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Electronic Supplementary Information

Quinoxaline: a new directing group for *ortho* C-H alkenylation / intramolecular *ortho* C–H cycloamination under open air leading to bioactive polynuclear *N*-heteroarenes

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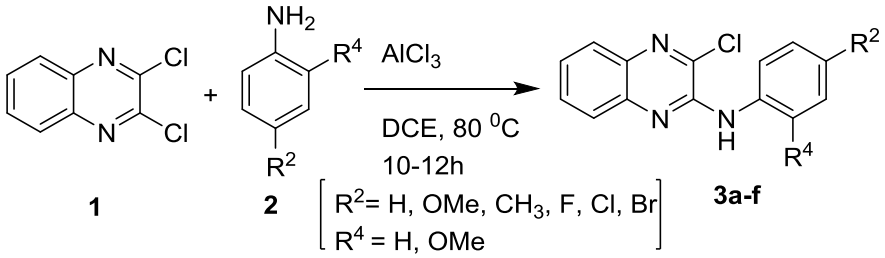
Chemistry

General methods: Unless stated otherwise, reactions were performed under nitrogen atmosphere using oven dried glassware. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (230-400 mesh) using distilled hexane, ethyl acetate. ^{1}H NMR and ^{13}C NMR spectra were recodred in $CDCl_3$ or DMSO-d_6 solution by using 400 or 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), dd (doublet of doublet), td (triplet of doublet), t (triplet) and m (multiplet) as well as b (broad). Coupling constants (*J*) are given in hertz. MS spectra were obtained on a Agilent 6430 series Triple Quard LC-MS / MS spectrometer. Melting points (mp) were by using Buchi B-540 melting point apparatus and are uncorrected. Chromatographic purity by HPLC (Agilent 1200 series Chem Station software) was determined by using area normalization method and the condition specified in each case: column, mobile phase (range used), flow rate, detection wavelength, and retention times.

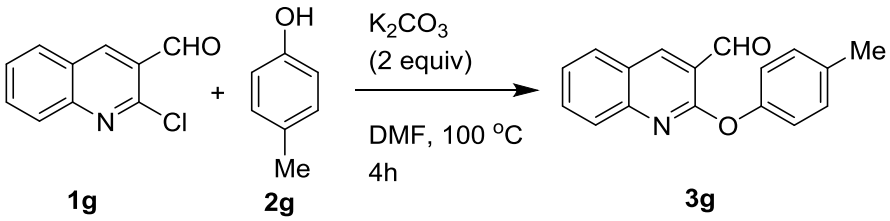
General Procedure for the preparation of 3-chloro-*N*-aryl substituted quinoxalin-2-amine (3a-f)[1]



A mixture of 2,3-dichloroquinoxaline **1** (1.0 mmol), an appropriate amine **2** (1.0 mmol) and $AlCl_3$ (1.25 mmol) in 1,2-dichloroethane (5mL) was stirred at 80°C for 10-12 h under a nitrogen atmosphere. After completion of the reaction, the mixture was cooled to room temperature, poured into ice-cold water (15 mL), stirred for 10 min and then extracted with ethylacetate (3 × 10 mL). The combined organic layers were washed with cold water (2 × 10 mL), brine (4mL) and dried over anhydrous Na_2SO_4 and concentrated under vacuum. The residue obtained was purified by column chromatography on silica gel (230-400 mesh) using

ethylacetate/hexane to give the desired product **3a-f**.

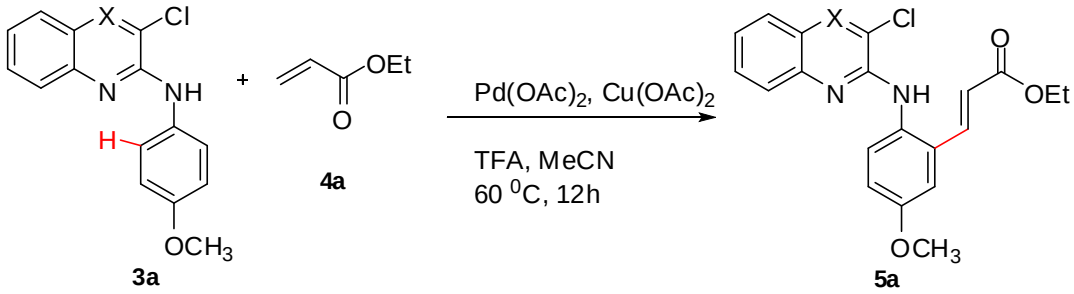
Typical procedure for the preparation of 2-(*p*-tolyloxy)quinoline-3-carbaldehyde (3g)[2]



1g **2g** **3g**

A100 mL round bottomed flask, fitted with a reflux condenser, was charged with a mixture of 2-chloro-3-formylquinoline **1g** (1 mmol), phenol **2g** (1 mmol), anhydrous potassium carbonate (2 mmol) and dimethyl formamide (5 mL). The mixture was heated at 100 ^{0}C for 4h and the progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was cooled to room temperature and then poured into chilled water (50 mL) with continuous stirring followed by neutralization with 1.5N HCl until pH ~ 7 resulted. The solid mass separated was collected by filtration, washed well with water, dried and crystallized from ethylacetate to give the title compound.

Typical procedure for the preparation of (*E*)-ethyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methoxyphenyl)acrylate (5a)

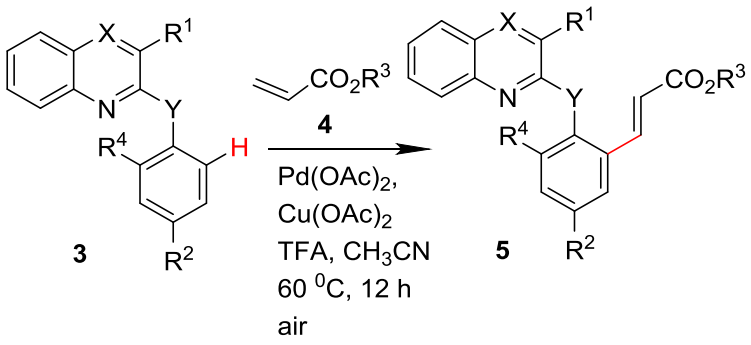


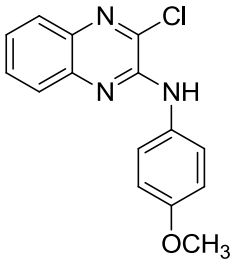
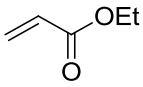
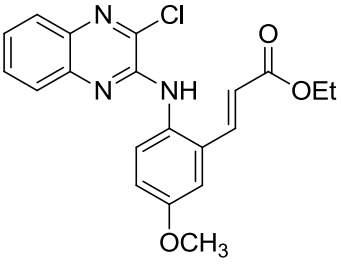
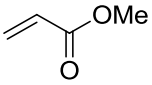
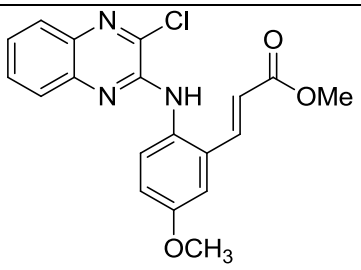
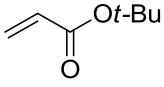
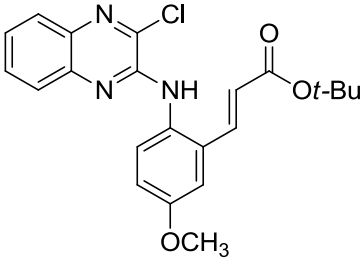
3a **5a**

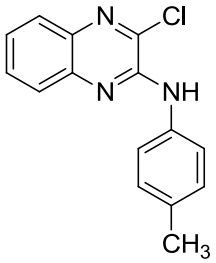
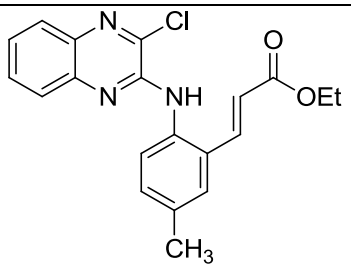
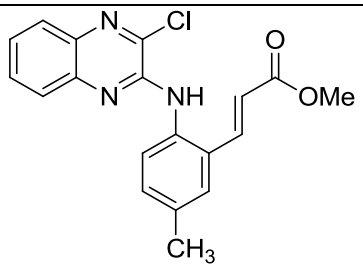
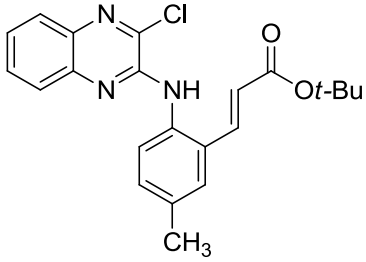
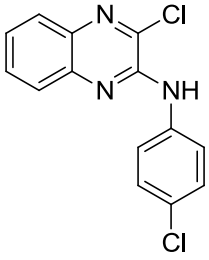
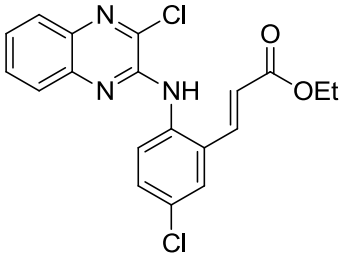
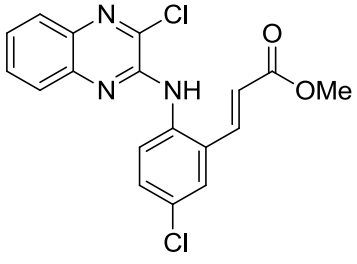
A mixture of 3-chloro-*N*-(4-methoxyphenyl)quinoxalin-2-amine **3a** (0.350 mmol), ethyl acrylate **4a** (0.526 mmol) **,** $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (0.526 mmol), TFA (0.42 mmol) in CH_3CN (2.5 mL) was heated at 60 °C in air for 12h. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to RT, diluted with ethyl acetate (15 mL) and passed through celite. The resulting solution was washed with water (3 x 15 mL) followed by brine solution (25 mL), dried over anhydrous Na_2SO_4, filtered and concentrated

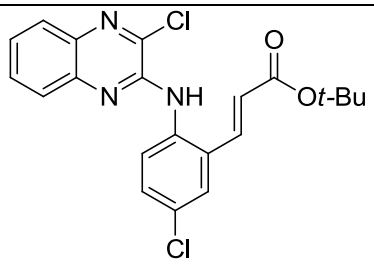
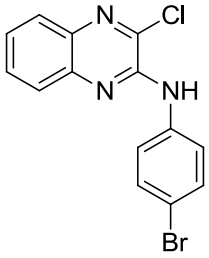
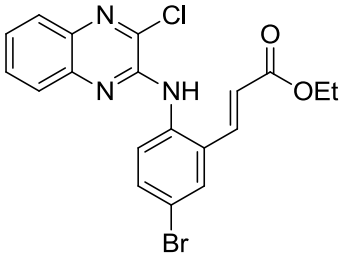
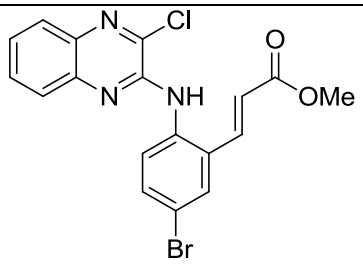
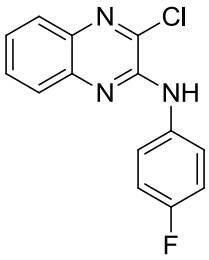
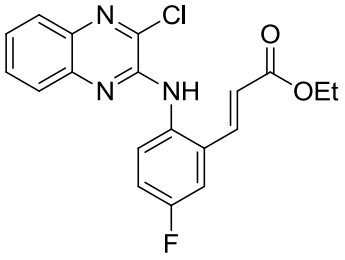
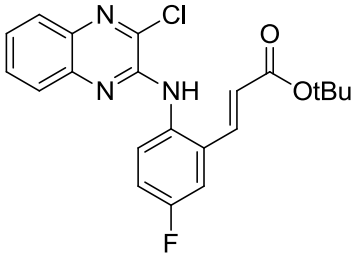
under reduced pressure. The residue was purified by column chromatography using ethyl acetate–hexane to give desired compound **5a**.

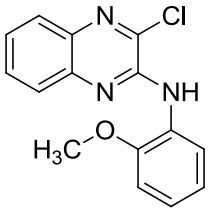
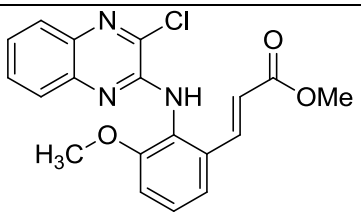
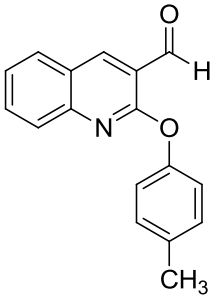
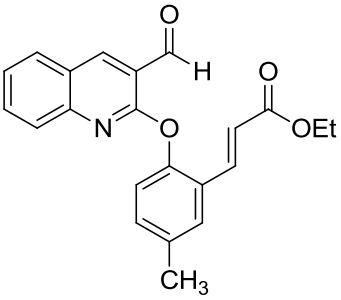
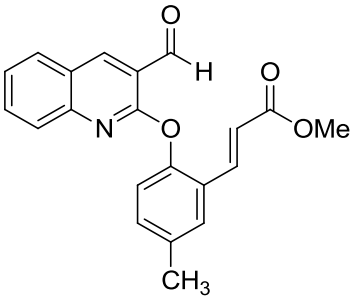
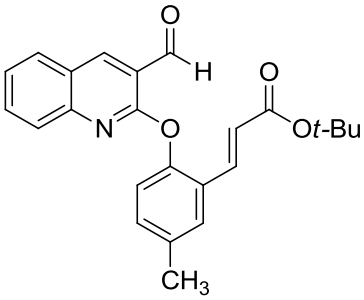
Table S-1: synthesis of compound 5.[a]



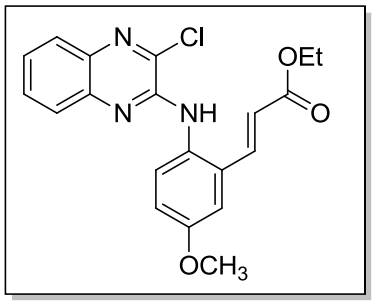
Entry	Substrate (**3**)	Acrylate (**4**)	Product (**5**)	Yield[b] (%)
1	 **3a**	 **4a**	 **5a**	84
2	**3a**	 **4b**	 **5b**	82
3	**3a**	 **4c**	 **5c**	67

4	 **3b**	**4a**	 **5d**	75
5	**3b**	**4b**	 **5e**	80
6	**3b**	**4c**	 **5f**	62
7	 **3c**	**4a**	 **5g**	77
8	**3c**	**4b**	 **5h**	71

9	**3c**	**4c**	 **5i**	59
10	 **3d**	**4a**	 **5j**	78
11	**3d**	**4b**	 **5k**	74
12	 **3e**	**4a**	 **5l**	79
14	**3e**	**4c**	 **5m**	74

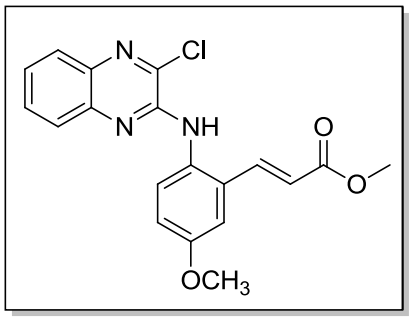
15	 **3f**	**4b**	 **5n**	55
16	 **3g**	**4a**	 **5o**	68
17	**3g**	**4b**	 **5p**	72
18	**3g**	**4c**	 **5q**	61

[a]All the reactions are carried out using compound **3** (1 mmol), alkene **4** (1.5 mmol), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (1.5 mmol) and TFA (1.2 mmol) in CH_3CN (2.5 mL) at 60 °C, under air.
[b]Isolated yield.



Yield: 84%; Light yellow; mp: 117-179 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 7.6 Hz, 1H), 7.86-7.84 (m, 2H), 7.69-7.67 (m, 1H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 1H), 7.25 (s, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.05 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 157.3, 146.0, 140.4, 139.4, 137.6, 137.3, 130.2, 130.0, 129.8, 127.8, 126.5 (2C), 126.0, 120.9, 116.8, 111.5, 60.6, 55.5, 14.1; MS (ES mass): 384.1 (M+1); HPLC: 98.8%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/50, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 3.8 min.

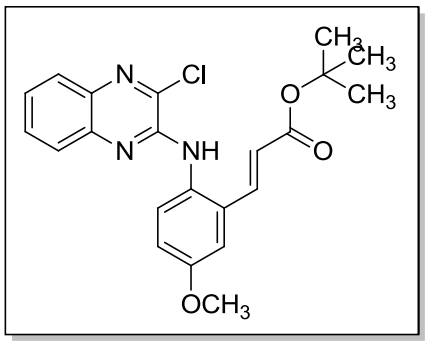
(*E*)-Ethyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methoxyphenyl)acrylate (5b)



Compound **5b** was synthesized from **3a** following a procedure similar to that of compound **5a**
Yield: 82%; Light yellow; mp: 156-158 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90-7.84 (m, 3H), 7.69-7.67 (m, 1H), 7.61-7.56 (m, 1H), 7.49-7.45 (m, 1H), 7.23 (s, 1H), 7.16 (d, *J* = 3.2 Hz, 1H), 7.06 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 157.3, 146.1, 140.5, 139.7, 137.6, 137.3, 130.2, 129.8, 127.8, 126.6, 126.5, 126.1, 120.5, 116.8, 111.6, 109.9, 55.5, 51.7; MS (ES mass): 370.0 (M+1); HPLC: 98.3%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile

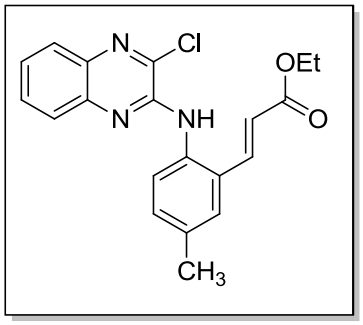
phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 3/20, 8/40, 15/95, 20/95, 25/20, 30/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 255.0 nm, retention time 3.6 min.

(*E*)-*tert*-butyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methoxyphenyl)acrylate (5c)



Compound **5c** was synthesized from **3a** following a procedure similar to that of compound **5a** Yield: 67%; Light yellow; mp: 115-117 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.8 Hz, 1H), 7.86-7.84 (m, 1H), 7.78 (d, *J* = 16.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.60-7.56 (m, 1H), 7.48-7.44 (m, 1H), 7.27 (s, 1H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.04 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.88 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.6, 157.2, 146.0, 140.5, 138.2, 137.6, 137.2, 130.2, 130.0, 129.7, 127.8, 126.5, 126.3, 126.0, 122.8, 116.6, 111.4, 80.7, 55.5, 28.0; MS (ES mass): 412.1 (M+1); HPLC: 98.7%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/50, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.1 min.

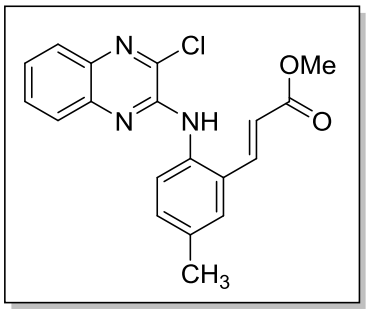
(*E*)-Ethyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methylphenyl)acrylate (5d)



Compound **5d** was synthesized from **3b** following a procedure similar to that of compound **5a**

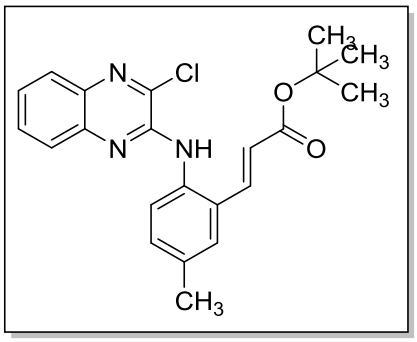
Yield: 75%; Light yellow; mp: 129-131 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 16.0 Hz, 1H),7.84 (d, *J* = 8.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51-7.46 (m, 2H), 7.41 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 145.6, 140.4, 139.4 (2C), 137.7, 137.3, 135.1, 134.2, 131.5, 130.3, 128.0, 127.8, 126.6, 126.2, 124.0, 120.8, 60.5, 21.0, 14.2; MS (ES mass): 368.1 (M+1); HPLC: 95.0%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/10, 2/10, 10/95, 20/95, 22/10, 25/10; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.0 min.

(*E*)-Methyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methylphenyl)acrylate (5e)



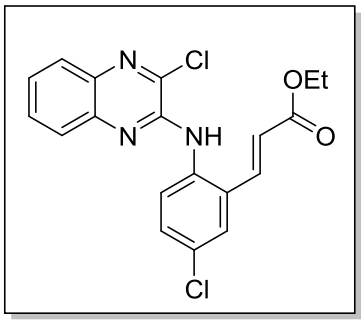
Compound **5e** was synthesized from **3b** following a procedure similar to that of compound **5a**
Yield: 80%; Light yellow; mp: 168-170 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 16.0 Hz, 1H),7.87-7.85 (m, 1H), 7.72-7.70 (m, 1H), 7.62-7.58 (m, 1H), 7.50-7.44 (m, 2H), 7.37 (s, 1H), 7.31-7.29 (m, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 145.6, 140.3, 139.7, 137.7, 137.3, 135.1, 134.2, 131.5, 130.3, 128.0, 127.8 (2C), 126.5, 126.2, 124.0, 120.2, 51.7, 20.9; MS (ES mass): 354.1 (M+1); HPLC: 99.9%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 10/95, 10.5/95, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 230.0 nm, retention time 3.7 min.

(*E*)-*tert*-butyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-methylphenyl)acrylate (5f)



Compound **5f** was synthesized from **3b** following a procedure similar to that of compound **5a** Yield: 62%; Light yellow; mp: 112-114 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, *J* = 8.0 Hz, 1H), 7.87-7.84 (m, 1H), 7.80 (d, *J* = 16.0 Hz, 1H), 7.73-7.71 (m, 1H), 7.64-7.58 (m, 1H), 7.49-7.44 (m, 2H), 7.42 (s, 1H), 7.29-7.27 (m, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.7, 145.6, 140.4, 138.2, 137.2, 134.9, 134.0, 131.2, 130.2, 127.8 (2C), 127.7, 126.5, 126.1, 123.7, 122.6, 120.0, 80.6, 28.0, 20.9; MS (ES mass): 396.1 (M+1); HPLC: 98.3%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 265.0 nm, retention time 3.1 min.

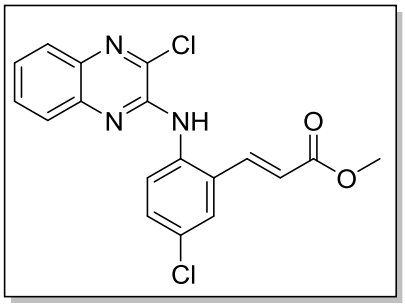
(*E*)-Ethyl 3-(5-chloro-2-((3-chloroquinoxalin-2-yl)amino)phenyl)acrylate (5g)



Compound **5g** was synthesized from **3c** following a procedure similar to that of compound **5a** Yield: 77%; Light yellow; mp: 207-209 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 8.4 Hz, 1H), 7.89-7.83 (m, 2H), 7.76-7.74 (m, 1H), 7.66-7.62 (m, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.54-7.50 (m, 1H), 7.46-7.43 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 145.0,

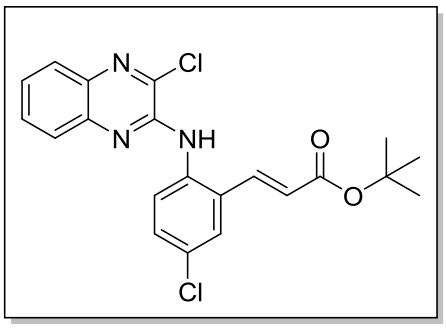
140.0, 137.8, 137.6, 137.4, 135.2, 130.5, 130.4, 130.3, 128.9, 127.9, 127.3, 126.7, 126.5, 124.6, 122.5, 60.8, 14.1; MS (ES mass): 388.1 (M+1); HPLC: 95.5%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/10, 2/10, 10/95, 20/95, 22/10, 25/10; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.2 min.

(*E*)-Methyl 3-(5-chloro-2-((3-chloroquinoxalin-2-yl)amino)phenyl)acrylate (5h)



Compound **5h** was synthesized from **3c** following a procedure similar to that of compound **5a** Yield: 71%; Light yellow; mp: 201-203 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.8 Hz, 1H), 7.89-7.83 (m, 2H), 7.75-7.73 (m, 1H), 7.65-7.61 (m, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.53-7.49 (m, 1H), 7.46-7.43 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 145.0, 140.0, 138.1, 137.6, 137.5, 135.2, 130.5, 130.4, 130.3, 128.9, 127.9, 127.3, 126.7, 126.5, 124.7, 122.0, 51.9; MS (ES mass): 374.0 (M+1); HPLC: 97.8%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 3.9 min.

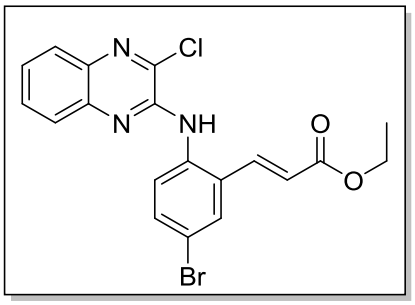
(*E*)-*tert*-butyl 3-(5-chloro-2-((3-chloroquinoxalin-2-yl)amino)phenyl)acrylate (5i)



Compound **5i** was synthesized from **3c** following a procedure similar to that of compound **5a**

Yield: 59%; Light yellow; mp: 147-149 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, *J* = 8.8Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79-7.76 (m, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.60 (s, 1H), 7.55-7.44 (m, 3H), 6.43 (d, *J* = 16.0 Hz, 1H), 1.52 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.2, 145.0, 140.1, 137.6, 137.5, 136.6, 135.1, 130.5, 130.2 (2C), 128.9, 127.9, 127.2, 126.6 (2C), 124.5, 124.4, 81.1, 28.1; MS (ES mass): 416.1 (M+1); HPLC: 98.2%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.7 min.

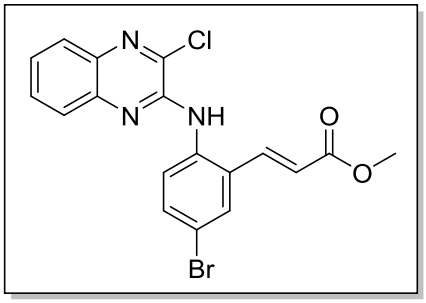
(*E*)-Ethyl 3-(5-bromo-2-((3-chloroquinoxalin-2-yl)amino)phenyl)acrylate (5j)



Compound **5j** was synthesized from **3d** following a procedure similar to that of compound **5a**

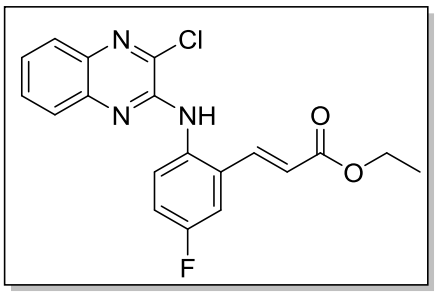
Yield: 78%; Light yellow; mp: 129-131 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, *J* = 8.8 Hz, 1H), 7.89-7.82 (m, 2H), 7.76-7.72 (m, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.59-7.57 (m, 1H), 7.54-7.49 (m, 1H), 7.46 (s, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 144.9, 140.0, 137.7, 137.6, 137.5, 135.7, 133.3, 130.6, 130.3, 129.1, 127.9, 126.7, 126.6, 124.6, 122.6, 117.8, 60.8, 14.2; MS (ES mass): 434.0 (M+3); HPLC: 95.9%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/10, 2/10, 10/95, 20/95, 22/10, 25/10; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.7 min.

(*E*)-Methyl 3-(5-bromo-2-((3-chloroquinoxalin-2-yl)amino)phenyl)acrylate (5k)



Compound **5k** was synthesized from **3d** following a procedure similar to that of compound **5a** Yield: 74%; Light yellow; mp: 125-127 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (d, *J* = 8.8 Hz, 1H), 7.89-7.83 (m, 2H), 7.76-7.72 (m, 2H), 7.66-7.62 (m, 1H), 7.60-7.59 (m, 1H), 7.54-7.50 (m, 1H), 7.45 (s, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 144.9, 140.0, 138.0, 137.6, 137.4, 135.7, 133.3, 130.5, 130.3, 129.1, 127.9, 126.7, 126.6, 124.7, 122.1, 117.8, 51.9; MS (ES mass): 420.0 (M+3); HPLC: 93.6%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/10, 2/10, 10/95, 20/95, 22/10, 25/10; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.0 min.

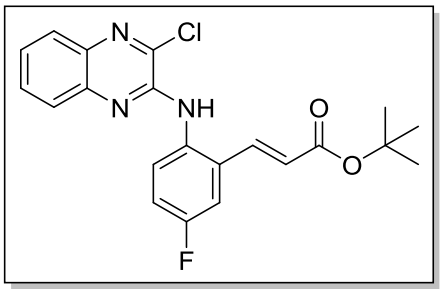
(*E*)-Ethyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-fluorophenyl)acrylate (5l)



Compound **5l** was synthesized from **3e** following a procedure similar to that of compound **5a** Yield: 79%; Light yellow; mp: 177-179 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.88-7.83 (m, 2H), 7.72-7.69 (m, 1H), 7.63-7.59 (m, 1H), 7.52-7.48 (m, 1H), 7.35=7.32 (m, 2H), 7.22-7.17 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 161.1 (C-F *J* = 244.5Hz), 158.7, 145.5, 140.2, 138.1, 137.5 (C-F *J* = 7.8 Hz), 137.4, 132.7 (2C), 130.4, 130.2 (C-F *J* = 7.9 Hz),, 130.1, 127.8, 126.5 (C-F *J* = 7.4 Hz), 126.4, 126.3, 126.2 , 122.1, 117.6 (C-F *J* = 22.7 Hz), 117.4, 113.7 (C-F *J* = 23.2 Hz), 113.5, 60.7, 14.1; MS (ES mass): 372.0 (M+1); HPLC: 99.7%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 %

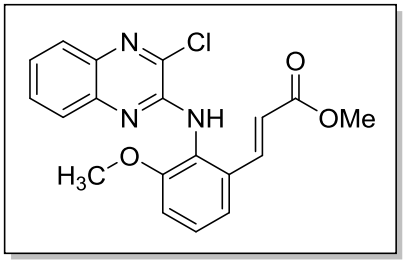
TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 3.8 min.

(*E*)-*tert*-butyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-5-fluorophenyl)acrylate (5m)



Compound **5m** was synthesized from **3e** following a procedure similar to that of compound **5a** Yield: 74%; Light yellow; mp: 167-169 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.88-7.85 (m, 1H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.72-7.70 (m, 1H), 7.63-7.59 (m, 1H), 7.51-7.47 (m, 1H), 7.36 (s, 1H), 7.32 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.22-7.14 (m, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 165.2, 161.1 (C-F *J* = 244.1Hz), 158.6, 148.8, 145.5, 140.2, 137.5, 137.4, 137.0, 132.6 , 130.4, 130.2, 127.8, 126.5, 126.3, 126.2 (C-F *J* = 8.4 Hz), 126.1, 124.0, 117.4 (C-F *J* = 22.5 Hz), 117.1, 113.6 (C-F *J* = 23.3 Hz), 113.4, 109.9, 80.9, 28.0; MS (ES mass): 400.2 (M+1); HPLC: 99.7%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 3.0 min.

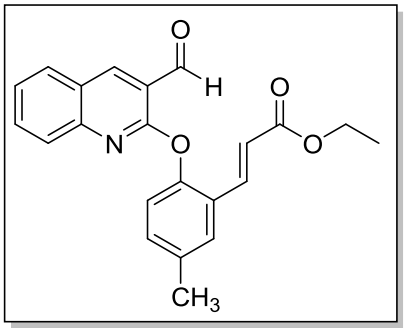
(*E*)-Methyl 3-(2-((3-chloroquinoxalin-2-yl)amino)-3-methoxyphenyl)acrylate (5n)



Compound **5n** was synthesized from **3f** following a procedure similar to that of compound **5a** Yield: 55%; Pale yellow; mp: 124-126 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.83 (m, 1H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.56-7.49 (m, 2H), 7.45-7.41 (m,

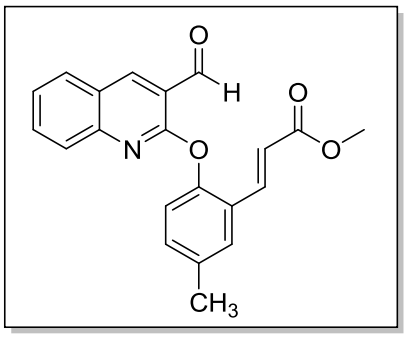
1H), 7.36-7.30 (m, 2H), 7.25 (s, 1H), 7.02-7.00 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 3.85 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.4, 157.3, 146.0, 140.4, 139.4, 137.6, 137.3, 130.2, 130.0, 129.8, 127.8, 126.5 (2C), 126.0, 120.9, 116.8, 111.5, 60.6, 55.5; MS (ES mass): 370.1 (M+1); HPLC: 99.9%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.8 min.

(*E*)-Ethyl 3-(2-((3-formylquinolin-2-yl)oxy)-5-methylphenyl)acrylate (5o)



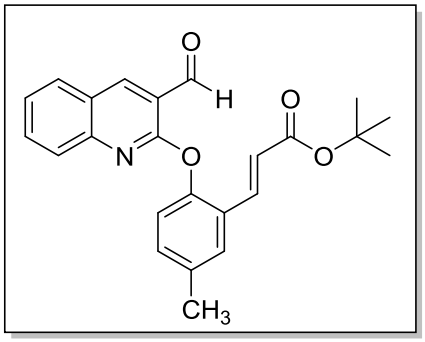
Compound **5o** was synthesized from **3g** following a procedure similar to that of compound **5a** Yield:68%; pink; mp: 160-162 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.71 (s, 1H), 8.78 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H),7.87 (d, *J* = 16.0 Hz, 1H) 7.71-7.70 (m, 2H), 7.55 (s, 1H), 7.50-7.46 (m, 1H), 7.30 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.23-4.15 (m, 2H), 2.45 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.5, 166.7, 160.4, 149.6, 148.5, 140.8, 138.5, 135.2, 132.7, 131.8, 129.6, 128.0, 127.8, 127.2, 125.8, 125.2, 122.9, 120.0, 119.7, 60.4, 20.9, 14.2; MS (ES mass): 362.1 (M+1); HPLC: 98.1%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.9 min.

(*E*)-Methyl 3-(2-((3-formylquinolin-2-yl)oxy)-5-methylphenyl)acrylate (5p)



Compound **5p** was synthesized from **3g** following a procedure similar to that of compound **5a** Yield:72%; white; mp: 136-138 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.71 (s, 1H), 8.79 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 4.4 Hz, 2H), 7.56 (s, 1H), 7.50-7.46 (m, 1H), 7.31 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.5, 167.1, 160.4, 149.6, 148.5, 140.8, 138.8, 135.3, 132.7, 131.9, 129.6, 128.1, 127.8, 127.2, 125.8, 125.2, 122.9, 120.0, 119.3, 51.6, 20.9; MS (ES mass): 348.1 (M+1); HPLC: 96.1%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 3.8 min.

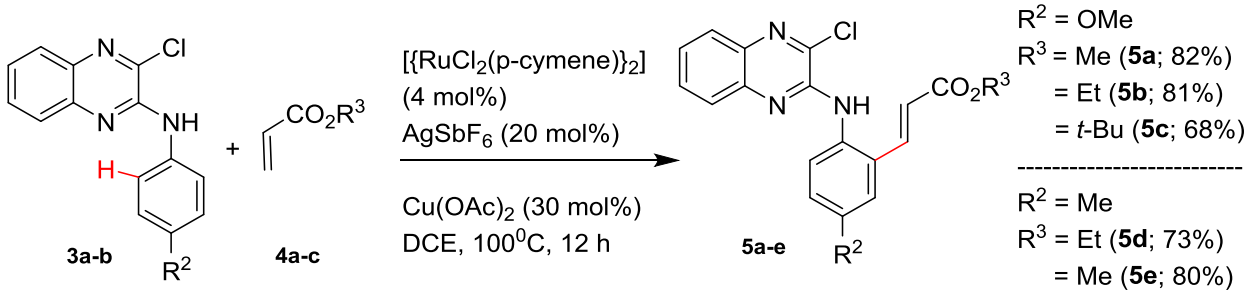
(*E*)-*tert*-butyl 3-(2-((3-formylquinolin-2-yl)oxy)-5-methylphenyl)acrylateacrylate (5q)



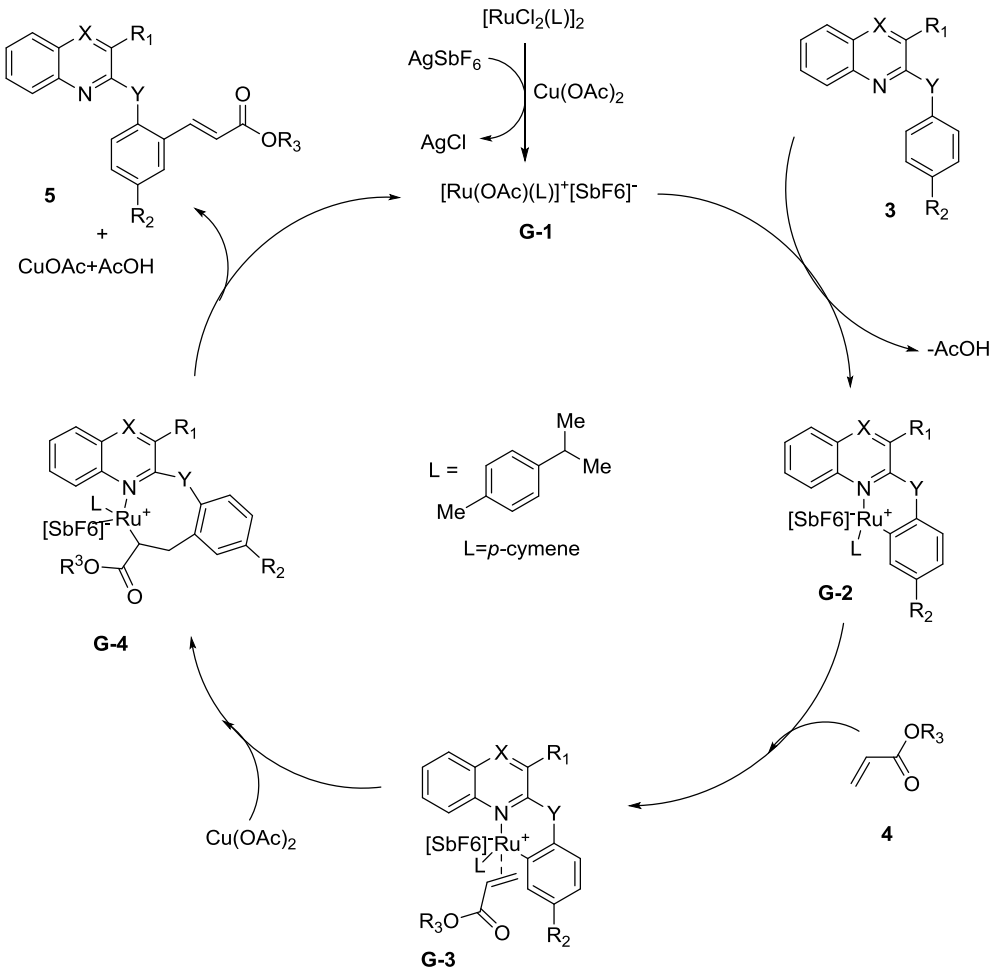
Compound **5q** was synthesized from **3g** following a procedure similar to that of compound **5a** Yield: 61%; Pink; mp: 126-127 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.70 (s, 1H), 8.77 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.70 (d, *J* = 4.6 Hz, 2H), 7.55 (s, 1H), 7.49-7.45 (m, 1H), 7.28 (s, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 16.0 Hz, 1H), 2.44 (s, 3H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 188.5, 165.9, 160.4, 149.5, 148.5, 140.7, 137.4, 135.1, 132.6, 131.6, 129.9, 129.5, 127.8, 127.3, 125.7, 125.1,

122.9, 121.4, 119.9, 80.4, 28.0, 20.9; MS (ES mass): 388.0 (M-1); HPLC: 97.6%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 260.0 nm, retention time 4.2 min.

General procedure for the Ru-catalyzed direct *ortho* C-H alkenylation of 3a-b

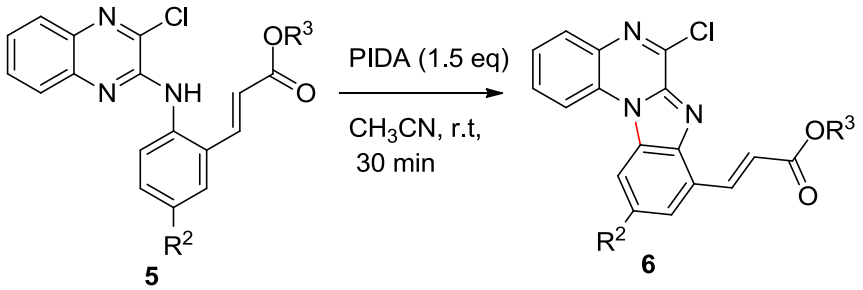


To a mixture of $[\{RuCl_2(p\text{-cymene})\}_2]$ (0.04 mmol, 4 mol %), $AgSbF_6$ (0.20 mmol, 20 mol %), $Cu(OAc)_2$ (0.30 mmol, 30 mol %) and 3-chloro-*N*-aryl quinoxalin-2-amine **3a-b** (1.0 equiv), taken in a sealed tube (fitted with a septum) was added acrylate **4a-c (**1.5 equiv) and then dichloroethane (3.0 mL) via a syringe under nitrogen. The mixture was allowed to stir for 5 min at room temperature. Then, the septum was taken off and the reaction mixture was stirred under an open air for an additional 10 min. The tube was covered with a screw cap and the reaction mixture was allowed to stir at 100 °C for 12 h. After completion of the reaction the mixture was cooled to room temperature, transferred to an RB flask and solvent was evaporated. The residue was diluted with ethylacetate (5 mL) and filtered through Celite. The filtrate was washed with water (3 x 15 mL) followed by brine solution (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue obtained was purified by column chromatography on silica gel (230-400 mesh) using ethylacetate/hexane to give the desired product **5a-e**.



Scheme S-1. The proposed reaction mechanism for Ru-catalyzed direct *ortho* C-H alkenylation of **3a-b**.

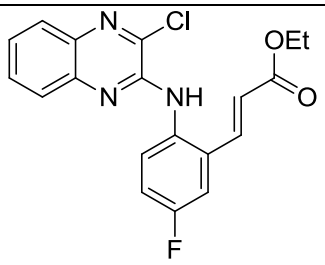
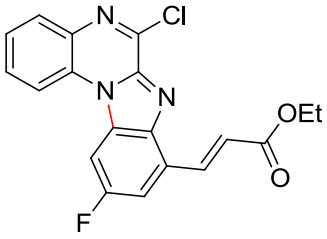
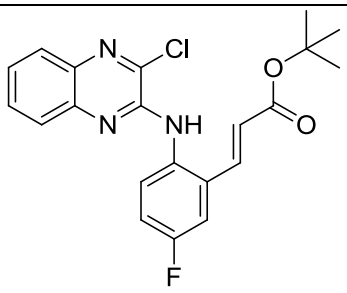
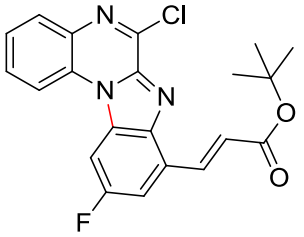
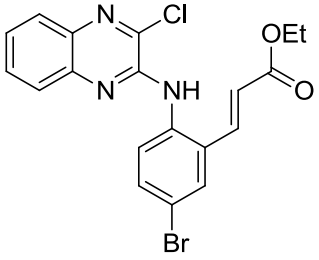
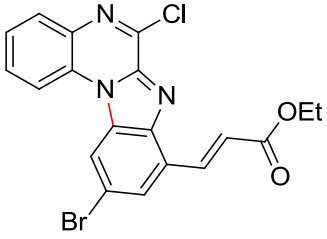
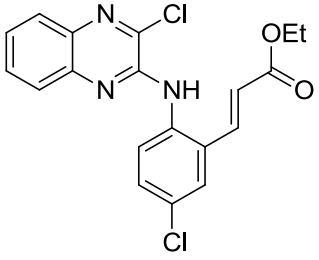
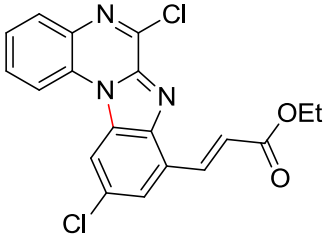
General procedure for the preparation of (*E*)-Alkyl 3-(10-substituted-6-chlorobenzo[4,5]imidazo[1,2-*a*]quinoxalin-8-yl)acrylate (6a-d)



To a solution of **5** (1.0 mmol) in acetonitrile (5 mL) was added PIDA (1.5 mmol) and the solution was allowed to stirred at room temperature for 30 min. After completion of the reaction

(indicated by TLC), the mixture was extracted with ethylacetate (3 x 10 mL). The combined organic phase was collected, washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate–hexane to give desired compound **6**.

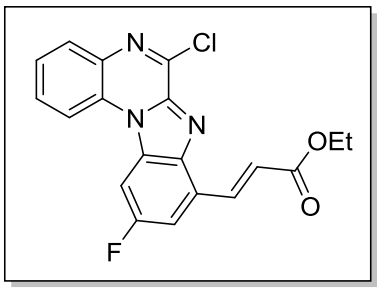
Table S-2: Synthesis of compound **6**[a]

Entry	Substrate **(5)**	Product **(6)**	Yield[b] **(%)**
1	 **5l**	 **6a**	90
2	 **5m**	 **6b**	85
3	 **5j**	 **6c**	91
4			82

	5g	**6d**	

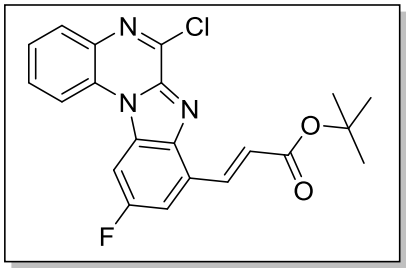
[a]All the reactions are carried out using compound **5** (1 mmol), PIDA (1.5 mmol) in CH_3CN (2.5 mL) at room temparature in 30 min, under air.
[b]Isolated yield.

(*E*)-Ethyl 3-(6-chloro-10-fluorobenzo[4,5]imidazo[1,2-*a*]quinoxalin-8-yl)acrylate (6a)



Yield: 90%; white solid; mp: 221-223 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 16.0 Hz, 1H), 8.14-8.08 (m, 2H), 7.84-7.79 (m, 1H), 7.68-7.64 (m, 1H), 7.56 (dd, *J* = 9.8, 2.0 Hz, 1H), 7.43 (d, *J* = 16.0 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 161.4 (C-F *J* = 244.5Hz), 159.0, 144.7, 139.2, 138.7, 138.6, 134.5, 131.3, 131.2, 130.6 (C-F *J* = 40.6Hz), 130.2, 129.7, 129.6, 128.9 (C-F *J* = 9.6Hz), 126.7, 124.3, 114.7 (C-F *J* = 25.6Hz), 114.4 (2C), 102.1(C-F *J* = 29.0 Hz), 101.8, 60.8, 14.3; MS (ES mass): 370.1 (M+1); HPLC: 97.4%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20,; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.8 min.

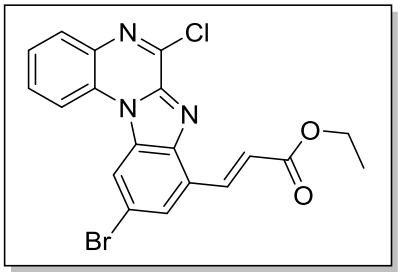
(*E*)-*tert*-butyl 3-(6-chloro-10-fluorobenzo[4,5]imidazo[1,2-*a*]quinoxalin-8-yl)acrylate (6b)



Yield: 85%; white solid; mp: 198-200 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 16.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.84-7.80 (m, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 9.8, 1.9 Hz, 1H),

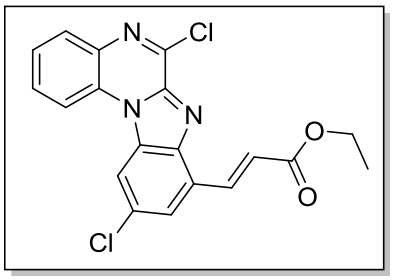
7.32 (d, *J* = 16.0 Hz, 1H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.1, 161.5, 159.0 (C-F *J* = 243.6 Hz), 144.7, 139.3, 139.2, 137.6 (2C), 134.5, 130.5, 130.1, 128.9, 128.2, 126.6, 126.1, 114.4, 114.2, 101.8, 101.5 (C-F *J* = 28.9 Hz), 80.9, 28.2; MS (ES mass): 398.0 (M+1); HPLC: 99.9%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20,; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.8 min.

(*E*)-Ethyl 3-(10-bromo-6-chlorobenzo[4,5]imidazo[1,2-*a*]quinoxalin-8-yl)acrylate (6c)



Yield: 91%; white solid; mp: 209-211 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.20-8.12 (m, 2H), 7.88 (s, 1H), 7.86-7.82 (m, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 16.0 Hz, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 144.6, 141.4, 139.2, 138.5, 134.6, 132.3, 131.0, 130.6, 130.3, 129.3, 128.8, 126.8, 124.4, 118.6, 117.9, 114.6, 60.7, 14.3; MS (ES mass): 431.9 (M+3); HPLC: 99.9%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20,; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.8 min.

(*E*)-Ethyl 3-(6,10-dichlorobenzo[4,5]imidazo[1,2-*a*]quinoxalin-8-yl)acrylate (6d)



Yield: 82%; white solid; mp: 185-187 °C; R_f = 0.2 (10% EtOAc/ *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41-8.39 (m, 2H), 8.21 (d, *J* = 16.0 Hz, 1H), 8.15 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.86-7.82

(m, 1H), 7.77 (s, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 16.0 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.8, 144.7, 138.6, 134.6, 131.9, 131.2, 130.6, 130.3, 129.8, 129.4, 126.8, 126.7, 125.8, 125.7, 124.4, 114.9, 114.6, 60.7, 14.3; MS (ES mass): 385.9 (M+1); HPLC: 99.8%, Column: Symmetry C-18 75 * 4.6 mm, 3.5µm, mobile phase A: 0.1 % TFA in water, mobile phase B: CH_3CN (T/%B): 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20,; flow rate: 1.0 mL/min; Diluent: ACN: WATER (90:10); UV 220.0 nm, retention time 4.4 min.

References:

1. B. Prasad, K. S. Kumar, P. VijayaBabu, K. Anusha, D. Rambabu, A. Kandale, G. R. Vanaja, A. M. Kalle and M. Pal, *Tetrahedron Lett*., **2012**, *53*, 6059.

2. D. C. Mungra, M. P. Patel, D. P. Rajani, and R. G. Patel, *Eur. J. Med. Chem*., **2011**, *46*, 4192.

Pharmacology

In vitro assay for PDE4B

Cells and Reagents: Sf9 cells were obtained from ATCC (Washington D.C., USA) and were routinely maintained in Grace's supplemented medium (Invitrogen) with 10% FBS. cAMP was purchased from SISCO Research Laboratories (Mumbai, India). PDElight HTS cAMP phosphodiesterase assay kit was procured from Lonza (Basel, Switzerland). PDE4B1 clone was procured from OriGene Technologies (Rockville, MD, USA). PDE4D2 enzyme was purchased from BPS Bioscience (San Diego, CA, USA).

PDE4B protein production and purification: PDE4B1 cDNA was sub-cloned into pFAST Bac HTB vector (Invitrogen) and transformed into DH10Bac (Invitrogen) competent cells. Recombinant bacmids were tested for integration by PCR analysis. Sf9 cells were transfected with bacmid using Lipofectamine 2000 (Invitrogen) according to manufacturer's instructions. Subsequently, P3 viral titer was amplified, cells were infected and 48 h post infection cells were lysed in lysis buffer (50 mM Tris-HCl pH 8.5, 10 mM 2-Mercaptoethanol, 1 % protease inhibitor cocktail (Roche), 1 % NP40). Recombinant His-tagged PDE4B protein was purified as previously described elsewhere (Wang et al., 1997). Briefly, lysate was centrifuged at 10,000 rpm for 10 min at 4˚C and supernatant was collected. Supernatant was mixed with Ni-NTA resin

(GE Life Sciences) in a ratio of 4:1 (v/v) and equilibrated with binding buffer (20 mM Tris-HCl pH 8.0, 500 mM-KCl, 5 mM imidazole, 10 mM 2-mercaptoethanol and 10 % glycerol) in a ratio of 2:1 (v/v) and mixed gently on rotary shaker for 1 hour at 4˚C. After incubation, lysate-Ni-NTA mixture was centrifuged at 4,500 rpm for 5 min at 4˚C and the supernatant was collected as the flow-through fraction. Resin was washed twice with wash buffer (20 mM Tris-HCl pH 8.5, 1 M KCl, 10 mM 2-Mercaptoethanol and 10% glycerol). Protein was eluted sequentially twice using elution buffers (Buffer I: 20 mM Tris-HCl pH 8.5, 100 mM KCl, 250 mM imidazole, 10 mM 2-mercaptoethanol, 10% glycerol, Buffer II: 20 mM Tris-HCl pH 8.5, 100 mM KCl, 500 mM imidazole, 10 mM 2-mercaptoethanol, 10% glycerol). Eluates were collected in four fractions and analyzed by SDS-PAGE. Eluates containing PDE4B protein were pooled and stored at -80˚C in 50% glycerol until further use.

PDE4 enzymatic assay: The inhibition of PDE4 enzyme was measured using PDE light HTS cAMP phosphodiesterase assay kit (Lonza) according to manufacturer's recommendations. Briefly, 10 ng of in house purified PDE4B1 enzyme was pre-incubated either with DMSO (vehicle control) or compound for 15 min before incubation with the substrate cAMP (5 µM) for 1 hour. The reaction was halted with stop solution and reaction mix was incubated with detection reagent for 10 minutes in dark. Luminescence values (RLUs) were measured by a Multilabel plate reader (Perklin Elmer 1420 Multilabel counter).The percentage of inhibition was calculated using the following formula:

$$\%\ inhibition = \frac{(RLU\ of\ vehicle\ control - RLU\ of\ inhibitior)}{RLU\ of\ vehicle\ control} X\ 100$$

Copies of ^{1}H and ^{13}C NMR spectra

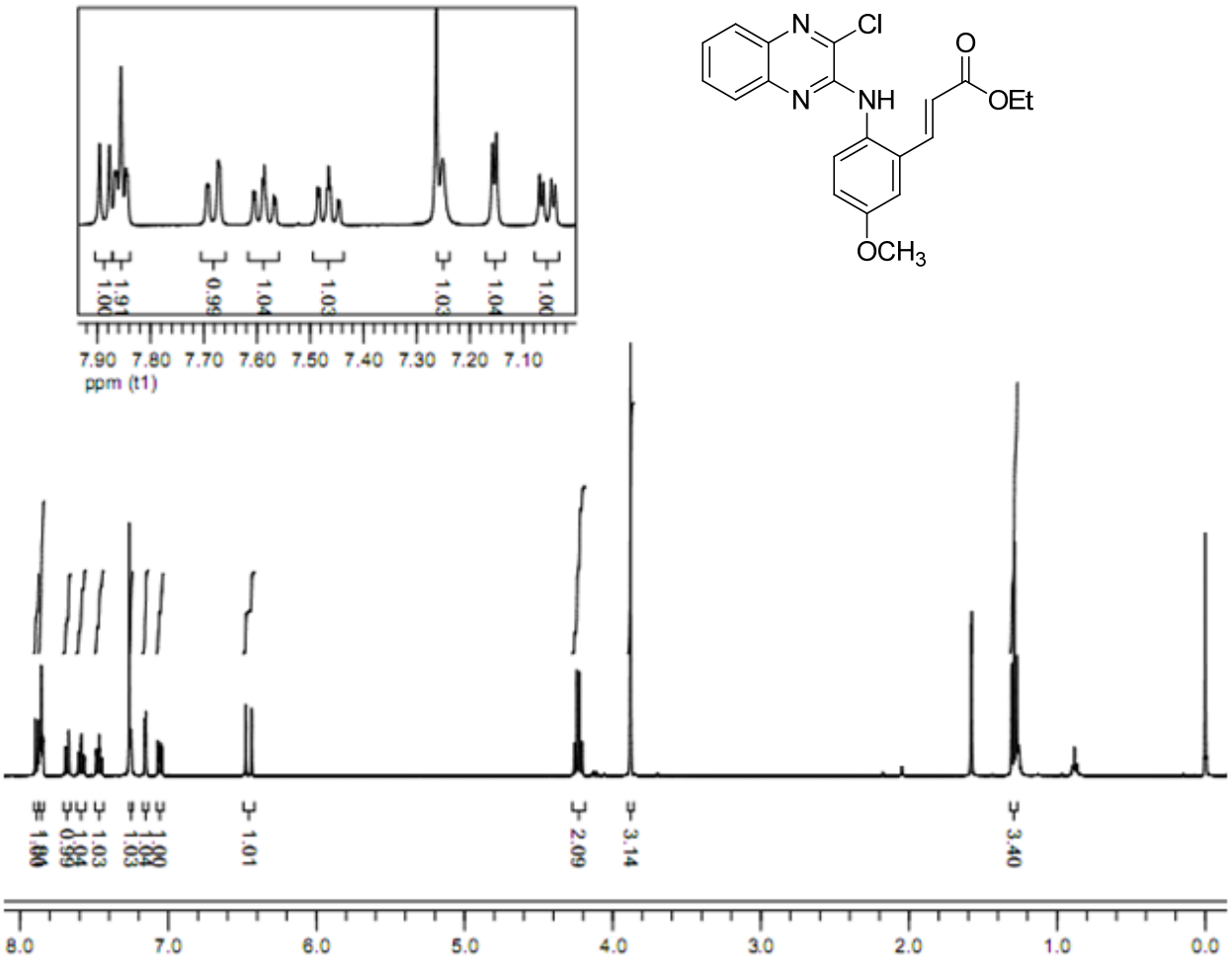


Fig. 1: ^{1}H NMR spectra of compound **5a** ($CDCl_3$, 400 MHz)

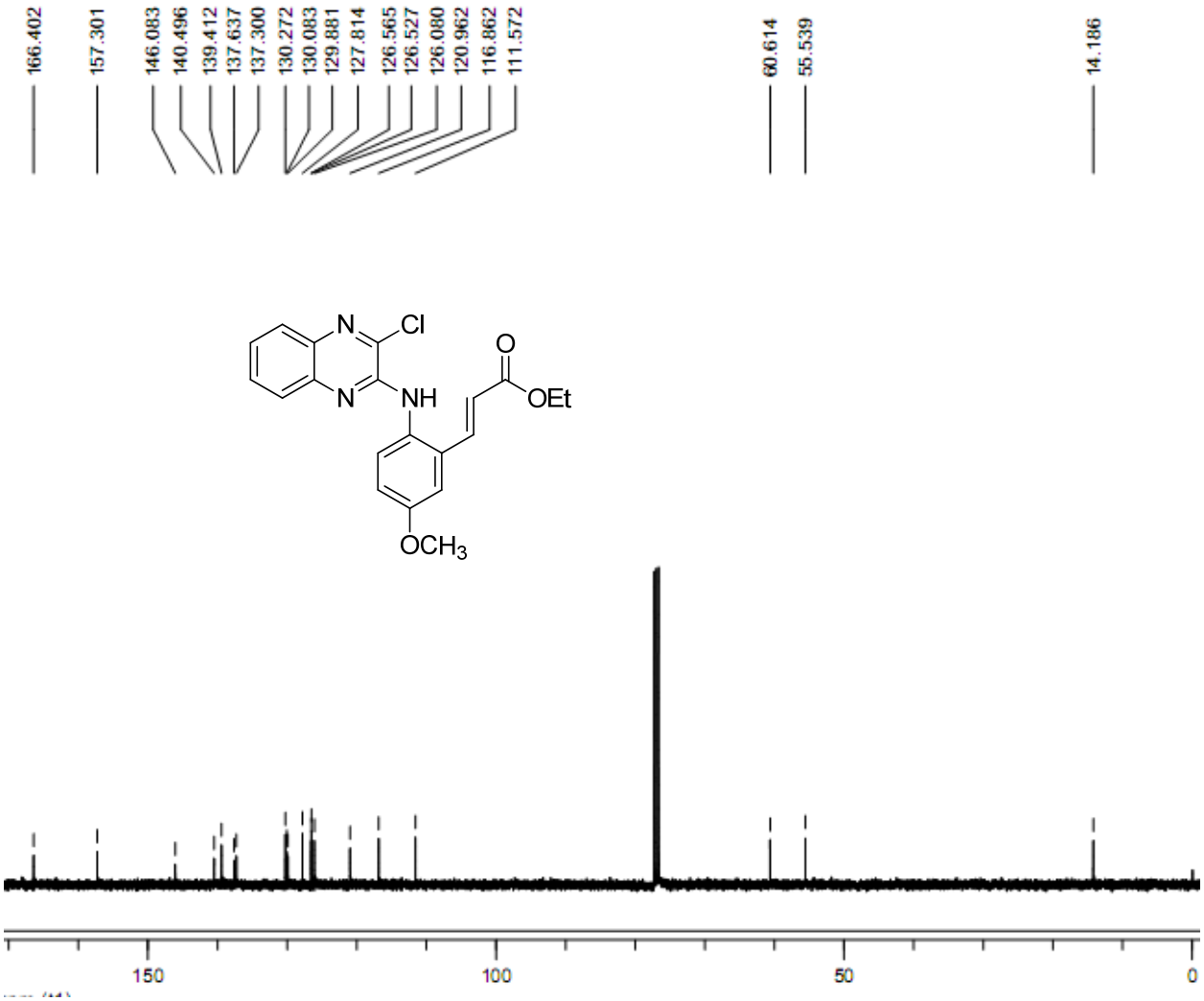


Fig. 2: ^{13}C NMR spectra of compound **5a** ($CDCl_3$, 100 MHz)

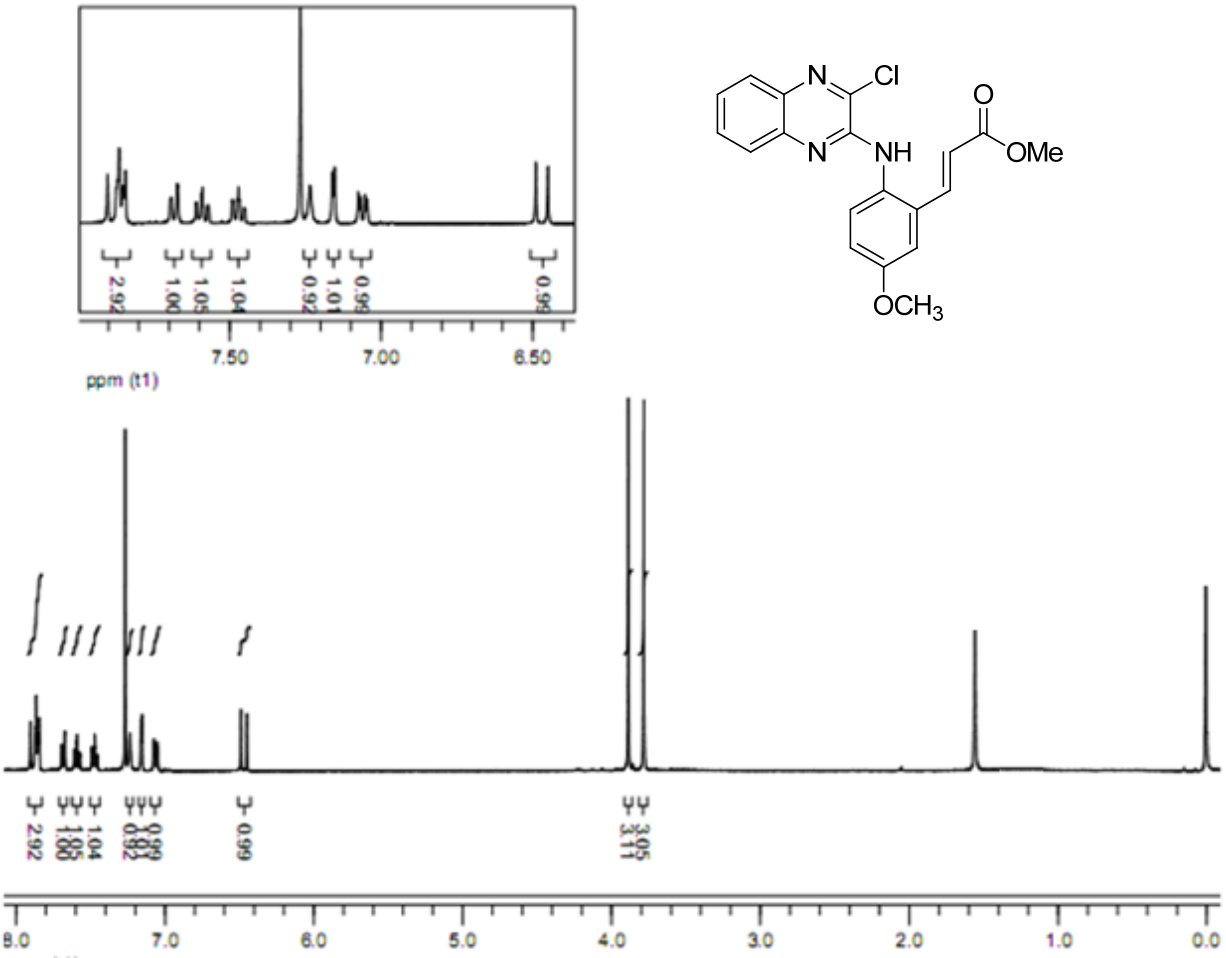


Fig. 3: ^{1}H NMR spectra of compound **5b** ($CDCl_3$, 400 MHz)

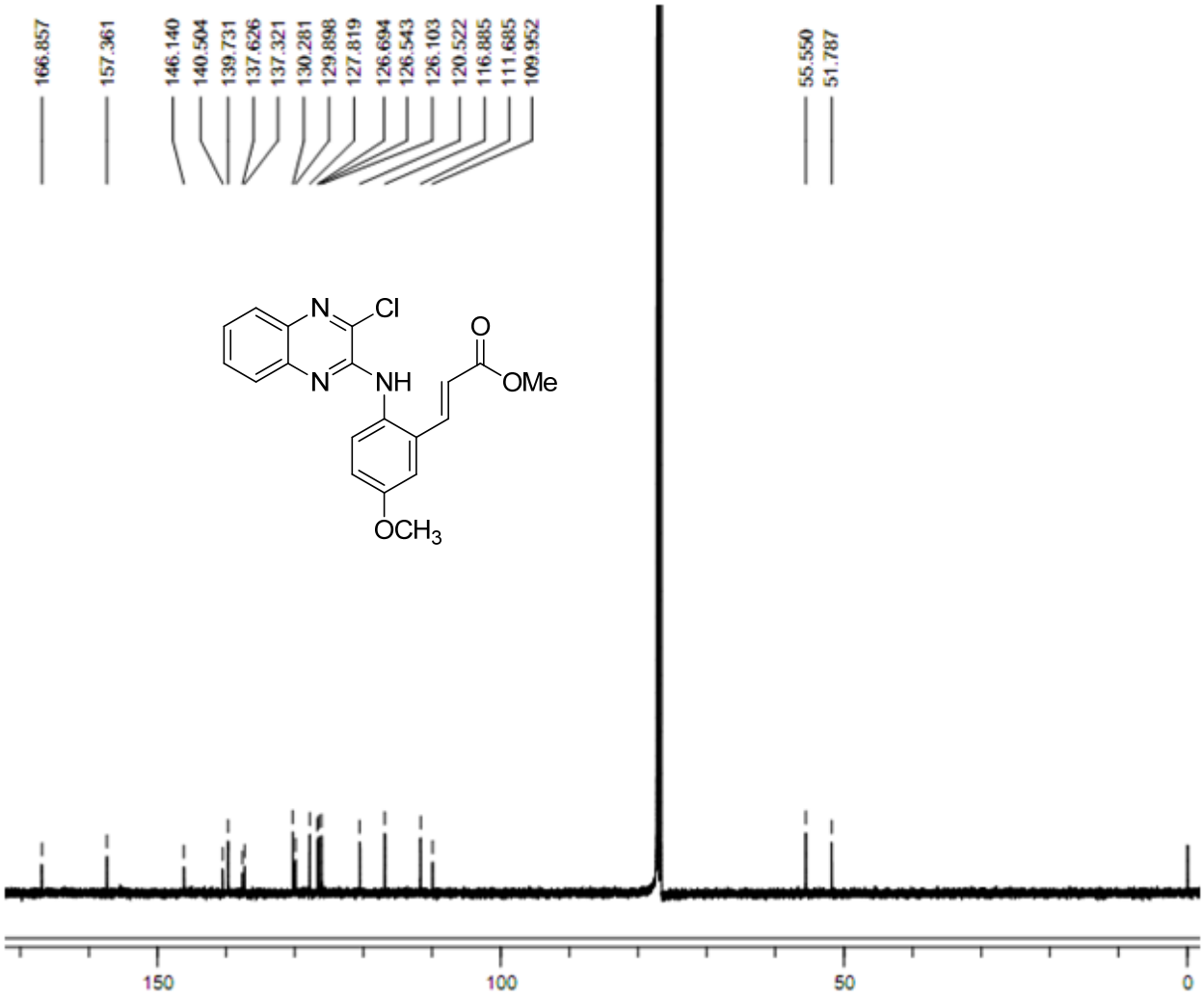


Fig. 4: ^{13}C NMR spectra of compound **5b** ($CDCl_3$, 100 MHz)

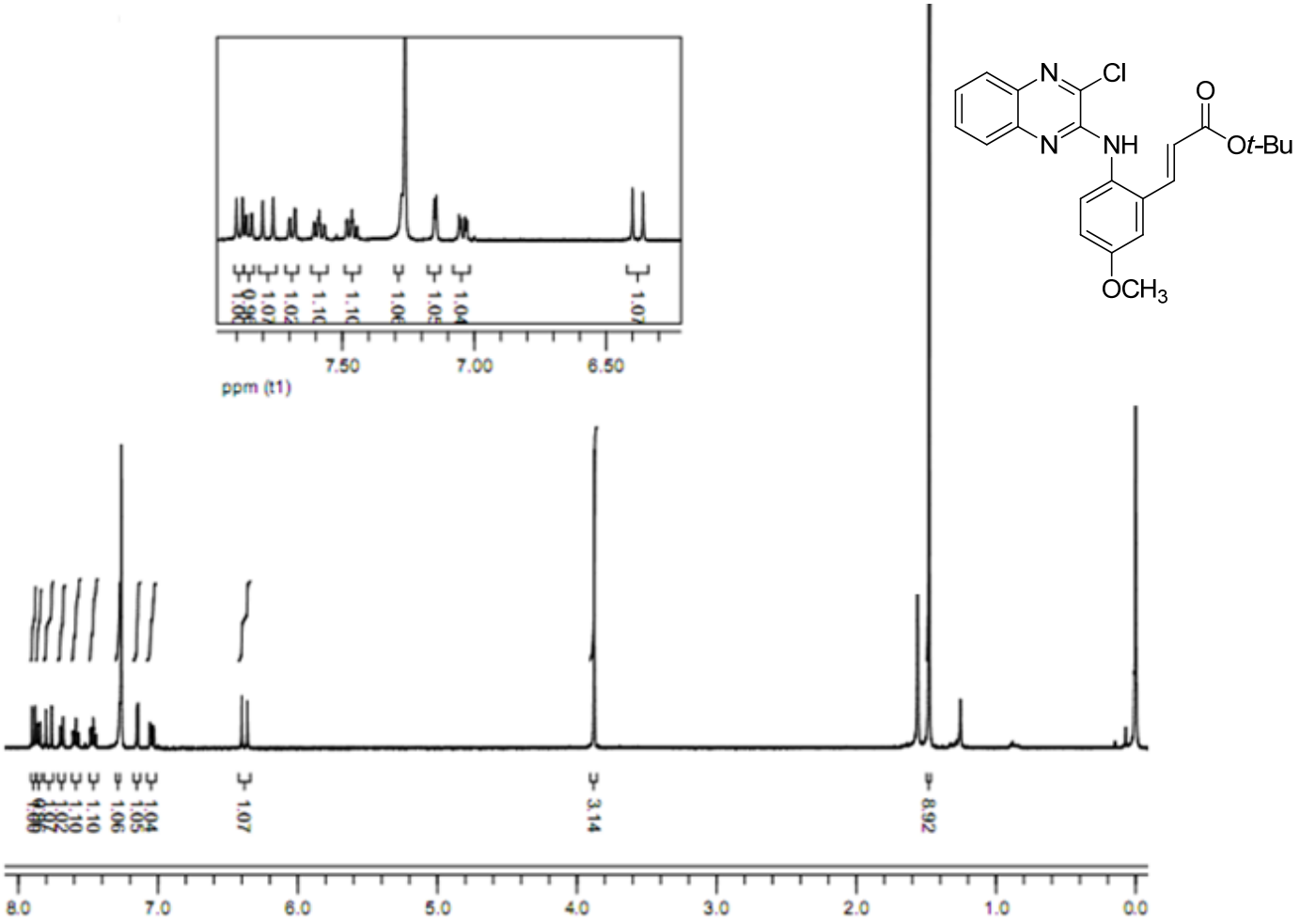


Fig. 5: ^{1}H NMR spectra of compound **5c** ($CDCl_3$, 400 MHz)

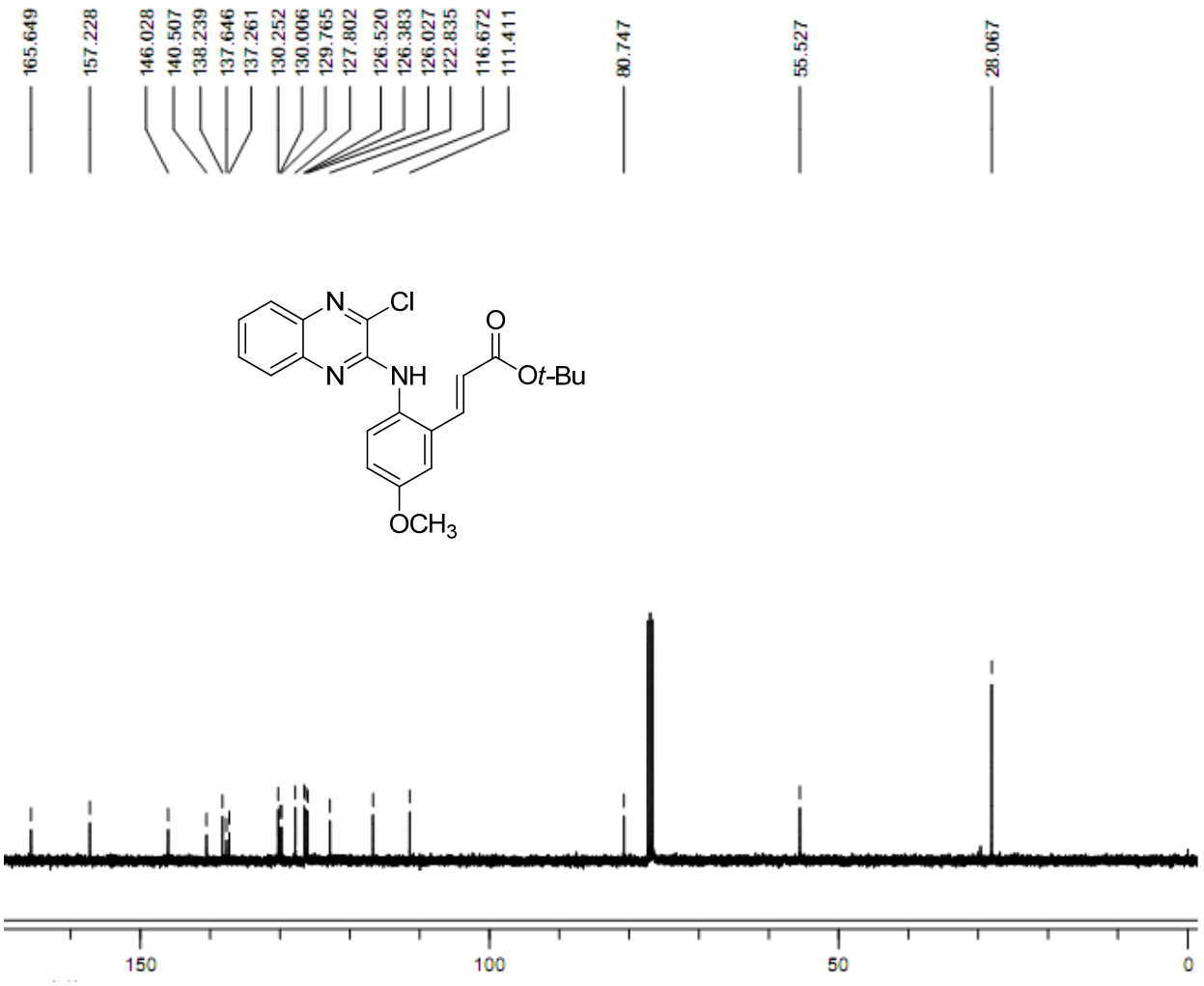


Fig.6: ^{13}C NMR spectra of compound **5c** ($CDCl_3$, 100 MHz)

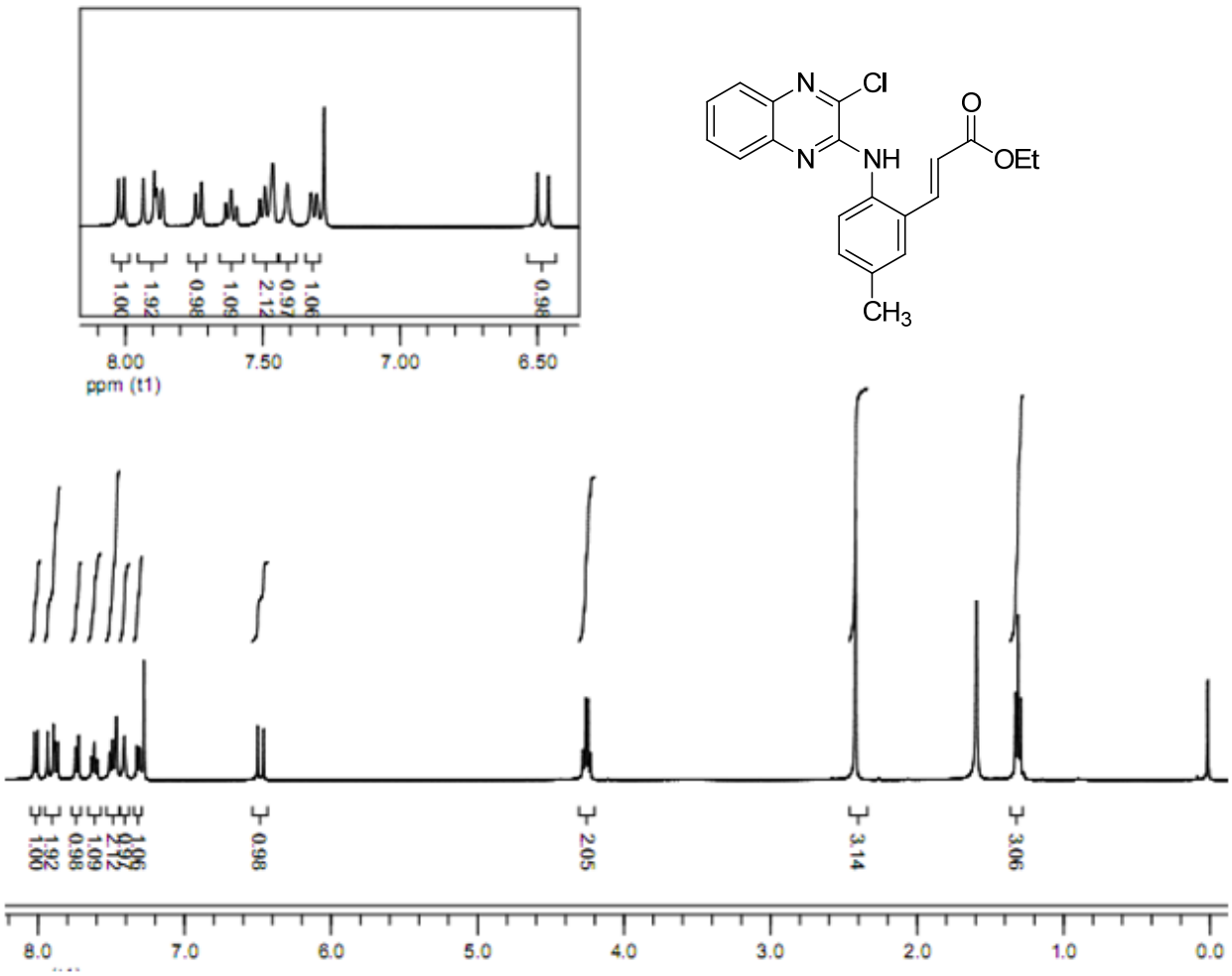


Fig. 7: ^{1}H NMR spectra of compound **5d** ($CDCl_3$, 400 MHz)

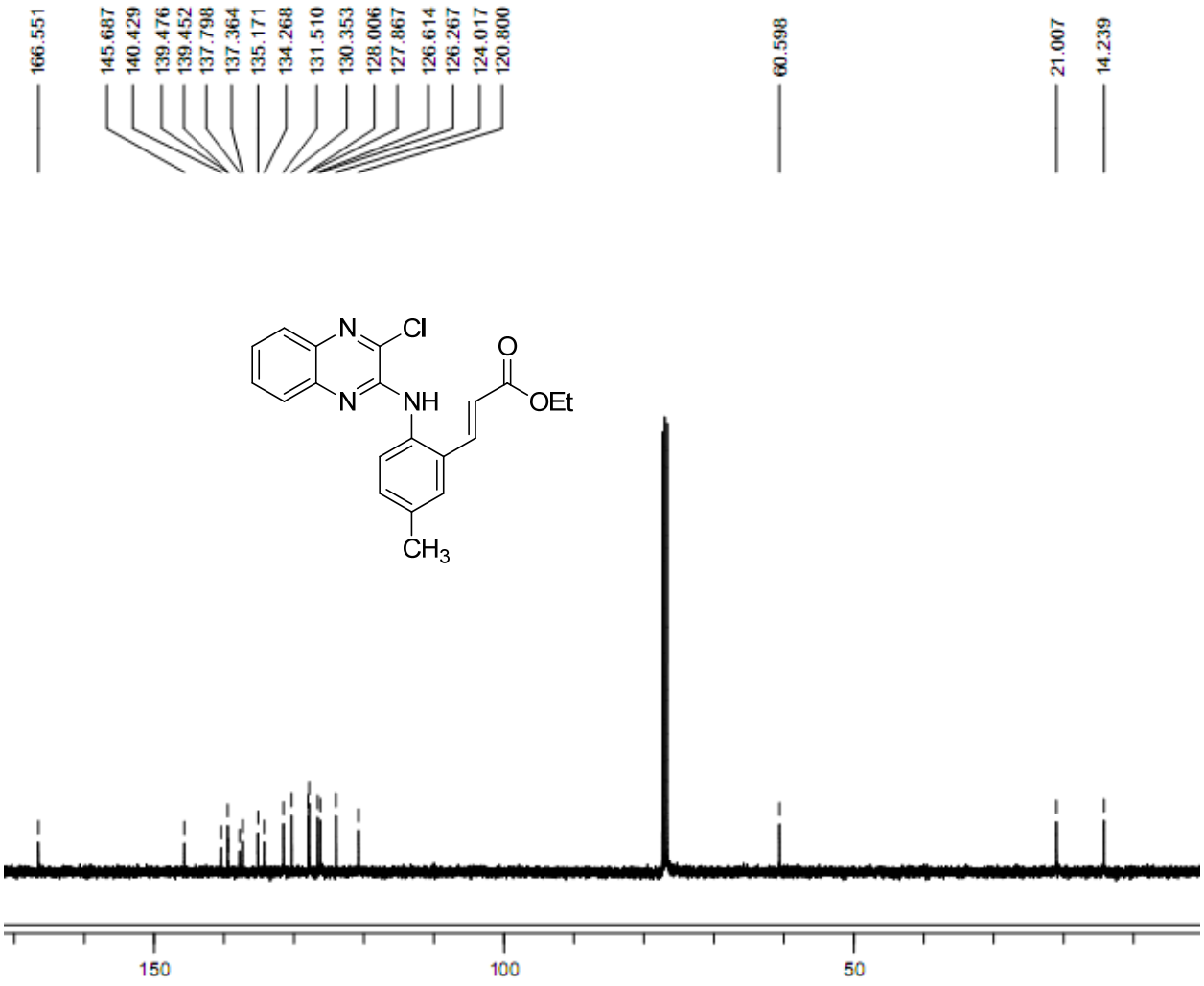


Fig. 8: ^{13}C NMR spectra of compound **5d** ($CDCl_3$, 100 MHz)

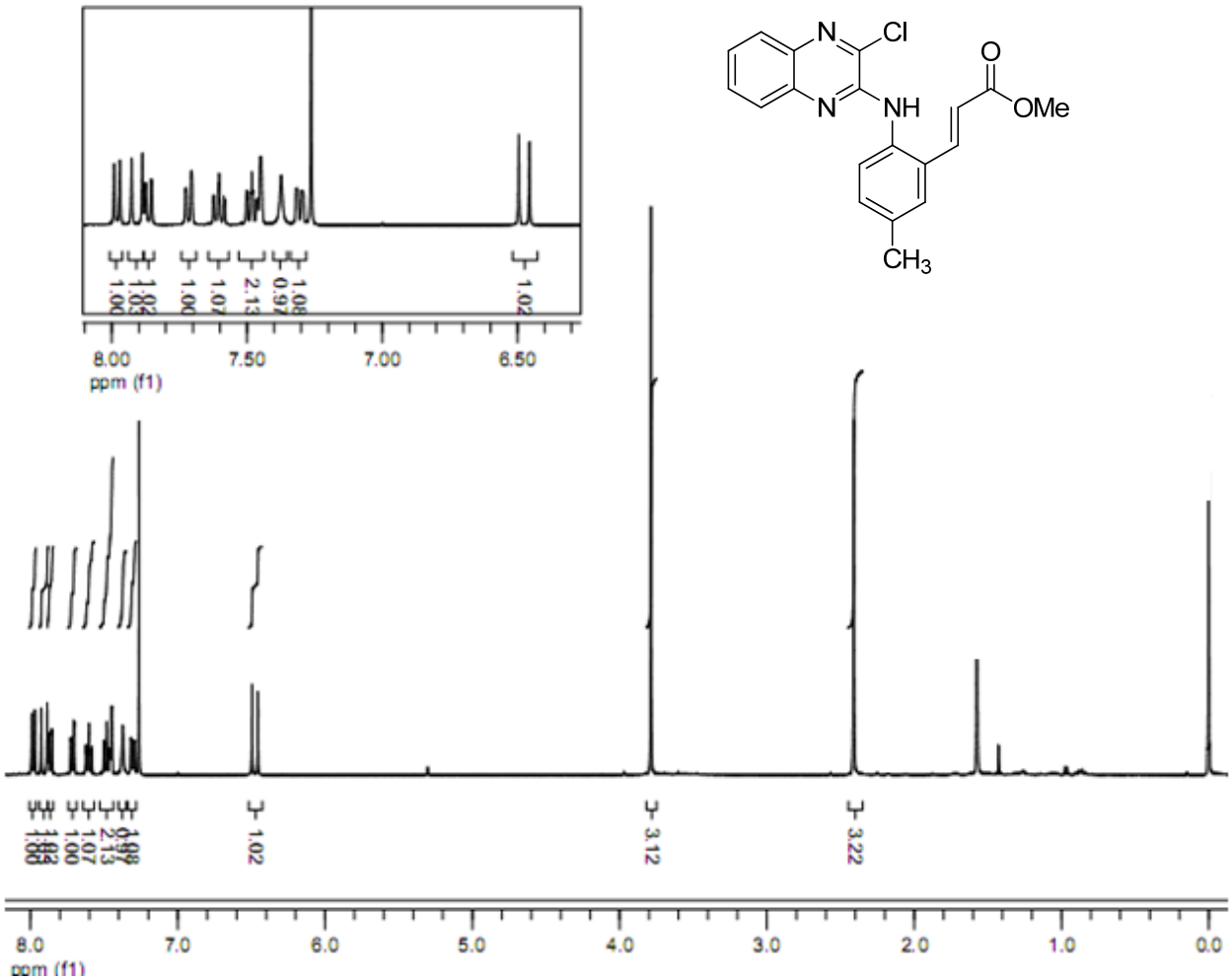


Fig. 9: ^{1}H NMR spectra of compound **5e** ($CDCl_3$, 400 MHz)

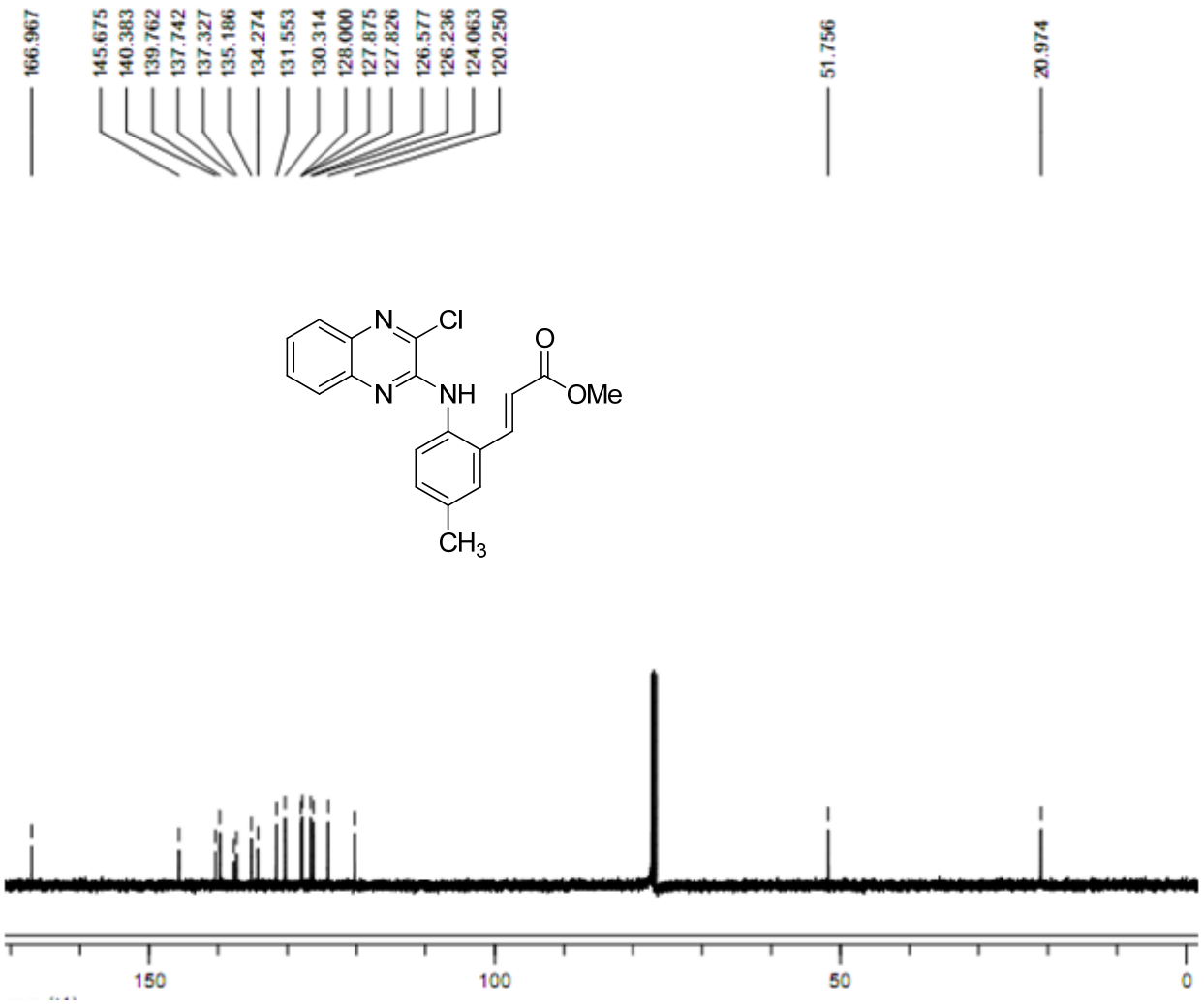


Fig. 10: ^{13}C NMR spectra of compound **5e** ($CDCl_3$, 100 MHz)

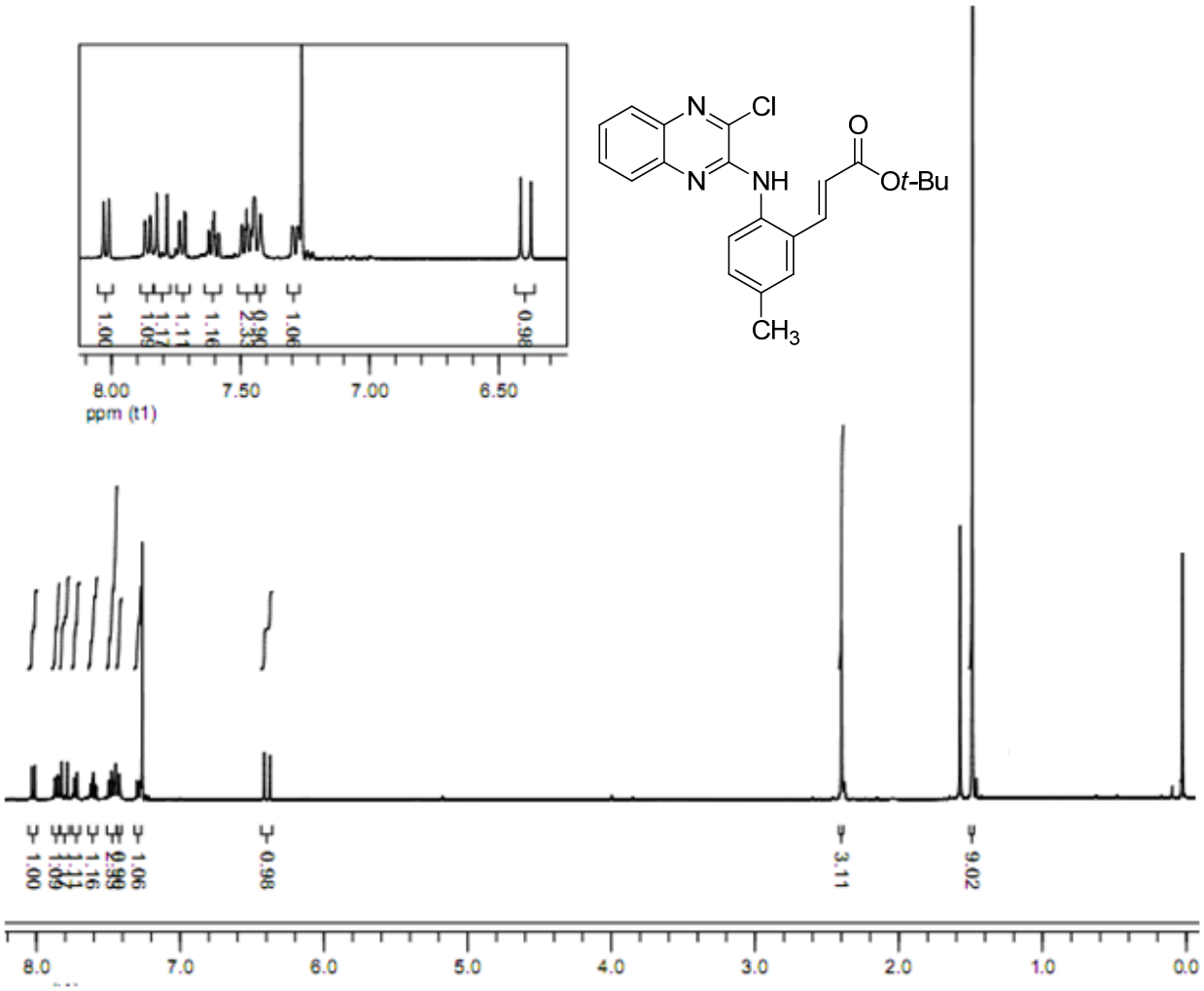


Fig. 11: ^{1}H NMR spectra of compound **5f** ($CDCl_3$, 400 MHz)

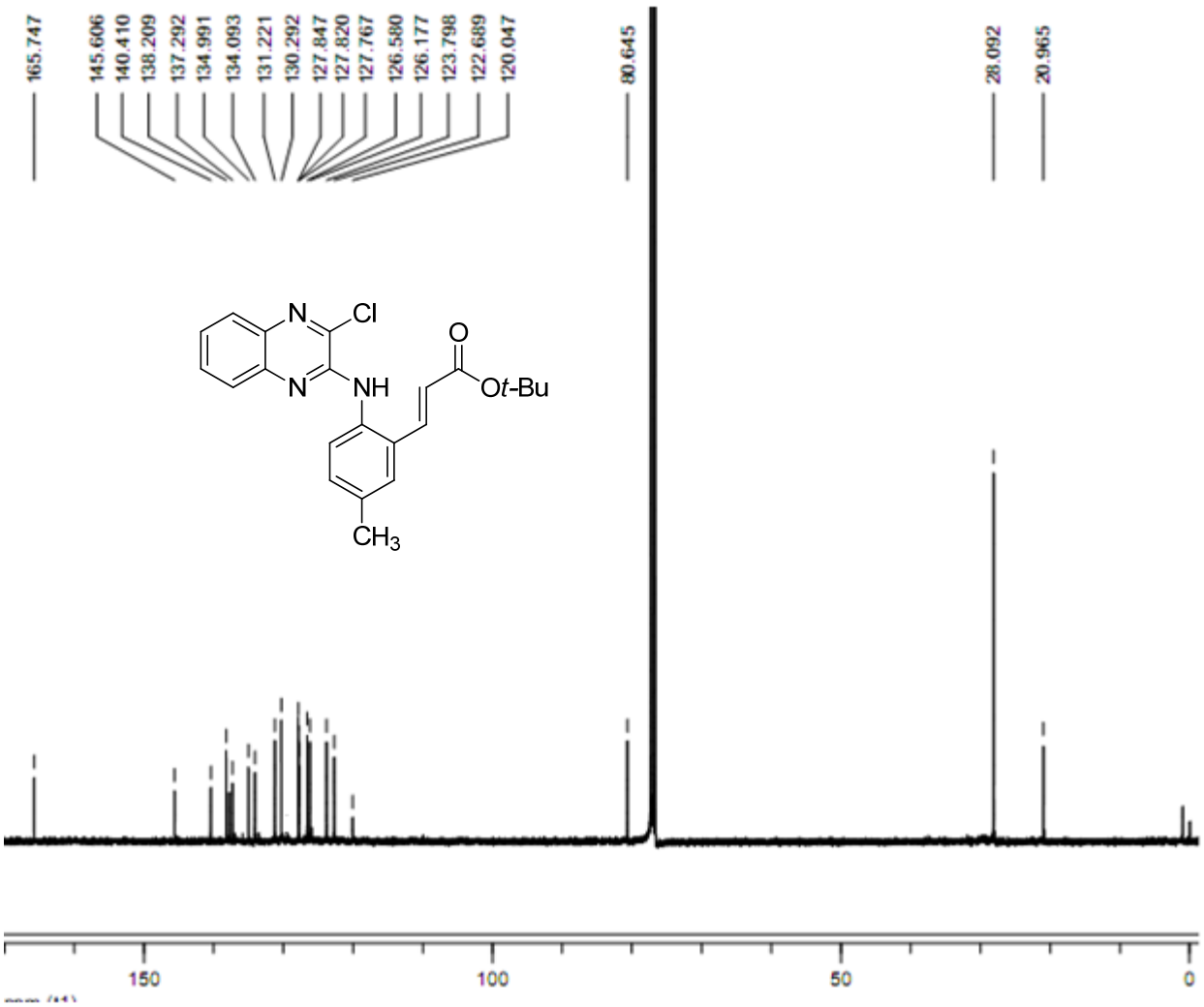


Fig. 12: ^{13}C NMR spectra of compound **5f** ($CDCl_3$, 100 MHz)

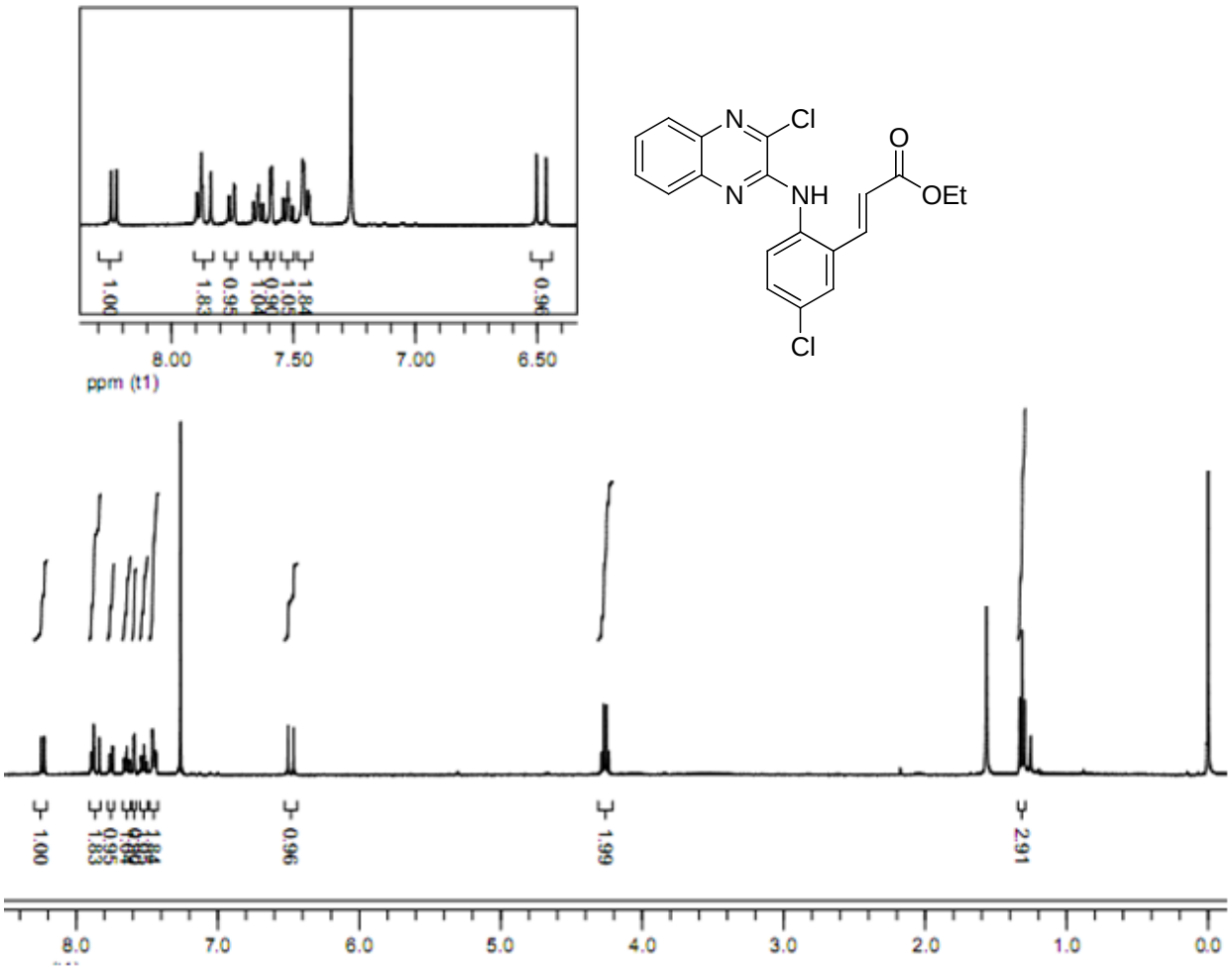


Fig. 13: ^{1}H NMR spectra of compound **5g** ($CDCl_3$, 400 MHz)

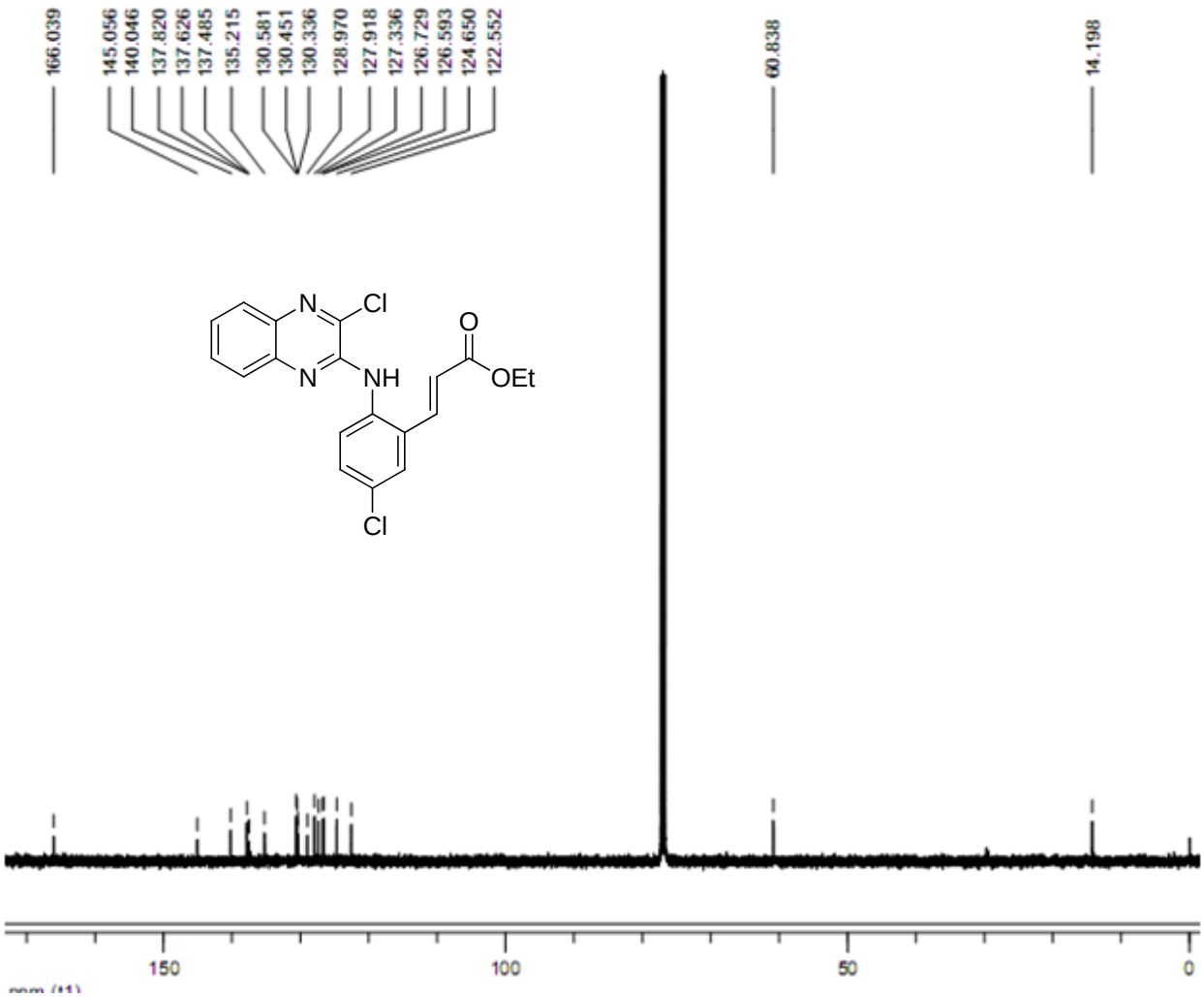


Fig. 14: ^{13}C NMR spectra of compound **5g** ($CDCl_3$, 100 MHz)

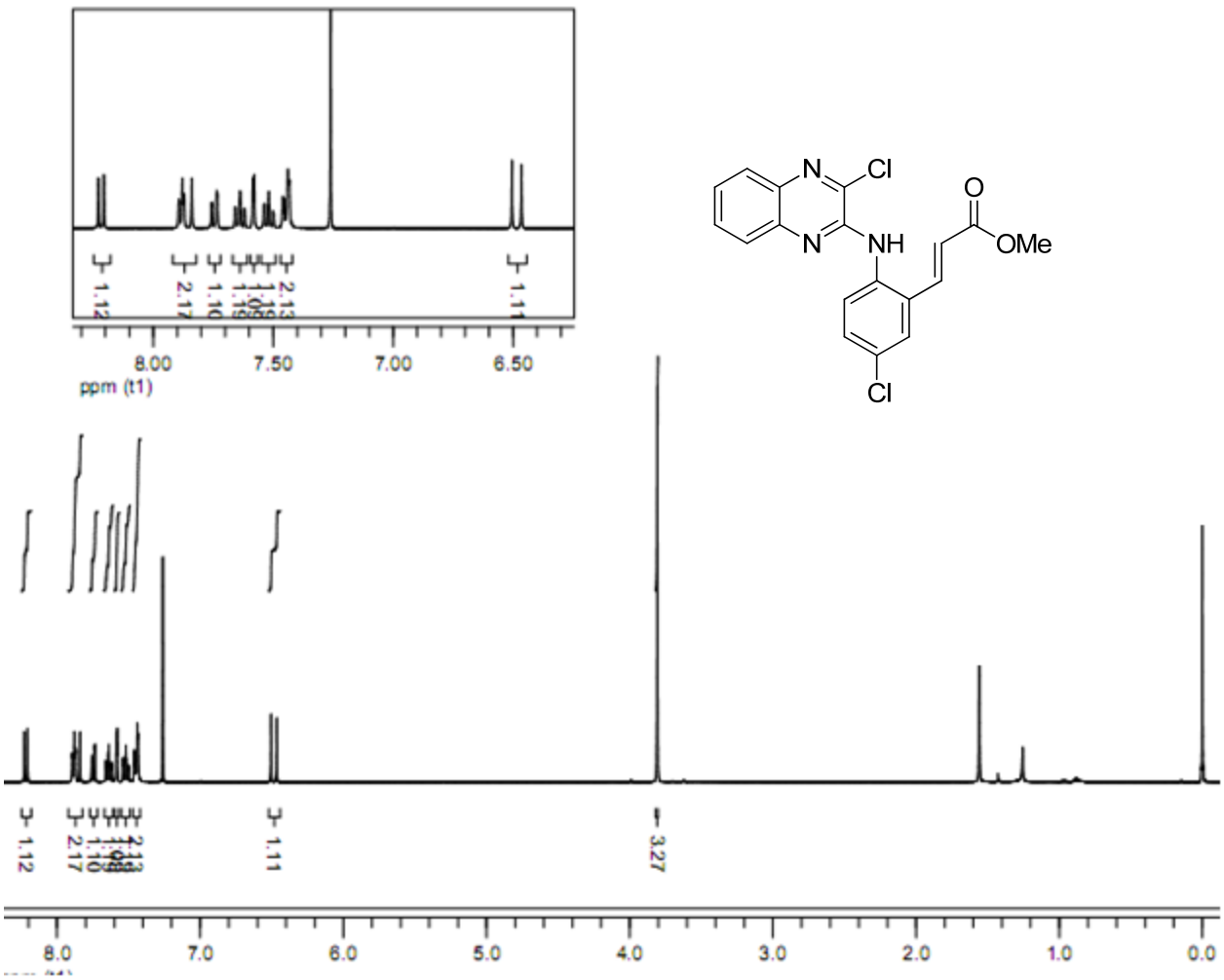


Fig. 15: ^{1}H NMR spectra of compound **5h** ($CDCl_3$, 400 MHz)

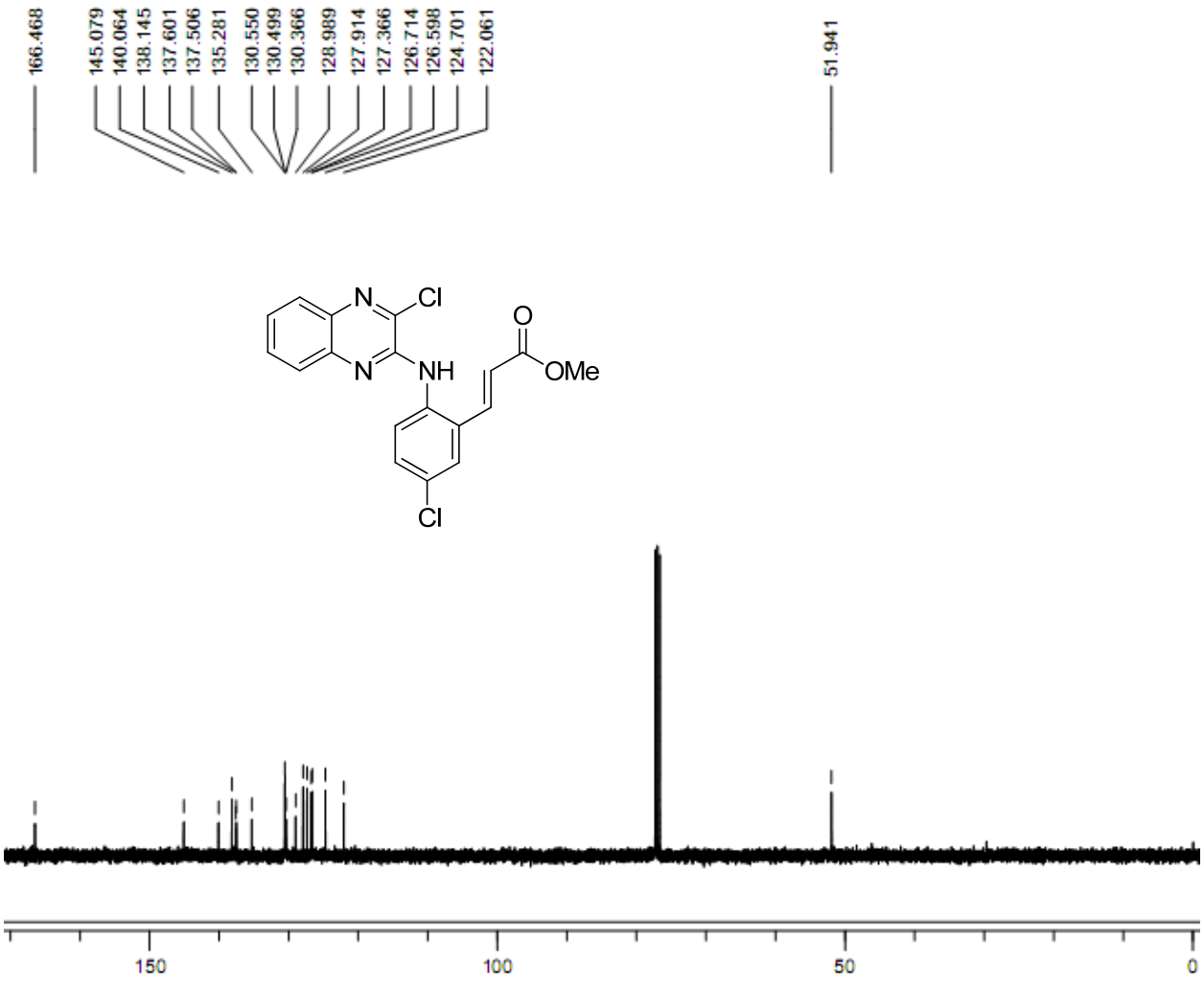


Fig. 16: ^{13}C NMR spectra of compound **5h** ($CDCl_3$, 100 MHz)

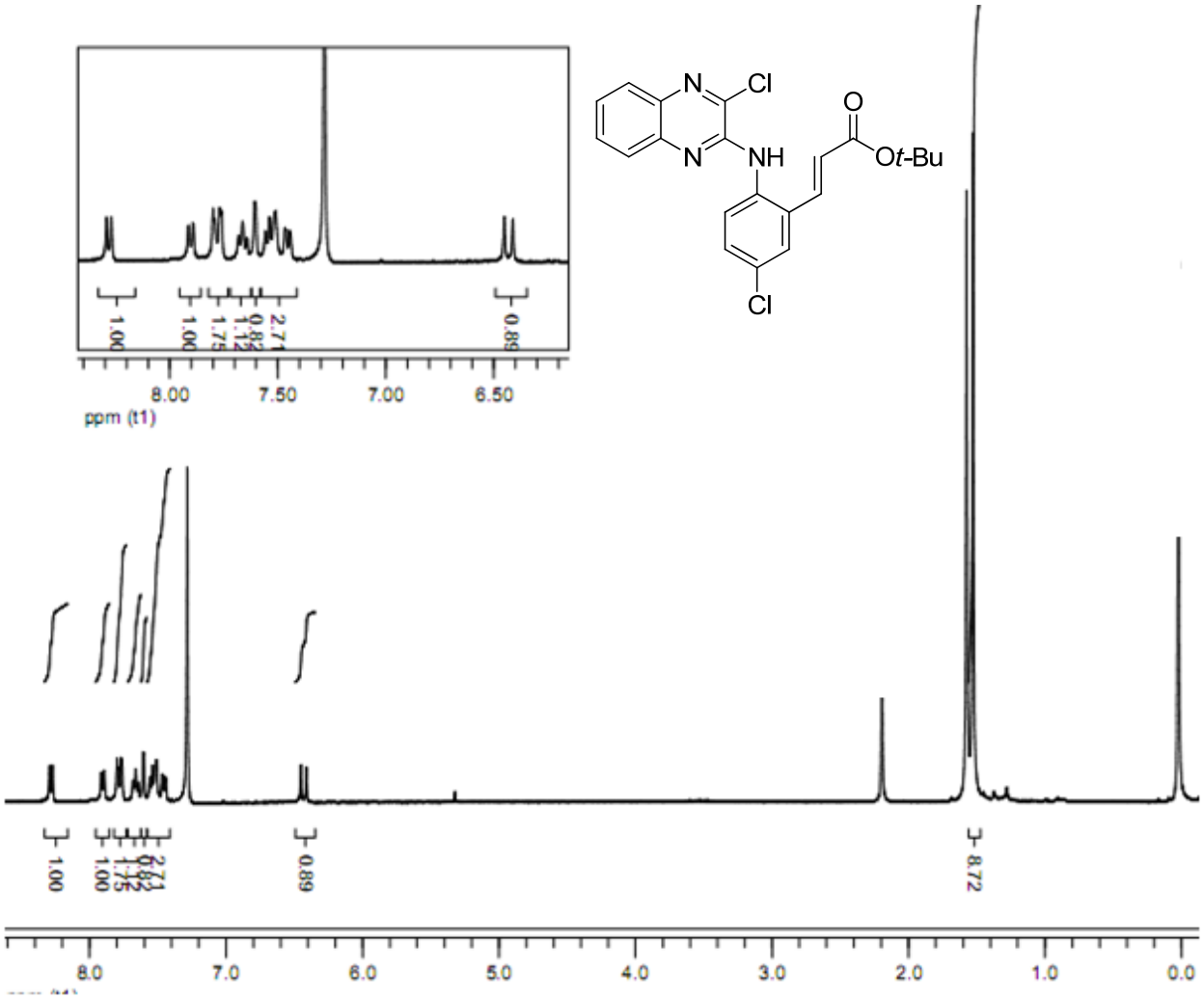


Fig. 17: ^{1}H NMR spectra of compound **5i** ($CDCl_3$, 400 MHz)

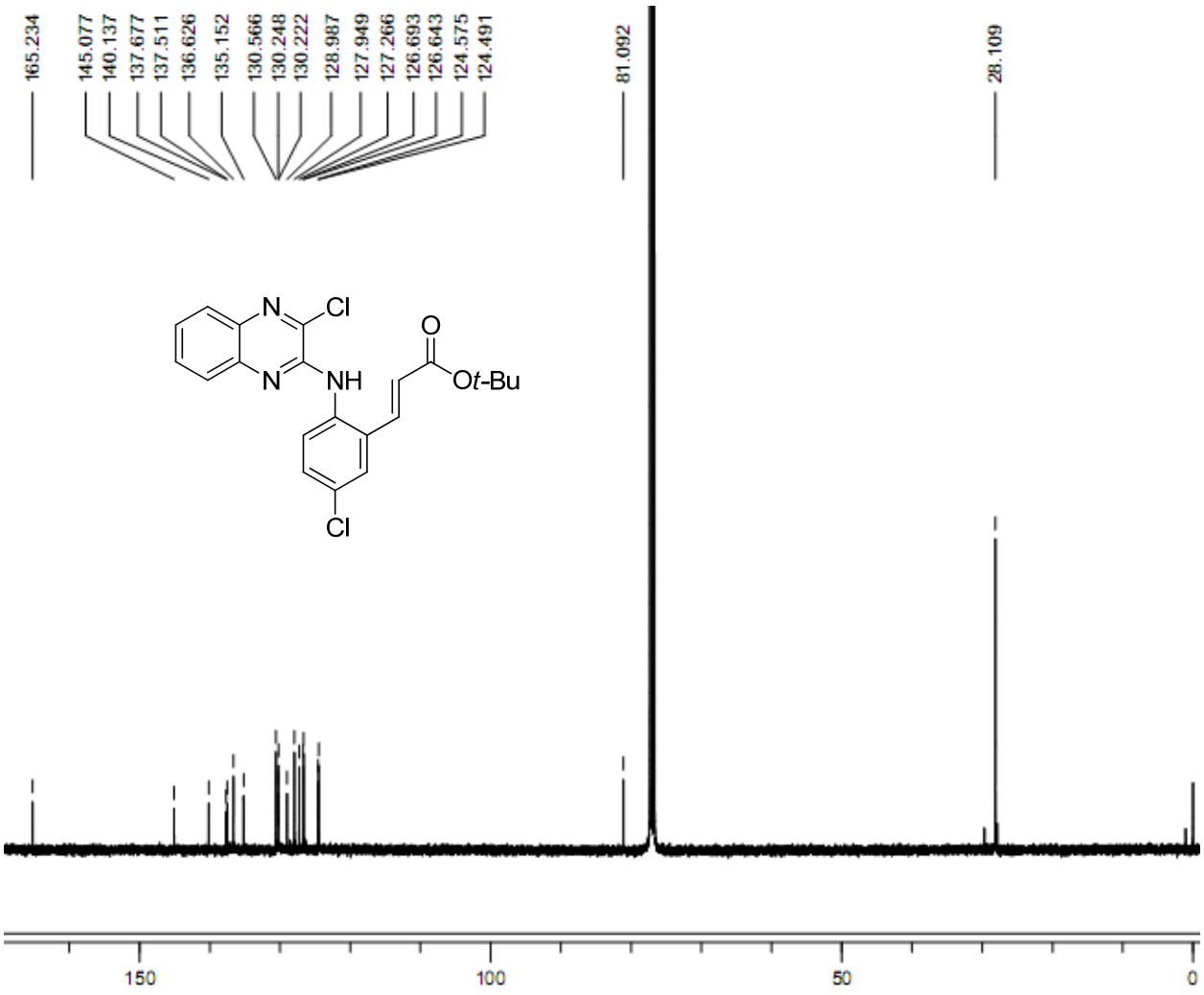


Fig. 18: ^{13}C NMR spectra of compound **5i** ($CDCl_3$, 100 MHz)

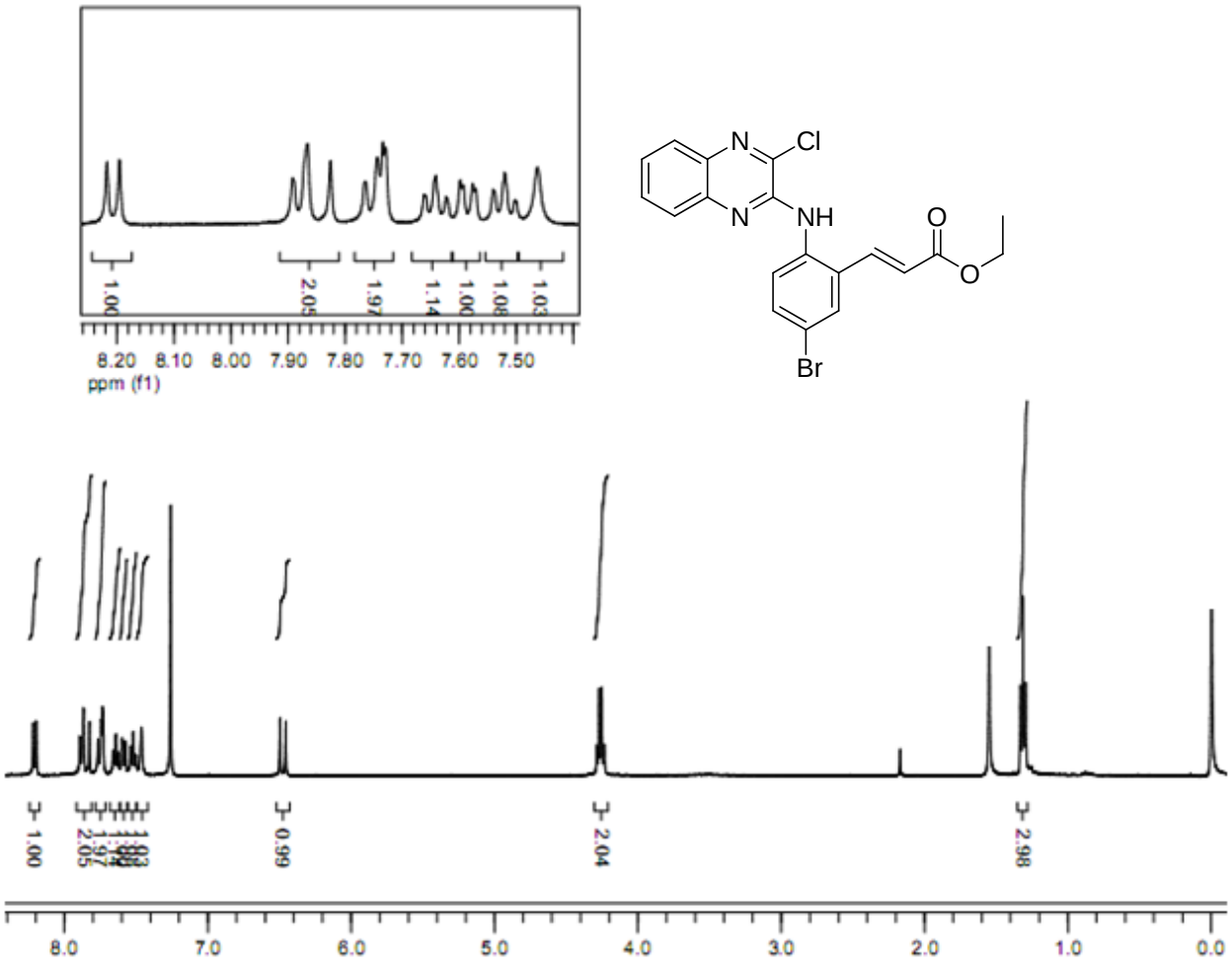


Fig. 19: ^{1}H NMR spectra of compound **5j** ($CDCl_3$, 400 MHz)

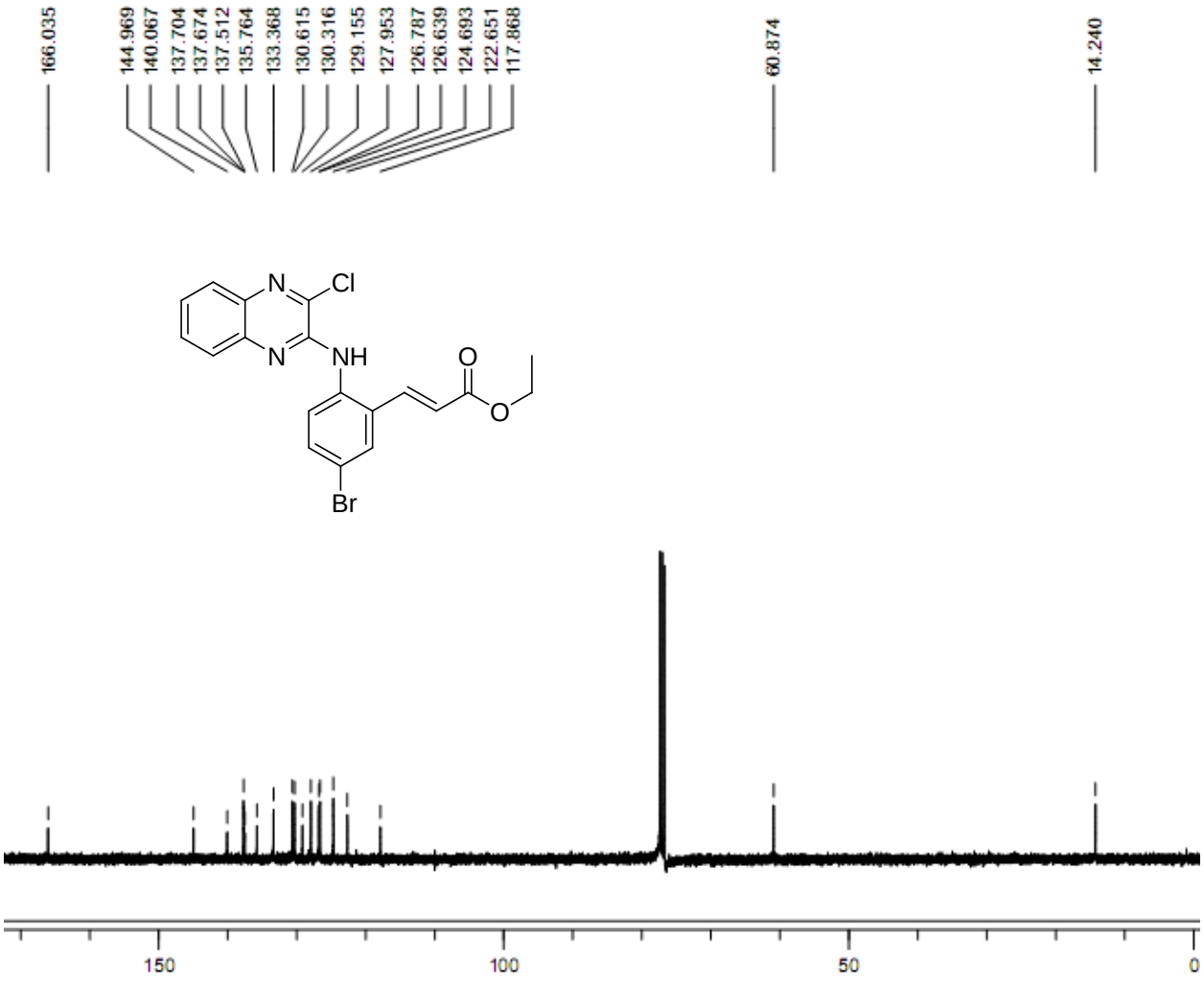


Fig. 20: ^{13}C NMR spectra of compound **5j** ($CDCl_3$, 100 MHz)

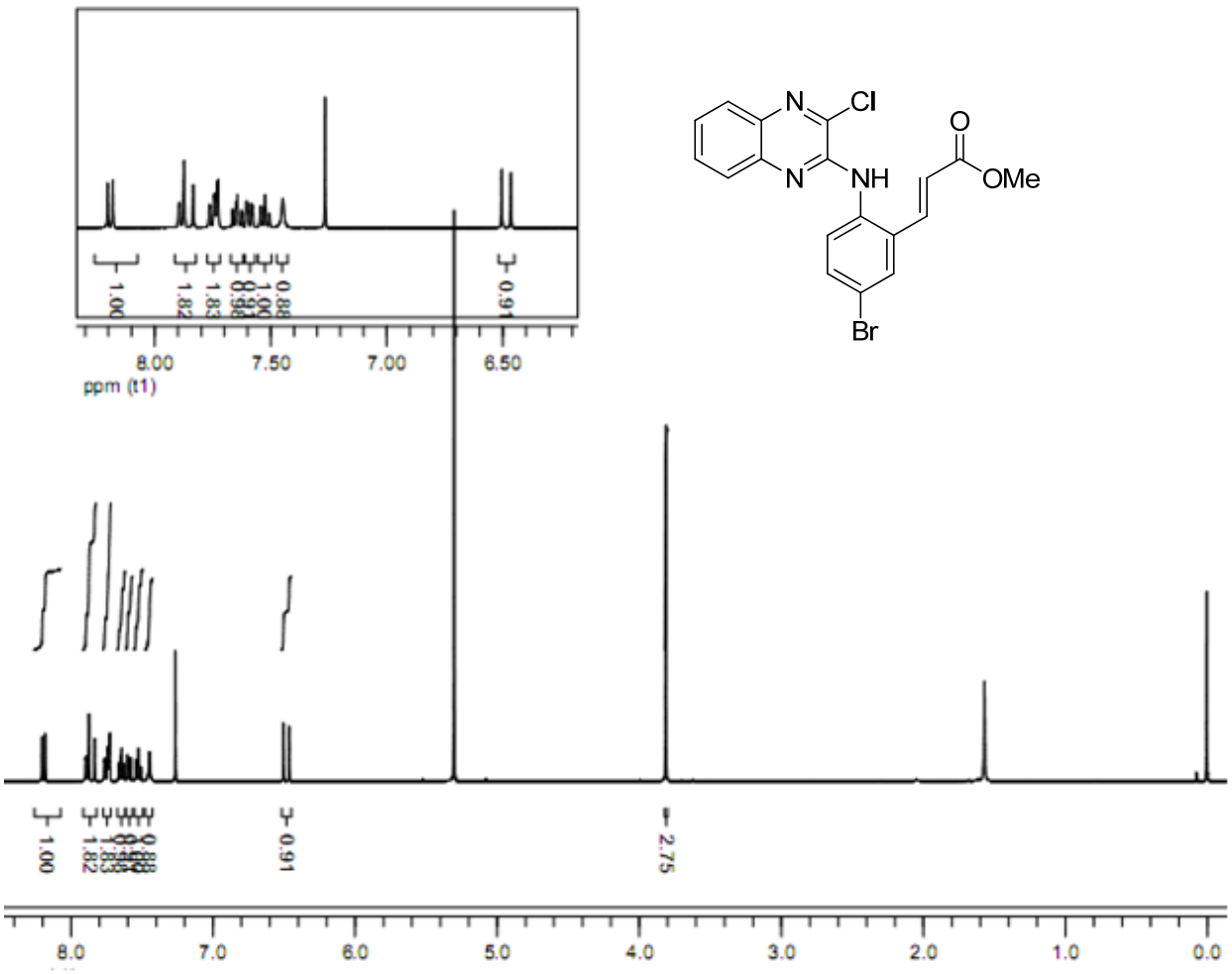


Fig. 21: ^{1}H NMR spectra of compound **5k** ($CDCl_3$, 400 MHz)

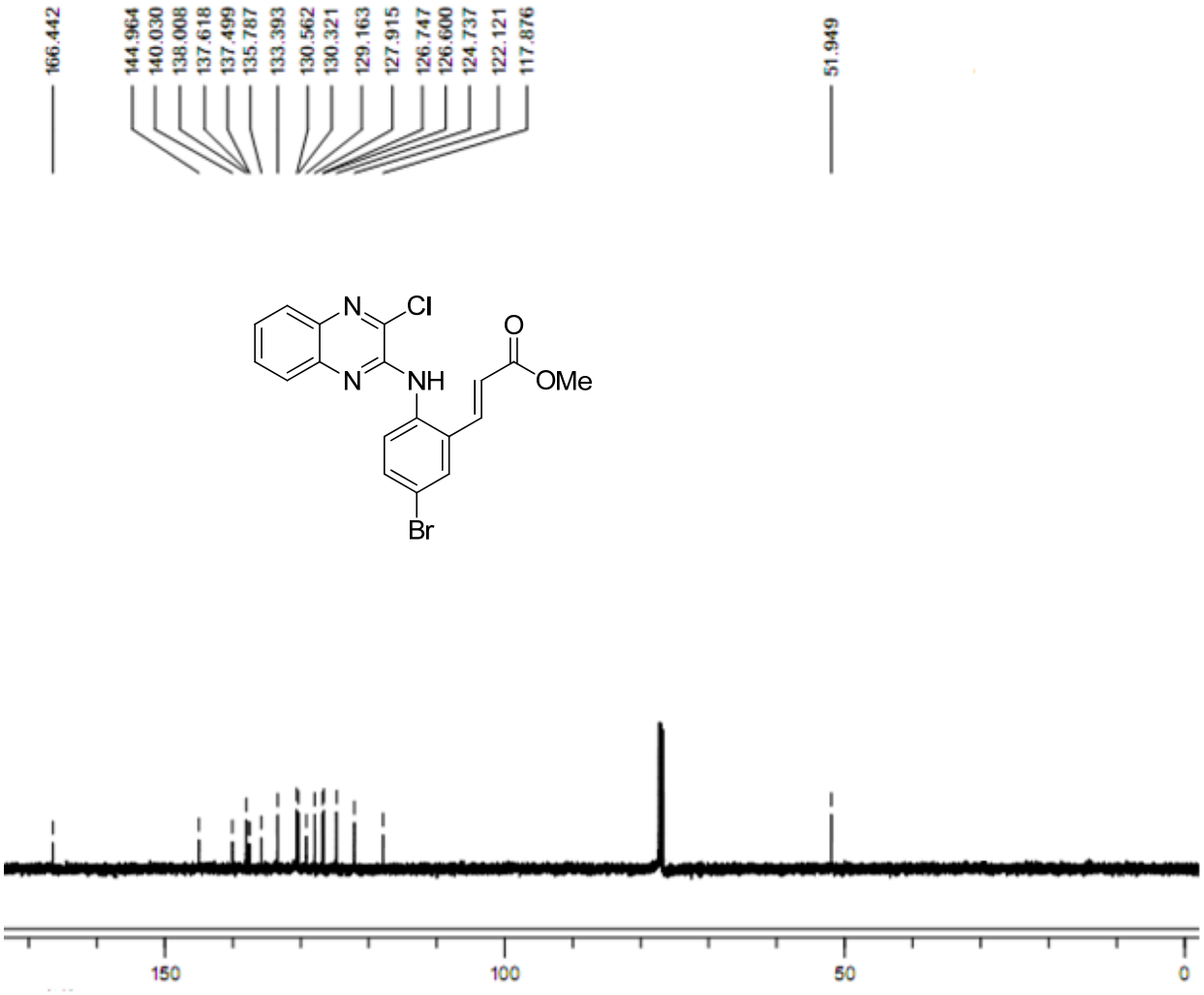


Fig. 22: ^{13}C NMR spectra of compound **5k** ($CDCl_3$, 100 MHz)

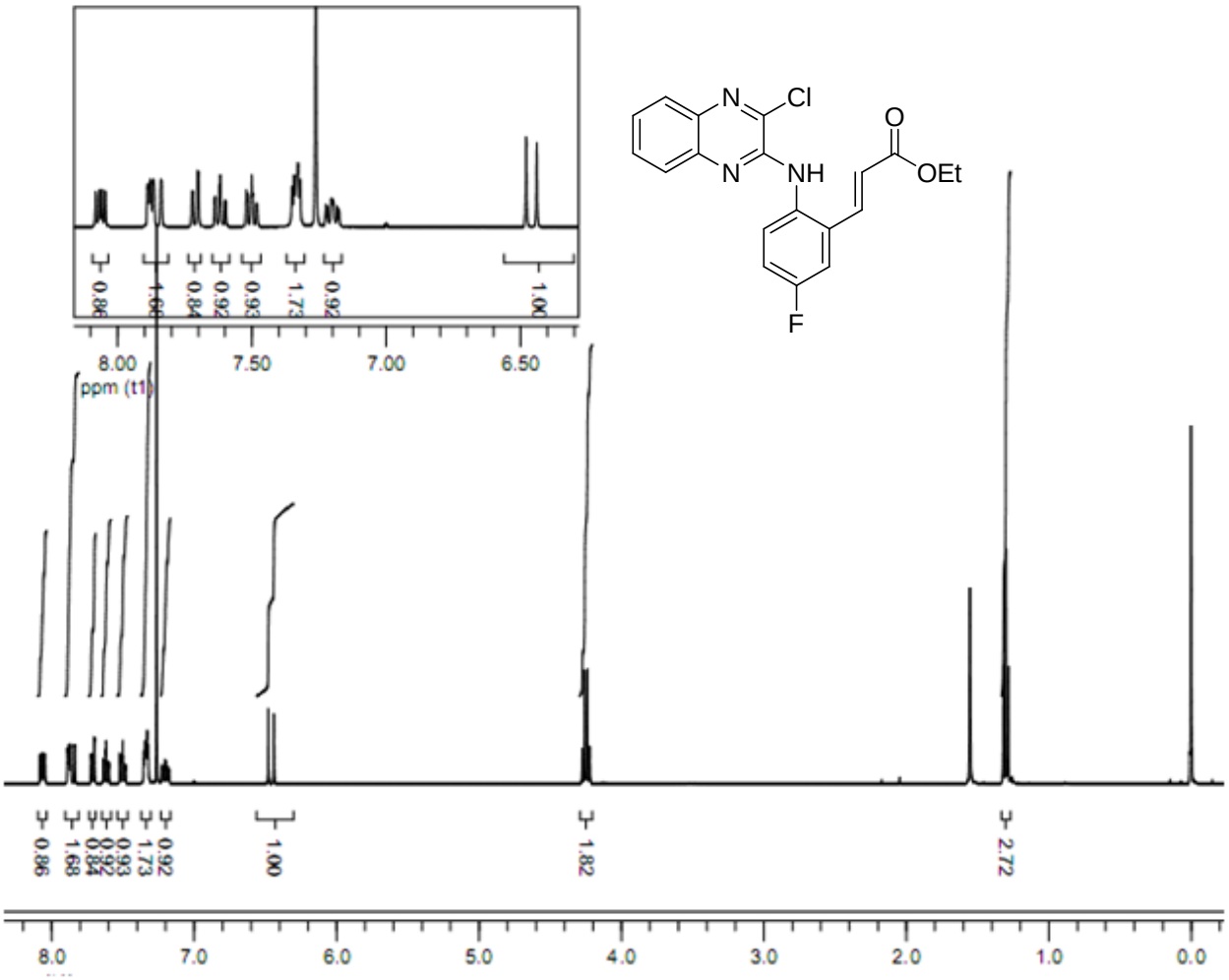


Fig. 23: ^{1}H NMR spectra of compound **5l** ($CDCl_3$, 400 MHz)

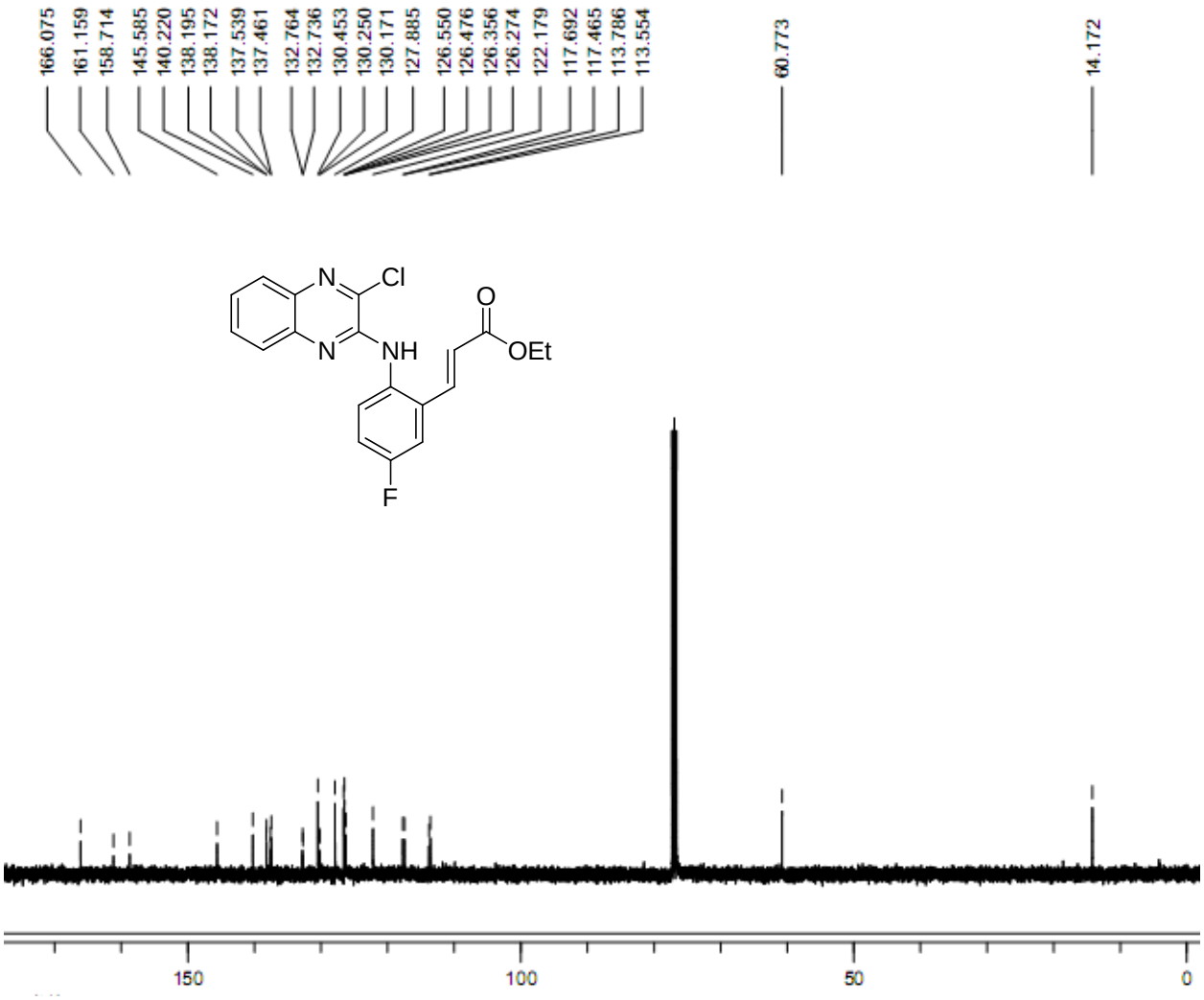


Fig. 24: ^{13}C NMR spectra of compound **5l** ($CDCl_3$, 100 MHz)

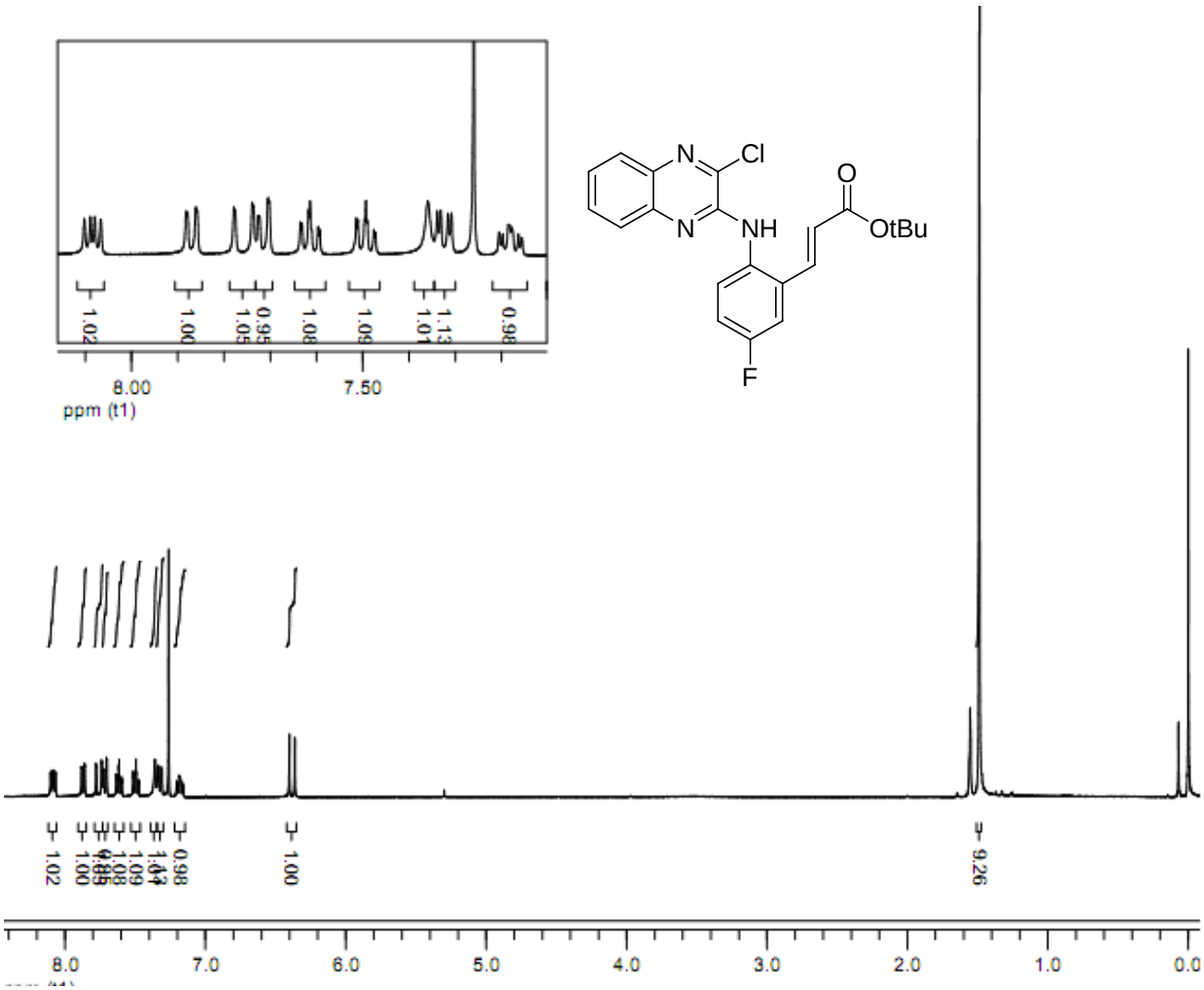


Fig. 25: ^{1}H NMR spectra of compound **5m** ($CDCl_3$, 400 MHz)

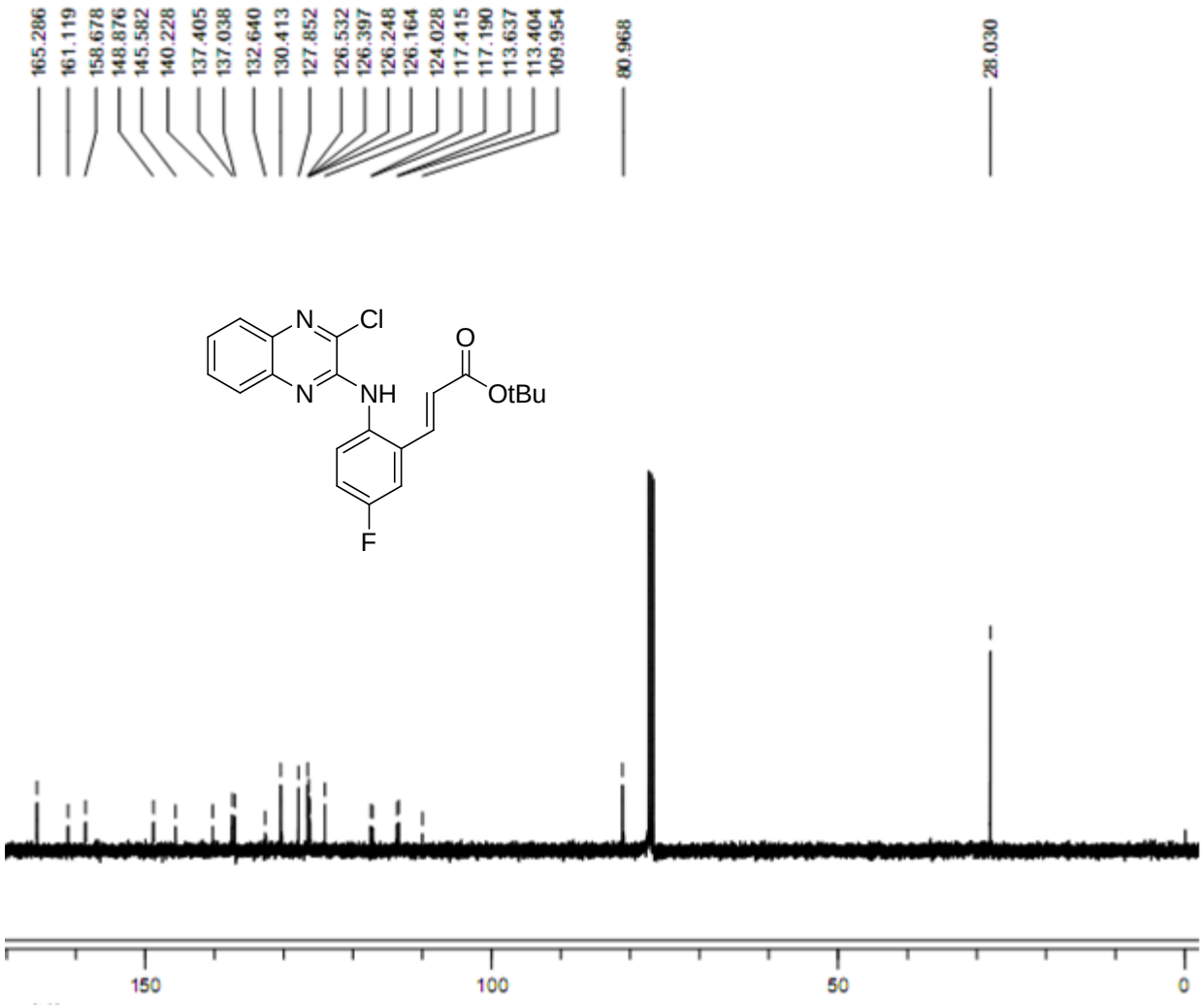


Fig. 26: ^{13}C NMR spectra of compound **5m** ($CDCl_3$, 100 MHz)

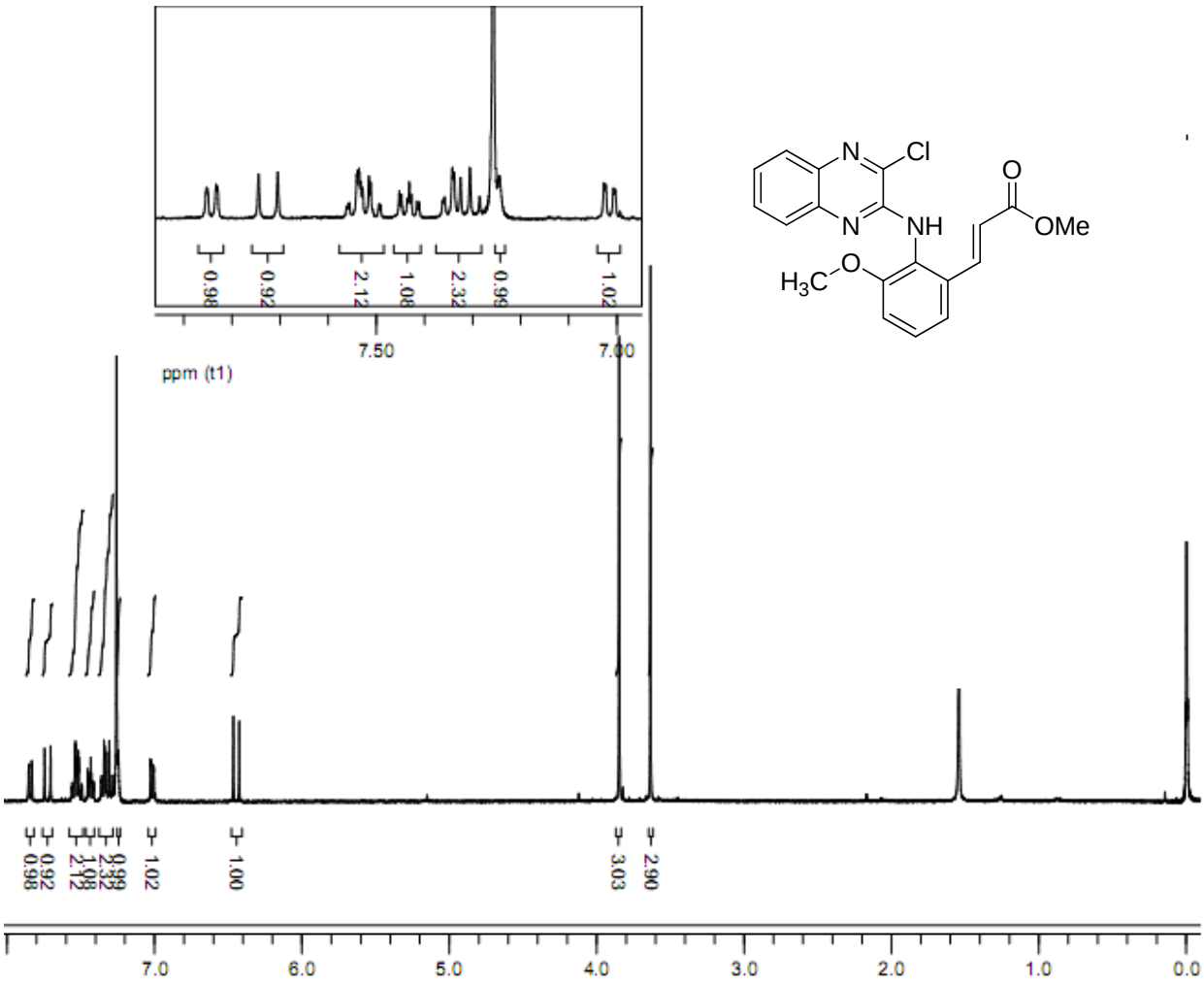


Fig. 27: ^{1}H NMR spectra of compound **5n** ($CDCl_3$, 400 MHz)

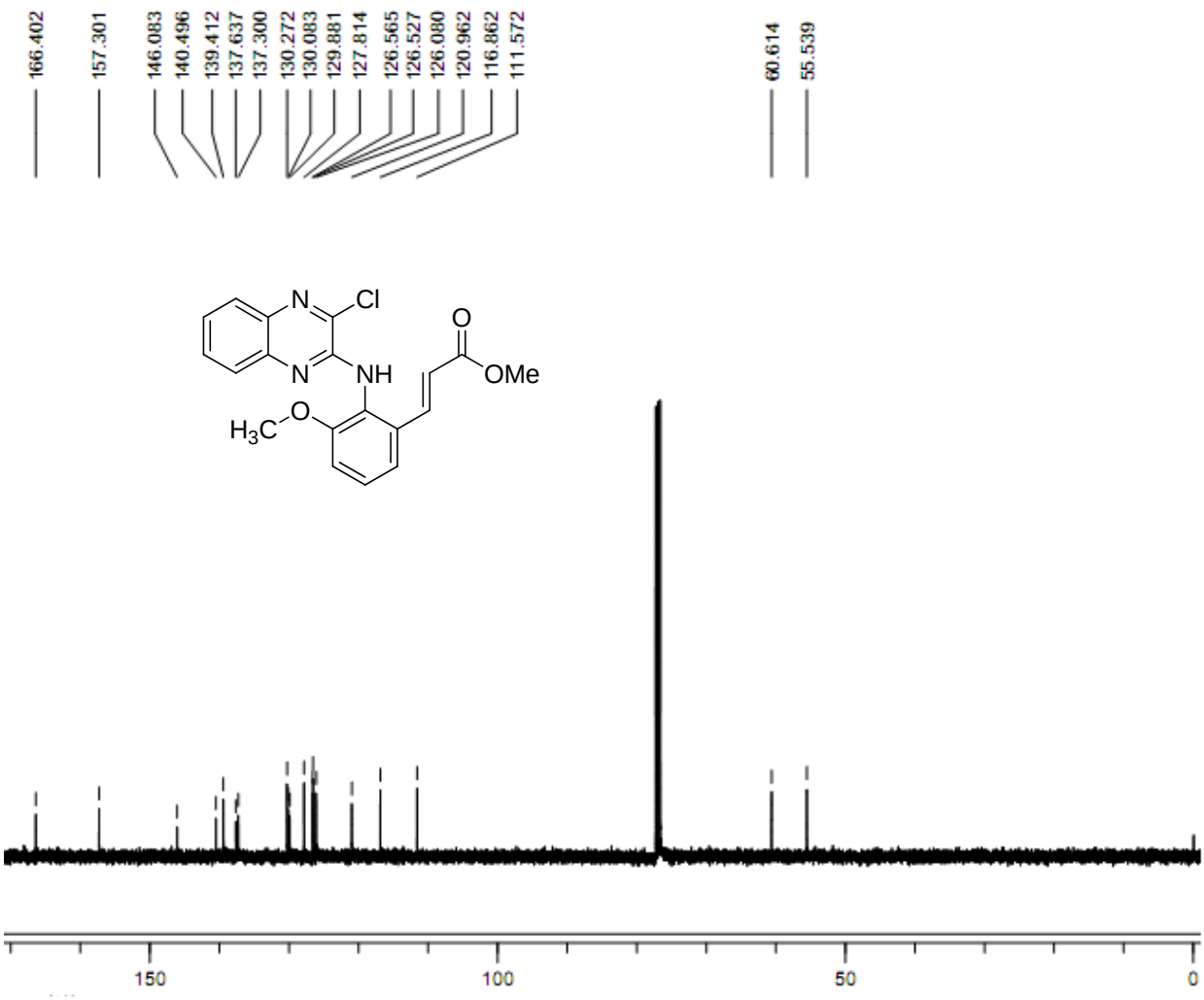


Fig. 28: ^{13}C NMR spectra of compound **5n** ($CDCl_3$, 100 MHz)

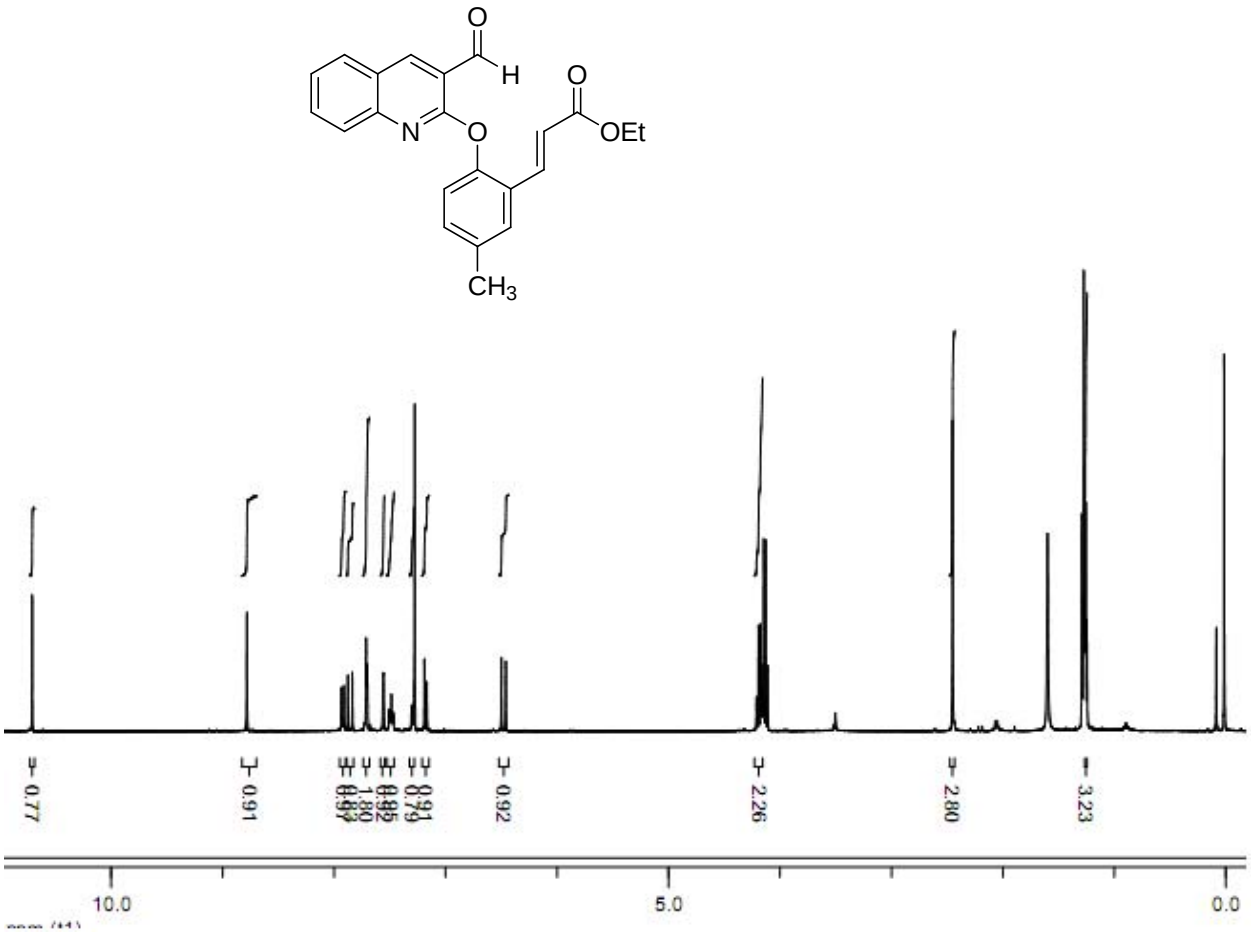


Fig. 29: ^{1}H NMR spectra of compound **5o** ($CDCl_3$, 400 MHz)

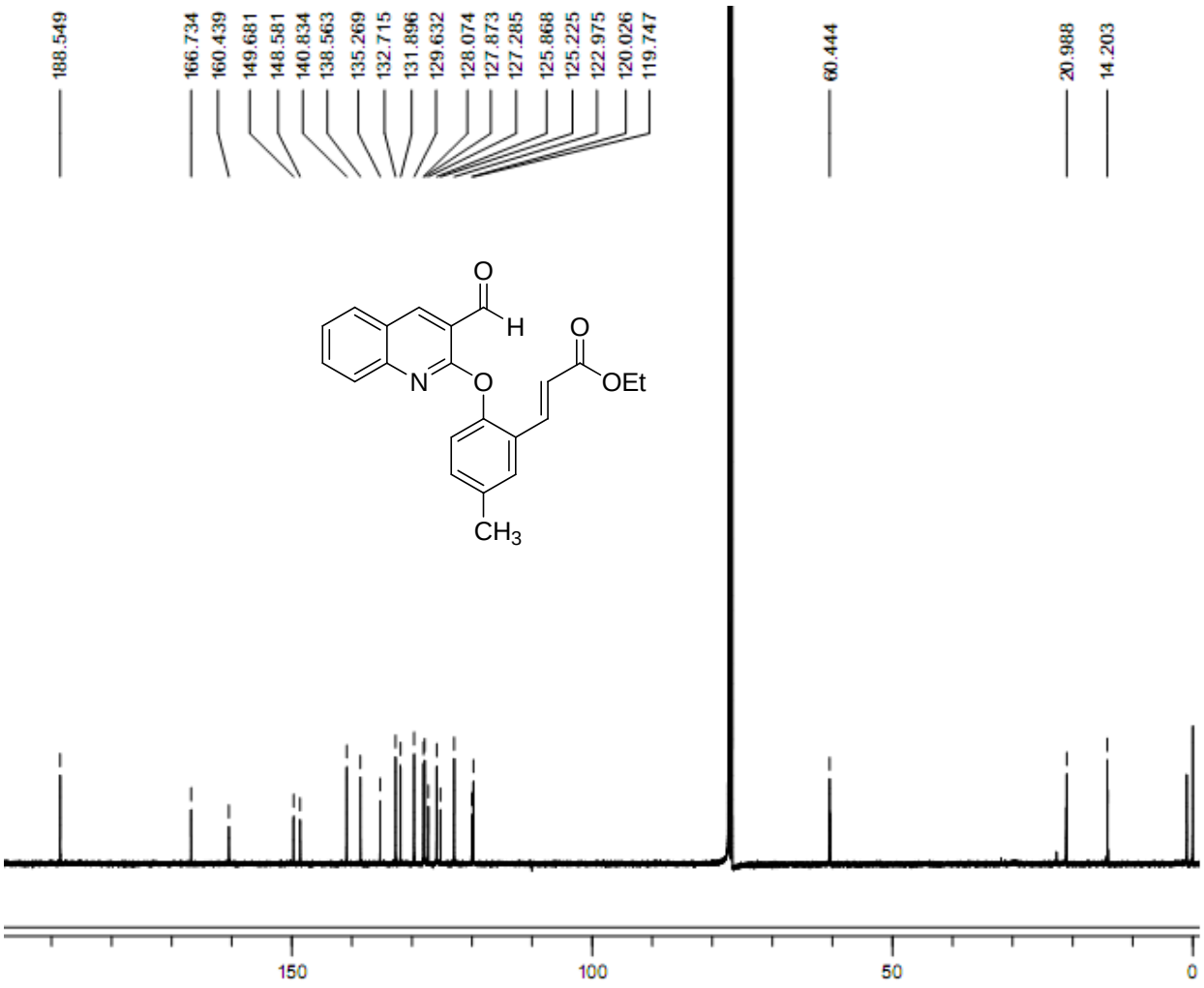


Fig. 30: ^{13}C NMR spectra of compound **5o** ($CDCl_3$, 100 MHz)

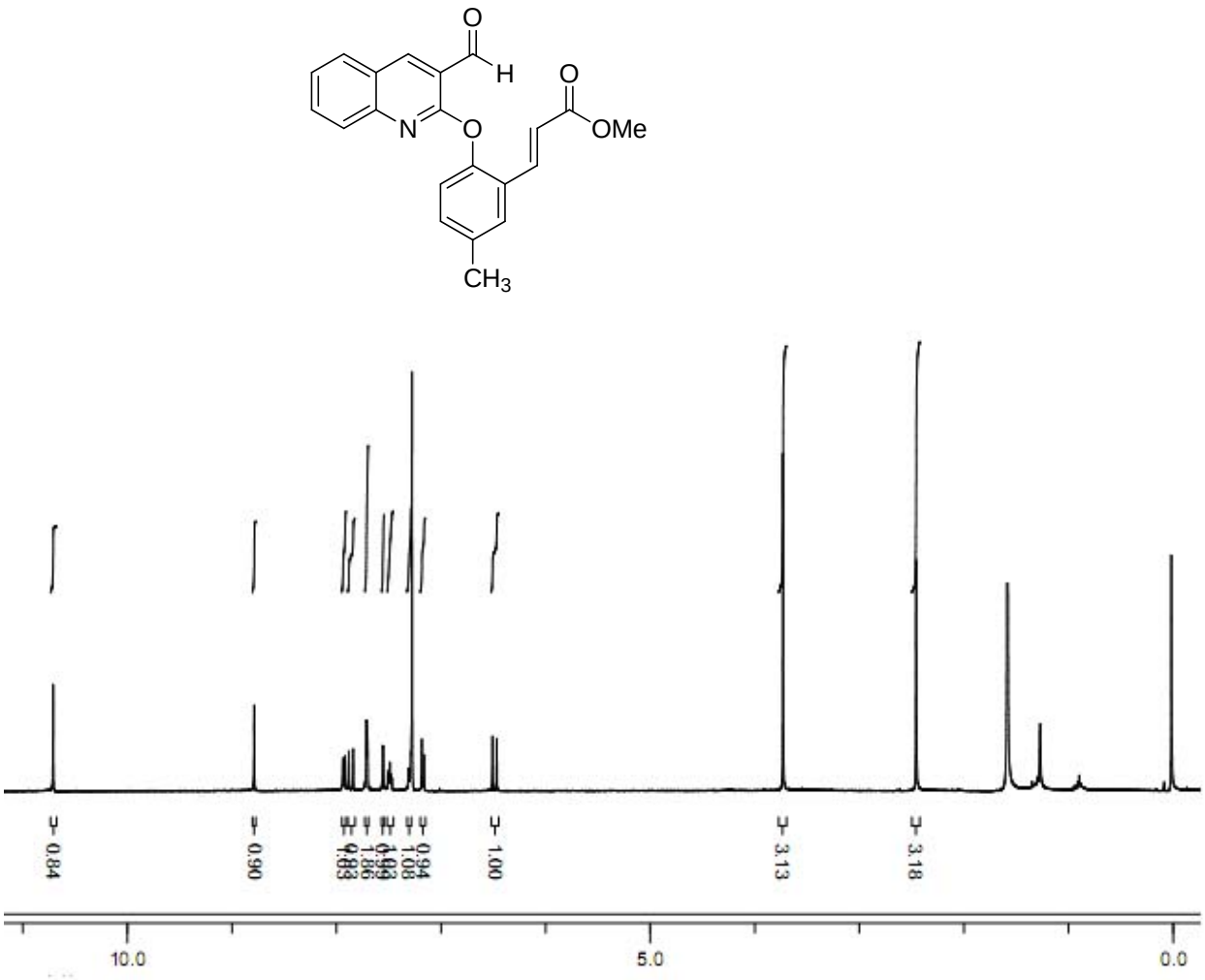


Fig. 31: ^{1}H NMR spectra of compound **5p** ($CDCl_3$, 400 MHz)

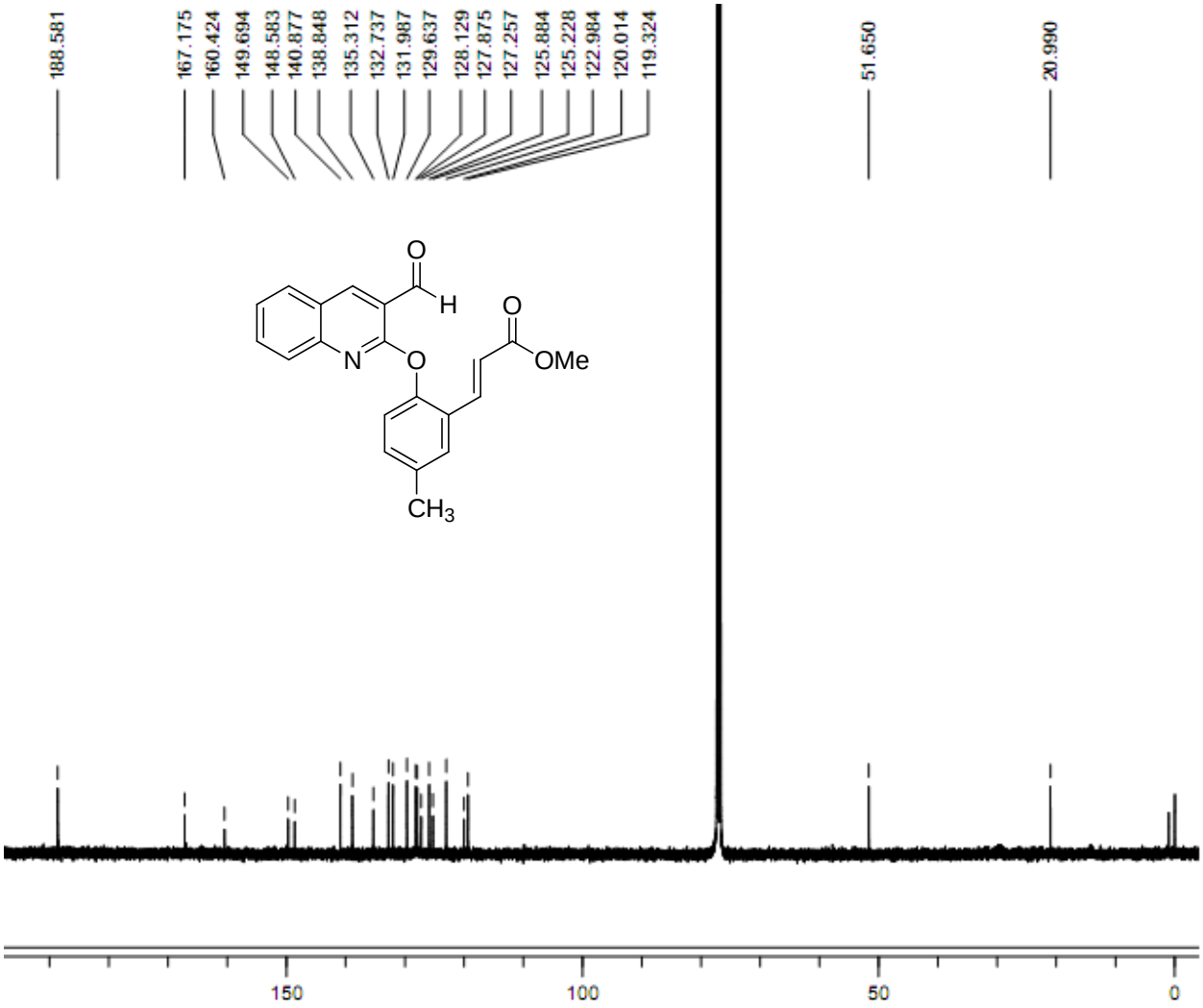


Fig. 32: ^{13}C NMR spectra of compound **5p** ($CDCl_3$, 100 MHz)

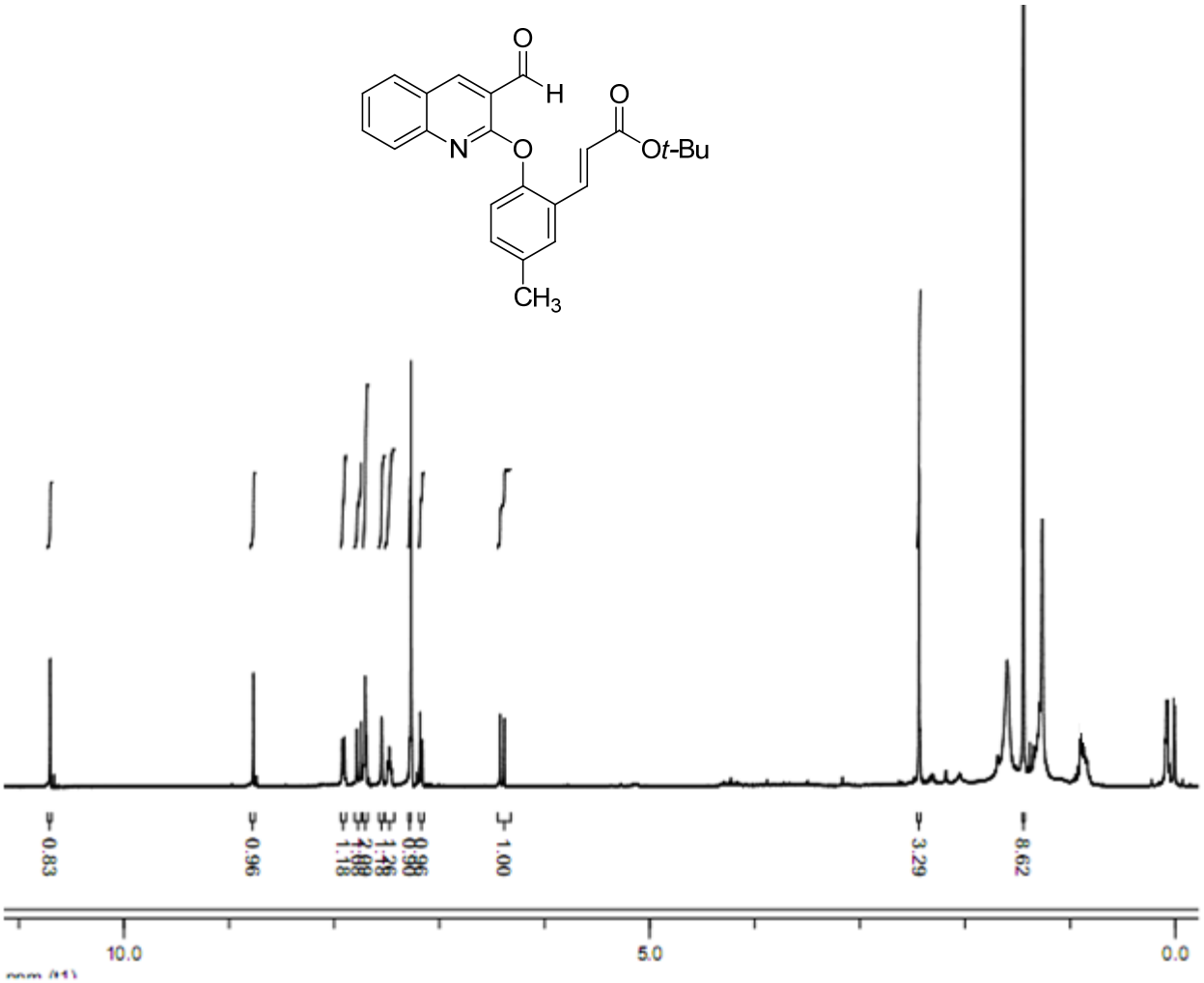


Fig. 33: ^{1}H NMR spectra of compound **5q** ($CDCl_3$, 400 MHz)

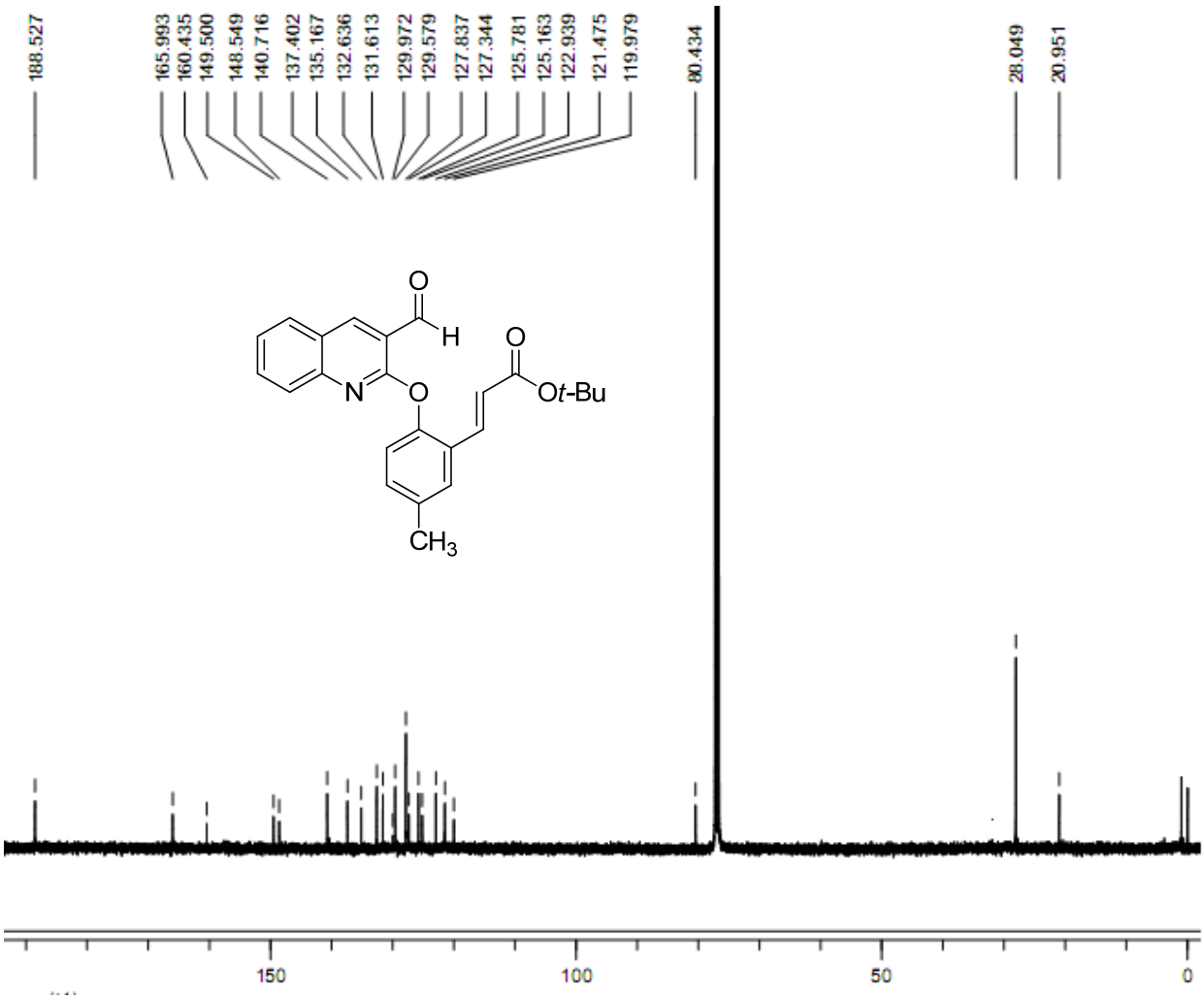


Fig. 34: ^{13}C NMR spectra of compound **5q** ($CDCl_3$, 100 MHz)

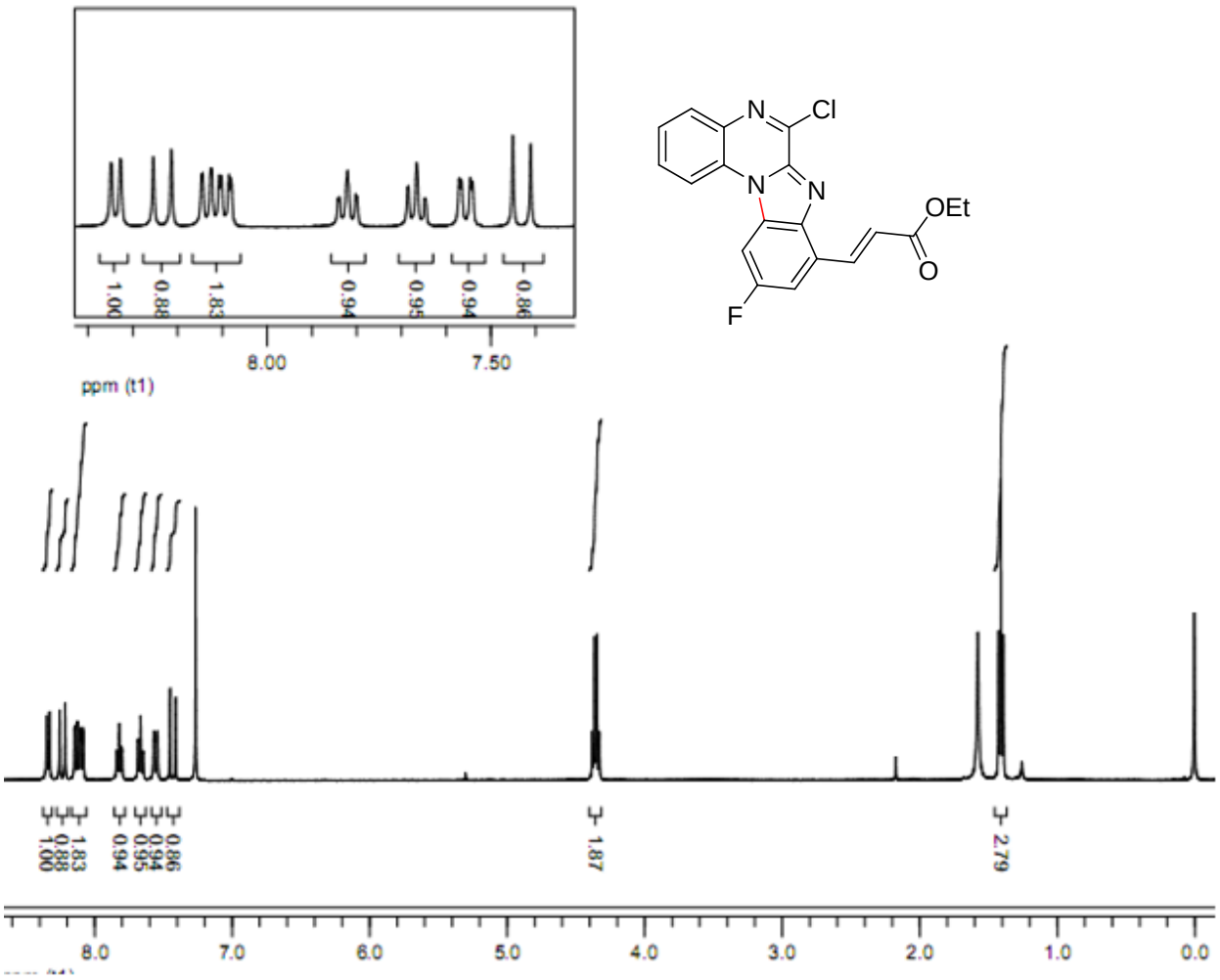


Fig. 35: ^{1}H NMR spectra of compound **6a** ($CDCl_3$, 400 MHz)

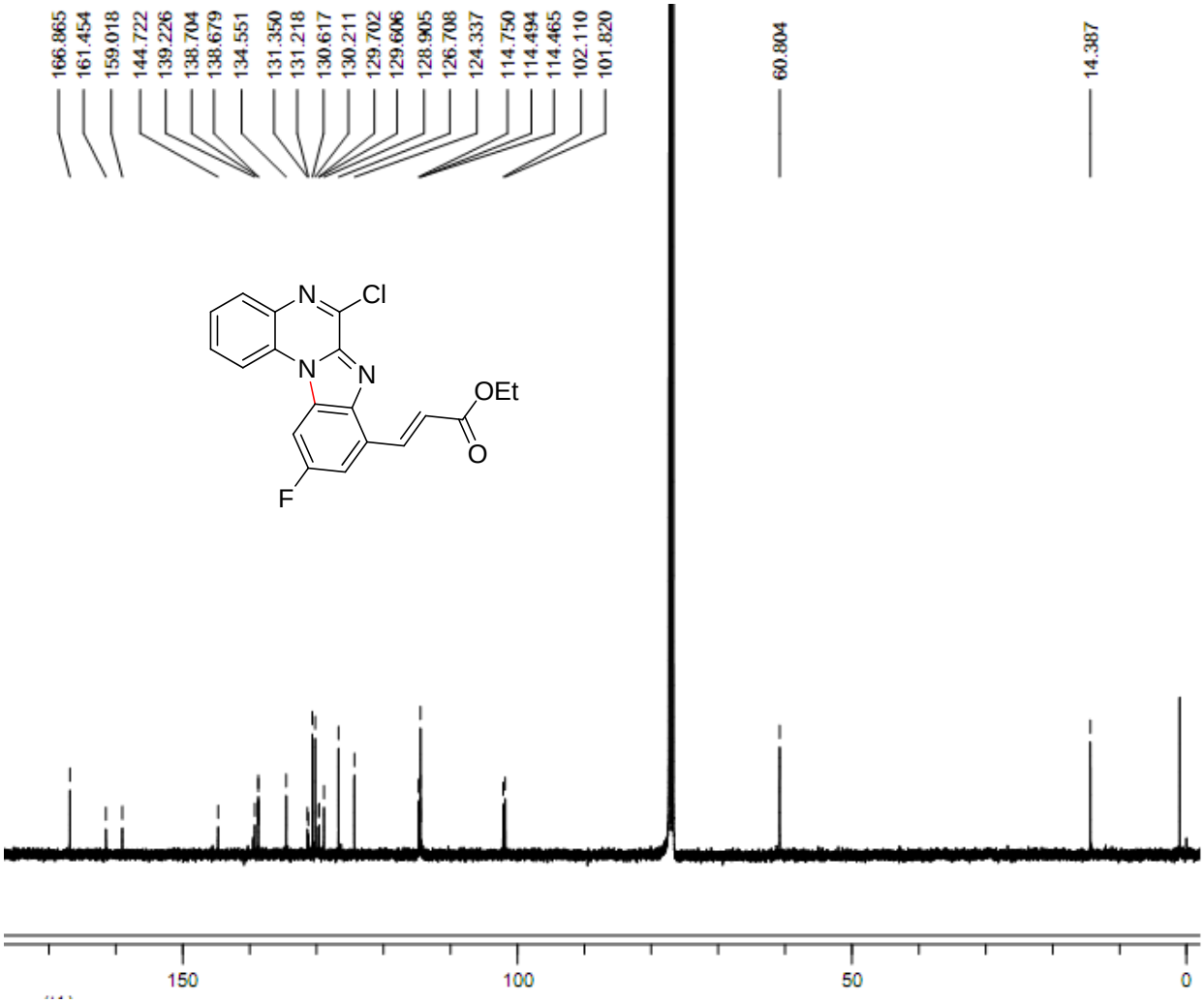


Fig. 36: ^{13}C NMR spectra of compound **6a** ($CDCl_3$, 100 MHz)

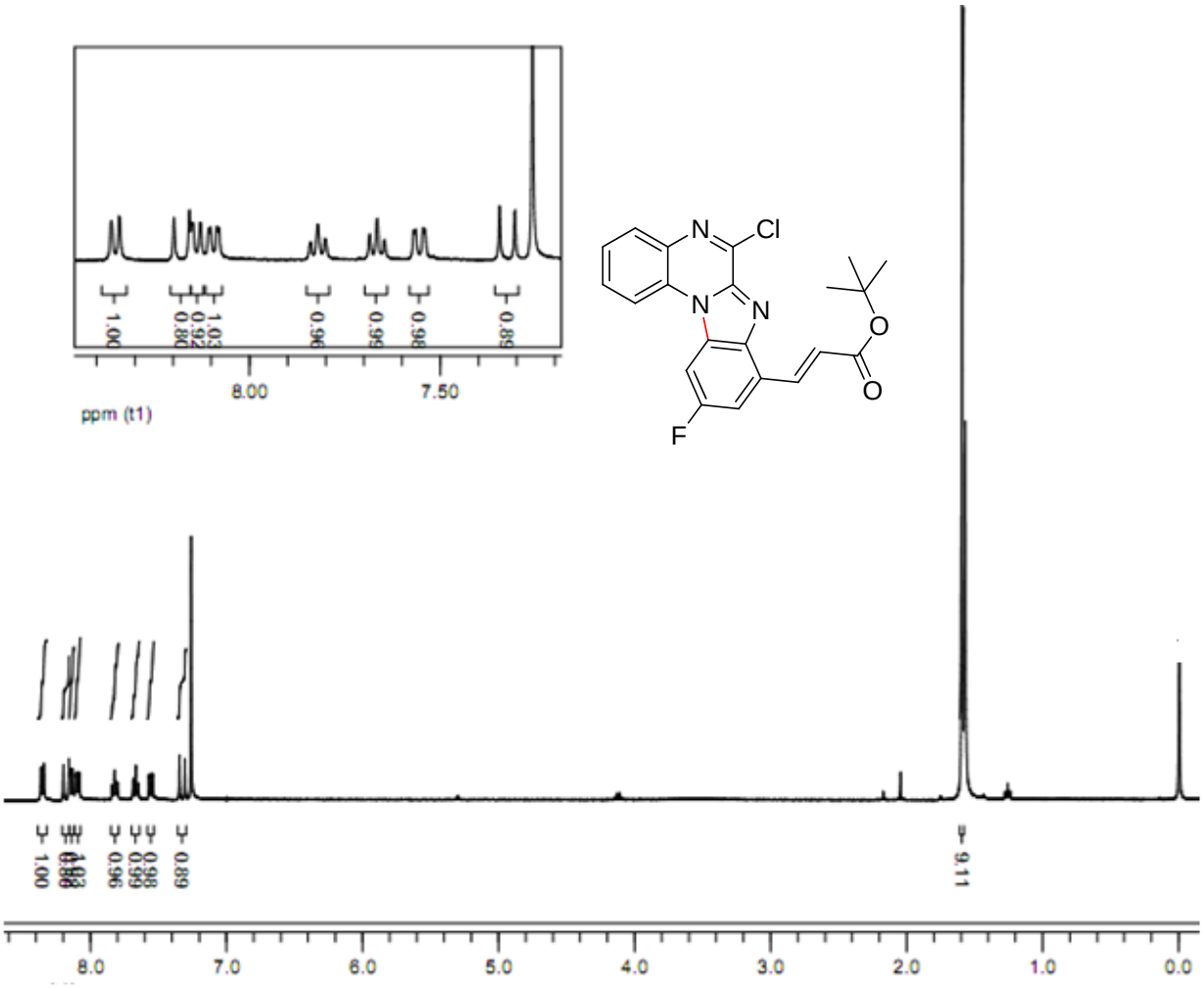


Fig. 37: ^{1}H NMR spectra of compound **6b** ($CDCl_3$, 400 MHz)

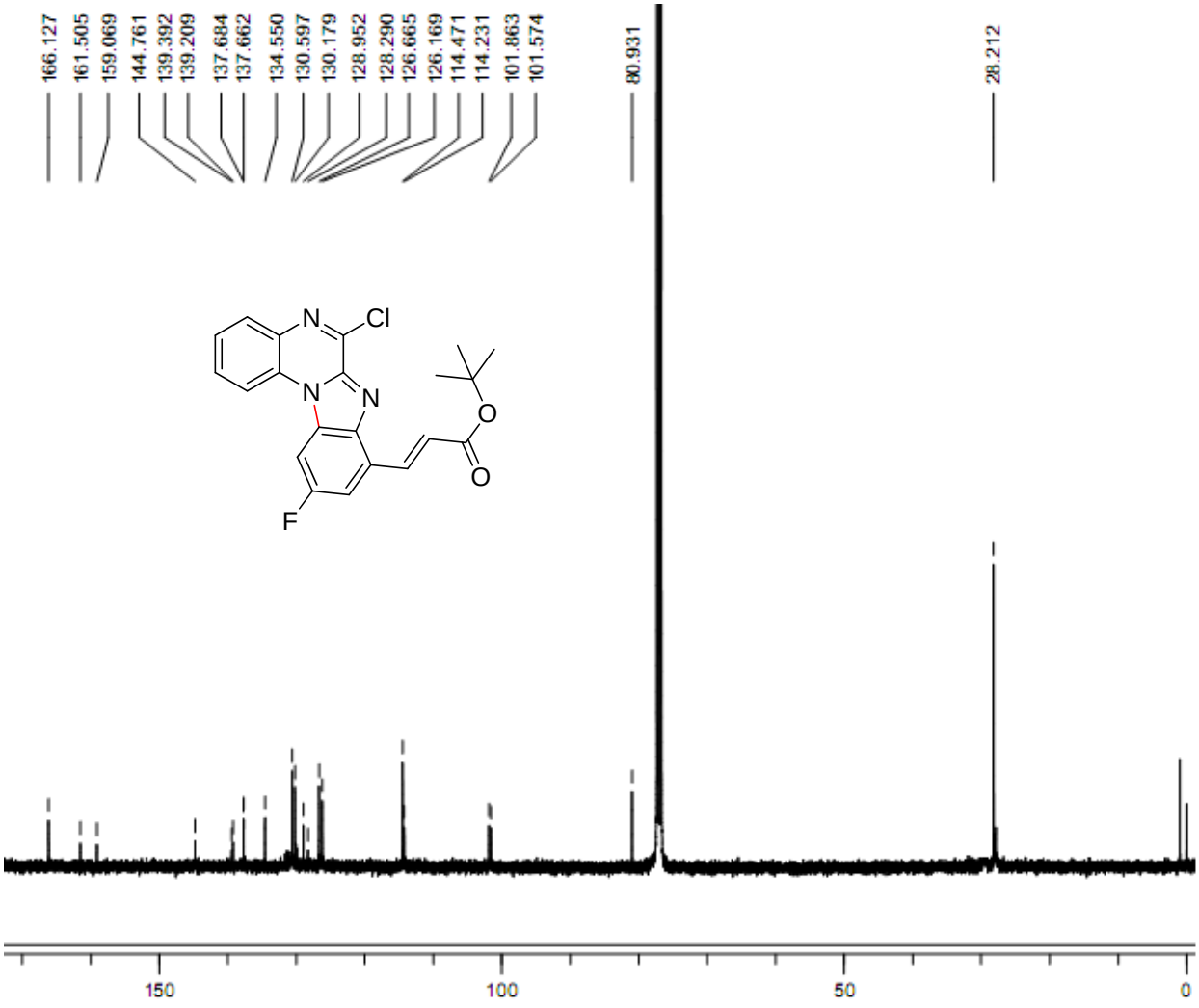


Fig. 38: ^{13}C NMR spectra of compound **6b** ($CDCl_3$, 100 MHz)

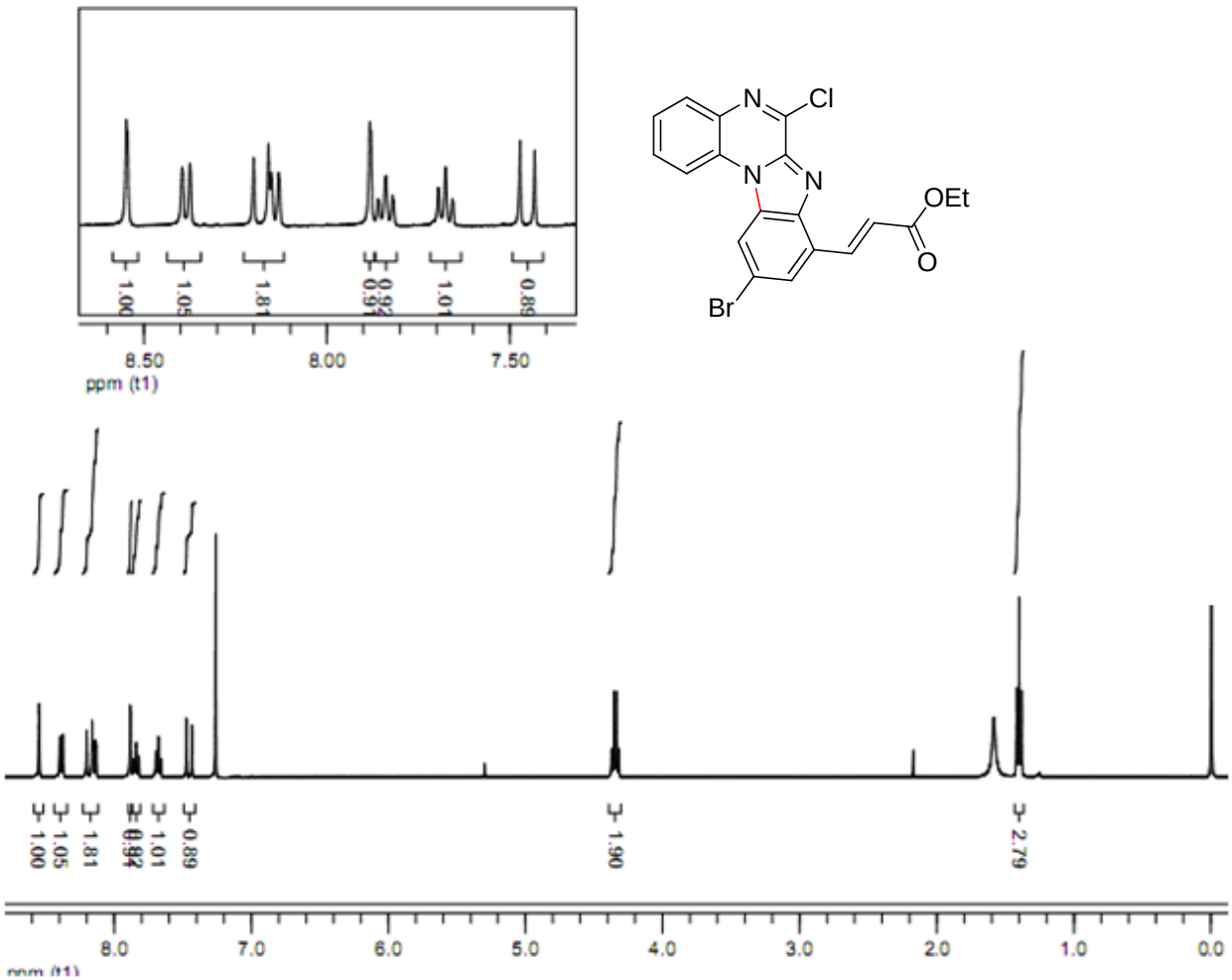


Fig. 39: ^{1}H NMR spectra of compound **6c** ($CDCl_3$, 400 MHz)

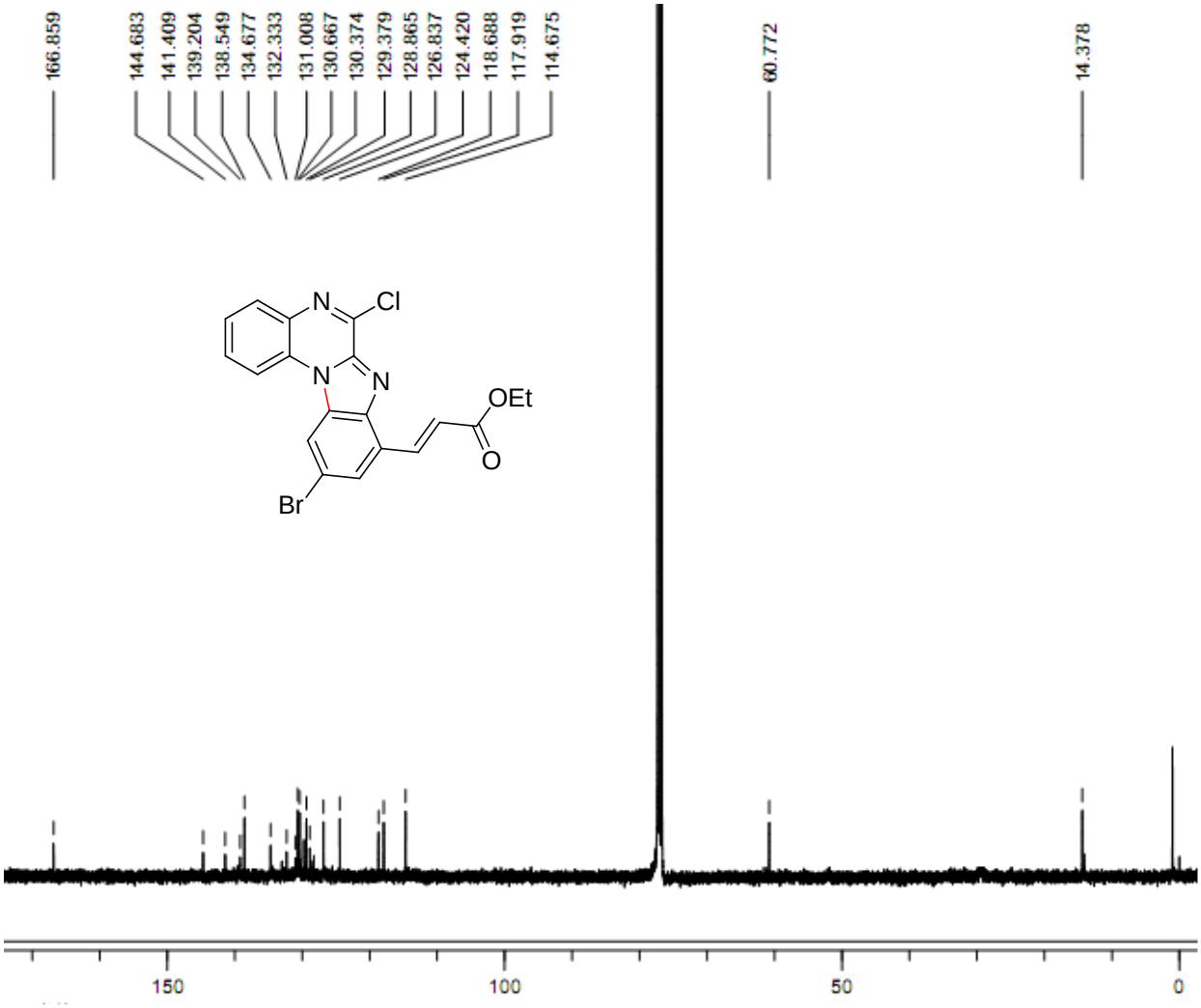


Fig. 40: ^{13}C NMR spectra of compound **6c** ($CDCl_3$, 100 MHz)

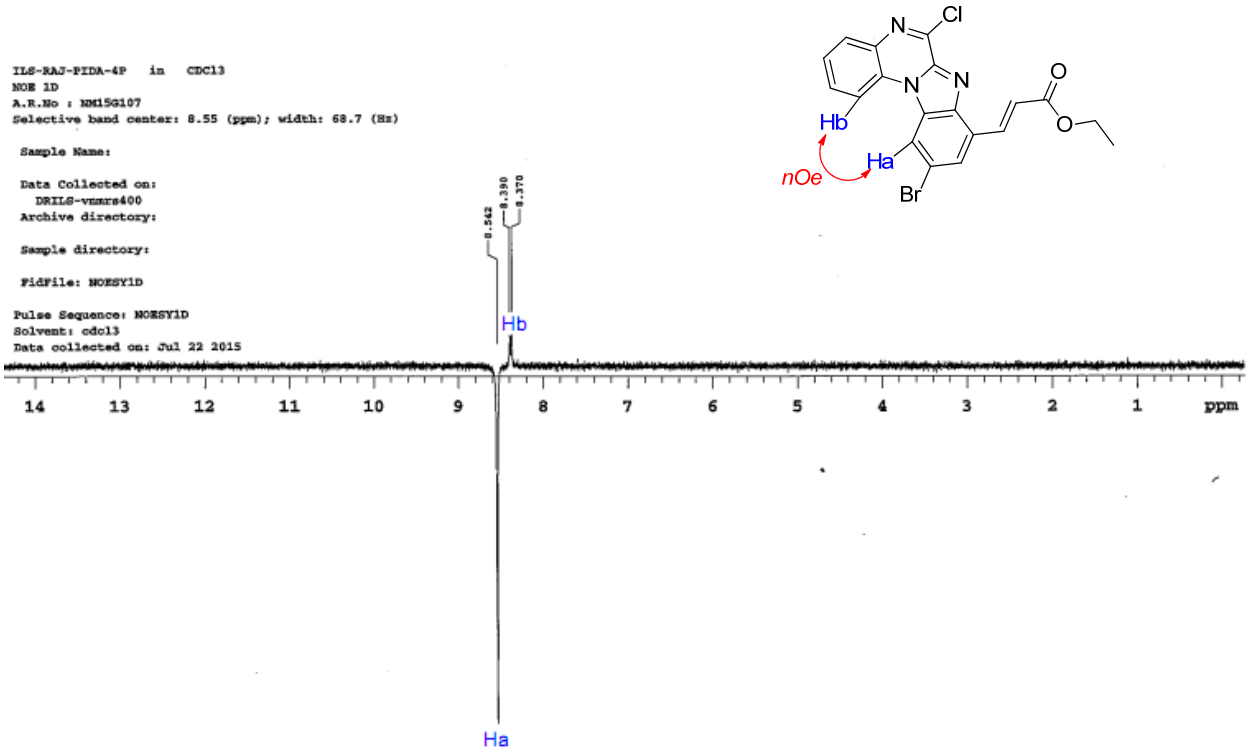


Fig. 41: 1D-NOE spectra of compound **6c**

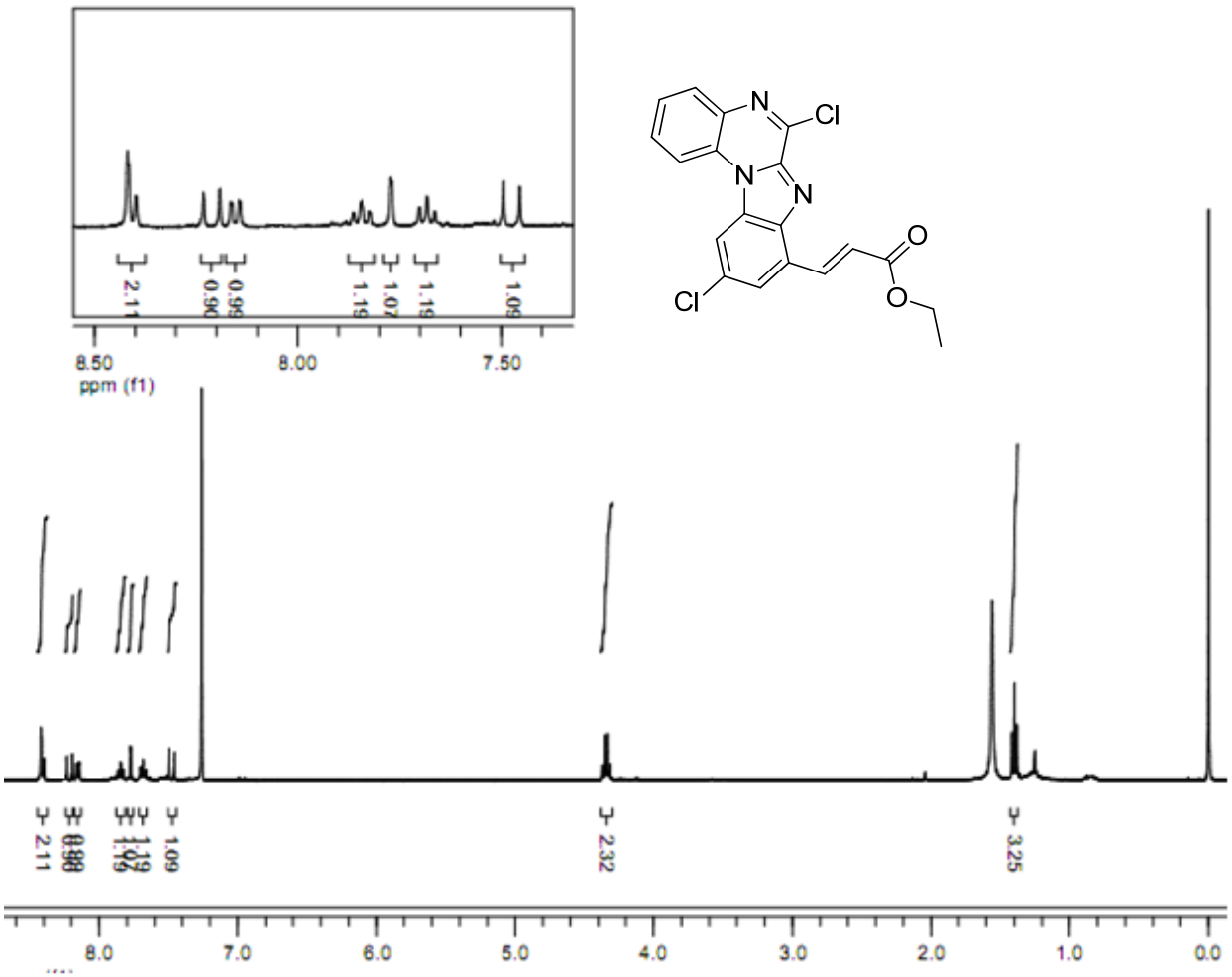


Fig. 42: ^{1}H NMR spectra of compound **6d** ($CDCl_3$, 400 MHz)

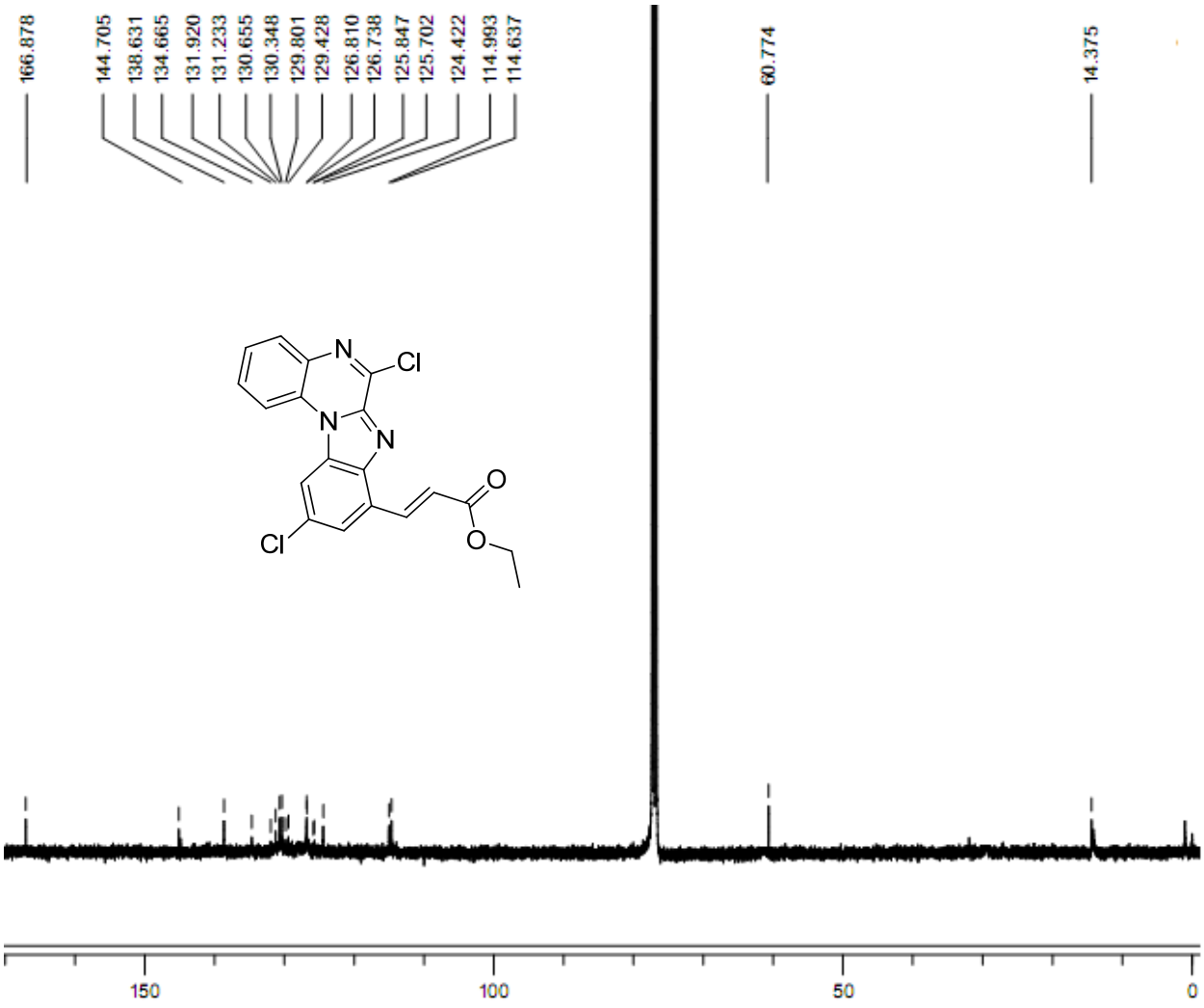
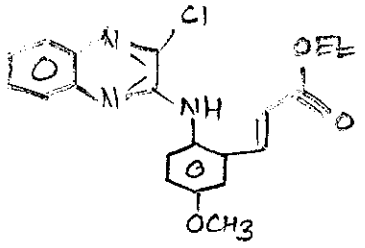


Fig. 43: ^{13}C NMR spectra of compound **6d** ($CDCl_3$, 100 MHz)

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-OCH3-ET	Acquired By:	System
A R Number:	CM14K010	Sample Set Name:	251114_3
Vial:	35	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO0
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/26/2014 3:12:54 AM IST		
Date Processed:	11/26/2014 3:28:29 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	3.825	5252909	98.89	831020
2	4.373	59013	1.11	9387

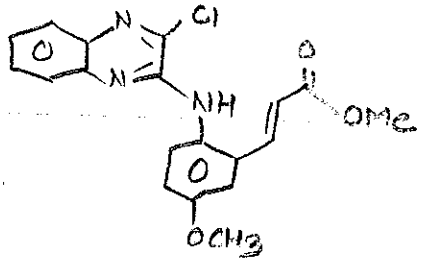
Analysed By: Checked By:

26/11/14

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-S2-6F		
AR Number:	CM14L007		
Vial:	18	Sample Set Name:	161214
Injection #:	1	Acq. Method Set:	MC
Injection Volume:	5.00 ul	Processing Method:	MC_PRO
Run Time:	12.0 Minutes	Channel Name:	255.0nm
		Proc. Chnl. Descr.:	PDA 255.0 nm
Date Acquired:	12/16/2014 2:48:27 PM IST		
Date Processed:	12/17/2014 11:04:02 AM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 3/20, 8/40,15/95, 20/95, 25/20, 30/20
Flow: 1.0 ml/min, Diluent: ACN



	RT	Area	% Area	Height
1	3.686	5613755	98.33	890135
2	3.900	87188	1.53	13382
3	8.098	7873	0.14	955

13/12/14

Analysed By:

Checked By:

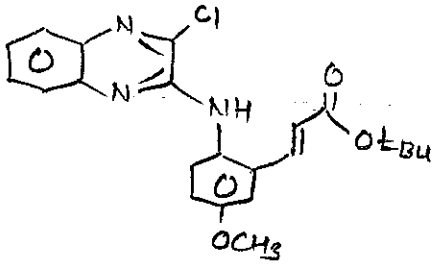
Empower 2 software

CPRI@DRILS

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-OME-T-BU	Acquired By:	System
A R Number:	CM14K011	Sample Set Name:	251114_3
Vial:	36	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO0
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/26/2014 3:28:38 AM IST		
Date Processed:	11/26/2014 3:29:27 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
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4	4.350	10733	0.17	2117
5	4.677	5209	0.08	795
6	5.190	5030	0.08	721
7	5.351	4872	0.08	727

26/11/14

Analysed By:

Checked By:

Reported by User: System
Report Method: CPRI@DRILS
Report Method ID: 3574
Page: 1 of 1

Project Name: NOB_2014
Date Printed:
11/26/2014
3:36:26 PM Asia/Calcutta

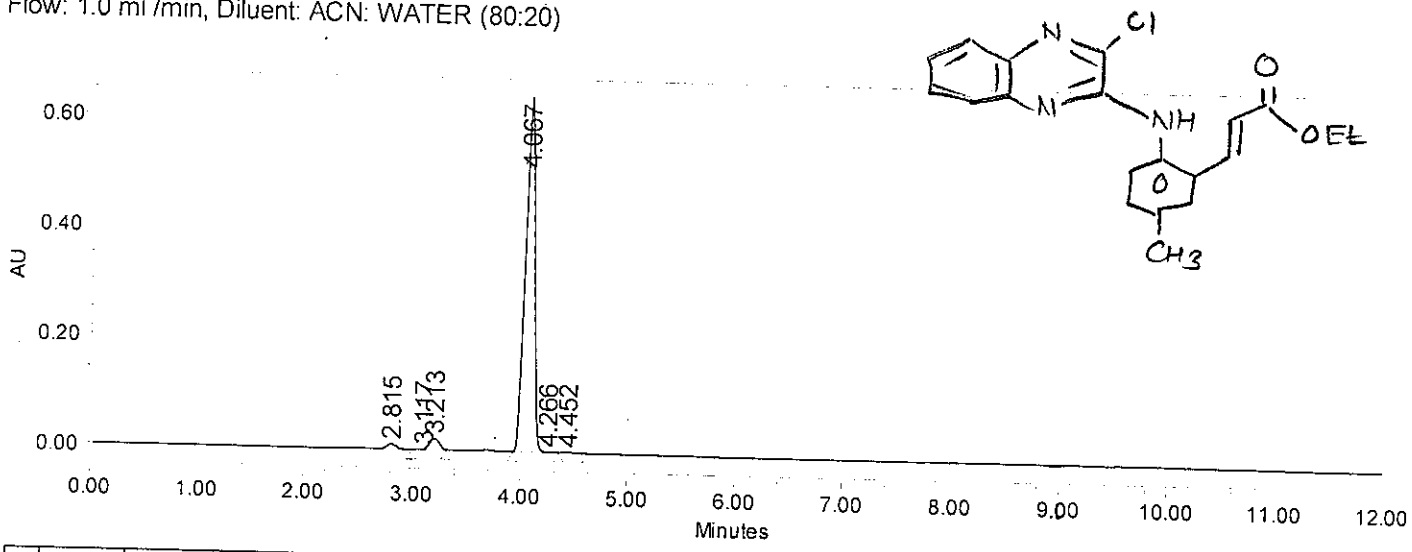
Empower 2 software

CPRI@DRILS

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-S2-4F	Acquired By:	System
A R Number:	CM14K007	Sample Set Name:	241114
Vial:	16	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/24/2014 2:30:07 PM IST		
Date Processed:	11/24/2014 2:59:29 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/10, 2/10, 10/95, 20/95, 22/10, 25/10
Flow: 1.0 ml /min, Diluent: ACN: WATER (80:20)



	RT	Area	% Area	Height
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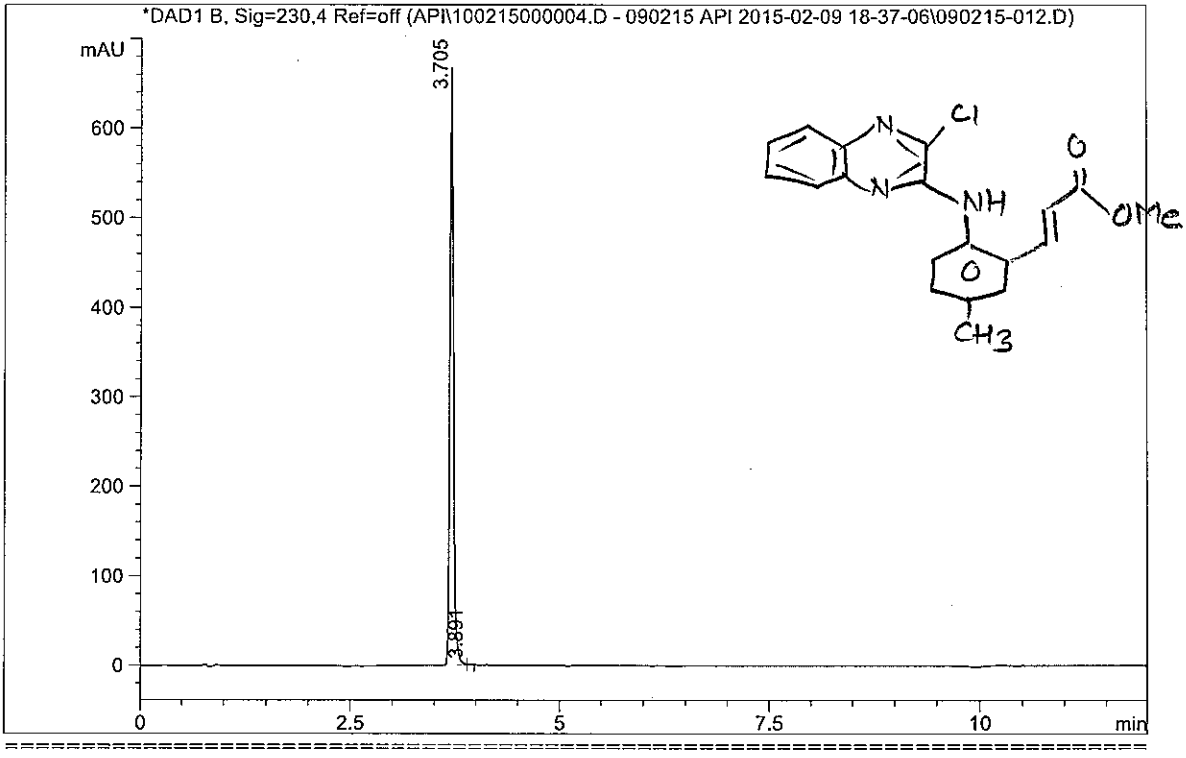
3	3.213	122312	3.01	20479
4	4.067	3855740	95.00	635411
5	4.266	8102	0.20	1550
6	4.452	10850	0.27	1955

Analysed By: Checked By:

CPRI @ DRILS
HPLC ANALYSIS REPORT

Inj Date : Tue, 10. Feb. 2015 Acq Operator: SHASHIDHAR
Sample Name : ILS-RAJ-me[redacted] Vial 14
A R Number : CM15B015 ->Inj. Vol. : 5µL
Acq. Method : D:\CHEM32_002\1\METHODS\MC.M
Analysis Method : D:\CHEM32_002\1\METHODS\MC.M
Method Info : Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water ,B) ACN
T/%B:0/20,0.5/20,2/95,10/95,10.5/20,12/20
Flow:1.0mL/min Diluent: ACN:Water(80:20)



Signal 1: DAD1 B, Sig=230,4 Ref=off

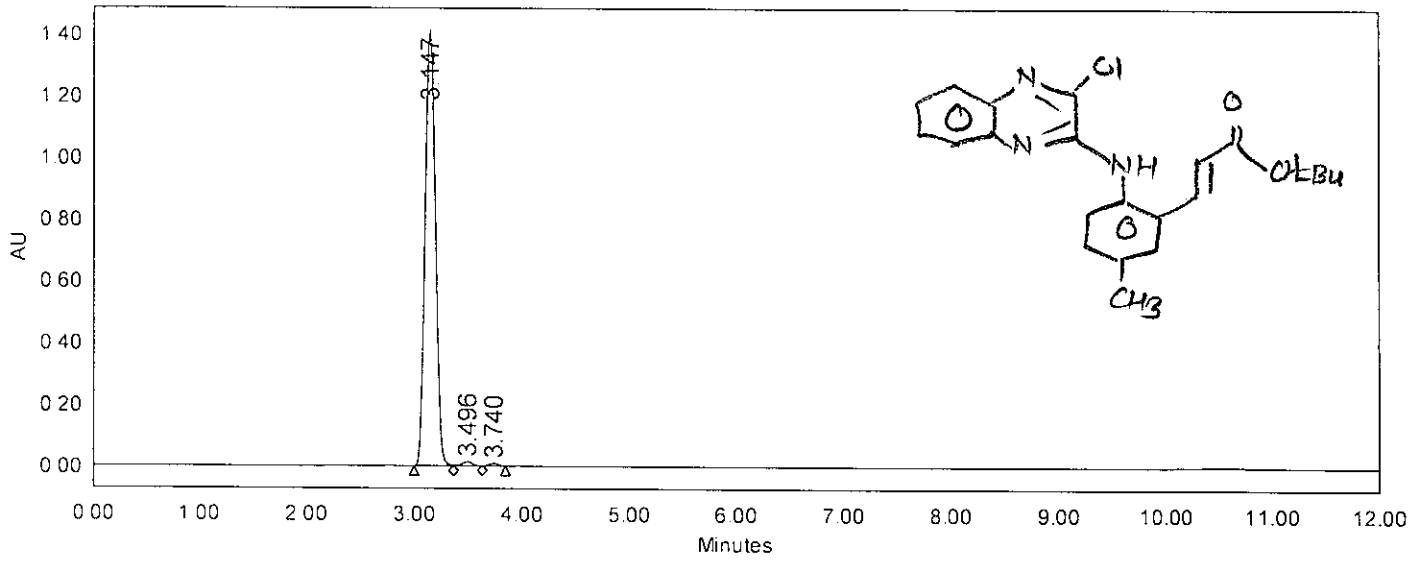
Peak #	RT [min]	Area	Area %
1	3.705	2106.615	99.907
2	3.891	1.960	0.093

Analysed by : Checked by :

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-Me-tBu		
AR Number:	CM15D022	Sample Set Name:	300415
Vial:	11	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume:	6.00 ul	Channel Name:	265.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 265.0 nm
Date Acquired:	4/30/2015 3:12:56 PM IST		
Date Processed:	4/30/2015 4:51:20 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase. A) 0.1% TFA in water B) ACN
T/%B. 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	3.147	9296297	98.39	1409602
2	3.496	98842	1.05	13267
3	3 740	52976	0.56	8274

Analyzed By: 30/04/15

Checked By:

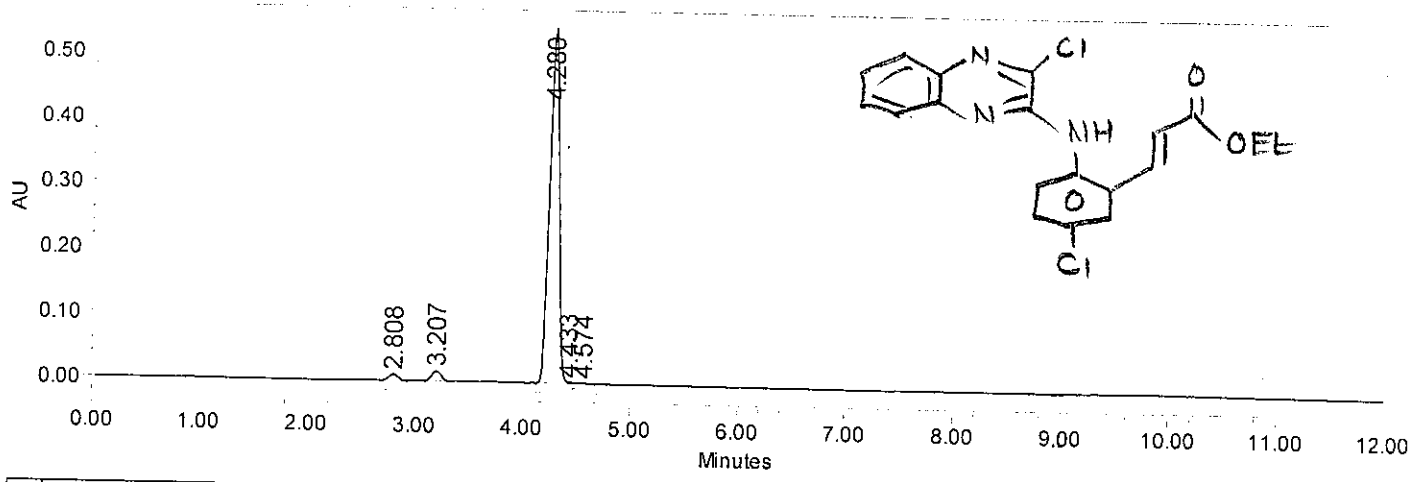
Empower 2 software

CPRI@DRILS

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-BR-ET	Acquired By:	System
A R Number:	CM14K003	Sample Set Name:	241114
Vial:	12	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/24/2014 1:26:38 PM IST		
Date Processed:	11/24/2014 2:41:53 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/10, 2/10, 10/95, 20/95, 22/10, 25/10
Flow: 1.0 ml /min, Diluent: ACN: WATER (80:20)



	RT	Area	% Area	Height
1	2.808	55335	1.60	9314
2	3.207	86969	2.52	14837
3	4.280	3301406	95.49	540398
4	4.433	8369	0.24	2010
5	4.574	5407	0.16	903

24/11/14

Analysed By: Checked By:

Reported by User: System
Report Method: CPRI@DRILS
Report Method ID: 3109
Page: 1 of 1

Project Name: NOB_2014
Date Printed:
11/24/2014
2:46:18 PM Asia/Calcutta

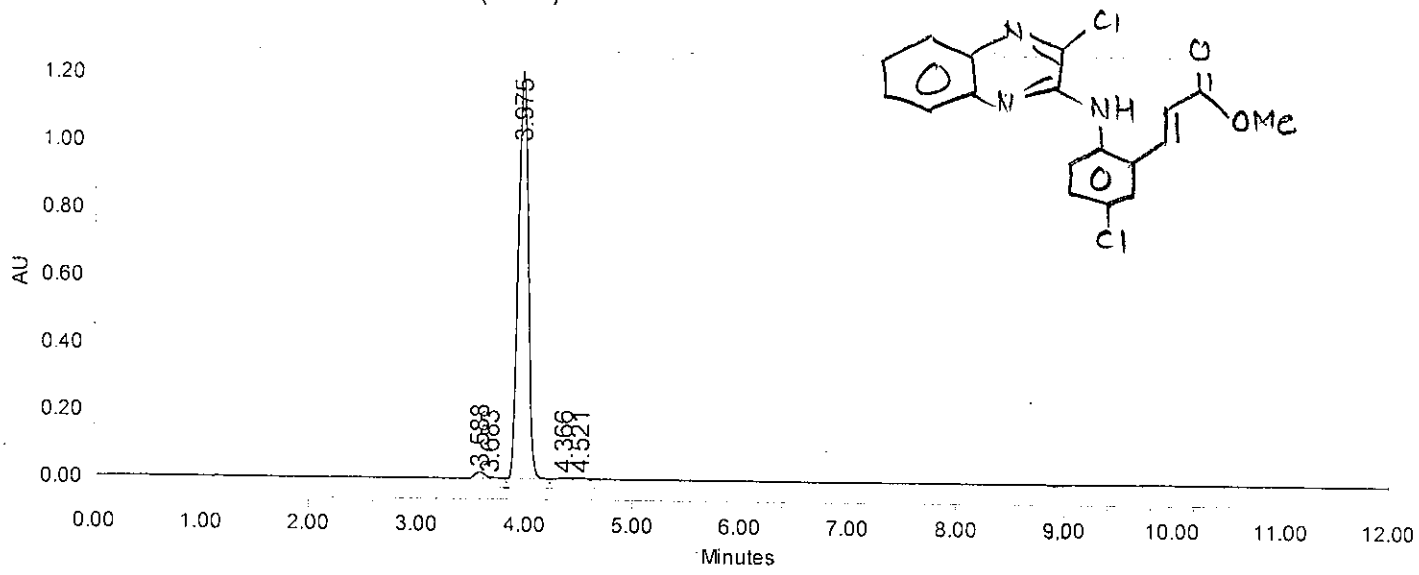
Empower 2 software

CPRI@DRILS

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-CL-ME	Acquired By:	System
A R Number:	CM14K014	Sample Set Name:	251114_3
Vial:	39	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO0
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/26/2014 4:16:23 AM IST		
Date Processed:	11/26/2014 3:31:00 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	3.588	116605	1.48	18864
2	3.683	8221	0.10	2183
3	3.975	7723046	97.87	1211200
4	4.366	21113	0.27	3410
5	4.521	21985	0.28	3781

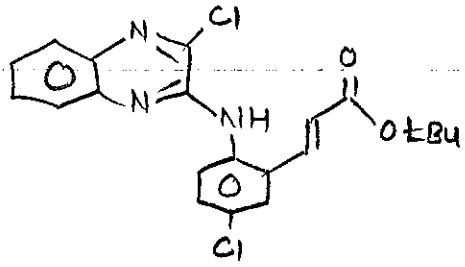
26/11/14

Analysed By: Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-CL-T-BU	Acquired By:	System
A R Number:	CM14K013	Sample Set Name:	251114_3
Vial:	38	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO0
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/26/2014 4:00:06 AM IST		
Date Processed:	11/26/2014 3:30:28 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.117	37445	0.40	4797
2	4.381	93618	1.01	12722
3	4.720	9098385	98.32	1380371
4	4.917	14238	0.15	3237
5	5.177	10376	0.11	1650

26/11/14

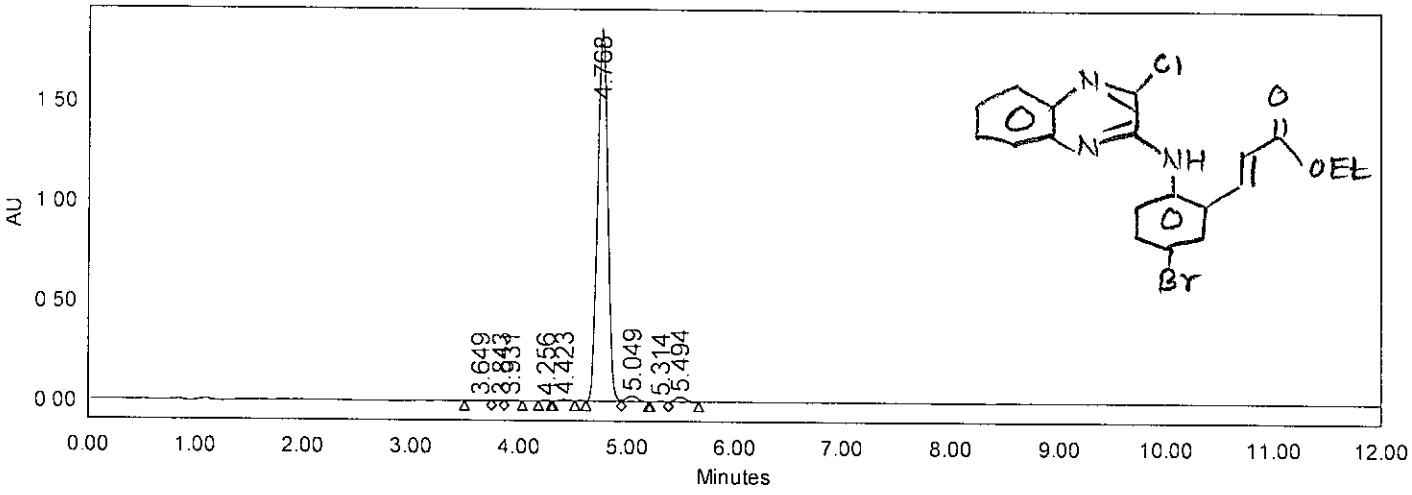
Analysed By:

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-[illegible]		
A R Number:	CM15C037	Sample Set Name:	310315
Vial:	32	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume:	10.00 ul	Channel Name:	220.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm Blank Subtracted
Date Acquired:	3/31/2015 3:01:22 PM IST		
Date Processed:	3/31/2015 5:48:09 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	3.649	28885	0.22	2827
2	3.843	23926	0.18	4050
3	3.931	32873	0.25	5040
4	4.256	7654	0.06	1884
5	4.423	40632	0.31	7404
6	4.768	12420818	95.95	1866613
7	5.049	202757	1.57	27321
8	5.314	18077	0.14	3123
9	5.494	168859	1.30	24565

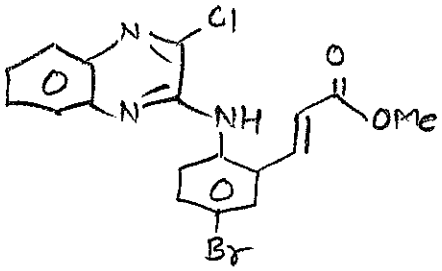
Analyzed By: 31/03/15

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-BR-ME	Acquired By:	System
A R Number:	CM14K004	Sample Set Name:	241114
Vial:	13	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/24/2014 1:42:22 PM IST		
Date Processed:	11/24/2014 2:43:32 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/10, 2/10, 10/95, 20/95, 22/10, 25/10
Flow: 1.0 ml /min, Diluent: ACN: WATER (80:20)



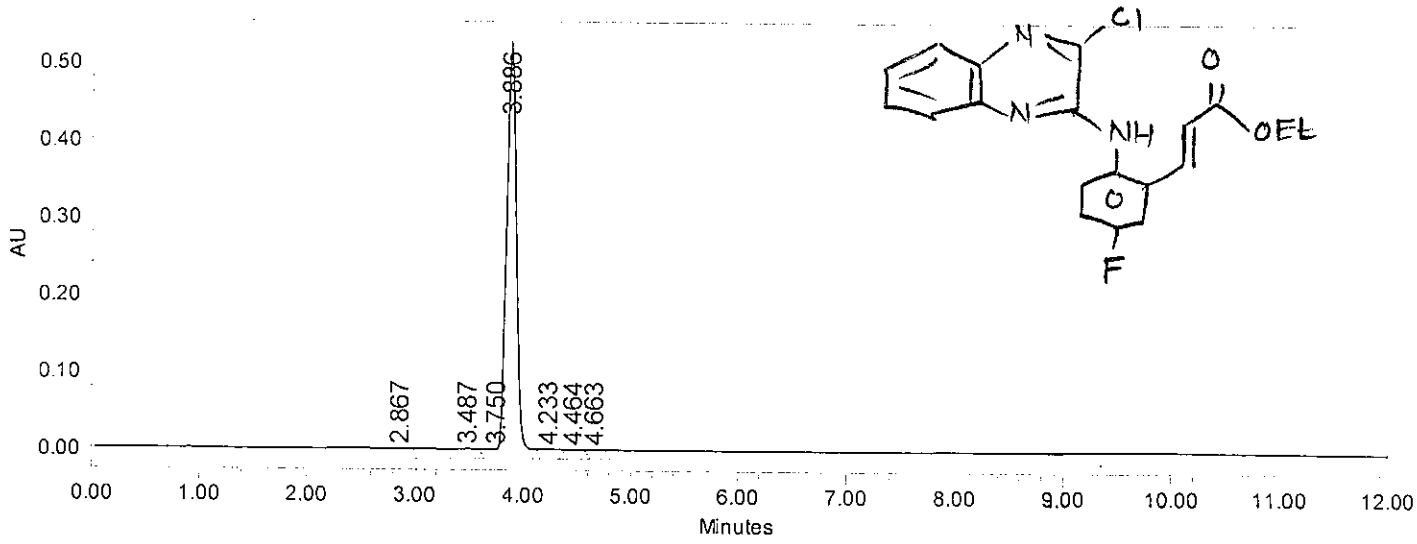
	RT	Area	% Area	Height
1	2.823	52643	1.63	8905
2	3.091	3343	0.10	763
3	3.222	110998	3.45	18609
4	3.700	20961	0.65	2283
5	4.071	3014646	93.63	497425
6	4.217	17220	0.53	3115

Analysed By: Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-F-ME	Acquired By:	System
A R Number:	CM14K009	Sample Set Name:	251114_3
Vial:	34	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO0
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/26/2014 2:57:11 AM IST		
Date Processed:	11/26/2014 3:27:00 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	2.867	1750	0.05	245
2	3.487	4528	0.14	734
3	3.750	1067	0.03	288
4	3.886	3266739	99.71	520515
5	4.233	1031	0.03	152
6	4.464	716	0.02	127
7	4.663	493	0.02	87

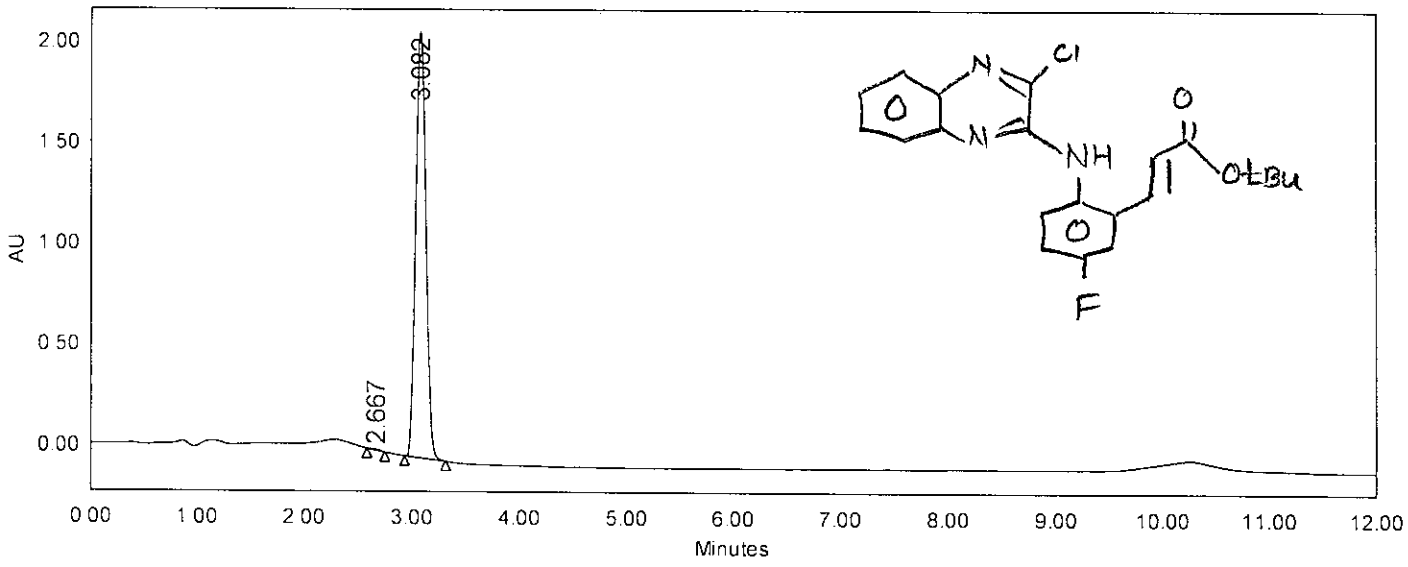
26/11/14
Analysed By:

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-F-TBu		
AR Number:	CM15D024	Sample Set Name:	300415
Vial:	13	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume	6.00 ul	Channel Name:	220.0nm@1
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	4/30/2015 3:42:27 PM IST		
Date Processed:	4/30/2015 4:52:02 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	2.667	29378	0.21	5534
2	3.082	13888294	99.79	2129593

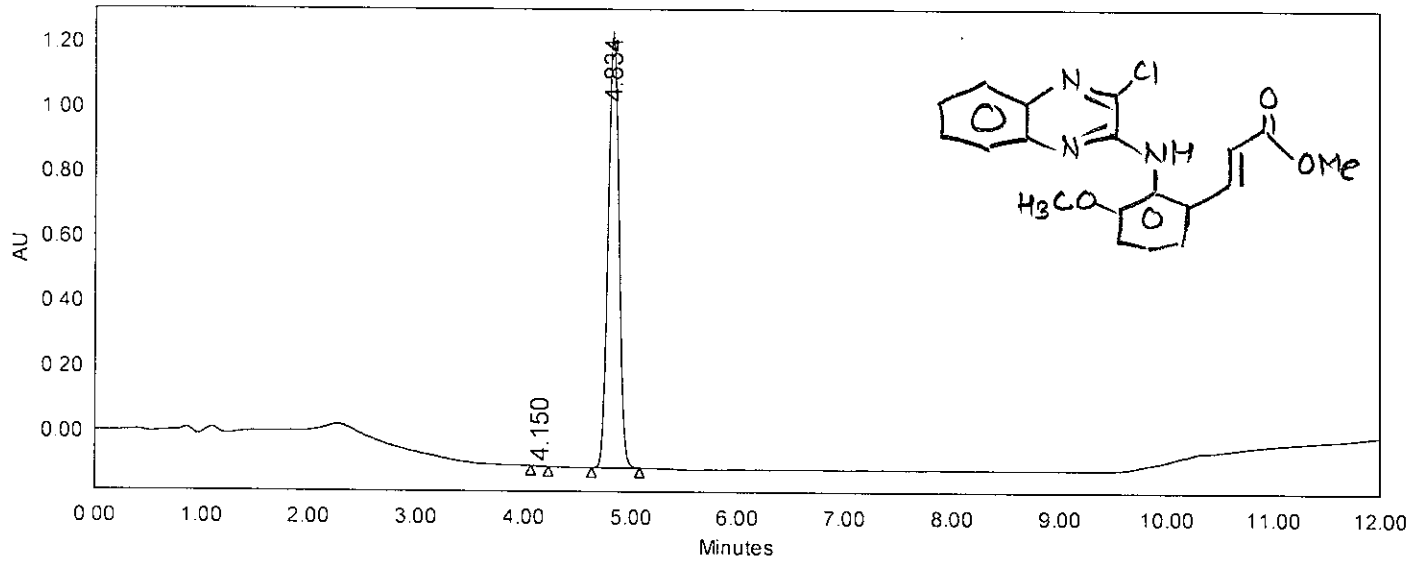
Analyzed By:

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-O-CH3		
AR Number:	CM15D019	Sample Set Name:	300415
Vial:	8	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume:	4.00 ul	Channel Name:	220.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	4/30/2015 2:12:56 PM IST		
Date Processed:	4/30/2015 4:50:44 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.150	4173	0.04	751
2	4.834	9411670	99.96	1341008

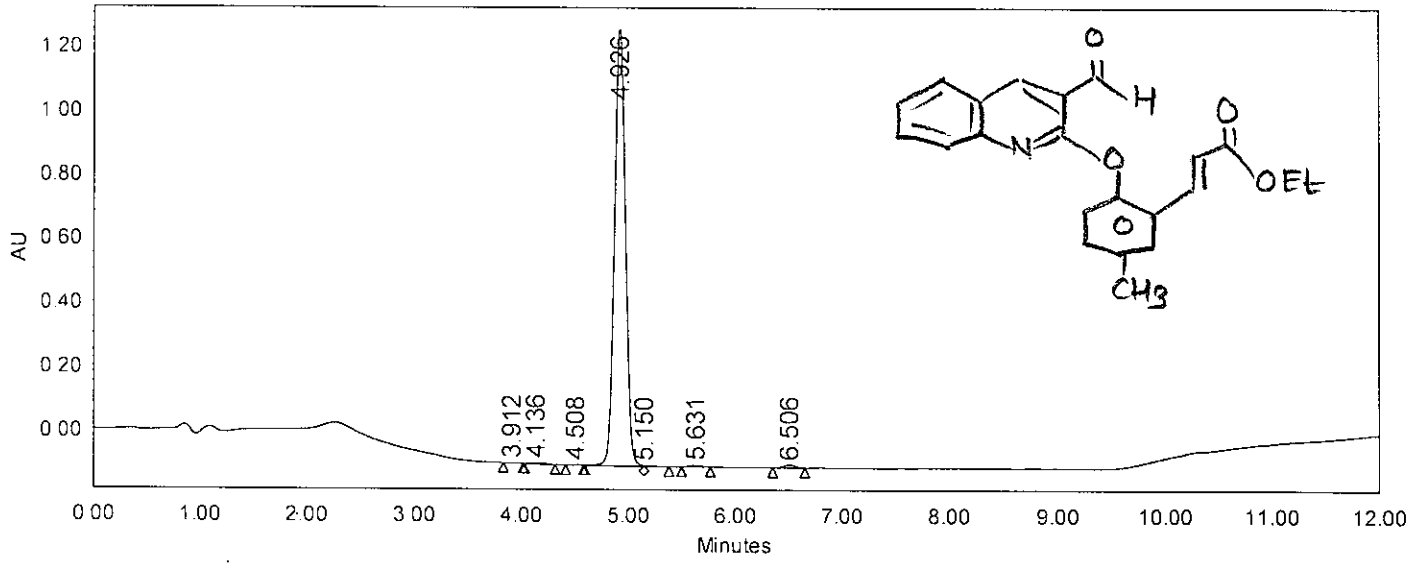
Analyzed By: Checked By:

30/04/15

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-AR		
AR Number:	CM15D018	Sample Set Name:	300415
Vial:	7	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume:	6.00 ul	Channel Name:	220.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	4/30/2015 1:58:11 PM IST		
Date Processed:	4/30/2015 4:50:34 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	3.912	4099	0.04	612
2	4.136	39336	0.40	4512
3	4.508	5541	0.06	990
4	4.926	9687044	98.16	1370827
5	5.150	14850	0.15	2701
6	5.631	43818	0.44	6110
7	6.506	73567	0.75	9066

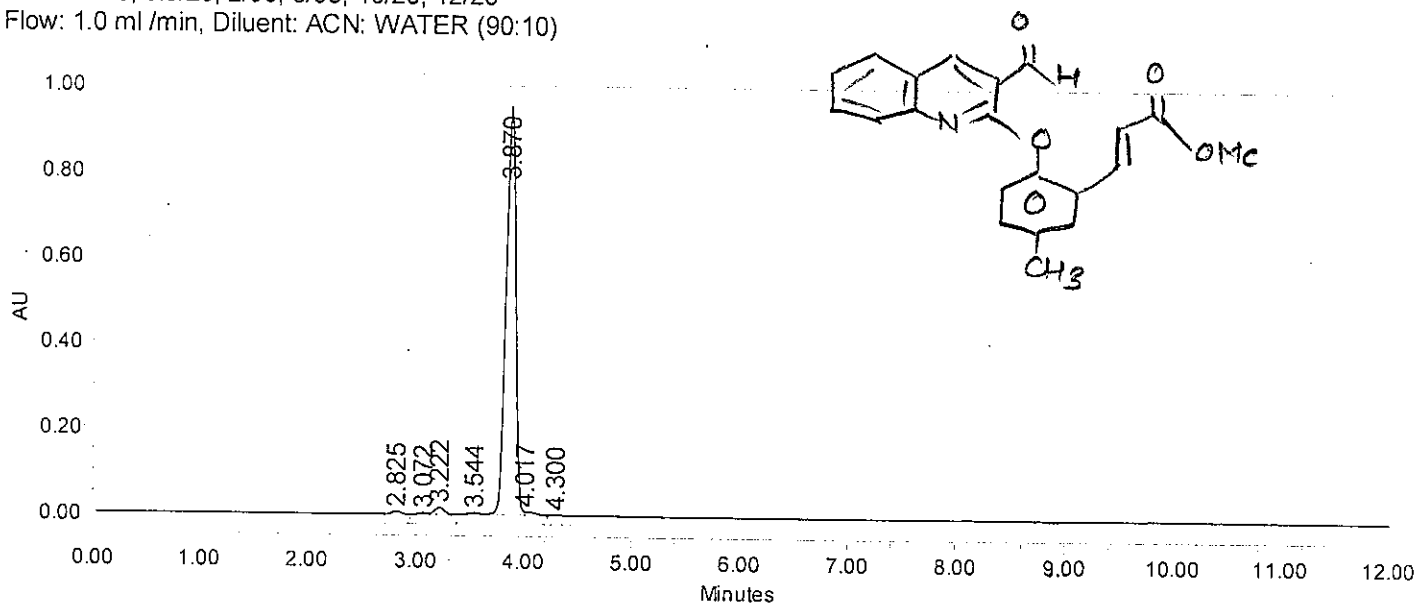
Analyzed By: Checked By:

30/04/15

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-S2-2F	Acquired By:	System
A R Number:	CM14K008	Sample Set Name.	241114
Vial:	17	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC PRO
Injection Volume:	5.00 ul	Channel Name:	260.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	11/24/2014 2:46:09 PM IST		
Date Processed:	11/26/2014 3:46:11 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	2.825	41210	0.67	6857
2	3.072	19563	0.32	3219
3	3.222	97192	1.57	15991
4	3.544	29735	0.48	3906
5	3.870	5952079	96.10	944607
6	4.017	48893	0.79	7351
7	4.300	4652	0.08	878

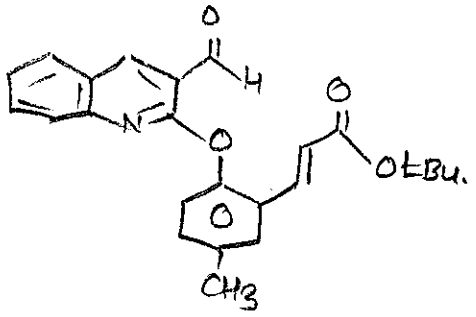
26/11/14

Analysed By: Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-[redacted]-tBu		
A R Number:	CM14L018		
Vial:	7	Sample Set Name:	020115
Injection #:	1	Acq. Method Set:	MC
Injection Volume:	5.00 ul	Processing Method:	MC_PRO
Run Time:	12.0 Minutes	Channel Name:	260.0nm
		Proc. Chnl. Descr.:	PDA 260.0 nm
Date Acquired:	1/2/2015 5:07:43 PM IST		
Date Processed:	1/2/2015 5:15:12 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	2.821	42204	0.53	7247
2	3.238	16163	0.20	2516
3	3.317	2665	0.03	932
4	3.617	635	0.01	168
5	3.784	6612	0.08	1006
6	3.996	29564	0.37	5104
7	4.260	7743188	97.64	1259739
8	4.468	58250	0.73	9952

	RT	Area	% Area	Height
9	4.703	13480	0.17	2309
10	5.549	17222	0.22	2199

05/01/15

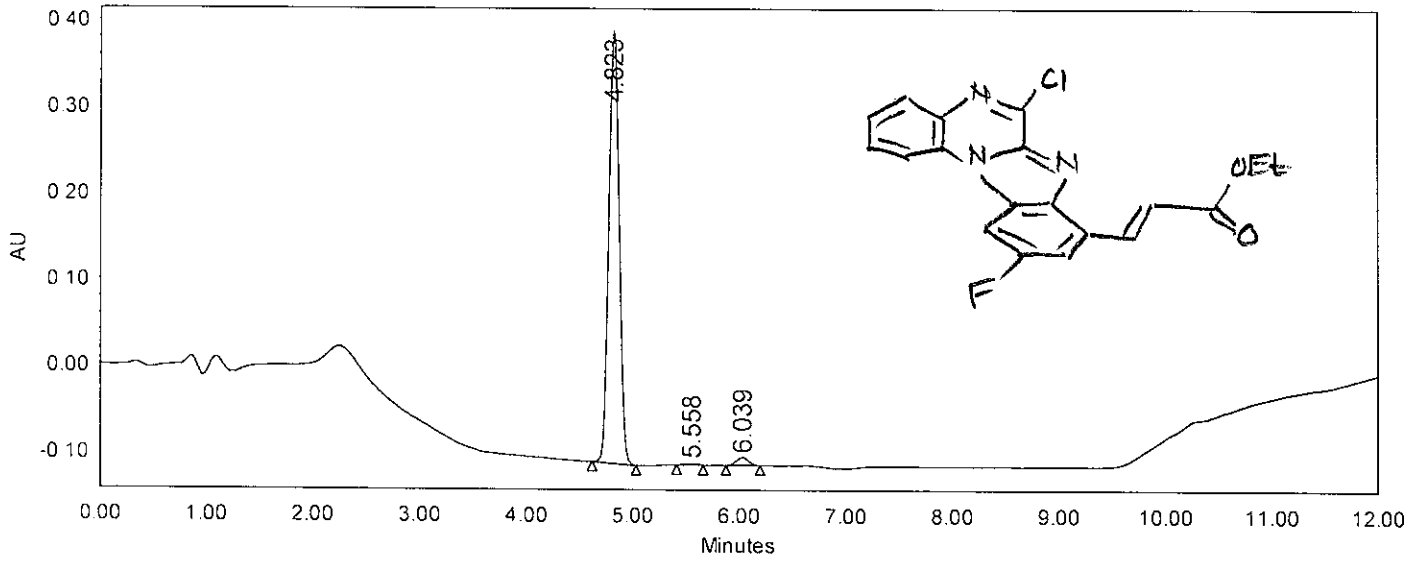
Analysed By:

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-P-F-PIDA		
AR Number:	CM15D021	Sample Set Name:	300415
Vial:	10	Acq. Method Set:	MC
Injection #:	1	Processing Method:	MC_PRO
Injection Volume:	6.00 ul	Channel Name:	220.0nm
Run Time:	12.0 Minutes	Proc. Chnl. Descr.:	PDA 220.0 nm
Date Acquired:	4/30/2015 2:58:14 PM IST		
Date Processed:	4/30/2015 4:51:06 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.823	3421820	97.49	502349
2	5.558	15521	0.44	1941
3	6.039	72615	2.07	9284

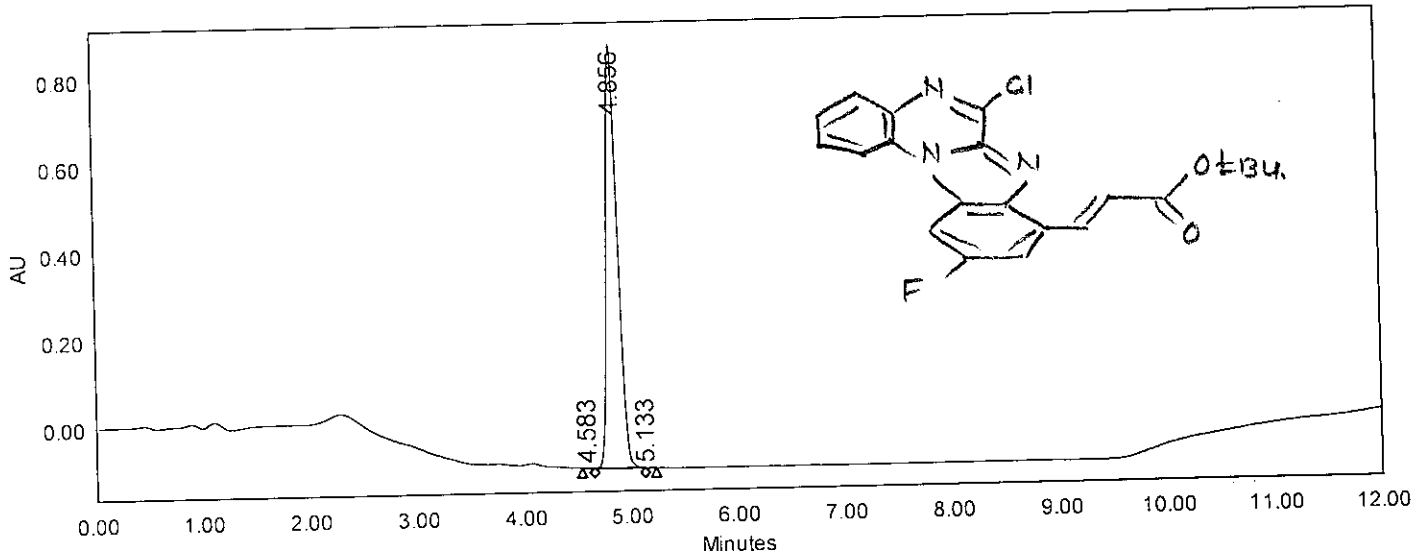
Analyzed By: Checked By:

30/04/15

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-N	Sample Set Name:	130515_2
Sample Type:	CM15E009	Acq. Method Set:	MC
Vial:	17	Processing Method:	MC PRO
Injection #:	1	Channel Name:	220.0nm
Injection Volume:	1.20 ul	Proc. Chnl. Descr.:	PDA 220.0 nm
Run Time:	12.0 Minutes		
Date Acquired:	5/13/2015 2:54:45 PM IST		
Date Processed:	5/13/2015 3:24:29 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.583	1396	0.02	262
2	4.856	7230575	99.96	979920
3	5.133	1746	0.02	686

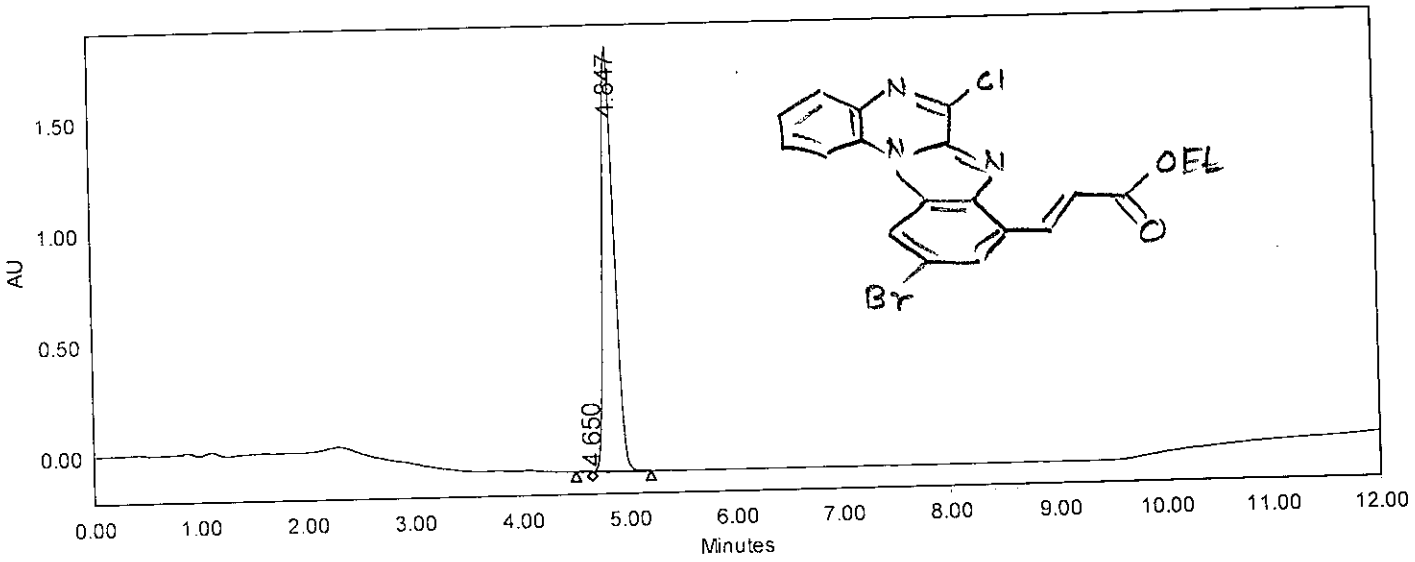
Analyzed By: 13/05/15

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-PIDA-4P	Sample Set Name:	130515_2
Sample Type:	CM15E008	Acq. Method Set:	MC
Vial:	16	Processing Method:	MC_PRO
Injection #:	1	Channel Name:	220.0nm@1
Injection Volume:	1.50 ul	Proc. Chnl. Descr.:	PDA 220.0 nm
Run Time:	12.0 Minutes		
Date Acquired:	5/13/2015 2:39:49 PM IST		
Date Processed:	5/13/2015 3:24:16 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.650	5609	0.04	975
2	4.847	14561299	99.96	1910323

Analyzed By:

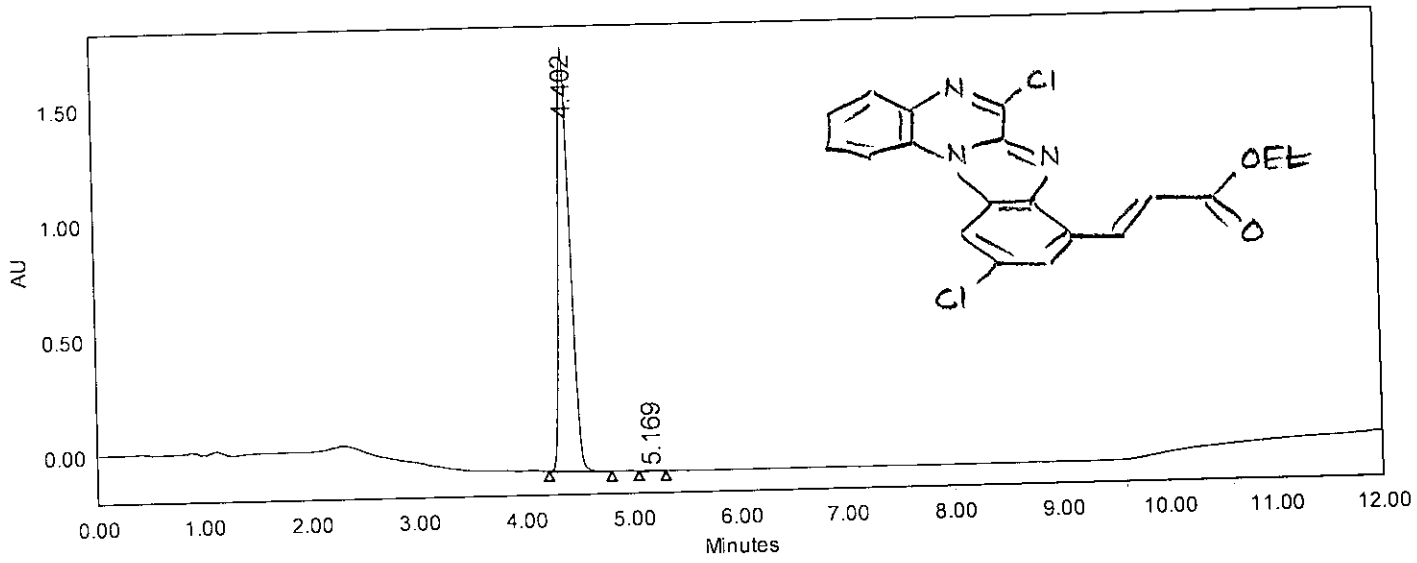
13/05/15

Checked By:

SAMPLE INFORMATION

Sample Name:	ILS-RAJ-PIDA-2	Sample Set Name:	130515_2
Sample Type:	CM15E010	Acq. Method Set:	MC
Vial:	18	Processing Method:	MC PRO
Injection #:	1	Channel Name:	220.0nm
Injection Volume:	1.20 ul	Proc. Chnl. Descr.:	PDA 220.0 nm
Run Time:	12.0 Minutes		
Date Acquired:	5/13/2015 3:09:28 PM IST		
Date Processed:	5/13/2015 3:25:30 PM IST		

Column: Symmetry C-18 75*4.6mm 3.5µm
Mobile phase: A) 0.1% TFA in water B) ACN
T/%B: 0/20, 0.5/20, 2/95, 8/95, 10/20, 12/20
Flow: 1.0 ml /min, Diluent: ACN: WATER (90:10)



	RT	Area	% Area	Height
1	4.402	13577888	99.86	1837954
2	5.169	18676	0.14	2752

Analyzed By:

13/05/15

Checked By: