Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Convenient synthesis of 2-chloro-3-substituted quinoxalines by visible-light-induced radical cascade cyclization of *ortho*-diisocyanoarenes with sulfinic acids

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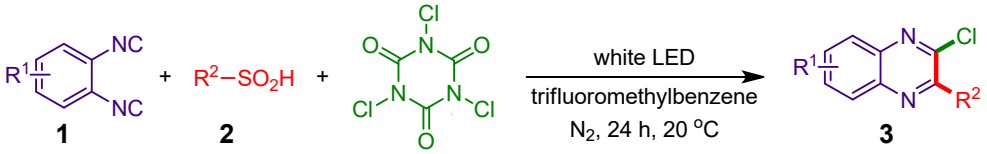
TABLE OF CONTENTS

General Information

Unless otherwise stated, all reagents and some precursors were purchased from commercial sources with the best quality and they were used without further purification. All the reactions were carried out under N_2 gas atmosphere using oven-dried glassware. All solvents were distilled prior to use and stored over 3 Å/4 Å molecular sieves.[1] The progress of the optimization reactions were monitored by gas chromatography. The progress of the substrate scope was monitored by analytical thin layer chromatography and visualization was accomplished by irradiation with short wave UV light at 254 nm and by staining in phosphomolybdic acid. Products were purified by column chromatography on 100-200 mesh silica gels. All products were characterized by NMR spectra. Chemical shifts are expressed as δ-value in parts per million (ppm) and were calibrated using the residual protonated solvent as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet and so on. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectroscopic (HRMS) data of new products were collected on Agilent Technologies Accurate-Mass Q-TOF LC/MS using ESI.

Experimental Section

General procedure for the synthesis of 2-chloro-3-substituted quinoxalines (3)

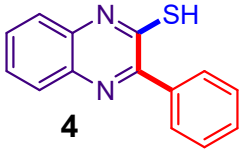


R^1 = H, EDG or EWG
R^2 = alkyl or aryl

An oven-dried glass vial equipped with a magnetic stir bar was evacuated and backfilled with nitrogen was added *ortho*-diisocyanoarenes (**1**, 0.5 mmol, 1.0 equiv.), alkyl(aryl)sulfinic acid (**2**, 1.5 mmol, 3.0 equiv.), and trichloroisocyanuric acid (CCA, 81 mg, 0.35 mmol, 0.7 equiv.) in BTF (2.5 mL). Resultant mixture was stirred few minutes to dissolve well and then with stirring irradiated through the plane bottom side of the vial using 24 W white LEDs at a distance of 2 cm under nitrogen gas atmosphere at 20 °C. After 24 h, the volatiles were completely removed by vacuum evaporation. Subsequently, aqueous $NaHCO_3$ solution (10 mL) was added, sonicated and product was extracted with ethyl acetate, dried over anhydrous sodium sulphate, filtered and

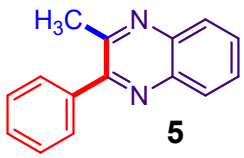
concentrated. The resulting crude mixture was purified by column chromatography on silica gel using 20-30% ethyl acetate in hexane to provide the desired product **3**.

Follow-up transformations of product 3b



4

Procedure for the preparation of 3-phenylquinoxaline-2-thiol (4):[2] To an oven-dried Schlenk-tube were added 2-chloro-3-phenylquinoxaline (**3b**, 120 mg, 0.5 mmol), potassium hydrosulfide (72 mg, 1.0 mmol) and ethanol-water (8:2, v/v, 2mL). The resulting mixture was stirred and refluxed for 24 h. Subsequently, the mixture was cooled to room temperature followed by cooled to 5 °C in a freezer. The precipitate obtained was collected by filtration and recrystallized using ethyl acetate and hexane mixture to afford product **4** (109 mg, 91% Yield). Pale-yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.4 (bs, 1H), 7.88 (dd, J = 8.2, 1.2 Hz, 1H), 7.87-7.81 (m, 2H), 7.68-7.65 (m, 1H), 7.62 (dd, J = 8.2, 1.2 Hz, 1H), 7.53-7.49 (m, 1H), 7.48-7.40 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.8, 160.6, 139.0, 135.8, 132.3, 131.6, 129.8, 129.6, 129.2, 127.7, 126.3, 116.2. Spectra data are consistent with those reported in the literature.

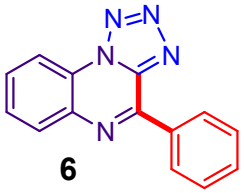


5

Procedure for the preparation of 2-methyl-3-phenylquinoxaline (5):[3] To an oven-dried Schlenk-tube was added 2-chloro-3-phenylquinoxaline (**3b**, 120 mg, 0.5 mmol), methylboronic acid (60 mg, 1.0 mmol), $Pd(PPh_3)_4$ (3 mol%) and toluene-ethanol (1:1, 3 mL). The resulting mixture was refluxed for 24 h at 110 °C and then solvents were removed under reduced pressure. Residue obtained was treated with water and then extracted with ethyl acetate (3 × 10 mL), the organic phase was dried over sodium sulfate and evaporated under reduced pressure to get the crude product which was purified by filtration thru a short-pad of silica gel column (hexane-ethyl acetate) to afford **5** (97 mg, 88%). Pale-yellow semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.10 (m, 1H), 8.09-8.05 (m, 1H), 7.78-7.71 (m, 2H), 7.68-7.63 (m, 2H), 7.56-7.50 (m, 3H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 152.6, 141.3, 141.1, 139.2, 129.8, 129.4, 129.3, 129.1, 129.0, 128.6, 128.4, 24.4. Spectra data are consistent with those reported in the literature.

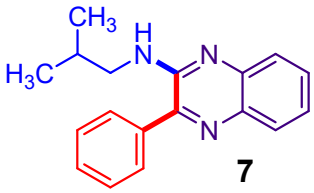
Procedure for the preparation of 4-phenyltetrazolo[1,5-a]quinoxaline (6):[4] To an oven-dried Schlenk-tube was added 2-chloro-3-phenylquinoxaline (**3b**, 120 mg, 0.5 mmol), NaN_3 (65 mg,

1.0 mmol), and DMF (2 mL). The resulting mixture was heated to 80 °C and stirred vigorously for 4 h. Subsequently, the mixture was cooled to room temperature and then admixed with cold brine solution. Organic matter (product) precipitated was collected by filtration and washed with cold water (3 mL) followed by recrystallized using water-ethanol mixture to afford product **6** (110 mg, 89% Yield). Colorless solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93-8.88 (m, 2H), 8.64-8.59 (m, 1H), 8.31-8.26 (m, 1H), 7.86-7.81 (m, 2H), 7.64-7.60 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.0, 142.1, 136.7, 134.0, 132.2, 130.6, 130.4, 130.0, 129.6, 128.9, 124.2, 116.1. Spectra data are consistent with those reported in the literature.



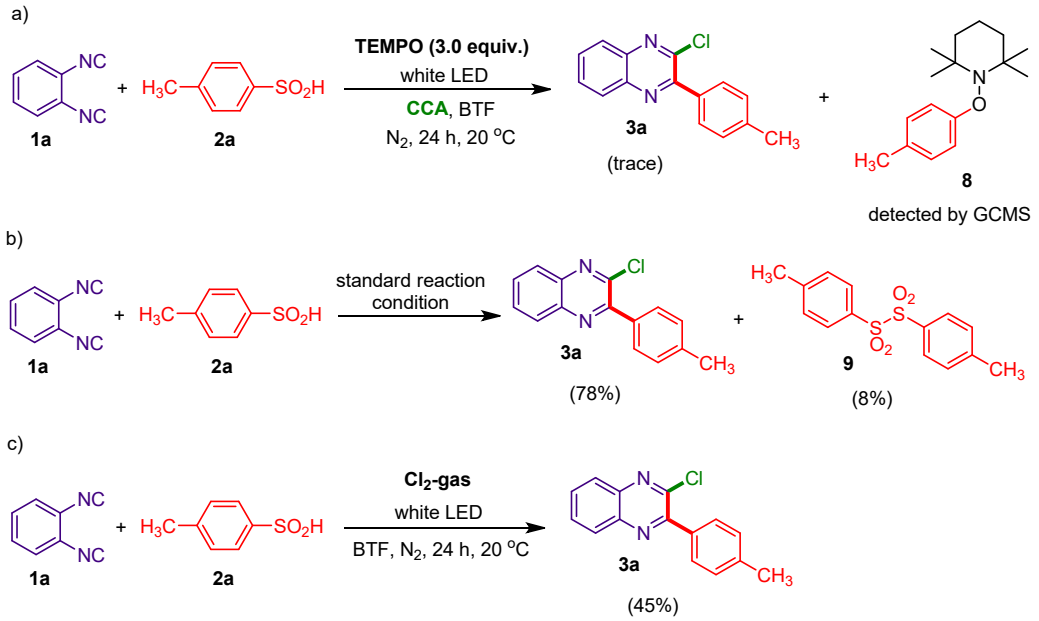
6

Procedure for the preparation of N-isobutyl-3-phenylquinoxalin-2-amine (7):[5] To an oven-dried Schlenk-tube was added 2-chloro-3-phenylquinoxaline (**3b**, 120 mg, 0.5 mmol), CuI (5 mol%), 9-10-phenanthroline (10 mol%), K_2CO_3 (138 mg, 1.0 mmol) and dioxane (5 mL). Then 2-methylpropan-1-amine (145 mg, 2.0 mmol) was added at room temperature. Subsequently, the reaction mixture was refluxed for 24 h and then solvents were removed under reduced pressure. Residue obtained was treated with water and then extracted with ethyl acetate (3 × 10 mL), the organic phase was dried over sodium sulfate and evaporated under reduced pressure to get the crude product which was purified by filtration thru a short-pad of silica gel column (hexane-ethyl acetate) to afford **7** (104 mg, 75%). Colorless semi-solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 1H), 7.74-7.71 (m, 3H), 7.58-7.52 (m, 4H), 7.38-7.35 (m, 1H), 5.12 (bs, 1H), 3.40-3.37 (m, 2H), 1.95 (t, J = 6.4 Hz, 1H), 0.96 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 150.3, 146.7, 141.8, 136.8, 129.6, 129.5, 129.3, 128.8, 128.4, 125.9, 124.1, 48.7, 31.9, 20.4. Spectra data are consistent with those reported in the literature.



7

Procedure for control experiments



A radical scavenger (2,2,6,6-tetramethylpiperidinoxy, TEMPO, 3.0 equiv.), 1,2-diisocyanobenzene (**1a**, 64 mg, 0.5 mmol, 1.0 equiv.), 4-methylbenzenesulfinic acid (**2a**, 234 mg, 1.5 mmol, 3.0 equiv.), and trichloroisocyanuric acid (CCA, 81 mg, 0.35 mmol, 0.7 equiv.) in BTF (2.5 mL) were irradiated through the plane bottom side of the vial using 24 W white LEDs at a distance of 2 cm under nitrogen gas atmosphere. After 24 h, the crude reaction mixture was analyzed by GCMS. In MS spectra (Figure S1), the peak at m/z = 247 was detected corresponding to the adduct **8**.

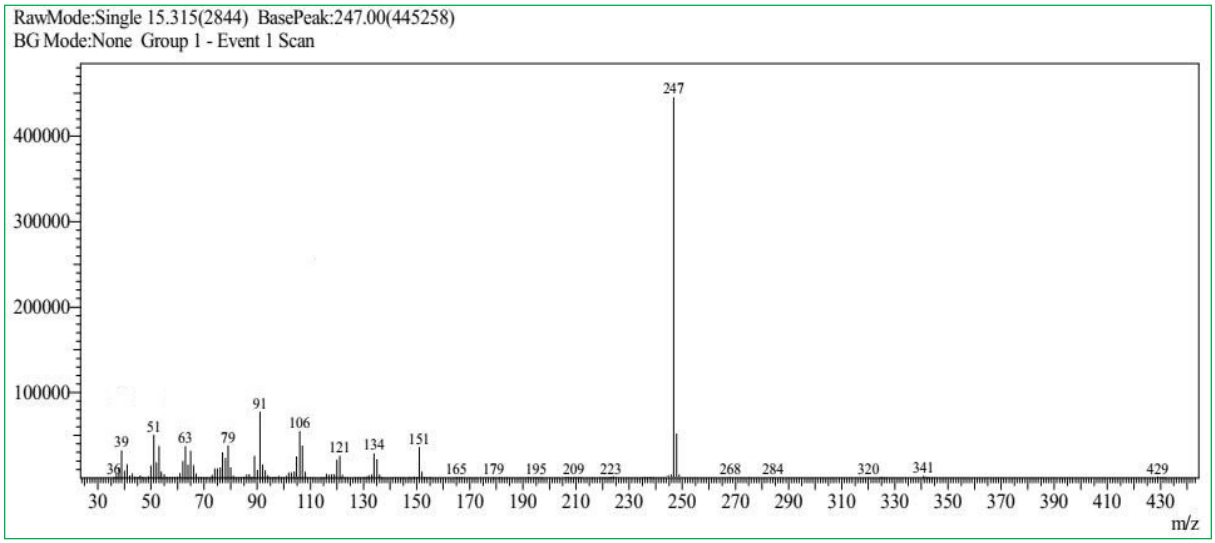


Figure S1. The mass spectra of compound **8**.

Procedure for measuring the UV/Vis absorption spectra of EDA complexes: The UV/Vis absorption spectra of individual compounds such as 1,2-diisocyanobenzene (**1a**, 3.2 mg, 0.5 mmol, 1.0 equiv.), 4-methylbenzenesulfinic acid (**2a**, 11.7 mg, 1.5 mmol, 3.0 equiv.), and trichloroisocyanuric acid (CCA, 4 mg, 0.35 mmol, 0.7 equiv.) in BTF (1.0 mL) as well as their same concentration proportion were recorded in 1 cm path quartz cuvettes by using a Hitachi UV/Vis spectrometer.

Procedure for Job's plot measurements: We measured the absorption at 520 nm of BTF solution with different donor/acceptor ratios in a constant concentration (0.10 M) of the two components. All the absorption spectra were recorded in 1 mm path quartz cuvettes by using a Hitachi UV/Vis spectrometer. The absorbance values were plotted against the molar fraction (%) of 1,2-diisocyanobenzene (**1a**). The maximum absorbance was obtained with a 1:1 mixture, indicating that it is the stoichiometry of the EDA complex in solution.

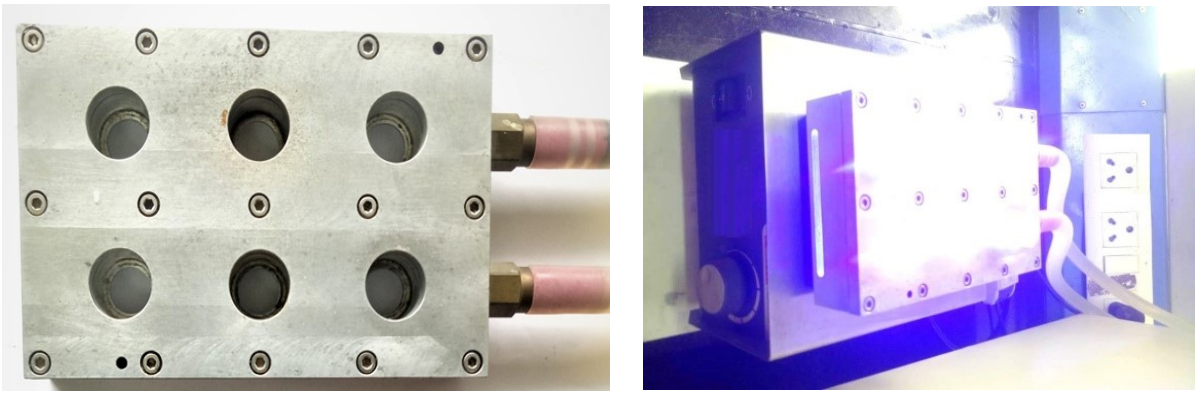
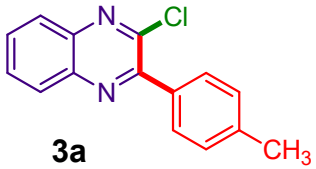


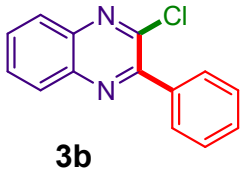
Figure S2. Photochemical reaction set-up. The photographs of parts of a custom made photochemical reactor setup used to perform reactions described in this work. holding *cum* water-cooling unit (left) and a complete reaction setup under running conditions with turn-on white LEDs with water inlet/outlet (right).

Experimental characterization data for products



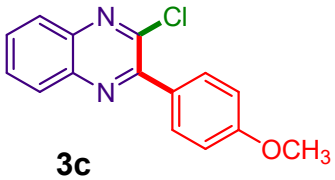
3a

2-Chloro-3-(*para*-tolyl)quinoxaline (3a):[6] Synthesized by following a general procedure. Colorless solid (100 mg, 78% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.13 (m, 1H), 8.08-8.02 (m, 1H), 7.82-7.74 (m, 4H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 146.2, 141.0, 140.9, 140.0, 133.8, 130.7, 130.4, 129.6, 129.2, 129.0, 128.1, 21.5. Spectra data are consistent with those reported in the literature.



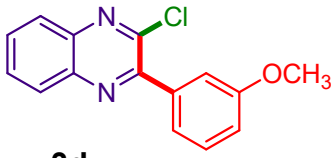
3b

2-Chloro-3-phenylquinoxaline (3b):[7] Synthesized by following a general procedure. Colorless solid (89 mg, 74% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 8.09-8.04 (m, 1H), 7.91-7.86 (m, 2H), 7.83-7.78 (m, 2H), 7.58-7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 146.1, 141.03, 141.01, 136.8, 130.8, 130.5, 129.8, 129.6, 129.1, 128.3, 128.1. Spectra data are consistent with those reported in the literature.



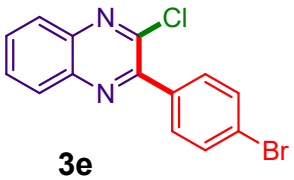
3c

2-Chloro-3-(para-methoxyphenyl)quinoxaline (3c):[8] Synthesized by following a general procedure. Colorless solid (114 mg, 84% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.14 (m, 3H), 8.09-8.05 (m, 1H), 7.81-7.76 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 153.0, 146.2, 141.0, 140.9, 130.8, 130.5, 128.9, 128.4, 128.1, 114.7, 103.2, 55.6. HRMS (ESI) m/z calculated for $C_{15}H_{12}ClN_2O$ [$(M+H)^+$] 271.0641, found 271.0648.



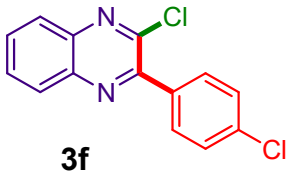
3d

2-Chloro-3-(3-methoxyphenyl)quinoxaline (3d): Synthesized by following a general procedure. Pale-yellow solid (98 mg, 72% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 8.08-8.05 (m, 1H), 7.82-7.71 (m, 4H), 7.44 (t, J = 8.0 Hz, 1H), 7.03 (dd, J = 8.0, 2.0 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 153.0, 146.1, 141.0, 140.9, 138.1, 130.7, 130.4, 129.2, 128.5, 128.1, 119.9, 116.3, 112.6, 55.6. HRMS (ESI) m/z calculated for $C_{15}H_{12}ClN_2O$ $[(M+H)^+]$ 271.0641, found 271.0633.



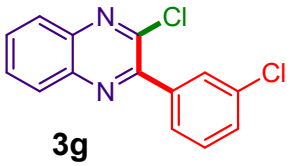
3e

2-(4-Bromophenyl)-3-chloroquinoxaline (3e): Synthesized by following a general procedure. Pale-yellow solid (110 mg, 69% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 8.08-8.03 (m, 3H), 7.81-7.76 (m, 2H), 7.66 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 146.3, 140.94, 140.9, 135.3, 132.3, 130.8, 130.4, 128.4, 128.1, 125.2, 124.9. HRMS (ESI) m/z calculated for $C_{14}H_9BrClN_2$ $[(M+H)^+]$ 318.9641, found 318.9639.



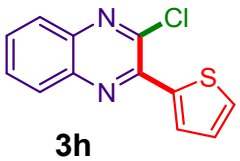
3f

2-Chloro-3-(4-chlorophenyl)quinoxaline (3f):[8] Synthesized by following a general procedure. Colorless semi-solid (78 mg, 57% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.14 (m, 3H), 8.09-8.05 (m, 1H), 7.82-7.76 (m, 2H), 7.55 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 146.2, 141.0, 140.9, 136.6, 135.1, 130.9, 130.5, 130.4, 128.7, 128.4, 128.0. HRMS (ESI) m/z calculated for $C_{14}H_9Cl_2N_2$ $[(M+H)^+]$ 275.0147, found 275.0153.



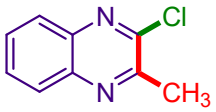
3g

2-Chloro-3-(3-chlorophenyl)quinoxaline (3g): Synthesized by following a general procedure. Colorless sticky oil (85 mg, 62% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.23 (m, 1H), 8.17-8.14 (m, 1H), 8.09-8.05 (m, 2H), 7.81-7.77 (m, 2H), 7.51 (d, J = 3.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 146.3, 140.9, 140.8, 138.5, 135.3, 130.8, 130.5, 130.2, 129.1, 128.4, 128.1, 127.6, 125.5. HRMS (ESI) m/z calculated for $C_{14}H_9Cl_2N_2$ [$(M+H)^+$] 275.0147, found 275.0151.



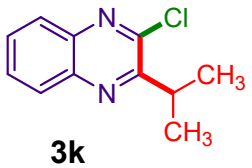
3h

2-Chloro-3-(thiophen-2-yl)quinoxaline (3h): Synthesized by following a general procedure. Pale-yellow sticky oil (93 mg, 75% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 1H), 8.08-8.05 (m, 1H), 7.86 (d, J = 3.6 Hz, 1H), 7.82-7.77 (m, 2H), 7.55 (d, J = 5.0, 1H), 7.23-7.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 145.3, 142.2, 140.5, 140.1, 130.4, 130.0, 129.1, 128.5, 128.3, 128.0, 127.2. HRMS (ESI) m/z calculated for $C_{12}H_8ClN_2S$ [$(M+H)^+$] 247.0101, found 247.0107.



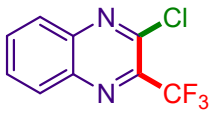
3j

2-Chloro-3-methylquinoxaline (3j):[9] Synthesized by following a general procedure. Colorless solid (77 mg, 86% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 1H), 7.98-7.95 (m, 1H), 7.75-7.71 (m, 2H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 147.8, 140.9, 140.8, 130.1, 129.9, 128.4, 128.1, 23.3. Spectra data are consistent with those reported in the literature.



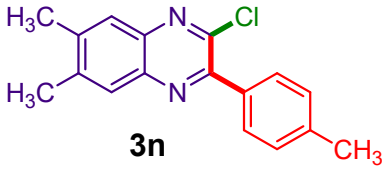
3k

2-Chloro-3-isopropylquinoxaline (3k):[4] Synthesized by following a general procedure. Colorless solid (84 mg, 81% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-8.02 (m, 1H), 7.98-7.93 (m, 1H), 7.75-7.66 (m, 2H), 3.71 (hept, J = 6.6 Hz, 1H), 1.40 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 147.3, 141.0, 140.7, 129.8, 129.8, 128.8, 128.0, 32.5, 21.0. Spectra data are consistent with those reported in the literature.



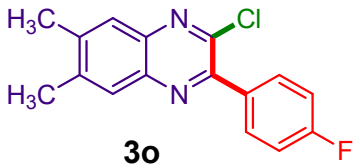
3l

2-Chloro-3-(trifluoromethyl)quinoxaline (3l):[4] Synthesized by following a general procedure. Colorless solid (47 mg, 40% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.22 (m, 1H), 8.13-8.10 (m, 1H), 7.98-7.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.7, 140.3 (q, J = 36.6 Hz), 138.8, 133.5, 131.5, 129.9, 128.2, 120.3 (q, J = 274.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.4. Spectra data are consistent with those reported in the literature.



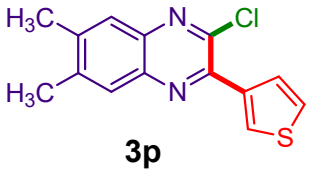
3n

2-Chloro-6,7-dimethyl-3-(p-tolyl)quinoxaline (3n): Synthesized by following a general procedure. Pale-yellow solid (93 mg, 66% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.94 (s, 1H), 7.86 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 2.52 (s, 3H), 2.50 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 145.9, 141.3, 140.6, 140.4, 140.1, 139.8, 134.4, 129.8, 128.7, 128.2, 127.3, 21.5, 20.4, 20.3. HRMS (ESI) m/z calculated for $C_{17}H_{16}ClN_2$ $[(M+H)^+]$ 283.1005, found 283.0998.



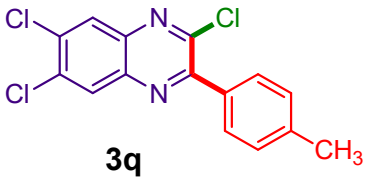
3o

2-Chloro-3-(4-fluorophenyl)-6,7-dimethylquinoxaline (3o): Synthesized by following a general procedure. Beige solid (48 mg, 33% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.8, 5.4 Hz, 2H), 8.13 (s, 1H), 7.94 (s, 1H), 7.25 (dd, J = 8.8, 5.4 Hz, 2H), 2.53 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, J = 251.5 Hz), 153.0, 146.1, 140.7, 140.6, 140.1, 139.9, 132.9 (d, J = 1.0 Hz), 129.4, 128.6, 128.2, 116.2 (d, J = 22.4 Hz), 20.4, 20.3. HRMS (ESI) m/z calculated for $C_{16}H_{13}ClFN_2$ $[(M+H)^+]$ 287.0753, found 287.0761.



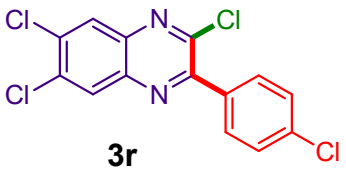
3p

2-Chloro-6,7-dimethyl-3-(thiophen-3-yl)quinoxaline (3p): Synthesized by following a general procedure. Beige solid (70 mg, 51% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.93 (s, 1H), 7.89-7.82 (m, 2H), 7.52 (dd, *J* = 5.0, 2.8 Hz, 1H), 2.52 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 147.4, 141.3, 140.8, 140.4, 140.0, 139.8, 128.5, 128.2, 126.9, 126.4, 125.1, 20.4, 20.3. HRMS (ESI) m/z calculated for $C_{14}H_{12}ClN_2S$ $[(M+H)^+]$ 275.0414, found 275.0408.



3q

2,6,7-Trichloro-3-(p-tolyl)quinoxaline (3q): Synthesized by following a general procedure. Brown solid (134 mg, 83% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.21 (s, 1H), 7.87 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.6 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 146.1, 141.3, 140.7, 140.6, 134.7, 134.5, 133.8, 129.7, 128.6, 128.3, 127.2, 21.4. HRMS (ESI) m/z calculated for $C_{15}H_{10}Cl_3N_2$ $[(M+H)^+]$ 322.9913, found 322.9919.



3r

2,6,7-Trichloro-3-(4-chlorophenyl)quinoxaline (3r): Synthesized by following a general procedure. Brown solid (106 mg, 62% yield). R_f (ethyl acetate:n-hexane, 2:8): 0.33. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.22 (s, 1H), 8.16 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 146.1, 140.8, 140.5, 136.6, 135.1, 134.5, 133.8, 128.7, 128.6, 128.3, 128.0. HRMS (ESI) m/z calculated for $C_{14}H_7Cl_4N_2$ $[(M+H)^+]$ 342.9369, found 342.9373.

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Copies of NMR spectra of products

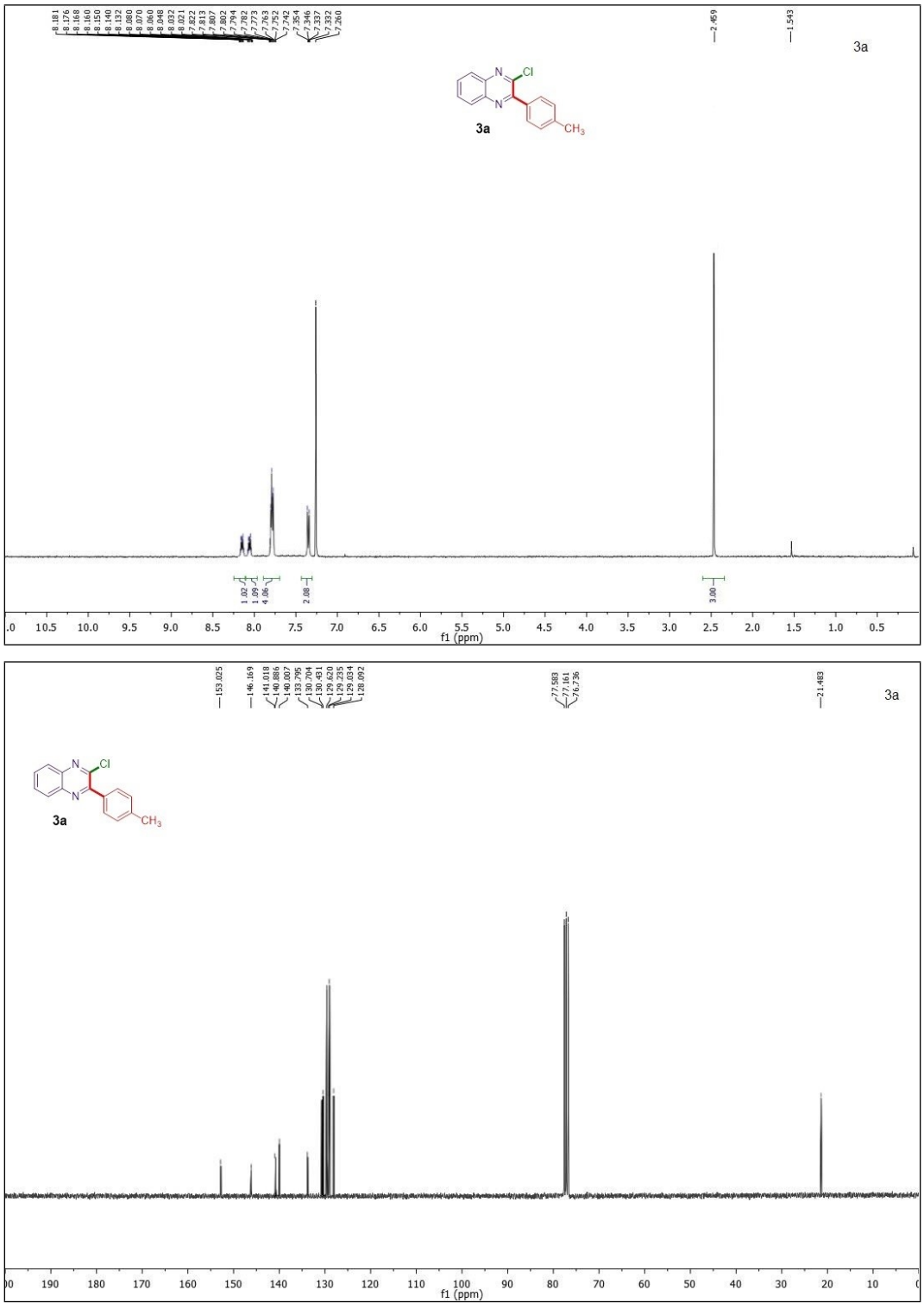

Figure S3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3a** in $CDCl_3$.

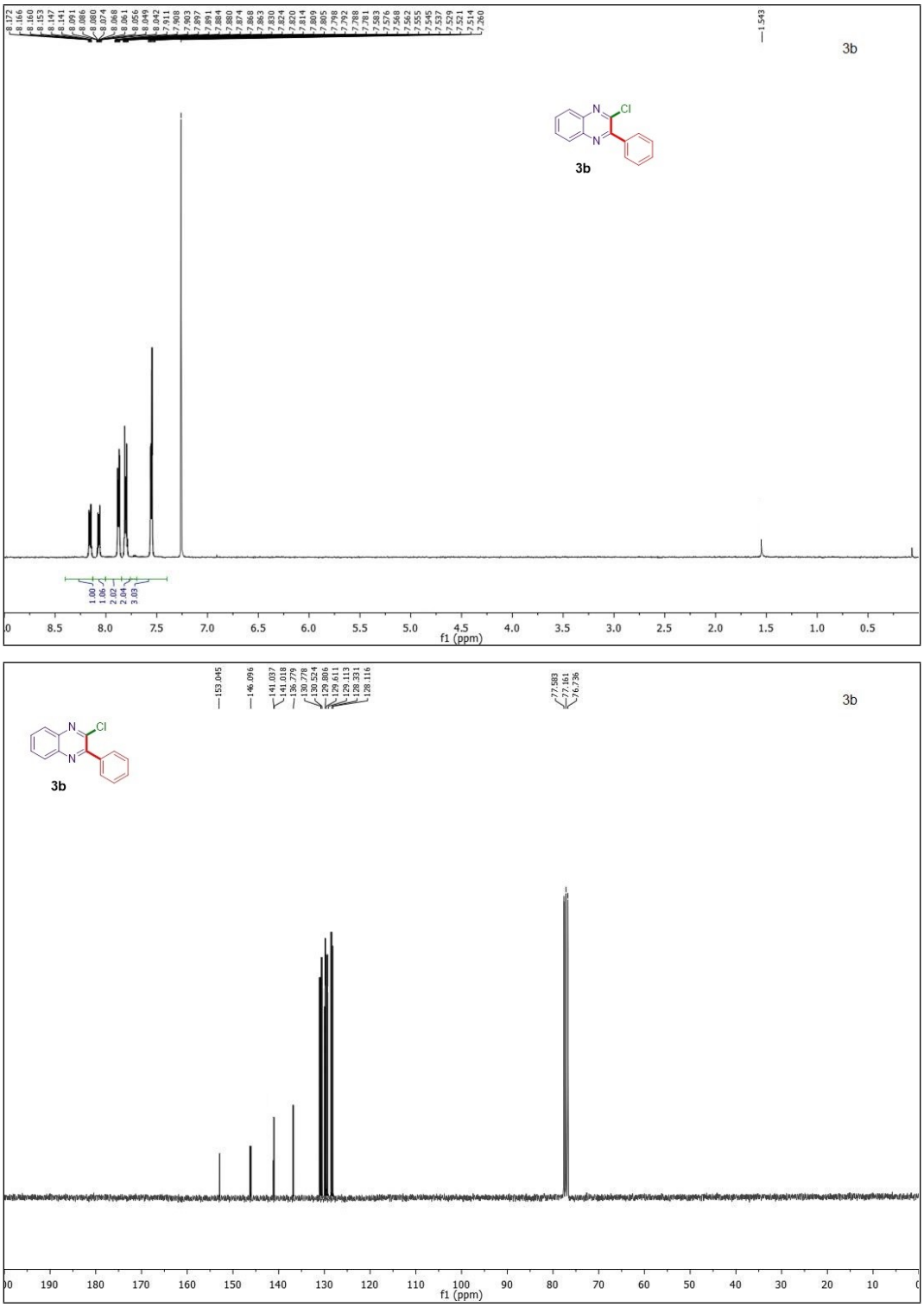

Figure S4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3b** in $CDCl_3$.

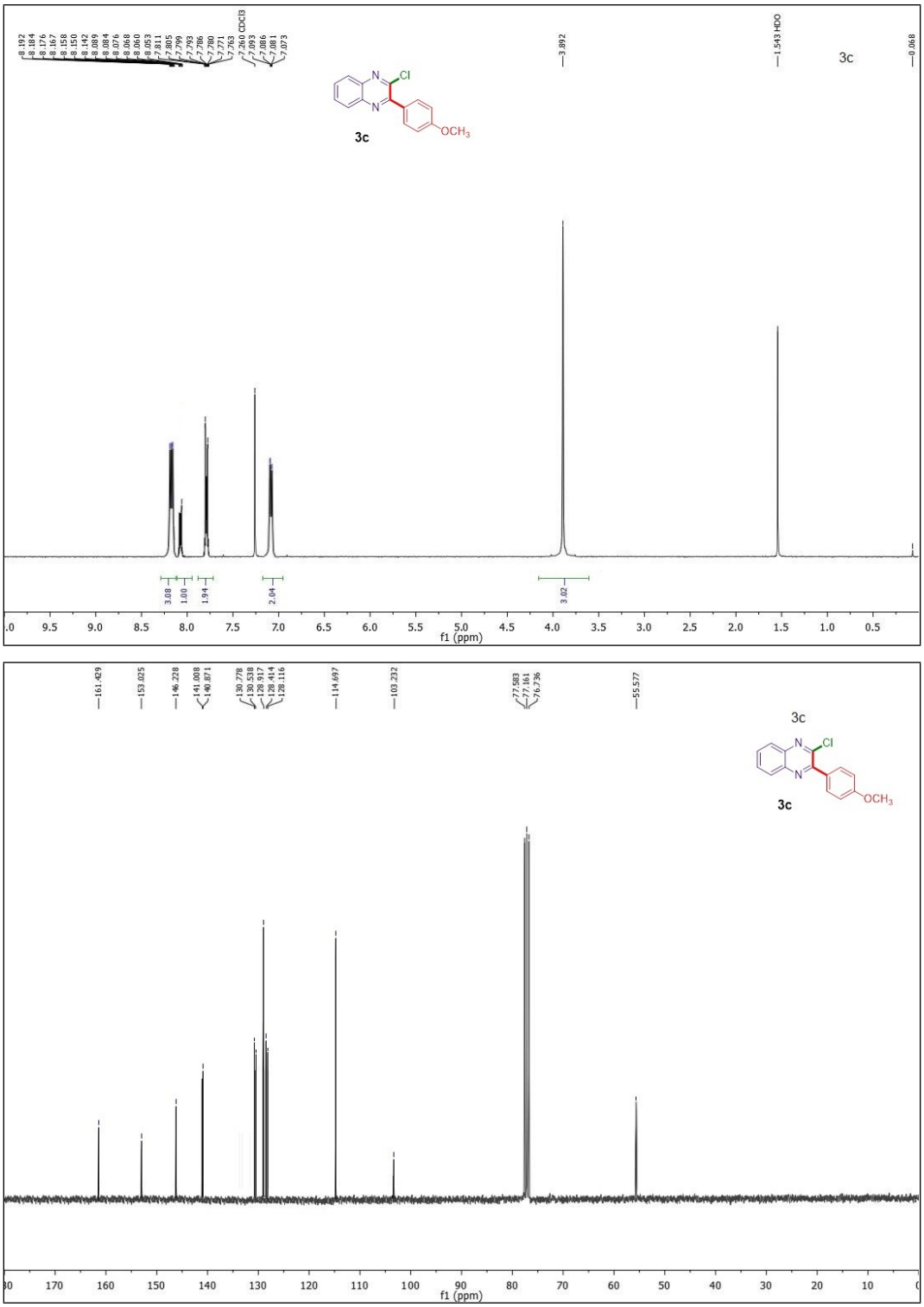

Figure S5. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3c** in $CDCl_3$.

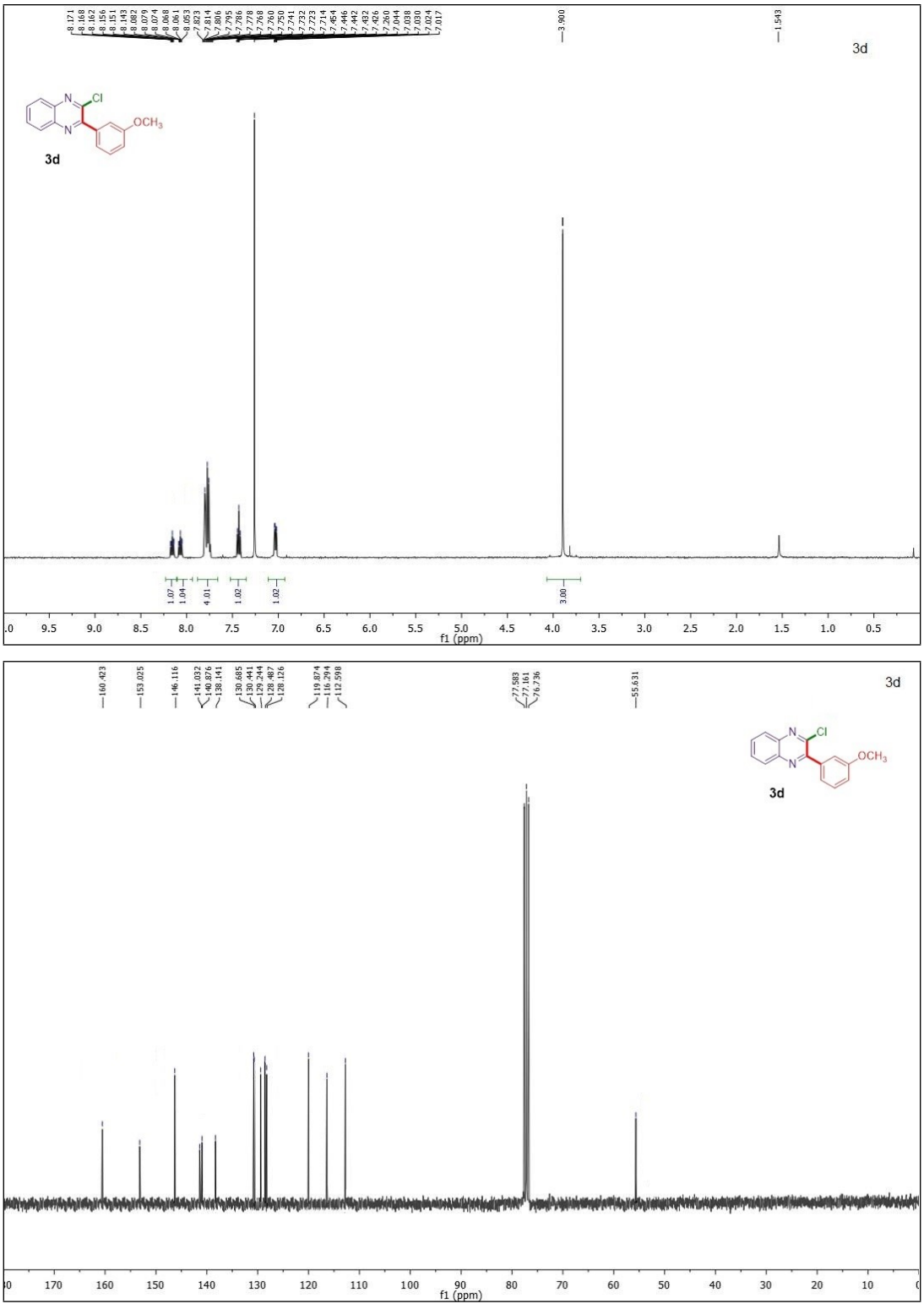

Figure S6. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3d** in $CDCl_3$.

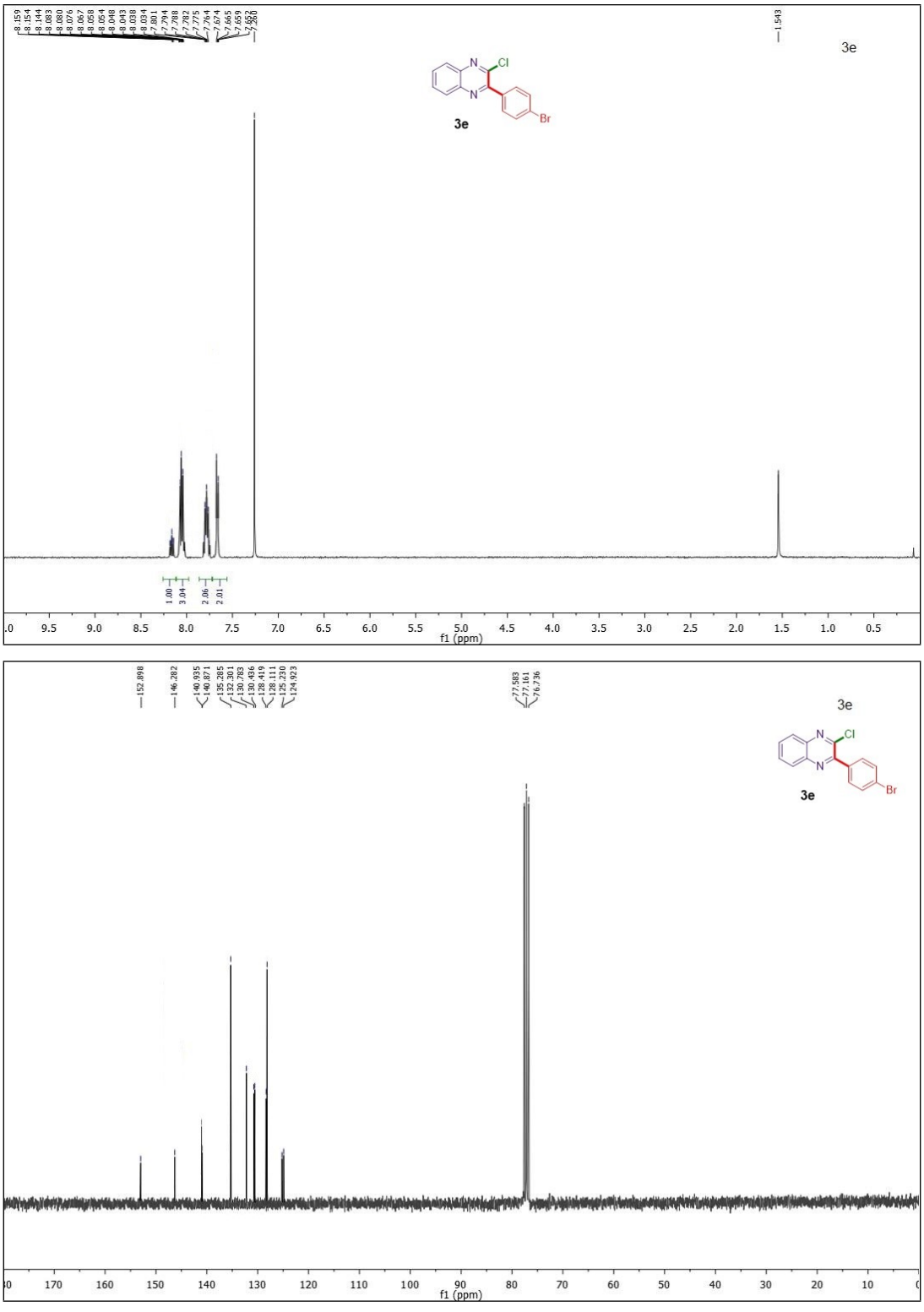

Figure S7. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3e** in $CDCl_3$.

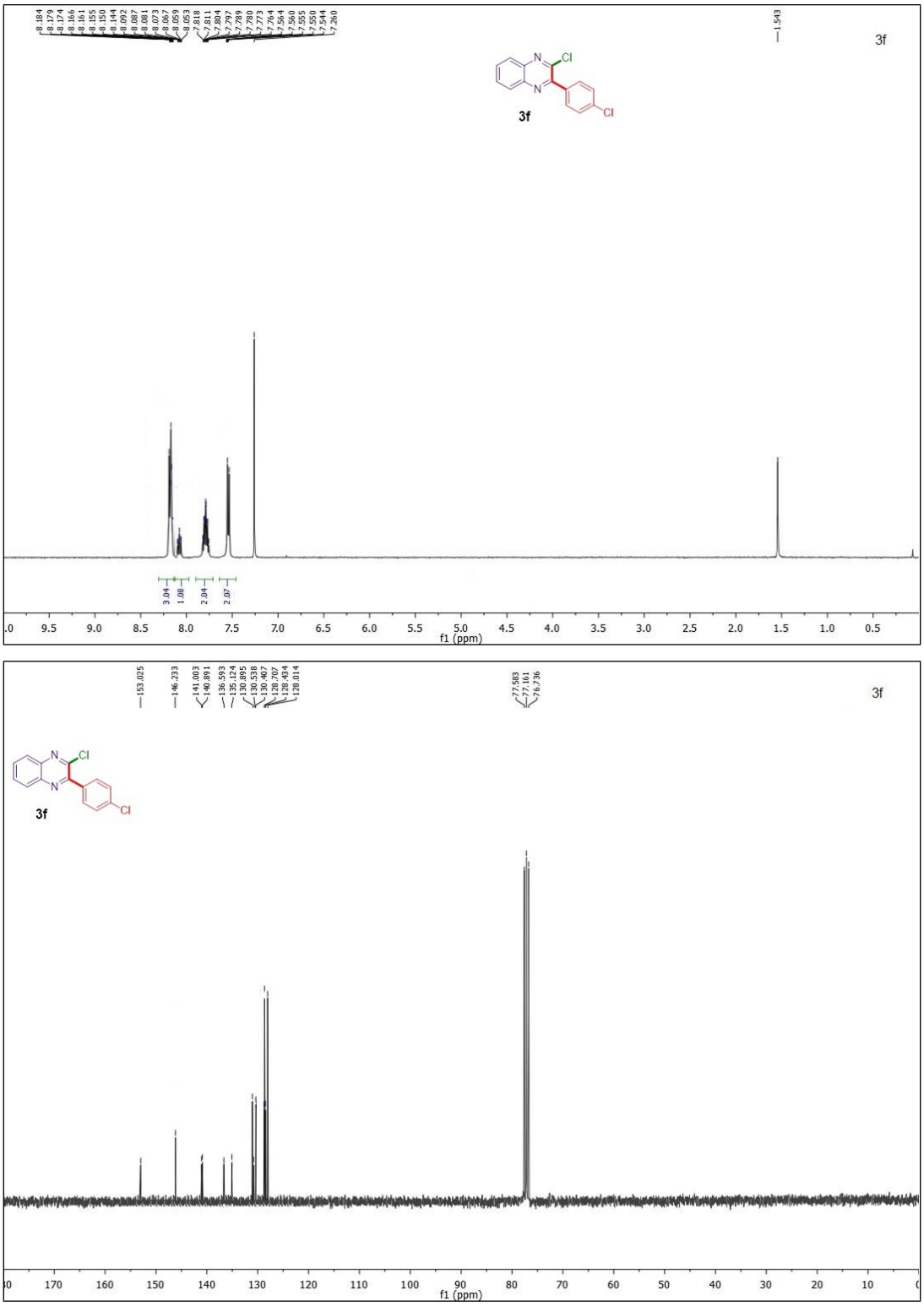

Figure S8. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3f** in $CDCl_3$.

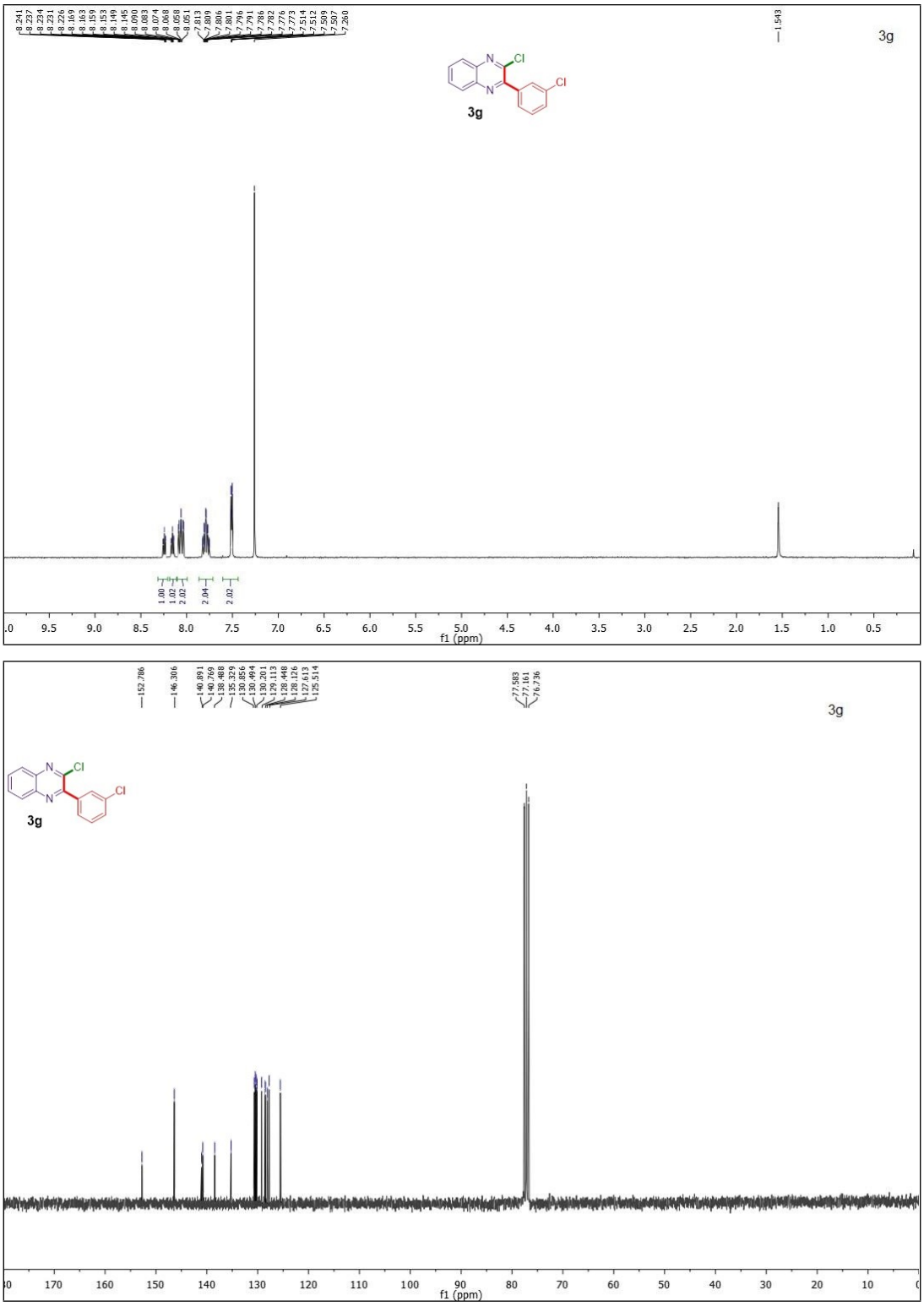

Figure S9. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3g** in $CDCl_3$.

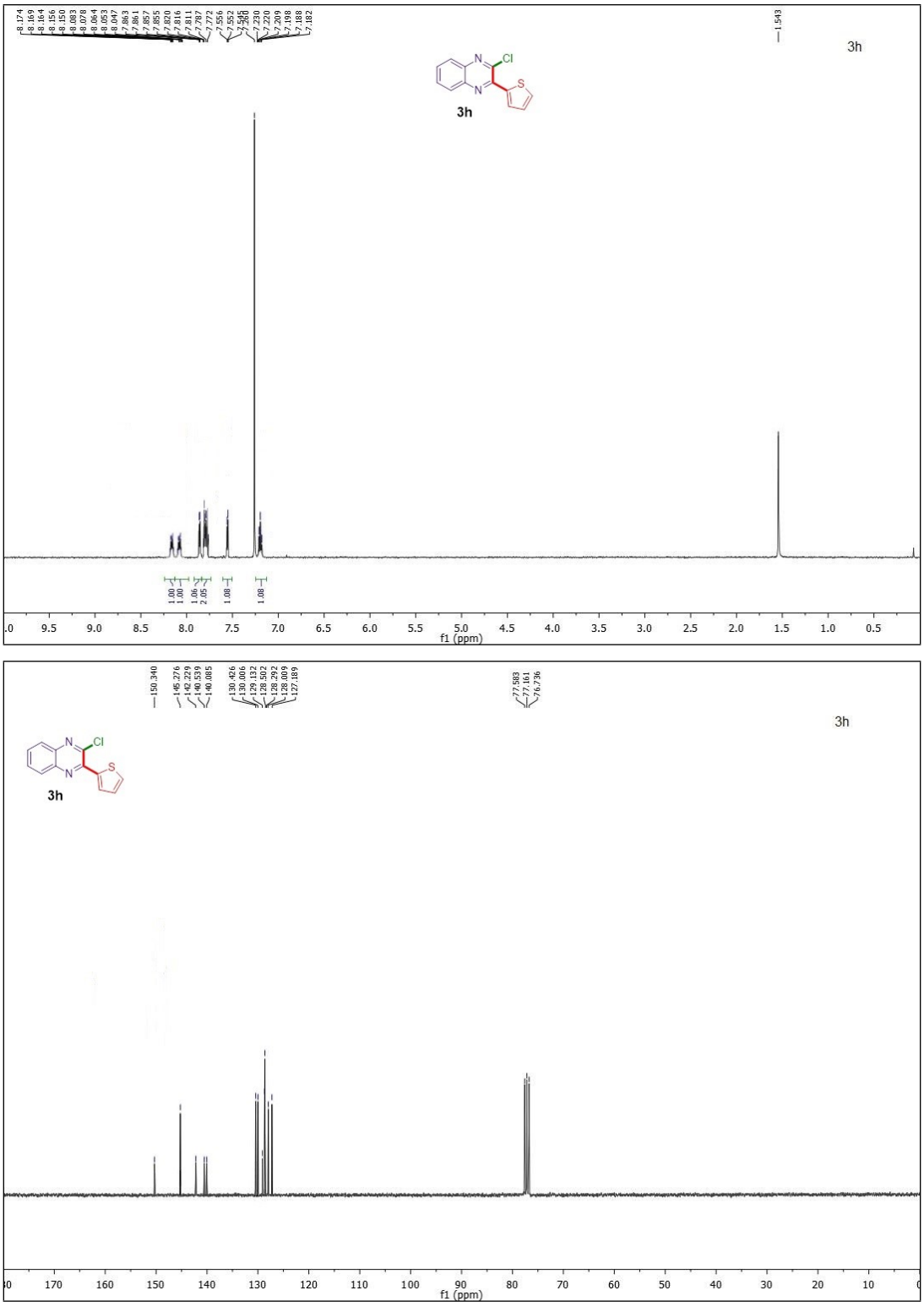

Figure S10. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3h** in $CDCl_3$.

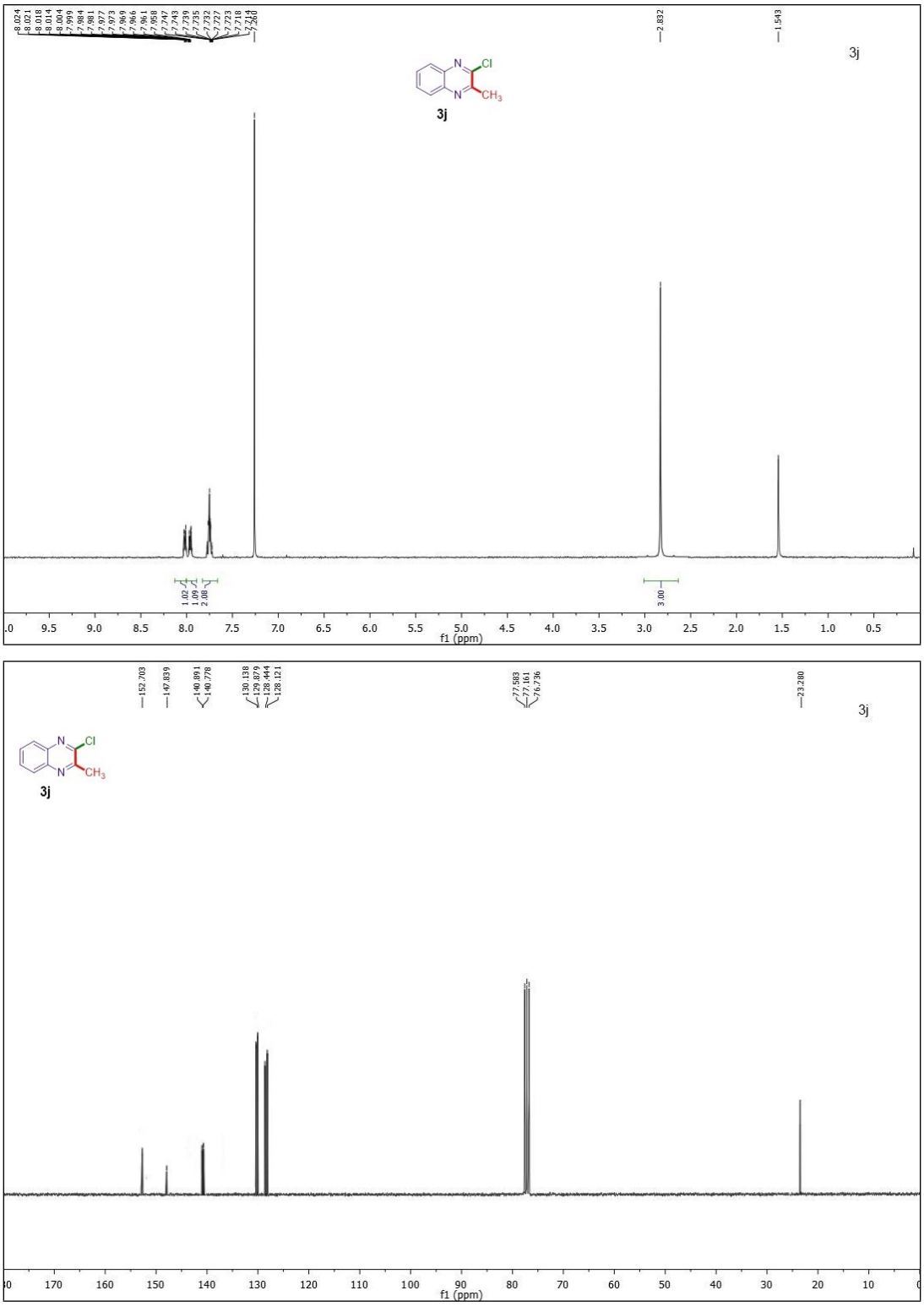

Figure S11. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3j** in $CDCl_3$.

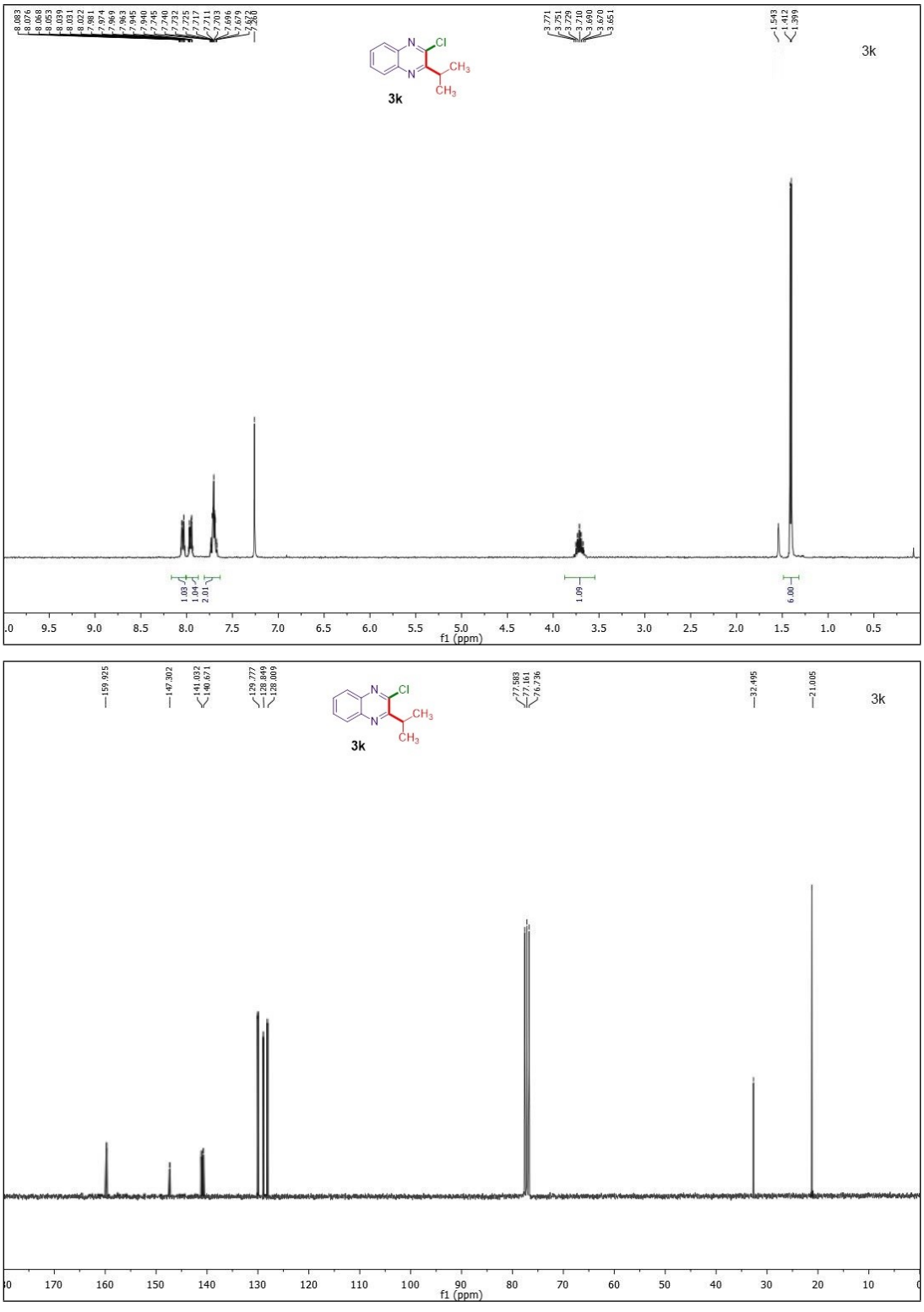

Figure S12. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3k** in $CDCl_3$.

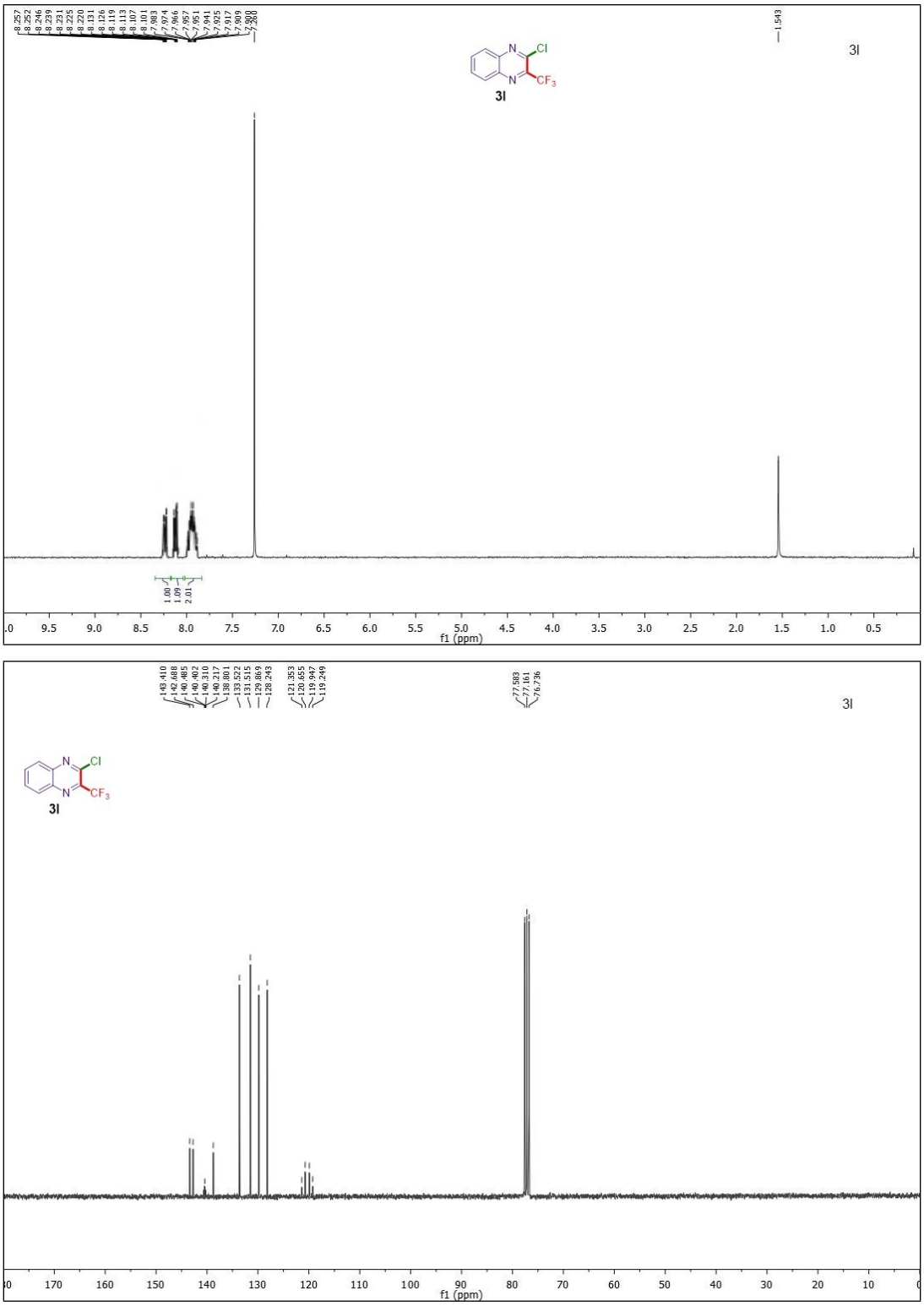

Figure S13. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3l** in $CDCl_3$.

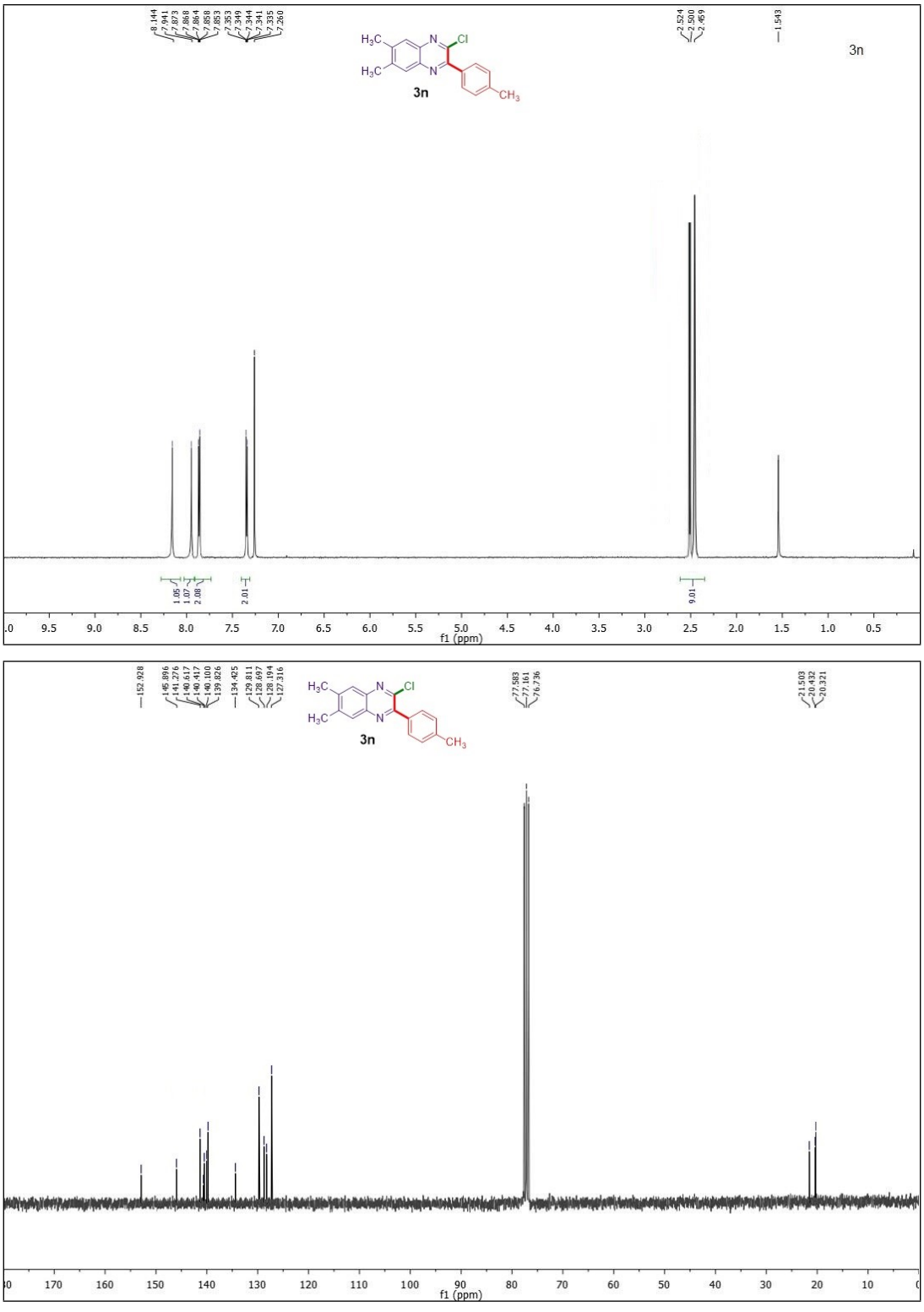

Figure S14. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3n** in $CDCl_3$.

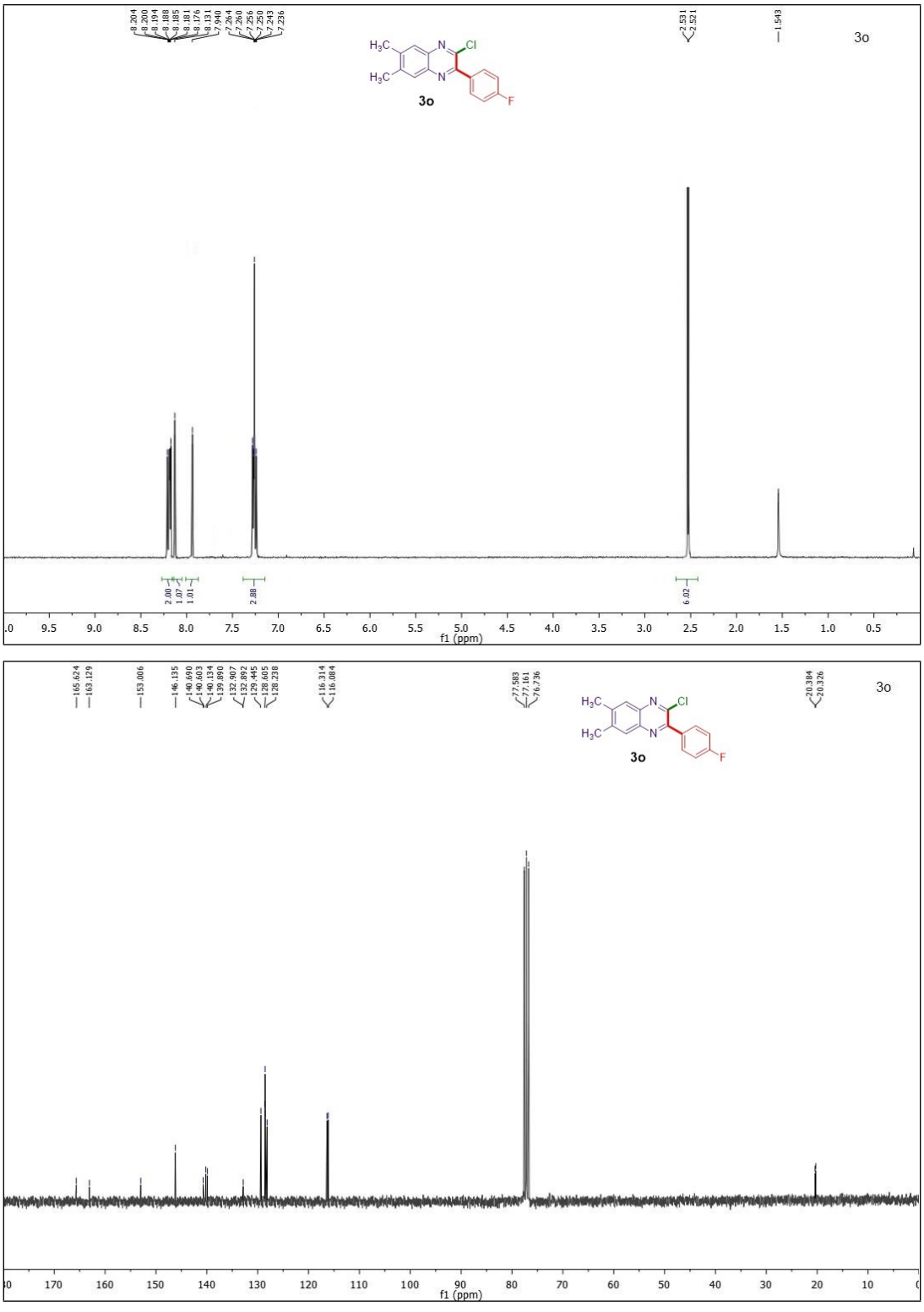

Figure S15. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3o** in $CDCl_3$.

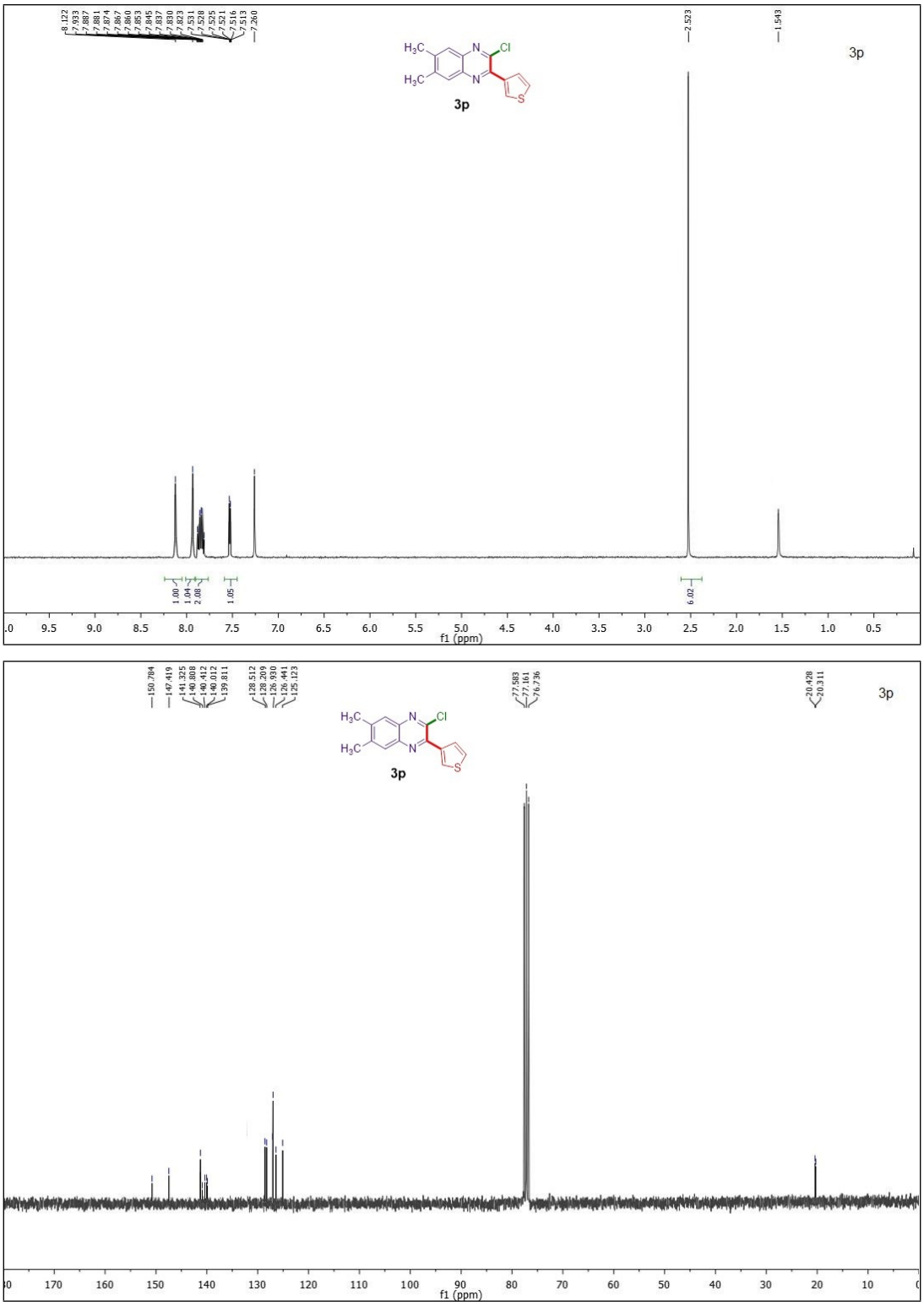

Figure S16. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3p** in $CDCl_3$.

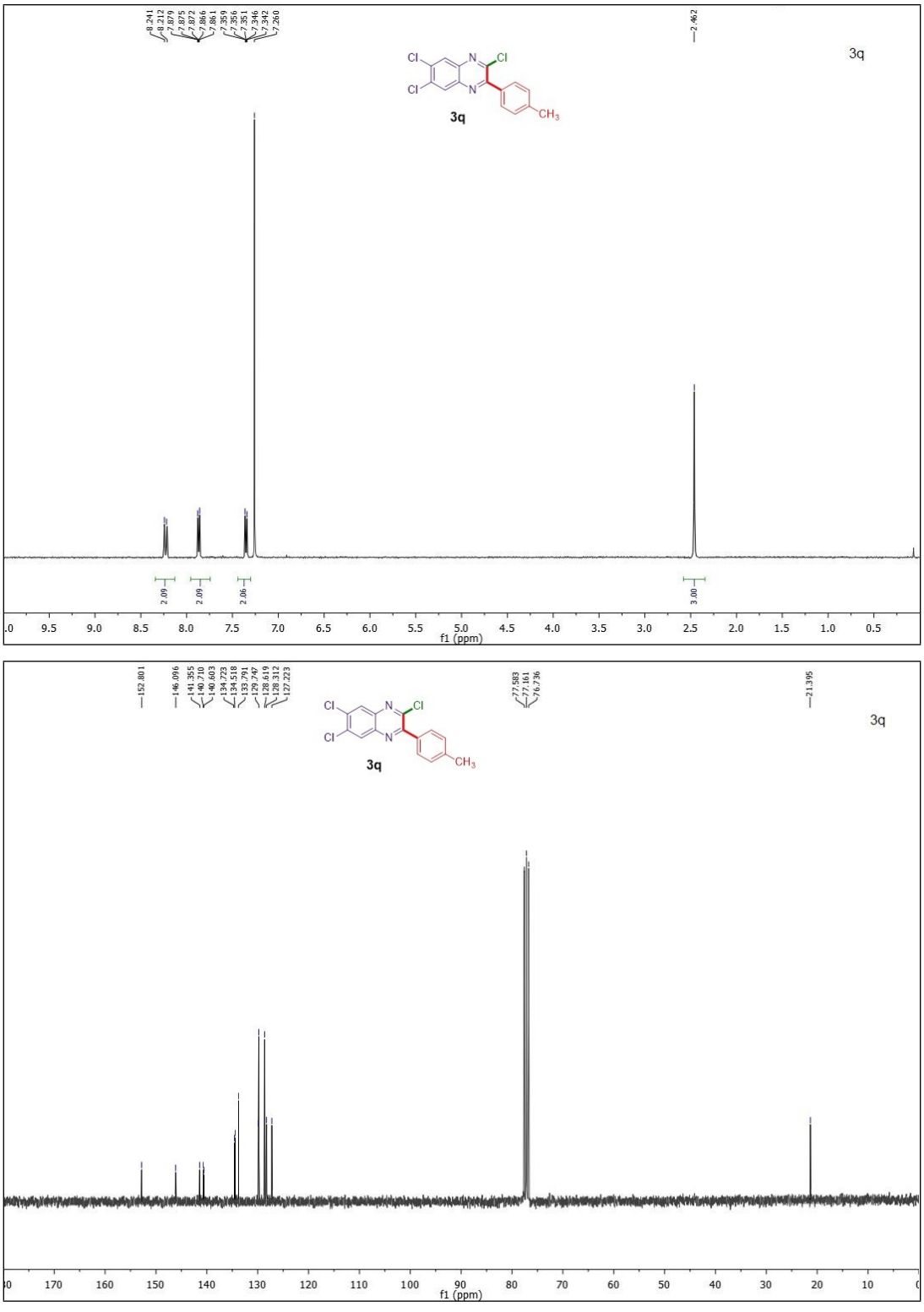

Figure S17. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3q** in $CDCl_3$.

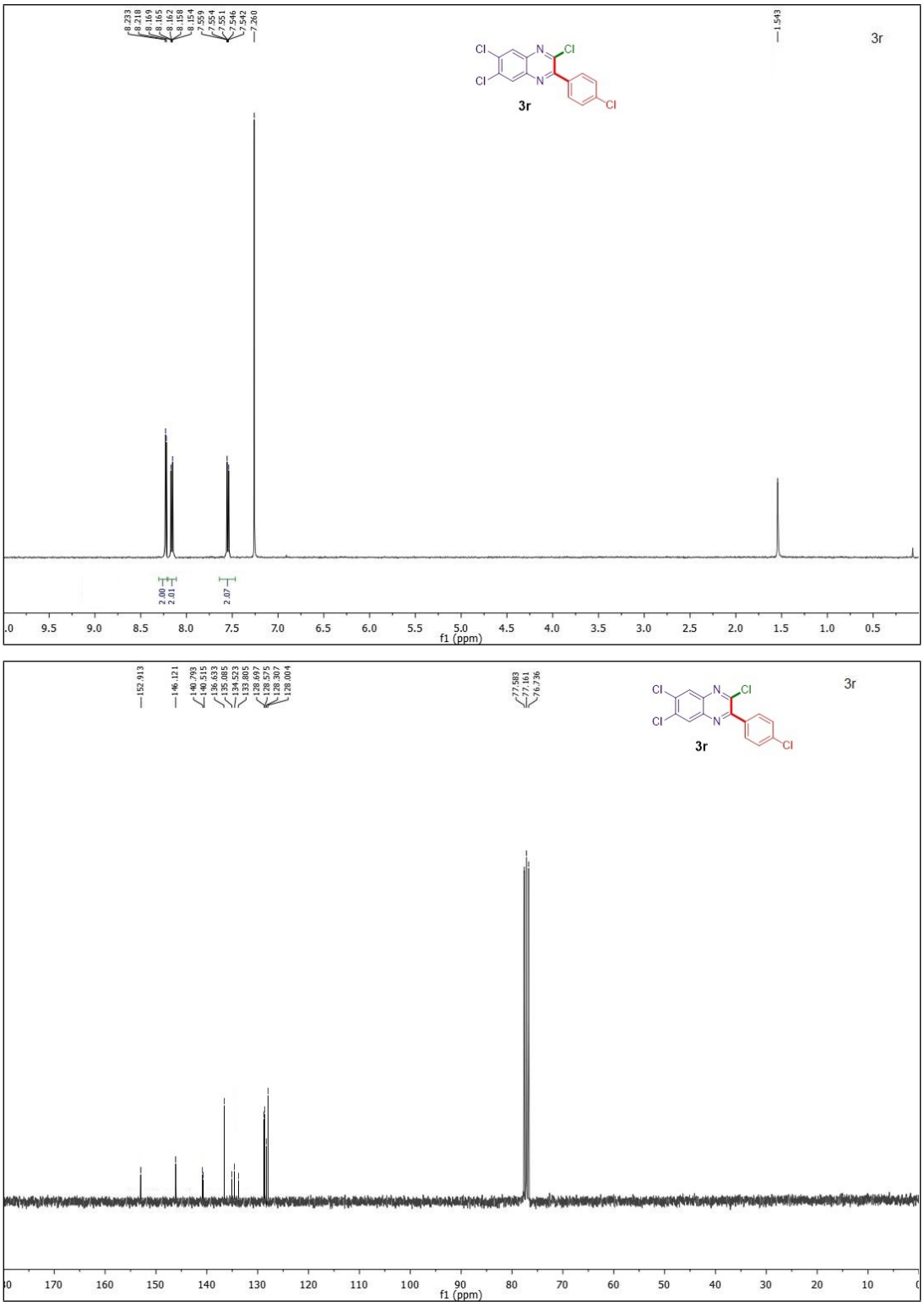

Figure S18. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **3r** in $CDCl_3$.

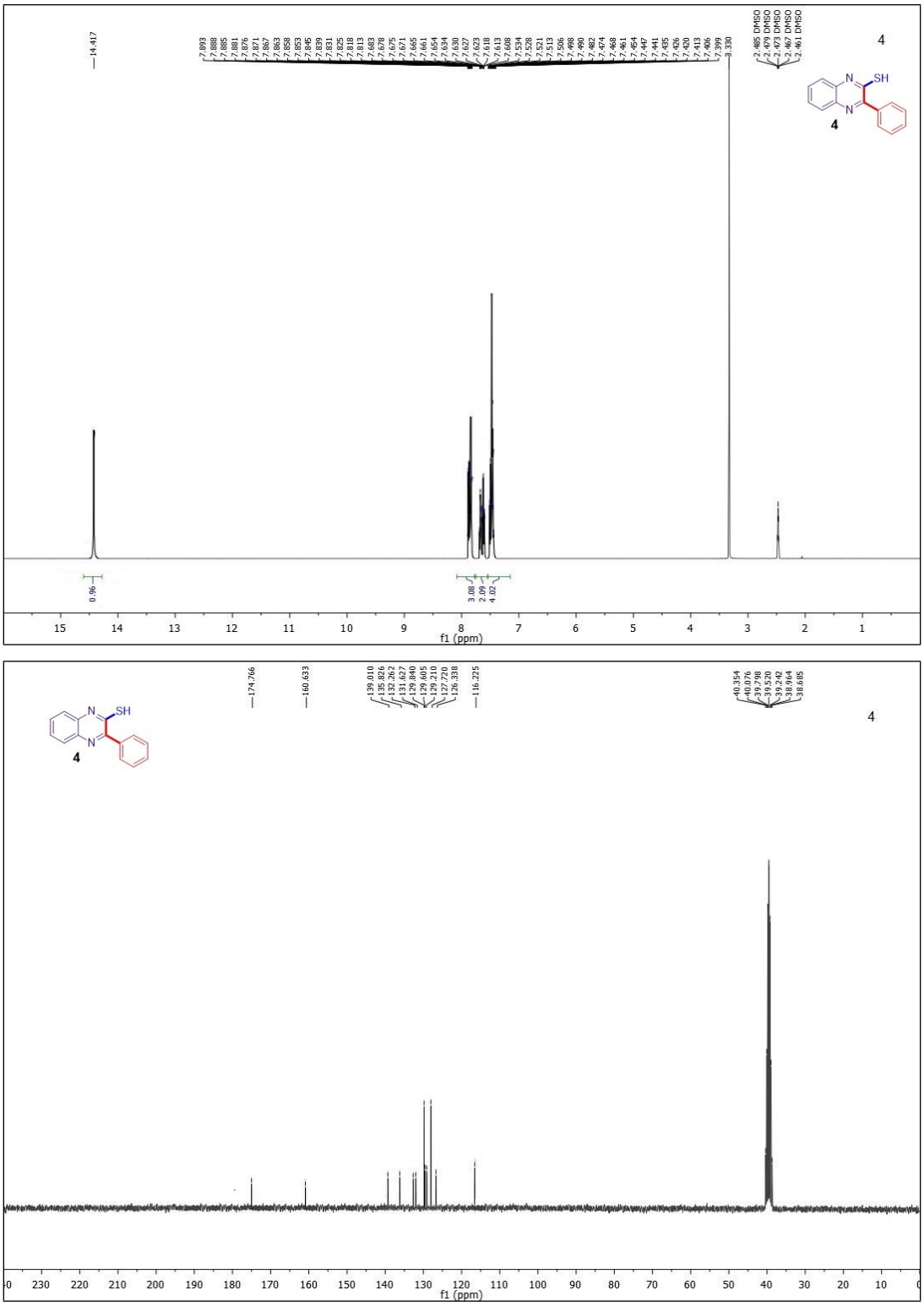

Figure S19. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **4** in $CDCl_3$.

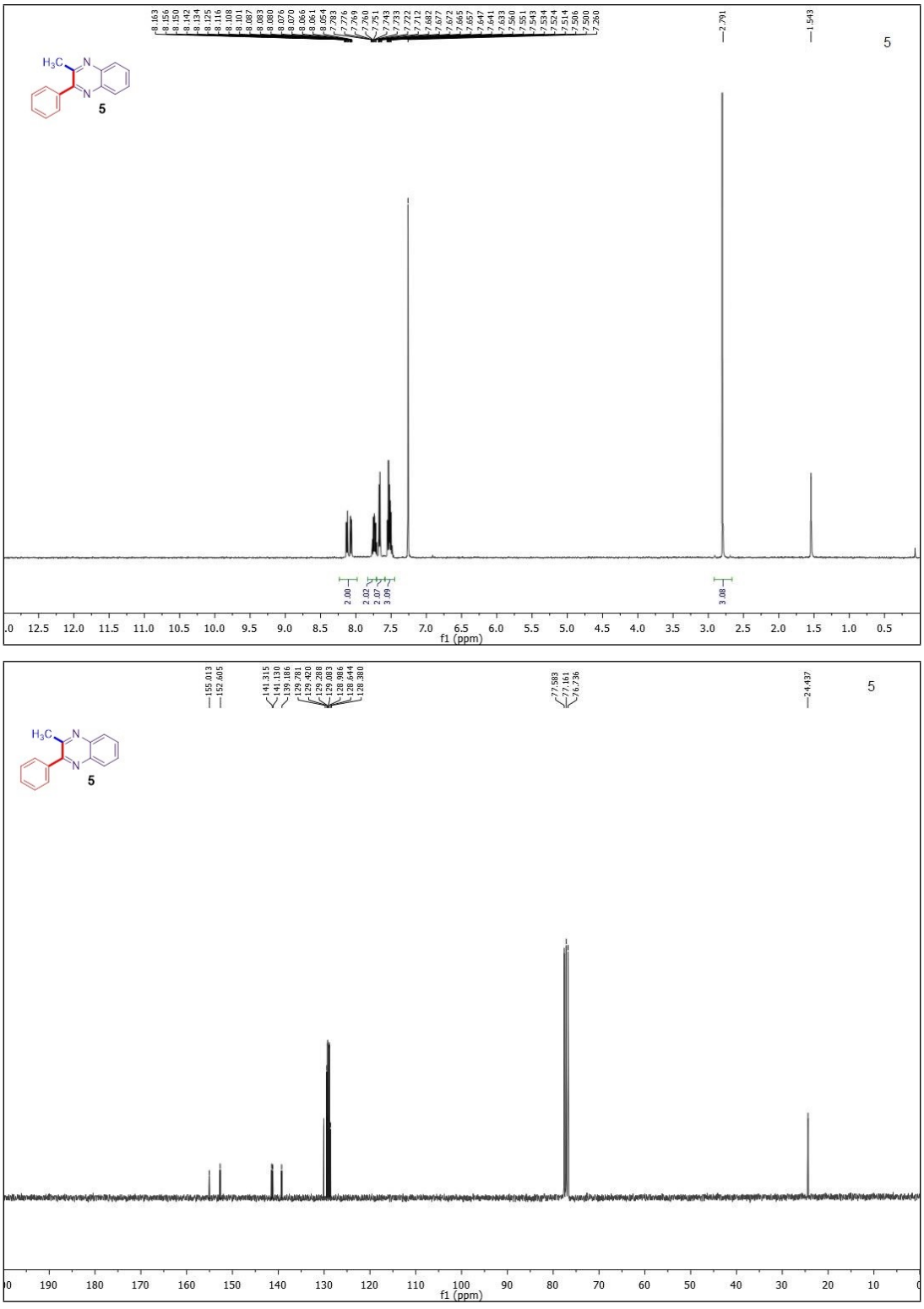

Figure S20. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **5** in $CDCl_3$.

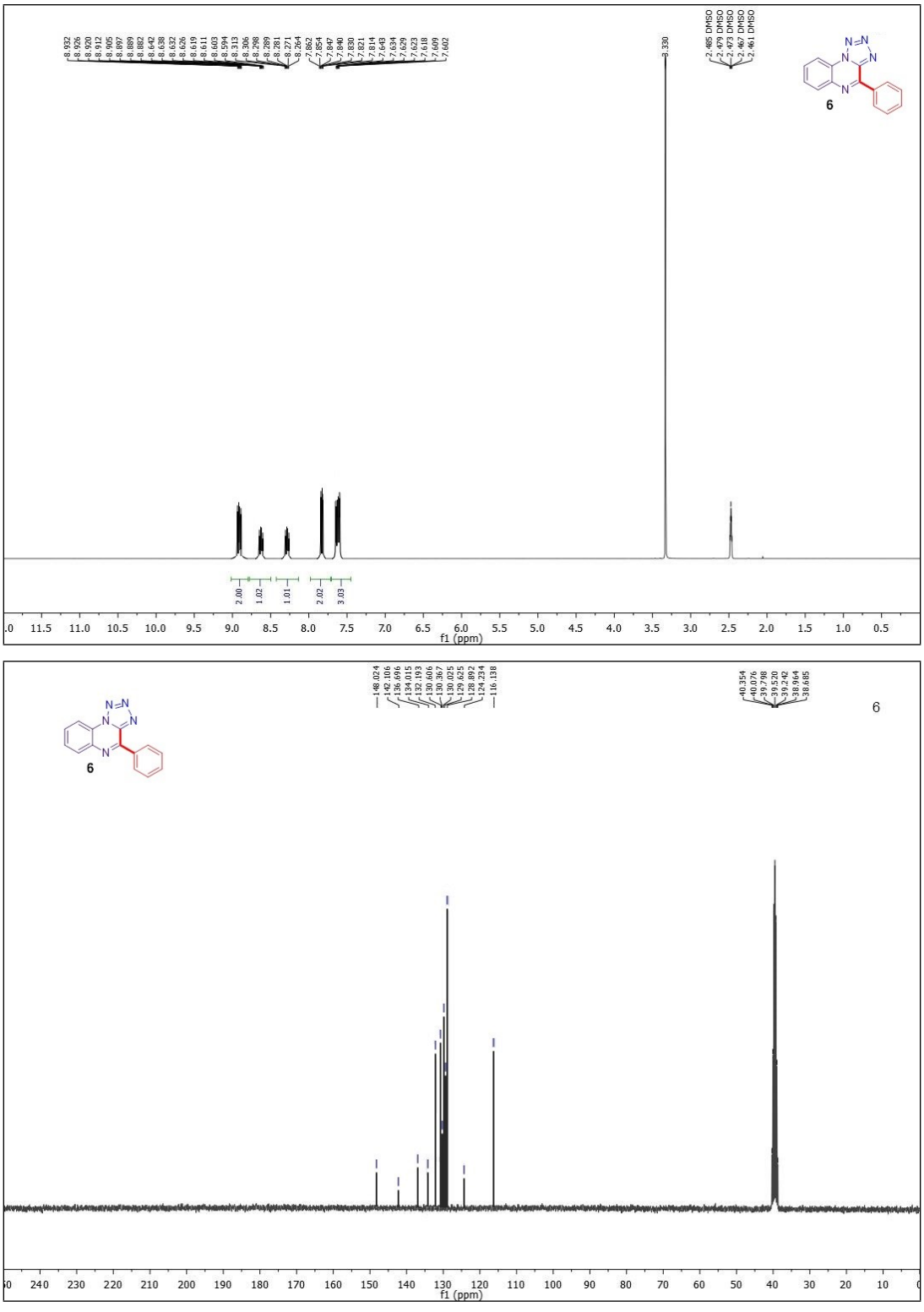

Figure S21. ^{1}H (top) and ^{13}C (bottom) NMR spectra of compound **6** in $CDCl_3$.