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Facile regioselective oxidative selenocyanation of N-aryl enaminones under transition metal free conditions

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Supporting information

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General experimental

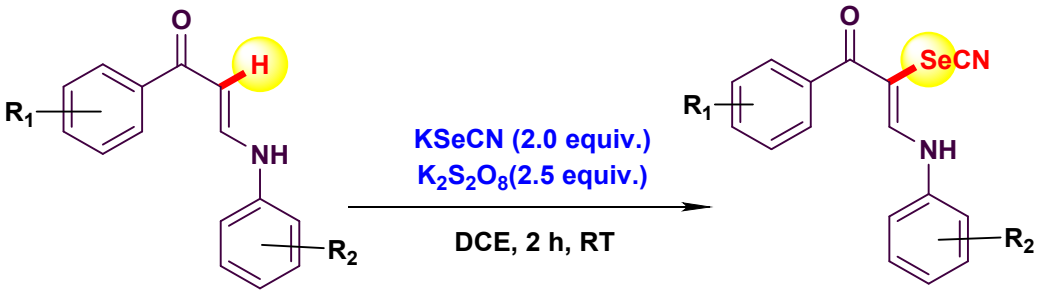
All reactions were carried out in oven-dried glassware, all compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker-400 spectrometers, (^{1}H: 400 MHz, ^{13}C: 100 MHz), and were referenced to the residual peaks of $CDCl_3$ at 7.26 ppm (^{1}H NMR) and $CDCl_3$ at 77.23 ppm (^{13}C NMR). Chemical shifts (δ) are expressed in ppm, and J values are given in Hz. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, db = doublet broad, m = multiplet), coupling constant (Hz), and integration. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points (m.p.) were determined on digital melting point apparatus and are uncorrected. Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Column chromatography was carried out using commercially available silica gel (230-400 mesh) under pressure.

Materials

Unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification. PE refers to petroleum ether (b.p. 60-90 °C) and EA refers to ethyl acetate, and all reaction solvents were freshly distilled prior to use.

All substrates **1a** were synthesized according to the literature[1].

Typical experimental procedure for selenocyanation of *N*-aryl enaminones

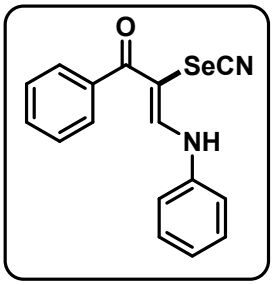


1a **2a**

N-aryl enaminone (0.60 mmol), KSeCN (2 equiv., 1.20 mmol), $K_2S_2O_8$ (1.50 mmol) in ethylene dichloride (DCE) (3 mL) were stirred at room temperature for 2 hrs. After completion of the reaction (monitored by TLC) reaction mixture was quenched using saturated solution of $NaHCO_3$ then it was extracted with dichloromethane (3x15 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified on a silica gel by column chromatography using hexane/EtOAc to get the pure product.

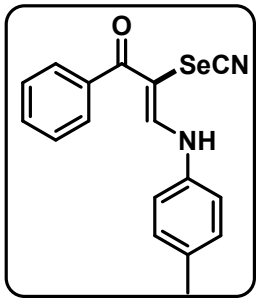
Spectroscopic Data of *α*-selenocynated enaminones 2

1-Phenyl-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2a)



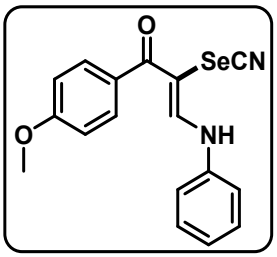
Yellow solid; m.p. 181–183 °C; 96%, 211 mg, R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 - 7.44 (m, 4H, ArH), 7.45 - 7.49 (m, 4H, ArH), 7.50 - 7.57 (m, 2H, ArH), 7.68 – 7.72 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.9, 116.7, 116.8, 124.1, 128.4, 128.6, 130.7, 139.8, 139.9, 153.06, 188.9; MS(ESI): *m/z* calcd for $C_{16}H_{12}N_2OSe$ 328.01; found 329.00 [M+H].

1-Phenyl-2-selenocyanato-3-(p-tolylamino)prop-2-en-1-one-(2b)



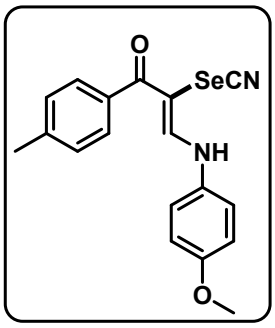
Yellow solid; m.p. 165–167 °C; 94%, 212 mg, R_f = 0.28 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H, -Me), 7.27 - 7.32 (m, 5H, ArH), 7.41 - 7.48 (m, 3H, ArH), 7.50 - 7.55 (m, 1H, ArH), 7.68 – 7.72 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 108.4, 116.4, 127.3, 128.4, 130.3, 131.5, 137.9, 139.4, 145.3, 146.9, 187.9; MS(ESI): *m/z* calcd for $C_{17}H_{14}N_2OSe$ 342.02; found 342.95 [M+H].

1-(4-Methoxyphenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2c)



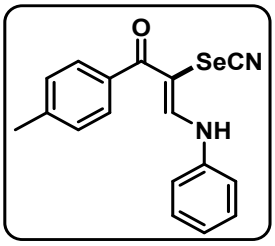
Yellow semi solid; 98%, 208 mg, R_f = 0.32 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.84 (s, 3H, -OMe), 6.92 - 6.97 (m, 2H, ArH), 7.32 (s, 1H, ArH), 7.37 - 7.53 (m, 6H, ArH), 7.68 - 7.73 (m,2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 108.9, 113.6, 114.9, 116.8, 118.3, 128.4, 128.5, 130.7, 130.9, 138.8, 143.2, 145.0, 156.3, 189.9; MS(ESI): *m/z* calcd for $C_{17}H_{14}N_2O_2Se$ 358.02; found 359.00 [M+H].

3-(4-Methoxyphenyl)amino-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2d)



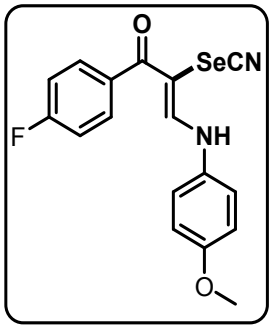
Brown viscous liquid; 95%, 198 mg, R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, -Me), 3.81 (s, 3H, -OMe), 6.95 - 6.99 (m, 2H, ArH), 7.16 - 7.34 (m, 7H, -NH + ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 55.4, 108.9, 113.7, 116.5, 130.4, 130.7, 131.3, 133.8, 136.9, 143.0, 145.5, 189.8; MS(ESI): *m/z* calcd for $C_{18}H_{16}N_2O_2Se$ 372.03; found 373.02 [M+H].

3-(Phenylamino)-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2e)



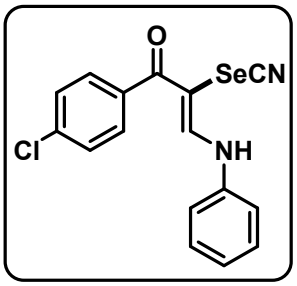
Brown viscous liquid; 92%, 199 mg, R_f = 0.30 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H, -Me), 7.23 - 7.33 (m, 4H, ArH) 7.36 - 7.43 (m, 3H, ArH), 7.43 - 7.52 (m, 2H, ArH), 7.61 (d, *J* = 8.0 Hz), 7.64 - 7.74 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.7, 108.8, 116.45, 127.3, 128.4, 130.3, 131.5, 133.5, 137.8, 139.4, 145.3, 146.9, 187.1; MS(ESI): *m/z* calcd for $C_{17}H_{14}N_2OSe$ 342.02; found 343.03 [M+H].

1-(4-Fluorophenyl)-3-(4-methoxyphenyl)amino)-2-selenocyanatoprop-2-en-1-one-(2f)



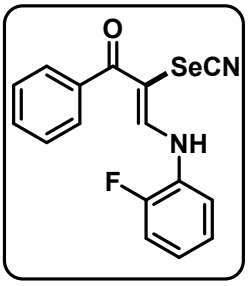
Yellow viscous liquid; 90%, 187 mg, R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3H, -OMe), 6.96 - 7.01 (m, 2H, ArH) 7.10 - 7.17 (m, 3H, ArH), 7.30 - 7.35 (m, 2H, ArH), 7.70 - 7.76 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 109.2, 115.1, 115.2, 115.5, 118.0, 129.5 (d, J = 10.0 Hz), 134.7 (d, J = 191.0 Hz), 143.5, 146.1, 156.2, 164.8 (d, J = 251.0 Hz), 186.59; MS(ESI): *m/z* calcd for $C_{17}H_{13}FN_2O_2Se$ 376.01; found 377.02 [M+H].

1-(4-Chlorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2g)



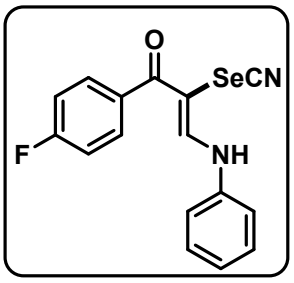
Brown viscous liquid; 93%, 199 mg, R_f = 0.30 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1H, ArH), 7.38 - 7.44 (m, 5H, ArH) 7.45 - 7.51 (m, 3H, ArH), 7.62 - 7.67 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.8, 116.3, 116.5, 123.9, 128.7, 128.7, 129.8, 137.6, 137.8, 140.1, 145.4, 186.9; MS(ESI): *m/z* calcd for $C_{16}H_{11}ClN_2OSe$ 361.97; found 362.99 [M+H].

3-(2-Fluorophenyl)amino-1-phenyl-2-selenocyanatoprop-2-en-1-one-(2h)



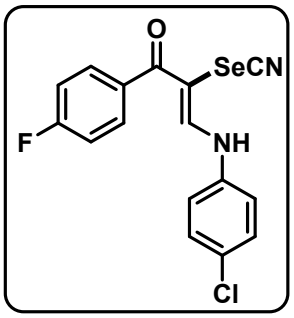
Yellow semi solid; 90%, 187 mg, R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22 - 7.28 (m, 3H, ArH), 7.38 - 7.56 (m, 6H, ArH+NH), 7.69 - 7.73 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.1, 115.5, 116.2 (d, J = 18.7 Hz), 123.6 (d, J = 7.0 Hz), 124.8 (d, J = 4.0 Hz), 127.4, 128.4, 128.9 (d, J = 10.8 Hz), 131.7, 139.0, 144.0, 151.2 (d, J = 245.0 Hz), 188.5; MS(ESI): *m/z* calcd $C_{16}H_{11}FN_2OSe$ 346.00; found 347.01 [M+H].

1-(4-Fluorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2i)



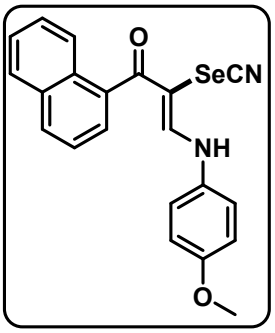
Yellow semi solid; 98%, 211 mg, R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.0 - 7.16 (m, 2H, ArH), 7.29 (s, 1H, ArH), 7.33 - 7.55 (m, 6H, ArH), 7.70 - 7.75 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.8, 115.9, 116.0, 116.2, 124.1 (d, J = 7.3 Hz), 125.0 (d, J = 4.0 Hz), 128.4, 128.4, 131.1, 138.4, 141.8, 142.5, 151.0 (d, J = 243.0 Hz), 153.5 (d, J = 243Hz), 188.2; MS(ESI): *m/z* calcd $C_{16}H_{11}FN_2OSe$ 346.00; found 346.90 [M+H].

3-(4-Chlorophenyl)amino-1-(4-fluorophenyl)-2-selenocyanatoprop-2-en-1-one-(2j)



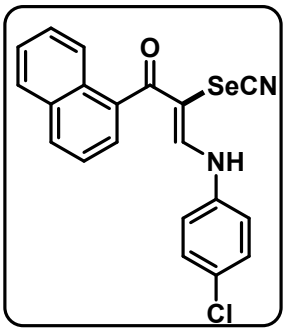
Yellow semi solid; 95%, 196 mg, R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.08 - 7.19 (m, 3H, ArH), 7.25 - 7.28 (m, 1H, ArH), 7.36 - 7.41 (m, 2H, ArH), 7.42 - 7.47 (m, 2H, ArH), 7.71 - 7.76 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 109.8, 115.4, 115.6, 117.5, 128.9, 129.7, 129.8, 129.8, 135.3 (d, J = 3.0 Hz), 138.9, 165.0 (d, J = 250.8 Hz), 186.8; MS(ESI): *m/z* calcd $C_{16}H_{10}ClFN_2OSe$ 379.96; found 380.95 [M+H].

3-(4-Methoxyphenyl)amino-1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2k)



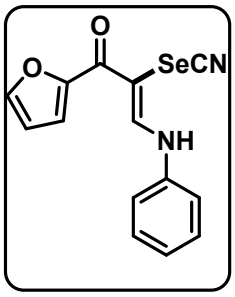
Dark brown semi-solid; 94%, 189 mg, R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H, -OMe), 6.9 (d, *J* = 8.8 Hz, 2H, ArH), 7.07 (s, 1H, ArH), 7.23 (d, *J* = 8.8 Hz, 2H, ArH), 7.46 (t, *J* = 7.6 Hz, 1H, ArH), 7.51 - 7.57 (m, 2H, ArH), 7.61 (d, *J* = 6.8 Hz, 1H, ArH), 7.85 - 7.95 (m, 3H, ArH), 8.12 (d, *J* = 9.2 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 109.2, 115.1, 118.1, 124.8, 125.8, 126.0, 126.1, 126.8, 128.3, 130.2, 130.5, 133.8, 133.9, 139.2, 145.6, 156.5, 188.3; MS(ESI): *m/z* calcd for $C_{21}H_{16}N_2O_2Se$ 408.03; found 408.95 [M+H].

3-(4-Chlorophenyl)amino -1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2l)



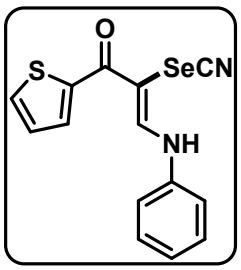
Dark brown semi-solid; 92%, 185 mg, R_f = 0.28 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07 (s, 1H, ArH), 7.27 - 7.30 (m, 2H, ArH), 7.34 - 7.38 (m, 2H, ArH), 7.44 - 7.50 (m, 2H, ArH), 7.52 - 7.57 (m, 2H, ArH), 7.60 - 7.63 (m, 1H, ArH), 7.86 - 7.90 (m, 1H, ArH), 7.95 (d, *J* = 8.0 Hz, 1H, ArH), 8.10 - 8.40 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 108.9, 117.5, 117.5, 124.7, 125.8, 126.0, 126.1, 126.9, 128.3, 128.8, 129.8, 130.1, 130.8, 133.8, 138.7, 138.9, 144.2, 189.2; MS(ESI): *m/z* calcd for $C_{20}H1_3ClN_2OSe$ 411.98; found 412.95 [M+H].

1-(Furan-2-yl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2m)



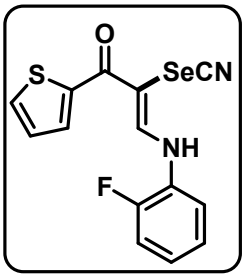
Yellow gum; 83%, 185 mg, R_f = 0.32 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.55 (dd, *J* = 2.0 Hz, 4.0 Hz,1H, ArH), 7.27 (d, *J* = 3.62 Hz, 1H, ArH), 7.43 - 7.46 (m, 7H, ArH), 8.07 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 107.9, 111.9, 115.2, 117.3, 118.5, 123.0, 132.9, 144.8, 145.0, 148.9, 156.7, 173.0; MS(ESI): *m/z* calcd for $C_{14}H_{10}N_2O_2Se$ 317.99; found 318.97 [M+H].

3-(Phenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2n)



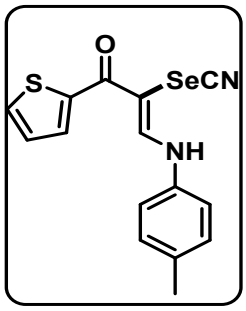
Yellow gum; 85%, 186 mg, R_f = 0.32 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (dd, *J* = 4.0 Hz, 3.6Hz, 1H, ArH), 7.39 - 7.54 (m, 6H, ArH+NH), 7.58 - 7.61 (m, 1H, ArH), 7.63 (s, 1H, ArH), 7.66 - 7.69 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 108.9, 116.1, 123.6, 127.9, 128.9, 129.6, 129.6, 131.4, 147.2,179.8; MS(ESI): *m/z* calcd for $C_{14}H_{10}N_2OSSe$ 333.96; found 334.90 [M+H].

3-(2-Fluorophenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2o)



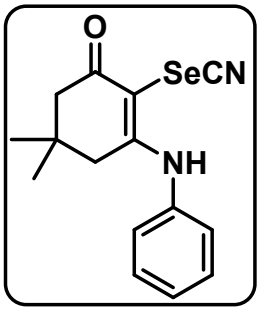
Brown semi solid; 85%, 186 mg, R_f = 0.32 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.12 - 7.15 (m, 1H, ArH), 7.25 - 7.32 (m, 2H, ArH), 7.41 - 7.57 (m, 4H, ArH+NH), 7.61 (dd, *J* = 0.8 Hz, 1.2 Hz,1H, ArH), 7.68 (dd, *J* = 0.8 Hz, *J* = 1.2 Hz,1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 109.7, 115.3, 116.1, 116.3, 123.6 (d, *J* = 7.2 Hz), 124.8 (d, *J* = 3.7 Hz), 128.0, 128.8, 128.9, 129.3, 131.8, 143.6, 145.2, 151.2 (d, *J* = 244.0 Hz), 178.9; MS(ESI): *m/z* calcd for $C_{14}H_9FN_2OSSe$ 351.95; found 352.90 [M+H].

2-Selenocyanato-1-(thiophen-2-yl)-3-(p-tolylamino)prop-2-en-1-one-(2p)



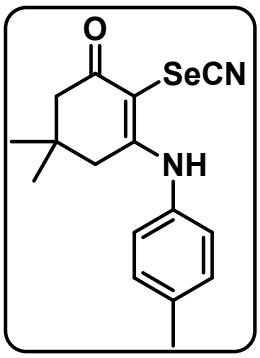
Yellow gum; 88%, 188 mg, R_f = 0.32 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H, -Me), 7.11 (dd, J = 3.6 Hz, 4.0 Hz,1H, ArH), 7.27 - 7.38 (m, 5H, ArH+NH), 7.59 (dd, J = 1.2 Hz, J = 1.2 Hz,1H, ArH), 7.61 (s, 1H, ArH), 7.66 (dd, J = 1.2 Hz, 0.8 Hz,1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 20.75, 108.5, 114.0, 116.7, 116.7, 126.9, 127.6, 130.1, 132.7, 144.4, 145.3, 146.7, 178.2; MS(ESI): *m/z* calcd for $C_{15}H_{12}N_2OSSe$ 347.98; found 348.95 [M+H].

5,5-Dimethyl-3-(phenylamino)-2-selenocyanatocyclohex-2-en-1-one-(4a)



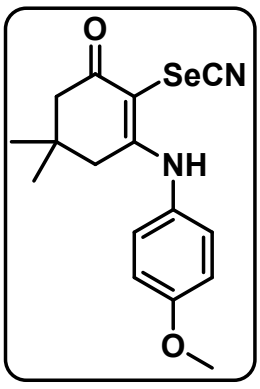
Pale yellow gum; 88%, 196 mg, R_f = 0.30 in 50% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 6H), 2.08 (s, 2H), 2.36 (s, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.51-7.42 (m, 3H);^{13}C NMR (100 MHz, $CDCl_3$); δ = 28.3, 34.3, 40.0, 50.9, 109.1, 128.7, 129.6, 130.2, 136.0, 153.4, 162.7, 190.3; MS(ESI): *m/z* calcd for $C_{15}H_{16}N_2OSe$ 319.27; found 320.96 [M+H].

5,5-Mimethyl-2-selenocyanato-3-(p-tolylamino)cyclohex-2-en-1-one-(4b)



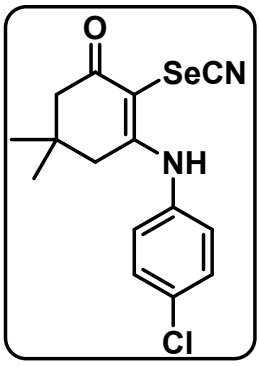
Dark brown liquid; 92%, 201 mg, R_f = 0.33 in 50% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 6H), 2.08 (s, 2H), 2.34 (d, J = 5.4 Hz, 5H), 7.07 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 21.3, 28.3, 29.6, 34.2, 40.0, 50.9, 108.8, 128.3, 130.9, 133.2, 139.7, 153.7, 162.9, 190.3; MS(ESI): *m/z* calcd for $C_{16}H_{18}N_2OSe$ 333.29; found 333.95 [M+H].

3-(4-Methoxyphenyl)amino-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4c)



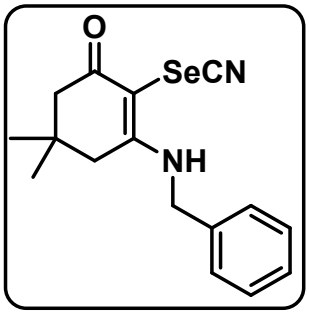
Pale brown liquid; 95%, 203 mg, R_f = 0.38 in 50% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 6H), 2.07 (s, 2H), 2.34 (s, 2H), 3.79 (s, 3H), 6.99 - 6.96 (m, 2H), 7.12 - 7.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$); δ = 28.3, 34.4, 40.0, 50.8, 55.9, 108.6, 115.4, 128.2, 129.9, 153.9, 160.1, 163.4, 190.3; MS(ESI): *m/z* calcd for $C_{16}H_{18}N_2O_2Se$ 349.29; found 351.00 [M+H].

3-(4-Chlorophenyl)amino-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4d)



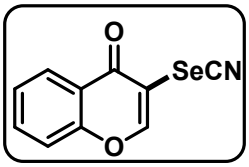
Pale yellow liquid; 92%, 196 mg, R_f = 0.34 in 50% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 6H), 2.06 (s, 2H), 2.33 (s, 2H), 7.16 (dd, J = 6.8, 1.8 Hz, 2H), 7.43 (dd, J = 6.7, 1.9 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$); δ = 28.3, 34.3, 40.0, 50.8, 109.4, 130.1, 130.3, 134.6, 135.4, 153.0, 162.2, 190.3; MS(ESI): *m/z* calcd for $C_{15}H1_5ClN_2OSe$ 353.71; found 354.95 [M+H].

3-(Benzylamino)-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4e)



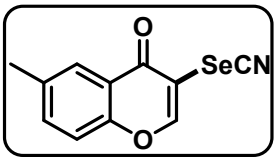
Pale yellow liquid; 92%, 177 mg, R_f = 0.38 in 50% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 6H), 2.36 (d, J = 6.7 Hz, 4H), 5.08 (s, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H); δ = 28.4, 34.2, 39.1, 46.9, 50.7, 108.6, 126.0, 127.6, 128.9, 135.9, 154.0, 161.7, 189.8; MS(ESI): *m/z* calcd for $C_{16}H_{18}N_2OSe$ 333.29; found 334.45 [M+H].

3-Selenocyanato-4H-chromen-4-one-(6a)[2]



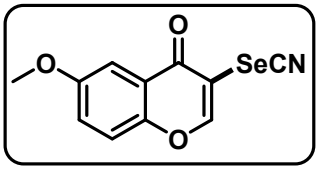
Light brown solid; m.p. 134-136^{o}C (lit.136-137^{o}C); 89%, 229 mg; R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 - 7.58 (m, 2H, ArH), 7.74-7.82 (m, 1H, ArH), 8.19 (dd, J = 1.2 Hz, 1.2 Hz, 1H, ArH), 8.25 (s, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): 99.8, 112.6, 118.4, 121.9, 125.7, 126.4, 134.9, 153.0, 156.6, 174.1.

6-Methyl-3-selenocyanato-4H-chromen-4-one-(6b)[2]



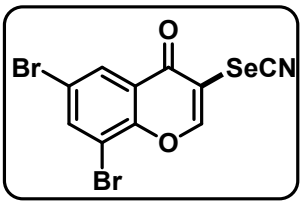
Light yellow solid; m.p. 142-144^{o}C (lit.145^{o}C); 93%, 231 mg; R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3H, -Me), 7.43 (d, J = 8.4Hz, 1H, ArH), 7.56 (dd, J = 2.0Hz, J = 2.0 Hz, 1H, ArH), 7.96 (s, 1H, ArH), 8.21 (s, 1H, ArH).

6-Methoxy-3-selenocyanato-4H-chromen-4-one-(6c)[2]



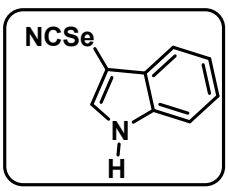
Light yellow solid; m.p. 143-145^{o}C (lit.145-146^{o}C); 93%, 221 mg; R_f = 0.35 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H, -OMe), 7.33 (d, J = 3.2 Hz, 1H, ArH),7.46 - 7.49 (m, 2H, ArH), 8.21 (s, 1H, ArH).

6,8-Dibromo-3-selenocyanato-4H-chromen-4-one-(6d)[2]



Light yellow solid; m.p. 131-133^{o}C (lit.135^{o}C); 96%, 194 mg; R_f = 0.38 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 2.4Hz, 1H, ArH), 8.06 (d, J = 2.4Hz, 1H, ArH), 8.32 (s, 1H, ArH.

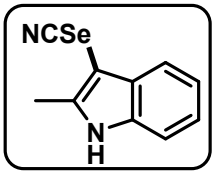
3-Selenocyanato-1H-indole-(7a)[3]



Light yellow solid; m.p. 97-99°C (lit. 99-100°C); 96%, 273 mg; R_f = 0.54 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.29 (m, 2H, ArH), 7.35-7.40 (m, 2H, ArH); 7.69 - 7.73 (m, 1H, ArH), 8.84 (br, s, 1H, NH).

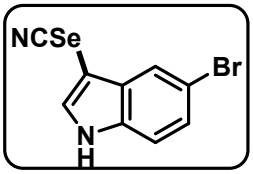
2-Methyl-3-selenocyanato-1H-indole-(7b)[3]

Light brown solid; m.p. 124-126°C (lit.124-126°C); 99%, 288 mg; R_f = 0.44 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.55 (s, 3H, -Me); 7.21-7.25 (m, 2H, ArH), 7.30 - 7.33 (m, 1H, ArH); 7.60 - 7.64 (m, 1H, ArH), 8.50 (br, s, 1H, NH).



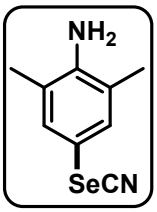
5-Bromo-3-selenocyanato-1H-indole-(7c)[3]

Light brown solid; m.p. 138-140°C (lit.140-142°C); 98%, 227 mg; R_f = 0.41 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.8Hz, 1H, ArH), 7.39 - 7.43 (m, 1H, ArH), 7.55 (d, J = 2.8 Hz, 1H, ArH), 7.88 (d, J = 2.0 Hz, 1H, ArH), 8.68 (br, s, 1H, NH).



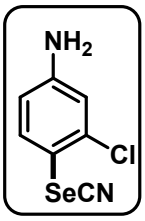
2,6-Dimethyl-4-selenocyanatoaniline-(8a) [3]

Light yellow liquid; 70%, 195 mg; R_f = 0.38 in 15% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 6H, -Me), 3.83 (s, 2H, ArH).



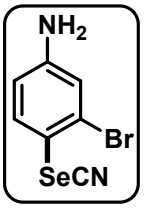
3-Chloro-4-selenocyanatoaniline-(8b) [3]

Light yellow liquid; 72%, 197 mg; R_f = 0.34 in 15% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.99 (s, 2H, ArH), 6.50 - 6.60 (m, 1H, ArH), 6.76 (d, J = 2.4 Hz, 1H, ArH),7.48 (d, J = 8.4 Hz, 1H, ArH).



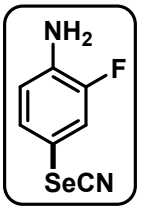
3-Bromo-4-selenocyanatoaniline(8c) [3]

Light yellow liquid; 72%, 173 mg; R_f = 0.36 in 15% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.98 (s, 2H, ArH), 6.55 - 6.63 (m, 1H, ArH), 6.92 (d, J = 2.4 Hz, 1H, ArH),7.48 (d, J = 8.8 Hz, 1H, ArH).



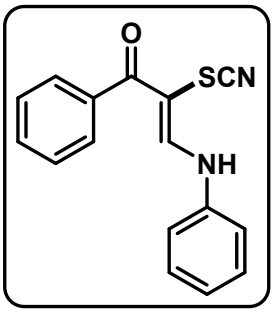
2-Fluoro-4-selenocyanatoaniline(8d) [3]

Light yellow liquid; 73%, 212 mg; R_f = 0.32 in 15% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.05 (s, 2H, ArH), 6.69 - 6.74 (m, 1H, ArH), 7.19 - 7.23 (m, 1H, ArH), 7.27 -7.31 (m, 1H, ArH).



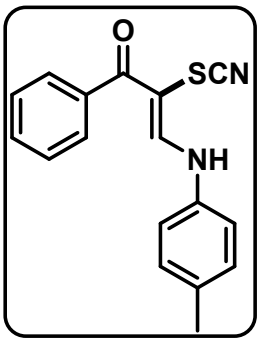
1-Phenyl-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9a)

Yellow oil; 79%, 150 mg, R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.09 (t, J = 7.6 Hz, 1H, ArH), 7.18 (d, J = 7.6 Hz, 2H, ArH), 7.31 (t, J = 8.4 Hz, 2H, ArH), 7.43 – 7.54 (m, 3H, ArH), 7.57 - 7.62 (m, 2H,



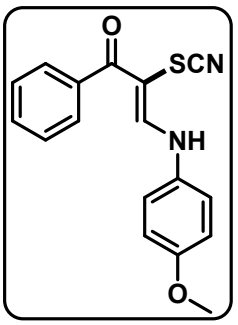
ArH), 8.07 (d, *J* = 13.6 Hz, 1H, C=CH), 11.25 (d, *J* = 13.6 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 107.9, 116.8 116.8, 124.2, 128.4, 128.7, 129.7, 130.8, 139.9, 139.9, 153.13, 195.4; MS(ESI): *m/z* calcd for $C_{16}H_{12}N_2OS$ 280.0670; found 281.03 [M+H].

1-Phenyl-2-thiocyanato-3-(p-tolylamino)prop-2-en-1-one-(9b)



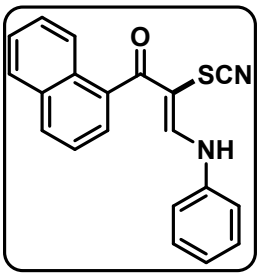
Yellow dark oil; 89%, 165 mg, R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H, -Me), 7.19 - 7.24 (m, 1H, ArH), 7.27 - 7.33 (m, 4H, ArH), 7.44 (t, *J* = 7.6 Hz, 3H, ArH), 7.51 - 7.54 (m, 2H, ArH), 7.63 - 7.73 (m, 2H, AH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.71, 107.8, 116.4 127.2, 128.4, 129.7, 130.2, 131.4, 133.4, 137.8, 139.3, 145.3, 147.1; MS(ESI): *m/z* calcd for $C_{17}H_{14}N_2OS$ 294.08; found 295.05 [M+H].

3-(4-Methoxyphenyl)amino-1-phenyl-2-thiocyanatoprop-2-en-1-one-(9c)



Dark brown semi solid ; 87%, 165 mg, R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3H, -OMe), 6.85 (d, *J* = 8.8 Hz, 2H, ArH), 7.11 (d, *J* = 8.8 Hz, 2H, ArH), 7.42 - 7.45 (m, 3H, ArH), 7.55 - 7.59 (m, 2H, ArH), 7.97 (d, *J* = 13.6 Hz, 1H, C=CH), 11.23 (d, *J* = 13.6 Hz, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 107.1, 114.9 118.2, 128.4, 128.6, 130.0, 130.6, 133.5, 140.1, 153.5, 145.3, 156.7, 195.0; MS(ESI): *m/z* calcd for $C_{17}H_{14}N_2O_2S$ 310.0776; found 311.04 [M+H].

1-(Naphthalen-1-yl)-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9d)



Brown semi solid ; 89%, 161mg; R_f = 0.31 in 30% (EtOAc:PET); Stain $KMnO_4$ Active; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 - 7.25 (m, 1H, ArH), 7.28 - 7.33 (m, 3H, ArH), 7.33 - 7.39 (m, 2H, ArH), 7.47 - 7.54 (m, 3H, ArH), 7.59 (d, *J* = 6.4 Hz, H, ArH), 7.82 - 7.86 (m, 1H, ArH), 7.91 (d, *J* = 8.4 Hz, 1H,ArH), 8.11 - 8.16 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.6, 116.5, 123.8, 124.8, 125.9, 126.1, 126.9, 128.3, 129.8, 130.2, 130.7, 133.9, 139.0, 140.3, 144.6, 184.32; MS(ESI): *m/z* calcd for $C_{20}H_{14}N_2OS$ 330.0827; found 331.00 [M+H].

Reference:

1. (a) Xie, Y. B.; Ye, S. P.; Chen, W. F.; Hu, Y. L.; D. J. Li.; Wang, L. *Asian J. Org. Chem.,* **2017**, *6*, 746-750; (b) Sorabad, G. S.; Maddani, M. R. *New J. Chem.,* **2019**, *43*, 6563-6568.
2. Kosso, A. R. O.; Broggi, J.; Redon, S.; Vanelle, P. *Synlett* **2018**, *29*, 1215–1218.
3. Muniraj, N.; Dhineshkumar, J.; and Prabhu, K R. *Chemistry Select* **2016**, *5*, 1033-1038.

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

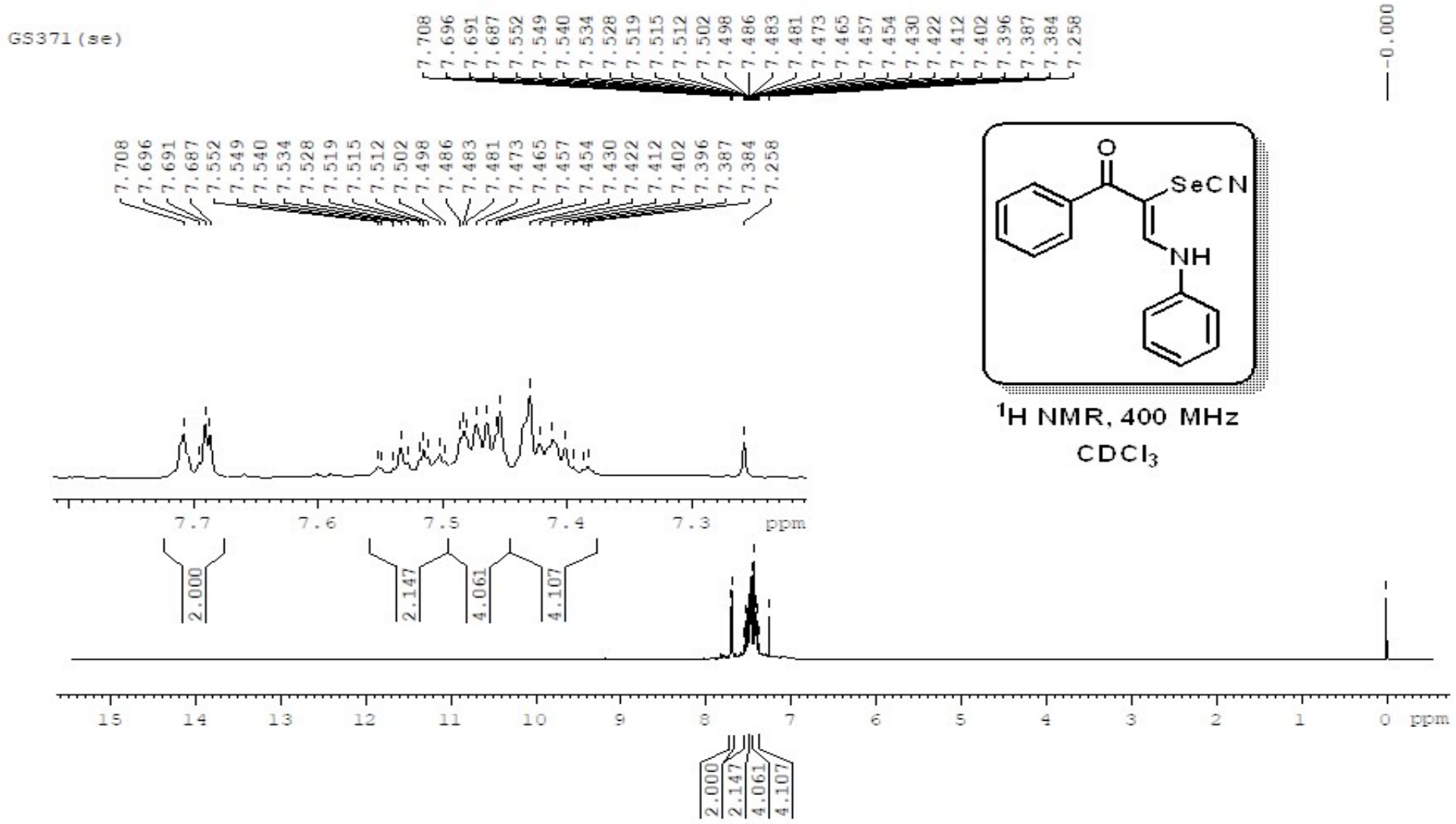


Fig 1. ^{1}H-NMR Spectrum of 1-Phenyl-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2a)

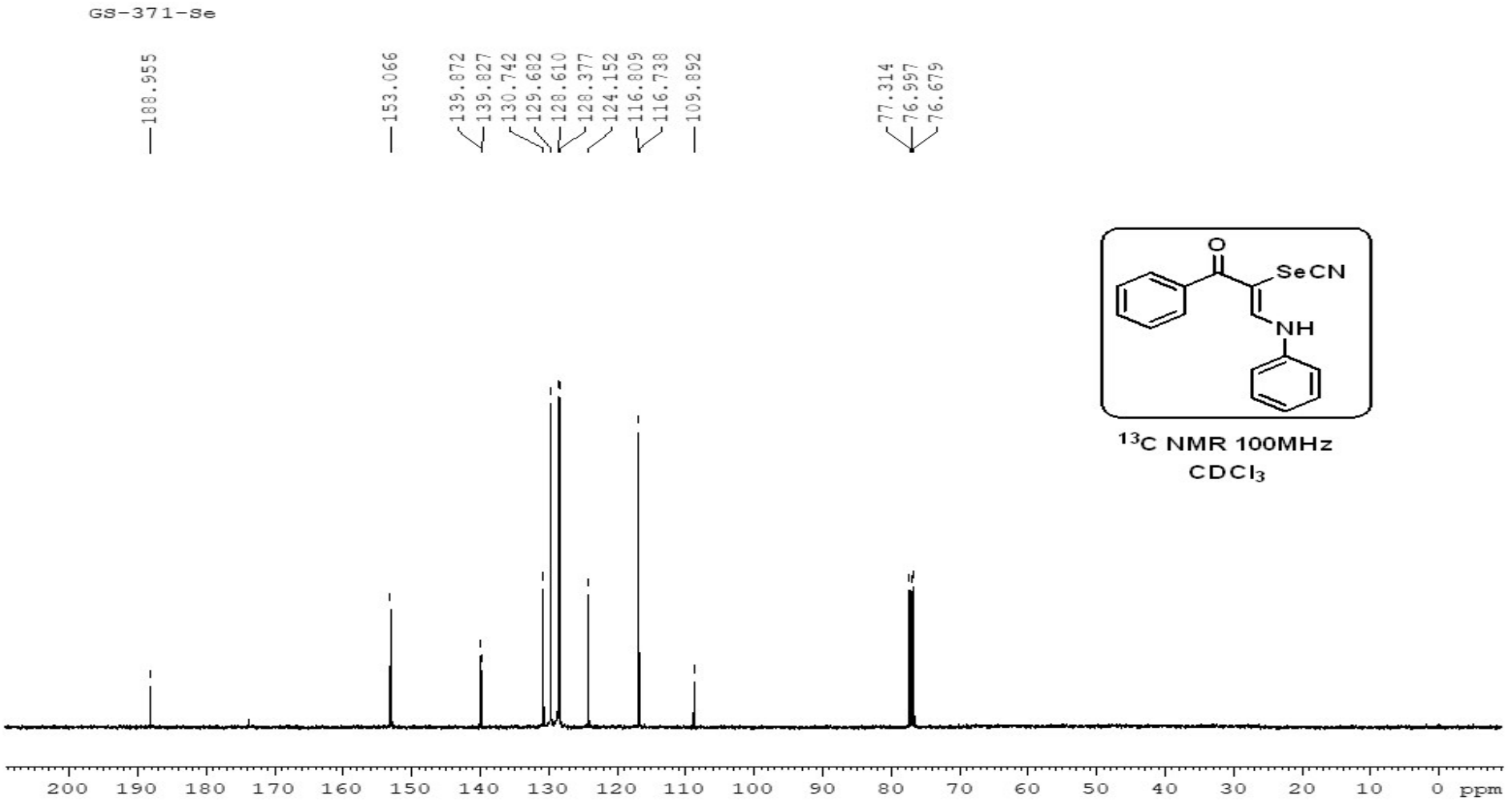


Fig 2. ^{13}C-NMR Spectrum of 1-Phenyl-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2a)

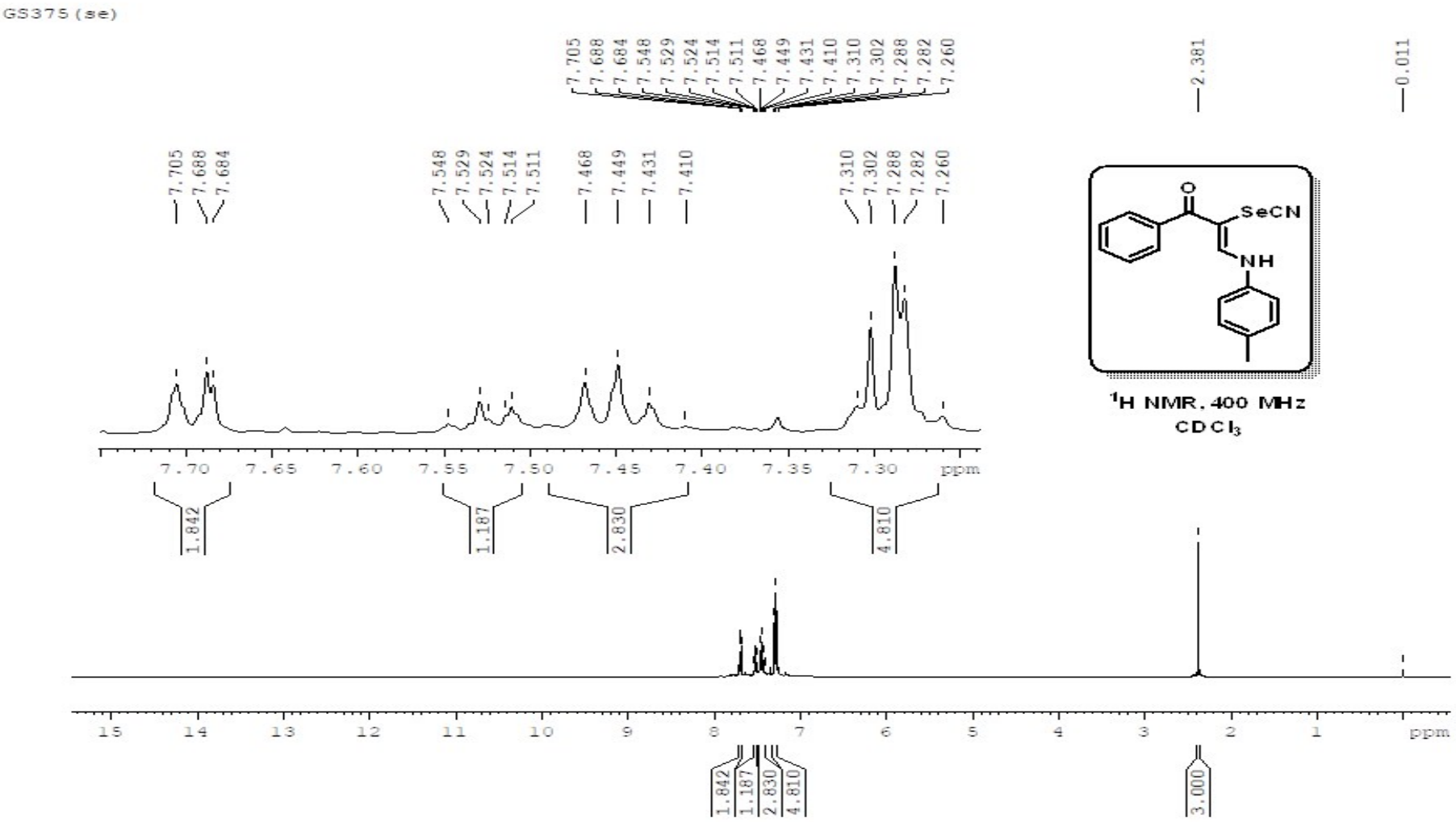


Fig 3. [1]H-NMR Spectrum of 1-Phenyl-2-selenocyanato-3-(p-tolylamino)prop-2-en-1-one-(2b)

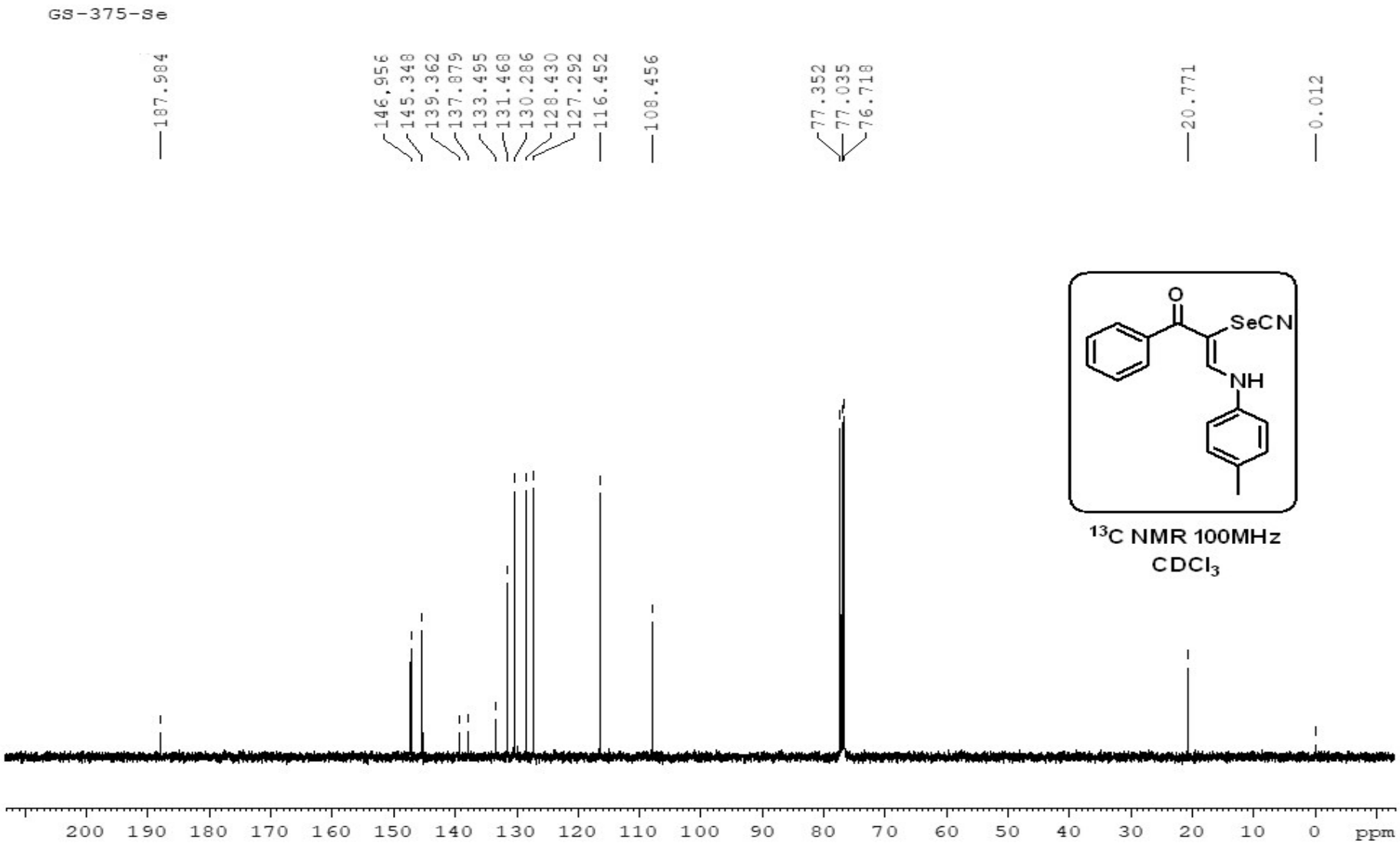


Fig 4. ^{13}C-NMR Spectrum of 1-Phenyl-2-selenocyanato-3-(p-tolylamino)prop-2-en-1-one-(2b)

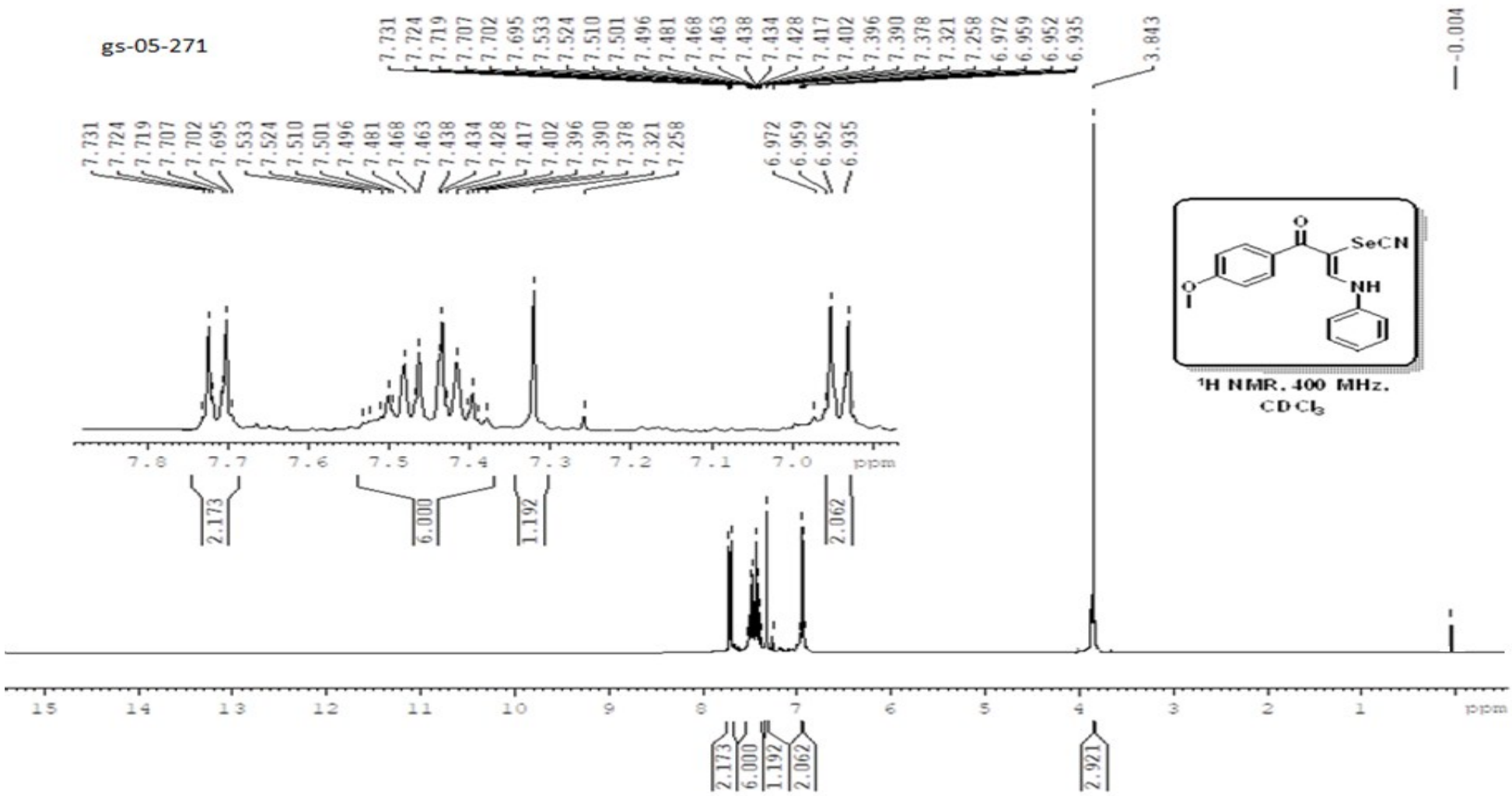


Fig 5. [1]H-NMR Spectrum of 1-(4-Methoxyphenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2c)

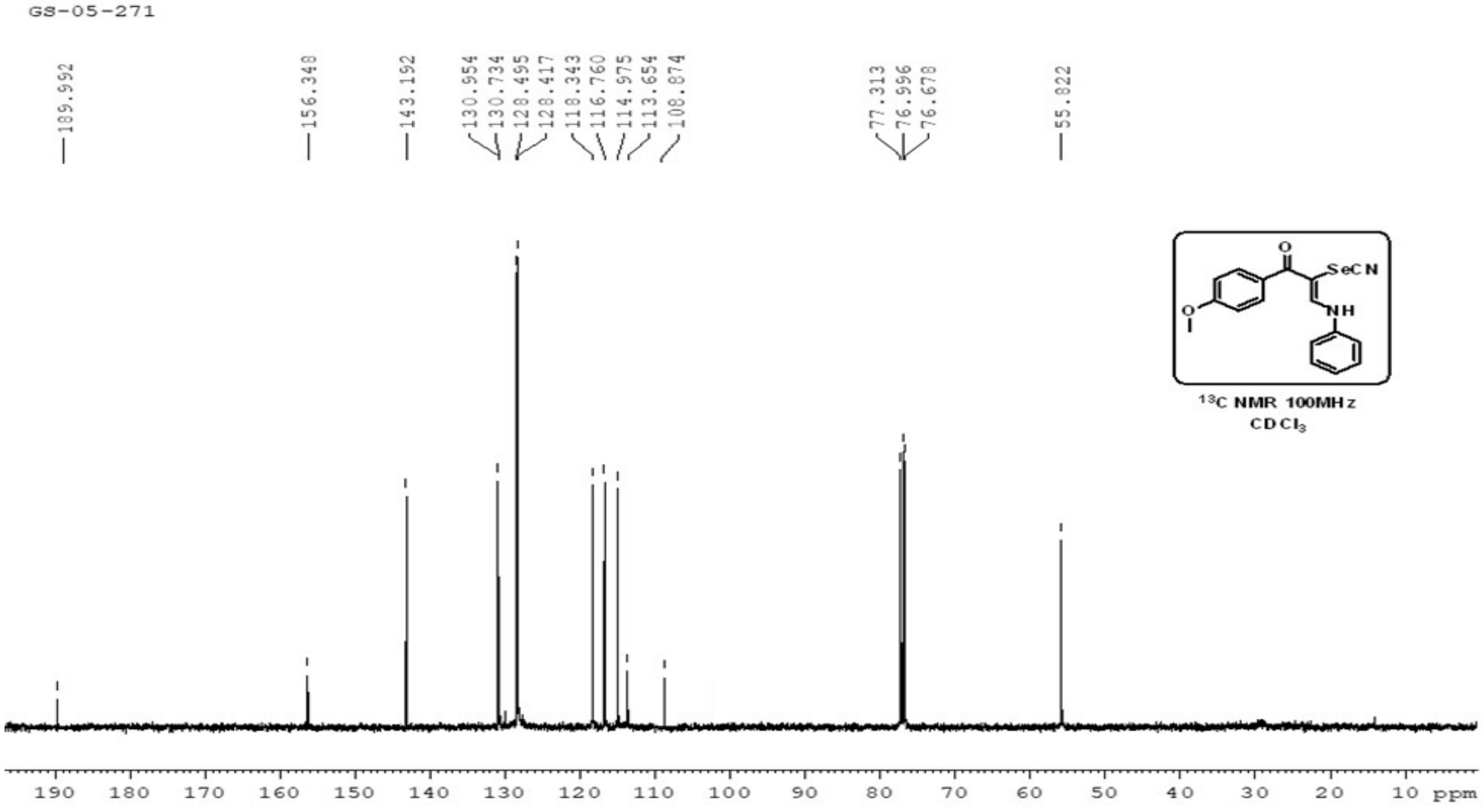


Fig 6. ^{13}C-NMR Spectrum of 1-(4-Methoxyphenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2c)

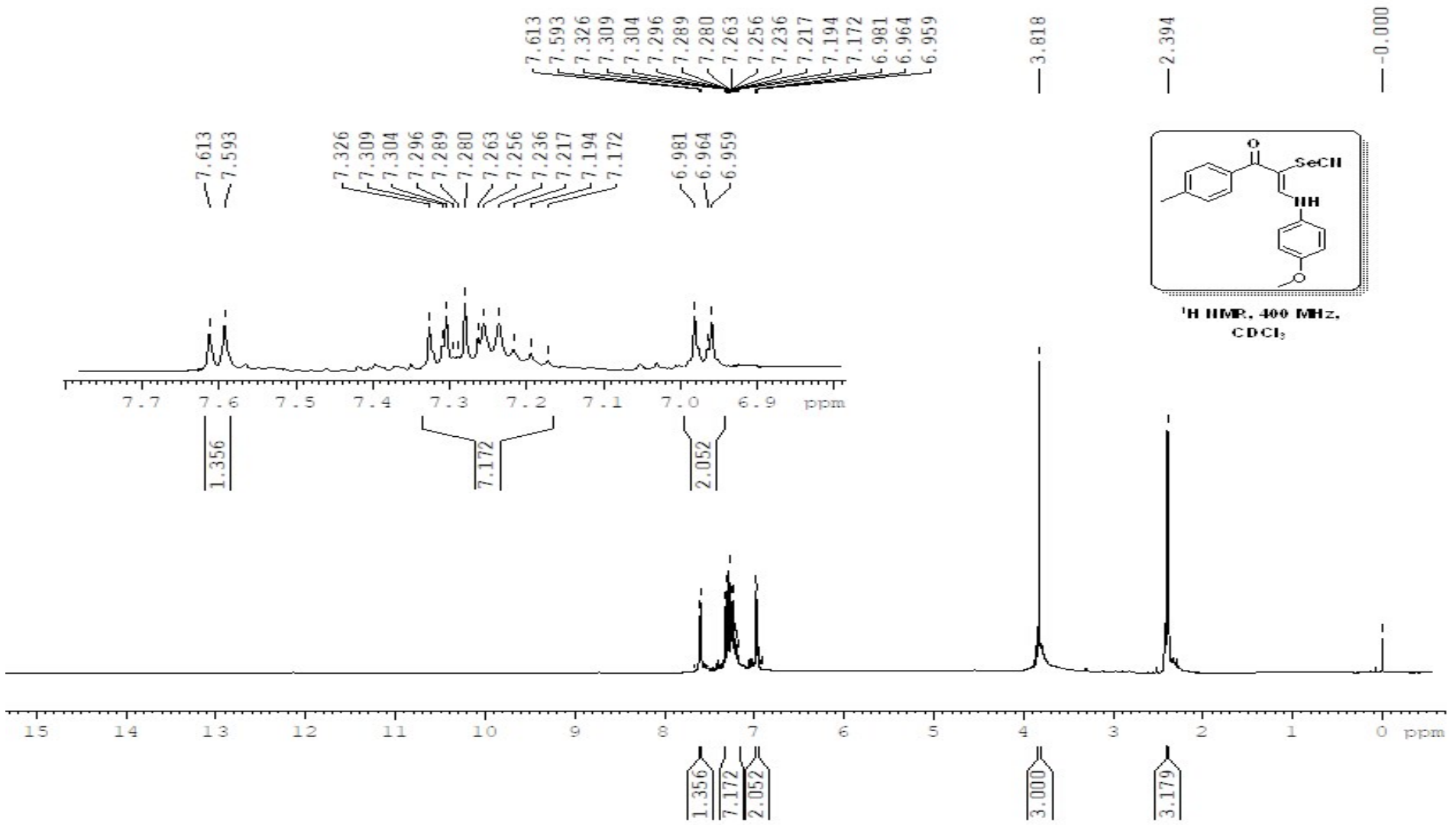


Fig 7. [1]H-NMR Spectrum of 3-(4-Methoxyphenyl)amino)-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2d)

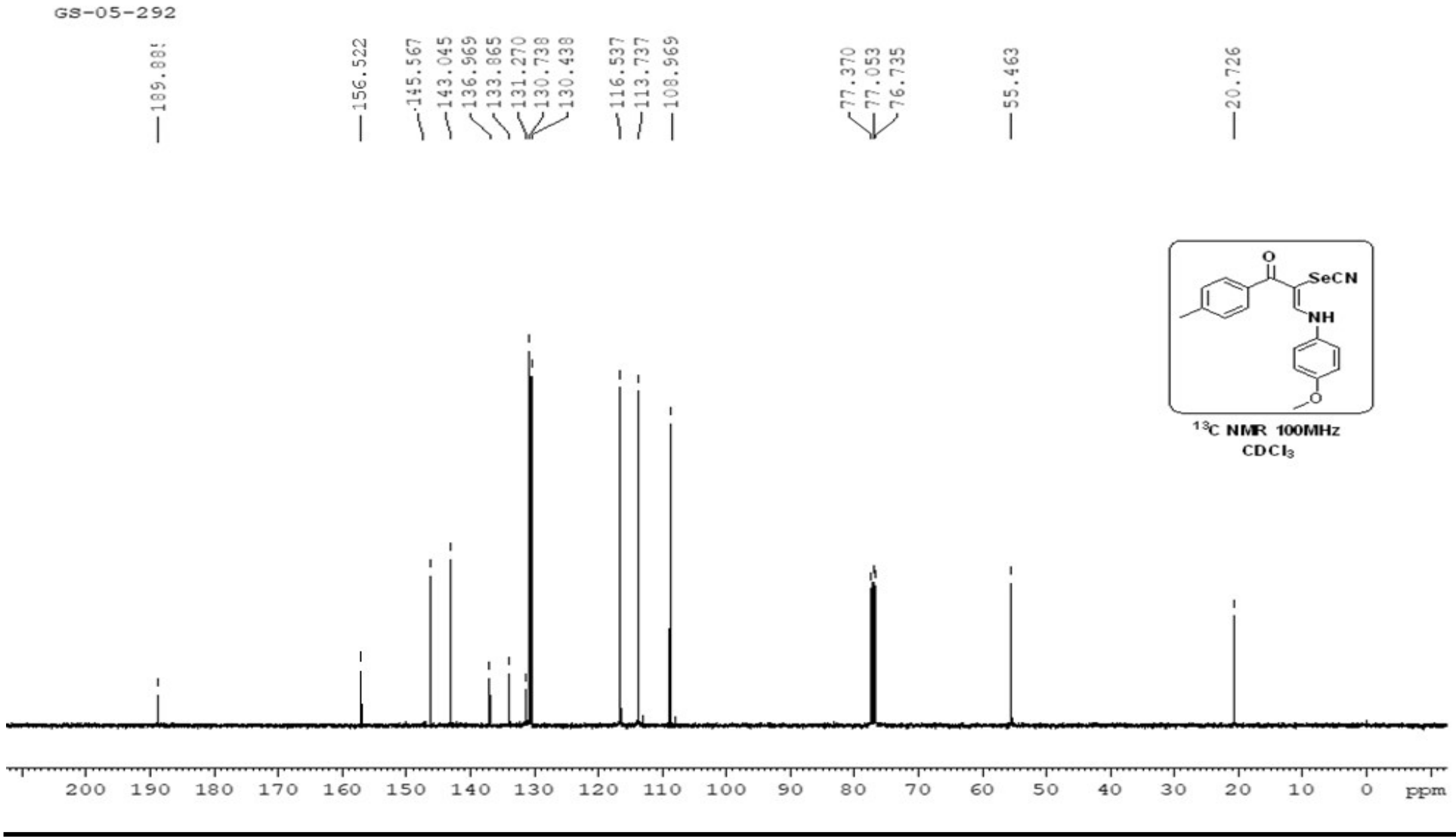


Fig 8. ^{13}C-NMR Spectrum of 3-(4-Methoxyphenyl)amino)-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2d)

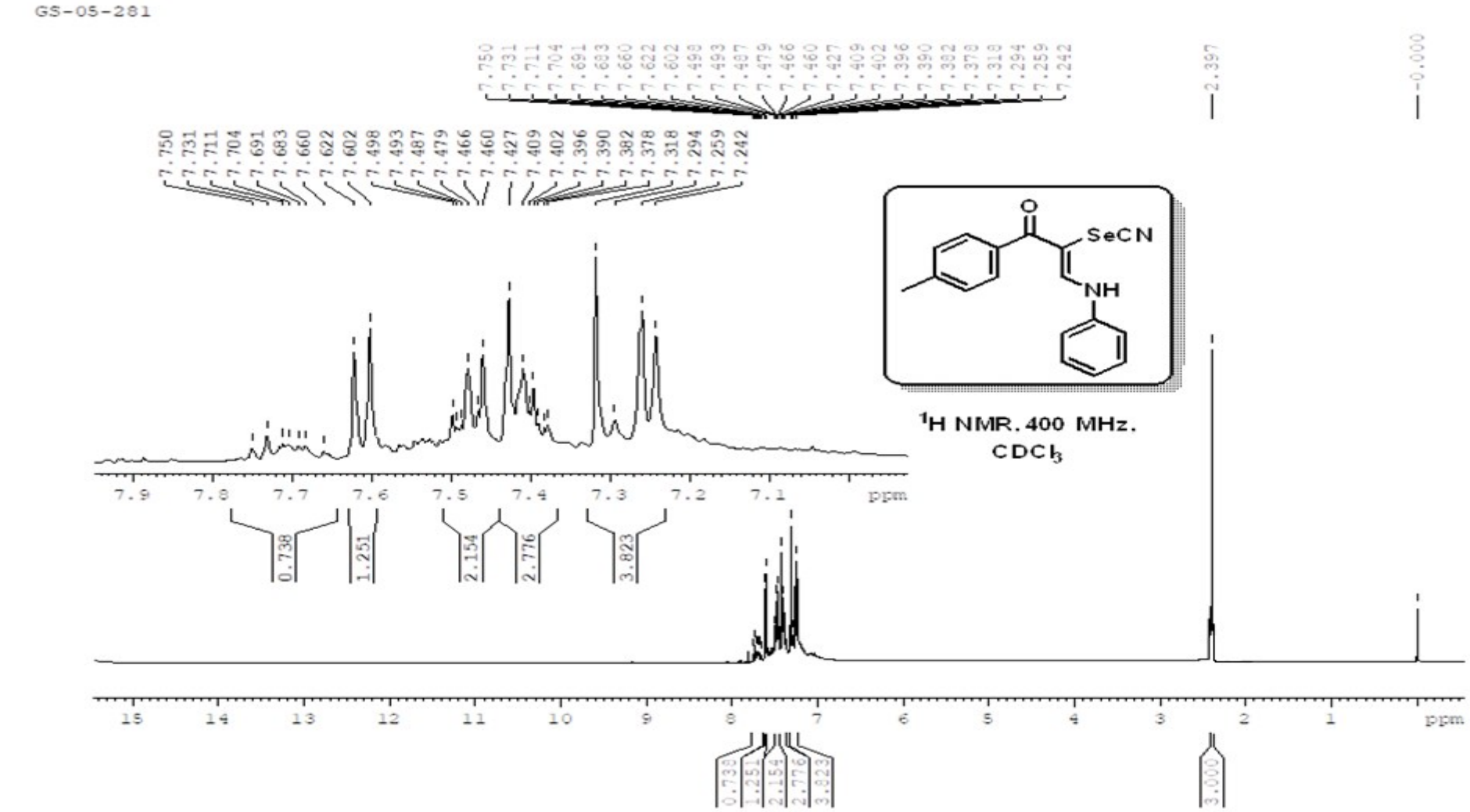


Fig 9. [1]H-NMR Spectrum of 3-(Phenylamino)-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2e)

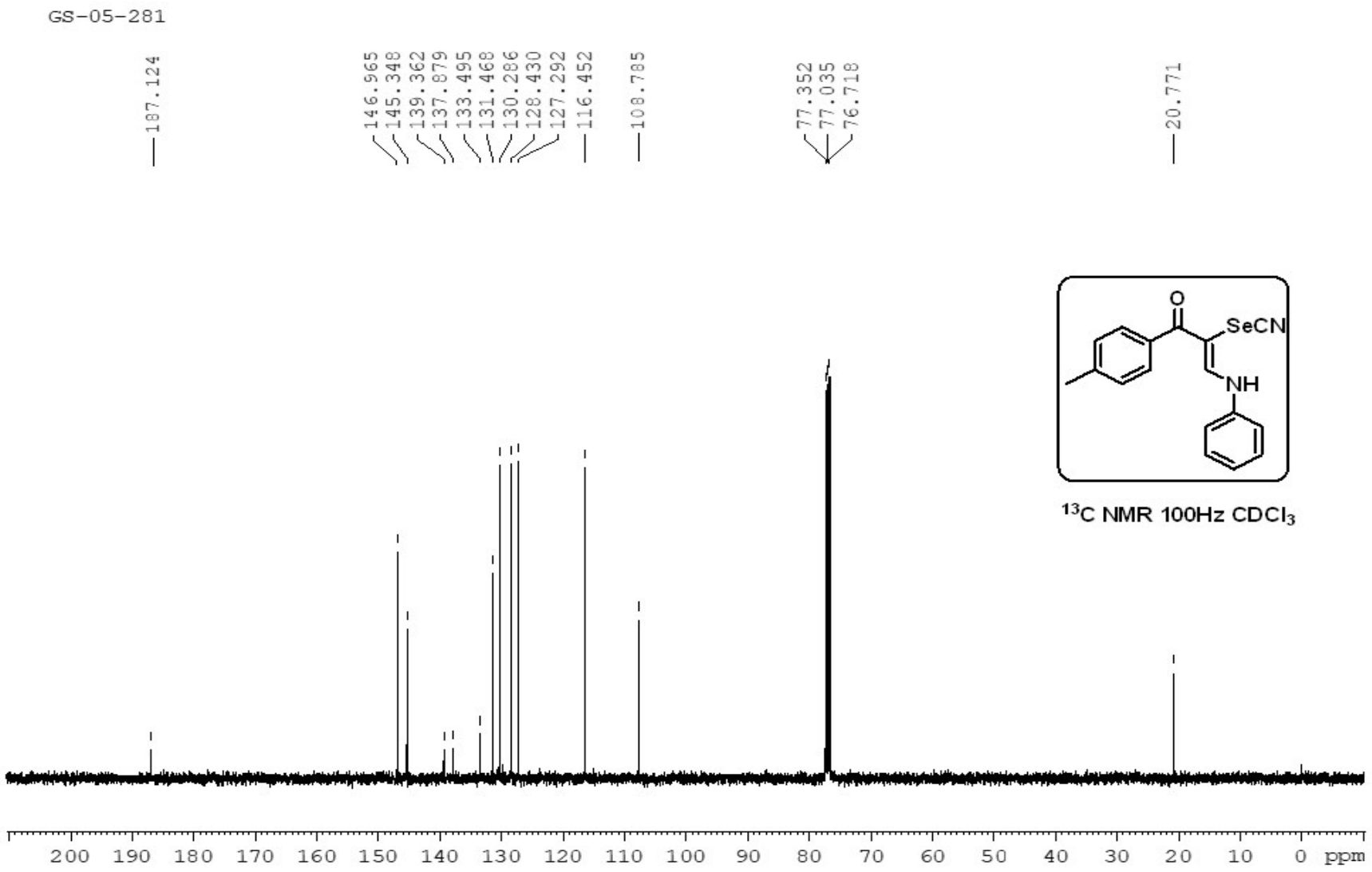


Fig 10. ^{13}C-NMR Spectrum of 3-(Phenylamino)-2-selenocyanato-1-(p-tolyl)prop-2-en-1-one-(2e)

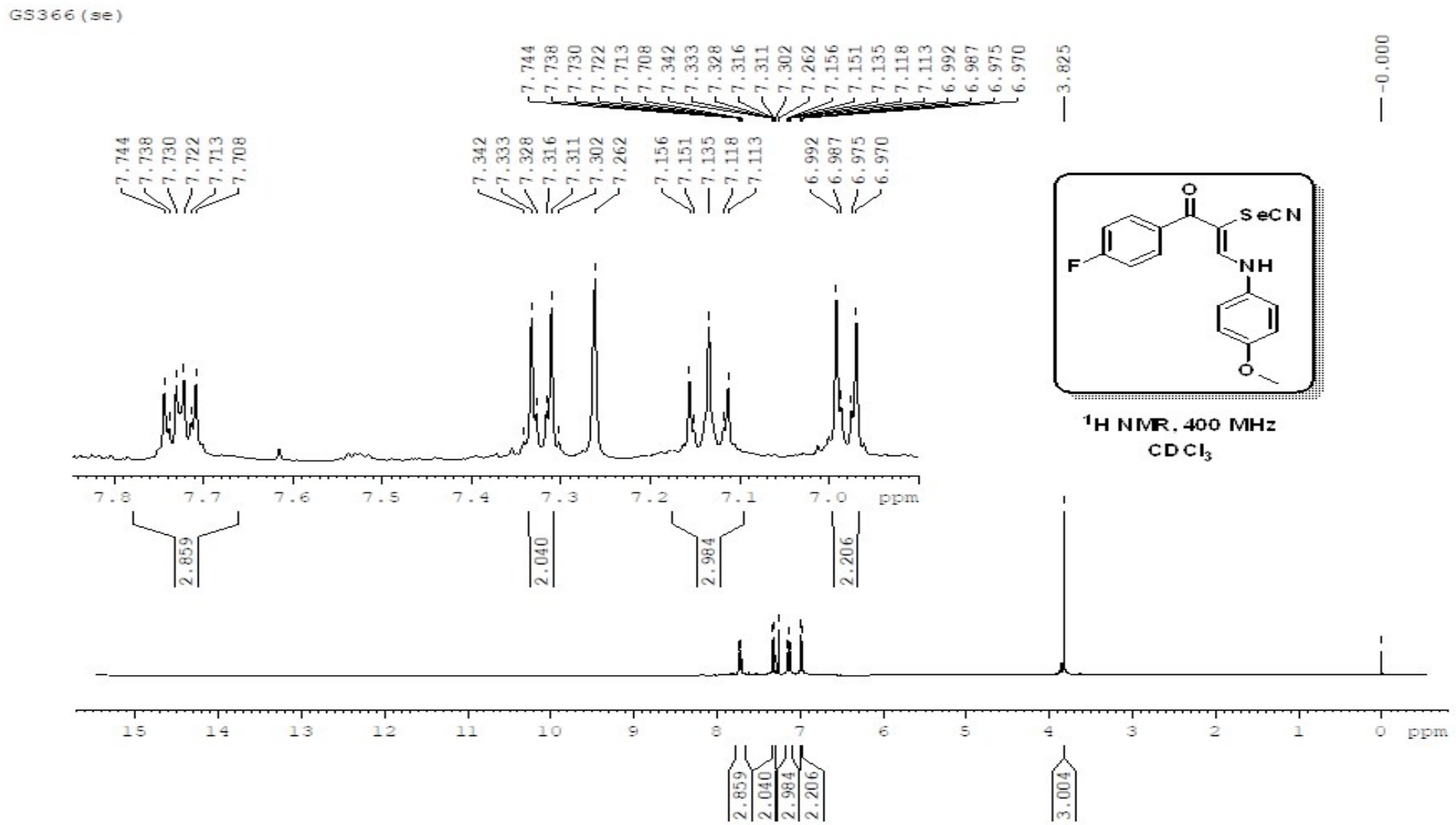


Fig 11. [1]H-NMR Spectrum of 1-(4-Fluorophenyl)-3-(4-methoxyphenyl)amino)-2-selenocyanatoprop-2-en-1-one-(2f)

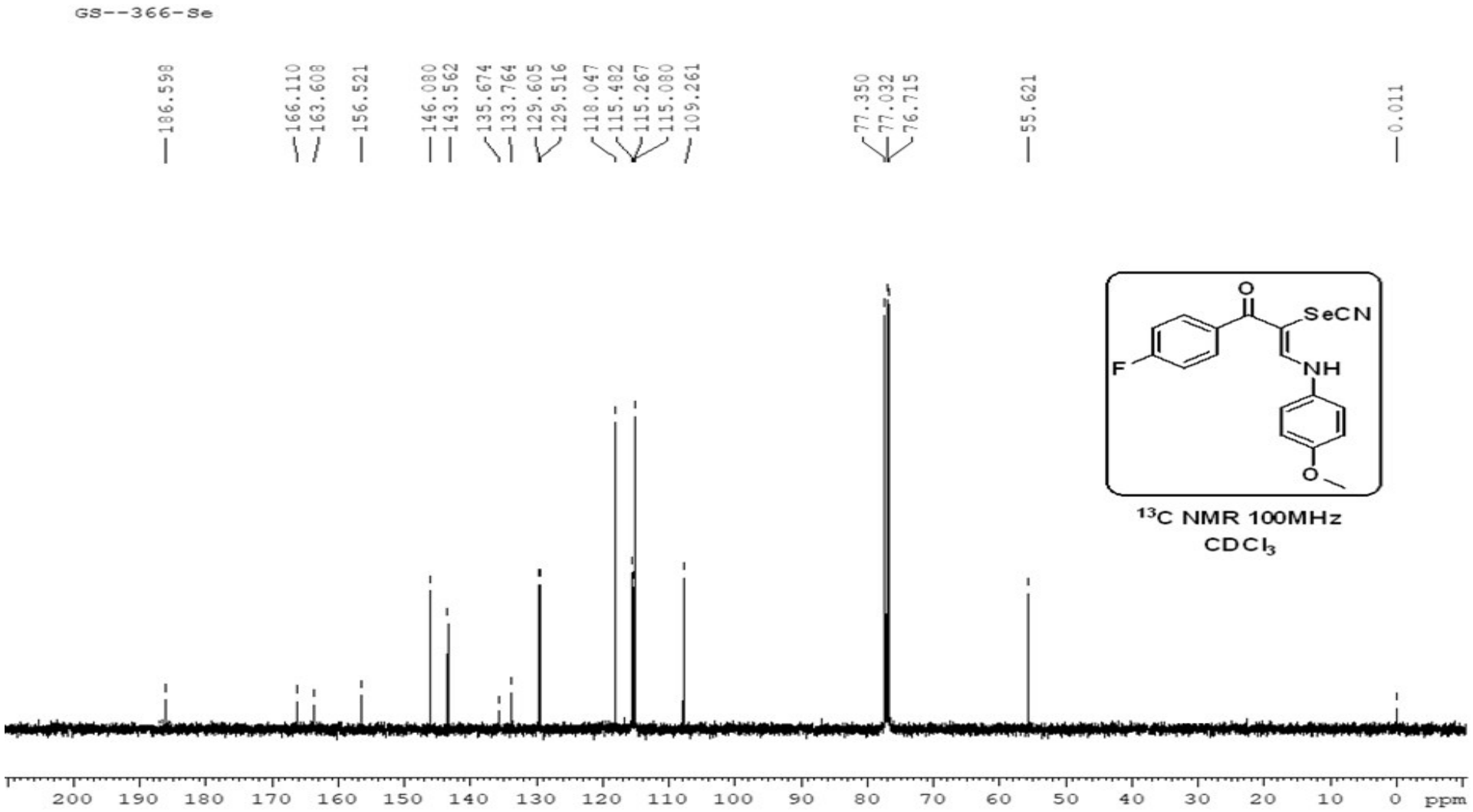


Fig 12. ^{13}C-NMR Spectrum of 1-(4-Fluorophenyl)-3-(4-methoxyphenyl)amino)-2-selenocyanatoprop-2-en-1-one-(2f)

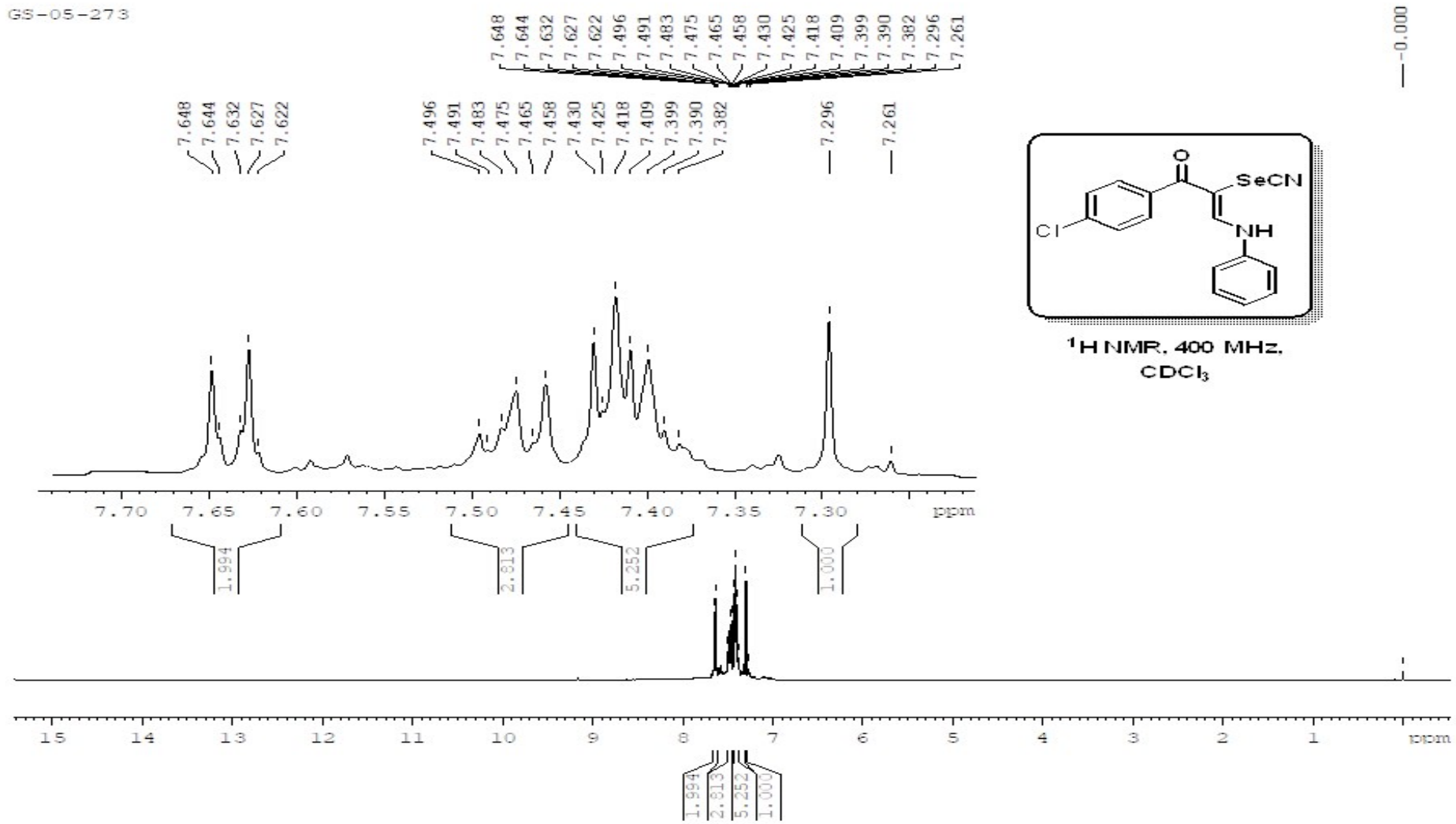


Fig 13. [1]H-NMR Spectrum of 1-(4-Chlorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2g)

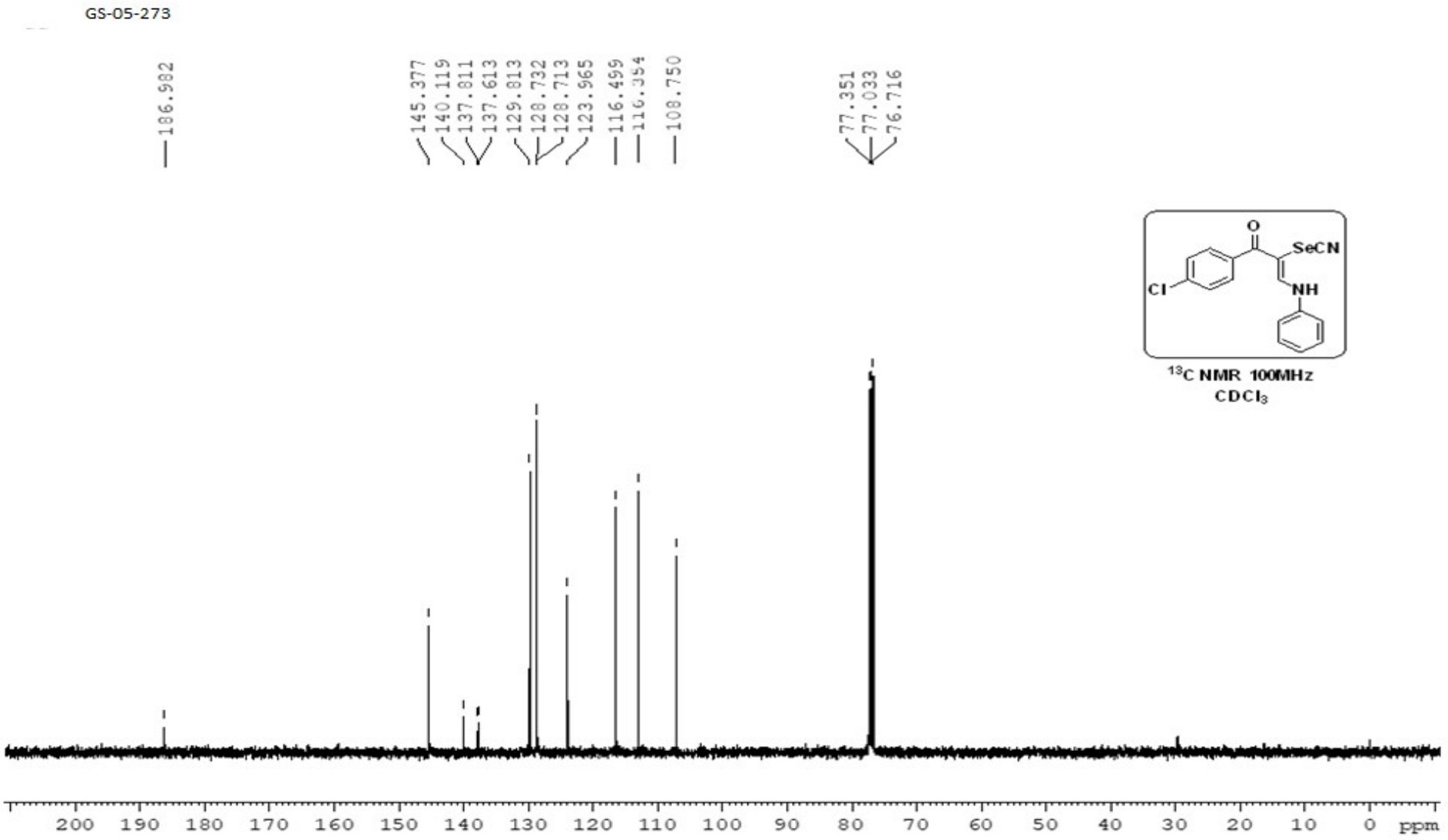


Fig 14. ^{13}C-NMR Spectrum of 1-(4-Chlorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2g)

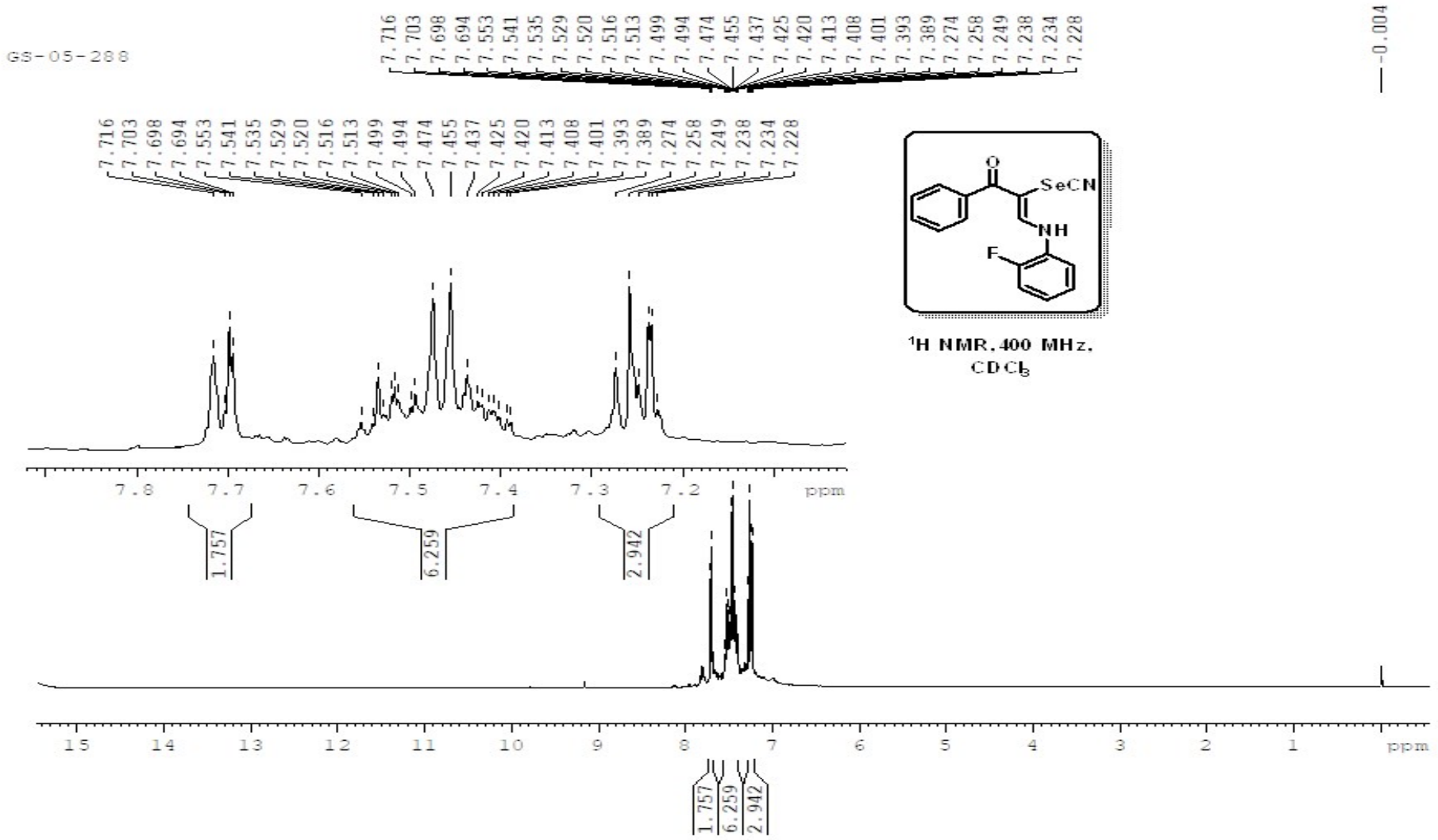


Fig 15. ^{1}H-NMR Spectrum of 3-(2-Fluorophenyl)amino-1-phenyl-2-selenocyanatoprop-2-en-1-one-(2h)

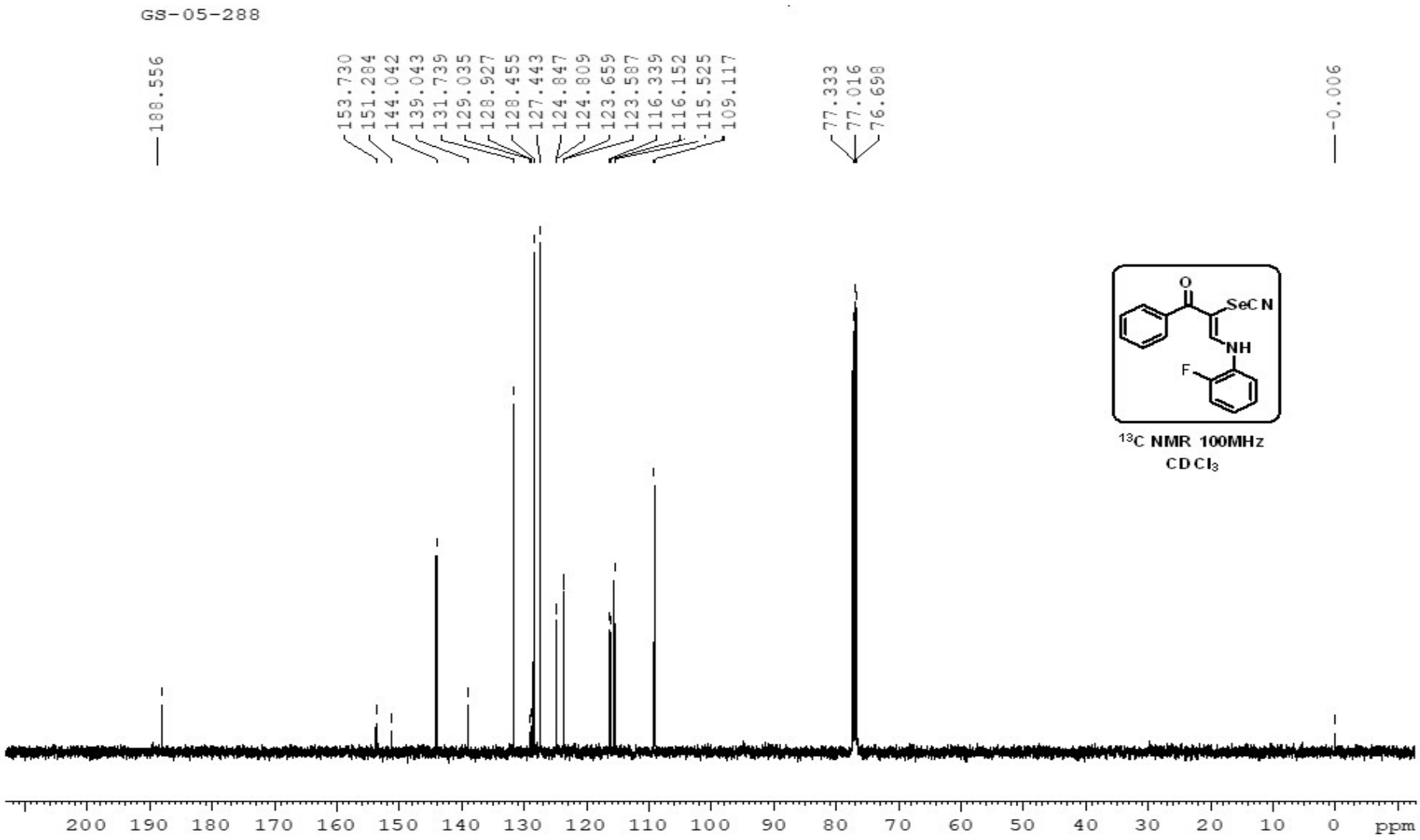


Fig 16. ^{13}C-NMR Spectrum of 3-(2-Fluorophenyl)amino-1-phenyl-2-selenocyanatoprop-2-en-1-one-(2h)

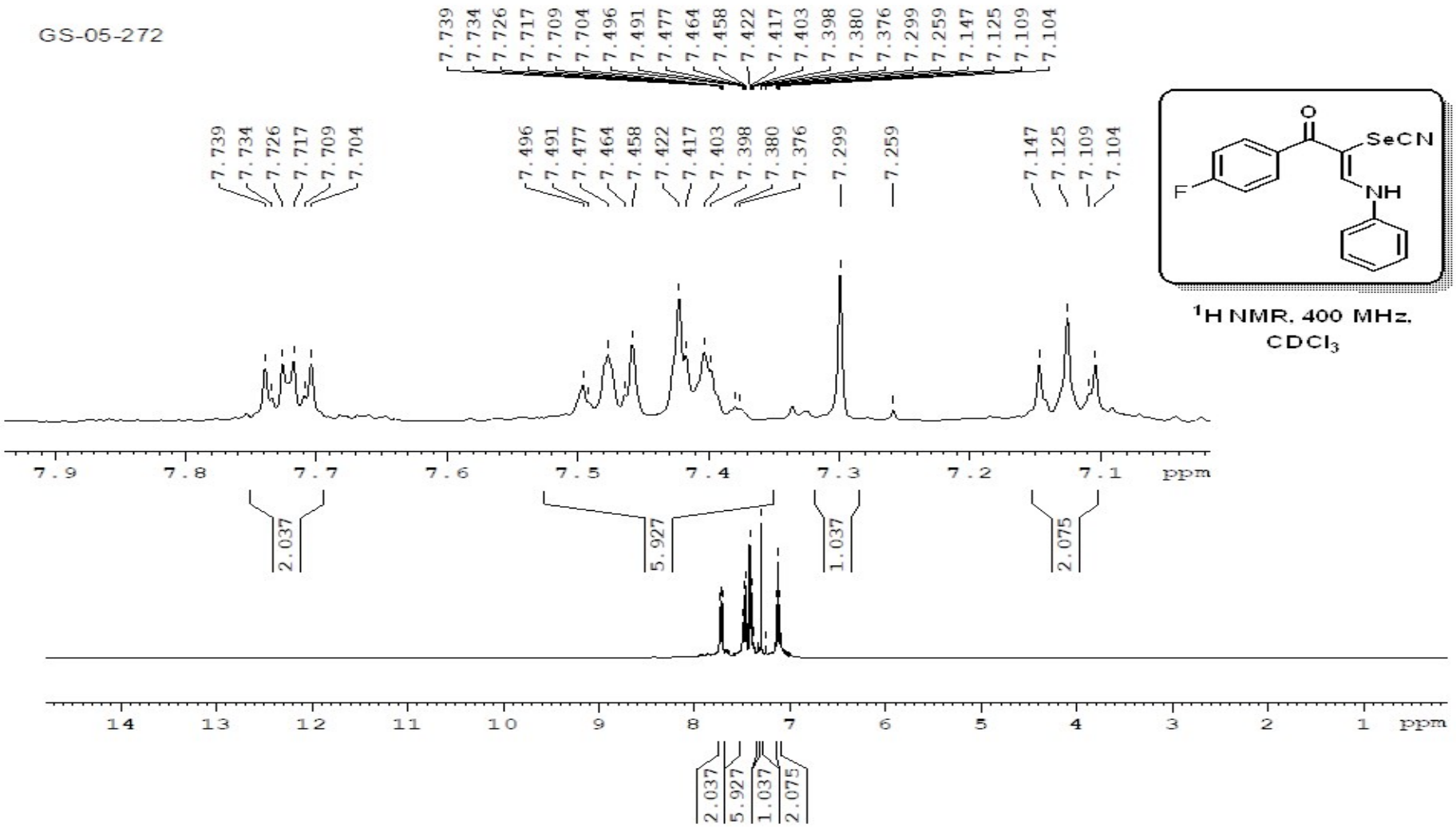


Fig 17. [1]H-NMR Spectrum of 1-(4-Fluorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2i)

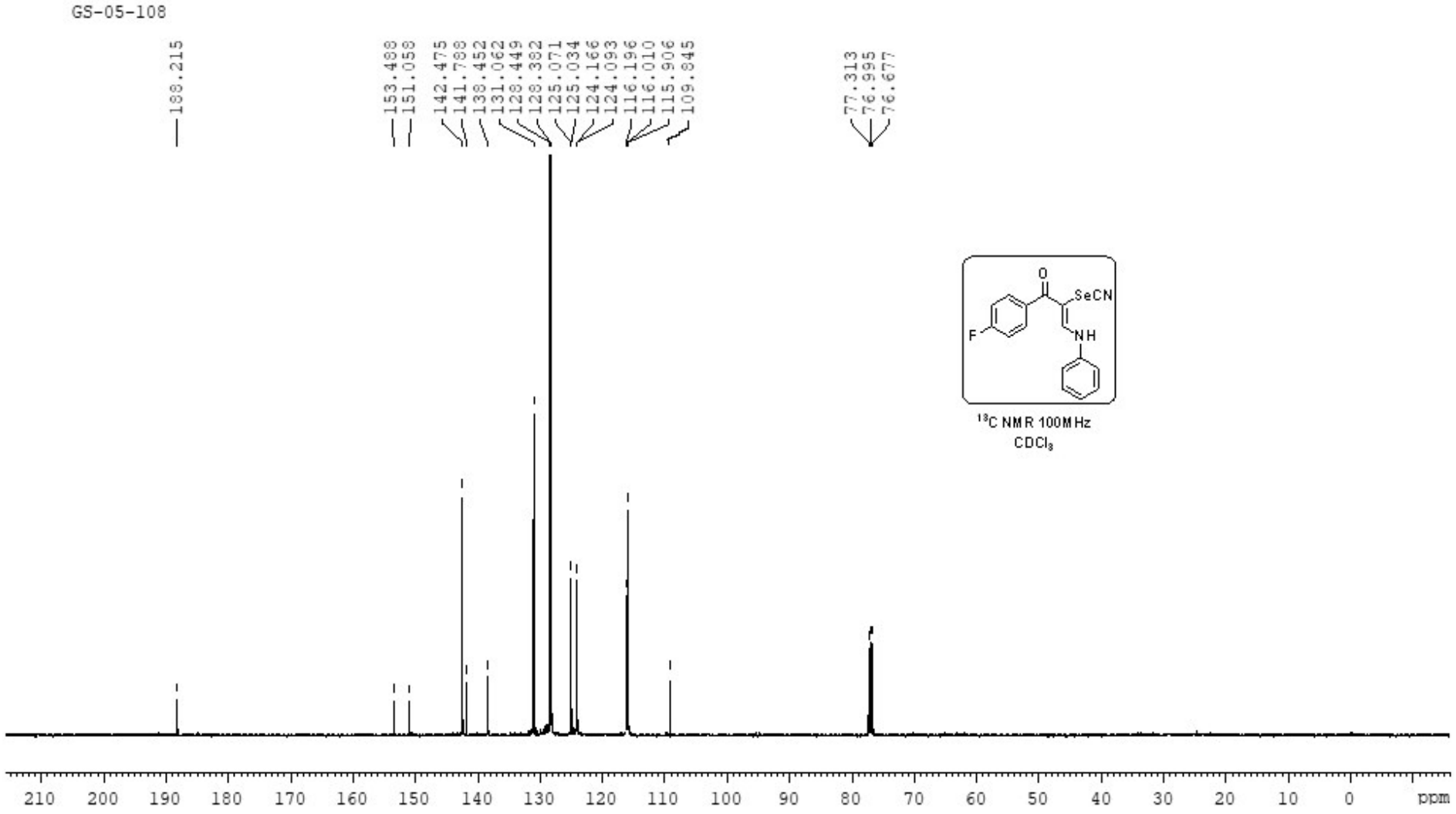


Fig 18. ^{13}C-NMR Spectrum of 1-(4-Fluorophenyl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2i)

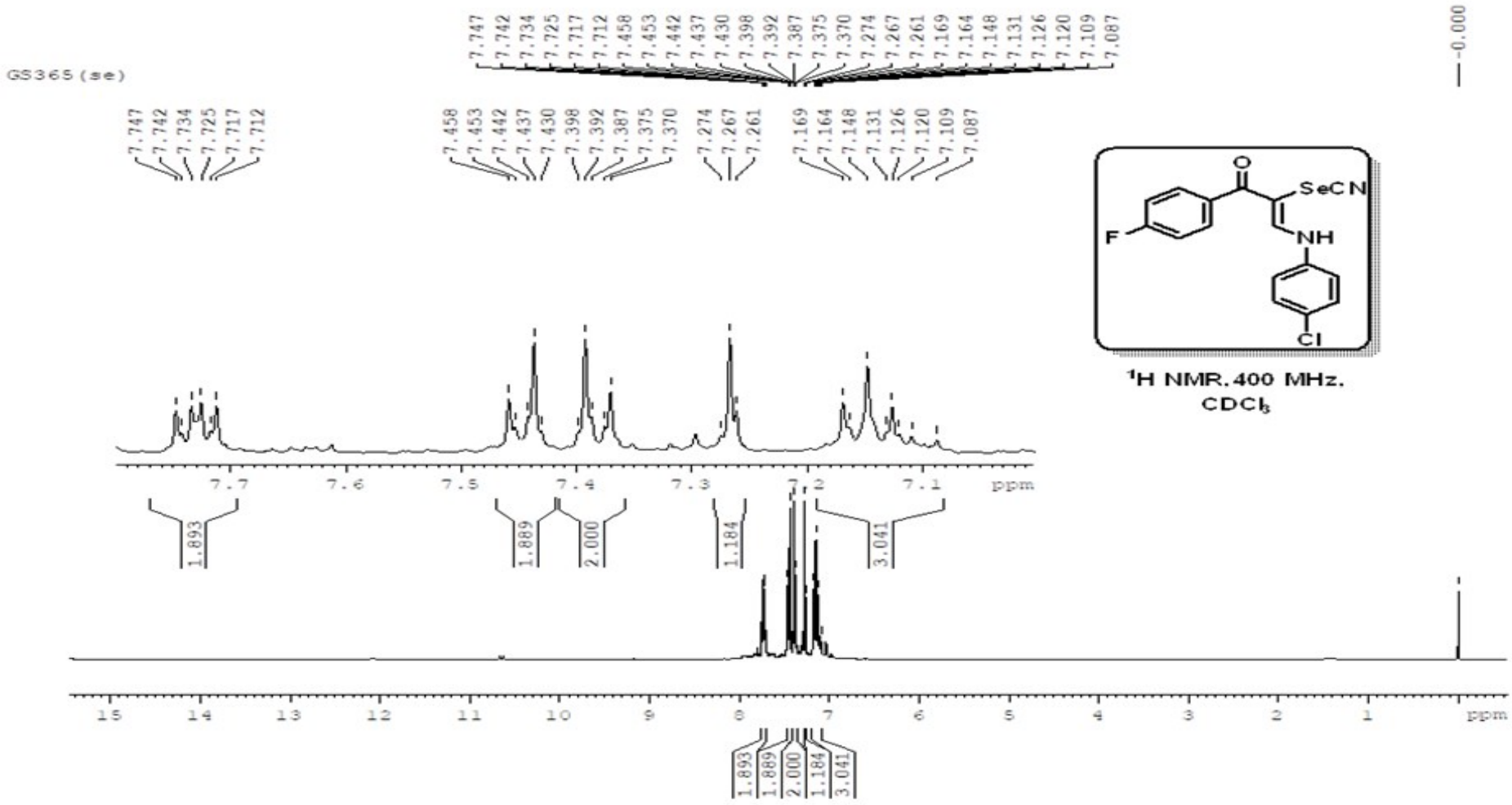


Fig 19. ^{1}H-NMR Spectrum of 3-(4-Chlorophenyl)amino-1-(4-fluorophenyl)-2-selenocyanatoprop-2-en-1-one-(2j)

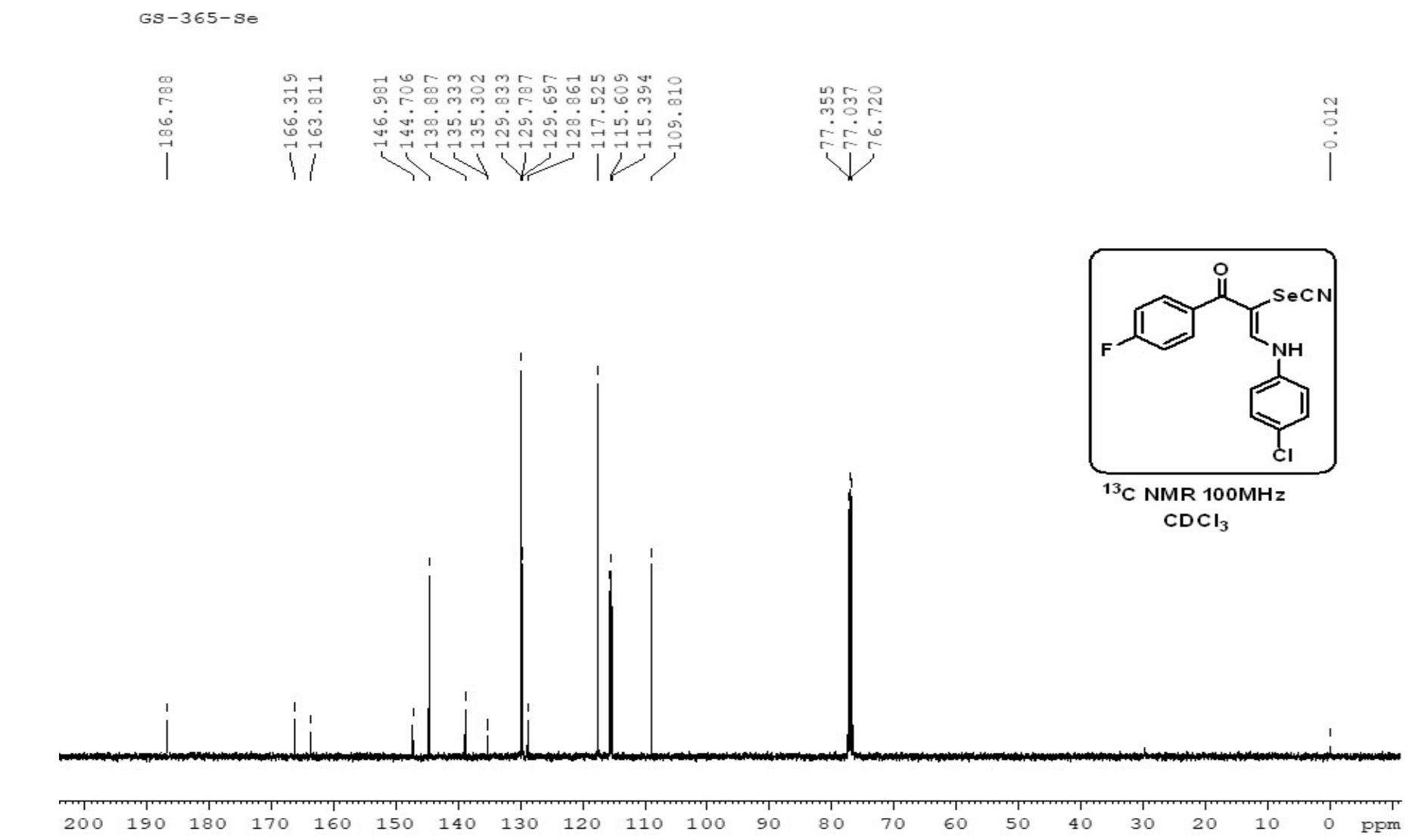


Fig 20. ^{13}C-NMR Spectrum of 3-(4-Chlorophenyl)amino-1-(4-fluorophenyl)-2-selenocyanatoprop-2-en-1-one-(2j)

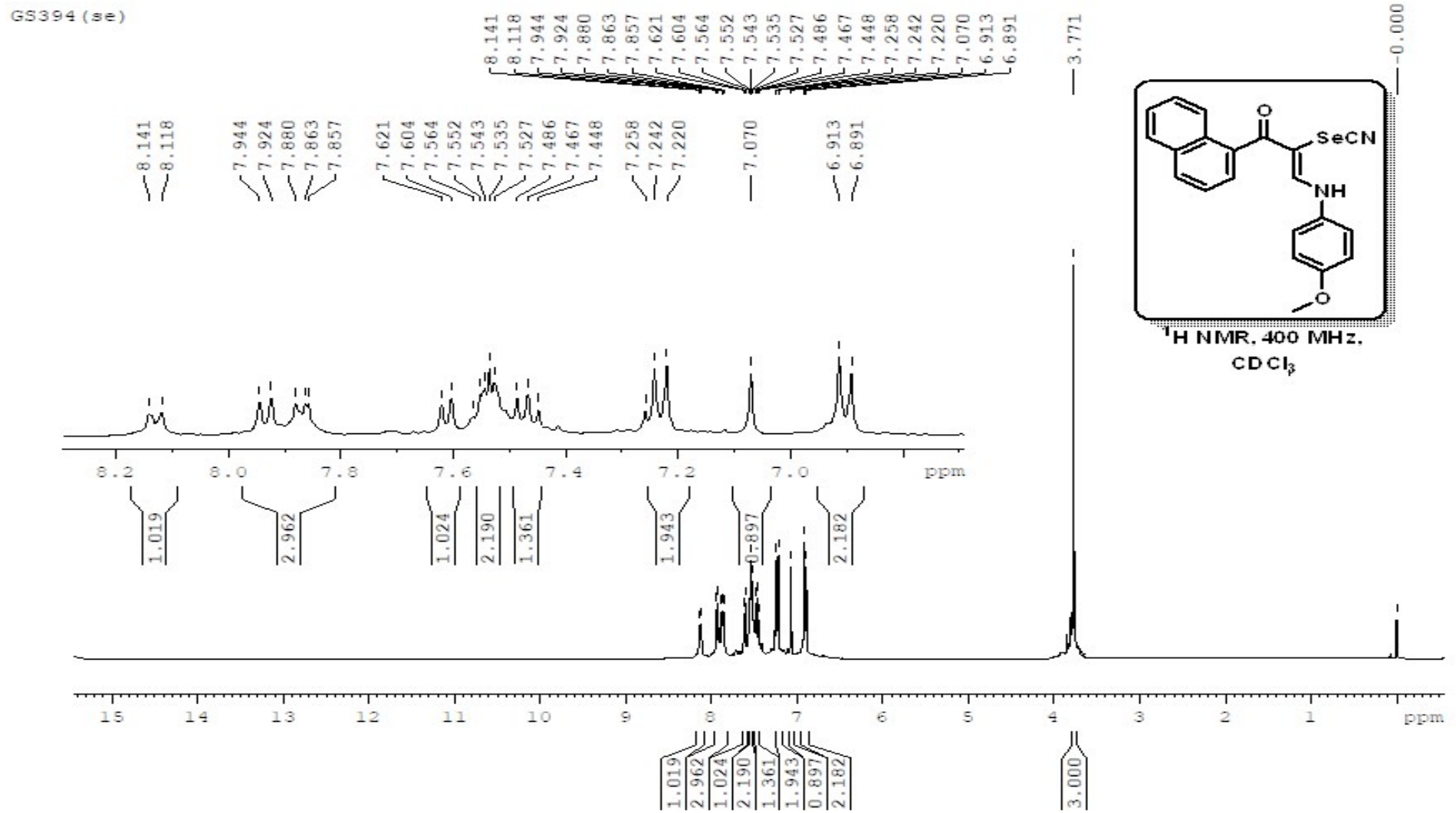


Fig 21. ^{1}H-NMR Spectrum of 3-(4-Methoxyphenyl)amino-1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2k)

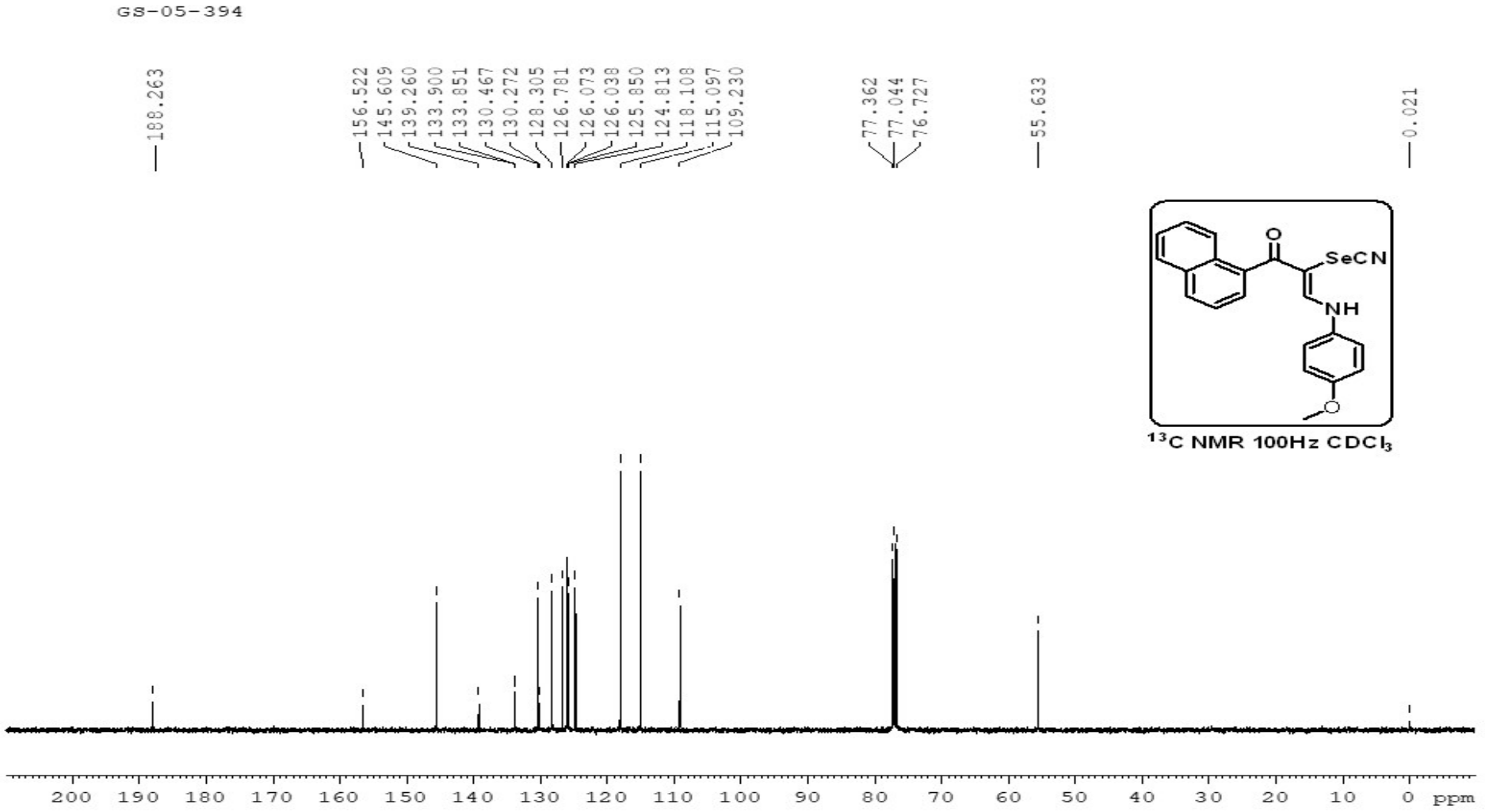


Fig 22. ^{13}C-NMR Spectrum of 3-(4-Methoxyphenyl)amino-1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2k)

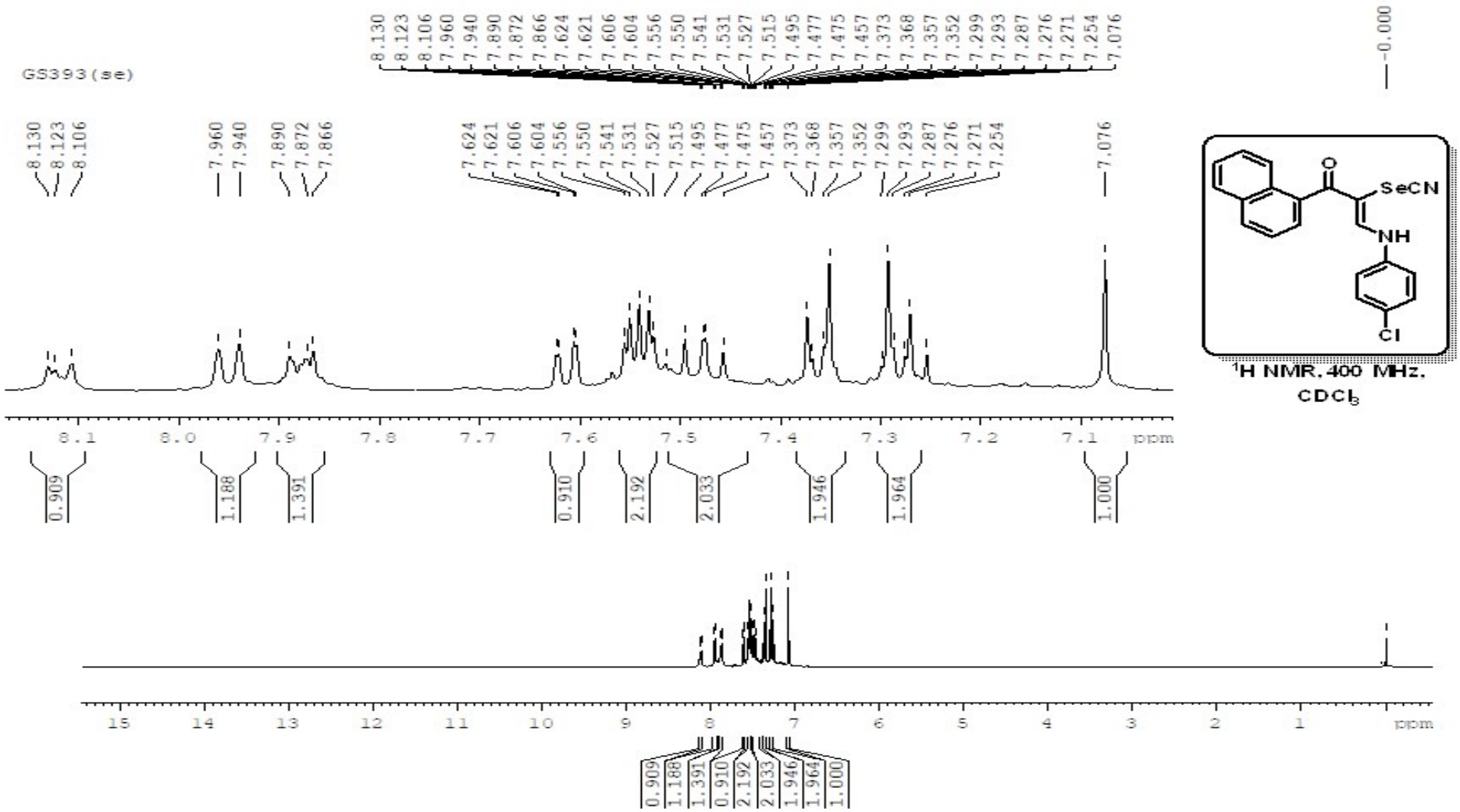


Fig 23. ^{1}H-NMR Spectrum of 3-(4-Chlorophenyl)amino -1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2l)

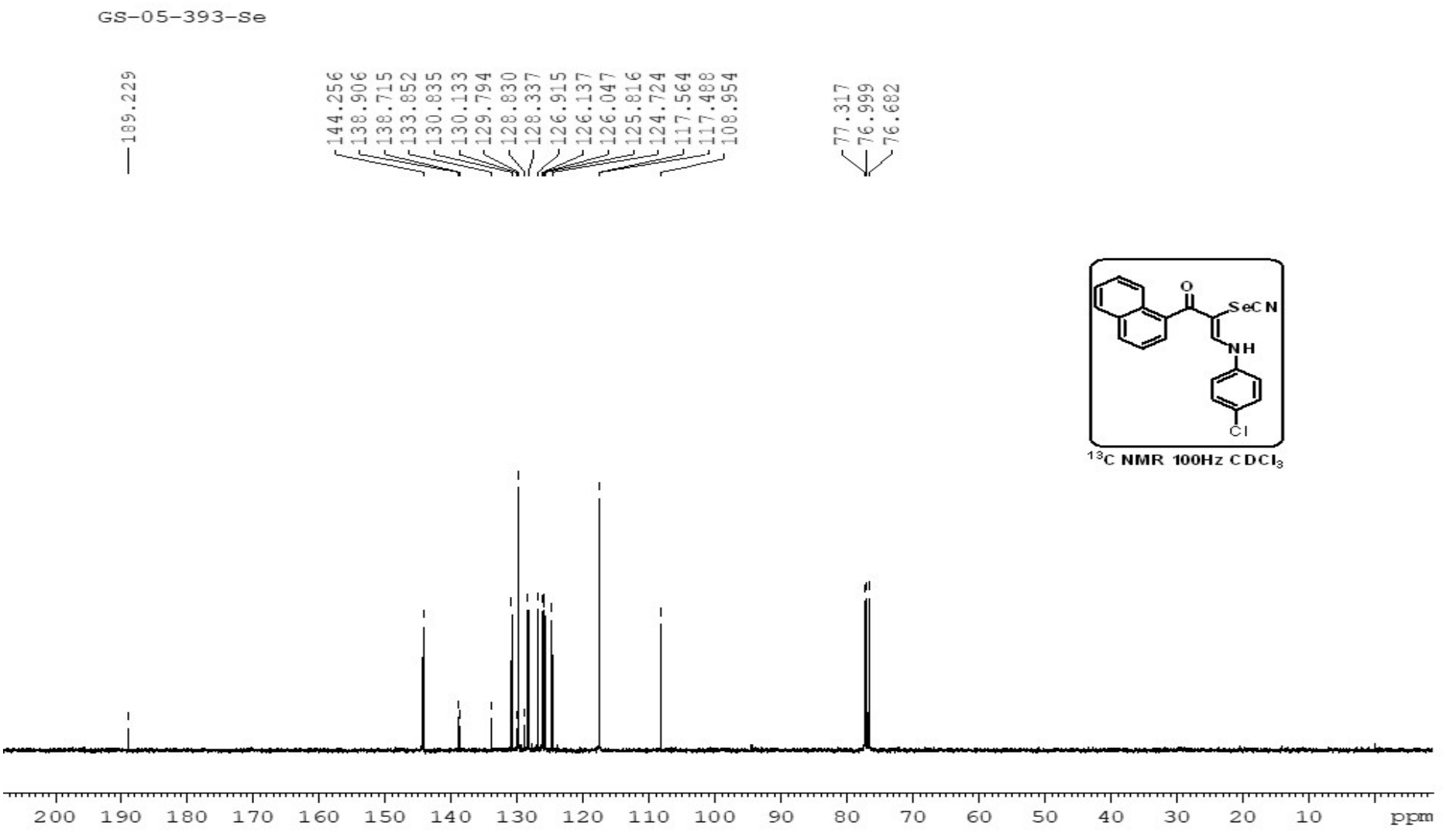


Fig 24. ^{13}C-NMR Spectrum of 3-(4-Chlorophenyl)amino -1-(naphthalen-1-yl)-2-selenocyanatoprop-2-en-1-one-(2l)

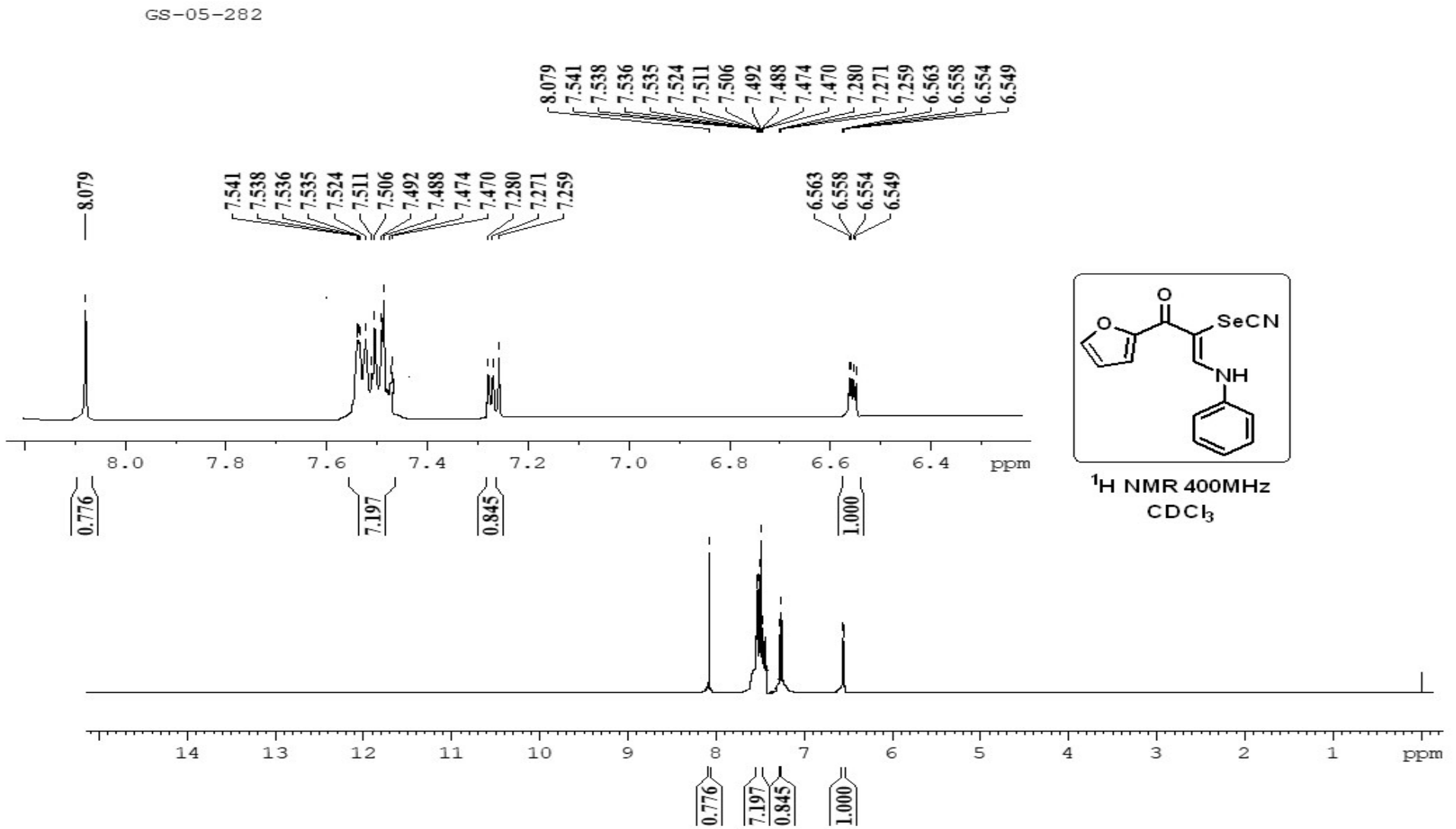


Fig 25. ^{1}H-NMR Spectrum of 1-(Furan-2-yl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2m)

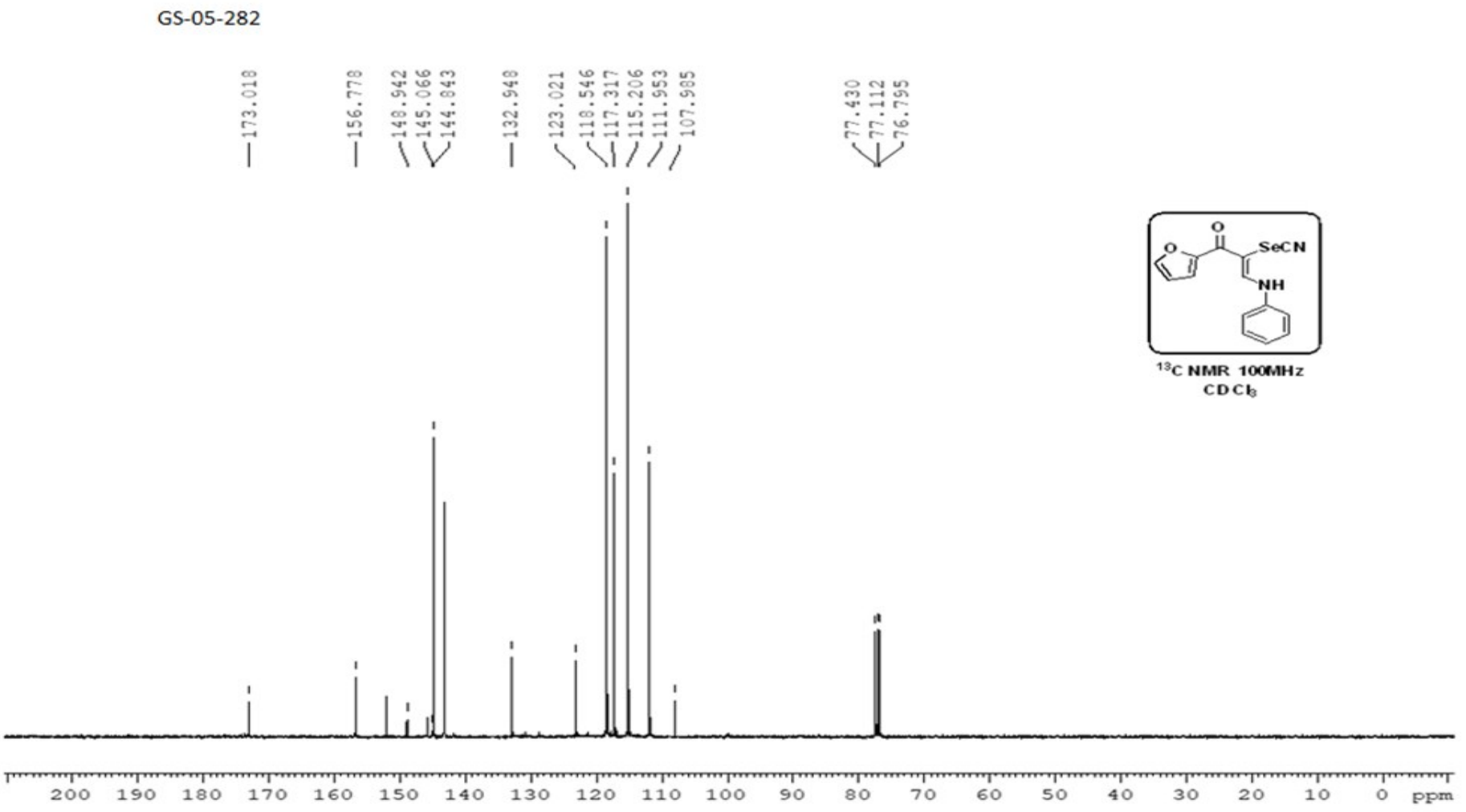


Fig 26. ^{13}C-NMR Spectrum of 1-(Furan-2-yl)-3-(phenylamino)-2-selenocyanatoprop-2-en-1-one-(2m)

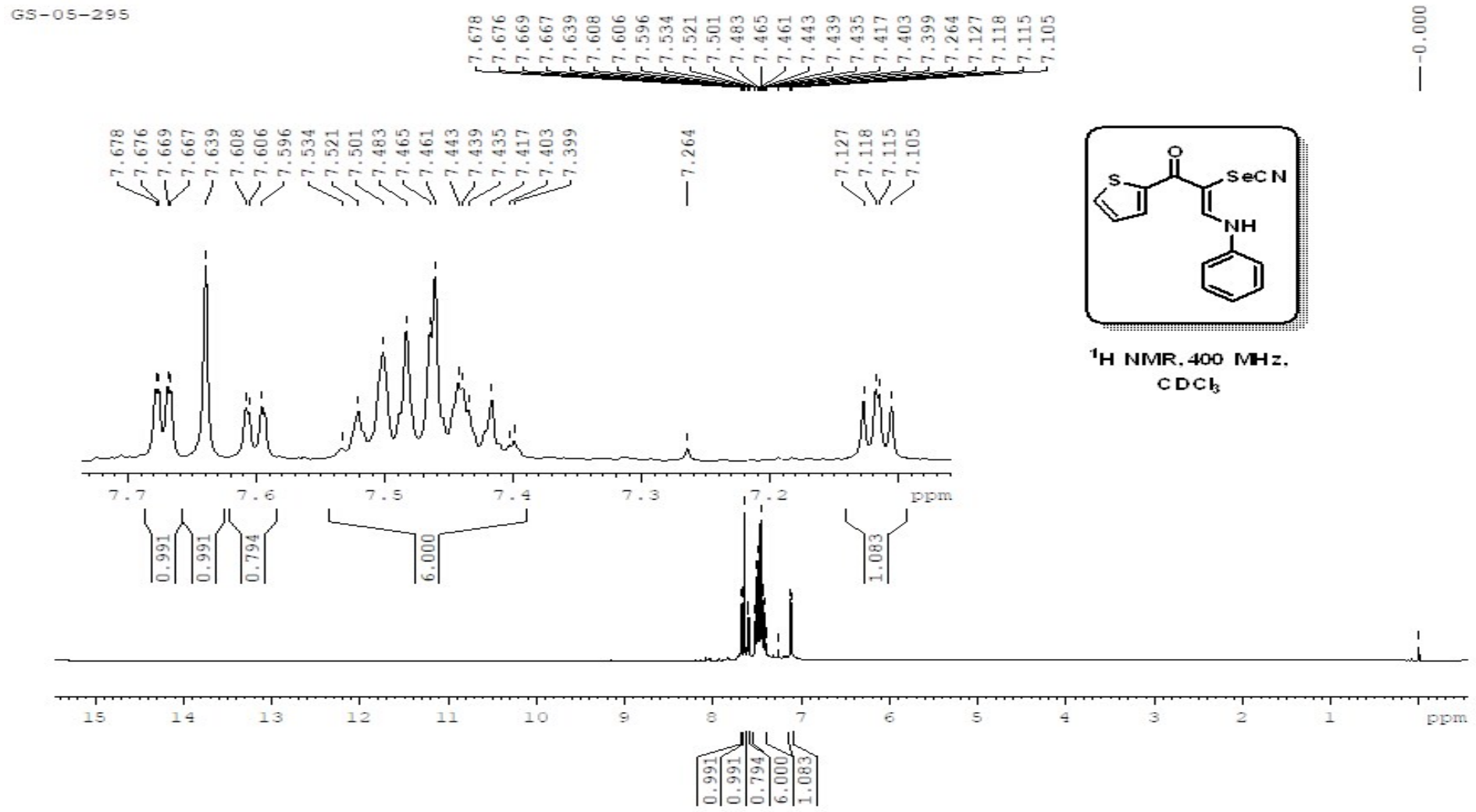


Fig 27. [1]H-NMR Spectrum of 3-(Phenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2n)

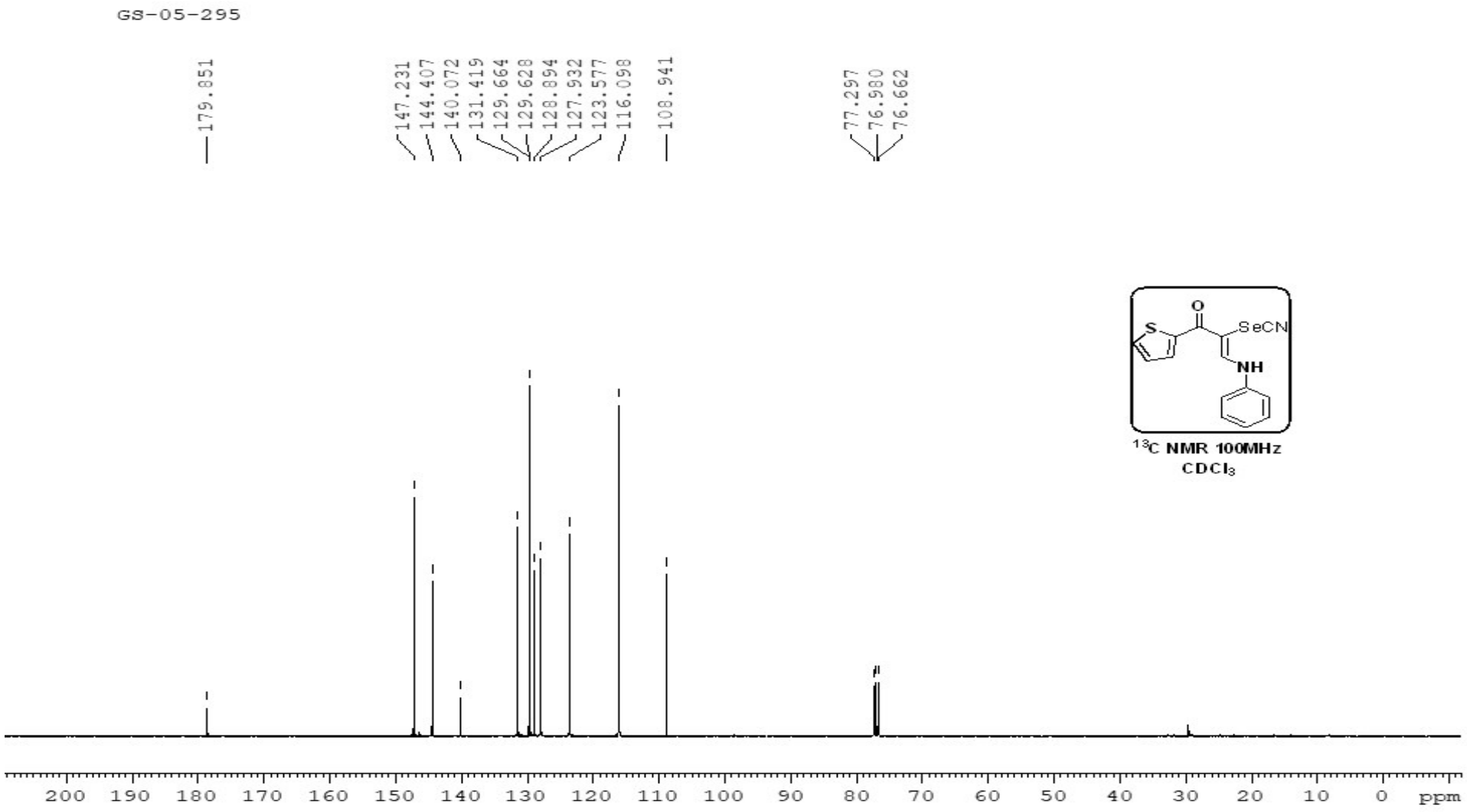


Fig 28. [1]C-NMR Spectrum of 3-(Phenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2n)

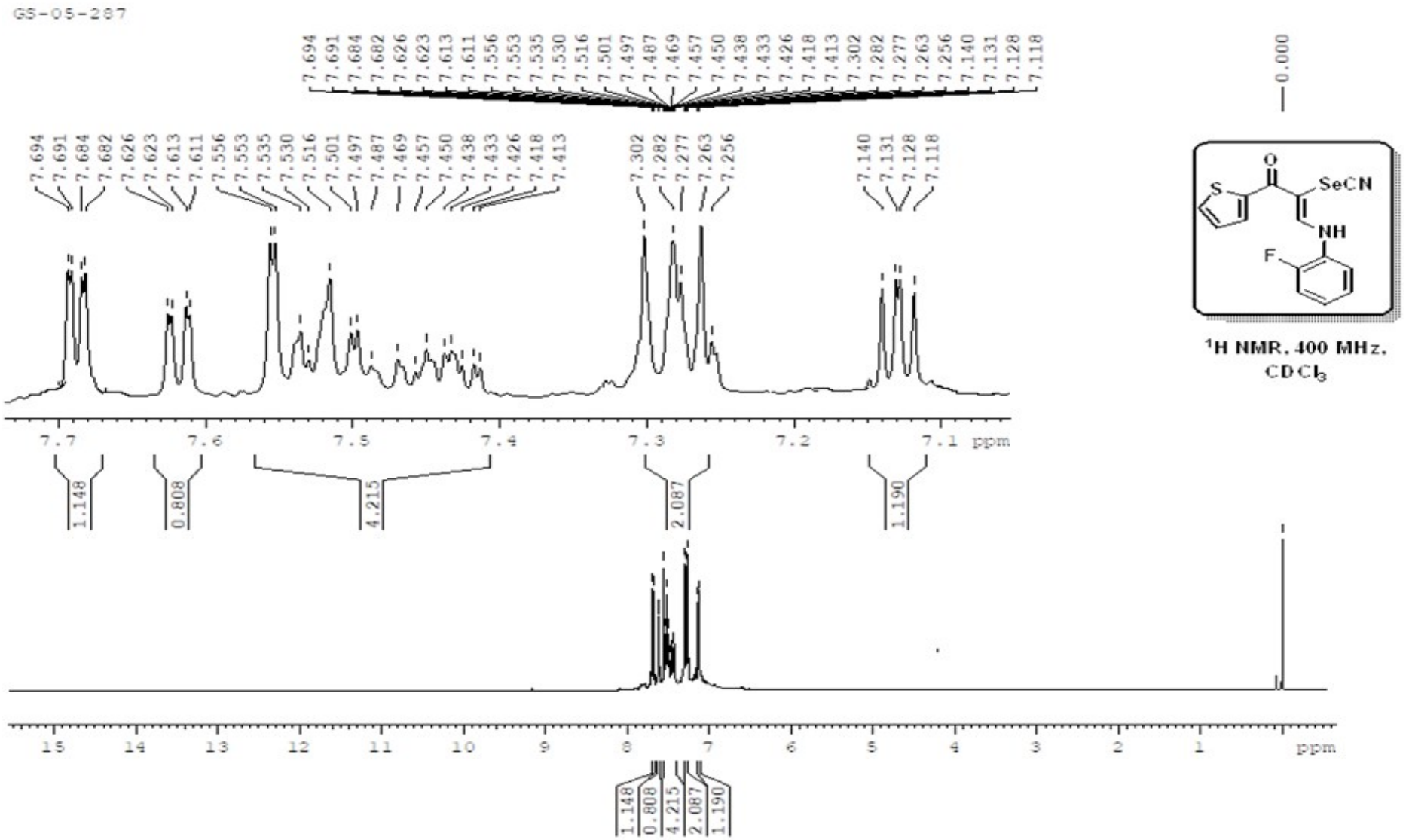


Fig.29 [1]H-NMR Spectrum of 3-(2-Fluorophenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2o)

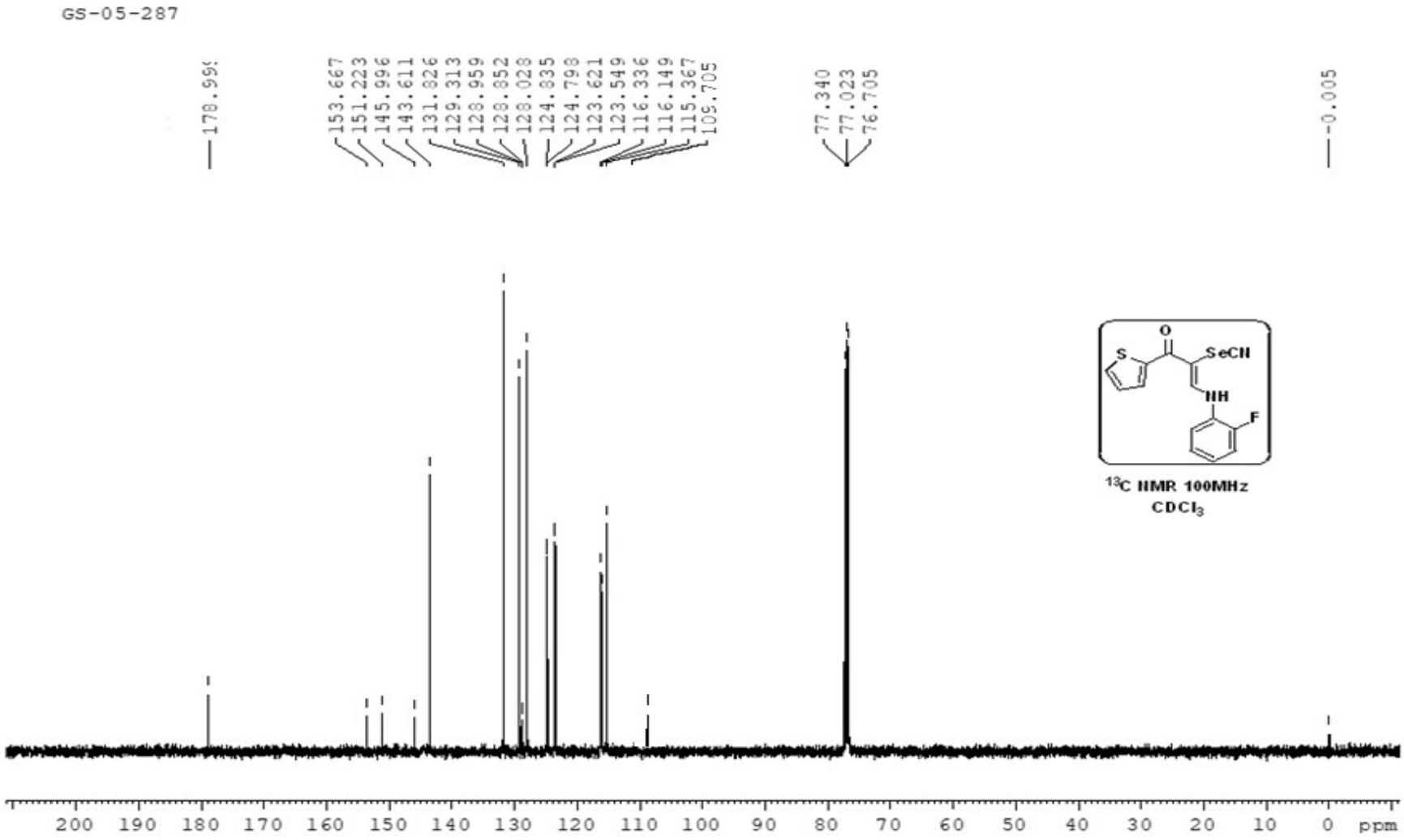


Fig 30. ^{13}C-NMR Spectrum of 3-(2-Fluorophenylamino)-2-selenocyanato-1-(thiophen-2-yl)prop-2-en-1-one-(2o)

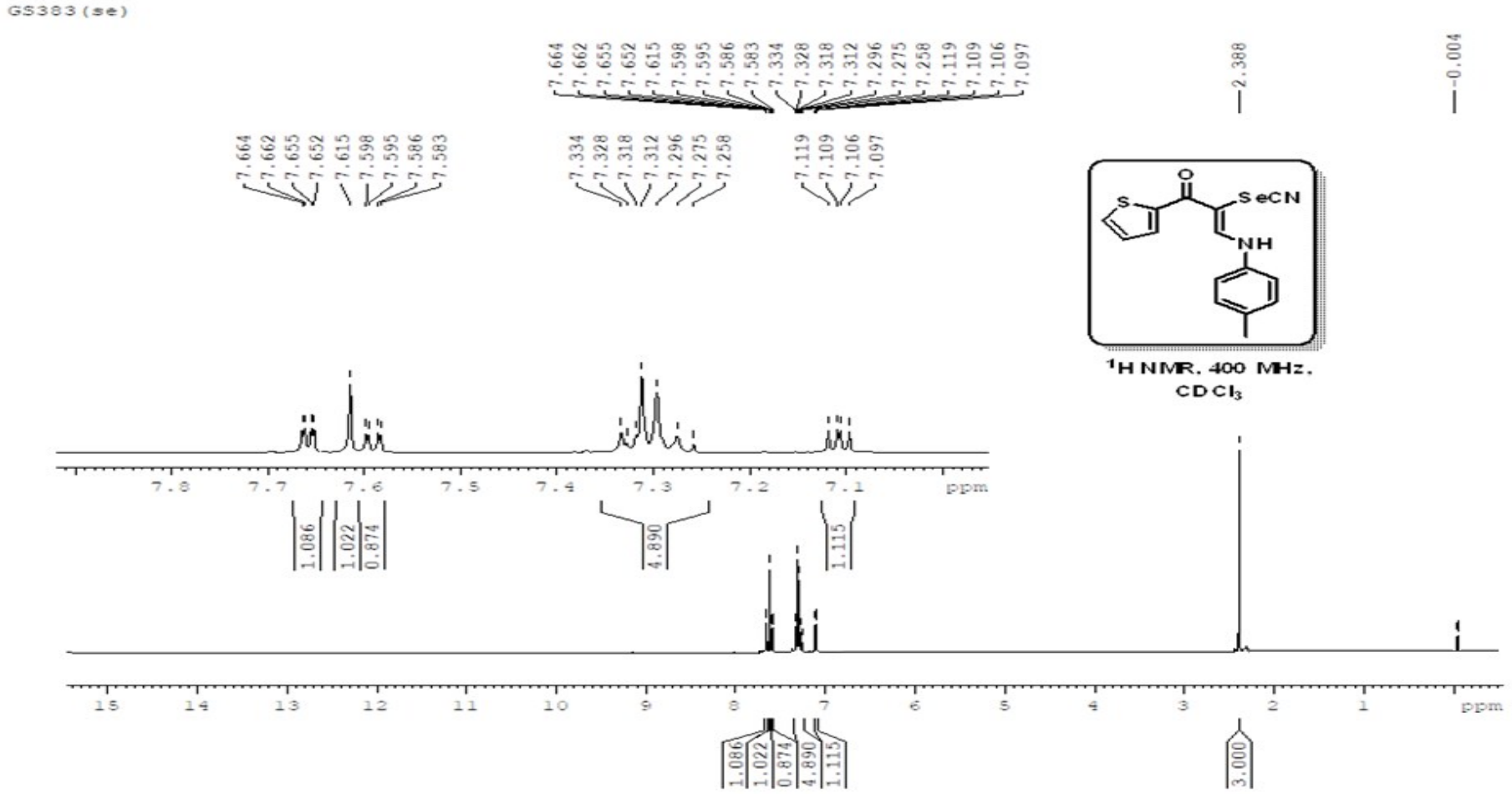


Fig 31. [1]H-NMR Spectrum of 2-Selenocyanato-1-(thiophen-2-yl)-3-(p-tolylamino)prop-2-en-1-one-(2p)

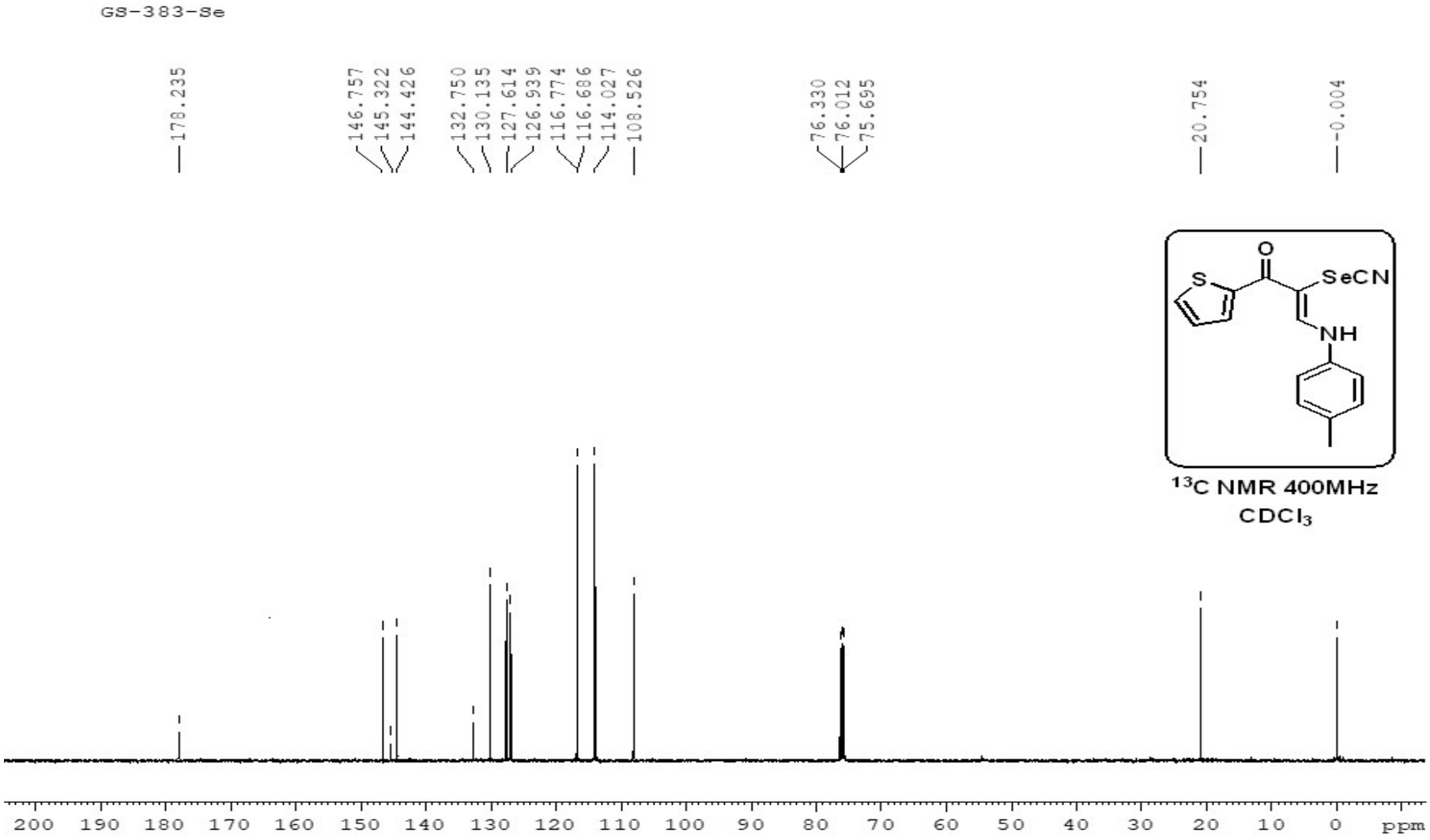


Fig 32. ^{13}C-NMR Spectrum of 2-Selenocyanato-1-(thiophen-2-yl)-3-(p-tolylamino)prop-2-en-1-one-(2p)

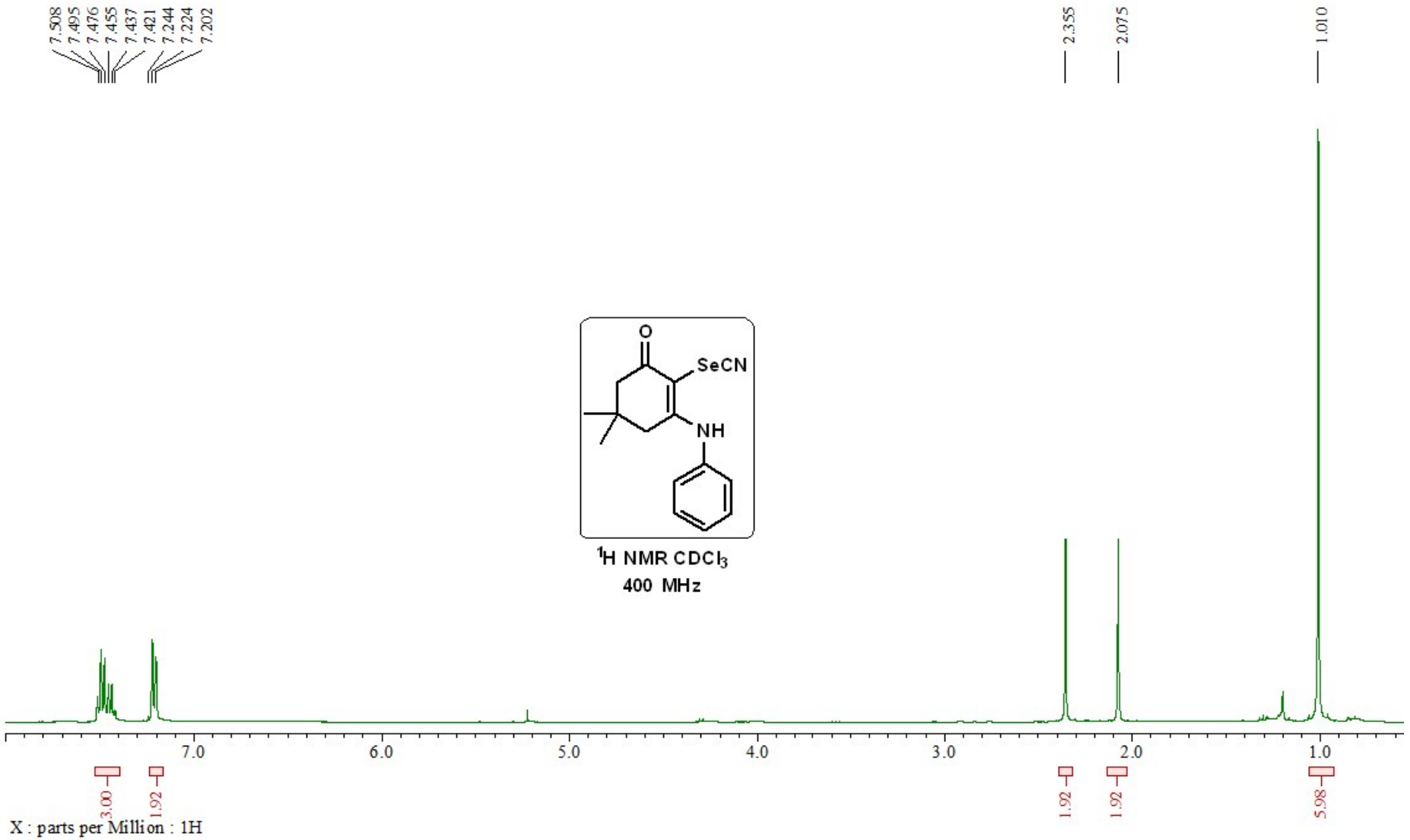


Fig 33. ^{1}H-NMR Spectrum of 5,5-Dimethyl-3-(phenylamino)-2-selenocyanatocyclohex-2-en-1-one-(4a)

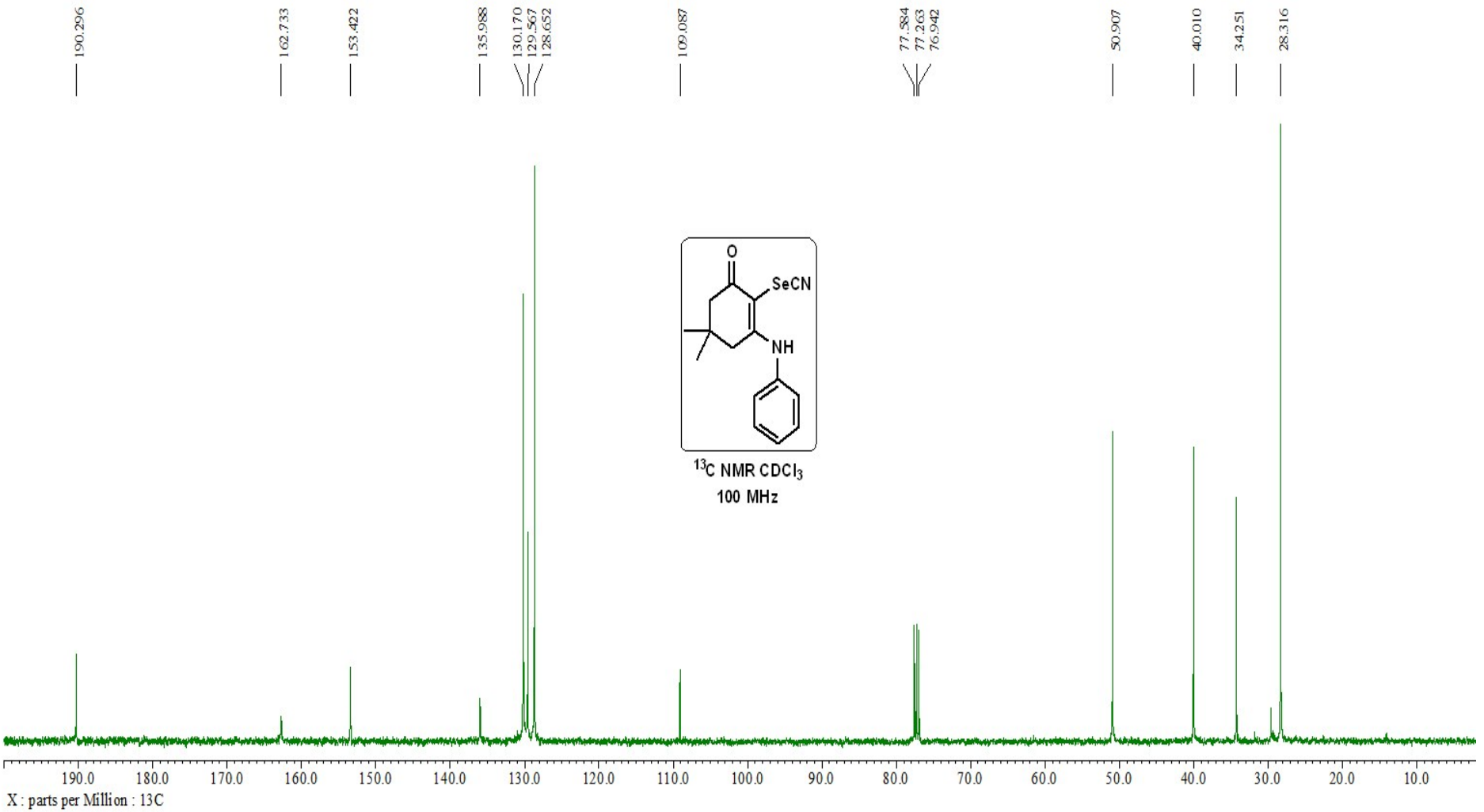


Fig 34. ^{13}C-NMR Spectrum of 5,5-Dimethyl-3-(phenylamino)-2-selenocyanatocyclohex-2-en-1-one-(4a)

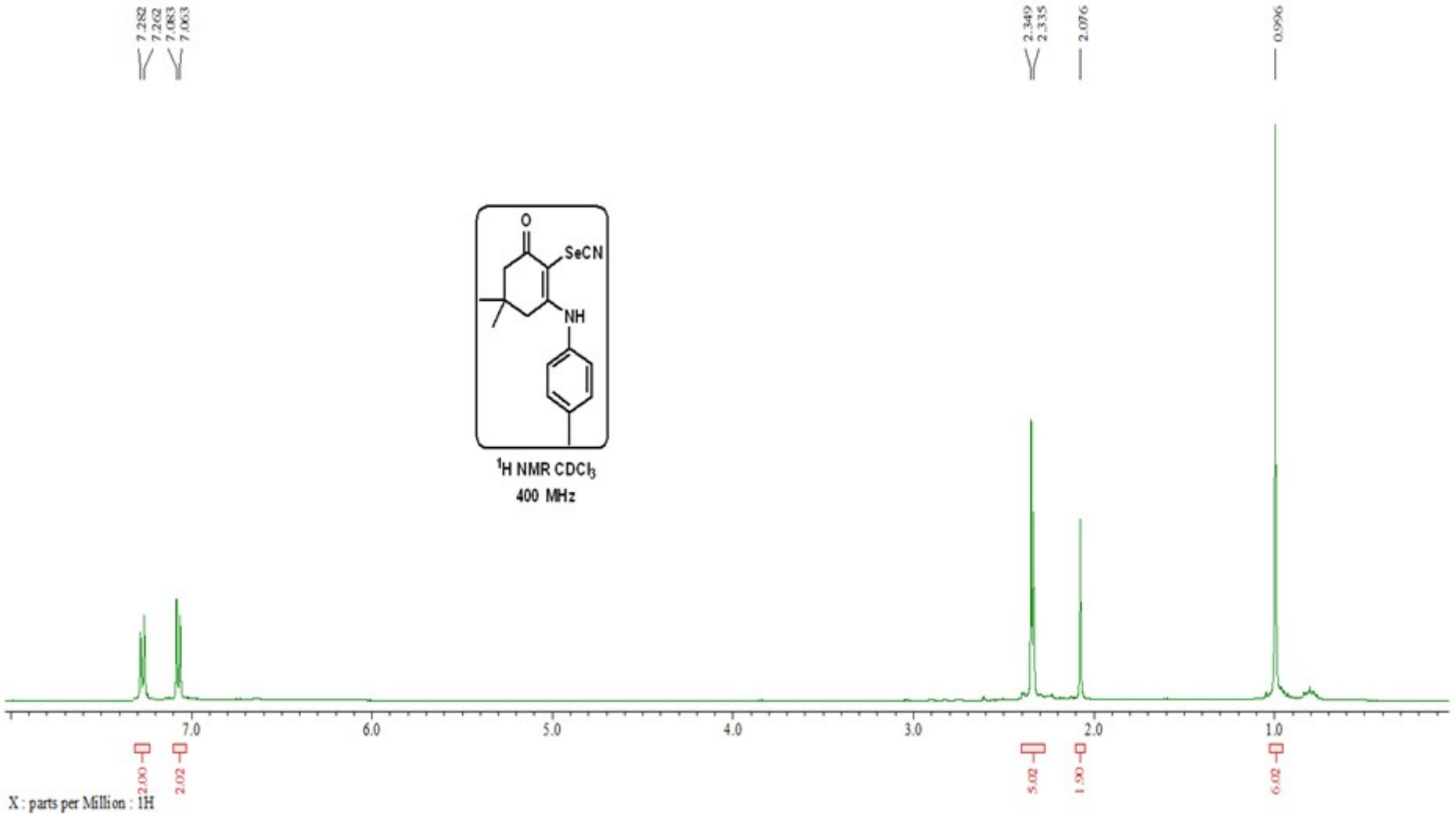


Fig 35. ^{1}H-NMR Spectrum of 5,5-Dimethyl-2-selenocyanato-3-(p-tolylamino)cyclohex-2-en-1-one-(4b)

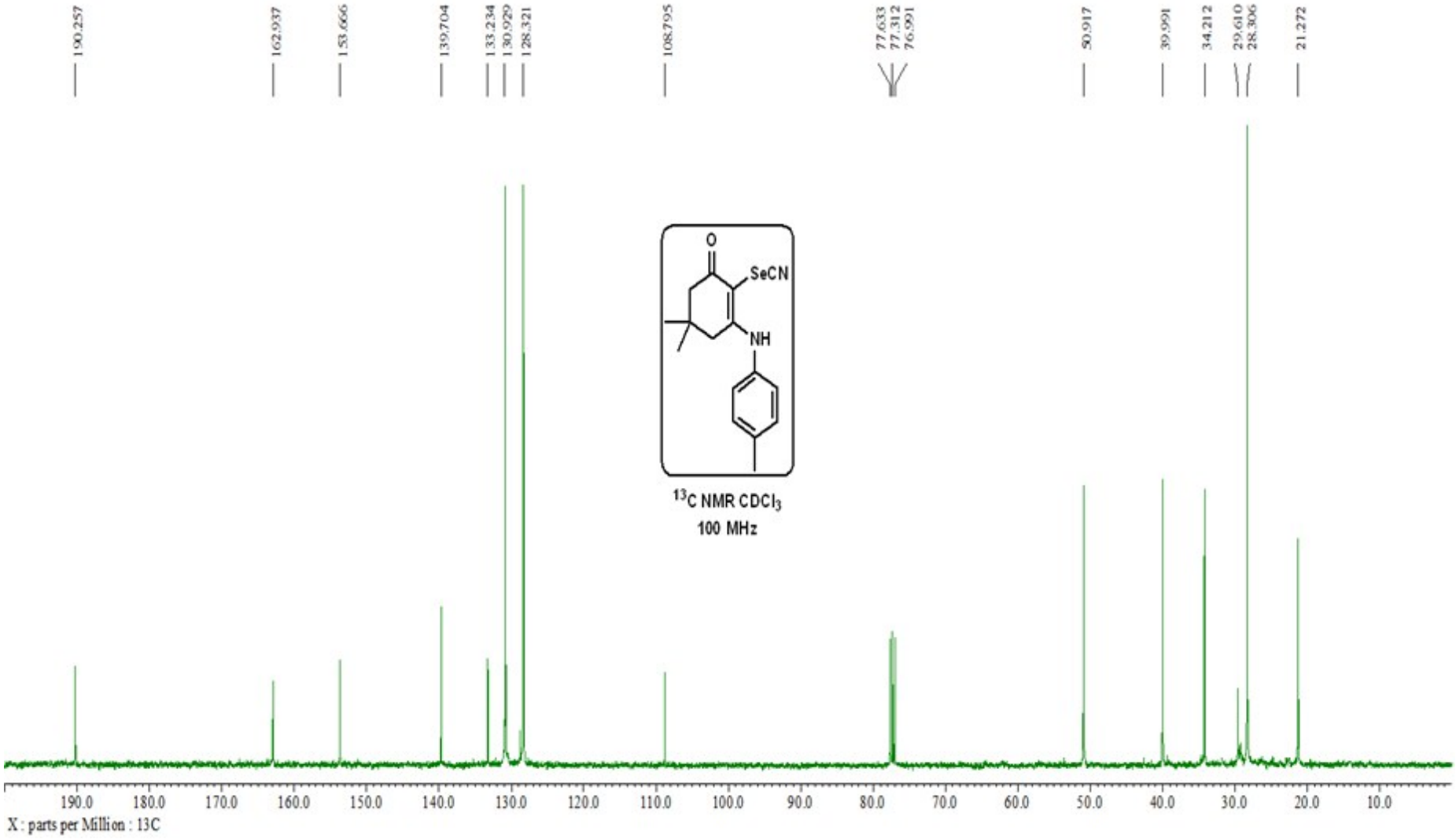


Fig 36. ^{13}C-NMR Spectrum of 5,5-Dimethyl-2-selenocyanato-3-(p-tolylamino)cyclohex-2-en-1-one-(4b)

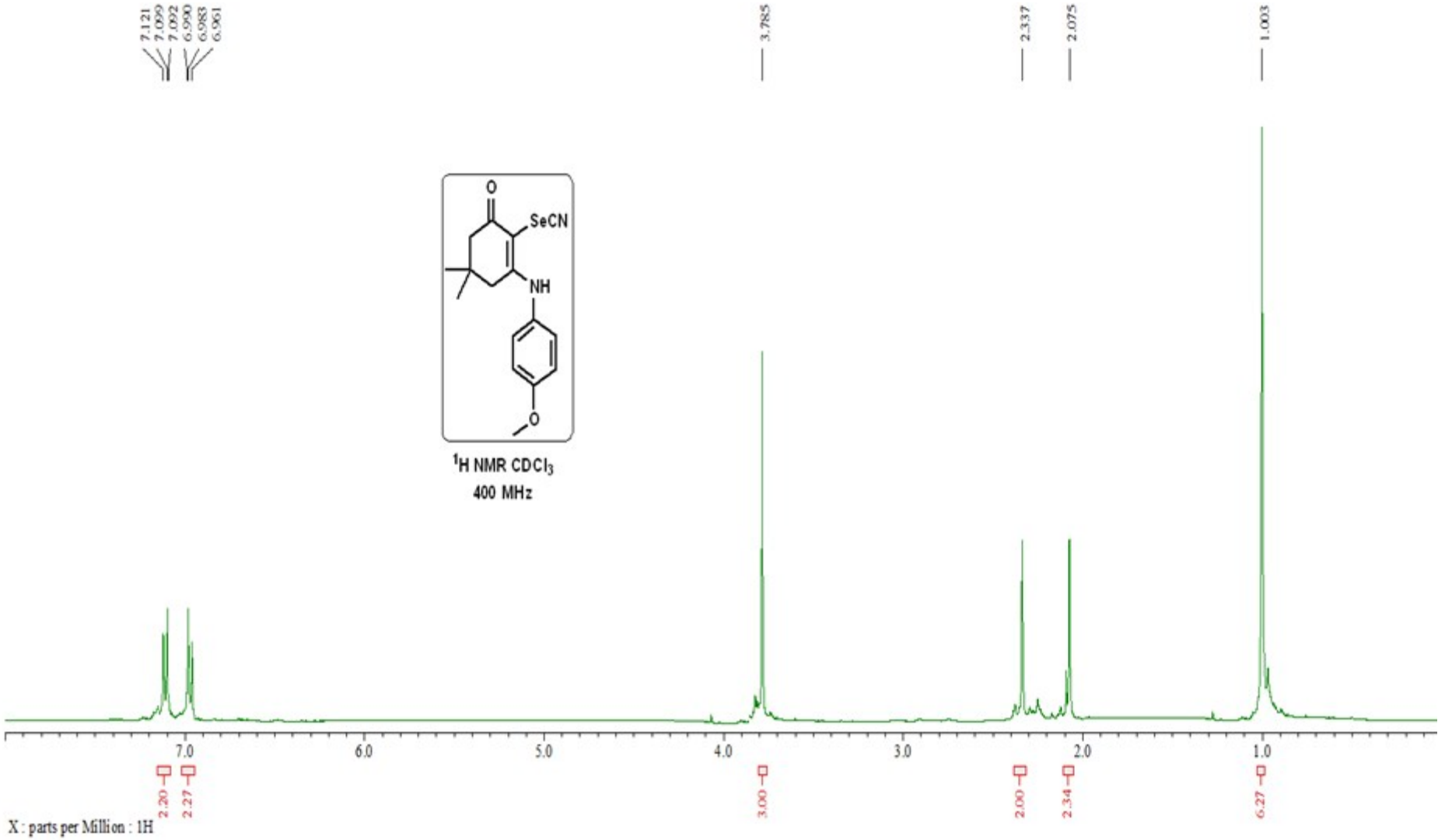


Fig 37. ^{1}H-NMR Spectrum of 3-((4-Methoxyphenyl)amino)-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4c)

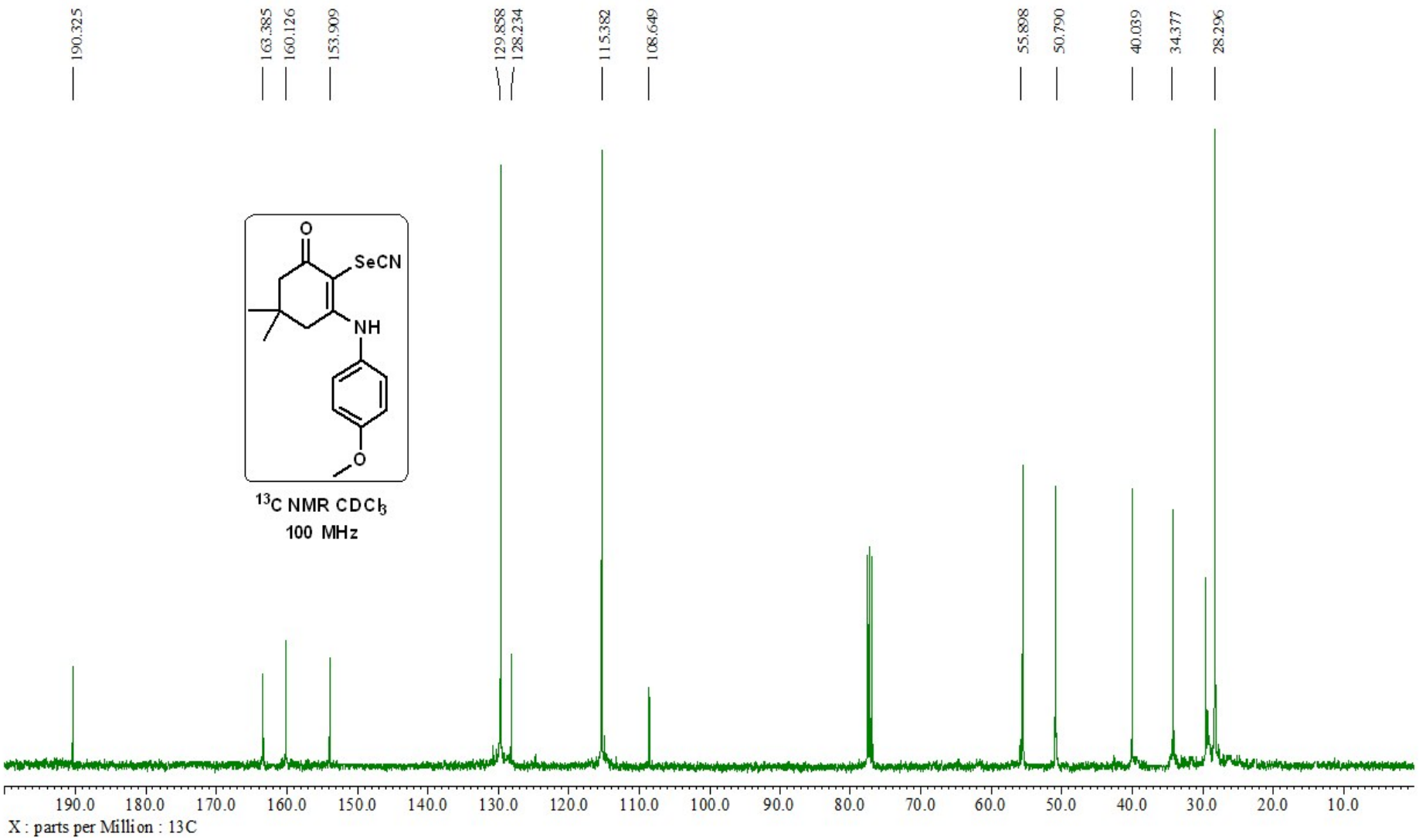


Fig 38. ^{13}C-NMR Spectrum of 3-(4-Methoxyphenyl)amino-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4c)

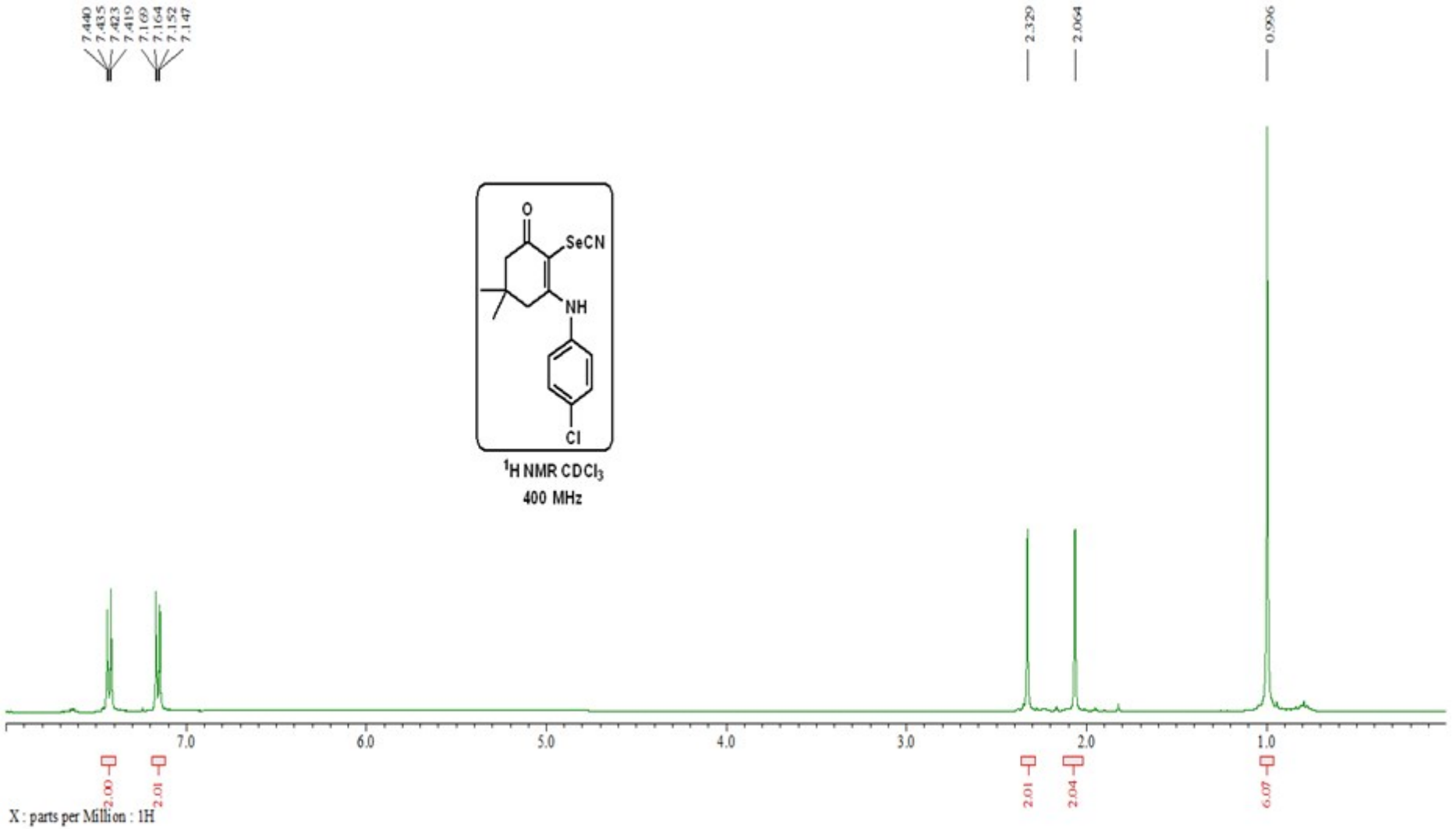


Fig 39. ^{1}H-NMR Spectrum of 3-(4-Chlorophenyl)amino-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4d)

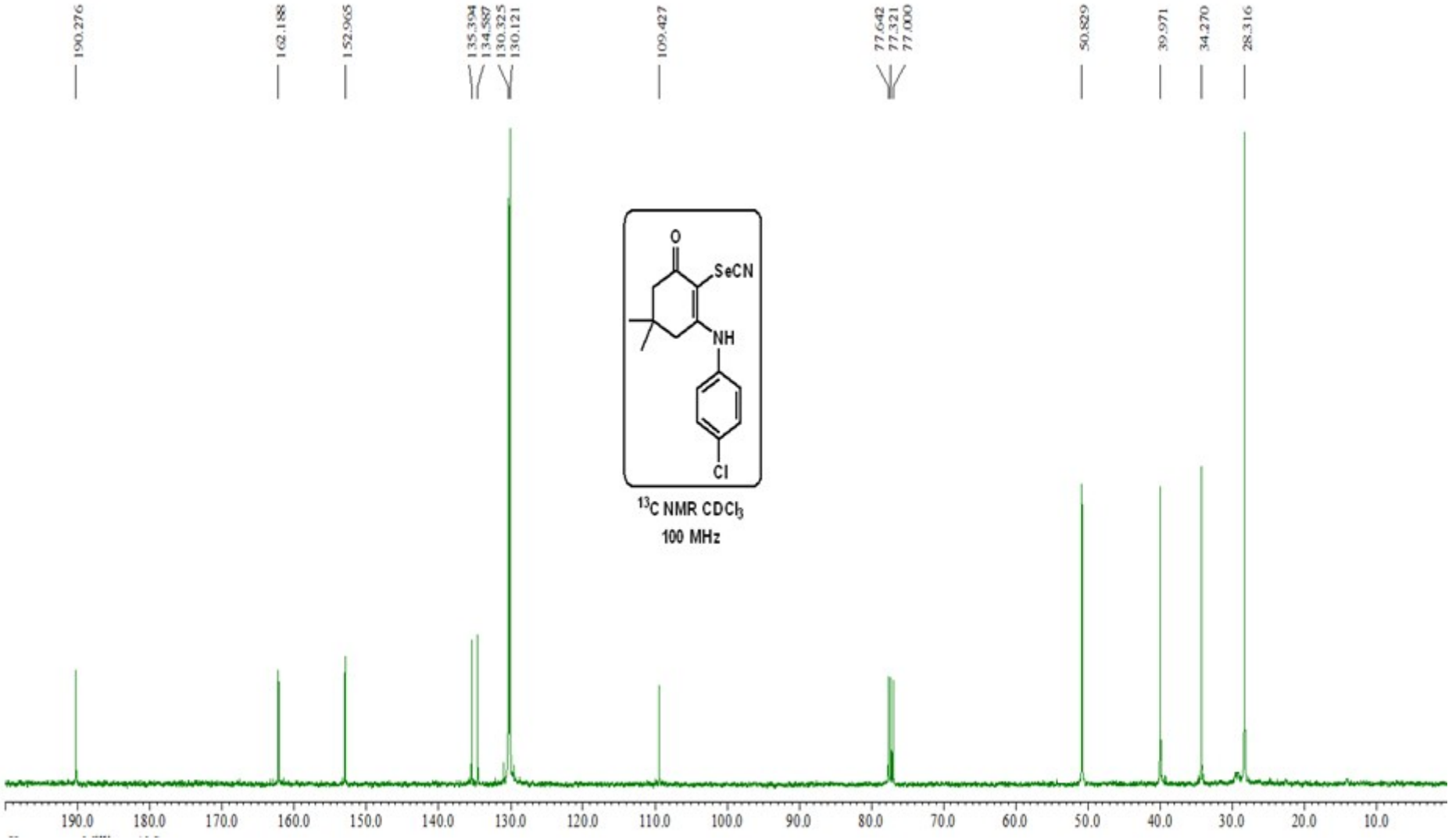


Fig 40. ^{13}C-NMR Spectrum of 3-(4-Chlorophenyl)amino-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4d)

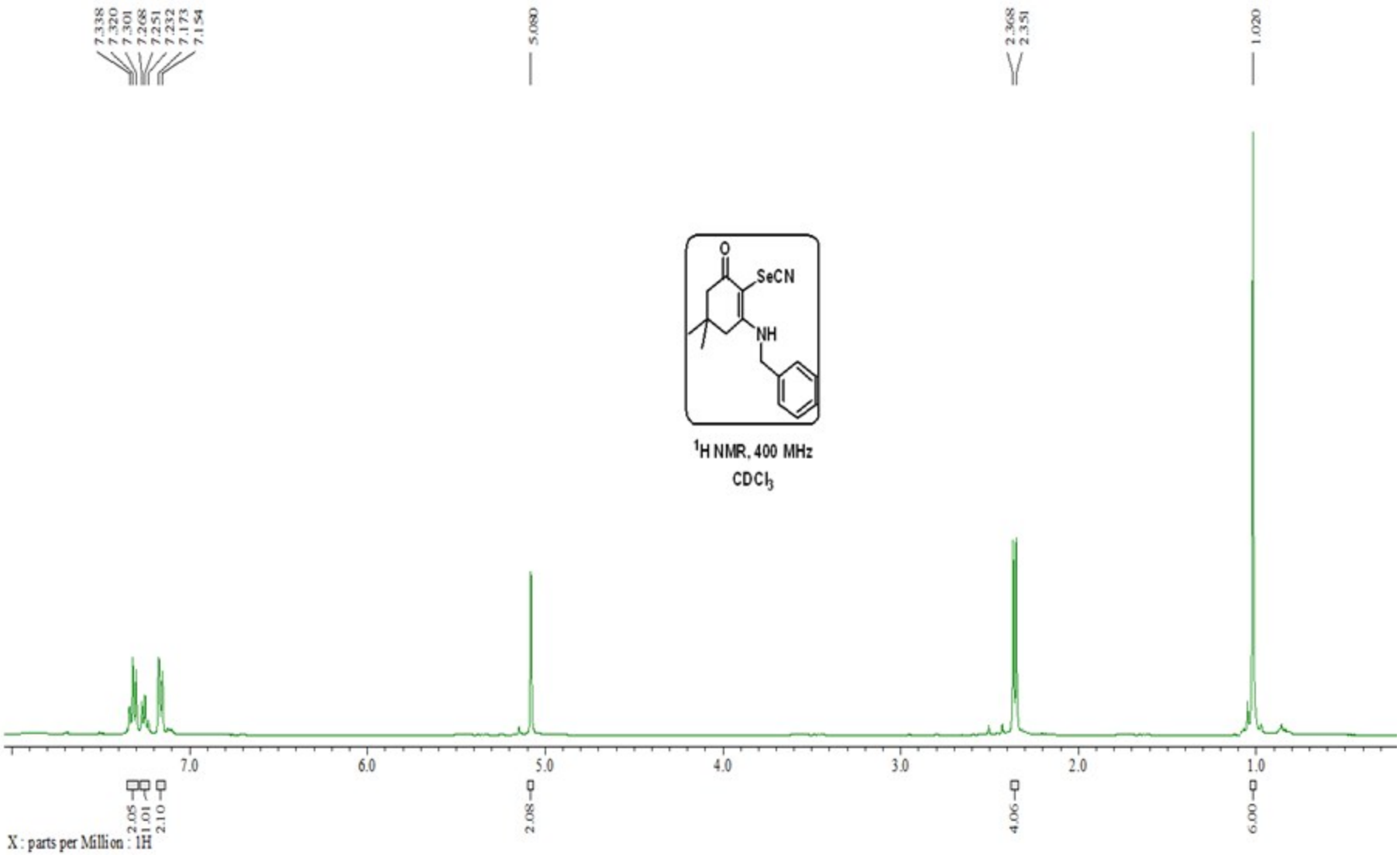


Fig 41. ^{1}H-NMR Spectrum of 3-(Benzylamino)-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4e)

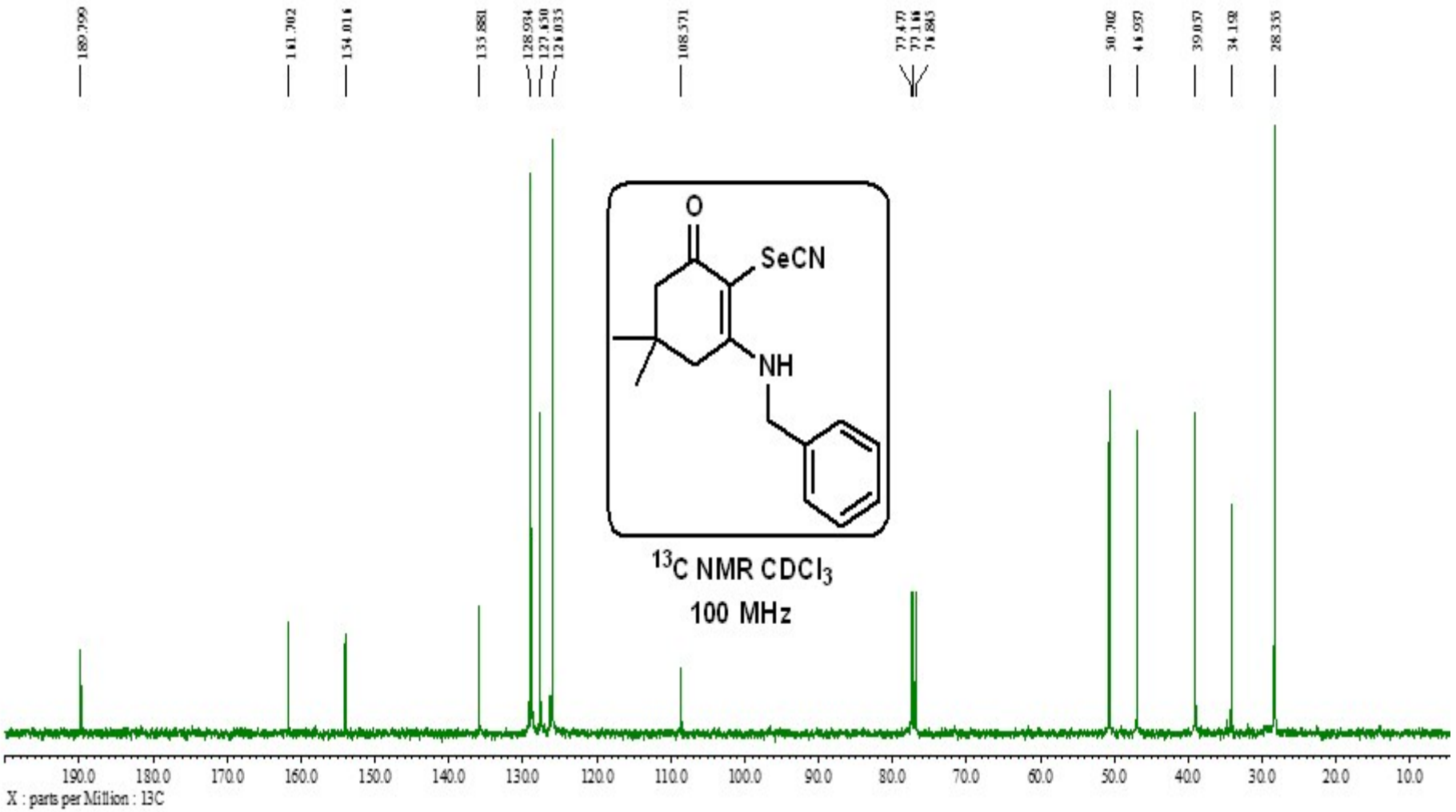


Fig 42. ^{13}C-NMR Spectrum of 3-(Benzylamino)-5,5-dimethyl-2-selenocyanatocyclohex-2-en-1-one-(4e)

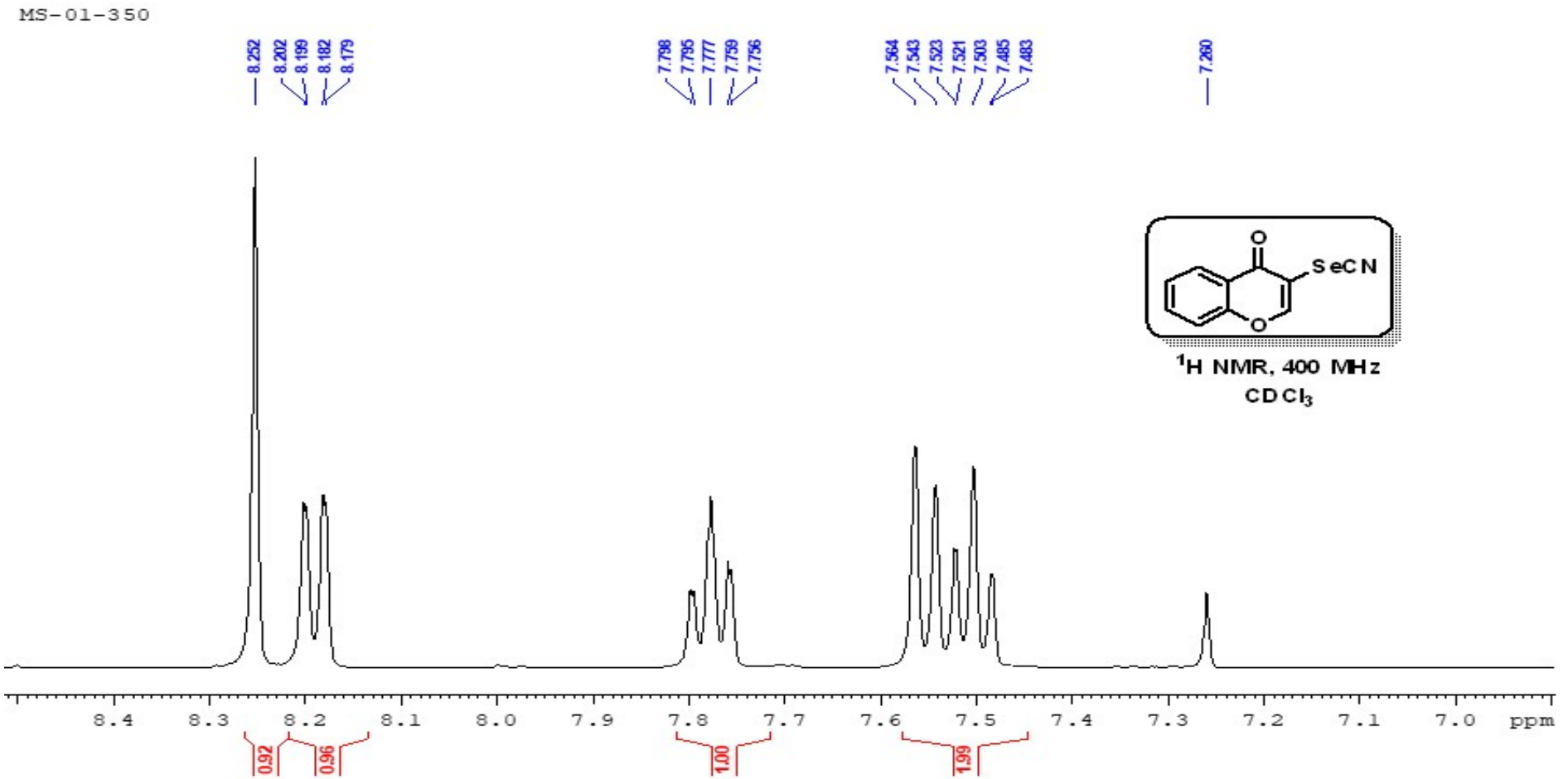


Fig 43. ^{1}H-NMR Spectrum of 3-Selenocyanato-4H-chromen-4-one-(6a)

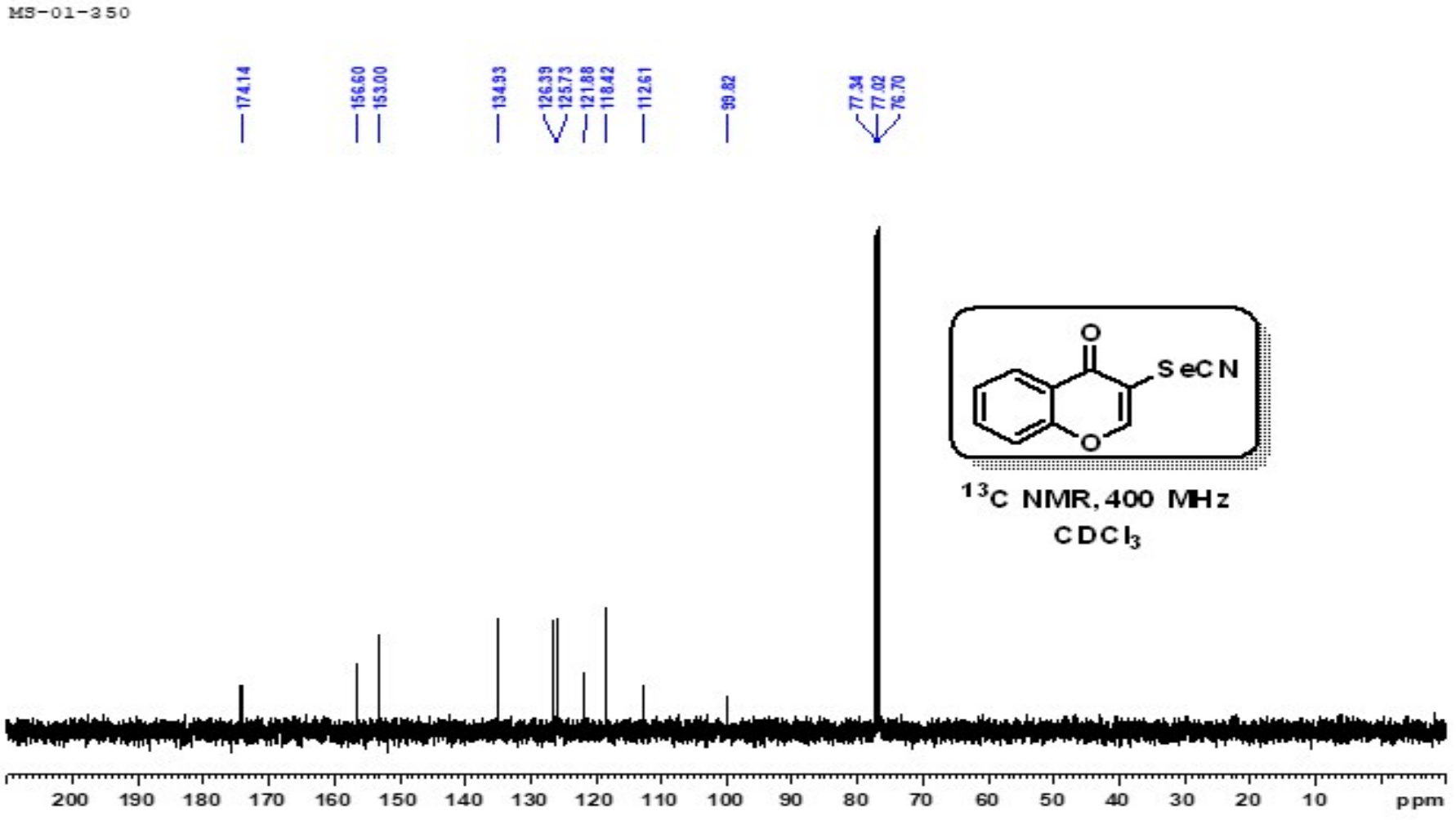


Fig 44. ^{13}C-NMR Spectrum of 3-Selenocyanato-4H-chromen-4-one-(6a)

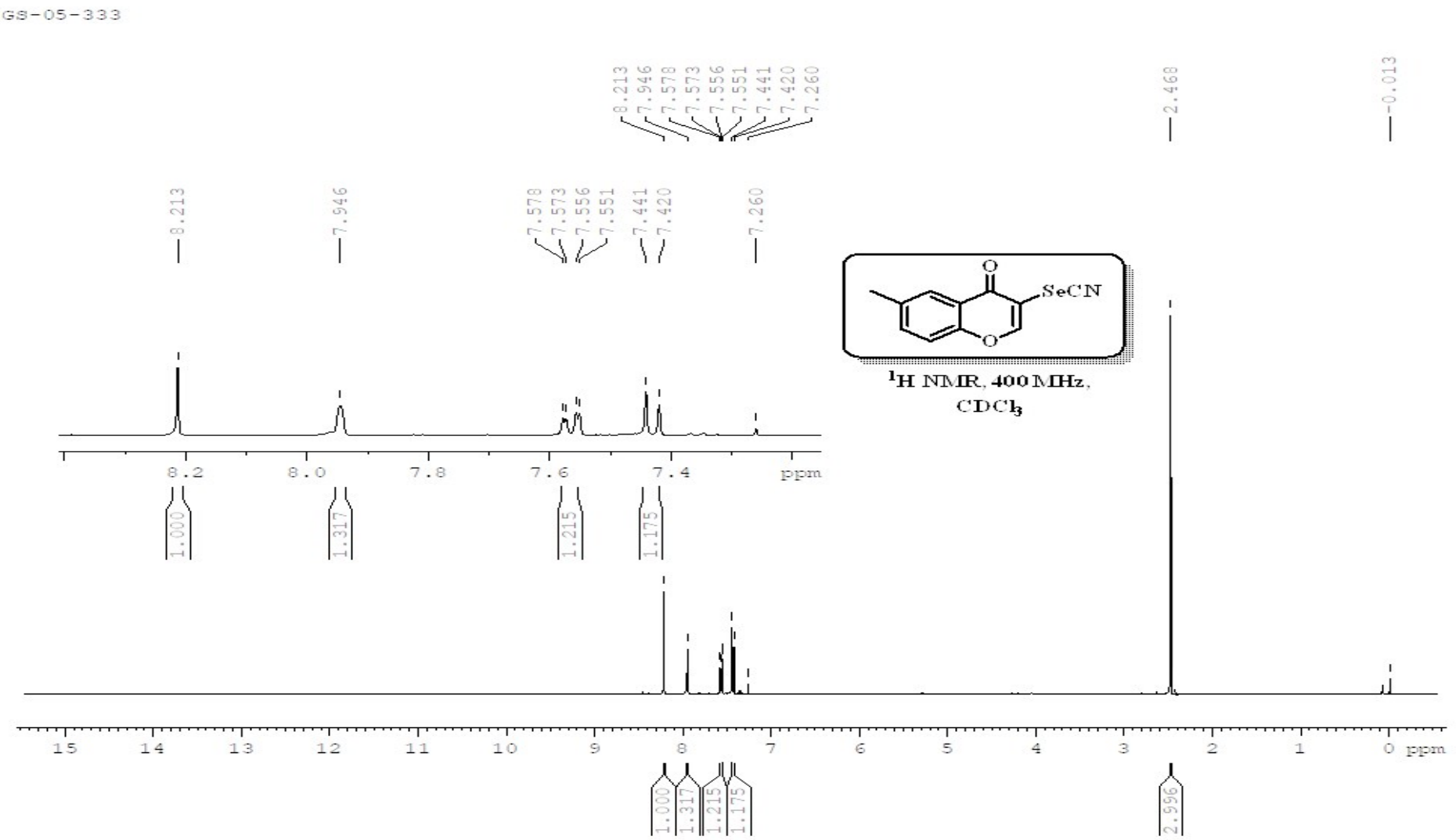


Fig 45. [1]H-NMR Spectrum of 6-Methyl-3-selenocyanato-4H-chromen-4-one-(6b)

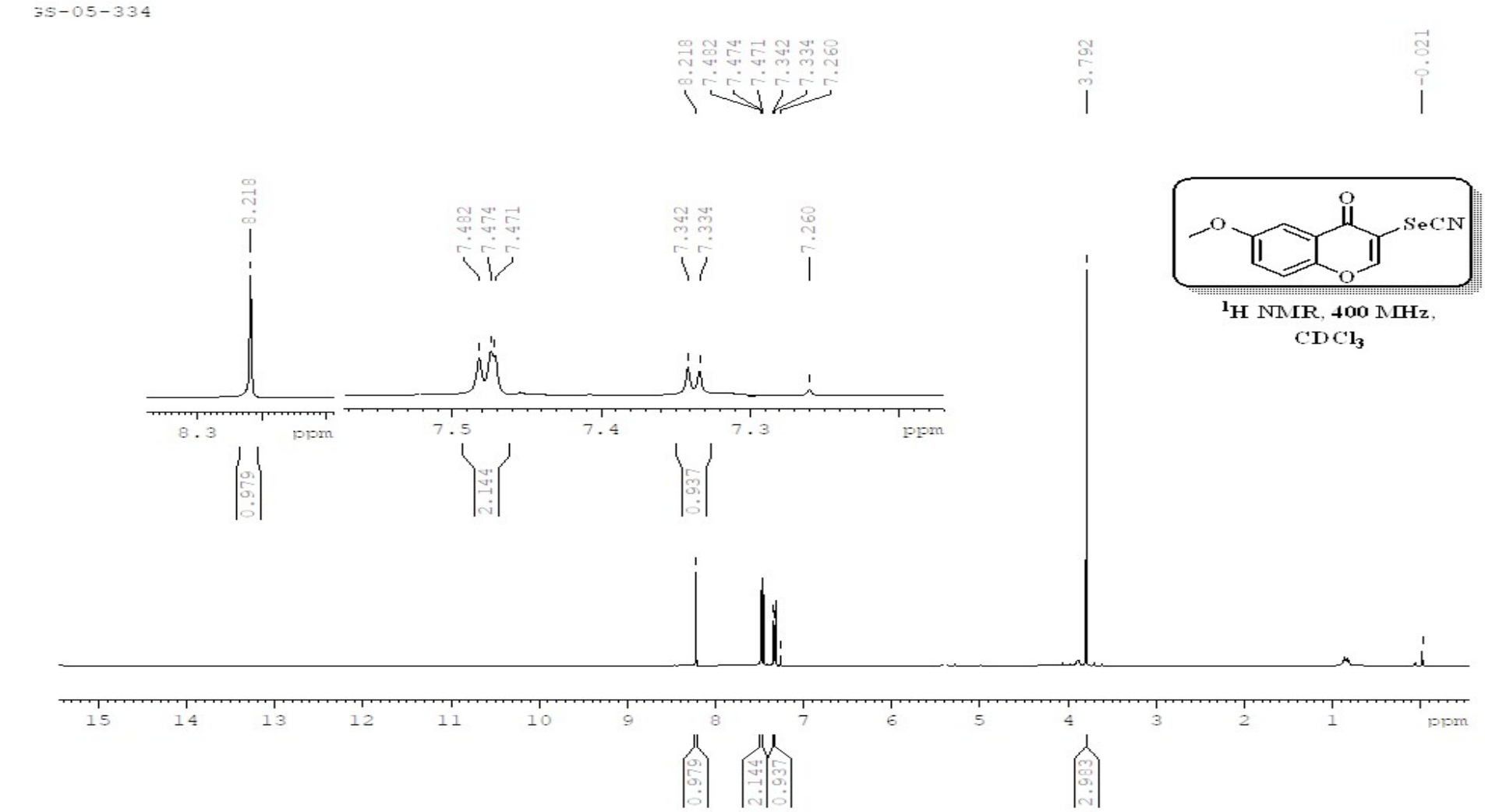


Fig 46. ^{1}H-NMR Spectrum of 6-Methoxy-3-selenocyanato-4H-chromen-4-one-(6c)

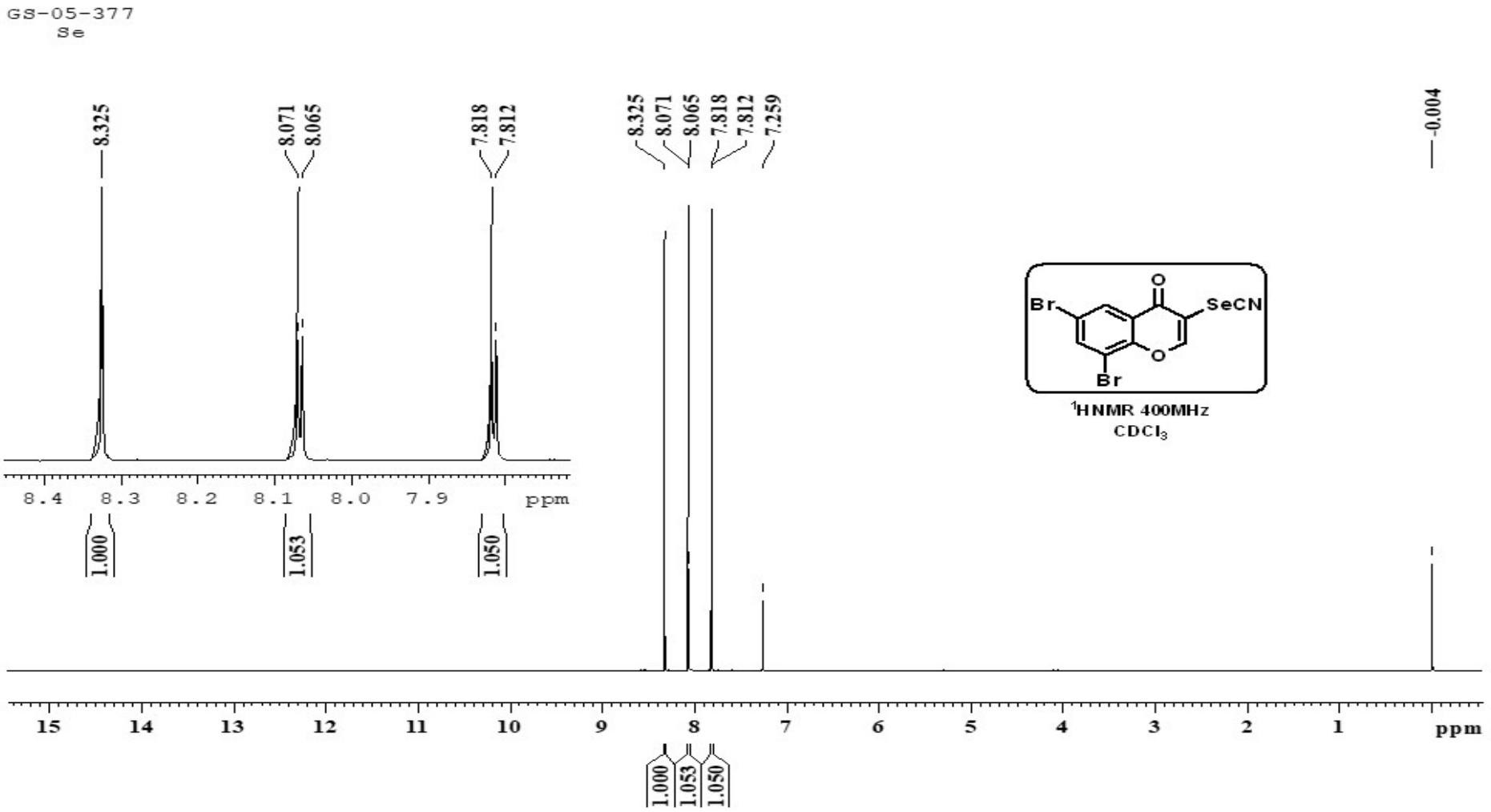


Fig 47. [1]H-NMR Spectrum of 6,8-Dibromo-3-selenocyanato-4H-chromen-4-one-(6d)

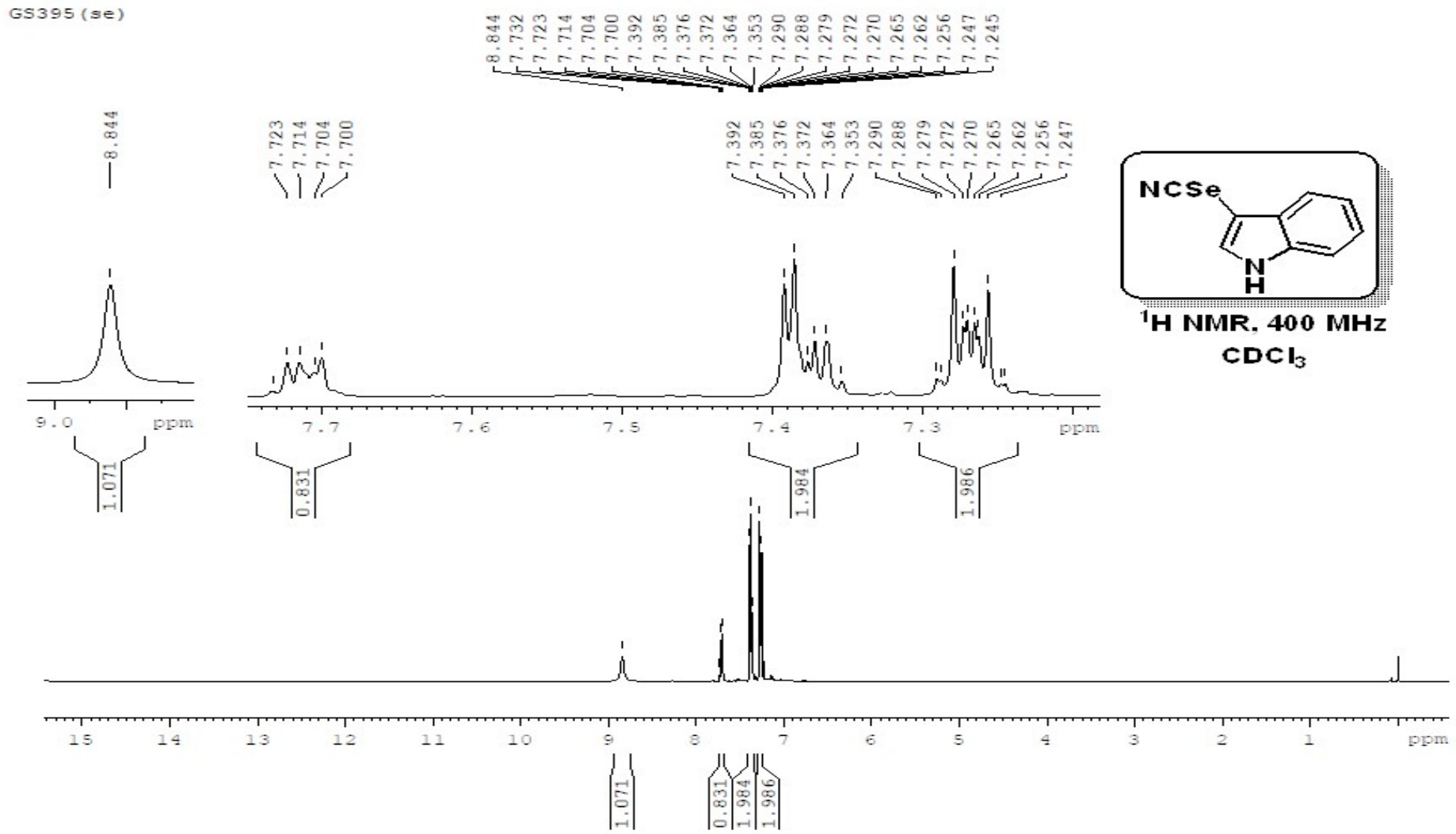


Fig 48. [1]H-NMR Spectrum of 3-Selenocyanato-1H-indole-(7a)

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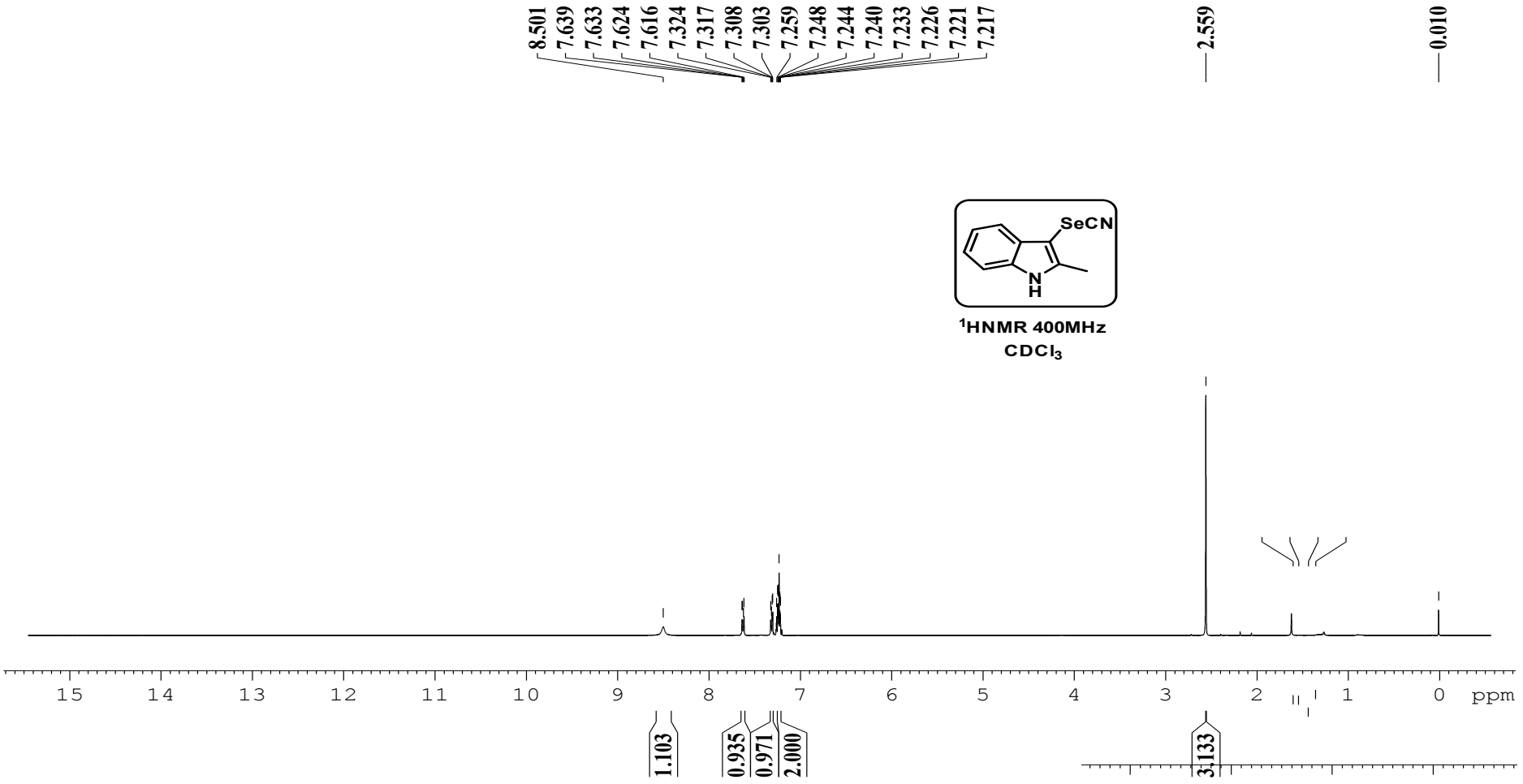

Fig 49. [1]H-NMR Spectrum of 2-Methyl-3-selenocyanato-1H-indole-(7b)

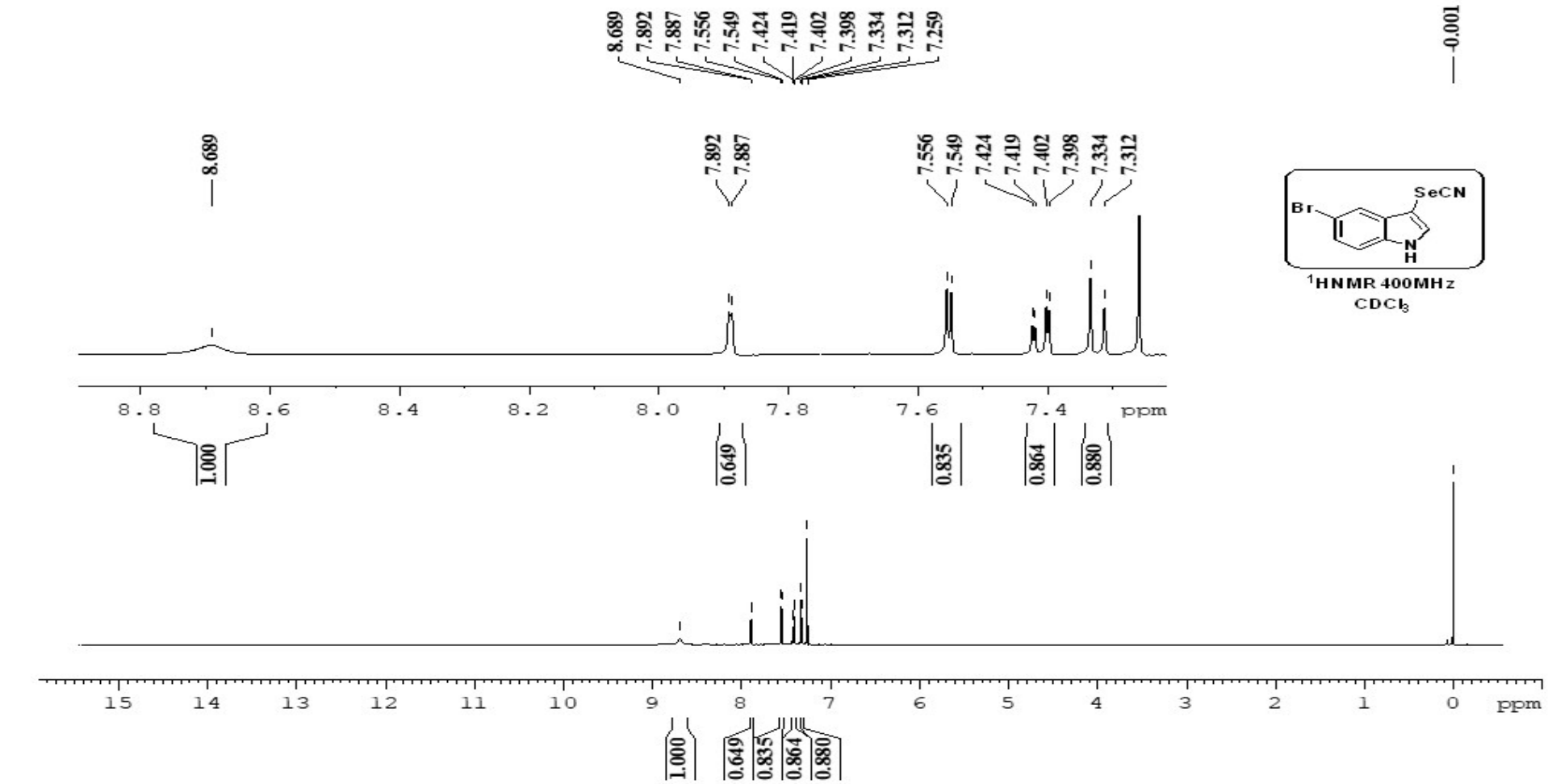

Fig 50. [1]H-NMR Spectrum of 5-Bromo-3-selenocyanato-1H-indole-(7c)

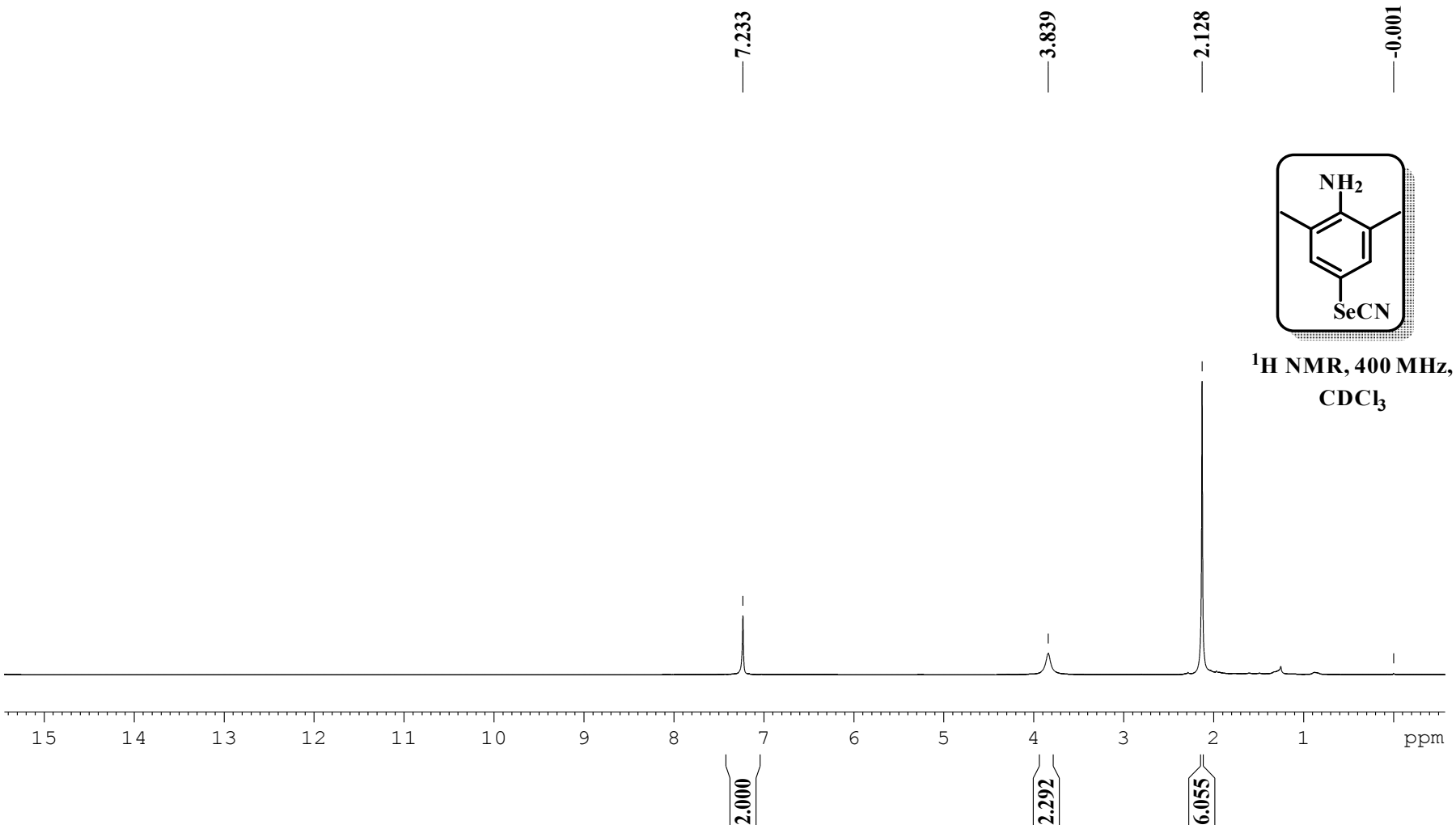

Fig 51. ^{1}H-NMR Spectrum of 2,6-Dimethyl-4-selenocyanatoaniline-(8a)

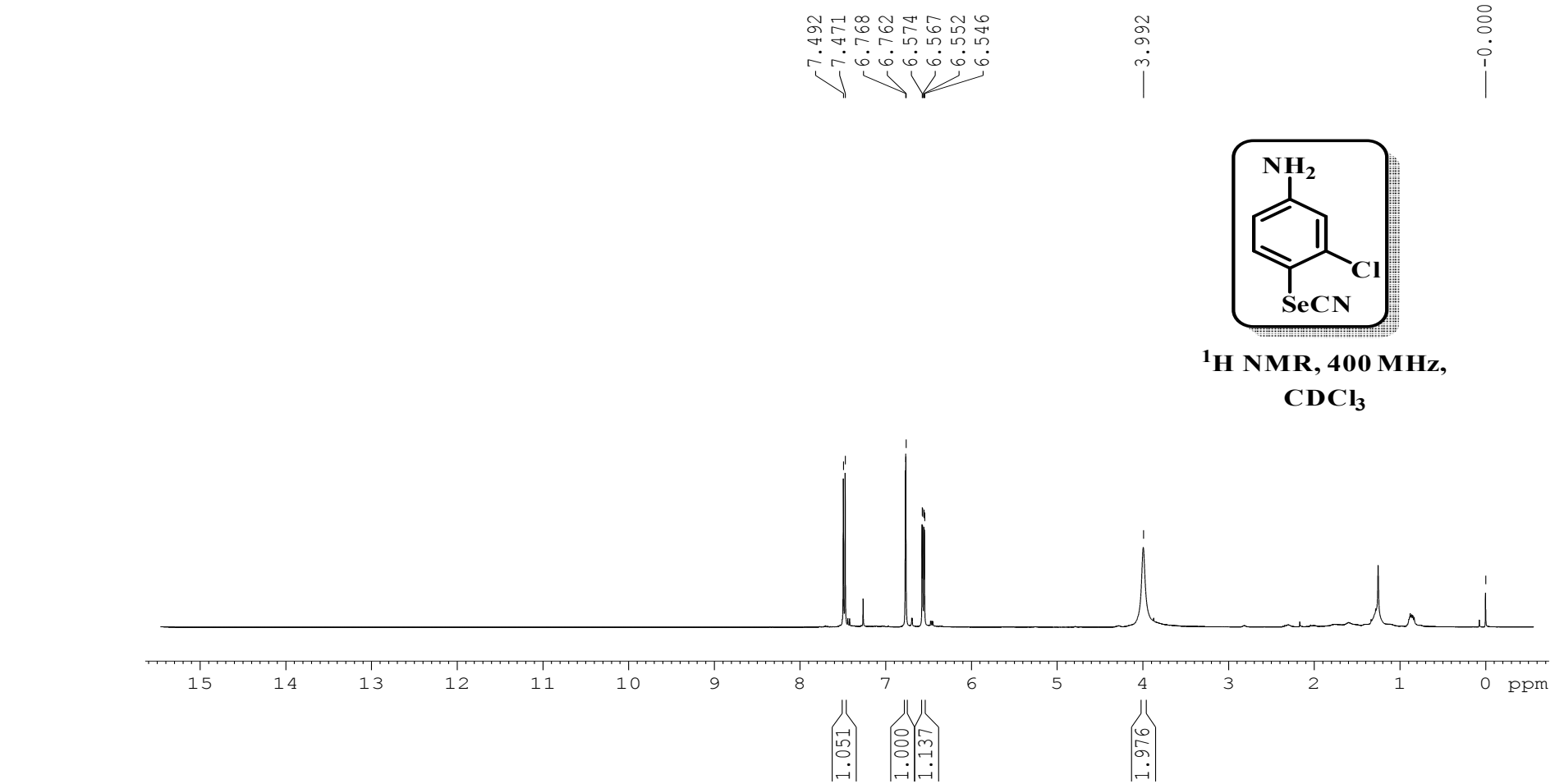

Fig 52. ^{1}H-NMR Spectrum of Chloro-4-selenocyanatoaniline-(8b)

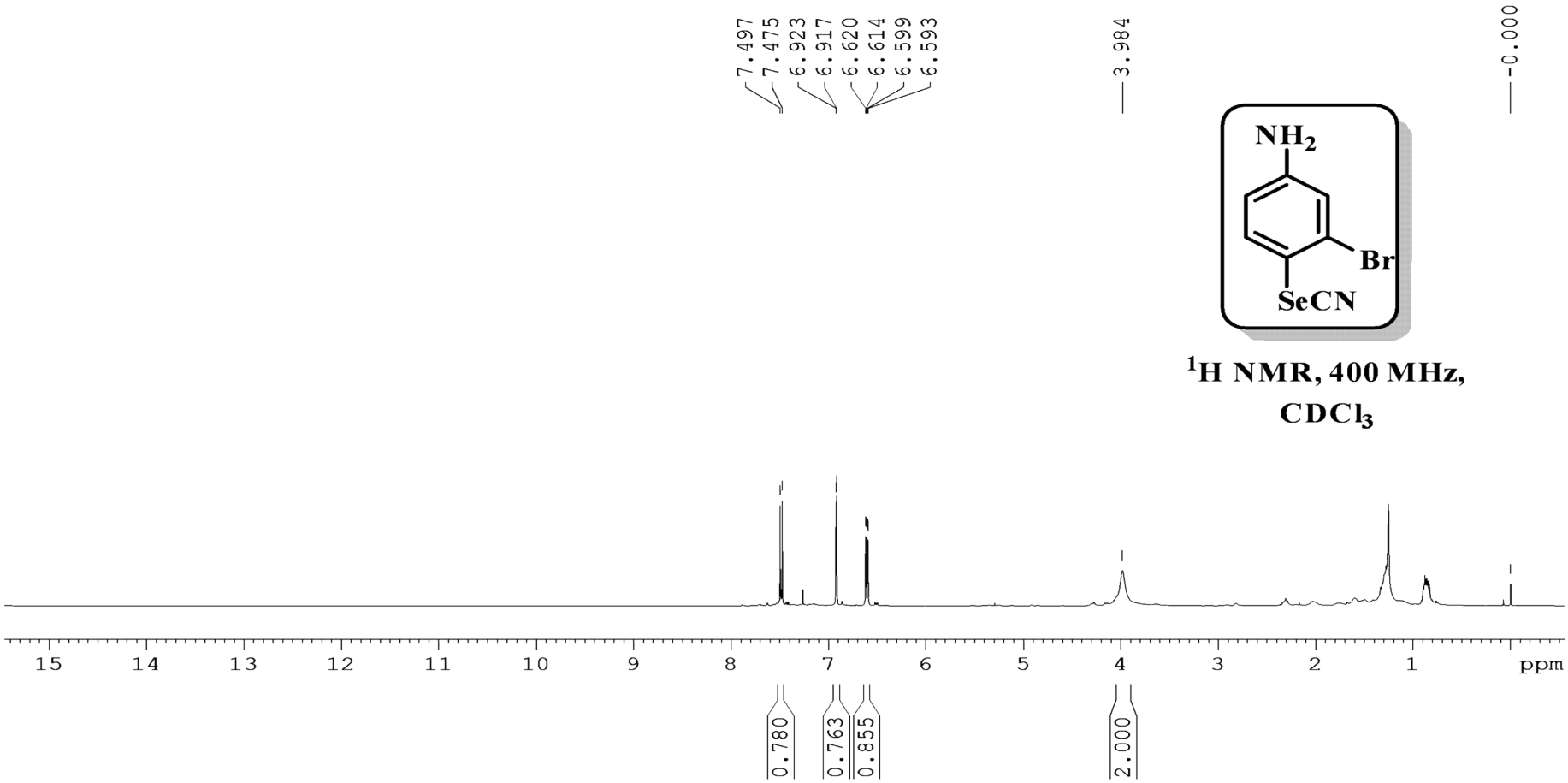

Fig 53. ^{1}H-NMR Spectrum of 3-Bromo-4-selenocyanatoaniline(8c)

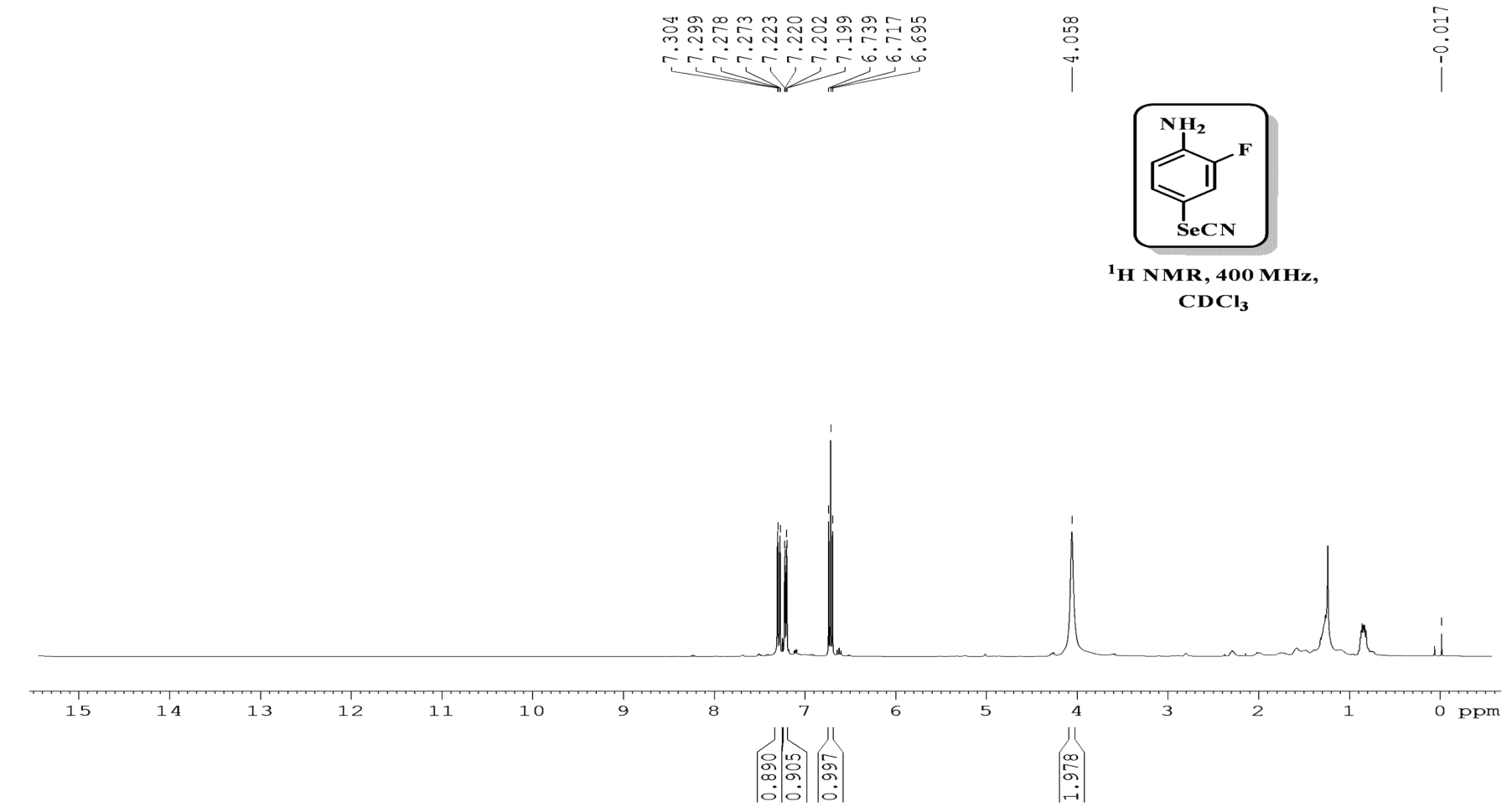

Fig 54. ^{1}H-NMR Spectrum of 2-Fluoro-4-selenocyanatoaniline(8d)

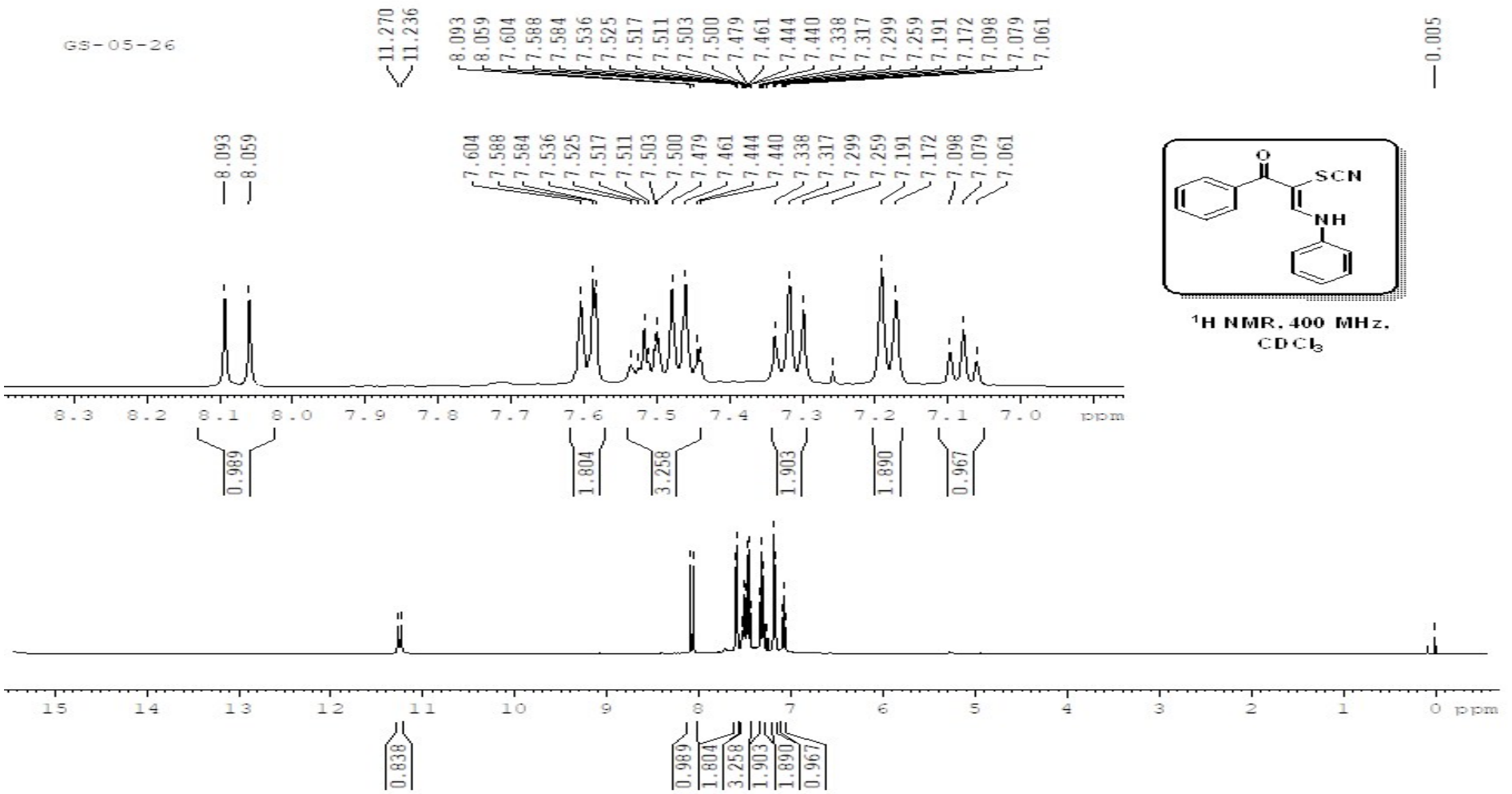

Fig 55. [1]H-NMR Spectrum of 1-Phenyl-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9a)

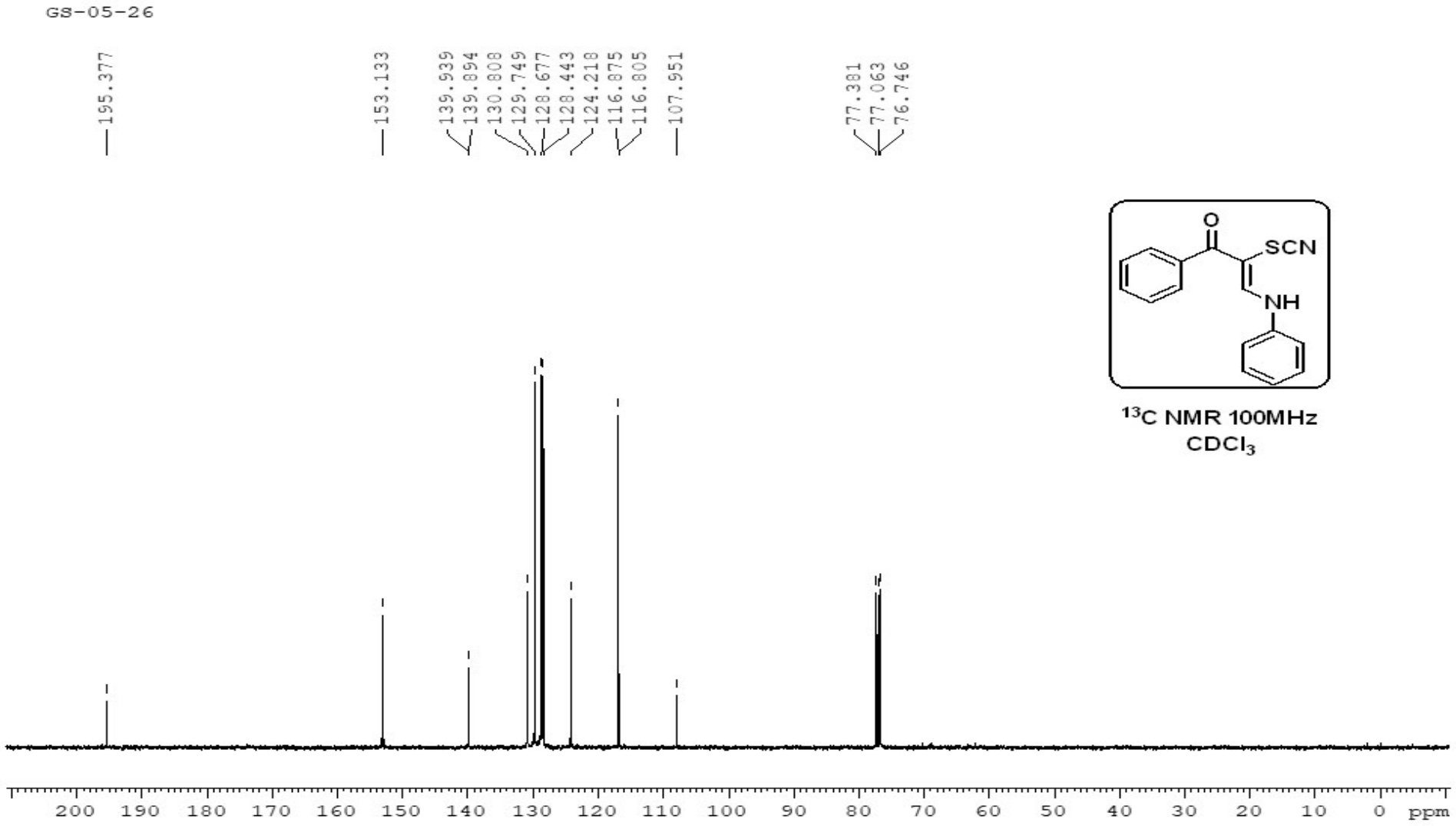

Fig 56. ^{13}C-NMR Spectrum of 1-Phenyl-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9a)

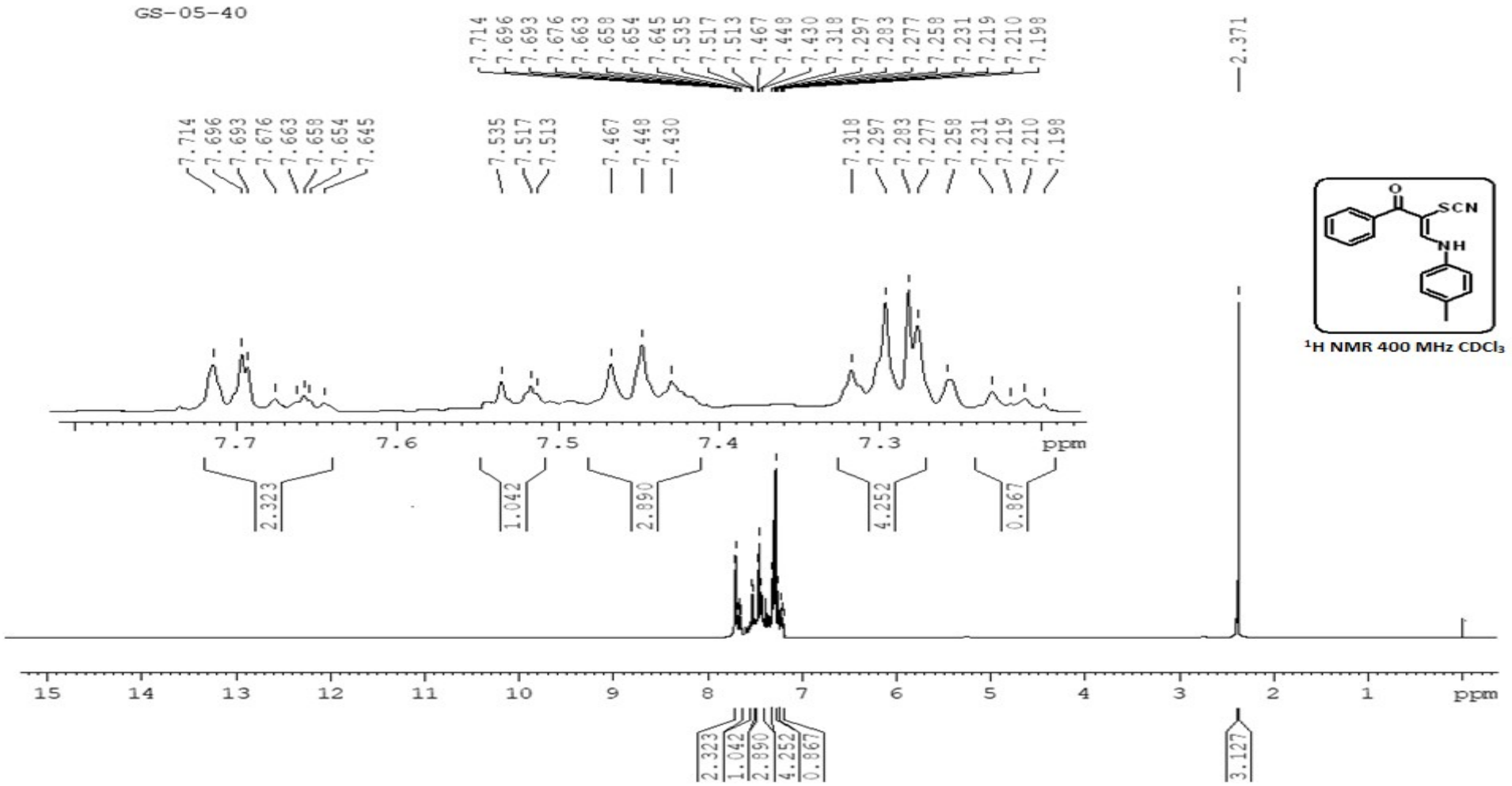

Fig 57. ^{1}H-NMR Spectrum of 1-Phenyl-2-thiocyanato-3-(p-tolylamino)prop-2-en-1-one-(9b)

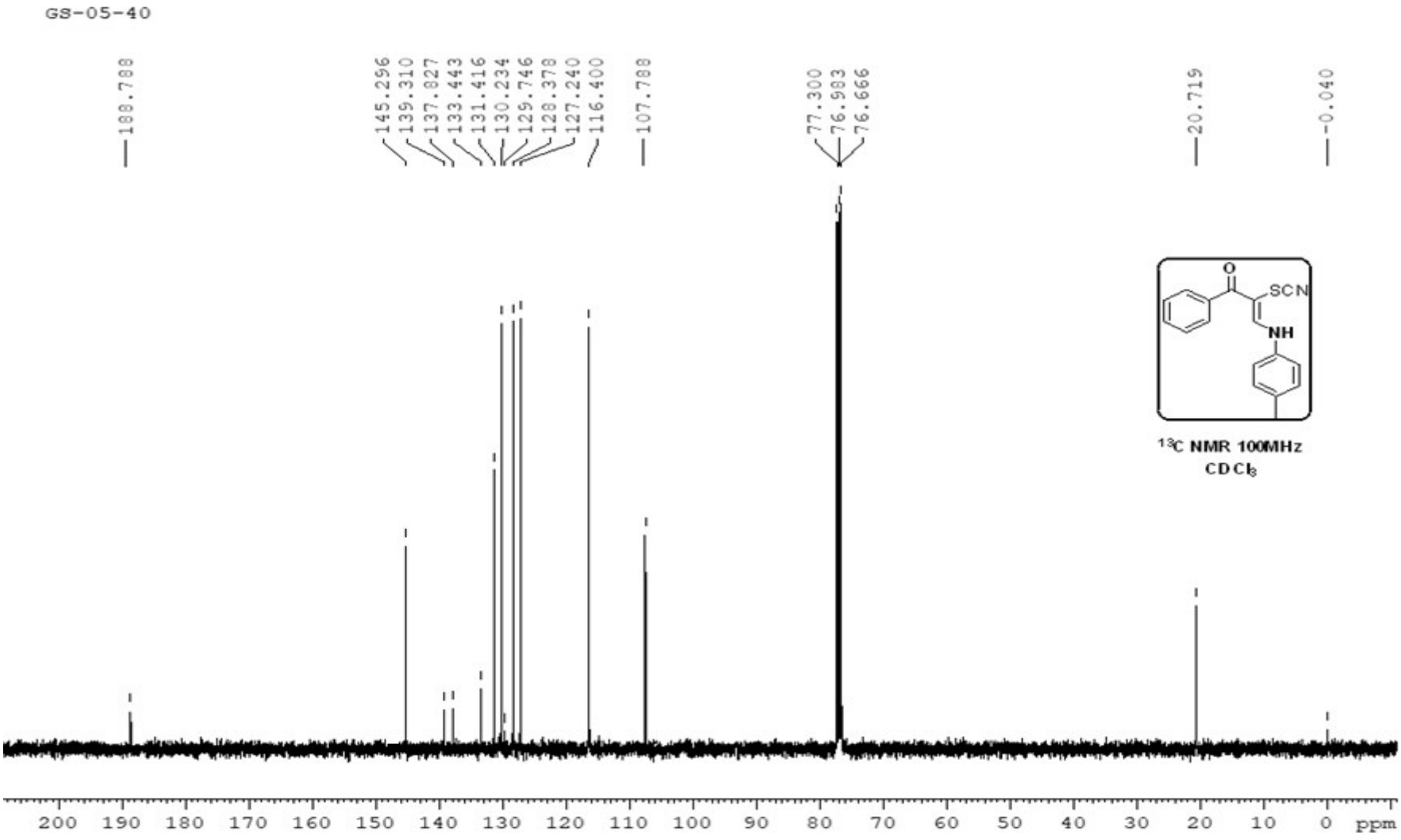

Fig 58. ^{13}C-NMR Spectrum of 1-Phenyl-2-thiocyanato-3-(p-tolylamino)prop-2-en-1-one-(9b)

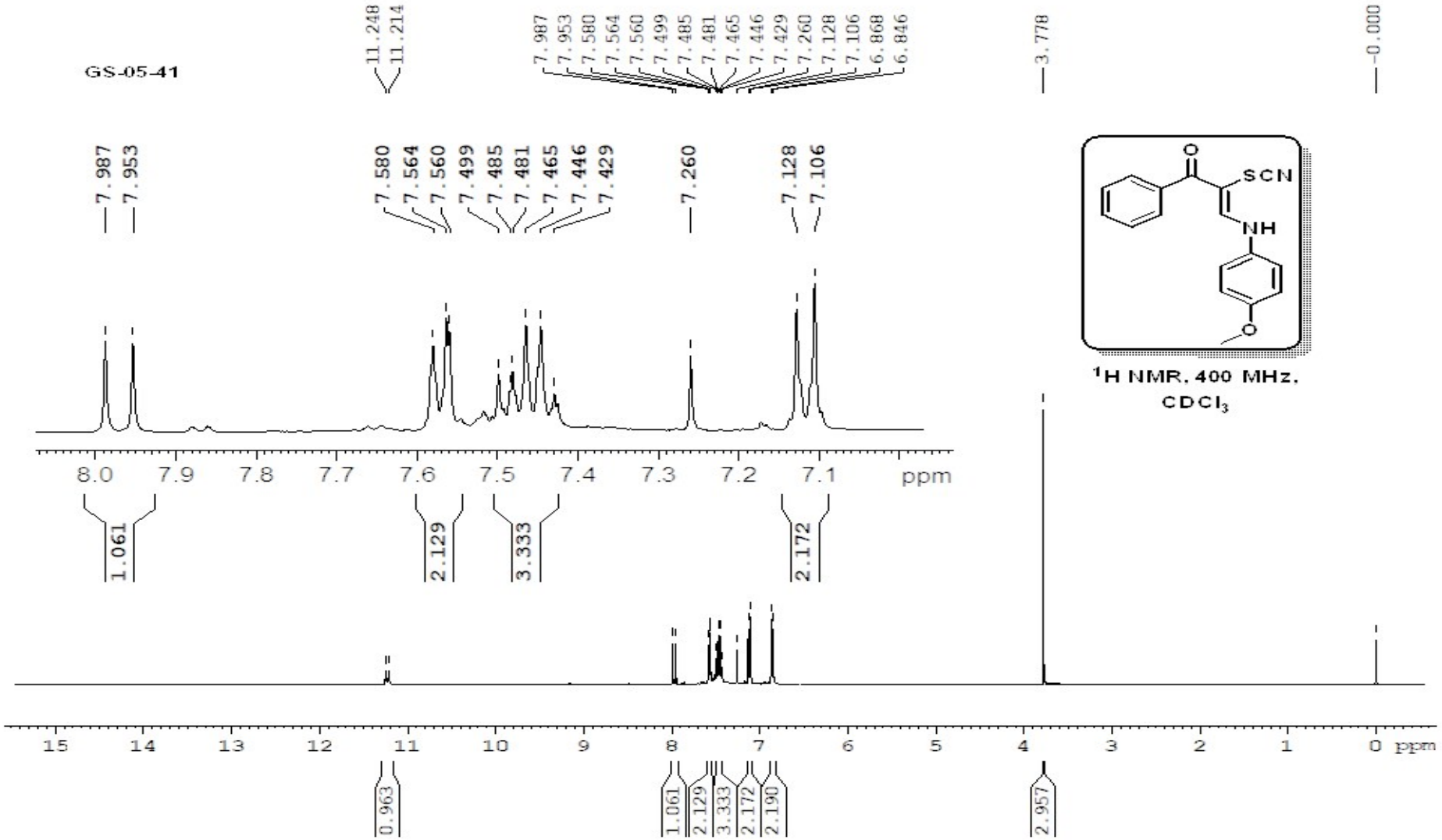

Fig 59. ^{1}H-NMR Spectrum of 3-(4-Methoxyphenyl)amino-1-phenyl-2-thiocyanatoprop-2-en-1-one-(9c)

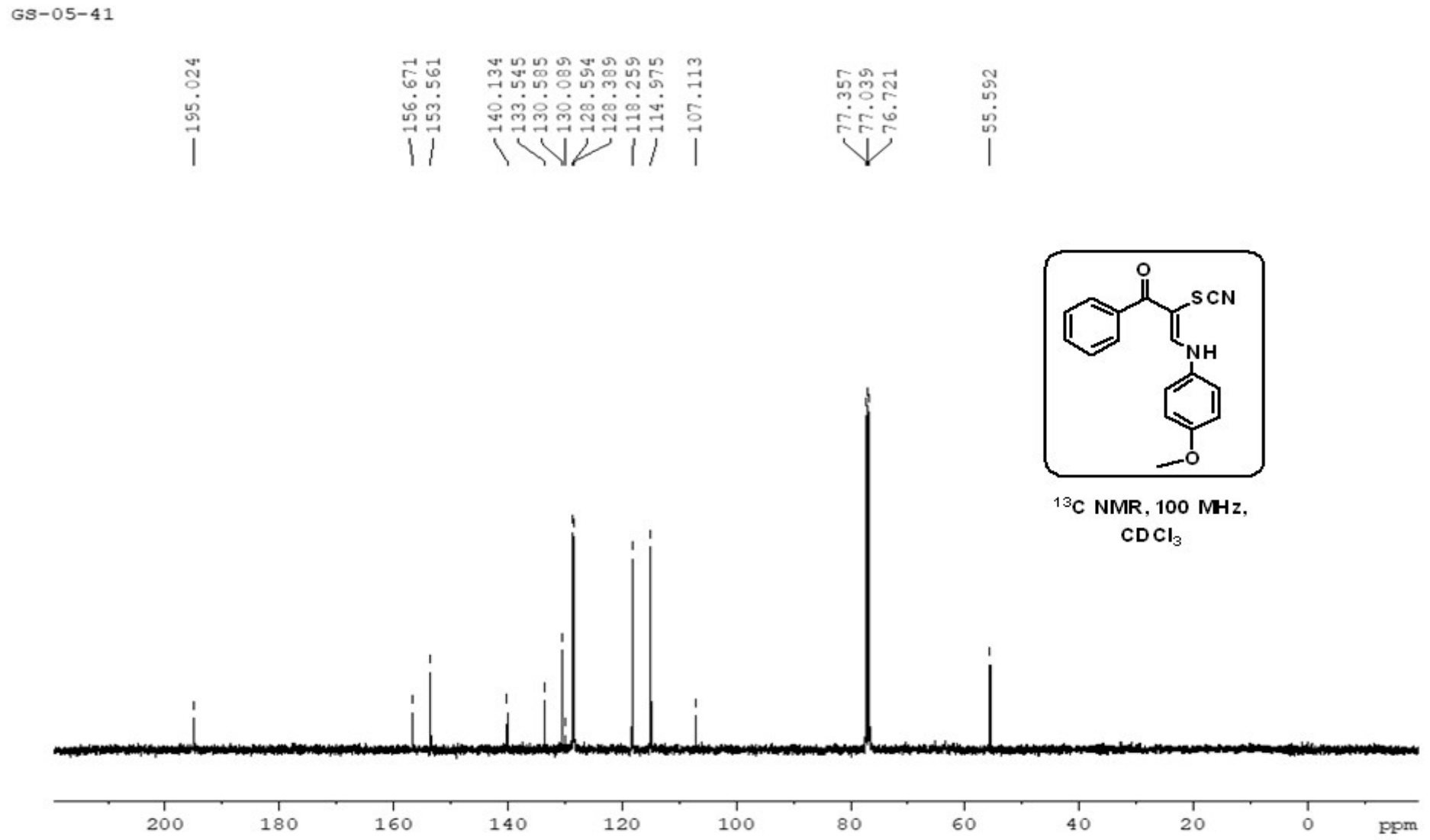

Fig 60. ^{13}C-NMR Spectrum of 3-(4-Methoxyphenyl)amino-1-phenyl-2-thiocyanatoprop-2-en-1-one-(9c)

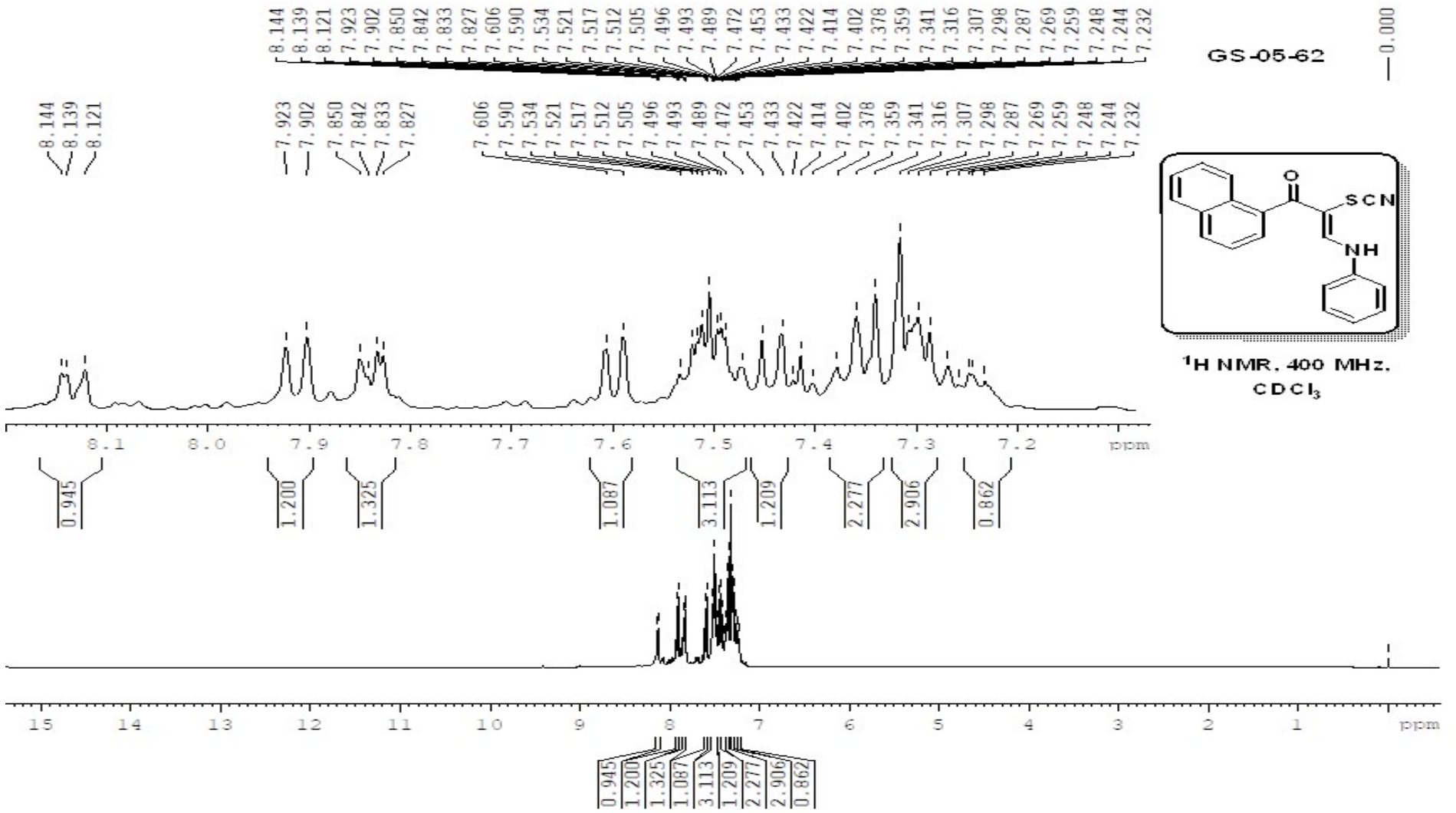

Fig 61. [1]H-NMR Spectrum of 1-(Naphthalen-1-yl)-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9d)

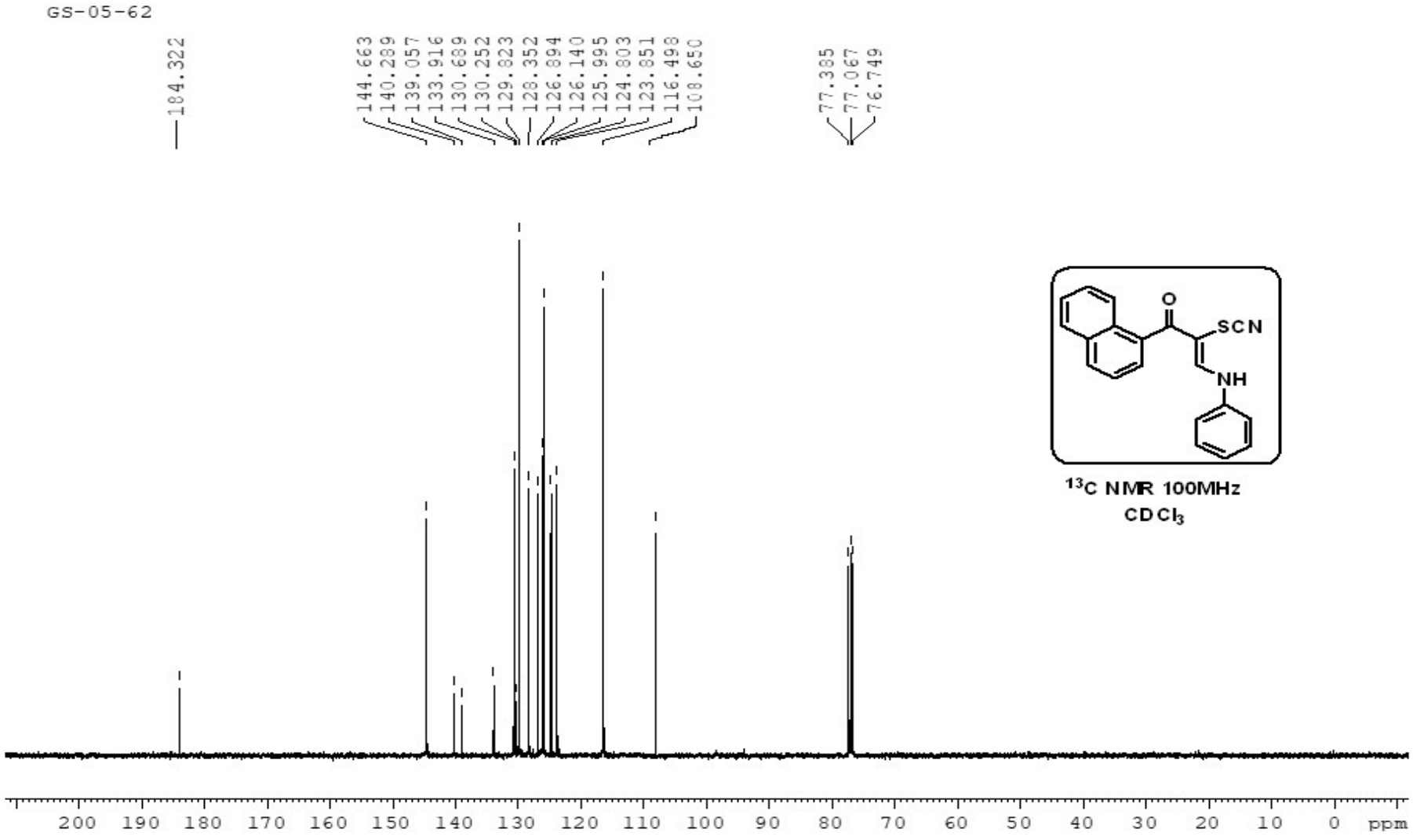

Fig 62. ^{13}C-NMR Spectrum 1-(Naphthalen-1-yl)-3-(phenylamino)-2-thiocyanatoprop-2-en-1-one-(9d)