Supporting Information

An Atom-economical and Regioselective Metal-free C-5 Chalcogenation of 8-Aminoquinolines under Mild Conditions

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General Information

All the reactions were carried out in presence of air unless stated otherwise and all the glass wares were oven dried at 100°C. The commercially available reagents and chemicals were used without further purification. The solvents were dried before use following standard procedures. The thin layer chromatography (TLC) was done using TLC Silica gel F254 plates purchased by Merck. All the products were purified by column chromatography using either silica gel (mesh 100-200) or thin layer chromatography. The NMR spectra of products were recorded on Bruker spectrometer (600 MHz, 500 MHz, 400 MHz and 300 MHz). The Chemical shifts of ^{1}H are given in ppm relative to internal standards $CDCl_3$ at 7.24 ppm and DMSO-d_6 at 2.50 ppm. The chemical shifts for ^{13}C are given in ppm relative to internal standards $CDCl_3$ at 77.00 ppm and DMSO-d_6 at 39.53 ppm. All ^{13}C NMRs are proton-decoupled data. HRMS were measured on Bruker Daltonics micrOTOF ESI-MS mass spectrometer. HPLC (Agilent, 1220 Infinity LC Gradient System VL, reverse phage chromatography, C_{18} column, gradient system water: acetonitrile, UV absorbance 250 nm) was used for the analysis of purity for substrates and products as well as conversion in controlled experiments. All the dialkyl/diaryl diselenides and dialkyl/diaryl disulphides were mostly purchased from Sigma Aldrich. Bis(2-methoxyphenyl)diselenide[1(a)] and bis(3-nitrophenyl)diselenide[1(b)] were synthesized according to the reported method and the spectroscopic data (^{1}H and ^{13}C NMR) were matched with literature report (purity was analyzed with HPLC, Figure S5, SI).[1] 8-Aminoquinolineband primaquine biphosphate were purchased from Sigma Aldrich and used without further purification. The substituted 8-aminoquinoline derivatives such as 6-methoxy/6-methyl-8-aminoquinoline used as substrate were synthesized by following literature method[2] while *N*-methyl-8-aminoquinoline[2(b)] and *N*-Boc primaquine[2(c)] were synthesized with modification in literature report. The spectroscopic data (^{1}H NMR, ^{13}C NMR and HRMS) were matched with the literature report and found the same. The purity of substituted 8-aminoquinoline derivatives was analyzed with HPLC.

General procedure for the chalcogenation of 8-aminoquinoline derivatives:

To a 50 mL round bottom flask 8-aminoquinoline derivative (**1**, 1.0 mmol, 1 equiv), diarylselenides/diarylsulphides (**2**, 0.5 mmol, 0.5 equiv) in 5 mL acetonitrile was taken. To this stirred solution 10 mol% (25.38 mg, 0.1 mmol, 0.1 equiv) iodine and 50 mol% (0.5 mmol, 0.5 equiv) *tert*-butylhydroperoxide (TBHP) was added. The reaction mixture was stirred at room temperature (25 °C) in air and monitored by TLC. After completion of the reaction, 20 mL of ethylacetate was added and washed with saturated solution of sodium thiosulfate. The organic layer was separated and dried over sodium sulfate. The solvent was evaporated and the reaction mixture was further purified using column chromatography (dichloromethane: hexane/ ethyl acetate: hexane) or thin layer chromatography (TLC) to afford **3a-3w**.

Procedure for the synthesis of *N*-methyl-8-aminoquinoline from 8-aminoquinoline[2(b)]

8-aminoquinoline (144.18 mg, 1 mmol, 1 equiv) and K_2CO_3 (138.20 mg, 1 mmol, 1 equiv) in 5 mL of DMF was taken in 25 mL of round bottom flask and stirred it at room temperature (25 °C) for 30 minutes. To this reaction mixture, methyl iodide (170.33 mg, 1.2 mmol, 1.2 equiv) was added dropwise and stirred it at room temperature for overnight. After completion of reaction the reaction was quenched with water and extracted the organic layer with ethyl acetate. The organic layer was washed with brine solution three times and dried with anhydrous sodium sulfate. The solvent was evaporated and purified the crude with silica gel chromatography (ethyl acetate/hexane 1:4) to obtain *N*-methyl-8-aminoquinoline in 61% yield (0.6 mmol). The spectroscopic data (^{1}H and ^{13}C NMR) were matched with literature report and purity of product was analyzed by HPLC (Figure S3, SI).

General procedure for the synthesis of *tert*-butyl (4-((6-methoxyquinolin-8-yl)amino)pentyl)carbamate (*N*-Boc primaquine)[2(c)]

To a solution of primaquine biphosphate (200 mg, 0.439 mmol, 1.0 equiv,) in DCM (20 mL), di-*tert*-butyl dicarbonate (287.6 mg, 1.317 mmol, 3 equiv,) and triethylamine (0.367 mL, 2.634 mmol, 6.0 equiv,) were added. The resulting reaction mixture was stirred at room temperature for overnight. After completion of reaction DCM was evaporated and the crude product was purified using silica gel chromatography (ethylacetate/hexane 1:4). Yield: 145 mg, 91 % (0.393 mmol). The spectroscopic data (^{1}H and ^{13}C NMR) were matched with literature report and purity of product was analyzed by HPLC (Figure S4, SI).

Fate of reaction in presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and BHT (3,5-di-*tert*-4-butylhydroxytoluene)

Following the general procedure of chalcogenation of 8-aminoquinoline, we performed a set of reactions with and without TEMPO. In order to perform the reaction in presence of 0.2 equiv of TEMPO, a 50 mL round bottom flask 8-aminoquinoline

derivative (**1**, 1.0 mmol, 1 equiv), diarylselenides/diarylsulphides (**2**, 0.5 mmol, 0.5 equiv) in 5 mL acetonitrile was taken. To this stirred solution 10 mol% (25.38 mg, 0.1 equiv) iodine and 50 mol% (0.5 equiv) *tert*-butylhydroperoxide (TBHP) was added followed by TEMPO (0.2 mmol, 0.2 equiv). The reaction mixture was stirred at room temperature (25 ^{o}C) in air and monitored by TLC. After completion of the reaction, 20 mL of ethylacetate was added and washed with saturated solution of sodium thiosufate. The organic layer was separated and dried over sodium sulfate. The solvent was evaporated and HPLC analysis was performed with crude product (**3a**) (Figure S8, see SI). The reaction mixture was further purified using column chromatography (dichloromethane: hexane 1:1) to obtain **3a** in 81% yield.

The controlled reaction was performed both with 0.2 and 1.0 equiv of TEMPO to analyze the variation in the yield of product **3a.** In addition, BHT (0.2 and 1.0 equiv) was also incorporated as radical quencher instead of TEMPO to analyze the variation in the yield of product **3a** following the general procedure. We found that there was neither significant change in the yield of product, nor the formation of side product as monitored by HPLC (Figure S1 to figure S10 in SI). It proves that the reaction does not follow a radical pathway.

General procedure for the preparation of 5,7-Di-deuteriated-8-aminoquinoline[3]

In a 15 mL sealed tube with a magnetic stir bar, 8-aminoquinoline (144.18 mg, 1 mmol) and conc. DCl in D_2O (1 mmol) were added. The reaction mixture was heated at 150 ^{o}C for 12 h. in oil bath. Then it was cooled to room temperature and diluted with 20 mL distilled water. The product was extracted with ethyl acetate (10mL x 3 mL) and dried over anhydrous sodium sulfate. The solvent was evaporated to get the solid **1aD** (96% Deuterium incorporation based on 1D NMR).

Intramolecular Kinetic Isotope Effect

Following the procedure of chalcogenation, 8-aminoquinoline (**1a**, 1 mmol, 0.5 equiv), 8-aminoquinoline-d_2 (**1aD**, 1 mmol, 0.5 equiv) and *p*-tolyldisulphide (**2m**, 1 mmol, 0.5 equiv) were taken in 5 mL of acetonitrile. To this solution iodine (25.38 mg, 10 mol%, 0.1 equiv) and TBHP (50 mol%, 0.5 equiv) were added and the reaction mixture was stirred at room temperature. After 45 min, the reaction was quenched by adding sodium thiousulfate solution. The products were extracted with ethylacetate and dried over sodium sulfate. The solvent was evaporated and the product was purified with silica gel chromatography (ethyl acetate/hexane, 2:3) to get the solid product (yield: 0.8 mmol, 40%). The ^{1}H NMR revealed the existence of H/D (**3m**: **3mD**) in 1:1 ratio at the 7-position of 8-Aminoquinoline.

Analytical Data for Synthesized Products:

*5-(Phenylselanyl)quinoline-8-amine (**3a**).* Light brown solid, mp 55-56 ^{o}C; 239.4 mg; 85% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (dd, *J* = 4.1 Hz, 1.3 Hz, 1H), 8.59 (dd, *J* = 8.5 Hz, 1.1 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.13 – 7.06 (m, 5H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.24 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.5, 146.0, 138.8, 138.6, 137.0, 134.0, 131.0, 129.1, 129.0, 125.8, 122.5, 112.5, 109.8. ^{77}Se NMR (114 MHz, $CDCl_3$): δ 322.70; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}N_2SeNa$ 323.0058; found 323.0061.

*5-(Benzylselanyl)quinoline-8-amine (**3b**).* Off-white solid; mp 77-78 ^{o}C; 234.9 mg; 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (dd, *J* = 4.2 Hz, 1.8 Hz, 1H), 8.54 (dd, *J* = 8.5 Hz, 1.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 8.7 Hz, 4.0 Hz, 1H), 7.10 - 7.09 (m, 3H), 6.95 – 6.94 (m, 2H), 6.76 (d, *J* = 7.8 Hz, 1H), 5.13 (br, 2H), 3.89 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.1, 145.2, 139.1, 138.4, 137.9, 136.8, 131.1, 128.6, 128.1, 126.4, 121.8, 113.8, 109.6, 33.3; ^{77}Se NMR (114 MHz, $CDCl_3$): δ 300.81; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2Se$ 315.0395; found 315.0397.

*5-(p-Tolylselanyl)quinoline-8-amine(**3c**).* Light brown solid; mp 132-134 ^{o}C; 194.2 mg; 62% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.71 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.60 (dd, *J* = 8.5 Hz, 1.6 Hz, 1H), 7.81 – 7.80 (m, 1H), 7.36 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 7.8 Hz, 1H), 5.27 (br, 2H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.3, 145.7, 138.8, 138.1, 137.0, 135.7, 130.8, 129.9, 129.8, 129.4, 122.3, 113.1, 109.8, 20.9; ^{77}Se NMR (114 MHz, $CDCl_3$): δ 317.27; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{16}H_{14}N_2SeNa$ 337.0215; found 337.0215.

*5-((2-Methoxyphenyl)selanyl)quinolin-8-amine(**3d**).*Dark brown sticky semi solid; 215 mg; 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (dd, *J* = 4.2 Hz, 1.4 Hz, 1H), 8.55 (dd, *J* = 8.6 Hz, 1.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.34 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 7.05 – 6.87 (m, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.56 – 6.41 (m, 1H), 6.39 (d, *J* = 1.2 Hz, 1H), 5.26 (br, 2H), 3.93 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8, 147.5, 146.1, 139.3, 138.9, 137.0, 131.4, 128.2, 126.3, 123.4, 122.4, 121.5, 110.3, 110.0, 109.9, 55.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}N_2OSe$ 331.0345; found 331.0326.

*5-((4-Chlorophenyl)selanyl)quinoline-8-amine(**3e**).* Brown solid; mp 105-107 ^{o}C; 216.9 mg; 70% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (d, *J* = 3.0 Hz, 1H), 8.53 (d, *J* = 2.5 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 8.4 Hz, 4.0 Hz, 1H), 7.07 - 7.02

(m, 4H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.27 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.4, 146.1, 138.6, 136.8, 132.2, 131.7, 130.7, 130.1, 129.1, 122.5, 111.9, 109.7;^{77}Se NMR (114 MHz, $CDCl_3$): δ 323.82; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{15}H_{12}ClN_2Se$ 334.9849; found 334.9850.

*5-((3-Nitrophenyl)selanyl)quinoline-8-amine(**3f**).* Dark brown solid; mp 155-157 °C; 258 mg; 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.5 Hz, 1H), 8.51 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 8.02 (s, 1H), 7.91 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.32 (s, 1H), 7.26 (s, 1H), 7.25 (d, *J* = 8.0Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.34 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 147.7, 146.8, 139.2, 138.9, 136.8, 136.2, 134.3, 130.7, 129.6, 123.2, 122.9, 120.6, 110.4, 109.6; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{15}H_{12}N_3O_2Se$ 346.0090; found 346.0105.

*6-Methoxy-5-(phenylselanyl)quinoline-8-amine (**3g**).* Black sticky solid; 124.7 mg; 76% yield; ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.56 – 8.47 (m, 2H), 7.42 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.13 – 6.91 (m, 6H), 6.58 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 160.7, 149.4, 144.6, 134.9, 134.2, 131.9, 129.1, 127.7, 125.2, 123.2, 95.1, 93.4, 56.3; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2OSe$ 331.0345; found 331.0353.

*6-Methoxy-5-(3-nitrophenylselanyl)quinoline-8-amine (**3h**).* Brown Solid; mp 190-192 °C; 210 mg; 56% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 – 8.57 (m, 2H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.89 (d, *J* = 1.0 Hz, 1H), 7.37 – 7.36 (m, 2H), 7.24 – 7.23 (m, 1H), 6.79 (s, 1H), 5.44 (br, 2H), 3.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.6, 148.6, 148.3, 145.4, 136.8, 135.3, 134.9, 134.0, 132.1, 129.4, 123.3, 123.0, 120.3, 96.1, 96.7, 56.7; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{14}N_3O_3Se$ 376.0195; found 376.0187

*6-methyl-5-(phenylselanyl)quinolin-8-amine (**3i**).* Brown solid; mp 145- 147 °C; 224.8 mg; 72% yield; ^{1}H NMR (400 MHz, DMSO-d_6 and CD_3OD): δ 8.67 (s, 1H), 8.60 (d, *J* = 8.4 Hz, 1H), 7.48 – 7.46 (m, 1H), 7.13 – 7.08 (m, 3H), 7.00 – 6.96 (m, 3H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 146.2, 144.6, 136.9, 135.9, 133.6, 131.2, 129.3, 127.7, 125.5, 122.8, 110.6, 108.9, 24.4; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2Se$ 315.0395; found 315.0402.

*N-methyl-5-(phenylselanyl)quinolin-8-amine (**3j**).* Brown solid; mp 82-84 °C; 156.6 mg; 50% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, *J* = 3.9 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.4 Hz, 3.9 Hz, 1H), 7.11 – 7.07 (m, 5H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.44 (br, 1H), 3.06 (d, *J* = 3.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5, 146.9, 139.3, 138.8, 136.9, 134.3, 130.5, 129.0, 128.7, 125.6, 122.5, 109.7, 104.0, 29.7; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2Se$ 315.0395, found 315.0400.

*5-(Methylselanyl)quinoline-8-amine (**3k**).* Off-white solid; mp 65-67 °C; 106.7 mg; 45% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.01 (dd, *J* = 8.3 Hz, 1.6 Hz, 1H), 7.60 (d, 8.5 Hz, 1H), 7.34 (dd, 8.3 Hz, 4.2 Hz, 1H), 7.02 (d, 8.5 Hz, 1H), 5.66 (br, 2H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.5, 145.8, 137.3, 136.0, 133.8, 128.5, 121.5, 115.3, 109.8, 7.7. ^{77}Se NMR (114 MHz, $CDCl_3$): δ 106.47; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{10}H_{11}N_2Se$ 239.0082; found 239.0084.

*5-(Phenylthio)quinolin-8-amine (**3l**).*[4] Black sticky compound; 156.4 mg; 62% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.75 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.59 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.36 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.05 – 7.02 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 5.23 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.4, 146.1, 139.5, 138.9, 137.6, 134.6, 130.6, 128.7, 125.9, 124.8, 122.3, 113.9, 109.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{15}H_{12}N_2SNa$ 275.0614; found 275.0616.

*5-(p-Tolylthio)quinolin-8-amine (**3m**).*[4] Brown solid; mp 80-81 °C; 207.5 mg; 78% yield;^{1}H NMR (600 MHz, $CDCl_3$): δ 8.74 (d, *J* = 3.9 Hz, 1H), 8.60 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.36 (m, 1H), 6.96 – 6.88 (m, 5H), 5.27 (br, 2H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.4, 145.9, 138.9, 137.3, 135.8, 134.8, 134.7, 130.5, 129.6, 126.5, 122.3, 114.9, 109.5, 20.8.

*5-((4-Methoxyphenyl)thio)quinolin-8-amine (**3n**).*[4] Brown sticky solid; 198 mg; 70% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.62 (dd, *J* = 8.5 Hz, 1.6 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.02 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 1H), 6.71 (dd, *J* = 6.8 Hz, 2.0 Hz, 2H), 5.27 (br, 2H), 3.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 157.9, 147.3, 145.7, 138.8, 136.5, 134.7, 130.2, 129.5, 128.9, 122.2, 116.2, 114.6, 109.4, 55.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{16}H_{14}N_2OSNa$ 305.0720; found 305.0717.

*5-((4-Aminophenyl)thio)quinolin-8-amine (**3o**).*Light yellow solid; mp 164-167 °C; 160 mg; 60% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.2 Hz, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.37 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.36 (br, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.3, 145.1, 144.8,

138.9, 135.6, 134.6, 130.0, 126.2, 122.0, 117.5, 115.8, 109.5; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{15}H_{13}N_2OS$ 268.0903; found 268.0910.

*3-((8-Aminoquinolin-5-yl)thio)phenol (**3p**).* Brown solid; mp 181-183 °C; 155 mg; 58% yield; ^{1}H NMR (600 MHz, DMSO-d_6): δ 9.34 (d, *J* = 5.4 Hz, 1H), 8.77 (d, *J* = 3.6 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.54 - 7.53 (m, 1H), 7.01 – 6.91 (m, 2H), 6.49 – 6.43 (m, 4H), 6.23 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ 157.8, 147.9, 147.2, 140.3, 138.1, 138.0, 133.7, 130.2, 129.8, 122.7, 116.1, 112.2, 112.0, 109.6, 108.3; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{15}H_{13}N_2OS$ 269.0744; found 269.0740.

***5-((4-Nitrophenyl)thio)quinolin-8-amine** (**3q**).*[4] Yellow solid; mp 167-168 °C; 214 mg; 72% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 4.1 Hz, 1.6 Hz, 1H), 8.41 (dd, *J* = 8.5 Hz, 1.6 Hz, 1H), 7.95 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 6.97 – 6.95 (m, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 5.43 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.0, 147.8, 147.1, 144.9, 138.8, 138.3, 133.9, 130.4, 125.1, 123.9, 122.9, 110.6, 109.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{15}H_{11}N_3O_2SNa$ 320.0465; found 320.0465.

*5-((4-Chlorophenyl)thio)quinolin-8-amine (**3r**).*[4] Brown solid; mp 131-132 °C; 215 mg; 75% yield; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.75 (dd, *J* = 4.1 Hz, 1.5 Hz, 1H), 8.51 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 8.5 Hz, 4.1 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.87 (m, 3H), 5.27 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.5, 146.3, 138.8, 138.1, 137.7, 134.5, 130.6, 130.4, 128.8, 127.2, 122.5, 113.8, 109.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{15}H_{11}N_2ClSNa$ 309.0224; found 309.0225.

*6-Methyl-5-(phenylthio)quinolin-8-amine (**3s**).*[4] Brown solid; mp 72-75 °C; 159 mg; 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 – 8.68 (m, 2H), 7.36 (dd, *J* = 6.3 Hz, 3.0 Hz, 1H), 7.11 (t, *J* = 5.5 Hz, 2H), 7.00 (t, *J* = 5.5 Hz, 1H), 6.92 – 6.89 (m, 3H), 5.21 (br, 2H), 2.56 (s, 3H); HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2S$ 267.0956; found 267.0977.

*6-Methoxy-5-(phenylthio)quinolin-8-amine (**3t**).* Black sticky solid; 225 mg; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 – 8.42 (m, 2H), 7.23 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.90 – 6.86 (m, 3H), 6.63 (s, 1H), 5.30 (br, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.2, 147.9, 145.2, 139.3, 134.8, 133.8, 132.3, 128.7, 125.5, 124.5, 123.1, 97.7, 96.5, 56.6; HRMS (ESI-TOF) m/z: $[M+H]^+$calcd for $C_{16}H_{15}N_2OS$ 283.0900; found 283.0917.

*5-(Propylthio)quinolone-8-amine (**3u**).* Viscous yellow liquid; 100 mg; 46% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72 – 8.68 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 5.03 (br, 2H), 2.63 (t, *J* = 7.0 Hz, 2H), 1.51 – 1.39 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ147.29, 144.68, 138.88, 135.25, 134.53, 130.40, 121.78, 118.36, 109.40, 39.00, 22.83, 13.25; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{15}N_2S$ 219.0951; found 219.0936.

*tert-Butyl(4-((6-methoxy-5-((2-methoxyphenyl)selanyl)quinolin-8-yl)amino)pentyl)carbamate (**3v**).* Sticky yellow liquid; 155mg; 50% yield; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 – 8.52 (m, 1H), 8.41 (dd, *J* = 11.6 Hz, 1.2 Hz, 1H), 7.40 (d, *J* = 11.4 Hz, 1H), 7.02 – 6.99 (m, 1H), 6.89 (d, *J* = 10.8 Hz, 1H), 6.81 (s, 1H), 6.71 – 6.66 (m, 2H), 6.57 – 6.55 (m, 1H), 6.25 (d, *J* = 0.8 Hz, 1H), 3.89 (d, *J* = 11.2 Hz, 6H), 3.46 (br, 1H), 3.00 (d, *J* = 6.8 Hz, 2H), 1.57 – 1.45 (m, 4H), 1.39 (s, 9H), 1.28 (d, *J* = 8.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.7, 155.9, 155.7, 147.3, 144.3, 135.1, 134.5, 132.1, 126.6, 125.9, 123.3, 122.8, 121.3, 110.4, 91.9, 90.5, 77.3, 56.5, 55.7, 47.1, 36.2, 33.5, 28.2, 26.4, 20.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$calcd for $C_{27}H_{35}N_3O_4SeNa$ 568.1690; found 568.1713.

*tert-Butyl(4-((6-methoxy-5-(phenylthio)quinolin-8-yl)amno)pentyl)carbamate (**3w**).* Yellow viscous liquid; 234 mg; 90% yield; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.57 – 8.56 (m, 1H), 8.45 (dd, *J* = 11.6 Hz, 1.2 Hz, 1H), 7.46 (d, *J* = 11.4 Hz, *J* = 5.4 Hz 1H), 7.16 – 7.11 (m, 2H), 7.02 – 6.97 (m, 1H), 6.90 (d, *J* = 10.4 Hz, 2H), 6.84 – 6.81 (m, 1H), 6.76 (d, *J* = 11.6 Hz ,1H), 6.64 (s, 1H), 3.94 (s, 3H), 3.86-3.89 (m, 1H), 3.00 (d, *J* = 7.2 Hz, 2H), 1.60 – 1.51 (m, 4H), 1.35 (s, 9H), 1.28 (d, *J* = 8.0 Hz 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9, 155.6, 147.4, 144.3, 139.4, 134.3, 132.7, 131.5, 128.8, 124.9, 124.3, 123.3, 92.7, 91.7, 77.3, 56.4, 47.0, 36.2, 33.4, 28.2, 26.3, 20.2; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{34}N_3O_3S$ 468.2316; found 468.2330.

*5,7-bis(phenylselanyl)quinoline-8-amine (**4a**)*. Off white; mp 106-108 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (dd, J = 4.1 Hz, 1.2 Hz, 1H), 8.60 (dd, J = 7.2 Hz, 1.8 Hz, 1H), 8.23 (d, J = 9.6 Hz, 1H), 7.40 (dd, J = 9.0 Hz, 4.2 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.20 – 7.15 (m, 5H), 7.13 – 7.10 (m, 3H), 5.99 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.8, 147.8, 145.9, 138.2, 137.0, 133.6, 131.3, 131.2, 129.6, 129.3, 129.1, 126.5, 125.9, 123.1, 111.9, 106.8. ^{77}Se NMR (114 MHz, $CDCl_3$): δ 327.59, 312.48; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}N_2Se_2$ 456.9722; found 456.9701.

*5,7-Di-deuteriated-8-aminoquinoline (**1aD**).*[3] ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.75 (d, *J* = 3.5 Hz, 1H), 8.05 – 8.03 (m, 1H), 7.35 – 7.33 (m, 2H), 4.93 (br, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.3, 143.8, 138.3, 135.9, 128.7, 127.1, 121.3, 115.7 (1:1:1, t, *J* = 24.9 Hz, 1C), 109.7 (1:1:1, t, *J* = 24.2 Hz, 1C).

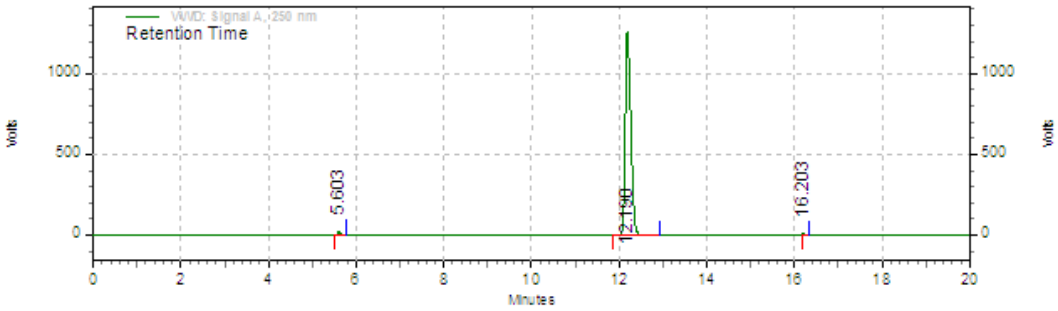
References:

1. (a) D. Singh, A. Deobald, L. Camargo, G. Tabarelli, O. Rodrigues and A. Braga, *Org. Lett.*, 2010, **12**, 3288-3291. (b) G. ten Brink, B. Fernandes, M. vanVliet, I. Arends and R. Sheldon, *J. Chem. Soc., Perkin Trans. 1*, 2001, 224-228.
2. (a) Z. Wu, Y. He, C. Ma, X. Zhou, X. Liu, Y. Li, T. Hu, P. Wen and G. Huang, *Asian J. Org. Chem.*, 2016, **5**, 724-728. (b) Q. Yan, Y. Fang, Y. Jia and X. Duan, *New J. Chem.* 2017, **41**, 2372-2377. (c) H. Shiraki, M. Kozar, V. Melendez, T. Hudson, C. Ohrt, A. Magill and A. Lin, *J. Med. Chem.*, 2011, **54**, 131-142.
3. A. M. Suess, M. Z. Ertem, C. J. Cramer and S. S. Stahl, *J. Am. Chem. Soc.*, 2013, **135**, 9797-9804.
4. Q. Yu, Y. Yang, J. Wan and Y. Liu, *J. Org. Chem.* 2018, **83**, 11385-11391.

Figure S1: HPLC data (area % report) for 6-methoxy-8-aminoquinoline:

Area % Report

Data File: D:\chalcogenation\6-OMe-8-aminoquinoline_22-Feb-19 9-59-30 AM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
Acquired: 2/22/2019 10:01:35 AM
Printed: 8/2/2019 5:42:16 PM



VWD: Signal A, 250 nm Results

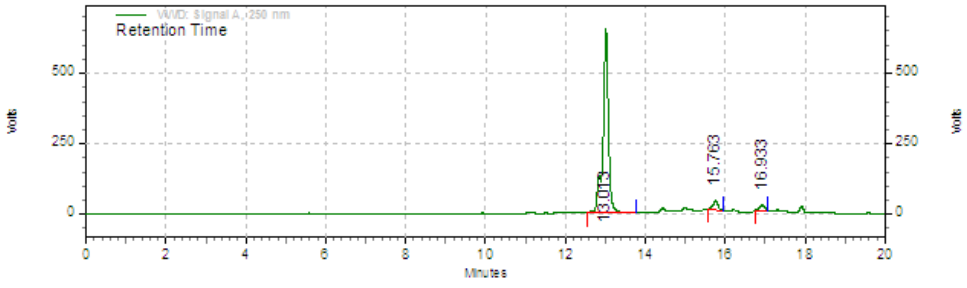
Retention Time	Area	Area %	Height	Height %
5.603	1009261	0.55	290845	1.35
12.190	182620809	99.27	21143189	98.35
16.203	325352	0.18	63180	0.29
Totals				

Note: The HPLC data is given for pure 6-methoxy-8-aminoquinoline. The peak value with retention time (rt) of 12.190 corresponds to 6-methoxy-8-aminoquinoline.

Figure S2: HPLC data (area % report) for 6-methyl-8-aminoquinoline:

Area % Report

Data File: D:\chalcogenation\6-methyl-8-aminoquinoline 8-2-2019 10-59-29 AM
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
Acquired: 8/2/2019 11:01:25 AM
Printed: 8/2/2019 5:25:51 PM



VWD: Signal A, 250 nm Results

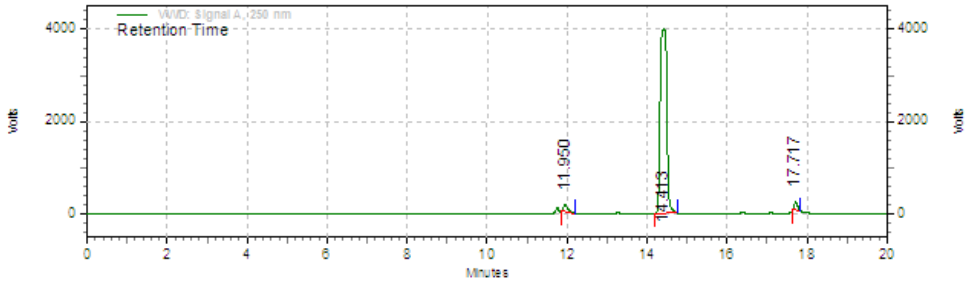
Retention Time	Area	Area %	Height	Height %
13.013	106118401	93.28	10967056	92.78
15.763	4669366	4.10	538526	4.56
16.933	2977740	2.62	314692	2.66
Totals				

Note: The HPLC data is given for pure 6-methyl-8-aminoquinoline. The peak value with retention time (rt) of 13.013 corresponds to 6-methyl-8-aminoquinoline.

Figure S3: HPLC data (area % report) for *N*-methyl-8-aminoquinoline:

Area % Report

Data File: D:\chalcogenation\N-methyl aminoquinoline 8-2-2019 10-30-40 AM
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
Acquired: 8/2/2019 10:32:07 AM
Printed: 8/2/2019 5:48:09 PM



VWD: Signal A, 250 nm Results

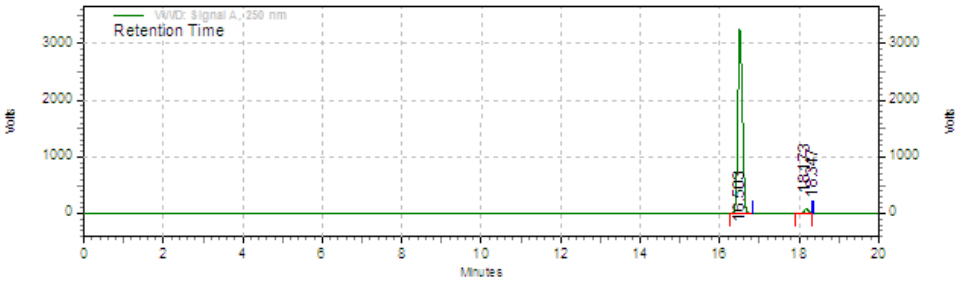
Retention Time	Area	Area %	Height	Height %
11.950	17836857	2.23	2460518	3.39
14.413	764958408	95.53	67110301	92.58
17.717	17930457	2.24	2917521	4.02
Totals				

Note: The HPLC data is given for pure *N*-methyl-8-aminoquinoline. The peak value with retention time (rt) of 14.413 corresponds to *N*-methyl-8-aminoquinoline.

Figure S4: HPLC data (area % report) for *tert*-butyl (4-((6-methoxyquinolin-8-yl)amino)pentyl)carbamate (*N*-Boc primaquine)

Area % Report

Data File: D:\chalcogenation\Ex 155 6-1-2019 3-41-30 PM
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
Acquired: 6/1/2019 3:51:03 PM
Printed: 8/5/2019 12:54:42 PM



VWD: Signal A, 250 nm Results

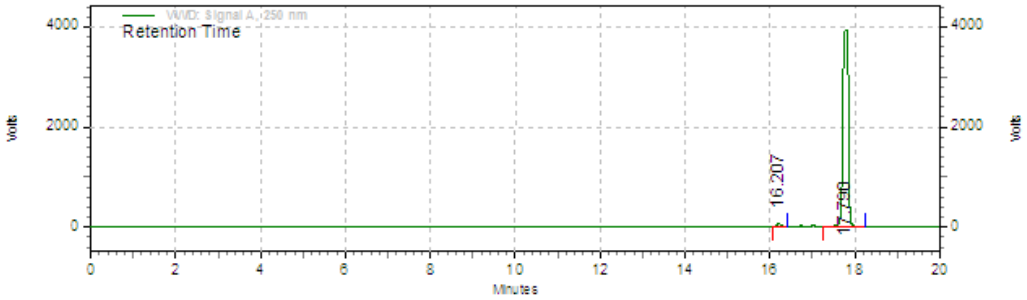
Retention Time	Area	Area %	Height	Height %
16.503	446122076	97.88	54540189	97.52
18.173	9658935	2.12	1383558	2.47
18.347	4473	0.00	3415	0.01
Totals	455785484	100.00	55927162	100.00

Note: The HPLC data is given for pure *N*-Boc primaquine. The peak value with retention time (rt) of 16.503 corresponds to *N*-Boc primaquine.

Figure S5: HPLC data (area % report) for bis(2-methoxyphenyl)diselenide:

Area % Report

Data File: D:\chalcogenation\ortho methoxyphenyl diselenide 8-2-2019 9-56-12 AM
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
Acquired: 8/2/2019 9:59:16 AM
Printed: 8/2/2019 5:33:58 PM



VWD: Signal A, 250 nm Results

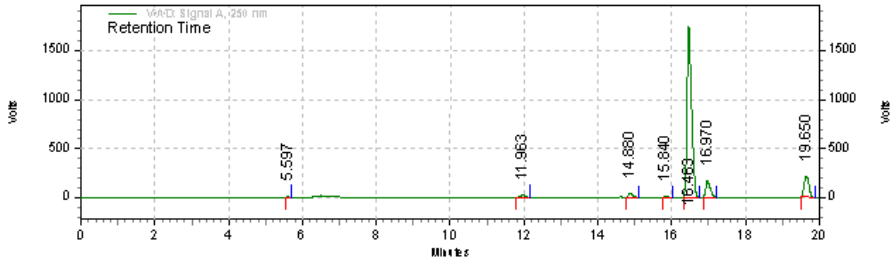
Retention Time	Area	Area %	Height	Height %
16.207	7964788	1.29	1056861	1.58
17.790	608636791	98.71	66024652	98.42
Totals	616601579	100.00	67081513	100.00

Note: The HPLC data is given for pure bis(2-methoxyphenyl)diselenide. The peak value with retention time (rt) of 17.790 corresponds to bis(2-methoxyphenyl)diselenide.

Figure S6: HPLC data (area % report) for crude reaction mixture under standardized condition

Area % Report

Data File: D:\chalcogenation\136 b_01-Mar-19 5-38-01 PM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\untitled.met
Acquired: 01-Mar-19 5:40:06 PM
Printed: 02-Mar-19 3:03:10 PM



VWD: Signal A, 250 nm Results

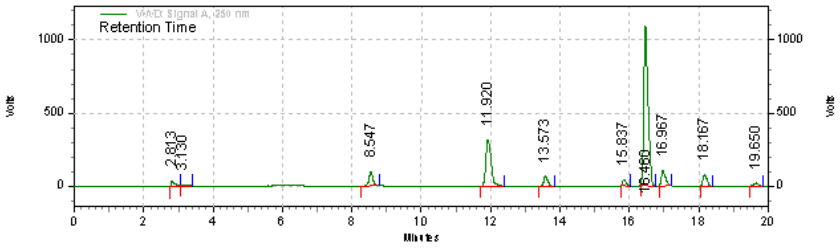
Retention Time	Area	Area %	Height	Height %
5.597	966392	0.30	315127	0.84
11.963	4161794	1.31	434984	1.16
14.880	6288611	1.97	761093	2.03
15.840	2137107	0.67	280649	0.75
16.463	247676131	77.77	29263137	77.95
16.970	24010346	7.54	2852961	7.60
19.650	33240520	10.44	3634433	9.68
Totals	318480901	100.00	37542384	100.00

Note: The HPLC data is given for crude reaction mixture. The peak value corresponds to retention time (rt) of 11.903 for 8-aminoquinoline, 16.46 for product **3a** and18.16 for diphenyldiselenide

Figure S7: HPLC data (area % report) of crude product for the reaction in presence of 1.0 equiv TEMPO

Area % Report

Data File: D:\chalcogenation\136 a with tempo_01-Mar-19 6-05-50 PM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\136 b.met
Acquired: 01-Mar-19 6:08:11 PM
Printed: 02-Mar-19 3:24:28 PM



VWD: Signal A, 250 nm Results

Retention Time	Area	Area %	Height	Height %
2.813	5469108	1.99	690924	2.20
3.130	2040678	0.74	160695	0.51
8.547	13244341	4.81	1586651	5.06
11.920	56584045	20.56	5330176	16.99
13.573	9801487	3.56	1171701	3.73
15.837	5425700	1.97	732055	2.33
16.460	153546716	55.80	18242536	58.15
16.967	14553605	5.29	1727693	5.51
18.167	10743548	3.90	1351040	4.31
19.650	3758566	1.37	377535	1.20
Totals	275167794	100.00	31371006	100.00

Note: The HPLC data is given for crude reaction mixture. The peak value corresponds to retention time (rt) of 11.903 for 8-aminoquinoline, 13.56 for TEMPO, 16.46 for product **3a** and18.16 for diphenyldiselenide.

Figure S8: HPLC data (area % report) of crude product for the reaction in presence of 0.2 equiv TEMPO

Area % Report

Data File: D:\chalcogenation\137_05-Mar-19 3-47-25 PM.dat
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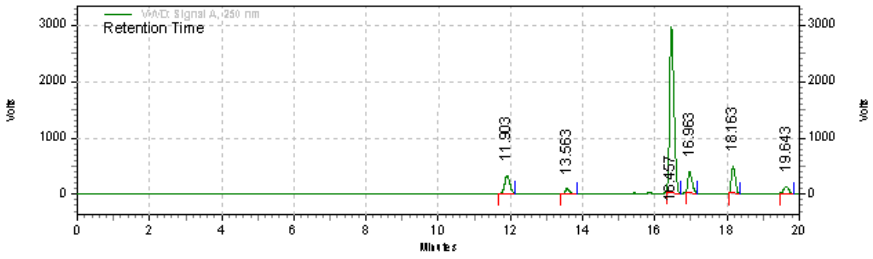
Acquired: 05-Mar-19 3:53:36 PM
Printed: 05-Mar-19 4:26:08 PM



VWD: Signal A, 250 nm Results

Retention Time	Area	Area %	Height	Height %
11.903	54558763	8.96	5372429	7.37
13.563	13069593	2.15	1588722	2.18
16.457	411166317	67.53	49487988	67.85
16.963	48912816	8.03	6257592	8.58
18.163	60472080	9.93	8062723	11.05
19.643	20692285	3.40	2163927	2.97
Totals	608871854	100.00	72933381	100.00

Note: The HPLCdata is given for crude reaction mixture. The peak value corresponds to retention time (rt) of 11.903 for 8-aminoquinoline, 13.56 for TEMPO, 16.45 for product **3a** and 18.16 for diphenyldiselenide.

Figure S9: HPLC data (area % report) of crude product for the reaction in presence of0.2 equiv BHT

Area % Report

Data File: D:\chalcogenation\Ex 159 5-23-2019 5-07-50 PM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\Ex 158.met
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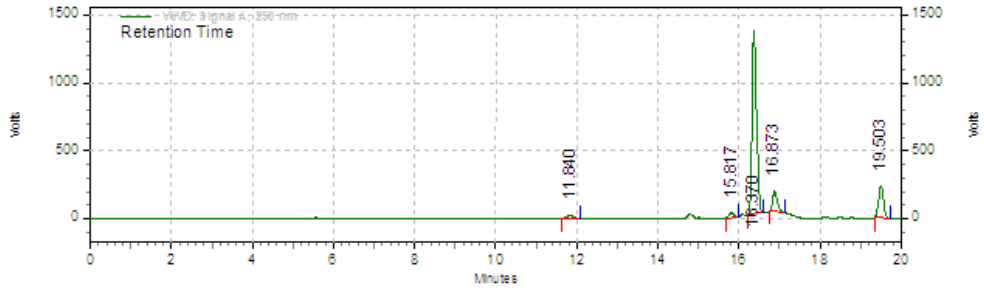
Printed: 5/24/2019 10:22:51 AM



VWD: Signal A, 250 nm Results

Retention Time	Area	Area %	Height	Height %
11.840	4701178	2.02	412890	1.38
15.817	5097212	2.19	601086	2.01
16.370	170984046	73.38	22638598	75.59
16.873	19035916	8.17	2438397	8.14
19.503	33187287	14.24	3859104	12.89
Totals	233005639	100.00	29950075	100.00

Note: The HPLC data is given for crude reaction mixture. The peak value corresponds to retention time (rt) of 11.86 for 8-aminoquinoline, 18.10 for BHT, 16.397 for product **3a** and 19.55 for diphenyldiselenide.

Figure S10: HPLC data (area % report) of crude product for the reaction in presence of 1.0 equiv BHT

Area % Report

Data File: D:\chalcogenation\EX 158 5-23-2019 4-20-05 PM.dat
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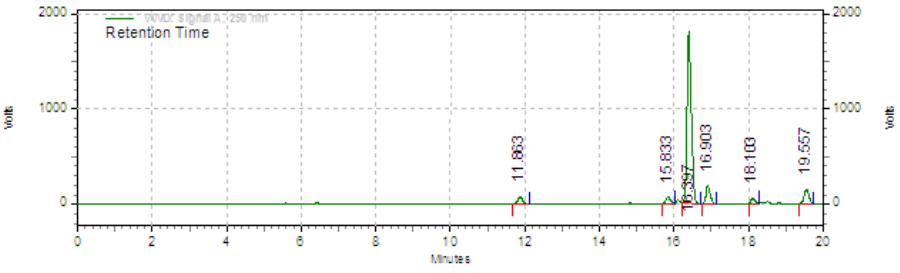
Printed: 5/24/2019 10:16:55 AM



VWD: Signal A, 250 nm Results

Retention Time	Area	Area %	Height	Height %
11.863	12377519	3.95	1291308	3.27
15.833	9935977	3.17	1152136	2.92
16.397	235563969	75.22	30301469	76.74
16.903	24432542	7.80	3173535	8.04
18.103	7313569	2.34	969975	2.46
19.557	23551305	7.52	2597042	6.58
Totals	313174881	100.00	39485465	100.00

Note: The HPLC data is given for crude reaction mixture. The peak value corresponds to retention time (rt) of 11.86 for 8-aminoquinoline, 18.10 for BHT, 16.397 for product **3a** and 19.55 for diphenyldiselenide.

Figure S11: HPLC data (area % report) for the purified product *tert*-Butyl(4-((6-methoxy-5-((2-methoxyphenyl)selanyl)quinolin-8-yl)amino)pentyl)carbamate (3v):

Area % Report

Data File: D:\chalcogenation\Ex 164A 6-20-2019 10-36-57 AM
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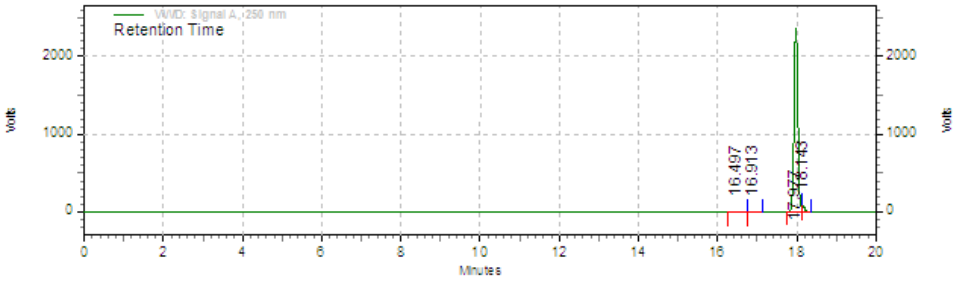
Acquired: 6/20/2019 10:40:01 AM
Printed: 7/27/2019 2:03:24 PM



VWD: Signal A, 250 nm Results

Retention Time	Area	Area %	Height	Height %
16.497	1526348	0.56	196694	0.48
16.913	921781	0.34	138175	0.33
17.977	261152718	96.21	39612220	95.79
18.143	7851842	2.89	1405118	3.40
Totals	271452689	100.00	41352207	100.00

Note: The HPLC data is given for purified product **3v**. The peak value corresponds to retention time (rt) of 17.977 for*tert*-Butyl(4-((6-methoxy-5-((2-methoxyphenyl)selanyl)quinolin-8-yl)amino)pentyl)carbamate **(3v)**

Figure S12: HPLC data (area % report) for purified*tert*-Butyl(4-((6-methoxy-5-(phenylthio)quinolin-8-yl)amino)pentyl)carbamate (3w):

Area % Report

Data File: D:\chalcogenation\Ex 163A 6-17-2019 11-40-34 AM
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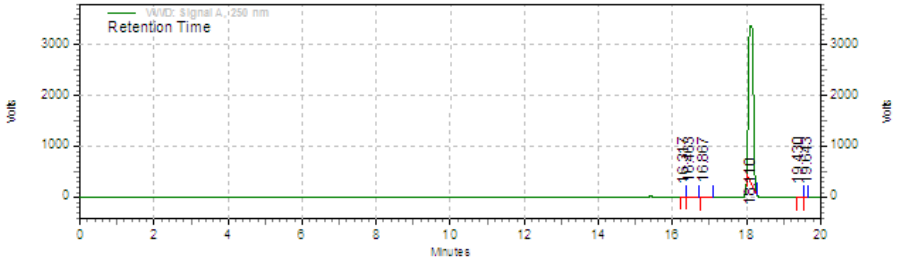
Acquired: 6/17/2019 11:42:07 AM
Printed: 7/27/2019 1:57:11 PM



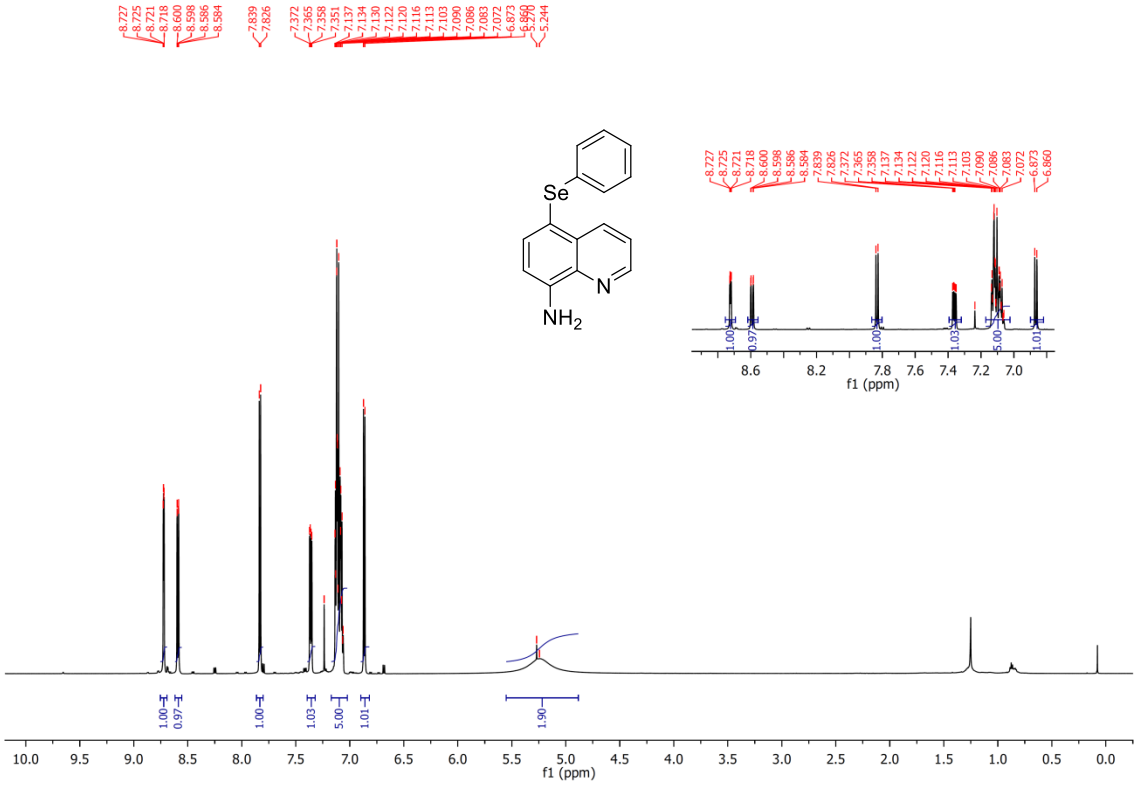
VWD: Signal A, 250 nm Results

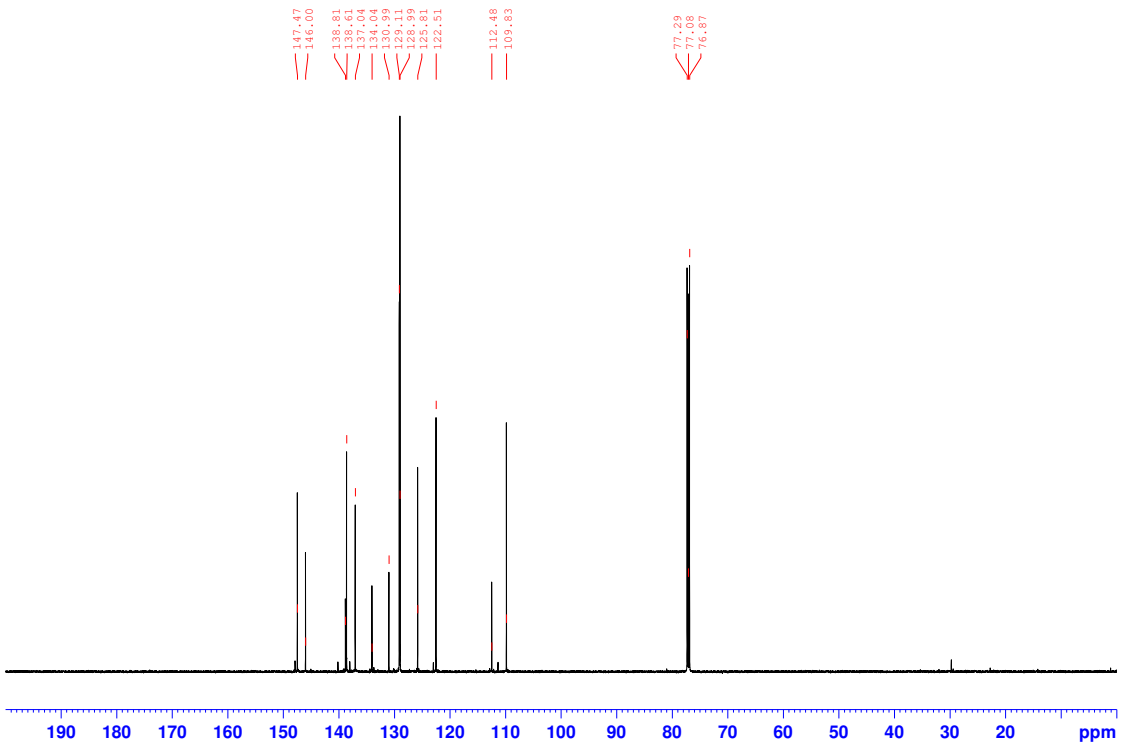
Retention Time	Area	Area %	Height	Height %
16.317	172423	0.04	30575	0.06
16.463	938849	0.20	120211	0.23
16.867	820090	0.18	116237	0.22
18.110	464742746	99.58	51633072	99.47
19.430	29603	0.01	5154	0.01
19.643	15196	0.00	3157	0.01
Totals	466718907	100.00	51908406	100.00

Note: The HPLC data is given for purified product **3w**. The peak value corresponds to retention time (rt) of 18.110 for *tert*-Butyl(4-((6-methoxy-5-(phenylthio)quinolin-8-yl)amino)pentyl)carbamate (**3w**)

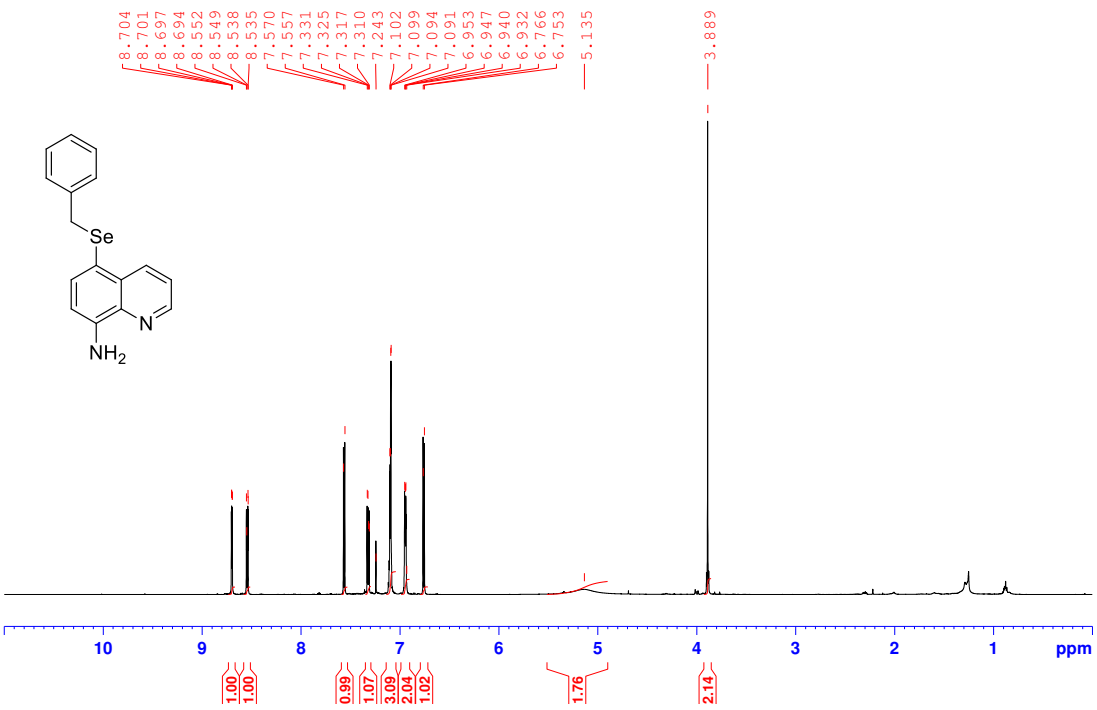
1D and 2Dspectrum for the products:

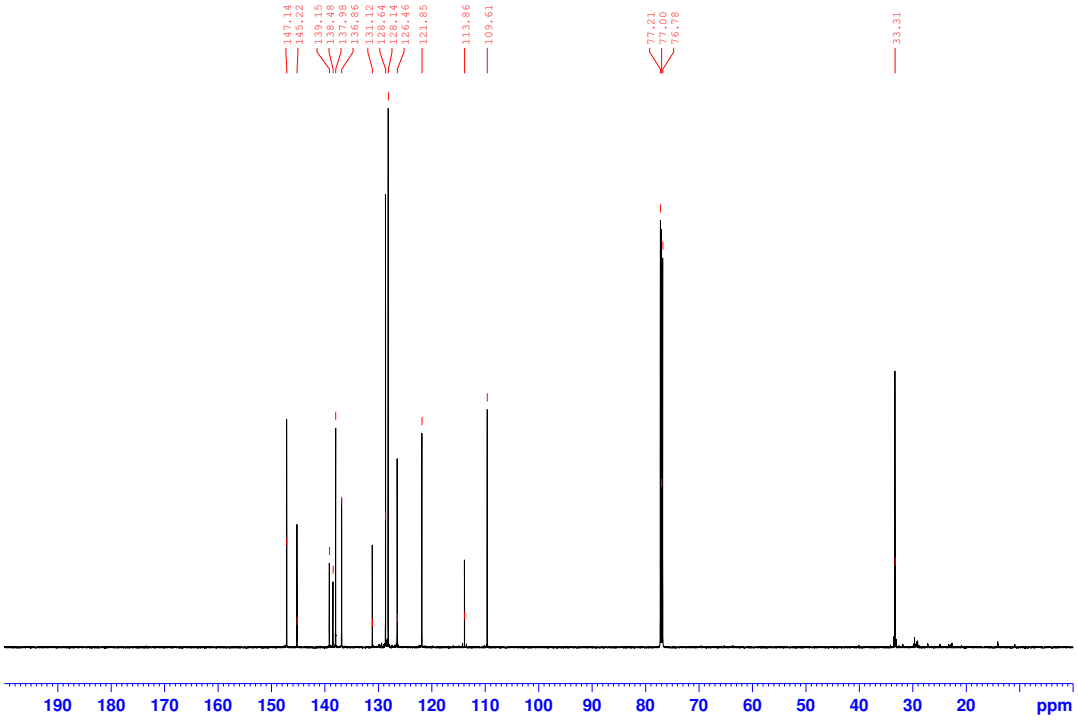
^{1}H and ^{13}C NMR of 5-(phenylselanyl)quinoline-8-amine (**3a)**



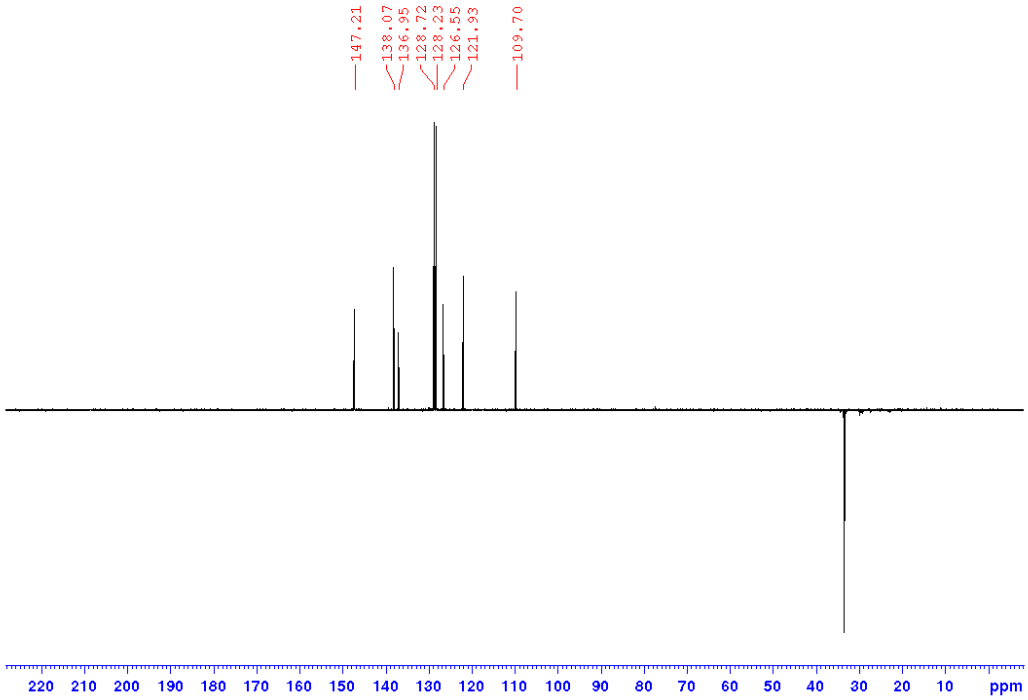


^{1}H and ^{13}C NMR of 5-(benzylselanyl)quinoline-8-amine (**3b**)

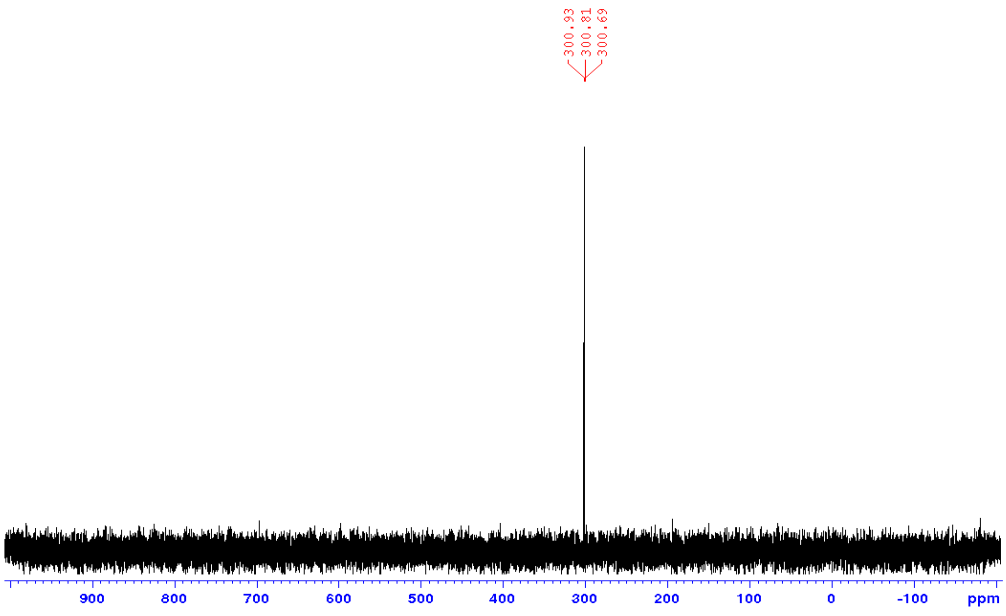




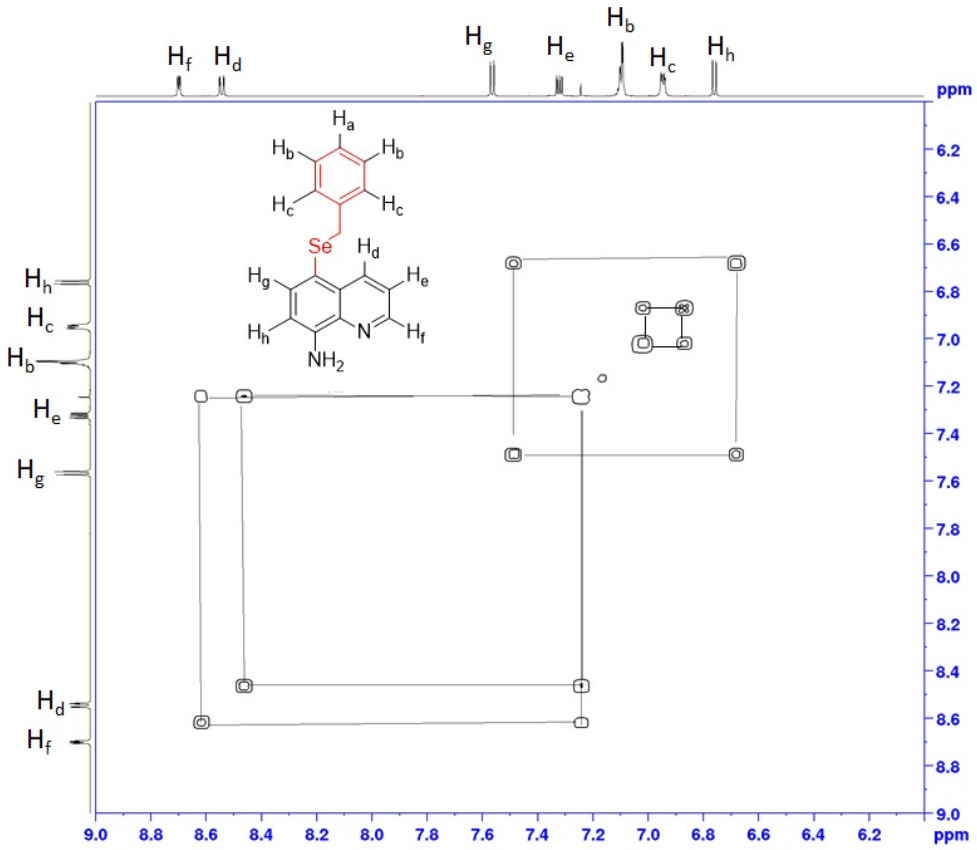
DEPT-135 for **3b**



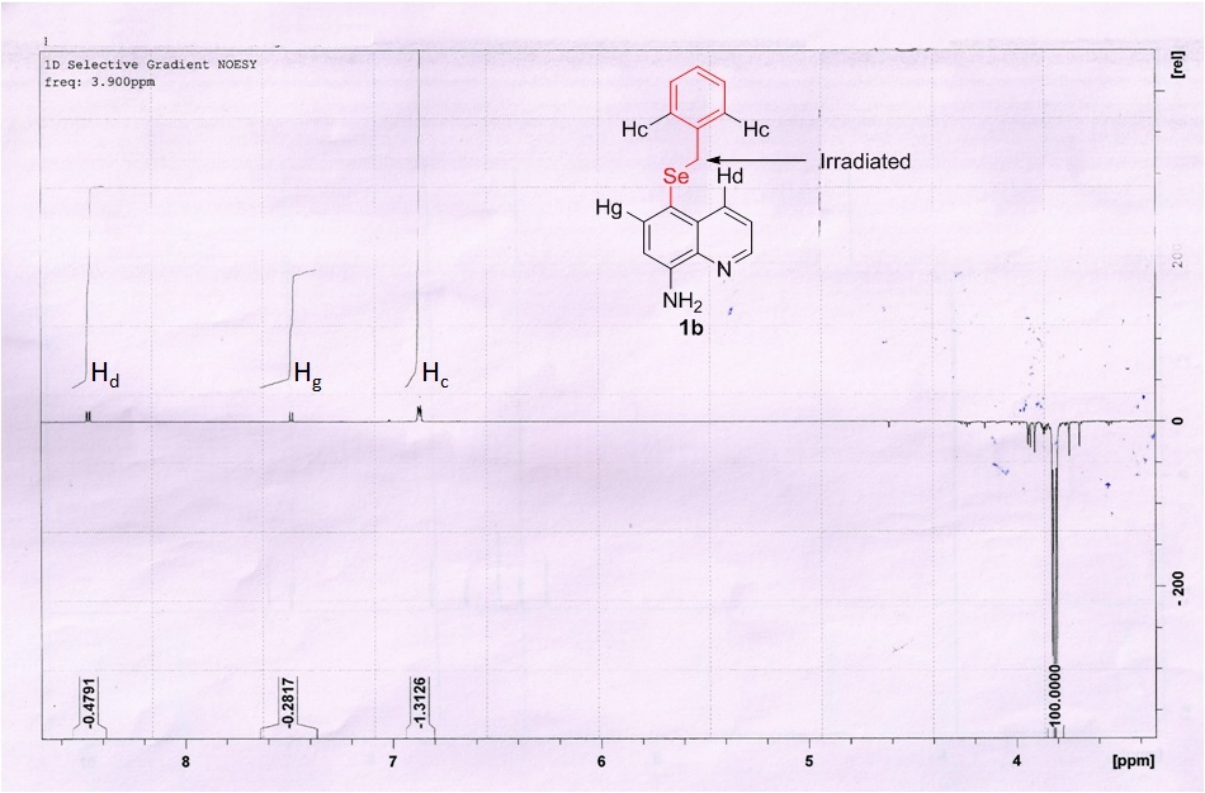
^{77}Se Spectra for **3b**



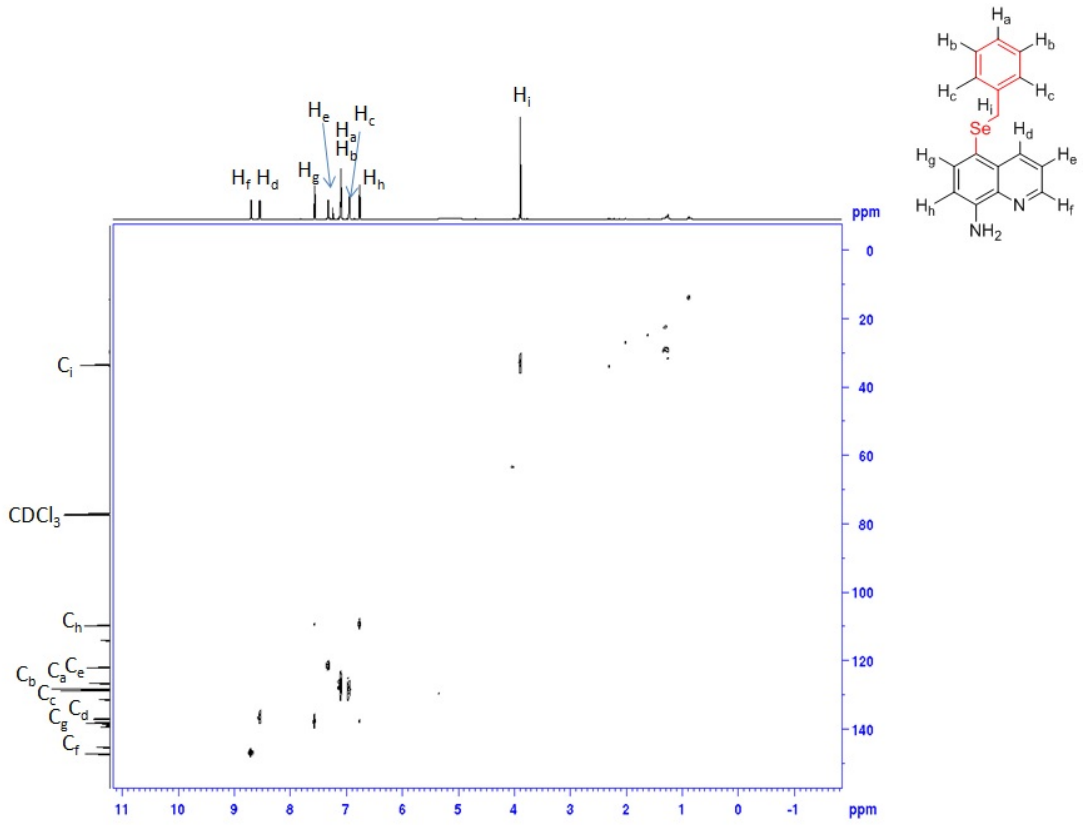
Cosy spectra for **3b**



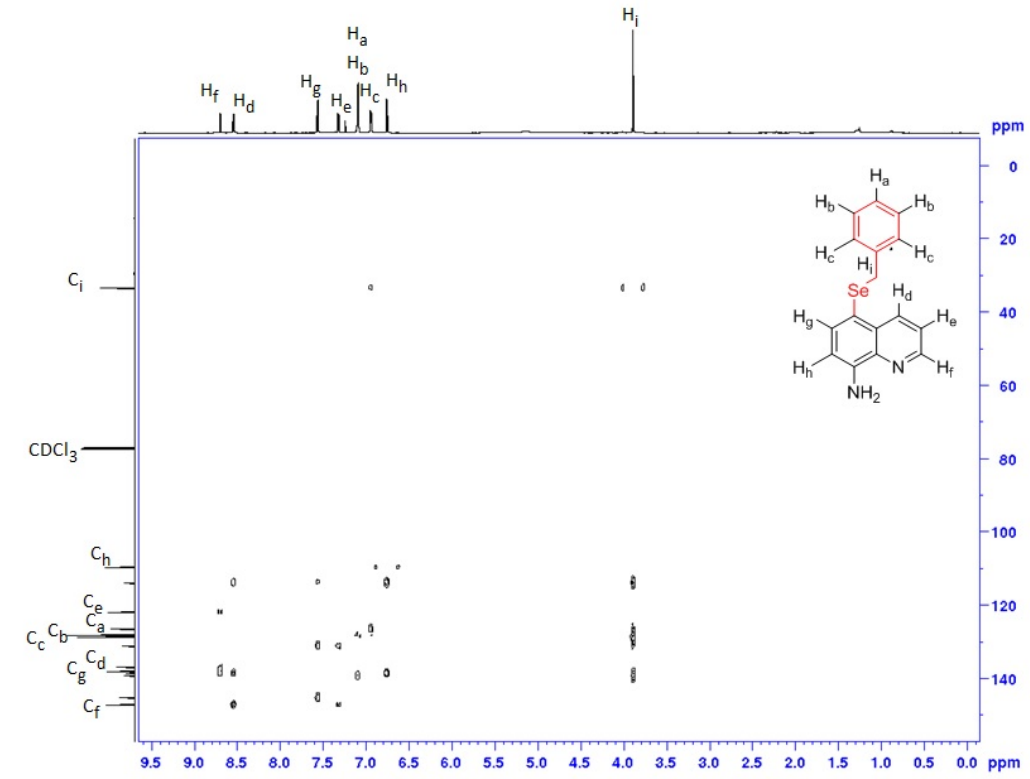
NOE spectra for **3b**



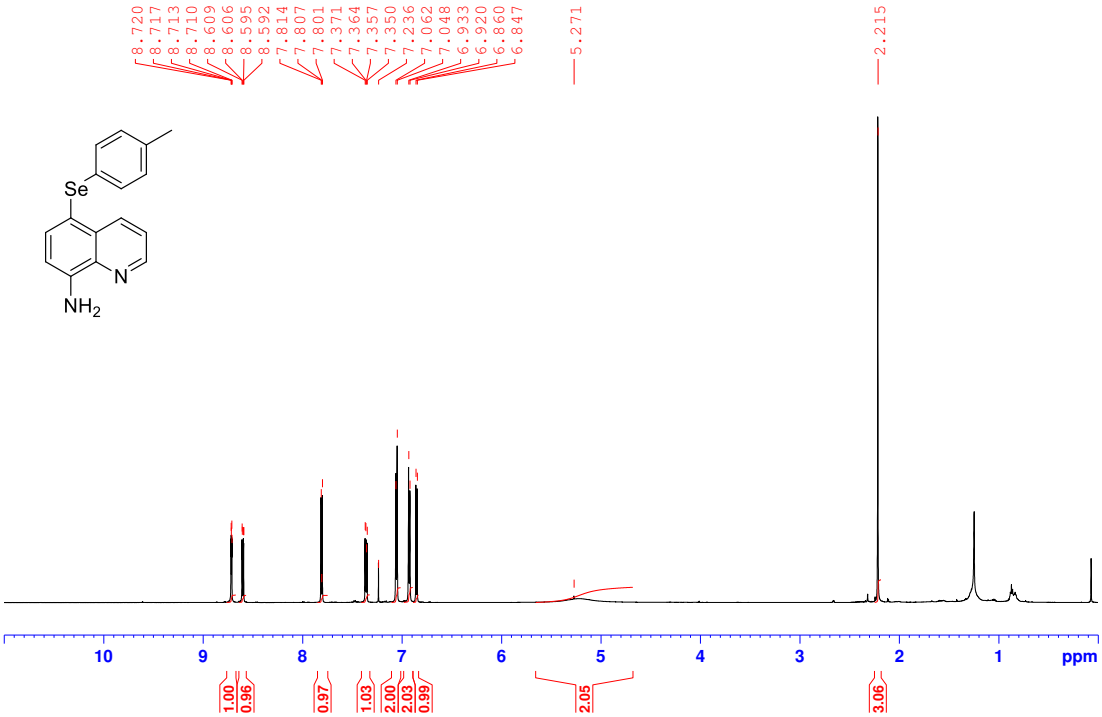
HSQC spectra for **3b**

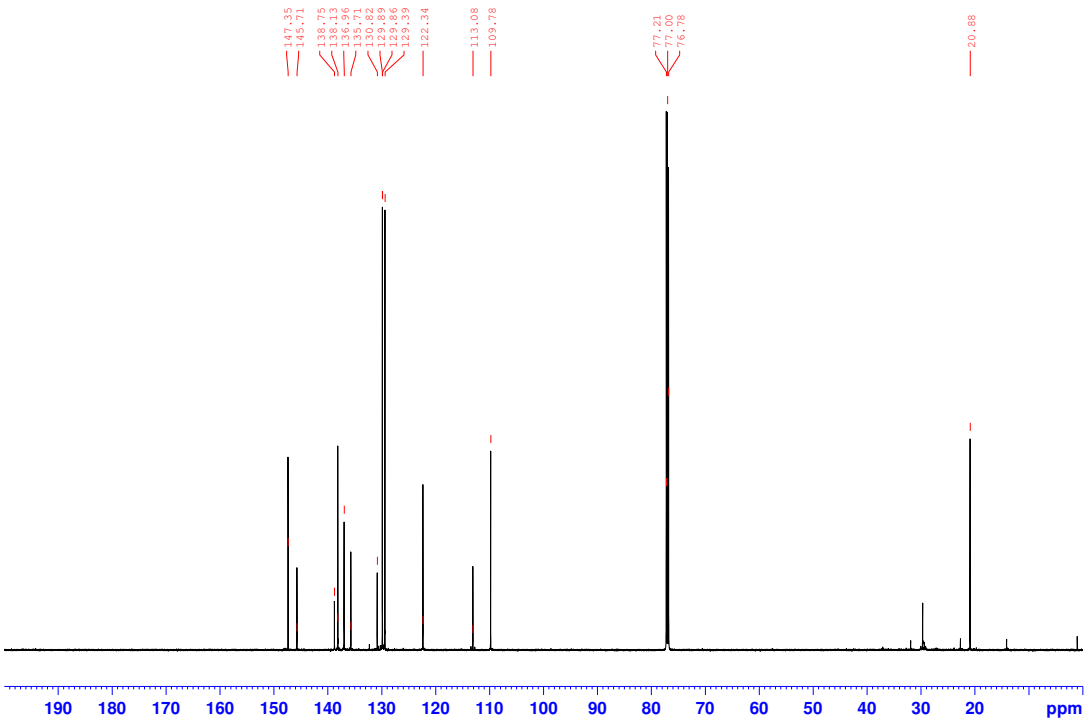


HMBC spectra for **3b**

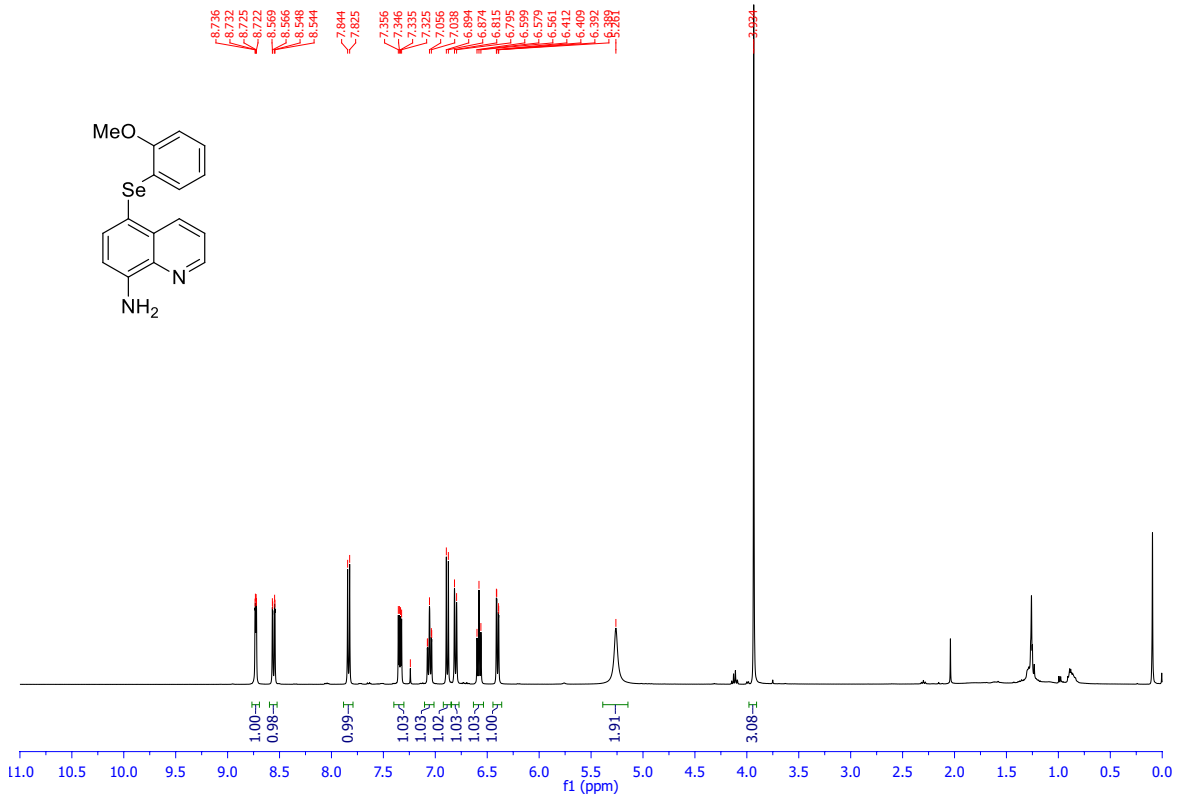


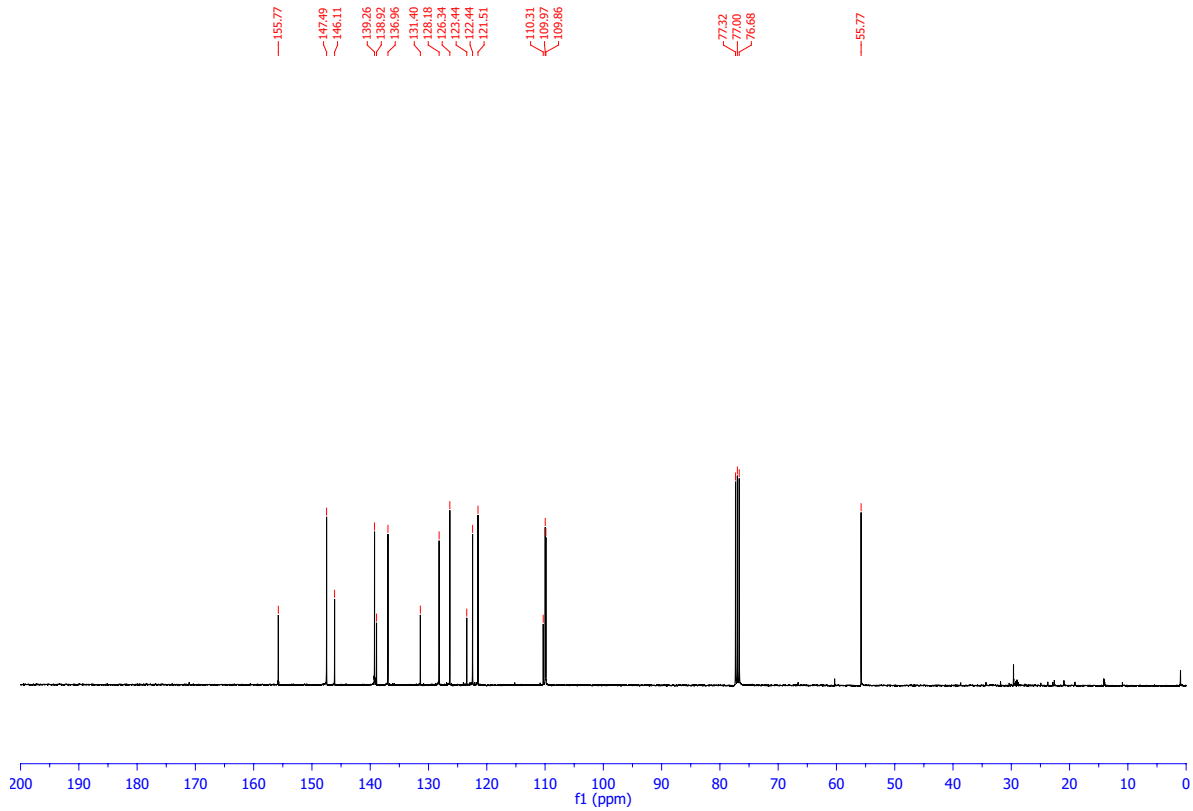
^{1}H and ^{13}C NMR of 5-(*p*-tolylselanyl)quinoline-8-amine (**3c**)



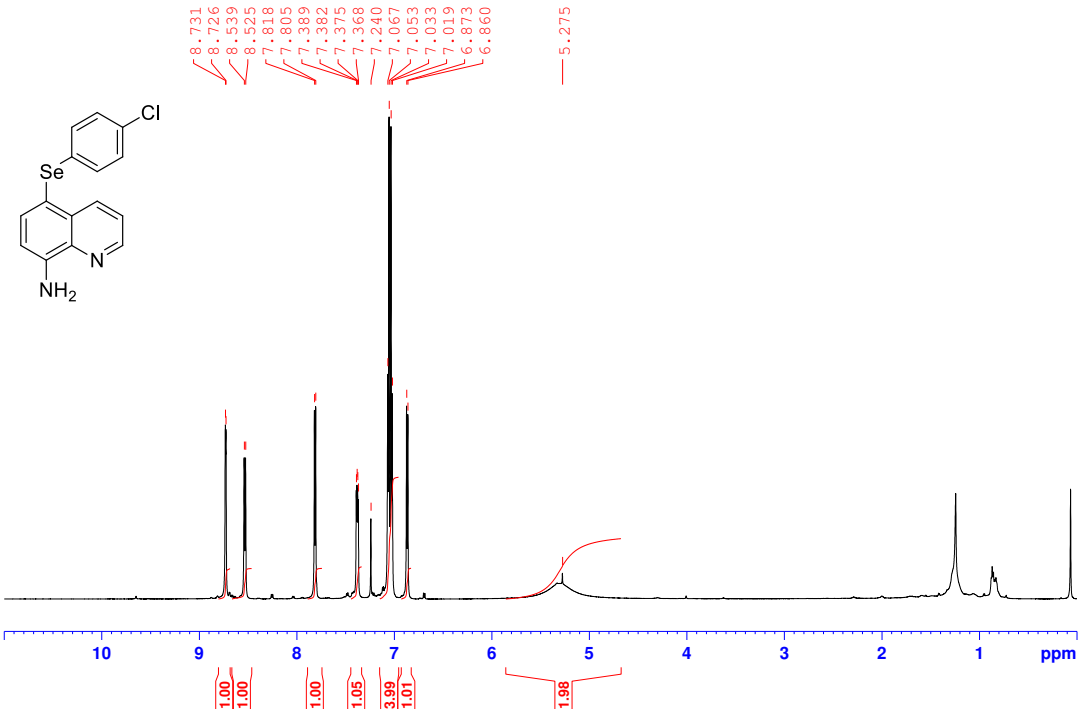


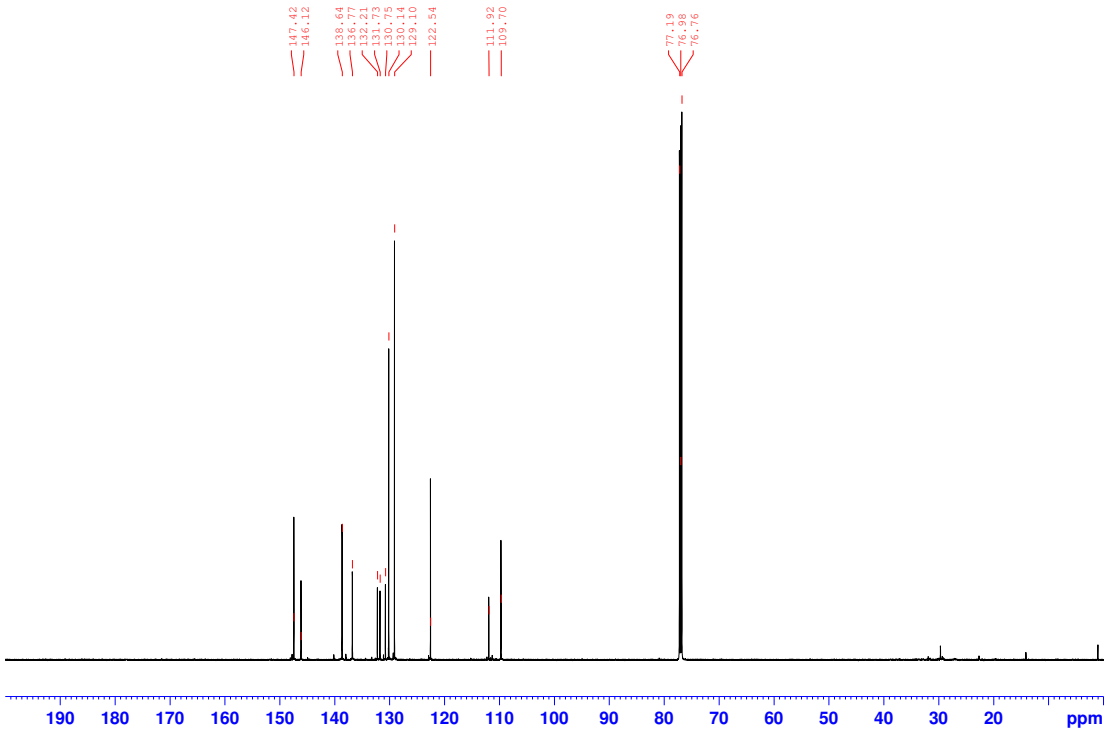
^{1}H and ^{13}C NMR of 5-((2-methoxyphenyl)selanyl)quinolin-8-amine (**3d**)



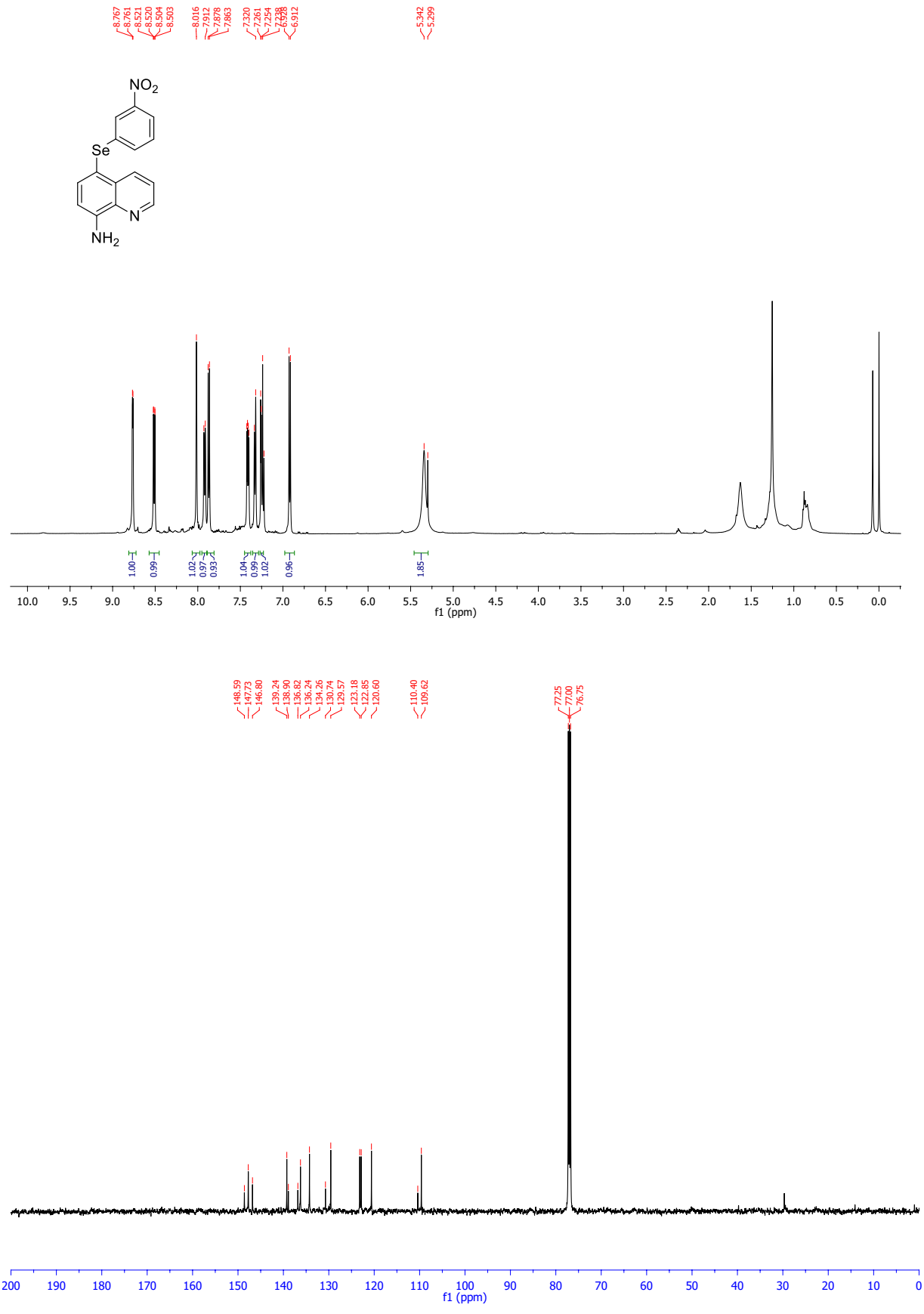


^{1}H and ^{13}C NMR of 5-((4-chlorophenyl)selanyl)quinoline-8-amine (**3e**)

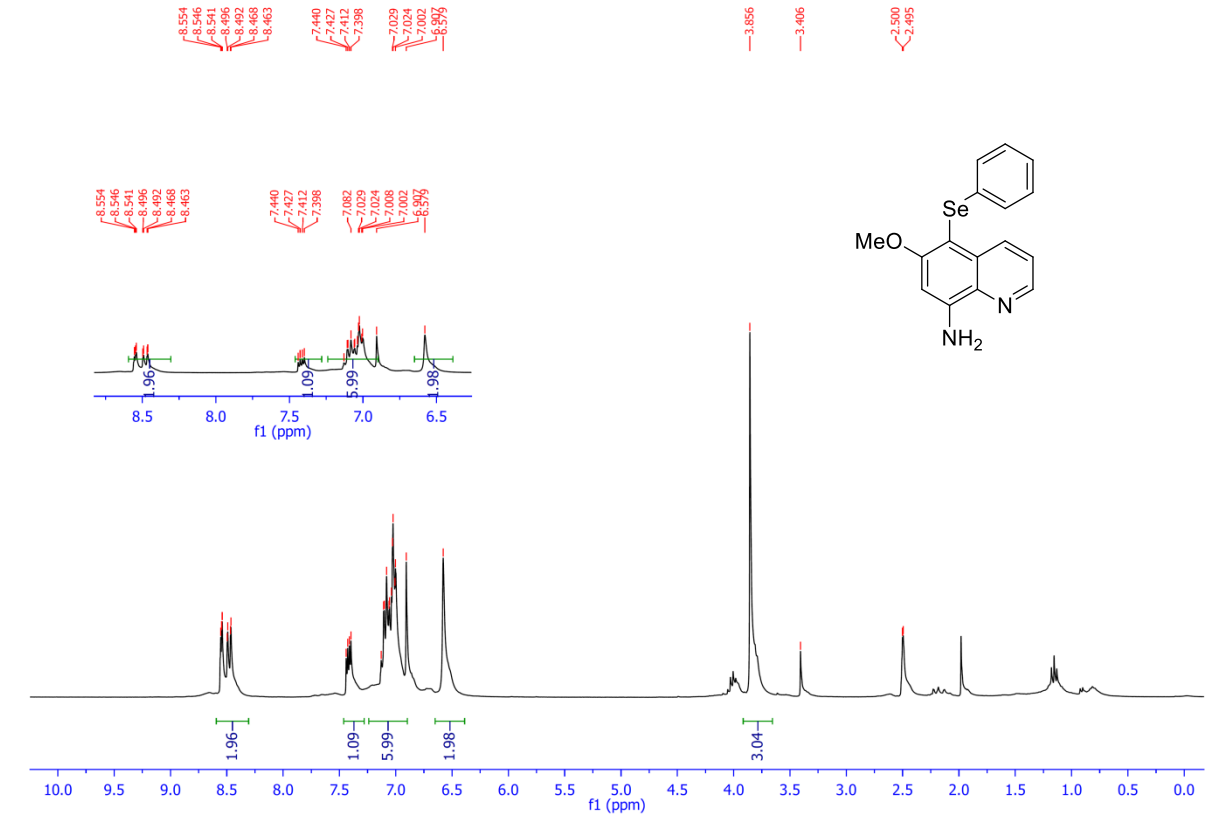




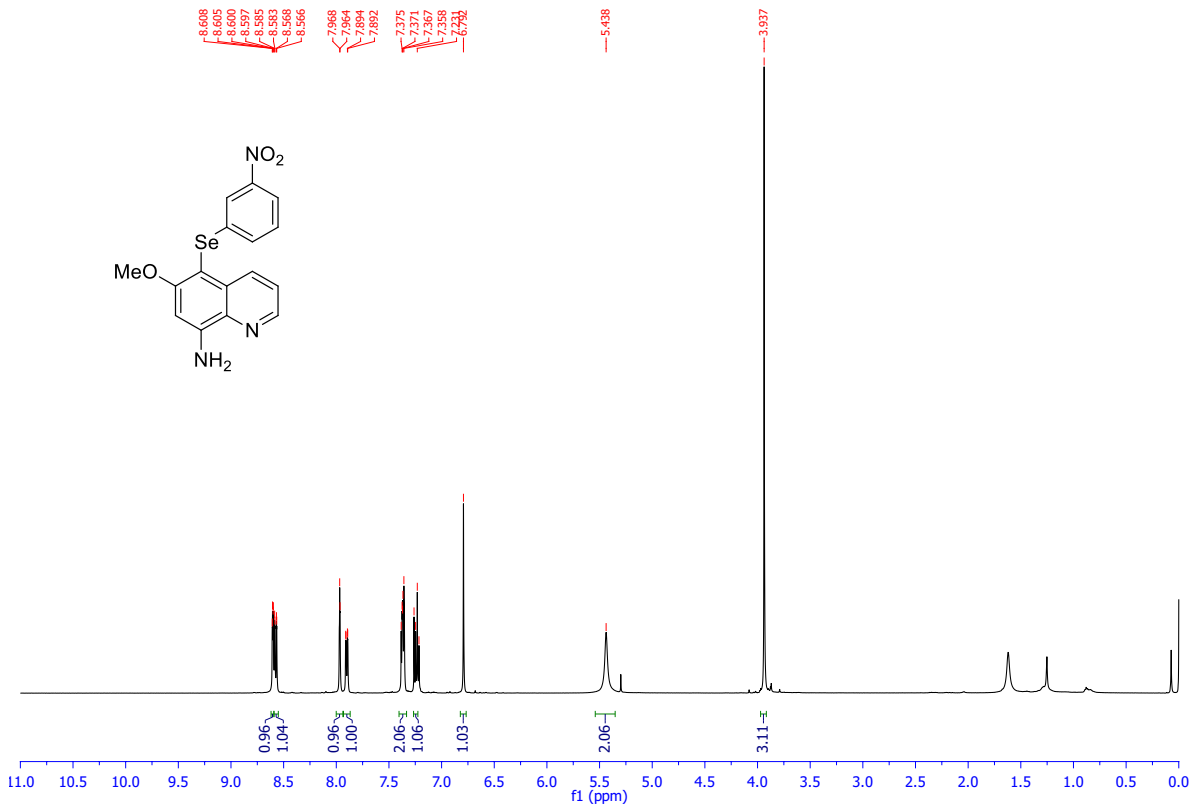
^{1}H and ^{13}C NMR of 5-((3-Nitrophenyl)selanyl)quinoline-8-amine (**3f**)

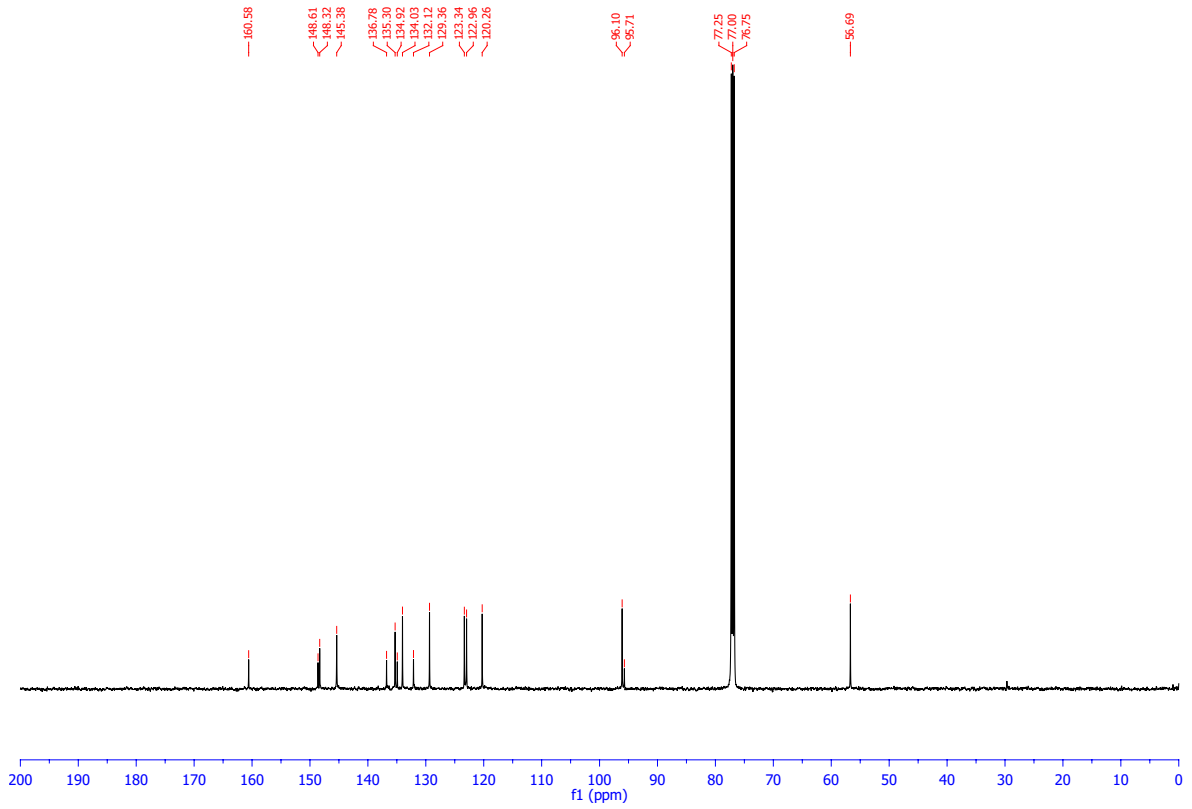


^{1}H and ^{13}C NMR of 6-Methoxy-5-(phenylselanyl)quinoline-8-amine (**3g**)

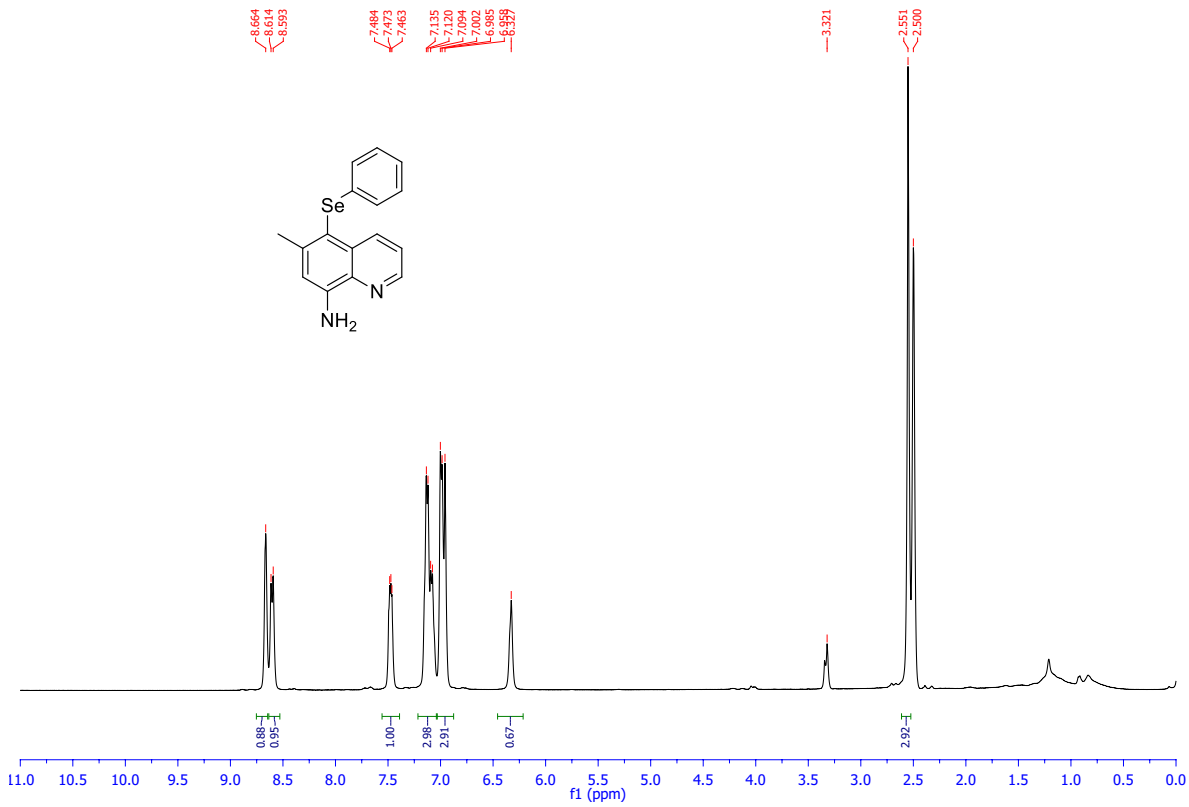


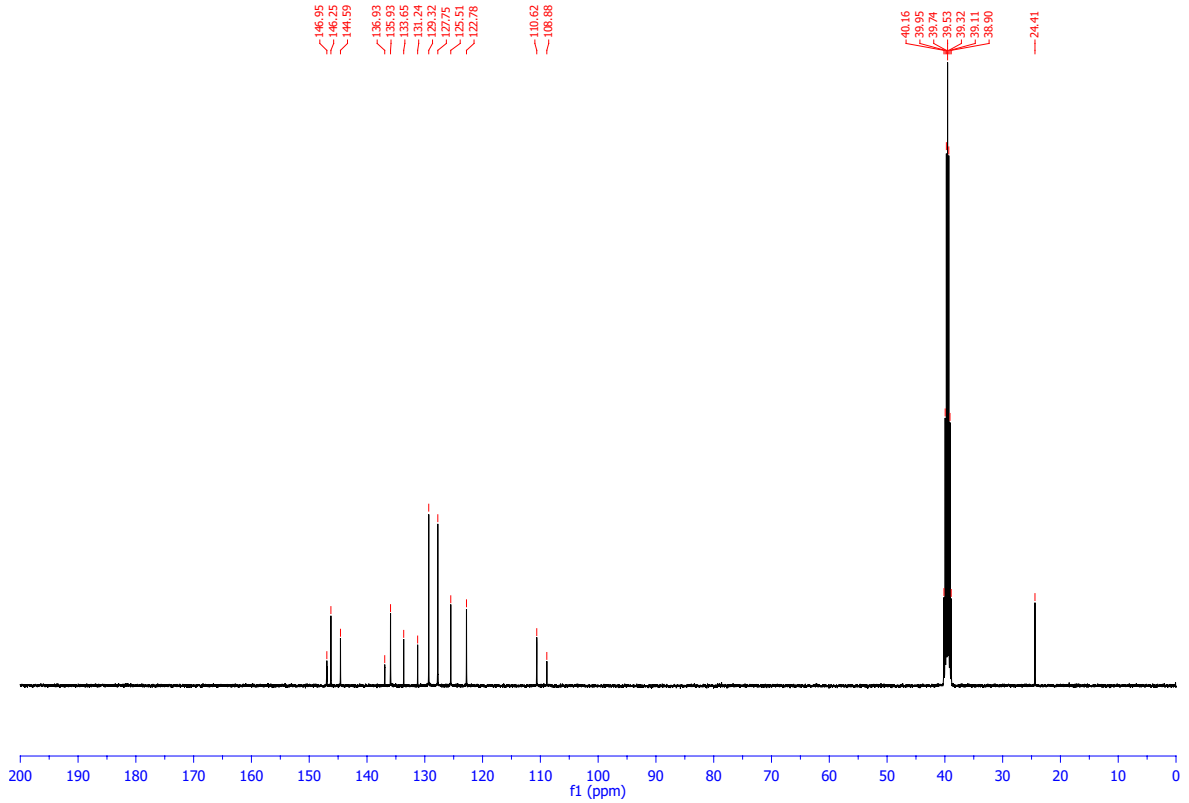
^{1}H and ^{13}C NMR of 6-Methoxy-5-(3-nitrophenylselanyl)quinoline-8-amine (**3h**)



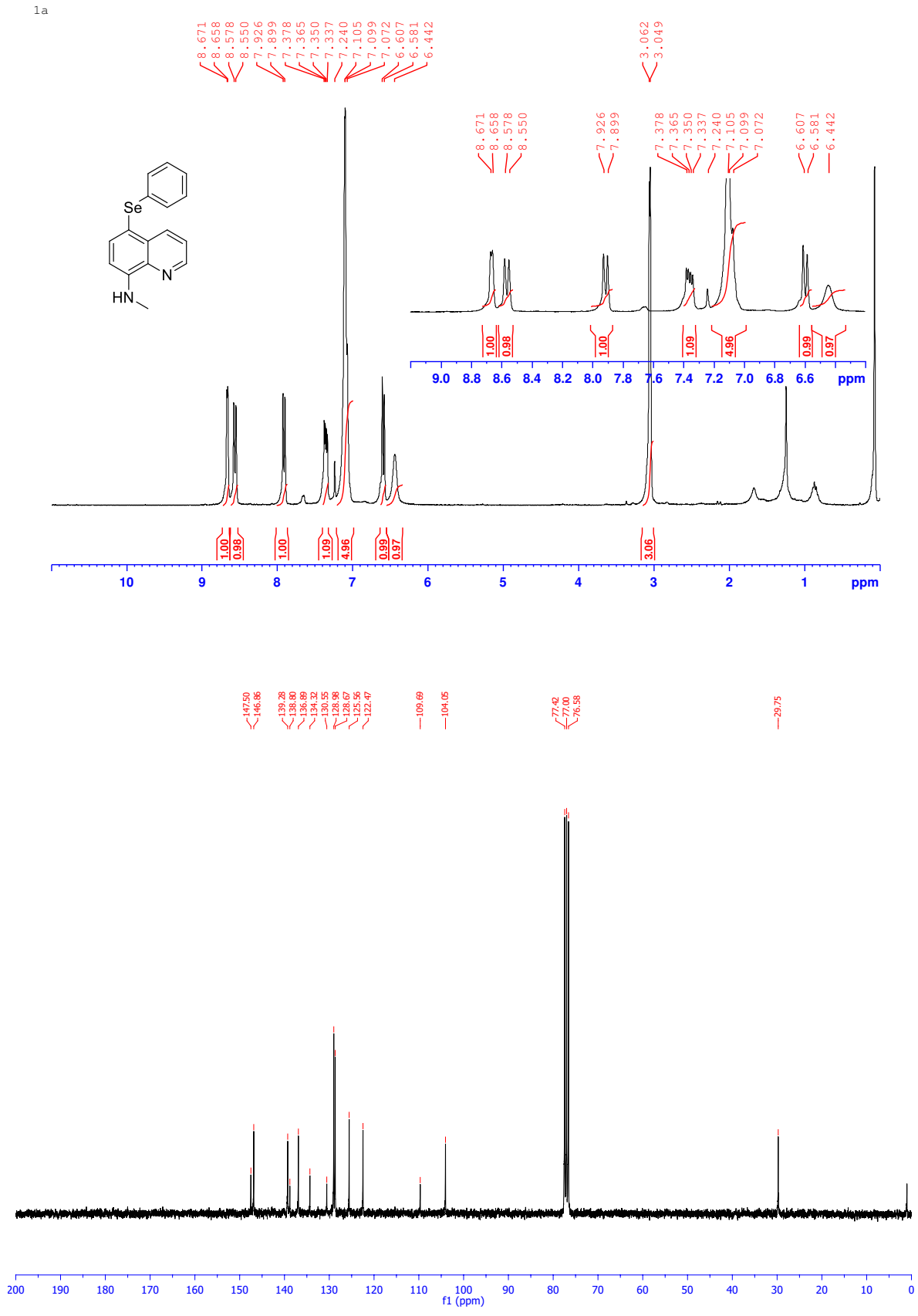


^{1}H and ^{13}C NMR of 6-Methyl-5-(phenylselanyl)quinolin-8-amine (**3i**)

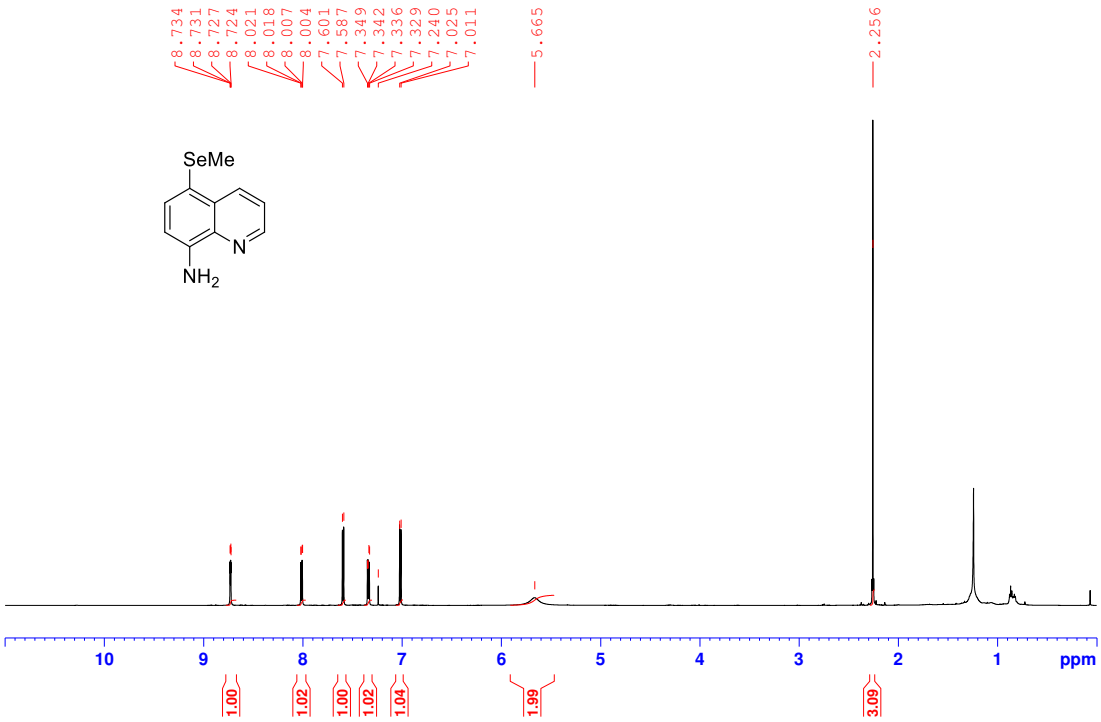


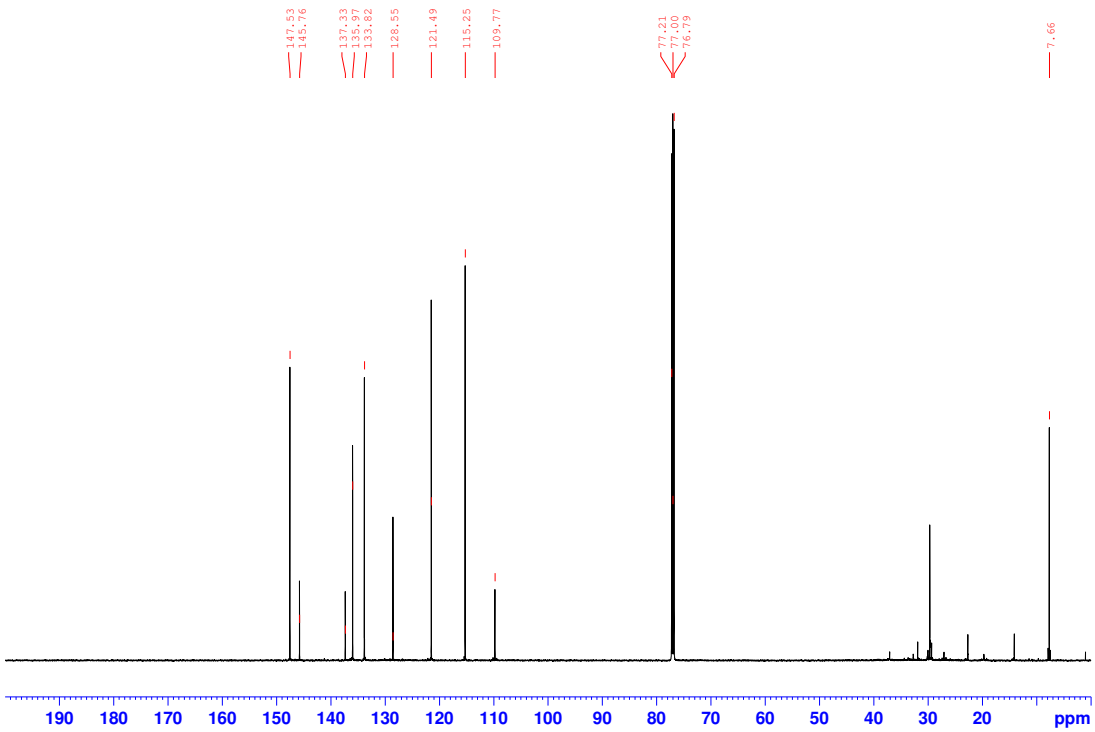


^{1}H and ^{13}C NMR of *N*-methyl-5-(phenylselanyl)quinolin-8-amine (**3j**)

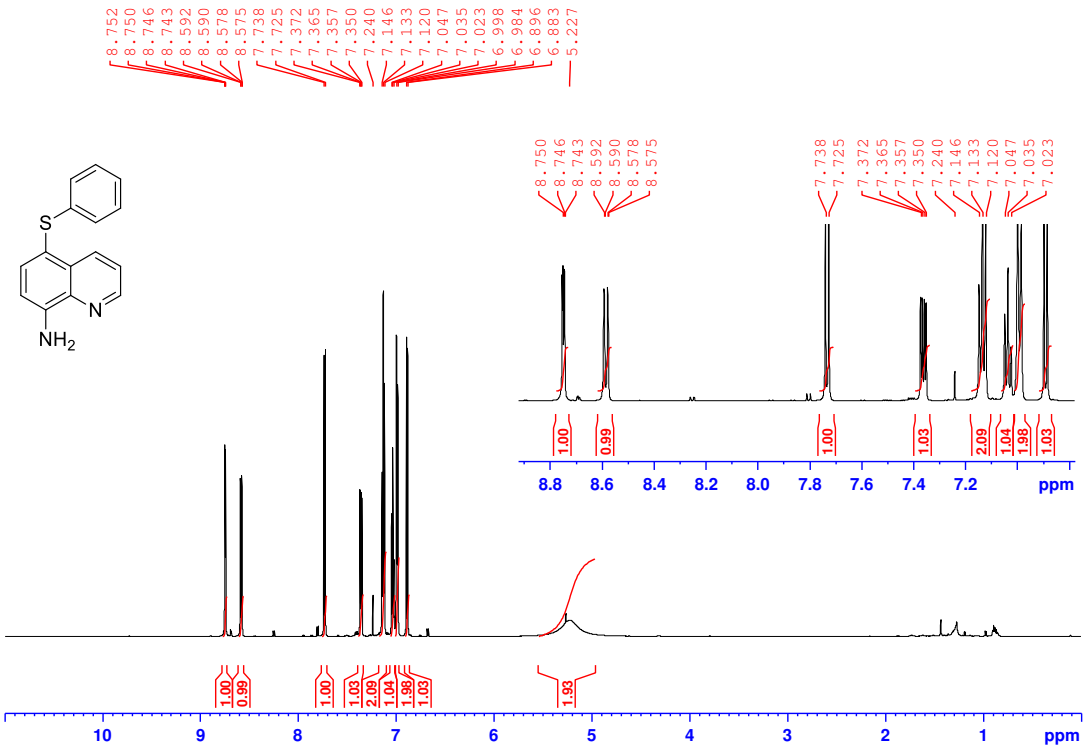


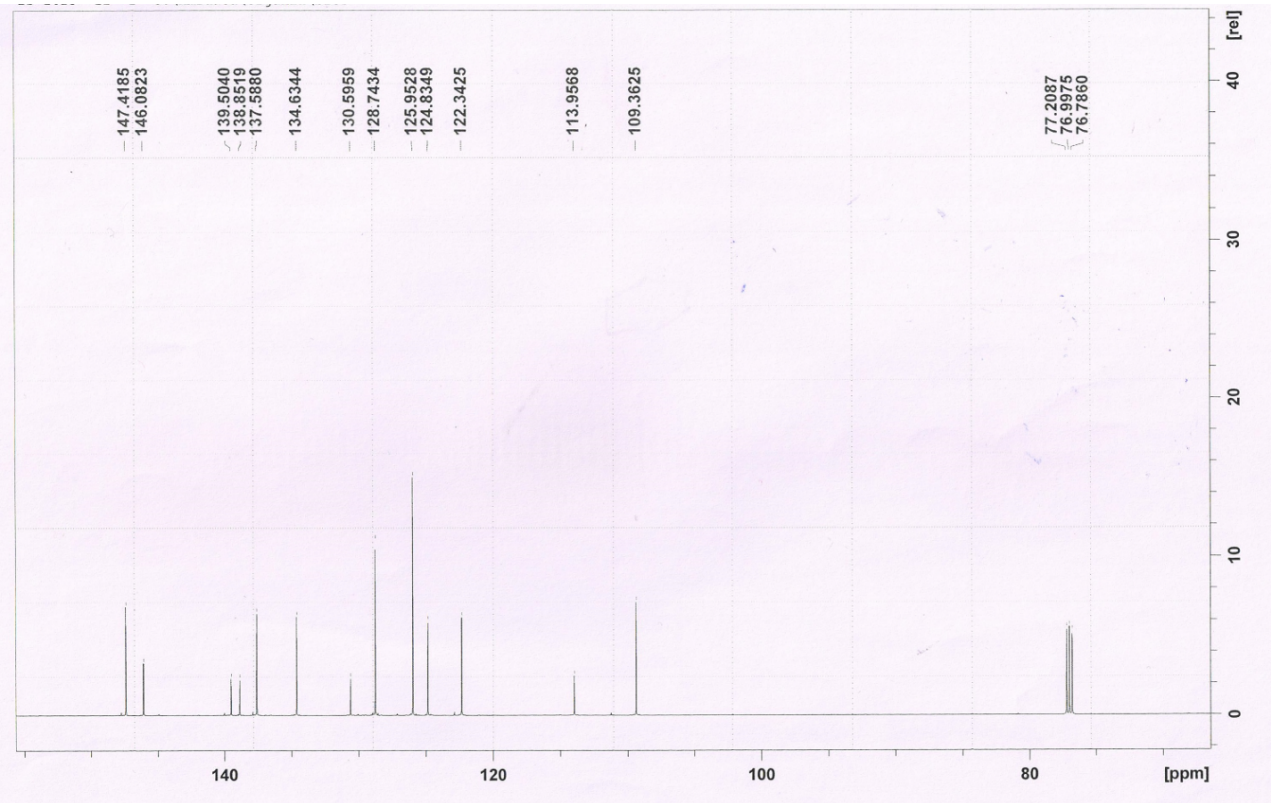
^{1}H and ^{13}C NMR of 5-(Methylselanyl)quinoline-8-amine (**3k**)



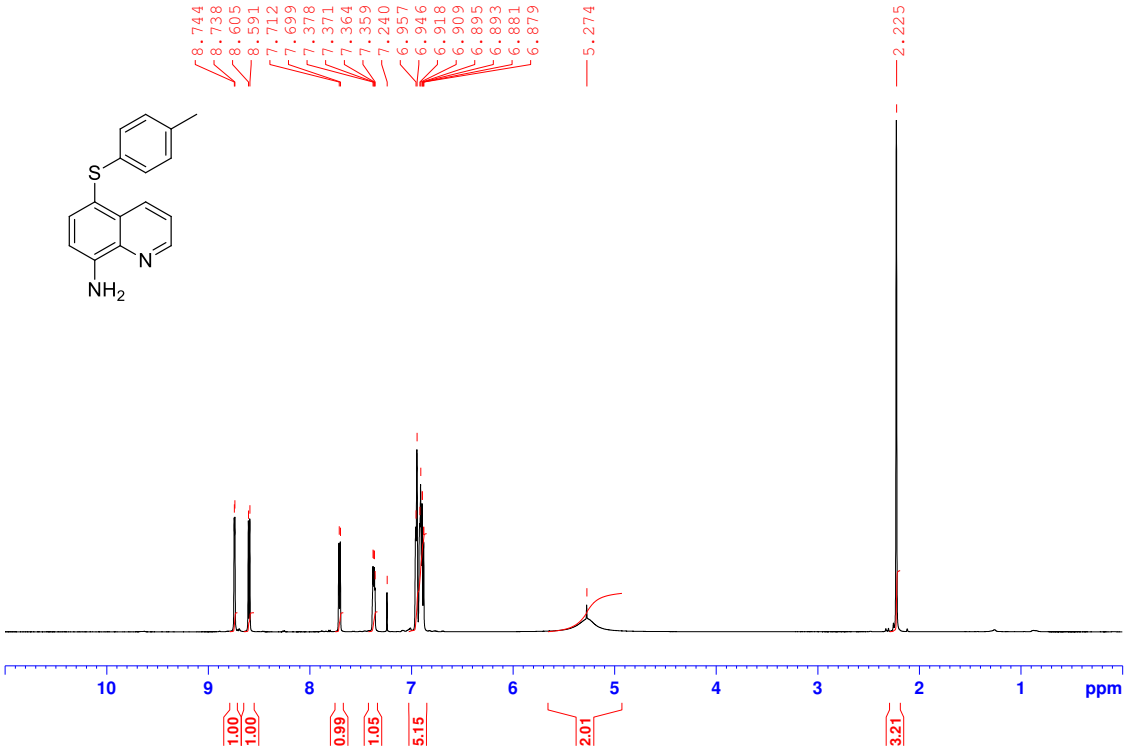


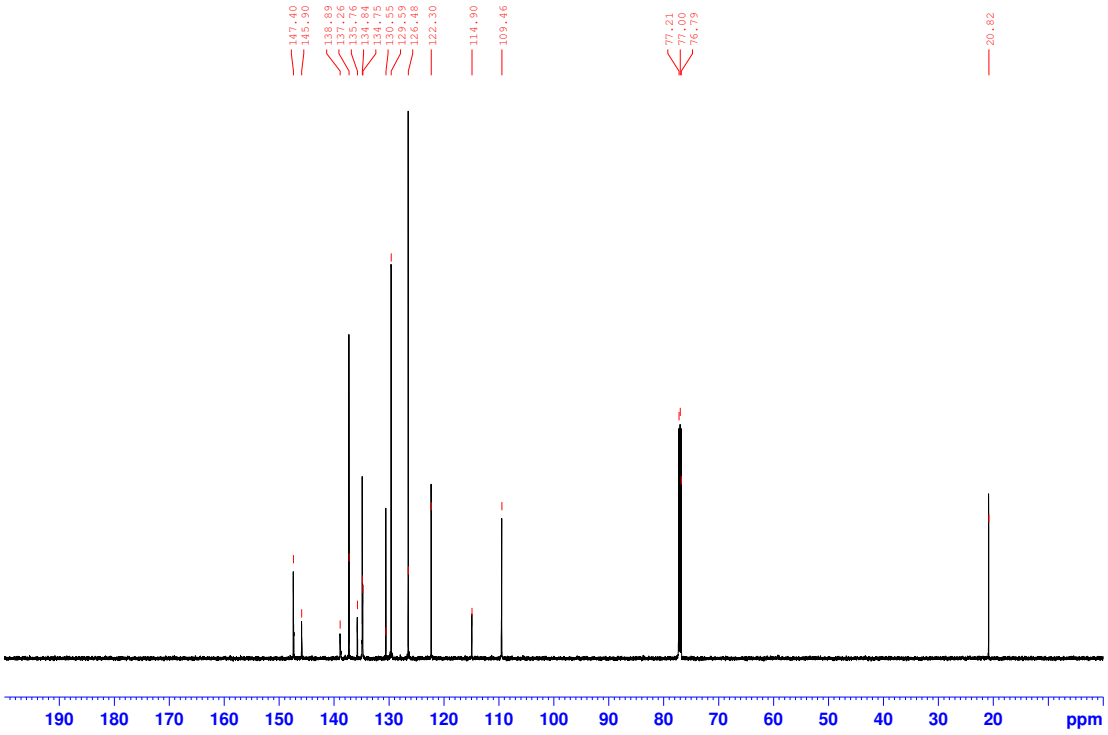
^{1}H and ^{13}C NMR of 5-(Phenylthio)quinolin-8-amine (**3l**)



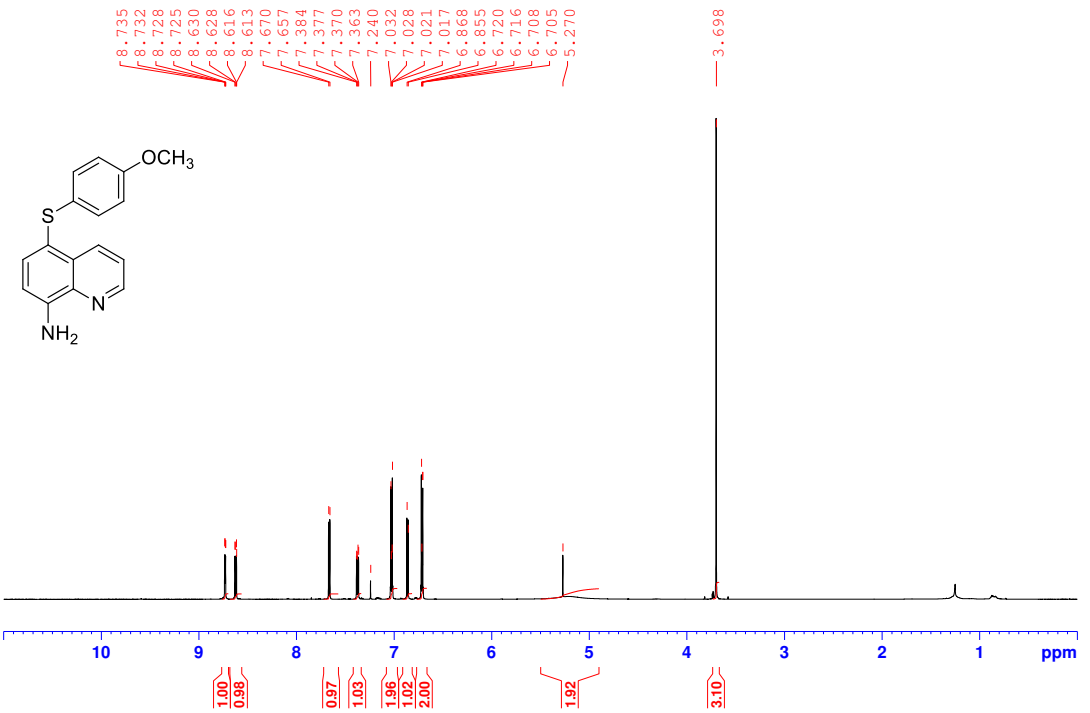


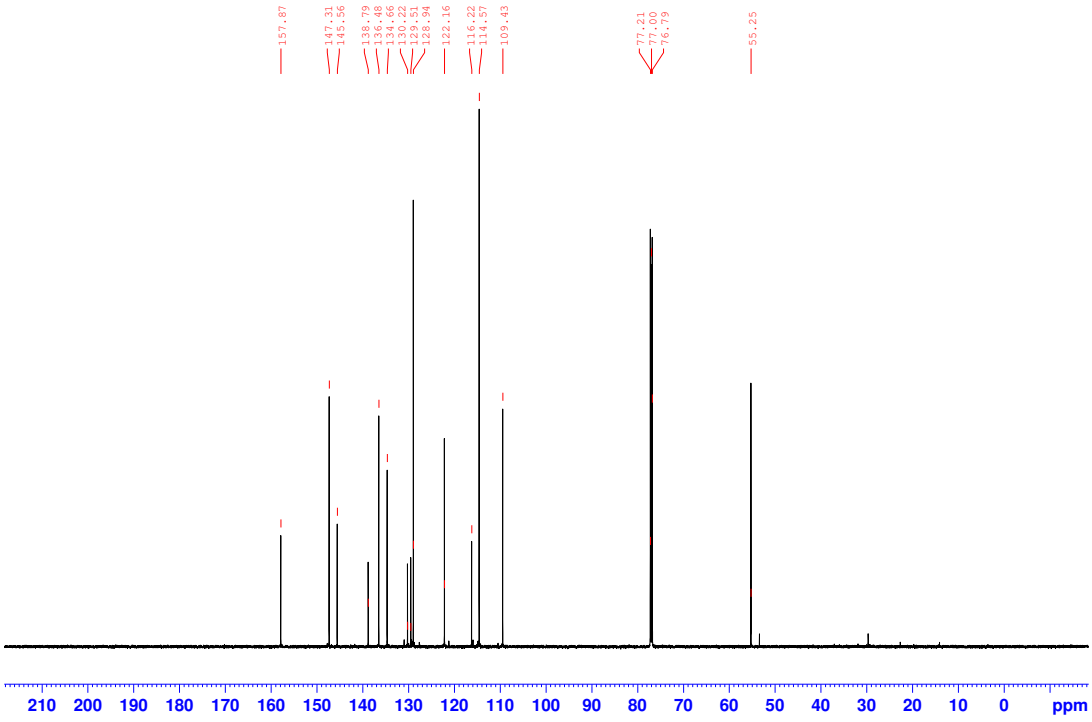
^{1}H and ^{13}C NMR of 5-(p-Tolylthio)quinolin-8-amine (**3m**)



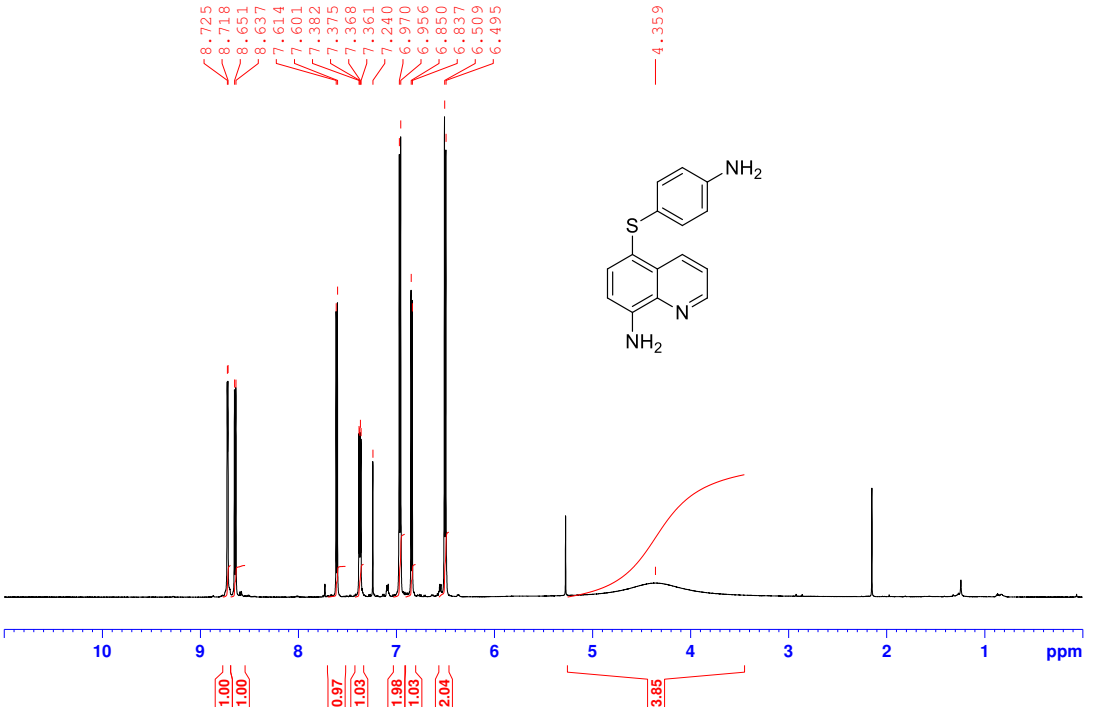


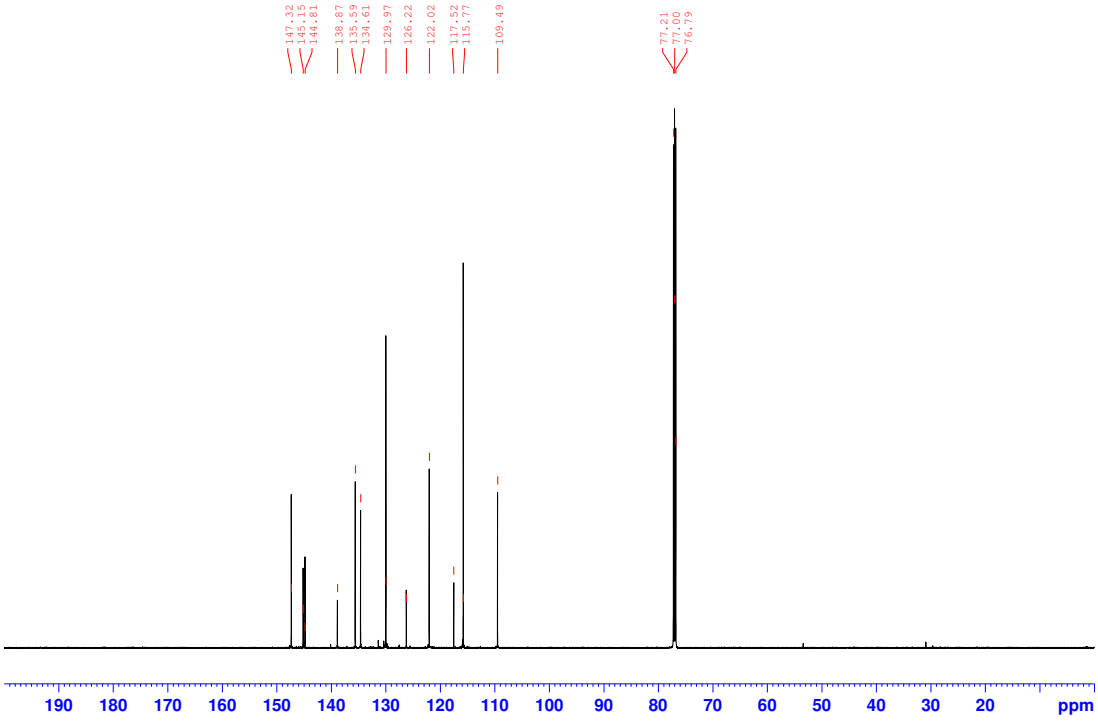
^{1}H and ^{13}C NMR of 5-((4-Methoxyphenyl)thio)quinolin-8-amine (**3n**)



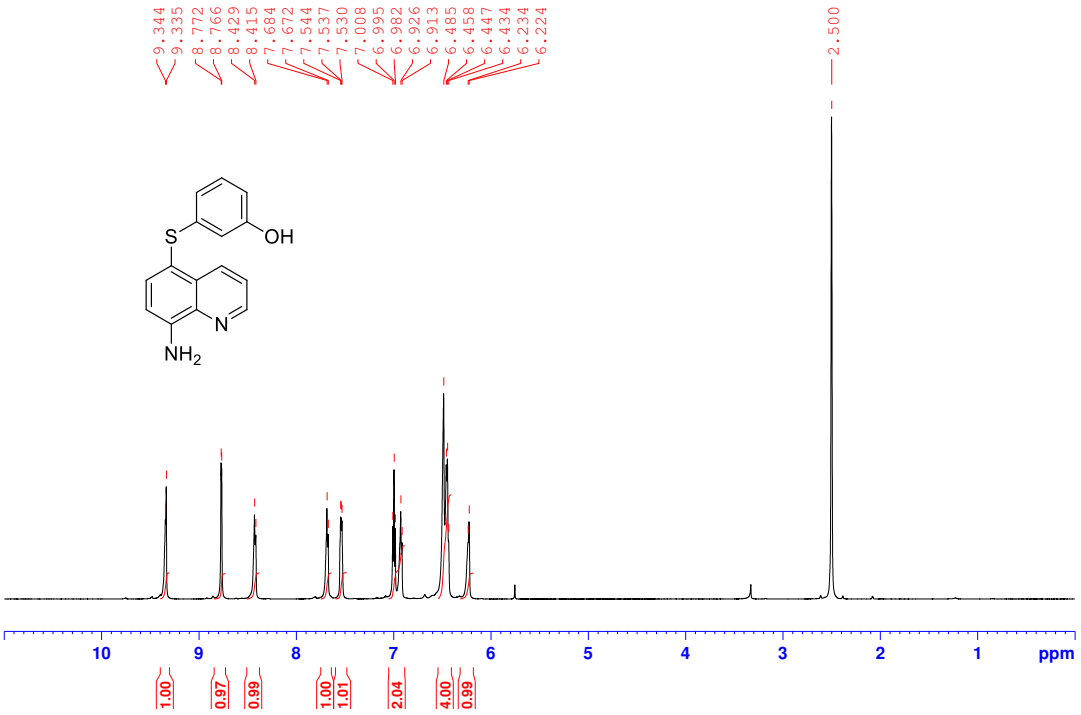


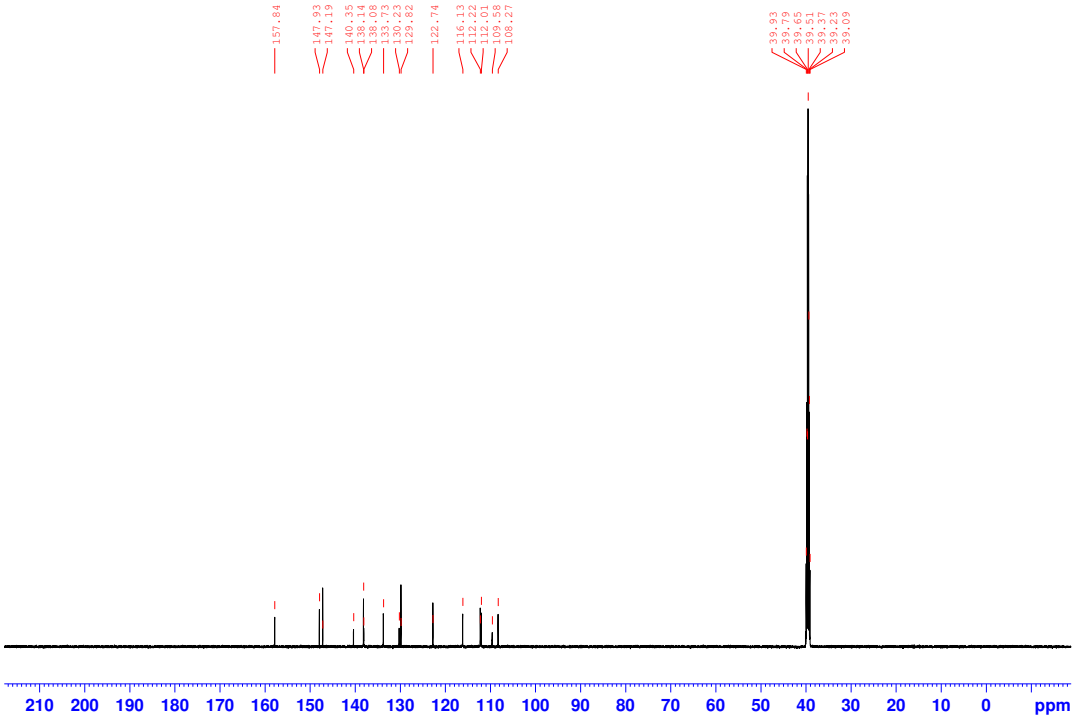
^{1}H and ^{13}C NMR of 5-((4-Aminophenyl)thio)quinolin-8-amine (**3o**)



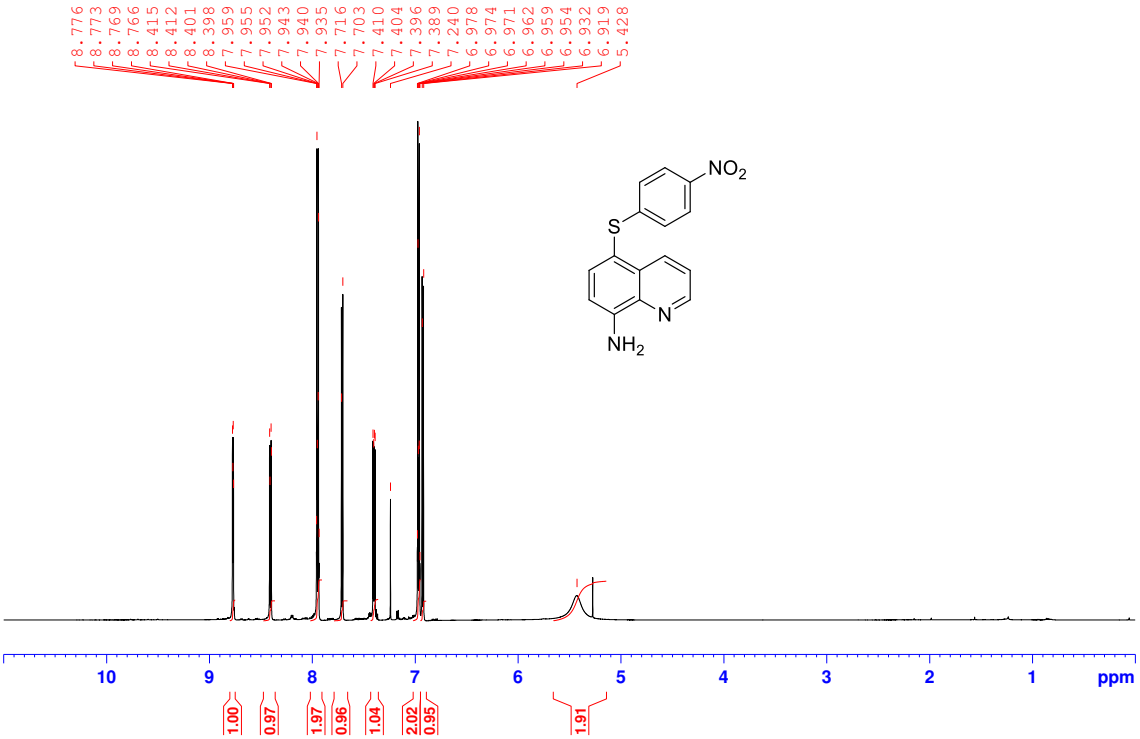


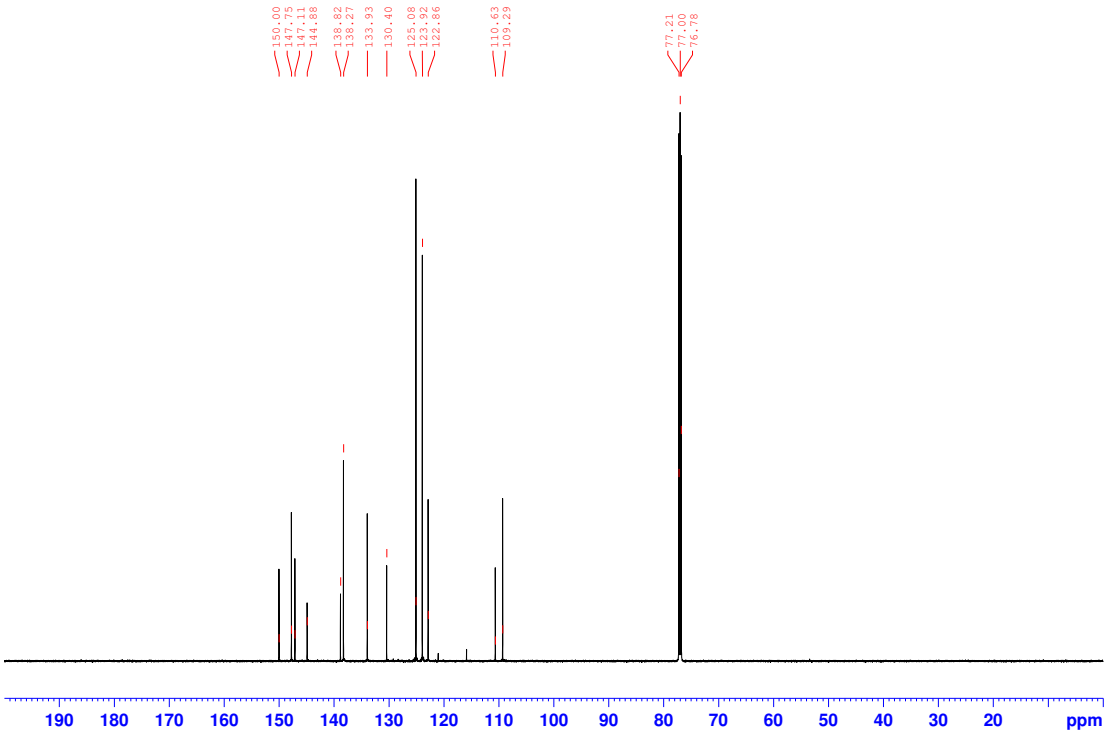
^{1}H and ^{13}C NMR of 3-((8-Aminoquinolin-5-yl)thio)phenol (**3p**)



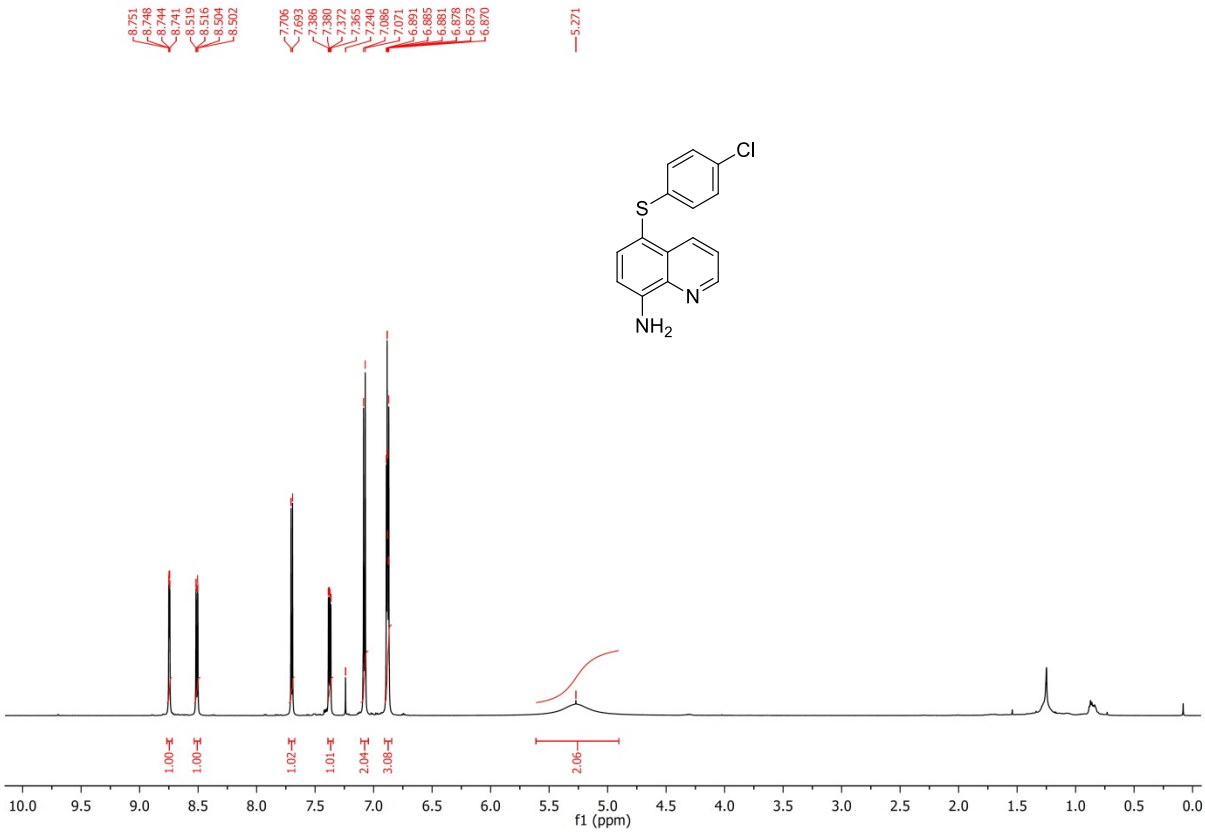


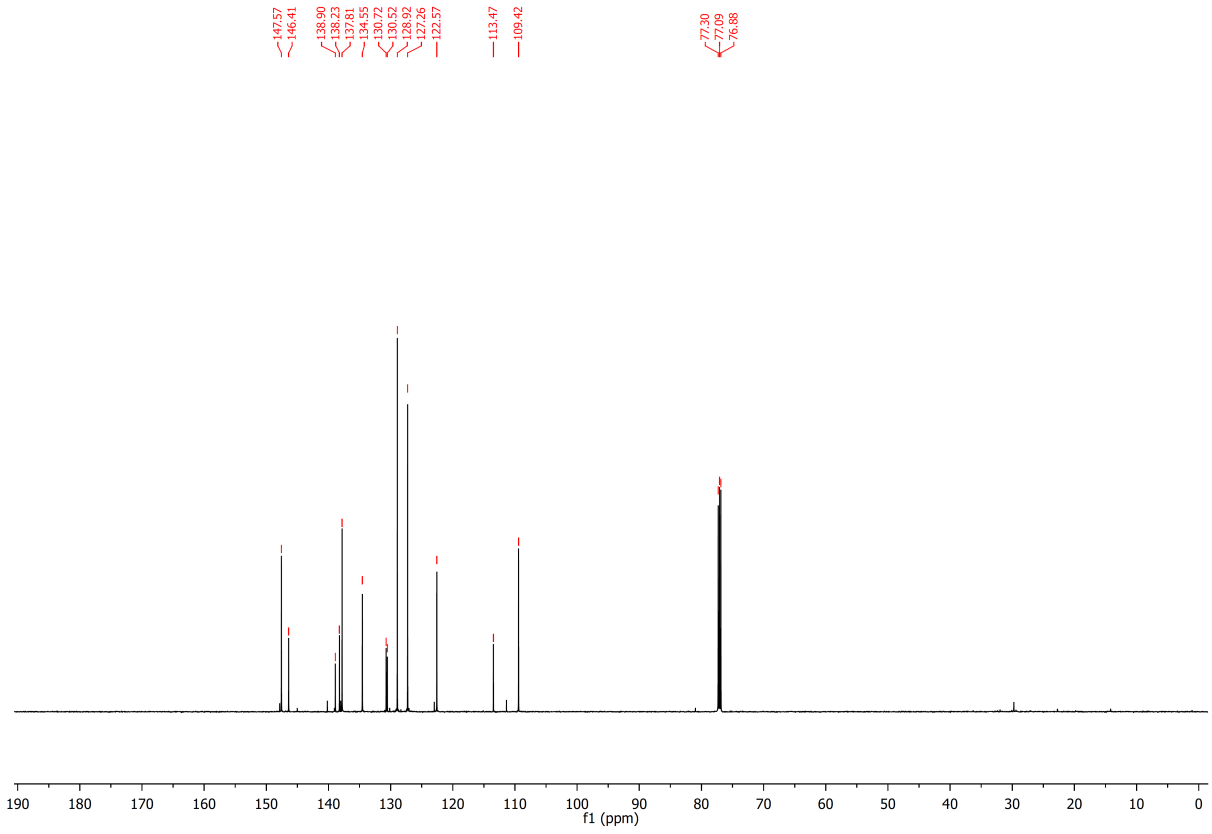
^{1}H and ^{13}C NMR of 5-((4-Nitrophenyl)thio)quinolin-8-amine (**3q**)



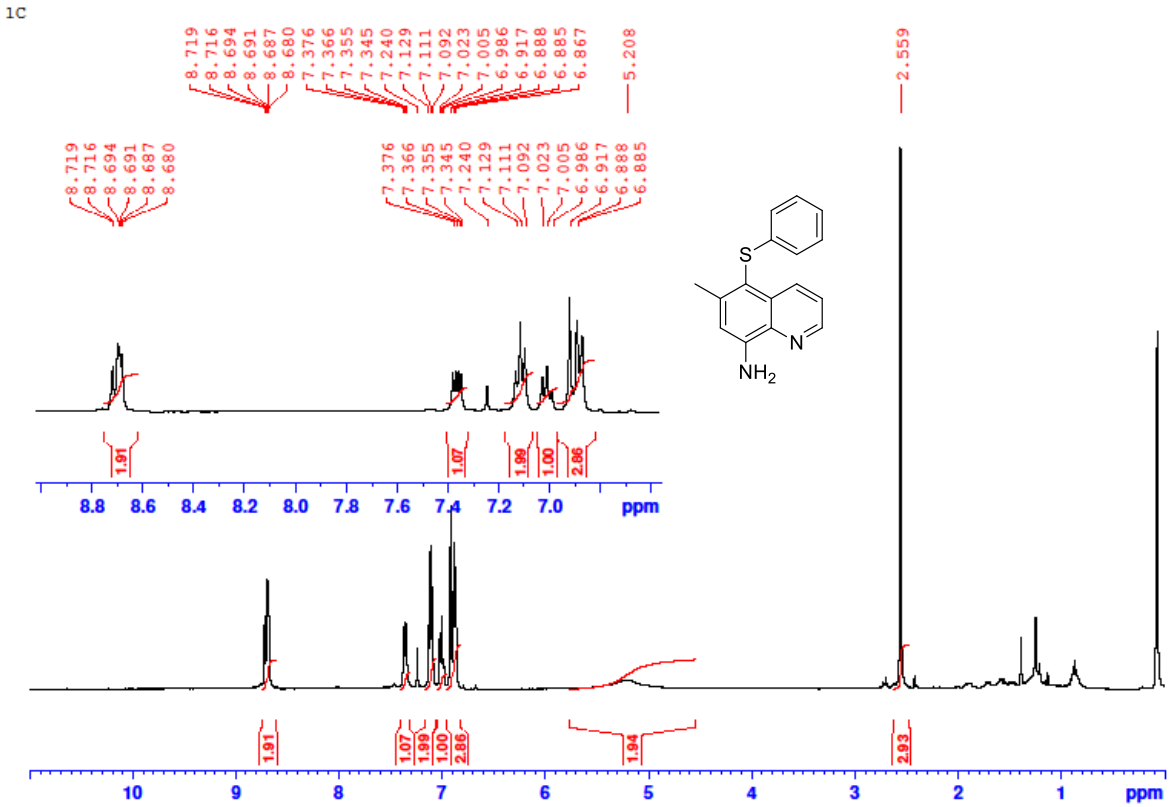


^{1}H and ^{13}C NMR of 5-((4-Chlorophenyl)thio)quinolin-8-amine (**3r**)

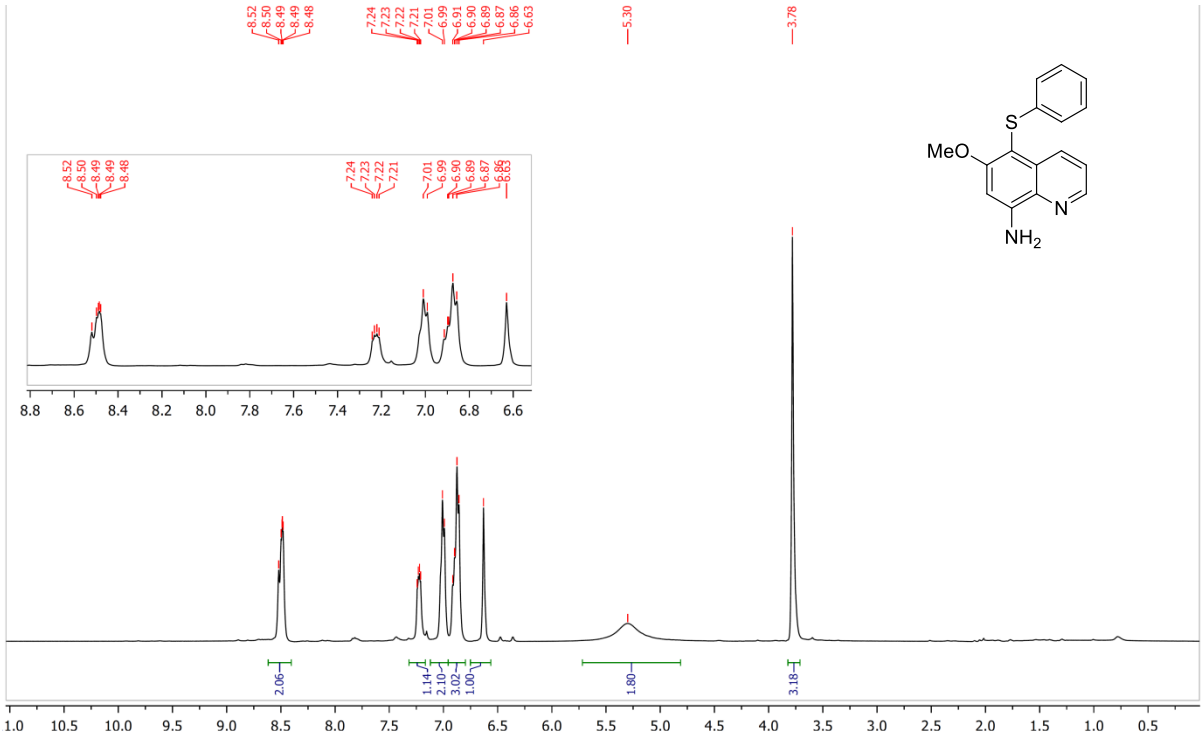


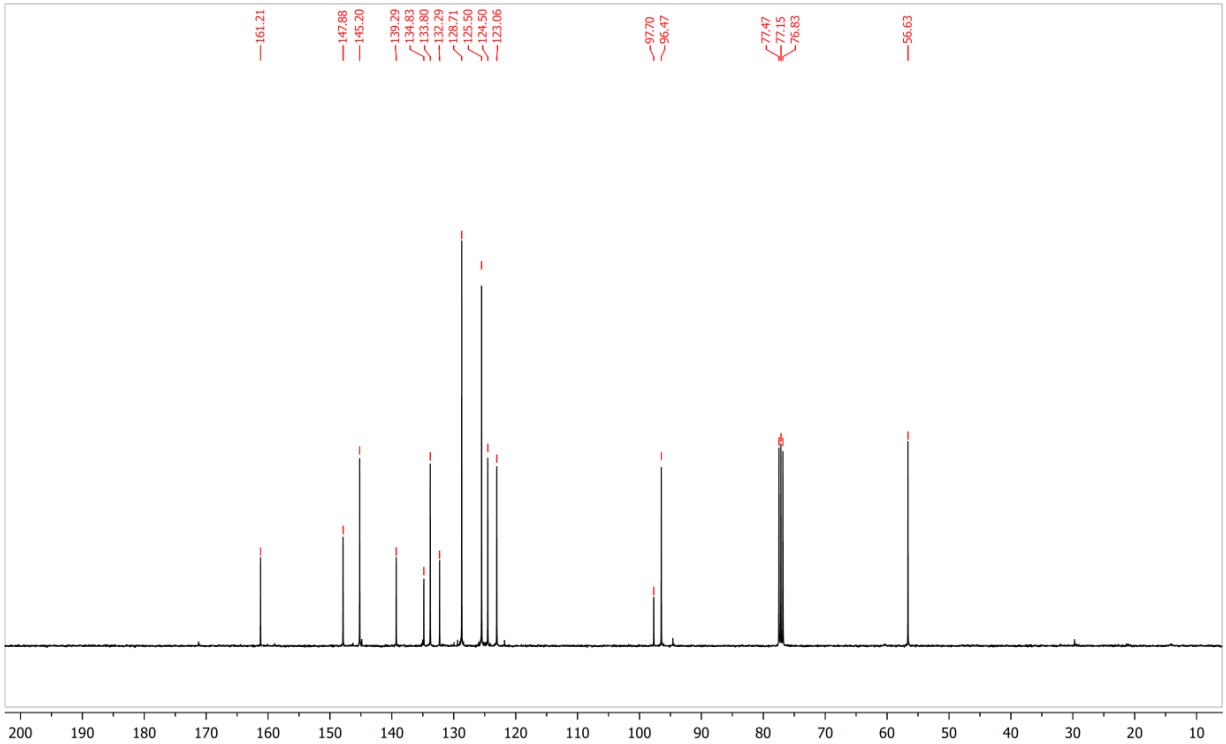


^{1}H NMR of 6-Methyl-5-(phenylthio)quinolin-8-amine (**3s**)

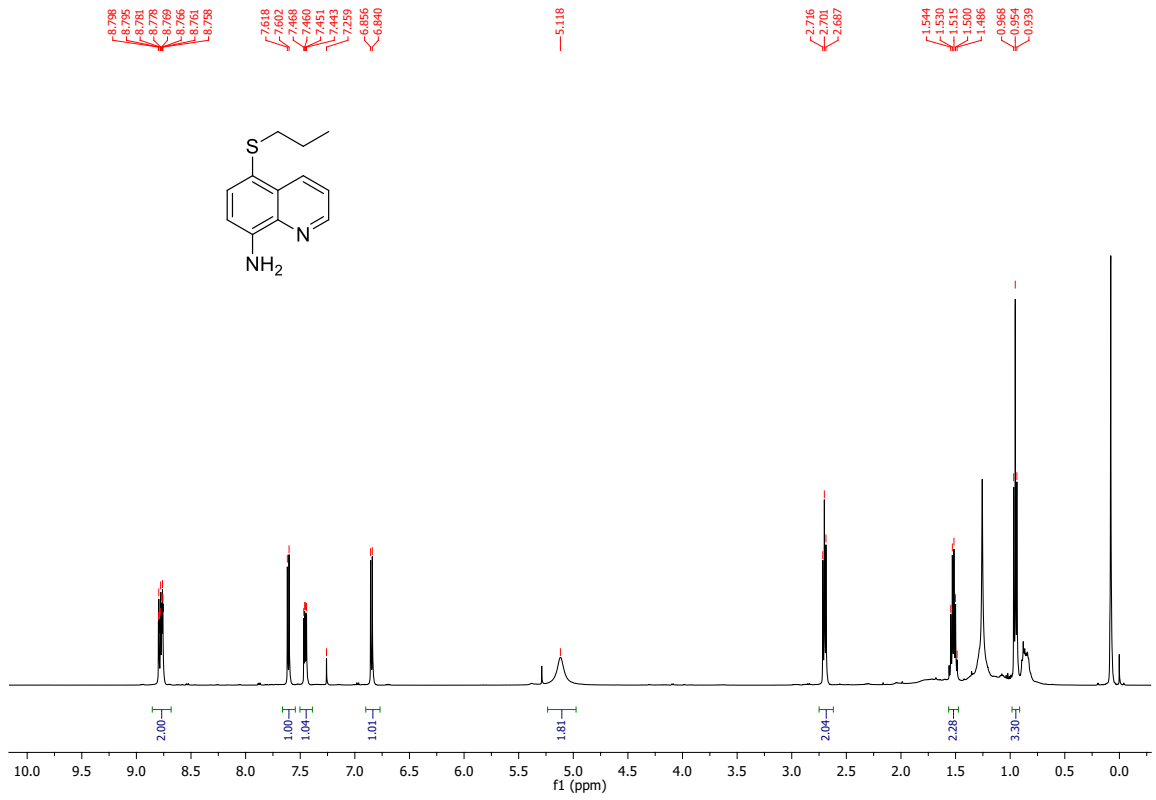


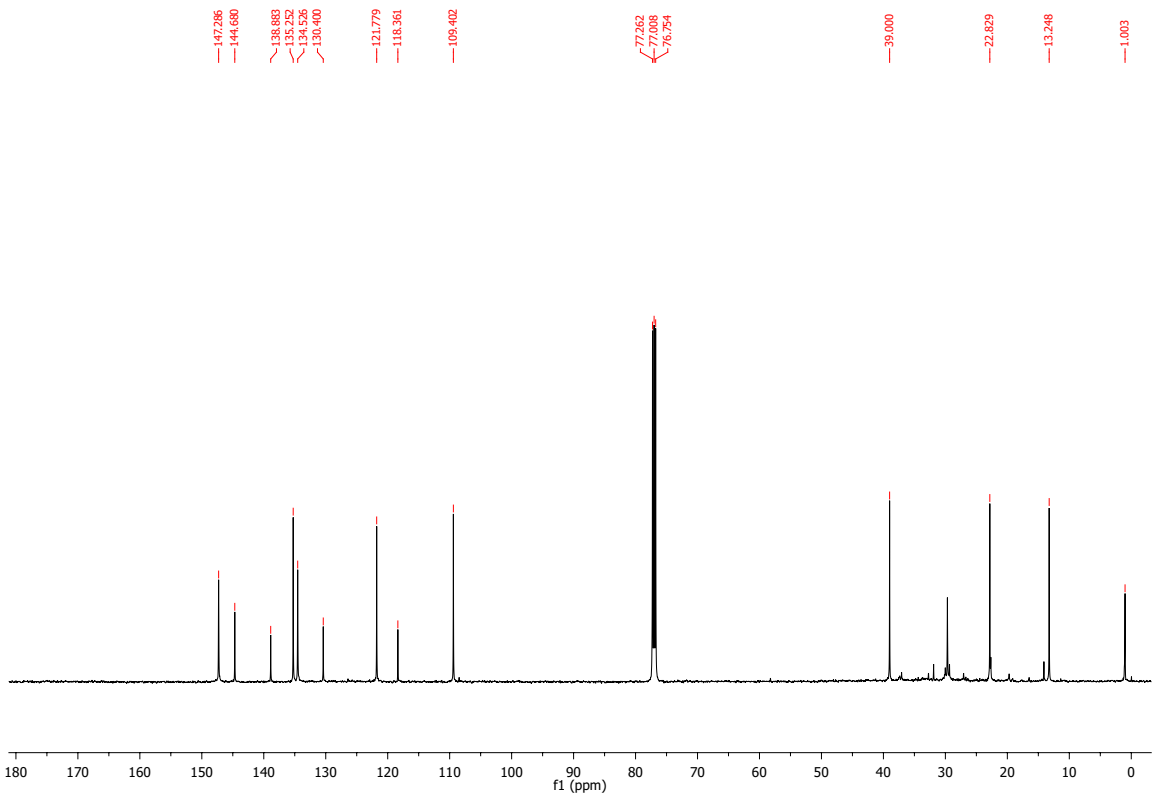
^{1}H and ^{13}C NMR of 6-Methoxy-5-(phenylthio)quinolin-8-amine (**3t**)



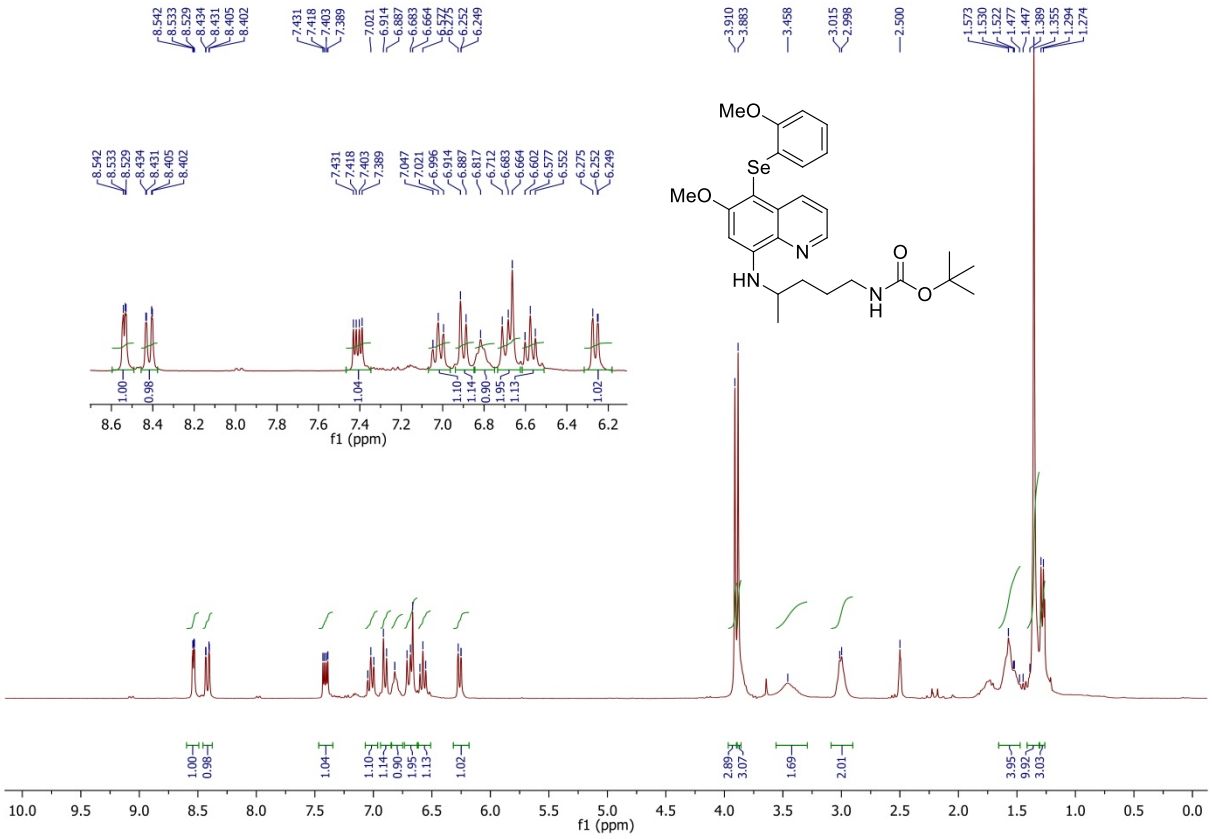


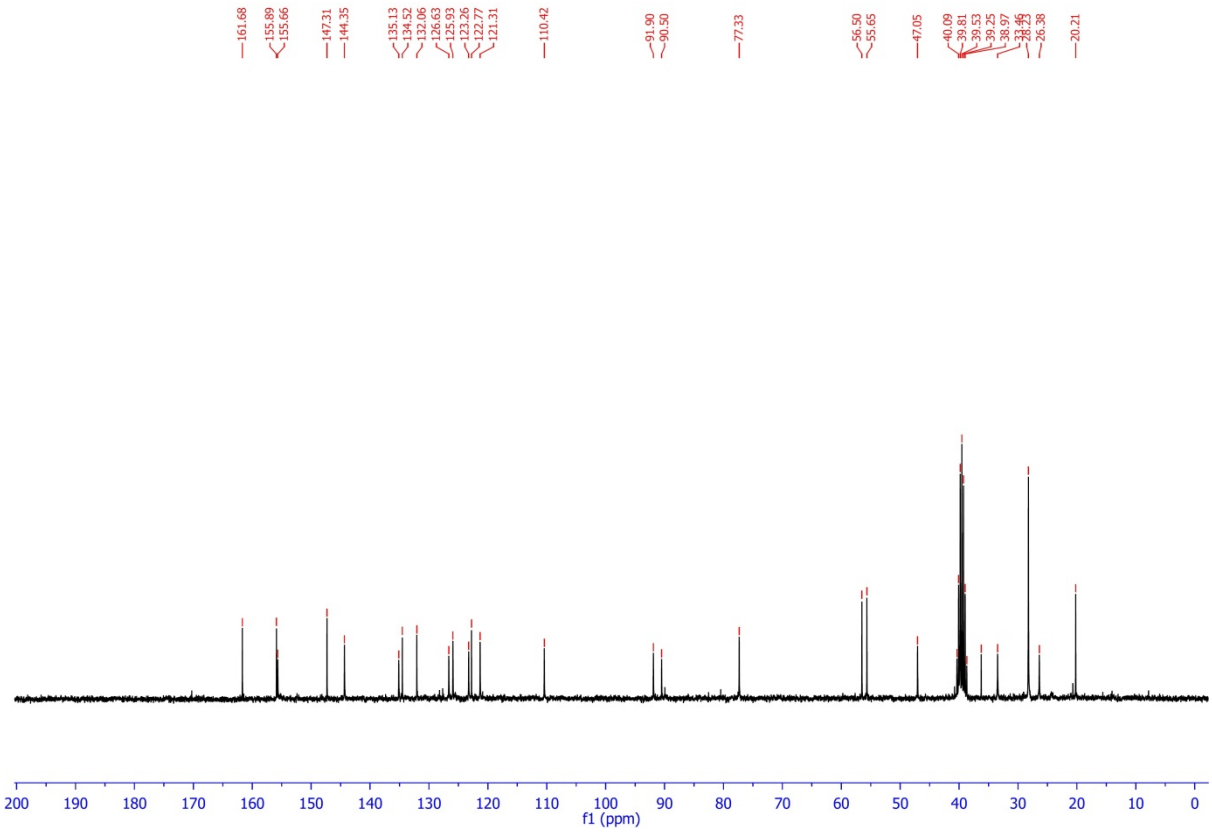
^{1}H and ^{13}C NMR of 5-(Propylthio)quinoline-8-amine (**3u**)



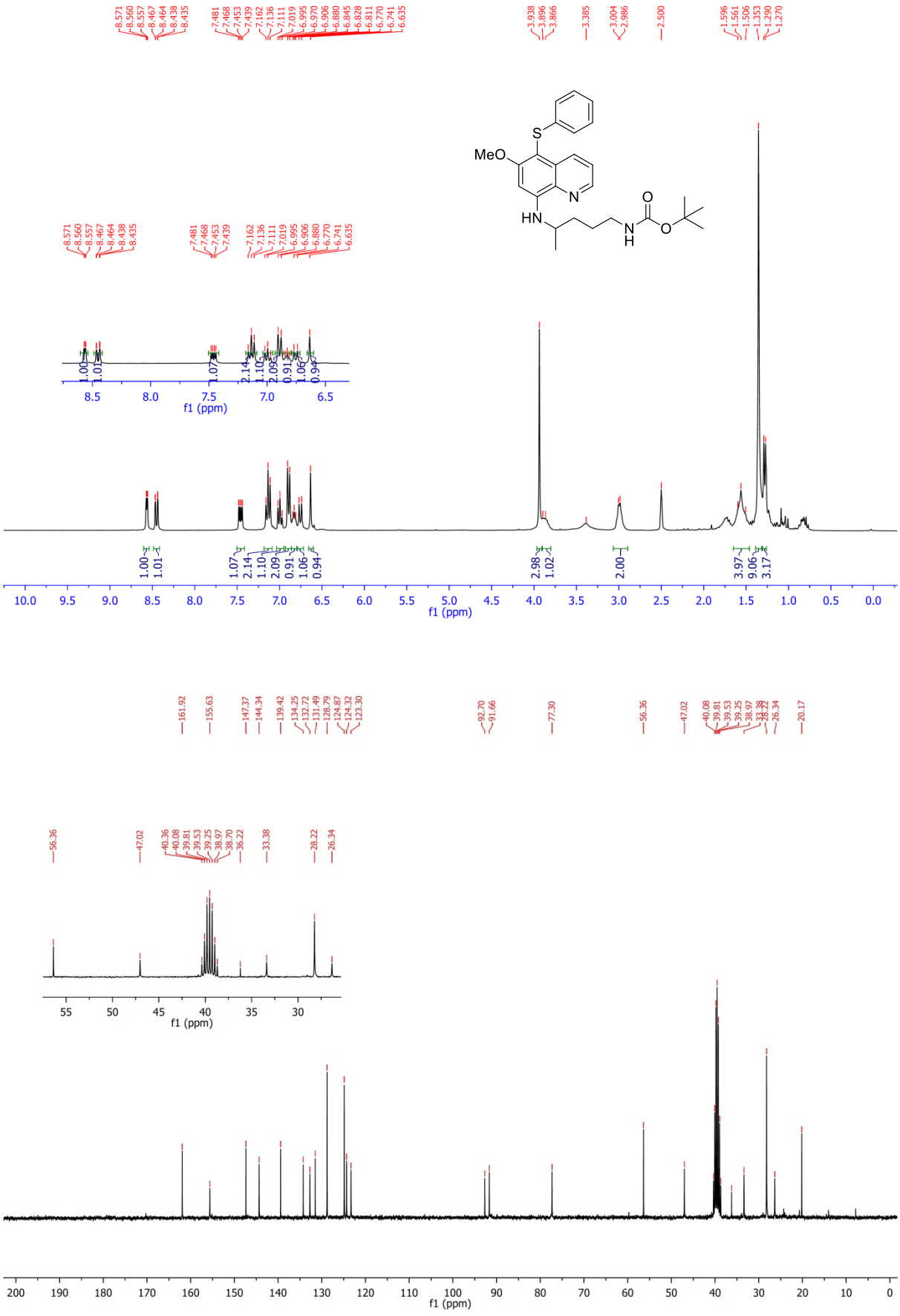


^{1}H and ^{13}C NMR of *tert*-Butyl(4-((6-methoxy-5-((2-methoxyphenyl)selanyl)quinolin-8-yl)amino)pentyl)carbamate (**3v**)

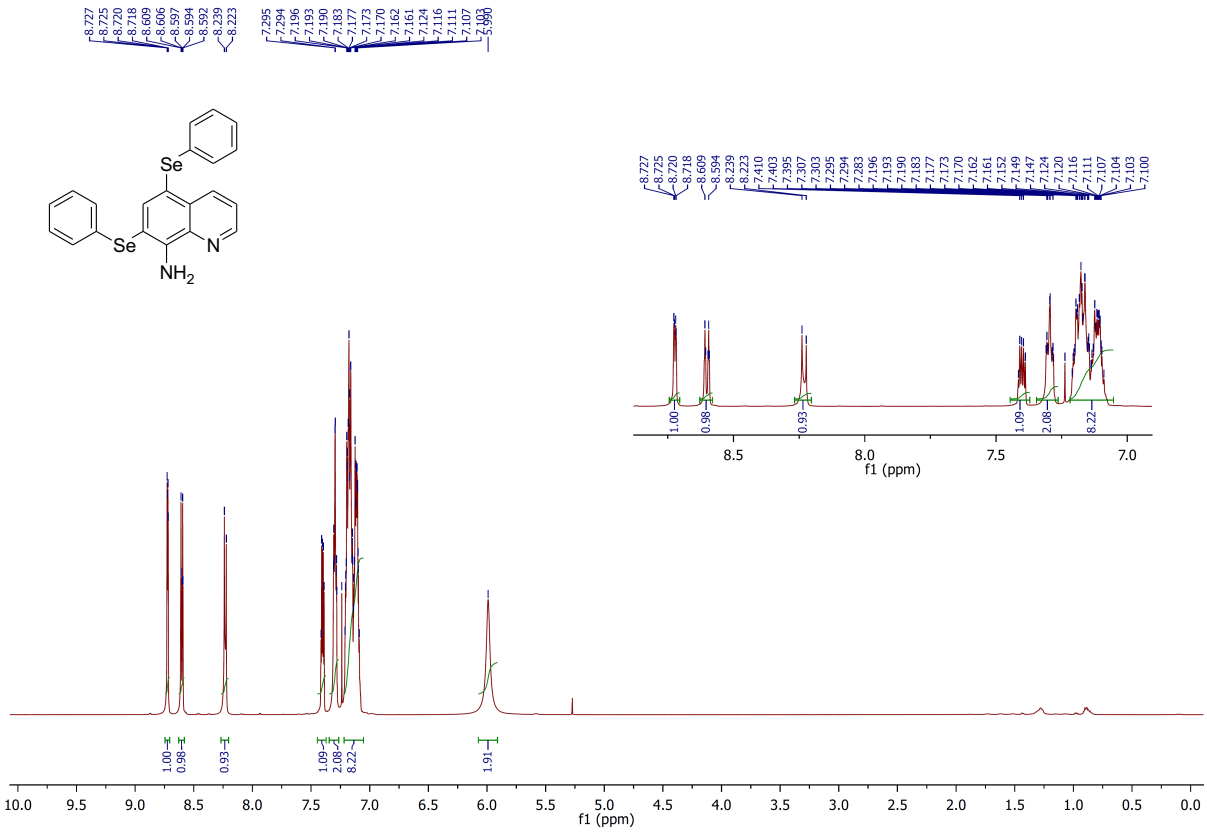


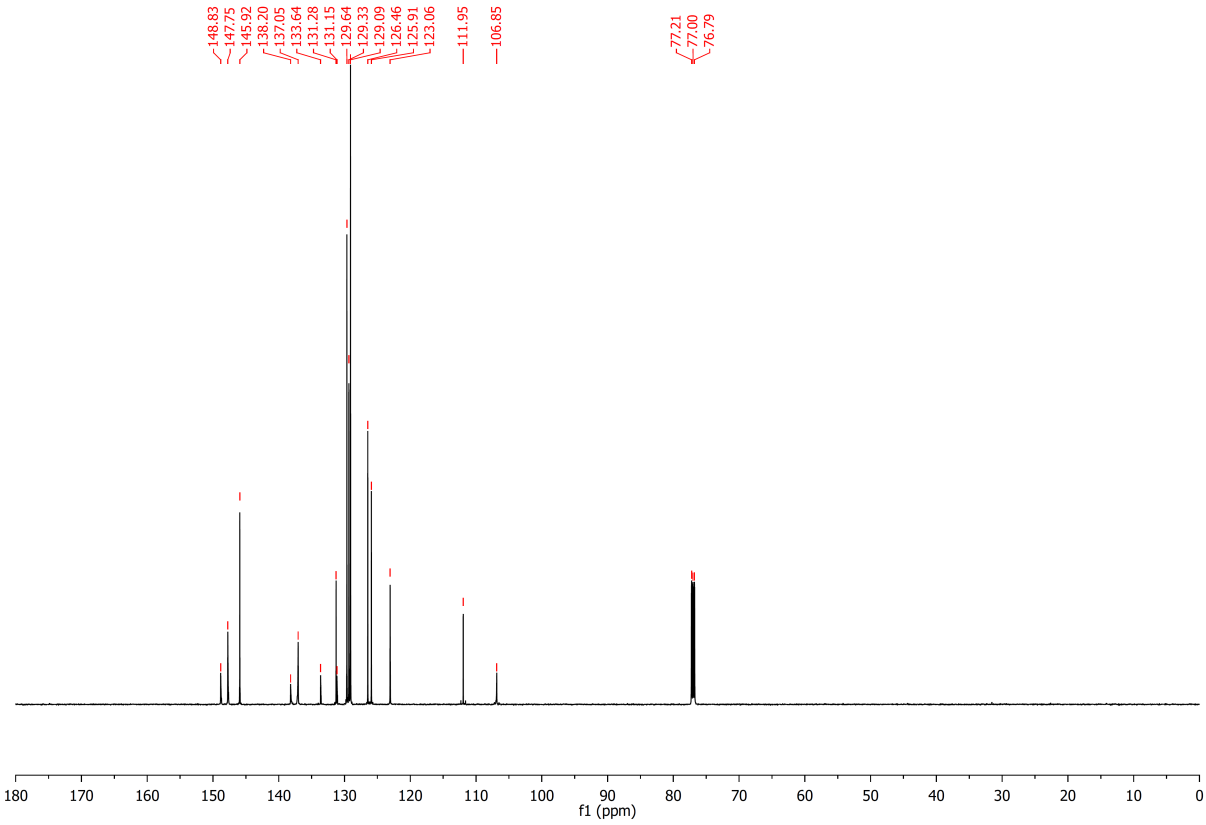


^{1}H and ^{13}C NMR of *tert*-Butyl(4-((6-methoxy-5-(phenylthio)quinolin-8-yl)amino)pentyl)carbamate (**3w**)

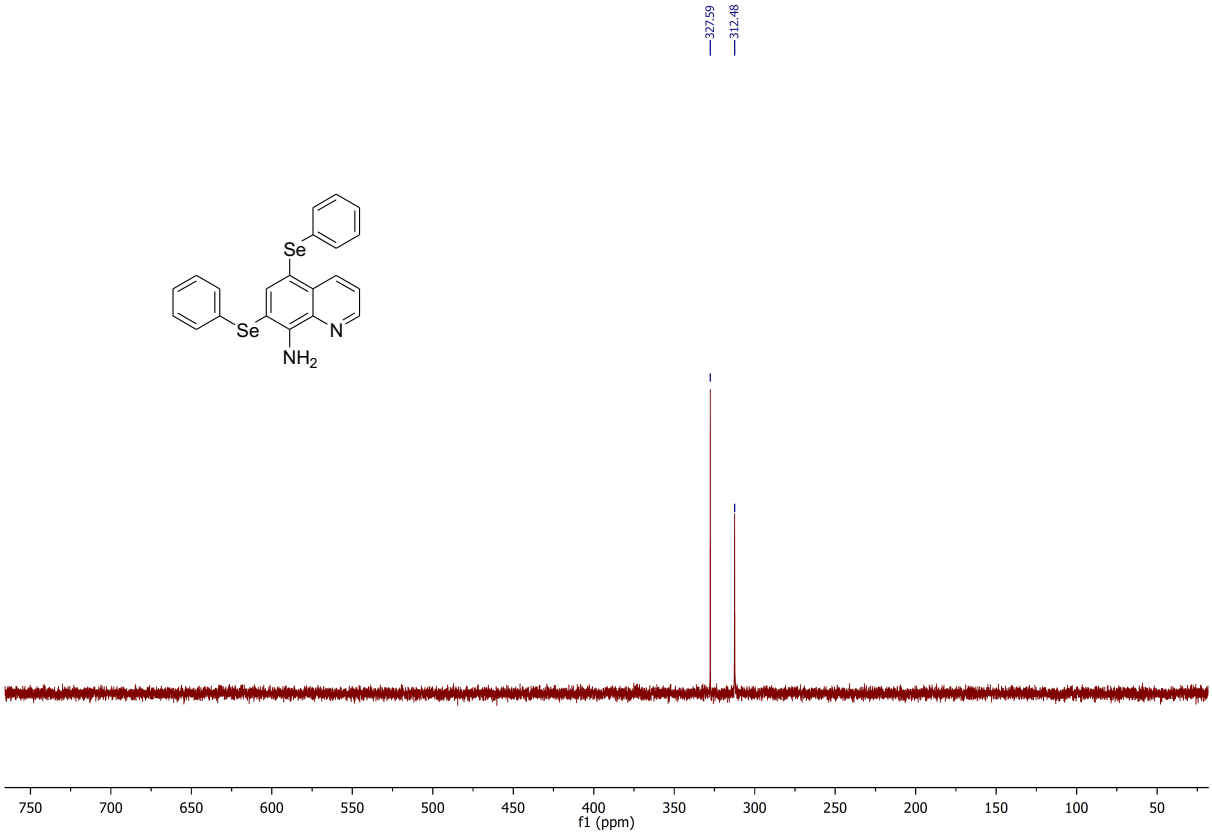


^{1}H and ^{13}C NMR of 5,7-bis(phenylselanyl)quinoline-8-amine (**4a**)

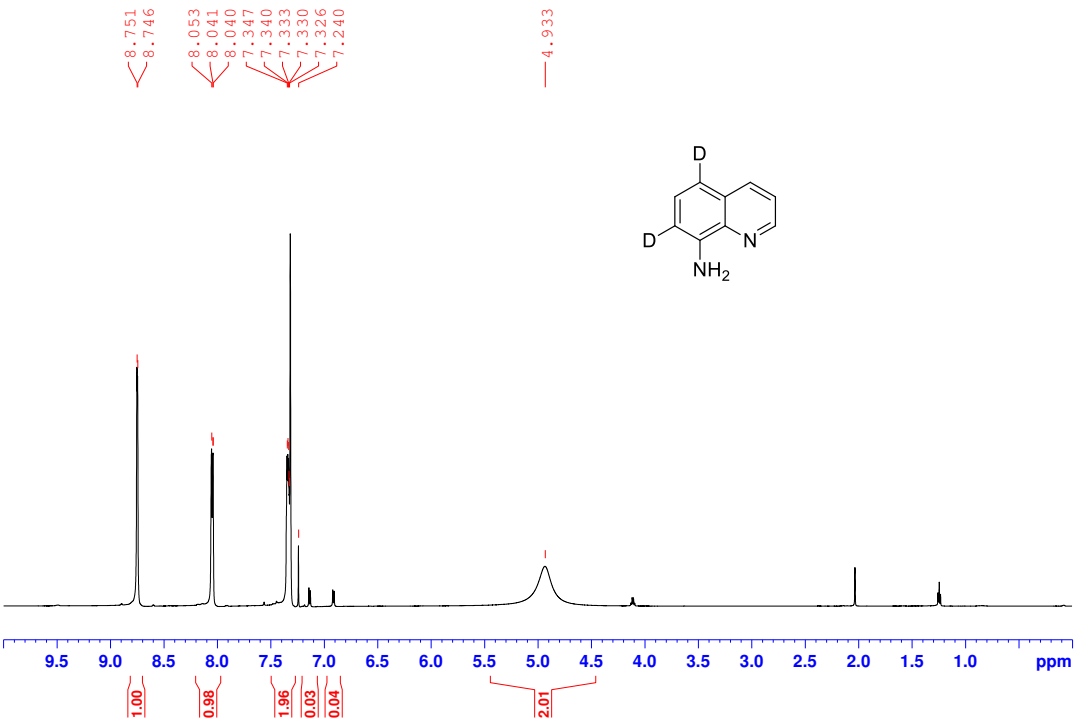




^{77}Se of 5,7-bis(phenylselanyl)quinoline-8-amine (**4a**)



^{1}H and ^{13}C NMR of 5,7-Di-deuteriated-8-aminoquinoline (**1aD**)



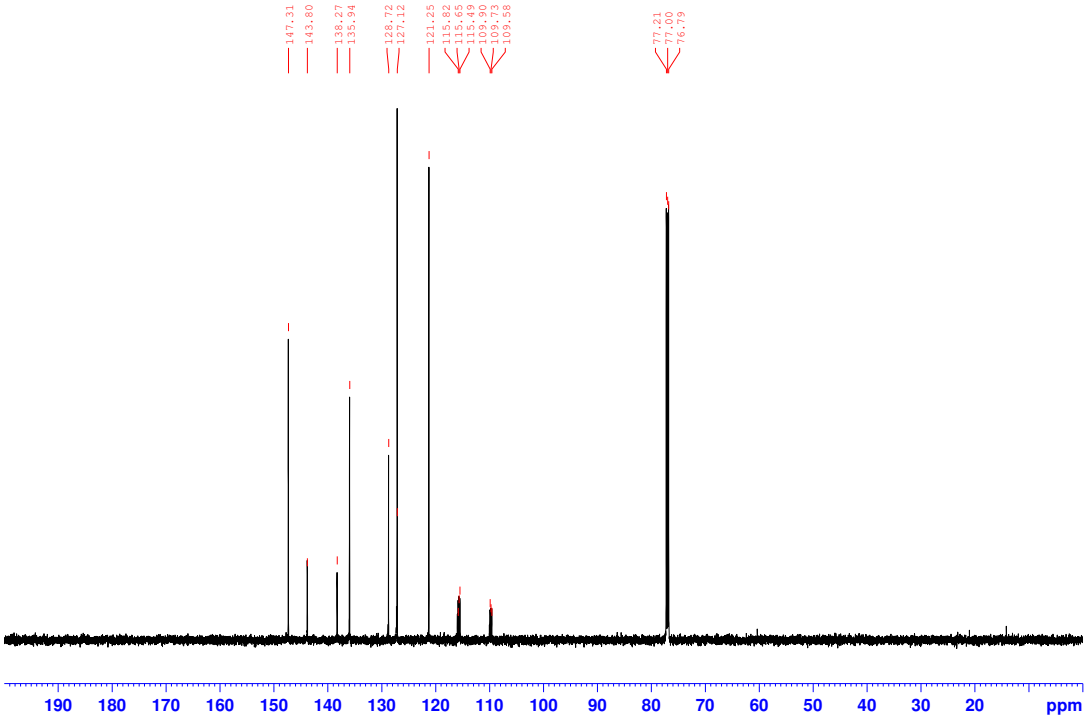


Figure S8. ^{1}H NMR of the products 3m and 3mD for KIE experiment