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Microwave-assisted Palladium-catalysed isonitrile insertion in 2-bromophenylureas for efficient synthesis of 4-substituted imino 4*H*-benzo[*d*][1,3]oxazin-2-amines

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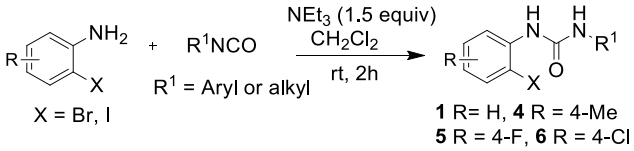
Experimental

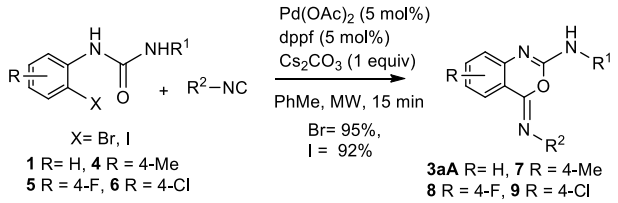
General- All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Melting points are uncorrected and were determined in capillary tubes on a melting point apparatus containing silicon oil. IR spectra were recorded using a Perkin-Elmer FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometer, using TMS as an internal standard (chemical shifts in δ). The ESI-MS were recorded on Thermo Finnigan LCQ Advantage, Ion Trap Mas a s spectrometer. The HRMS spectra were recorded as a ESI-HRMS on Agilent 6520 Q-TOF, LC-MS/MS mass spectrometer. The reactions under microwave heating were carried out in Biotage initiator 2.5 microwave synthesizer using low absorption mode. The temperature in this instrument is determined by a calibrated external infrared sensor. All reagents and solvents were used as obtained commercially.

General procedure for the synthesis of 2-halophenylureas as exemplified for 1a[1]



To the flask containing aryl / alkyl isocyanate (5.0 mmol) in CH_2Cl_2 (5 mL), 2-bromoaniline (5 mmol) and triethylamine (1.5 equiv) were added under stirring at room temperature. The reaction was allowed to continue for 2h, after which the precipitated product separated from the reaction mixture was filtered, washed with hexane and dried under vaccum.

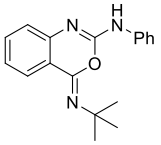
General procedure for the synthesis substituted 4*H*-benzo[*d*][1,3]oxazin-2-amines as exemplified for synthesis of 3aA



A 5 mL microwave vessel was charged with the 2-bromophenylurea **1a** (0.1 g, 0.34 mmol), *tert*-butyl isocyanide **2A** (0.06 mL, 0.52 mmol), $Pd(OAc)_2$ (0.038 g, 5 mol %), dppf (0.094 g, 5 mol%), Cs_2CO_3 (0.1 g, 0.34 mmol) and anhydrous toluene (2.0 mL). The vessel was degassed, refilled with nitrogen and sealed. The mixture was heated to 110 °C for 15 min under microwave irradiation. After cooling, the reaction mixture was filtered on a bed of Celite with EtOAc and the solvent removed under vacuum to obtain a residue which was

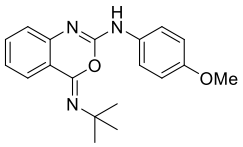
purified via silica gel column chromatography (hexanes/ EtOAc, 95:5, v/v) to furnish **3aA** (0.09 g, 95 %) as a white solid.

4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aA). Mp = 105-107 °C ;



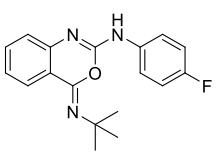
R_f = 0.55 (hexanes: EtOAc, 80:20, v/v); ν_{max} (KBr) 669, 921, 1215, 1605, 1647, 3434, 3683 cm $^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =1.50 (s, 9H), 6.23 (s, 1H), 7.00-7.04 (m, 1H), 7.42-7.56 (m, 5H), 8.02 (dd, 2H, J_1= 1.7 Hz, J_2= 1.2 Hz), 8.72 (d, 1H, J = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.9, 52.3, 121.8, 122.5, 122.9, 126.7, 127.5, 128.9, 131.9, 132.3, 135.0, 139.6, 151.9, 154.9; MS (ESI+) *m/z* 294.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{19}N_3O$ $[MH]^+$ 294.1606, Found 294.1608.

4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3bA). 81%



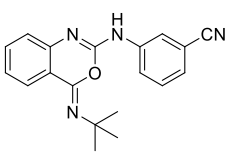
(0.078 g from 0.1 g) as a white solid; mp = 123-125 °C; R_f = 0.43 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 757, 1084, 1384, 1449, 1513, 1602, 1650, 3019, 3434 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.50 (s, 9H), 3.87 (s, 3H), 6.20 (s, 1H), 6.98-7.04 (m, 3H), 7.41-7.48 (m, 2H), 7.97-8.00 (m, 2H), 8.70-8.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.9, 52.3, 55.6, 114.1, 121.7, 122.4, 122.6, 126.7, 127.3, 129.4, 132.2, 139.7, 153.4, 155.1, 165.2; MS (ESI+) *m/z* = 324.0 $(M+H)^+$; ES-HRMS calcd. for $C_{19}H_{21}N_3O$ $[MH]^+$ 324.1484, Found 324.1486.

4-(*tert*-Butylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3cA). 93%



(0.089 g from 0.1 g) as a white solid; mp = 111-113 °C; R_f = 0.55 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 758, 1068, 1215, 1384, 1635, 1649, 3439, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.53 (s, 9H), 6.21 (s, 1H), 7.04-7.08 (m, 1H), 7.33-7.36 (m, 1H), 7.45-7.57 (m, 4H), 8.05 (dd, 2H, J_1= 1.6 Hz, J_2= 1.2 Hz), 8.76 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.2, 52.8, 113.2, 115.3 (d, J = 22 Hz), 118.3, 120.7, 122.1, 123.6, 128.0, 132.1 (d, J = 31 Hz), 135.4, 137.2, 152.3, 154.9, 158.4 (d, J = 237.3 Hz); MS (ESI+) *m/z* = 312.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{18}FN_3O$ $[MH]^+$ 312.1512, Found 312.1515.

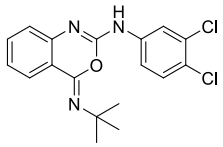
3-(4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (3dA). 97% (0.093



g from 0.1 g) as a white solid; mp = 125-127 °C; R_f = 0.51 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 758, 1068, 1511, 1523, 1626, 3367, 3400, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.78 (s, 9H), 6.62-6.67 (m, 2H), 6.88-6.95 (m, 2H), 6.99 (bs, 1H), 7.23-7.32 (m, 2H), 8.20 (d, 1H, J=7.3 Hz);

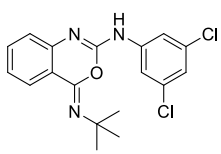
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.6, 61.2, 115.4, 118.9, 121.5, 123.2, 124.5, 126.6, 127.2, 130.4, 131.8, 137.9, 153.3, 157.4; MS (ESI+) *m/z* = 318.0 $(M+H)^+$; ES-HRMS calcd. for $C_{19}H_{17}N_4O$ $[MH]^+$ 318.1481, Found 318.1483.

4-(*tert*-Butylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3eA). 83%



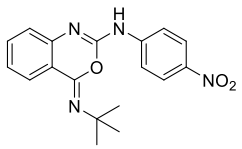
(0.08 g from 0.1 g) as a white solid; mp = 95-97 °C; R_f = 0.53 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 670, 929, 1026, 1215, 1523, 1626, 3367 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.51 (s, 9H), 7.25-7.29 (m, 1H), 7.43 (d, 1H, *J*=7.6 Hz), 7.52-7.54 (m, 2H), 8.07 (dd, 2H, J_1= 1.5 Hz, J_2= 1.8 Hz), 8.45 (d, 1H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.0, 50.6, 114.2, 116.4, 117.0, 118.3, 120.5, 122.9, 128.0, 130.2, 130.7, 134.5, 138.3, 151.8, 155.0; MS (ESI+) *m/z* = 362.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{17}Cl_2N_3O$ $[MH]^+$ 362.0827, Found 362.0831.

4-(*tert*-Butylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3fA). 86%



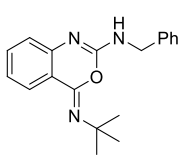
(0.083 g from 0.1 g) as a white solid; mp = 101-103 °C; R_f = 0.51 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 931, 1033, 1511, 1626, 1643, 2401, 3367, 3684 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.81 (s, 9H), 6.97 (d, 2H, *J* = 7.9 Hz), 7.16-7.21 (m, 2H, *J* = 7.7 Hz), 7.54-7.58 (m, 2H), 8.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.7, 52.0, 122.1, 124.3, 127.2, 128.5, 129.2, 129.9, 132.5, 135.0, 137.3, 138.2, 152.2, 156.4; MS (ESI+) *m/z* = 362.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{17}Cl_2N_3O$ $[MH]^+$ 362.0827, Found 362.0831.

4-(*tert*-Butylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3gA). 89%



(0.086 g from 0.1 g) as a yellow solid; mp = 115-117 °C; R_f = 0.41 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 725, 1089, 1499, 1511, 1626, 2553, 3367 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.65 (s, 9H), 3.89 (s, 1H), 6.99-7.02 (m, 2H), 7.34-7.38 (m, 1H), 7.56-7.58 (m, 2H), 7.89-7.92 (m, 2H), 8.39 (s, 1H), 8.53-8.55(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.5, 51.4, 114.5, 121.6, 123.3, 128.4, 129.2, 129.8, 133.3, 137.1, 140.0, 153.0, 155.2; MS (ESI+) *m/z* = 339.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{18}N_4O_3$ $[MH]^+$ 339.1457, Found 339.1459.

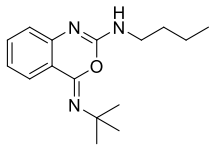
***N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3hA).** 86% (0.082 g from



0.1 g) as a white solid; mp = 135-137 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 765, 1039, 1411, 1504, 1633, 1649, 3019, 3407 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.47 (s, 9H), 4.41 (s, 2H), 7.02-7.06 (m, 2H), 7.26-7.43 (m, 7H), 8.49-8.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.9, 44.6, 52.3, 121.0, 121.8, 122.8, 123.8, 126.5, 127.9, 128.8, 129.3, 132.3, 139.3, 150.5, 155.2;

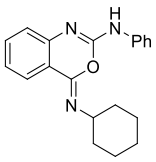
MS (ESI+) *m/z* = 308.0 $(M+H)^+$; ES-HRMS calcd. for $C_{19}H_{21}N_3O$ $[MH]^+$ 308.1763, Found 308.1768.

***N*-butyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3iA).** 91% (0.087 g from



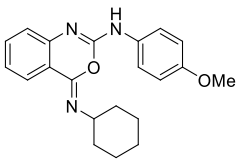
0.1 g) as a white solid; mp = 119-121 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 786, 1039, 1543, 1633, 1649, 3367 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.93 (t, 3H, *J* = 7.3 Hz), 1.37 (t, 2H, *J* = 7.6 Hz), 1.46 (s, 9H), 1.49-1.55 (m, 2H), 3.22-3.27 (m, 2H), 4.70 (s, 1H), 6.91 (t, 1H, *J* = 7.3 Hz), 7.32-7.39 (m, 2H), 8.37 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.8, 20.0, 29.6, 32.1, 40.3, 52.0, 121.0, 122.7, 126.8, 131.8, 152.5, 155.7; MS (ESI+) *m/z* = 274.0 $(M+H)^+$; ES-HRMS calcd. for $C_{16}H_{23}N_3O$ $[MH]^+$ 274.1919, Found 274.1921.

4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aB). 81% (0.084 g



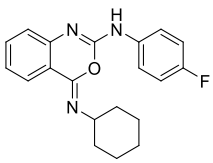
from 0.1 g) as a white solid; mp = 119-117 °C; R_f = 0.55 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 768, 1099, 1412, 1523, 1639, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) =1.23-1.31 (m, 4H), 1.43-1.47 (m, 2H), 1.65-1.80 (m, 3H, CH), 2.02-2.06 (m, 2H), 6.18 (s, 1H), 7.07-7.11 (m, 1H), 7.46-7.54 (m, 5H), 8.02-8.05 (m, 2H), 8.78 (dd, 1H, J_1= 0.8 Hz, J_2= 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.0, 25.6, 33.2, 66.7, 121.2, 121.8, 122.9, 126.6, 127.5, 128.9, 131.9, 132.6, 135.0, 140.0, 152.1, 155.7; MS (ESI+) *m/z*= 320.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{21}N_3O$ $[MH]^+$ 320.1763, Found 320.1769.

4-(Cyclohexylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3bB). 79%



(0.083 g from 0.1 g) as a white solid; mp = 133-137 °C; R_f = 0.51 (hexane: EtOAc, 75:25, v/v); ν_{max} (KBr) 768, 1099, 1512, 1523, 1699, 3320 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.18-1.31 (m, 4H), 1.39-1.43 (m, 3H), 1.76-1.79 (m, 2H), 2.03-2.04 (m, 2H), 3.88 (s, 3H), 6.12 (s, 1H), 7.00 (d, 2H, *J* = 7.3 Hz), 7.10 (d, 1H, *J* = 7.6 Hz), 7.46-7.53 (m, 2H), 8.01 (d, 2H, *J* = 8.6 Hz), 8.78 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.0, 25.6, 33.2, 55.6, 64.9, 114.1, 121.0, 121.7, 122.7, 126.2, 126.5, 127.4, 129.4, 132.7, 136.1, 151.1, 155.0, 165.3; MS (ESI+) *m/z*= 350.0 $(M+H)^+$; ES-HRMS calcd. for $C_{21}H_{23}N_3O$ $[MH]^+$ 350.1869, Found 350.1871.

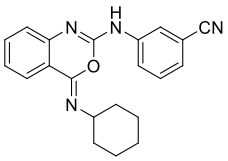
4-(Cyclohexylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cB).** 87%



(0.091 g from 0.1 g) as a white solid; mp = 105-107 °C; R_f = 0.56 (hexane: EtOAc, 85:15, v/v); ν_{max} (KBr) 967, 1098, 1512, 1533, 3019, 3434 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.01-1.25 (m, 4H), 1.27-1.34 (m, 2H),

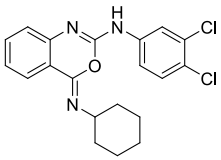
1.51-1.63 (m, 3H), 1.81-1.88 (m, 2H), 5.98 (s, 1H), 7.30-7.32 (m, 2H), 7.39-7.47 (m, 3H), 7.52-7.56 (m, 2H), 8.02 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.9, 25.5, 33.9, 63.6, 115.4 (d, *J* = 21.8 Hz), 118.6, 125.4, 128.3, 129.7 (d, *J* = 7.3 Hz), 130.2, 132.3, 132.8, 132.9, 149.4, 152.1, 154.0 (d, *J* = 279 Hz); MS (ESI+) *m/z* = 338.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{20}FN_3O$ $[MH]^+$ 338.1669, Found 338.1670.

3-(4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (3dB). 88%



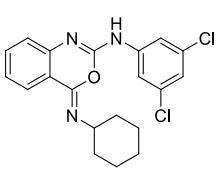
(0.092 g from 0.1 g) as a white solid; mp = 129-131 ^{o}C; R_f = 0.55 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 669, 1099, 1412, 1533, 1597, 1642, 2220, 3420, 3439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.48-1.54 (m, 3H), 1.65-1.71 (m, 2H), 1.94-2.00 (m, 3H), 2.26 (bs, 2H), 6.39 (s, 1H), 6.86-6.90 (m, 1H), 7.70-7.74 (m, 3H), 7.81-7.88 (m, 3H), 8.08-8.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.8, 25.5, 33.1, 62.9, 114.2, 116.3, 123.6, 127.5, 127.6, 128.7, 128.8, 129.3, 133.7, 135.4, 137.5, 151.3, 155.4; MS (ESI+) *m/z* = 345.0 $(M+H)^+$; ES-HRMS calcd. for $C_{21}H_{20}N_4O$ $[MH]^+$ 345.1715, Found 345.1712.

4-(Cyclohexylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3eB).



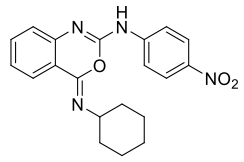
91% (0.094 g from 0.1 g) as a white solid; mp = 119-121 $^{\circ}$C; R_f = 0.53 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 799, 967, 1512, 1626, 3200, 3367, 3400 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26-1.30 (m, 4H), 1.38-1.44 (m, 2H), 1.70-1.79 (m, 3H), 1.85-1.90 (m, 2H), 6.77-6.81 (m, 1H), 6.93-6.97 (m, 1H), 7.03-7.05 (m, 1H), 7.16-7.26 (m, 1H), 7.34-7.39 (m, 1H), 7.57-7.61 (m, 1H), 8.11-8.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.1, 25.1, 32.0, 62.1, 114.2, 117.0, 118.3, 120.5, 122.9, 128.0, 130.2, 130.7, 134.5, 138.3, 151.8, 155.0; MS (ESI+) *m/z* = 388.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{19}Cl_2N_3O$ $[MH]^+$ 388.0983, Found 388.0980.

4-(Cyclohexylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3fB).



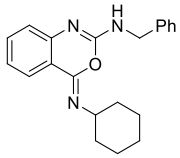
92% (0.095 g from 0.1 g) as a white solid; mp = 112-114 $^{\circ}$C; R_f = 0.51 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 787, 1039, 1507, 1659, 3320, 3300 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =1.15-1.40 (m, 6H), 1.63-1.76 (m, 3H), 1.92-1.94 (m, 2H), 5.53 (s, 1H), 7.45-7.47 (m, 2H), 7.58-7.61 (m, 2H), 7.80-7.82 (m, 2H), 8.09-8.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.6, 26.6, 34.8, 61.8, 114.7, 118.9, 121.0, 121.9, 123.3, 128.6, 129.0, 131.3, 132.8, 134.9, 138.8, 152.3, 155.5; MS (ESI+) *m/z*= 388.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{19}Cl_2N_3O$ $[MH]^+$ 388.0983, Found 388.0985.

4-(Cyclohexylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3gB). 87%



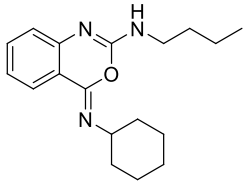
(0.09 g from 0.1 g) as a yellow solid; mp = 126-128 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 766, 1307, 1423, 1512, 1607, 1625, 3367, 3400, 3551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.88-2.01 (m, 6H), 2.10-2.14 (m, 3H), 2.36-2.39 (m, 2H), 4.54 (s, 1H), 7.31-7.40 (m, 2H), 7.42-7.44 (m, 1H), 7.70-7.75 (m, 1H), 8.06-8.08 (m, 1H), 8.39-8.42 (m, 2H), 8.72 (d, 1H, *J*= 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.9, 25.6, 32.9, 64.4, 126.3, 127.2, 128.0, 128.5, 131.2, 132.4, 133.1, 134.3, 136.0, 143.9, 153.0, 154.9; MS (ESI+) *m/z* = 365.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{20}N_4O_3$ $[MH]^+$ 365.1614, Found 365.1619.

***N*-benzyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3hB).** 76% (0.079 g



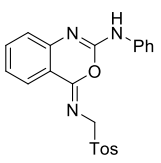
from 0.1 g) as a white solid; mp = 131-133 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 669, 723, 967, 1099, 1449, 1626, 1639, 3367, 3400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.85-0.90 (m, 3H), 1.05-1.56 1.62- 1.85 (m, 3H), 1.85-1.92 (m, 2H), 5.48 (s, 2H), 5.62 (s, 1H), 6.83-6.87 (m, 2H), 6.96-7.00 (m, 3H), 7.37-8.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.4, 26.6, 32.0, 46.4, 63.4, 118.1, 122.0, 122.7, 123.8, 124.7, 127.2, 127.6, 127.9, 128.2, 128.6, 132.3, 134.2, 138.6, 152.5, 155.3; MS (ESI+) *m/z* = 334.0 $(M+H)^+$; ES-HRMS calcd. for $C_{21}H_{23}N_3O$ $[MH]^+$ 334.1919, Found 334.1914.

***N*-butyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3iB).** 81% (0.085 g from



0.1 g) as a white solid; mp = 121-123 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 868, 967, 1099, 1423, 1608, 1626, 3367, 3400, 3500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.81-0.91 (m, 3H), 1.04-1.07 (m, 2H), 1.21-1.38 (m, 6H), 1.59-1.68 (m, 6H), 1.70-1.72 (m, 1H), 1.73-1.98 (m, 2H), 4.91 (s, 1H), 7.16-7.19 (m, 1H), 7.33-7.36 (m, 1H), 7.37-7.42 (m, 1H), 8.44 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.8, 20.1, 24.9, 25.0, 32.3, 32.9, 40.7, 62.9, 121.4, 122.8, 126.8, 128.9, 132.2, 154.2, 155.7; MS (ESI+) *m/z* = 300.1 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{25}N_3O$ $[MH]^+$ 300.2076, Found 300.2067.

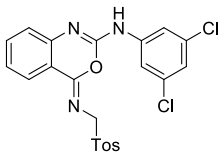
***N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aC).** 78% (0.1 g from



0.1 g) as a white solid; mp = 143-145 °C; R_f = 0.53 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 507, 967, 1211, 1403, 1599, 1623, 1640, 1994, 3421, 3367, 3409 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.64 (s, 3H), 5.32 (s, 1H), 6.62 (s, 2H), 7.29-7.43 (m, 5H), 7.46-7.54 (m, 3H), 7.61-7.69 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.9, 75.0, 112.6, 122.9, 127.0, 128.5, 128.7, 128.8,

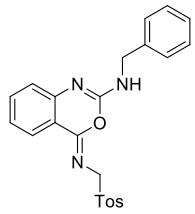
129.5, 129.9, 133.8, 134.7, 135.9, 140.3, 142.2, 152.7, 154.0; MS (ESI+) *m/z* = 406.1 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{19}N_3O_3S$ $[MH]^+$ 406.1225, Found 406.1229.

***N*-(3,5-Dichlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3fC).**



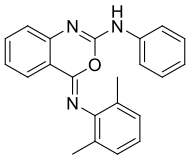
85% (0.11 g from 0.1 g) as a white solid; mp = 139-141 °C; R_f = 0.51 (hexane: EtOAc, 75:25, v/v); ν_{max} (KBr) 536, 727, 967, 1033, 1299, 1599, 1626, 1900, 3367, 3400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.38 (s, 3H), 4.08 (s, 1H), 6.49 (s, 2H), 6.85-6.92 (m, 2H), 7.22-7.48 (m, 7H), 7.80 (s, 1H), 8.09-8.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 23.1, 73.9, 114.5, 122.2, 127.1, 127.3, 128.2, 128.5, 128.6, 130.0, 135.0, 136.3, 141.6, 142.2, 152.5, 155.8; MS (ESI+) *m/z* = 474.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{17}Cl_2N_3O_3S$ $[MH]^+$ 474.0446, Found 474.0451.

***N*-Benzyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3hC).** 73% (0.091g



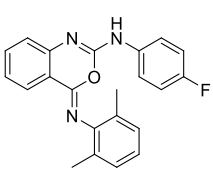
from 0.1 g) as a white solid; mp = 119-121 °C; R_f = 0.56 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 587, 789, 976, 1088, 1223, 1511, 1626, 3321, 3467, 3500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.91 (s, 3H), 4.29 (s, 2H), 6.47 (s, 2H), 7.08-7.12 (m, 1H), 7.18-7.34 (m, 11H), 7.52-7.56 (m, 1H), 7.95-7.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.5, 44.2, 72.6, 117.2, 122.7, 126.5, 127.2, 127.3, 127.5, 127.7, 128.6, 128.7, 134.7, 138.2, 139.2, 142.1, 151.4, 154.5; MS (ESI+) *m/z* = 420.1 $(M+H)^+$; ES-HRMS calcd. for $C_{23}H_{21}N_3O_3S$ $[MH]^+$ 420.1382, Found 420.1385.

4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aD). 86%



(0.096 g from 0.1 g) as a white solid; mp = 116-118 °C; R_f = 0.56 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 773, 1200, 1523, 1626, 1633, 3367, 3433, 3500 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.24 (s, 6H), 6.92-7.02 (m, 3H), 7.18-7.22 (m, 4H), 7.34-7.36 (m, 4H), 7.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.5, 119.0, 122.4, 128.3, 128.8, 131.3, 132.5, 134.3, 136.5, 138.0, 152.9, 153.3, 156.4; MS (ESI+) *m/z* = 342.1 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{19}N_3O$ $[MH]^+$ 342.1606, Found 342.1609.

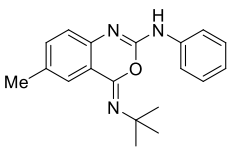
4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (3cD). 83%



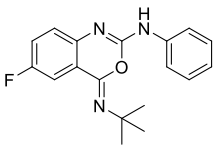
(0.093 g from 0.1 g) as a white solid; mp = 149-151 °C; R_f = 0.55 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 667, 1099, 1133, 1599, 1626, 3367, 3400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.51 (s, 6H), 6.74-6.78 (m, 2H), 6.83-6.87 (m, 2H), 7.13-7.17 (m, 1H), 7.30-7.33 (m, 2H), 7.37-7.39 (m, 1H), 7.69 (s,

1H), 8.05 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.9, 112.9, 115.1 (d, *J* = 22.1 Hz), 120.2 (d, *J* = 7.4 Hz), 121.9, 123.4, 127.8, 132.1, 135.3, 137.0, 152.0, 152.8, 156.9, 158.1 (d, *J* = 239.7 Hz); MS (ESI+) *m/z* = 360.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{18}FN_3O$ $[MH]^+$ 360.1512, Found 360.1516.

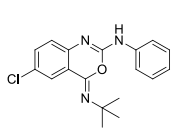
4-(*tert*-butylimino)-6-methyl-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (7). 93% (0.089 g from 0.1 g) as white solid; mp = 109-111 °C; R_f = 0.45 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 676, 968, 1015, 1684, 1699, 1733, 3412, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.57 (s, 9H), 2.29 (s, 3H), 6.58 (s, 1H, NH), 6.91 (s, 1H), 7.07-7.12 (m, 1H), 7.26 (s, 1H), 7.34-7.40 (m, 4H), 7.97 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.8, 29.5, 50.6, 120.1, 120.3, 123.0, 123.1, 127.6, 128.1, 129.0, 129.1, 134.4, 139.0, 139.4, 152.4, 155.7; MS (ESI+) *m/z* = 312.0 $(M+H)^+$; ES-HRMS calcd. for $C_{19}H_{21}N_3O$ $[MH]^+$ 308.1763, Found 308.1766.



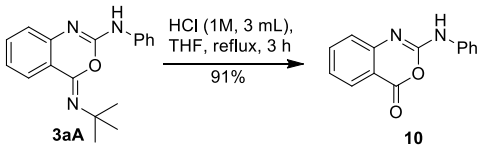
4-(*tert*-Butylimino)-6-fluoro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (8). 86% (0.083 g from 0.1 g) as white solid; mp = 125-127 °C; R_f = 0.51 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 838, 968, 1019, 1311, 1640, 1699, 3569, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.51 (s, 9H), 6.55 (s, 1H), 6.95-7.00 (m, 1H), 7.12-7.15 (m, 1H), 7.18-7.21 (m, 2H), 7.31-7.32 (m, 3H), 8.03-8.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 30.0, 51.8, 110.9 (d, *J* = 31.4 Hz), 115.9 (d, *J* = 21.4 Hz), 126.7, 128.7, 130.1, 131.0, 131.5 (d, *J* = 7.7 Hz), 136.1, 144.0, 152.1, 156.0, 161.4 (d, *J* = 243.6 Hz), MS (ESI+) *m/z* = 312.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{18}FN_3O$ $[MH]^+$ 312.1519, Found 312.1521.



4-(*tert*-butylimino)-6-chloro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (9). 89% (0.085 g from 0.1 g) as white solid; mp = 134-135 °C; R_f = 0.55 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 758, 1033, 1515, 1589, 1635, 1649, 3132, 3400, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.49 (s, 9H), 6.55 (s, 1H), 7.10 (t, 1H, *J* = 7.7 Hz), 7.45 (d, 1H, *J* = 7.8 Hz), 7.49-7.55 (m, 4H), 8.02-8.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.6, 55.0, 121.7, 122.1, 123.7, 124.2, 124.6, 129.1, 129.4, 130.5, 136.0, 142.6, 147.1, 152.8, 158.3; MS (ESI+) *m/z* = 328.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{18}ClN_3O$ $[M+H]^+$ 328.1217, Found 328.1215.



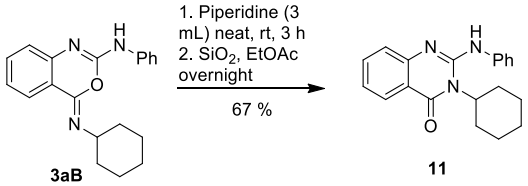
General procedure for the synthesis of 2-(phenylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one (10)[2]



A mixture of (*Z*)-4-(*tert*-butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **3aA** (0.1 g, 0.34 mmol) and hydrochloric acid (1.0 M, 3 mL) in THF (10 mL) was heated at reflux for 3 h. Thereafter the mixture was diluted with water (20 mL) and extracted with EtOAc (2 X 35 mL). The organic layers were combined, dried over Na_2SO_4 and evaporated to obtain a residue which upon purification via silica gel column chromatography using hexanes/ EtOAc (93:7, v/v) as an eluent furnished the **10** (0.07 g, 91%) as a white solid.

2-(Phenylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one (10). Mp = 109-111 $^{\circ}$C; R_f = 0.51 (hexane: EtOAc, 70:30, v/v); ν_{max} (KBr) 667, 779, 1019, 1033, 1612, 1642, 1679, 1686, 1735, 3431 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.12 (s, 1H), 7.01-7.05 (m, 2H), 7.51-7.55 (m, 2H), 8.02-8.04 (m, 2H), 8.44-8.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 119.8, 122.9, 125.6, 128.3, 131.4, 134.4, 138.1, 145.5, 152.6; MS (ESI+) *m/z* = 239.0 $(M+H)^+$; ES-HRMS calcd. for $C_{14}H_{10}N_2O_2$ $[MH]^+$ 239.0821, Found 239.0823.

Typical procedure for the synthesis of 3-Cyclohexyl-2-(phenylamino)quinazolin-4(3*H*)-one (11) [3]



A solution of **3aB** (0.1 mg, 0.31 mmol) in piperidine (3 mL) was stirred at room temperature for 1h. After completion of the reaction, the resulting mixture was evaporated under reduced pressure to obtain a residue which was dissolved in EtOAc (5 mL) followed by addition of silica gel (100-200 mesh, 75 mg). The mixture was stirred at room-temperature overnight and then silica gel was filtered off. The filtrate was evaporated under reduced pressure to afford a residue which was purified upon silica gel column chromatography using hexanes/ EtOAc (80:20, v/v) as the eluent to furnish 0.07 mg (67%) of **11** as a white solid.

3-Cyclohexyl-2-(phenylamino)quinazolin-4(3*H*)-one (11). Mp = 109-111 ^{o}C; R_f = 0.51 (hexane: EtOAc, 70:30, v/v); ν_{max} (KBr) 967, 1601, 1630, 3056, 3189, 3297 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.14-1.25 (m, 3H), 1.33-143 (m, 2H) 1.97-1.98 (m, 2H), 6.10 (s, 1H), 7.00-7.04 (m, 1H), 7.39-7.47 (m, 5H), 7.95-7.97 (m, 2H), 8.72 (d, 1H, *J* = 6.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.0, 25.6, 33.2, 48.9, 121.2, 121.8, 122.9, 126.6,

127.5, 128.9, 131.9, 132.7, 135.0, 140.0, 153.5, 160.9; MS (ESI+) *m/z* = 320.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{21}N_3O_2$ $[MH]^+$ 320.1763, Found 320.176.

References

1. J. Clayden, H.Turner, M. Pickworth, T. Adler, *Org. Lett.*, 2005**, 7**, 3147-3151
2. X. D. Fe, Z.-Y. Ge, T. Tang , Y.-M. Zhu, S. -J. Ji, *J. Org. Chem.* 2012, **77**, 10321−10328
3. F. He, B. B. Snider, *J Org. Chem.* 1999**, 64**, 1397-1399.

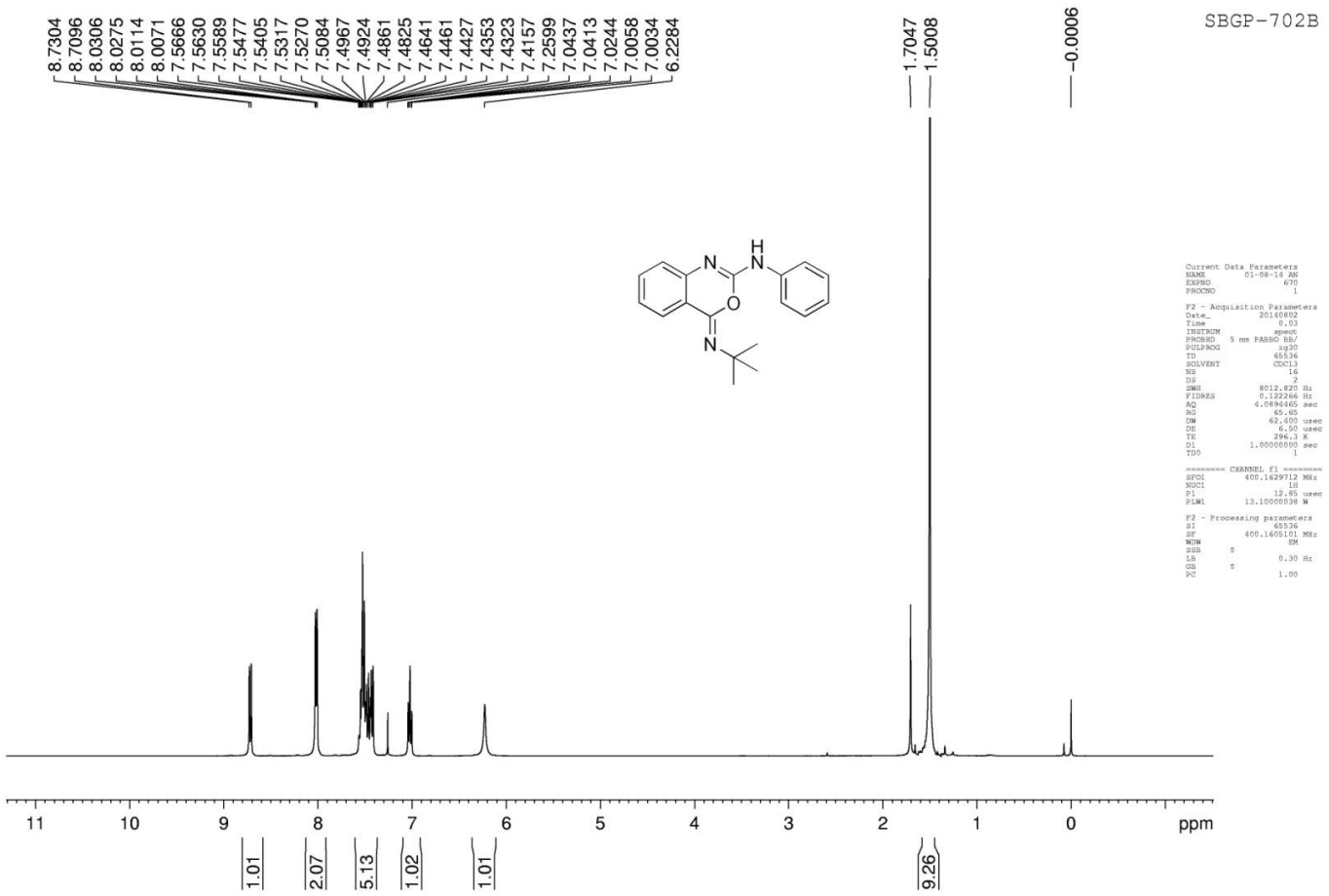


Fig: S-1 ^{1}H spectrum of 4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aA)**

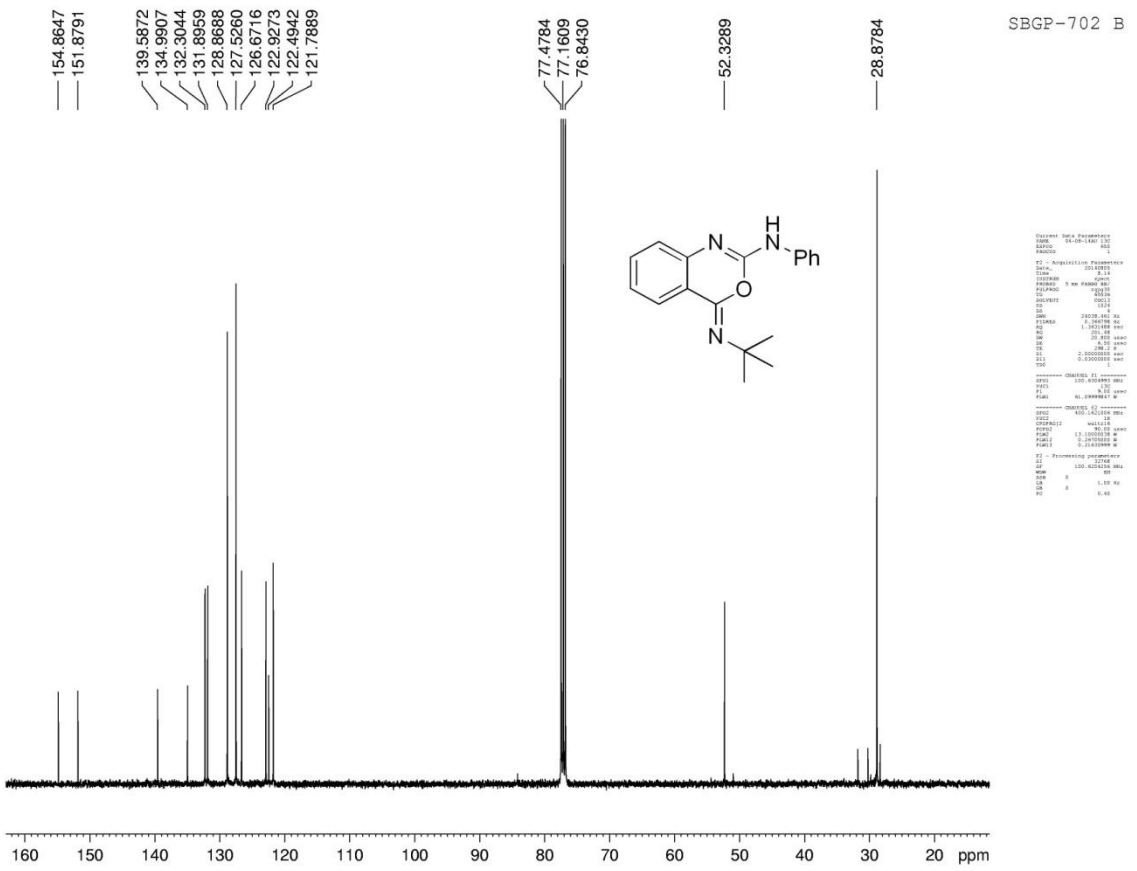


Fig: S-2 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aA)**

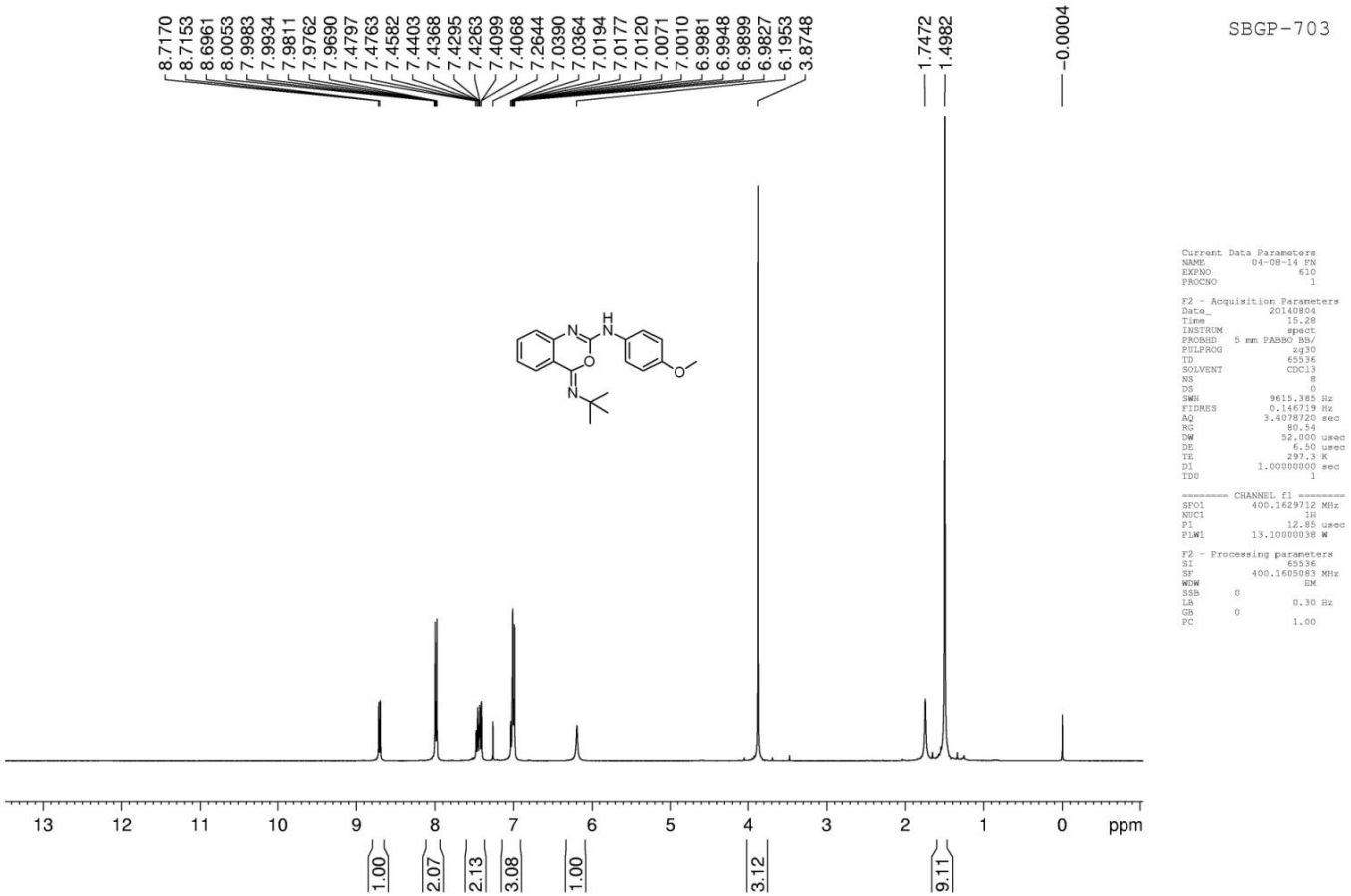


Fig: S-3 ^{1}H spectrum of 4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3bA)**

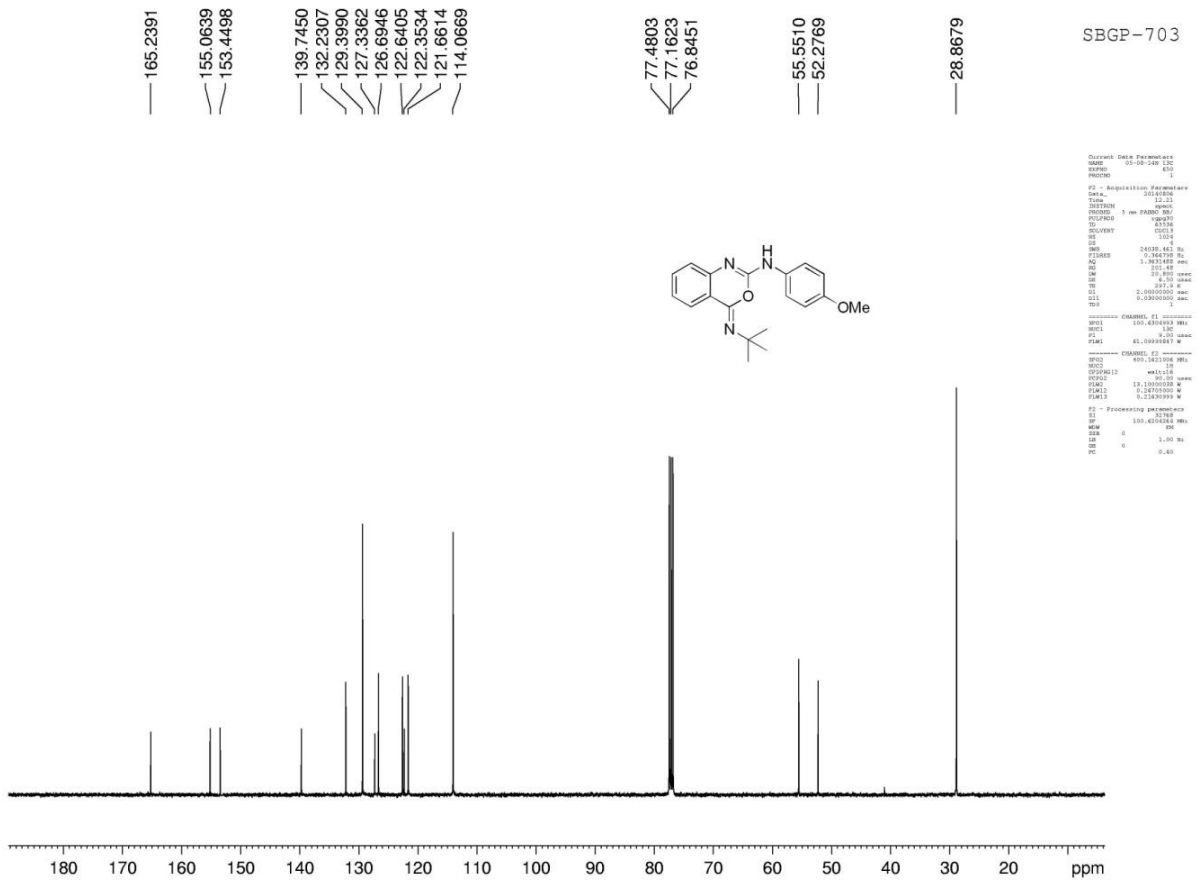


Fig: S-4 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3bA)**

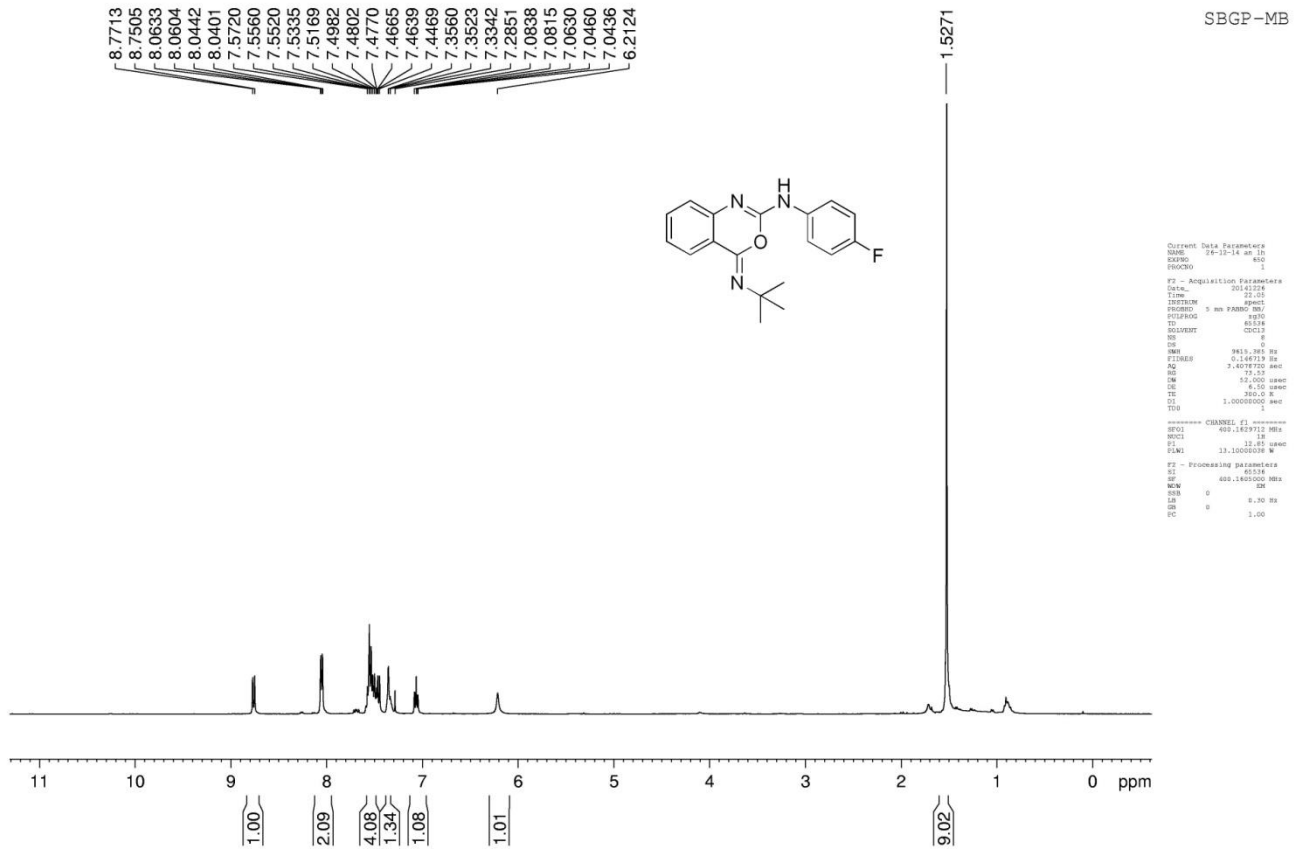


Fig: S-5 ^{1}H spectrum of 4-(*tert*-Butylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3cA)**

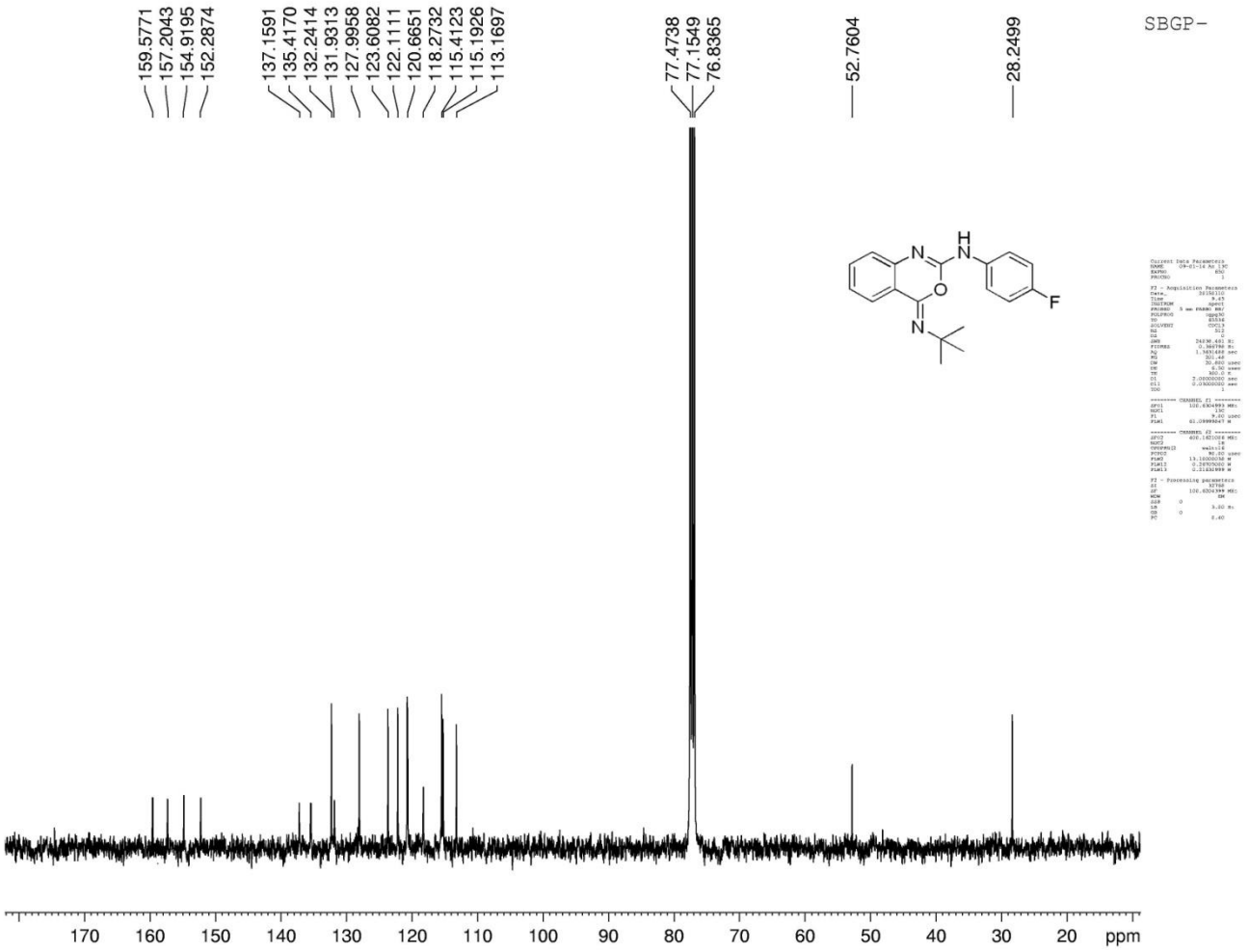


Fig: S-6 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3cA)**

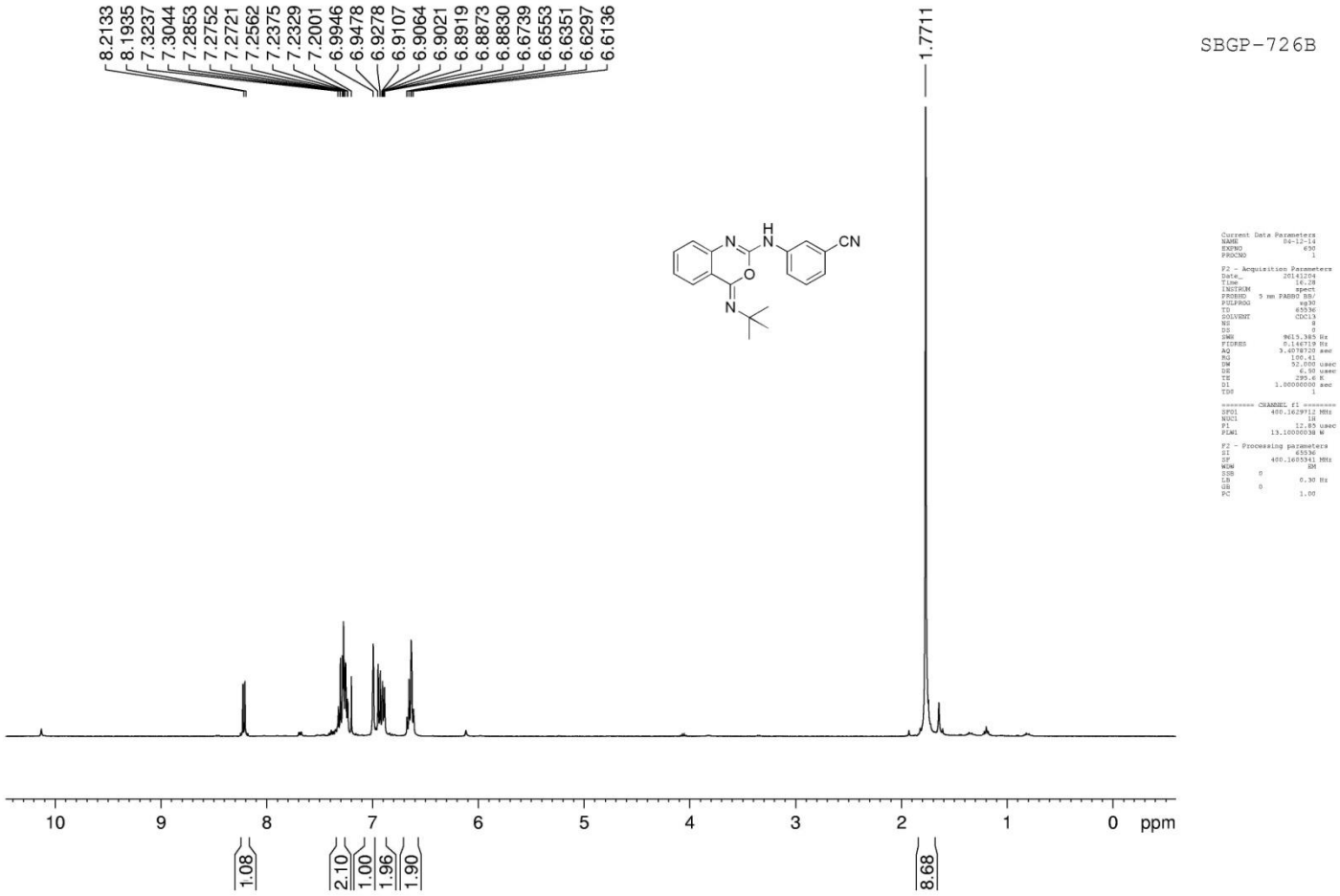


Fig: S-7 ^{1}H spectrum of 3-(4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile **(3dA)**

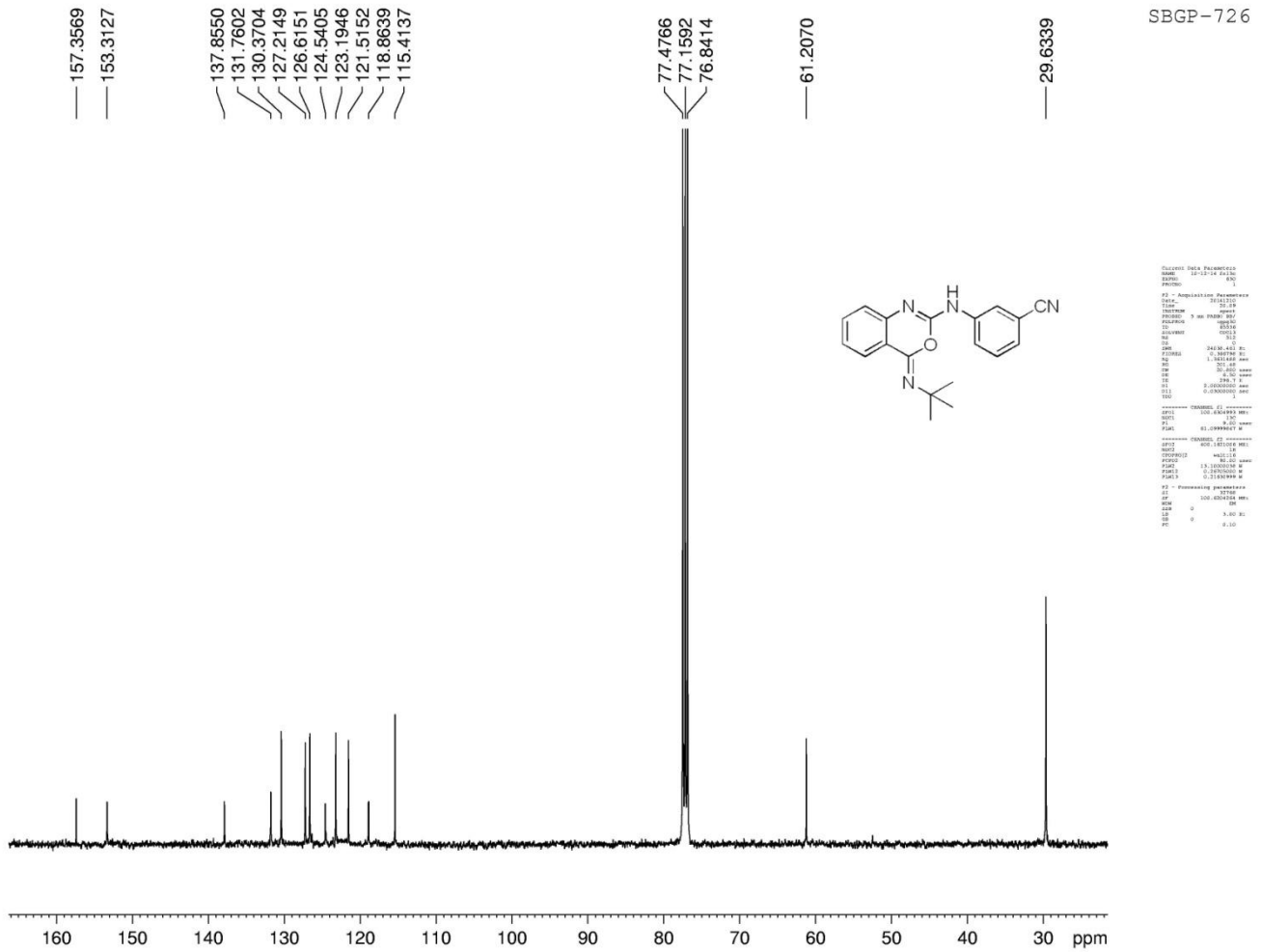


Fig: S-8 ^{13}C spectrum of 3-(4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile **(3dA)**

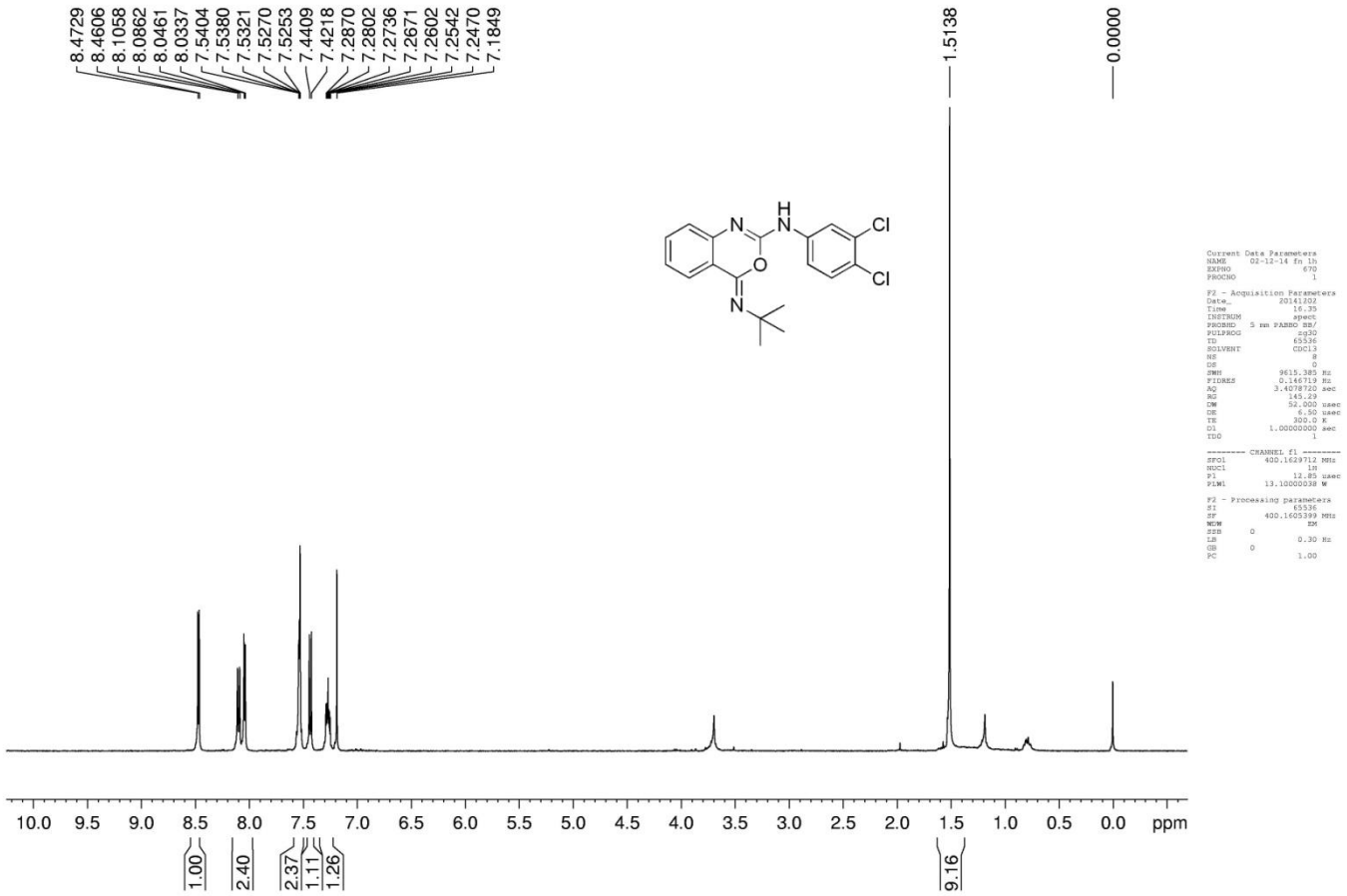


Fig: S-9 ^{1}H spectrum of 4-(*tert*-Butylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3eA)**

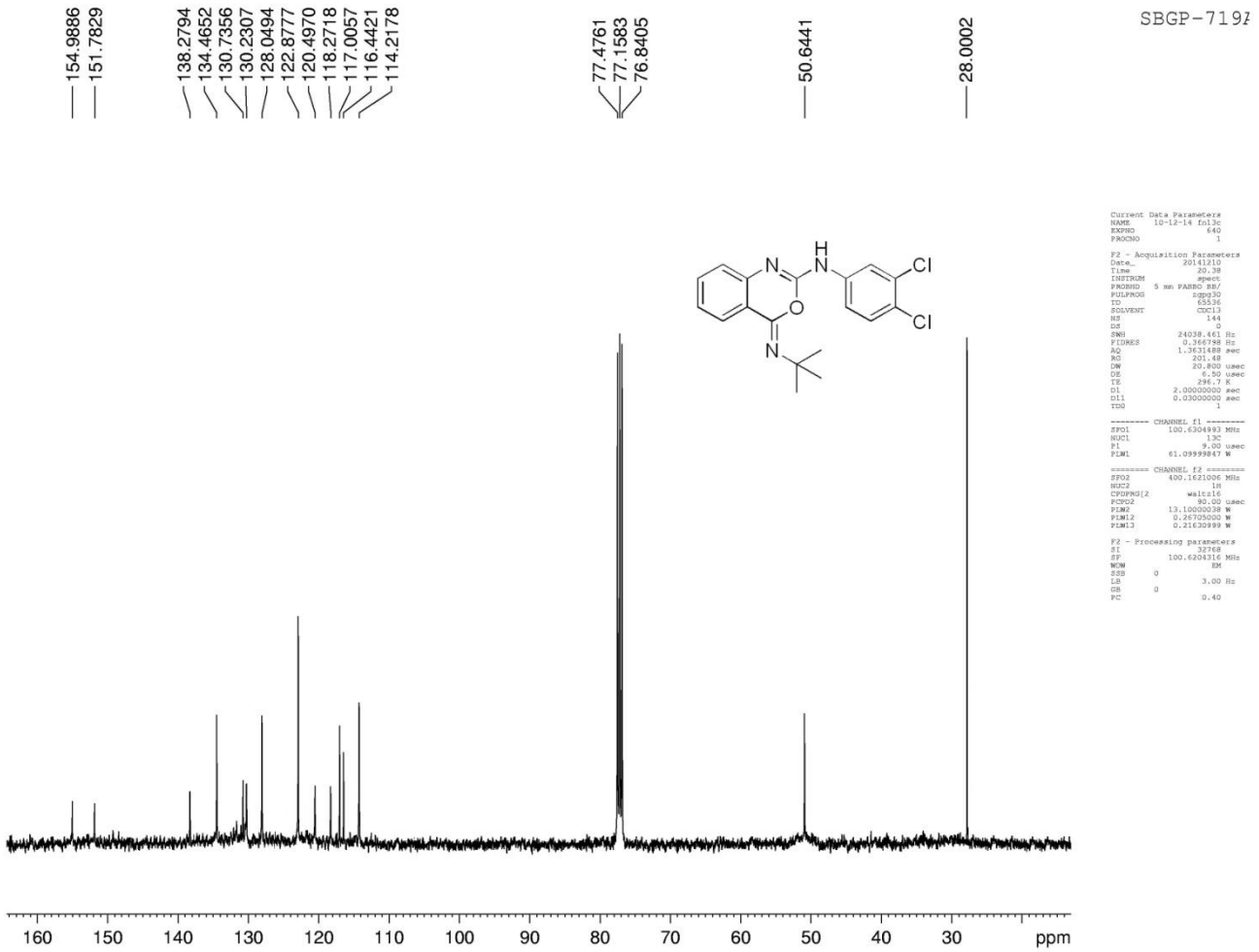


Fig: S-10 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3eA)**

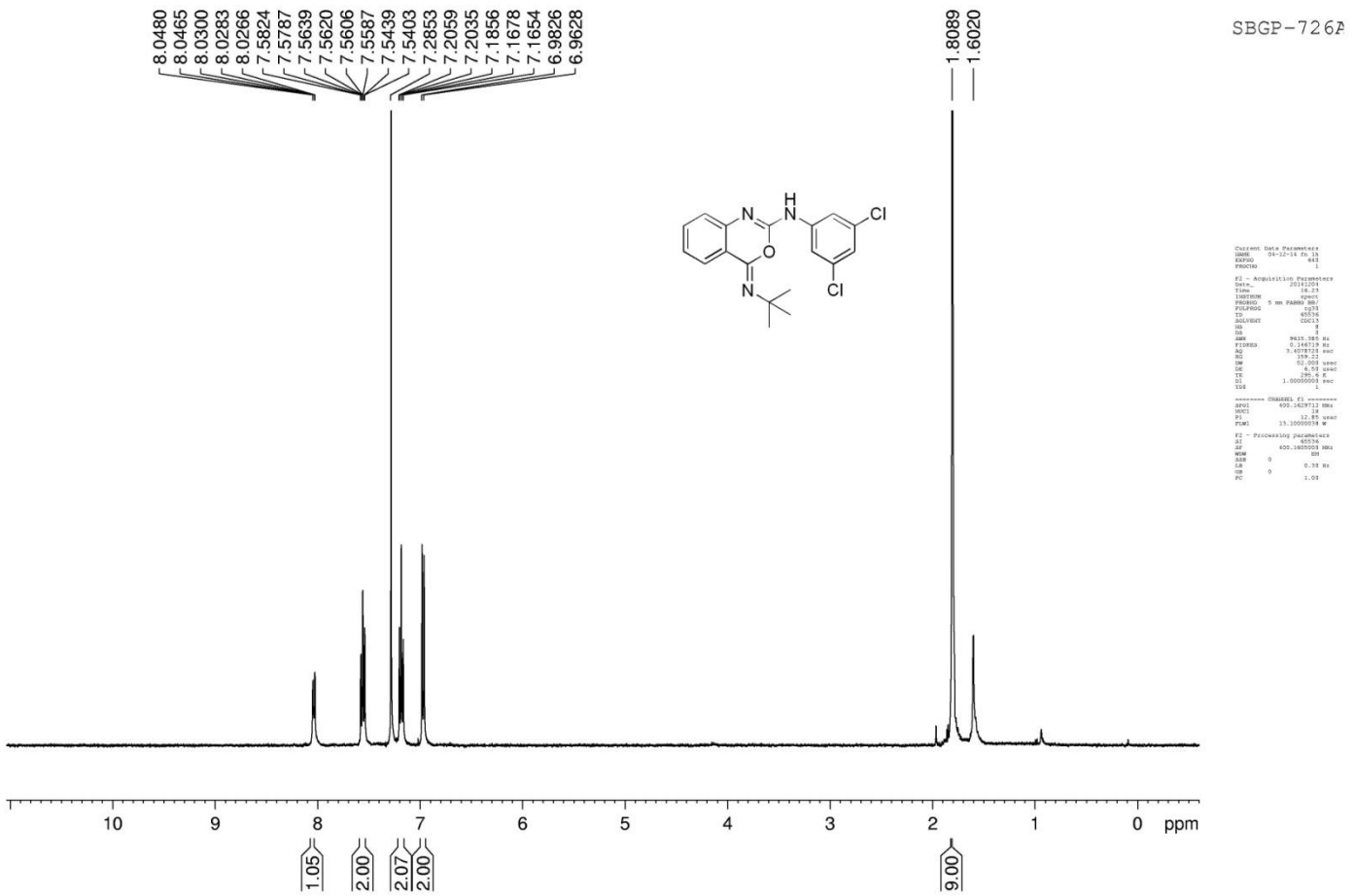


Fig: S-11 [1]H spectrum of 4-(*tert*-Butylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fA)**

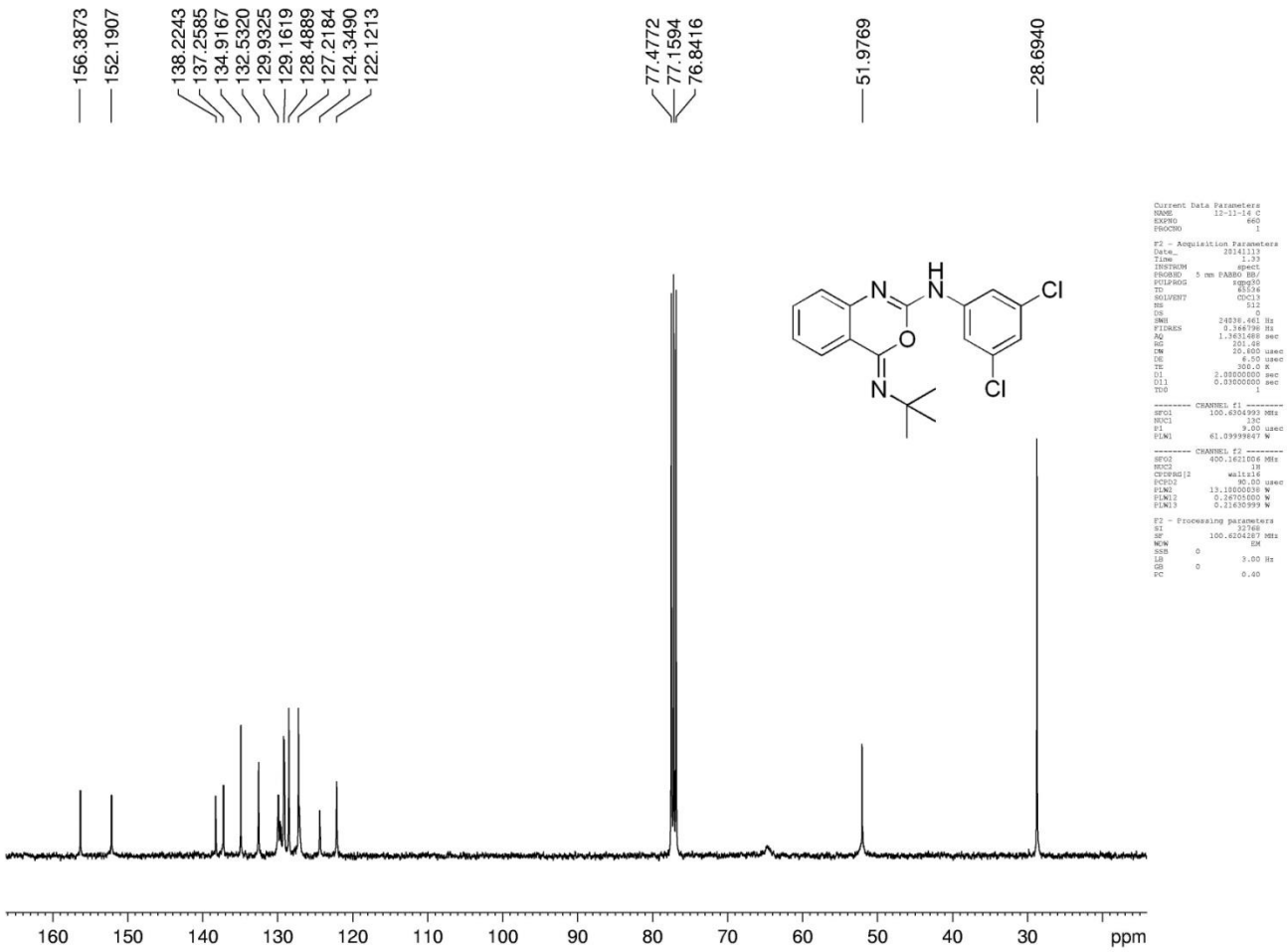


Fig: S-12 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fA)**

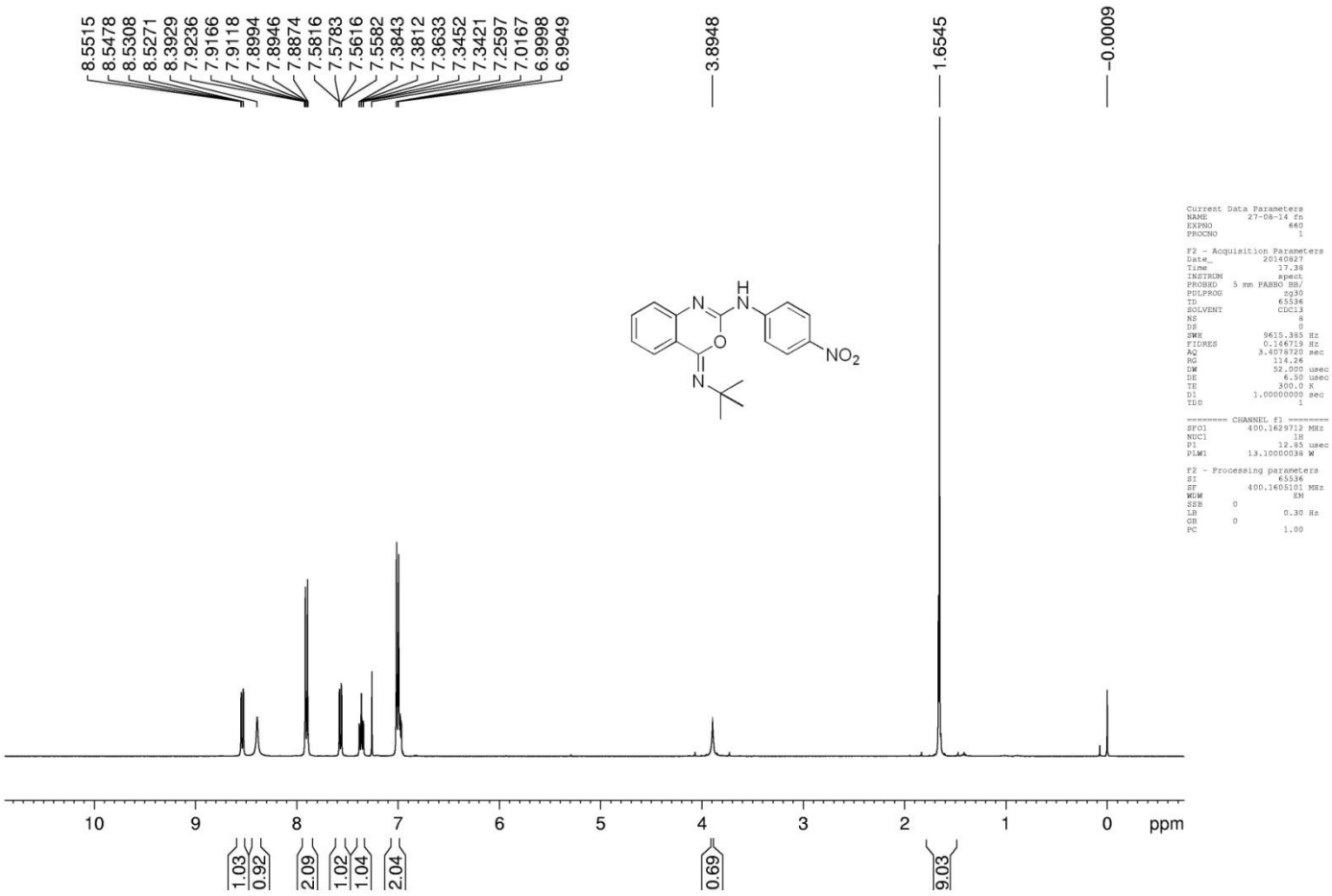


Fig: S-13 ^{1}H spectrum of 4-(*tert*-Butylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3gA)**

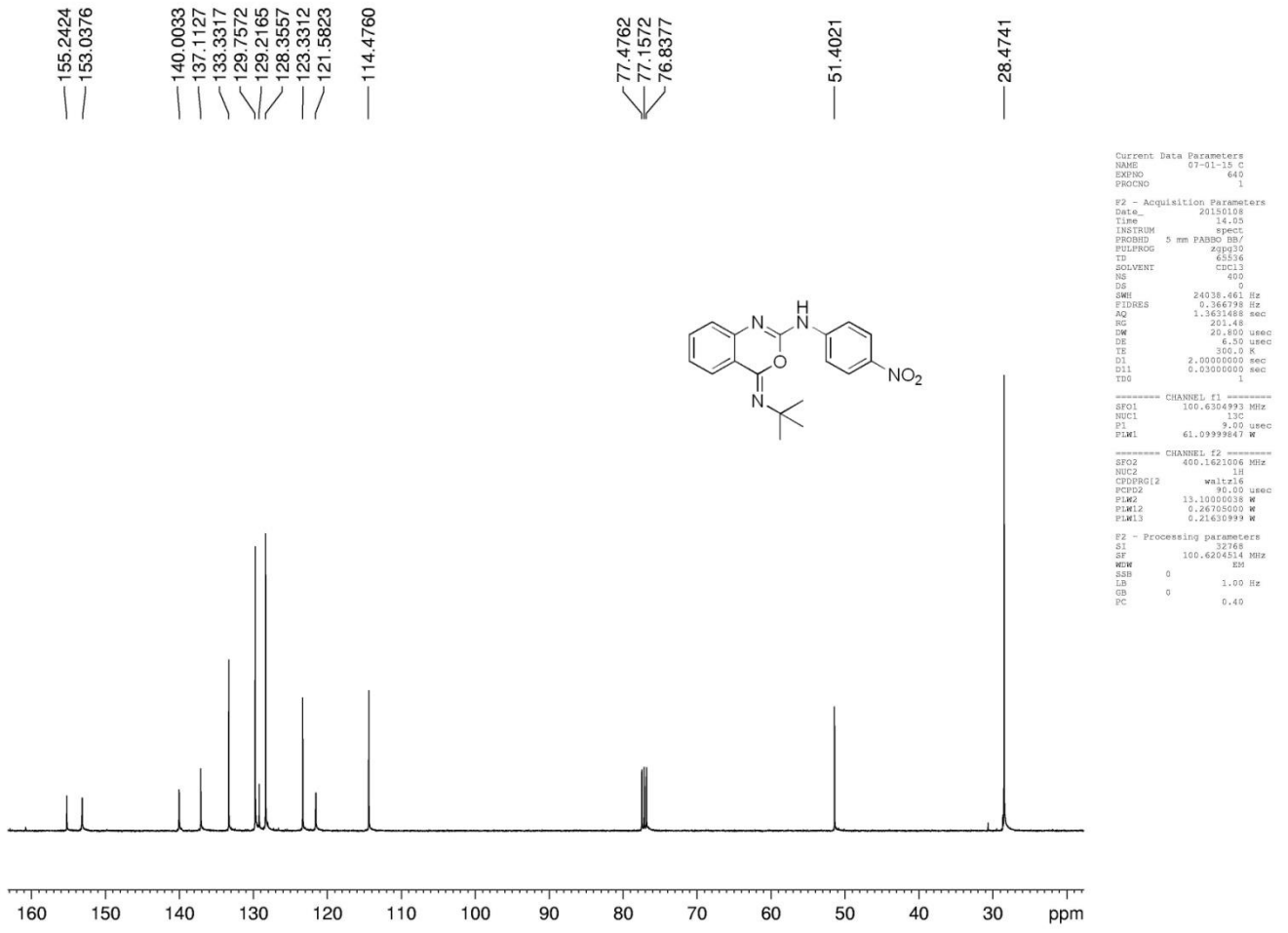


Fig: S-14 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3gA)**

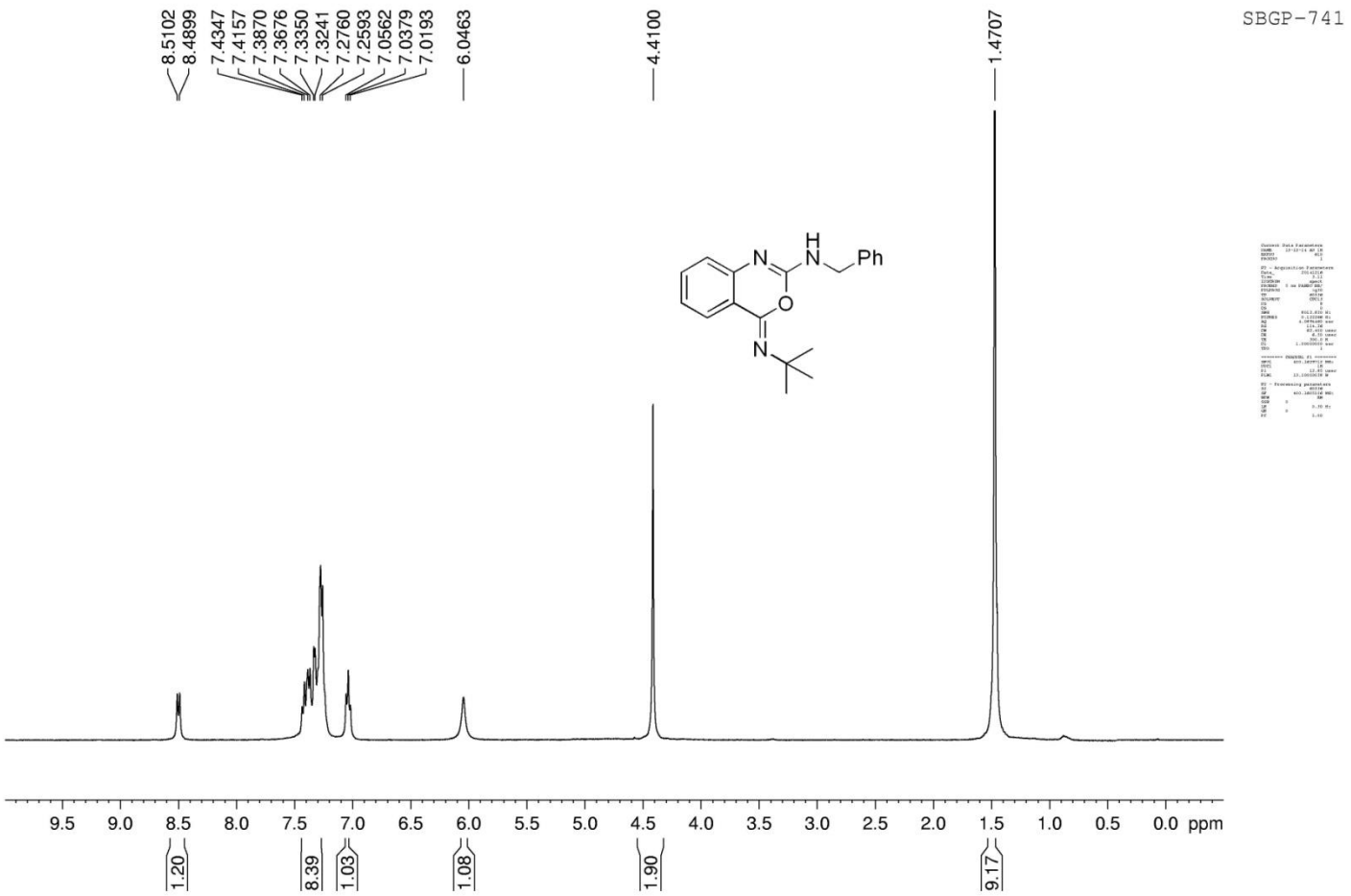


Fig: S-15 ^{1}H spectrum of *N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hA)**

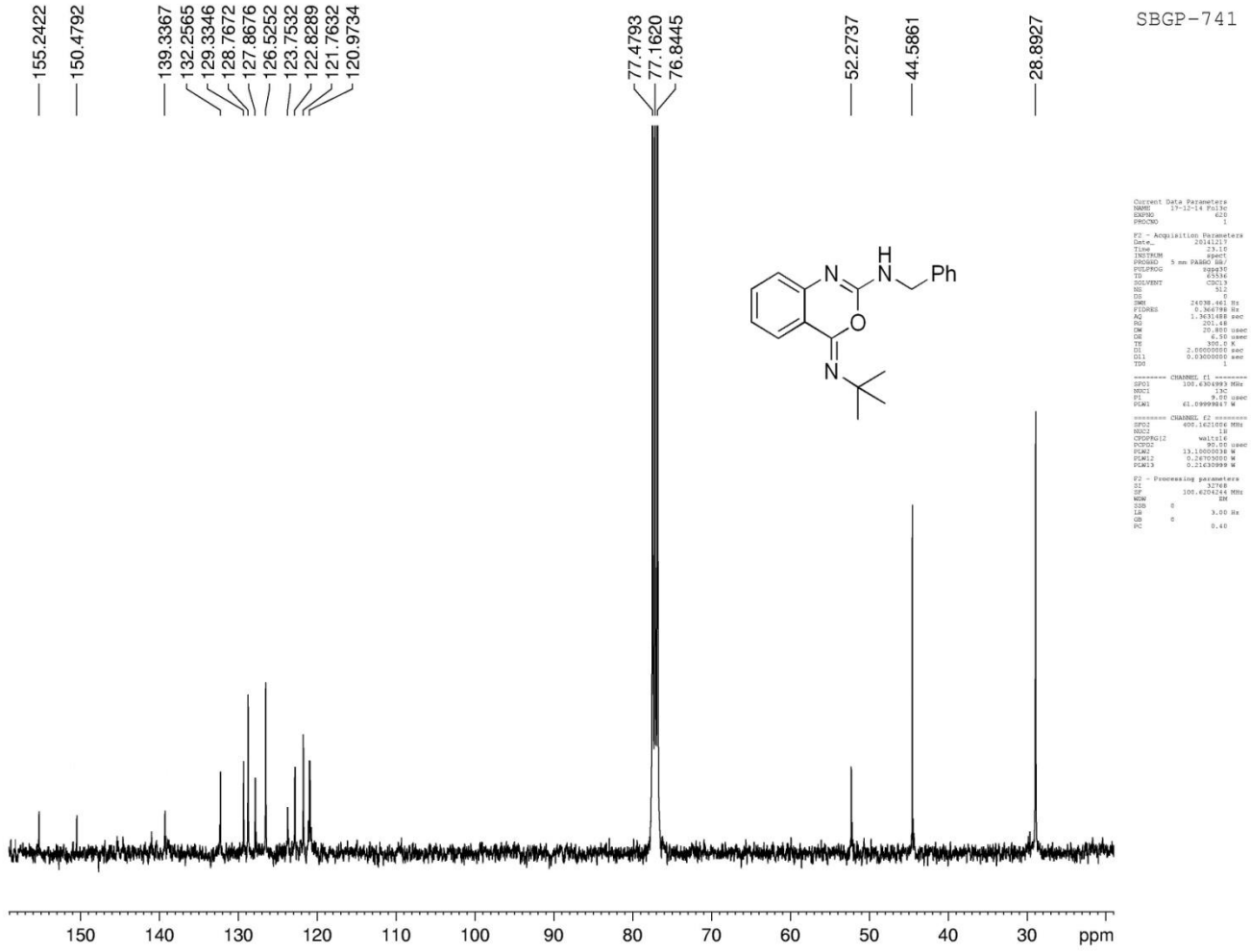


Fig: S-16 ^{13}C spectrum of *N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hA)**

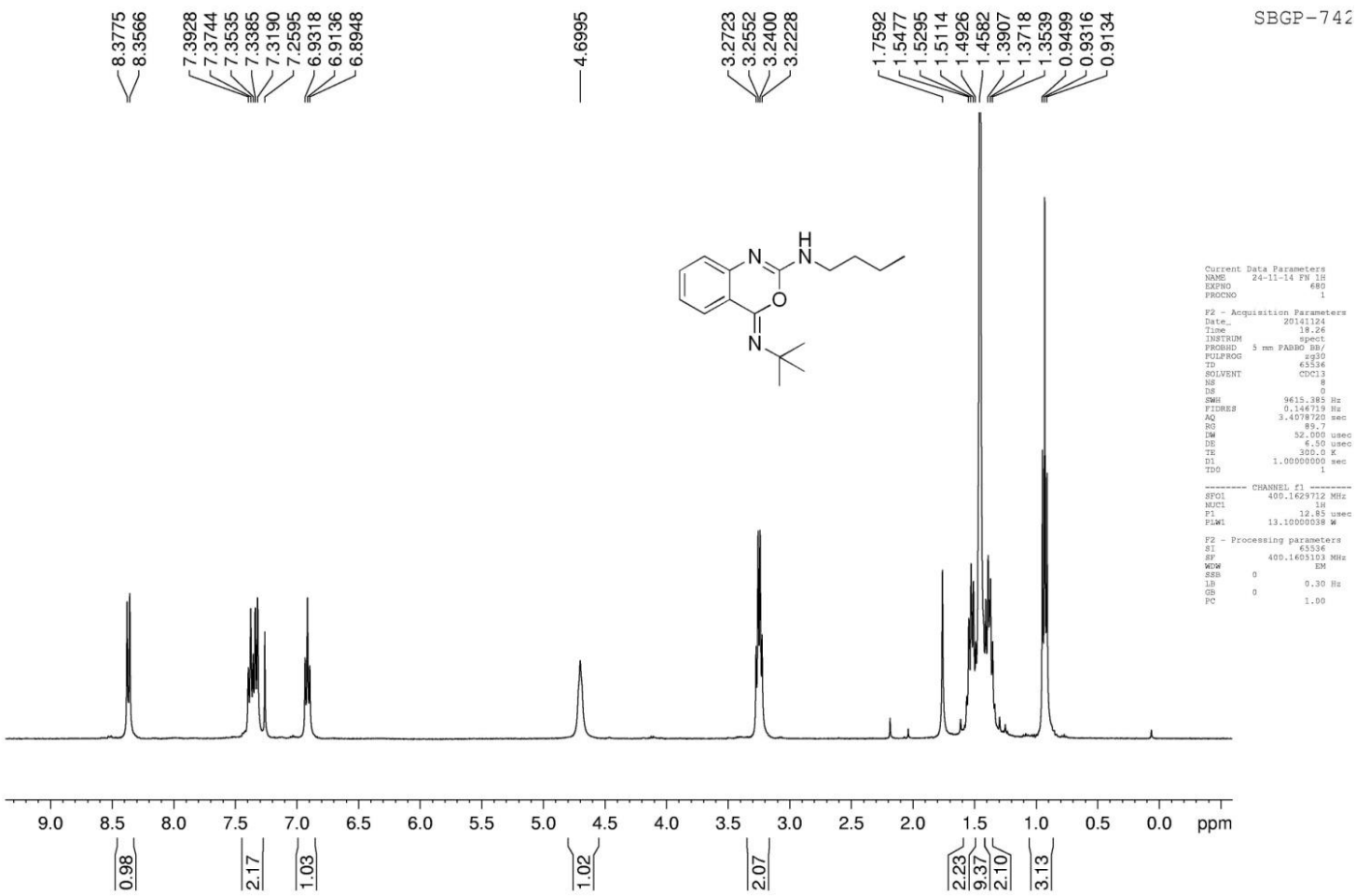


Fig: S-17 ^{1}H spectrum of *N*-butyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3iA)**

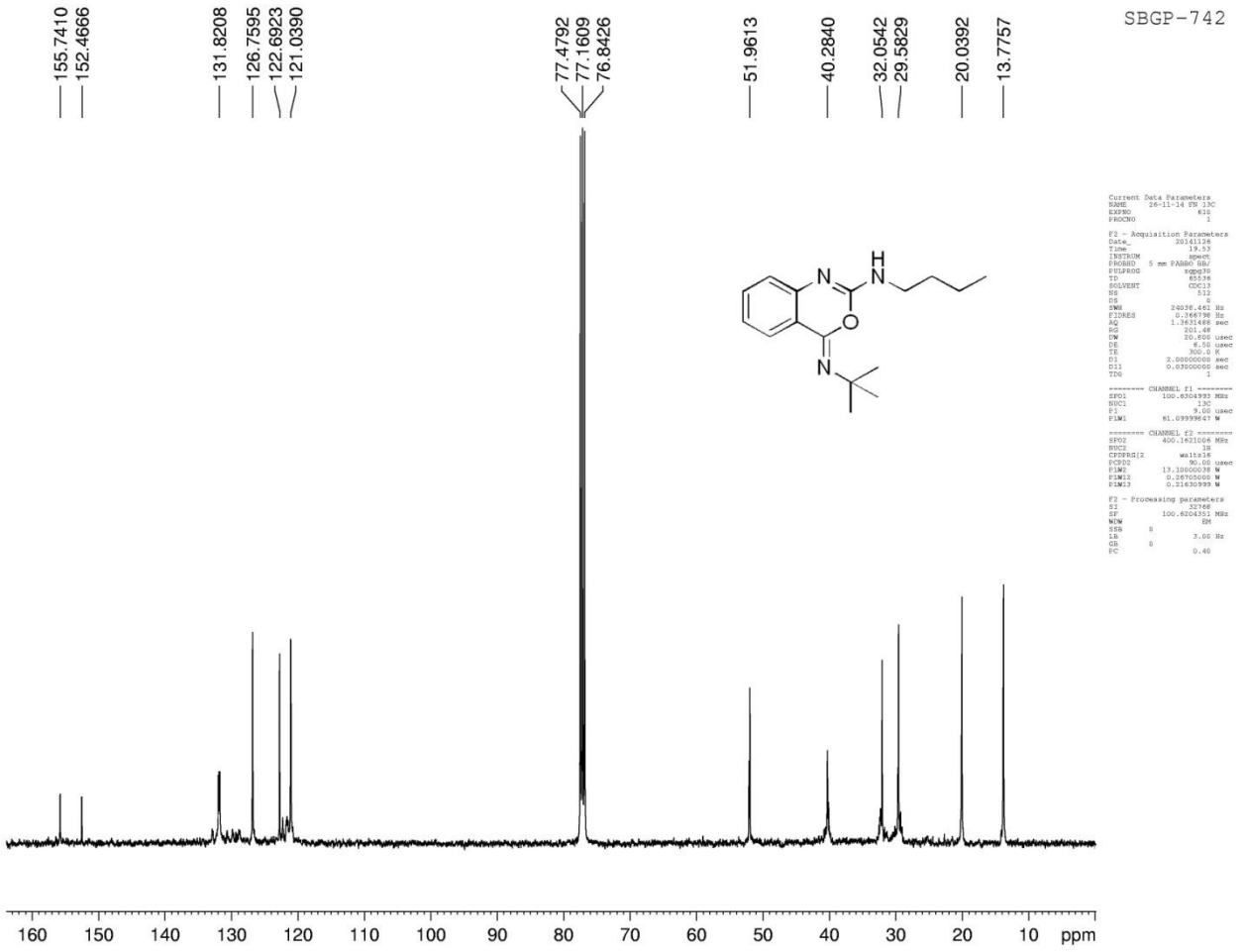


Fig: S-18 ^{13}C spectrum of *N*-butyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3iA)**

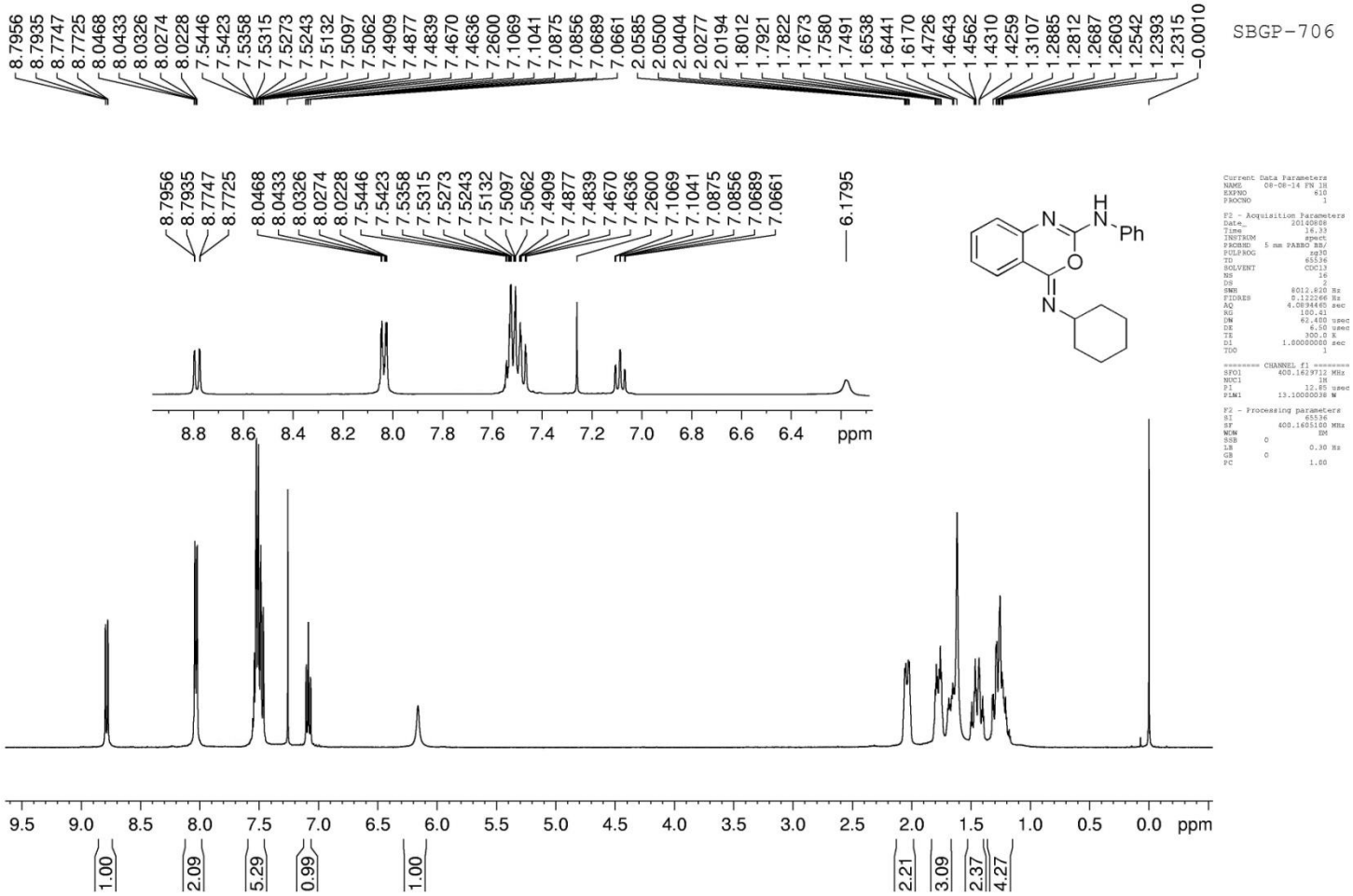


Fig: S-19 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aB)**

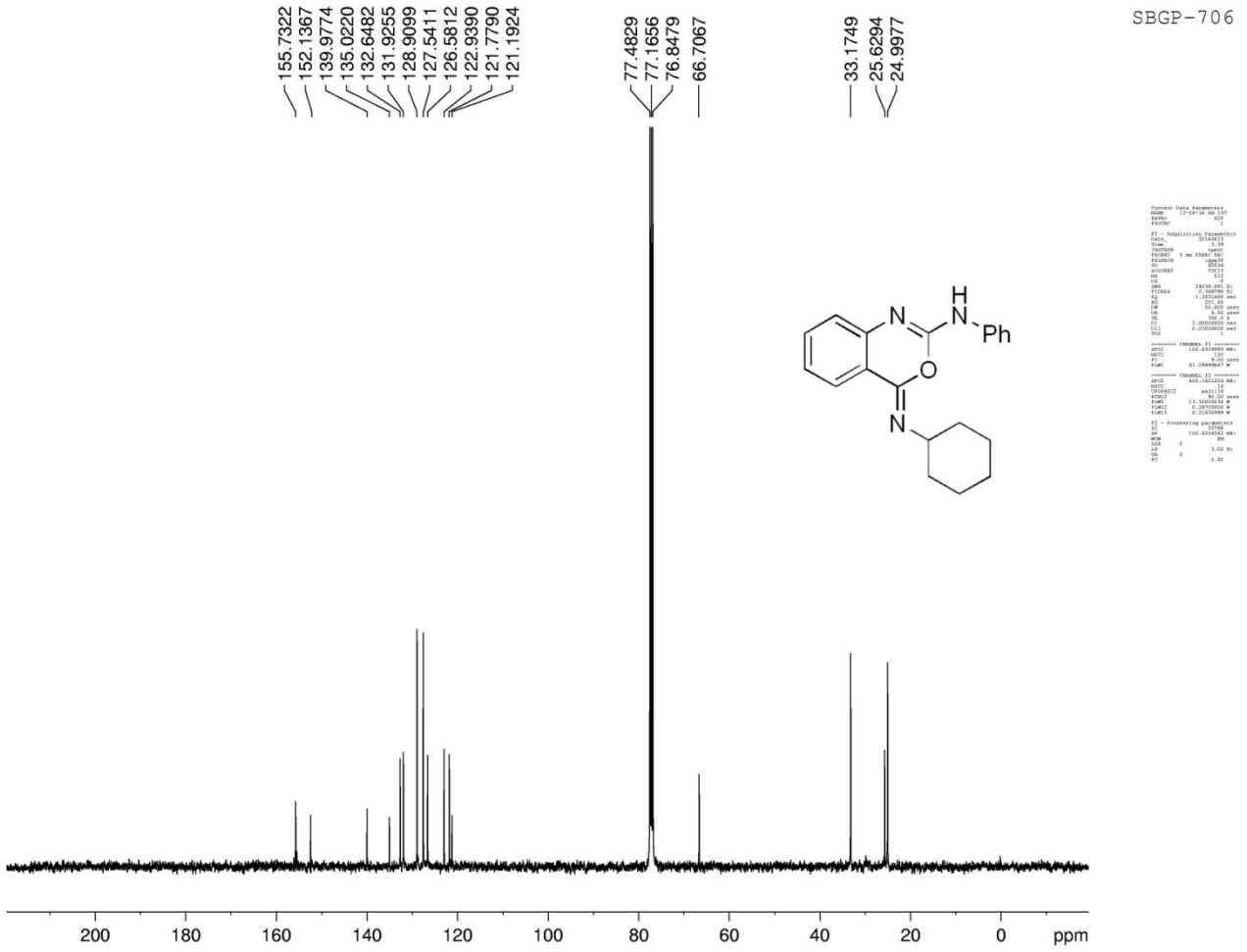


Fig: S-20 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aB)**

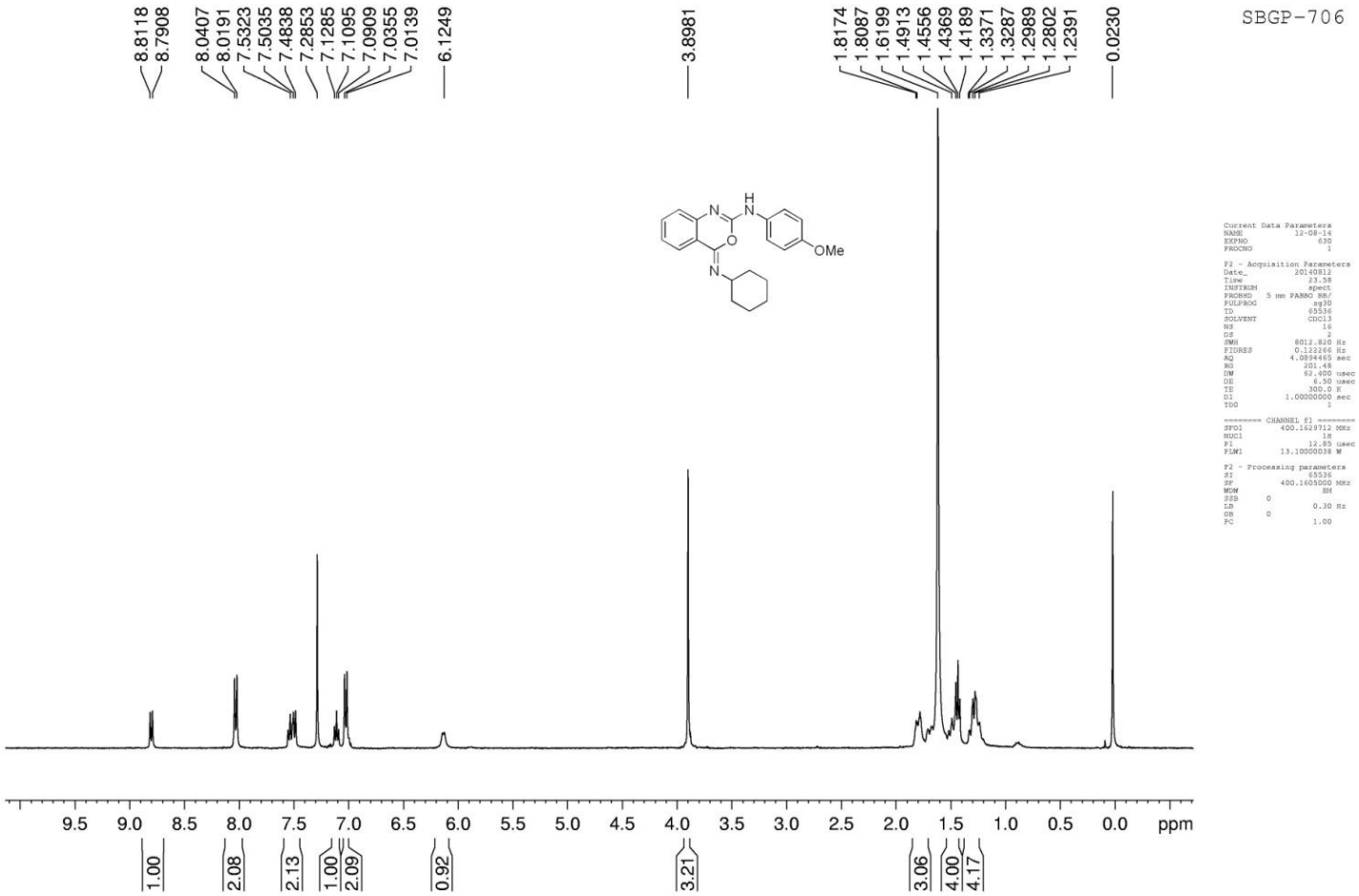


Fig: S-21 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3bB)**

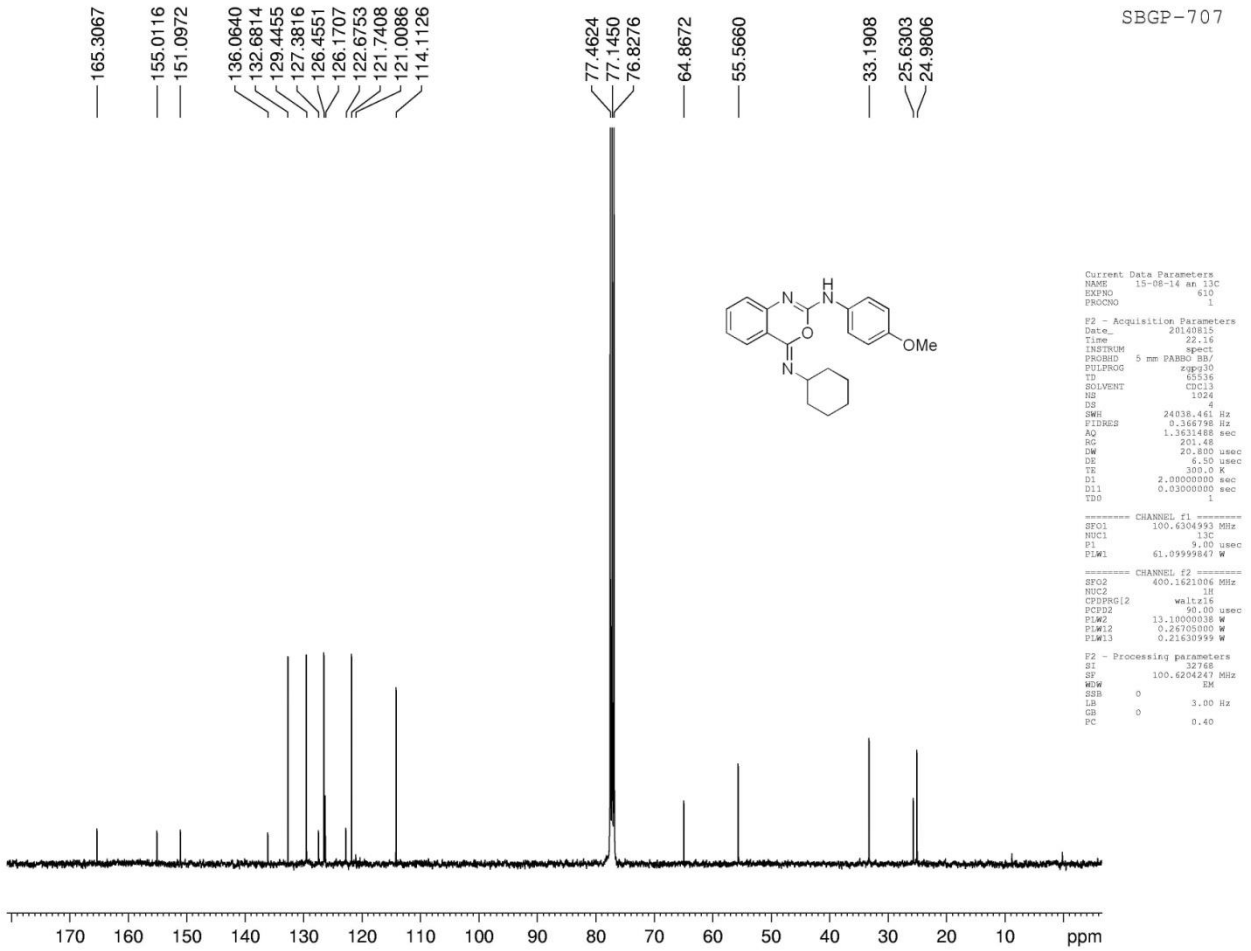


Fig: S-22 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3bB)**

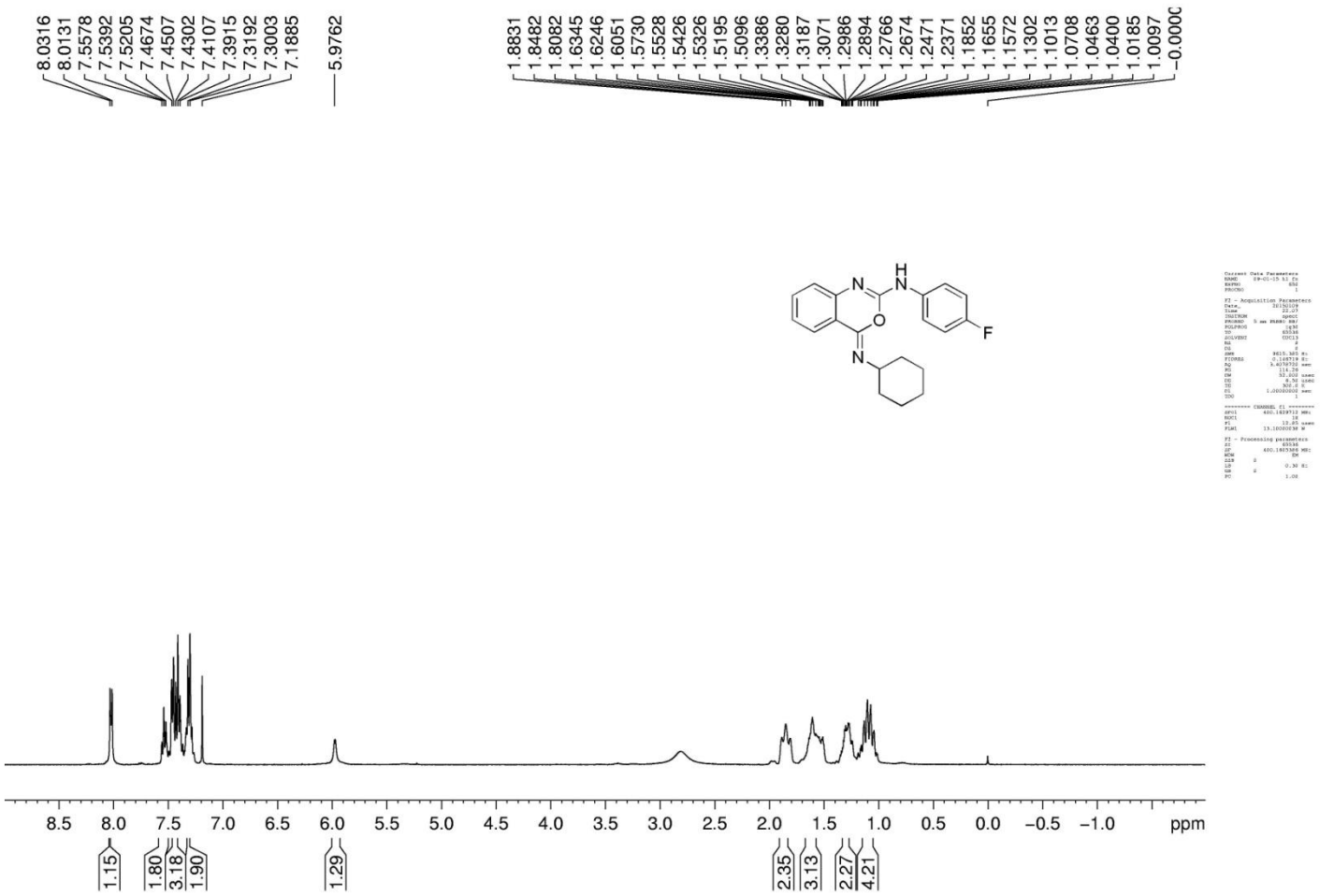


Fig: S-23 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cB)**

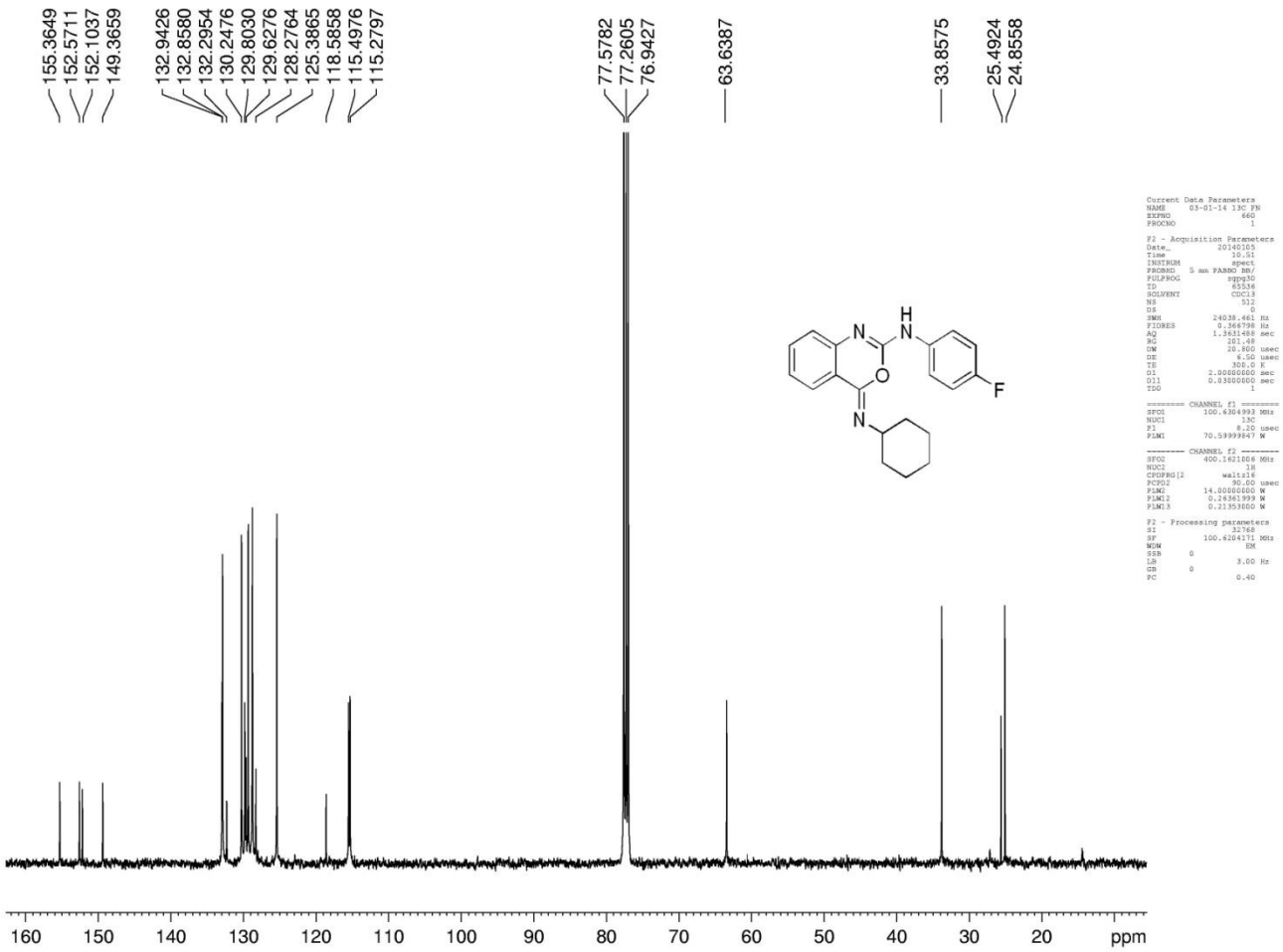


Fig: S-24 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cB)**

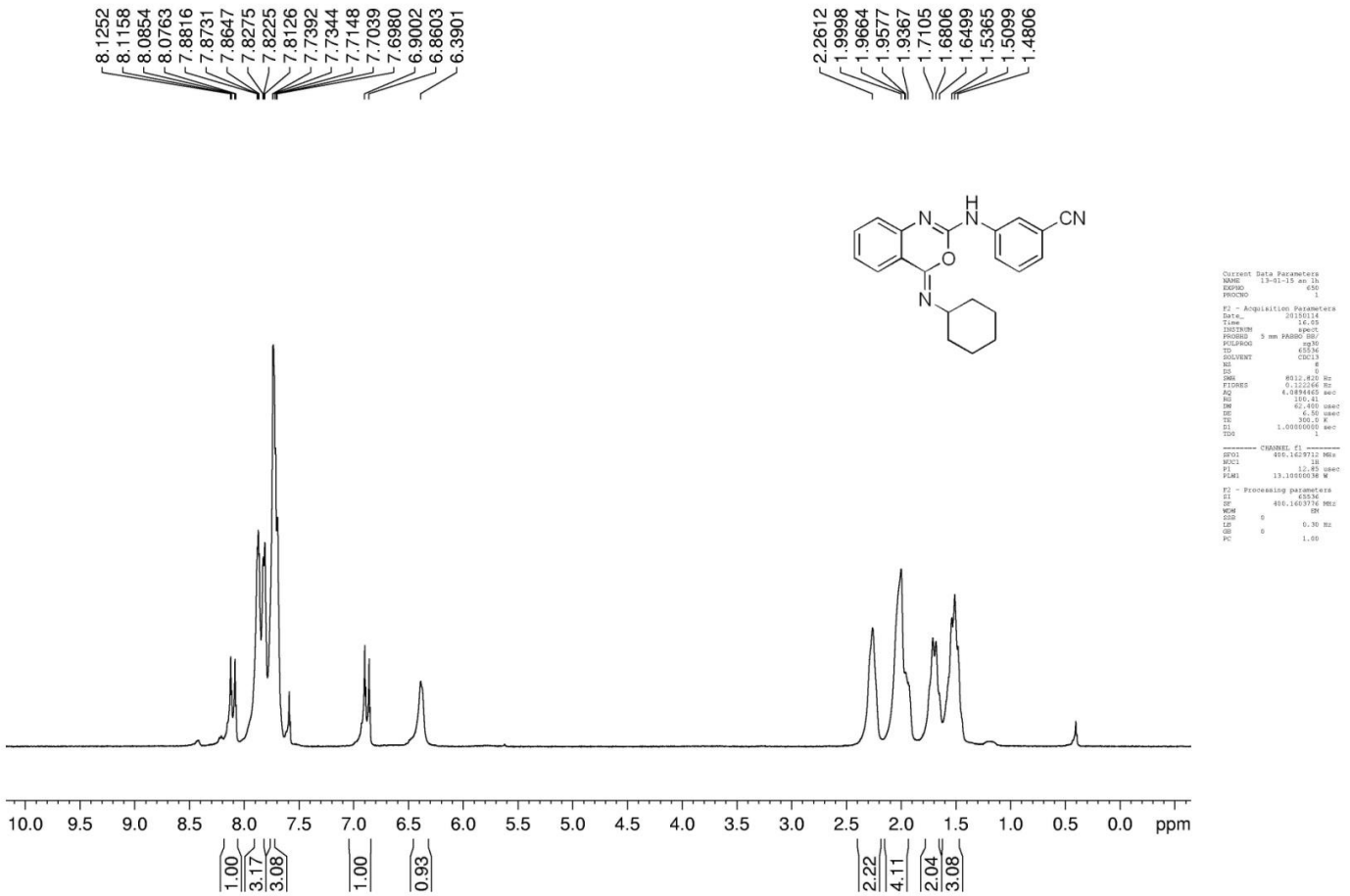


Fig: S-25 ^{1}H spectrum of 3-(4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (**3dB)**

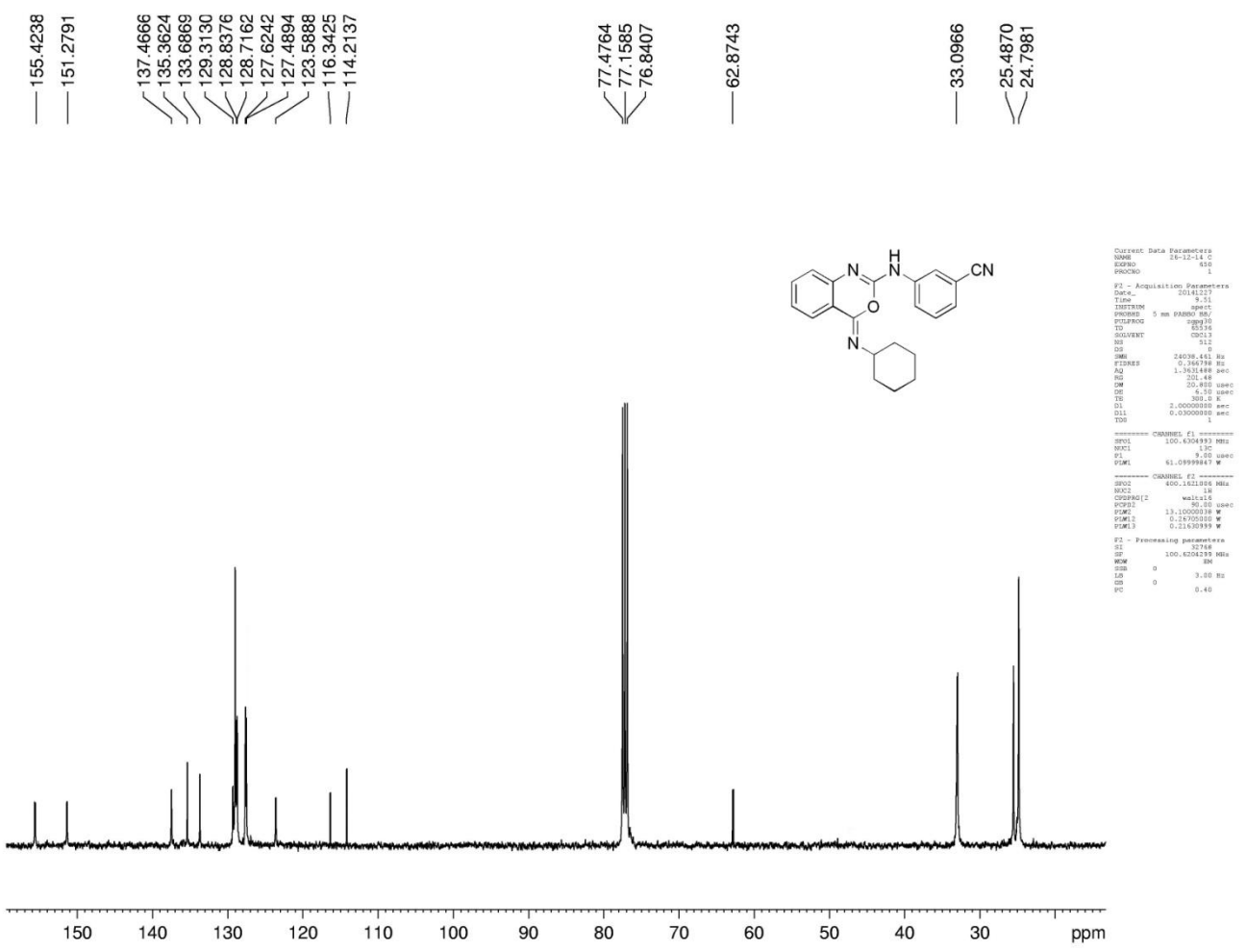


Fig: S-26 ^{13}C spectrum of 3-(4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (**3dB)**

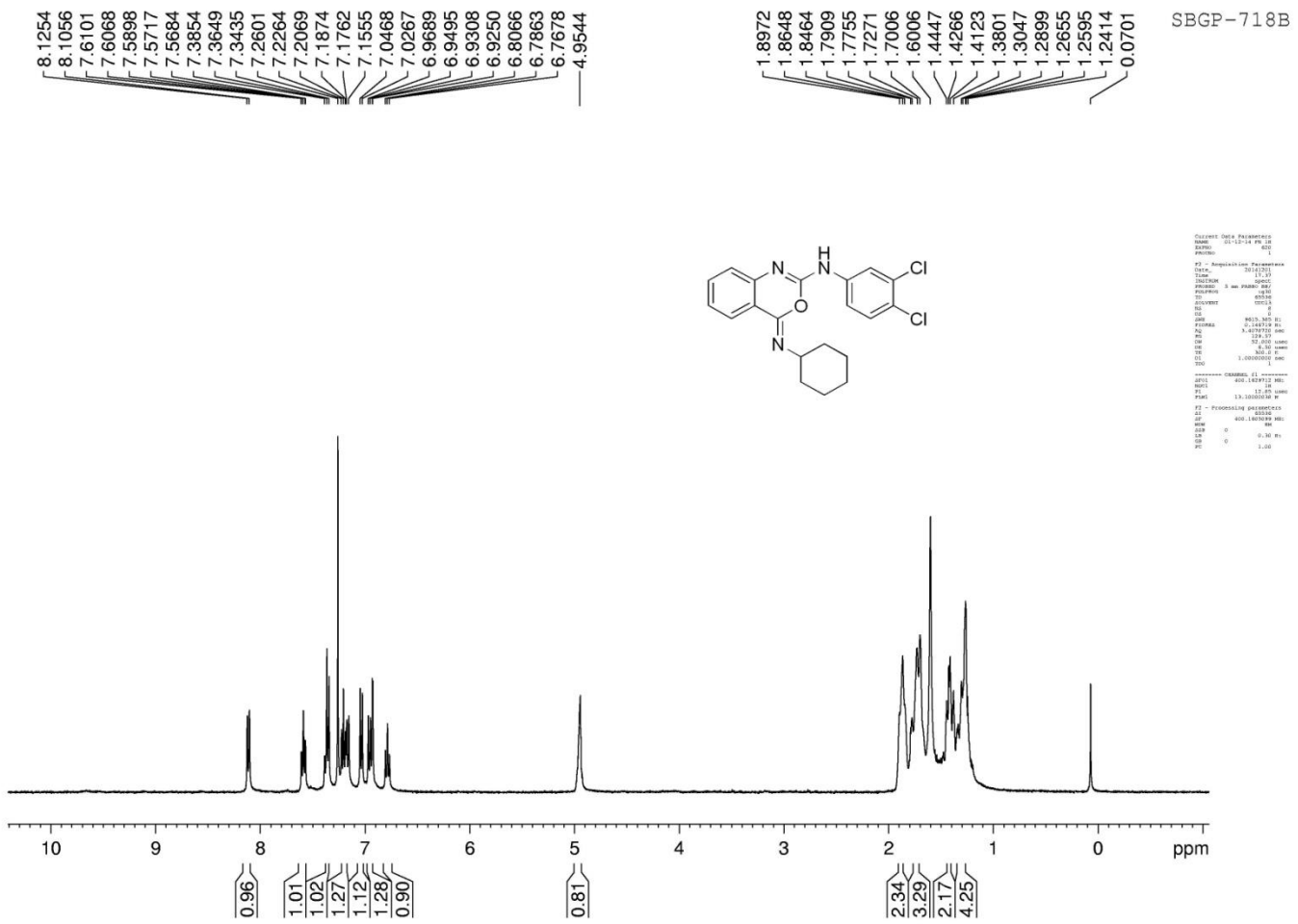


Fig: S-27 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3eB)**

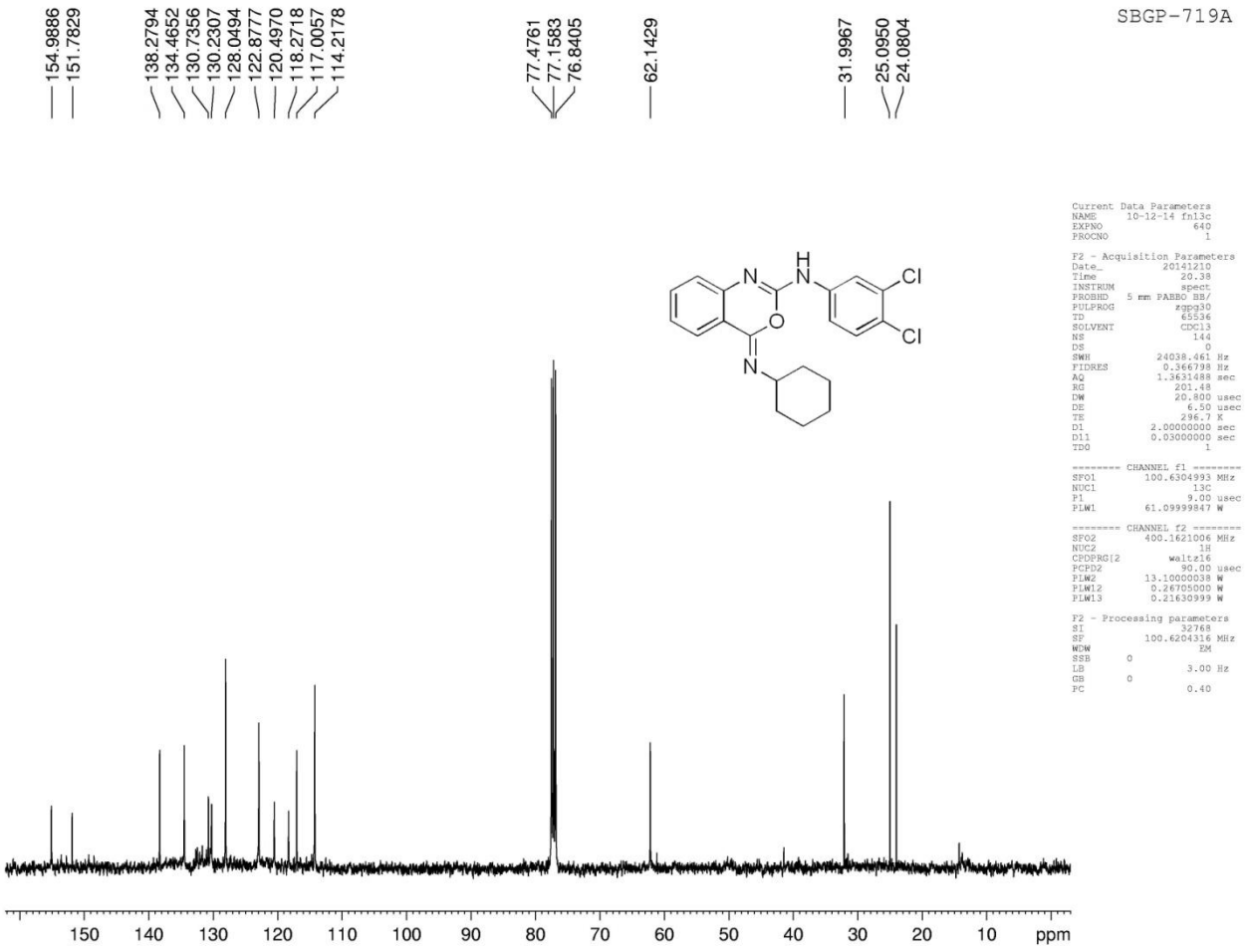


Fig: S-28 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3eB)**

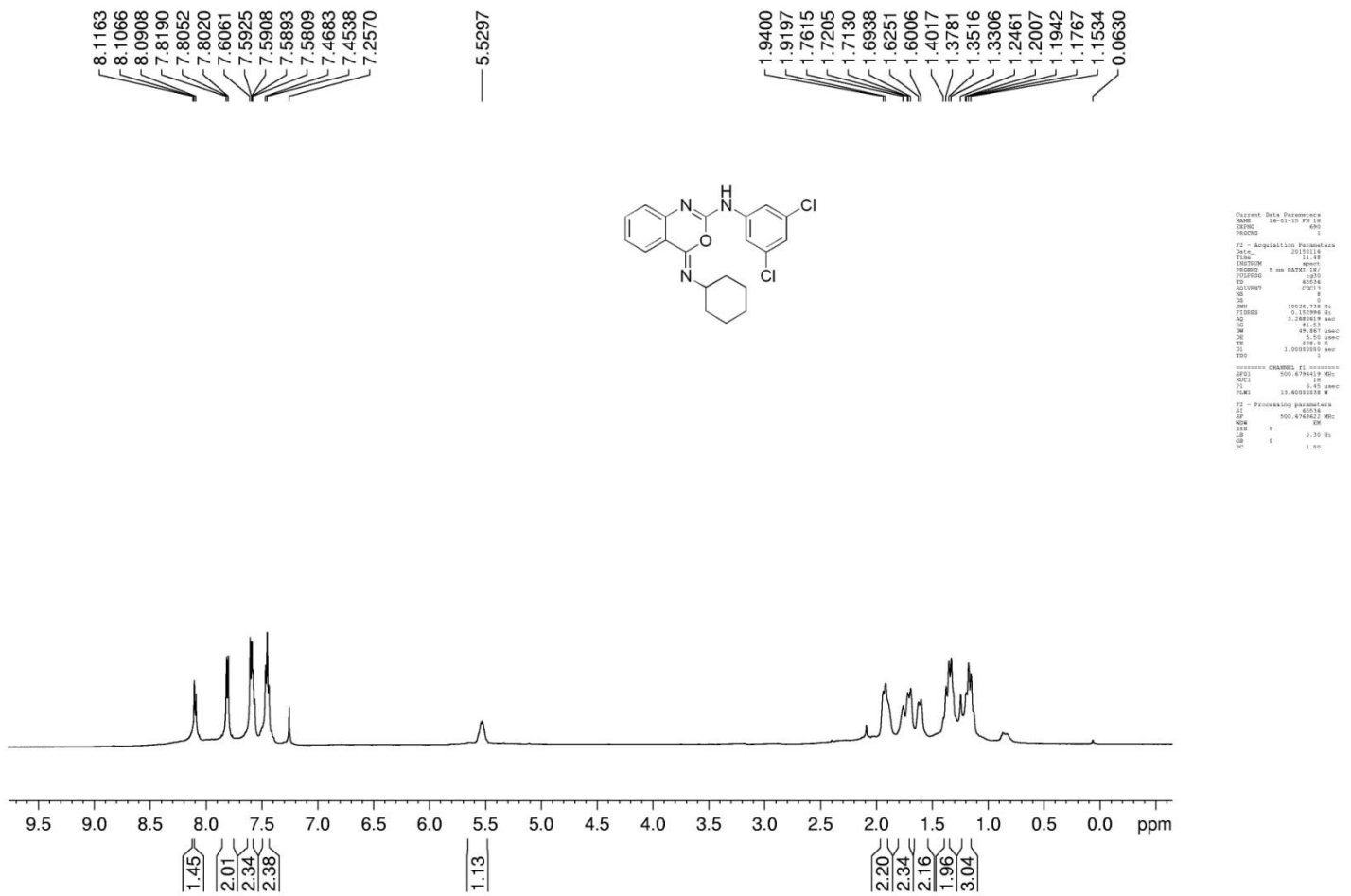


Fig: S-29 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-(3, 5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fB)**

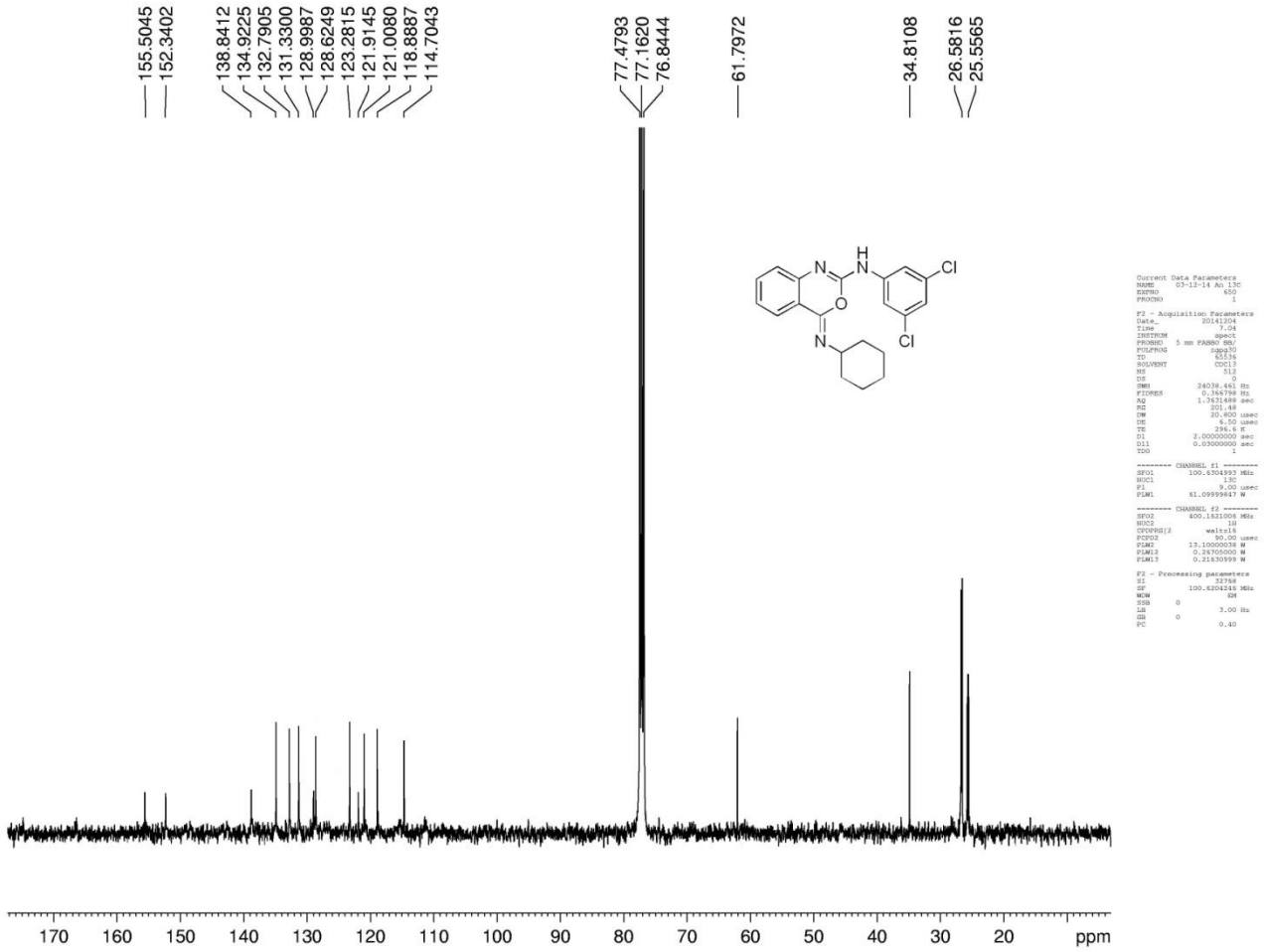


Fig: S-30 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(3, 5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fB)**

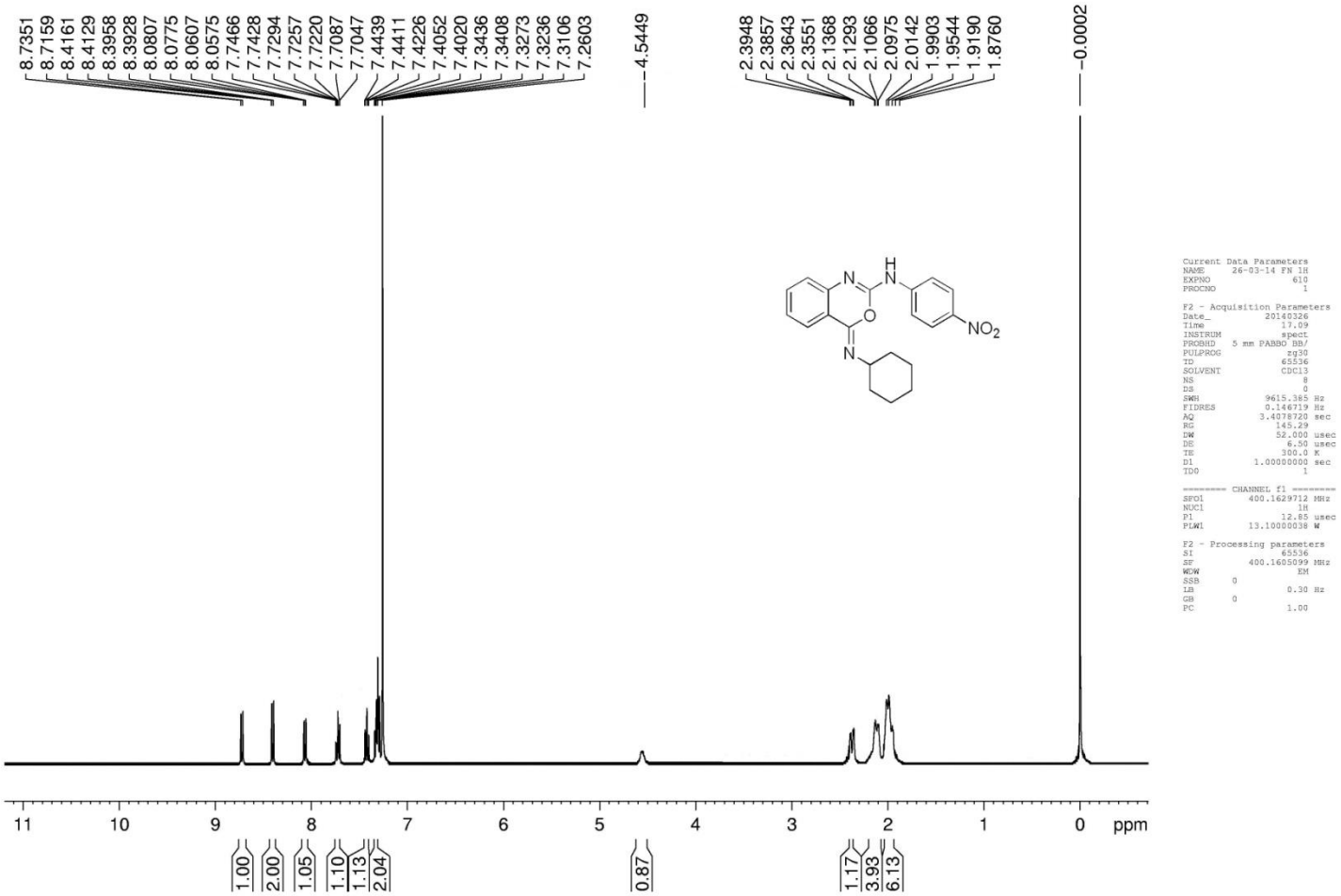


Fig: S-31 ^{1}H spectrum of 4-(Cyclohexylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3gB)**

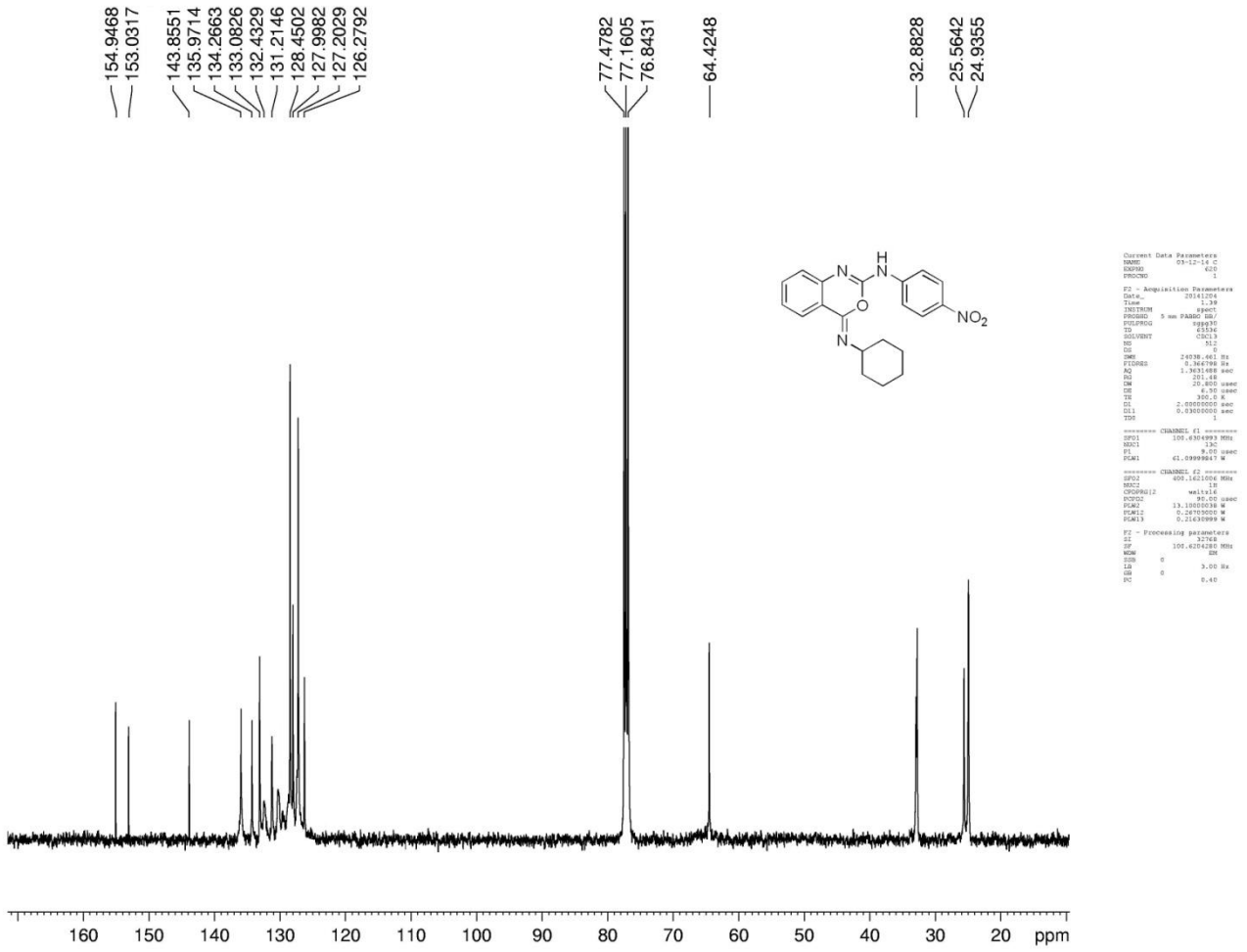


Fig: S-32 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3gB)**

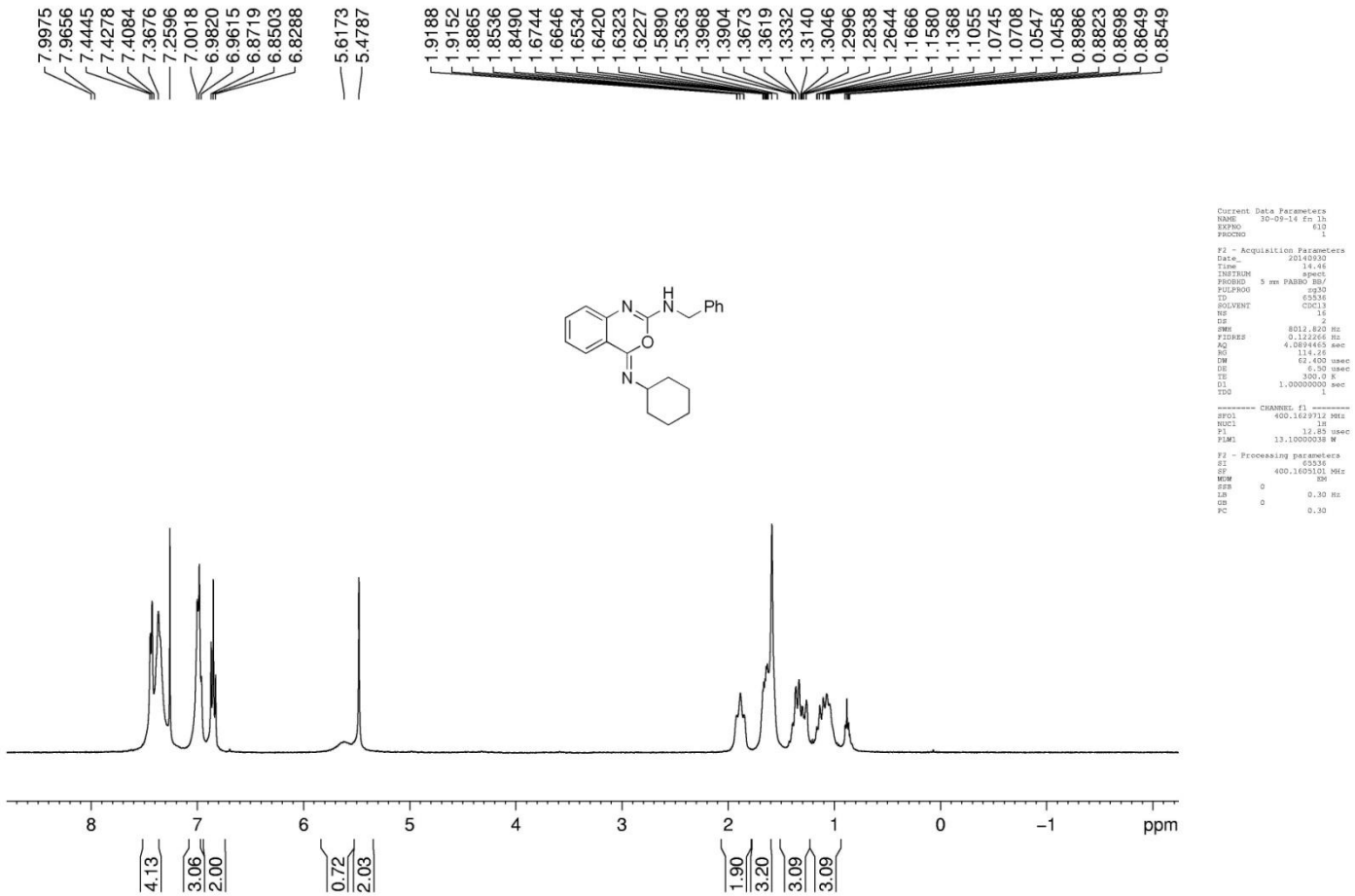


Fig: S-33 ^{1}H spectrum of *N*-benzyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hB)**

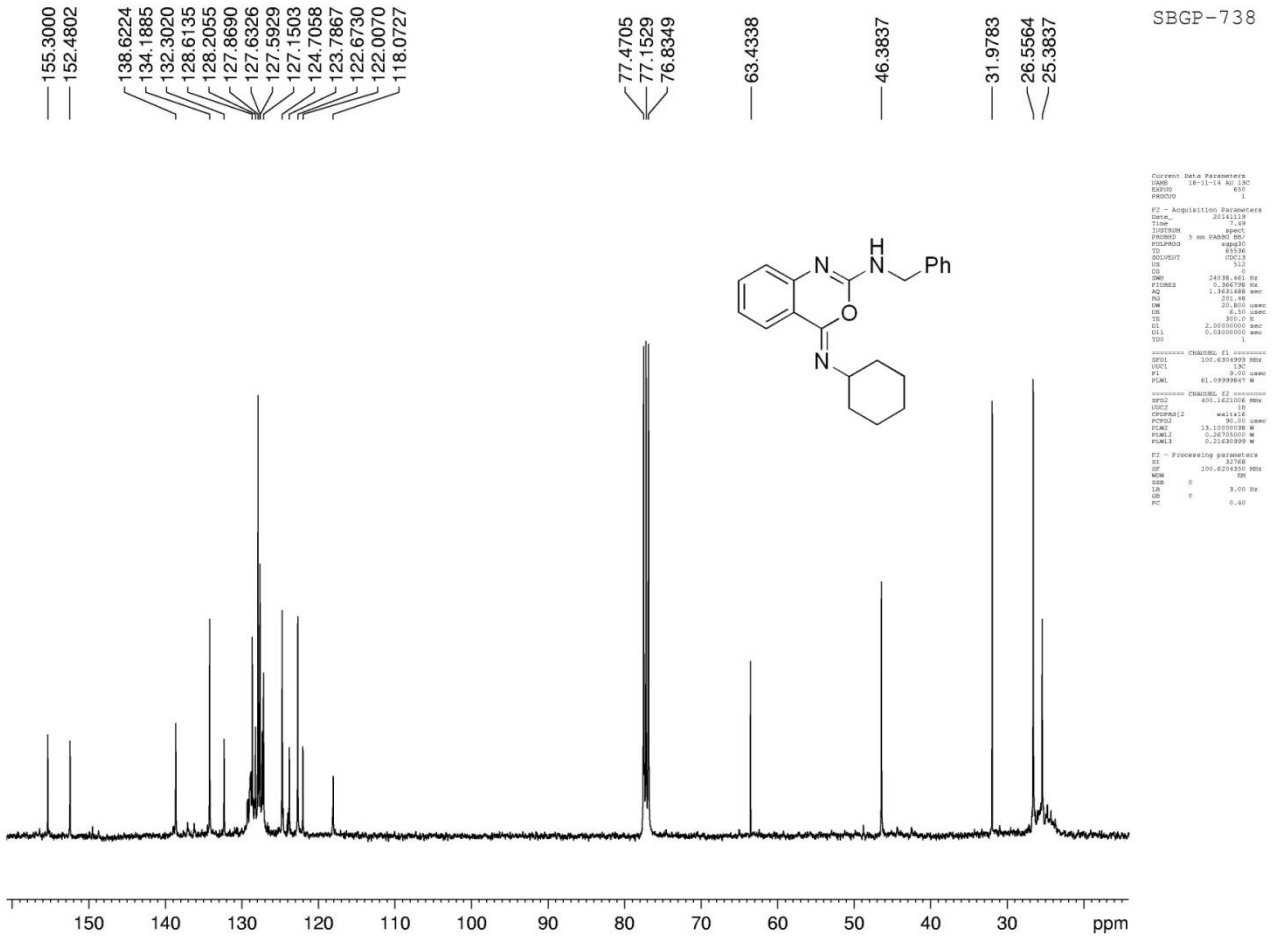


Fig: S-34 ^{13}C spectrum of *N*-benzyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hB)**

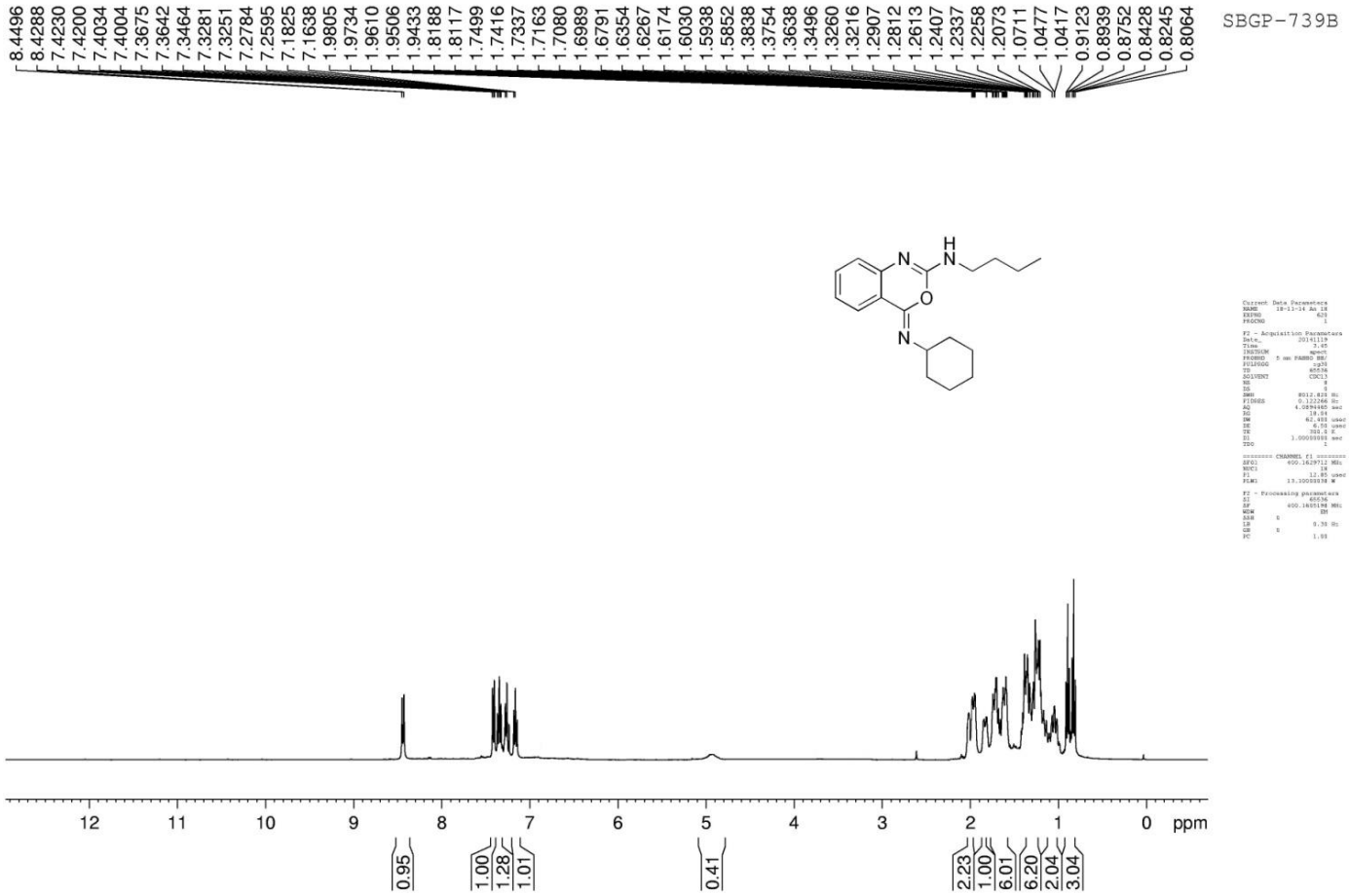


Fig: S-35 ^{1}H spectrum of *N*-butyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3iB)**

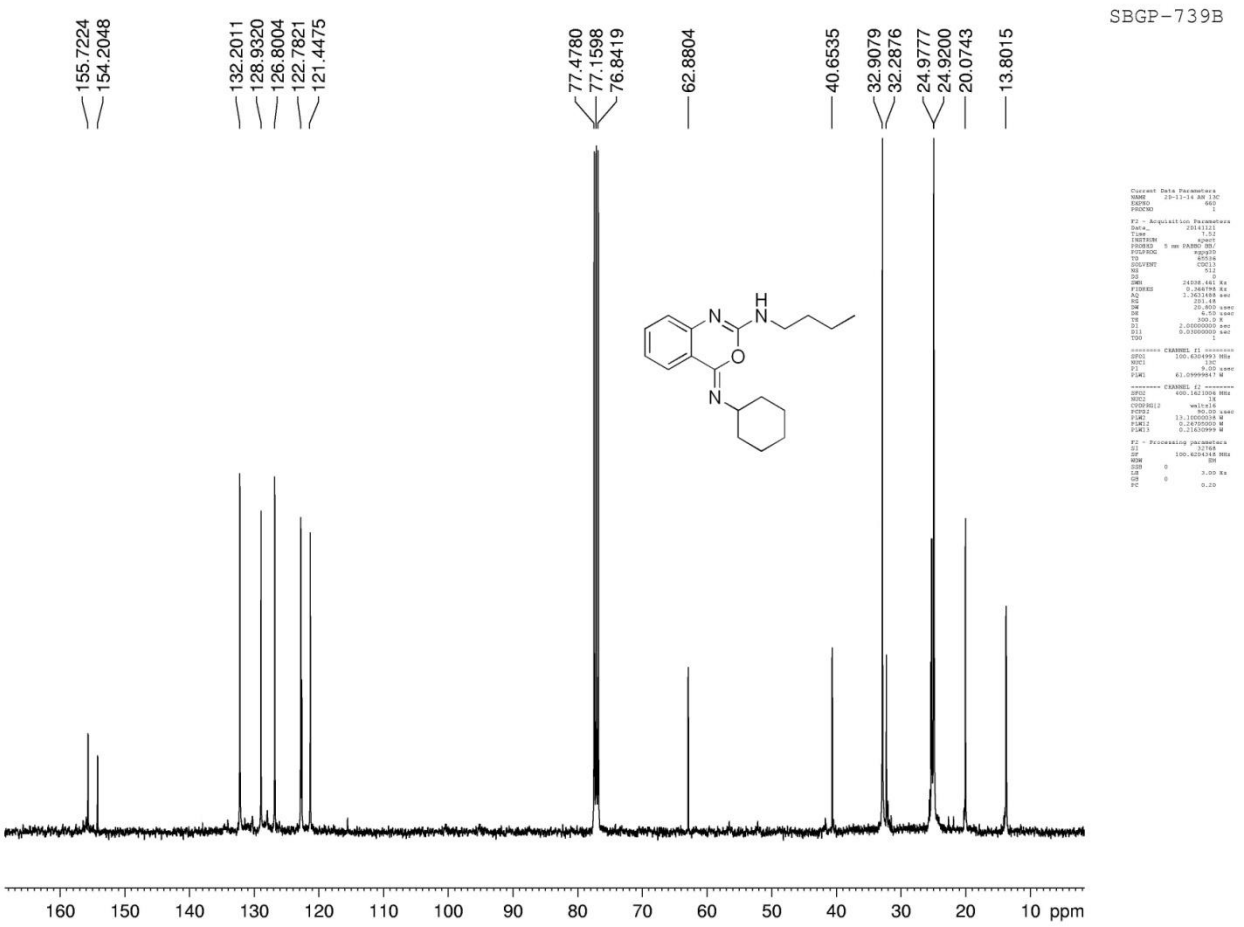


Fig: S-36 ^{13}C spectrum of *N*-butyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3iB)**

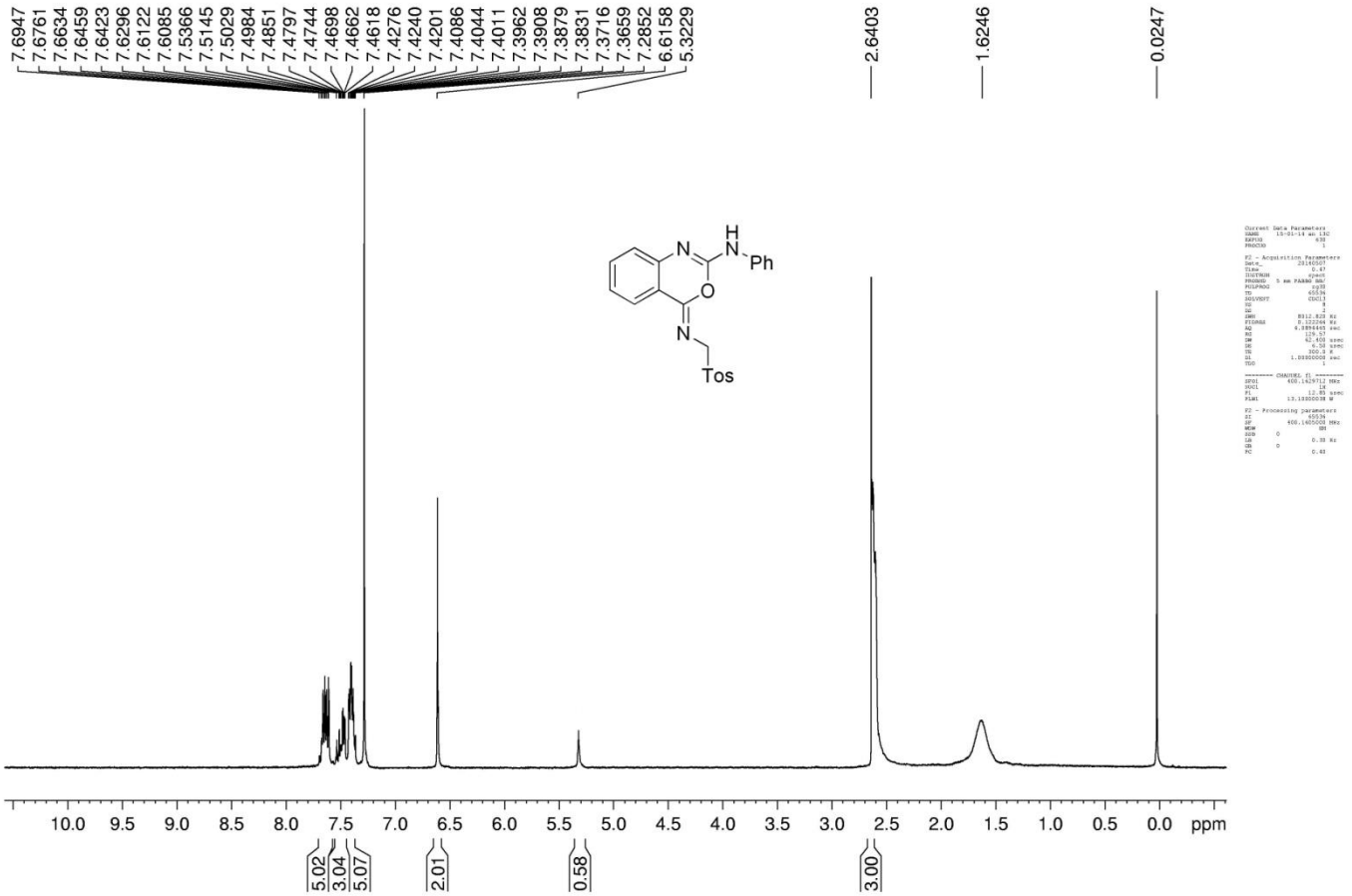


Fig: S-37 ^{1}H spectrum of *N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aC)**

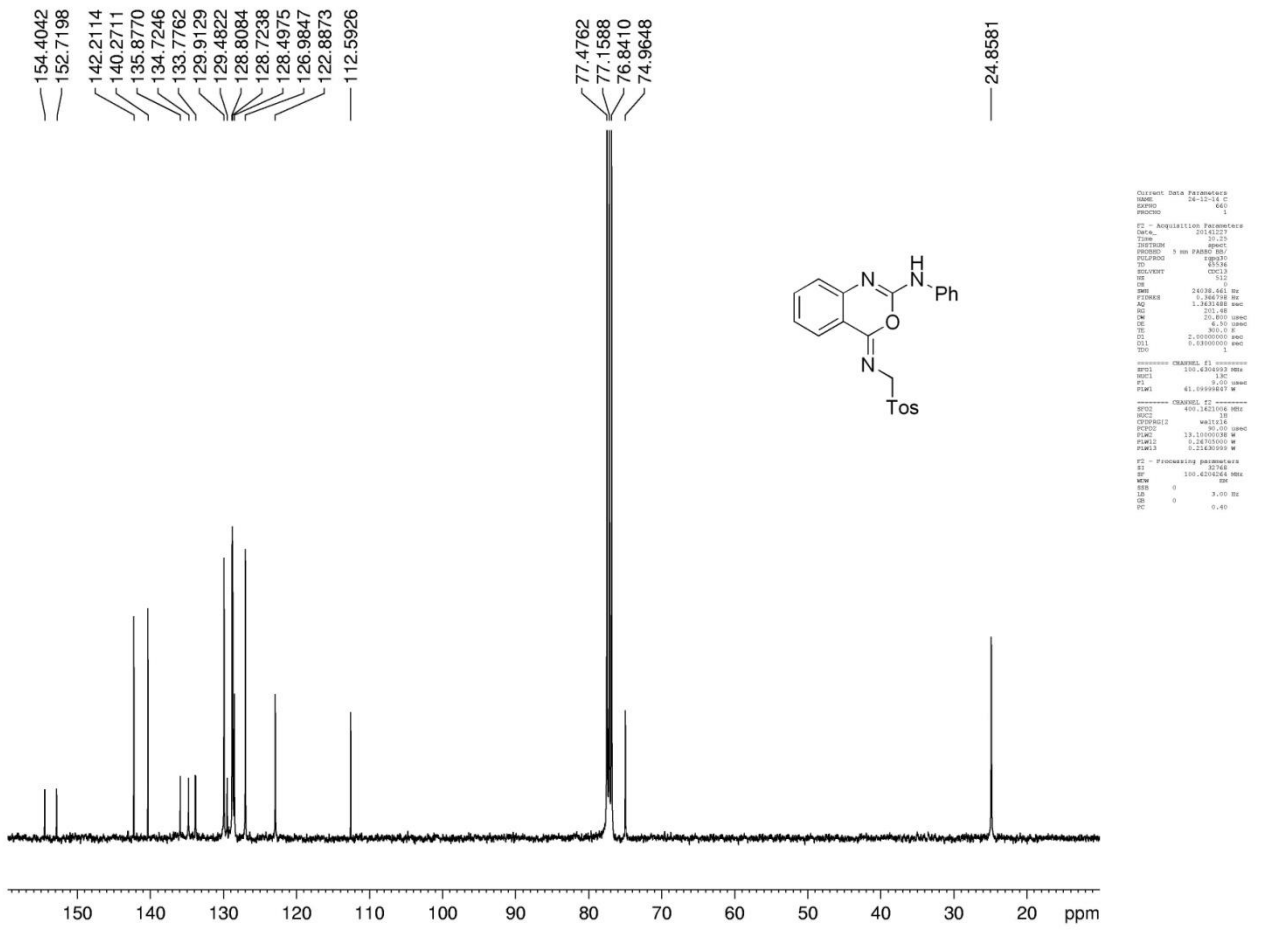


Fig: S-38 ^{13}C spectrum of *N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aC)**

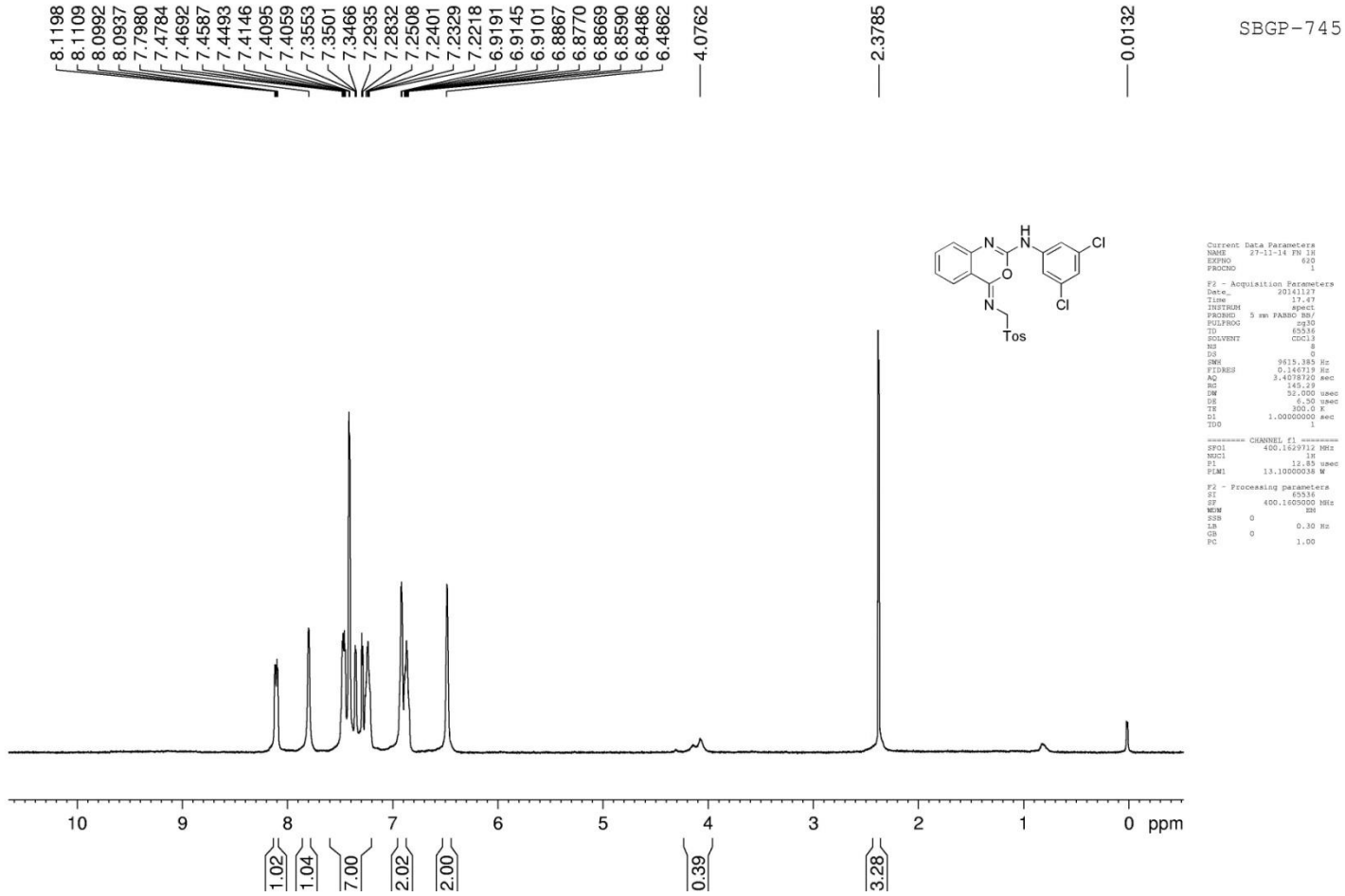


Fig: S-39 ^{1}H spectrum of *N*-(3,5-Dichlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fC)**

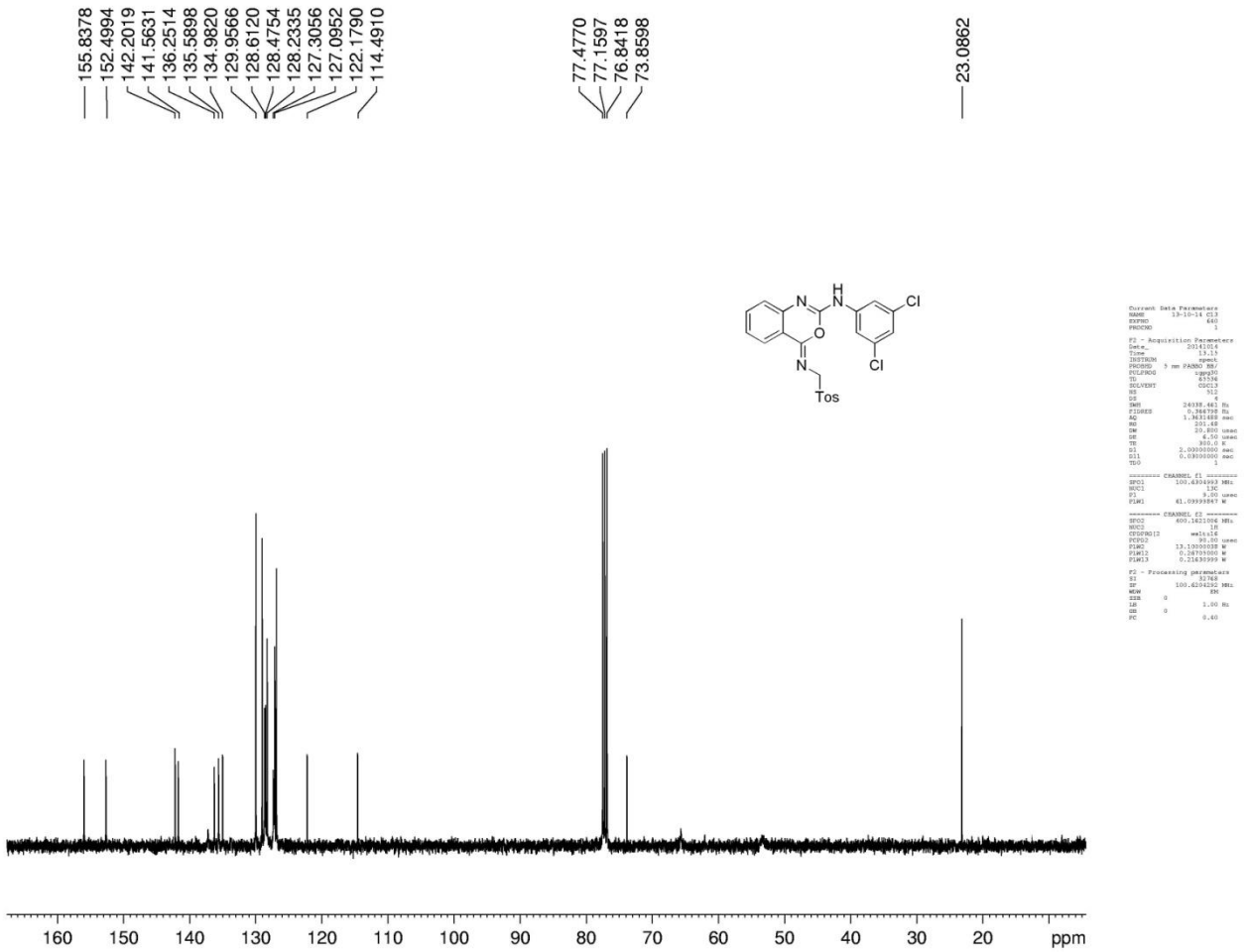


Fig: S-40 ^{13}C spectrum of *N*-(3,5-Dichlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3fC)**

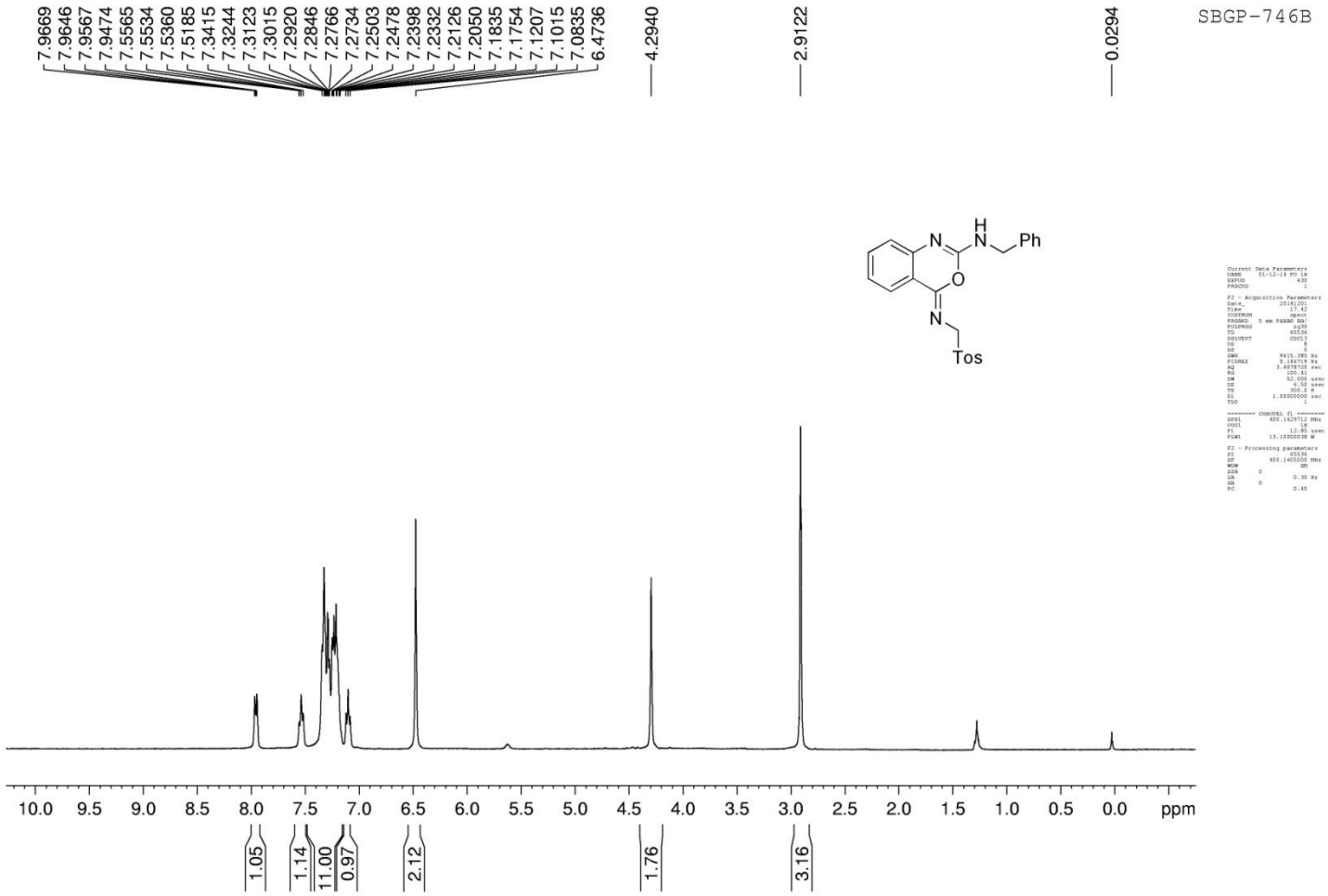


Fig: S-41 ^{1}H spectrum of *N*-benzyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hC)**

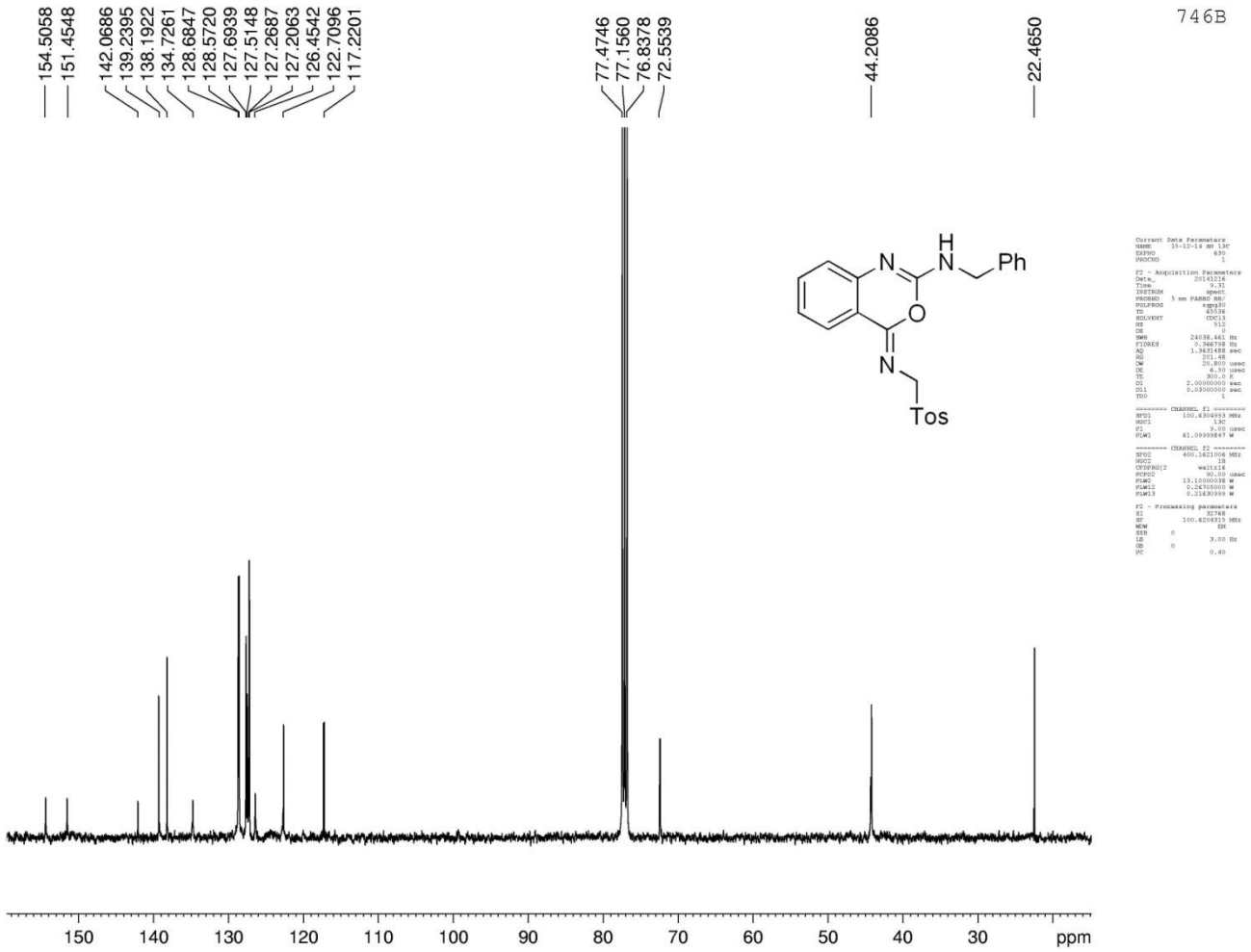


Fig: S-42 ^{13}C spectrum of *N*-benzyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3hC)**

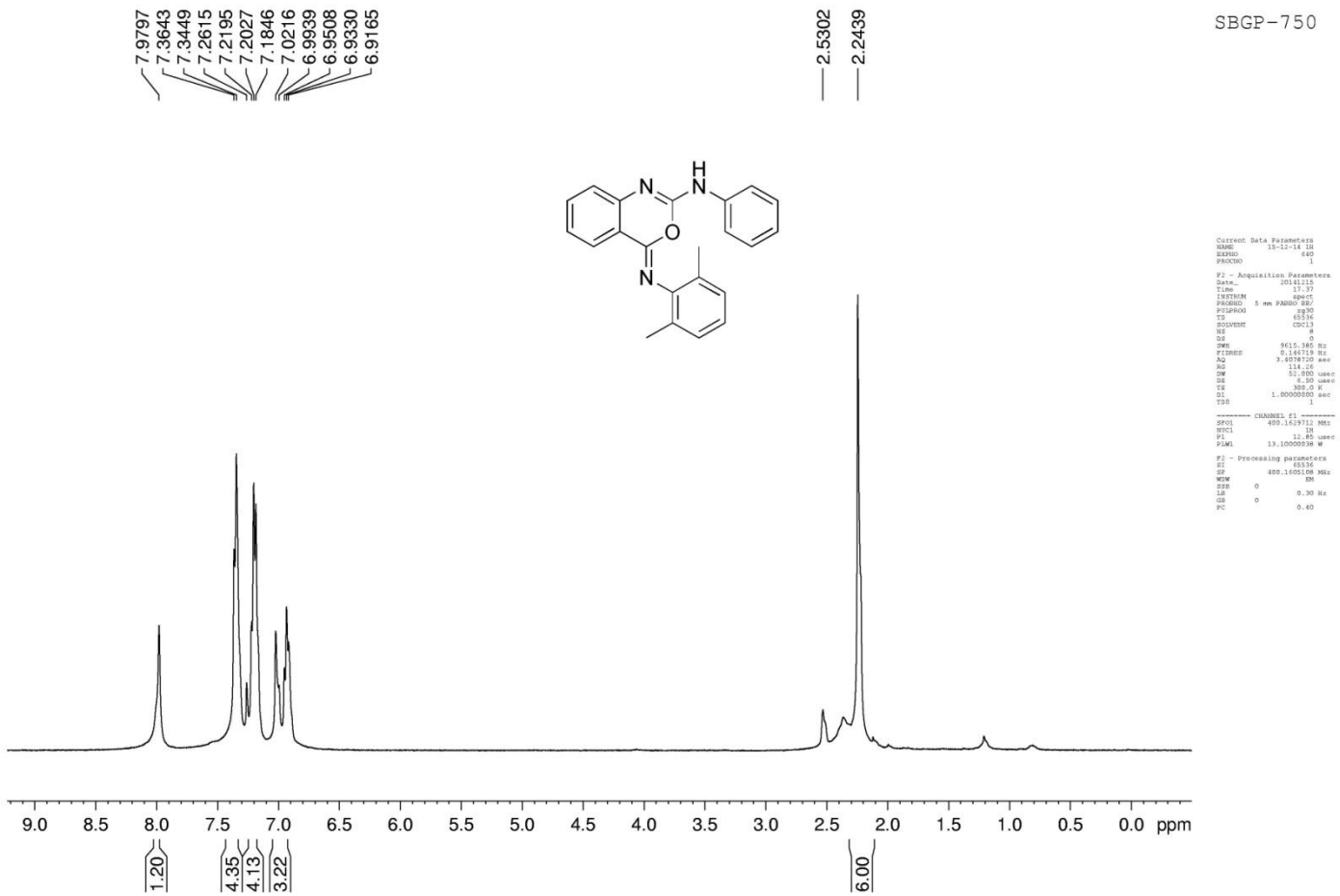


Fig: S-43 ^{1}H spectrum of (2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aD)**

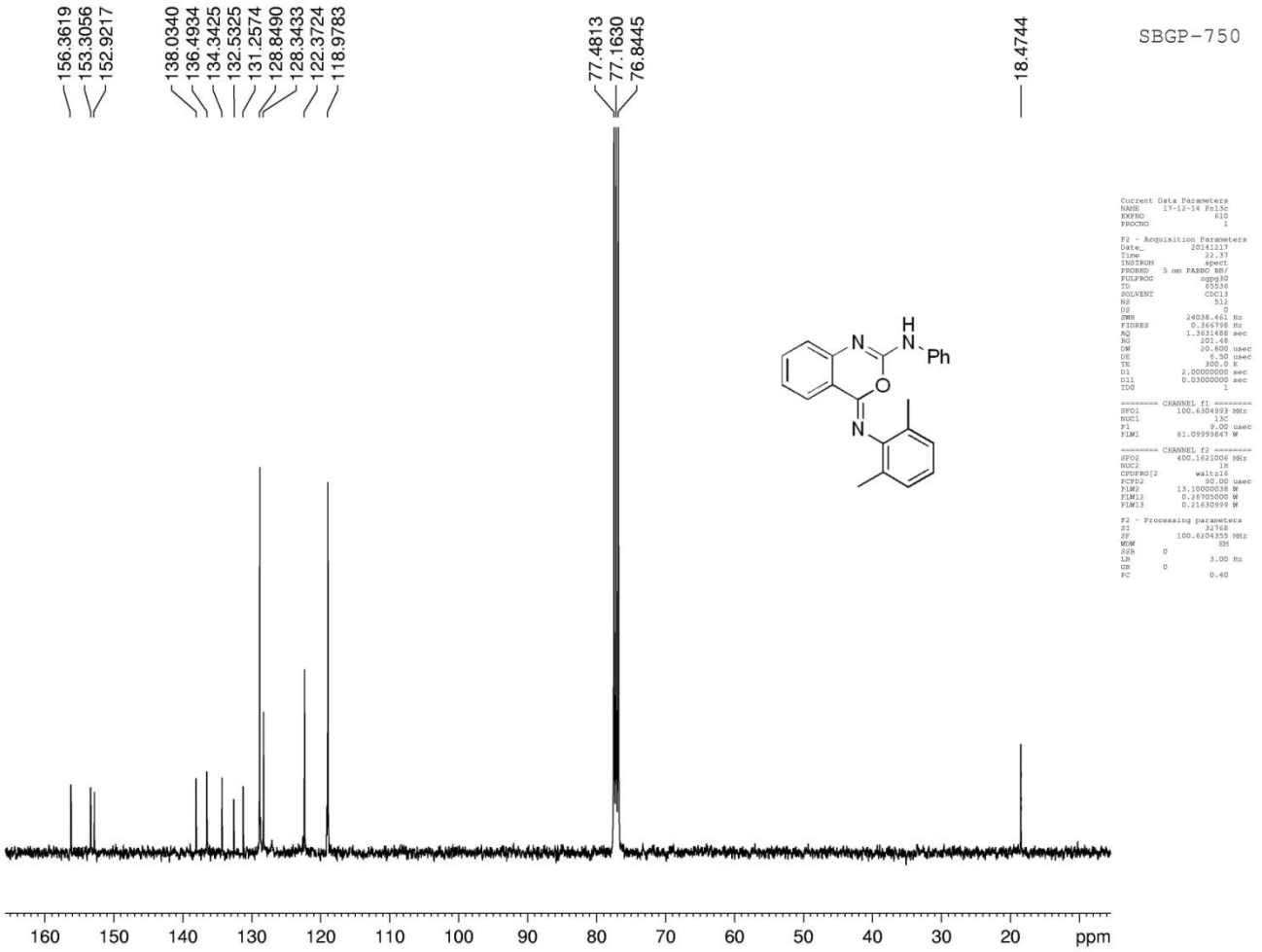


Fig: S-44 ^{13}C spectrum of 4-(2, 6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3aD)**

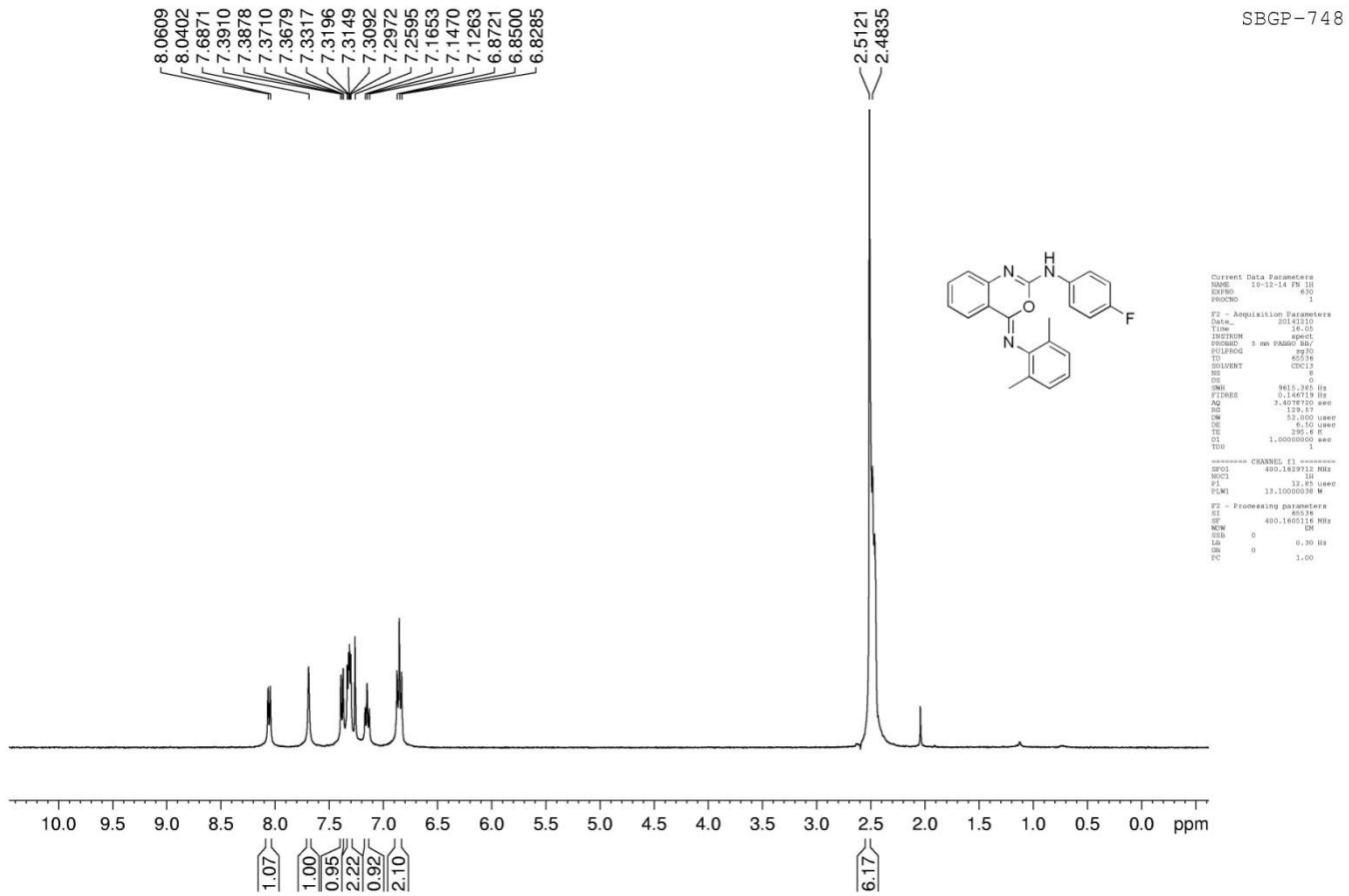


Fig: S-45 ^{1}H spectrum of 4-(2, 6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3cD)**

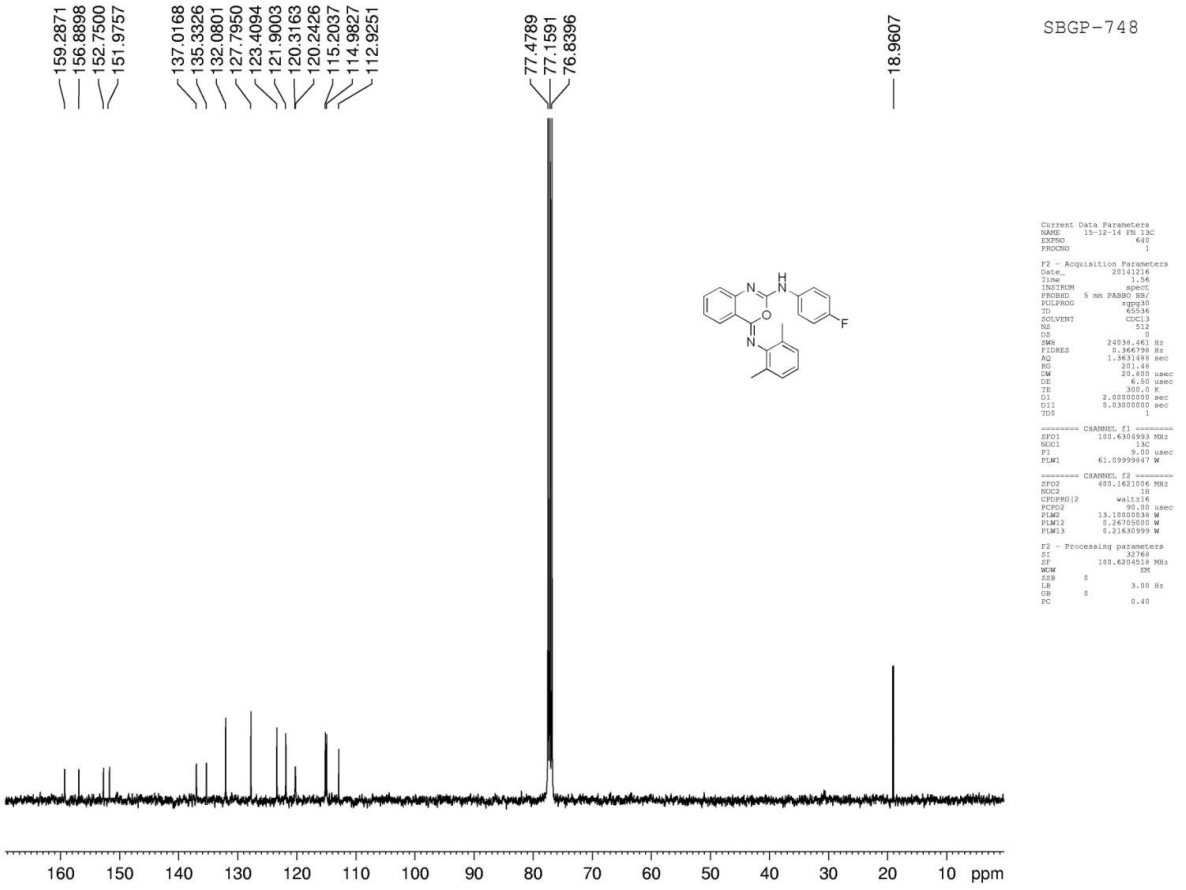


Fig: S-46 ^{13}C spectrum of 4-(2, 6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(3cD)**

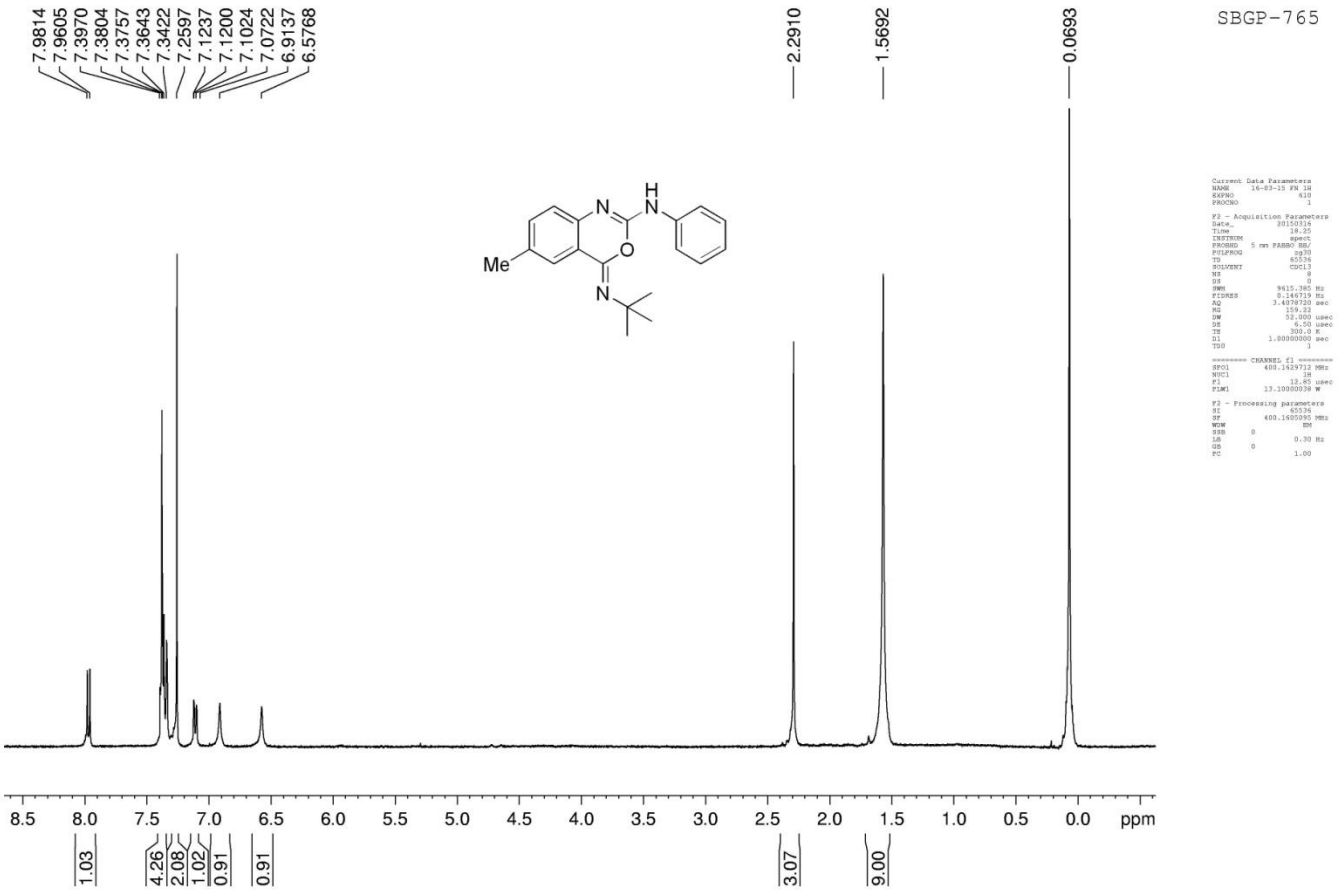


Fig: S-47 ^{1}H spectrum of 4-(*tert*-butylimino)-6-methyl-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(7)**

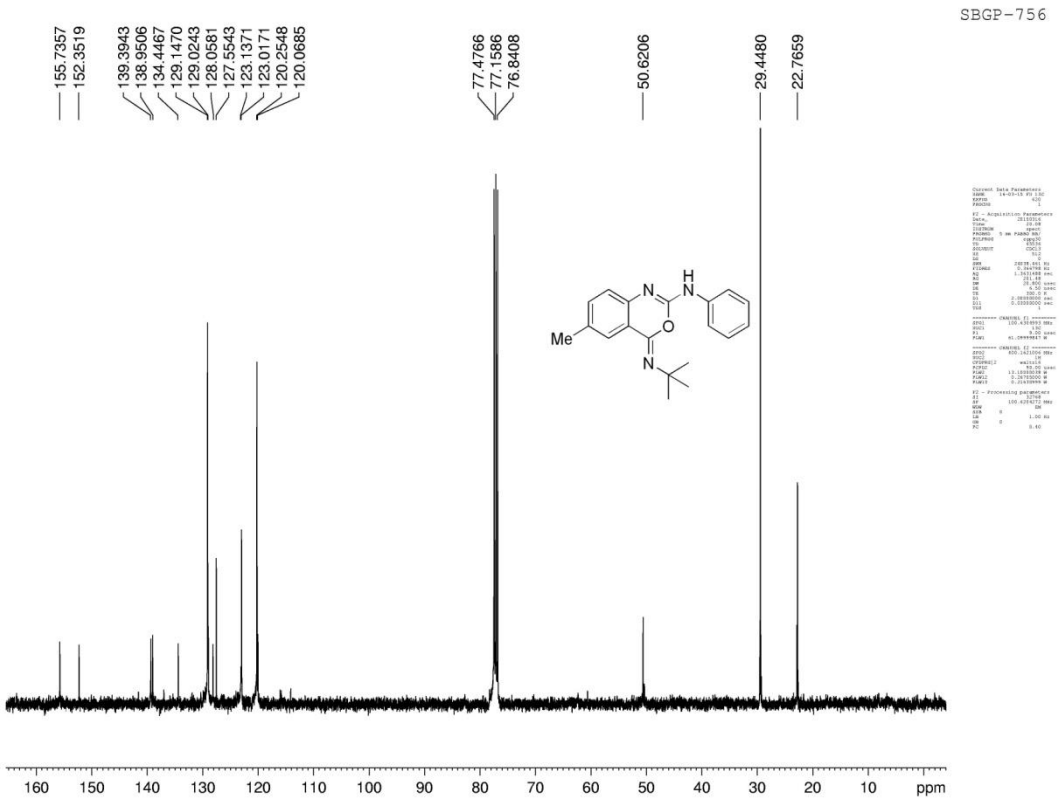


Fig: S-48 ^{13}C spectrum of 4-(*tert*-butylimino)-6-methyl-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(7)**

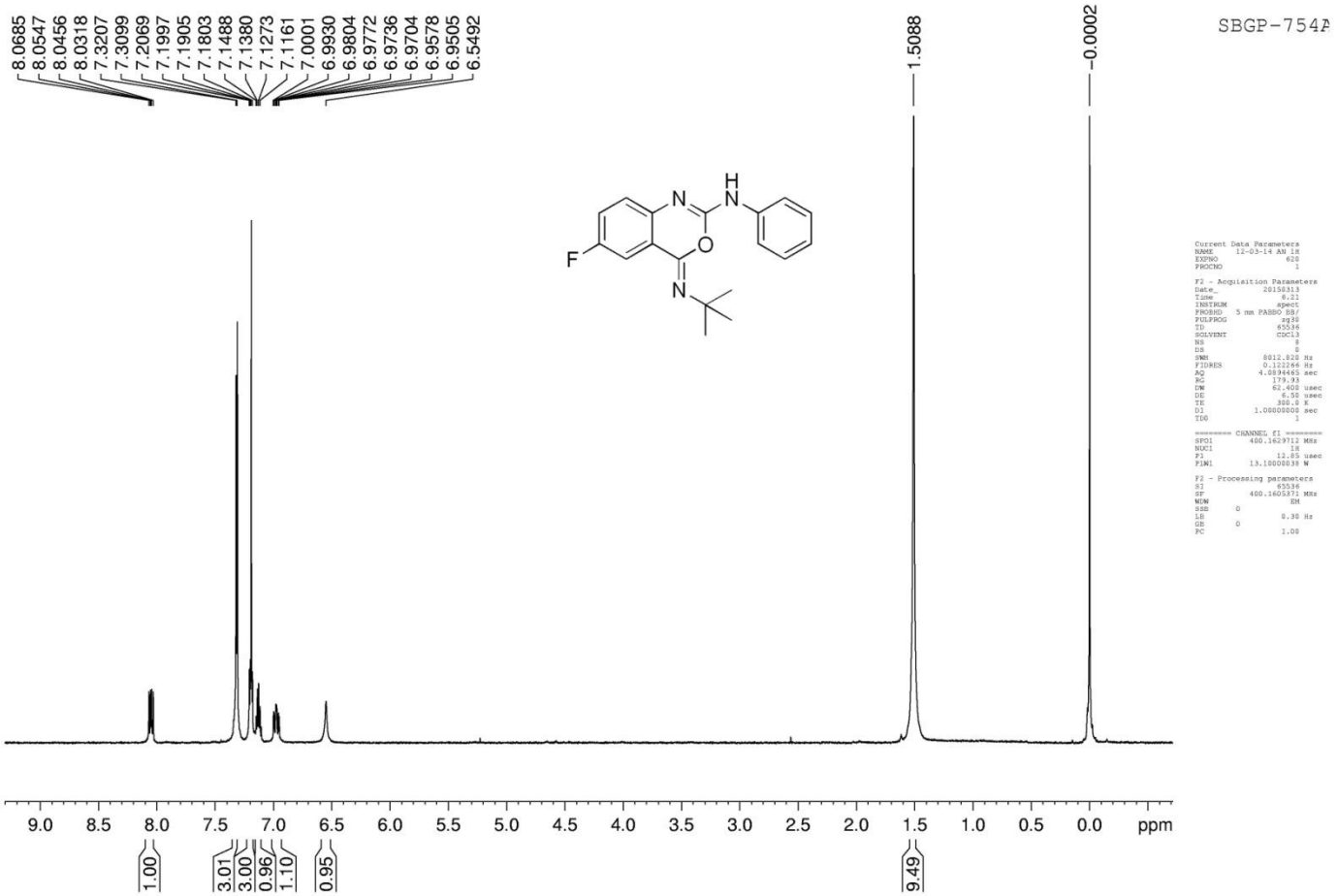


Fig: S-49 ^{1}H spectrum of 4-(*tert*-butylimino)-6-fluoro-*N*-phenyl-4*H*-benzo[d][1,3]oxazin-2-amine **(8)**

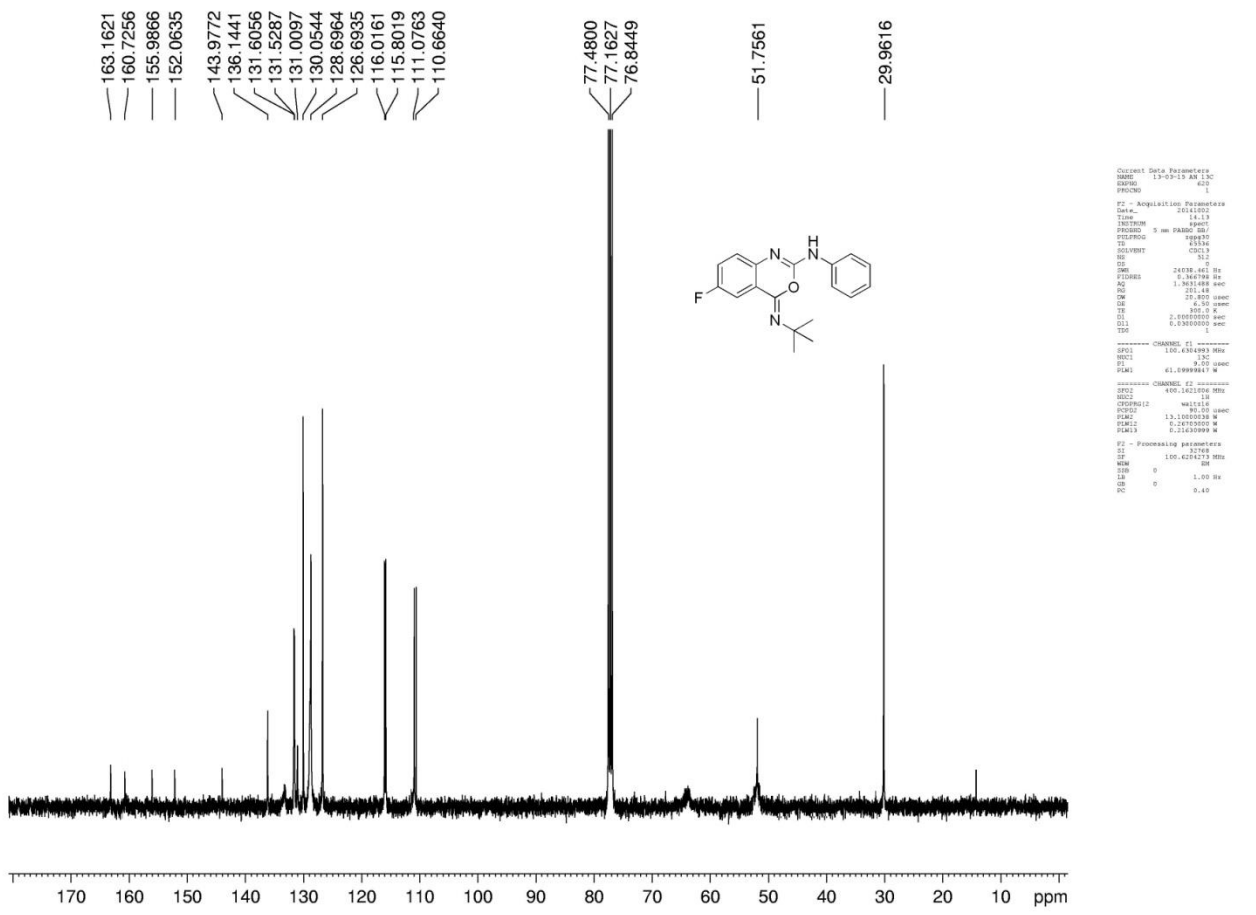


Fig: S-50 ^{13}C spectrum of 4-(*tert*-butylimino)-6-fluoro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(8)**

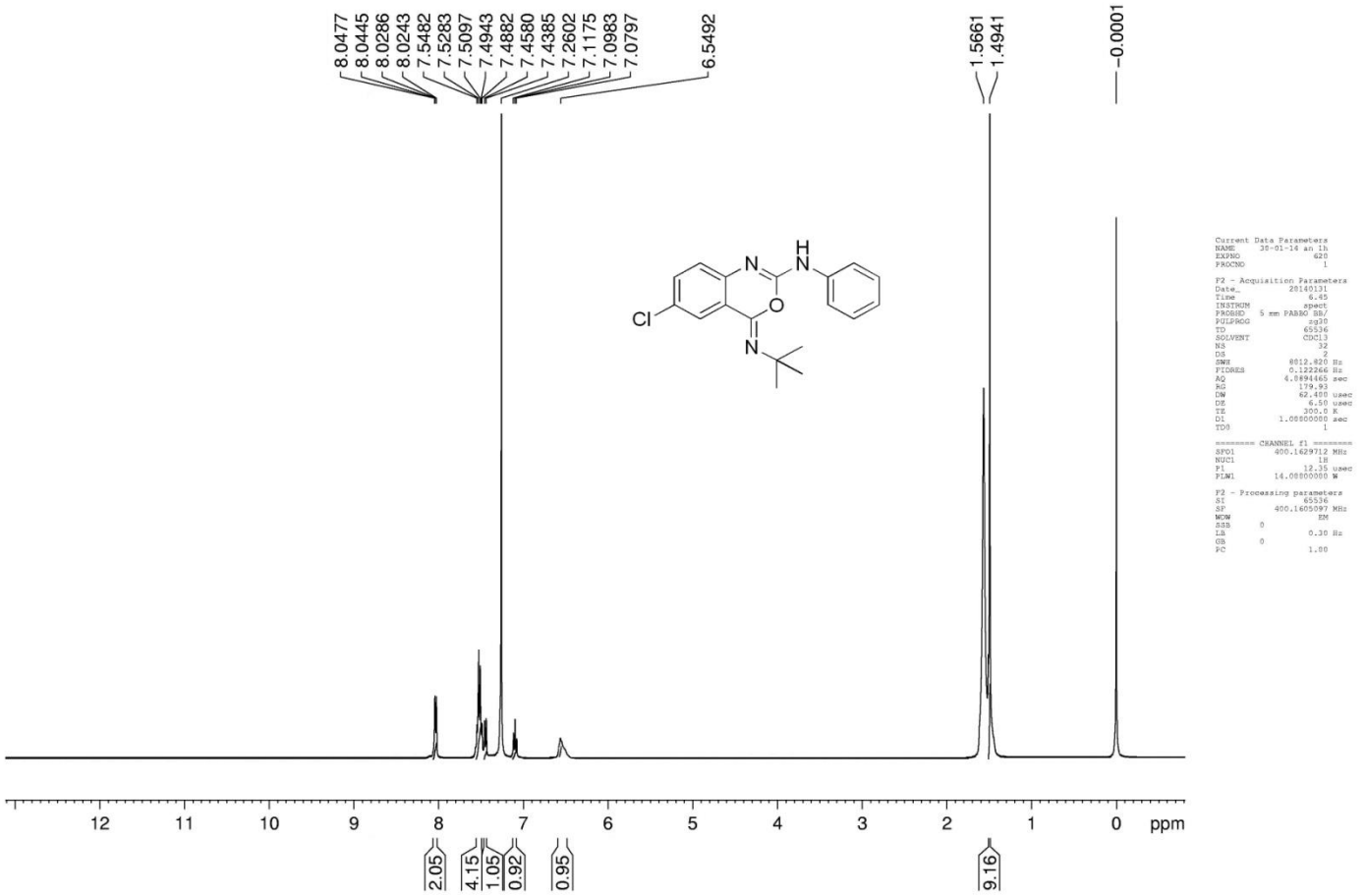


Fig: S-51 ^{1}H spectrum of 4-(*tert*-butylimino)-6-chloro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(9)**

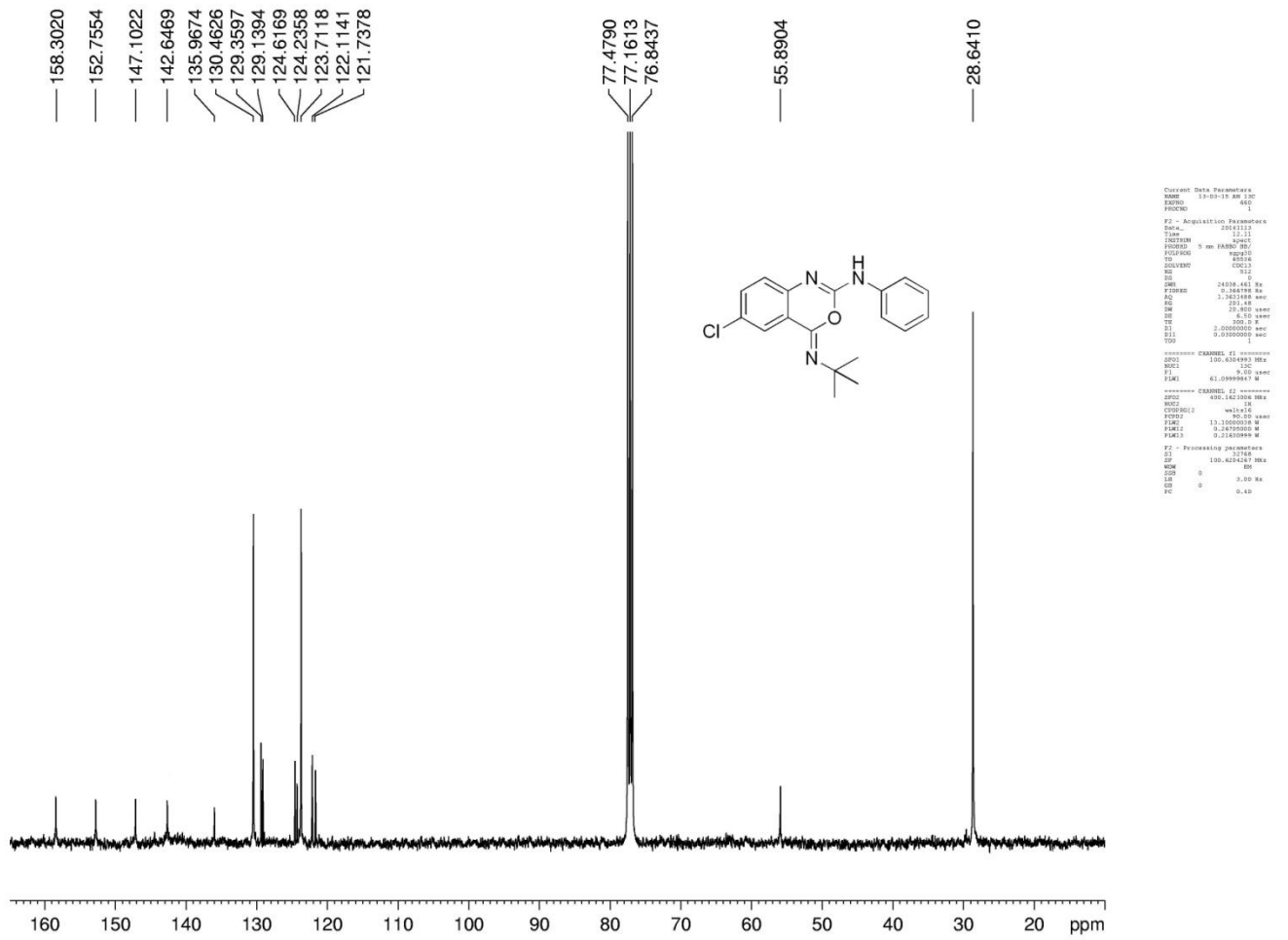


Fig: S-52 ^{13}C spectrum of 4-(*tert*-butylimino)-6-chloro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine **(9)**

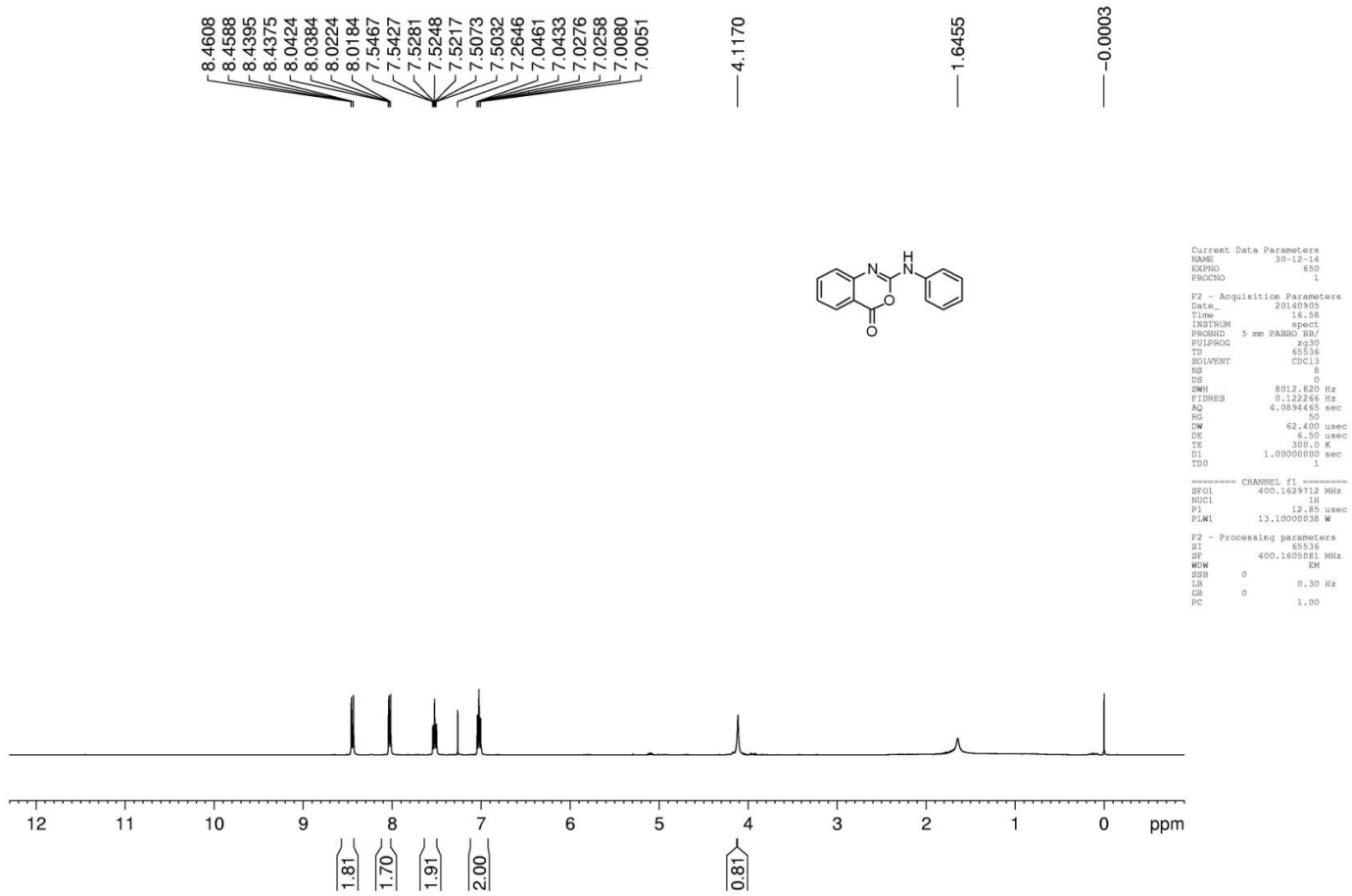


Fig: S-53 ^{1}H spectrum of 2-(phenylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one **(10)**

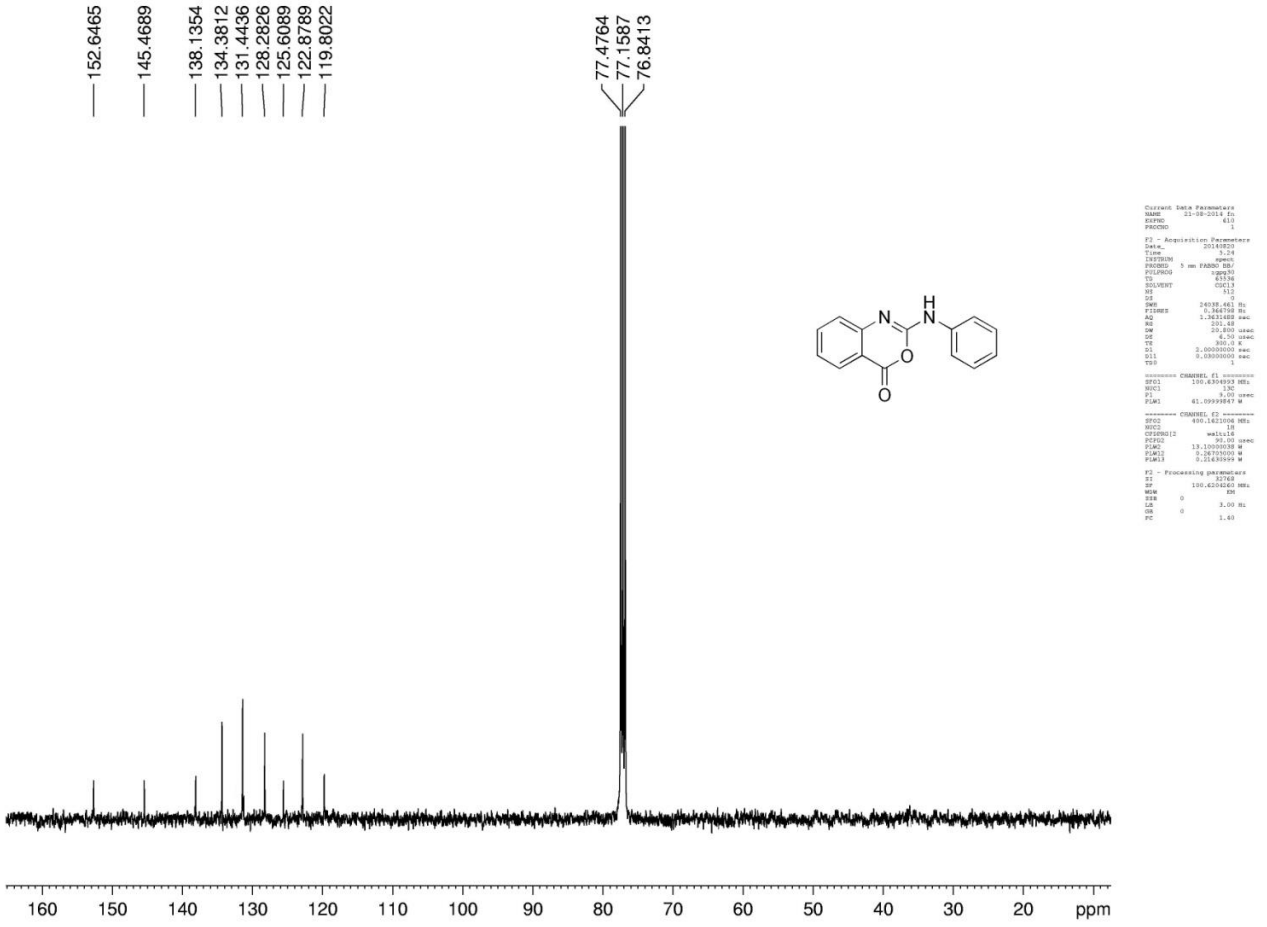


Fig: S-54 ^{13}C spectrum of 2-(phenylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one **(10)**

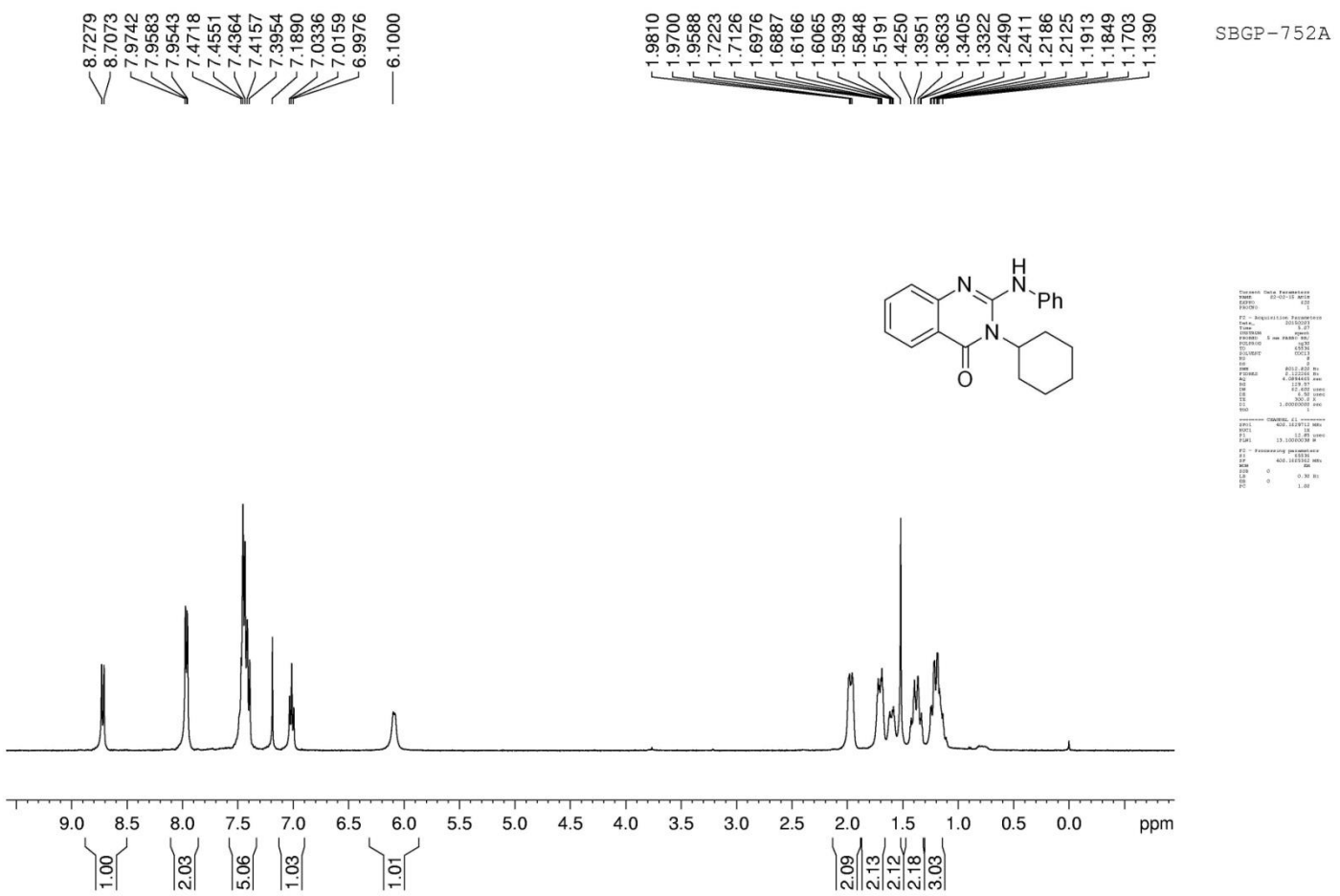


Fig: S-55 ^{1}H spectrum of 3-cyclohexyl-2-(phenylamino)quinazolin-4(3*H*)-one **(11)**

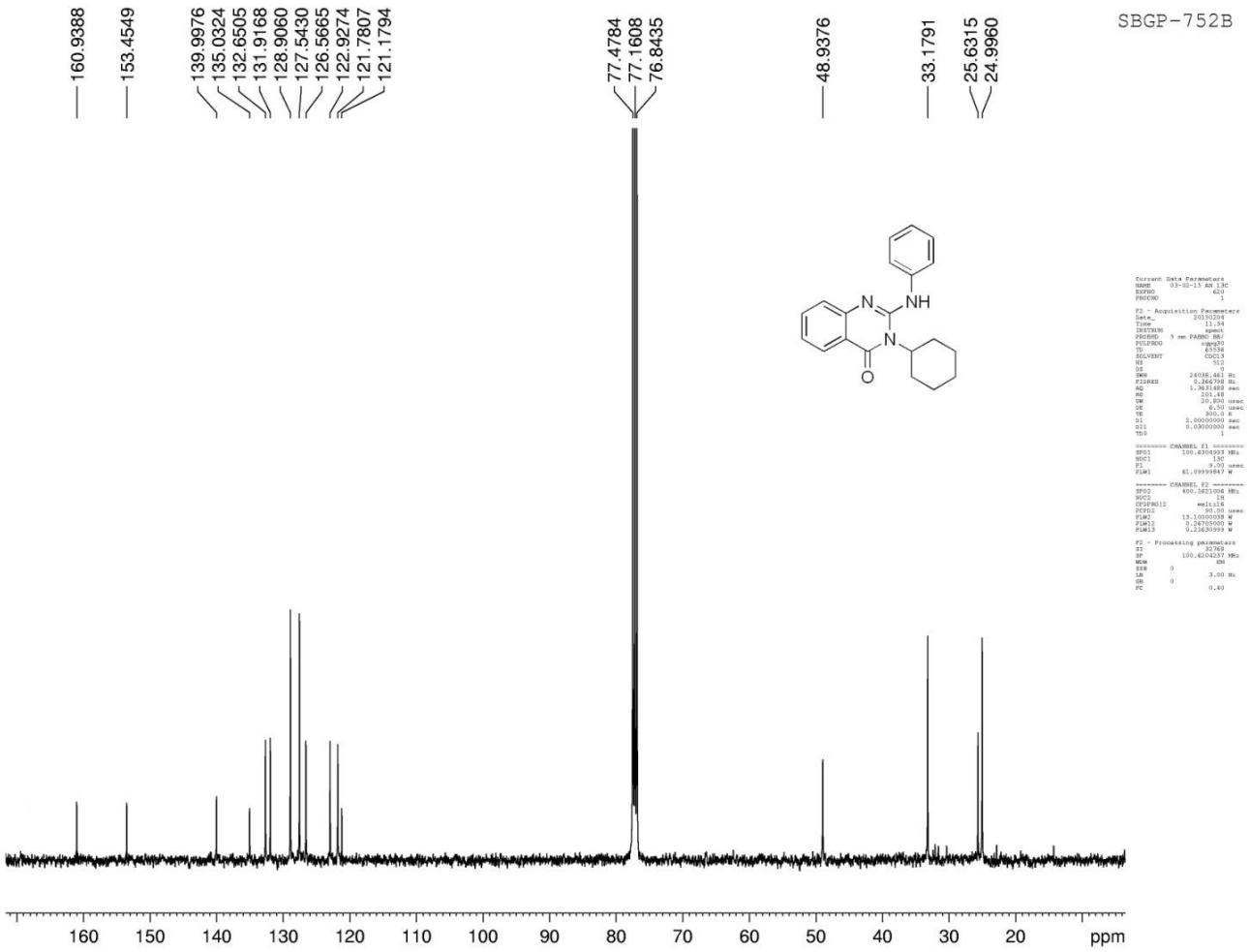


Fig: S-56 ^{13}C spectrum of 3-cyclohexyl-2-(phenylamino)quinazolin-4(3*H*)-one **(11)**