

Synthesis of allyl-aziridines from α -Halo Oxime Ethers and Allyl zinc bromides

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Supporting information

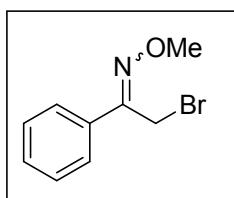
General details.....	1
General procedure for Synthesis of α -halo oxime ethers (1a-1o).....	2
General procedure for Synthesis of Aziridines:.....	4
References:.....	10
^1H and ^{13}C of all compounds	11

General details

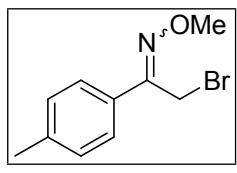
Zinc powder must be activated and all other chemicals were purchased from a commercial source without further purification before use. Solvents were purchased from commercial source, without further purification before use. Petroleum ether (PE) used refers to the 60-90°C boiling point fraction of petroleum. Tetrahydrofuran (THF) was distilled from sodium and benzophenone immediately prior to use. The flash column chromatography was carried out on silica gel (300-400 mesh). ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a 400 MHz spectrometer. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, $\delta = 0.00\text{ppm}$). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal ($\delta = 77.0\text{ppm}$). IR spectra were recorded on F-1000 spectrometer in KBr with absorptions in cm^{-1} . HRMS were obtained with a TOF-Q III instrument.

General procedure for Synthesis of α -halo oxime ethers (1a-1o).¹

The appropriate α -haloketone (10.0mmol) and O-methyl (or Benzyl) hydroxylamine hydrochloride (15.0 mmol) were dissolved in ethanol (30 mL) containing one drop of concentrated sulphuric acid. The mixture was stirred at room temperature for 2-12 h. The reaction progress was monitored by TLC. When the starting material disappeared, the solvent was evaporated in vacuum to near dryness. Ether (50 mL) was added and the solution was washed with 1 M aqueous KHSO₄ (2 × 20 ml), saturated aqueous NaHCO₃ (20 ml) and water (20 ml). The organic phase was dried over Na₂SO₄, filtered and the solvent evaporated in vacuum. The residue was purified by column chromatography (PE/dichloromethane) through deactivated silica gel. Finally, solvents were removed in vacuum affording the corresponding α - halo oxime ethers.

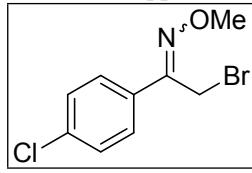


Yield 89 %; colorless liquid; The Z/E ratio was 70:30. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.71 - 7.68 (m, 2H), 7.39 - 7.37 (m, 3H), 4.51 & 4.33 (s, 2H), 4.07 & 4.05 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 152.54, 152.47, 133.36, 133.32, 129.62, 129.60, 128.59, 128.27, 126.06, 125.95, 62.72, 62.65, 32.46, 17.94 ppm



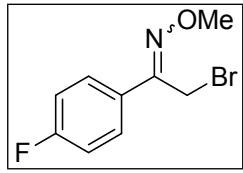
(Z/E)-2-bromo-1-(p-tolyl) ethanone O-methyl oxime (1b)

Yield 83 %; colorless liquid; The Z/E ratio was 38:62. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.59 - 7.57 (d, 2H, J = 8 Hz), 7.19 - 7.17 (d, 2H, J = 8 Hz), 4.50 & 4.31 (s, 2H), 4.06 & 4.04 (s, 3H), 2.35(s, 3 H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 152.48, 152.41, 139.72, 139.69, 130.45, 130.42, 129.28, 129.26, 125.93, 125.82, 62.60, 62.52, 32.42, 21.24, 17.97ppm



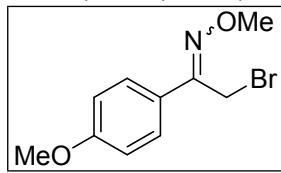
(Z/E)-2-bromo-1-(4-chlorophenyl)ethanone O-methyl oxime (1c)

Yield 80 %; white solid; The Z/E ratio was 29:71. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.64 - 7.61 (m, 2H), 7.37 - 7.34 (m, 2H), 4.49 & 4.30 (s, 2H), 4.07 & 4.06 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 151.46, 151.39, 135.62, 135.60, 131.77, 131.73, 128.79, 128.77, 127.34, 127.22ppm



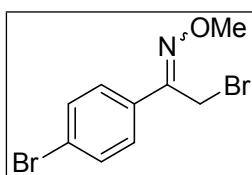
(Z/E)-2-bromo-1-(4-fluorophenyl)ethanone O-methyl oxime (1d)

Yield 77 %; white solid; The Z/E ratio was 24:76. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.71 - 7.67 (m, 2H), 7.11 - 7.05 (m, 2H), 4.51 & 4.32 (s, 2H), 4.07 & 4.06 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 164.78, 164.76, 162.30, 162.27, 151.49, 151.41, 129.48, 129.44, 129.40, 128.01, 127.93, 127.89, 127.81, 115.68, 115.66, 115.46, 115.44, 62.69, 62.61, 32.28, 17.72ppm



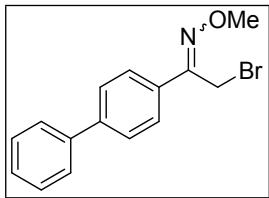
(Z/E)-2-bromo-1-(4-methoxyphenyl)ethanone O-methyl oxime (1e)

Yield 82 %; white solid; The Z/E ratio was 60:40. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.64 - 7.61(m, 2H), 6.90 - 6.86 (m, 2H), 4.48 & 4.30 (s, 2H), 4.04 & 4.02 (s, 3H), 3.78(s,3H)ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 160.68, 160.65, 152.05, 151.96, 127.39, 127.27, 125.67, 125.65, 113.90, 113.88, 62.45, 62.38, 55.14, 32.32, 17.91ppm



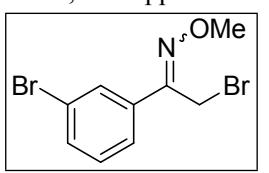
(Z/E)-2-bromo-1-(4-bromophenyl)ethanone O-methyl oxime (1f)

Yield 88 %; white solid; The Z/E ratio was 46:54. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.57 - 7.55 (m, 2H), 7.51 - 7.49 (m, 2H), 4.48 & 4.29 (s, 2H), 4.07 & 4.05 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 151.50, 151.43, 132.19, 132.15, 131.72, 131.70, 127.56, 127.44, 123.93, 123.92, 62.87, 62.79, 32.08, 17.47 ppm



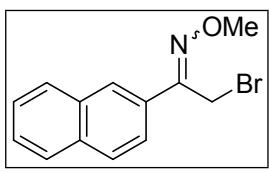
(Z/E)-1-((1,1'-biphenyl)-4-yl)-2-bromoethanone O-methyl oxime (1g)

Yield 71 %; white solid; The Z/E ratio was 35:65. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.76 - 7.74 (d, 2H, J = 8 Hz), 7.57 (t, 4H, J = 8 Hz), 7.40 (t, 2H, J = 8 Hz), 7.32 (t, 1H, J = 8 Hz), 4.51 & 4.32 (s, 2H), 4.06 & 4.05 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 152.14, 152.07, 142.25, 142.23, 140.13, 132.11, 132.09, 128.77, 127.60, 127.16, 126.93, 126.43, 126.31, 62.73, 62.65, 32.28, 17.79 ppm



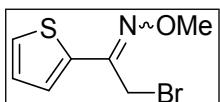
(Z/E)-2-bromo-1-(3-bromophenyl)ethanone O-methyl oxime (1h)

Yield 80 %; colorless liquid; The Z/E ratio was 46:54. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.87 - 7.86 (m, 1H), 7.59 - 7.57 (m, 1H), 7.50 - 7.47 (m, 1H), 7.22 (t, 1H, J = 8 Hz), 4.46 & 4.27 (s, 2H), 4.07 & 4.05 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 151.06, 150.99, 135.25, 135.21, 132.42, 132.40, 129.99, 129.97, 128.91, 128.81, 124.56, 124.43, 122.71, 122.69, 62.90, 62.82, 32.06, 17.44 ppm



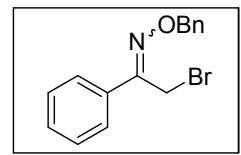
(Z/E)-2-bromo-1-(naphthalen-2-yl)ethanone O-methyl oxime (1i)

Yield 85 %; white solid; The Z/E ratio was 62:38. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.07 (s, 1H), 7.92 - 7.85 (m, 2H), 7.82 - 7.80 (m, 2H), 7.50 - 7.46 (m, 2H), 4.62 & 4.44 (s, 2H), 4.12 & 4.11 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 152.33, 152.25, 133.71, 133.69, 132.93, 130.52, 128.46, 128.25, 128.23, 127.54, 126.78, 126.36, 125.84, 125.67, 123.09, 123.04, 62.78, 62.70, 32.18, 17.68 ppm.



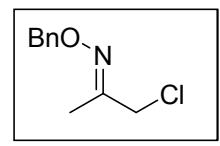
(Z/E)-2-bromo-1-(thiophen-2-yl)ethanone O-methyl oxime (1k)

Yield 53 %; white solid; The Z/E ratio was 68:32. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.32 - 7.29 (m, 2H), 7.05 - 7.02 (m, 1H), 4.48 & 4.31 (s, 2H), 4.04 & 4.03 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 149.03, 148.86, 136.95, 136.92, 127.41, 127.39, 127.19, 127.17, 126.75, 126.50, 62.81, 62.74, 32.43, 17.59 ppm.



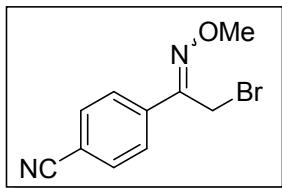
(Z/E)-2-bromo-1-phenylethanone O-benzyl oxime (1l)

Yield 88 %; colorless liquid; The Z/E ratio was 44:56. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.71 - 7.67 (m, 2H), 7.44 - 7.28 (m, 8H), 5.32 & 5.31 (s, 2H), 4.55 & 4.37 (s, 2H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 152.91, 152.85, 137.38, 137.33, 133.44, 133.37, 129.66, 129.64, 128.58, 128.56, 128.39, 128.38, 128.12, 128.07, 127.95, 127.93, 126.15, 126.03, 76.97, 76.91, 32.69, 18.19 ppm.



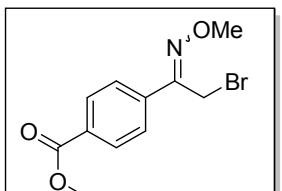
(Z/E)-1-chloropropan-2-one O-benzyl oxime (1m).

Yield 85 %; colorless liquid; The Z/E ratio was 93:7. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.36 - 7.26 (m, 5H), 5.10 & 5.09 (s, 2H), 4.22 & 4.03 (s, 2H), 1.99 & 1.97 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 153.38, 137.50, 128.31, 127.96, 127.92, 127.80, 75.99, 75.92, 45.93, 36.90, 18.13, 12.51 ppm.



(Z/E)- 4-(2-bromo-1-(methoxyimino)ethyl)benzonitrile (1n)

Yield 83 %; white solid; The Z/E ratio was 48:52. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.85 - 7.82 (m, 2H), 7.70 - 7.67 (m, 2H), 4.53 & 4.34 (s, 2H), 4.13 & 4.11 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 150.90, 150.85, 137.56, 137.52, 132.32, 132.30, 126.61, 126.48, 118.42, 113.02, 113.00, 63.28, 63.20, 31.83, 17.06 ppm

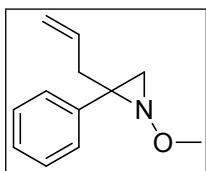


(Z/E)- methyl 4-(2-bromo-1-(methoxyimino)ethyl)benzoate (1o)

Yield 86 %; white solid; The Z/E ratio was 25:75. ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.08 – 8.04 (m, 2H), 7.80 - 7.77 (m, 2H), 4.54 & 4.36 (s, 2H), 4.12 & 4.10 (s, 3H), 3.93 (s, 3H) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 166.53, 151.73, 151.67, , 137.54, 137.50, 130.93, 130.90, 129.82, 129.79, 126.02, 125.90, 63.08, 63.00, 52.22, 32.18, 17.52 ppm.

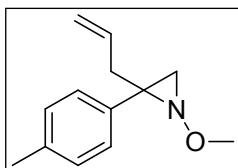
General procedure for Synthesis of Aziridines:

Allyl bromide (1 mmol) and Zinc powder (1.2 mmol, 78.5mg) were suspended in dry THF (4 mL) under a N₂ atmosphere at RT. The mixture was stirred for about 15-30 min, and the zinc powder disappeared. Stirring was continued for one hour to complete the synthesis of the organozinc reagent; Stirring was stopped, allowed to stand for 5 minutes. The supernatant was transferred to a dry flask containing 1(0.5mmol), the mixture was stirred under a N₂ atmosphere at RT for 14h and then was quenched with 10mL H₂O .The resulting mixture was extracted with Et₂O(3×15 mL) The organic phase was dried over Na₂SO₄, filtered and the solvent evaporated in vacuum. The residue was purified by column chromatography (PE/EA) through deactivated silica gel. Finally, solvents were removed in vacuum affording the corresponding aziridines.



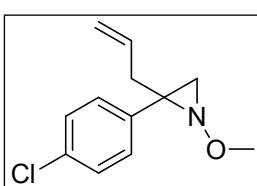
2-allyl-1-methoxy-2-phenylaziridine (3a)

colorless liquid; 80mg (85%); IR (KBr): 3062, 3028, 2982, 2939, 2894, 2808, 1640,1603, 1495, 1447, 996, 916, 760,698cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.32 - 7.27 (m, 4H), 7.23 - 7.21 (m, 1H), 5.83 - 5.73 (m, 1H), 5.04 - 4.99 (m, 2H), 3.65(s, 3H), 2.86 - 2.75(m, 2H) ,2.26 - 2.25 (m, 1H), 2.095(d, 1H, J=4Hz) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 141.0 , 134.7 , 128.2 , 127.8 , 127.0 , 117.2 , 60.3 , 49.9 , 42.8 , 35.5 ppm ; HRMS (ESI) m/z (M+H⁺) calcd for C₁₂H₁₆NO 190.1226, found 190.1240.



2-allyl-1-methoxy-2-(p-tolyl)aziridine (3b)

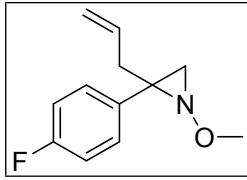
colorless liquid; 87mg (86%); IR (KBr):3073, 3026, 2983, 2939, 2898, 2805, 1647, 1608, 1506, 1445, 993,909, 828cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.19 (s, 1H), 7.19 (s, 1H), 7.10 (d, 2H, J = 8Hz), 5.83 - 5.73 (m, 1H), 5.04 - 4.99 (m, 2H), 3.64(s, 3H), 2.84 - 2.74 (m, 2H) , 2.30(s, 3H), 2.24 - 2.23 (m, 1H), 2.065(d, 1H, J=4Hz) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 138.0 , 136.6 , 134.9 , 128.9 , 127.6 , 117.1 , 60.3 , 49.6 , 42.8 , 35.5, 21.0 ppm ; HRMS (ESI) m/z (M+H⁺) calcd for C₁₃H₁₈NO 204.1383, found 204.1380.



2-allyl-2-(4-chlorophenyl)-1-methoxyaziridine (3c)

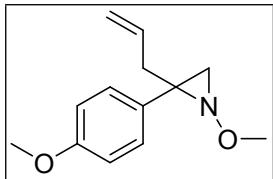
colorless liquid; 93mg (83%); IR (KBr): 3077, 2983, 2939, 2894, 2808,

1640, 1598, 1493, 1466, 977, 918, 832cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.28 - 7.23 (m, 4H), 5.80 - 5.70 (m, 1H), 5.03 - 4.98 (m, 2H), 3.64 (s, 3H), 2.85 - 2.71(m, 2H) , 2.21 - 2.20 (m, 1H), 2.095 (d, 1H,*J*=4Hz) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 139.6 , 134.4 , 132.8 , 129.2 , 128.4 , 117.6 , 60.4 , 49.2 , 43.1 , 35.4 ppm ; HRMS (ESI) m/z (M+H⁺) calcd for C₁₂H₁₅ClNO 224.0837, found 224.0837.



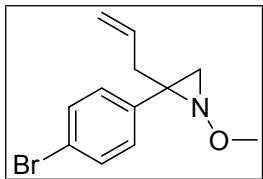
2-allyl-2-(4-fluorophenyl)-1-methoxyaziridine (3d)

colorless liquid; 83mg (80%); IR (KBr): 3076, 2983, 2940, 2895, 2809, 1641, 1605, 1512, 1467, 977, 919, 838cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.30 - 7.26 (m, 2H), 7.00 - 6.95 (m, 2H), 5.81 - 5.71 (m, 1H), 5.02 - 4.98 (m, 2H), 3.65(s, 3H), 2.84 - 2.71(m, 2H) , 2.22 - 2.21 (m, 1H), 2.09 (d, 1H, *J* = 3Hz) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 161.8 (¹J(C,F) = 245 Hz) , 136.8 (⁴J(C,F)=3 Hz) , 134.5 , 129.5 (³J(C,F)=8Hz) , 117.5 , 115.1 (²J(C,F)=21 Hz) , 60.4 , 49.4 , 42.9 , 35.7 ppm ; HRMS (ESI) m/z (M+H⁺) calcd for C₁₂H₁₅FNO 208.1132, found 208.1131.



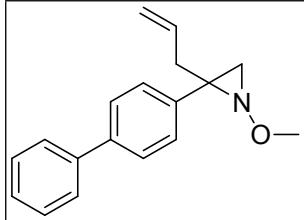
2-allyl-1-methoxy-2-(4-methoxyphenyl)aziridine (3e)

colorless liquid; 88mg (80%); IR (KBr): 3074, 2981, 2937, 2835, 2808, 1640, 1612, 1515, 1465, 977, 914, 833cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.17 - 7.13 (m, 2H), 6.77 - 6.74 (m, 2H), 5.75 - 5.65 (m, 1H), 4.96 - 4.91 (m, 2H) , 3.69 (s, 3H), 3.57 (s, 3H), 2.74 - 2.65(m, 2H) , 2.16 - 2.15 (m, 1H), 1.98(d, 1H, *J*=3Hz) ppm ; ¹³C NMR (100 MHz, CDCl₃) δ 158.5 , 134.9 , 133.1 , 128.9 , 117.1 , 113.6 , 60.3 , 55.2 , 49.4 , 42.8, 35.7 ppm ; HRMS (ESI) m/z (M+H⁺) calcd for C₁₃H₁₈NO₂ 220.1332, found 220.1336.



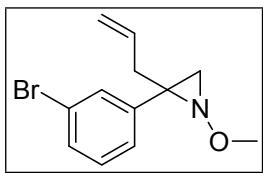
2-allyl-2-(4-bromophenyl)-1-methoxyaziridine (3f)

colorless liquid; 124mg (93%); IR (KBr): 3078, 2961, 2900, 2808, 1640, 1592, 1490, 1466, 996, 918, 823cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.42 - 7.40 (m, 2H), 7.20 - 7.18 (m, 2H), 5.80 - 5.70 (m, 1H), 5.02 - 4.98 (m, 2H), 3.64 (s, 3H), 2.84 - 2.79 (m, 1H), 2.76 - 2.70(m, 1H), 2.20 - 2.19(m, 1H), 2.10(d, 1H, *J*=3Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.1, 134.3, 131.3, 129.5, 120.9, 117.6, 60.4, 49.2, 43.0, 35.2ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₂H₁₅⁷⁹BrNO 268.0337, found 268.0334; C₁₂H₁₅⁸¹BrNO 270.0317, found 270.0323.



2-([1,1'-biphenyl]-4-yl)-2-allyl-1-methoxyaziridine (3g)

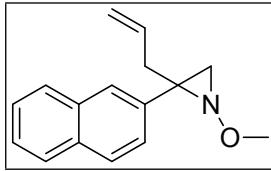
colorless liquid; 112mg (85%); IR (KBr): 3076, 3029, 2982, 2938, 2893, 2807, 1640, 1599, 1486, 1465, 995, 913, 843cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.56 - 7.51 (m, 4H), 7.41 - 7.36 (m, 4H), 7.32 - 7.28 (m, 1H), 5.87 - 5.77(m, 1H), 5.07 - 5.02 (m, 2H), 3.66 (s, 3H), 2.89 - 2.78 (m, 2H), 2.28 - 2.27(m, 1H), 2.12 (d, 1H, *J*=3Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.7, 140.1, 139.9, 134.7, 128.7, 128.1, 127.2, 127.0, 126.9, 117.3, 60.3, 49.4, 43.0, 35.3; HRMS (ESI) m/z (M+H⁺) calcd for C₁₈H₂₀NO 266.1539, found 266.1544.



2-allyl-2-(3-bromophenyl)-1-methoxyaziridine (3h)

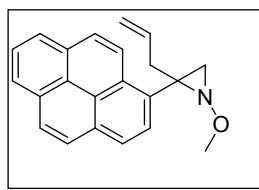
colorless liquid; 118mg (88%); IR (KBr): 3075, 2983, 2939, 2893, 2808,

1640, 1595, 1476, 1466, 978, 915, 883, 790, 694cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.47 - 7.46 (m, 1H), 7.36 - 7.33 (m, 1H), 7.26 - 7.23 (m, 1H), 7.17 - 7.14 (m, 1H), 5.81 - 5.70 (m, 1H), 5.04 - 4.99 (m, 2H), 3.65 (s, 3H), 2.86 - 2.80 (m, 1H), 2.77 - 2.71 (m, 1H), 2.21 - 2.20 (m, 1H), 2.095 (d, 1H, *J*=4Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 143.4, 134.2, 130.9, 130.1, 129.7, 126.5, 122.3, 117.7, 60.4, 49.2, 43.1, 35.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₂H₁₅⁷⁹BrNO 268.0337, found 268.0329; C₁₂H₁₅⁸¹BrNO 270.0317, found 270.0310



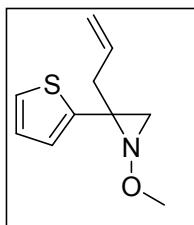
2-allyl-1-methoxy-2-(naphthalen-2-yl) aziridine (3i)

colorless liquid; 106mg (89%); IR (KBr): 3057, 2981, 2938, 2893, 2807, 1640, 1600, 1506, 1466, 995, 913cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.79 - 7.74 (m, 4H), 7.48 - 7.41 (m, 3H), 5.86 - 5.75 (m, 1H), 5.04 - 4.97 (m, 2H), 3.70 (s, 3H), 2.95 - 2.83 (m, 2H), 2.35 - 2.34 (m, 1H), 2.155 (d, 1H, *J*=4Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 134.7, 133.1, 132.5, 128.0, 127.8, 127.6, 126.7, 126.0, 125.8, 117.3, 60.4, 50.1, 43.0, 35.5 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₆H₁₈NO 240.1383, found 240.1385.



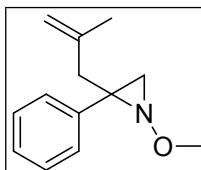
2-allyl-1-methoxy-2-(pyren-1-yl)aziridine (3j):

pale yellow oil; 63mg (40%); IR (KBr): 3074, 2970, 2919, 2849, 2808, 1632, 1488, 1001, 911cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 8.43 (d, 1H, *J*=4Hz), 8.18 - 8.10 (m, 4H), 8.03 - 7.95 (m, 4H), 5.82 - 5.72 (m, 1H), 4.91 - 4.83 (m, 2H), 3.85 (s, 3H), 3.11 - 2.98 (m, 2H), 2.48 - 2.42 (m, 2H), 1.34 (s, 1H), 1.28 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 134.3, 131.2, 130.7, 130.6, 128.6, 127.7, 127.5, 127.4, 127.2, 125.9, 125.2, 125.1, 124.9, 124.8, 124.4, 123.5, 117.4, 60.5, 50.2, 43.2, 37.3 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₂₂H₂₀NO 314.1539, found 314.1537.



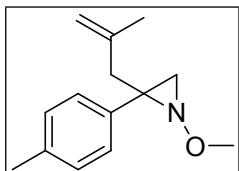
2-allyl-1-methoxy-2-(thiophen-2-yl)aziridine (3k)

colorless liquid; 53mg (54%); IR (KBr): 3075, 2898, 2937, 2895, 2808, 1640, 1533, 1465, 1435, 995, 918cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.17 - 7.15 (m, 1H), 6.93 - 6.91 (m, 2H), 5.94 - 5.84 (m, 1H), 5.18 - 5.07 (m, 2H), 3.63 (s, 3H), 2.87 - 2.84 (m, 2H), 2.395 (d, 1H, *J*=4Hz), 2.185 (d, 1H, *J*=4Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 146.0, 134.6, 126.7, 124.6, 124.3, 117.5, 60.5, 45.9, 45.2, 34.9 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₀H₁₄NOS 196.0791, found 196.0790.



1-methoxy-2-(2-methylallyl)-2-phenylaziridine (3l)

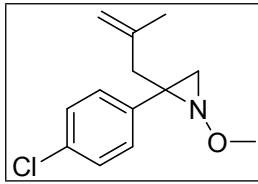
colorless liquid; 77mg (76%); IR (KBr): 3062, 3028, 2982, 2939, 2894, 2808, 1648, 1495, 1447, 890, 778, 698cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.31 - 7.18 (m, 5H), 4.73 (s, 1H), 4.64 (s, 1H), 3.65 (s, 3H), 2.79 (m, 2H), 2.41 - 2.40 (m, 1H), 2.16 (d, 1H, *J*=3Hz), 1.71 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 142.2, 141.1, 128.1, 127.5, 126.9, 113.4, 60.2, 48.7, 43.2, 38.3, 23.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₃H₁₈NO 204.1383, found 204.1380.



1-methoxy-2-(2-methylallyl)-2-(p-tolyl)aziridine (3m)

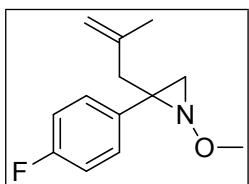
colorless liquid; 75mg (69%); IR (KBr): 3073, 3026, 2982, 2939, 2897, 2807, 1649, 1516, 1465, 889, 820cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS)

δ 7.19 - 7.17 (m, 4H), 7.08 (d, 2H, J =8Hz), 4.73 (s, 1H), 4.65 (s, 1H), 3.63 (s, 3H), 2.78 (m, 2H), 2.40 - 2.39 (m, 1H), 2.29 (s, 3H), 2.13 (d, 1H, J =3Hz), 1.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 138.1, 136.5, 128.8, 127.3, 113.3, 60.2, 48.4, 43.1, 38.3, 23.2, 21.0 ppm; HRMS (ESI) m/z (M+H $^+$) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}$ 218.1539, found 218.1540.



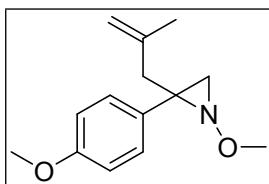
2-(4-chlorophenyl)-1-methoxy-2-(2-methylallyl)aziridine (3n)

colorless liquid; 75mg (63%); IR (KBr): 3075, 2984, 2939, 2894, 2808, 1649, 1598, 1494, 1465, 892, 831cm $^{-1}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.26 - 7.21 (m, 4H), 4.74 (s, 1H), 4.62 (s, 1H), 3.63 (s, 3H), 2.80 - 2.72 (m, 2H), 2.35 (d, 1H, J =4Hz), 2.16 (d, 1H, J =3Hz), 1.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 139.8, 132.7, 128.9, 128.3, 113.7, 60.3, 48.1, 43.4, 38.2, 23.2 ppm; HRMS (ESI) m/z (M+H $^+$) calcd for $\text{C}_{13}\text{H}_{17}\text{ClNO}$ 238.0993, found 238.0996.



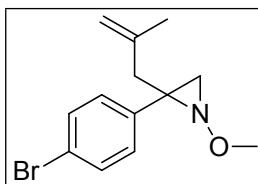
2-(4-fluorophenyl)-1-methoxy-2-(2-methylallyl)aziridine (3o)

colorless liquid; 73mg (66%); IR (KBr): 3074, 2987, 2940, 2896, 2810, 1650, 1605, 1512, 1466, 893, 838cm $^{-1}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.28 - 7.23 (m, 2H), 6.99-6.94 (m, 2H), 4.74 (s, 1H), 4.62 (s, 1H), 3.64 (s, 3H), 2.80 - 2.71 (m, 2H), 2.36-2.35 (m, 1H), 2.16 (d, 1H, J =3Hz), 1.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 161.7 ($^1J(\text{C},\text{F})$ =244Hz), 142.0, 137.0 ($^4J(\text{C},\text{F})$ =3Hz), 129.2 ($^3J(\text{C},\text{F})$ =8Hz), 115.0 ($^2J(\text{C},\text{F})$ =21 Hz), 113.6, 60.2, 48.2, 43.2, 38.5, 23.1 ppm; HRMS (ESI) m/z (M+H $^+$) calcd for $\text{C}_{13}\text{H}_{17}\text{FNO}$ 222.1289, found 222.1291.



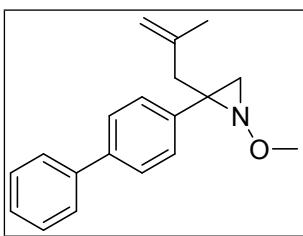
1-methoxy-2-(4-methoxyphenyl)-2-(2-methylallyl)aziridine (3p)

colorless liquid; 65mg (56%); IR (KBr): 3073, 3037, 2937, 2835, 2808, 1648, 1612, 1515, 1464, 890, 832cm $^{-1}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.25 - 7.19 (m, 2H), 6.83 - 6.80 (m, 2H), 4.73 (s, 1H), 4.64 (s, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 2.82 - 2.69 (m, 2H), 2.40 - 2.39 (m, 1H), 2.13 (d, 1H, J =3Hz), 1.70 (s, 3H) ppm; ^{13}C NMR (100MHz, CDCl_3) δ 158.5, 142.4, 133.2, 128.7, 113.5, 113.3, 60.2, 55.1, 48.3, 43.0, 38.5, 23.2 ppm; HRMS (ESI) m/z (M+H $^+$) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_2$ 234.1489, found 234.1492.



2-(4-bromophenyl)-1-methoxy-2-(2-methylallyl)aziridine (3q)

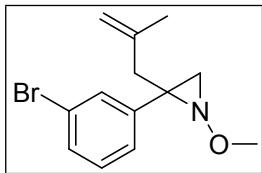
colorless liquid; 96mg (68%); IR (KBr): 3074, 2939, 2893, 2808, 1649, 1592, 1491, 1465, 892, 828cm $^{-1}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.41 - 7.39 (m, 2H), 7.18 - 7.16 (m, 2H), 4.74 (s, 1H), 4.62 (s, 1H), 3.64 (s, 3H), 2.80 - 2.72 (m, 2H), 2.34 - 2.33 (m, 1H), 2.16 (d, 1H, J =3Hz), 1.71 (s, 3H) ppm; ^{13}C NMR (100MHz, CDCl_3) δ 141.9, 140.3, 131.2, 129.2, 120.8, 113.7, 60.3, 48.0, 43.4, 38.7, 23.2 ppm; HRMS (ESI) m/z (M+H $^+$) calcd for $\text{C}_{13}\text{H}_{17}^{79}\text{BrNO}$ 282.0494, found 282.0493; $\text{C}_{13}\text{H}_{17}^{81}\text{BrNO}$ 284.0473, found 284.0471.



2-([1,1'-biphenyl]-4-yl)-1-methoxy-2-(2-methylallyl)aziridine (3r)

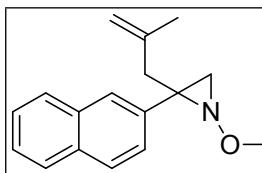
colorless liquid; 113mg (81%); IR (KBr): 3074, 3029, 2983, 2938, 2893, 2807, 1650, 1600, 1512, 1465, 891, 843cm $^{-1}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.56 - 7.50 (m, 4H), 7.41 - 7.34 (m, 4H), 7.32 -

7.28 (m, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 3.65 (s, 3H), 2.89 - 2.76 (m, 2H), 2.44 - 2.43 (m, 1H), 2.19 (d, 1H, *J*=3Hz), 1.74 (s, 3H) ppm; ¹³C NMR (100MHz, CDCl₃) δ 142.2, 140.7, 140.2, 139.7, 128.6, 127.8, 127.1, 127.0, 126.8, 113.4, 60.2, 48.2, 43.4, 38.0, 23.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₉H₂₂NO 280.1696, found 280.1702.



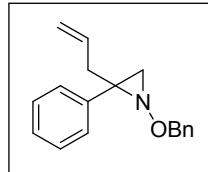
2-(3-bromophenyl)-1-methoxy-2-(2-methylallyl)aziridine (3s)

colorless liquid; 100mg (71%); IR (KBr): 3073, 2938, 2894, 2808, 1650, 1595, 1477, 1466, 890, 892, 791, 693cm⁻¹; ¹H NMR (400MHz, CDCl₃, TMS) δ 7.44 - 7.43 (m, 1H), 7.35 - 7.32(m, 1H), 7.24 - 7.21 (m, 1H), 7.16 - 7.12 (t, 1H), 4.76 (s, 1H), 4.64 (s, 1H), 3.64 (s, 3H), 2.80 - 2.72 (t, 2H), 2.35 - 2.34 (m, 1H), 2.16 (d, 1H, *J*=3Hz), 1.72 (s, 3H) ppm; ¹³C NMR (100MHz, CDCl₃) δ 143.6, 141.8, 130.6, 130.1, 129.6, 126.2, 122.2, 113.7, 60.3, 48.0, 43.4, 38.00, 23.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₃H₁₇⁷⁹BrNO 282.0494, found 282.0499; C₁₃H₁₇⁸¹BrNO 284.0473, found 284.0467.



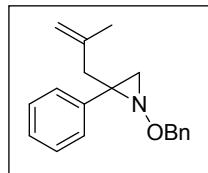
1-methoxy-2-(2-methylallyl)-2-(naphthalen-2-yl)aziridine (3t)

colorless liquid; 87mg (69%); IR (KBr): 3057, 3020, 2938, 2893, 2807, 1649, 1600, 1507, 1465, 892cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.78 - 7.76 (m, 3H), 7.70- 7.70 (m, 1H), 7.48 - 7.40 (m, 3H), 4.71 (s, 1H), 4.66 (s, 1H), 3.69 (s, 3H), 2.95 - 2.82 (m, 2H), 2.51 - 2.50(m, 1H), 2.23 (d, 1H, *J*=3Hz), 1.73 (s, 3H) ppm; ¹³C NMR (100MHz, CDCl₃) δ 142.2, 138.6, 133.1, 132.5, 127.9, 127.8, 127.5, 126.4, 125.9, 125.7, 125.6, 113.6, 60.3, 48.9, 43.3, 38.3, 23.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₇H₂₀NO 254.1539, found 254.1540.



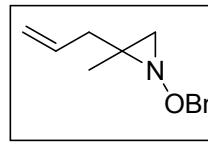
2-allyl-1-(benzyloxy)-2-phenylaziridine (3u):

colorless liquid; 93mg (70%); IR (KBr): 3063, 3030, 2979, 2914, 2855, 1640, 1602, 1495, 1453, 976, 914, 750, 700cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 87.40 - 7.18 (m,10H), 5.81 - 5.71 (m,1H), 5.01 - 4.82 (m, 4H), 2.88 - 2.82 (m, 1H), 2.76 - 2.70 (m, 1H), 2.29 - 2.28 (m, 1H), 2.16 - 2.15 (m, 1H) ppm; ¹³C NMR (100MHz, CDCl₃) δ 141.0, 137.5, 134.8, 128.6, 128.5, 128.3, 128.1, 127.8, 127.0, 117.2, 75.2, 49.7, 42.9, 35.9 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₈H₂₀NO 266.1539, found 266.1544.



1-(benzyloxy)-2-(2-methylallyl)-2-phenylaziridine (3v):

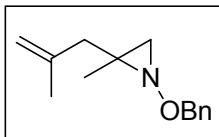
colorless liquid; 88mg (63%); IR (KBr): 3063, 3030, 2967, 2915, 2855, 1649, 1603, 1495, 1453, 890, 749, 697cm⁻¹; ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.40 - 7.30 (m, 5H), 7.25- 7.17 (m, 5H), 4.87 (m, 2H), 4.71 - 4.70 (m, 1H), 4.61 - 4.60 (m, 1H), 2.76 (m, 2H), 2.44 - 2.43 (m, 1H), 2.23 - 2.22 (m, 1H), 1.69 (s, 3H) ppm; ¹³C NMR (100MHz, CDCl₃) δ 142.3, 141.1, 137.5, 128.7, 128.3, 128.0, 127.9, 127.5, 126.9, 75.2, 48.6, 43.2, 38.9, 23.2 ppm; HRMS (ESI) m/z (M+H⁺) calcd for C₁₉H₂₂NO 280.1696, found 280.1702.



2-allyl-1-(benzyloxy)-2-methylaziridine (3w):

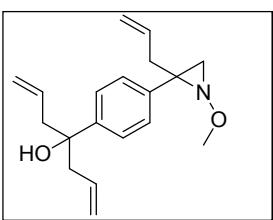
colorless liquid; 84mg (83%); ¹H NMR (400MHz, CDCl₃, TMS) δ 7.36 - 7.27 (m, 5H), 5.89 - 5.69 (m, 1H), 5.13 - 5.04 (m, 2H), 4.78 - 4.68 (m, 2H),

2.48 - 2.42 & 2.33 - 2.27 & 2.09 - 1.96 (m, 2H), 1.86 - 1.81 (m, 1H), 1.75 - 1.70 (m, 1H), 1.30 & 1.08 (s, 1H) ppm; ^{13}C NMR (100MHz, CDCl_3) δ 137.5, 137.5, 135.3, 133.9, 128.5, 128.5, 128.2, 128.2, 127.7, 117.3, 117.0, 43.5, 43.4, 42.6, 42.4, 42.0, 36.0, 21.9, 15.2 ppm; HRMS (ESI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ 204.1383, found 204.1380.



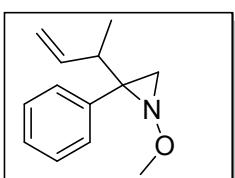
1-(benzyloxy)-2-methyl-2-(2-methylallyl)aziridine (3x):

colorless liquid; 93mg (86%); ^1H NMR (400MHz, CDCl_3 , TMS) δ 7.37 - 7.24 (m, 5H), 4.81 - 4.71 (m, 4H), 2.38 - 2.27 & 2.12 - 2.08 & 1.74 - 1.71 (m, 2H), 1.91 - 1.86 (m, 2H), 1.73 (s, 3H), 1.30 & 1.04 (s, 3H) ppm; ^{13}C NMR (100MHz, CDCl_3) δ 142.6, 141.9, 137.2, 137.1, 128.1, 128.1, 127.8, 127.4, 127.3, 112.5, 112.5, 74.4, 74.4, 45.8, 42.7, 42.5, 42.2, 41.9, 39.1, 22.5, 22.2, 21.6, 14.7 ppm; HRMS (ESI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{14}\text{H}_{20}\text{NO}$ 218.1539, found 218.1540.



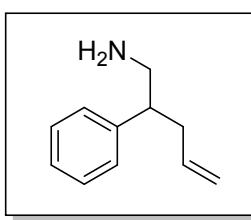
4-(4-(2-allyl-1-methoxyaziridin-2-yl)phenyl)hepta-1,6-dien-4-ol (3y)

colorless liquid; 90mg (60%); ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.34 - 7.32 (m, 2H), 7.29 - 7.26 (m, 2H), 5.83 - 5.72 (m, 1H), 5.63 - 5.52 (m, 2H), 5.11 - 4.98 (m, 6H), 3.65 (s, 3H), 2.85 - 2.75 (m, 2H), 2.68 - 2.62 (m, 2H), 2.51 - 2.45 (m, 2H), 2.27 - 2.26 (m, 1H), 2.20 (s, 1H), 2.10 - 2.09 (m, 1H) ppm ; ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 139.2, 134.7, 133.3, 127.5, 125.2, 119.1, 119.0, 117.1, 74.9, 60.3, 49.6, 46.7, 46.6, 42.8, 35.4 ppm ; HRMS (ESI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_2$ 300.1958, found 300.1955.



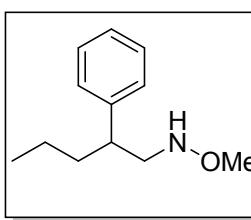
2-(but-3-en-2-yl)-1-methoxy-2-phenylaziridine (3z)

colorless liquid; 31mg (31%); ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.31 - 7.2 (m, 5H), 5.92 - 5.84 (m, 1H), 5.05 - 4.97 (m, 2H), 3.71 (s, 3H), 2.78 - 2.70 (m, 1H), 2.17(d, 1H, $J=2.4\text{Hz}$), 2.06(d, 1H, $J=2.4\text{Hz}$), 1.03(d, 3H, $J=6.8\text{Hz}$) ppm ; ^{13}C NMR (100 MHz, CDCl_3) δ 141.1, 138.5, 129.8, 127.6, 127.1, 114.4, 60.4, 54.8, 43.1, 38.8, 16.3 ppm ; HRMS (ESI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ 204.1383, found 204.1380.



2-phenylpent-4-en-1-amine (4aa)

colorless liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.34 - 7.30 (m, 2H), 7.25 - 7.18 (m, 3H), 5.72 - 5.62 (m, 1H), 5.04 - 4.94 (m, 2H), 3.24 (s, 2H), 3.07 - 3.02 (m, 1H), 2.92 - 2.78 (m, 2H), 2.47 - 2.33 (m, 2H) ppm ; ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 135.9, 128.7, 127.9, 126.9, 116.7, 47.5, 46.4, 38.2 ppm ; LC-MS (EI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}$ 162.1, found 162.2.



O-methyl-N-(2-phenylpentyl)hydroxylamine (4ab)

colorless liquid; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.33 - 7.29 (m, 2H), 7.23 - 7.17 (m, 3H), 5.34 (s, 1H), 3.48 (s, 3H), 3.24 - 3.20 (m, 1H), 3.01 - 2.87 (m, 2H), 1.68 - 1.51 (m, 2H), 1.23 - 1.15 (m, 2H), 0.86 (t, 3H, $J=8\text{Hz}$) ppm ; ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 128.5, 127.8, 126.5, 61.4, 57.5, 42.9, 36.5, 20.5, 14.0 ppm ; HRMS (ESI) m/z ($\text{M}+\text{H}^+$) calcd for $\text{C}_{12}\text{H}_{20}\text{NO}$

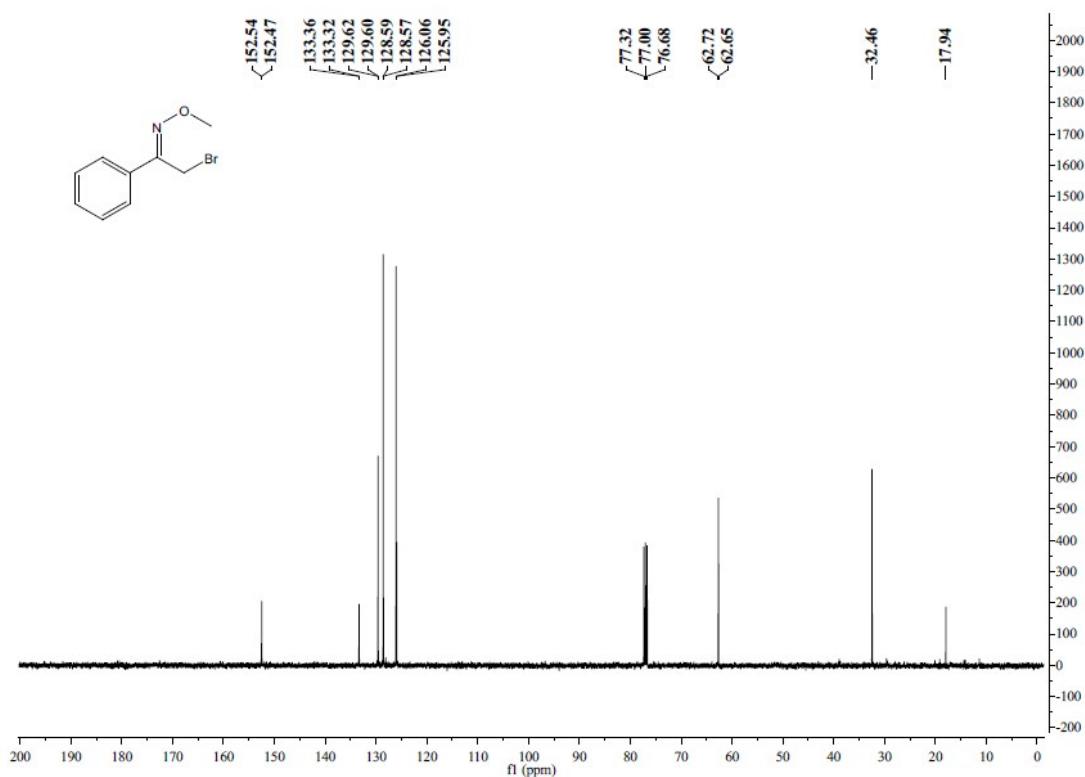
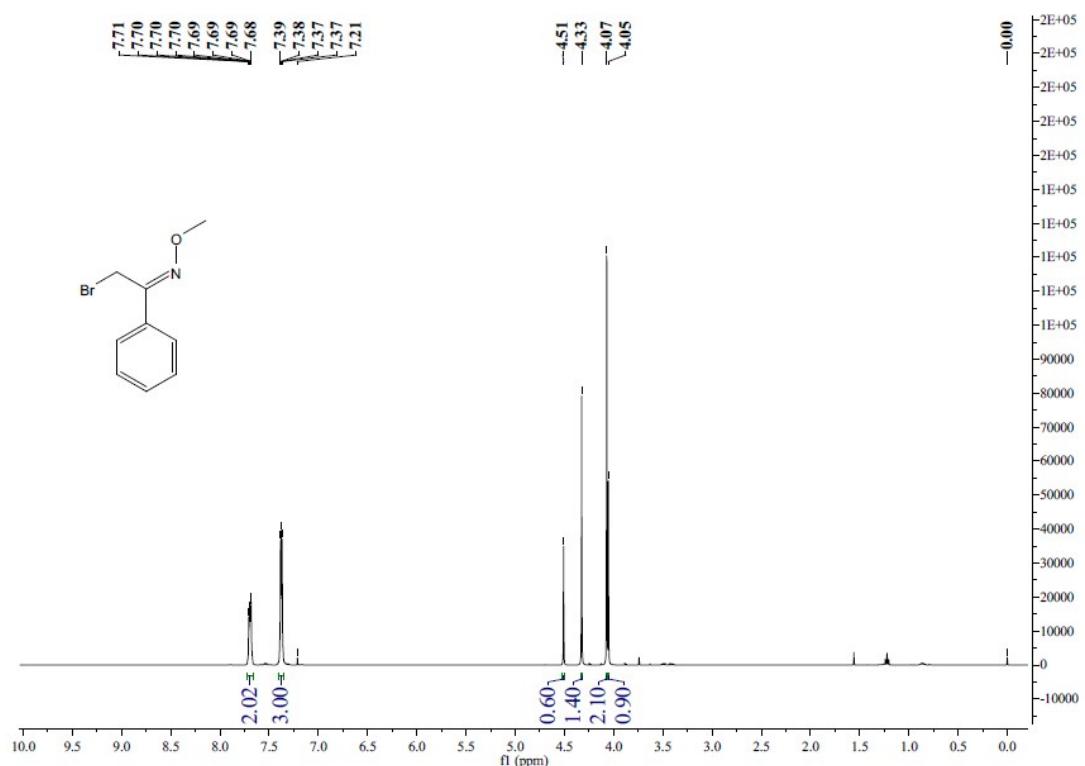
194.1539, found 194.1534.

References:

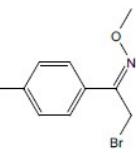
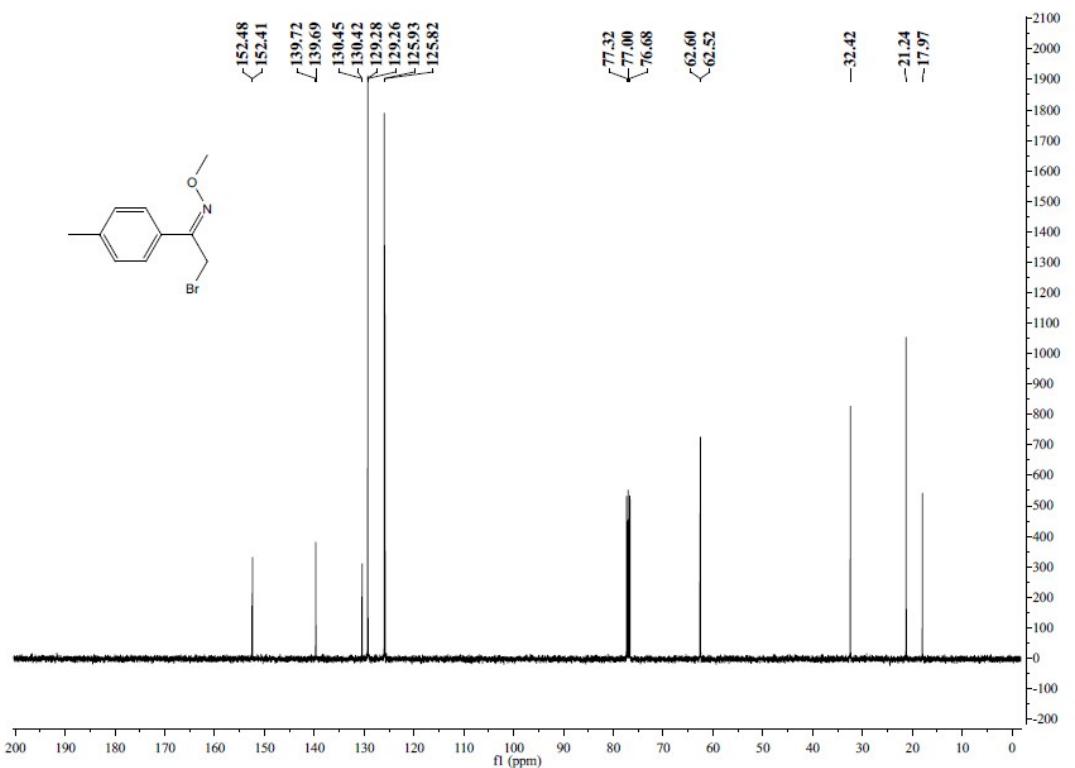
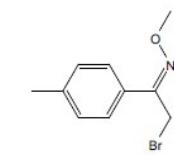
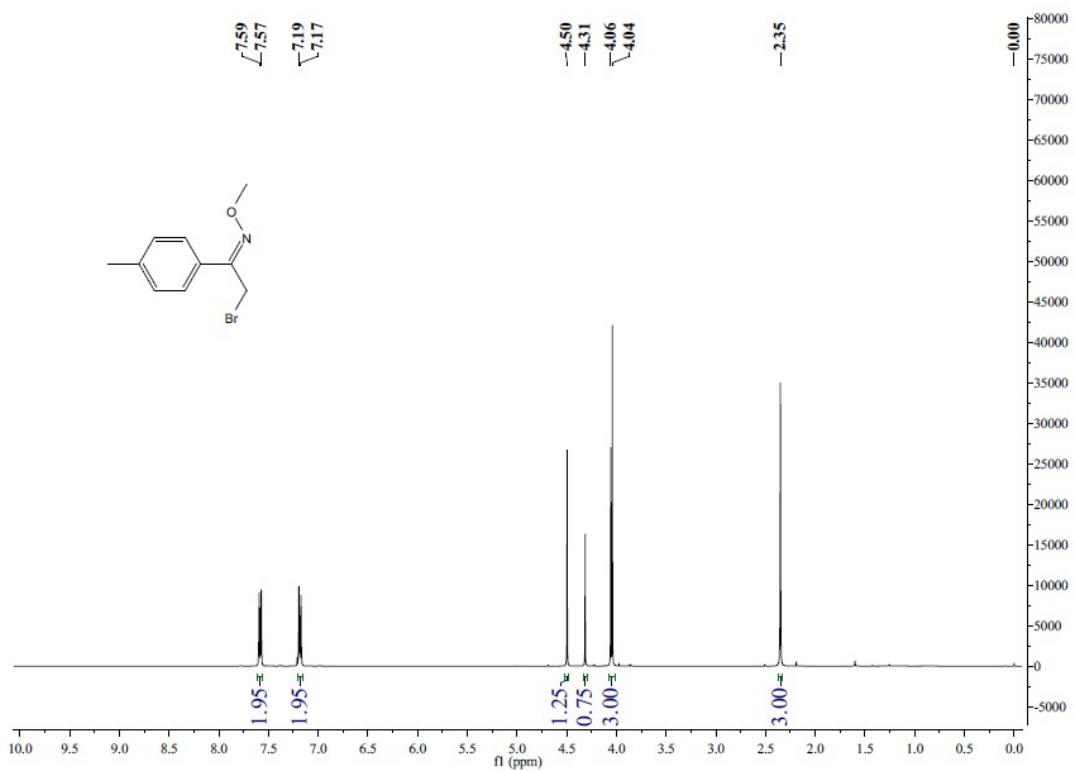
- [1] (a) T. C. Wabnitz, S. Saaby, K. A. Jørgensen *Org. Biomol. Chem.*, **2014**, *2*, 828;(b) X. X. Qi, L. Dai, C. M. Park, *Chem. Commun.*, **2012**, *48*, 11244; (c) B. Noverges, C. Mollar, M. Medio-Simón, G. Asensio *Adv. Synth. Catal.* **2015**, *357*, 430; (d) T. Tsuritani, K. Yagi, H. Shinokubo, K. Oshima *Angew. Chem.* **2003**, *115*, 5771.

¹H and ¹³C of all compounds

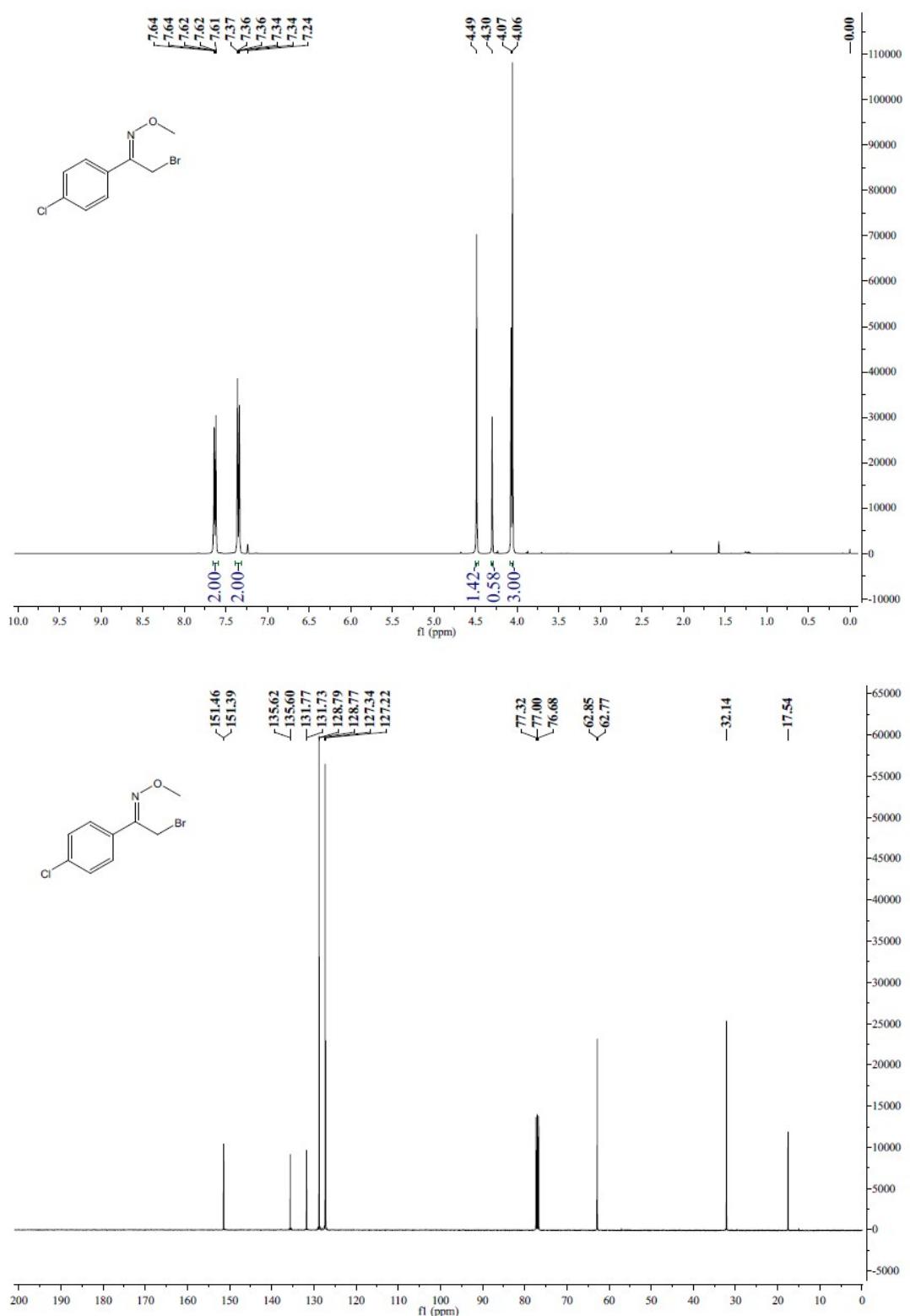
¹H and ¹³C of 1a



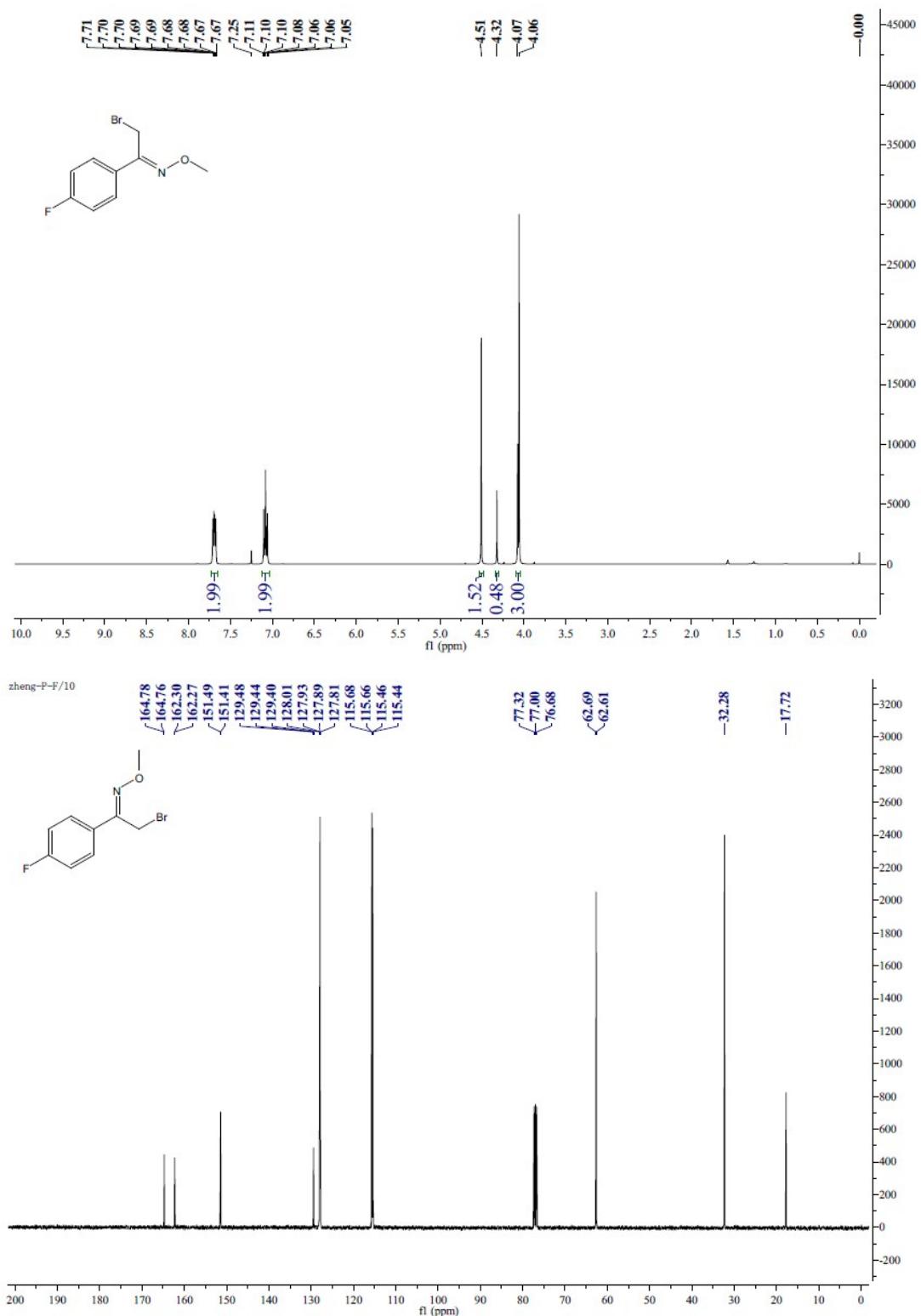
¹H and ¹³C of **1b**



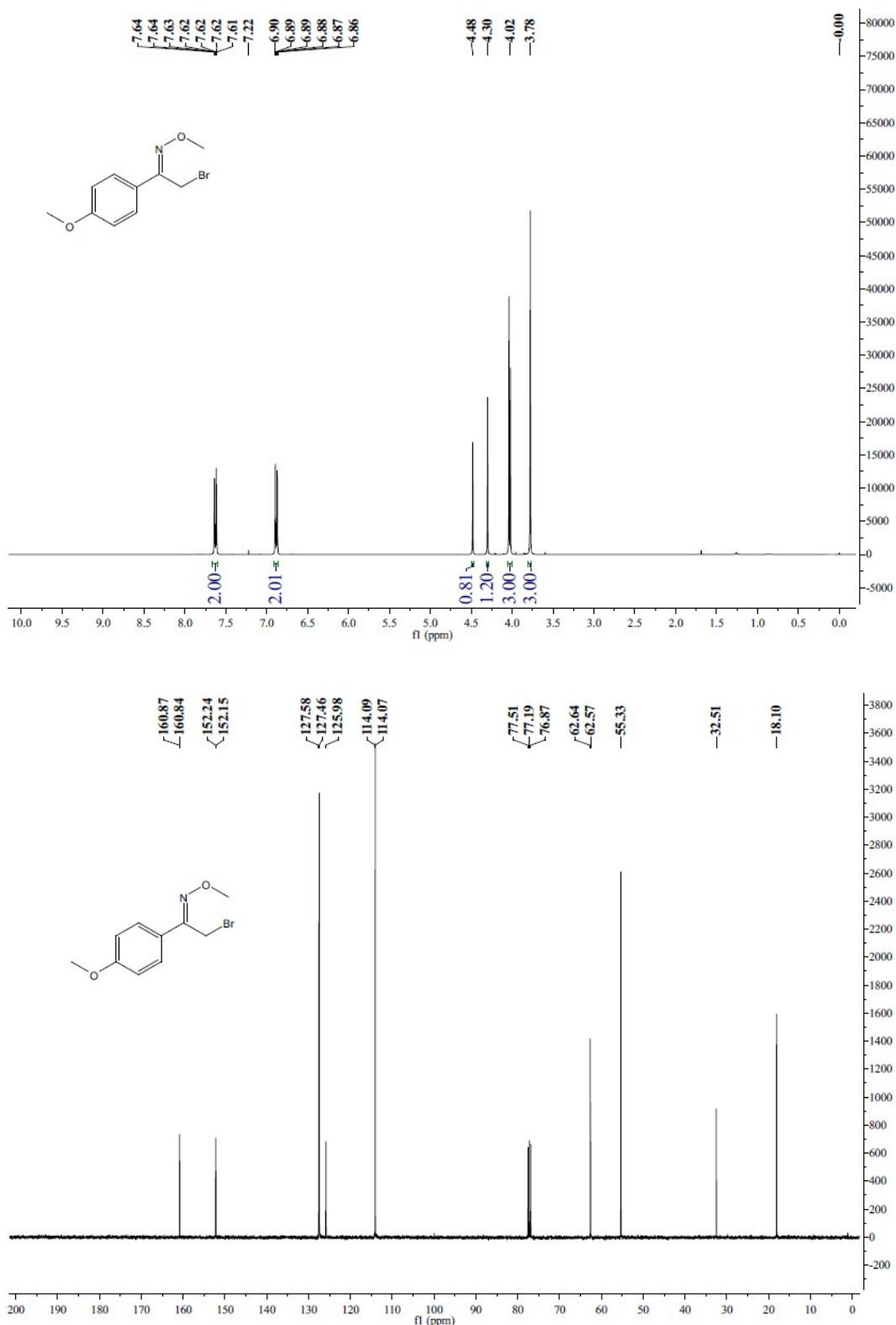
¹H and ¹³C of **1c**



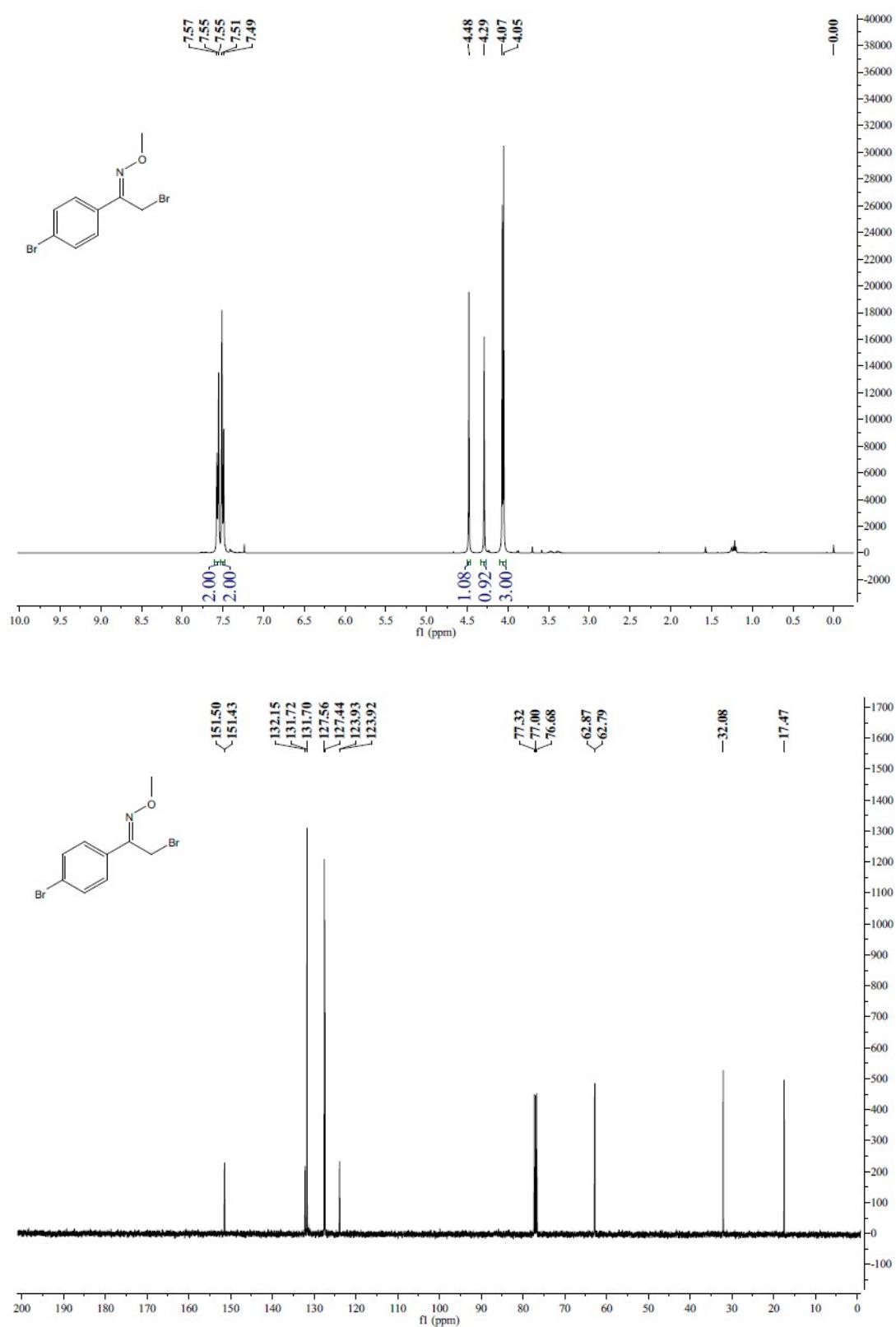
¹H and ¹³C of **1d**



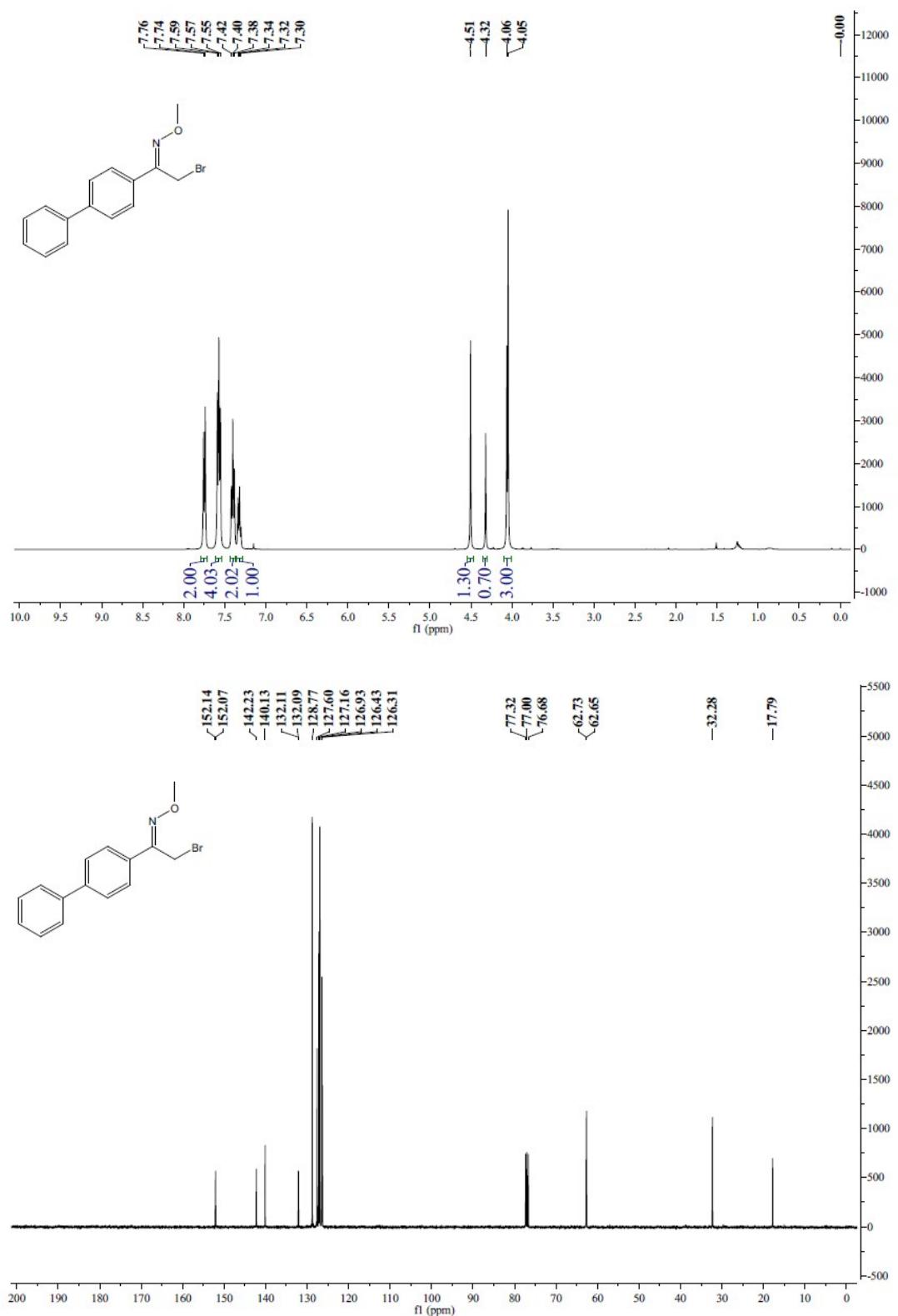
¹H and ¹³C of **1e**



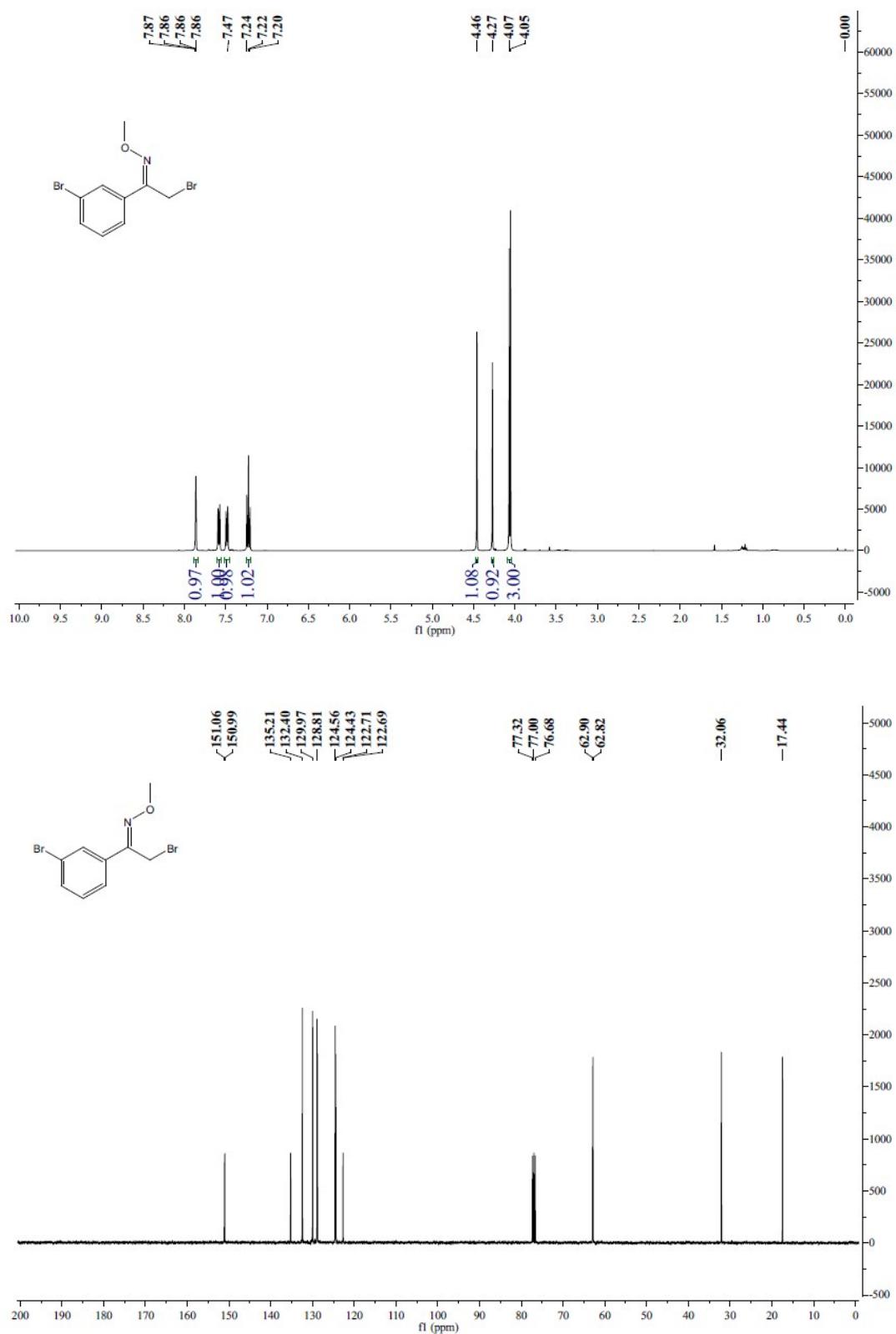
¹H and ¹³C of **1f**



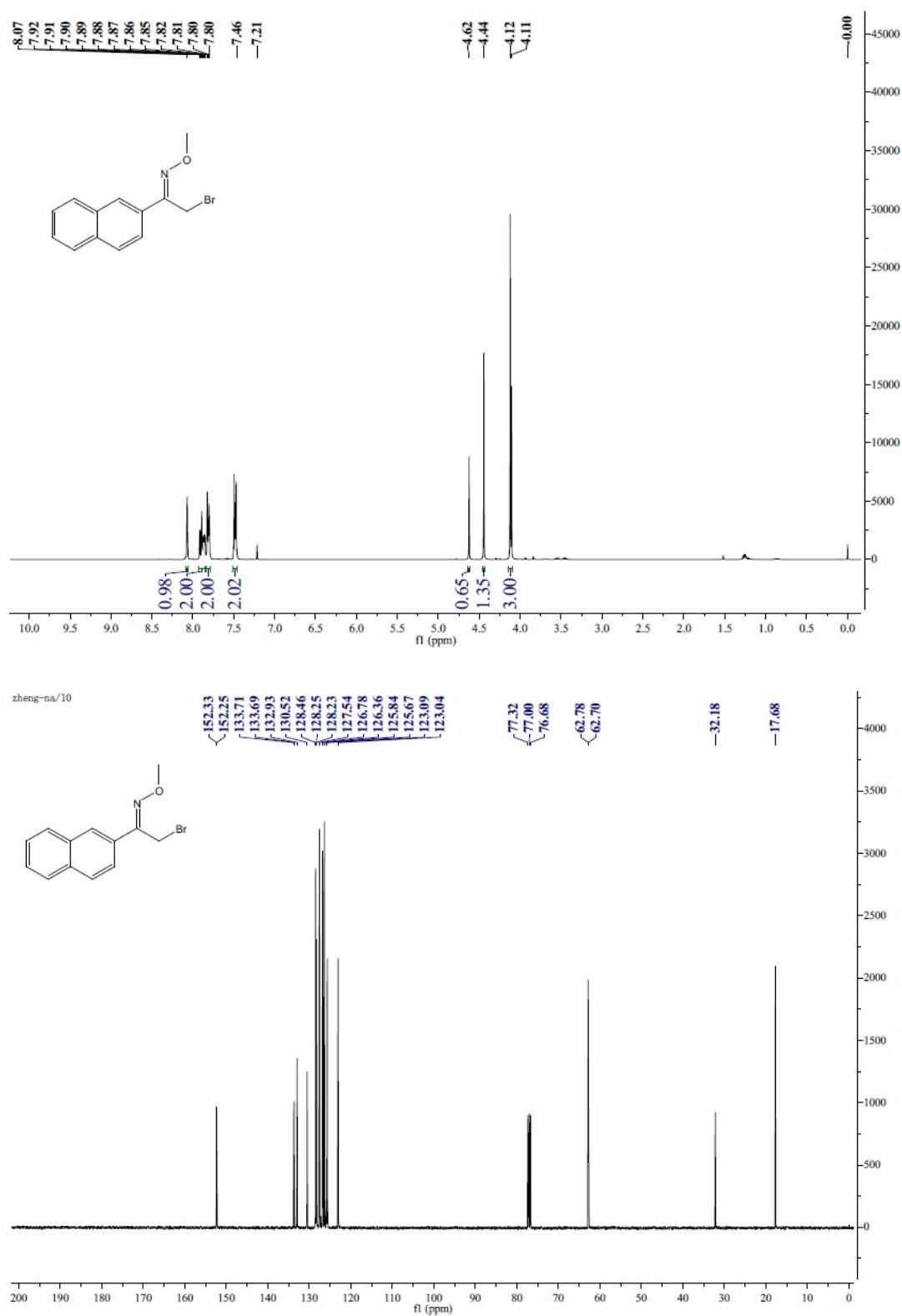
¹H and ¹³C of **1g**



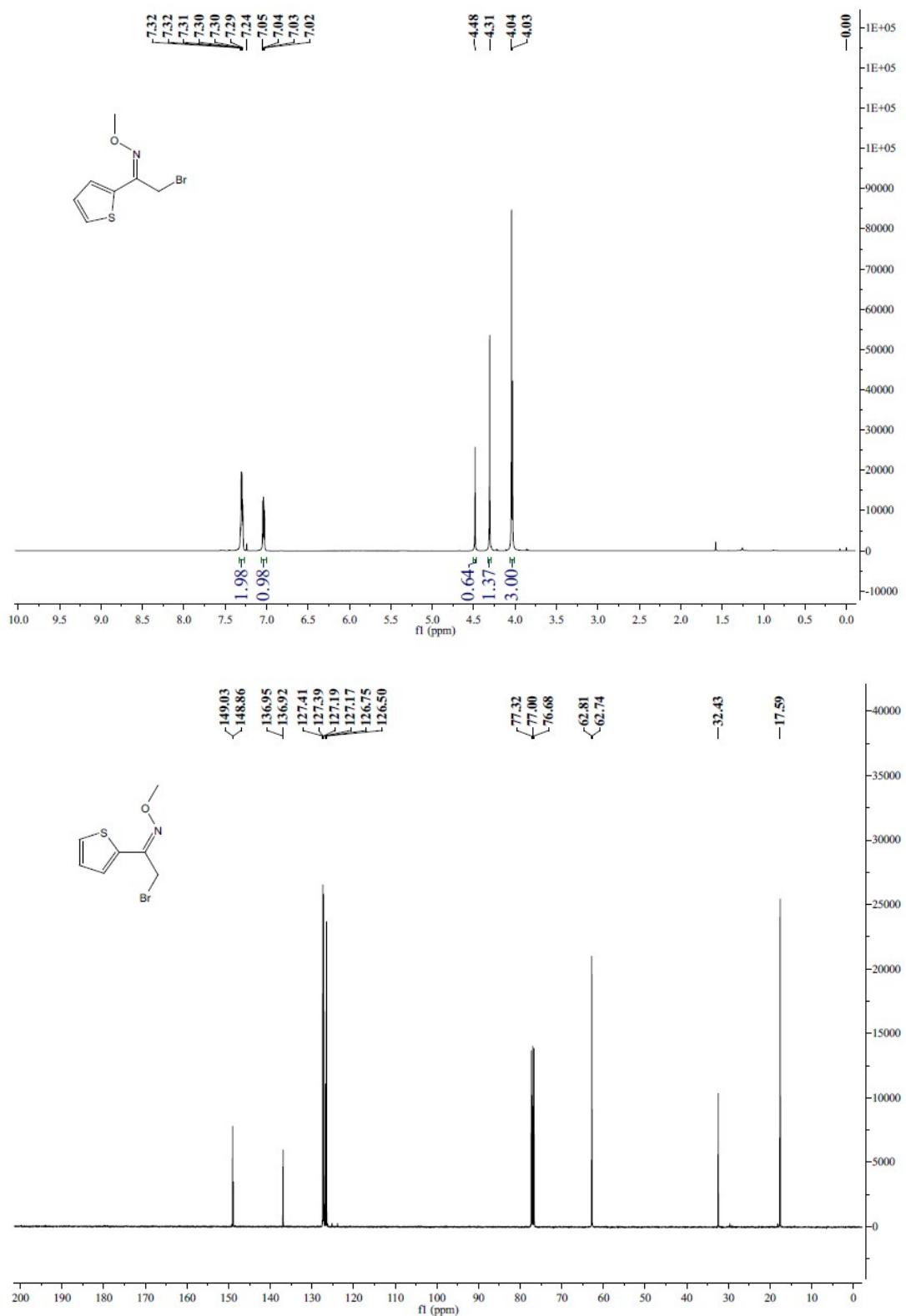
¹H and ¹³C of **1h**



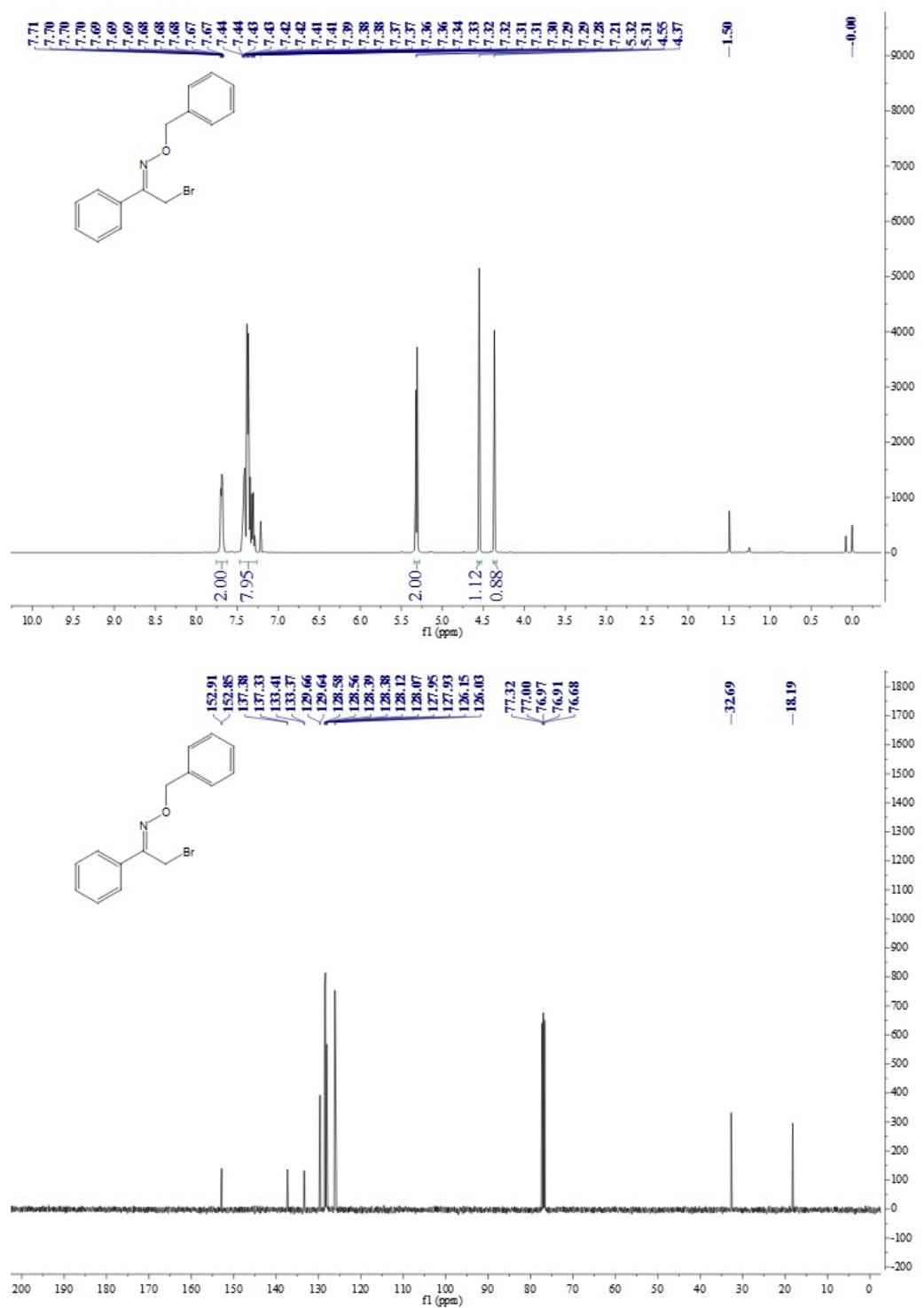
¹H and ¹³C of **1i**



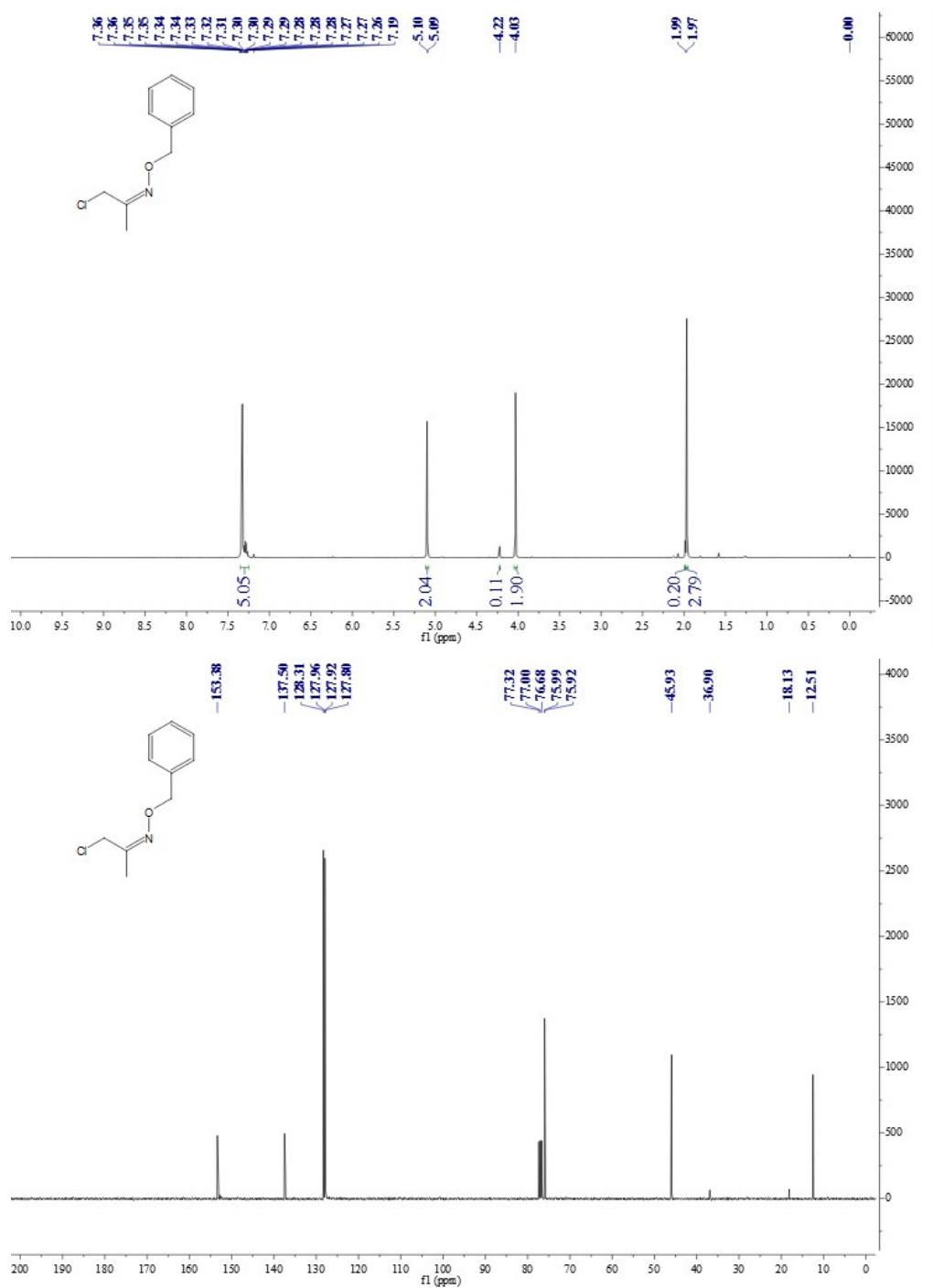
¹H and ¹³C of **1k**



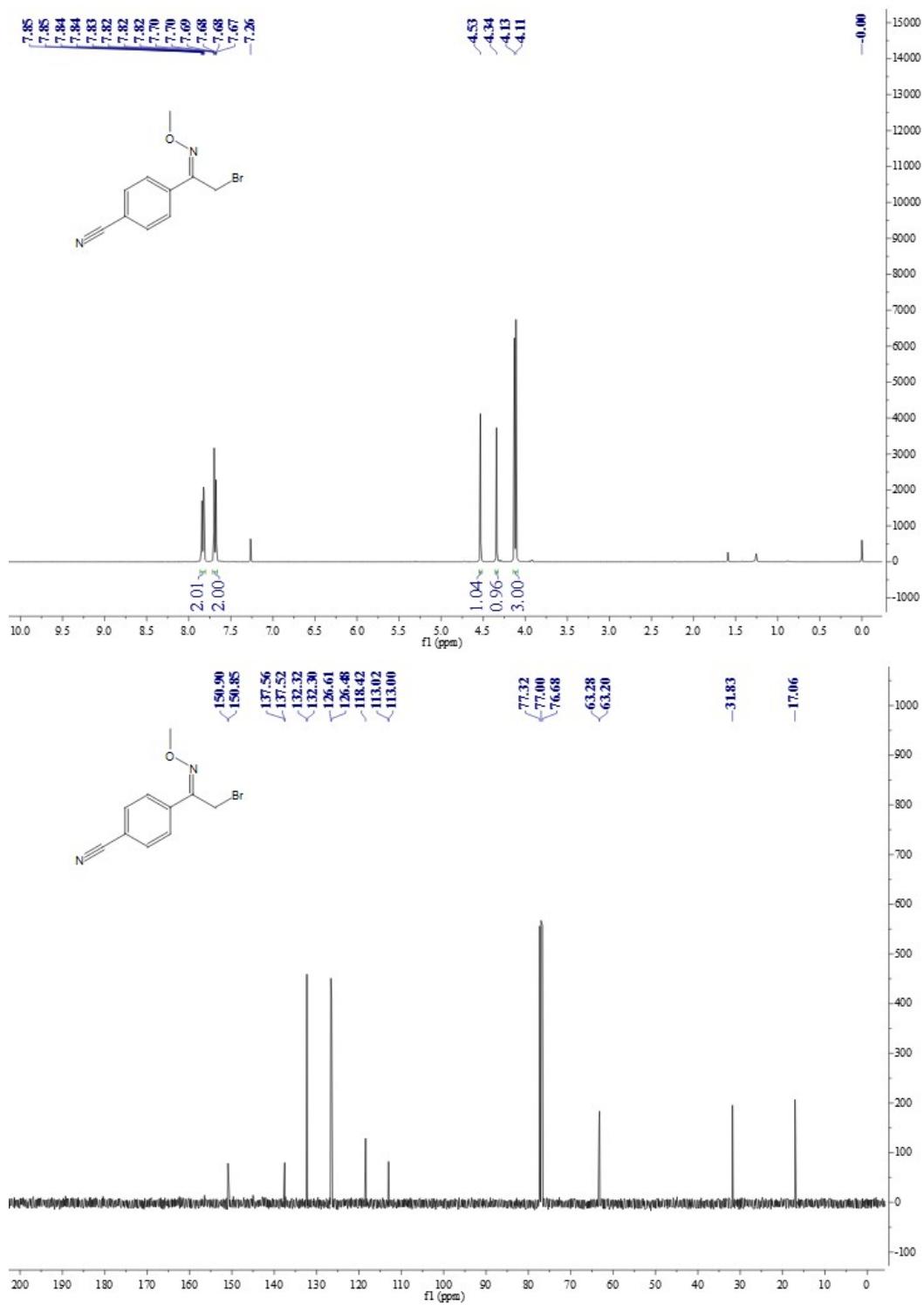
¹H and ¹³C of **1I**



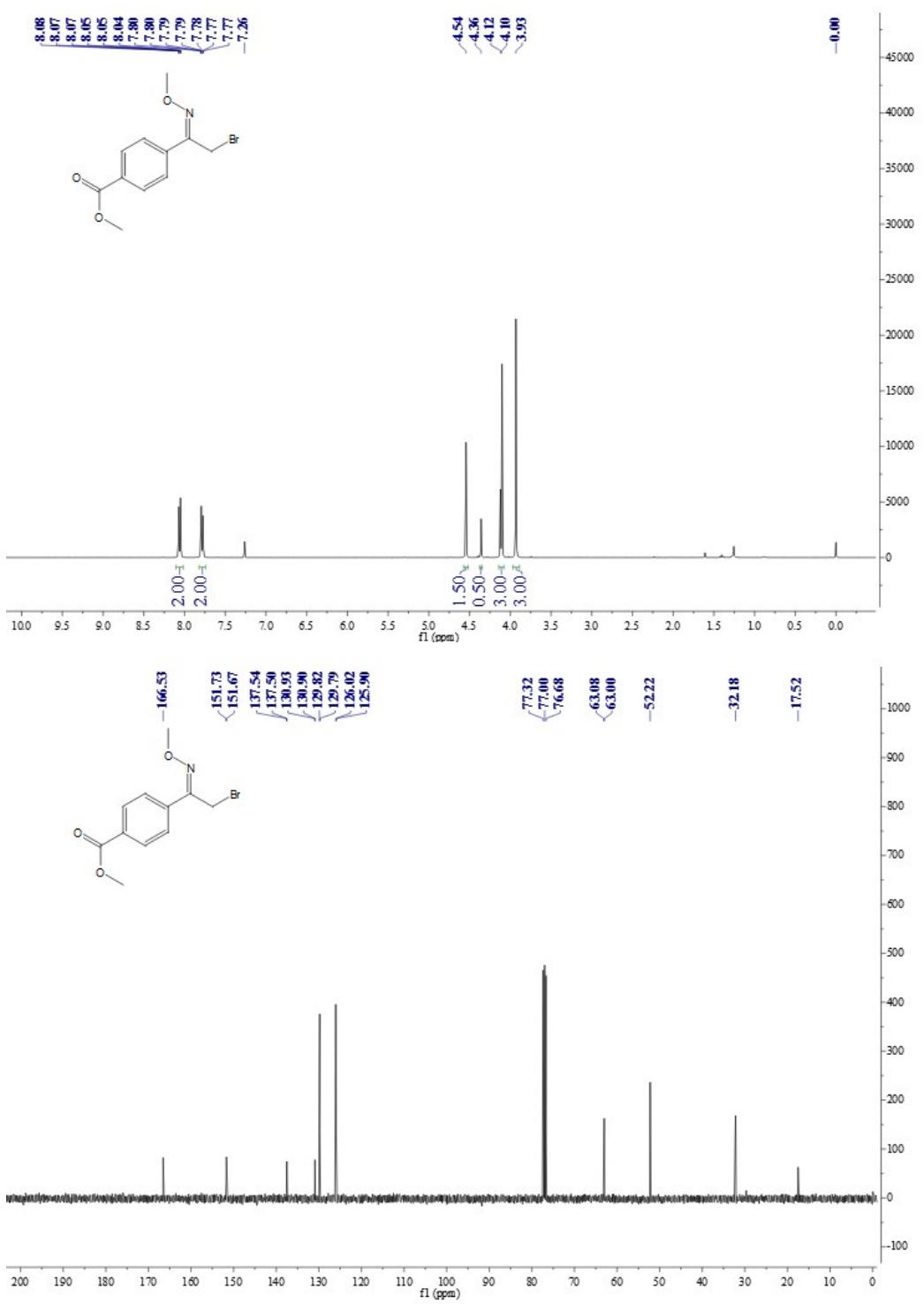
¹H and ¹³C of **1m**



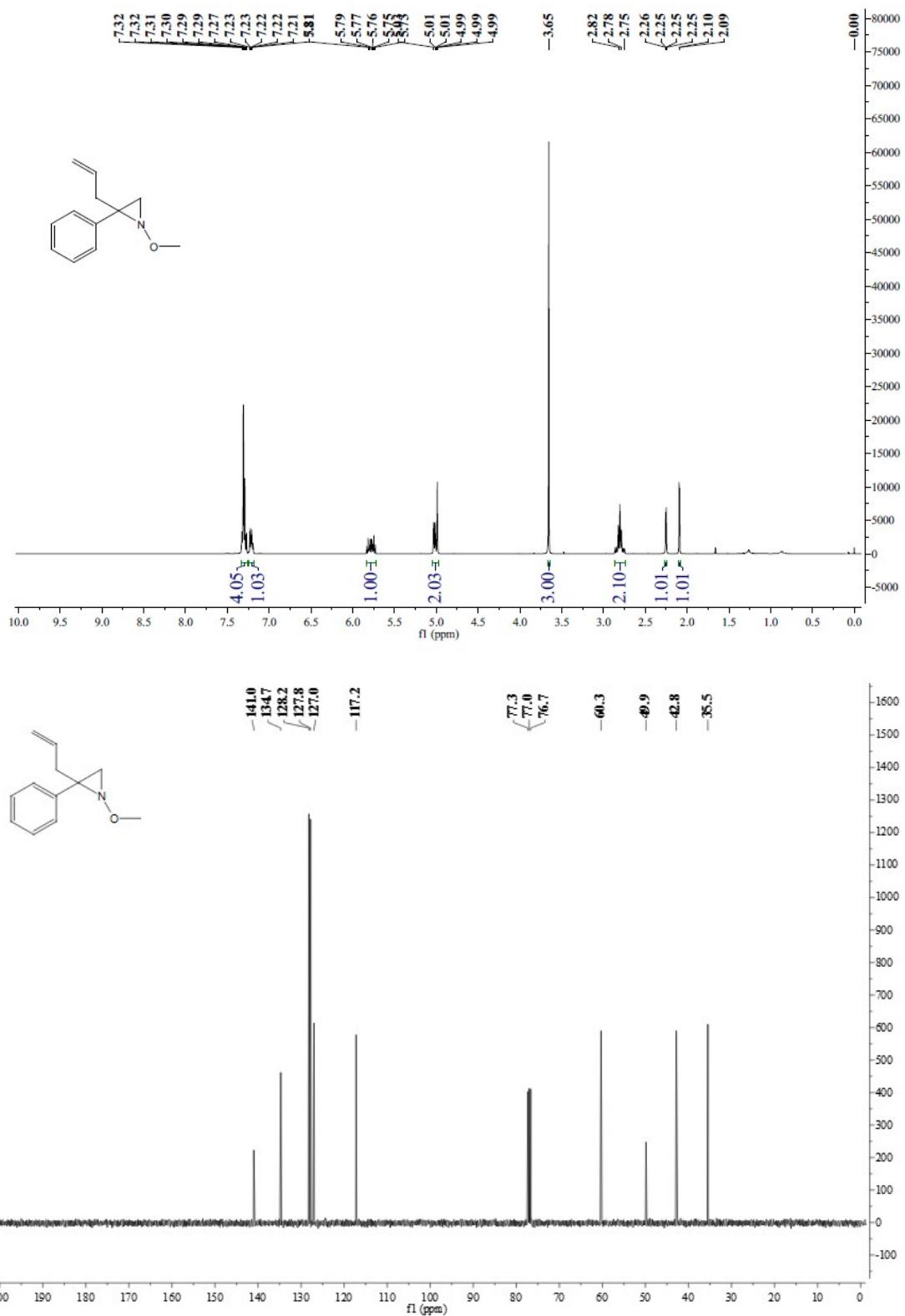
¹H and ¹³C of **1n**



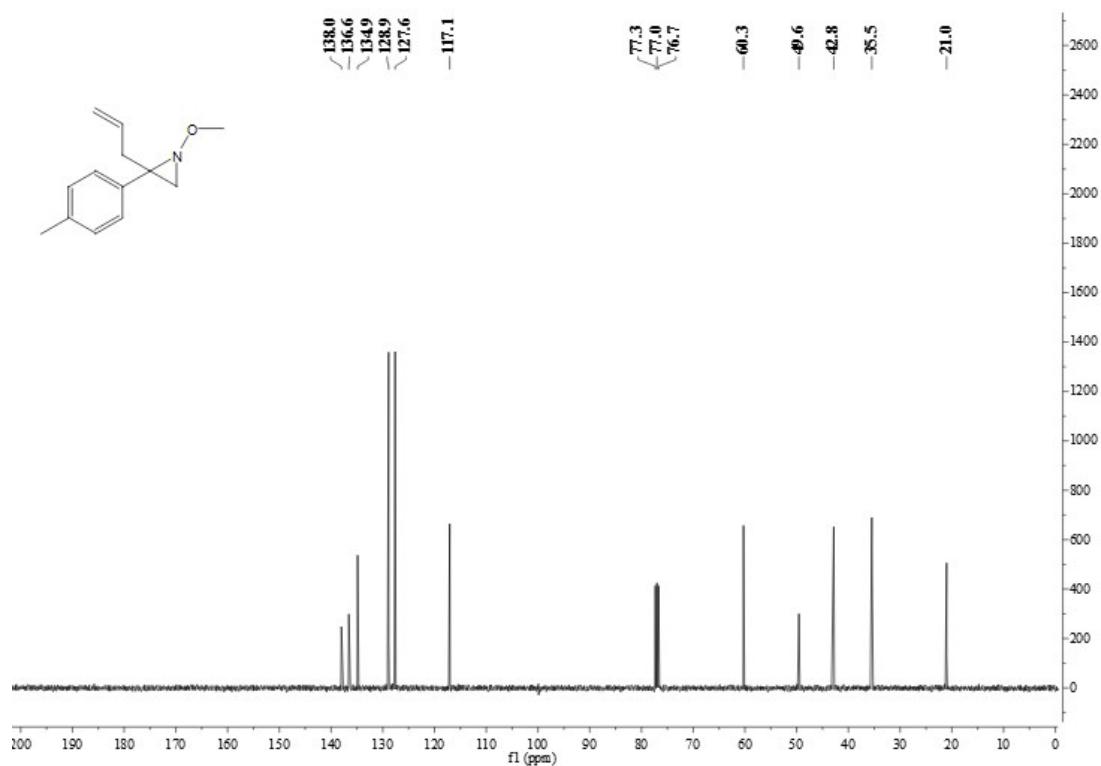
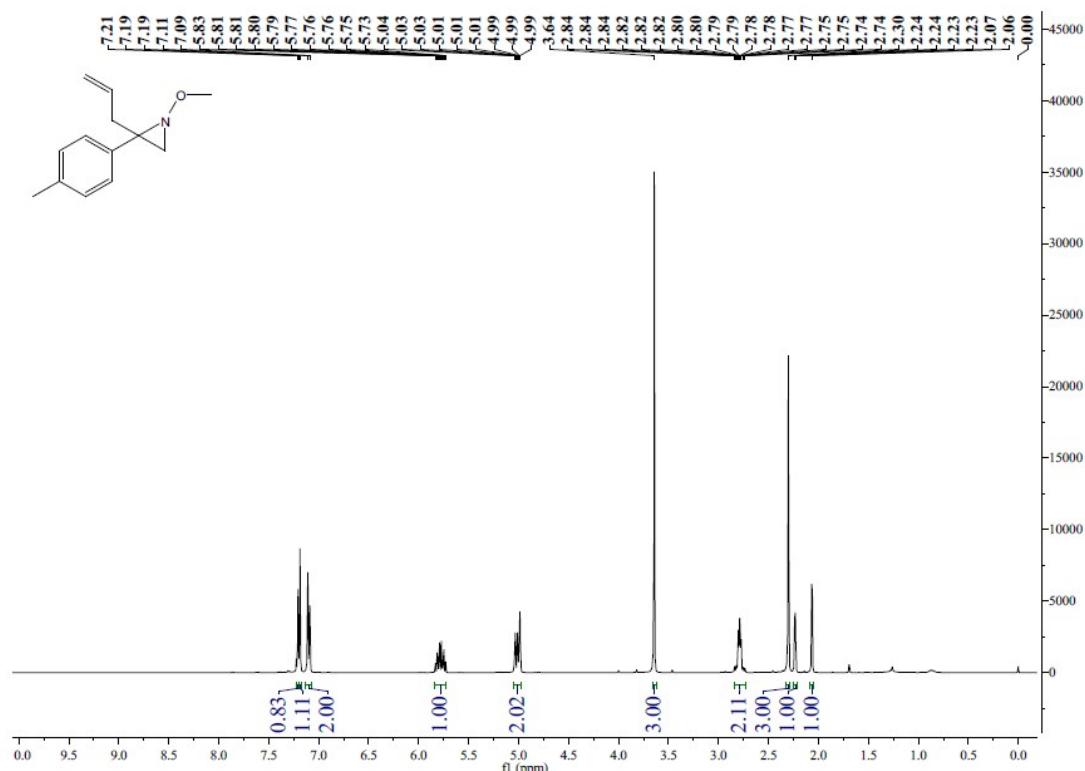
¹H and ¹³C of **1o**



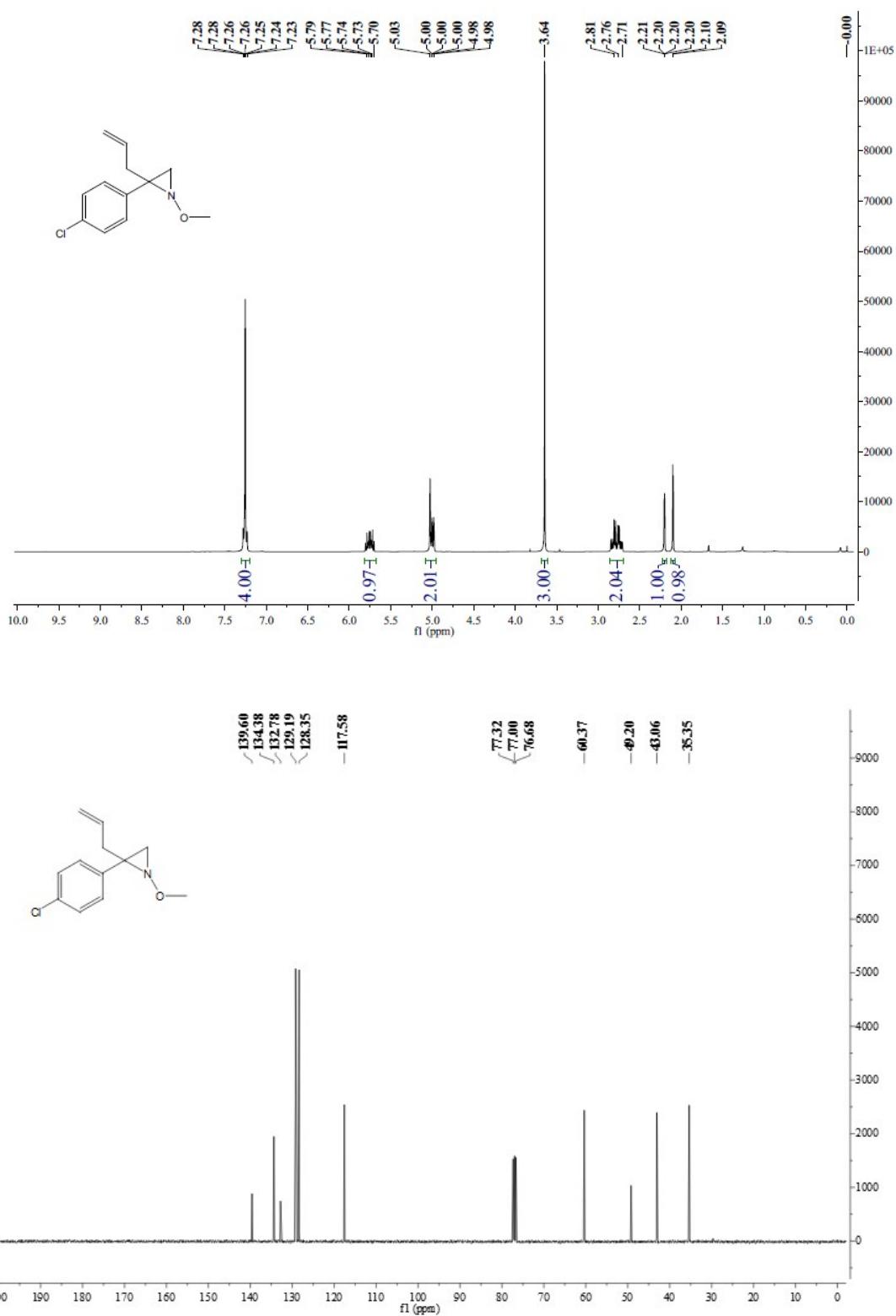
¹H and ¹³C of **3a**



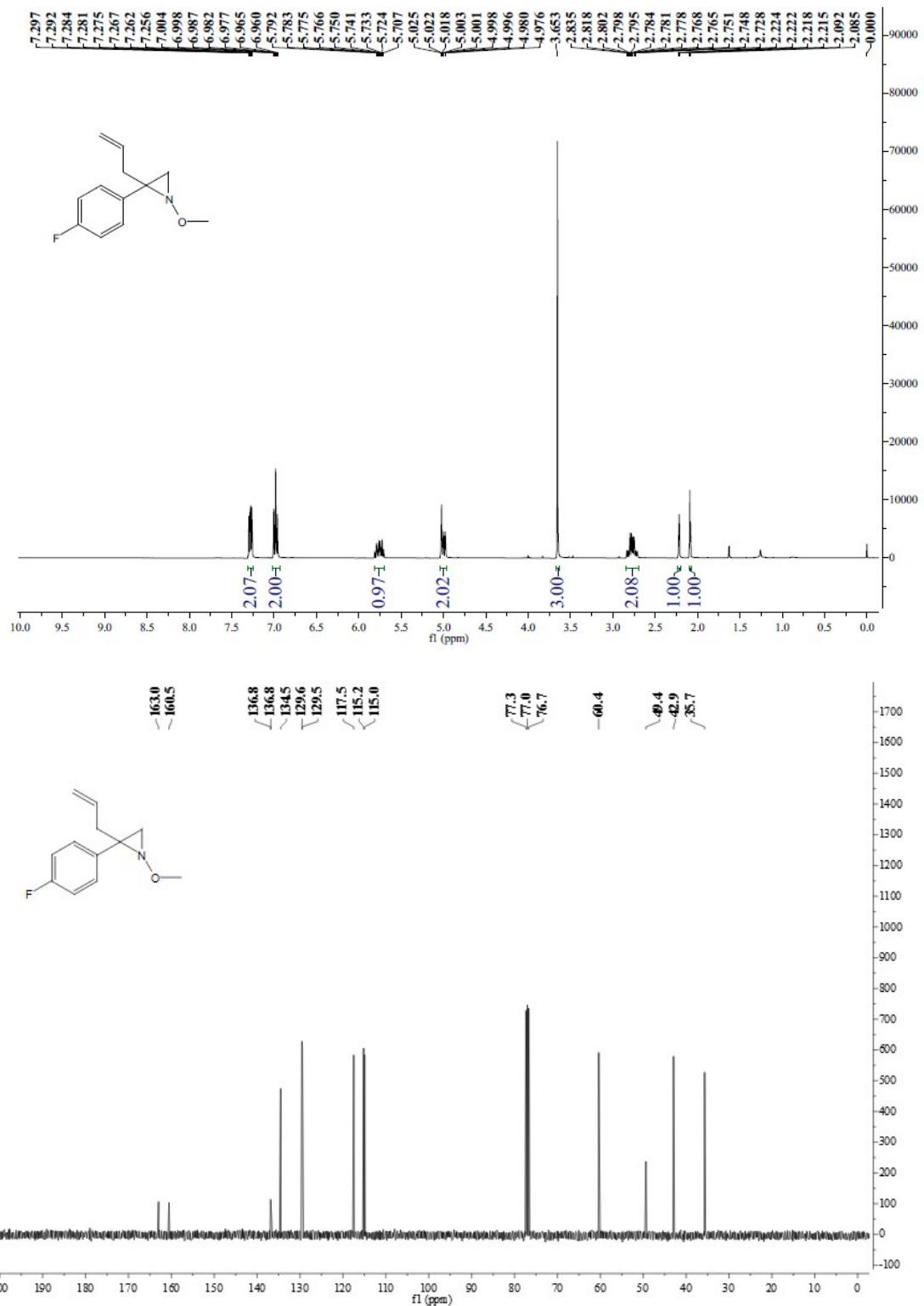
¹H and ¹³C of **3b**



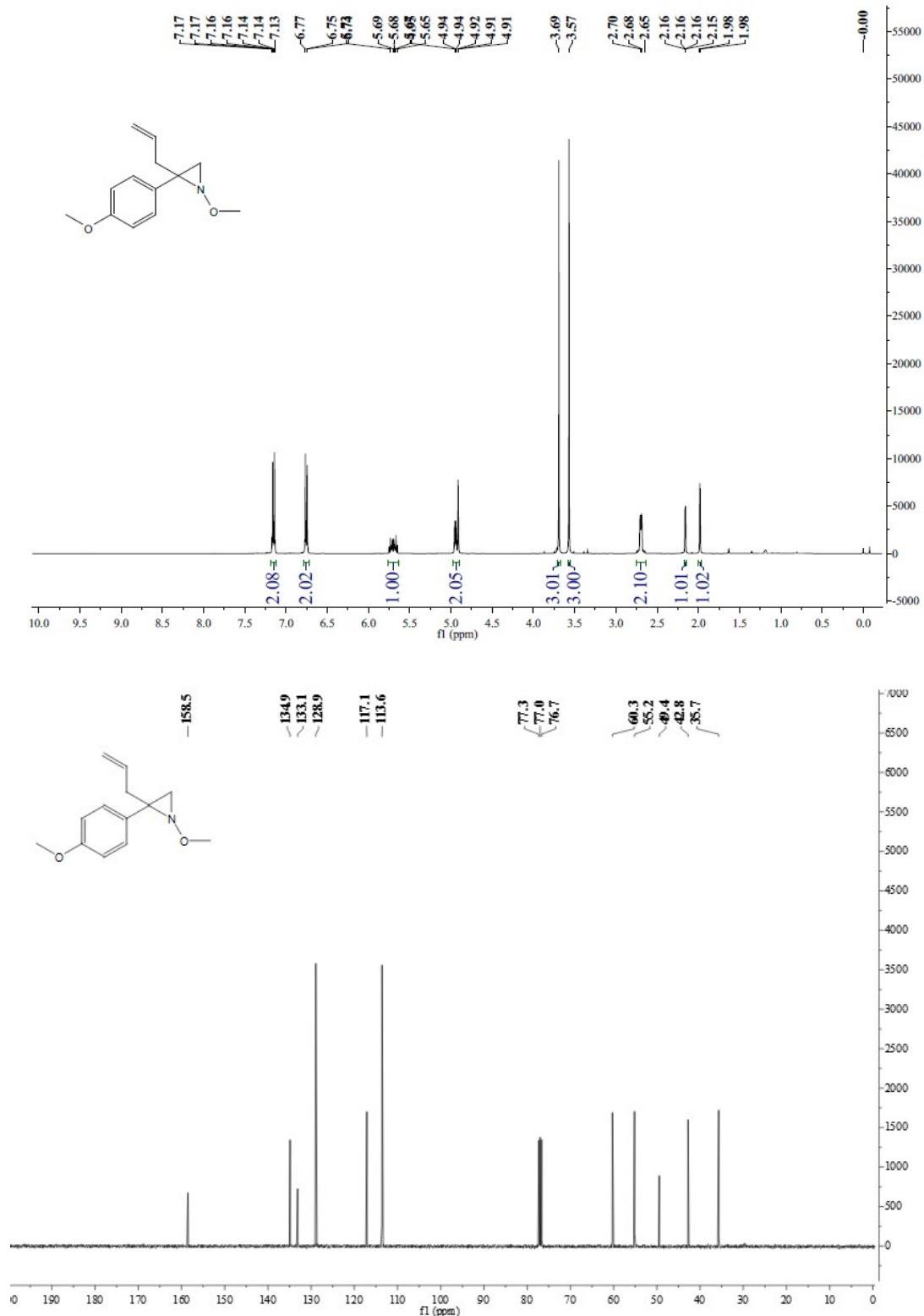
¹H and ¹³C of 3c



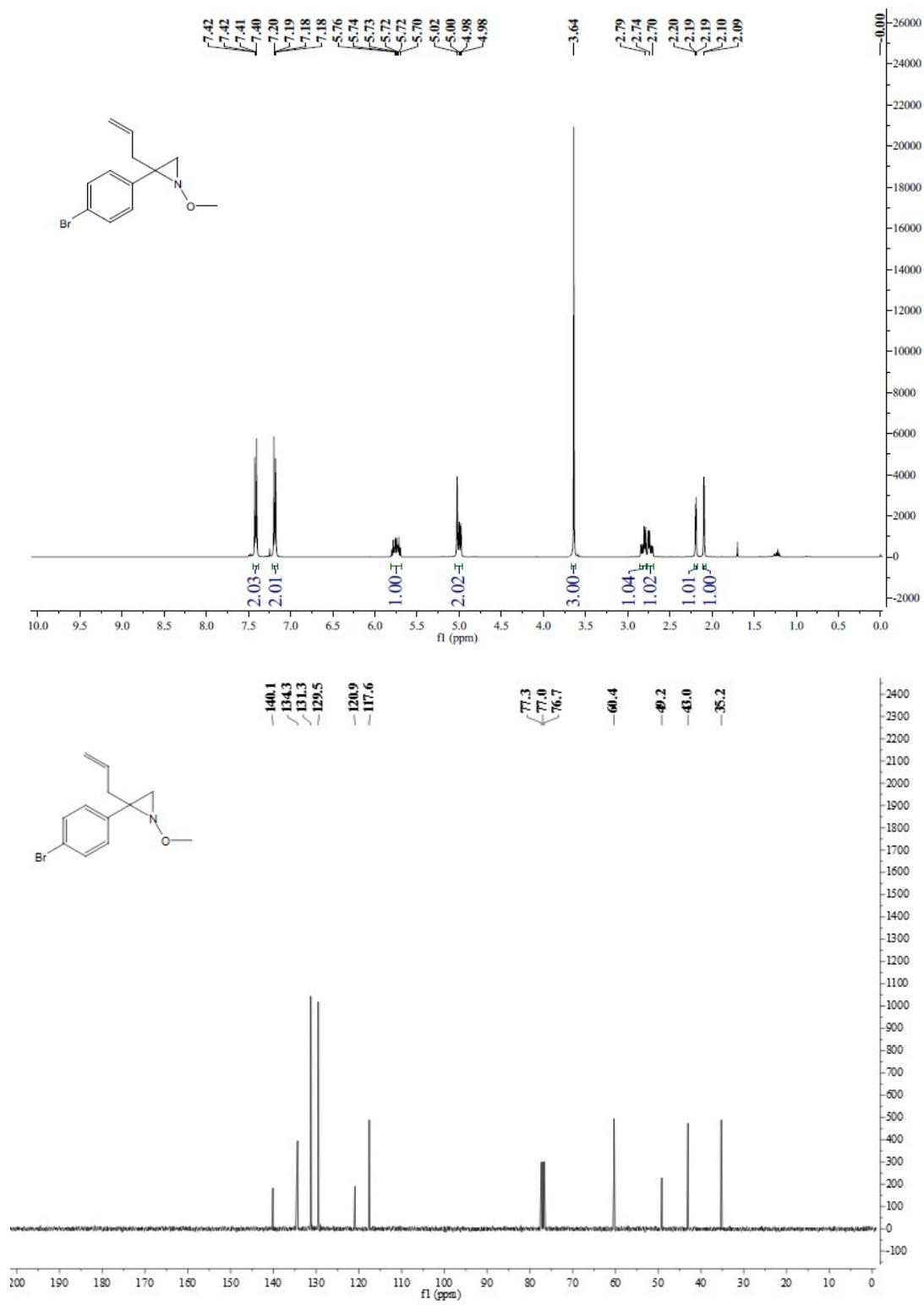
¹H and ¹³C of **3d**



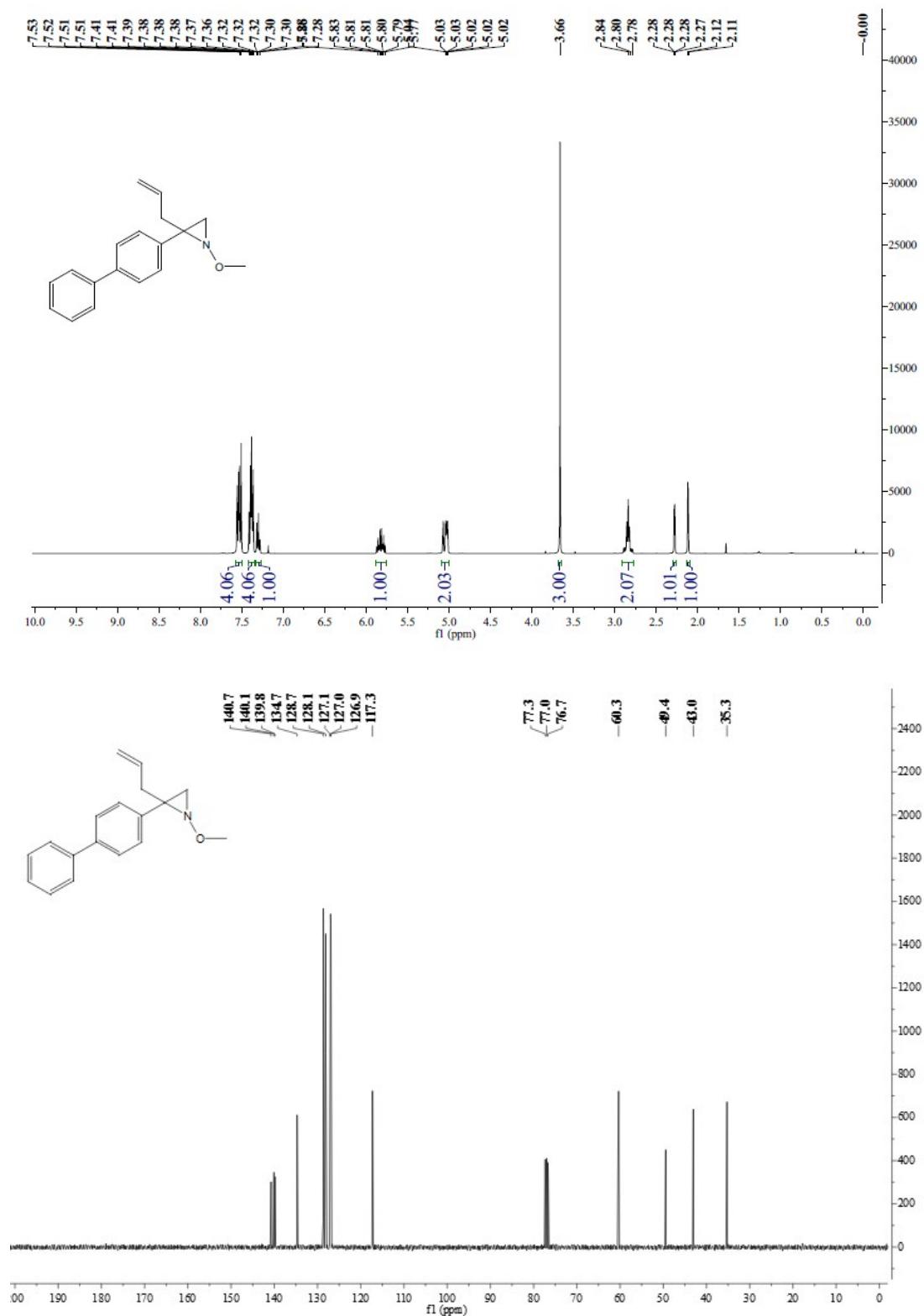
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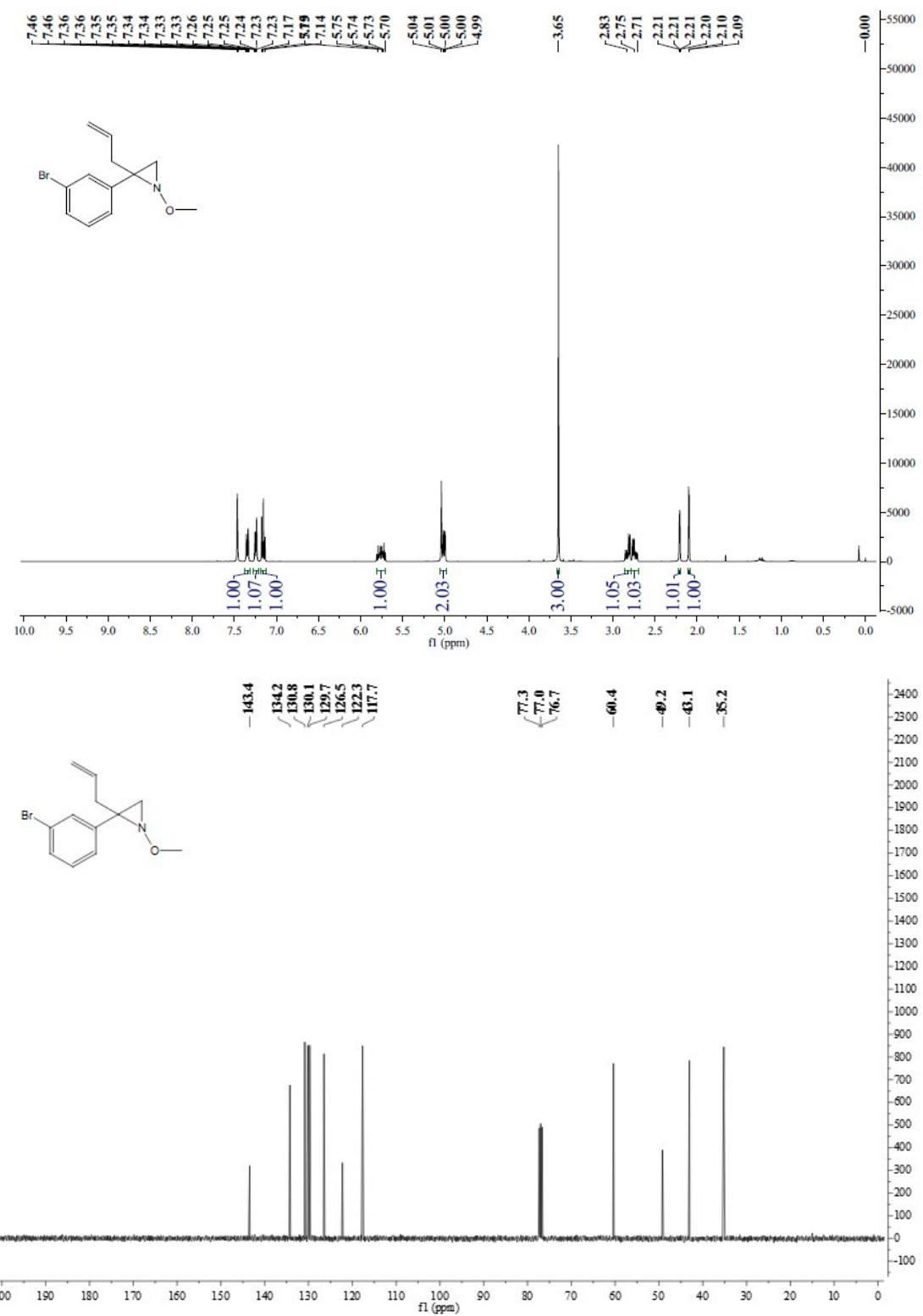
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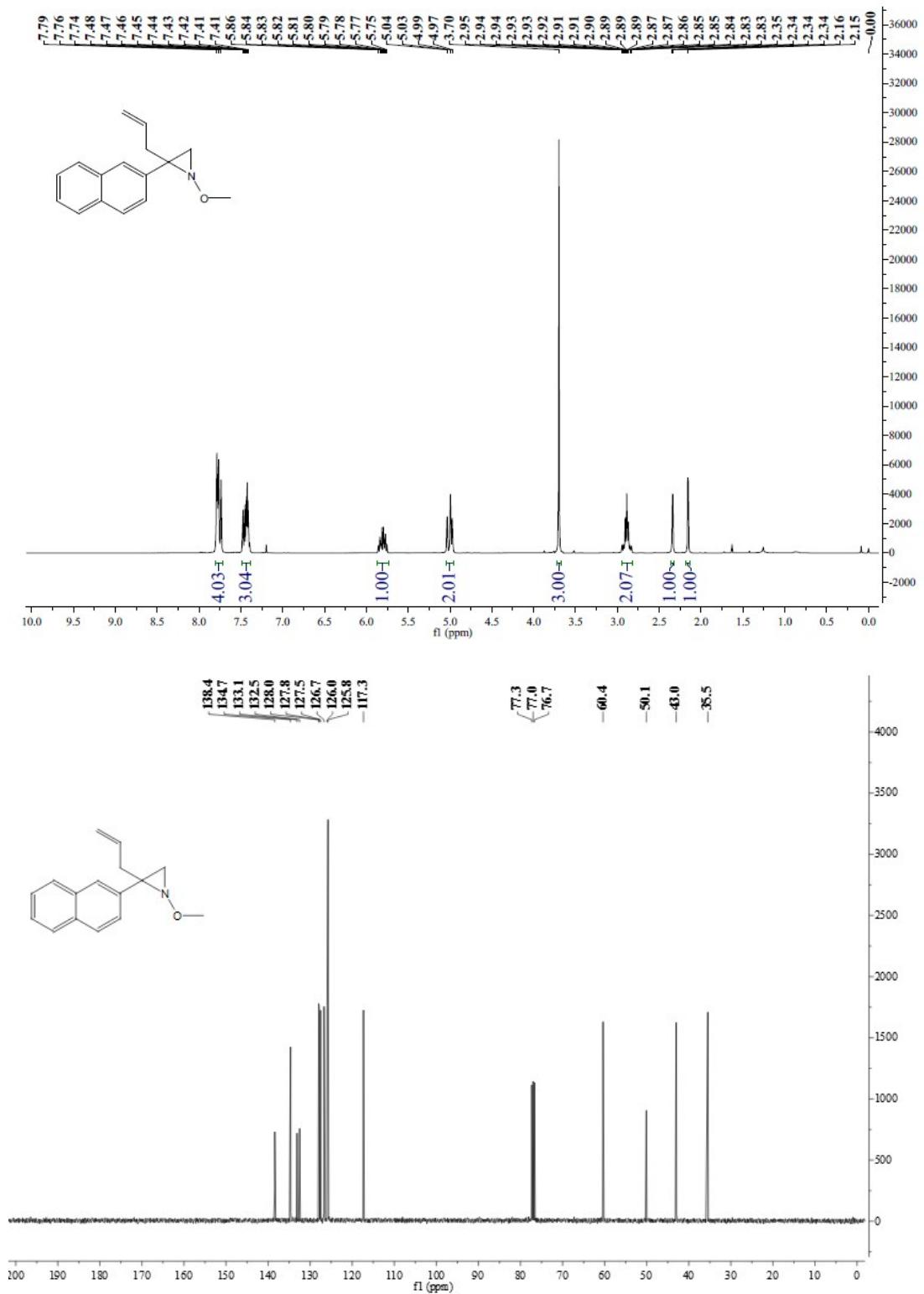
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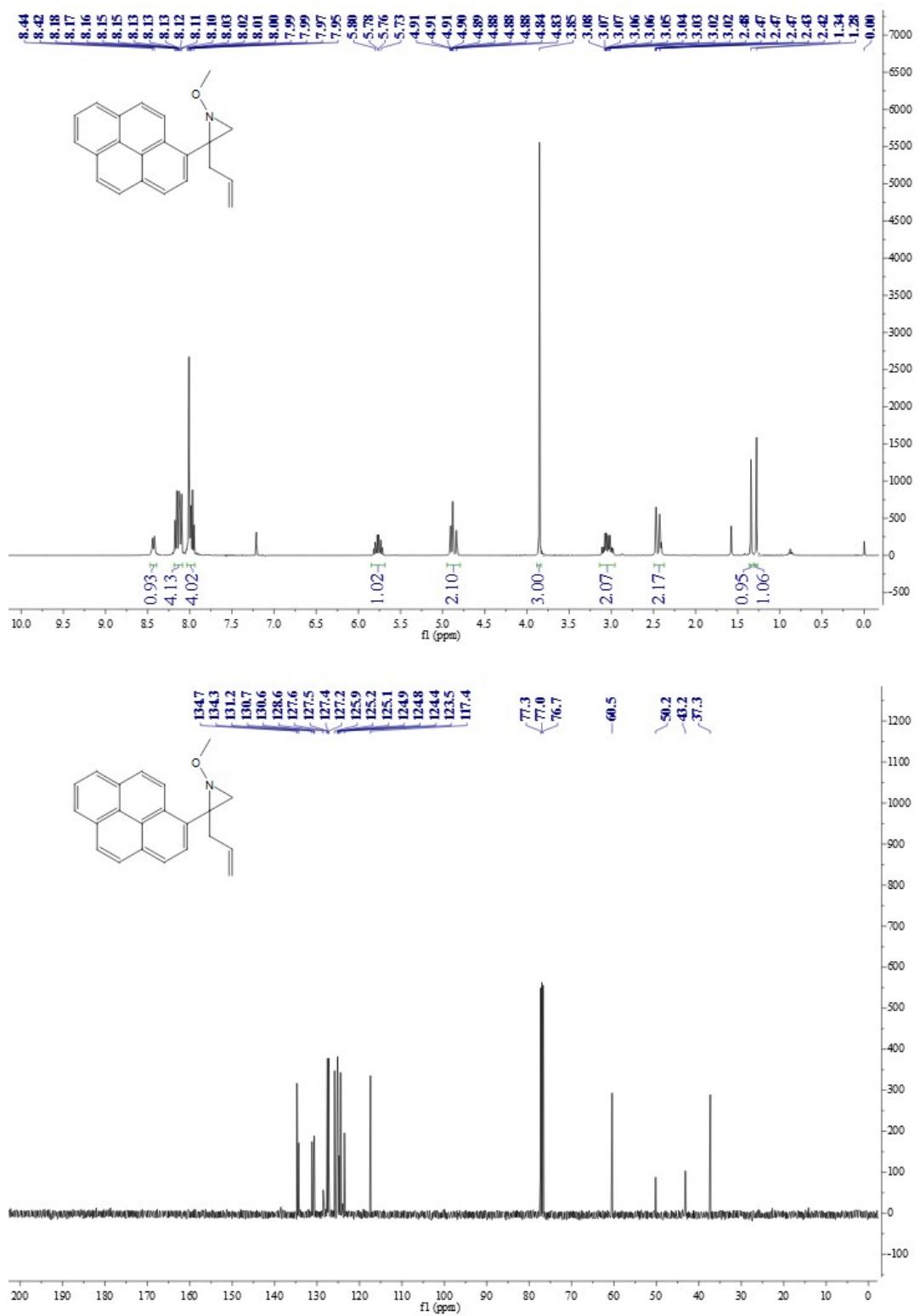
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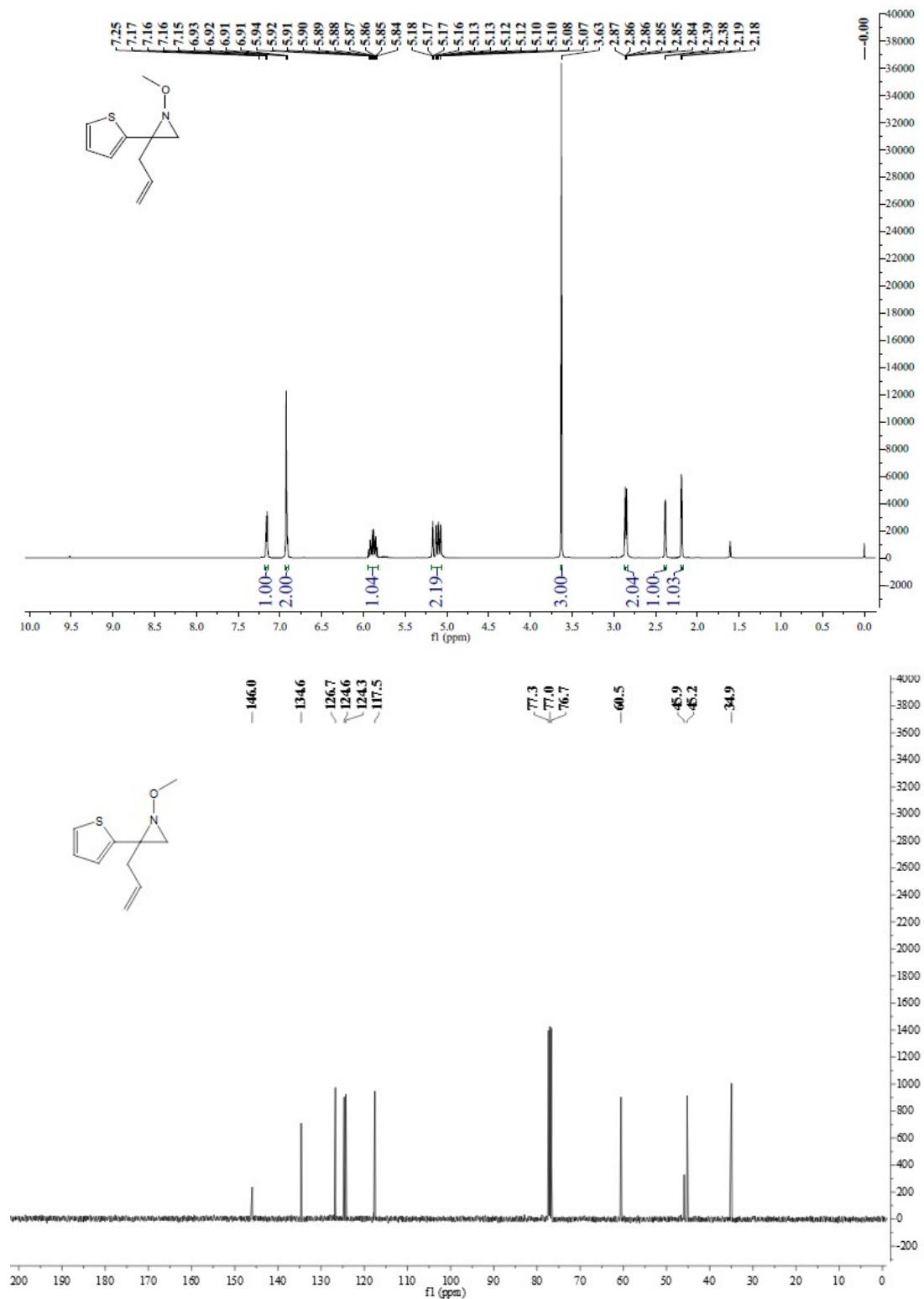
¹H and ¹³C of 3i



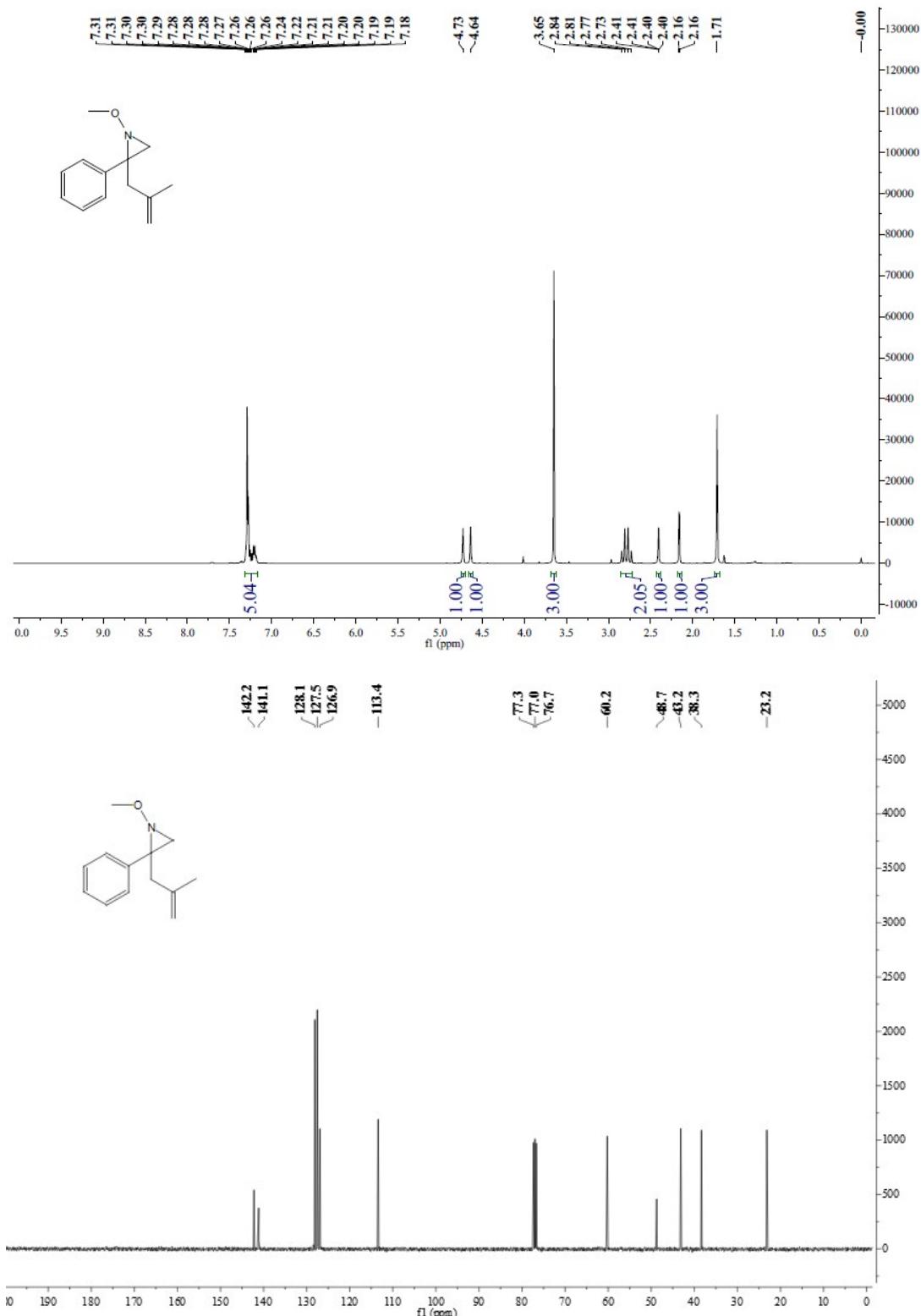
¹H and ¹³C of **3j**



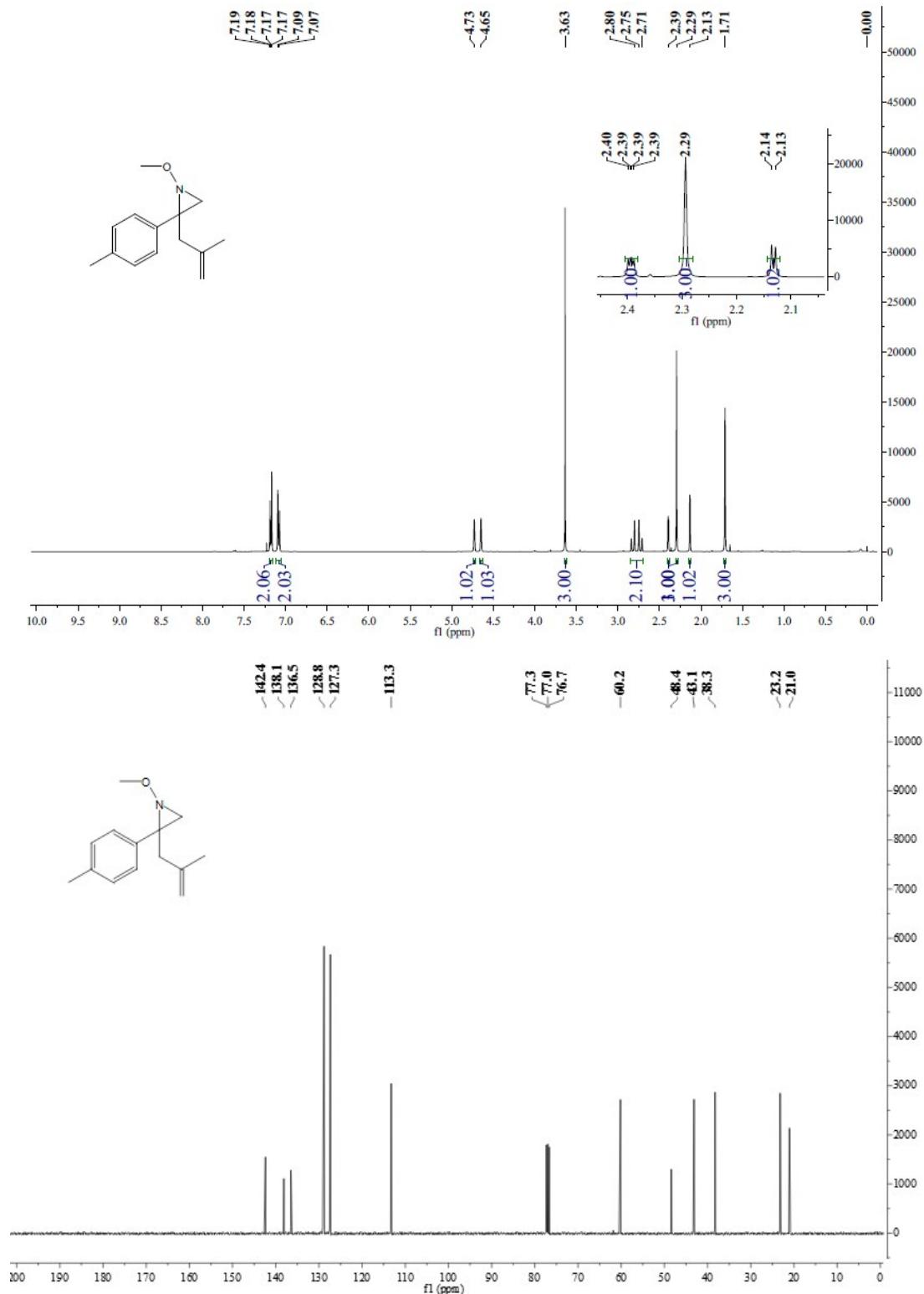
¹H and ¹³C of **3k**



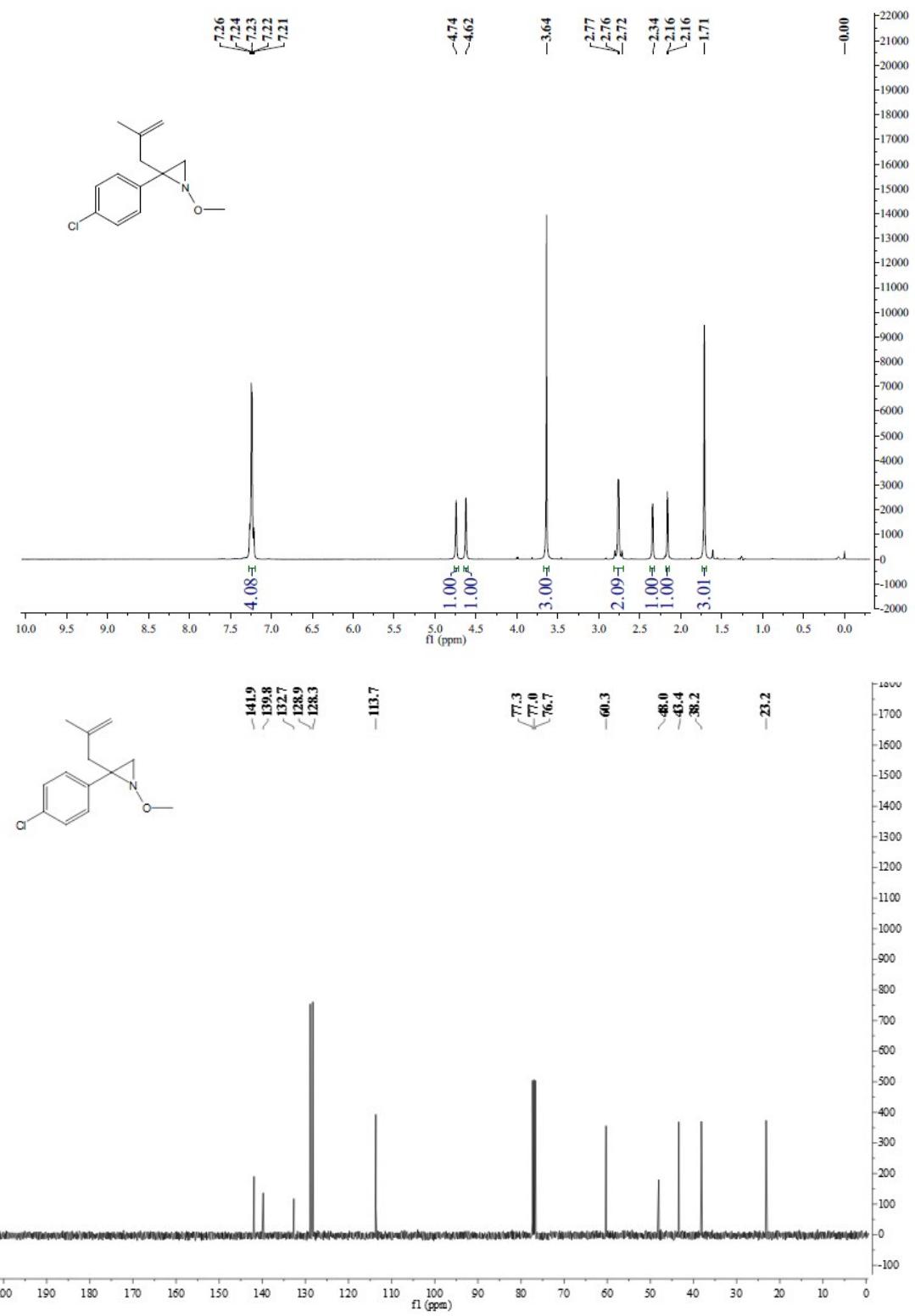
¹H and ¹³C of **3l**



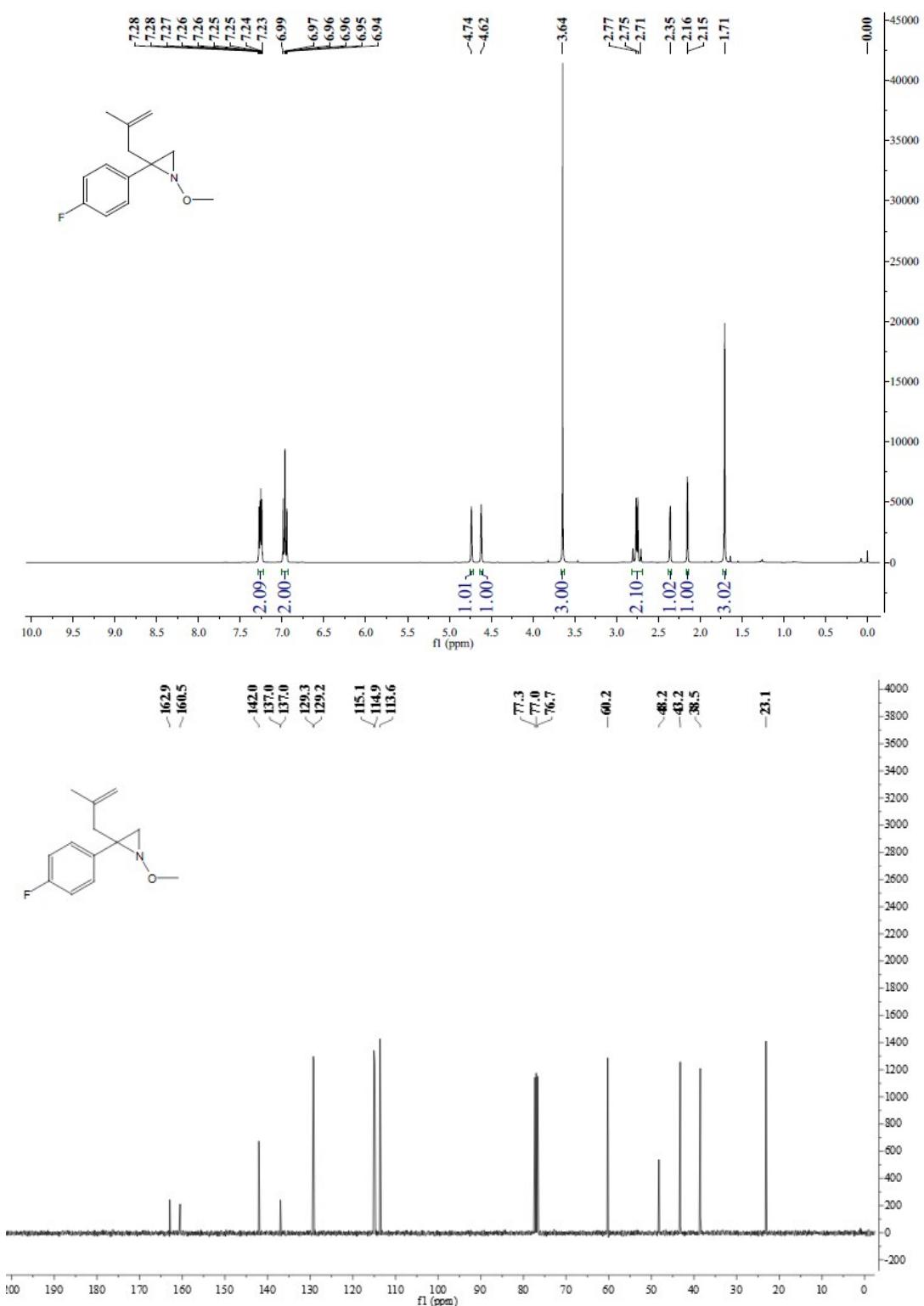
¹H and ¹³C of **3m**



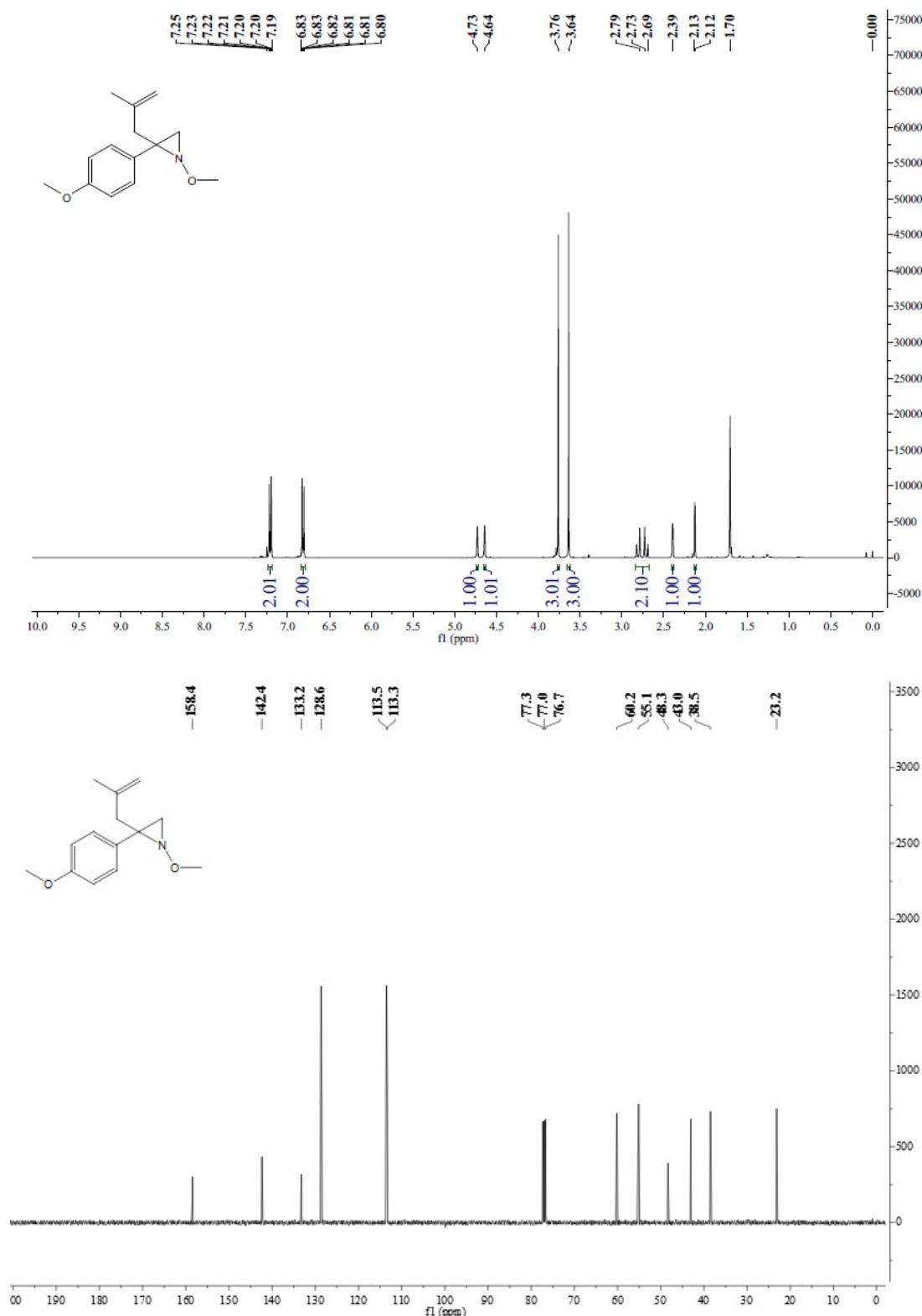
¹H and ¹³C of **3n**



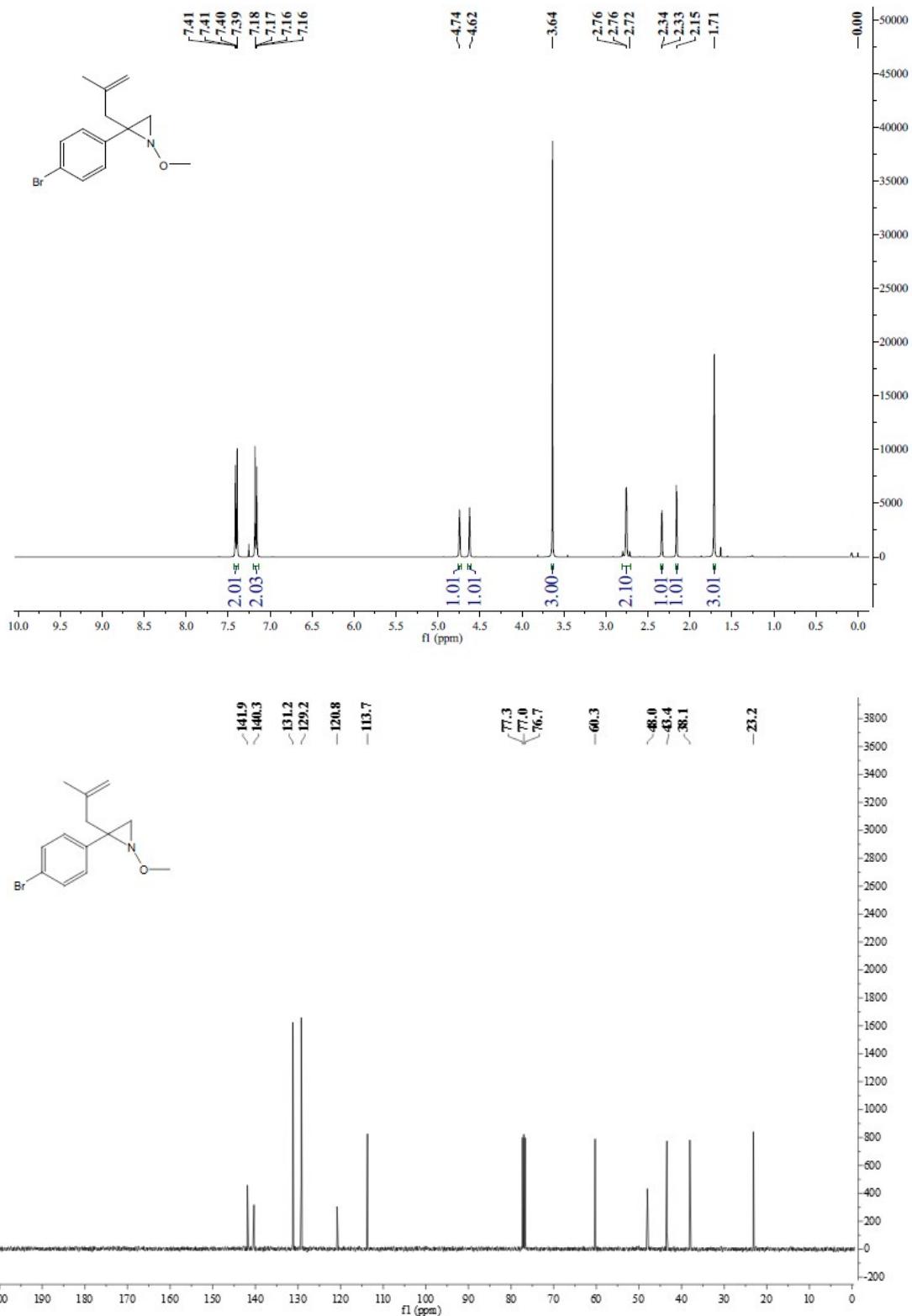
¹H and ¹³C of **3o**



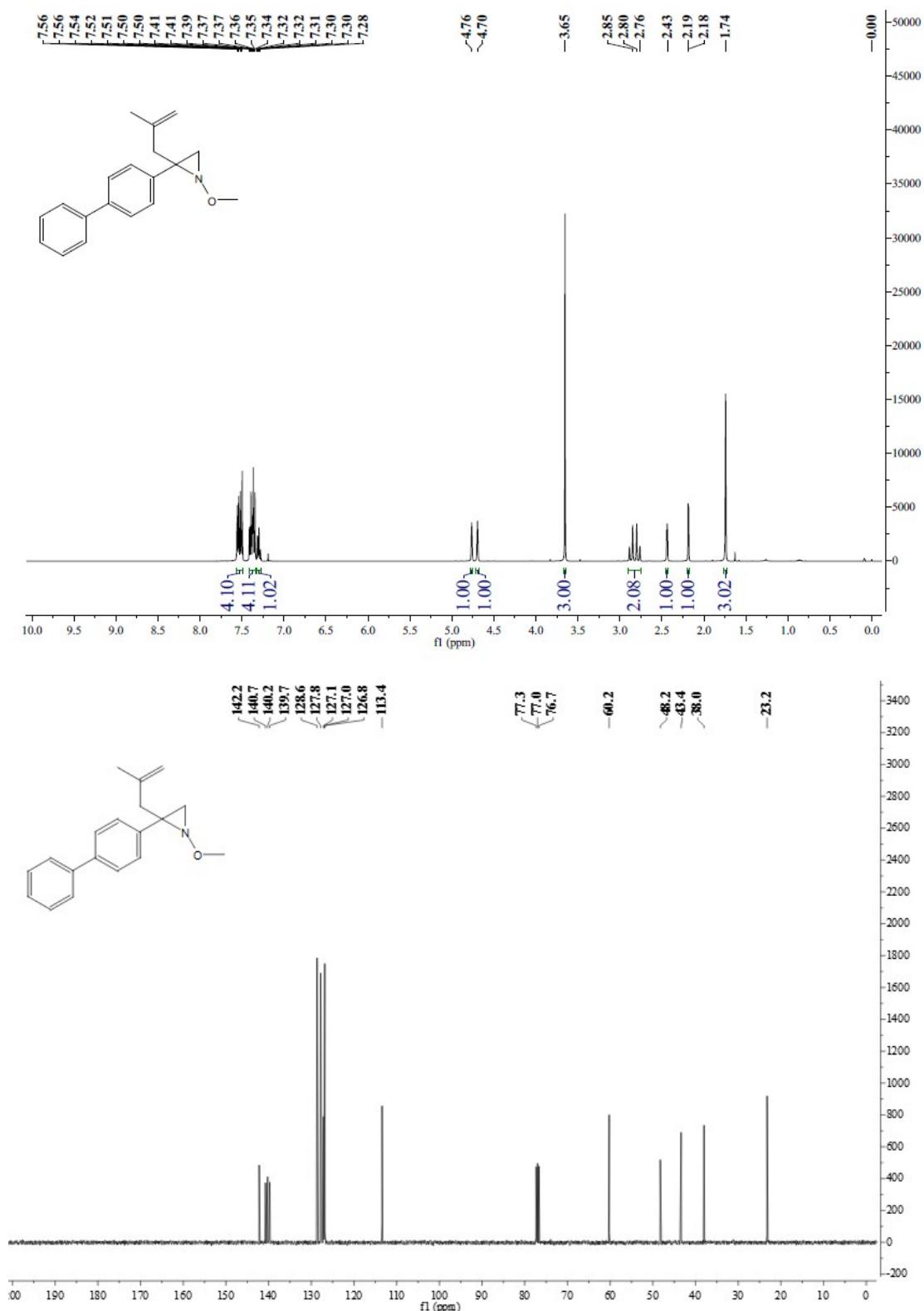
¹H and ¹³C of 3p



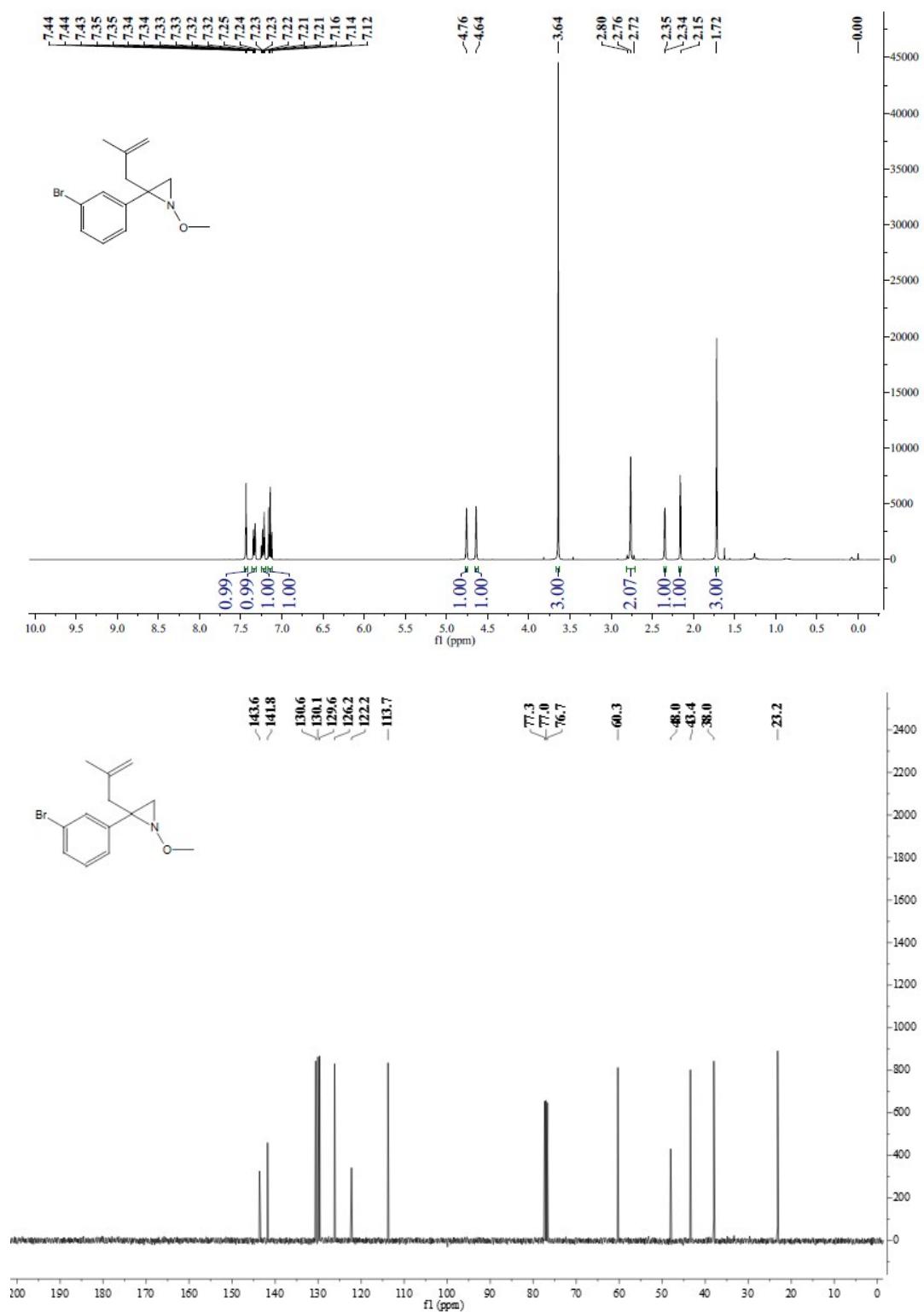
¹H and ¹³C of **3q**



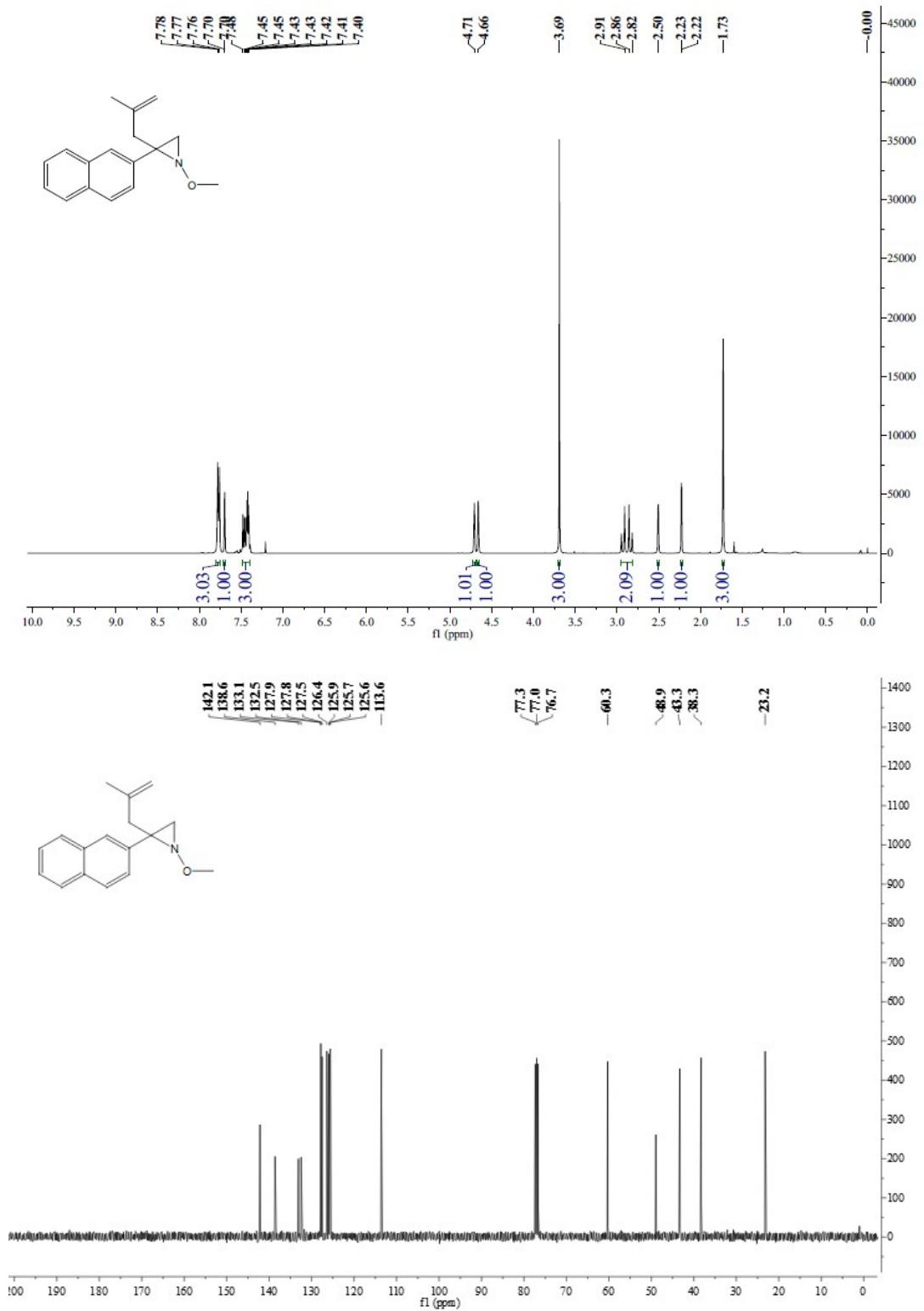
¹H and ¹³C of **3r**



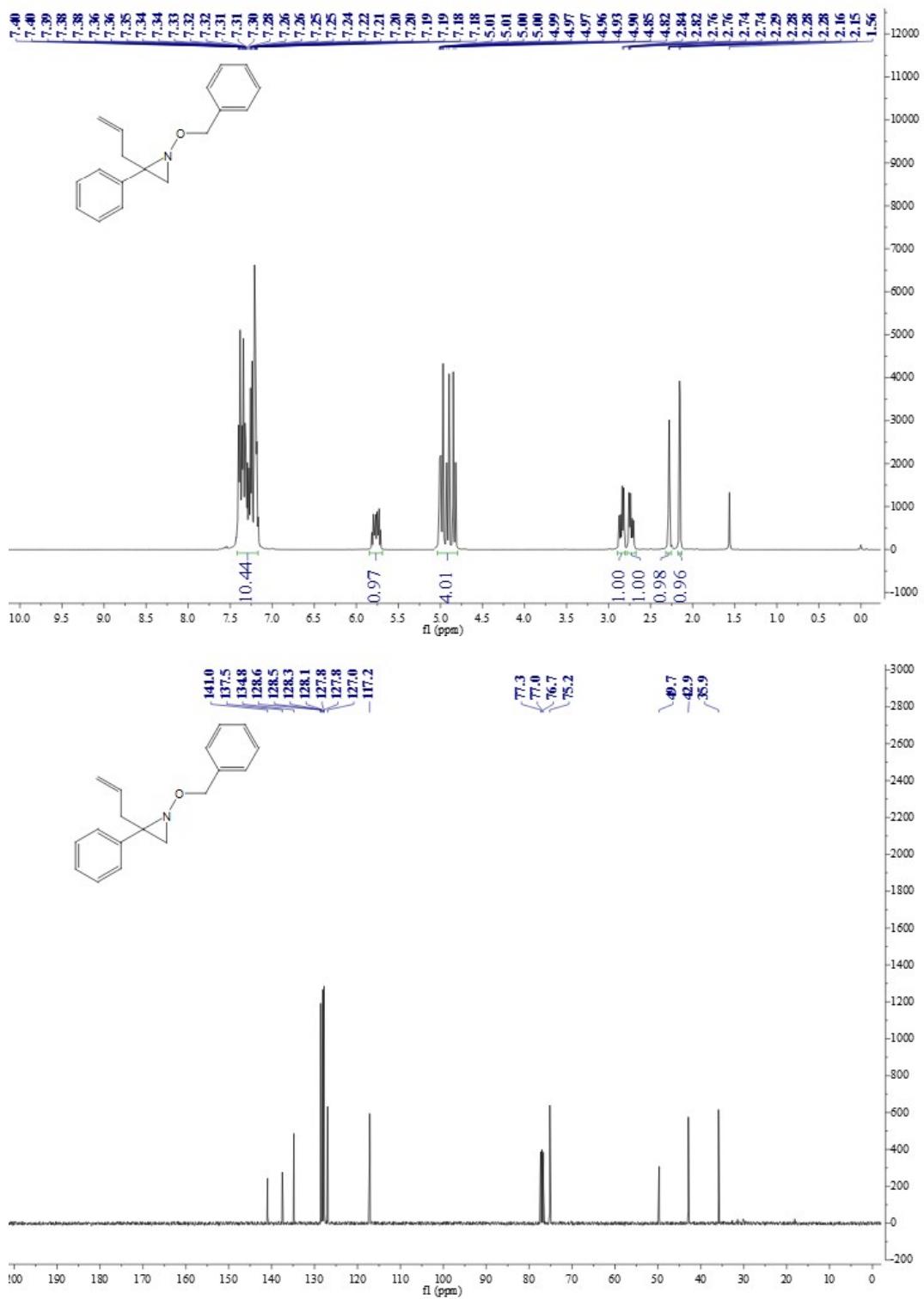
¹H and ¹³C of **3s**



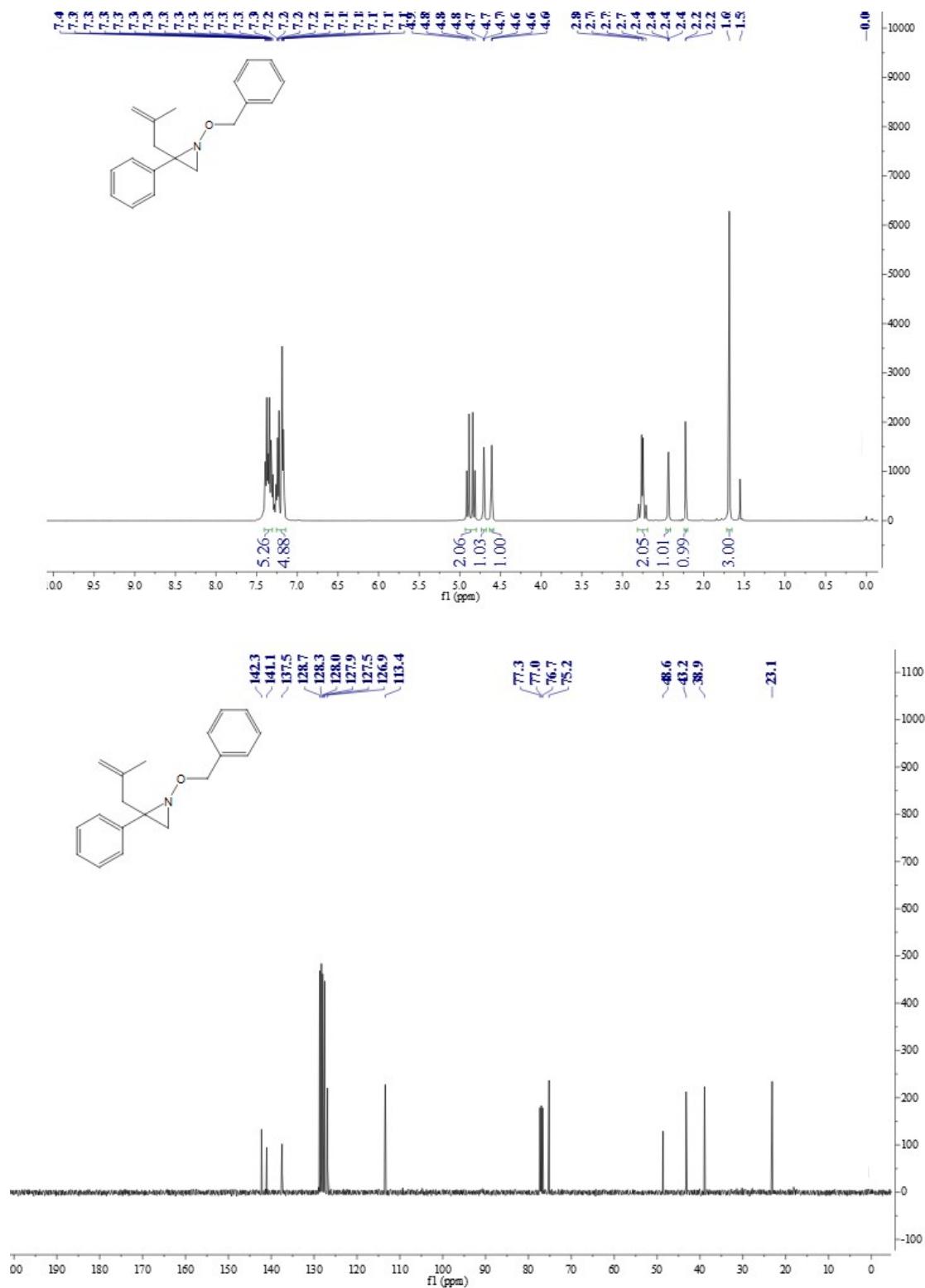
¹H and ¹³C of 3t



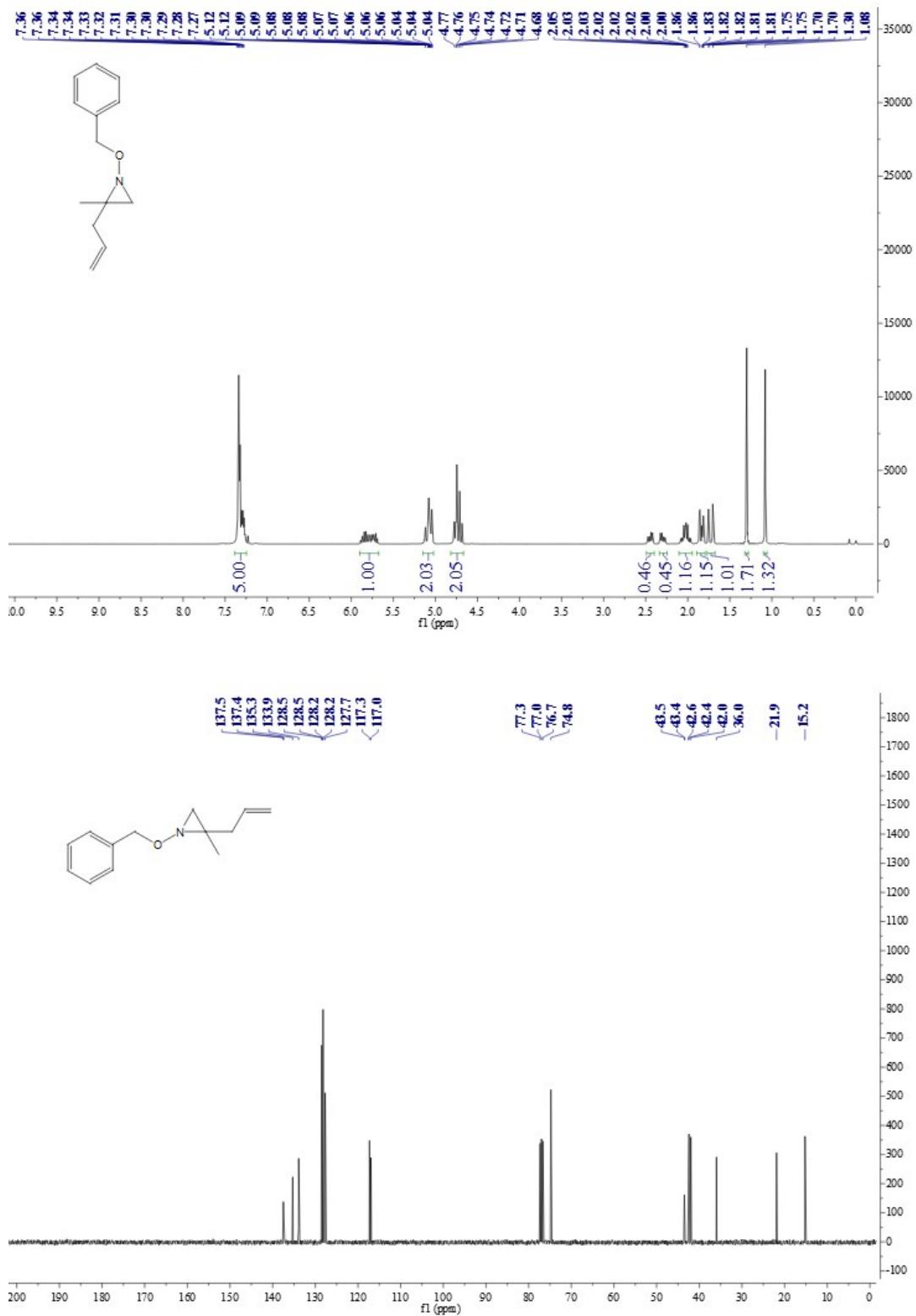
¹H and ¹³C of **3u**



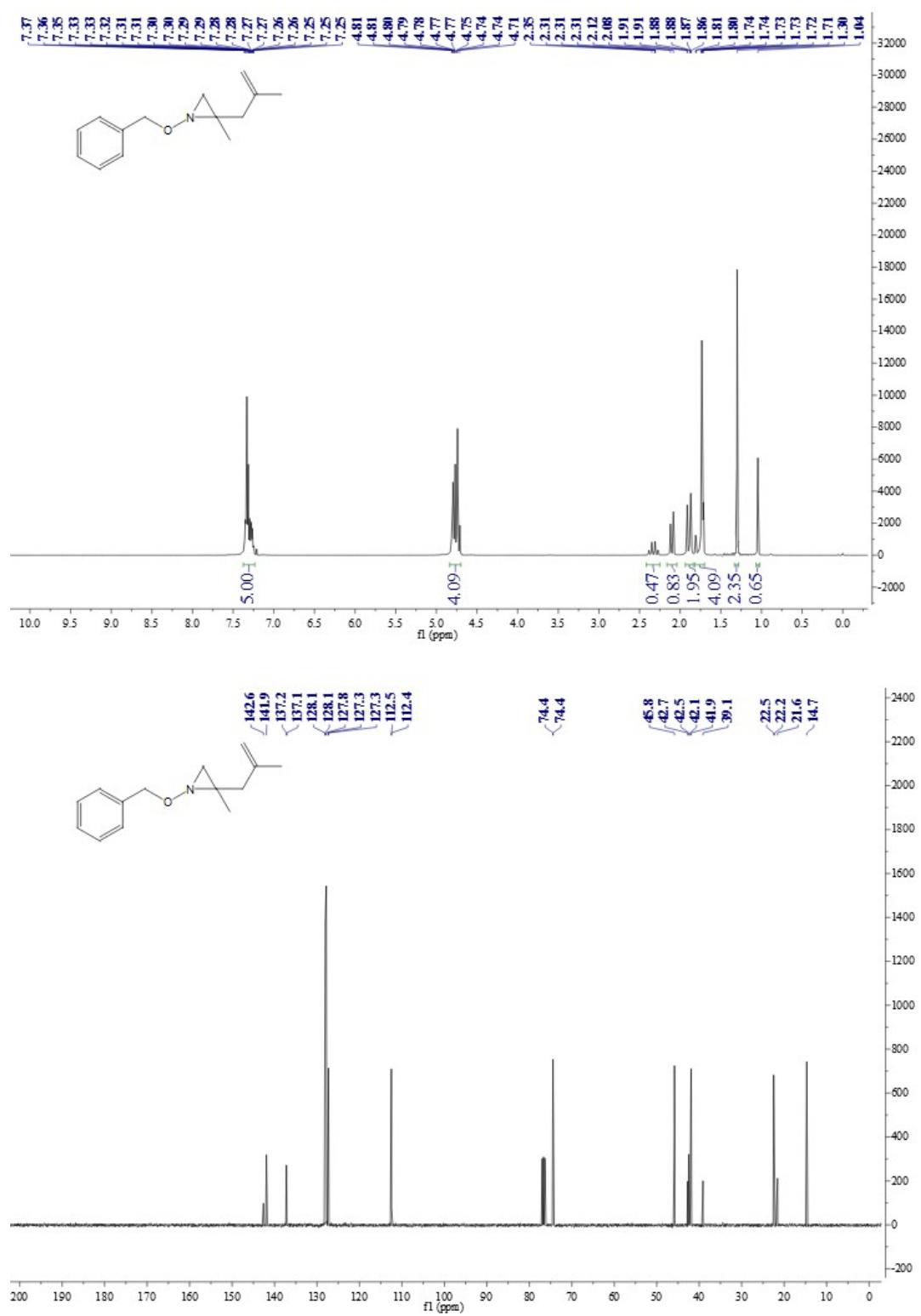
¹H and ¹³C of 3v



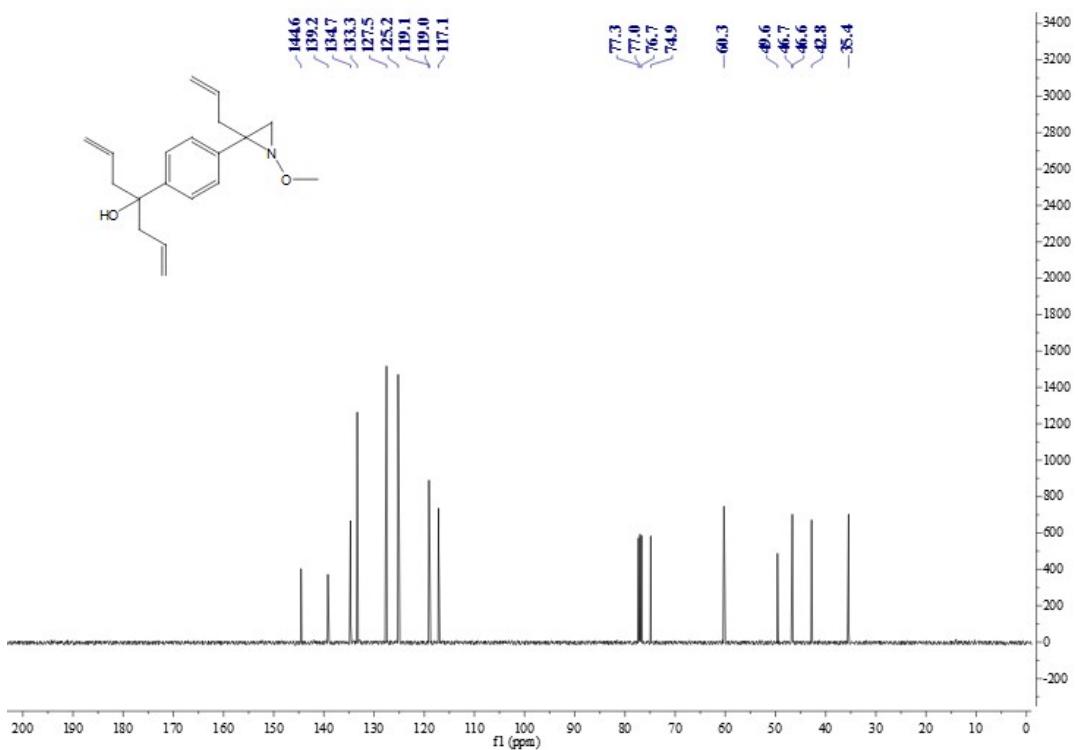
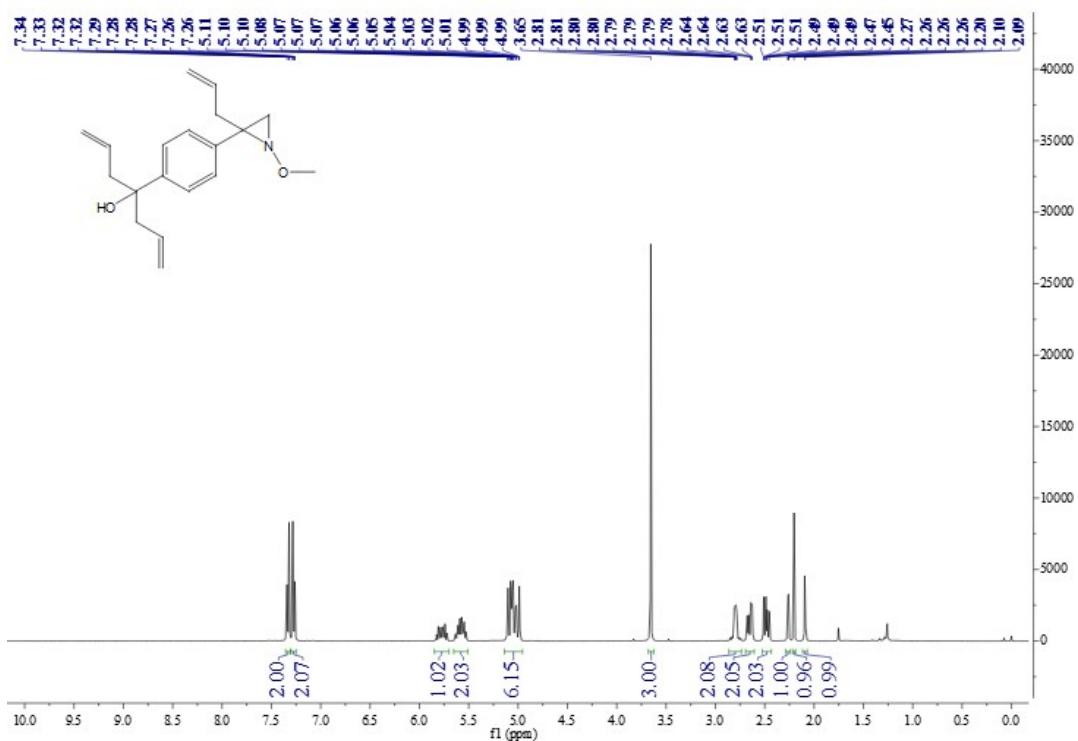
¹H and ¹³C of 3w



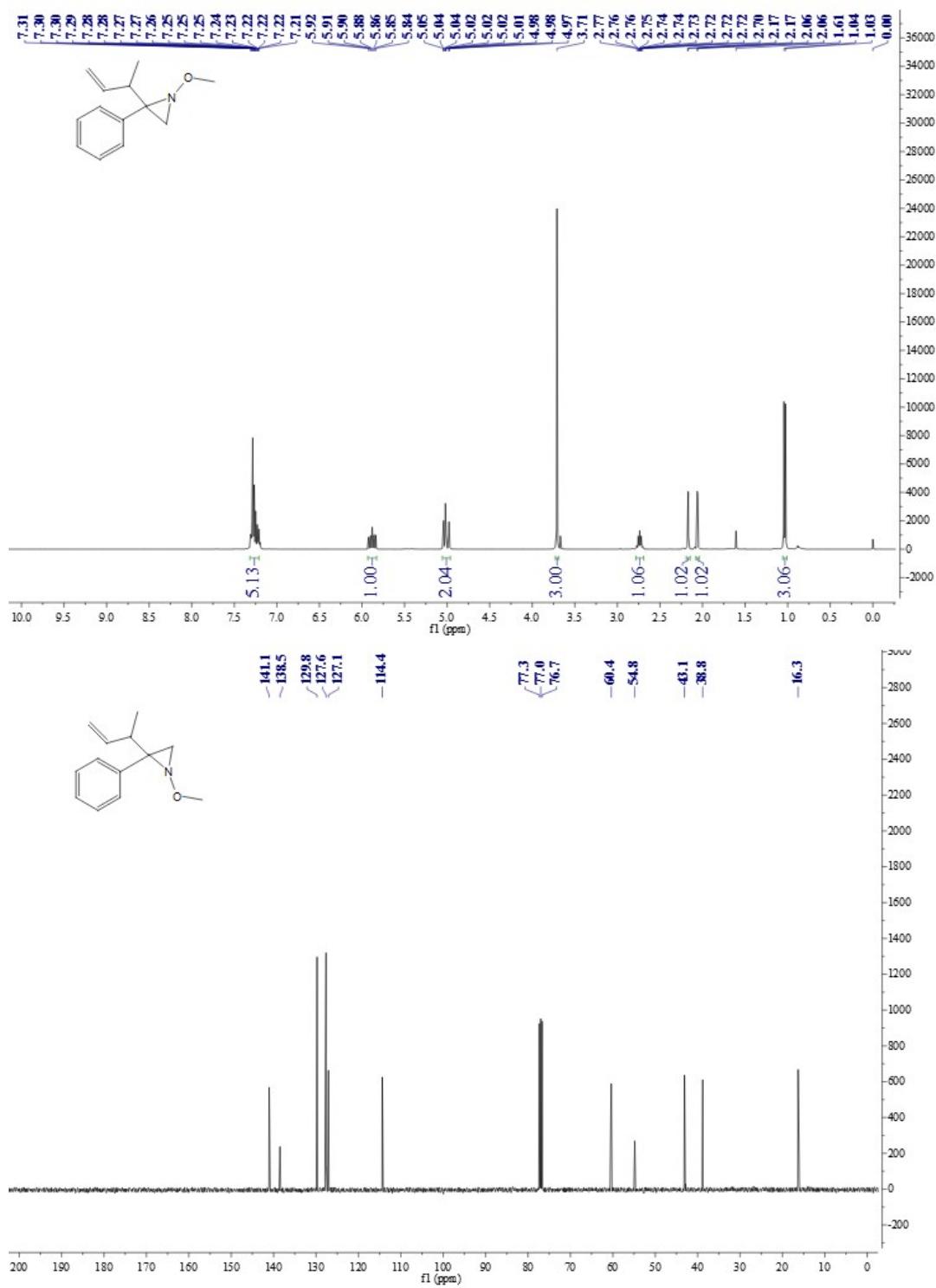
¹H and ¹³C of **3x**



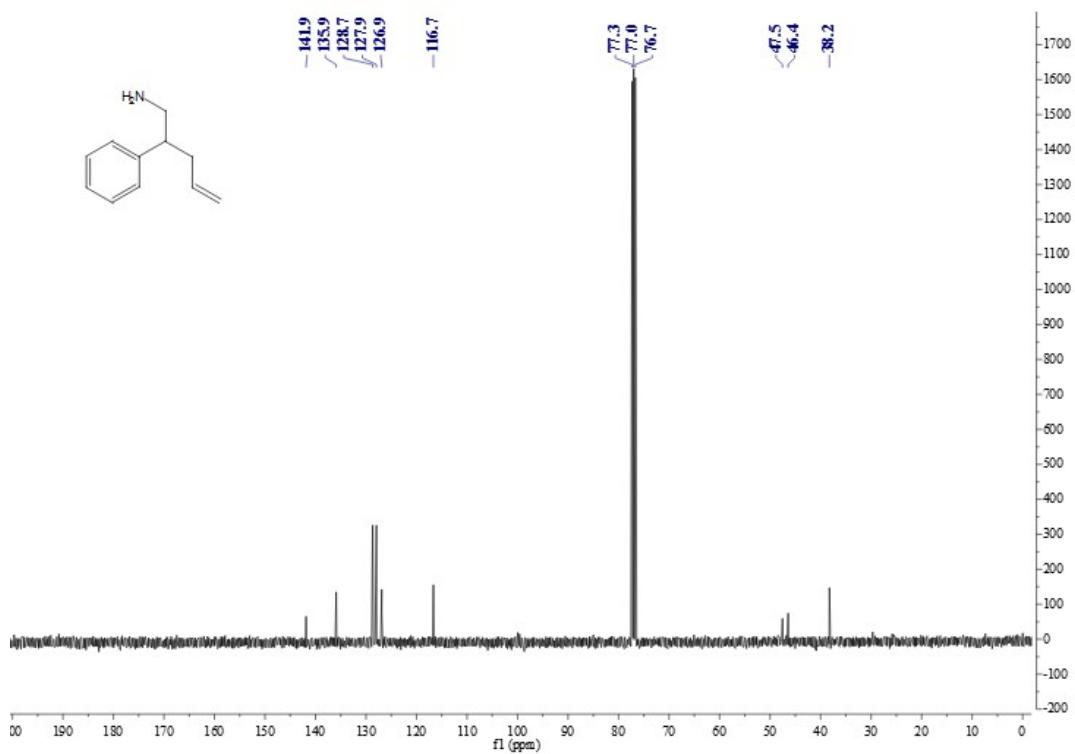
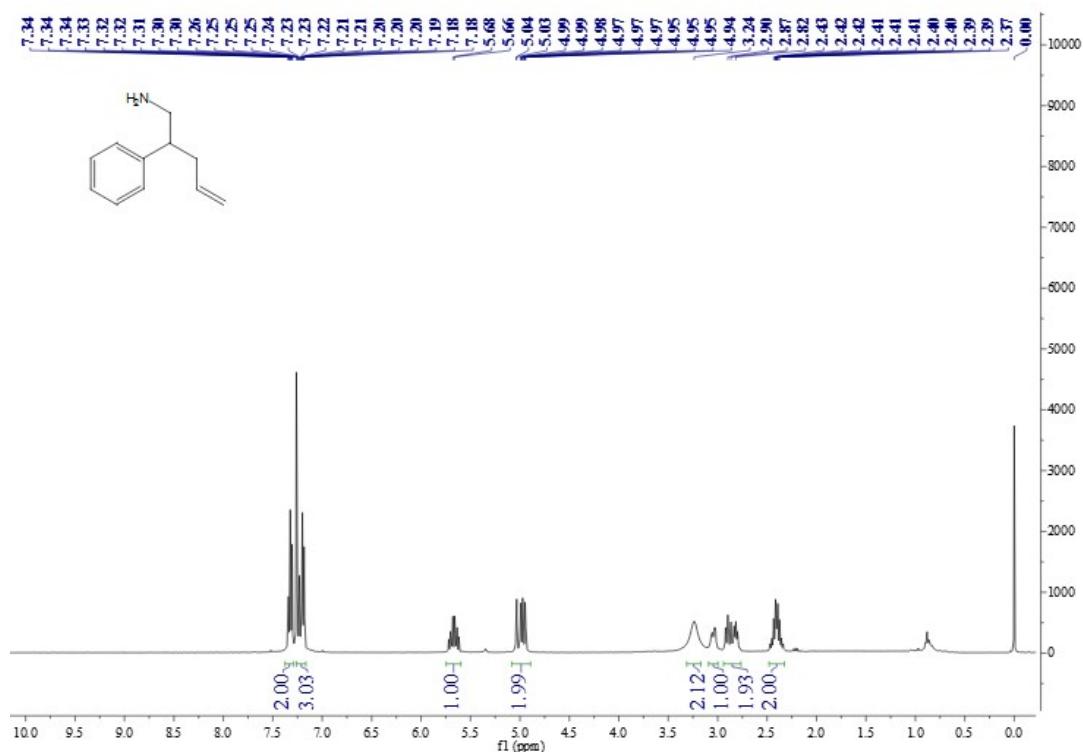
¹H and ¹³C of 3y



¹H and ¹³C of **3z**



¹H and ¹³C of **4aa**



¹H and ¹³C of **4ab**

