Synthesis of bis-exocyclic conjugated diene containing 1,2,3,4-tetrahydroquinoline derivatives *via* palladium-catalyzed intramolecular Heck cyclization

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Supplementary Data

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General remarks

All reactions were carried out using oven-dried glassware and commercial grade reagents without further purification. Solvents were dried and distilled following standard protocols prior to use. All yields refer to isolated yields after column purification. Chromatographic separation was done using 60-120 mesh silica gel (Merck). Precoated silica gel 60 F254 TLC sheets (Merck) were used for reaction monitoring. ^{1}H NMR spectra were recorded on BRUKER-200 (200 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 7.26 ppm). ^{1}H NMR data of compounds are reported using the following abbreviations: chemical shifts (δ), multiplicity (s = singlet, br = broad singlet, d = doublet, t = triplet, dd = doublet of doublet, q = quartet, m = multiplet), and coupling constant (*J* in Hz). In case of ^{13}C NMR data, chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: 77.23 ppm). EIMS (70 ev) spectra were taken using a VG Autospec mass spectrometer. Petroleum ether refers to the fraction boiling in the range 60-80 ^{0}C.

General procedure for Pd-catalysed Sonogashira Coupling:

To a solution of 2-iodoaniline (1 mmol) in dry Et_3N (6 mL), ethynyl benzene (1.1 mmol), $PdCl_2(PPh_3)_2$ (5 mol %) and CuI (5 mol %) were added and refluxed for 4-5 h in argon atmosphere. The reaction mixture was cooled to rt and extracted with EtOAc (3×20ml).Combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified through column chromatography using silica gel (60-120 mesh) and pet ether/EtOAc as eluent.

General procedure for the synthesis of (2-Bromo-allyl)-(2-phenylethynyl-phenyl)-amines (2a-2j):

Previously prepared (2-phenylethynyl-phenyl)-amine (1 mmol) and K_2CO_3 (2 mmol) were taken in a two-necked round bottom flask in argon atmosphere. 2,3-dibromopropene (1 mmol) and acetonitrile (5 mL) were added and the mixture was refluxed for 10-12 h. After cooling to rt, the reaction mixture was extracted with EtOAc (3×20ml).Combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude

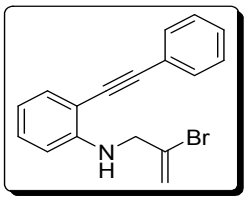
product was purified through column chromatography using silica gel (60-120 mesh) and pet ether/EtOAc as eluent.

General procedure for Heck cyclization:

Compound **2a** (100 mg, 0.32 mmol), HCOONa (32.7 mg, 0.48 mmol), PPh_3 (42.0 mg, 0.16 mmol), and Pd $(OAc)_2$ (5 mol %, 3.6 mg) were taken in a two-necked round bottomed flask in argon atmosphere. 5 mL of dry DMF was added to the reaction mixture and heated at 80 ^{0}C for 4 h. Progress of the reaction was monitored by TLC. After the completion of the reaction the reaction mixture was cooled to rt and extracted with EtOAc (3x20ml).Combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified through column chromatography using silica gel (60-120 mesh) and pet ether:EtOAc (10:1) as eluent.

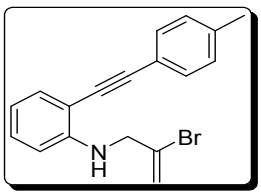
Spectral data for compounds 2a-2m:

(2-Bromo-allyl)-(2-phenylethynyl-phenyl)-amine (2a):



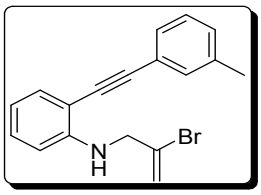
Yellow liquid, Yield = 72%; ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.66-7.62 (m, 3H), 7.61-7.48 (m, 1H), 7.45-7.33 (m, 3H), 6.84-6.77 (m, 1H), 6.73-6.64 (m, 1H), 5.96 (d, *J* = 1.6 Hz, 1H), 5.66 (s, 1H), 5.33 (br, 1H), 4.17 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 147.5, 132.4, 131.6 (2C), 130.5, 130.1, 128.6, 128.5, 124.8, 123.2, 117.5, 116.7, 110.2, 108.0, 95.6, 85.7, 51.8. Anal. Calcd. for $C_{17}H_{14}NBr$: C: 65.40; H : 4.52; N : 4.49 %; Found : C : 65.32; H : 4.56; N : 4.38 %. HRMS Calcd. for $C_{17}H_{15}BrN^+$ $[M+H]^+$: 312.0382, Found : 312.0395.

(2-Bromo-allyl)-(2-*p*-tolylethynyl-phenyl)-amine (2b):



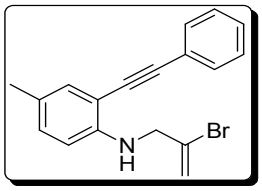
Yellow liquid, Yield = 76%; ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.51-7.42(m, 3H), 7.30-7.20 (m, 3H), 6.77 (t, *J* =7.5 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 5.93 (d, *J* = 2.0 Hz, 1H), 5.63 (s, 1H), 5.21 (br, 1H), 4.14(s, 2H), 2.43 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 147.4, 138.6, 132.3, 131.5 (2C), 129.9, 129.3 (2C), 124.9, 120.1, 117.5, 116.7, 110.1, 108.2, 95.72, 85.0, 51.8, 21.7. Anal. Calcd. for $C_{18}H_{16}NBr$: C: 66.27: H : 4.94; N : 4.29 %; Found : C : 66.15, H : 4.99, N : 4.22 %. HRMS Calcd. for $C_{18}H_{17}BrN^+$ $[M+H]^+$: 326.0539; Found : 326.0548.

(2-Bromo-allyl)-(2-*m*-tolylethynyl-phenyl)-amine (2c):



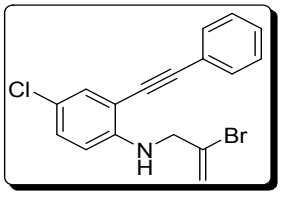
Reddish-yellow liquid, Yield = 68%; ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.55- 7.38 (m, 3H), 7.35-7.26 (m, 4H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.70 (d, *J* = 1.2 Hz, 1H), 5.33 (br, 1H), 4.22 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 147.5, 138.3, 132.4, 132.2, 130.5, 129.4, 128.7, 128.5, 124.9, 123.0, 117.6, 116.7, 110.2, 108.1, 95.8, 85.3, 51.8, 21.4. Anal. Calcd. for $C_{18}H_{16}NBr$: C : 66.27: H : 4.9; N : 4.29 %; Found : C : 66.19, H : 4.97, N : 4.19 %. HRMS Calcd. for $C_{18}H_{17}BrN^+$ $[M+H]^+$: 326.0539; Found : 326.0552.

(2-Bromo-allyl)-(4-methyl-2-phenylethynyl-phenyl)-amine (2d):



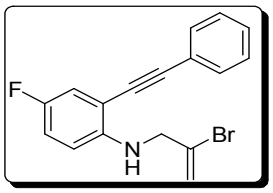
Yellow liquid, Yield = 70%; ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.61-7.56 (m, 2H), 7.41-7.37 (m, 3H), 7.27 (s, 1H), 7.06 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 5.91 (d, *J* = 1.8 Hz, 1H), 5.61 (d, *J* = 1.2 Hz, 1H), 5.11 (br, 1H), 4.11 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 145.4, 132.6, 131.6 (2C), 130.9 (2C), 128.6, 128.4 (2C), 126.7, 123.3, 116.6, 110.4, 108.0, 95.3, 85.9, 52.0, 20.4. Anal. Calcd. for $C_{18}H_{16}NBr$: C : 66.27: H : 4.94; N : 4.29 %; Found : C : 66.22, H : 4.95, N : 4.24 %. HRMS Calcd. for $C_{18}H_{17}BrN^+$ $[M+H]^+$: 326.0539; Found : 326.0550.

(2-Bromo-allyl)-(4-chloro-2-phenylethynyl-phenyl)-amine (2e):



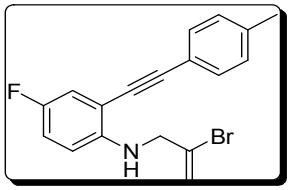
Yellow liquid, Yield = 65%; ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.58-7.53 (m, 2H), 7.40-7.37 (m, 4H), 7.16 (dd, J_1 = 2.6 Hz, J_2 = 8.8 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 5.86 (d, *J* = 2.0 Hz, 1H), 5.60 (d, *J* = 1.2 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 146.1, 131.7 (2C), 131.7, 130.1, 129.9, 128.9 (2C), 128.6, 122.7, 122.0, 117.0, 111.4, 109.4, 96.5, 84.4, 51.8. Anal. Calcd. for $C_{17}H_{13}NClBr$: C : 76.26, H : 5.27, N : 5.23 %; Found : C : 76.13, H : 5.31, N : 5.11 %. HRMS Calcd. for $C_{17}H_{14}BrClN^+$ $[M+H]^+$: 345.9993; Found : 346.0009.

(2-Bromo-allyl)-(4-fluoro-2-phenylethynyl-phenyl)-amine (2f):



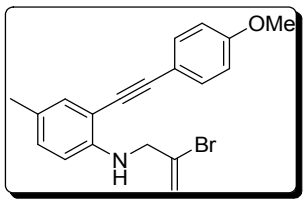
Yellow liquid, Yield = 62%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.57-7.52 (m, 2H), 7.39-7.36 (m, 3H), 7.12 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H), 6.99-6.89 (m, 1H), 6.50 (q, J = 4.6 Hz, 1H), 5.87 (d, J = 1.6 Hz,1H), 5.58 (s, 1H), 5.05 (br, 1H), 4.08 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 152.7, 144.2, 131.7 (2C), 130.5, 128.8, 128.6, 124.9 (J = 6.0 Hz), 122.8, 118.4 (J = 24.0 Hz), 117.2, 116.9 (J = 5.5 Hz), 111.2 (J = 8.0 Hz), 108.8 (J = 9.0 Hz), 96.2, 84.7 (J = 3.0 Hz). 52.3. Anal. Calcd. for $C_{17}H_{13}BrFN$: C : 61.84, H : 3.97, N : 4.24 %; Found : C : 61.80, H : 4.02, N : 4.13 %. HRMS Calcd. for $C_{17}H_{14}BrFN^{+}$ $[M+H]^{+}$: 330.0288; Found : 330.0302.

(2-Bromo-allyl)-(4-fluoro-2-*p*-tolylethynyl-phenyl)-amine (2g):



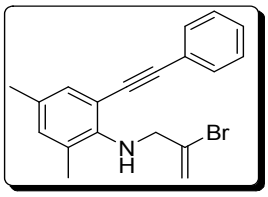
Yellow liquid, Yield = 66%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.44 (d, J = 7.4 Hz, 2H), 7.21-7.09 (m, 3H), 6.98-6.89 (m, 1H), 6.45 (q, J = 4.6 Hz, 1H), 5.87 (s, 1H), 5.59 (s, 1H), 5.05 (br, 1H), 4.07 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 152.6, 144.1, 139.0, 131.6 (2C), 130.6, 129.4 (2C), 124.8, 119.7, 118.3 (J = 23.5 Hz), 116.9 (J = 9.0 Hz), 111.1 (J = 7.5 Hz), 109.0 (J = 9.0 Hz), 96.5, 84.1, 52.2, 21.7. Anal. Calcd. for $C_{18}H_{15}BrFN$: C : 62.81, H : 4.39, N : 4.07 %; Found : C : 62.76, H : 4.41, N : 3.98 %. HRMS Calcd. for $C_{18}H_{16}BrNF^{+}$ $[M+H]^{+}$: 344.0445; Found : 344.0451.

(2-Bromo-allyl)-[2-(4-methoxy-phenylethynyl)-4-methyl-phenyl]-amine (2h):



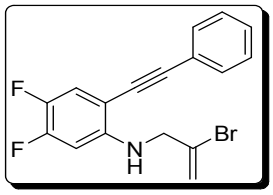
Reddish-yellow liquid, Yield = 75%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.51 (d, J = 8.8 Hz, 2H), 7.25 (s, 1H), 7.04 (dd, J_1 = 1.8 Hz, J_2 = 8.4 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 6.53 (d, J = 8.4 Hz, 1H), 5.90 (d, J = 1.8 Hz, 1H), 5.60 (s, 1H), 5.12 (t, J = 6.0 Hz, 1H), 3.85 (s,5H), 2.28 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 159.5, 145.1, 132.9 (2C), 132.3, 130.9, 130.4, 126.3, 116.4, 115.2, 114.0 (2C), 110.2, 108.1, 95.1, 84.5, 55.1, 51.8, 20.2. Anal. Calcd. for $C_{19}H_{18}BrNO$: C : 64.06, H : 5.09, N : 3.93 %; Found : C : 63.91, H : 5.14, N : 3.87 %. HRMS Calcd. for $C_{19}H_{19}BrNO^{+}$ $[M+H]^{+}$: 356.0645; Found : 356.0649.

(2-Bromo-allyl)-(2,4-dimethyl-6-phenylethynyl-phenyl)-amine (2i):



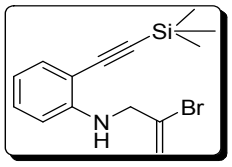
Yellow liquid, Yield = 63%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.56-7.51(m, 2H), 7.37-7.34 (m, 3H), 7.16 (s, 1H), 6.93 (s, 1H), 5.90 (s, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 4.23 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 144.6, 132.9, 132.3, 131.3, 131.1, 130.0, 128.4, 128.2, 127.4, 123.5, 119.4, 117.7, 113.0, 108.6, 93.9, 87.9, 55.6, 20.4, 18.7. Anal. Calcd. for $C_{19}H_{18}BrN$: C : 67.07, 5.33, 4.12 %; Found : C : 66.94, H : 5.36, N : 3.99 %. HRMS Calcd. for $C_{19}H_{19}BrN^{+}$ $[M+H]^{+}$: 340.0695; Found : 340.0711.

(2-Bromo-allyl)-(4,5-difluoro-2-phenylethynyl-phenyl)-amine (2j):



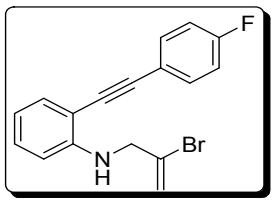
Reddish-yellow liquid, Yield = 60%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.61-7.55 (m, 3H), 7.44-7.21 (m, 3H), 6.40 (q, *J* = 7.0 Hz, 1H), 5.92 (d, *J* = 1.6 Hz, 1H), 5.66 (s, 1H), 5.19 (br, 1H), 4.07 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 149.1 (*J* = 13.5 Hz), 145.0 (*J* = 9.0 Hz), 140.0 (*J* = 13.5 Hz), 131.6 (2C), 129.8, 128.6 (*J* = 10.5 Hz) (2C), 124.7, 122.6, 120.3 (*J* = 18.5 Hz), 117.2, 103.4 (*J* = 4.5 Hz), 99.4 (*J* = 22.0 Hz), 95.8, 83.8, 52.0. Anal. Calcd. for $C_{17}H_{12}BrF_2N$: C : 58.64, H : 3.47, N : 4.02 %; Found : C : 58.61, H : 3.51, N : 3.89 %. HRMS Calcd. for $C_{17}H_{13}BrF_2N^{+}$ $[M+H]^{+}$: 348.0194; Found : 348.0210.

(2-Bromo-allyl)-(2-trimethylsilanylethynyl-phenyl)-amine (2k):



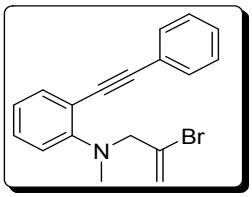
Yellow liquid, Yield = 66 %, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.34-7.22 (m, 1H), 7.18-7.14 (m, 1H), 6.69-6.62 (m, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 5.86 (d, J = 2.0 Hz, 1H), 5.56 (s, 1H), 5.15 (br, 1H), 4.07 (d, *J* = 3.8 Hz, 2H), 0.27 (s, 9H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 148.0, 132.5, 130.4, 130.3, 117.3, 116.7, 110.0, 107.9, 101.8, 100.7, 51.7, 0.3 (3C). Anal. Calcd. for $C_{14}H_{18}BrNSi$: C : 54.54, H : 5.89, N : 4.54 %; Found : C : 54.48, H : 5.91, N : 4.50 %. HRMS Calcd. for$C_{14}H_{19}BrNSi^{+}$: $[M+H]^{+}$: 308.0465; Found : 308.478.

(2-Bromo-allyl)-[2-(4-fluoro-phenylethynyl)-phenyl]-amine (2l):



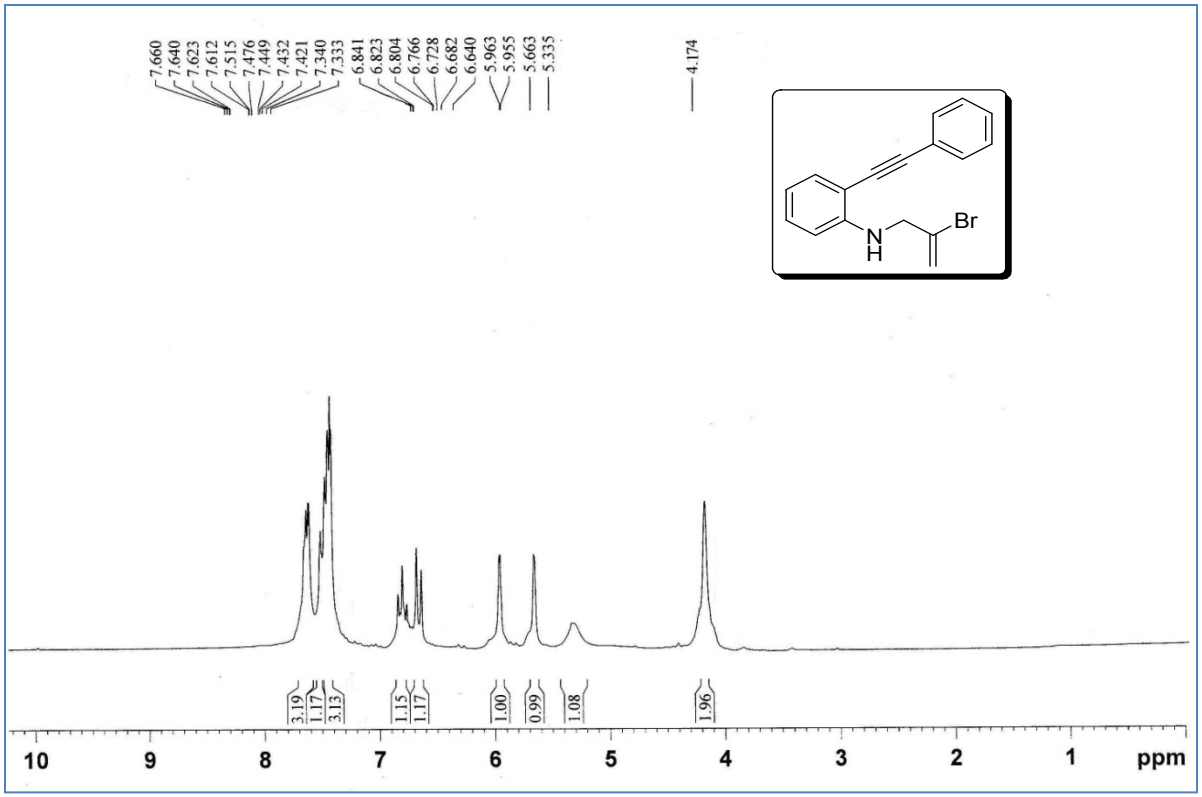
Yellow liquid, Yield = 61 % , ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.56-7.49 (m, 2H), 7.39 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 7.22-7.18 (m, 1H), 7.06 (t, J = 8.6 Hz, 2H), 6.72 (td, J_1 = 1.0 Hz, J_2 = 7.6 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 5.88 (d, J = 1.8 Hz, 1H), 5.59 (d, J = 0.6 Hz, 1H), 5.18 (br, 1H), 4.11 (d, J = 5.2 Hz, 2H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 164.9, 147.4, 133.5, 133.3, 132.3, 130.5, 130.1, 119.3 (J = 3.5 Hz), 117.5, 116.6, 115.9, 115.5, 110.2, 107.7, 94.4, 85.5, 51.6. Anal. Calcd. for $C_{17}H_{13}BrFN$: C : 61.84, H : 3.97, N : 4.24 %; Found : C : 61.82, H : 4.01, N : 4.18 %. HRMS Calcd. for $C_{17}H_{14}BrFN^{+}$ $[M+H]^{+}$: 330.0288; Found : 330.0299.

(2-Bromo-allyl)-methyl-(2-phenylethynyl-phenyl)-amine (2m):

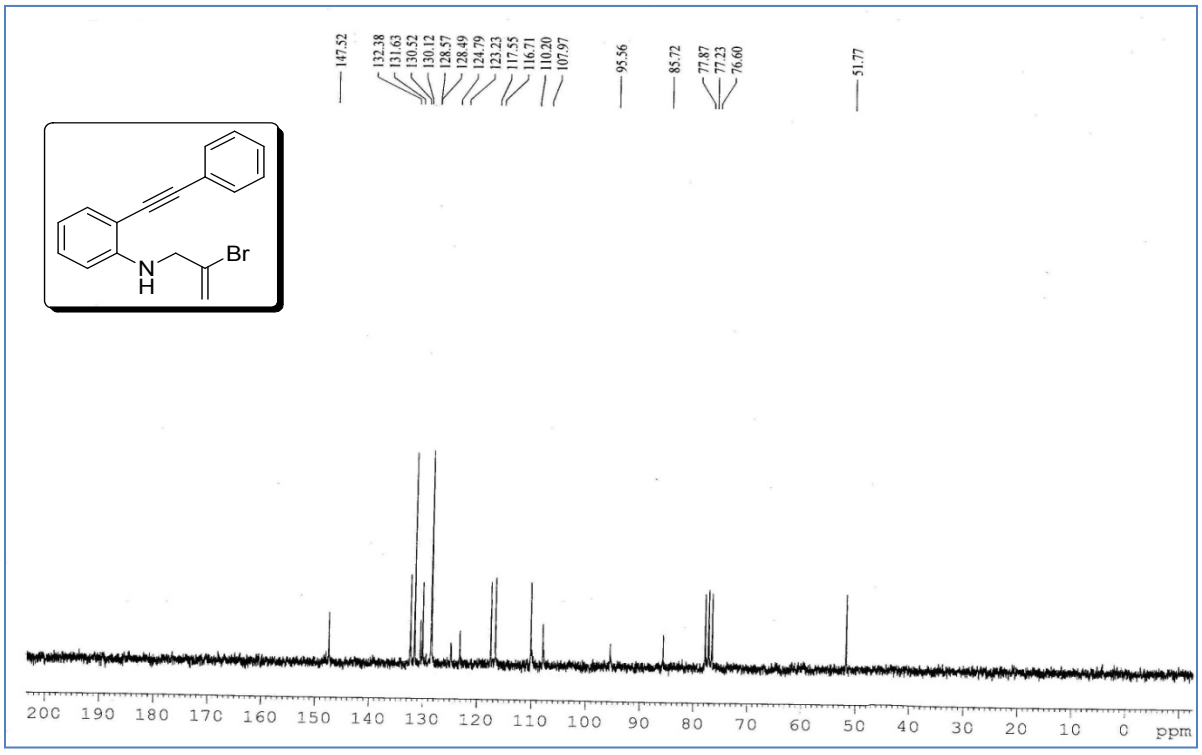


Light yellow liquid, Yield = 70 %, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.56-7.52 (m, 3H), 7.34 (dd, J_1 = 2.0 Hz, J_2 = 5.0 Hz, 5H), 6.97 (d, J = 7.6 Hz, 1H), 6.02 (d, J = 1.6 Hz, 1H), 5.63 (d, J = 1.4 Hz, 1H), 4.30 (s, 2H), 2.99 (s, 3H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 152.6, 134.7, 131.5, 131.4, 130.7, 129.3, 128.5, 128.3, 128.1, 123.8, 120.7, 117.7, 117.2, 114.2, 94.7, 88.6, 63.3, 39.5. Anal. Calcd. For $C_{18}H_{16}BrN$: C : 66.27, H : 4.94, N : 4.29 %; Found : C : 66.25, H : 5.03, N : 4.18 %. HRMS Calcd. for $C_{18}H_{17}BrN^{+}$ $[M+H]^{+}$: 326.0539; Found : 326.0555.

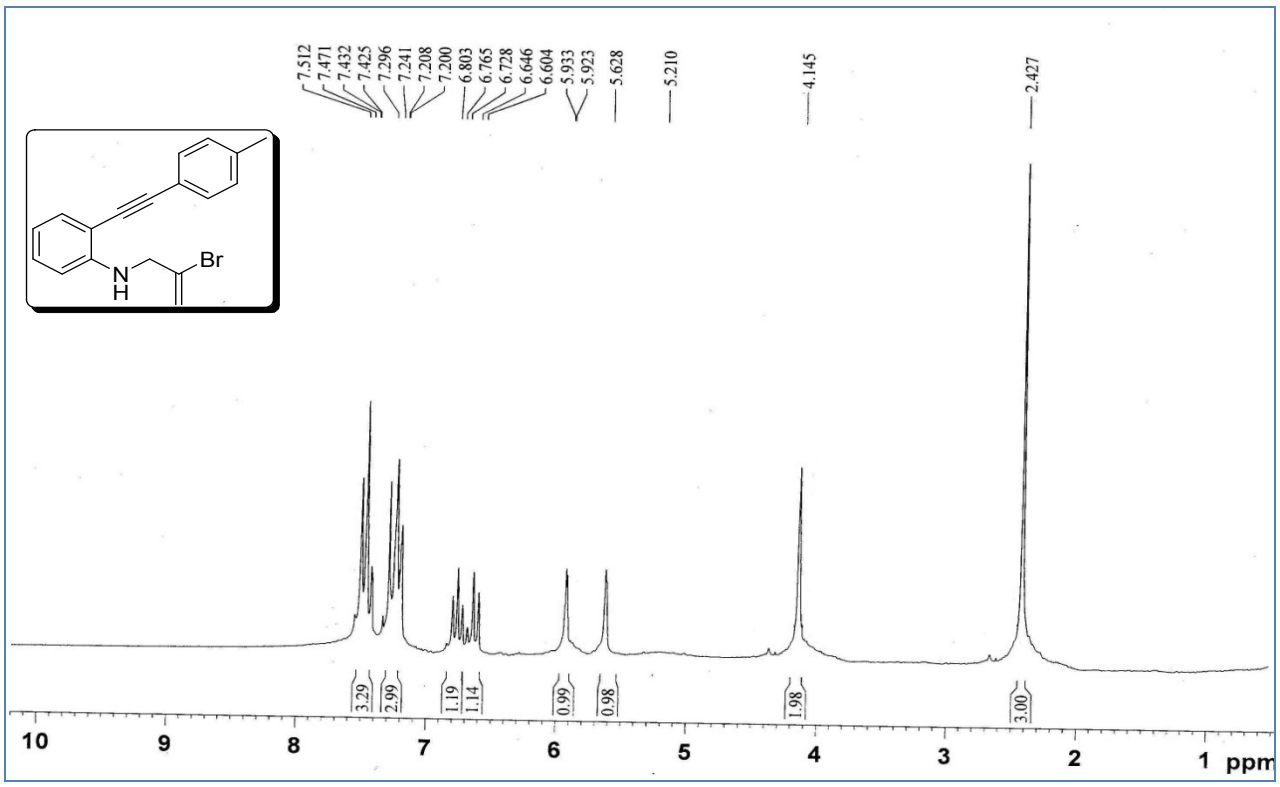
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2a):



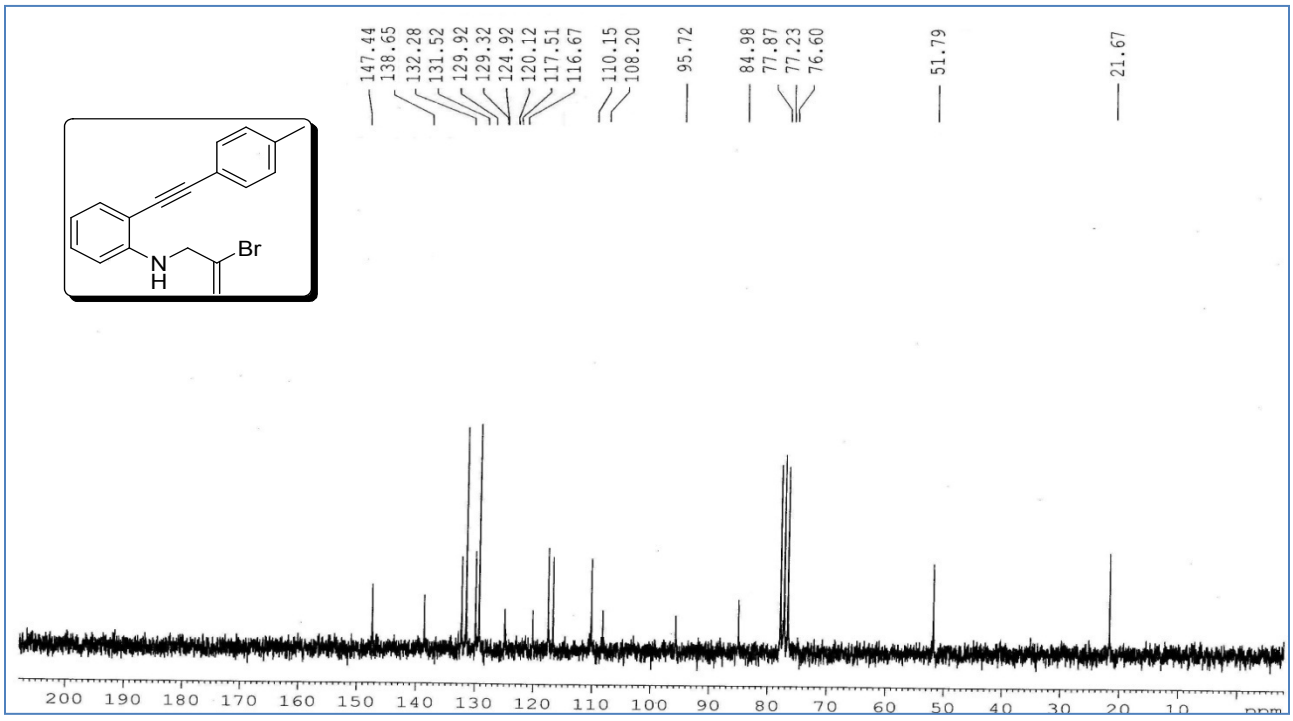
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2a):



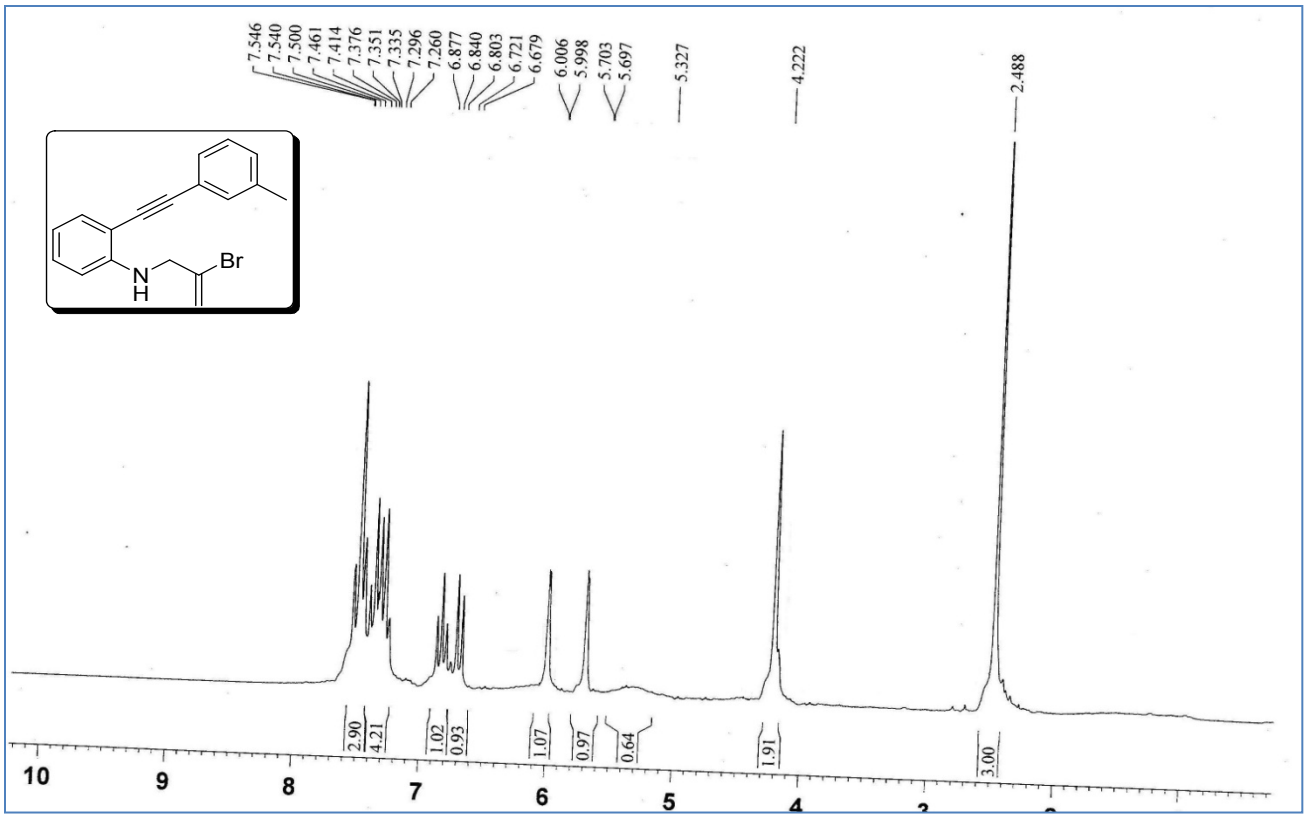
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2b):



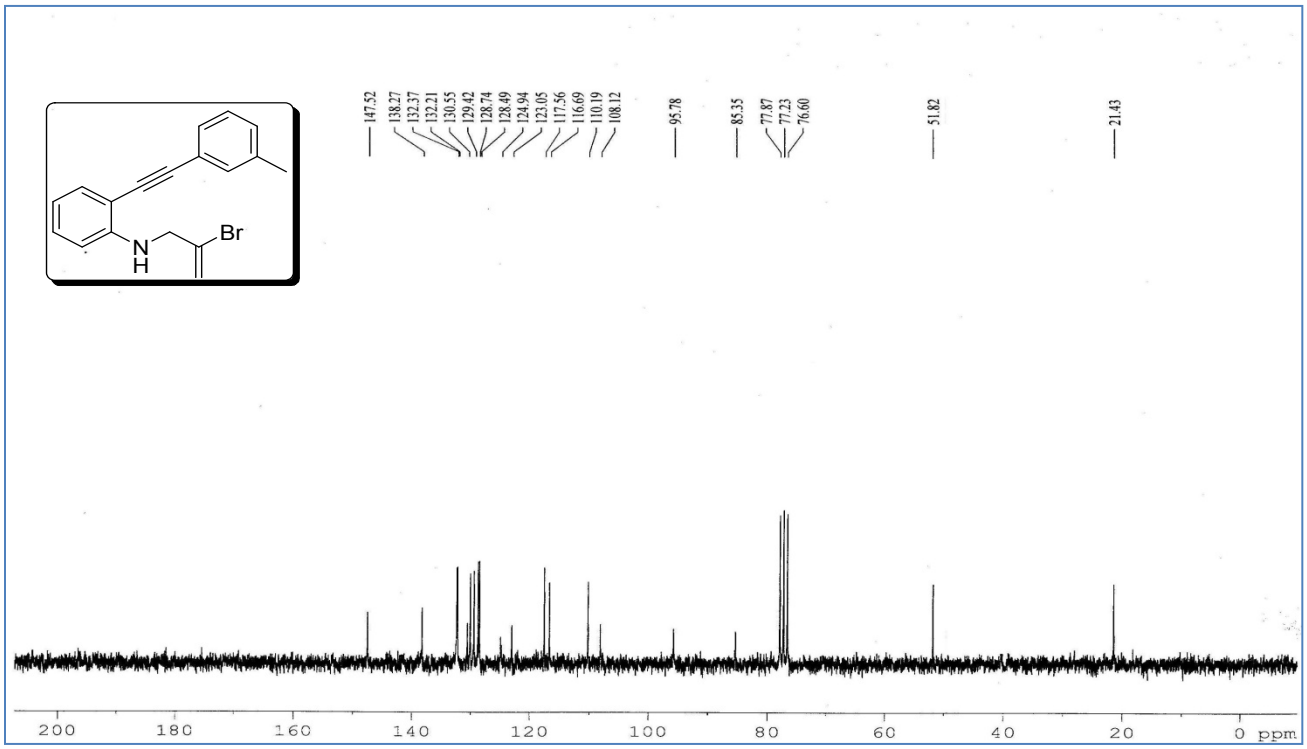
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2b):



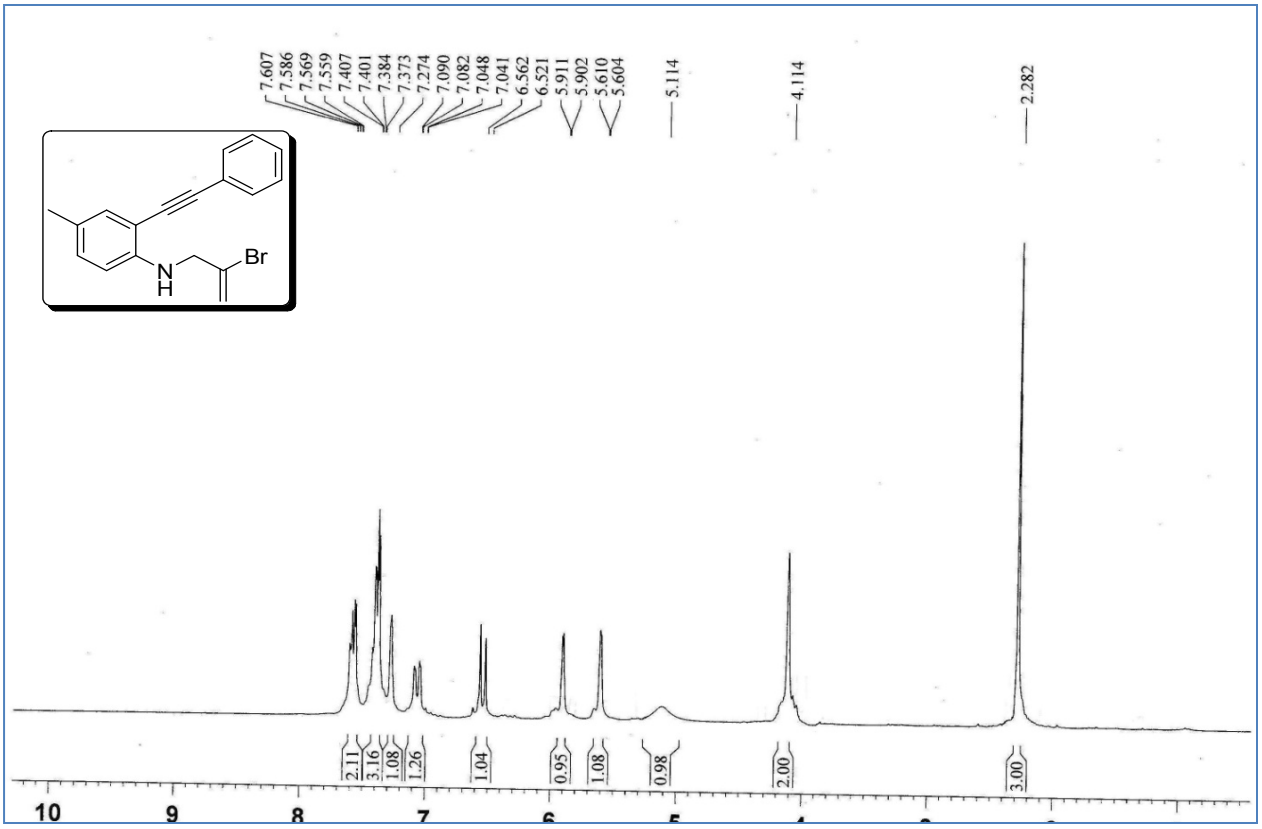
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2c):



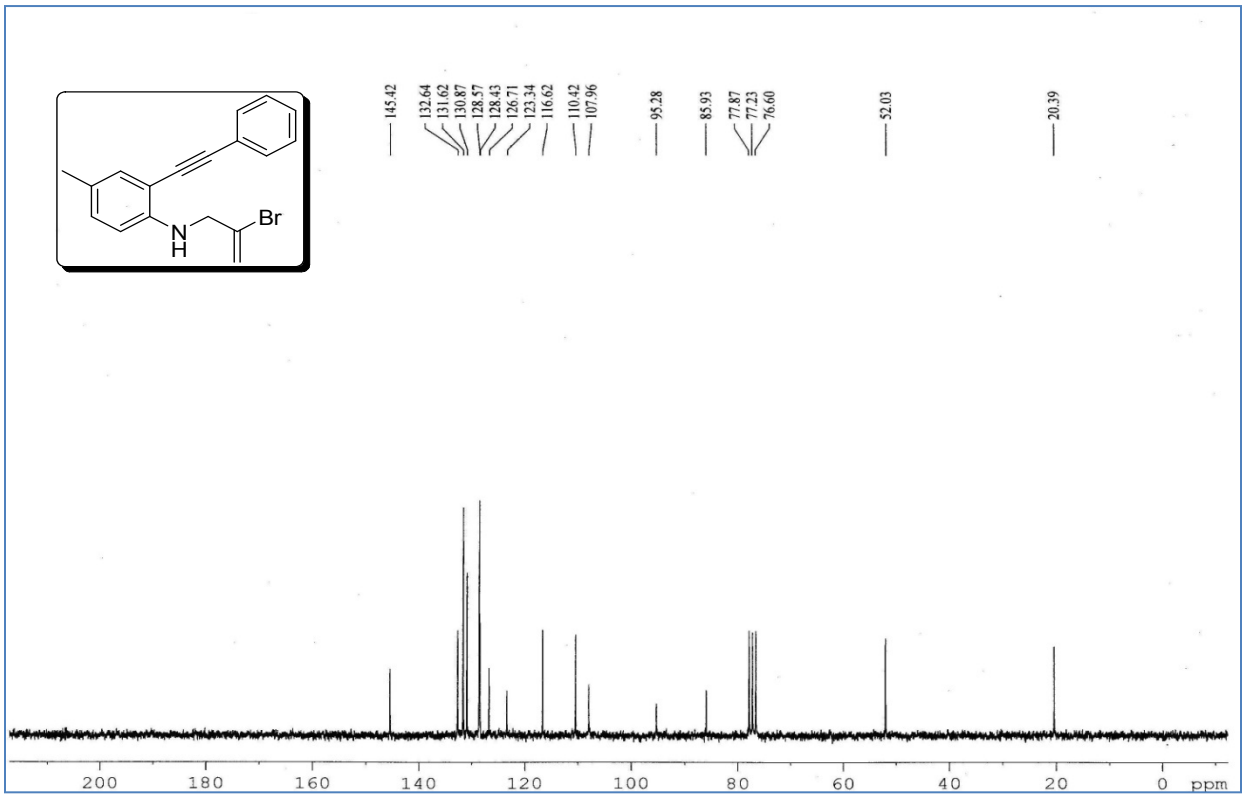
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2c):



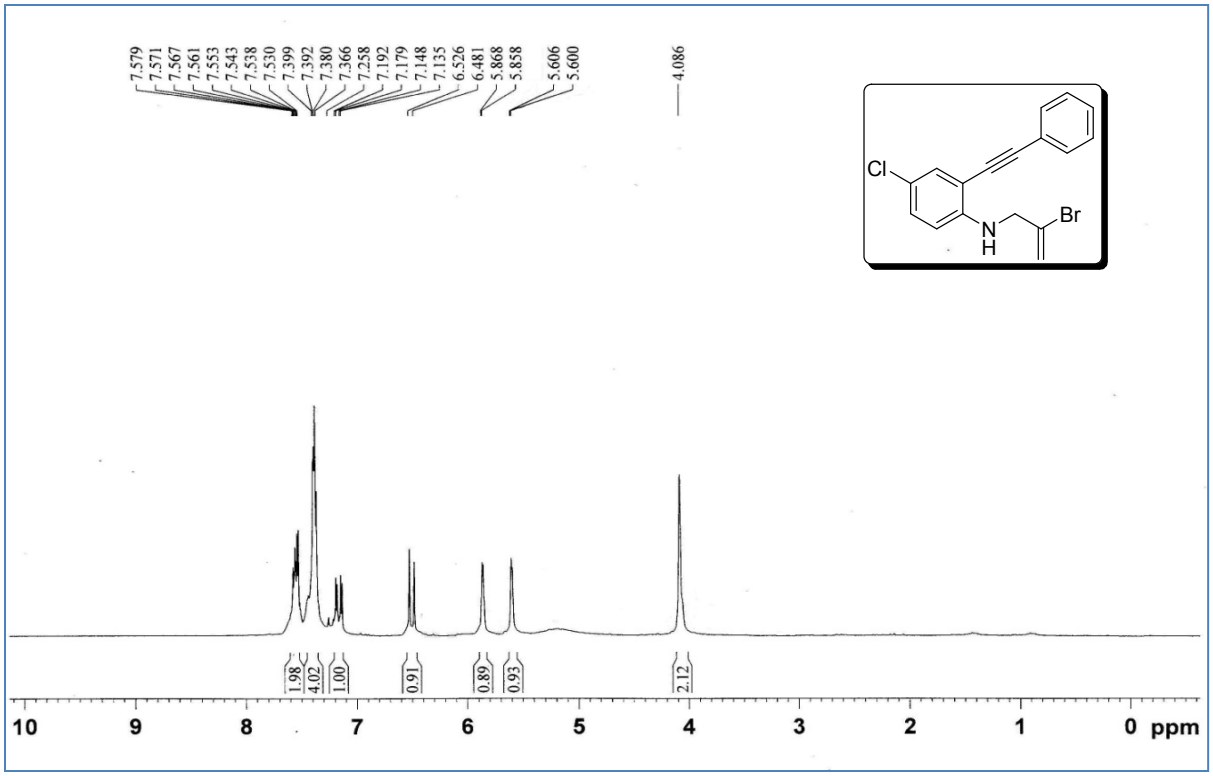
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2d):



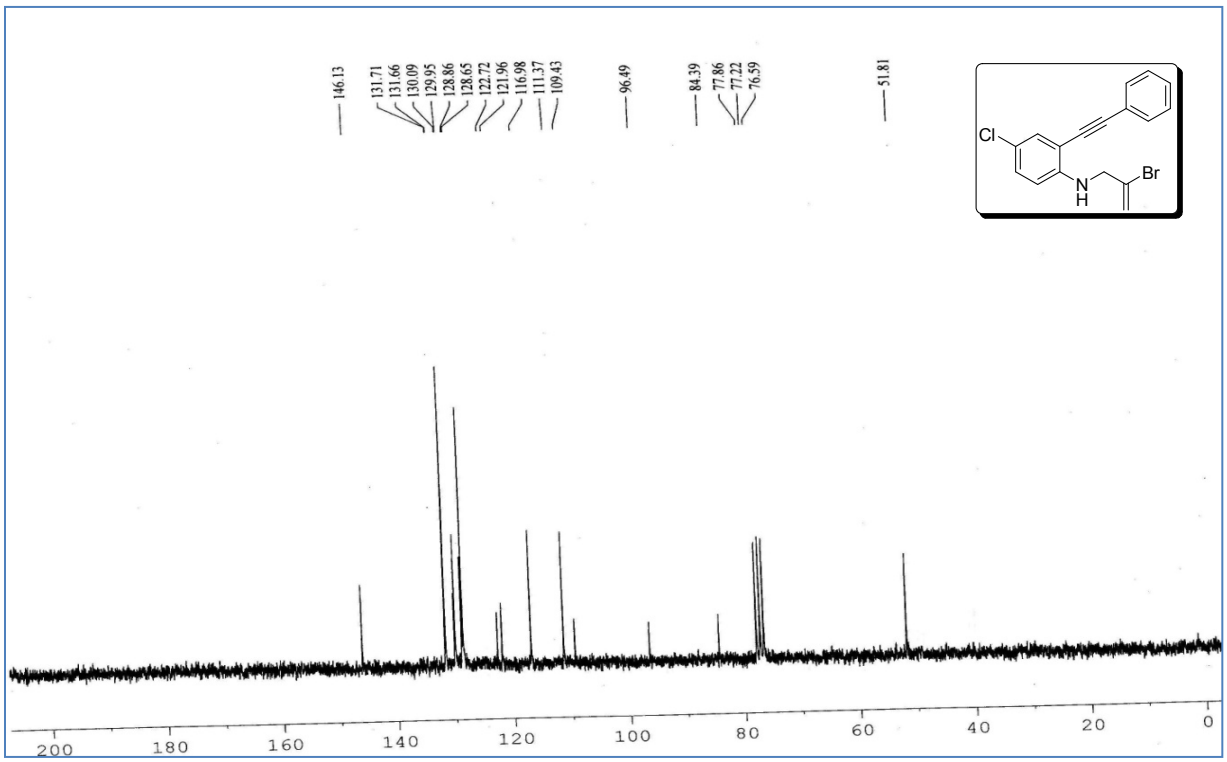
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2d):



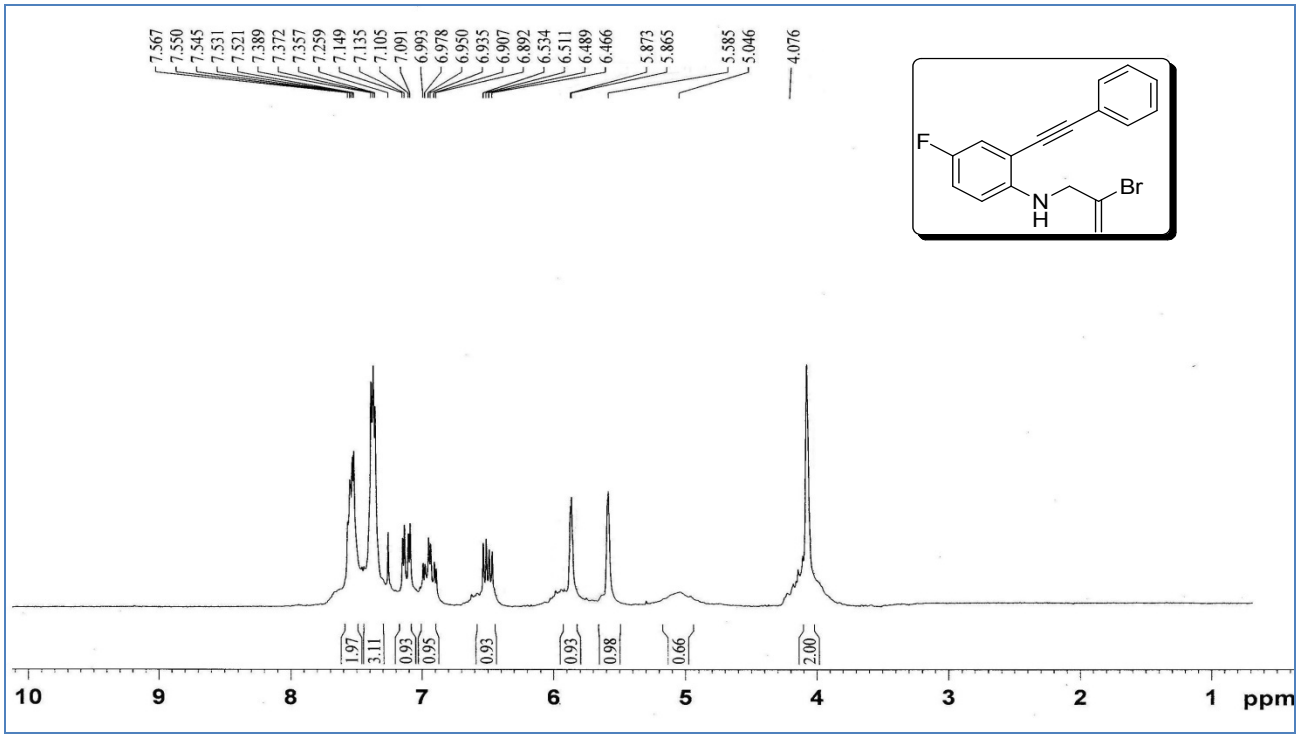
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2e):



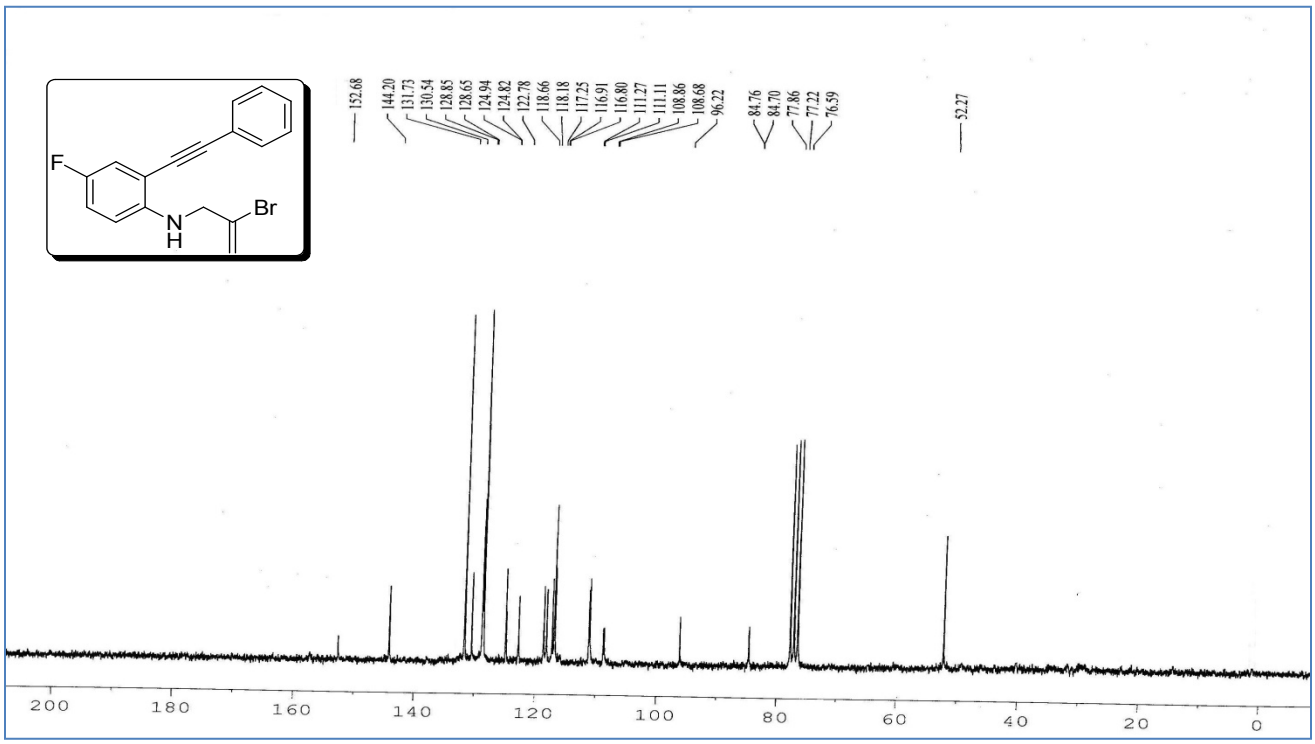
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2e):



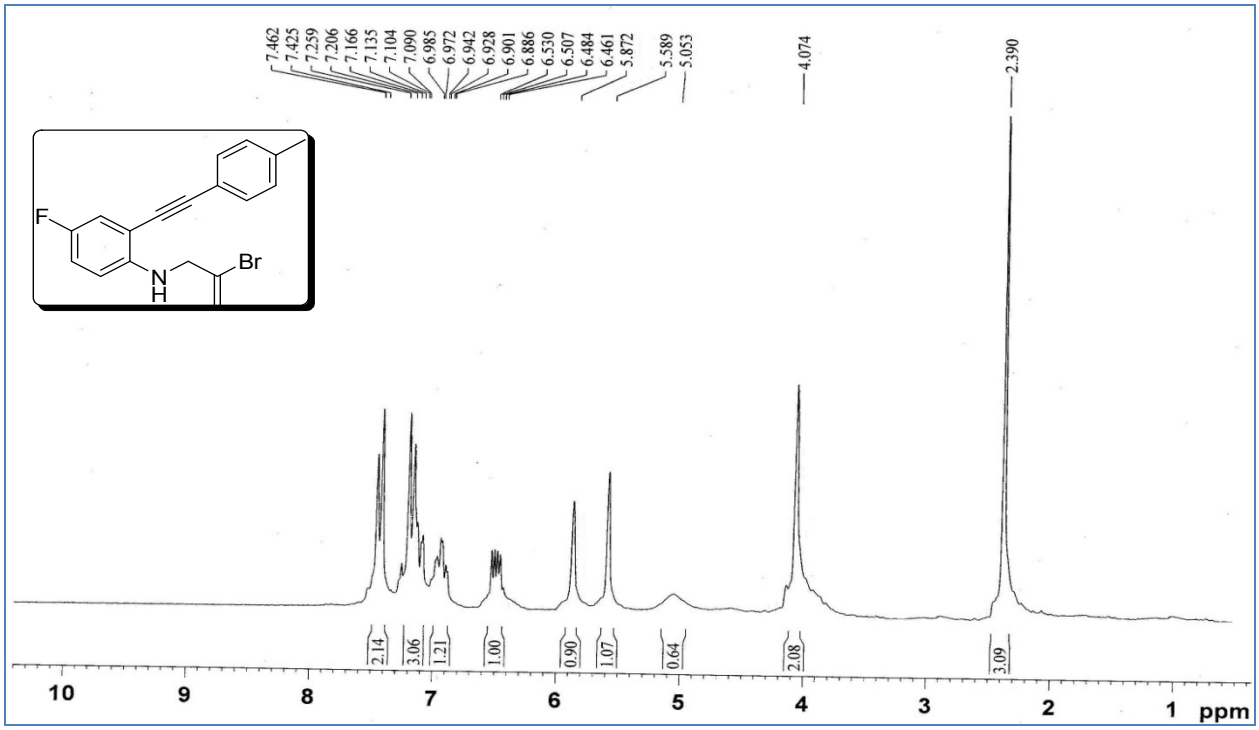
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2f):



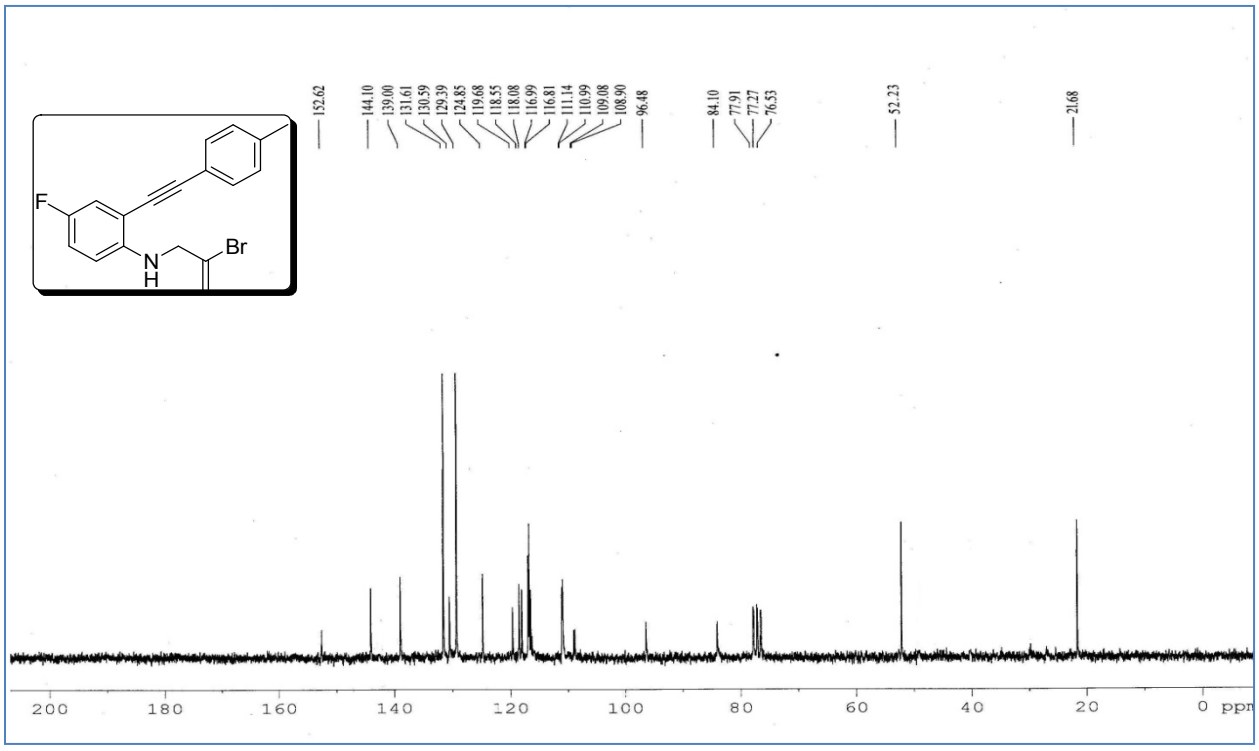
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2f):



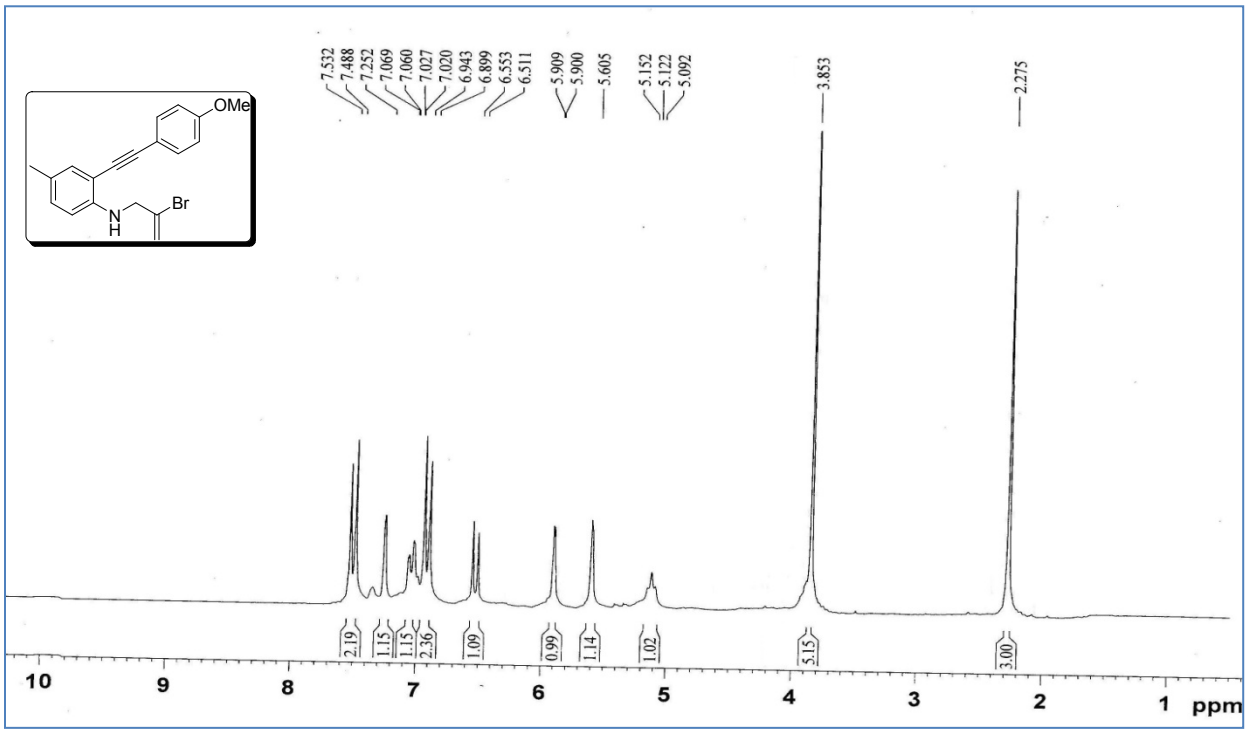
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2g):



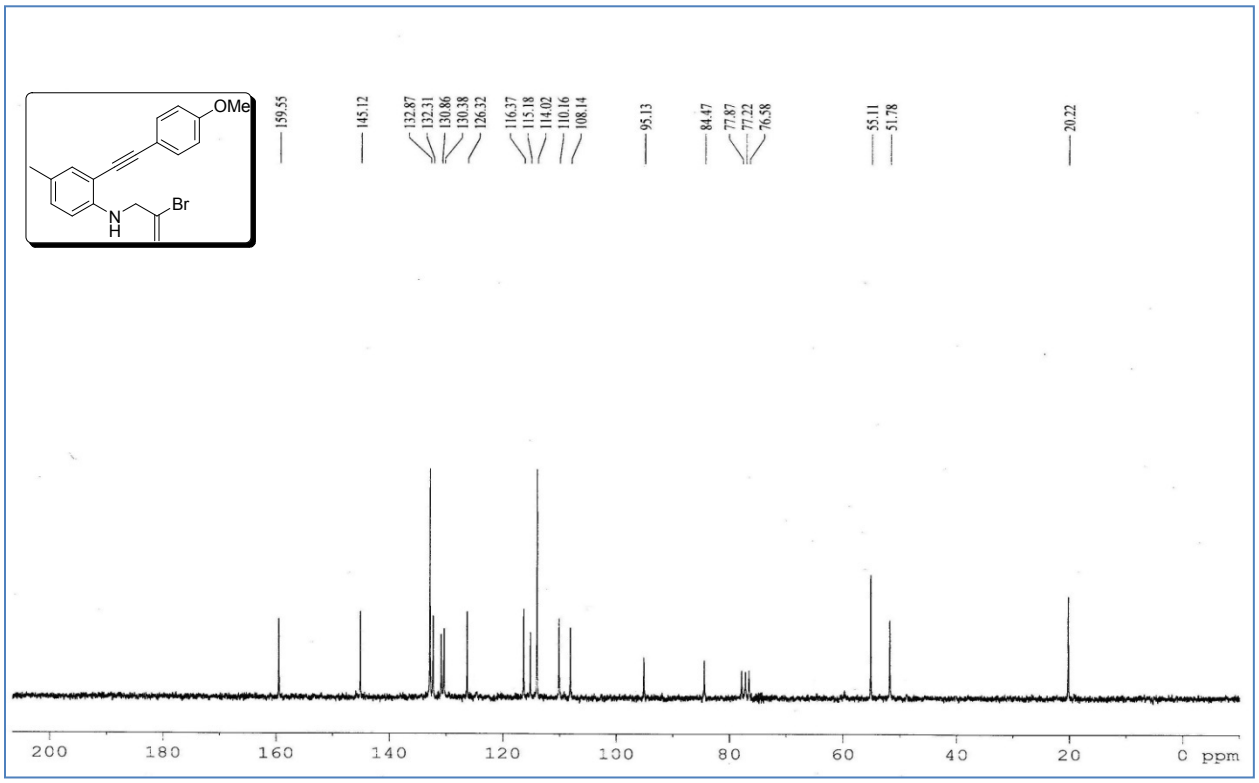
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2g):



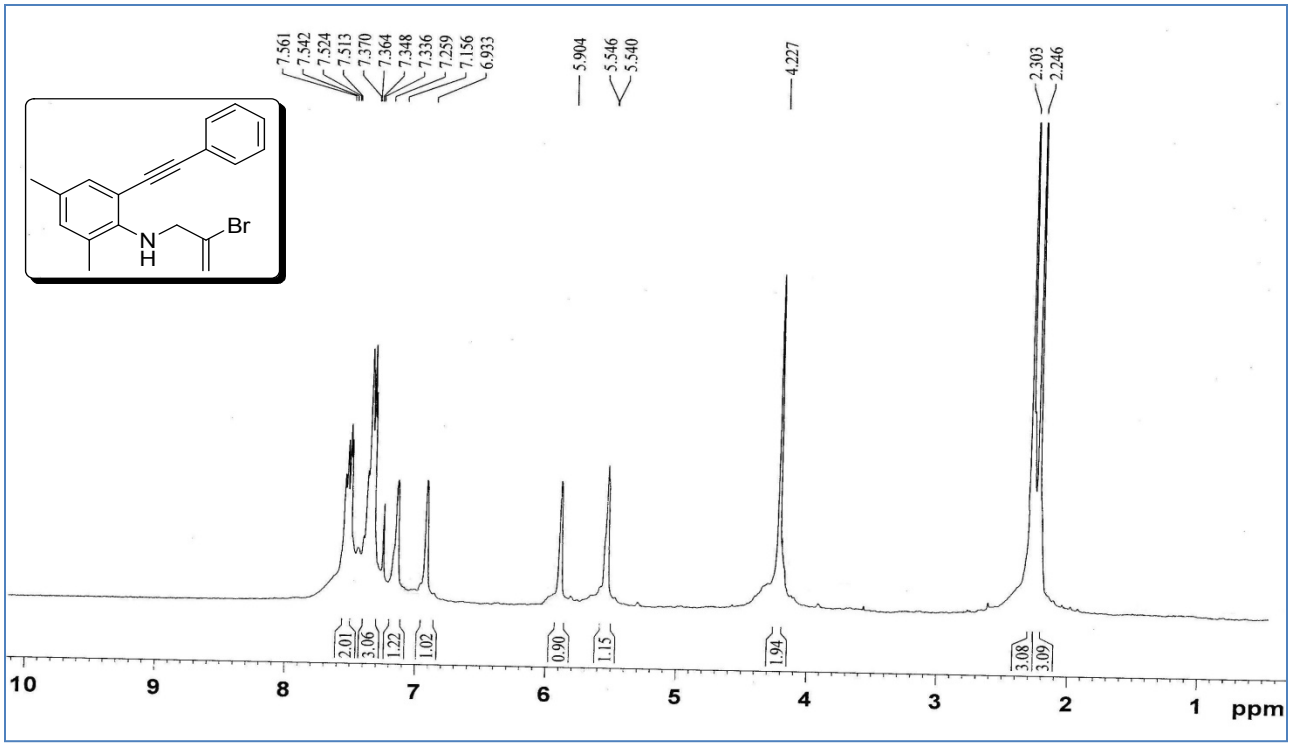
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2h):



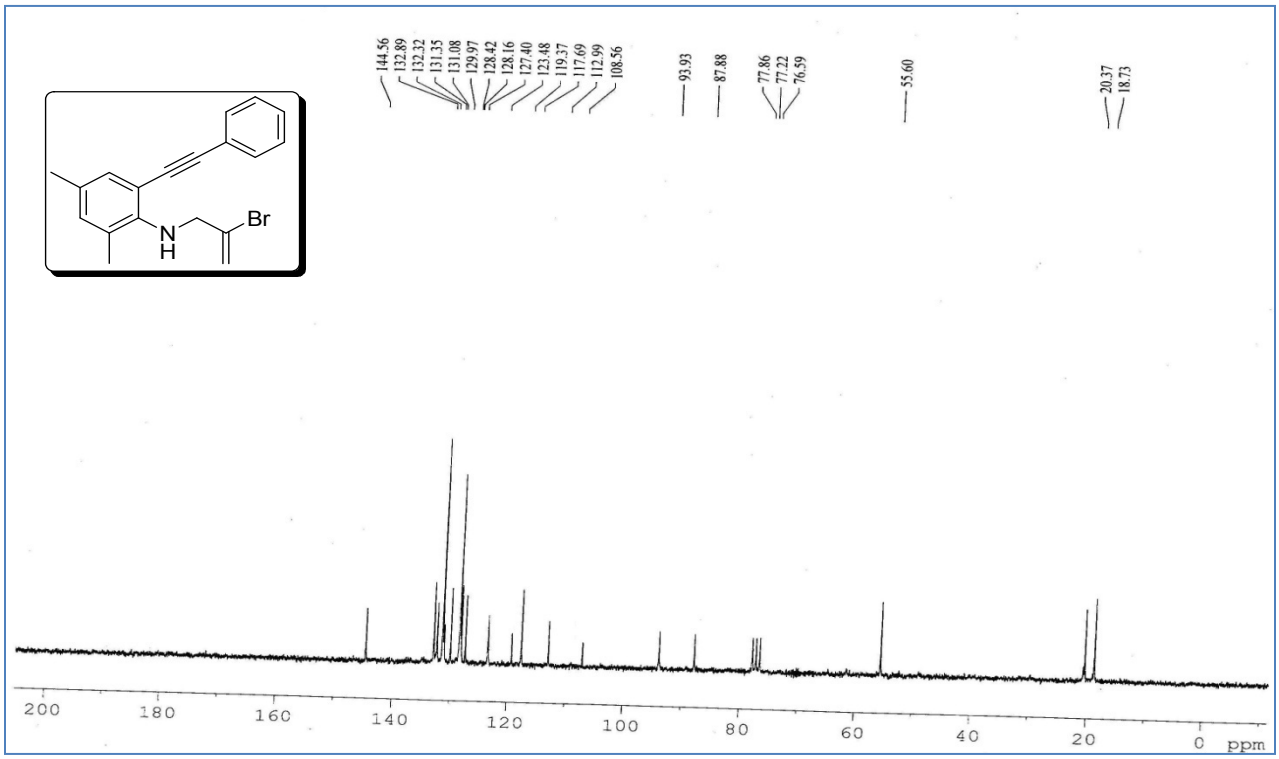
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2h):



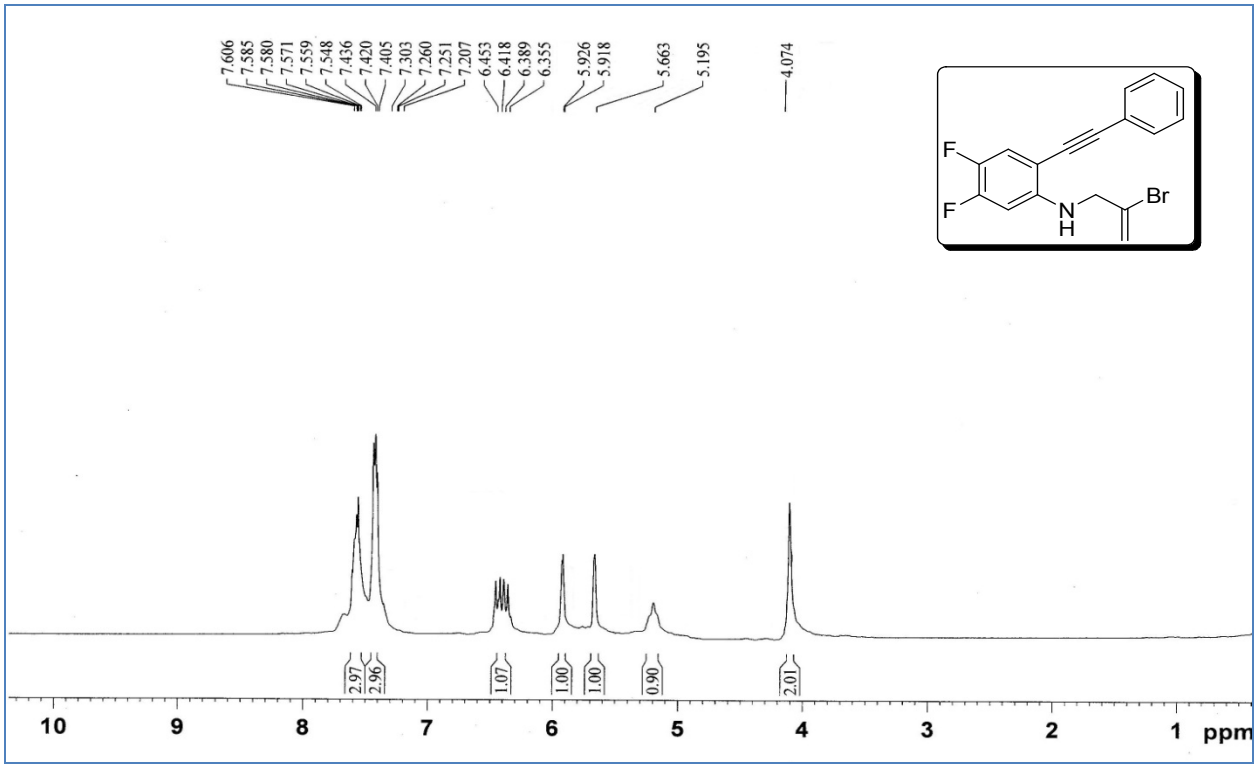
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2i):



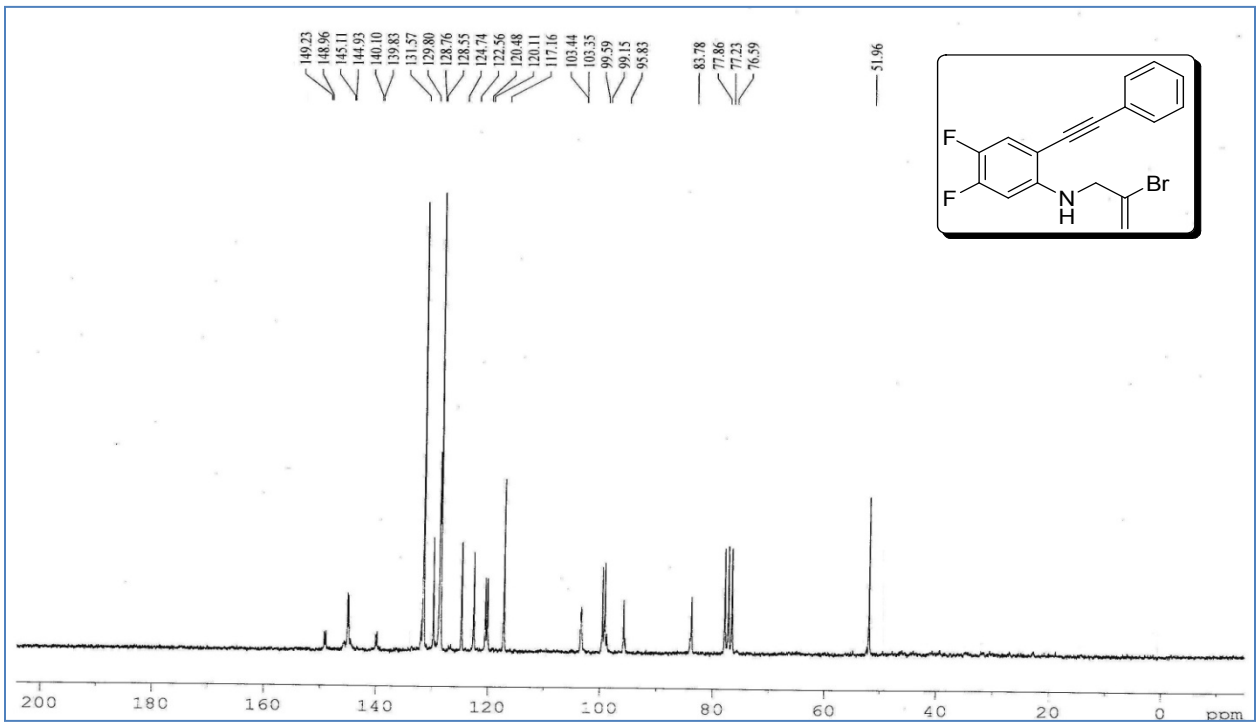
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2i):



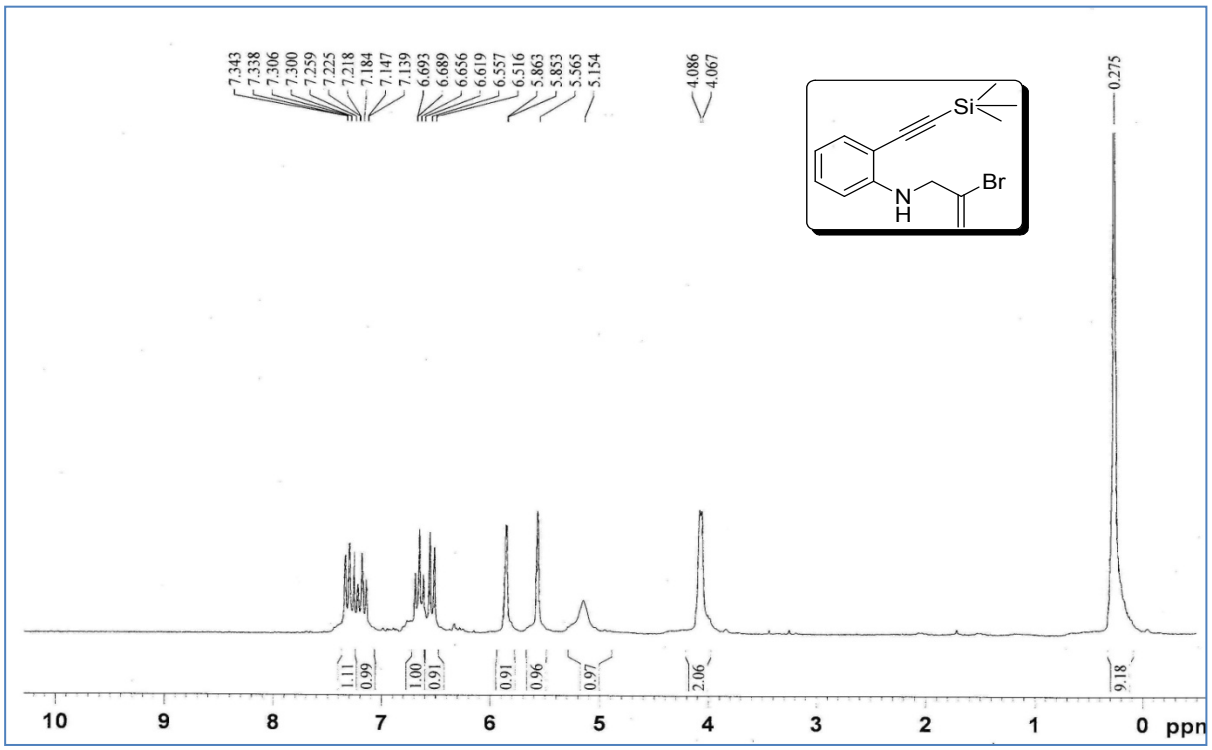
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2j):



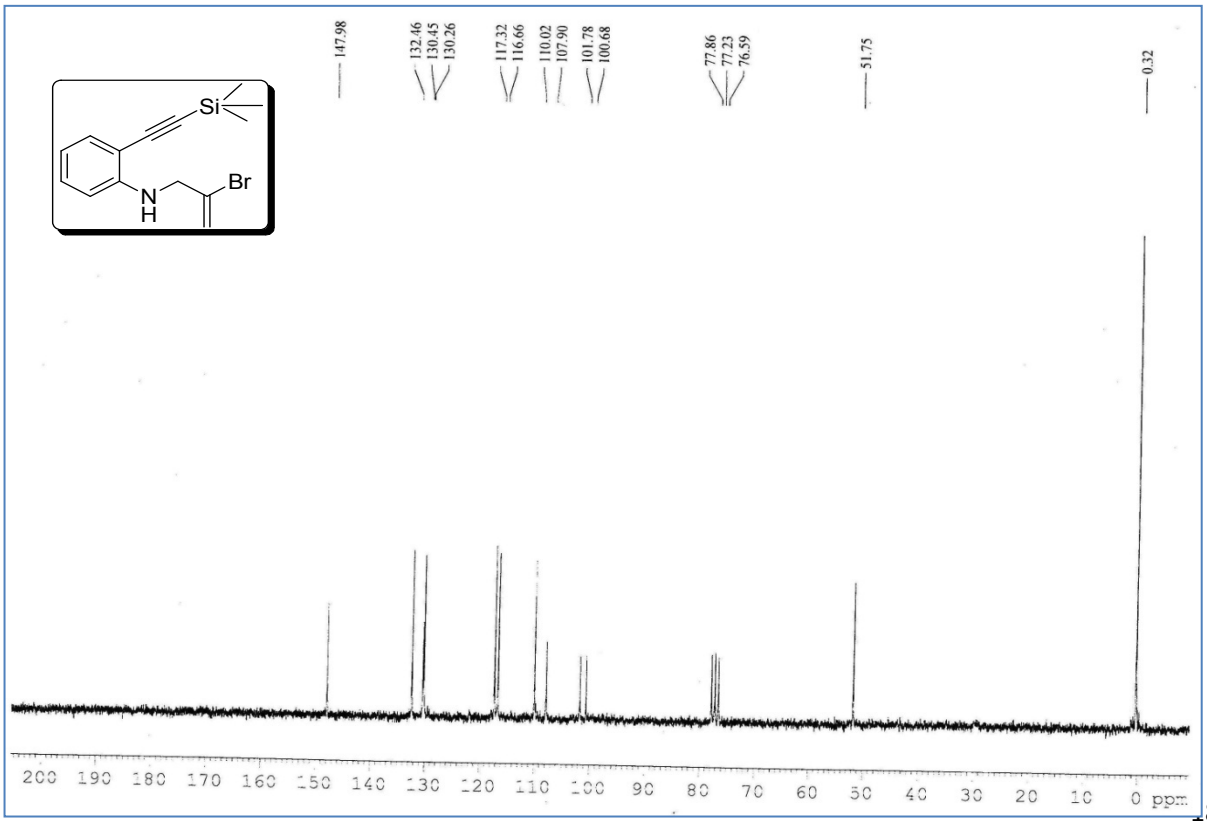
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2j):



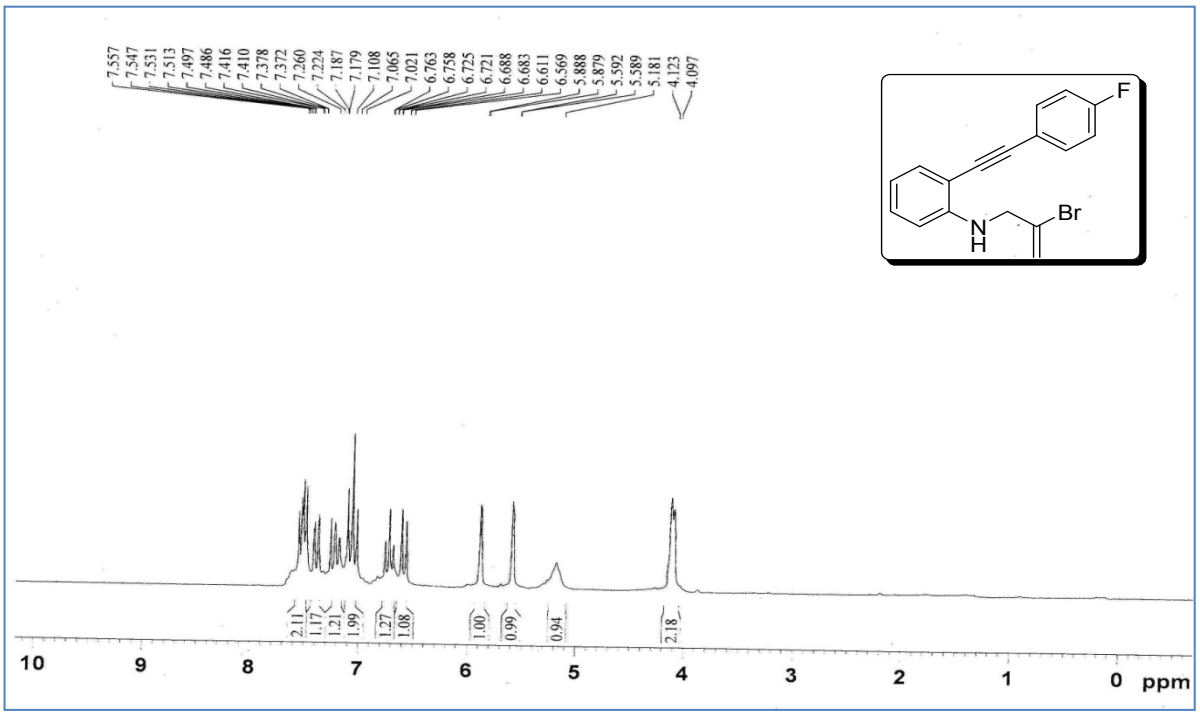
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2k):



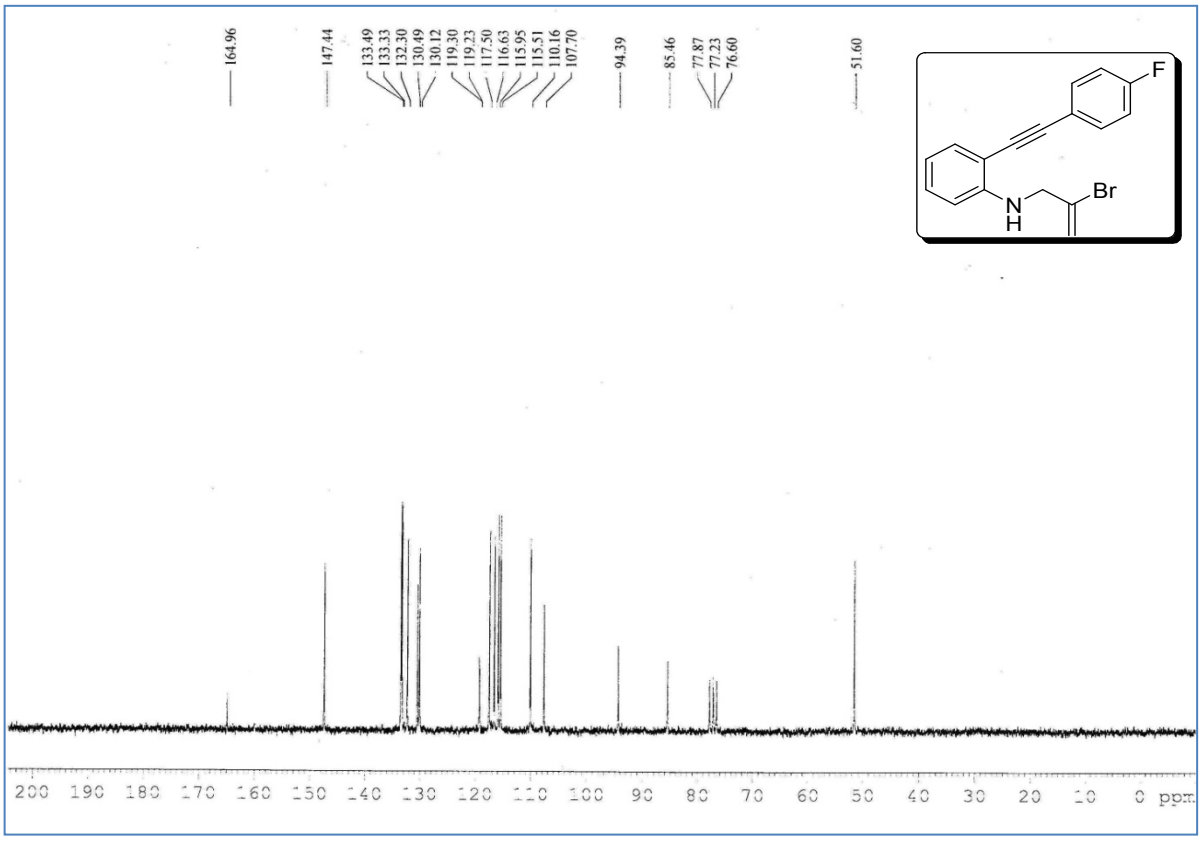
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2k):



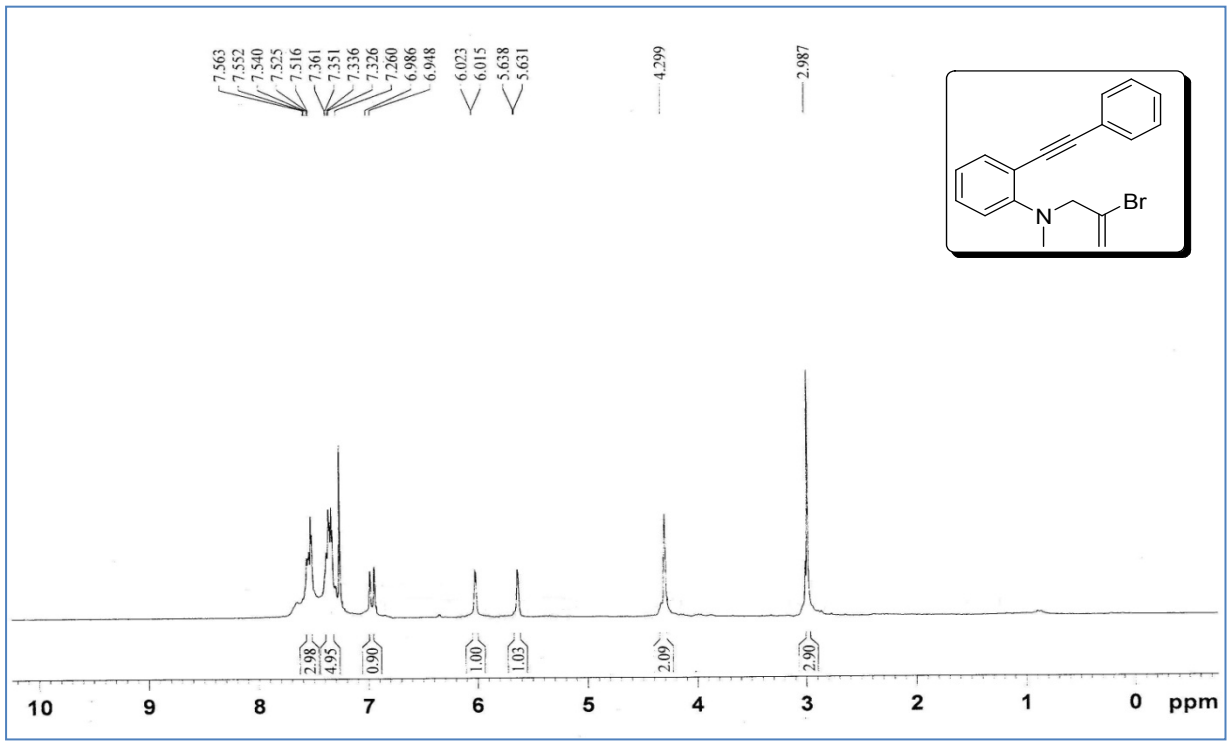
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2l):



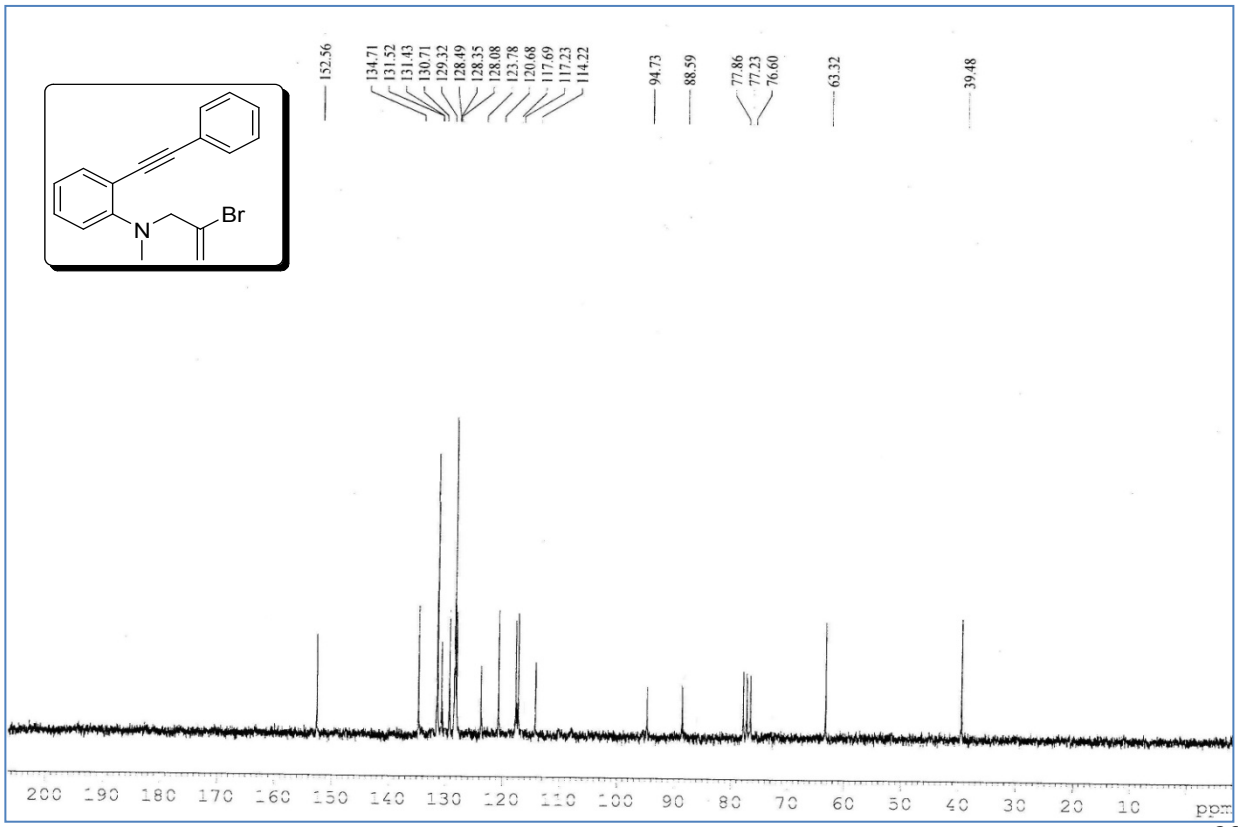
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2l):



^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (2m):

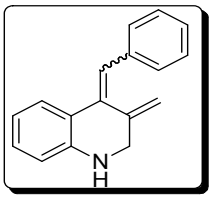


^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (2m):



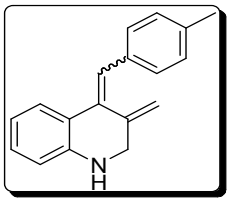
Spectral data for compounds 3a-3m:

4-Benzylidene-3-methylene-1,2,3,4-tetrahydroquinoline (3a):



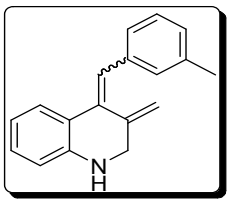
Yellow liquid, Yield = 82%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.66-7.62 (m, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.37-7.26 (m, 5H), 7.10-7.06 (m, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.66-6.59 (m, 1H), 5.18 (s, 1H), 5.10 (s, 1H), 4.04 (s, 2H), 3.81 (br, 1H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 144.7, 138.2, 134.7, 131.7, 129.0 (2C), 128.9, 128.5, 128.3 (2C), 126.7, 123.8, 121.8, 118.4, 116.3, 115.6, 50.0. Anal. Calcd. for $C_{17}H_{15}N$: C : 87.52, H : 6.48, N : 6.00 %; Found : C : 87.39, H : 6.51, N : 5.91 %. HRMS Calcd. for $C_{17}H_{16}N^+$ [M+ H]$^+$: 234.1277; Found: 234.1318.

4-(4-Methyl-benzylidene)-3-methylene-1,2,3,4-tetrahydroquinoline (3b):



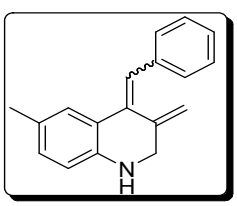
Yellow liquid, Yield = 80%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.49-7.37 (m, 3H), 7.26-7.09 (m, 5H), 6.78-6.74 (m, 2H), 5.18 (s, 1H), 5.13 (s, 1H), 4.03 (s, 2H), 3.70 (br, 1H), 2.37 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 147.9, 144.5, 138.5, 132.2, 131.5 (2C), 130.0, 129.7 (2C), 129.3, 129.0, 128.9, 123.7, 120.4, 118.1, 114.5, 49.9, 21.7. Anal. Calcd. for $C_{18}H_{17}N$: C : 87.41, H : 6.93, N : 5.66 %; Found : C : 87.33, H : 6.99, N : 5.55 %. HRMS Calcd. for $C_{18}H_{18}N^+$ [M+H]$^+$: 248.1434; Found : 248.1449.

4-(3-Methyl-benzylidene)-3-methylene-1,2,3,4-tetrahydroquinoline (3c):



Yellow liquid, Yield = 72%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 1H), 7.30-7.00 (m, 6H), 6.87-6.75 (m, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.19 (s, 1H), 5.13 (s, 1H), 4.04 (s, 2H), 3.07 (br, 1H), 2.38 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 144.6, 138.2, 137.8, 135.6, 129.7, 129.2, 128.8, 128.1, 127.7, 127.4, 126.0, 123.8, 122.0, 118.4, 116.3, 115.6, 50.0, 21.6. Anal. Calcd. for $C_{18}H_{17}N$: C : 87.41, H : 6.93, N : 5.66 %; Found : C : 87.36, H : 6.94, N : 5.57 %. HRMS Calcd. for $C_{18}H_{18}N^+$ [M+H]$^+$: 248.1434; Found : 28.1453.

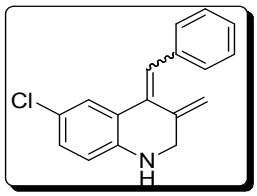
4-Benzylidene-6-methyl-3-methylene-1,2,3,4-tetrahydroquinoline (3d):



Yellow liquid, Yield = 76%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.49 (d, *J* = 7.8 Hz, 3H), 7.40-7.26 (m, 4H), 7.02-6.91 (m, 2H), 6.55 (d, *J* = 8.2 Hz, 1H),

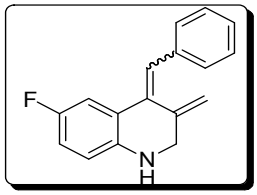
5.17 (s, 1H), 5.09 (s, 1H), 4.00 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 142.5, 138.5, 138.3, 134.7, 131.6, 129.8, 129.6, 129.0, 128.3 (2C), 127.6, 126.6, 123.9, 121.5, 116.3, 115.8, 50.1, 20.9. Anal. Calcd. for $C_{18}H_{17}N$: C : 87.41, H : 6.93, N : 5.66 %; Found : C : 87. 28, H : 6.91, N : 5.60 %. HRMS Calcd. for $C_{18}H_{18}N^+$ $[M+H]^+$: 248.1434; Found : 248.1450.

4-Benzylidene-6-chloro-3-methylene-1,2,3,4-tetrahydroquinoline (3e):



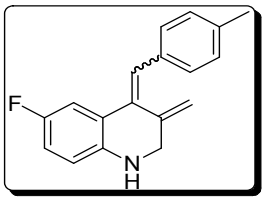
Yellow liquid, Yield = 74%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.54-7.51 (m, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.37-7.22 (m, 4H), 7.07-6.93 (m, 2H), 6.48 (dd, J_1 = 1.4 Hz, J_2 = 8.6 Hz, 1H), 5.15 (s, 1H), 5.07 (s, 1H), 4.25 (br, 1H), 3.98 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 143.1, 137.7, 137.3, 133.6, 131.7, 129.0 (2C), 128.6 (2C), 128.4 (2C), 126.9, 123.5, 122.8, 116.8, 116.6, 49.7. Anal. Calcd. for $C_{17}H_{14}ClN$: C: 76.26, H : 5.27, N : 5.23 %; Found : C : 76.23, H : 5.29, N : 5.16 %. HRMS Calcd. for $C_{17}H_{15}ClN^+$ $[M+H]^+$: 268.0888; Found : 268.0882.

4-Benzylidene-6-fluoro-3-methylene-1,2,3,4-tetrahydroquinoline (3f):



Yellow liquid, Yield = 64%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.44 (d, J = 7.4 Hz, 2H), 7.33-7.26 (m, 5H), 6.93 (s, 1H), 6.84-6.75 (m, 1H), 6.52 (dd, J_1 = 5.0 Hz, J_2 = 8.8 Hz, 1H), 5.16 (s, 1H), 5.07 (s, 1H), 3.96 (s, 2H), 3.11 (br, 1H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 152.7, 144.2, 139.0, 131.7 (2C), 130.5, 128.7 (J = 10.0 Hz) (3C), 124.9 (J = 6.0 Hz), 122.8, 118.4 (J = 24.0 Hz), 117.2, 116.8 (J = 5.5 Hz) (2C), 111.2 (J = 8.0 Hz), 49.3. Anal. Calcd.for $C_{17}H_{14}FN$: C : 81.25, H : 5.62, N : 5.57 %; Found : C : 81.17, H : 5.66, N : 5.49 %. HRMS Calcd. for $C_{17}H_{15}FN^+$ $[M+H]^+$: 252.1183; Found : 252.1227.

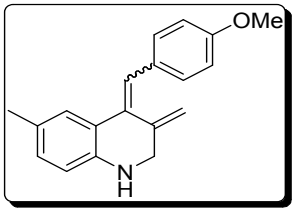
6-Fluoro-(4-methyl-benzylidene)-3-methylene-1,2,3,4-tetrahydroquinoline (3g):



Yellow liquid, Yield = 67%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.47-7.32 (m, 3H), 7.13 (d, J = 7.6 Hz, 3H), 6.91(s, 1H), 6.50 (dd, J_1 = 5.0 Hz, J_2 = 8.8 Hz, 1H), 5.17 (s, 1H), 5.14 (s, J = 1.2 Hz, 1H), 3.94 (s, 2H), 3.72 (br, 1H), 2.36 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 154.2, 140.9, 138.9, 137.9, 134.7, 131.6 (2C), 129.2 (J = 14.5 Hz) (2C), 128.8 (J = 7.0 Hz) (2C), 122.8, 117.3 (J = 28.0 Hz), 116.6 (J = 9.0 Hz), 115.6 (J = 23.0 Hz), 109.5 (J = 23.0 Hz), 49.9, 21.4. Anal. Calcd.

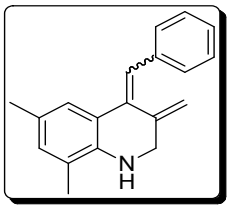
for $C_{18}H_{16}FN$: C : 81.48, H : 6.08, N : 5.28 %; Found : C : 81.37, H : 6.13, N : 5.19 %. HRMS Calcd. for $C_{18}H_{17}FN^+$ $[M+H]^+$: 266.1340; Found : 266.1361.

4-(4-Methoxy-benzylidene)-6-methyl-3-methylene-1,2,3,4-tetrahydroquinoline (3h):



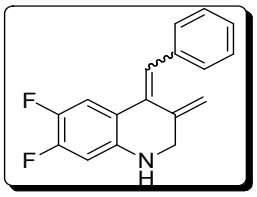
Yellow liquid, Yield = 73%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.43 (d, *J* = 8.8 Hz, 2H), 6.94-6.83 (m, 5H), 6.50 (d, *J* = 8.0 Hz, 1H), 5.16 (s, 1H), 5.13 (s, 1H), 3.96 (s, 2H), 3.82 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 158.4, 142.3, 138.9, 133.3, 133.0, 130.6, 130.2 (2C), 129.4, 127.4, 123.7, 122.1, 121.2, 115.8, 113.7 (2C), 55.3, 50.1, 20.9. Anal. Calcd. for $C_{19}H_{19}NO$: C : 82.28, H : 6.90, N : 5.05 %; Found : C : 82.17, H : 6.92, N : 4.99 %. HRMS Calcd. for $C_{19}H_{20}NO^+$ [M+H]+ : 278.1539; Found : 278.1566.

4-Benzylidene-6, 8-dimethyl-3-methylene-1,2,3,4-tetrahydroquinoline (3i):



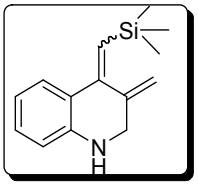
Yellow liquid, Yield = 69%, ^{1}H NMR (200 NMR in $CDCl_3$): δ = 7.50 (d, *J* = 7.4 Hz, 2H), 7.37-7.26 (m, 5H), 7.03 (s, 1H), 6.87 (s, 1H), 5.19 (s, 1H), 5.09 (s, 1H), 4.09 (s, 2H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 140.5, 138.7, 138.5, 135.3, 131.0, 129.0 (2C), 128.3 (2C), 127.0, 126.5, 122.7, 121.9, 121.5 (2C), 115.8, 50.2, 20.8, 17.5. Anal. Calcd. for $C_{19}H_{19}N$: C : 87.31, H : 7.33, N : 5.36 %; Found : C : 87.23, H : 7.35, N : 5.23 %. HRMS Calcd. for $C_{19}H_{20}N^+$ $[M+H]^+$: 262.1590; Found : 262.1573.

4-Benzylidene-6, 7-difluoro-3-methylene-1,2,3,4-tetrahydroquinoline (3j):



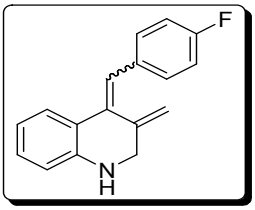
Yellow liquid; Yield = 60%, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.44-7.30 (m, 5H), 6.86 (s, 1H), 6.55 (dd, J_1 = 7.0 Hz, J_2 = 11.8 Hz, 1H), 6.38 (dd, J_1 = 7.0 Hz, J_2 = 11.8 Hz, 1H), 5.20 (s, 1H), 5.11 (s, 1H), 4.23 (br, 1H), 4.00 (s, 2H). ^{13}C NMR (50 MHz in $CDCl_3$): δ = 148.2 (*J* = 14.0 Hz), 145.2 (*J* = 7.5 Hz), 137.6 (*J* = 4.5 Hz), 137.2, 131.7 (2C), 128.9 (*J* = 7.5 Hz) (2C), 128.5 (*J* = 12.5 Hz) (2C), 126.9, 122.6 (*J* = 24.0 Hz), 120.1 (*J* = 19.0 Hz), 117.0, 111.9 (*J* = 18.5 Hz), 103.2 (*J* = 5.5 Hz), 49.7. Anal. Calcd. for $C_{17}H_{13}F_2N$: C : 75.82, H : 4.87, N : 5.20 %; Found : 75.76, H : 4.89, N ; 5.09 %. HRMS Calcd. for $C_{17}H_{14}F_2N^+$ $[M+H]^+$: 270.1089; Found : 270.2011.

3-Methylene-4-trimethylsilanylmethylene-1,2,3,4-tetrahydroquinoline (3k):



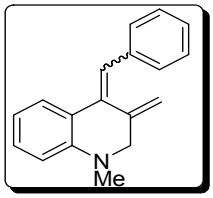
Yellow liquid, Yield = 74 %, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.15-6.98 (m, 2H), 6.69 (dd, J_1 = 7.4Hz, J_2 = 14.8 Hz, 2H), 6.57-6.45 (m, 1H), 5.35 (d, J = 1.4 Hz, 1H), 5.29 (d, J = 0.6 Hz, 1H), 3.9 (s, 2H), 0.20 (s, 3H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 149.8, 144.3, 142.0, 129.2, 124.4, 122.5, 118.2, 118.0, 115.4, 113.6, 49.3, 0.7 (3C). Anal. Calcd. for $C_{14}H_{19}NSi$: C : 73.30, H : 8.35, N ; 6.11 %; Found : C : 73.19, H : 8.42, N : 5.98 %. HRMS Calcd. for $C_{14}H_{20}NSi^+$: $[M+H]^+$: 230.1360; Found : 230.1369.

4-(4-Fluoro-benzylidene)-3-methylene-1,2,3,4-tetrahydroquinoline (3l):



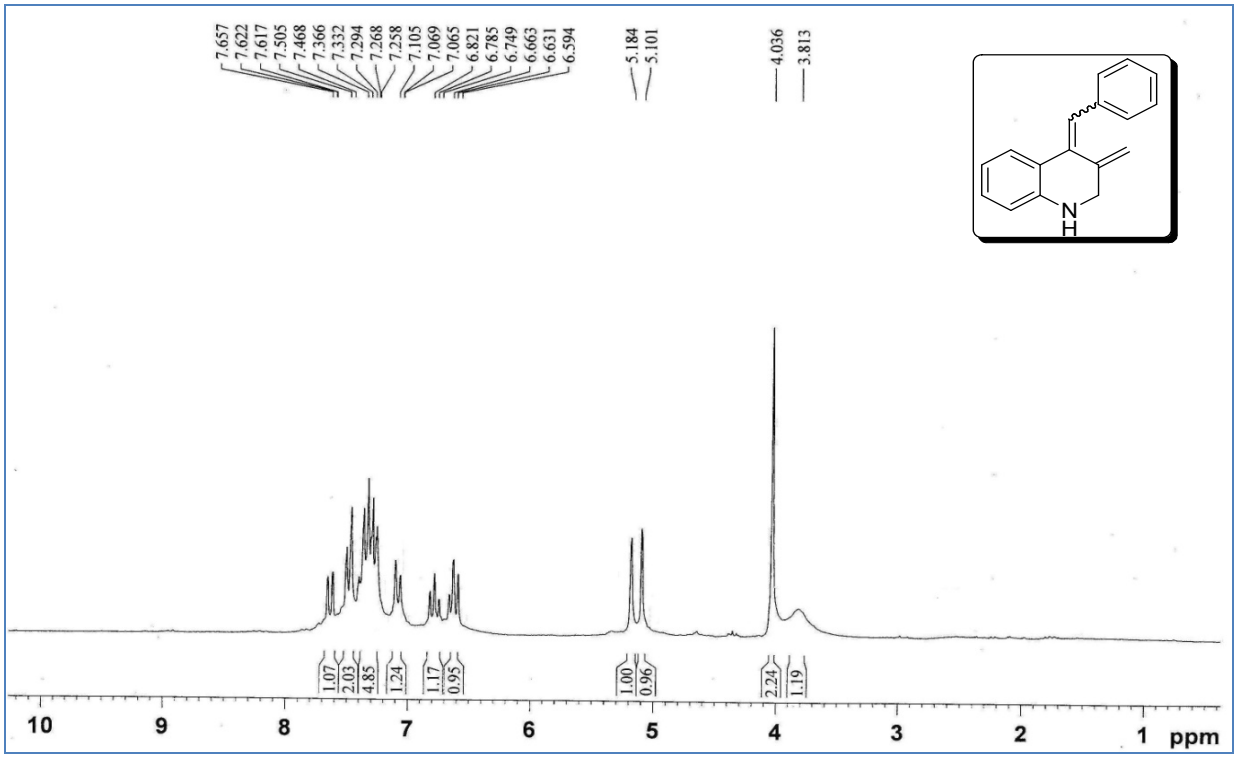
Yellow solid, Yield = 69 %, mp = 126^{0}C, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.58-7.50 (m, 2H), 7.40 (dd, J_1 = 5.6 Hz, J_2 = 8.4 Hz, 2H), 7.09-6.92 (m, 3H), 6.77-6.69 (m, 1H), 6.57 (d, J = 8.0 Hz, 1H), 5.15 (d, J = 1.0 Hz, 1H), 5.03 (s, 1H), 3.99 (s, 2H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 164.1, 144.6, 138.1, 134.7, 134.1 (J = 3.5 Hz), 133.5 (J = 8.0 Hz), 130.6 (J = 7.5 Hz) (2C), 128.9 (2C), 123.7, 120.5, 118.3 (J = 7.5 Hz), 116.4, 115.5 (J = 8.5 Hz) (2C), 49.9. Anal. Calcd. for $C_{17}H_{14}FN$: C : 81.25, H : 5.62, N : 5.57 %; Found : C : 81.14, H : 5.66, N : 5.49 %. HRMS Calcd. for $C_{17}H_{15}FN^+$: $[M+H]^+$: 252.1183; Found : 252.1195.

4-Benzylidene-1-methyl-3-methylene-1,2,3,4-tetrahydroquinoline (3m):

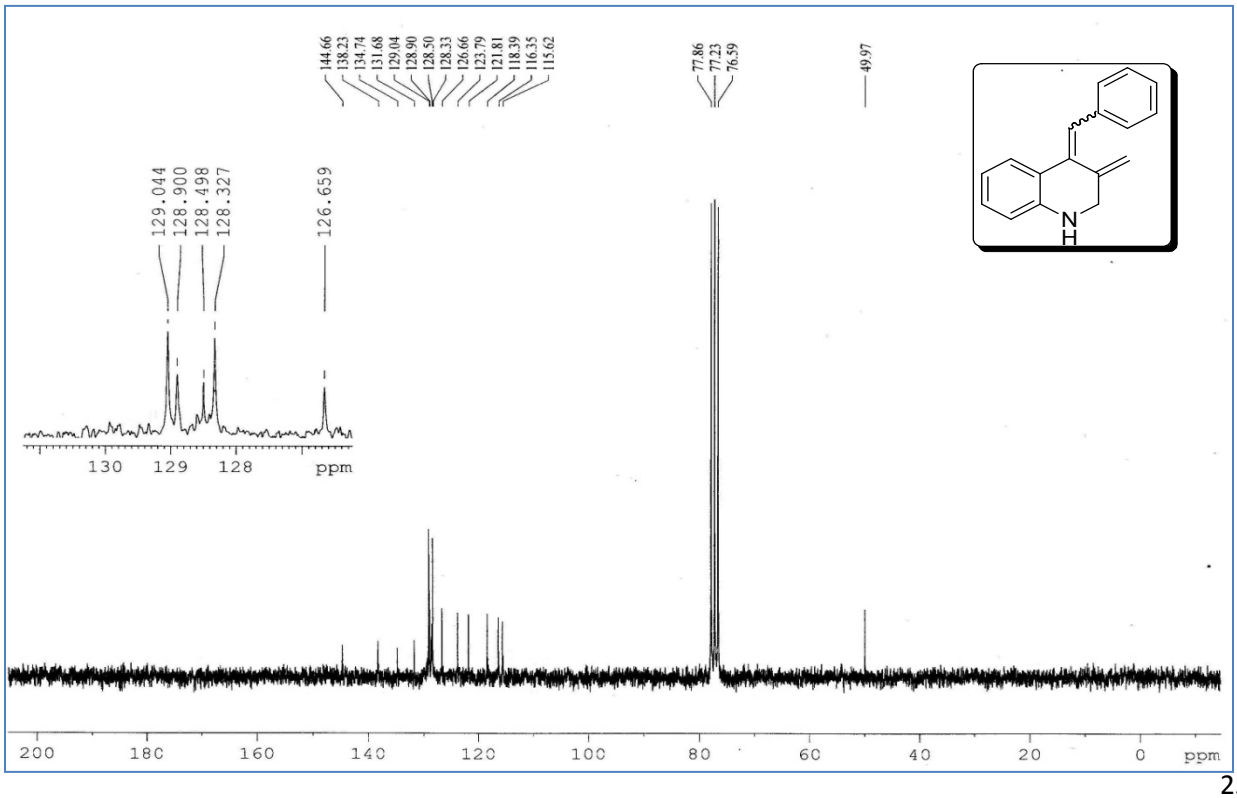


Yellow liquid, Yield = 68 %, ^{1}H NMR (200 MHz in $CDCl_3$): δ = 7.59 (dd, J_1 = 1.4 Hz, J_2 = 7.8 Hz, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.30-7.19 (m, 4H), 6.91 (d, J = 8.2 Hz, 1H), 6.81-6.67 (m, 2H), 5.12 (d, J = 1.2 Hz, 1H), 5.05 (s, 1H), 3.93 (s, 2H), 2.95 (s, 3H), ^{13}C NMR (50 MHz in $CDCl_3$): δ = 146.5, 138.6, 138.2, 135.4, 128.9 (2C), 128.3 (3C), 126.6, 123.7, 122.2, 117.8, 115.4, 112.4, 106.2, 58.6, 39.0. Anal. Calcd. for $C_{18}H_{17}N$: C : 87.41, H : 6.93, N : 5.66 %; Found : C : 87.36, H : 6.97, N : 5.52 %. HRMS Calcd. for $C_{18}H_{18}N^+$ $[M+H]^+$; 248.1434; Found : 248. 1446.

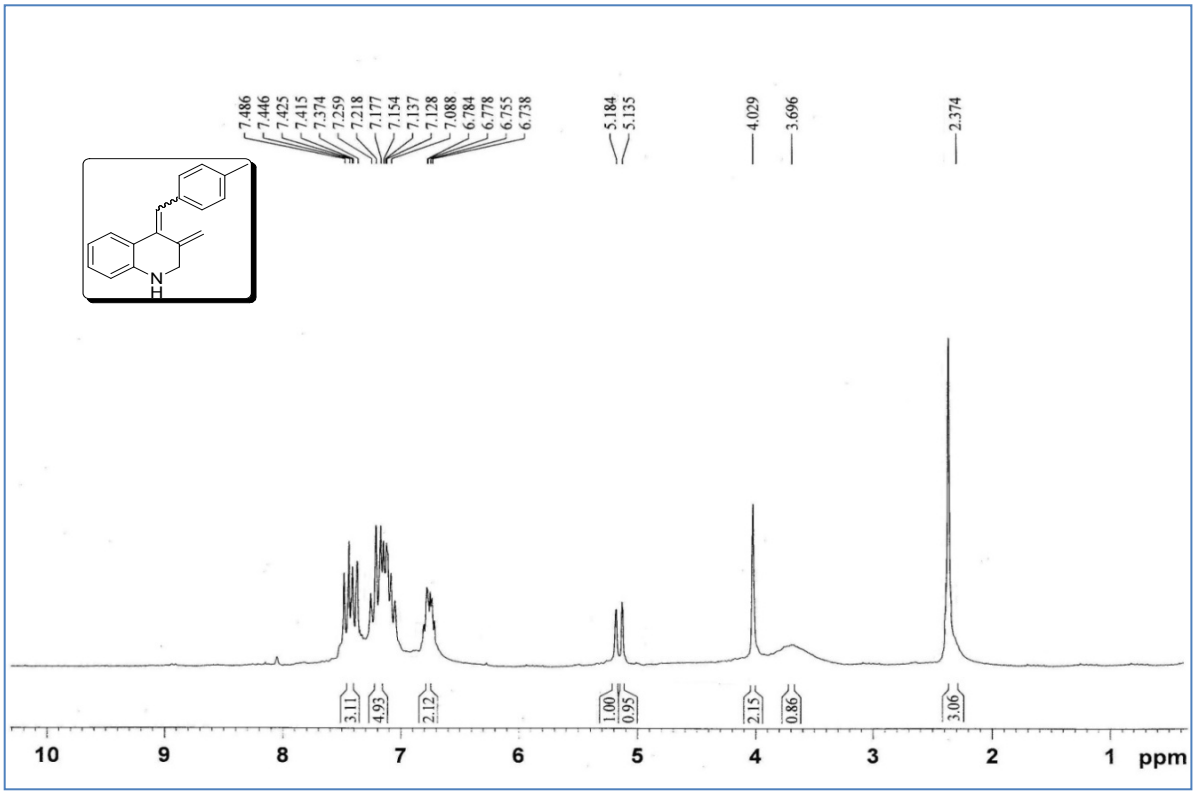
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3a):



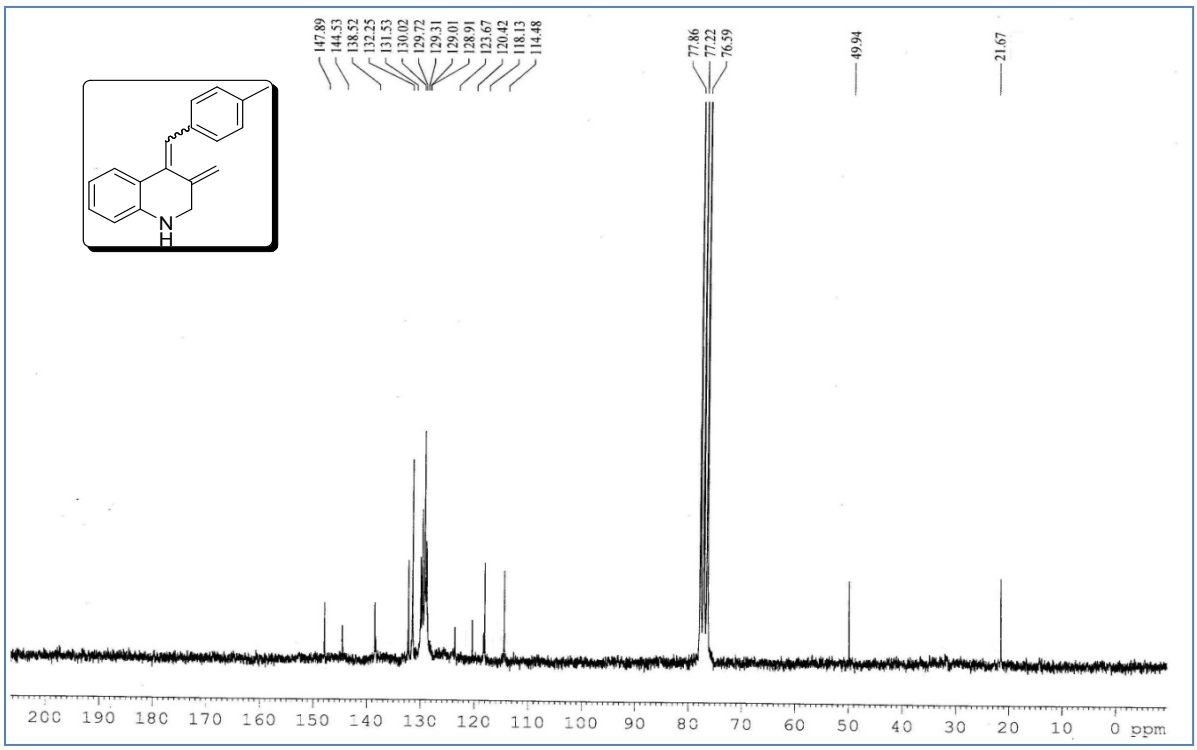
^{13}CNMR ($CDCl_3$, 50 MHz) Spectrum of (3a):



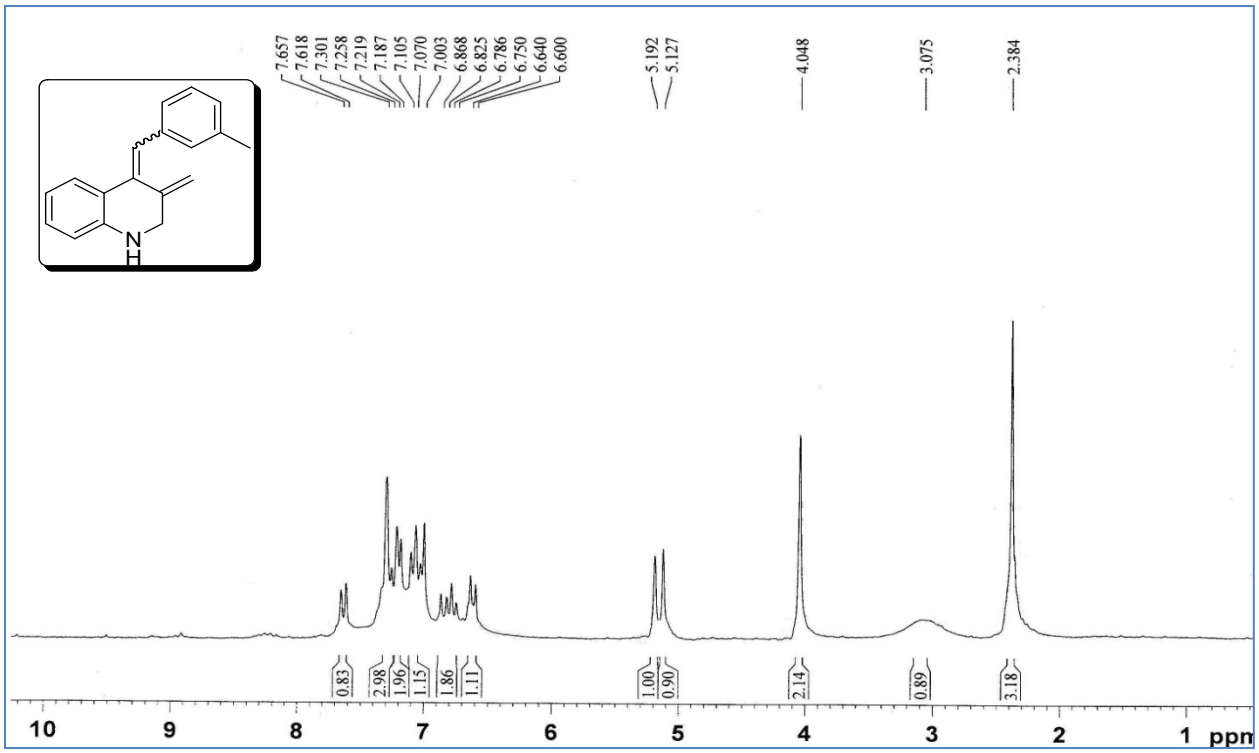
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3b):



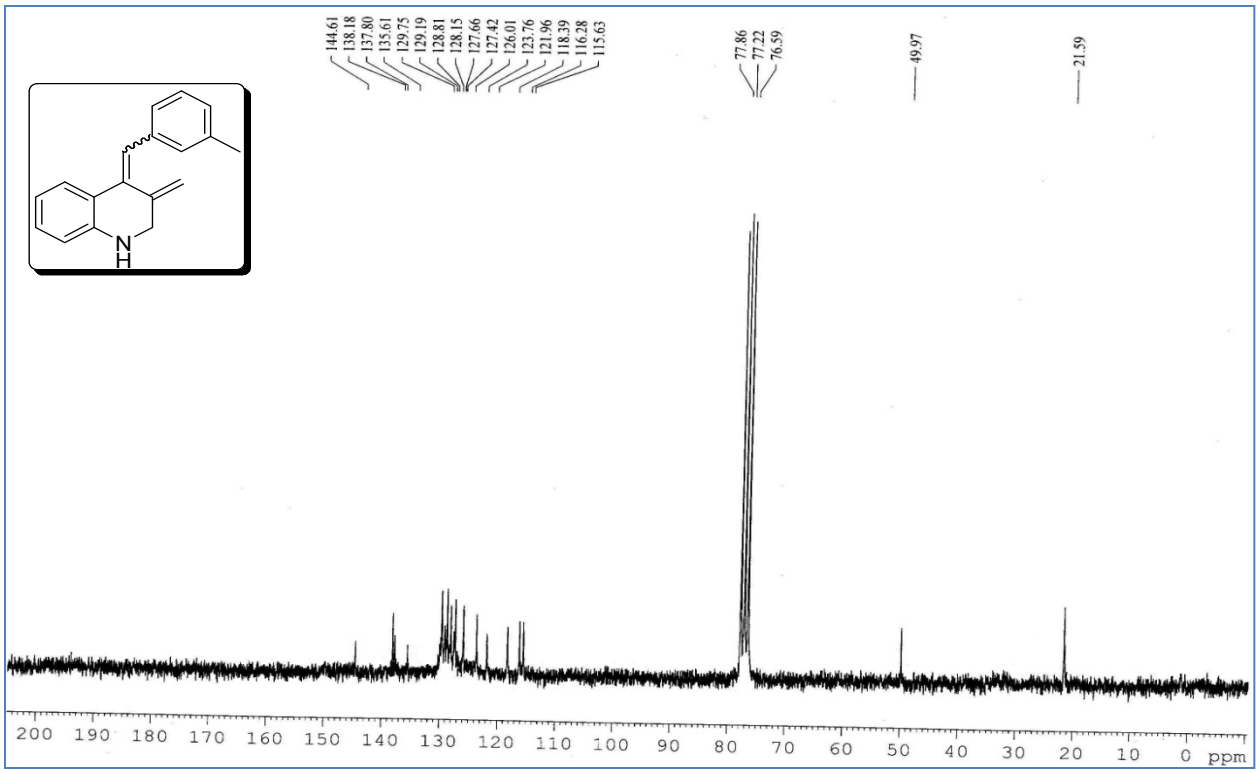
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3b):



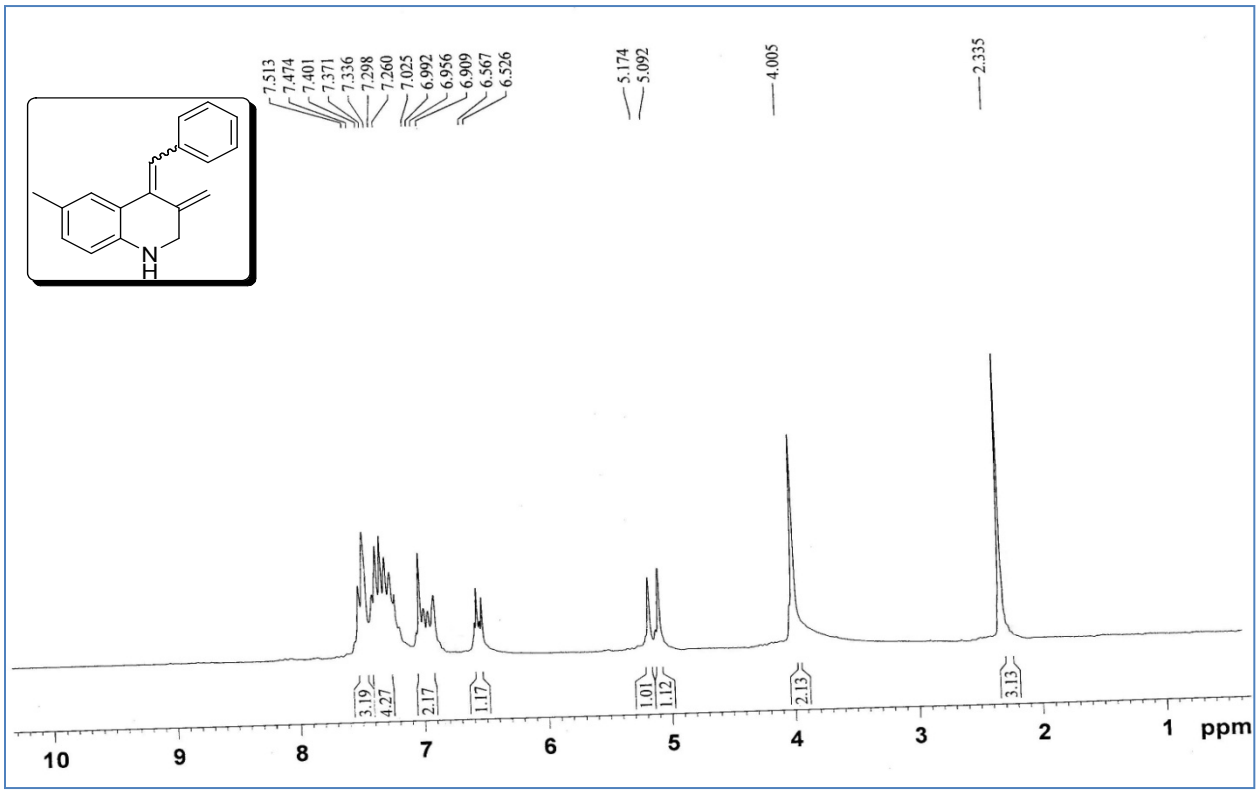
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3c):



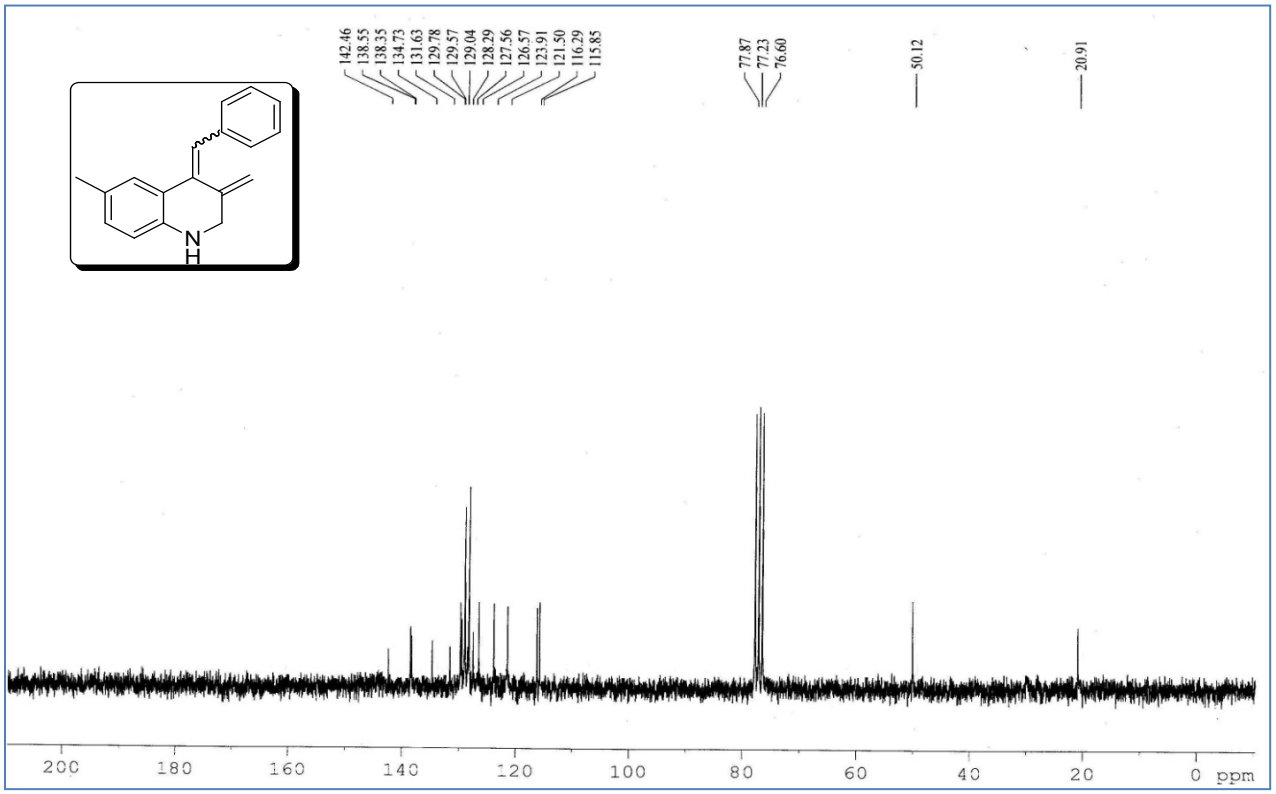
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3c):



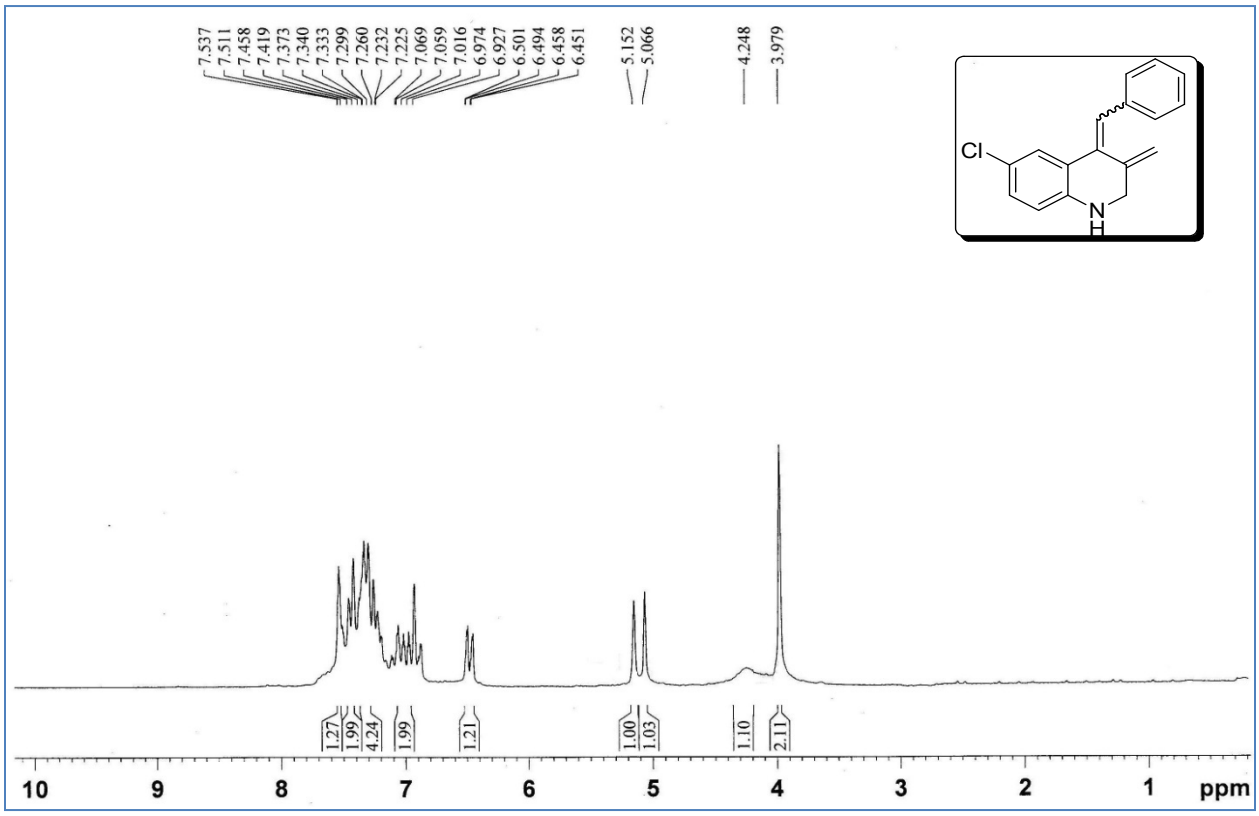
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3d):



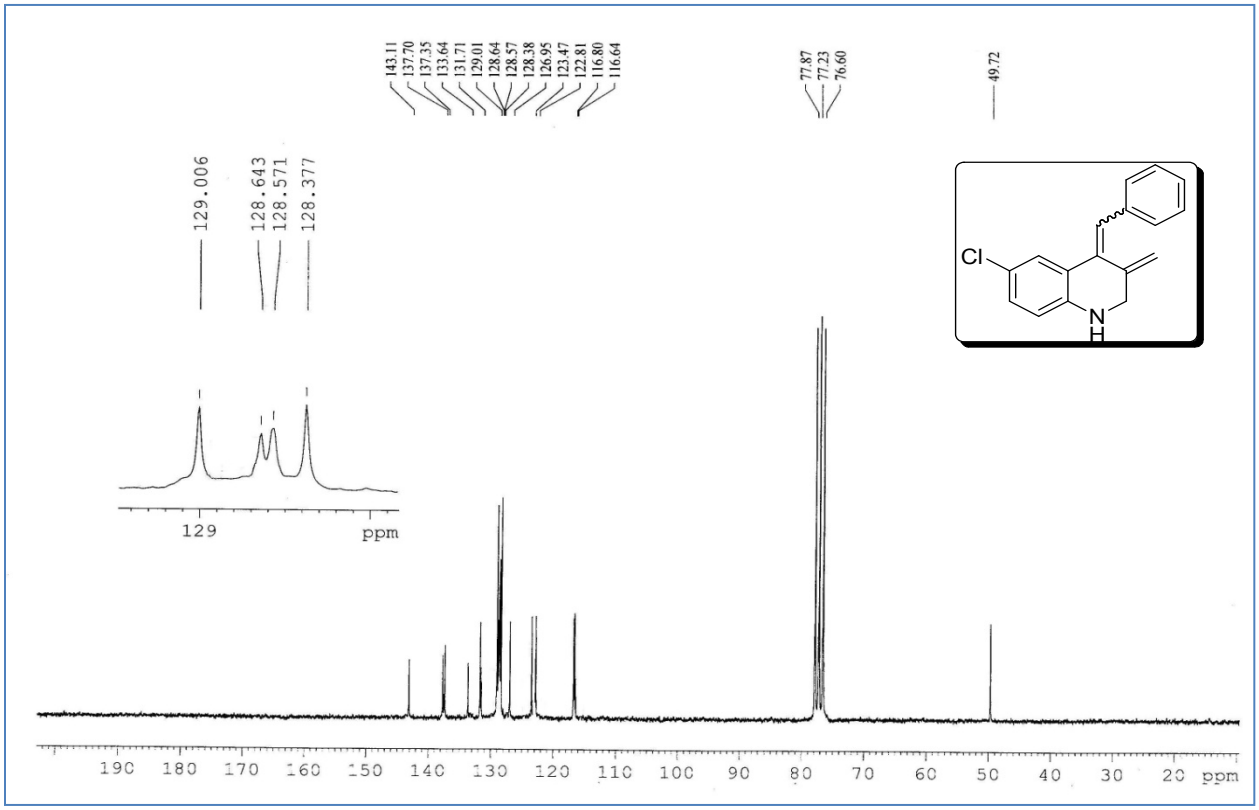
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3d):



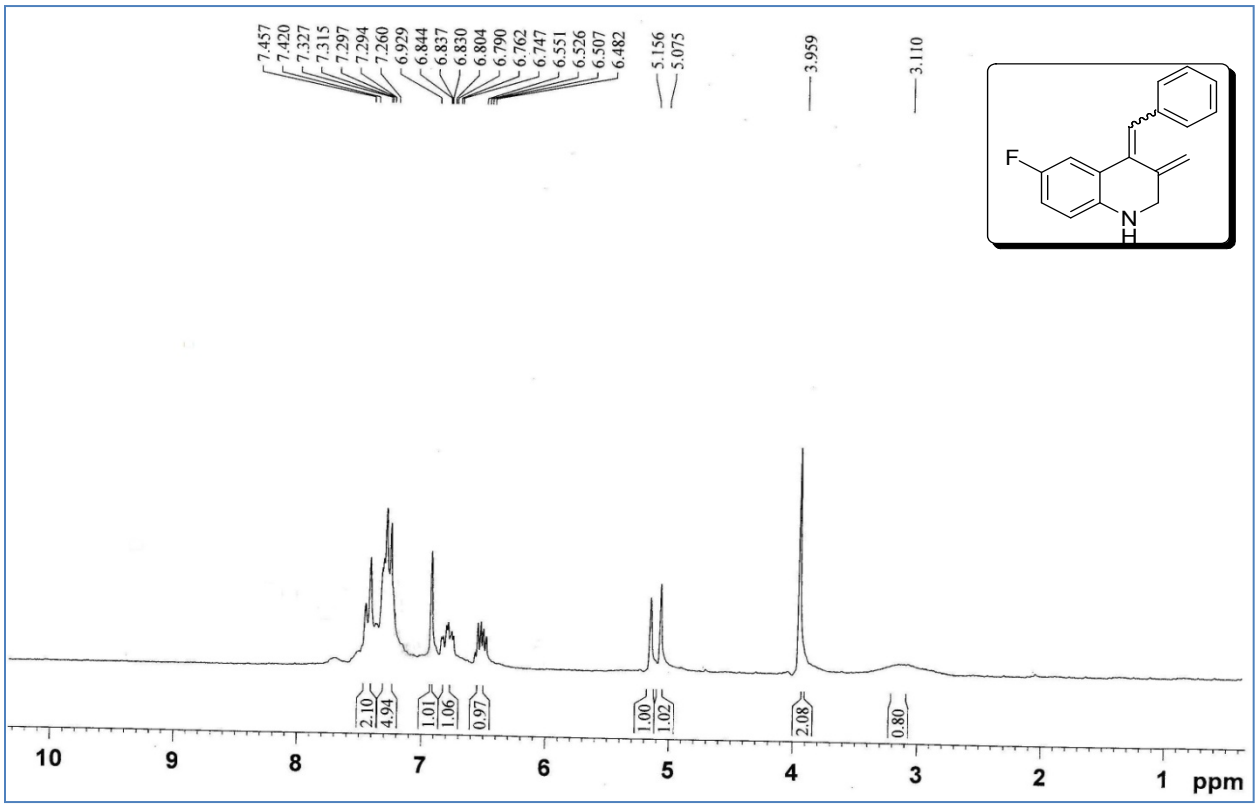
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3e):



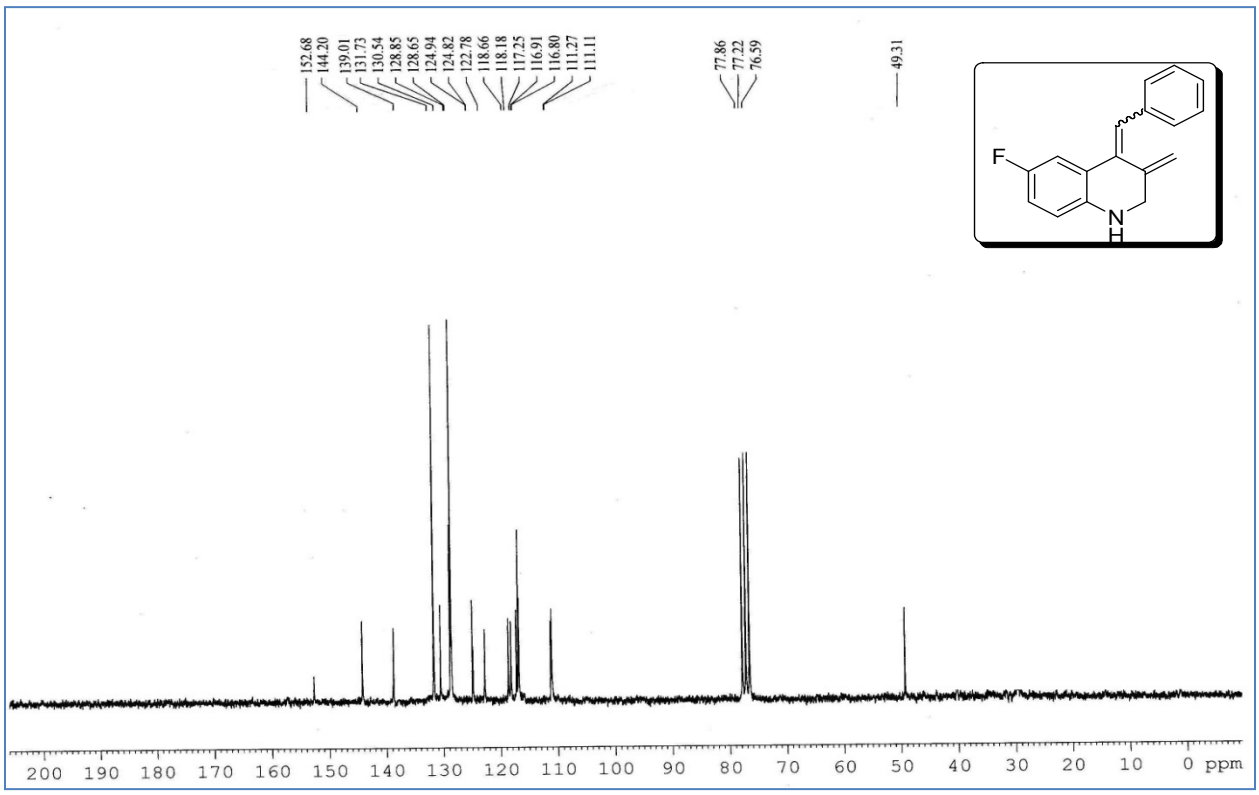
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3e):



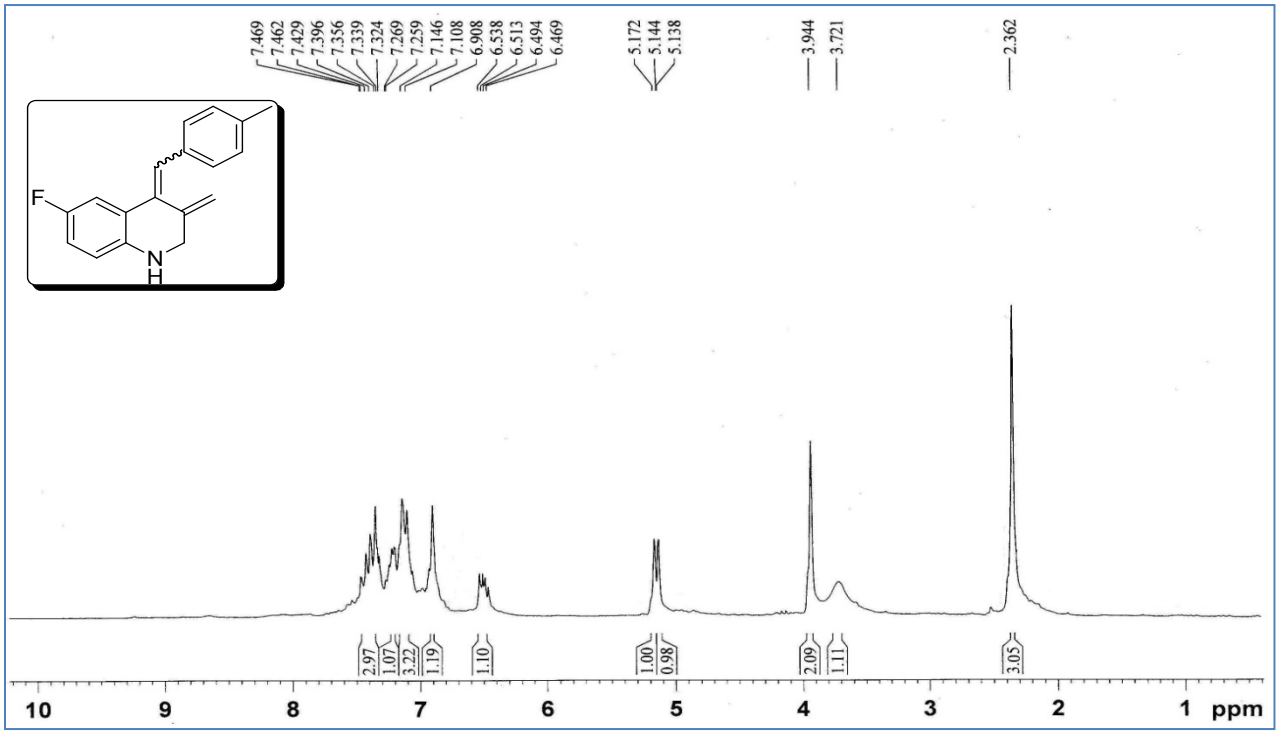
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3f):



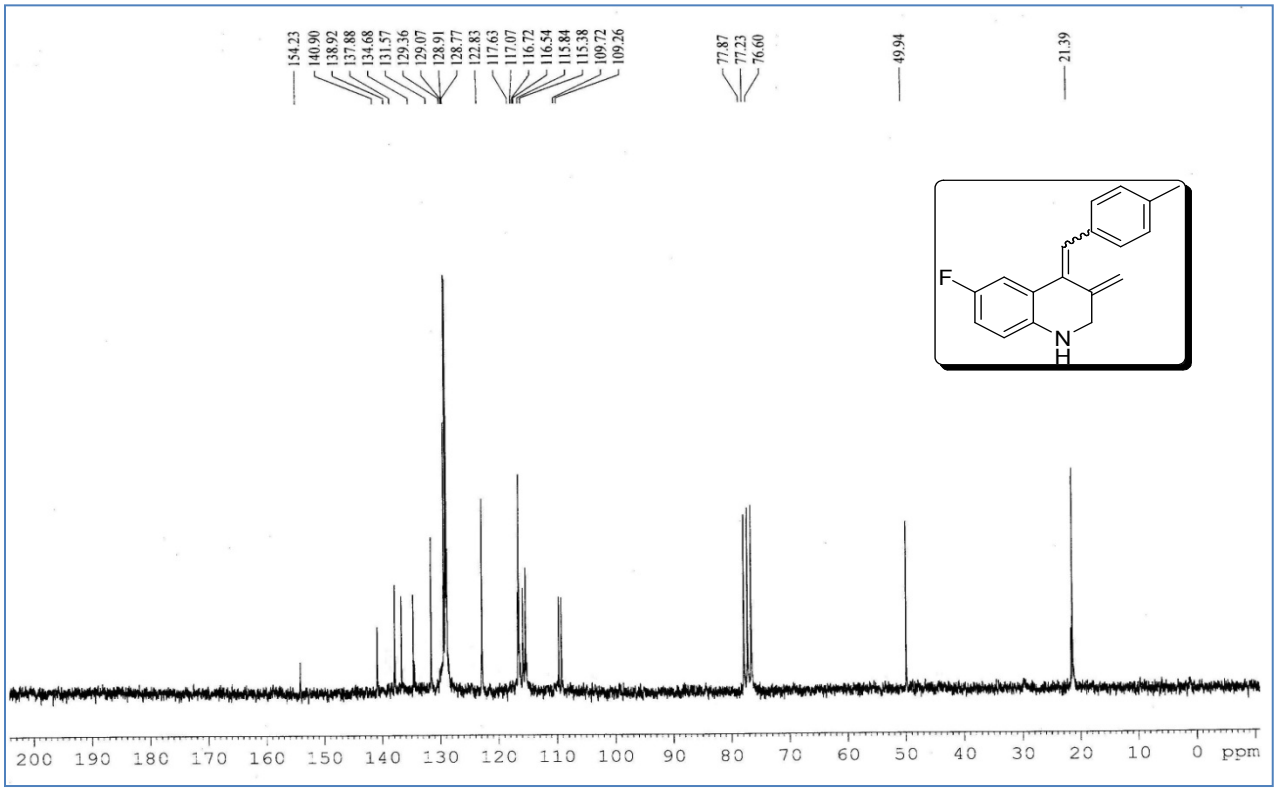
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3f):



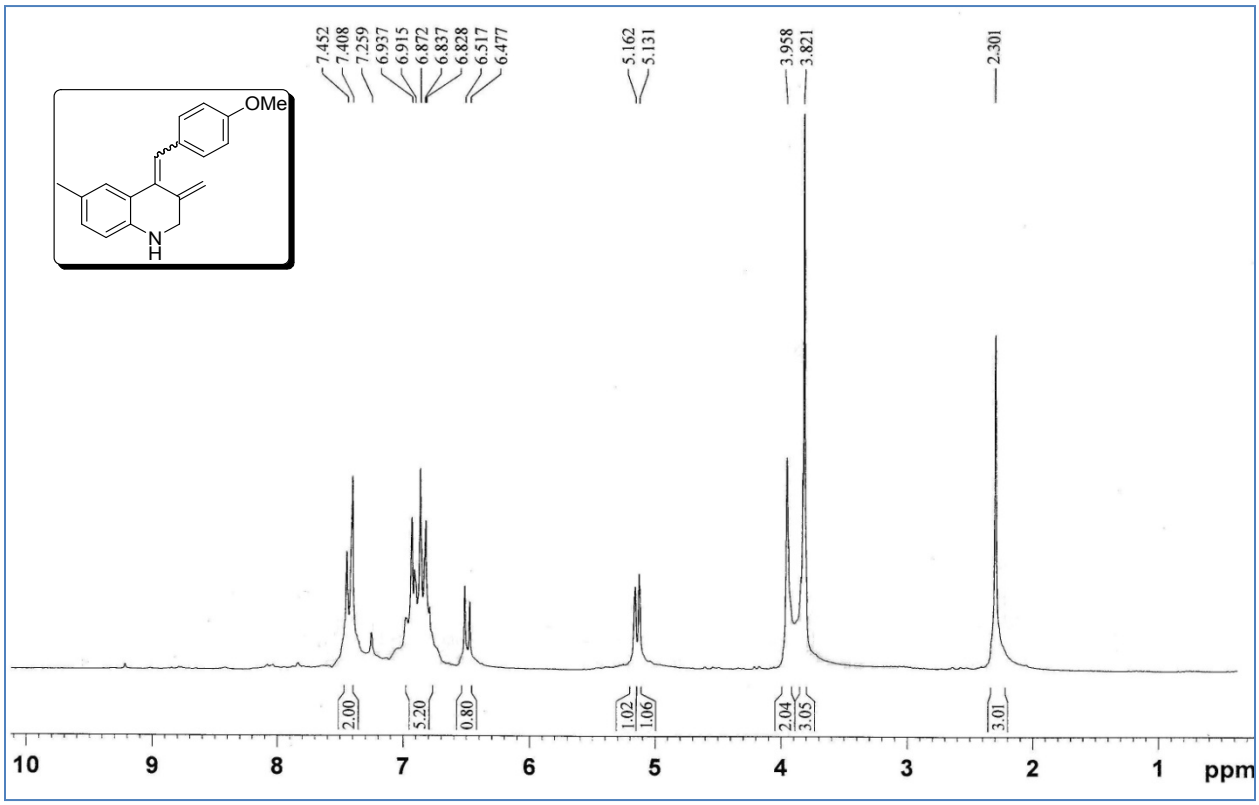
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3g):



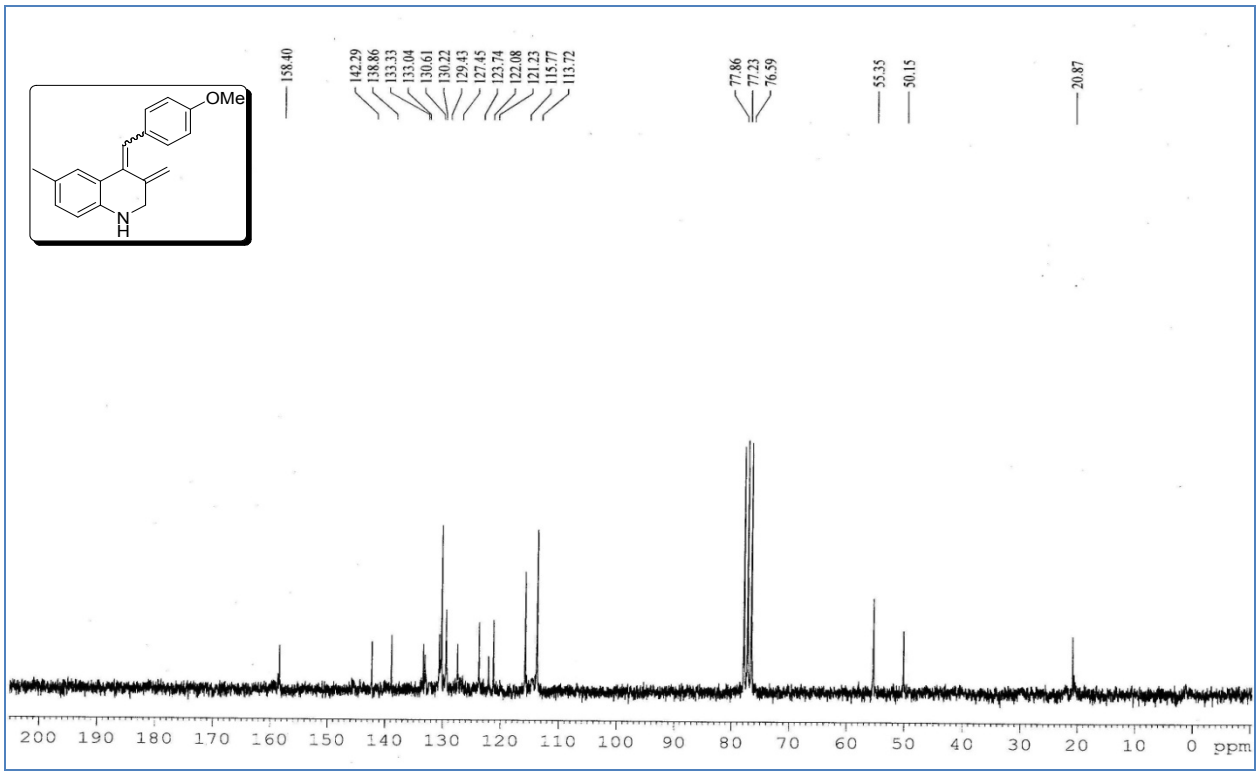
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3g):



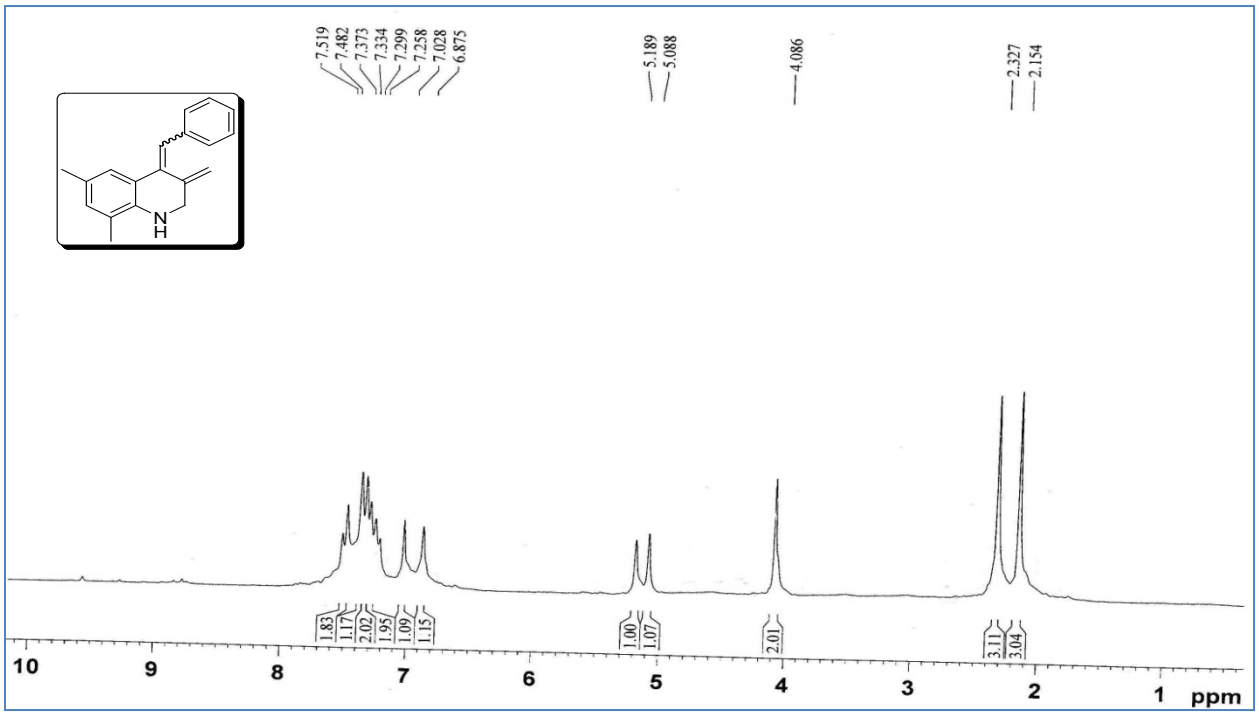
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3h):



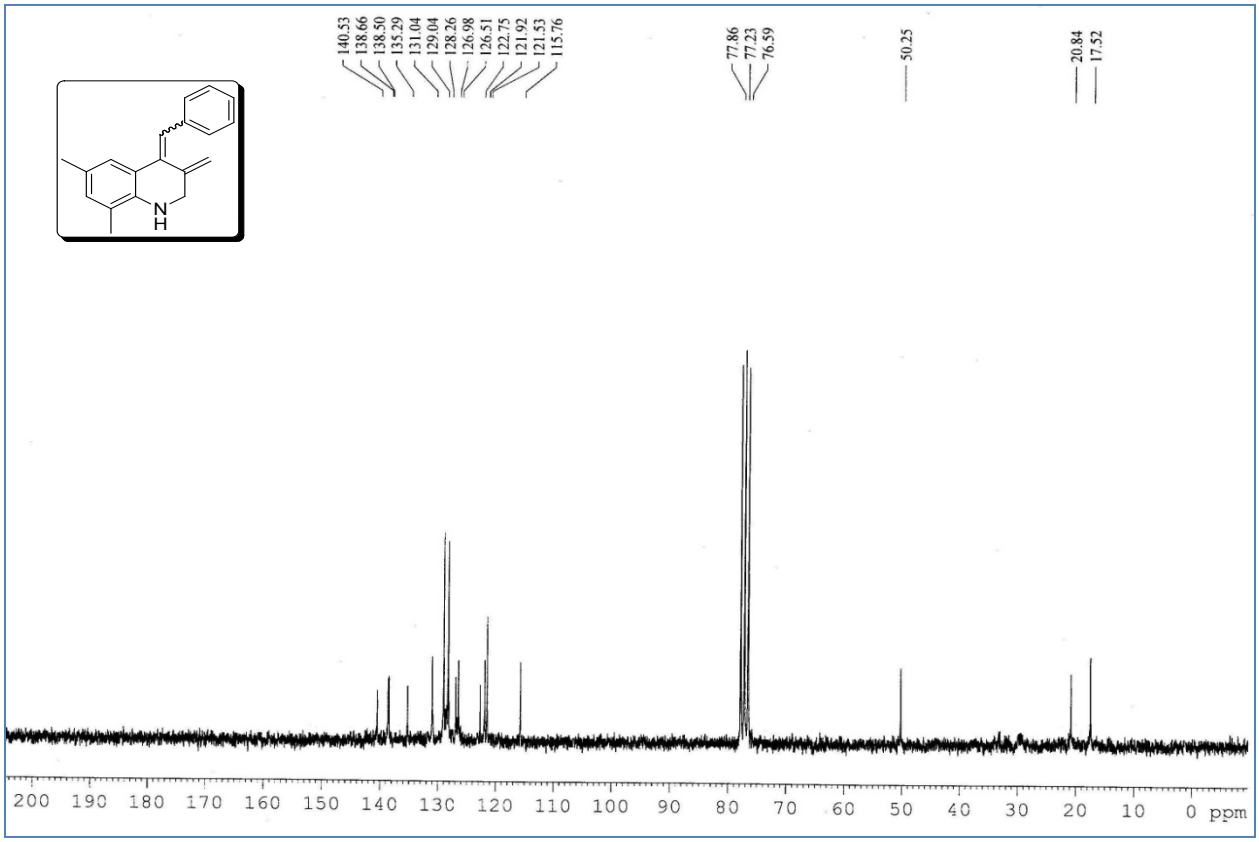
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3h):



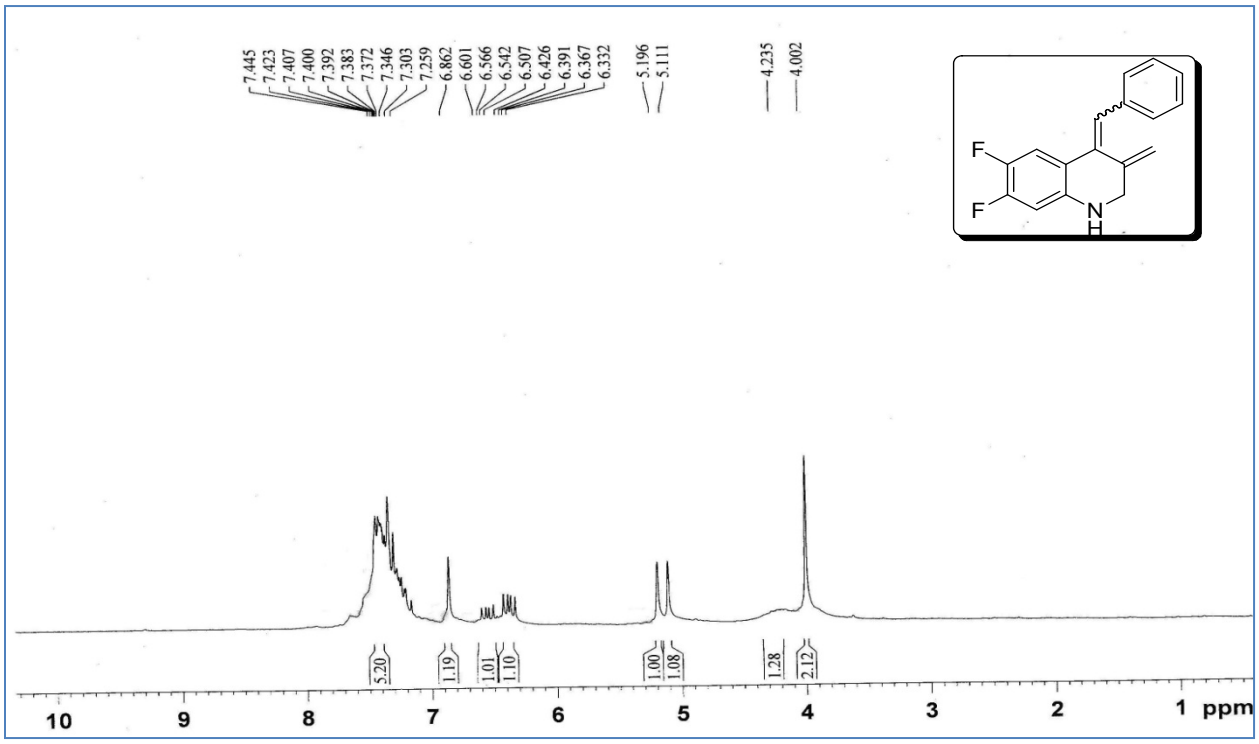
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3i):



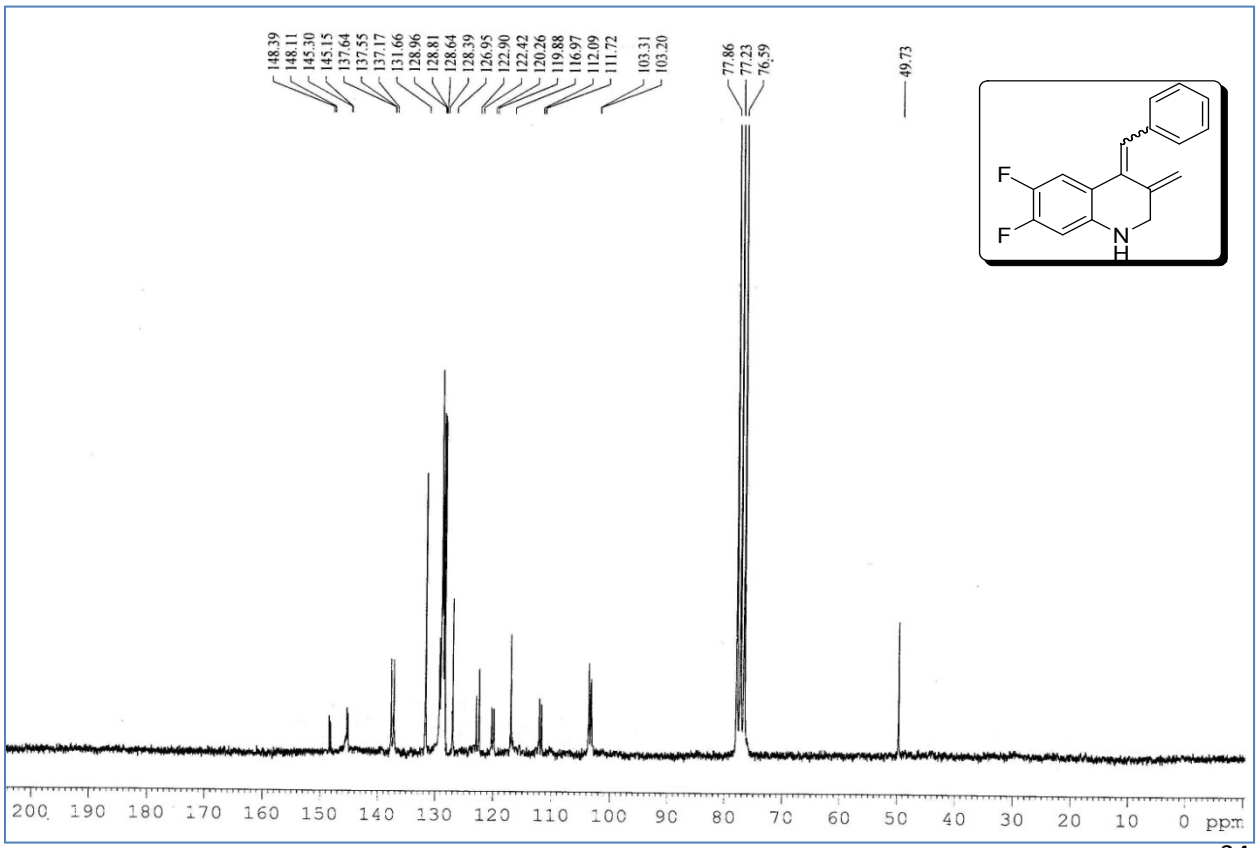
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3i):



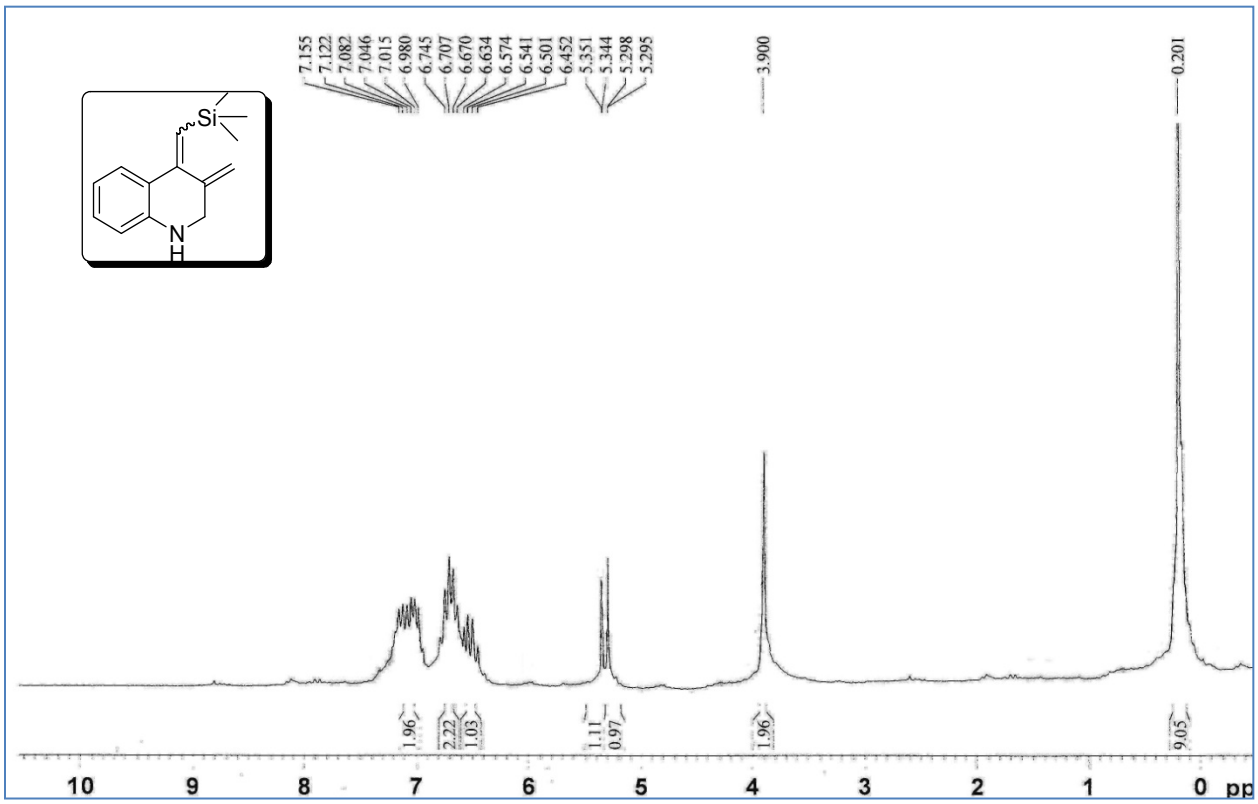
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3j):



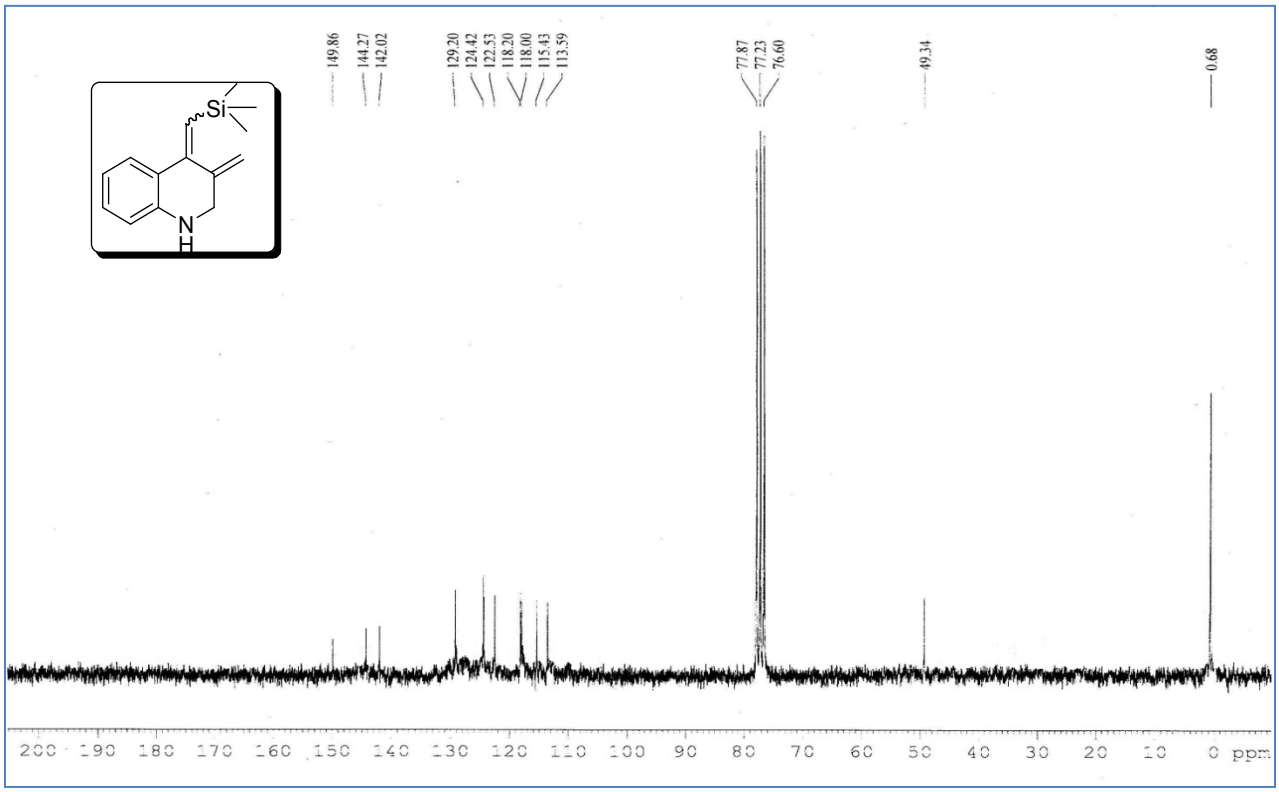
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3j):



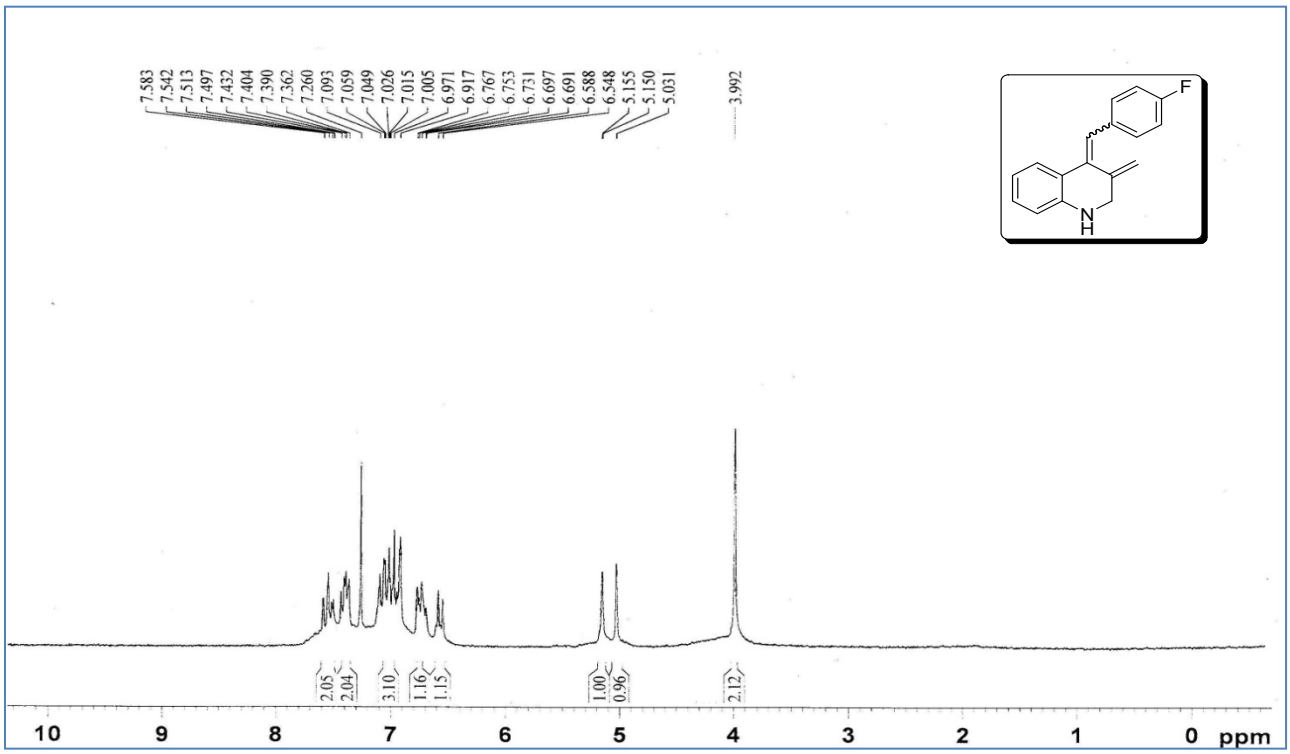
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3k):



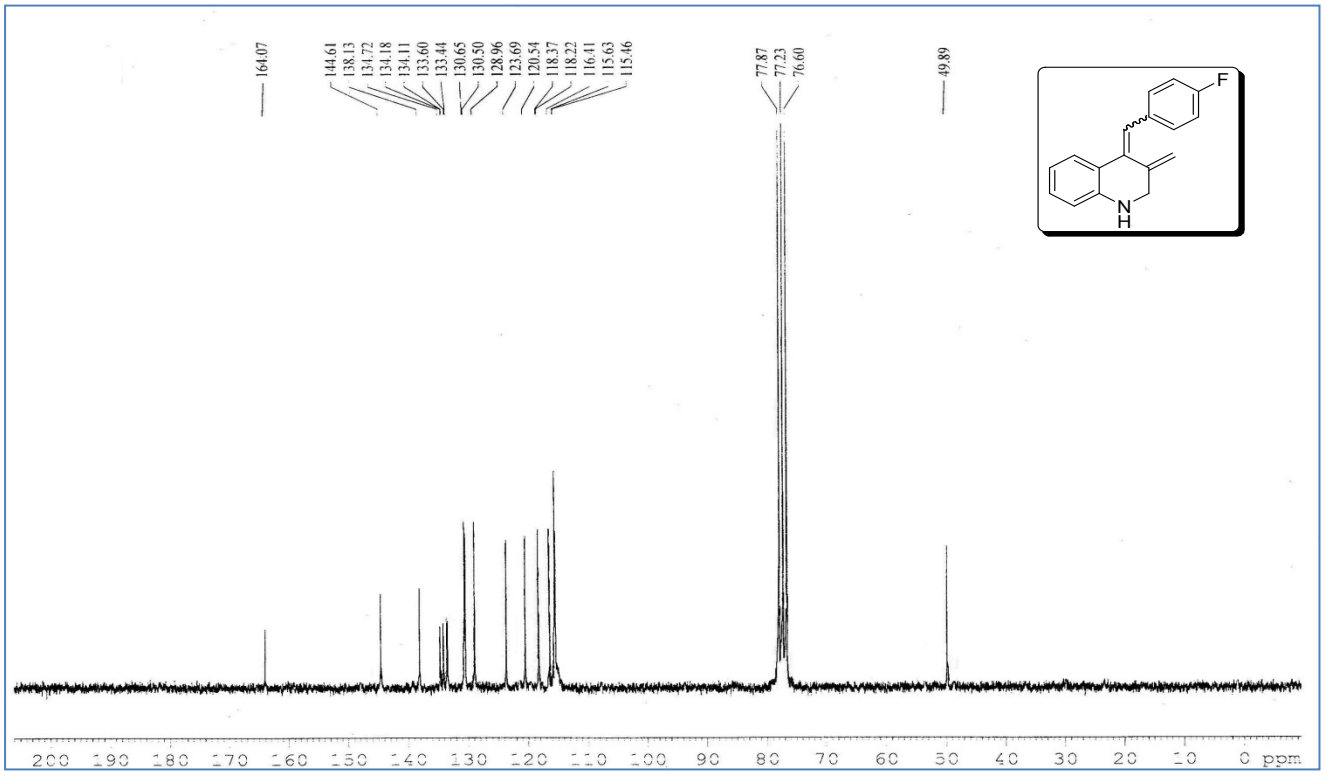
^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3k):



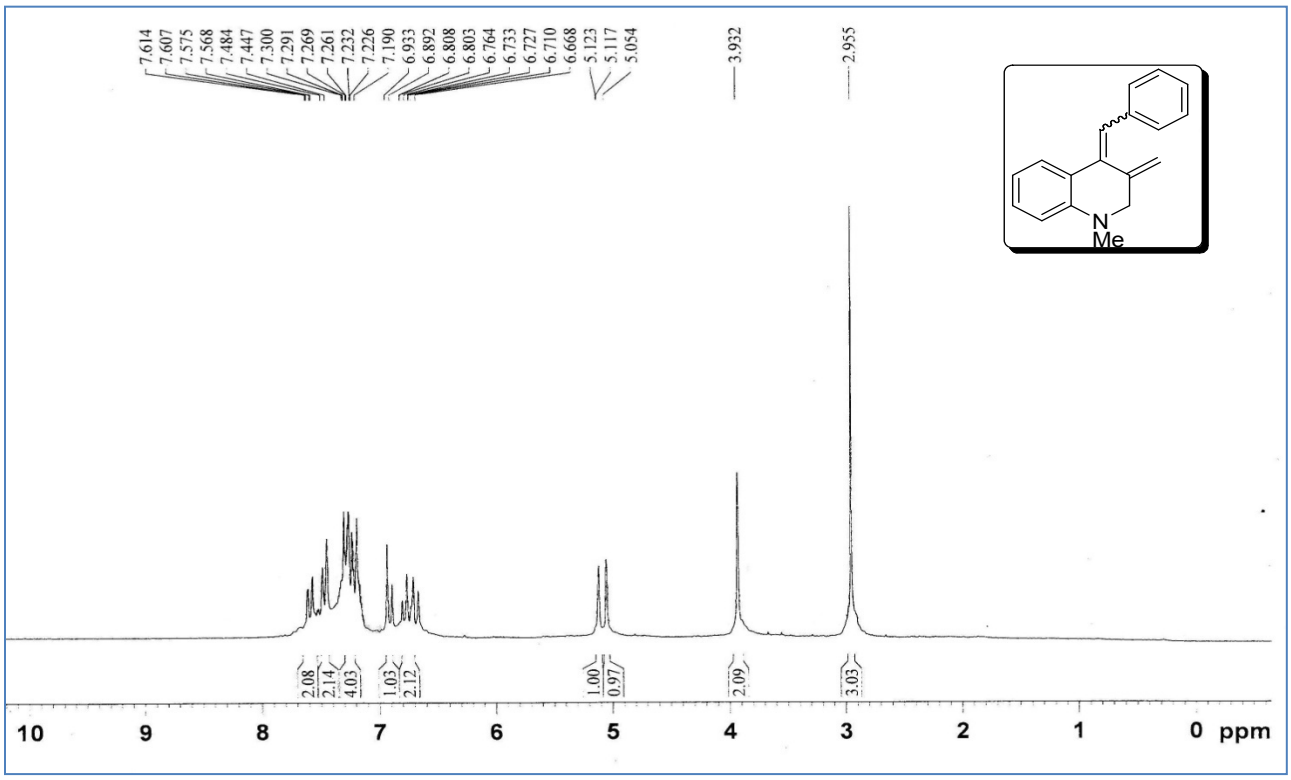
^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3l):



^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3l):



^{1}H NMR ($CDCl_3$, 200 MHz) Spectrum of (3m):



^{13}C NMR ($CDCl_3$, 50 MHz) Spectrum of (3m):