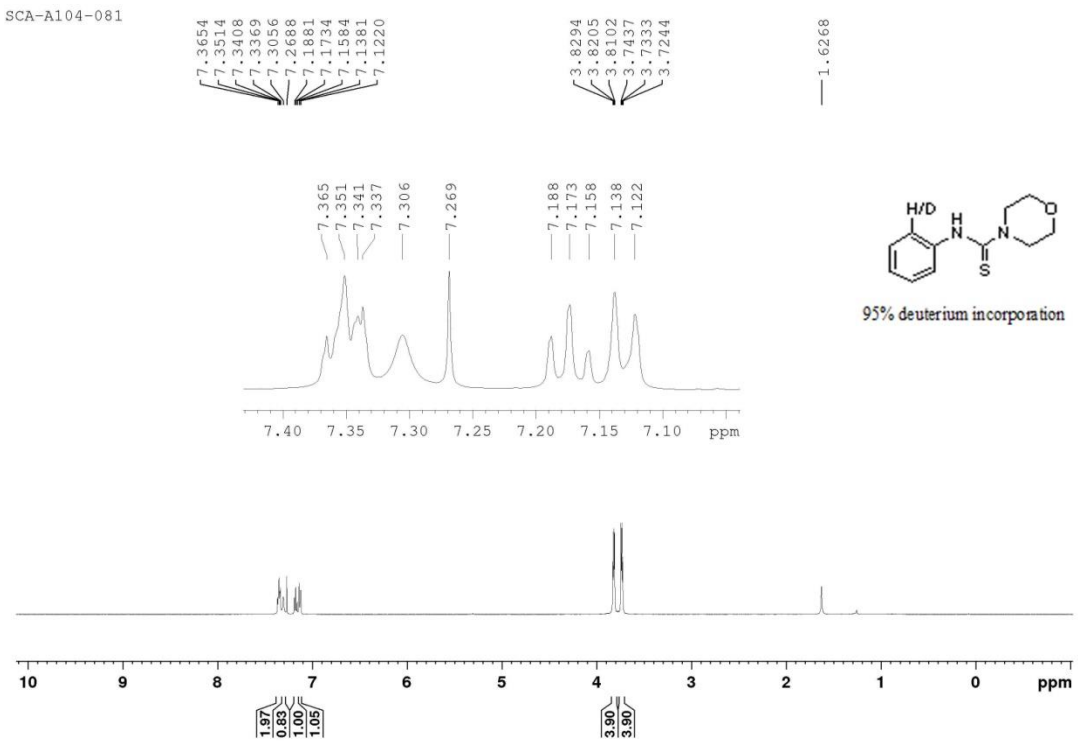


Figure S56: ^{1}H NMR spectra of *N*-2-deutriumphenylmorpholine-4-carbothioamide (**8a-*d*$_1$**).

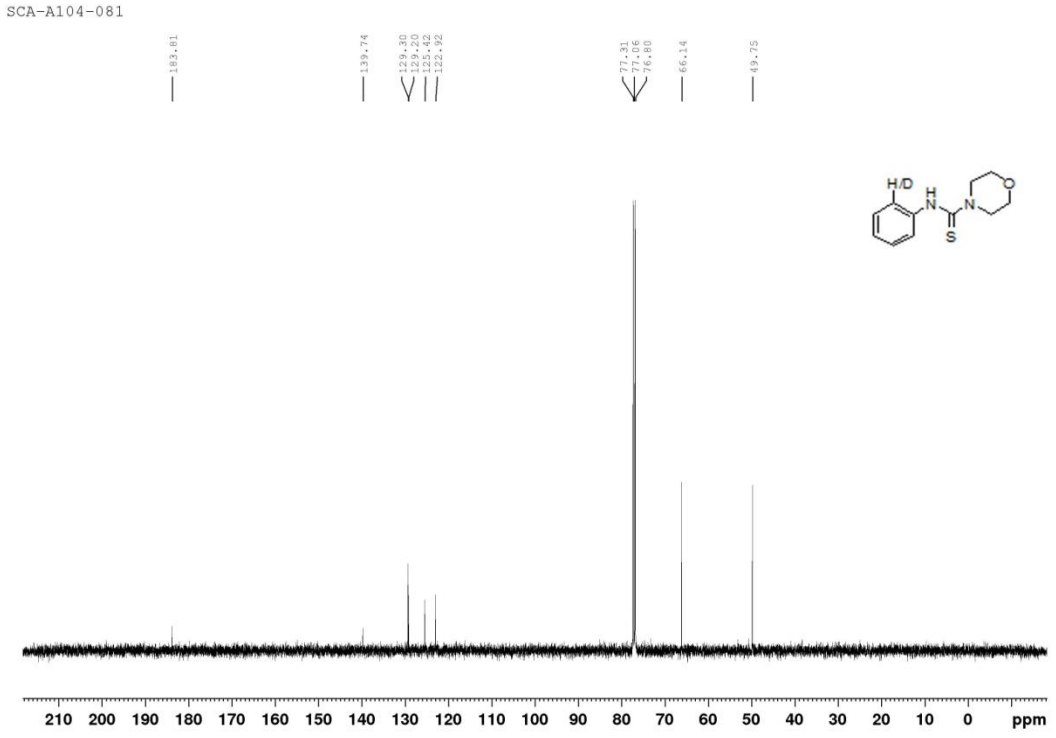


Figure S57:^{13}C NMR spectra of *N*-2-deutriumphenylmorpholine-4-carbothioamide (**8a- *d*$_1$**).

5.4. Determination of Kinetic Isotope Effect (KIE) in 2-aminobenzothiazole experiment

A schlenk tube equipped with a stir-bar was charged with *N*-(2-dueteriopenyl)morpholine-4-carbothioamide **8a-*d*$_1$** (0.05 g, 0.223 mmol) and DCE (2 mL) as a solvent. The reaction tube was purged with argon. Then after 5-10 min Oxone (0.068 g, 0.223 mmol) and $RuCl_3$ (0.002 g, 0.011 mmol) was added to the reaction mixture followed by argon purging, then argon was replaced by air and the mixture was stirred at 110 ^oC for 4 hrs. After cooling to room temperature, the reaction mixture was passed through Celite bed and concentrated under reduced pressure and then purified by silica gel chromatography (EtOAc: petroleum ether = 1:9) to give inseparable mixture of **9a**-*d* and **9a**. The ratio of **9a**-*d*$_1$ and **9a** was determined by ^1H NMR spectrum as **9a-*d*$_1$**: **9a**= 45: (50+5) (KIE = 45/(55-5)_= 0.9).

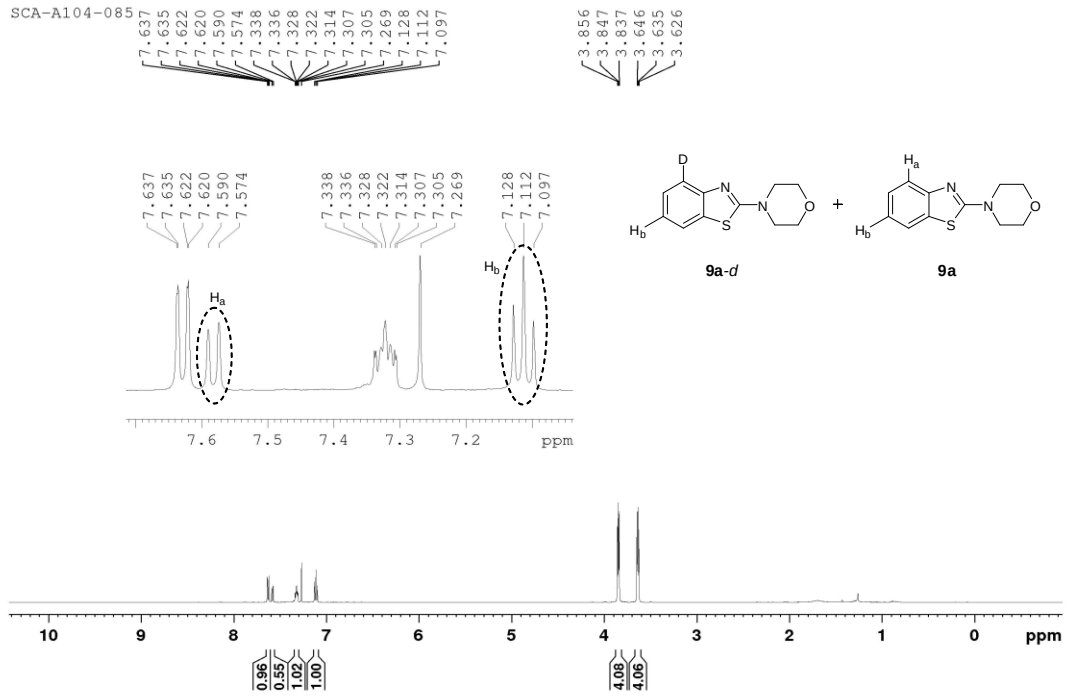
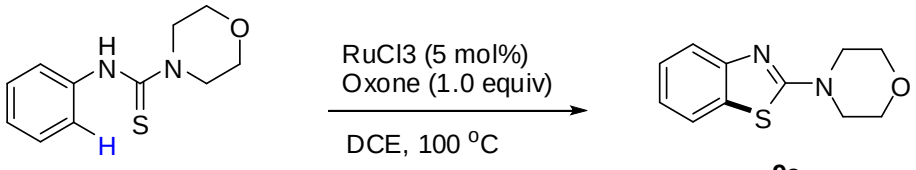


Figure S58: ^1H NMR spectra of Kinetic isotopic effect experiment showing mixture of **9a** and **9a-*d*$_1$**.

6. Radical Trap Experiment

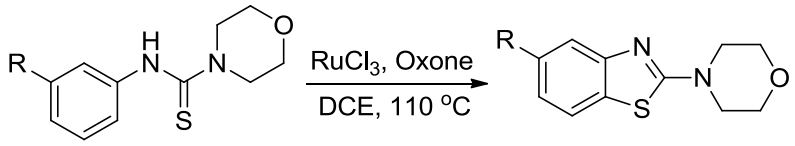


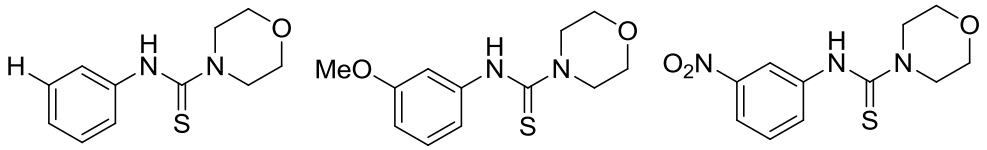
8a **9a**

Condition:	
None-	87%
TEMPO-	85%
Galvinoxyl-	83%

PROCEDURE: The reactions were been carried out as per the protocol reported in Section 3 in the presence of either TEMPO or Galvinoxyl (free radical scavenger). The product was purified by silica-gel column chromatography (EtOAc: hexane) to produce the isolated yields of **9a**.

7. Table S7: Kinetic Studies





8a **8i** **8j**

Time	**8a** (Yield%)	**8i** (Yield%)	**8j** (Yield%)
0	0	0	0
2.5	21.86	48.9	3
0.5	46.6	75	8
1	65	85	10
1.5	72	87	15
2	81	90	28
2.5	83	91	37
3	86	91	54
4	87	91	65
6	87	91	77
8	87	91	77
10	87	91	77

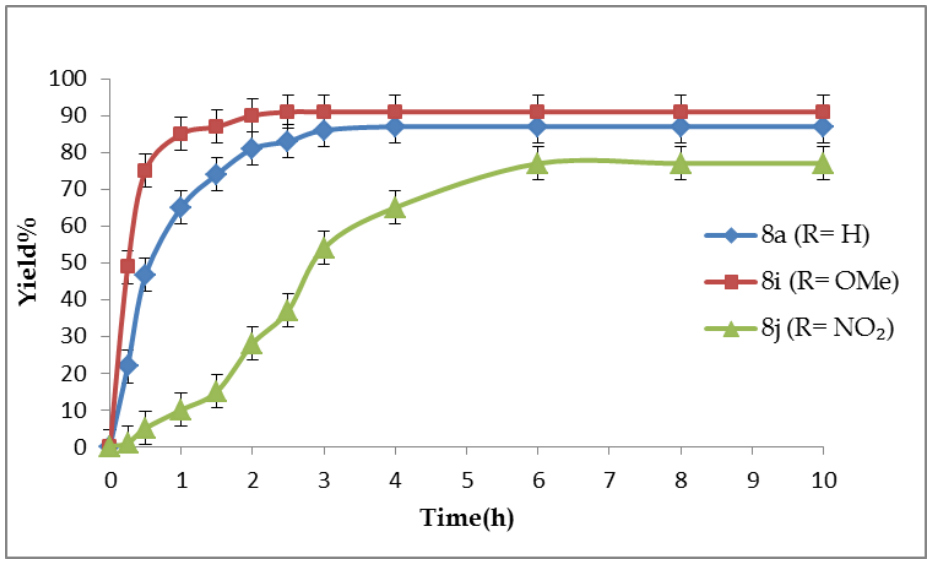


Figure S59: Plot of yield *vs.* time in the cyclizations of **8a**, **8i**, **8j**.

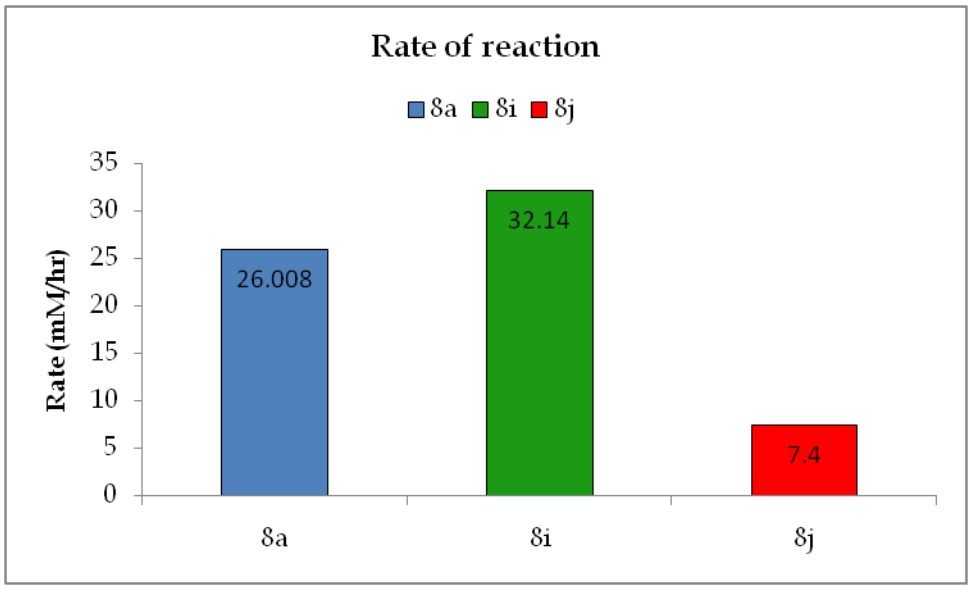


Figure S60: Comparison in the rate of the reaction of 8a, 8i and 8j

8. Crystallographic Data

Crystals of **9q** and **9u** suitable for Single Crystal X-ray Analysis were obtained by slow evaporation in their acetonitrile solutions. Crystal data were collected on Bruker APEX II CCD diffractometer (MoKα, λ = 0.71073 Å). Complete hemispheres of data were collected using ω-scans (0.3º, up to 30 seconds/frame). Integrated intensities were obtained with SAINT+[7] and when they were corrected for absorption SADABS was used.[8] Structure solution and refinement was performed with the SHELXTL-package.[9] The structures were solved by direct methods and completed by iterative cycles of DF syntheses and full-matrix least-squares refinement against

F^2.[10] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. Details of the data collection and refinement parameters are given in Table S7. CCDC 1418622 (**9q**) and 1418623 (**9u**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S8: Crystal data and refinement parameters for compounds **9q and 9u**.

Compound	**9q**	**9u**
Formula	$C_{13}H_{10}N_2S$	$C_{14}H_{12}N_2OS$
Formula weight	226.29	256.32
Crystal system	Triclinic	Monoclinic
Space group	P-1	P21/c
Temperature (K)	296(2)	296(2)
a (Å)	3.9105(6)	13.1514(9)
b (Å)	10.8964(17)	12.8014(9)
c (Å)	12.403(2)	7.2224(6)
α (º)	97.328(3)	90
β (º)	94.957(3)	105.094(2)
γ (º)	92.265(3)	90
Volume (Å^3)	521.54(14)	1173.99(15)
Z	2	4
Reflections collected/unique	3145	7716
R_{int}	0.0186	0.0272
Data/restraints/parameters	1873/0/149	2062/0/168
Goodness-of-fit on F^2	1.067	1.063
Final *R* indices [$I>2\sigma(I)$][a]	R_1 = 0.0311, wR_2 = 0.0732	R_1 = 0.0299, wR_2= 0.0759
R indices (all data)[a]	R_1 = 0.0369, wR_2 = 0.0762	R_1 = 0.0350, wR_2 = 0.0792
Largest residuals (e.Å^{-3})	0.19/-0.29	0.25/-0.30

[a] $R_1 = \Sigma \| \|F_0\| - \|F_c\| \| / \Sigma |F_0|$; $wR_2 = \{[\Sigma w(|F_0|^2 |F_c|^2)^2]/[\Sigma w(|F_0|^2)^2]\}^{1/2}$

9. **Computational details**

For all the theoretical investigations the density functional theory (DFT) based Becke three-parameter hybrid (B3) functional was used along with Lee-Yang-Parr (LYP) correction B3LYP formalisms.[11] The standard 6-31+G(d,p) basis set[12] was used to describe the H, C, N, O and Cl atoms and Def2-TZVP for Ru.[13] The effective core potential variation was used for Ru. The free geometry optimizations for all the species have been performed followed by harmonic vibrational frequencies. Systematic conformational search have been performed to determine the lowest energy conformers for each extrema. Frequency calculations on each equilibriumgeometry show the true minima for reactant and product. Transition state is determined with a vibrational frequency corresponds to the reaction coordinate. Zero-point energies were included to calculate the activation barrier at room temperature. All the theoretical calculations have been performed using the GAUSSIAN09 package.[14]

9.1. Cartesian coordinates for intermediate (reactant), transition state and intermediate (product).

The listed cartesian coordinates correspond to optimizations performed at B3LYP level with Def2-TZVP for Ru and 6-31+G** for all other atoms.

Reactant (**12**):

6	-0.170850	-2.500981	-1.345319
6	0.303306	-2.186779	-0.046155
6	1.690389	-1.901477	0.153232
6	2.543793	-1.883296	-0.977210
6	2.043526	-2.163955	-2.241894
6	0.681747	-2.475040	-2.440667
1	-1.214597	-2.781191	-1.452120
1	3.600353	-1.687974	-0.822382
1	2.721207	-2.163308	-3.092380
1	0.316649	-2.718757	-3.433907
7	2.241133	-1.767872	1.405092
6	1.641468	-1.184208	2.390819

1	2.100585	-1.299543	3.375501
16	0.241020	-0.156938	2.451326
44	-0.694197	0.056515	0.255824
1	-0.299208	-2.480624	0.806098
17	-2.565532	-1.276780	1.038960
6	-1.186792	0.711002	-1.865288
6	0.194376	0.908021	-1.541032
6	0.617129	1.751292	-0.474844
6	-0.412632	2.216856	0.394915
6	-1.785698	1.931819	0.149734
6	-2.196207	1.230305	-1.034897
1	-1.453108	0.078023	-2.704168
1	0.946236	0.410771	-2.146069
1	-0.149173	2.736801	1.308697
1	-2.534271	2.251796	0.866752
6	2.093640	2.088042	-0.313968
1	2.645883	1.151347	-0.462218
6	-3.654016	0.986002	-1.304285
1	-3.794477	0.310831	-2.151595
1	-4.132055	0.538702	-0.428130
1	-4.153388	1.935968	-1.529972
6	2.518715	3.066305	-1.432550
1	3.591886	3.274118	-1.362981
1	2.317210	2.660507	-2.429230
1	1.984945	4.019716	-1.341936

6	2.473269	2.650738	1.062779
1	3.559042	2.778895	1.118437
1	2.022636	3.636301	1.232767
1	2.167121	1.984459	1.873198

Transition state (**13**):

6	1.753758	-0.118680	-1.855695
6	1.362086	-0.724660	-0.617512
6	2.440697	-1.141430	0.235877
6	3.783365	-0.817308	-0.100325
6	4.089249	-0.135702	-1.260817
6	3.061105	0.191207	-2.171892
1	0.984398	0.067367	-2.598264
1	4.561295	-1.150704	0.579334
1	5.123055	0.103300	-1.495105
1	3.301377	0.654767	-3.124782
7	2.331466	-1.955323	1.345993
6	1.303584	-2.081688	2.104686
1	1.352843	-2.849651	2.879034
16	-0.177057	-1.157173	2.167916
44	-0.525314	-0.059062	0.200133
1	0.472893	-1.734813	-0.943587
17	-0.311645	-3.003865	-1.611807
6	-1.845229	0.374464	-1.546019
6	-1.005565	1.493136	-1.378433
6	-0.827753	2.096813	-0.097599

6	-1.673721	1.640783	0.970929
6	-2.589470	0.583059	0.781471
6	-2.626870	-0.131436	-0.453499
1	-1.837932	-0.175416	-2.481555
1	-0.374224	1.815281	-2.198623
1	-1.556378	2.062029	1.962854
1	-3.150244	0.204353	1.629755
6	0.141946	3.257111	0.067667
1	0.924179	3.117001	-0.688842
6	-3.500060	-1.344002	-0.635942
1	-2.979897	-2.103407	-1.224700
1	-3.775029	-1.781473	0.326753
1	-4.421236	-1.057342	-1.159672
6	-0.590232	4.581379	-0.243725
1	0.111140	5.420872	-0.193706
1	-1.037535	4.572312	-1.243161
1	-1.389812	4.767369	0.482759
6	0.827791	3.314796	1.441637
1	1.589906	4.100455	1.438370
1	0.119884	3.556731	2.242634
1	1.314813	2.367060	1.687405

Product (**14**):

6	1.458595	0.830954	-1.749723
6	1.208364	0.788976	-0.340368
6	2.133820	1.557257	0.450889

6	3.173536	2.305214	-0.176487
6	3.348041	2.320016	-1.544437
6	2.476012	1.560103	-2.344948
1	0.822626	0.255758	-2.412798
1	3.832155	2.863307	0.481403
1	4.151272	2.898257	-1.992373
1	2.598895	1.536216	-3.424817
7	2.193770	1.689579	1.832351
6	1.392389	1.164237	2.690875
1	1.605410	1.363800	3.743382
16	-0.018298	0.171238	2.477331
44	-0.445923	-0.272531	0.299280
1	2.761428	-1.104633	-0.580019
17	3.492956	-2.165649	-0.745936
6	-0.842161	-1.602558	-1.459191
6	-1.568917	-0.410071	-1.642338
6	-2.408191	0.106975	-0.604833
6	-2.656112	-0.733812	0.533607
6	-1.955888	-1.935867	0.705536
6	-0.954873	-2.341627	-0.236855
1	-0.116902	-1.918438	-2.202145
1	-1.401391	0.194299	-2.527564
1	-3.298784	-0.379625	1.331647
1	-2.064135	-2.490634	1.632108
6	-3.138422	1.426110	-0.812889

1	-2.519745	2.015024	-1.501791
6	-0.149932	-3.595632	-0.013339
1	0.829595	-3.530293	-0.492337
1	0.003273	-3.780595	1.052853
1	-0.682192	-4.458195	-0.435535
6	-4.495450	1.161127	-1.501603
1	-5.000156	2.108060	-1.720619
1	-4.371449	0.616570	-2.443554
1	-5.154940	0.570505	-0.855030
6	-3.320421	2.252487	0.469778
1	-3.749187	3.228853	0.221529
1	-4.006981	1.768909	1.174255
1	-2.366366	2.414434	0.978898

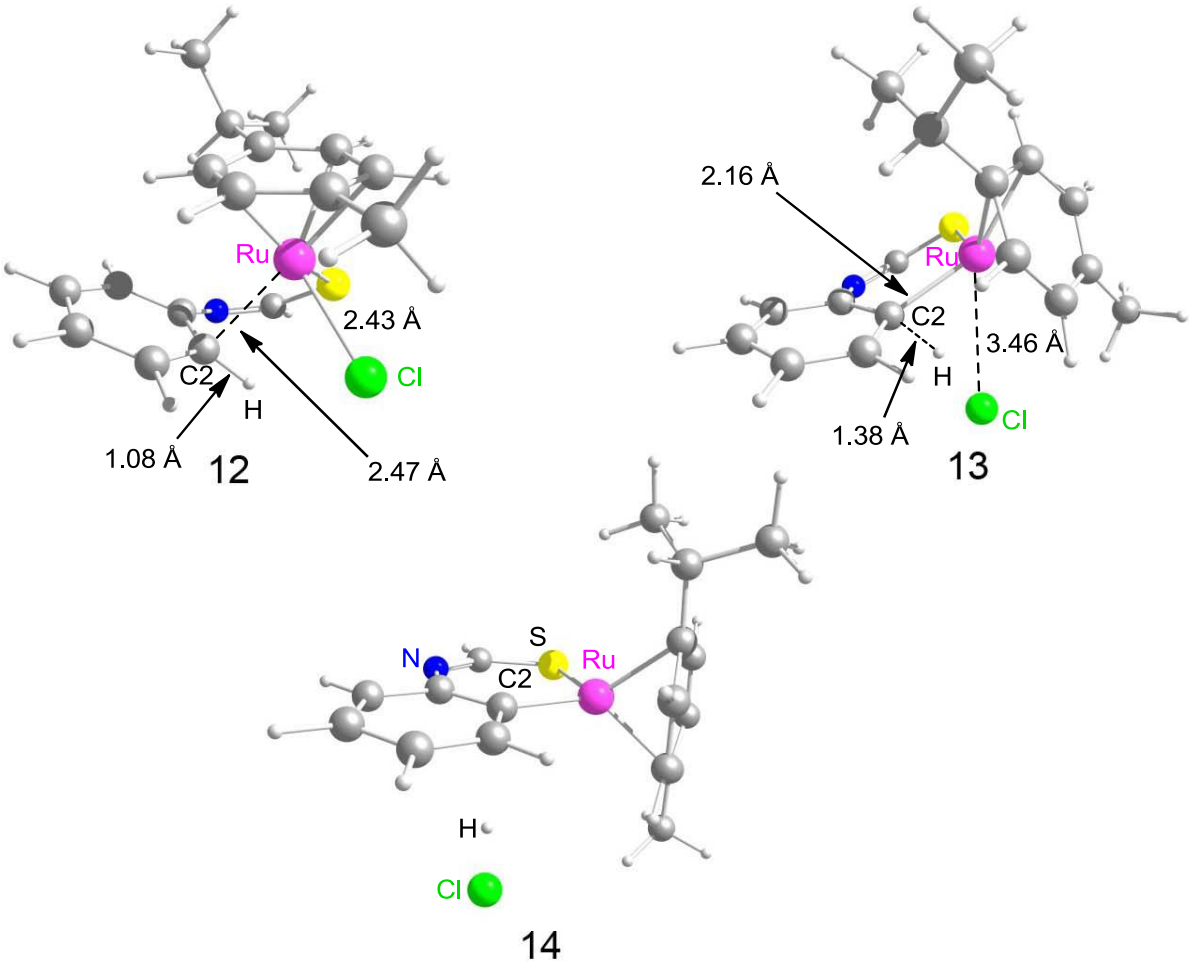


Figure S61. Calculated structures of **12**, **13** and **14**.

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