Supporting Information

Ligand-controlled palladium catalysis enables switch between mono- and di-arylation of primary aromatic amines with 2-halobenzothiazoles

Yan-Qiu Zhu[a], Rui Zhang[a], Wei Sang[b], Hua-Jing Wang[b], Yuan Wu[c], Bao-Yi Yu[d], Jun-Chao Zhang[a], Hua Cheng*[a] and Cheng Chen*[b]

[a] Department of Chemical Engineering and Food Science, Hubei University of Arts and Science, Xiangyang 441053, P. R. China;
[b] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, Wuhan 430070, P. R. China;
[c] Key Laboratory of Pesticide & Chemical Biology, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China;
[d] Key Laboratory of Urban Agriculture (North China), Ministry of Agriculture, Beijing University of Agriculture, Beinong Road 7, Beijing 102206, P. R. China

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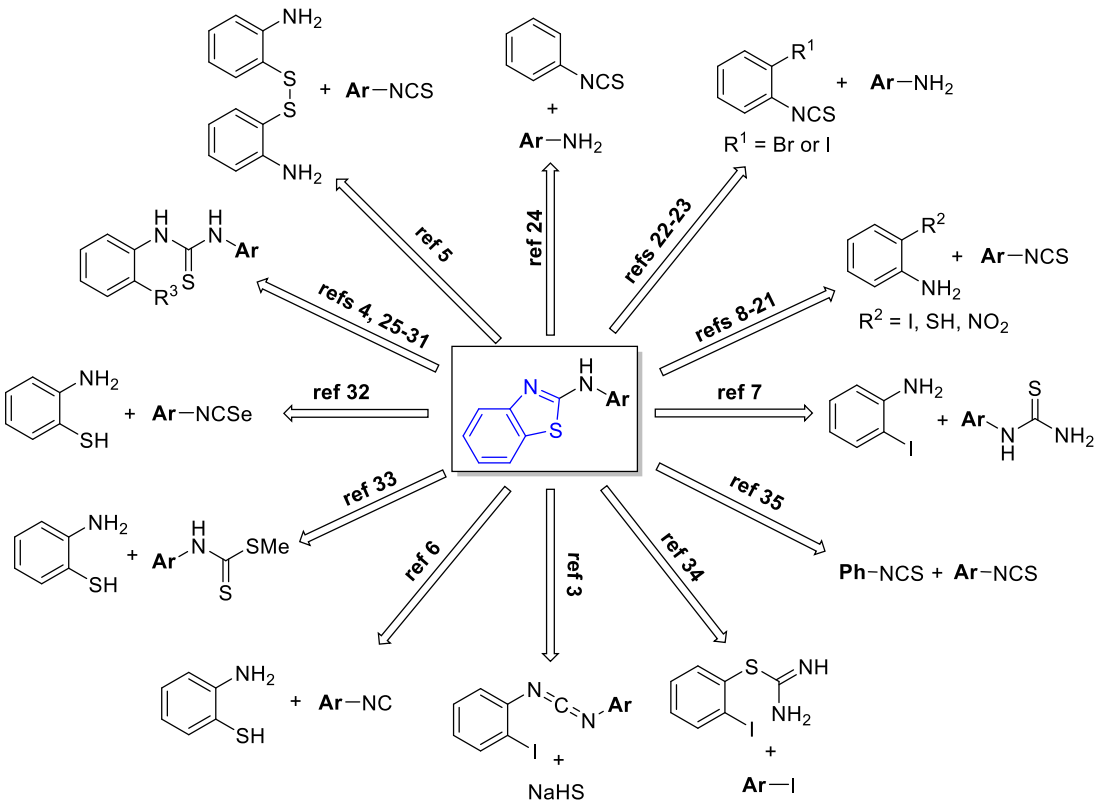
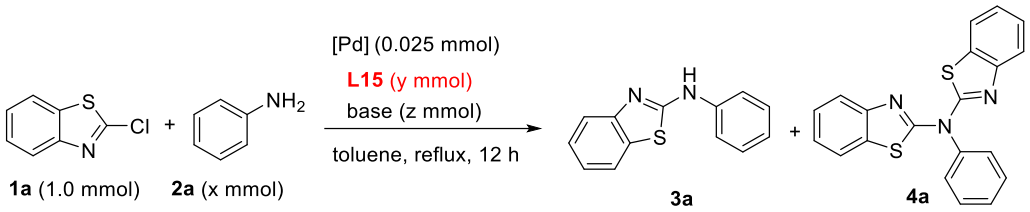


Figure S1. Synthesis of 2-aminoarylbenzothiazoles via construction of the benzothiazole ring.

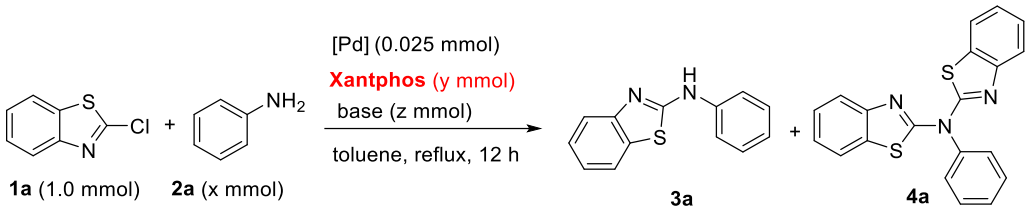
Table S1. Optimization of **L15**-based catalytic systems[a]



Entry	[Pd]	Base (z)	x	y	Yields (%)[b]		
					3a	**4a**	**1a**
1	**$Pd(OAc)_2$**	**NaH (1.00)**	**1.00**	**0.025**	**-**	**94**	**-**
2	$Pd(OAc)_2$	NaO*t*Bu (1.00)	1.00	0.025	-	80	18
3	$Pd(OAc)_2$	Cs_2CO_3 (1.00)	1.00	0.025	3	18	66
4	$Pd(OAc)_2$	NaH (1.50)	1.00	0.025	3	79	-
5	$Pd(OAc)_2$	NaH (2.00)	1.00	0.025	31	61	-
6	$Pd(OAc)_2$	NaH (1.00)	1.00	0.050	-	72	18
7	$Pd(OAc)_2$	NaH (1.00)	1.00	0.075	-	70	22
8	$PdCl_2$	NaH (1.00)	1.00	0.025	-	55	33
9	$Pd_2(dba)_3$	NaH (1.00)	1.00	0.025	3	51	26
10	$Pd(OAc)_2$	NaH (1.00)	0.50	0.025	-	71	18
11	$Pd(OAc)_2$	NaH (1.00)	2.00	0.025	1	92	-
12[c]	$Pd(OAc)_2$	NaH (1.00)	1.00	0.025	-	75	19

[a] **Conditions:** (1) [Pd] (0.025 mmol), **L15** (y mmol), base (z mmol) and toluene (2.5 mL) were heated at reflux under argon for 30 min; (2) **1a** (1.00 mmol) and **2a** (x mmol) were added and the mixture was heated at the same temperature for 12 h. [b] NMR yields using 1,3,5-trimethoxybenzene as an internal standard (average of two consistent runs); [c] $Pd(OAc)_2$ (0.0125 mmol) and **L15** (0.0125 mmol) were used.

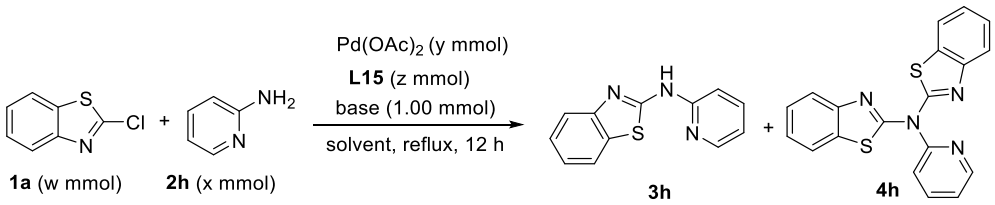
Table S2. Optimization of Xantphos-based catalytic systems[a]



Entry	[Pd]	Base (z)	x	y	Yields (%)[b]		
					3a	**4a**	**1a**
1	$Pd(OAc)_2$	NaH (1.00)	1.00	0.025	83	11	-
2	$Pd(OAc)_2$	NaO*t*Bu (1.00)	1.00	0.025	71	19	8
3	$Pd(OAc)_2$	Cs_2CO_3 (1.00)	1.00	0.025	45	52	-
4	$Pd(OAc)_2$	NaH (1.50)	1.00	0.025	81	15	-
5	$Pd(OAc)_2$	NaH (2.00)	1.00	0.025	86	10	-
6	$PdCl_2$	NaH (1.00)	1.00	0.025	76	12	-
7	$Pd_2(dba)_3$	NaH (1.00)	1.00	0.025	81	11	-
8	**$Pd(OAc)_2$**	**NaH (1.00)**	**1.00**	**0.050**	**92**	**5**	**-**
9	$Pd(OAc)_2$	NaH (1.00)	1.00	0.075	93	5	-
10	$Pd(OAc)_2$	NaH (1.00)	0.50	0.005	86	8	17
11	$Pd(OAc)_2$	NaH (1.00)	2.00	0.050	93	5	-
12	$Pd(OAc)_2$	NaH (1.00)	3.00	0.050	94	4	-
13[c]	$Pd(OAc)_2$	NaH (1.00)	1.00	0.025	72	19	-

[a] [Pd] (0.025 mmol), Xantphos (y mmol), base (z mmol), **1a** (1.00 mmol), **2a** (x mmol) and toluene (2.5 mL) were heated at reflux under argon for 12 h. [b] NMR yields using 1,3,5-trimethoxybenzene as an internal standard (average of two consistent runs); [c] $Pd(OAc)_2$ (0.0125 mmol) and Xantphos (0.025 mmol) were used.

Table S3. The reactions of 2-chlorobenzothiazole (**1a**) and 2-aminoaniline (**2h**) applying the **L15**-based systems[a]

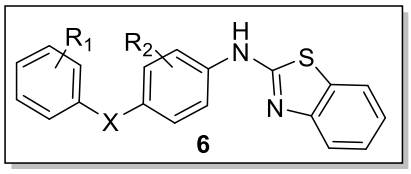


Entry	w	x	y	z	solvent	Yields (%)[a]	
						3h	**4h**
1	**1.00**	**1.00**	**0.025**	**0.025**	**toluene**	**70**	**-**
2	1.00	0.50	0.025	0.025	toluene	64	-
3	2.00	0.50	0.025	0.025	toluene	58	-
4	2.00	1.00	0.025	0.025	toluene	46	-
5	1.00	1.00	0.050	0.050	toluene	67	-
6	1.00	1.00	0.025	0.025	*m*-xylene	48	-

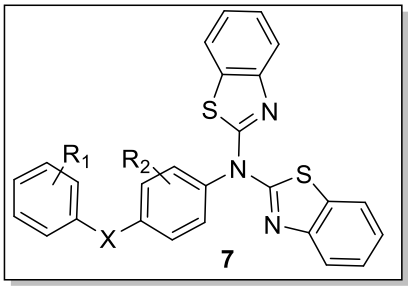
[a] NMR yields using 1,3,5-trimethoxybenzene as an internal standard (average of two consistent runs).

Inhibitory activity of compounds **6** and **7** was tested against SCR, with an initial concentration of 10 μM for preliminary studies (as listed in Table S4). For compounds possessing inhibitory percentages no less than 50%, their IC_{50} values were further determined (as listed in Table S3). The bioassays revealed that the mono-arylated products generally demonstrated certain inhibitory activity against SCR (entries 1-11). Especially, compounds **6d**-**6g** and **6i** exhibited high potency with their IC_{50} values ranging from 0.13 μM to 0.51 μM (entries 4-7, 9), which was comparable with the commercial SCR inhibitor, azoxystrobin (entry 23). Unfortunately, all the di-arylated target compounds were unsuitable for the bioassay tests due to the poor solubility of these compounds in DMSO or DMSO/H_2O (entries 12-22).

Table S4. Inhibitory activity of compounds **6** and **7** against SCR



6



7

Entry	Compound No.	IC_{50} (μM)	Entry	Compound No.	IC_{50} (μM)
1	**6a**	>10	12	**7a**	-[a]
2	**6b**	>10	13	**7b**	-[a]
3	**6c**	>10	14	**7c**	-[a]
4	**6d**	0.49 ± 0.04	15	**7d**	-[a]
5	**6e**	0.13 ± 0.01	16	**7e**	-[a]
6	**6f**	0.51 ± 0.04	17	**7f**	-[a]
7	**6g**	0.29 ± 0.03	18	**7g**	-[a]
8	**6h**	>10	19	**7h**	-[a]
9	**6i**	0.48 ± 0.02	20	**7i**	-[a]
10	**6j**	>10	21	**7j**	-[a]
11	**6k**	>10	22	**7k**	-[a]
23	**Azoxystrobin**				0.31 ± 0.02

[a] IC_{50} values cannot be determined due to the poor solubility of these compounds in DMSO or DMSO/H_2O.

1,3-Dimethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (**L1**),[1] 3-ethyl-1-methyl-1*H*-benzo[d]imidazol-3-ium iodide (**L2**),[2] 3-isopropyl-1-methyl-1*H*-benzo[*d*]imidazol-3-ium iodide (**L3**),[2] 1,3,5,6-tetramethyl-1*H*-benzo[*d*]imidazol-3-ium iodide (**L4**),[1] 5,6-dichloro-1,3-dimethyl-1H-benzo[d]imidazol-3-ium iodide (**L5**),[2] 3-methyl-1-phenyl-1H-benzo[d]imidazol-3-ium iodide (**L6**),[3] 3-methyl-1-(*o*-tolyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L7**),[3] 3-methyl-1-(*m*-tolyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L8**),[3] 3-methyl-1-(*p*-tolyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L9**),[3] 3-methyl-1-(4-nitrophenyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L10**),[3] 1-(4-ethylphenyl)-3-methyl-1*H*-benzo[*d*]imidazol-3-ium iodide (**L11**), [3] 3-ethyl-1-(4-ethylphenyl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L12**),[3] 1-(4-ethylphenyl)-3-isopropyl-1*H*-benzo[*d*]imidazol-3-ium iodide (**L13**),[3] 2-(1-methyl-1*H*-benzo[*d*]imidazol-3-ium-3-yl)acetate (**L14**),[4] 3-methyl-1-(pyridin-2-yl)-1*H*-benzo[*d*]imidazol-3-ium iodide (**L15**),[5] 2-(4-aminophenoxy)benzonitrile (**5b**),[6] 4-(2,4-dichlorophenoxy)aniline (**5c**),[6] 3-chloro-4-(2,4-dichlorophenoxy)aniline (**5d**),[6] 3-chloro-4-(2-chloro-4-(trifluoromethyl)phenoxy)aniline (**5e**),[6] 3,5-dichloro-4-(2,4-dichlorophenoxy)aniline (**5f**),[6] 3-chloro-4-(2,4,6-trichlorophenoxy)aniline (**5g**),[6] 3-fluoro-4-(2,4,6-trichlorophenoxy)aniline (**5h**),[6] 3,5-dichloro-4-(2,4,6-trichlorophenoxy)aniline (**5i**),[6] 4-(naphthalen-2-yloxy)aniline (**5j**)[7] were synthesized using the literature procedures.

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2. Characterization data for compounds 3, 4, 6, 7 and 9

*N-phenylbenzo[d]thiazol-2-amine (**3a**).* White solid, m.p. 159.5-160.3℃. Isolated yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.57 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.37 (m, 2H), 7.32 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 1H), 7.23 – 7.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 151.5, 139.8, 130.0, 129.5, 126.1, 124.3, 122.4, 120.8, 120.1, 119.5. HRMS (ESI): calculated for $C_{13}H_{11}N_2S$ $[M+H]^+$: 227.06375; Found: 227.06369.

*N-(p-tolyl)benzo[d]thiazol-2-amine (**3b**).* White solid, m.p. 182.1-182.6℃. Isolated yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.3, 151.6, 137.3, 134.5, 130.1, 130.0, 126.1, 122.2, 120.9, 120.8, 119.3, 20.9. HRMS (ESI): calculated for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.07940; Found: 241.07929.

*N-(4-(tert-butyl)phenyl)benzo[d]thiazol-2-amine (**3c**).* White solid, m.p. 136.3-137.1℃. Isolated yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.41 (s, 4H), 7.33 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 151.6, 147.5, 137.1, 130.0, 126.4, 126.1, 122.2, 120.8, 120.1, 119.3, 34.4, 31.4. HRMS (ESI): calculated for $C_{17}H_{19}N_2S$ $[M+H]^+$: 283.12635; Found: 283.12622.

*N-(4-fluorophenyl)benzo[d]thiazol-2-amine (**3d**).* White solid, m.p. 201.2-202.0 ℃. Isolated yield: 80%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.51 (s, 1H), 7.82 (dd, *J* = 9.5, 5.7 Hz, 3H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 8.7 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.1, 157.8 (d, *J* = 238.7 Hz), 152.5, 137.6, 130.4, 126.3, 122.7, 121.5, 119.8 (d, *J* = 7.6 Hz), 119.6, 116.0 (d, *J* = 22.3 Hz). HRMS (ESI): calculated for $C_{13}H_{10}FN_2S$ $[M+H]^+$: 245.05432; Found: 245.05421.

*N-(4-(trifluoromethyl)phenyl)benzo[d]thiazol-2-amine (**3e**).* White solid, m.p. 191.8-192.4℃. Isolated yield: 56%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.77

– 7.59 (m, 6H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 151.0, 142.6, 130.0, 126.7 (q, *J* = 3.7 Hz), 126.5, 125.2 (q, *J* = 32.8 Hz), 124.1 (d, *J* = 271.6 Hz), 123.3, 120.9, 120.1, 118.2. HRMS (ESI): calculated for $C_{14}H_{10}F_3N_2S$ $[M+H]^+$: 295.05113; Found: 295.05095.

*N-(m-tolyl)benzo[d]thiazol-2-amine (**3f**).* White solid, m.p. 122.4-123.2℃. Isolated yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 7.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.37 – 7.25 (m, 4H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 6.99 (d, *J* = 6.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 151.3, 139.8, 139.6, 129.9, 129.4, 126.1, 125.3, 122.2, 121.1, 120.8, 119.2, 117.4, 21.5. HRMS (ESI): calculated for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.07940; Found: 241.07928.

*N-(o-tolyl)benzo[d]thiazol-2-amine (**3g**).* White solid, m.p. 119.4-120.0℃. Isolated yield: 55%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.65 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.20 (td, *J* = 7.3, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 151.7, 138.2, 132.2, 131.2, 130.2, 127.3, 126.3, 126.0, 124.0, 122.0, 120.8, 118.9, 17.9. HRMS (ESI): calculated for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.07940; Found: 241.07932.

*N-(pyridin-2-yl)benzo[d]thiazol-2-amine (**3h**).* White solid, m.p. 239.1-239.9℃. Isolated yields: 41% for Condition A and 70% for Condition B. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.57 (s, 1H), 8.36 (d, *J* = 5.0 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.86 – 7.71 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.11 (m, 2H), 7.01 (dd, *J* = 7.2, 5.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.8, 152.1, 149.9, 147.0, 138.8, 132.1, 126.2, 122.5, 121.6, 119.6, 117.3, 111.7. HRMS (ESI): calculated for $C_{12}H_{10}N_3S$ $[M+H]^+$: 228.05899; Found: 228.05891.

*6-Methyl-N-phenylbenzo[d]thiazol-2-amine (**3i**).* White solid, m.p. 166.1-167.0℃. Isolated yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.52 – 7.46 (m, 3H), 7.43 (s, 1H), 7.42 – 7.36 (m, 2H), 7.14 (tt, *J* = 7.1, 1.1 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 149.4, 139.9, 132.3, 130.1, 129.5, 127.4, 124.0, 120.8, 119.7, 119.2, 21.3. HRMS (ESI): calculated for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.07940; Found: 241.07924.

*6-Methoxy-N-phenylbenzo[d]thiazol-2-amine (**3j**)*. White solid, m.p. 115.0-115.8℃. Isolated yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.49 (dd, *J* = 8.6, 1.1 Hz, 2H), 7.38 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.17 (d, *J* = 2.6 Hz, 1H), 7.13 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.95 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 155.9, 145.9, 139.9, 131.2, 129.5, 123.8, 120.2, 119.4, 113.9, 105.1, 55.9. HRMS (ESI): calculated for $C_{14}H_{13}N_2OS$ $[M+H]^+$: 257.07431; Found: 257.07420.

*6-Chloro-N-phenylbenzo[d]thiazol-2-amine (**3k**)*. White solid, m.p. 190.9-191.7℃. Isolated yield: 77%. In addition, 10% of the di-substituted product (**4k**) was also isolated. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.60 (d, *J* = 2.1 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.30 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 150.3, 139.4, 131.3, 129.6, 127.7, 126.7, 124.6, 120.5, 120.2, 120.2. HRMS (ESI): calculated for $C_{13}H_{10}ClN_2S$ $[M+H]^+$: 261.02477; Found: 261.02468.

*N-(benzo[d]thiazol-2-yl)-N-phenylbenzo[d]thiazol-2-amine (**4a**)*. White solid, m.p. 202.8-204.1℃. Isolated yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.72 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.67 – 7.59 (m, 3H), 7.58 – 7.52 (m, 2H), 7.40 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.27 – 7.23 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 150.1, 141.7, 132.5, 130.5, 130.0, 129.3, 126.1, 123.5, 121.2, 120.7. HRMS (APCI): calculated for $C_{20}H_{14}N_3S_2$ $[M+H]^+$: 360.06237; Found: 360.06173.

*N-(benzo[d]thiazol-2-yl)-N-(p-tolyl)benzo[d]thiazol-2-amine (**4b**)*. White solid, m.p. 189.5-190.3℃. Isolated yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.43 (s, 4H), 7.39 (ddd, *J* = 8.4, 7.3, 1.2 Hz, 2H), 7.27 – 7.21 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 150.2, 140.1, 139.2, 132.5, 131.1, 129.0, 126.1, 123.4, 121.2, 120.7, 21.5. HRMS (APCI): calculated for $C_{21}H_{16}N_3S_2$ $[M+H]^+$: 374.07802; Found: 374.07760.

*N-(benzo[d]thiazol-2-yl)-N-(4-(tert-butyl)phenyl)benzo[d]thiazol-2-amine (**4c**)*. White solid, m.p. 272.5-273.6℃. Isolated yield: 93%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.72 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.49 – 7.43 (m, 2H), 7.40 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 2H), 7.28 – 7.21 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 153.0, 150.1, 139.1, 132.5, 128.6, 127.4, 126.0, 123.4, 121.2, 120.7, 35.0, 31.4. HRMS (APCI): calculated for $C_{24}H_{22}N_3S_2$ $[M+H]^+$: 416.12497; Found: 416.12451.

N-(benzo[d]thiazol-2-yl)-N-(4-fluorophenyl)benzo[d]thiazol-2-amine ***(4d)***. White solid, m.p. 200.0-200.8 ℃. Isolated yield: 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.73 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.58 – 7.50 (m, 2H), 7.41 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.22 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 250.6 Hz), 162.7, 150.0, 137.5 (d, *J* = 3.4 Hz), 132.4, 131.4 (d, *J* = 9.0 Hz), 126.2, 123.6, 121.3, 120.8, 117.6 (d, *J* = 23.1 Hz). HRMS (APCI): calculated for $C_{20}H_{13}FN_3S_2$ $[M+H]^+$: 378.05294; Found: 378.05236.

N-(benzo[d]thiazol-2-yl)-N-(4-(trifluoromethyl)phenyl)benzo[d]thiazol-2-amine ***(4e)***. White solid, m.p. 230.3-231.1 ℃. Isolated yield: 30%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.42 (ddd, *J* = 8.4, 7.3, 1.3 Hz, 2H), 7.27 (td, *J* = 7.7, 1.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 149.9, 144.5, 132.4, 131.9 (q, *J* = 33.1 Hz), 130.1, 127.7 (q, *J* = 3.7 Hz), 126.9, 126.3, 123.7 (q, *J* = 272.6 Hz), 121.3, 120.8. HRMS (APCI): calculated for $C_{21}H_{13}F_3N_3S_2$ $[M+H]^+$: 428.04975; Found: 428.04931.

N-(benzo[d]thiazol-2-yl)-N-(m-tolyl)benzo[d]thiazol-2-amine ***(4f)***. White solid, m.p. 194.5-195.2℃. Isolated yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.72 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.53 (dd, *J* = 9.0, 7.3 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.37 – 7.33 (m, 2H), 7.28 – 7.21 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 150.1, 141.7, 140.6, 132.5, 130.8, 130.2, 129.7, 126.2, 126.1, 123.4, 121.2, 120.7, 21.5. HRMS (APCI): $C_{21}H_{16}N_3S_2$ $[M+H]^+$: calculated for 374.07802; Found: 374.07772.

N-(benzo[d]thiazol-2-yl)-N-(o-tolyl)benzo[d]thiazol-2-amine ***(4g)***. White solid, m.p. 193.6-194.8℃. Isolated yield: 62%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.73 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.57 – 7.44 (m, 4H), 7.40 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.27 – 7.23 (m, 2H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 150.3, 140.6, 137.4, 132.5, 132.2, 130.4, 129.5, 128.1, 126.1, 123.4, 121.2, 120.8,

17.5. HRMS (APCI): calculated for $C_{21}H_{16}N_3S_2$ $[M+H]^+$: 374.07802; Found: 374.07748.

6-Methyl-N-(6-methylbenzo[d]thiazol-2-yl)-N-phenylbenzo[d]thiazol-2-amine ***(4i)***. White solid, m.p. 192.0-193.6℃. Isolated yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.58 (m, 3H), 7.55 (dd, *J* = 6.7, 1.8 Hz, 2H), 7.50 (s, 2H), 7.20 (dd, *J* = 8.2, 1.7 Hz, 2H), 2.44 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 148.1, 141.8, 133.3, 132.5, 130.4, 129.8, 129.4, 127.4, 120.8, 120.6, 21.5. HRMS (APCI): calculated for $C_{22}H_{18}N_3S_2$ $[M+H]^+$: 388.09367; Found: 388.09298.

6-Methoxy-N-(6-methoxybenzo[d]thiazol-2-yl)-N-phenylbenzo[d]thiazol-2-amine ***(4j)***. White solid, m.p. 165.7-168.4 ℃. Isolated yield: 56%. In addition, 26% of the mono-substituted product (**3j**) was also obtained. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.9 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.54 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.20 (d, *J* = 2.6 Hz, 2H), 6.99 (dd, *J* = 8.9, 2.6 Hz, 2H), 3.84 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 156.3, 144.4, 141.7, 133.5, 130.4, 129.8, 129.4, 121.7, 114.4, 104.3, 55.8. HRMS (APCI): calculated for $C_{22}H_{18}N_3O_2S_2$ $[M+H]^+$: 420.08349; Found: 420.08270.

6-Chloro-N-(6-chlorobenzo[d]thiazol-2-yl)-N-phenylbenzo[d]thiazol-2-amine ***(4k)***. White solid, m.p. 244.0-245.0℃. Isolated yield: 84%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.12 (d, *J* = 2.3 Hz, 2H), 7.75 – 7.65 (m, 7H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.6, 148.8, 141.6, 134.0, 131.1, 130.8, 129.8, 128.1, 127.3, 122.2, 121.8. HRMS (APCI): calculated for $C_{20}H_{12}Cl_2N_3S_2$ $[M+H]^+$: 427.98442; Found: 427.98388.

Diethyl 2,2'-(phenylazanediyl)bis(benzo[d]thiazole-6-carboxylate) ***(4l)***. White solid, m.p. 238.7-239.3℃. Isolated yields: 55% for Condition A and 75% for Condition B. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 1.8 Hz, 2H), 8.11 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.73 – 7.63 (m, 3H), 7.56 (dd, *J* = 7.8, 1.9 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.1, 153.3, 141.2, 132.4, 130.7, 130.4, 129.1, 127.7, 125.8, 123.0, 120.9, 61.1, 14.4. HRMS (APCI): calculated for $C_{26}H_{22}N_3O_4S_2$ $[M+H]^+$: 504.10462; Found: 504.10369.

N-(4-phenoxyphenyl)benzo[d]thiazol-2-amine ***(6a)***. White solid, m.p.

158.8-159.4℃. Isolated yield: 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.15 (t, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.09 – 6.98 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 157.3, 154.1, 151.7, 135.2, 130.1, 129.8, 126.1, 123.3, 122.5, 122.4, 120.8, 120.0, 119.5, 118.7. HRMS (ESI): calculated for $C_{19}H_{15}N_2OS$ $[M+H]^+$: 319.08996; Found: 319.08979.

*2-(4-(Benzo[d]thiazol-2-ylamino)phenoxy)benzonitrile (**6b**).* White solid, m.p. 174.3-174.9℃. Isolated yield: 72%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.57 (s, 1H), 7.95 – 7.86 (m, 3H), 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.64 (ddd, *J* = 8.9, 7.4, 1.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.33 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.6, 160.4, 152.8, 149.9, 138.7, 136.2, 134.9, 130.8, 126.9, 124.2, 123.3, 121.9, 121.5, 120.5, 120.1, 117.4, 117.0, 102.9. HRMS (ESI): calculated for $C_{20}H_{14}N_3OS$ $[M+H]^+$: 344.08521; Found: 344.08515.

N-(4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (***6c***). Brown solid, m.p. 184.9-186.5℃. Isolated yield: 75%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.88 – 7.77 (m, 3H), 7.75 (d, *J* = 2.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.32 (td, *J* = 7.6, 1.4 Hz, 1H), 7.15 (td, *J* = 7.7, 1.2 Hz, 1H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.1, 152.5, 152.4, 150.6, 137.7, 130.5, 130.5, 129.1, 128.0, 126.4, 125.1, 122.7, 121.5, 120.9, 119.9, 119.8, 119.6. HRMS (ESI): calculated for $C_{19}H_{13}Cl_2N_2OS$ $[M+H]^+$: 387.01202; Found: 387.01194.

*N-(3-chloro-4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**6d**).* White solid, m.p. 165.0-165.8℃. Isolated yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.79 (d, *J* = 2.7 Hz, 1H), 7.65 (dd, *J* = 7.6, 5.3 Hz, 2H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.17 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 151.5, 151.4, 147.6, 137.1, 130.5, 130.0, 128.9, 127.9, 126.4, 126.4, 125.3, 123.0, 122.0, 121.1, 120.9, 119.9, 119.3, 119.1. HRMS (ESI): calculated for $C_{19}H_{12}Cl_3N_2OS$ $[M+H]^+$: 420.97304; Found: 420.97287.

N-(3,5-dichloro-4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine ***(6e)***. White solid, m.p. 192.1-193.0℃. Isolated yield: 82%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.35 (s, 1H), 7.26 – 7.22 (m, 1H), 7.09 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.45 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 151.3, 151.2, 142.0, 138.4, 130.5, 130.1, 130.0, 127.8, 127.5, 126.5, 123.5, 123.4, 120.9, 120.3, 119.0, 115.0. HRMS (ESI): calculated for $C_{19}H_{11}Cl_4N_2OS$ $[M+H]^+$: 454.93407; Found: 454.93389.

N-(3-chloro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine ***(6f)***. White solid, m.p. 201.5-202.9℃. Isolated yield: 83%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.58 (s, 1H), 8.20 (d, *J* = 2.6 Hz, 1H), 7.91 (s, 2H), 7.81 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.47 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.4, 1.3 Hz, 1H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 6.66 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.9, 152.3, 146.7, 146.0, 137.2, 131.4, 130.4, 130.0, 129.8, 126.4, 122.9, 121.6, 121.6, 119.9, 119.8, 118.2, 115.5. HRMS (ESI): calculated for $C_{19}H_{11}Cl_4N_2OS$ $[M+H]^+$: 454.93407; Found: 454.93380.

N-(3-fluoro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine ***(6g)***. White solid, m.p. 205.3-207.0℃. Isolated yield: 81%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.65 (s, 1H), 8.14 – 8.00 (m, 1H), 7.89 (s, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 9.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 9.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.8, 152.3, 151.1 (d, *J* = 243.7 Hz), 146.0, 138.6 (d, *J* = 11.5 Hz), 137.2 (d, *J* = 9.8 Hz), 131.3, 130.4, 130.0, 129.8, 126.4, 122.9, 121.6, 119.8, 116.6, 114.3 (d, *J* = 3.3 Hz), 107.2 (d, *J* = 22.7 Hz). HRMS (ESI): calculated for $C_{19}H_{10}Cl_3FN_2OS$ $[M+H]^+$: 438.96362: Found: 438.96341.

N-(3,5-dichloro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine ***(6h)***. Brown solid, m.p. 192.5-193.1℃. Isolated yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.83 (s, 1H), 7.95 (s, 2H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.76 (s, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.4, 152.0, 147.4, 142.0, 138.5, 130.4, 129.9, 129.9,

129.3, 126.6, 126.1, 123.4, 121.7, 120.3, 118.2. HRMS (ESI): calculated for $C_{19}H_{10}Cl_5N_2OS$ $[M+H]^+$; Exact Mass: 488.89510; Found: 488.89477.

N-(3,5-difluoro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine ***(6i)***. White solid, m.p. 227.4-228.0℃. Isolated yield: 84%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.82 (s, 2H), 7.72 – 7.58 (m, 3H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.5, 153.5 (dd, *J* = 244.7, 6.7 Hz), 152.0, 148.1, 137.6 (t, *J* = 13.2 Hz), 130.4, 130.4, 129.8, 127.9, 127.0 (t, *J* = 13.7 Hz), 126.5, 123.3, 121.7, 120.2, 102.2 (dd, *J* = 20.0, 6.3 Hz). HRMS (ESI): calculated for $C_{19}H_{10}Cl_3F_2N_2OS$ $[M+H]^+$: 456.95420; Found: 456.95393.

N-(4-(naphthalen-2-yloxy)phenyl)benzo[d]thiazol-2-amine ***(6j)***. White solid, m.p. 173.2-173.7℃. Isolated yield: 60%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.52 (s, 1H), 7.96 (d, *J* = 9.4 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 4.6 Hz, 1H), 7.79 (d, *J* = 4.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.47 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.0, 6.7, 1.3 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.20 – 7.12 (m, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.1, 156.1, 152.6, 151.0, 137.5, 134.4, 130.5, 130.5, 129.9, 128.1, 127.4, 127.1, 126.4, 125.0, 122.7, 121.5, 120.8, 119.9, 119.7, 119.6, 112.5. HRMS (ESI): calculated for $C_{23}H_{17}N_2OS$ $[M+H]^+$: 369.10561; Found: 369.10552.

N_1-(benzo[d]thiazol-2-yl)-N_4-phenylbenzene-1,4-diamine ***(6k)***. Brown solid, m.p. 181.3-182.6℃. Isolated yield: 52%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.27 (s, 1H), 8.04 (s, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.36 – 7.25 (m, 1H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 152.8, 144.7, 138.5, 134.3, 130.4, 129.6, 126.2, 122.3, 121.4, 119.9, 119.3, 119.3, 119.0, 116.0. HRMS (ESI): calculated for $C_{19}H_{16}N_3S$ $[M+H]^+$: 318.10594; Found: 318.10591.

N-(benzo[d]thiazol-2-yl)-N-(4-phenoxyphenyl)benzo[d]thiazol-2-amine ***(7a)***. White solid, m.p. 217.1-217.7℃. Isolated yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.47 – 7.37 (m,

4H), 7.30 – 7.24 (m, 3H), 7.24 – 7.16 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 158.8, 155.9, 150.1, 136.1, 132.5, 130.8, 130.0, 126.1, 124.4, 123.5, 121.2, 120.8, 120.1, 119.4. HRMS (APCI): calculated for $C_{26}H_{18}N_3OS_2$ $[M+H]^+$: 452.08858; Found: 452.08744.

*2-(4-(Bis(benzo[d]thiazol-2-yl)amino)phenoxy)benzonitrile (**7b**).* White solid, m.p. 205.9-208.0℃. Isolated yield: 73%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.75 (t, *J* = 7.6 Hz, 3H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.19 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 158.5, 156.4, 150.1, 137.9, 134.4, 134.1, 132.5, 131.3, 126.2, 124.0, 123.6, 121.3, 121.0, 120.8, 118.5, 115.6, 104.9. HRMS (ESI): calculated for $C_{27}H_{17}N_4OS_2$ $[M+H]^+$: 477.08383; Found: 477.08349.

*N-(benzo[d]thiazol-2-yl)-N-(4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7c**).* White solid, m.p. 174.4-175.8℃. Isolated yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.30 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.11 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 157.7, 150.3, 150.1, 136.7, 132.4, 131.0, 130.7, 130.3, 128.4, 127.4, 126.1, 123.5, 122.7, 121.2, 120.8, 118.8. HRMS (APCI): calculated for $C_{26}H_{16}Cl_2N_3OS_2$ $[M+H]^+$: 520.01064; Found: 520.00994.

*N-(benzo[d]thiazol-2-yl)-N-(3-chloro-4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7d**).* White solid, m.p. 215.3-216.4℃. Isolated yield: 51%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.19 (d, *J* = 2.6 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.72 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.58 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 1H), 7.32 (ddd, *J* = 8.2, 7.3, 1.2 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.9, 153.2, 149.9, 137.7, 132.7, 132.4, 131.0, 130.9, 130.3, 129.7, 126.9, 126.4, 125.9, 124.3, 124.2, 123.2, 122.1, 121.1, 119.6. HRMS (APCI): calculated for $C_{26}H_{15}Cl_3N_3OS_2$ $[M+H]^+$: 553.97166: Found: 553.97070.

*N-(benzo[d]thiazol-2-yl)-N-(3,5-dichloro-4-(2,4-dichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7e**).* White solid, m.p. 216.0-216.4℃. Isolated yield: 82%. ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.66 (s, 2H), 7.53 (d, *J* = 2.5 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.3, 1.3 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.21 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.63 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 150.7, 149.8, 148.1, 139.2, 132.3, 130.9, 130.7, 130.7, 128.4, 127.8, 126.5, 124.0, 123.8, 121.4, 120.9, 115.4. HRMS (APCI): calculated for $C_{26}H_{14}Cl_4N_3OS_2$ $[M+H]^+$: 587.93269; Found: 587.93182.

*N-(benzo[d]thiazol-2-yl)-N-(3-chloro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7f**).* White solid, m.p. 256.2-257.7℃. Isolated yield: 81%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 2.5 Hz, 1H), 7.48 (s, 2H), 7.46 – 7.38 (m, 2H), 7.33 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.69 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 152.9, 150.0, 145.9, 136.6, 132.5, 132.1, 132.0, 130.3, 129.3, 128.9, 126.3, 124.4, 123.7, 121.3, 120.8, 115.6. HRMS (APCI): calculated for $C_{26}H_{14}Cl_4N_3OS_2$ $[M+H]^+$: 587.93269; Found: 587.93194.

*N-(benzo[d]thiazol-2-yl)-N-(3-fluoro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7g**).* White solid, m.p. 198.1-199.0℃. Isolated yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.47 (s, 2H), 7.46 – 7.38 (m, 3H), 7.31 – 7.25 (m, 2H), 7.22 (dt, *J* = 8.8, 2.2 Hz, 1H), 6.80 (t, *J* = 8.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5, 152.3 (d, *J* = 252.4 Hz), 150.0, 145.8, 145.4 (d, *J* = 10.9 Hz), 136.3 (d, *J* = 8.3 Hz), 132.5, 131.9, 130.2, 129.3, 126.3, 125.7 (d, *J* = 3.6 Hz), 123.7, 121.3, 120.8, 118.8 (d, *J* = 19.2 Hz), 116.9. HRMS (APCI): calculated for $C_{26}H_{13}Cl_3FN_3OS_2$ $[M+H]^+$: 571.96224; Found: 571.96136.

*N-(benzo[d]thiazol-2-yl)-N-(3,5-dichloro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d]thiazol-2-amine (**7h**).* White solid, m.p. 227.8-228.7℃. Isolated yield: 78%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.55 (s, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.38 (s, 2H), 7.29 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 149.9, 149.4, 147.2, 137.5, 132.4, 130.6, 129.9, 129.2, 127.9, 127.3, 126.4, 123.9, 121.4, 120.9. HRMS (APCI): calculated for $C_{26}H_{13}Cl_5N_3OS_2$ $[M+H]^+$: 621.89372; Found: 621.89258.

N-(benzo[d]thiazol-2-yl)-N-(3,5-difluoro-4-(2,4,6-trichlorophenoxy)phenyl)benzo[d

*]thiazol-2-amine (**7i**).* Yellow solid, m.p. 221.0-224.1℃. Isolated yield: 82%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.02 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.92 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 154.3 (dd, *J* = 252.9, 5.8 Hz), 149.9, 147.8, 136.1 (t, *J* = 11.4 Hz), 134.6 (t, *J* = 12.6 Hz), 132.4, 130.9, 129.0, 128.4, 126.4, 123.9, 121.4, 120.9, 114.6 (dd, *J* = 18.9, 5.0 Hz). HRMS (APCI): calculated for $C_{26}H_{12}Cl_3F_2N_3OS_2$ $[M+H]^+$: 589.95282; Found: 589.95178.

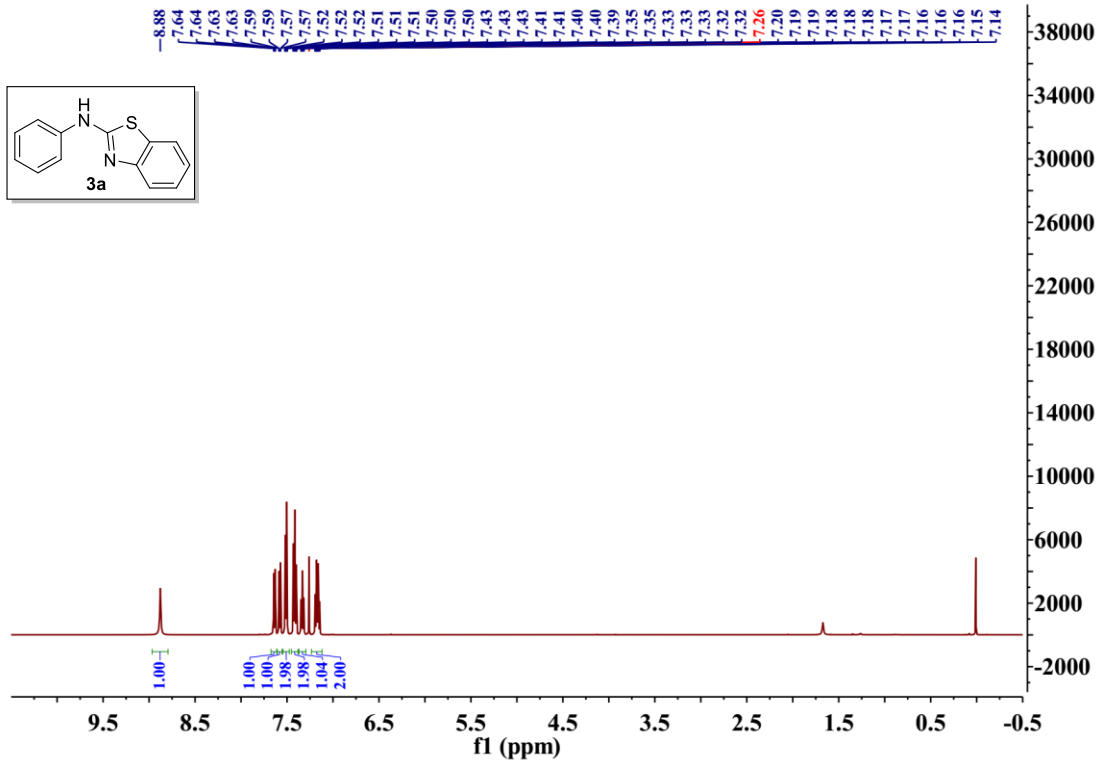
*N-(benzo[d]thiazol-2-yl)-N-(4-(naphthalen-2-yloxy)phenyl)benzo[d]thiazol-2-amin e (**7j**).* White solid, m.p. 218.7-219.4℃. Isolated yield: 46%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.09 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 3H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.79 – 7.69 (m, 5H), 7.57 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.52 (ddd, *J* = 8.0, 6.8, 1.4 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.35 – 7.27 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.2, 158.8, 153.5, 150.0, 136.7, 134.5, 132.4, 131.9, 131.0, 130.9, 128.3, 127.8, 127.3, 126.9, 125.9, 124.1, 122.1, 121.0, 120.9, 119.7, 116.4. HRMS (APCI): calculated for $C_{30}H_{20}N_3OS_2$ $[M+H]^+$: 502.10423; Found: 502.10339.

*N_1,N_1-bis(benzo[d]thiazol-2-yl)-N_4-phenylbenzene-1,4-diamine (**7k**).* White solid, m.p. 202.3-203.4 ℃. Isolated yield: 26%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.24 – 7.20 (m, 4H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.13 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 150.2, 145.1, 141.6, 133.5, 132.6, 130.1, 129.5, 126.1, 123.4, 122.2, 121.1, 120.8, 119.4, 117.4. HRMS (APCI): calculated for $C_{26}H_{19}N_4S_2$ $[M+H]^+$: 451.10456; Found: 451.10373.

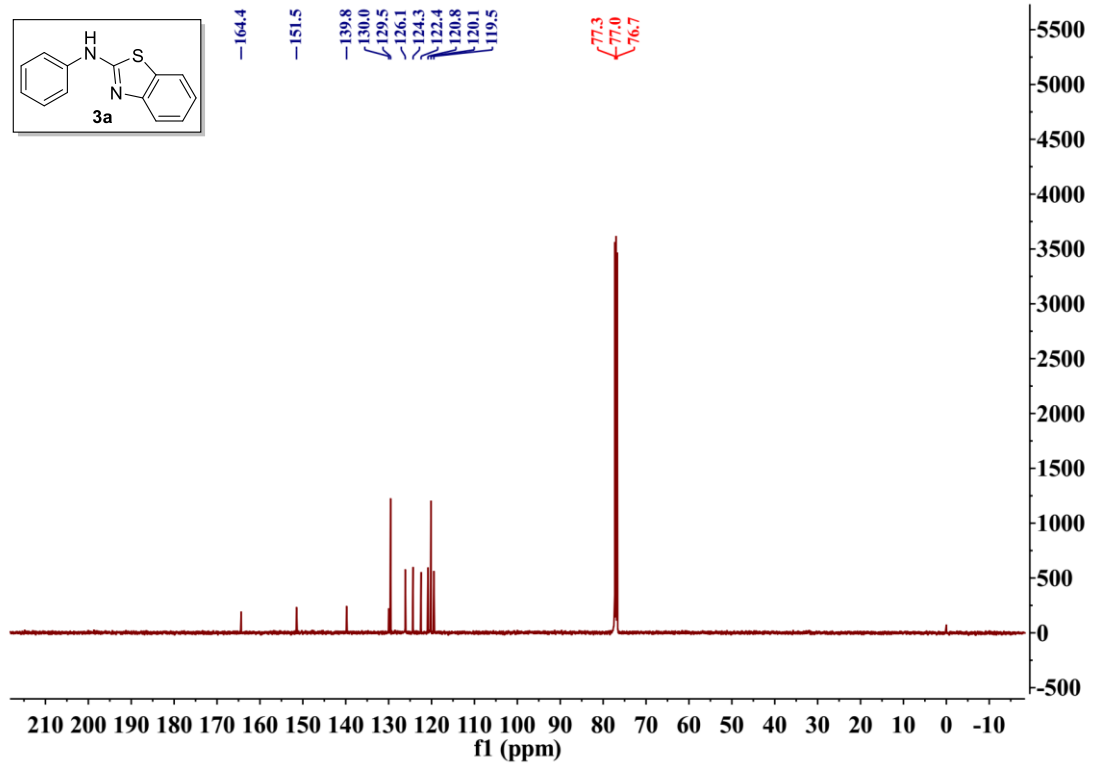
*N,N-diphenylbenzo[d]thiazol-2-amine (**9**).* Yellow solid, m.p. 120.1-120.9 ℃. Isolated yields: 80% for Condition A and 75% for Condition B. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.48 – 7.37 (m, 8H), 7.34 – 7.26 (m, 3H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 152.2, 144.7, 131.9, 129.6, 126.5, 126.4, 125.9, 122.5, 120.4, 120.3. HRMS (APCI): calculated for $C_{19}H_{15}N_2S$ $[M+H]^+$: 303.09505; Found: 303.09460.

3. Original NMR and HRMS spectra for 3, 4, 6, 7 and 9

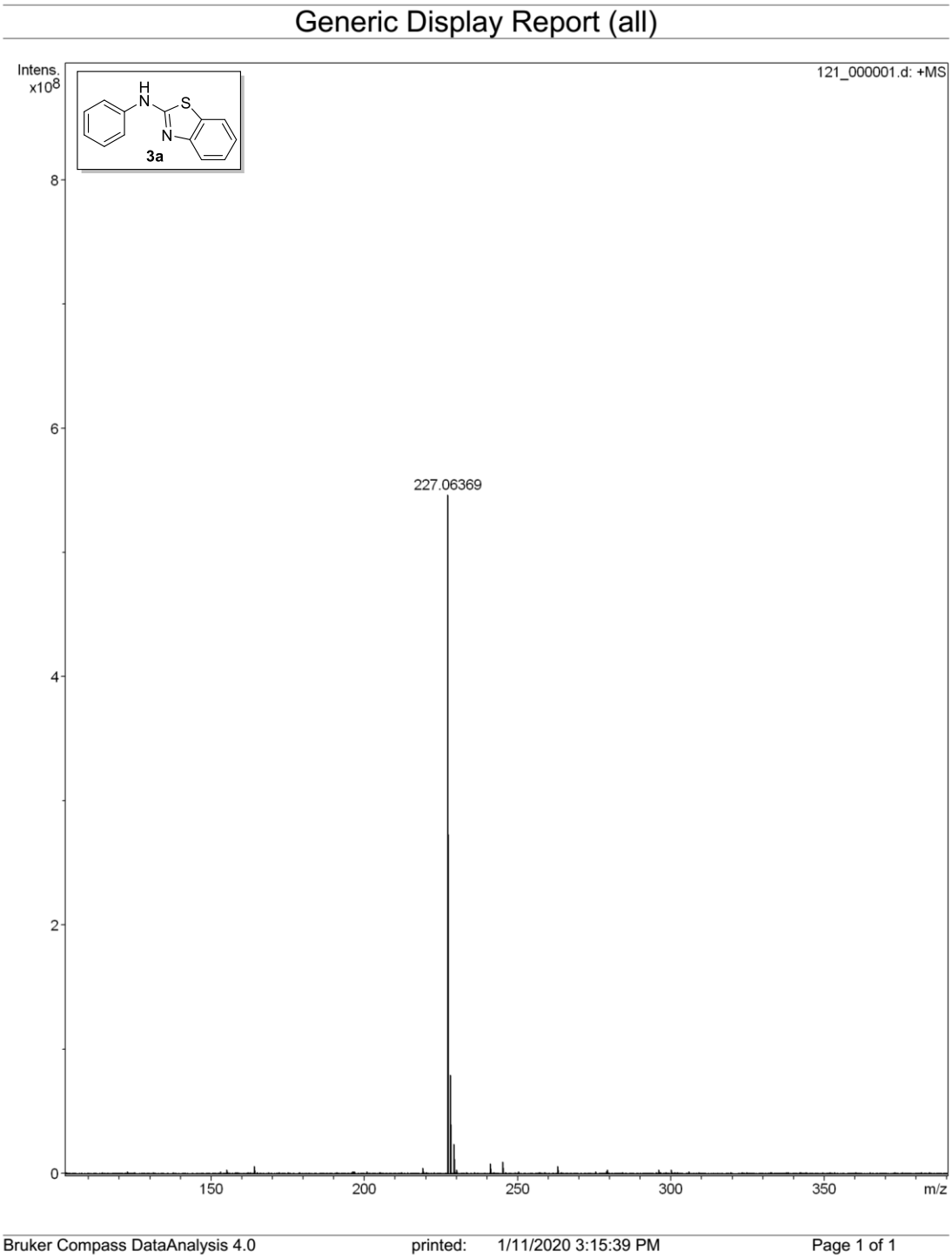
- ^{1}H NMR spectrum for **3a**



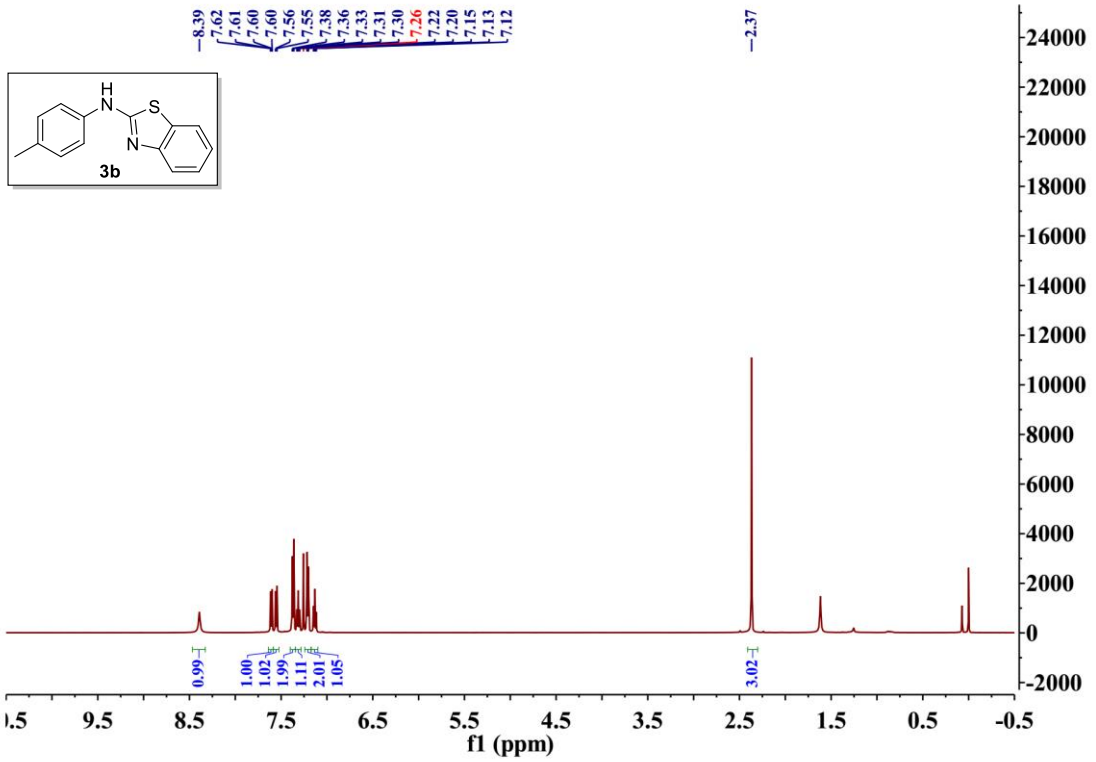
- ^{13}C NMR spectrum for **3a**



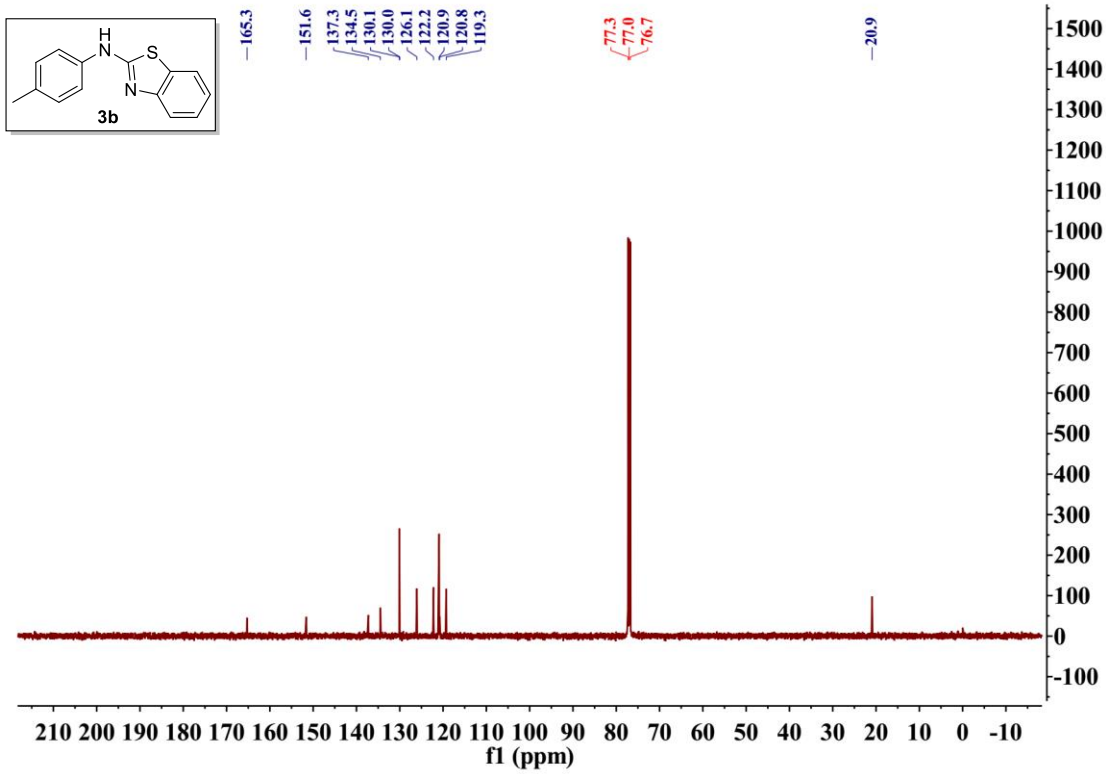
- HRMS spectrum for **3a**



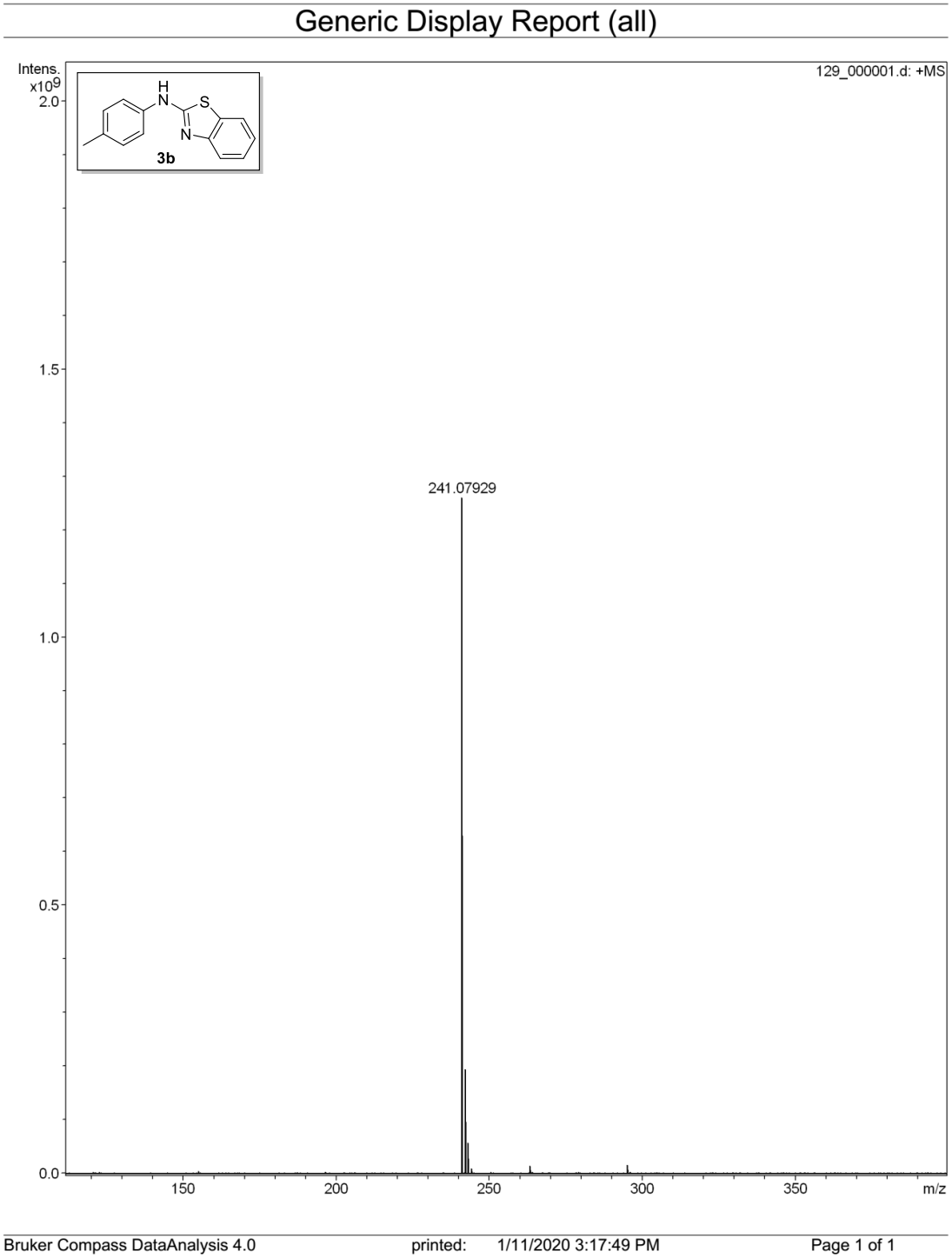
➢ ^{1}H NMR spectrum for **3b**



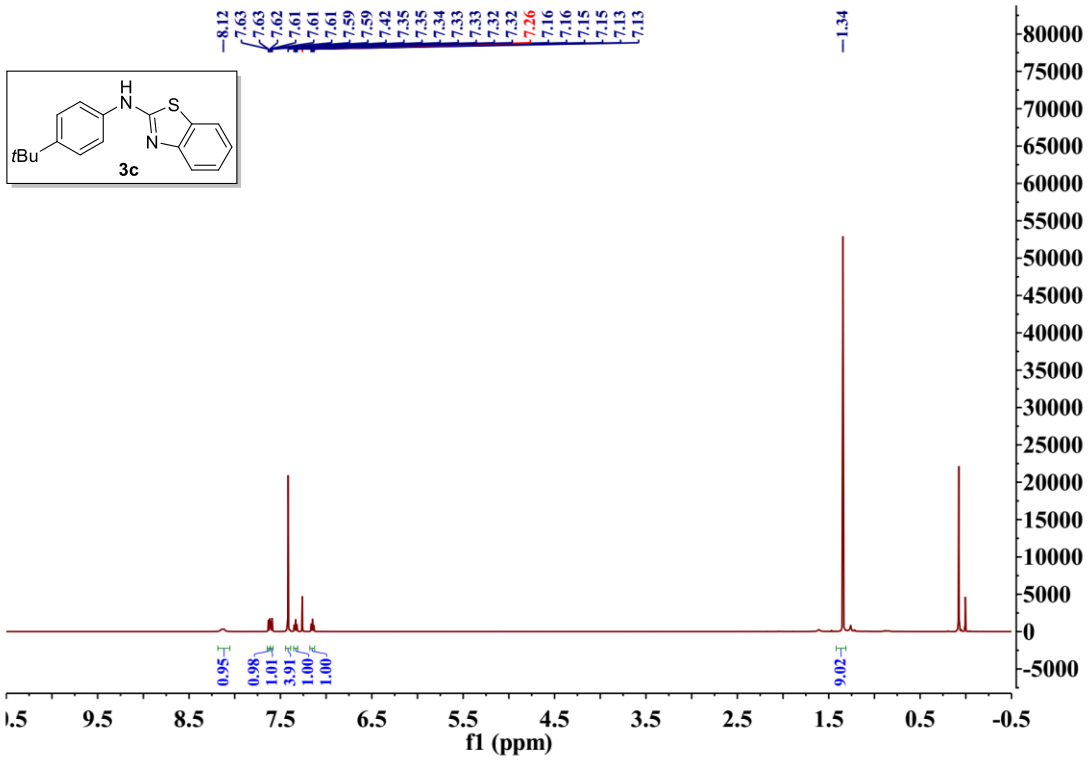
➢ ^{13}C NMR spectrum for **3b**



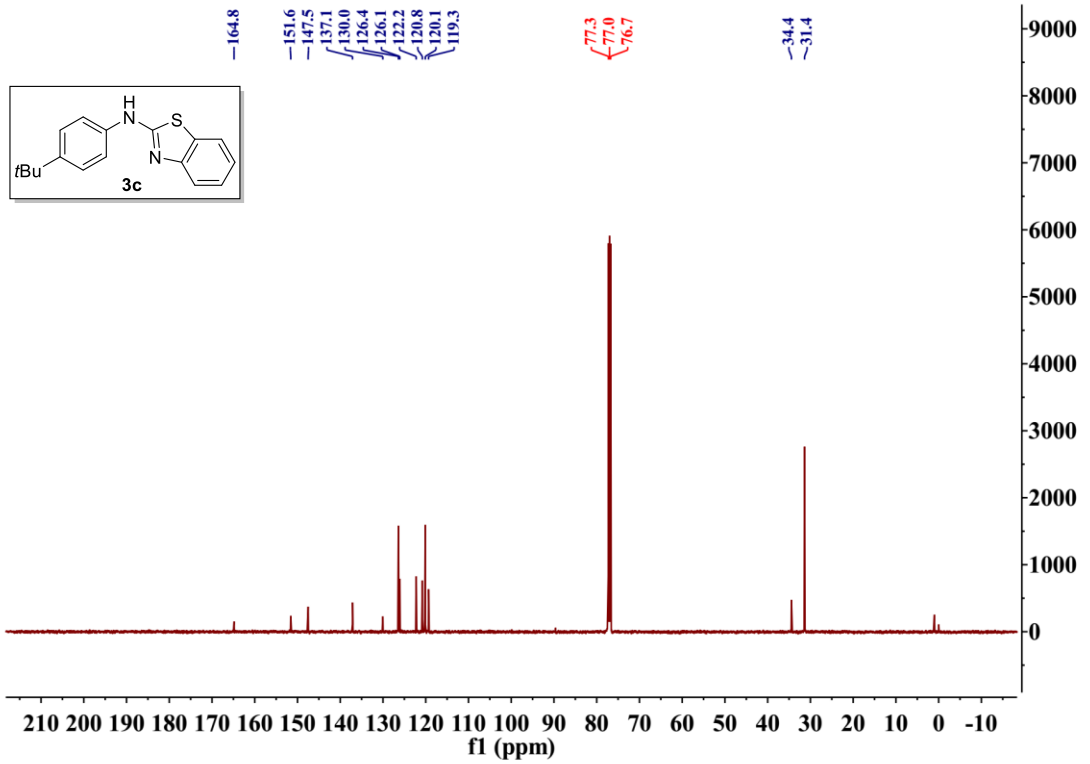
- HRMS spectrum for **3b**



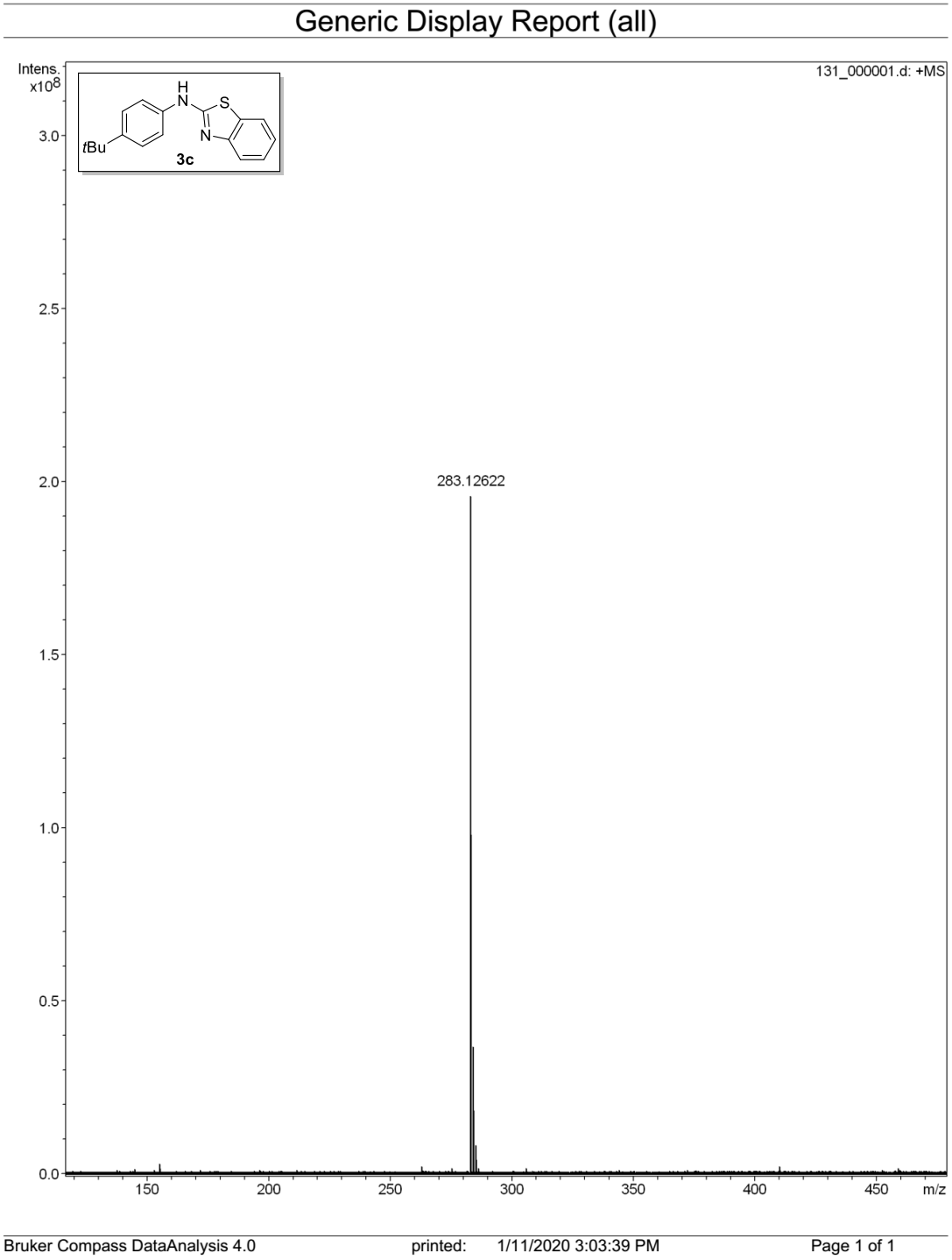
➢ ^{1}H NMR spectrum for **3c**



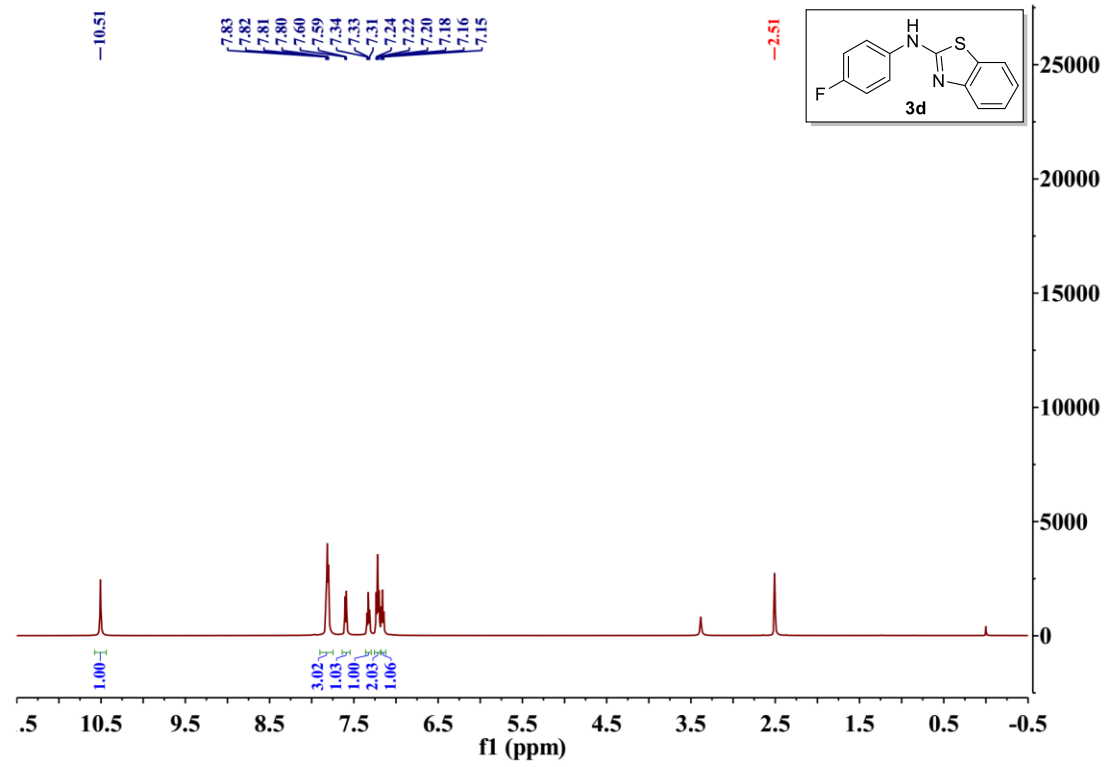
➢ ^{13}C NMR spectrum for **3c**



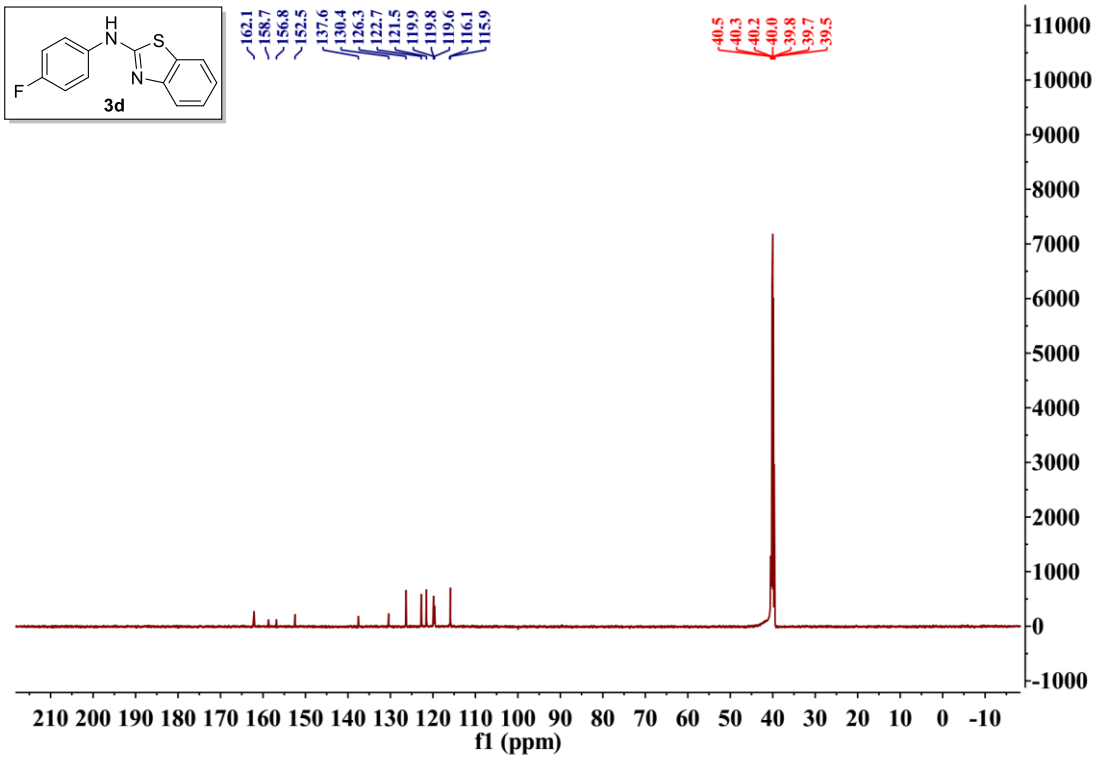
- HRMS spectrum for **3c**



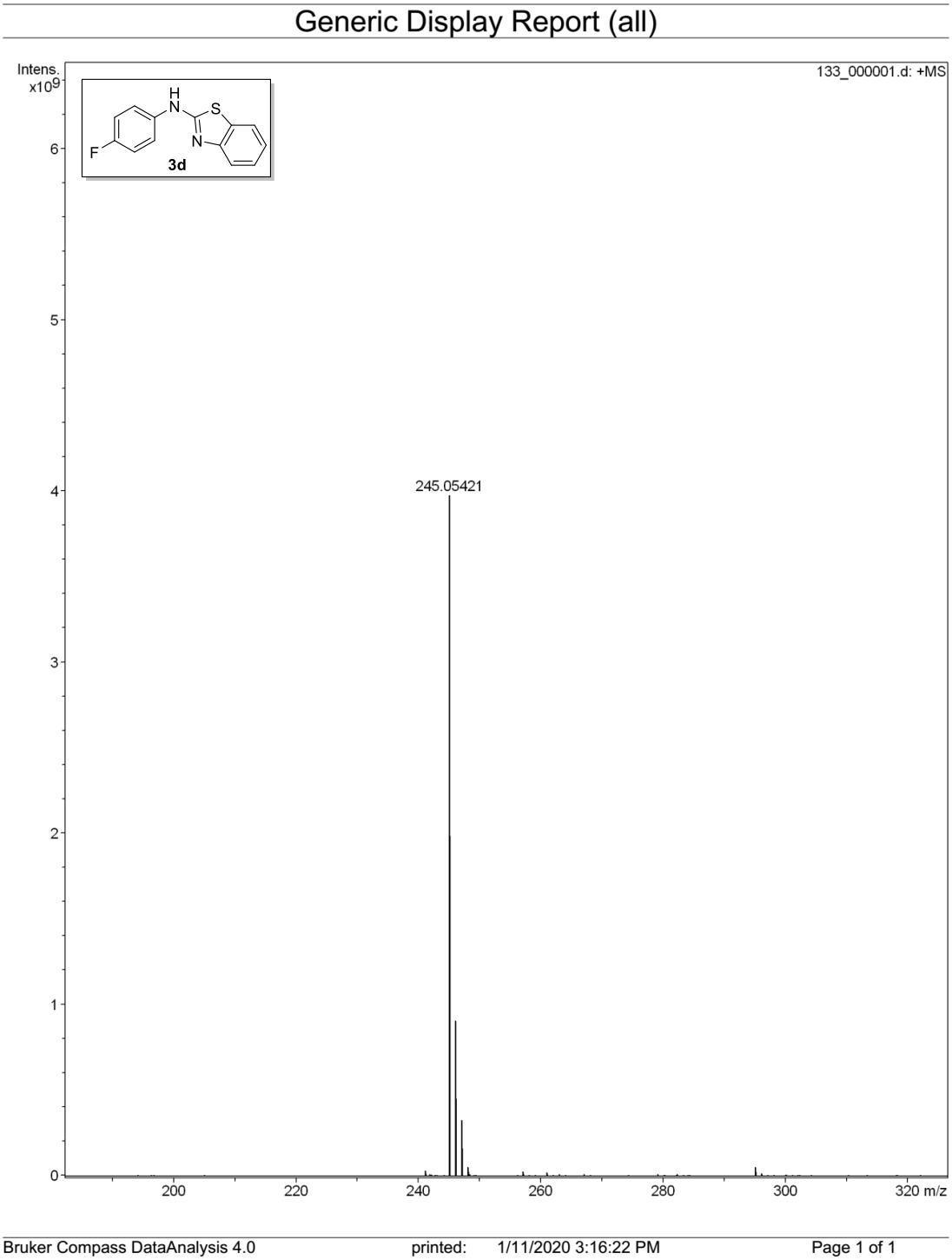
➢ ^{1}H NMR spectrum for **3d**



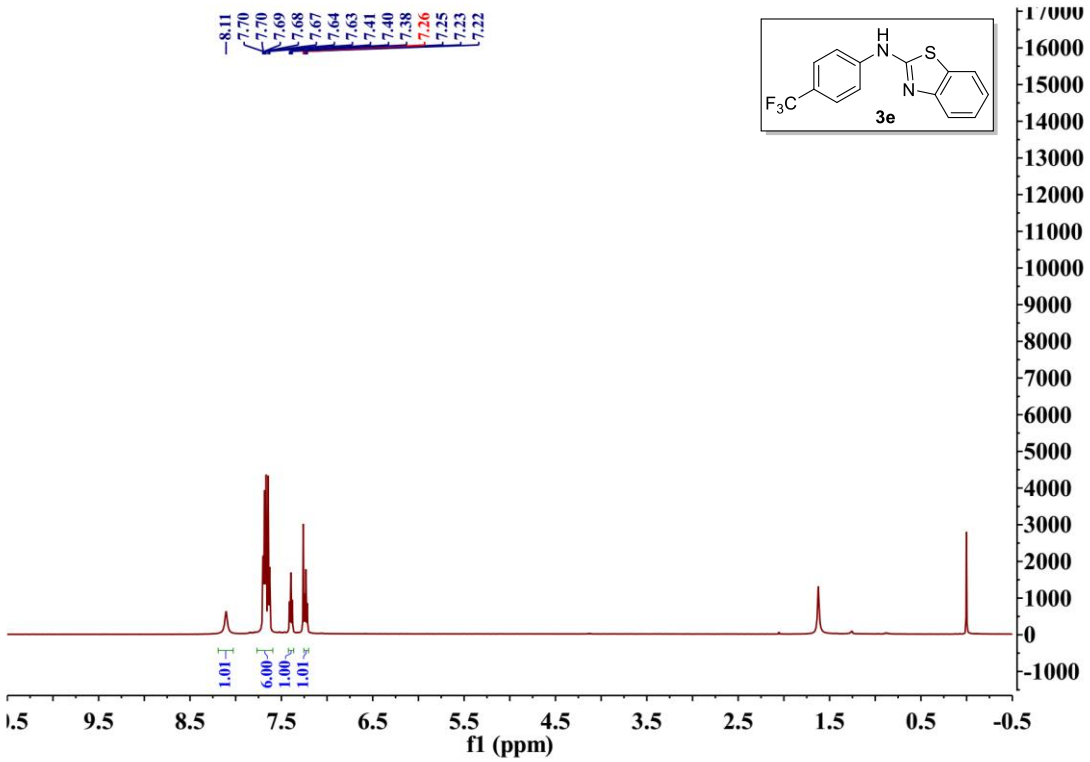
➢ ^{13}C NMR spectrum for **3d**



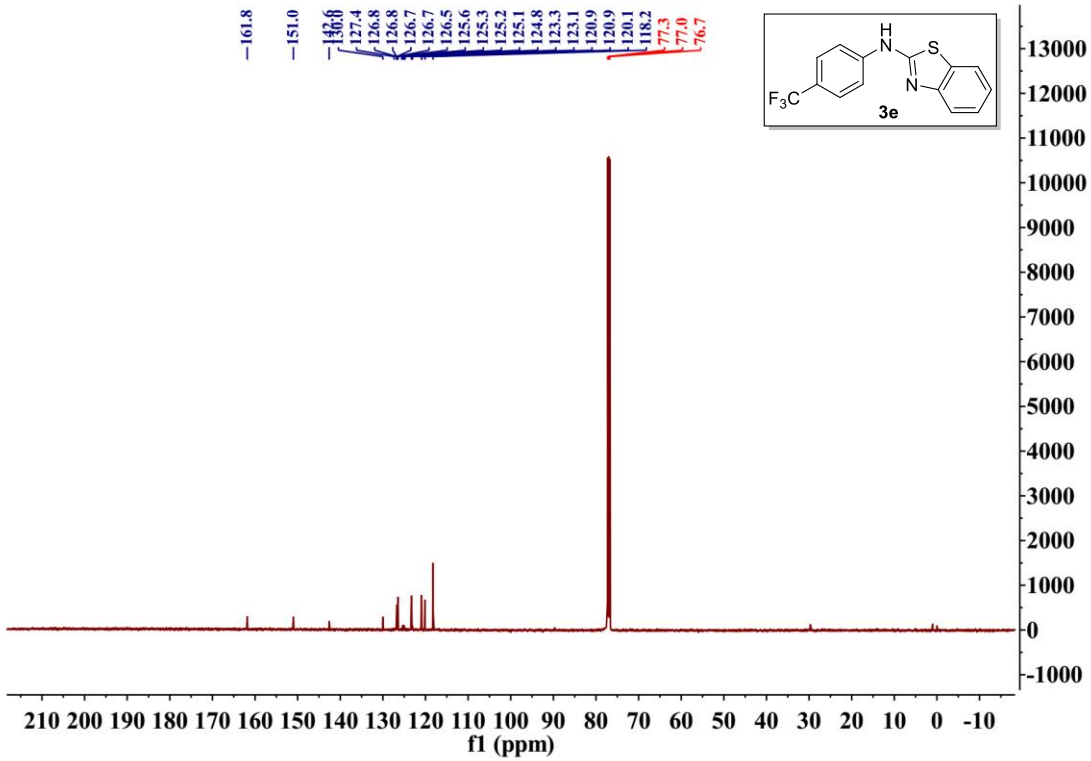
- HRMS spectrum for **3d**



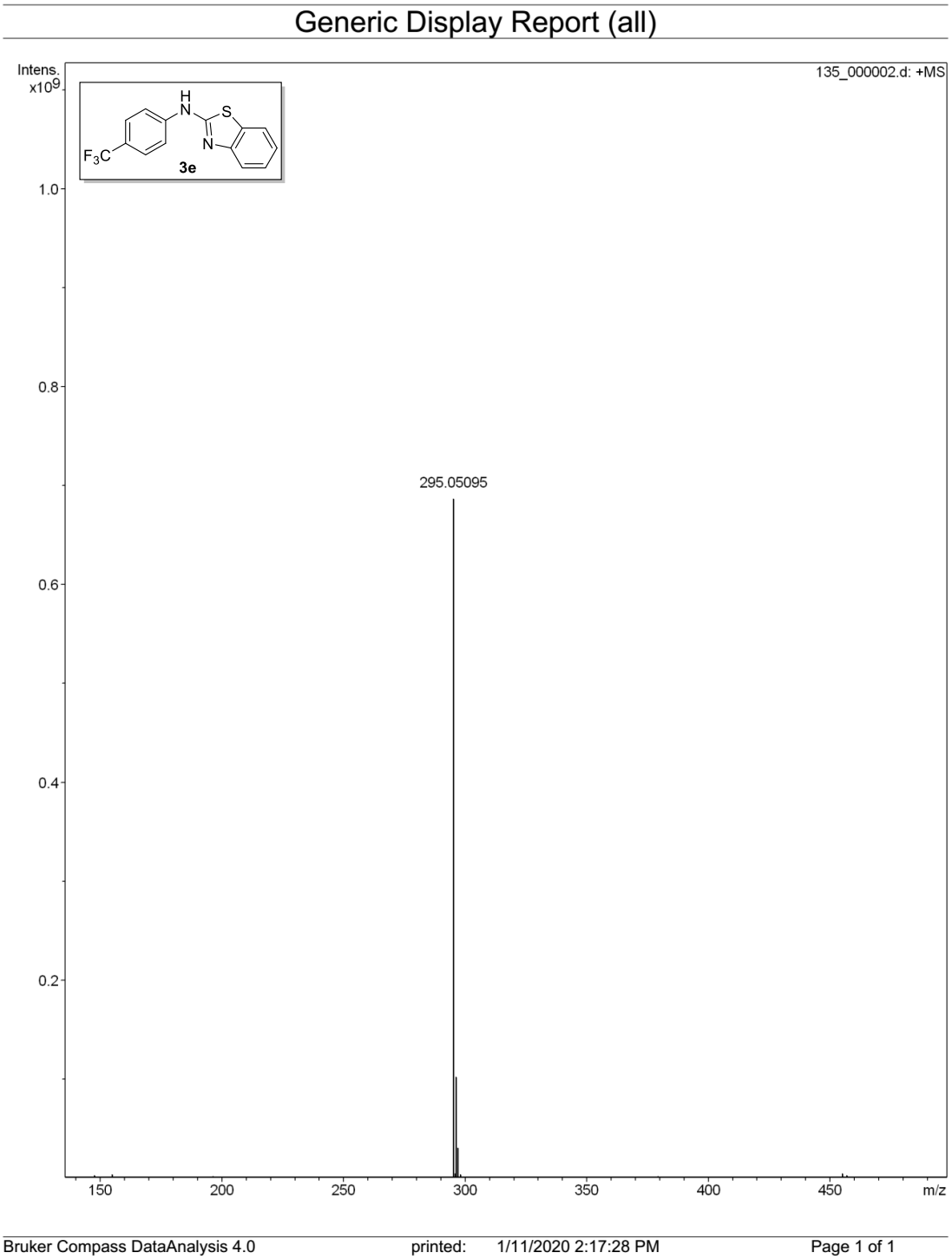
➢ ^{1}H NMR spectrum for **3e**



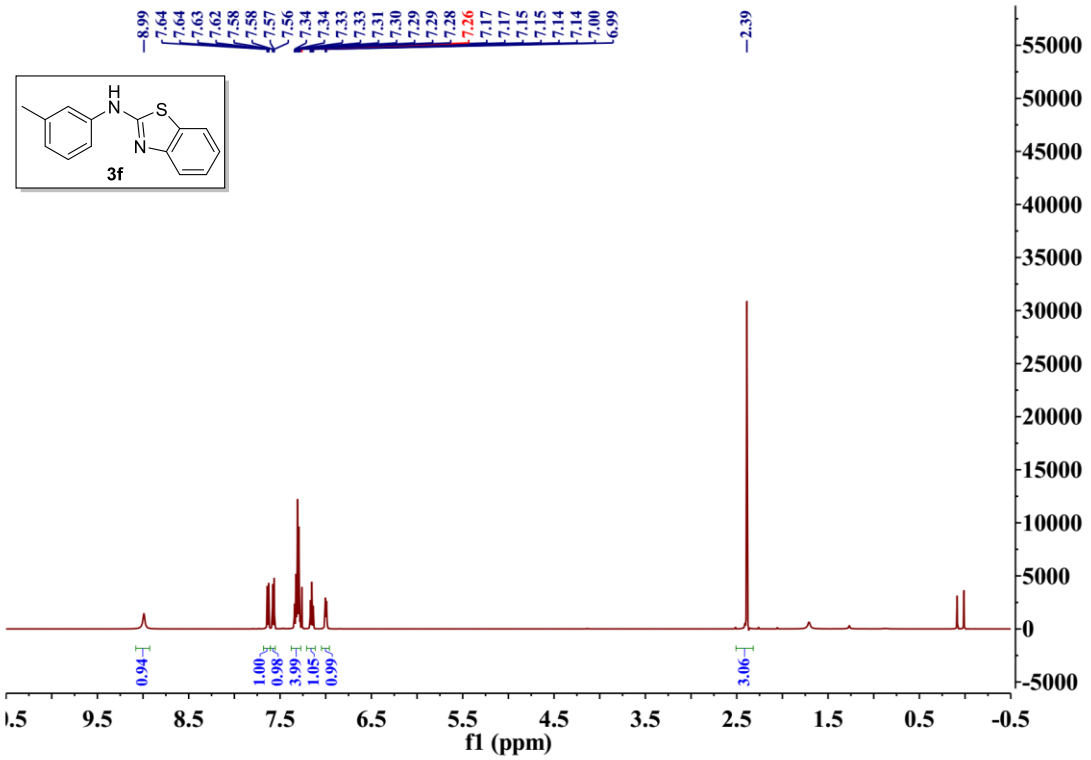
➢ ^{13}C NMR spectrum for **3e**



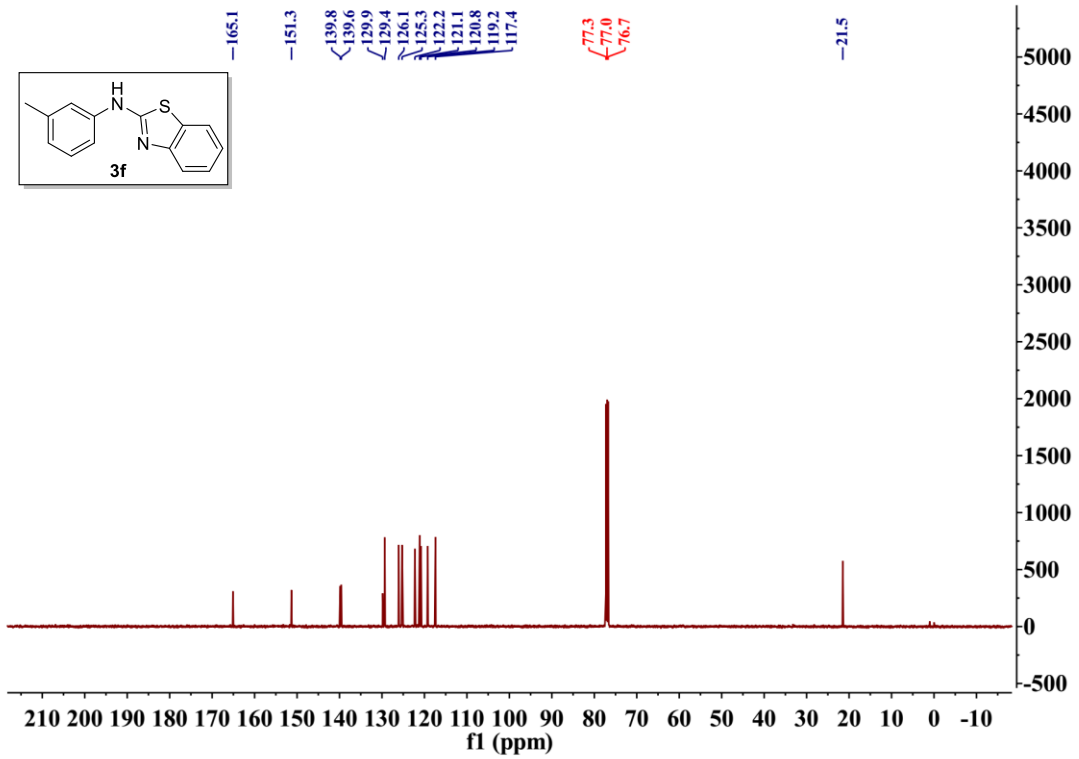
- HRMS spectrum for **3e**



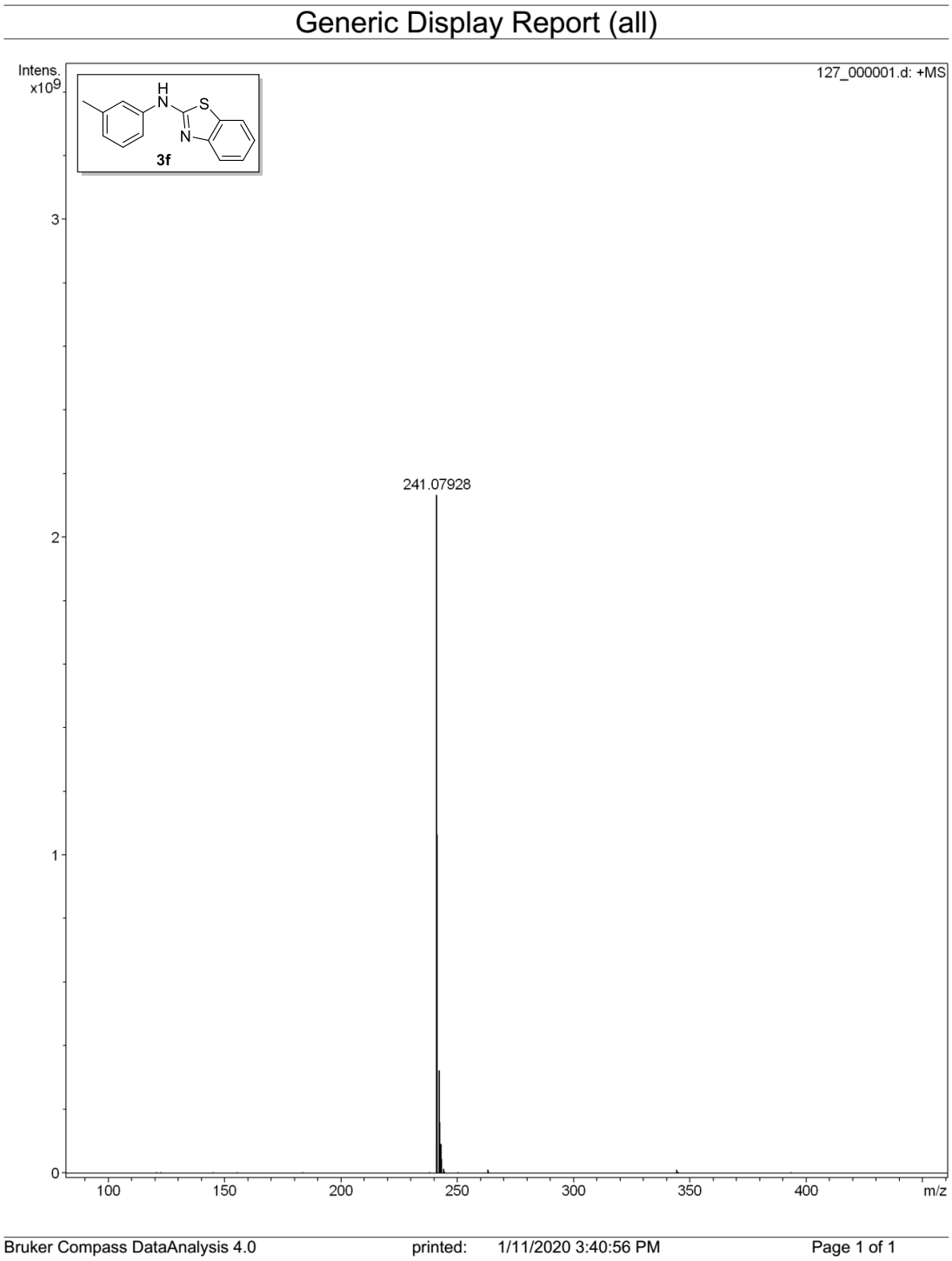
➢ ^{1}H NMR spectrum for **3f**



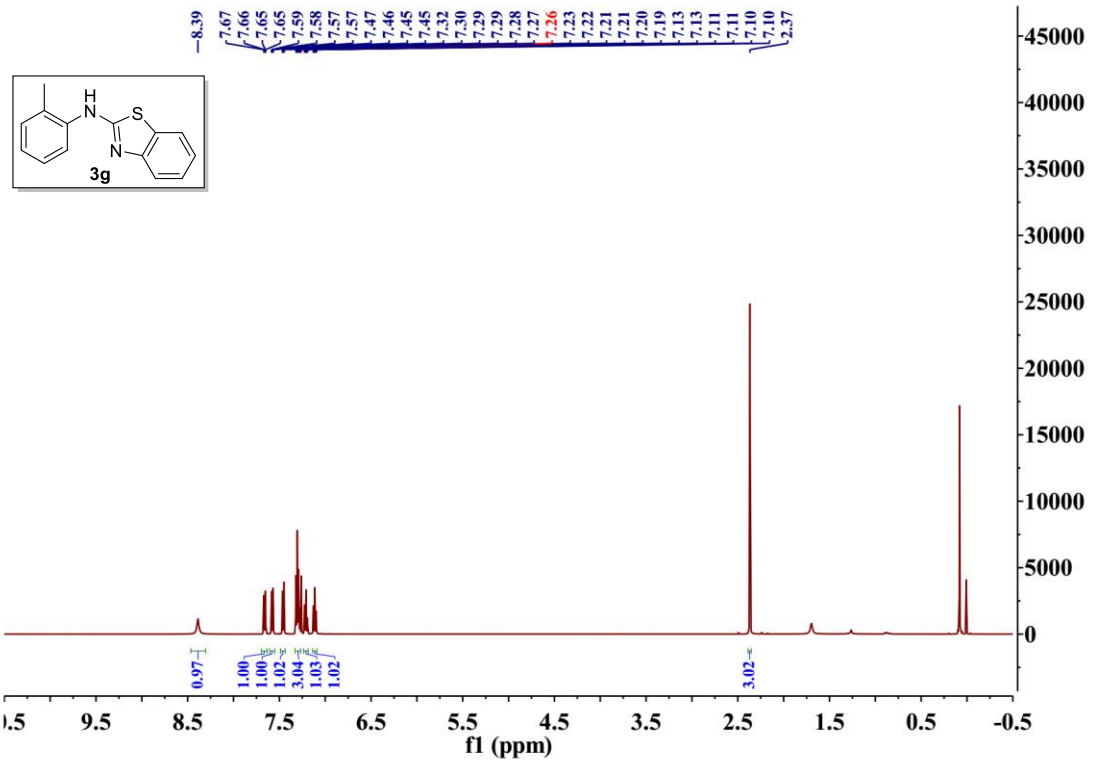
➢ ^{13}C NMR spectrum for **3f**



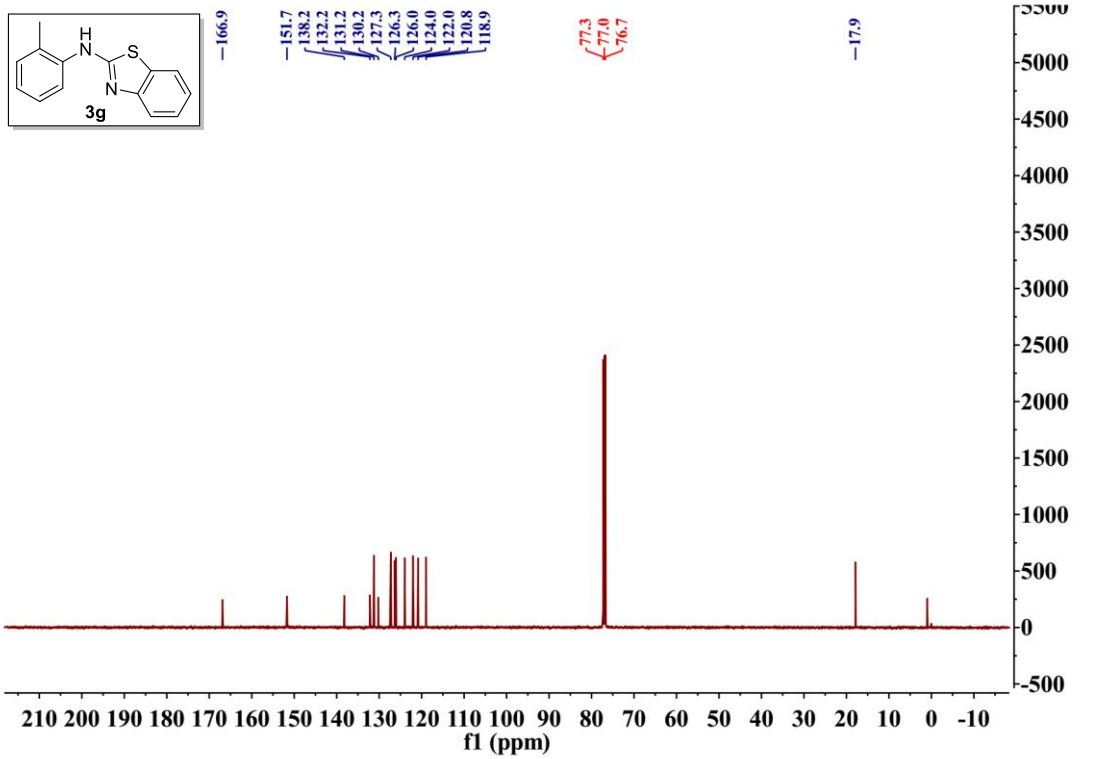
- HRMS spectrum for **3f**



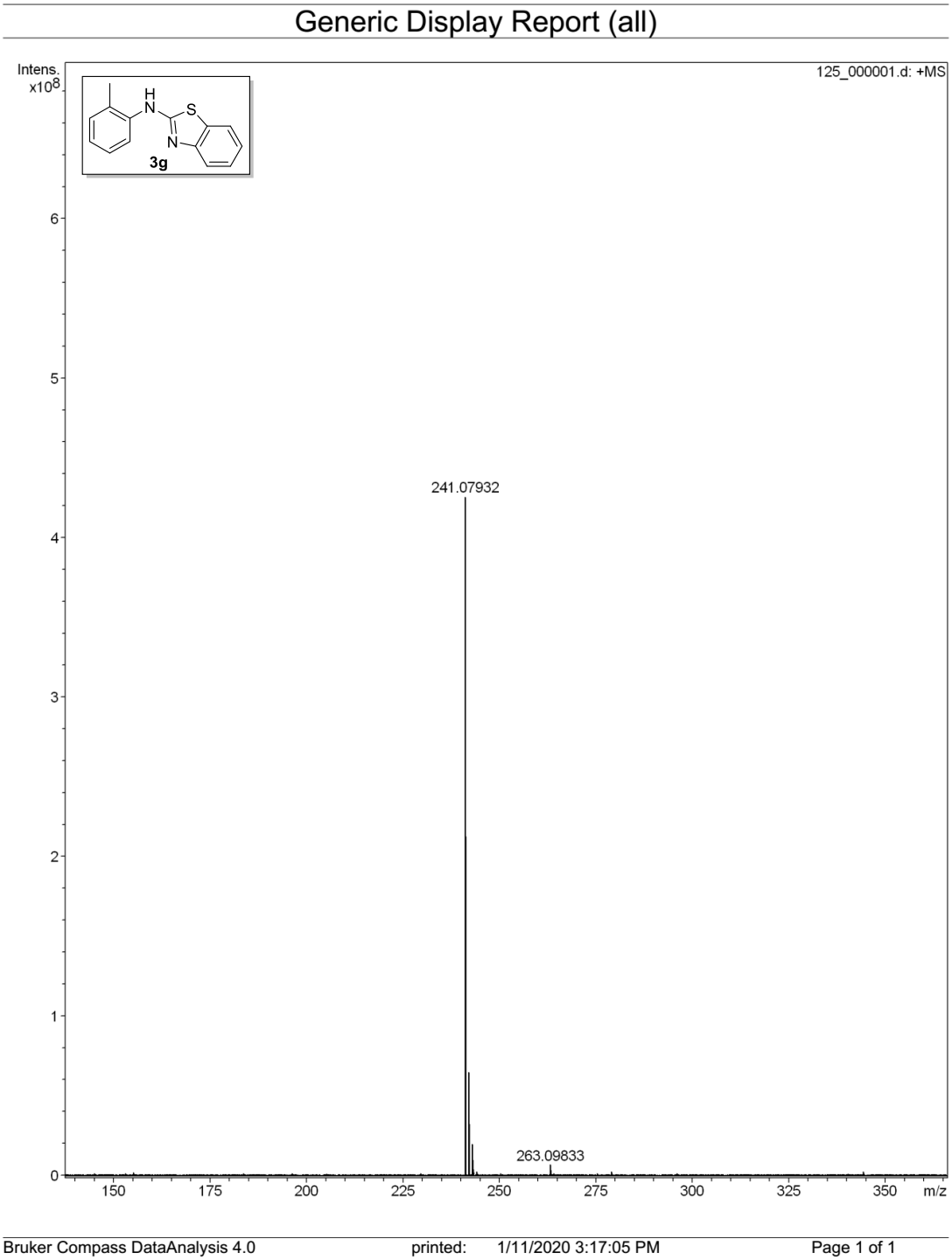
➢ ^{1}H NMR spectrum for **3g**



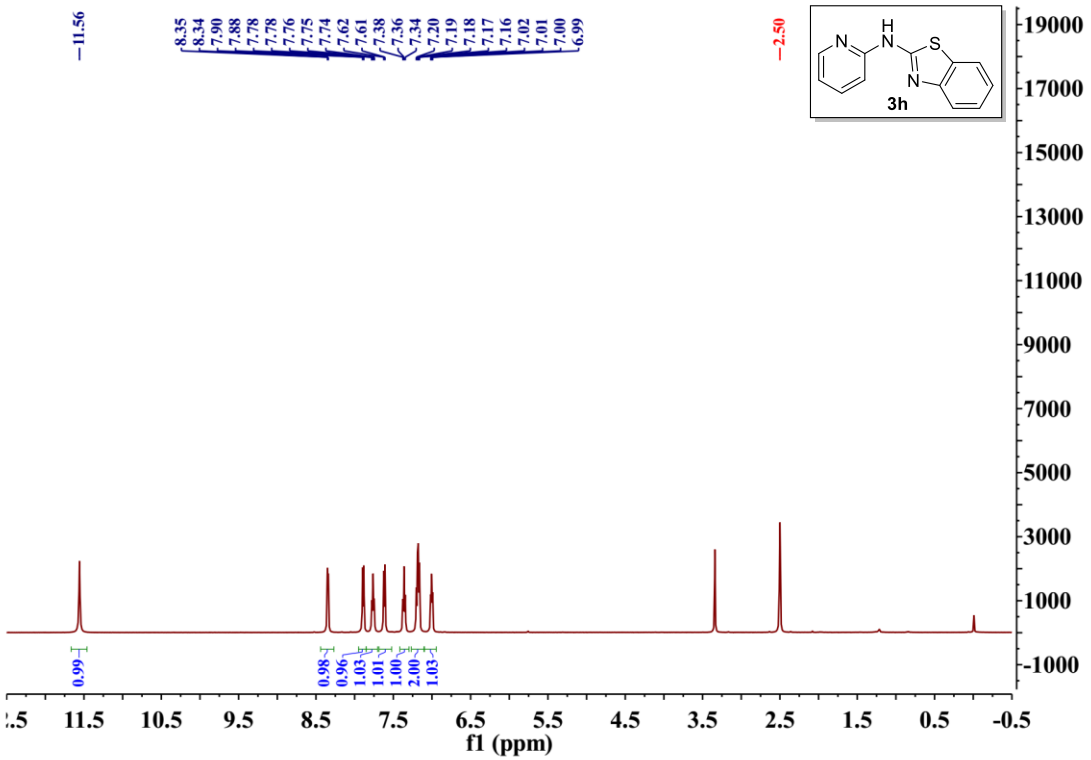
➢ ^{13}C NMR spectrum for **3g**



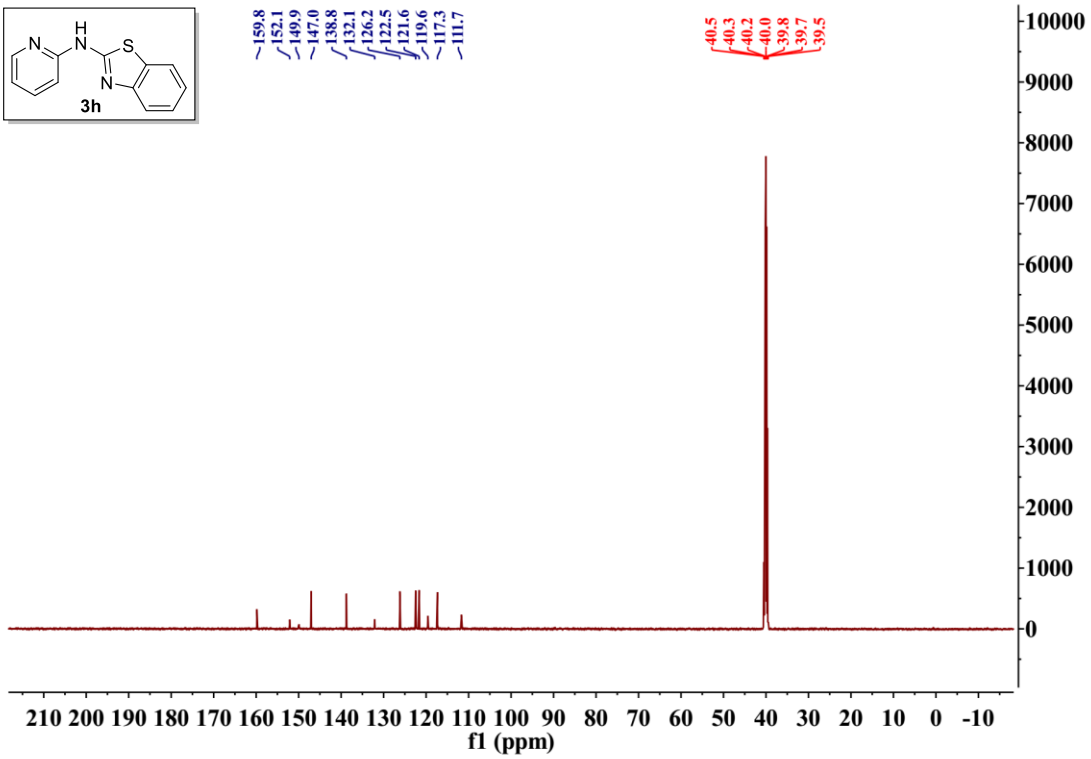
- HRMS spectrum for **3g**



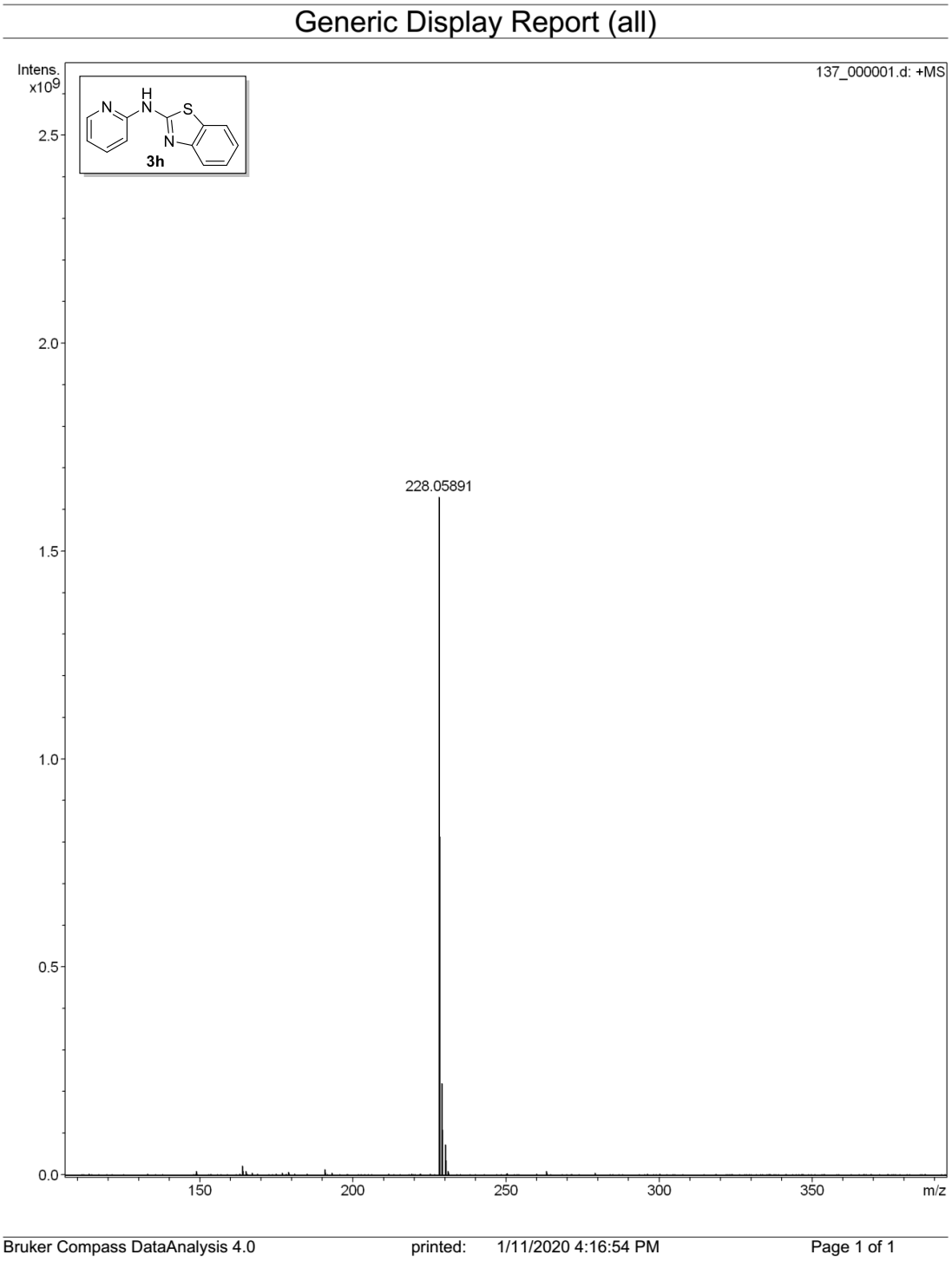
➢ ^{1}H NMR spectrum for **3h**



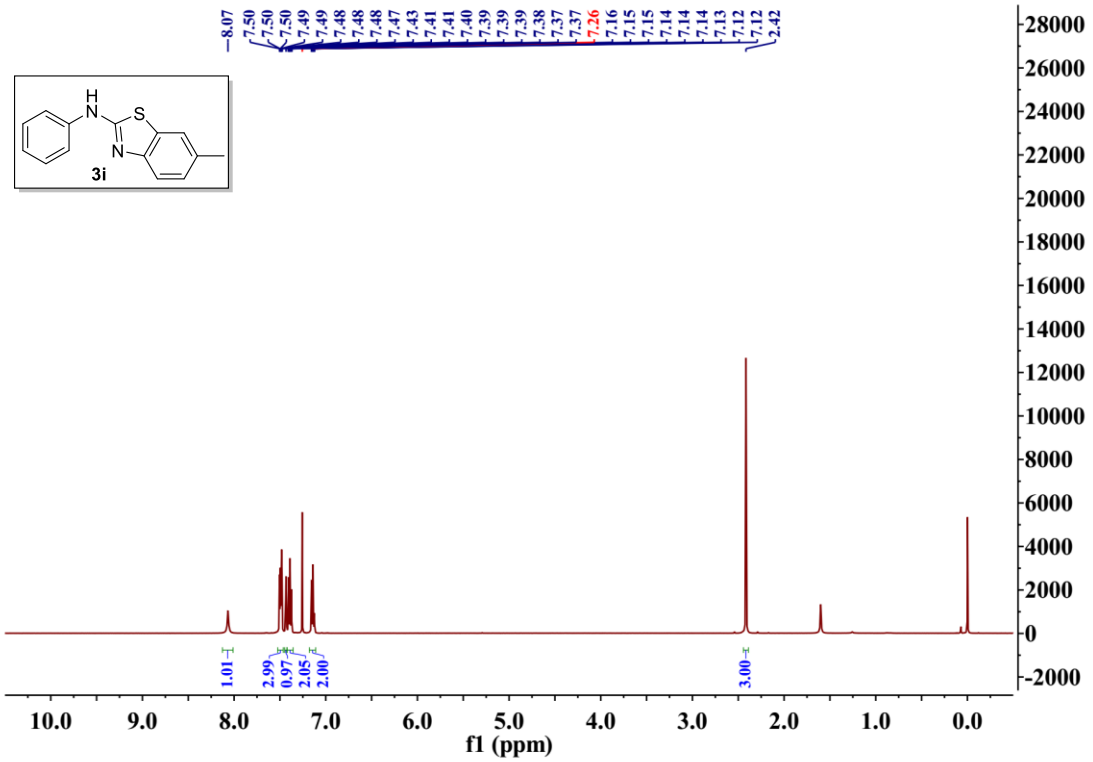
➢ ^{13}C NMR spectrum for **3h**



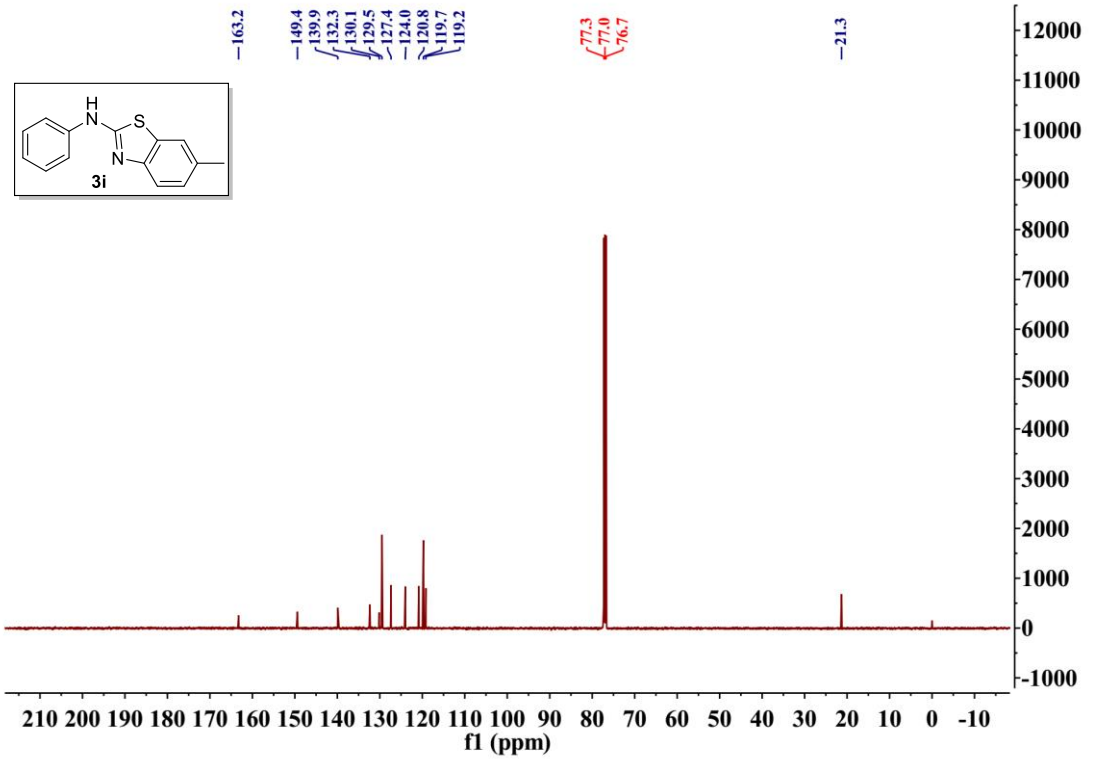
➢ HRMS spectrum for **3h**



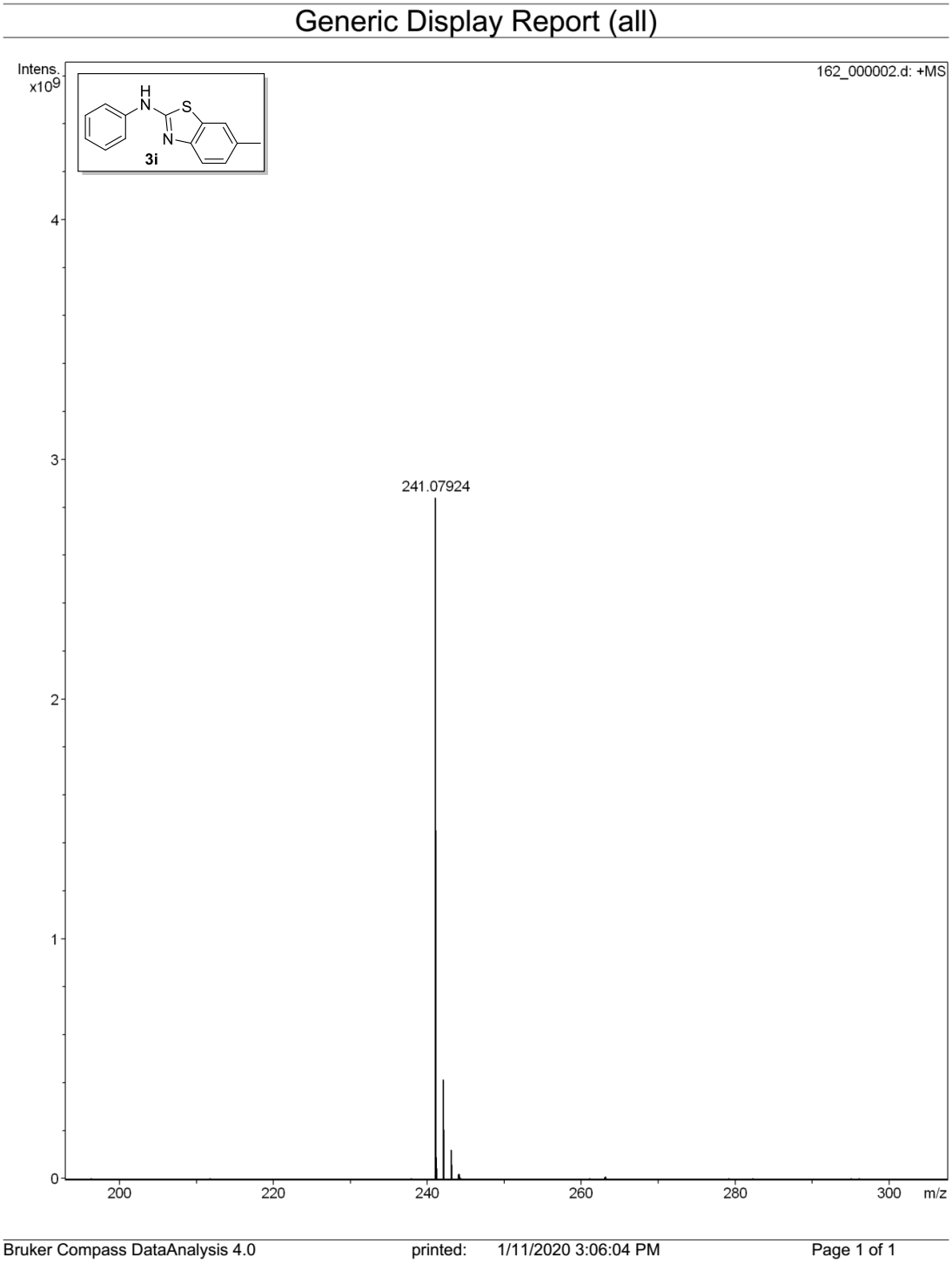
➢ ^{1}H NMR spectrum for **3i**



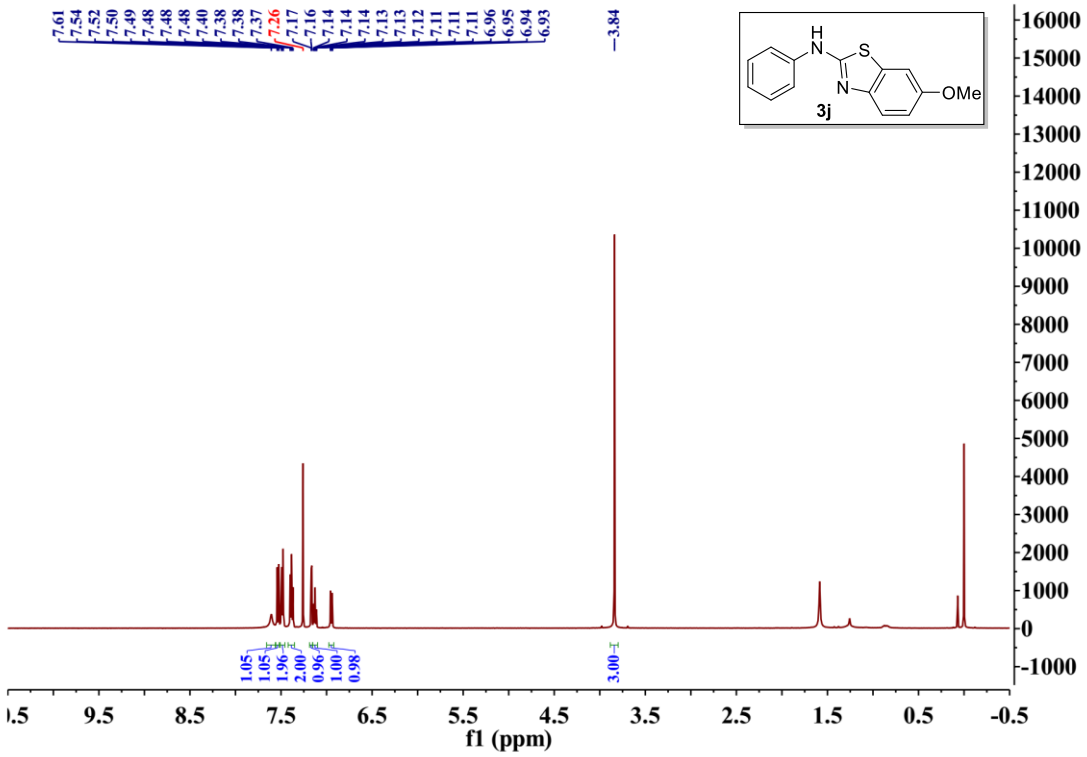
➢ ^{13}C NMR spectrum for **3i**



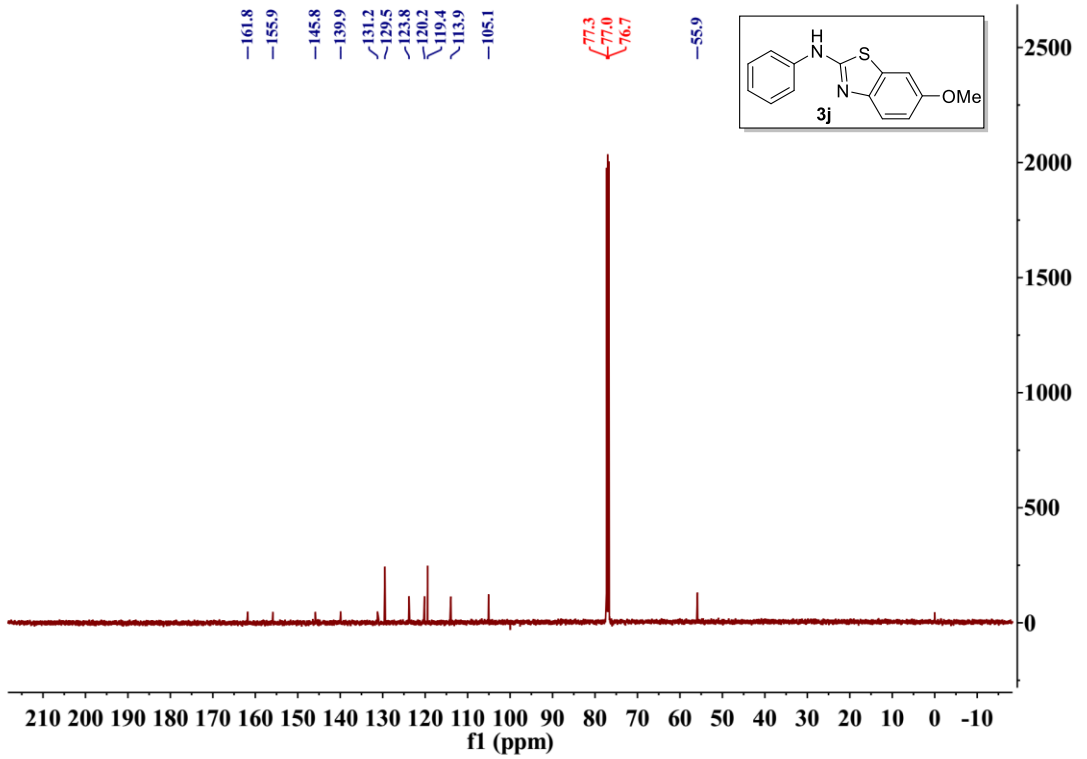
- HRMS spectrum for **3i**



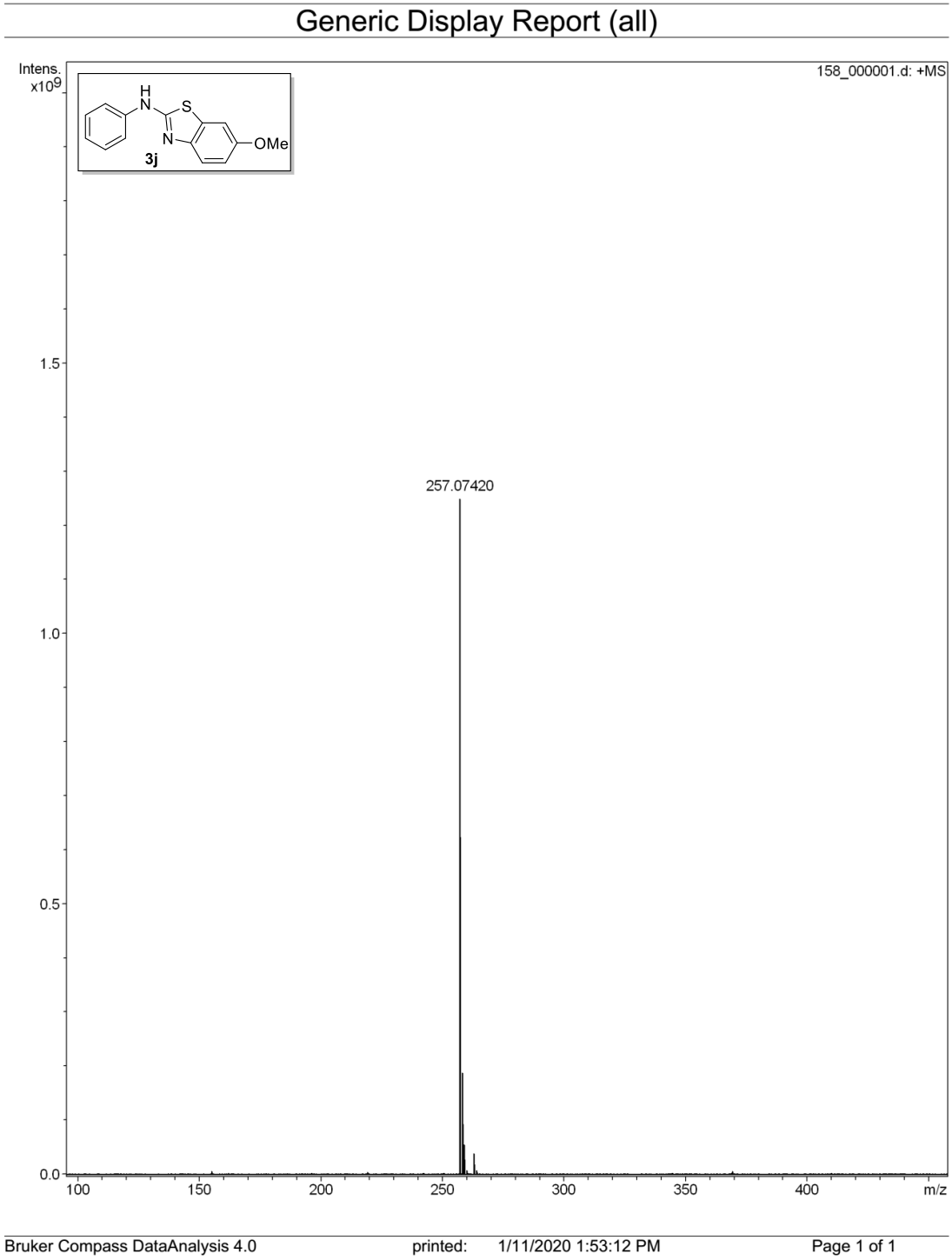
➢ ^{1}H NMR spectrum for **3j**



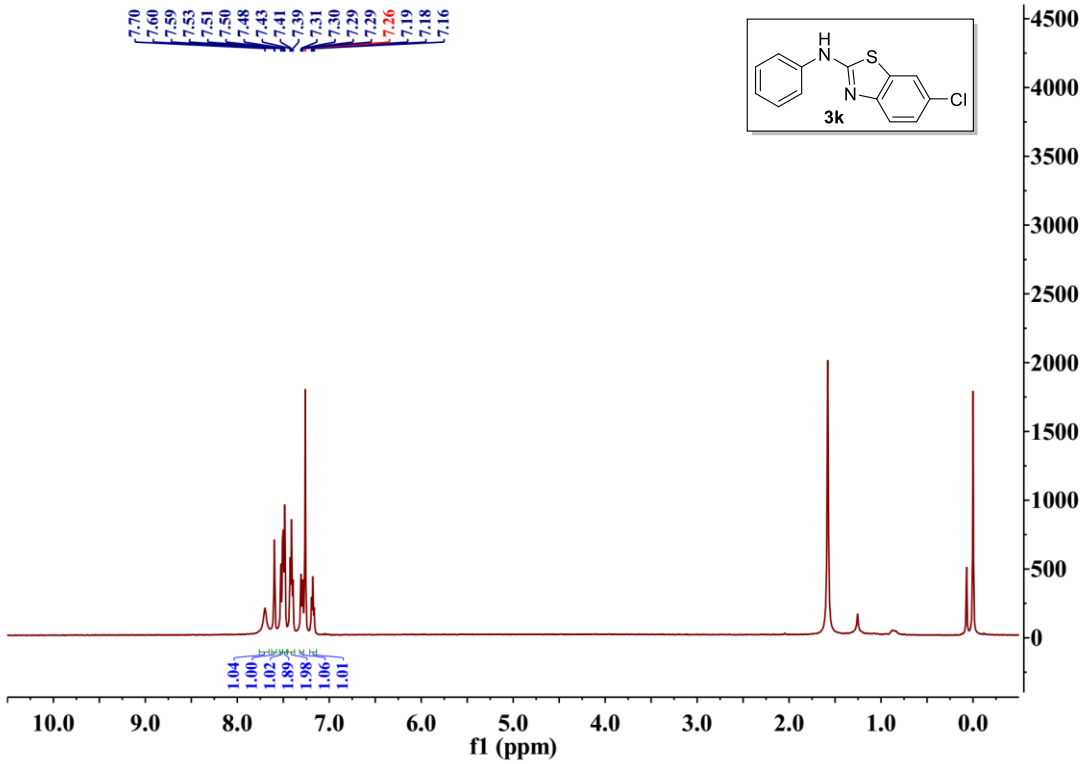
➢ ^{13}C NMR spectrum for **3j**



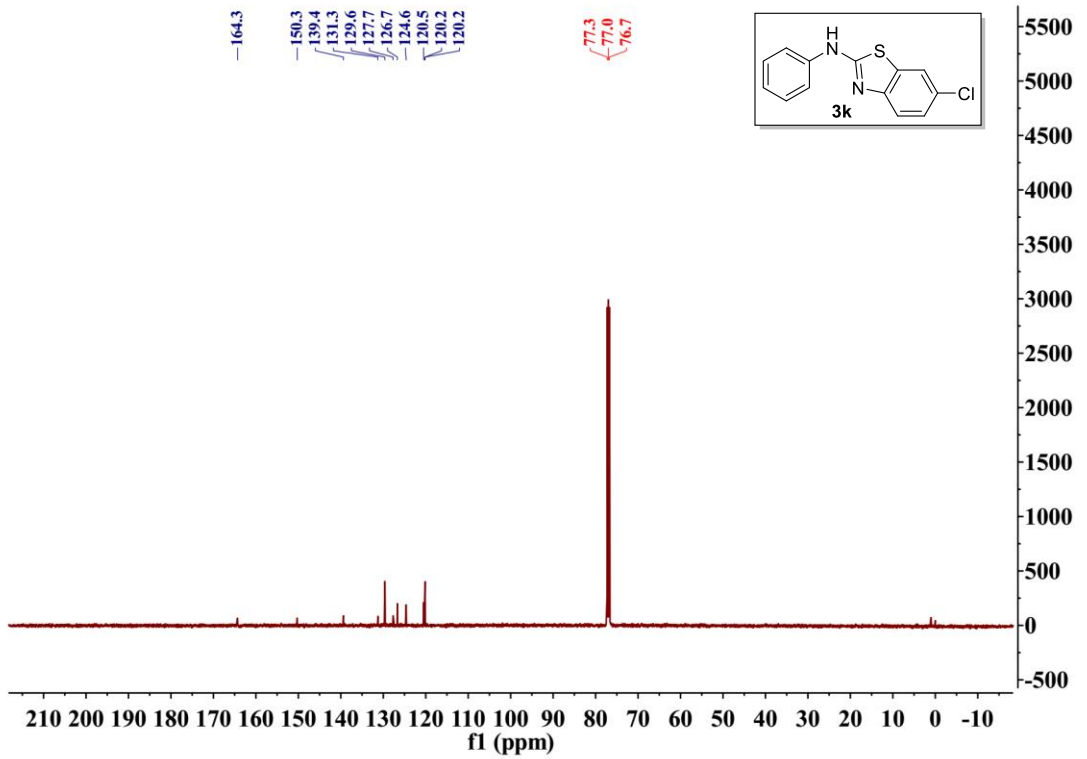
- HRMS spectrum for **3j**



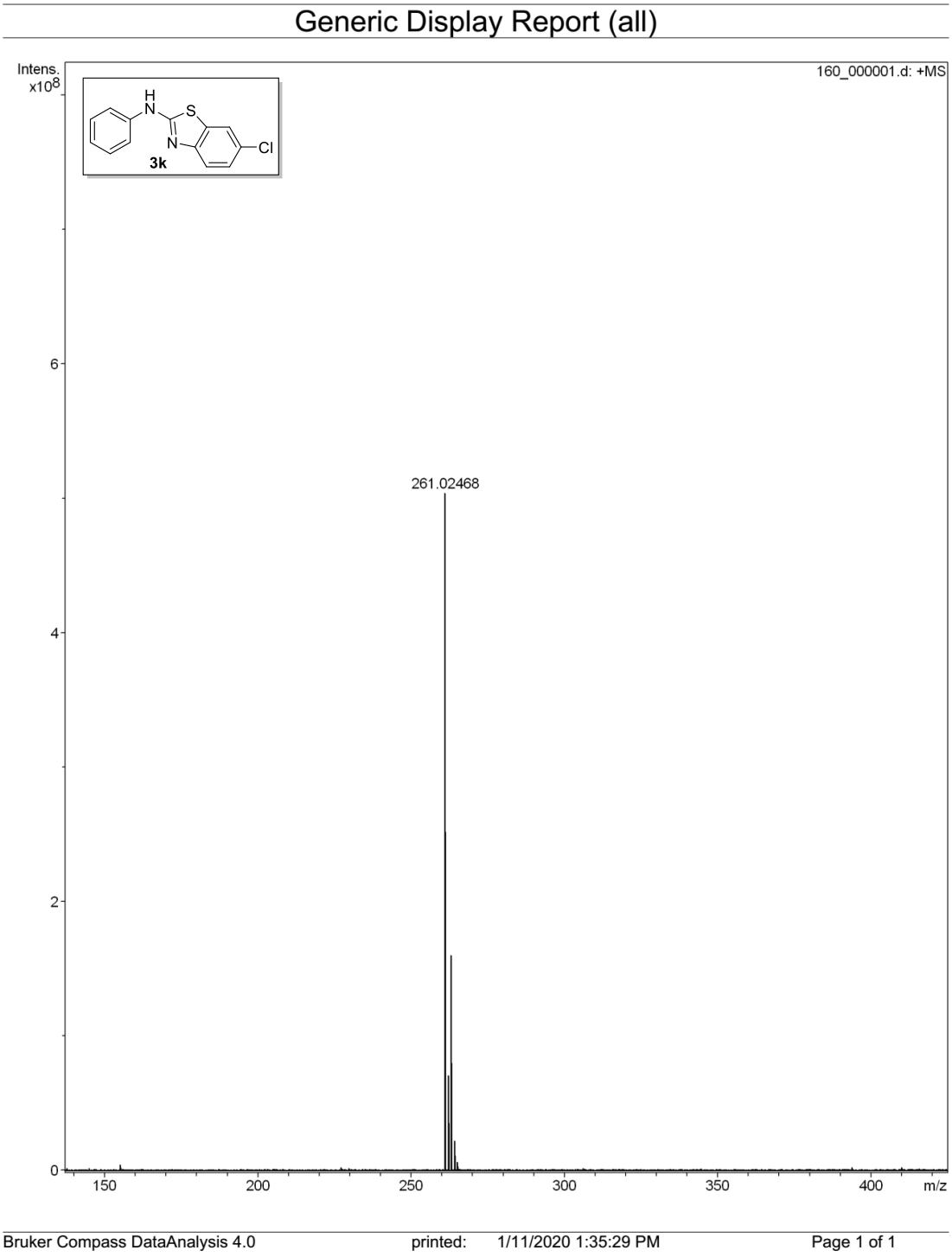
➢ ^{1}H NMR spectrum for **3k**



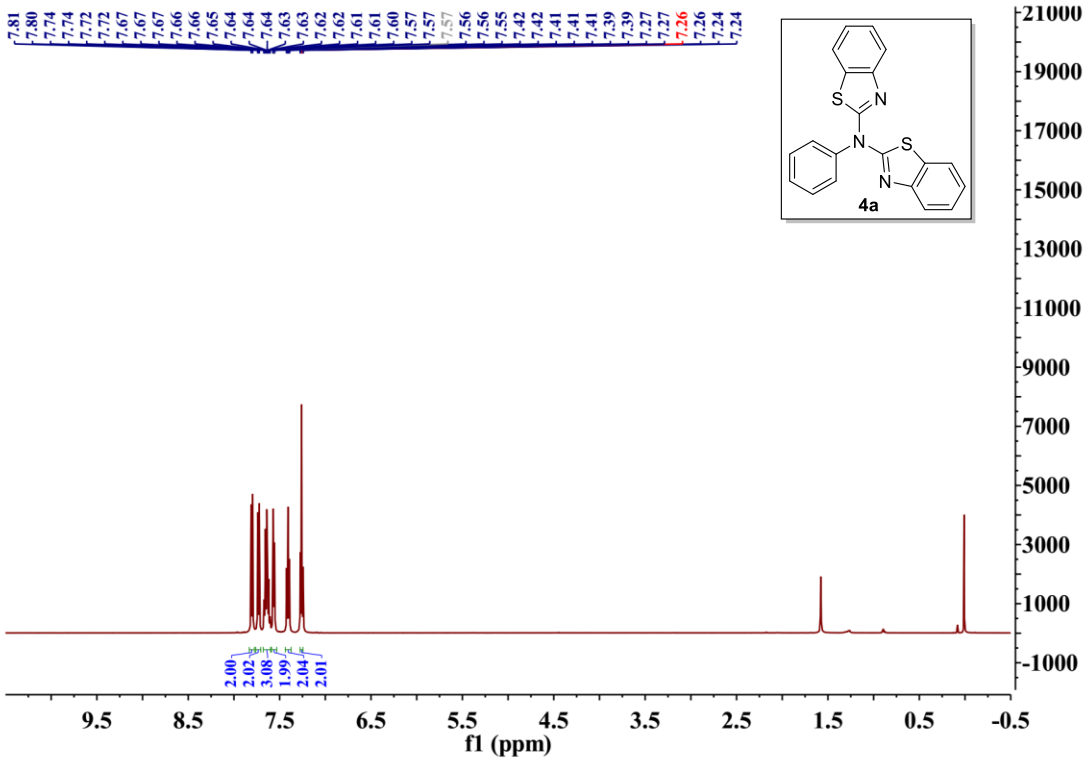
➢ ^{13}C NMR spectrum for **3k**



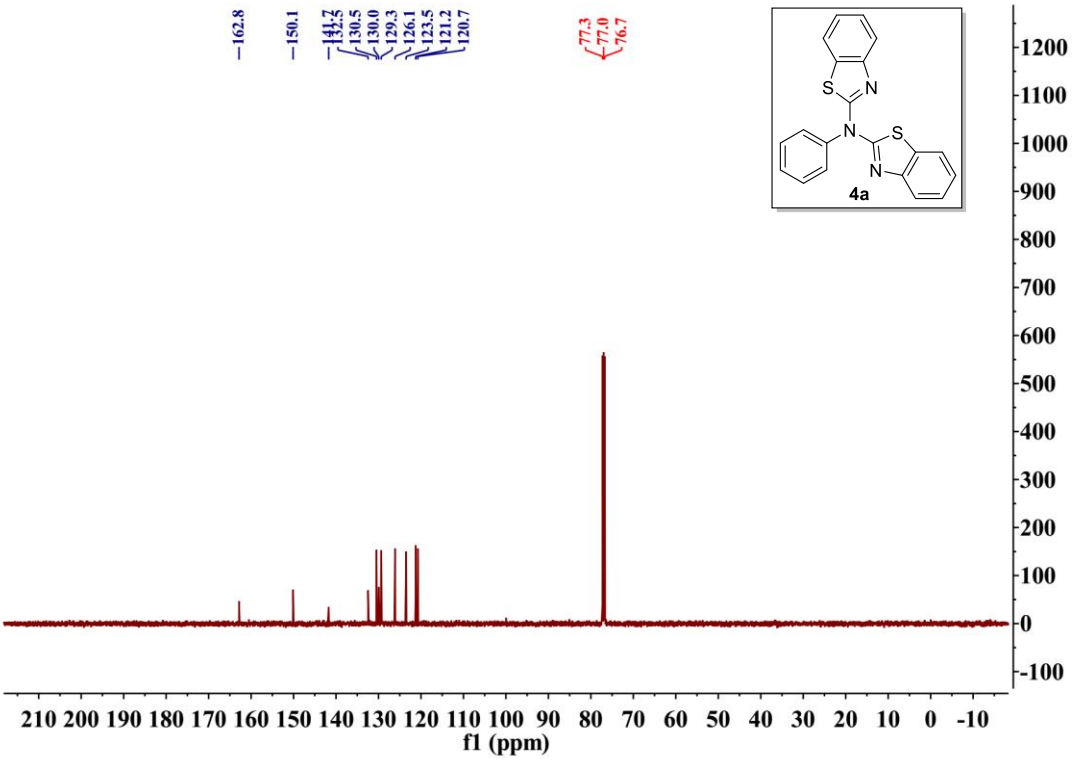
- HRMS spectrum for **3k**



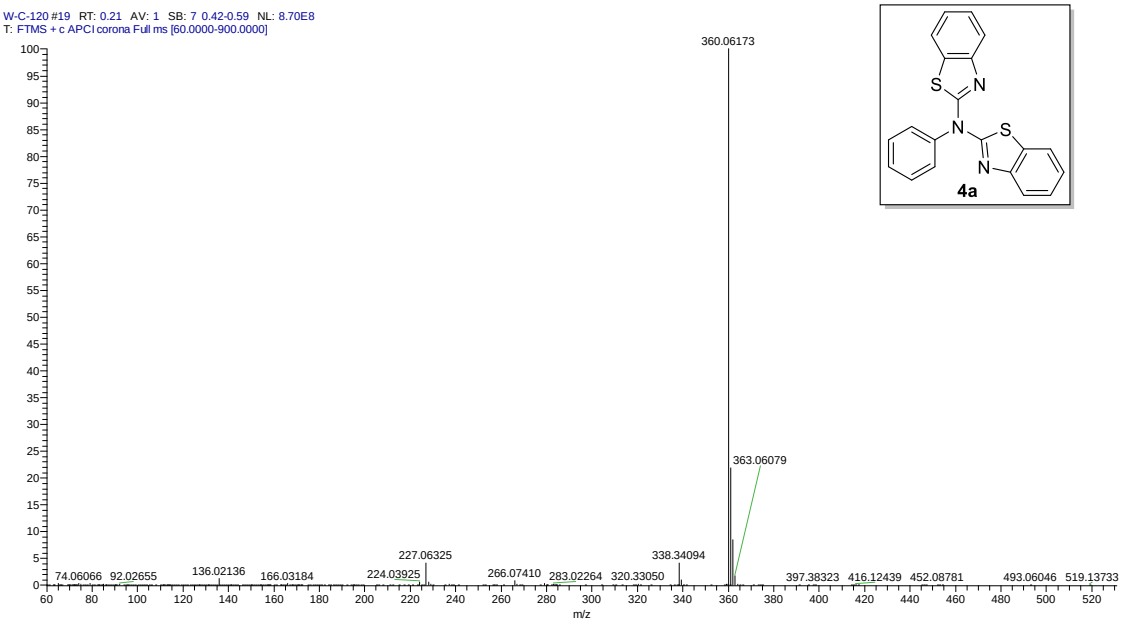
➢ ^{1}H NMR spectrum for **4a**



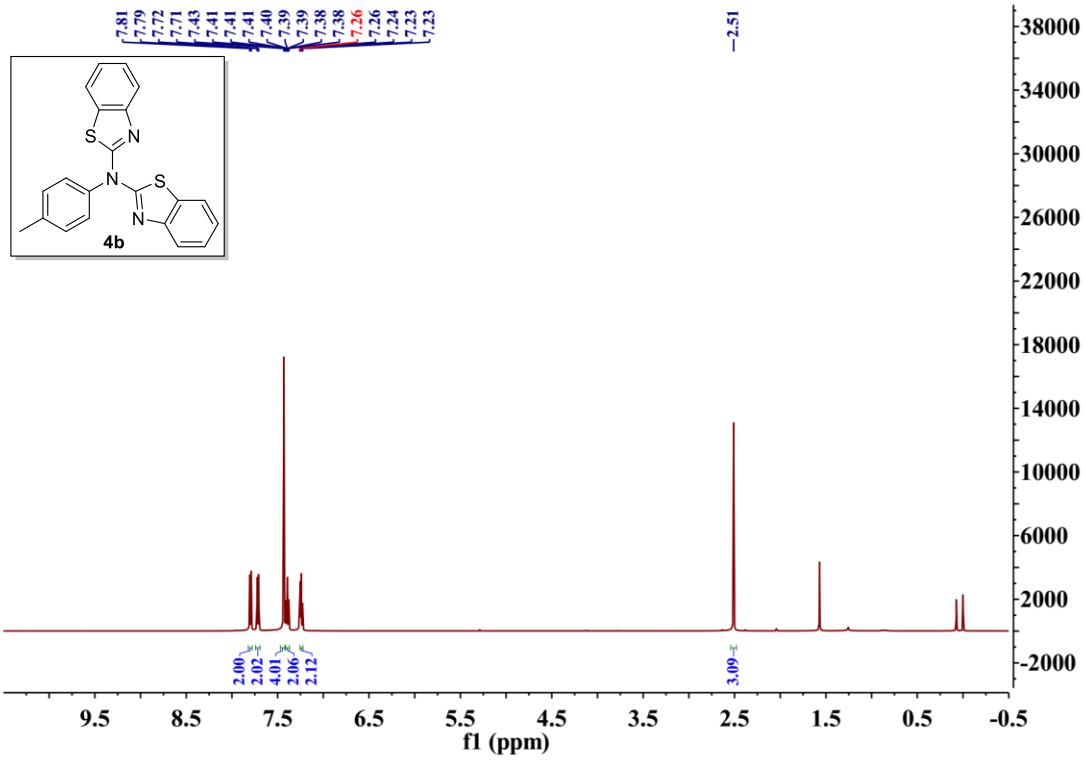
➢ ^{13}C NMR spectrum for **4a**



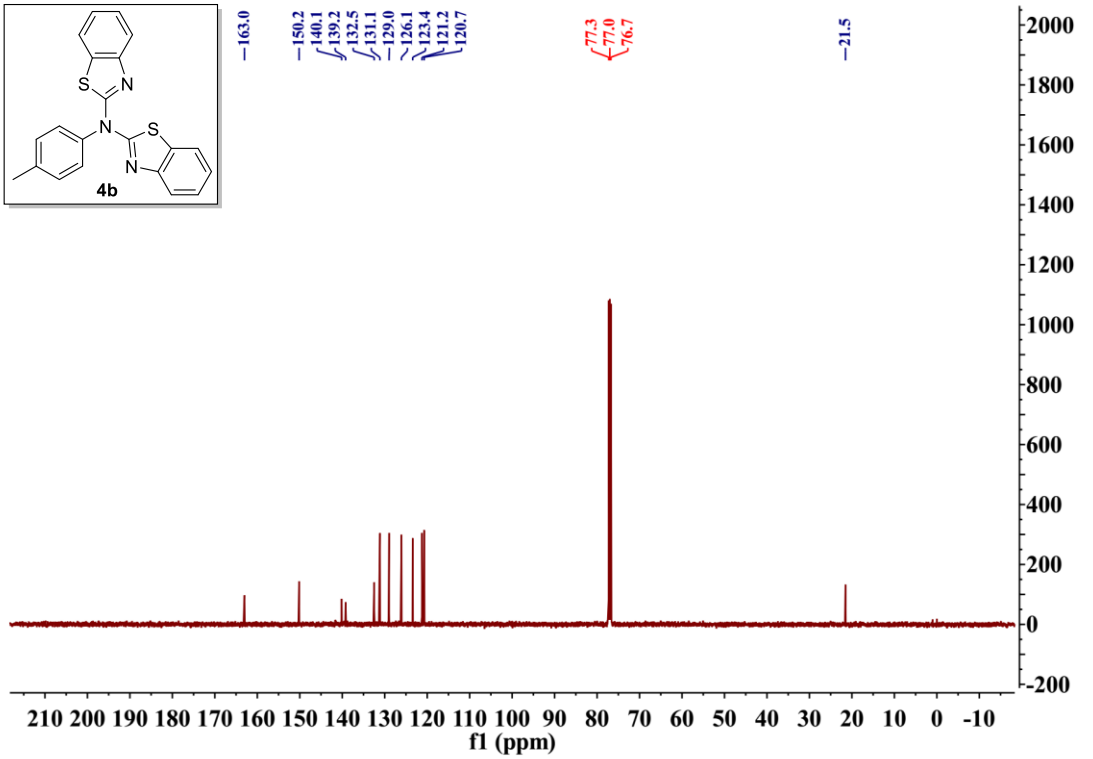
➢ HRMS spectrum for **4a**



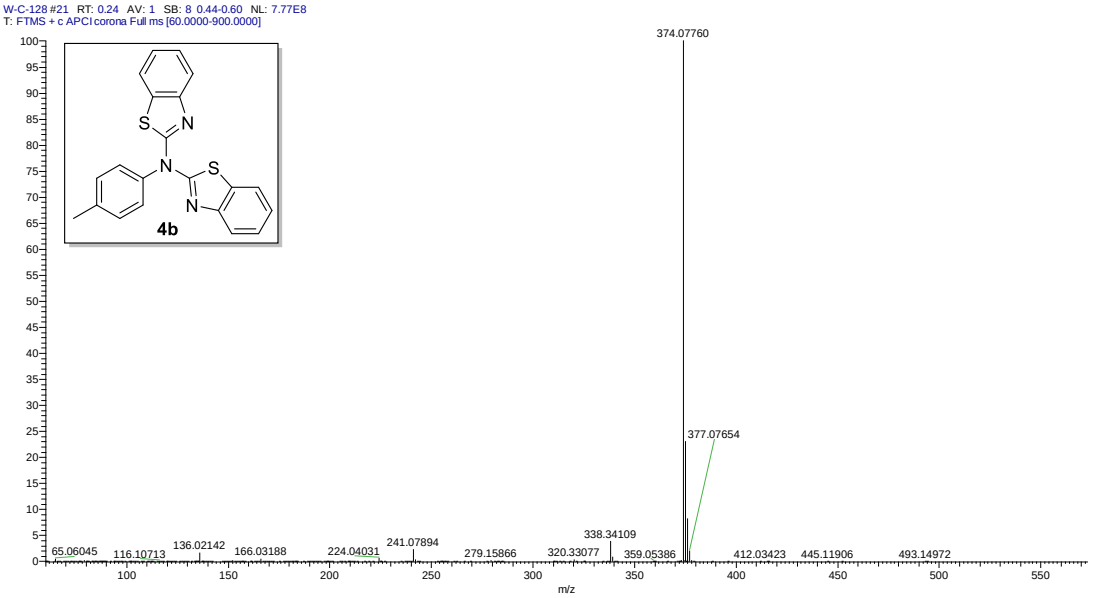
➢ ^{1}H NMR spectrum for **4b**



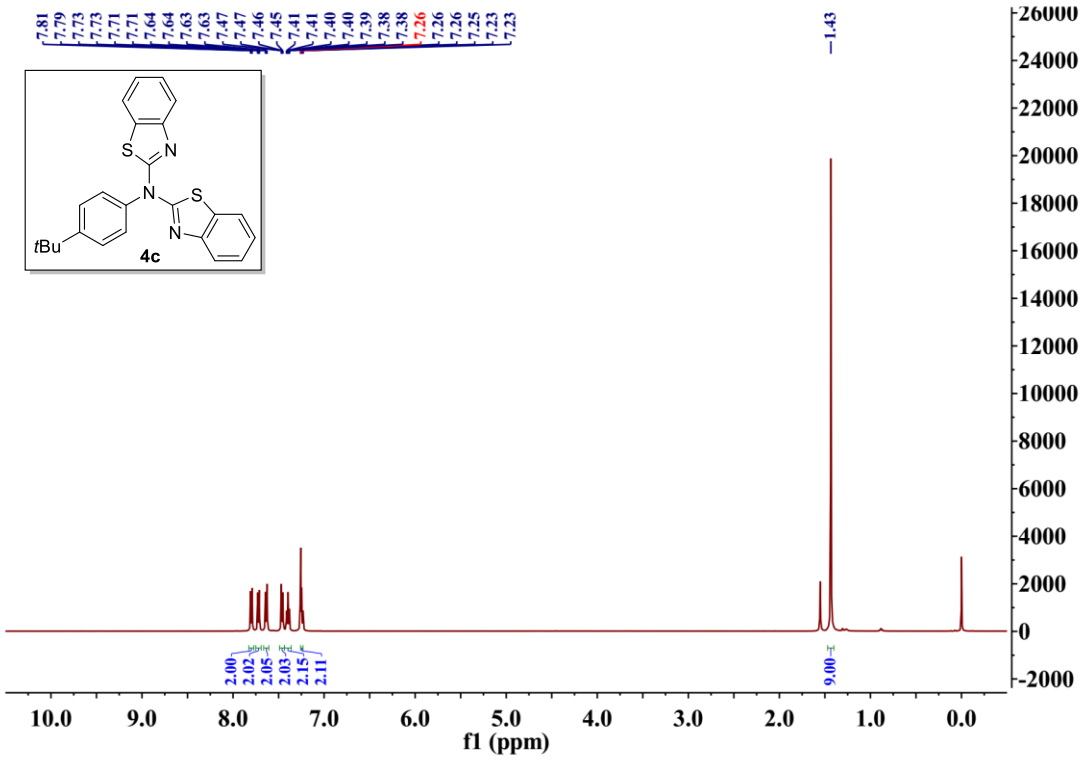
➢ ^{13}C NMR spectrum for **4b**



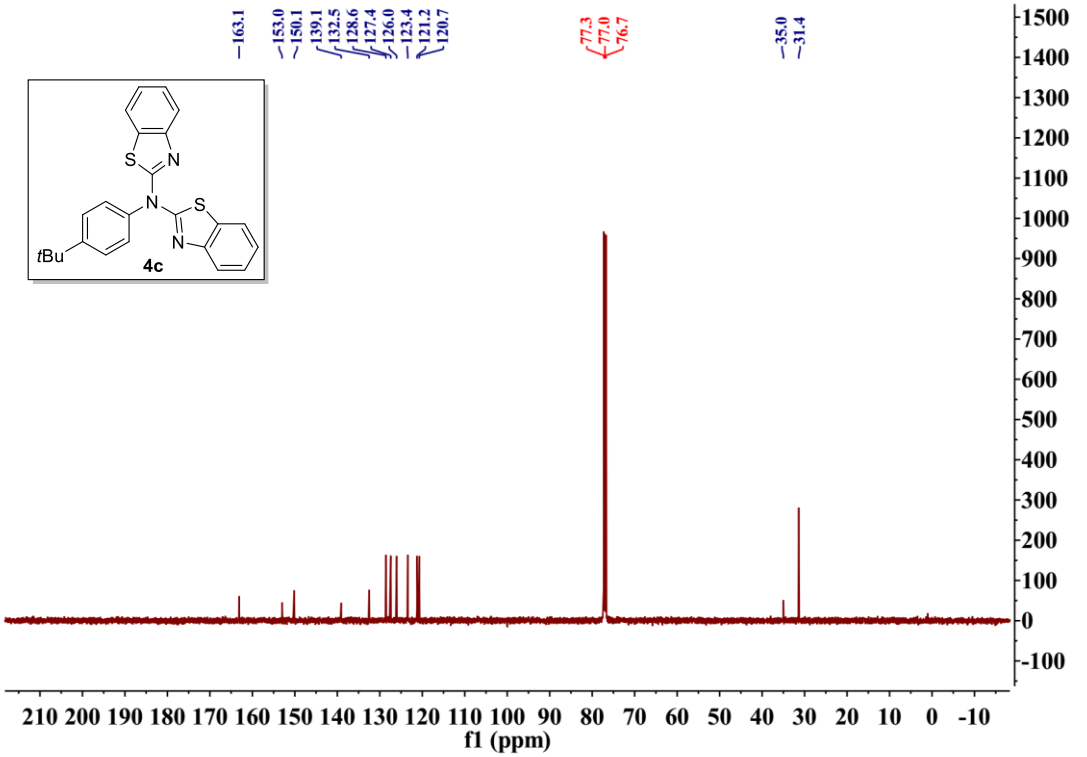
➢ HRMS spectrum for **4b**



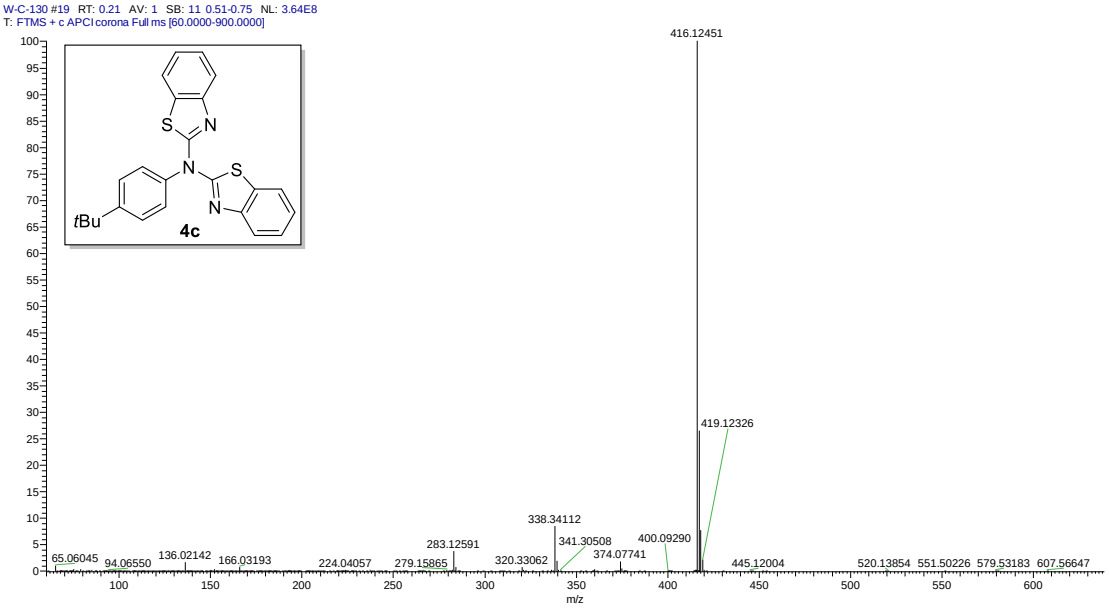
➢ ^{1}H NMR spectrum for **4c**



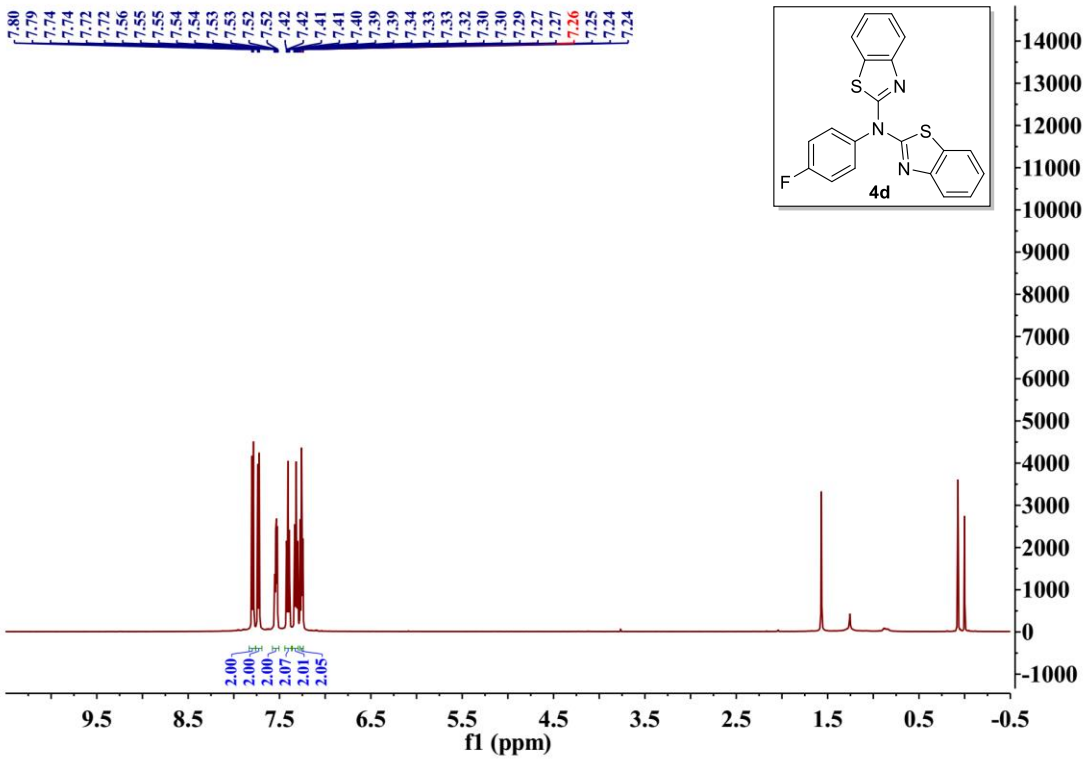
➢ ^{13}C NMR spectrum for **4c**



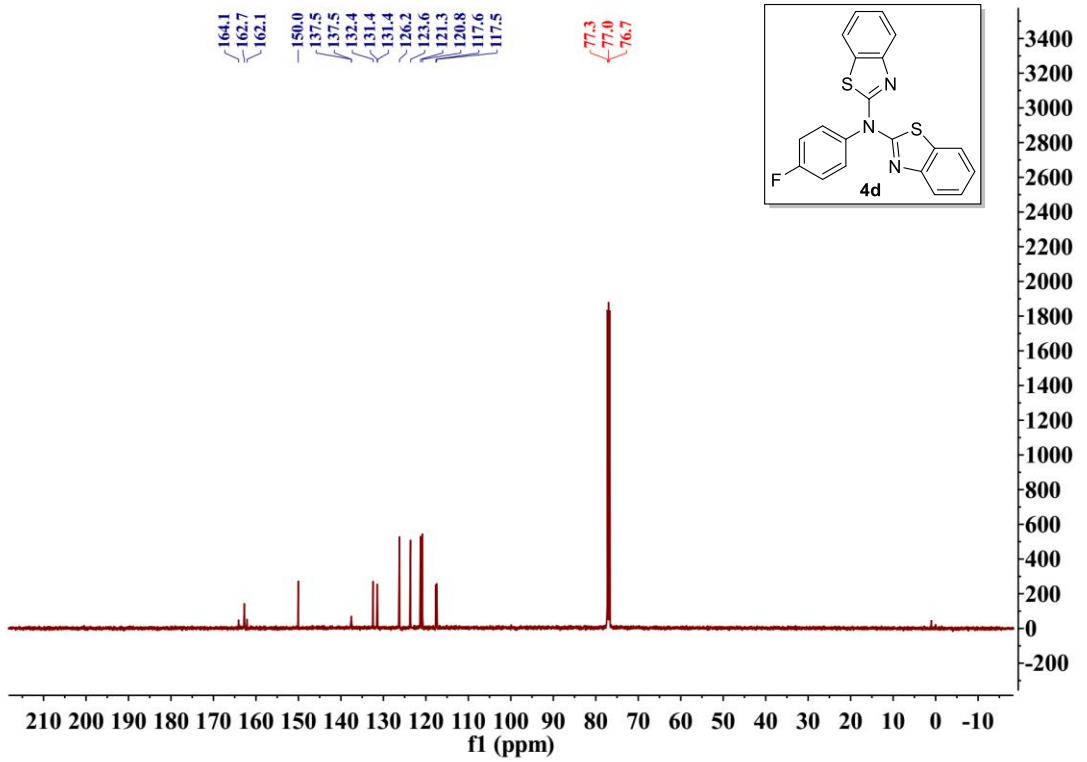
➢ HRMS spectrum for **4c**



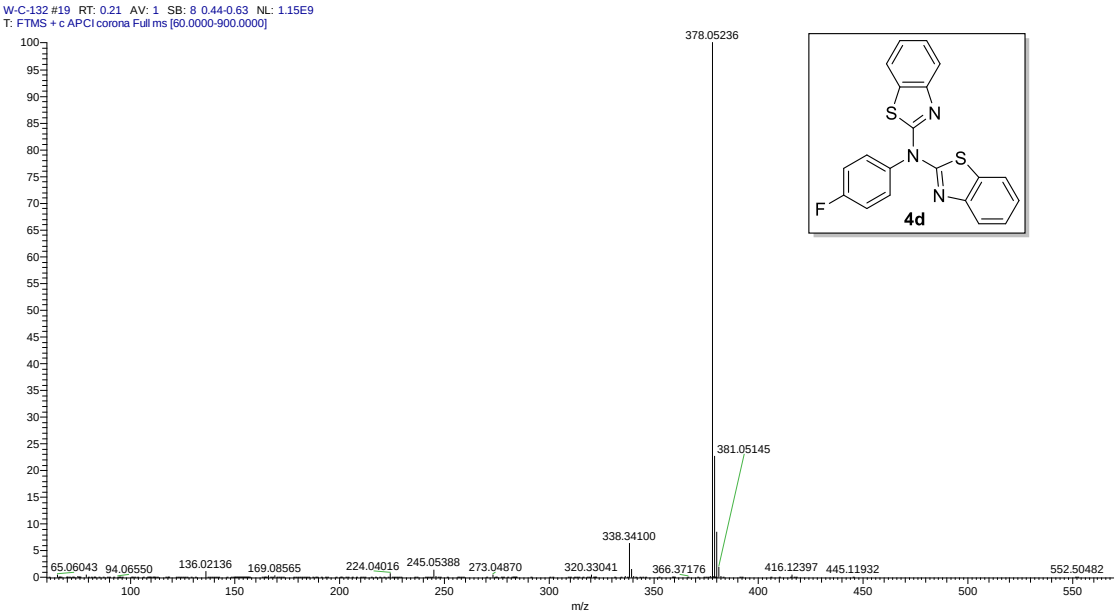
➢ ^{1}H NMR spectrum for **4d**



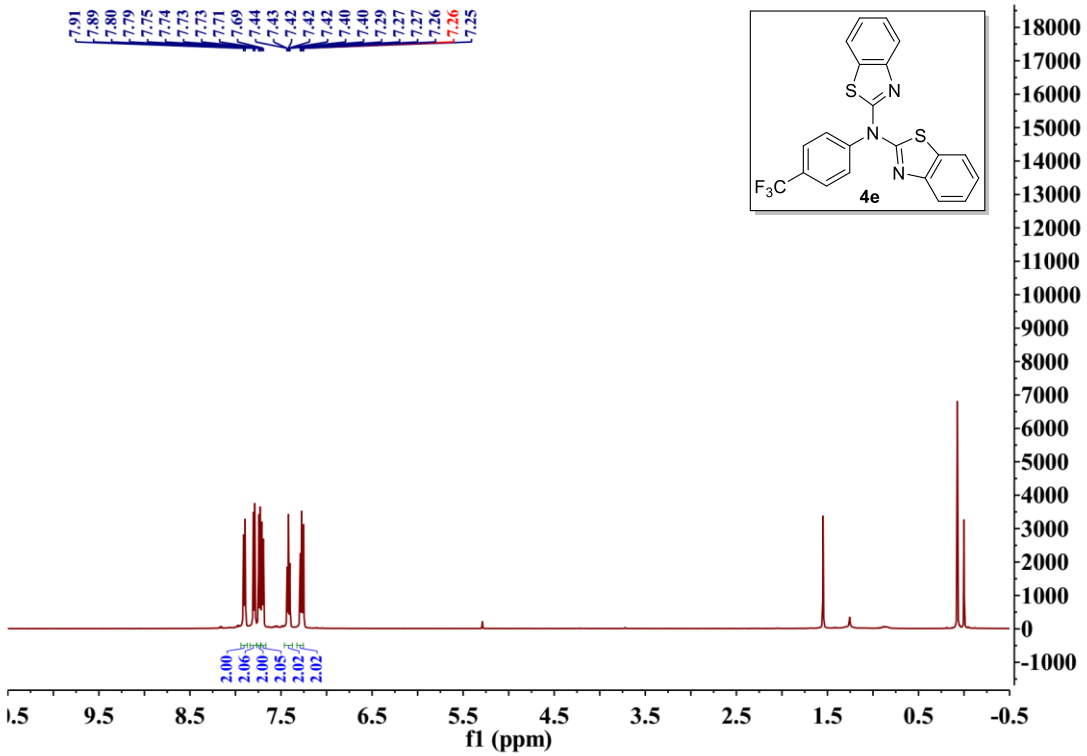
➢ ^{13}C NMR spectrum for **4d**



➢ HRMS spectrum for **4d**



➢ ^{1}H NMR spectrum for **4e**



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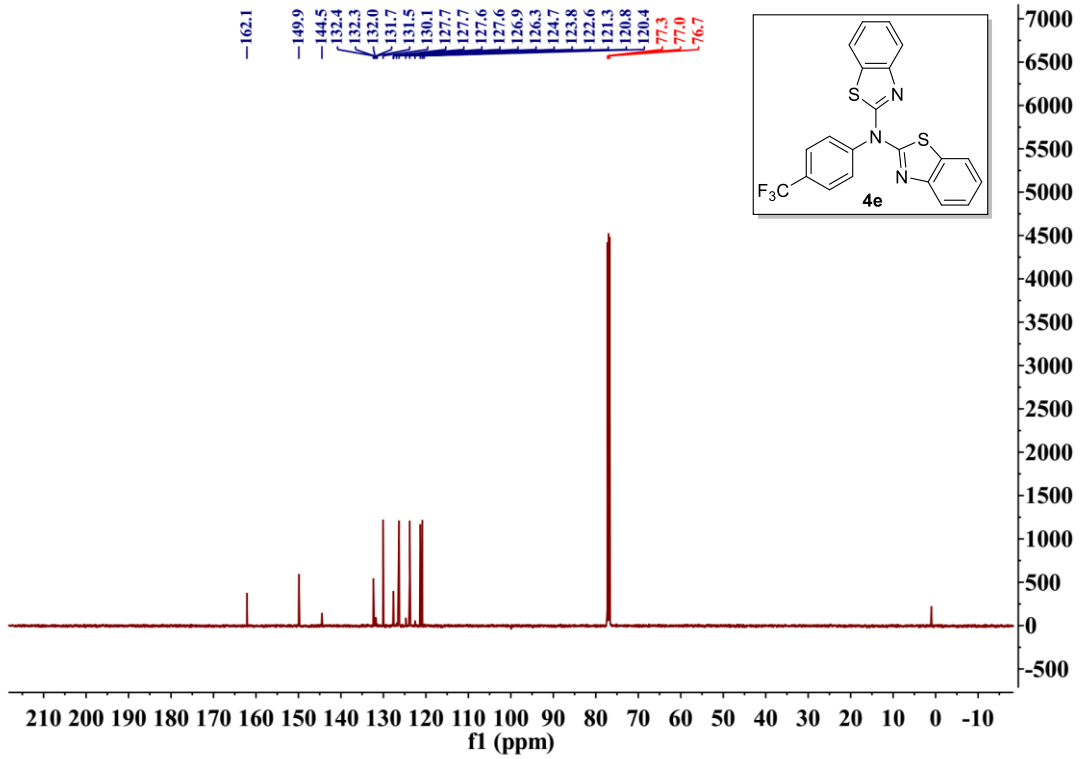

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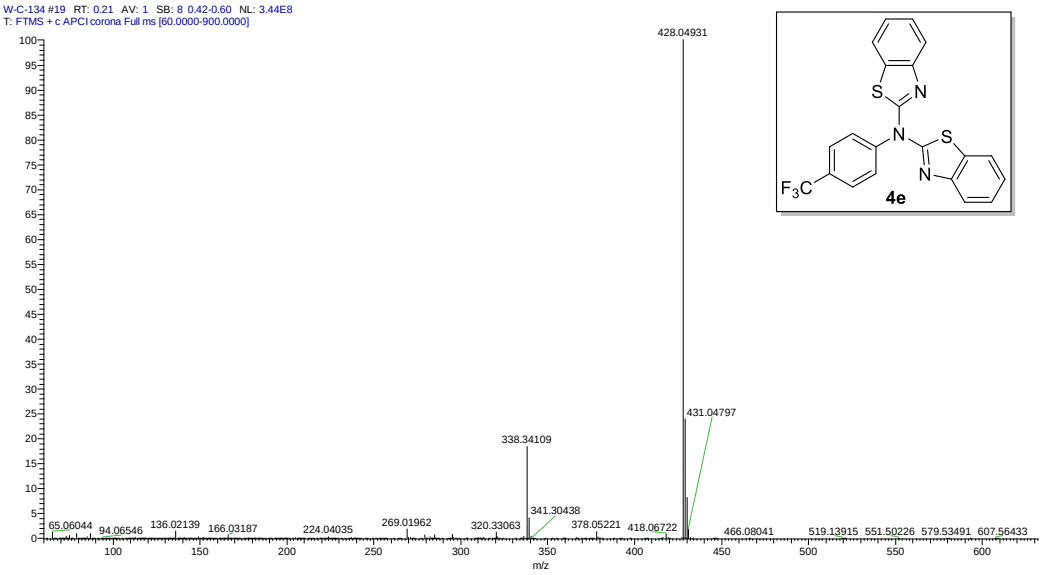
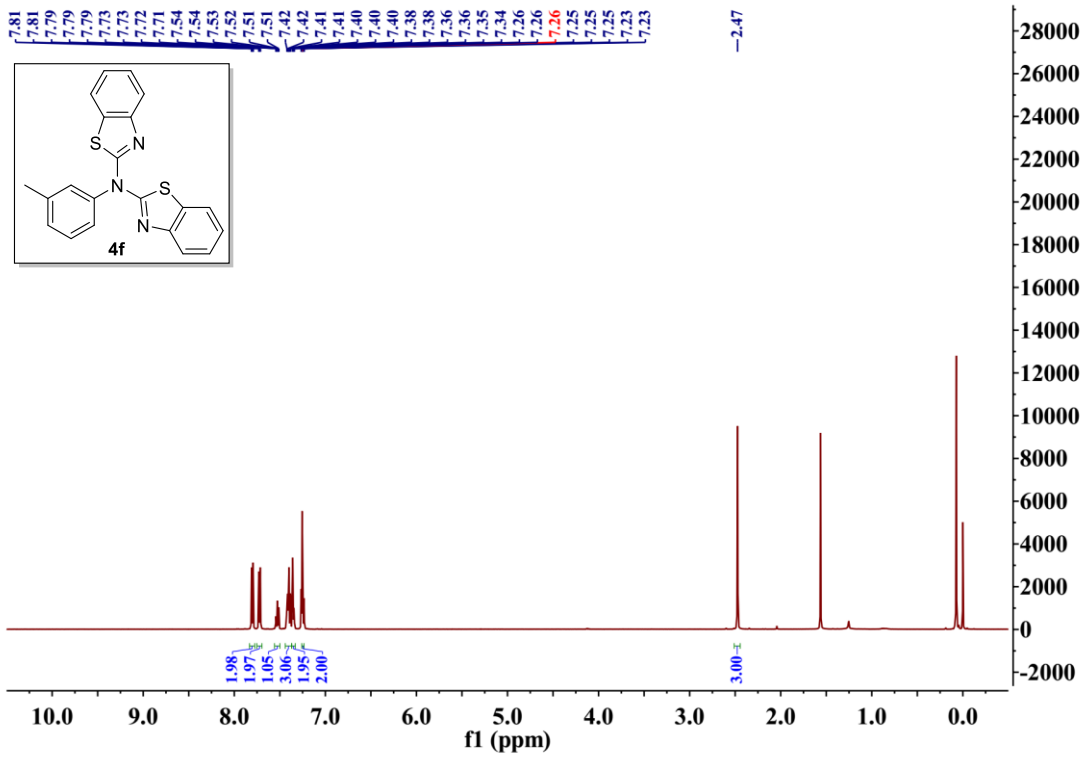
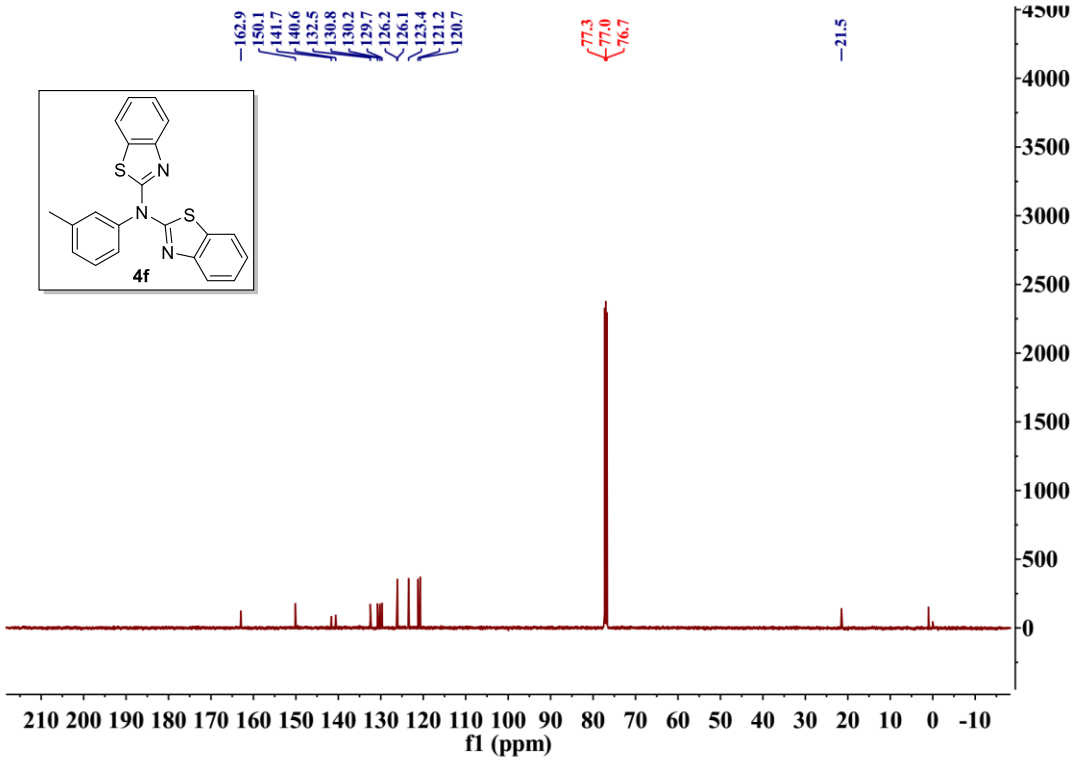


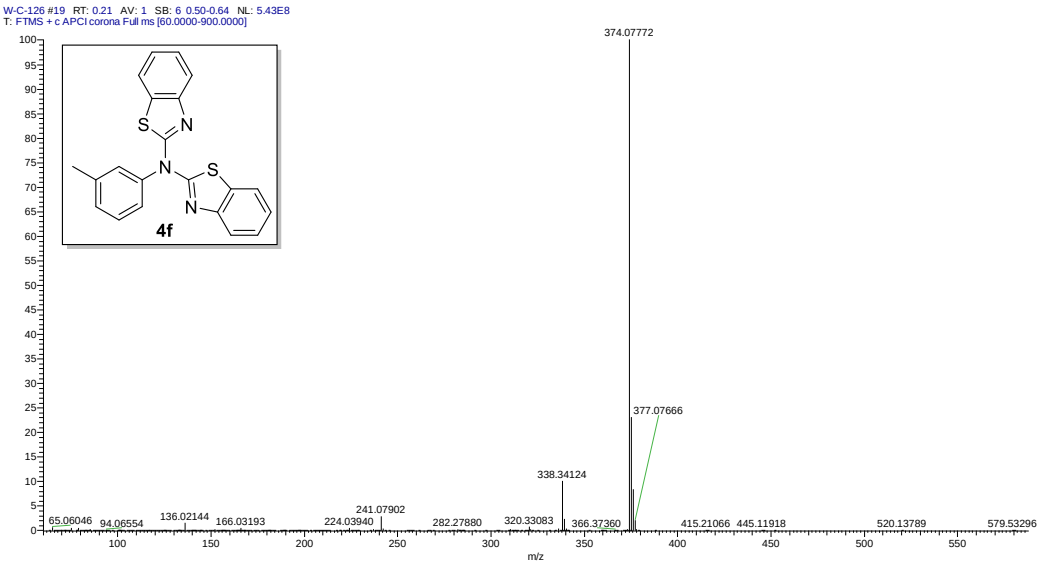
➢ ^{1}H NMR spectrum for **4f**



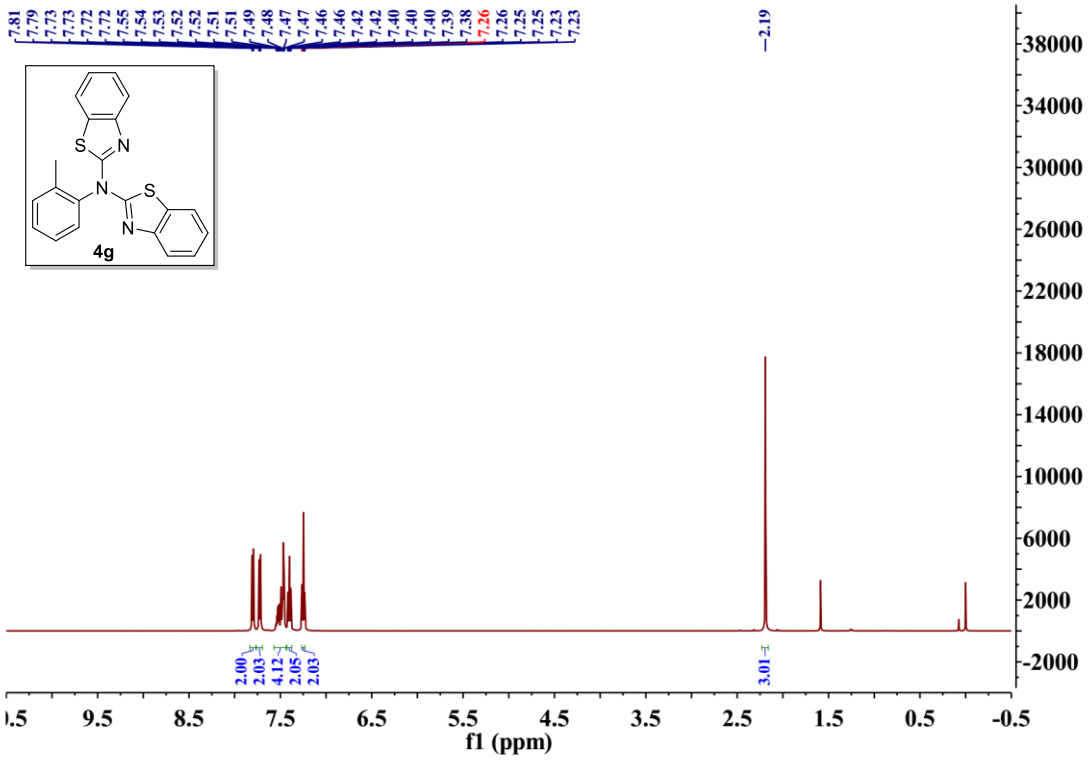
➢ ^{13}C NMR spectrum for **4f**



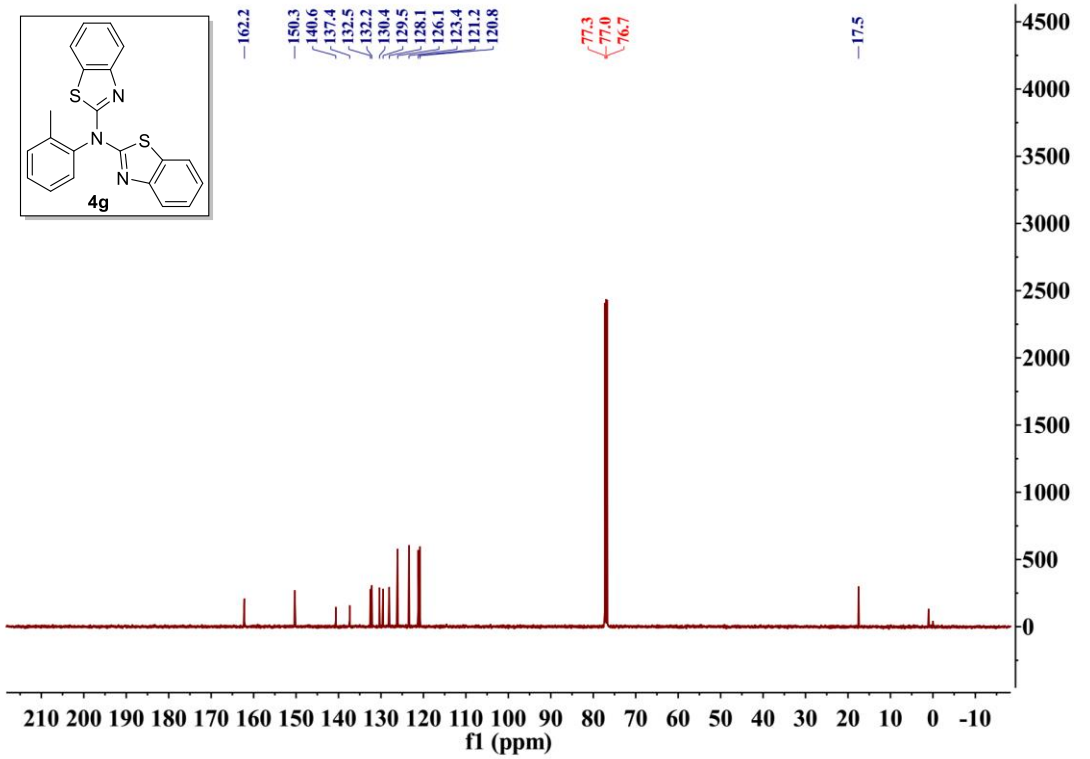
➢ HRMS spectrum for **4f**



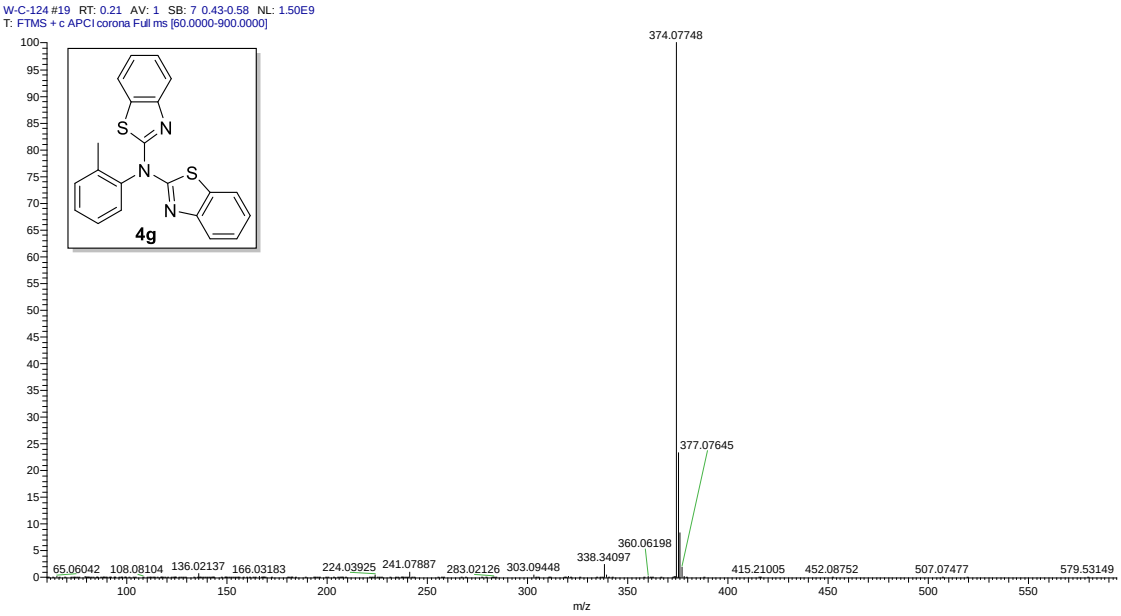
➢ ^{1}H NMR spectrum for **4g**



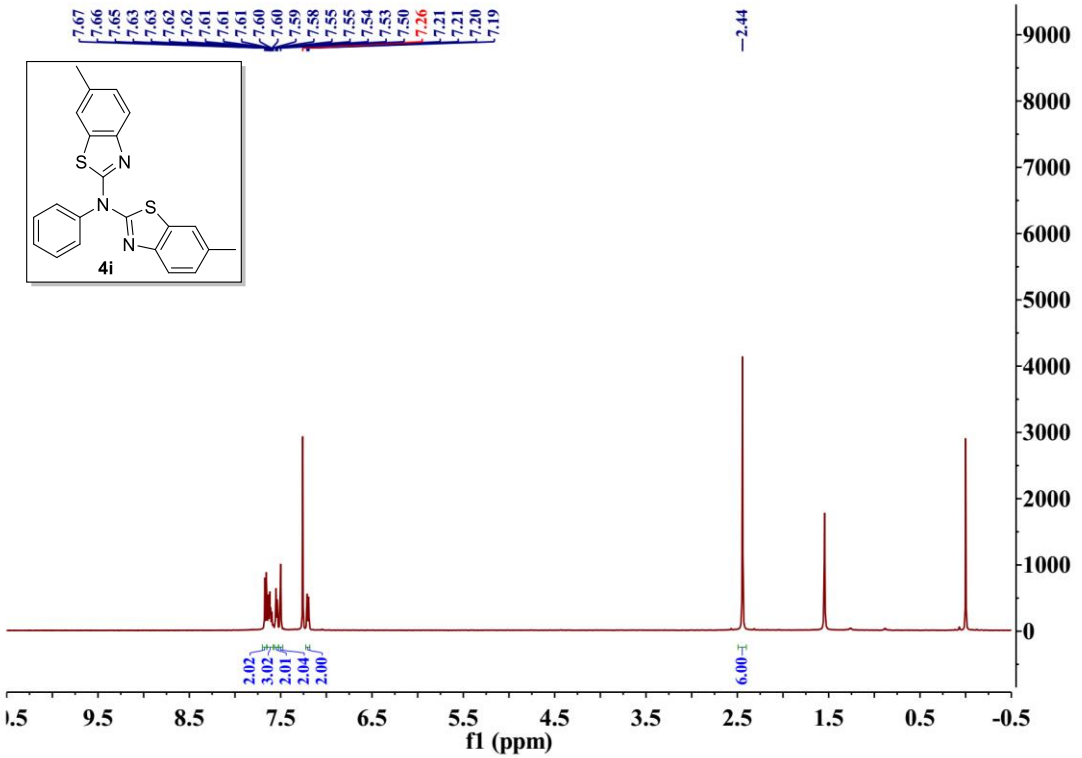
➢ ^{13}C NMR spectrum for **4g**



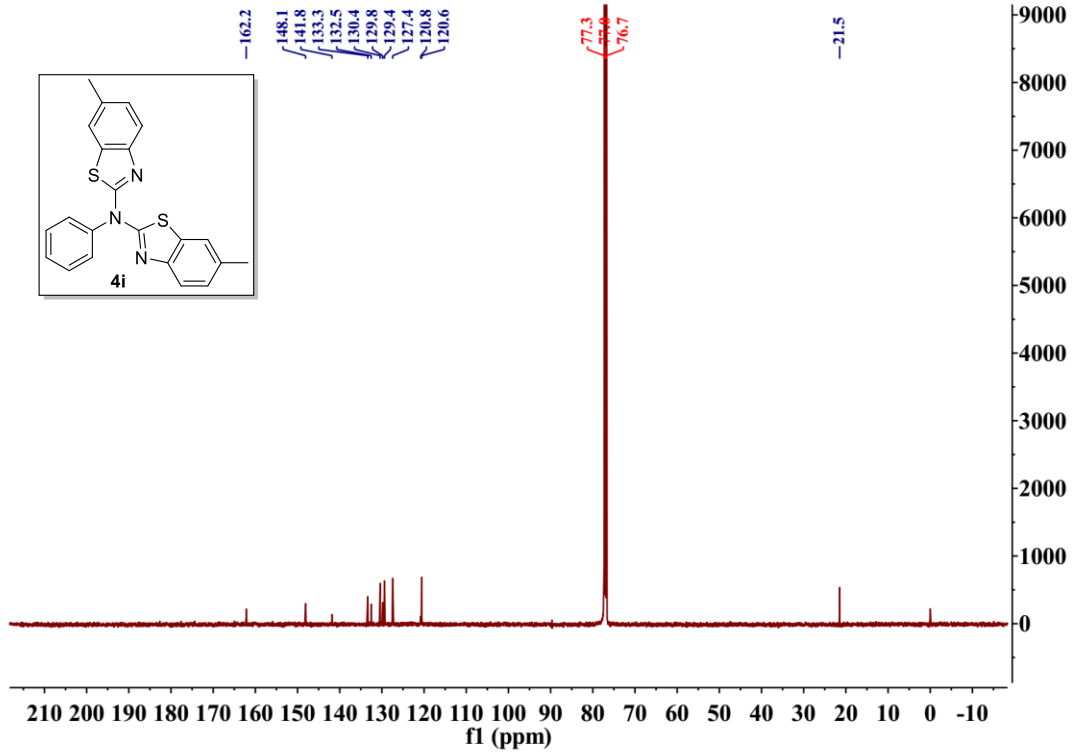
➢ HRMS spectrum for **4g**



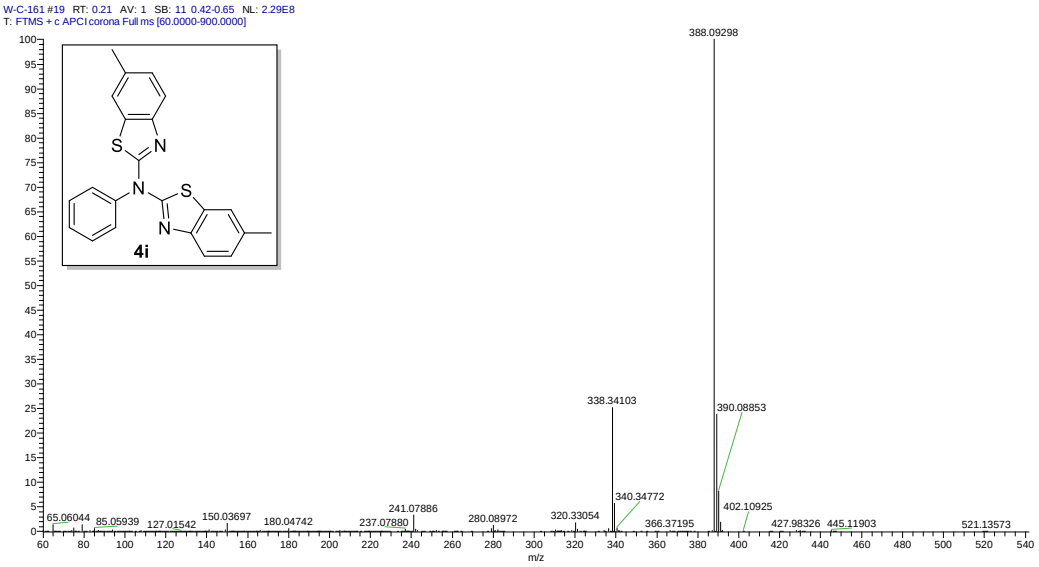
➢ ^{1}H NMR spectrum for **4i**



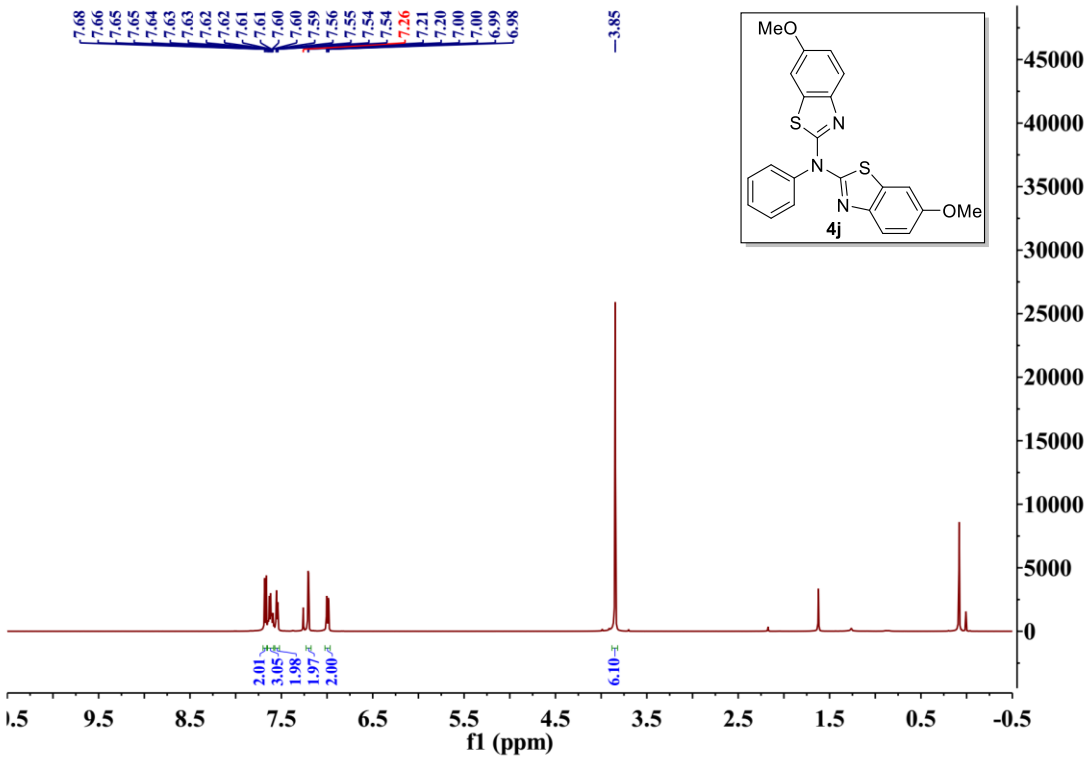
➢ ^{13}C NMR spectrum for **4i**



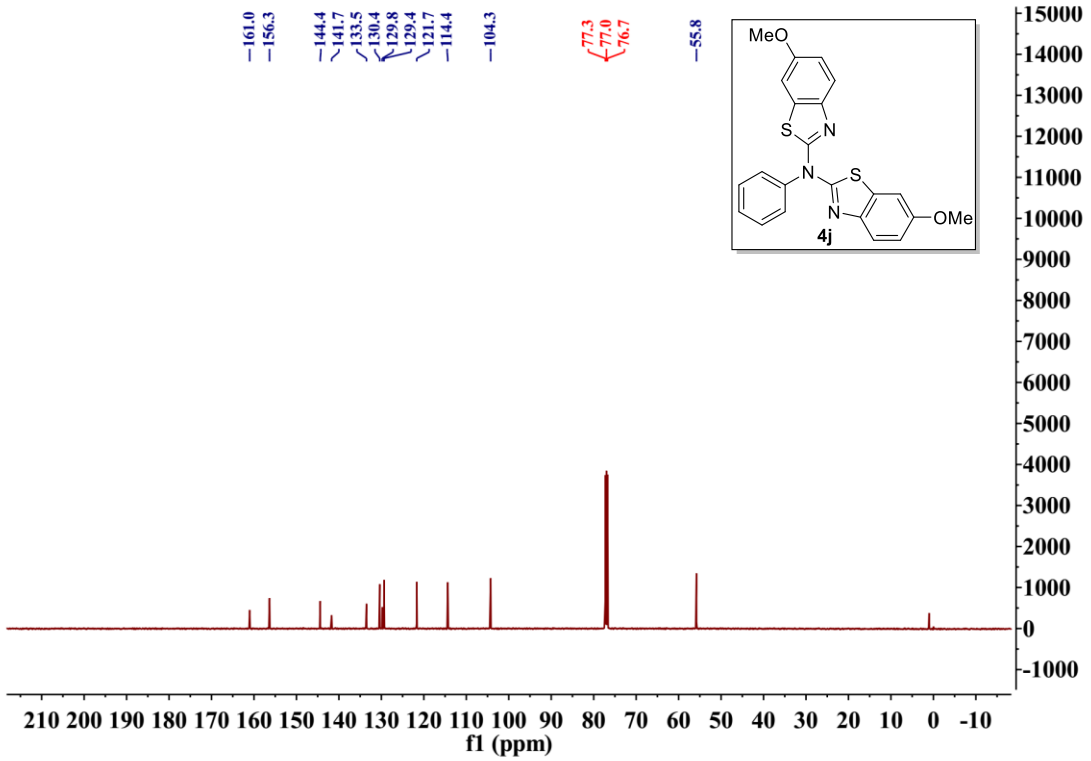
➢ HRMS spectrum for **4i**



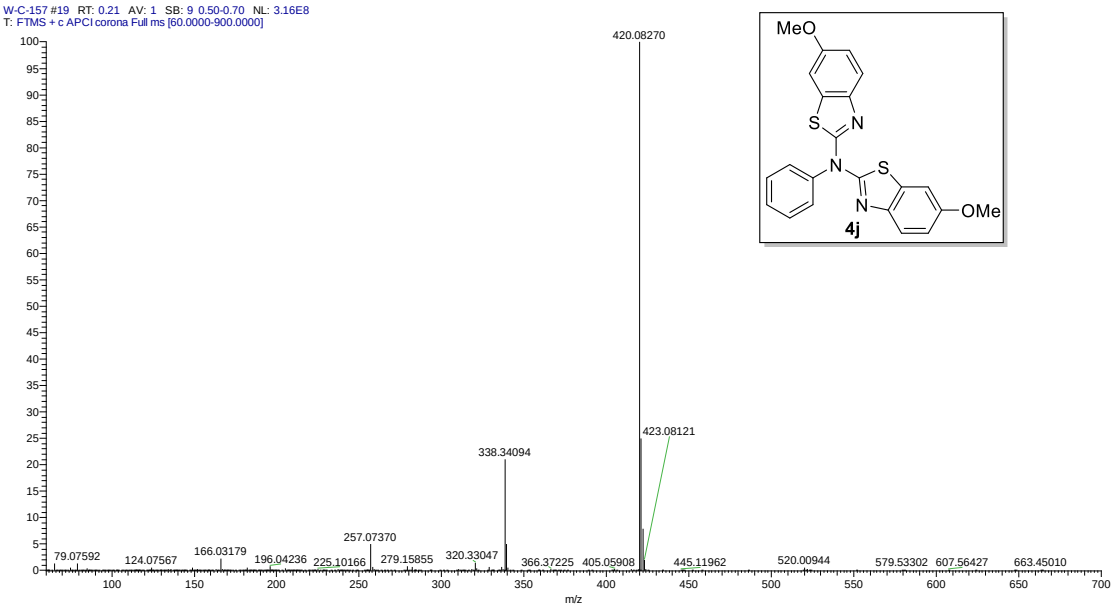
➢ ^{1}H NMR spectrum for **4j**



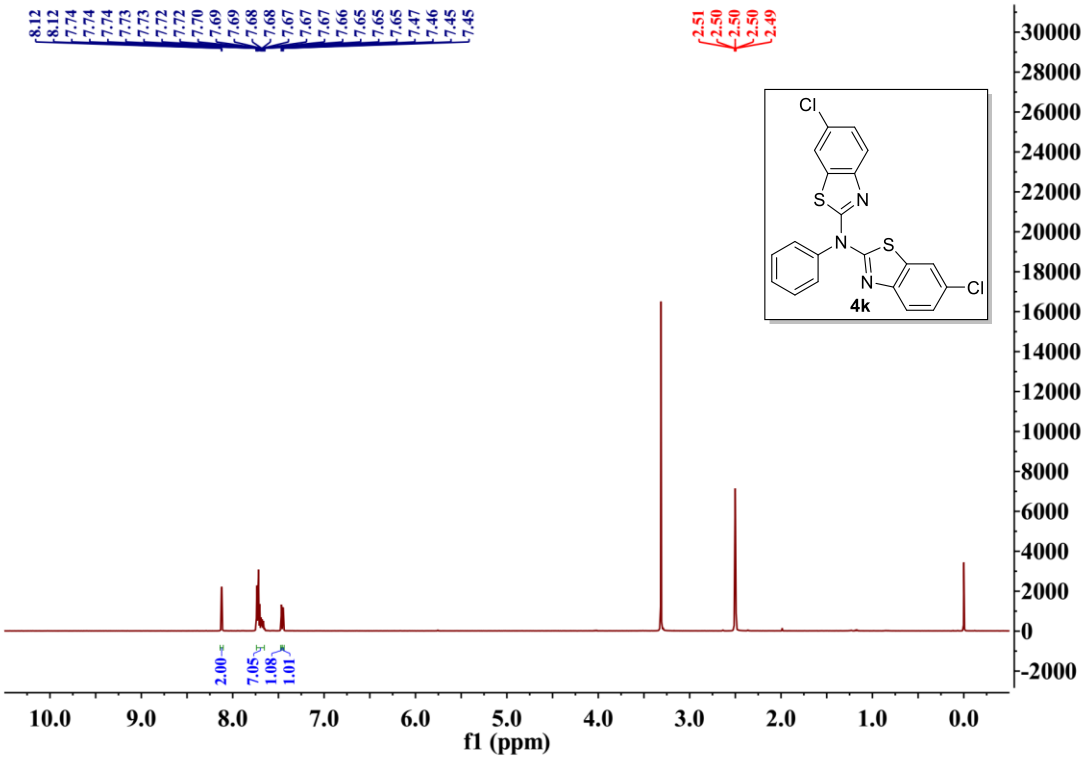
➢ ^{13}C NMR spectrum for **4j**



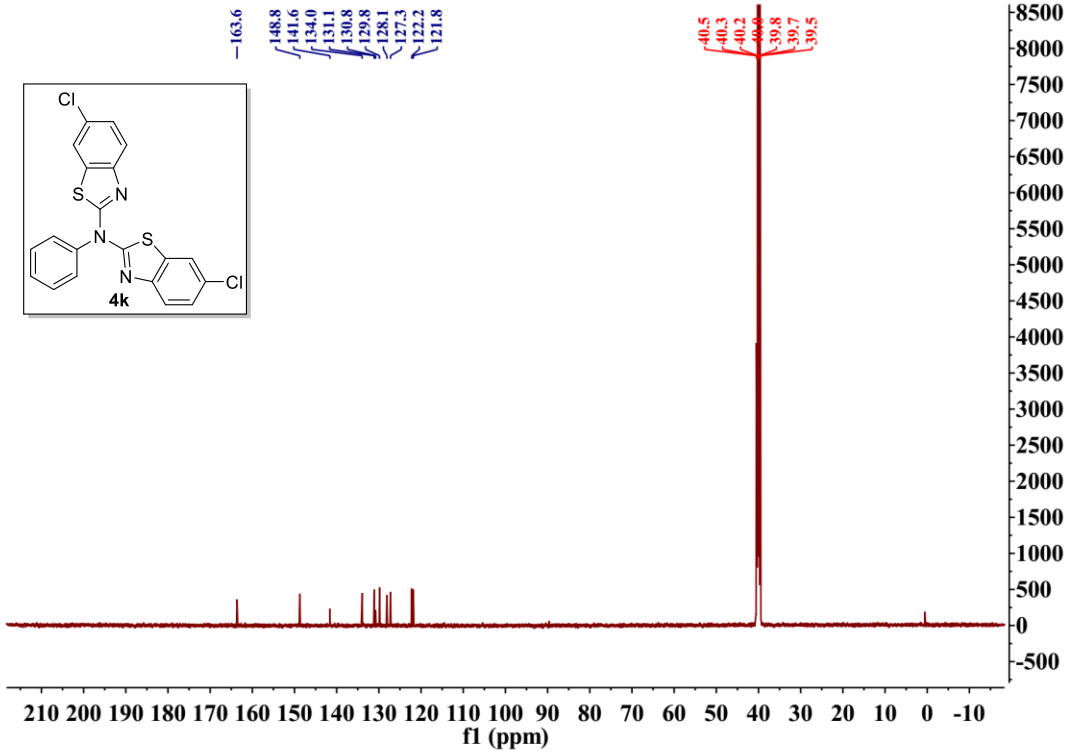
➢ HRMS spectrum for **4j**



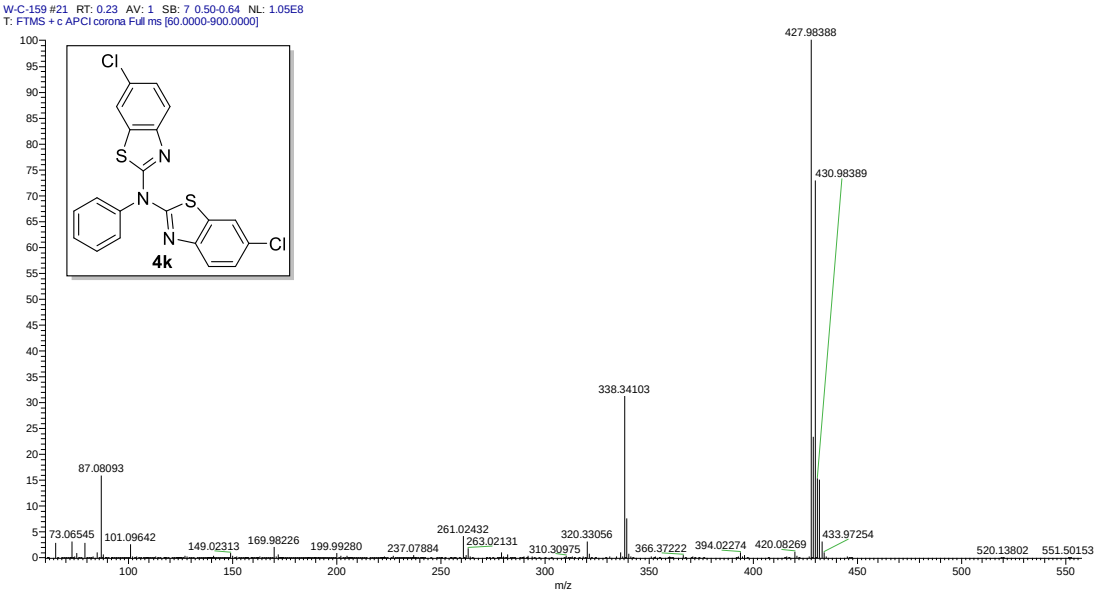
➢ ^{1}H NMR spectrum for **4k**



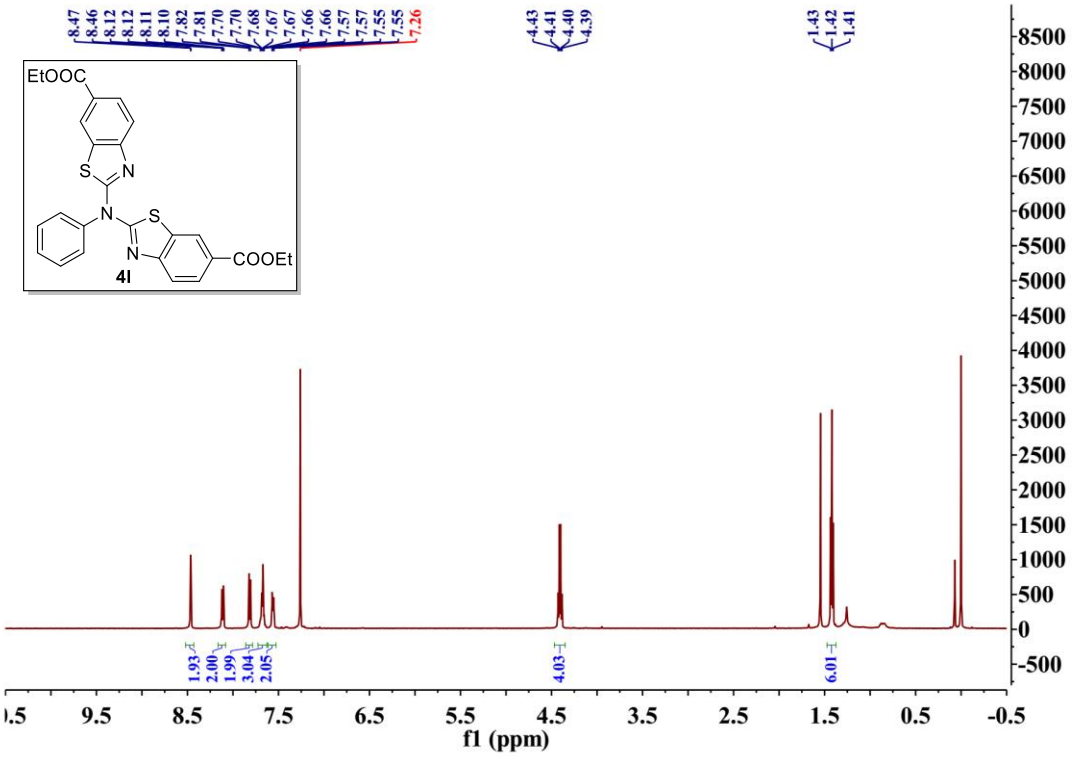
➢ ^{13}C NMR spectrum for **4k**



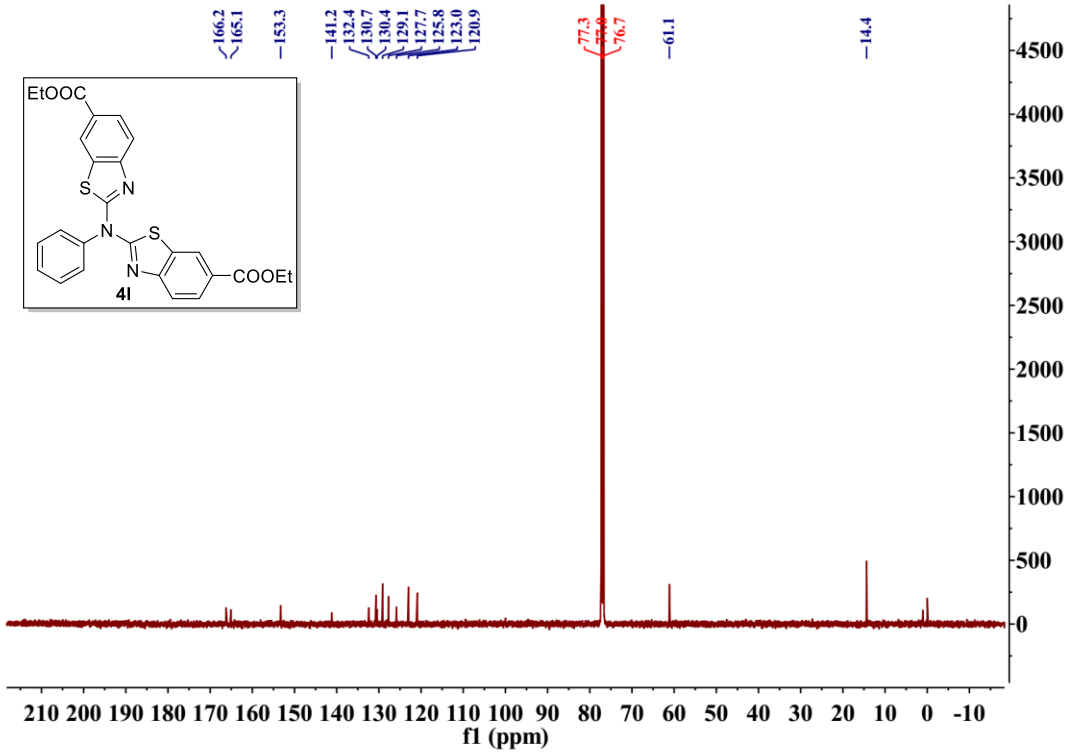
➢ HRMS spectrum for **4k**



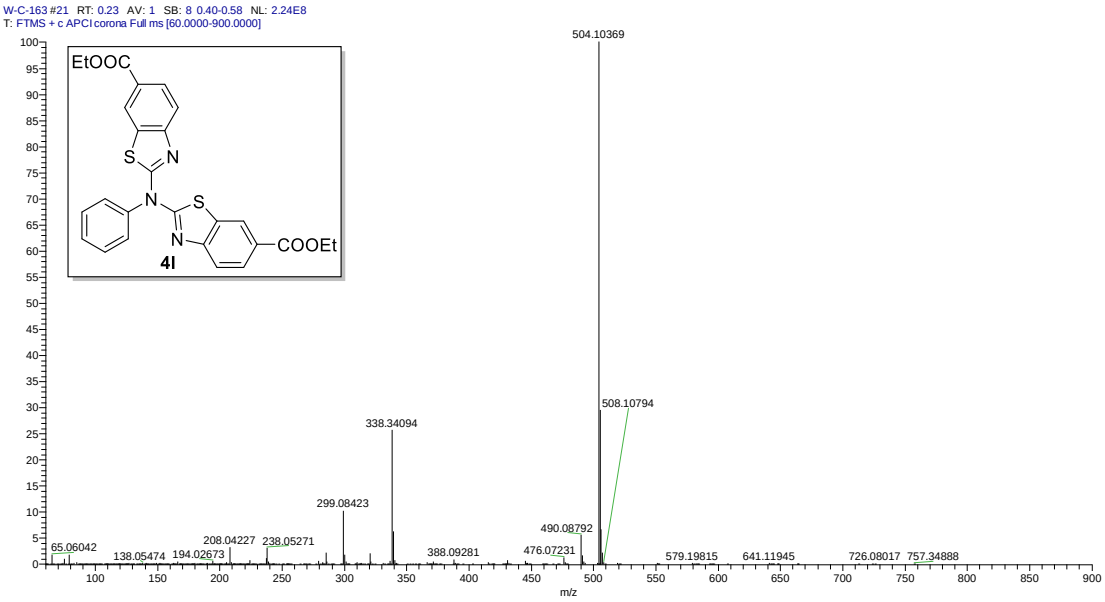
➢ ^{1}H NMR spectrum for **4l**



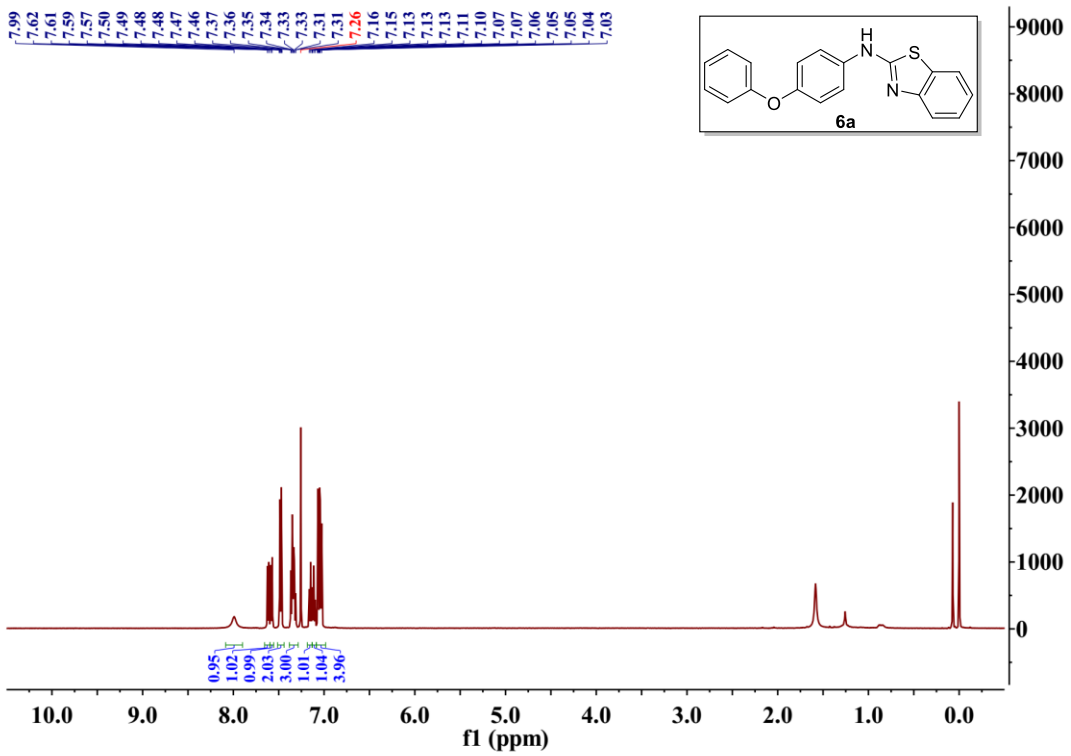
➢ ^{13}C NMR spectrum for **4l**



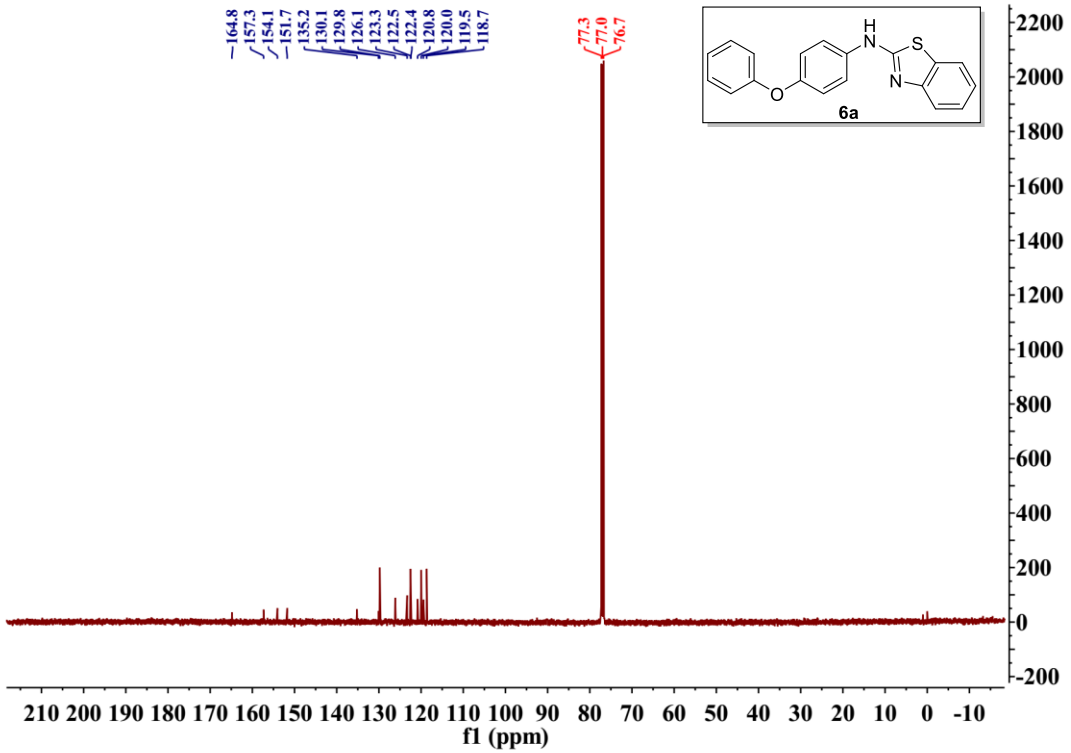
➢ HRMS spectrum for **4l**



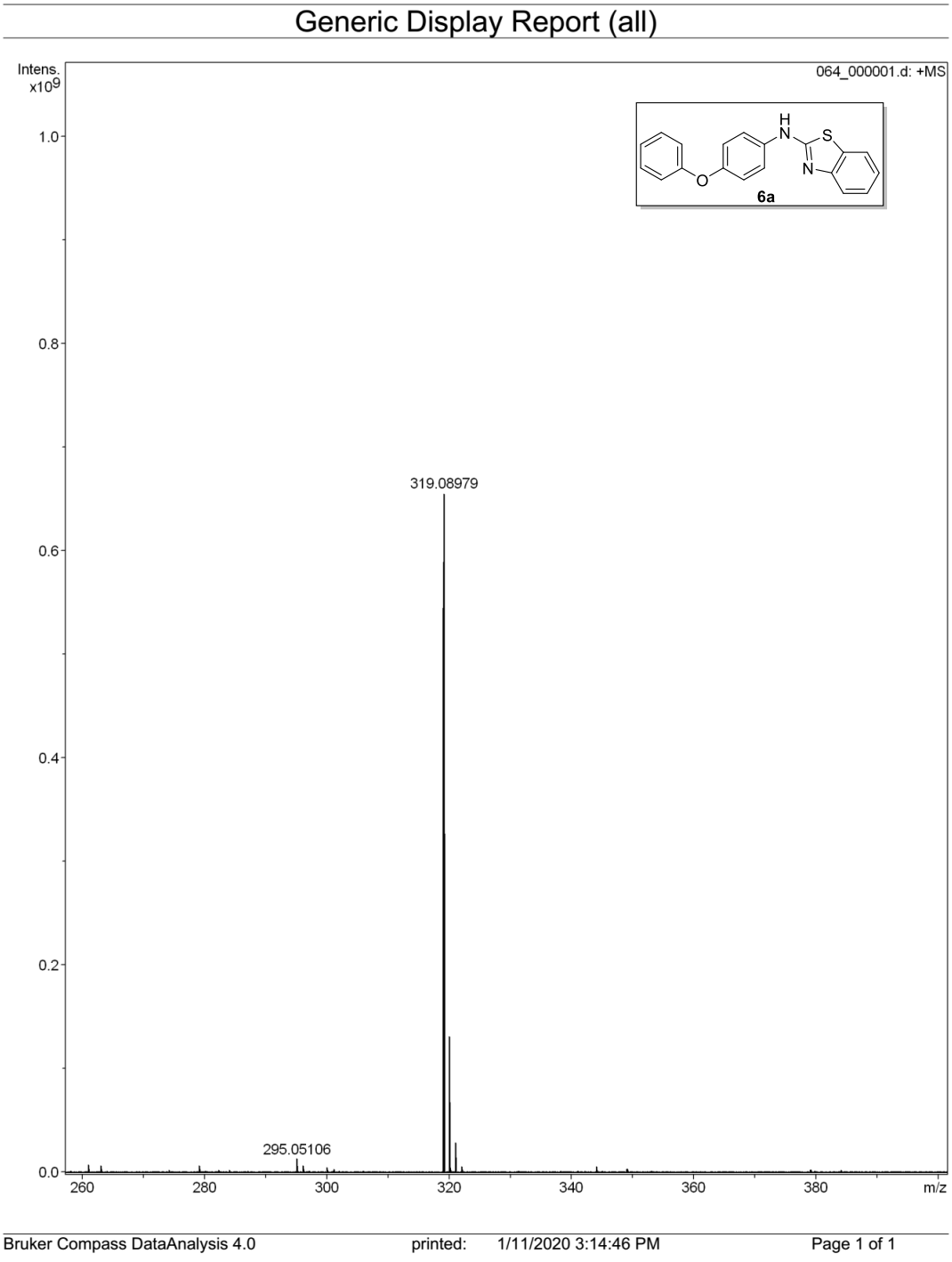
➢ ^{1}H NMR spectrum for **6a**



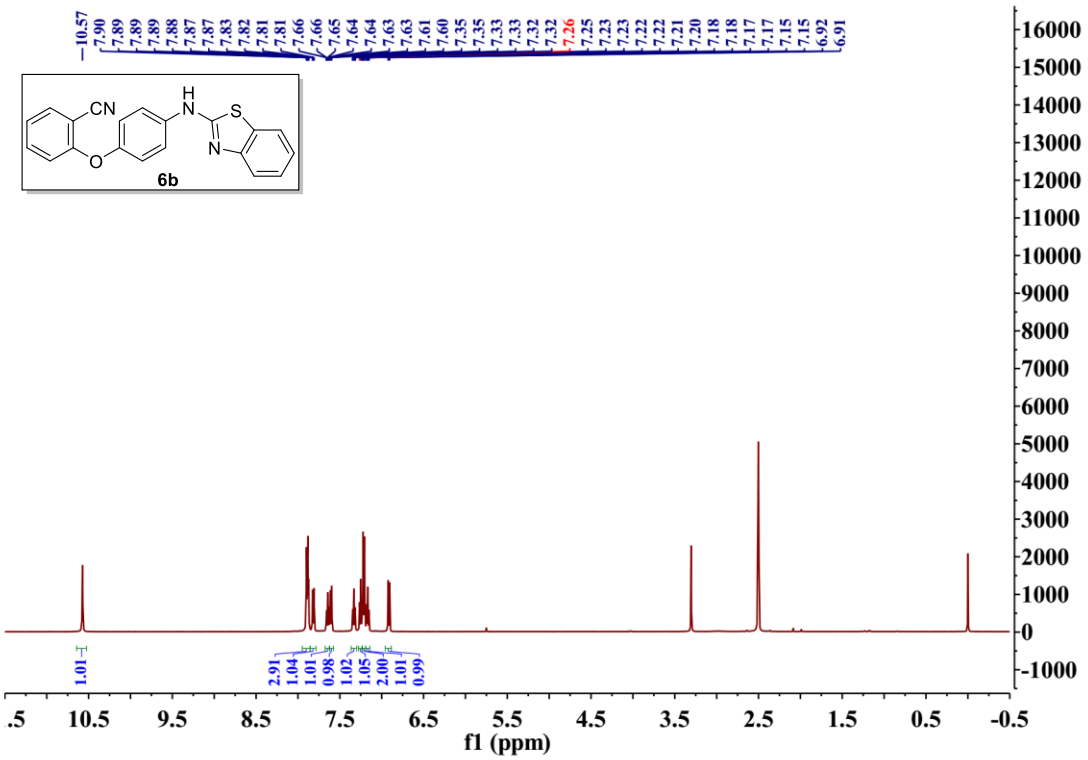
➢ ^{13}C NMR spectrum for **6a**



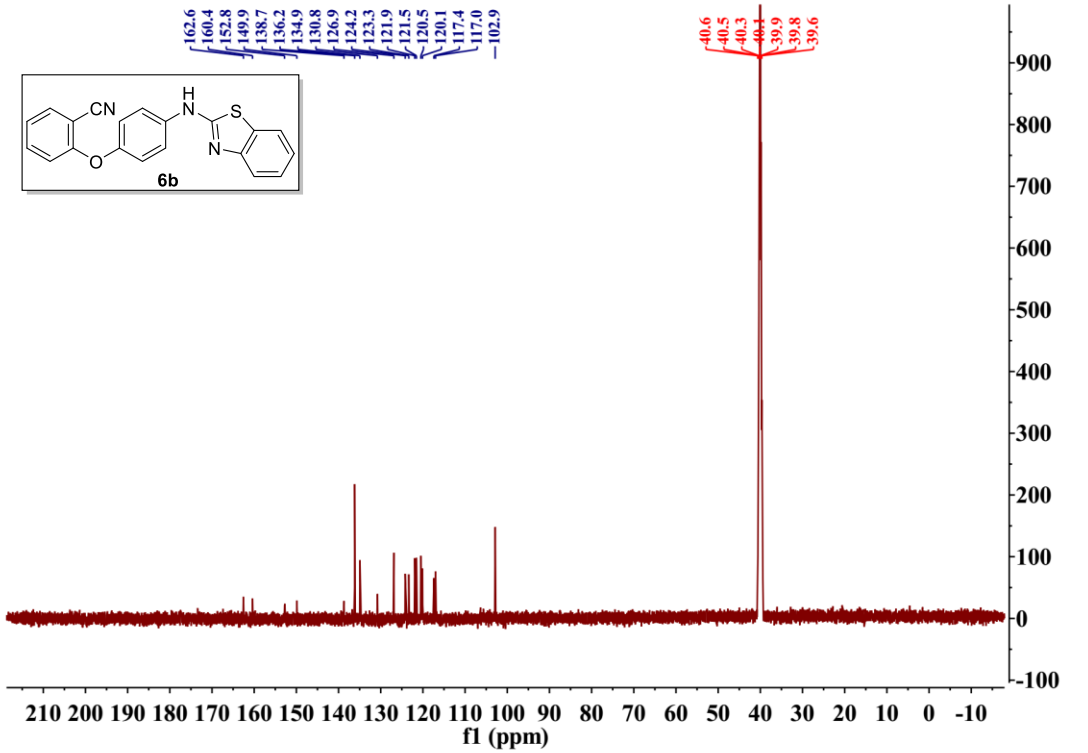
- HRMS spectrum for **6a**



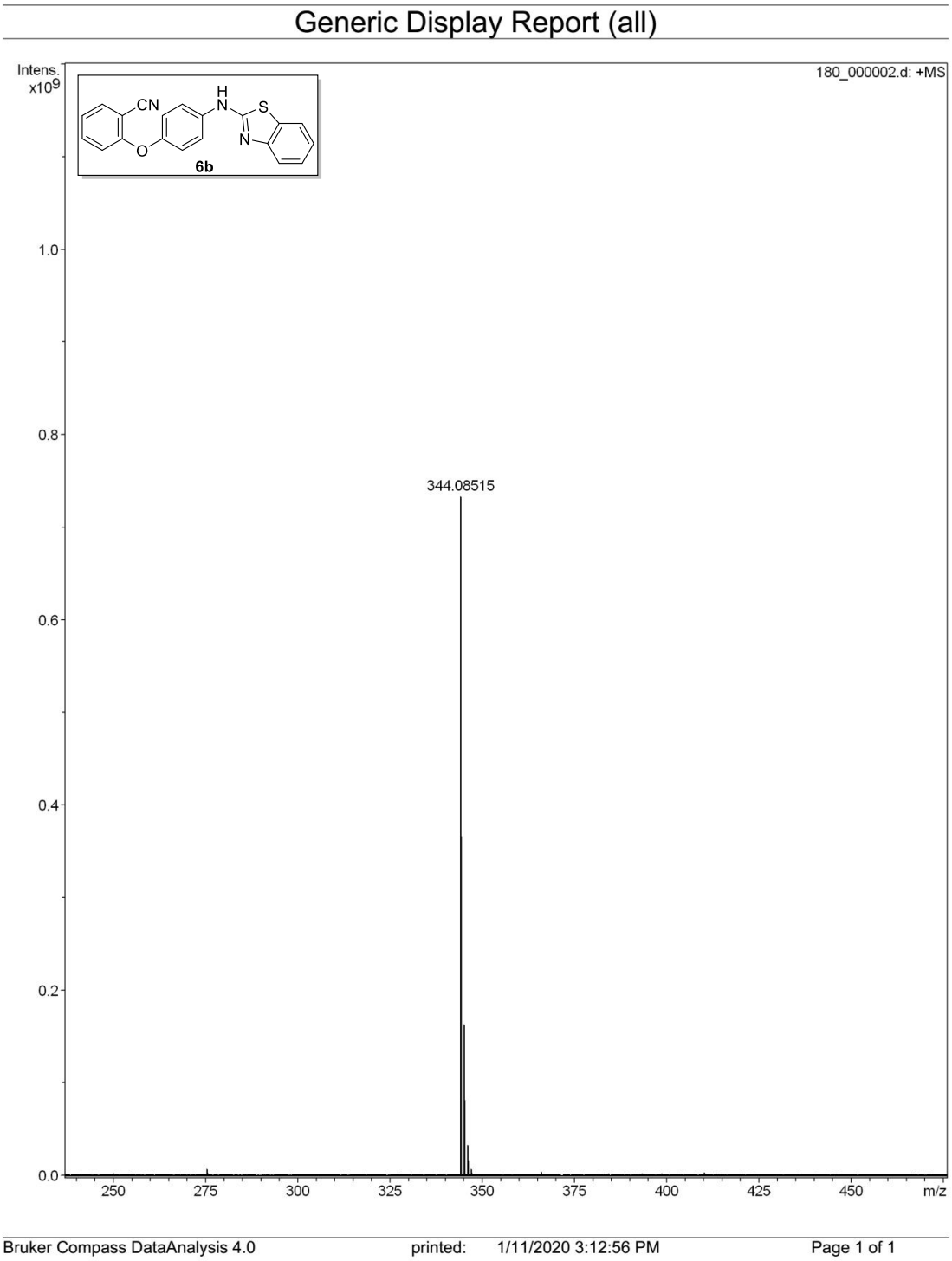
➢ ^{1}H NMR spectrum for **6b**



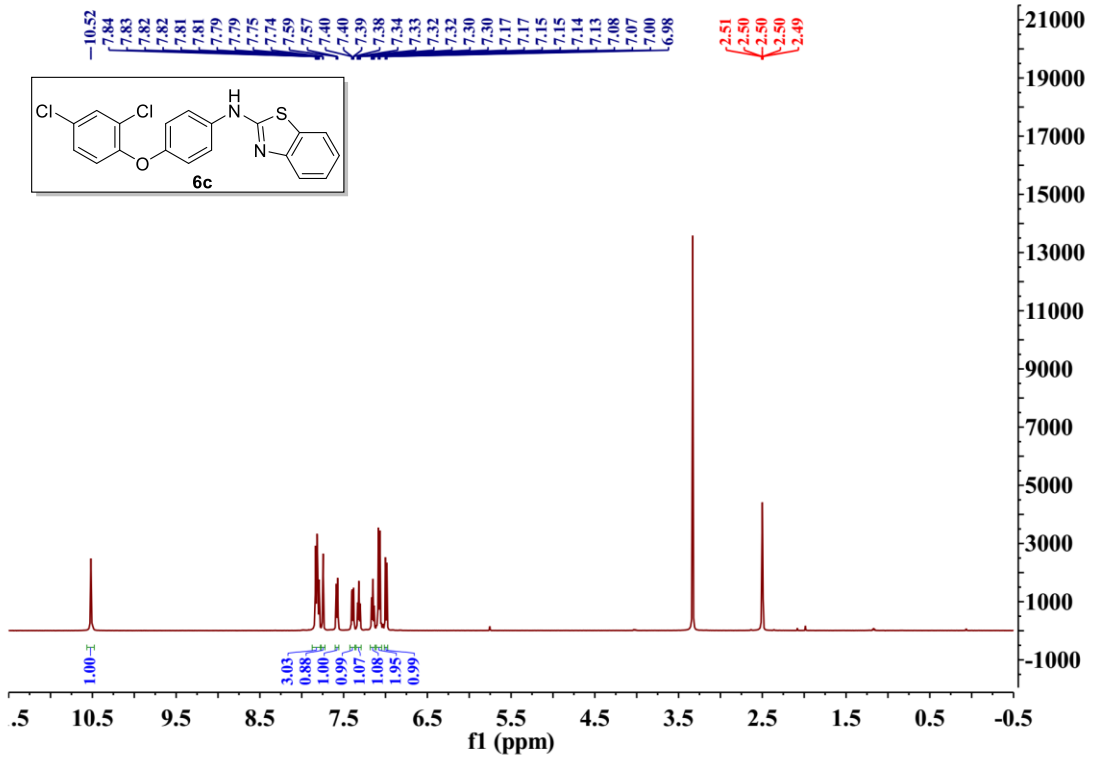
➢ ^{13}C NMR spectrum for **6b**



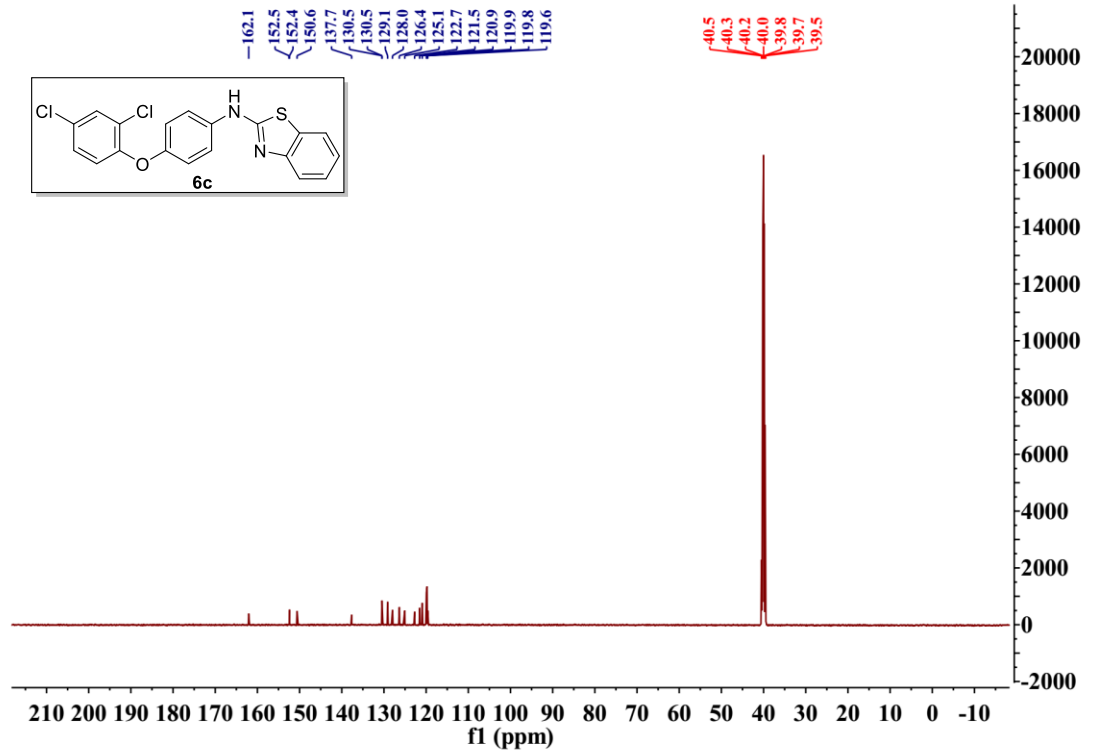
- HRMS spectrum for **6b**



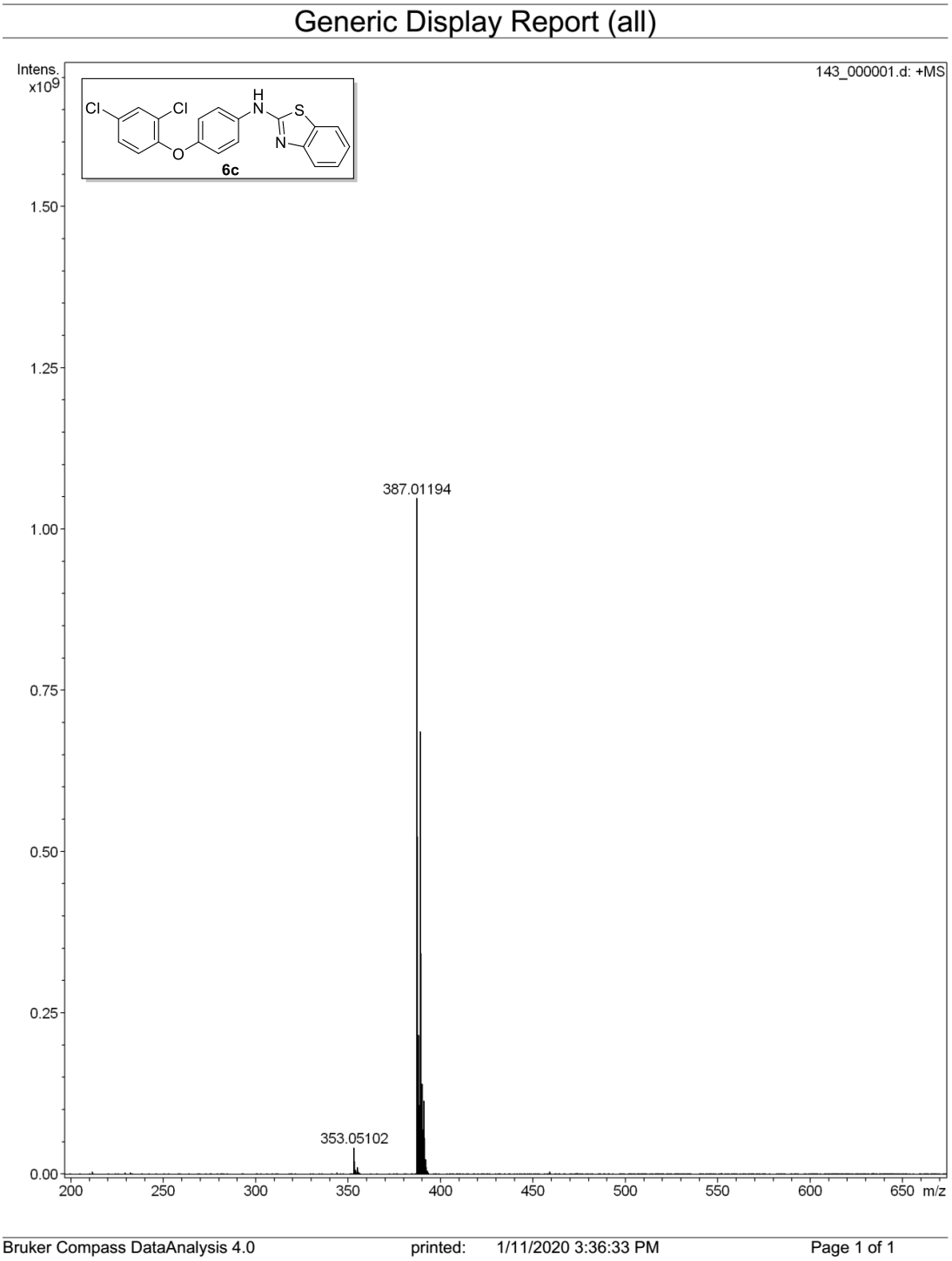
➢ ^{1}H NMR spectrum for **6c**



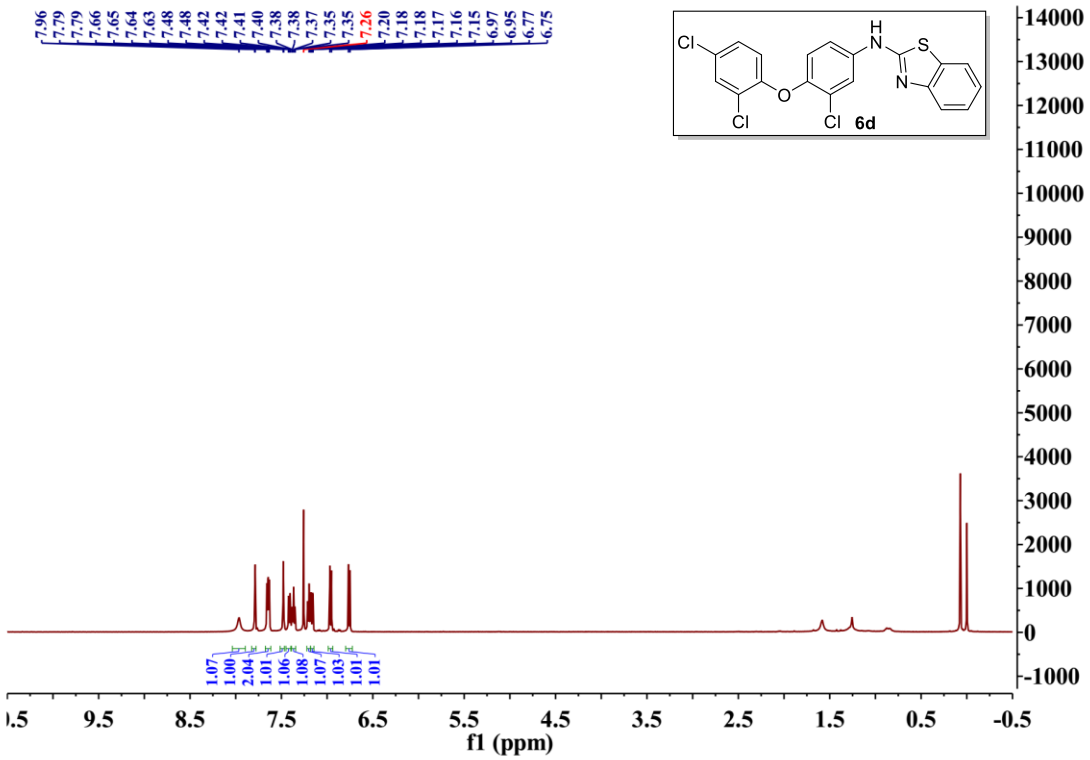
➢ ^{13}C NMR spectrum for **6c**



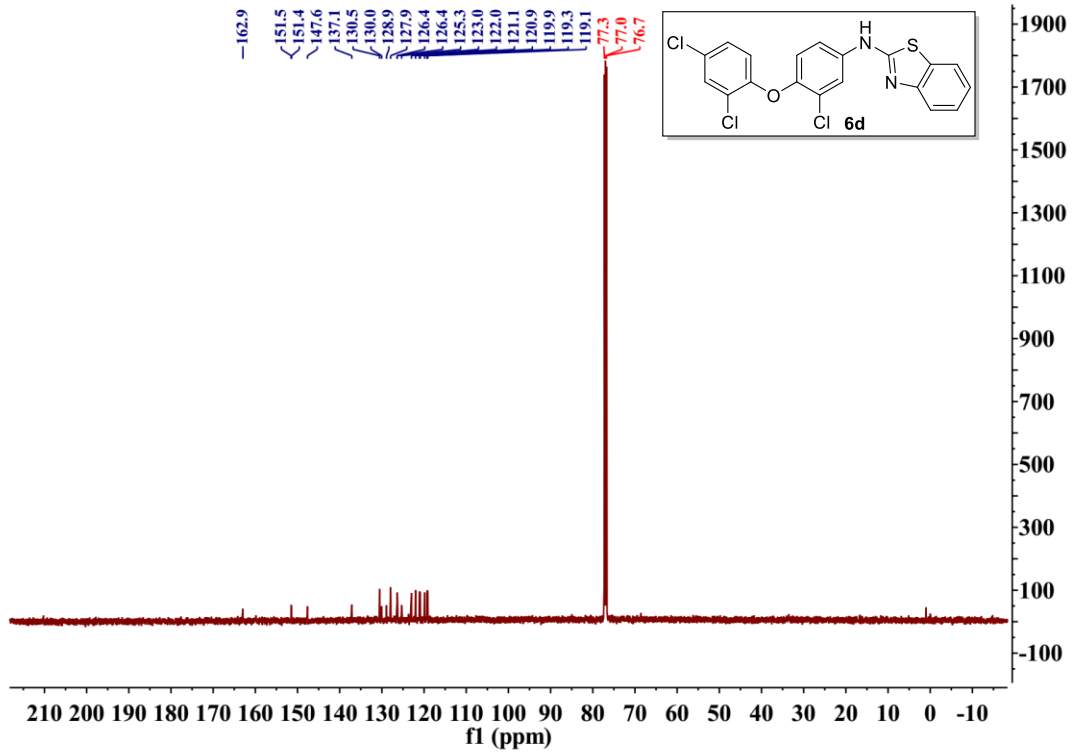
- HRMS spectrum for **6c**



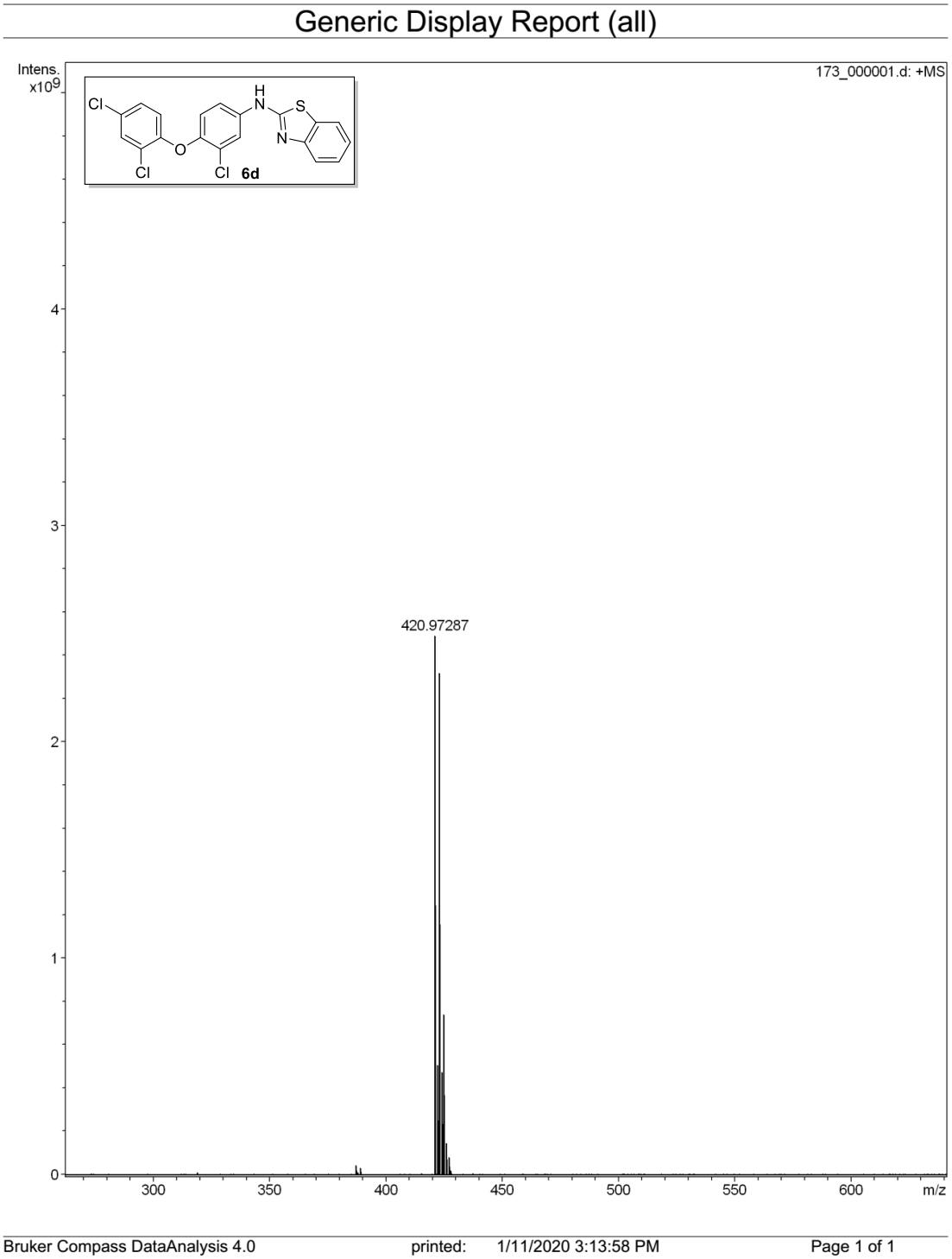
➢ ^{1}H NMR spectrum for **6d**



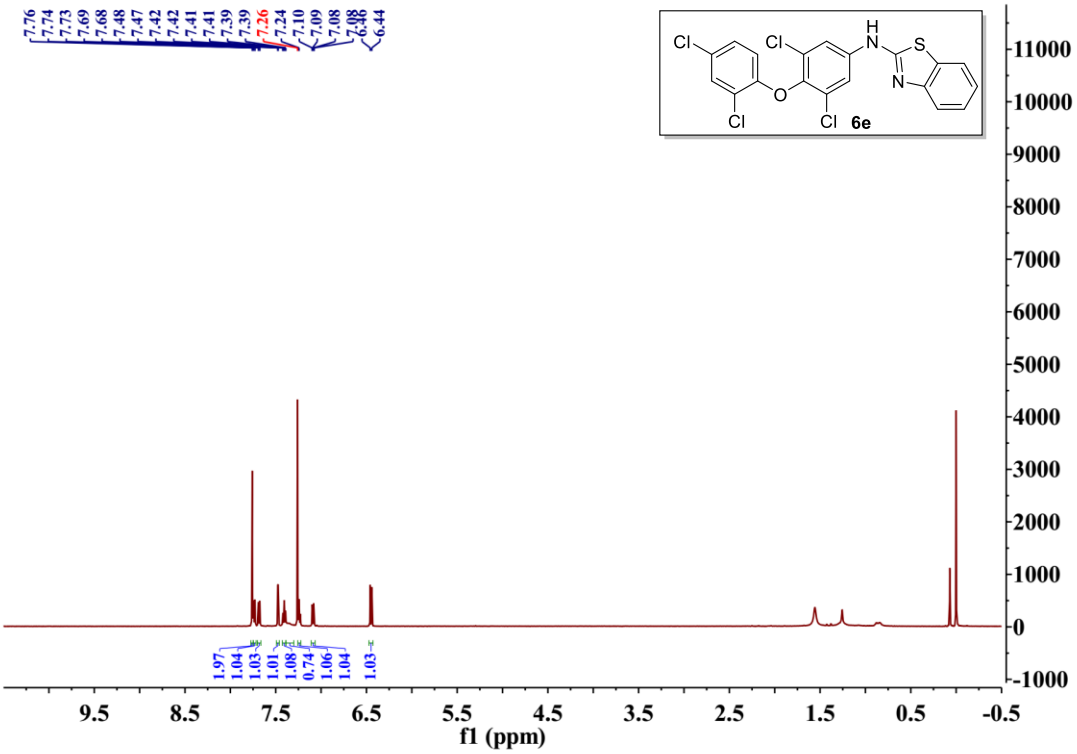
➢ ^{13}C NMR spectrum for **6d**



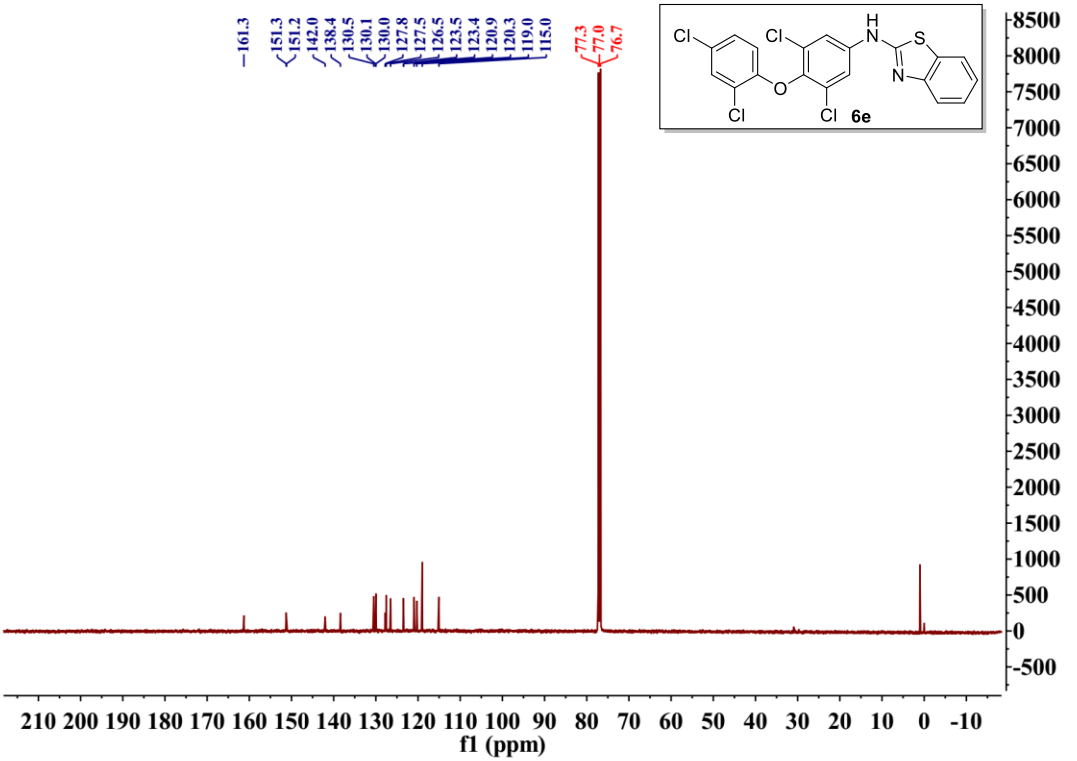
➢ HRMS spectrum for **6d**



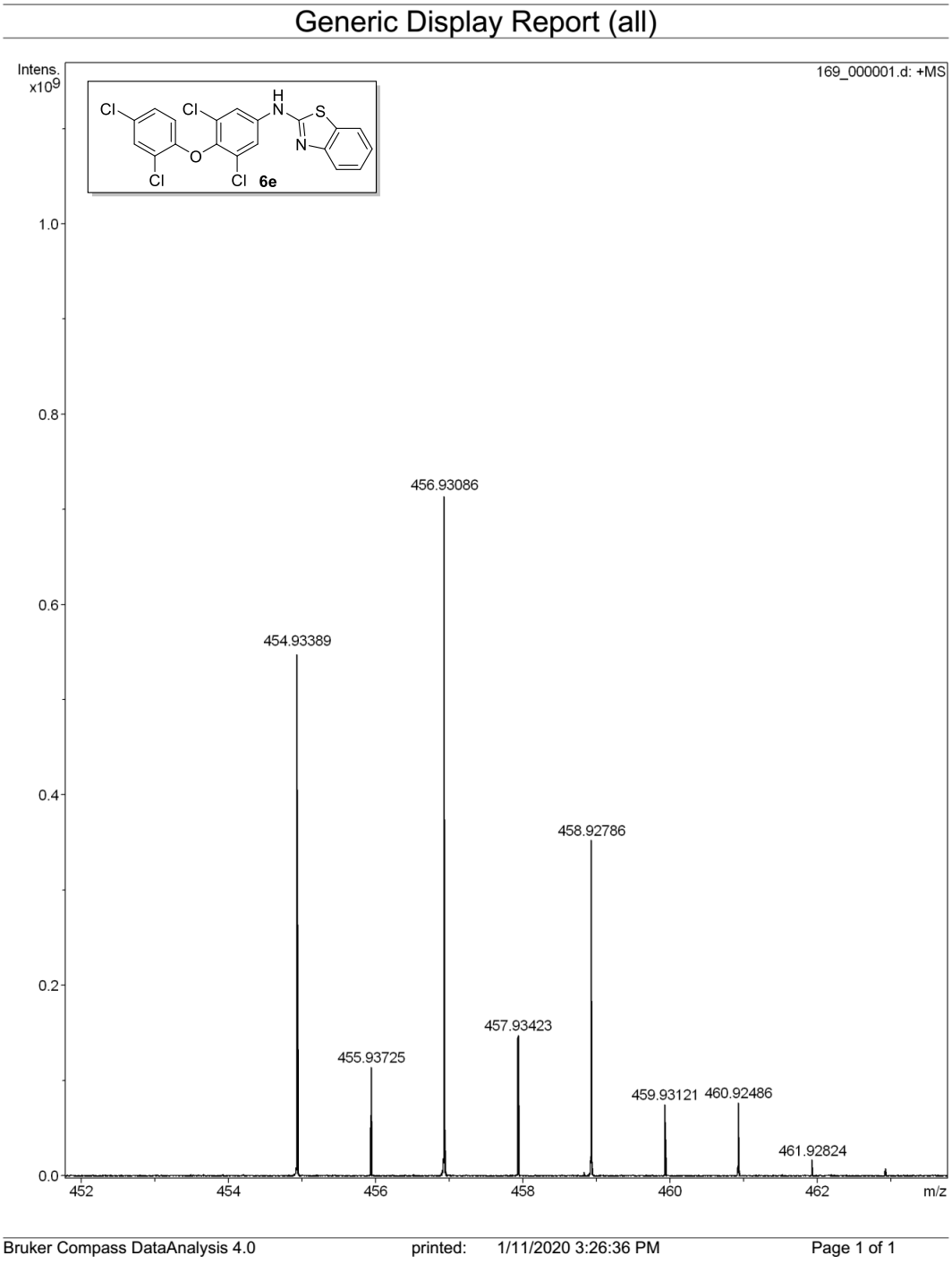
➢ ^{1}H NMR spectrum for **6e**



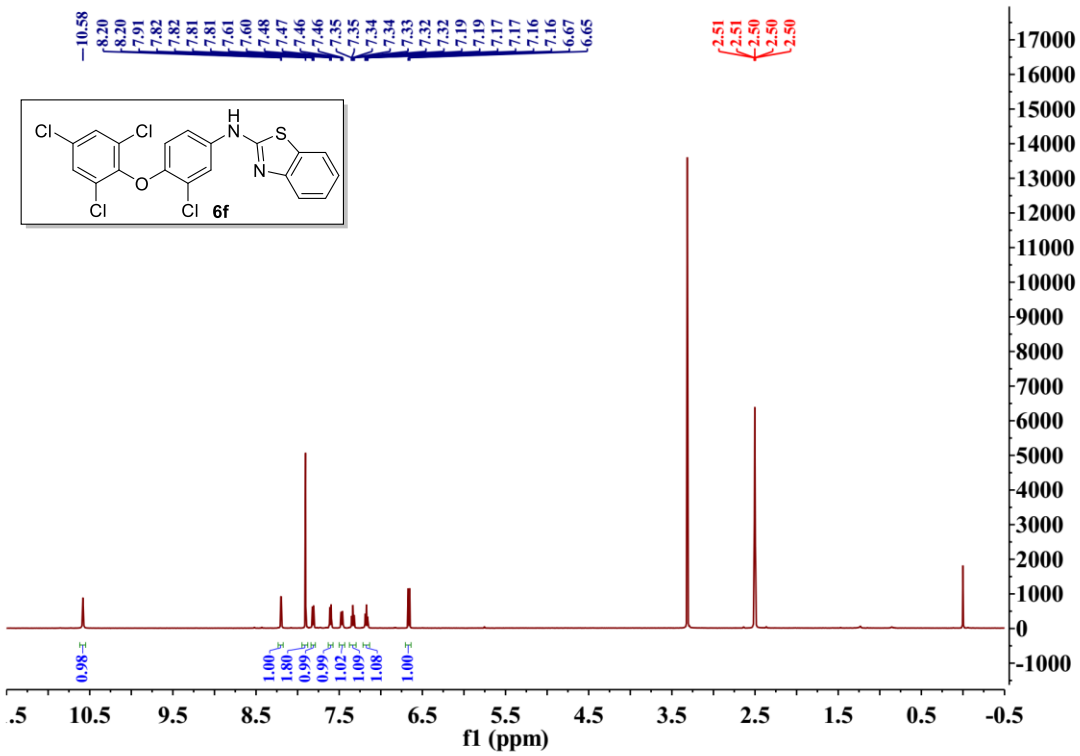
➢ ^{13}C NMR spectrum for **6e**



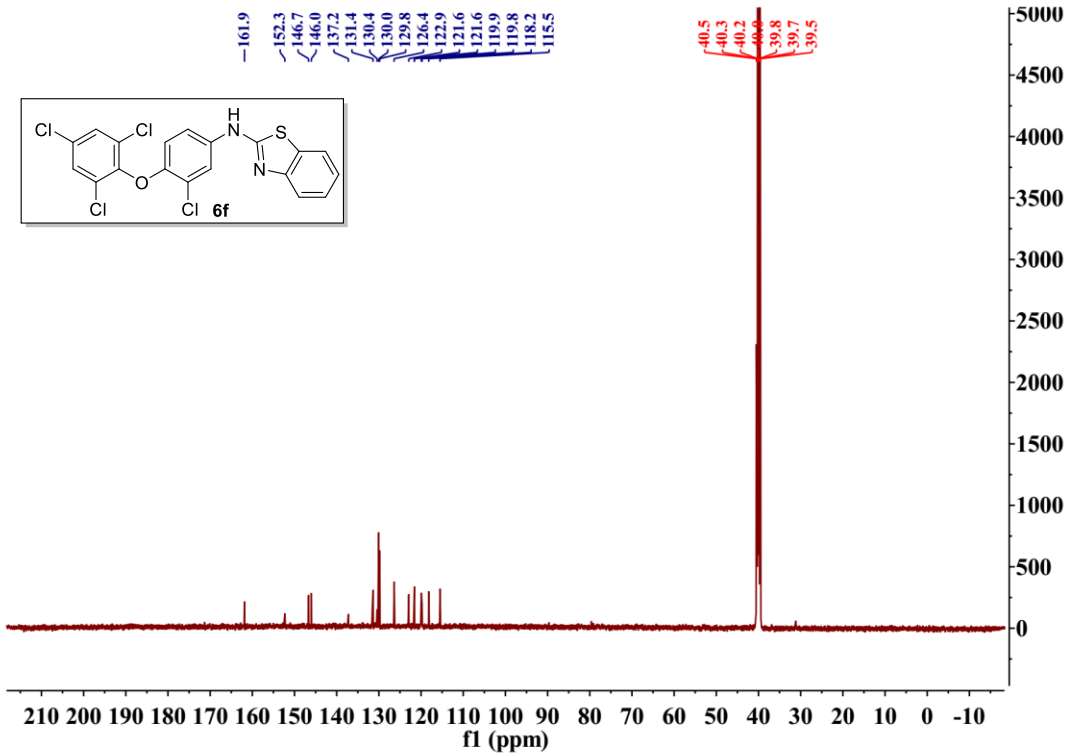
- HRMS spectrum for **6e**



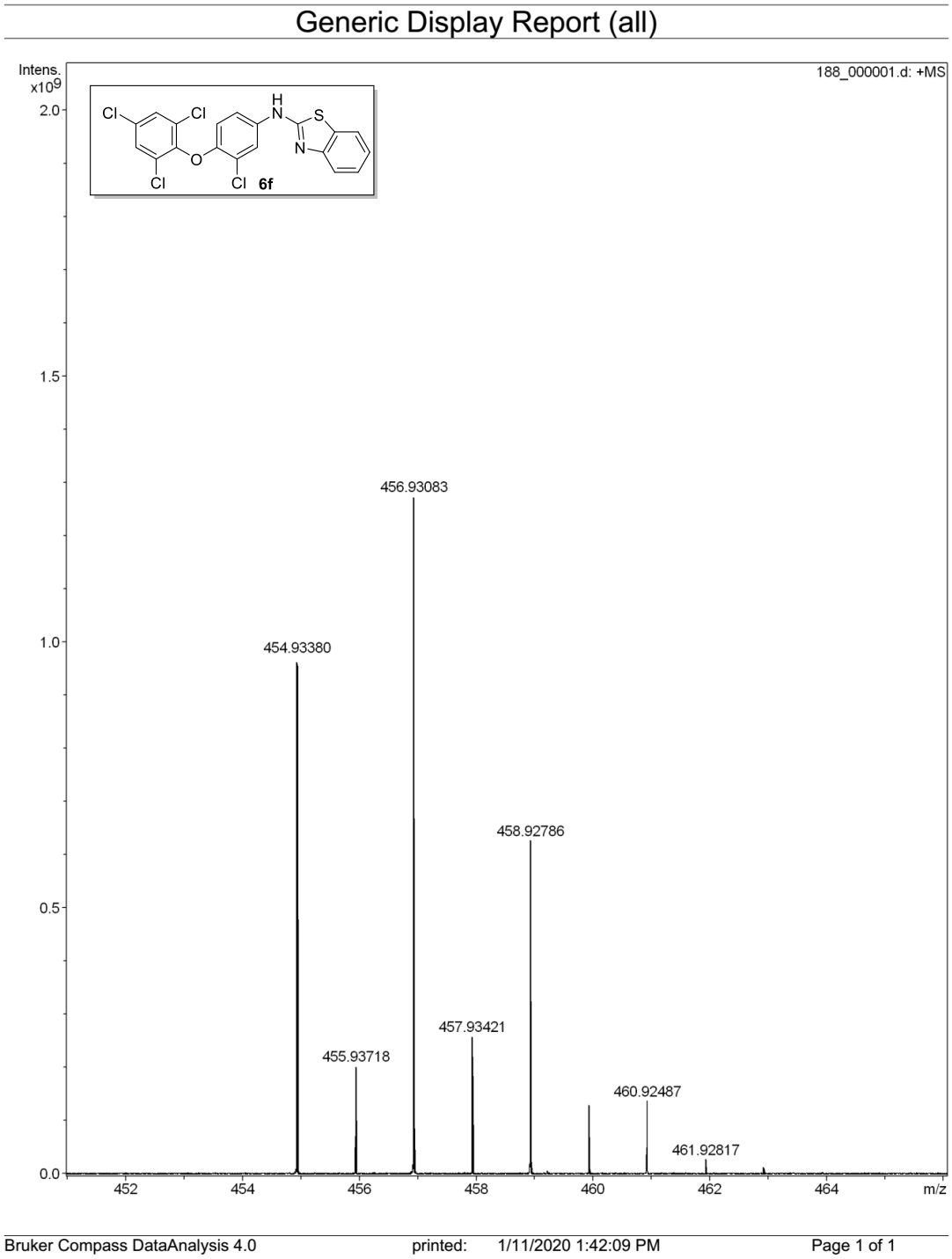
➢ ^{1}H NMR spectrum for **6f**



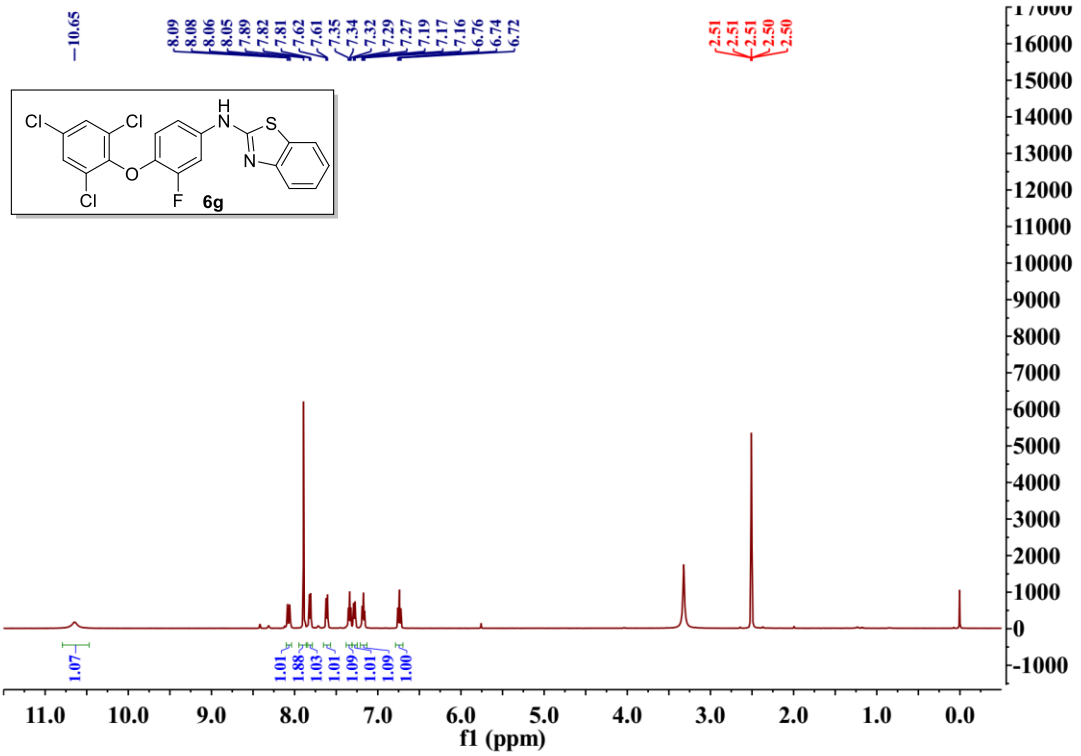
➢ ^{13}C NMR spectrum for **6f**



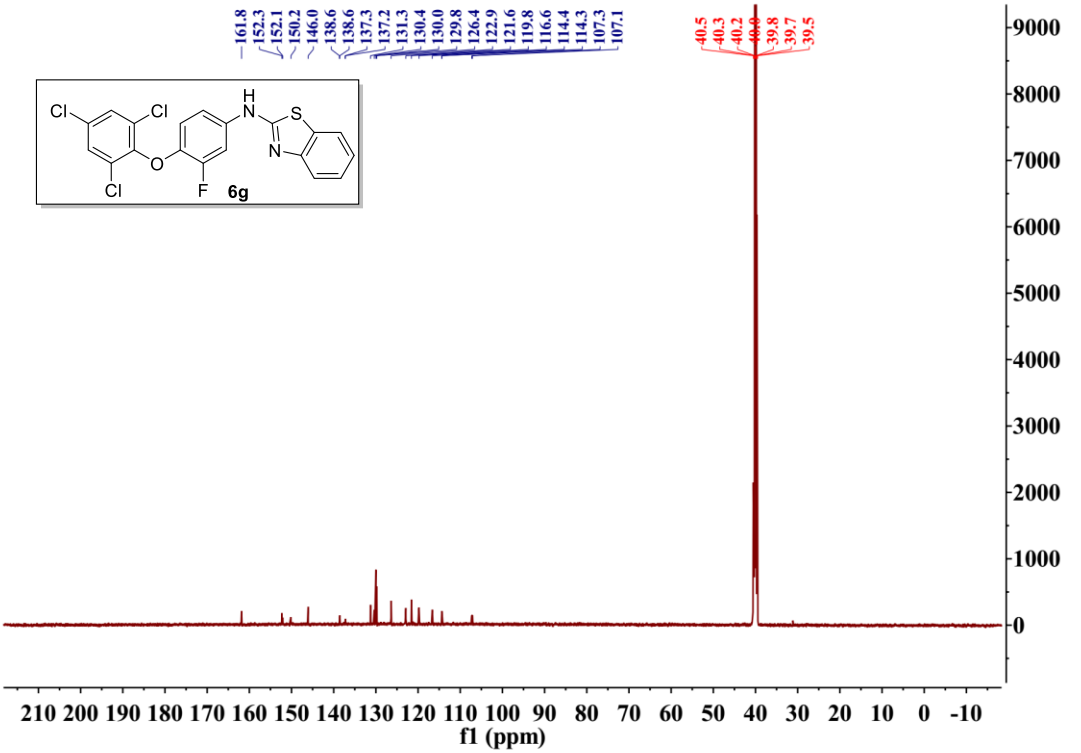
- HRMS spectrum for **6f**



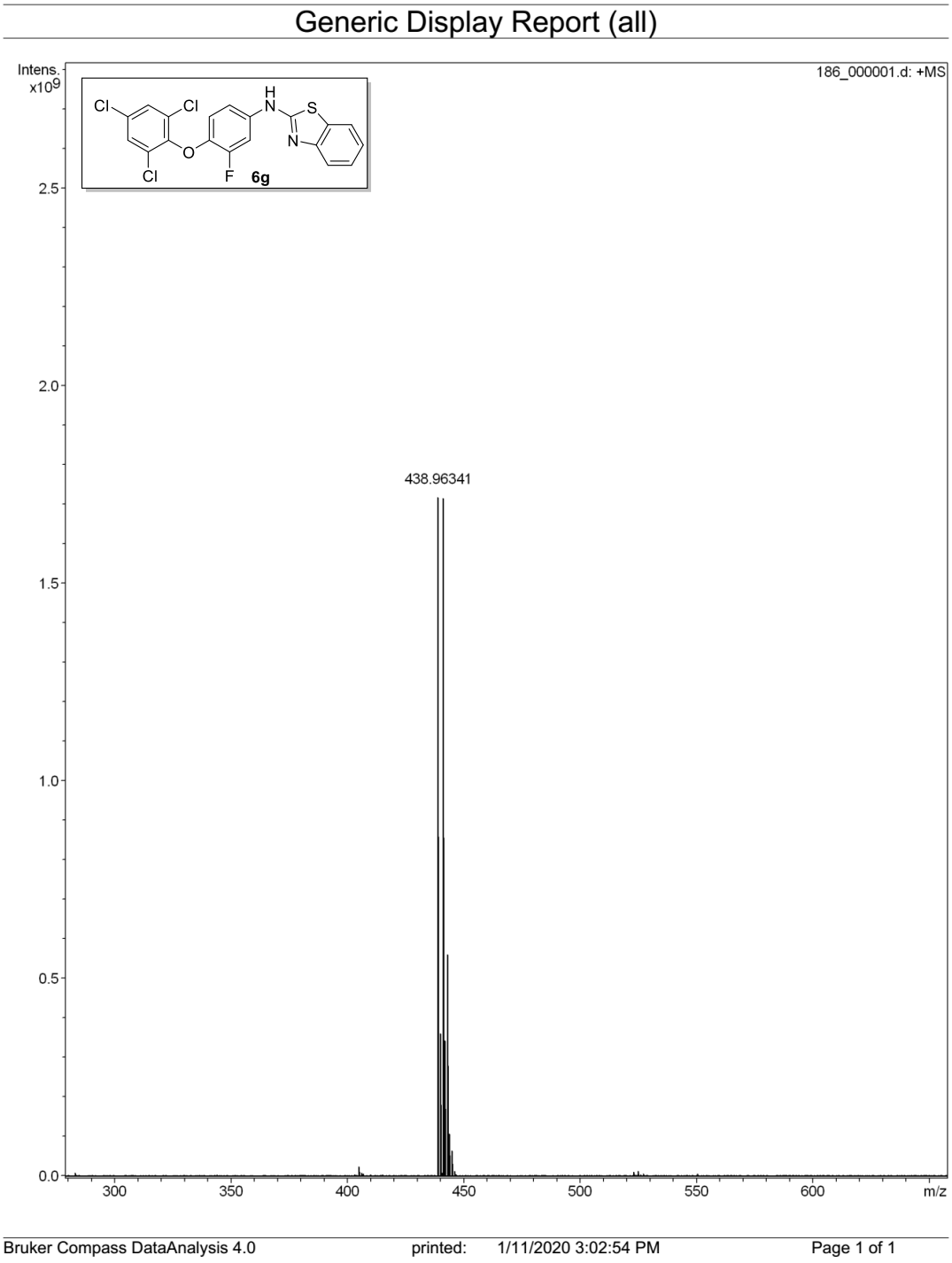
➢ ^{1}H NMR spectrum for **6g**



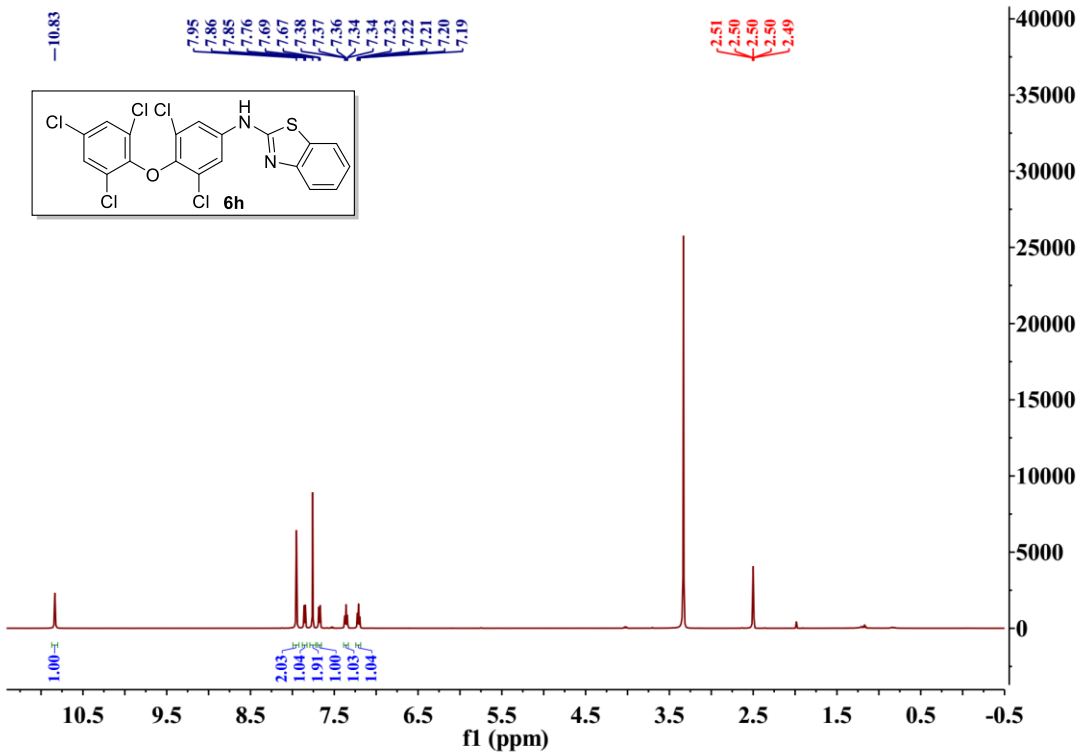
➢ ^{13}C NMR spectrum for **6g**



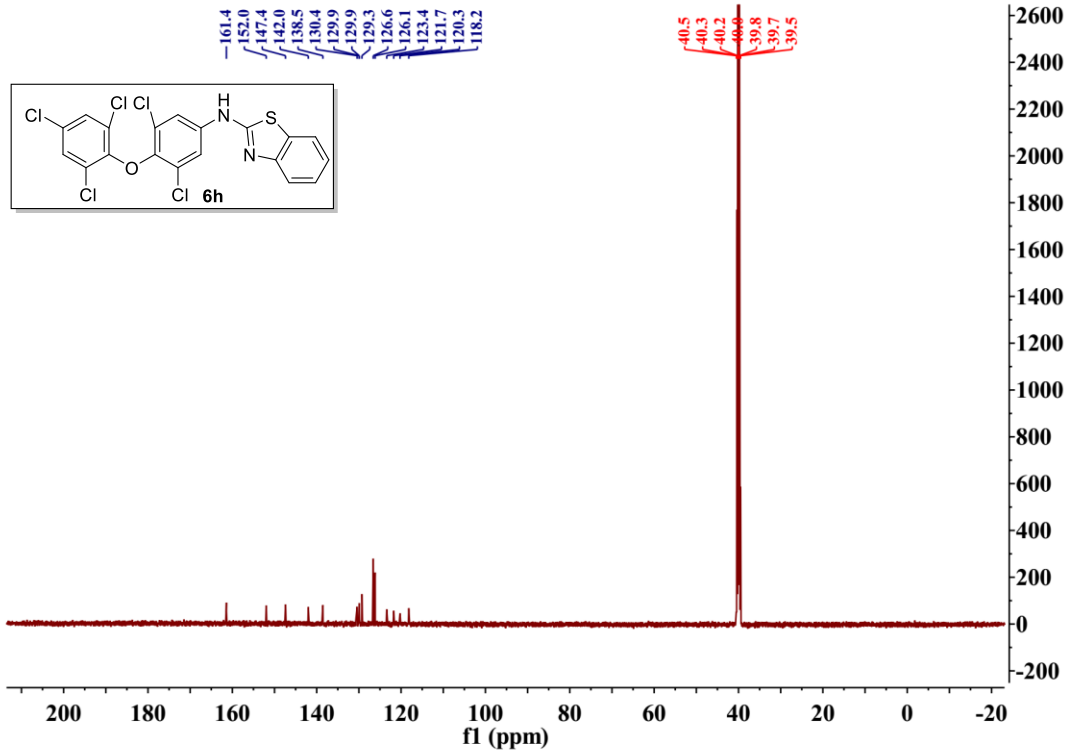
- HRMS spectrum for **6g**



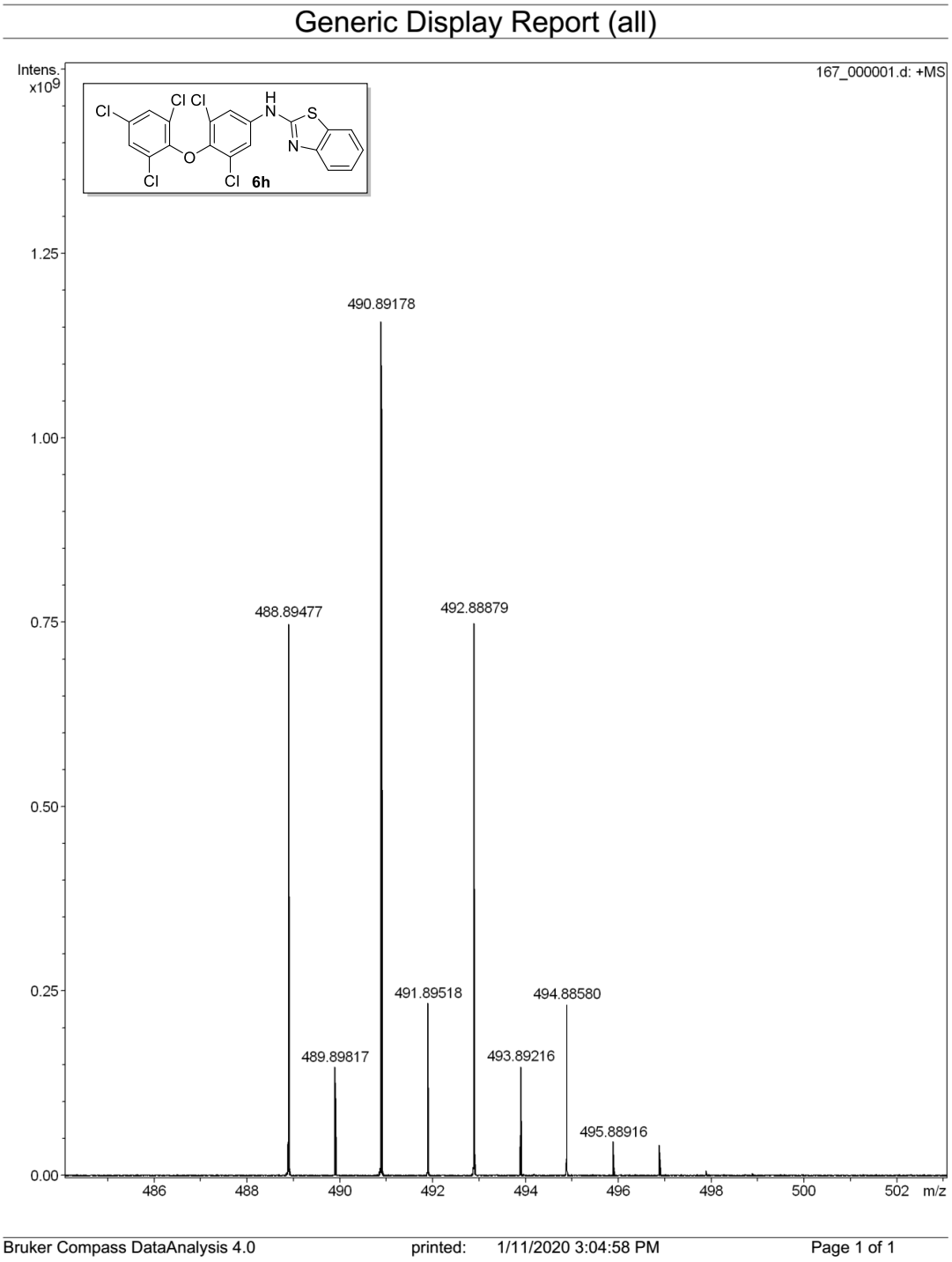
➢ ^{1}H NMR spectrum for **6h**



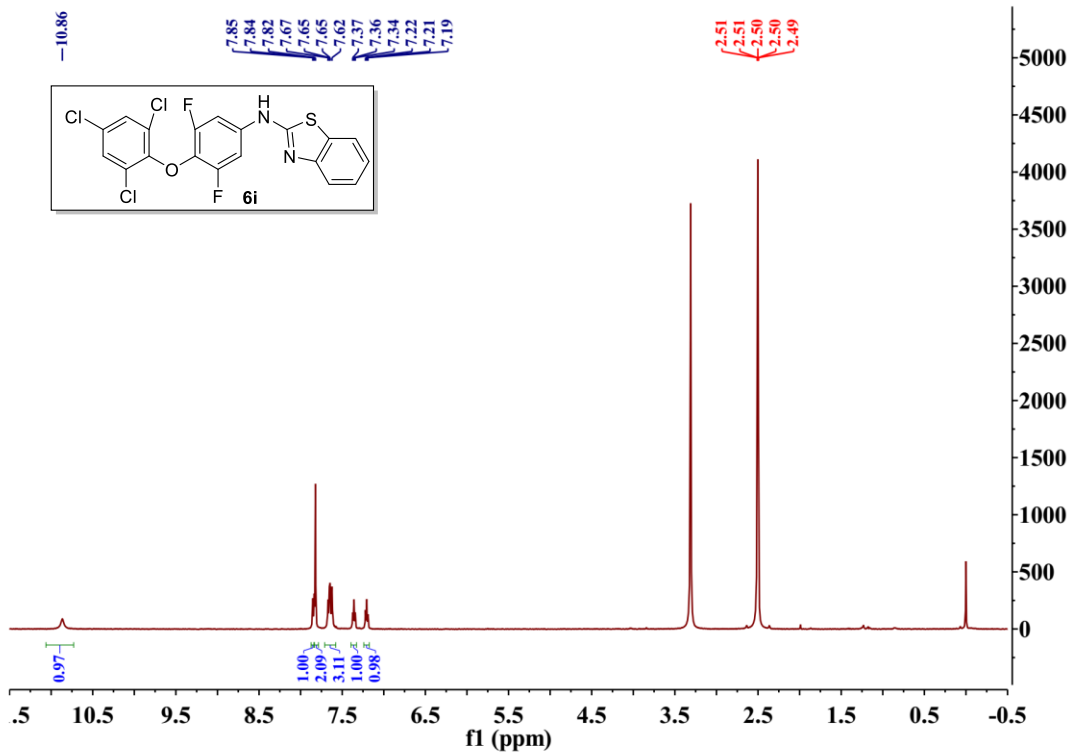
➢ ^{13}C NMR spectrum for **6h**



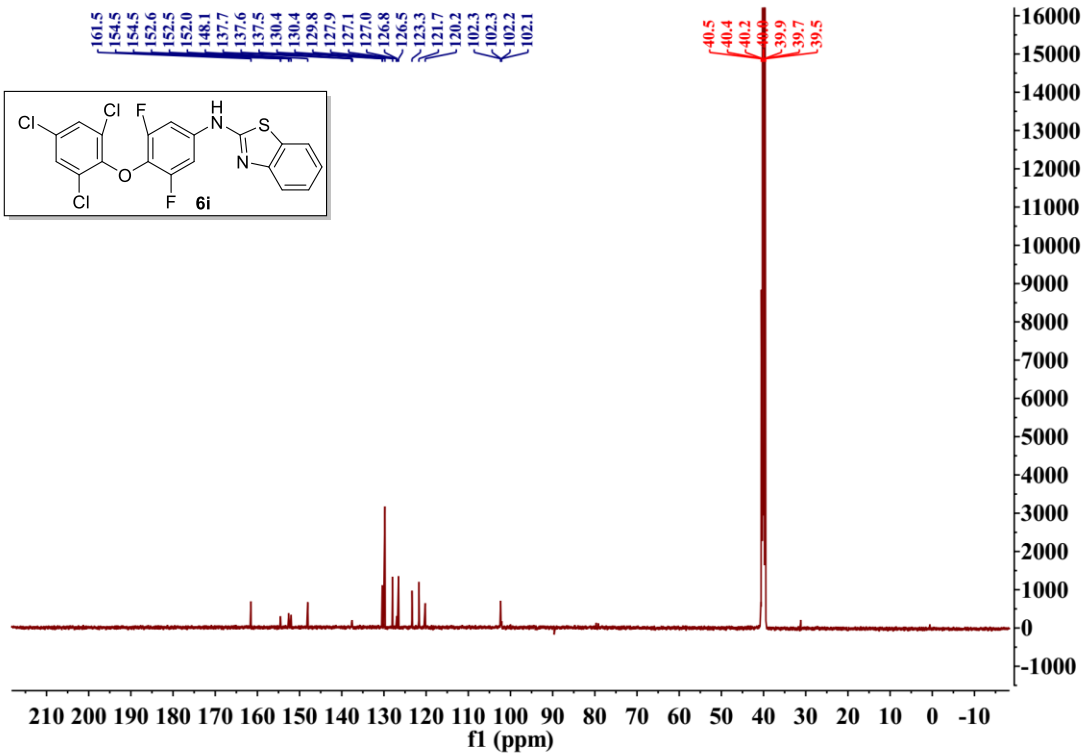
➢ HRMS spectrum for **6h**



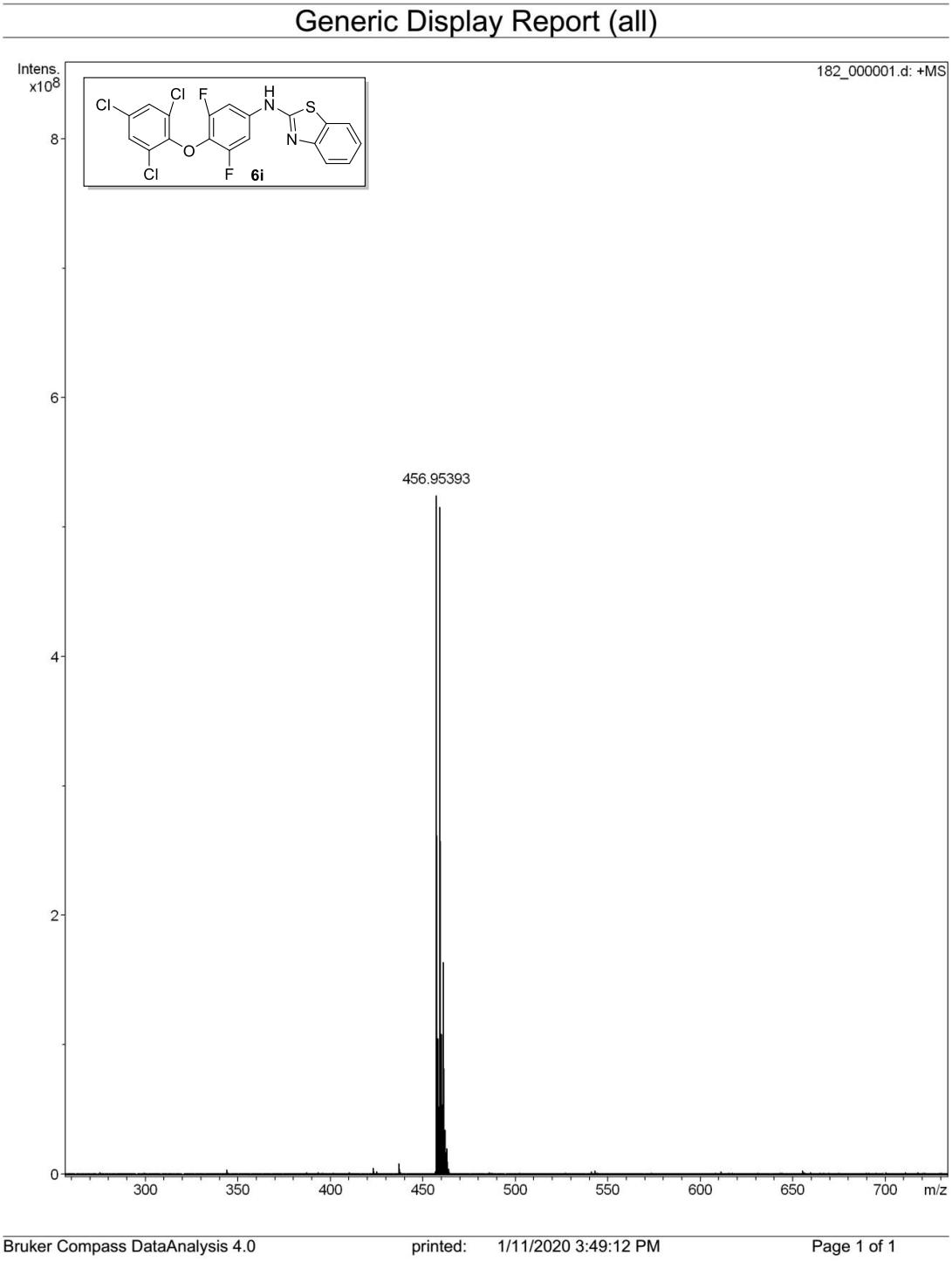
➢ ^{1}H NMR spectrum for **6i**



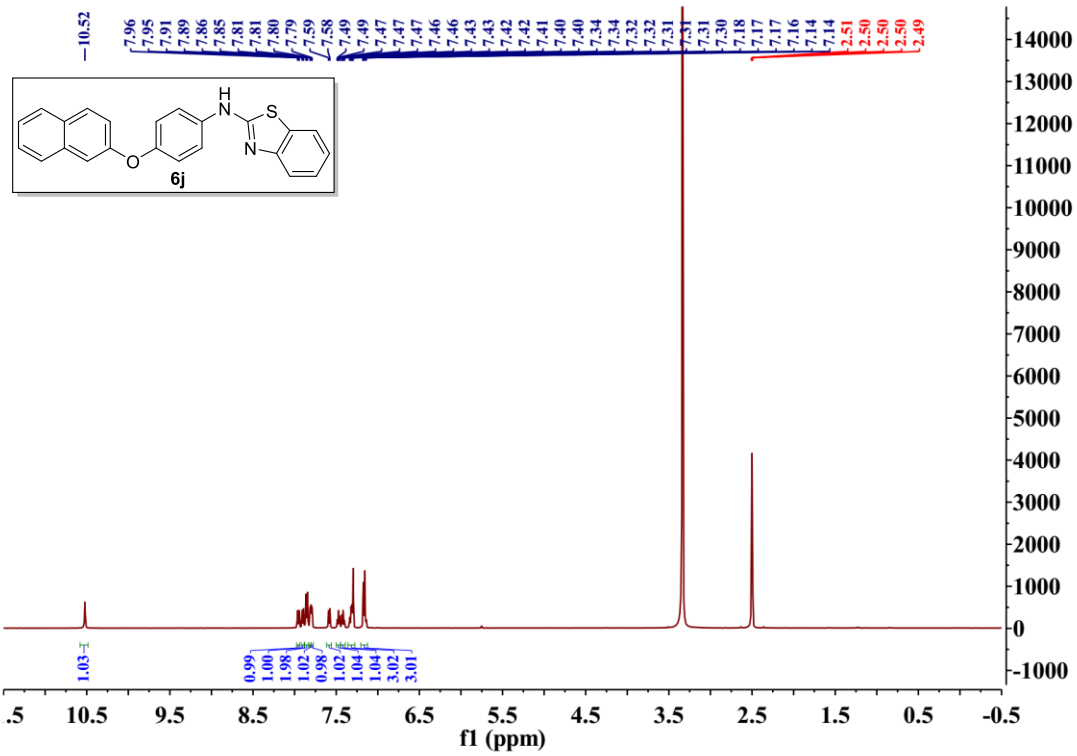
➢ ^{13}C NMR spectrum for **6i**



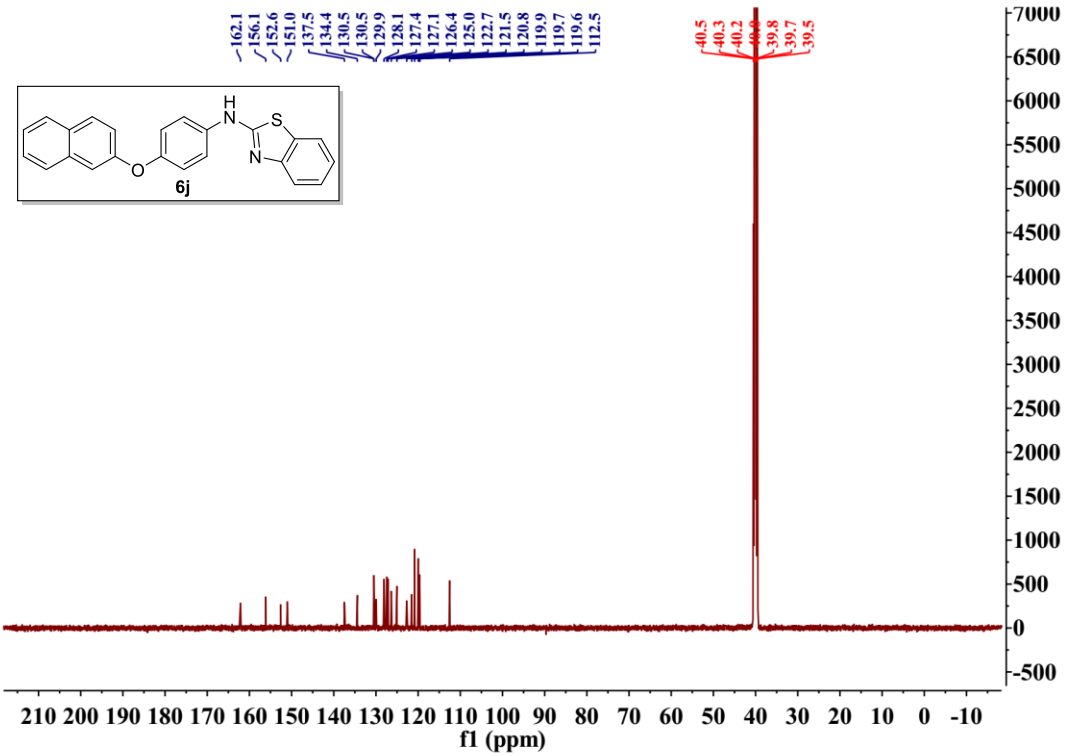
- HRMS spectrum for **6i**



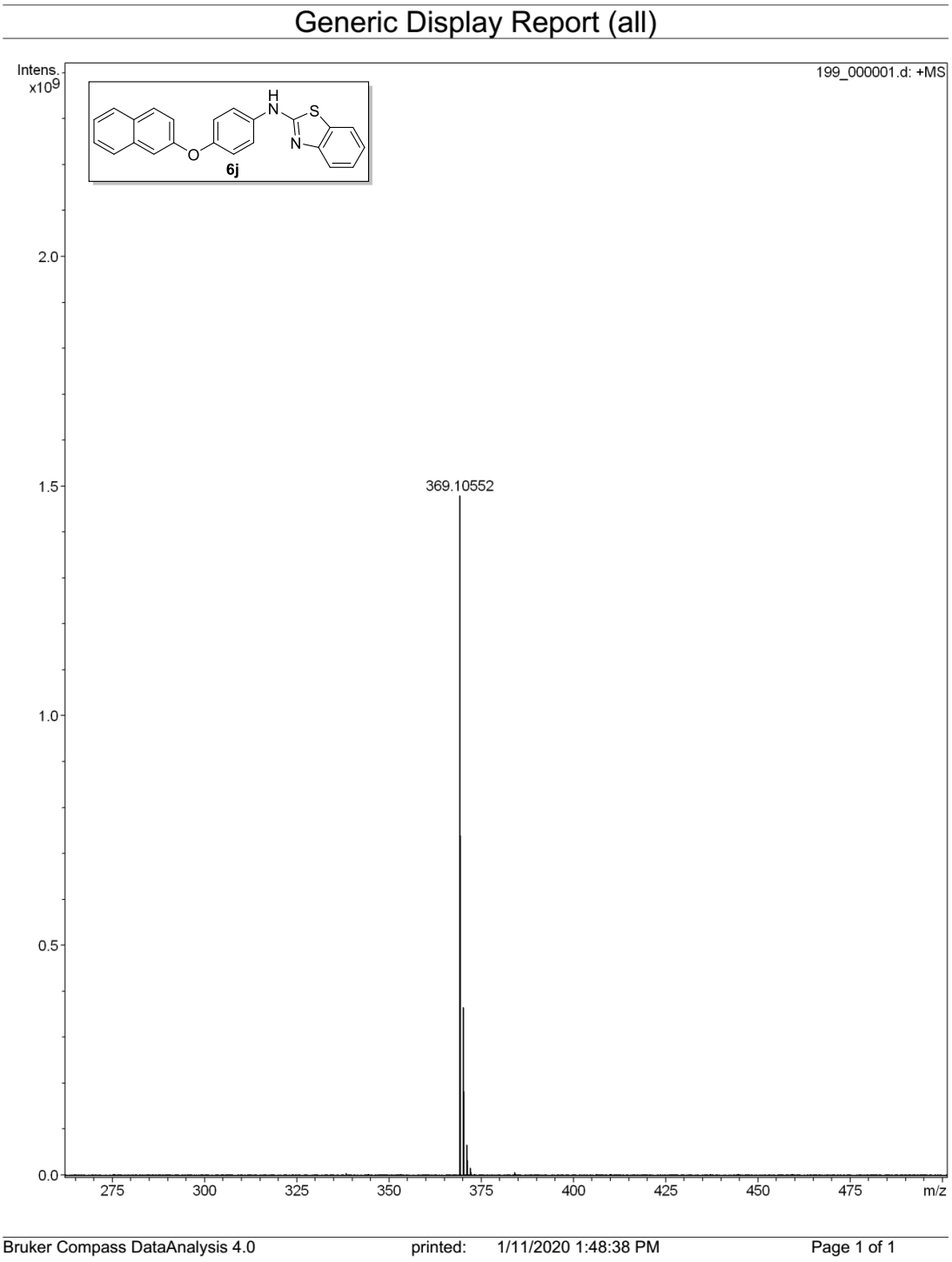
➢ ^{1}H NMR spectrum for **6j**



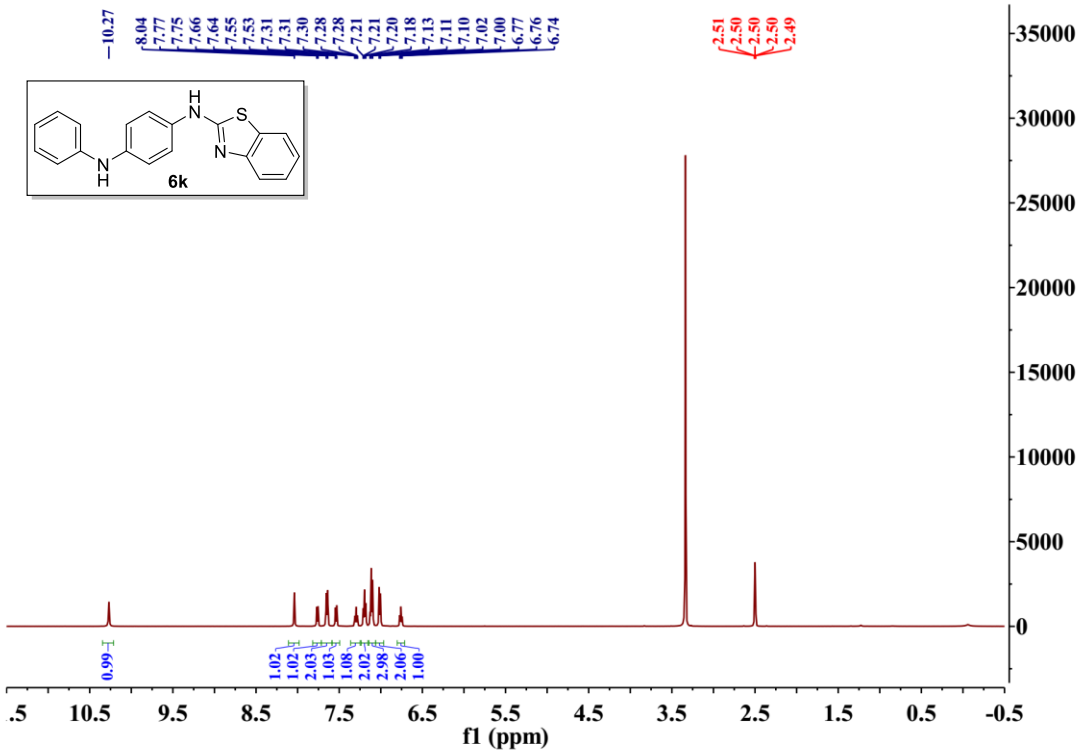
➢ ^{13}C NMR spectrum for **6j**



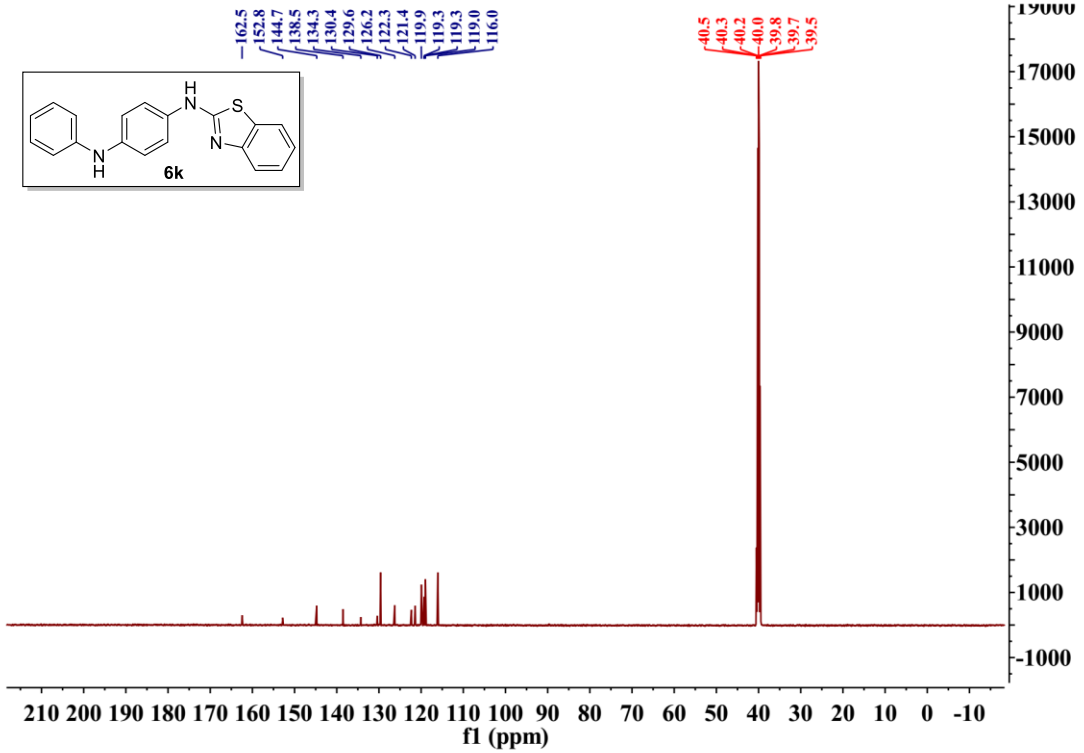
- HRMS spectrum for **6j**



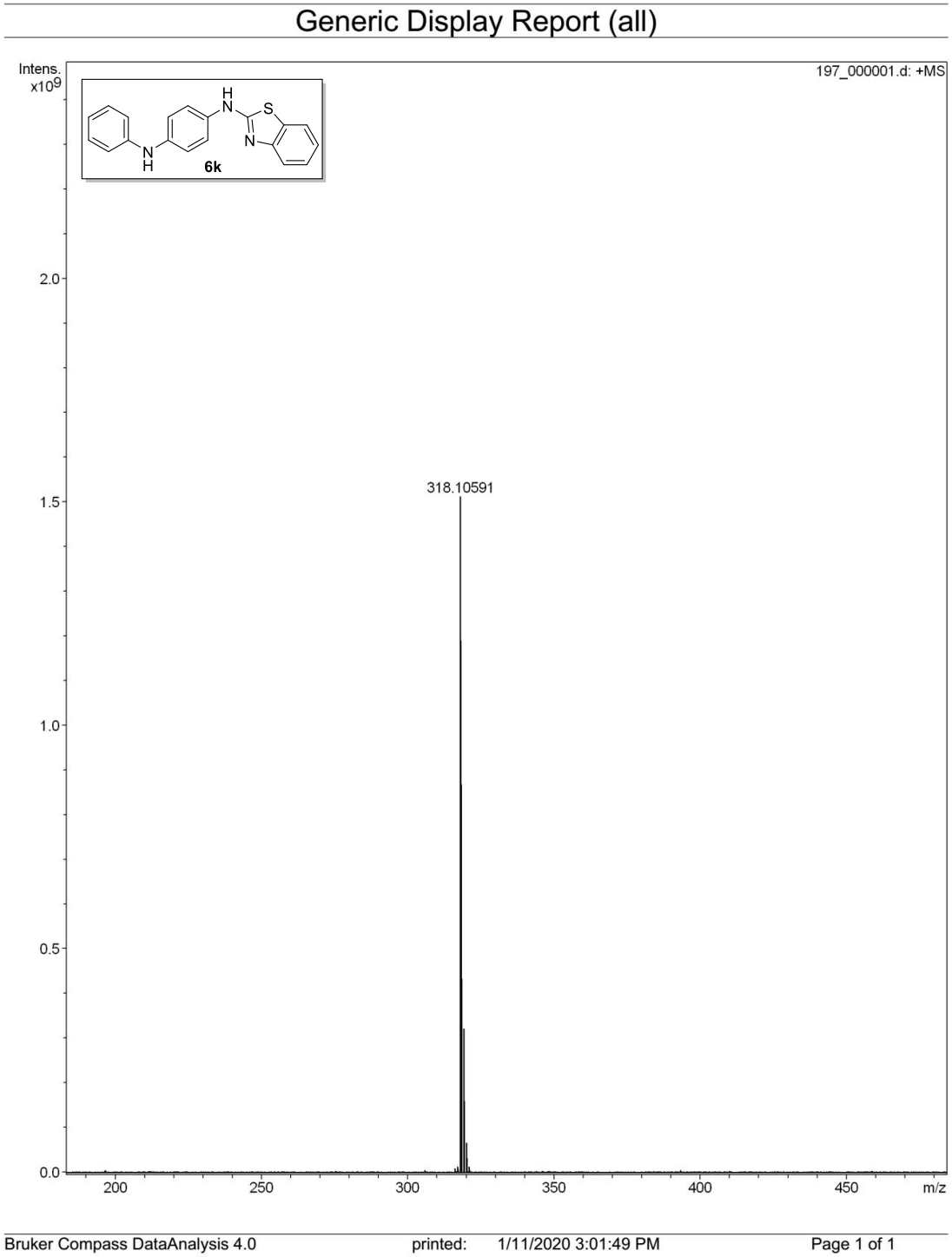
➢ ^{1}H NMR spectrum for **6k**



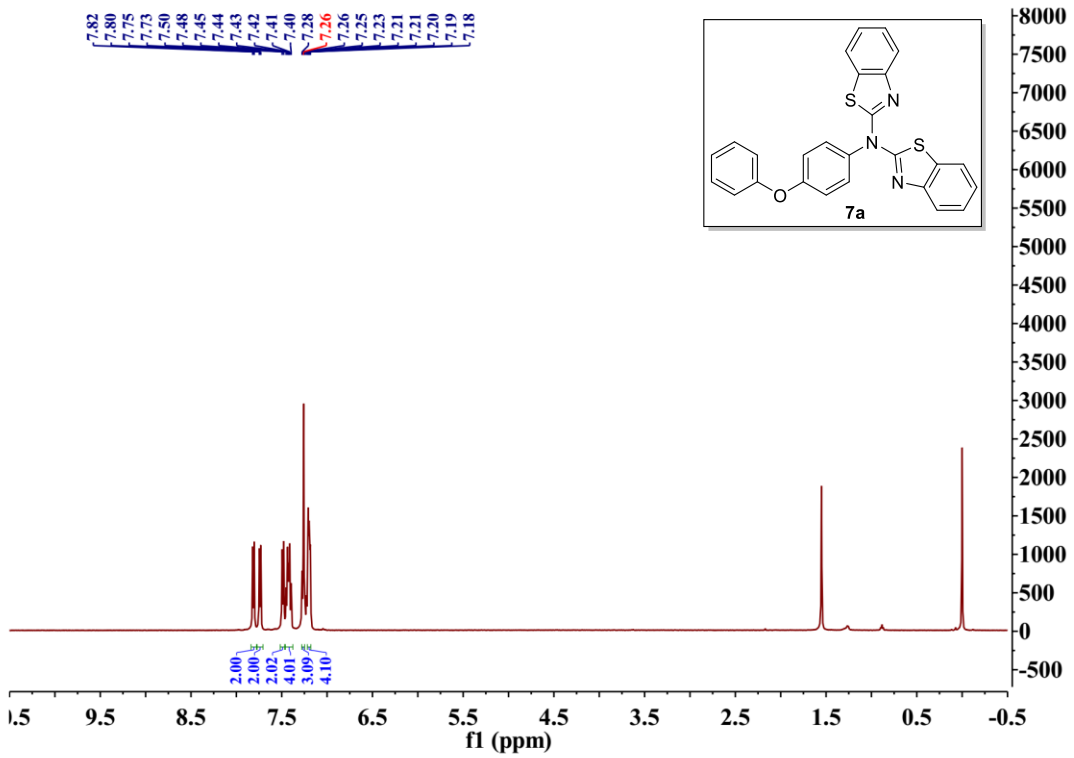
➢ ^{13}C NMR spectrum for **6k**



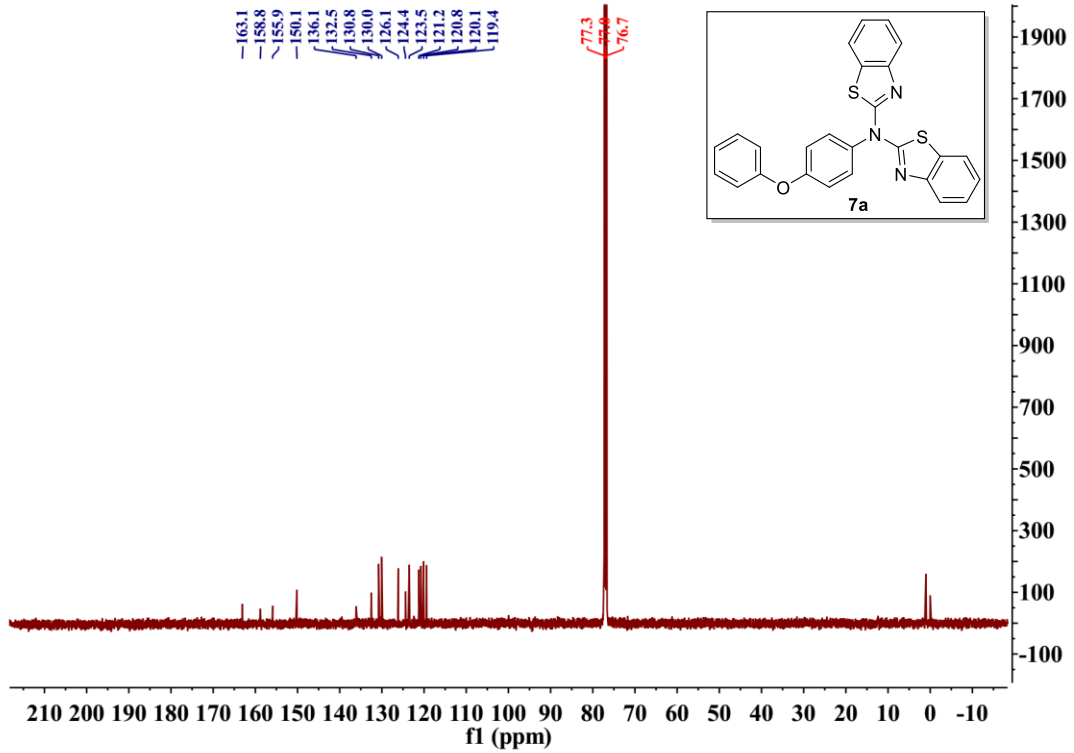
- HRMS spectrum for **6k**



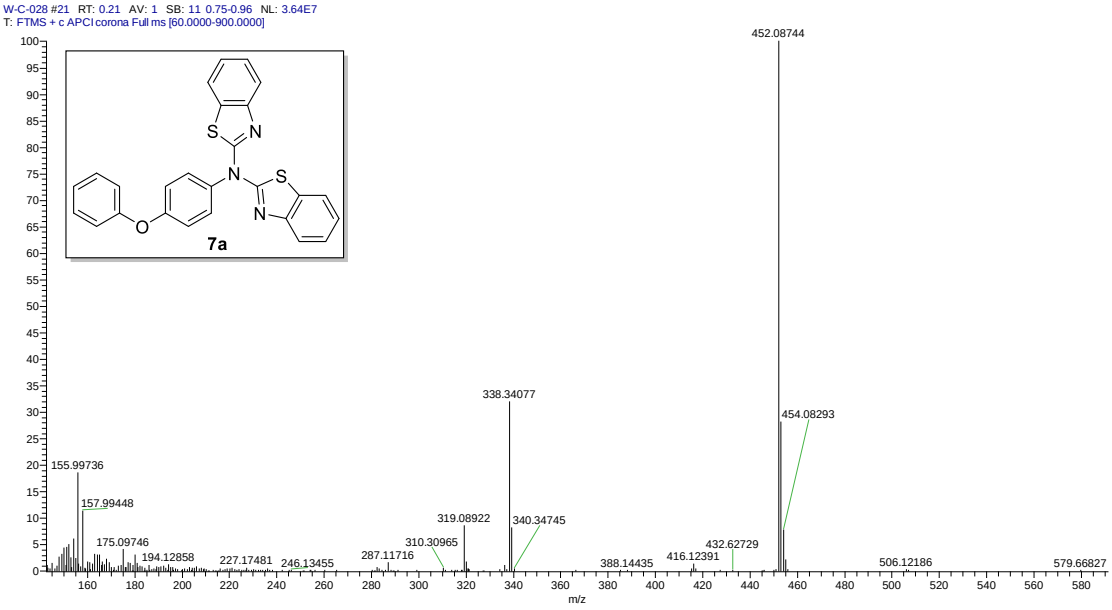
➢ ^{1}H NMR spectrum for **7a**



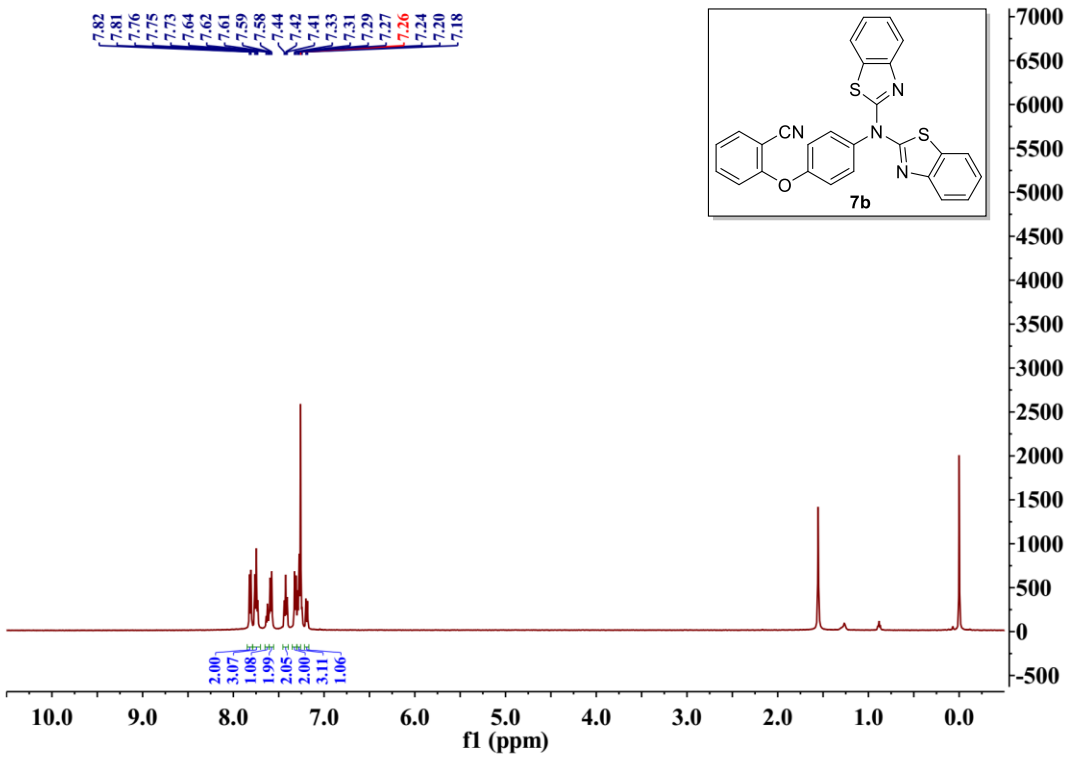
➢ ^{13}C NMR spectrum for **7a**



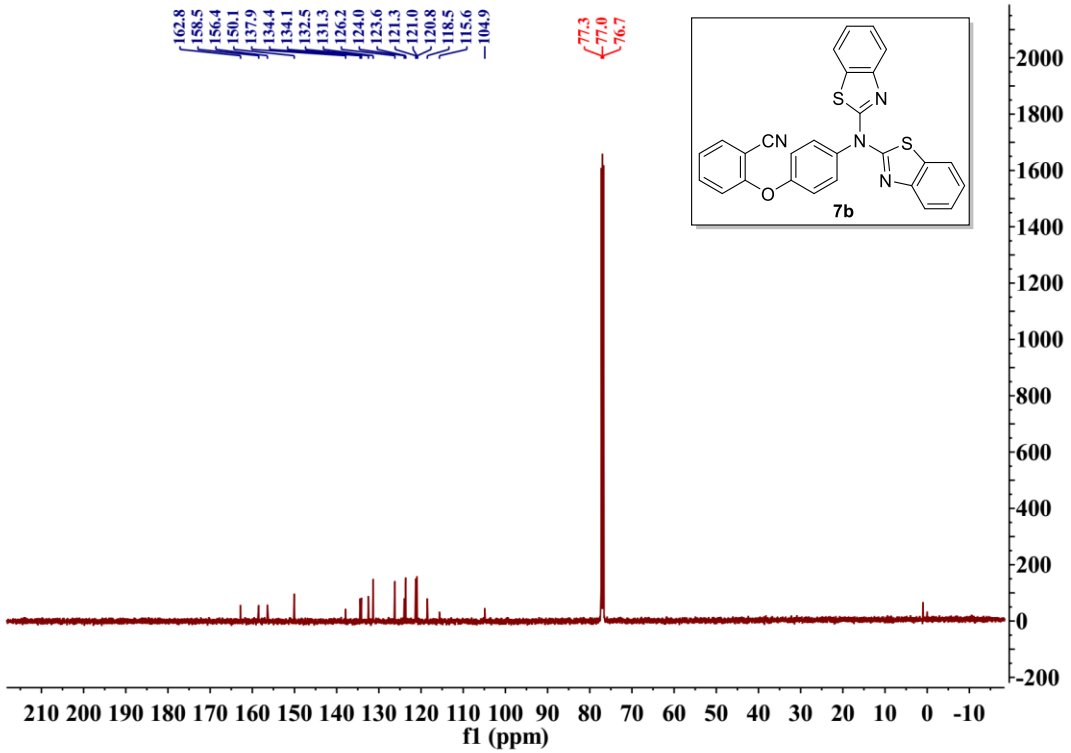
➢ HRMS spectrum for **7a**



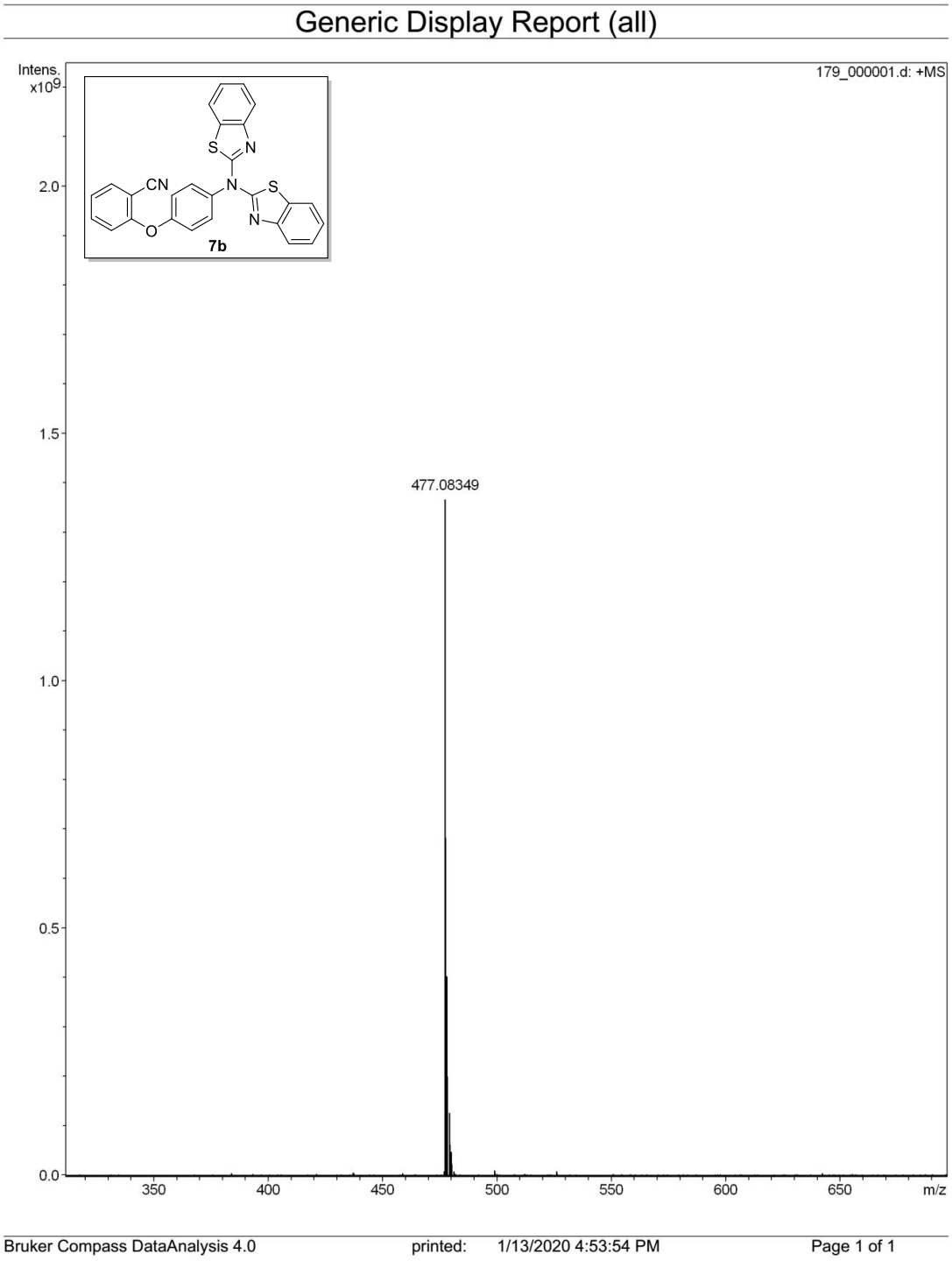
➢ ^{1}H NMR spectrum for **7b**



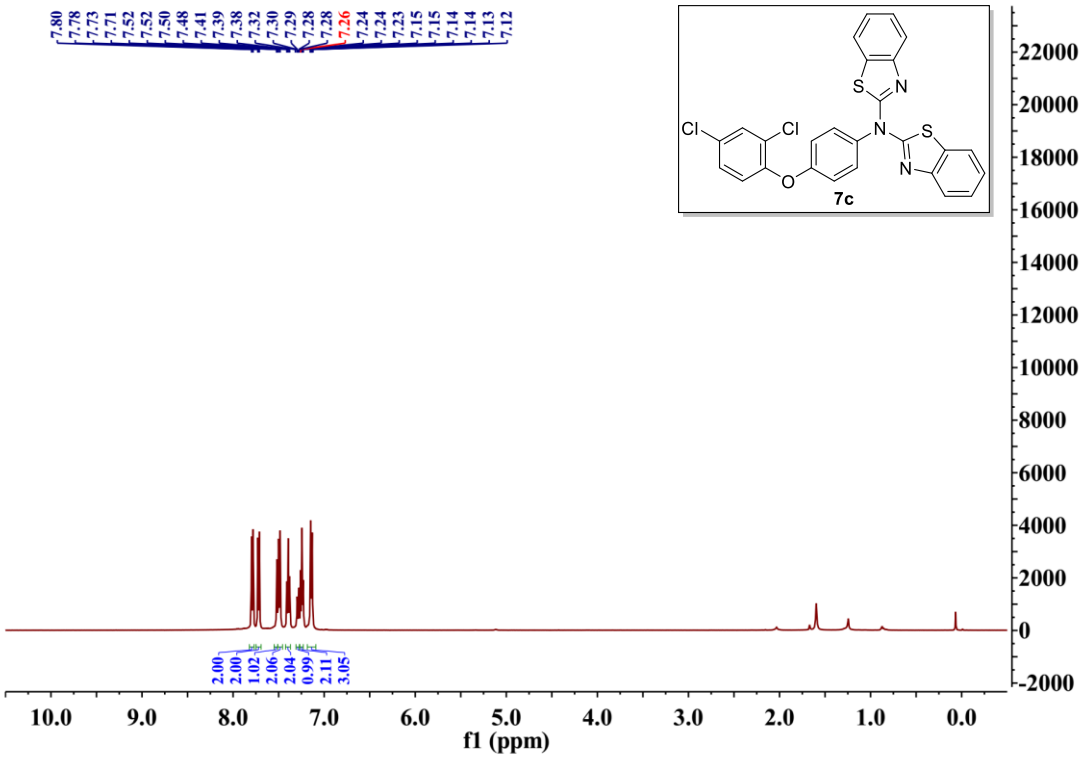
➢ ^{13}C NMR spectrum for **7b**



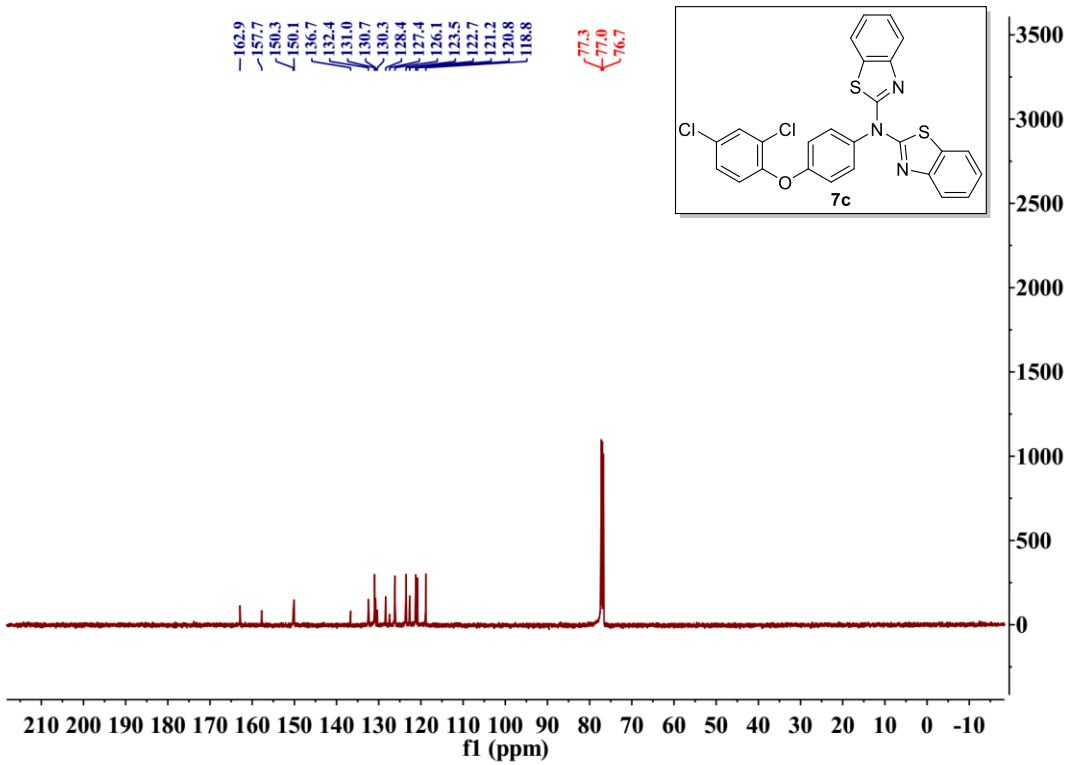
- HRMS spectrum for **7b**



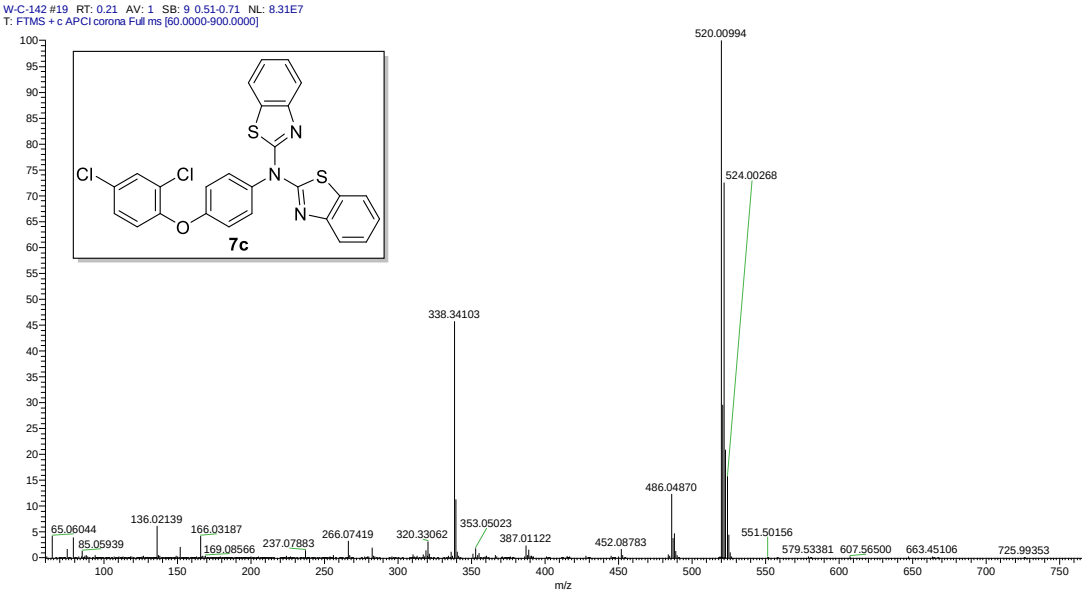
➢ ^{1}H NMR spectrum for **7c**



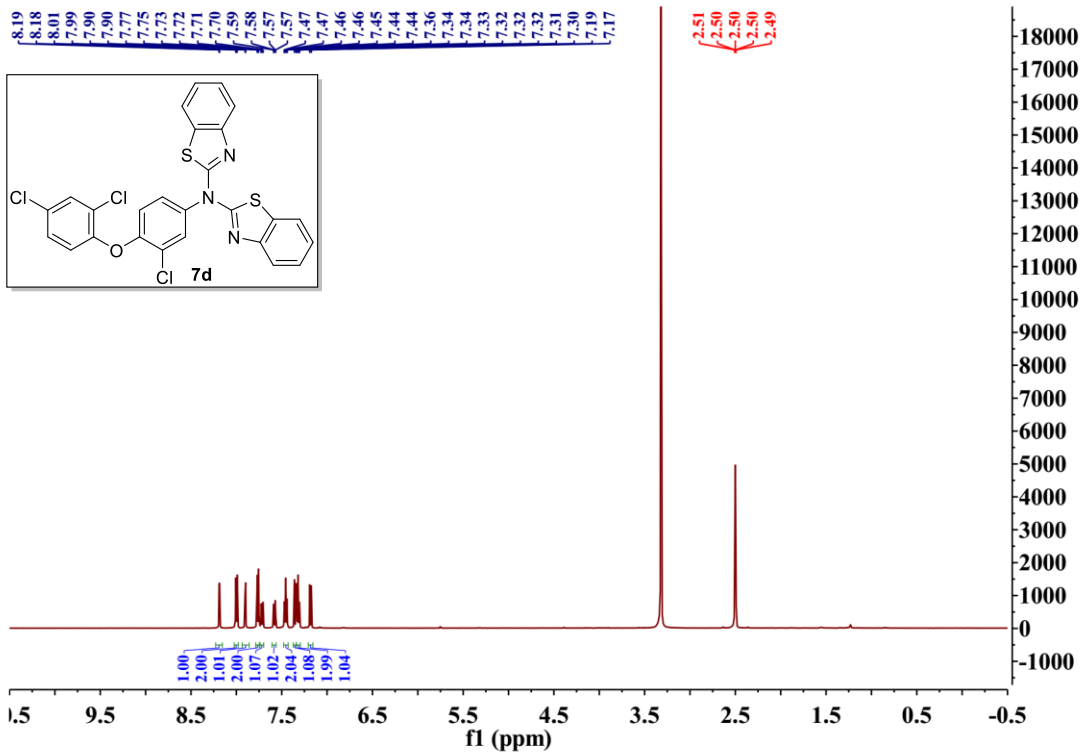
➢ ^{13}C NMR spectrum for **7c**



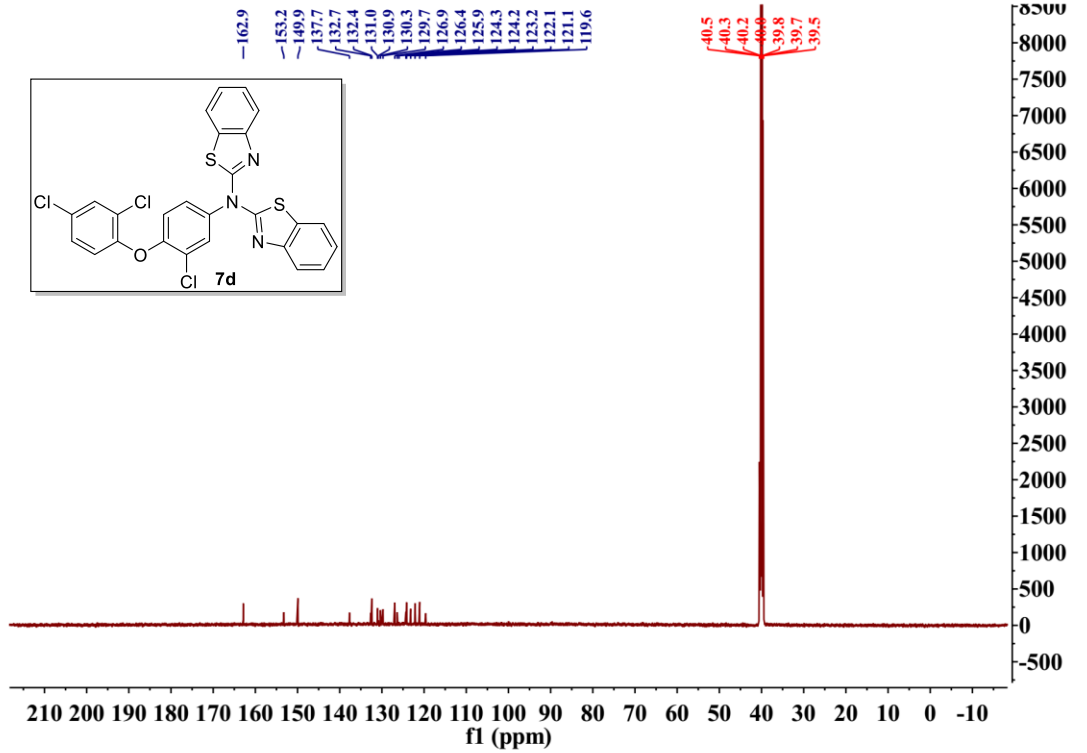
➢ HRMS spectrum for **7c**



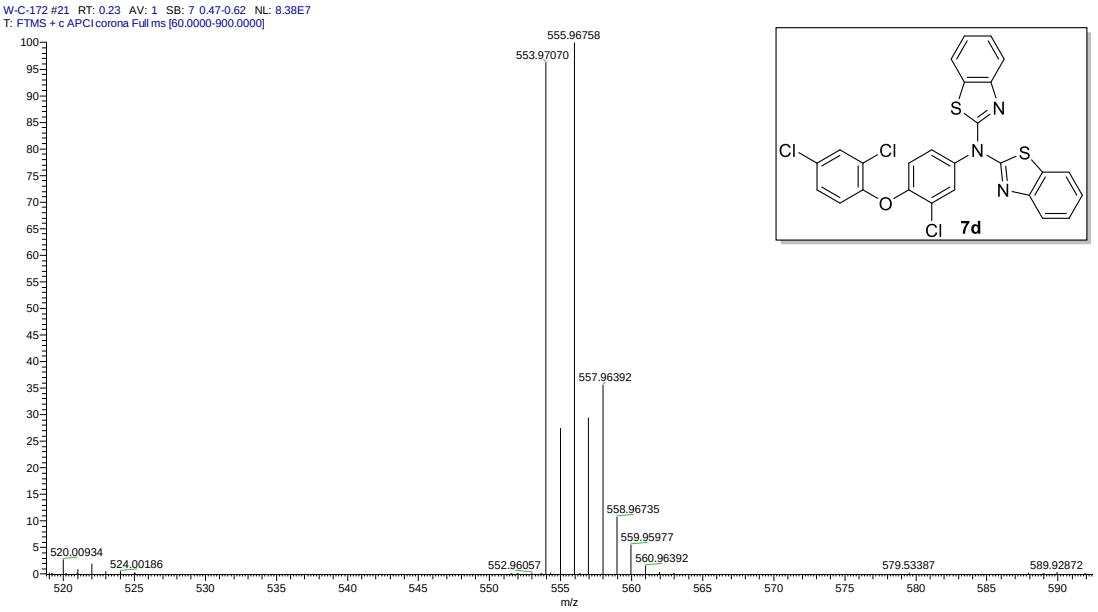
➢ ^{1}H NMR spectrum for **7d**



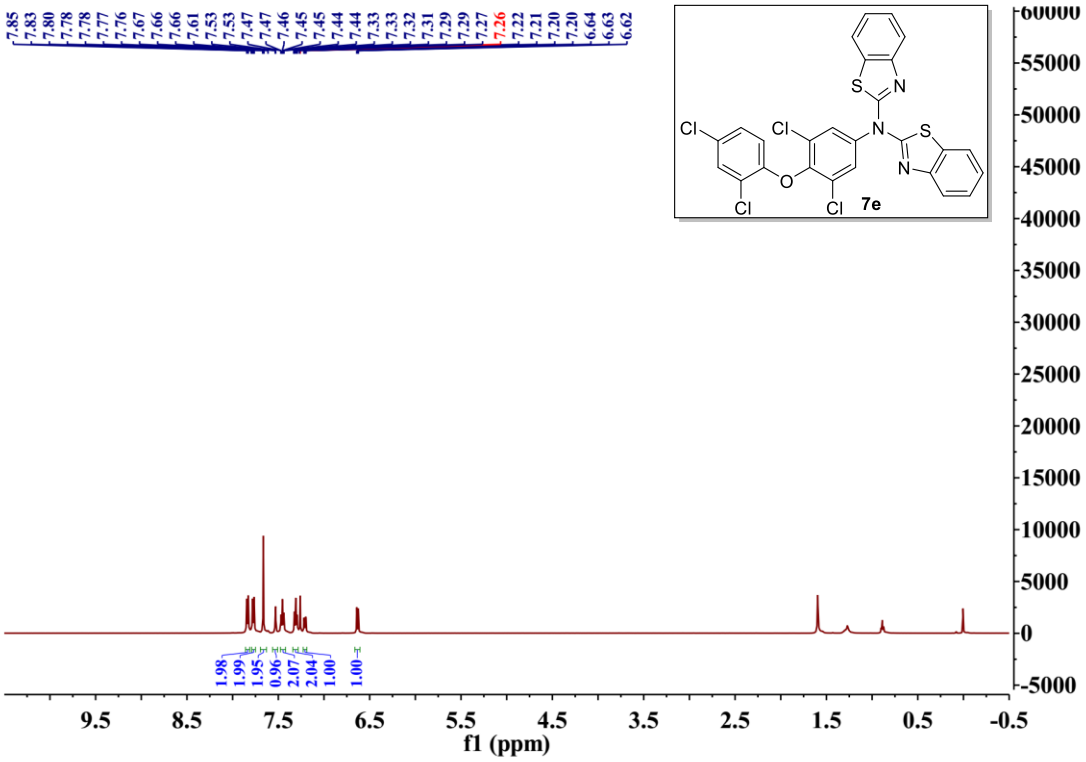
➢ ^{13}C NMR spectrum for **7d**



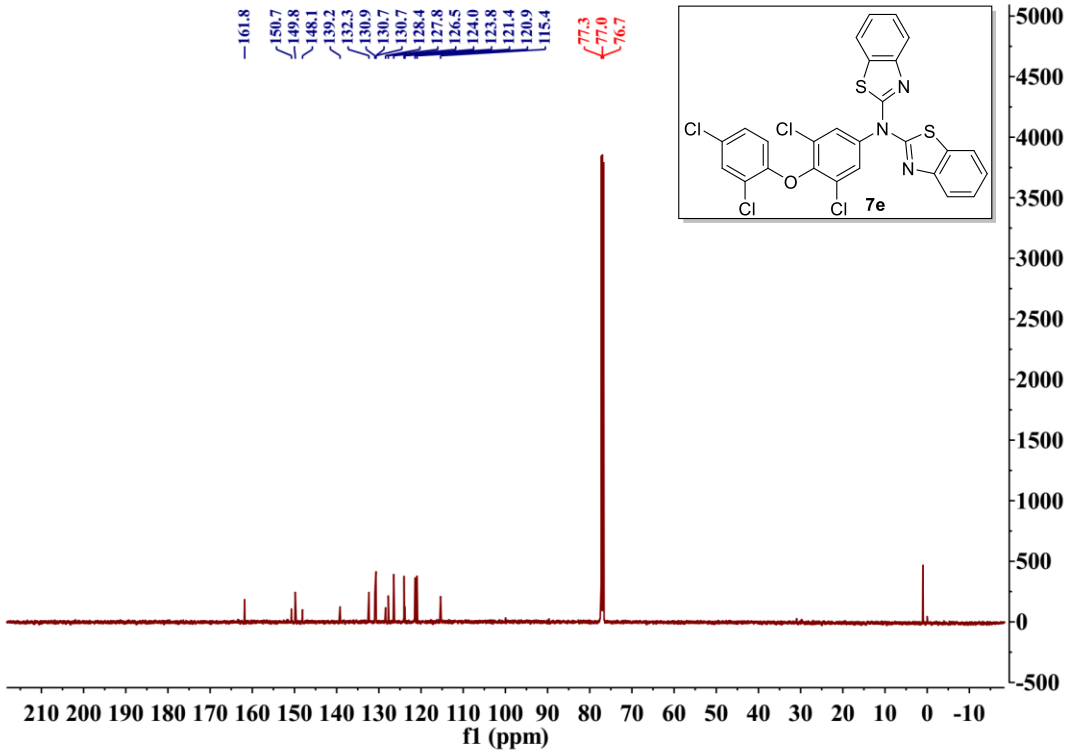
➢ HRMS spectrum for **7d**



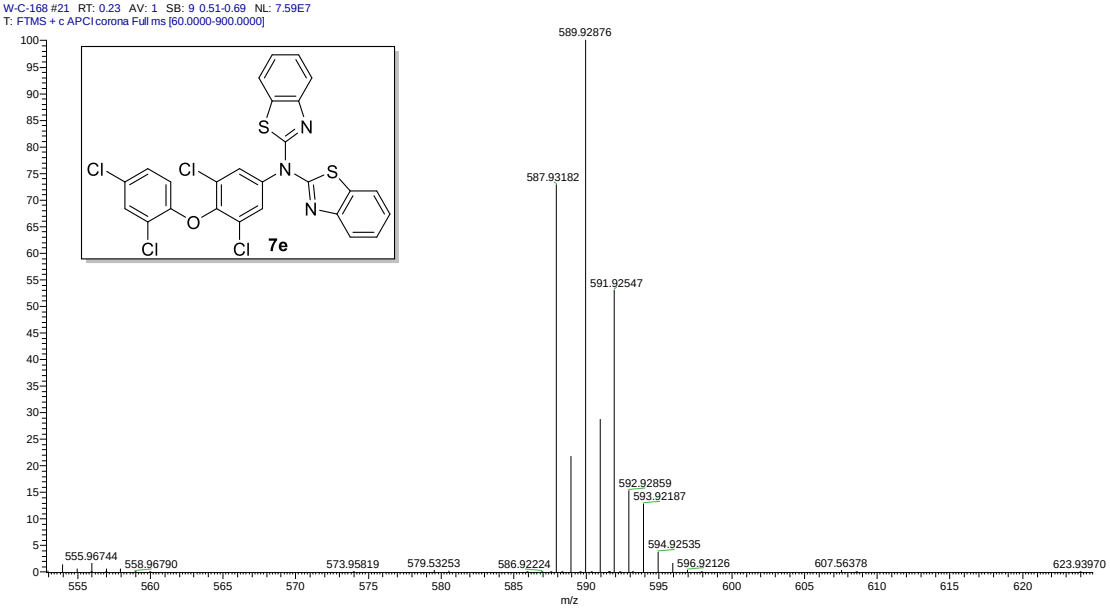
➢ ^{1}H NMR spectrum for **7e**



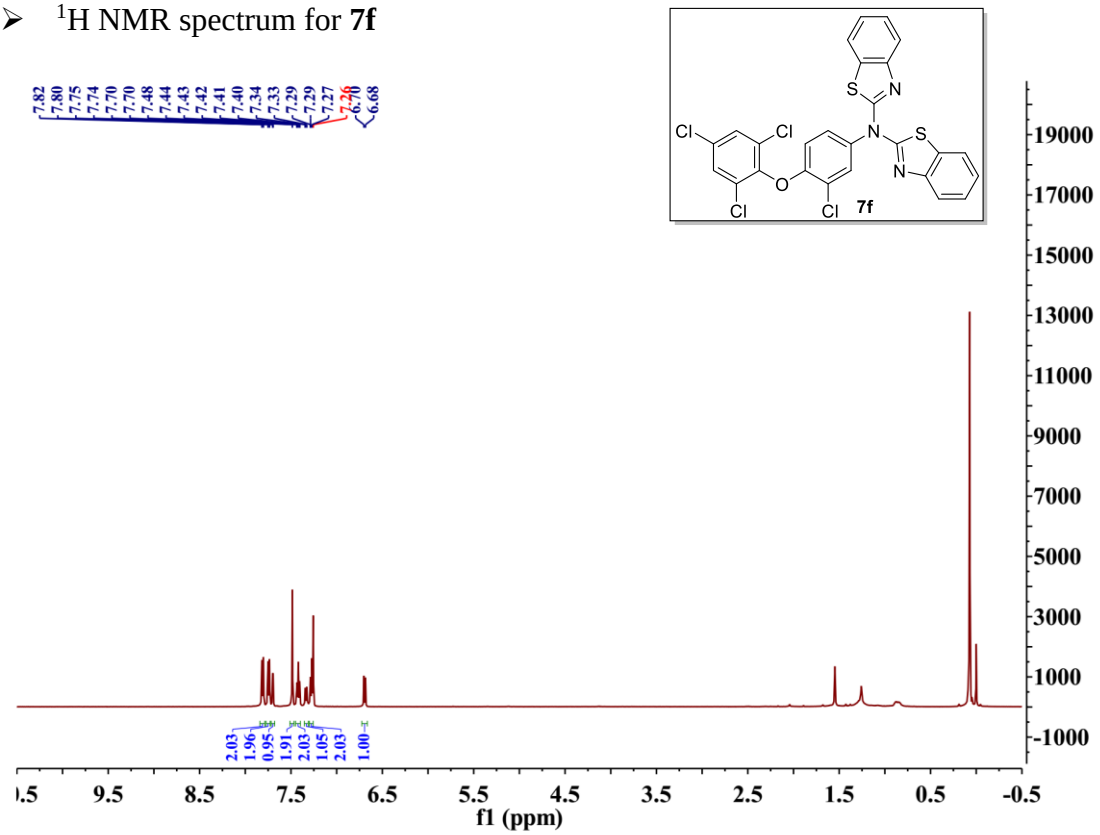
➢ ^{13}C NMR spectrum for **7e**



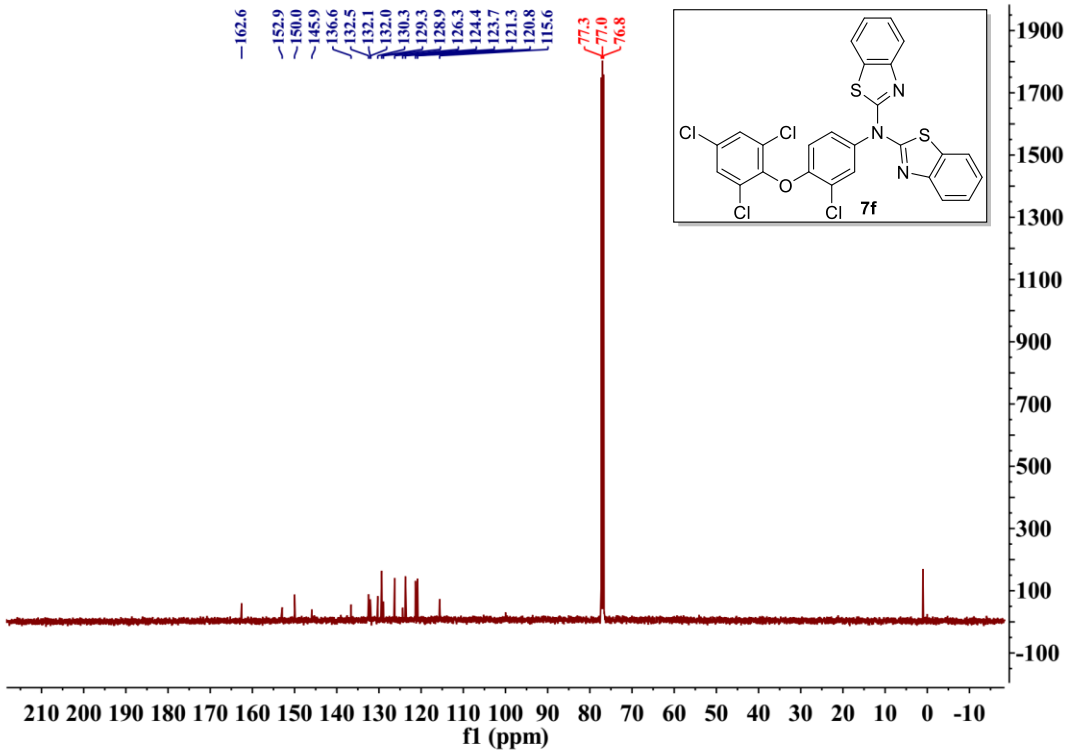
➢ HRMS spectrum for **7e**



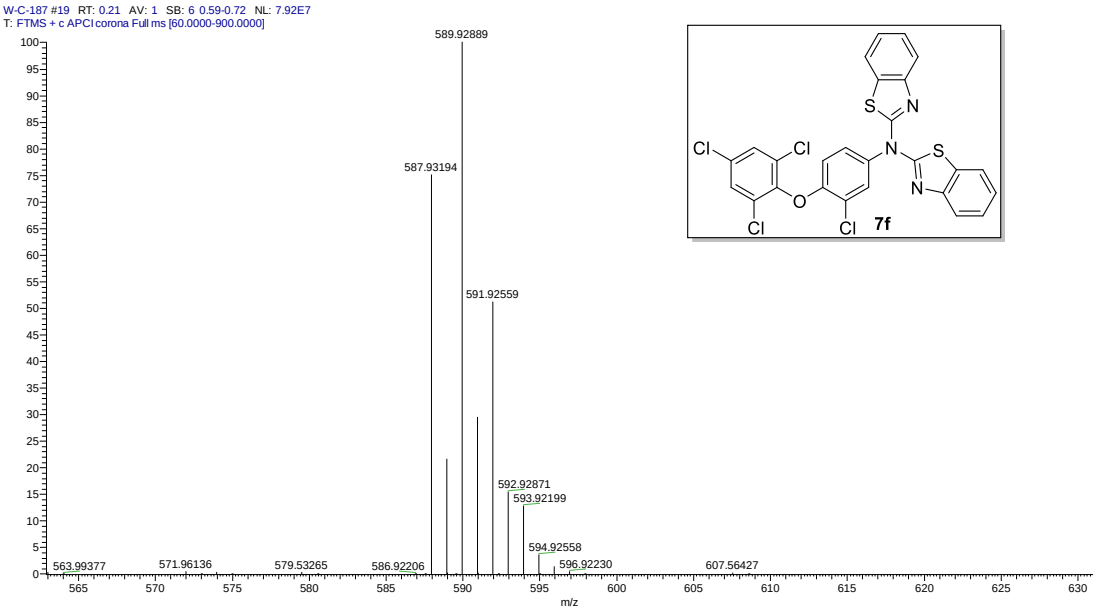
➢ ^{1}H NMR spectrum for **7f**



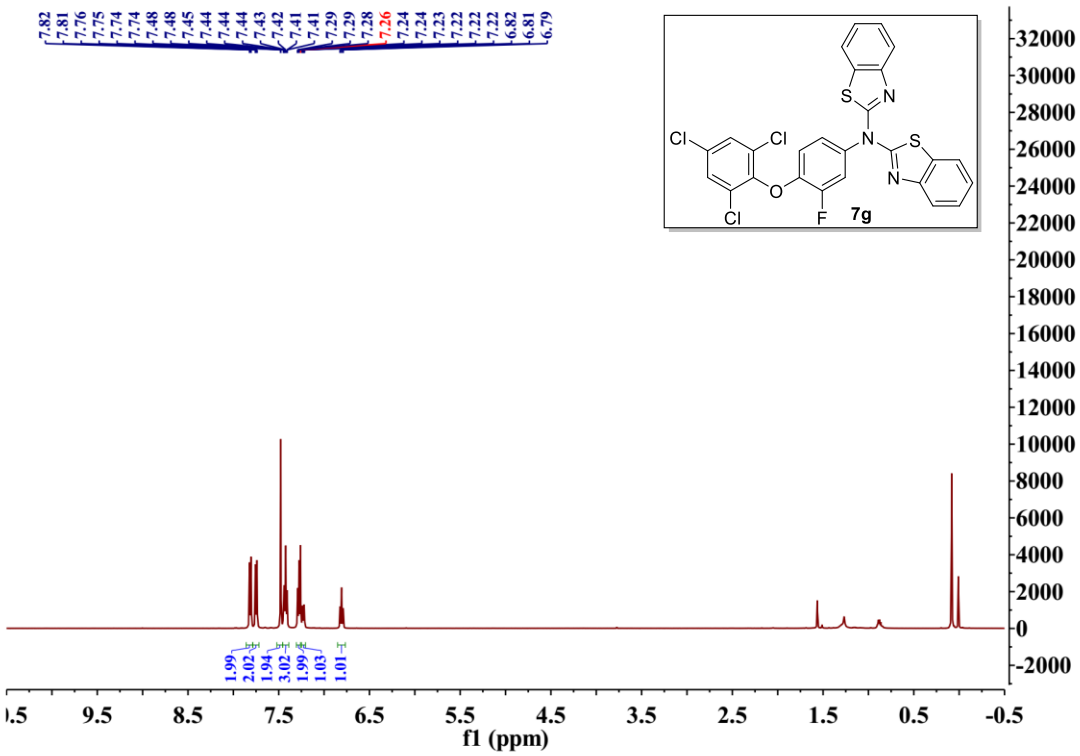
➢ ^{13}C NMR spectrum for **7f**



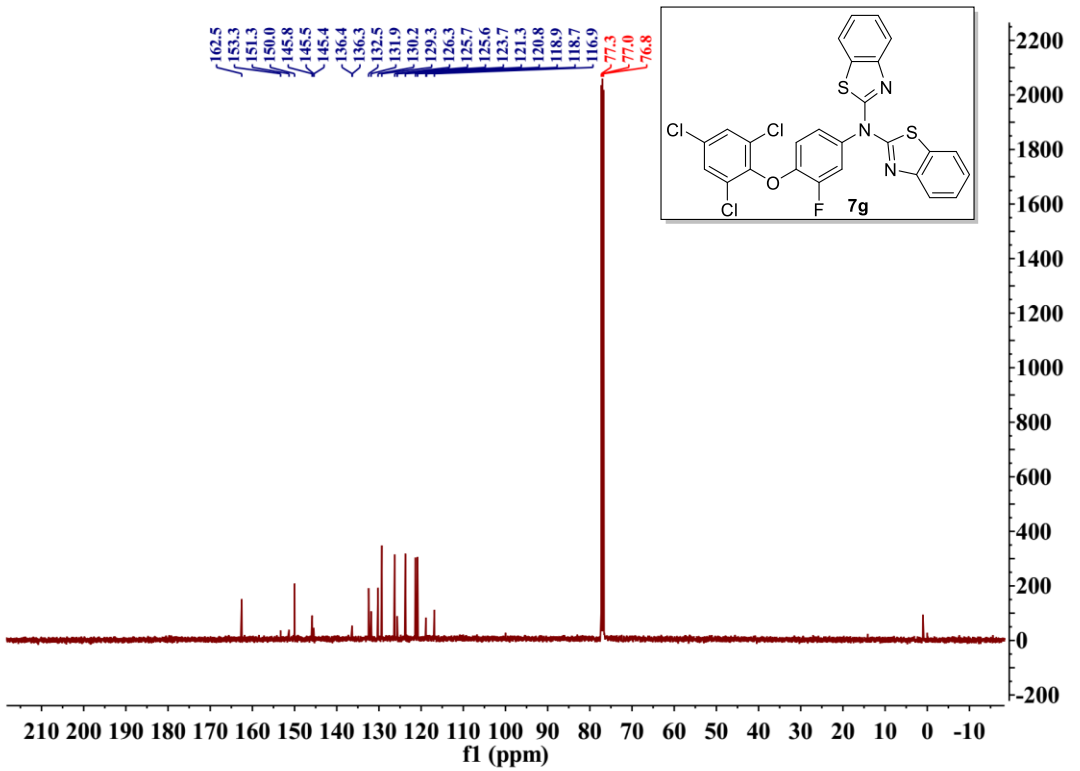
➢ HRMS spectrum for **7f**



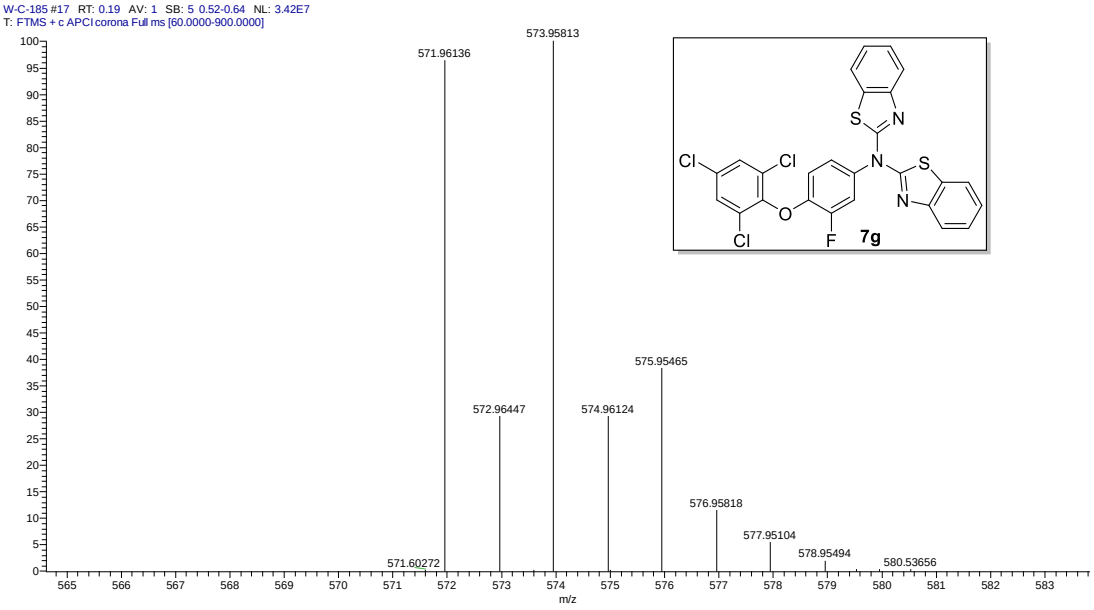
➢ ^{1}H NMR spectrum for **7g**



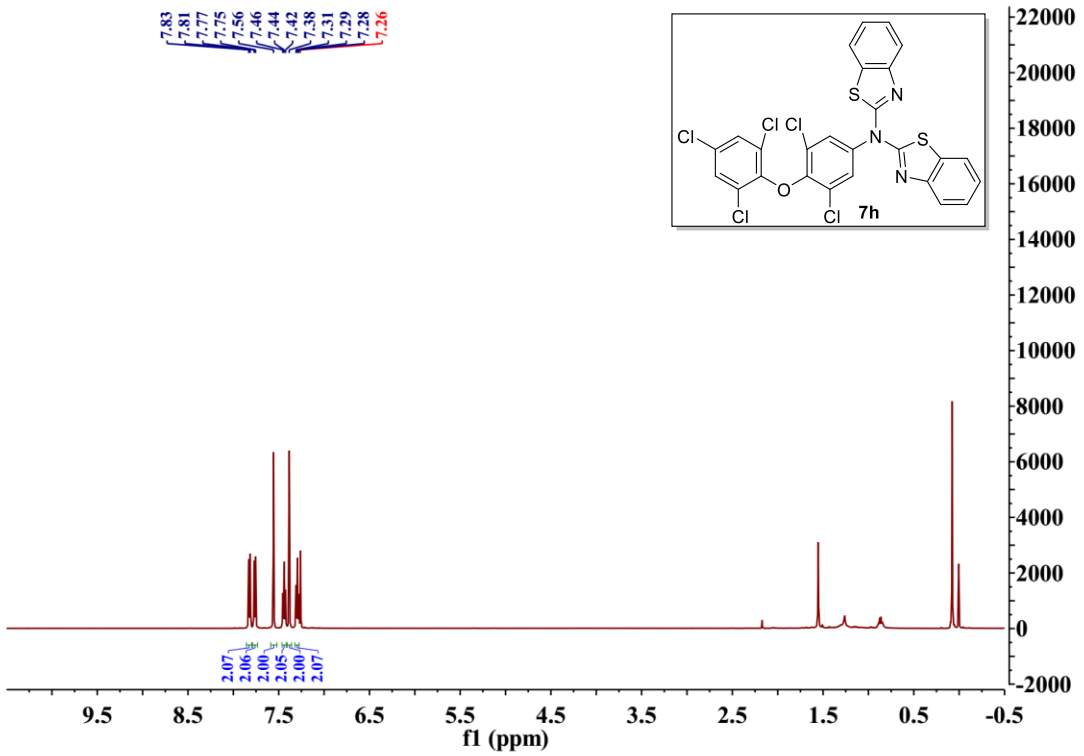
➢ ^{13}C NMR spectrum for **7g**



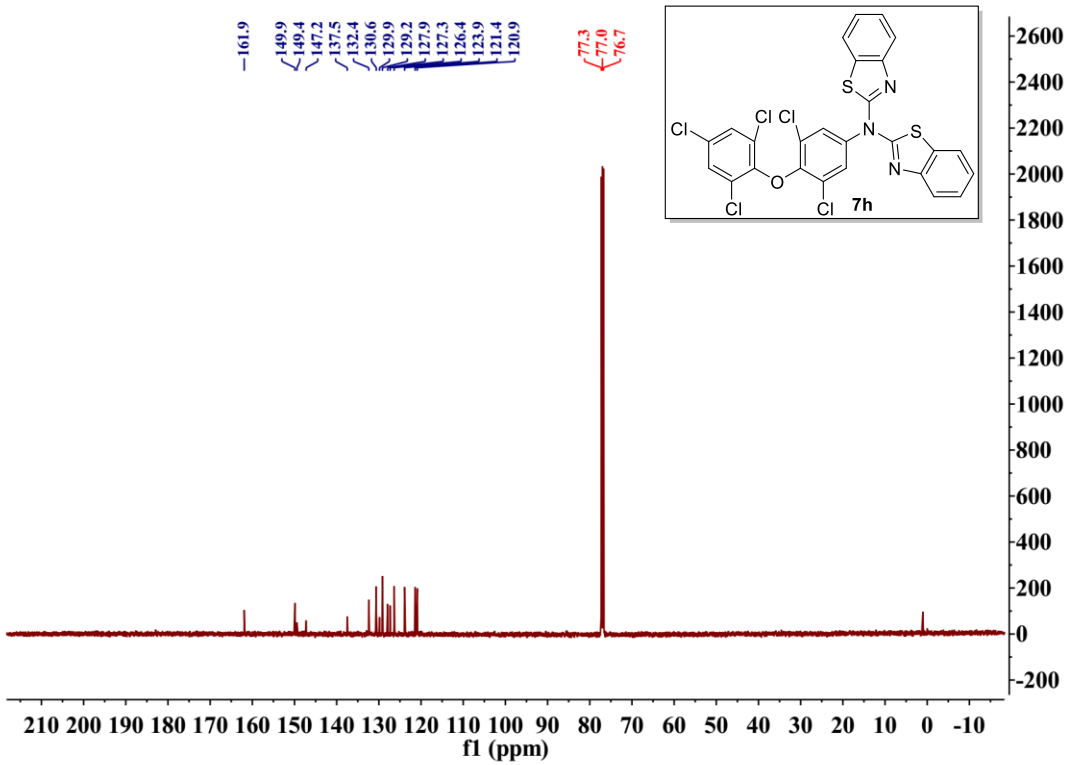
➢ HRMS spectrum for **7g**



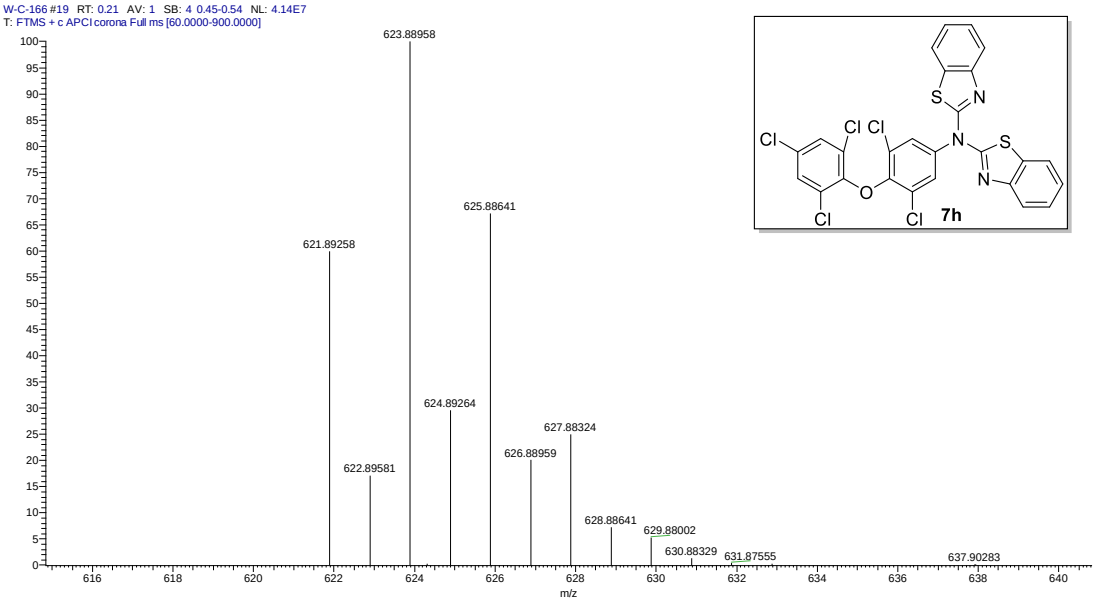
➢ ^{1}H NMR spectrum for **7h**



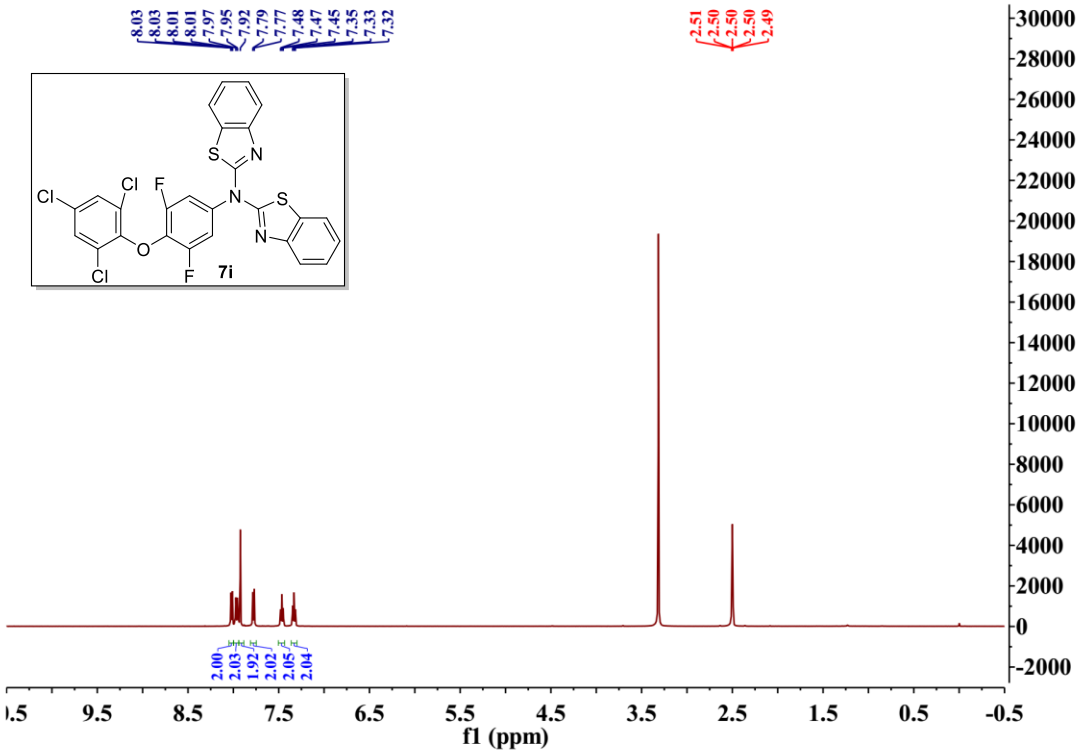
➢ ^{13}C NMR spectrum for **7h**



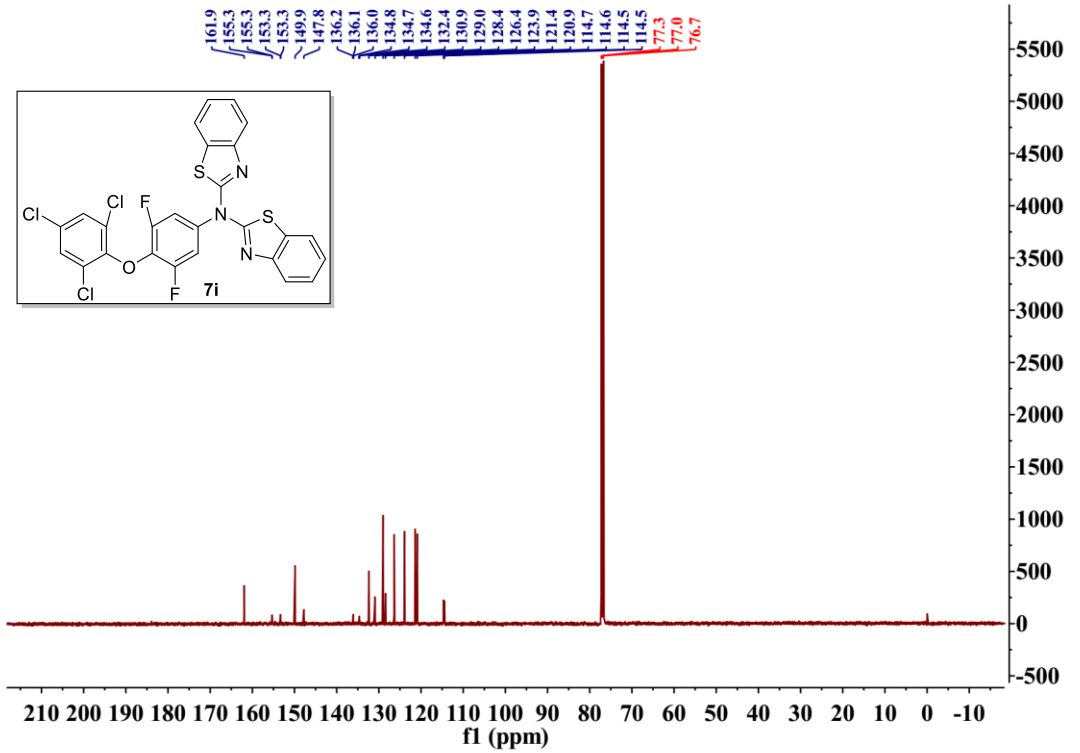
➢ HRMS spectrum for **7h**



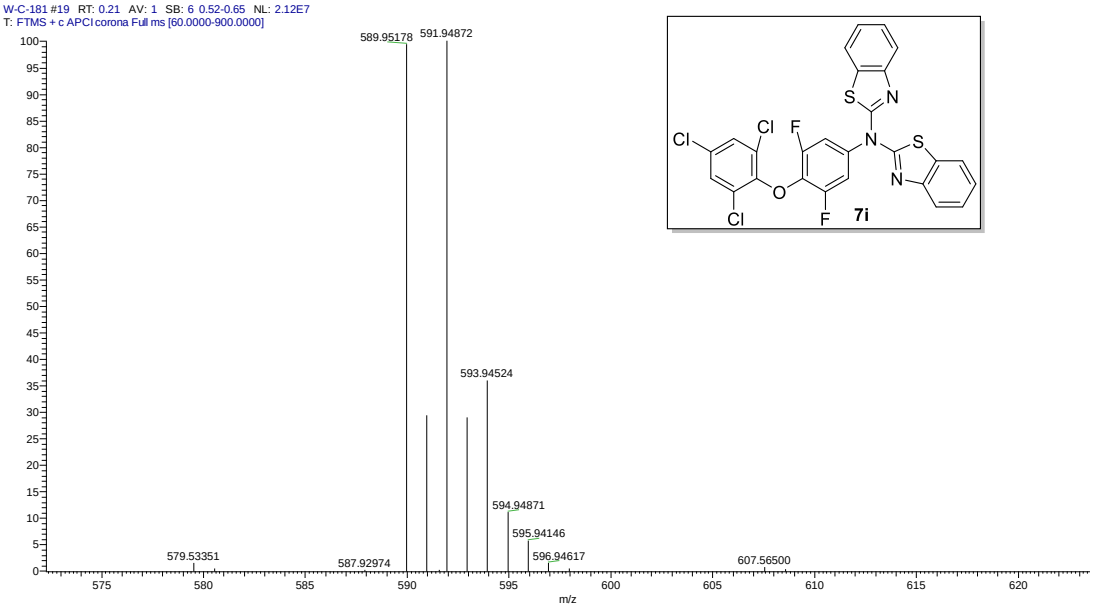
➢ ^{1}H NMR spectrum for **7i**



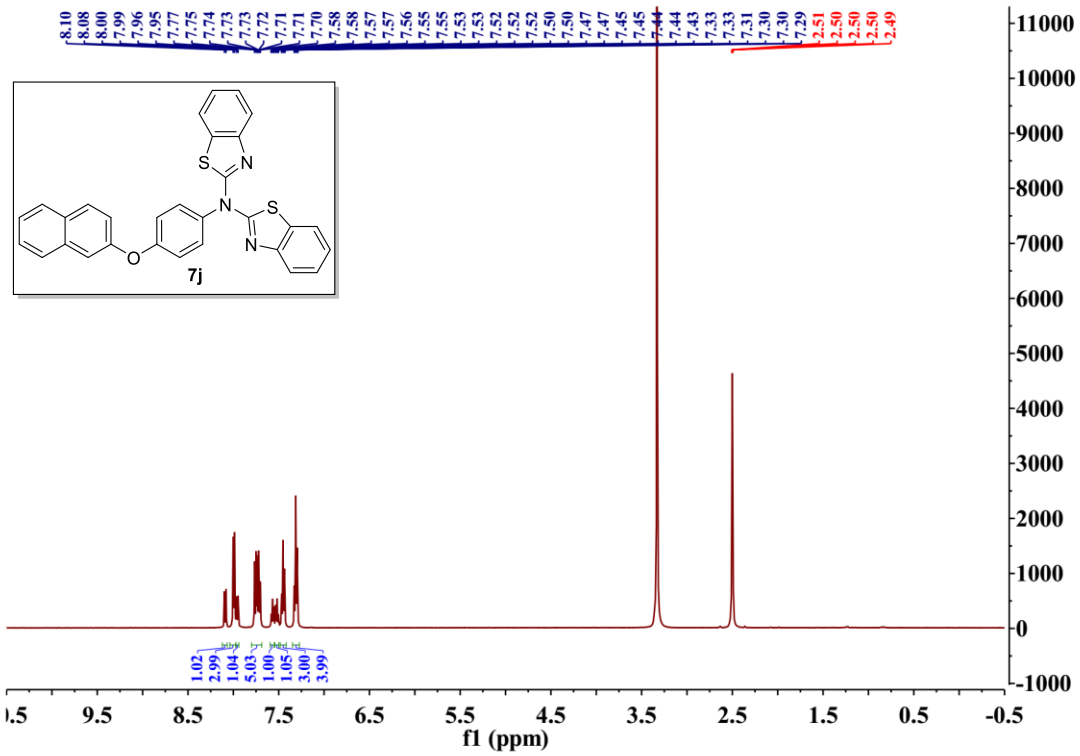
➢ ^{13}C NMR spectrum for **7i**



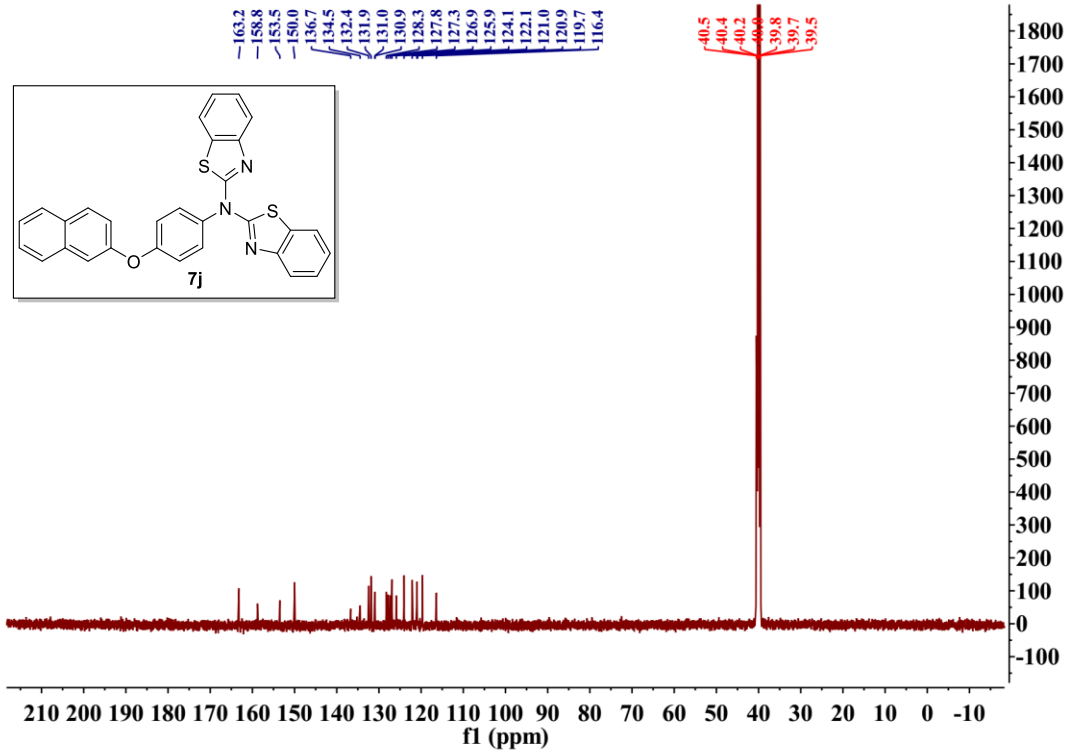
➢ HRMS spectrum for **7i**



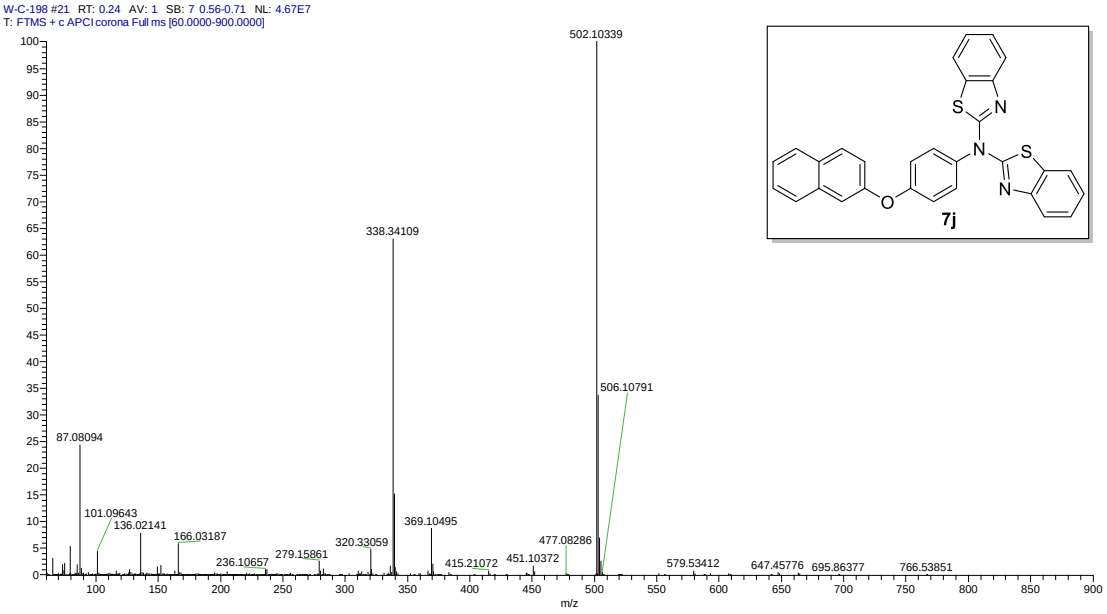
➢ ^{1}H NMR spectrum for **7j**



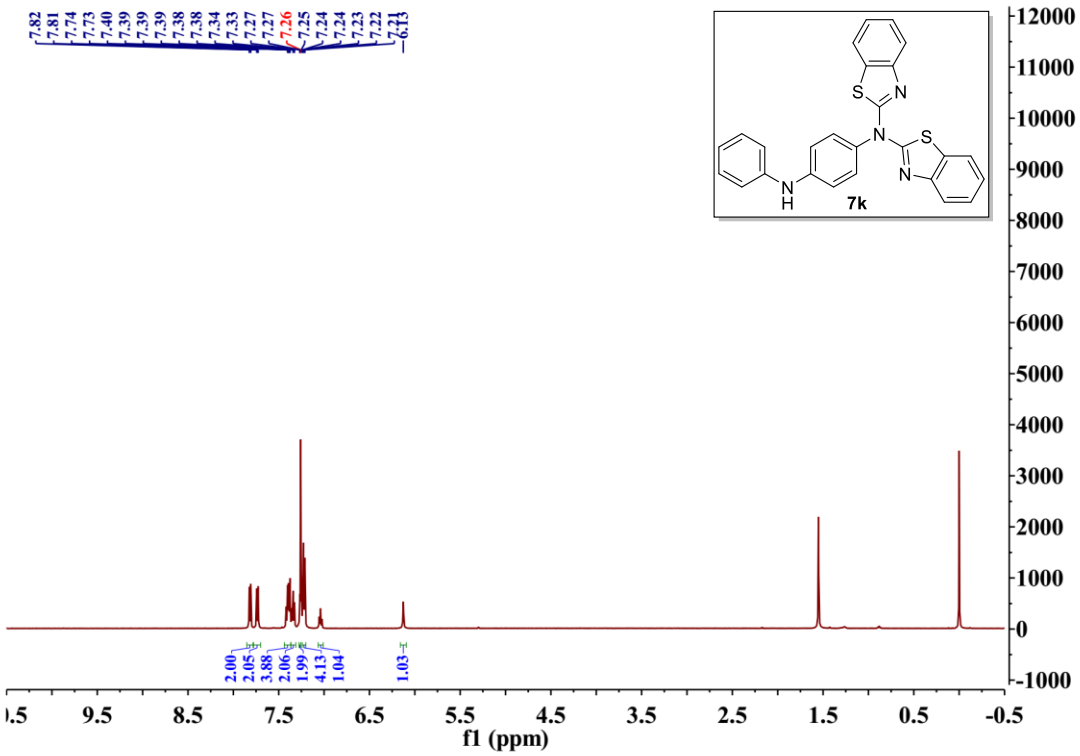
➢ ^{13}C NMR spectrum for **7j**



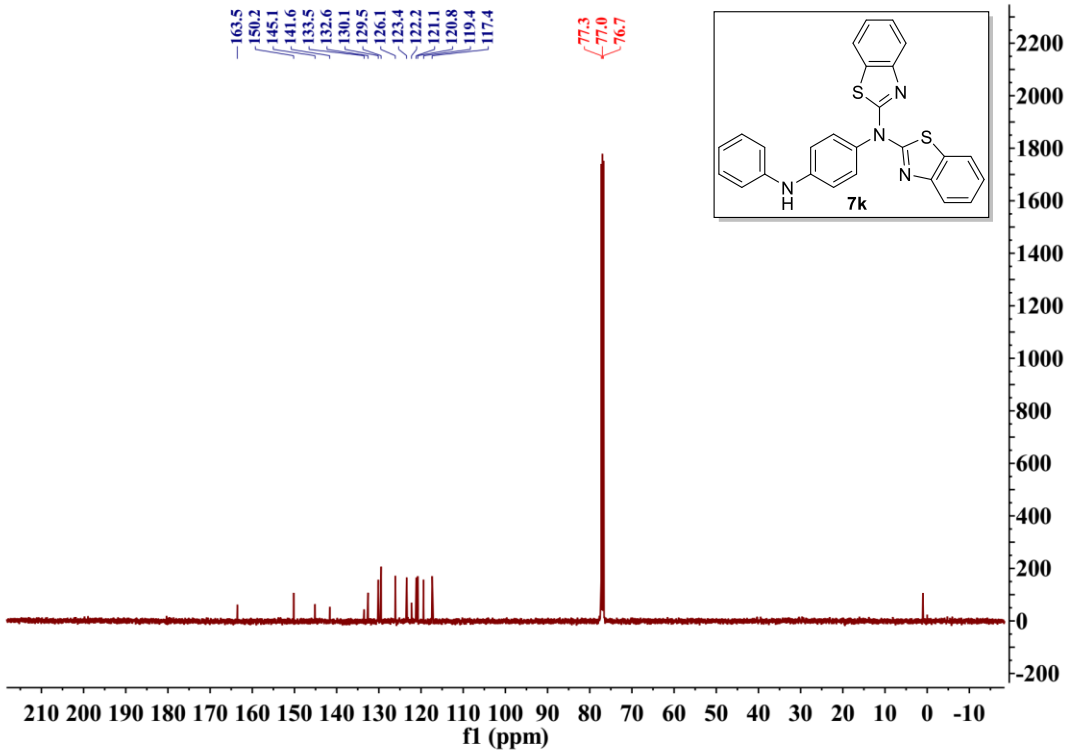
➢ HRMS spectrum for **7j**



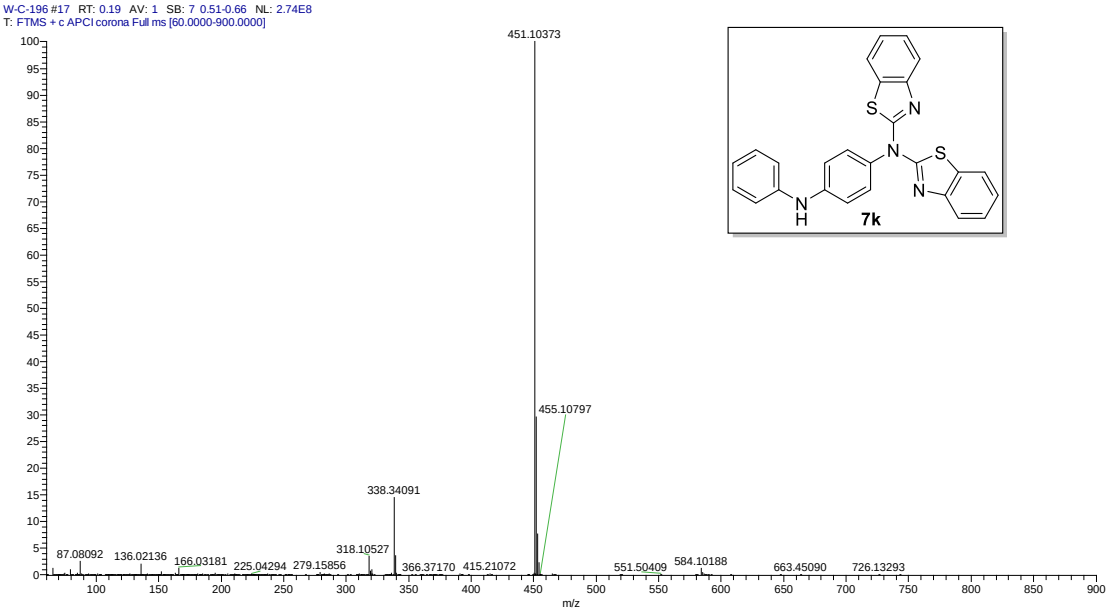
➢ ^{1}H NMR spectrum for **7k**



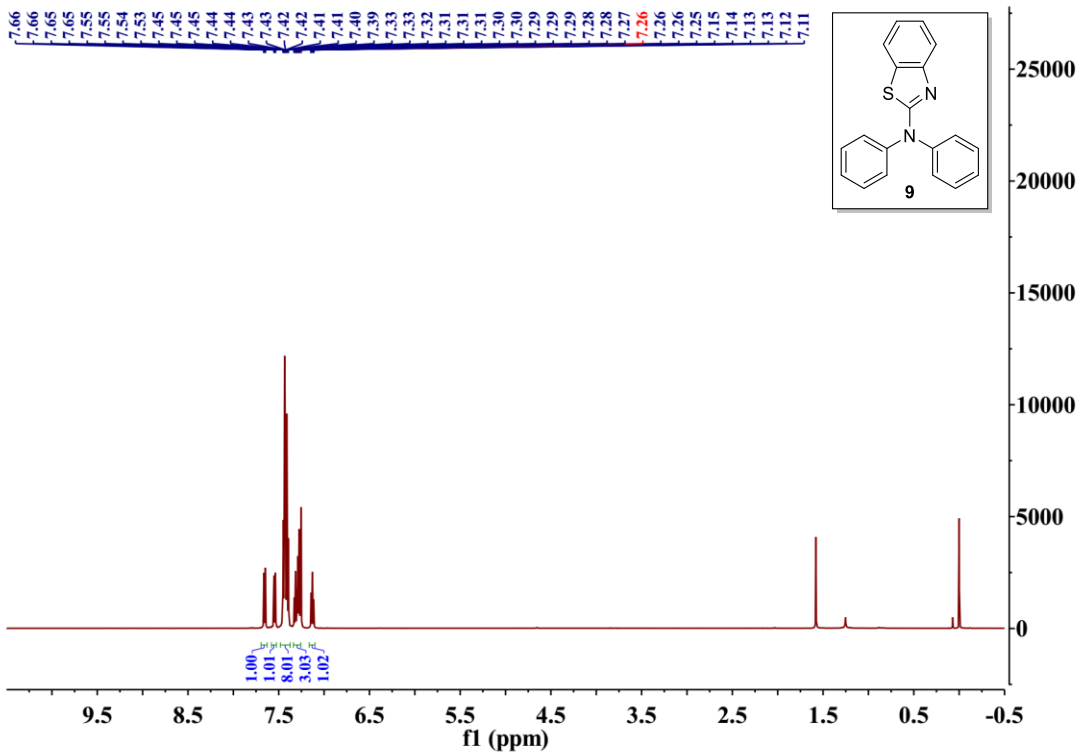
➢ ^{13}C NMR spectrum for **7k**



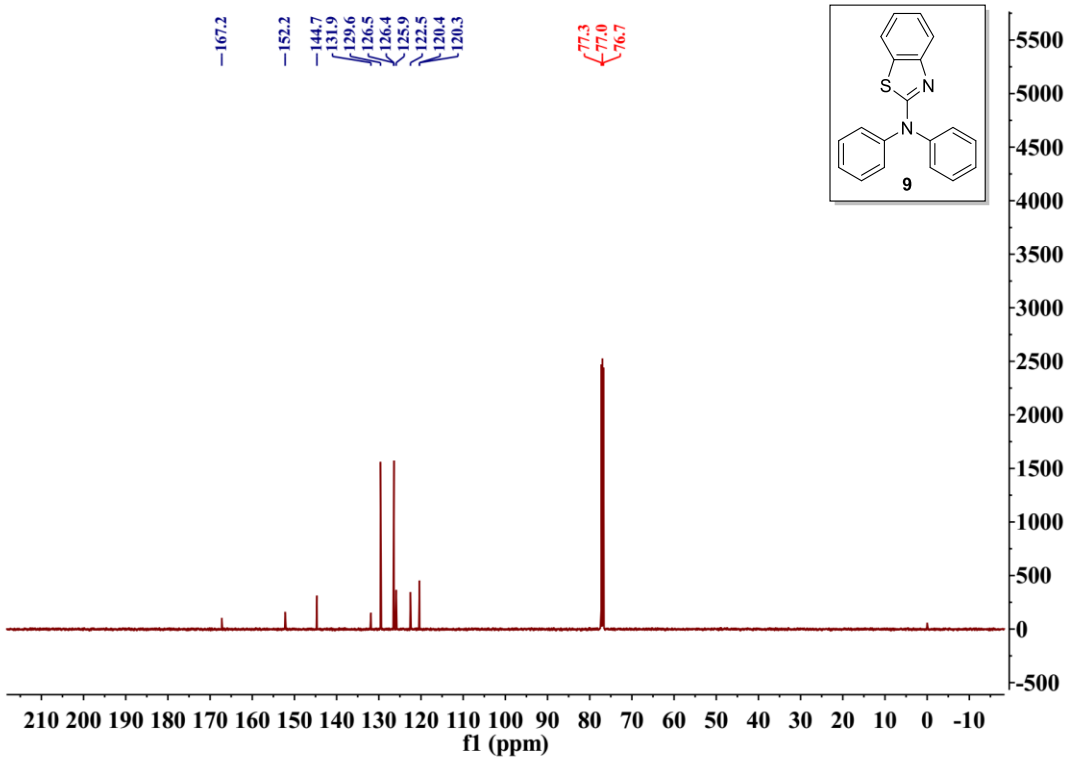
➢ HRMS spectrum for **7k**



➢ ^{1}H NMR spectrum for **9**



➢ ^{13}C NMR spectrum for **9**



➢ HRMS spectrum for **9**