Rhodium-catalyzed selenylation and sulfenylation of quinoxalinones 'on water'

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Supporting Information

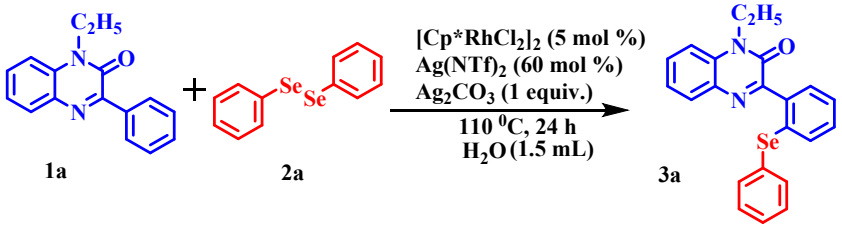
Content

1. General Information

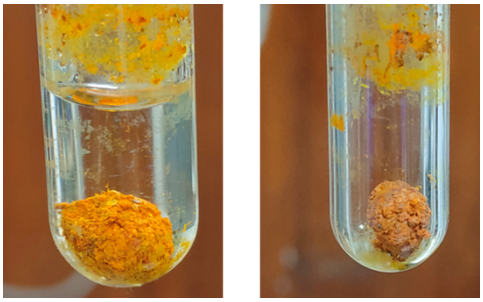
All the experiments were carried out in an oven-dried screw-capped reaction vial under conventional heating. Commercial reagents were purchased from Sigma-Aldrich, Alfa Aeser, Acros, TCI and other commercial suppliers and used as received without further purification. The analytical TLC was performed using 0.20 mm silica gel 60F plates with a 254 nm fluorescent indicator. The TLC plates were visualised by using ultra-violet light. Column chromatography was done using 150-230 mesh silica gel. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on JEOL ECX-400P NMR or Brucker at 400 MHz and 100 MHz respectively using TMS as the internal standard and are reported as chemical shifts (δ) in parts per million (ppm). The spectra were measured in $CDCl_3$ (TMS, ^{1}H δ = 0; $CDCl_3$, ^{1}H δ = 7.26, ^{13}C δ = 77.16) or DMSO-d_6 (TMS, ^{1}H δ = 0; DMSO-d_6, ^{1}H δ = 2.50, ^{13}C δ = 39.52). The coupling constants (*J*) are reported in Hz. The following abbreviations are used for explaining the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS (m/z) were recorded using an Agilent Technology 6530, Accurate mass, Q-TOF LCMS spectrometer. Melting points were recorded on a Buchi M-560 melting point apparatus and are uncorrected. Single crystal was recorded in a Bruker Kappa APEC2 CCD Diffractometer with MoKα radiation. The structures were solved by SHELXT and refined with SHELX. 1-alkyl-3-phenylquinoxalin-2(1*H*)-ones were prepared following the literature procedure. [1-3]

2. Experimental Section

2.1 General procedure for the synthesis of compounds 3a-3n and 5a-5r:



In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of 1-ethyl-3-phenylquinoxalin-2(1*H*)-one **1a** (0.2 mmol, 1.0 equiv.), diphenyl disulfides/diphenyl diselenides **2a/4a** (0.4 mmol, 2 equiv.), silver triflimide (60 mol%), Ag_2CO_3 (0.2 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. After 24 h, the reaction



a. **b.**

Figure 1. Pictures of the reaction vial **a**. before decanting water **b**. after decanting water

was stopped and the reaction mixture was cooled to ambient temperature. As shown in the above Figure 1, the water from the reaction vial was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane /ethyl acetate as eluent to afford the targeted products **3a-3n** and **5a-5r**.

2.2 Procedure for late-stage modification to afford compound 7

Compound **6** was prepared as per the available literature.[3] In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of **6** (0.128 mmol), diphenyl disulfide (2 equiv.), silver triflimide (60 mol %), Ag_2CO_3 (1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. After 24 h reaction was stopped and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane/ethyl acetate as eluent to give the pure targeted product in 52% yield.

2.3 Procedure for late-stage modification to afford compound 10

Compound **8** was prepared as per the available literature.[3] In an oven-dried screw-capped **10** mL reaction vial with a stirring bar was charged with a mixture of **8**, (0.1468 mmol), diphenyl disulfide (2 equiv.), silver triflimide (60 mol %), Ag_2CO_3 (1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. After 24 h reaction was stopped and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane/ethyl acetate as eluent to give the pure targeted product **10** in 58% yield.

2.4 Procedure for late-stage modification to afford compound 11

Compound **9** was prepared as per the available literature.[4] In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of **9,** (0.1621 mmol), diphenyl diselenide (2 equiv.), silver triflimide (60 mol %), Ag_2CO_3 (1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. After 24 h reaction was stopped and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane/ethyl acetate as eluent to afford the pure targeted product **11** in 91% yield.

2.5 Procedure for late-stage modification to afford compound 12

Compound **9** was prepared as per the available literature.[4] In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of **9,** (0.1621 mmol), diphenyl

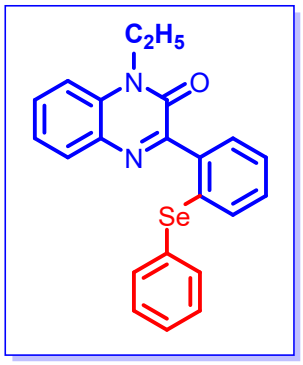
disulfide (2 equiv.), silver triflimide (60 mol %), Ag_2CO_3 (1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. After 24 h reaction was stopped and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane/ethyl acetate as eluent to afford the pure targeted product **12** in 88% yield.

2.6 Procedure for the synthesis of compounds 14

Compound **13** was prepared as per the available literature.[5] In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of **13,** (0.242 mmol), diphenyl diselenide (2 equiv.), silver triflimide (60 mol %), Ag_2CO_3 (1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %) and 1.5 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by slowly heating at 110 °C (oil bath temperature). The progress of the reaction was monitored using TLC. Then after the reaction was stopped and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane/ethyl acetate as eluent to afford the pure targeted product **14** in 56% yield.

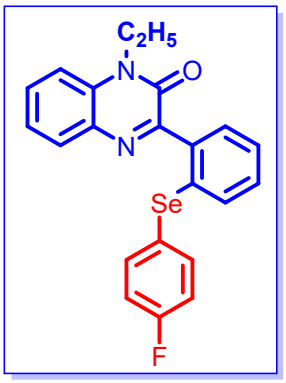
3. Analytical data

1-ethyl-3-(2-(phenylselanyl)phenyl)quinoxalin-2(1*H*)-one (3a)



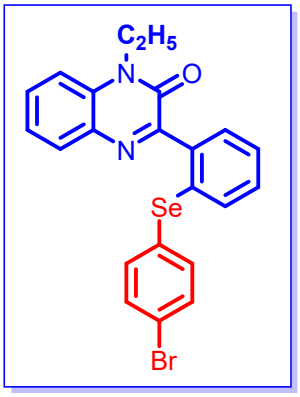
Colour and physical state: Pale yellow solid
Yield: 94% (76 mg)
Melting point:139-141 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.00 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59 (td, *J* = 7.7, 1.6 Hz, 1H), 7.54 (dd, *J* = 7.4, 2.0 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.32 (m, *J* = 15.4, 7.6, 7.1, 1.3 Hz, 3H), 7.27 – 7.26 (m, 1H), 7.25 (d, *J* = 1.2 Hz, 1H), 7.21 (m, *J* = 7.6, 1.6 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.31, 154.17, 136.94, 135.57, 135.04, 132.93, 132.67, 132.60, 132.38, 130.80, 130.70, 130.56, 130.23, 129.38, 127.97, 126.16, 123.82, 113.70, 37.89, 12.57. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OSe$ $[M+H]^+$: 407.0657; found: 407.0659

1-ethyl-3-(2-((4-fluorophenyl)selanyl)phenyl)quinoxalin-2(1*H*)-one (3b)



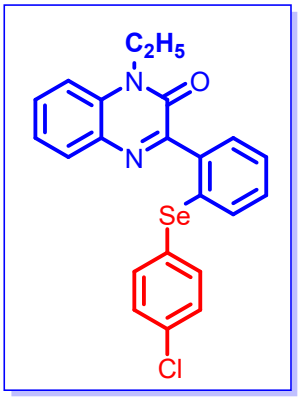
Colour and physical state: Pale yellow solid
Yield: 92% (78 mg)
Melting point: 116-118 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d)* δ 8.12 (d, *J* = 7.6 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.27 (td, *J* = 18.3, 17.2, 7.3 Hz, 3H), 6.97 (t, *J* = 8.4 Hz, 2H), 4.40 (q, *J* = 7.3 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.22, 161.75, 155.08, 154.17, 137.46, 137.38, 136.68, 135.93, 132.64, 132.46, 130.86, 130.53, 130.28, 127.10, 127.06, 126.12, 123.86, 116.73, 116.52, 113.73, 37.91, 12.57. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -113.39. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}FN_2OSe$ $[M+H]^+$: 425.0563; found: 425.0565.

3-(2-((4-bromophenyl)selanyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (3c)



Colour and physical state: Yellow solid
Yield: 84% (81 mg)
Melting point: 156-158 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 6.4 Hz, 1H), 7.99 (d, *J* = 6.8 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.40 (d, *J* = 1.7 Hz, 1H), 7.38 (dd, *J* = 5.1, 2.2 Hz, 5H), 7.34 (dd, *J* = 4.3, 2.7 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.27 – 7.22 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.21, 154.18, 137.26, 136.41, 134.96, 133.14, 132.67, 132.63, 132.49, 131.63, 130.91, 130.84, 130.57, 130.38, 126.57, 123.89, 122.37, 113.75, 37.92, 12.58. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}BrN_2OSe$ $[M+H]^+$: 484.9762; found: 484.9757.

3-(2-((4-chlorophenyl)selanyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (3d)



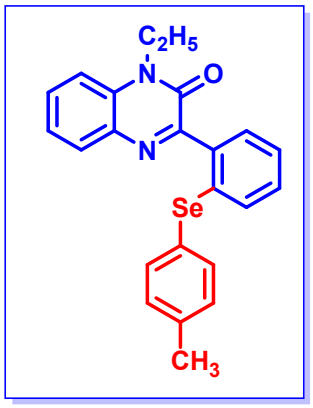
Colour and physical state: Yellow solid

Yield:77% (68 mg)

Melting point: 138-140 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.61 (td, *J* = 7.7, 1.6 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.37 (m, 2H), 7.33 (dd, *J* = 7.8, 6.5 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.21 (d, *J* = 2.0 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.14, 154.16, 137.11, 136.25, 135.18, 134.23, 132.99, 132.62, 130.90, 130.85, 130.55, 130.36, 129.57, 126.47, 123.89, 113.74, 37.92, 12.58. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}ClN_2OSe$ $[M+H]^+$: 441.0267; found: 441.0268.

1-ethyl-3-(2-(p-tolylselanyl)phenyl)quinoxalin-2(1H)-one (3e)



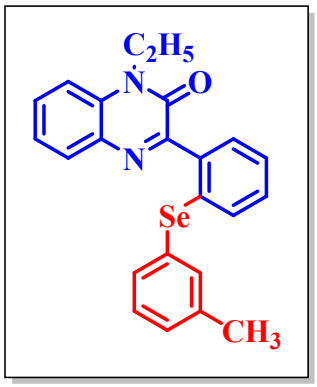
Colour and physical state: Yellow solid

Yield: 81% (68 mg)

Melting point: 150-152 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.07 (m, 1H), 8.02 (dd, J = 8.3, 1.6 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.33 – 7.25 (m, 2H), 7.23 – 7.16 (m, 1H), 7.09 (d, J = 7.5 Hz, 2H), 4.40 (q, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.19, 154.12, 138.15, 136.49, 136.28, 135.51, 132.63, 132.57, 132.40, 130.75, 130.70, 130.52, 130.25, 130.14, 128.44, 125.80, 123.78, 113.67, 37.86, 21.35, 12.55. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2OSe$ $[M+H]^+$: 421.0814; found: 421.0838.

1-ethyl-3-(2-(m-tolylselanyl)phenyl)quinoxalin-2(1H)-one (3f)



Colour and physical state: Yellow solid

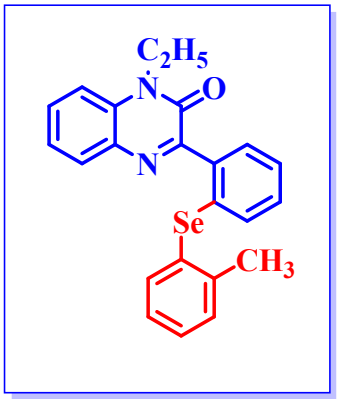
Yield: 80% (67 mg)

Melting point: 102-104 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) 1H NMR (400 MHz, Chloroform-d) δ 8.07 (dd, J = 7.7, 1.6 Hz, 1H), 8.01 (dd, J = 8.3, 1.5 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.41 – 7.35 (m, 4H), 7.35 – 7.33 (m, 1H), 7.33 – 7.28 (m, 1H), 7.24 – 7.19 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.12 – 7.06 (m, 1H), 4.40 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, *Chloroform-d*) δ 155.36, 154.16, 139.16, 136.87, 135.74, 135.71, 132.92, 132.69, 132.61, 132.17, 132.04, 130.76, 130.68, 130.58, 130.17, 129.18, 128.84, 126.06, 123.79, 113.68, 37.87, 21.35,

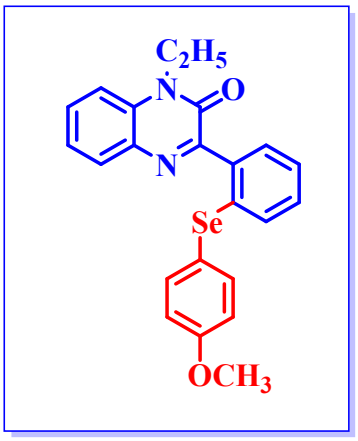
12.57. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2OSe$ $[M+H]^+$: 421.0814; found: 421.0821.

1-ethyl-3-(2-(o-tolylselanyl)phenyl)quinoxalin-2(1H)-one (3g)



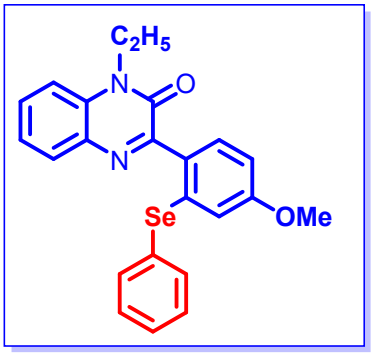
Colour and physical state: Yellow solid
Yield: 85% (71 mg)
Melting point: 97-99 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, 1H), 8.03 (dd, J = 8.1, 1.6 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.44 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 7.24 – 7.18 (m, 4H), 7.12 – 7.05 (m, 1H), 4.40 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.25, 154.11, 141.63, 136.87, 136.47, 135.07, 132.73, 132.67, 132.58, 132.18, 130.85, 130.73, 130.54, 130.30, 130.21, 128.64, 126.76, 126.01, 123.75, 113.66, 37.84, 22.79, 12.55. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2OSe$ $[M+H]^+$: 421.0814; found: 421.0820.

1-ethyl-3-(2-(p-tolylselanyl)phenyl)quinoxalin-2(1H)-one (3h)



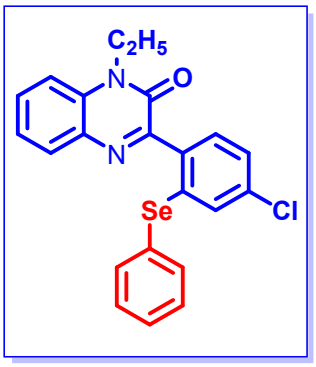
Colour and physical state: Yellow solid
Yield: 77% (67 mg)
Melting point: 118-120 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (dd, J = 7.7, 1.5 Hz, 1H), 8.02 (dd, J = 8.4, 1.5 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.35 (m, 2H), 7.26 (s, 2H), 7.22 – 7.16 (m, 1H), 4.41 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 1.45 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.00, 155.04, 154.15, 137.65, 137.08, 135.97, 132.62, 131.81, 130.79, 130.54, 130.15, 125.54, 123.84, 122.21, 115.15, 113.71, 55.39, 37.91, 12.59. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2O_2Se$ $[M+H]^+$: 437.0763; found: 437.0786.

1-ethyl-3-(4-methoxy-2-(phenylselanyl)phenyl)quinoxalin-2(1*H*)-one (3i)



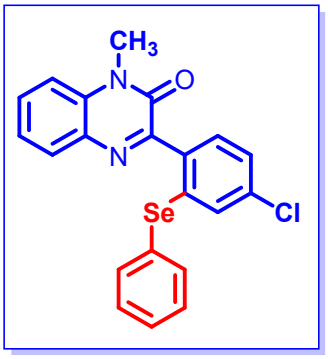
Colour and physical state: Yellow solid
Yield: 83% (72 mg)
Melting point: 113-115 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.7 Hz, 1H), 8.02 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.57 (ddd, *J* = 8.7, 7.2, 1.5 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 6.81 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 3.64 (s, 3H), 1.44 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 160.77, 154.31, 153.90, 138.77, 135.89, 132.60, 132.36, 132.32, 132.30, 130.32, 130.13, 129.50, 128.89, 128.38, 123.79, 117.54, 113.65, 111.41, 55.31, 37.88, 12.58. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2O_2Se$ $[M+H]^+$: 437.0763; found: 437.0761.

3-(4-chloro-2-(phenylselanyl)phenyl)-1-ethylquinoxalin-2(1*H*)-one (3j)



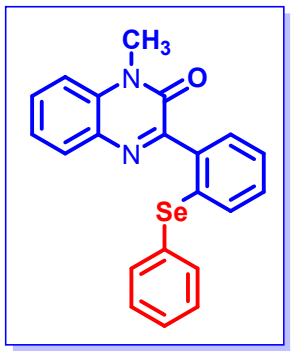
Colour and physical state: Yellow solid
Yield: 74% (74 mg)
Melting point: 118-120 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.4 Hz, 1H), 8.02 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.42 – 7.37 (m, 2H), 7.37 – 7.31 (m, 3H), 7.26 (d, *J* = 2.9 Hz, 1H), 7.25 – 7.19 (m, 1H), 4.41 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.05, 153.75, 138.54, 136.30, 135.66, 134.47, 132.56, 131.93, 131.69, 131.54, 131.06, 130.49, 129.73, 128.69, 125.93, 124.00, 113.78, 37.99, 12.59. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}ClN_2OSe$ $[M+H]^+$: 441.0267; found: 441.0255.

3-(4-chloro-2-(phenylselanyl)phenyl)-1-methylquinoxalin-2(1*H*)-one (3k)



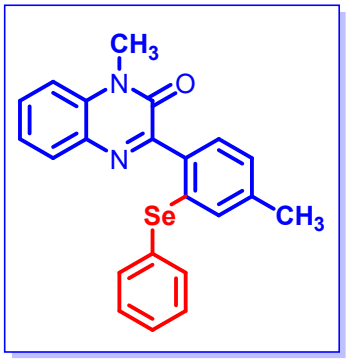
Colour and physical state: Pale yellow solid
Yield: 61% (61 mg)
Melting point: 127-129 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.43 – 7.35 (m, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.22 (d, *J* = 2.1 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.56, 153.86, 138.41, 136.32, 135.66, 134.55, 133.62, 132.20, 131.87, 131.71, 131.45, 131.09, 130.24, 129.73, 128.69, 125.98, 124.19, 113.96, 29.66. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{15}ClN_2OSe$ $[M+H]^+$: 427.0111; found: 427.0095.

1-methyl-3-(2-(phenylselanyl)phenyl)quinoxalin-2(1*H*)-one (3l)



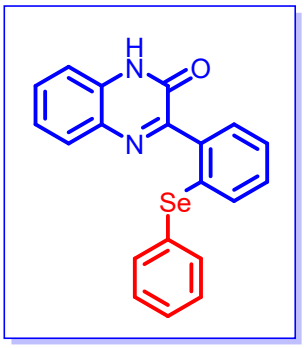
Colour and physical state: Pale yellow solid
Yield: 92% (76 mg)
Melting point: 133-135 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.60 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.34 (m, 3H), 7.34 – 7.29 (m, 1H), 7.28 – 7.19 (m, 4H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.52, 154.72, 137.19, 135.39, 135.00, 133.74, 133.06, 132.46, 132.39, 130.83, 130.66, 130.37, 130.23, 129.39, 127.95, 126.25, 124.00, 113.87, 29.59. **HRMS** (ESI+) m/z: calculated for **$C_{21}H_{16}N_2OSe$** $[M+H]^+$: 393.0501; found: 393.0504.

1-methyl-3-(4-methyl-2-(phenylselanyl)phenyl)quinoxalin-2(1*H*)-one (3m)



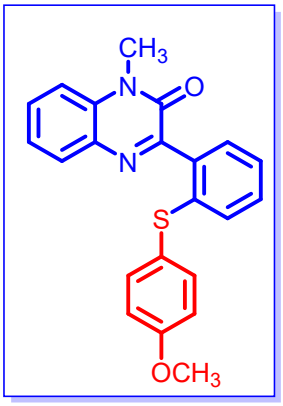
Colour and physical state: Yellow solid
Yield: 87% (70 mg)
Melting point: 149-151 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 2H), 7.59 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.41 – 7.32 (m, 2H), 7.30 – 7.21 (m, 3H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.13 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.77 (s, 3H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.42, 154.78, 140.50, 135.08, 134.79, 134.49, 133.60, 132.56, 132.44, 130.61, 130.50, 130.22, 129.32, 127.81, 127.26, 123.94, 113.82, 29.58, 21.47. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OSe$ $[M+H]^+$: 407.0657; found: 407.0664.

3-(2-(phenylselanyl)phenyl)quinoxalin-2(1*H*)-one (3n)



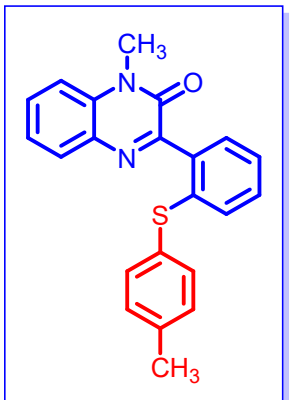
Colour and physical state: Pale yellow solid
Yield: 63% (53 mg)
Melting point: 246-248 ^{0}C
^{1}H NMR (400 MHz, DMSO-d_6) : δ 12.69 (s, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 6.7 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 7.37 – 7.33 (m, 5H), 7.32 – 7.30 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 156.09, 154.43, 136.90, 134.29, 134.14, 132.25, 131.71, 131.25, 130.81, 130.67, 130.17, 129.64, 129.19, 128.49, 128.12, 126.17, 123.65, 115.41. **HRMS** (ESI+) m/z: calculated for $C_{20}H_{14}N_2OSe$ $[M+H]^+$: 379.0344; found: 379.0345.

3-(2-((4-methoxyphenyl)thio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5a)



Colour and physical state: Pale yellow solid
Yield: 78% (62 mg)
Melting point: 148-150 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 6.5 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.42 – 7.31 (m, 4H), 7.30 – 7.24 (m, 2H), 7.23 – 7.13 (m, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.67, 156.69, 154.61, 138.92, 136.38, 135.32, 133.80, 132.79, 130.80, 130.67, 130.53, 129.95, 126.03, 125.88, 123.88, 114.84, 113.81, 55.39, 29.51. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2O_2S$ $[M+H]^+$: 375.1162; found: 375.1162.

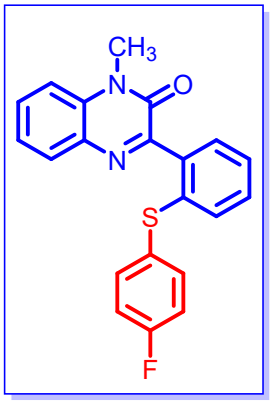
1-methyl-3-(2-(p-tolylthio)phenyl)quinoxalin-2(1*H*)-one (5b)



Colour and physical state: Pale yellow solid
Yield: 76% (58 mg)
Melting point: 107-109 ^{0}C

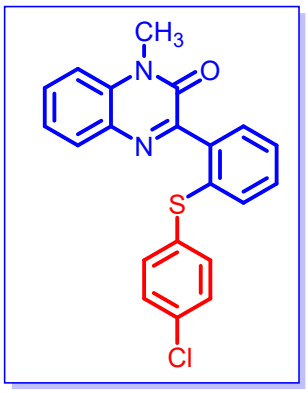
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.61 (dt, *J* = 12.6, 6.1 Hz, 2H), 7.37 (q, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.5 Hz, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 3.76 (s, 3H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.80, 154.66, 137.78, 137.58, 137.32, 133.79, 132.80, 132.67, 132.38, 131.75, 130.81, 130.54, 130.05, 129.96, 126.60, 123.88, 113.82, 29.55, 21.23. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OS$ $[M+Na]^+$:381.1032; found: 381.1004

3-(2-((4-fluorophenyl)thio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5c)



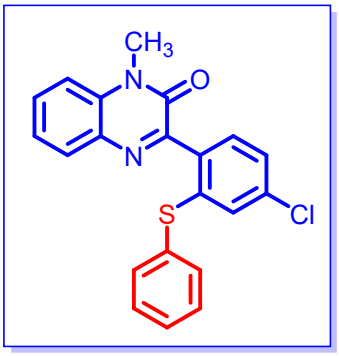
Colour and physical state: Yellow solid
Yield: 68 % (52 mg)
Melting point: 131-133 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.67 – 7.57 (m, 2H), 7.42 – 7.36 (m, 2H), 7.36 – 7.31 (m, 4H), 7.30 (d, *J* = 6.2 Hz, 1H), 6.92 (t, *J* = 8.7 Hz, 2H), 3.76 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 163.64, 156.68, 154.67, 137.63, 137.24, 134.46, 134.38, 133.81, 132.80, 132.03, 130.93, 130.57, 130.18, 130.11, 127.01, 123.98, 116.39, 116.17, 113.88, 29.58. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -114.18. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{15}FN_2OS$ $[M+Na]^+$: 385.0781; found: 385.0785

3-(2-((4-chlorophenyl)thio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5d)



Colour and physical state: Brown solid
Yield: 67% (54 mg)
Melting point: 152-154 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.69 – 7.56 (m, 2H), 7.41 – 7.38 (m, 1H), 7.38 – 7.35 (m, 3H), 7.34 (d, *J* = 1.3 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.17 – 7.13 (m, 2H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.67, 154.66, 138.44, 136.01, 135.45, 133.78, 133.10, 132.98, 132.81, 132.73, 130.96, 130.57, 130.28, 130.23, 129.19, 127.61, 124.00, 113.88, 29.59. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{15}ClN_2OS$ $[M+H]^+$: 379.0666; found: 379.0673.

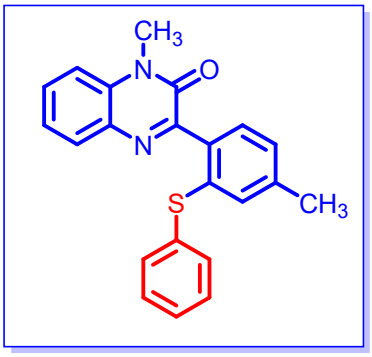
3-(4-chloro-2-(phenylthio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5e)



Colour and physical state: Brown solid
Yield: 51% (36 mg)
Melting point: 105-107 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (t, *J* = 8.1 Hz, 2H), 7.39 – 7.33 (m, 4H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.25 (d, *J* = 3.0 Hz, 2H), 7.22 (d, *J* = 2.1 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.94, 154.56, 140.13, 136.17, 135.44, 134.66,

133.81, 132.85, 131.35, 131.12, 130.62, 129.47, 128.50, 128.08, 126.77, 124.05, 113.91, 29.62. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{15}ClN_2OS$ $[M+H]^+$: 379.0666; found: 379.0653.

1-methyl-3-(4-methyl-2-(phenylthio)phenyl)quinoxalin-2(1*H*)-one (5f)



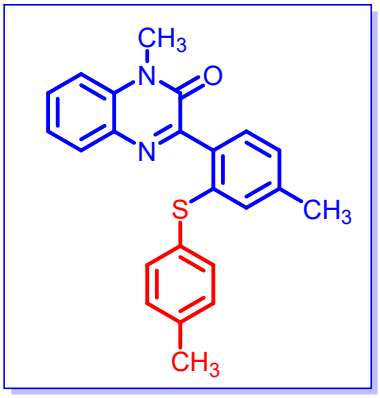
Colour and physical state: Pale yellow solid

Yield: 68% (49 mg)

Melting point: 120-122 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.38 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.22 – 7.14 (m, 5H), 3.73 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.90, 154.80, 140.35, 136.99, 136.01, 135.68, 133.79, 133.49, 132.86, 131.34, 130.63, 130.50, 129.97, 129.01, 128.27, 126.89, 123.78, 113.77, 29.53, 21.42. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OS$ $[M+H]^+$: 359.1213; found: 359.1217.

1-methyl-3-(4-methyl-2-(p-tolylthio)phenyl)quinoxalin-2(1*H*)-one (5g)

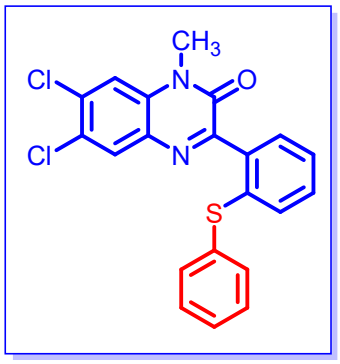


Colour and physical state: Pale yellow semi-solid

Yield: 62% (46 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 – 7.55 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 3.73 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.93, 154.77, 140.21, 137.25, 137.10, 134.95, 133.80, 132.88, 132.82, 132.60, 132.24, 130.60, 130.50, 129.91, 129.87, 127.74, 123.77, 113.74, 29.52, 21.44, 21.22. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2OS$ $[M+H]^+$: 373.1369; found: 373.1374.

6,7-dichloro-1-methyl-3-(2-(phenylthio)phenyl)quinoxalin-2(1*H*)-one (5h)



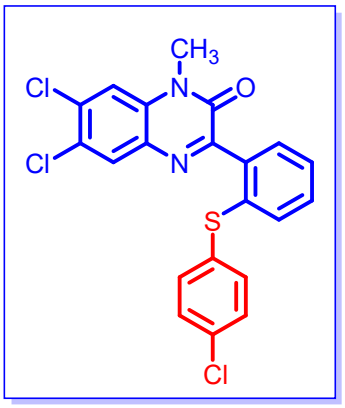
Colour and physical state: White solid

Yield: 54% (37 mg)

Melting point: 141-143 ^{0}C

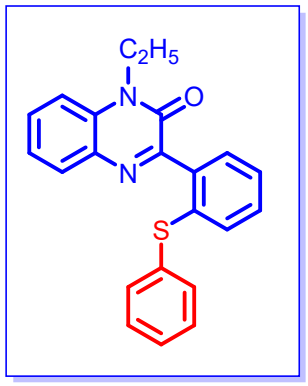
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.68 – 7.55 (m, 1H), 7.43 (s, 1H), 7.36 (d, *J* = 3.4 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.17 (m, 3H), 3.69 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.96, 154.12, 137.44, 136.77, 136.37, 134.93, 133.17, 132.84, 131.82, 131.70, 131.24, 130.52, 130.03, 129.18, 127.69, 127.31, 127.18, 115.34, 29.83. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{14}Cl_2N_2OS$ $[M+H]^+$: 413.0277; found: 413.0272.

6,7-dichloro-3-(2-((4-chlorophenyl)thio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5i)



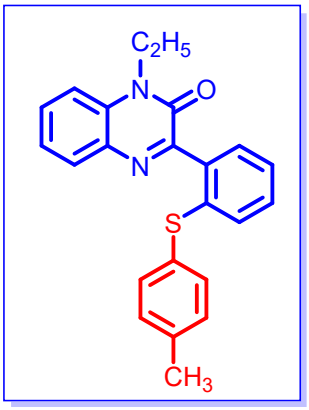
Colour and physical state: White solid
Yield: 66% (48 mg)
Melting point: 119-121 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.65 – 7.59 (m, 1H), 7.44 (s, 1H), 7.37 (q, *J* = 3.2 Hz, 3H), 7.24 – 7.14 (m, 4H), 3.69 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.83, 154.08, 137.73, 136.17, 135.21, 135.09, 133.33, 133.16, 133.03, 132.74, 131.81, 131.25, 130.64, 130.18, 129.31, 127.81, 127.57, 115.38, 29.83. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{13}Cl_3N_2OS$ $[M+H]^+$: 446.9887; found: 446.9872.

1-ethyl-3-(2-(phenylthio)phenyl)quinoxalin-2(1*H*)-one (5j)



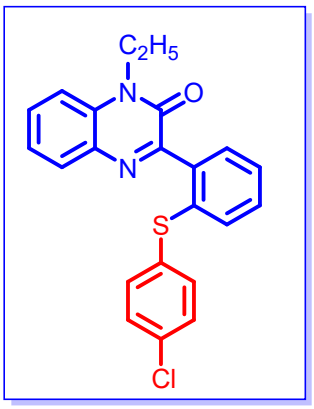
Colour and physical state: White solid
Yield: 84% (60 mg)
Melting point: 145-147 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.59 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.36 (d, *J* = 1.4 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.31 (d, *J* = 1.4 Hz, 1H), 7.23 – 7.14 (m, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.78, 154.17, 138.11, 136.78, 136.69, 133.11, 132.75, 132.70, 131.72, 130.82, 130.76, 130.12, 129.09, 127.14, 123.65, 113.64, 37.76, 12.55. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OS$ $[M+H]^+$: 359.1213; found: 359.1210.

1-ethyl-3-(2-(p-tolylthio)phenyl)quinoxalin-2(1*H*)-one (5k)



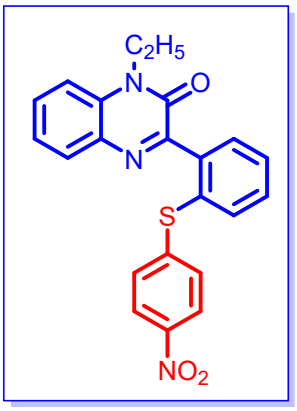
Colour and physical state: Pale yellow solid
Yield: 77% (57 mg)
Melting point: 99-101 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.69 – 7.64 (m, 1H), 7.59 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.30 – 7.28 (m, 2H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.24 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.75, 154.13, 137.88, 137.54, 137.33, 133.11, 132.75, 132.64, 132.54, 131.79, 130.81, 130.72, 130.06, 130.00, 129.95, 126.56, 123.62, 113.62, 37.75, 21.22, 12.54. **HRMS** (ESI+) m/z: calculated for $C_{23}H_{20}N_2OS$ $[M+H]^+$: 373.1369; found: 373.1343.

3-(2-((4-chlorophenyl)thio)phenyl)-1-ethylquinoxalin-2(1*H*)-one (5l)



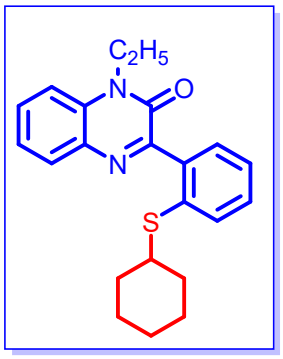
Colour and physical state: White solid
Yield: 75% (59 mg)
Melting point: 108-110 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.71 – 7.65 (m, 1H), 7.63 – 7.56 (m, 1H), 7.42 – 7.34 (m, 5H), 7.24 – 7.20 (m, 2H), 7.18 – 7.12 (m, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 156.63, 154.12, 138.41, 136.10, 135.55, 133.09, 132.97, 132.71, 130.86, 130.81, 130.29, 130.24, 129.19, 127.57, 123.72, 113.66, 37.78, 12.54. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}ClN_2OS$ $[M+H]^{]+}$: 393.0823; found: 393.0826.

1-ethyl-3-(2-((4-nitrophenyl)thio)phenyl)quinoxalin-2(1H)-one (5m)



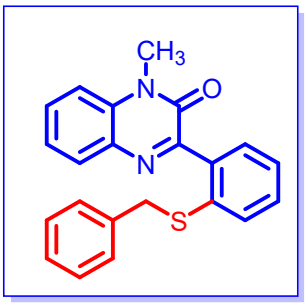
Colour and physical state: Pale yellow solid
Yield: 72% (58 mg)
Melting point: 245-247 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 2H), 4.33 (q, *J* = 7.3 Hz, 2H), 1.37 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d)* δ 156.46, 154.11, 148.50, 145.50, 141.04, 135.65, 133.05, 132.71, 131.54, 131.08, 130.81, 130.74, 129.80, 127.91, 123.88, 123.82, 113.73, 37.77, 12.50. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}N_3O_3S$ $[M+H]^+$: 404.1063; found: 404.1065.

3-(2-(cyclohexylthio)phenyl)-1-ethylquinoxalin-2(1*H*)-one (5n)



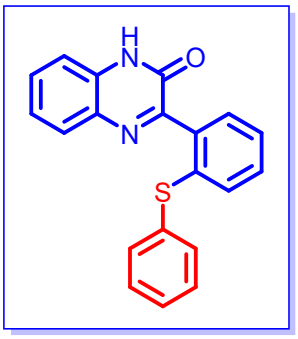
Colour and physical state: White solid
Yield: 62% (45 mg)
Melting point: 96-98 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.50 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.43 – 7.31 (m, 4H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.09 – 3.01 (m, 1H), 1.91 – 1.83 (m, 2H), 1.68 – 1.64 (m, 2H), 1.57 – 1.49 (m, 1H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.31 – 1.11 (m, 5H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 158.31, 154.25, 140.27, 135.07, 133.31, 133.20, 132.84, 130.75, 130.51, 129.58, 129.42, 127.25, 123.48, 113.64, 47.95, 37.59, 33.41, 26.12, 25.80, 12.50. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{24}N_2OS$ $[M+H]^+$: 365.1682; found: 365.1682.

3-(2-(benzylthio)phenyl)-1-methylquinoxalin-2(1*H*)-one (5o)



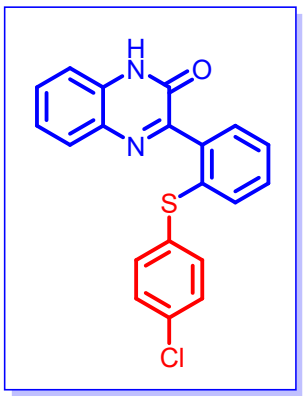
Colour and physical state: Brown solid
Yield: 51% (39 mg)
Melting point: 104-106 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.60 (td, *J* = 7.8, 1.6 Hz, 1H), 7.56 – 7.49 (m, 1H), 7.46 – 7.39 (m, 1H), 7.39 – 7.32 (m, 4H), 7.24 – 7.16 (m, 4H), 6.82 – 6.72 (m, 1H), 4.06 (s, 2H), 3.77 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.81, 138.93, 137.42, 136.05, 133.88, 132.87, 132.07, 130.77, 130.60, 129.87, 129.59, 129.23, 128.49, 127.22, 127.16, 123.87, 113.90, 40.60, 29.56. **HRMS** (ESI+) m/z: calculated for $C_{22}H_{18}N_2OS$ $[M+H]^+$: 359.1213; found: 359.1219.

3-(2-(phenylthio)phenyl)quinoxalin-2(1*H*)-one (5p)



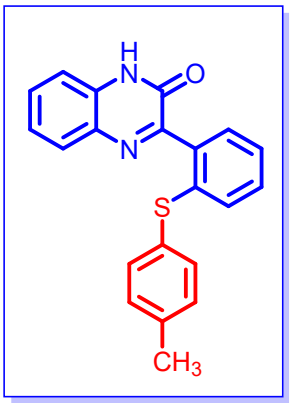
Colour and physical state: Pale yellow solid
Yield: 64% (48 mg)
Melting point: 228-230 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.26 (s, 1H), 7.96 – 7.88 (m, 1H), 7.72 – 7.65 (m, 1H), 7.55 – 7.48 (m, 1H), 7.44 – 7.37 (m, 4H), 7.36 – 7.32 (m, 1H), 7.31 – 7.28 (m, 2H), 7.21 – 7.11 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.15, 156.33, 137.72, 136.83, 136.66, 133.08, 133.02, 131.52, 130.96, 130.35, 130.26, 129.58, 129.13, 127.65, 127.40, 127.18, 124.69, 116.11. **HRMS** (ESI+) m/z: calculated for $C_{20}H_{14}N_2OS$ $[M+H]^+$: 331.0900; found: 331.0916.

3-(2-((4-chlorophenyl)thio)phenyl)quinoxalin-2(1*H*)-one (5q)



Colour and physical state: Pale yellow solid
Yield: 62% (51 mg)
Melting point: 250-252 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.16 (s, 1H), 7.91 (td, *J* = 7.8, 1.4 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.57 – 7.49 (m, 1H), 7.46 – 7.38 (m, 2H), 7.38 – 7.32 (m, 1H), 7.28 – 7.25 (m, 4H), 7.24 – 7.20 (m, 1H), 7.18 – 7.13 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-D_6) δ 157.81, 154.44, 139.09, 135.61, 134.08, 133.07, 132.39, 131.83, 131.76, 131.70, 130.82, 130.37, 130.31, 129.26, 128.84, 127.98, 123.54, 115.46. HRMS (ESI+) m/z: calculated for $C_{20}H_{13}ClN_2OS$ $[M+Na]^+$: 387.0329; found: 387.0310.

3-(2-(p-tolylthio)phenyl)quinoxalin-2(1*H*)-one (5r)



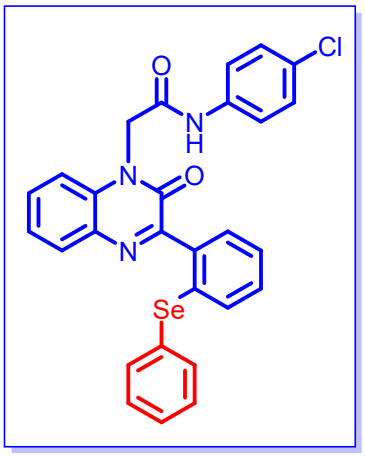
Colour and physical state: Pale yellow solid

Yield: 68% (53 mg)

Melting point: 240-242 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.18 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.66 (m, 1H), 7.56 – 7.46 (m, 2H), 7.41 – 7.31 (m, 4H), 7.24 (d, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 157.66, 156.29, 137.90, 137.56, 137.12, 136.21, 132.42, 132.16, 131.67, 130.84, 130.16, 129.99, 129.65, 128.36, 126.88, 124.49, 116.01, 21.20. **HRMS** (ESI+) m/z: calculated for $C_{21}H_{16}N_2OS$ $[M+Na]^+$: 367.0876; found: 367.0851

N-(4-chlorophenyl)-2-(2-oxo-3-(2-(phenylselanyl)phenyl)quinoxalin-1(2H)-yl)acetamide (Compound 7)



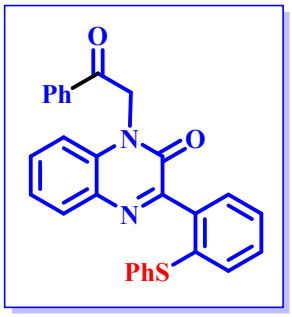
Colour and physical state: White solid

Yield: 52% (36 mg)

Melting point: 205-207 ^{0}C

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.50 – 7.43 (m, 4H), 7.39 (t, *J* = 8.2 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.22 – 7.18 (m, 2H), 5.07 (s, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 164.88, 155.47, 155.40, 137.31, 135.98, 134.60, 134.22, 133.89, 133.02, 132.64, 132.18, 131.67, 130.68, 130.56, 130.36, 129.80, 129.49, 129.10, 127.98, 127.03, 125.20, 121.39, 114.82, 49.22.
HRMS (ESI+) m/z: calculated for $C_{28}H_{20}ClN_3O_2Se$ $[M+H]^+$: 546.0482; found: 546.0490.

1-(2-oxo-2-phenylethyl)-3-(2-(phenylthio)phenyl)quinoxalin-2(1H)-one (Compound 10)



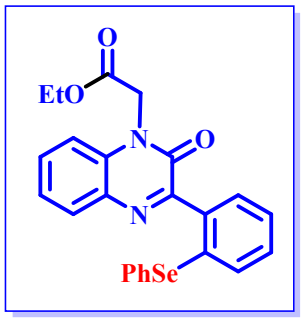
Colour and physical state: White solid

Yield: 58% (38 mg)

Melting point: 183-185 ^{0}C

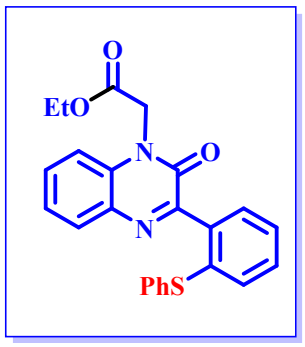
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.58 – 7.52 (m, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.31 (m, 6H), 7.25 – 7.15 (m, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.77 (s, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.54, 156.51, 154.47, 138.04, 136.81, 136.71, 134.78, 134.42, 133.30, 133.04, 132.76, 131.85, 130.88, 130.27, 130.24, 129.19, 129.13, 128.39, 127.22, 127.19, 124.05, 113.79, 48.93. **HRMS** (ESI+) m/z: calculated for $C_{28}H_{20}N_2O_2S$ $[M+H]^+$: 449.1318; found: 449.1314.

ethyl 2-(2-oxo-3-(2-(phenylselanyl)phenyl)quinoxalin-1(2H)-yl)acetate (Compound 11)



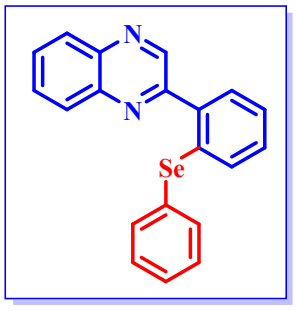
Colour and physical state: White solid
Yield: 91% (68 mg)
Melting point: 175-177 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 6.1 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.51 (m, 3H), 7.43 – 7.35 (m, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.18 (m, 4H), 7.13 (d, *J* = 7.3 Hz, 1H), 5.08 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.25, 154.97, 154.26, 136.54, 135.76, 135.15, 132.87, 132.79, 132.42, 132.30, 130.95, 130.79, 130.58, 130.34, 129.40, 128.03, 126.11, 124.31, 113.32, 62.23, 44.07, 14.26. **HRMS** (ESI+) m/z: calculated for $C_{24}H_{20}N_2O_3Se$ $[M+H]^+$: 465.0712; found: 465.0715.

ethyl 2-(2-oxo-3-(2-(phenylthio)phenyl)quinoxalin-1(2H)-yl)acetate (Compound 12)



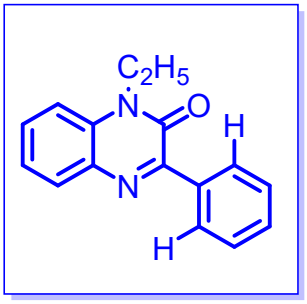
Colour and physical state: White solid
Yield: 88% (59 mg)
Melting point: 168-170 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.73 – 7.64 (m, 1H), 7.56 (t, *J* = 7.1 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.23 – 7.15 (m, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 5.06 (s, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.25 (t, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 167.23, 156.57, 154.28, 137.82, 136.85, 136.61, 132.97, 132.89, 132.73, 131.82, 130.95, 130.89, 130.26, 130.19, 129.11, 127.19, 127.16, 124.16, 113.29, 62.20, 43.99, 14.24. **HRMS** (ESI+) m/z: calculated for $C_{24}H_{20}N_2O_3S$ $[M+H]^+$: 417.1267; found: 417.1266.

2-(2-(phenylselanyl)phenyl)quinoxaline (Compound 14)



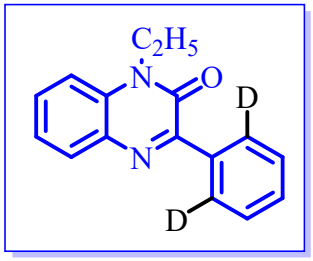
Colour and physical state: Pale yellow
Yield: 47% (41 mg)
Melting point: 174-176 ^{0}C
^{1}H NMR (400 MHz, Chloroform-d) δ 9.26 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.15 (d, J = 9.8 Hz, 1H), 7.84 (d, J = 9.1 Hz, 1H), 7.82 – 7.77 (m, 2H), 7.56 (dd, J = 7.6, 1.9 Hz, 2H), 7.42 – 7.36 (m, 1H), 7.36 – 7.33 (m, 1H), 7.31 (d, J = 1.9 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.27 – 7.24 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.23, 144.92, 141.20, 141.12, 137.20, 135.71, 135.61, 132.74, 131.37, 130.51, 130.13, 130.04, 129.82, 129.61, 129.37, 129.32, 128.40, 126.71. **HRMS** (ESI+) m/z: calculated for $C_{20}H_{14}N_2Se$ $[M+H]^+$: 363.0395; found: 363.0383.

1-ethyl-3-phenylquinoxalin-2(1*H*)-one (1a)



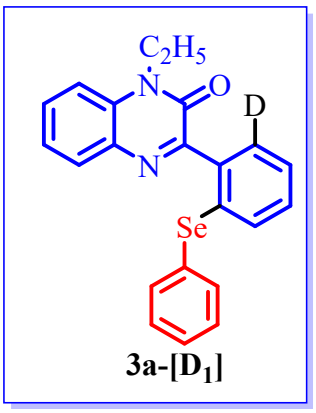
Colour and physical state: White solid
Yield: 86 %
Melting point: 180-182 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.96 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.56 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.36 (dd, *J* = 8.2, 5.8 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.33, 154.30, 136.19, 133.56, 132.44, 130.87, 130.41, 129.71, 128.19, 123.66, 113.54, 37.71, 12.53. **HRMS** (ESI+) m/z: calculated for $C_{16}H_{14}N_2O$ $[M+H]^+$: 251.1179; found: 251.1161.

1-ethyl-3-(phenyl-2,6-*d*$_2$)quinoxalin-2(1H)-one (1a [D$_2$])



Colour and physical state: White solid
Yield: 86 % (43 mg)
Melting point: 95-97 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 8.3 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.49 (s, 3H), 7.44 – 7.33 (m, 2H), 4.40 (q, J = 7.2 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 154.32, 154.24, 135.99, 133.54, 132.42, 130.85, 130.42, 128.08, 123.66, 113.54, 37.71, 12.53. **HRMS** (ESI+) m/z: calculated for $C_{16}H_{12}D_2N_2O$ $[M+H]^+$: 253.1304; found: 253.1304.

1-ethyl-3-(2-(phenylselanyl)phenyl-6-d)quinoxalin-2(1H)-one (3a [D$_1$])



3a-[D$_1$]

Colour and physical state: White solid
Yield: 85% (69 mg)
Melting point: 130-132 ^{0}C
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.49 (s, 3H), 7.44 – 7.33 (m, 2H), 4.40 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **HRMS** (ESI+) m/z: calculated for $C_{22}H_{17}DN_2OSe$ $[M+H]^+$: 408.0720; found: 408.0737.

4. Copies of ^{1}H, ^{13}C NMR and ^{19}F NMR spectra

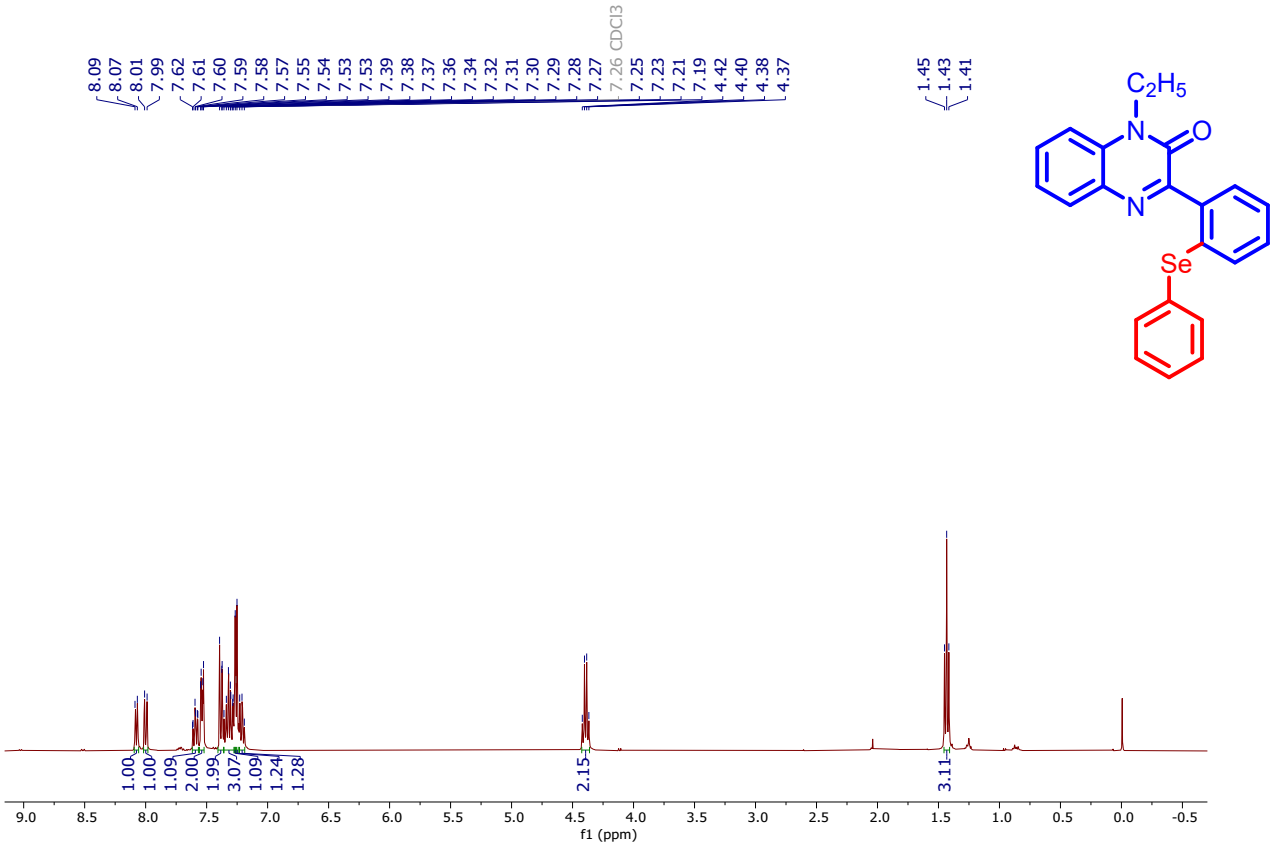


Figure 2: ^{1}H NMR spectrum of compound **3a** ($CDCl_3$, 400 MHz)

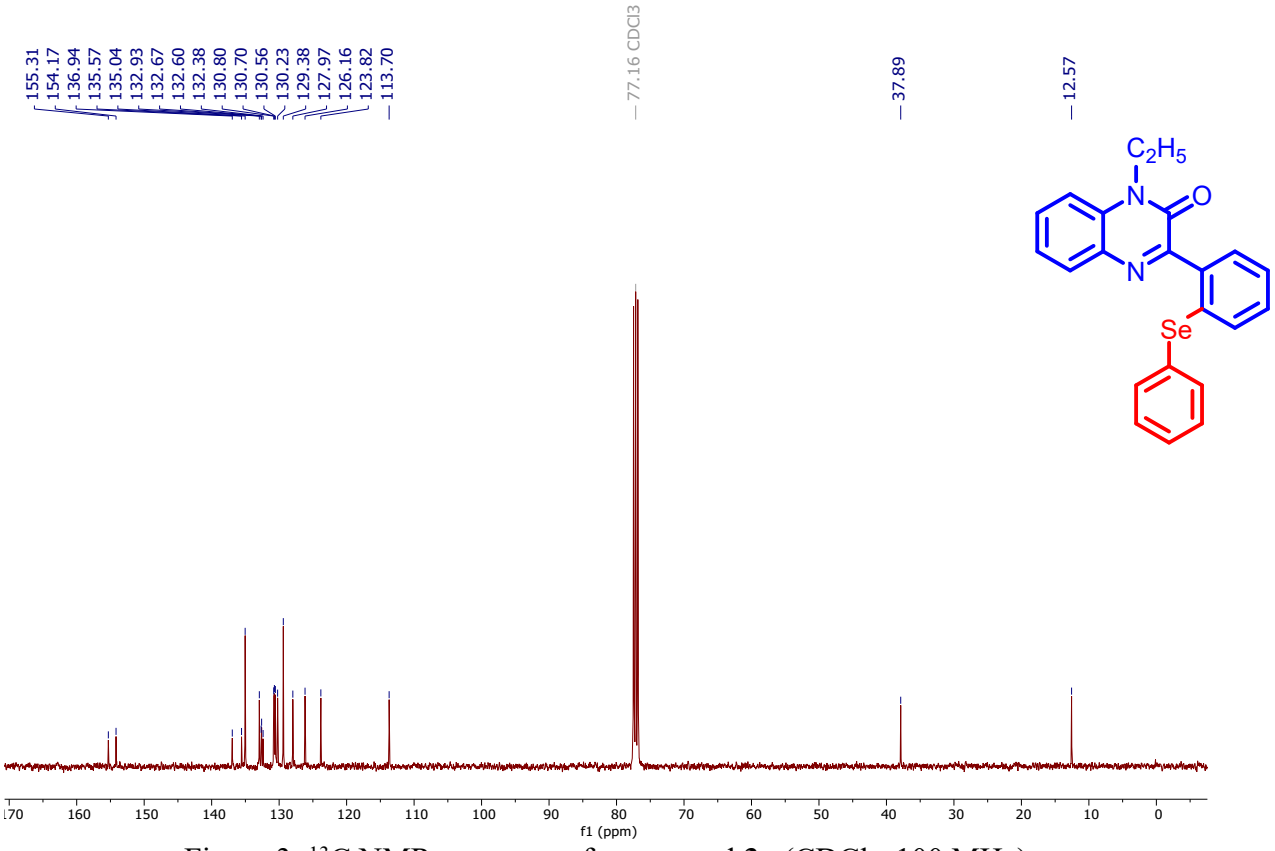


Figure 3: ^{13}C NMR spectrum of compound **3a** ($CDCl_3$, 100 MHz)

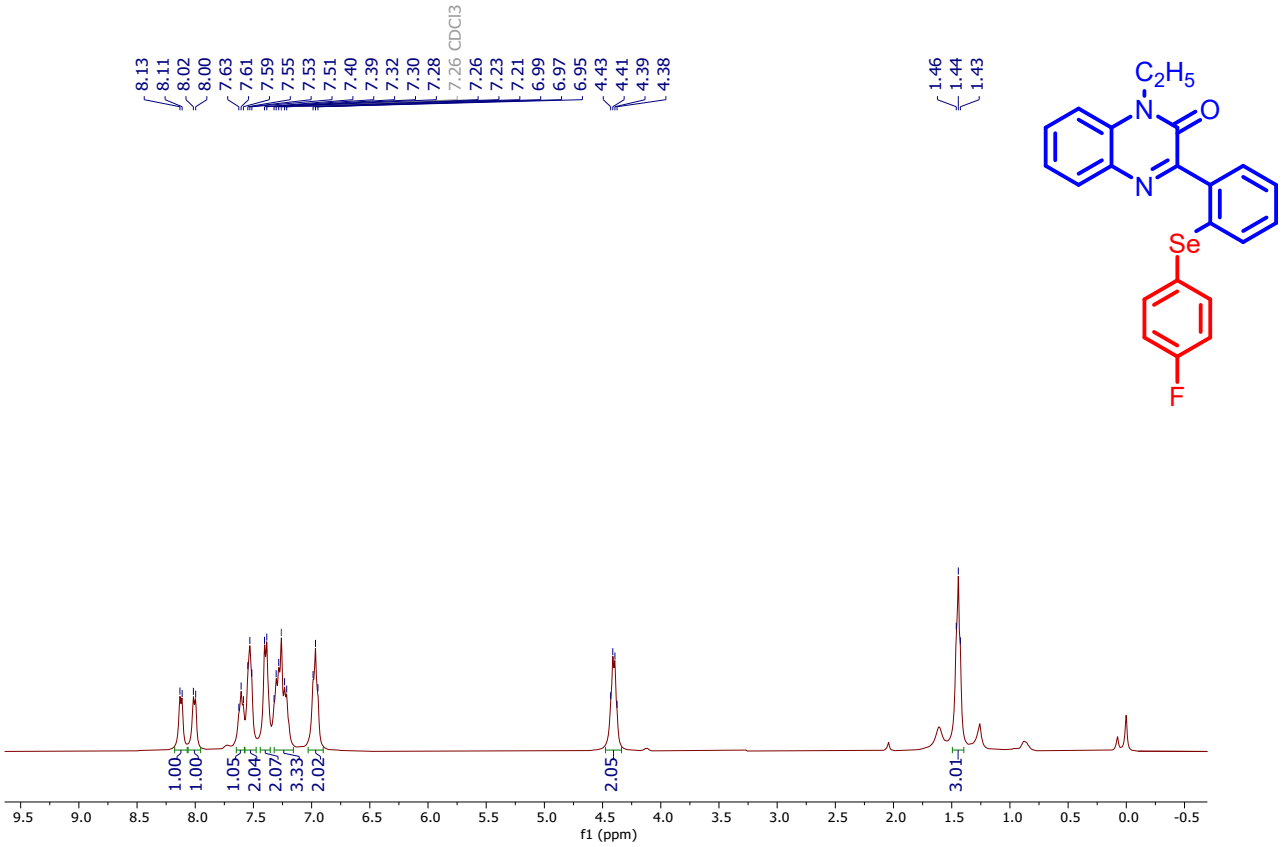


Figure 4: ^{1}H NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)

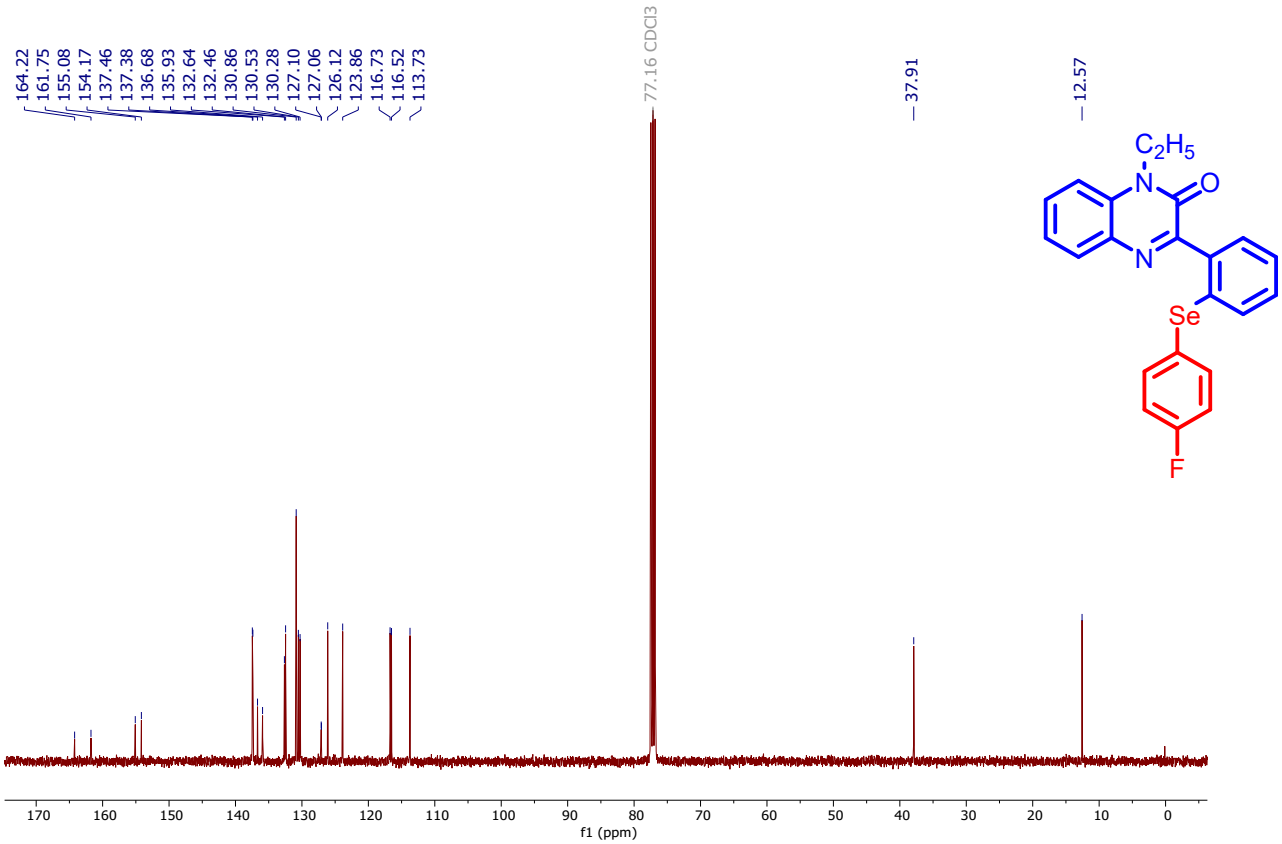


Figure 5: ^{13}C NMR spectrum of compound **3b** ($CDCl_3$, 100 MHz)

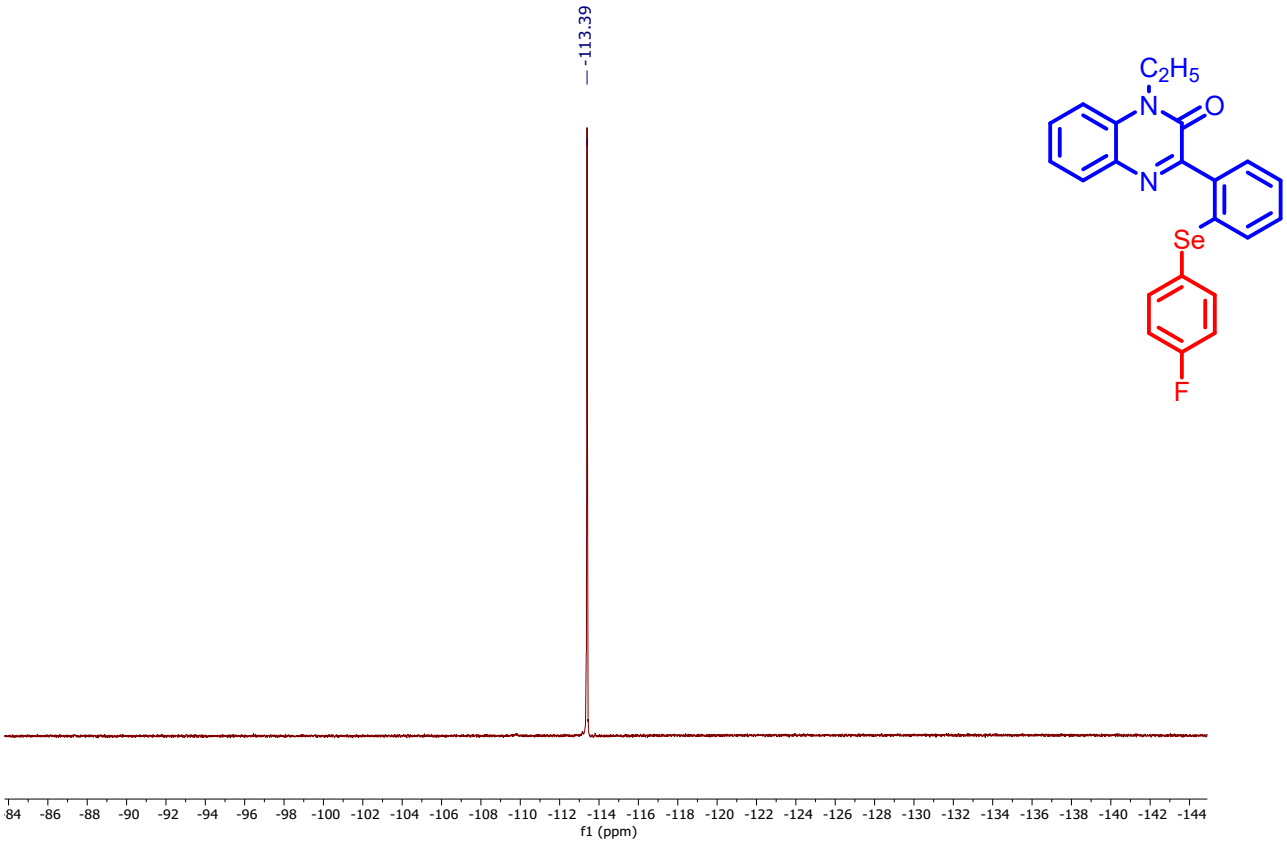


Figure 6: ^{19}F NMR spectrum of compound **3b** ($CDCl_3$, 400 MHz)

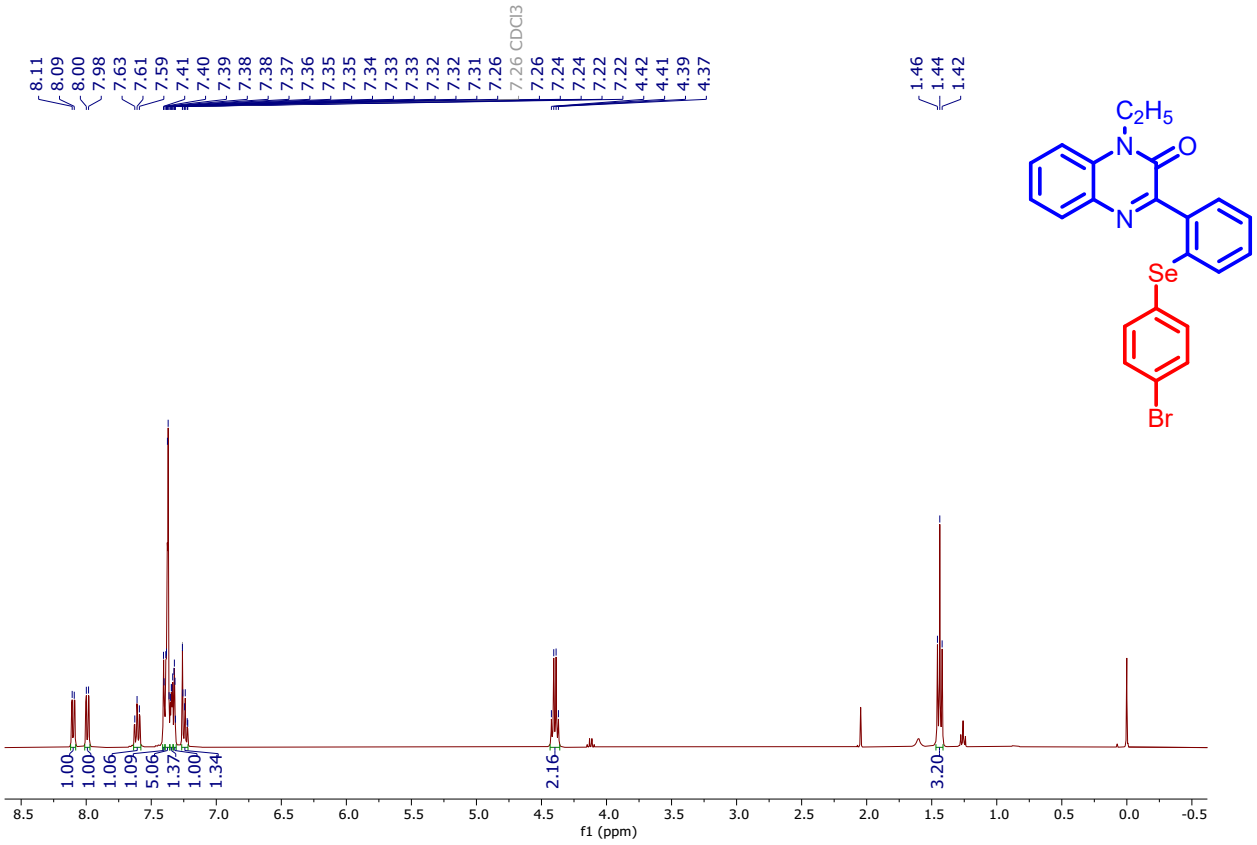


Figure 7: ^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 400 MHz)

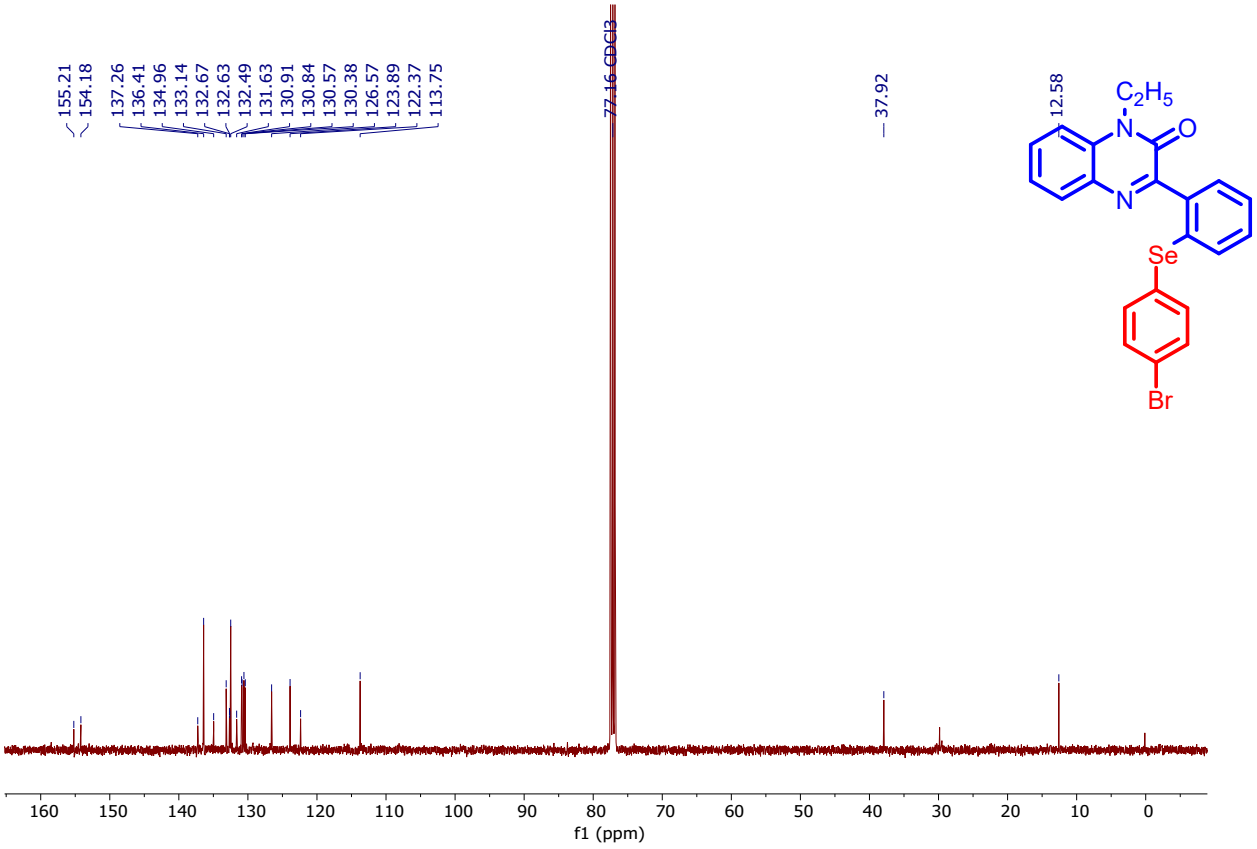


Figure 8: ^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 100 MHz)

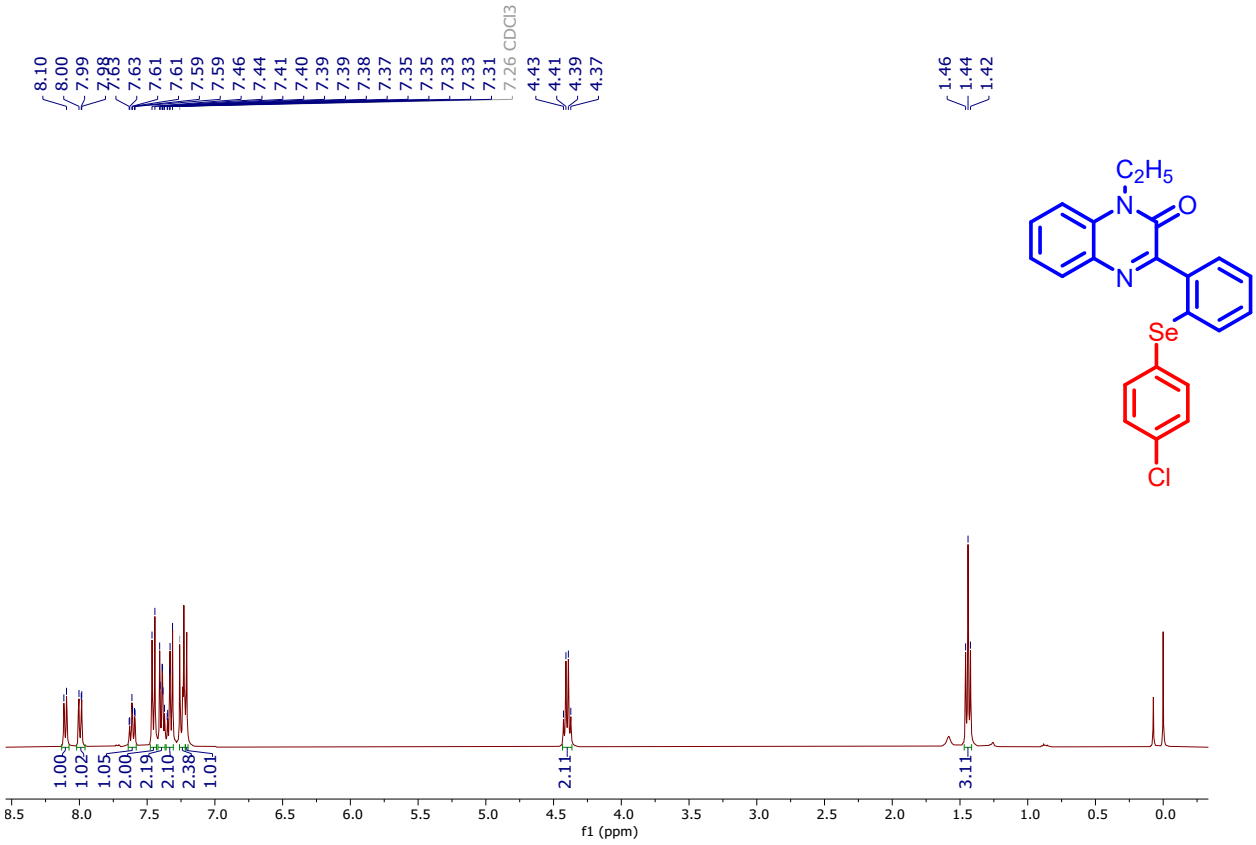


Figure 9: ^{1}H NMR spectrum of compound **3d** ($CDCl_3$, 400 MHz)

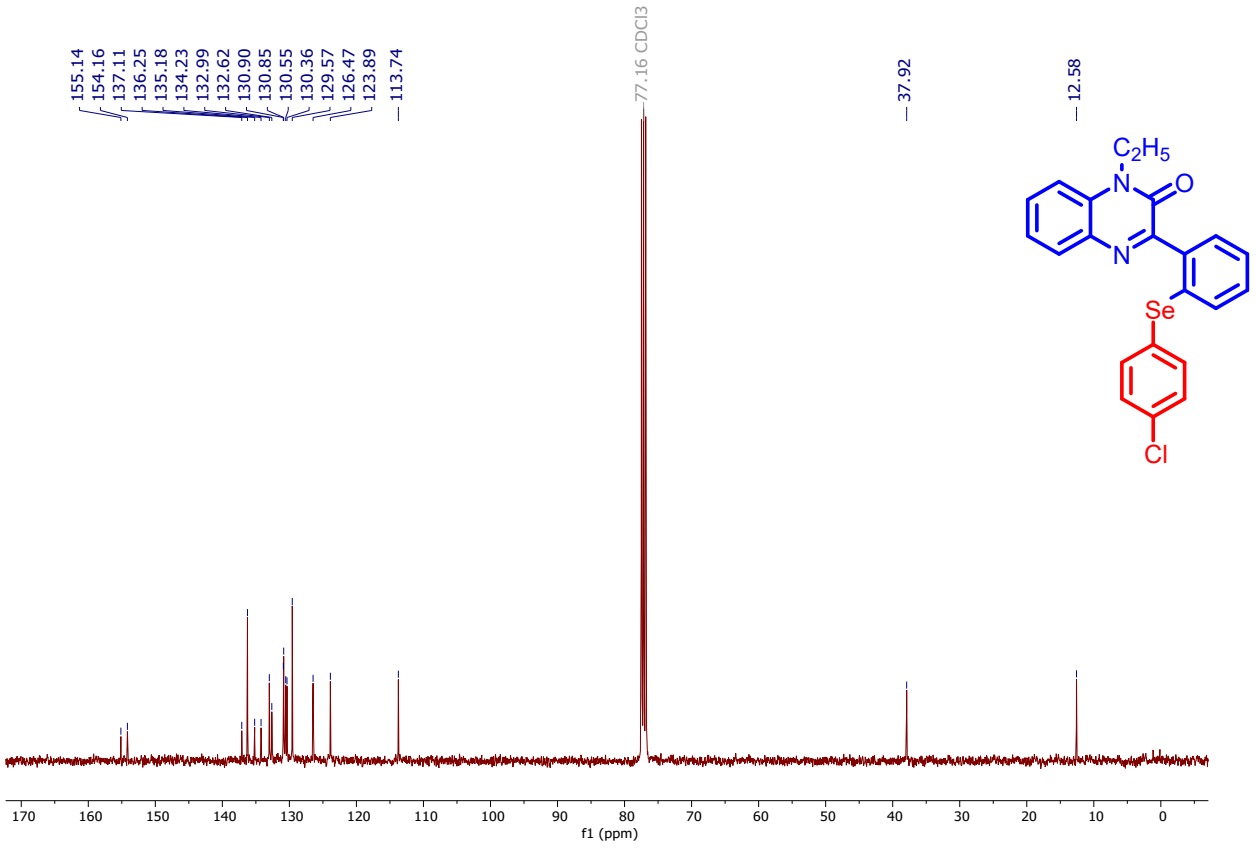


Figure 10: ^{13}C NMR spectrum of compound **3d** ($CDCl_3$, 100 MHz)

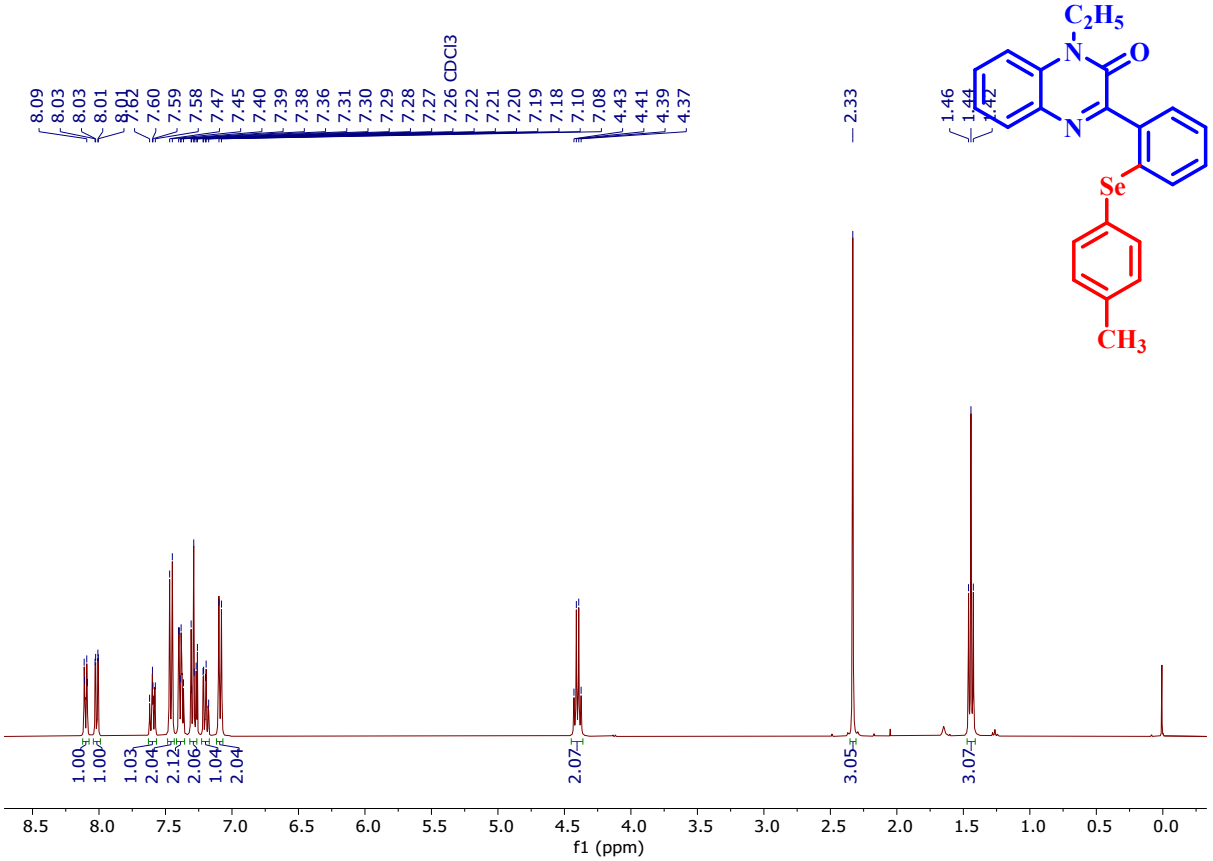


Figure 11: ^{1}H NMR spectrum of compound **3e** ($CDCl_3$, 400 MHz)

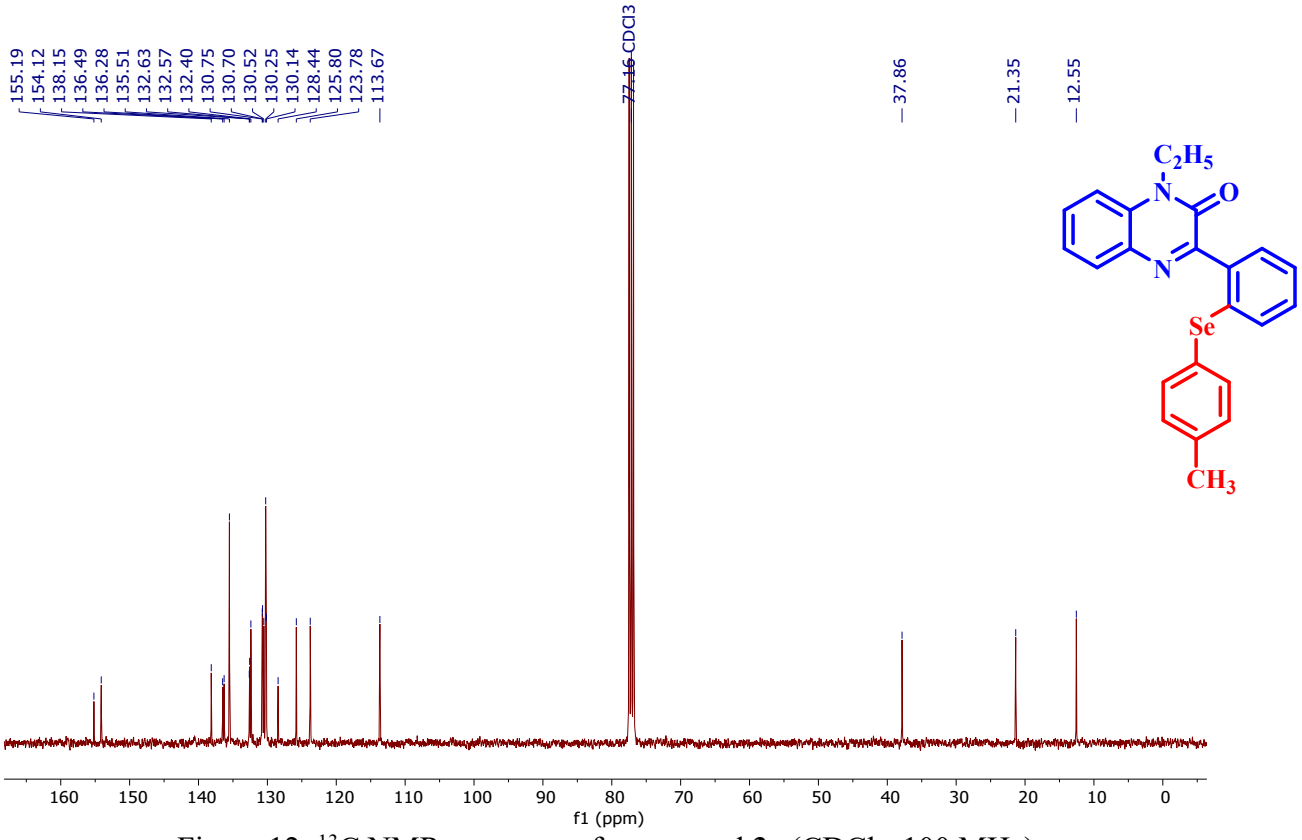


Figure 12: ^{13}C NMR spectrum of compound **3e** ($CDCl_3$, 100 MHz)

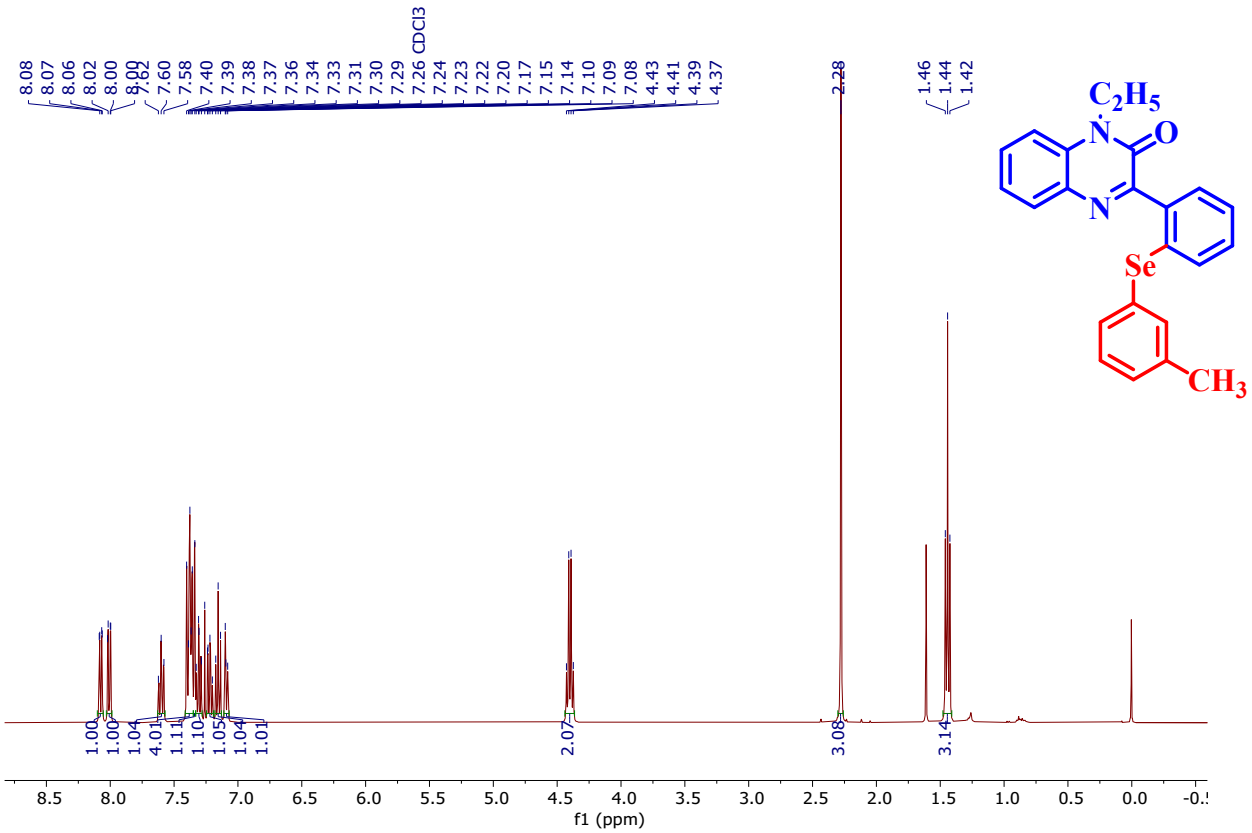


Figure 13: ^{1}H NMR spectrum of compound **3f** ($CDCl_3$, 400 MHz)

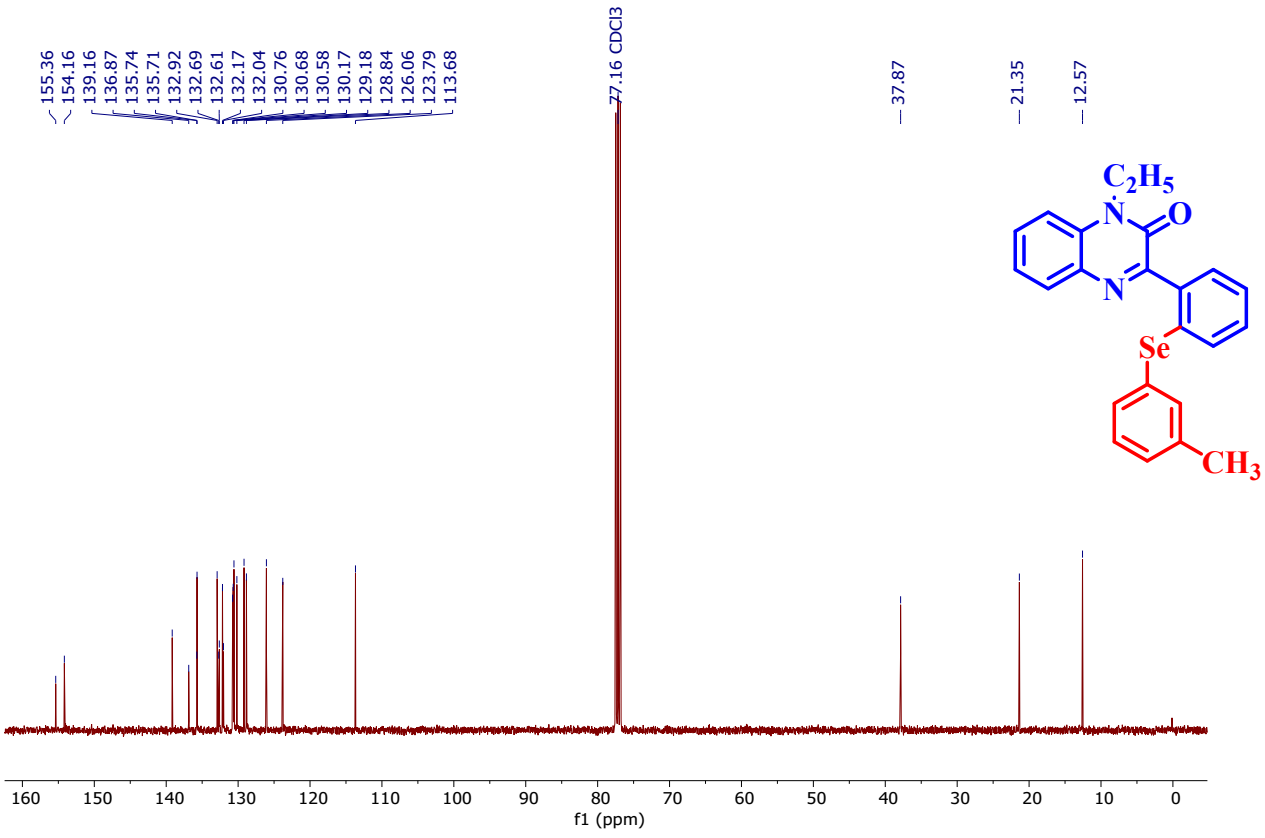


Figure 14: ^{13}C NMR spectrum of compound **3f** ($CDCl_3$, 100 MHz)

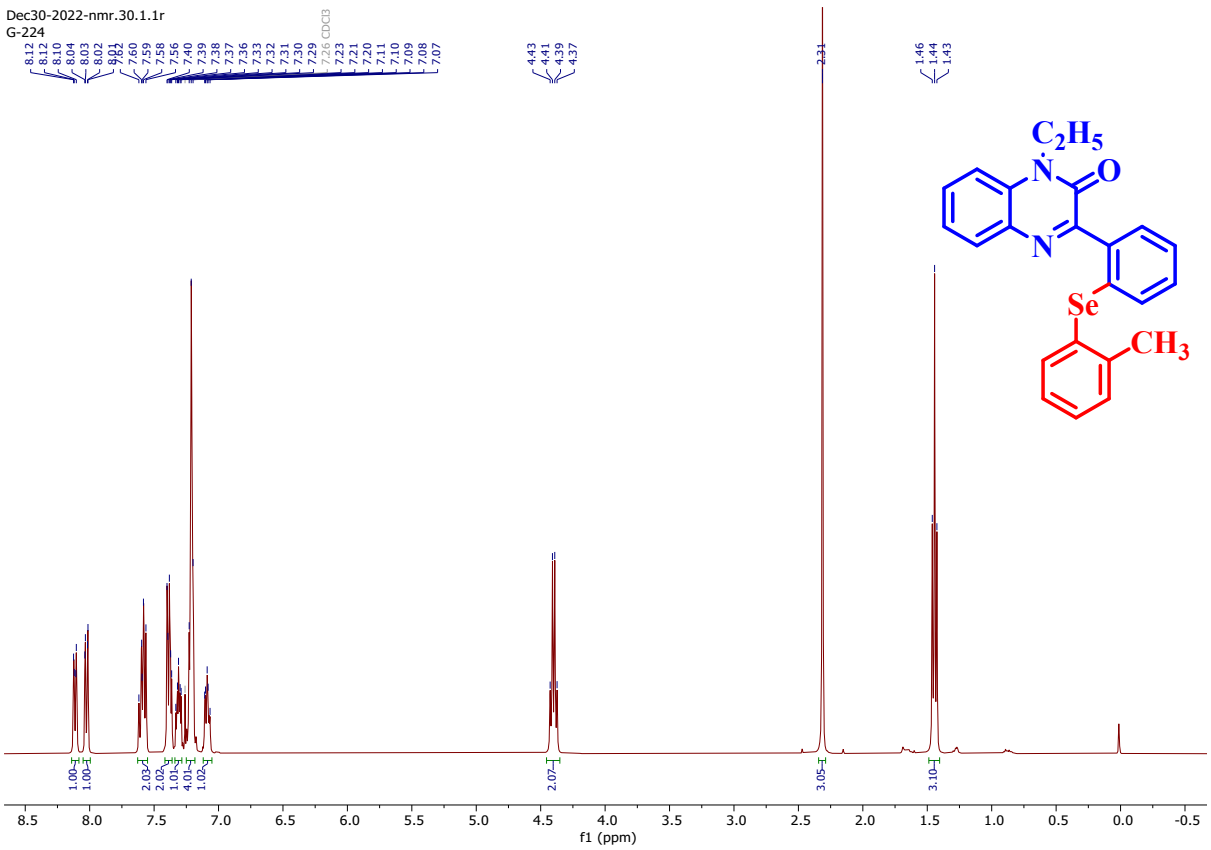


Figure 15: ^{1}H NMR spectrum of compound **3g** ($CDCl_3$, 400 MHz)

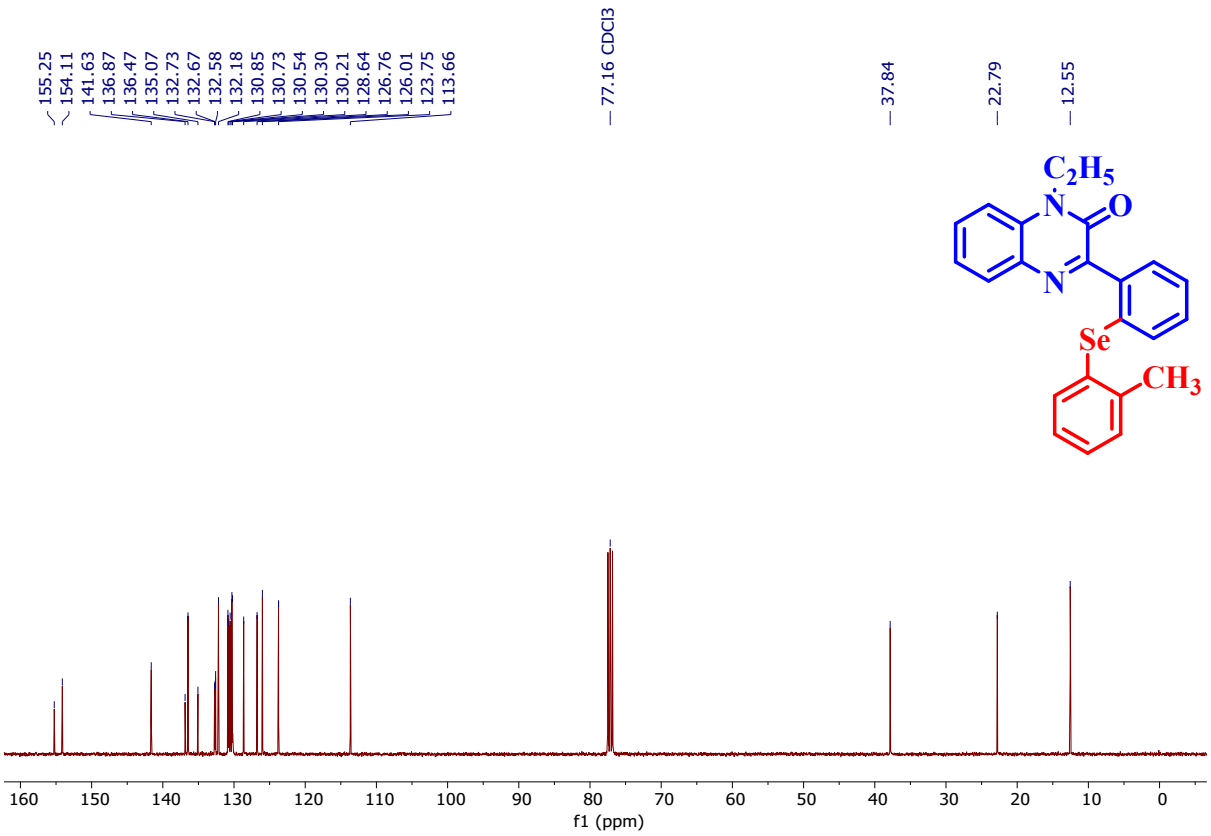


Figure 16: ^{13}C NMR spectrum of compound **3g** ($CDCl_3$, 100 MHz)

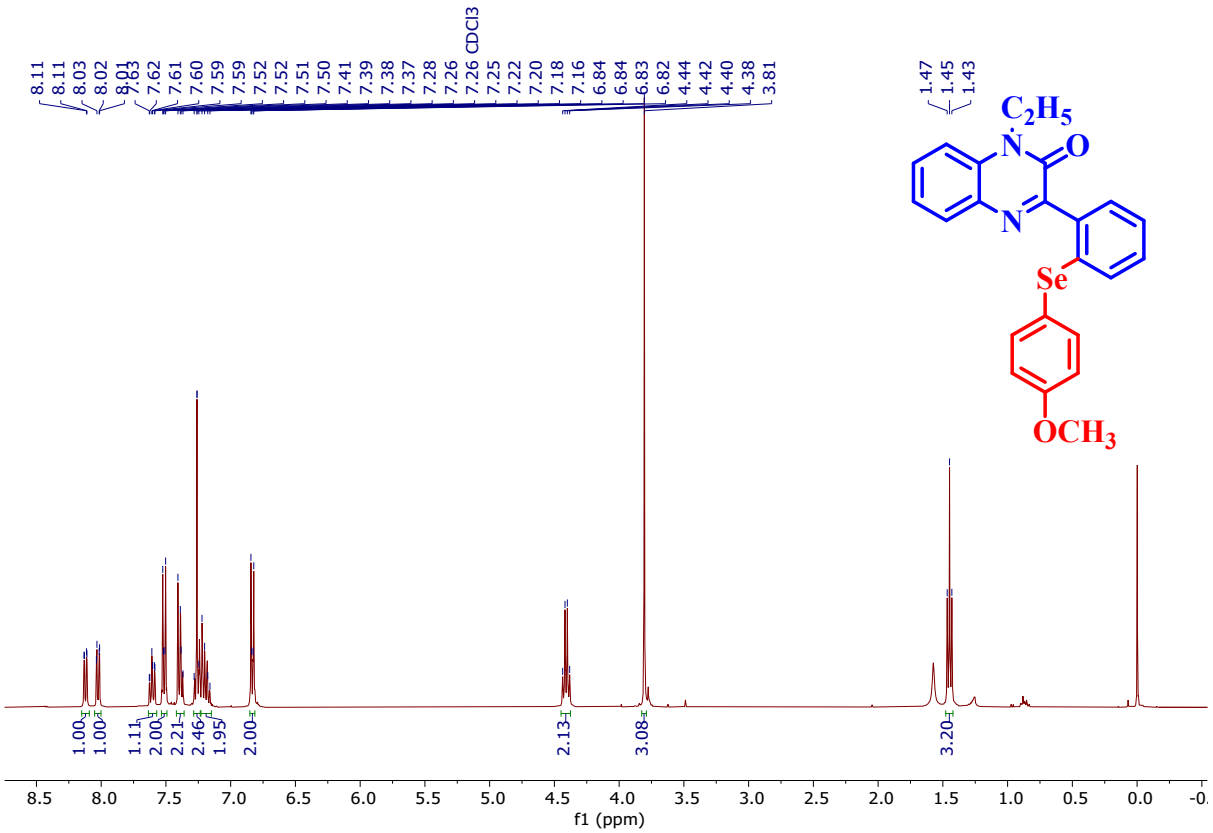


Figure 17: ^{1}H NMR spectrum of compound **3h** ($CDCl_3$, 400 MHz)

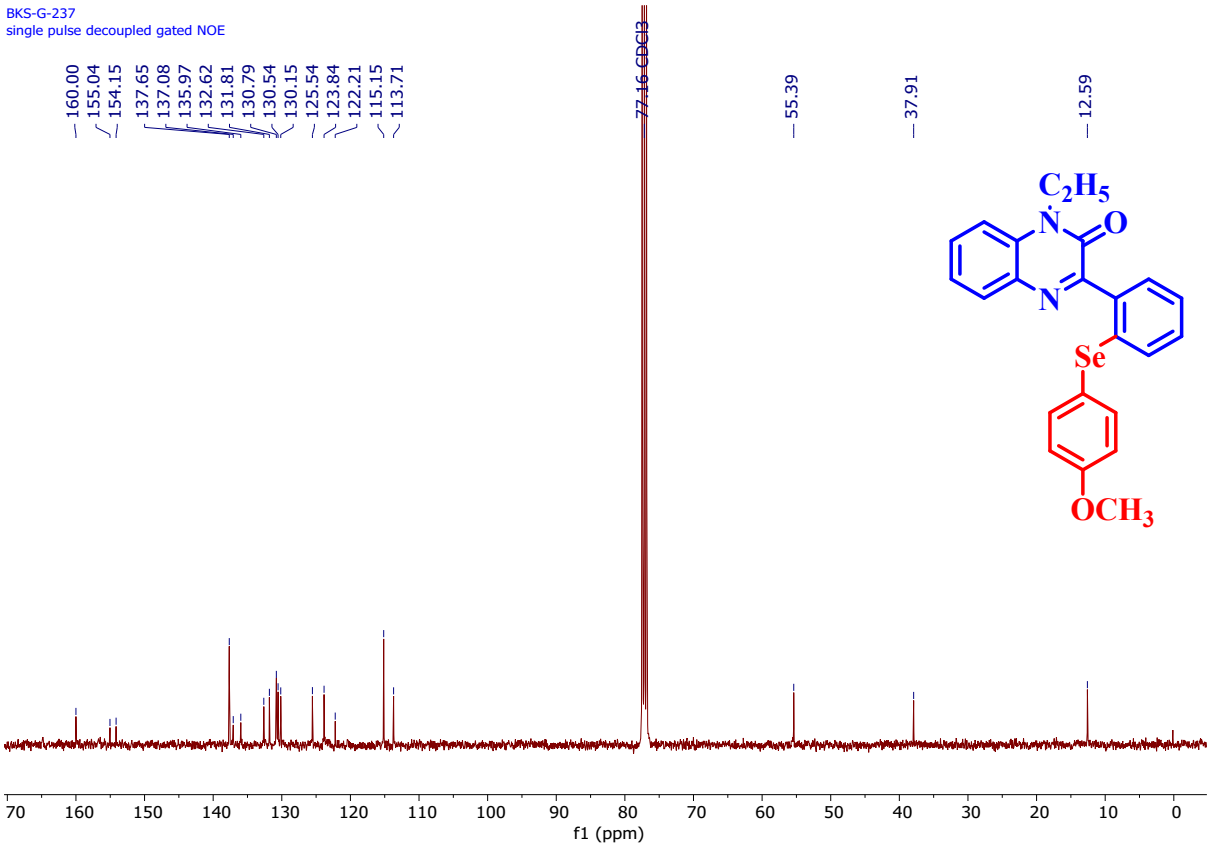


Figure 18: ^{13}C NMR spectrum of compound **3h** ($CDCl_3$, 100 MHz)

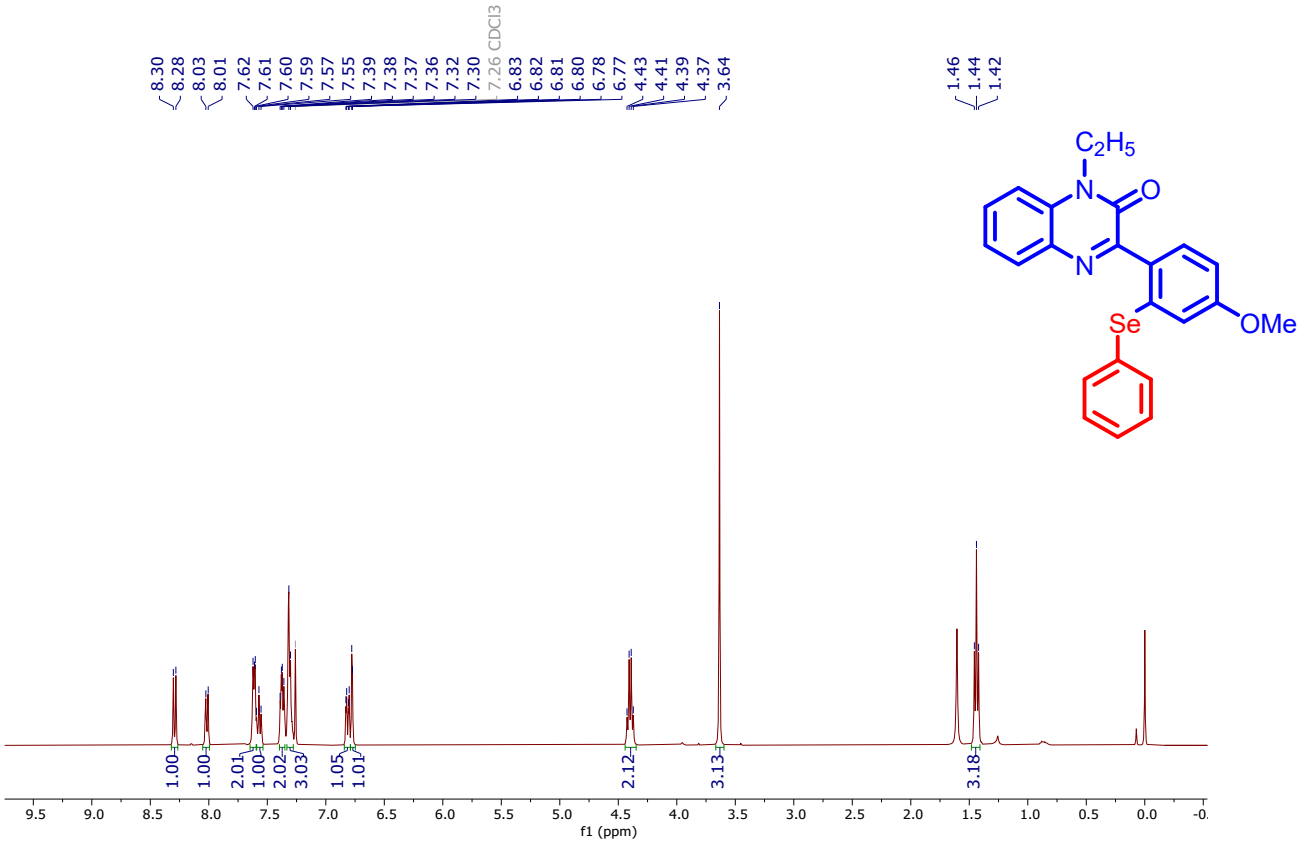


Figure 19: ^{1}H NMR spectrum of compound **3i** ($CDCl_3$, 400 MHz)

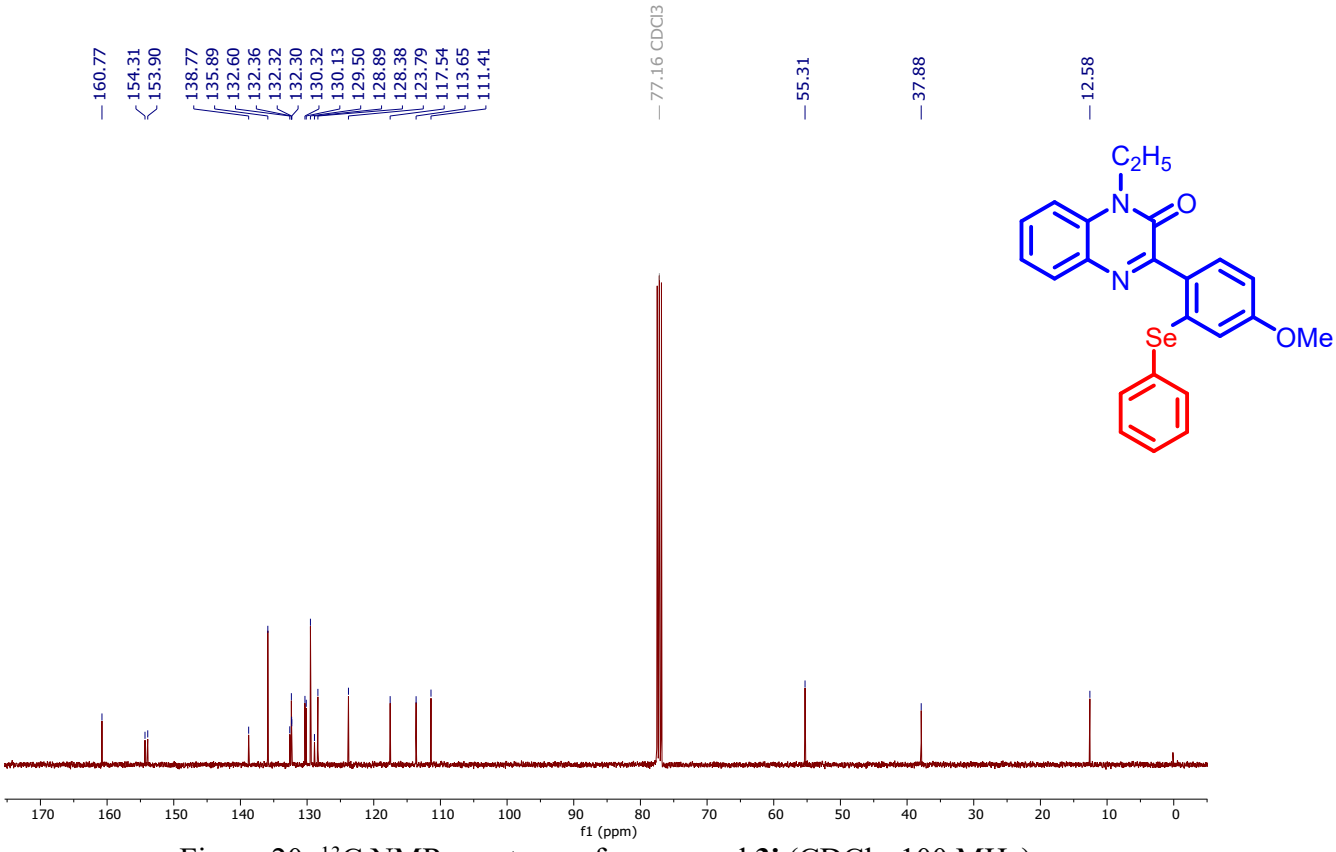


Figure 20: ^{13}C NMR spectrum of compound **3i** ($CDCl_3$, 100 MHz)

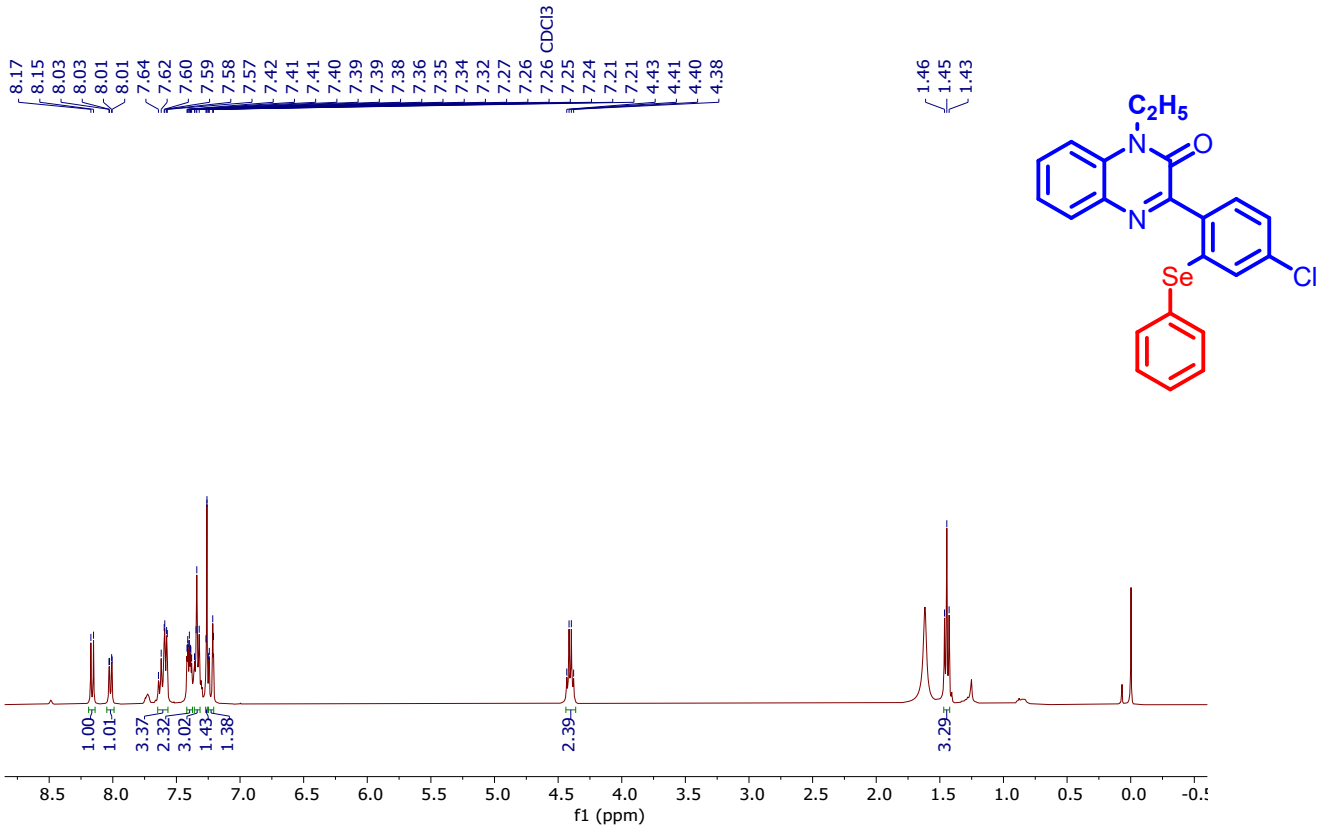


Figure 21: ^{1}H NMR spectrum of compound **3j** ($CDCl_3$, 400 MHz)

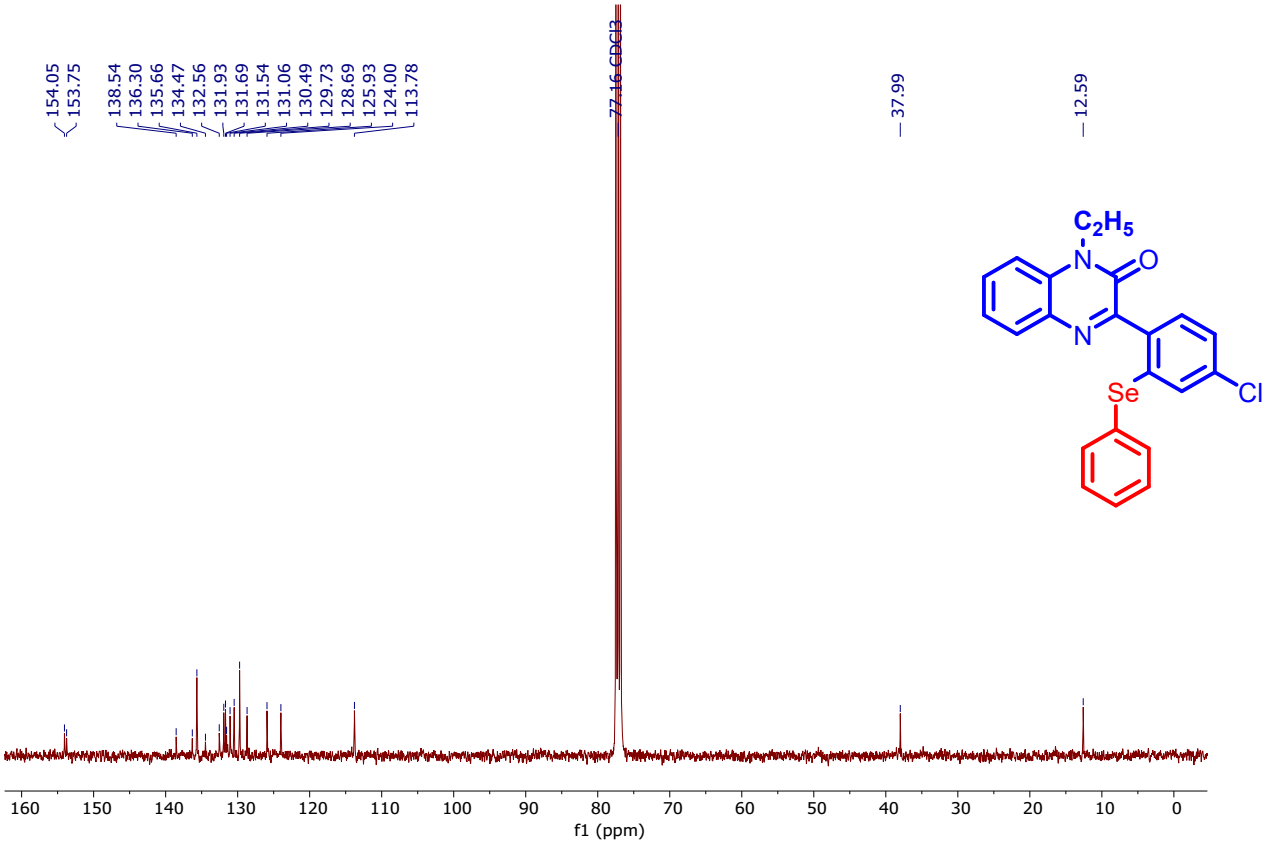


Figure 22: ^{13}C NMR spectrum of compound **3j** ($CDCl_3$, 100 MHz)

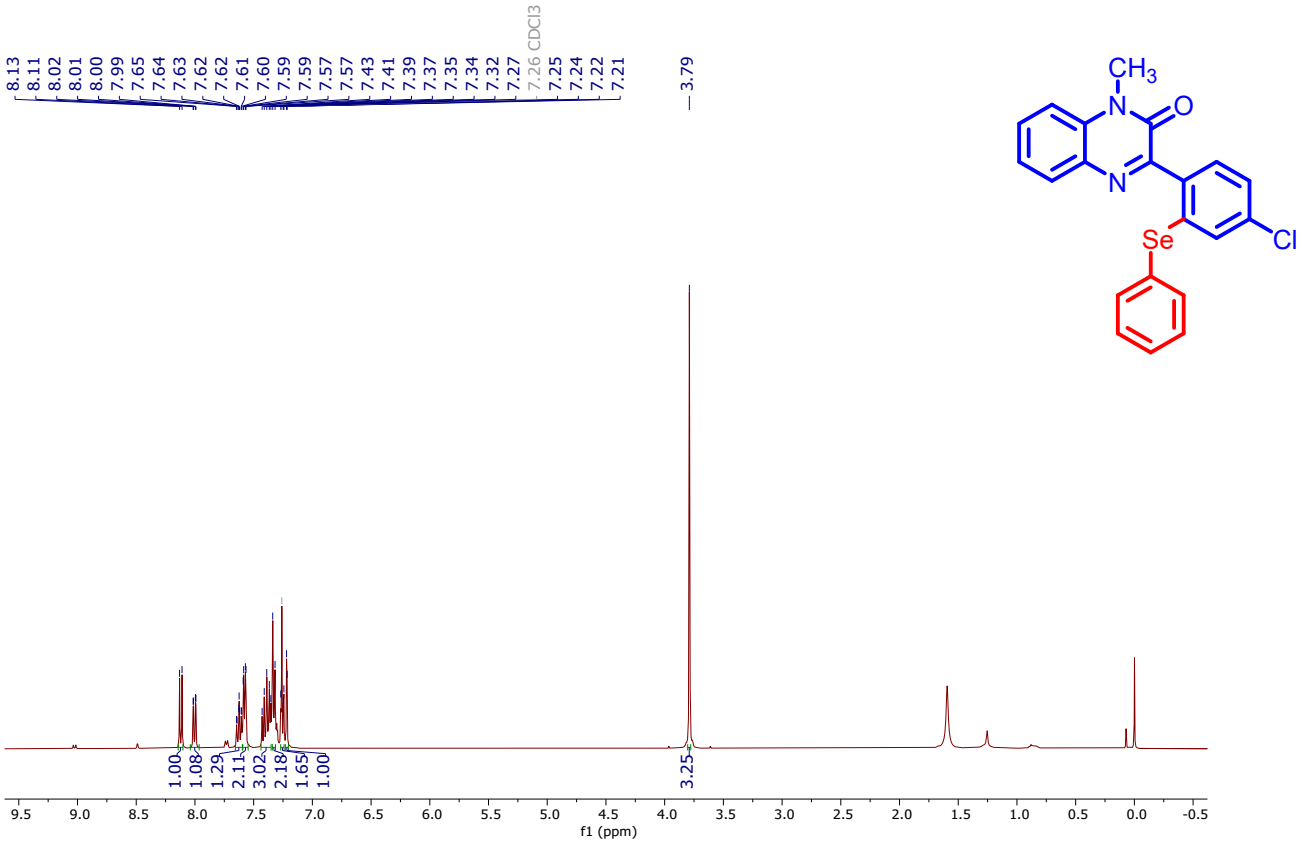


Figure 23: ^{1}H NMR spectrum of compound **3k** ($CDCl_3$, 400 MHz)

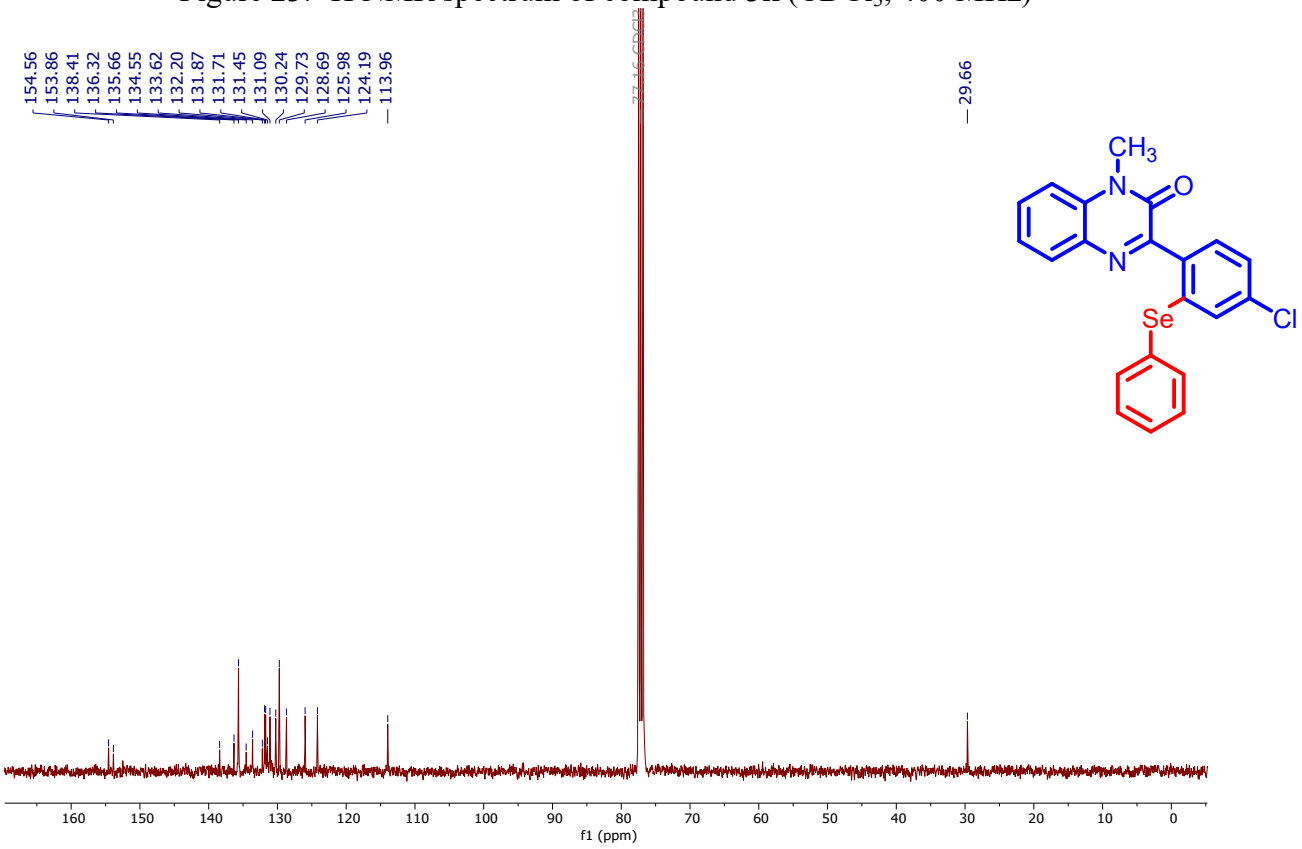


Figure 24: ^{13}C NMR spectrum of compound **3k** (CDCl3, 100 MHz)

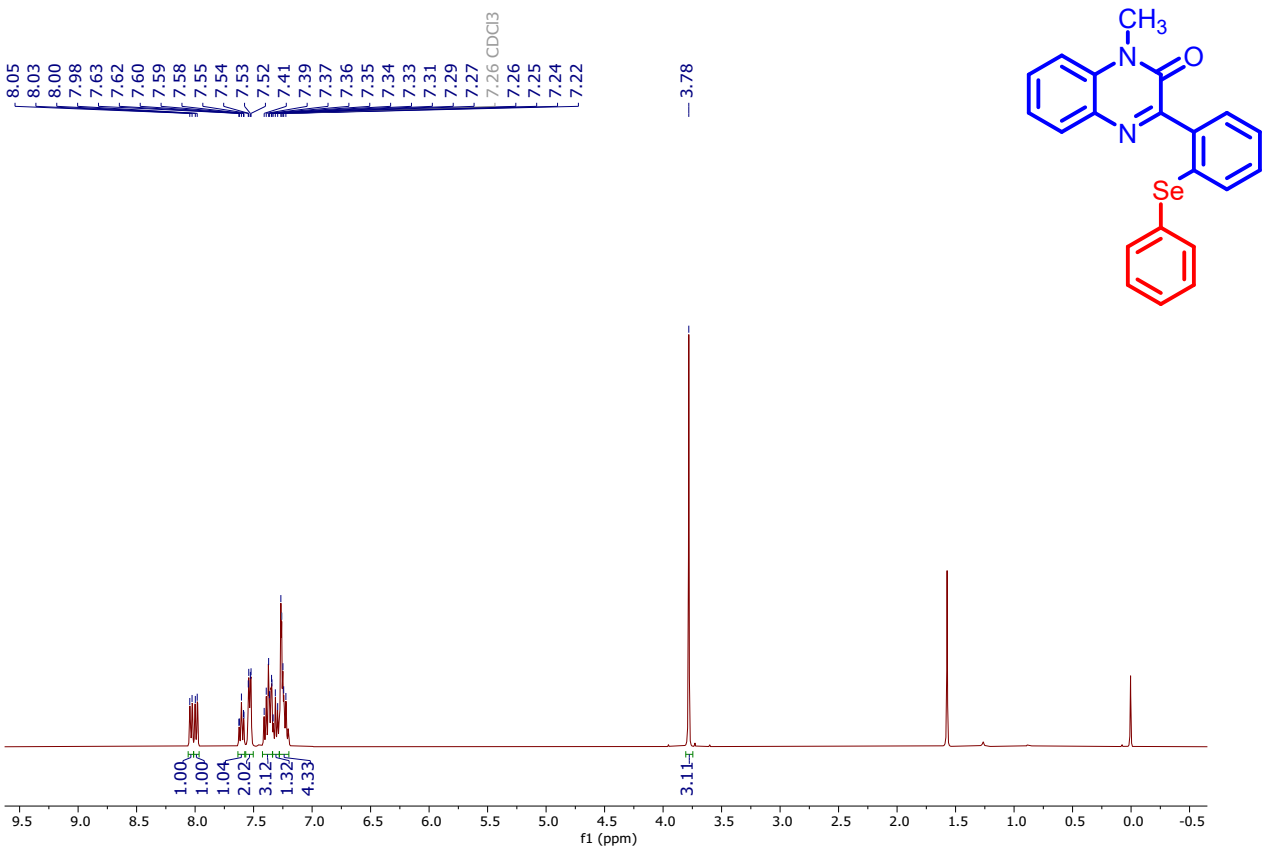


Figure 25: ^{1}H NMR spectrum of compound **3l** ($CDCl_3$, 400 MHz)

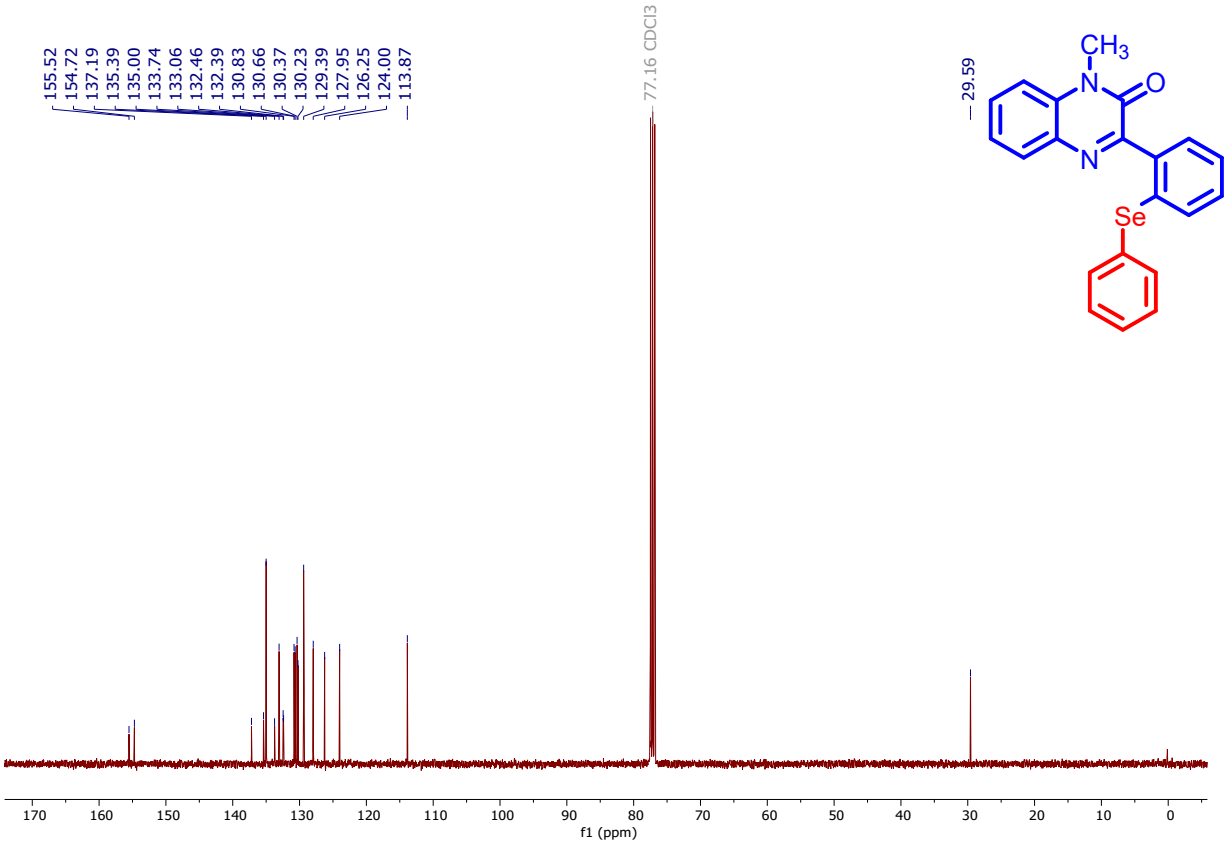


Figure 26: ^{13}C NMR spectrum of compound **3l** ($CDCl_3$, 100 MHz)

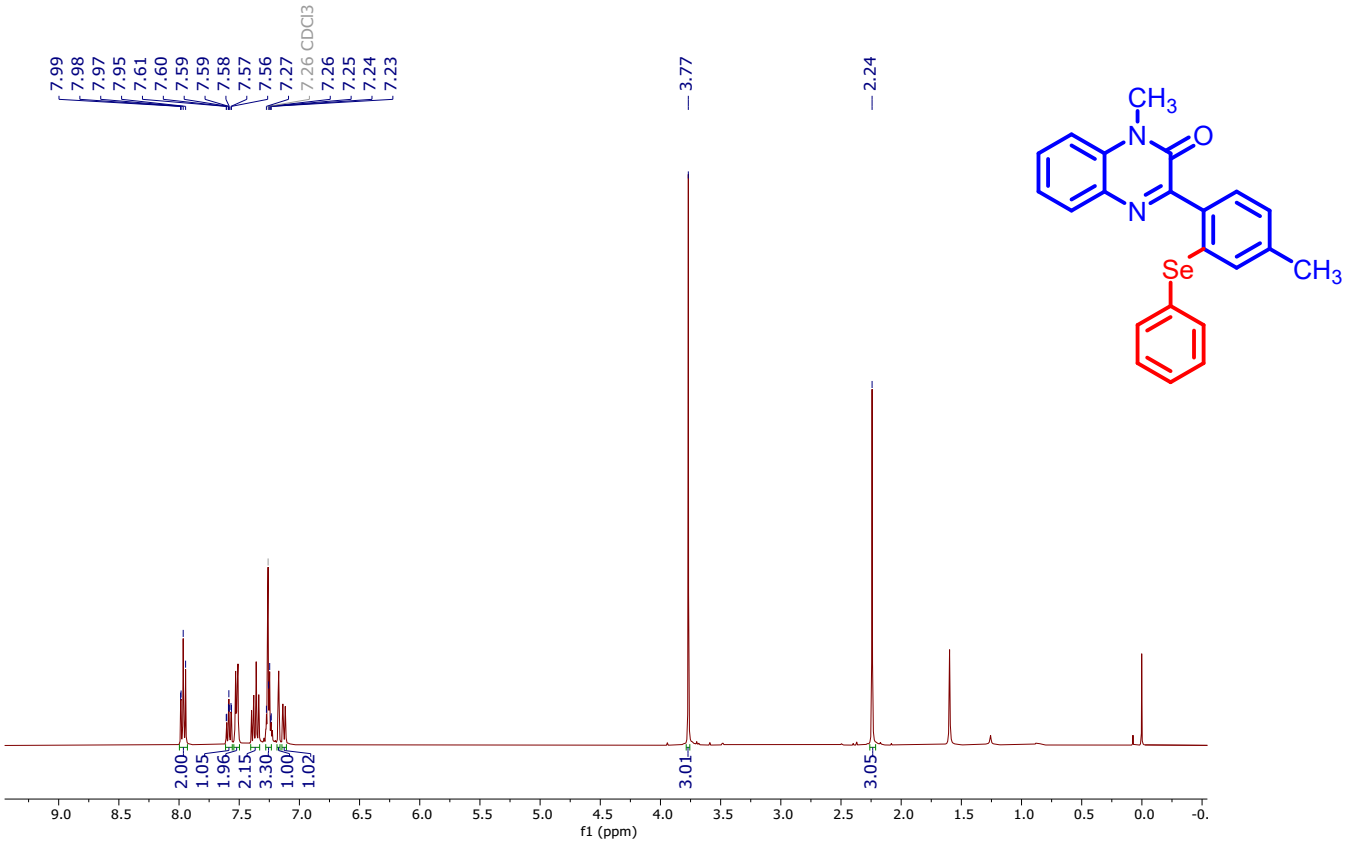


Figure 27: ^{1}H NMR spectrum of compound **3m** ($CDCl_3$, 400 MHz)

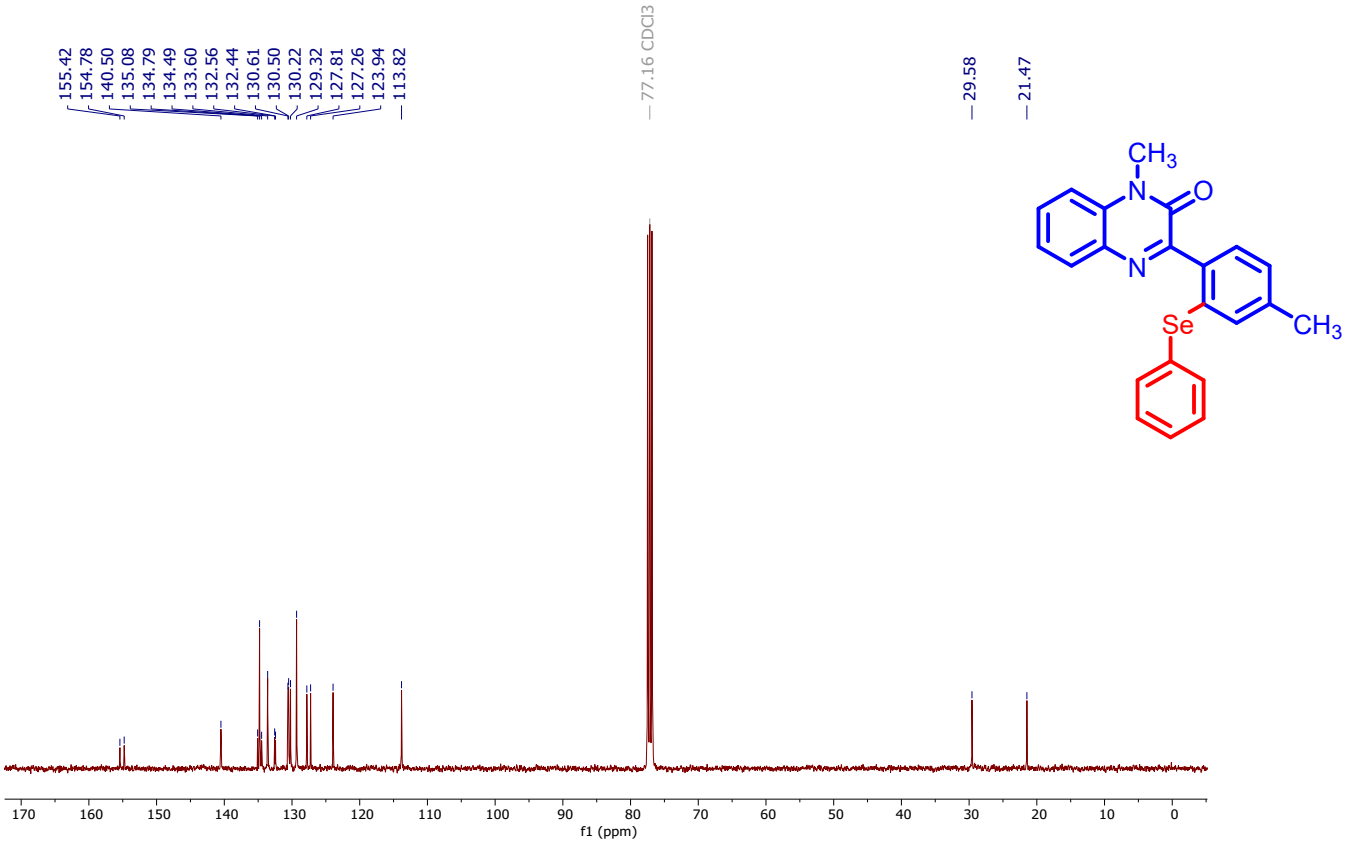


Figure 28: ^{13}C NMR spectrum of compound **3m** (CDCl3, 100 MHz)

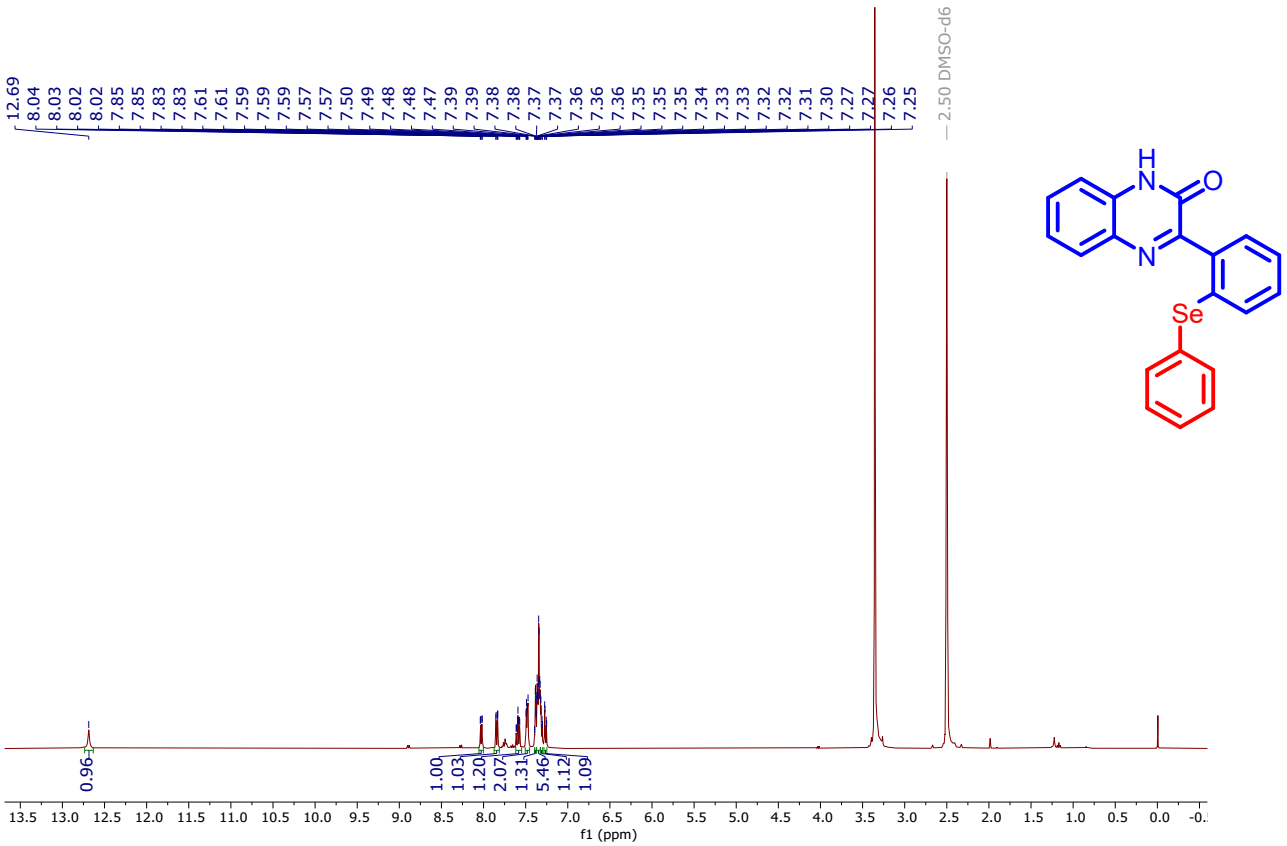


Figure 29: ^{1}H NMR spectrum of compound **3n** ($CDCl_3$, 400 MHz)

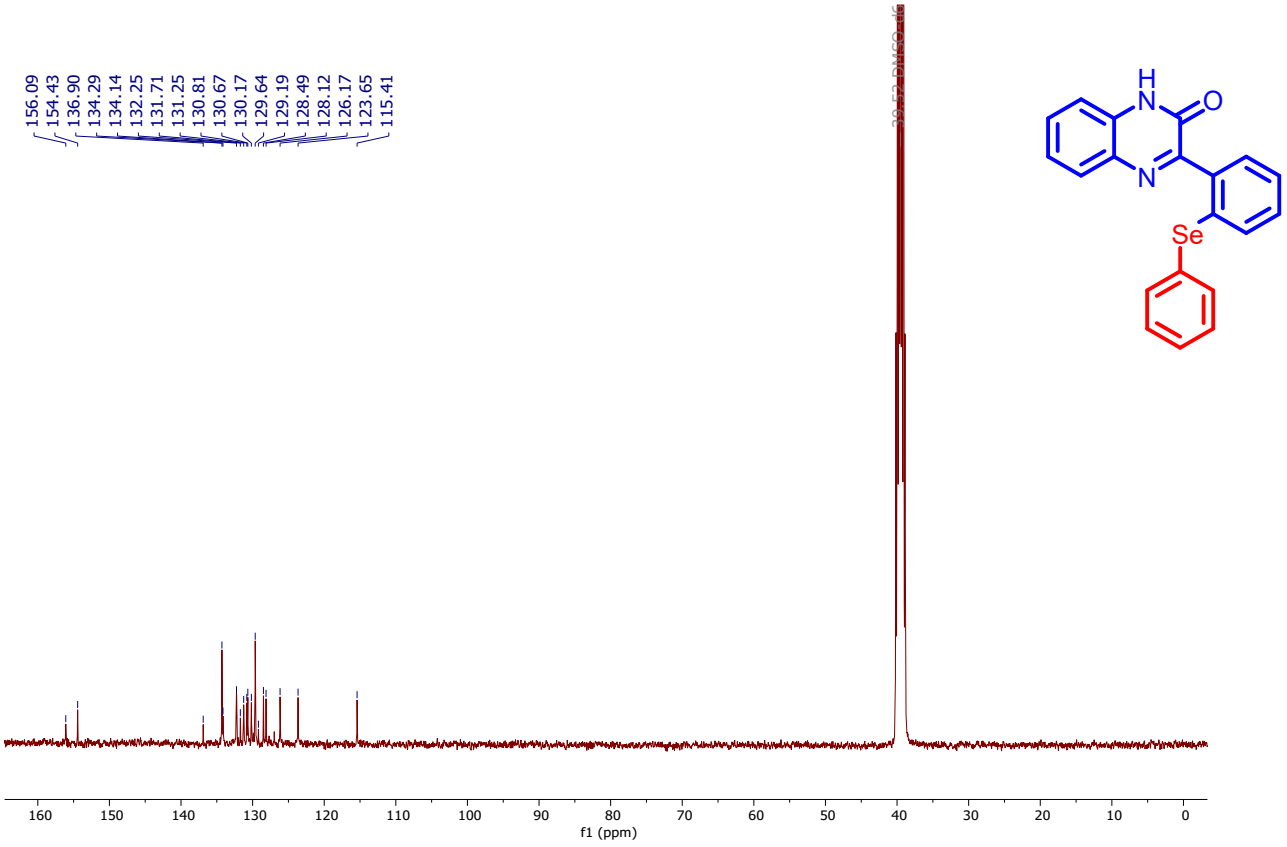


Figure 30: ^{13}C NMR spectrum of compound **3n** ($CDCl_3$, 100 MHz)

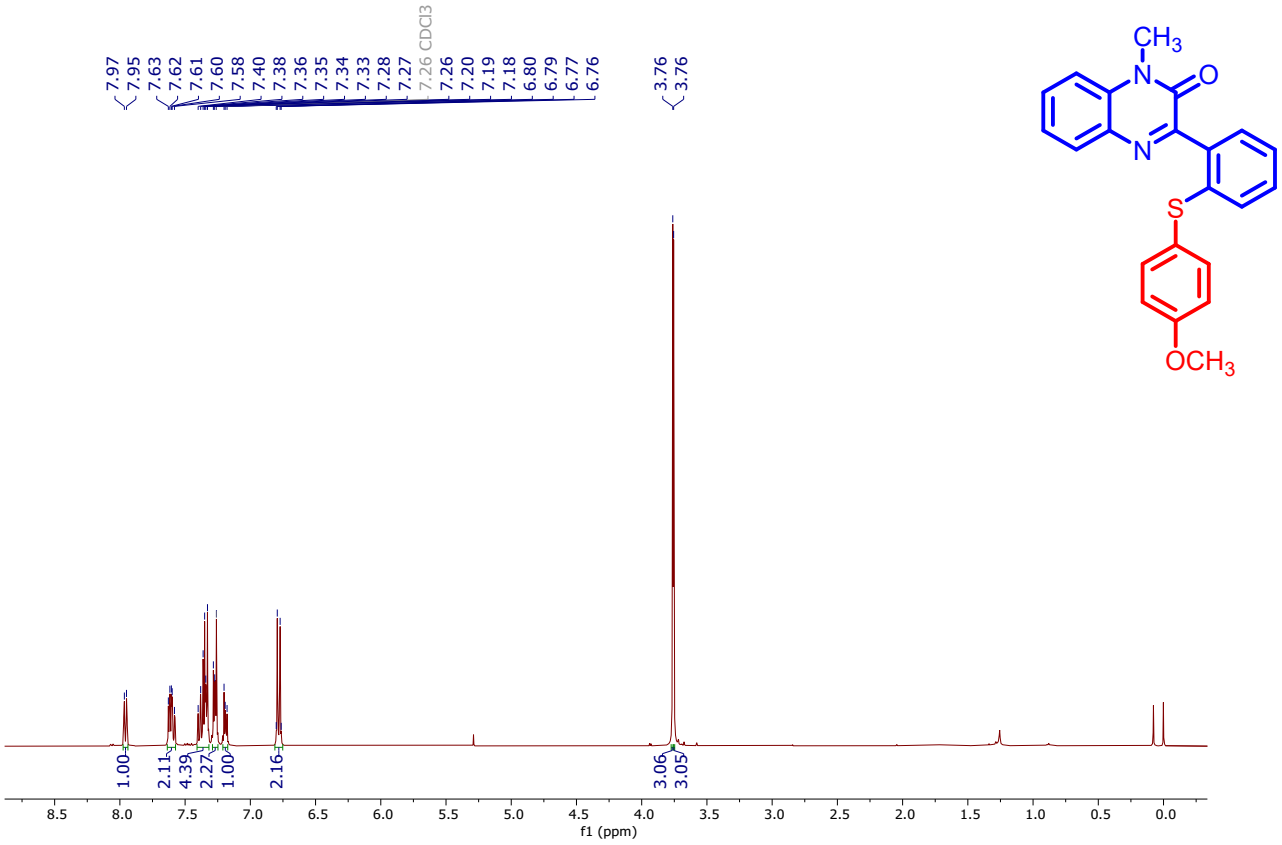


Figure 31: ^{1}H NMR spectrum of compound **5a** ($CDCl_3$, 400 MHz)

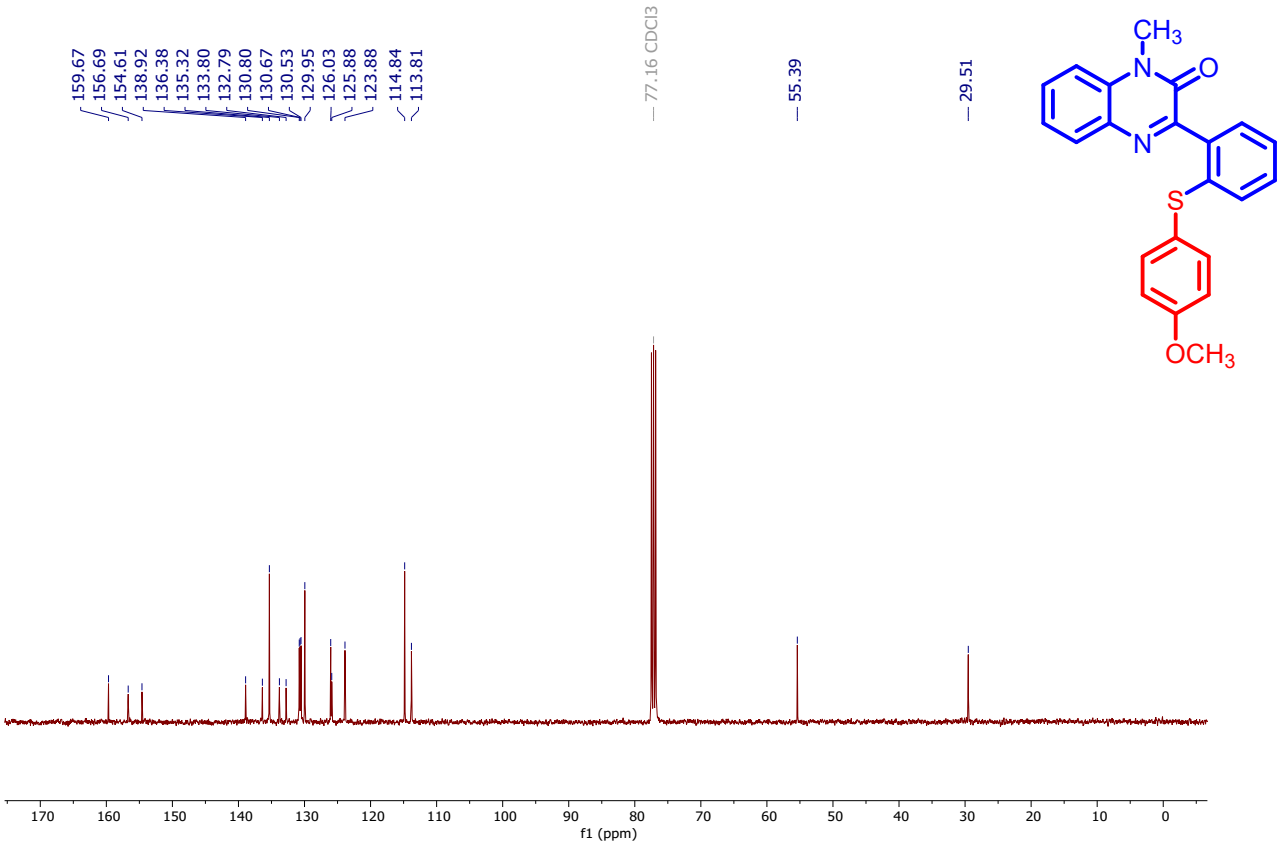


Figure 32: ^{13}C NMR spectrum of compound **5a** ($CDCl_3$, 100 MHz)

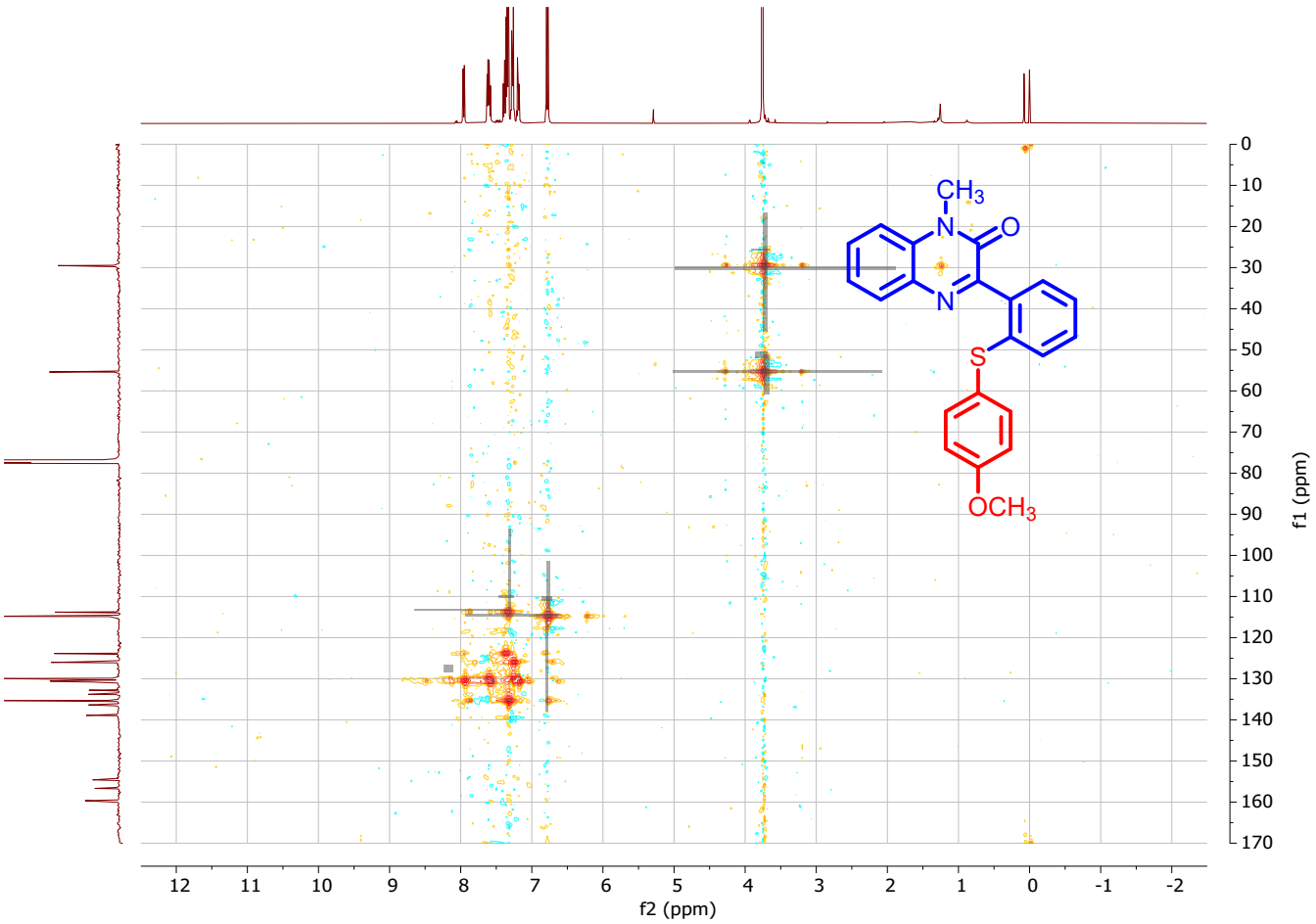


Figure 33: HSQC spectrum of compound **5a** ($CDCl_3$, 400 MHz)

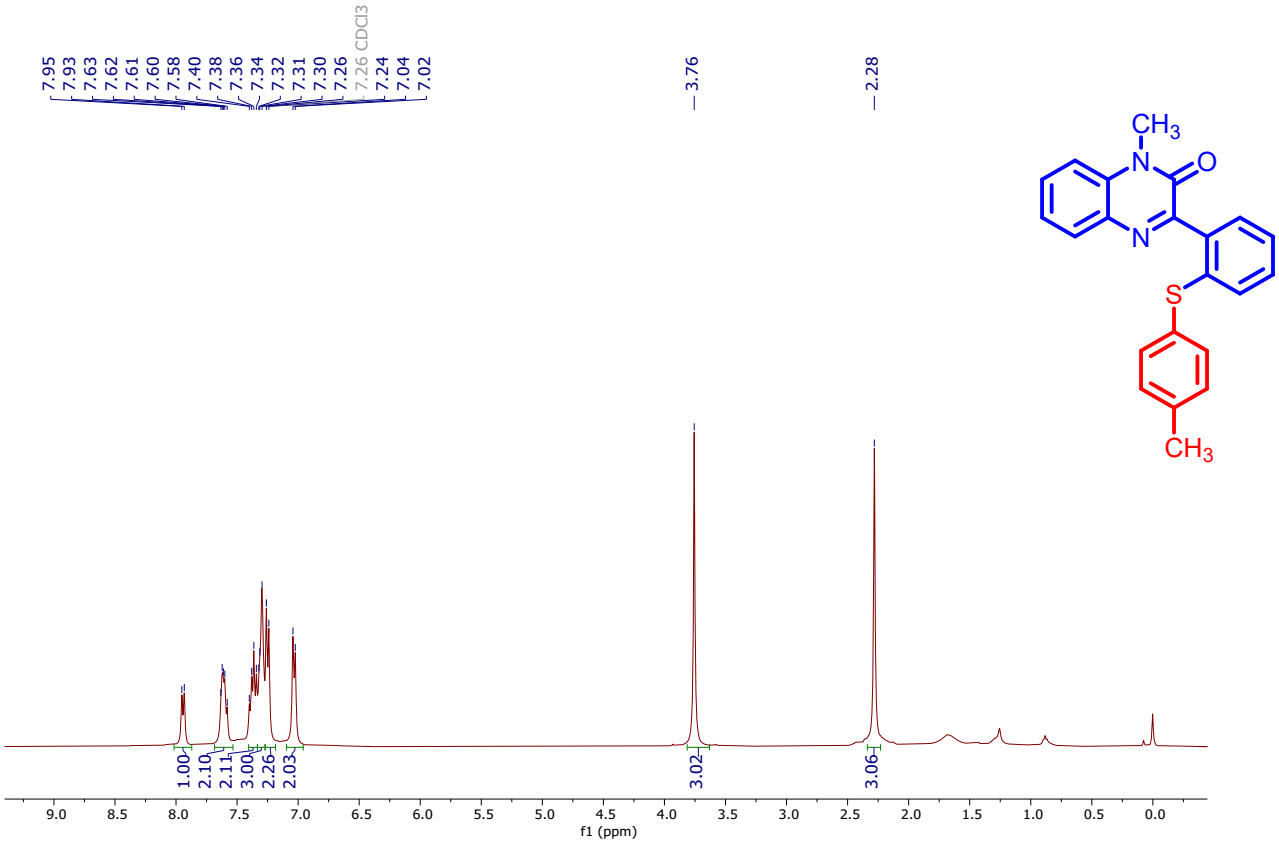


Figure 34: ^{1}H NMR spectrum of compound **5b** ($CDCl_3$, 400 MHz)

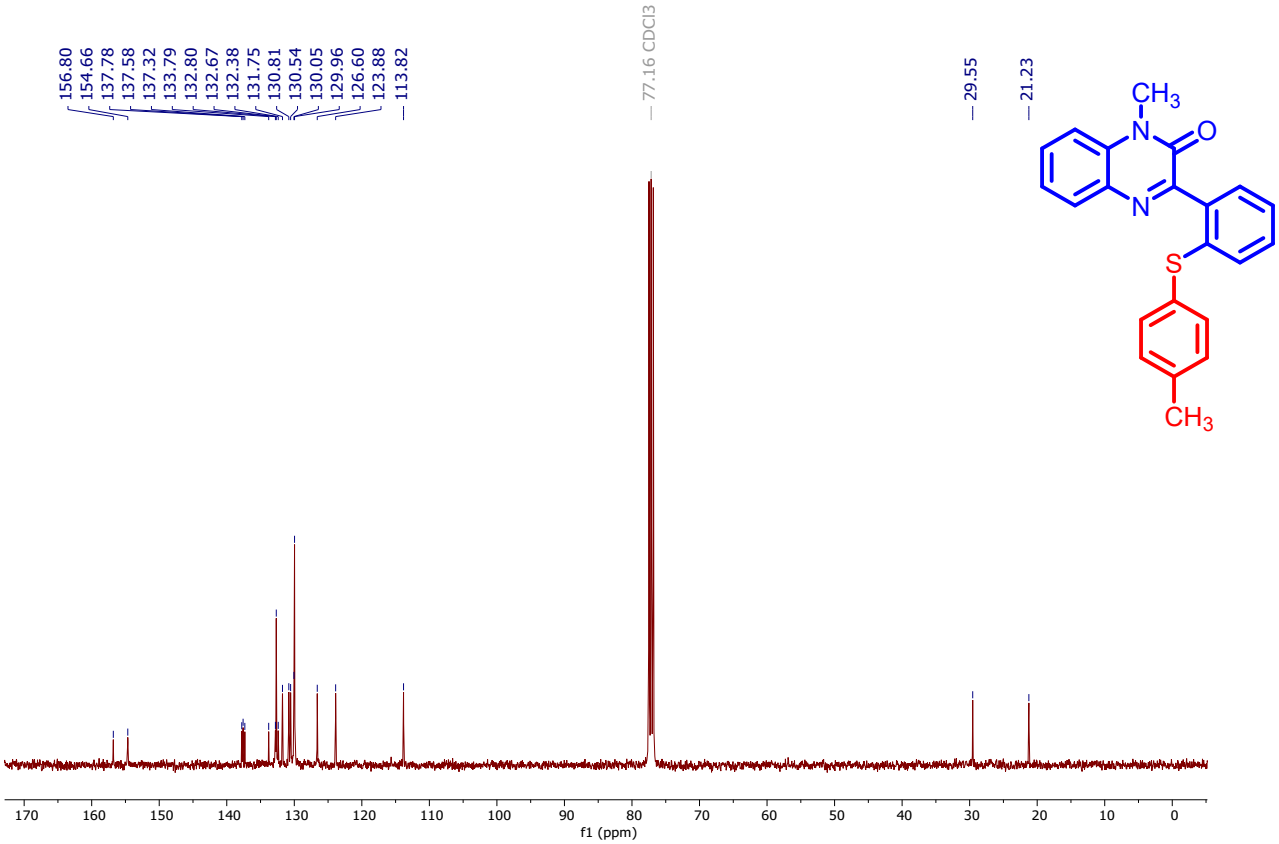


Figure 35: ^{13}C NMR spectrum of compound **5b** ($CDCl_3$, 100 MHz)

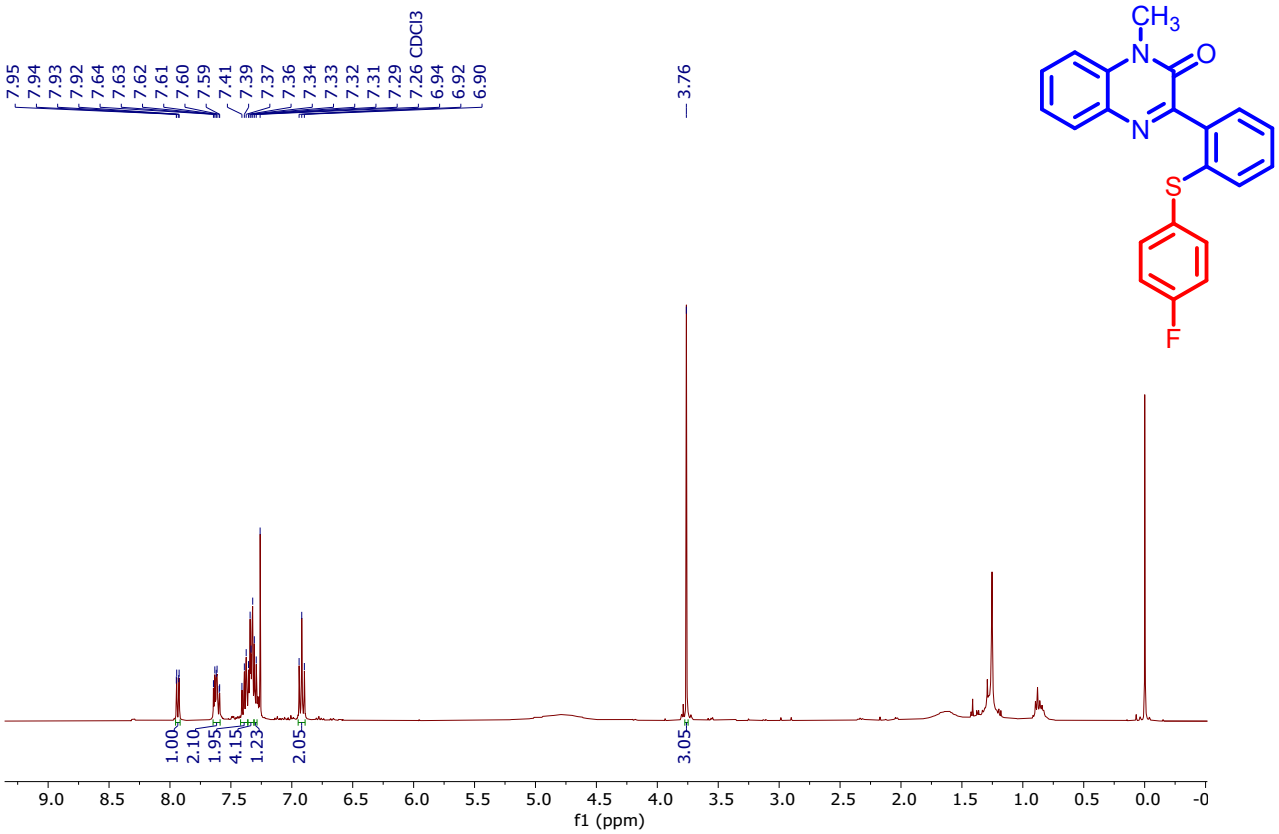


Figure 36: ^{1}H NMR spectrum of compound **5c** ($CDCl_3$, 400 MHz)

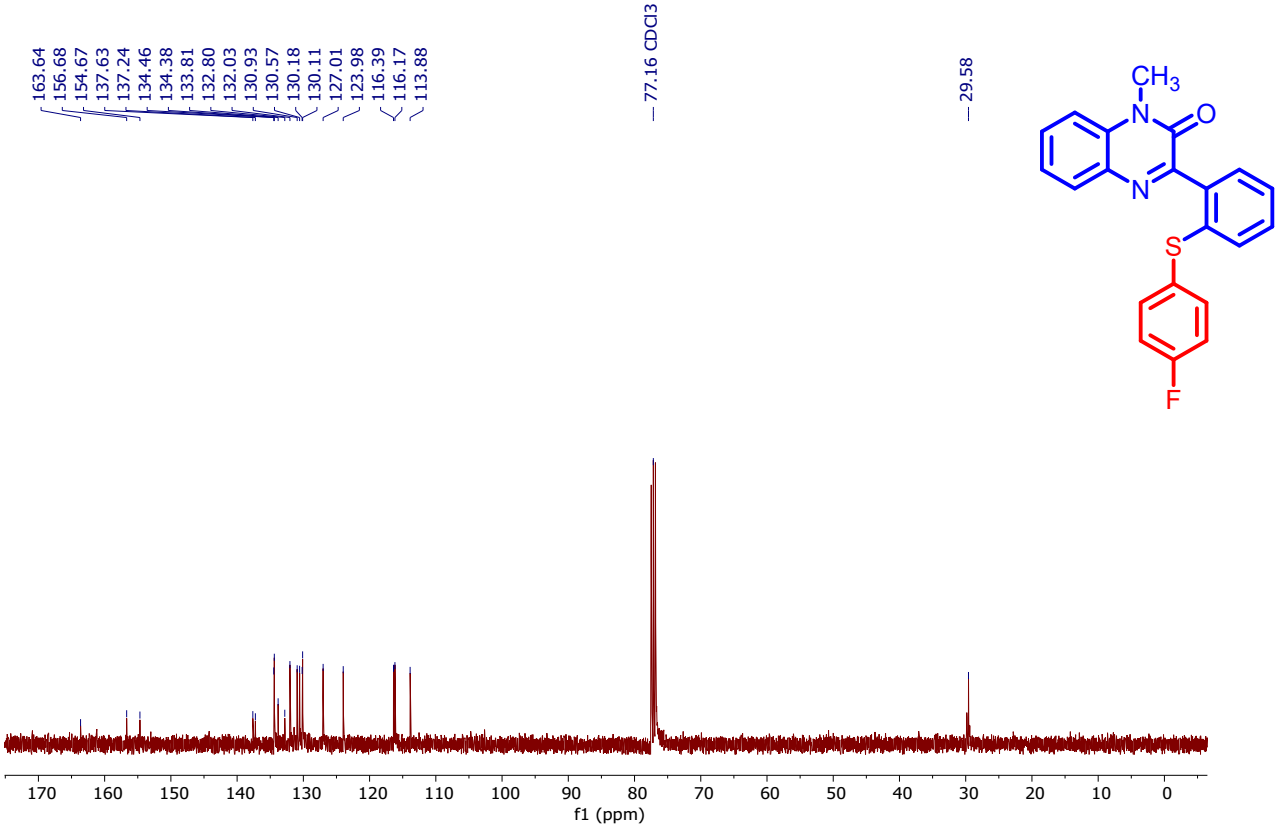


Figure 37: ^{13}C NMR spectrum of compound **5c** ($CDCl_3$, 100 MHz)

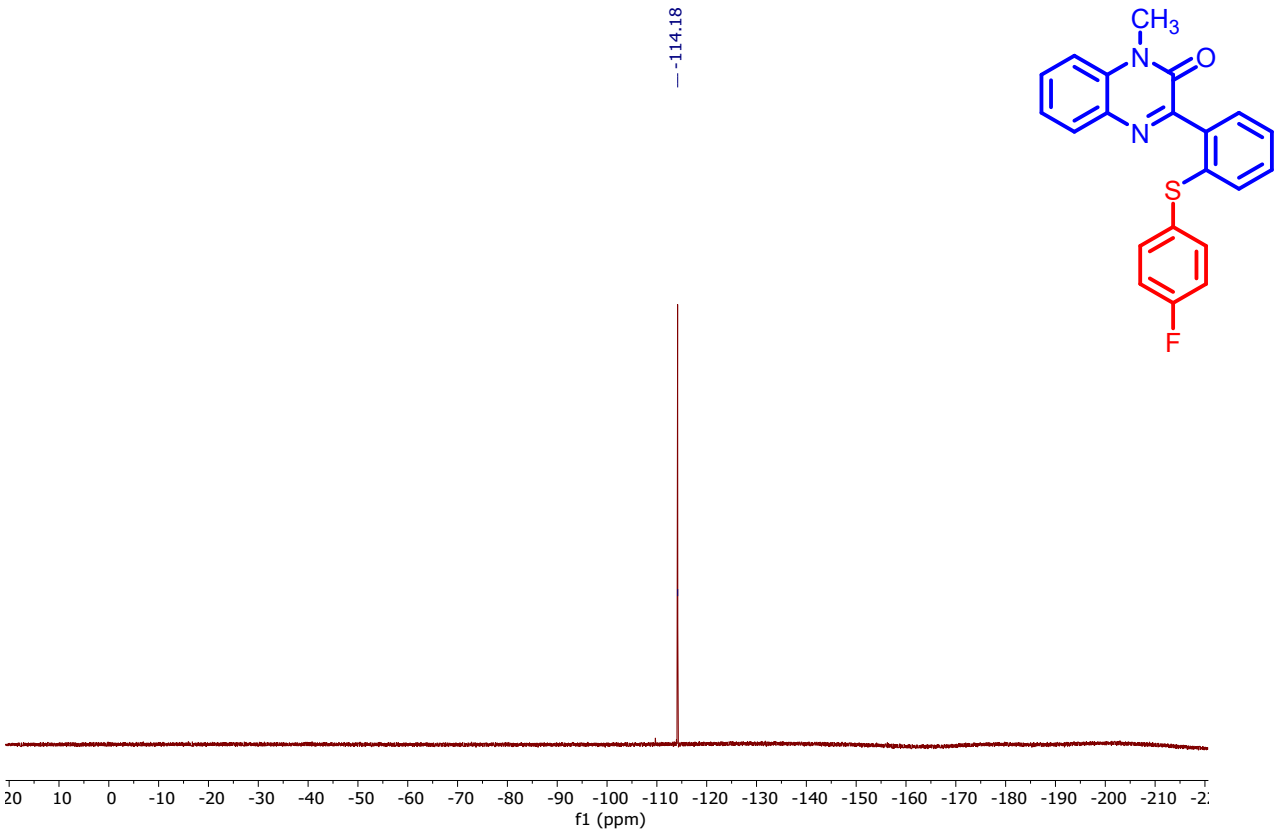


Figure 38: ^{19}F NMR spectrum of compound **5c** ($CDCl_3$, 376 MHz)

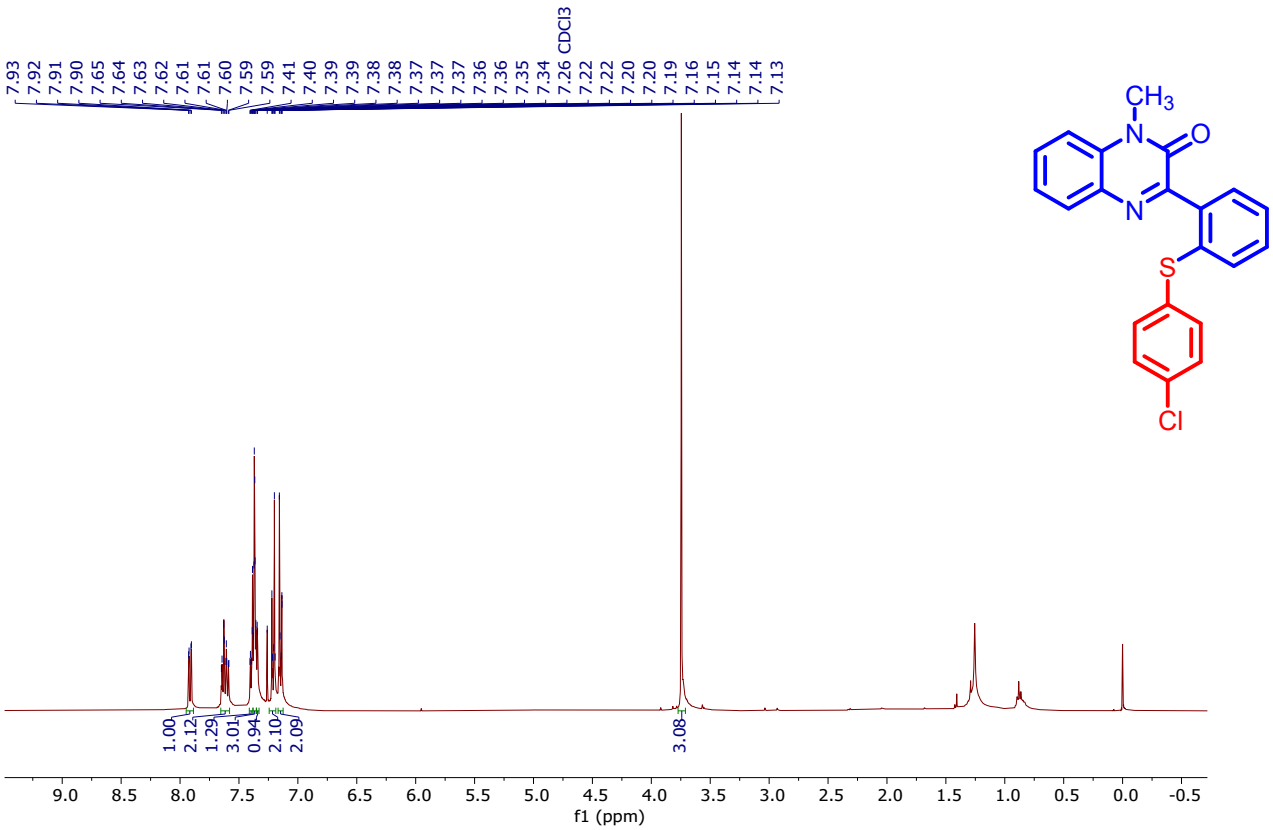


Figure 39: ^{1}H NMR spectrum of compound **5d** ($CDCl_3$, 400 MHz)

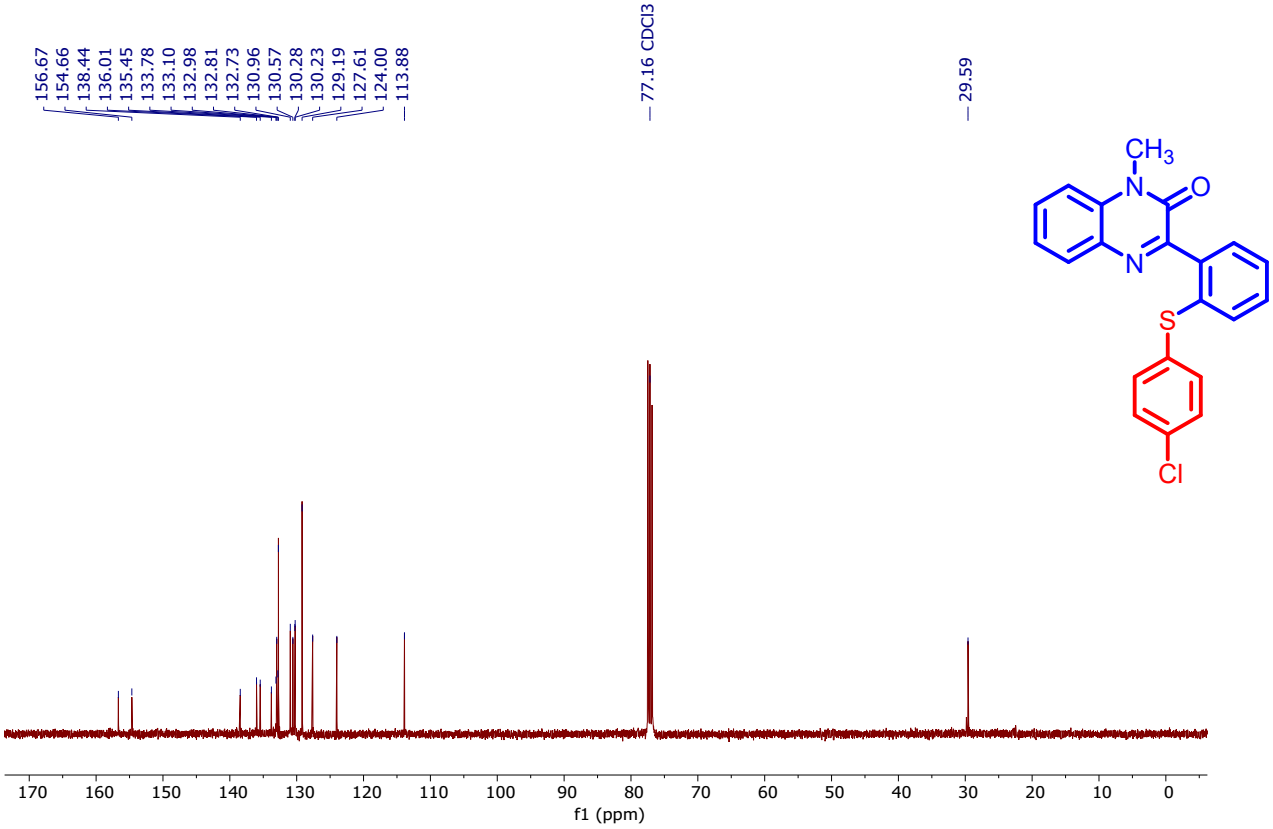


Figure 40: ^{13}C NMR spectrum of compound **5d** ($CDCl_3$, 100 MHz)

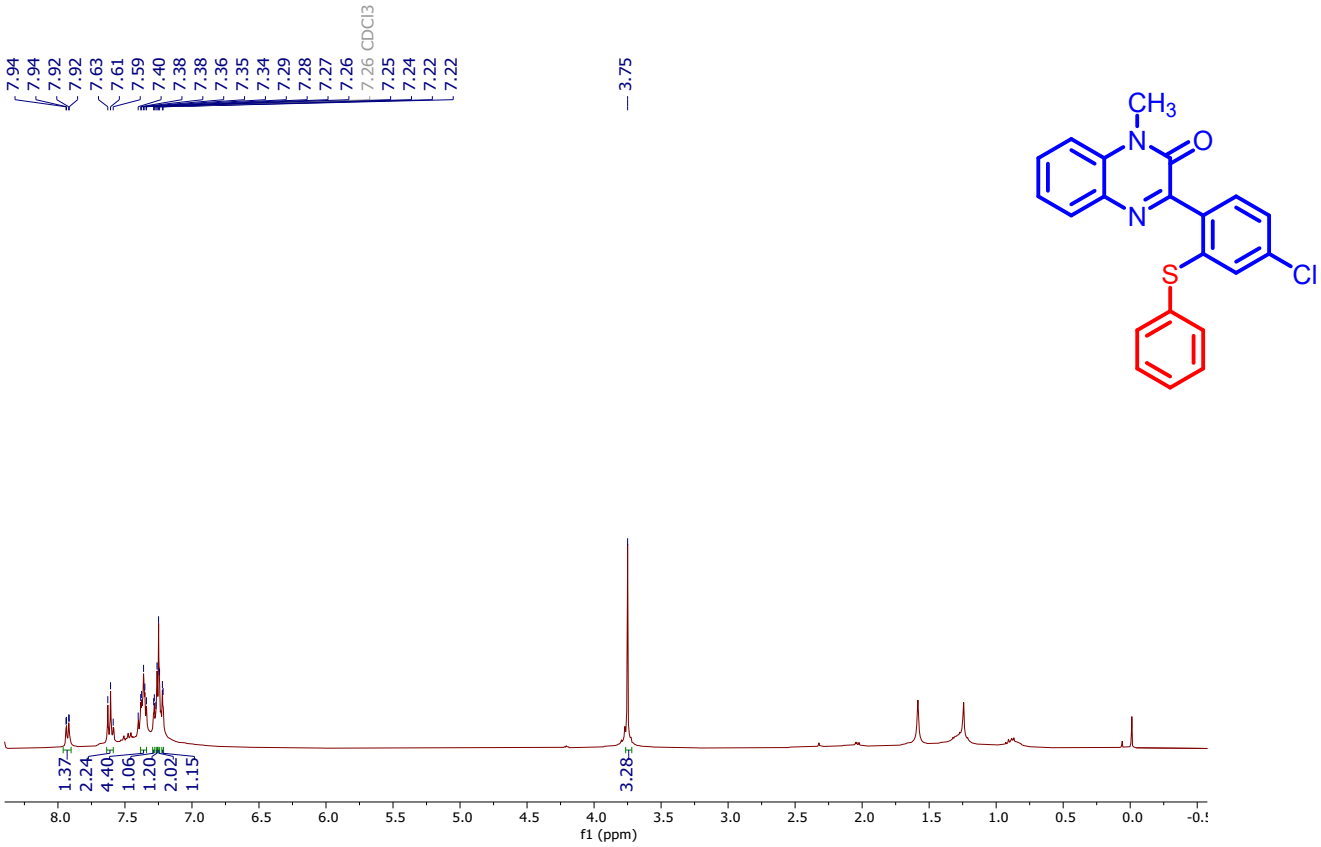


Figure 41: ^{1}H NMR spectrum of compound **5e** ($CDCl_3$, 400 MHz)

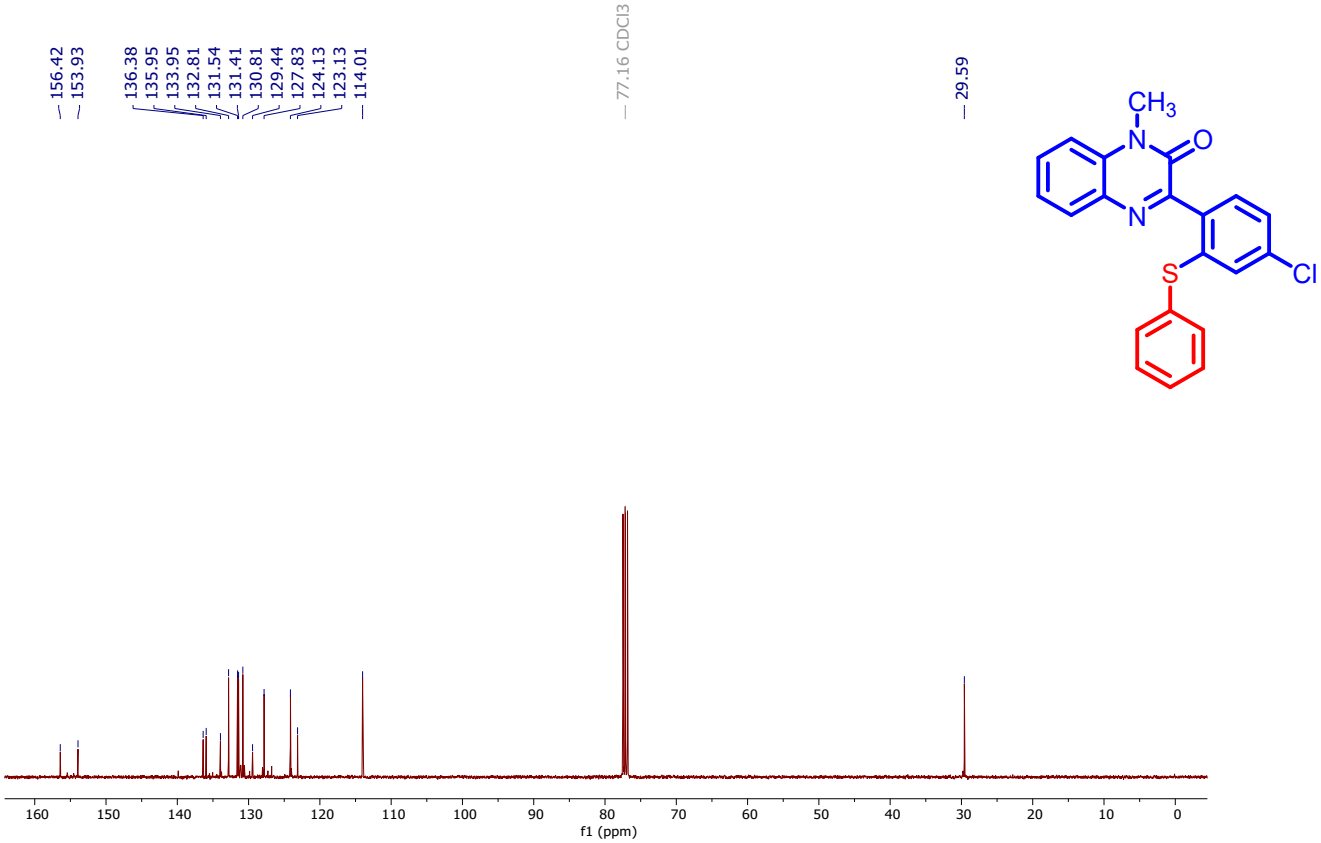


Figure 42: ^{13}C NMR spectrum of compound **5e** ($CDCl_3$, 100 MHz)

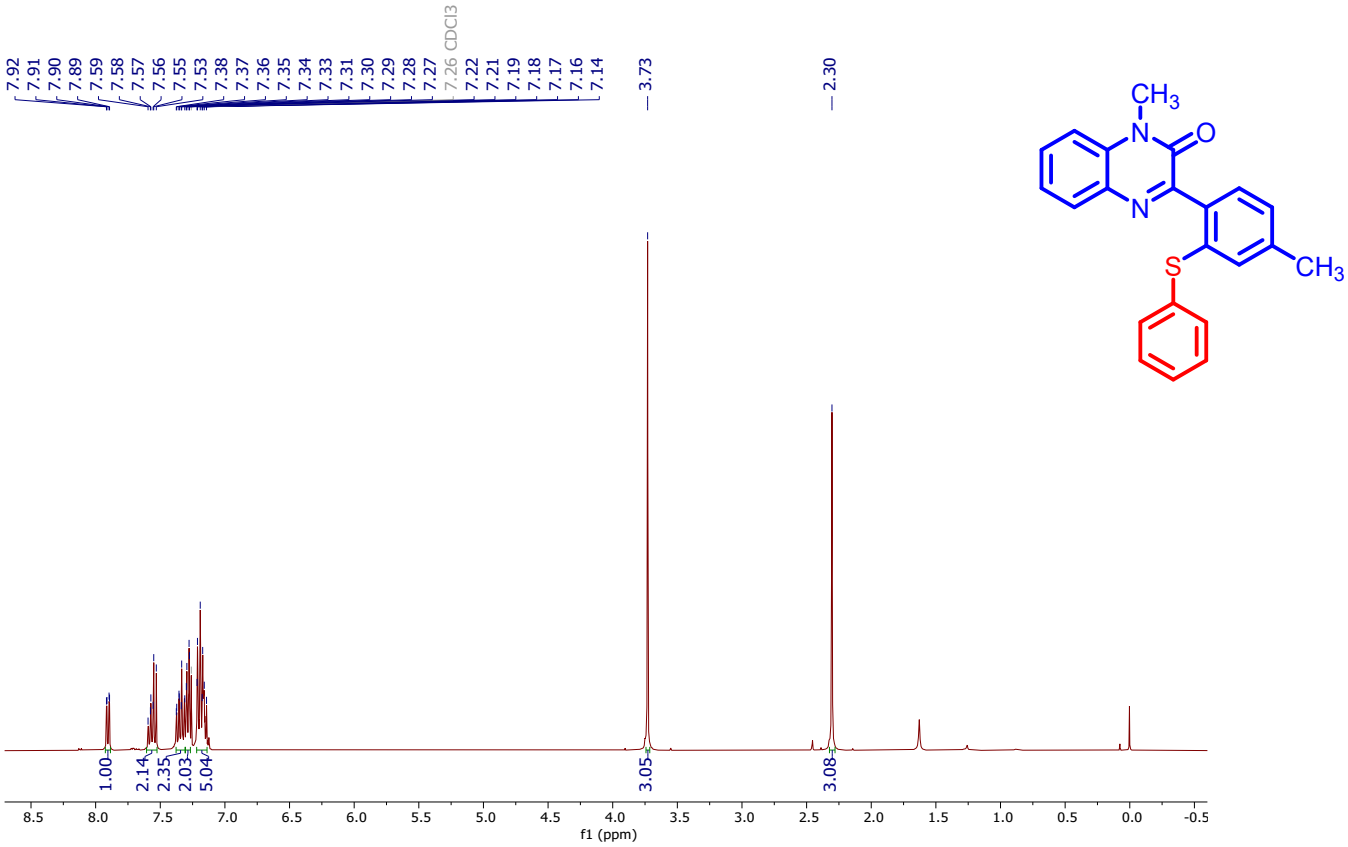


Figure 43: ^{1}H NMR spectrum of compound **5f** ($CDCl_3$, 400 MHz)

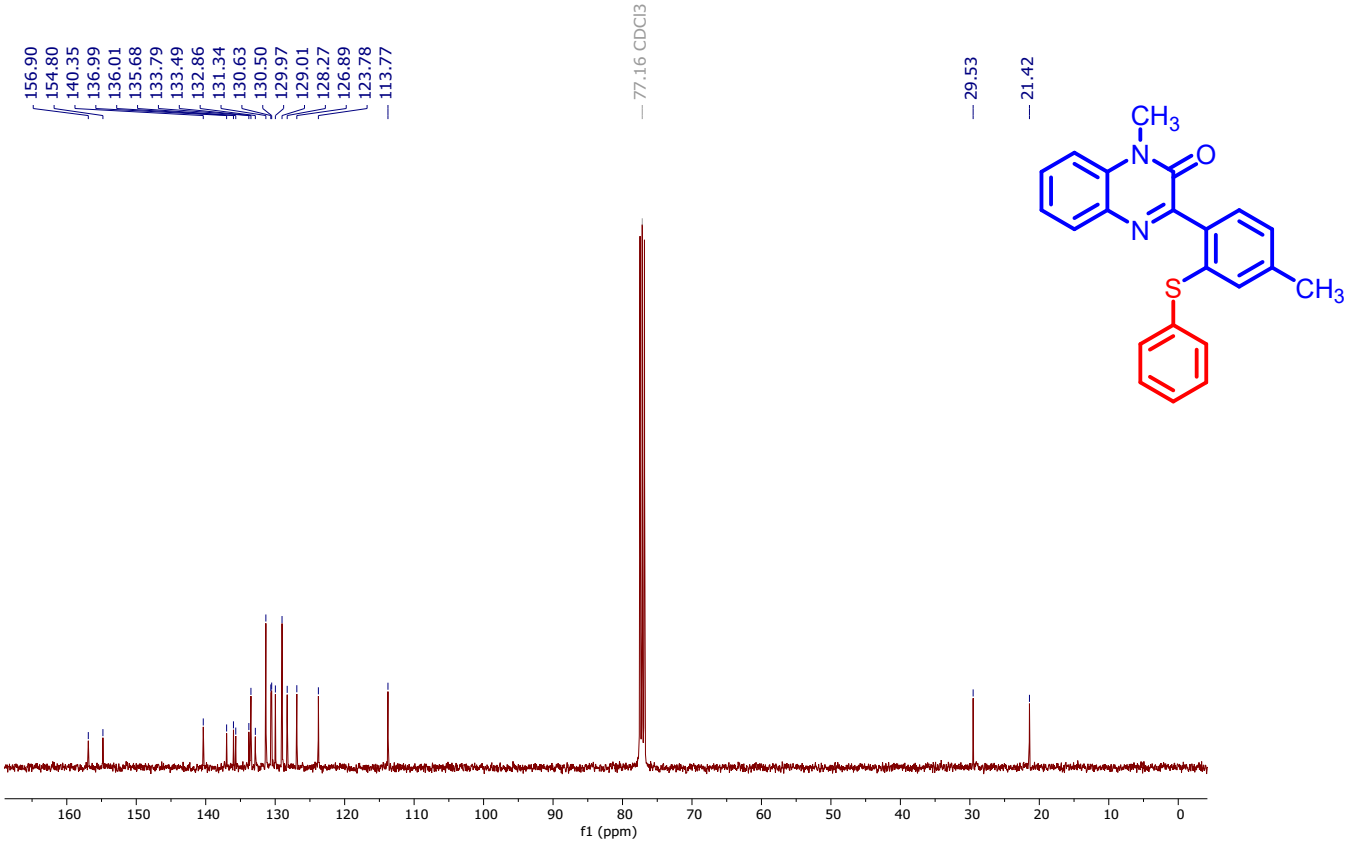


Figure 44: ^{13}C NMR spectrum of compound **5f** ($CDCl_3$, 100 MHz)

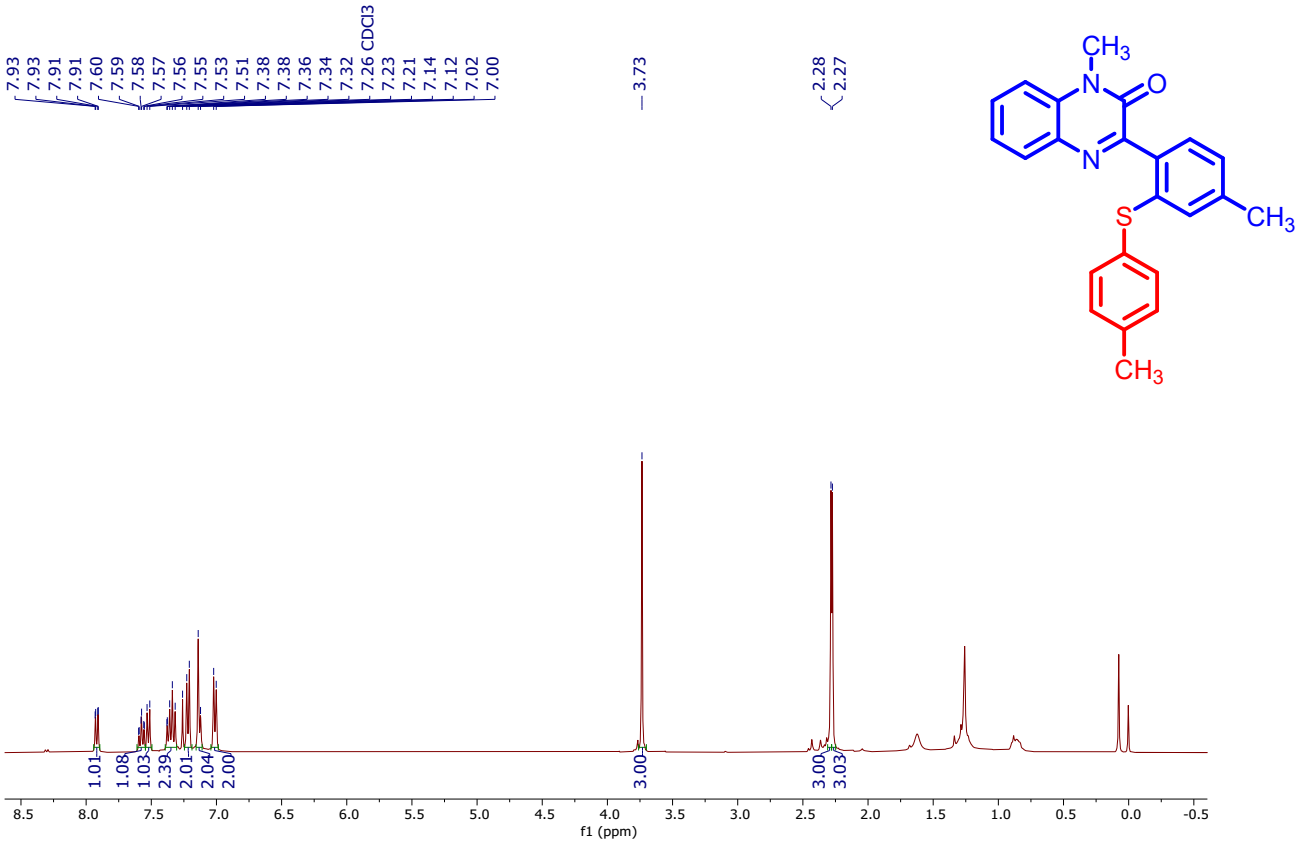


Figure 45: ^{1}H NMR spectrum of compound **5g** ($CDCl_3$, 400 MHz)

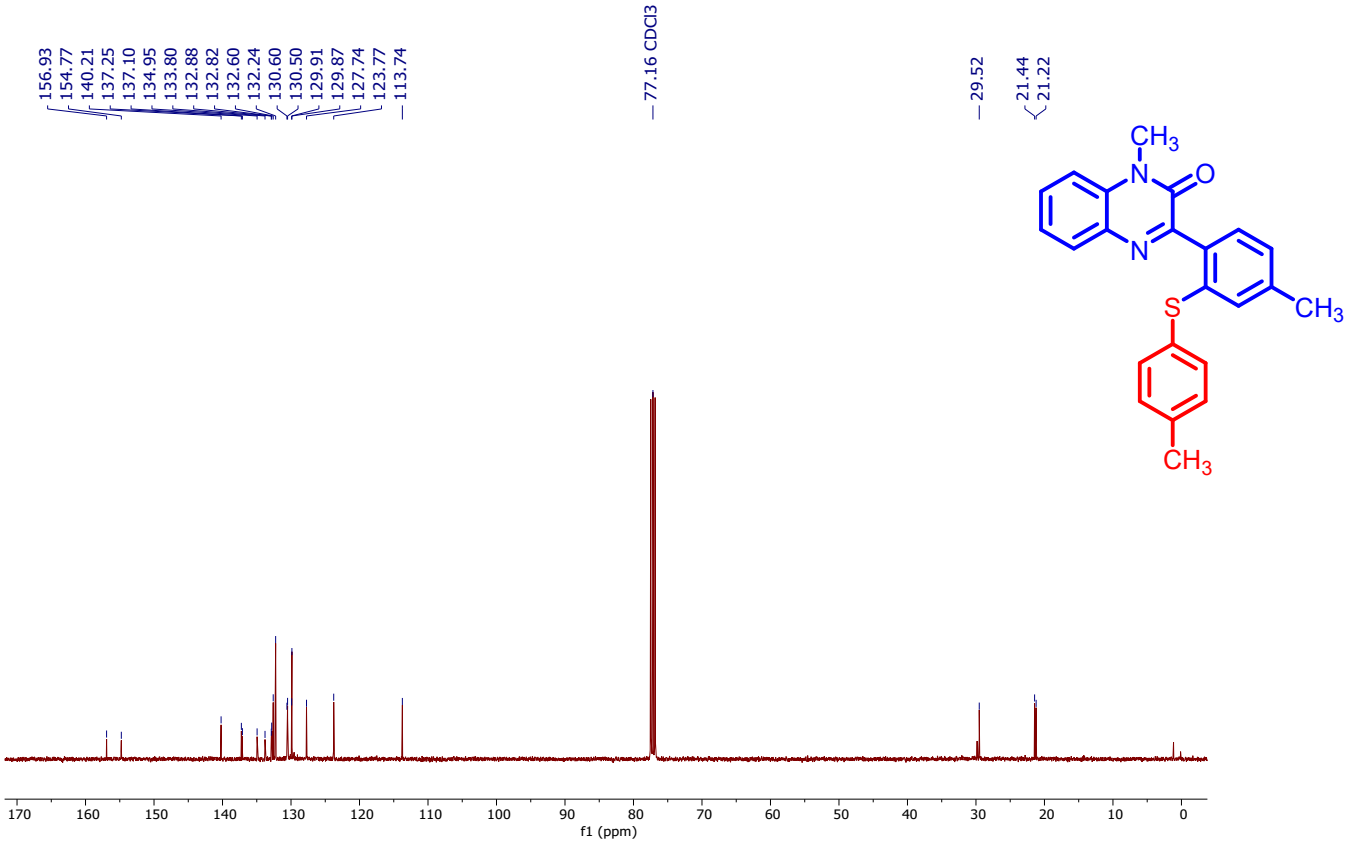


Figure 46: ^{13}C NMR spectrum of compound **5g** ($CDCl_3$, 100 MHz)

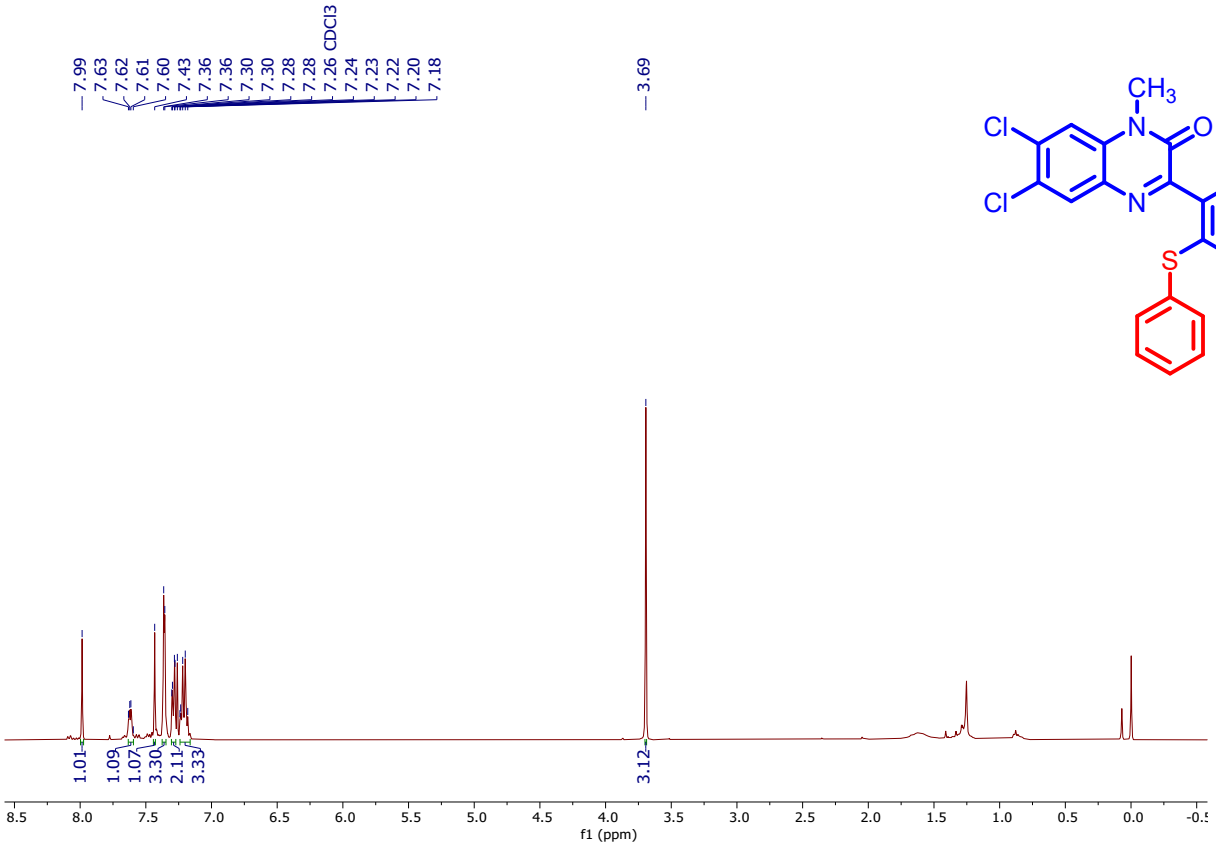


Figure 47: ^{1}H NMR spectrum of compound **5h** ($CDCl_3$, 400 MHz)

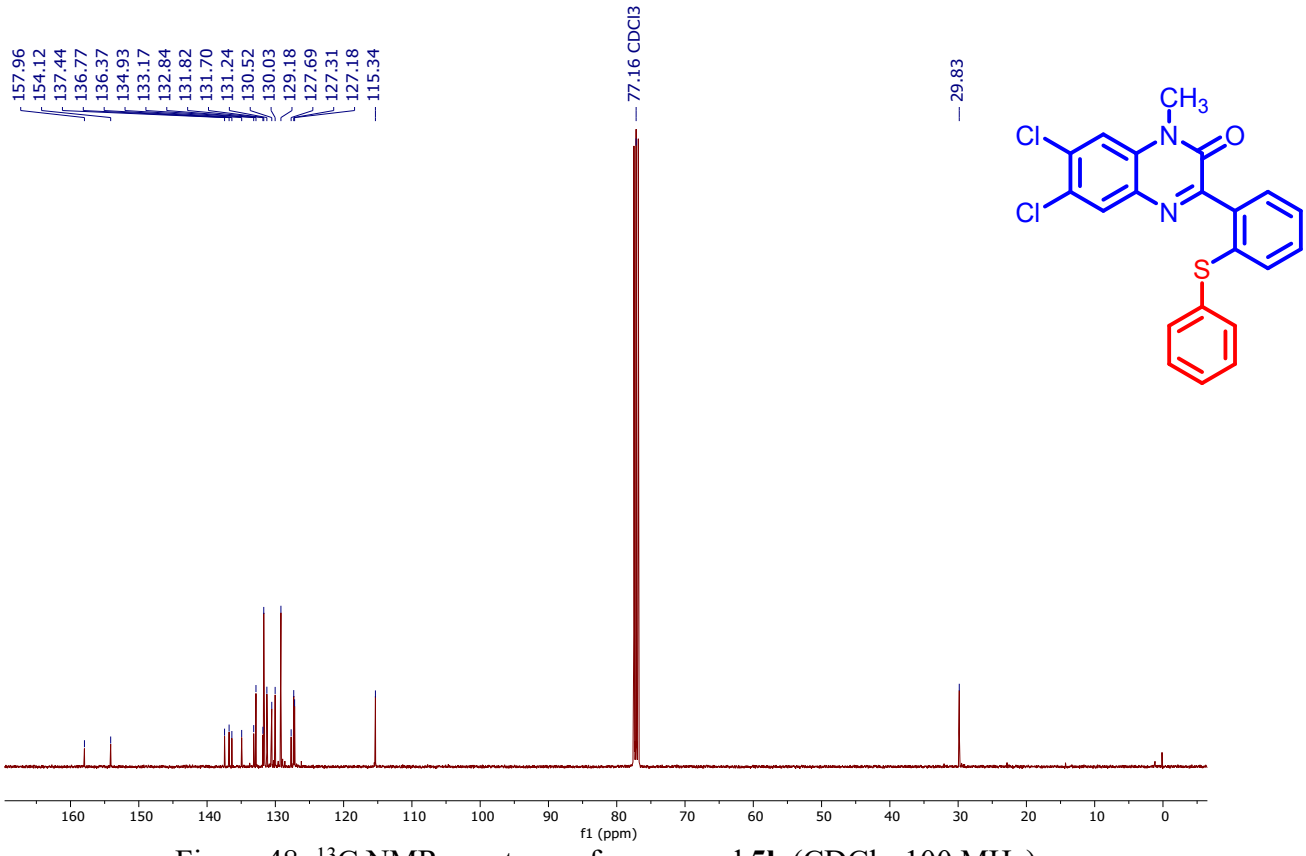


Figure 48: ^{13}C NMR spectrum of compound **5h** ($CDCl_3$, 100 MHz)

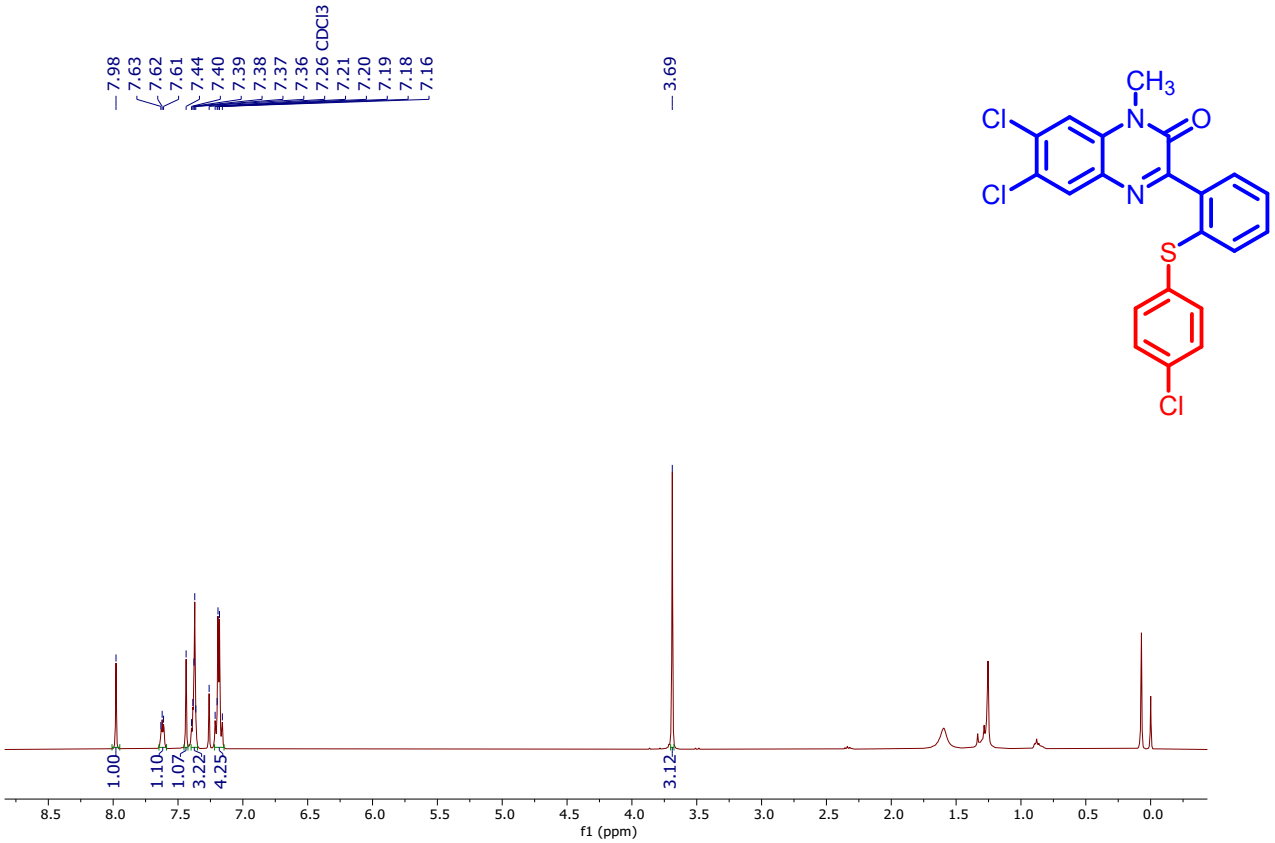


Figure 49: ^{1}H NMR spectrum of compound **5i** ($CDCl_3$, 400 MHz)

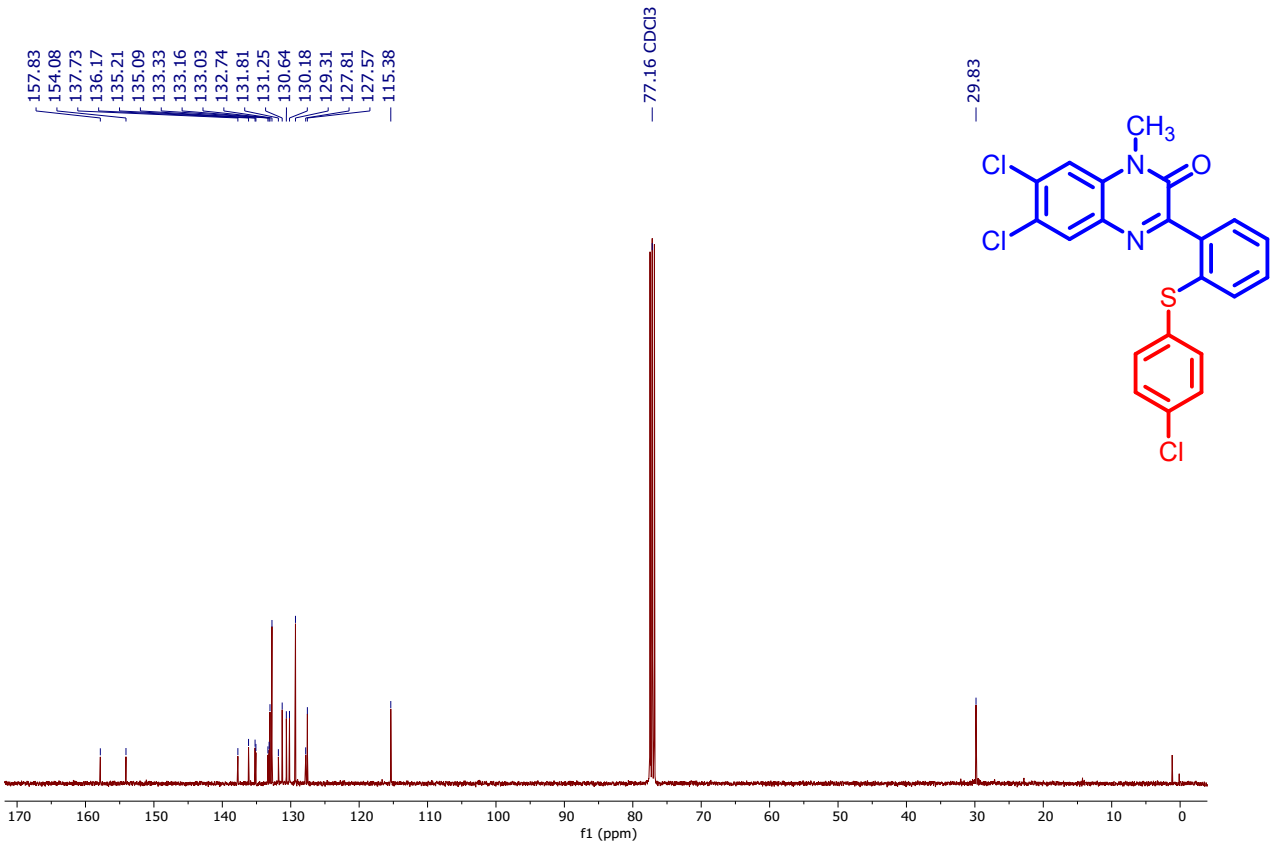


Figure 50: ^{13}C NMR spectrum of compound **5i** ($CDCl_3$, 100 MHz)

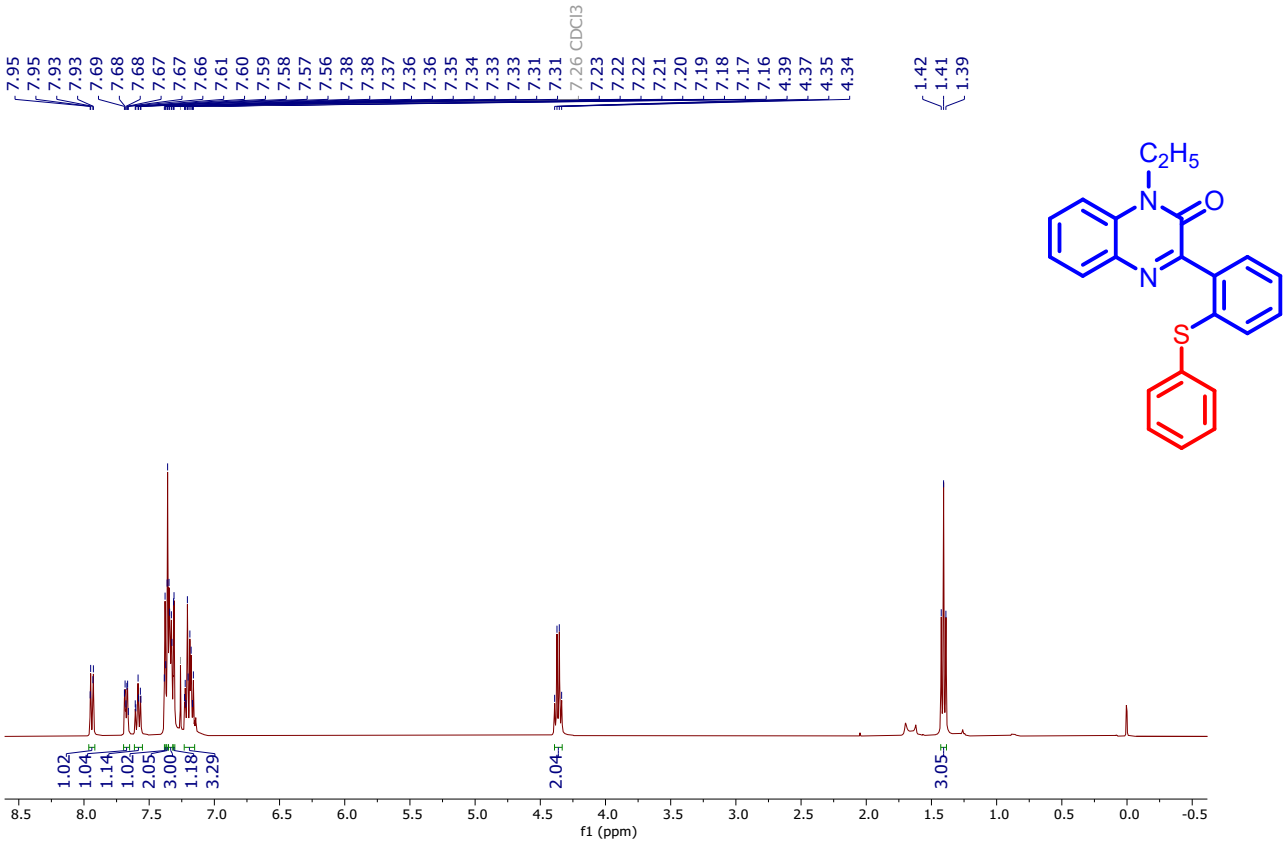


Figure 51: ^{1}H NMR spectrum of compound **5j** ($CDCl_3$, 400 MHz)

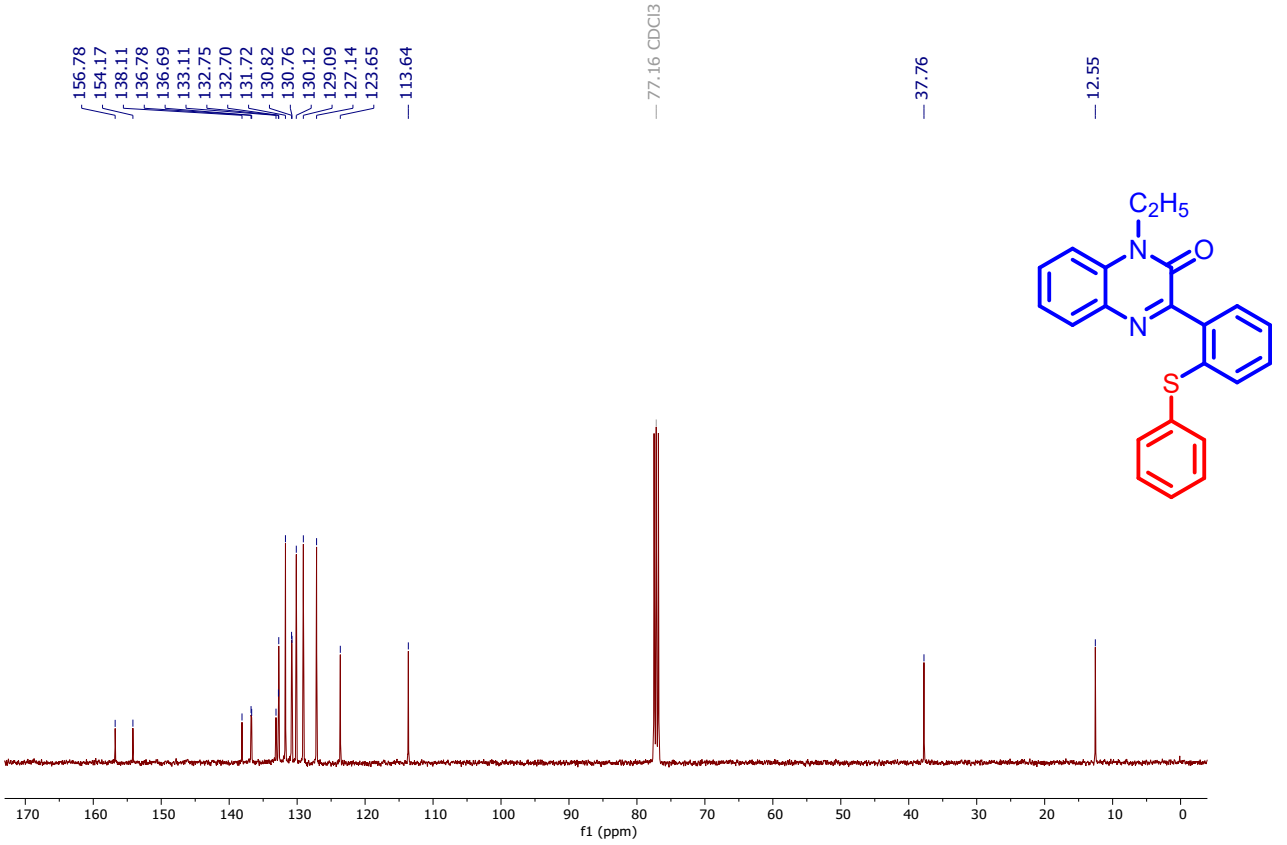


Figure 52: ^{13}C NMR spectrum of compound **5j** ($CDCl_3$, 100 MHz)

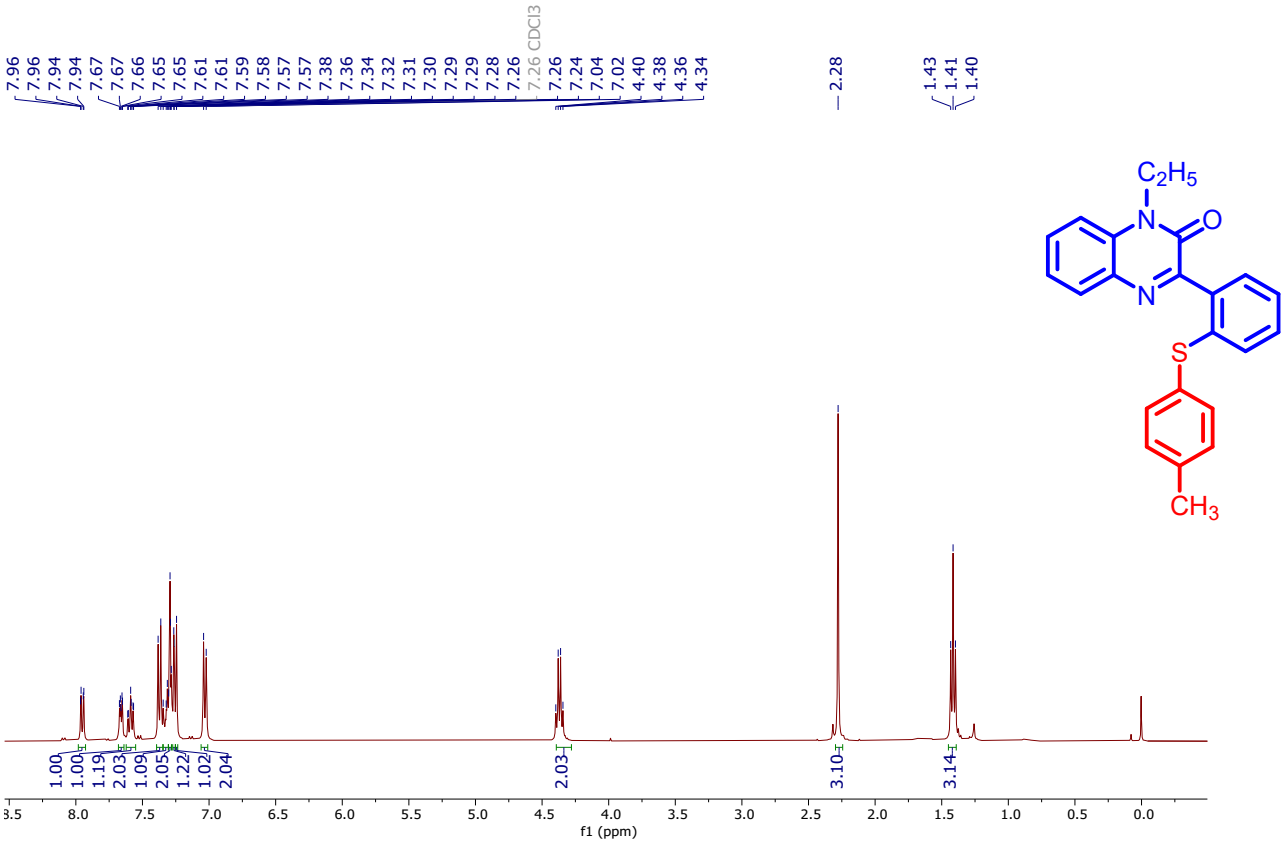


Figure 53: ^{1}H NMR spectrum of compound **5k** ($CDCl_3$, 400 MHz)

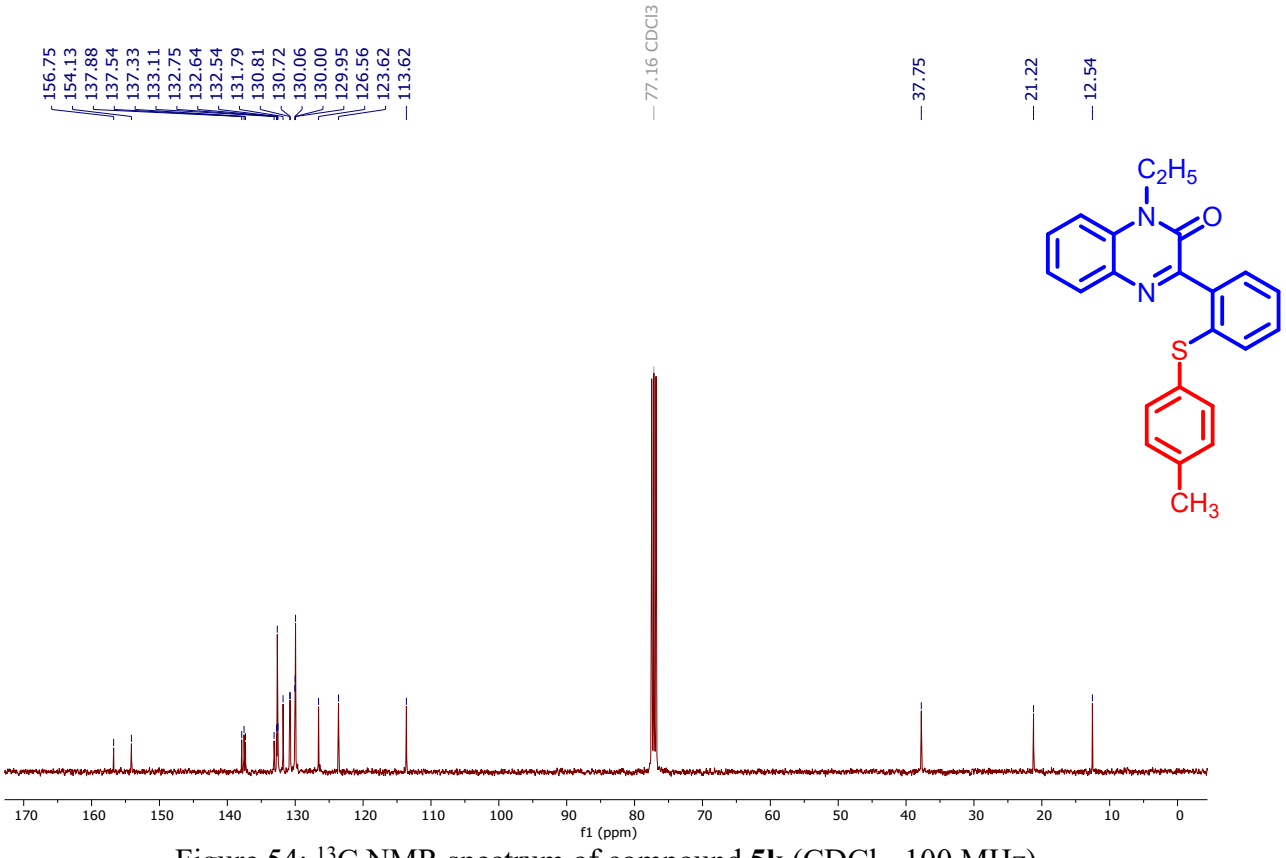


Figure 54: ^{13}C NMR spectrum of compound **5k** ($CDCl_3$, 100 MHz)

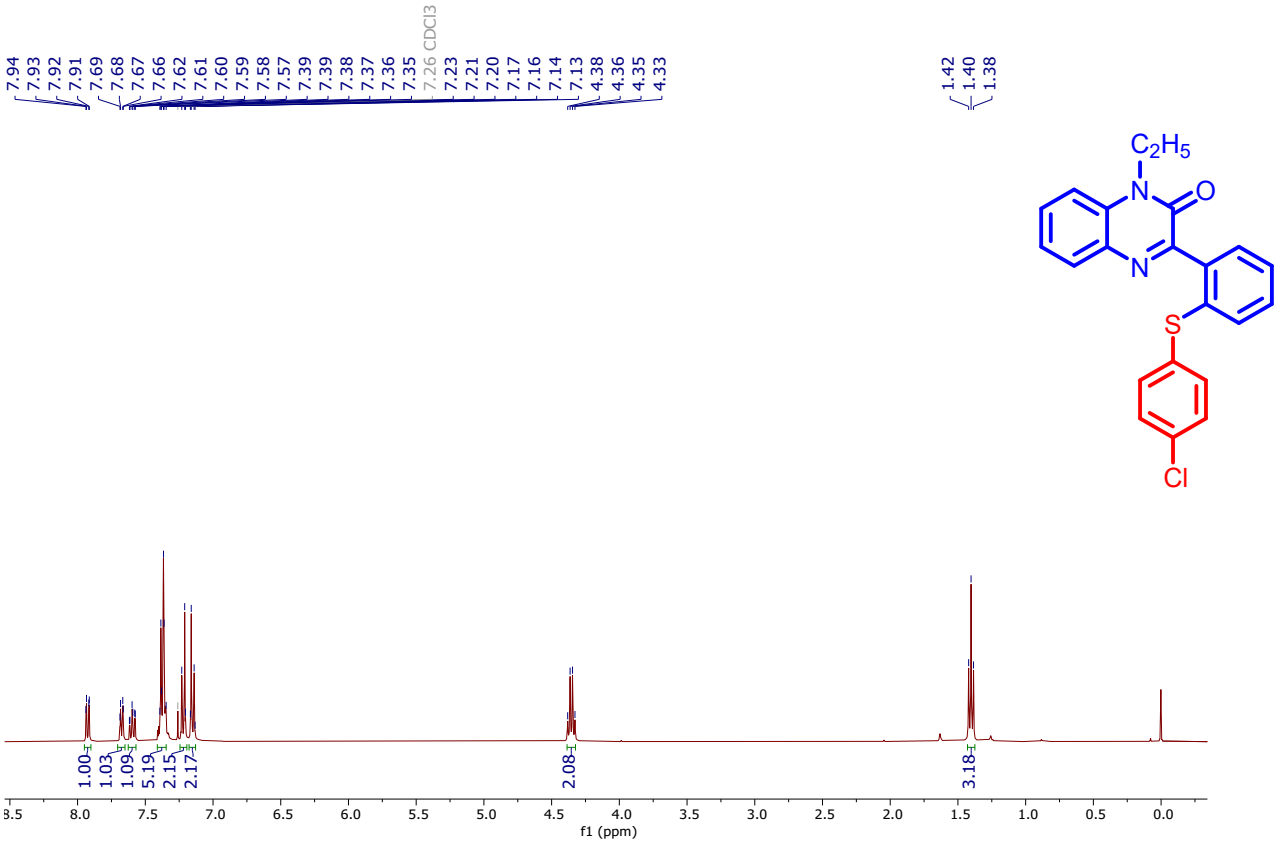


Figure 55: ^{1}H NMR spectrum of compound **5l** ($CDCl_3$, 400 MHz)

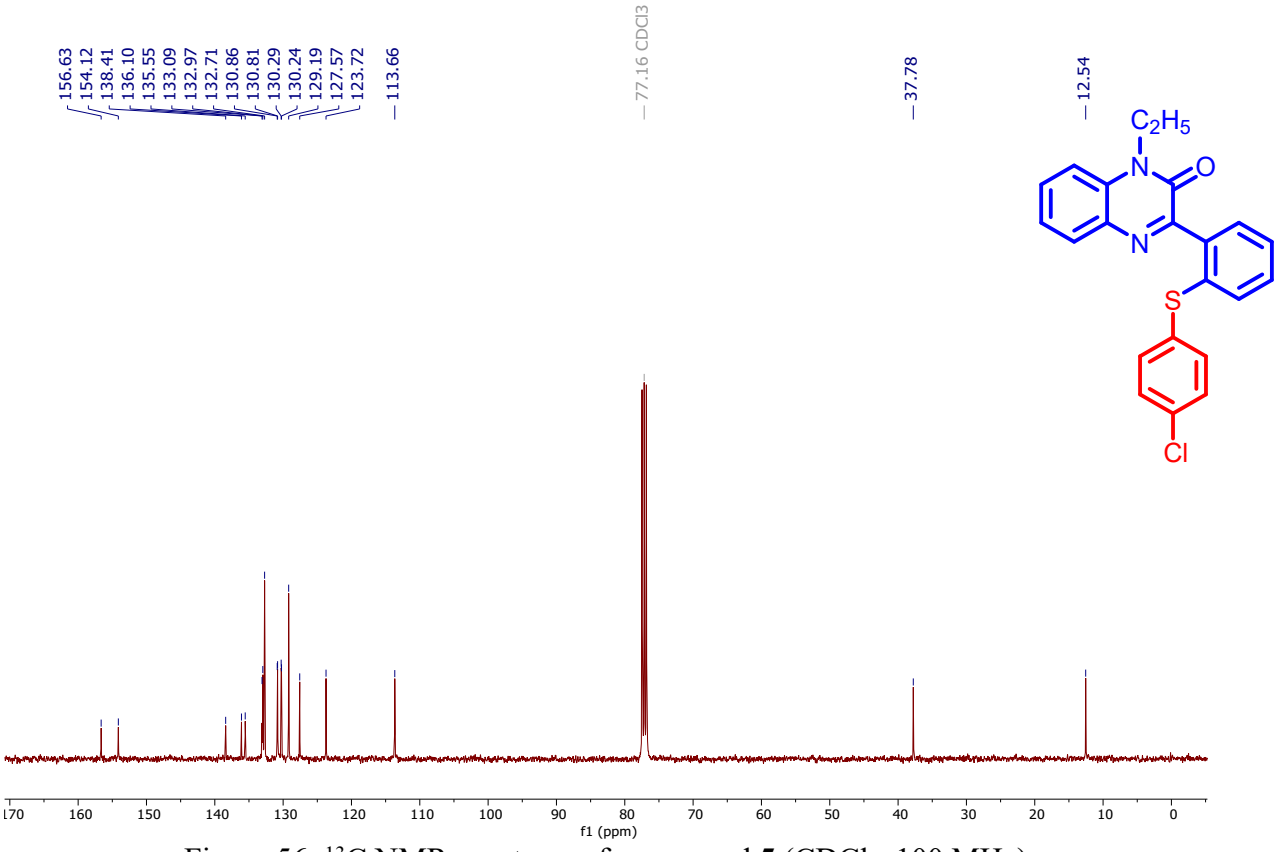


Figure 56: ^{13}C NMR spectrum of compound **5** ($CDCl_3$, 100 MHz)

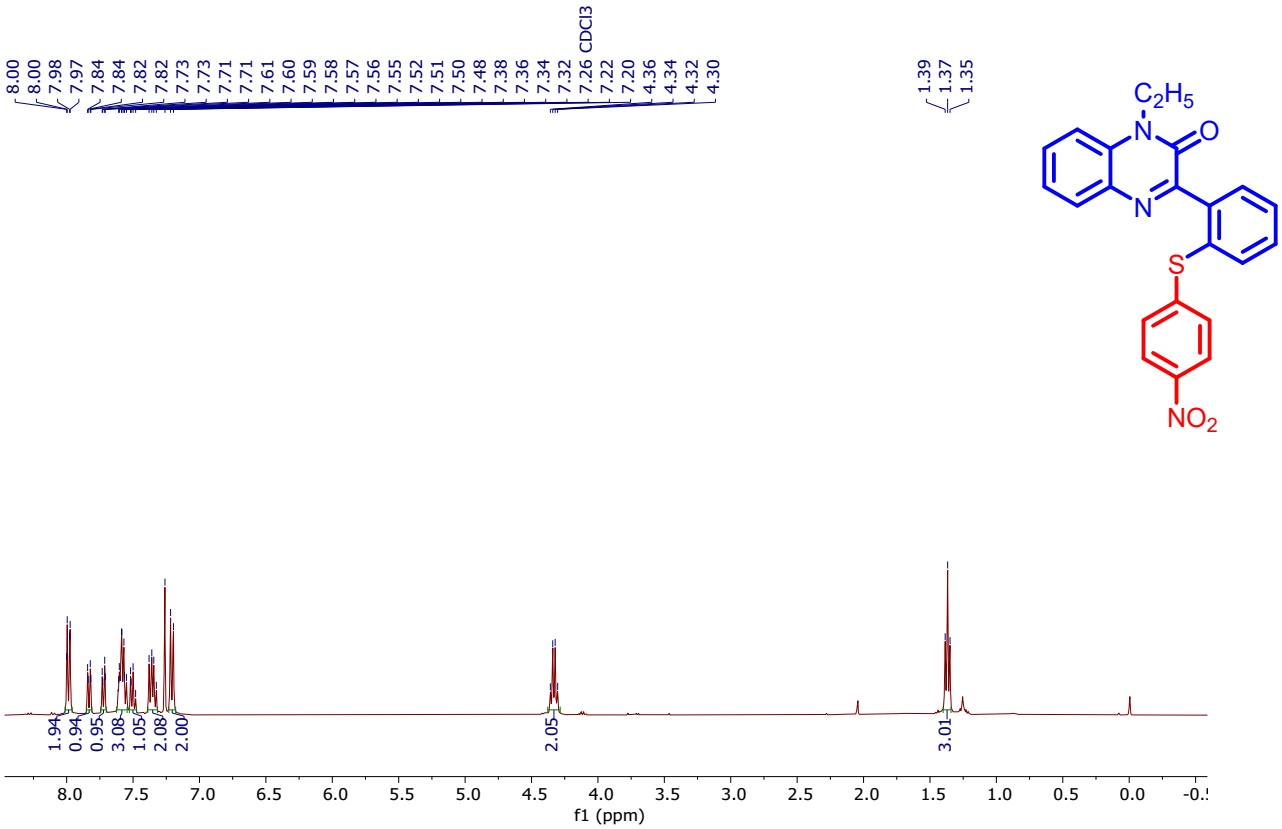


Figure 57: ^{1}H NMR spectrum of compound **5m** ($CDCl_3$, 400 MHz)

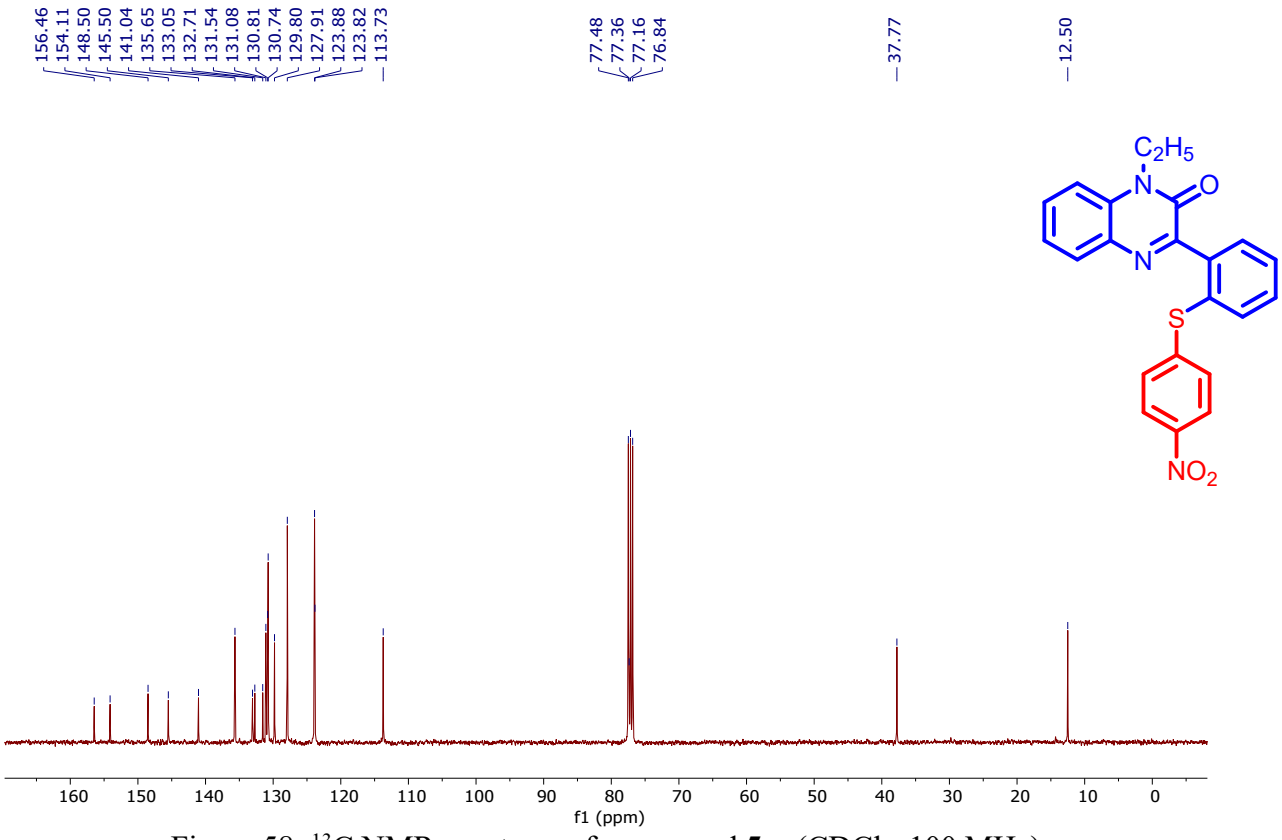


Figure 58: ^{13}C NMR spectrum of compound **5m** ($CDCl_3$, 100 MHz)

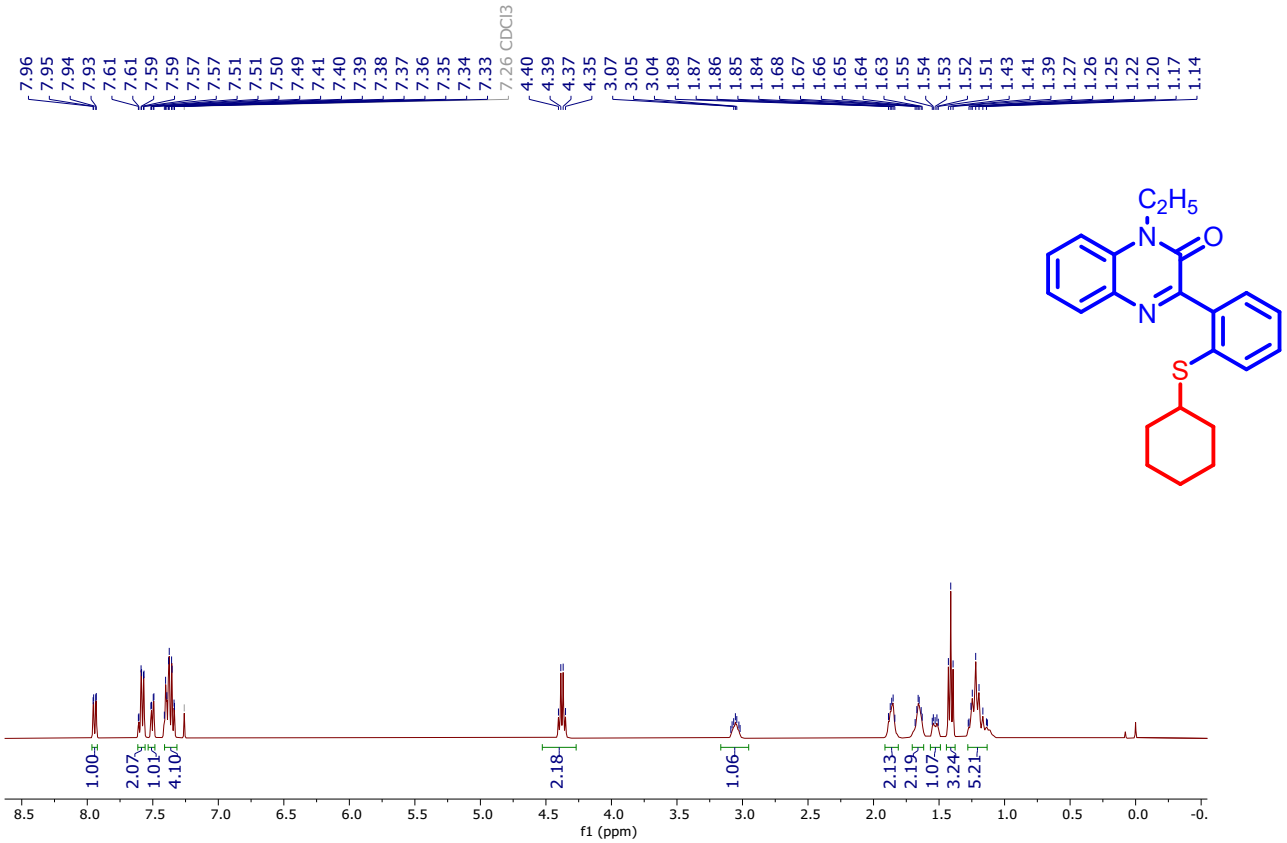


Figure 59: ^{1}H NMR spectrum of compound **5n** ($CDCl_3$, 400 MHz)

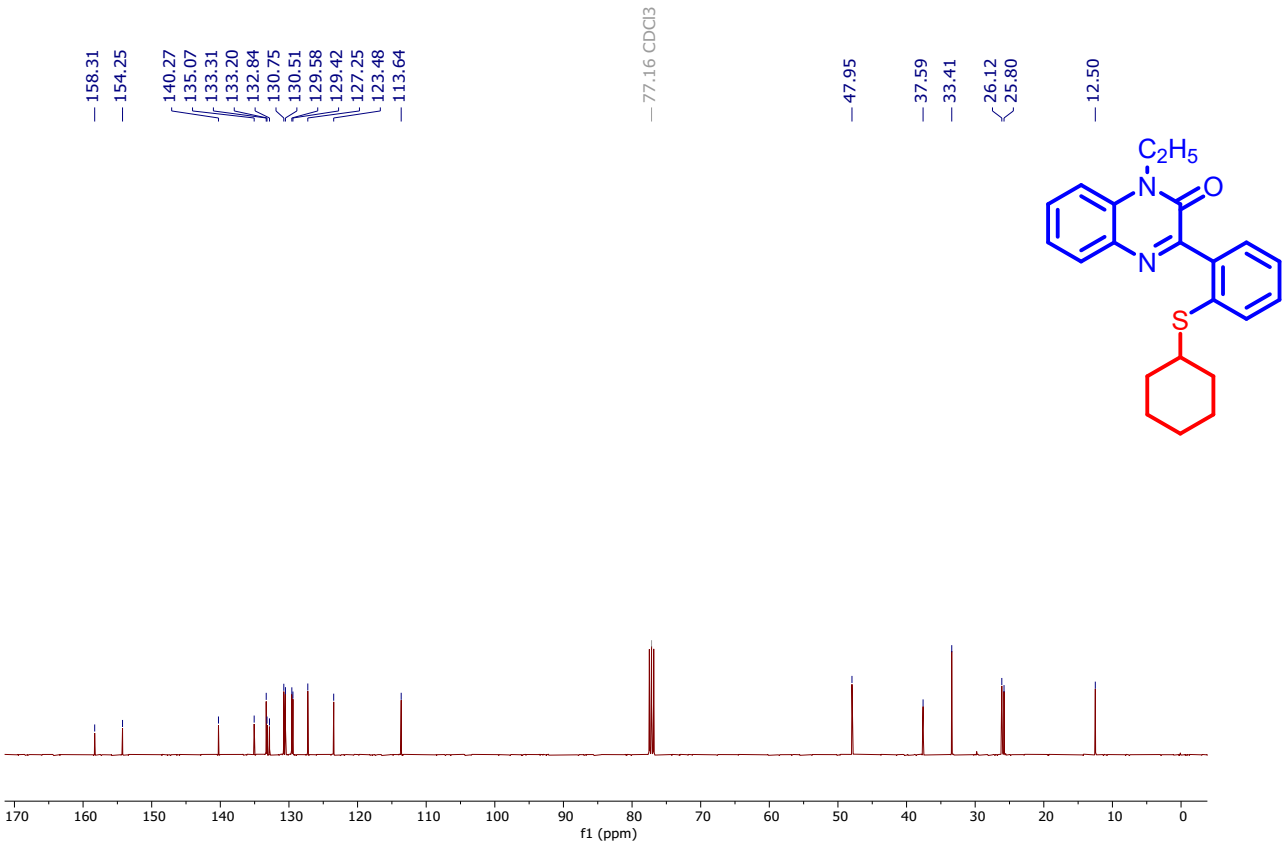


Figure 60: ^{13}C NMR spectrum of compound **5n** ($CDCl_3$, 100 MHz)

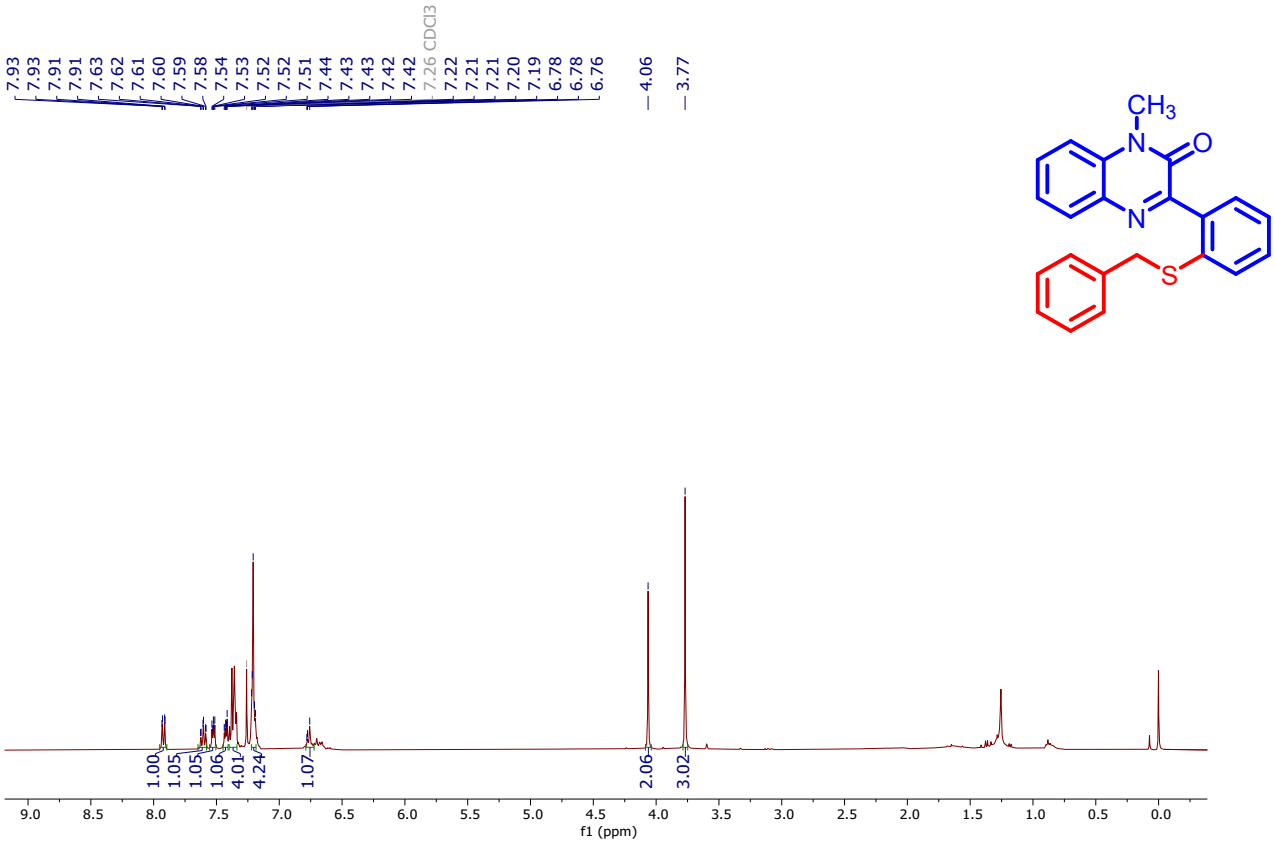


Figure 61: ^{1}H NMR spectrum of compound **5o** ($CDCl_3$, 400 MHz)

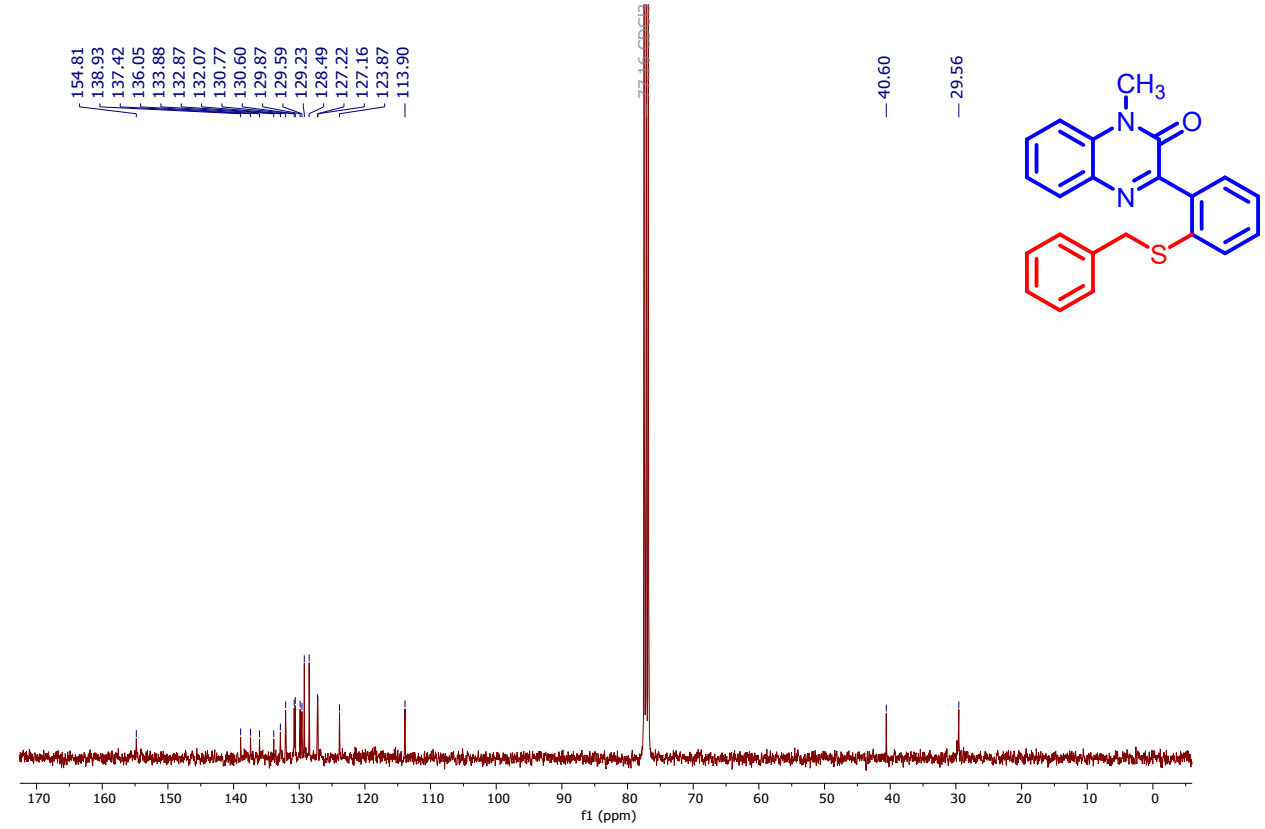


Figure 62: ^{13}C NMR spectrum of compound **5o** ($CDCl_3$, 100 MHz)

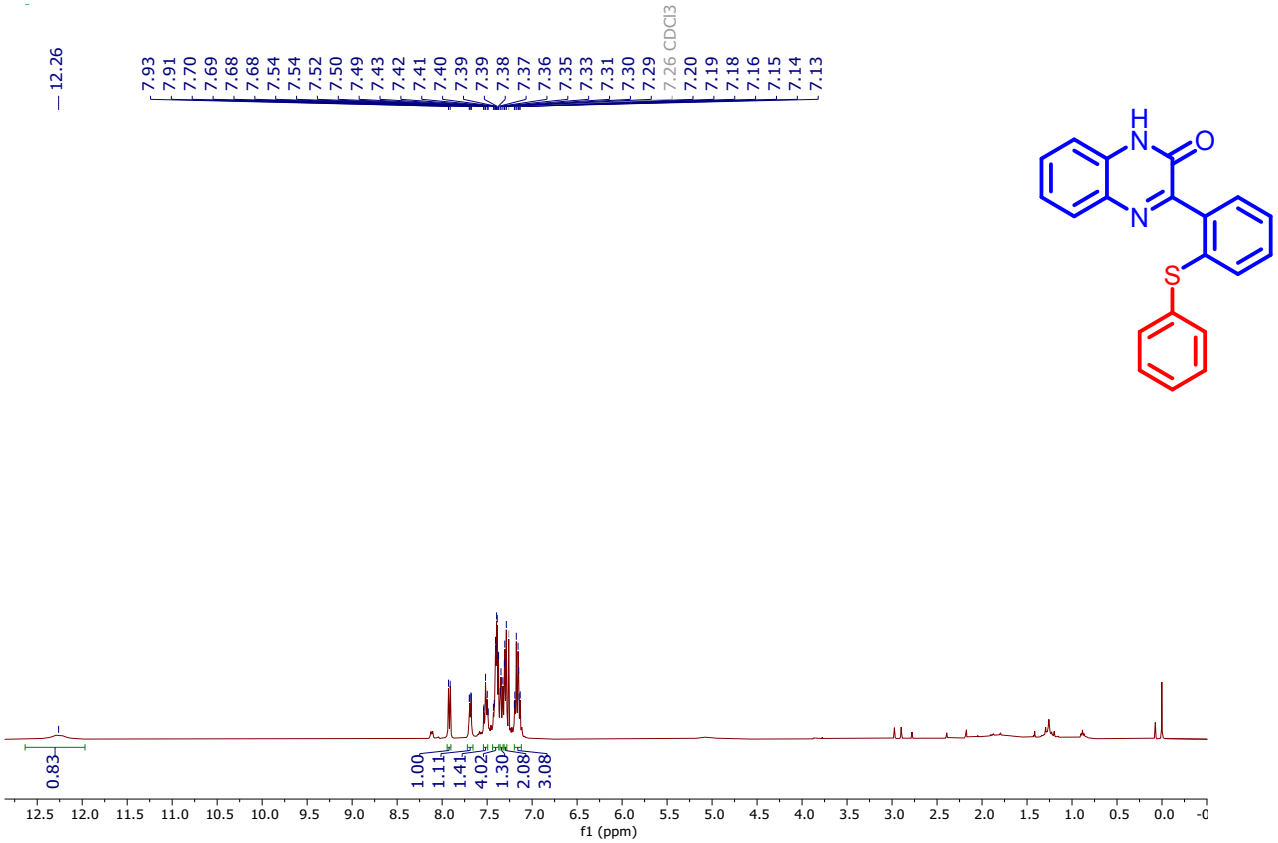


Figure 63: ^{1}H NMR spectrum of compound **5p** ($CDCl_3$, 400 MHz)

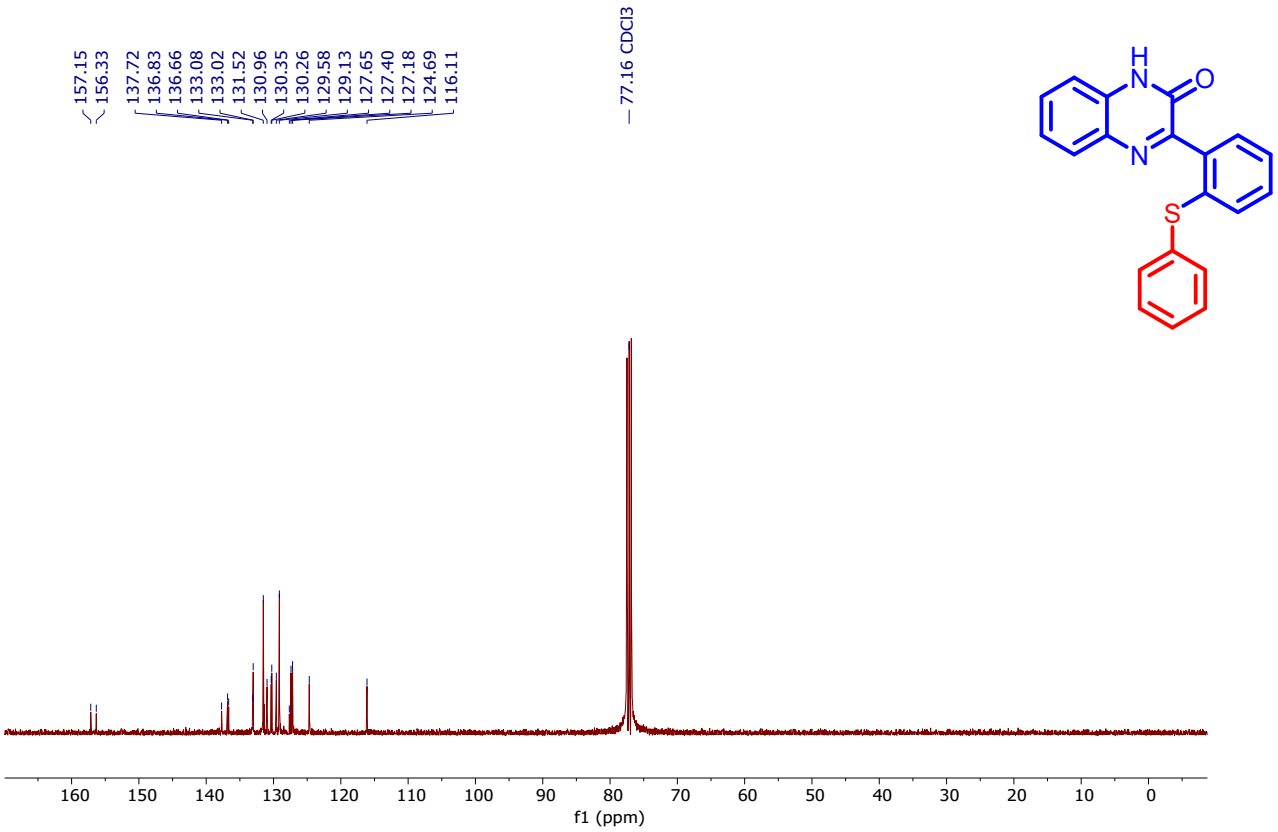


Figure 64: ^{13}C NMR spectrum of compound **5p** ($CDCl_3$, 100 MHz)

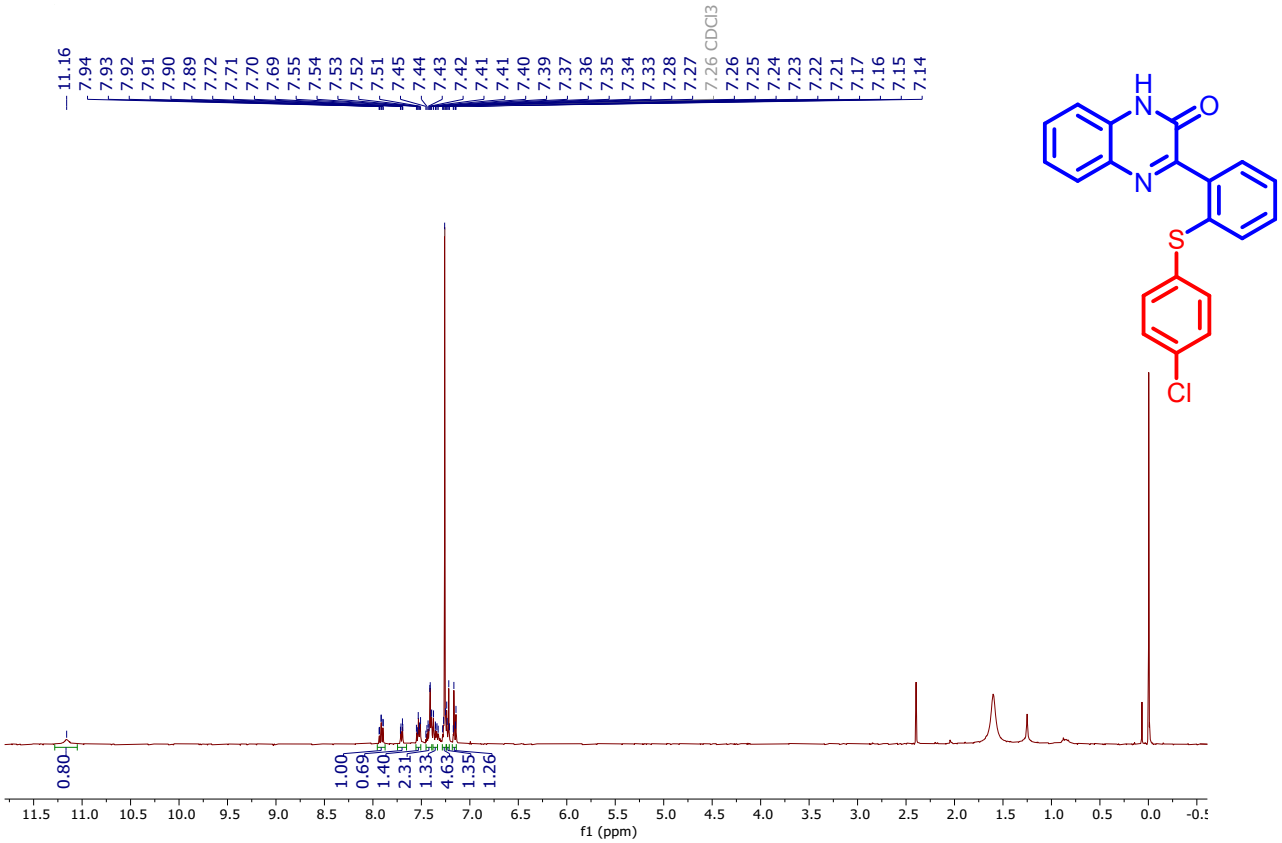


Figure 65: ^{1}H NMR spectrum of compound **5q** ($CDCl_3$, 400 MHz)

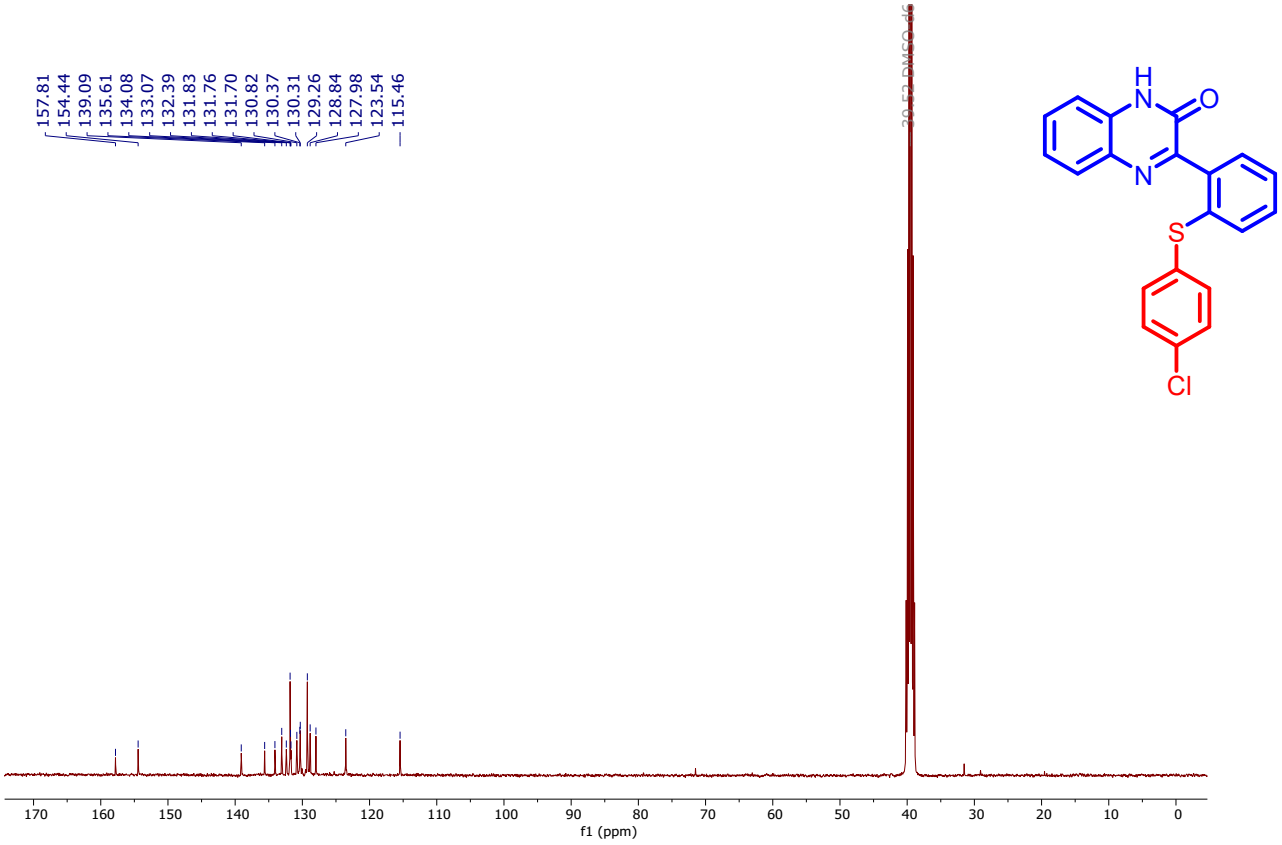


Figure 66: ^{13}C NMR spectrum of compound **5q** (DMSO, 100 MHz)

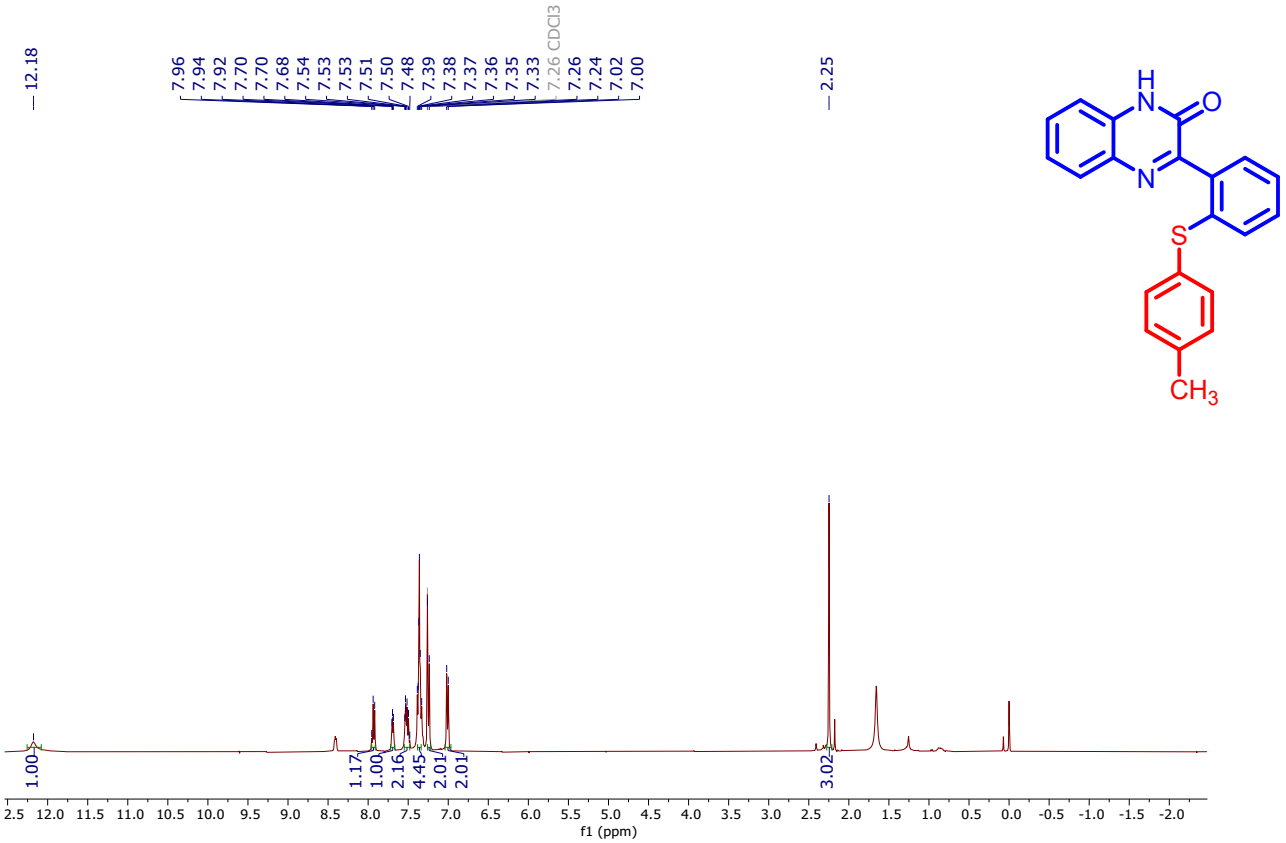


Figure 67: ^{1}H NMR spectrum of compound **5r** ($CDCl_3$, 400 MHz)

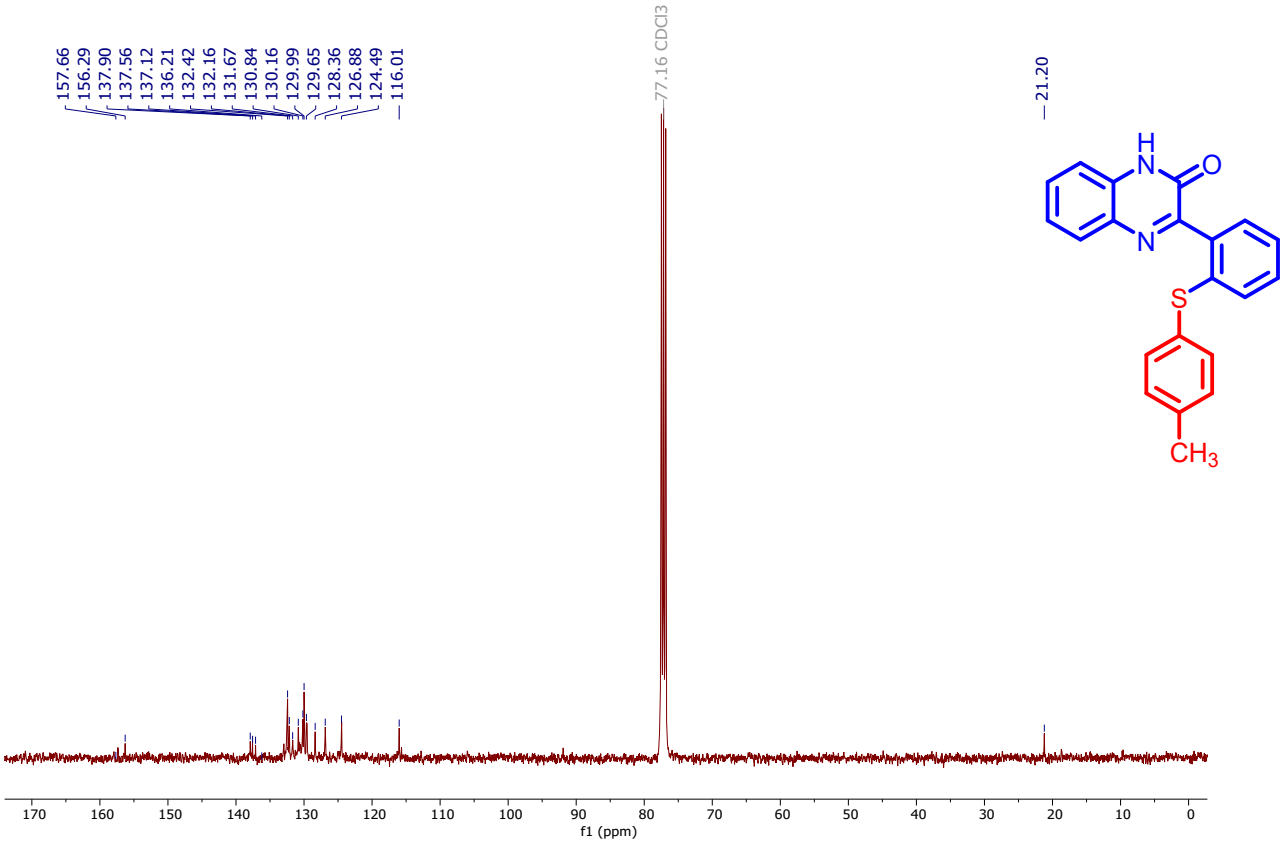


Figure 68: ^{13}C NMR spectrum of compound **5r** ($CDCl_3$, 100 MHz)

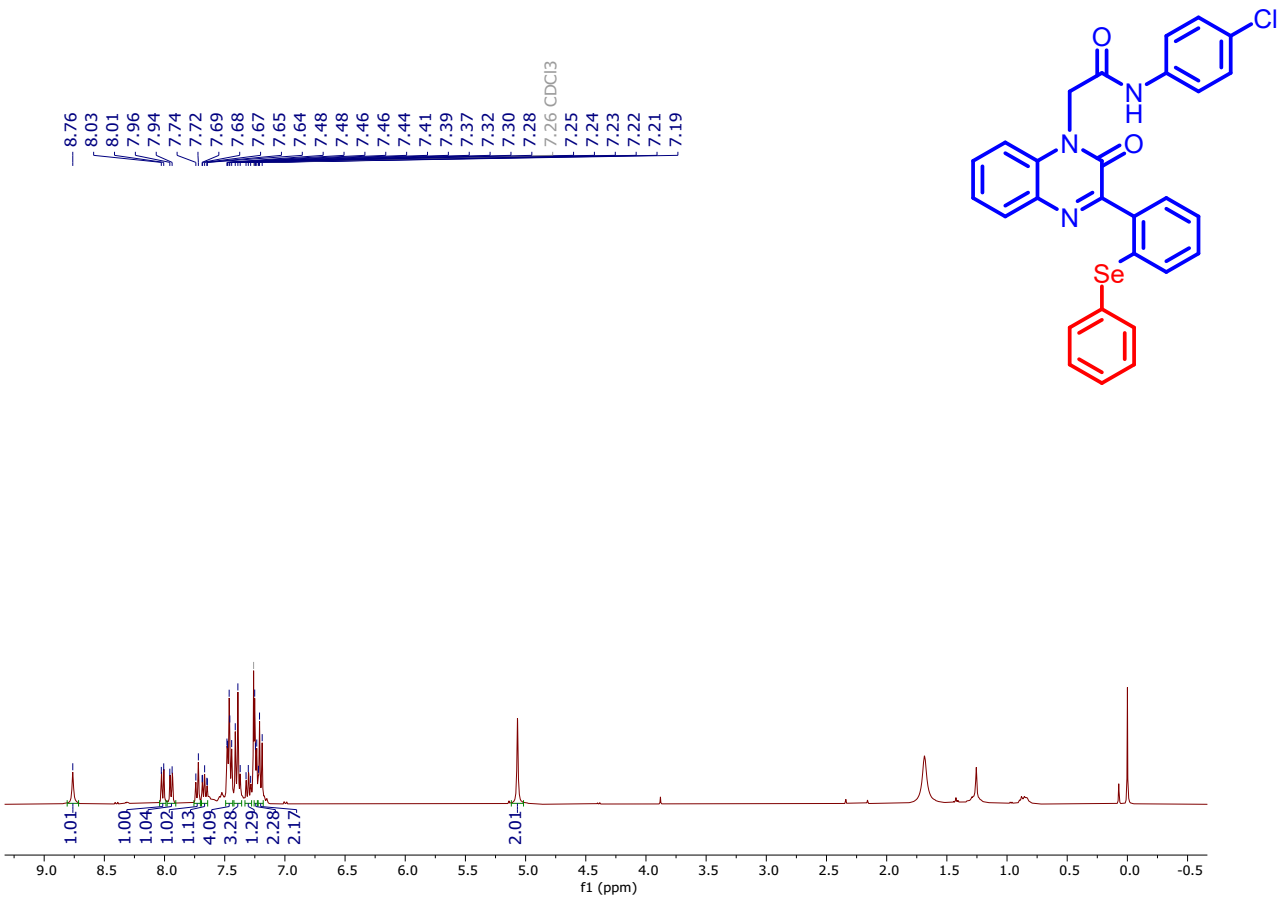


Figure 69: ^{1}H NMR spectrum of compound **7** ($CDCl_3$, 400 MHz)

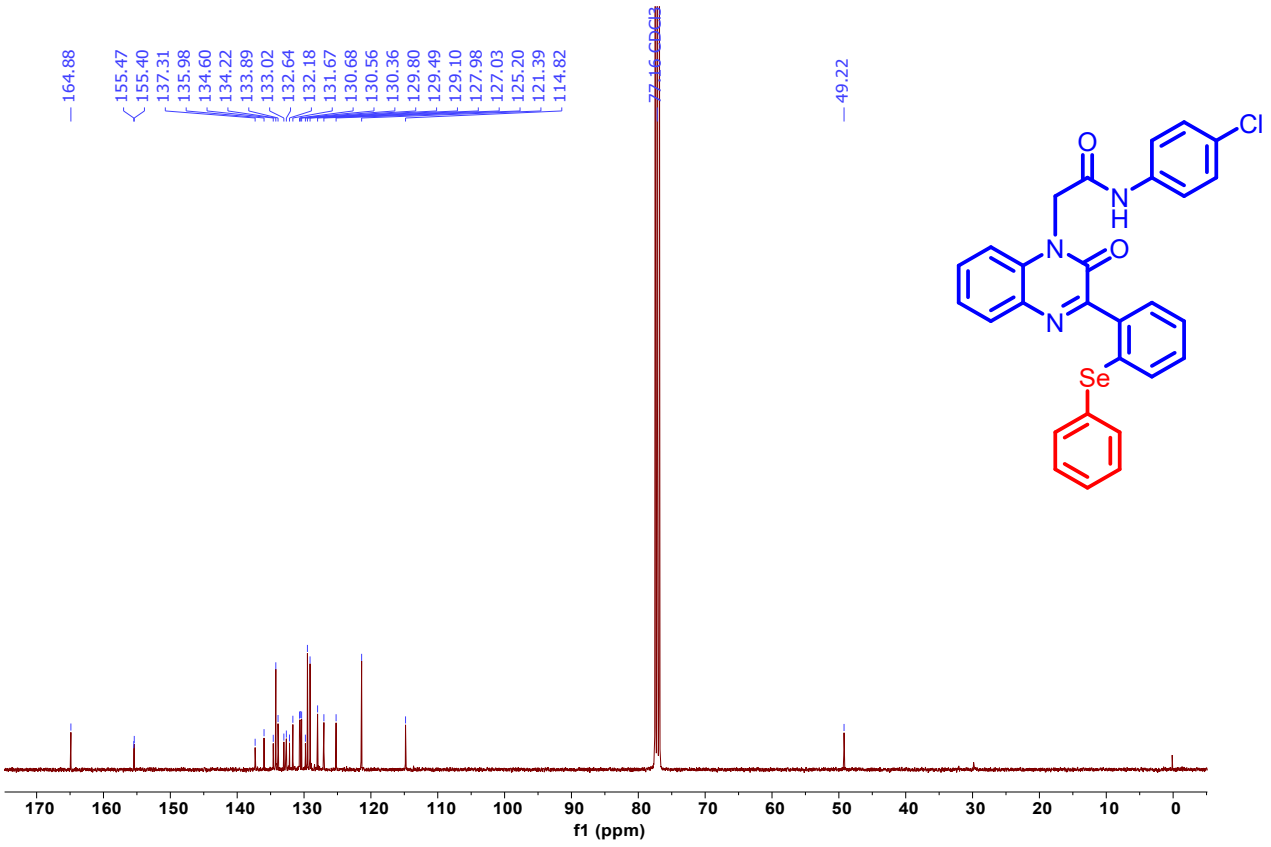


Figure 70: ^{13}C NMR spectrum of compound **7** ($CDCl_3$, 100 MHz)

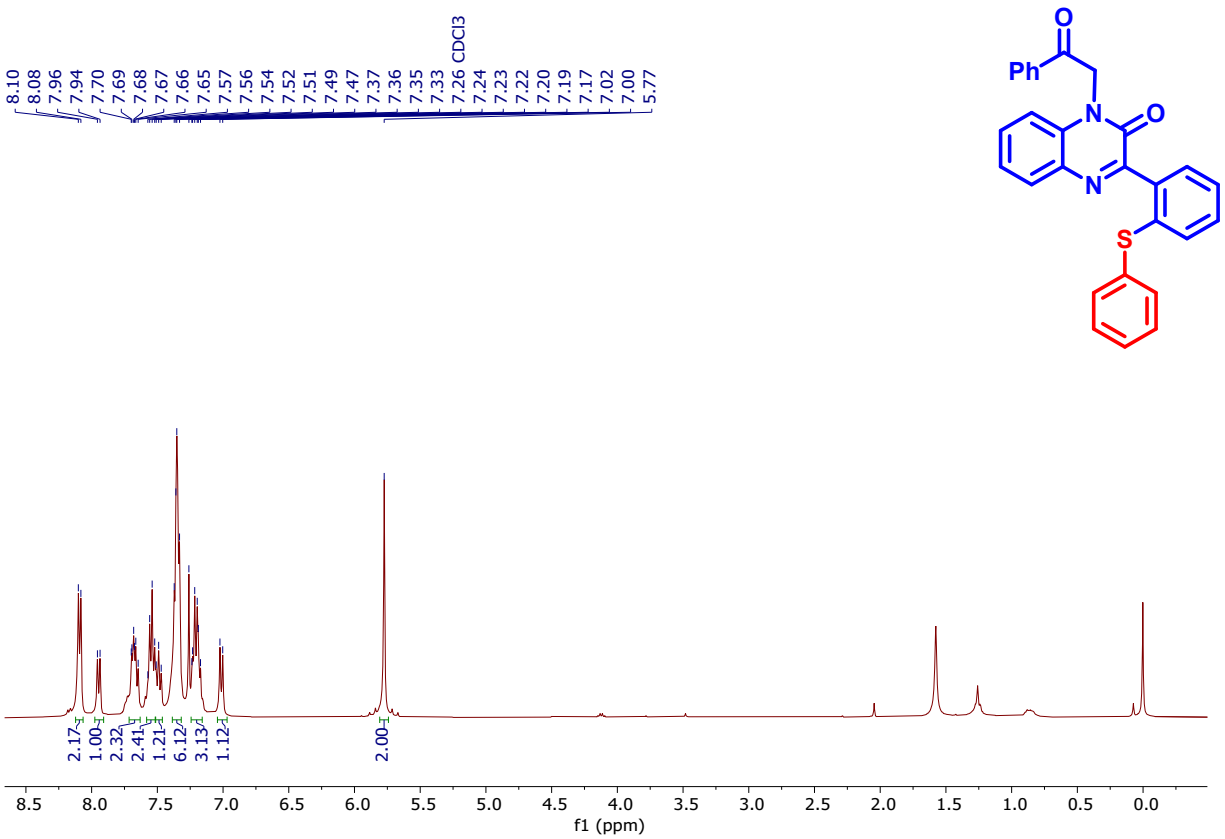


Figure 71: ^{1}H NMR spectrum of compound **10** ($CDCl_3$, 400 MHz)

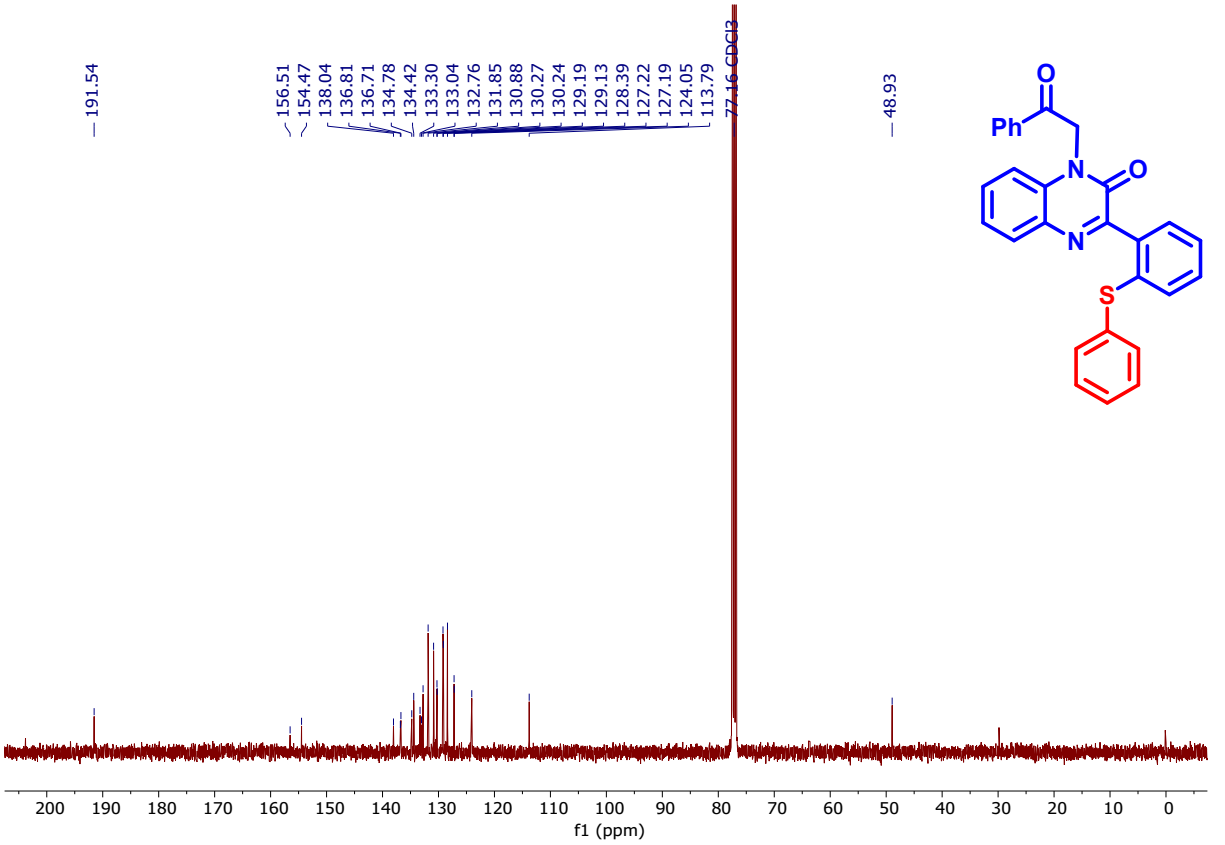


Figure 72: ^{13}C NMR spectrum of compound **10** ($CDCl_3$, 100 MHz)

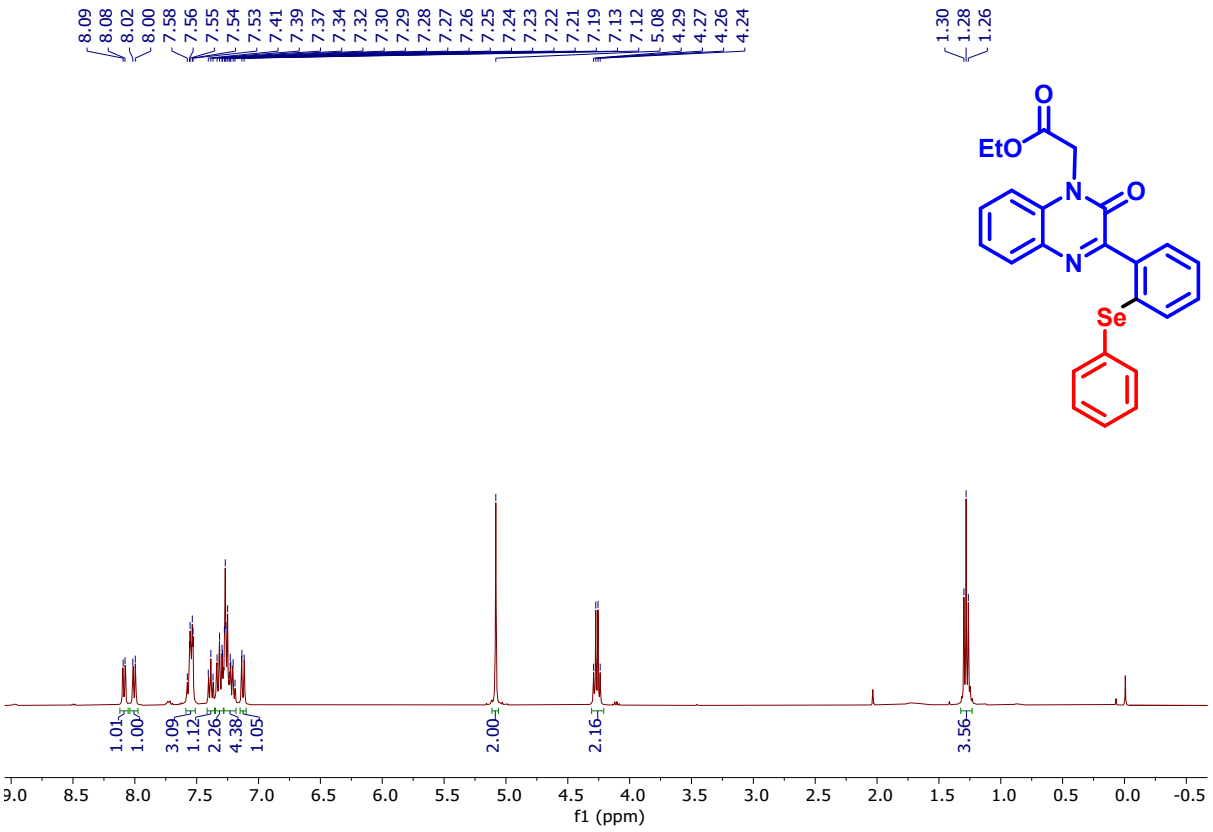


Figure 73: ^{1}H NMR spectrum of compound **11** ($CDCl_3$, 400 MHz)

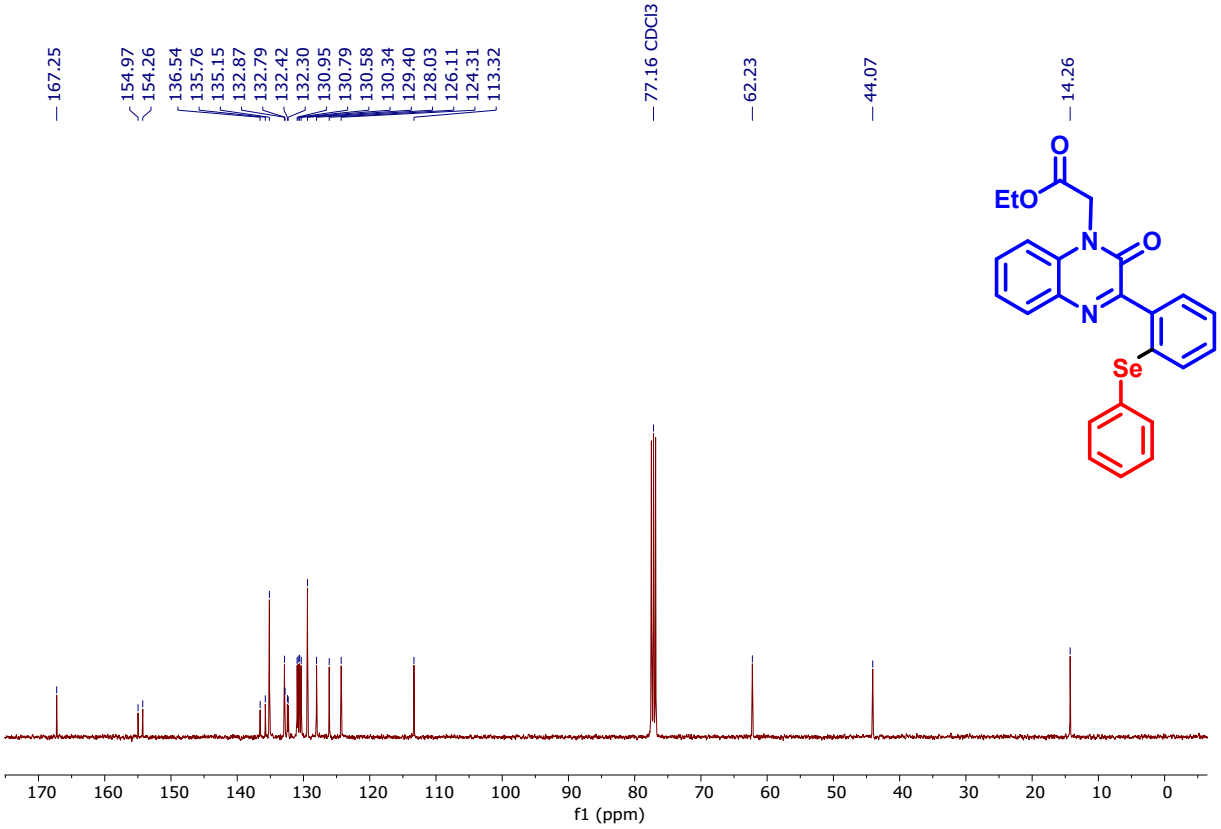


Figure 74: ^{13}C NMR spectrum of compound **11** ($CDCl_3$, 100 MHz)

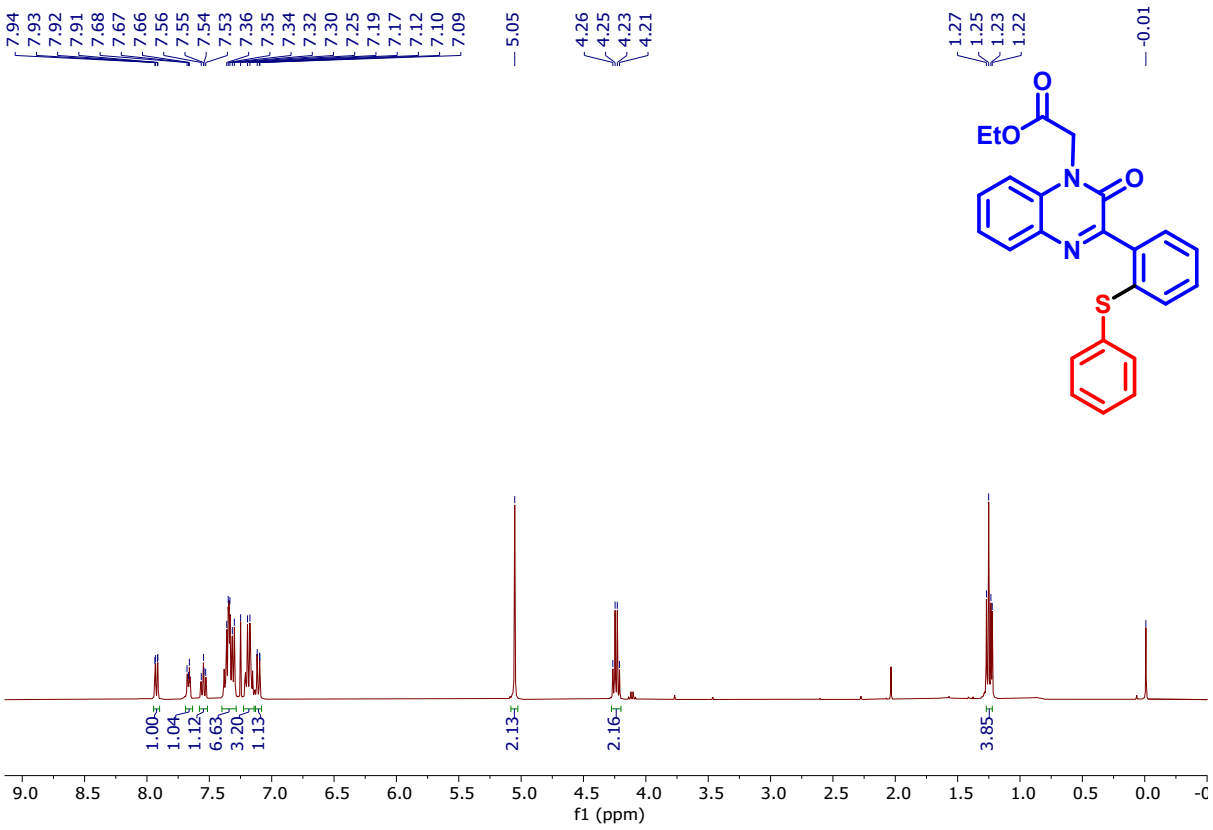


Figure 75: ^{1}H NMR spectrum of compound **12** ($CDCl_3$, 400 MHz)

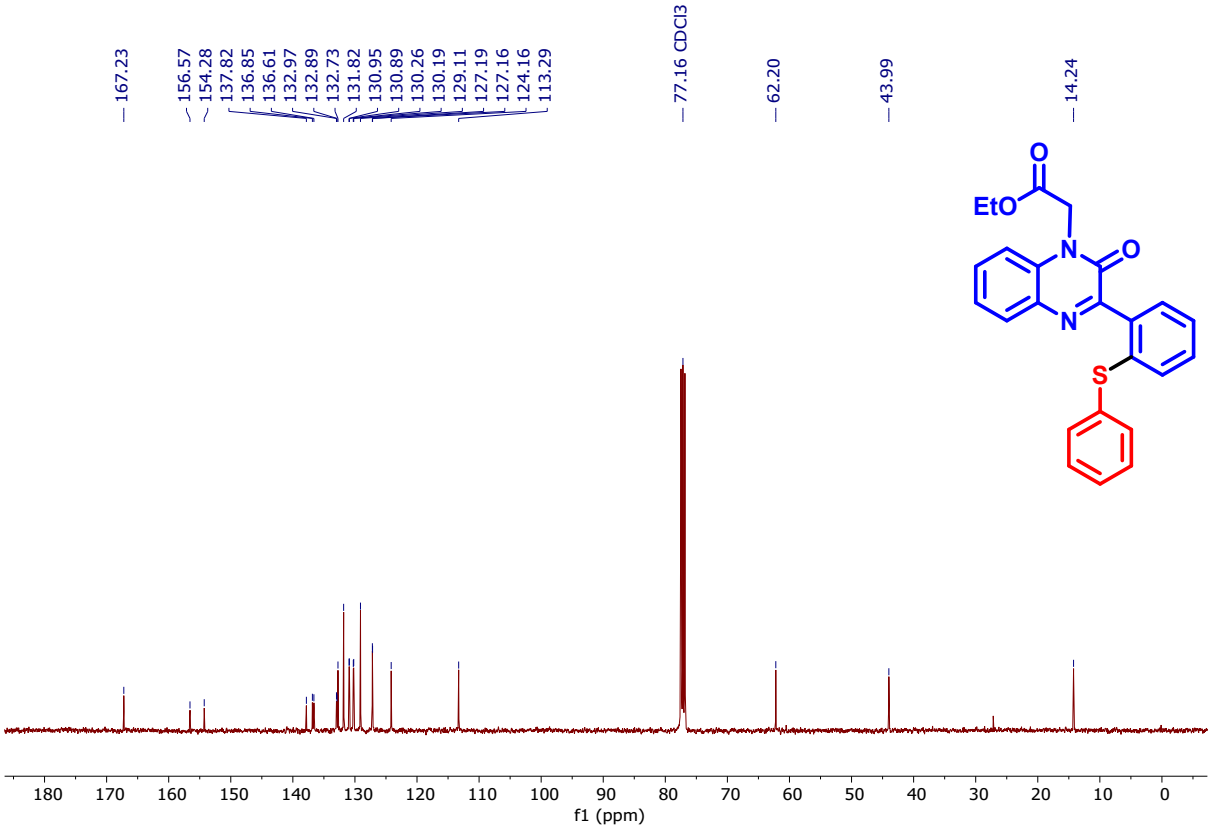


Figure 76: ^{13}C NMR spectrum of compound **12** ($CDCl_3$, 100 MHz)

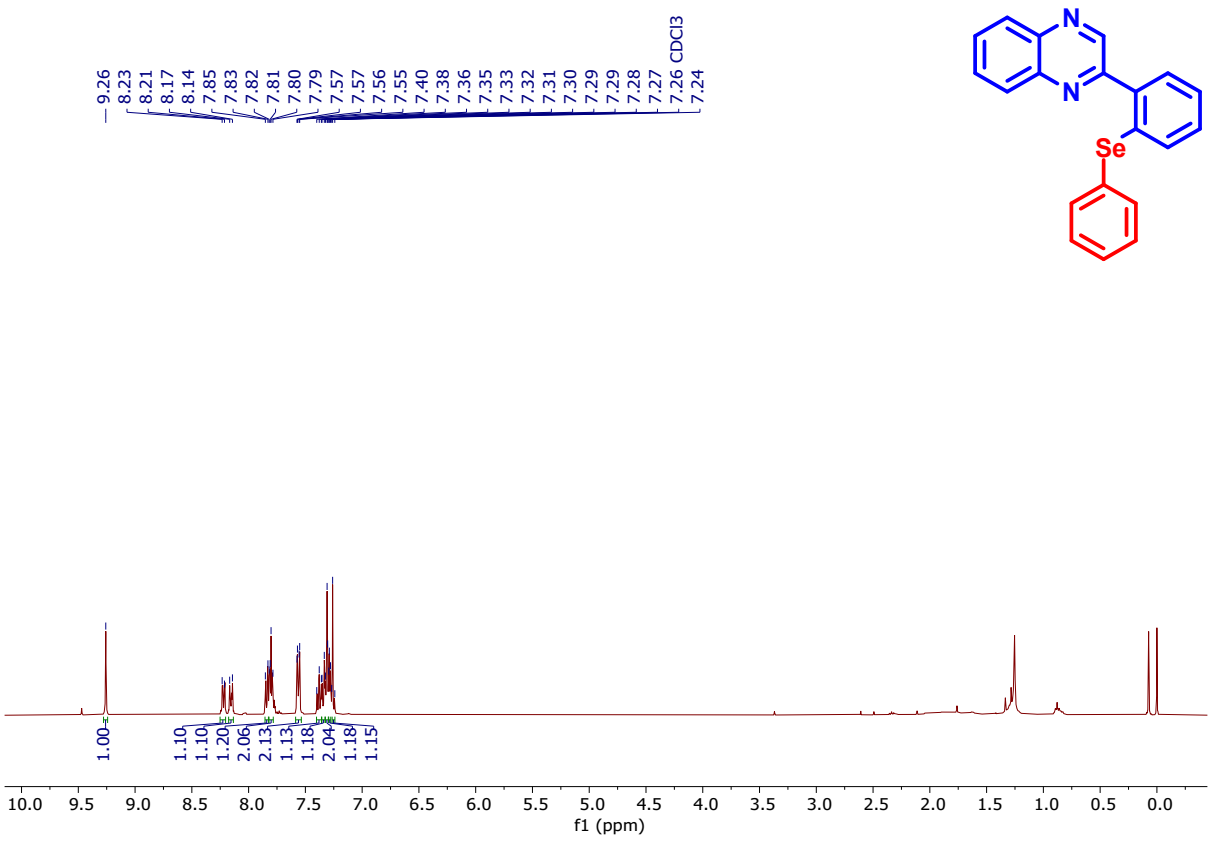


Figure 77: ^{1}H NMR spectrum of compound **14** ($CDCl_3$, 400 MHz)

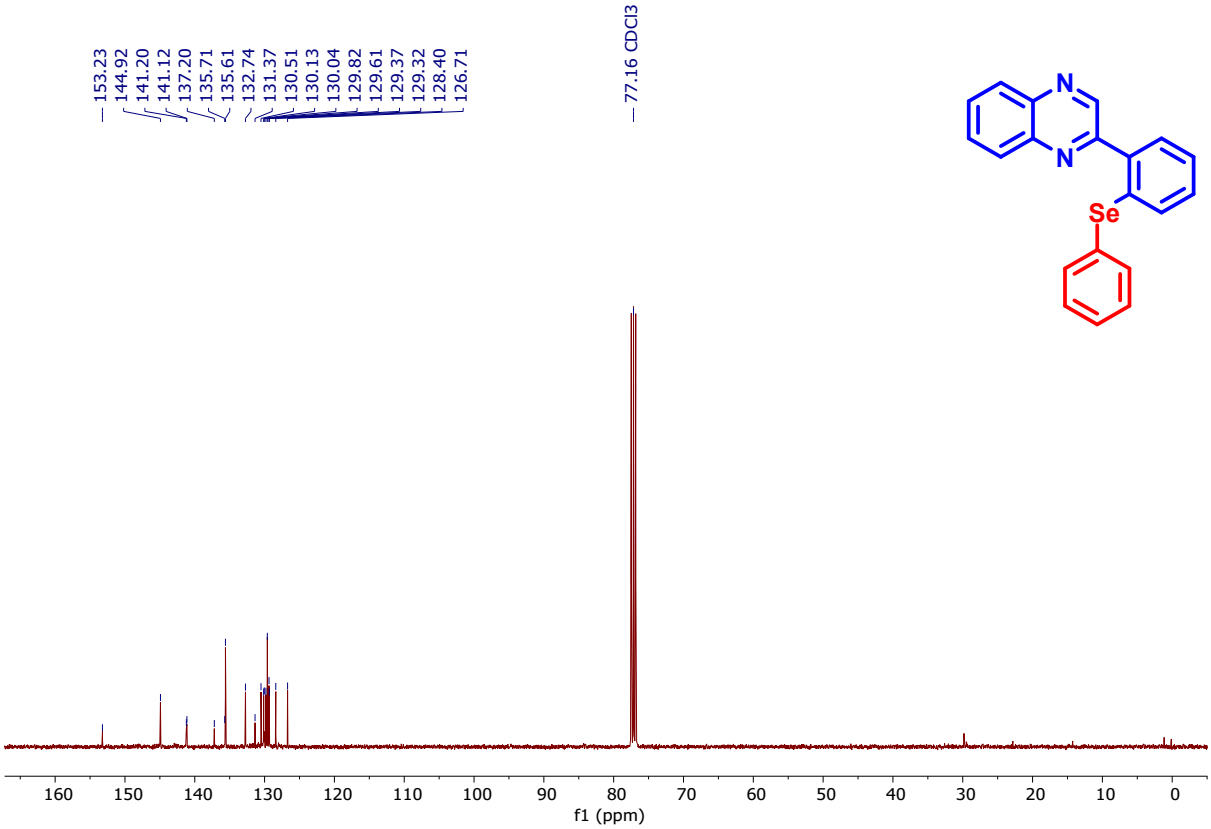


Figure 78: ^{13}C NMR spectrum of compound **14** ($CDCl_3$, 100 MHz)

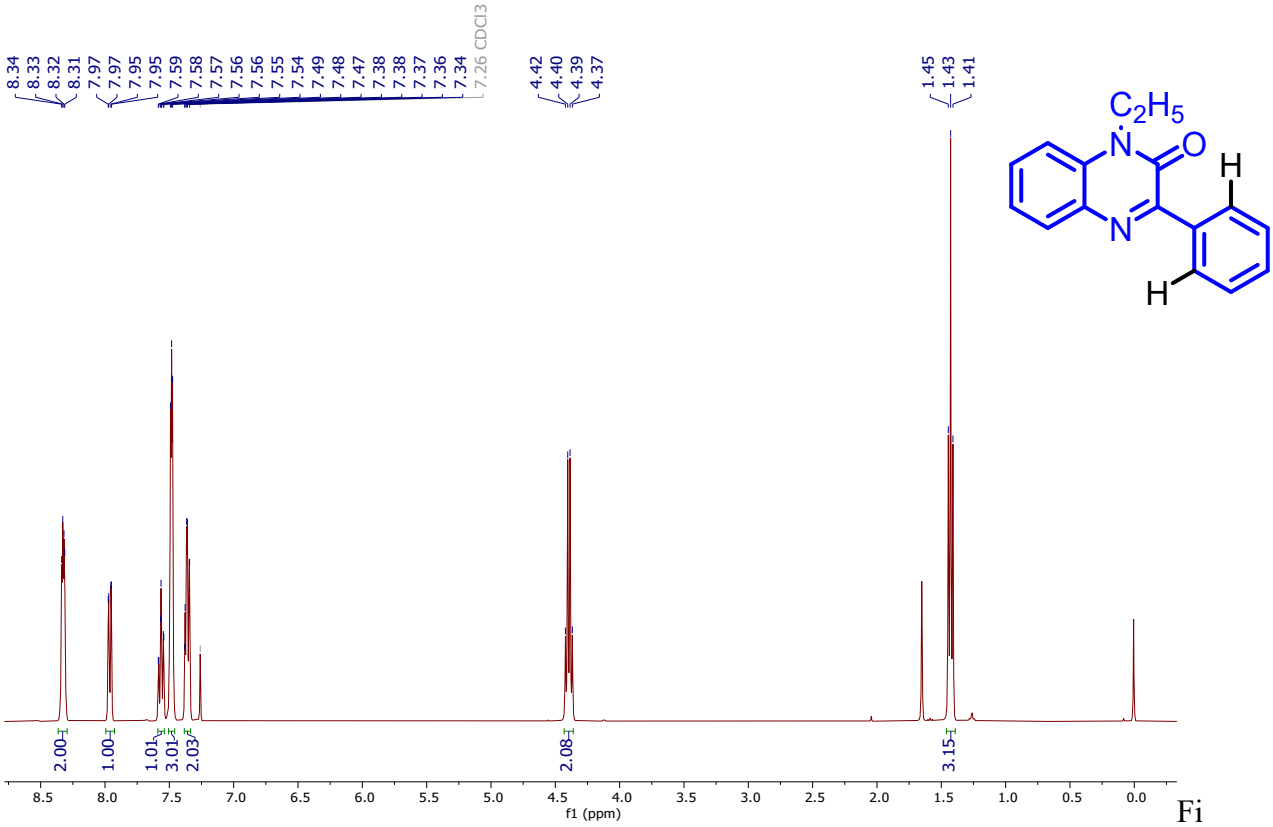


Figure 79. Standard ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$)

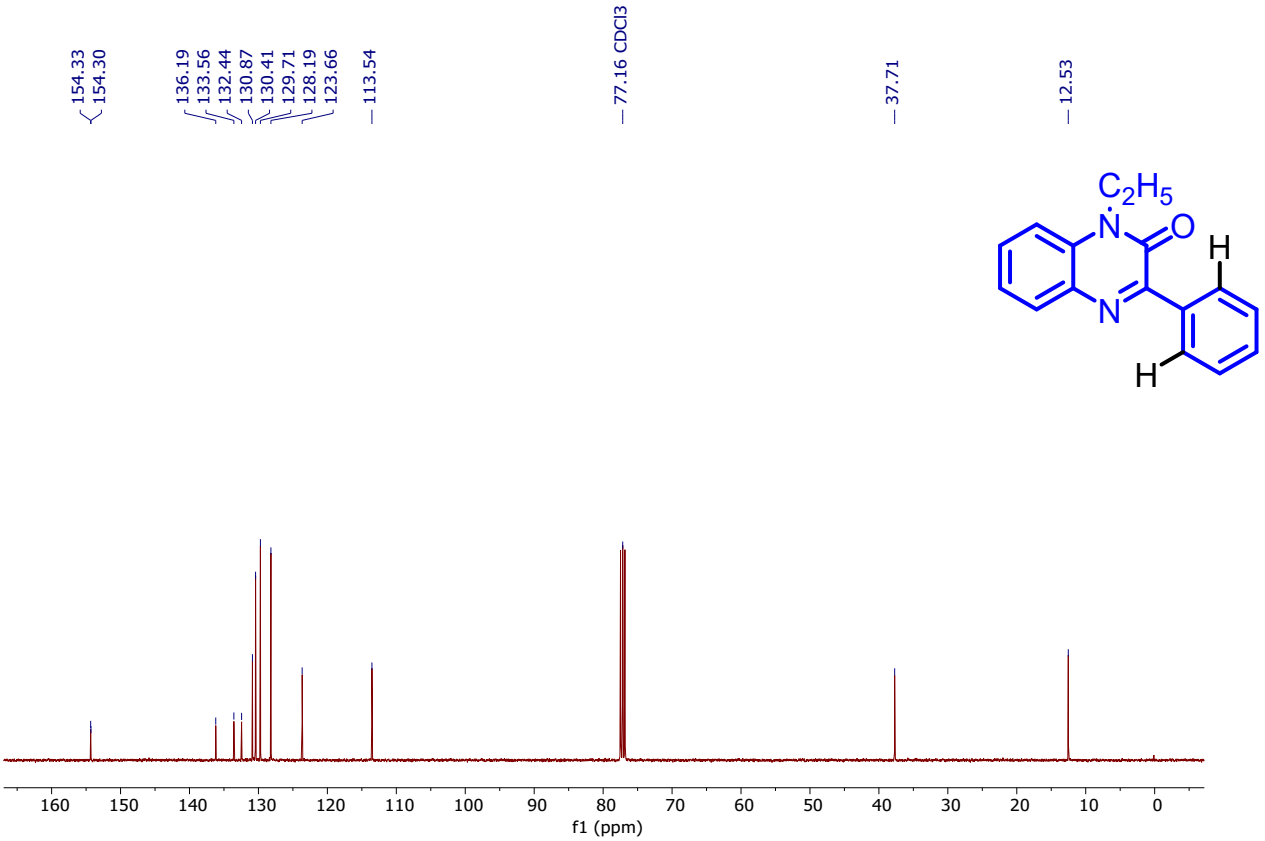


Figure 80: ^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100 MHz)

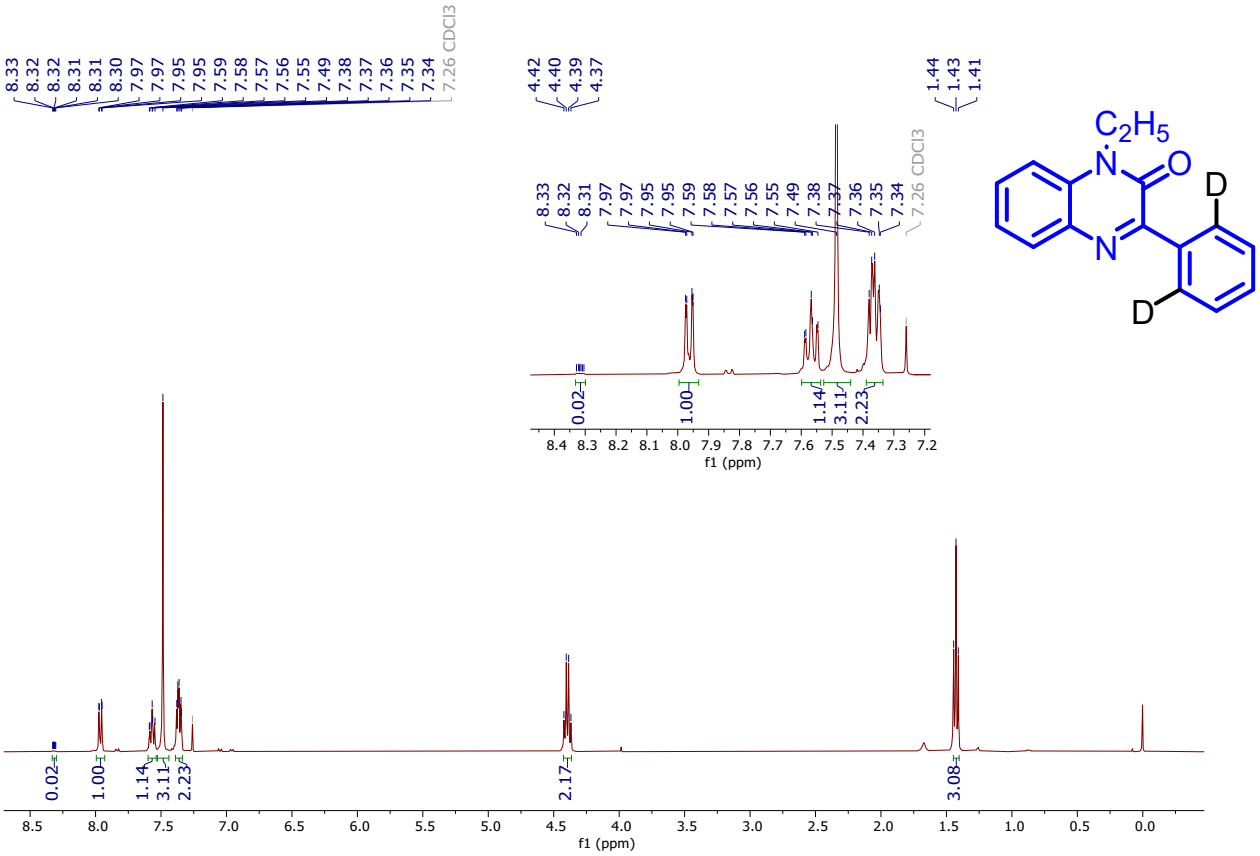


Figure 81: ^{1}H NMR spectrum of compound **1a-[D$_2$]** ($CDCl_3$, 400 MHz)

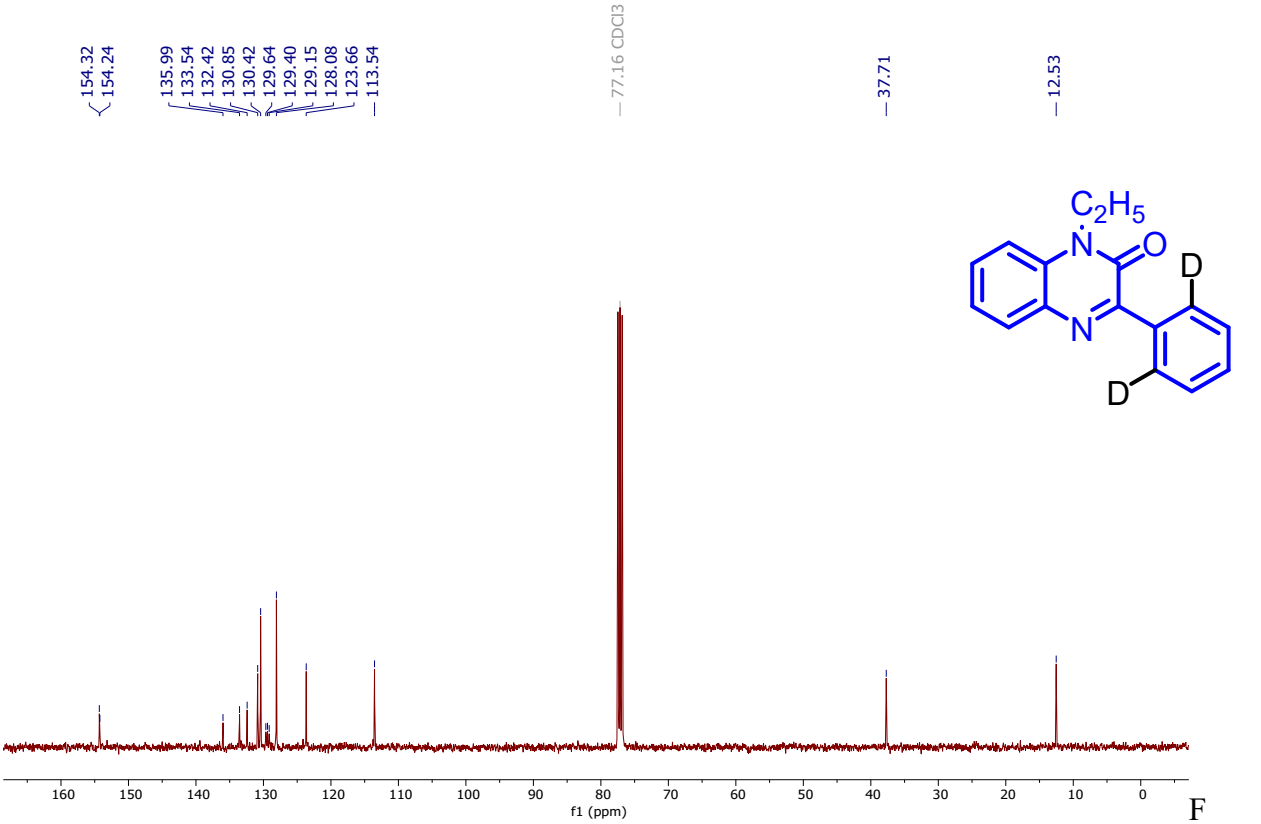


Figure 82: ^{13}C NMR spectrum of compound **1a-[D$_2$]** ($CDCl_3$, 100 MHz)

5. Investigation of deuterium kinetic isotope effects

5.1 Preparation of deuterium-labelled 1-ethyl-3-phenylquinoxalin-2(1H)-one and calculation of percentage purity (3a [D_2])

The compound deuterium labelled compound **3a-[D_2]** was prepared using the same procedure as was used for the standard reaction except that the coupling partner diphenyl diselenide was not added and that the reaction was carried out in D_2O instead of water.

The purity of the deuterium labelling of **1a-[D_2]** (Figure 81) was determined by ^{1}H NMR spectroscopy viz-a viz the standard ^{1}H NMR spectrum of **1a** (Figure 79)[6].

Fig. 79 Fig. 81

Amount of **1a-D_{ortho}**, ie **1a-[D_2]** = $\frac{(2.00 - 0.02)}{2.00}$ x 100 % = 99 % for **1a-[D_2]** purity

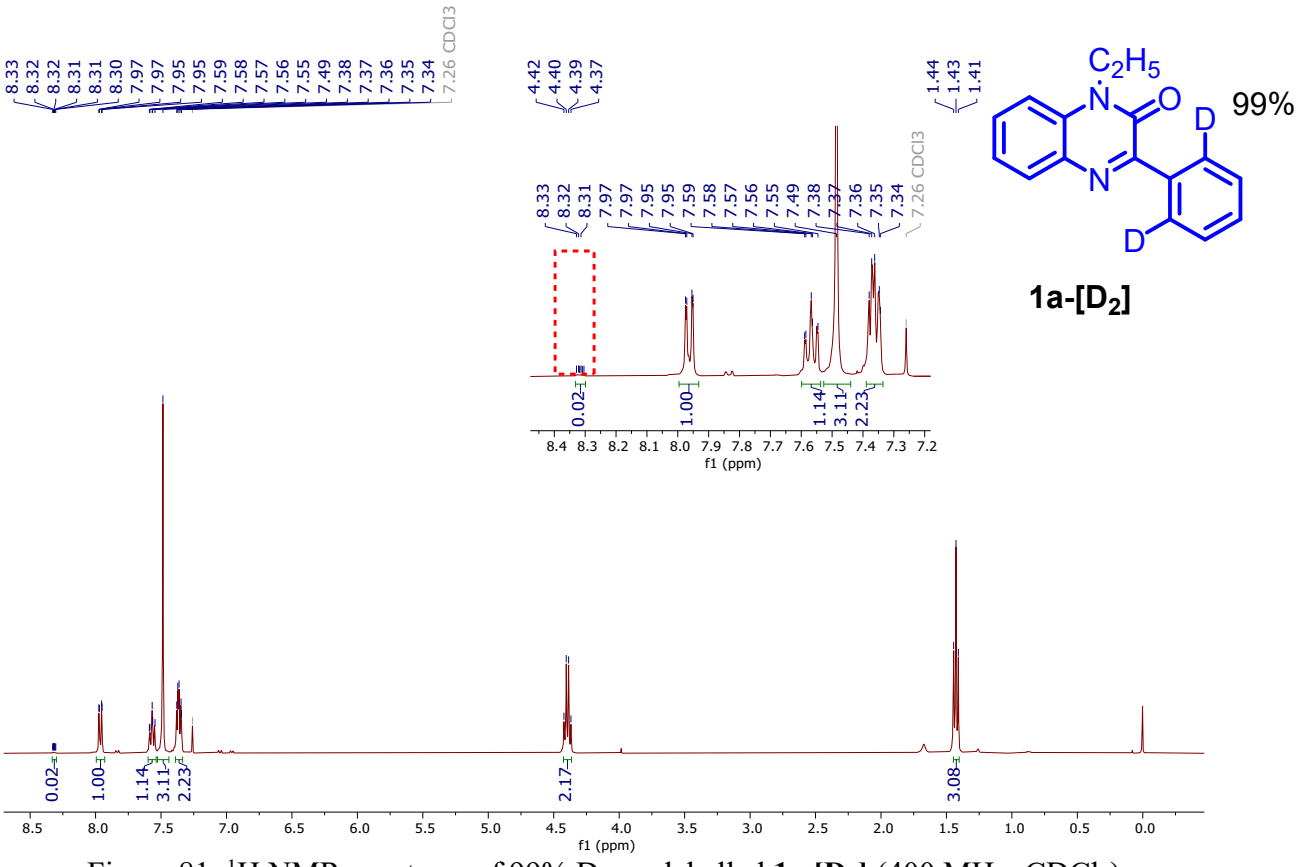


Figure 81. ^{1}H NMR spectrum of 99% D_{ortho} -labelled **1a [D_2]** (400 MHz, $CDCl_3$)

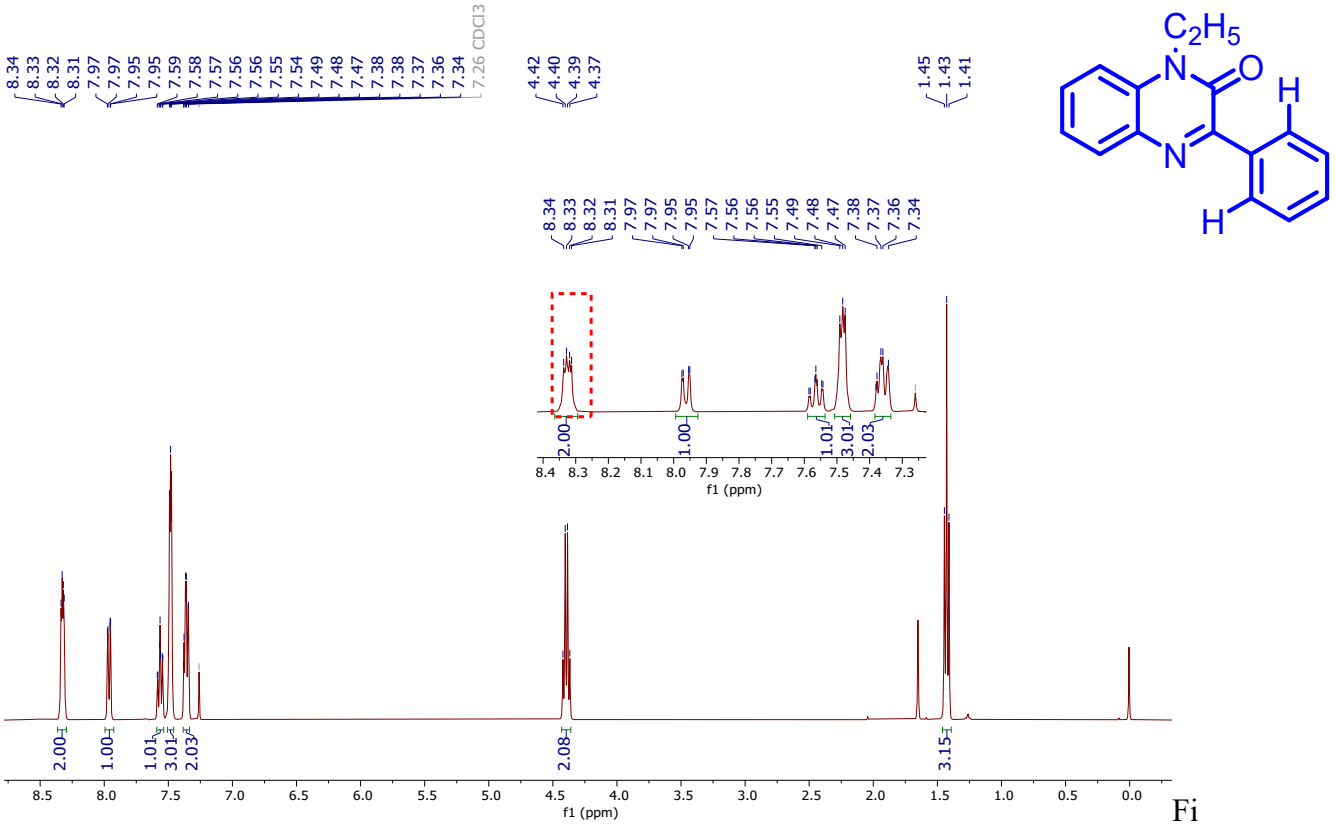


Figure 79. Standard ^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$).

5.2 H/D exchange experiment in the presence of **2a**.

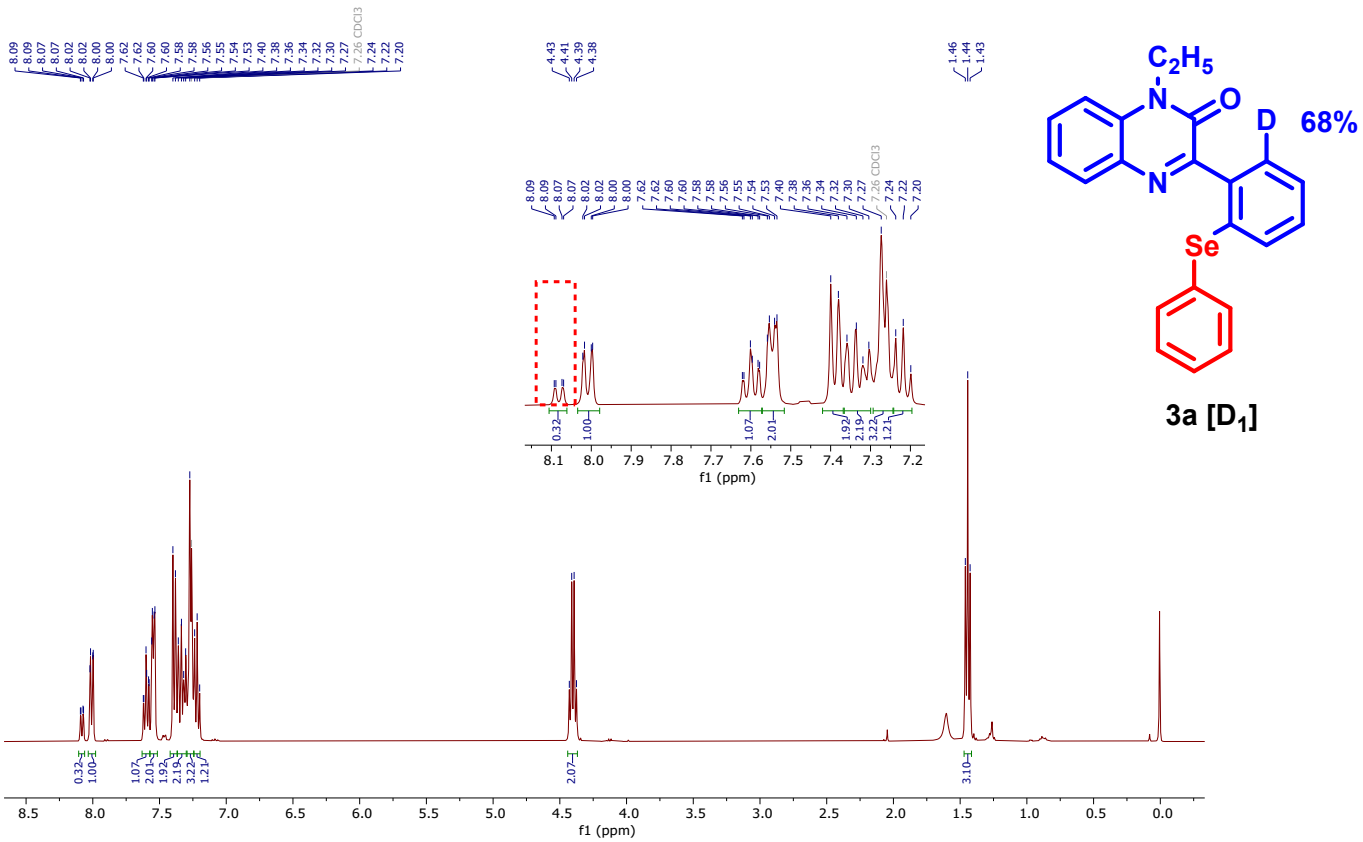


Figure 83. ^{1}H NMR spectrum of compound **3a [D_1]** ($CDCl_3$, 400 MHz) with 68% deuteration

5.3 Deuterium kinetic isotope studies

Procedure for Intermolecular Competition: In an oven-dried screw-capped 10 mL reaction vial with a stirring bar was charged with a mixture of **1a** (0.0793 mmol, 1.0 equiv.) and/or **1a [D_2] (**99% deuterated**)** (0.0793 mmol, 1.0 equiv.), diphenyl diselenide **2a** (0.1586 mmol, 2 equiv.), silver triflimide (60 mol%), Ag_2CO_3 (0.0793 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%) and 0.8 mL distilled water as solvent. The reaction vial was closed and kept for stirring in an oil bath by heating at 110 °C (oil bath temperature). After 80 minutes, the reaction was stopped, and the reaction mixture was cooled to ambient temperature. Water was decanted and the reaction mixture was directly charged into the silica gel column and purification was done using n-hexane /ethyl acetate as eluent to afford a mixture of **3a [D_1]** and **3a**. (See figures 85 and 84 respectively). The intermolecular $\boldsymbol{k_H/k_D}$ values were eventually determined by ^{1}H NMR spectroscopy compared to the standard ^{1}H NMR spectrum of **3a** (Figure 2).

Procedure for the Parallel reactions: In oven-dried screw-capped 10 mL reaction vials with a stirring bar were charged with a mixture of **1a** (0.0793 mmol, 1.0 equiv.) or **1a [D_2] (**99% deuterated**)** (0.0793 mmol, 1.0 equiv.), diphenyl diselenide **2a** (0.1586 mmol, 2 equiv.), silver triflimide (60 mol%), Ag_2CO_3 (0.0793 mmol, 1 equiv.), $[Cp^*RhCl_2]_2$ (5 mol%) and 0.8 mL distilled water as solvent. The reaction vials were closed and kept for stirring in the same oil bath by heating at 110 °C (oil bath temperature). After 80 minutes, the reactions were stopped and the reaction mixture were cooled to ambient temperature. Water was decanted and the reaction mixtures were mixed together and the resultant reaction mixture was directly charged into the silica gel column and purification was done using n-hexane /ethyl acetate as eluent to afford a mixture of **3a [D_1]** and **3a**. (See figures 86). The $\boldsymbol{k_H/k_D}$ values for the Parallel Reaction was eventually determined by ^{1}H NMR spectroscopy compared to the standard ^{1}H NMR spectrum of **3a** (Figure 2).

The $\boldsymbol{k_H/k_D}$ calculation based on the reaction of 1a and 1a [D_2] with 2a:

Assume the molar fraction of **1a** is X and that of **1a [D_2]** is (1 - X)

The pattern between 8.05 and 8.11 ppm was employed to calculate $\boldsymbol{k_H/k_D}$:

for Intermolecular Competition Reaction

Fig.2 Fig. 84 Fig. 85

X + 0.21 (1-X) = 0.75

X= 0.6835
1-X= 0.3164
k_H/k_D= 2.16

For Parallel Reaction

Fig.2 Fig. 84 Fig. 86

X + 0.21(1-X) = 0.76

X= 0.6962
1-X= 0.3037
k_H/k_D= 2.29

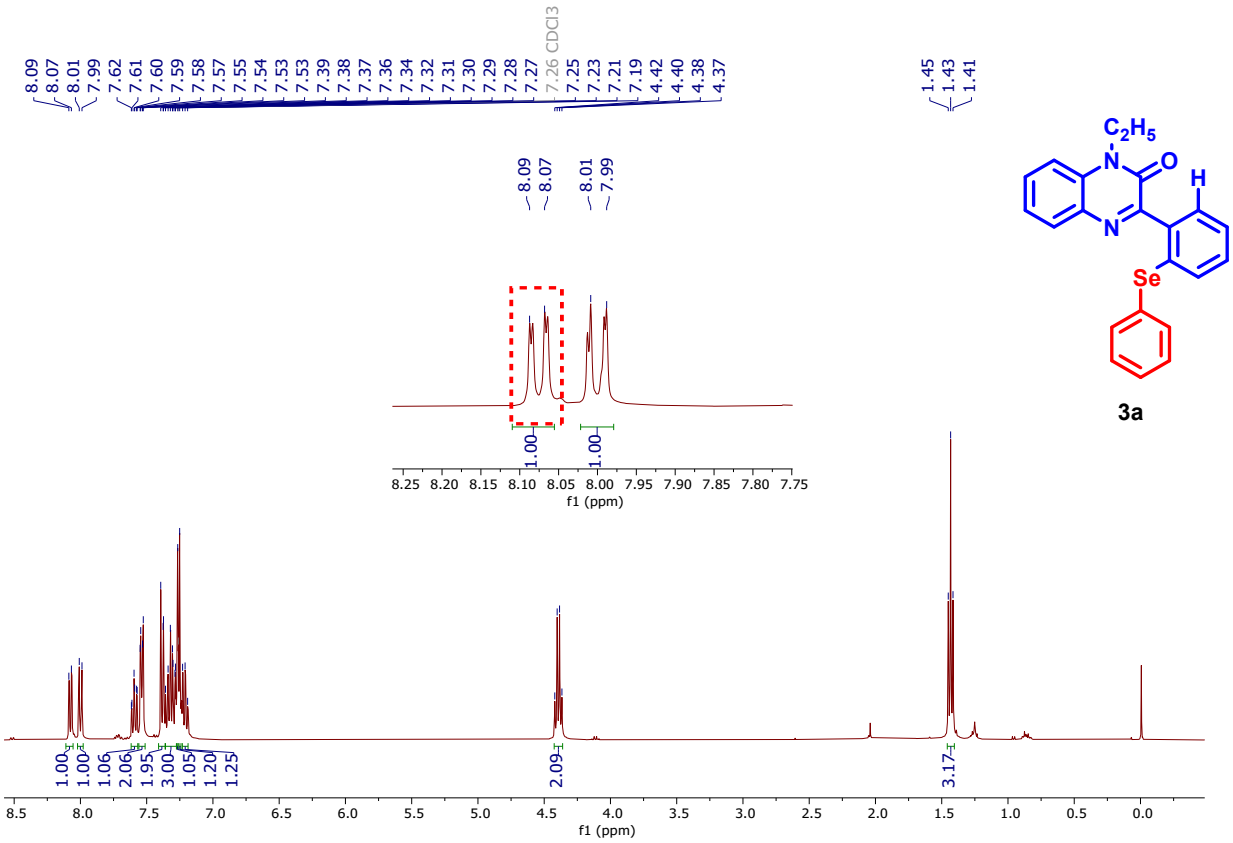


Figure 2. Standard ^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)

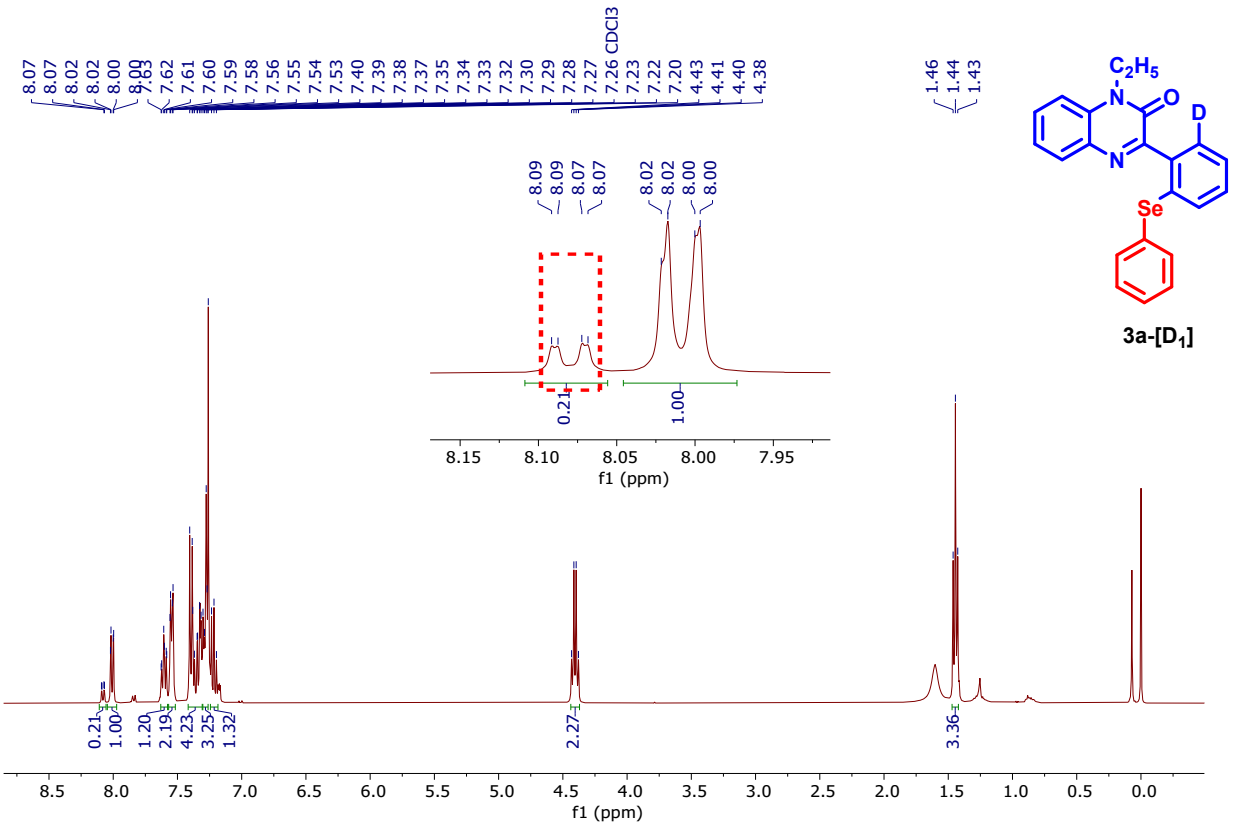


Figure 84. ^{1}H NMR spectrum of **3a [D_1]** (400 MHz, $CDCl_3$)

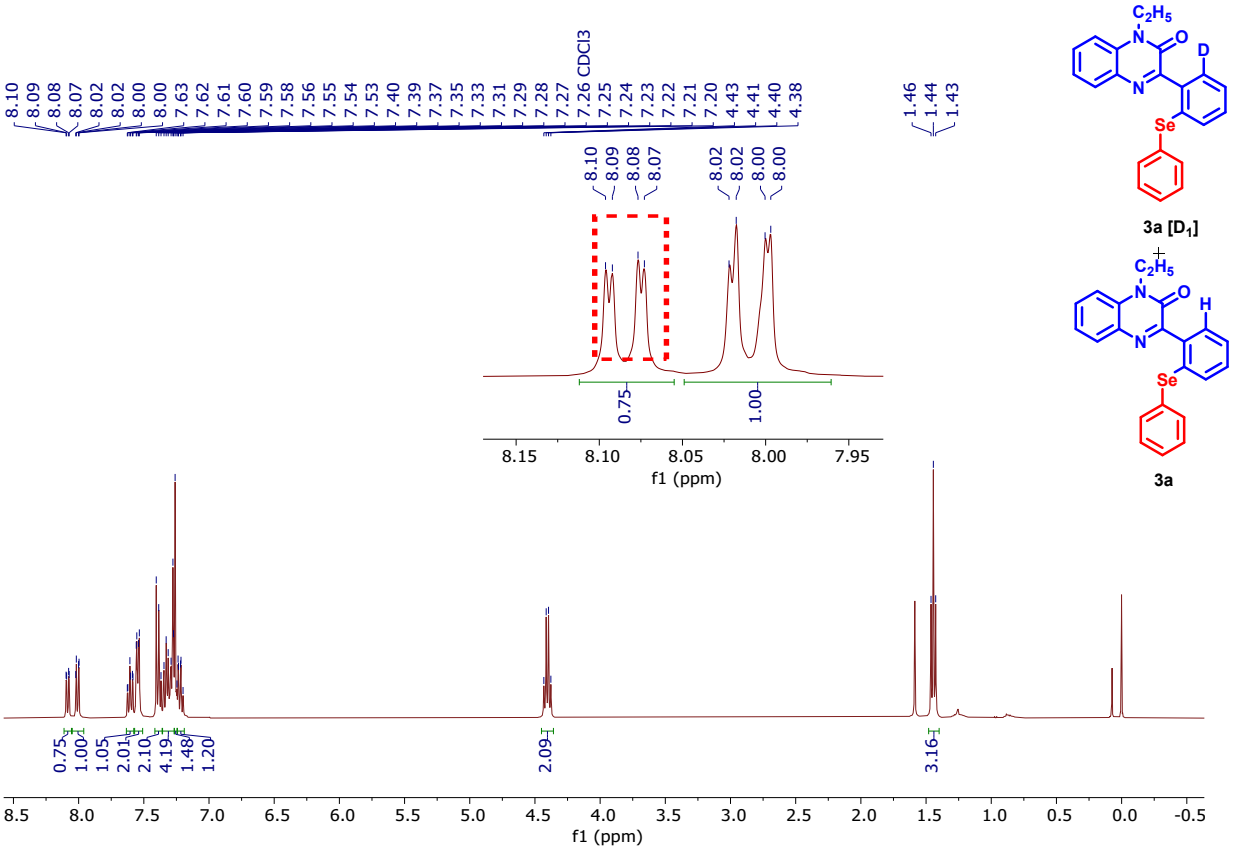


Figure 85. ^{1}H NMR spectrum of **3a [D_1]** (400 MHz, $CDCl_3$)

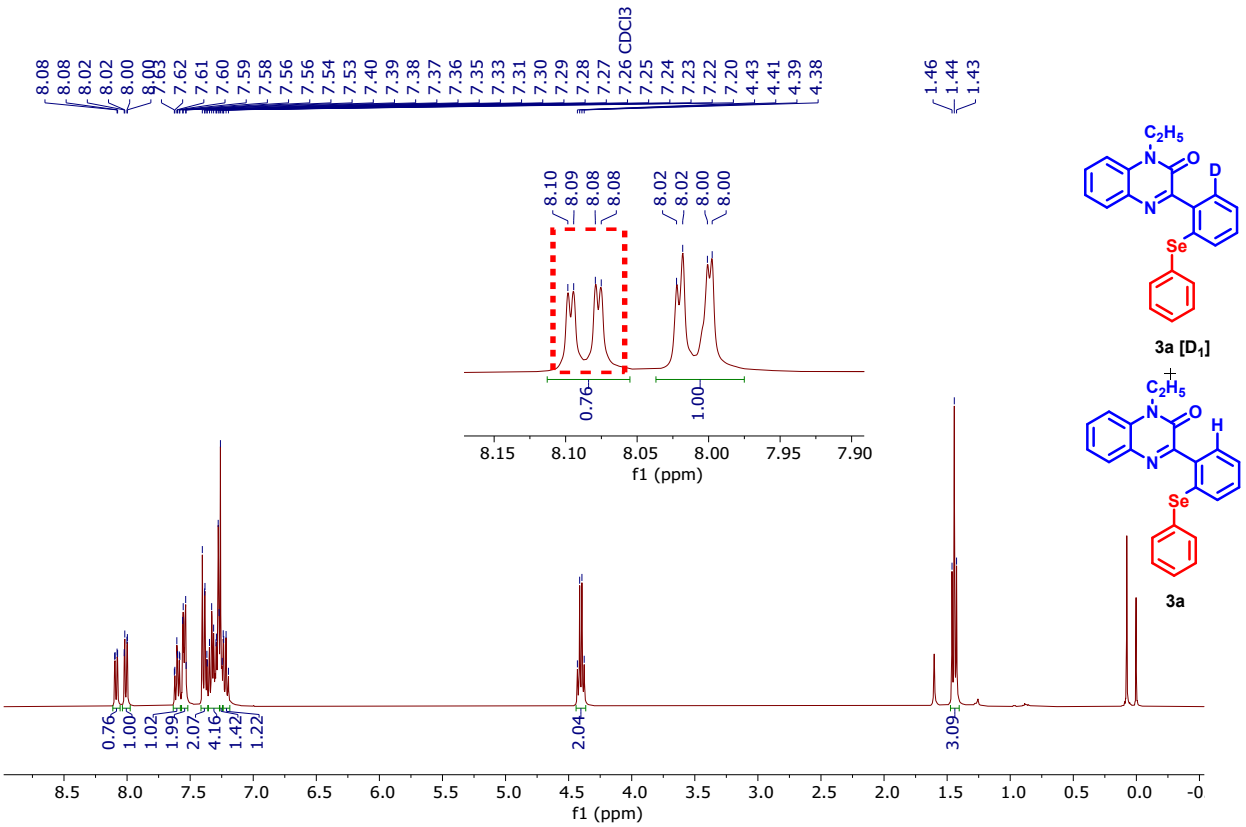


Figure 86. ^{1}H NMR spectrum of **3a [D_1]** (400 MHz, $CDCl_3$)

6. X-ray Structure of 3a, 3c[7-9]

The single crystals were grown by slow evaporation at room temperature using petroleum: ethyl acetate (2:1, v/v) for compounds **3a** and **3c**. The data for X-ray intensity were collected at room temperature (298 K) on Bruker CCD diffractometer and MoKα radiation having wavelength 0.71073 was used. The structures were solved by SHELXL. All the non-hydrogens were refined by full matrix least square on F2 using SHELXL-2018/3. The ORTEP diagrams were generated using the Mercury. The CCDC numbers are 2214690 and 2215006 respectively for compound 3a and 3c. The supplementary crystallographic data can be obtained via CCDC www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S3. Crystal data and structure refinement for **3a** and **3b.**

Identification code	**3a**	**3b**
Emperical Formula	C_{22} H_{18} N_2 O Se	C_{22} H_{17} F N_2 O Se
Formula weight	405.34	423.33
Temperature	298 K	298 K
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P 21/n	P-1
Unit cell dimentions	a/Å = 11.2232 (3) b/Å = 10.9897 (2) c/Å = 15.9803 (4) α/° = 90 β/° = 109.770 (3) γ/° = 90	a/Å = 9.8962 (7) b/Å = 10.3482 (6) c/Å = 21.7111 (10) α/° = 99.181 (5) β/° = 91.413 (5) γ/° = 114.770 (7)
volume	1854.83	1982.6
Z	4	4
Density (calculated)	1.452	1.418
Absorption coefficient	2.037	1.916
F(000)	824	856
Crystal size	0.210 x 0.190 x 0.180 mm^3	0.210 x 0.190 x 0.180 mm^3
Theta ranges	3.3-29.2	3.14-23.9560
Reflections collected	17099	20772
Independent Reflections	4533	9130 [R(int) = 0.0539]
Index ranges	-14≤ h≤ 14 -14 ≤ k ≤ 14 -21≤ l≤ 21	-13 ≤ h≤ 12 -13 ≤ k ≤ 12 -27 ≤ l≤ 27
Completeness of data	0.905	0.848
Absorption correction	none	none
Refinement method	SHELXL-2018/3 (Sheldrick, 2018)	SHELXL-2018/3 (Sheldrick, 2018)
Data/restraint/parameters	4533/0/235	9130/0/489
Goodness of fit on F^2	1.083	1.017
Final R indices	R1=0.0335, wR2=0.761	R1=0.0539, wR2=0.0935

[I>2sigma(I)]		
R indices (all data)	R1=0.0491, wR2=0.0835	R1=0.1233, wR2=0.1266
Absolute structure parameter	235	489
Largest diff. peak and hole [e Å^{-3}]	0.519/-0.356	0.530/-0.574

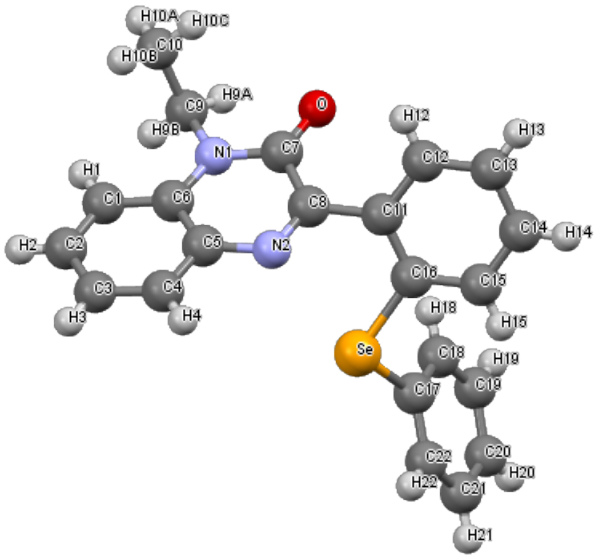


Figure 87. ORTEP diagram of the compound **3a (CCDC 2214690)**.

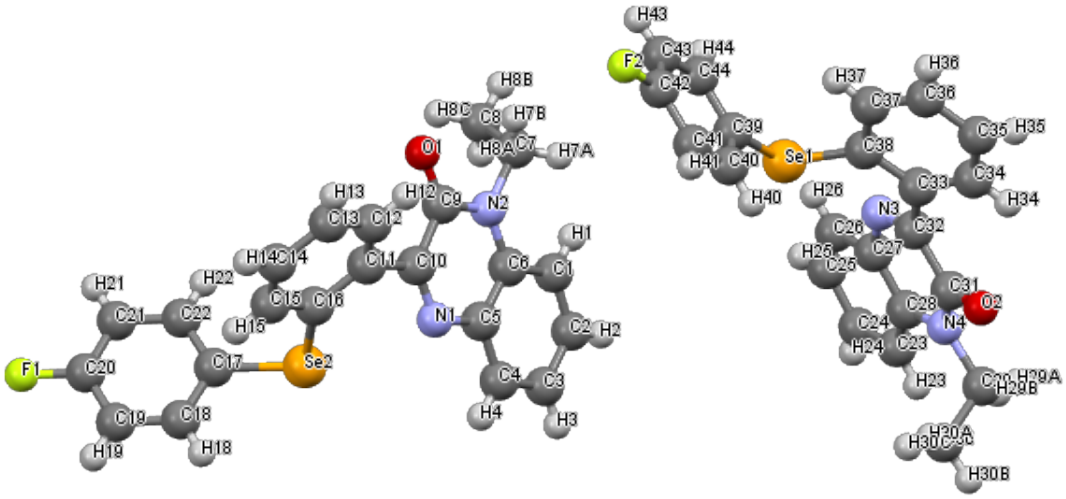


Figure 88. ORTEP diagram of the compound **3b (CCDC 2215006)**.

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