

A rapid construction of 1,3,2-benzodiazaborininones [R-B(aam)] from boronic acids and anthranilamides

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1. General information

Commercial reagents were purchased from Meyer Reagent Co., Ltd. (Shanghai, China), Macklin Reagent Co., Ltd. (Shanghai, China), Chongqing Chuandong Chemical Co., Ltd. (Chongqing, China), etc., and used as received without further purification. ^1H and ^{13}C spectra were recorded at Bruker Avance-III spectrometer (600 MHz, 151 MHz and 193 MHz) using TMS as internal standard. Chemical shifts were reported in ppm and coupling constants (J) in Hz. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), triplet (t) and broad singlet (brs). TLC plates were visualized by exposing UV light or by iodine. Purification of crude compounds and separation of reaction mixtures were carried out by column chromatography using silica gel (200-300 meshes, Shanghai, China).

2. Experimental procedure

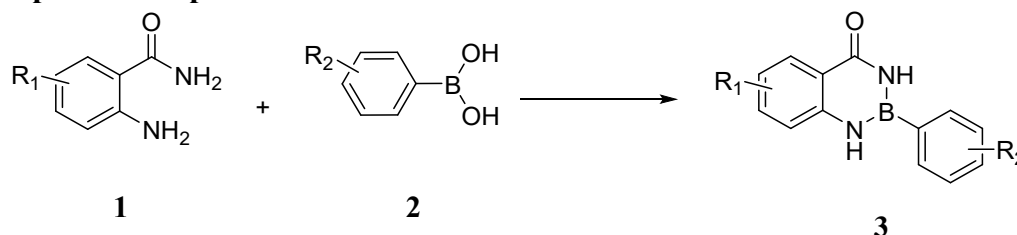


Fig 1 the synthesis of R-B (aam)

2.1 General procedure for the synthesis of R-B (aam) 3

A round-bottom flask or glass tube was charged with anthranilamide **1a** (0.14 g, 1 mmol, 1.2 equiv), phenylboronic **2a** (0.1 g 0.83 mmol 1 equiv.) and ethyl acetate (3ml). The mixture was stirred at room temperature for 3h. Reaction was monitored by TLC. When the reaction reached completion, the desired product **3a** precipitated from the ethyl acetate after can be isolated by simple filtration. (**Fig 2**) The collected filtrate concentrated in vacuum with silica gel added. The residue was separated by chromatography (dichloromethane / petroleum ether 10:1) to obtain the desired product **3a**. It was nothing that we use ethyl acetate/petroleum ether as the developing solvent to detect the product during the experiment by TLC. In this system, no matter what proportion of solvent is used, the product and phenylboronic acid have an approximate R_f value (Figure 3 a), but if you change the system to detect (DCM: EA = 10:1), you will find that there are obvious product spots (Figure 3 b, Figure 3 c)

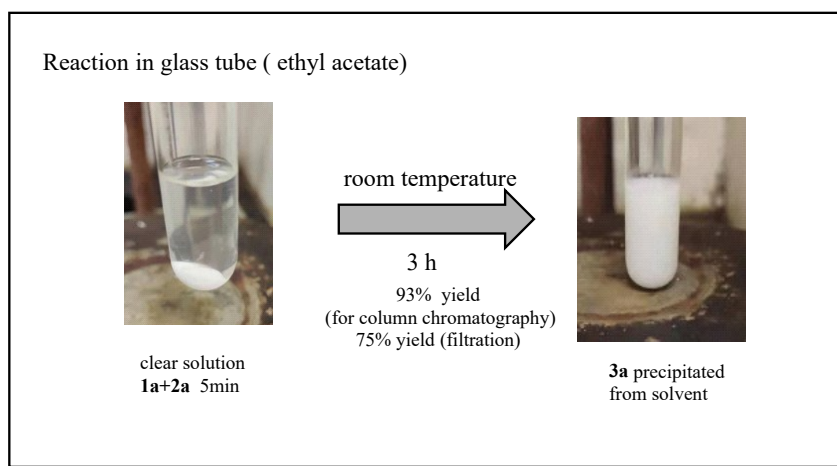


Fig 2. Reaction phenomenons and results.

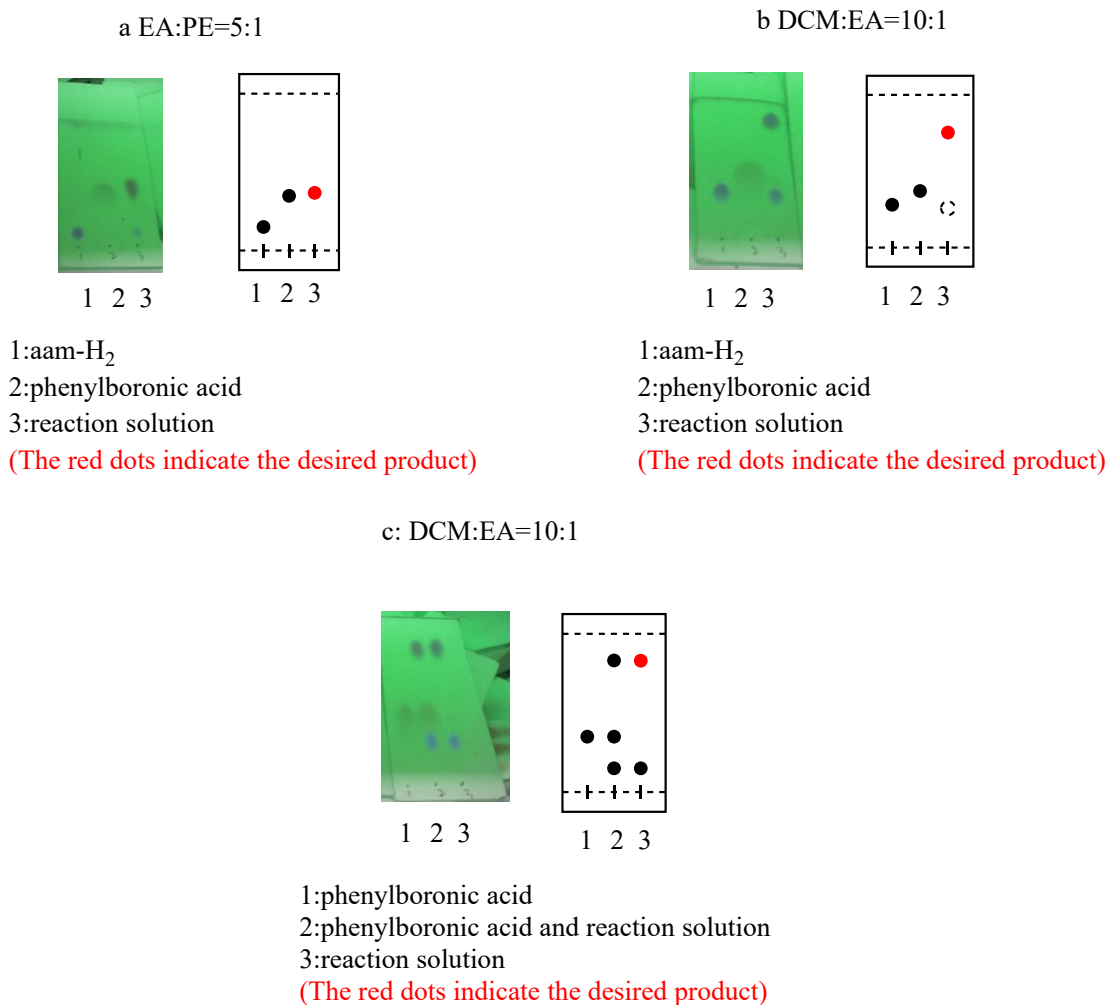
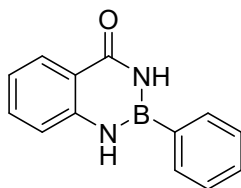


Fig 3

2.2 The gram-scale reaction

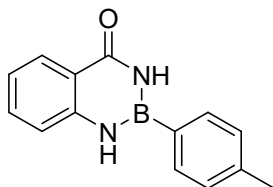
A round-bottom flask (250ml) was charged with anthranilamide **1a** (5.00 g, 36.7 mmol, 1.2 equiv), phenylboronic **2a** (4.00 g 32.8 mmol 1 equiv.) and ethyl acetate(80ml). The mixture was stirred at room temperature for 3h. When the reaction reached completion, the solvent was completely removed by vacuum distillation. Then, the reaction tubes were put at -10°C for 8h, and 15ml of ethyl acetate was added. the desired product **3a** precipitated from the ethyl acetate after can be isolated by simple filtration. The collected filtrate concentrated in vacuum with silica gel added. The residue was separated by chromatography (dichloromethane / petroleum ether 10:1) to obtain the desired product **3a**.

3. Analytic Data of Products



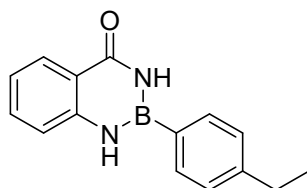
2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3a), white solid, m.p.209.8-212°C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.70 (s, 1H), 9.33 (s, 1H), 8.05 (dd, *J* = 14.6, 7.6 Hz, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 (dt, *J* = 25.7, 7.6 Hz, 4H), 7.12 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.78, 145.95, 133.85, 133.78, 130.98, 128.41, 128.28, 121.29, 119.25, 118.62. HRMS (ESI): *m/z* [M+H]⁺ calculated for C₁₃H₁₂BN₂O: 223.10372 found: 223.1031



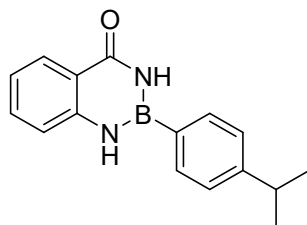
2-(*p*-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one

2-(*p*-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3b), white solid, m.p.265-266°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.64 (s, 1H), 9.30 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.76, 145.98, 137.14, 134.39, 133.83, 131.58, 130.87, 128.40, 128.21, 121.23, 119.24, 118.60, 21.58.



2-(4-ethylphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one

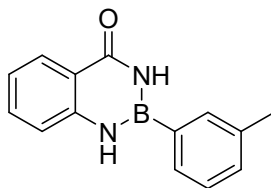
2-(4-ethylphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3c), white solid, m.p.242.8-243.5°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.63 (s, 1H), 9.26 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.07 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.78, 146.87, 146.01, 133.91, 133.81, 128.39, 127.78, 121.16, 119.19, 118.56, 28.74, 15.93.



2-(4-isopropylphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one

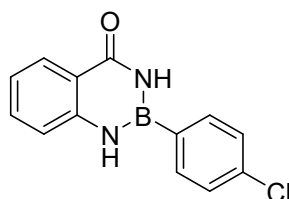
2-(4-isopropylphenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3d) gray solid m.p.224.0-226.5°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.63 (s, 1H), 9.25 (s, 1H), 8.01 (d, *J* = 6.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 2.92 (p, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.78, 151.45, 146.01, 133.93, 133.81, 128.39, 126.31, 121.17, 119.19, 118.56, 33.99, 24.21. ¹¹B

NMR (193 MHz, DMSO- d_6) δ 29.91.



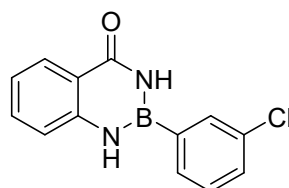
2-(*m*-tolyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

2-(*m*-tolyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one(3e) white soild,m.p.219.1-221.6°C
 ^1H NMR (600 MHz, DMSO- d_6) δ 9.63 (s, 1H), 9.28 (s, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.89 (s, 1H), 7.84 (d, $J = 7.3$ Hz, 1H), 7.59 – 7.54 (m, 1H), 7.44 (d, $J = 8.1$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.10 (t, $J = 7.5$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 166.76, 145.98, 137.14, 134.39, 133.83, 131.58, 130.87, 128.40, 128.21, 121.23, 119.24, 118.60, 21.58.



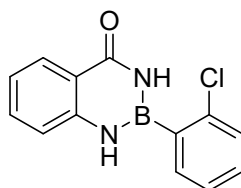
2-(4-chlorophenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

2-(4-chlorophenyl)-2,3-dihydrobenzo[*d*][1,3,2] diazaborinin-4(1*H*)-one(3g) white soild,m.p.256-257°C ^1H NMR (600 MHz, DMSO- d_6) δ 9.77 (s, 1H), 9.39 (s, 1H), 8.08 (d, $J = 8.4$ Hz, 2H), 8.03 (d, $J = 7.9$ Hz, 1H), 7.58 (t, $J = 6.8$ Hz, 1H), 7.54 (s, 2H), 7.43 (d, $J = 8.3$ Hz, 1H), 7.14 – 7.09 (m, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 165.65, 144.75, 135.05, 134.62, 132.84, 127.35, 127.29, 120.37, 118.21, 117.56.



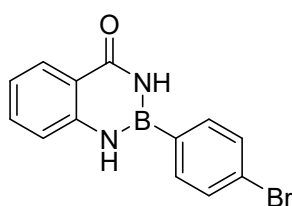
2-(3-chlorophenyl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

2-(3-chlorophenyl)-2,3-dihydrobenzo[*d*][1,3,2] diazaborinin-4(1*H*)-one(3h) white soild,m.p.245.6-248.9°C ^1H NMR (600 MHz, DMSO- d_6) δ 9.82 (s, 1H), 9.44 (s, 1H), 8.17 – 8.13 (m, 1H), 8.07 – 8.01 (m, 2H), 7.60 (t, $J = 6.8$ Hz, 1H), 7.55 (d, $J = 9.1$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 1H), 7.14 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 166.70, 145.76, 133.94, 133.75, 133.36, 132.29, 130.76, 130.30, 128.42, 121.52, 119.35, 118.65.



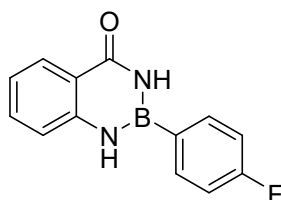
2-(2-chlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(2-chlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3i) white soild,m.p.181.6-183.1°C ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 9.50 (s, 1H), 9.32 (s, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.56 (t, $J = 7.7$ Hz, 2H), 7.49 – 7.44 (m, 2H), 7.38 (t, $J = 7.0$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 1H), 7.13 (t, $J = 7.0$ Hz, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 166.21, 145.63, 137.14, 135.22, 133.84, 131.47, 129.05, 128.40, 126.81, 121.57, 119.36, 118.61.



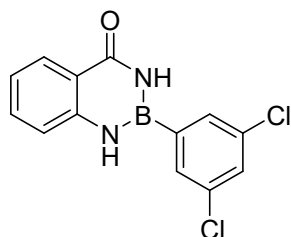
2-(4-bromophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(4-bromophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3j) white soild,m.p.257-258°C ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 9.76 (s, 1H), 9.38 (s, 1H), 8.01 (dd, $J = 12.1, 8.9$ Hz, 3H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.60 – 7.56 (m, 1H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 166.70, 145.80, 135.89, 133.92, 131.27, 128.41, 125.14, 121.45, 119.28, 118.62.



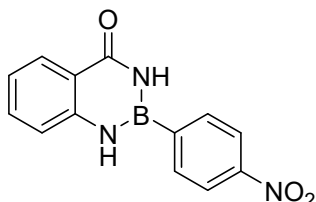
2-(4-fluorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(4-fluorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3k) white soild,m.p.257.6-262.3°C ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 9.73 (s, 1H), 9.33 (s, 1H), 8.15 – 8.09 (m, 2H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.60 – 7.55 (m, 1H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.29 (t, $J = 9.0$ Hz, 2H), 7.11 (t, $J = 8.1$ Hz, 1H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 165.67, 164.22, 162.58, 144.82, 135.28, 135.23, 132.81, 127.33, 120.26, 118.11, 117.50, 114.30, 114.17.



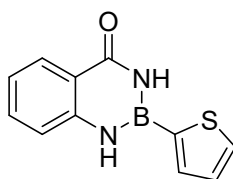
2-(3,5-dichlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(3,5-dichlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3l) white solid 286-287°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.87 (s, 1H), 9.49 (s, 1H), 8.11 (d, *J* = 1.9 Hz, 2H), 8.02 (d, *J* = 6.4 Hz, 1H), 7.71 (s, 1H), 7.62 – 7.57 (m, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.16 – 7.12 (m, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.57, 145.57, 134.65, 134.03, 132.16, 130.24, 128.42, 121.74, 119.44, 118.67.



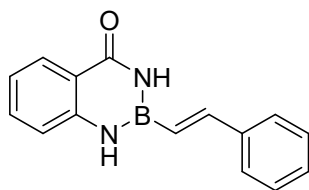
2-(4-nitrophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(4-nitrophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3o) yellow solid, m.p > 300°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.94 (s, 1H), 9.60 (s, 1H), 8.30 (q, *J* = 8.7 Hz, 4H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.13 (m, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.63, 149.31, 145.62, 135.12, 134.01, 128.43, 122.79, 121.79, 119.49, 118.78.



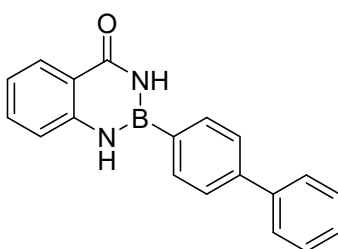
2-(thiophen-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

2-(thiophen-2-yl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3p) white solid, m.p. 201-202.3°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.85 (s, 1H), 9.43 (s, 1H), 8.04 (t, *J* = 8.2 Hz, 3H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.09, 147.04, 138.36, 133.78, 131.19, 130.51, 128.34, 121.46, 118.17, 117.90.



(*E*)-2-styryl-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

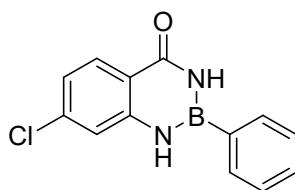
(*E*)-2-styryl-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one(3q) white soild, m.p.199.8-203.1°C
¹H NMR (600 MHz, DMSO-*d*₆) δ 9.71 (s, 1H), 9.33 (s, 1H), 8.05 (dd, *J* = 15.5, 7.1 Hz, 3H), 7.57 (dd, *J* = 16.4, 7.4 Hz, 3H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.14 – 7.09 (m, 1H), 6.79 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.97 (d, *J* = 17.6 Hz, 1H), 5.35 (d, *J* = 11.0 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 165.70, 144.89, 138.45, 135.97, 133.07, 132.79, 127.35, 124.95, 120.22, 118.19, 117.54, 114.75.



2-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

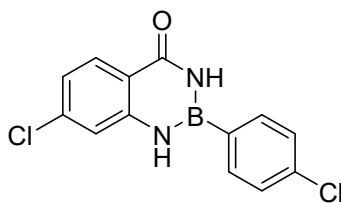
2-([1,1'-biphenyl]-4-yl)-2,3-dihydrobenzo[*d*][1,3,2] diazaborinin-4(1*H*)-one(3r)

white soild, m.p.287-287.5°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.76 (s, 1H), 9.39 (s, 1H), 8.17 (d, *J* = 7.9 Hz, 2H), 8.04 (d, *J* = 6.3 Hz, 1H), 7.76 (dd, *J* = 7.6, 4.4 Hz, 4H), 7.59 (t, *J* = 8.4 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.79, 145.98, 142.50, 140.29, 134.49, 133.87, 129.45, 128.43, 128.25, 127.25, 126.49, 121.31, 119.29, 118.63.



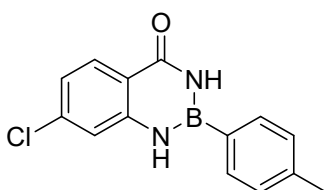
7-chloro-2-phenyl-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one

7-chloro-2-phenyl-2,3-dihydrobenzo[*d*][1,3,2]diazaborinin-4(1*H*)-one(3s) white soild, m.p.289.4-290.3°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.75 (s, 1H), 9.29 (s, 1H), 8.02 (dd, *J* = 10.2, 5.6 Hz, 2H), 7.94 (d, *J* = 4.6 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.31 (t, *J* = 4.0 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.49, 145.87, 136.81, 133.87, 132.94, 129.09, 128.41, 121.30, 119.26, 118.60.



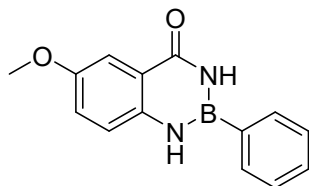
7-chloro-2-(4-chlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

7-chloro-2-(4-chlorophenyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3t) white soild m.p.>300°C ^1H NMR (600 MHz, DMSO- d_6) δ 9.88 (s, 1H), 9.47 (s, 1H), 8.03 (dd, $J = 22.1, 8.2$ Hz, 3H), 7.54 (d, $J = 7.9$ Hz, 2H), 7.48 (s, 1H), 7.15 (d, $J = 8.5$ Hz, 1H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 166.00, 146.92, 138.39, 136.33, 135.68, 130.52, 128.43, 121.60, 118.19, 117.89.



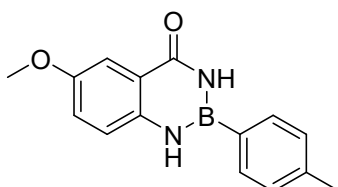
7-chloro-2-(p-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

7-chloro-2-(p-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3u) white soild m.p.>300°C ^1H NMR (600 MHz, DMSO- d_6) δ 9.76 (s, 1H), 9.35 (s, 1H), 7.96 (dd, $J = 39.2, 8.0$ Hz, 3H), 7.48 (s, 1H), 7.27 (d, $J = 7.6$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 166.06, 147.10, 140.93, 138.31, 133.86, 130.52, 129.05, 121.36, 118.10, 117.82, 21.67.



6-methoxy-2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

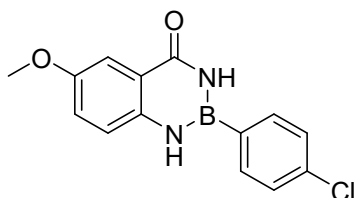
6-methoxy-2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3v) white soild m.p.224.7-225.5°C ^1H NMR (600 MHz, DMSO- d_6) δ 9.77 (s, 1H), 9.28 (s, 1H), 8.08 (d, $J = 7.4$ Hz, 2H), 7.55 (s, 1H), 7.51 – 7.43 (m, 4H), 7.26 (dd, $J = 8.8, 2.9$ Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, DMSO- d_6) δ 166.73, 154.09, 140.17, 133.66, 130.80, 128.26, 122.77, 120.08, 119.57, 109.45, 55.77.



6-methoxy-2-(p-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one

6-methoxy-2-(p-tolyl)-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(3w) white soild

m.p.262.2-264.5°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.67 (s, 1H), 9.19 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 3.0 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.29 – 7.20 (m, 3H), 3.81 (s, 3H), 2.36 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.70, 153.99, 140.39, 140.22, 133.71, 128.96, 122.73, 120.00, 119.48, 109.44, 55.77, 21.64.



2-(4-chlorophenyl)-6-methoxy-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one

2-(4-chlorophenyl)-6-methoxy-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1*H*)-one(3x) white solid
 m.p.298.3-299.2°C ¹H NMR (600 MHz, DMSO-*d*₆) δ 9.79 (s, 1H), 9.35 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.43 (m, 3H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.24 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 166.61, 154.16, 140.00, 135.92, 135.55, 128.33, 122.81, 120.07, 119.60, 109.43, 55.79.

4.Copies of 1H NMR and 13C NMR for the products

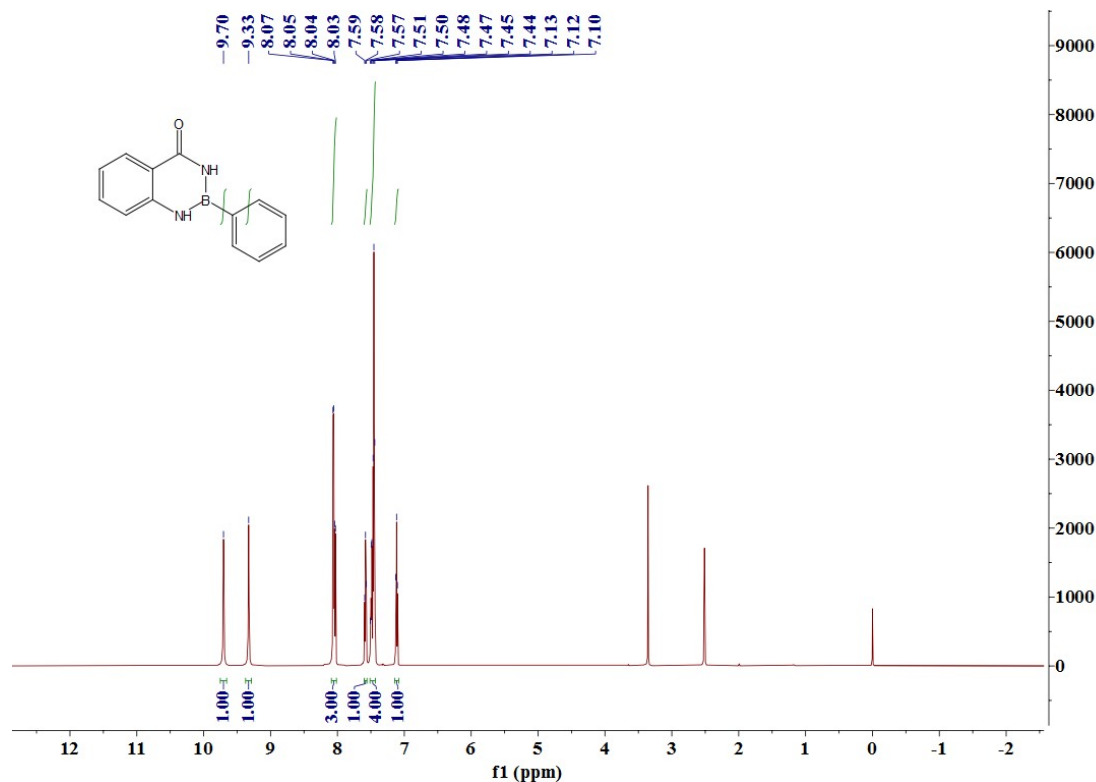


Figure 1. ¹H NMR spectrum of **3a** (solvent: DMSO-*d*₆)

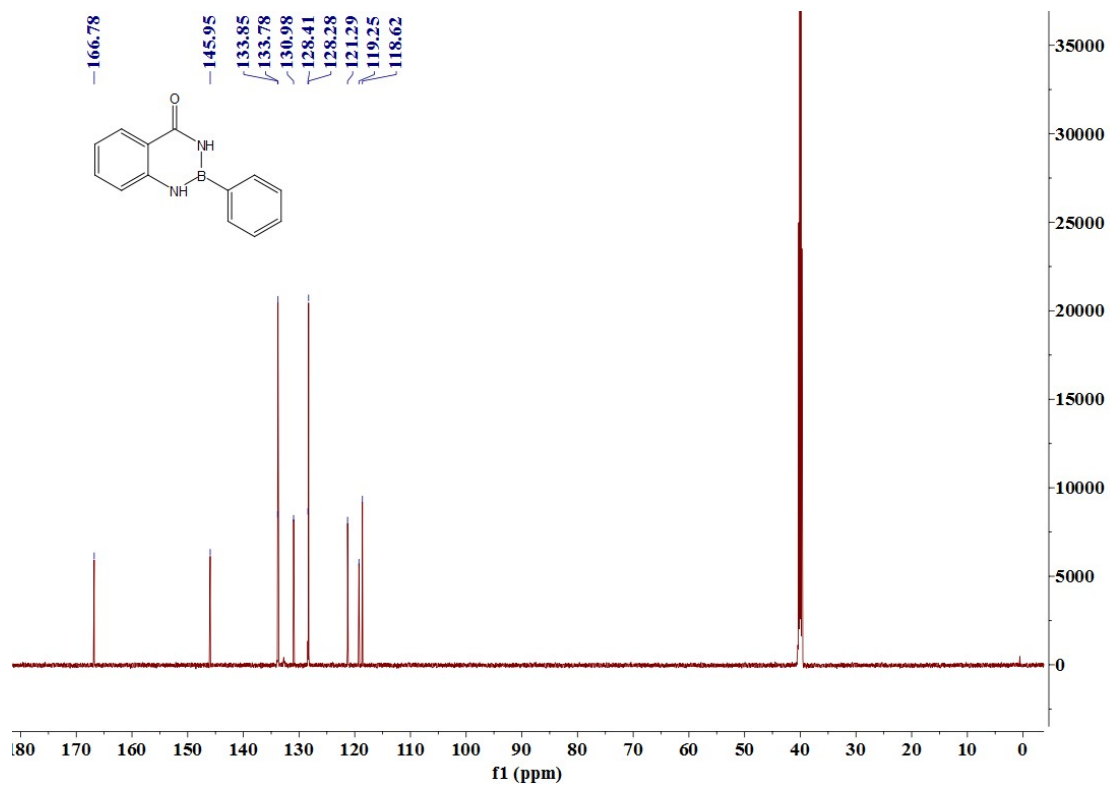


Figure 2. ^{13}C NMR spectrum of **3a** (solvent: DMSO-d₆)

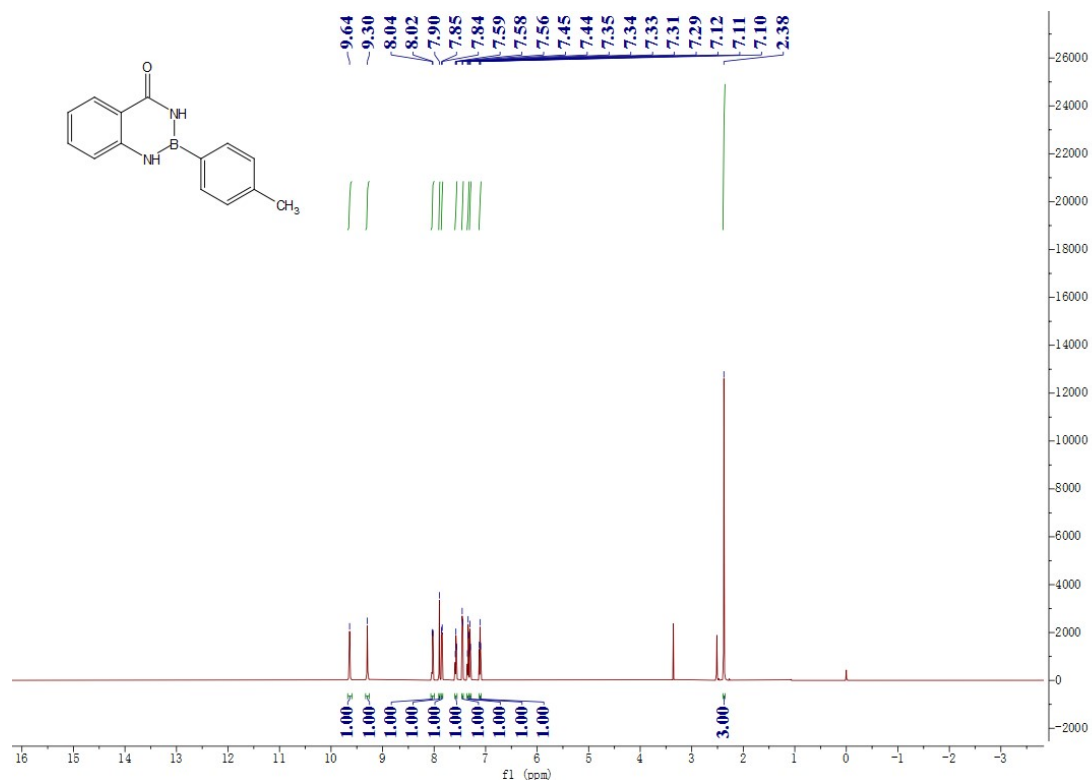


Figure 3. ^1H NMR spectrum of **3b** (solvent: DMSO-d₆)

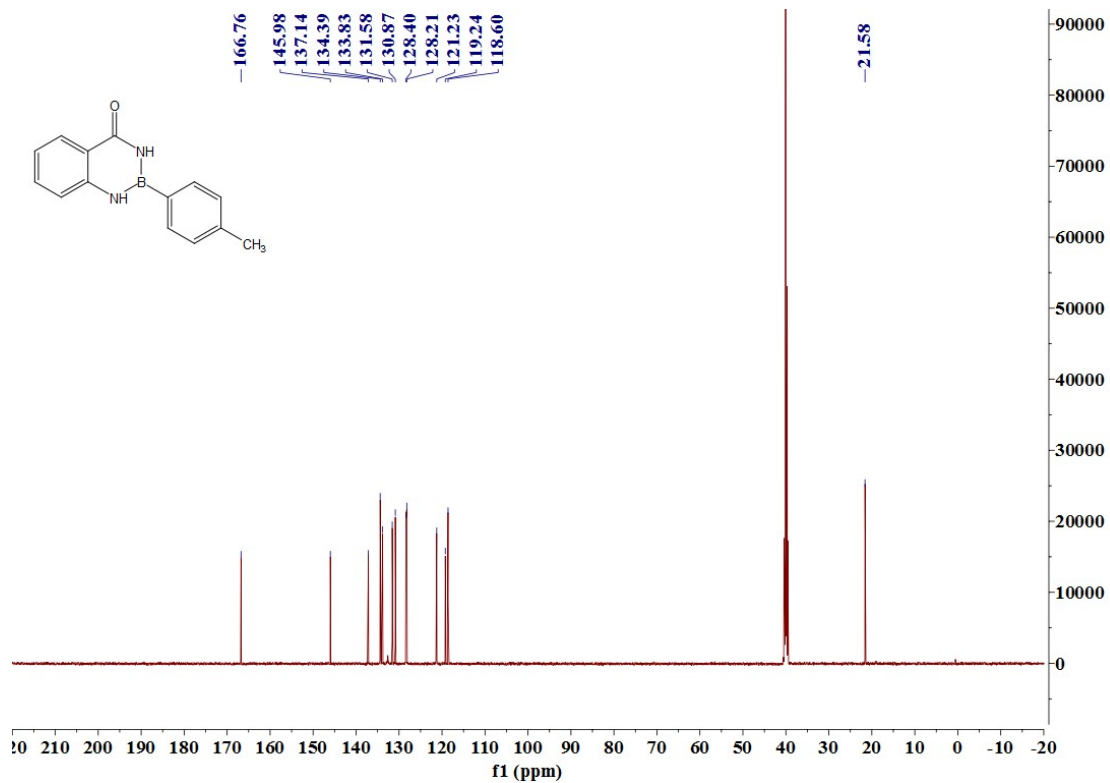


Figure 4. ¹³C NMR spectrum of **3b** (solvent: DMSO-d6)

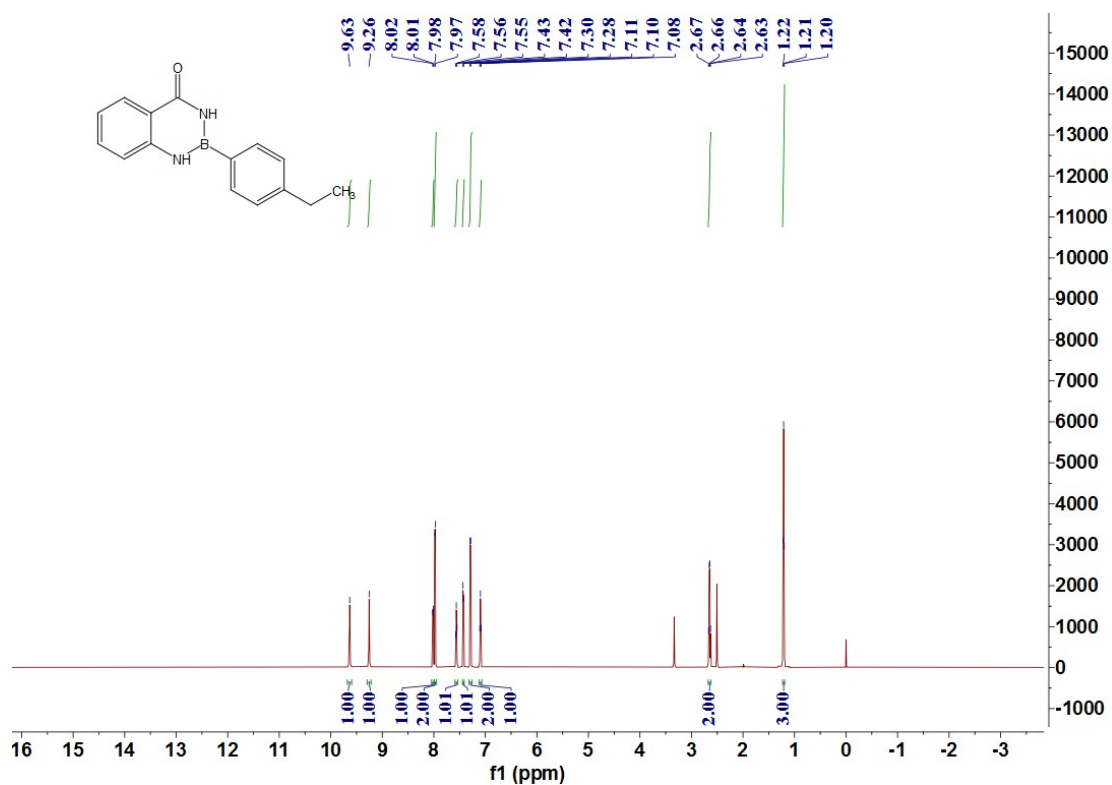


Figure 5. ¹H NMR spectrum of **3c** (solvent: DMSO-d6)

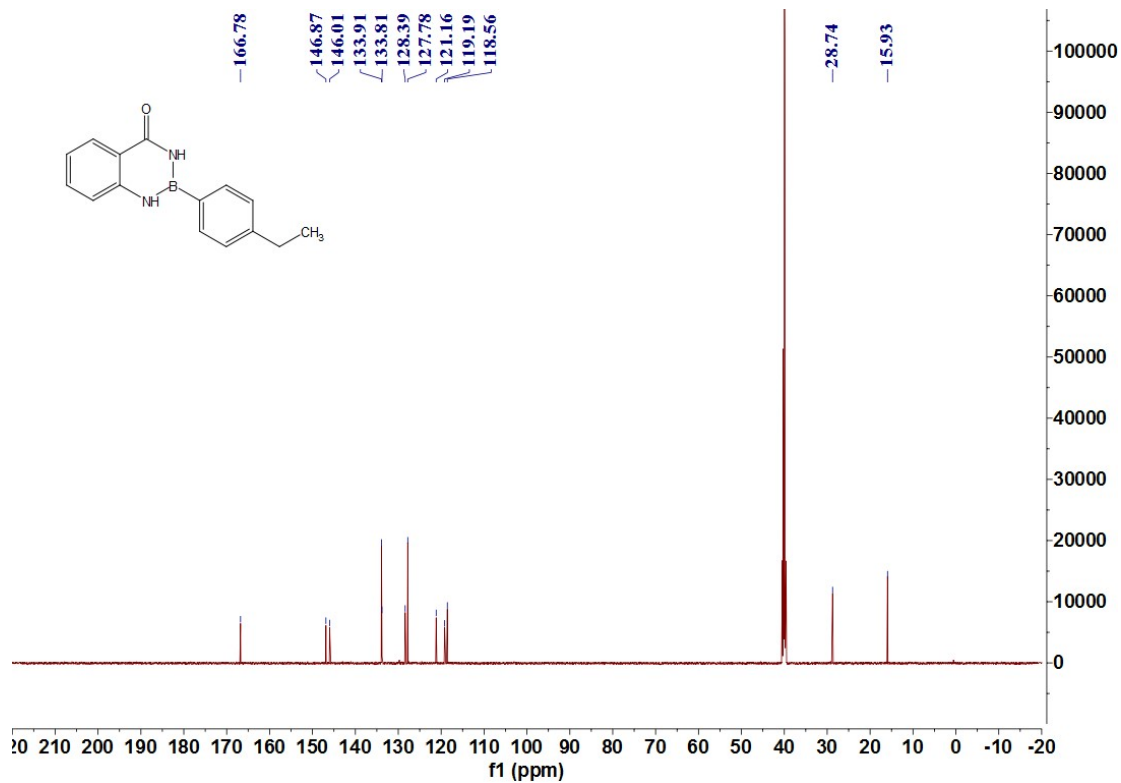


Figure 6. ¹³C NMR spectrum of 3c (solvent: DMSO-d6)

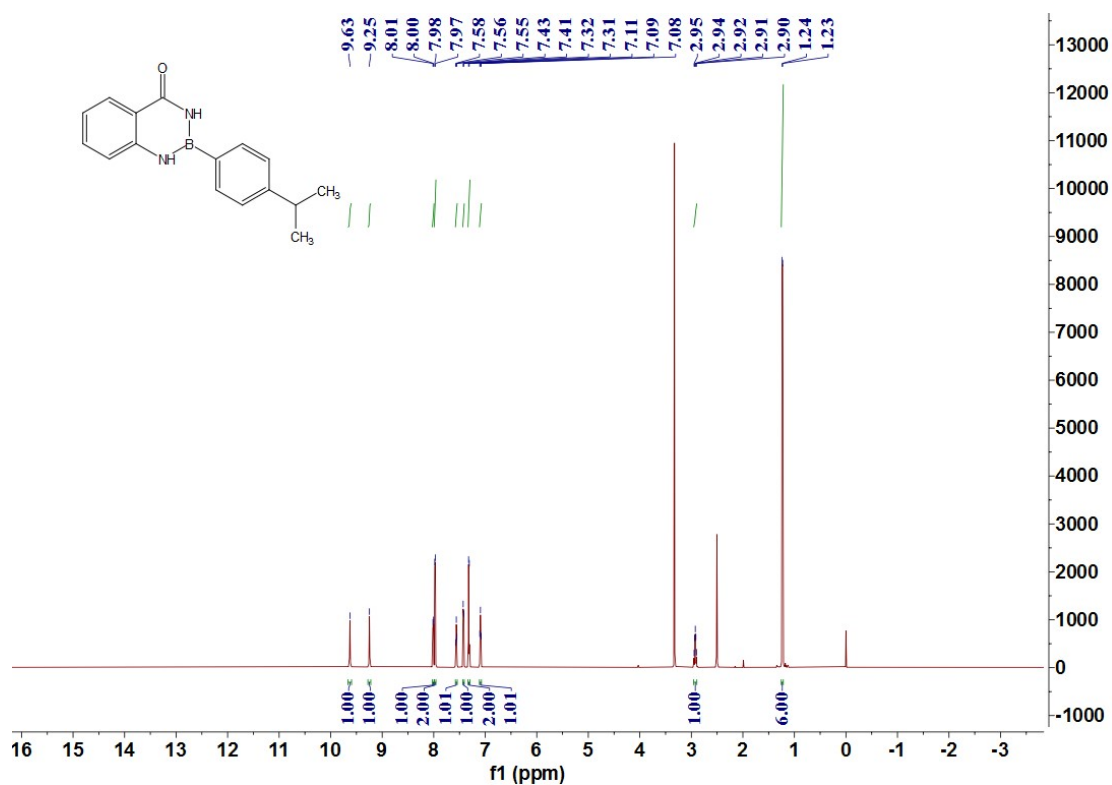
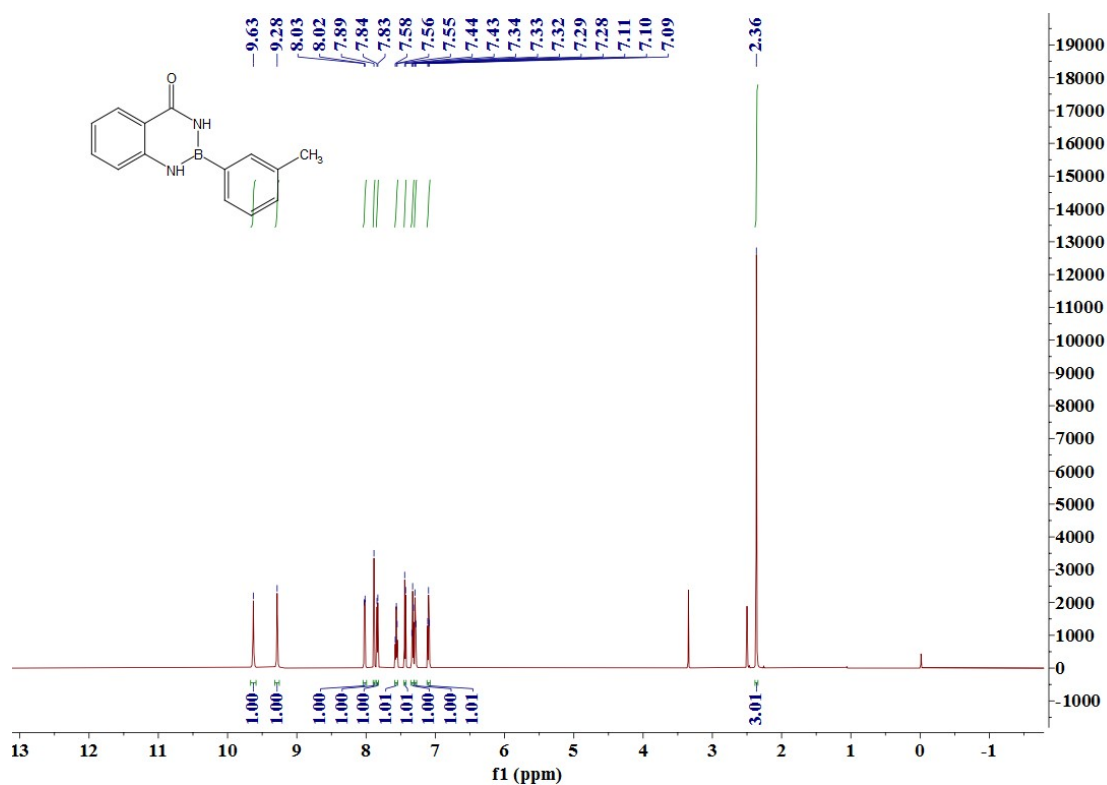
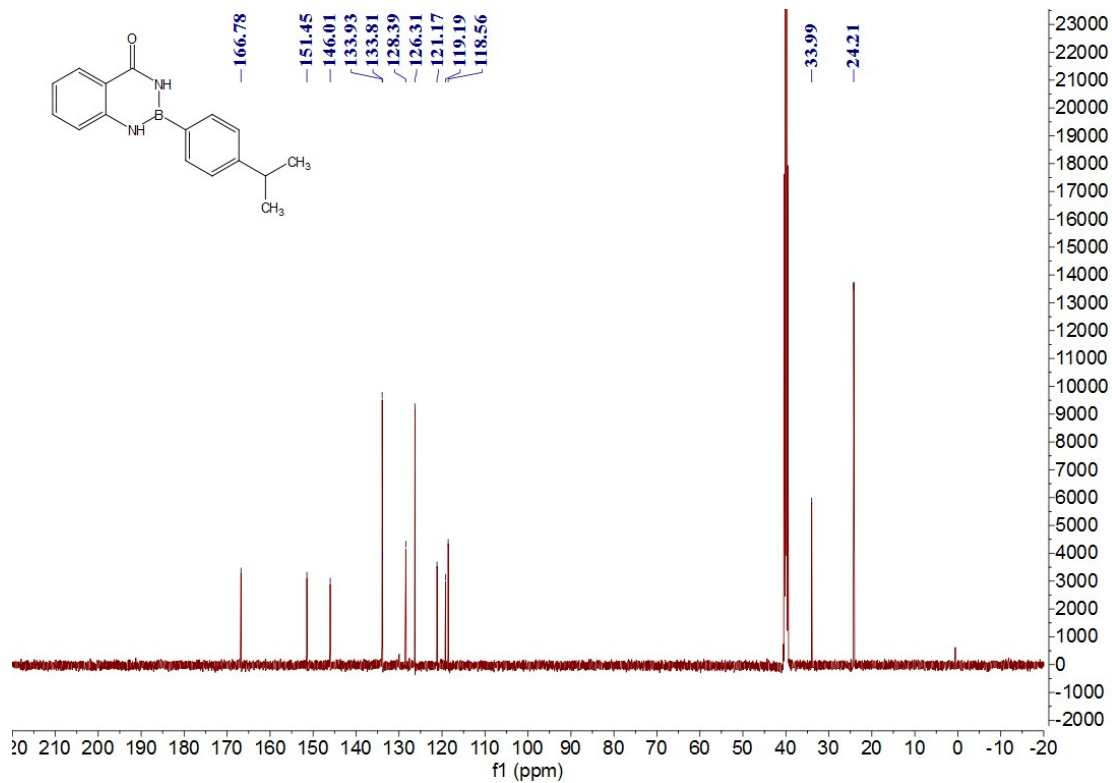
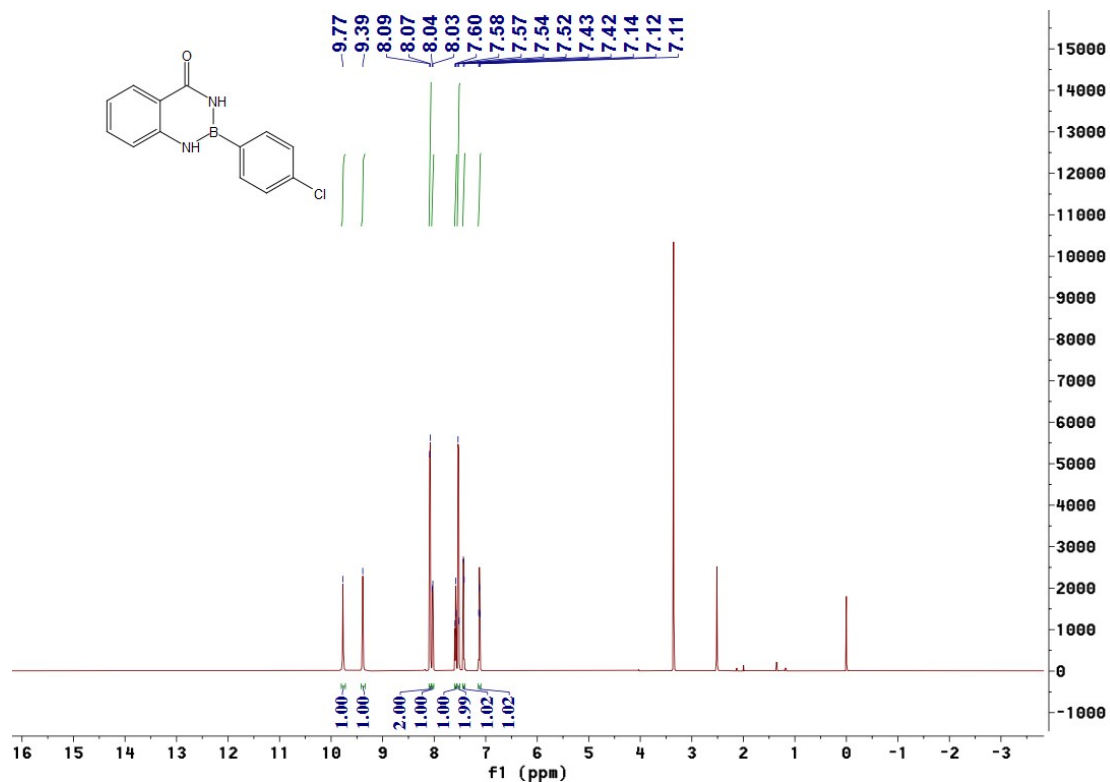
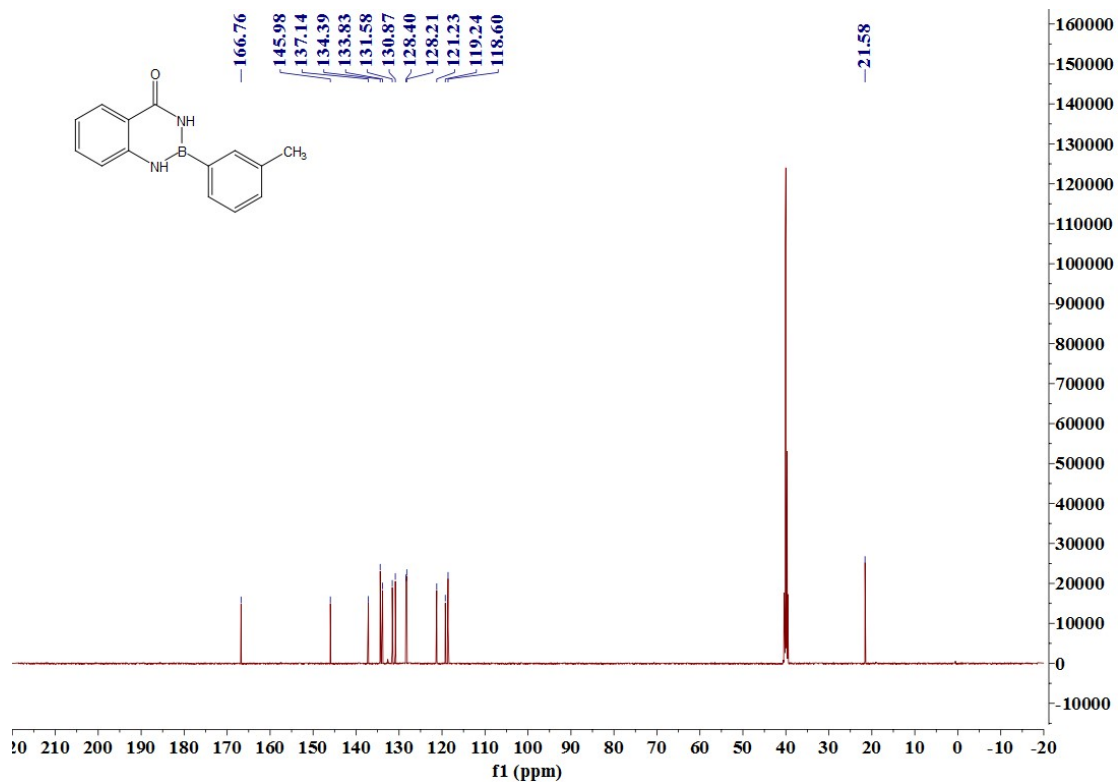


Figure 7. ¹H NMR spectrum of 3d (solvent: DMSO-d6)





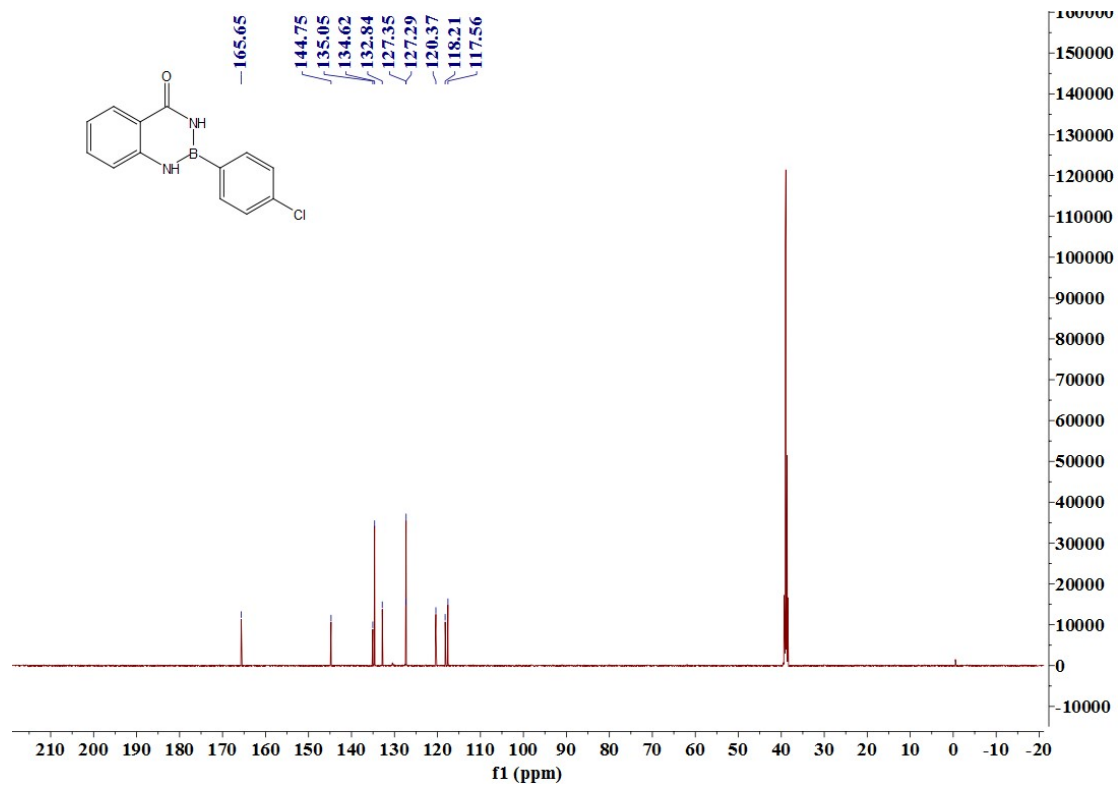


Figure 12. ¹³C NMR spectrum of **3g** (solvent: DMSO-d₆)

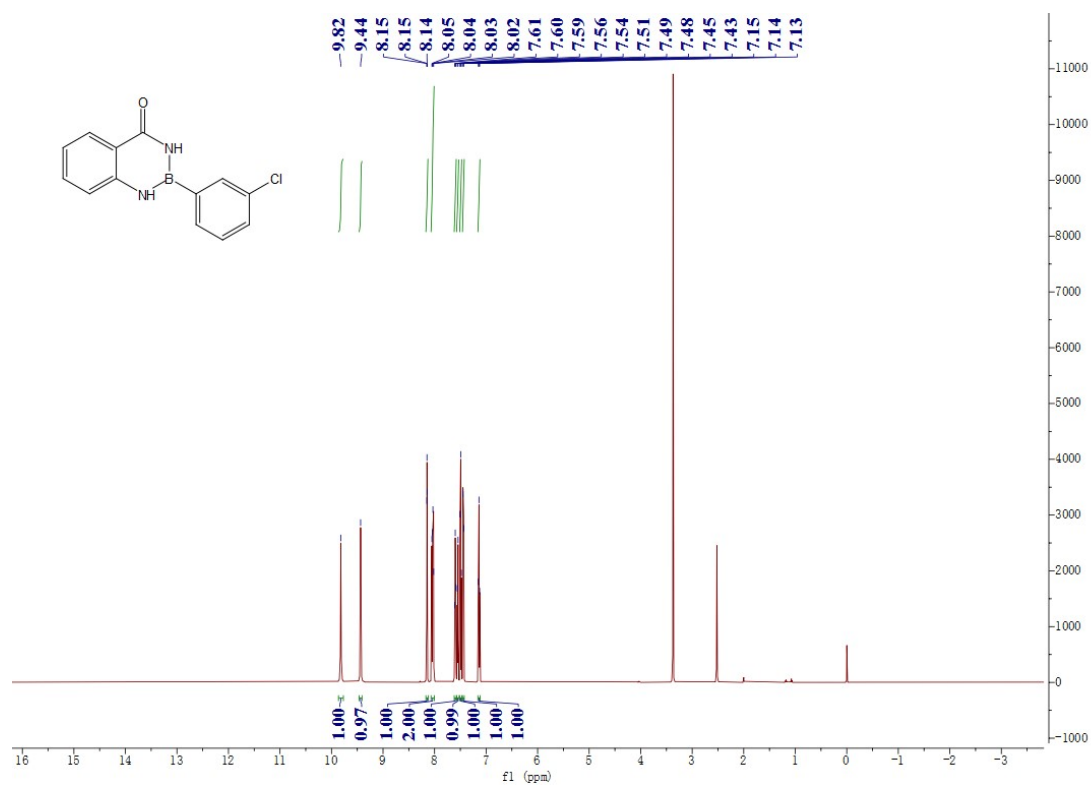


Figure 13. ¹H NMR spectrum of **3h** (solvent: DMSO-d₆)

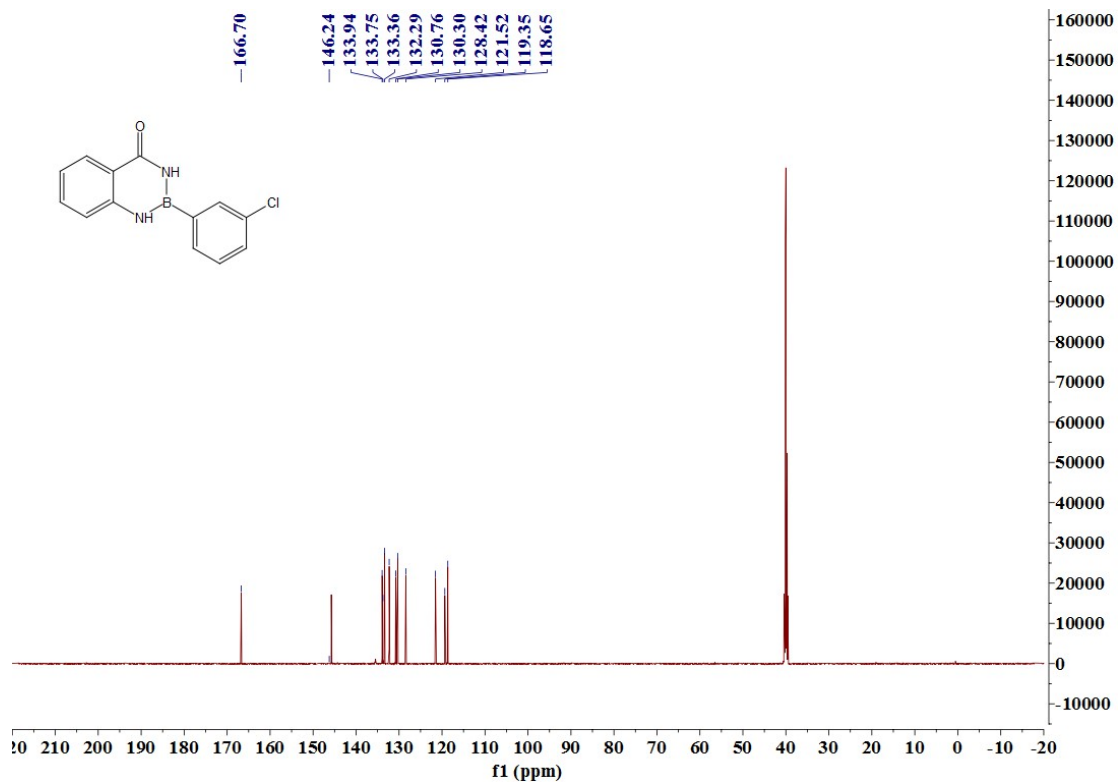


Figure 14. ¹³C NMR spectrum of **3h** (solvent: DMSO-d₆)

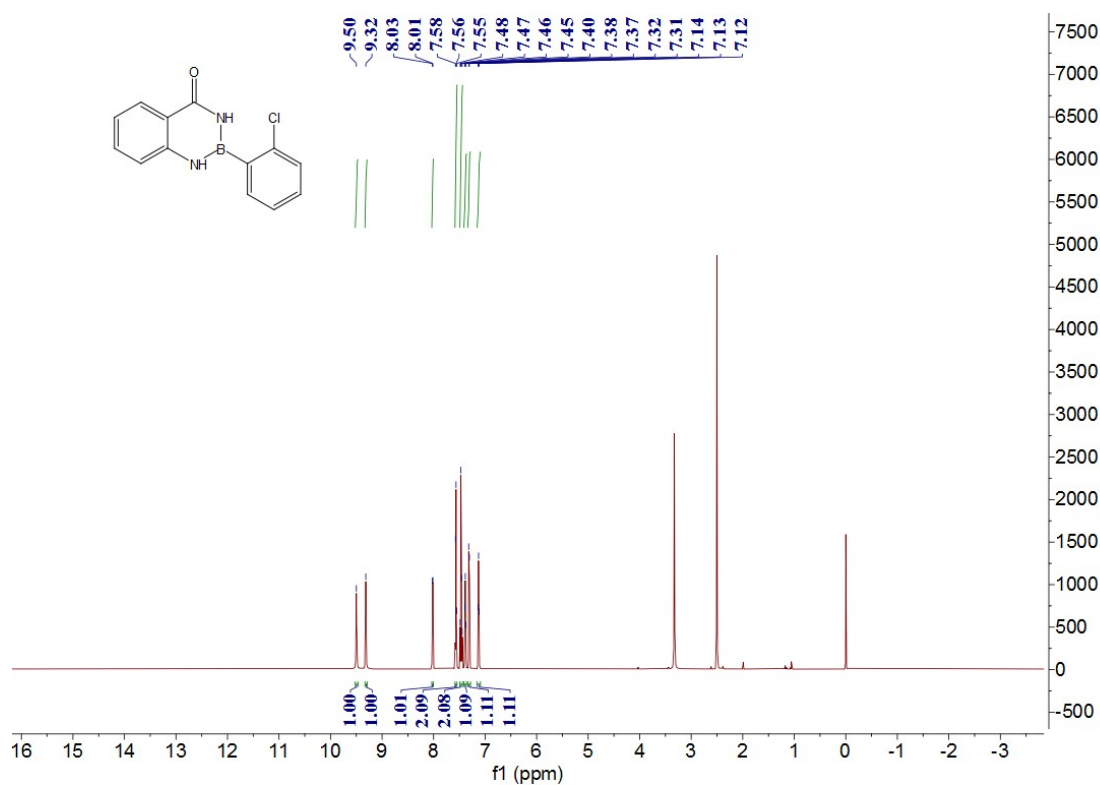


Figure 15. ¹H NMR spectrum of **3i** (solvent: DMSO-d₆)

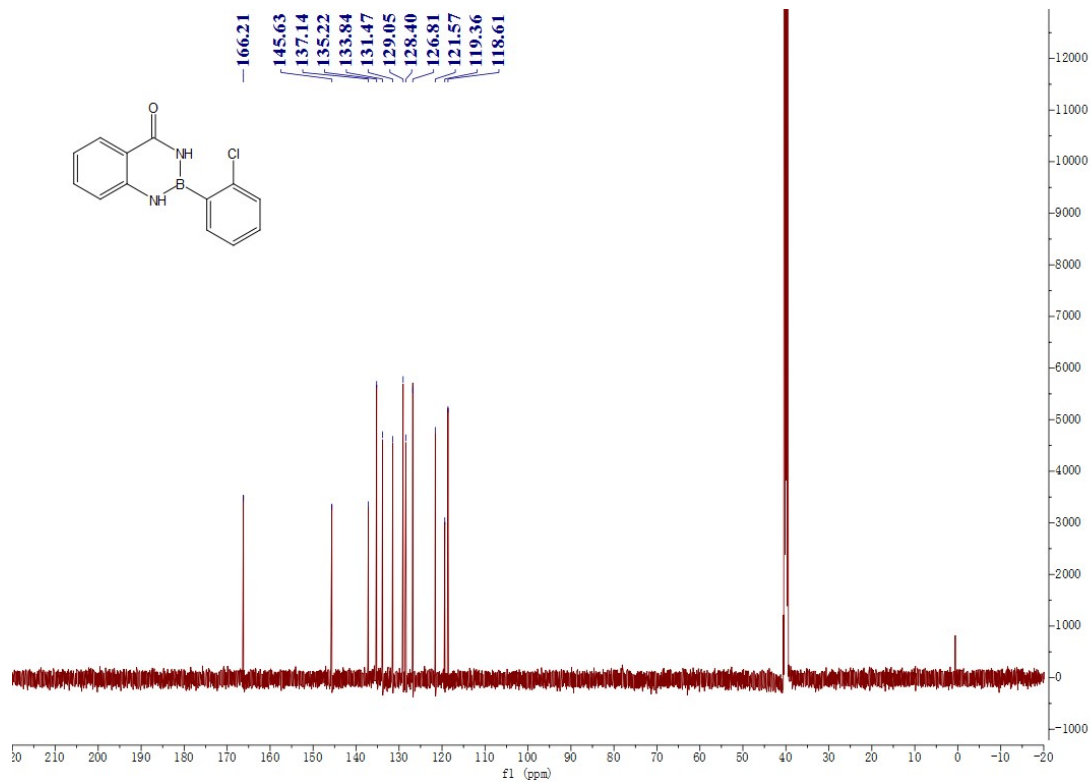


Figure 16. ¹³C NMR spectrum of **3i** (solvent: DMSO-d₆)

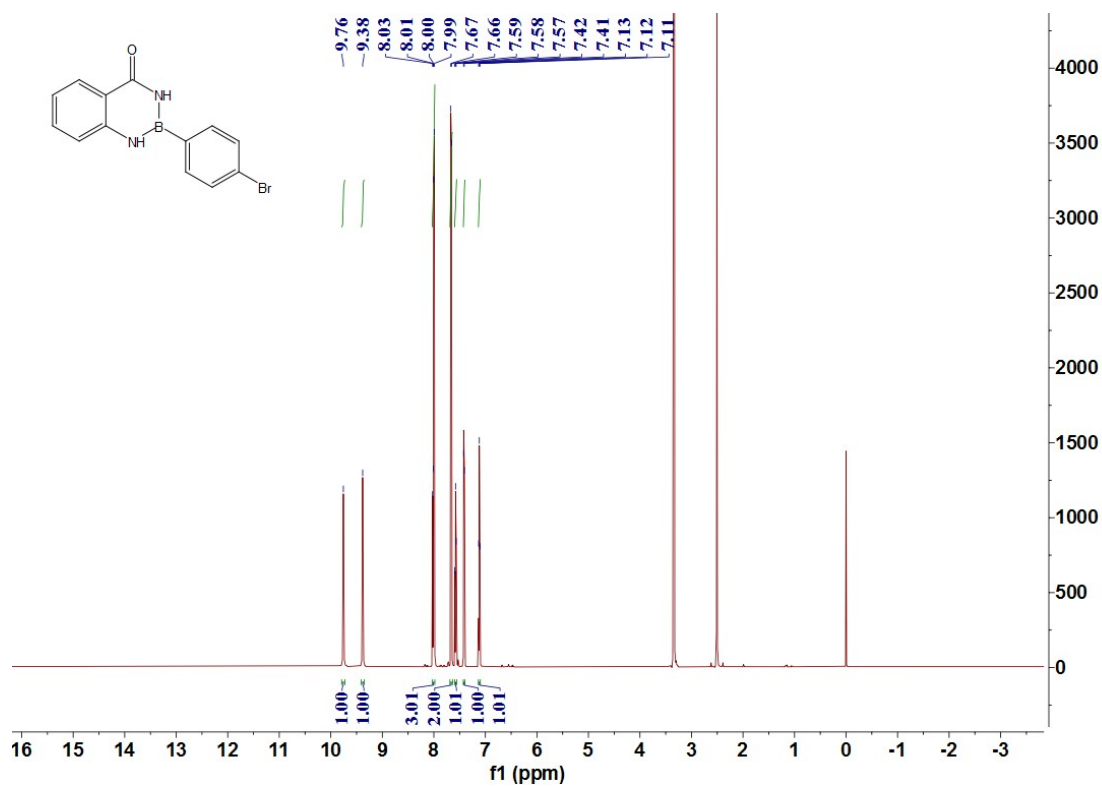


Figure 17. ¹H NMR spectrum of **3j** (solvent: DMSO-d₆)

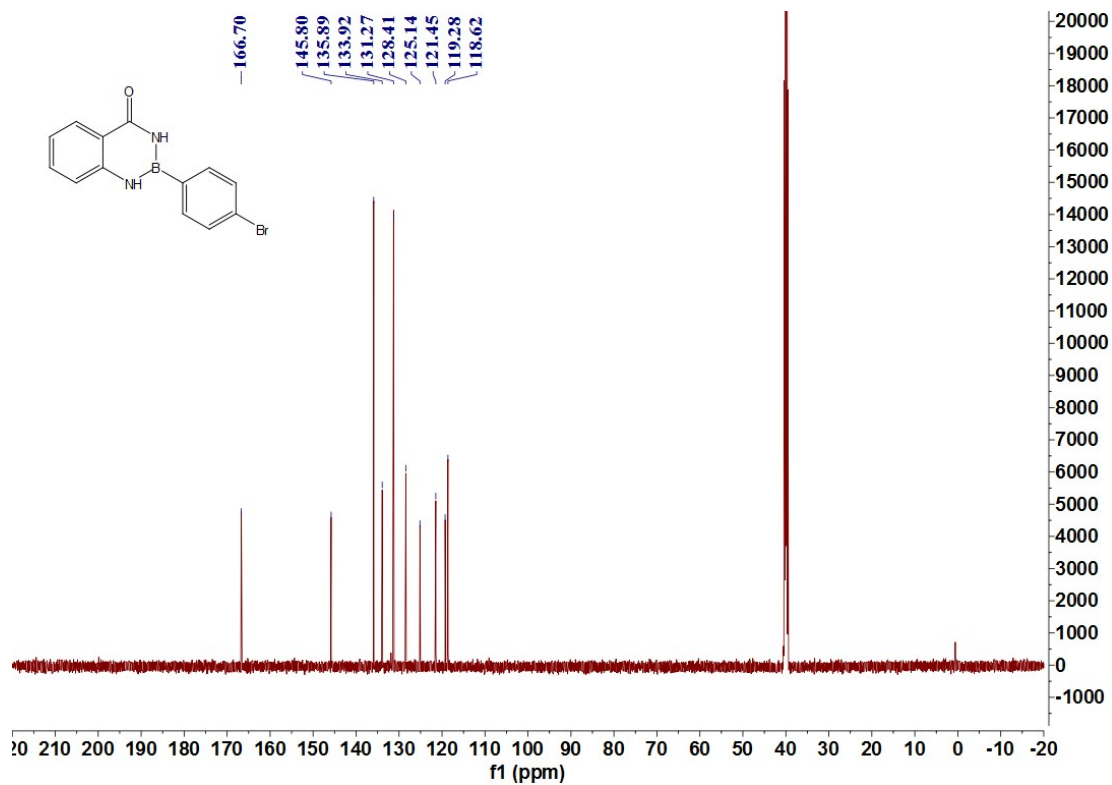


Figure 18. ^{13}C NMR spectrum of **3j** (solvent: DMSO-d₆)

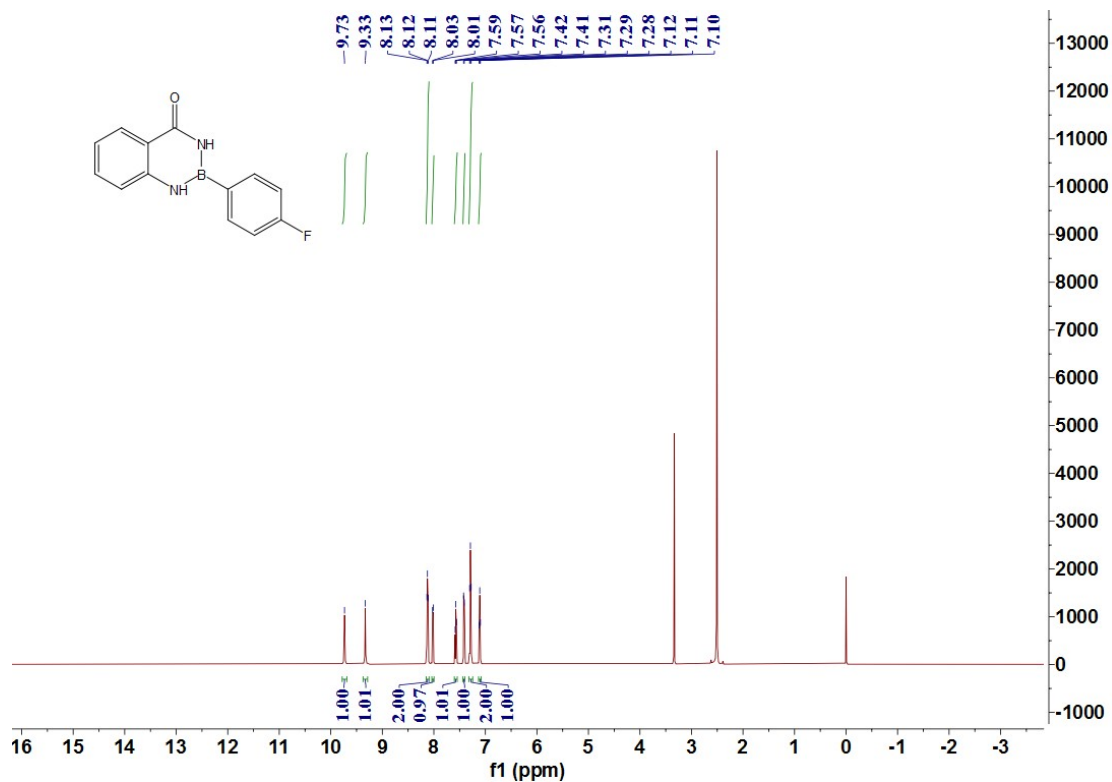


Figure 19. ^1H NMR spectrum of **3k** (solvent: DMSO-d₆)

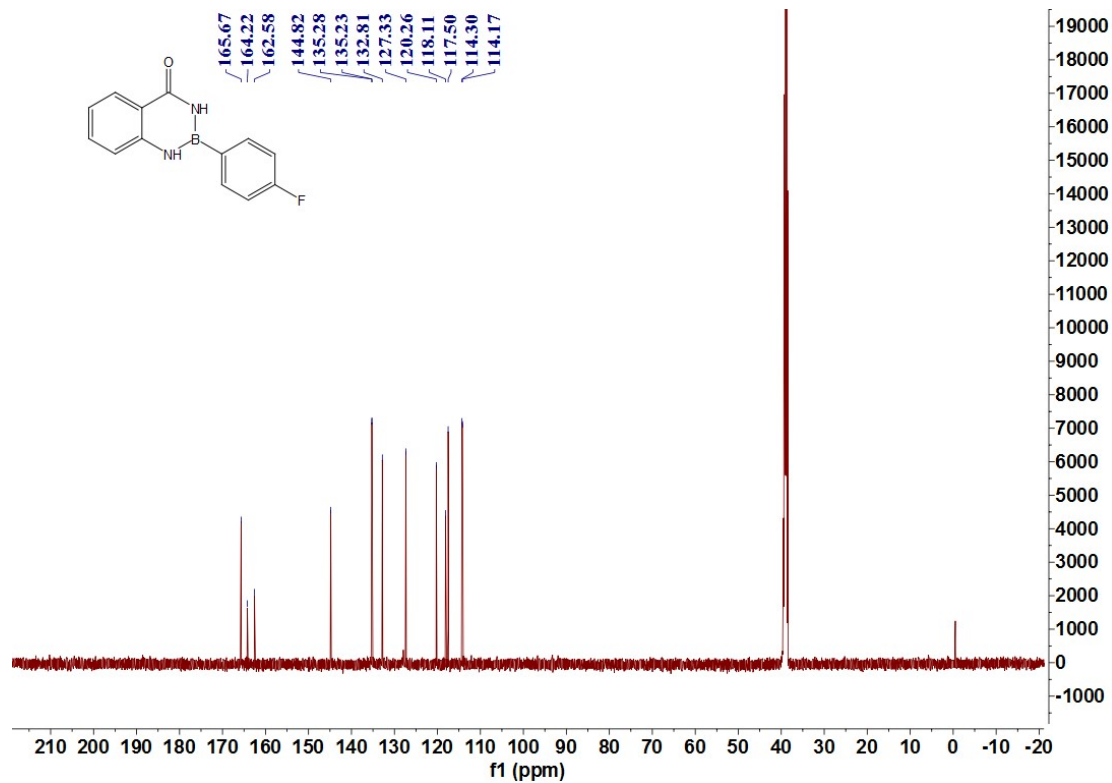


Figure 20. ¹³C NMR spectrum of **3k** (solvent: DMSO-d₆)

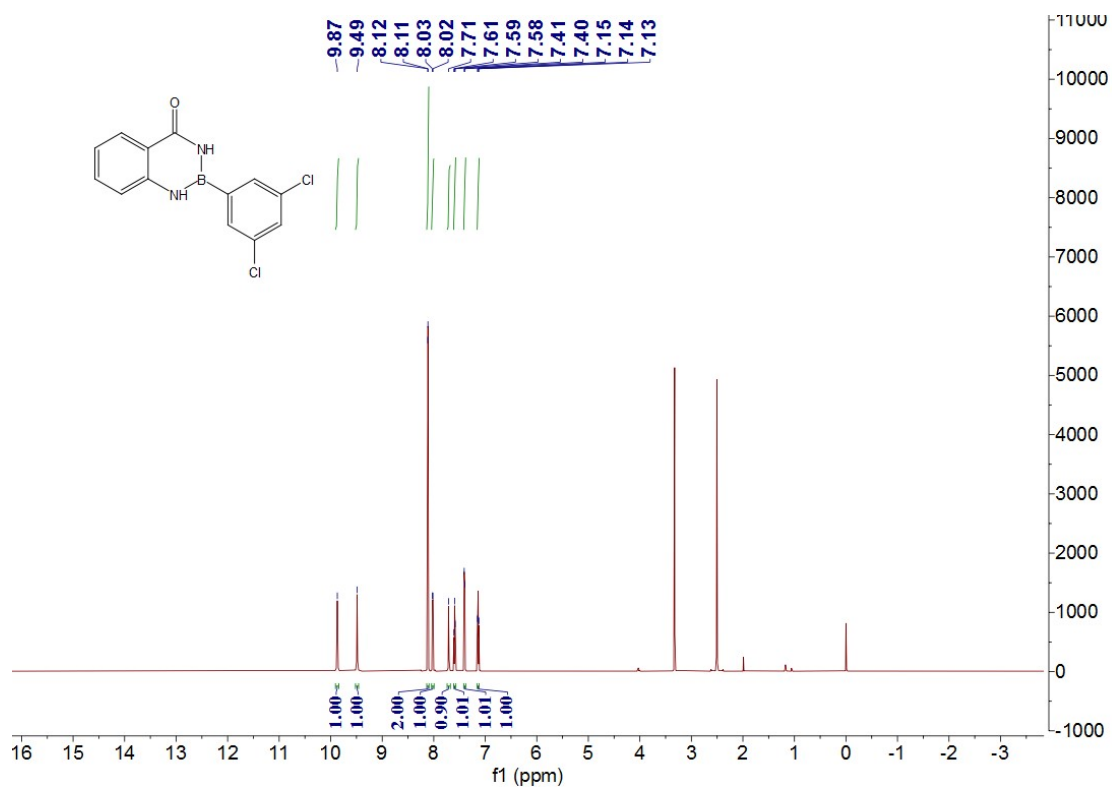


Figure 21. ¹H NMR spectrum of **3l** (solvent: DMSO-d₆)

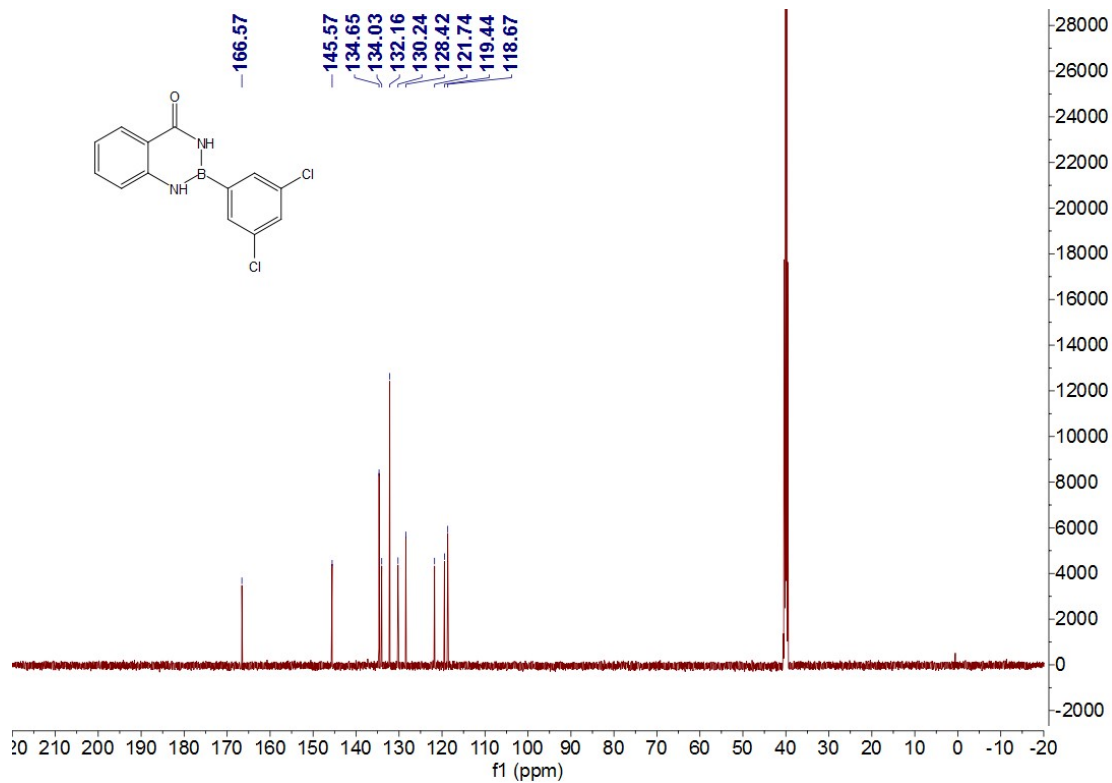


Figure 22. ¹³C NMR spectrum of **3i** (solvent: DMSO-d₆)

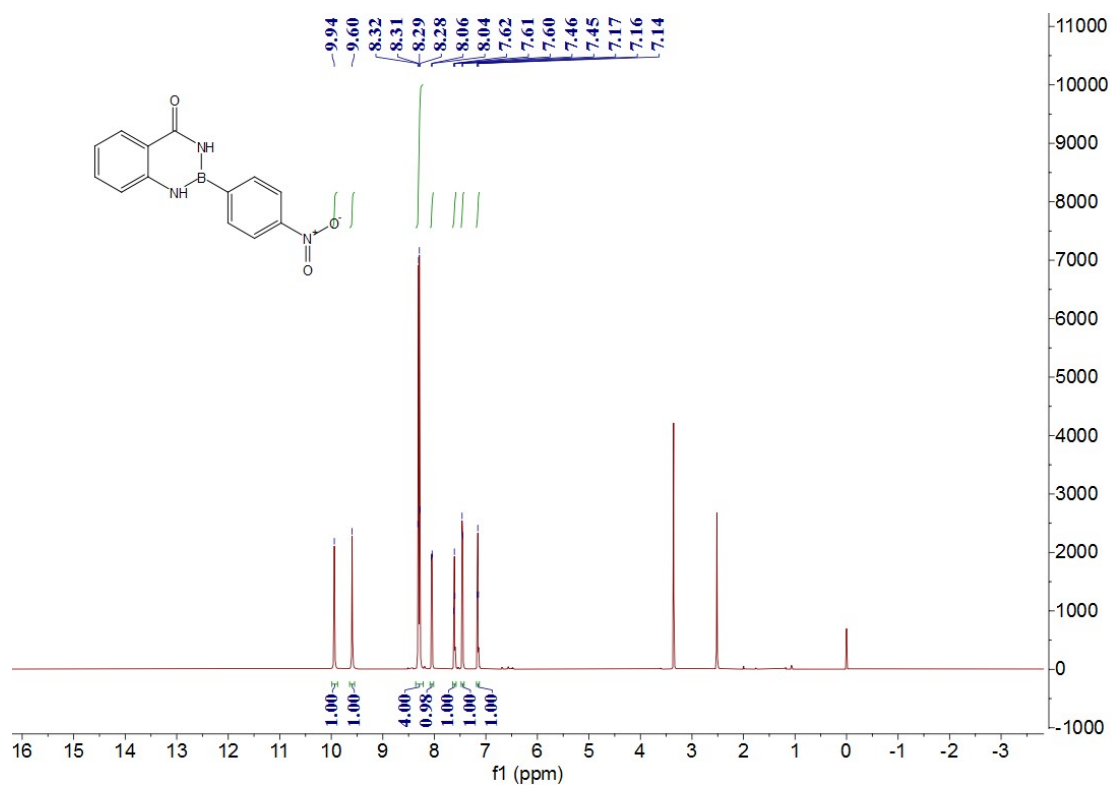


Figure 23. ¹H NMR spectrum of **3o** (solvent: DMSO-d₆)

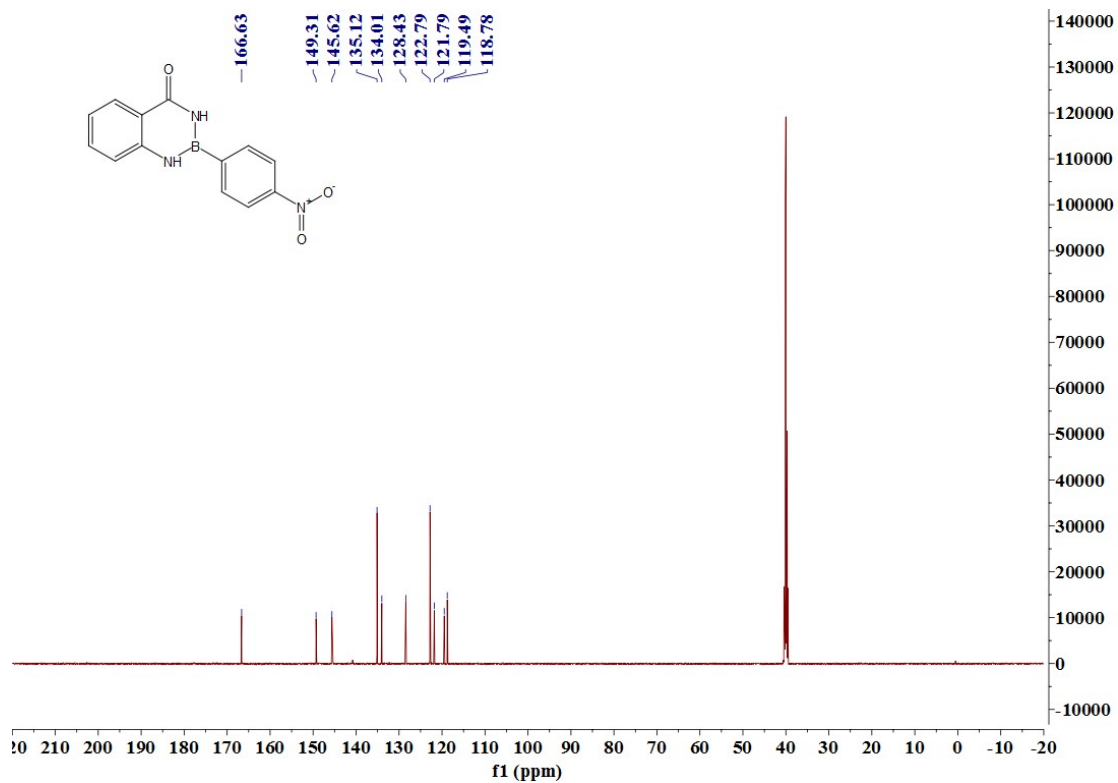


Figure 24. ¹³C NMR spectrum of **3o** (solvent: DMSO-d₆)

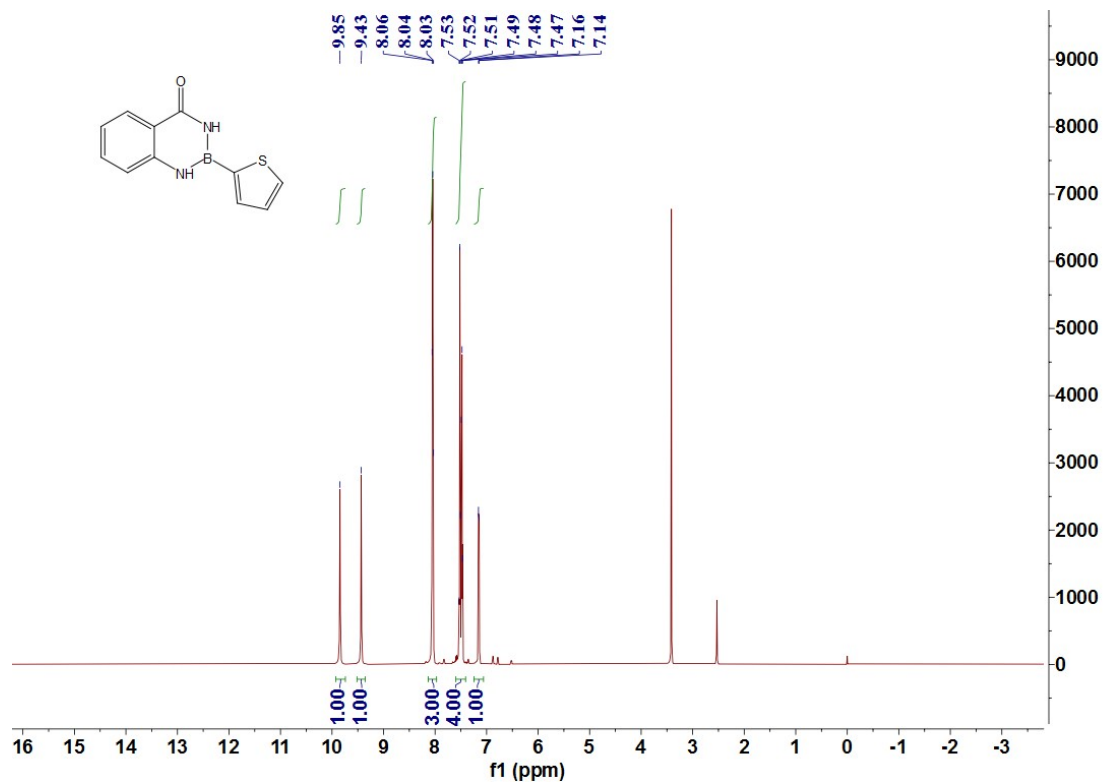


Figure 25. ¹H NMR spectrum of **3p** (solvent: DMSO-d₆)

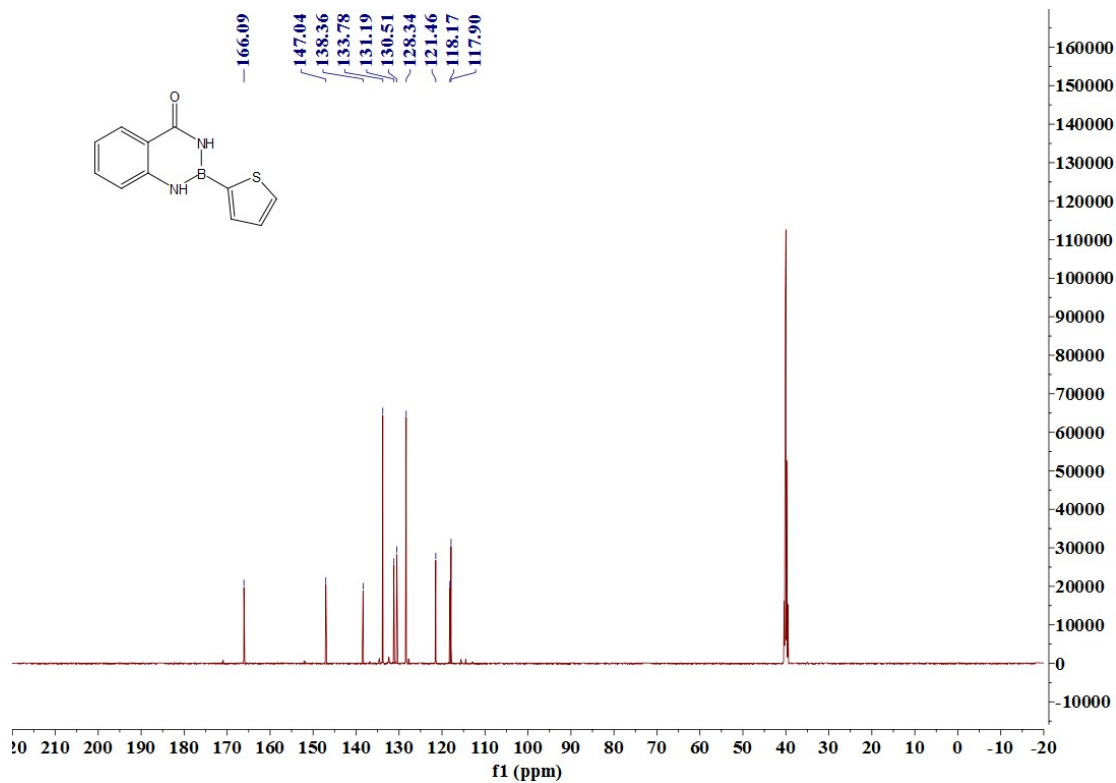


Figure 26. ^{13}C NMR spectrum of **3p** (solvent: DMSO- d_6)

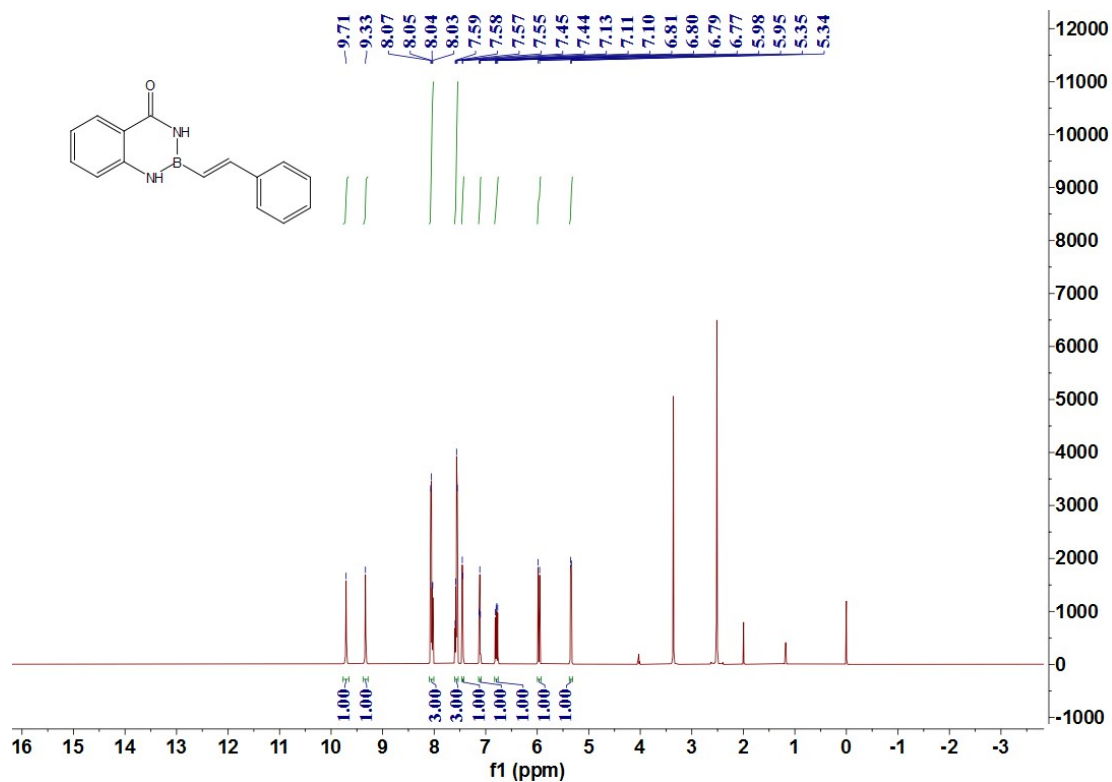


Figure 27. ^1H NMR spectrum of **3q** (solvent: DMSO- d_6)

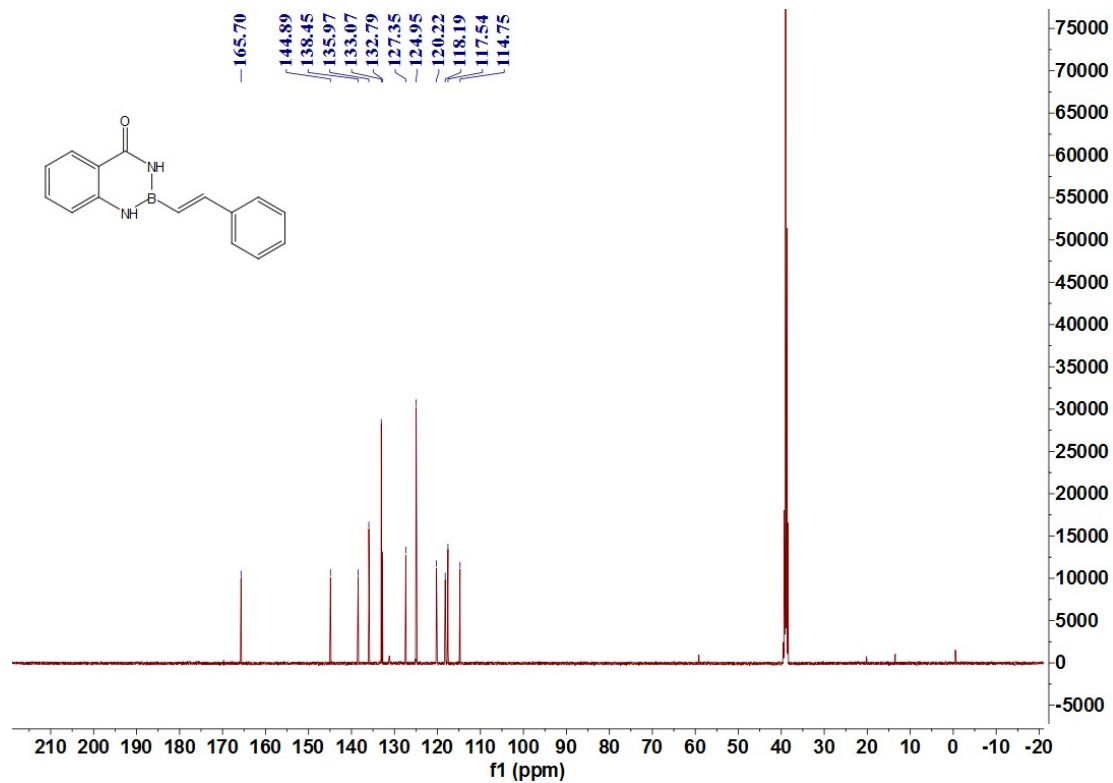


Figure 28. ¹³C NMR spectrum of **3q** (solvent: DMSO-d₆)

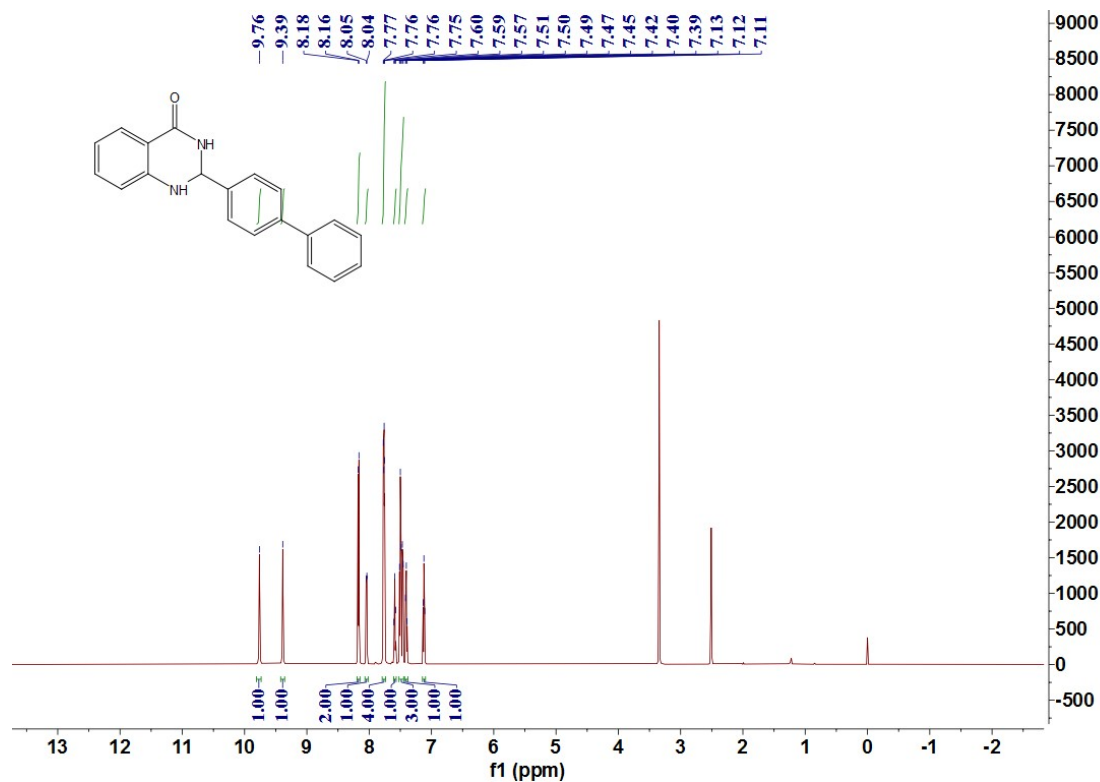


Figure 29. ¹H NMR spectrum of **3r** (solvent: DMSO-d₆)

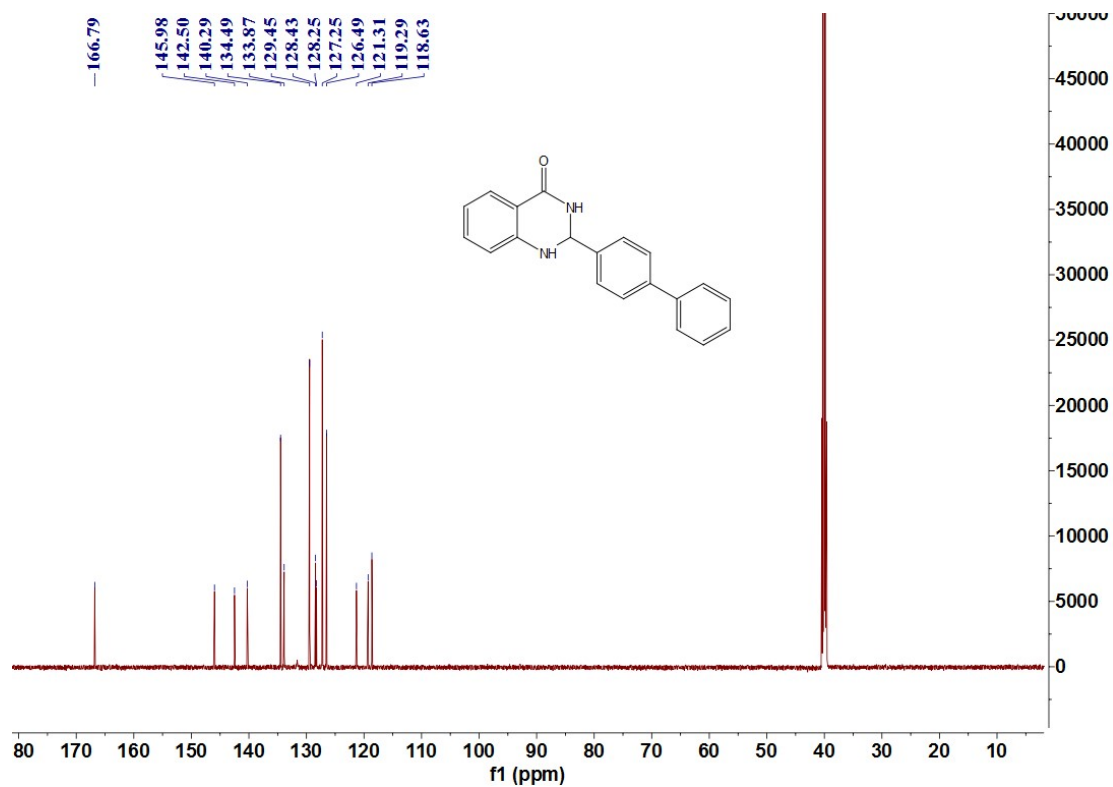


Figure 30. ¹³C NMR spectrum of 3r(solvent: DMSO-d6)

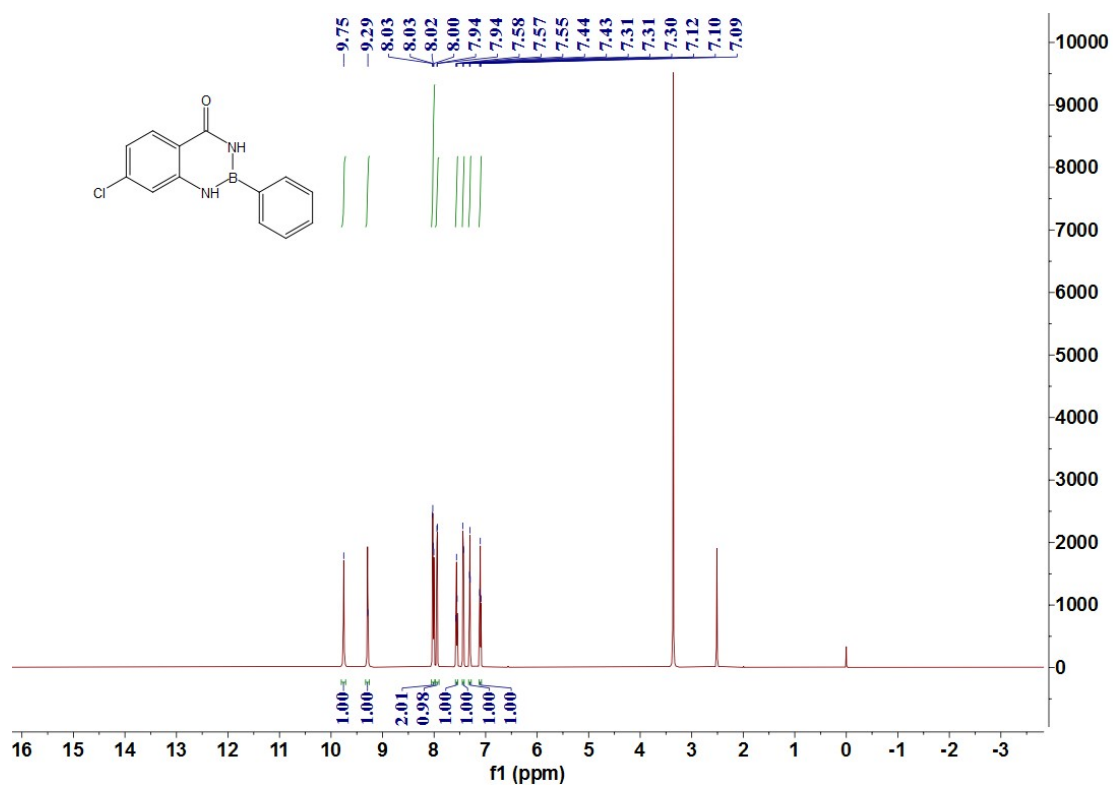


Figure 31. ¹H NMR spectrum of 3s (solvent: DMSO-d6)

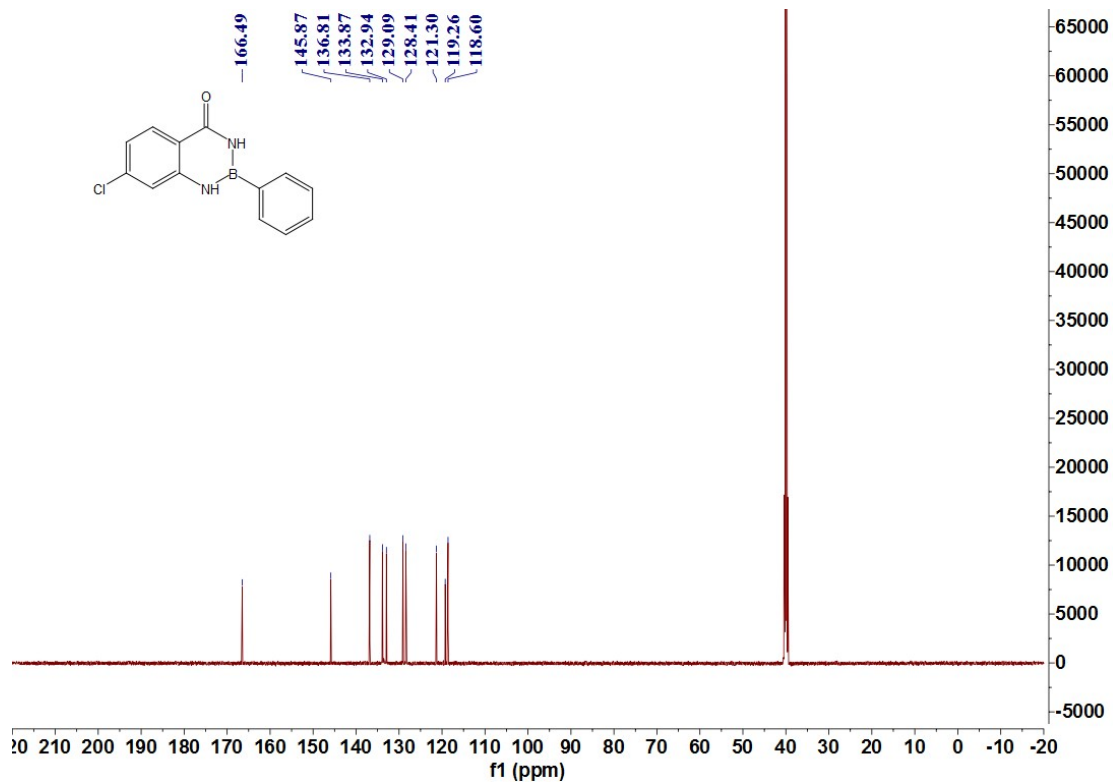


Figure 32. ¹³C NMR spectrum of 3s (solvent: DMSO-d6)

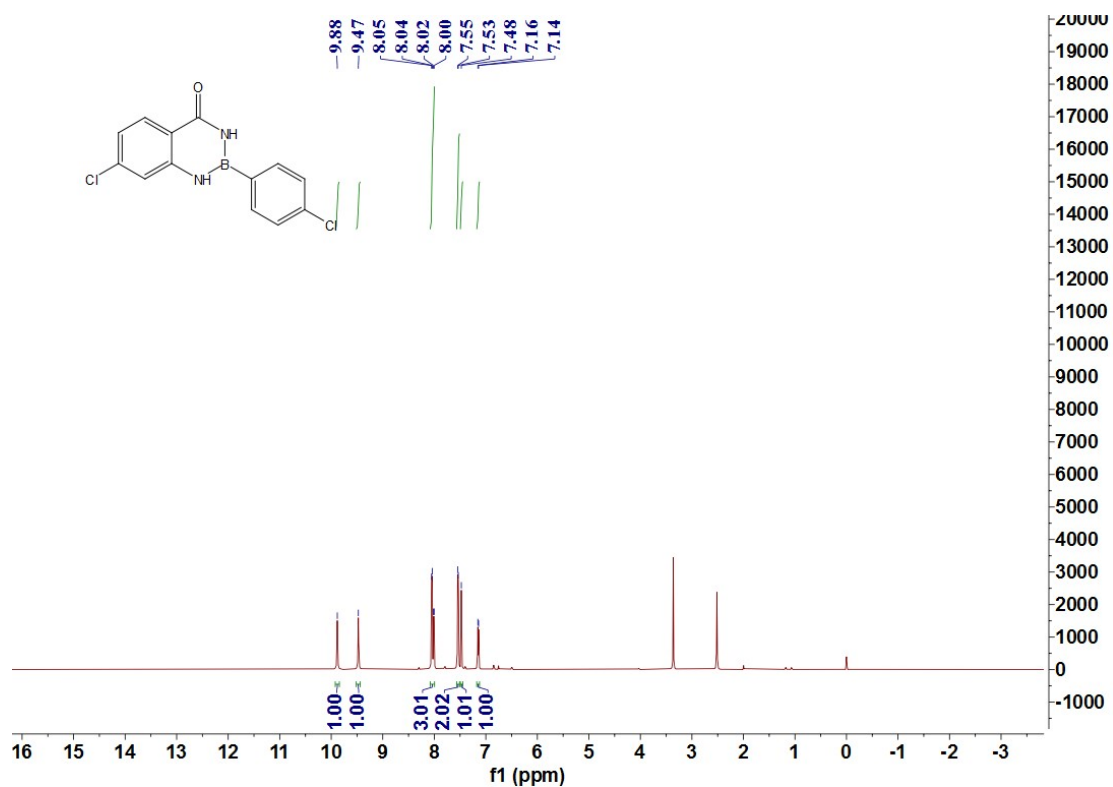


Figure 33. ¹H NMR spectrum of 3t (solvent: DMSO-d6)

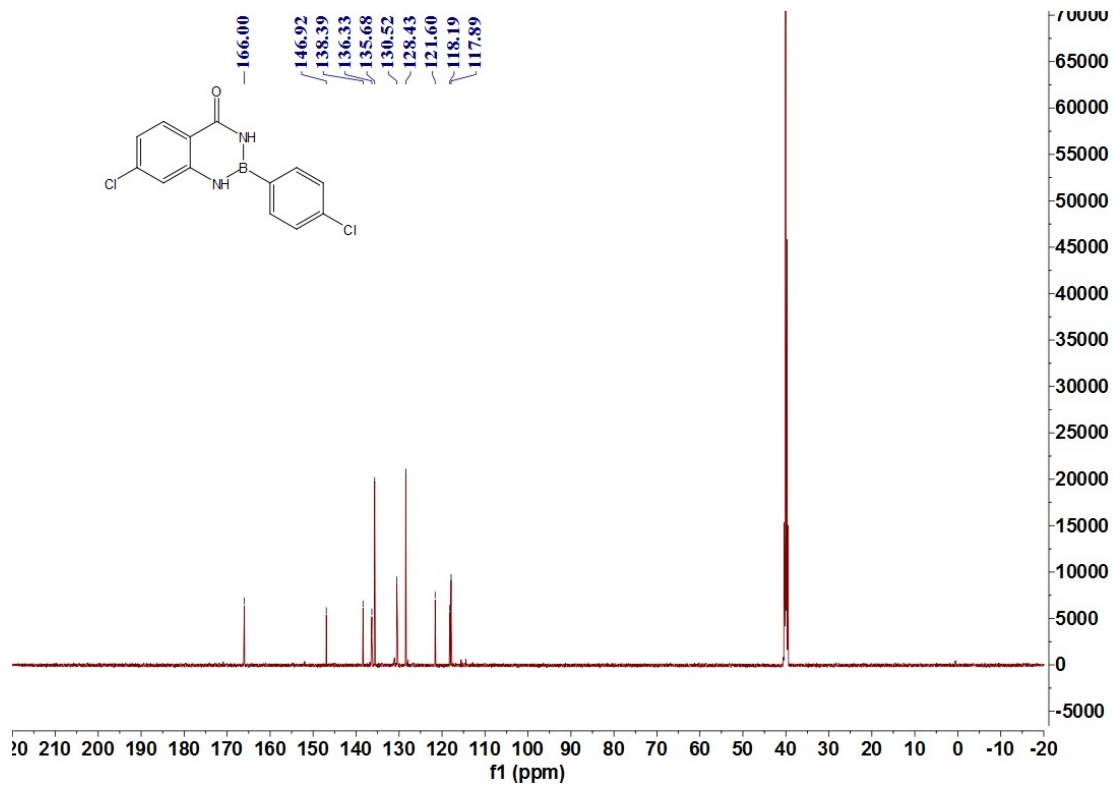


Figure 34. ¹³C NMR spectrum of **3t** (solvent: DMSO-d₆)

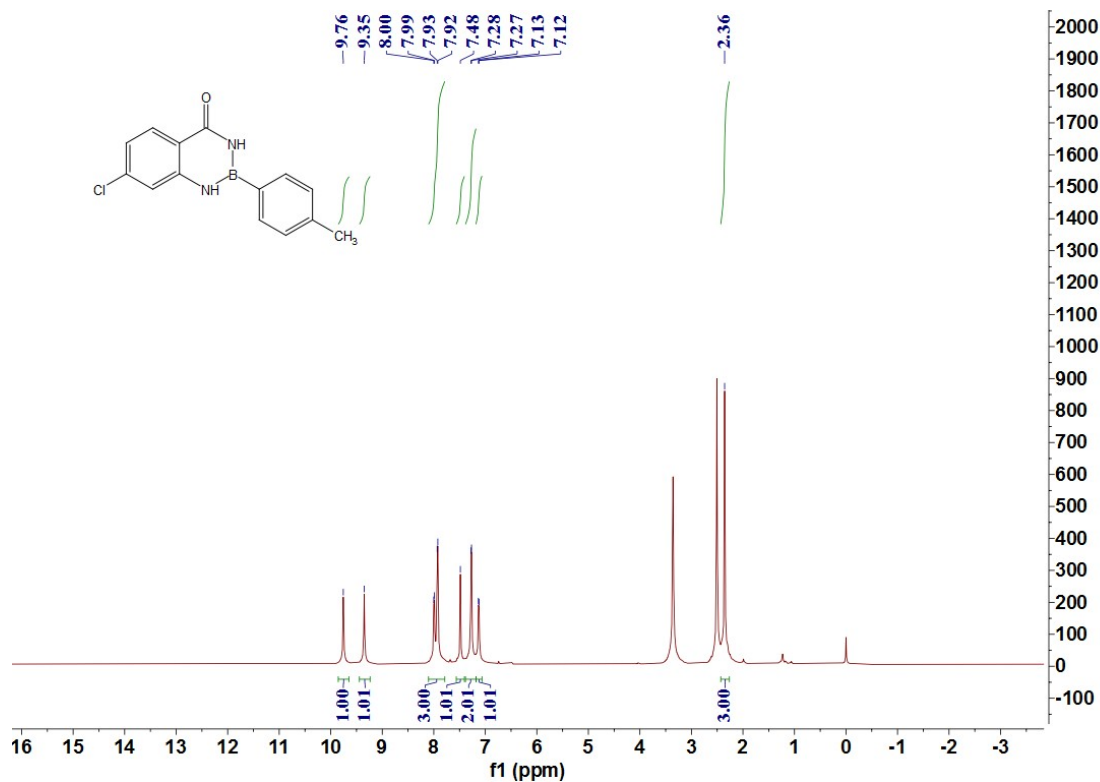


Figure 35. ¹H NMR spectrum of **3u** (solvent: DMSO-d₆)

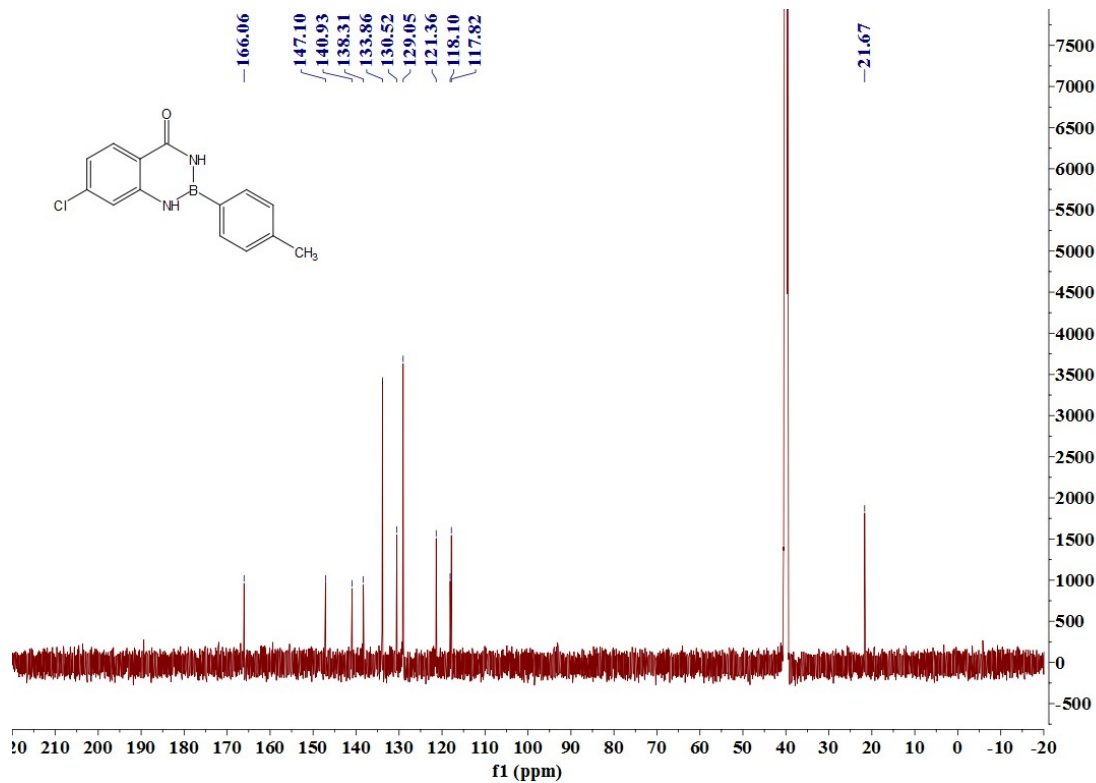


Figure 36. ¹³C NMR spectrum of **3u** (solvent: DMSO-d₆)

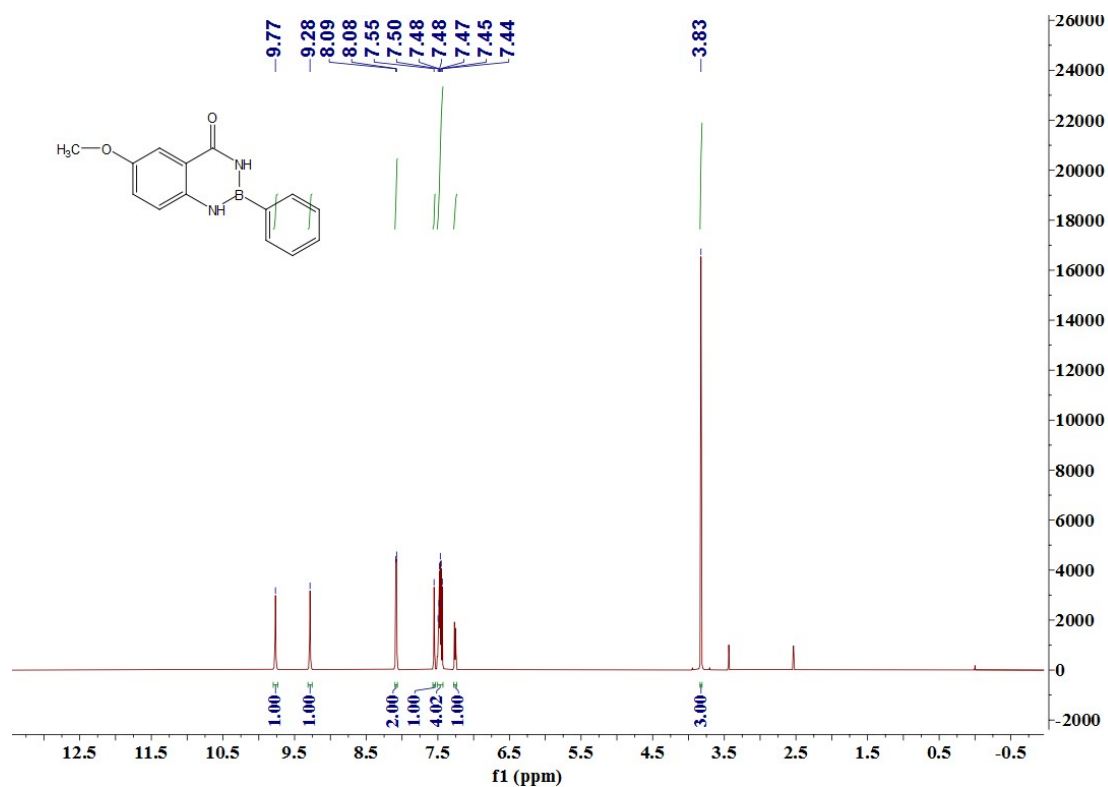


Figure 37. ¹H NMR spectrum of **3v** (solvent: DMSO-d₆)

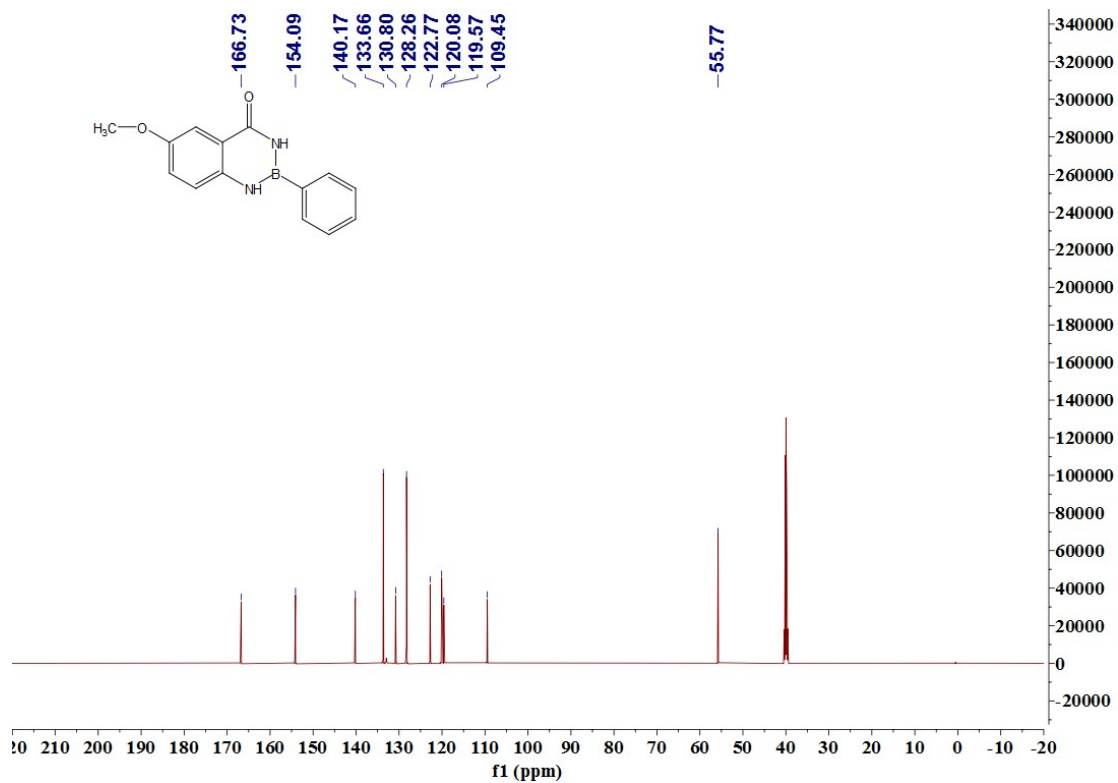


Figure 38. ¹³C NMR spectrum of **3v** (solvent: DMSO-d₆)

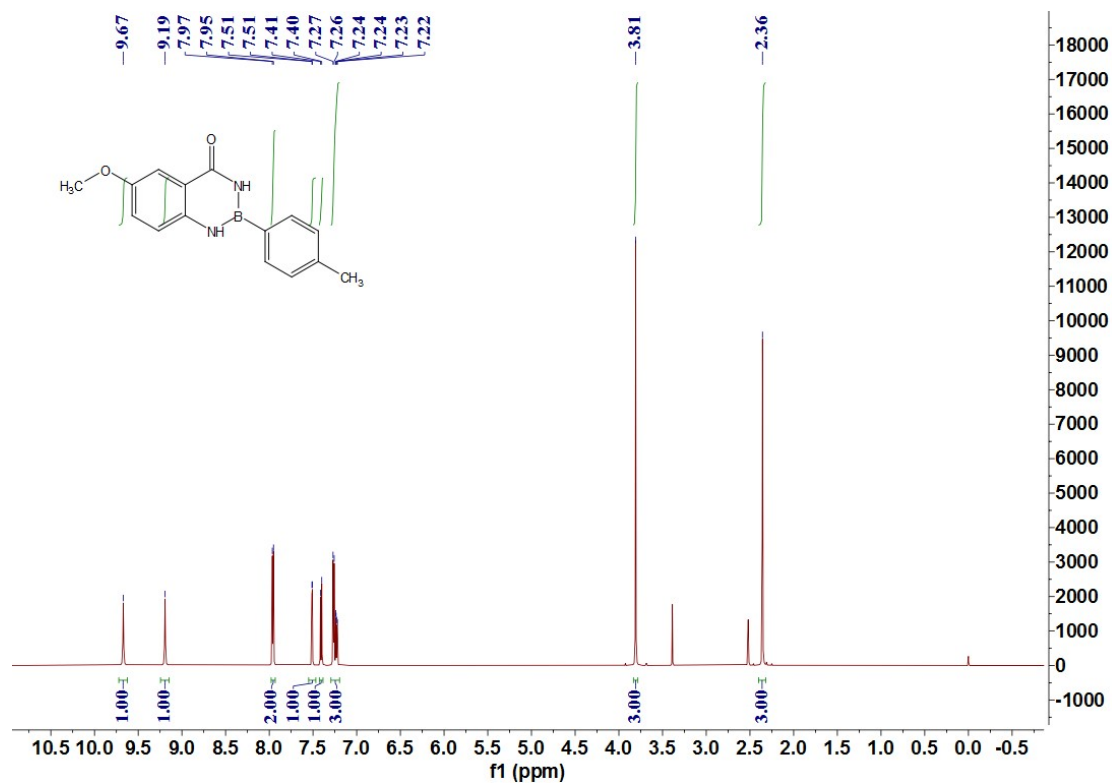


Figure 39. ¹H NMR spectrum of **3w** (solvent: DMSO-d₆)

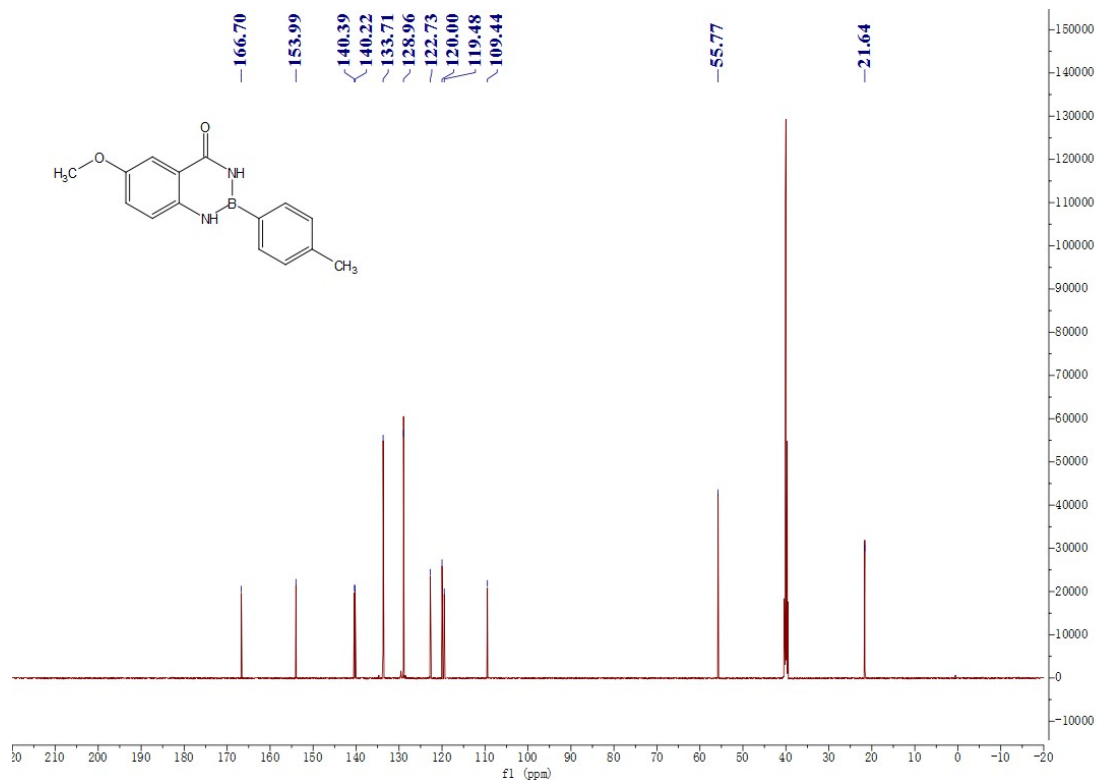


Figure 40. ¹³C NMR spectrum of **3w** (solvent: DMSO-d₆)

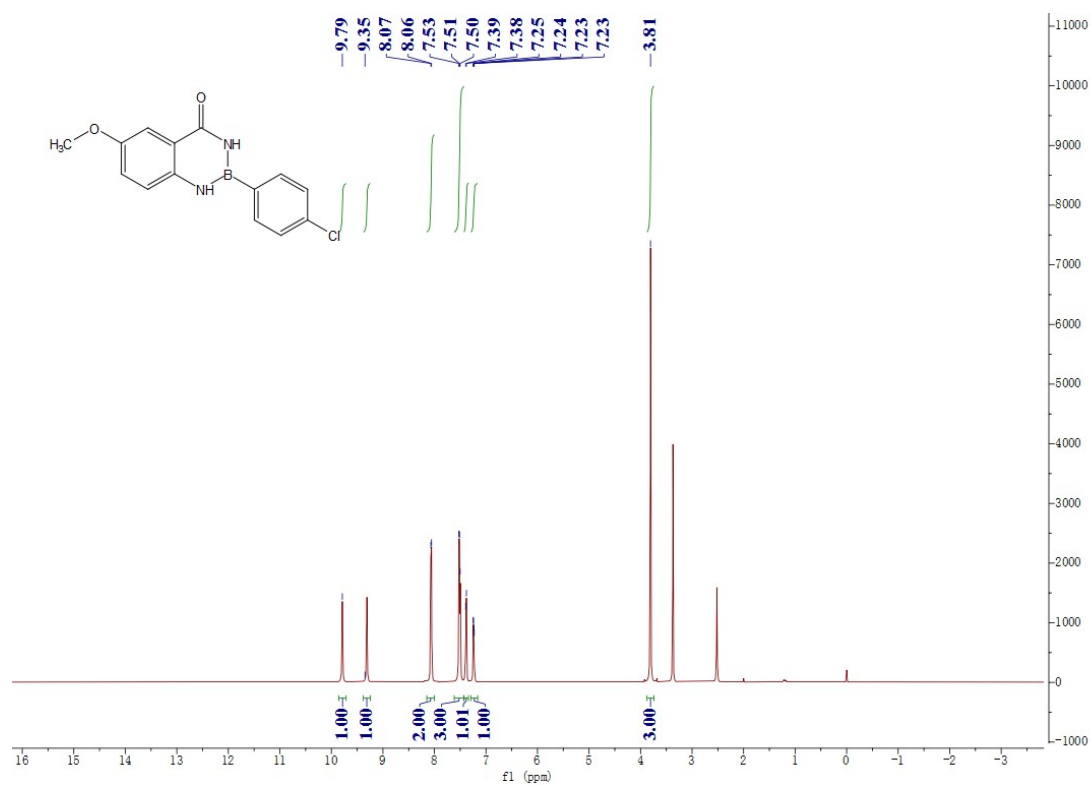


Figure 41. ¹H NMR spectrum of **3x** (solvent: DMSO-d₆)

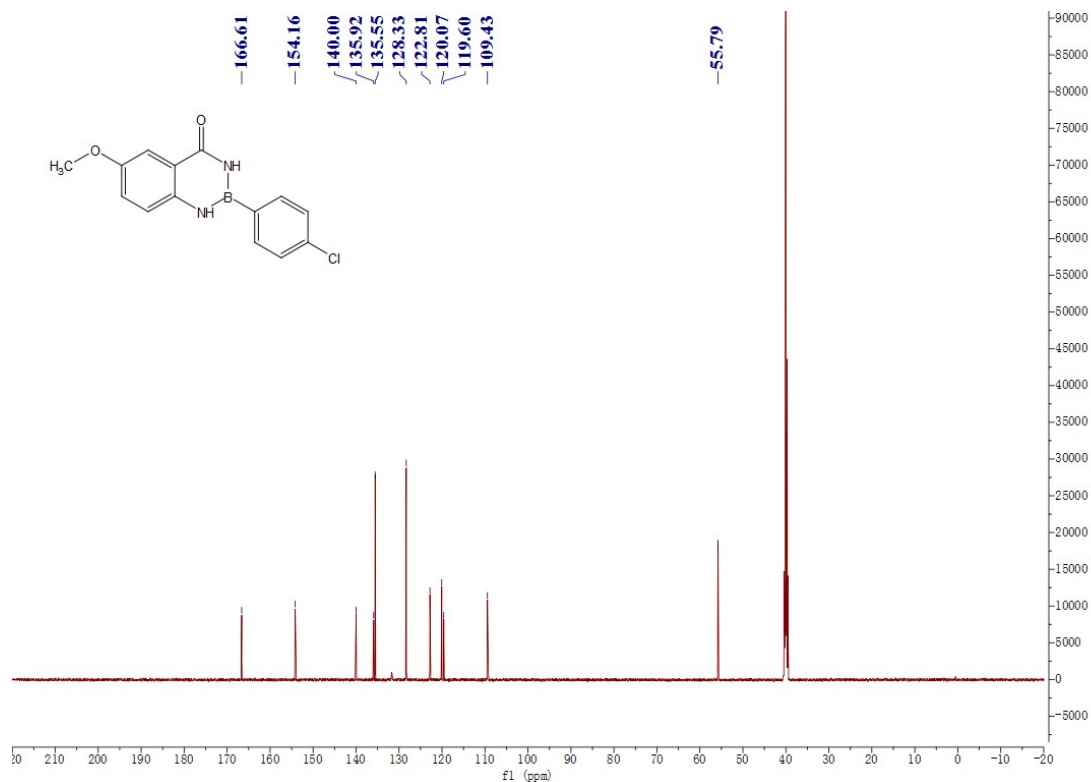


Figure 42. ^{13}C NMR spectrum of **3x** (solvent: DMSO- d_6)

5 Copies of ^{11}B -NMR NMR for the product

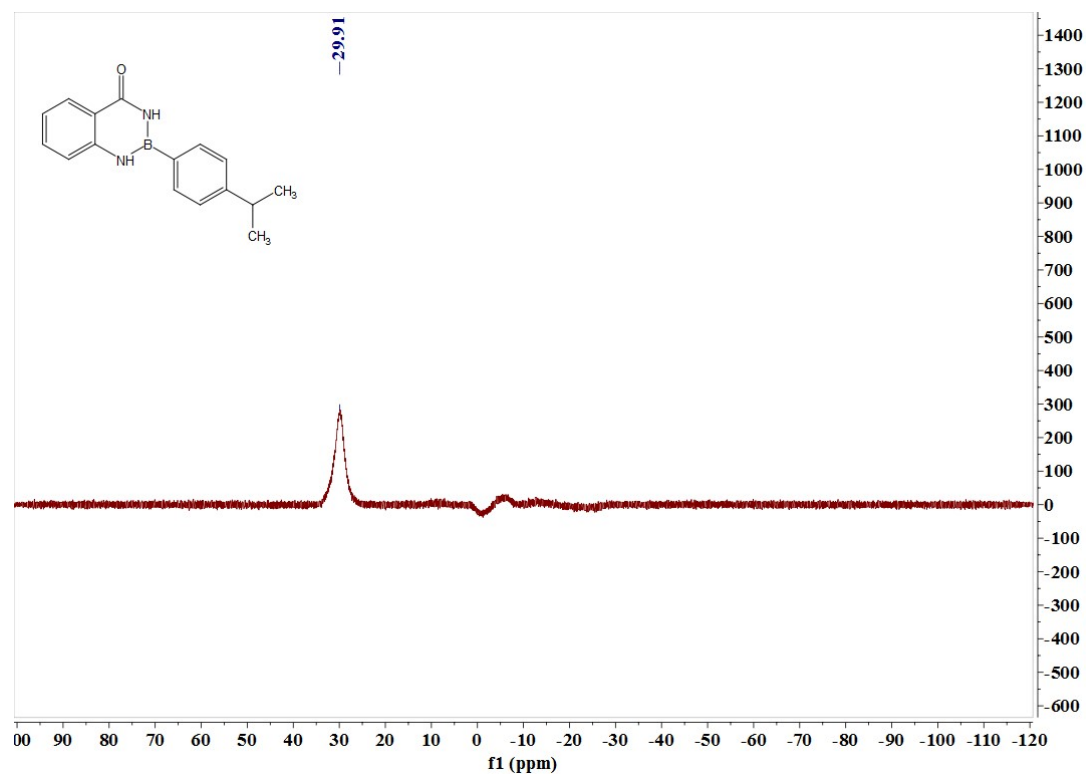


Figure 1 ^{11}B NMR spectrum of **3d** (solvent: DMSO- d_6)

6 High-resolution mss spectra of products

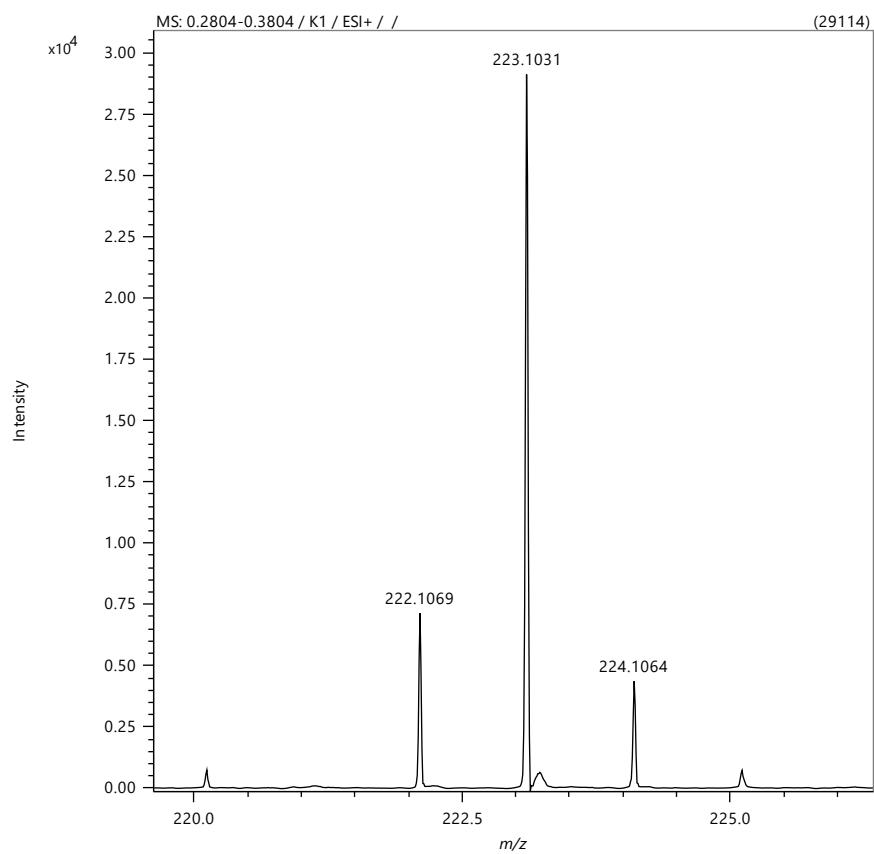


Figure 1 2-phenyl-2,3-dihydrobenzo[d][1,3,2]diazaborinin-4(1H)-one(**3a**)