Supporting information

Imine-directed Ru(II)-Catalyzed *ortho*-C(sp²)–H Amidation of 3-arylquinoxalin-2(1*H*)-ones via Nitrene Transfer from Acyl/Heteroacyl Azides

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1. **General Information:**

   All chemicals and solvents were purchased from Alfa-Aesar, Thermo Fischer Scientific, India Pvt. Limited, Sigma-Aldrich Chemicals Pvt. Limited India and from local commercial sources, and were used without any further purification unless otherwise specified. Solvents for column chromatography were dried and distilled before use. Solvents were removed under reduced pressure using rotary evaporator, followed by further removal of the residual solvent under high vacuum. Column chromatography was performed on silica gel (100-200 mesh size). Melting points were determined on Buchi M-560 instrument and are uncorrected. HRMS analysis was carried out using Agilent G6530AA LC Q-TOF mass spectrometer using ESI method. The IR spectra of compounds were recorded on Perkin-Elmer model 2000 FT-IR spectrometer and are expressed as wavenumber (cm^{-1}). R_f values of compounds are reported from analytical TLC study using the specified solvents and 0.25 mm silica gel 60 F_{254} plates that were visualized by UV irradiation. The ^1H- and the ^{13}C-NMR spectra were recorded on Bruker-Avance Neo 400 FT-NMR spectrometers by using tetramethylsilane (TMS) as internal standard. The chemical shift values are on δ scale and the coupling constant (J) are in Hz. 1-alkyl-3-phenylquinoxalin-2(1*H*)-ones derivatives were well known compounds and were prepared according to protocol reported in literature[a-c]. Benzoylzides were synthesized using the literature protocol.[d]

2. **General Procedure for the synthesis of compounds 3aa-fb, 4ga-hd, 5ae-ge, 5ef, 5ld & 5ma**

   An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of 1-alkyl-3-phenylquinoxalin-2(1*H*)-ones **1** (1.0 equiv.), Benzoylazides **2** (1.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%), $AgSbF_6$ (20 mol%), anhydrous $Cu(OAc)_2$ (10 mol%) and DCE (3.0 mL). The resulting reaction mixture was stirred at 110 ^oC for 10 h. The progress of the reaction was monitored by analytical TLC. After completion of the reaction, the reaction mixture was cooled to ambient temperature, diluted with water and extracted with EtOAc (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the crude product. The crude product thus obtained was purified on a silica gel column using hexane/ethyl acetate as eluent to afford the pure products **3aa-fb**, **4ga-hd, 5ae-ge, 5ef, 5ld** & **5ma** in 60-90% yields.

3. **General Procedure for the synthesis of compound 5ag**

   An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of 3-arylquinoxalin-2(1*H*)-ones **1a** (1.0 equiv.), acetyl azide **2g** (1.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%), $AgSbF_6$ (20 mol%), anhydrous $Cu(OAc)_2$ (10 mol%) and DCE (3.0

mL). The resulting reaction mixture was stirred at 110 °C for 10 h. The progress of the reaction was monitored by analytical TLC examination. But no product was obtained.

4. **General Procedure for the synthesis of compound 6ie**

An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of ethyl 2-(2-oxo-3-phenyl-quinoxalin-1(2*H*)-yl acetate **1i** (1.0 equiv.), Theonylazide **2e** (1.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%), $AgSbF_6$ (20 mol%), anhydrous $Cu(OAc)_2$ (10 mol%) and DCE (3.0 mL). The resulting reaction mixture was stirred at 110 °C for 10 h. The progress of the reaction was monitored by analytical TLC examination. After completion of the reaction, the reaction mixture was cooled to ambient temperature, diluted with water and extracted with EtOAc (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the crude product. The crude product thus obtained was purified on a silica gel column using hexane/ethyl acetate as eluent to afford the pure product **6ie** in 75% yield.

5. **General Procedure for the synthesis of compound 6ja**

An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of 1-(2-oxo-2-phenylethyl)-3-phenylquinoxalin-2(1*H*)-ones **1j** (1.0 equiv.), Benzoylazide **2a** (1.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%), $AgSbF_6$ (20 mol%), anhydrous $Cu(OAc)_2$ (10 mol%) and DCE (3.0 mL). The resulting reaction mixture was stirred at 110 °C for 10 h. The progress of the reaction was monitored by analytical TLC examination. After completion of the reaction, the reaction mixture was cooled to ambient temperature, diluted with water and extracted with EtOAc (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the crude product. The crude product thus obtained was purified on a silica gel column using hexane/ethyl acetate as eluent to afford the pure product **6ja** in 78% yield.

6. **General Procedure for the synthesis of compound 6ka**

An oven dried 10 mL screw capped reaction vial with a small stirring bar was charged with a mixture of 2-phenylpyridine **1k** (1.0 equiv.), Benzoylazide **2a** (1.5 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (10 mol%), $AgSbF_6$ (20 mol%), anhydrous $Cu(OAc)_2$ (10 mol%) and DCE (3.0 mL). The resulting reaction mixture was stirred at 110 °C for 10 h. The progress of the reaction was monitored by analytical TLC examination. After completion of the reaction, the reaction mixture was cooled to ambient temperature, diluted with water and extracted with EtOAc (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated on a rotary evaporator to obtain the crude product. The

crude product thus obtained was purified on a silica gel column using hexane/ethyl acetate as eluent to afford the pure product **6ka** in 75% yield.

7. Key References

a) Yan S., Ye L., Liu M., Chen J., Ding J., Gao W., Huang X and Wu H. Unexpected TFA-catalyzed tandem reaction of benzo [d] oxazoles with 2-oxo-2-arylacetic acids: synthesis of 3-aryl-2 H-benzo [b][1, 4] oxazin-2-ones and cephalandole A. *RSC Adv*, **2014**, *4*, 16705-16709.

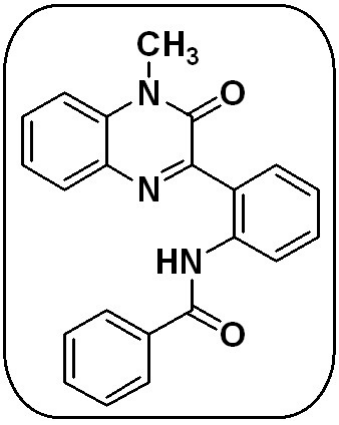
b) Xue Z Y., Jiang Y., Peng X Z., Yuan W C and Zhang X M. The first general, highly enantioselective Lewis base organo-catalyzed hydrosilylation of benzoxazinones and quinoxalinones. *Adv. Synth. Catal.*, **2010**, *352*, 2132-2136.

c) Nonell S., Ferreras L R., Cañete A., Lemp E., Günther G., Pizarro N. and Zanocco A.L. Photophysics and photochemistry of naphthoxazinone derivatives. *J. Org. Chem.*, **2008**, *73*, 5371-5378.

d) Banert K., Berndt C., Hagedorn M., Liu H., Anacker T., Friedrich J. and Rauhut G., Experimental and theoretical studies on the synthesis, spectroscopic data, and reactions of formyl azide. *Angew. Chem. Int. Ed.*, **2012**, *51*, 4718-4721.

Analytical Data

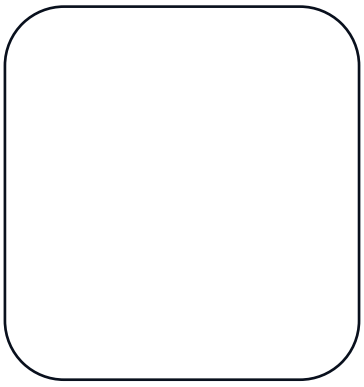
3-(2-amino-*N*-(benzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3aa)



It was obtained as light yellow solid having melting point 170-172 ^{o}C with 85% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3567, 2885, 1670, 1641.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.53 (s, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.21 (d, J =8.0 Hz, 1H), 7.95 (d, J = 7.5 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.54-7.52 (m, 2H), 7.48-7.39 (m, 5H), 3.81 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 165.42, 154.77, 154.60, 137.68, 135.40, 133.26, 131.99, 131.73, 131.68, 131.31, 131.12, 130.21, 129.64, 129.19, 128.63, 127.32, 124.87, 124.26, 123.49, 122.89, 114.02, 29.87. **HRMS (ESI^{+}):** m/z [M+H]$^{+}$ calculated for $C_{22}H_{18}N_3O_2^{+}$: 356.1394; found: 356.1392.

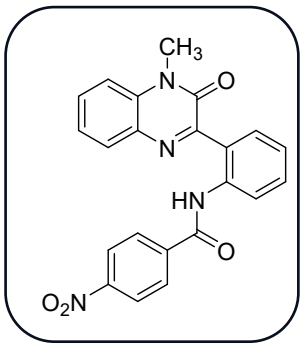
3-(2-amino-N-(4-methoxybenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3ab)



It was obtained as yellow solid having melting point 195-197 ^{o}C with 84% yield. R_f= 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3261, 2987, 2887, 1672, 1643.

^{1}H NMR (400 MHz, Chloroform-d): δ 12.34 (s, 1H), 8.41-8.38 (m, 2H), 8.00-7.97 (m, 2H), 7.83 (dd, J = 8.1, 1.5 Hz, 1H), 7.61-7.45 (m, 4H), 7.41-7.36 (m, 2H), 6.79 (dd, J = 9.0, 2.7 Hz, 1H), 3.94 (s, 3H), 3.80 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 165.81, 142.80, 140.28, 133.93, 133.26, 131.76, 130.39, 128.94, 128.64, 127.41, 125.35, 125.09, 124.02, 121.17, 113.89, 110.01, 106.24, 55.52, 29.83. **HRMS (ESI^{+}):** m/z [M+H]$^{+}$ calculated for $C_{23}H_{20}N_3O_3^{+}$: 386.1499; found: 386.1498.

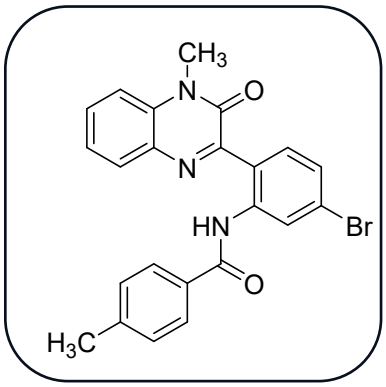
3-(2-amino-*N*-(4-nitrobenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3ac)



It was obtained as light yellow solid having melting point 199-201 °C with 62% yield. R_f = 0.33 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3122, 2124, 1648, 1560, 1505.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.46 (s, 1H), 8.45 (d, J = 8.3 Hz, 1H), 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 7.98-7.94 (m, 2H), 7.88 (dd, J = 8.0, 1.5 Hz, 1H), 7.65 (m, 1H), 7.56-7.51 (m, 1H), 7.46-7.40 (m, 2H), 7.13 (t, J = 8.6 Hz, 2H), 7.00 (t, J = 8.6 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d):** δ 164.36, 154.64, 154.07, 153.41, 137.55, 133.24, 131.79, 131.33, 131.21, 129.69, 125.16, 124.37, 124.01, 123.69, 122.96, 115.78, 115.56, 114.07, 29.89. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{22}H_{17}N_4O_4^+$: 401.1244; found: 401.1240.

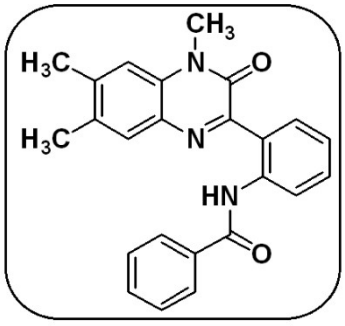
3-(2-amino-4-bromo-*N*-(4-methylbenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one. (3dd)



It was obtained as light yellow solid having melting point 176-178 °C with 80% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3162, 2984, 2885, 1672, 1643, 682.

^{1}H NMR (400 MHz, Chloroform-d): δ 9.76 (s, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.74 (d, J =7.9 Hz, 3H), 7.34 (s, 2H), 7.13 (d, J = 8.0 Hz, 3H), 6.73 (s, 1H), 6.54 (s, 1H), 3.49 (s, 3H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 163.74, 154.52, 149.62, 141.33, 136.24, 134.56, 133.43, 129.07, 128.90, 128.68, 128.54, 128.45, 128.32, 126.54, 124.73, 123.33, 121.00, 120.24, 120.24, 120.01, 20.62, 19.82. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}BrN_3O_2^+$: 448.0655; found: 448.0650.

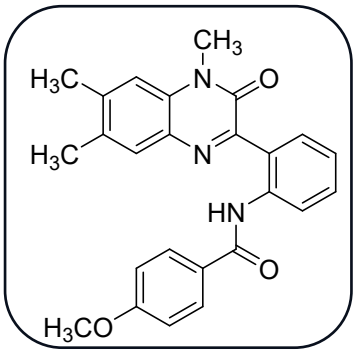
3-(2-amino-*N*-(benzoyl)phenyl)-6,7-dimethyl-1-methylquinoxalin-2(1*H*)-one (3ba)



It was obtained as light yellow solid having melting point 178-180 °C with 81% yield. R_f = 0.36 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3300, 2989, 2967, 1656, 1643.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.69 (s, 1H), 8.52 (d, J = 8.3 Hz, 1H), 8.22 (dd, J =7.9, 1.6 Hz, 1H), 7.97 (dd, J = 7.1, 1.8 Hz, 2H), 7.65 (s, 1H), 7.55-7.50 (m, 2H), 7.47-7.44 (m, 2H), 7.24-7.22 (m, 1H), 7.15 (s, 1H), 3.78 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 165.33, 154.84, 153.13, 141.38, 137.70, 135.70, 135.53, 133.38, 131.67, 131.64, 131.35, 131.00, 130.42, 129.67, 128.54, 127.42, 125.01, 123.40, 122.68, 114.48, 29.77, 20.78, 19.32. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{24}H_{22}N_3O_2^+$: 384.1707; found: 384.1706.

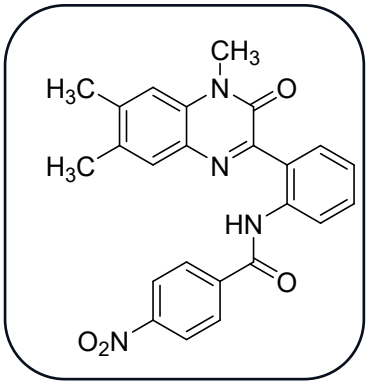
3-(2-amino-N-(4-methoxybenzoyl)phenyl)-6,7-dimethyl-1-methylquinoxalin-2(1*H*)-one (3bb)



It was obtained as yellow solid having melting point 193-195 °C with 80% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3294, 2836, 1632, 1606, 1554.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.54 (s, 1H), 8.48 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 7.15 (s, 1H), 6.94 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), 3.78 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.95, 162.35, 141.29, 137.87, 133.33, 131.61, 130.95, 130.50, 129.69, 129.25, 127.85, 123.21, 122.73, 122.23, 114.55, 114.47, 114.34, 113.72, 55.44, 29.75, 20.74, 19.30. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{25}H_{24}N_3O_3^+$: 414.1812; found: 414.1810.

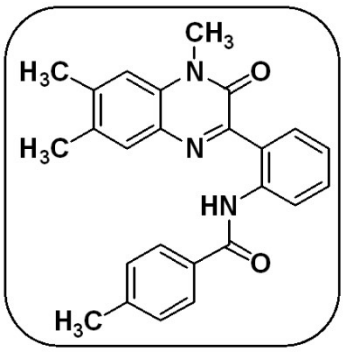
3-(2-amino-*N*-(4-nitrobenzoyl)phenyl)-6,7-dimethyl-1-methylquinoxalin-2(1*H*)-one (3bc)



It was obtained as light yellow solid having melting point 201-203 °C with 65% yield. R_f = 0.36 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3260, 2918, 1672, 1632.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.78 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.24 (dd, J = 8.0, 1.6 Hz, 1H), 7.79-7.76 (m, 1H), 7.70-7.68 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 1H), 7.26-7.20 (m, 2H), 7.16 (s, 1H), 3.79 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 161.57, 154.84, 153.00, 141.53, 137.43, 133.61, 131.73, 131.35, 131.04, 130.37, 130.28, 130.20, 129.64, 124.95, 123.62, 123.21, 122.57, 118.72, 118.51, 114.50, 114.28, 29.78, 20.78, 19.19. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{24}H_{21}N_4O_4^+$: 429.1557; found: 429.1555.

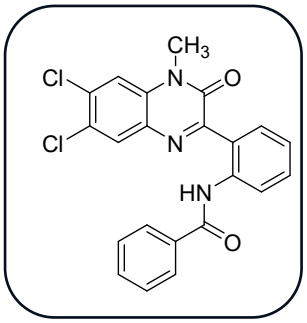
3-(2-amino-*N*-(4-methylbenzoyl)phenyl)-6,7-dimethyl-1-methylquinoxalin-2(1*H*)-one (3bd)



It was obtained as light yellow solid having melting point 181-183 °C with 83% yield. R_f = 0.37 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3265, 2836, 2887, 2869, 1667, 1636.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.59 (s, 1H), 8.50 (d, J = 8.3 Hz, 1H), 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 7.99 (d, J =7.9 Hz, 1H), 7.86 (d, J =7.9 Hz, 2H), 7.66 (s, 1H), 7.53-7.48 (m, 1H), 7.23 (d, J = 2.6 Hz, 2H), 7.14 (s, 1H), 3.78 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d):** δ 165.34, 154.85, 153.19, 142.12, 141.33, 137.74, 133.35, 132.65, 131.59, 131.33, 130.95, 130.11, 129.70, 129.21, 129.09, 127.43, 125.06, 123.30, 122.75, 114.47, 29.75, 21.53, 20.77, 19.30. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{25}H_{24}N_3O_2^+$: 398.1863; found: 398.1862.

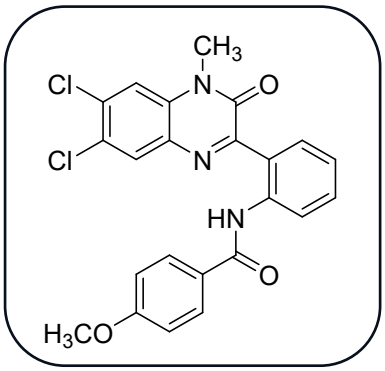
3-(2-amino-*N*-(benzoyl)phenyl)-6,7-dichloro-1-methylquinoxalin-2(1*H*)-one (3ca)



It was obtained as light yellow solid having melting point 188-190 °C with 75% yield. R_f = 0.36 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3123, 2889, 2767, 1636, 1543, 749.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.82 (s, 1H), 8.65 (d, J = 2.2 Hz, 1H), 8.42-8.34 (m, 1H), 8.26 (d, J = 8.7 Hz, 1H), 7.96 (d, J = 3.6 Hz, 1H), 7.85 (dd, J = 8.1, 1.4 Hz, 1H), 7.69-7.65 (m, 1H), 7.45-7.41 (m, 2H), 7.23 (d, J = 6.4 Hz, 1H), 7.16 (d, J = 6.5 Hz, 2H), 3.82 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 175.96, 165.58, 154.64, 153.42, 134.58, 133.25, 132.86, 132.38, 131.72, 131.41, 131.00, 129.76, 129.67, 129.37, 128.31, 124.44, 123.55, 122.32, 115.87, 115.65, 114.15, 29.95. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{22}H_{16}Cl_2N_3O_2^+$: 424.0614; found: 424.0610.

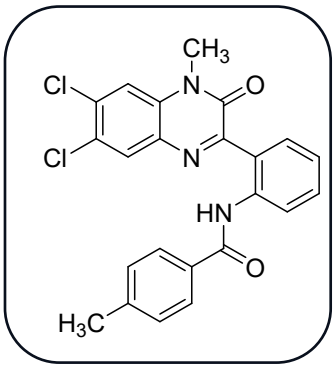
3-(2-amino-N-(4-methoxybenzoyl)phenyl)-6,7-dichloro-1-methylquinoxalin-2(1*H*)-one (3cb)



It was obtained as yellow solid having melting point 189-191 °C with 82% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3360, 2885, 2786, 1650, 1620, 1025, 850.

^{1}H NMR (400 MHz, Chloroform-d): δ 10.76 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.35-7.29 (m, 2H), 7.21 (d, J = 8.3 Hz, 1H), 7.06 (d, J = 8.3 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 6.90 (d, J = 8.6 Hz, 1H), 6.83 (s, 2H), 3.88 (d, J =10.2 Hz, 3H), 3.80 (d, J =13.6 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 174.73, 165.81, 142.80, 140.28, 133.93, 133.26, 131.76, 130.39, 128.94, 128.64, 127.41, 125.35, 125.09, 124.02, 121.17, 113.89, 110.01, 106.24, 55.52, 29.83. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{18}Cl_2N_3O_3^+$: 454.0720; found: 454.0718.

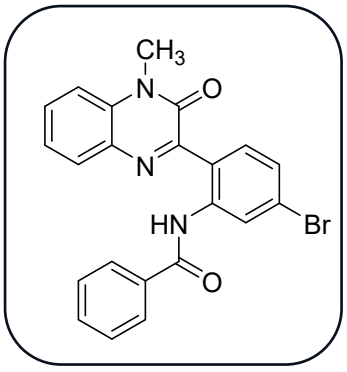
3-(2-amino-*N*-(4-methylbenzoyl)phenyl)-6,7-dichloro-1-methylquinoxalin-2(1*H*)-one (3cd)



It was obtained as light yellow solid having melting point 200-202 °C with 72% yield. R_f = 0.33 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3260, 2760, 1653, 1610, 564.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.67 (s, 1H), 8.35 (s, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.98-7.95 (m, 1H), 7.85 (dd, J = 8.1, 1.5 Hz, 1H), 7.65-7.61 (m, 1H), 7.44-7.38 (m, 2H), 7.16-7.11 (m, 2H), 7.07 (dd, J = 8.2, 1.7 Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d):** δ 163.34, 141.10, 132.13, 130.91, 130.66, 129.89, 128.67, 128.58, 128.29, 123.46, 123.22, 122.05, 120.96, 114.73, 114.52, 113.00, 28.83, 20.82. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{18}Cl_2N_3O_2^+$: 438.0771; found: 438.0770.

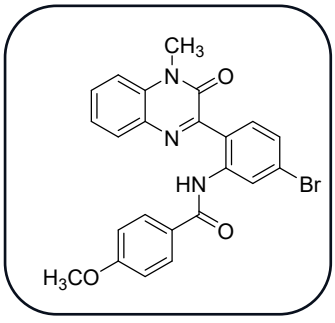
3-(2-amino-4-bromo-*N*-(benzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3da)



It was obtained as light yellow solid having melting point 166-168 °C with 78% yield. R_f = 0.30 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3258, 2981, 2851, 1670, 1640, 690.

^{1}H NMR (400 MHz, Chloroform-d): δ 10.77 (s, 1H), 8.27 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 8.6 Hz, 1H), 7.88 (d, J = 5.6 Hz, 2H), 7.51 (d, J = 6.5 Hz, 2H), 7.46 (s, 1H), 7.30 (d, J = 8.0 Hz, 3H), 7.19 (s, 1H), 7.05 (s, 1H), 3.71 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 168.19, 154.64, 136.57, 134.47, 133.45, 133.03, 131.01, 130.59, 130.52, 129.83, 129.31, 129.05, 128.30, 127.66, 125.64, 123.89, 121.09, 120.67, 120.46, 119.40, 113.64, 29.34. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{22}H_{17}BrN_3O_2^+$: 434.0499; found: 434.0498

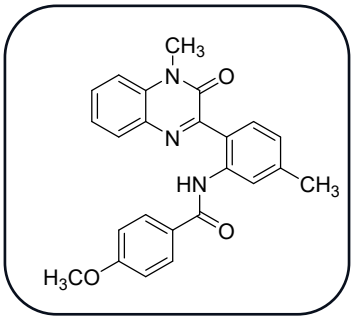
3-(2-amino-4-bromo-N-(4-methoxybenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3db)



It was obtained as yellow solid having melting point 190-192 °C with 79% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3161, 2920, 2881, 1672, 1643, 845.

^{1}H NMR (400 MHz, Chloroform-d): δ 10.69 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.42 (d, J = 8.5 Hz, 1H), 7.28-7.19 (m, 3H), 7.14 (d, J

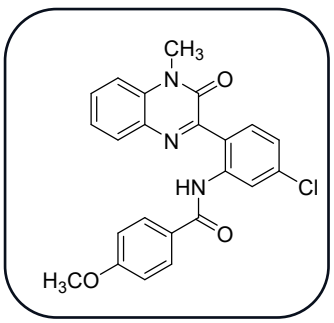
= 8.3 Hz, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 6.84-6.76 (m, 2H), 3.81 (d, *J* = 10.2 Hz, 3H), 3.72 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.90, 141.89, 139.37, 133.02, 132.25, 130.85, 129.48, 128.03, 127.73, 126.50, 124.44, 124.18, 123.11, 120.26, 112.98, 109.10, 105.33, 54.61, 28.92. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}BrN_3O_3^+$: 464.0604; found: 464.0601.



3-(2-amino-4-methyl-*N*-(4-methoxybenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3eb)

It was obtained as yellow solid having melting point 200-201 ^{o}C with 85% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3250, 2765, 1670, 1634, 1554.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.61 (s, 1H), 8.38 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 14.9, 8.2 Hz, 3H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.43-7.37 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.80, 141.79, 139.27, 132.92, 132.25, 130.75, 129.38, 127.93, 127.63, 126.40, 124.34, 124.08, 123.01, 120.16, 112.88, 109.00, 105.23, 54.51, 28.82. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{24}H_{22}N_3O_3^+$: 400.1656; found: 400.1611.

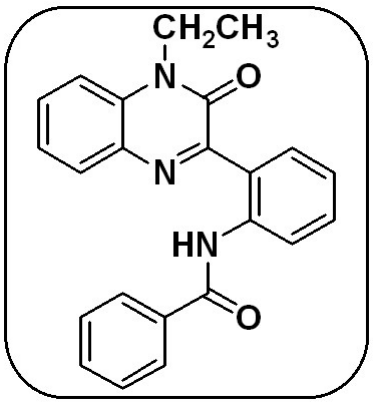


3-(2-amino-4-chloro-*N*-(4-methoxybenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3fb)

It was obtained as yellow solid having melting point 173-175 ^{o}C with 81% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3267, 2767, 2850, 1654, 1620, 1166, 689.

^{1}H NMR (400 MHz, Chloroform-d): δ 8.85 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.35-7.26 (m, 4H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.88 (d, *J* = 10.1 Hz, 3H), 3.78 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.86, 157.53, 152.72, 149.89, 141.85, 139.33, 132.98, 132.31, 130.81, 129.44, 127.99, 127.69, 126.46, 124.40, 124.14, 123.07, 120.22, 112.94, 109.06, 105.29, 54.57, 28.88. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}ClN_3O_3^+$: 420.1109; found: 420.1100.

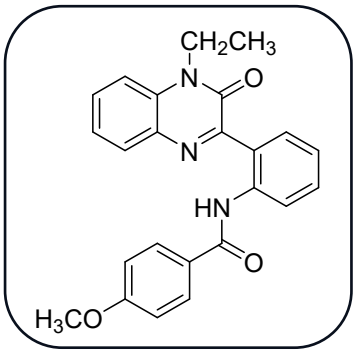
3-(2-amino-*N*-(benzoyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (4ga)



It was obtained as light yellow solid having melting point 194-196 °C with 84% yield. R_f = 0.36 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3256, 2687, 1672, 1643.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.47 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.19 (dd, J =8.0, 1.6 Hz, 1H), 7.96 (d, J = 7.1 Hz, 1H), 7.93 (dd, J =8.2, 1.5 Hz, 1H), 7.66-7.61 (m, 1H), 7.56-7.50 (m, 2H), 7.48-7.40 (m, 4H), 7.36-7.28 (m, 2H), 4.44 (q, J =7.1 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 165.33, 154.30, 137.70, 135.39, 132.44, 132.18, 131.76, 131.70, 131.25, 131.09, 130.04, 128.60, 127.31, 125.27, 124.10, 123.57, 123.03, 113.81, 38.27, 12.42. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{20}N_3O_2^+$: 370.1550; found: 370.1550.

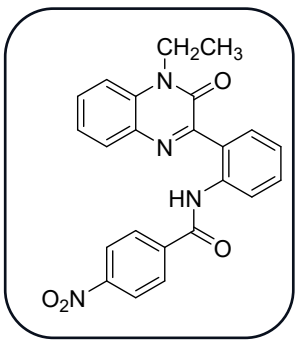
3-(2-amino-N-(4-methoxybenzoyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (4gb)



It was obtained as yellow solid having melting point 193-195 °C with 83% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3165, 2980, 2877, 1652, 1623, 1166.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.35 (s, 1H), 8.46 (d, J = 8.3 Hz, 1H), 8.17 (d, J = 7.9 Hz, 1H), 7.95-7.92 (m, 3H), 7.63 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.44-7.41 (m, 2H), 7.26 (s, 1H), 6.94 (d, J = 8.5 Hz, 2H) 4.44 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 1.17-1.12 (m, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.90, 162.36, 154.80, 137.87, 132.46, 131.71, 131.22, 131.07, 130.02, 129.17, 127.67, 125.20, 124.13, 123.35, 123.04, 113.82, 113.78, 55.47, 31.62, 14.15. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{24}H_{22}N_3O_3^+$: 400.1656; found: 400.1655.

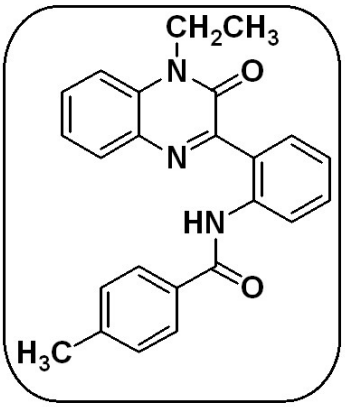
3-(2-amino-*N*-(4-nitrobenzoyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (4gc)



It was obtained as light yellow solid having melting point 205-207 °C with 56% yield. R_f = 0.34 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3650, 2967, 2887, 1652, 1023.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.33 (s, 1H), 8.34 (dd, J = 8.3, 1.3 Hz, 1H), 8.10 (dd, J = 7.9, 1.6 Hz, 1H), 7.92-7.87 (m, 2H), 7.83 (dd, J = 8.3, 1.5 Hz, 1H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 1H), 7.41-7.34 (m, 2H), 7.23-7.14 (m, 2H), 7.08-7.04 (m, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H) . **^{13}C NMR (100 MHz, Chloroform-d):** δ 165.13, 163.28, 153.65, 153.32, 136.49, 131.47, 131.09, 130.83, 130.22, 130.17, 129.28, 128.97, 128.67, 128.58, 127.05, 1243.58, 123.20, 122.77, 122.10, 114.72, 114.50, 112.84, 37.29, 11.41. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}N_4O_4^+$: 415.1401; found: 415.1400.

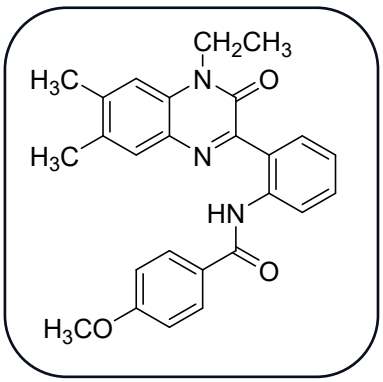
3-(2-amino-*N*-(4-methylbenzoyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (4gd)



It was obtained as light yellow solid having melting point 186-188 ^{o}C with 81% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3258, 2981, 2886, 1670, 1640.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.40 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.17 (dd, J =8.0, 1.6 Hz, 1H), 7.95-7.93 (m, J = 8.0, 1H), 7.86 (d, 2H), 7.66-7.61 (m, 1H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.25-7.23 (m, 3H), 4.43 (q, J =7.2 Hz, 2H), 2.41 (s, 3H), 1.44 (t, J =7.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 165.26, 154.74, 154.28, 142.17, 137.78, 132.52, 132.43, 132.18, 131.69, 131.22, 131.04, 130.02, 129.25, 127.32, 125.16, 124.10, 123.40, 123.01, 113.80, 38.26, 21.50, 12.44. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{24}H_{22}N_3O_2^+$: 384.1707; found: 384.1705.

3-(2-amino-*N*-(4-methoxybenzoyl)phenyl)-6,7-dimethyl-1-ethylquinoxalin-2(1*H*)-one (4hb)

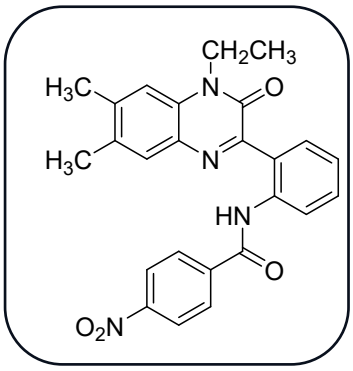


It was obtained as yellow solid having melting point 193-195 ^{o}C with 81% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3160, 2680, 2587, 1672, 1629, 1056.

^{1}H NMR (400 MHz, Chloroform-d): δ 8.86 (s, 1H), 7.35-7.29 (m, 5H), 7.07-7.05 (m, 2H), 6.85-6.82 (m, 3H), 3.86 (s, 3H), 3.77 (s, 6H), 1.62 (s, 1H), 1.31-1.22 (m, 2H), 0.94-0.80 (m, 2H).**^{13}C NMR (100 MHz, Chloroform-d)** δ 164.83, 141.81, 139.29, 132.95, 132.28, 130.78,

129.41, 127.96, 127.65, 126.43, 124.11, 123.04, 120.19, 112.91, 109.02, 105.25, 54.53, 44.20, 28.84, 28.71. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{26}H_{26}N_3O_3^+$: 428.1969; found: 428.1965.

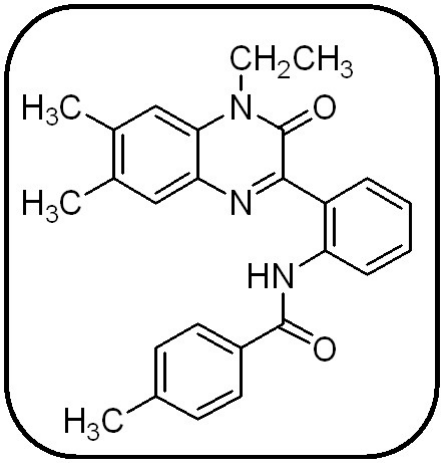
3-(2-amino-*N*-(4-nitrobenzoyl)phenyl)-6,7-dimethyl-1-ethylquinoxalin-2(1*H*)-one (4hc)



It was obtained as light yellow solid having melting point 210-212 ^oC with 62% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3350, 2765, 1642, 1021.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.68 (s, 1H), 8.58 (dd, J = 8.4, 1.2 Hz, 1H), 8.33 (dd, J = 8.0, 1.6 Hz, 1H), 8.17-8.13 (m, 2H), 7.82 (s, 1H), 7.70-7.66 (m, 1H), 7.42 (s, 1H), 7.34 (s, 1H), 7.30-7.26 (m, 2H), 4.57 (q, J = 7.1 Hz, 2H), 2.63 (s, 3H), 2.56 (s, 3H), 1.59 (t, J = 7.2 Hz, 3H) . **^{13}C NMR (100 MHz, Chloroform-d)**: δ 164.19, 156.73, 151.51, 154.40, 153.29, 148.27, 141.47, 137.52, 133.40, 131.79, 131.01, 130.93, 130.20, 129.99, 129.76, 129.68, 125.82, 123.72, 122.97, 115.62, 115.40, 114.22, 38.15, 20.83, 19.31, 12.48. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{25}H_{23}N_4O_4^+$: 443.1714; found: 443.1711.

3-(2-amino-*N*-(4-methylbenzoyl)phenyl)-6,7-dimethyl-1-ethylquinoxalin-2(1*H*)-one (4hd)

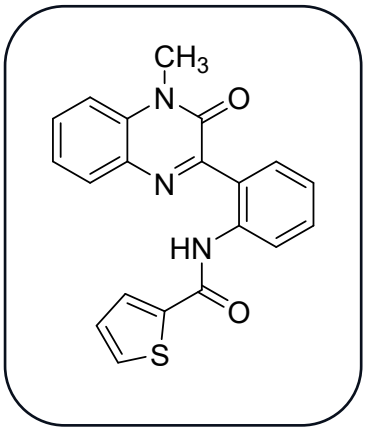


It was obtained as light yellow solid having melting point 190-192 ^oC with 79% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3235, 2811, 2884, 2869, 1667.

^{1}H NMR (400 MHz, Chloroform-d): δ 9.28 (s, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.21 (s, 2H), 7.14 (d, J = 7.2 Hz, 3H), 6.64 (s, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 2.31 (s, 2H), 2.17

(s, 3H), 1.25 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 168.79, 156.13, 151.85, 143.19, 140.37, 132.11, 130.22, 129.92, 129.53, 129.20, 128.60, 128.60, 127.20, 121.96, 120.02, 39.14, 21.75, 21.60, 20.86, 13.95. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{26}H_{26}N_3O_2$: 412.2020; found: 412.2018.

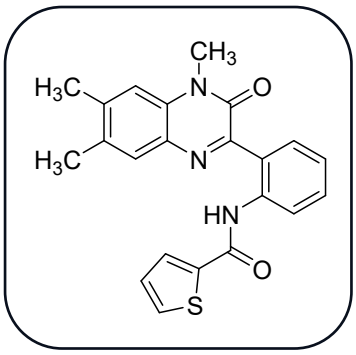
3-(2-amino-N-(thiophene-2-carbonyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (5ae)



It was obtained as yellow solid having melting point 193-195 ^{o}C with 84% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3093, 2918, 2851, 1643, 726.

^{1}H NMR (400 MHz, Chloroform-d): *δ* 11.24 (s, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.97 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.65-7.60 (m, 2H), 7.53-7.48 (m, 2H), 7.44-7.38 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 4.3 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** *δ* 159.86, 154.78, 154.61, 140.25, 137.21, 133.20, 132.13, 131.69, 131.15, 130.46, 129.80, 128.50, 127.67, 125.28, 124.31, 123.59, 123.10, 114.02, 113.56, 29.85. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{20}H_{16}N_3O_2S^+$: 362.0958; found: 362.0955.

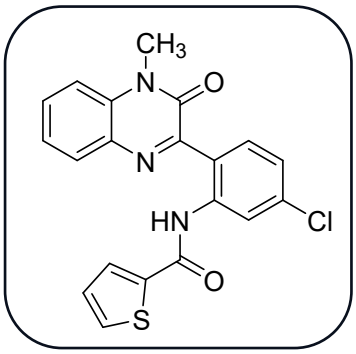
3-(2-amino-N-(thiophene-2-carbonyl)phenyl)-6,7-dimethyl-1-methylquinoxalin-2(1*H*)-one (5be)



It was obtained as yellow solid having melting point 183-185 ^{o}C with 86% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3046, 2910, 2723, 1654, 790.

^{1}H NMR (400 MHz, Chloroform-d): *δ* 11.30 (s, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72 (s, 1H), 7.65 (d, *J* = 3.7 Hz, 1H), 7.53-7.47 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 (s, 1H), 7.10-7.06 (m, 1H), 3.80 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** *δ* 159.87, 154.90, 153.25, 141.46, 140.50, 137.14, 133.48, 131.66, 131.26, 130.84, 130.72, 130.43, 129.87, 128.32, 127.55, 125.79, 123.63, 123.04, 114.48, 29.77, 20.77, 19.32. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{22}H_{20}N_3O_2S^+$: 390.1271; found: 390.1270.

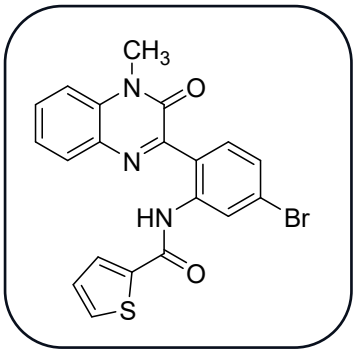
3-(2-amino-4-chloro-N-(thiophene-2-carbonyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (5ce)



It was obtained as yellow solid having melting point 193-195 °C with 80% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3094, 2922, 2847, 1672, 845.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.53 (s, 1H), 8.57 (d, J = 2.2 Hz, 1H), 8.18 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.69-7.66 (m, 2H), 7.53 (d, J = 5.3 Hz, 1H), 7.48-7.41 (m, 2H), 7.23-7.19 (m, 1H), 7.12-7.10 (m, 1H), 3.83 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.38, 154.66, 154.09, 153.43, 137.57, 133.26, 131.81, 131.35, 131.23, 129.71, 129.62, 125.18, 124.39, 124.03, 123.71, 122.98, 115.80, 115.58, 114.09, 29.91. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{20}H_{15}ClN_3O_2S^+$: 396.0568; found: 396.0565.

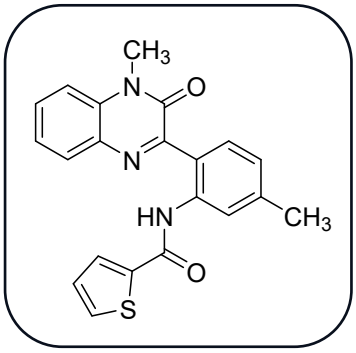
3-(2-amino-4-bromo-N-(thiophene-2-carbonyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (5de)



It was obtained as yellow solid having melting point 193-195 °C with 81% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3134, 2867, 2732, 1667, 867.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.54 (s, 1H), 8.58 (d, J = 2.2 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.54 (d, J = 5.3 Hz, 1H), 7.49-7.42 (m, 2H), 7.22 (d, J = 7.8 Hz, 1H), 7.13-7.12 (m, 1H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 164.35, 154.63, 154.06, 153.40, 157.54, 133.23, 131.78, 131.32, 131.20, 129.69, 129.60, 125.15, 124.36, 124.00, 123.68, 122.96, 115.77, 115.55, 114.07, 29.88. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{20}H_{15}BrN_3O_2S^+$: 440.0063; found: 440.0060.

3-(2-amino-4-methyl-N-(thiophene-2-carbonyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (5ee)

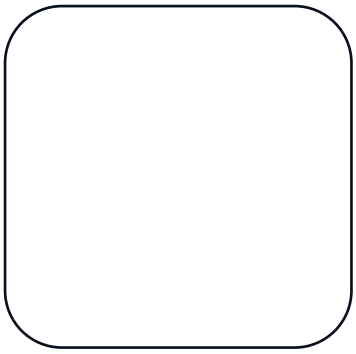


It was obtained as yellow solid having melting point 193-195 °C with 84% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3178, 2876, 2699, 1662, 765.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.41 (s, 1H), 8.28 (d, J = 1.8 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.97 (dd, J = 8.0, 1.5 Hz, 1H), 7.66 (dd, J = 3.7, 1.2 Hz, 1H), 7.64-7.60 (m, 1H), 7.50 (d, J

= 5.0, 1.2 Hz, 1H), 7.45-7.38 (m, 2H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.82 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 159.90, 154.82, 154.69, 141.94, 140.45, 137.22, 133.14, 131.32, 131.20, 129.69, 129.60, 125.15, 124.36, 124.00, 123.68, 122.96, 115.77, 115.55, 114.07, 29.88. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{21}H_{18}N_3O_2S^+$: 376.1114; found: 376.1112.

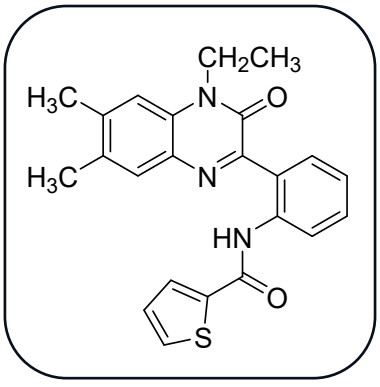
3-(2-amino-N-(thiophene-2-carbonyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (5fe)



It was obtained as yellow solid having melting point 195-197 ^{o}C with 81% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3061, 2936, 2818, 1672, 821.

^{1}H NMR (400 MHz, Chloroform-d): δ 10.73 (s, 1H), 8.49 (s, 1H), 8.47 (s, 1H), 8.23-8.05 (m, 7H), 7.89 (d, *J* = 10.4 Hz, 2H), 2.79-2.73 (m, 2H), 1.23-1.17 (m, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 167.52, 159.96, 157.46, 145.82, 140.19, 137.10, 136.83, 132.61, 131.77, 131.15, 130.50, 130.24, 128.53, 127.66, 124.21, 123.82, 123.35, 113.82, 38.31, 12.48. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{21}H_{18}N_3O_2S^+$: 376.1114; found: 376.1110.

3-(2-amino-N-(thiophene-2-carbonyl)phenyl)-6,7-dimethyl-1-ethylquinoxalin-2(1*H*)-one (5ge)

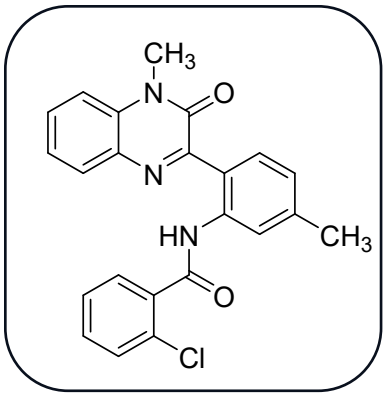


It was obtained as yellow solid having melting point 193-195 ^{o}C with 83% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3159, 2938, 2812, 1632, 789.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.26 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.08 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75-7.70 (m, 2H), 7.51-7.48 (m, 1H), 7.19 (s, 1H), 7.13-7.09 (m, 1H), 6.88 (t, *J* = 6.1 Hz, 1H), 6.82-6.79 (m, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 2.39 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 165.54, 152.00, 143.14, 132.09, 130.54, 129.82, 129.31, 129.27, 129.04, 128.88, 128.75, 128.68, 128.16, 127.36, 124.55,

124.08, 120.96, 120.68, 112.48, 31.94, 29.70, 19.50, 14.41. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{22}N_3O_2S^+$: 404.1427; found: 404.1425.

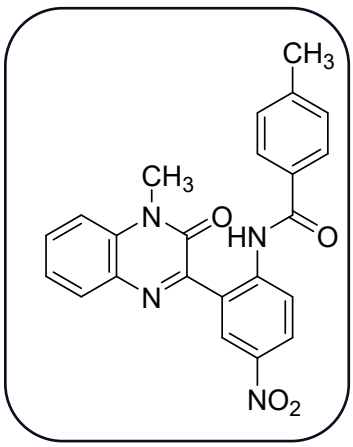
3-(2-amino-4-*N*-(2-chlorobenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one. (5ef)



It was obtained as light yellow solid having melting point 165-167 ^oC with 71% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3160, 2664, 1612, 1643, 692.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.67 (s, 1H), 8.34 (d, J = 1.5 Hz, 1H), 8.15 (d, J =8.2 Hz, 1H), 7.98-7.95 (m, 2H), 7.85 (dd, J = 8.1, 1.5 Hz, 1H), 7.65-7.61 (m, 1H), 7.44-7.38 (m, 2H), 7.16-7.11 (m, 2H), 7.07 (dd, J = 8.2, 1.7 Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 163.15, 140.92, 131.95, 130.73, 130.47, 129.71, 128.49, 128.39, 128.11, 123.28, 123.04, 121.86, 120.78, 114.55, 114.33, 112.82, 28.65, 20.64. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}ClN_3O_2^+$: 404.1160; found: 404.1159.

3-(2-amino-3-nitro-*N*-(4-methylbenzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one. (5ld)

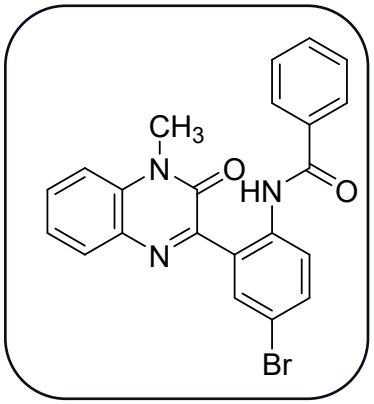


It was obtained as light yellow solid having melting point 180-182 ^oC with 60% yield. R_f = 0.25 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3010, 2944, 2785, 1672.

^{1}H NMR (400 MHz, Chloroform-d): δ 9.27 (t, J = 2.0 Hz, 1H), 8.78 (dt, J = 7.8, 1.4 Hz, 1H), 8.33-8.30 (m, 1H), 7.98 (dd, J =

8.0, 1.5 Hz, 1H), 7.67-7.62 (m, 1H), 7.45-7.36 (m, 3H), 7.09 (dd, *J* = 8.8, 3.8 Hz, 2H), 3.80 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 154.48, 151.13, 148.19, 137.50, 135.48, 133.56, 132.86, 131.38, 130.84, 129.03, 124.75, 124.67, 124.19, 113.82, 29.46, 20.86. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{19}N_4O_4^+$: 415.1401; found: 415.1400.

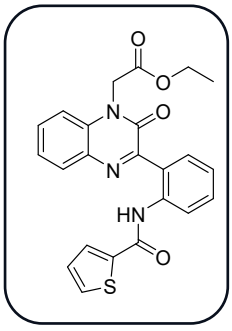
3-(2-amino-3-bromo-*N*-(benzoyl)phenyl)-1-methylquinoxalin-2(1*H*)-one. (5ma)



It was obtained as light yellow solid having melting point 166-168 ^{o}C with 72% yield. R_f = 0.35 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3100, 2884, 2745, 1670, 672.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.91 (s, 1H), 8.75 (s, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 8.08-8.04 (m, 2H), 7.95 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.78-7.74 (m, 1H), 7.57-7.51 (m, 3H), 7.32 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.25 (t, *J* = 8.6 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR (100 MHz, Chloroform-d)**: δ 174.97, 164.59, 153.65, 133.59, 132.26, 131.87, 131.39, 130.73, 130.42, 130.01, 128.77, 128.68, 128.38, 127.31, 123.45, 122.56, 121.33, 114.88, 114.66, 113.15, 28.95. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{22}H_{17}BrN_3O_2^+$: 434.0499; found: 434.0490.

3-(2-amino-N-(thiophene-2-carbonyl)phenyl)-1-ethyl-(2-oxo-quinoxalin-1(2*H*)-yl)acetate (6ie)

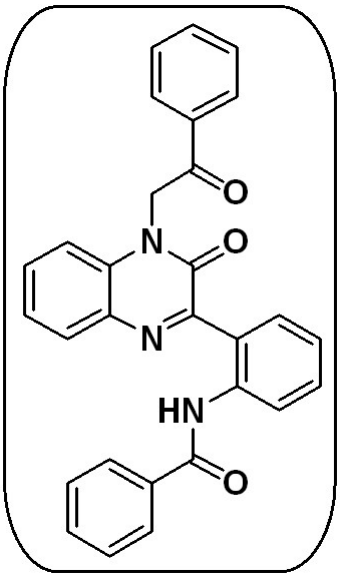


It was obtained as yellow solid having melting point 198-200 ^{o}C with 75% yield. R_f = 0.32 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3149, 2985, 1740, 1647, 1576, 1021.

^{1}H NMR (400 MHz, Chloroform-d): δ 11.53 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.96-7.90 (m, 2H), 7.62-7.57 (m, 1H), 7.53 (q, *J* = 8.0, 7.2 Hz, 2H), 7.48-7.40 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 166.85, 165.48, 154.46, 154.36, 137.88, 135.49, 132.48, 132.03, 131.73, 131.69, 131.48, 131.20, 129.90, 128.59, 127.35, 124.49, 124.31, 123.37,

122.78, 113.43, 62.25, 44.27, 14.11. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{23}H_{20}N_3O_4S^+$: 434.1169; found: 434.160.

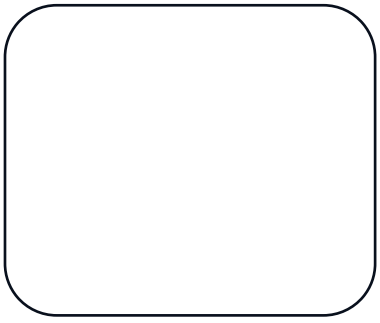
3-(2-amino-*N*-(benzoyl)phenyl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1*H*)-one (6ja)



It was obtained as light yellow solid having melting point 200-202 ^oC with 78% yield. R_f = 0.36 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1}):** 3260, 2887, 2687, 1643, 1542.

^{1}H NMR (400 MHz, Chloroform-d): δ 13.13 (s, 1H), 10.10 (d, J = 8.3 Hz, 1H), 9.80 (d, J = 7.9 Hz, 1H), 9.55 (d, J = 7.8 Hz, 2H), 9.50 (d, J = 8.0 Hz, 1H), 9.33 (d, J = 7.7 Hz, 1H), 9.22 (d, J = 7.9 Hz, 1H), 9.14-9.10 (m, 2H), 9.07-8.98 (m, 6H), 8.87-8.85 (m, 3H), 5.41 (s, 2H). **^{13}C NMR (100 MHz, Chloroform-d):** δ 198.58, 162.78, 159.97, 137.32, 136.73, 129.96, 128.59, 128.35, 128.18, 128.02, 127.83, 127.67, 127.46, 127.11, 126.80, 125.61, 122.84, 119.73, 118.89, 114.43, 28.68. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated for $C_{29}H_{22}N_3O_3^+$: 460.1656; found: 460.1656.

***N*-(2-(pyridin-2-yl)phenyl)benzamide (6ka)**



It was obtained as white solid having melting point 84-86 ^oC with 75% yield. R_f = 0.30 (20% ethyl acetate in hexane); **IR (KBr, cm^{-1})**: 3100, 1650, 1276.

^{1}H NMR (400 MHz, Chloroform-d): δ 10.79 (s, 1H), 7.94 (d, J = 7.1 Hz, 1H), 7.58 (d, J = 1.3 Hz, 1H), 7.56-7.52 (m, 2H), 7.47-7.45 (m, 1H), 7.40-7.37 (m, 3H), 7.35 (s, 1H), 7.33 (s,1H),

7.31(s, 1H), 7.15-7.11 (m, 2H). **^{13}C NMR (100 MHz, Chloroform-d)** δ 163.01, 154.78, 137.88, 132.45, 129.36, 129.12, 129.09, 129.03, 127.59, 124.54, 124.45, 121.40, 120.69, 120.62, 120.59. **HRMS (ESI$^+$):** m/z $[M+H]^+$ calculated For $C_{18}H_{15}N_2O^+$: 275.1179; found: 275.1175.

Spectra

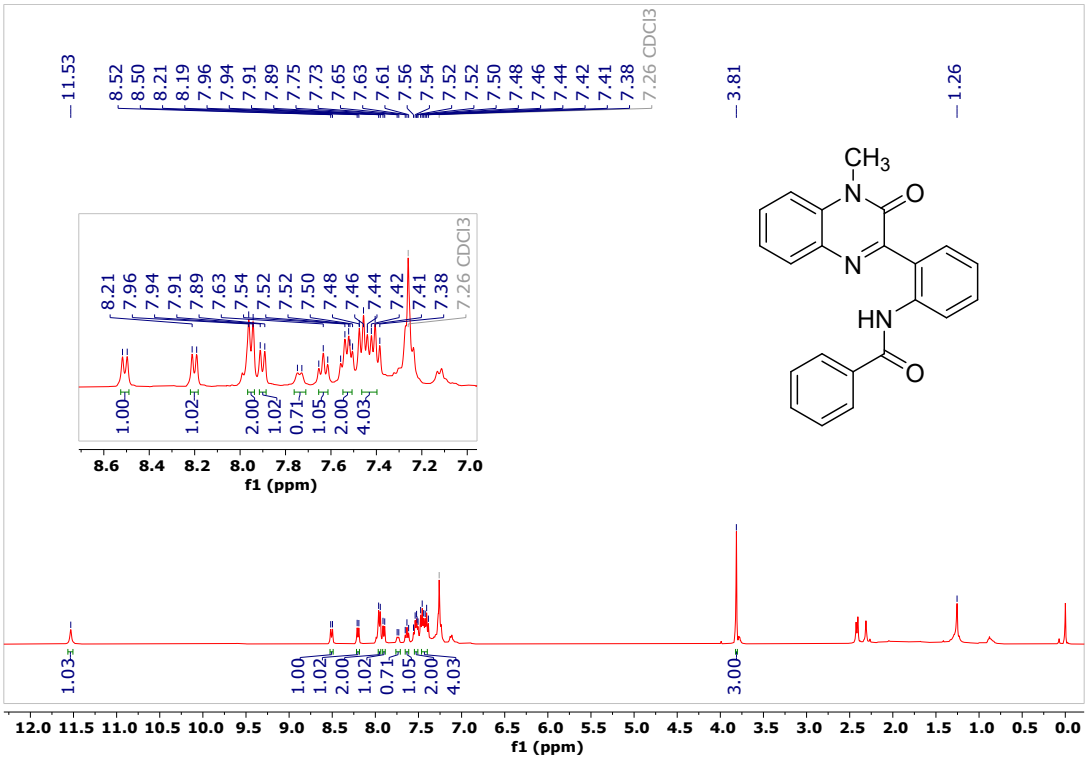


Figure 1: ^{1}H NMR spectrum of compound **3aa** (400 MHz, $CDCl_3$).

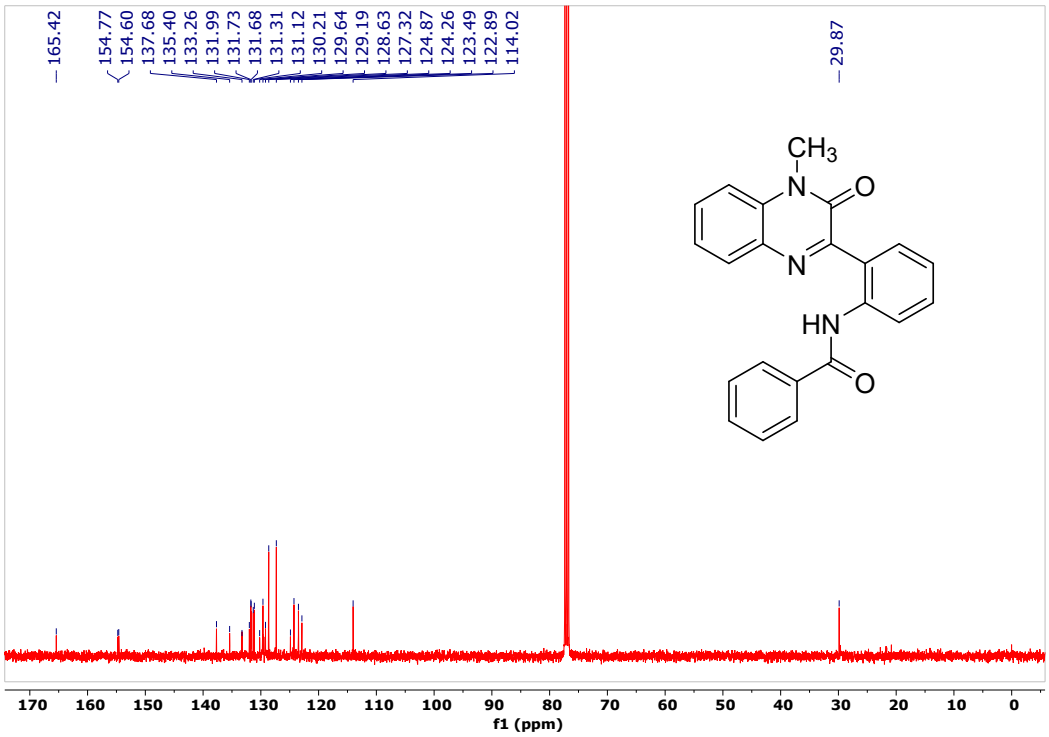


Figure 2: ^{13}C NMR spectrum of compound **3aa** (100 MHz, $CDCl_3$).

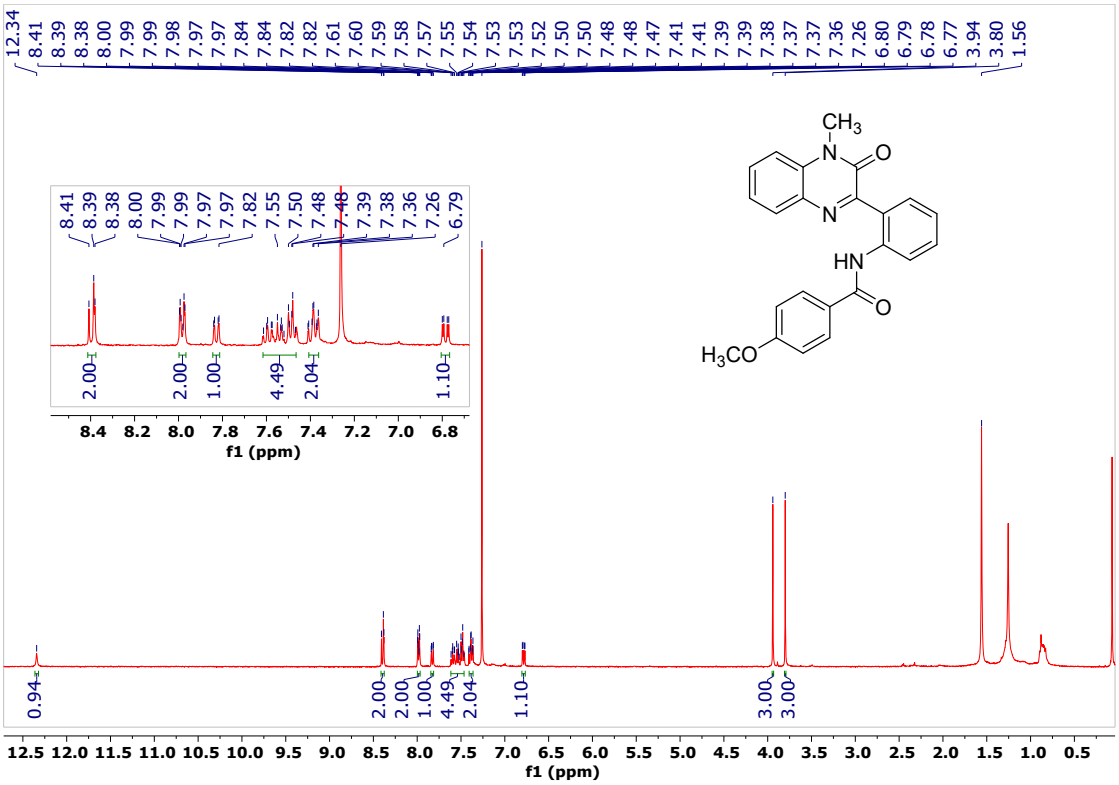


Figure 3: ^{1}H NMR spectrum of compound **3ab** (400 MHz, $CDCl_3$).

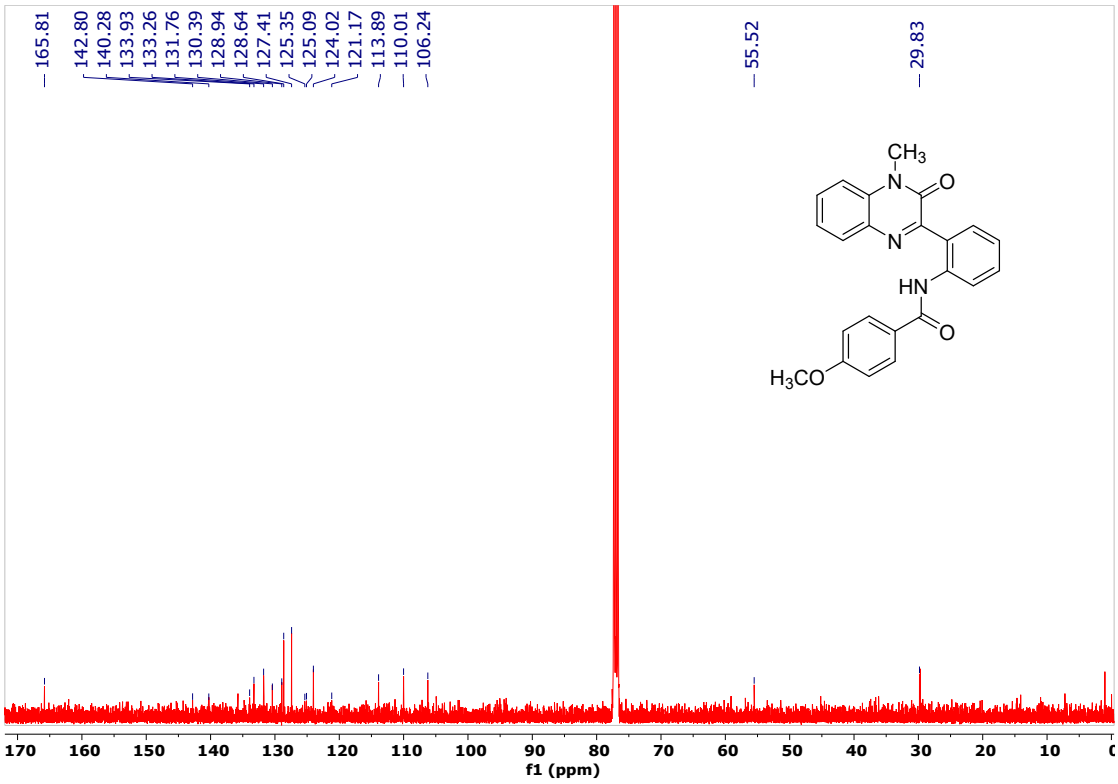


Figure 4: ^{13}C NMR spectrum of compound **3ab** (100 MHz, $CDCl_3$).

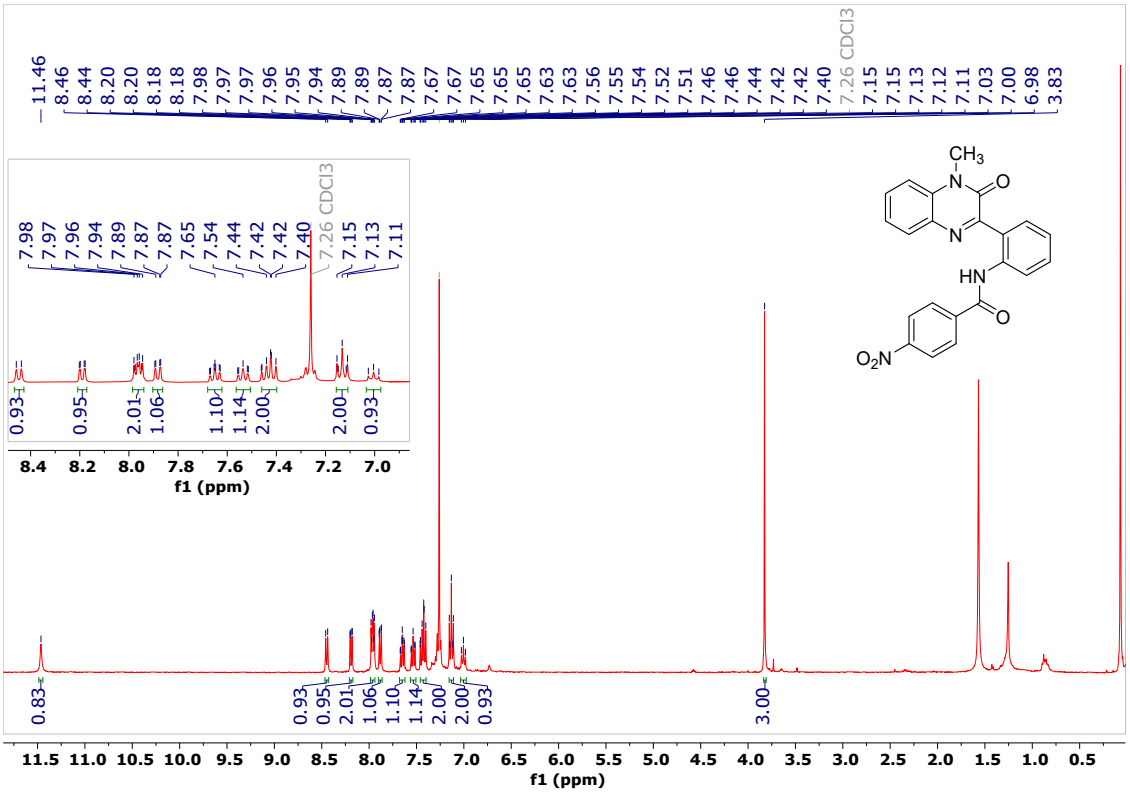


Figure 5: ^{1}H NMR spectrum of compound **3ac** (400 MHz, $CDCl_3$).

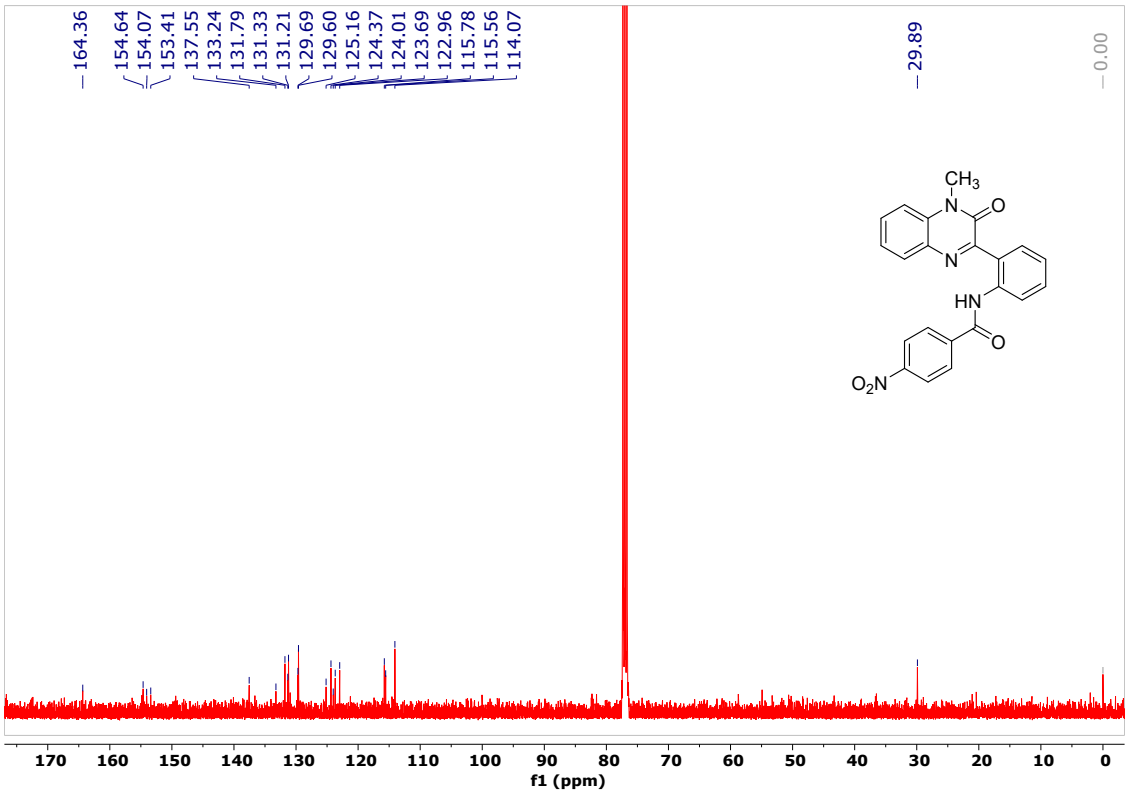


Figure 6: ^{13}C NMR spectrum of compound **3ac** (100 MHz, $CDCl_3$).

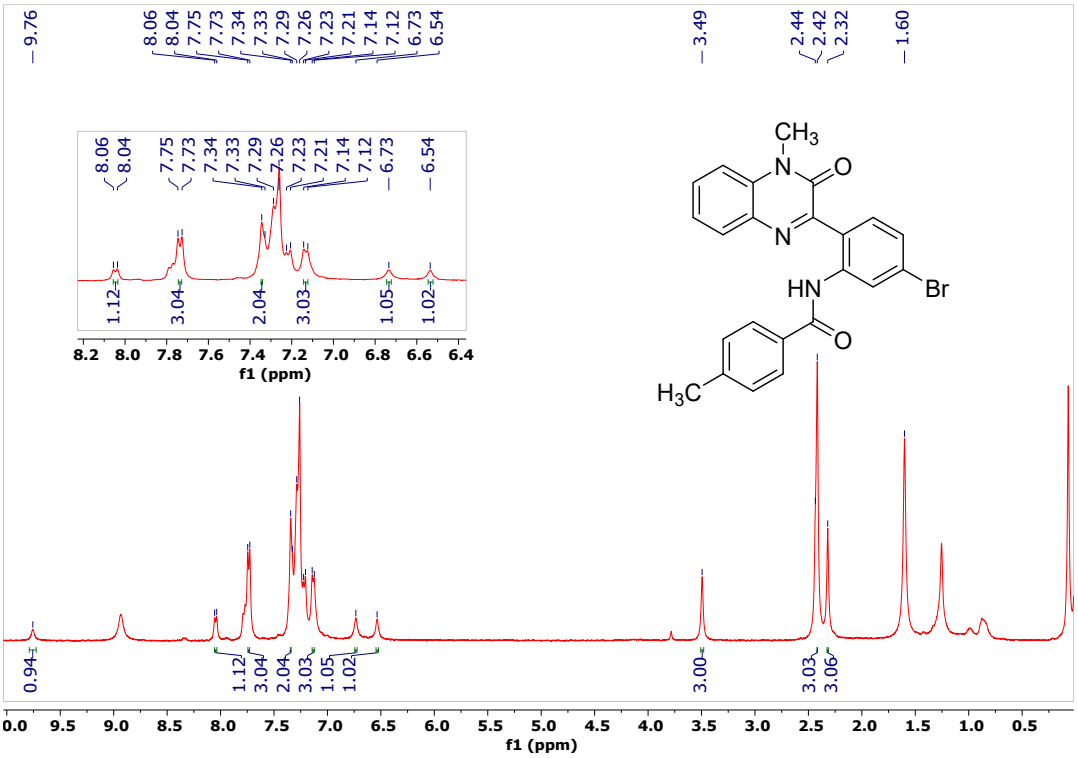


Figure 7: ^{1}H NMR spectrum of compound **3ad** (400 MHz, $CDCl_3$).

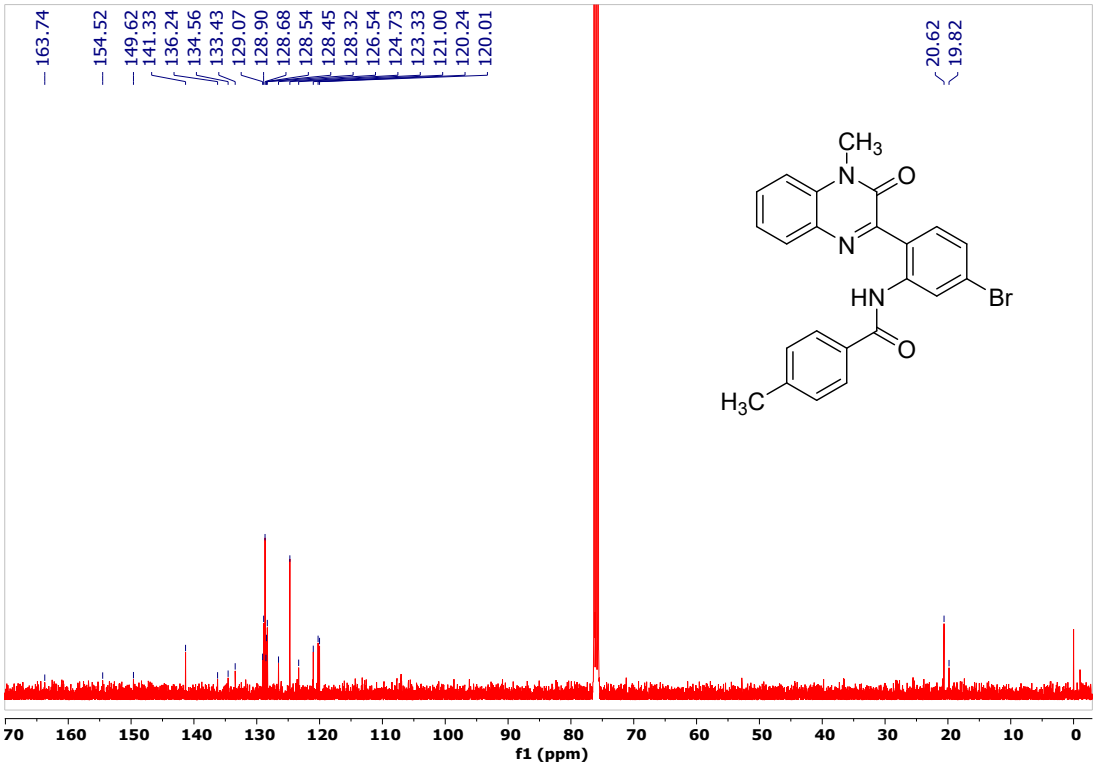


Figure 8: ^{13}C NMR spectrum of compound **3ad** (100 MHz, $CDCl_3$).

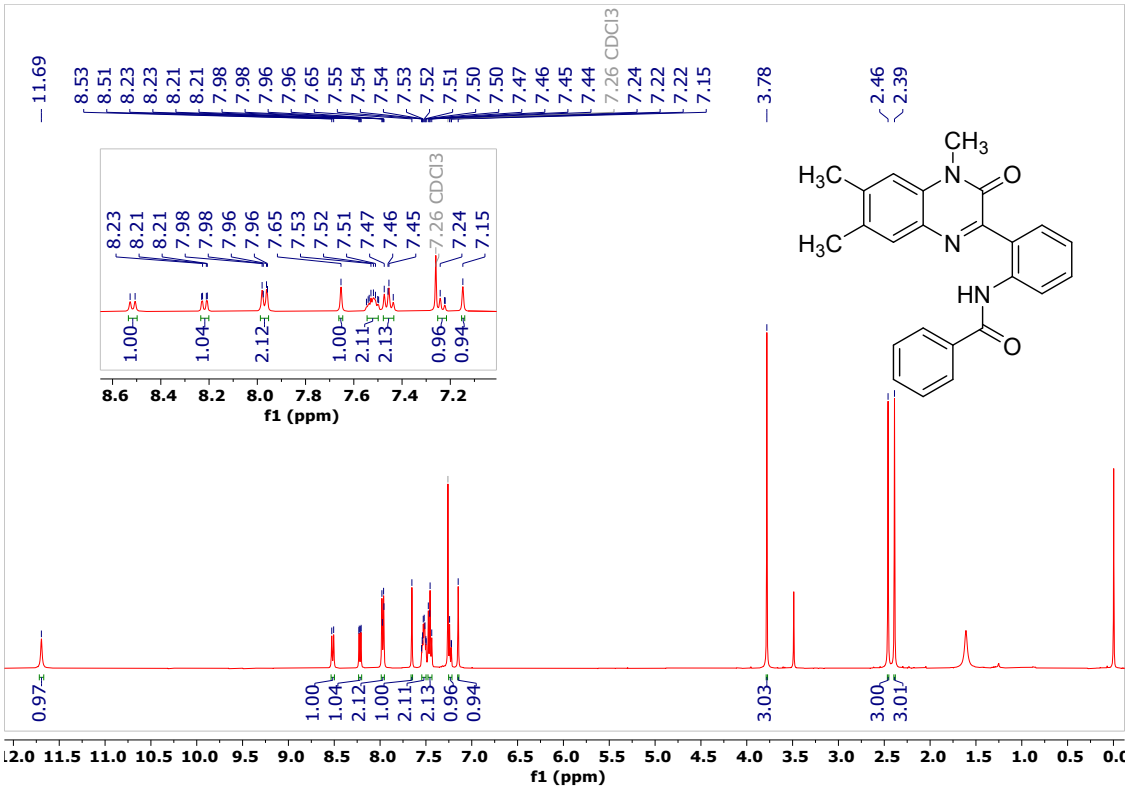


Figure 9: ^{1}H NMR spectrum of compound **3ba** (400 MHz, $CDCl_3$).

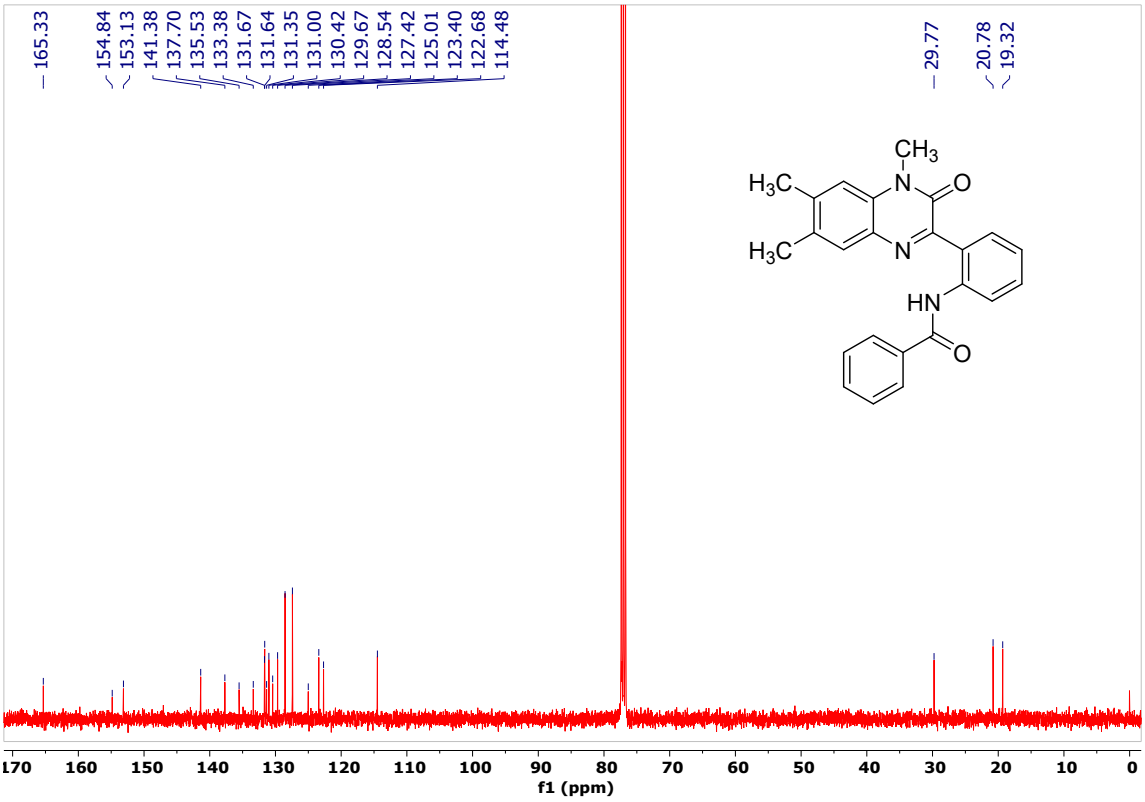


Figure 10: ^{13}C NMR spectrum of compound **3ba** (100 MHz, $CDCl_3$).

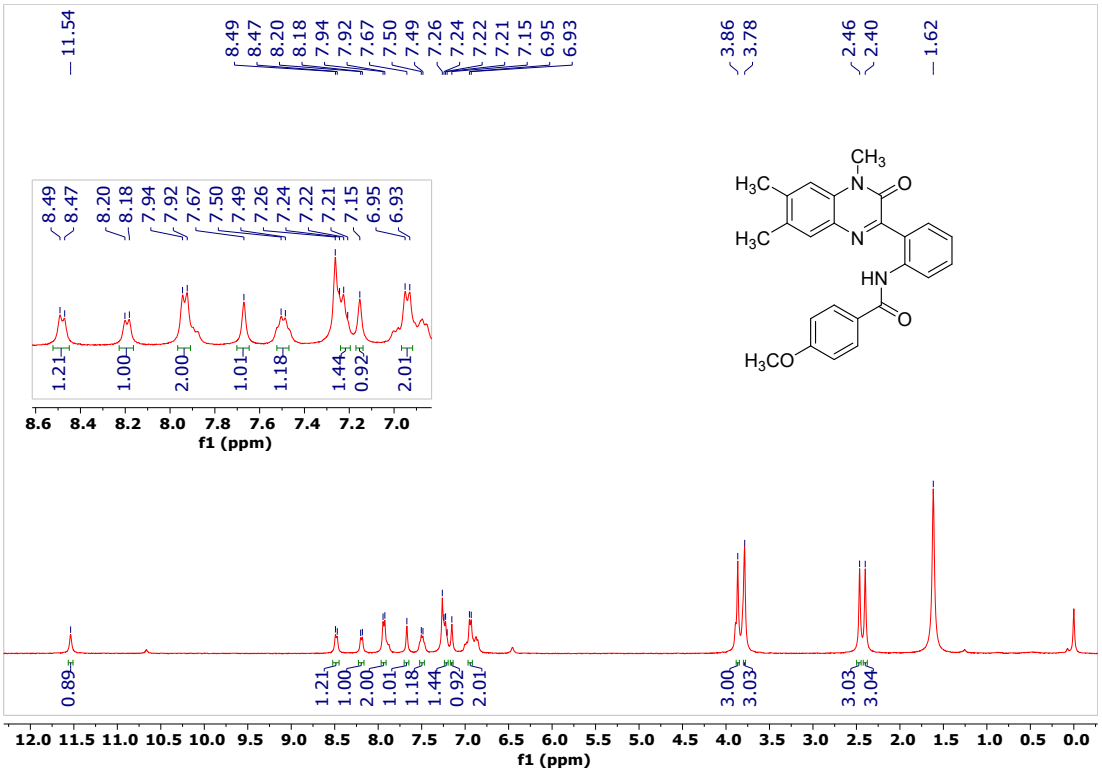


Figure 11: ^{1}H NMR spectrum of compound **3bb** (400 MHz, $CDCl_3$).

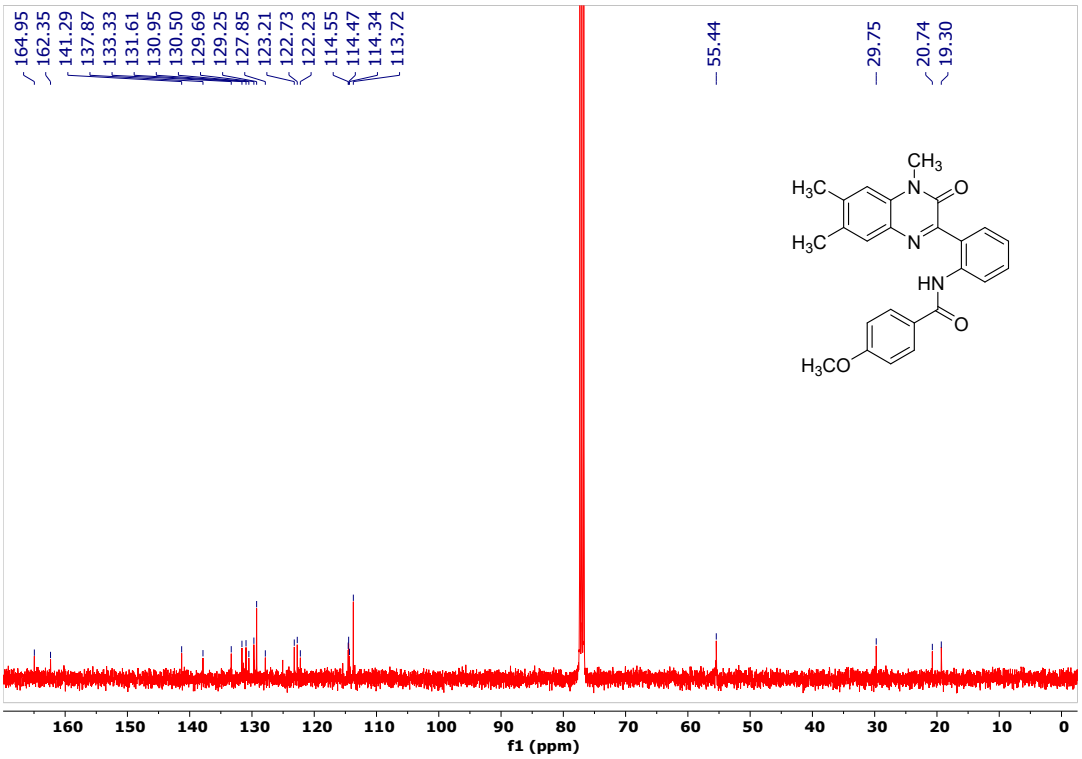


Figure 12: ^{13}C NMR spectrum of compound **3bb** (100 MHz, $CDCl_3$).

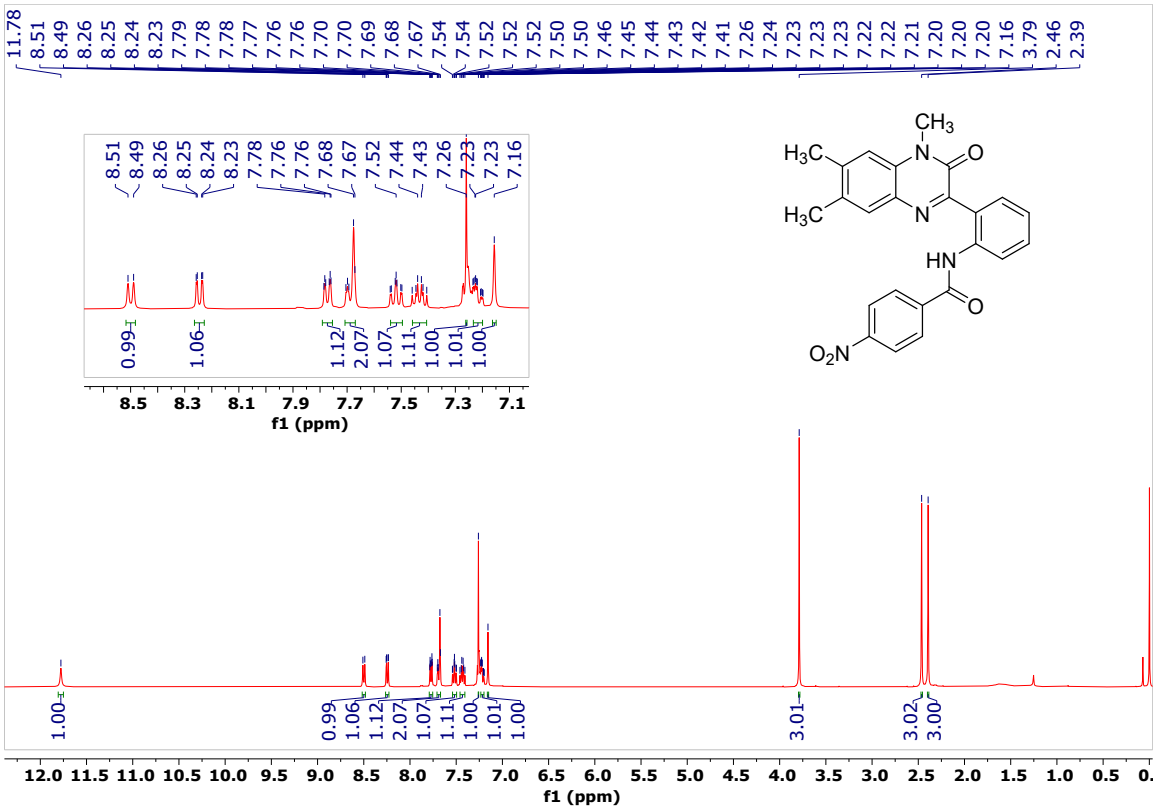


Figure 13: ^{1}H NMR spectrum of compound **3bc** (400 MHz, $CDCl_3$).

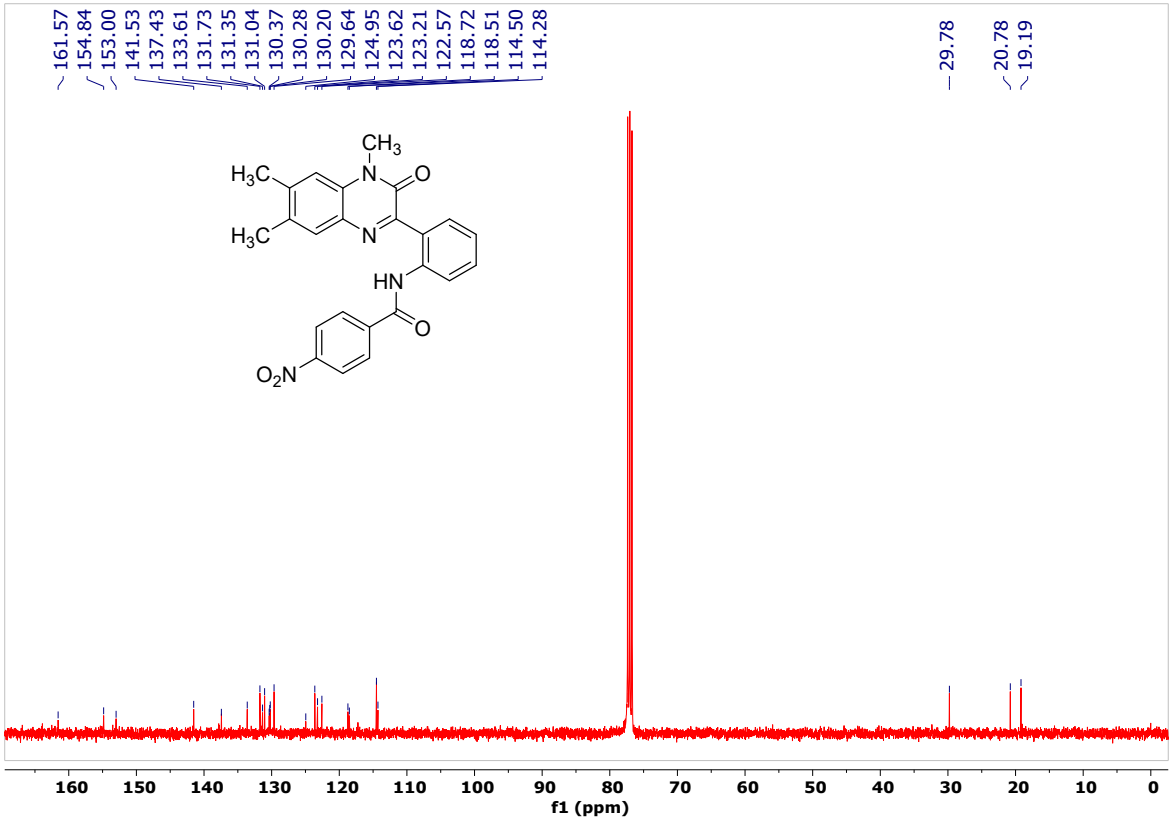


Figure 14: ^{13}C NMR spectrum of compound **3bc** (100 MHz, $CDCl_3$).

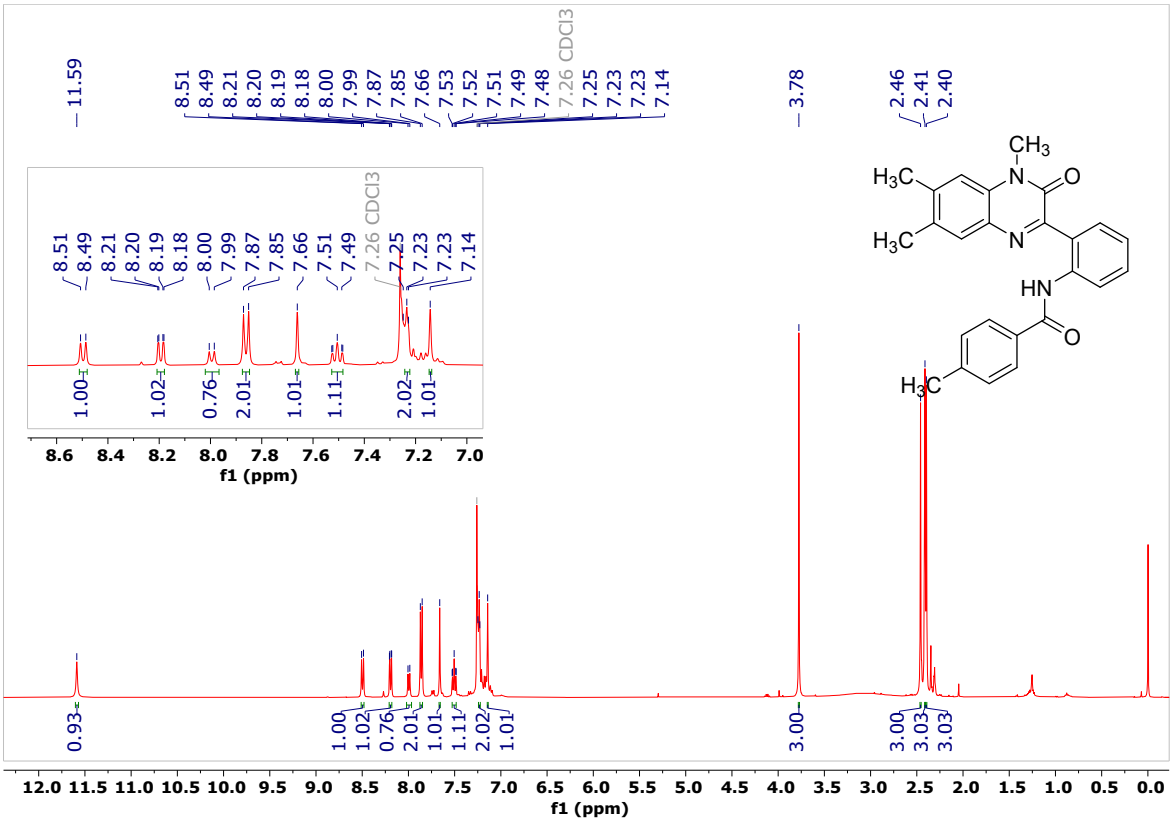


Figure 15: ^{1}H NMR spectrum of compound **3bd** (400 MHz, $CDCl_3$).

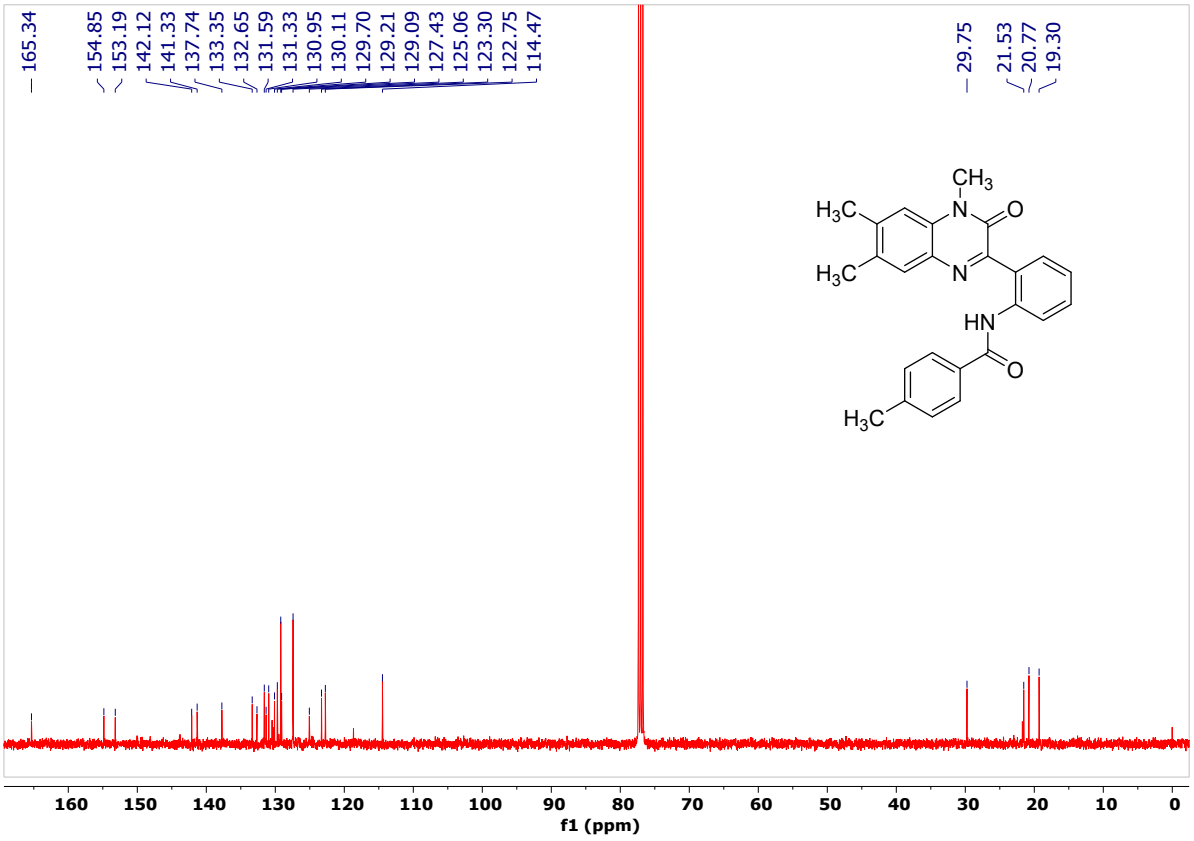


Figure 16: ^{13}C NMR spectrum of compound **3bd** (100 MHz, $CDCl_3$).

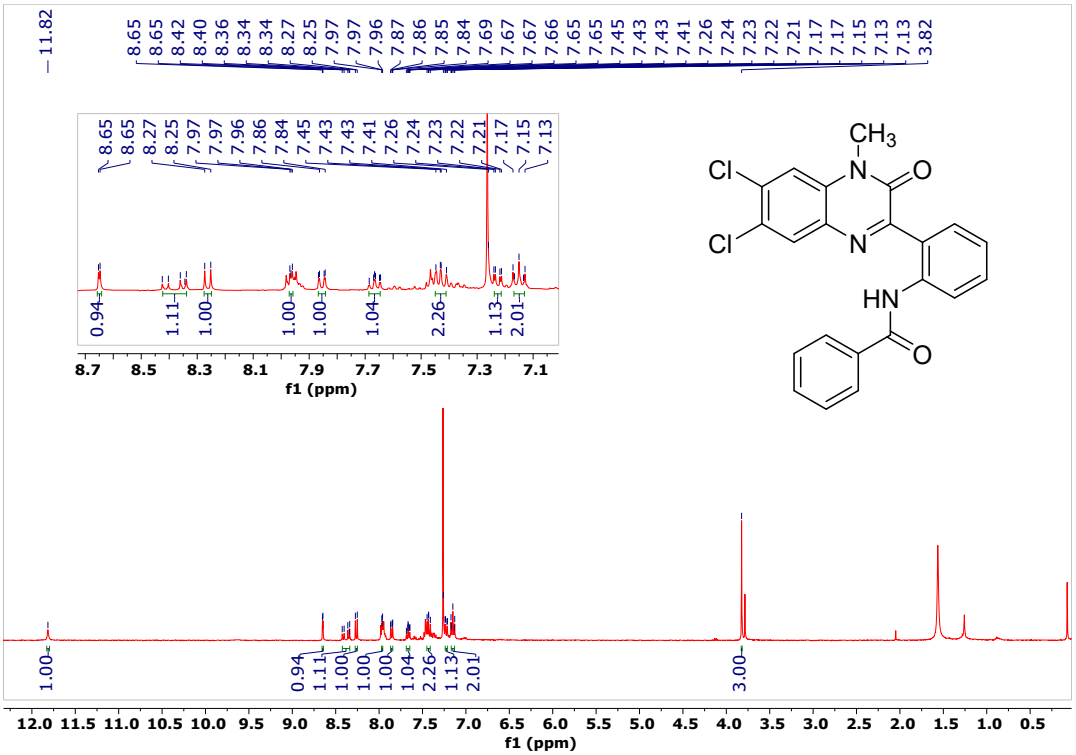


Figure 17: ^{1}H NMR spectrum of compound **3ca** (400 MHz, $CDCl_3$).

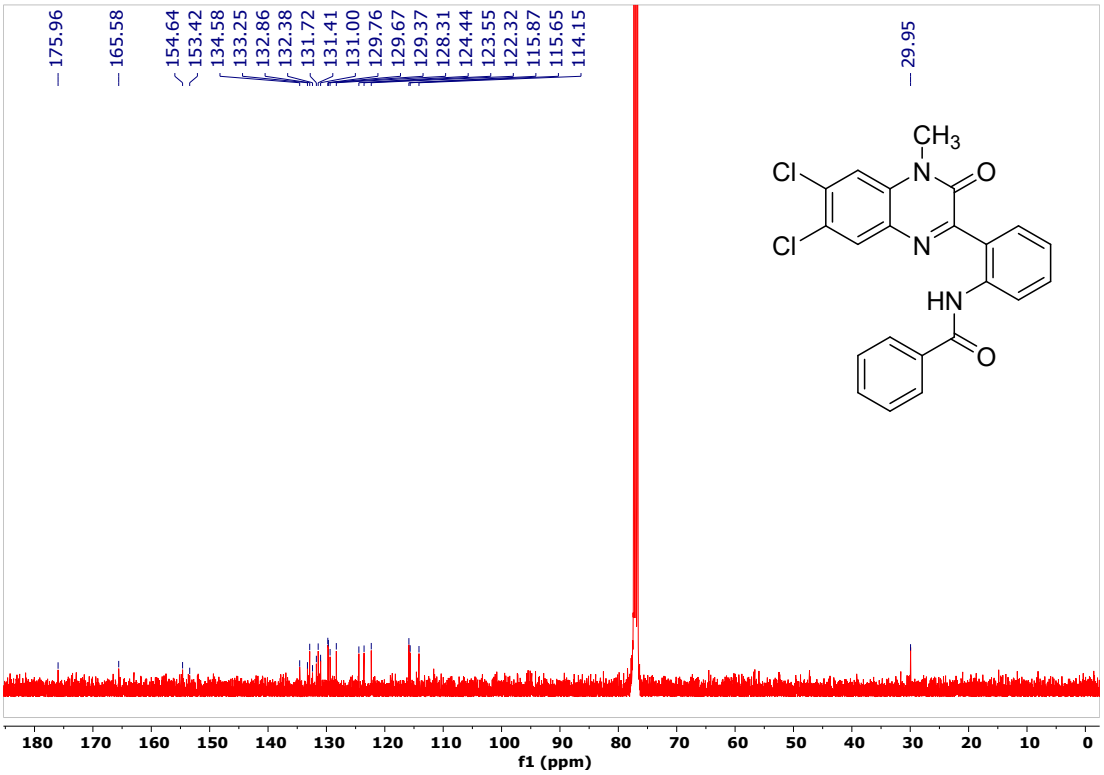


Figure 18: ^{13}C NMR spectrum of compound **3ca** (100 MHz, $CDCl_3$).

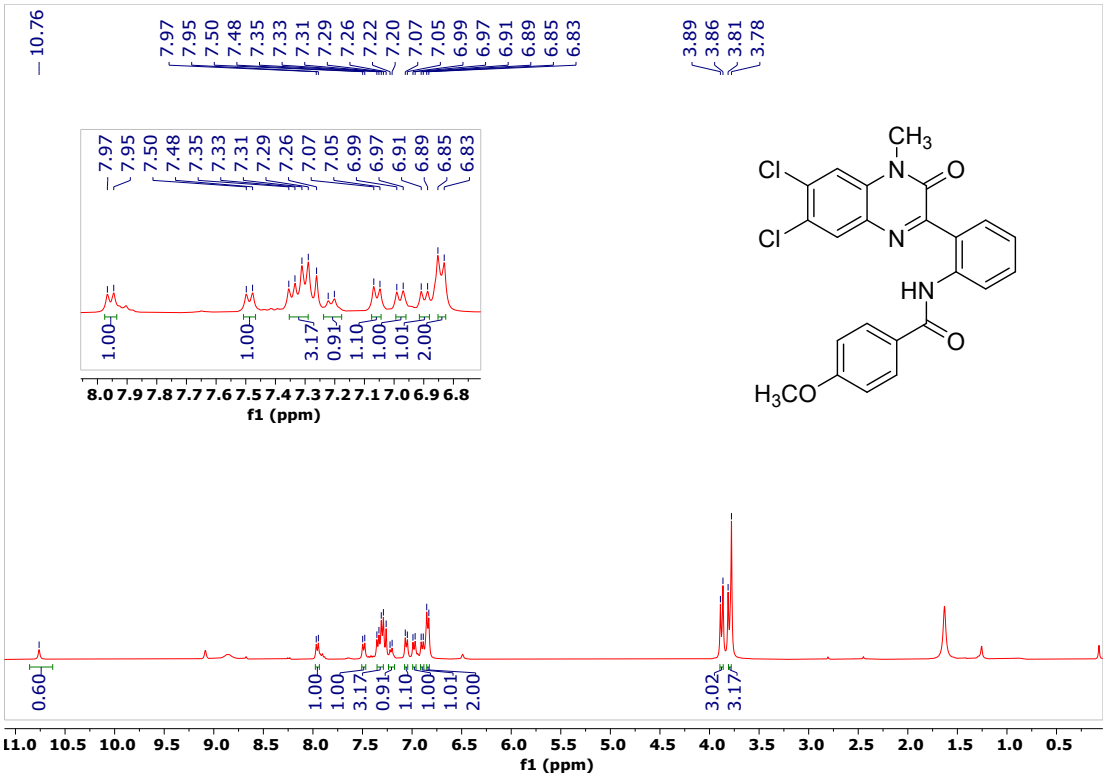


Figure 19: ^{1}H NMR spectrum of compound **3cb** (400 MHz, $CDCl_3$).

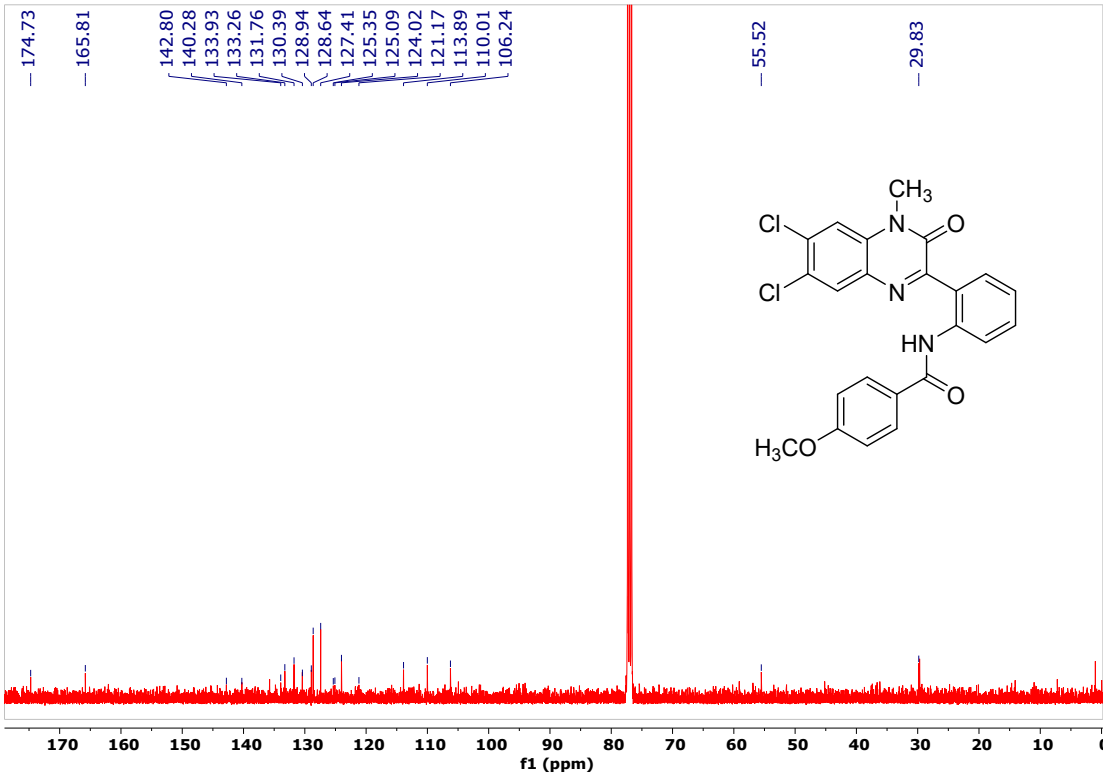


Figure 20: ^{13}C NMR spectrum of compound **3cb** (100 MHz, $CDCl_3$).

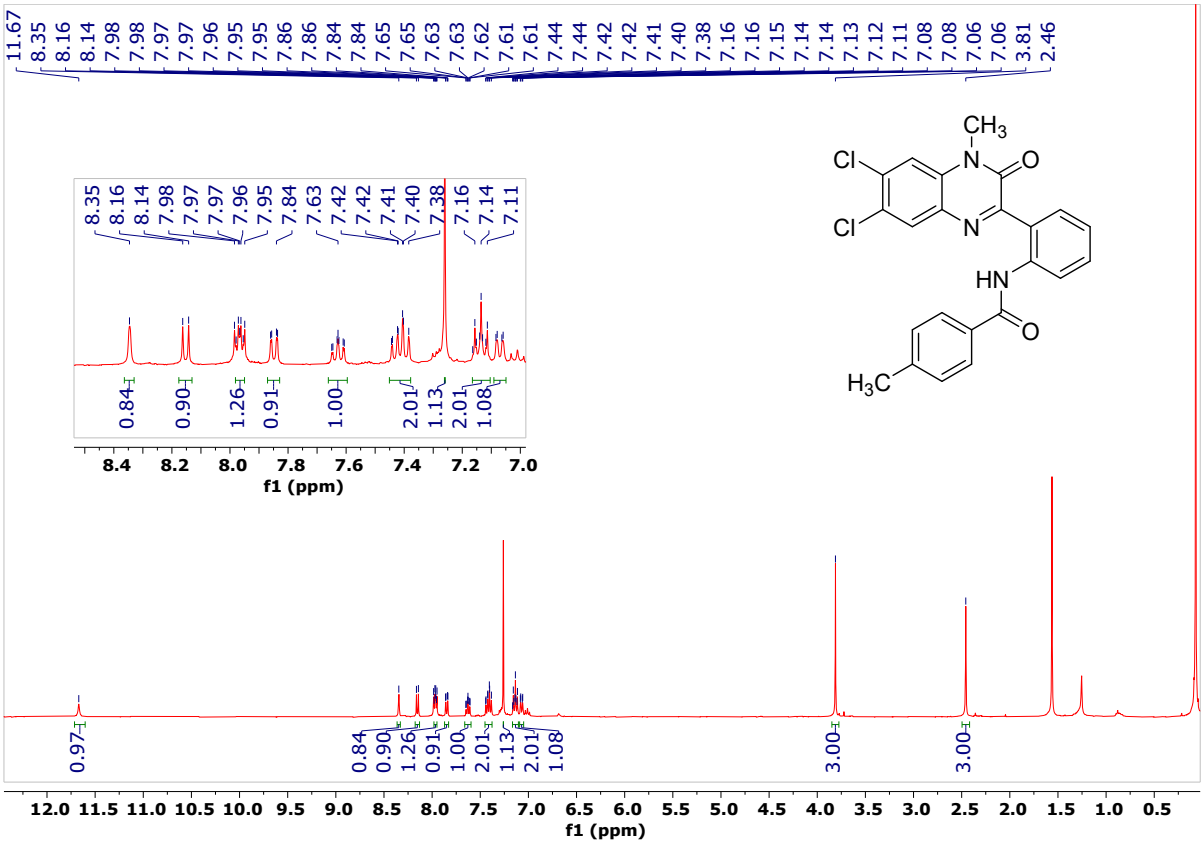


Figure 21: ^{1}H NMR spectrum of compound **3cd** (400 MHz, $CDCl_3$).

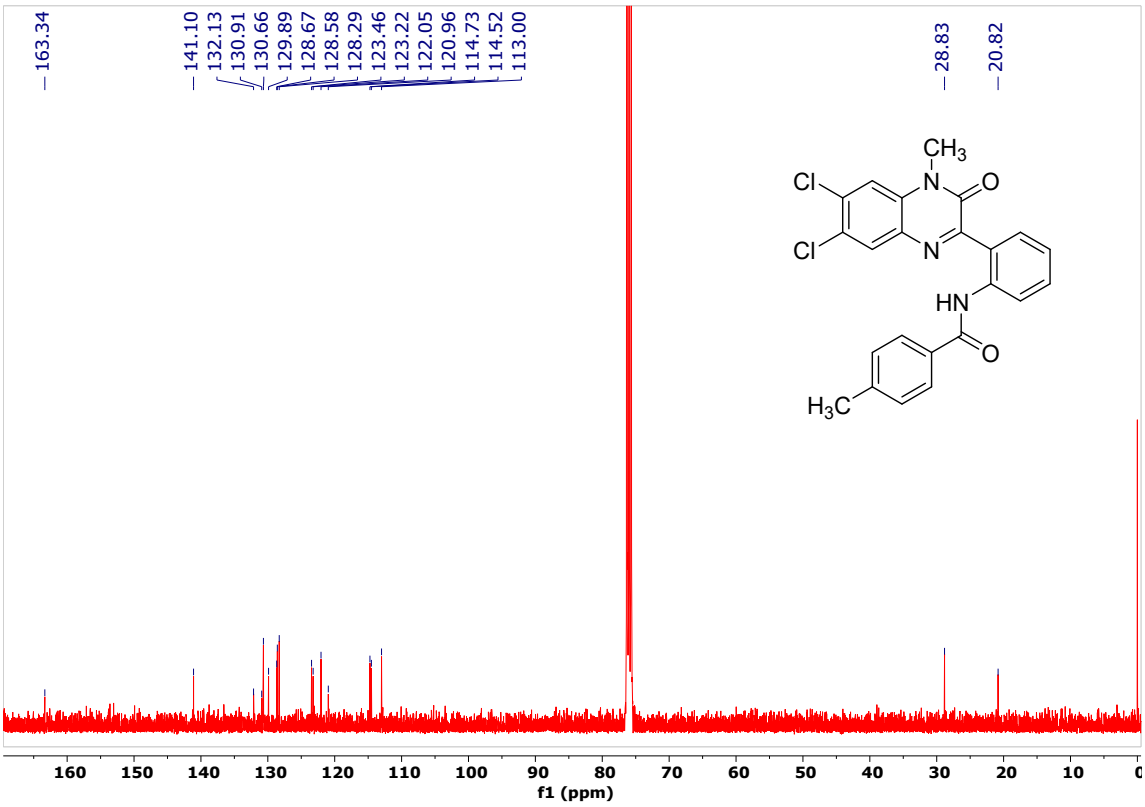


Figure 22: ^{13}C NMR spectrum of compound **3cd** (100 MHz, $CDCl_3$).

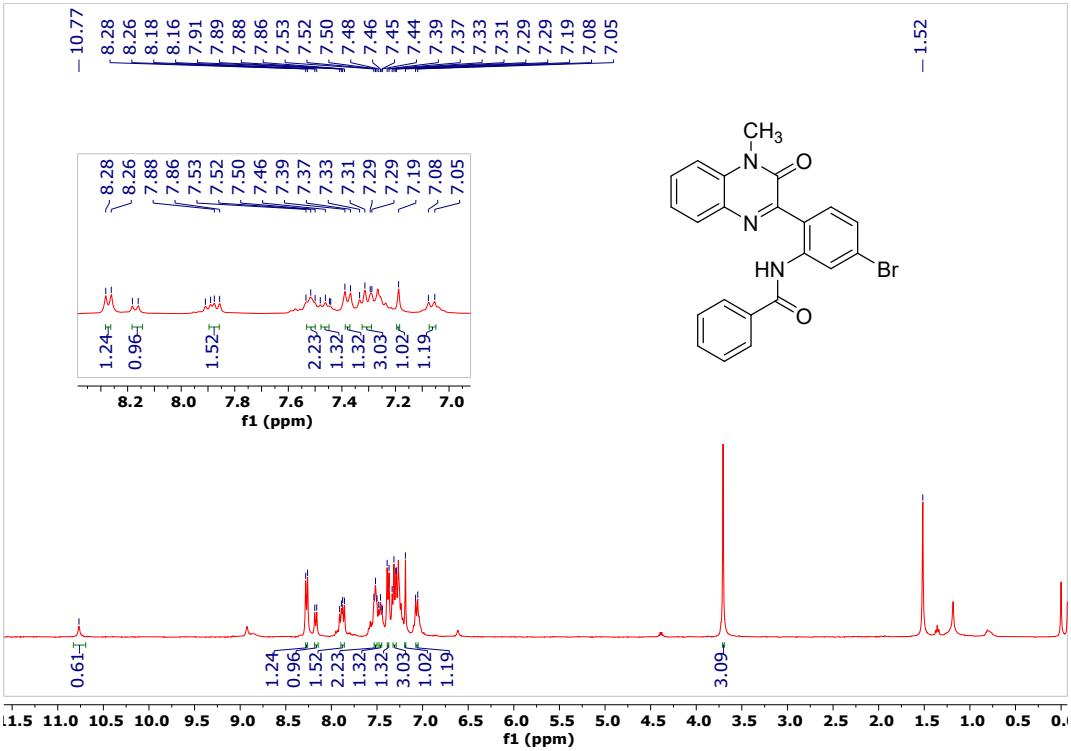


Figure 23: ^{1}H NMR spectrum of compound **3da** (400 MHz, $CDCl_3$).

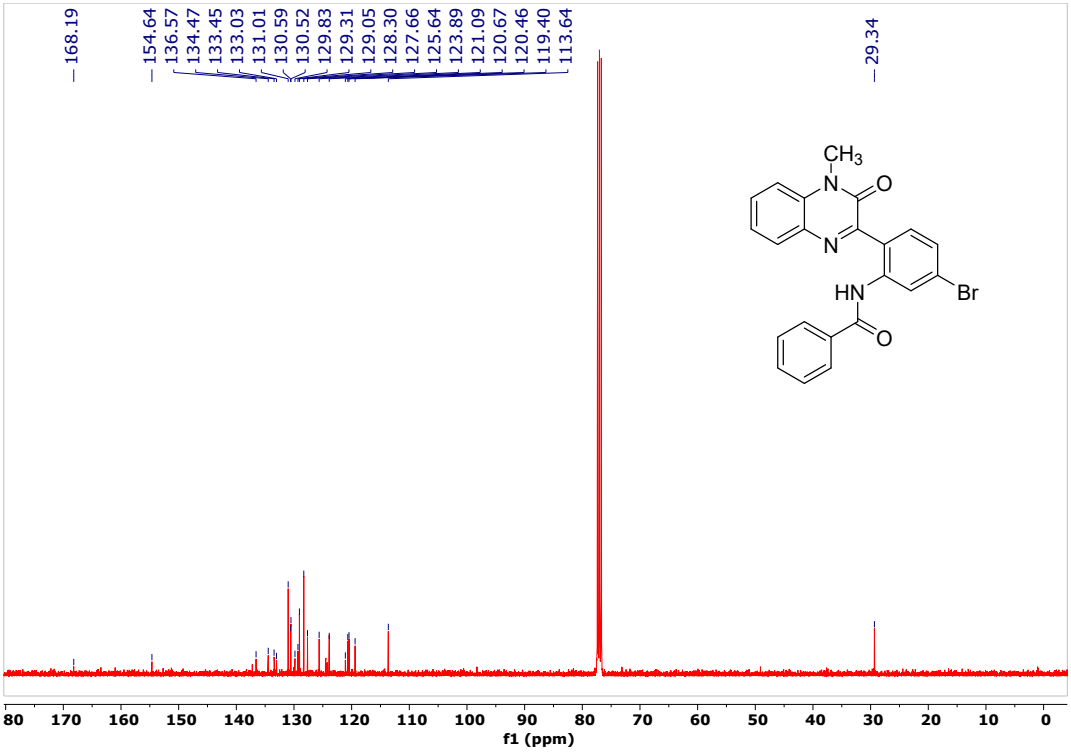


Figure 24: ^{13}C NMR spectrum of compound **3da** (100 MHz, $CDCl_3$).

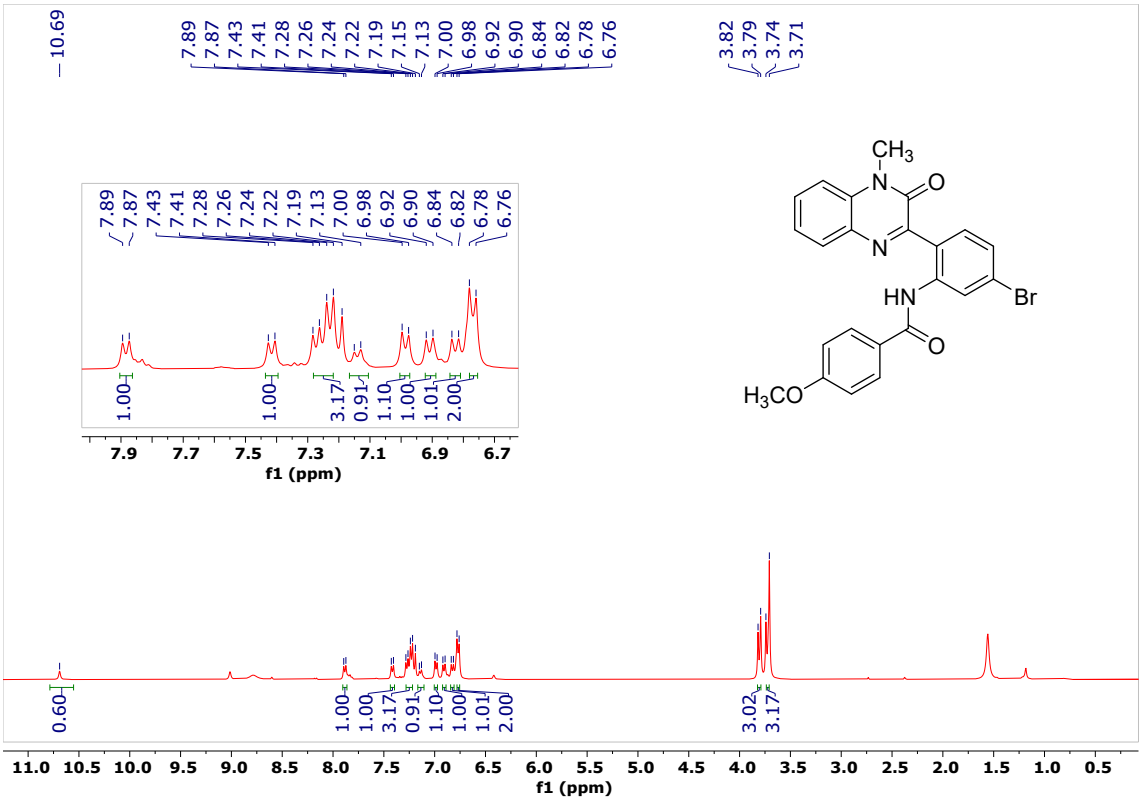


Figure 25: ^{1}H NMR spectrum of compound **3db** (400 MHz, $CDCl_3$).

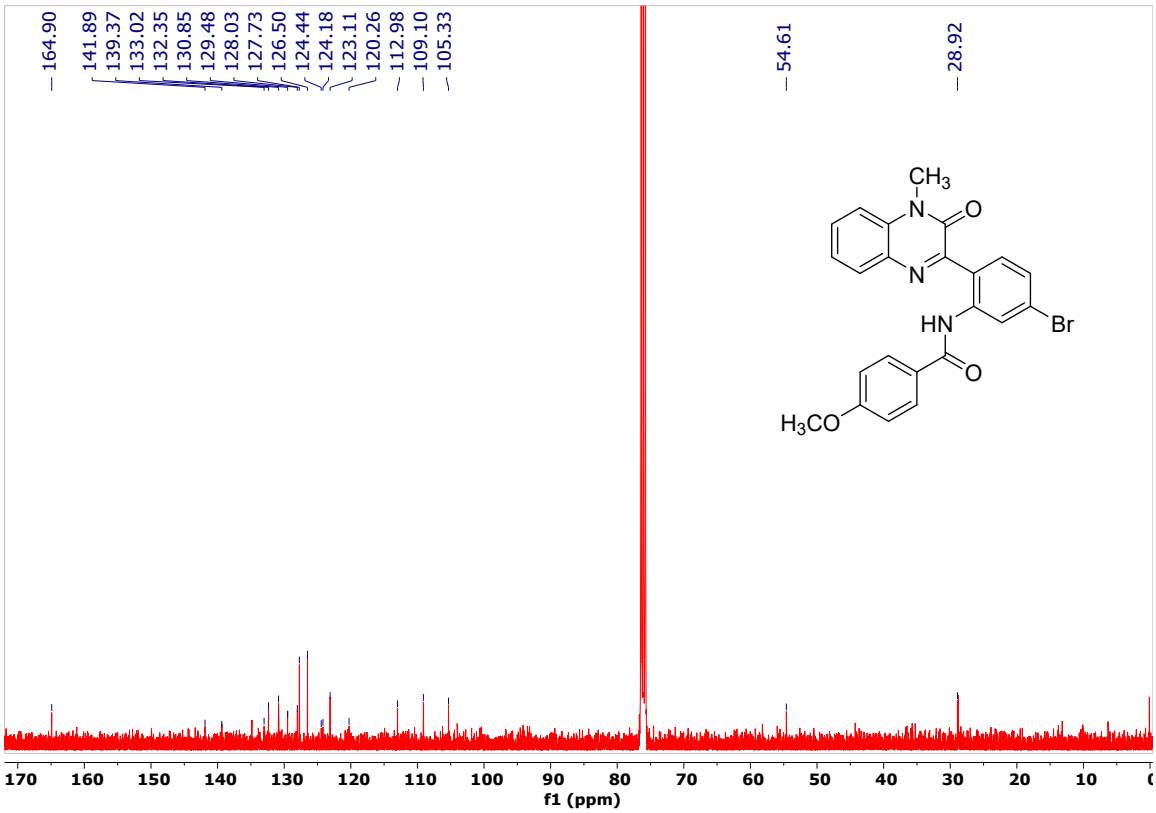


Figure 26: ^{13}C NMR spectrum of compound **3db** (100 MHz, $CDCl_3$).

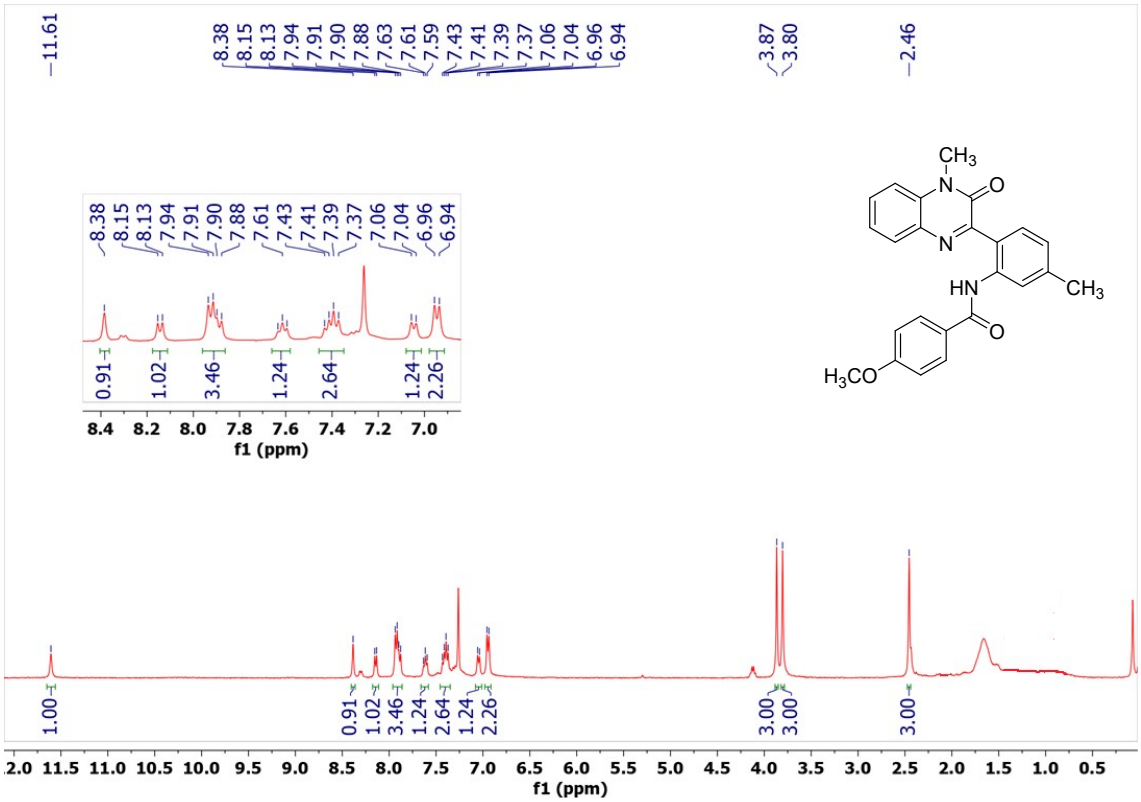


Figure 27: ^{1}H NMR spectrum of compound **3eb** (400 MHz, $CDCl_3$).

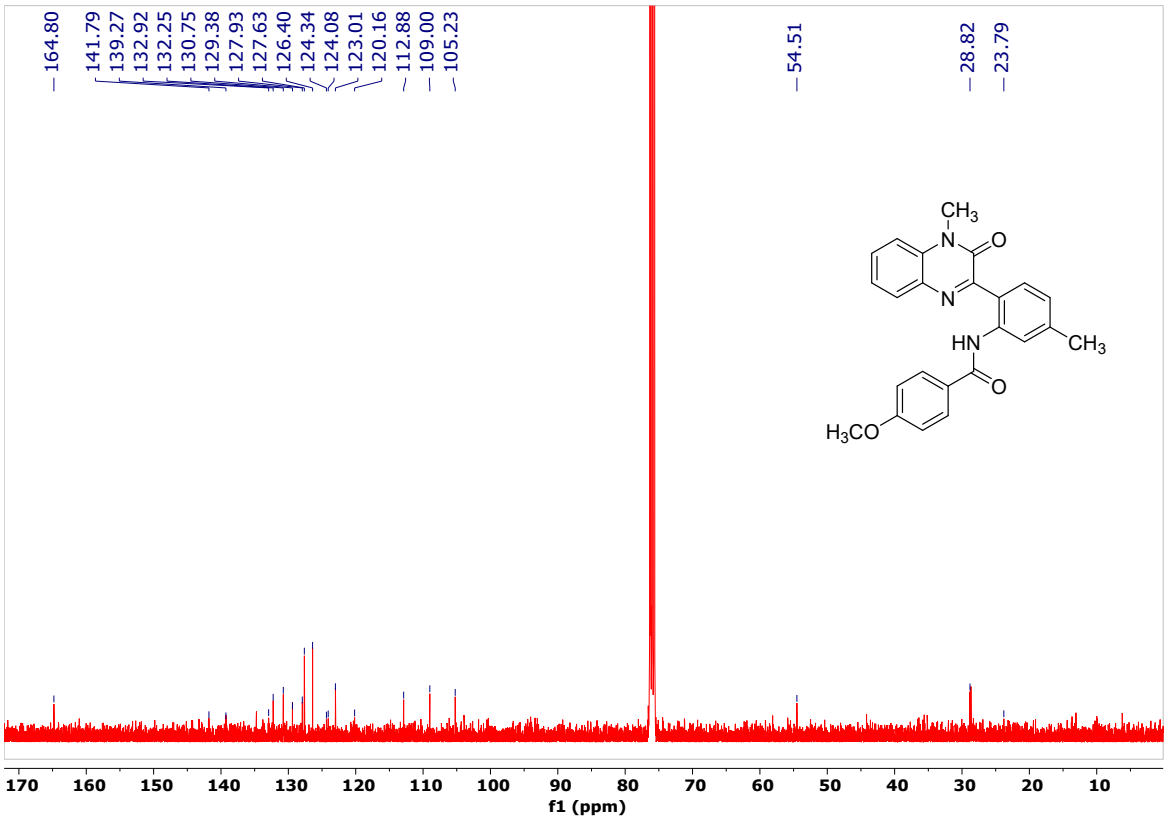


Figure 28: ^{13}C NMR spectrum of compound **3eb** (100 MHz, $CDCl_3$).

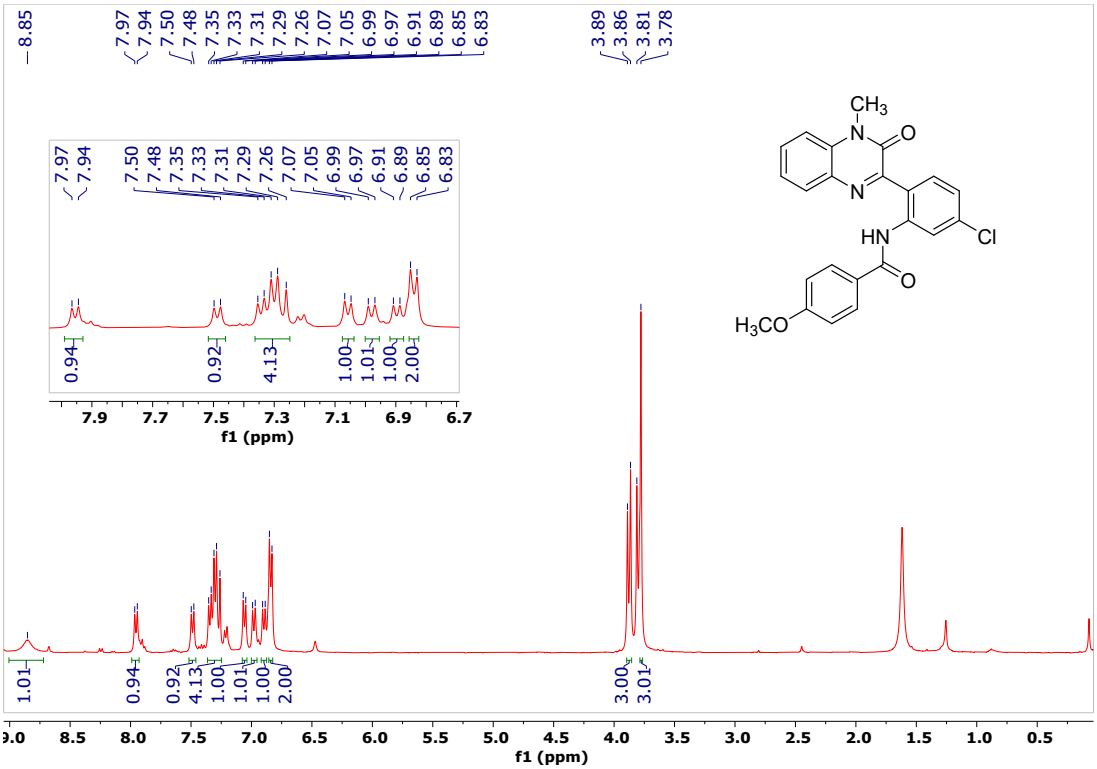


Figure 29: ^{1}H NMR spectrum of compound **3f b** (400 MHz, $CDCl_3$).

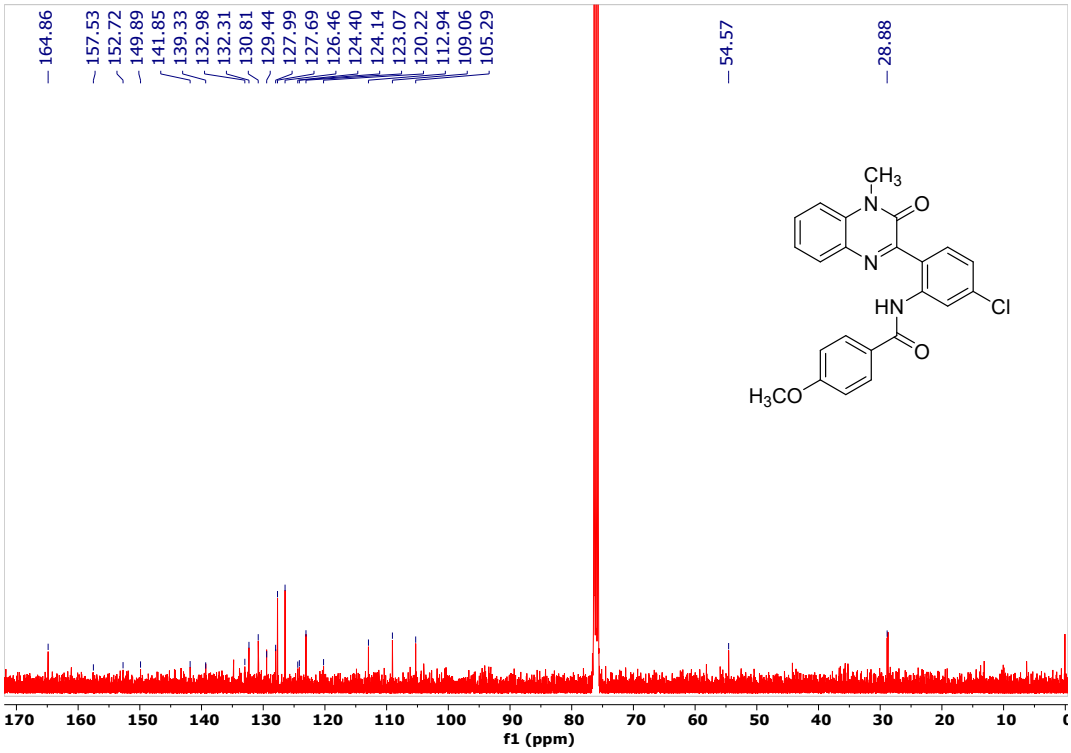


Figure 30: ^{13}C NMR spectrum of compound **3f b** (100 MHz, $CDCl_3$).

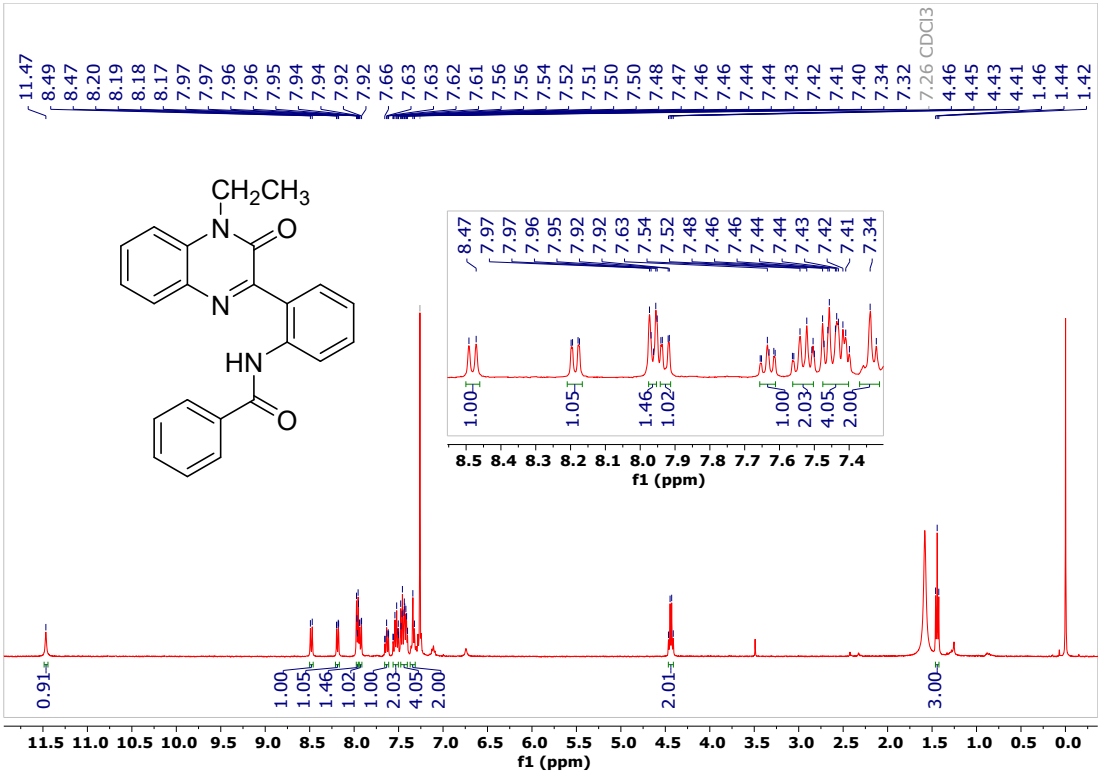


Figure 31: ^{1}H NMR spectrum of compound **4ga** (400 MHz, $CDCl_3$).

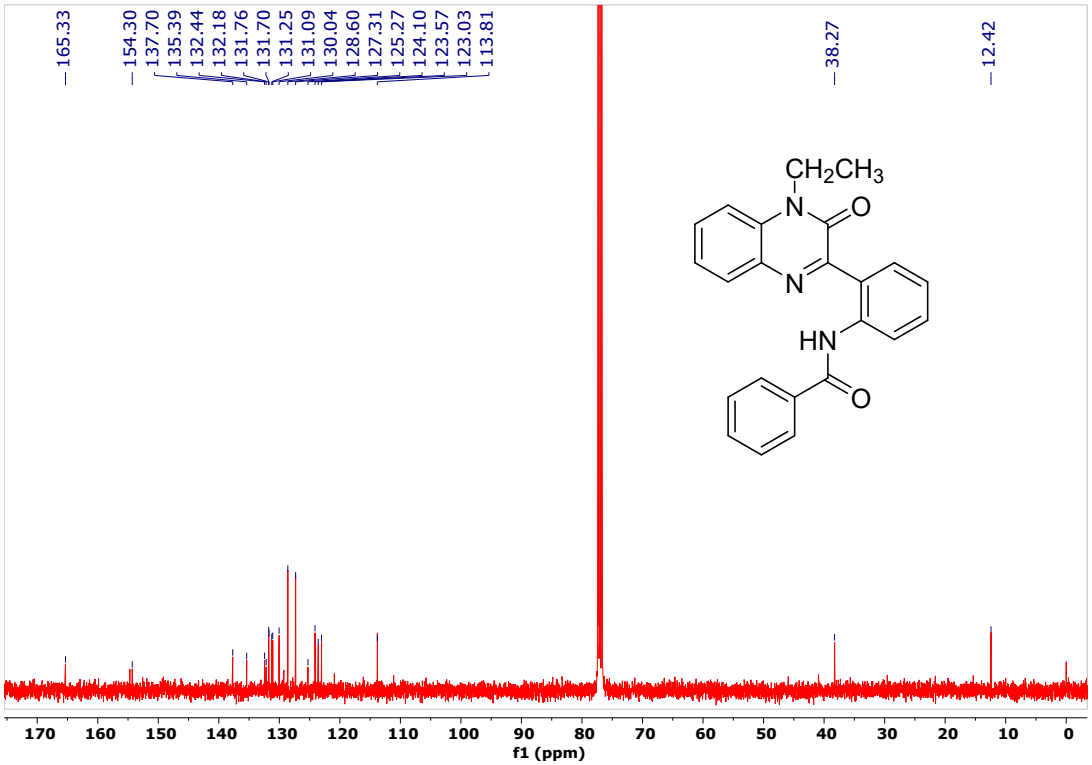


Figure 32: ^{13}C NMR spectrum of compound **4ga** (100 MHz, $CDCl_3$).

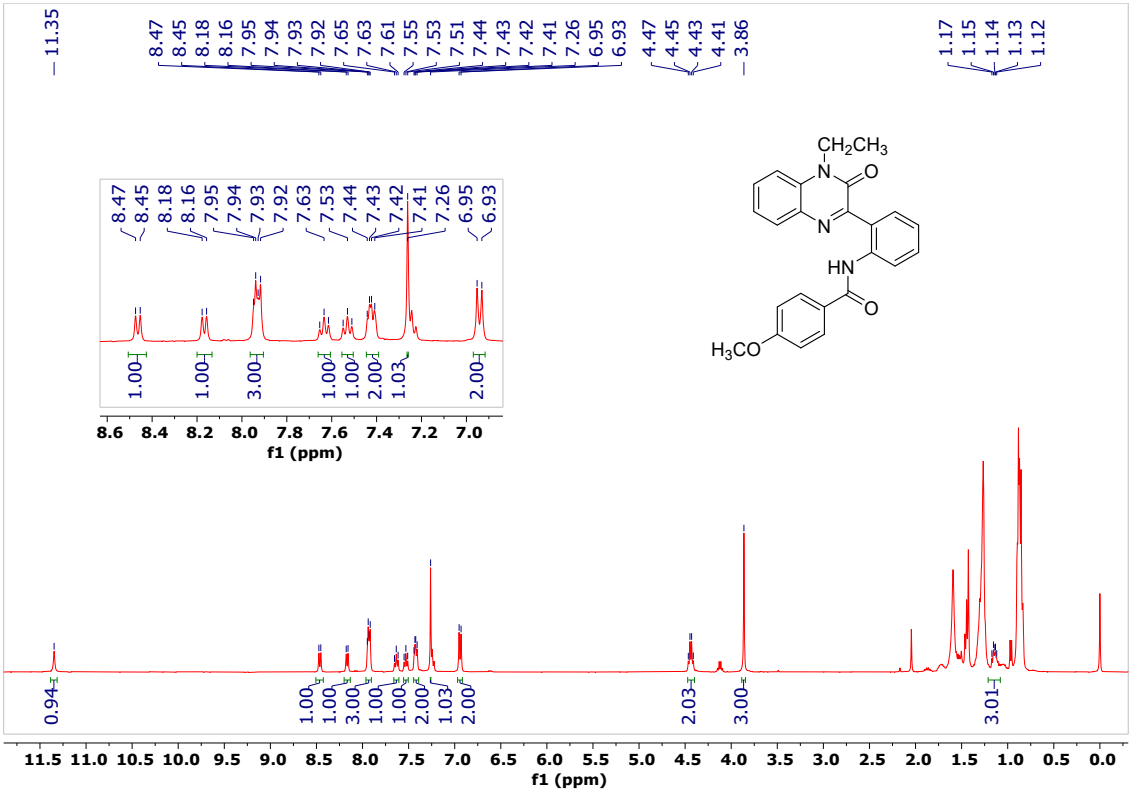


Figure 33: ^{1}H NMR spectrum of compound **4gb** (400 MHz, $CDCl_3$).

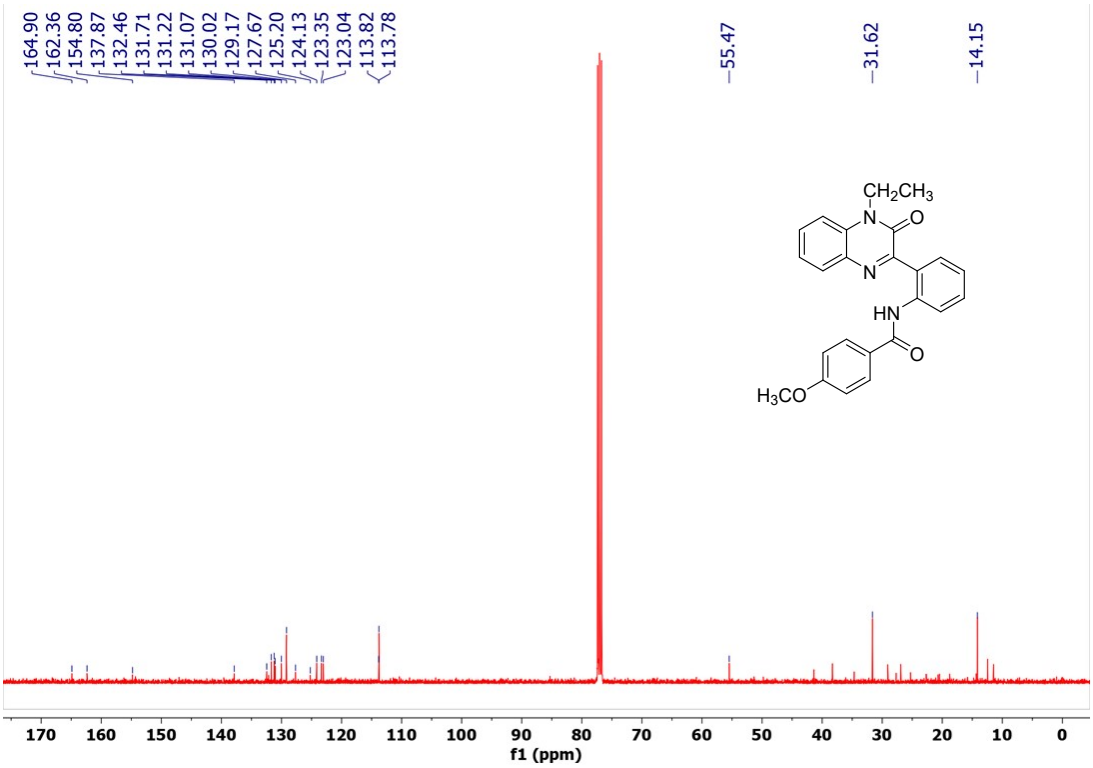


Figure 34: ^{13}C NMR spectrum of compound **4gb** (100 MHz, $CDCl_3$).

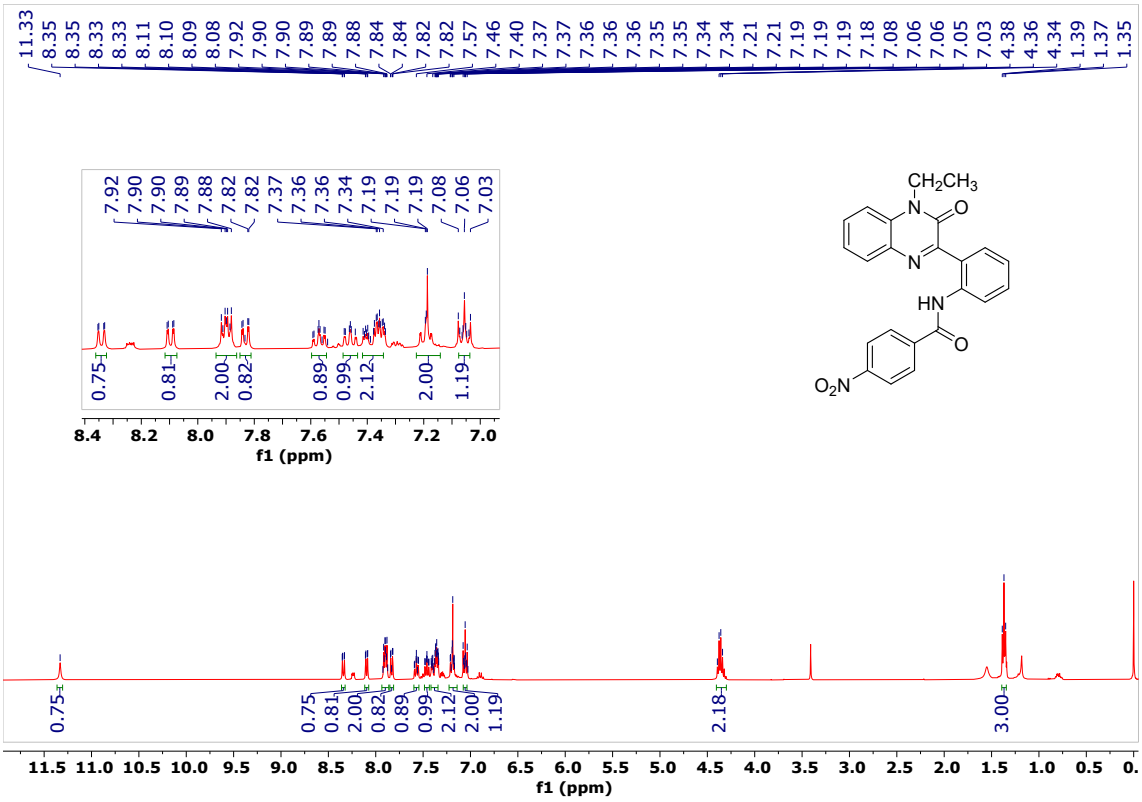


Figure 35: ^{1}H NMR spectrum of compound **4gc** (400 MHz, $CDCl_3$).

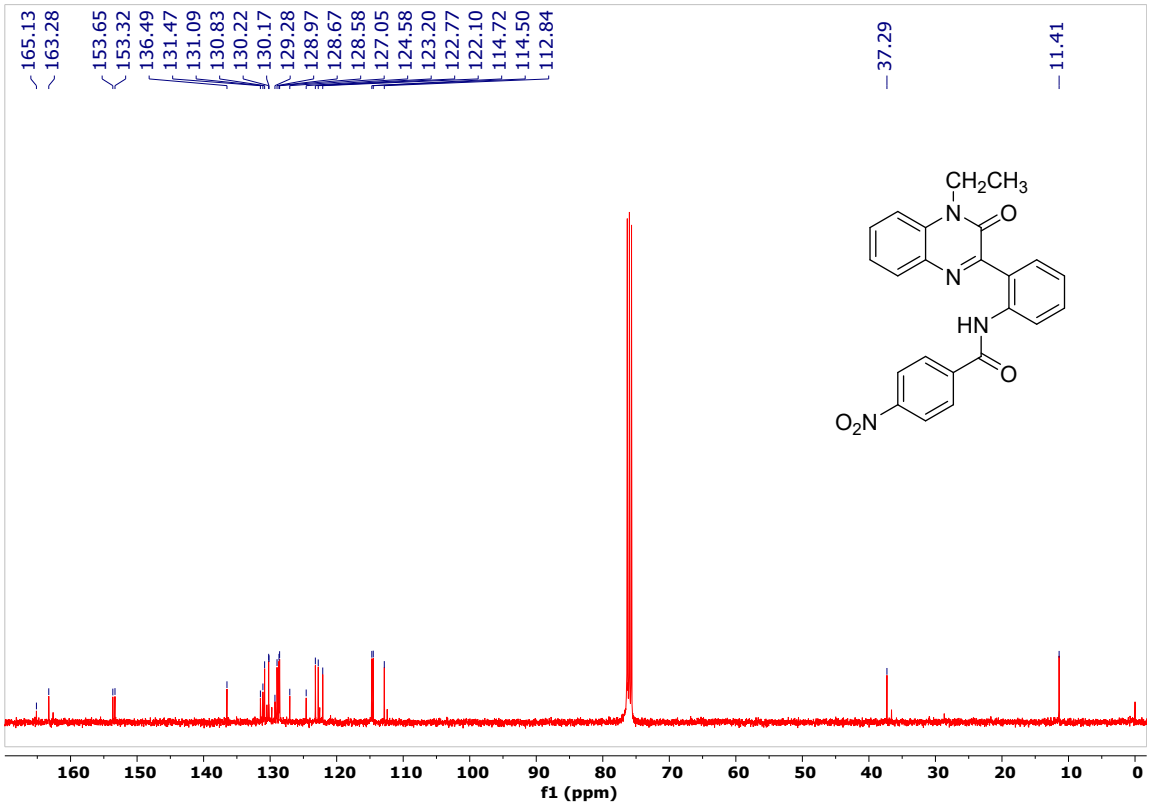


Figure 36: ^{13}C NMR spectrum of compound **4gc** (100 MHz, $CDCl_3$).

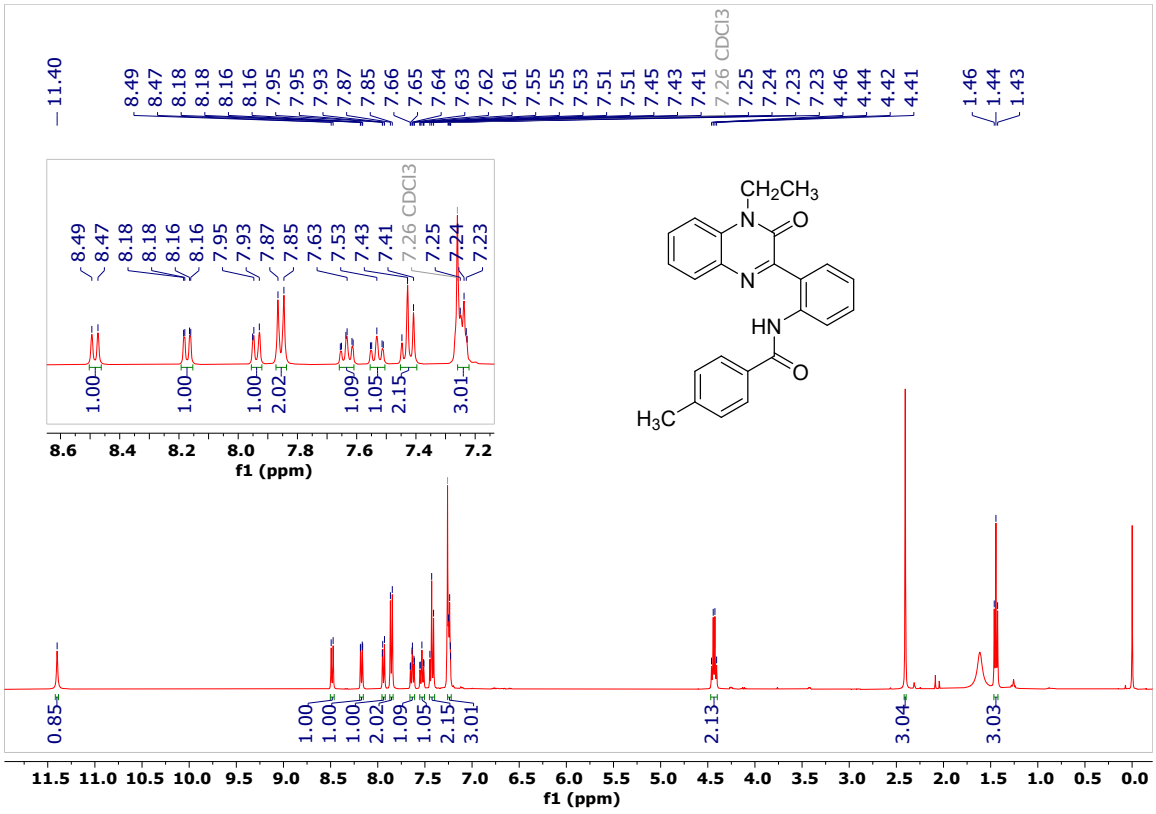


Figure 37: ^{1}H NMR spectrum of compound **4gd** (400 MHz, $CDCl_3$).

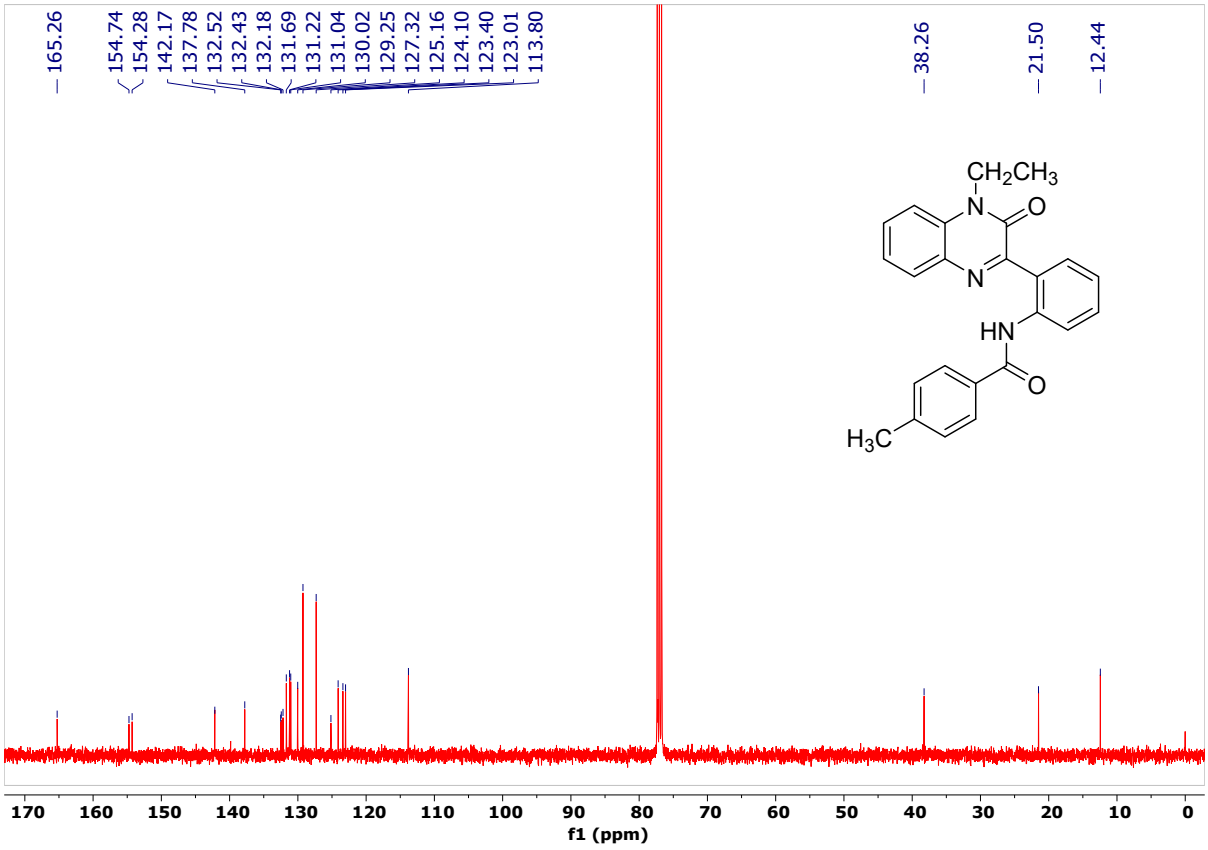


Figure 38: ^{13}C NMR spectrum of compound **4gd** (100 MHz, $CDCl_3$).

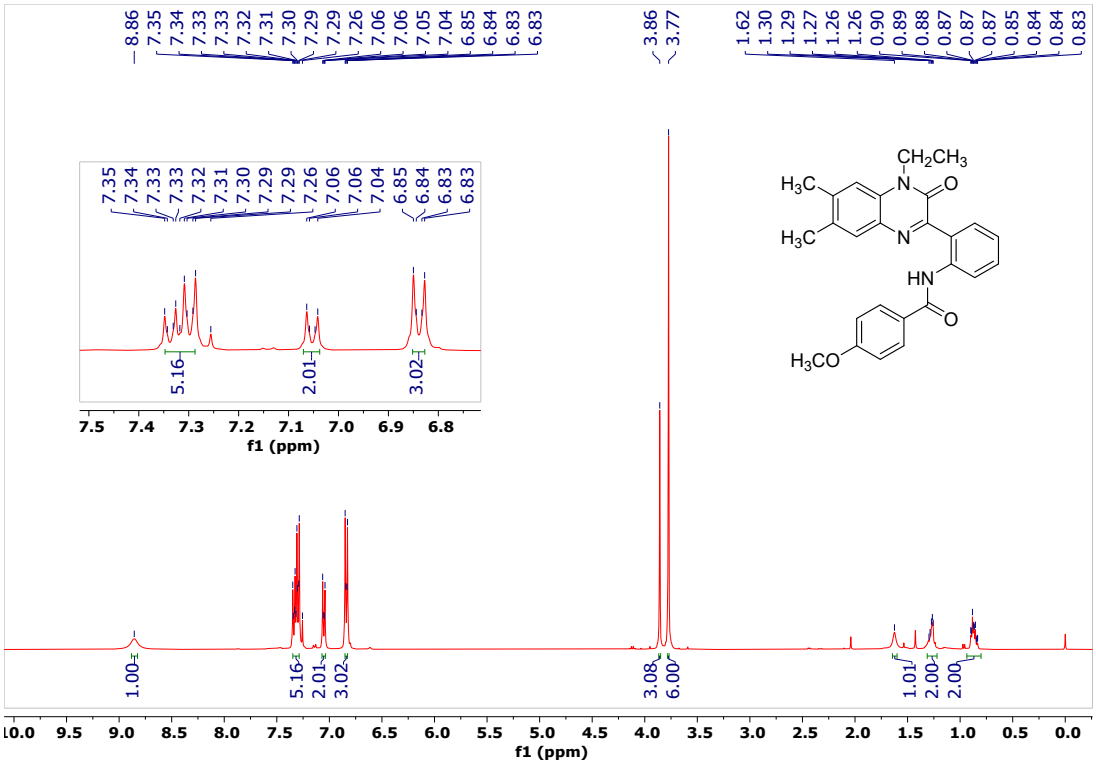


Figure 39: ^{1}H NMR spectrum of compound **4hb** (400 MHz, $CDCl_3$).

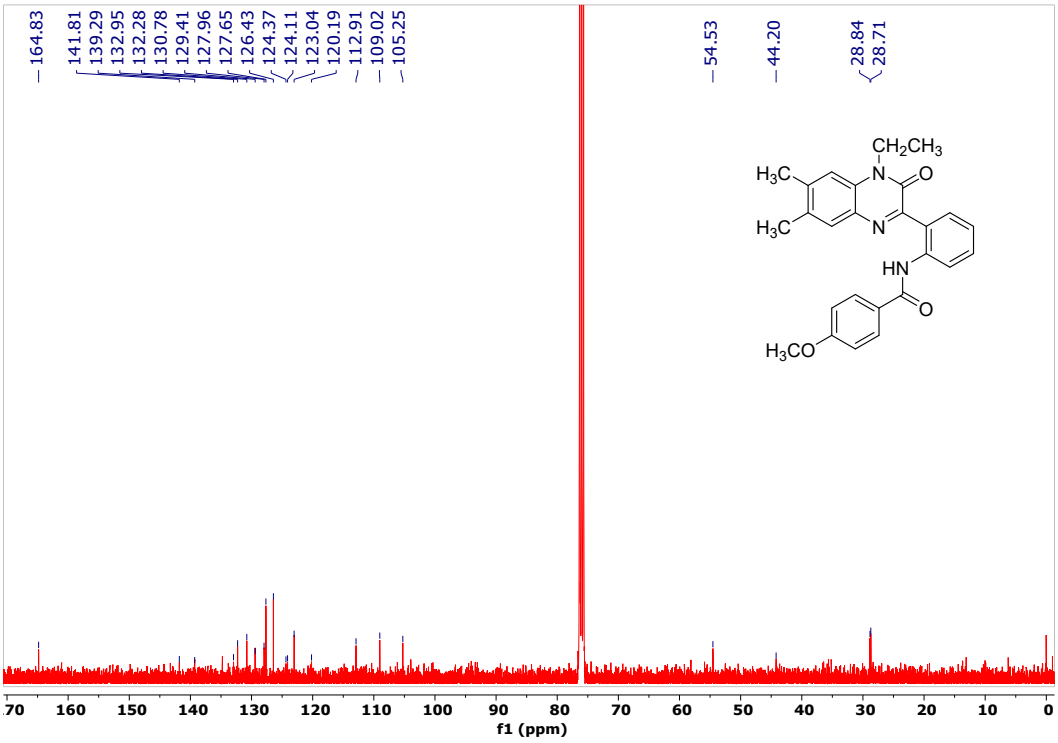


Figure 40: ^{13}C NMR spectrum of compound **4hb** (100 MHz, $CDCl_3$).

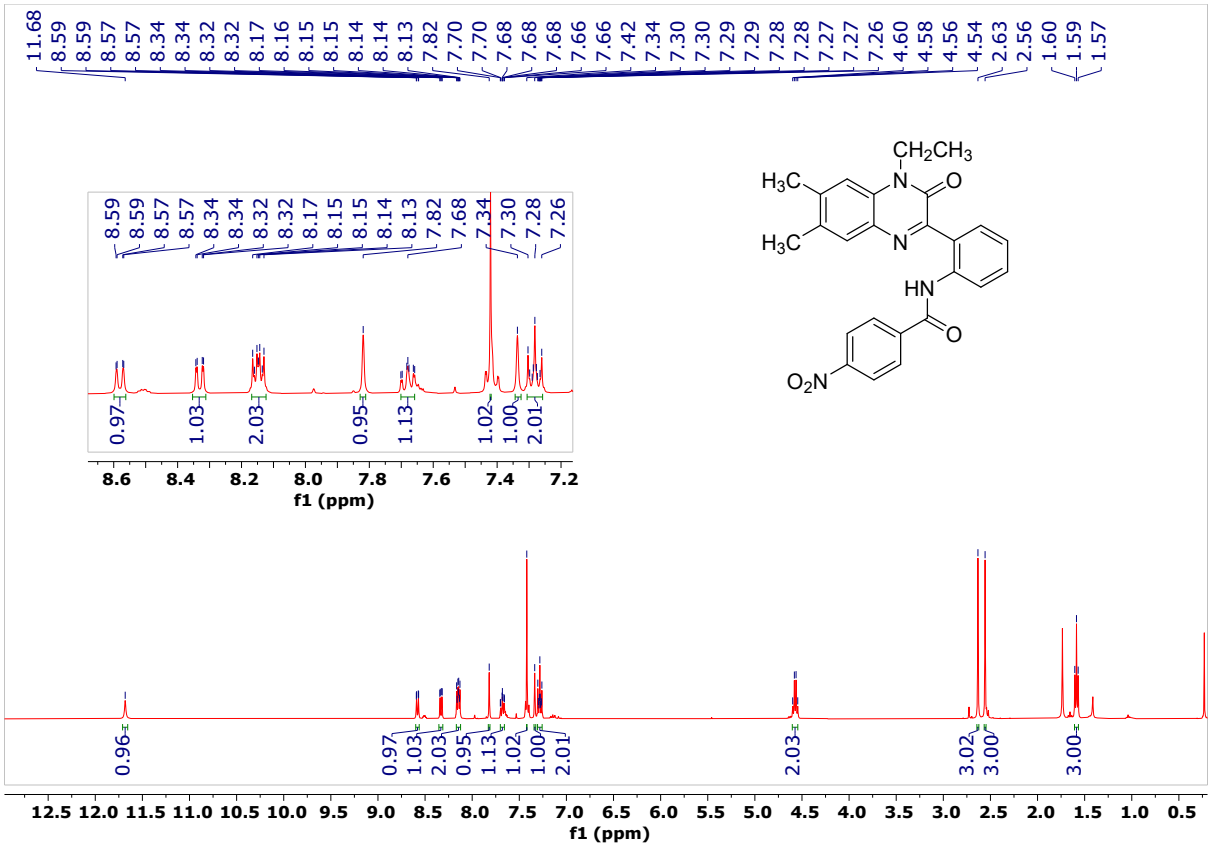


Figure 41: ^{1}H NMR spectrum of compound **4hc** (400 MHz, $CDCl_3$).

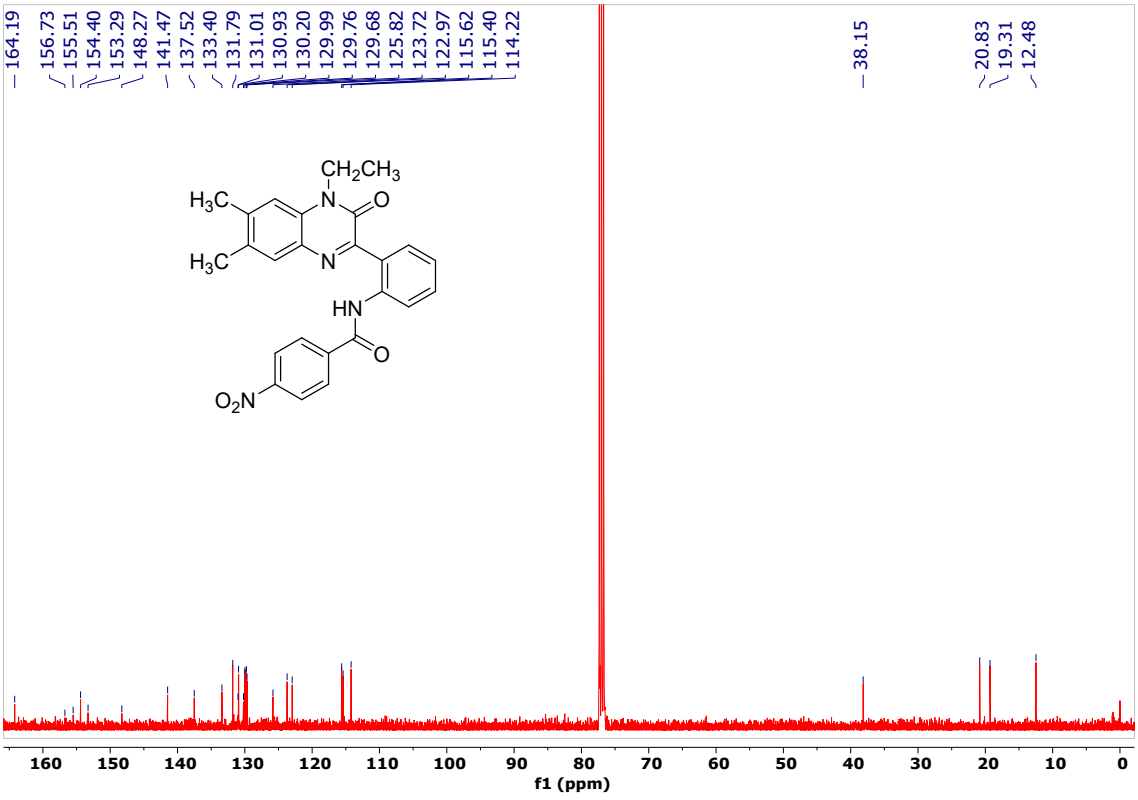


Figure 42: ^{13}C NMR spectrum of compound **4hc** (100 MHz, $CDCl_3$).

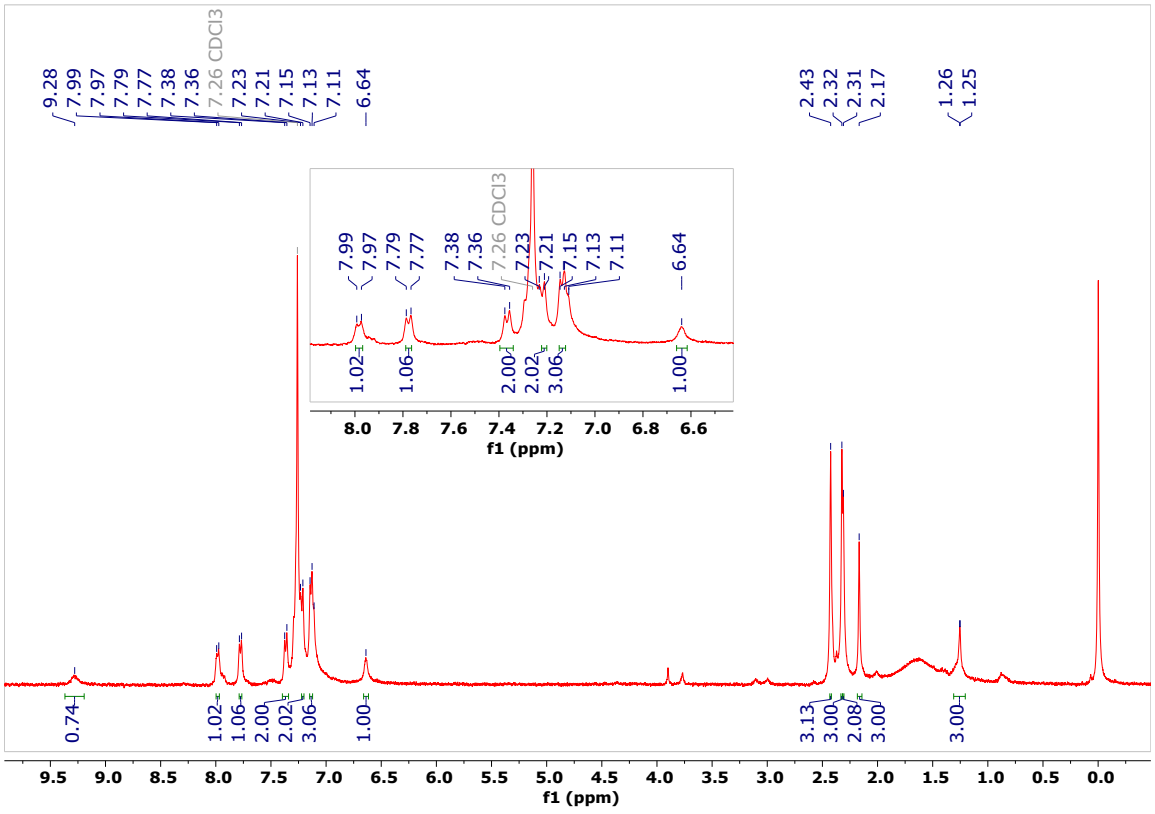


Figure 43: ^{1}H NMR spectrum of compound **4hd** (400 MHz, $CDCl_3$).

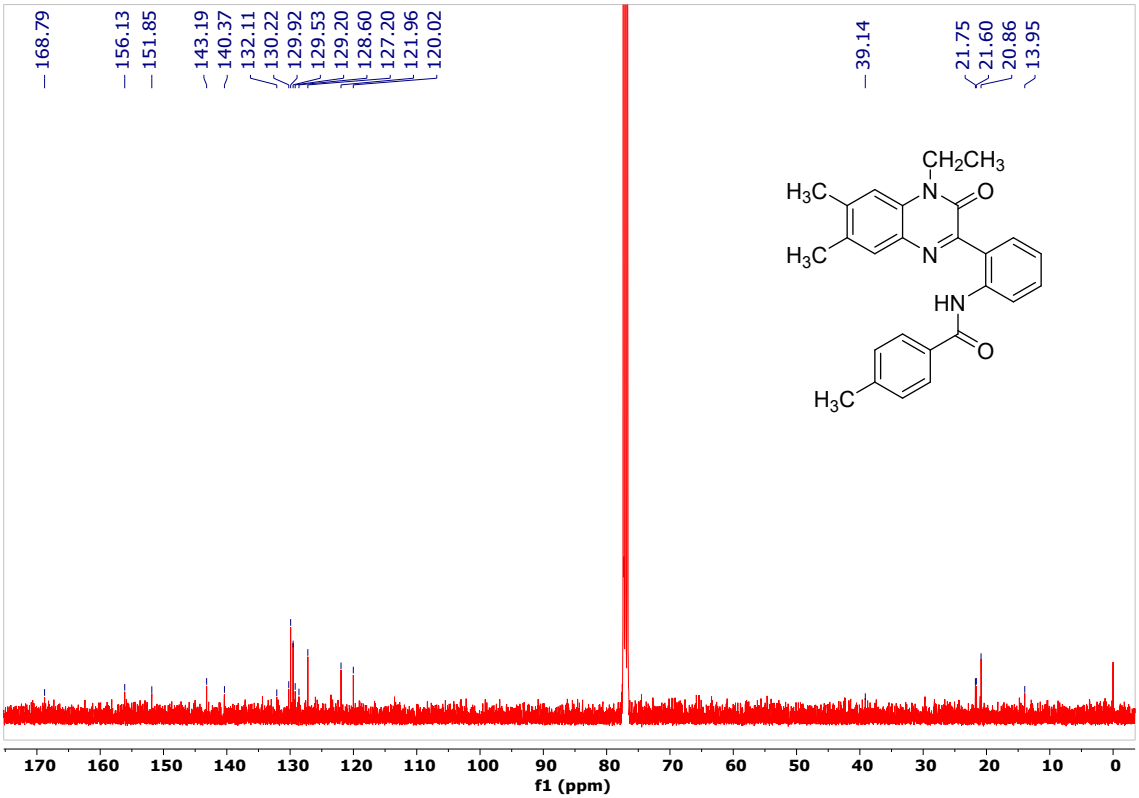


Figure 44: ^{13}C NMR spectrum of compound **4hd** (100 MHz, $CDCl_3$).

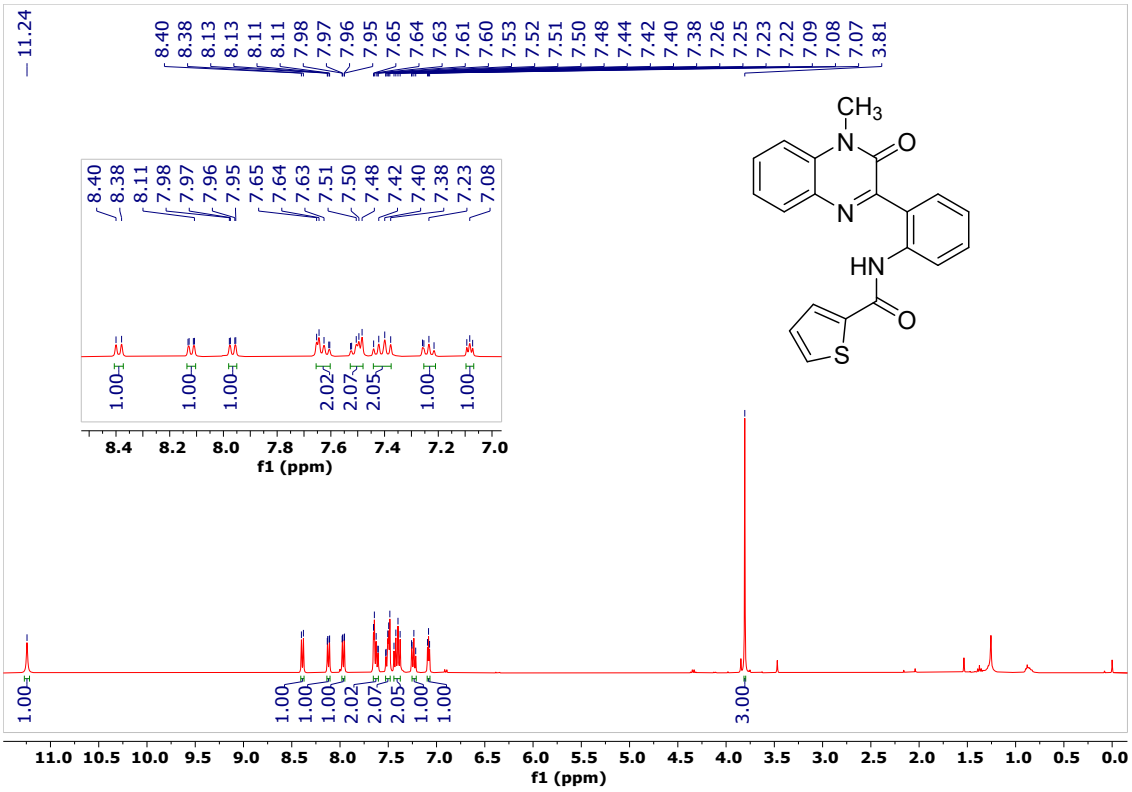


Figure 45: ^{1}H NMR spectrum of compound **5ae** (400 MHz, $CDCl_3$).

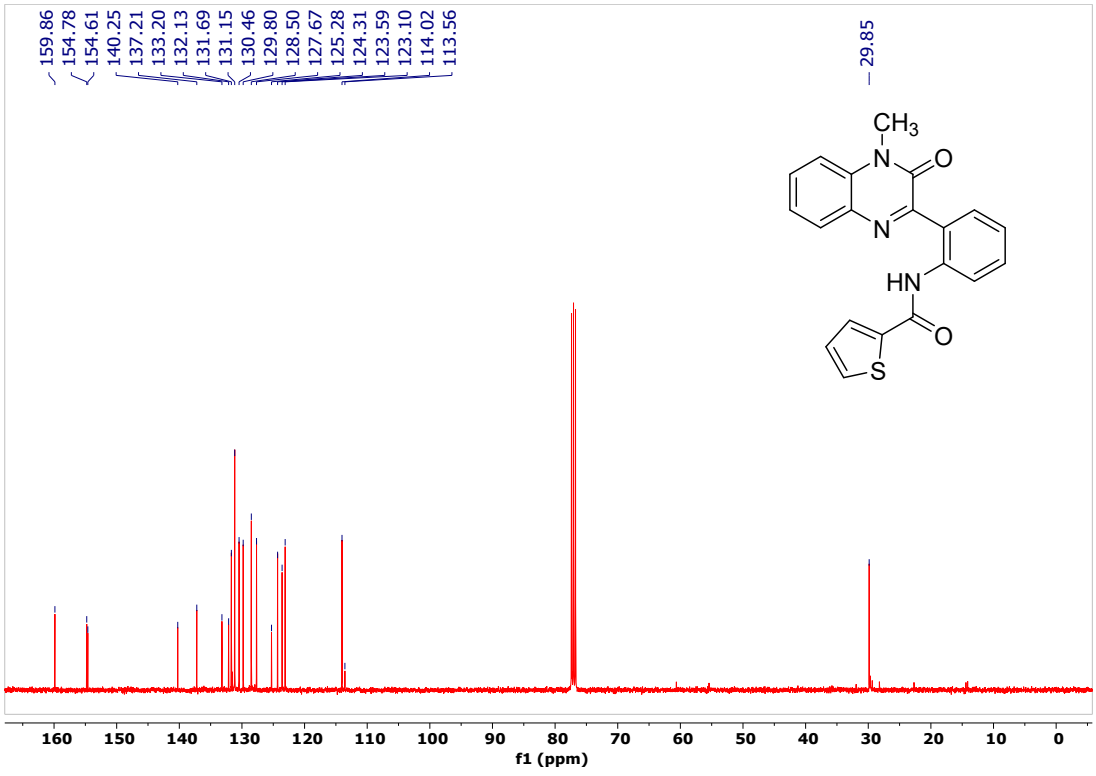


Figure 46: ^{13}C NMR spectrum of compound **5ae** (100 MHz, $CDCl_3$).

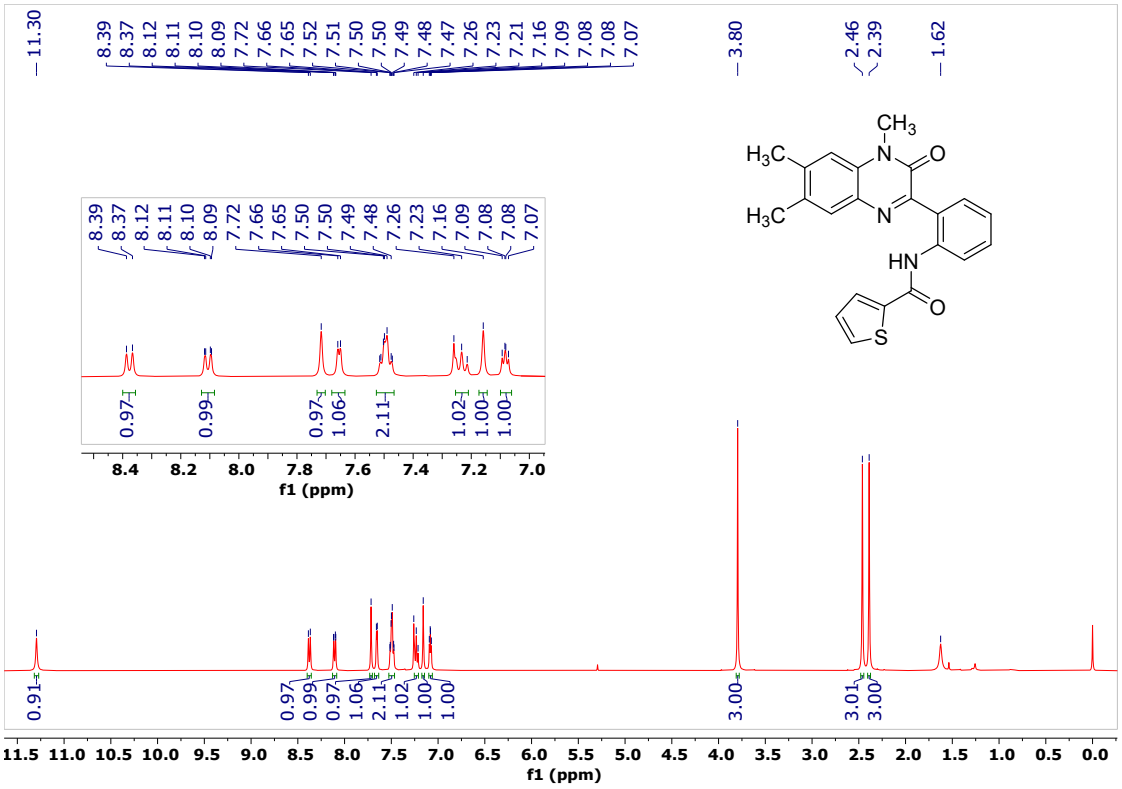


Figure 47: ^{1}H NMR spectrum of compound **5be** (400 MHz, $CDCl_3$).

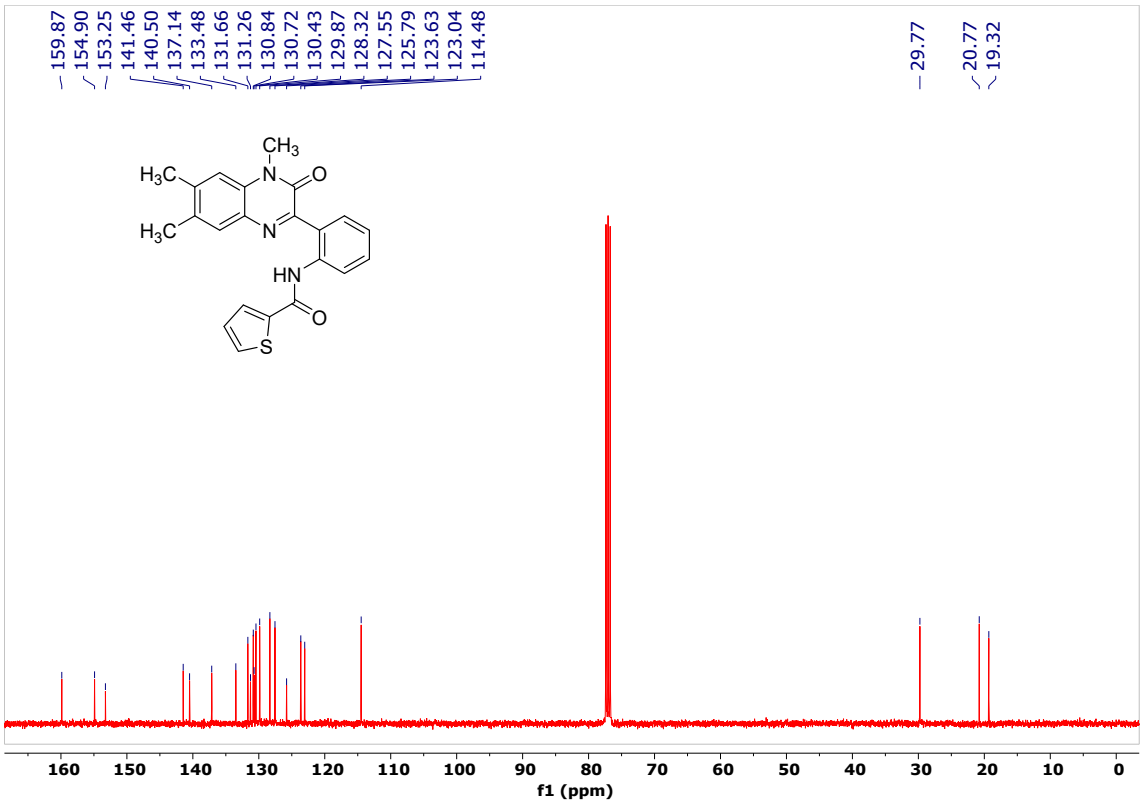


Figure 48: ^{13}C NMR spectrum of compound **5be** (100 MHz, $CDCl_3$).

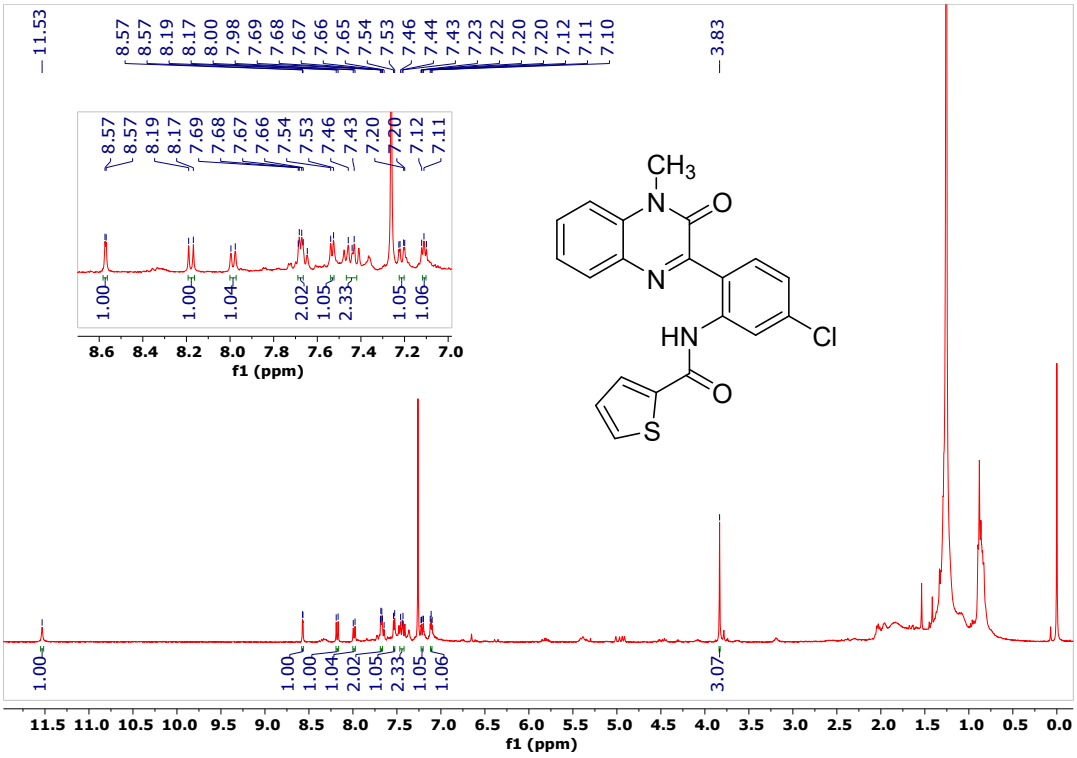


Figure 49: ^{1}H NMR spectrum of compound **5ce** (400 MHz, $CDCl_3$).

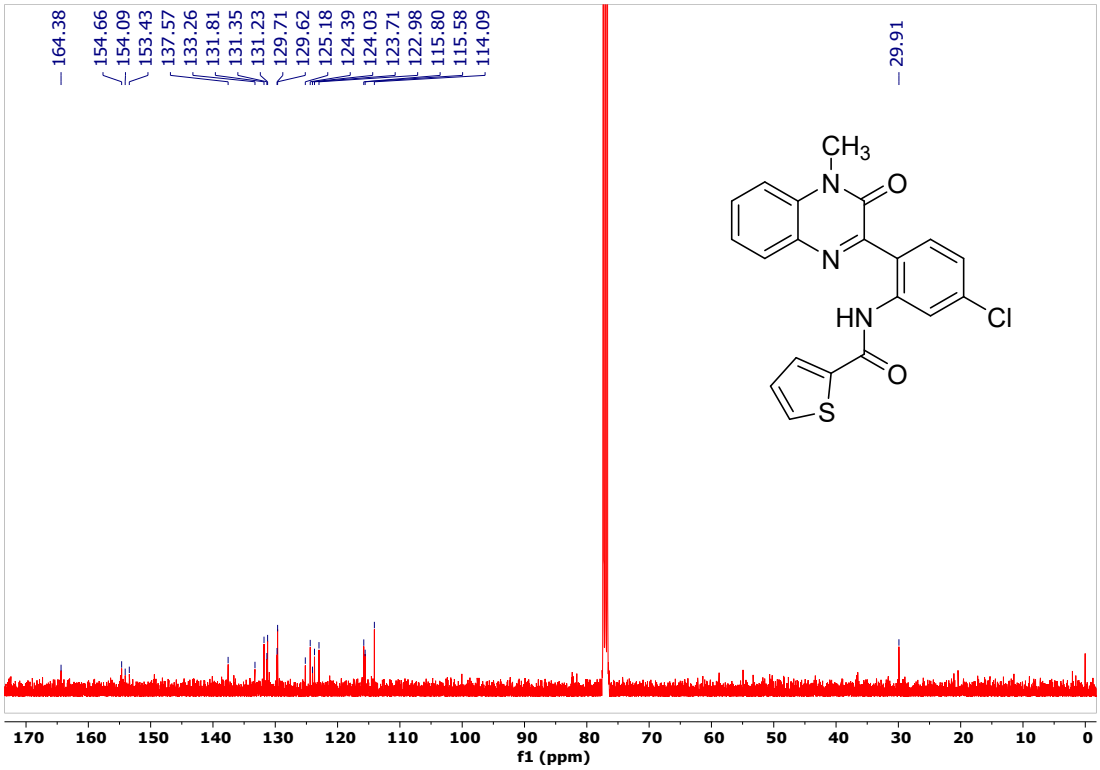


Figure 50: ^{13}C NMR spectrum of compound **5ce** (100 MHz, $CDCl_3$).

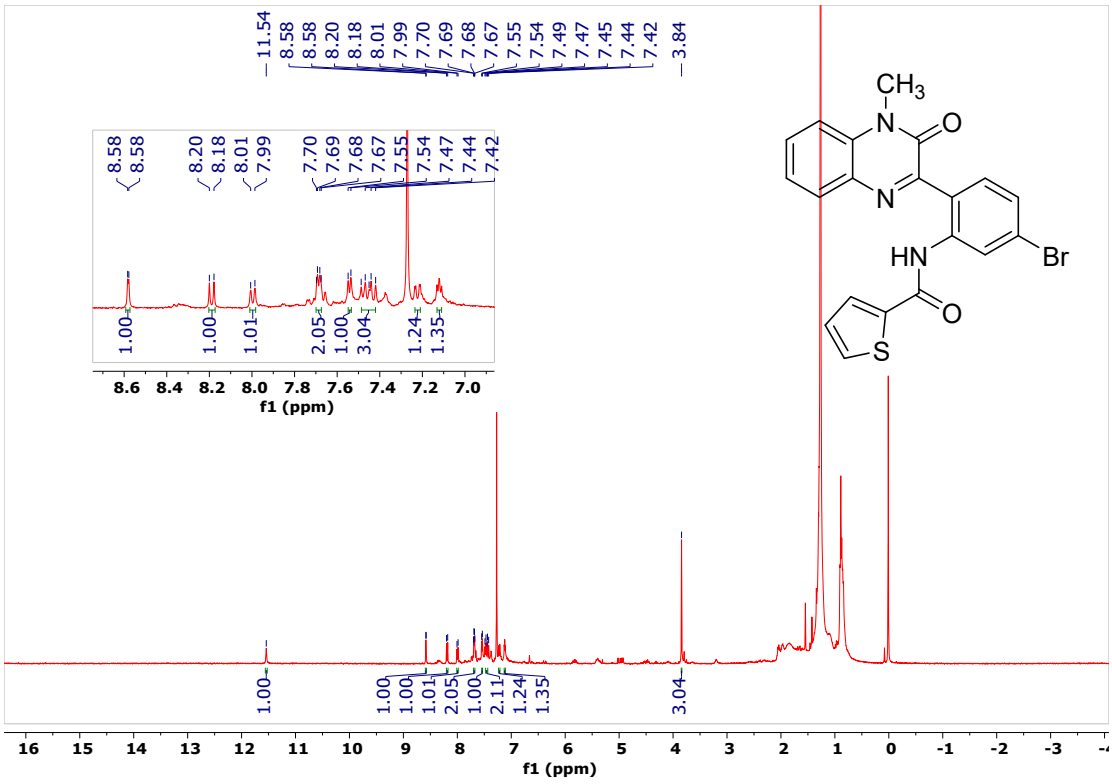


Figure 51: ^{1}H NMR spectrum of compound **5de** (400 MHz, $CDCl_3$).

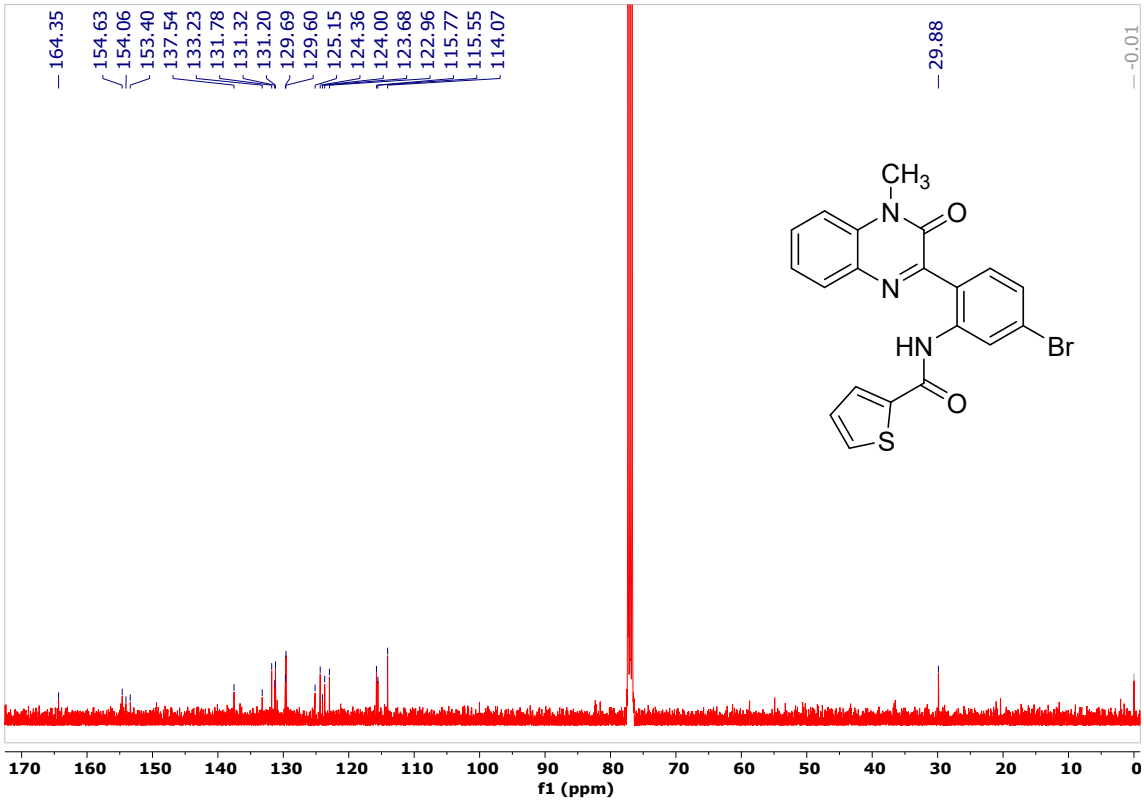


Figure 52: ^{13}C NMR spectrum of compound **5de** (100 MHz, $CDCl_3$).

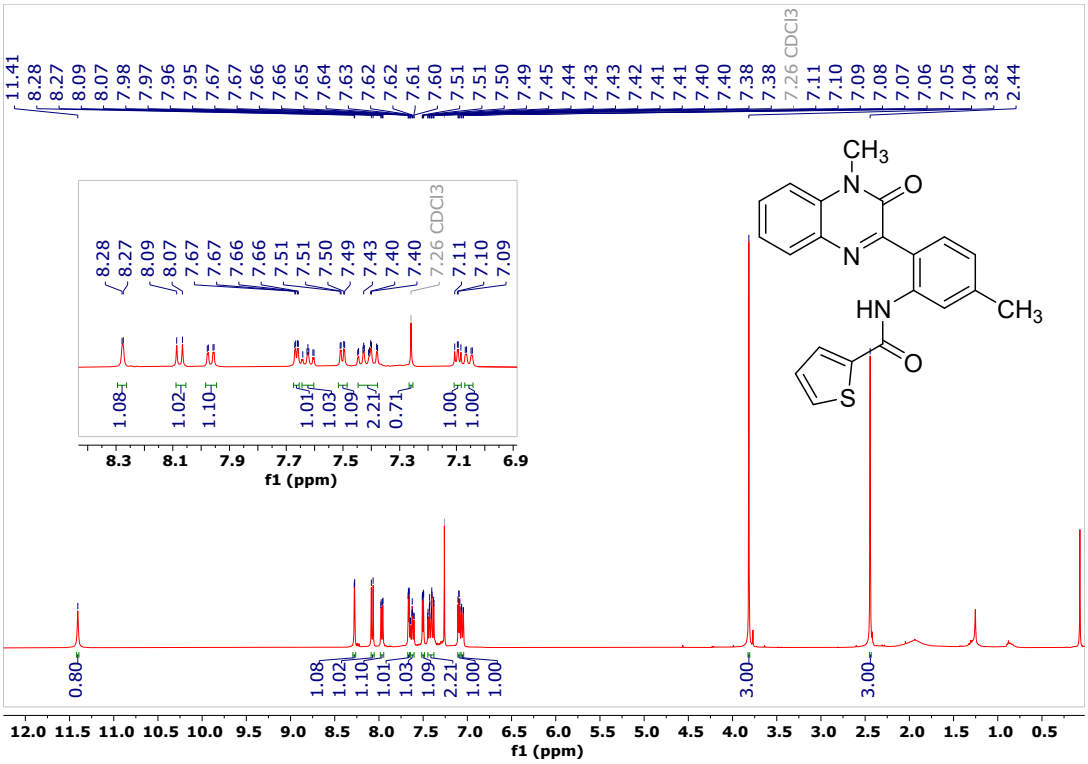


Figure 53: ^{1}H NMR spectrum of compound **5ee** (400 MHz, $CDCl_3$).

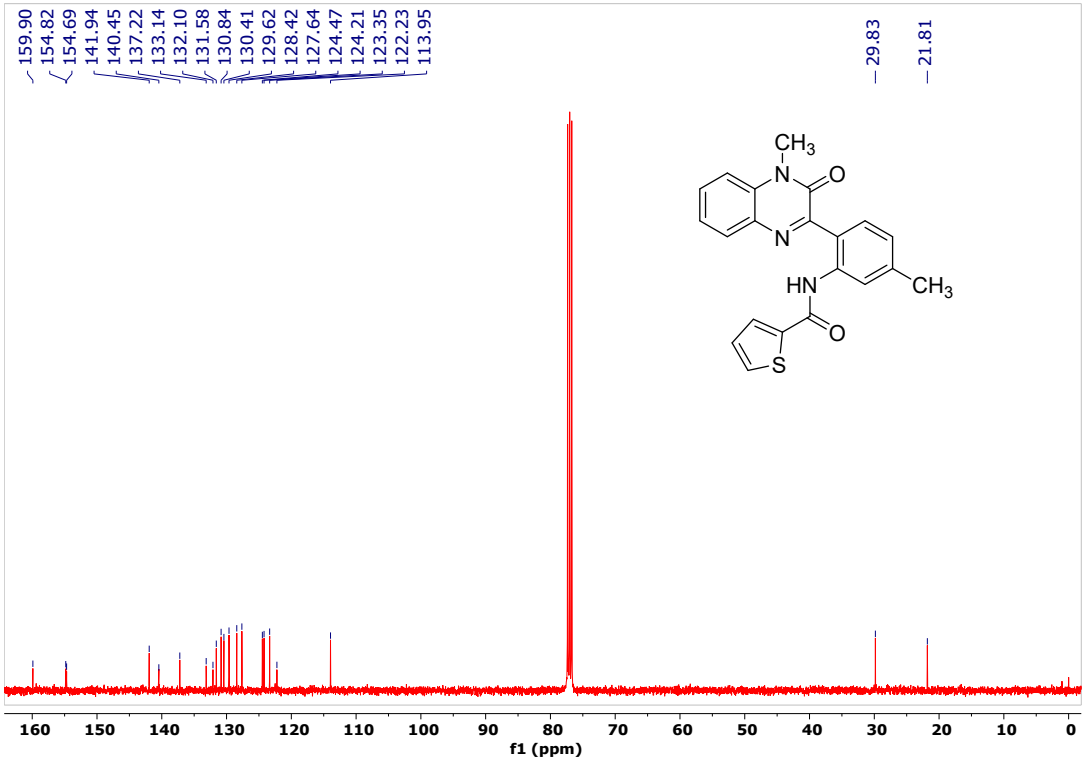


Figure 54: ^{13}C NMR spectrum of compound **5ee** (100 MHz, $CDCl_3$).

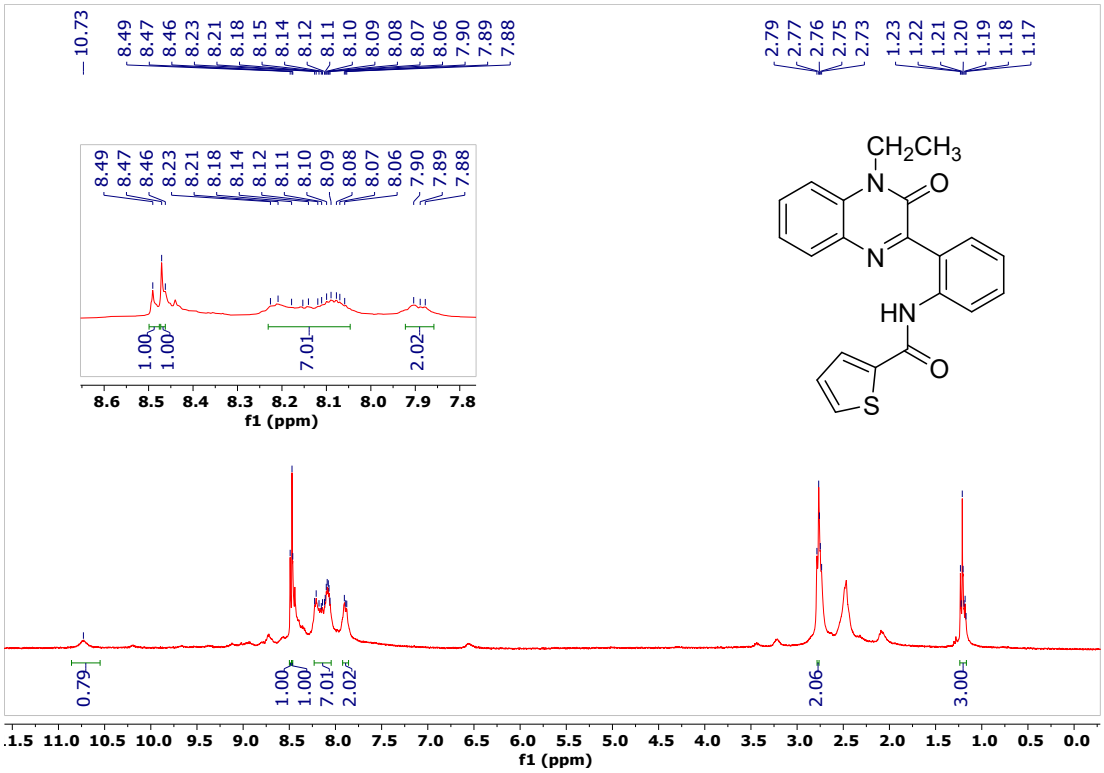


Figure 55: ^{1}H NMR spectrum of compound **5fe** (400 MHz, $CDCl_3$).

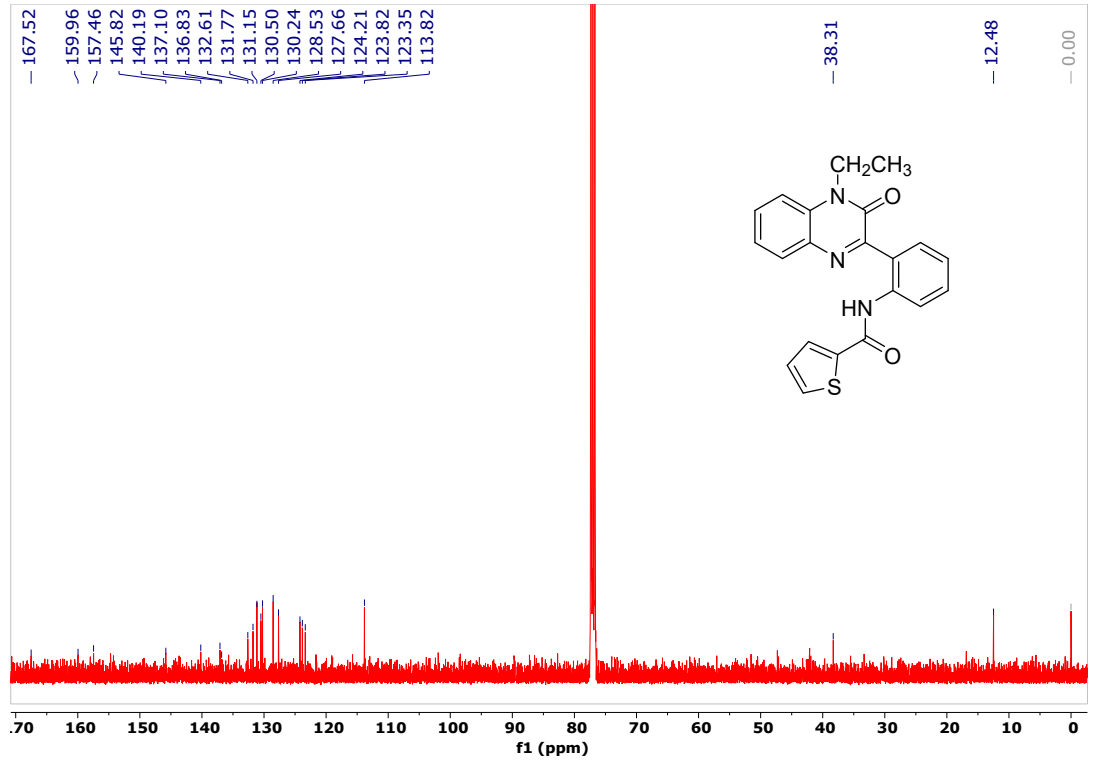


Figure 56: ^{13}C NMR spectrum of compound **5fe** (100 MHz, $CDCl_3$).

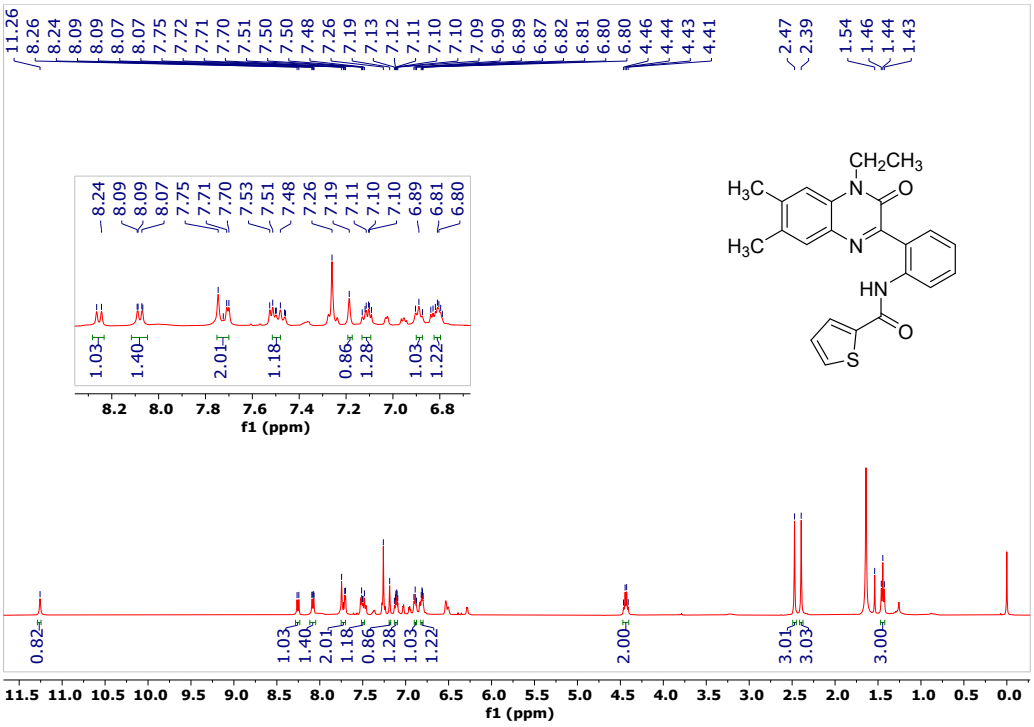


Figure 57: ^{1}H NMR spectrum of compound **5ge** (400 MHz, $CDCl_3$).

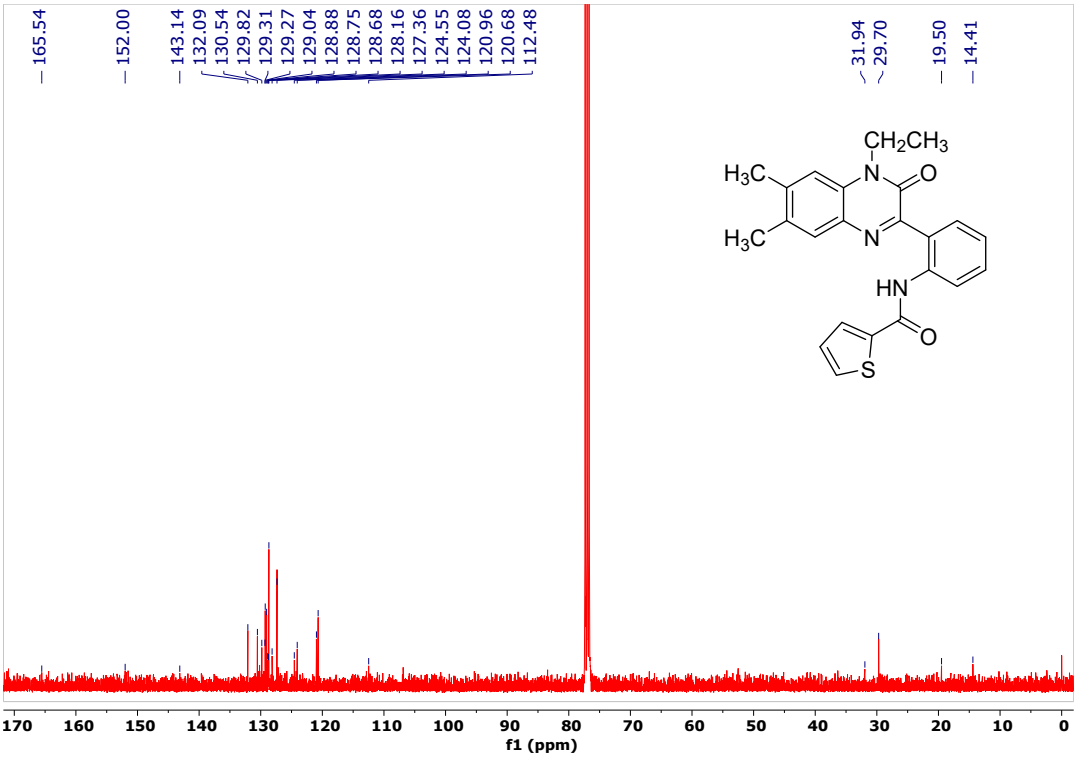


Figure 58: ^{13}C NMR spectrum of compound **5ge** (100 MHz, $CDCl_3$).

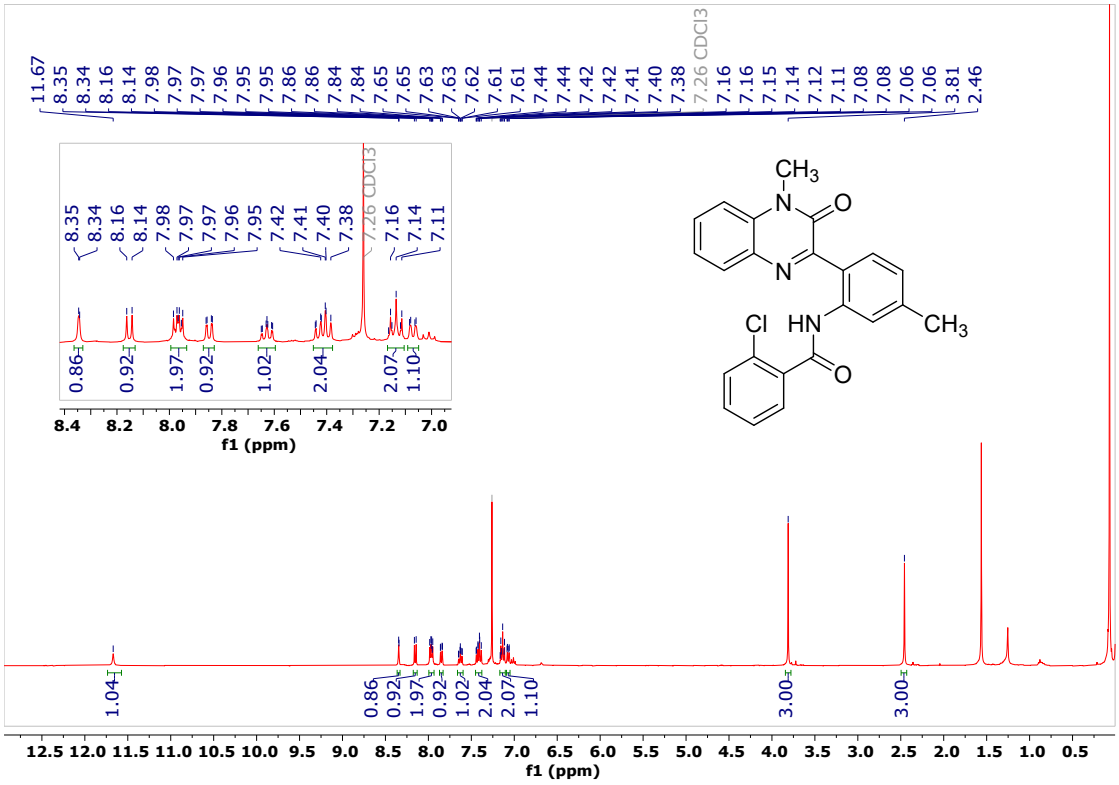


Figure 59: ^{1}H NMR spectrum of compound **5ef** (400 MHz, $CDCl_3$).

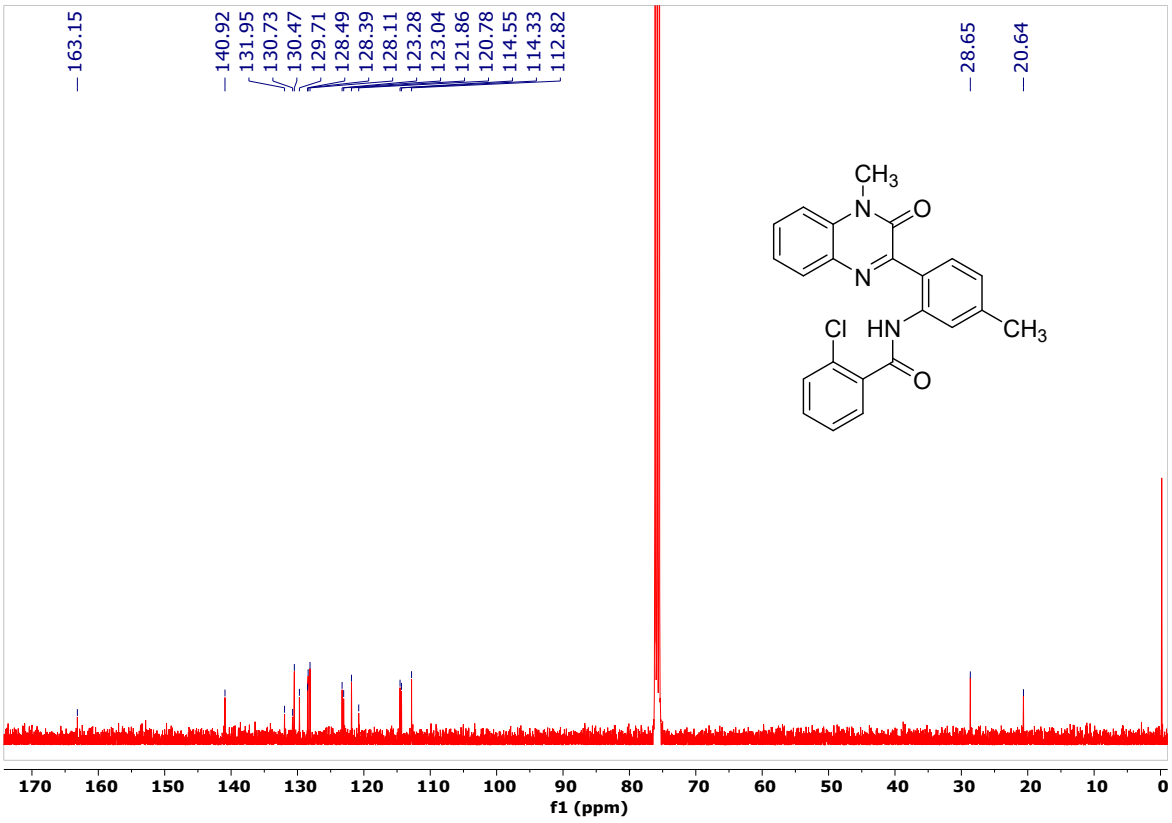


Figure 60: ^{13}C NMR spectrum of compound **5ef** (100 MHz, $CDCl_3$).

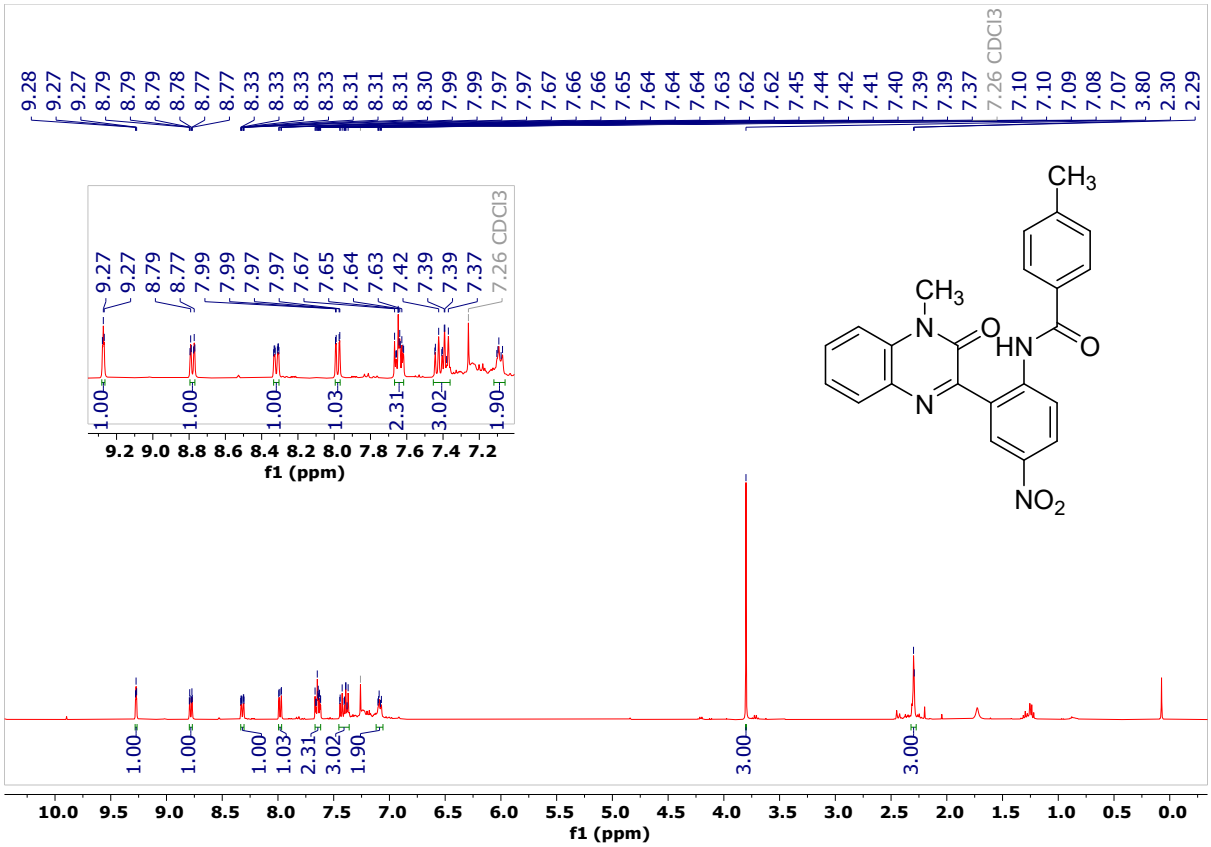


Figure 61: ^{1}H NMR spectrum of compound **5ld** (400 MHz, $CDCl_3$).

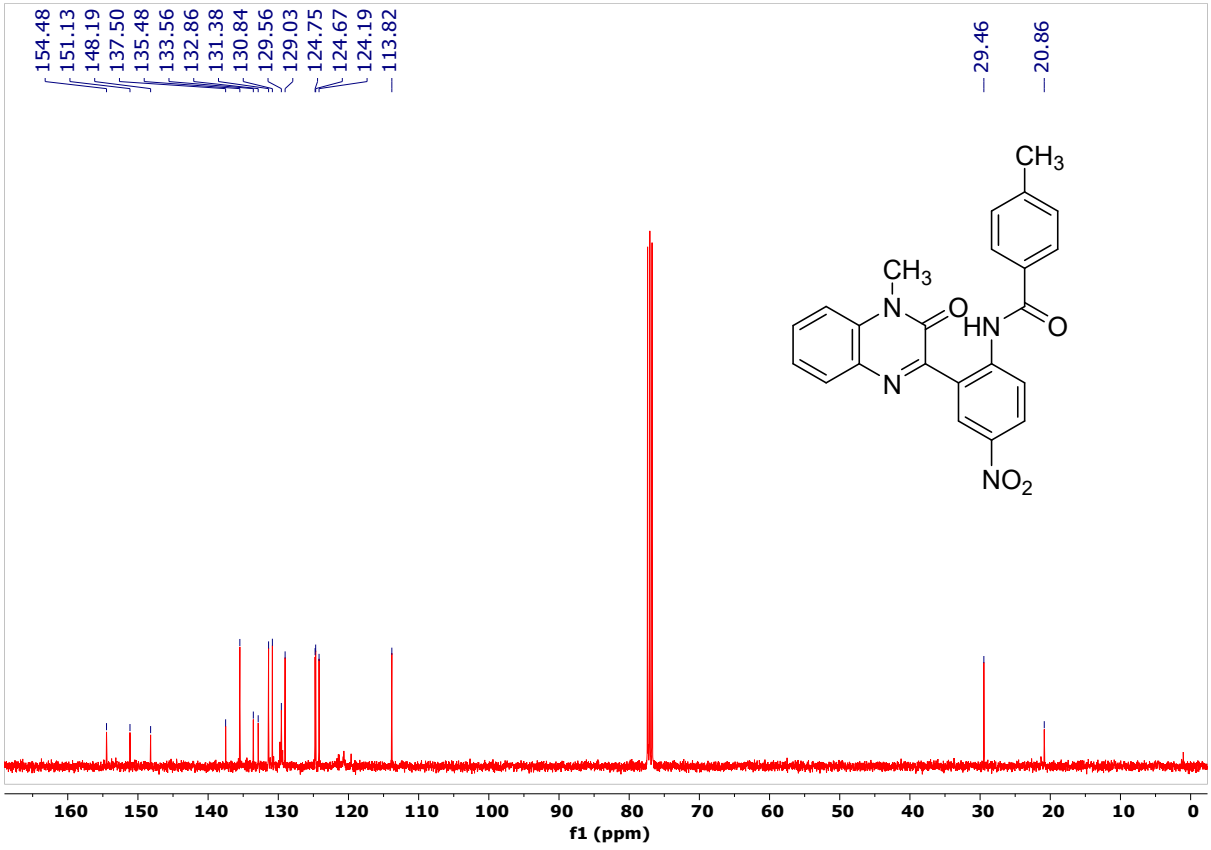


Figure 62: ^{13}C NMR spectrum of compound **5ld** (100 MHz, $CDCl_3$).

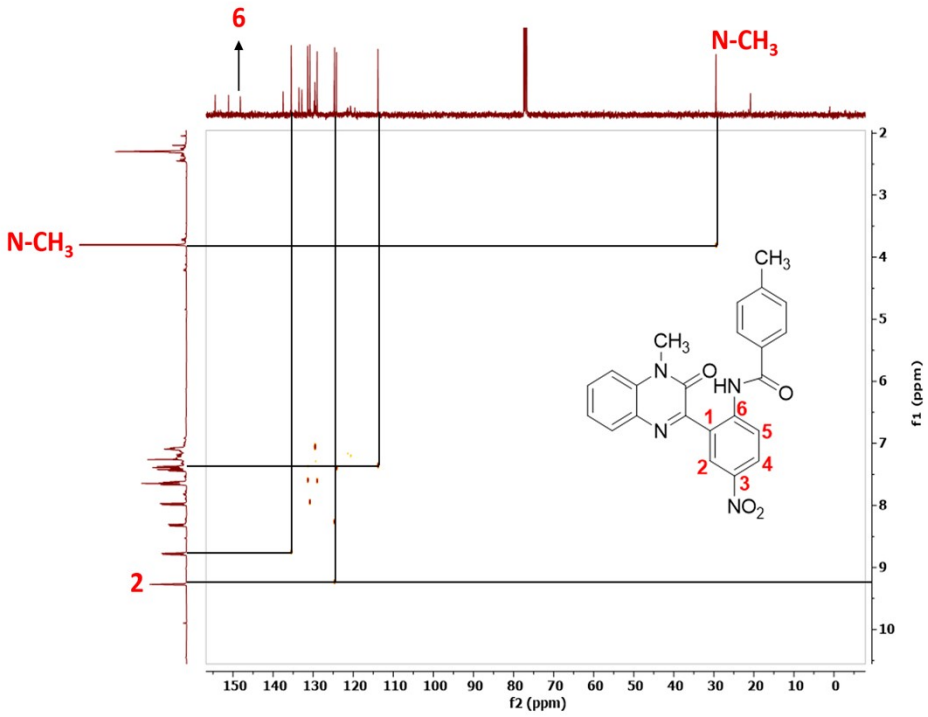


Figure 63: HETCOR SPECTRA OF COMPOUND 5ld.

In the HETCOR spectrum of compound **5ld**, the C-2 carbon signal at δ 124.67 ppm showed correlation with the proton that appeared at δ 9.27 ppm, confirming that amidation did not occur at the C-2 position. In contrast, the absence of proton correlation at the C-6 carbon along with its quaternary nature indicated preferential amidation had taken place at the C-6 position in **5ld**, likely due to steric hindrance.

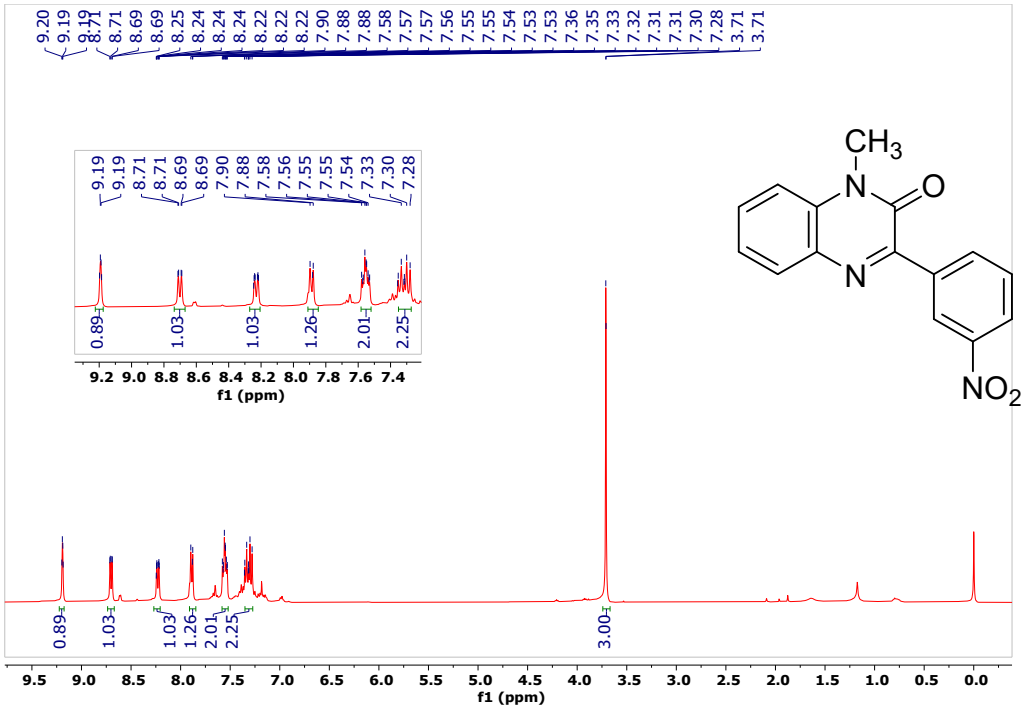


Figure 64: ^{1}H NMR spectrum of compound **1l** (400 MHz, $CDCl_3$).

^{1}H NMR (400 MHz, Chloroform-d): δ 9.19 (s, 1H), 8.70 (dd, J = 7.9, 1.6 Hz, 1H), 8.27-8.21 (m, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.58-7.52 (m, 2H), 7.31 (dd, J = 13.8, 8.0 Hz, 2H), 3.71 (s, 3H).

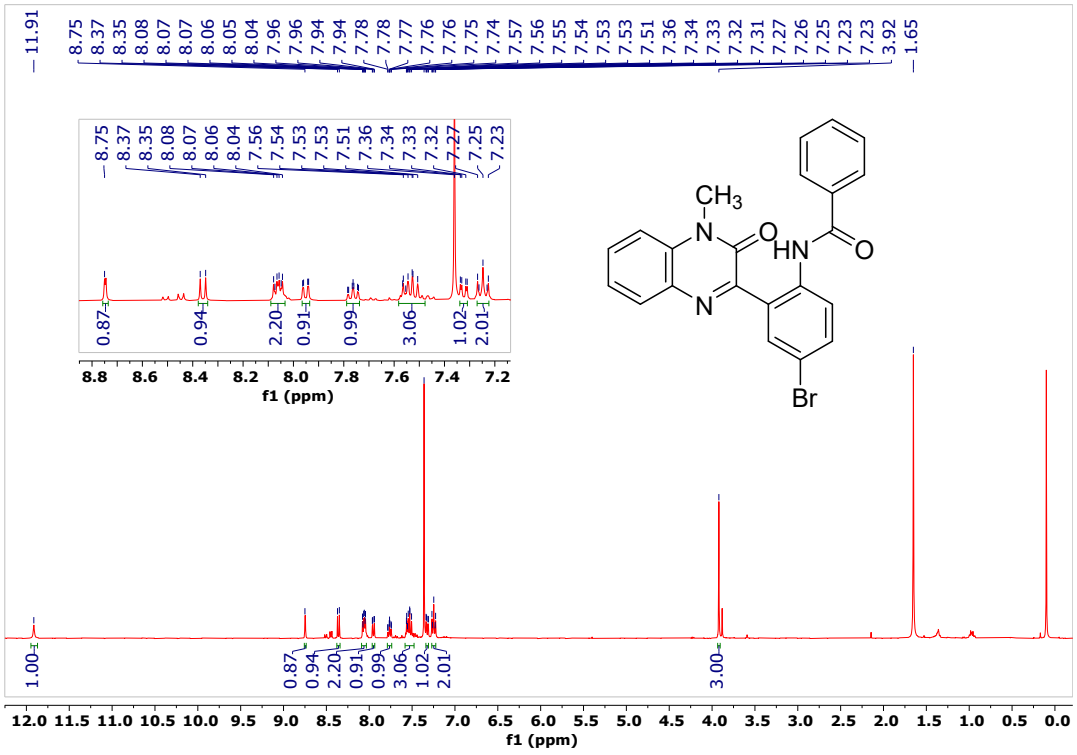


Figure 65: ^{1}H NMR spectrum of compound **5ma** (400 MHz, $CDCl_3$).

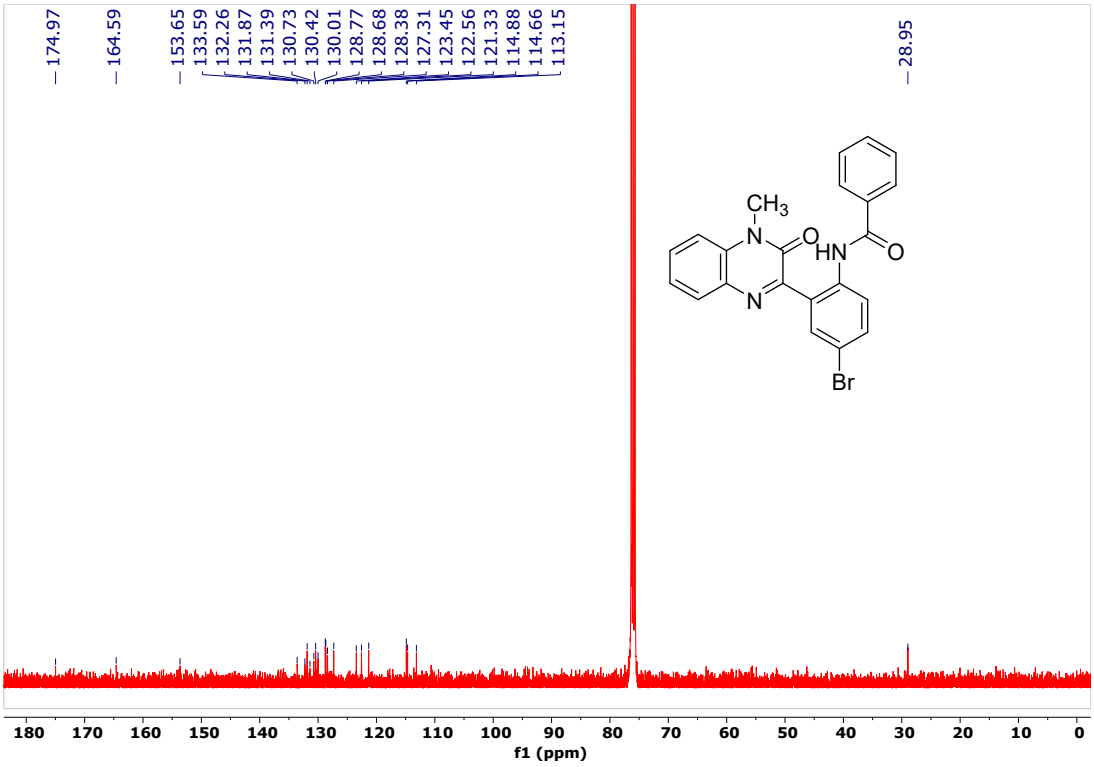


Figure 66: ^{13}C NMR spectrum of compound **5ma** (100 MHz, $CDCl_3$).

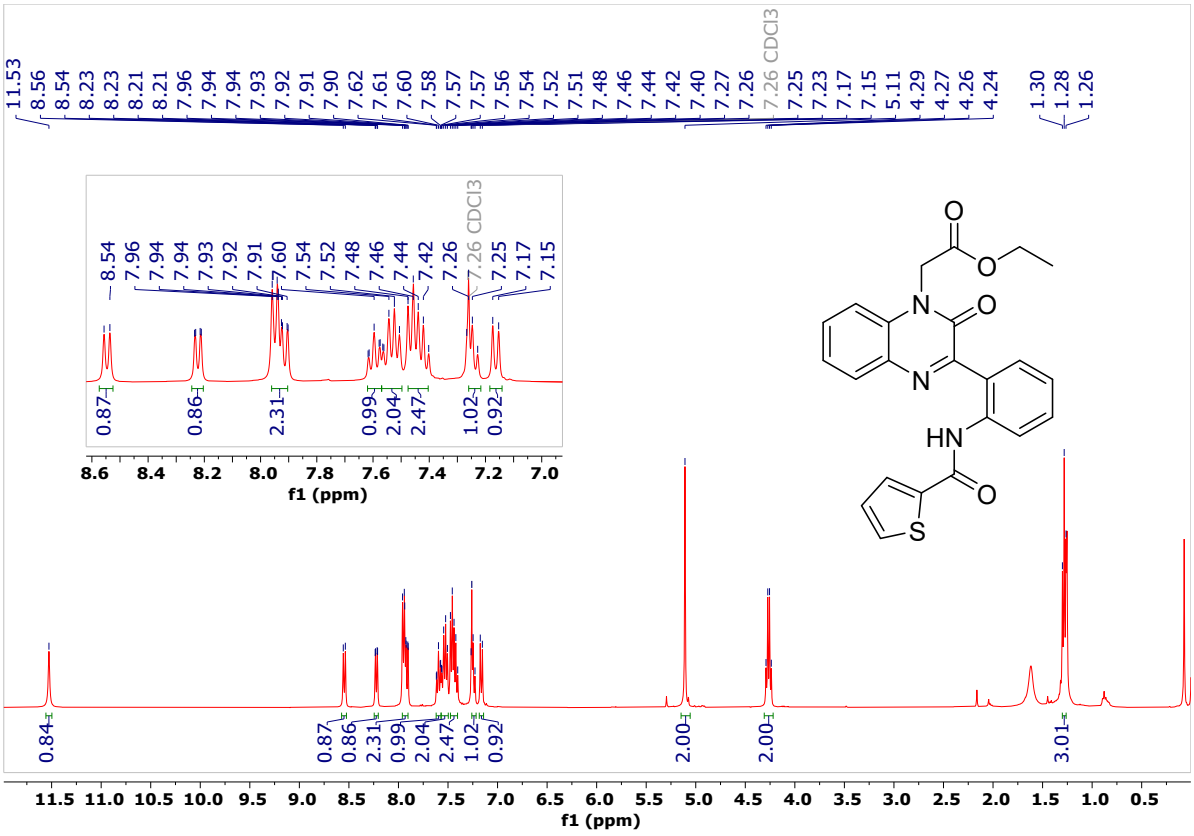


Figure 67: ^{1}H NMR spectrum of compound **6ie** (400 MHz, $CDCl_3$).

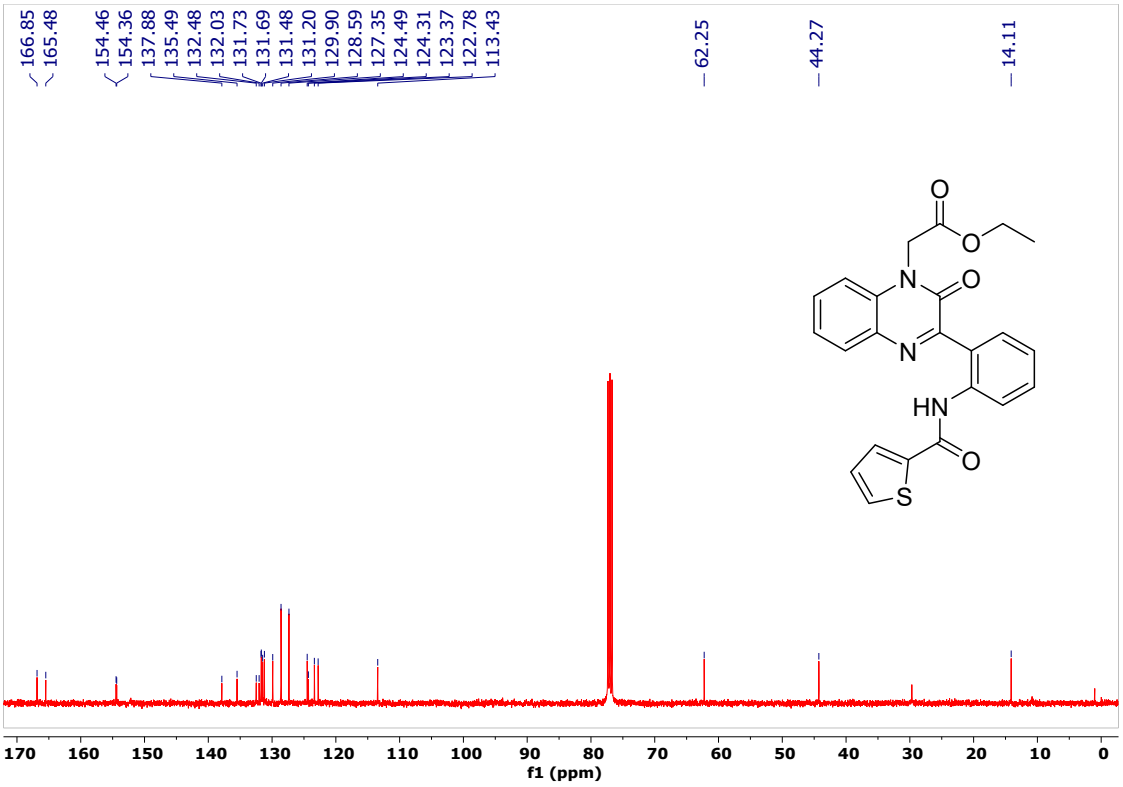


Figure 68: ^{13}C NMR spectrum of compound **6ie** (100 MHz, $CDCl_3$).

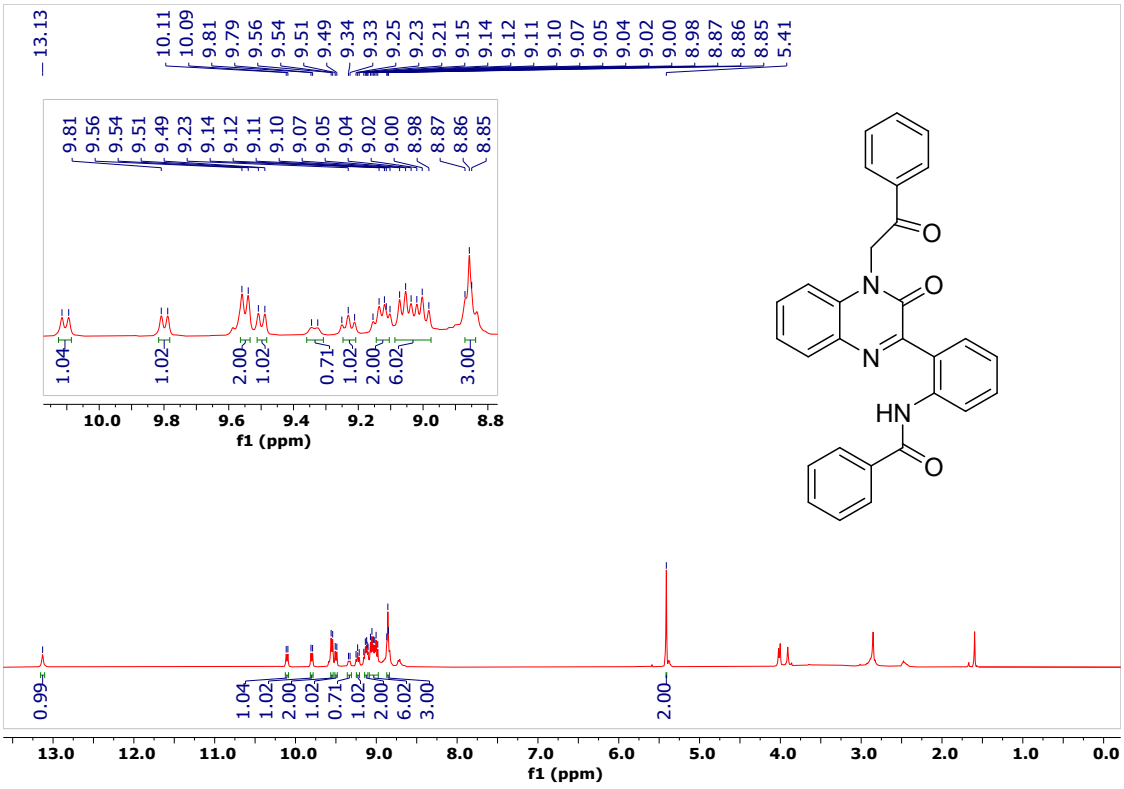


Figure 69: ^{1}H NMR spectrum of compound **6ja** (400 MHz, $CDCl_3$).

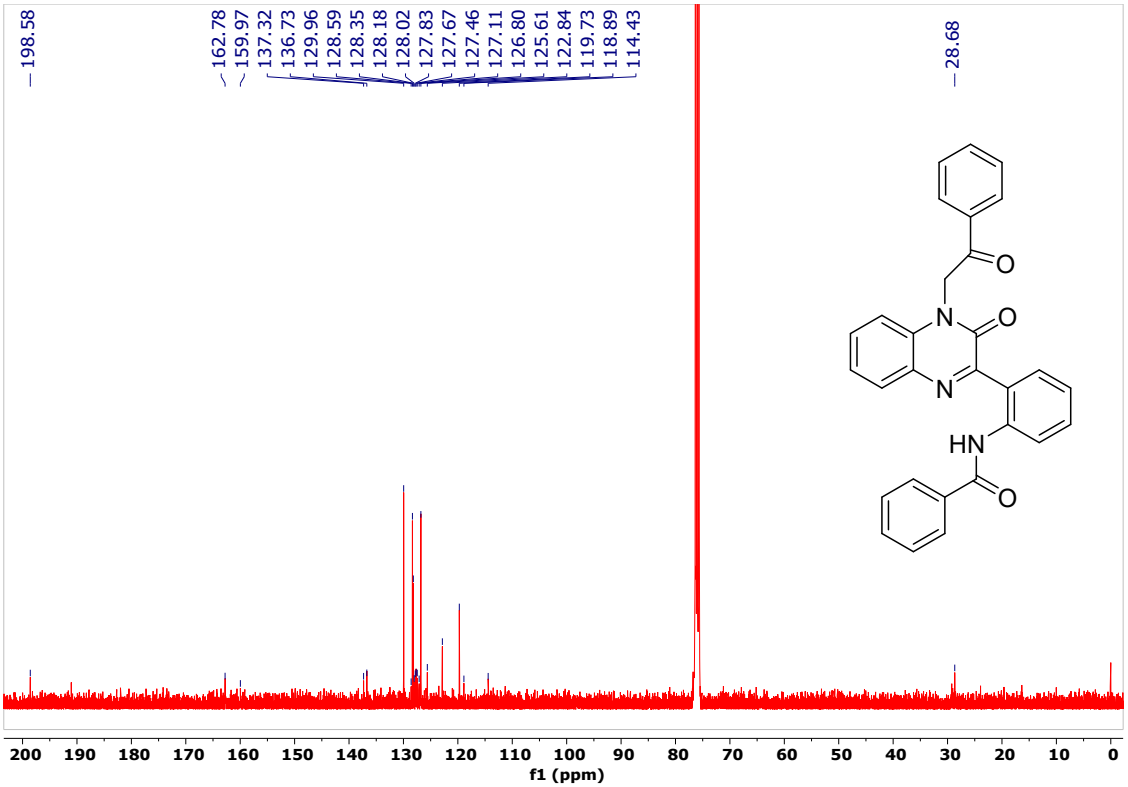


Figure 70: ^{13}C NMR spectrum of compound **6ja** (100 MHz, $CDCl_3$).

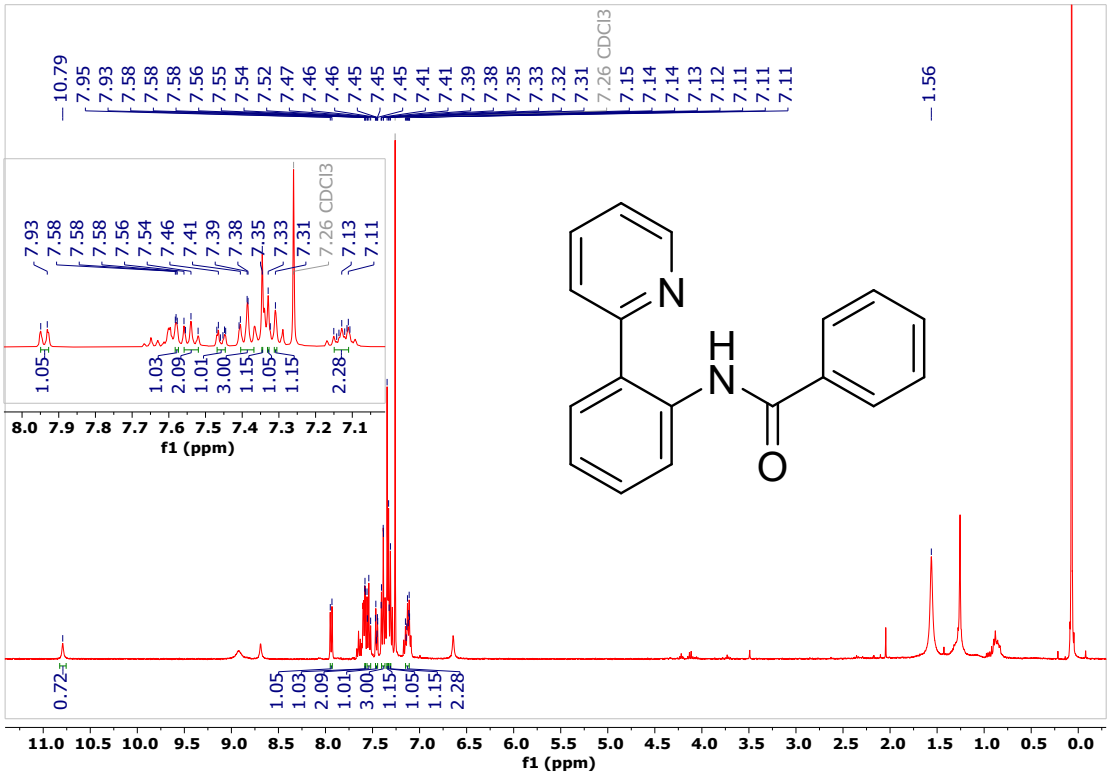


Figure 71: ^{1}H NMR spectrum of compound **6ka** (400 MHz, $CDCl_3$).

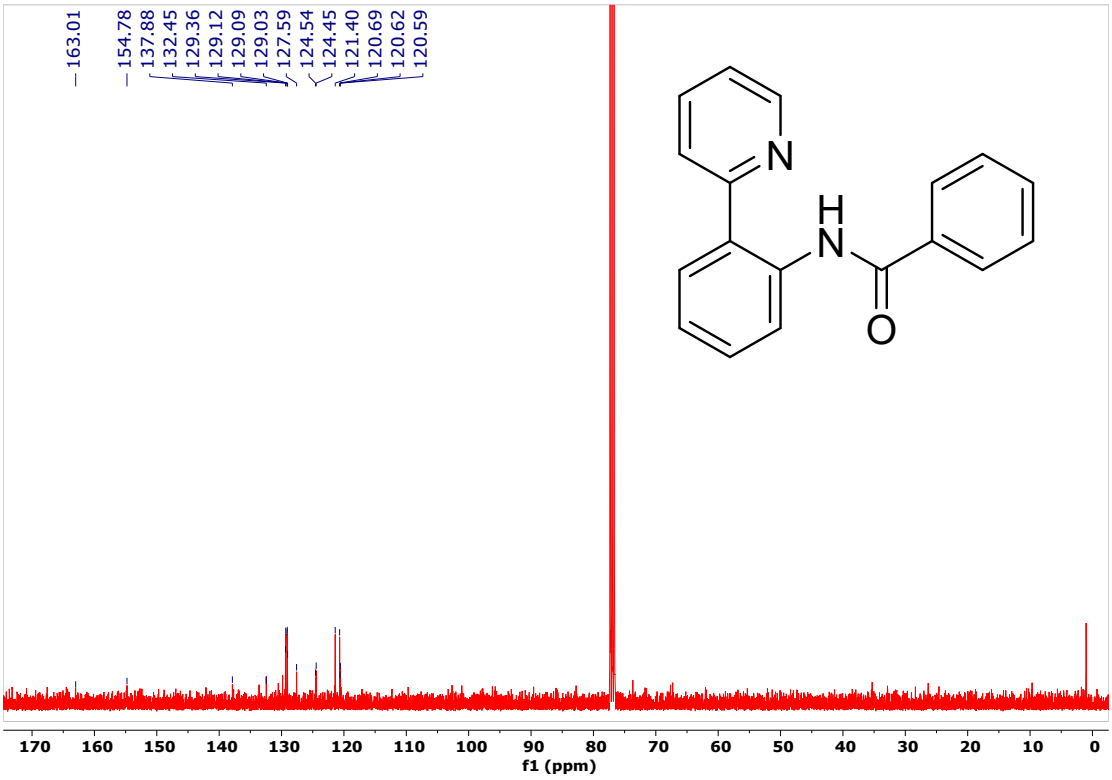


Figure 72: ^{13}C NMR spectrum of compound **6ka** (100 MHz, $CDCl_3$).

Single crystal X-ray diffraction analysis of compound

Table S1: Single crystal X-ray diffraction analysis of compound

Identification code	exp_2520_auto	
Empirical formula	$C_{20}H_{15}N_3O_2S$	
Formula weight	361.41	
Temperature/K	293(2)	
Crystal system	orthorhombic	
Space group	Pca21	
Unit cell dimensions/Å	a = 11.3360(8)	α = 90
	b = 7.3440(5)	β = 90
	c = 20.122(3)	γ = 90
Volume/$Å^3$	1675.2(3)	
Z	4	
Density (calculated)/g/cm^3	1.433	
Absorption coefficient/mm^{-1}	0.214	
F(000)	752.0	
Crystal size/mm^3		
Theta range for data collection/°	4.048 to 61.986	
Index ranges	$-14 \leq h \leq 16$, $-8 \leq k \leq 10$, $-25 \leq l \leq 26$	
Reflections collected	9326	
Independent reflections	3688 [Rint = 0.0377, Rsigma = 0.0502]	
Data /restraints /parameters	3688/1/240	
Goodness-of-fit on F^2	1.042	
Final R indices [I>=2σ (I)]	R_1= 0.0660 , wR_2 = 0.1742	
R indices (all data)	R_1=0.1189 , wR_2 = 0.2111	
Largest diff. peak and hole/$e.Å^{-3}$	0.12/-0.43	