CHAPTER 4

EXPERIMENTAL

General Techniques

1. Solvent

All solvents were purified according to standard procedures before used.

2. Spectroscopy

2.1. Infrared (IR) Spectra. IR spectra were recorded on a Perkin-Elmer Spectrum GX 60237. Spectra of samples were recorded as CH_2Cl_2 film on KBr.

2.2. Nuclear Magnetic Resonance (NMR) Spectra. The ^{1}H and ^{13}C spectra were measured with a Bruker AVANCE 400 spectrometer operating at 400 MHz. The chemical shifts (δ_H and δ_C) were recorded in ppm with reference to residual solvent signal, $CDCl_3$ (δ_H 7.24, δ_C 77.00) where appropriated.

2.3. Mass Spectra. The electrospray mass spectra (ESMS) were recorded on a Finnigan LC-Q mass spectrometer.

3. Physical Constant

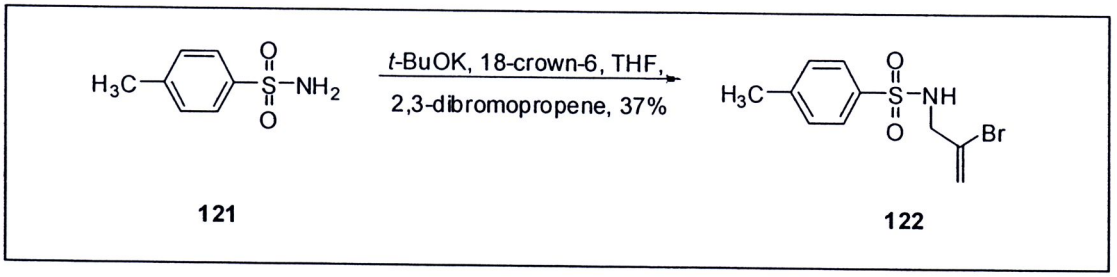
Melting points were determined on an Electrothermal melting point apparatus and were uncorrected. The temperature was given in degree Celsius.

Synthesis

1. Synthesis of Cyclic Amine Containing Vinyl Bromo-Olefin

1.1 5-Membered Ring of Cyclic Amine Containing Vinyl Bromo-Olefin

1.1.1 *Preparation of N-(2-Bromoally)-4-methylbenzenesulfonamide* **122**



121 **122**

To a solution of $TsNH_2$ (1.715 g, 10 mmol) in CH_3CN (30 mL) was added *t*-BuOK (280.5 mg, 2.50 mmol) and 18-crown-6 (165 mg, 0.62 mmol) at 0 °C. After stirring for 10 minutes, 2,3-dibromopropene (258.5 μL, 2.64 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the

crude product as a yellow solid. Purification was accomplished by column chromatography eluting with 14% EtOAc/hexane to give compound **122** (230.4 mg, 32%) as a white solid and dialkylation (375.5 mg, 37%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (2H, d, J = 8.1 Hz, Ar**H**$C_{Ar}(SO_2)$), 7.28 (2H, d, J = 8.1 Hz, Ar**H**$C_{Ar}CH_3$), 5.77 (1H, br s, BrC=C**H**H), 5.45 (1H, br s, BrC=CH**H**), 4.79 (1H, br t, J = 5.5 Hz, N**H**), 3.82 (2H, d, J = 6.4 Hz, CH_2CBr), 2.41 (3H, s, CH_3).

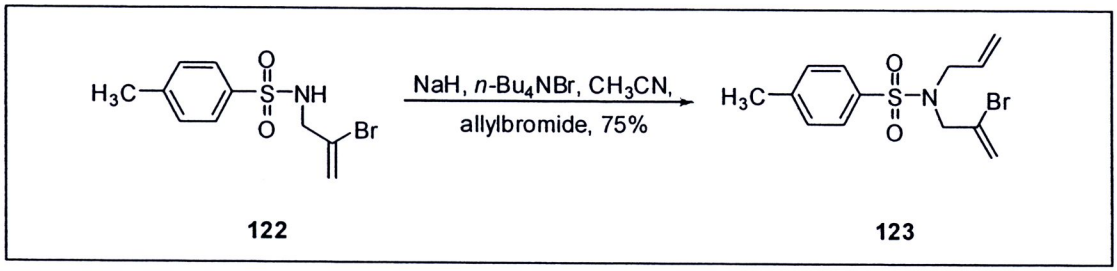
^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.8 (CH_3C_{Ar}), 137.0 (2xC_{Ar}), 129.7 (CH_{Ar}), 128.0 (BrC=CH_2), 127.2 (2xC_{Ar}), 118.9 (BrC=CH_2), 50.8 (NHCH_2), 21.5 (CH_3).

IR ν_{max} (cm^{-1}) 1629 (w), 1598 (w), 1494 (w), 1441 (w), 1346 (m).

ESMS (+ve): m/z (% rel. intensity) 291.8 $[M+H]^+$ (100).

m.p. 66-68 °C.

1.1.2 *Preparation of N-Allyl-N-(2-bromoallyl)-4-methylbenzenesulfonamide* **123**



122 **123**

To a solution of compound **122** (100 mg, 0.34 mmol) in CH_3CN (5 mL) was added NaH (8.27 mg, 0.34 mmol) and *n*-Bu_4NBr (22.21 mg, 0.07 mmol) at 0 °C. After stirring for 10 minutes, allyl bromide (30 µL, 0.34 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 6% EtOAc/hexane to give compound **123** (84.3 mg, 75%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (2H, d, J = 8.2 Hz, Ar**H**$C_{Ar}(SO_2)$), 7.28 (2H, d, J = 8.1 Hz, Ar**H** $C_{Ar}CH_3$), 5.82 (1H, d, J = 1.7 Hz, BrC=C**H**H), 5.58 (1H, d, J = 1.7 Hz, BrC=CH**H**), 5.56 (1H, ddt, J = 16.9, 10.1, 6.6 Hz, **H**C=CHH), 5.17 (1H, d, J = 10.1 Hz, HC=C**H**H), 5.12 (1H, d, J = 16.9 Hz, HC=CH**H**), 4.00 (2H, s, CH_2CBr=CH_2), 3.82 (2H, d, J = 6.6 Hz, CH_2CH=CH_2), 2.41 (3H, s, CH_3).

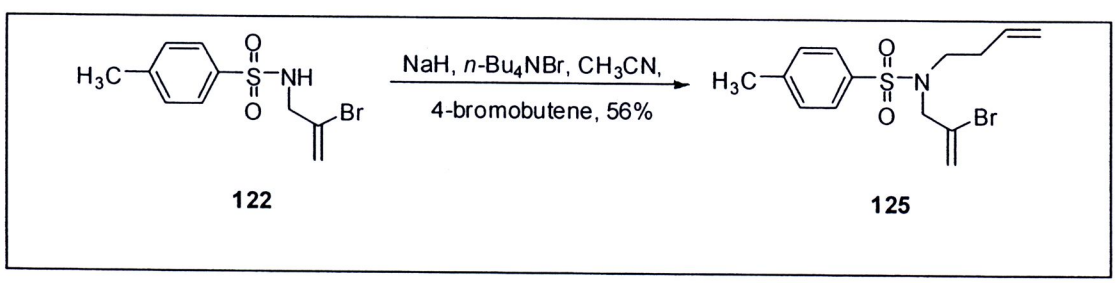
^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6 (CH_3C_{Ar}), 137.2 (C_{Ar}), 131.9 ($HC{=}CH_2$), 129.7 (2xCH_{Ar}), 127.9 ($BrC{=}CH_2$), 127.3 (2xCH_{Ar}), 119.9 ($BrC{=}CH_2$), 119.3 ($HC{=}CH_2$), 53.8 (NCH_2CBr), 50.0 (NCH_2CH), 21.5 (CH_3).

IR ν_{max} (cm^{-1}) 3083 (w), 2922 (w), 1692 (w), 1598 (w), 1494 (w), 1441 (w).

ESMS (+ve): m/z (% rel. intensity) 330.0, 331.9 $[M+H]^+$ (100), (97).

1.2 6-Membered Ring of Cyclic Amine Containing Vinyl Bromo-Olefin

1.2.1 *Preperation of N-(2-Bromoallyl)-N-(but-3-ebyl)-4-methylbenzenesulfona mide* **125**



122 **125**

To a solution of compound **122** (127.3 mg, 0.44 mmol) in CH_3CN (10 mL) was added NaH (10.5 mg, 0.44 mmol) and *n*-Bu_4NBr (14.1 mg, 0.044 mmol) at 0 °C. After stirring for 10 minutes, 4-bromobutene (45 µL, 0.44 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under

reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 10% EtOAc/hexane to give compound **125** (84.9 mg, 56%) as a colorless oil.

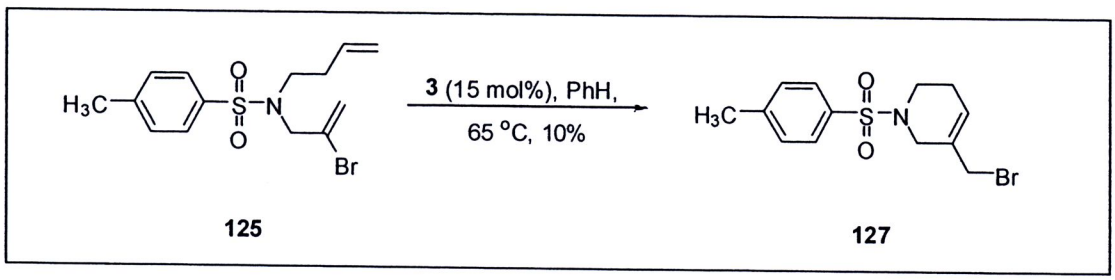
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (2H, d, J = 8.2 Hz, Ar**H**SO_2), 7.28 (2H, d, J = 8.0 Hz, Ar**H**CH_3), 5.85 (1H, br s, BrC=C**H**H), 5.64 (1H, ddt, J = 17.1, 10.2, 6.8 Hz, **H**C=CH_2), 5.59 (1H, br s, BrC=CH**H**), 5.01 (1H, d, J = 10.2 HC=C**H**H), 5.00 (1H, br s, HC=CH**H**), 4.02 (2H, s, NC**H**$_2$CBr=CH_2), 3.21(2H, t, J = 7.6 Hz, NC**H**$_2$$CH_2$CH=$CH_2$), 2.40 (3H, s, C**H**$_3$), 2.25 (2H, q, J = 10.1, 7.6 Hz, NCH_2C**H**$_2$CH=CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5 (CH_3**C**$_{Ar}$), 136.9 (C$_{Ar}$), 134.4 (H**C**=CH_2), 129.7 (2x**C**H$_{Ar}$), 128.2 (BrC=**C**H_2), 127.3 (2x**C**H$_{Ar}$), 119.2 (Br**C**=CH_2), 117.3 (HC=**C**H_2), 55.5 (**C**H_2CBr), 47.6 (N**C**$H_2$$CH_2$), 32.7 (NC$H_2$**C**$H_2$), 21.5 (**C**$H_3$).

IR ν_{max} (cm^{-1}) 2922 (w), 1635 (w), 1597 (w), 1350 (m).

ESMS (+ve): m/z (% rel. intensity) 344.0, 345.9 $[M]^+$ (86), (60).

1.2.2 *Preparation of 5-(Bromomethyl)-1-tosyl-1,2,3,6-tetrahydropyridine* **127**



125 **127**

To a solution of compound **125** (23.9 mg, 0.07 mmol) in benzene (0.6 mL) was added a solution of Grubbs catalyst **3** (6.0 mg, 7.0 μmol) in benzene (0.8 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 65 °C for 18 hours. Another portion of the Grubbs catalyst **3** (3.0 mg, 3.5 μmol) in benzene (0.8 mL) was added and then the reaction mixture was continue stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 4% EtOAc/hexane to give cyclized product **127** (2.3 mg, 10%) as a white oil and recovered starting material (16.8 mg, 70%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (2H, d, J = 8.0 Hz, Ar**H**SO_2), 7.31 (2H, d, J = 8.0 Hz, Ar**H**CH_3), 5.84 (1H, br s, $NCH_2C(CH_2Br)$=C**H**), 3.97 (2H, s, N**C**$H_2C(CH_2Br)$=CH), 3.65 (2H, s, CH_2Br), 3.13 (2H, t, J = 5.7 Hz, N**C**H_2CH_2), 2.42 (3H, s, C**H**$_3$), 2.28-2.18 (2H, br s, NCH_2C**H**$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.5 (CH_3**C**$_{Ar}$), 131.17 (CH_2**C**(CH_2Br)=CH), 130.9 (**C**$_{Ar}$), 129.7 (2x**C**H$_{Ar}$), 127.7 (2x**C**H$_{Ar}$), 125.8 (**C**H$_{Ar}$), 46.8

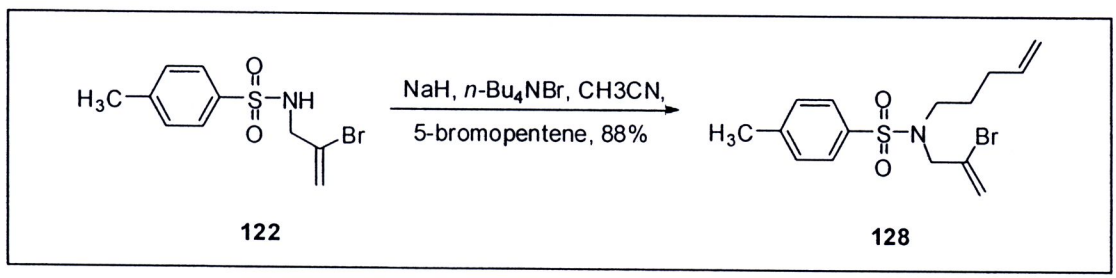
($NCH_2C(CH_2Br)=CH$), 45.4 (NCH_2CH_2), 42.2 (CH_2Br), 25.1 (NCH_2CH_2), 21.5 CH_3).

IR ν_{max} (cm^{-1}) 2921(W), 2851 (w), 1443 (w), 1338 (m).

ESMS (+ve): m/z (% rel. intensity) 659.2 $[2M]^+$ (98).

1.3 7-Membered Ring of Cyclic Amine Containing Vinyl Bromo-Olefin

1.3.1 *Preparation of N-(2-Bromoallyl)-4-methyl-N-(pent-4-enyl)benzenesulfonamide* **128**



122 **128**

To a solution of compound **122** (150 mg, 0.52 mmol) in CH_3CN (5 mL) was added NaH (12 mg, 0.52 mmol) and *n*-Bu_4NBr (33 mg, 0.10 mmol) at 0 °C. After stirring for 10 minutes, 5-bromo-1-pentene (60 μL, 0.52 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by

column chromatography eluting with 4% EtOAc/hexane to give compound **128** (163.7 mg, 88%) as a colorless oil.

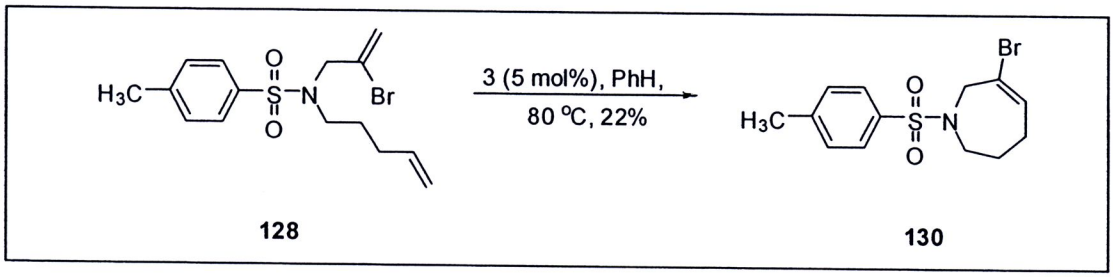
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (2H, d, J = 8.2 Hz, Ar**H**SO_2), 7.28 (2H, d, J = 8.0 Hz, Ar**H**CH_3), 5.85 (1H, br s, BrC=C**H**H), 5.71 (1H, ddt, J = 17.0, 10.3, 6.6 Hz, **H**C=CH_2), 5.58 (1H, br s, BrC=CH**H**), 5.01-4.91 (2H, m, HC=C**H**$_2$), 3.99 (2H, s, C**H**$_2$CBr=CH_2), 3.14 (2H, t, J = 7.8 Hz, NC**H**$_2$$CH_2$$CH_2$), 2.40 (3H, s, CH_3), 1.99 (2H, q, J = 14.1, 7.1 Hz, NCH$_2$CH$_2$C**H**$_2$CH=CH_2), 1.64-1.55 (2H, m, NCH$_2$C**H**$_2$$CH_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.4 (CH_3**C**$_{Ar}$), 137.2 (**C**$_{Ar}$), 137.2 (**H**C=CH_2), 129.6 (2x**C**H$_{Ar}$), 128.3 (BrC=**C**H_2), 127.2 (2x**C**H$_{Ar}$), 119.1 (Br**C**=CH_2), 115.3 (HC=**C**H_2), 55.5 (N**C**H_2CBr), 47.9 (N**C**$H_2$$CH_2$$CH_2$), 30.7 (NCH$_2CH_2$**C**$H_2$), 27.2 (NCH$_2$**C**$H_2$$CH_2$), 21.4 (**C**$H_3$).

IR ν_{max} (cm^{-1}) 3077 (w), 2924 (w), 1641 (w), 1573 (w), 1443 (w), 1341 (m).

ESMS (+ve): m/z (% rel. intensity) 359.0, 360.2 $[M+H]^+$ (53), (100).

1.3.2 *Preparation of (E)-6-Bromo-1-tosyl-2,3,4,7-tetrahydro-1H-azepine* **130**



128 **130**

To a solution of compound **128** (21.8 mg, 0.06 mmol) in benzene (4 mL) was added a solution of Grubbs catalyst (5.0 mg, 6.0 μmol) in benzene (2 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 80 °C for 18 hours. Another portion of the Grubbs catalyst **3** (2.5 mg, 3.0 μmol) in benzene (1 mL) was added and then the reaction mixture was continue stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give cyclized product **130** (4.4 mg, 22%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (2H, d, J = 8.0 Hz, 2xAr**H**SO_2), 7.28 (2H, d, J = 8.0 Hz, 2xAr**H**CH_3), 6.06 (1H, t, J = 5.8 Hz, CH_2CBr=C**H**), 4.16 (2H, s, C**H**$_2$CBr), 3.39 (2H, t, J = 6.4 Hz, CBr=CHCH$_2$CH$_2$C**H**$_2$), 2.40 (3H, s, C**H**$_3$), 2.10-2.00 (2H, m, CBr=CHC**H**$_2$CH$_2$), 1.87-1.75 (2H, m, CBr=CHCH$_2$C**H**$_2$).

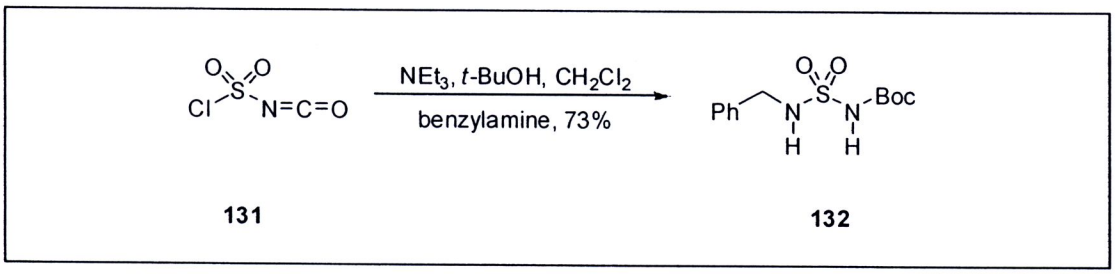
^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.4 (2xC_{Ar}), 129.6 (2xCH_{Ar}), 127.6 ($CH_2CBr{=}CH$), 127.1 (2xCH_{Ar}), 114.6 ($CH_2CBr{=}CH$), 54.2 ($CBr{=}CHCH_2CH_2CH_2$), 48.4 ($CH_2CBr{=}CH$), 26.8 ($CBr{=}CHCH_2CH_2CH_2$), 26.5 ($CBr{=}CHCH_2CH_2CH_2$), 21.5 (CH_3).

IR ν_{max} (cm^{-1}) 2924 (w), 1335 (m), 841 (w).

ESMS (+ve): m/z (% rel. intensity) 329.8, 331.7 $[M]^+$ (100), (97).

2. Synthesis of Cyclic Sulfamide Containing Vinyl Bromo-Olefin

2.1 *Preparation of tert-Butyl(benzylsulfamoyl)carbamate* 132



131 132

To a solution of chlorosulfonyl isocyanate (CSI) (410 µL, 4.67 mmol) in CH_2Cl_2 (29 mL) was added *t*-BuOH (440 µL, 4.67 mmol) at 0 °C. After stirring for 10 minutes, NEt_3 (650 µL, 4.67 mmol) and benzylamine (510 µL, 4.67 mmol) were added. The reaction mixture was stirred for 15 hours at room temperature and before doing diluted with CH_2Cl_2 (15 mL). The organic phases were washed with 1 M HCl (3x15 mL) and water (2x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow solid. Purification

was accomplished by column chromatography eluting with 15% EtOAc/hexane to give compound **132** (978.4 mg, 73%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.23 (5H, m, Ar**H**), 7.17 (1H, s, **H**NBoc), 5.41 (1H, br t, J = 5.7 Hz, $PhCH_2N\mathbf{H}$), 4.18 (2H, d, J = 6.2 Hz, $PhC\mathbf{H}_2$), 1.39 (9H, s, $CO_2C(C\mathbf{H}_3)_3$).

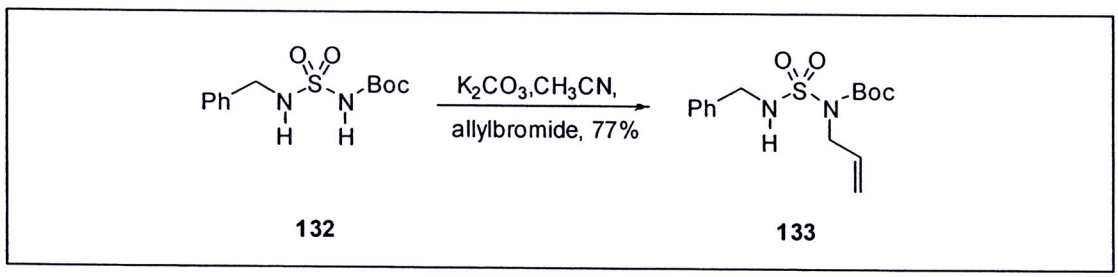
^{13}C NMR ($CDCl_3$, 100MHz) δ 150.1 (CO), 135.6 (C_{Ar}), 128.9 (2xCH_{Ar}), 128.8 (CH_{Ar}), 128.1 (2xCH_{Ar}), 83.8 ($C(CH_3)_3$), 47.9 ($PhCH_2$), 27.9 ($C(CH_3)_3$).

IR ν_{max} (cm^{-1}) 3295 (m), 3268 s, 1712 s, 1448 (m), 1427 (m), 1351 (m).

ESMS (-ve): m/z (% rel. intensity) 285.4 $[M-H]^-$ (75), 286.3 $[M]^-$ (64).

m.p. 127-128°C.

2.2 *Preparation of tert-butyl(Benzylsulfamoyl)prop-2-en-1-ylcarbamate* **133**



132 **133**

To a solution of compound **132** (200 mg, 0.70 mmol) in CH_3CN (15 mL) was added K_2CO_3 (97 mg, 0.70 mmol) at 0 °C. After stirring for 10 minutes, allyl bromide (60 µL, 0.70 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15

mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow solid. Purification was accomplished by column chromatography eluting with 15% EtOAc/hexane to give compound **133** (176.8 mg, 77%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.22 (5H, m, Ar**H**), 5.84 (1H, ddt, J = 17.0, 10.3, 5.9 Hz, **H**C=CH_2), 5.55 (1H, br t, J = 5.8 Hz, PhCH_2N**H**), 5.27 (1H, d, J = 17.0 Hz, HC=C**H**H), 5.19 (1H, d, J = 10.3 Hz, HC=CH**H**), 4.16 (2H, d, J = 5.9 Hz, C**H**$_2$CH=CH_2), 4.12 (2H, d, J = 6.3 Hz, PhC**H**$_2$NH), 1.46 (9H, s, C(C**H**$_3$)$_3$).

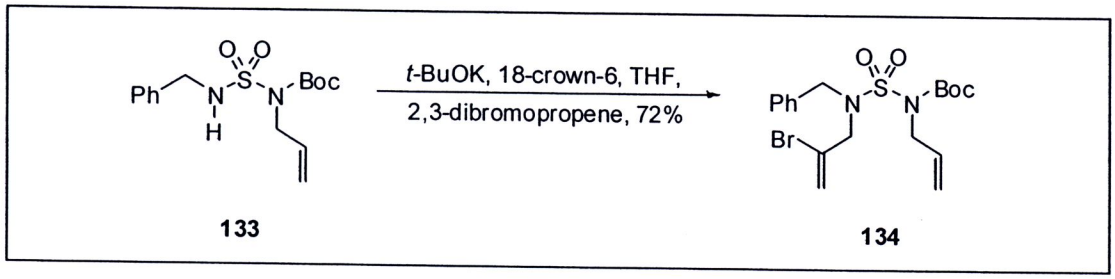
^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.7 (CO), 135.6 (**C**$_{Ar}$), 132.9 (**H**C=CH_2), 128.8 (2x**C**H$_{Ar}$), 128.2 (**C**H$_{Ar}$), 128.1 (2x**C**H$_{Ar}$), 118.1 (HC=**C**H_2), 84.1 (**C**(CH_3)$_3$), 49.6 (Ph**C**H_2), 48.1 (**C**H_2CH=CH_2), 28.0 (C(**C**H_3)$_3$).

IR ν_{max} (cm^{-1}) 3281 (m), 1741 s, 1457 (w), 1359 s.

ESMS (-ve): m/z (% rel. intensity) 325.1 $[M-H]^-$ (100).

m.p. 71-79 °C.

2.3 *Preparation of tert-Butylallyl(N-benzyl-N-(2-bromoallyl)sulfamoyl)carba mate* **134**



133 **134**

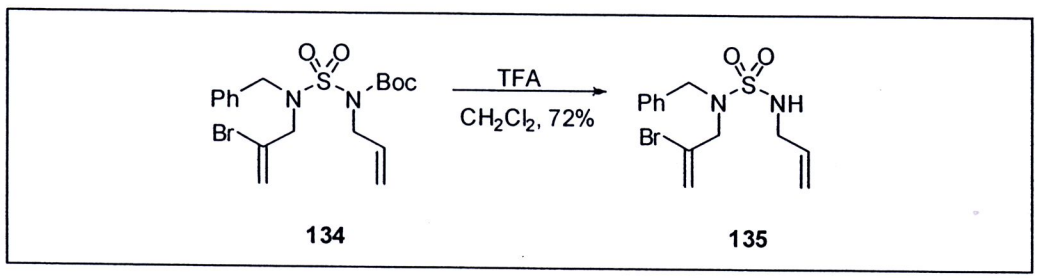
To a solution of compound **133** (177 mg, 0.54 mmol) in THF (10 mL) was added *t*-BuOK (61 mg, 0.54 mmol) and 18-crown-6 (36 mg, 0.14 mmol) at 0 °C. After stirring for 10 minutes, 2,3-dibromopropene (32 μL, 0.54 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 8% EtOAc/hexane to give compound **134** (150 mg, 72%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.22 (5H, m, ArH), 5.86 (1H, ddt, J = 17.1, 10.2, 5.9 Hz, $CH_2C\mathbf{H}=CH_2$), 5.76 (1H, br s, $CH_2CBr=C\mathbf{H}H$), 5.60 (1H, br s, $CH_2CBr=CH\mathbf{H}$), 5.28 (1H, d, J = 17.1, $CH_2CH=C\mathbf{H}H$), 5.17 (1H, d, J = 10.2 Hz, $CH_2CH=CH\mathbf{H}$), 4.54 ($PhC\mathbf{H}_2$), 4.23 (2H, d J = 5.9 Hz, $C\mathbf{H}_2CH=CH_2$), 4.08 (2H, s, $C\mathbf{H}_2CBr=CH_2$), 1.52-1.46 (9H, m, $C(C\mathbf{H}_3)_3$).

IR ν_{max} (cm^{-1}) 1714 s, 1479 (m), 1448 (m).

ESMS (+ve): m/z (% rel. intensity) 462.0, 464.0 $[M+NH_3]^+$ (100), (69).

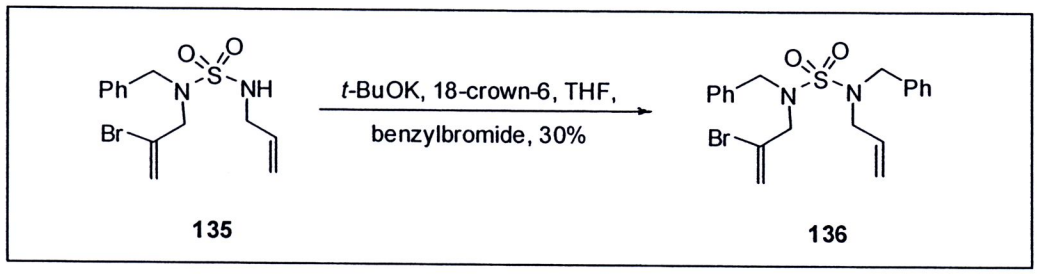
2.4 *Preparation of N–Benzyl-N-(2-bromoprop-2-en-1-yl)-N'-prop-2-en-1-ylsulfuric diamide* **135**



134 **135**

To a solution of compound **134** (150 mg, 0.30 mmol) in CH_2Cl_2 (4 mL) was added TFA (1 mL). The solution mixture was stirred at room temperature for an hour and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 10% EtOAc/hexane to give compound **135** (75.5 mg, 72%) as a colorless oil.

2.5 *Preparation of N,N'-Dibenzyl-N-(2-bromoprop-2-en-1-yl)-N'-prop-2-en-1-ylsulfuric diamide* **136**



135 **136**

To a solution of compound **135** (76 mg, 0.22 mmol) in THF (5 mL) was added *t*-BuOK (25 mg, 0.22 mmol) and 18-crown-6 (14 mg, 0.05 mmol) at 0 °C. After stirring for 10 minutes, benzyl bromide (26 μL, 0.22 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 4% EtOAc/hexane to give compound **136** (28.10 mg, 30%) as a colorless oil.

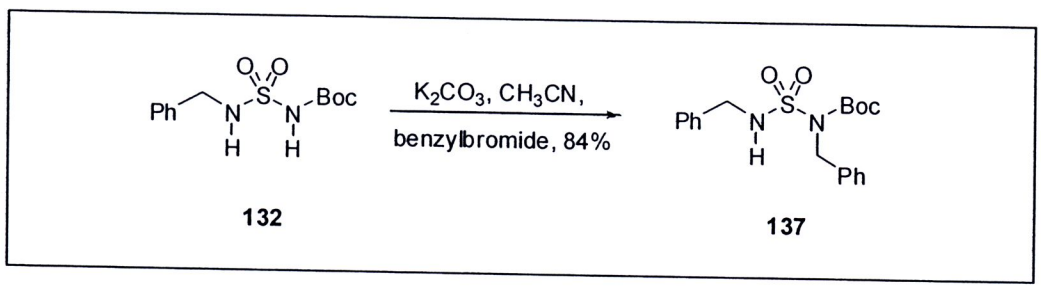
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.25 (10H, m, 2xAr**H**), 5.87-5.79 (1H, m, **H**C=CH_2), 5.78 (1H, s, BrC=C**H**H), 5.62 (1H, s, BrC=CH**H**), 5.20 (1H, d, J = 10.1 Hz, HC=C**H**H), 5.11 (1H, d, J = 17.1 Hz, HC=CH**H**), 4.45 (2H, s, PhC**H**$_2$NCH_2CBr), 4.40 (2H, s, PhC**H**$_2$NCH_2CH), 3.95 (2H, s, C**H**$_2$CBr), 3.72 (2H, d, J = 6.6 Hz, C**H**$_2$CH=CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1 (C_{Ar}), 136.1 (C_{Ar}), 135.3 (C_{Ar}), 132.8 ($CH_2CH=CH_2$), 128.9 (2xCH_{Ar}), 128.7 (2xCH_{Ar}), 128.6 (2xCH_{Ar}), 128.5 (2xCH_{Ar}), 128.0 (CH_{Ar}), 127.9 ($CBr=CH_2$), 127.8 (CH_{Ar}), 120.4 ($CBr=CH_2$), 119.6 ($HC=CH_2$), 54.5 ($CH_2CBr=CH_2$), 51.3 ($PhCH_2NCH_2CBr$), 50.7 ($PhCH_2NCH_2CH$), 49.9 ($CH_2CH=CH_2$).

IR ν_{max} (cm^{-1}): 2921 (w), 1639 (w), 1629 (w), 1496 (w), 1456 (w).

ESMS (+ve): m/z (% rel. intensity) 435.1, 437.2 $[M]^+$ (100), (95).

2.6 *Preparation of tert-butyl benzyl(benzylsulfamoyl)carbamate* 137



132 **137**

To a solution of compound **132** (250 mg, 0.87 mmol) in CH_3CN (10 mL) was added K_2CO_3 (121 mg, 0.87 mmol) at 0 °C. After stirring for 10 minutes, benzyl bromide (100 µL, 0.87 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow solid.

Purification was accomplished by column chromatography eluting with 20% EtOAc/hexane to give compound **137** (276.7 mg, 84%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.18 (10H, m, 2xAr**H**), 5.54 (1H, br t, J = 6.2 Hz, PhN**H**), 4.75 (2H, s, PhC**H**$_2$NBoc), 3.96 (2H, d, J = 6.2 Hz, PhC**H**$_2$NH), 1.41 (9H, s, 3xC**H**$_3$).

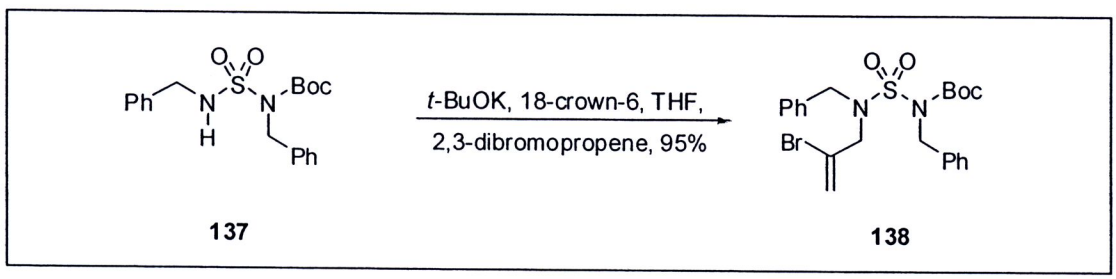
^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.9 (CO), 137.5 (**C**$_{Ar}$), 135.6 (**C**$_{Ar}$), 128.8 (2x**C**H$_{Ar}$), 128.5 (2x**C**H$_{Ar}$), 128.2 (**C**H$_{Ar}$), 128.1 (4x**C**H$_{Ar}$), 127.7 (**C**H$_{Ar}$), 84.3 (**C**(CH$_3$)$_3$), 50.7 (PhCH$_2$NBoc), 47.9 (PhCH$_2$NH), 28.0 (C(**C**H$_3$)$_3$).

IR ν_{max} (cm^{-1}) 3318 (NH), 2984 (w), 1713 s, 1496 (w), 1455 (m).

ESMS (-ve): m/z (% rel. intensity) 375.2 $[M-H]^-$ (100).

m.p. 128-130 °C

2.7 *Preparation of tert-Butylbenzyl(N-benzyl-N-(2-bromoallyl)sulfamoyl)carba- mate* **138**



137 **138**

To a solution of compound **137** (260 mg, 0.69 mmol) in THF (10 mL) was added *t*-BuOK (78 mg, 0.69 mmol) and 18-crown-6 (36 mg, 0.14 mmol) at 0 °C. After stirring for 10 minutes, 2,3-dibromopropene (41 µL, 0.69 mmol) was added. The reaction mixture was stirred for 15 hours at room

temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give compound **138** (326.3 mg, 95%) as a colorless oil.

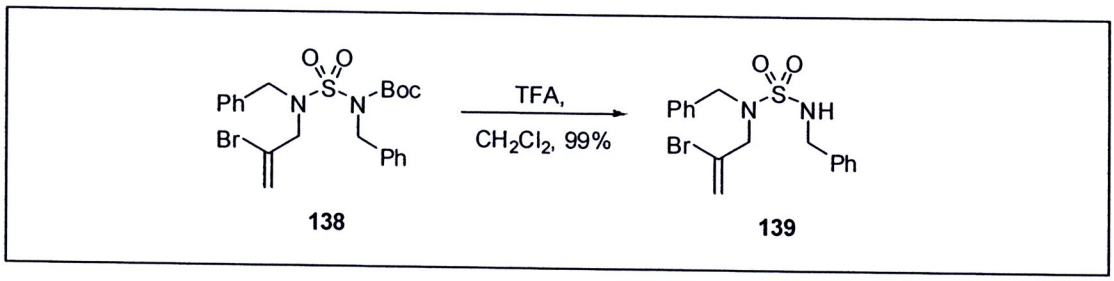
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.19 (10H, m, 2xAr**H**), 5.75 (1H, br s, BrC=C**H**H), 5.59 (1H, br s, BrC=CH**H**), 4.83 (2H, s, PhC**H**$_2$NBoc), 4.47 (2H, s, PhC**H**$_2$), 4.04 (2H, s, C**H**$_2$CBr), 1.43 (9H, s, 3xC**H**$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.5 (**C**O), 137.5 (**C**$_{Ar}$), 135.1 (**C**$_{Ar}$), 128.6 (2x**C**$_{Ar}$), 128.5 (2x**C**H$_{Ar}$), 128.4 (2x**C**H$_{Ar}$), 128.0 (**C**H$_{Ar}$), 127.8 (2x**C**H$_{Ar}$), 127.5 (**C**H$_{Ar}$), 119.6 (Br**C**=CH$_2$), 83.9 (**C**(CH$_3$)$_3$), 55.3 (**C**H$_2$BrC=CH$_2$), 52.0 (PhCH$_2$NBoc), 51.7 (PhCH$_2$), 28.1 (C(**C**H$_3$)$_3$).

IR ν_{max} (cm^{-1}): 2984 (w), 1711 s, 1487 (m), 1456 (m), 1418 (m).

ESMS (+ve): m/z (% rel. intensity) 1011.1, 1013.1 $[2M+Na]^+$ (36), (100).

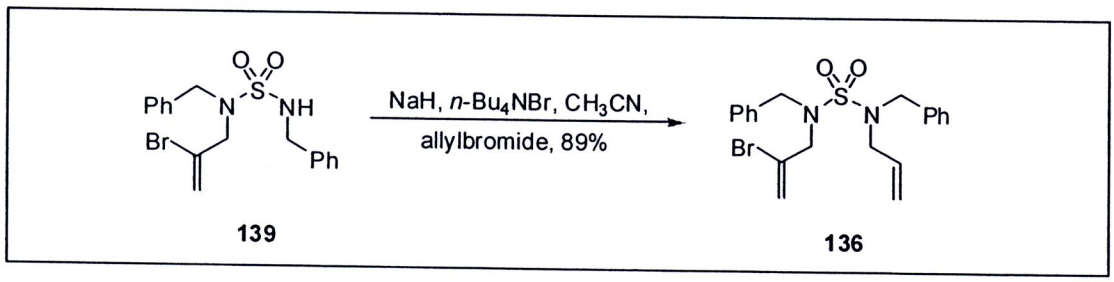
2.8 *Preparation of N,N'-Dibenzyl-N-(2-bromoprop-2-en-1-yl)sulfuric diamide* 139



138 139

To a solution of compound **138** (326.3 mg, 0.66 mmol) in CH_2Cl_2 (4 mL) was added TFA (1 mL). The solution mixture was stirred at room temperature for 1 hours and concentrated under reduced pressure to afford the crude product as a brown oil. Purification was accomplished by column chromatography eluting with 5% EtOAc/hexane to give compound **139** (257.2 mg, 99%) as a white solid.

2.9 *Preparation of N,N'-dibenzyl-N-(2-bromoprop-2-en-1-yl)-N'-prop-2-en-1-ylsulfuric diamide* **136**



139 **136**

To a solution of compound **139** (100 mg, 0.25 mmol) in CH_3CN (5 mL) were added NaH (6 mg, 0.25 mmol) and *n*-Bu_4NBr (16 mg, 0.05 mmol) at 0 °C. After stirring for 10 minutes, allyl bromide (22 μL, 0.25 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 4% EtOAc/hexane to give compound **136** (97.3 mg, 89%) as a colorless oil.

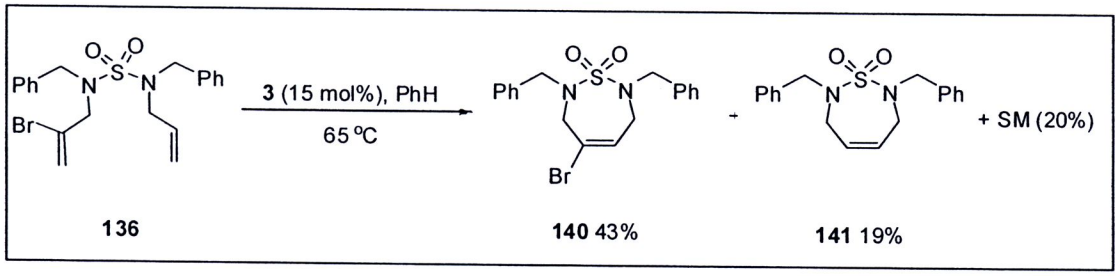
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.25 (10H, m, 2xAr**H**), 5.87-5.79 (1H, m, **H**C=CH_2), 5.78 (1H, s, BrC=C**H**H), 5.62 (1H, s, BrC=CH**H**), 5.20 (1H, d, J = 10.1 Hz, HC=C**H**H), 5.11 (1H, d, J = 17.1 Hz, HC=CH**H**), 4.45 (2H, s, PhC$\mathbf{H}_2$$NCH_2CBr$), 4.40 (2H, s, PhC$\mathbf{H}_2$$NCH_2CH$), 3.95 (2H, s, C$\mathbf{H}_2$CBr), 3.72 (2H, d, J = 6.6 Hz, C$\mathbf{H}_2$CH=CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1 (C_{Ar}), 136.1 (C_{Ar}), 135.3 (C_{Ar}), 132.8 ($CH_2CH=CH_2$), 128.9 (2xCH_{Ar}), 128.7 (2xCH_{Ar}), 128.6 (2xCH_{Ar}), 128.5 (2xCH_{Ar}), 128.0 (CH_{Ar}), 127.9 ($CBr=CH_2$), 127.8 (CH_{Ar}), 120.4 ($CBr=CH_2$), 119.6 ($HC=CH_2$), 54.5 ($CH_2CBr=CH_2$), 51.3 ($PhCH_2NCH_2CBr$), 50.7 ($PhCH_2NCH_2CH$), 49.9 ($CH_2CH=CH_2$).

IR ν_{max} (cm^{-1}): 2921 (w), 1639 (w), 1629 (w), 1496 (w), 1456 (w).

ESMS (+ve): m/z (% rel. intensity) 435.1, 437.2 $[M]^+$ (100), (95).

2.10 ***Preparation of 2,7-Dibenzyl-4-bromo-2,3,6,7-tetrahydro-1,2,7-thiadiazepine 1,1-dioxide*** **140** (Method 1)



136 **140** 43% **141** 19%

To a solution of compound **136** (30 mg, 0.07 mmol) in benzene (3 mL) was added a solution of the second generation Grubbs catalyst (6.0 mg, 7.0 μmol) in benzene (2 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 65 °C for 18 hours. Another portion of the Grubbs catalyst **3** (3.0 mg, 3.5 μmol) in benzene (1 mL) was added and then the reaction mixture was continue stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column

chromatography eluting with 4% EtOAc/hexane to give the cyclized product **140** (12.4 mg, 43%) as a white solid, minor product **141** (3.8 mg, 19%) as a colorless oil and recovered starting material (6.0 mg, 20%).

Compound **140**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.24 (10H, m, 2xAr**H**), 6.24 (1H, t, J = 5.7 Hz, **H**C=CBr), 4.52 (2H, s, PhC**H**$_2$NCH$_2$BrC=CH), 4.45 (2H, s, PhC**H**$_2$NCH$_2$CH=CBr), 4.03 (2H, s, C**H**$_2$BrC=CH), 3.60 (2H, d, J = 5.7 Hz, CBr=CHC**H**$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.6 (**C**$_{Ar}$), 135.3 (**C**$_{Ar}$), 130.5 (H**C**=CBr), 128.8 (2x**C**H$_{Ar}$), 128.7 (2x**C**H$_{Ar}$), 128.6 (2x**C**H$_{Ar}$), 128.3 (**C**H$_{Ar}$), 128.2 (**C**H$_{Ar}$), 122.7 (HC=**C**Br), 52.4 (2xPh**C**H$_2$), 52.1 (**C**H$_2$BrC=CH$_2$), 44.1 (CBr=CH**C**H$_2$).

IR ν_{max} (cm^{-1}): 3030 (w), 2919 (w), 1507 (w), 1456 (w), 1359 (w).

ESMS (-ve): m/z (% rel. intensity) 814.6 $[2M]^-$ (55)

m.p. 106-108 °C.

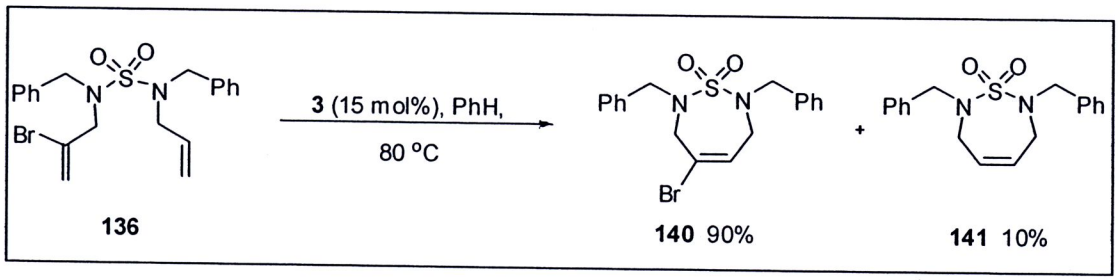
Compound **141**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.25 (10H, m, 2xAr**H**), 5.80 (2H, br t, J = 3.0 Hz, **H**C=C**H**), 4.45 (4H, s, 2xPhC**H**$_2$), 3.66 (4H, d, J = 3.0 Hz, 2xNC**H**$_2$CH=CH).

IR ν_{max} (cm^{-1}): 3032 (w), 2852 (w), 1631 (w), 1496 (w).

ESMS (+ve): m/z (% rel. intensity) 351.8 $[M+Na]^+$ (72).

2.11 ***Preparation of 2,7-Dibenzyl-4-bromo-2,3,6,7-tetrahydro-1,2,7-thiadiazepine 1,1-dioxide*** **140** (Method 2)



136 **140** 90% **141** 10%

To a solution of compound **136** (31.2 mg, 0.07 mmol) in benzene (5 mL) was added a solution of the second generation Grubbs catalyst (6.0 mg, 7.0 μmol) in benzene (2 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 80 °C for 18 hours. Another portion of the Grubbs catalyst **3** (3.0 mg, 3.5 μmol) in benzene (1 mL) was added and then the reaction mixture was continued stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give cyclized product **140** (25.8 mg, 90%) as a white solid and minor product **141** (2.3 mg, 10%) as a colorless oil.

Compound **140**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.24 (10H, m, 2xAr**H**), 6.24 (1H, t, J = 5.7 Hz, **H**C=CBr), 4.52 (2H, s, PhC**H**$_2$NCH$_2$BrC=CH), 4.45 (2H, s, PhC**H**$_2$NCH$_2$CH=CBr), 4.03 (2H, s, C**H**$_2$BrC=CH), 3.60 (2H, d, J = 5.68 Hz, CBr=CHC**H**$_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.6 (C_{Ar}), 135.3 (C_{Ar}), 130.5 (HC=CBr), 128.8 (2xCH_{Ar}), 128.7 (2xCH_{Ar}), 128.6 (2xCH_{Ar}), 128.3 (CH_{Ar}), 128.2 (CH_{Ar}), 122.7 (HC=CBr), 52.4 (2xPhCH_2), 52.1 (CH_2BrC=CH_2), 44.1 (CBr=CHCH_2).

IR ν_{max} (cm^{-1}) 3030 (w), 2919 (w), 1507 (w), 1456 (w), 1359 (w).

ESMS (-ve): m/z (% rel. intensity) 814.6 $[2M]^-$ (55)

m.p. 106-108 °C.

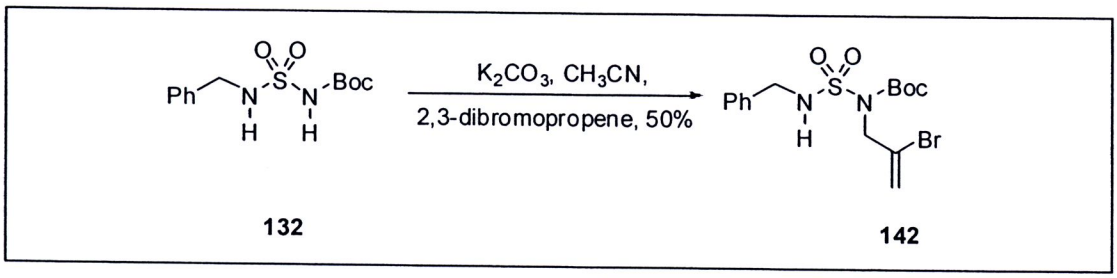
Compound **141**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.25 (10H, m, 2xAr**H**), 5.80 (2H, br t, 3.0 Hz, **H**C=C**H**), 4.45 (4H, s, 2xPhC$\mathbf{H}_2$), 3.66 (4H, d, J = 3.0 Hz, 2xNC$\mathbf{H}_2$CH=CH).

IR ν_{max} (cm^{-1}) 3032 (w), 2852 (w), 1631 (w), 1496 (w).

ESMS (+ve): m/z (% rel. intensity) 351.8 $[M+Na]^+$ (72).

2.12 *Preparation of tert-Butyl(benzylsulfamoyl)(2-bromoprop-2-en-1-yl)carba mate* 142



132 142

To a solution of compound **132** (500 mg, 1.77 mmol) in CH_3CN (25 mL) was added K_2CO_3 (240 mg, 1.77 mmol) at 0 °C. After stirring for 10 minutes, 2,3 dibromopropene (170 μL, 1.77 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow solid. Purification was accomplished by column chromatography eluting with 6% EtOAc/hexane to give compound **142** (356.3 mg, 50%) as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.27 (5H, m, ArH), 5.88 (1H, br (d), J = 2.1 Hz, BrC=C**H**H), 5.64-5.59 (1H, br t, J = 6.3 Hz, CH_2N**H**), 5.61 (1H, d, J = 2.1 Hz, BrC=CH**H**), 4.35 (2H, s, C**H**$_2$CBr), 4.20 (2H, d, J = 6.3 Hz, PhC**H**$_2$), 1.46 (9H, s, C(C**H**$_3$)$_3$).

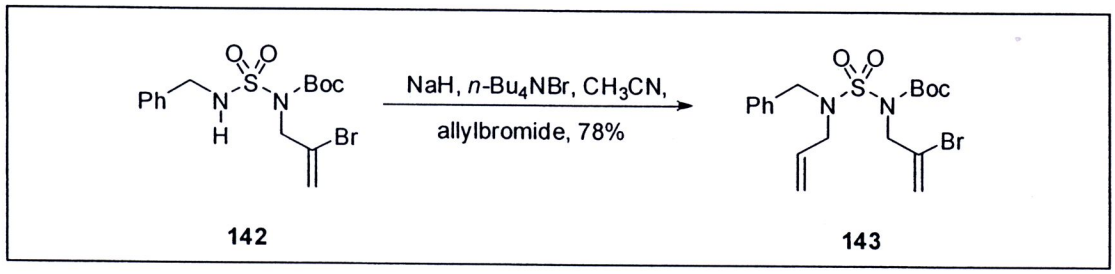
^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.3 (CO), 135.5 (**C**$_{Ar}$), 128.9 (2x**CH**$_{Ar}$), 128.3 (**CH**$_{Ar}$), 128.1 (2x**CH**$_{Ar}$), 127.6 (BrC=**CH**$_2$), 118.4 (Br**C**=CH$_2$), 84.7 (**C**(CH$_3$)$_3$), 53.9 (**CH**$_2$CBr), 48.1 (Ph**CH**$_2$), 27.9 (C(**CH**$_3$)$_3$).

IR ν_{max} (cm^{-1}) 3277 s, 3034 (w), 2975 (m), 1706 s, 1645 (w), 1496 (w), 1459 (m).

ESMS (+ve): m/z (% rel. intensity) 426.9, 428.9 $[M+Na]^+$ (100), (85).

m.p. 101-107°C.

2.13 *Preparation of tert-Butyl-N-allyl-N-benzylsulfamoyl(2-bromoallyl)carba mate* **143**



142 **143**

To a solution of compound **142** (100 mg, 0.25 mmol) in CH_3CN (5 mL) was added NaH (6 mg, 0.25 mmol) and *n*-Bu_4NBr (16 mg, 0.05 mmol) at 0 °C. After stirring for 10 minutes, allyl bromide (30 µL, 0.25 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (10 mL). The solution was extracted with EtOAc (3x15 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 8% EtOAc/hexane to give compound **143** (86.9 mg, 78%) as a colorless oil.

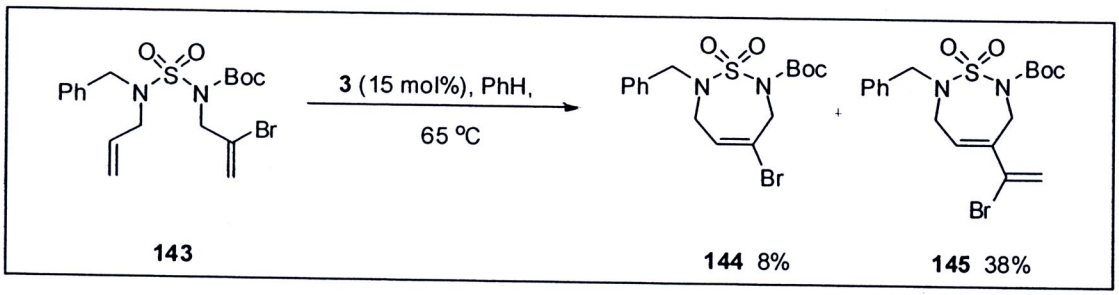
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.25 (5H, m, Ar**H**), 5.89 (1H, br (d), J = 1.0 Hz, BrC=C**H**H), 5.74 (1H, ddt, J = 17.1, 10.3, 6.5 Hz, **H**C=CH_2), 5.60 (1H, br (d), J = 1.0 Hz, BrC=CH**H**), 5.19 (1H, d, J = 10.3 Hz, HC=C**H**H), 5.13 (1H, d, J = 17.1 Hz, HC=CH**H**), 4.51 (2H, s, PhC$\mathbf{H}_2$), 4.44 (2H, s, C$\mathbf{H}_2$CBr), 3.83 (2H, d, J = 6.5 Hz, NC$\mathbf{H}_2$CH), 1.50 (9H, s, C(C$\mathbf{H}_3$)$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.0 (**C**O), 135.9 (**C**$_{Ar}$), 132.0 (**H**C=CH_2), 128.6 (2x**C**H$_{Ar}$), 128.3 (2x**C**H$_{Ar}$), 127.9 (Br**C**=CH_2), 127.8 (**C**H$_{Ar}$), 119.4 (BrC=**C**H_2), 117.5 (HC=**C**H_2), 84.2 (**C**(CH_3)$_3$), 55.1 (**C**H_2CBr=CH_2), 51.9 (**C**H_2Ph), 50.4 (**C**H_2CH=CH_2), 28.0 (C(**C**H_3)$_3$).

IR ν_{max} (cm^{-1}) 3032 (w), 2982 (m), 1735 s, 1643 (w), 1606 (w), 1496 (w), 1477 (m), 1367 s.

ESMS (+ve): m/z (% rel. intensity) 443.1, 444.1 $[M]^+$ (71), (19).

2.14 *Preparation of tert-Butyl-7-benzyl-4-bromo-6,7-dihydro-1,2,7-thiadiazepine-2(3H)-carboxylate 1,1-dioxide* **144**



143 **144** 8% **145** 38%

To a solution of compound **143** (30 mg, 0.07 mmol) in benzene (0.6 mL) was added a solution of the second generation Grubbs catalyst (6.0 mg, 7.0 μmol) in benzene (0.8 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 65 °C for 18 hours. Another portion of the Grubbs catalyst **3** (3.0 mg, 3.5 μmol) in benzene (0.5 mL) was added and then the reaction mixture was continue stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 4% EtOAc/hexane to give compound **144** (2.3 mg, 8%) as a colorless oil, compound **145** (11.9 mg, 38%) as a white solid and recovered starting material (16.7 mg, 56%).

Compound **144**

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.29 (5H, m, Ar**H**), 6.04 (1H, br t, J = 4.4 Hz, $CH_2CBr=C\mathbf{H}$), 4.57 (2H, s, $PhC\mathbf{H}_2NCH_2CH=CBr$), 4.47 (2H, s, $C\mathbf{H}_2CBr=CH$), 3.75 (2H, d, J = 4.4 Hz, $CBr=CHC\mathbf{H}_2$).

Compound **145**

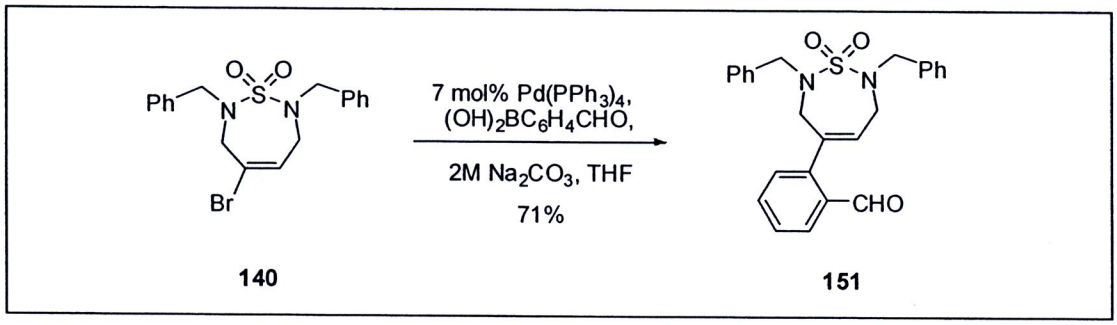
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.21 (5H, m, Ar**H**), 5.87 (1H, d, J = 1.04 Hz, $CBr=C\mathbf{H}H$), 5.59 (1H, d, J = 1.04 Hz, $CBr=CH\mathbf{H}$), 5.43 (1H, br t, J = Hz, $C\mathbf{H}=C(CH_2)CBr=CH_2$), 4.41 (2H, s, $CH=C(C\mathbf{H}_2)CBr=CH_2$), 4.38 (2H, s, $PhCH_2$), 3.82 (2H, $C\mathbf{H}_2CH=C(CH_2)CBr=CH_2$), 1.46 (9H, s, $C(C\mathbf{H}_3)_3$).

IR ν_{max} (cm^{-1}) 2978 (w), 2928 (w), 1731 s, 1368 s.

ESMS (+ve): m/z (% rel. intensity) 444.8 $[M+H]^+$ (100).

m.p. 126-130 °C.

2.15 ***Preparation of compound 2,7-Dibenzyl-4-(o-formylphenyl)-2,3,6,7-tetrahy dro-1,2,7-thiadiazepine 1,1-dioxide*** **151**



140 **151**

To a solution of compound **140** (25.4 mg, 0.06 mmol) in THF (2 ml) was added a solution of 2M Na_2CO_3 (1 ml) and 2-formylphenyl boronic acid (11 mg, 0.075 mmol). $Pd(PPh_3)_4$ (5 mg, 4 μmol) was added. The reaction mixture was heated at reflux for 2 hours before being quenched with water (5 ml) and then extracted with EtOAc (3x15 ml). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a brown oil. Purification was accomplished by column chromatography eluting with 14% EtOAc/hexane to give coupled product **151** (18.5 mg, 71%) as a yellow oil.

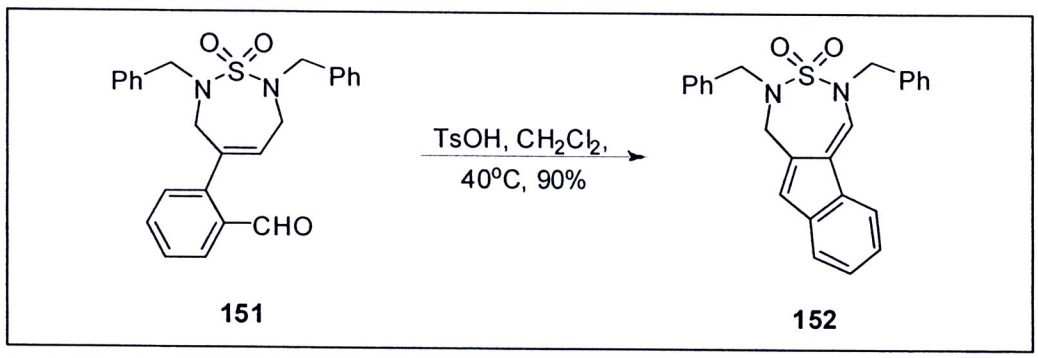
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.83 (1H, s, C**H**O), 7.78 (1H, d, J = 7.4 Hz, C_{Ar}(CHO)C**H**$_{Ar}$), 7.57-7.20 (12 H, m, C**H**$_{Ar}$), 6.93 (1H, d, J = 7.4 Hz, C**H**$_{Ar}$C(CH_2)=CH), 5.57 (1H, t, J = 4.8 Hz, CH_2C**H**=CBr), 4.60 (2H, s, Ph C**H**$_2$), 4.57 (2H, s, PhC**H**$_2$), 4.01 (2H, s, CH=CC**H**$_2$), 3.88 (2H, d, J = 4.8 Hz, C**H**$_2$CH=C).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.3 (CHO), 143.7 (C_{Ar}CHO), HC=C(Ar)CH_2), 136.3 (C_{Ar}), 136.2 (C_{Ar}), 133.8 (CH_{Ar}CHO), 133.7 (C_{Ar}CHO), 131.0 (CH_{Ar}CHO), 128.8 (2xCH_{Ar}), 128.7 (2xCH_{Ar}), 128.6 (CH_{Ar}), 128.4 (2xCH_{Ar}), 128.3 (CH_{Ar}CHO), 128.2 (2xCH_{Ar}), 128.1 (CH_{Ar}), 127.9 (CH_{Ar}CHO), 52.7 (2xPhCH_2), 48.6 (CH_2CH=C(ArCHO), 43.9 (HC=C(ArCHO)CH_2).

IR ν_{max} (cm^{-1}) 3031 (w), 2923 (w), 1698 s, 1595 (w), 1496 (w), 1456 (w).

ESMS (+ve): m/z (% rel. intensity) 443.0 $[M+H]^+$ (100).

2.16 *Preparation of compound* 152



151 **152**

To a solution of compound **151** (11.1 mg, mmol) in CH_2Cl_2 (3 ml) was added TsOH (4.5 mg, 0.026 mmol). The reaction mixture was heated at reflux for an hour before being quenched with water (5 ml) and then extracted with EtOAc (3x15 ml). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a brown oil. Purification was accomplished by column

chromatography eluting with% EtOAc/hexane to give compound **152** (9.6 mg, 90%) as a yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.11 (14H, m, Ar**H**), 7.09 (1H, s, $PhCH_2NCH$), 6.62 (1H, s, $PhCH_2NCH_2$), 4.98 (2H, s, $PhCH_2NCH$), 4.39 (2H, s, $PhCH_2NCH_2$), 4.10 (2H, s, $PhCH_2NCH_2$).

IR ν_{max} (cm^{-1}) 3066 (w), 2918 (w), 1620 s, 1456 (w)

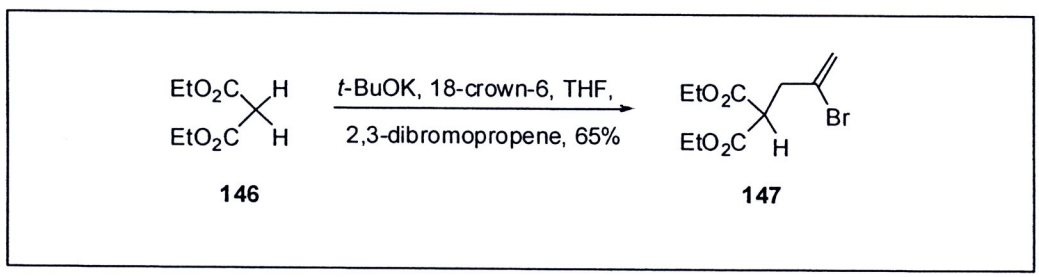
ESMS (+ve): m/z (% rel. intensity) 415.1 $[M+H]^+$ (100).

m.p. 153-154 °C.

3. Synthesis of Carbocyclic Containing Vinyl Bromo-Olefin

3.1 5-Membered Ring of Carbocyclic Containing Vinyl Bromo-Olefin

3.1.1 *Preparation of Diethyl-2-(2-bromoallyl)malonate* **147**



146 **147**

To a solution of diethylmalonate (9,514 µL, 6 mmol) in THF (30 mL) was added *t*-BuOK (224 mg, 2 mmol) and 18-crown-6 (105 mg, 0.40 mmol) at 0 °C. After stirring for 10 minutes, 2,3-dibromopropene (195 µL, 2 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The

solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give compound **147** (365.5 mg, 65%) as a colorless oil.

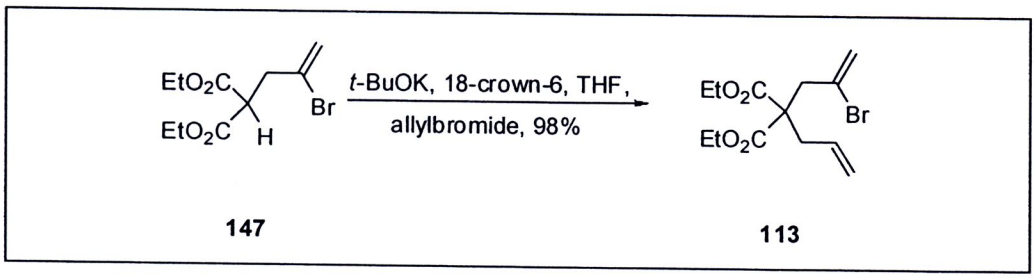
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.65 (1H, s, BrC=C**H**H), 5.44 (1H, s, BrC=CH**H**), 4.18 (4H, q, J = 14.1, 7.0 Hz, $(CO_2C\mathbf{H}_2CH_3)_2$), 3.74 (1H, t, J = 7.5 Hz, $(CO_2Et)_2C\mathbf{H}$), 2.99 (2H, d, J = 7.5 Hz, $CHC\mathbf{H}_2$), 1.24 (6H, t, J = 7.0 Hz, $(CO_2CH_2C\mathbf{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1 (2x**C**O), 129.4 (Br**C**=CH_2), 119.6 (BrC=$\mathbf{C}H_2$), 61.7 ($(CO_2\mathbf{C}H_2CH_3)_2$), 50.6 ($(CO_2Et)_2\mathbf{C}H$), 40.4 ($\mathbf{C}H_2CBr=CH_2$), 14.0 ($(CO_2CH_2\mathbf{C}H_3)_2$).

IR ν_{max} (cm^{-1}) 2924 (w), 1653 (w).

ESMS (+ve): m/z (% rel. intensity) 278.9, 280.9 $[M+H]^+$ (98), (100).

3.1.2 *Preparation of Diethyl-2-allyl-2-(2-bromoallyl)malonate* **113**



147 **113**

To a solution of compound **147** (250 µL, 1.25 mmol) in THF (10 mL) was added *t*-BuOK (140.10 mg, 1.25 mmol) and 18-crown-6 (66 mg, 0.25 mmol) at 0 °C. After stirring for 10 minutes,allyl bromide (74 µL, 1.25 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a yellow oil. Purification was accomplished by column chromatography eluting with 4% EtOAc/hexane to give compound **113** (390 mg, 98%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.70-5.60 (1H, m, **H**C=CH_2), 5.66 (1H, br s, BrC=C**H**H), 5.62 (1H, d, J = 1.4 Hz, BrC=C**H**H), 5.12 (1H, d, J = 8.8 Hz, CH_2CH=C**H**H), 5.08 (1H, br s, CH_2CH=CH**H**), 4.23-4.12 (4H, m, $(CO_2C\mathbf{H}_2CH_3)_2$), 3.12 (2H, s, $C\mathbf{H}_2CBr$), 2.75 (2H, d, J = 7.3 Hz, $C\mathbf{H}_2CH=CH_2$), 1.23 (6H, t, J = 7.1 Hz, $(CO_2CH_2C\mathbf{H}_3)_2$).

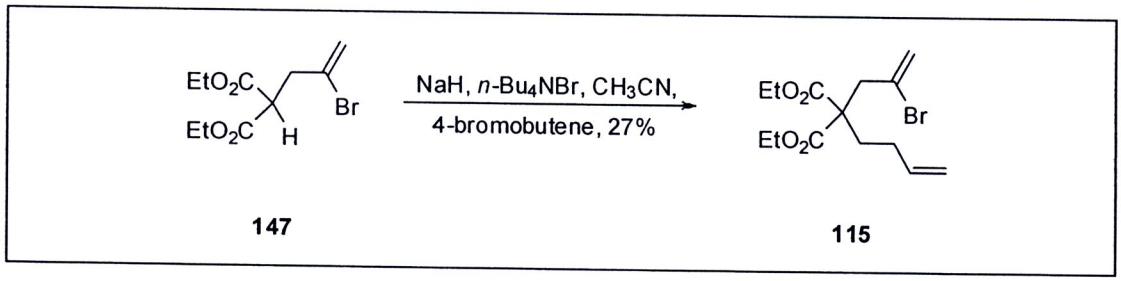
^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1 (2x**C**O), 132.1 (H**C**=CH_2), 127.3 (Br**C**=CH_2), 121.9 (BrC=**C**H_2), 119.5 (HC=**C**H_2), 61.6 (($CO_2CH_2CH_3)_2$), 56.9 (**C**$(CO_2Et)_2$), 42.9 (**C**H_2CBr=CH_2), 36.0 (**C**H_2CH=CH_2), 14.0 (($CO_2CH_2CH_3)_2$).

IR ν_{max} (cm^{-1}) 2959 (w), 2923 (w), 1734 (m), 1627 (m).

ESMS (+ve): m/z (% rel. intensity) 319.1 $[M]^+$ (100).

3.2 6-Membered Ring of Carbocyclic Containing Vinyl Bromo-Olefin

3.2.2 *Preparation of Diethyl-2-(2-bromoallyl)-2-(but-3-enyl)malonate* **115**



To a solution of compound **147** (100 mg, 0.36 mmol) in CH_3CN (5 mL) was added NaH (3.58 mg, 0.36 mmol) and *n*-Bu_4NBr (23 mg, 0.07 mmol) at 0 °C. After stirring for 10 minutes, 4-bromobutene (35 μL, 0.36 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to

afford the crude product as ayellow oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give compound **115** (54.7 mg, 46%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.76 (1H, ddt, J = 17.2, 10.3, 6.3 Hz, **H**C=CH_2), 5.63 (1H, br s, BrC=C**H**H), 5.56 (1H, br s, BrC=CH**H**), 5.01 (1H, d, J = 17.2 Hz, HC=C**H**H), 4.95 (1H, d, J = 10.3 Hz, HC=CH**H**), 4.23-4.13 (4H, m, (($CO_2C\mathbf{H}_2CH_3)_2$), 3.15 (2H, s, $C\mathbf{H}_2$CBr), 2.11-2.05 (2H, m, $C\mathbf{H}_2CH_2CH{=}CH_2$), 1.97-1.90 (2H, m, $CH_2C\mathbf{H}_2CH{=}CH_2$), 1.23 (6H, t, J = 7.1 Hz, $(CO_2CH_2C\mathbf{H}_3)_2$).

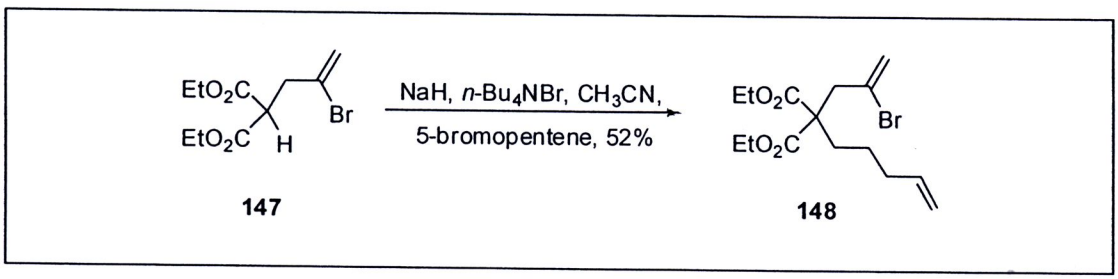
^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.5 (2x**C**O), 137.2 (H**C**=CH_2), 127.4 (Br**C**=CH_2), 121.6 (BrC=**C**H_2), 115.1 (HC=**C**H_2), 61.5 (($CO_2CH_2CH_3)_2$), 56.9 (**C**), 42.9 (CH_2BrC=CH_2), 30.6 ($CH_2CH_2CH{=}CH_2$), 28.4 ($CH_2CH_2CH{=}CH_2$), 14.0 (($CO_2CH_2CH_3)_2$).

IR ν_{max} (cm^{-1}) 2981(w), 1735 s, 1642 (w), 1626 (w), 1452 (w)910 (w).

ESMS (+ve): m/z (% rel. intensity) 333.0, 334.9 $[M]^+$ (92), (100).

3.3 7-Membered Ring of Carbocyclic Containing Vinyl Bromo-Olefin

3.3.1 *Preparation of Diethyl-2-(2-bromoallyl)-2-(pent-4-enyl)manolate* **148**



147 **148**

To a solution of compound **147** (150 mg, 0.54 mmol) in CH_3CN (5 mL) was added NaH (13 mg, 0.54 mmol) and n-Bu_4NBr (35 mg, 0.11 mmol) at 0 °C. After stirring for 10 minutes, 5-bromopentene (65 μL, 0.54 mmol) was added. The reaction mixture was stirred for 15 hours at room temperature and before doing quenched with water (15 mL). The solution was extracted with EtOAc (3x15 mL) and water (10 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as ayellow oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give compound **148** (98.5 mg, 52%) as a colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.75 (1H, ddt, J = 17.1, 10.1, 6.8 Hz, **H**C=CH_2), 5.61 (1H, br s, BrC=C**H**H), 5.54 (1H, d, J = 1.6 Hz, BrC=CH**H**), 4.99 (1H, dd, J = 17.1, 1.7 Hz, HC=C**H**H), 4.94 (1H, dd, J = 10.1, 1.7 Hz, HC=CH**H**), 4.20-4.02 (4H, m, (($CO_2C\mathbf{H}_2CH_3)_2$), 3.13 (2H, s, $NC\mathbf{H}_2CBr$),

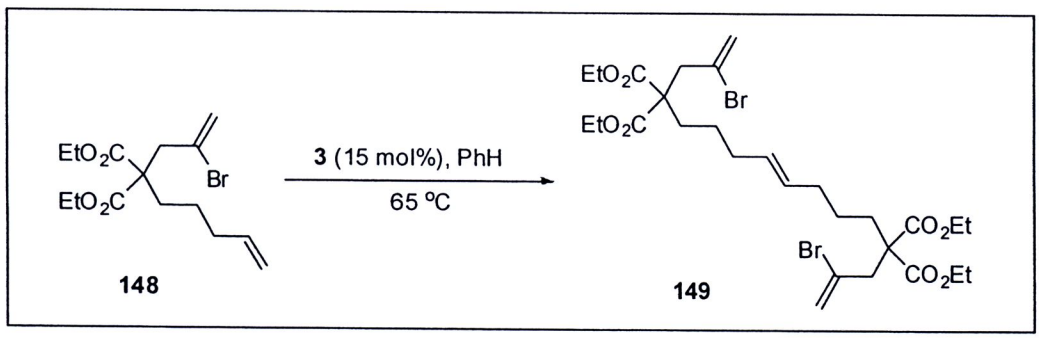
2.08-1.95 (4H, m, $NCH_2CH_2CH_2$), 1.30-1.20 (2H, m, $NCH_2CH_2CH_2$), 1.25 (6H, t, J = 6.1 Hz, $((CO_2CH_2CH_3)_2)$.

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6 (2xCO), 138.0 ($HC=CH_2$), 127.5 ($BrC=CH_2$), 121.5 ($BrC=CH_2$), 115.0 ($HC=CH_2$), 61.5 ($(COCH_2CH_3)_2$), 57.1 ($C(COCH_2CH_3)_2$), 42.9 (NCH_2CBr), 33.7 ($NCH_2CH_2CH_2$), 30.9 ($NCH_2CH_2CH_2$), 23.5 ($NCH_2CH_2CH_2$), 14.0 ($(COCH_2CH_3)_2$).

IR ν_{max} (cm^{-1}): 2982 (w), 1735 s, 1643 (w), 1626 (w), 1470 (w), 906 (w).

ESMS (+ve): m/z (% rel. intensity) 347.0, 348.8 $[M]^+$ (31), (100).

3.3.2 *Preparation of (E)-Tetraethyl-2,15-dibromohexadeca-1,8,15-triene-4,4,13,13-tetracarboxylate* **149**



To a solution of compound **148** (25.7 mg, 0.07 mmol) in benzene (2 mL) was added a solution of the second generation Grubbs catalyst (6.0 mg, 7.0 μmol) in benzene (1 mL). The reaction mixture was stirred and degassed for 2 minutes. The mixture was then heated at 65 °C for 18 hours. Another portion of the Grubbs catalyst **3** (3.0 mg, 3.5 μmol) in benzene (0.5 mL) was added and then the reaction mixture was continue stirring for

18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give cross product **149** (14.1 mg, 30%) as a colorless oil and recover starting material (11.4 mg, 44%) as a colorless oil.

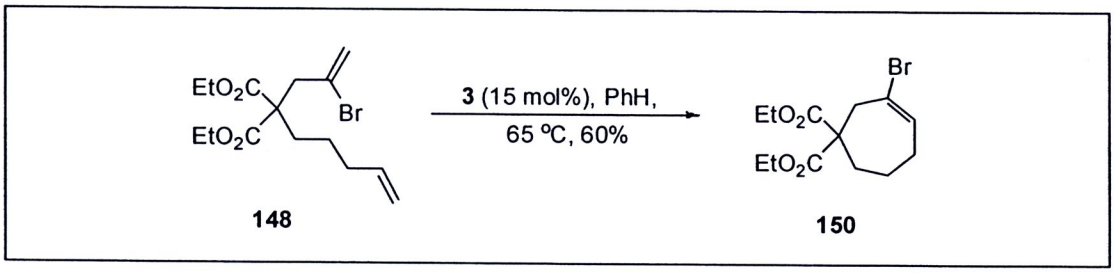
^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.61 (2H, d, J = 1.5 Hz, 2xBrC=C**H**H), 5.54 (2H, d, J = 1.5 Hz, 2xBrC=CH**H**), 5.34 (2H, t, J = 3.6 Hz, $CH_2CH_2CH_2C$**H**=C**H**), 4.21-4.13 (8H, m, 2xC(CO_2C**H**$_2CH_3)_2$), 3.12 (4H, s, 2xC**H**$_2$BrC=CH_2), 2.19-1.93 (8H, m, 2xC**H**$_2CH_2C$**H**$_2$CH=CH), 1.23 (12H, t, J = 7.13 Hz, 2xC(CO_2CH_2C**H**$_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6 (4x**C**O), 130.1 (2xBrC=**C**H_2), 127.5 (H**C**=**C**H), 121.5 (Br**C**=CH_2), 61.5 (2x(CO_2**C**$H_2CH_3)_2$), 57.1 (2x**C**(CO_2Et)), 42.8 (**C**H_2CBr=CH_2), 32.5 ($CH_2CH_2CH_2$**C**H=CH), 30.9 (**C**$H_2CH_2CH_2$CH=CH), 24.0 (CH_2**C**H_2CH_2CH=CH), 14.0 (2xCO_2CH_2**C**$H_3)_2$).

IR ν_{max} (cm^{-1}):2925 (w), 2853 (w), 1731 s, 1649(w).

ESMS (+ve): m/z (% rel. intensity) 689.2, 690.1, 691.5 $[M+Na]^+$(57), (56), (100).

3.3.3 *Preparation of (E)-Diethyl-3-bromocyclohept-3-ene-1,1dicarboxylate* **150**



148 **150**

To a solution of compound **148** (20.8 mg, 0.06 mmol) in benzene (4 mL) was added a solution of the second generation Grubbs catalyst (5.0 mg, 6.0 μmol) in benzene (2 mL). The reaction mixture was stirred and degassed for 30 second. The mixture was then heated at 65 °C for 18 hours. Another portion of the Grubbs catalyst **3** (2.5 mg, 3.0 μmol) in benzene (0.5 mL) was added and then the reaction mixture was continue stirring for 18 hours. The solution was concentrated under reduced pressure to afford the crude product as a black oil. Purification was accomplished by column chromatography eluting with 2% EtOAc/hexane to give the cyclized product **150** (11.5 mg, 60%) as a colorless oil and recovered starting material (7.3 mg, 35%) as a colorless oil.

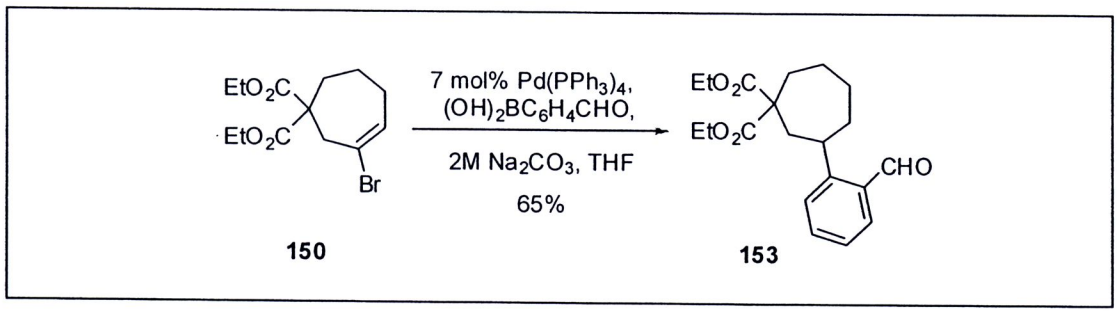
^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.22 (1H, t, J = 6.39 Hz, $H_2CHC{=}CBrCH_2$), 4.18 (4H, q, J = 14.20, 7.11 Hz, $C(CO_2CH_2CH_3)_2$), 3.19 ($HC{=}CBrCH_2$), 2.19 (2H, t, J = 6.04 Hz, $CH_2CH_2CH_2CH{=}CBr$), 2.09 (2H, q, J = 11.53, 6.34 Hz, $CH_2CH_2CH_2CH{=}CBr$), 1.73-1.66 (2H, m, $CH_2CH_2CH_2CH{=}CBr$), 1.25 (6H, t, J = 7.18 Hz, $C(CO_2CH_2CH_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.8 (2x**C**O), 135.1 (Br**C**=CH), 128.4 (Br**C**=CH), 61.5 (C($CO_2CH_2CH_3$)$_2$), 42.7 (**C**($CO_2CH_2CH_3$)$_2$), 42.7 (BrC=CH**C**H_2**C**H_2**C**H_2), 35.6 (**C**H_2Br=CH), 29.1 (BrC=CH**C**H_2**C**H_2**C**H_2), 21.8 (BrC=CHCH_2CH_2CH_2), 14.0 (C($CO_2CH_2CH_3$)$_2$).

IR ν_{max} (cm^{-1}): 2983 (w), 2924 (w), 1775 s.

ESMS (+ve): m/z (% rel. intensity) 318.8, 319.9, 320.9 $[M]^+$ (78), (13), (100).

3.3.4 *Preparation of Diethyl-3-(2-formylphenyl)cycloheptane-1,1-dicarboxylate* **153**



150 **153**

To a solution of compound **150** (8.7 mg, 0.027 mmol) in THF (1 ml) was added a solution of 2M Na_2CO_3 (1 ml) and 2-formylphenyl boronic acid (5 mg, 0.0324 mmol). $Pd(PPh_3)_4$ (2 mg, 1.89 μmol) was added. The reaction mixture was heated at reflux for 2 hours before being quenched with water (5 ml) and then extracted with EtOAc (3x10 ml). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude product as a brown oil. Purification was

accomplished by column chromatography eluting with 14% EtOAc/hexane to give compound **153** (6 mg, 65%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.03 (1H, s, C**H**O), 7.85 (1H, d, J = 7.7 Hz, C_{Ar}(CHO)C**H**$_{Ar}$), 7.49 (1H, t, J = 7.6 Hz, C**H**$_{Ar}$C$_{Ar}$C(CH_2)=CH), 7.35-7.19 (2H, m, 2xC**H**$_{Ar}$), 5.81 (1H, t, J = 6.4 Hz, PhC=C**H**CH_2), 4.06-4.02 (2H, m, $CO_2C\mathbf{H}_2CH_3$), 3.97-3.89 (2H, m, $CO_2C\mathbf{H}_2CH_3$), 3.18 (2H, s, C**H**$_2$C=CH), 2.39-2.26 (4H, m, PhC=CHC**H**$_2CH_2C\mathbf{H}_2$), 1.83-1.77 (2H, m, PhC=CH$CH_2C\mathbf{H}_2CH_2$), 1.04 (6H, t, J = 7.1 Hz, ($C(CO_2CH_2C\mathbf{H}_3)_2$).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.6 (**C**HO), 171.3 ($C(\mathbf{C}O_2Et)_2$, 149.2 (CH_2**C**Ph), 138.3 (**C**$_{Ar}$), 135.8 (**C**H$_{Ar}$), 133.1 (**C**H$_{Ar}$), 128.6 (**C**H$_{Ar}$), 128.4 (**C**H$_{Ar}$), 128.1 (**C**H$_{Ar}$), 126.7 (PhC=**C**H), 61.2 (($CO_2\mathbf{C}H_2CH_3)_2$), 55.4 ($\mathbf{C}(CO_2CH_2CH_3)_2$), 38.5 (PhC=CH$CH_2CH_2\mathbf{C}H_2$), 36.5 (**C**$H_2$Ph), 28.9 (PhC=CH**C**$H_2CH_2CH_2$), 22.3 (PhC=CH$CH_2\mathbf{C}H_2CH_2$), 13.7 (($CO_2CH_2\mathbf{C}H_3)_2$).

IR ν_{max} (cm^{-1}) 3062 (w), 2938 (m), 1735 s, 1689 s, 1671 (m), 1567 (w), 1477 (w), 1448 (m).

ESMS (+ve): m/z (% rel. intensity) 711.7 $[2M+Na]^+$ (100).

APPENDICES

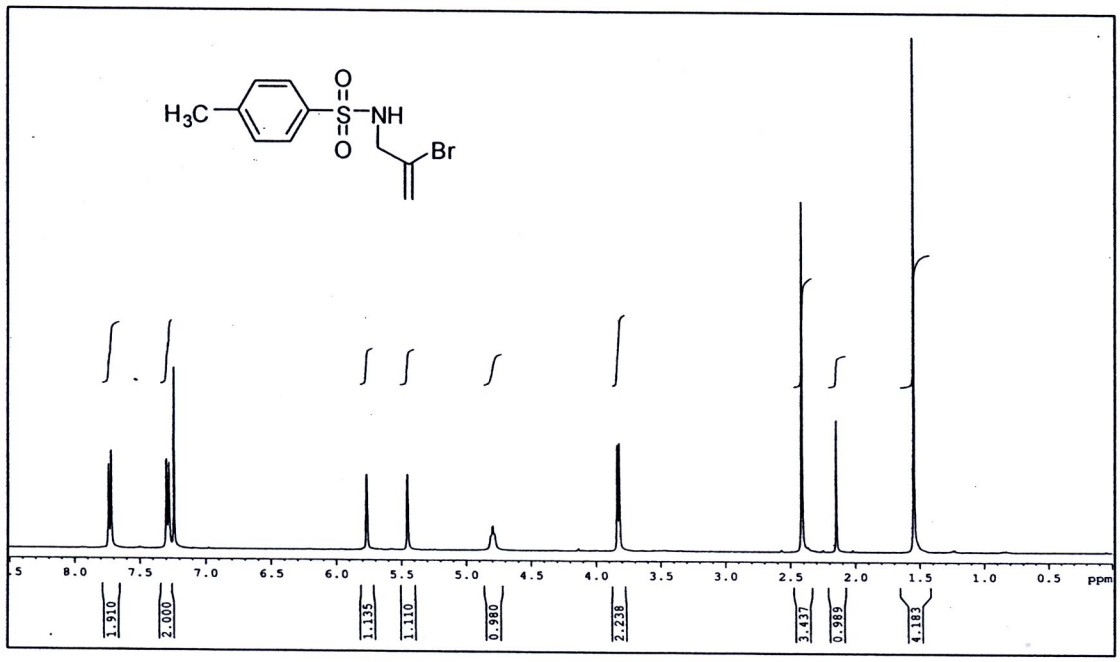


Figure 3 ^{1}H-NMR Spectrum of Compound **122** in $CDCl_3$

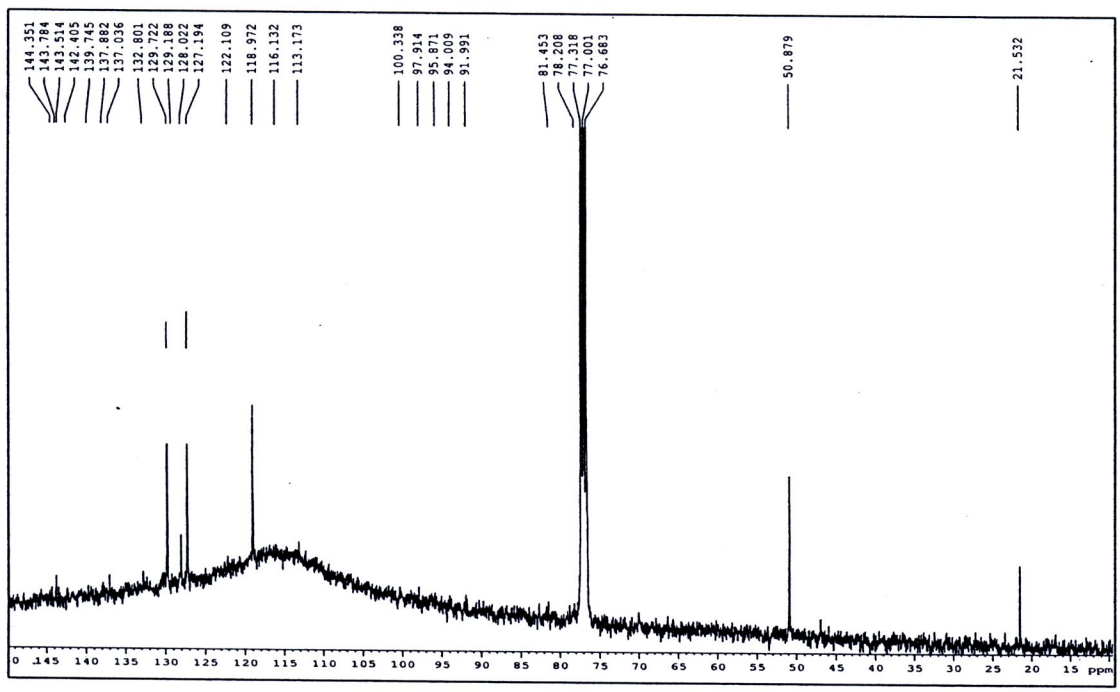


Figure 3a ^{13}C-NMR Spectrum of Compound **122** in $CDCl_3$

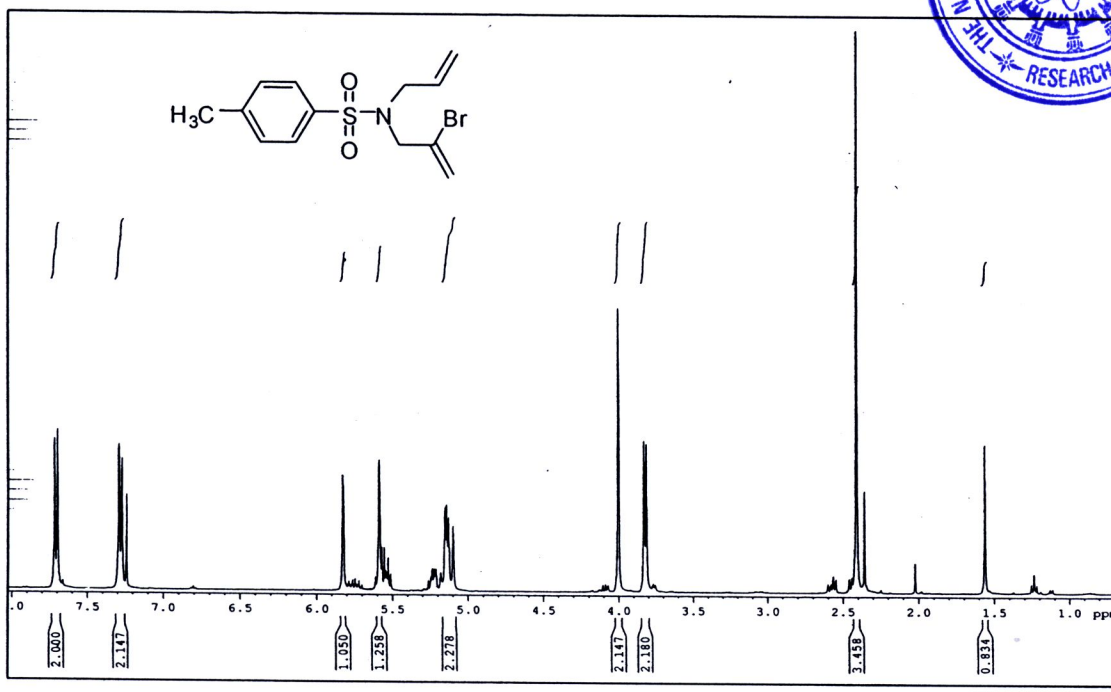


Figure 4 ^{1}H-NMR Spectrum of Compound **123** in $CDCl_3$

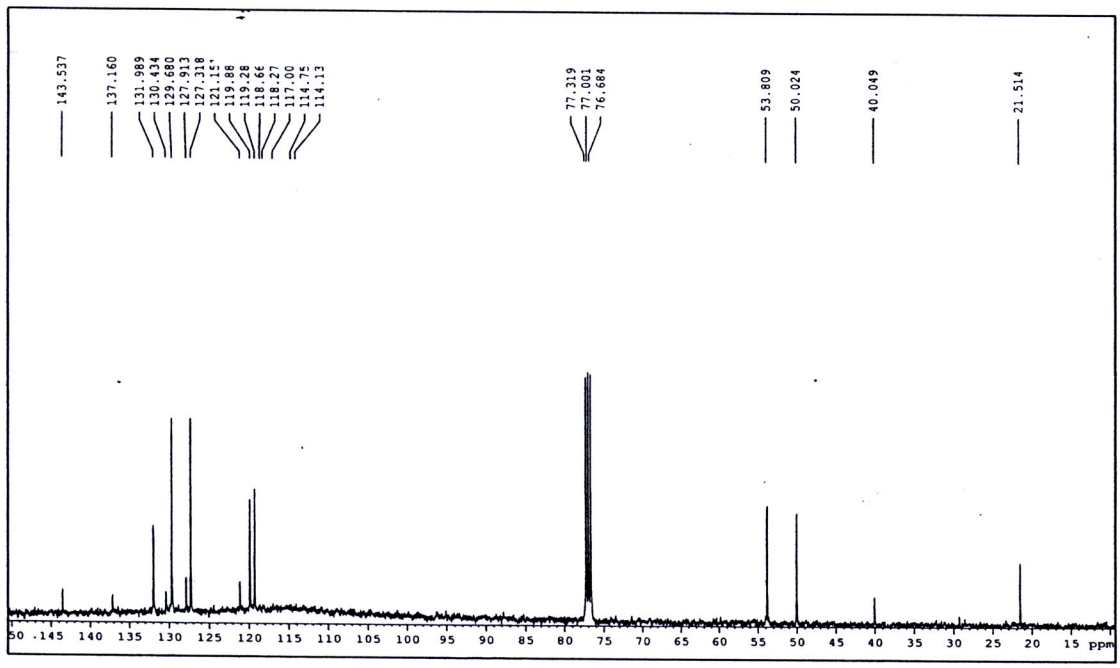


Figure 4a ^{13}C-NMR Spectrum of Compound **123** in $CDCl_3$

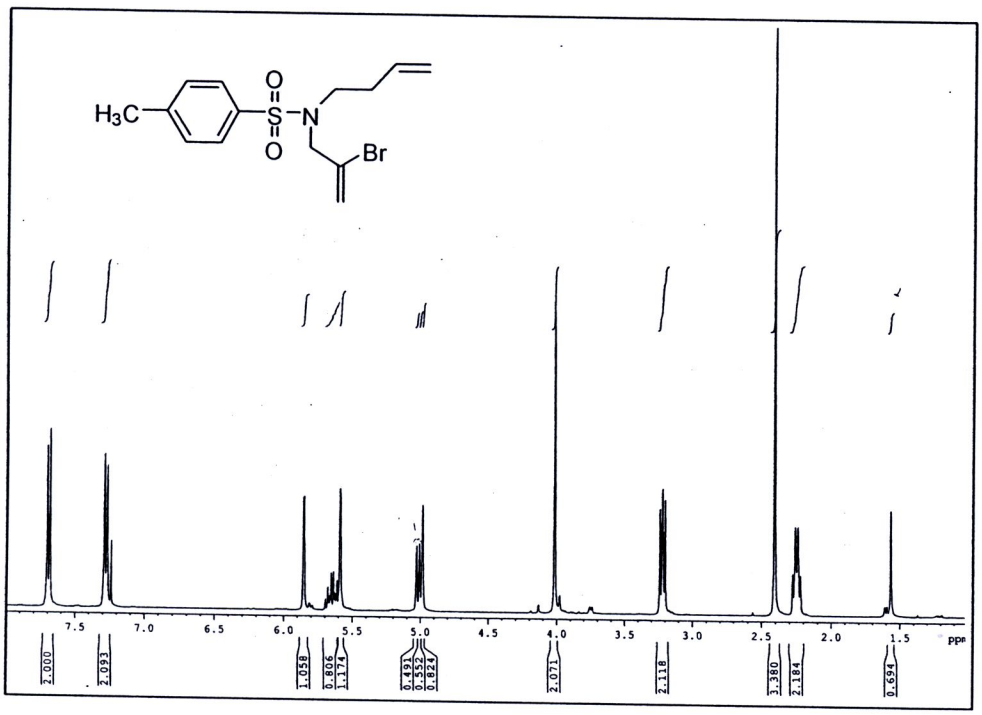


Figure 5 ^{1}H-NMR Spectrum of Compound **125** in $CDCl_3$

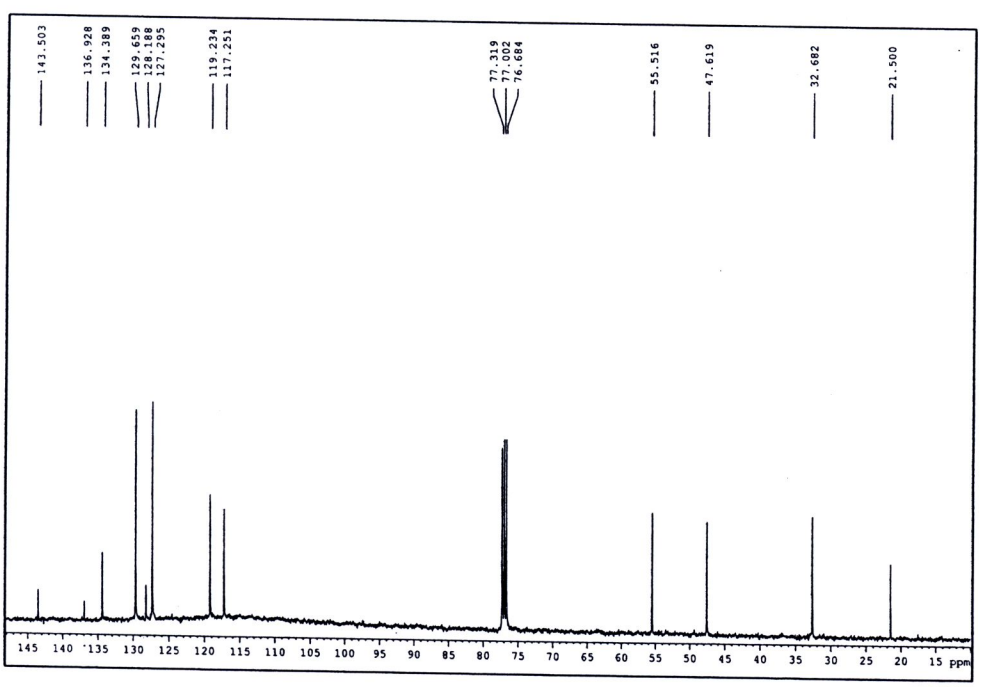


Figure 5a ^{13}C-NMR Spectrum of Compound **125** in $CDCl_3$

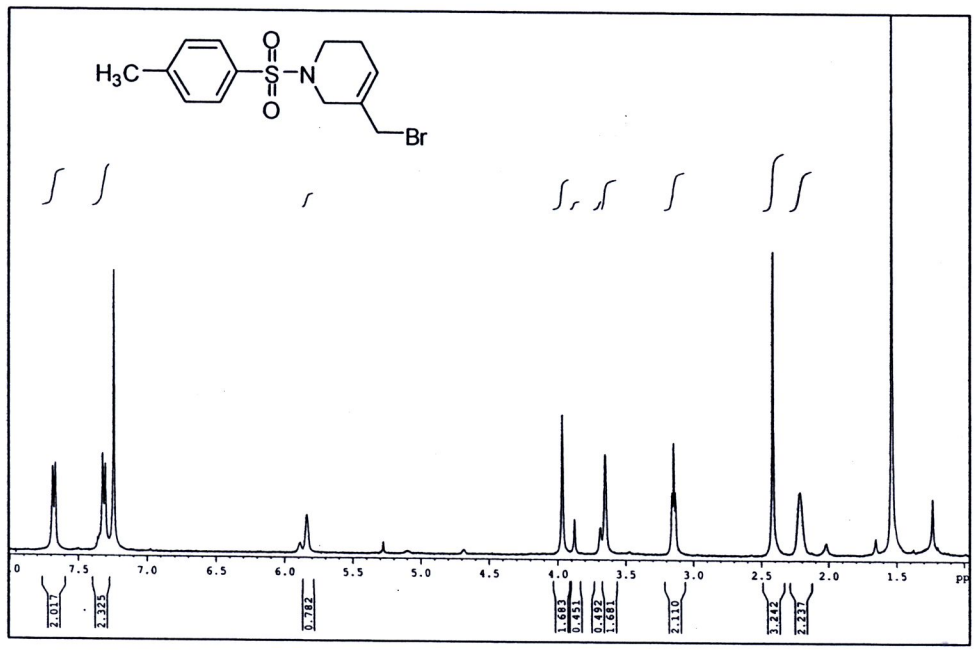


Figure 6 ^{1}H-NMR Spectrum of Compound **127** in $CDCl_3$

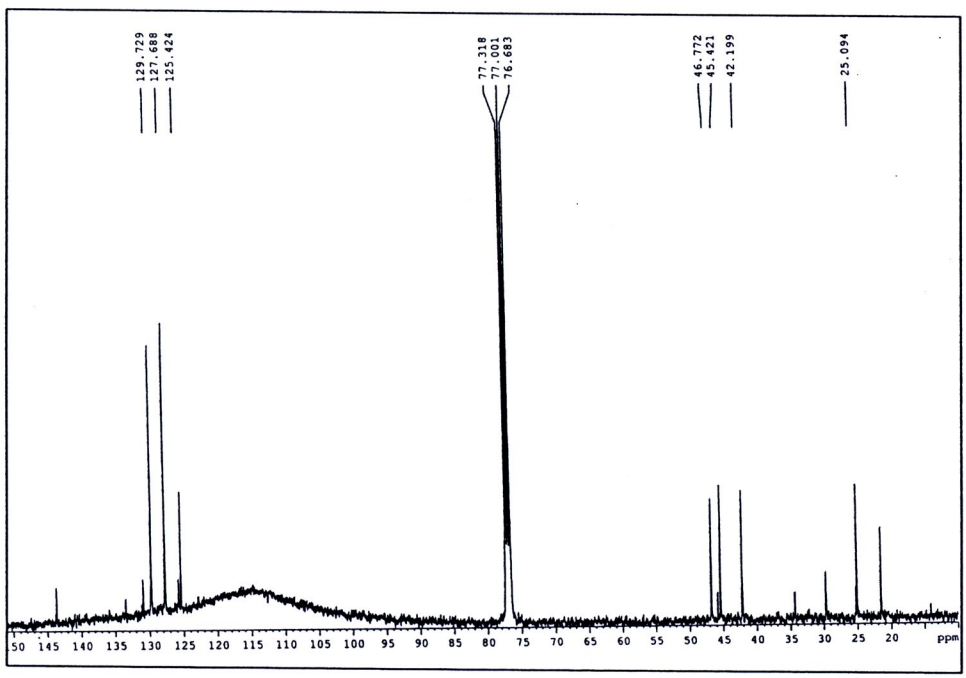


Figure 6a ^{13}C-NMR Spectrum of Compound **127** in $CDCl_3$

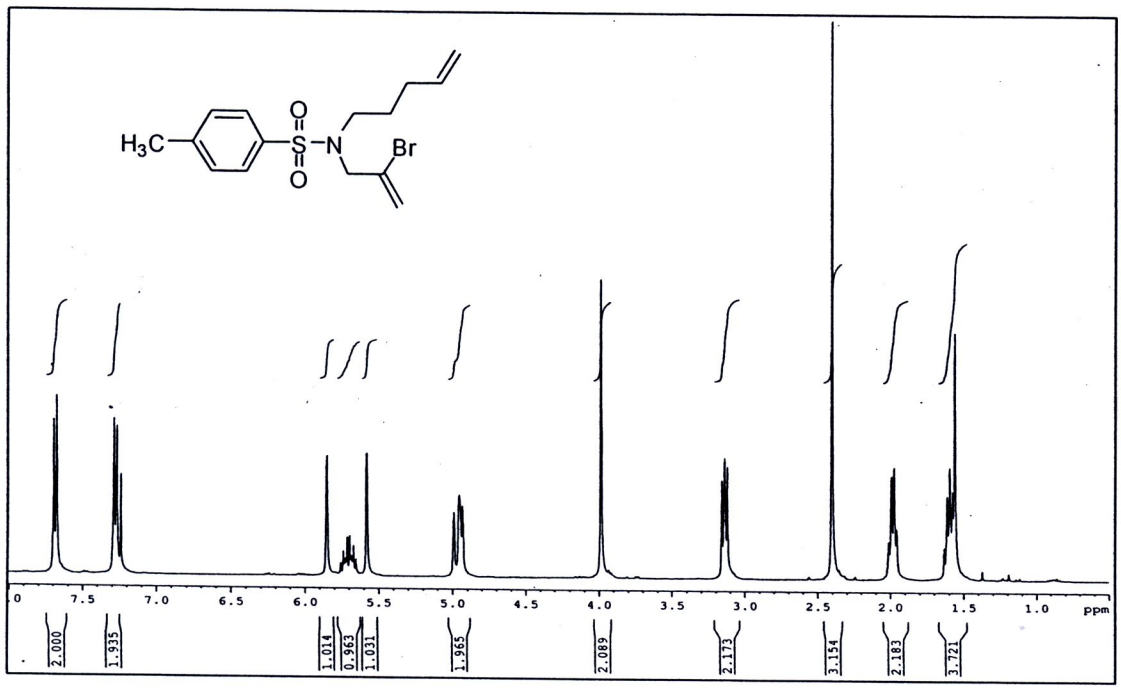


Figure 7 ^{1}H-NMR Spectrum of Compound **128** in $CDCl_3$

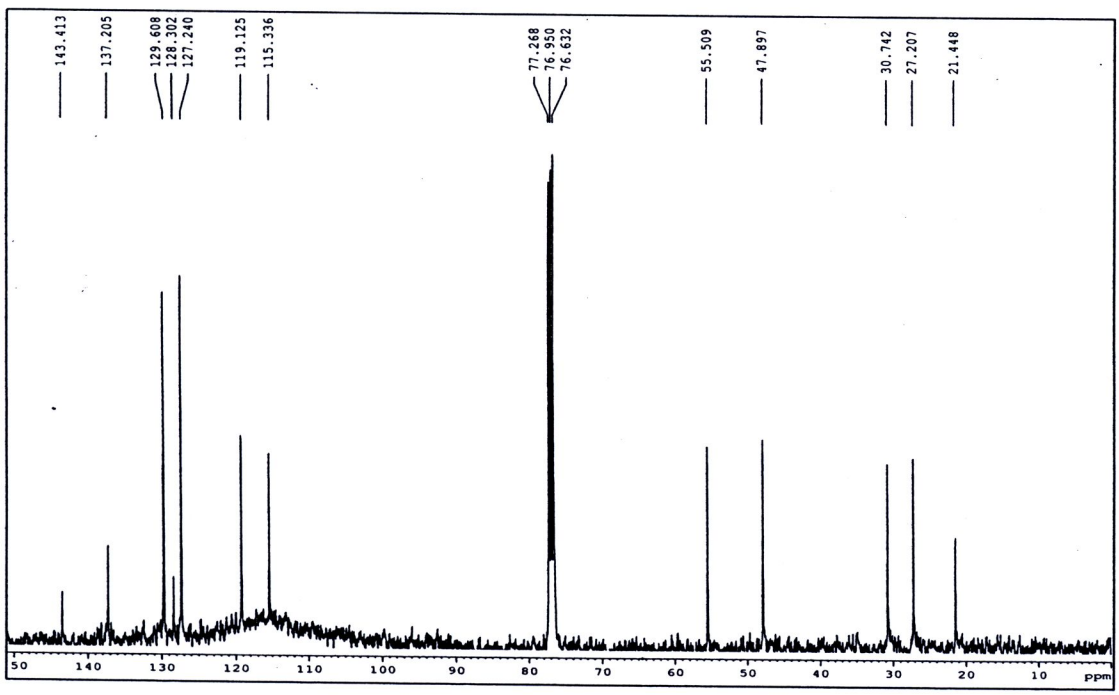


Figure 7a ^{13}C-NMR Spectrum of Compound **128** in $CDCl_3$

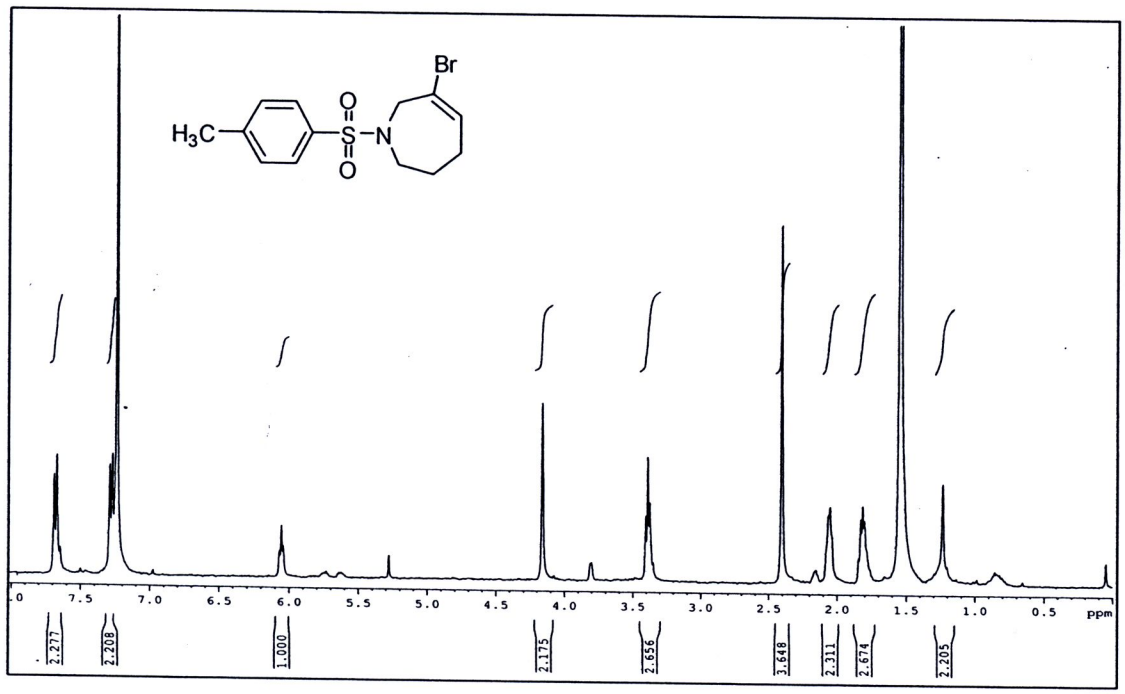


Figure 8 ^{1}H-NMR Spectrum of Compound 129 in $CDCl_3$

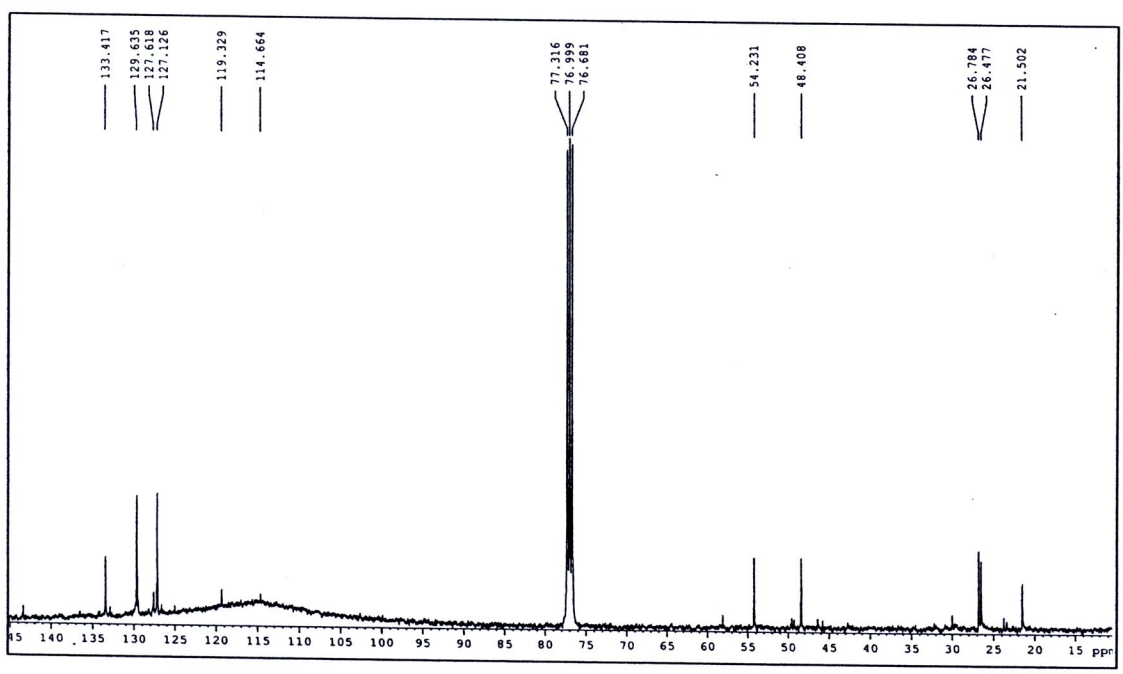


Figure 8a ^{13}C-NMR Spectrum of Compound **129** in $CDCl_3$

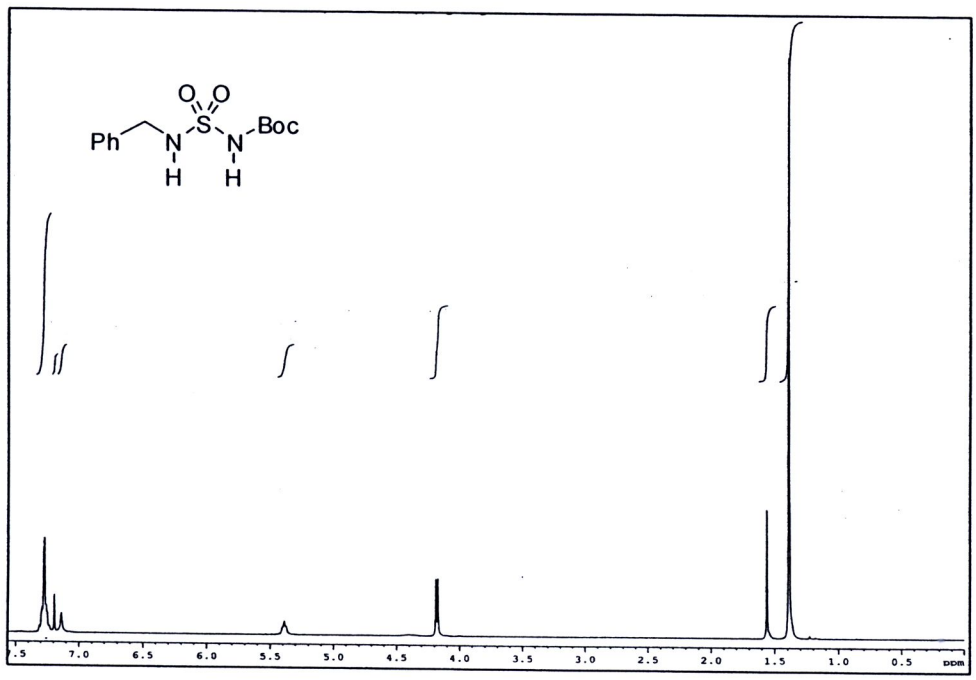


Figure 9 ^{1}H-NMR Spectrum of Compound **132** in $CDCl_3$

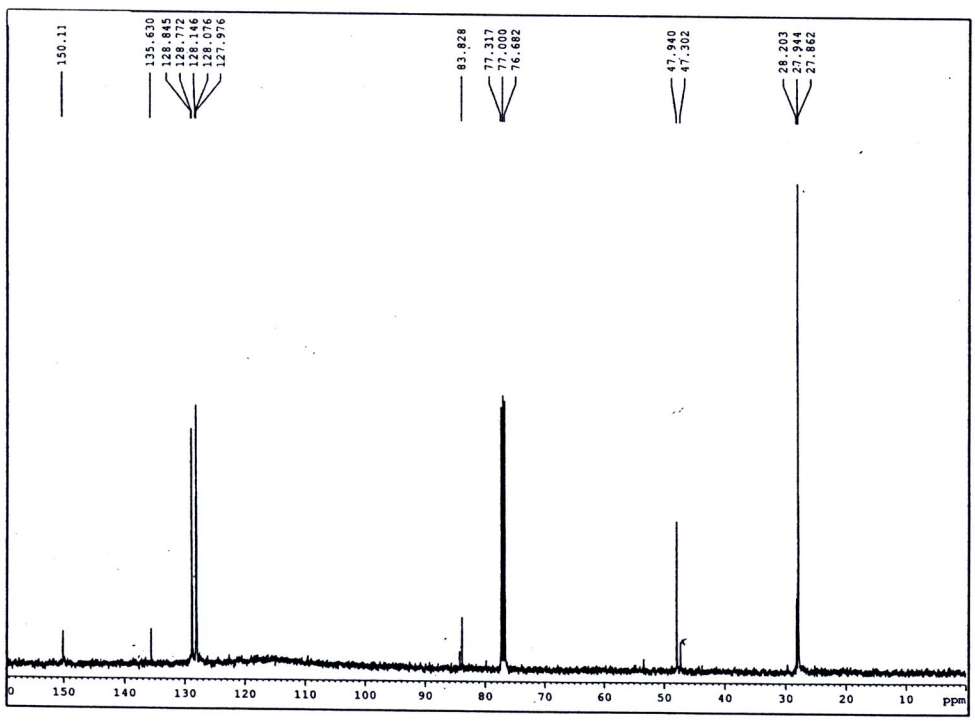


Figure 9a ^{13}C-NMR Spectrum of Compound **132** in $CDCl_3$

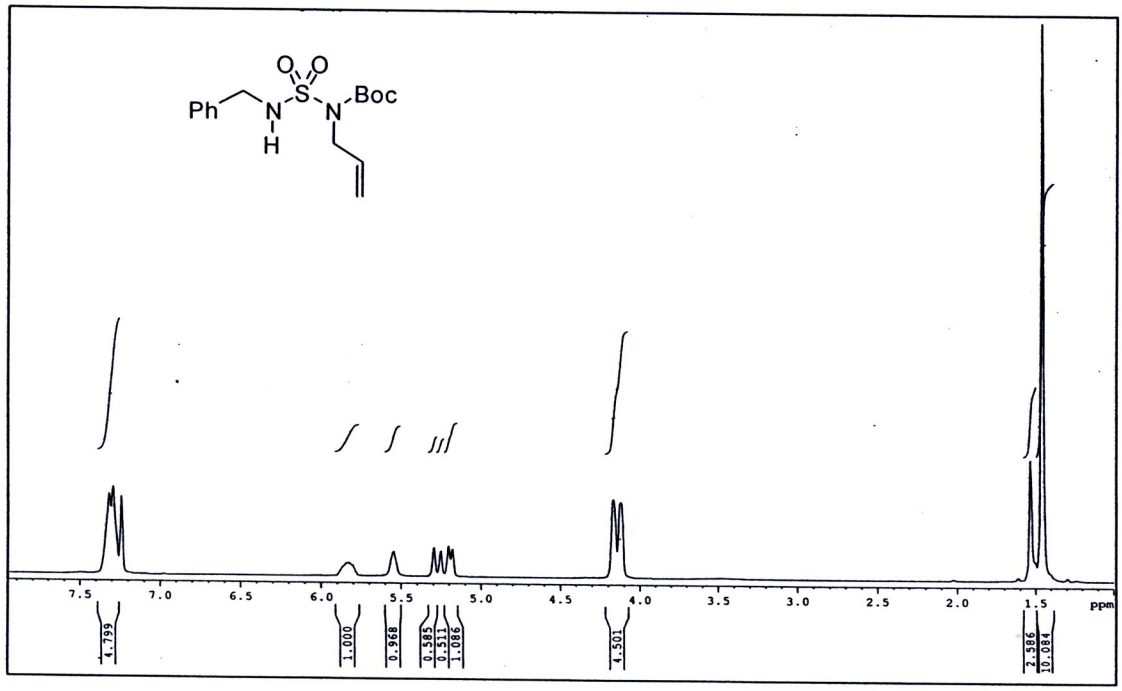


Figure 10 ^{1}H-NMR Spectrum of Compound **133** in $CDCl_3$

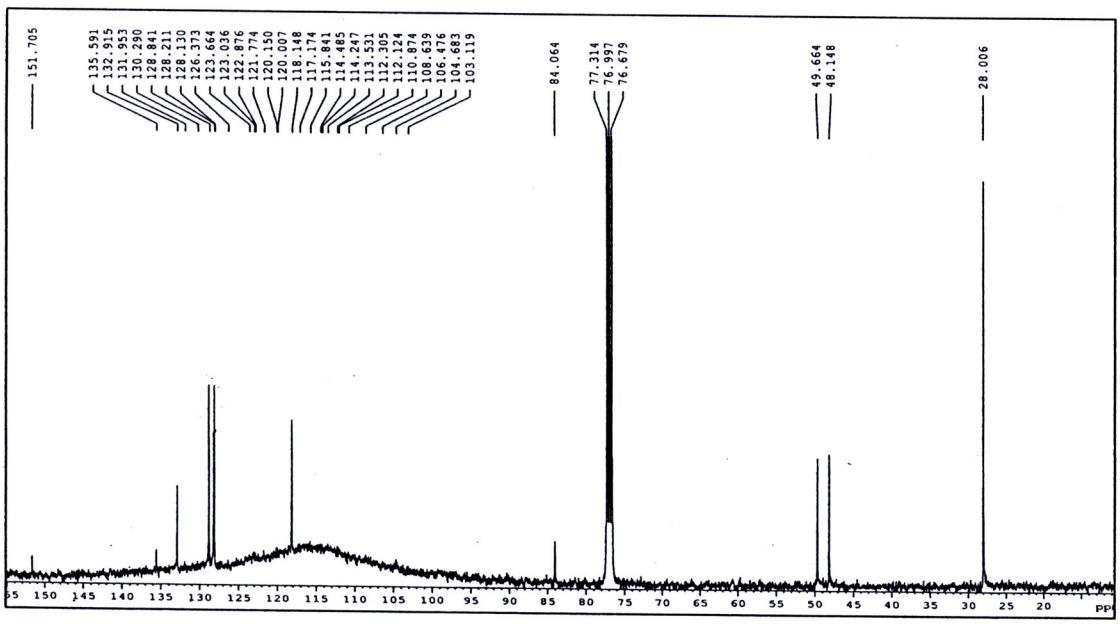


Figure 10a ^{13}C-NMR Spectrum of Compound **133** in $CDCl_3$

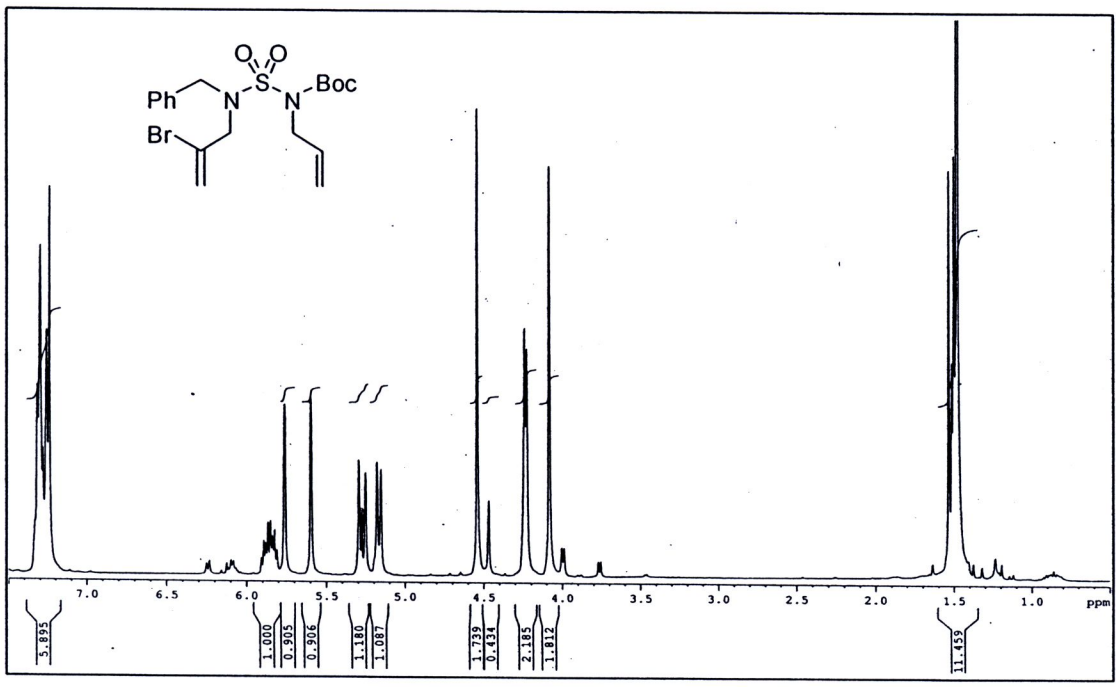


Figure 11 ^{1}H-NMR Spectrum of Compound **134** in $CDCl_3$

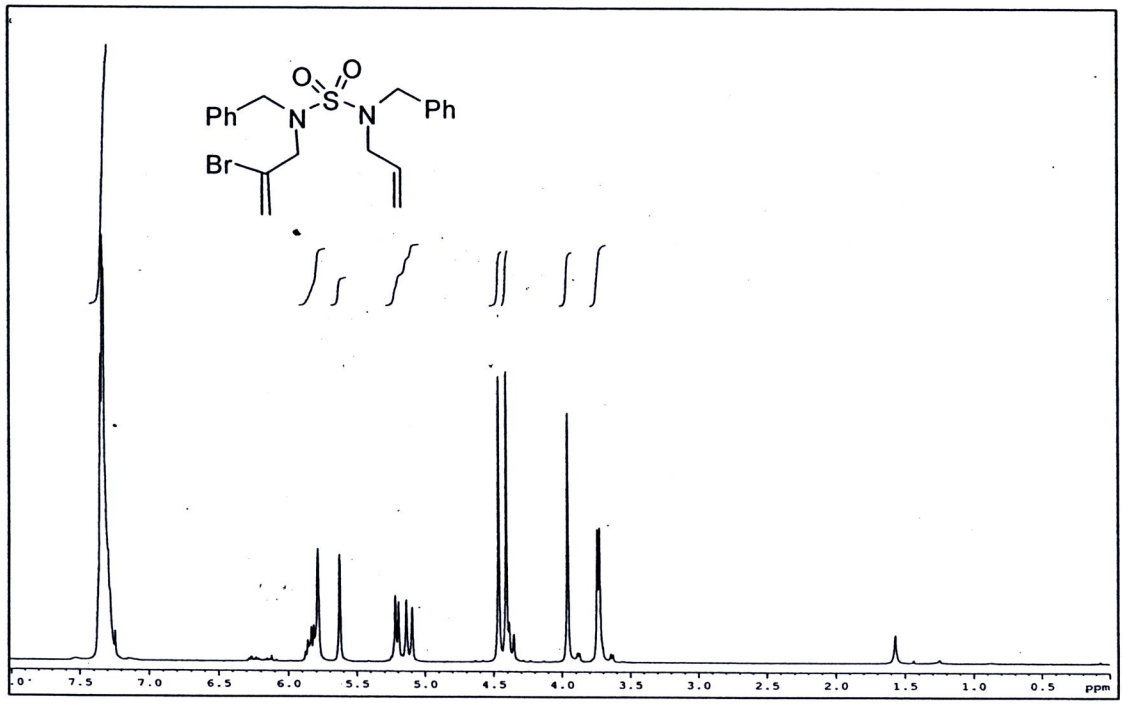


Figure 12 ^{1}H-NMR Spectrum of Compound **136** in $CDCl_3$

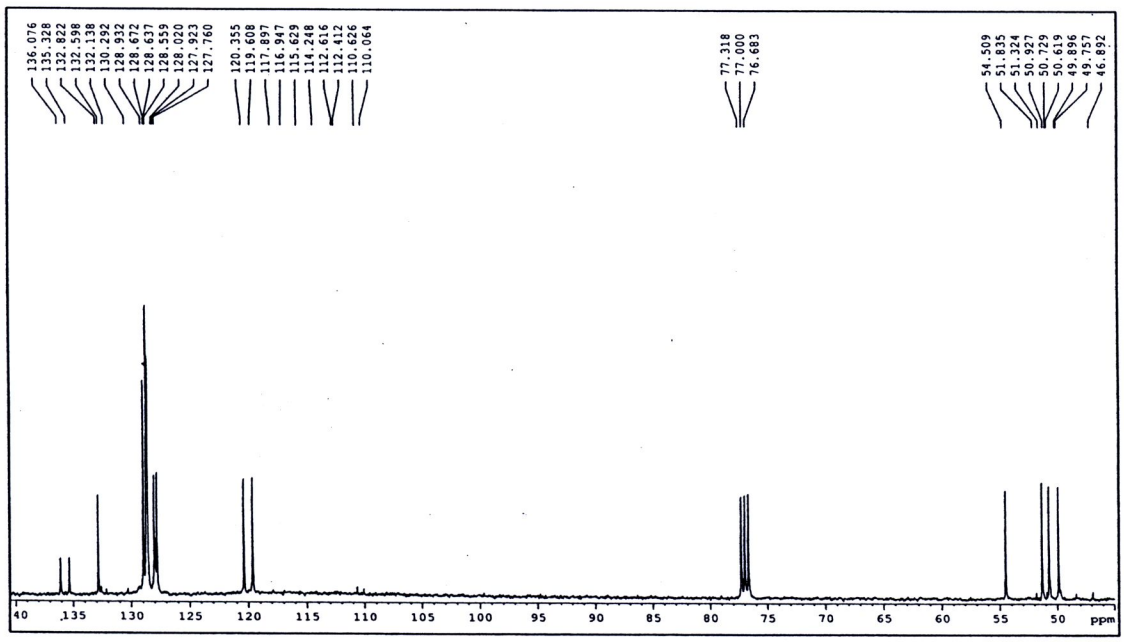


Figure 12a ^{13}C-NMR Spectrum of Compound **136** in $CDCl_3$

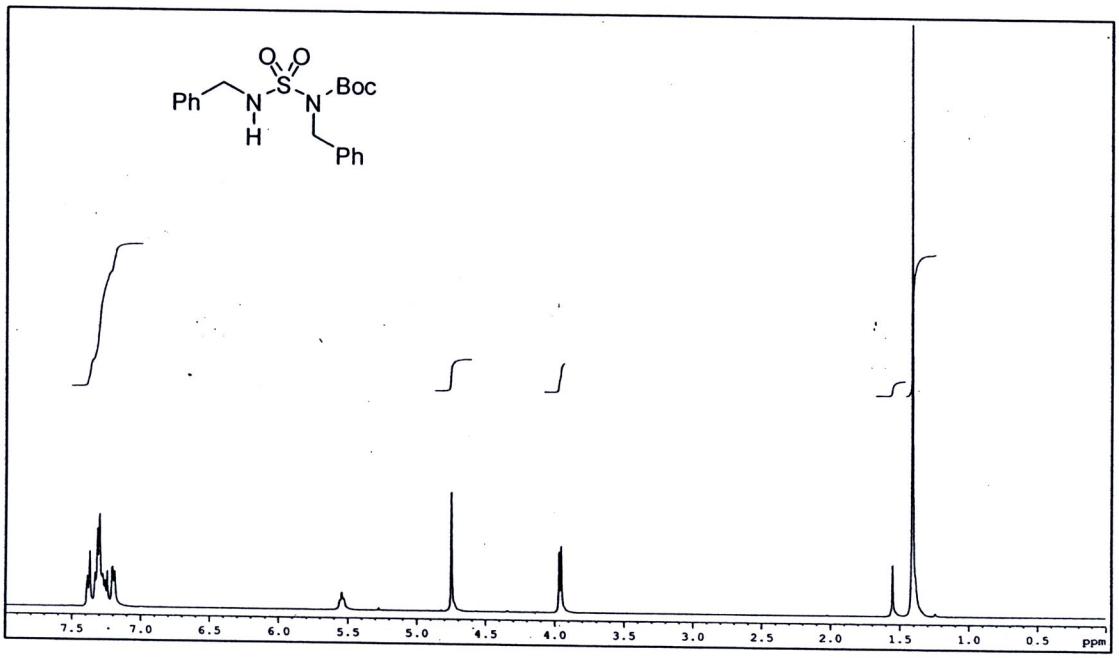


Figure 13 ^{1}H-NMR Spectrum of Compound **137** in $CDCl_3$

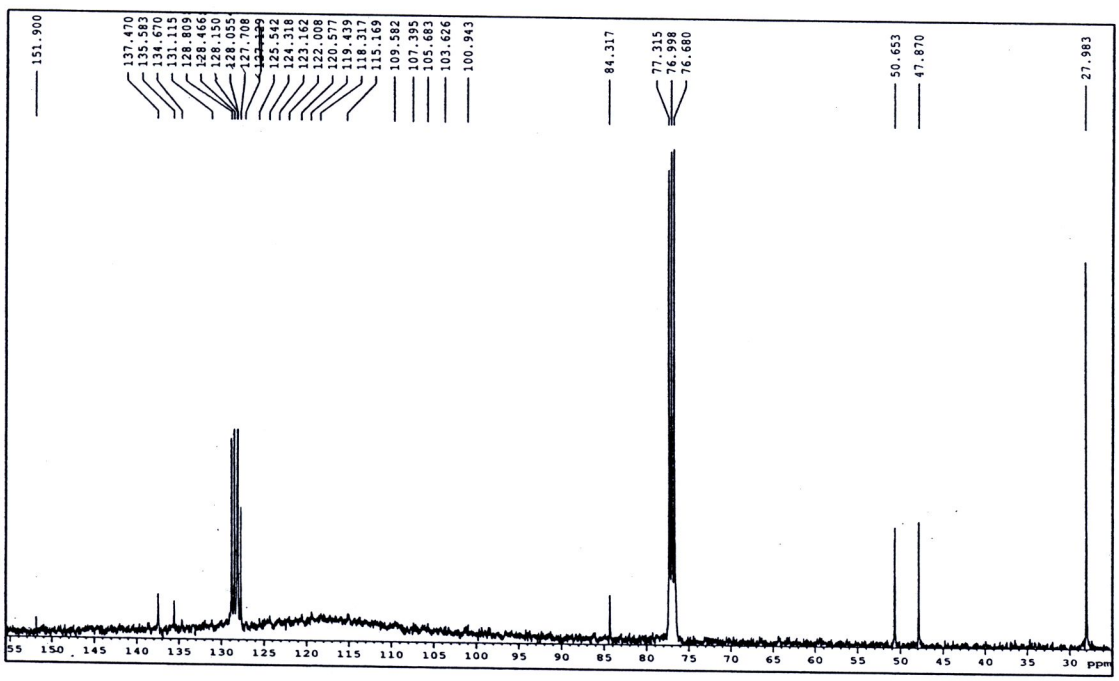


Figure 13a ^{13}C-NMR Spectrum of Compound **137** in $CDCl_3$

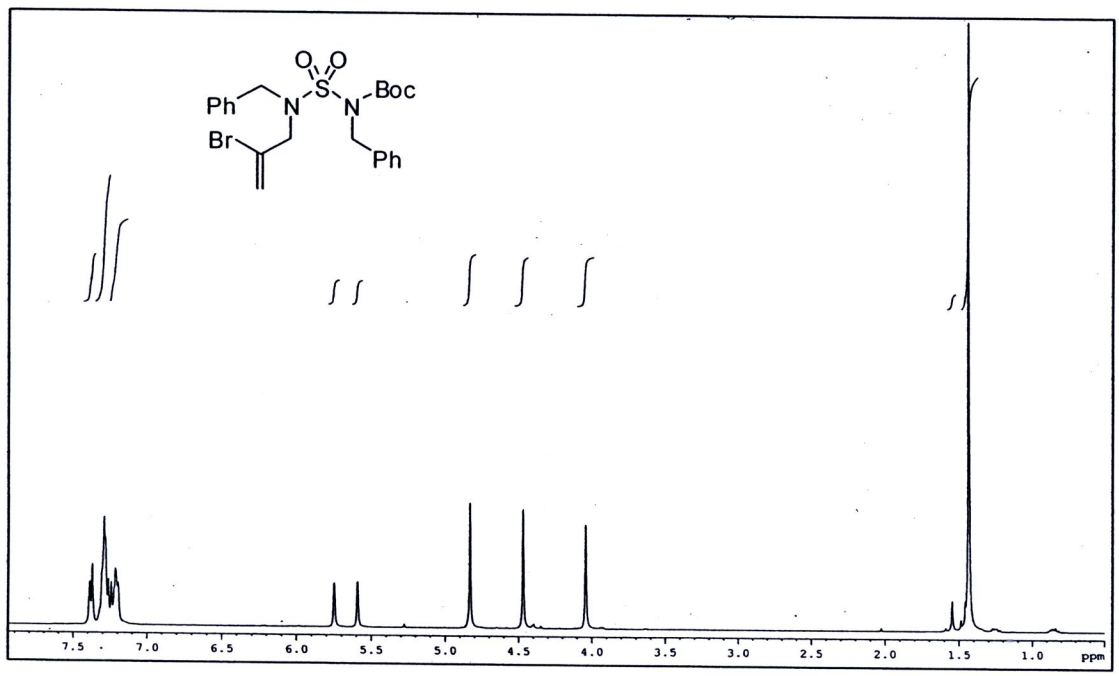


Figure 14 ^{1}H-NMR Spectrum of Compound **138** in $CDCl_3$

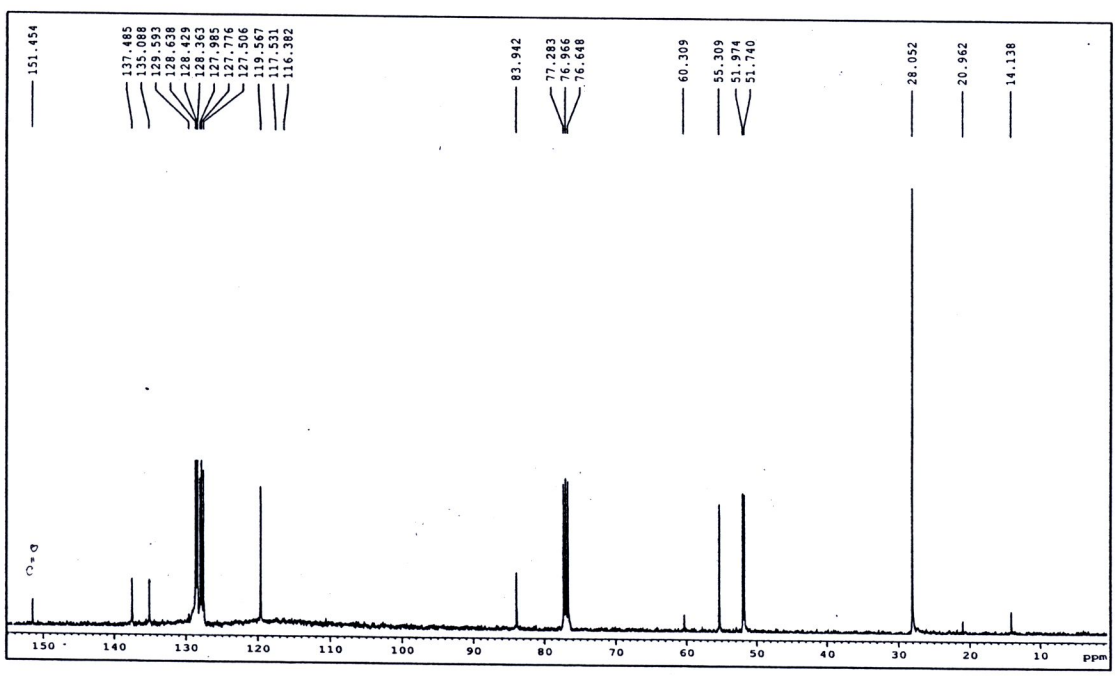


Figure 14a ^{13}C-NMR Spectrum of Compound **138** in $CDCl_3$

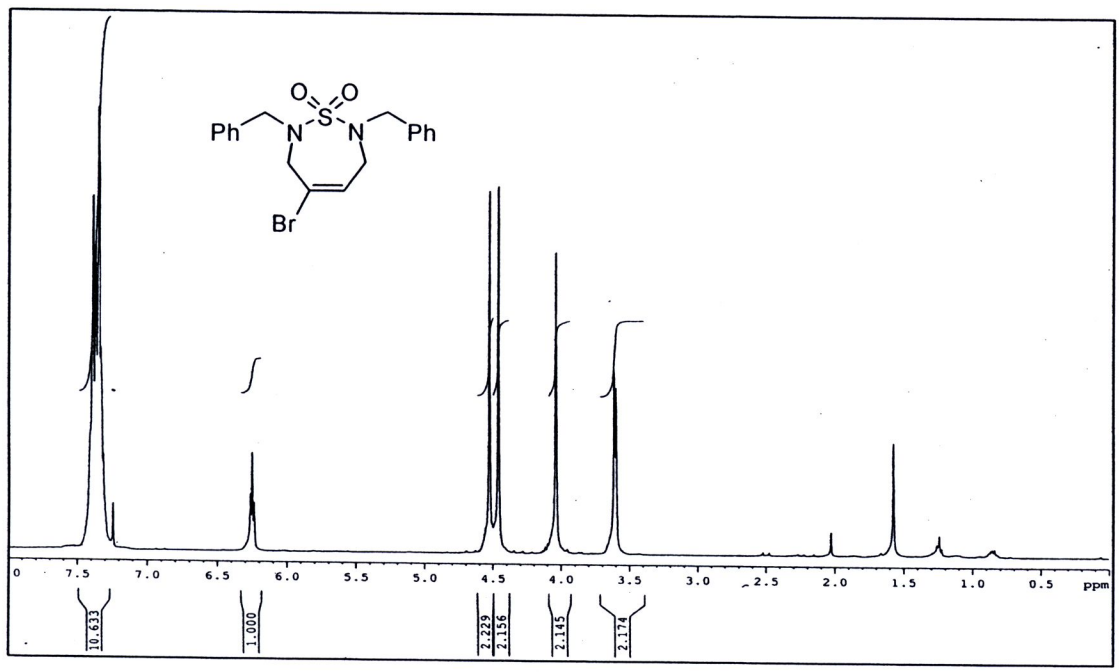


Figure 15 ^{1}H-NMR Spectrum of Compound **140** in $CDCl_3$

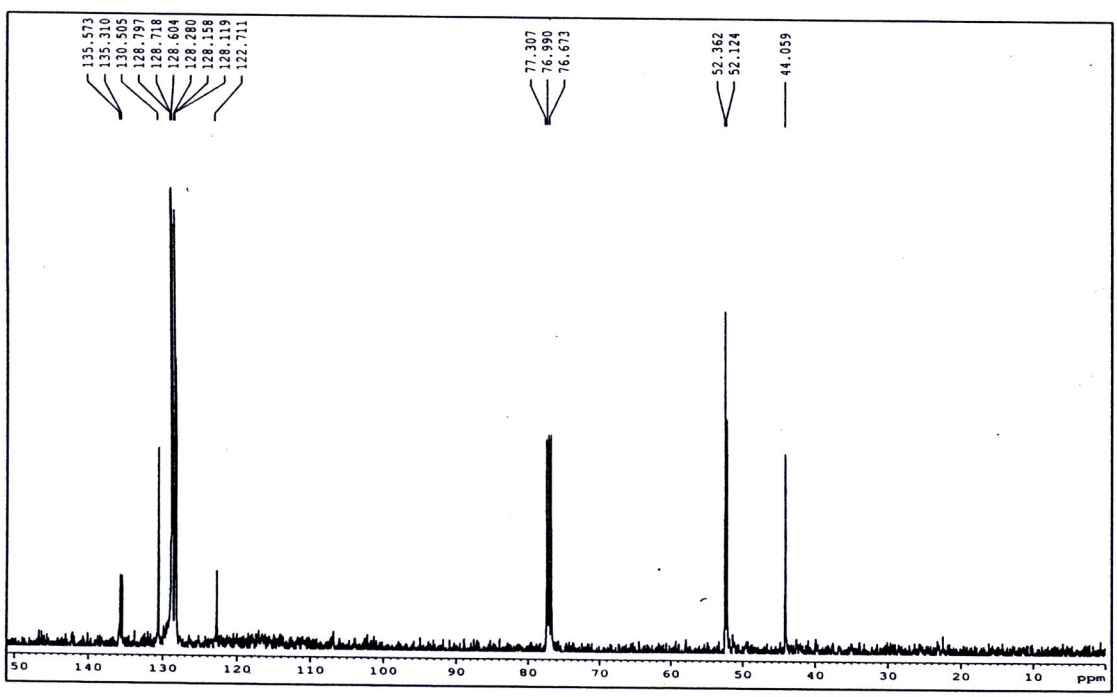


Figure 15a ^{13}C-NMR Spectrum of Compound **140** in $CDCl_3$

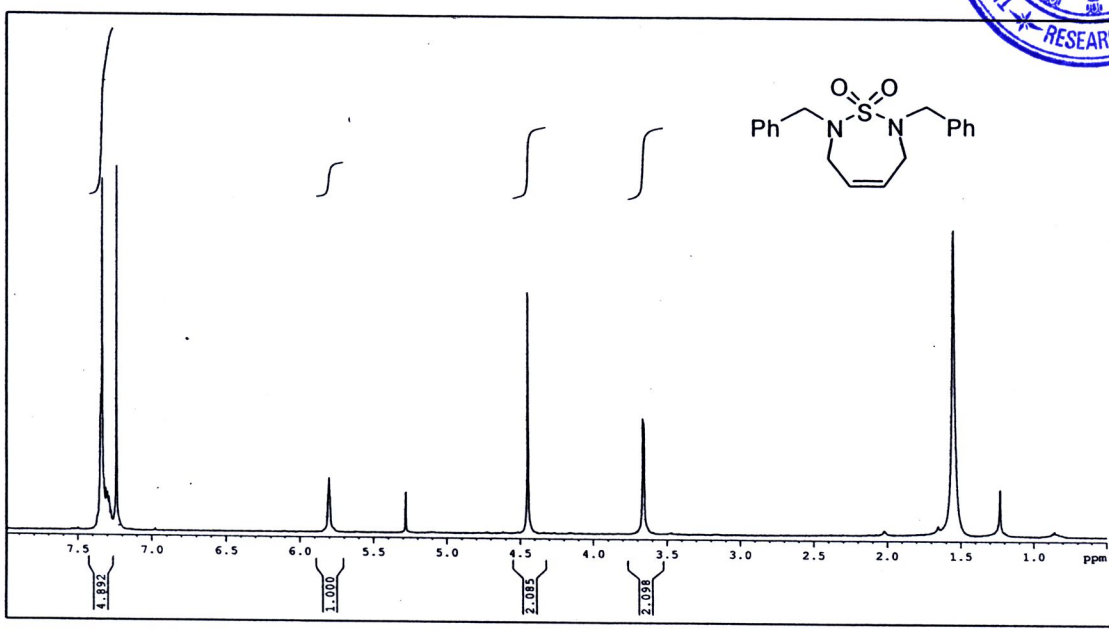


Figure 16 ^{1}H-NMR Spectrum of Compound **141** in $CDCl_3$

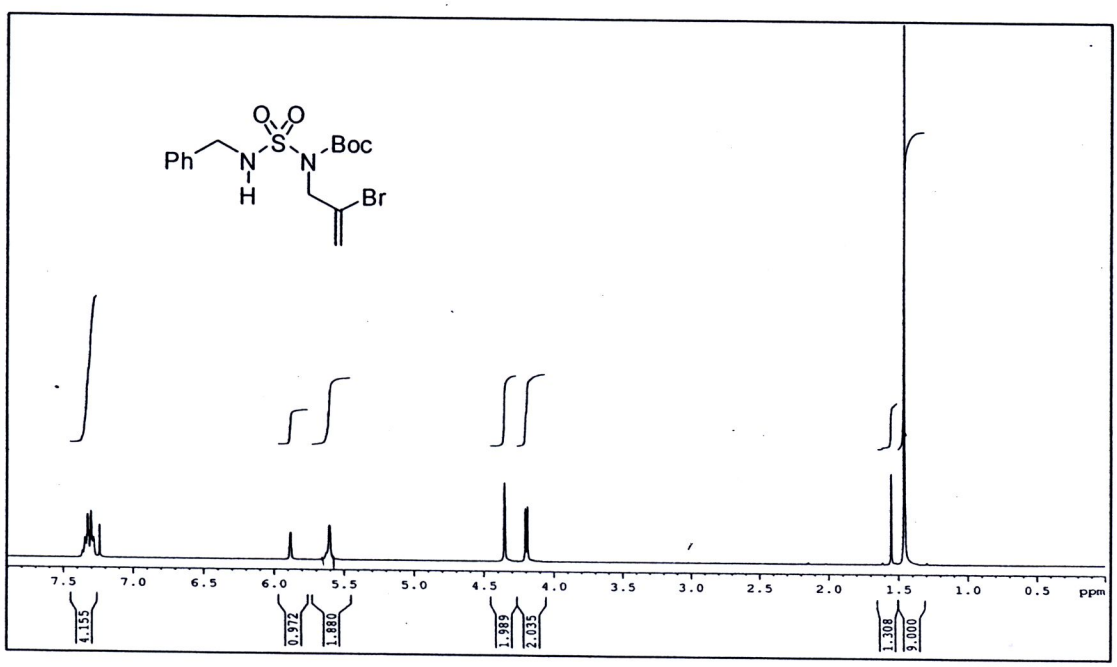


Figure 17 ^{1}H-NMR Spectrum of Compound **142** in $CDCl_3$

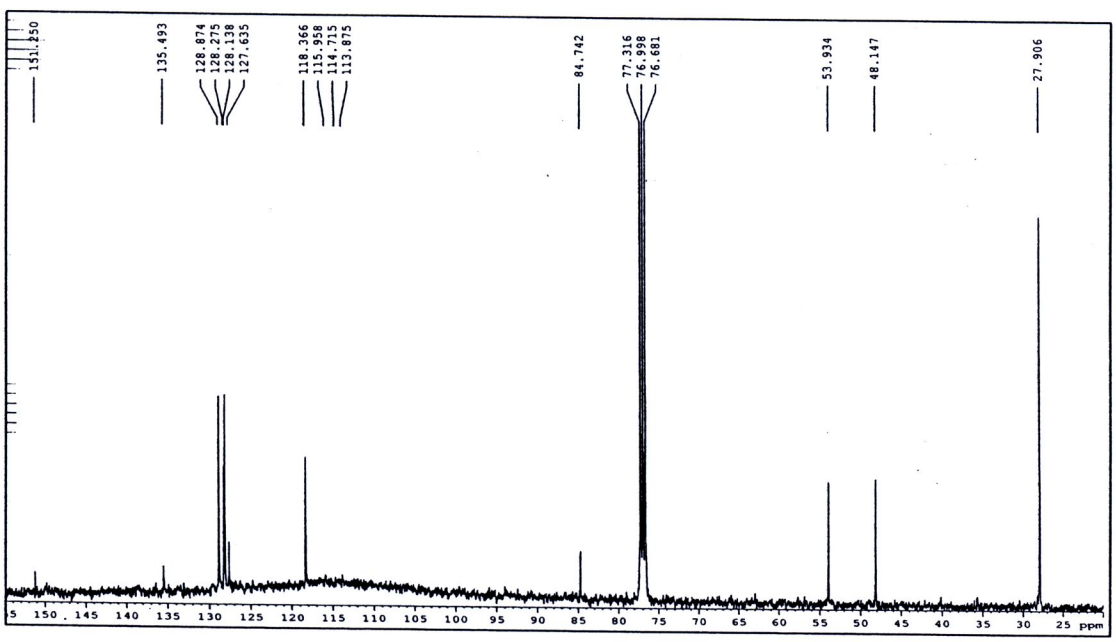


Figure 17a ^{13}C-NMR Spectrum of Compound **142** in $CDCl_3$

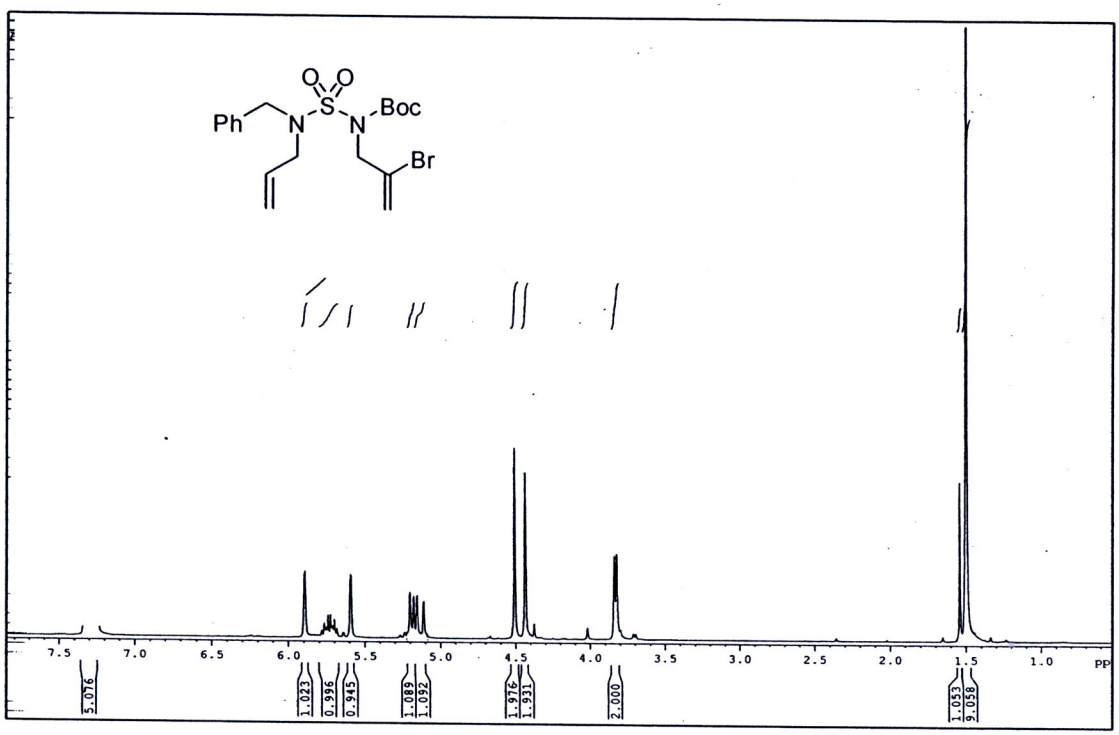


Figure 18 ^{1}H-NMR Spectrum of Compound **143** in $CDCl_3$

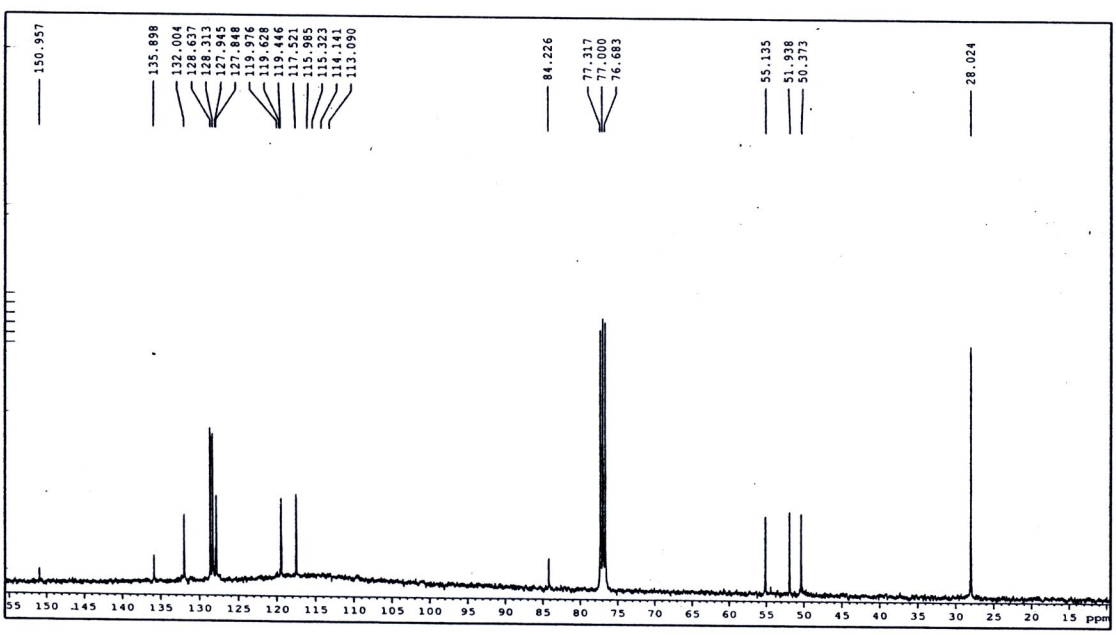


Figure 18a ^{13}C-NMR Spectrum of Compound **143** in $CDCl_3$

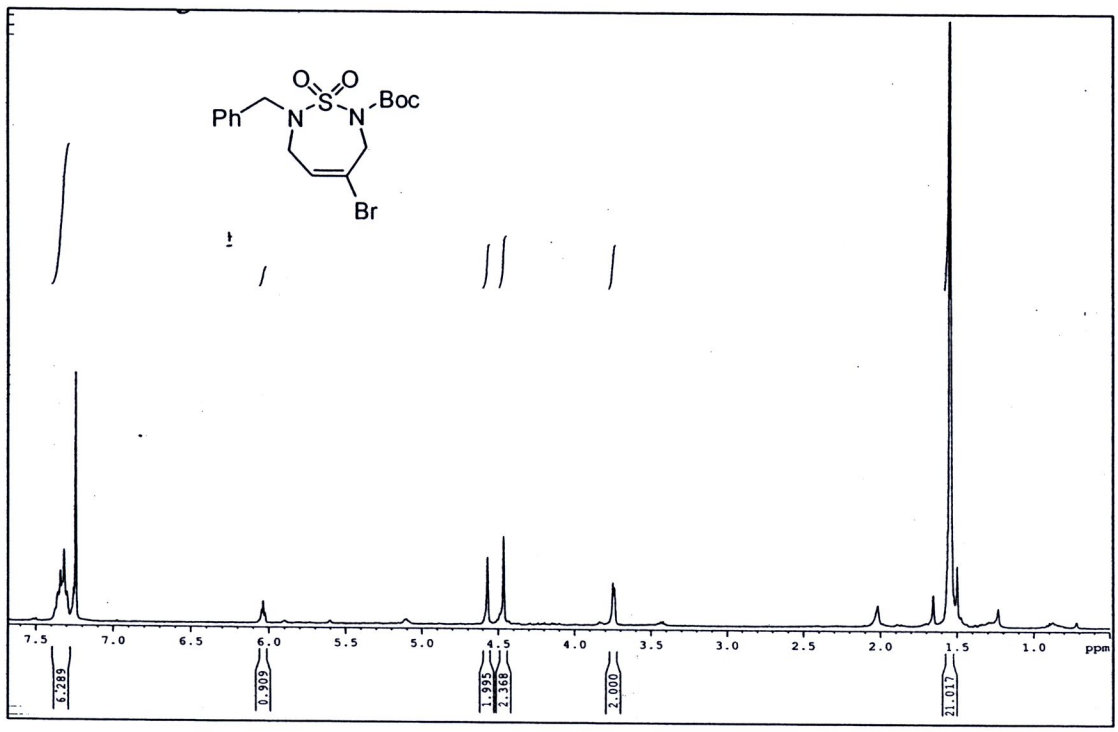


Figure 19 ^{1}H-NMR Spectrum of Compound **144** in $CDCl_3$

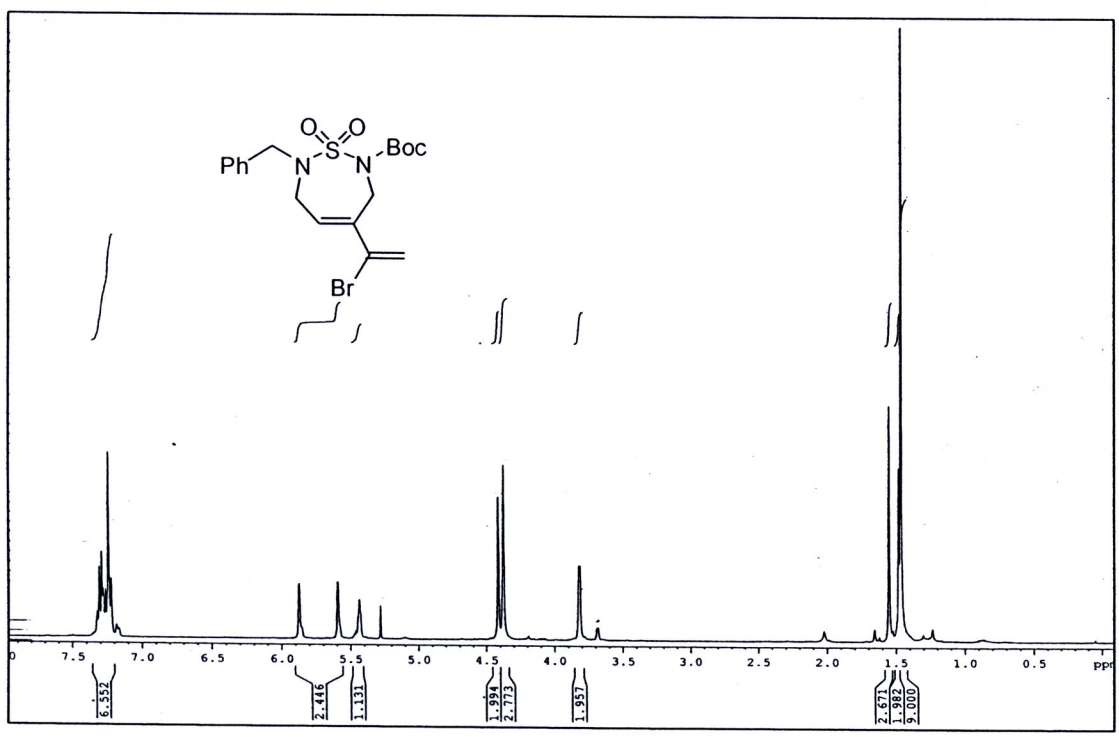


Figure 20 ^{1}H-NMR Spectrum of Compound **145** in $CDCl_3$

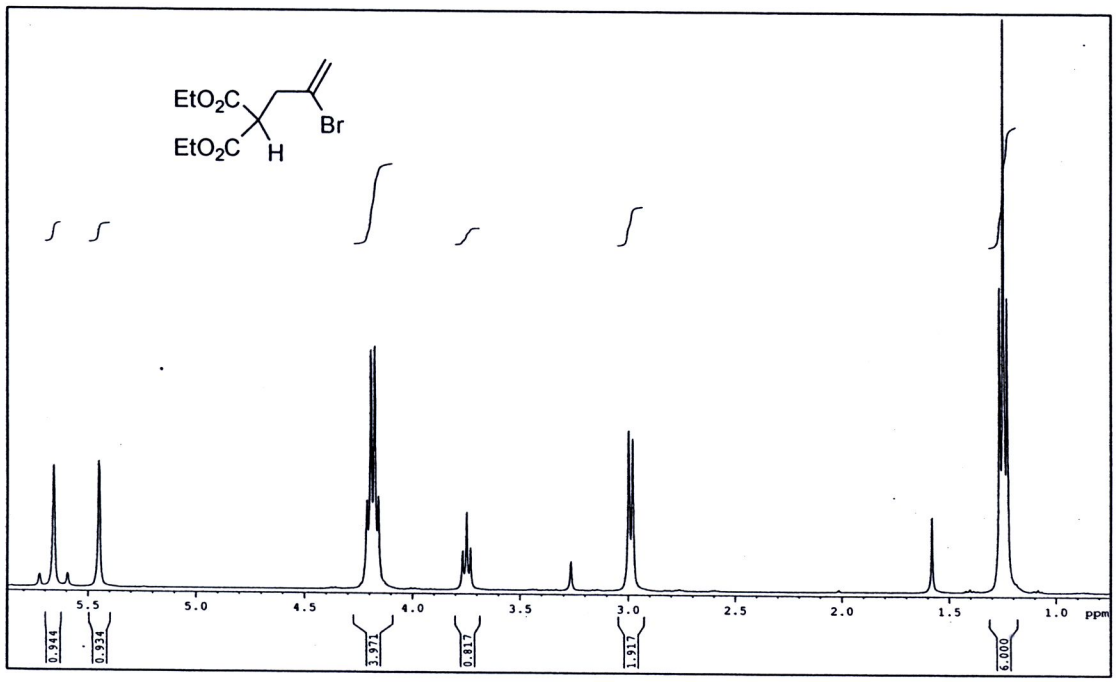


Figure 21 ^{1}H-NMR Spectrum of Compound **147** in $CDCl_3$

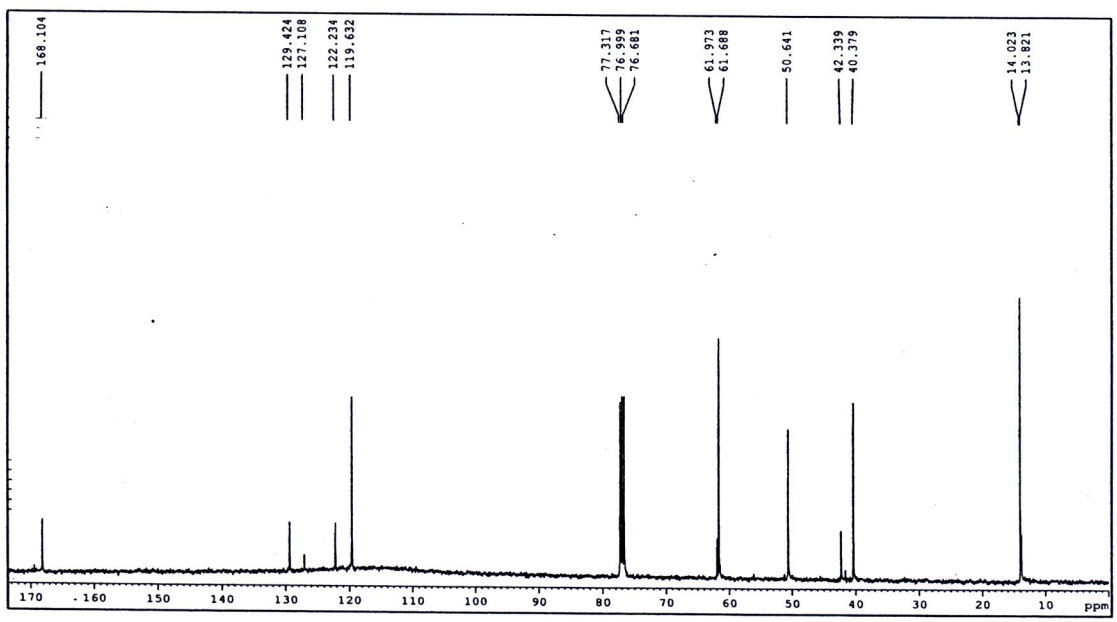


Figure 21a ^{13}C-NMR Spectrum of Compound **147** in $CDCl_3$

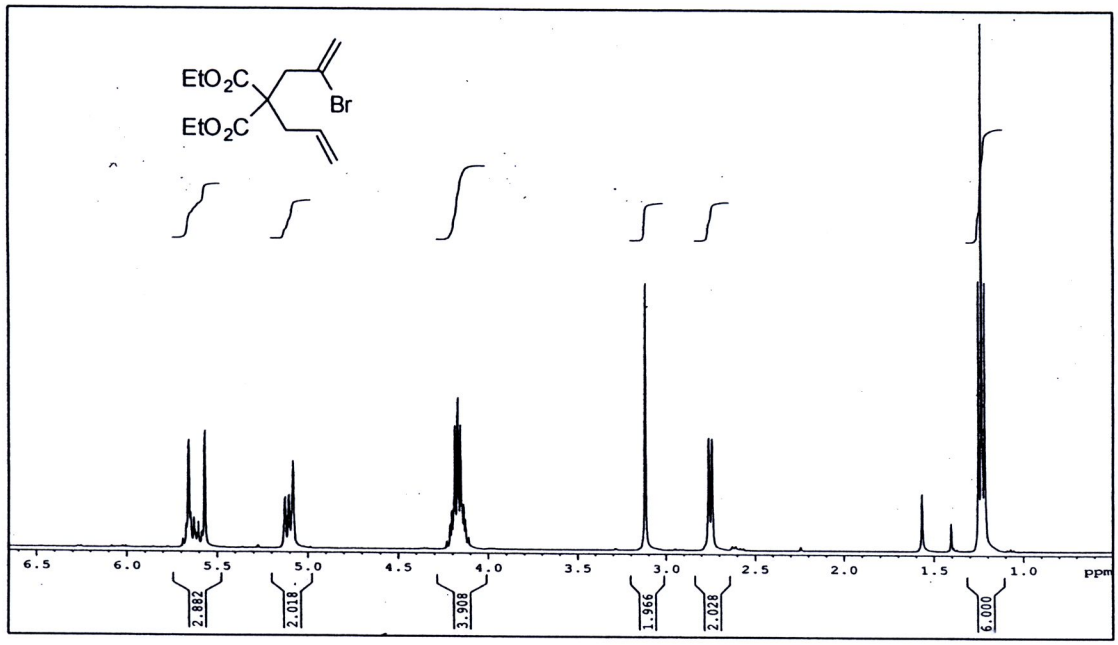


Figure 22 ^{1}H-NMR Spectrum of Compound **113** in $CDCl_3$

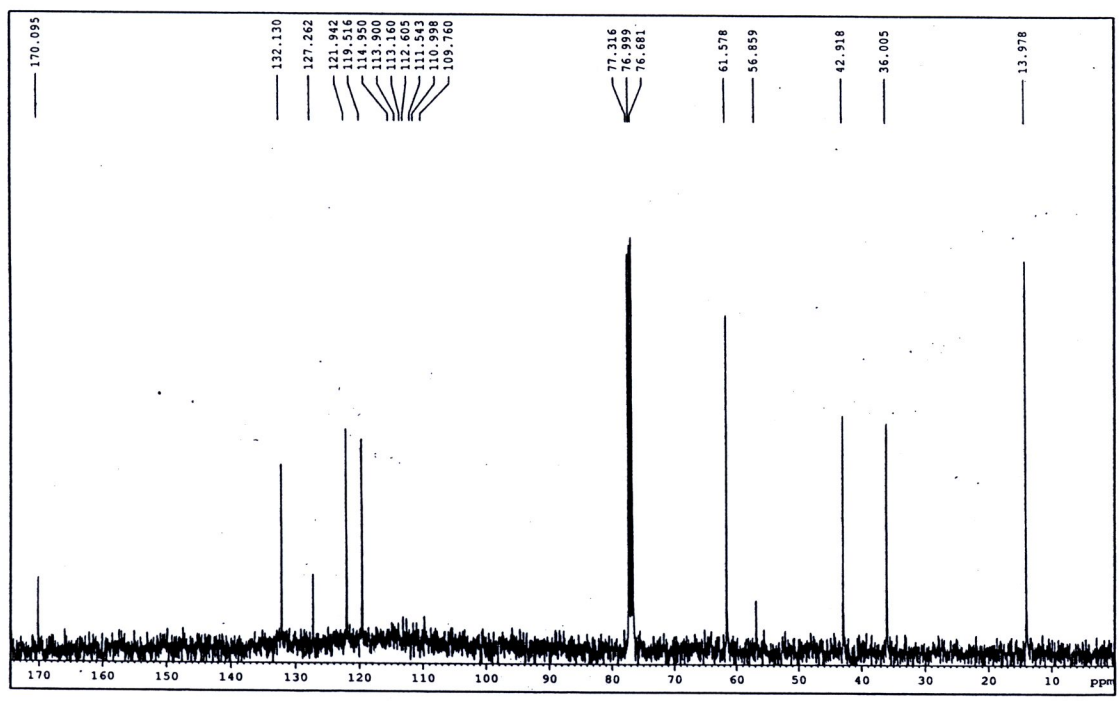


Figure 22a ^{13}C-NMR Spectrum of Compound **113** in $CDCl_3$

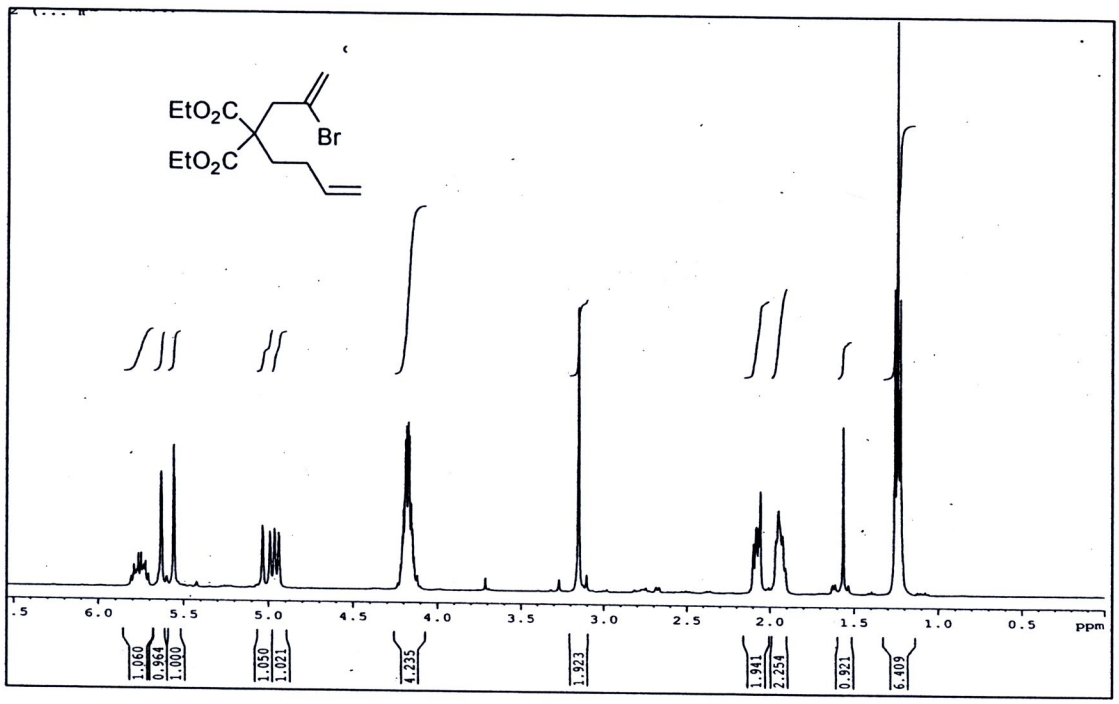


Figure 23 ^{1}H-NMR Spectrum of Compound **115** in $CDCl_3$

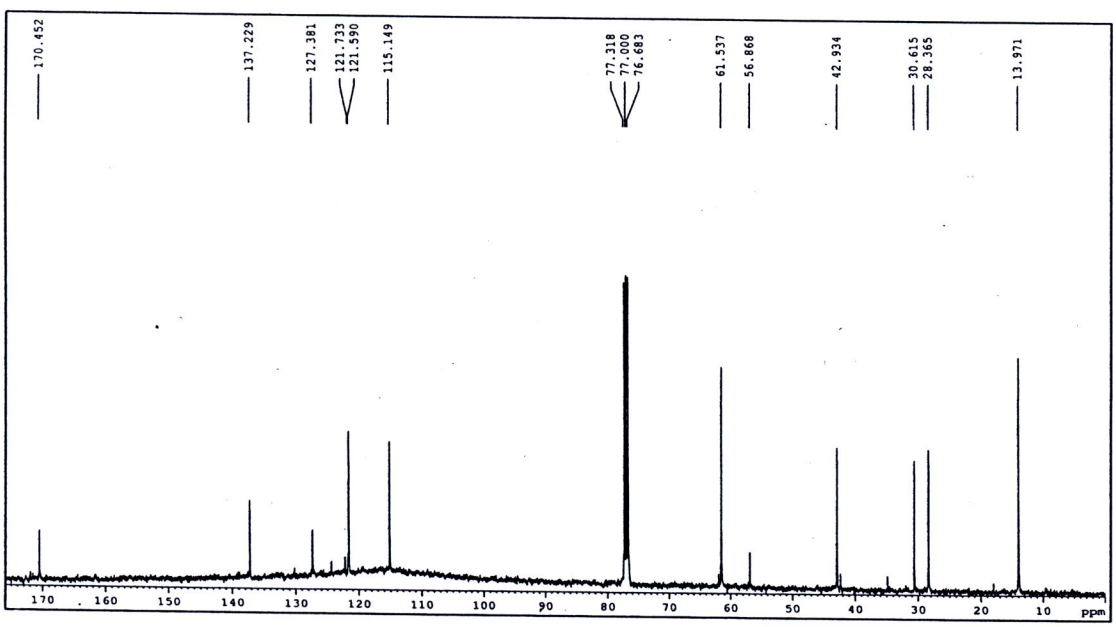


Figure 23a ^{13}C-NMR Spectrum of Compound **115** in $CDCl_3$

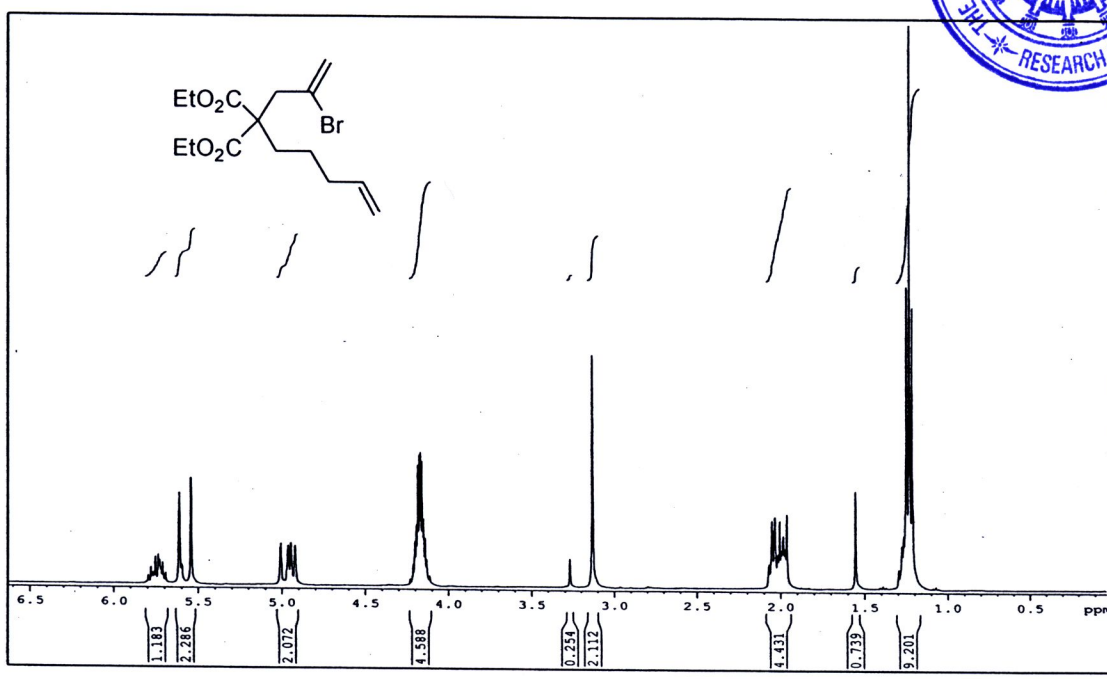


Figure 24 ^{1}H-NMR Spectrum of Compound **148** in $CDCl_3$

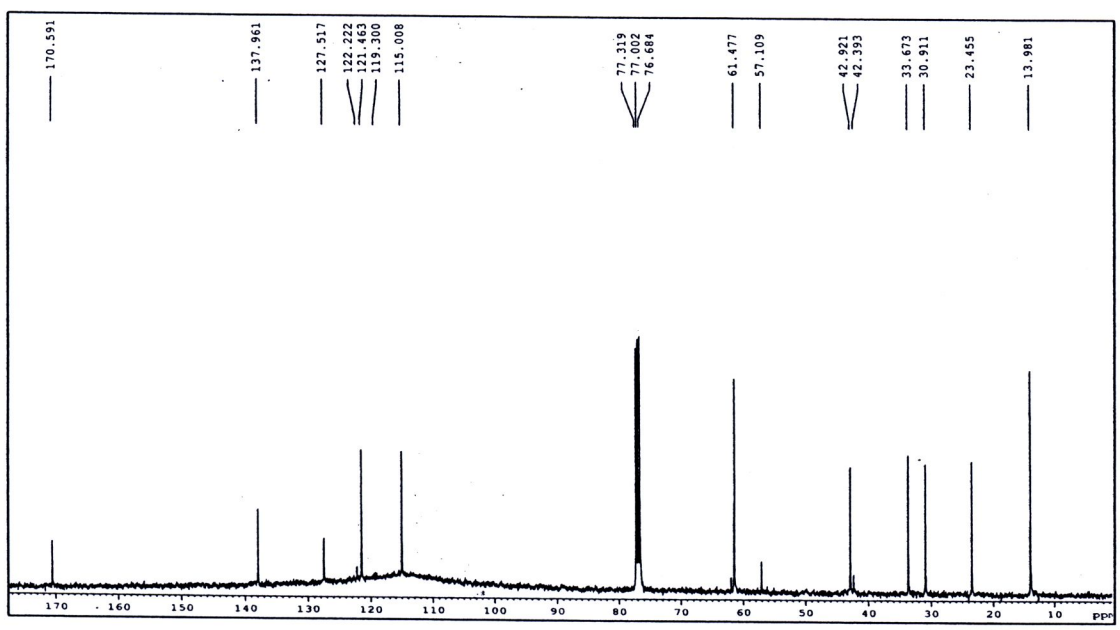


Figure 24a ^{13}C-NMR Spectrum of Compound **148** in $CDCl_3$

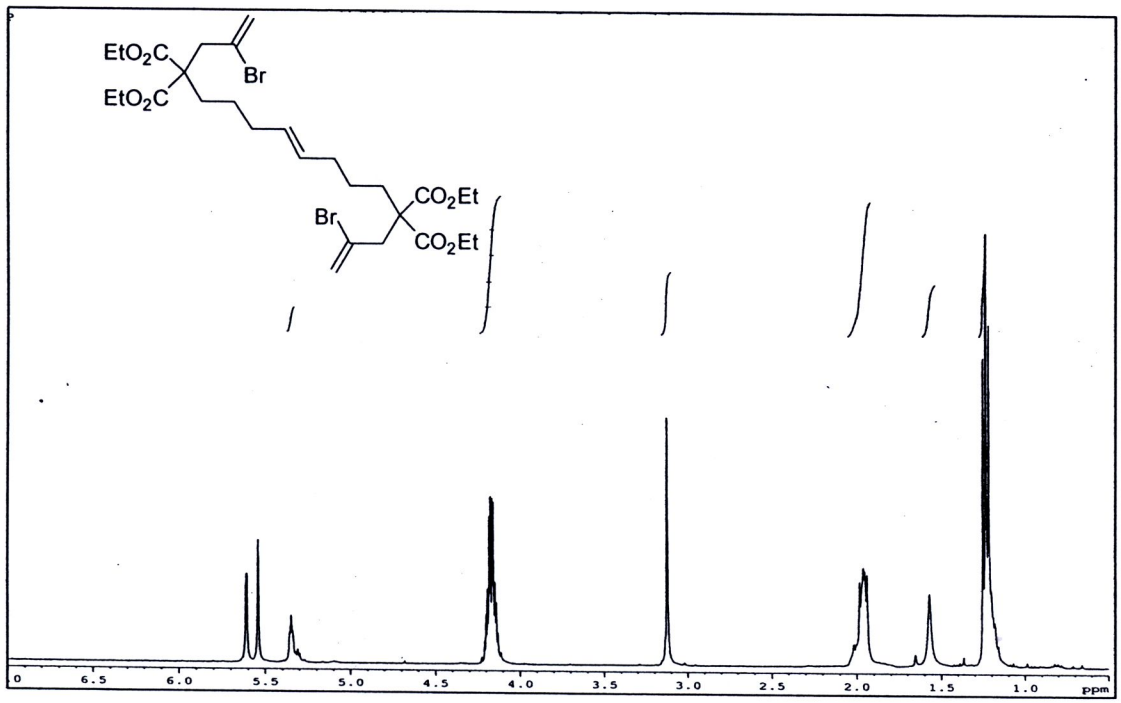


Figure 25 ^{1}H-NMR Spectrum of Compound **149** in $CDCl_3$

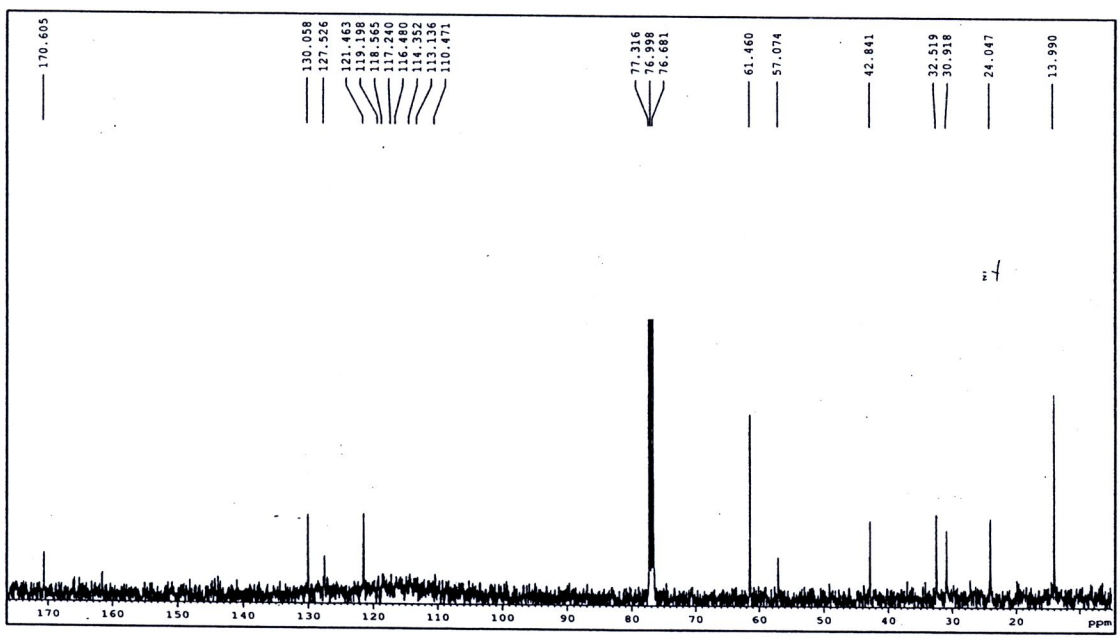


Figure 25a ^{13}C-NMR Spectrum of Compound **149** in $CDCl_3$

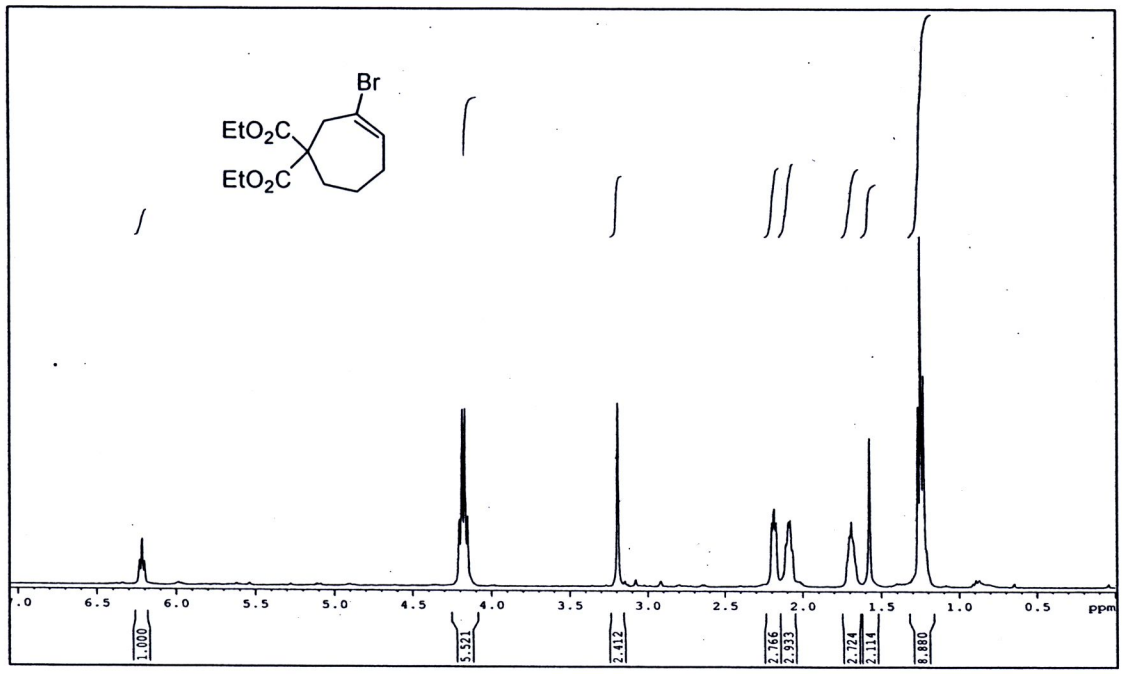


Figure 26 ^{1}H-NMR Spectrum of Compound **150** in $CDCl_3$

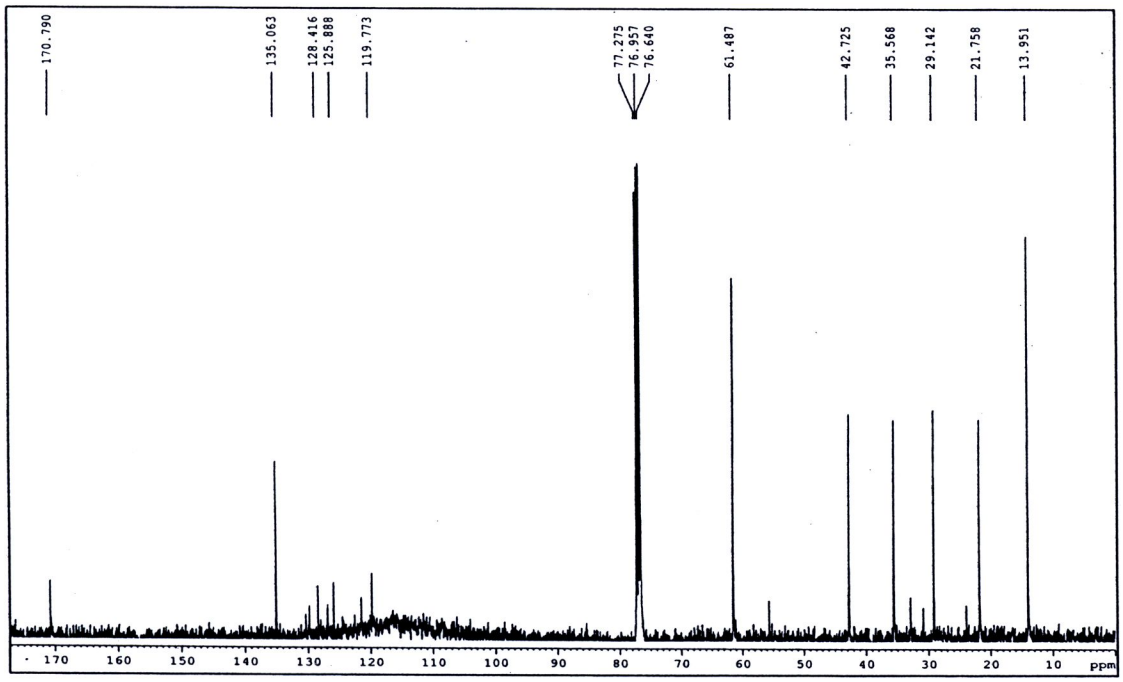


Figure 26a ^{13}C-NMR Spectrum of Compound **150** in $CDCl_3$

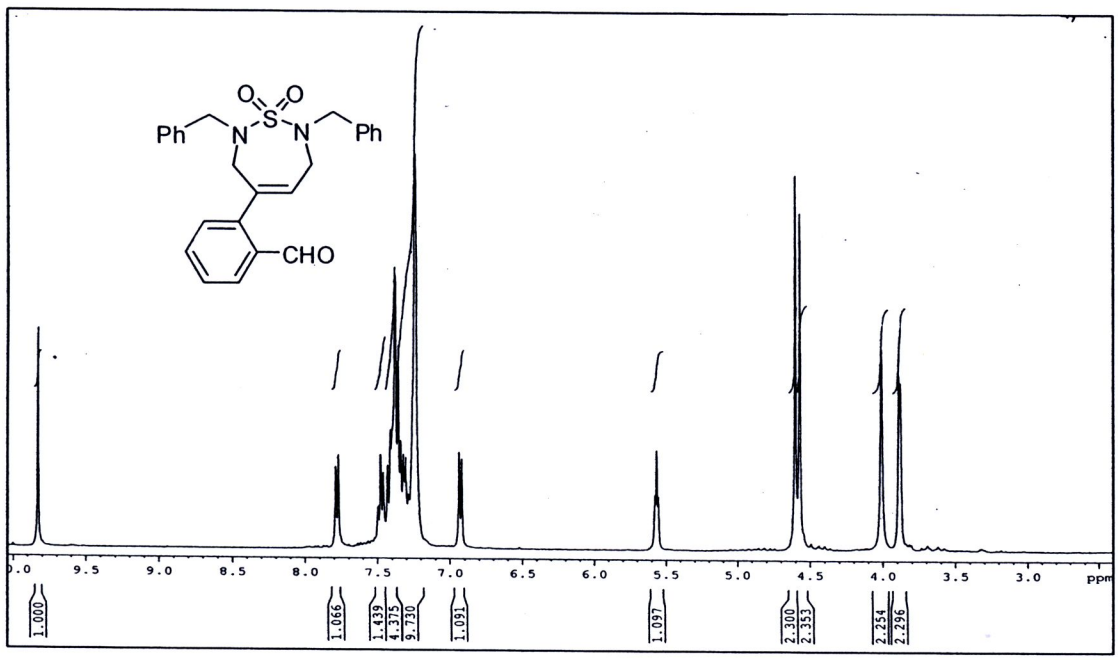


Figure 27 ^{1}H-NMR Spectrum of Compound **151** in $CDCl_3$

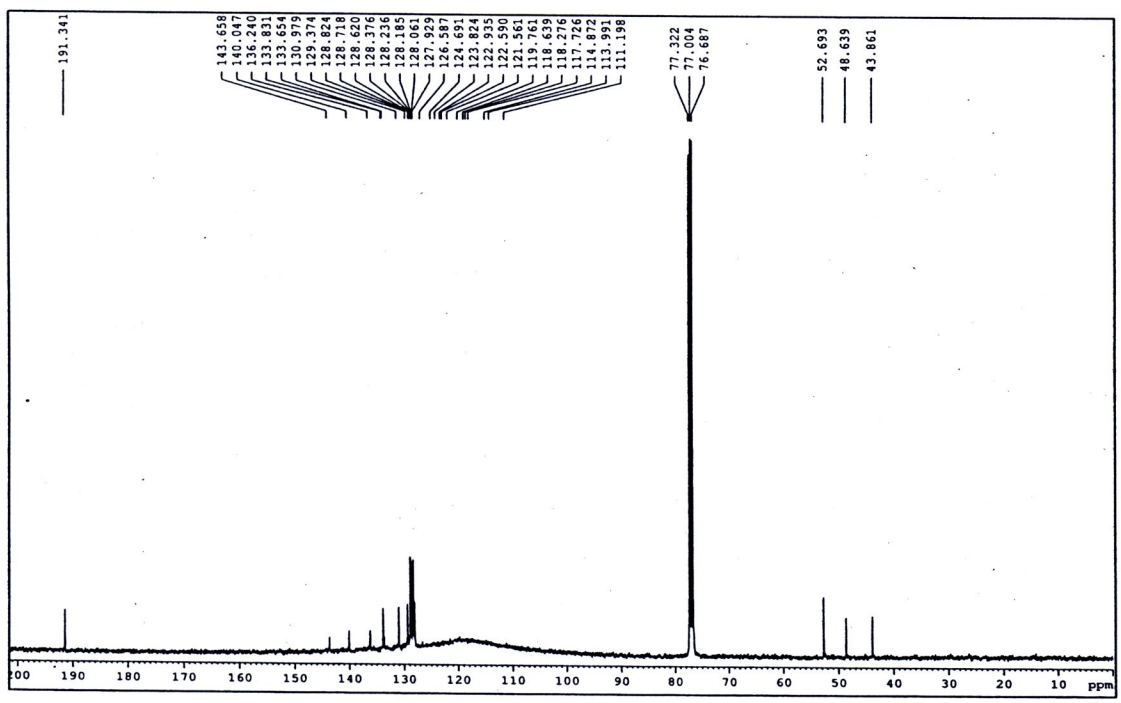


Figure 27a ^{13}C-NMR Spectrum of Compound **151** in $CDCl_3$

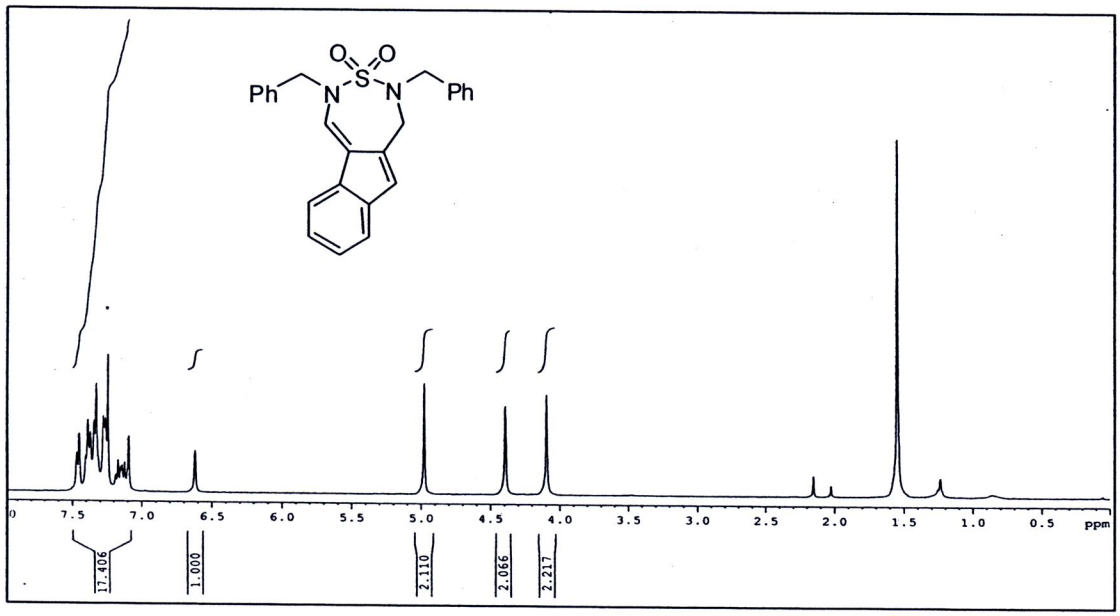


Figure 28 ^{1}H-NMR Spectrum of Compound **152** in $CDCl_3$

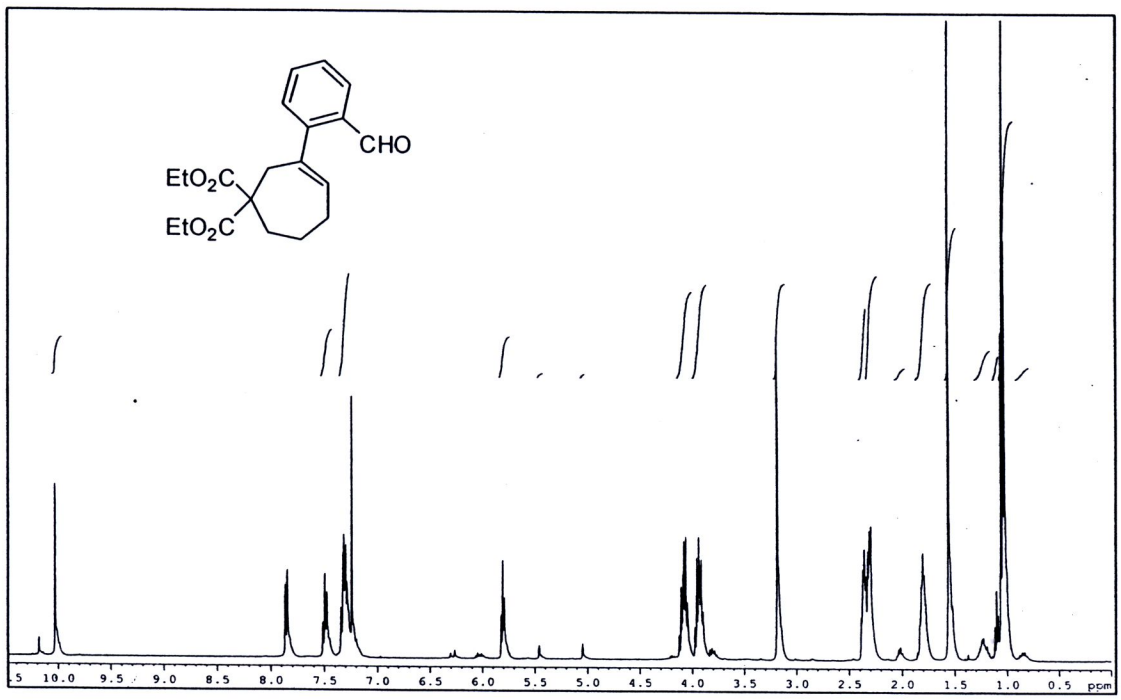


Figure 29 ^{1}H-NMR Spectrum of Compound **153** in $CDCl_3$

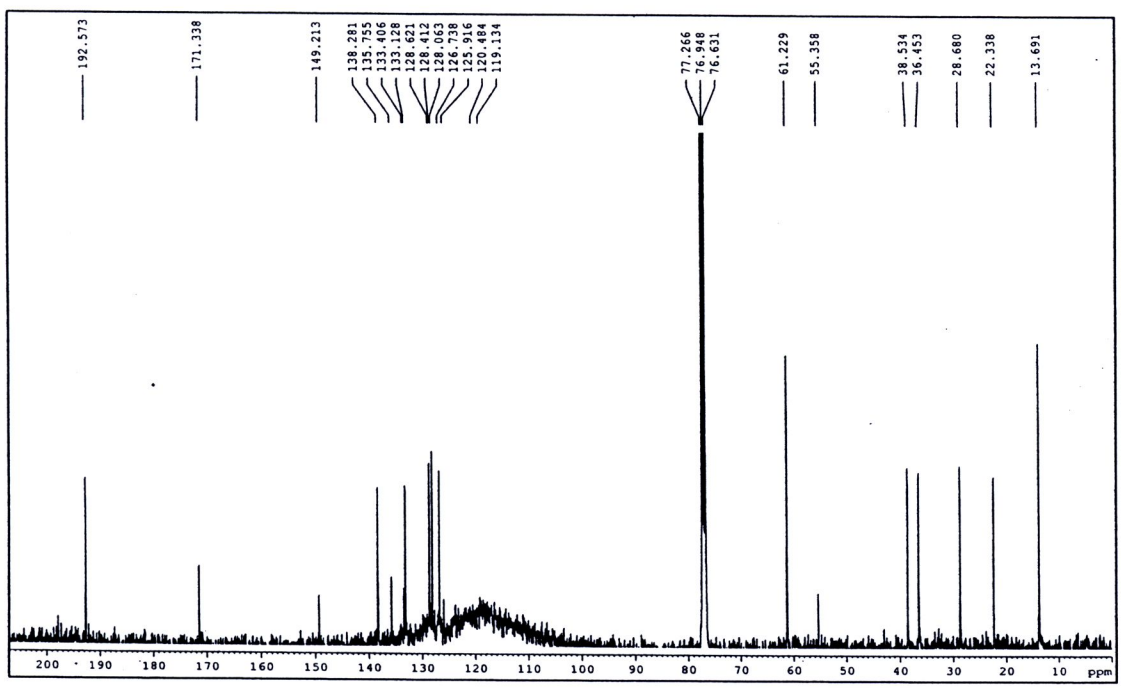


Figure 29a ^{13}C-NMR Spectrum of Compound **153** in $CDCl_3$