Electronic Supplementary Material (ESI) for ChemComm.

Syntheses of [1,2,4]triazolo[1,5-*a*]benzazoles Enabled by the Transition-Metal-Free Oxidative N-N Bond Formation

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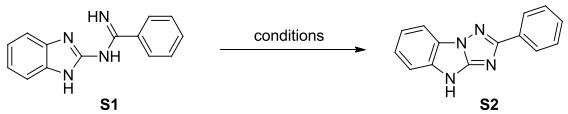
Supporting Information

Table of Contents

1. General information

^{1}H NMR and ^{13}C NMR data were obtained on AVANCE III Bruker 400 M Hz or 500 M Hz nuclear resonance spectrometers. DMSO-d6, $CDCl_3$, acetone-d6, THF-d8 were used as deuterated solvents and tetramethylsilane was used as the internal standard. ^{1}H NMR spectra are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm using the central peak of deuterated solvents as the internal standard. For chromatography, 200-300 mesh silica gel was employed. High resolution mass spectra were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). All other reagents were purchased from commercial sources and used as received.

2. Conditions screening



S1 S2

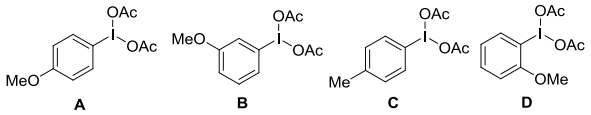
Entry	Condition[a]	Result[b]
1	$NaIO_4$, DCM/H_2O, rt	NR
2	$NaIO_4$, Dioxane/H_2O, rt	NR
3	$K_3[Fe(CN)_6]$, DCM/H_2O, rt	NR
4	$K_3[Fe(CN)_6]$, Dioxane/H_2O, rt	NR
5	IBX, DCM, rt	NR
6	IBX, DMSO, rt	NR
7	MnO_2, DCM, rt	NR
8	DDQ, DCM, rt	NR
9	CAN, DCM/H_2O, rt	NR
10	$Pb(OAc)_4$, benzene, rt	Trace Tm
11	DMP, DCM, rt	NR
12	Me_3COCl, DCM, 0 °C	Decomposed
13	PhIO, DCM, rt	Trace Tm
14	$PhIF_2$, DCM, rt	mix
15	PIDA, DCM, rt	17%
16	PIDA, toluene, rt	17%
17	PIDA, isopropyl alcohol, rt	12%
18	PIFA, DCM, rt	<10%
19	PIDA, HFIP, rt	Decomposed

20	PIDA, MeOH, rt	19%
21	**A**, MeOH, rt	32%
22	**B**, MeOH, rt	18%
23	**C**, MeOH, rt	11%
24	**D**, MeOH, rt	32%
25	n-BuLi, I_2, THF, -78 °C to rt	NR
26	n-BuLi, $FeCl_3$, THF/DMF, -78 °C to rt	NR
27	n-BuLi, $CuCl_2$, THF/DMF, -78 °C to rt	Decomposed
28	n-BuLi, Cu(2-ethylhexanoate), THF, -78 °C to rt	Decomposed
29	$K_2S_2O_8$, $AgNO_3$, MeCN/H_2O, 0 °C to rt	Mix
30	KOtBu (4 equ.), NBS, THF, -40 °C	Mix
31	KOtBu (4 equ.), NBS, THF, -78 °C	66%
32	KOtBu (4 equ.), NCS, THF, -78 °C	100% (99%[c])
33	KOtBu (3 equ.), NCS, THF, -78 °C	52%
34	NaOtBu (4 equ.), NCS, THF, -78 °C	16%

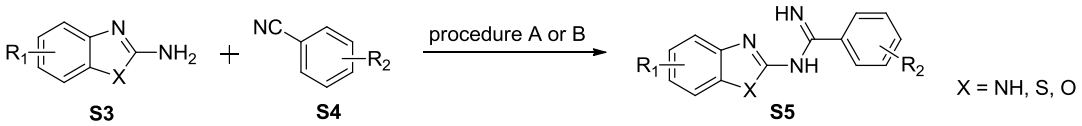
[a] General condition: **S1** (0.1 mmol), oxidant (0.12 mmol), solvent (2 mL);

[b] NMR yield with 1,3,5-Trimethoxybenzene as internal standard.

[c] Isolated yield



3. General procedure for substrate synthesis



3.1 General procedure A

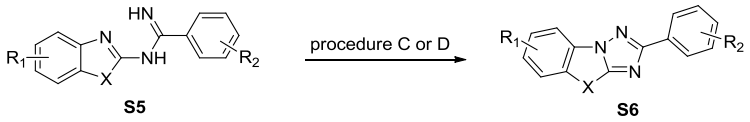
A mixture of 2-aminobenzimidazole/2-aminobenzoxazole/2-aminobenzothizole **S3** (1 mmol), benzonitrile **S4** (1 mmol) and anhydrous tin tetrachloride (3 mmol) in a sealed tube was heated at 130 °C under argon for 24 h. The mixture was then stirred at room temperature and dispersed into the ethyl acetate. The obtained ethyl acetate solution was poured into the ice cold aq. 20% NaOH gradually, and the resulting mixture was extracted with ethyl acetate (20 mL × 3). The organic layers were combined together, washed with water, brine, and dried over Na_2SO_4 successively. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography

on silica gel and eluted with petroleum ether–ethyl acetate as eluent to provide the amidine **S5**.

3.2 General procedure B

In a sealed tube, a solution of 2-aminobenzimidazole/2-aminobenzoxazole/2-aminobenzothizole **S3** (1 mmol), benzonitrile **S4** (1 mmol) and anhydrous tin tetrachloride (3 mmol) in toluene (2 mL) was heated at 130 °C for 24 h under argon. The mixture was then stirred at room temperature and diluted with ethyl acetate. The obtained ethyl acetate solution was poured into the ice cold aq. 20% NaOH gradually, and the resulting mixture was extracted with ethyl acetate (20 mL × 3). The organic solvent extracts were combined together, washed with water, brine, and dried over Na_2SO_4 successively. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate as eluent to provide the amidine **S5**.

4. General procedure for N-N bond formation



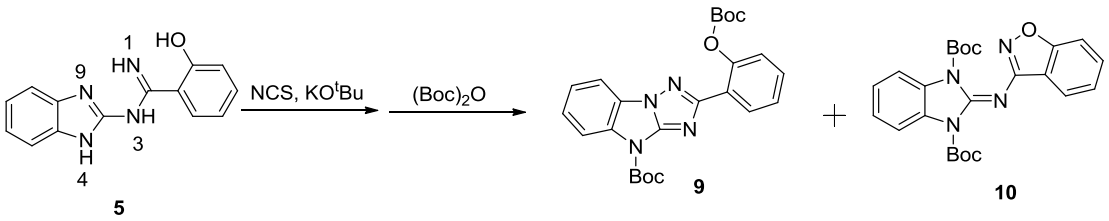
4.1 General procedure C

To a flame-dried 10 mL flask with a magnet, was added the amidine **S5** (0.1 mmol) and KO*t*Bu (0.4 mmol) under argon. The flask was cooled in a dry ice-acetone bath, and THF (2 mL) was then added with stirring. After 1 h stirring at same temperature, a solution of NCS (0.12 mmol) in THF (2 mL) was added and the result mixture was stirred until it finished by TLC monitor (about 0.5 ~ 1 h). The reaction was then quenched with saturated aqueous NH_4Cl (1 mL) and moved to room temperature. The system was diluted with ethyl acetate, washed with water, brine and dried over Na_2SO_4 successively. The dried solution was concentrated in vacuo to 2 mL, filtrated and washed with a small amount of ethyl acetate to obtain a large portion of the final product. The mother liquid was then purified by a short silica gel column chromatography to provide another portion of the final product. The two portions were combined together to afford **S6**.

4.2 General procedure D

To a flame-dried 10 mL flask with a magnet, was added the amidine **S5** (0.1 mmol) and KO*t*Bu (0.4 mmol) under argon. The flask was cooled in a dry ice-acetone bath, and THF (2 mL) was then added with stirring. After 0.5 h stirring at same temperature, a solution of NCS (0.12 mmol) in THF (2 mL) was added and the result mixture was stirred more 0.5 ~ 1 h. The reaction was then moved to 60 ^{o}C oil bath and stirred 20 min to 1 h until it finished by TLC monitor. And then, the mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl (1 mL). The system was diluted with ethyl acetate, washed with water, brine and dried over Na_2SO_4 successively. After evaporation of the solvent under reduced pressure, residue was subjected to column chromatography on silica gel and eluted with petroleum ether–ethyl acetate as eluent to afford the product **S6**.

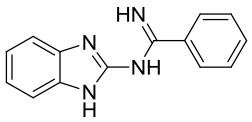
4.3 Procedure for mechanistic study



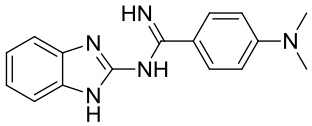
To a flame-dried 10 mL flask with a magnet, was added the amidine **S5** (0.1 mmol) and KO*t*Bu (0.5 mmol) under argon. The flask was cooled in a dry ice-acetone bath, and THF (1.5 mL) was then added with stirring. After 1 h stirring, a solution of NCS (0.15 mmol) in THF (1.5 mL) was added and the result mixture was stirred for 30 min under same temperature. A solution of di-*tert*-butyl dicarbonate (0.5 mmol) in THF (1 mL) was then added slowly, and the result mixture was moved to room temperature. After stirring at room temperature for 6 h, the reaction was quenched with saturated aqueous NH_4Cl (1 mL). The system was diluted with ethyl acetate, washed with water, brine and dried over Na_2SO_4 successively. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on a silica gel and eluted with PE/Acetone (19:1) as eluent to provide the products **9** (9.1 mg) as a white solid in 20% yield and **10** (12.0 mg) as a brown solid in 27% yield.

5. Characterization of compounds

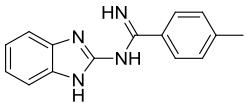
5.1 Characterization of Imidamides



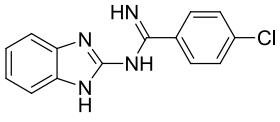
***N*-(1H-benzo[*d*]imidazol-2-yl)benzimidamide (2a).** According to the general procedure A, the reaction was finished in 24 h, and **2a** was obtained as a white solid in 42% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.89 (br, 1H), 10.43 (br, 1H), 8.65 (br, 1H), 8.09 (m, 2H), 7.58~7.47 (m, 4H), 7.28 (m, 1H), 7.08 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm):159.9, 157.6, 141.8, 135.2, 132.0, 130.9, 128.3, 127.2, 120.9, 120.6, 116.8, 109.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{13}N_4$: 237.1130, found: 237.1135. M. P. 225 °C.



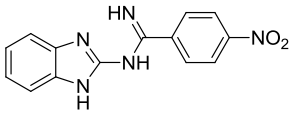
***N*-(1H-benzo[*d*]imidazol-2-yl)-4-(dimethylamino)benzimidamide (2b).** According to the general procedure B, the reaction was finished in 24 h, and **2b** was obtained as a yellow solid in 47% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.73 (br, 1H), 10.33 (br, 1H), 8.34 (br, 1H), 8.00 (d, *J* = 8 Hz, 2H), 7.45 (m, 1H), 7.24 (m, 1H), 7.05 (m, 2H), 6.78 (d, *J* = 8 Hz, 2H), 2.99 (s, 6H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm):160.0, 158.1, 152.0, 142.1, 132.0, 128.4, 121.5, 120.5, 120.4, 116.4, 110.9, 109.4, 39.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{16}H_{18}N_5$: 280.1552, found: 280.1557. M. P. 269~276 °C.



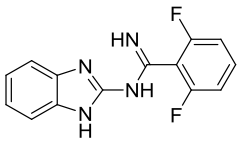
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-4-methylbenzimidamide (2c).** According to the general procedure B, the reaction was finished in 24 h, and **2c** was obtained as a white solid in 43% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.86 (br, 1H), 10.39 (br, 1H), 8.57 (br, 1H), 7.99 (d, *J* = 8 Hz, 2H), 7.46 (br, 1H), 7.33 (d, *J* = 8 Hz, 2H), 7.28 (br, 1H), 7.07(m, 2H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 159.9, 157.7, 141.9, 140.8, 132.3, 132.0, 128.8, 127.1, 120.7, 116.8, 109.6, 20.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{15}N_4$: 251.1286, found: 251.1291. M. P. 248~258 °C.



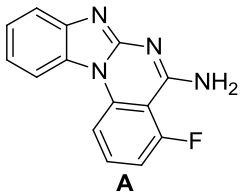
***N*-(1H-benzo[*d*]imidazol-2-yl)-4-chlorobenzimidamide (2d).** According to the general procedure B, the reaction was finished in 24 h, and **2d** was obtained as a white solid in 49% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.92 (br, 1H), 10.42 (br, 1H), 8.70 (br, 1H), 8.10 (d, *J* = 8 Hz, 2H), 7.61 (d, *J* = 8 Hz, 2H), 7.47 (br, 1H), 7.30 (br, 1H), 7.09 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 158.8, 157.3, 141.8, 135.7, 133.9, 132.0, 129.0, 128.4, 121.0, 120.7, 116.9, 109.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{12}ClN_4$: 271.0731, found: 271.0745. M. P. 265~269 ºC.



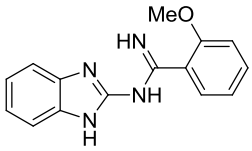
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-4-nitrobenzimidamide (2e).** According to the general procedure B, the reaction was finished in 24 h, and **2e** was obtained as an orange solid in 36% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.06 (br, 1H), 10.51 (br, 1H), 8.91 (br, 1H), 8.40 (d, *J* = 8 Hz, 2H), 8.32 (d, *J* = 8 Hz, 2H), 7.52 (m, 1H), 7.32 (br, 1H), 7.11 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 157.9, 157.0, 148.8, 141.7, 141.0, 132.0, 128.6, 123.5, 121.3, 120.9, 117.1, 109.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{12}N_5O_2$: 282.0982, found: 282.0985. M. P. 263~266 ºC.



***N*-(1*H*-benzo[*d*]imidazol-2-yl)-2,6-difluorobenzimidamide (2f).** According to the general procedure B, the reaction was finished in 24 h, and **2f** was obtained as a white solid in 36% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.96 (br, 1H), 10.31 (br, 1H), 8.89 (br, 1H), 7.61~7.51 (m, 2H), 7.30~7.22 (m, 3H), 7.11 (m, 2H). **^{13}C NMR (126 MHz, DMSO-*d6*)** (δ, ppm): 160.8 (d, *J* = 7.5 Hz), 158.8 (d, *J* = 7.5 Hz), 157.4, 153.8, 142.1, 132.3, 132.0 (t, *J* = 10 Hz), 121.7, 121.3, 117.6, 115.8 (t, *J* = 10 Hz), 112.4 (d, *J* = 5 Hz), 112.3 (d, *J* = 5 Hz), 110.4. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}F_2N_4$: 273.0941, found: 273.0946. M. P. **2f** was cyclized to compound **A** under 196~197 ºC. The M. P. of compound **A** is 336~337 ºC.

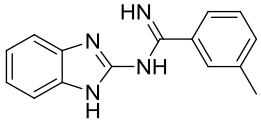


A

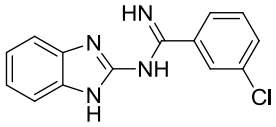


***N*-(1*H*-benzo[*d*]imidazol-2-yl)-2-methoxybenzimidamide (2g).** According to the general procedure B, the reaction was finished in 48 h, and **2g** was obtained as a yellow

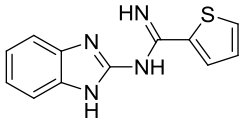
solid in 55% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.81 (br, 1H), 10.49 (br, 1H), 8.42 (br, 1H), 7.97 (dd, *J* = 8 Hz, 4 Hz, 1H), 7.52~7.44 (m, 2H), 7.26 (m, 1H), 7.18 (d, *J* = 8 Hz, 1H), 7.09~7.04 (m, 3H), 3.90 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 159.7, 157.7, 157.4, 141.9, 131.9, 131.8, 130.2, 123.8, 120.8, 120.5, 120.3, 116.7, 112.1, 109.6, 55.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{15}N_4O$: 267.1236, found: 267.1240. M. P. 251~254 °C.



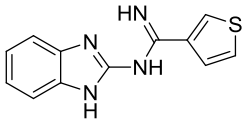
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-3-methylbenzimidamide (2h).** According to the general procedure A, the reaction was finished in 24 h, and **2h** was obtained as a yellow solid in 69% yield. **^{1}H NMR (400 MHz, THF-*d8*)** (δ, ppm): 11.55 (br, 1H), 10.79 (br, 1H), 7.92 (s, 1H), 7.87 (d, *J* = 8 Hz, 1H), 7.83 (br, 1H), 7.46 (br, 1H), 7.34~7.28 (m, 2H), 6.98 (br, 2H), 6.86 (br, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, THF-*d8*)** (δ, ppm): 161.7, 158.6, 143.4, 138.6, 136.9, 133.0, 131.9, 128.8, 128.5, 125.1, 121.2, 117.8, 110.0, 21.3. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{15}N_4$: 251.1287, found: 251.1291. M. P. 205~208 °C.



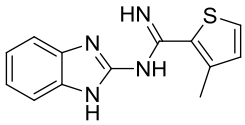
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-3-chlorobenzimidamide (2i).** According to the general procedure A, the reaction was finished in 24 h, and **2i** was obtained as a yellow solid in 67% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.97 (br, 1H), 10.45 (br, 1H), 8.78 (br, 1H), 8.16 (t, *J* = 4 Hz, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.64 (m, 1H), 7.57 (t, *J* = 8 Hz, 1H), 7.50 (br, 1H), 7.30 (br, 1H), 7.10 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 158.3, 157.2, 141.7, 137.1, 133.2, 131.9, 130.7, 130.3, 127.0, 125.8, 121.1, 120.7, 117.0, 109.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{12}ClN_4$: 271.0740, found: 271.0745. M. P. 237~239 °C.



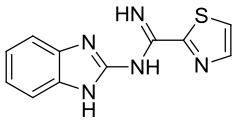
***N*-(1*H*-benzo[*d*]imidazol-2-yl)thiophene-2-carboximidamide (2j).** According to the general procedure B, the reaction was finished in 30 h, and **2j** was obtained as a yellow solid in 78% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.93 (br, 1H), 10.27 (br, 1H), 8.68 (br, 1H), 7.93 (dd, *J* = 4 Hz, 1.2 Hz, 1H), 7.76 (dd, *J* = 4 Hz, 1.2 Hz, 1H), 7.46 (m, 1H), 7.25 (m, 1H), 7.20 (m, 1H), 7.09~7.04 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 157.1, 155.2, 141.9, 140.4, 132.0, 130.8, 128.3, 128.0, 120.9, 120.6, 116.7, 109.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_{11}N_4S$: 243.0695, found: 243.0670. M. P. 287~290 °C.



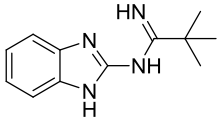
***N*-(1*H*-benzo[*d*]imidazol-2-yl)thiophene-3-carboximidamide (2k).** According to the general procedure B, the reaction was finished in 25 h, and **2k** was obtained as a white solid in 56% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.83 (br, 1H), 10.27 (br, 1H), 8.48 (br, 1H), 8.28 (dd, *J* = 2.8 Hz, 0.8 Hz, 1H), 7.71 (dd, *J* = 4.8 Hz, 0.8 Hz, 1H), 7.65 (dd, *J* = 4.8 Hz, 2.8 Hz, 1H), 7.45 (br, 1H), 7.27 (br, 1H), 7.07 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 157.7, 156.1, 141.9, 138.4, 132.0, 127.6, 126.9, 126.7, 120.8, 120.6, 116.8, 109.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_{11}N_4S$: 243.0696, found: 243.0699. M. P. 265~268 °C.



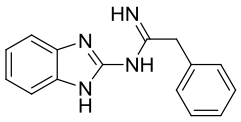
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-3-methylthiophene-2-carboximidamide (2l).** According to the general procedure B, the reaction was finished in 48 h, and **2l** was obtained as a white solid in 45% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.88 (br, 1H), 10.39 (br, 1H), 8.00 (br, 1H), 7.62 (d, *J* = 4.8 Hz, 1H), 7.46 (m, 1H), 7.26 (m, 1H), 7.07 (m, 2H), 7.01 (d, *J* = 4.8 Hz, 1H), 2.54 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 157.1, 156.6, 141.8, 138.6, 133.4, 131.9, 131.9, 127.7, 120.9, 120.6, 116.7, 109.7, 15.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{13}H_{13}N_4S$: 257.0852, found: 257.0855. M. P. 220~225 °C.



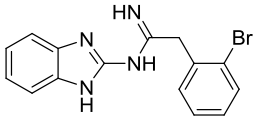
***N*-(1*H*-benzo[*d*]imidazol-2-yl)thiazole-2-carboximidamide (2m).** According to the general procedure B, the reaction was finished in 24 h, and **2m** was obtained as a yellow solid in 40% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.14 (br, 1H), 10.11 (br, 1H), 8.76 (br, 1H), 8.07 (d, *J* = 2.8 Hz, 1H), 8.02 (d, *J* = 2.8 Hz, 1H), 7.52 (m, 1H), 7.30 (m, 1H), 7.11 (m, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 164.3, 156.5, 153.1, 144.0, 141.8, 132.0, 125.1, 121.4, 121.0, 117.1, 110.0. HRMS: m/z: $[M+H]^+$, calculated for $C_{11}H_{10}N_5S$: 244.0649, found: 244.0651. M. P. 272 °C.



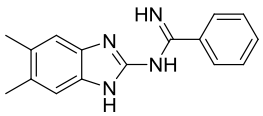
***N*-(1*H*-benzo[*d*]imidazol-2-yl)pivalimidamide (2n).** According to the general procedure A, the reaction was finished in 20 h, and **2n** was obtained as a yellow solid in 37% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.45 (br, 1H), 8.90 (br, 1H), 7.54 (m, 1H), 7.27 (m, 1H), 7.14 (m, 2H), 5.91 (br, 1H), 1.33 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 172.2, 157.9, 141.7, 131.8, 120.4, 116.5, 109.5, 37.6, 28.3. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_{17}N_4$: 217.1444, found: 217.1448. M. P. 242~244 °C.



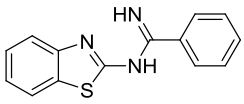
***N*-(1*H*-benzo[*d*]imidazol-2-yl)-2-phenylacetimidamide (2o).** According to the general procedure A, the reaction was finished in 24 h, and **2o** was obtained as a white solid in 84% yield. **^{1}H NMR (400 MHz, THF-*d8*)** (δ, ppm): 11.05 (br, 1H), 10.31 (br, 1H), 7.37 (m, 3H), 7.27 (m, 3H), 7.18 (m, 2H), 6.99 (m, 2H), 3.67 (s, 2H). **^{13}C NMR (101 MHz, THF-*d8*)** (δ, ppm): 165.1, 158.6, 143.5, 138.2, 132.9, 129.6, 128.9, 127.1, 121.1, 121.0, 117.7, 109.8, 44.3. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{15}N_4$: 251.1287, found: 251.1291. M. P. 205~207 ºC.



***N*-(1*H*-benzo[*d*]imidazol-2-yl)-2-(2-bromophenyl)acetimidamide (2p).** According to the general procedure B, the reaction was finished in 24 h, and **2p** was obtained as a yellow solid in 69% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.67 (br, 1H), 10.08 (br, 1H), 8.29 (br, 1H), 7.63 (dd, *J* = 8 Hz, 4Hz, 1H), 7.45~7.34 (m, 3H), 7.22 (m, 2H), 7.03 (m, 2H), 3.81 (s, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 163.5, 157.5, 141.7, 136.7, 132.3, 131.9, 131.4, 128.6, 127.7, 124.5, 120.5, 116.6, 109.6, 42.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{14}BrN_4$: 329.0389, found: 329.0396. M. P. 186~191 ºC.

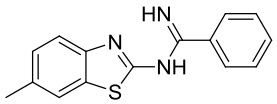


***N*-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)benzimidamide (2q).** According to the general procedure B, the reaction was finished in 30 h, and **2q** was obtained as a yellow solid in 44% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 11.66 (br, 1H), 10.40 (br, 1H), 8.52 (br, 1H), 8.07 (m, 2H), 7.57~7.49 (m, 3H), 7.16 (br, 2H), 2.28 (s, 6H). **^{13}C NMR (101 MHz, THF-*d8*)** (δ, ppm): 161.1, 157.9, 141.9, 137.2, 131.4, 131.1, 129.6, 129.1, 128.9, 127.9, 118.3, 110.6, 20.2. HRMS: m/z: $[M+H]^+$, calculated for $C_{16}H_{17}N_4$: 265.1444, found: 265.1448. M. P. 253~254 ºC.

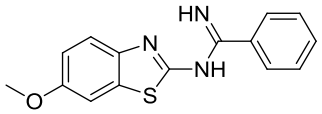


***N*-(benzo[*d*]thiazol-2-yl)benzimidamide (3a).** According to the general procedure A, the reaction was finished in 7 h, and **3a** was obtained as a white solid in 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.62 (br, 1H), 7.96 (m, 2H), 7.77 (m, 2H), 7.56~7.48 (m, 3H), 7.39 (m, 1H), 7.26 (m, 1H), 6.39 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 174.0, 160.2, 151.4, 135.2, 132.8, 131.6, 128.8, 127.2, 125.7, 123.6, 121.2, 120.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{12}N_3S$: 254.0744, found:

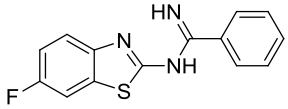
254.0746. M. P. 185 ºC.



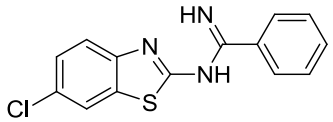
***N*-(6-methylbenzo[*d*]thiazol-2-yl)benzimidamide (3b).** According to the general procedure A, the reaction was finished in 7 h, and **3b** was obtained as a yellow solid in 89% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.56 (br, 1H), 7.95 (m, 2H), 7.66 (d, *J* = 8 Hz, 1H), 7.56 (s, 1H), 7.53~7.47 (m, 3H), 7.21 (dd, *J* = 8 Hz, 4Hz, 1H), 6.34 (br, 1H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 173.2, 159.9, 149.4, 135.2, 133.6, 132.9, 131.5, 128.8, 127.1, 121.1, 120.5, 21.5. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{14}N_3S$: 268.0901, found: 268.0903. M. P. 190~192 ºC.



***N*-(6-methoxybenzo[*d*]thiazol-2-yl)benzimidamide (3c).** According to the general procedure A, the reaction was finished in 36 h, and **3c** was obtained as a yellow solid in 76% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.46 (br, 1H), 7.95 (m, 2H), 7.66 (d, *J* = 8 Hz, 1H), 7.55~7.46 (m, 3H), 7.26 (d, *J* = 4 Hz, 1H), 7.00 (dd, *J* = 8 Hz, 4 Hz, 1H), 6.32 (br, 1H), 3.87 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 172.0, 159.6, 156.6, 145.7, 135.2, 134.0, 131.4, 128.8, 127.1, 121.5, 114.5, 104.4, 55.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{14}N_3OS$: 284.0847, found: 284.0852. M. P. 175~179 ºC.

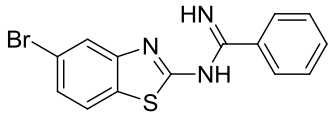


***N*-(6-fluorobenzo[*d*]thiazol-2-yl)benzimidamide (3d).** According to the general procedure A, the reaction was finished in 58 h, and **3d** was obtained as a yellow solid in 79% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.46 (br, 1H), 7.95 (m, 2H), 7.70 (q, *J* = 4 Hz, 1H), 7.56~7.47 (m, 3H), 7.45 (dd, *J* = 8 Hz, 4 Hz, 1H), 7.12 (dt, *J* = 8 Hz, 4 Hz, 1H), 6.39 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 173.6, 160.1, 159.5 (d, *J* = 240 Hz), 147.9, 135.0, 133.8 (d, *J* = 10 Hz), 131.6, 128.8, 127.1, 121.6 (d, *J* = 9 Hz), 113.9 (d, *J* = 20 Hz), 107.6 (d, *J* = 20 Hz). HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}FN_3S$: 272.0647, found: 272.0652. M. P. 198~201 ºC.

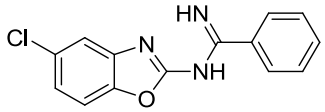


***N*-(6-chlorobenzo[*d*]thiazol-2-yl)benzimidamide (3e).** According to the general procedure A, the reaction was finished in 36 h, and **3e** was obtained as a yellow solid in 78% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.56 (br, 1H), 7.95 (m, 2H), 7.72 (d, *J* = 4 Hz, 1H), 7.67 (d, *J* = 8 Hz, 1H), 7.55~7.48 (m, 3H), 7.35 (dd, *J* = 8 Hz, 4 Hz, 1H), 6.42 (br, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** (δ, ppm): 174.3, 160.4, 150.0, 134.9,

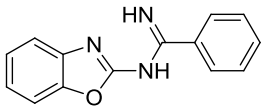
134.0, 131.7, 129.1, 128.9, 127.1, 126.3, 121.6, 120.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}ClN_3S$: 288.0351, found: 288.0357. M. P. 214~217 °C.



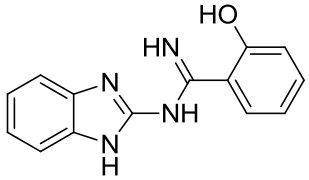
***N*-(5-bromobenzo[*d*]thiazol-2-yl)benzimidamide (3f).** According to the general procedure A, the reaction was finished in 20 h, and **3f** was obtained as a yellow solid in 35% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.52 (br, 1H), 7.96 (m, 2H), 7.92 (d, *J* = 4 Hz, 1H), 7.60 (d, *J* = 8 Hz, 1H), 7.57~7.48 (m, 3H), 7.37 (dd, *J* = 8 Hz, 4 Hz, 1H), 6.45 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 175.2, 160.6, 152.6, 134.9, 131.8, 131.6, 128.9, 127.2, 126.5, 123.7, 122.3, 119.1. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}BrN_3S$: 331.9849, found: 331.9852. M. P. 210~218 °C.



***N*-(5-chlorobenzo[*d*]oxazol-2-yl)benzimidamide (3g).** According to the general procedure A, the reaction was finished in 30 h, and **3g** was obtained as a white solid in 57% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.25 (br, 1H), 7.98 (m, 2H), 7.60~7.49 (m, 4H), 7.35 (d, *J* = 8 Hz, 1H), 7.20 (dd, *J* = 8 Hz, 4 Hz, 1H), 6.65 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 166.3, 163.3, 146.3, 142.8, 134.2, 132.2, 129.2, 128.9, 127.1, 123.5, 117.8, 110.6. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}ClN_3O$: 272.0583, found: 272.0585. M. P. 231~233 °C.



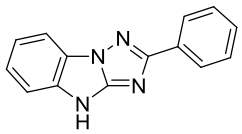
***N*-(benzo[*d*]oxazol-2-yl)benzimidamide (3h).** According to the general procedure A, the reaction was finished in 24 h, and **3h** was obtained as an orange solid in 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 10.33 (br, 1H), 8.00 (m, 2H), 7.59~7.49 (m, 4H), 7.45 (dd, *J* = 8 Hz, 4 Hz, 1H), 7.29~7.21 (m, 2H), 6.58 (br, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 165.3, 162.8, 147.7, 141.6, 134.5, 132.0, 128.8, 127.1, 123.8, 123.4, 117.8, 109.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{12}N_3O$: 238.0970, found: 238.0975. M. P. 183~188 °C.



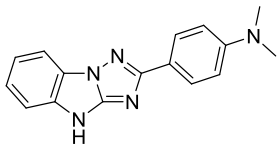
N-(1H-benzo[d]imidazol-2-yl)-2-hydroxybenzimidamide (5). According to the general procedure A, the reaction was finished in 24 h, and **5** was obtained as a light yellow solid in 35% yield. **^{1}H NMR (400 MHz, DMSO)** (δ, ppm): 14.73 (br, 1H),

12.29 (s, 1H), 10.64 (s, 1H), 8.95 (s, 1H), 7.96 (dd, *J* = 8 Hz, 4 Hz, 1H), 7.52 (m, 1H), 7.43~7.39 (m, 1H), 7.35 (m, 1H), 7.15~7.10 (m, 2H), 6.94~6.90 (m, 2H). **^{13}C NMR (126 MHz, DMSO)** (δ, ppm): 161.4, 160.9, 154.5, 141.5, 133.4, 131.8, 127.2, 121.5, 121.1, 118.1, 118.1, 117.1, 114.3, 110.1. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{13}N_4O$: 253.1084, found: 253.1084. M. P. 301~303 °C.

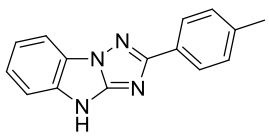
5.2 Characterization of Trizoles



2-phenyl-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1a). According to the general procedure C, the reaction was finished in 100 min, and **1a** was obtained as an orange solid in 99% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.42 (br, 1H), 8.13 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.53 ~ 7.43 (m, 3 H), 7.38 (m, 1H), 7.32 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 164.2, 154.0, 134.1, 131.8, 129.3, 128.7, 126.1, 124.0, 123.7, 121.3, 113.0, 110.4. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{11}N_4$: 235.0974, found: 235.0978. M. P. 330 °C.

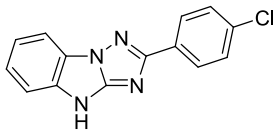


2-(4-*N*,*N*-dimethylanilinephenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1b). According to the general procedure C, the reaction was finished in 120 min, and **1b** was obtained as a brown solid in 94% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.27 (br, 1H), 7.94 (m, 2 H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.34 (m, 1H), 7.29 (m, 1H), 6.80 (m, 2H), 2.98 (s, 6H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 165.0, 154.0, 150.9, 134.0, 127.1, 123.9, 123.4, 121.1, 119.4, 112.8, 111.8, 110.0, 39.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{16}H_{16}N_5$: 278.1398, found: 278.1400. M. P. decomposed at 330 °C.

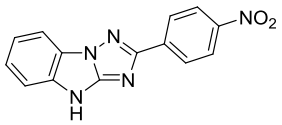


2-(4-methylphenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1c). According to the general procedure C, the reaction was finished in 100 min, and **1c** was obtained as a white solid in 92% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.38 (br, 1H), 8.02 (d, *J* = 8 Hz, 2H), 7.83 (d, *J* = 8 Hz, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.37 (m, 1H), 7.32 (m, 3H). 2.37 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 164.3, 154.0, 138.8, 134.1, 129.3, 129.1, 126.0, 123.9, 123.8, 121.3, 112.9, 110.3, 20.9. HRMS:

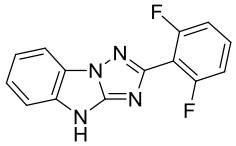
m/z: $[M+H]^+$, calculated for $C_{15}H_{13}N_4$: 249.1131, found: 249.1135. M. P. 331~332 ºC.



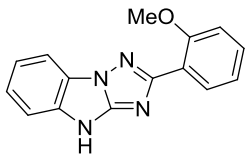
2-(4-chlorophenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1d). According to the general procedure C, the reaction was finished in 120 min, and **1d** was obtained as an orange solid in 93% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.50 (br, 1H), 8.13 (m, 2H), 7.86 (d, *J* = 8 Hz, 1H), 7.57 (m, 3H), 7.40 (m, 1H), 7.33 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 163.1, 154.0, 134.2, 133.9, 130.6, 128.8, 127.8, 124.1, 123.7, 121.4, 113.0, 110.5. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{10}ClN_4$: 269.0585, found: 269.0588. M. P. decomposed at 326~333 ºC.



2-(4-nitrophenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1e). According to the general procedure C, the reaction was finished in 100 min, and **1e** was obtained as a yellow solid in 93% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.63 (br, 1H), 8.37 (br, 4H), 7.91 (d, *J* = 8 Hz, 1H), 7.60 (d, *J* = 8 Hz, 1H), 7.43 (m, 1 H), 7.36 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 162.2, 154.1, 147.6, 137.8, 134.3, 127.0, 124.6, 124.2, 123.5, 121.6, 113.2, 110.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{10}N_5O_2$: 280.0826, found: 280.0829. M. P. > 350 ºC.

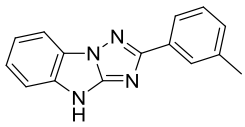


2-(2, 6-diflorophenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1f). According to the general procedure C, the reaction was finished in 120 min, and **1f** was obtained as an orange solid in 74% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.58 (br, 1H), 7.90 (d, *J* = 4 Hz, 1H), 7.66~7.58 (m, 2H), 7.43 (m, 1H), 7.37~7.27 (m, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 161.5 (d, *J* = 10 Hz), 159.0 (d, *J* = 10 Hz), 154.8, 153.5, 134.0, 131.9 (t, *J* = 10 Hz), 124.5, 123.5, 121.4, 113.2, 112.2 (d, *J* = 10 Hz), 112.0 (d, *J* = 10 Hz), 110.7, 110.2 (t, *J* = 10 Hz). HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_9F_2N_4$: 271.0788, found: 271.0790. M. P. 330~335 ºC.

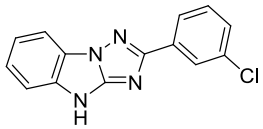


2-(2-methoxylphenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1g). According to the general procedure C, the reaction was finished in 100 min, and **1g** was obtained as

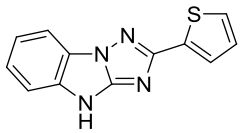
a white solid in 78% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.34 (br, 1H), 7.84 (m, 2H), 7.56 (d, *J* = 8 Hz, 1H), 7.44 (m, 1H), 7.38 (m, 1H), 7.31 (t, *J* = 8 Hz, 1H), 7.17 (d, *J* = 8 Hz, 1H), 7.06 (t, *J* = 8 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 162.8, 157.3, 153.4, 134.2, 130.8, 130.5, 123.8, 123.8, 121.1, 121.0, 120.2, 112.9, 112.2, 110.4, 55.6. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{13}N_4O$: 265.1082, found: 265.1084. M. P. 244~246 °C.



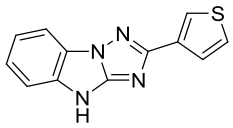
2-(3-methylphenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1h). According to the general procedure C, the reaction was finished in 100 min, and **1h** was obtained as an orange solid in 86% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.41 (br, 1H), 7.96 (s, 1H), 7.92 (d, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.38 (t, *J* = 8 Hz, 2H), 7.32 (m, 1H), 7.26 (d, *J* = 8 Hz, 1H), 2.40 (s, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 164.3, 154.0, 137.8, 134.1, 131.7, 129.9, 128.6, 126.6, 124.0, 123.7, 123.3, 121.3, 21.0. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{13}N_4$: 249.1131, found: 249.1135. M. P. 310~312 °C.



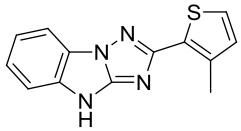
2-(3-chlorophenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1i). According to the general procedure C, the reaction was finished in 100 min, and **1i** was obtained as a white solid in 90% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.50 (br, 1H), 8.08 (m, 2H), 7.87 (d, *J* = 8 Hz, 1H), 7.59~7.51 (m, 3H), 7.40 (m, 1H), 7.33 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 162.7, 154.0, 134.3, 133.8, 133.5, 130.8, 129.1, 125.5, 124.6, 124.2, 123.6, 121.4, 113.1, 110.5. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{10}ClN_4$: 269.0585, found: 269.0588. M. P. 330~332 °C.



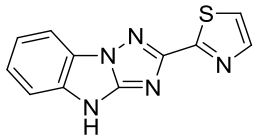
2-(thiophen-2-yl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1j). According to the general procedure C, the reaction was finished in 100 min, and **1j** was obtained as an orange solid in 97% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.45 (br, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.70 (dd, *J* = 4 Hz, 0.8 Hz, 1H), 7.65 (dd, *J* = 4 Hz, 0.8 Hz, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.38 (m, 1H), 7.32 (m, 1H), 7.19 (dd, *J* = 8 Hz, 4 Hz, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 160.2, 153.7, 134.6, 134.1, 128.0, 127.4, 126.2, 124.0, 123.6, 121.4, 113.0, 110.4. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_9N_4S$: 241.0540, found: 241.0542. M. P. > 350 °C.



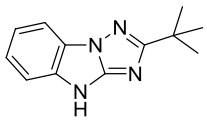
2-(thiophen-3-yl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1k). According to the general procedure C, the reaction was finished in 100 min, and **1k** was obtained as an orange solid in 93% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.39 (br, 1H), 8.10 (dd, *J* = 4 Hz, 1.6 Hz, 1H), 7.83 (d, *J* = 4 Hz, 1H), 7.67 (m, 2H), 7.56 (d, *J* = 8 Hz, 1H), 7.37 (m, 1H), 7.31 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 161.3, 153.8, 134.1, 133.9, 127.1, 126.0, 124.3, 123.9, 123.8, 121.3, 112.9, 110.3. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_9N_4S$: 241.0539, found: 241.0542. M. P. 340~350 °C.



2-(3-methylthiophen-3-yl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1l). According to the general procedure C, the reaction was finished in 120 min, and **1l** was obtained as a yellow solid in 95% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.42 (br, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.52 (d, *J* = 4 Hz, 1H), 7.37 (m, 1H), 7.31 (m, 1H), 7.02 (d, *J* = 8 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 161.0, 153.4, 137.0, 134.0, 131.6, 128.1, 125.9, 123.9, 123.6, 121.4, 113.0, 110.3, 15.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{13}H_{11}N_4S$: 255.0695, found: 255.0670. M. P. 353 °C.

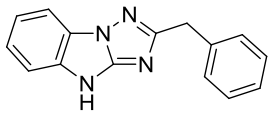


2-(thiazole-2-yl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1m). According to the general procedure C, the reaction was finished in 120 min, and **1m** was obtained as an orange solid in 93% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.63 (br, 1H), 8.02 (d, *J* = 4 Hz, 1H), 7.91 (m, 2H), 7.61 (d, *J* = 4 Hz, 1H), 7.43 (m, 1H), 7.36 (m, 1H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 159.2 (2C), 153.5, 144.1, 134.4, 124.6, 123.5, 121.7, 121.6, 113.2, 110.8. HRMS: m/z: $[M+H]^+$, calculated for $C_{11}H_8N_5S$: 242.0493, found: 242.0495. M. P. 333~338 °C.

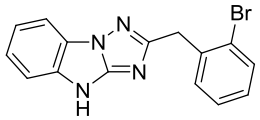


2-(*tert*-butyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1n). According to the general procedure C, the reaction was finished in 100 min, and **1n** was obtained as an orange solid in 93% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 13.10 (br, 1H), 7.84 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 8 Hz, 1H), 7.36 (m, 1H), 7.30 (m, 1H), 1.61 (s, 9H). **^{13}C NMR**

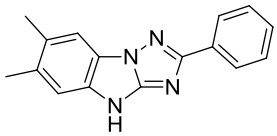
(101 MHz, $CDCl_3$) (δ, ppm): 175.0, 154.1, 133.9, 124.8, 123.7, 121.4, 112.6, 110.9, 34.2, 30.0. HRMS: m/z: $[M+H]^+$, calculated for $C_{12}H_{15}N_4$: 215.1288, found: 215.1291. M. P. 333~338 ºC.



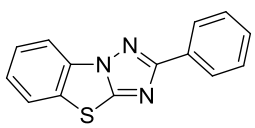
2-(benzyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1o). According to the general procedure C, the reaction was finished in 120 min, and **1o** was obtained as an orange solid in 71% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.22 (br, 1H), 7.74 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 8 Hz, 1H), 7.35~7.19 (m, 7H), 4.07 (s, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 166.2, 153.8, 138.3, 133.8, 128.8, 128.3, 126.2, 123.8, 123.6, 121.1, 112.8, 110.1, 35.4. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{13}N_4$: 249.1131, found: 249.1135. M. P. 250~258 ºC.



2-(2-bromobenzyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1p). According to the general procedure C, the reaction was finished in 100 min, and **1p** was obtained as an orange solid in 65% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.24 (br, 1H), 7.75 (d, *J* = 8 Hz, 1H), 7.63 (dd, *J* = 8 Hz, 1.6 Hz, 1H), 7.52 (d, *J* = 8 Hz, 1H), 7.42 (dd, *J* = 8 Hz, 1.6 Hz, 1H), 7.34 (m, 2H), 7.26 (m, 1H), 7.21 (m, 1H), 4.22 (s, 2H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 165.0, 153.7, 137.5, 133.8, 132.4, 131.5, 128.6, 127.7, 124.0, 123.7, 123.6, 121.1, 112.9, 110.2, 35.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{12}BrN_4$: 327.0238, found: 327.0240. M. P. 284~286 ºC.

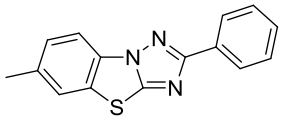


6,7-dimethyl-2-phenyl-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazole (1q). According to the general procedure C, the reaction was finished in 100 min, and **1q** was obtained as an orange solid in 95% yield. **^{1}H NMR (400 MHz, DMSO-*d6*)** (δ, ppm): 12.16 (br, 1H), 8.11 (m, 2H), 7.65 (s, 1H), 7.51~7.43 (m, 3H), 7.33 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d6*)** (δ, ppm): 163.7, 153.8, 132.5, 132.4, 131.9, 129.8, 129.1, 128.7, 126.0, 122.1, 113.3, 110.8, 19.8, 19.6. HRMS: m/z: $[M+H]^+$, calculated for $C_{16}H_{15}N_4$: 263.1287, found: 263.1291. M. P. decomposed at 345 ºC.

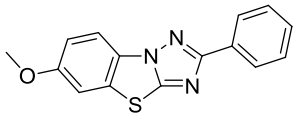


2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4a). According to the general

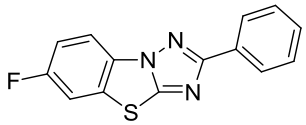
procedure D, the reaction was finished in 120 min, and **4a** was obtained as a yellow solid in 52% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.25 (m, 2H), 8.03 (d, *J* = 8 Hz, 1H), 7.79 (d, *J* = 8 Hz, 1H), 7.58 (m, 1H), 7.52~7.42 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 167.3, 156.3, 131.7, 130.9, 129.9, 129.4, 128.7, 127.1, 126.8, 125.7, 124.5, 113.5. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{10}N_3S$: 252.0593, found: 252.0590. M. P. decomposed at 181~183 °C.



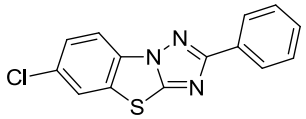
6-methyl-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4b). According to the general procedure D, the reaction was finished in 80 min, and **4b** was obtained as a yellow solid in 63% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.23 (m, 2H), 7.89 (d, *J* = 8 Hz, 1H), 7.56 (s, 1H), 7.51~7.44 (m, 3H), 7.36 (d, *J* = 8 Hz, 1H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 167.0, 156.0, 136.0, 131.0, 129.8, 129.7, 129.4, 128.7, 128.1, 126.7, 124.5, 113.0, 21.5. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{12}N_3S$: 266.0751, found: 266.0746. M. P. decomposed at 171~172 °C.



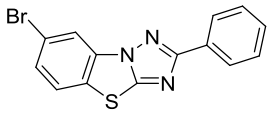
6-methoxyl-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4c). According to the general procedure D, the reaction was finished in 80 min, and **4c** was obtained as a yellow solid in 73% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.22 (m, 2H), 7.92 (d, *J* = 8 Hz, 1H), 7.51~7.44 (m, 3H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 8 Hz, 2.4 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 168.8, 157.9, 155.4, 131.1, 130.6, 129.7, 128.7, 126.6, 126.0, 114.5, 114.0, 108.7, 56.0. HRMS: m/z: $[M+H]^+$, calculated for $C_{15}H_{12}N_3OS$: 282.0693, found: 282.0696. M. P. decomposed at 147~149 °C.



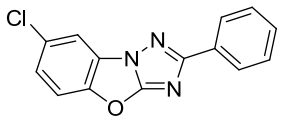
6-fluoro-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4d). According to the general procedure D, the reaction was finished in 80 min, and **4d** was obtained as a yellow solid in 65% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.23 (m, 2H), 7.99 (q, *J* = 4 Hz, 1H), 7.54~7.46 (m, 4H), 7.32 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 167.4, 160.2 (d, *J* = 240 Hz), 156.0, 130.8, 130.6 (d, *J* = 10 Hz), 130.0, 128.8, 128.3, 126.7, 115.1 (d, *J* = 30 Hz), 114.3 (d, *J* = 10 Hz), 111.6 (d, *J* = 20 Hz). HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_9FN_3S$: 270.0492, found: 270.0496. M. P. decomposed at 184~185 °C.



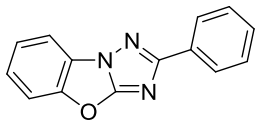
6-chloro-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4e). According to the general procedure D, the reaction was finished in 80 min, and **4e** was obtained as a yellow solid in 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.23 (m, 2H), 7.95 (d, *J* = 8 Hz, 1H), 7.79 (d, *J* = 2 Hz, 1H), 7.55 (dd, *J* = 8 Hz, 2 Hz, 1H), 7.52~7.46 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 167.6, 156.2, 131.3, 130.7, 130.6, 130.2, 130.0, 128.8, 127.6, 126.8, 124.3, 114.1. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_9ClN_3S$: 286.0197, found: 286.0200. M. P. decomposed at 234~236 °C.



7-bromo-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzothiazole (4f). According to the general procedure D, the reaction was finished in 80 min, and **4f** was obtained as a yellow solid in 40% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.22 (m, 3H), 7.65 (d, *J* = 8 Hz, 1H), 7.56 (dd, *J* = 8 Hz, 2 Hz, 1H), 7.53~7.47 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 167.6, 156.8, 132.4, 130.6, 130.1, 128.8, 128.8, 128.2, 126.8, 125.6, 120.7, 116.7. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_9BrN_3S$: 329.9691, found: 329.9695. M. P. decomposed at 212~213 °C.

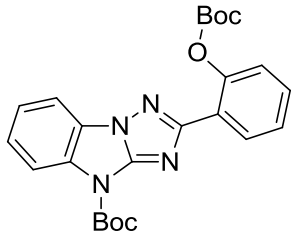


7-chloro-2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzoxazole (4g). According to the general procedure D, the reaction was finished in 80 min, and **4g** was obtained as a yellow solid in 26% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.17 (m, 2H), 7.81 (d, *J* = 2 Hz, 1H), 7.56 (d, *J* = 8 Hz, 1H), 7.51~7.45 (m, 3H), 7.38 (dd, *J* = 8 Hz, 2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 166.3, 162.8, 149.4, 131.1, 130.7, 130.2, 128.7, 126.7, 125.2, 114.0, 111.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_9ClN_3O$: 270.0432, found: 270.0429. M. P. decomposed at 175~177 °C.

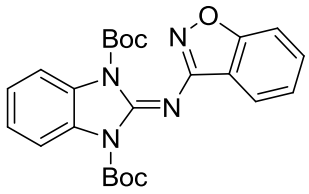


2-phenyl-[1,2,4]-triazolo[1,5-*a*]benzoxazole (4h). According to the general procedure D, the reaction was finished in 80 min, and **4h** was obtained as a yellow solid in 61% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 8.20 (m, 2H), 7.81 (dd, *J* = 8 Hz, 0.8 Hz, 1H), 7.64 (dd, *J* = 8 Hz, 0.8 Hz, 1H), 7.51~7.39 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** (δ, ppm): 165.9, 162.3, 151.0, 131.1, 130.0, 128.7, 126.6, 126.1, 125.3, 125.1, 113.2, 111.4. HRMS: m/z: $[M+H]^+$, calculated for $C_{14}H_{10}N_3O$: 236.0815, found: 236.0818. M. P. decomposed at 170~172 °C.

5.3 Characterization of the mechanistic study compounds



***tert*-butyl 2-(2-((*tert*-butoxycarbonyl)oxy)phenyl)-4H-benzo[4,5]imidazo[1,2-*b*][1,2,4]triazole-4-carboxylate (9). ^{1}H NMR (400 MHz, $CDCl_3$)** (δ, ppm): 7.93 (d, *J* = 8 Hz, 1H), 7.76 (d, *J* = 8 Hz, 1H), 7.65 (d, *J* = 8 Hz, 1H), 7.33~7.16 (m, 5H), 1.70 (s, 9H), 1.60 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** (δ, ppm): 151.0, 148.4, 148.2, 147.3, 143.8, 141.7, 132.3, 128.2, 124.9, 124.7, 124.1, 123.2, 118.9, 115.1, 114.5, 110.1, 86.3, 84.7, 28.2, 28.1. HRMS: m/z: $[M+H]^+$, calculated for $C_{24}H_{27}N_4O_5$: 451.1976, found: 451.1964.



di-*tert*-butyl 2-(benzo[*d*]isoxazol-3-ylimino)-1H-benzo[*d*]imidazole-1,3(2H)-dicarboxylate (10). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.76 (dd, *J* = 8 Hz, 4 Hz, 2H), 7.71 (d, *J* = 8 Hz, 1H), 7.53~7.46 (m, 2H), 7.27 (m, 1H), 7.21 (dd, *J* = 8 Hz, 4 Hz, 2H), 1.47 (s, 18H). **^{13}C NMR (126 MHz, $CDCl_3$)** (δ, ppm): 163.6, 161.0, 148.3, 143.6, 129.7, 128.5, 124.5, 123.0, 121.9, 119.6, 113.7, 109.9, 85.9, 27.9. HRMS: m/z: $[M+H]^+$, calculated for $C_{24}H_{27}N_4O_5$: 451.1976, found: 451.1967.

6. Crystal structures

6.1 Crystal structure of 1f

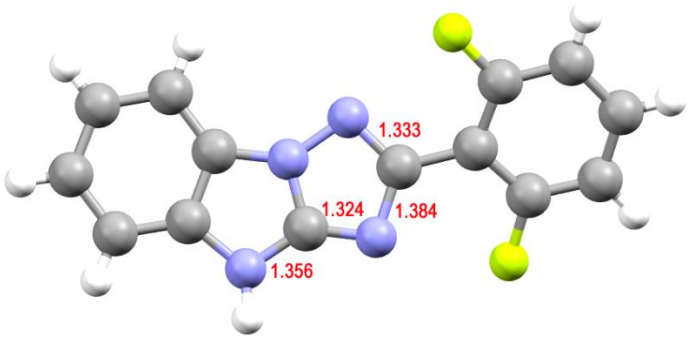


Table 1 Crystal data and structure refinement for compound 1f.

Identification code	CCDC 1441369
Empirical formula	$C_{14}H_8F_2N_4$
Formula weight	270.24
Temperature/K	141(50)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	4.3750(2)
b/Å	20.1126(13)
c/Å	13.1678(8)
α/°	90
β/°	98.317(6)
γ/°	90
Volume/Å^3	1146.50(12)
Z	4
ρ_{calc}g/cm^3	1.566
μ/mm^{-1}	0.121
F(000)	552.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.254 to 52.038
Index ranges	$-5 \le h \le 5$, $-24 \le k \le 24$, $-16 \le l \le 16$
Reflections collected	16603
Independent reflections	2269 [R_{int} = 0.0710, R_{sigma} = 0.0455]
Data/restraints/parameters	2269/0/185
Goodness-of-fit on F^2	1.046

Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0708, wR_2 = 0.1153
Largest diff. peak/hole / e Å^{-3}	0.21/-0.28

6.2 Crystal structure of 1q

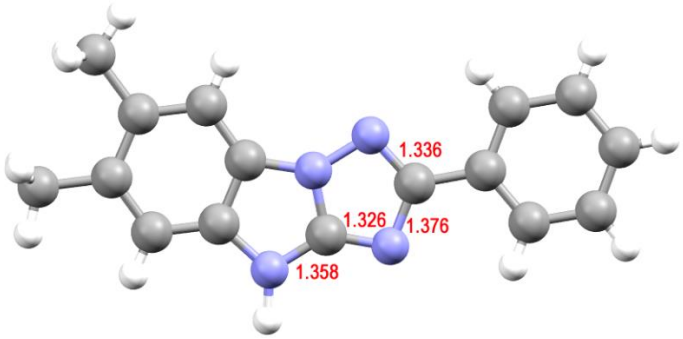


Table 1 Crystal data and structure refinement for compound 1q

Identification code	CCDC 1441371
Empirical formula	$C_{16}H_{14}N_4$
Formula weight	262.31
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.9753(6)
b/Å	15.9285(17)
c/Å	13.4470(13)
α/°	90
β/°	90.062(11)
γ/°	90
Volume/Å^3	1279.9(2)
Z	4
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.085
F(000)	552.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.284 to 50.048
Index ranges	-7 ≤ h ≤ 5, -18 ≤ k ≤ 12, -12 ≤ l ≤ 16
Reflections collected	3290
Independent reflections	2023 [R_{int} = 0.0273, R_{sigma} = 0.0566]
Data/restraints/parameters	2023/0/187

Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0502, wR_2 = 0.1100
Final R indexes [all data]	R_1 = 0.0848, wR_2 = 0.1324
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.20

6.3 Crystal structure of 4h

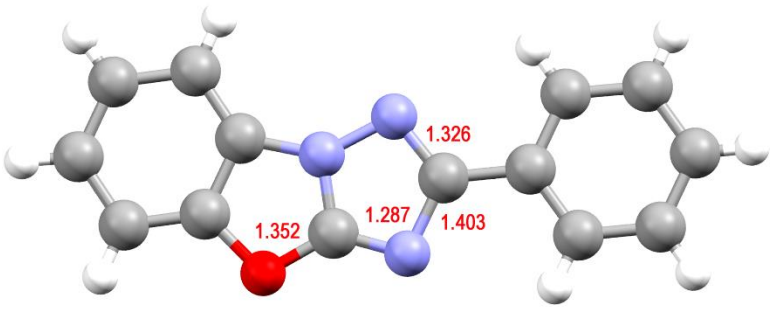


Table 1 Crystal data and structure refinement for compound 4h

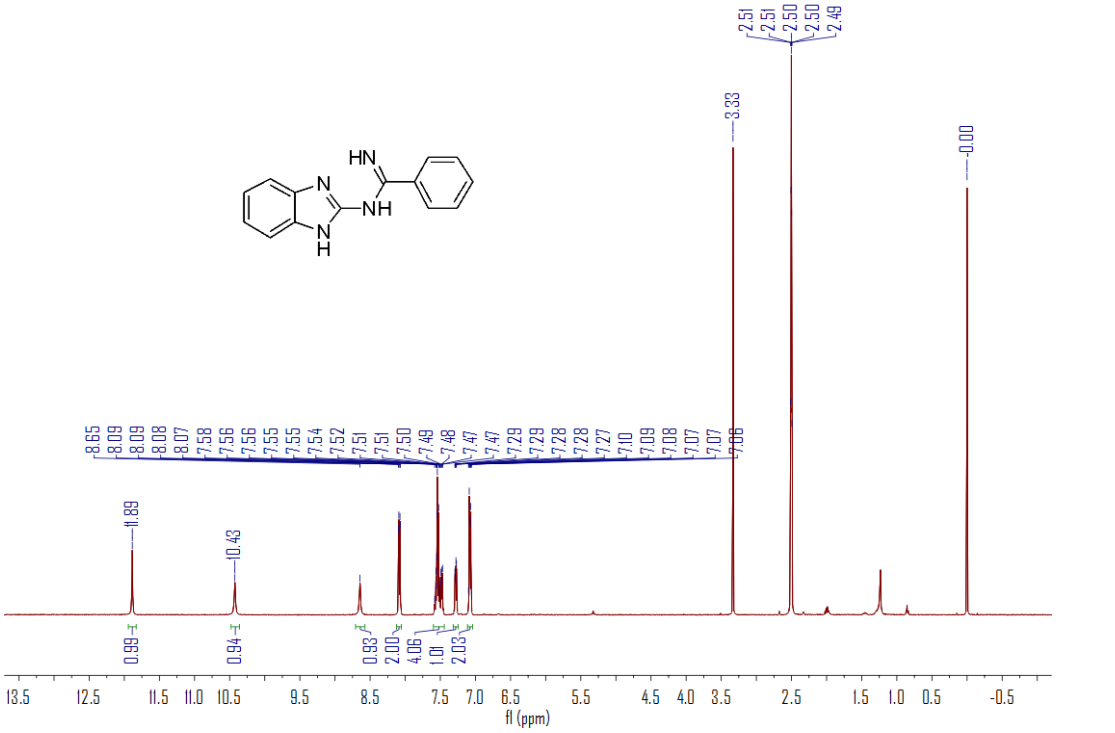
Identification code	CCDC 1441370
Empirical formula	$C_{14}H_9N_3O$
Formula weight	235.24
Temperature/K	179.99(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	21.401(2)
b/Å	4.7059(5)
c/Å	10.6453(10)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1072.10(19)
Z	4
$\rho_{calc}g/cm^3$	1.457
μ/mm^{-1}	0.096
F(000)	488.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.616 to 52.04
Index ranges	$-24 \le h \le 26$, $-5 \le k \le 5$, $-13 \le l \le 10$
Reflections collected	3244
Independent reflections	1646 [R_{int} = 0.0326, R_{sigma} = 0.0438]
Data/restraints/parameters	1646/1/164

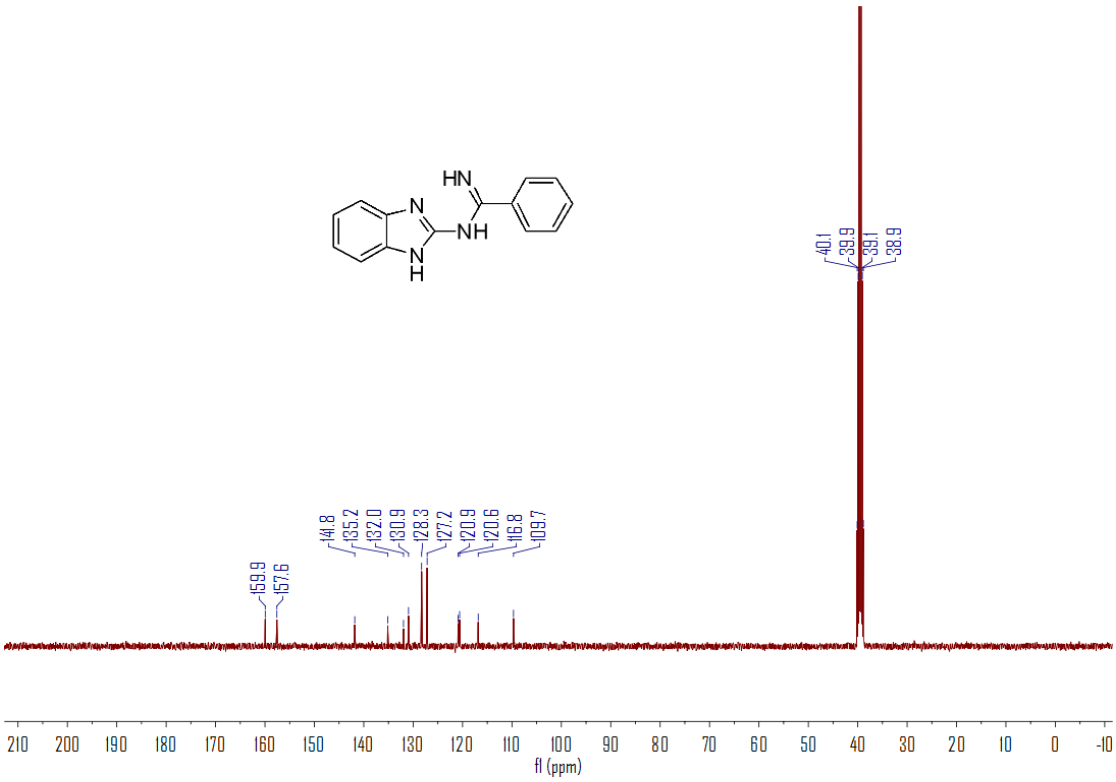
Goodness-of-fit on F^2	1.126
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1112
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.18
Flack parameter	-1.1(10)

7. NMR Spectra

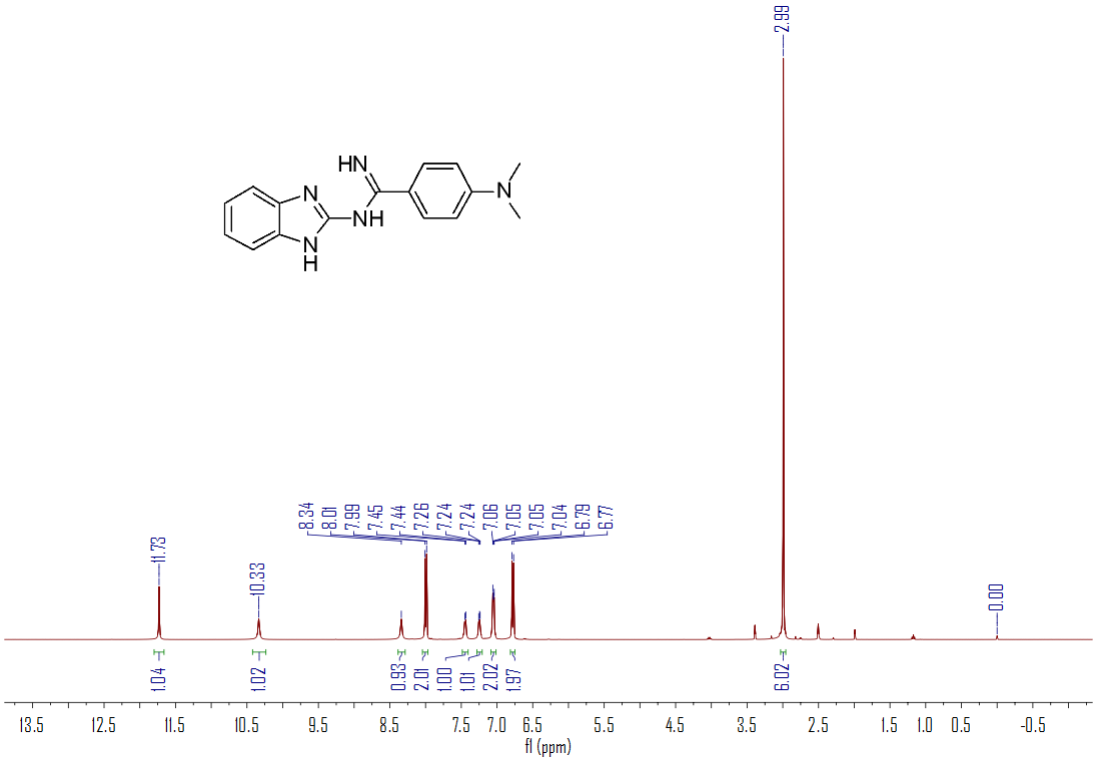
7.1 NMR Spectra of imidamides

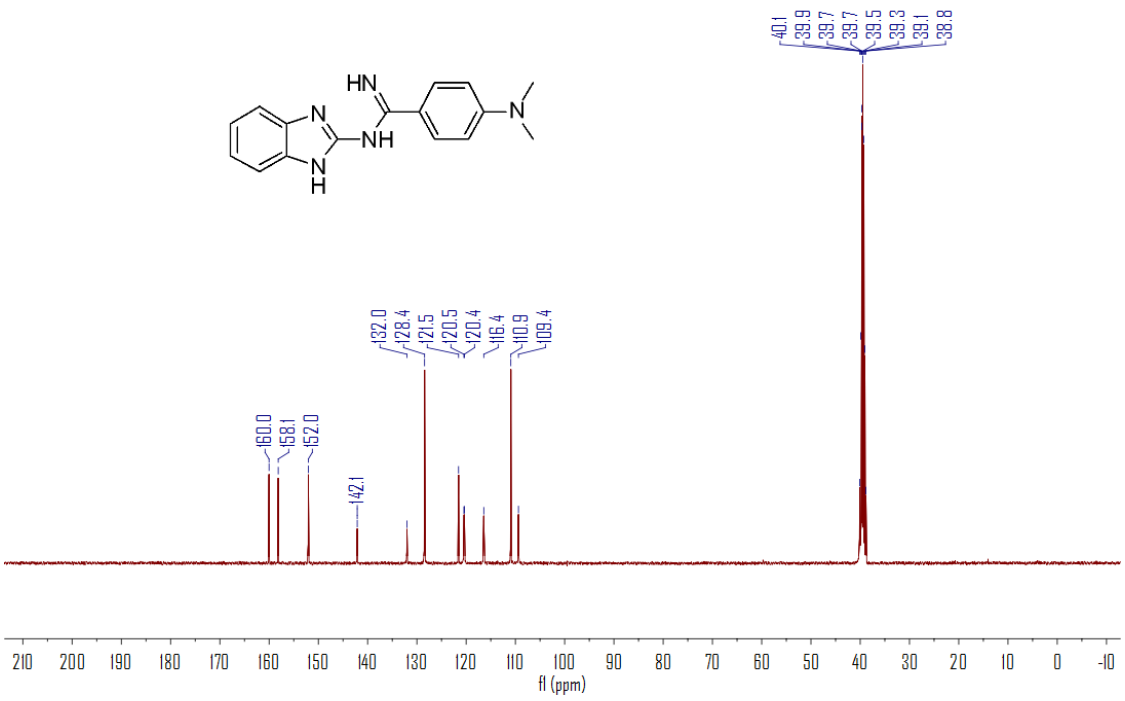
NMR spectra of **2a**:



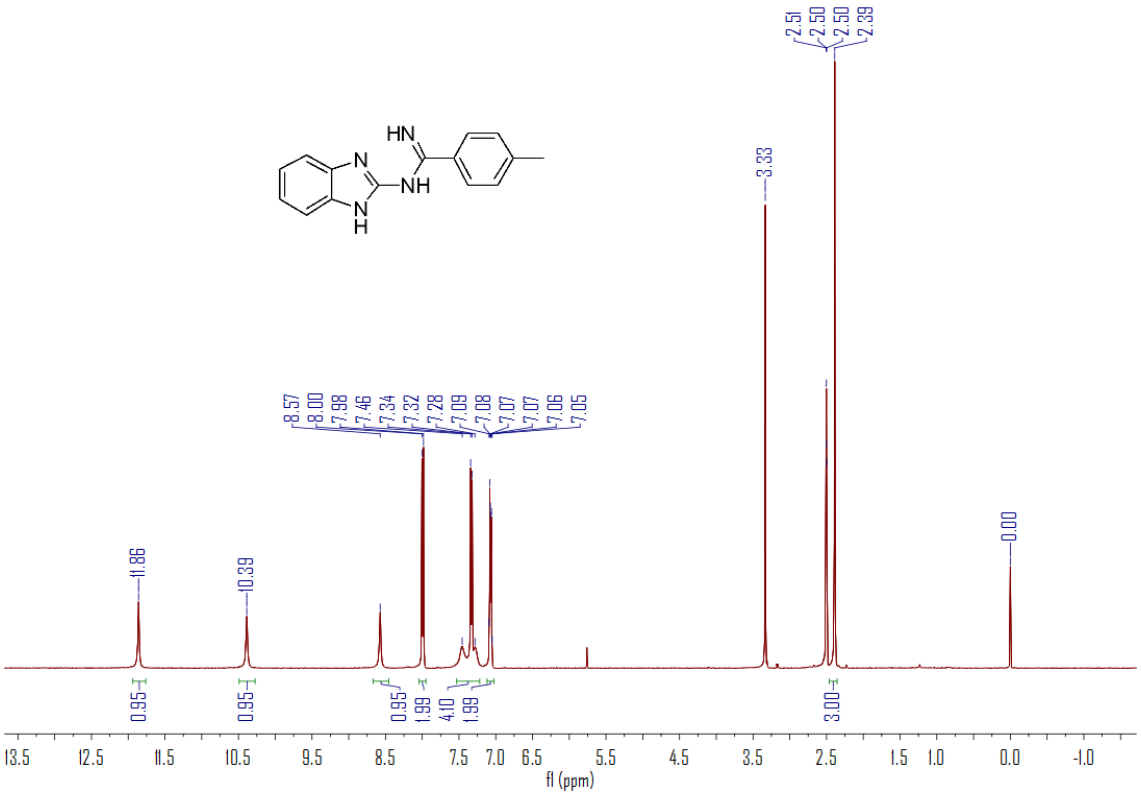


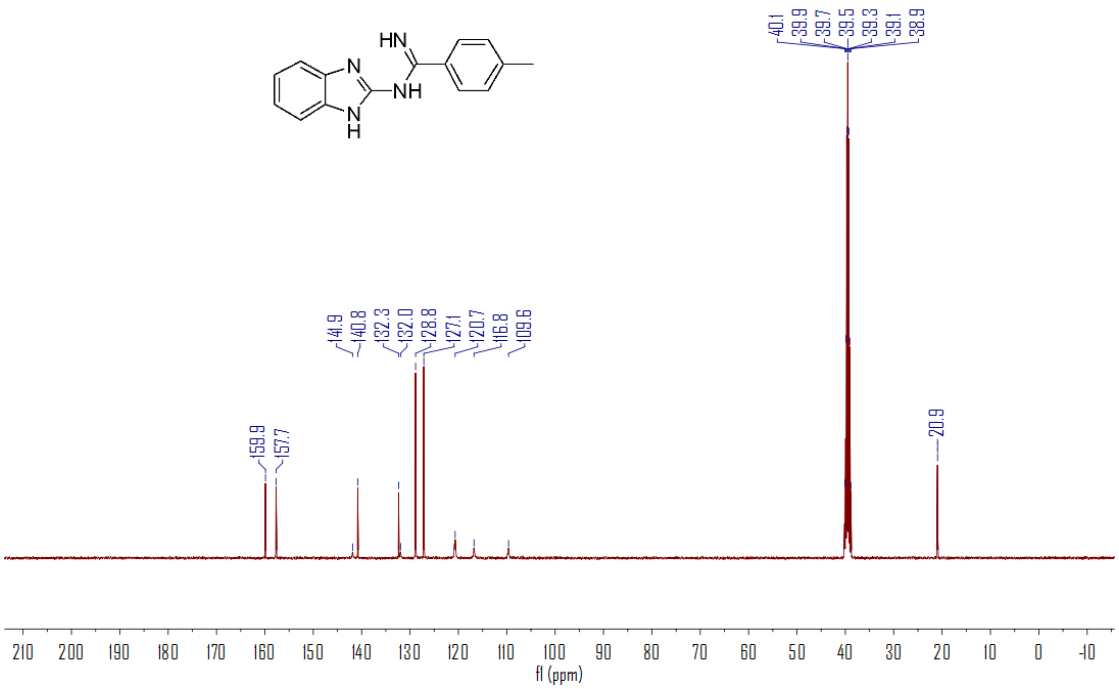
NMR spectra of **2b**:



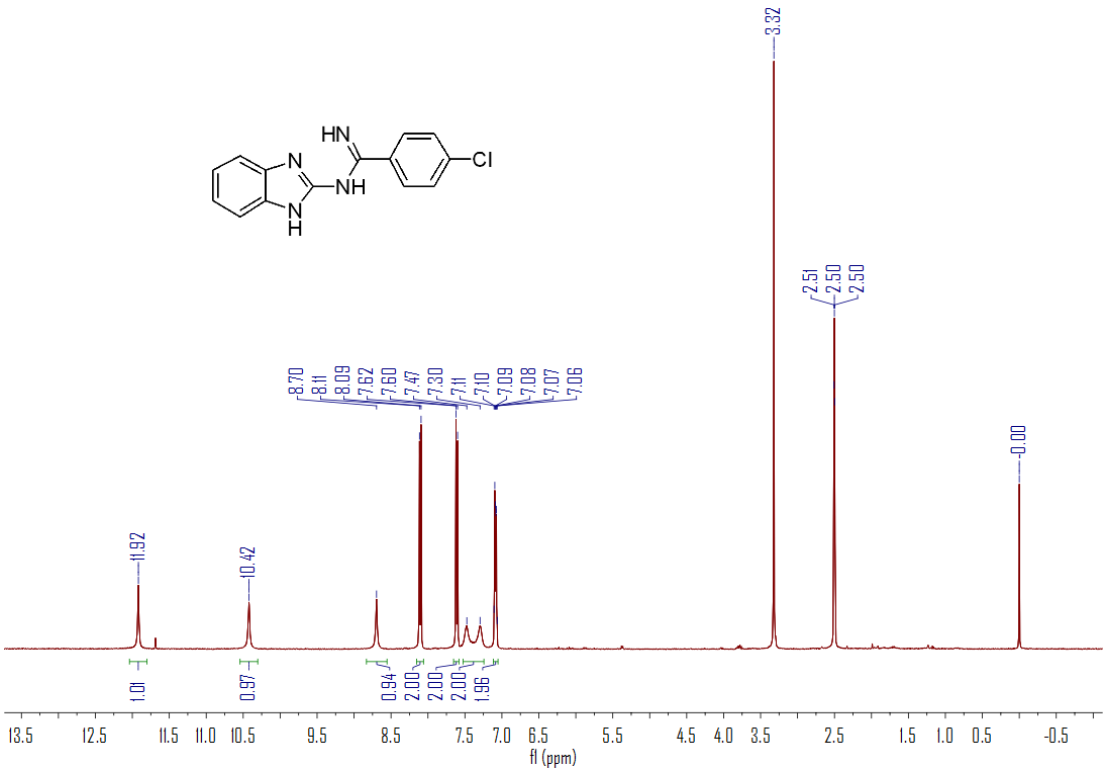


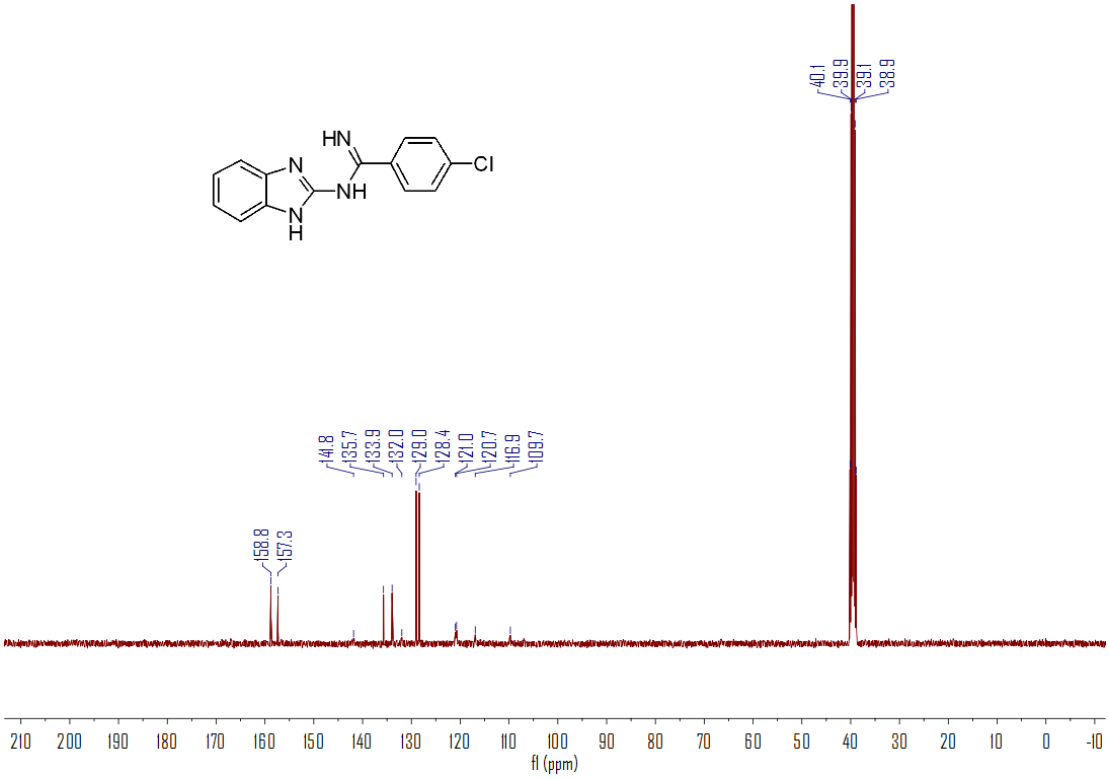
NMR spectra of **2c**:



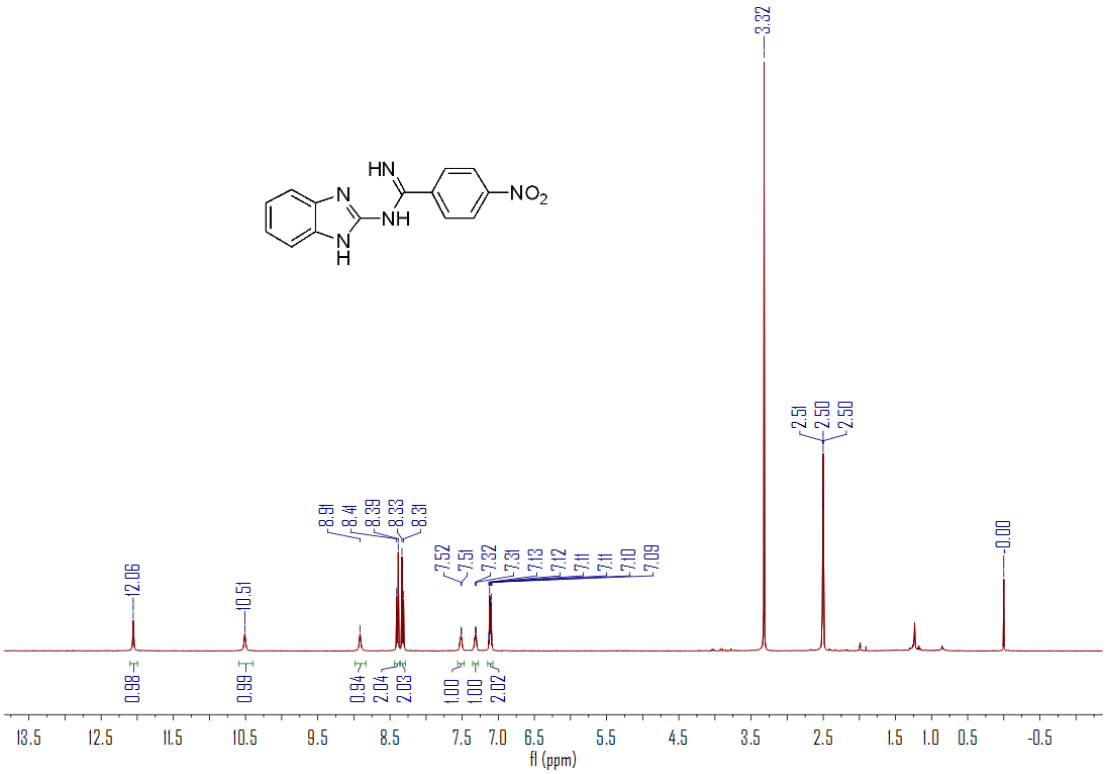


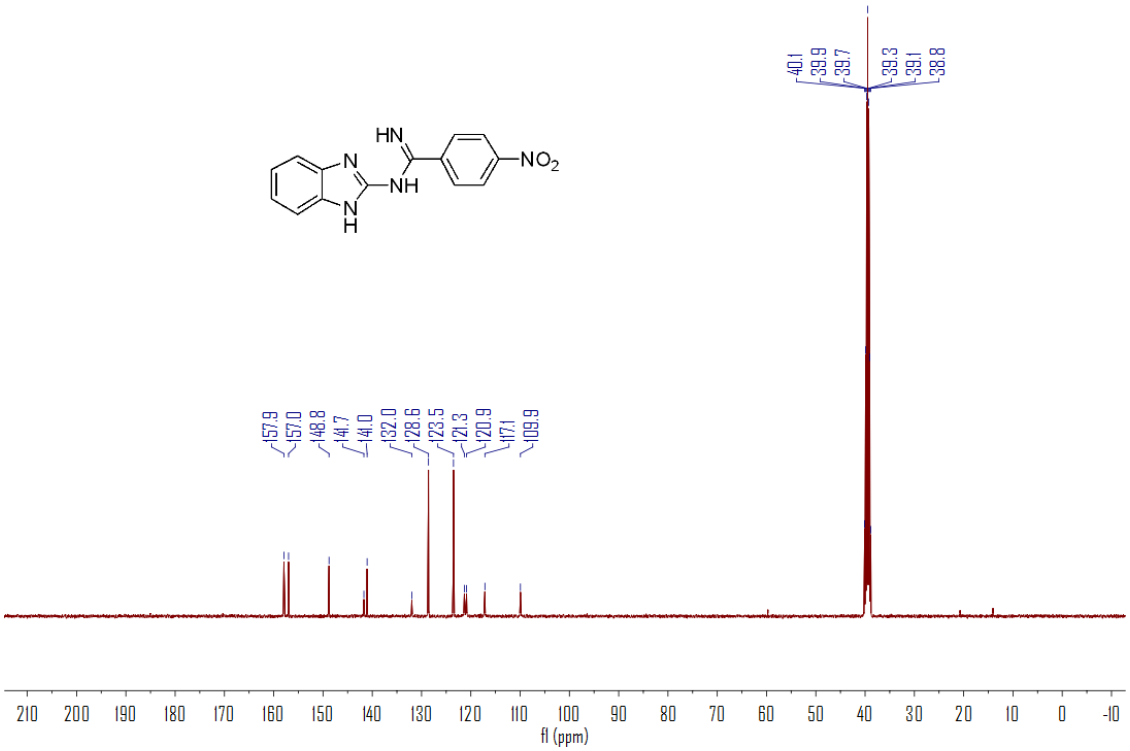
NMR spectra of **2d**:



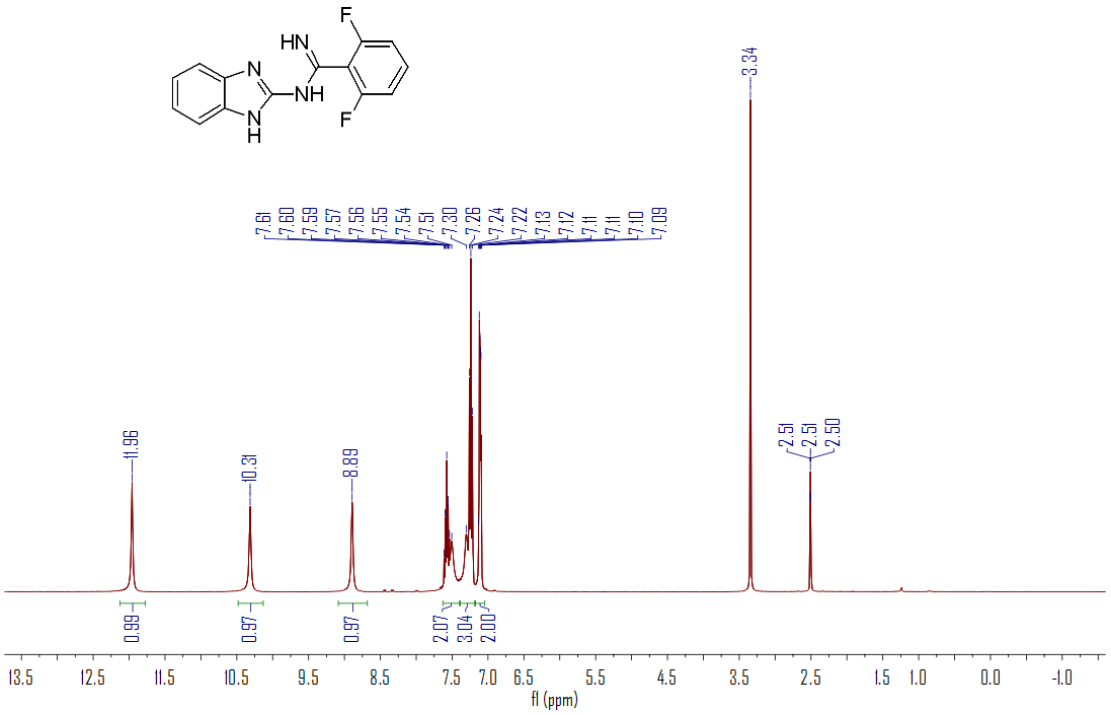


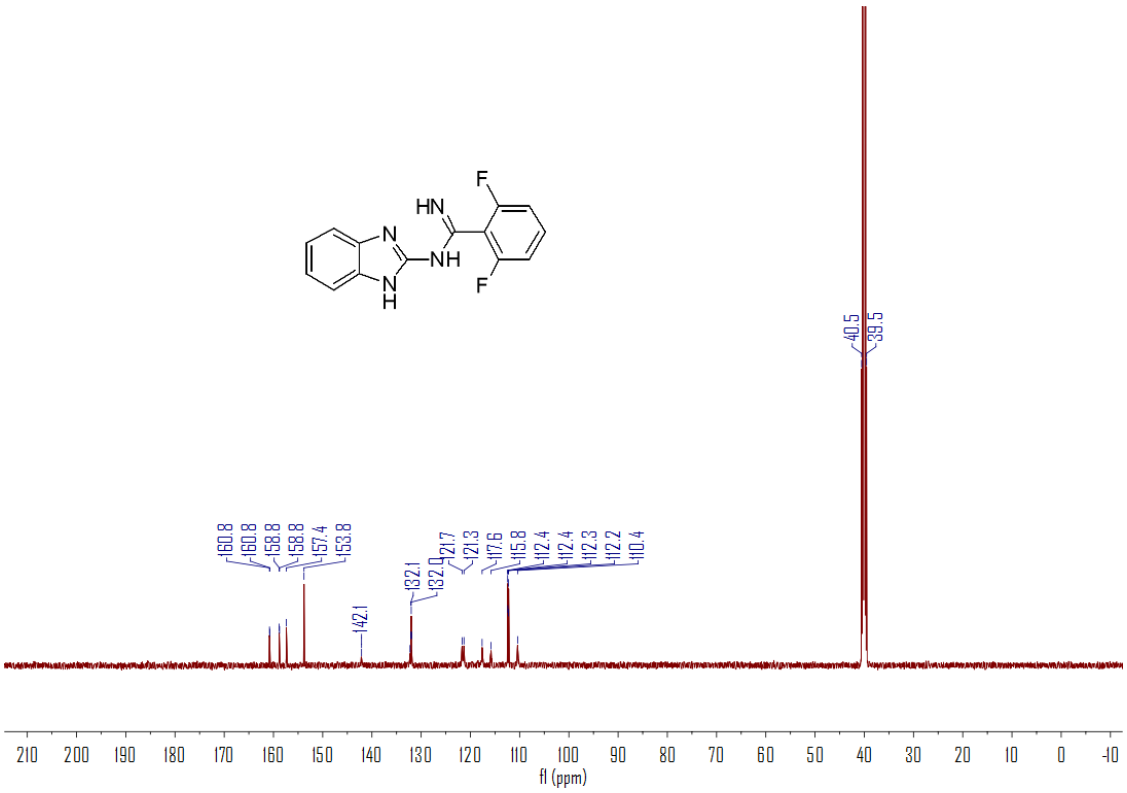
NMR spectra of **2e**:



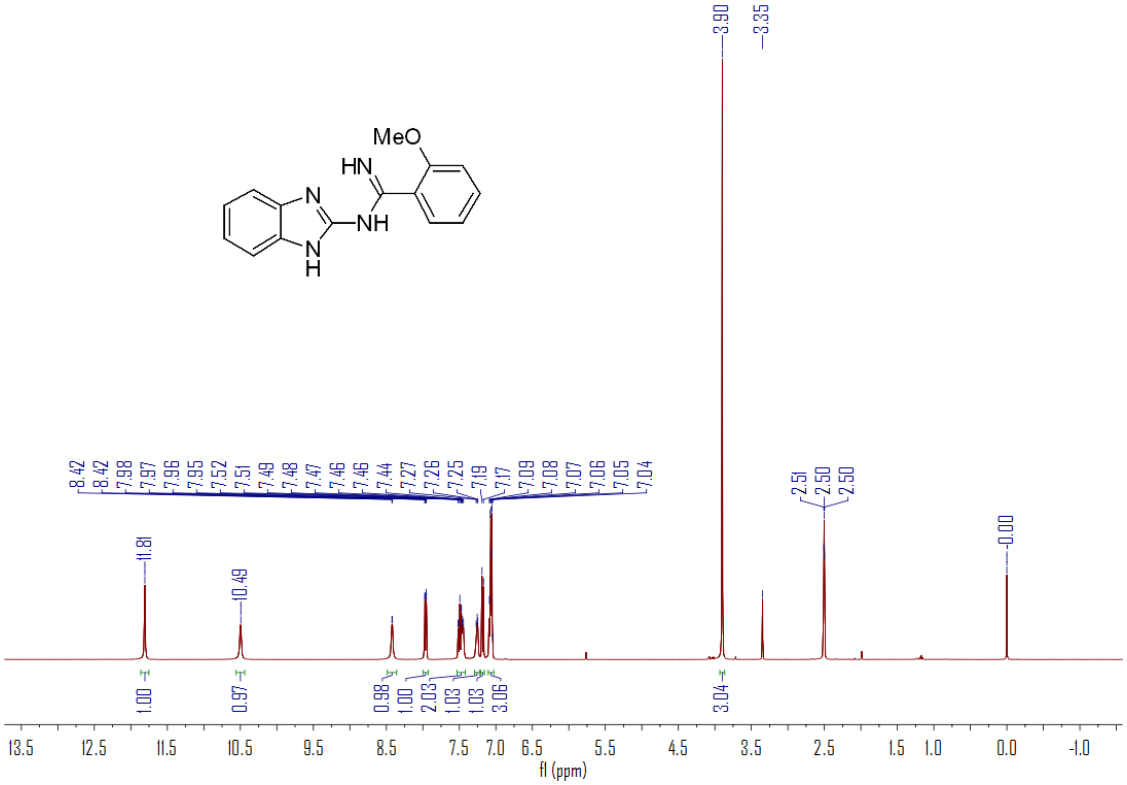


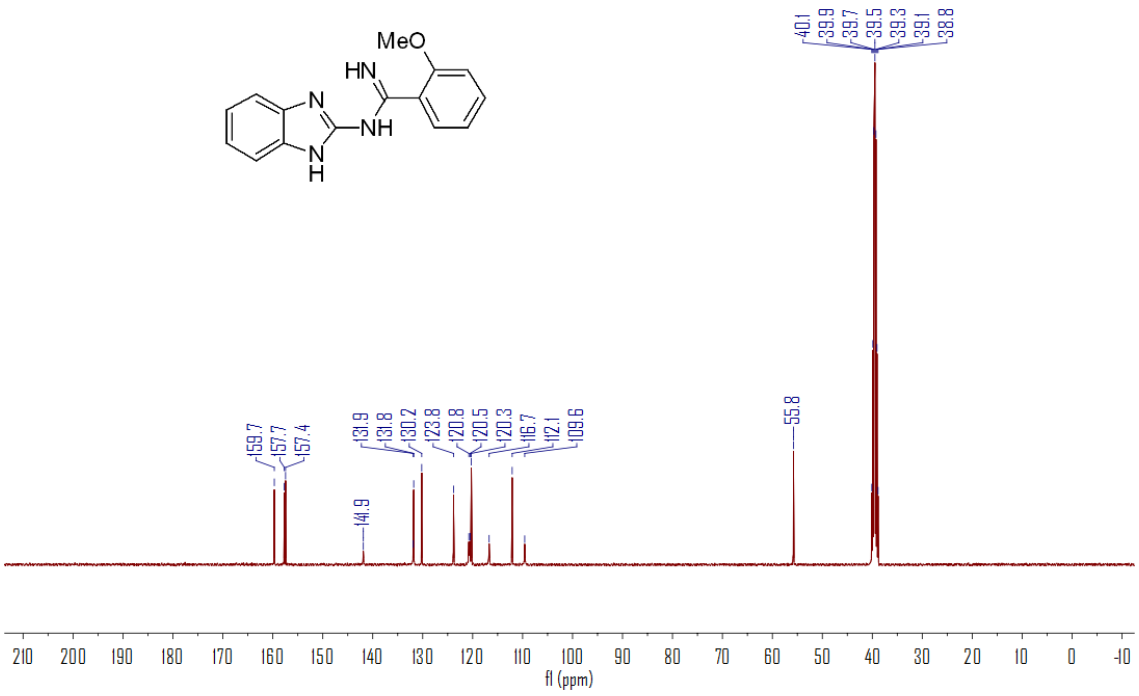
NMR spectra of **2f**:



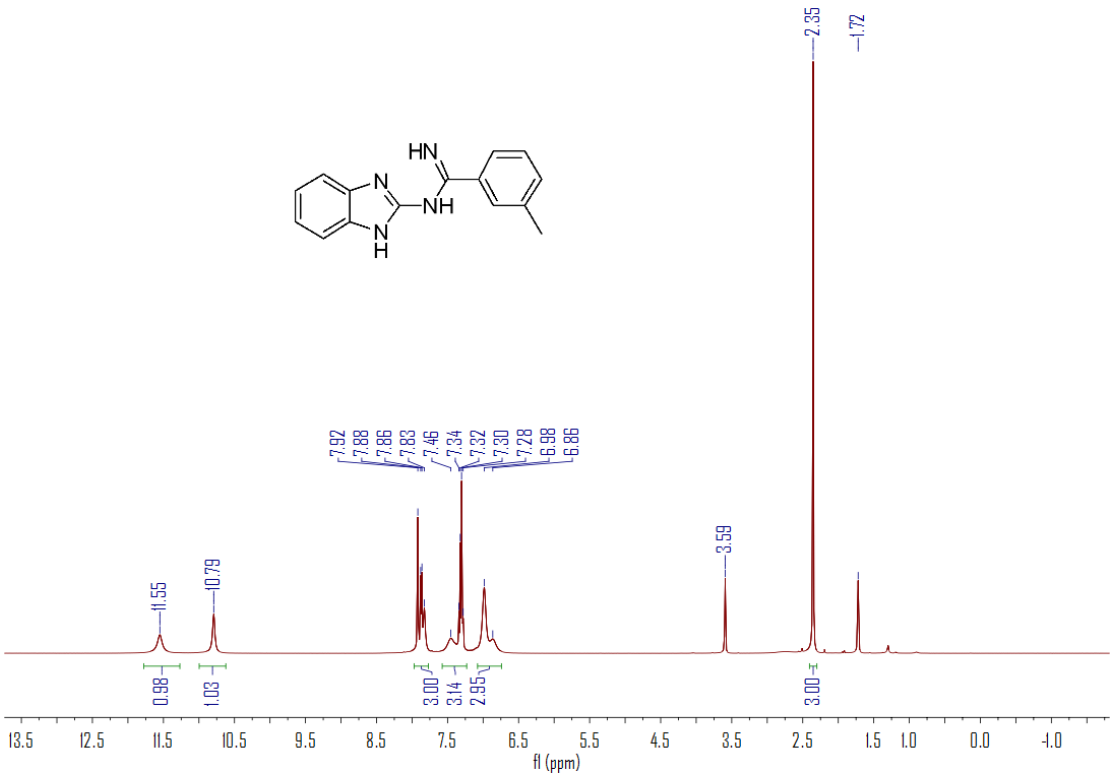


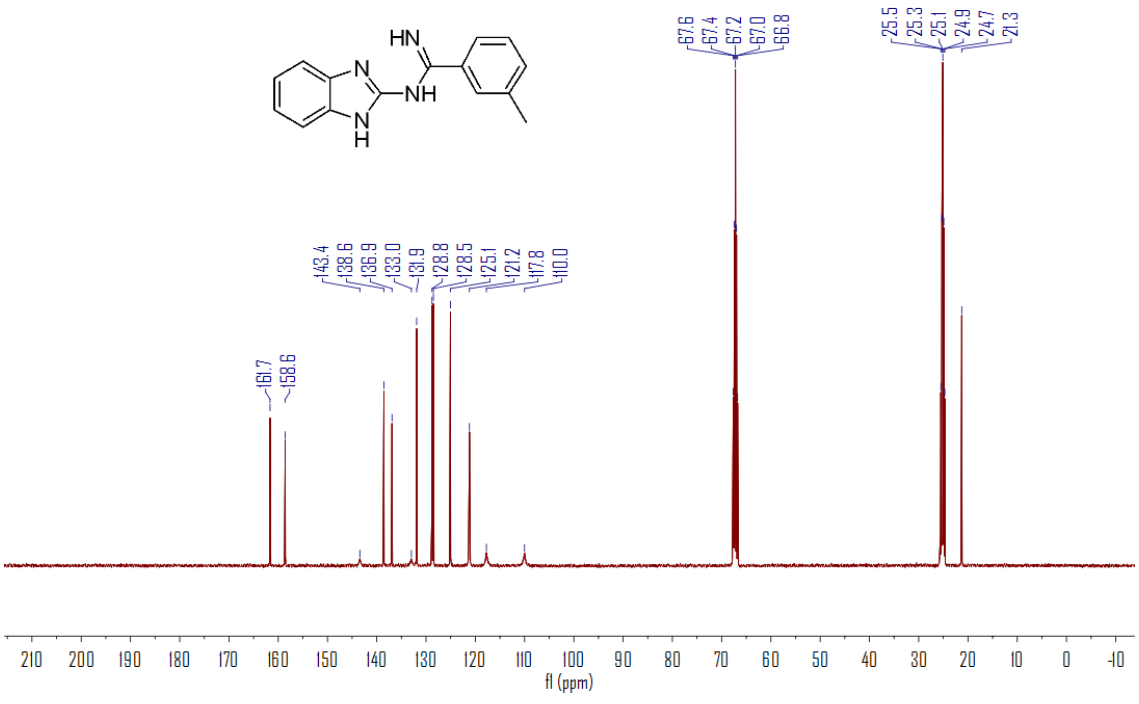
NMR spectra of **2g**:



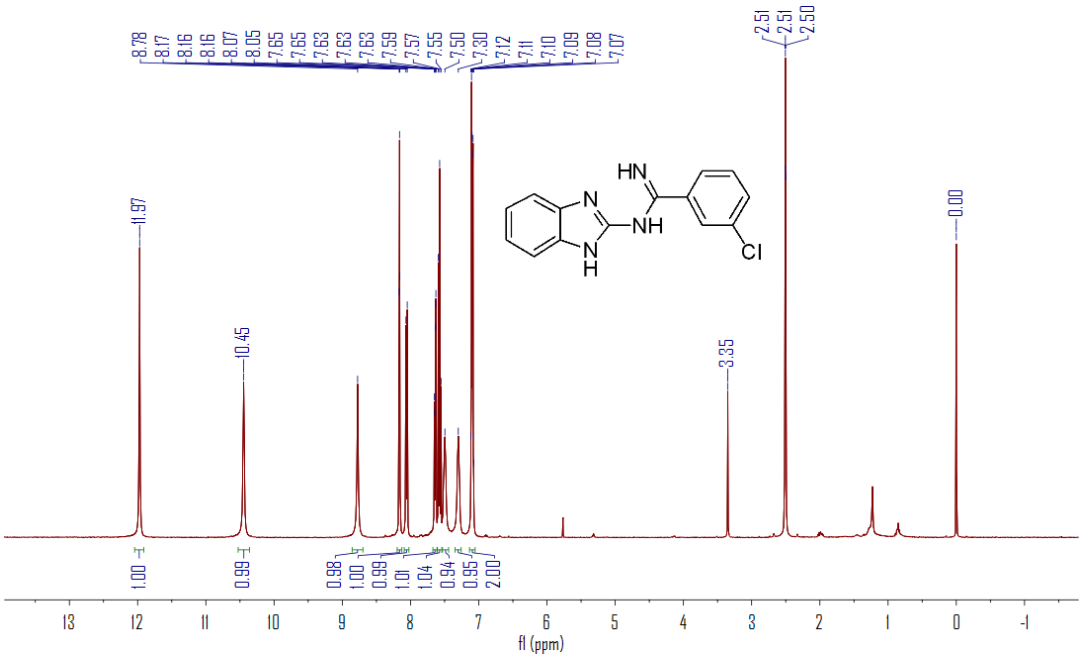


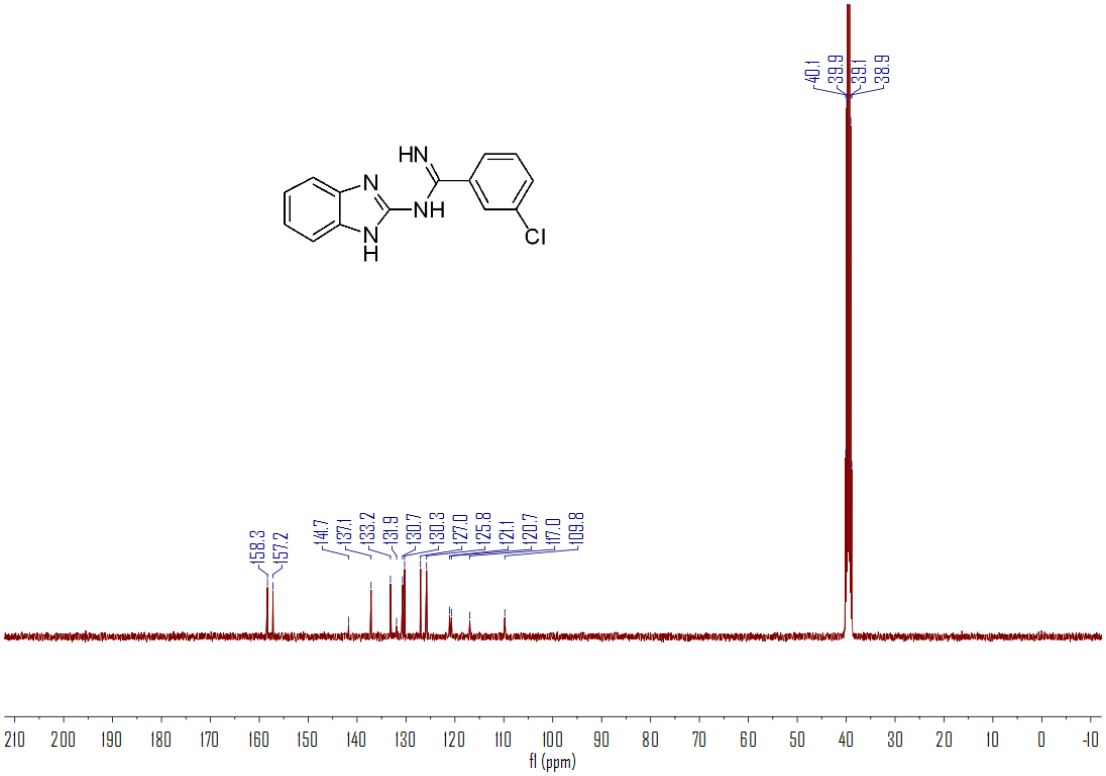
NMR spectra of **2h**:



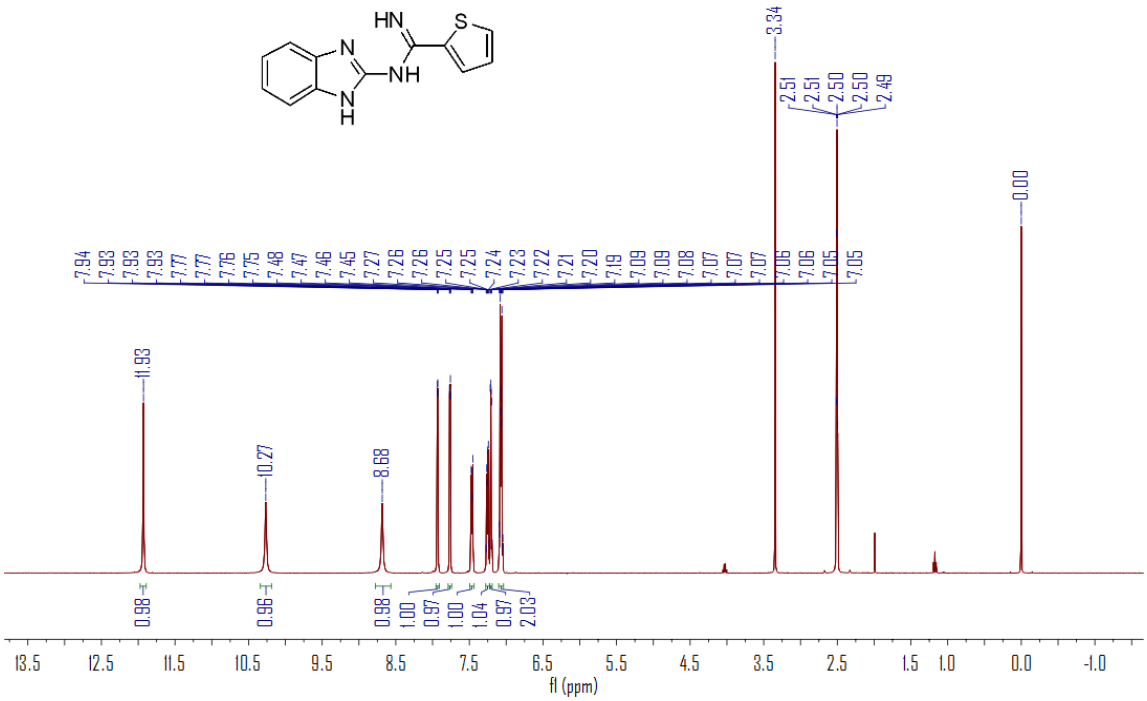


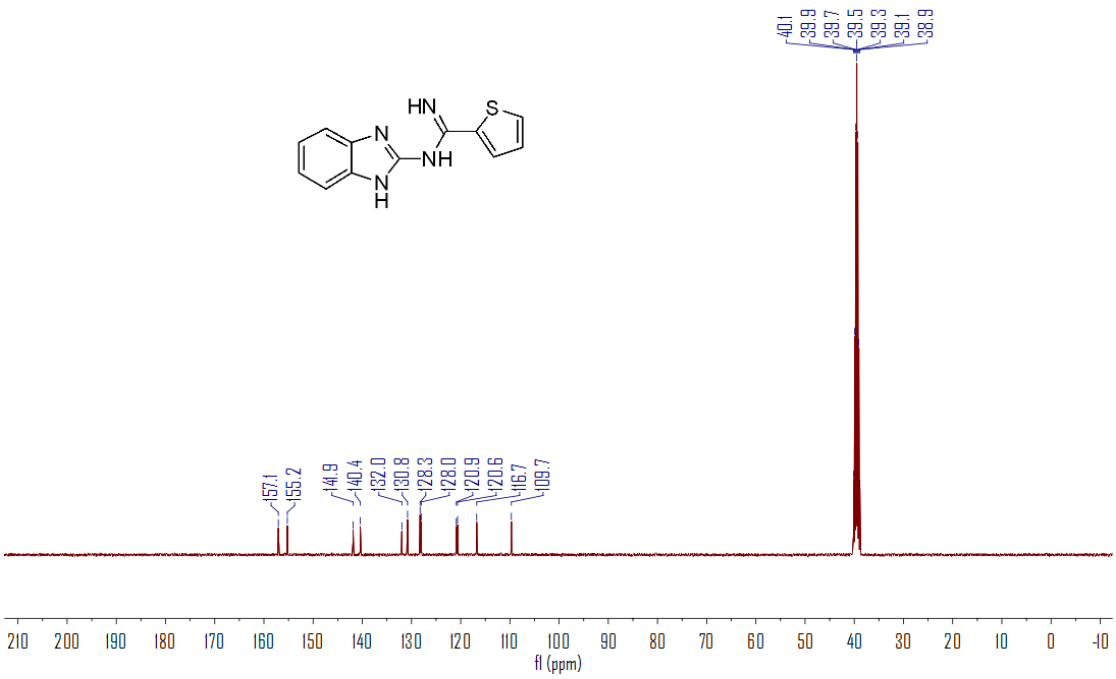
NMR spectra of **2i**:



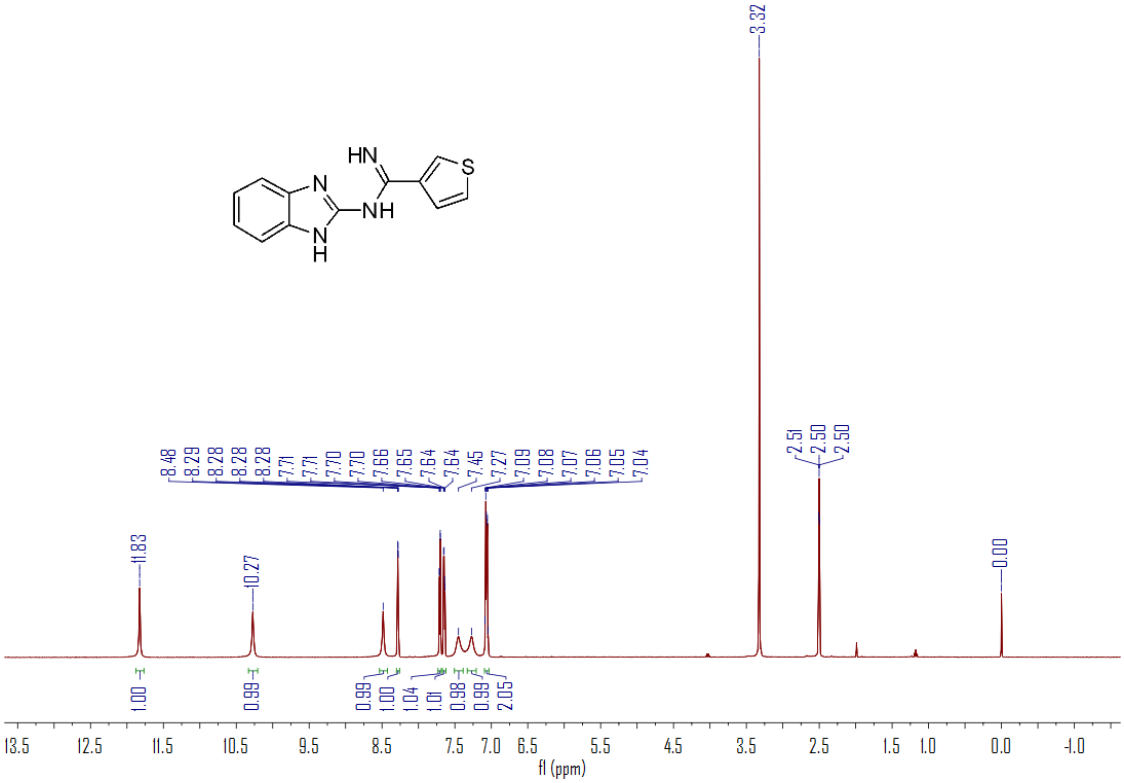


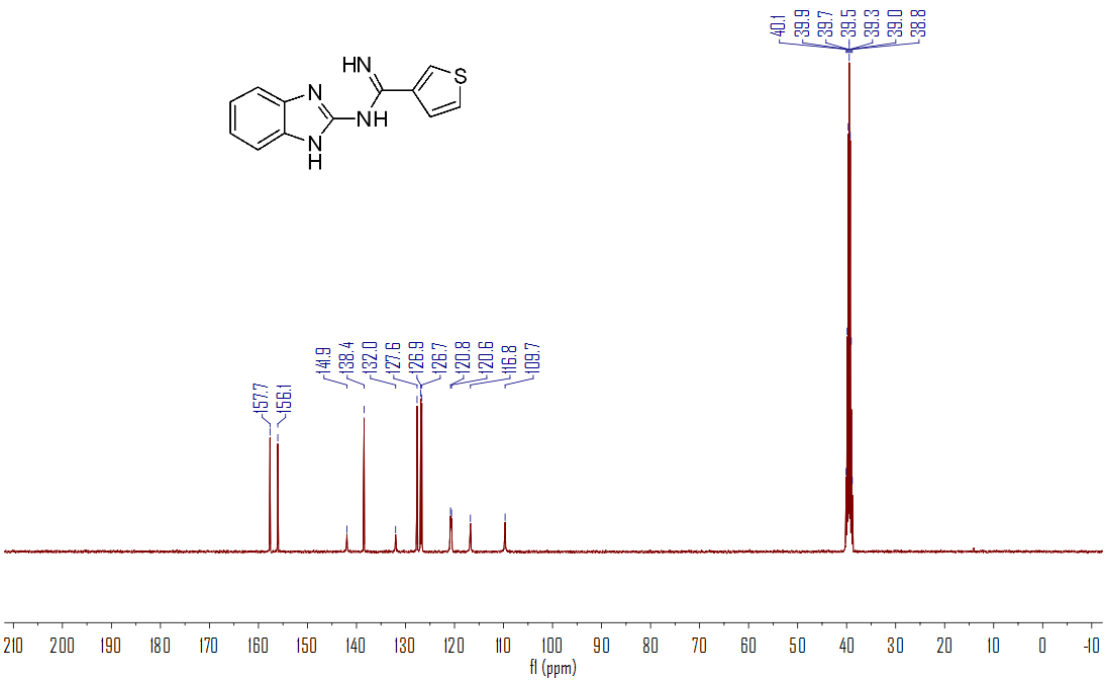
NMR spectra of **2j**:



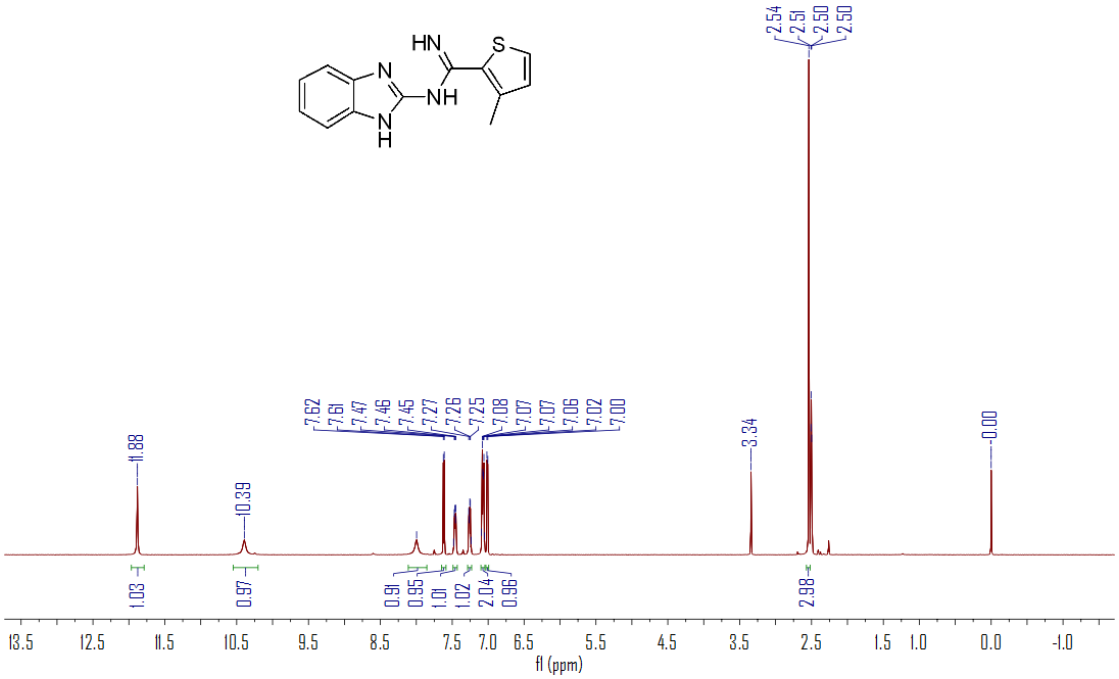


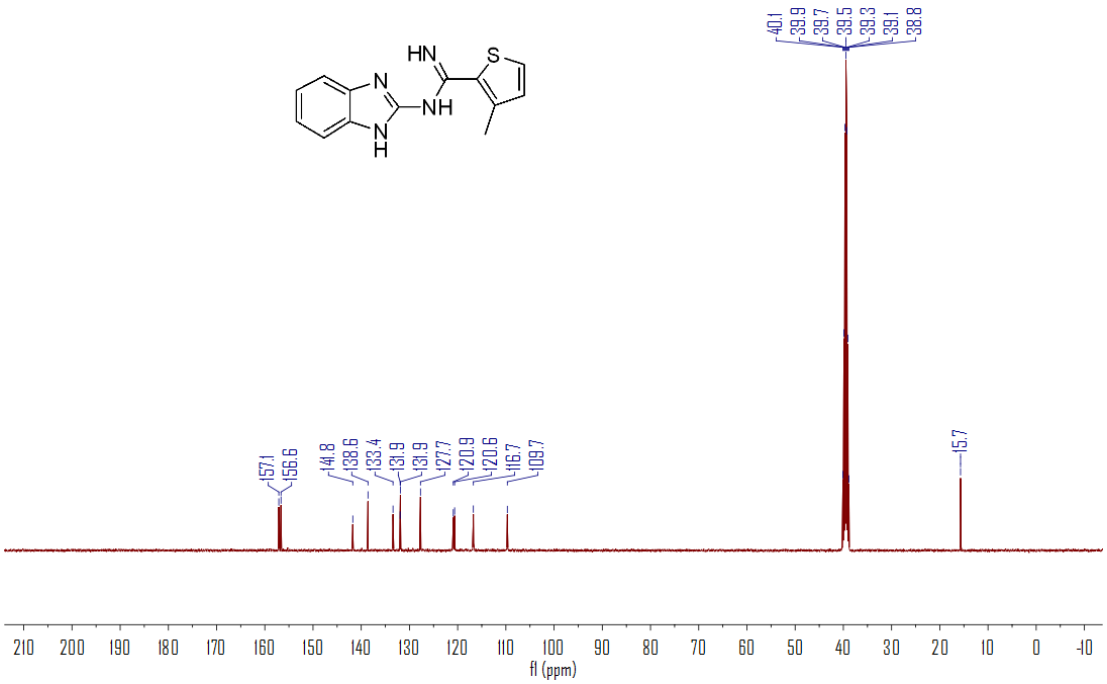
NMR spectra of **2k**:



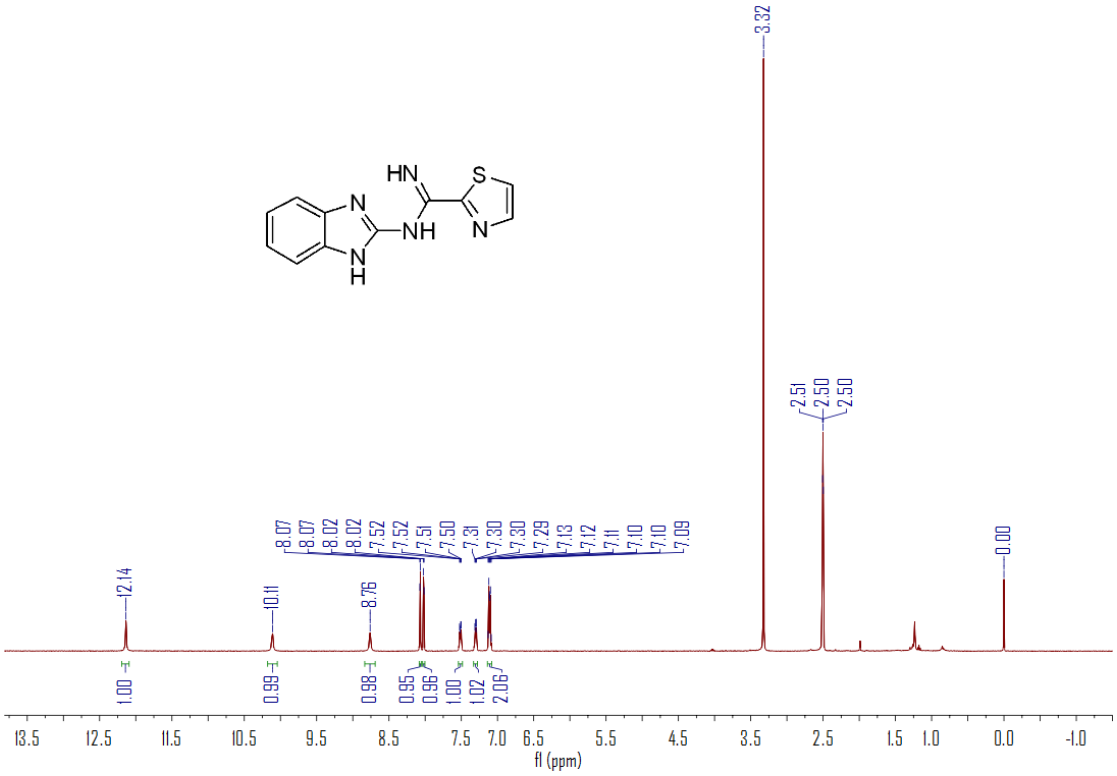


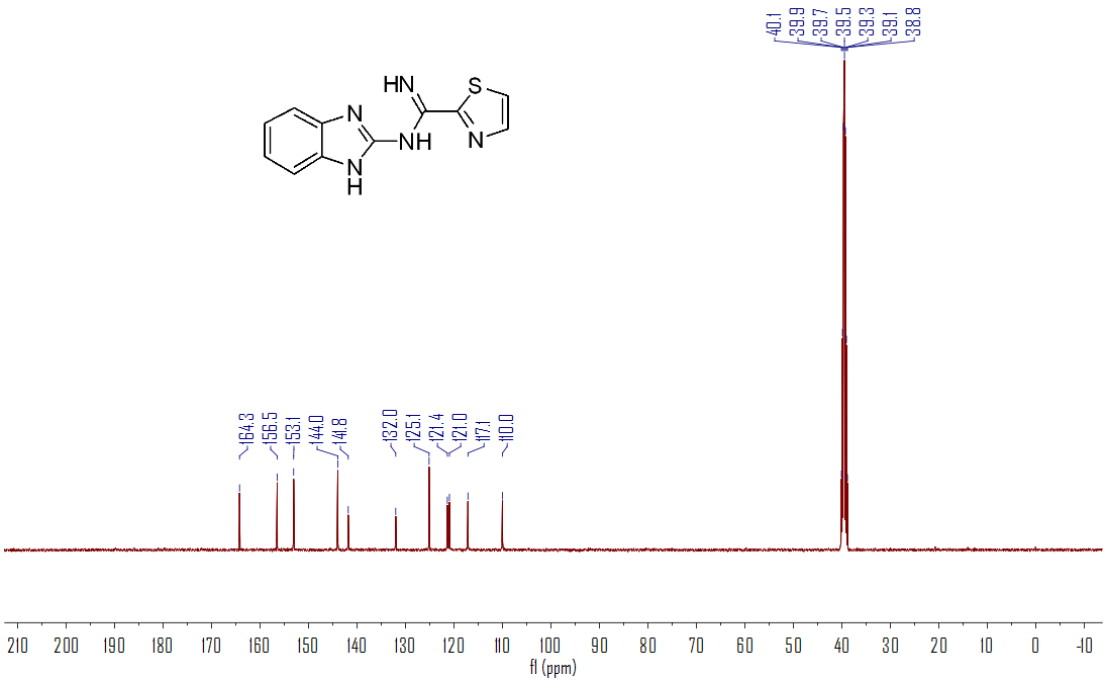
NMR spectra of **2l**:



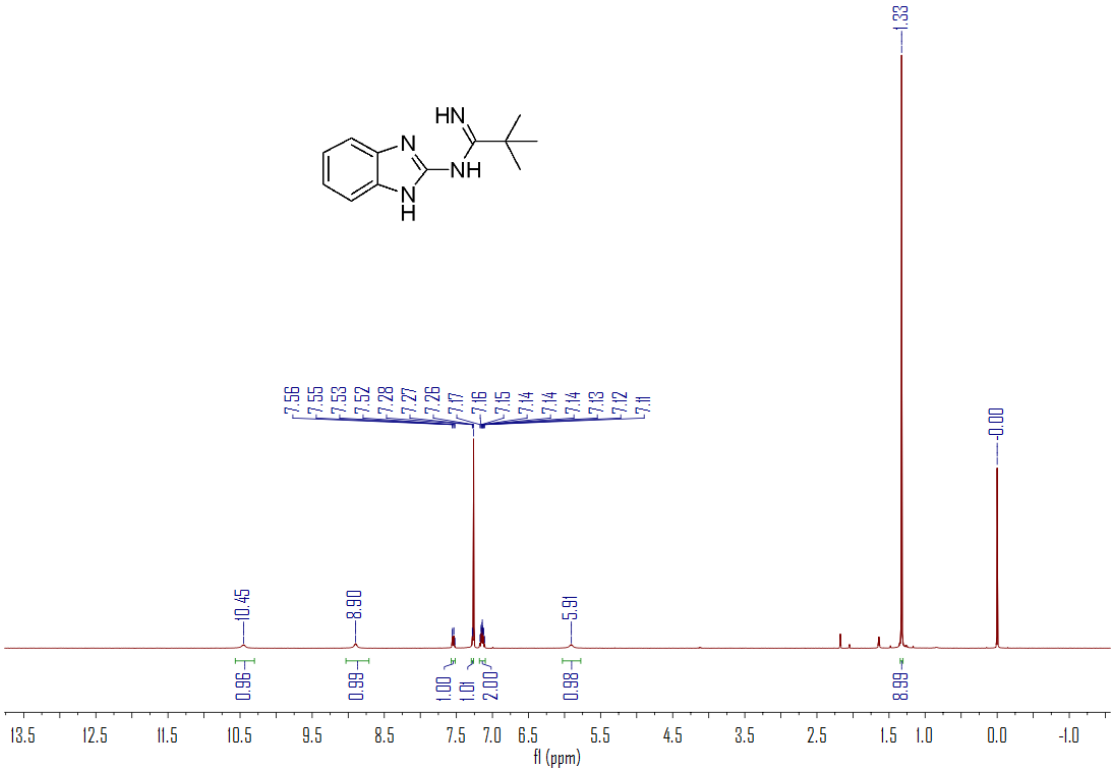


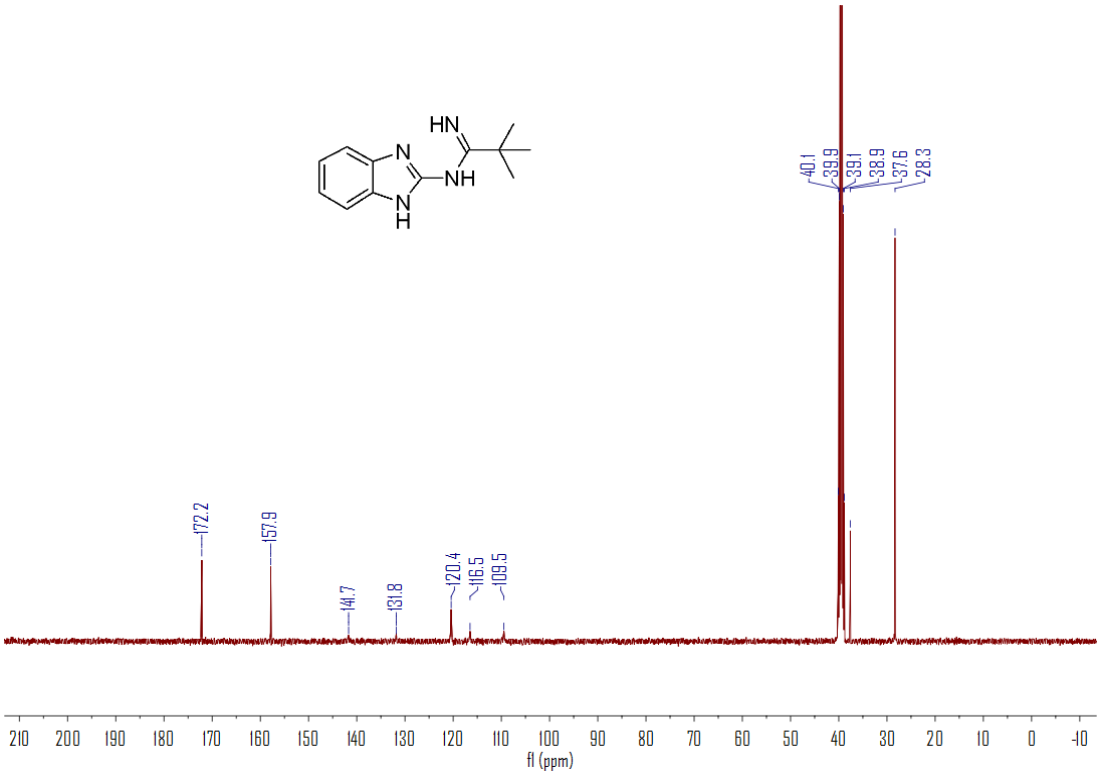
NMR spectra of **2m**:



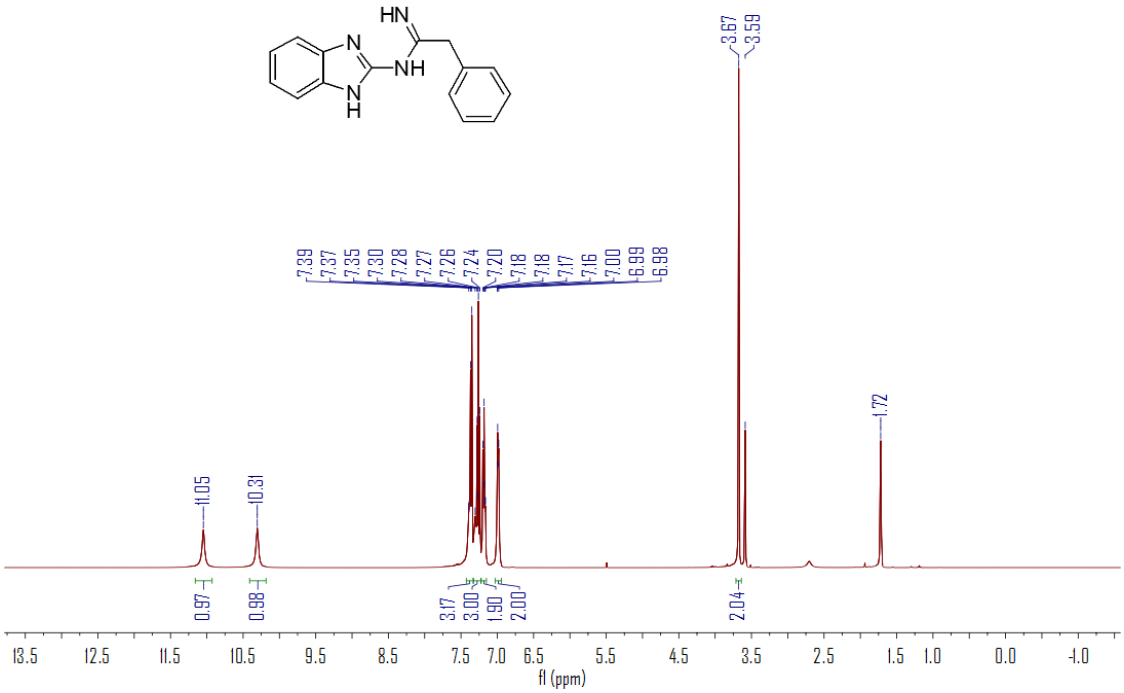


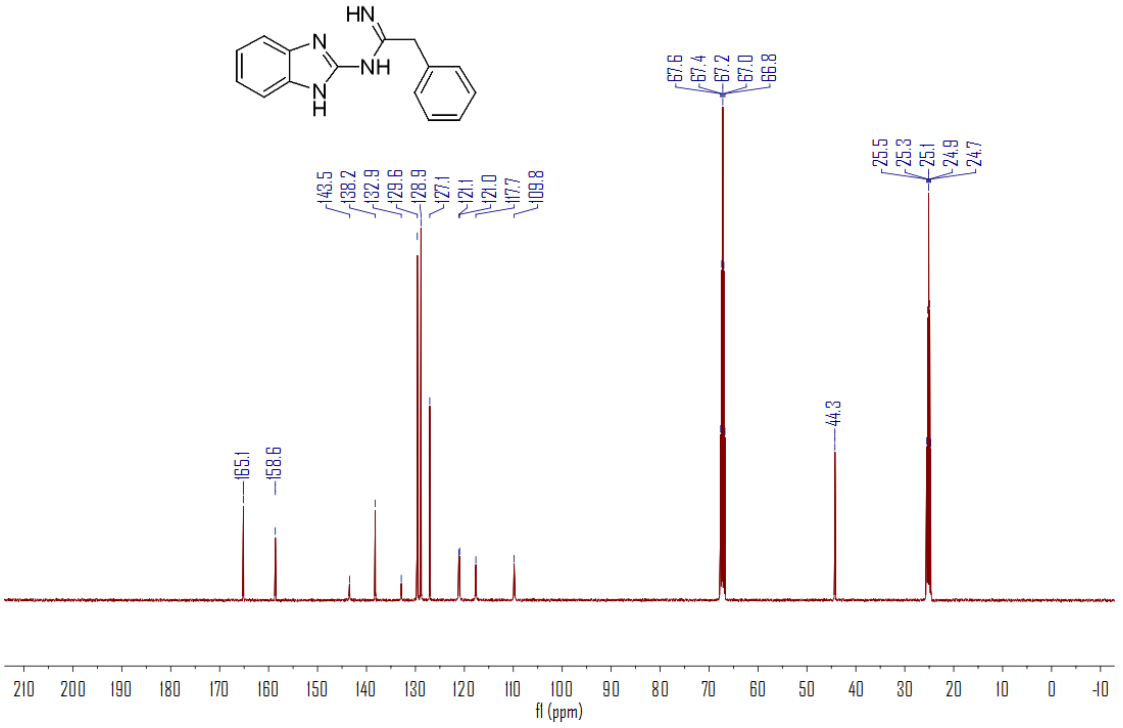
NMR spectra of **2n**:



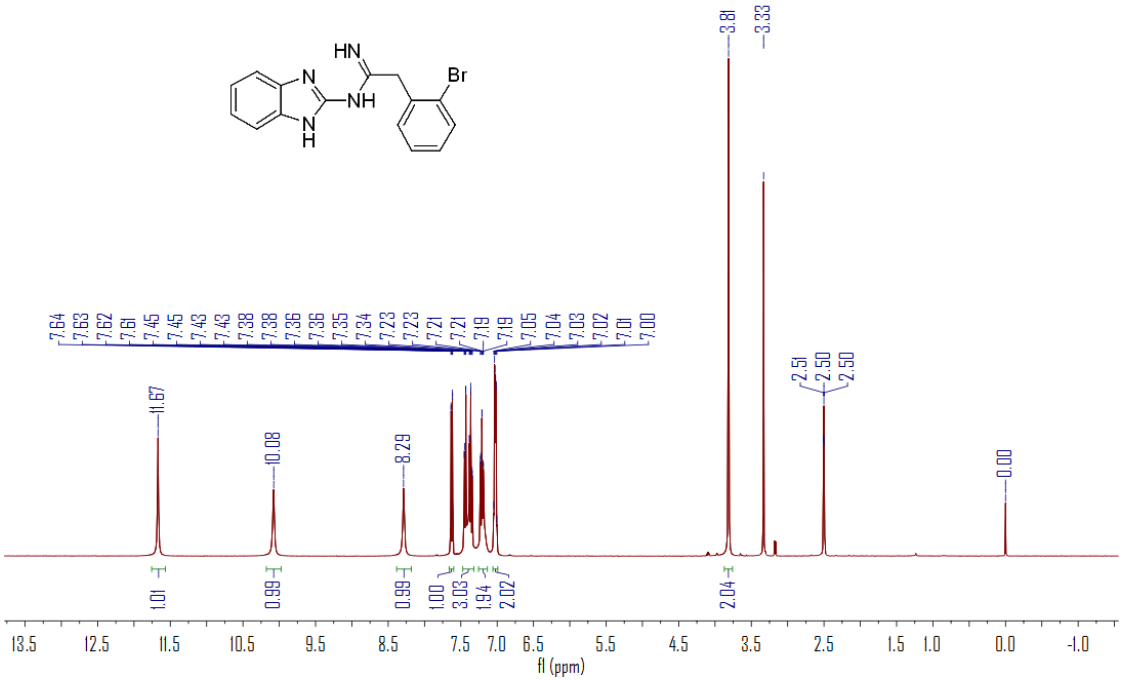


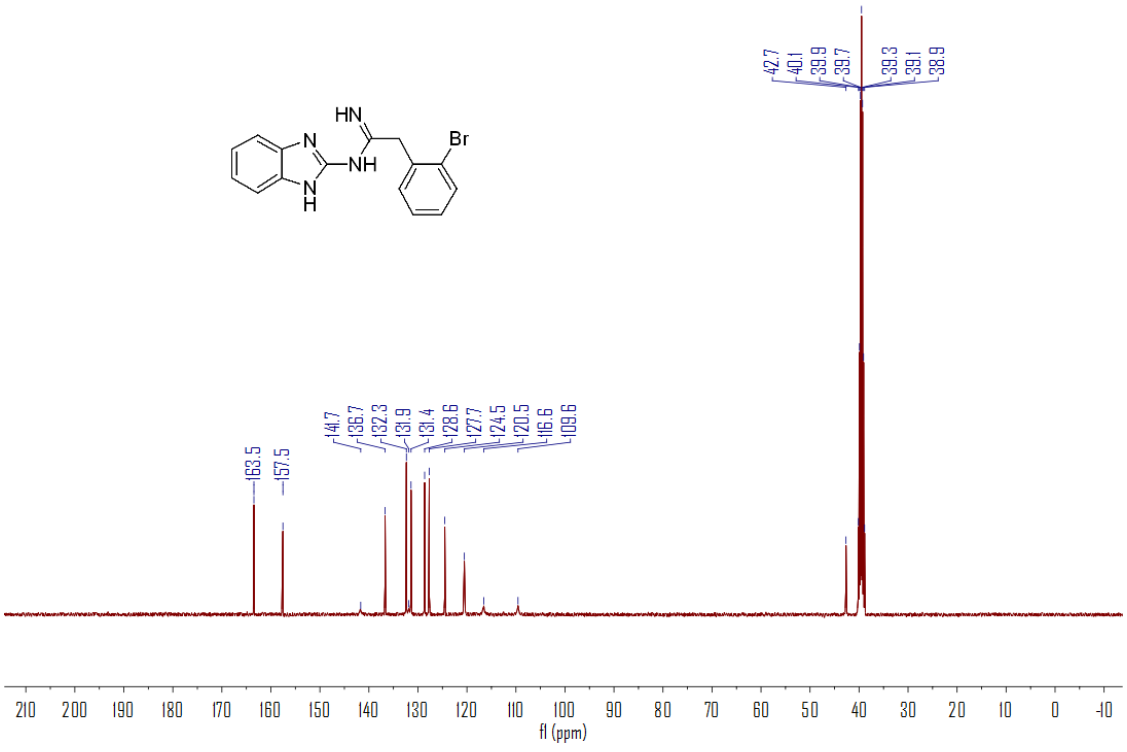
NMR spectra of **2o**:



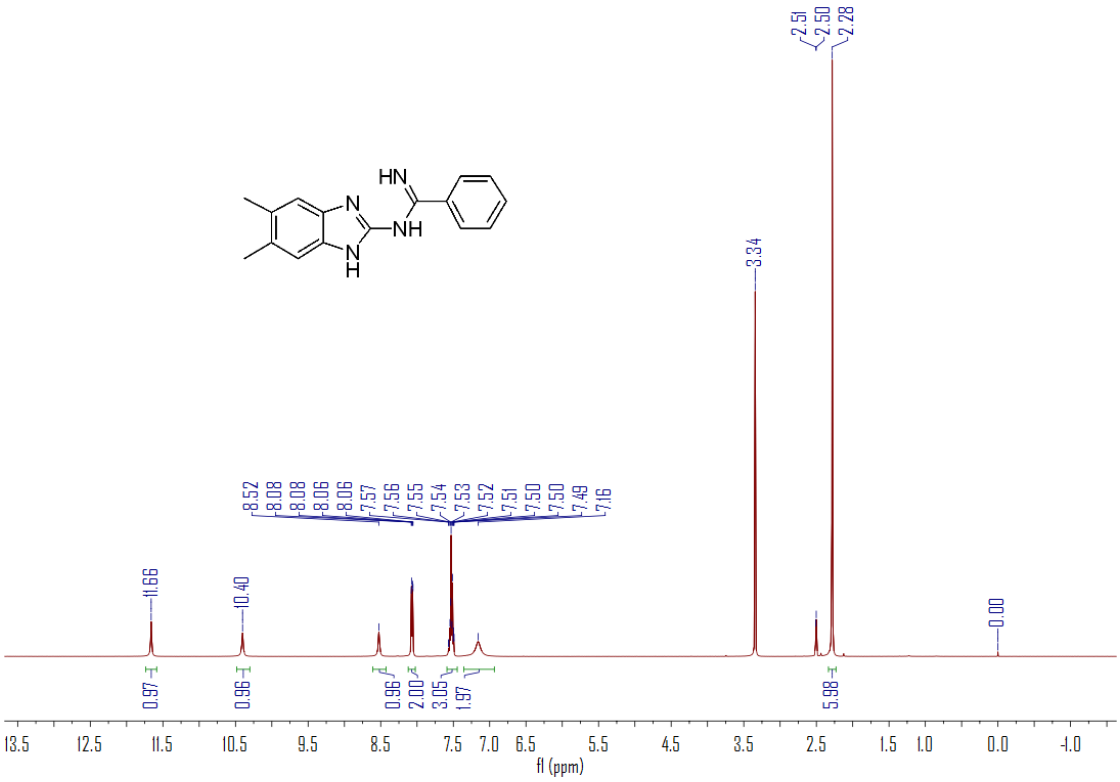


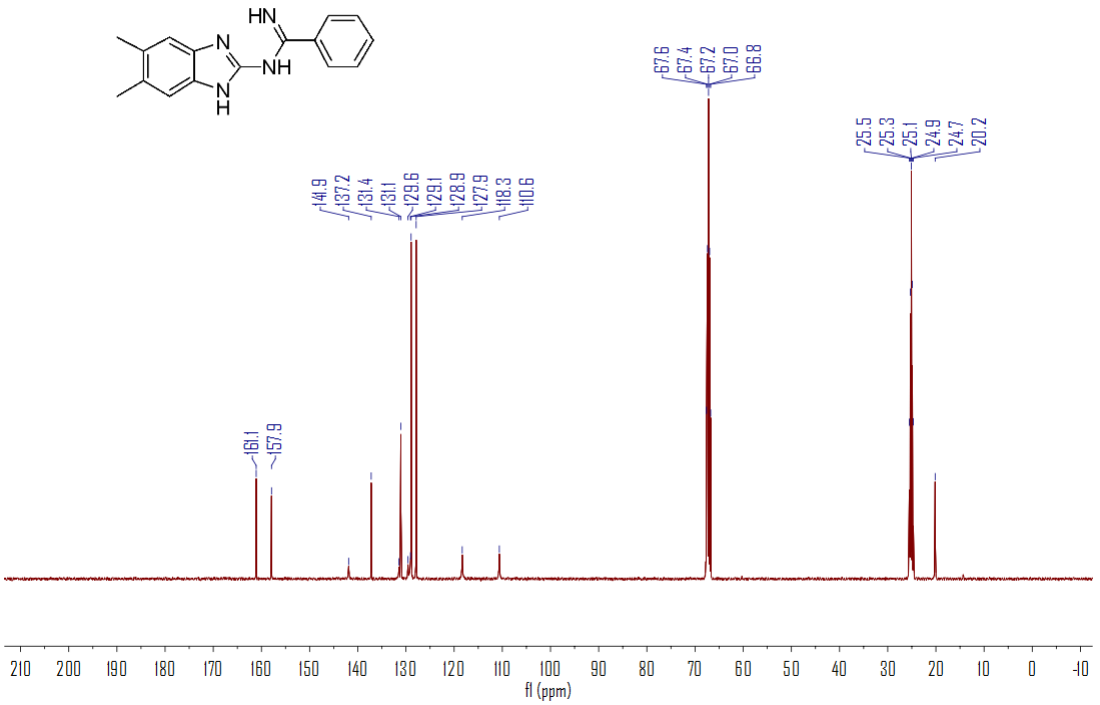
NMR spectra of **2p**:



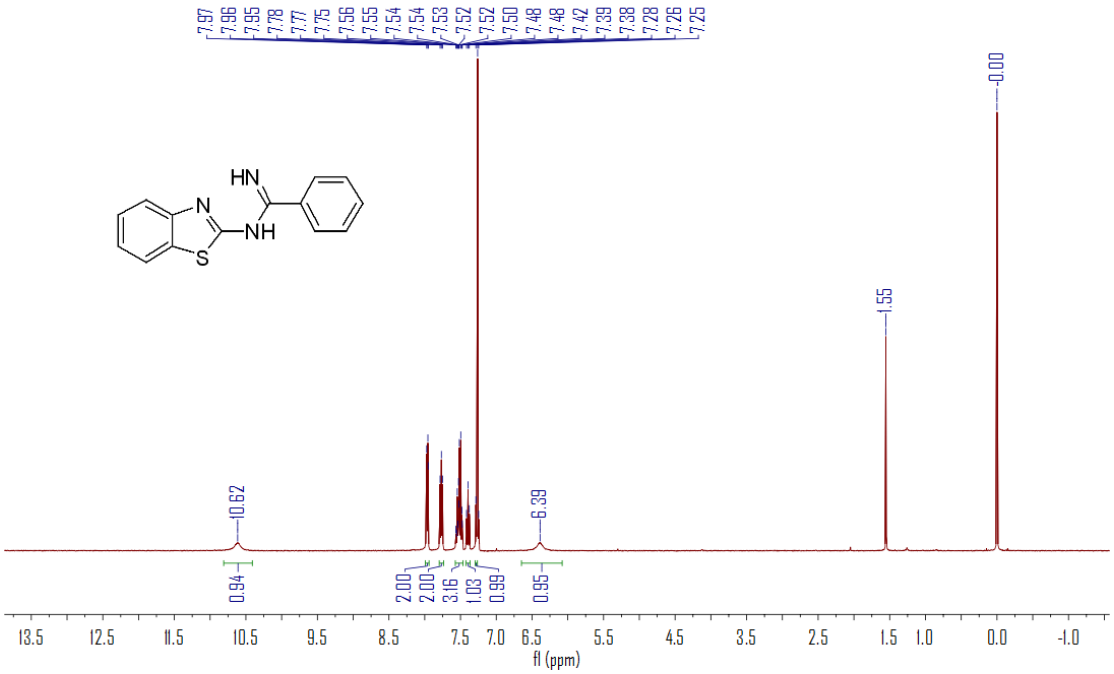


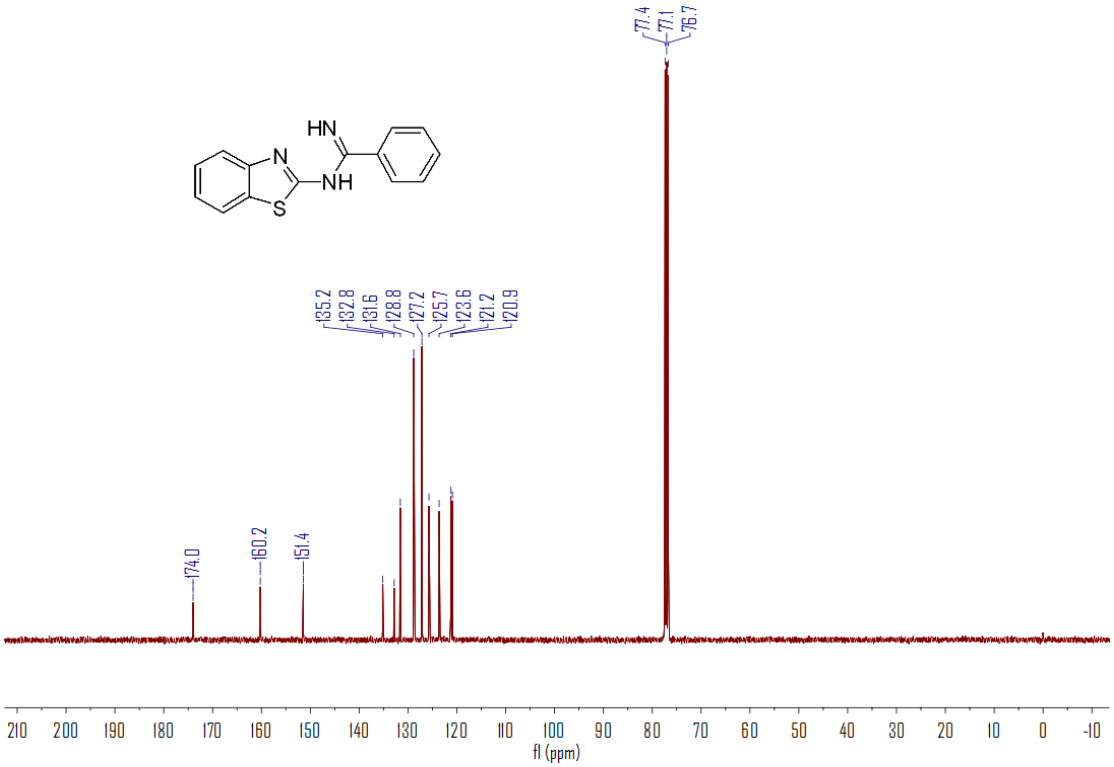
NMR spectra of **2q**:



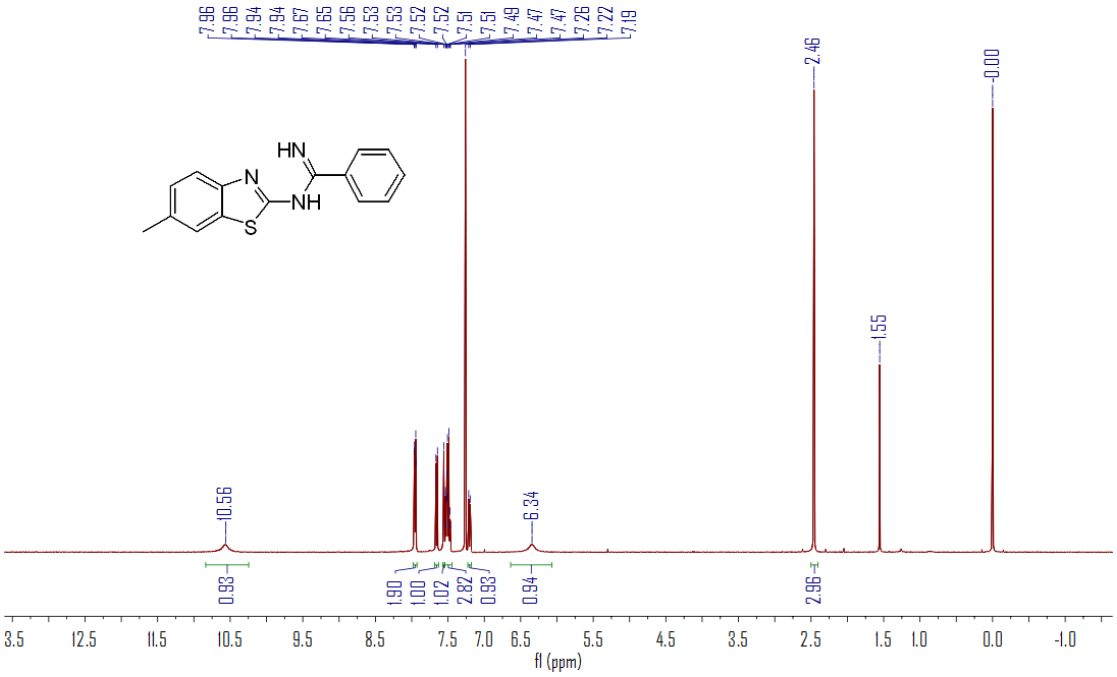


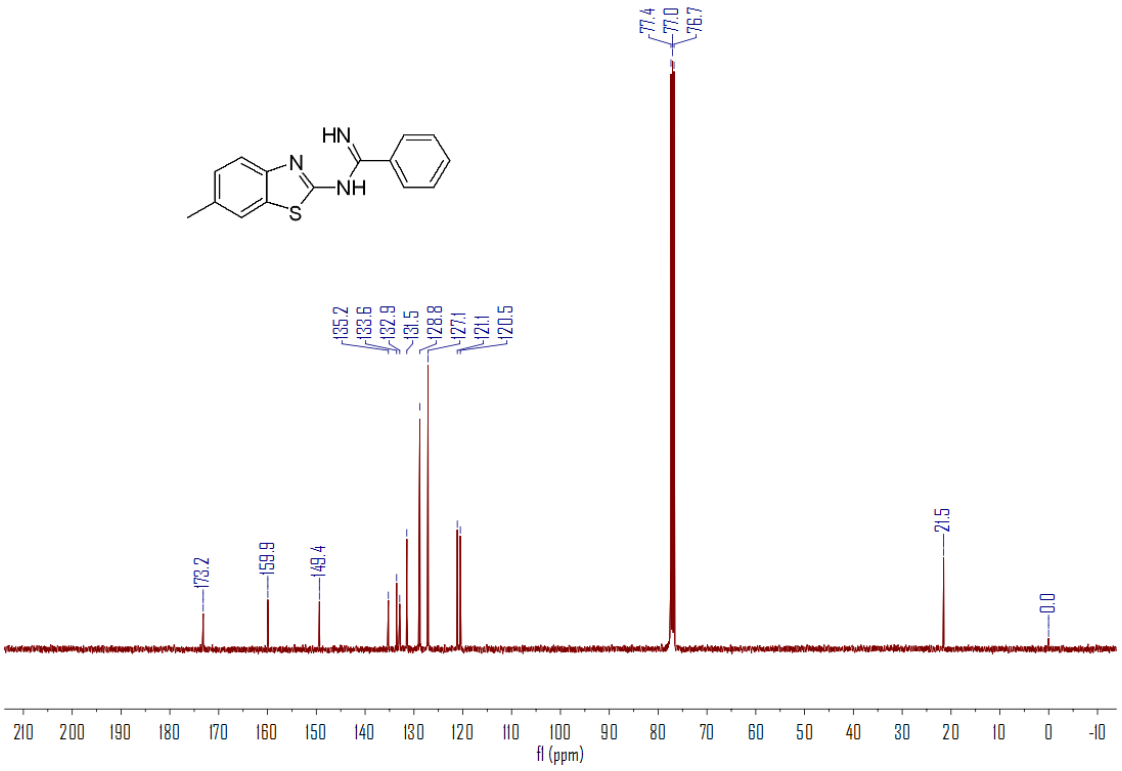
NMR spectra of **3a**:



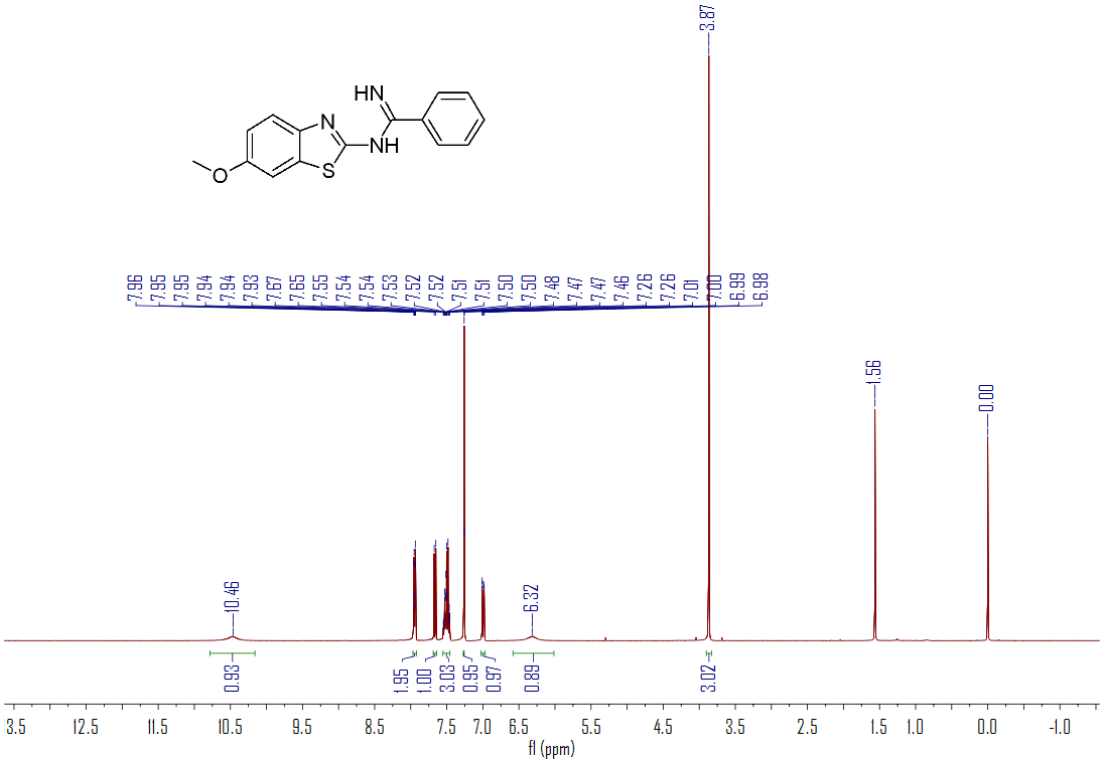


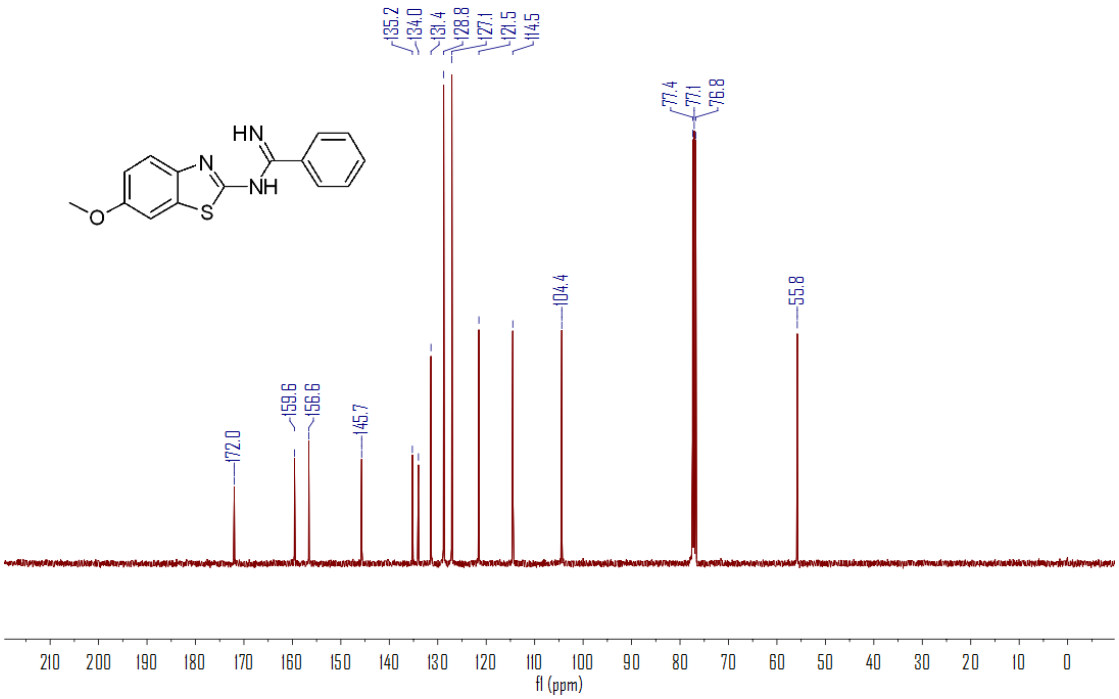
NMR spectra of **3b**:



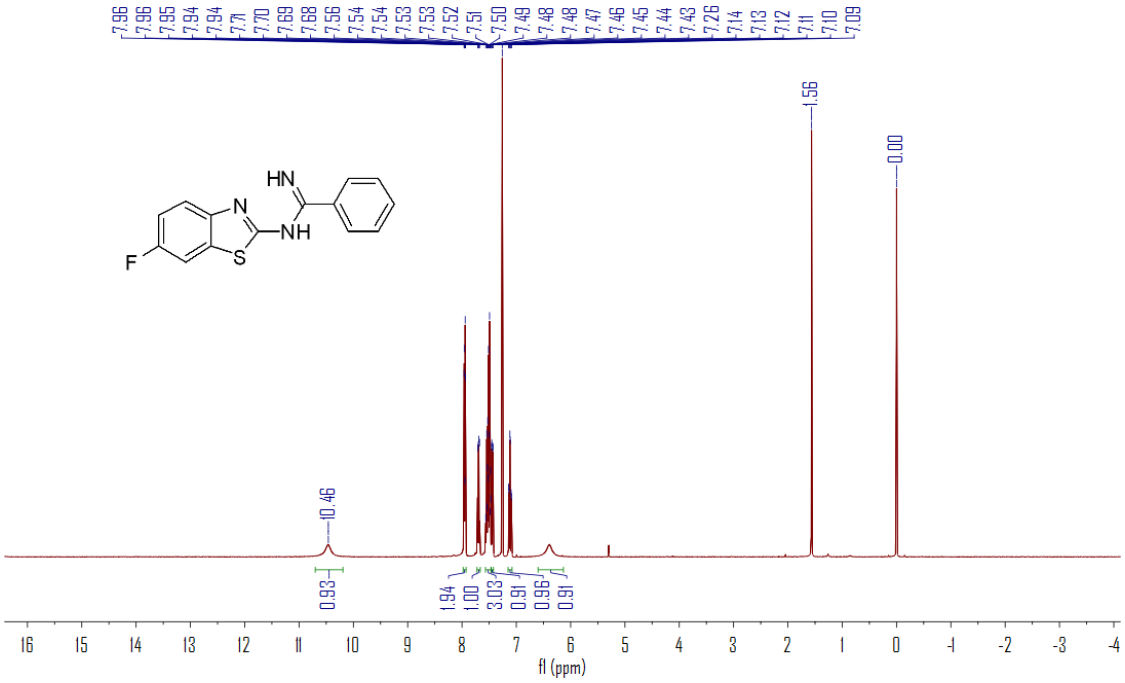


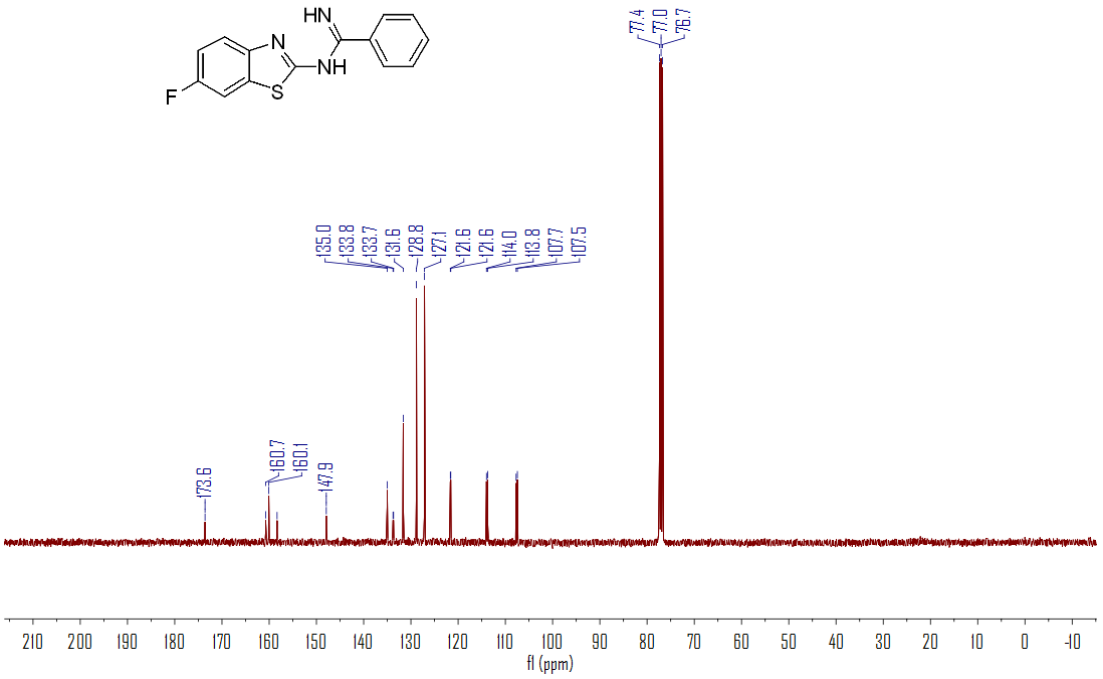
NMR spectra of **3c**:



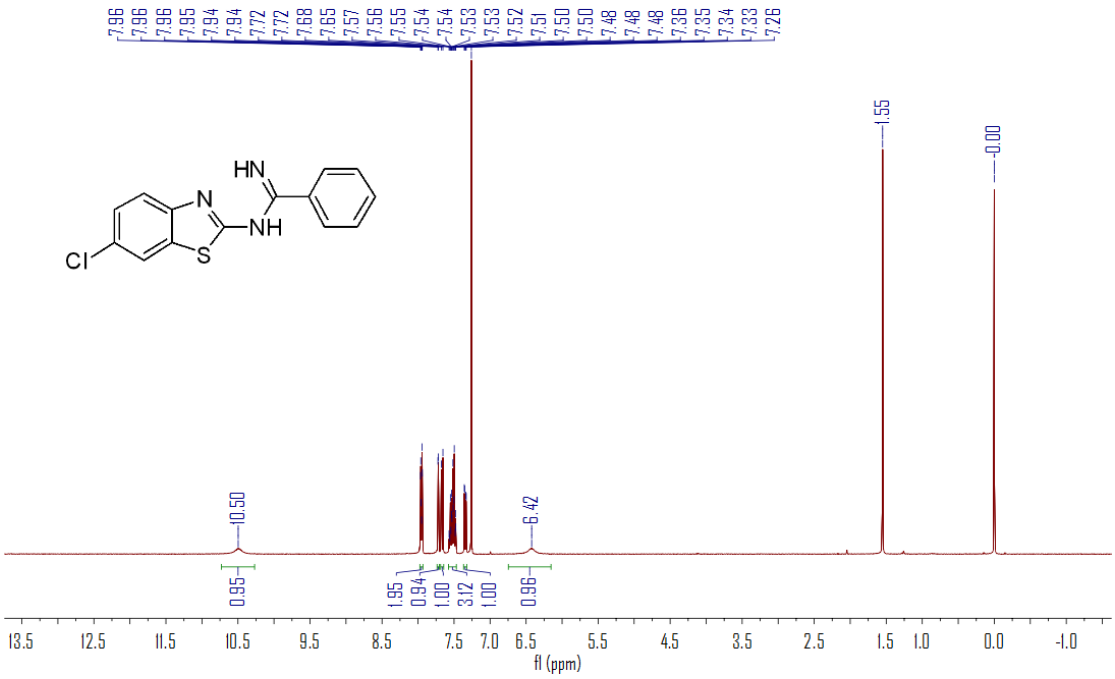


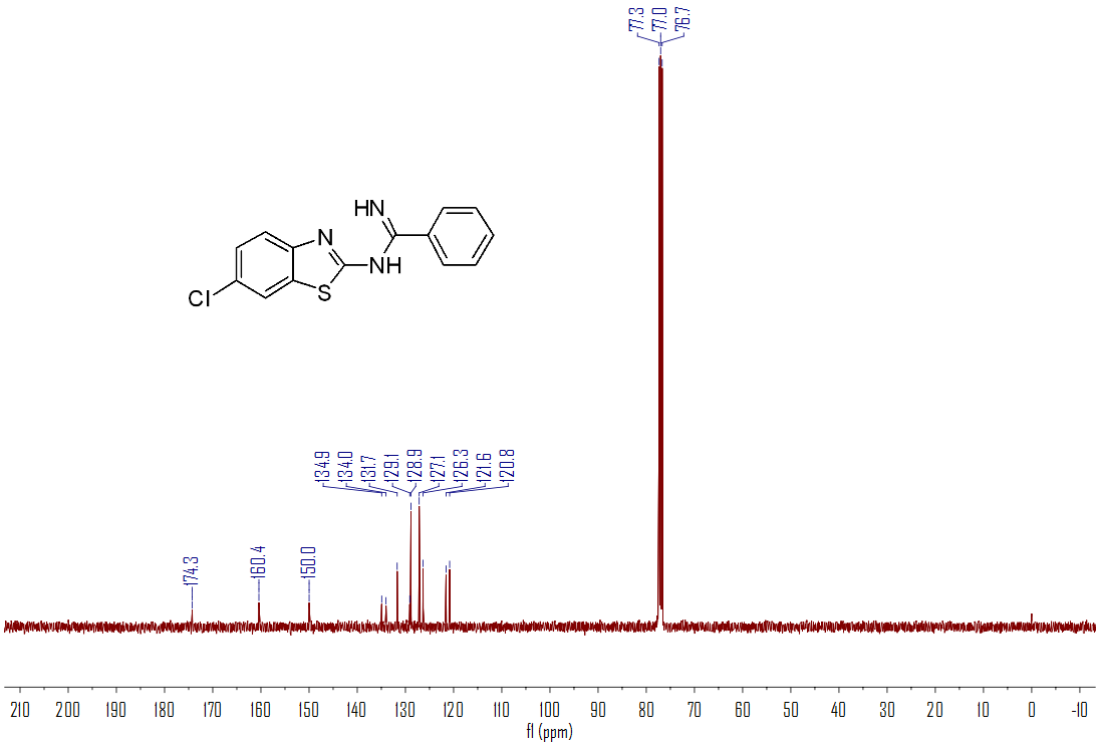
NMR spectra of **3d**:



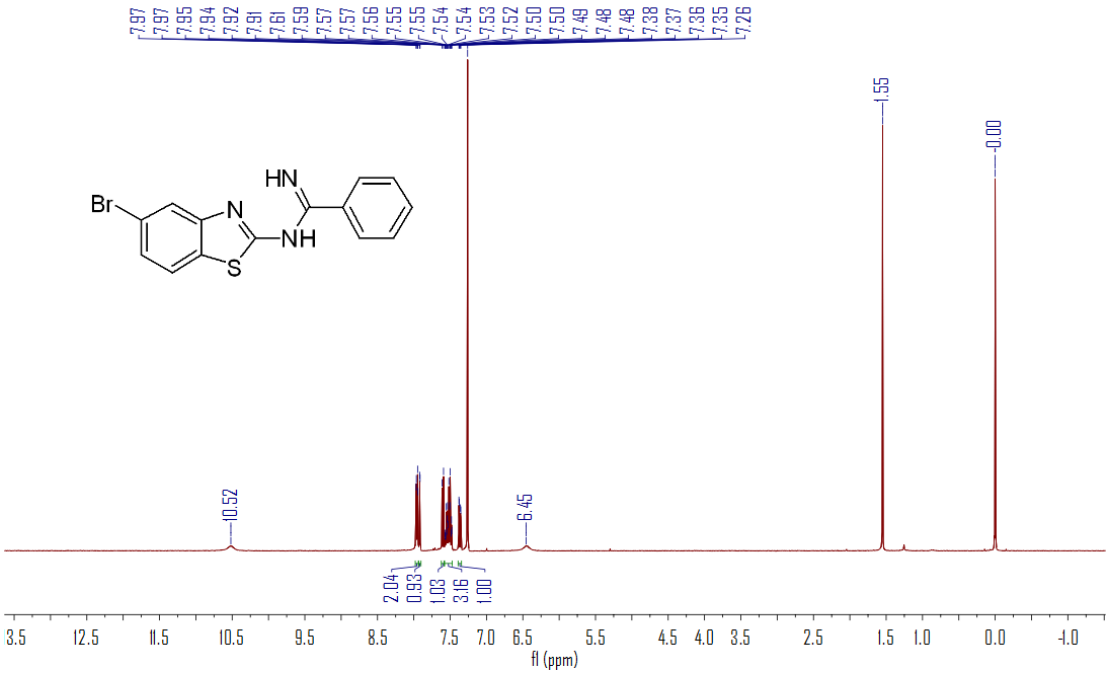


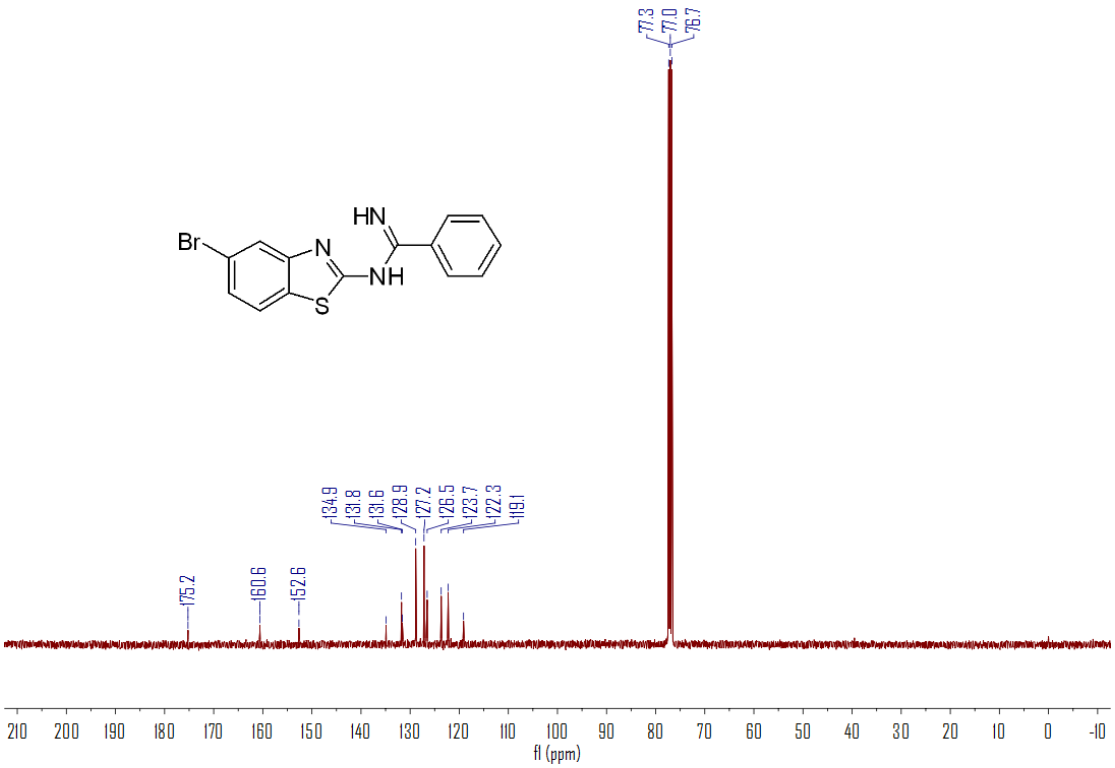
NMR spectra of **3e**:



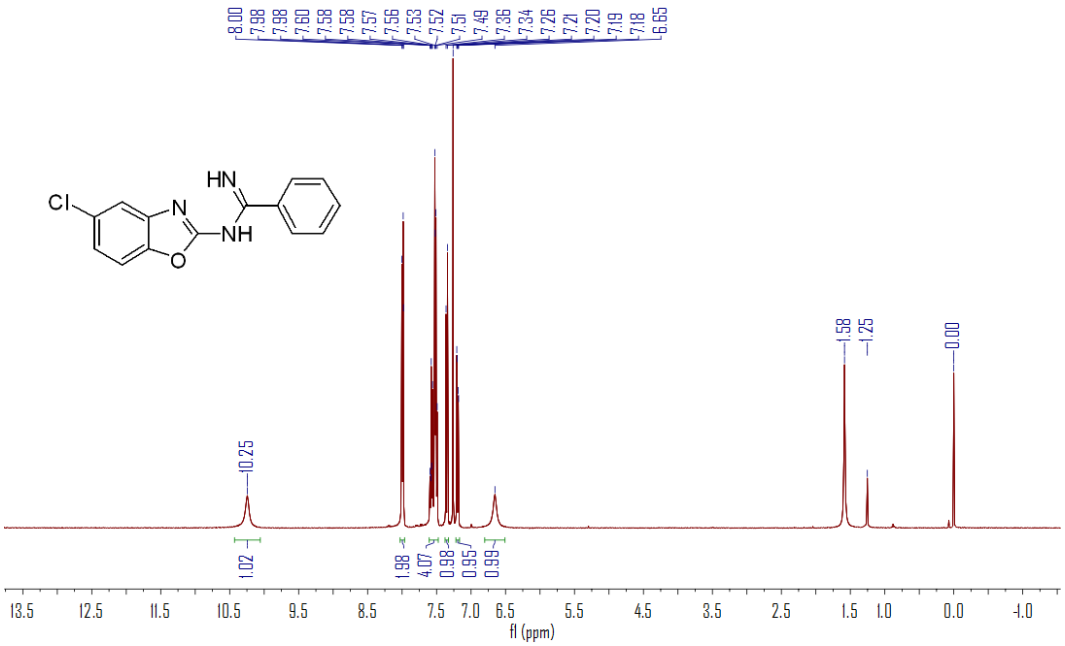


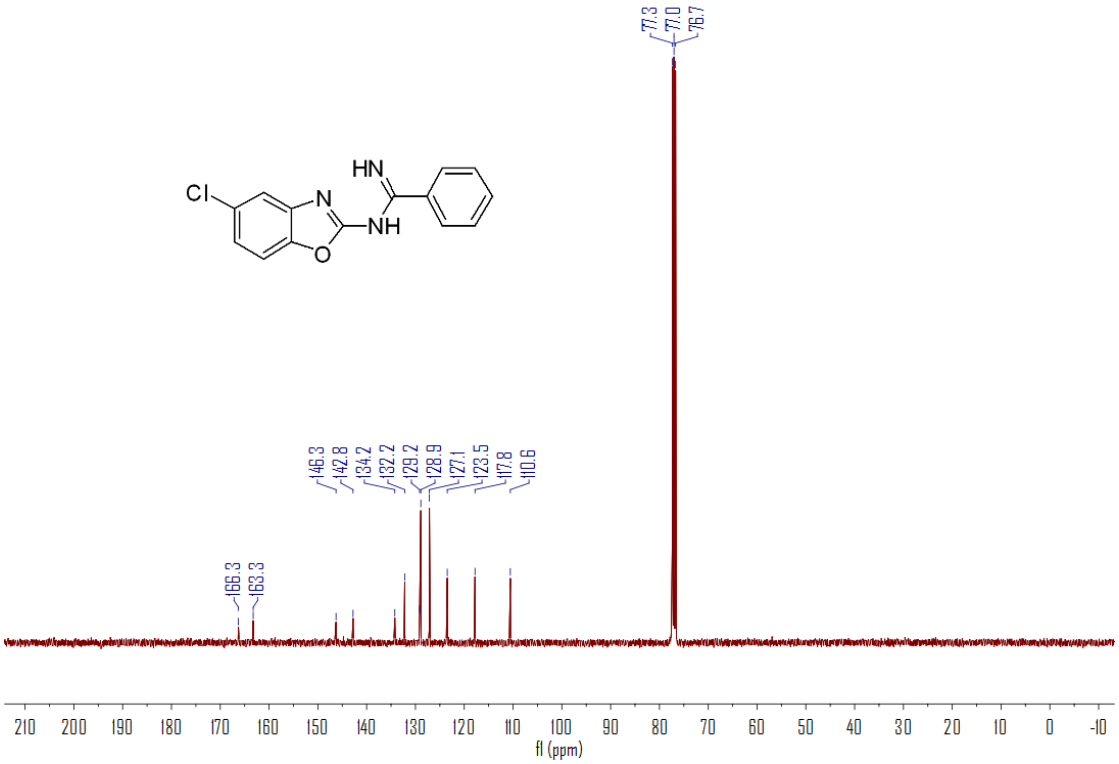
NMR spectra of **3f**:



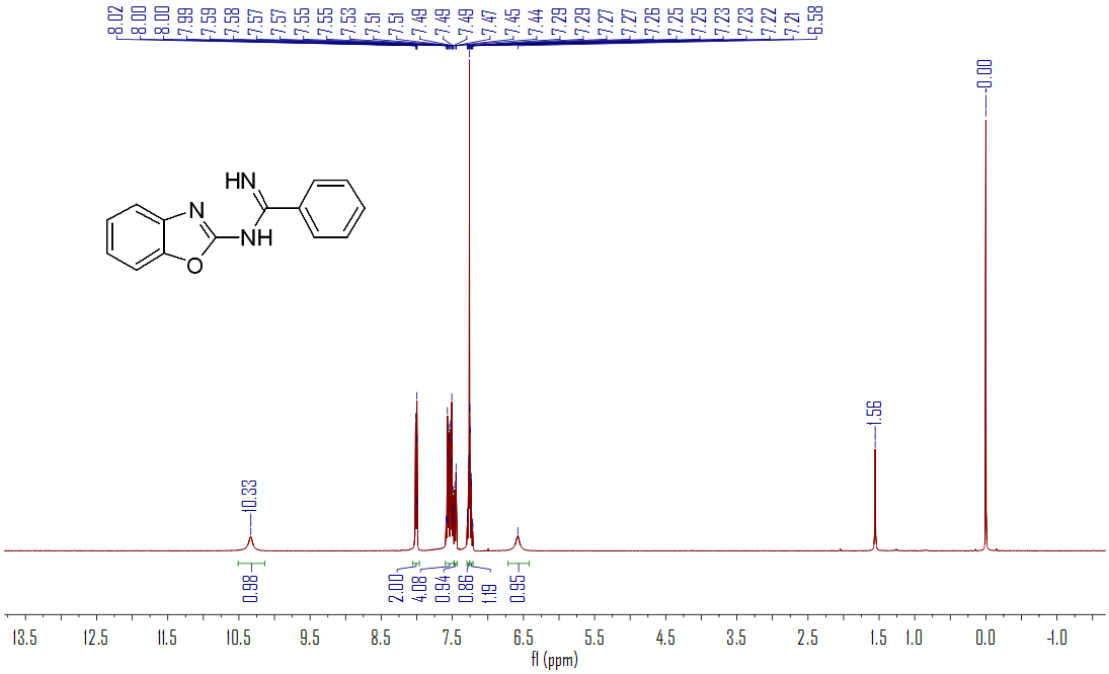


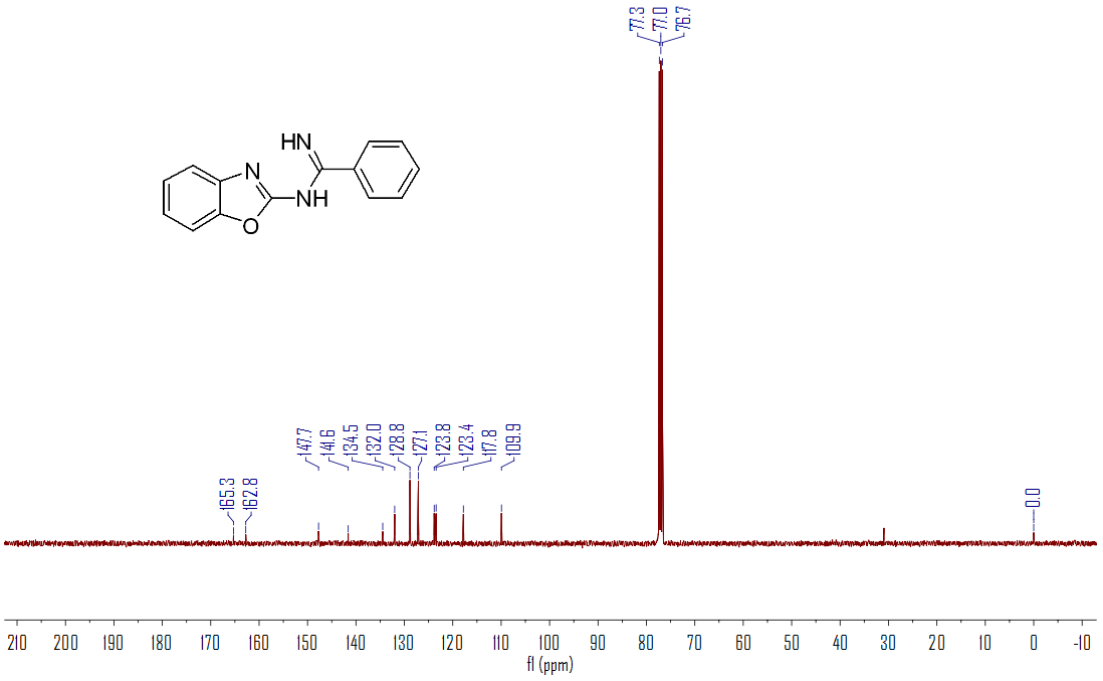
NMR spectra of **3g**:





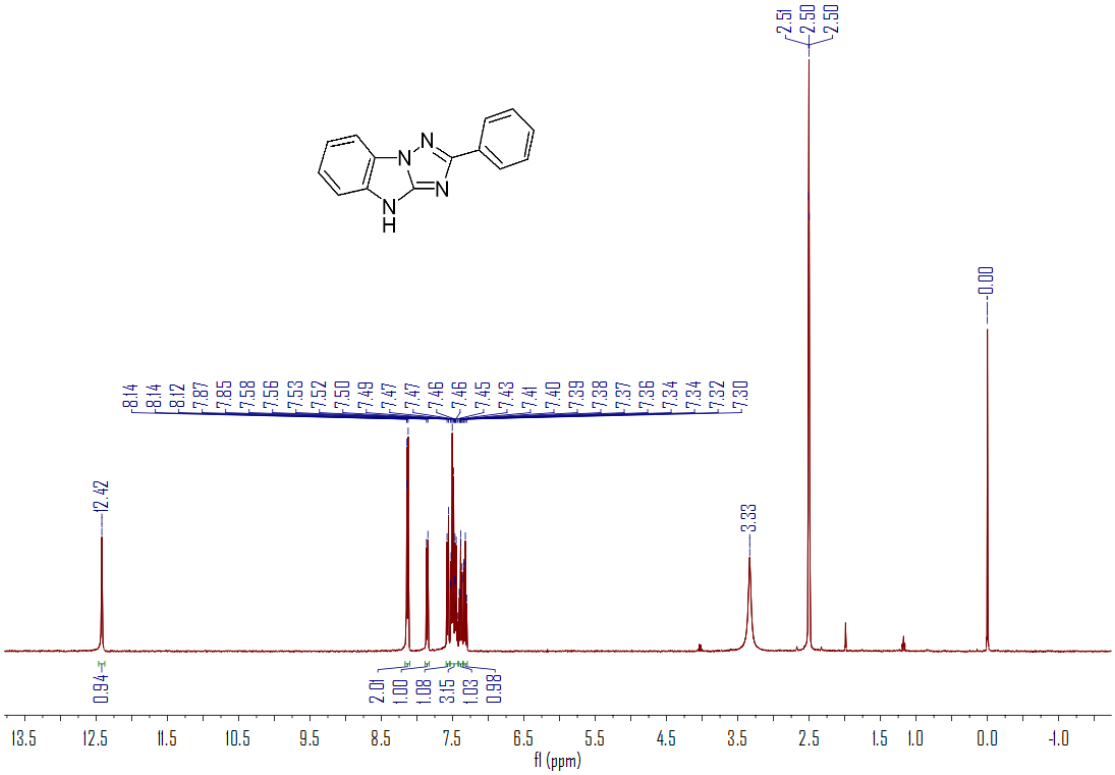
NMR spectra of **3h**:

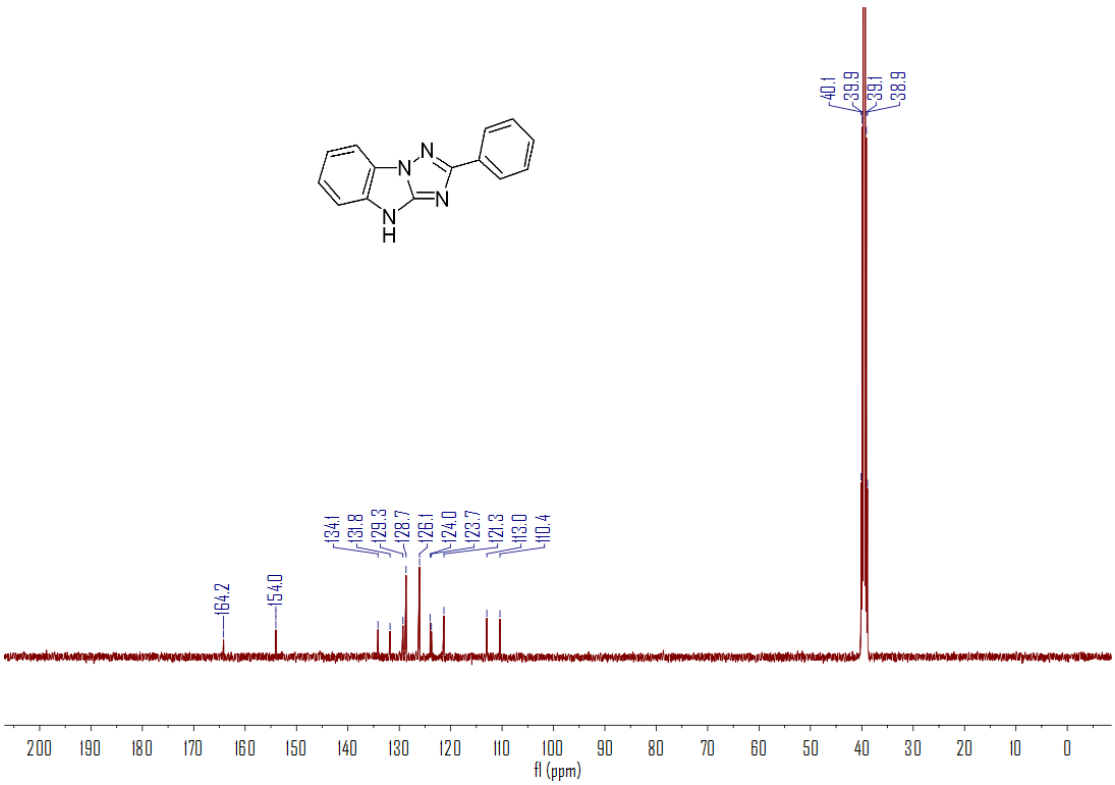




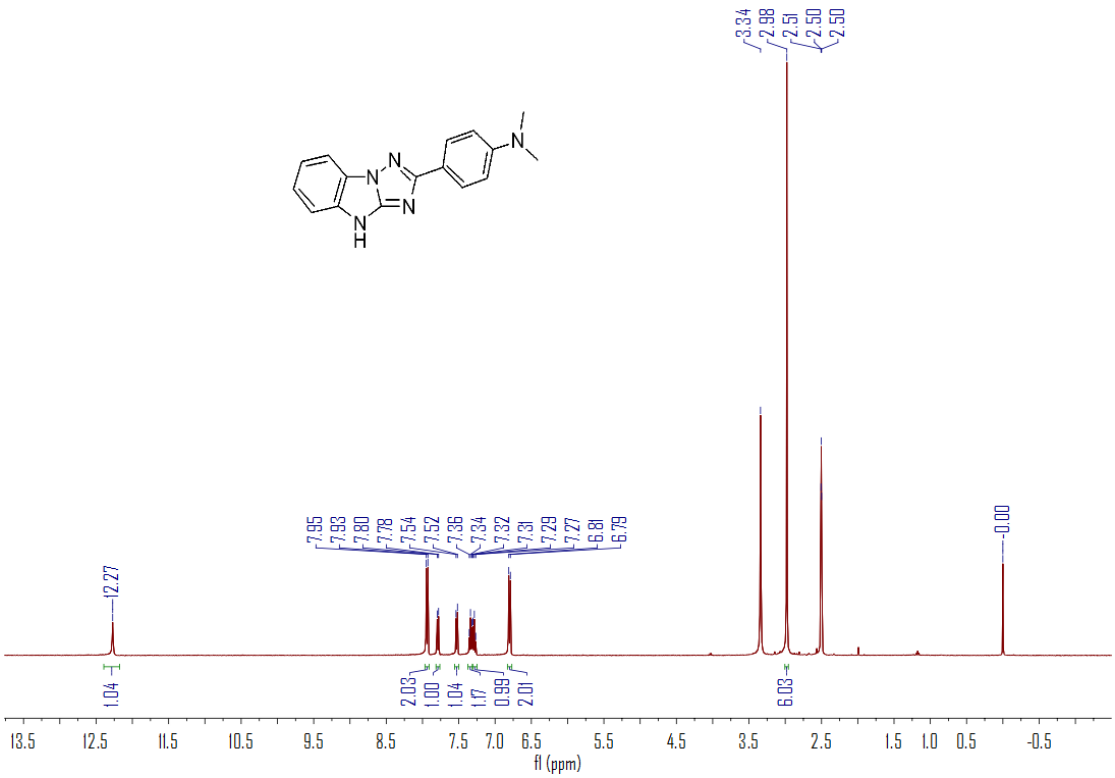
7.2 NMR spectra of trizoles

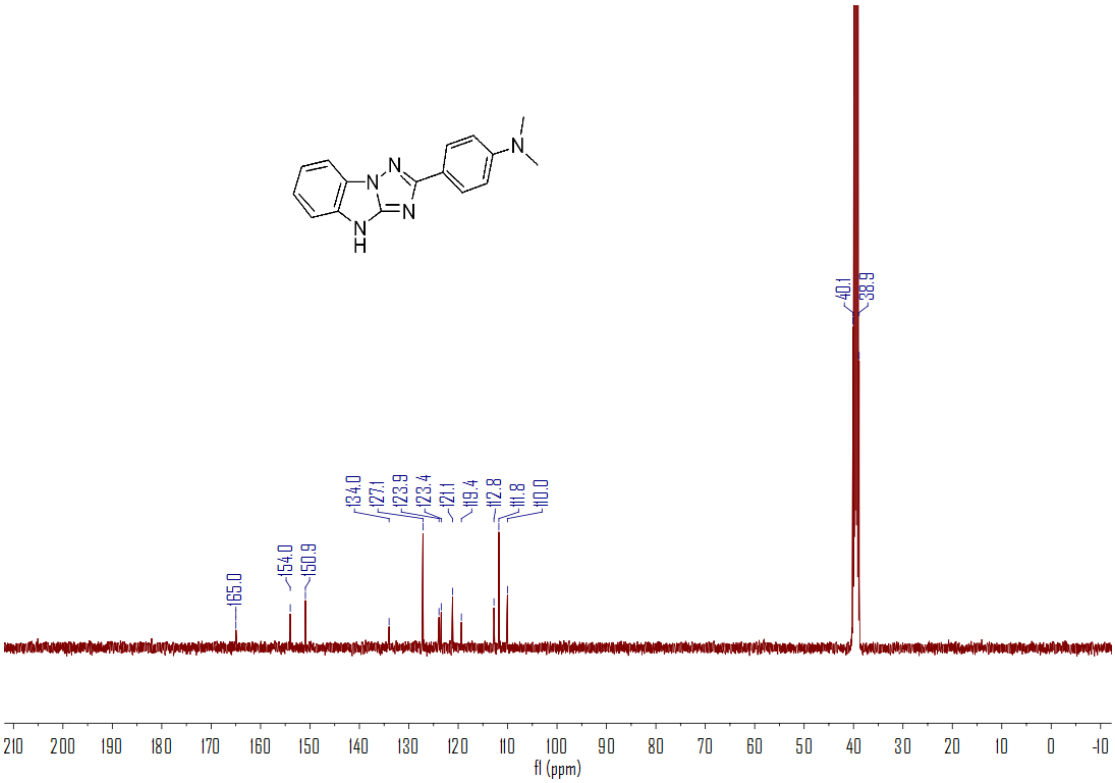
NMR spectra of **1a**:



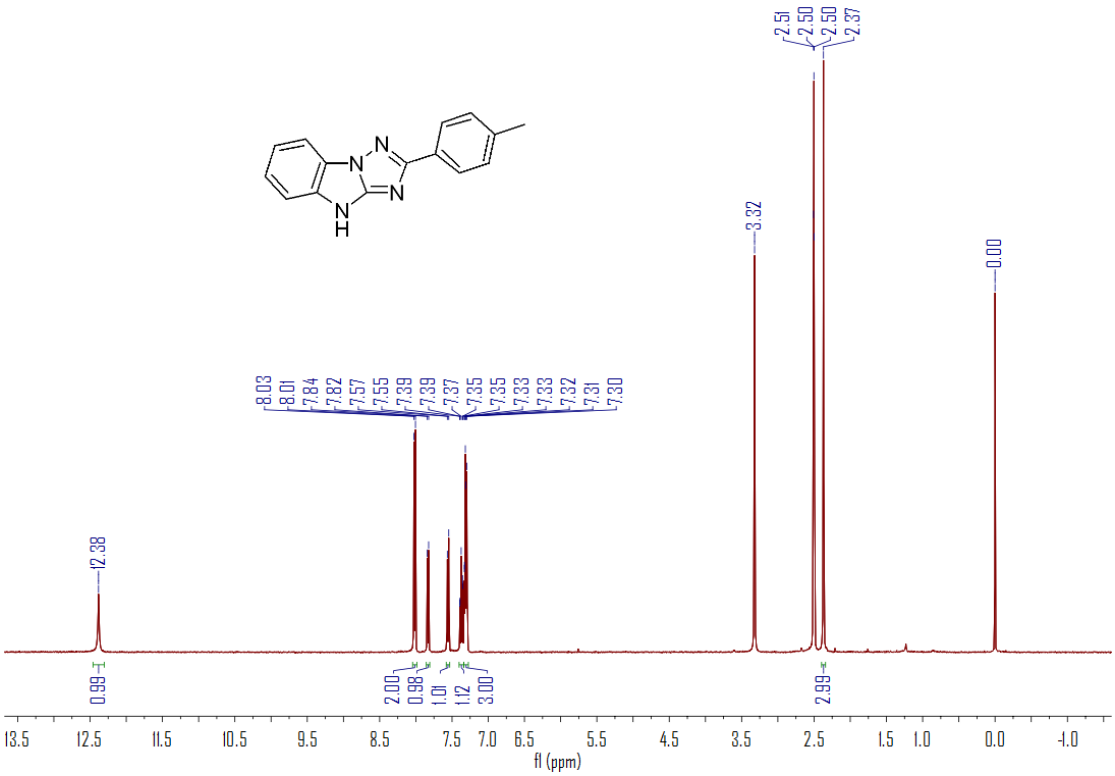


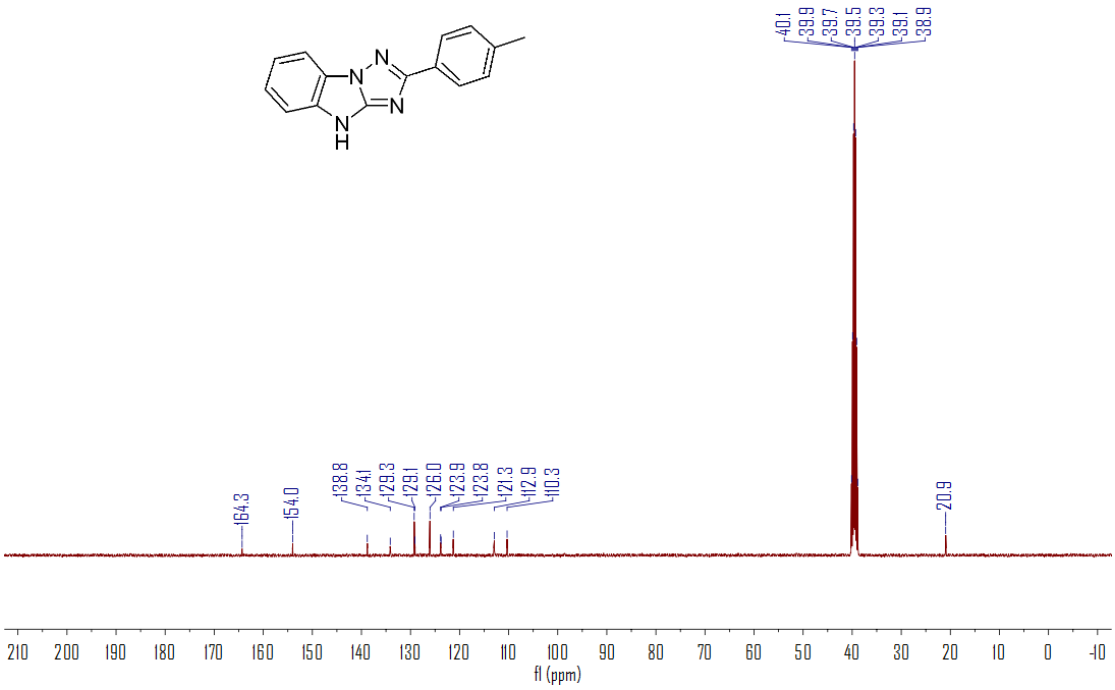
NMR spectra of **1b**:



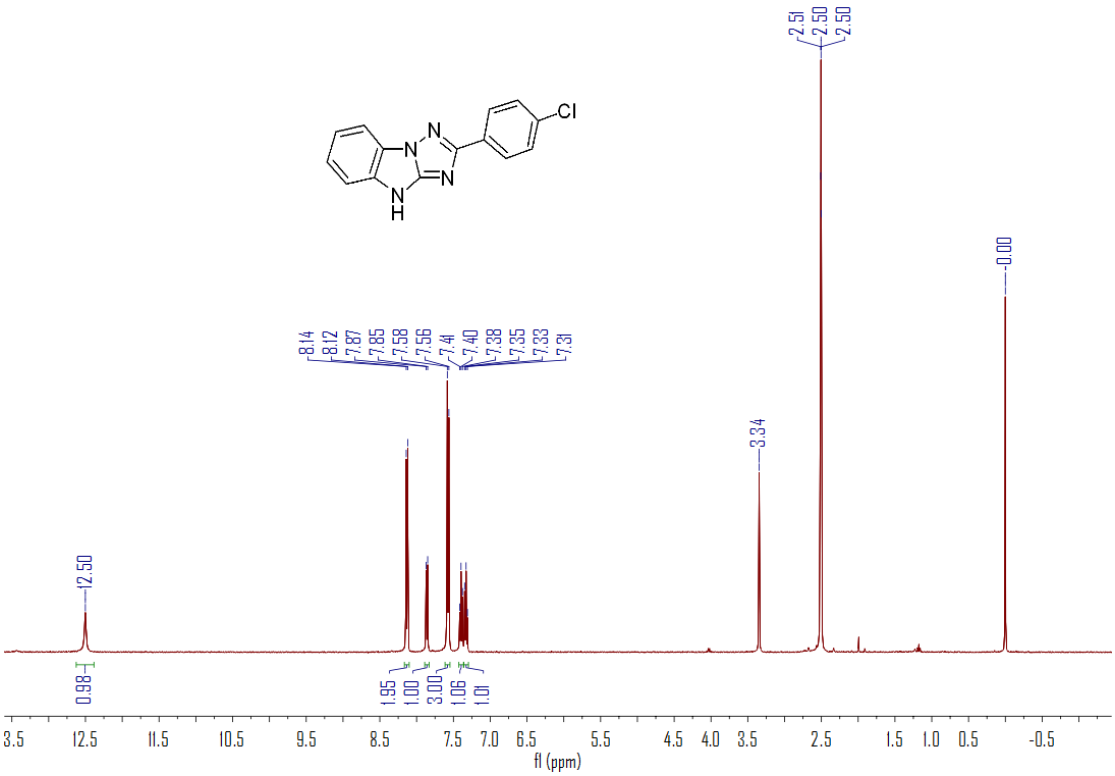


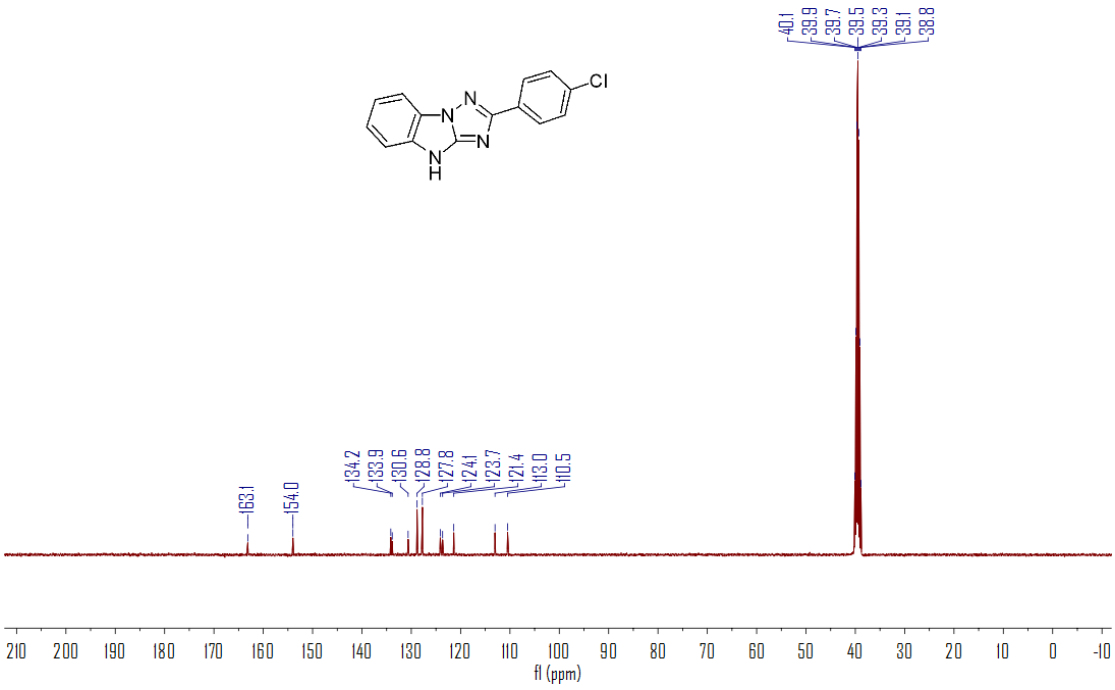
NMR spectra of **1c**:



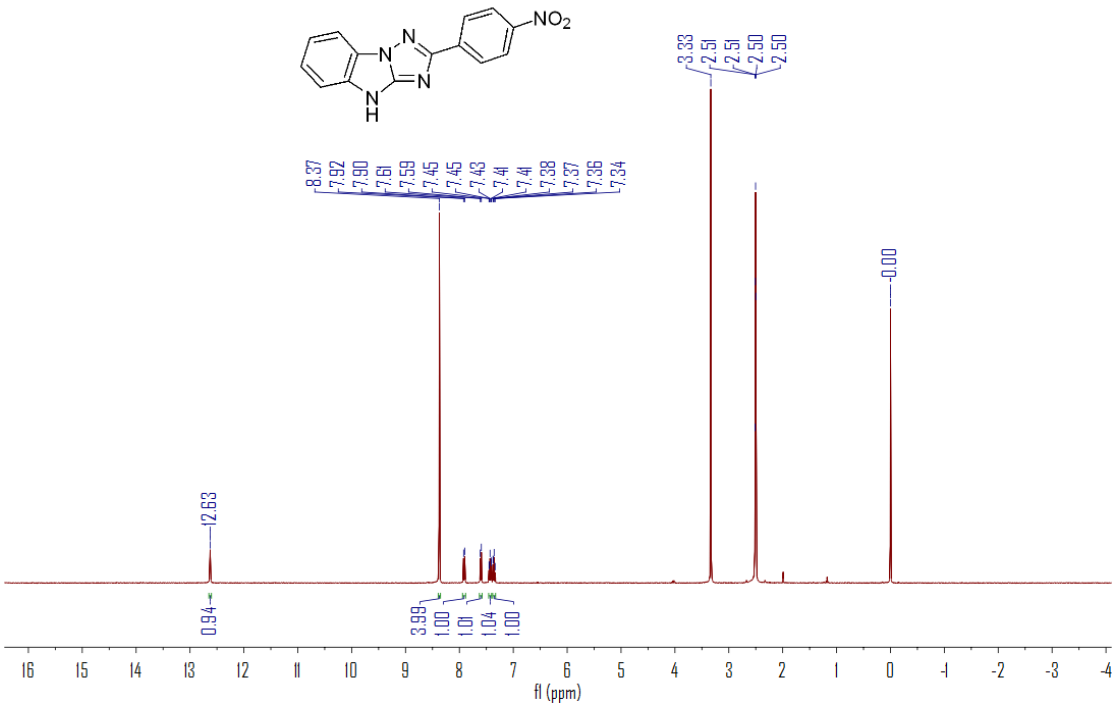


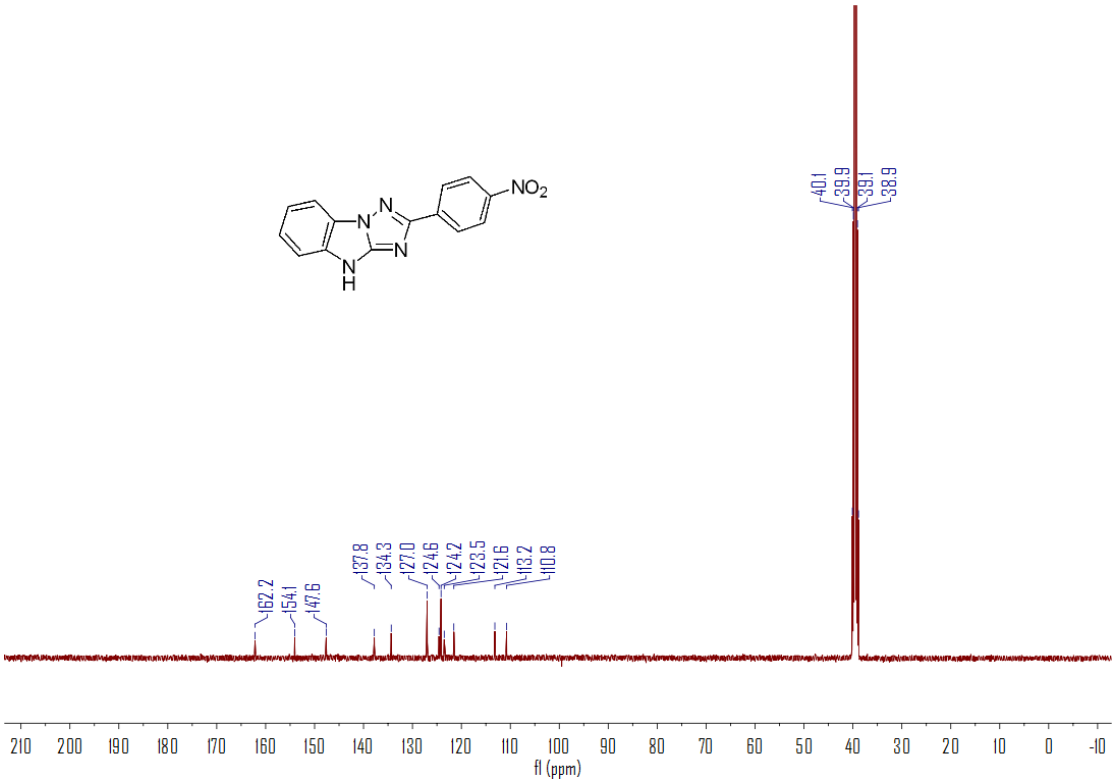
NMR spectra of **1d**:



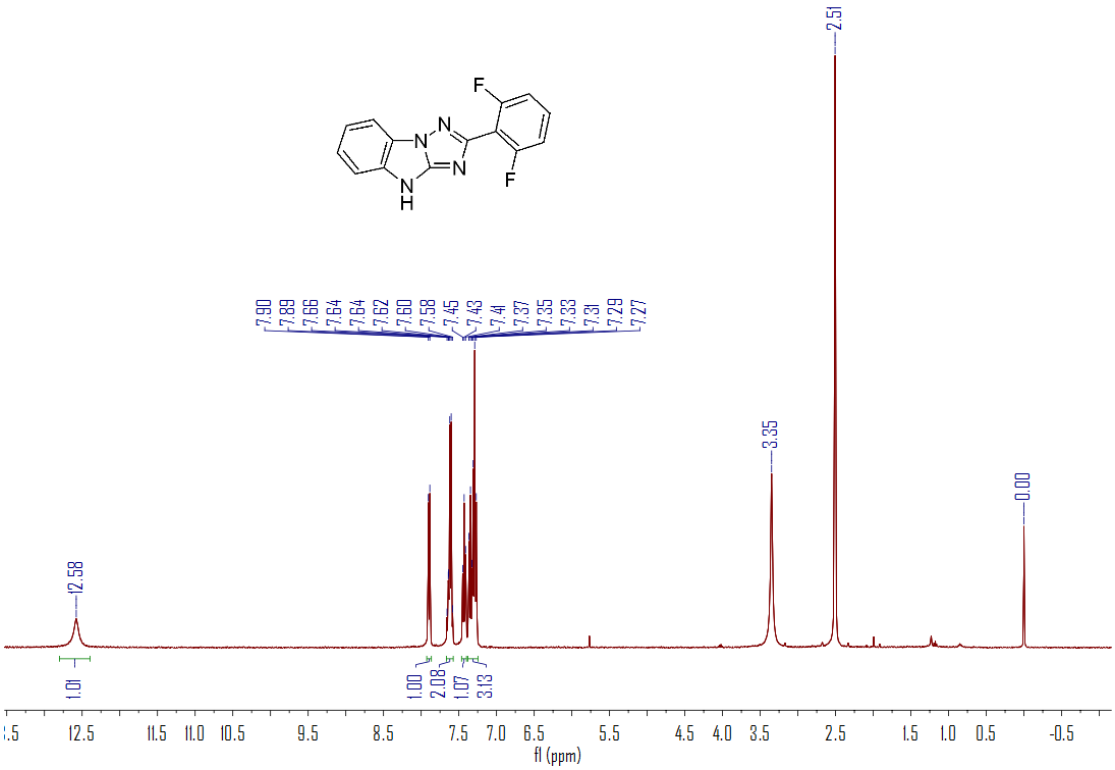


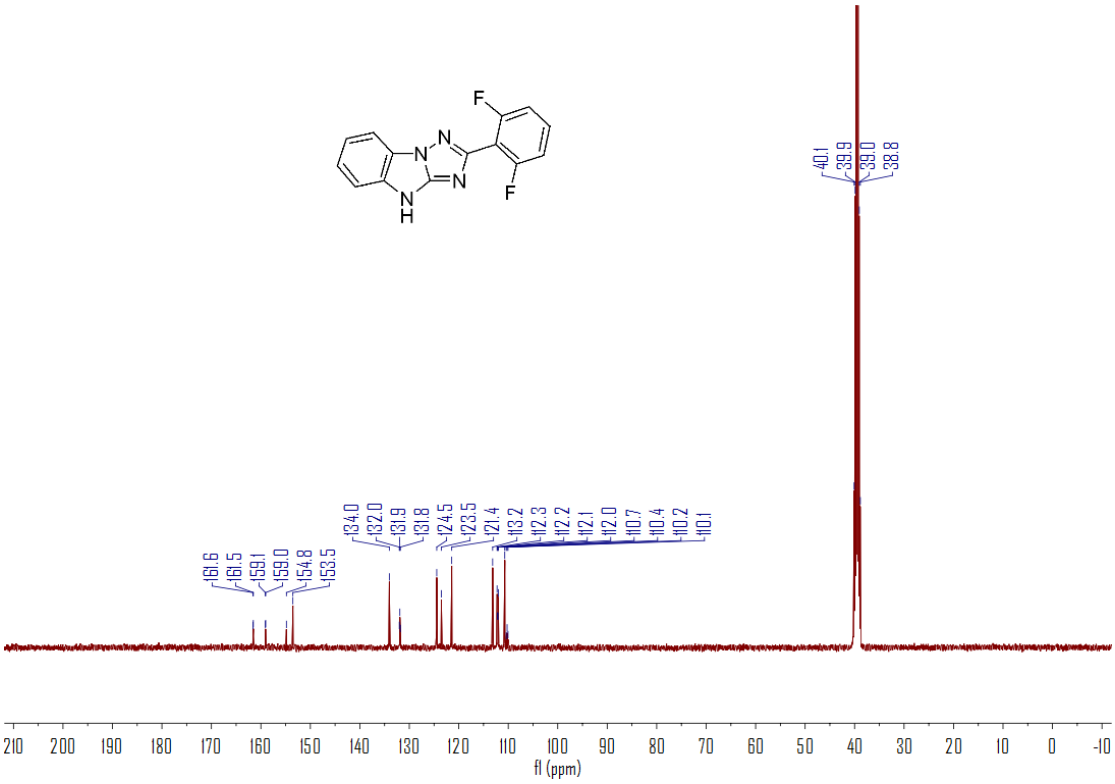
NMR spectra of **1e**:



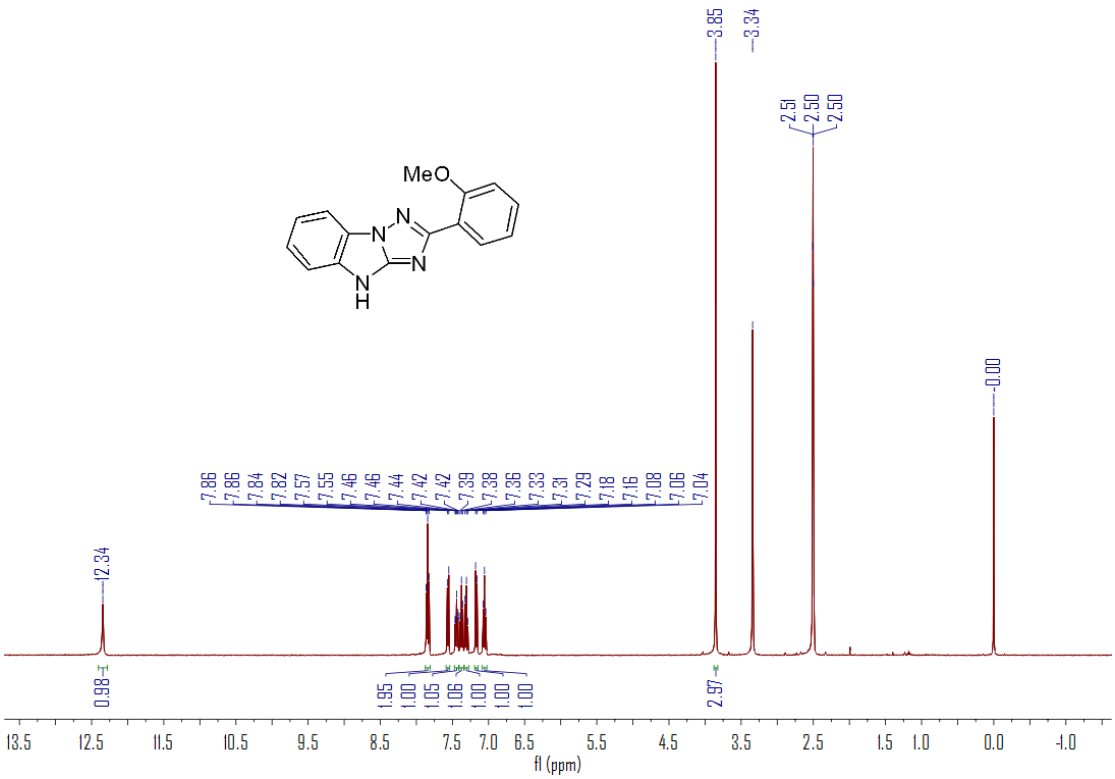


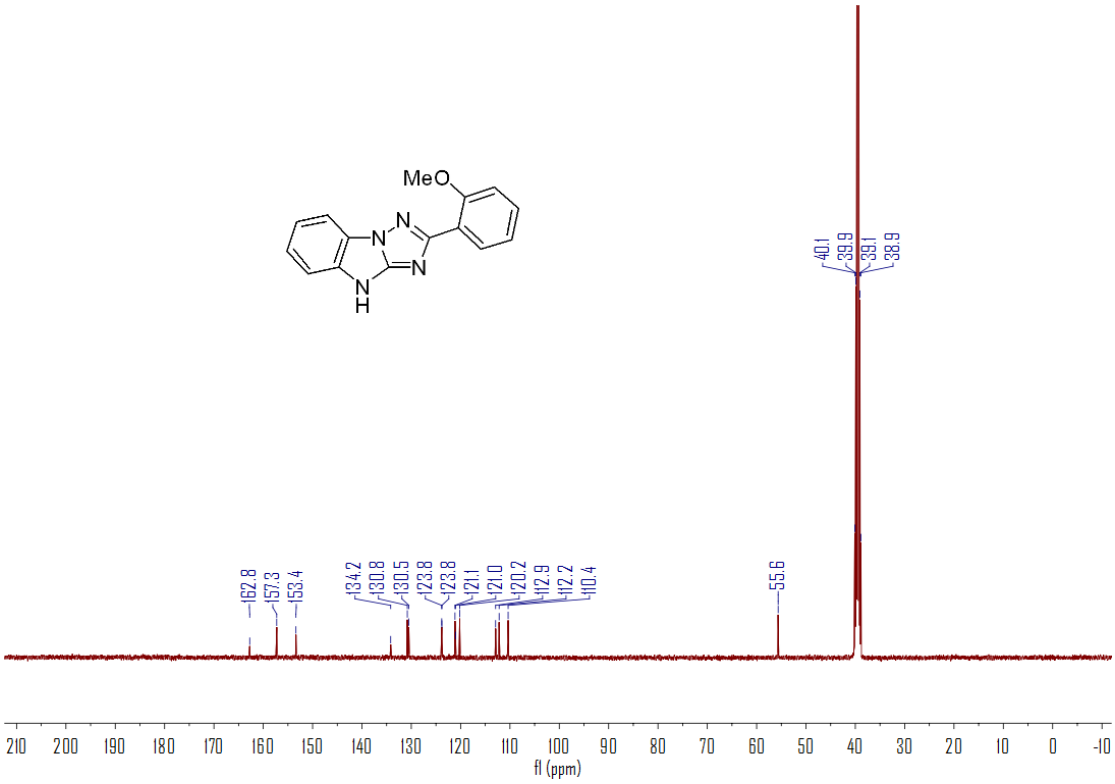
NMR spectra of **1f**:



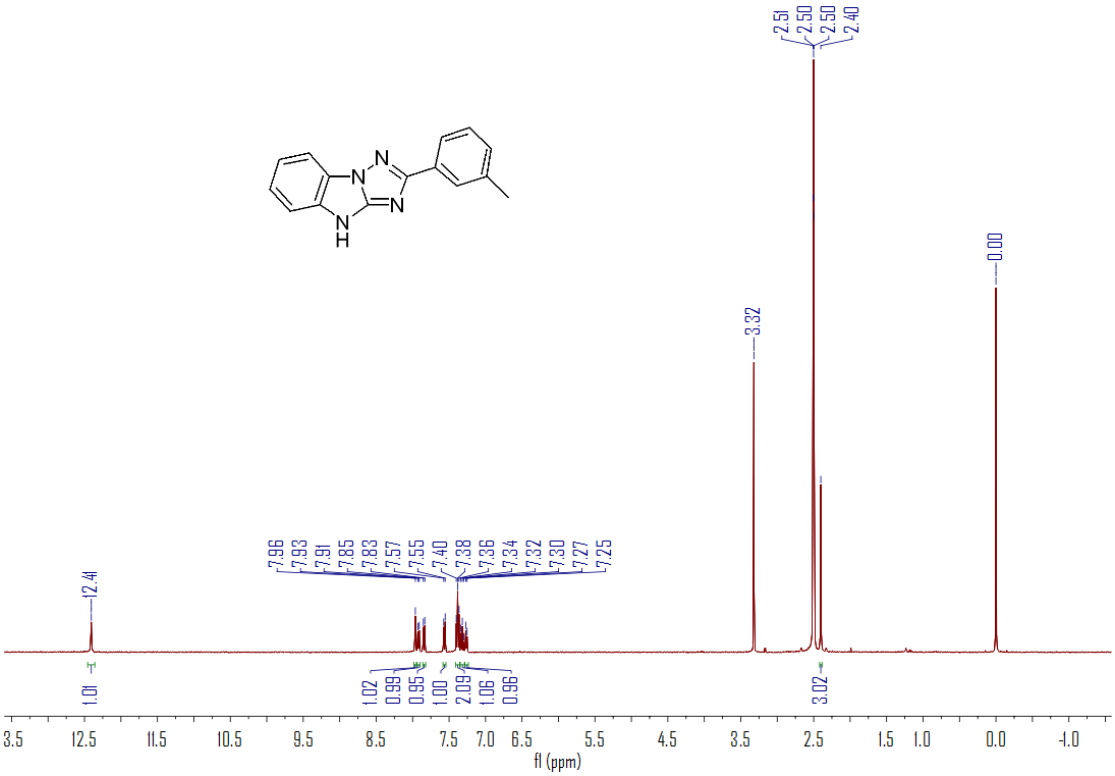


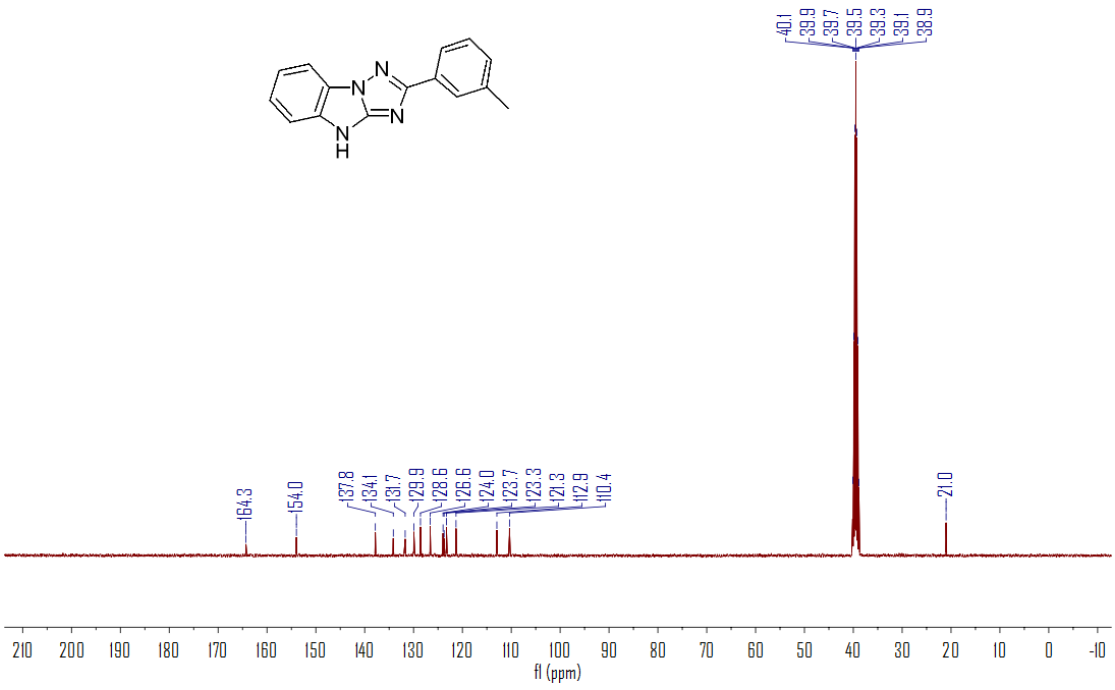
NMR spectra of **1g**:



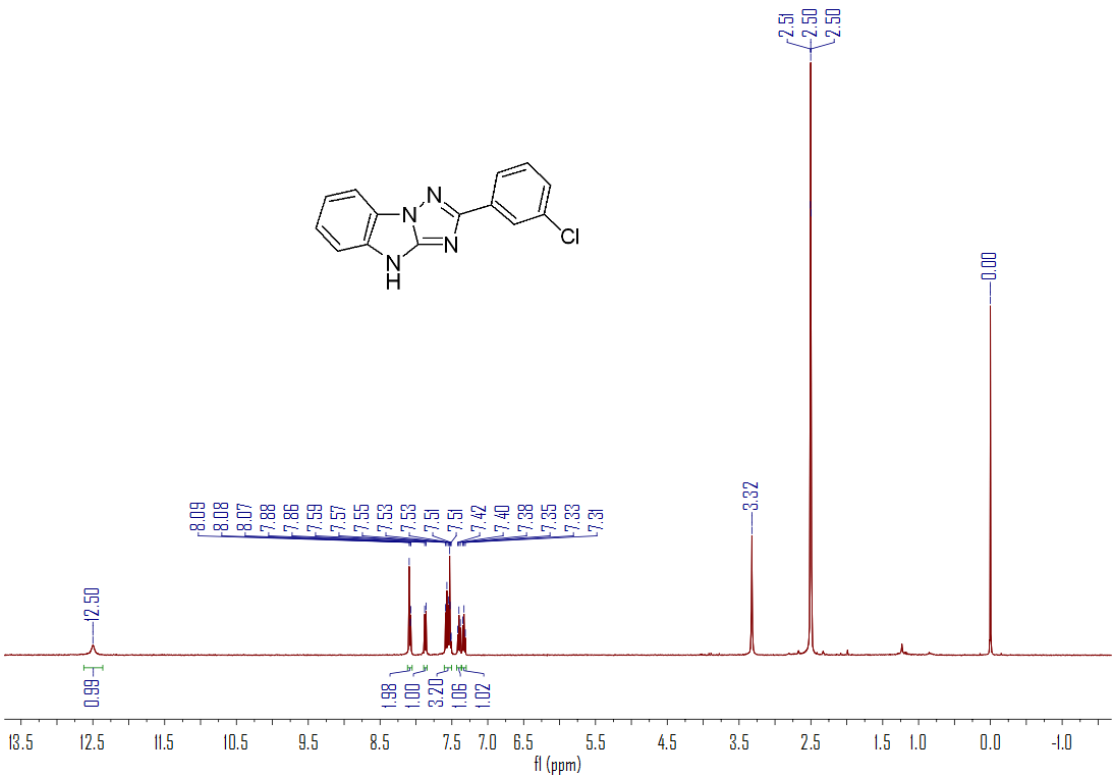


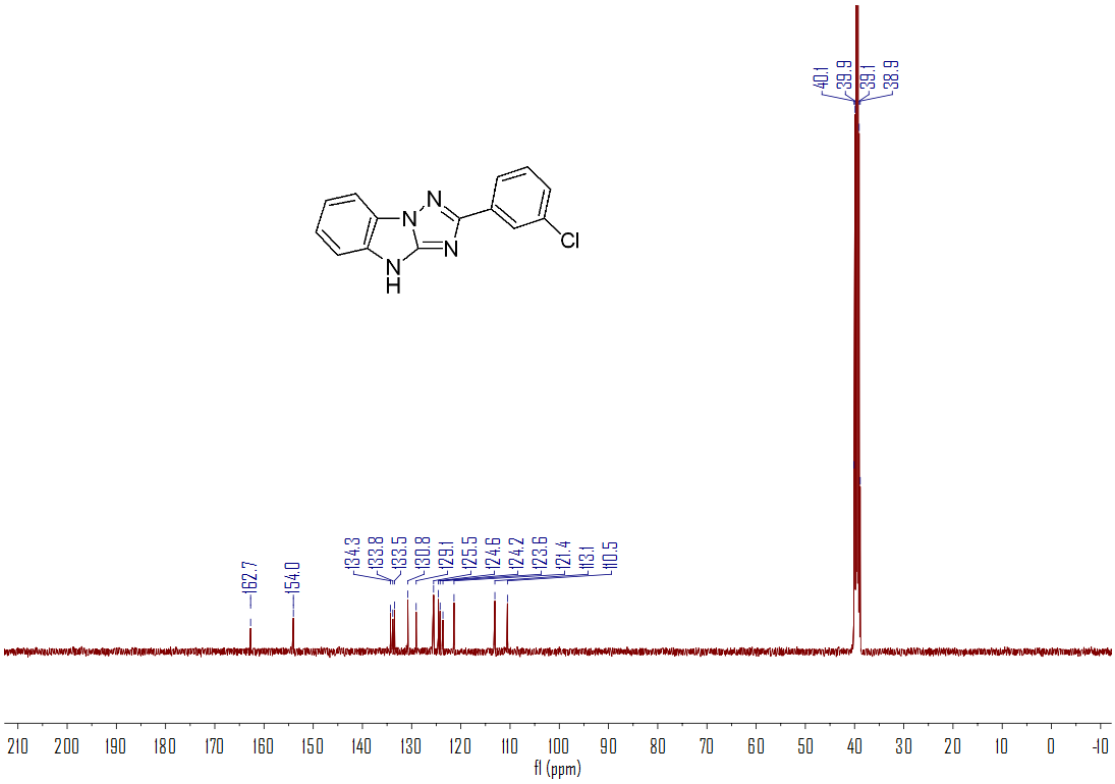
NMR spectra of **1h**:



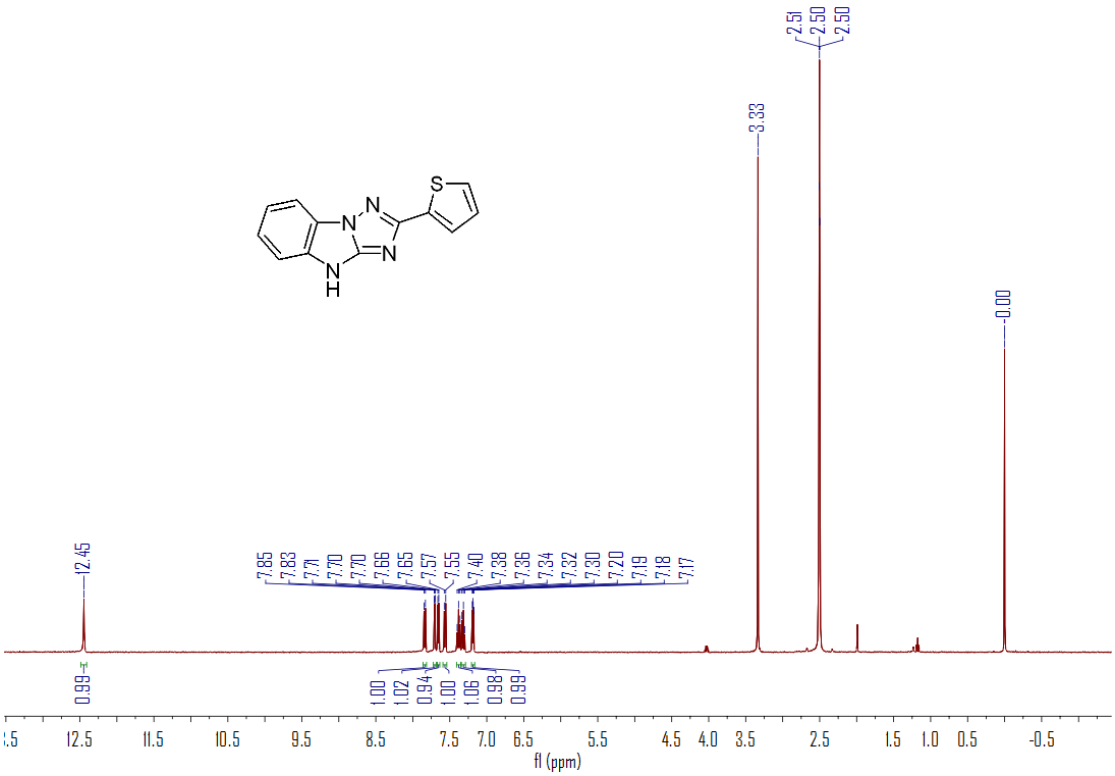


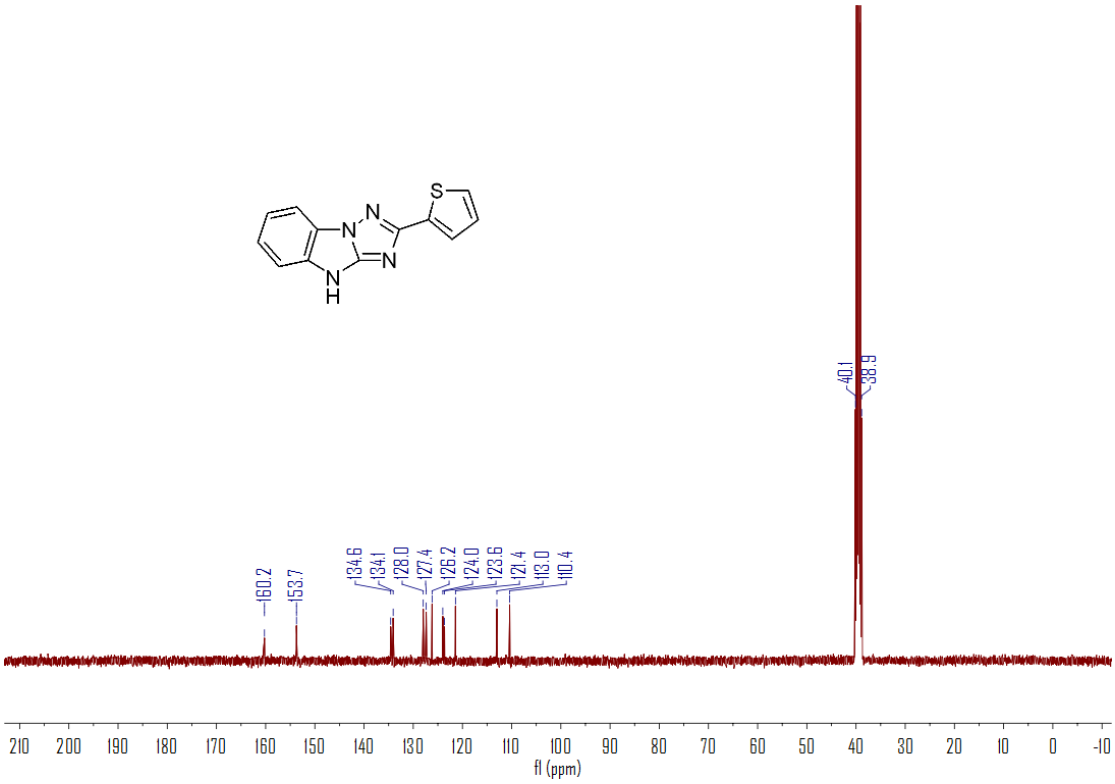
NMR spectra of **1i**:



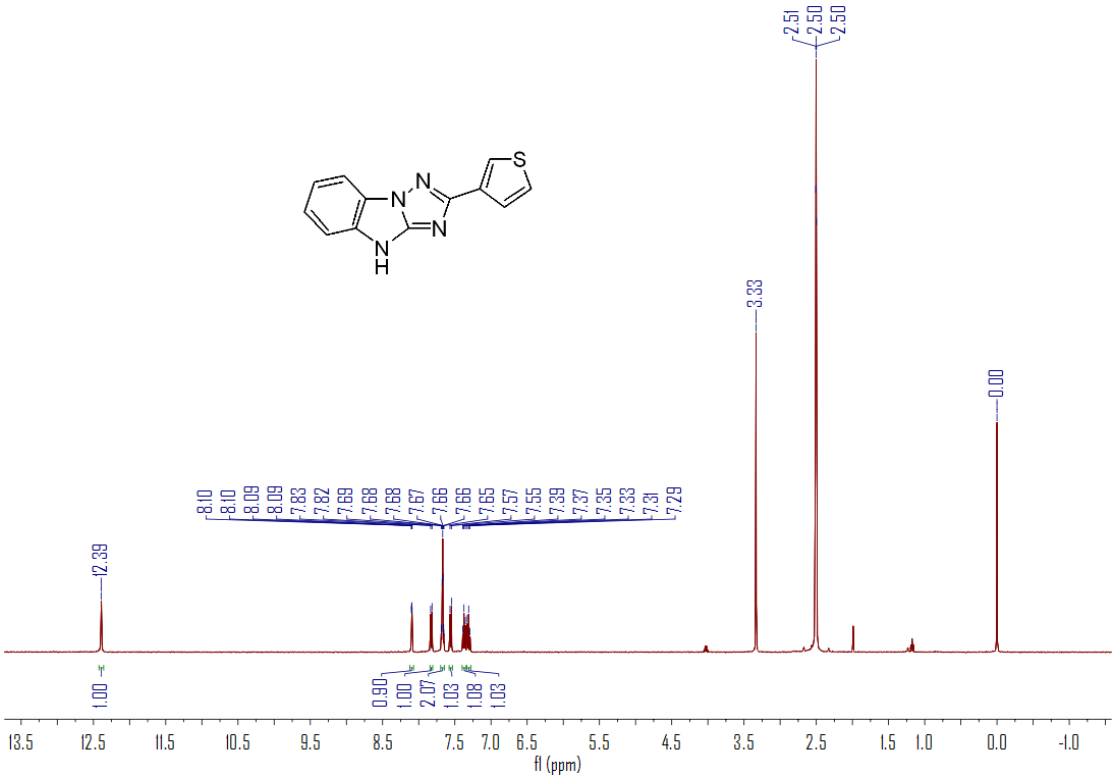


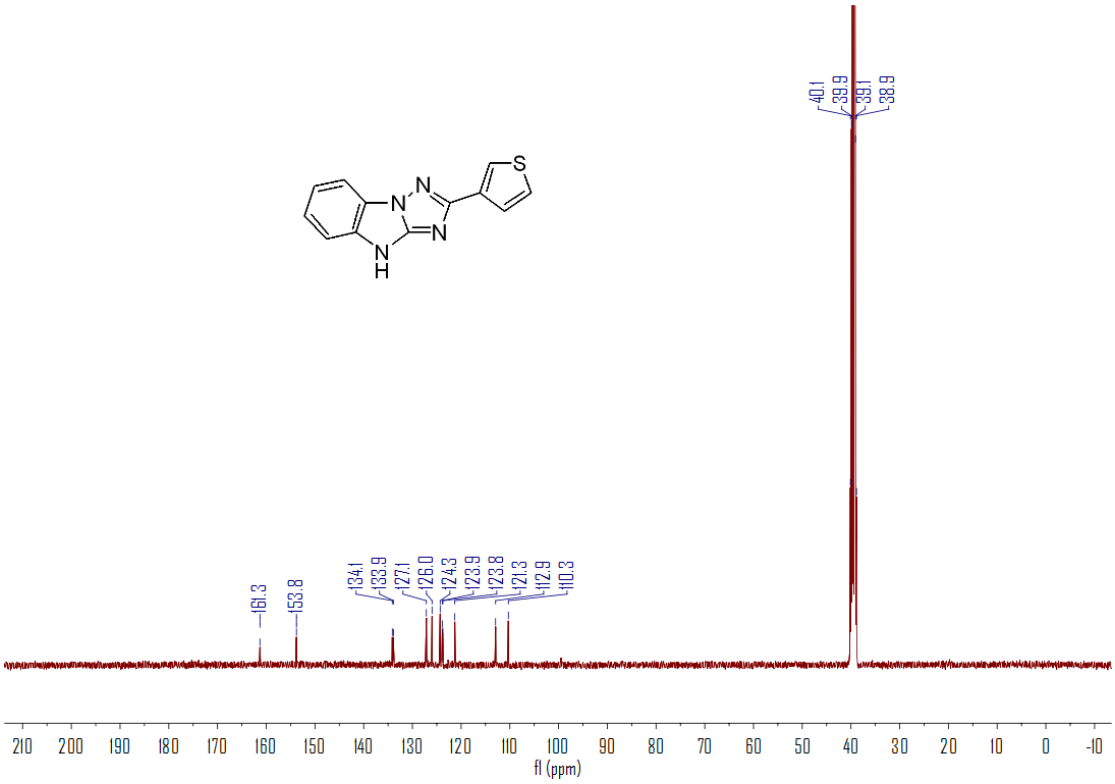
NMR spectra of **1j**:



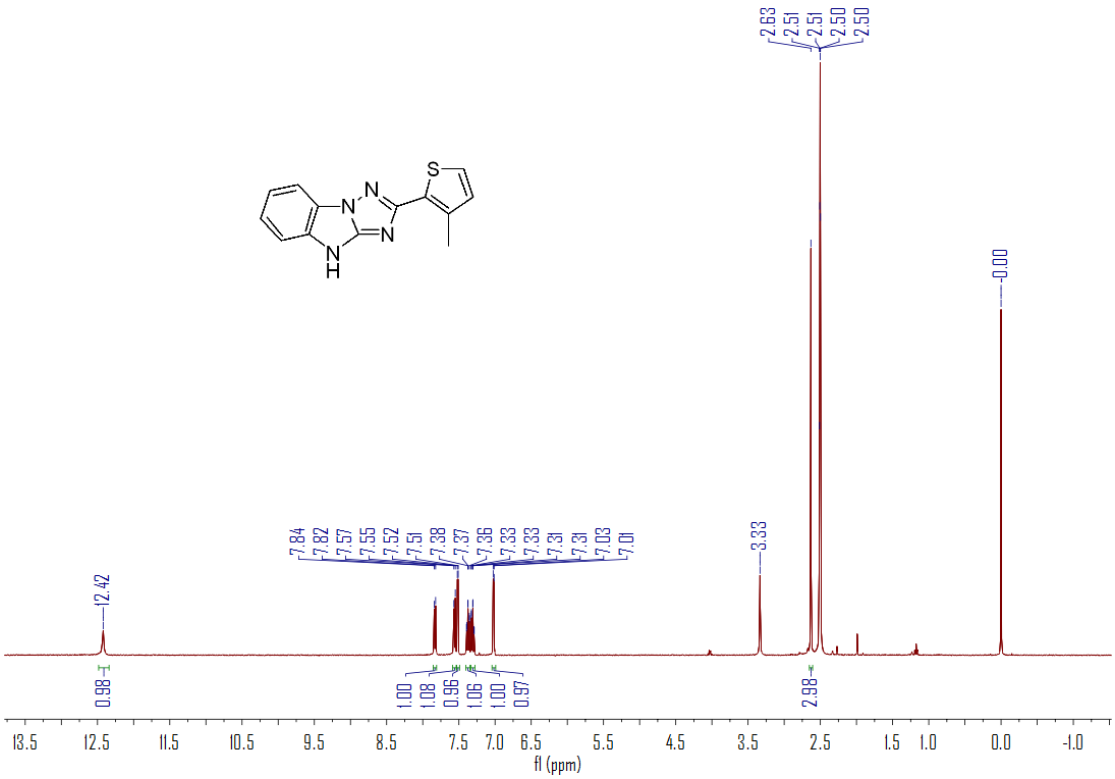


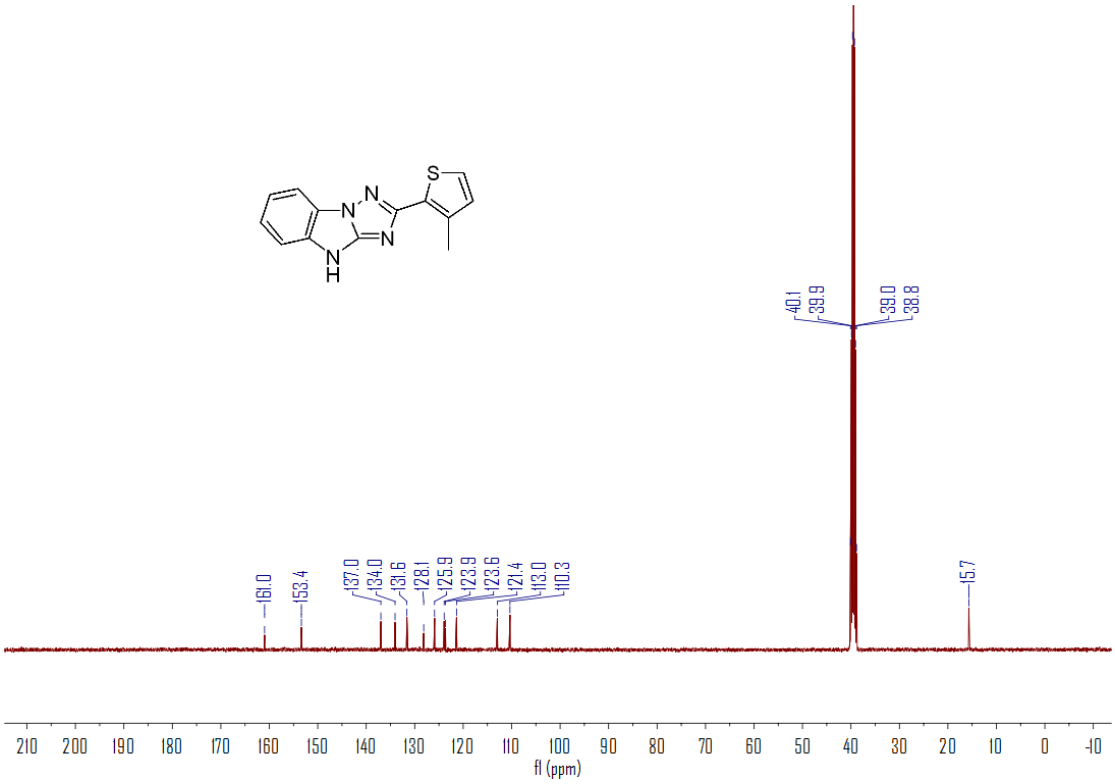
NMR spectra of **1k**:



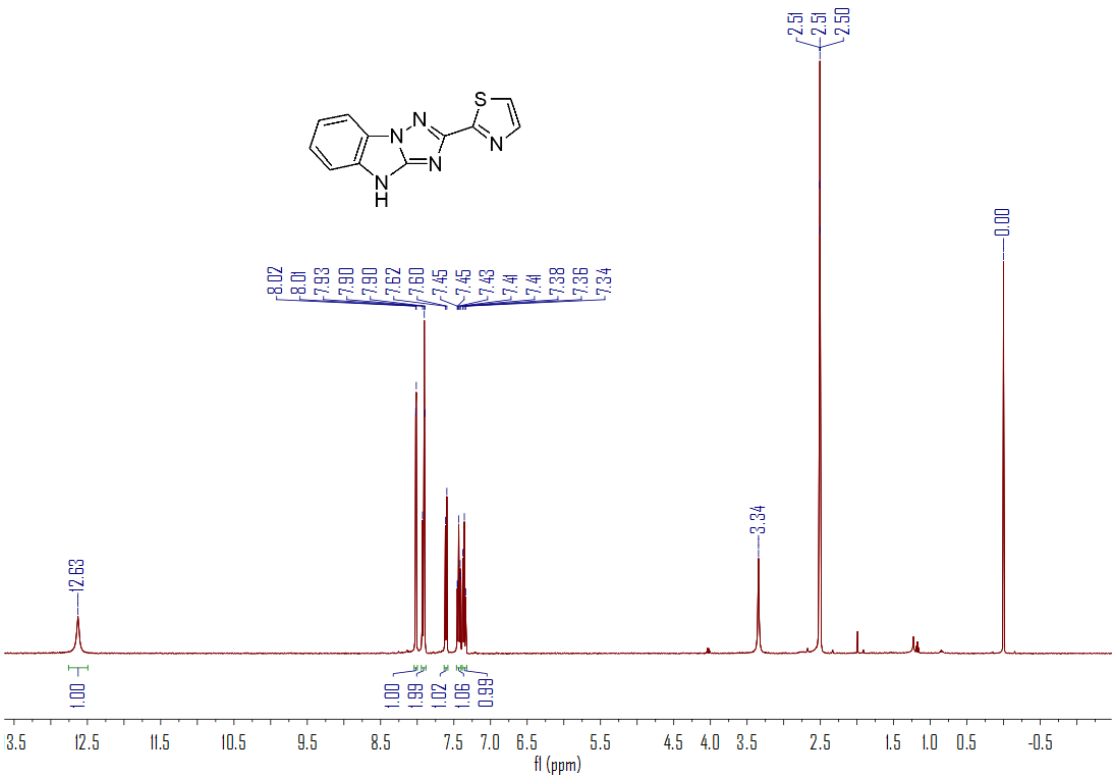


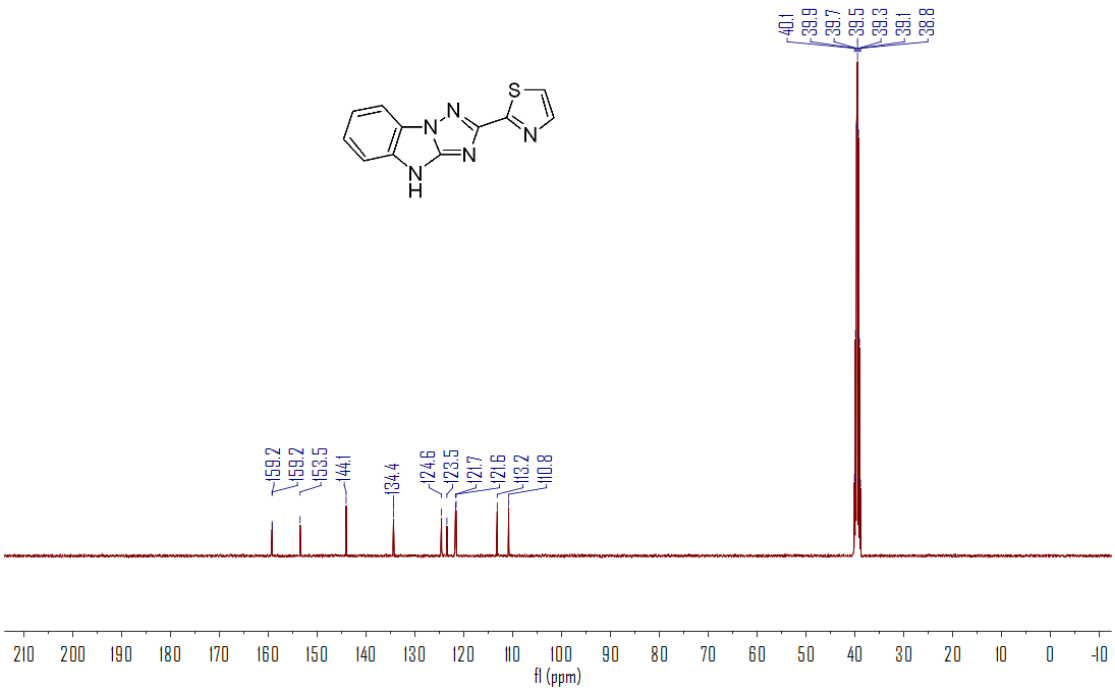
NMR spectra of **1l**:



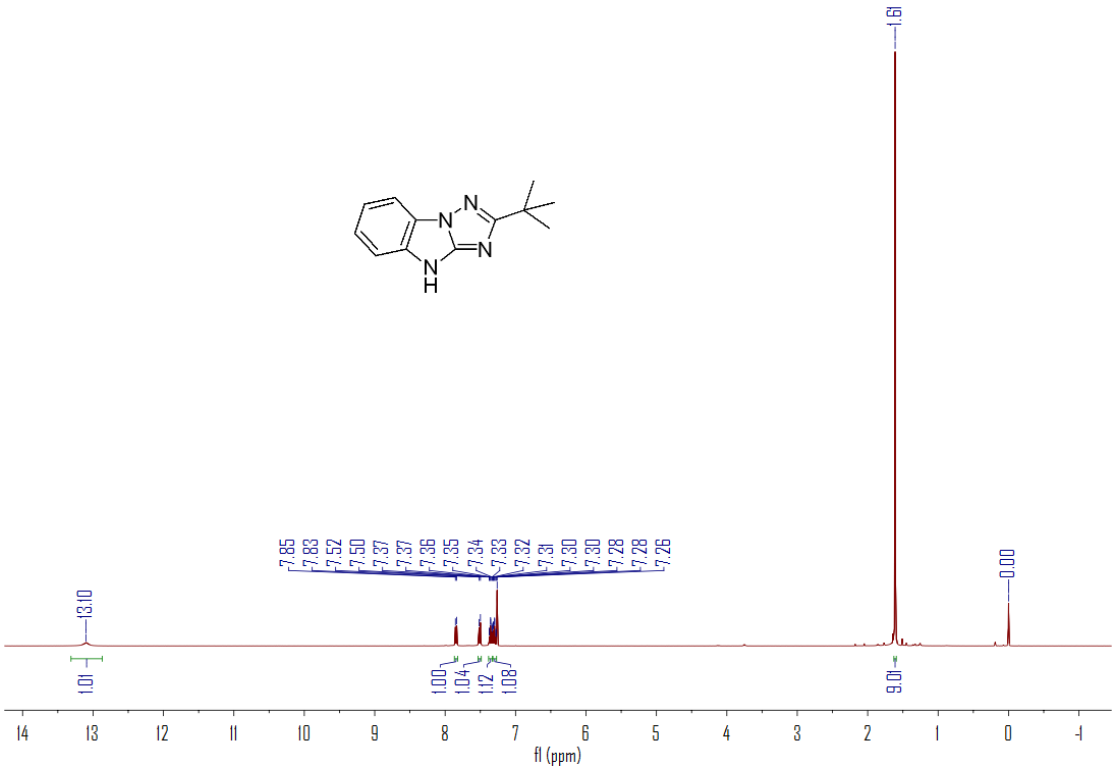


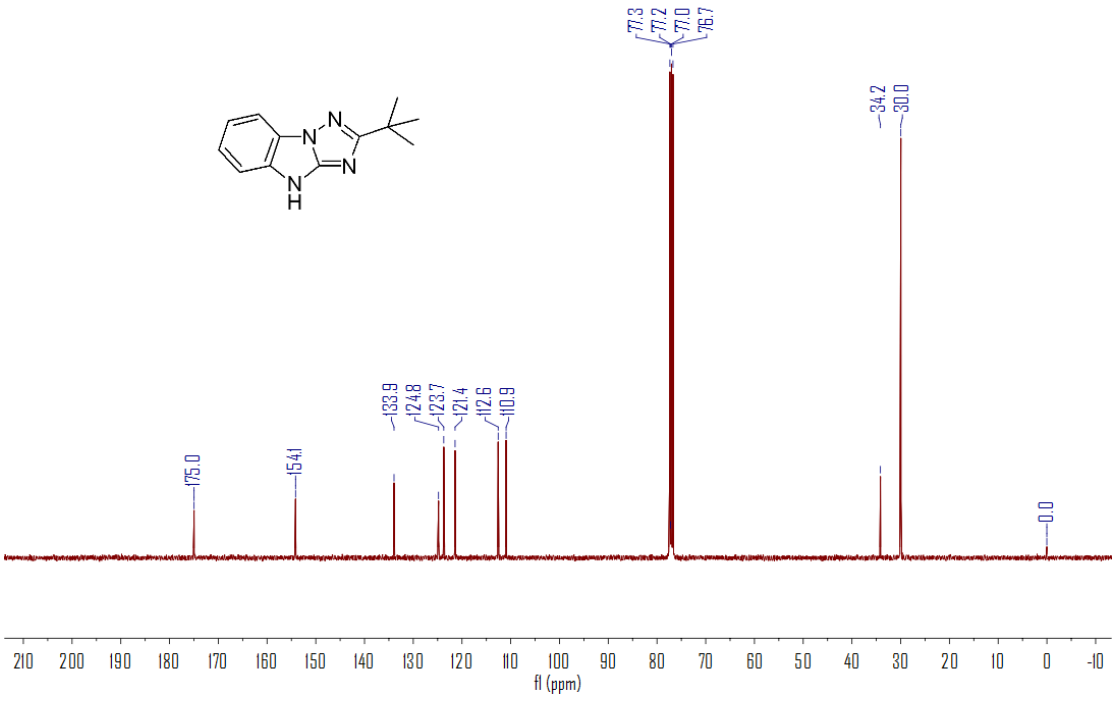
NMR spectra of **1m**:



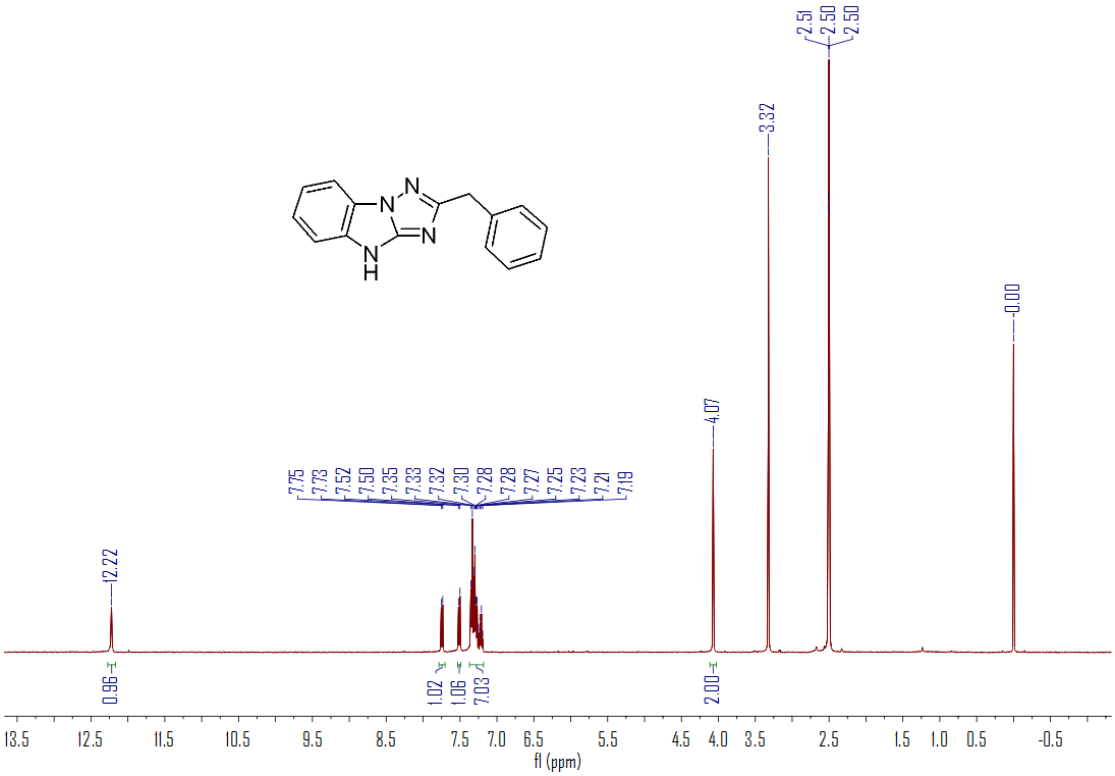


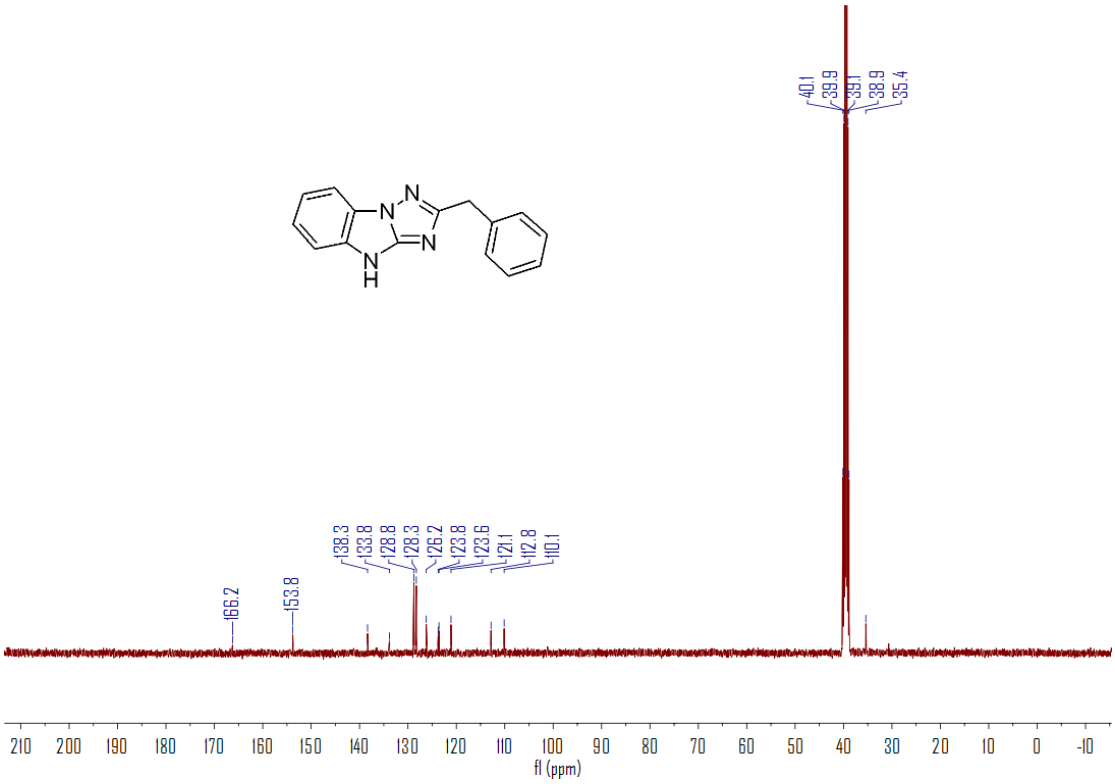
NMR spectra of **1n**:



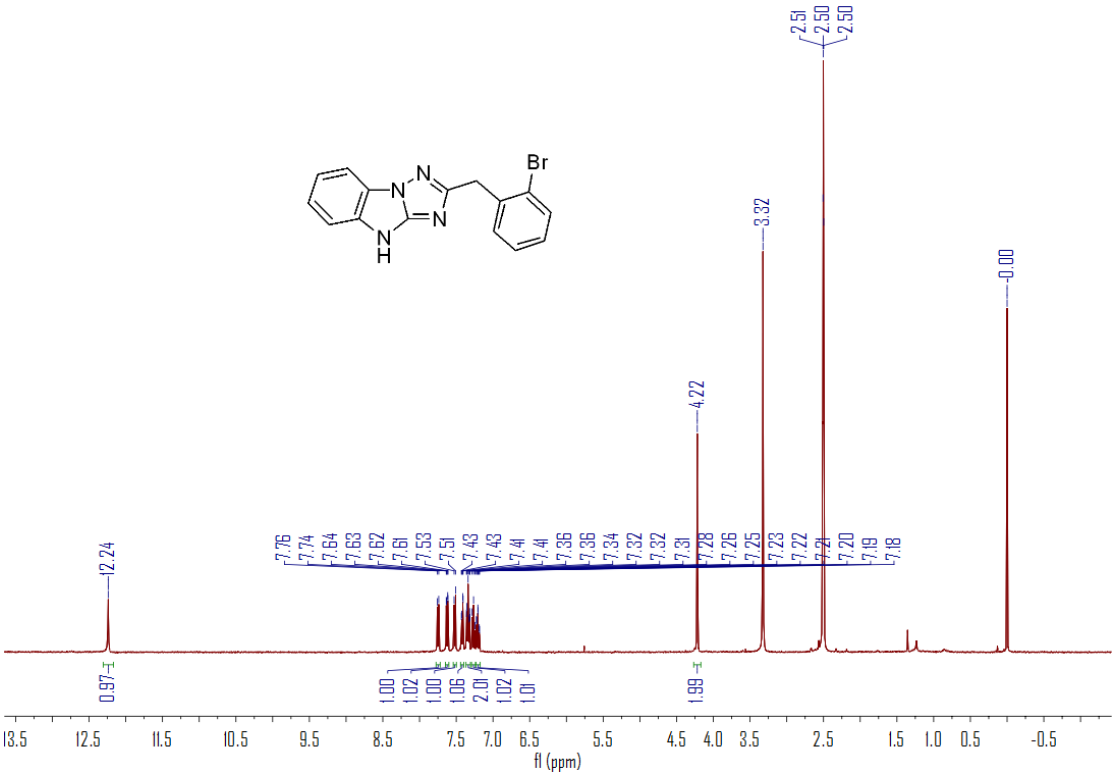


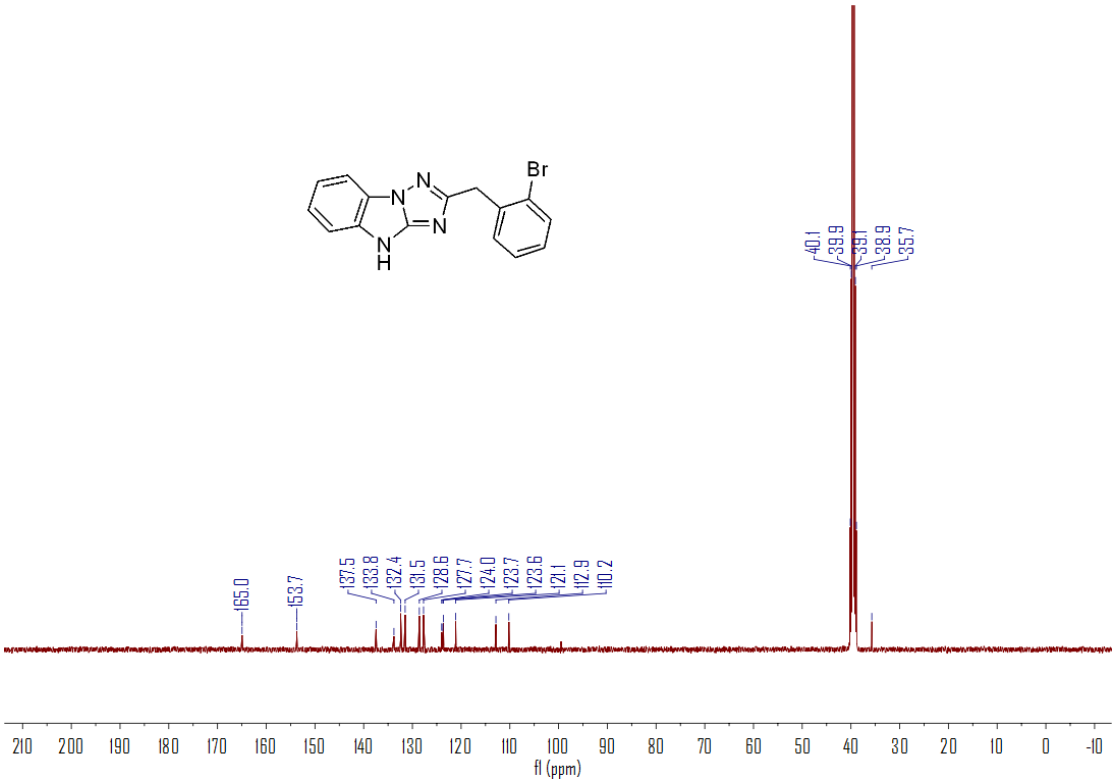
NMR spectra of **1o**:



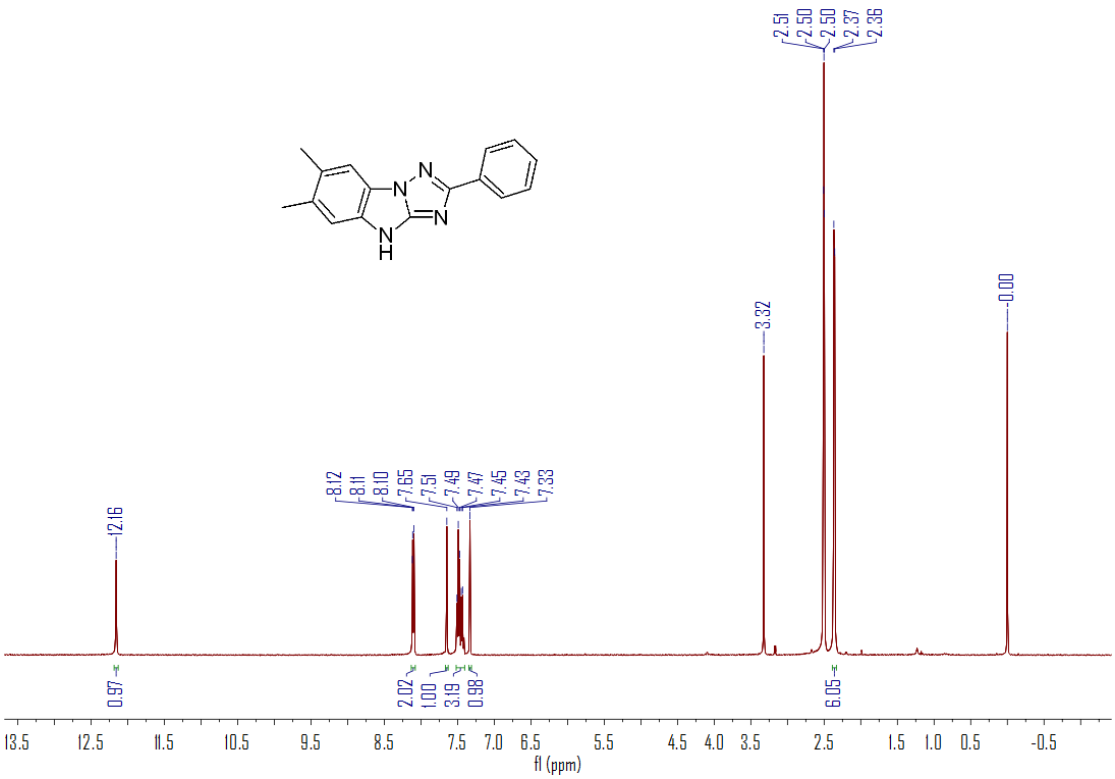


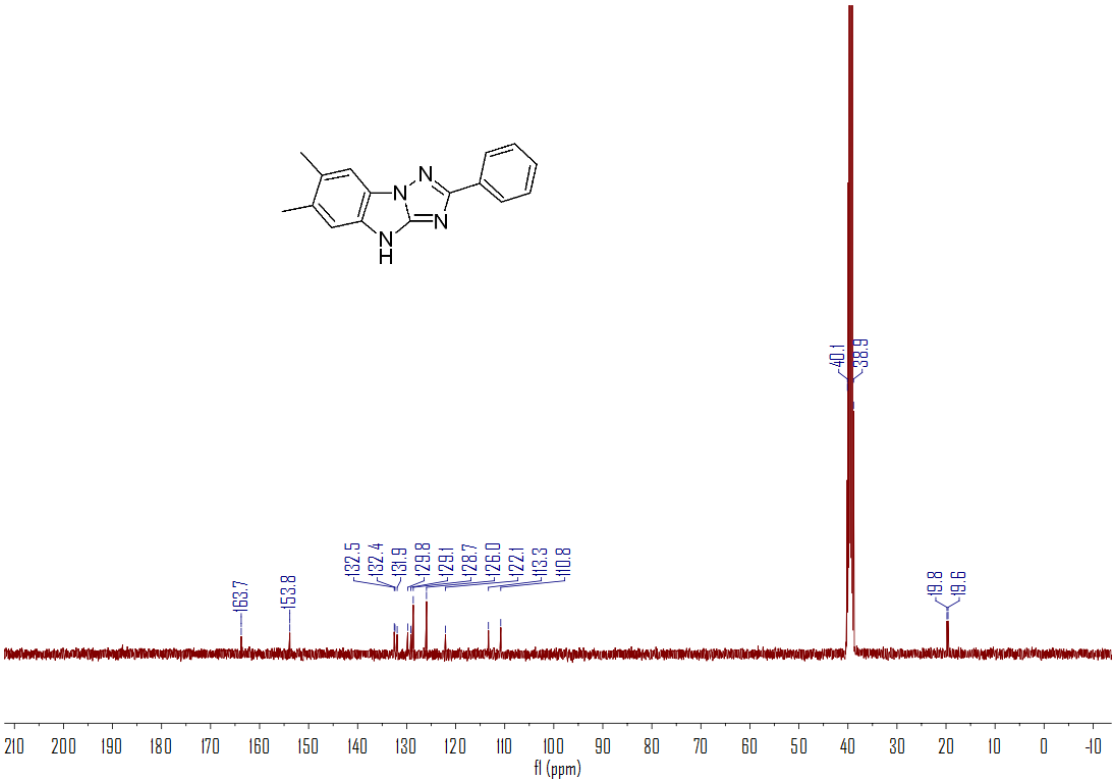
NMR spectra of **1p**:



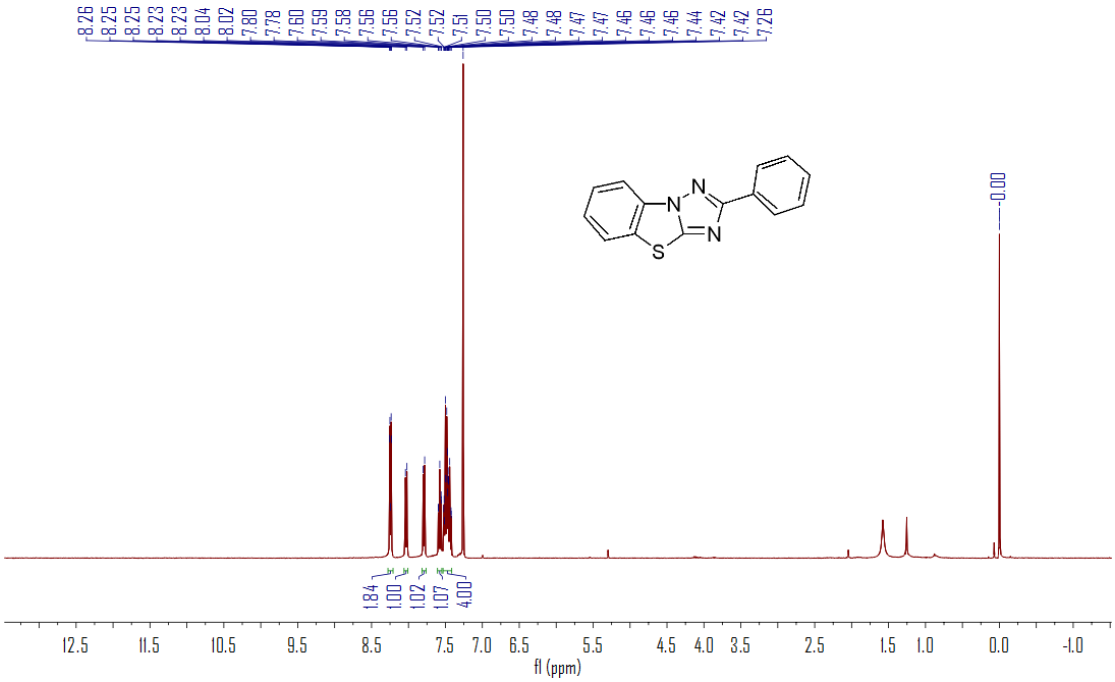


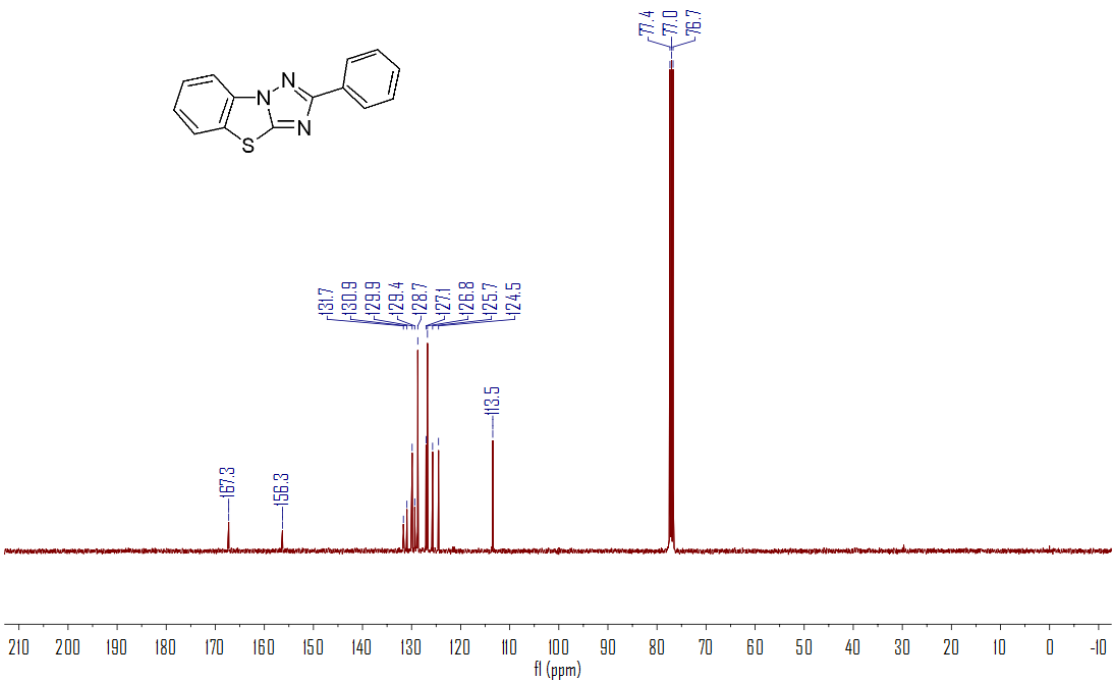
NMR spectra of **1q**:



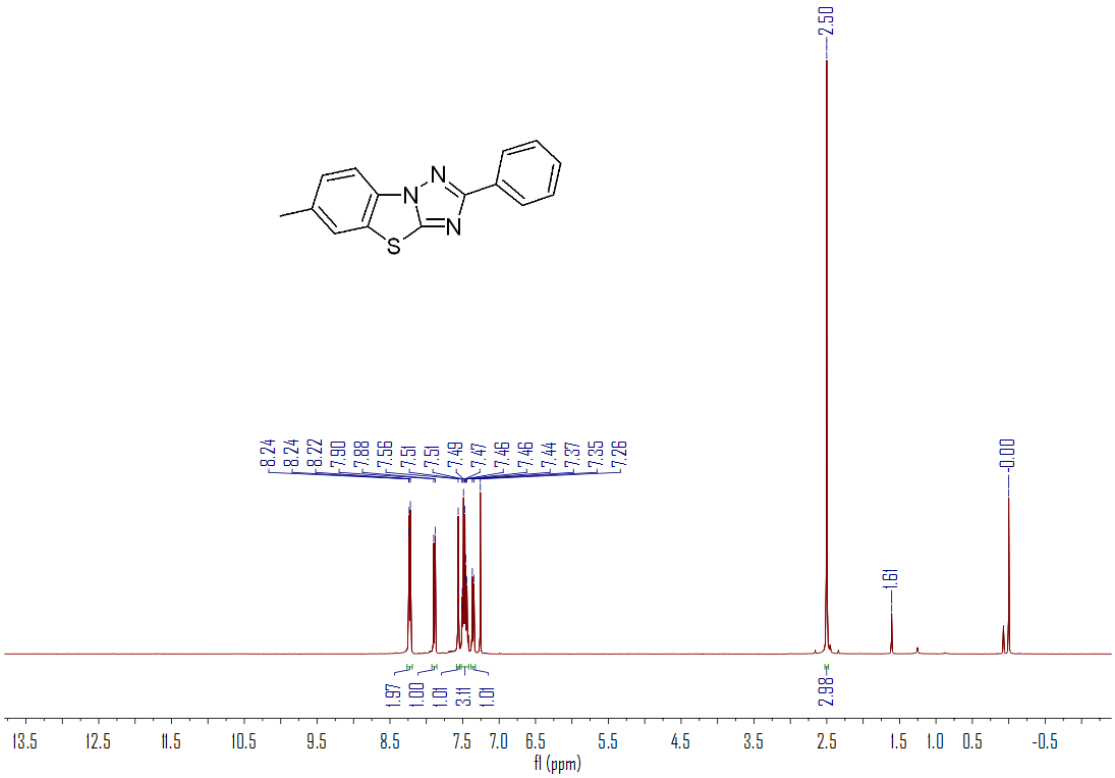


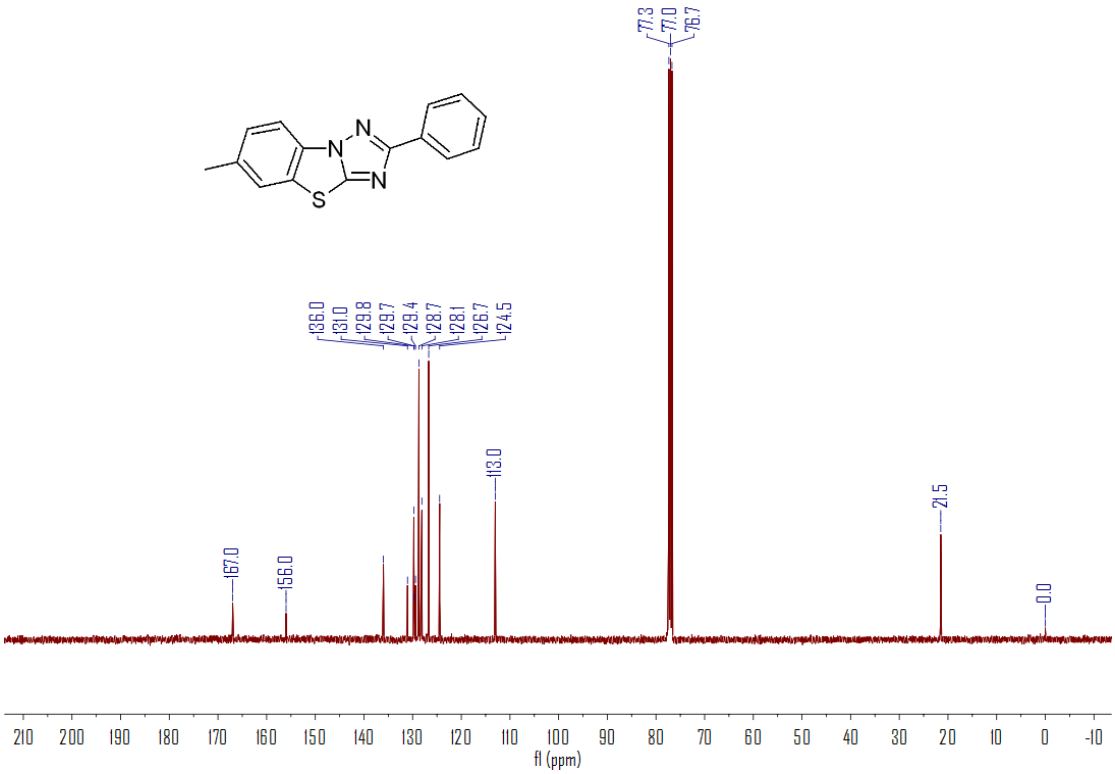
NMR spectra of **4a**:



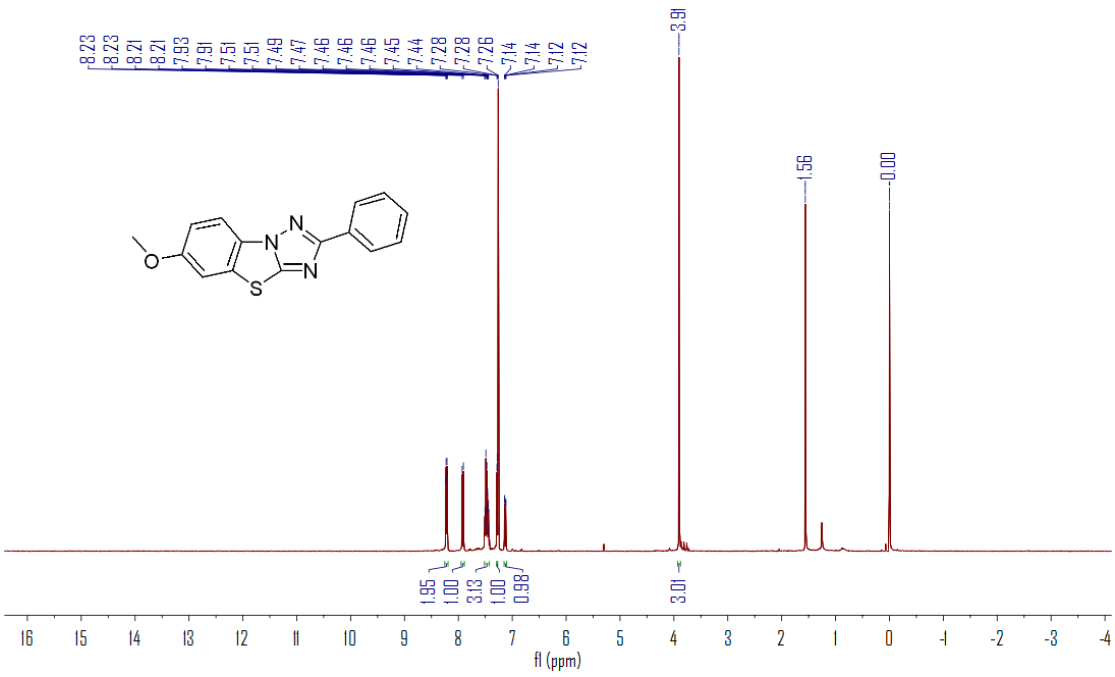


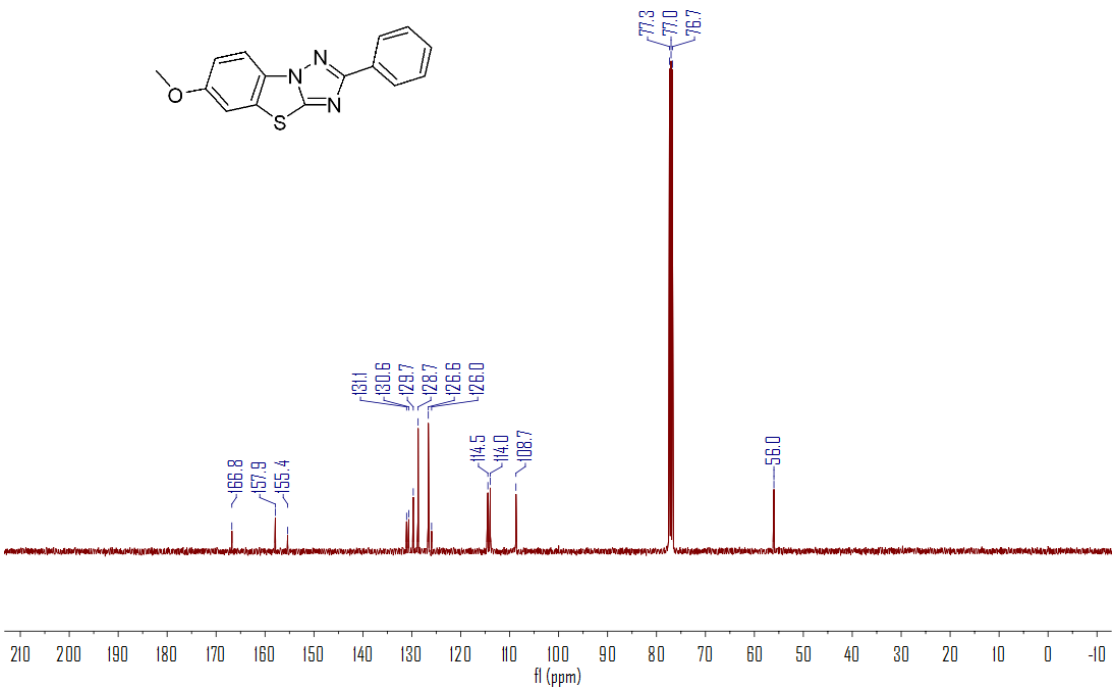
NMR spectra of **4b**:



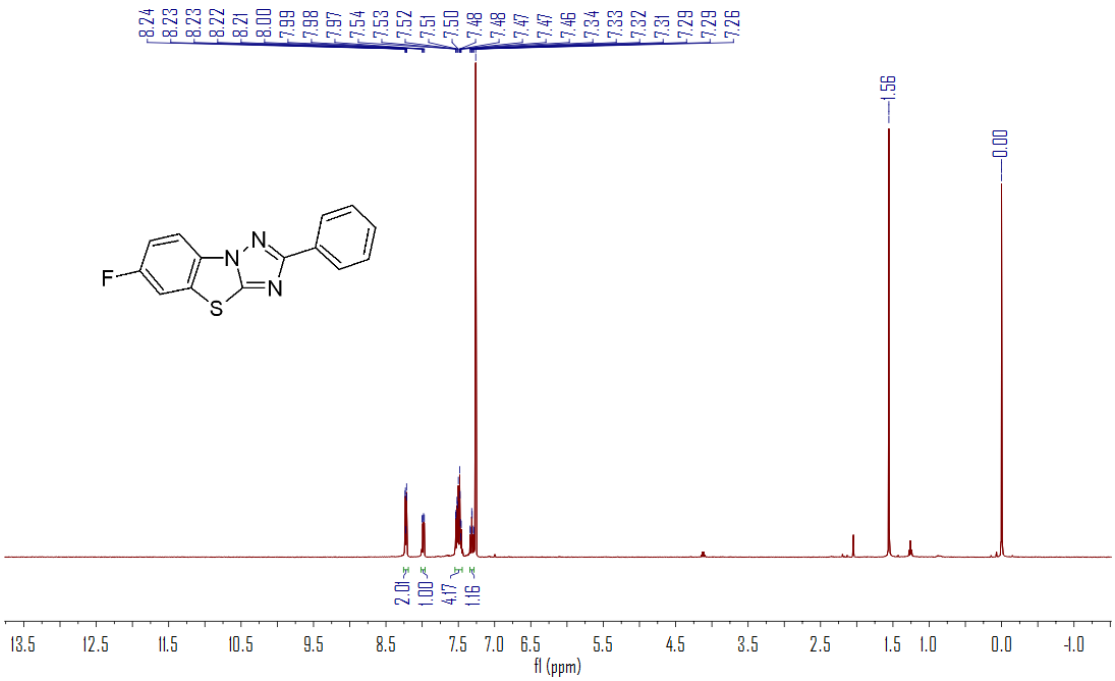


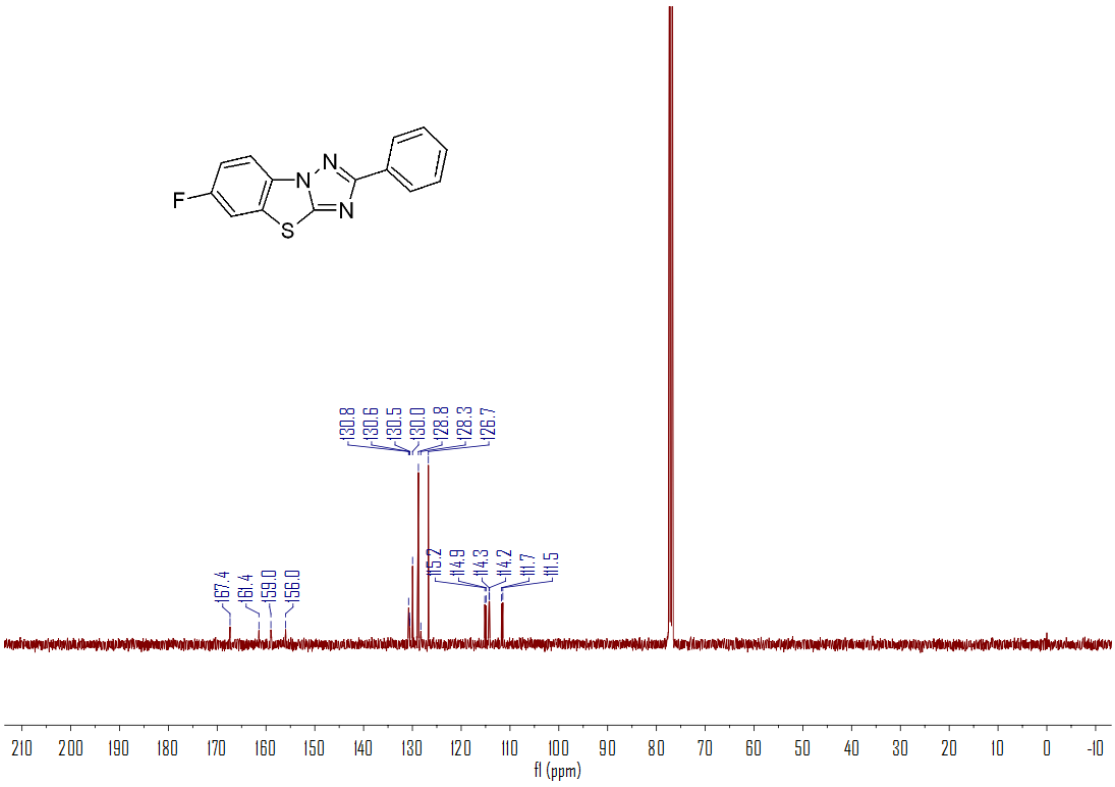
NMR spectra of **4c**:



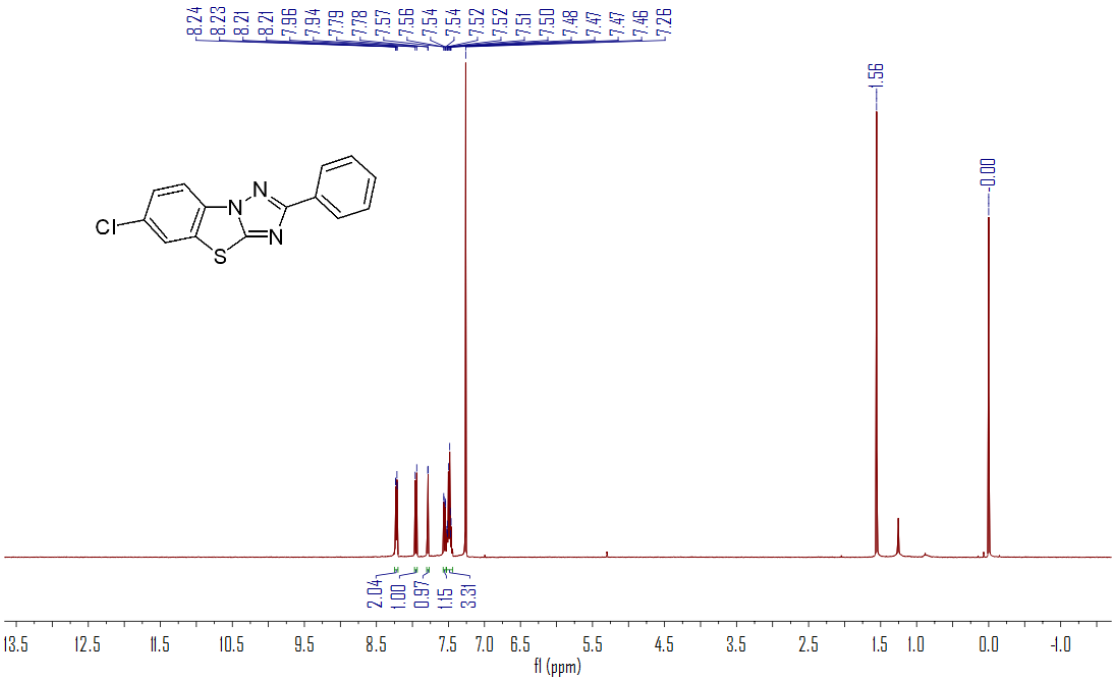


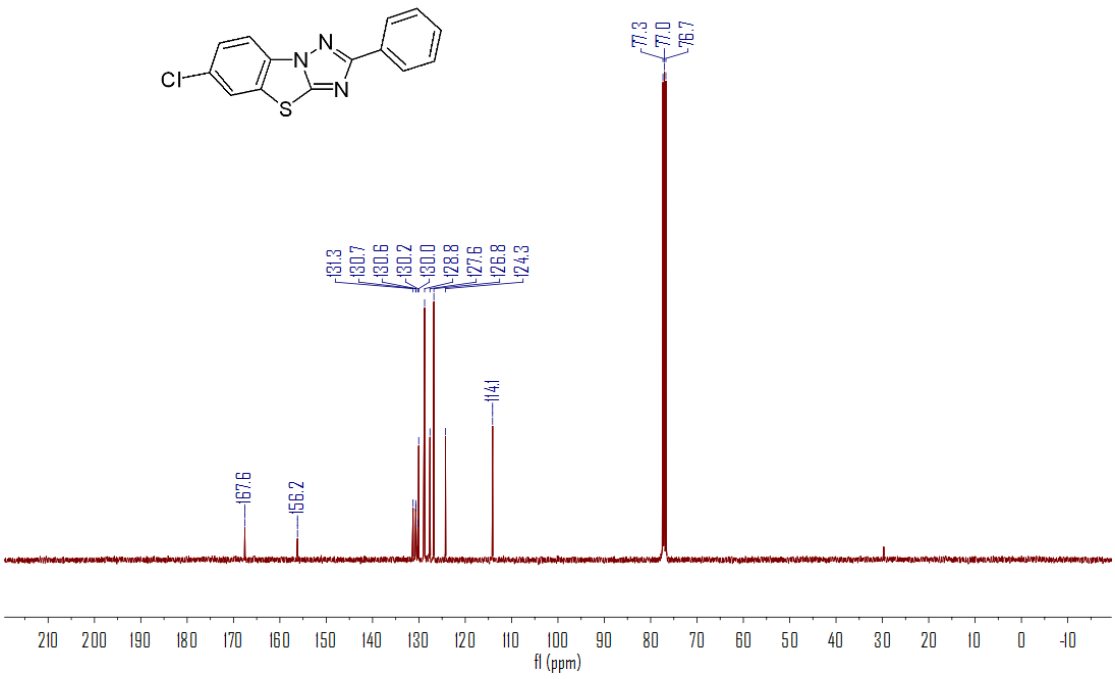
NMR spectra of **4d**:



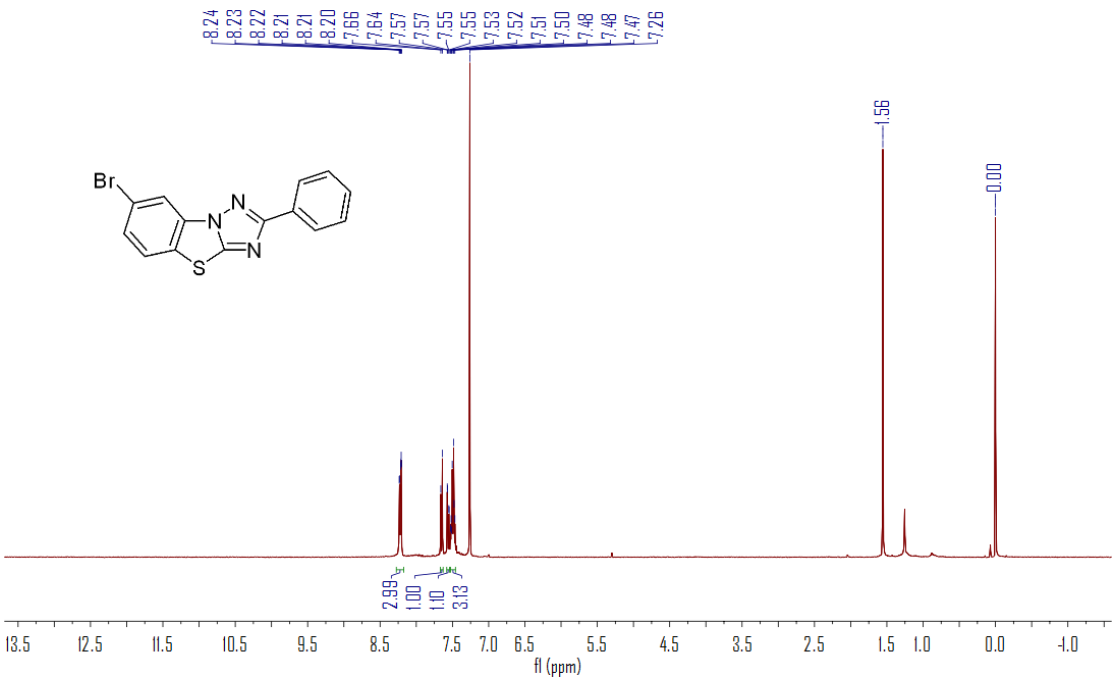


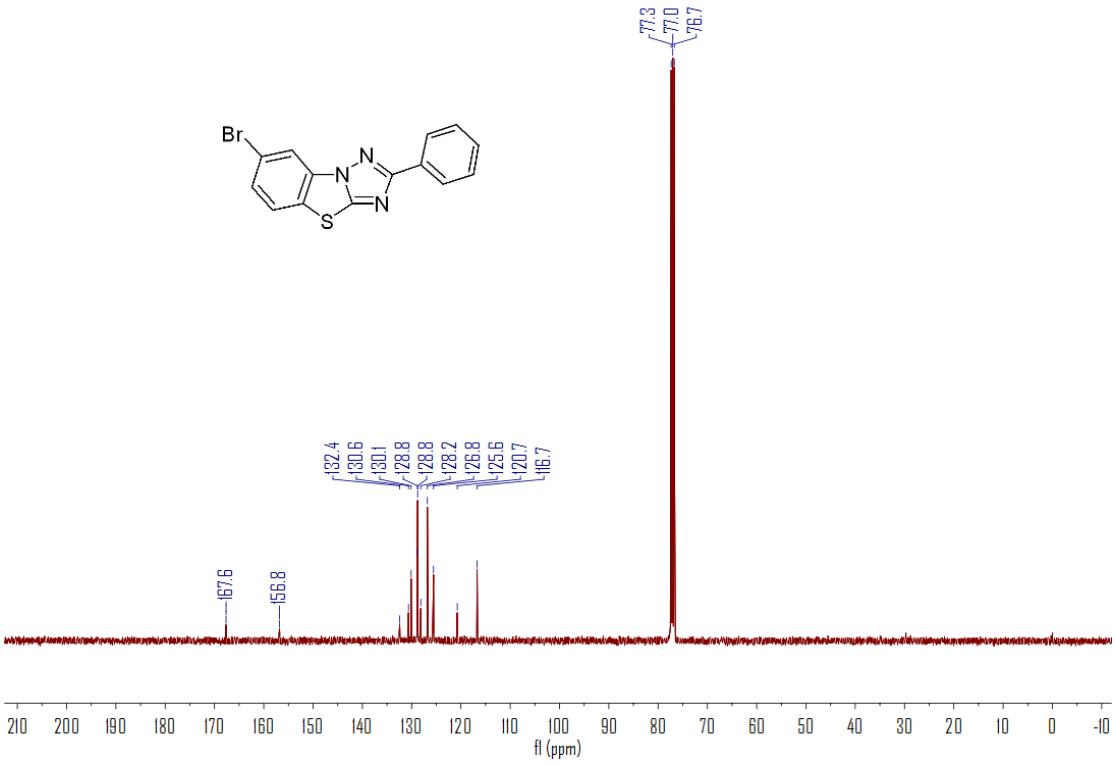
NMR spectra of **4e**:



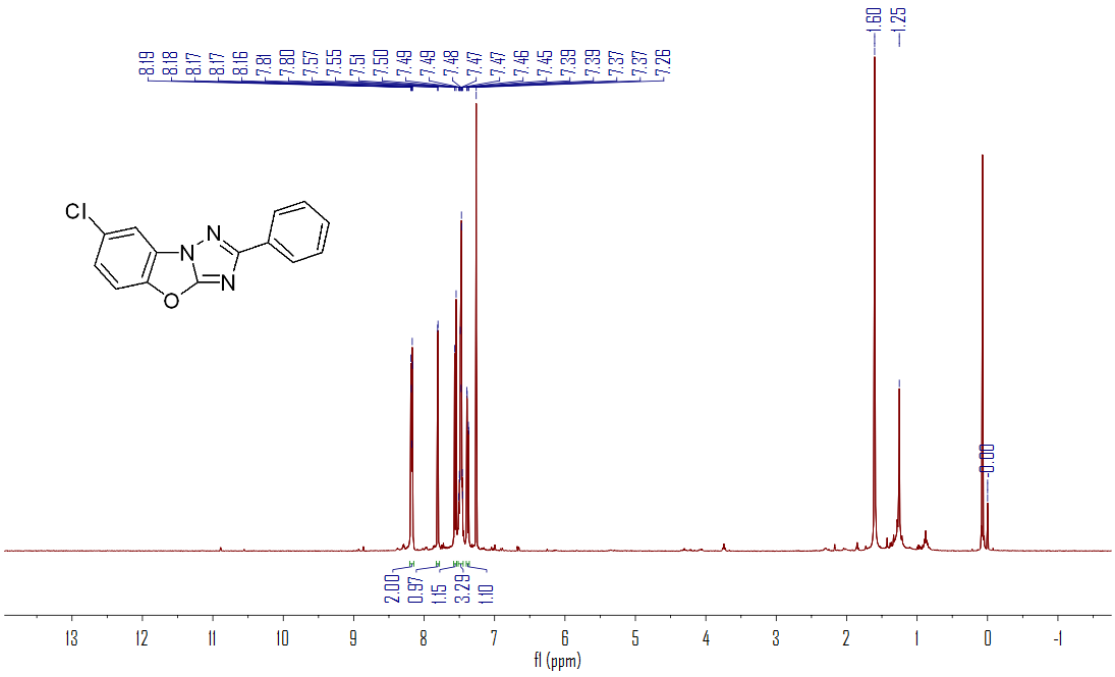


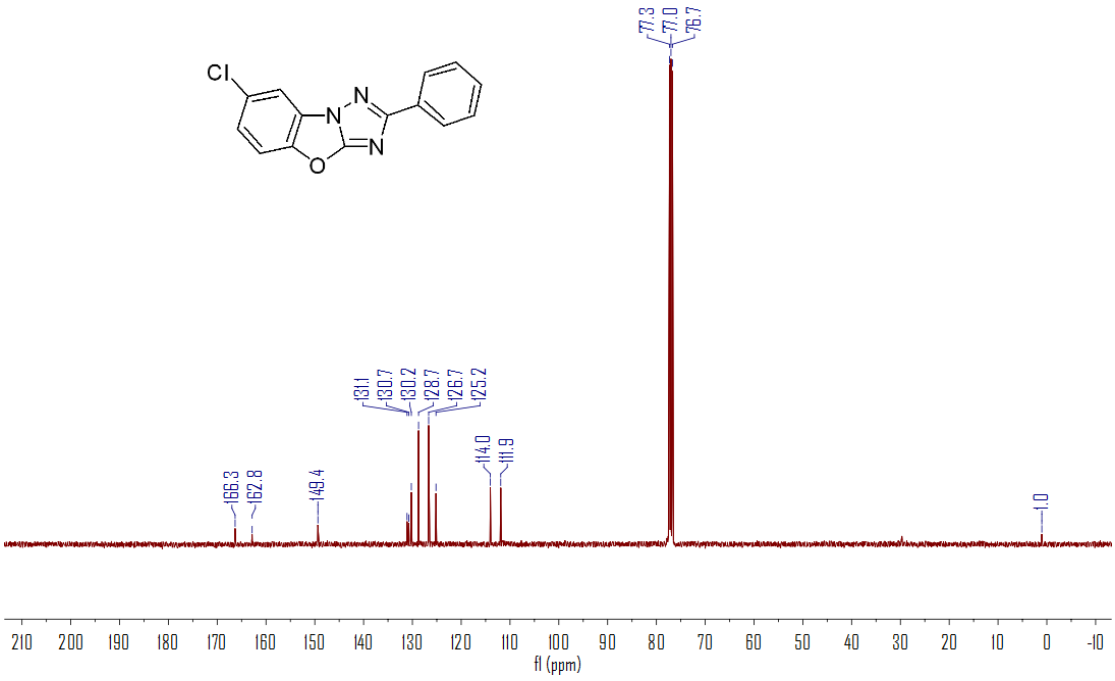
NMR spectra of **4f**:



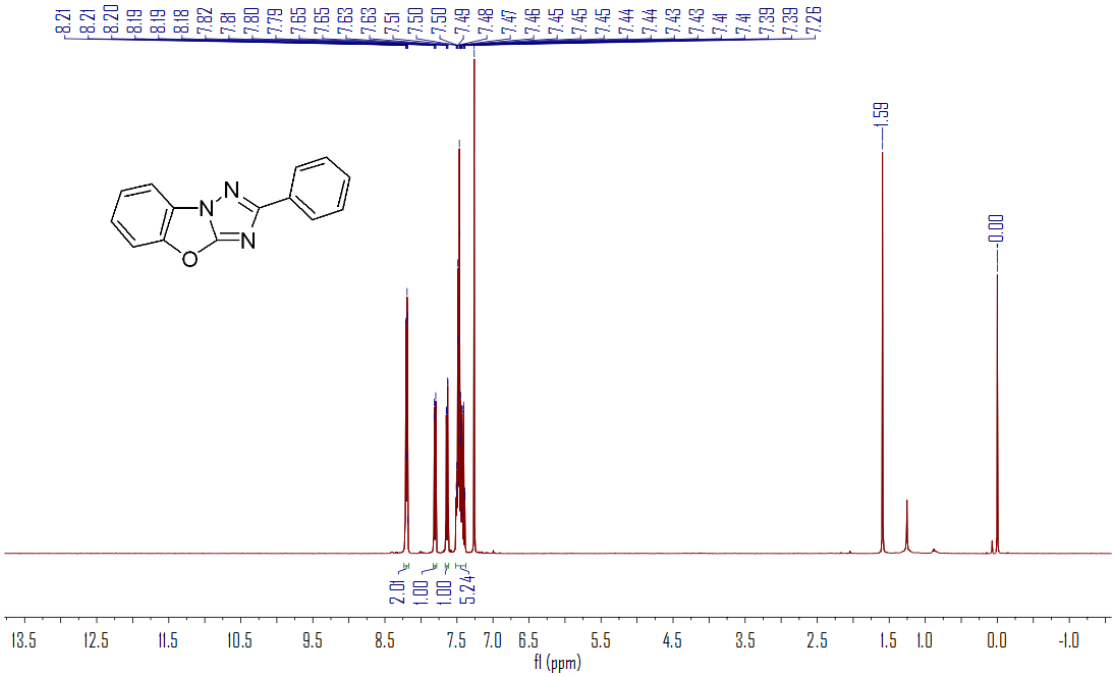


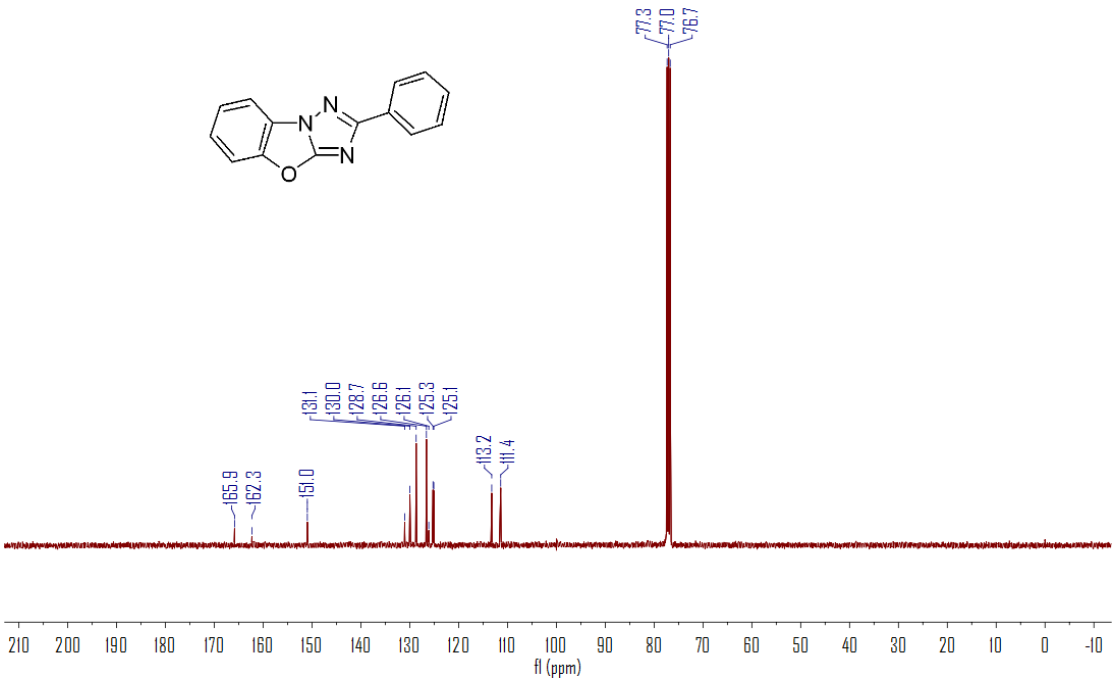
NMR spectra of **4g**:





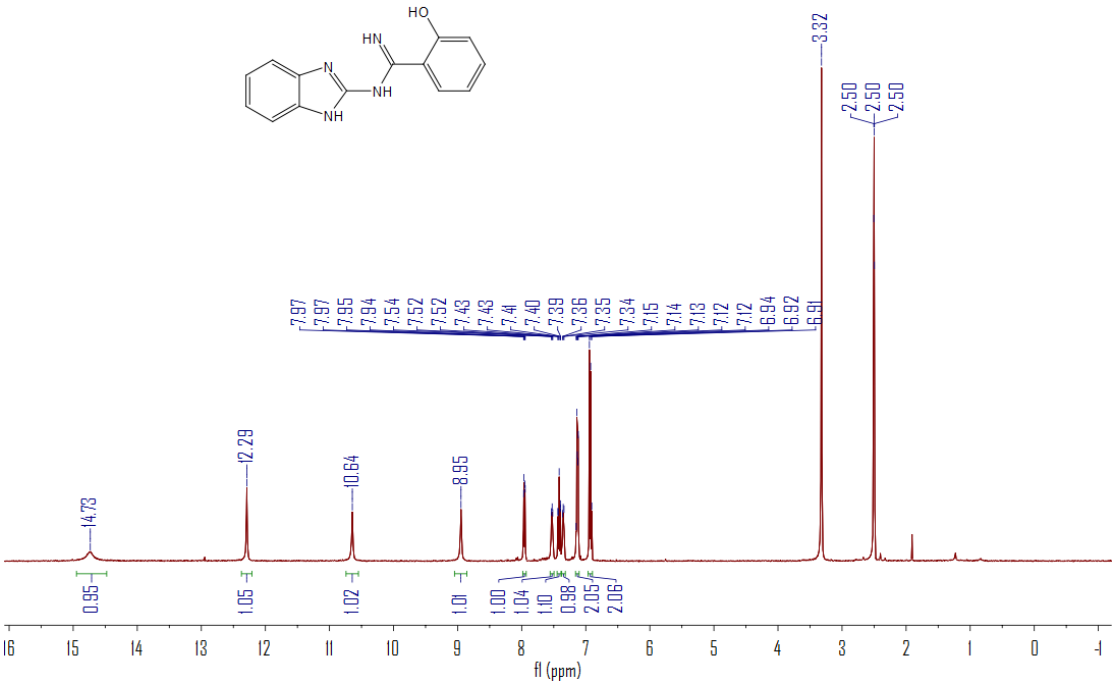
NMR spectra of **4h**:

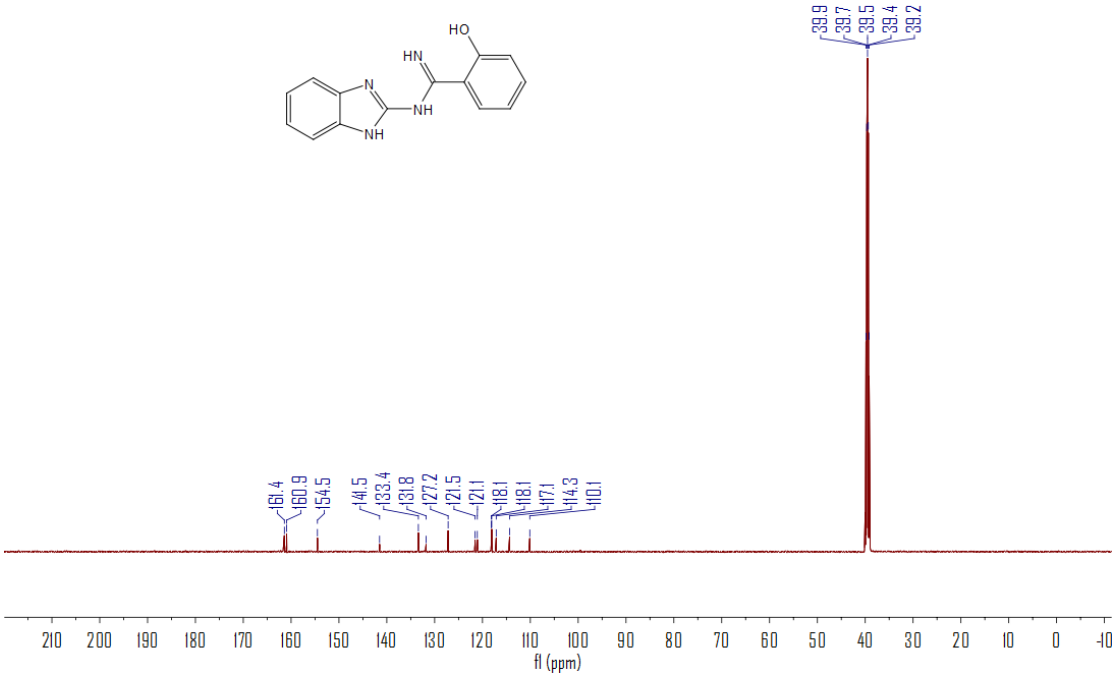




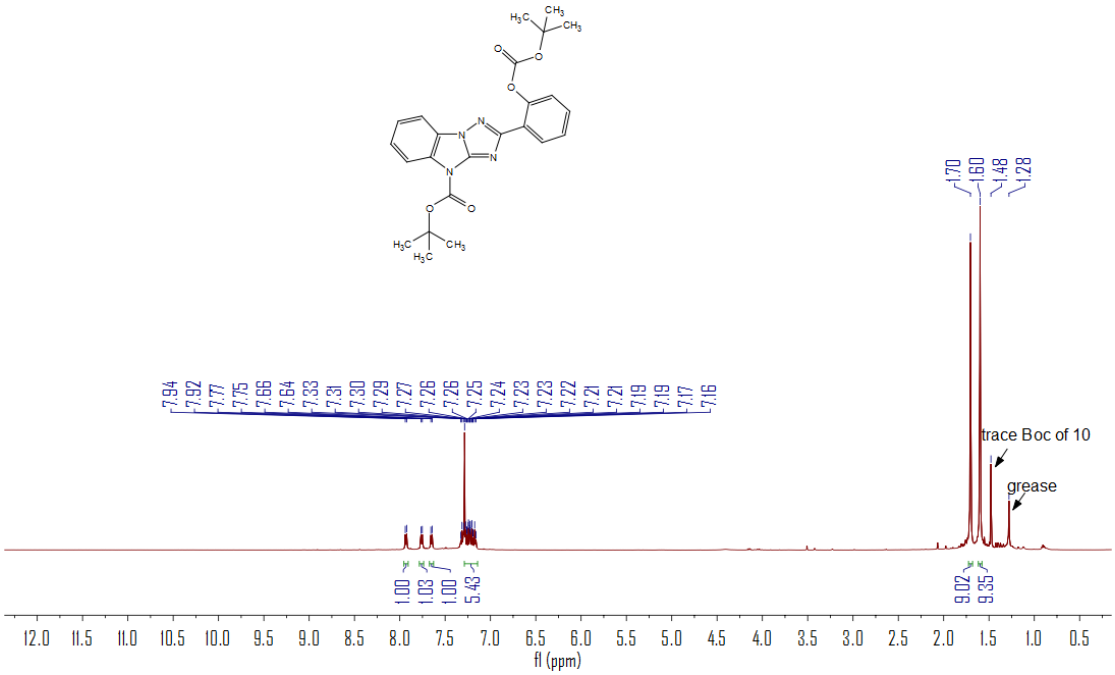
7.3 NMR spectra of mechanistic study compounds

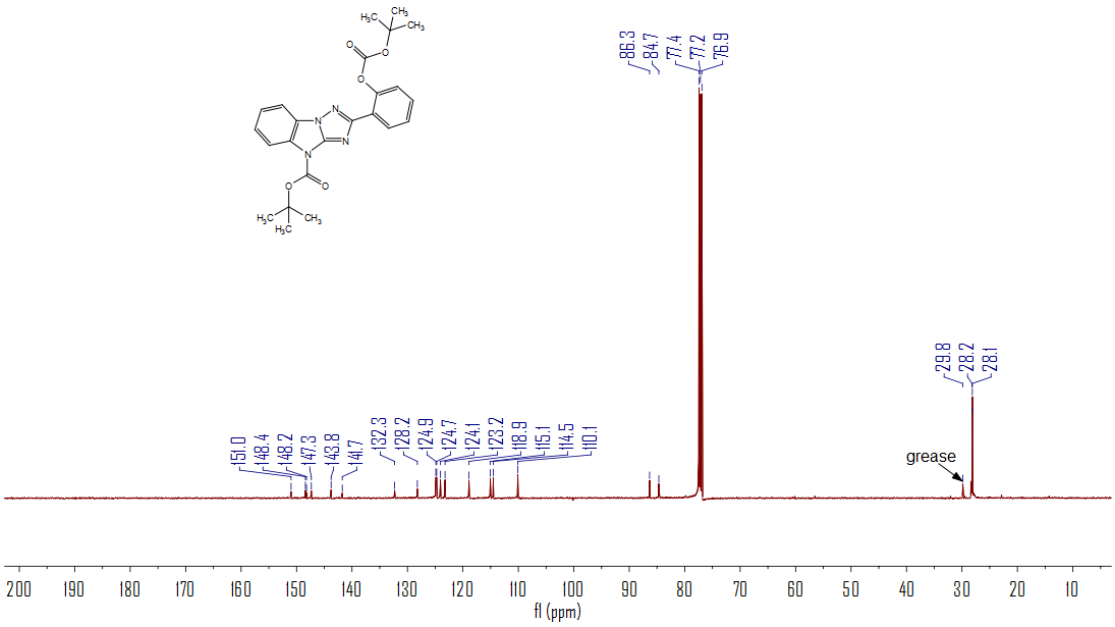
NMR spectra of **5**:





NMR spectra of **9**:





NMR spectra of **10**: