Supporting information

Iodine-Catalysed N-Centered [1,2]-Rearrangement of 3-Aminoindazoles with Anilines: Efficient Access to 1,2,3-Benzotriazins

Jie Ren,[†] Xinxin Yan,[†] Xiaofan Cui,[‡] Chao Pi,*[†] Yangjie Wu[†] and Xiuling Cui*[†]

[†]College of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P. R. China

[‡] Department of Biological and Chemical Engineering, Nanyang Institute of Technology, Nanyang 473004, P. R. China

E-mail: pichao@zzu.edu.cn.

E-mail: cuixl@zzu.edu.cn.

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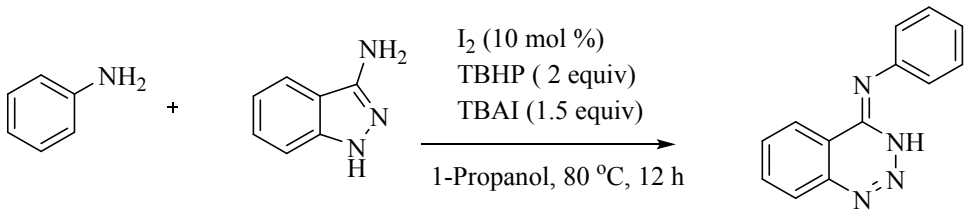
1. General Methods

Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without additional purification. Melting points were measured on a microscopic apparatus and were uncorrected. Silica gel was purchased from Qingdao Marine Chemical Co. Visualization on TLC was achieved by the use of UV light (254 nm). Column chromatography was undertaken on silica gel (200-300 mesh) using a proper eluent system. ^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) spectrometer in deuterated chloroform, deuterated acetone and deuterated dimethyl sulfoxide. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quarter), m (multiplet), dd (doublet and doublet), dt (doublet and triplet), td (triplet and doublet). Coupling constants (*J*) are reported in hertz (Hz).^{13}C NMR spectra were recorded at 100 MHz on Bruker DPX-400. ^{19}FNMR spectra were recorded using a 376 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on an Agilent LC- MSD- Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI).X-ray analysis was performed with a single-crystal X-ray diffractometer. 3-Aminoindazoles **2**[1] were prepared according to literatures.

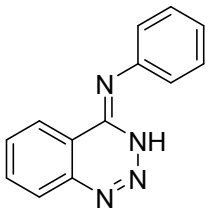
2. Typical Catalytic Procedure



1a **2a** **3aa**

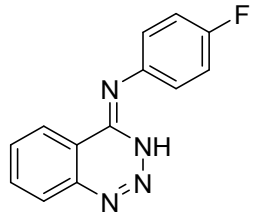
Underair atmosphere, a reaction tube (15 mL) equipped with a magnetic stirrer bar was charged with aniline (0.12 mmol), 3-aminoindazole (0.1 mmol), I_2 (10 mol %), TBHP (2 equiv) and TBAI (1.5 equiv) in anhydrous1-propanol (2 mL). The reaction mixture was stirred at 80 °C for 12 h. When the reaction was completed, the mixture was cooled to room temperature and then purified by column chromatography on silica gel (elute: EtOAc /petroleum ether) to give the desired product **3aa.**

3. Characterization of the Products

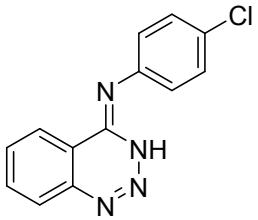


N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3aa), yellow solid, isolated yield 86% (19.1 mg); mp: 188.2-188.7 °C; ^{1}H NMR (400 MHz, Acetone-D6): δ 9.16 (s, 1H), 8.51 (d, *J* = 7.9Hz, 1H), 8.23 (dd, *J* = 8.2 Hz, *J* = 0.6 Hz1H), 8.11 (td, *J* = 7.8 Hz, *J* = 1.2 Hz 1H), 8.03 (dd, *J* = 8.8 Hz, *J* = 1.1 Hz 2H), 7.99 (td, *J* = 7.7 Hz, *J* = 1.2 Hz 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, Acetone-D6): δ 151.1, 143.9, 138.9, 134.1, 131.9,

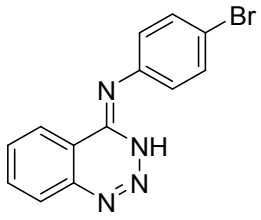
128.6, 127.9, 124.2, 122.2, 120.8, 109.2 ppm; HRMS (ESI): m/z calcd for $C_{13}H_{10}N_4$ $[M+H]^+$, 223.0978. Found: m/z 223.0980.



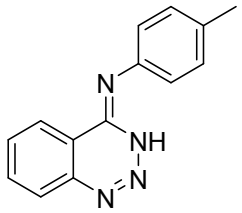
N-(4-fluorophenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ba), yellow solid, isolated yield 71% (17.1 mg); mp: 195.9-196.2 °C;^{1}H NMR (400 MHz, DMSO): δ 9.99 (s, 1H), 8.59 (d, *J* = 7.9 Hz, 1H), 8.21(dd, *J* = 8.3 Hz, *J* = 0.8 Hz 1H), 8.12(td, *J* = 7.7Hz,*J* = 1.2Hz 1H), 8.03 (td, *J* = 7.6 Hz, *J* = 1.3 Hz 1H), 7.90 (q, *J* = 4.1 Hz, 2H), 7.31 (t, *J* = 8.9Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 160.5, 158.1, 151.5, 143.8, 135.0, 132.6, 127.8, 125.4 (d, *J*= 8.0 Hz), 122.2, 115.8 (d, *J*= 22.3 Hz), 109.3 ppm; ^{19}F NMR (376 MHz, DMSO): -117.92 (s) ppm; HRMS (ESI): m/z calcd for $C_{13}H_9FN_4[M+H]^+$, 241.0884. Found: m/z 241.0886.



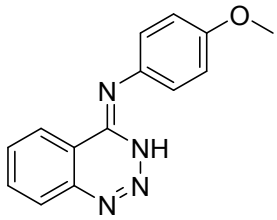
N-(4-chlorophenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ca), yellow solid, isolated yield 67% (17.2 mg); mp: 202.1-203.3 °C; ^{1}H NMR (400 MHz, DMSO): δ10.02 (s, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.13 (t, *J* = 7.8 Hz, 1H), 8.04 (t, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 151.4, 143.9, 138.0, 135.1, 132.7, 129.0, 128.4, 127.8, 124.7, 122.2, 109.4 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9ClN_4[M+H]^+$, 257.0589. Found: m/z 257.0590.



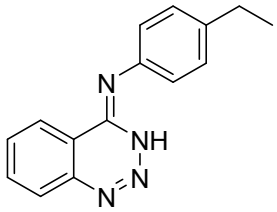
N-(4-bromophenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3da), yellow solid, isolated yield 62% (18.6mg); mp: 203.2-203.8°C;^{1}H NMR (400 MHz, DMSO): δ 10.01 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.13 (td, *J* = 7.5 Hz, *J* = 1.1 Hz 1H), 8.04 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 151.4, 143.9, 138.4, 135.1, 132.8, 131.9, 127.8, 125.0, 122.2, 116.5, 109.4 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9BrN_4[M+H]^+$, 301.0083. Found: m/z 301.0084.



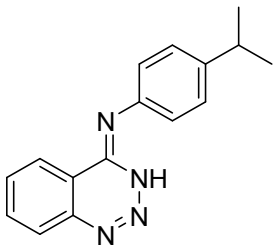
N-(4-methylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ea), yellow solid, isolated yield 90% (21.3mg); mp: 192.9-194.7°C;^{1}H NMR (400 MHz, Acetone-D6): δ 9.11 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.09 (td, *J* = 7.7 Hz, *J* = 1.2 Hz 1H), 7.97 (td, *J* = 7.8 Hz, *J* = 1.2 Hz 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, Acetone-D_6): δ 151.0, 143.9, 136.3, 134.0, 133.7, 131.8, 129.1, 127.8, 122.3, 120.8, 109.2, 20.03 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4[M+H]^+$, 237.1135. Found: m/z 237.1134.



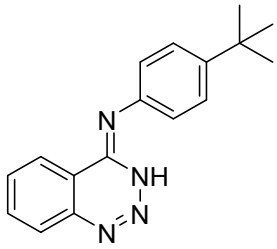
N-(4-methoxyphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3fa), yellow solid, isolated yield 87% (21.9 mg); mp: 184.1-185.3 °C; ^{1}H NMR (400 MHz, Acetone-D6): δ9.08 (s, 1H), 8.47 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.08 (td, *J* = 7.7 Hz, *J* = 1.2 Hz 1H), 7.95 (td, *J* = 7.7 Hz, *J* = 1.3 Hz 1H), 7.86 (d, *J* = 9.1 Hz, 2H), 7.01 (d, *J* = 9.1 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, Acetone-D_6): δ 156.8, 151.1, 143.8, 133.9, 131.7, 131.6, 127.8, 124.2, 120.8, 113.8, 109.2, 54.84 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4O$ $[M+H]^+$, 253.1084. Found: m/z 253.1083.



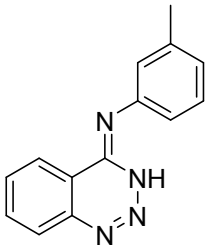
N-(4-ethylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ga), yellow solid, isolated yield 82% (19.4 mg); mp: 179.0-180.8 °C;^{1}H NMR (400 MHz, DMSO): δ 9.91 (s, 1H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.2 Hz, *J* = 0.7 Hz, 1H), 8.10 (td, *J* = 8.2Hz,*J* = 1.1Hz 1H), 8.01 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.13 (q, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 143.8, 140.5, 136.4, 134.9, 132.5, 128.3, 127.7, 123.5, 122.2, 109.4, 28.2, 16.2 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_4[M+H]^+$, 251.1291. Found: m/z 251.1292.



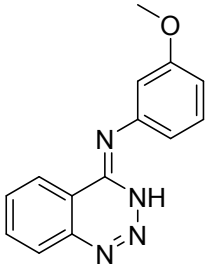
N-(4-isopropylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ha), yellow solid, isolated yield 80% (21.1 mg); mp: 183.2-184.6 °C; ^{1}H NMR (400 MHz, DMSO): δ9.91 (s, 1H), 8.61(d, *J* = 8.0 Hz, 1H), 8.19 (dd, *J* = 8.2 Hz, *J* = 0.7 Hz, 1H), 8.10 (td, *J* = 8.2 Hz, *J* = 1.1 Hz 1H), 8.01(td, *J* = 7.7 Hz, *J* = 1.2 Hz 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 2.99-2.87 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 145.1, 143.8, 136.5, 134.9, 132.5, 127.7, 126.9, 123.5, 122.2, 109.4, 33.5, 24.4 ppm; HRMS (ESI): m/z calcd for $C_{16}H_{16}N_4[M+H]^+$, 265.1448. Found: m/z 265.1449.



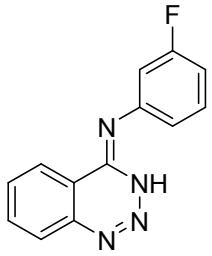
N-(4-(tert-butyl)phenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ia), yellow solid, isolated yield86% (23.9mg); mp: 196.3-197.5°C; ^{1}H NMR (400 MHz, DMSO): δ9.91(s, 1H), 8.61(d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.10 (t, *J* = 7.1 Hz, 1H), 8.01(t, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 147.3, 143.8, 136.2, 134.9, 132.5, 127.7, 125.8, 123.1, 122.2,109.4, 34.7, 31.7 ppm; HRMS (ESI): m/z calcd for $C_{17}H_{18}N_4[M+H]^+$, 279.1604. Found: m/z 279.1606.



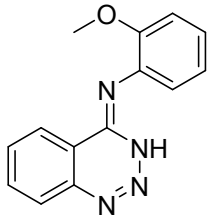
N-(3-methylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3la), yellow solid, isolated yield52% (12.3mg); mp: 188.2-189.4°C; ^{1}H NMR (400 MHz, DMSO): δ 9.88 (s, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.20 (dd, *J* = 8.4 Hz, *J* = 0.7 Hz, 1H), 8.11 (td, *J* = 8.4 Hz, *J* = 1.2 Hz 1H), 8.02 (td, *J* = 7.6Hz, *J* = 1.2 Hz 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 143.9, 138.8, 138.3, 134.9, 132.6, 129.0, 127.7, 125.6, 123.8, 122.2, 120.5, 109.4, 21.7 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4[M+H]^+$, 237.1135. Found: m/z 237.1135.



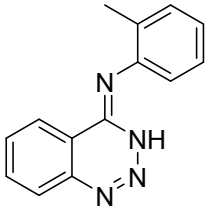
N-(3-methoxyphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ma), yellow solid, isolated yield 65% (16.4 mg); mp: 177.3-178.7 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.89 (s, 1H), 8.63 (d, *J* = 8.2 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.12 (t, *J* =7.9 Hz, 1H), 8.03 (t, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 2.1 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 8.2 Hz, 1H), 6.80 (dd, *J* = 8.2 Hz, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 159.9, 151.5, 143.9, 140.1, 135.0, 132.6, 129.9, 127.8, 122.2, 115.4, 110.2, 109.4, 109.0, 55.6 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4O$ $[M+H]^+$, 253.1084. Found: m/z 253.1083.



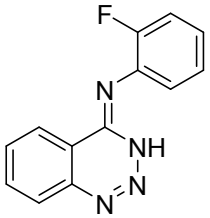
N-(3-fluorophenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3na), yellow solid, isolated yield 75% (18.0 mg); mp: 206.5-207.7 °C; ^{1}H NMR (400 MHz, DMSO): δ 10.05 (s, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.25 (dd, *J* = 8.3Hz,*J* = 0.8Hz, 1H), 8.14 (td, *J* = 8.3 Hz, *J* = 1.2 Hz 1H), 8.06 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.99 (dt, *J* = 11.7 Hz, *J* = 2.2 Hz 1H), 7.76 (dd, *J* = 8.2 Hz, *J* = 1.2Hz, 1H), 7.49 (q, *J* = 8.2 Hz, 1H), 7.03 (td, *J* = 8.6 Hz, *J* = 2.7 Hz 1H); ^{13}C NMR (100 MHz, DMSO): δ 163.7, 161.3, 151.5, 143.9, 140.8 (d, *J*= 11 Hz), 135.2, 132.8, 130.7 (d, *J*= 9.5 Hz), 127.9, 122.2, 118.5 (d, *J*= 2.5 Hz), 111.1 (d, *J*= 20.9 Hz), 109.6 (d, *J*= 18.3 Hz) ppm; ^{19}F NMR (376 MHz, DMSO):-112.36 (s) ppm; HRMS (ESI): m/z calcd for $C_{13}H_9FN_4[M+H]^+$, 241.0884. Found: m/z 241.0883.



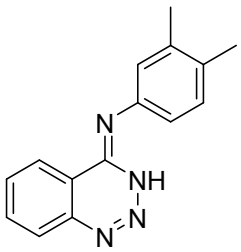
N-(2-methoxyphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3oa), yellow solid, isolated yield 80% (20.2 mg); mp: 162.4-163.7 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.68 (s, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.17 (dd, *J* = 8.4 Hz, *J* = 0.8 Hz, 1H), 8.09 (td, *J* = 8.3 Hz, *J* = 1.2 Hz 1H), 7.98 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.58 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.34 (td, *J* = 7.4 Hz, *J* = 1.7 Hz 1H), 7.19 (dd, *J* = 8.5 Hz, *J* = 1.1 Hz, 1H), 7.07 (td, *J* = 7.5 Hz, *J* = 1.2 Hz 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 154.4, 152.2, 143.8, 134.8, 132.4, 128.2, 128.0, 127.6, 126.7, 122.2, 120.8, 112.5, 109.2, 56.1 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4O[M+H]^+$, 253.1084. Found: m/z 253.1085.



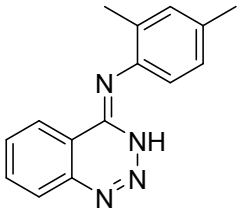
N-(2-methylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3pa), yellow solid, isolated yield 71% (16.8 mg); mp: 153.3-153.8 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.91 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.18 (dd, *J* = 8.0 Hz, *J* = 0.6 Hz, 1H), 8.10 (td, *J* =8.5 Hz, *J* = 1.1 Hz 1H), 8.00 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.38 (dd, *J* = 6.5 Hz, *J* = 2.2 Hz, 2H), 7.35-7.26 (m, 2H); ^{13}C NMR (100 MHz, DMSO): δ 152.2, 143.8, 136.8, 135.5, 134.9, 132.4, 131.1, 128.1, 127.6, 127.4, 126.9, 122.2, 109.1, 18.4 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4[M+H]^+$, 237.1135. Found: m/z 237.1136.



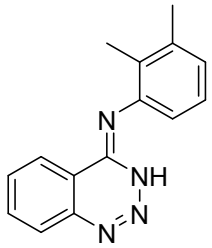
N-(2-fluorophenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3qa), yellow solid, isolated yield 45% (10.8 mg); mp: 174.9-175.5 °C; ^{1}H NMR (400 MHz, DMSO): δ 10.08 (s, 1H), 8.53 (d, *J* = 7.8 Hz, 1H), 8.22 (dd, *J* = 7.8 Hz, *J* = 0.7 Hz, 1H), 8.13 (td, *J* =8.4 Hz, *J* = 1.2 Hz 1H), 8.03 (td, *J* = 7.6 Hz, *J* = 1.3 Hz 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.43-7.36 (m, 2H), 7.36-7.29 (m, 1H); ^{13}C NMR (100 MHz, DMSO): δ152.1, 143.9, 135.2, 132.8, 129.0, 128.6, 128.5, 127.7, 125.9, 125.1, 122.3, 116.6 (d, *J*= 19.7 Hz), 109.1 ppm; ^{19}F NMR (376 MHz, DMSO): -118.81 (s) ppm; HRMS (ESI): m/z calcd for $C_{13}H_9FN_4[M+H]^+$,241.0884. Found: m/z241.0885.



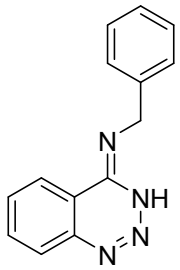
N-(3,4-dimethylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3ra), yellow solid, isolated yield 94% (23.5 mg); mp: 194.6-195.3°C; ^{1}H NMR (400 MHz, DMSO): δ 9.84 (s, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.09 (td, *J* = 8.1 Hz, *J* = 1.0 Hz 1H), 8.00 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.67-7.59 (m, 2H), 7.21 (d, *J* = 8.1 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 143.8, 136.8, 136.4, 134.8, 132.9, 132.4, 130.0, 127.7, 124.5, 122.2, 120.9, 109.4, 20.1, 19.4 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_4[M+H]^+$, 251.1291. Found: m/z251.1292.



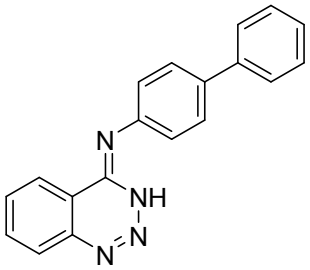
N-(2,4-dimethylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine (3sa), yellow solid, isolated yield 70% (17.5 mg); mp: 185.7-186.6 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.84 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.17 (dd, *J* = 8.4 Hz, *J* = 0.7 Hz, 1H), 8.09 (td, *J* = 8.4 Hz, *J* = 1.2 Hz 1H), 7.98 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.19 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 152.3, 143.8, 136.6, 135.2, 134.8, 134.2, 132.3, 131.6, 128.0, 127.6, 127.4, 122.2, 109.1, 21.1, 18.3 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_4[M+H]^+$, 251.1291. Found: m/z 251.1293.



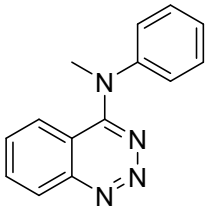
N-(2,3-dimethylphenyl)-1,2,3-benzotriazin-4(*3H*)-imine(3ta), yellow solid, isolated yield 76% (19.0 mg); mp: 190.4-191.7 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.93 (s, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 8.09 (td, *J* = 8.2 Hz, *J* = 1.0 Hz 1H), 7.99 (td, *J* = 8.0 Hz,*J* = 1.2 Hz 1H), 7.20 (s, 3H), 2.34 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 152.4, 143.8, 137.9, 136.7, 134.8, 134.2, 132.4, 128.8, 127.6, 126.2, 125.8, 122.2, 109.1, 20.6, 14.8 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_4[M+H]^+$, 251.1291. Found: m/z 251.1292.



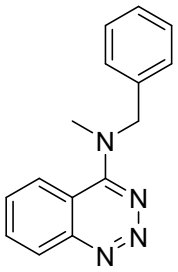
N-benzyl-1,2,3-benzotriazin-4(*3H*)-imine (3ua), yellow solid, isolated yield65% (15.4 mg); mp: 197.5-198.4 °C; ^{1}H NMR (400 MHz, DMSO): δ9.03 (t, *J* = 5.8 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 5.4 Hz, 1H), 8.03 (td, *J* = 8.2 Hz, *J* = 1.2 Hz 1H), 7.92 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 4.90 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ 152.4, 143.3, 139.3, 134.6, 132.0, 128.8, 127.8, 127.5, 127.4, 121.9, 109.2, 44.2 ppm; HRMS (ESI): m/z calcd for $C_{14}H_2N_4[M+H]^+$, 237.1135.Found: m/z 237.1136.



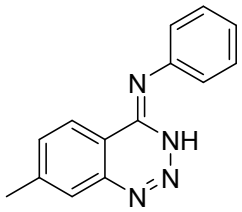
N-([1,1'-biphenyl]-4-yl)-1,2,3-benzotriazin-4(*3H*)-imine (3va), yellow solid, isolated yield 51% (15.2 mg); mp:212.8-213.7 °C; ^{1}H NMR (400 MHz, DMSO): δ 10.03 (s, 1H), 8.66 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 8.13 (td, *J* = 8.0 Hz, *J* = 1.0 Hz 1H), 8.05 (d, *J* = 8.7 Hz, 3H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.5, 143.9, 140.1, 138.4, 136.4, 135.2, 132.7, 129.4, 127.8, 127.7, 127.3, 126.9, 123.4, 122.3, 109.5 ppm; HRMS (ESI): m/z calcd for $C_{19}H_{14}N_4[M+H]^+$, 299.1291. Found: m/z 299.1292.



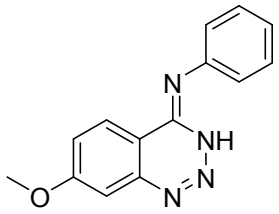
N-methyl-N-phenyl-1,2,3-benzotriazin-4-imine (3wa), yellow solid, isolated yield 63% (14.9 mg); mp:161.5-162.8 °C; ^{1}H NMR (400 MHz, DMSO): δ 8.17 (dd, *J* = 8.3 Hz, *J* = 0.7 Hz, 1H), 7.91 (td, *J* = 7.6 Hz, *J* = 1.2 Hz 1H), 7.49 (t, *J* = 7.1 Hz, 3H), 7.44-7.38 (m, 3H), 6.80 (d, *J* = 8.1 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 153.9, 147.2, 145.1, 134.2, 131.2, 130.9, 128.1, 128.0, 126.7, 124.4, 110.3, 42.6 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4[M+H]^+$, 237.1135. Found: m/z 237.1134.



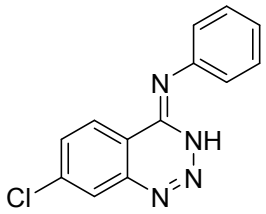
N-benzyl-N-methyl-1,2,3-benzotriazin-4-imine (3xa), yellow oily solid, isolated yield 72% (18.0 mg); ^{1}H NMR (400 MHz, DMSO): δ 8.15 (d, *J* = 8.4 Hz, 2H), 8.02 (td, *J* = 7.9 Hz, *J* = 1.0 Hz 1H), 7.79 (td, *J* = 7.8 Hz, *J* = 1.4 Hz 1H), 7.42-7.36 (m, 4H), 7.34-7.30 (m, 1H), 5.15 (s, 2H), 3.05 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 155.1, 145.4, 137.3, 134.3, 131.0, 129.2, 127.8, 127.6, 127.5, 124.8, 109.7, 55.8, 40.3 ppm; HRMS (ESI): m/z calcd for $C_{15}H_{14}N_4[M+H]^+$, 251.1291. Found: m/z 251.1292.



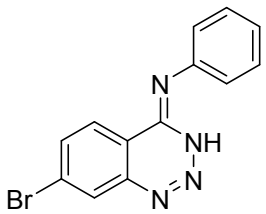
7-methyl-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ab), yellow solid, isolated yield 91% (21.5 mg); mp: 189.6-191.3 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.86 (s, 1H), 8.52 (d, *J* = 8.5 Hz, 1H), 8.00 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.86 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ151.4, 145.6, 144.2, 139.0, 134.3, 129.1, 126.6, 124.7, 123.1, 122.0, 107.3, 21.9 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4$[M+H]$^+$, 237.1135. Found: m/z 237.1136.



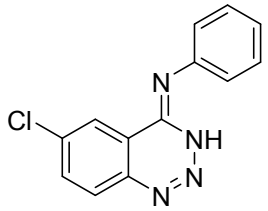
7-methoxy-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ac), yellow solid, isolated yield 84% (21.2 mg); mp: 211.5-213.2 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.82 (s, 1H), 8.54 (d, *J* = 9.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.62 (dd, *J* = 9.1 Hz, *J* = 2.6 Hz, 1H), 7.58 (d, *J* = 2.6 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 163.9, 151.1, 146.3, 139.0, 129.1, 124.6, 124.2, 123.9, 123.1, 106.4, 103.7, 56.6 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4O$ [M+H]$^+$, 253.1084. Found: m/z 253.1085.



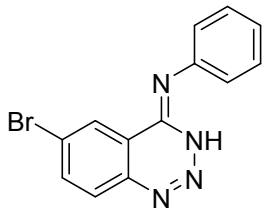
7-chloro-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ad), yellow solid, isolated yield 52% (13.3 mg); mp: 191.9-192.6 °C; ^{1}H NMR (400 MHz, DMSO): δ10.09 (s, 1H), 8.67 (d, *J* = 8.9 Hz, 1H), 8.29 (d, *J* = 2 Hz, 1H), 8.10 (dd, *J* = 9.0 Hz, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 8.1 Hz, 2H), 7.22 (2, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.2, 144.6, 139.3, 138.6, 132.9, 129.2, 126.6, 125.2, 125.0, 123.4, 108.2 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9ClN_4$[M+H]$^+$, 257.0589. Found: m/z 257.0592.



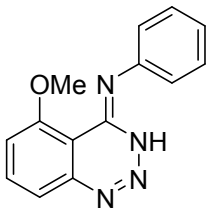
7-bromo-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ae), yellow solid, isolated yield 47% (14.1 mg); mp: 184.6-186.0 °C; ^{1}H NMR (400 MHz, DMSO): δ 10.09 (s, 1H), 8.59 (d, *J* = 8.9 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 8.21 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.88 (d, *J* =7.6 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 2H), 7.22(t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 151.3, 144.7, 138.6, 135.6, 129.8, 129.2, 128.2, 125.1, 124.9, 123.4, 108.4 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9BrN_4$[M+H]$^+$, 301.0083. Found: m/z 301.0084.



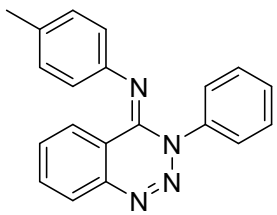
6-chloro-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3af), yellow solid, isolated yield 63% (16.1 mg); mp: 187.8-189.4°C; ^{1}H NMR (400 MHz, DMSO): δ 9.98 (s, 1H), 8.81 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 8.13 (dd, *J* = 8.8 Hz, *J* = 2.1 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 8.3 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 150.7 142.5, 138.6, 136.6, 135.4, 130.2, 129.2, 125.0, 123.1, 121.8, 110.5 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9ClN_4[M+H]^+$, 257.0589. Found: m/z 257.0590.



6-bromo-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ag), yellow solid, isolated yield 51% (15.3 mg); mp: 183.4-185.0 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.99 (s, 1H), 8.96 (d, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 8.7 Hz, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 150.4, 142.7, 138.6, 138.1, 130.1, 129.2, 125.5, 125.0, 124.9, 123.1, 110.8 ppm; HRMS (ESI): m/z calcd for $C_{13}H_9BrN_4[M+H]^+$, 301.0083.Found:m/z 301.0082.

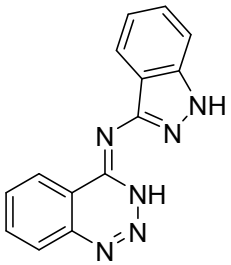


5-methoxy-N-phenyl-1,2,3-benzotriazin-4(*3H*)-imine (3ai), yellow solid, isolated yield 82% (20.7 mg); mp: 166.3-167.5 °C; ^{1}H NMR (400 MHz, DMSO): δ 9.76 (s, 1H), 8.01 (t, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.73 (dd, *J* = 8.3 Hz, *J* = 0.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 155.4, 151.2, 145.4, 138.4, 135.6, 129.2, 125.2, 123.7, 119.3, 112.3, 100.4, 57.7 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{12}N_4O[M+H]^+$, 253.1084. Found: m/z 253.1085.

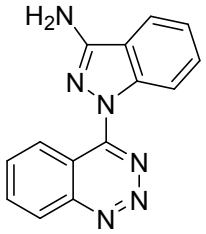


3-phenyl-N-(*p*-toly)-1,2,3-benzotriazin-4(*3H*)-imine (4aa), yellow solid, isolated yield 58% (18.1 mg); mp: 213.7-214.5 °C; ^{1}H NMR (400 MHz, DMSO): δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.00

(t, *J* = 7.5 Hz, 1H), 7.65 (td, *J* = 8.0 Hz, *J* = 1.2 Hz 1H), 7.43 (t, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 4H), 7.16 (d, *J* = 8.3 Hz, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ155.9, 146.4, 146.1, 143.7, 136.5, 134.8, 132.0, 130.9, 130.3, 128.3, 127.0, 127.0, 126.8, 124.4, 111.5, 21.1 ppm; HRMS (ESI): m/z calcd for $C_{20}H_{16}N_4$ $[M+H]^+$,313.1448. Found: m/z 314.1450.

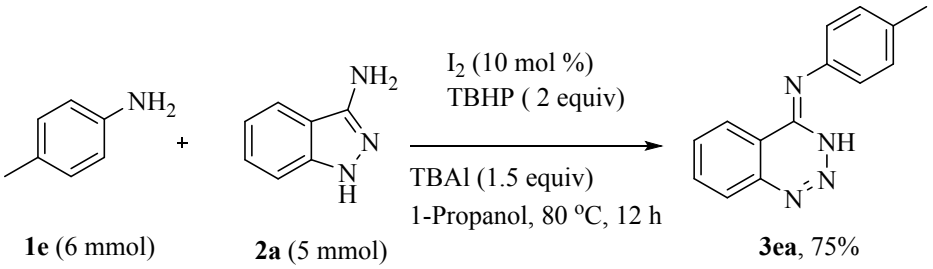


N-(1H-indazol-3-yl)1,2,3-benzotriazin-4(*3H*)-imine (5aa), yellow solid, isolated yield 90% (11.7 mg); mp: 223.6-224.6 °C; ^{1}H NMR (400 MHz, DMSO): δ 12.97 (s, 1H), 10.64 (s, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.14 (t, *J* = 7.7Hz, 1H), 8.03 (t, *J* = 7.3 Hz, 1H), 7.59-7.54 (m, 2H), 7.41(t, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 152.4, 144.0, 141.8, 140.0, 135.1, 132.7, 127.7, 126.9, 122.5, 121.8, 120.4, 118.1, 111.0, 109.1 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{10}N_6$ $[M+H]^+$, 263.1040. Found: m/z 263.1039.



1-(benzo[*d*][1,2,3]triazin-4-yl)-1*H*-indazol-3-amine (6aa), yellow solid, isolated yield 84% (11.0mg); mp: 239.4-240.7°C; ^{1}H NMR (400 MHz, DMSO): δ 9.73 (d, *J* = 8.4 Hz, 1H), 8.98 (d, *J* = 8.5 Hz, 1H), 8.33 (dd, *J* = 8.2 Hz, *J* = 0.7 Hz, 1H), 8.23-8.16 (m, 1H), 8.09-8.01 (m, 2H), 7.76-7.65 (m, 1H), 7.44 (td, *J* = 4.0 Hz, *J* = 0.8 Hz 1H), 6.86 (s, 2H); ^{13}C NMR (100 MHz, DMSO): δ 155.3, 150.2, 146.6, 141.1, 135.4, 132.7, 130.3, 128.2, 127.9, 124.4, 121.4, 120.1, 118.1, 110.3 ppm; HRMS (ESI): m/z calcd for $C_{14}H_{10}N_6$ $[M+H]^+$, 263.1040. Found: m/z 263.1041.

4. Gram-scale reaction



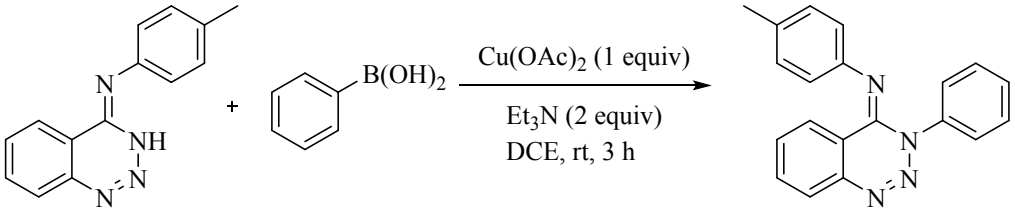
1e (6 mmol) **2a** (5 mmol) **3ea**, 75%

A mixture of *p*-toluidine **1e** (0.54 g, 6 mmol, 1.2 equiv), 3-aminoindazole**2a** (0.67 g, 5 mmol, 1.0 equiv), I_2 (0.13 g, 0.5 mmol, 10 mol %), TBHP (1.37 mL, 10 mmol, 2 equiv) and TBAI (2.77 g, 7.5 mmol, 1.5 equiv) was added in a dry round-bottomed flask under air

atmosphere. To the mixture, anhydrous1-propanol (20 mL) was added *via* a syringe and the reaction mixture was stirred at 80 °C for 12 h, which was monitored with TLC. After completion of the reaction, the solvent was removed under reduced pressure and the crude reaction mixture was purified by flash silica gel column chromatography (petroleum / EtOAc = 3:1-1:1) to afford the desired product **3ea** (0.89 g, 75%).

5. Chemical transformation of the product

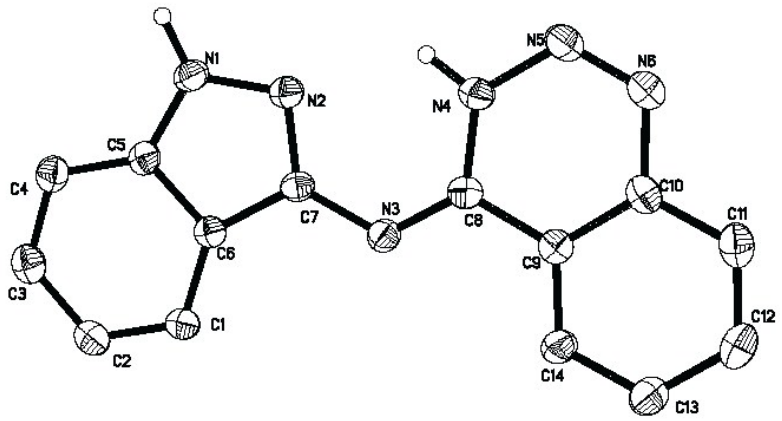
Experimental procedure for the synthesis of 4aa [2]



3ea (0.1 mmol) 0.15 mmol **4aa**, 58%

A mixture of **3ea** (0.1 mmol), $Cu(OAc)_2$ (1 equiv), Et_3N (2 equiv) and Phenylboronic acid (0.15 mmol) in DCE (2 mL) was stirred for 3 h at room temperature. It was diluted with EtOAc (10 mL) and washed brine. The combined organic phase was dried (Na_2SO_4). After evaporation of the solvents under reduced pressure, the crude product was purified on a silica gel column to give the desired product **4aa**.

6. X-Ray Crystallographic Data of 5aa



Single-crystal X-ray Molecular Structure of 5aa

The structure of **5aa** (containing little solvent) was determined by the X-ray diffraction. Recrystallized from acetone/pentane. Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data and assigned as CCDC 1955883.

Table 1 Crystal data and structure refinement for 5aa.

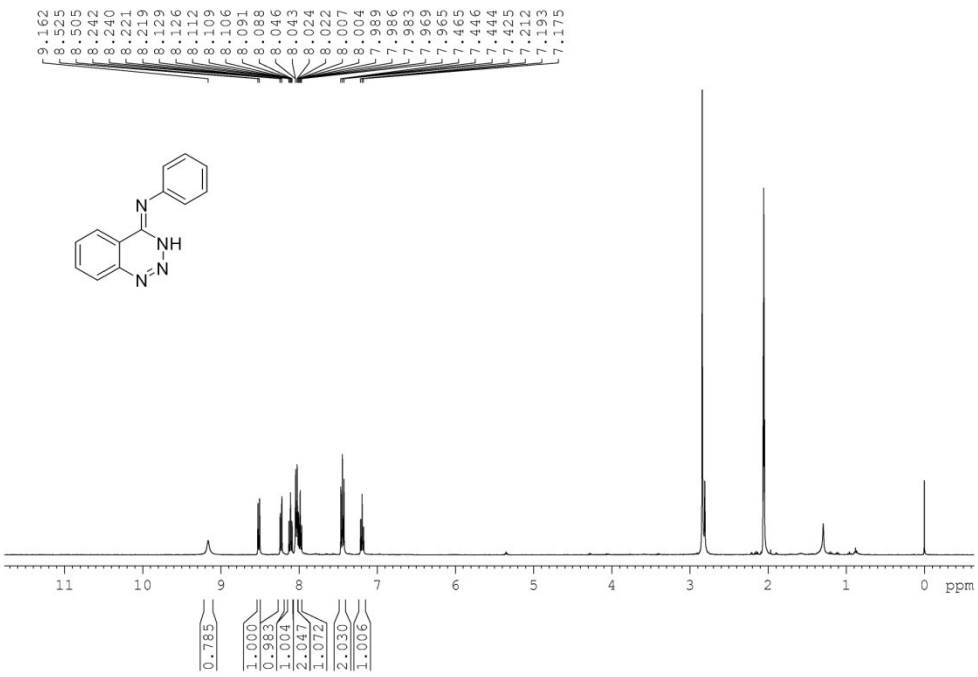
Identification code	**5aa**
Empirical formula	$C_{14}H_{10}N_6$
Formula weight	262.28
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	26.1795(13)
b/Å	4.5660(3)
c/Å	9.9140(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1185.08(11)
Z	4
ρ_{calc}g/cm^3	1.470
μ/mm^{-1}	0.777
F(000)	544.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.752 to 134.154
Index ranges	$-30 \le h \le 31$, $-5 \le k \le 2$, $-11 \le l \le 11$
Reflections collected	2801
Independent reflections	1651 [R_{int} = 0.0463, R_{sigma} = 0.0633]
Data/restraints/parameters	1651/1/189
Goodness-of-fit on F^2	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1069
Final R indexes [all data]	R_1 = 0.0608, wR_2 = 0.1135
Largest diff. peak/hole / e Å^{-3}	0.14/-0.16
Flack parameter	-0.2(6)

7. References

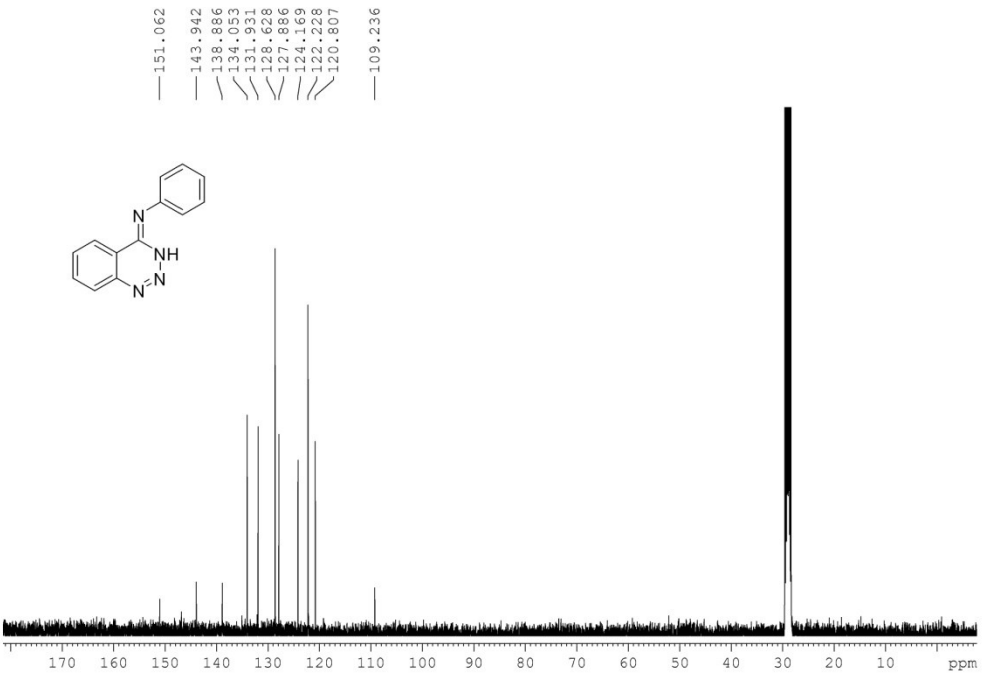
[1] Kong, W.; Zhou, Y.; Song, Q. *Adv. Synth. Catal*. **2018**, *360*, 1943.

[2] Kumar, K. S.; Adepu, R.; Sandra, S.; Rambabu, D.; Krishna, G. R.; Reddy, C. M.; Misra, P.; Pal, M. *Bioorg. Med. Chem. Lett.***2011**, *22*, 1146.

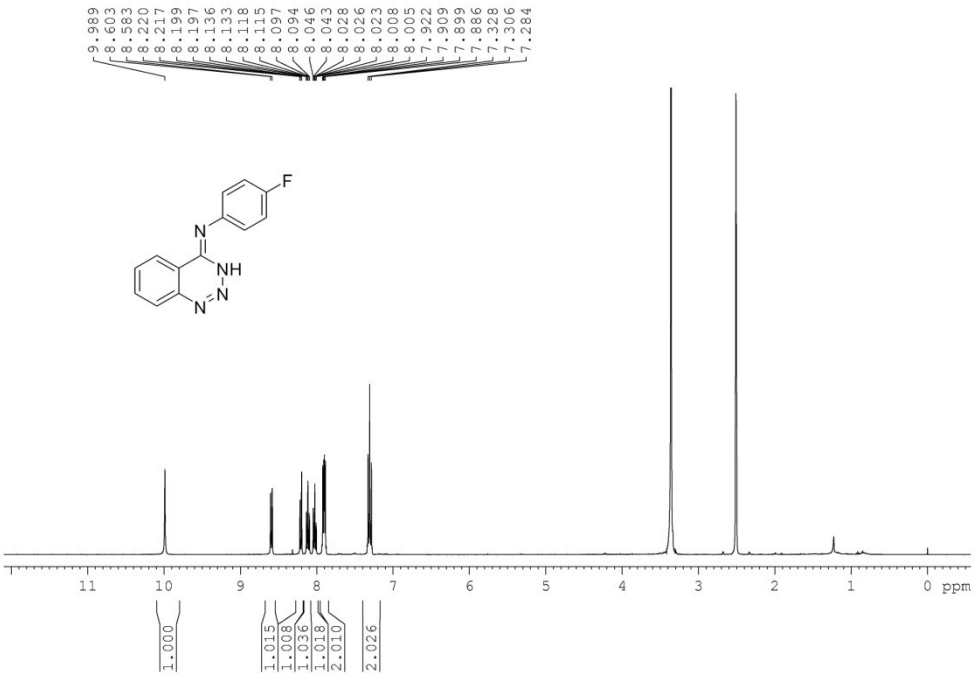
8. Copies of NMR Spectra



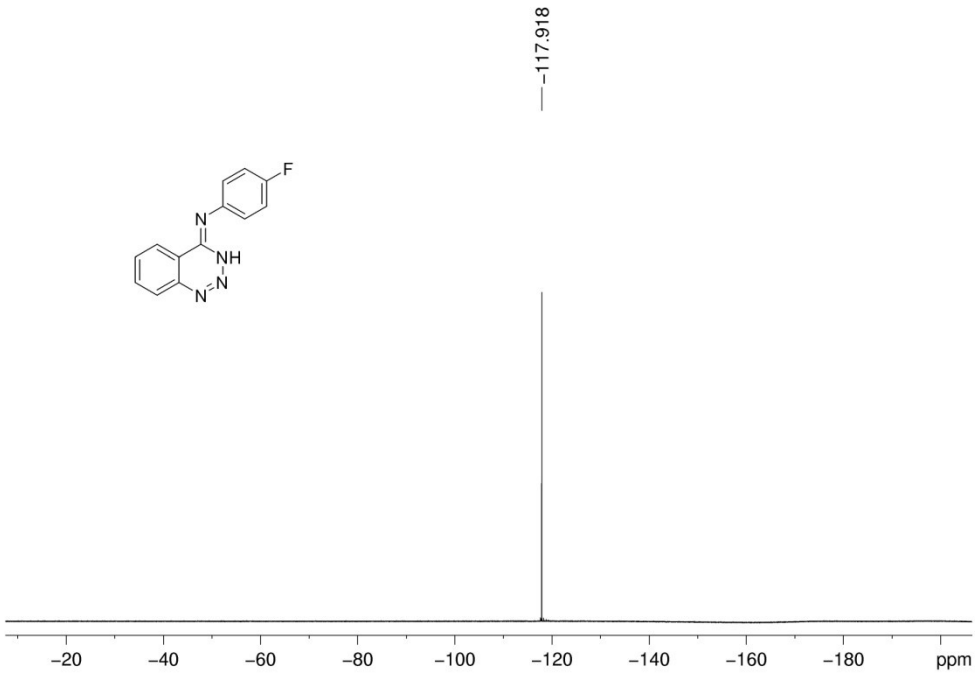
^{1}H NMR spectrum of compound 3aa



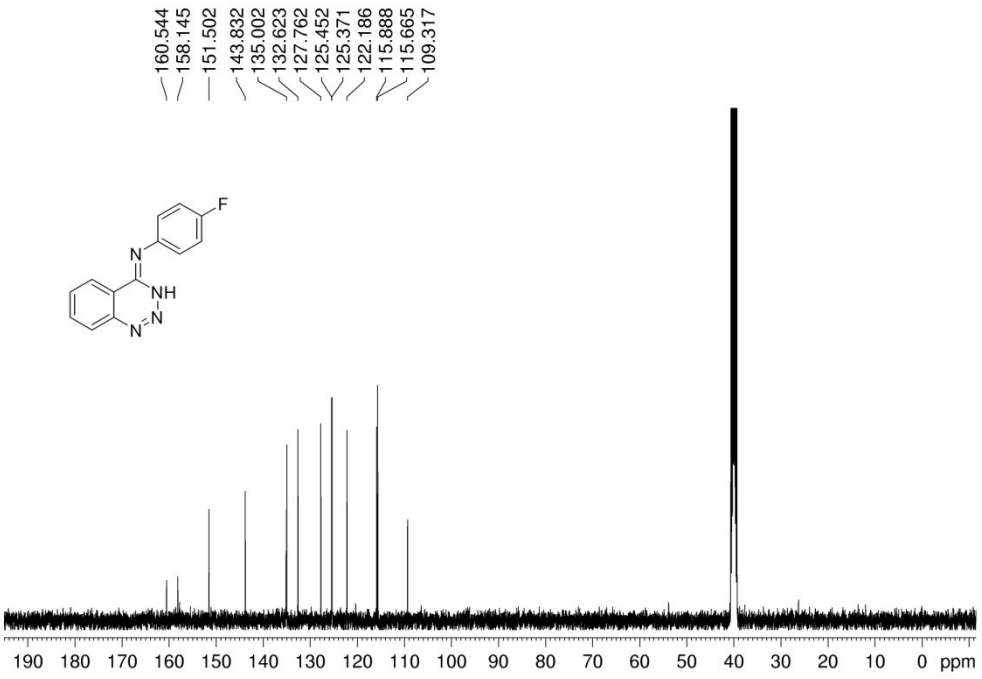
^{13}C NMR spectrum of compound 3aa



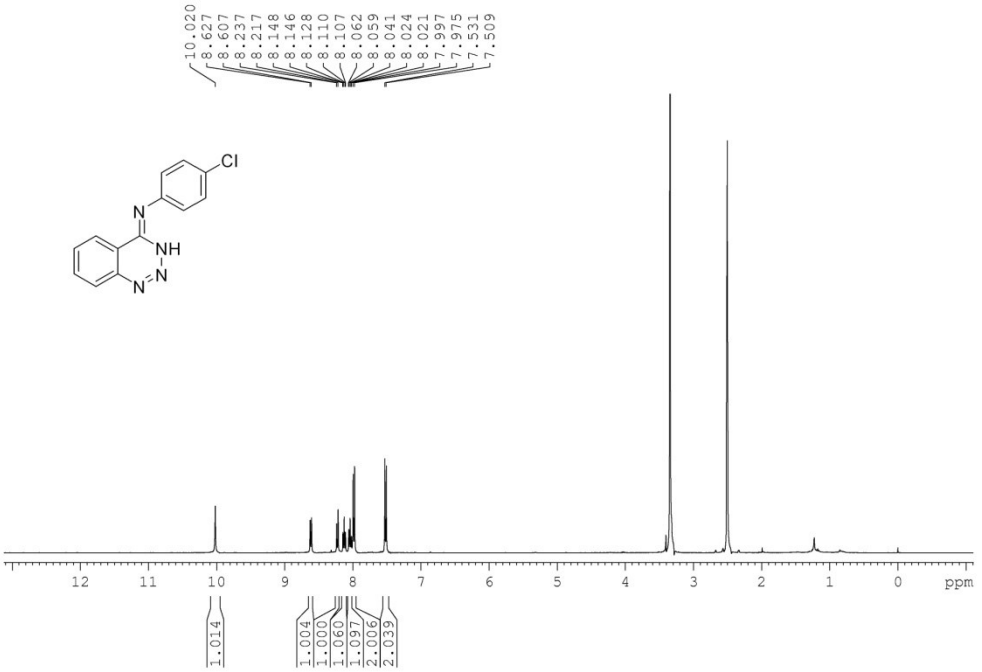
[1]H NMR spectrum of compound 3ba



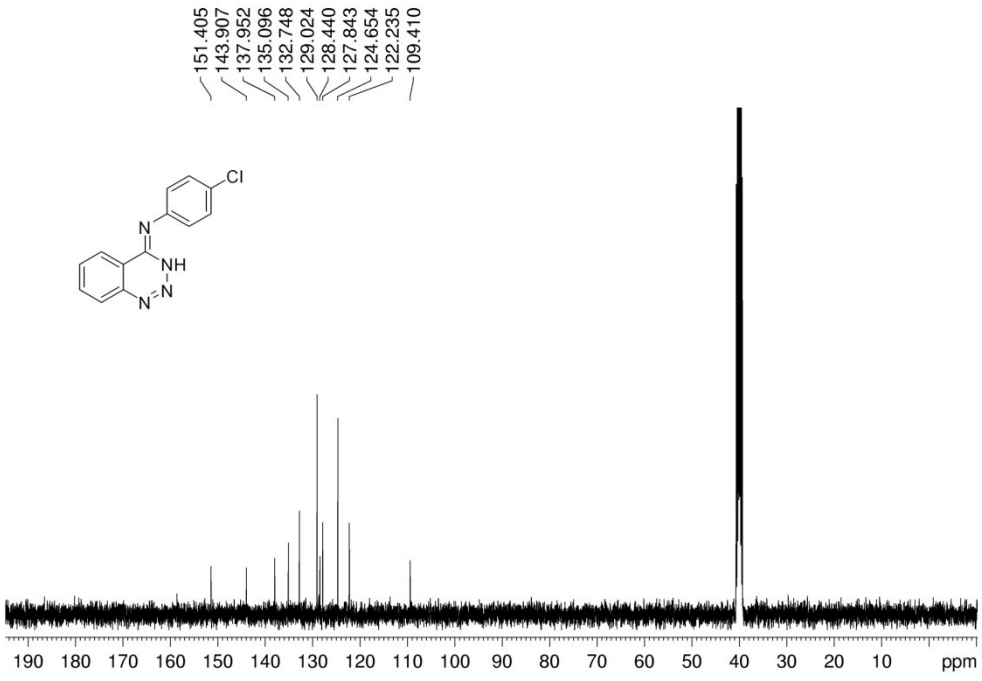
[19]F NMR spectrum of compound 3ba



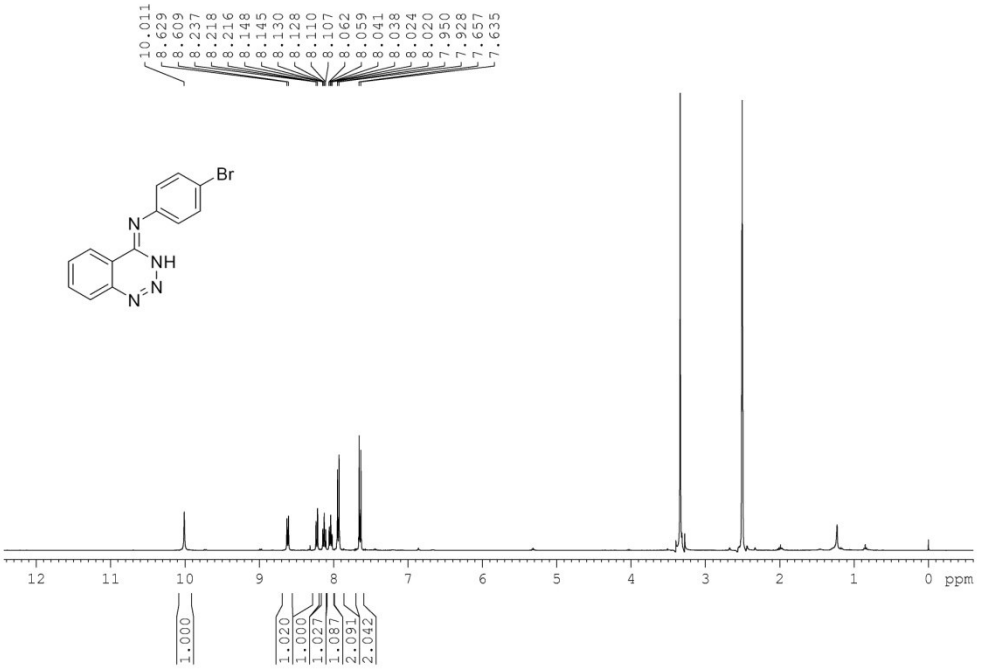
^{13}C NMR spectrum of compound 3ba



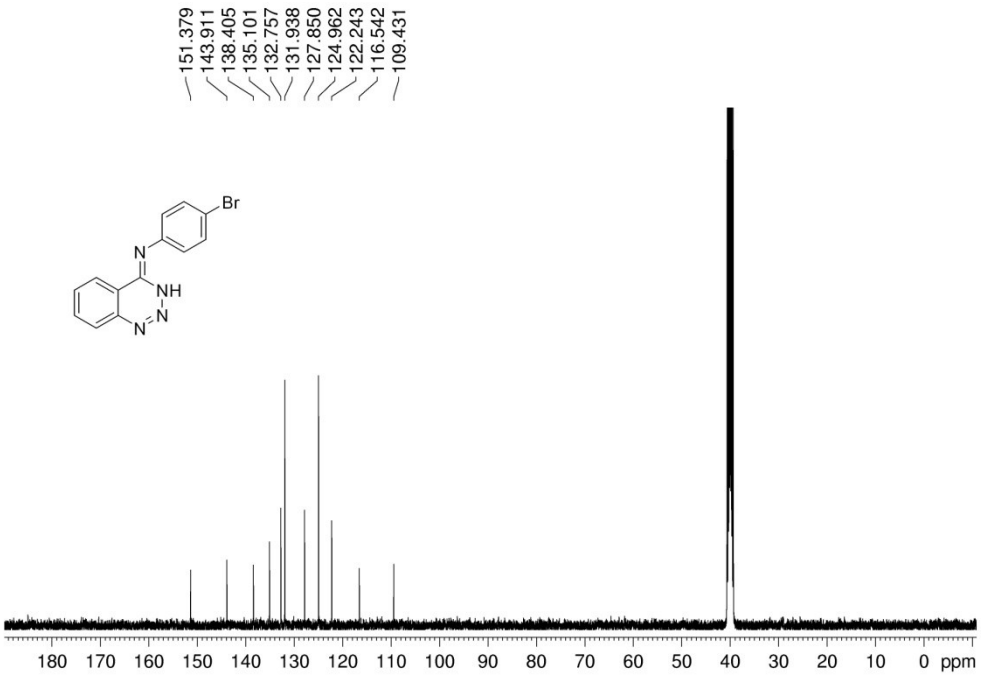
^{1}H NMR spectrum of compound 3ca



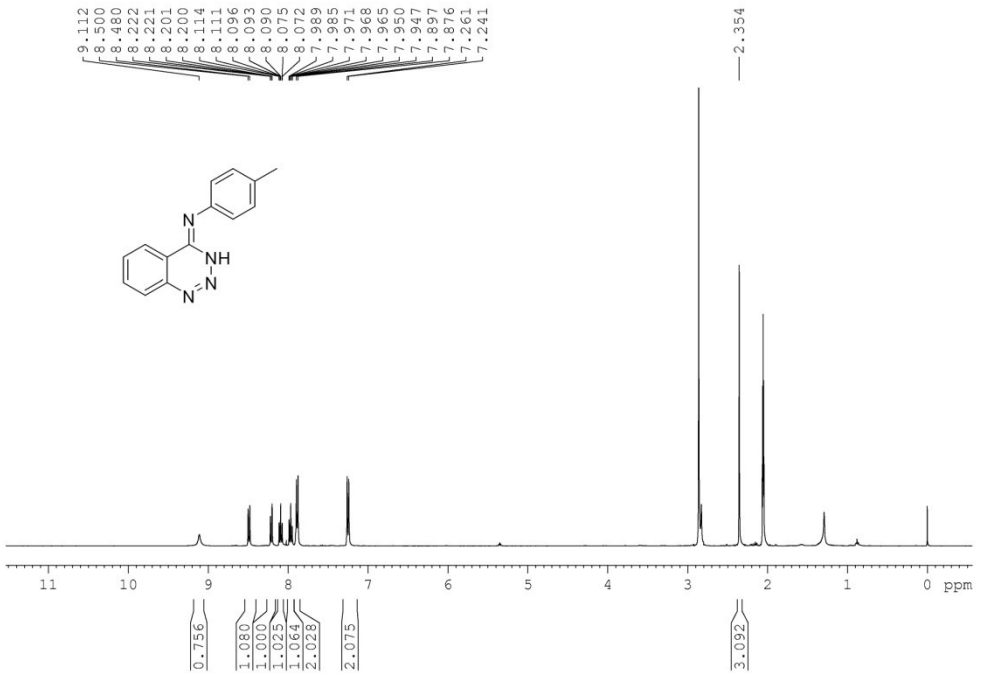
^{13}C NMR spectrum of compound 3ca



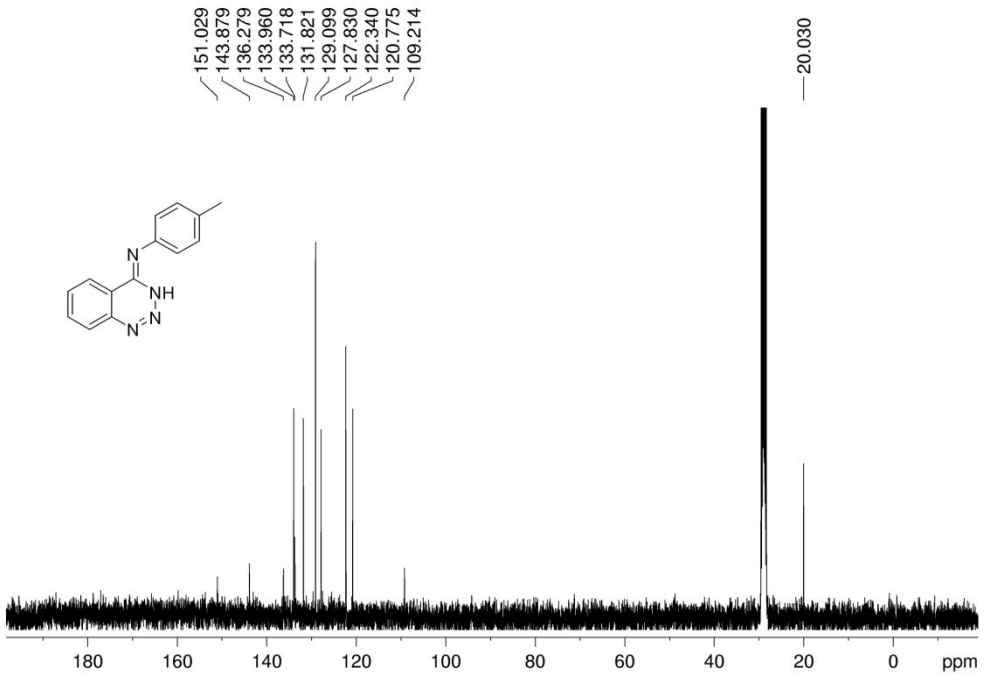
^{1}H NMR spectrum of compound 3da



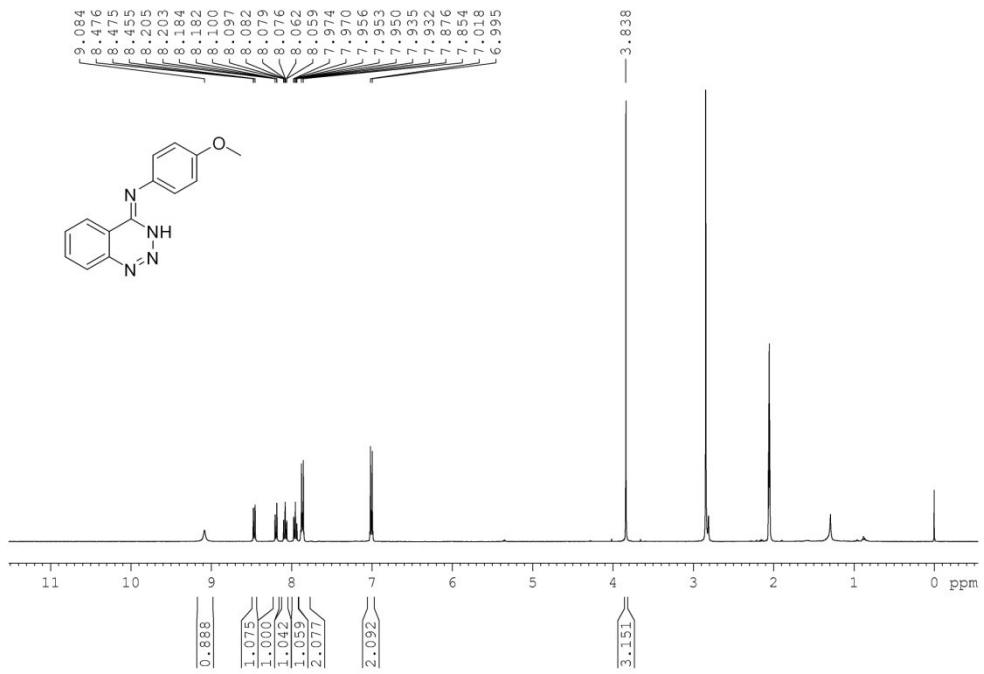
^{13}C NMR spectrum of compound 3da



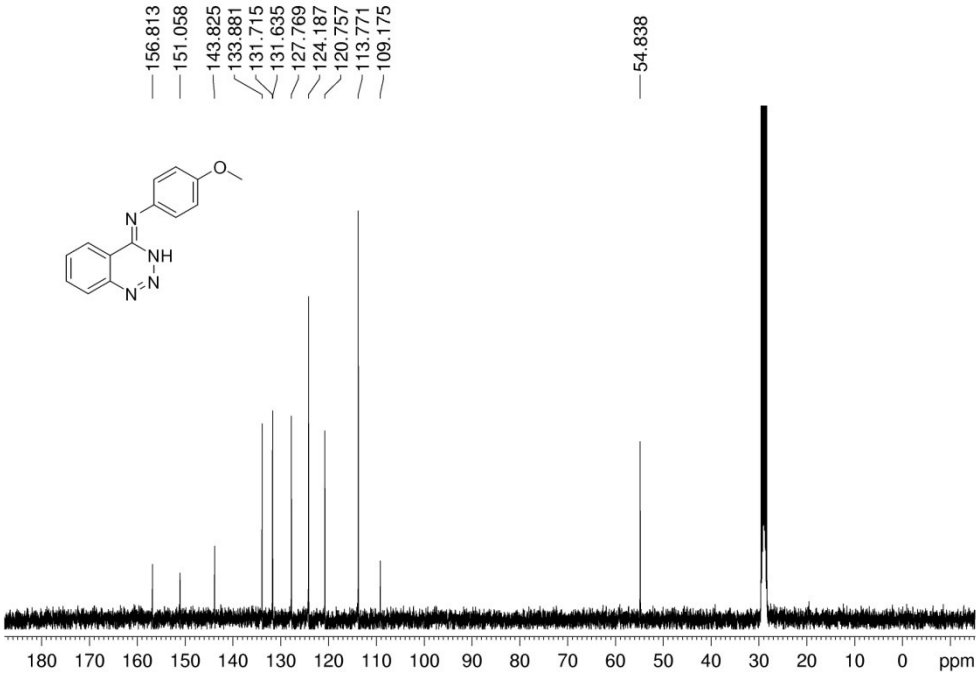
^{1}H NMR spectrum of compound 3ea



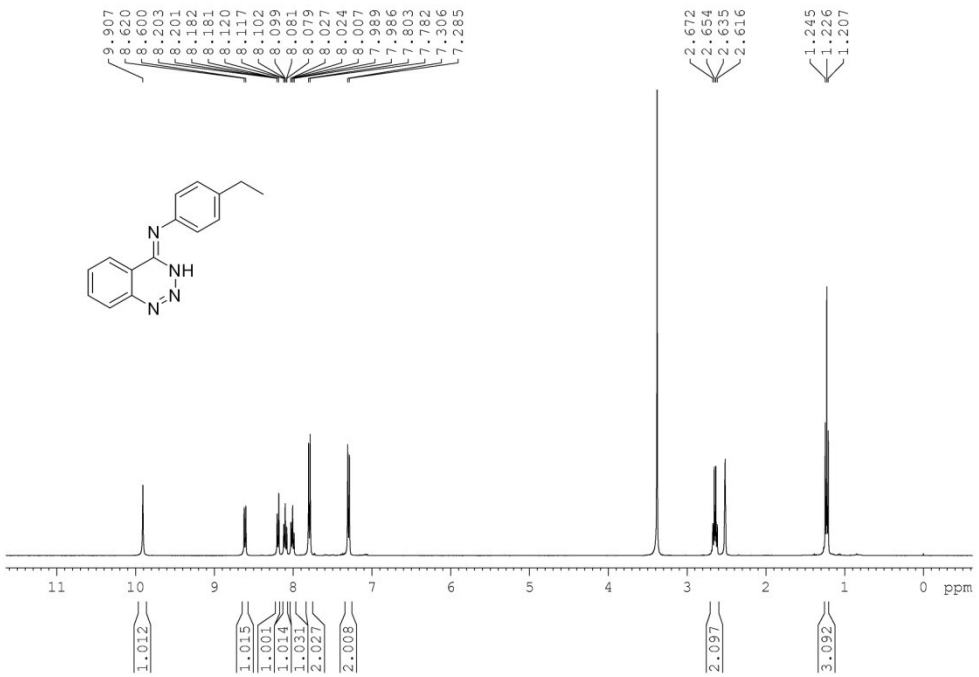
^{13}C NMR spectrum of compound 3ea



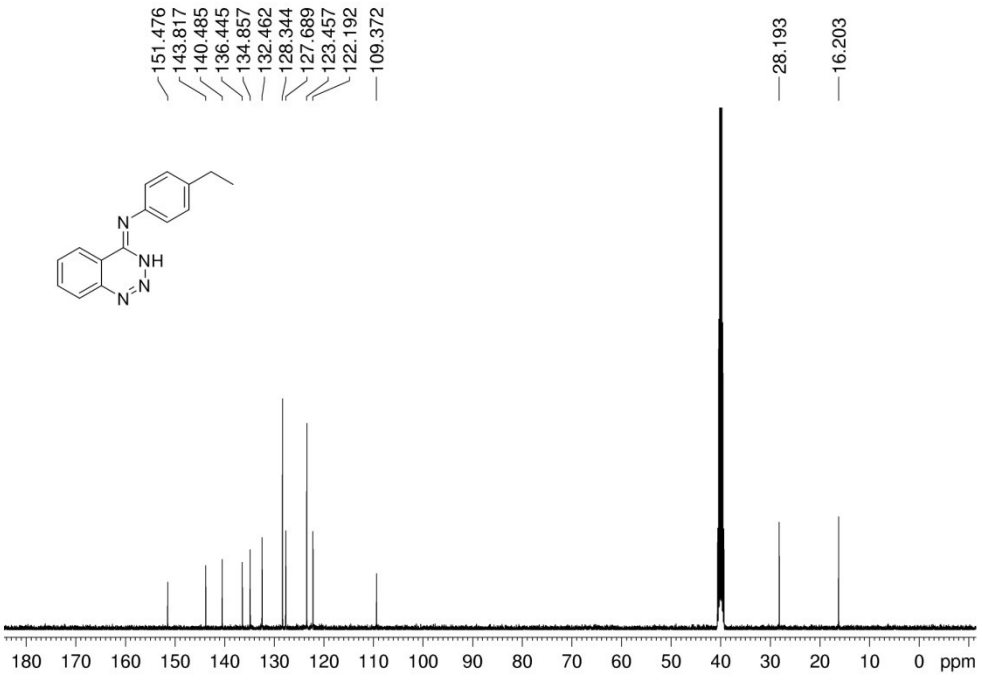
^{1}H NMR spectrum of compound 3fa



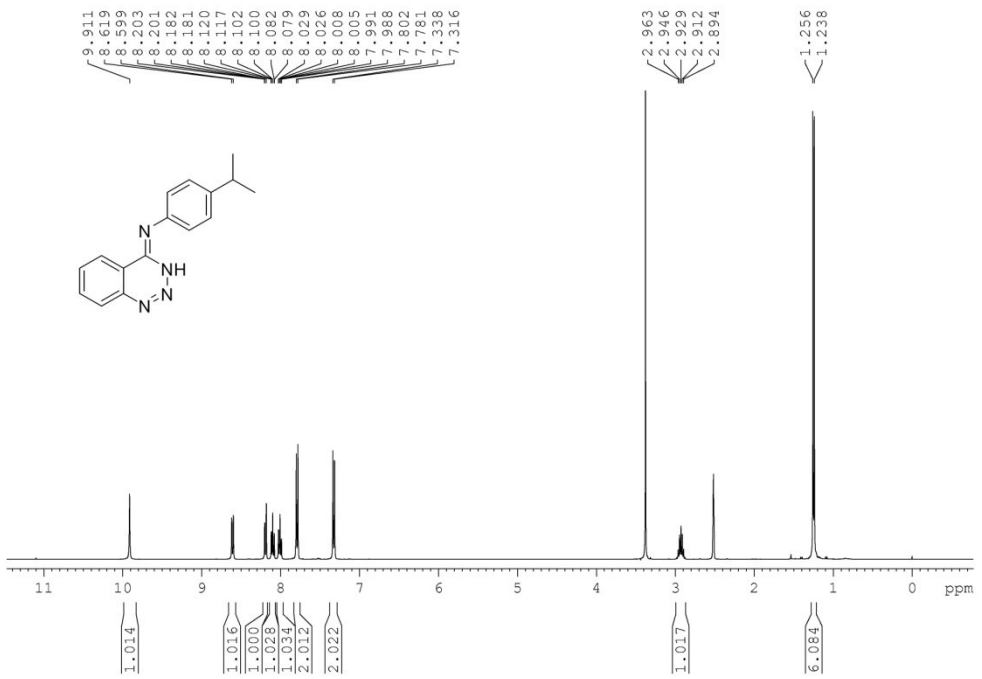
^{13}C NMR spectrum of compound 3fa



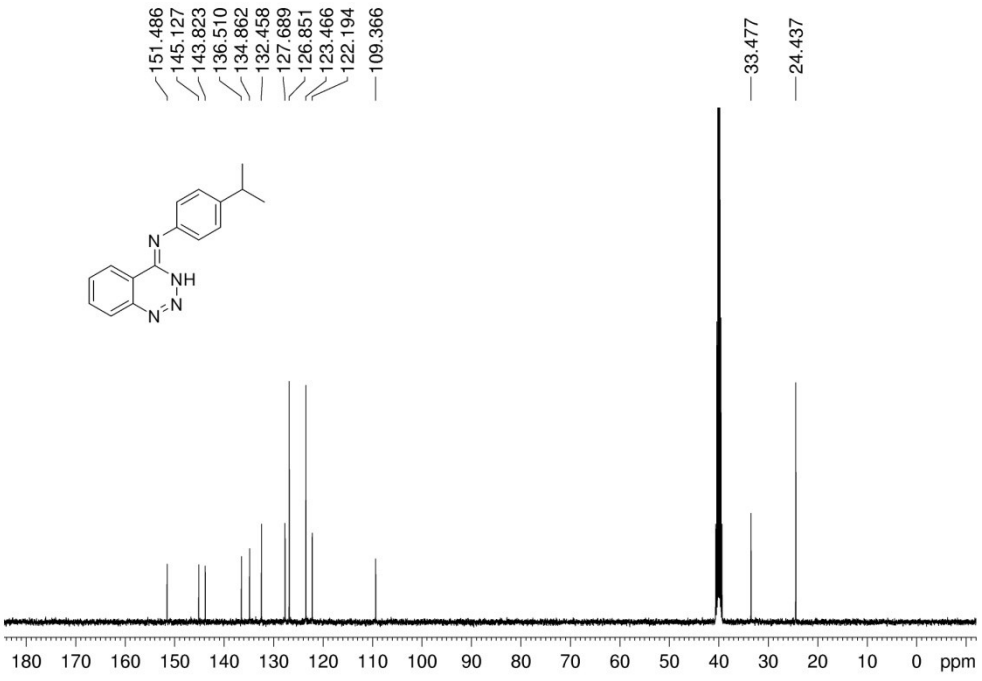
^{1}H NMR spectrum of compound 3ga



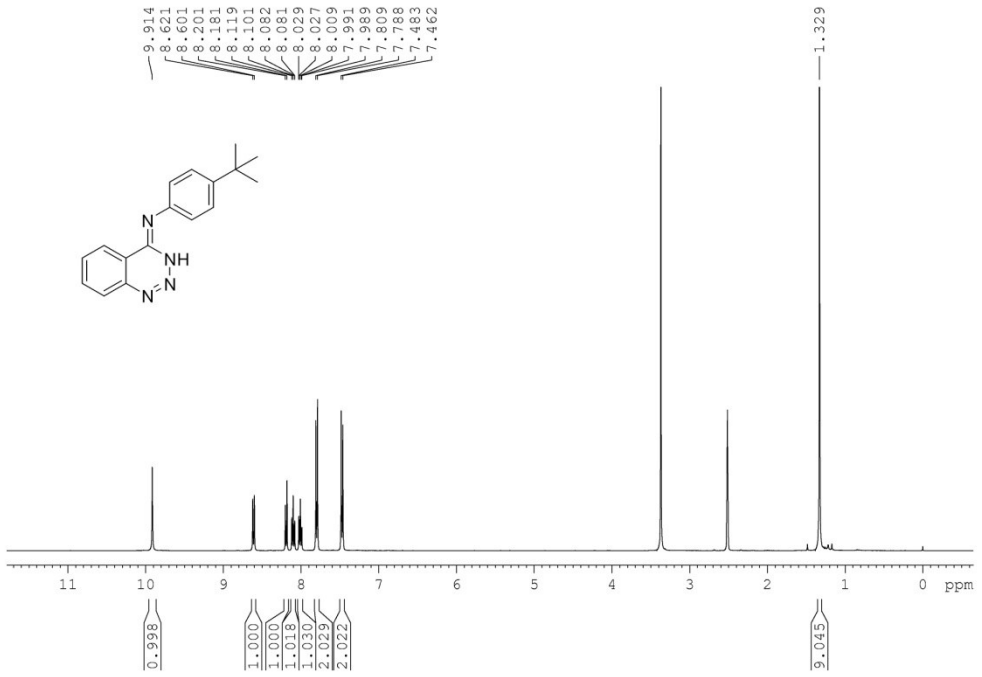
^{13}C NMR spectrum of compound 3ga



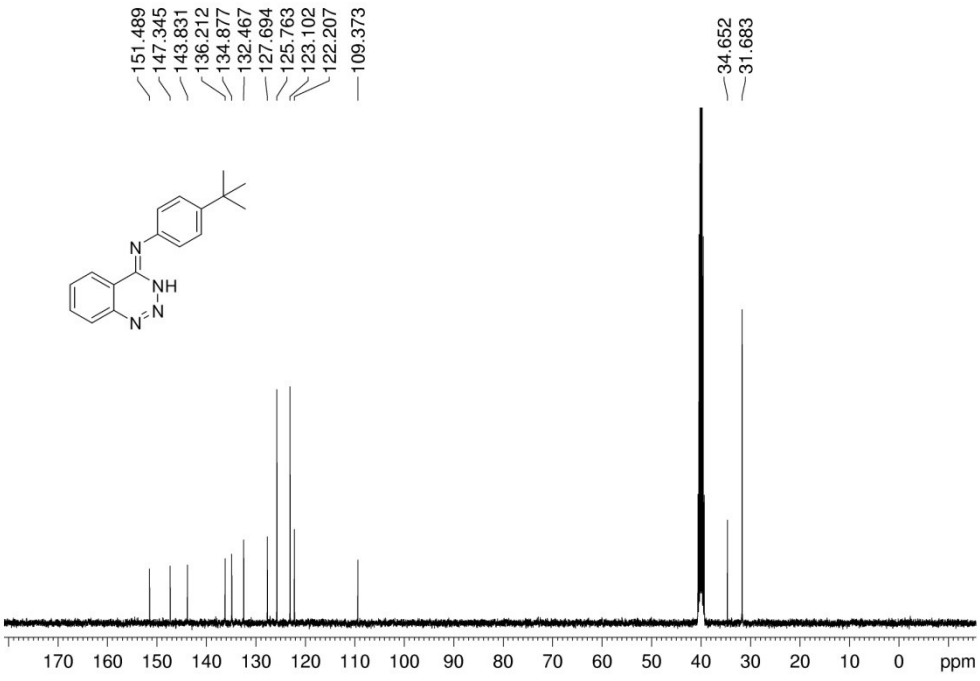
^{1}H NMR spectrum of compound 3ha



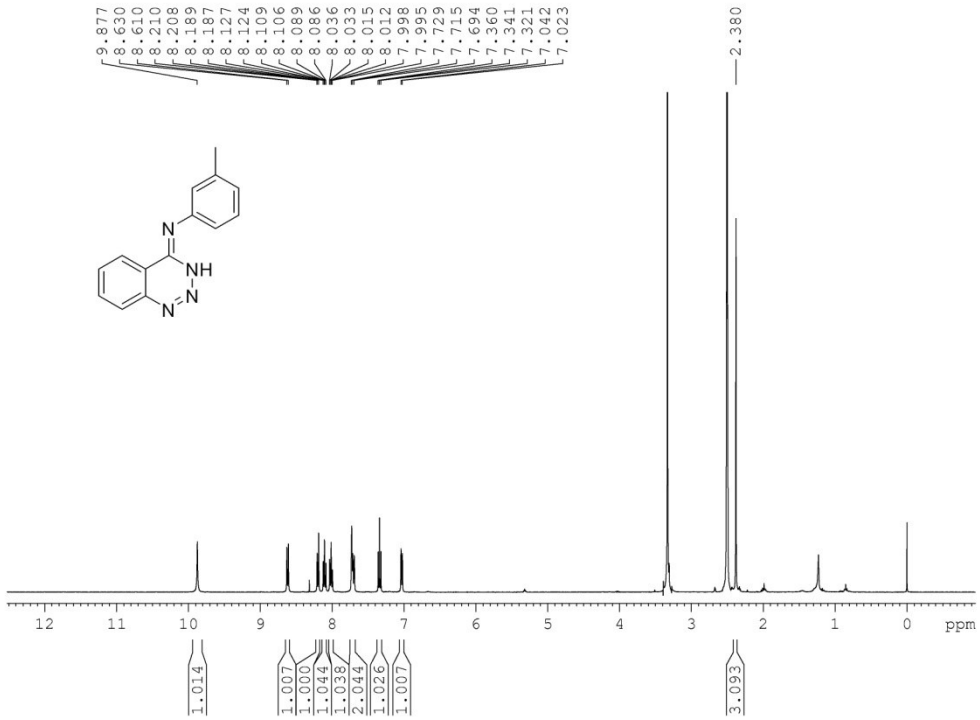
^{13}C NMR spectrum of compound 3ha



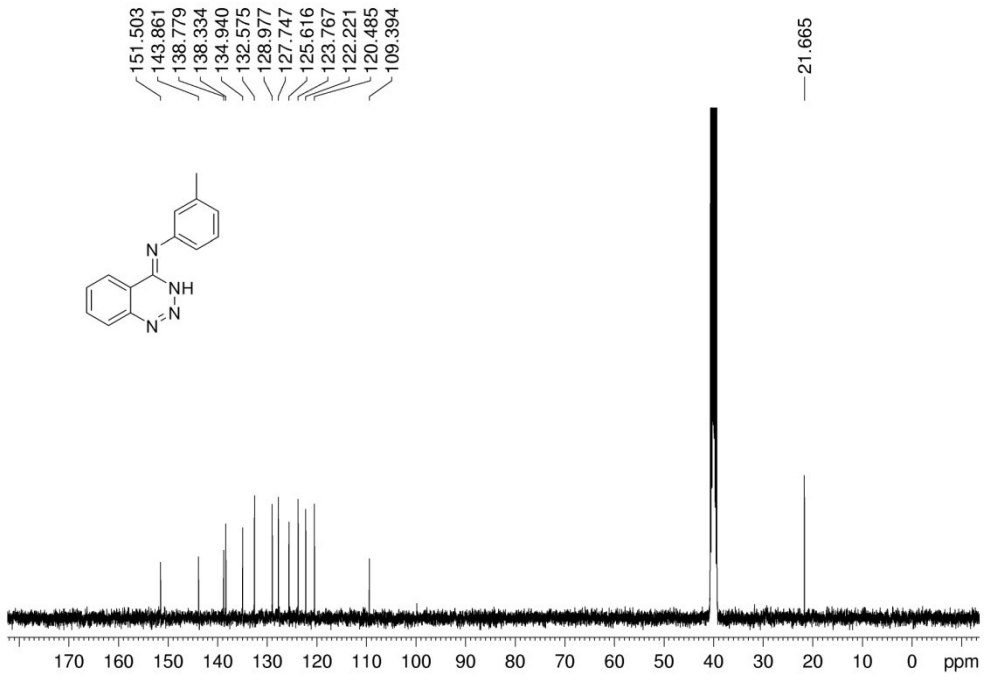
^{1}H NMR spectrum of compound 3ia



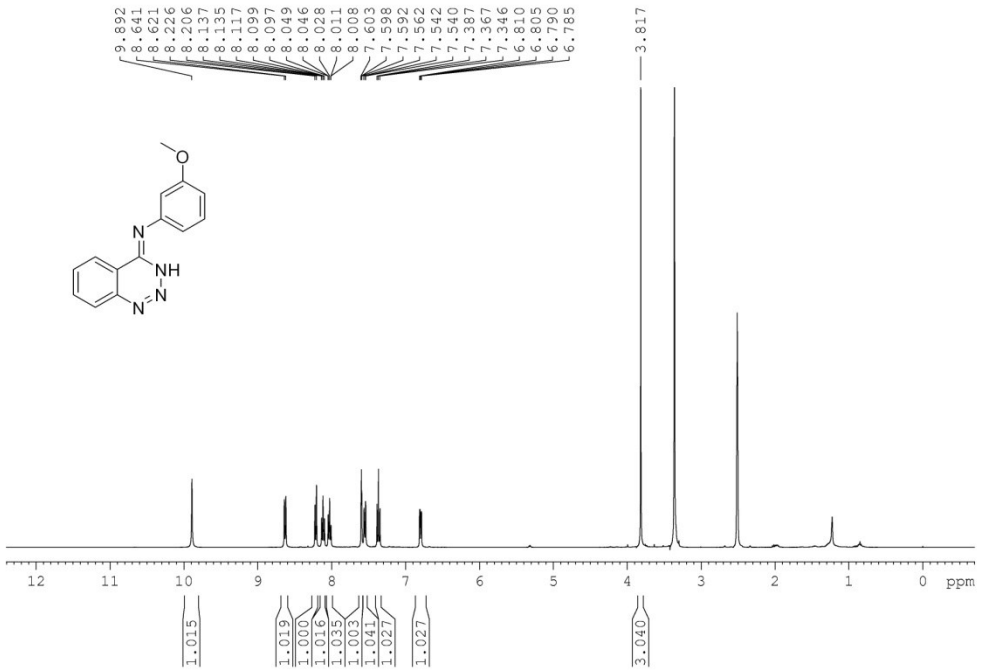
^{13}C NMR spectrum of compound 3ia



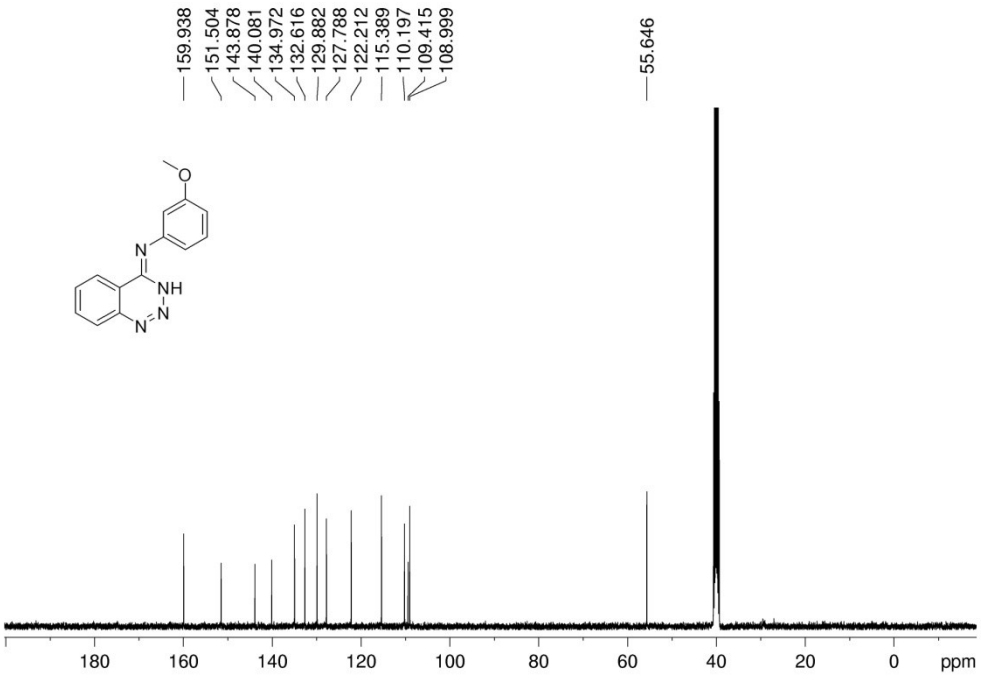
^{1}H NMR spectrum of compound 3la



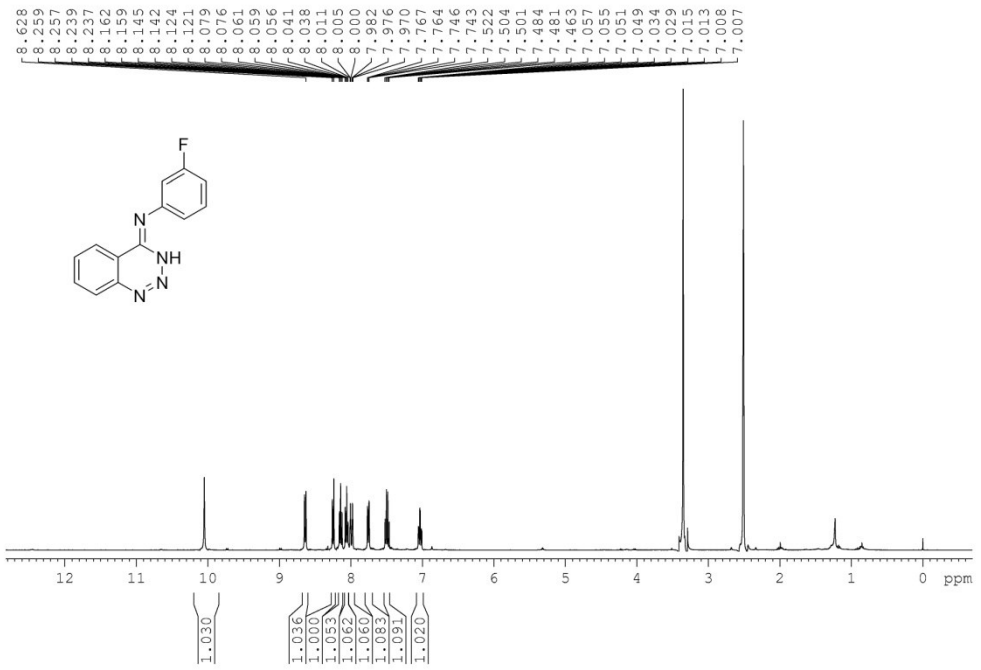
^{13}C NMR spectrum of compound 3la



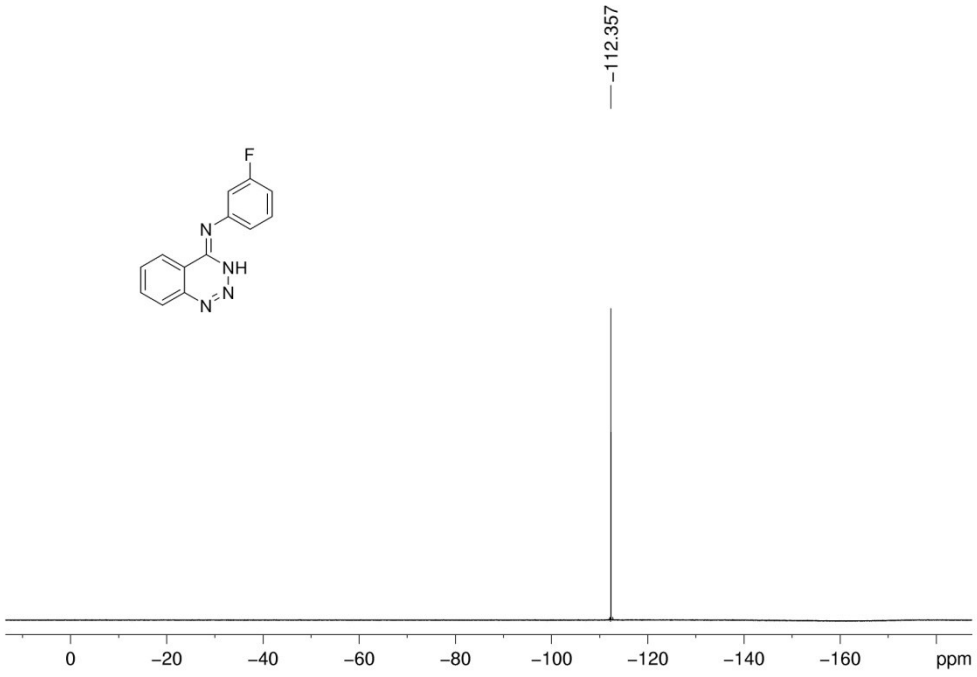
^{1}H NMR spectrum of compound 3ma



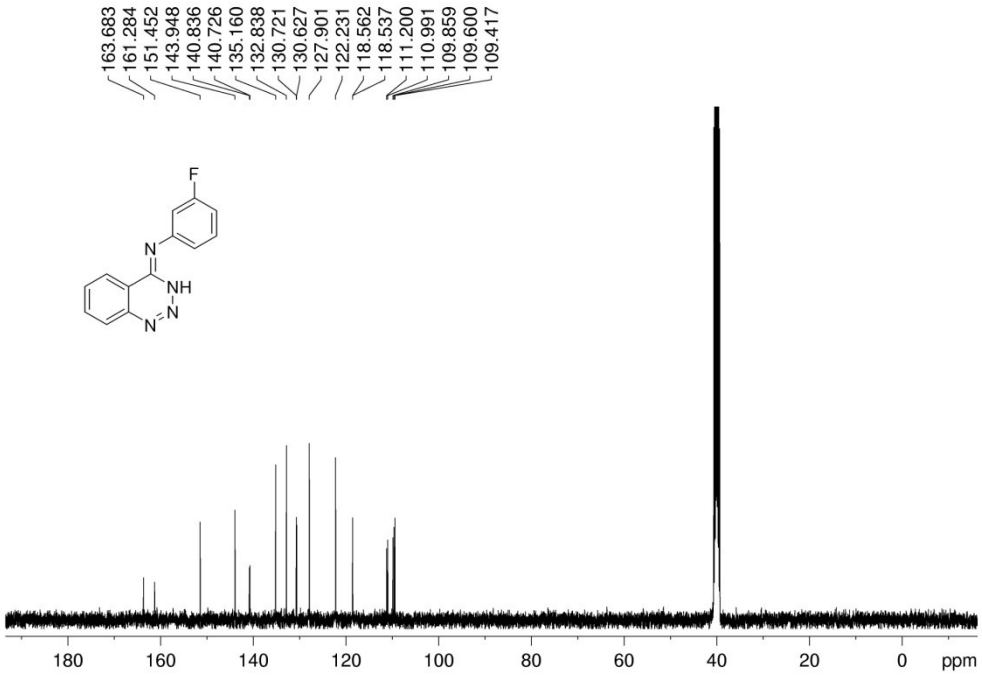
^{13}C NMR spectrum of compound 3ma



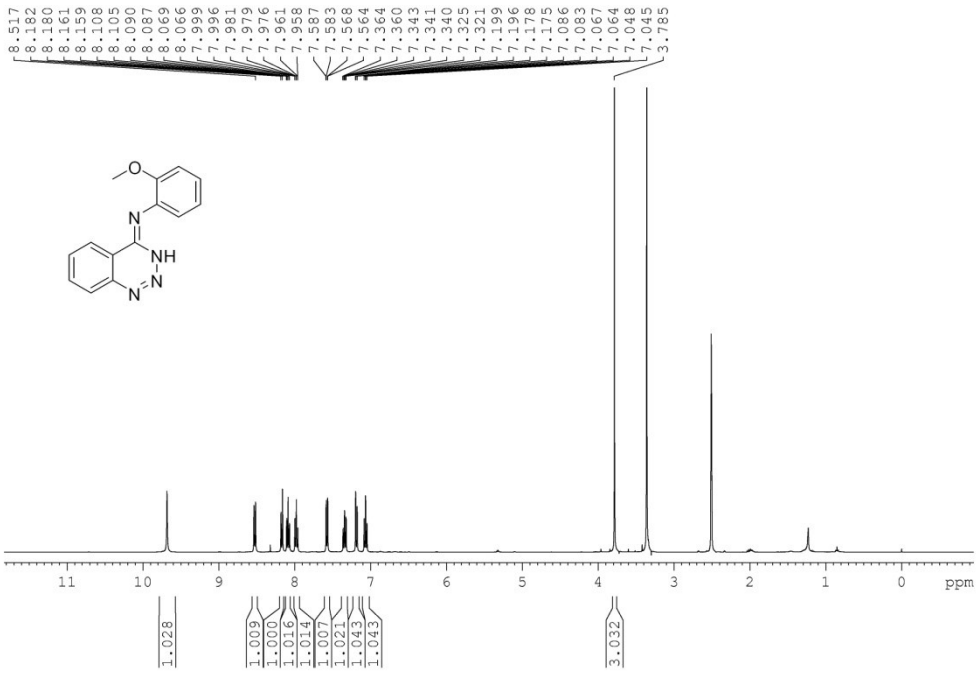
^{1}H NMR spectrum of compound 3na



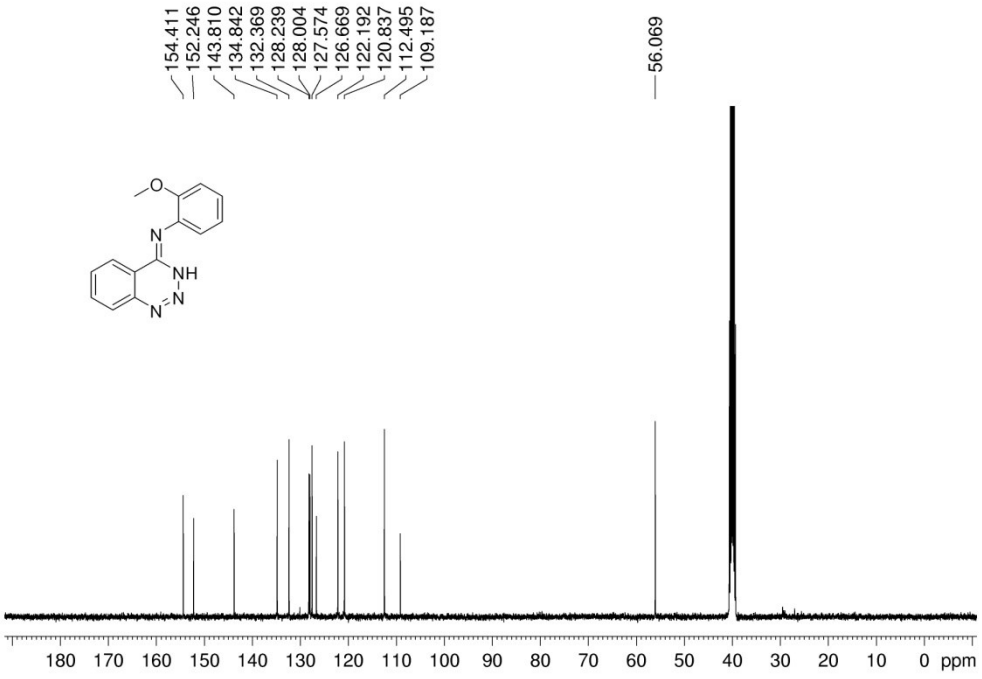
^{19}F NMR spectrum of compound 3na



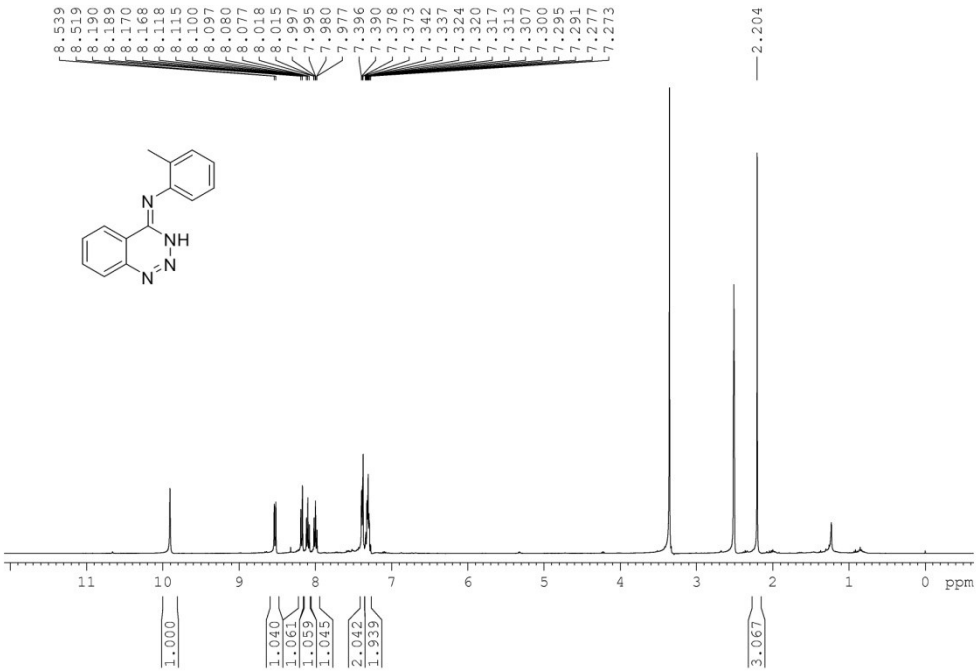
^{13}C NMR spectrum of compound 3na



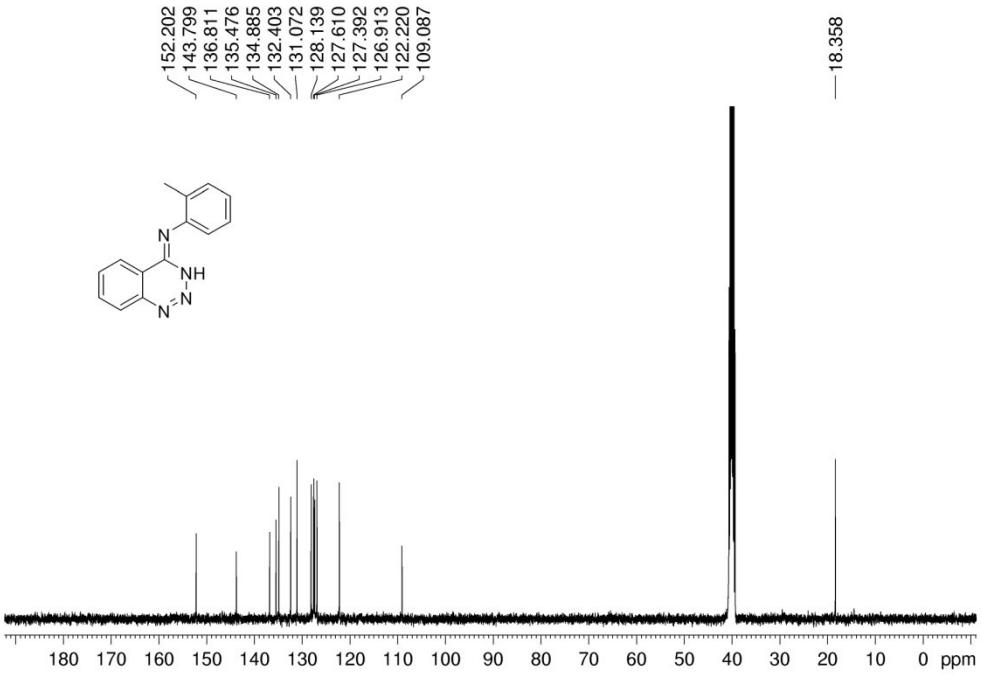
^{1}H NMR spectrum of compound 3oa



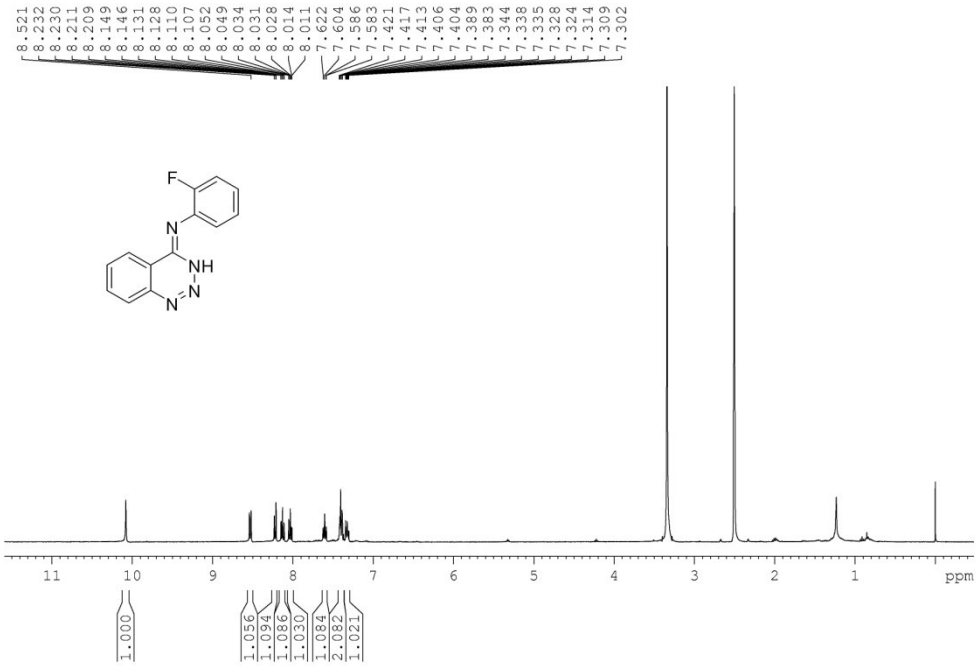
^{13}C NMR spectrum of compound 3oa



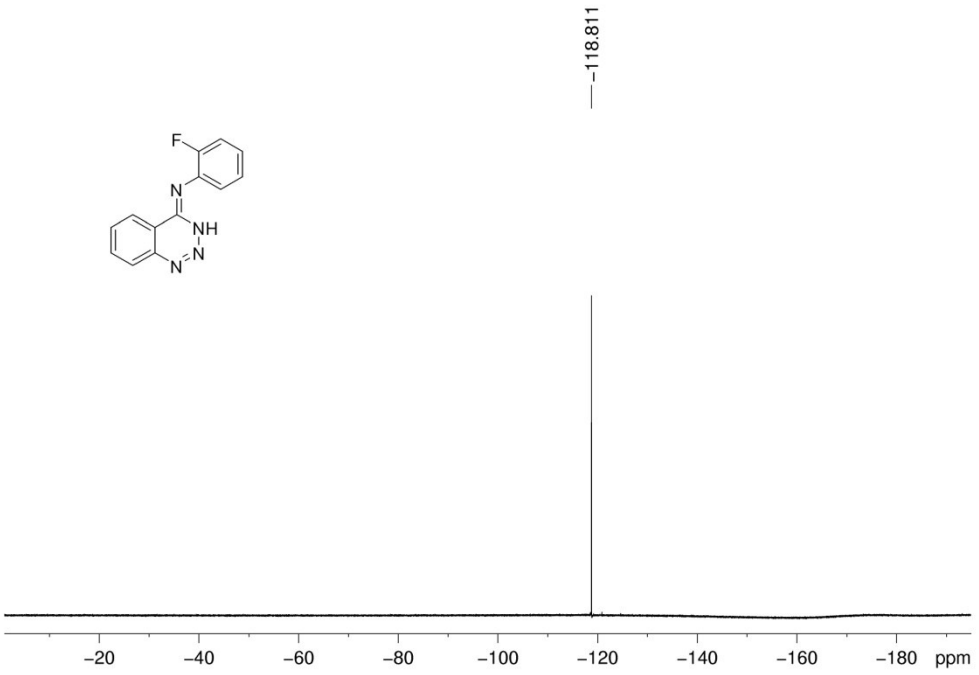
^{1}H NMR spectrum of compound 3pa



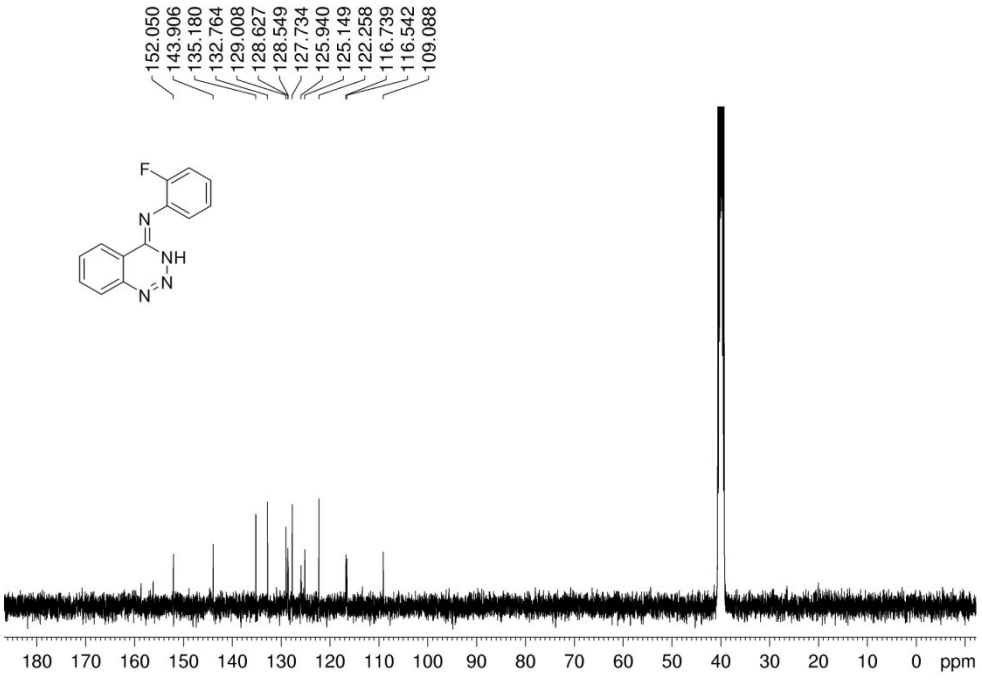
^{13}C NMR spectrum of compound 3pa



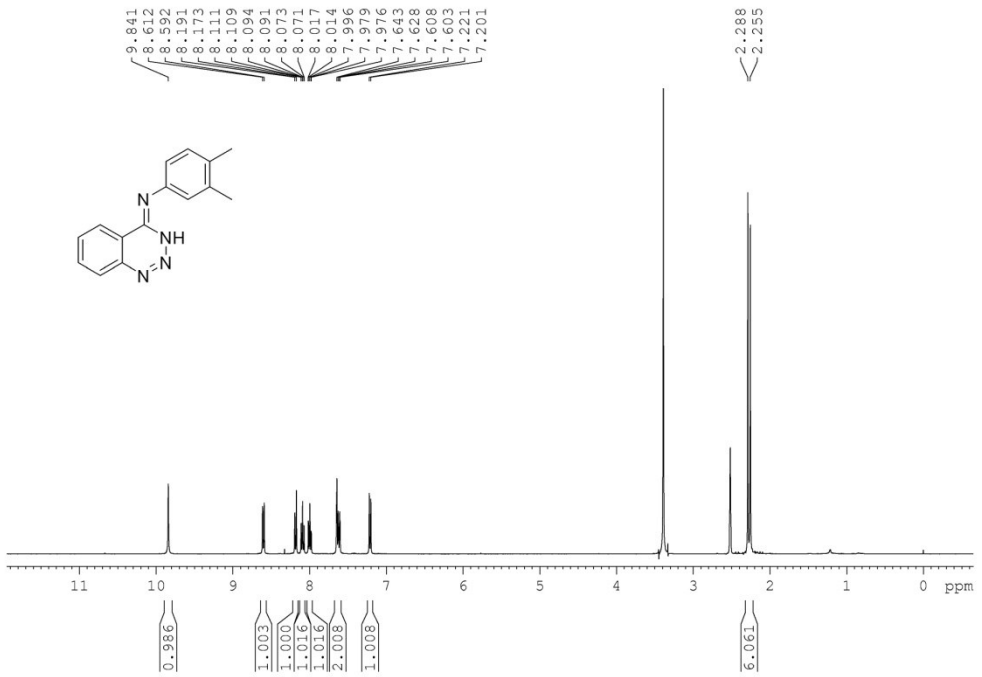
^{1}H NMR spectrum of compound 3qa



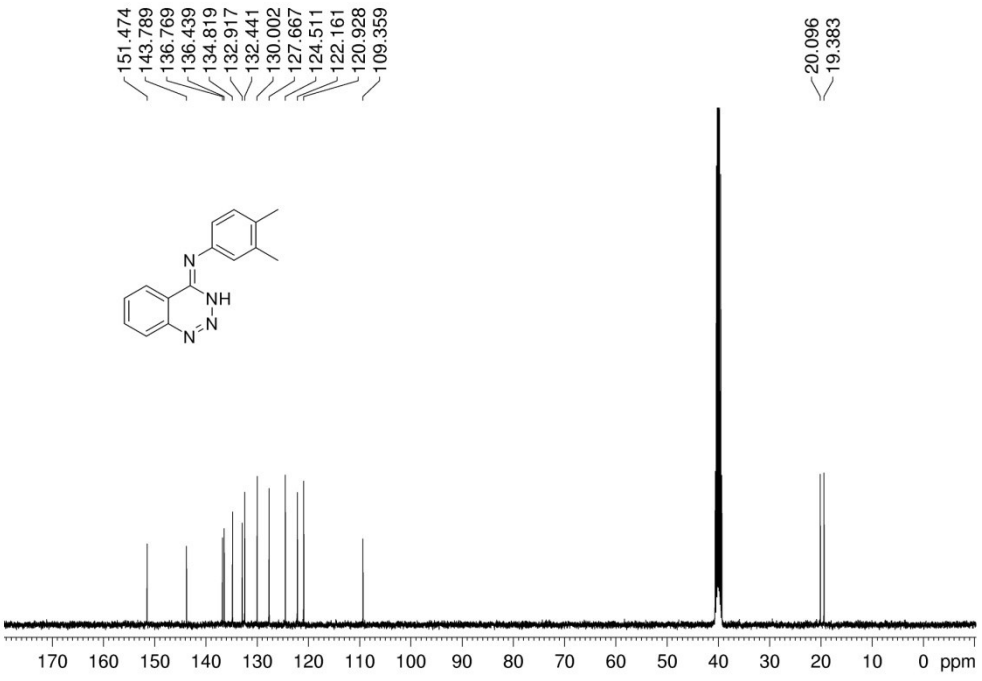
^{19}F NMR spectrum of compound 3qa



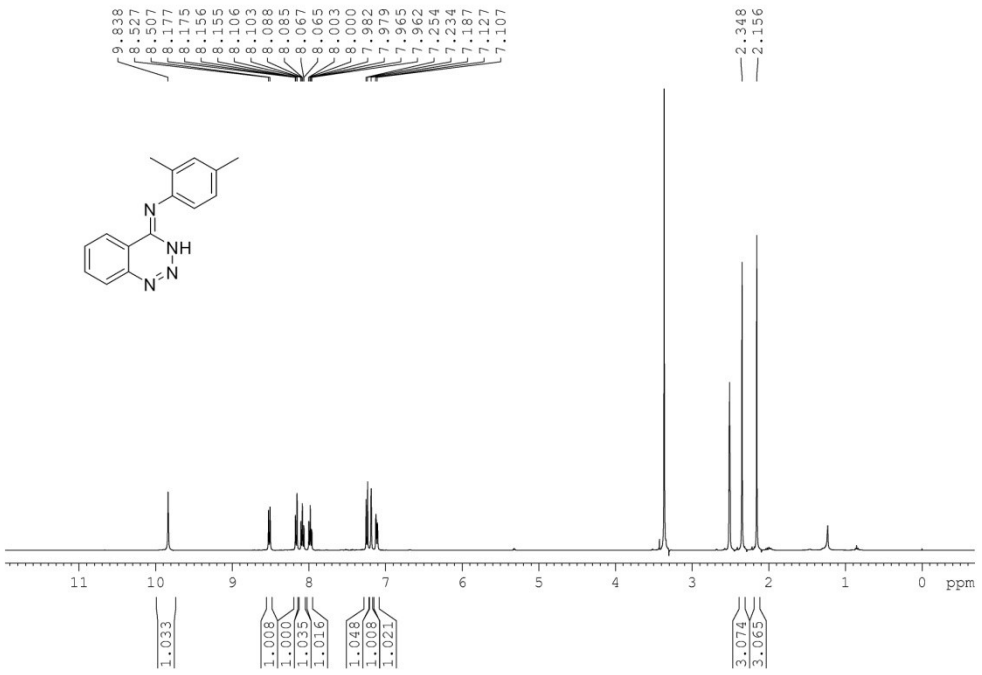
^{13}C NMR spectrum of compound 3qa



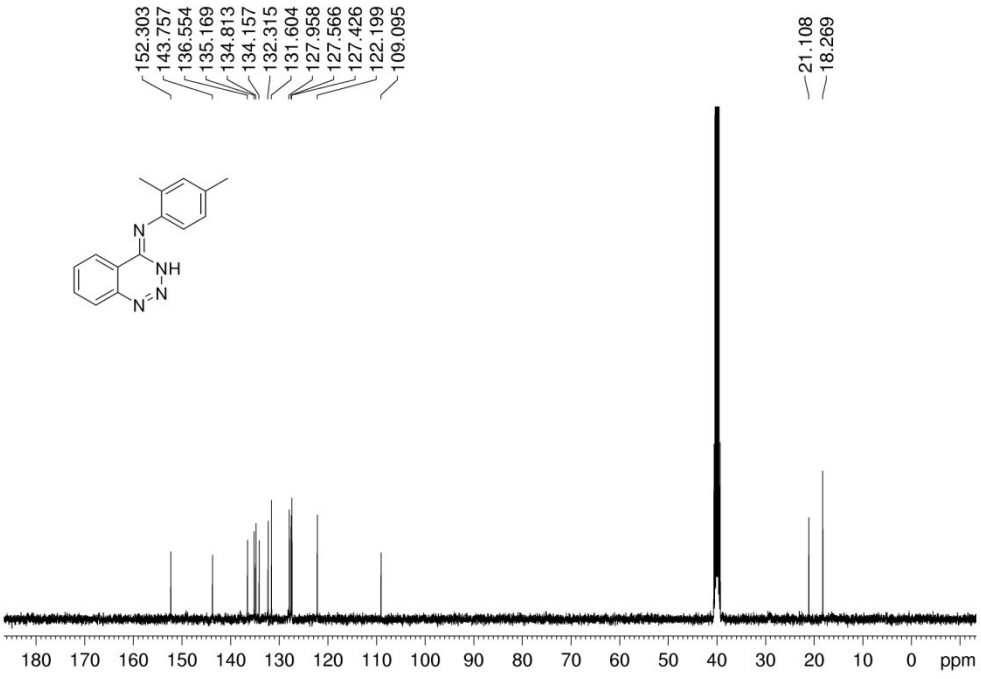
^{1}H NMR spectrum of compound 3ra



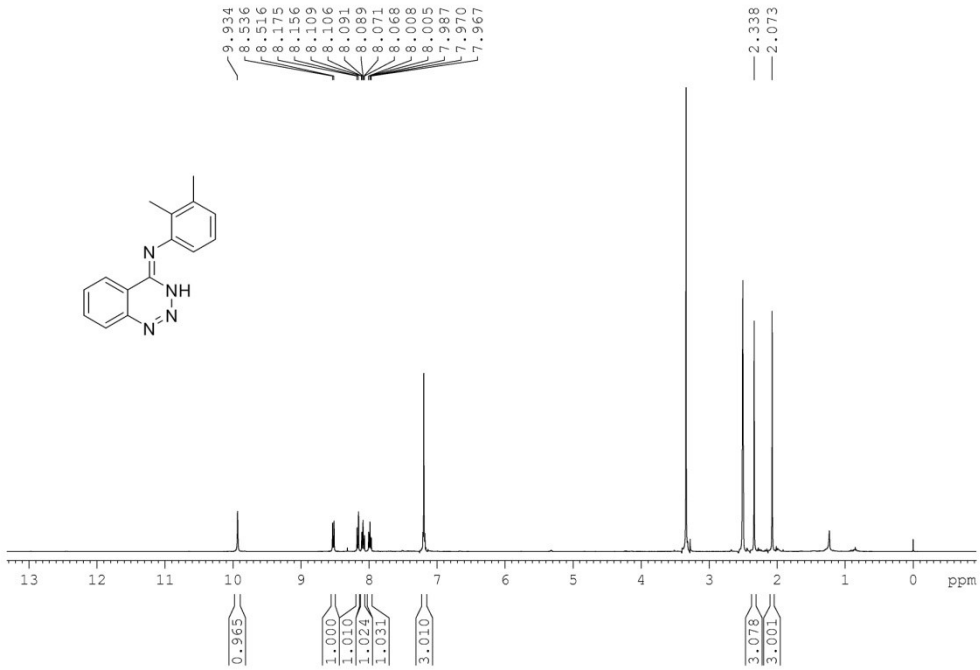
^{13}C NMR spectrum of compound 3ra



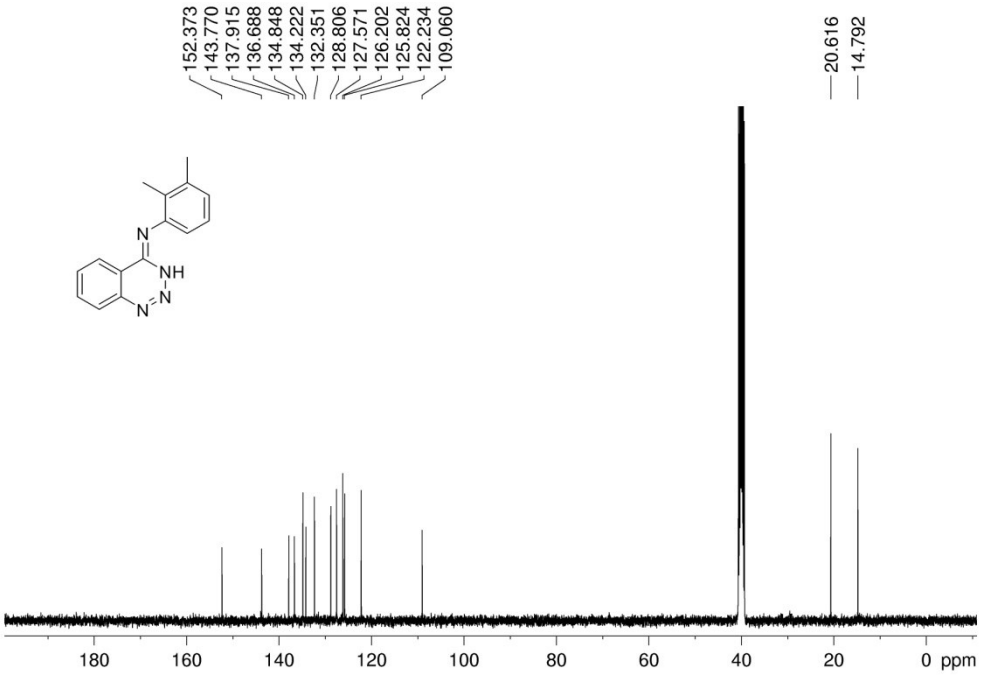
^{1}H NMR spectrum of compound 3sa



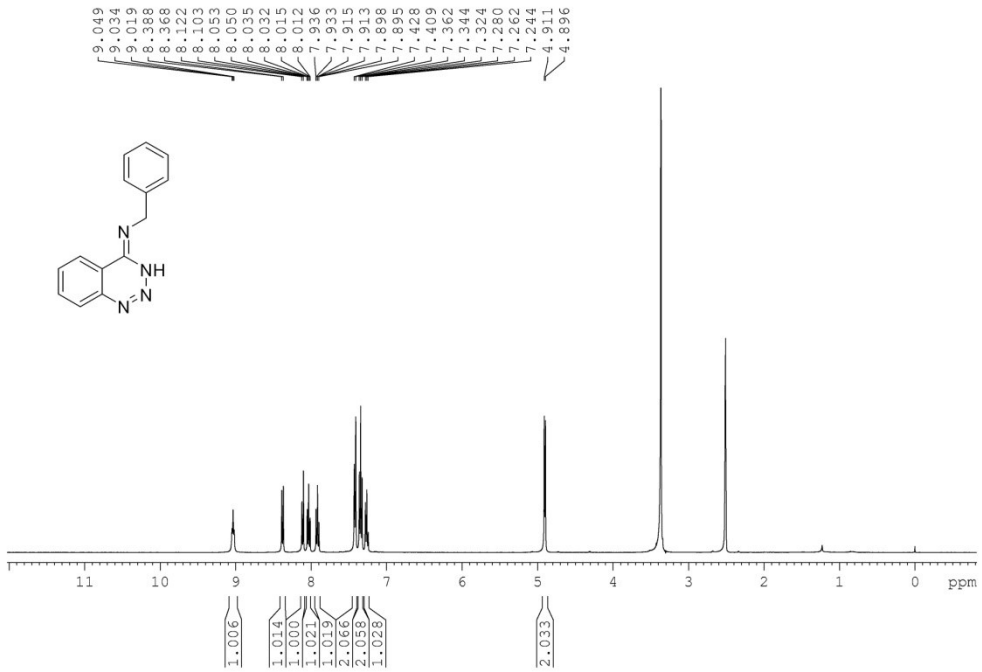
^{13}C NMR spectrum of compound 3sa



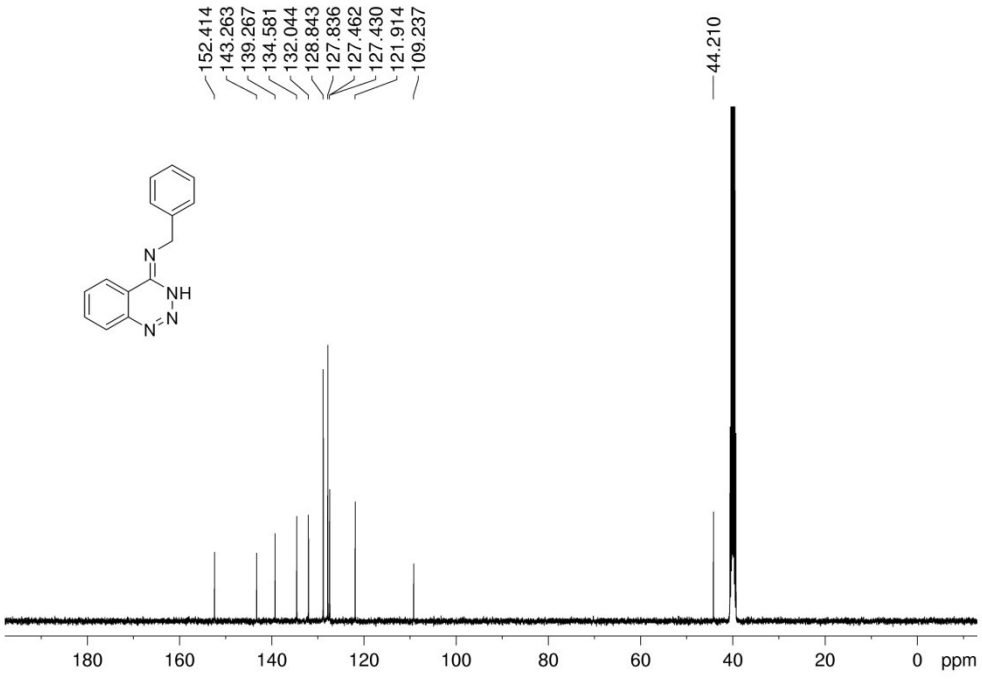
^{1}H NMR spectrum of compound 3ta



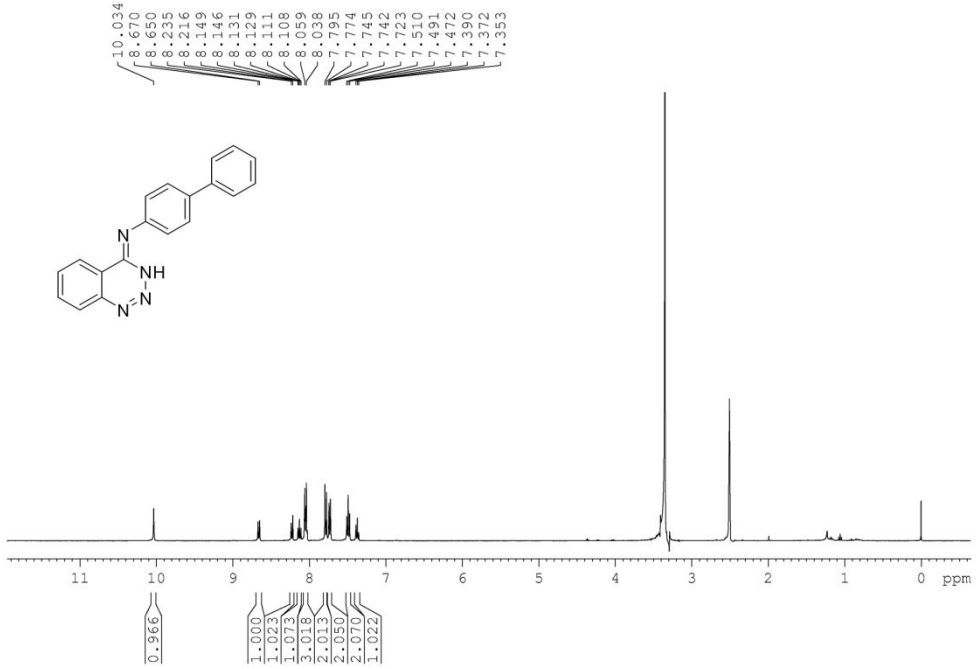
^{13}C NMR spectrum of compound 3ta



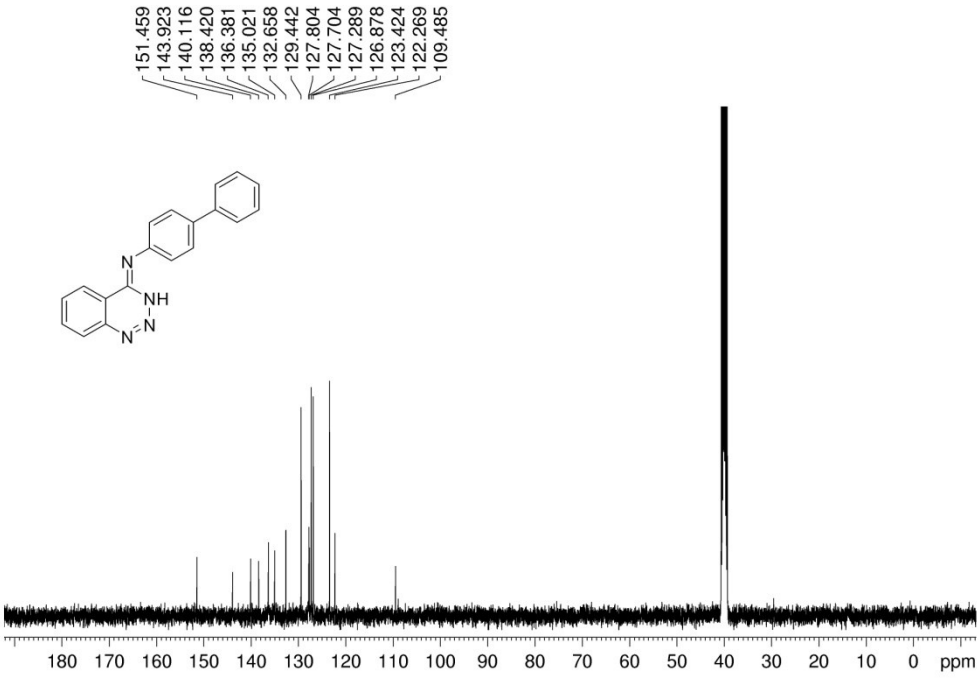
^{1}H NMR spectrum of compound 3ua



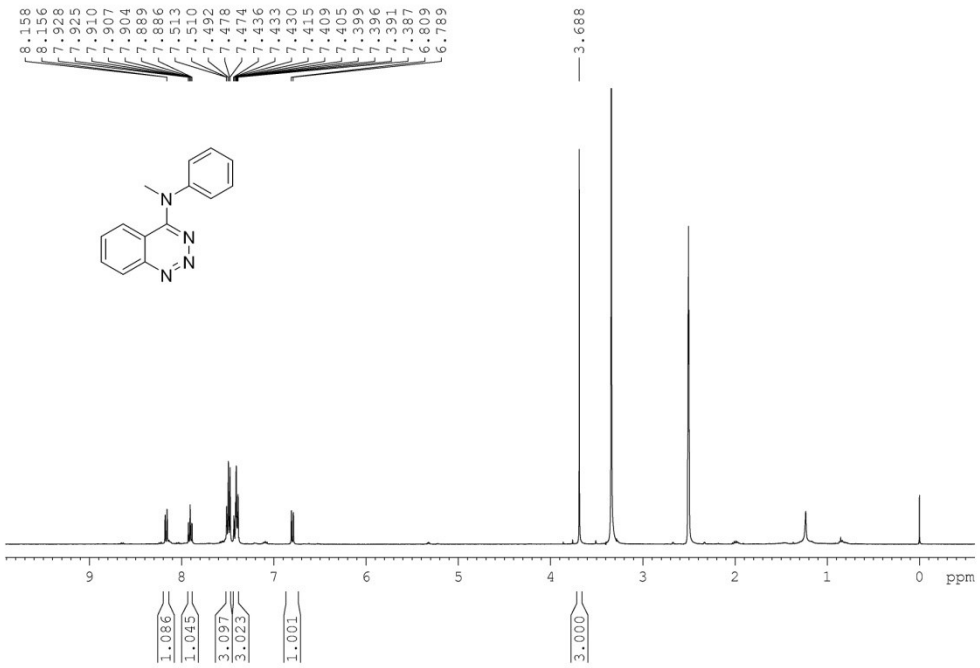
^{13}C NMR spectrum of compound 3ua



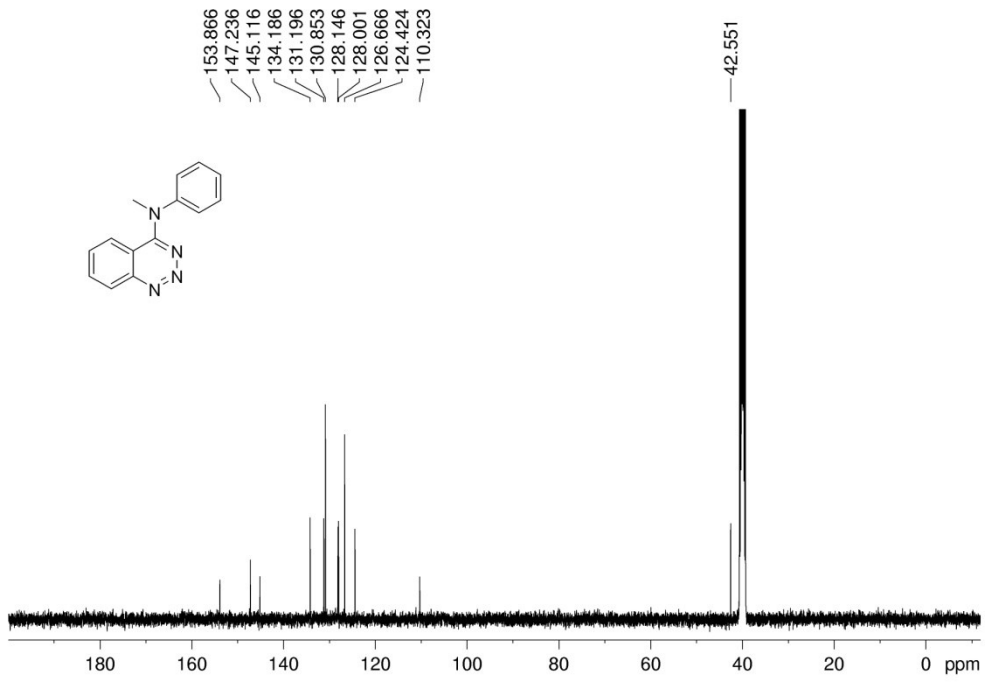
^{1}H NMR spectrum of compound 3va



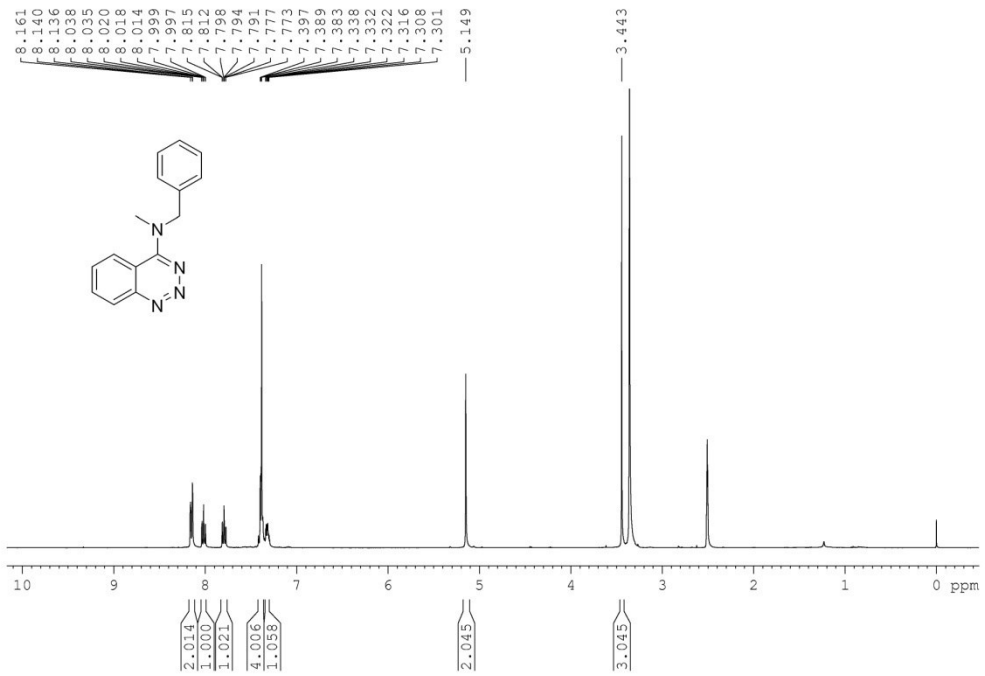
^{13}C NMR spectrum of compound 3va



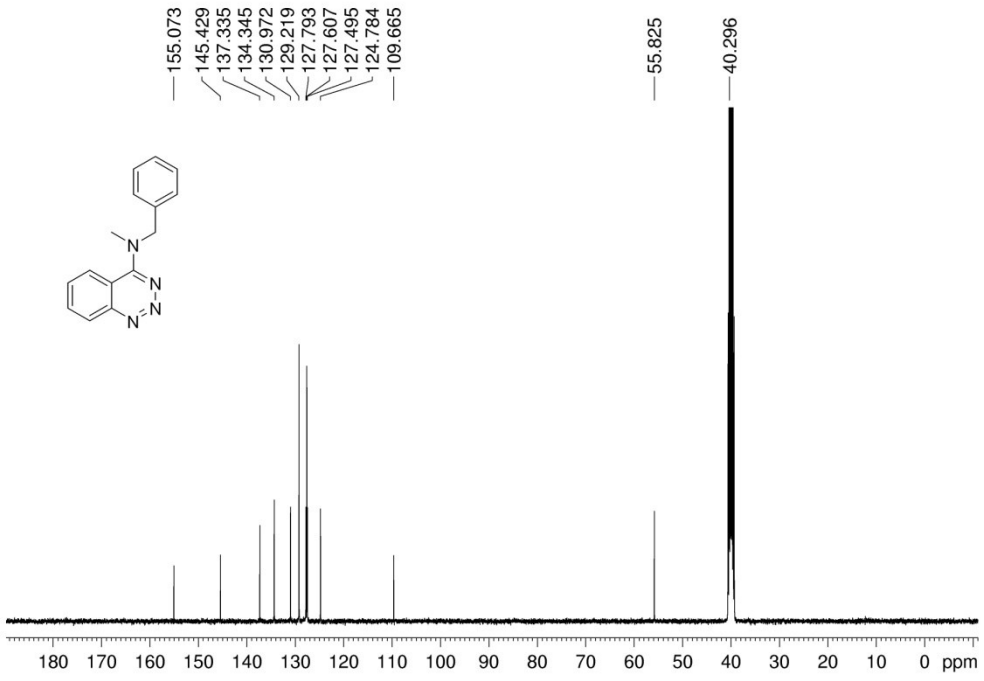
^{1}H NMR spectrum of compound 3wa



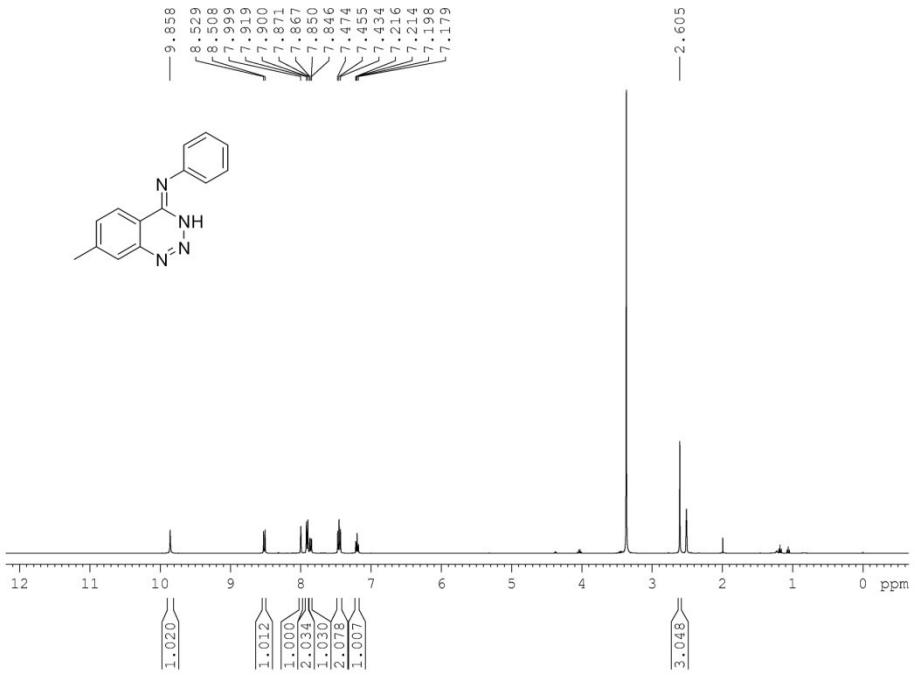
^{13}C NMR spectrum of compound 3wa



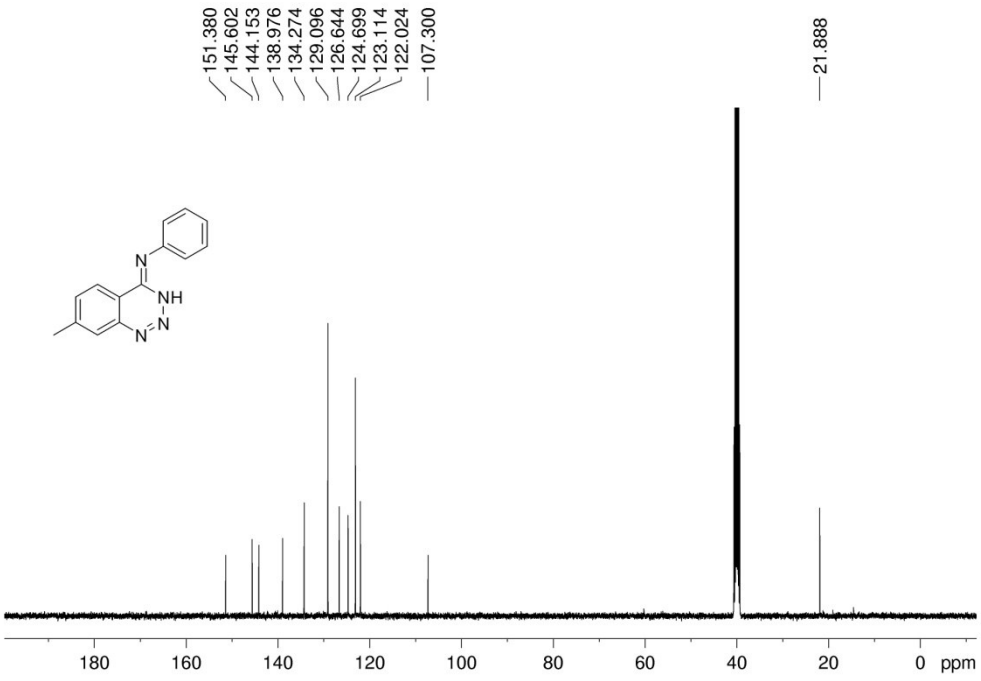
^{1}H NMR spectrum of compound 3xa



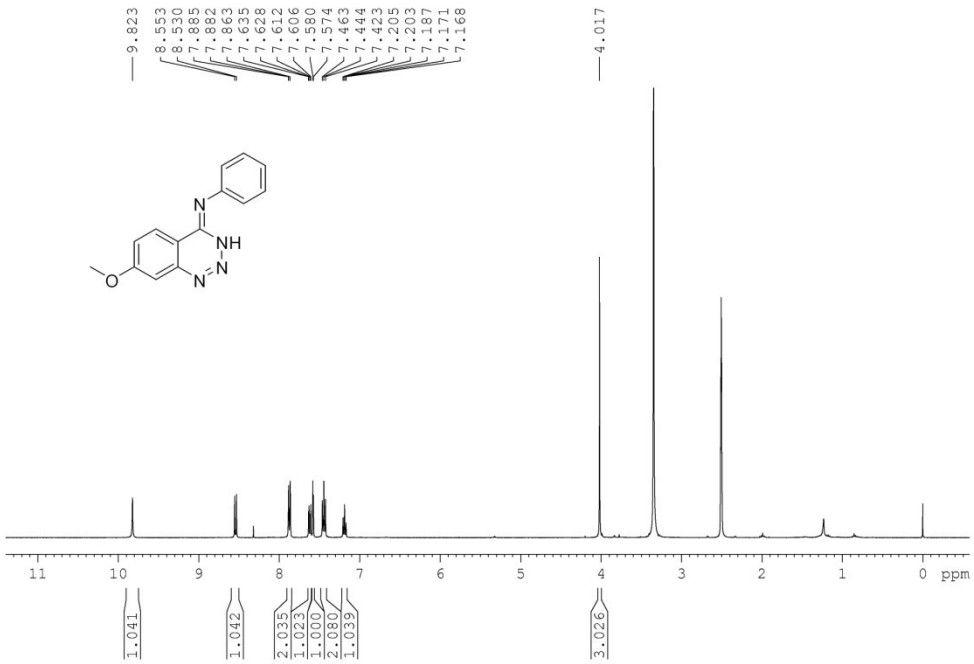
^{13}C NMR spectrum of compound 3wa



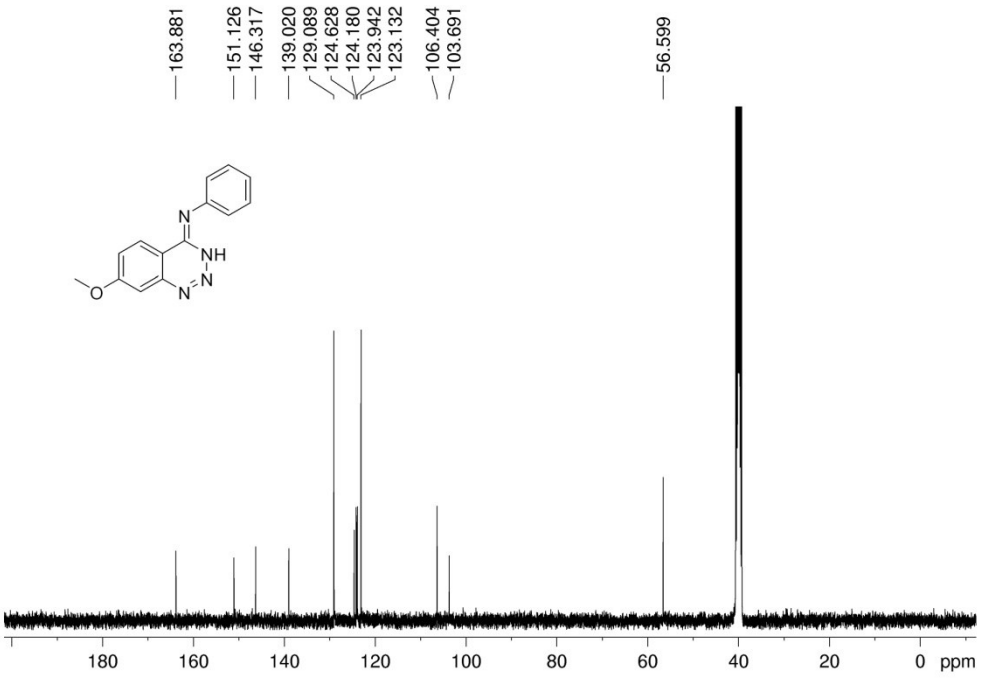
^{1}H NMR spectrum of compound 3ab



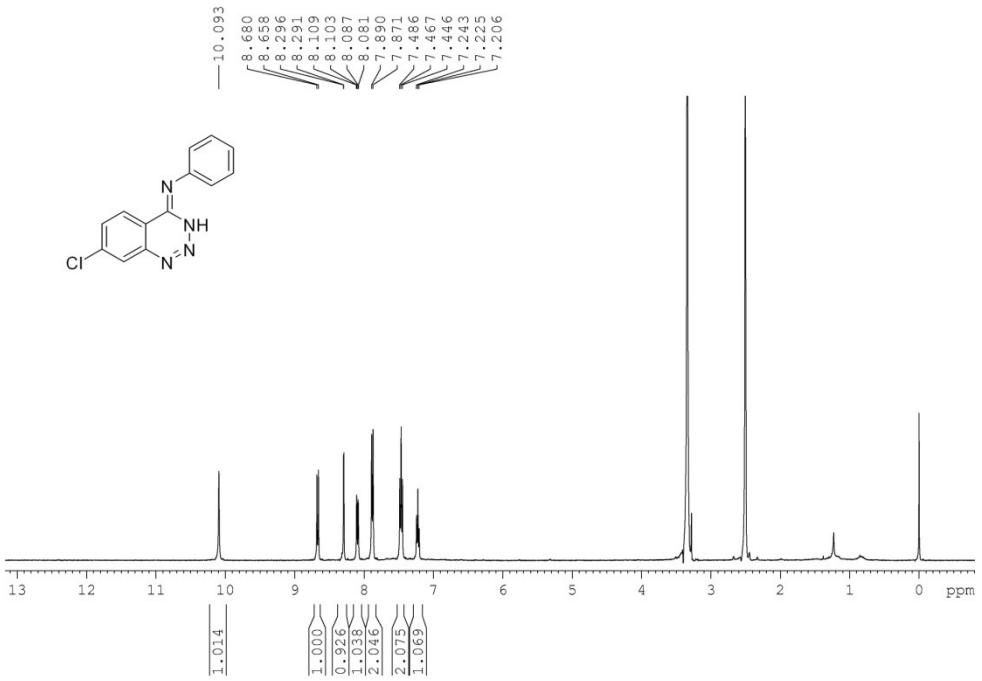
^{13}C NMR spectrum of compound 3ab



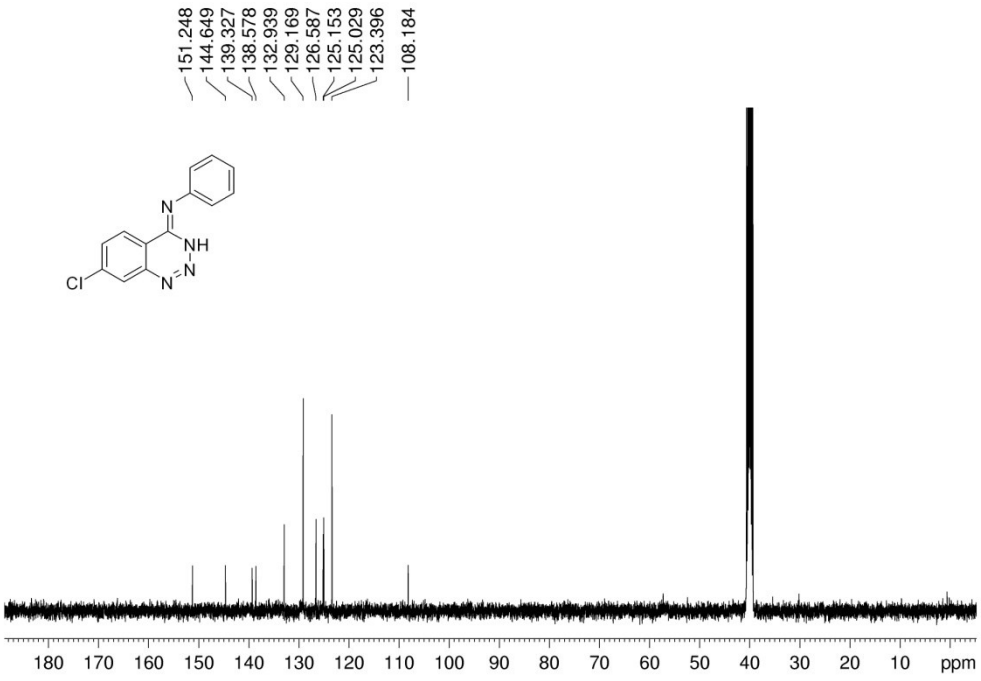
^{1}H NMR spectrum of compound 3ac



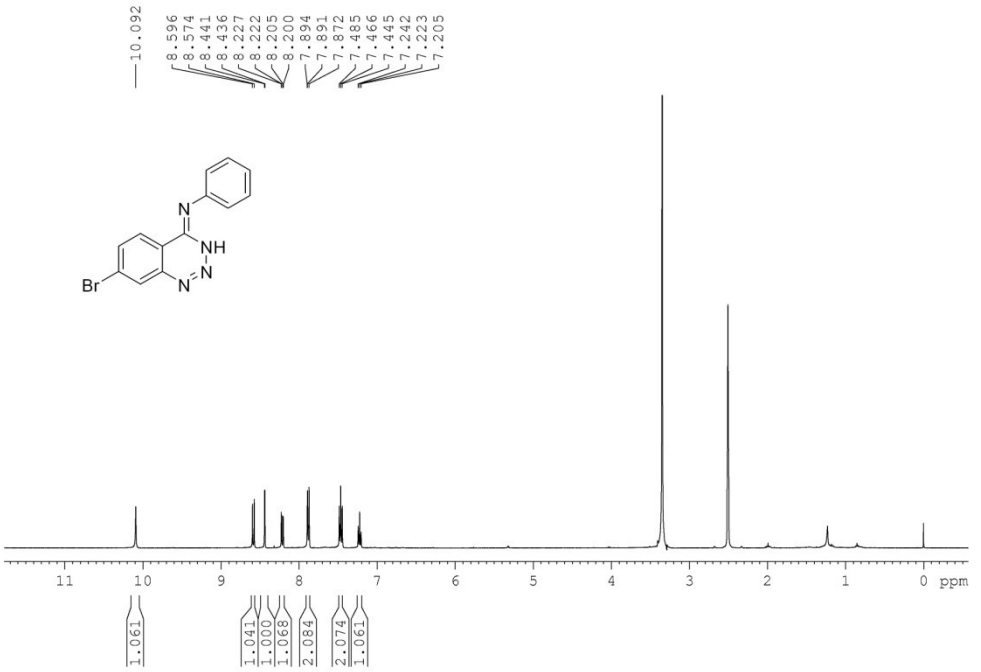
^{13}C NMR spectrum of compound 3ac



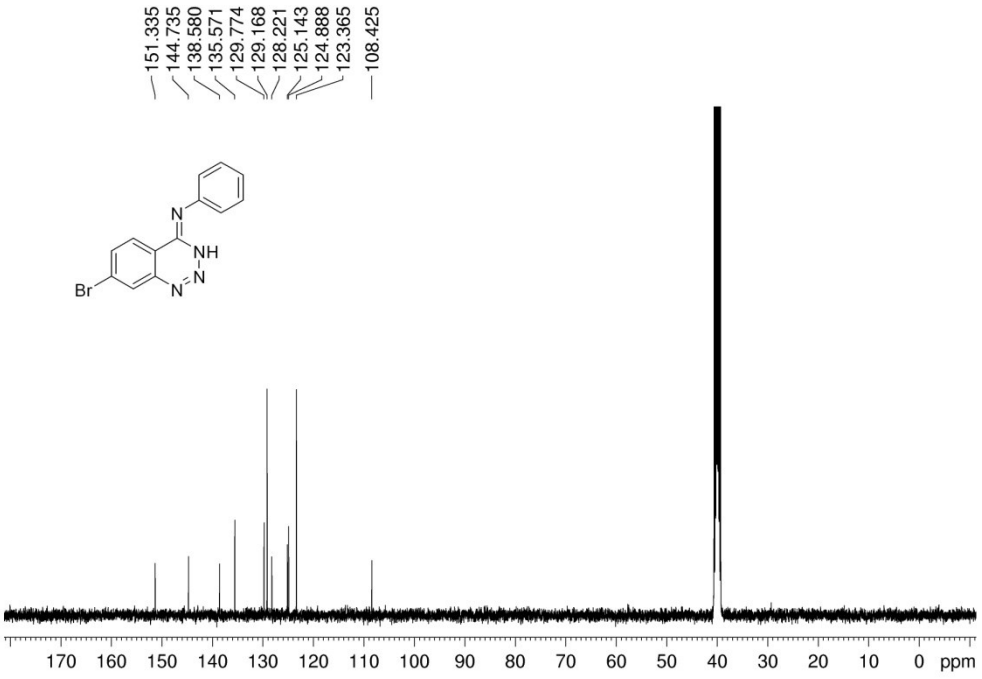
^{1}H NMR spectrum of compound 3ad



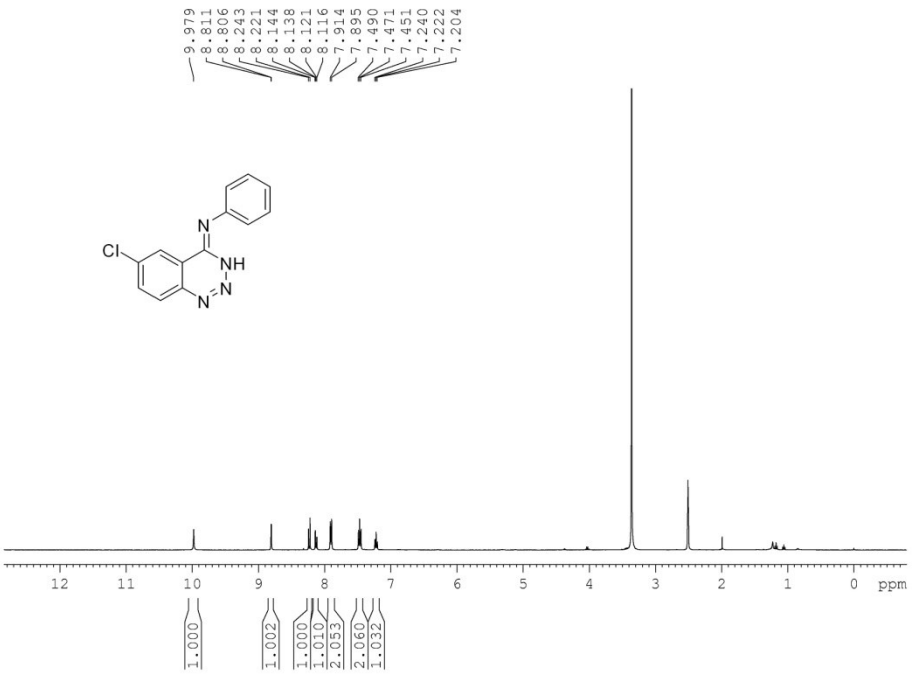
^{13}C NMR spectrum of compound 3ad



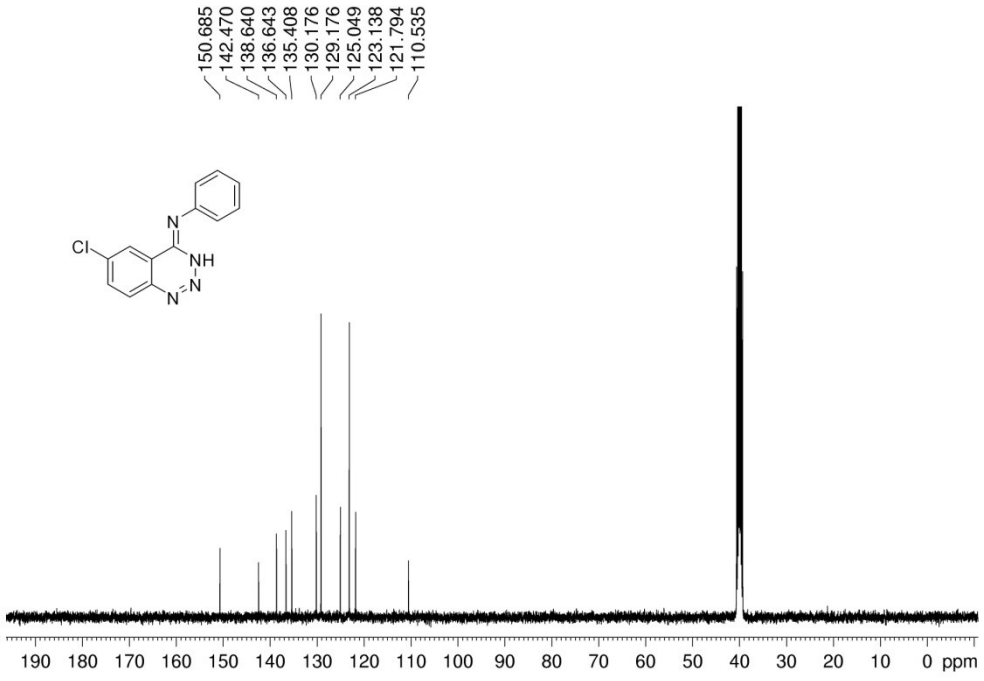
^{1}H NMR spectrum of compound 3ae



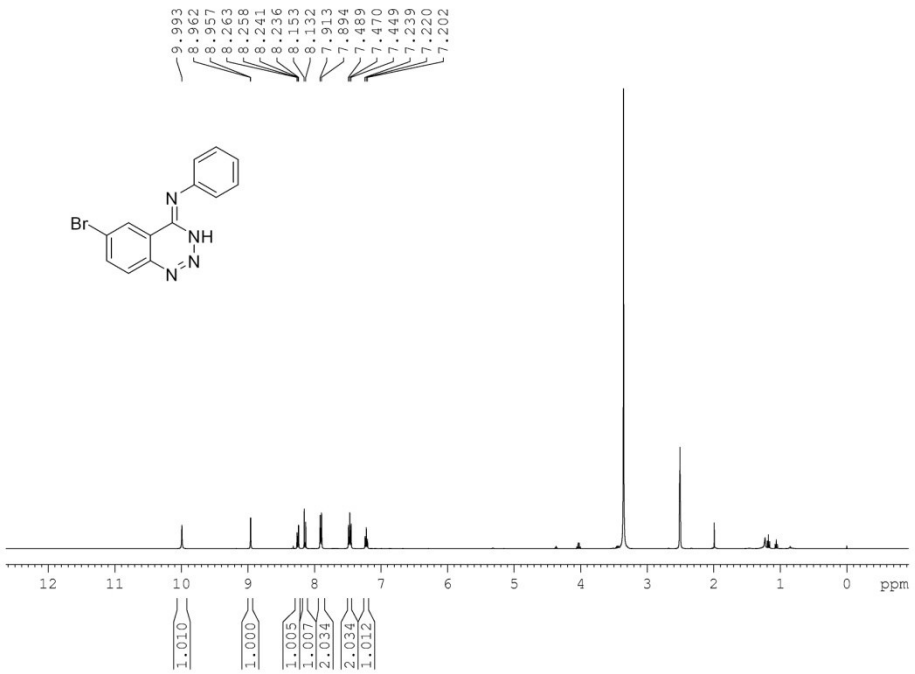
^{13}C NMR spectrum of compound 3ae



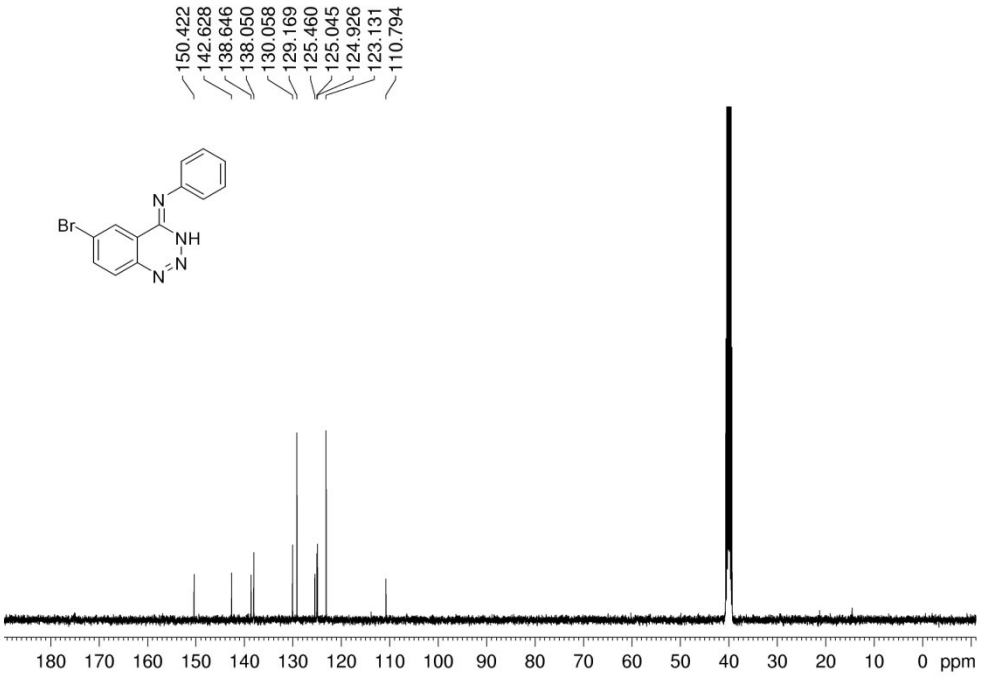
^{1}H NMR spectrum of compound 3af



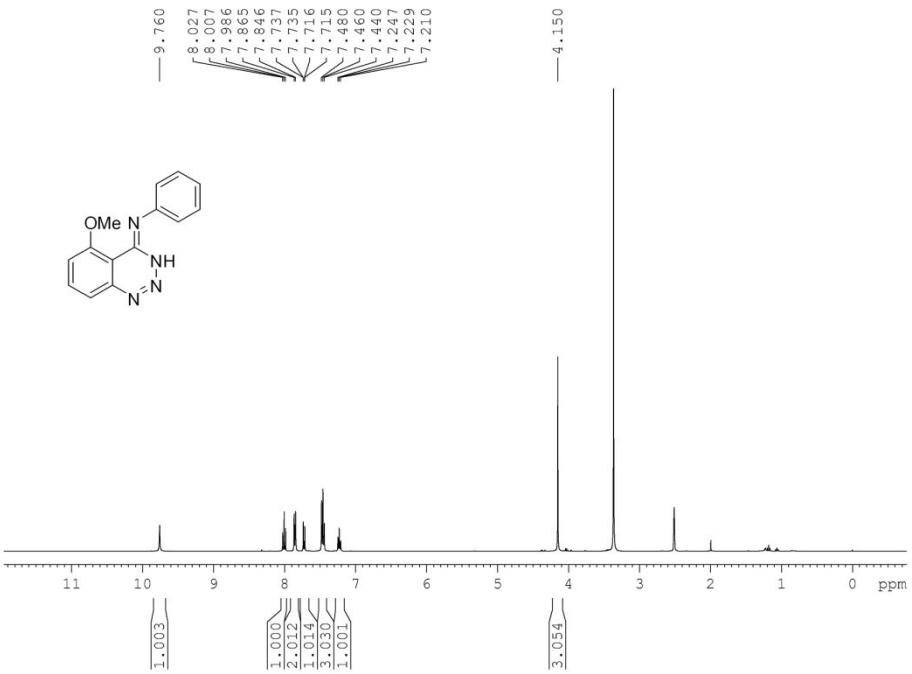
^{13}C NMR spectrum of compound 3af



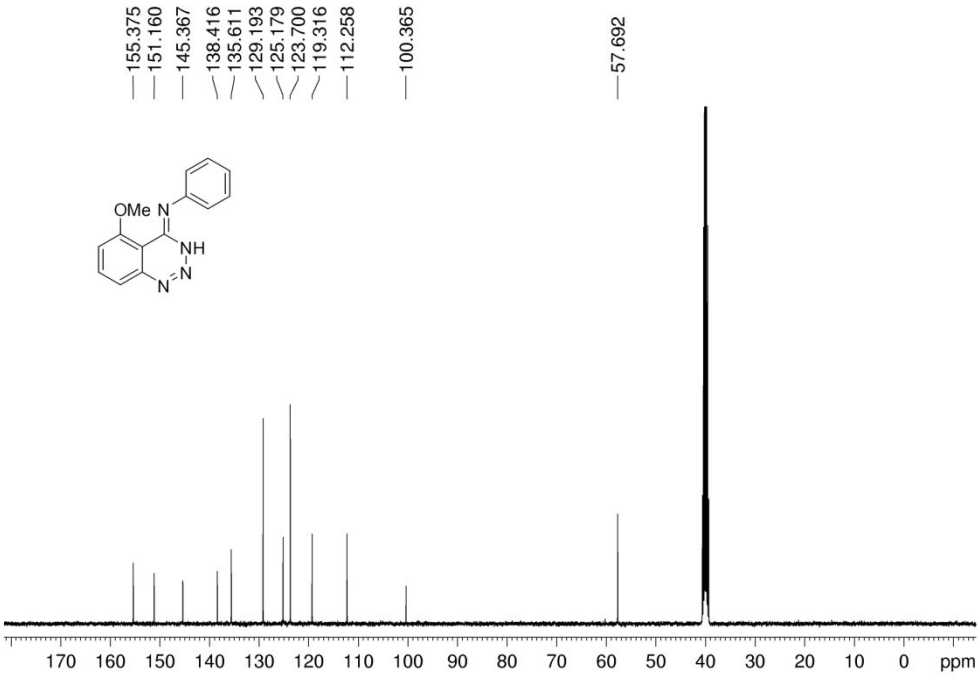
^{1}H NMR spectrum of compound 3ag



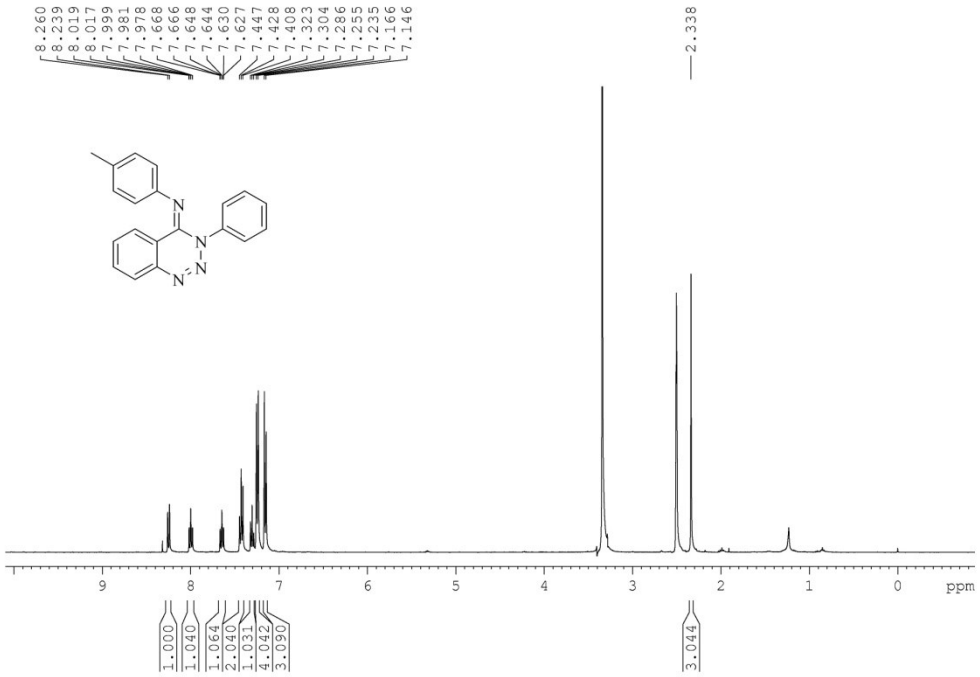
^{13}C NMR spectrum of compound 3ag



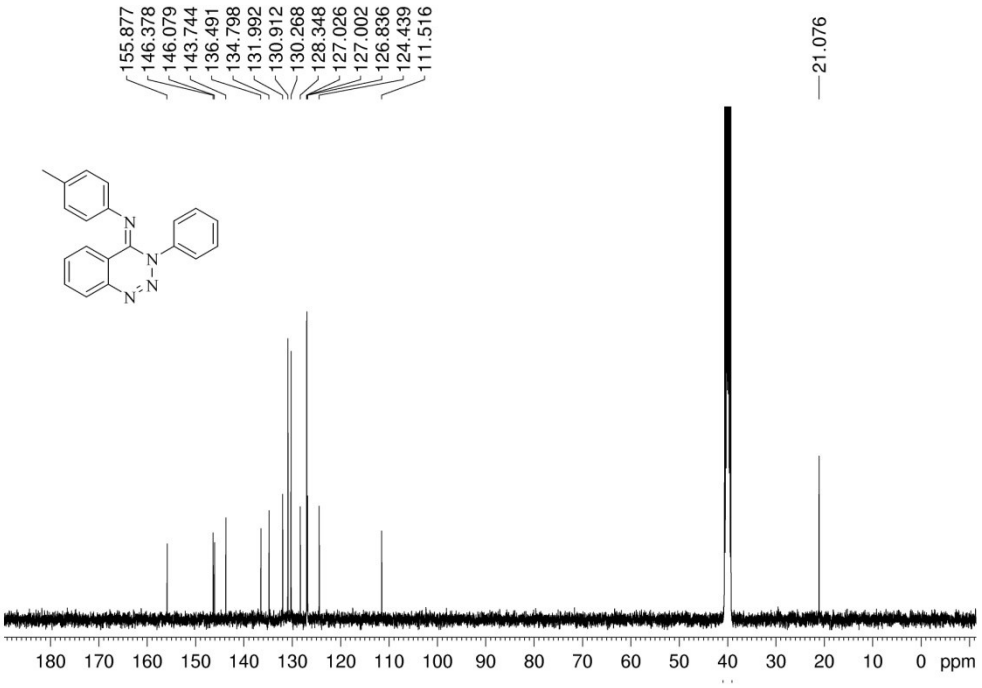
^{1}H NMR spectrum of compound 3ai



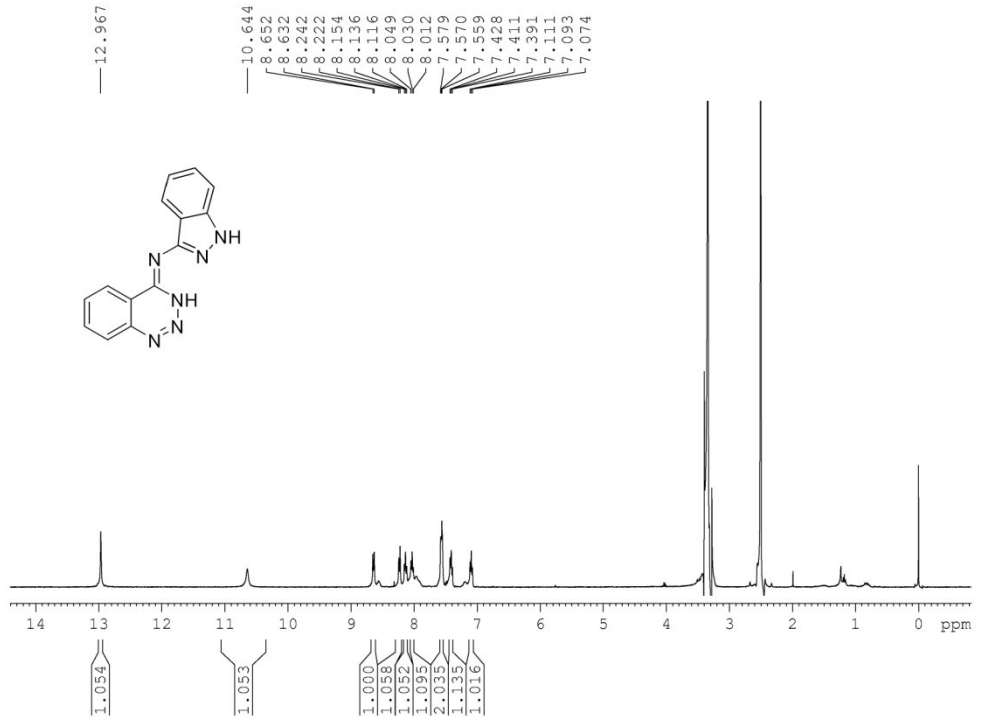
^{13}C NMR spectrum of compound 3ai



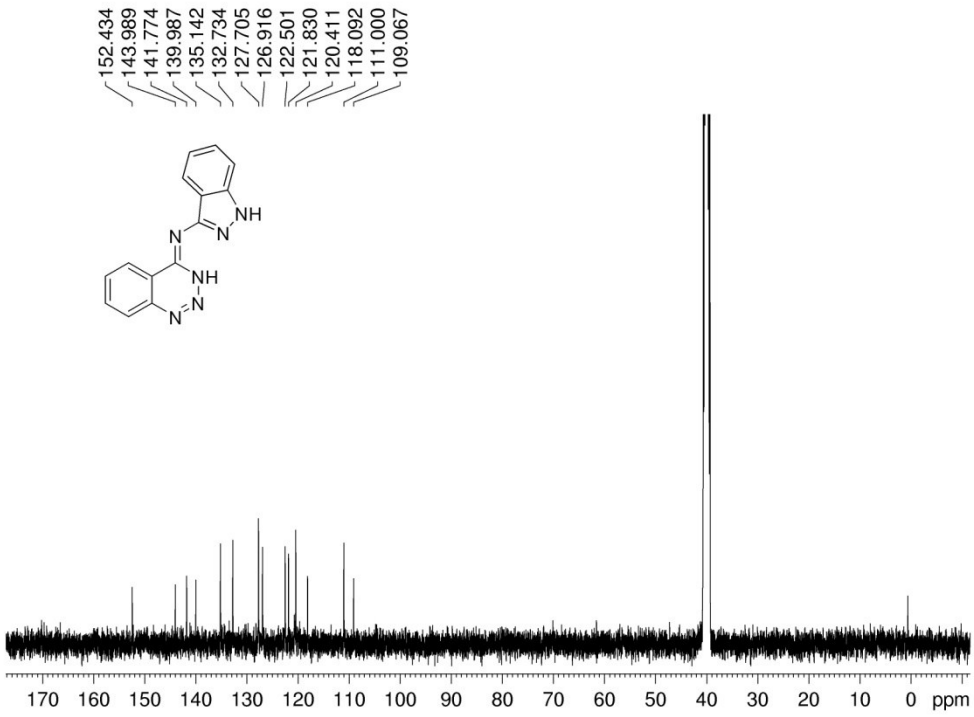
^{1}H NMR spectrum of compound 4aa



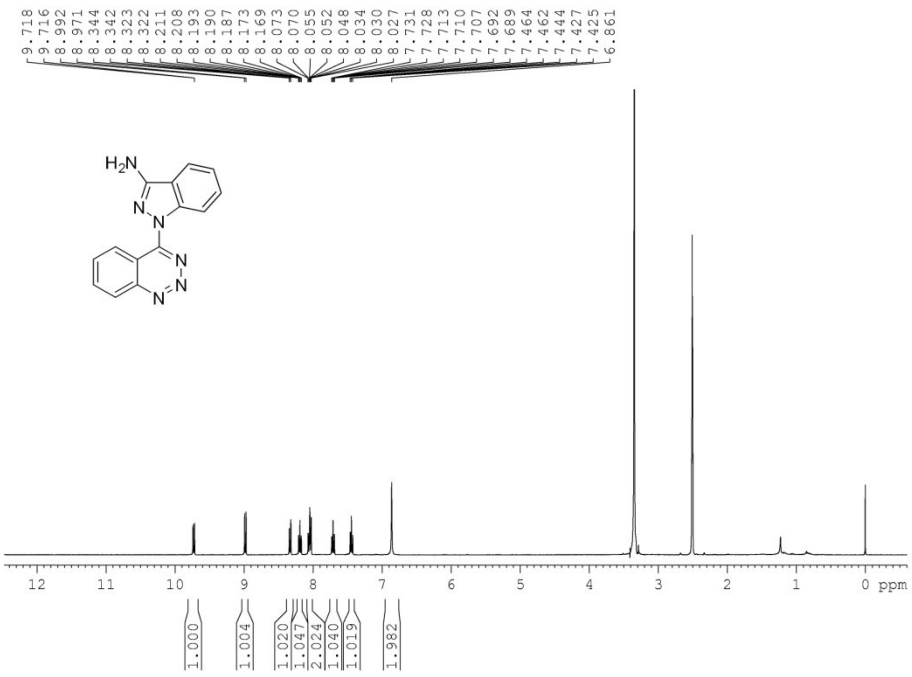
^{13}C NMR spectrum of compound 4aa



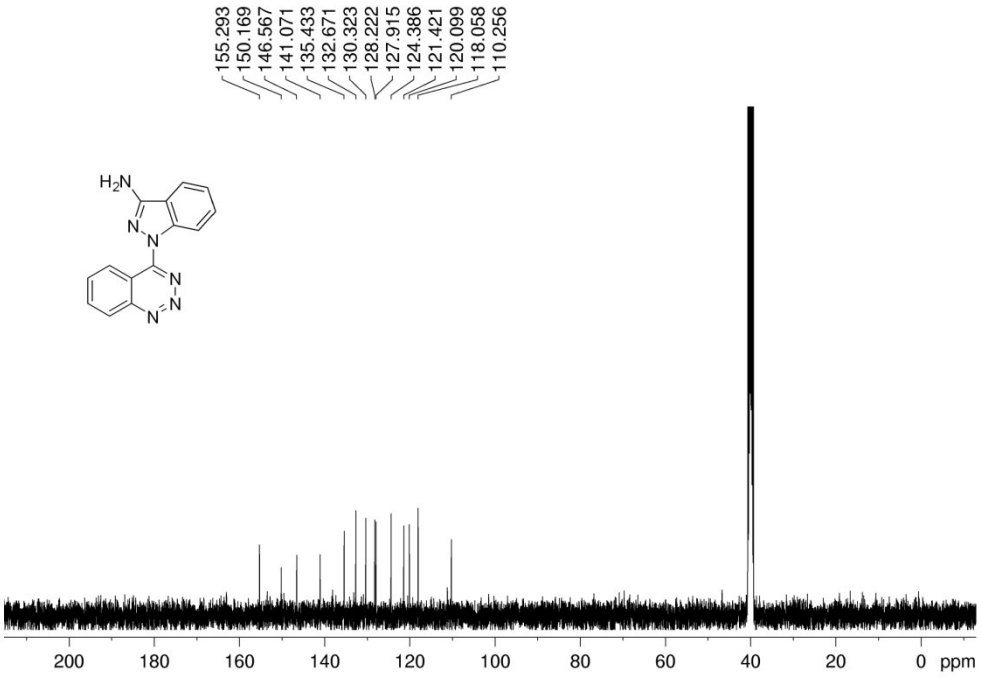
^{1}H NMR spectrum of compound 5aa



^{13}C NMR spectrum of compound 5aa



^{1}H NMR spectrum of compound 6aa



^{13}C NMR spectrum of compound 6aa