

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

Garima Pandey ^a and Sanjay Batra*^{a,b}

^a*Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, PO Box 173, B.S. 10/1, Sector 10, Jankipuram Extension, Sitapur Road, Lucknow-226031, India.*

^b*Academy of Scientific and Innovative Research, New Delhi, India*

e-mail: batra_san@yahoo.co.uk, s_batra@cdri.res.in

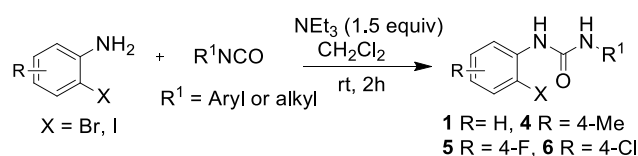
Contents

1. Experimental-General	S-2
2. General procedure for the synthesis of 2-halophenylthioureas	S-2
3. General procedure for the synthesis of substituted 4 <i>H</i> -benzo[<i>d</i>][1,3]oxazin-2-amines	S-2
4. Typical procedure for the synthesis of 2-(phenylamino)-4 <i>H</i> -benzo[<i>d</i>][1,3]oxazin-4-one (10)	S-9
5. Typical procedure for the synthesis of 3-cyclohexyl-2-(phenylamino)quinazolin-4(3 <i>H</i>)-one (11)	S-10
6. References	S-11
7. Copies of ¹ H and ¹³ C NMR spectra of synthesized compounds	S-12

Experimental

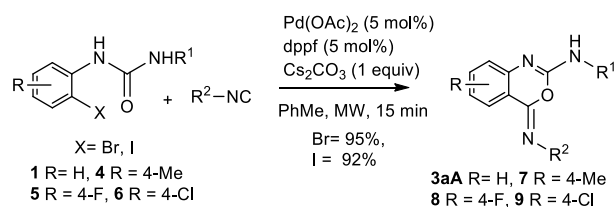
General- All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Melting points are uncorrected and were determined in capillary tubes on a melting point apparatus containing silicon oil. IR spectra were recorded using a Perkin-Elmer FTIR spectrophotometer. ¹H NMR and ¹³C 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 Mass 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 CH₂Cl₂ (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 vacuum.

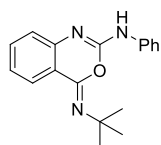
General procedure for the synthesis substituted 4H-benzo[d][1,3]oxazin-2-amines as exemplified for synthesis of **3aA**



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%), Cs₂CO₃ (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

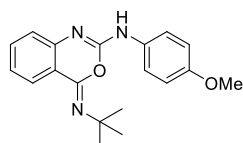
purified via silica gel column chromatography (hexanes/ EtOAc, 95:5, v/v) to furnish **3aA** (0.09 g, 95 %) as a white solid.

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



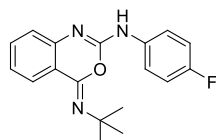
$R_f = 0.55$ (hexanes: EtOAc, 80:20, v/v); ν_{\max} (KBr) 669, 921, 1215, 1605, 1647, 3434, 3683 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 1.50 (s, 9H), 6.23 (s, 1H), 7.00-7.04 (m, 1H), 7.42-7.56 (m, 5H), 8.02 (dd, 2H, $J_1 = 1.7$ Hz, $J_2 = 1.2$ Hz), 8.72 (d, 1H, $J = 8.3$ Hz); $^{13}\text{C NMR}$ (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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}$ $[\text{MH}]^+$ 294.1606, Found 294.1608.

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



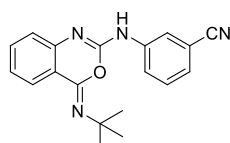
(0.078 g from 0.1 g) as a white solid; mp = 123-125 °C; $R_f = 0.43$ (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 757, 1084, 1384, 1449, 1513, 1602, 1650, 3019, 3434 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm) = 1.50 (s, 9H), 3.87 (s, 3H), 6.20 (s, 1H), 6.98-7.04 (m, 3H), 7.41-7.48 (m, 2H), 7.97-8.00 (m, 2H), 8.70-8.72 (m, 1H); $^{13}\text{C NMR}$ (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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}$ $[\text{MH}]^+$ 324.1484, Found 324.1486.

4-(tert-Butylimino)-N-(4-fluorophenyl)-4H-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} ; $^1\text{H NMR}$ (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); $^{13}\text{C NMR}$ (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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{FN}_3\text{O}$ $[\text{MH}]^+$ 312.1512, Found 312.1515.

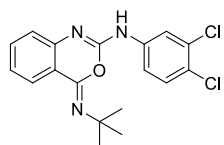
3-(4-(tert-Butylimino)-4H-benzo[d][1,3]oxazin-2-ylamino)benzotrile (3dA). 97% (0.093



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} ; $^1\text{H NMR}$ (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);

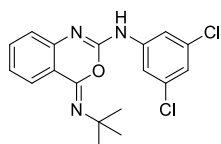
^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 29.6, 61.2, 115.4, 118.9, 121.5, 123.2, 124.5, 126.6, 127.2, 130.4, 131.8, 137.9, 153.3, 157.4; MS (ESI+) m/z = 318.0 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}$ [MH] $^+$ 318.1481, Found 318.1483.

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



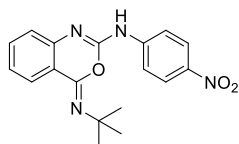
(0.08 g from 0.1 g) as a white solid; mp = 95-97 °C; R_f = 0.53 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 670, 929, 1026, 1215, 1523, 1626, 3367 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.51 (s, 9H), 7.25-7.29 (m, 1H), 7.43 (d, 1H, $J=7.6$ Hz), 7.52-7.54 (m, 2H), 8.07 (dd, 2H, $J_1=1.5$ Hz, $J_2=1.8$ 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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{N}_3\text{O}$ [MH] $^+$ 362.0827, Found 362.0831.

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



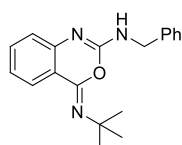
(0.083 g from 0.1 g) as a white solid; mp = 101-103 °C; R_f = 0.51 (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 931, 1033, 1511, 1626, 1643, 2401, 3367, 3684 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.81 (s, 9H), 6.97 (d, 2H, $J = 7.9$ Hz), 7.16-7.21 (m, 2H, $J = 7.7$ Hz), 7.54-7.58 (m, 2H), 8.04 (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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{N}_3\text{O}$ [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} ; ^1H 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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_3$ [MH] $^+$ 339.1457, Found 339.1459.

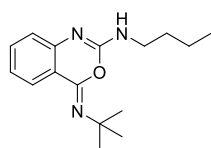
***N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3hA).** 86% (0.082 g from



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} ; ^1H 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;

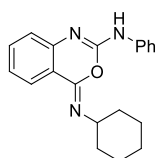
MS (ESI+) $m/z = 308.0$ (M+H)⁺; ES-HRMS calcd. for C₁₉H₂₁N₃O [MH]⁺ 308.1763, Found 308.1768.

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



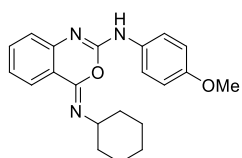
0.1 g) as a white solid; mp = 119-121 °C; $R_f = 0.49$ (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 786, 1039, 1543, 1633, 1649, 3367 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 0.93 (t, 3H, $J = 7.3$ Hz), 1.37 (t, 2H, $J = 7.6$ Hz), 1.46 (s, 9H), 1.49-1.55 (m, 2H), 3.22-3.27 (m, 2H), 4.70 (s, 1H), 6.91 (t, 1H, $J = 7.3$ Hz), 7.32-7.39 (m, 2H), 8.37 (d, 1H, $J = 8.4$ Hz); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₆H₂₃N₃O [MH]⁺ 274.1919, Found 274.1921.

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



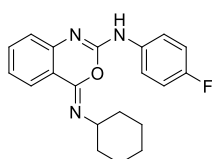
from 0.1 g) as a white solid; mp = 119-117 °C; $R_f = 0.55$ (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 768, 1099, 1412, 1523, 1639, 1699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 1.23-1.31 (m, 4H), 1.43-1.47 (m, 2H), 1.65-1.80 (m, 3H, CH), 2.02-2.06 (m, 2H), 6.18 (s, 1H), 7.07-7.11 (m, 1H), 7.46-7.54 (m, 5H), 8.02-8.05 (m, 2H), 8.78 (dd, 1H, $J_1 = 0.8$ Hz, $J_2 = 0.8$ Hz); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₀H₂₁N₃O [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, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₁H₂₃N₃O [MH]⁺ 350.1869, Found 350.1871.

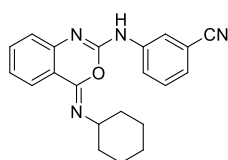
4-(Cyclohexylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3cB). 87%



(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, CDCl₃) δ (ppm) = 1.01-1.25 (m, 4H), 1.27-1.34 (m, 2H),

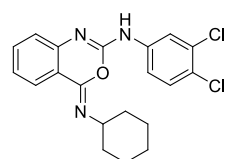
1.51-1.63 (m, 3H), 1.81-1.88 (m, 2H), 5.98 (s, 1H), 7.30-7.32 (m, 2H), 7.39-7.47 (m, 3H), 7.52-7.56 (m, 2H), 8.02 (d, 1H, $J = 8.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 24.9, 25.5, 33.9, 63.6, 115.4 (d, $J = 21.8$ Hz), 118.6, 125.4, 128.3, 129.7 (d, $J = 7.3$ Hz), 130.2, 132.3, 132.8, 132.9, 149.4, 152.1, 154.0 (d, $J = 279$ Hz); MS (ESI+) $m/z = 338.0$ (M+H) $^+$; ES-HRMS calcd. for $\text{C}_{20}\text{H}_{20}\text{FN}_3\text{O}$ [MH] $^+$ 338.1669, Found 338.1670.

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



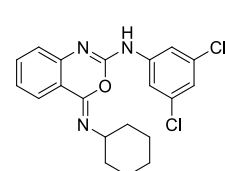
(0.092 g from 0.1 g) as a white solid; mp = 129-131 °C; $R_f = 0.55$ (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 669, 1099, 1412, 1533, 1597, 1642, 2220, 3420, 3439 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.48-1.54 (m, 3H), 1.65-1.71 (m, 2H), 1.94-2.00 (m, 3H), 2.26 (bs, 2H), 6.39 (s, 1H), 6.86-6.90 (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 $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}$ [MH] $^+$ 345.1715, Found 345.1712.

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



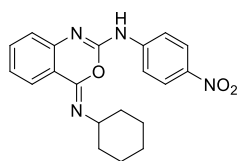
91% (0.094 g from 0.1 g) as a white solid; mp = 119-121 °C; $R_f = 0.53$ (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 799, 967, 1512, 1626, 3200, 3367, 3400 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.26-1.30 (m, 4H), 1.38-1.44 (m, 2H), 1.70-1.79 (m, 3H), 1.85-1.90 (m, 2H), 6.77-6.81 (m, 1H), 6.93-6.97 (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 $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}$ [MH] $^+$ 388.0983, Found 388.0980.

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



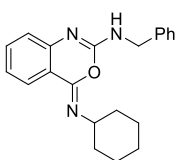
92% (0.095 g from 0.1 g) as a white solid; mp = 112-114 °C; $R_f = 0.51$ (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 787, 1039, 1507, 1659, 3320, 3300 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.15-1.40 (m, 6H), 1.63-1.76 (m, 3H), 1.92-1.94 (m, 2H), 5.53 (s, 1H), 7.45-7.47 (m, 2H), 7.58-7.61 (m, 2H), 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 $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{N}_3\text{O}$ [MH] $^+$ 388.0983, Found 388.0985.

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



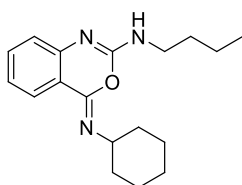
(0.09 g from 0.1 g) as a yellow solid; mp = 126-128 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 766, 1307, 1423, 1512, 1607, 1625, 3367, 3400, 3551 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.88-2.01 (m, 6H), 2.10-2.14 (m, 3H), 2.36-2.39 (m, 2H), 4.54 (s, 1H), 7.31-7.40 (m, 2H), 7.42-7.44 (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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_3$ [MH] $^+$ 365.1614, Found 365.1619.

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



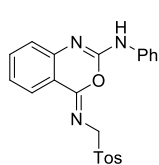
from 0.1 g) as a white solid; mp = 131-133 °C; R_f = 0.49 (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 669, 723, 967, 1099, 1449, 1626, 1639, 3367, 3400 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 0.85-0.90 (m, 3H), 1.05-1.56 (m, 2H), 1.62-1.85 (m, 3H), 1.85-1.92 (m, 2H), 5.48 (s, 2H), 5.62 (s, 1H), 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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{21}\text{H}_{23}\text{N}_3\text{O}$ [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 ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_3\text{O}$ [MH] $^+$ 300.2076, Found 300.2067.

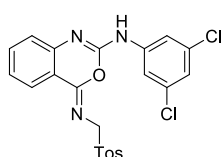
***N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aC).** 78% (0.1 g from



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 C₂₂H₁₉N₃O₃S [MH]⁺ 406.1225, Found 406.1229.

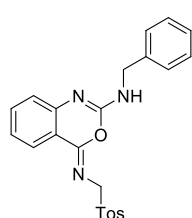
***N*-(3,5-Dichlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3fC).**



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, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₂H₁₇Cl₂N₃O₃S [MH]⁺ 474.0446, Found 474.0451.

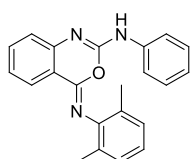
***N*-Benzyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3hC).** 73% (0.091g



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, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₃H₂₁N₃O₃S [MH]⁺ 420.1382, Found 420.1385.

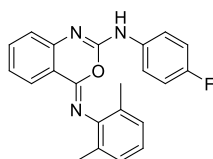
4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (3aD). 86%



(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, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₂H₁₉N₃O [MH]⁺ 342.1606, Found 342.1609.

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

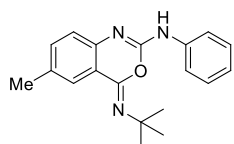


(0.093 g from 0.1 g) as a white solid; mp = 149-151 °C; $R_f = 0.55$ (hexane: EtOAc, 80:20, v/v); ν_{\max} (KBr) 667, 1099, 1133, 1599, 1626, 3367, 3400 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 2.51 (s, 6H), 6.74-6.78 (m,

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,

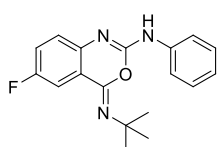
1H), 8.05 (d, 1H, $J = 8.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) = 18.9, 112.9, 115.1 (d, $J = 22.1$ Hz), 120.2 (d, $J = 7.4$ Hz), 121.9, 123.4, 127.8, 132.1, 135.3, 137.0, 152.0, 152.8, 156.9, 158.1 (d, $J = 239.7$ Hz); MS (ESI+) $m/z = 360.0$ ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{22}\text{H}_{18}\text{FN}_3\text{O}$ $[\text{MH}]^+$ 360.1512, Found 360.1516.

4-(tert-butylimino)-6-methyl-N-phenyl-4H-benzo[d][1,3]oxazin-2-amine (7). 93% (0.089



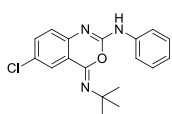
g from 0.1 g) as white solid; mp = 109-111 °C; $R_f = 0.45$ (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 676, 968, 1015, 1684, 1699, 1733, 3412, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.57 (s, 9H), 2.29 (s, 3H), 6.58 (s, 1H, NH), 6.91 (s, 1H), 7.07-7.12 (m, 1H), 7.26 (s, 1H), 7.34-7.40 (m, 4H), 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+) $m/z = 312.0$ ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}$ $[\text{MH}]^+$ 308.1763, Found 308.1766.

4-(tert-Butylimino)-6-fluoro-N-phenyl-4H-benzo[d][1,3]oxazin-2-amine (8). 86% (0.083 g



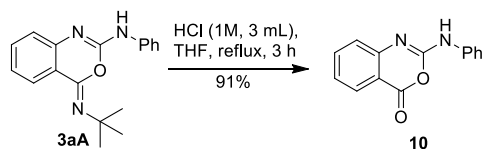
from 0.1 g) as white solid; mp = 125-127 °C; $R_f = 0.51$ (hexane: EtOAc, 80:20, v/v); ν_{max} (KBr) 838, 968, 1019, 1311, 1640, 1699, 3569, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ (ppm) = 1.51 (s, 9H), 6.55 (s, 1H), 6.95-7.00 (m, 1H), 7.12-7.15 (m, 1H), 7.18-7.21 (m, 2H), 7.31-7.32 (m, 3H), 8.03-8.07 (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+) $m/z = 312.0$ ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{FN}_3\text{O}$ $[\text{MH}]^+$ 312.1519, Found 312.1521.

4-(tert-butylimino)-6-chloro-N-phenyl-4H-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} ; ^1H 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+) $m/z = 328.0$ ($\text{M}+\text{H}$) $^+$; ES-HRMS calcd. for $\text{C}_{18}\text{H}_{18}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 328.1217, Found 328.1215.

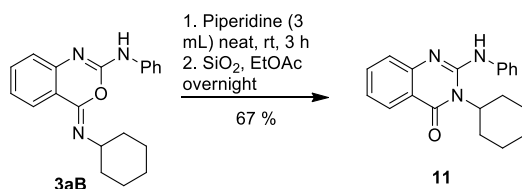
General procedure for the synthesis of 2-(phenylamino)-4H-benzo[d][1,3]oxazin-4-one (10)²



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 Na₂SO₄ 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 °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; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₄H₁₀N₂O₂ [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 °C; R_f = 0.51 (hexane: EtOAc, 70:30, v/v); ν_{max} (KBr) 967, 1601, 1630, 3056, 3189, 3297 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 1.14-1.25 (m, 3H), 1.33-1.43 (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); ¹³C NMR (100 MHz, CDCl₃) 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 C₂₀H₂₁N₃O₂ [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.

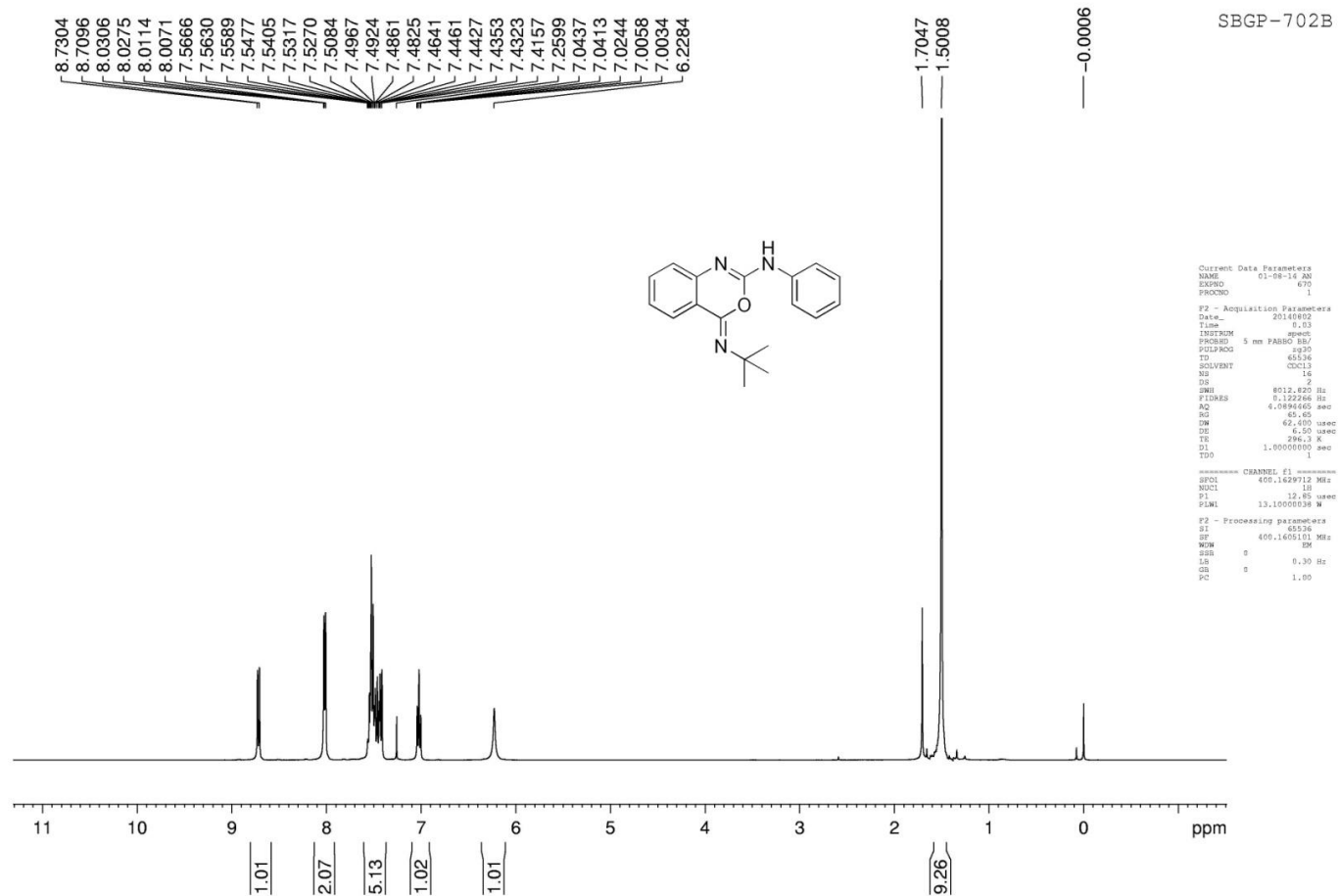


Fig. S-1 ^1H spectrum of 4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3aA**)

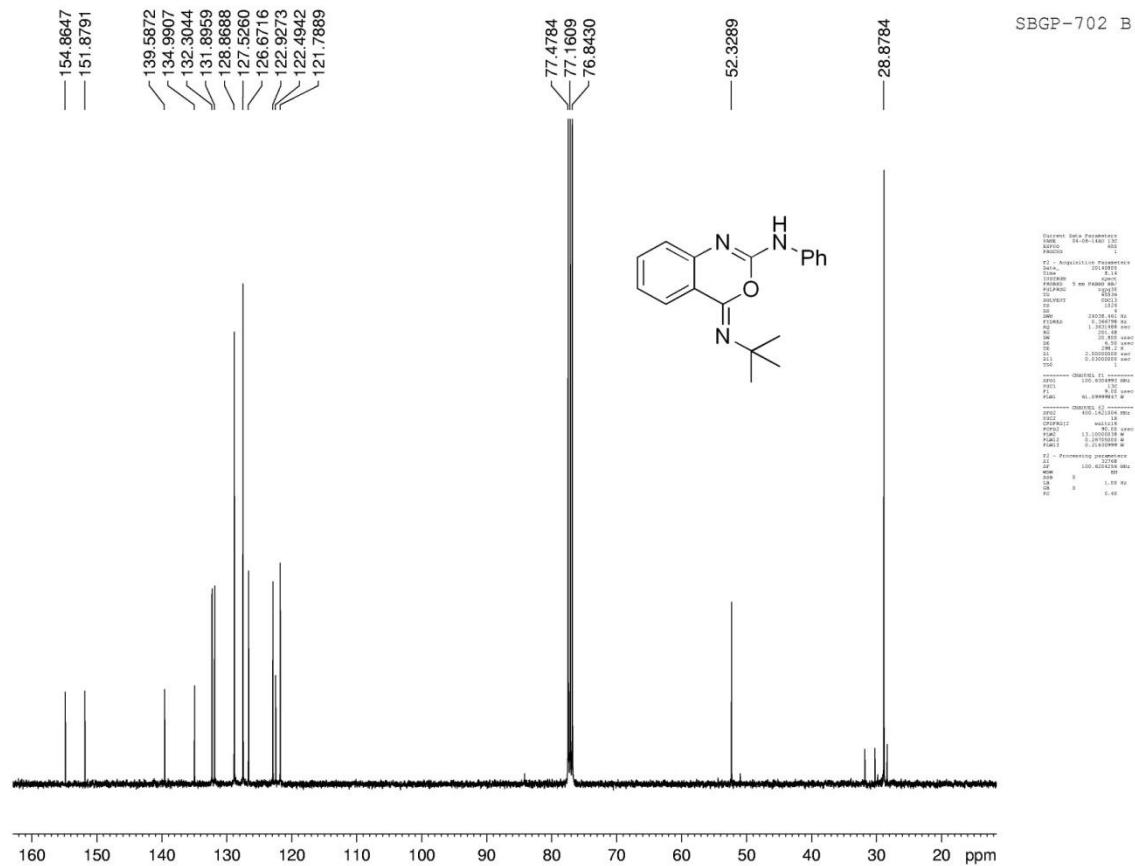


Fig: S-2 ^{13}C spectrum of 4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3aA**)

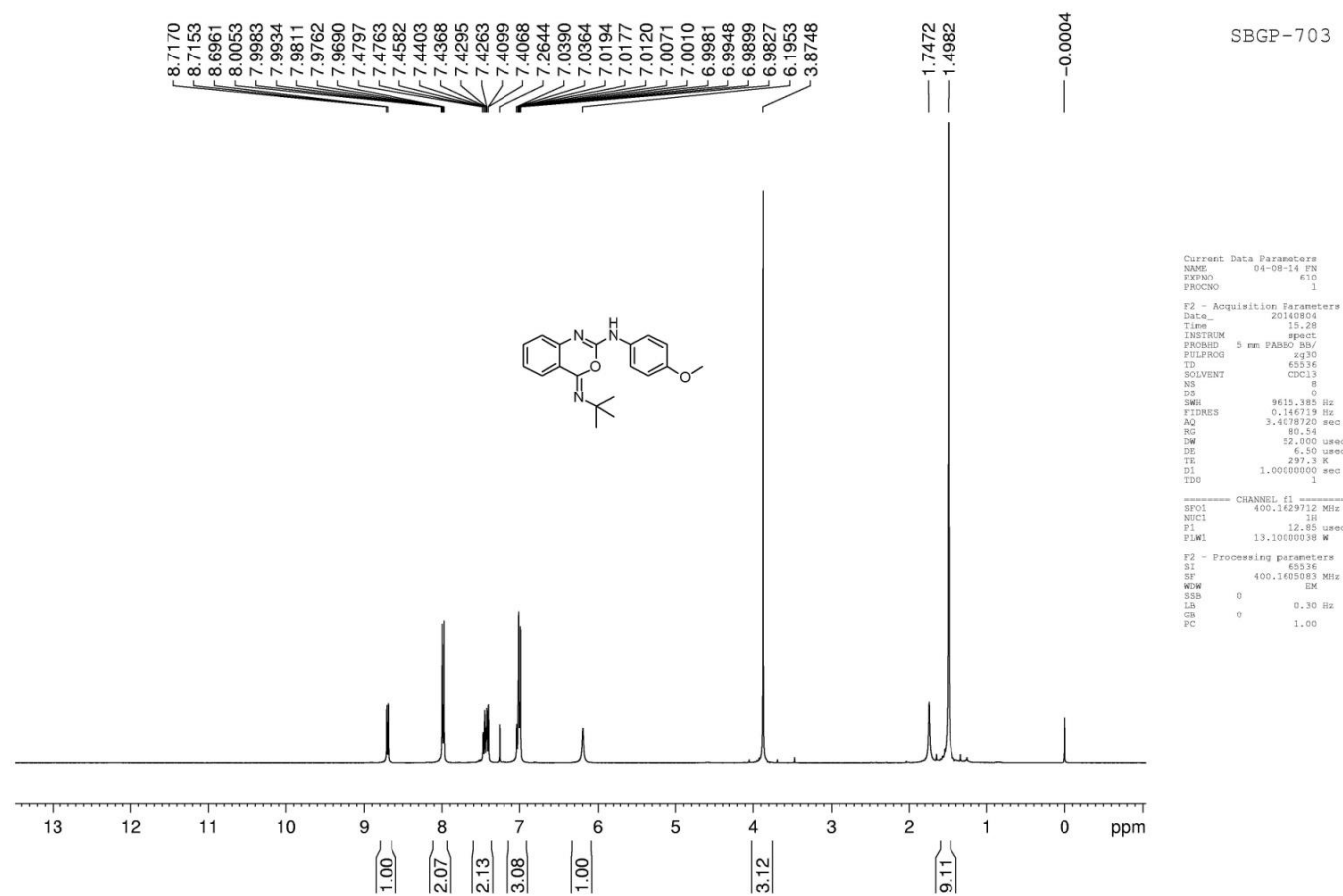


Fig: S-3 ^1H spectrum of 4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3bA**)

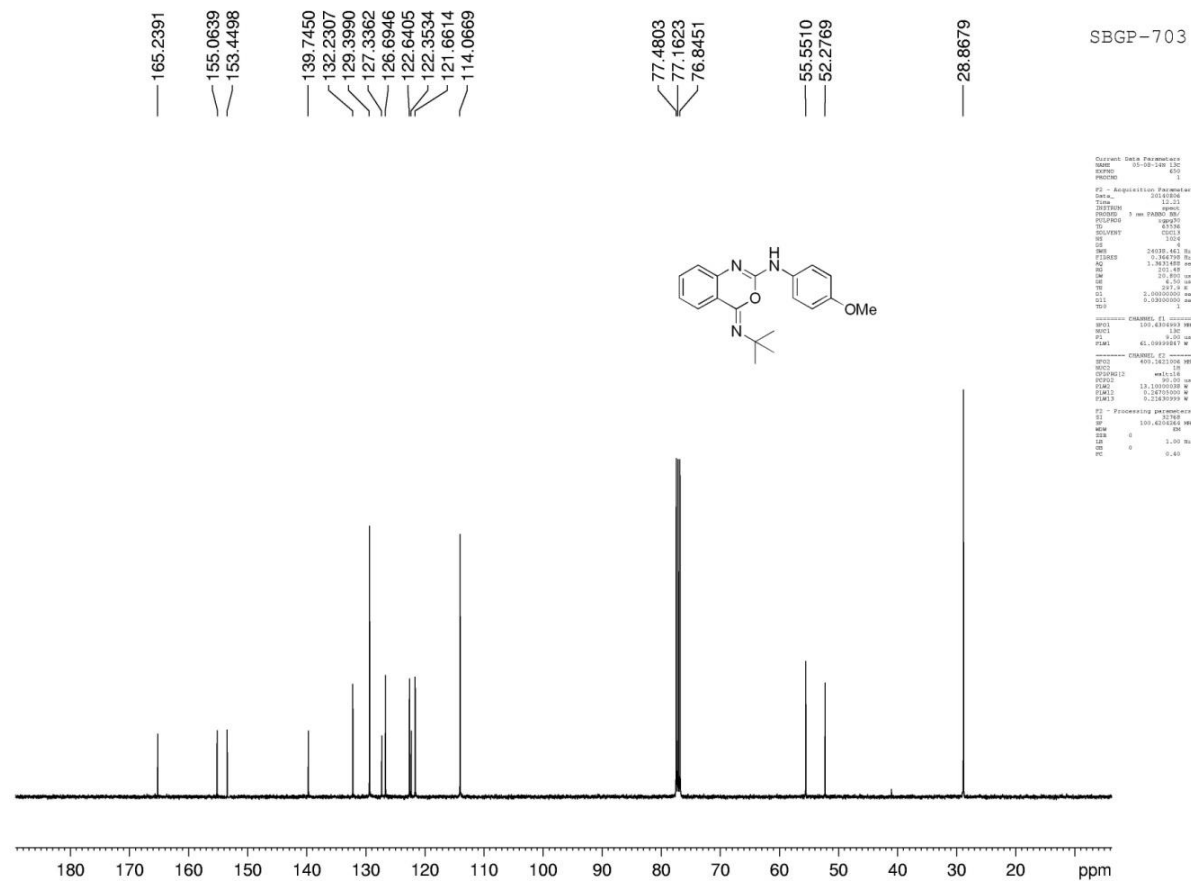


Fig: S-4 ¹³C spectrum of 4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3bA**)

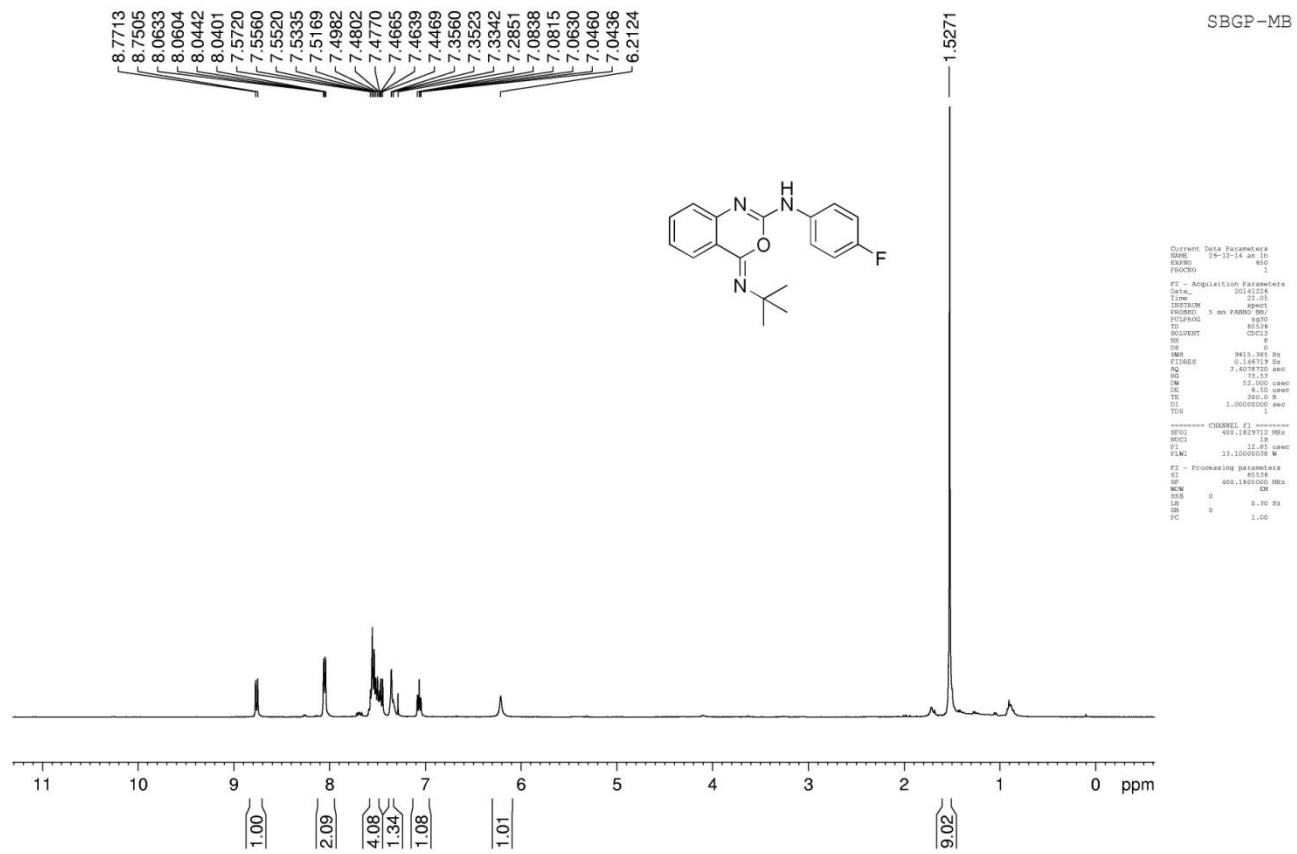


Fig: S-5 ^1H spectrum of 4-(*tert*-Butylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cA**)

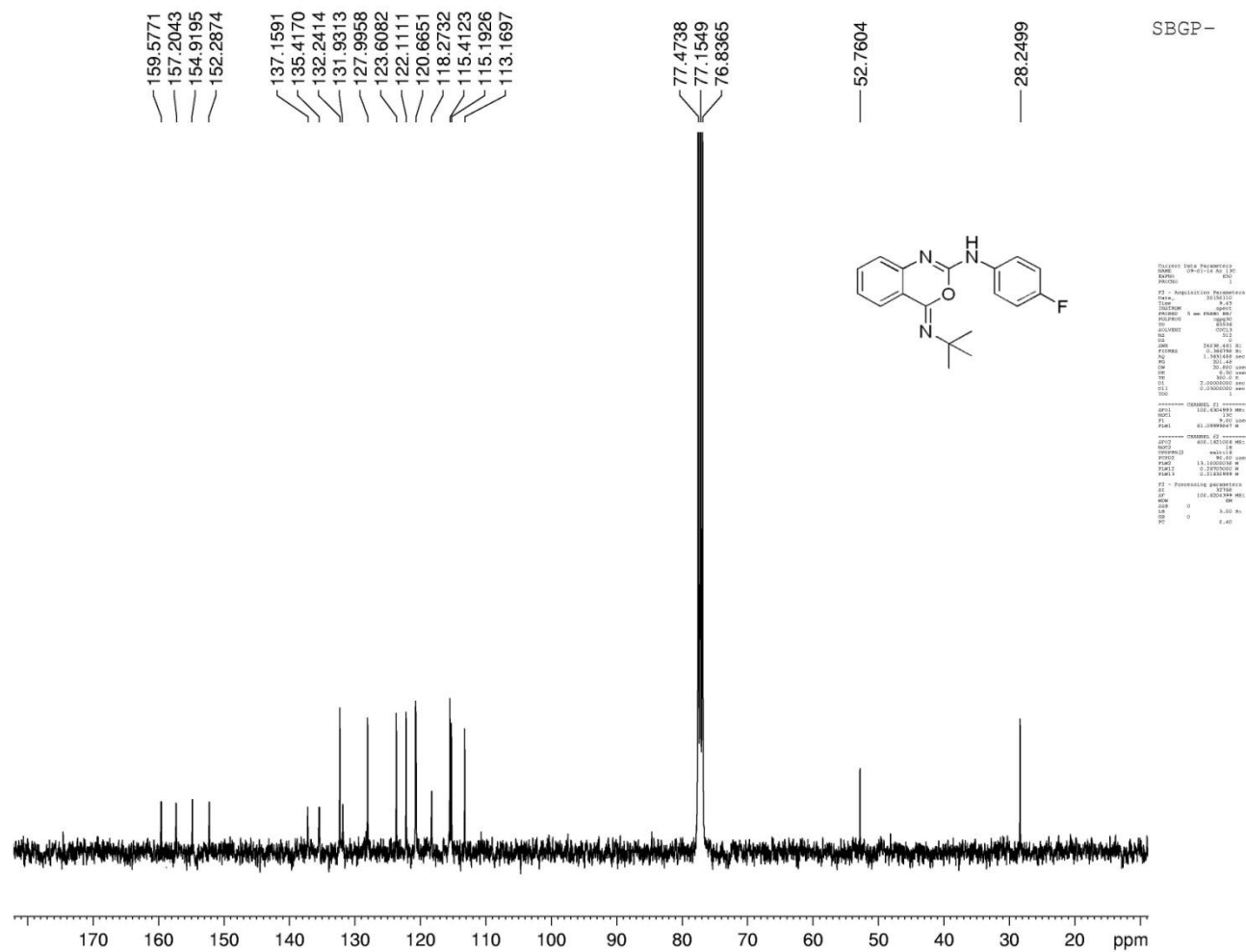


Fig: S-6 ¹³C spectrum of 4-(*tert*-Butylimino)-*N*-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cA**)

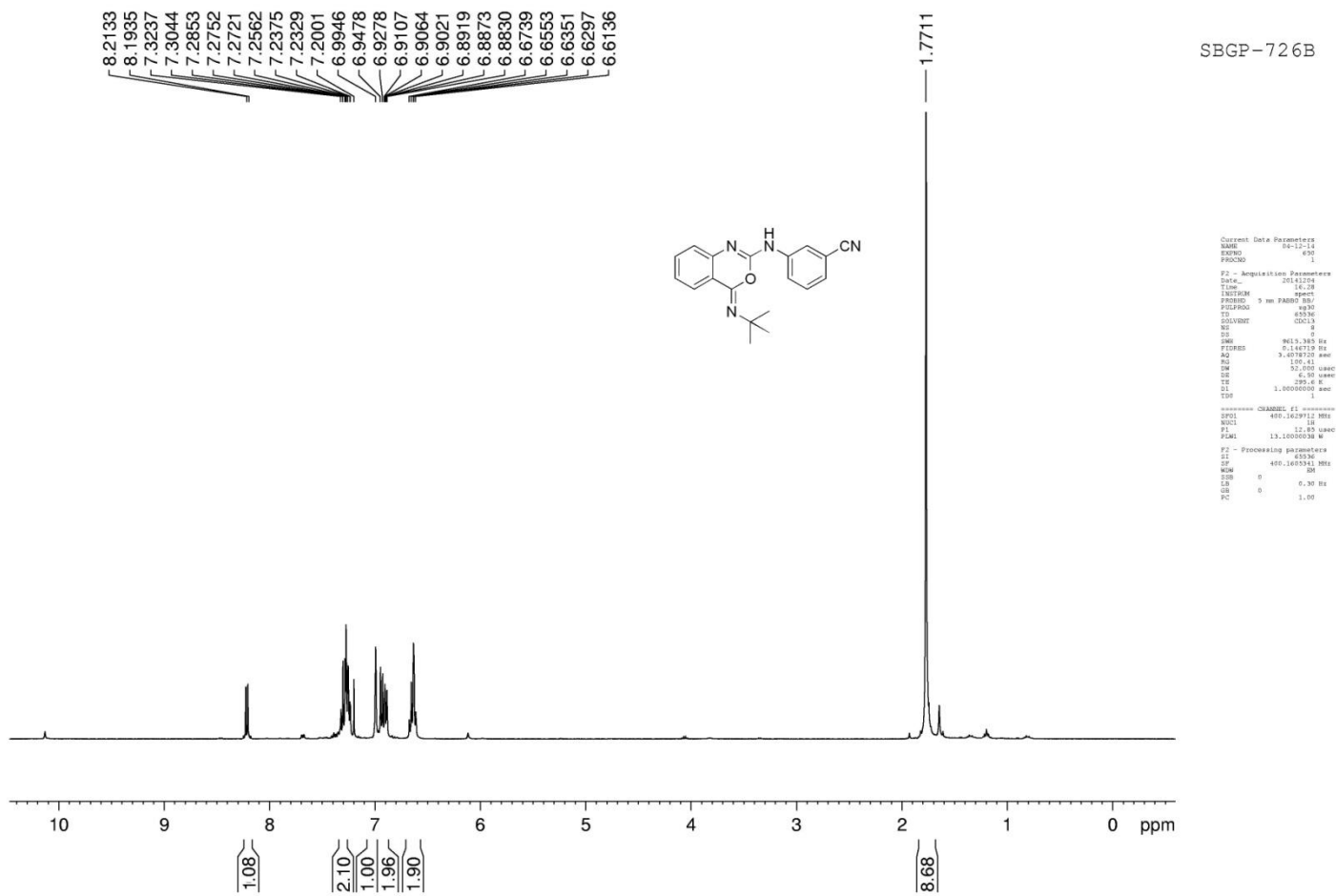


Fig: S-7 ^1H spectrum of 3-(4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (**3dA**)

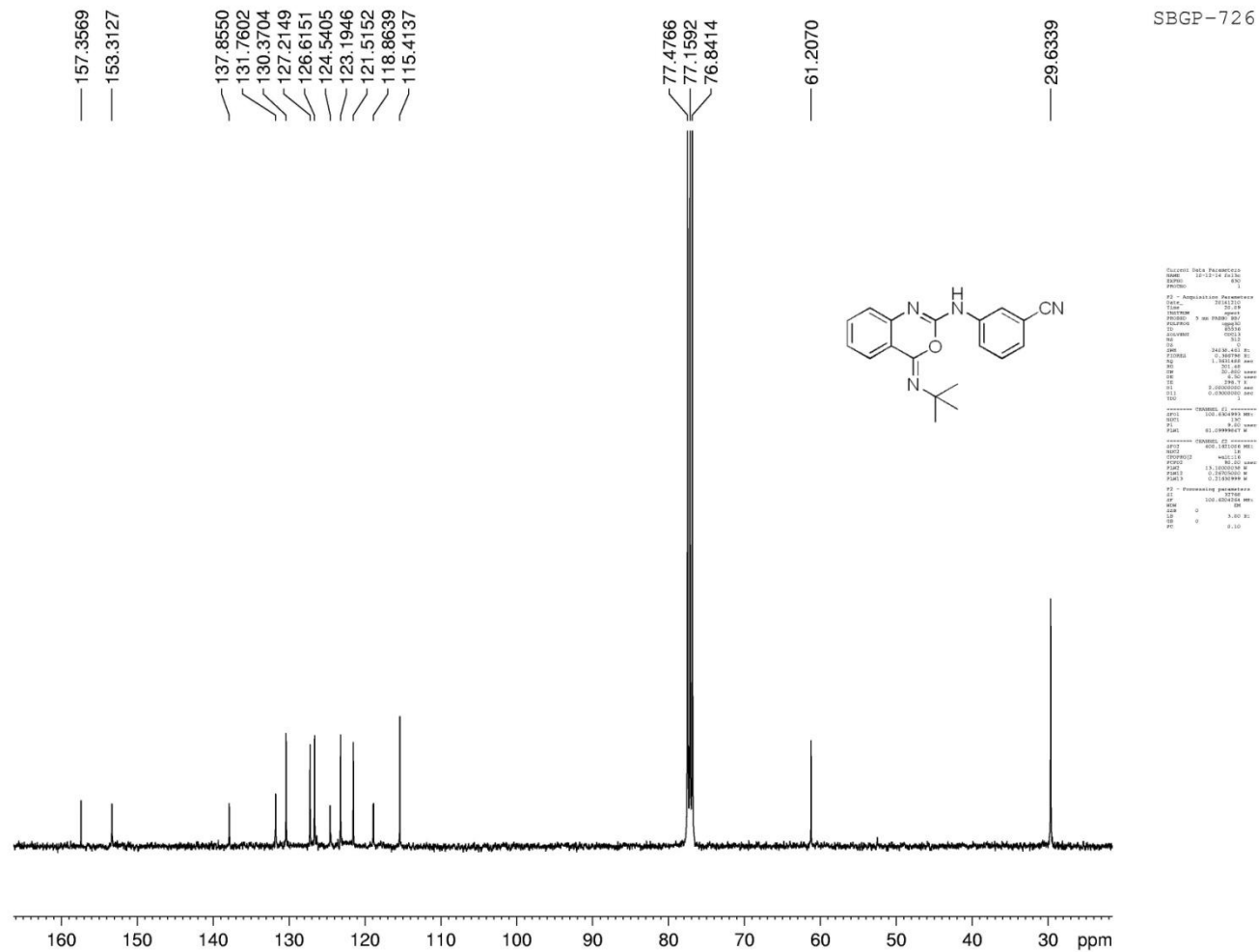


Fig: S-8 ^{13}C spectrum of 3-(4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-ylamino)benzonitrile (**3dA**)

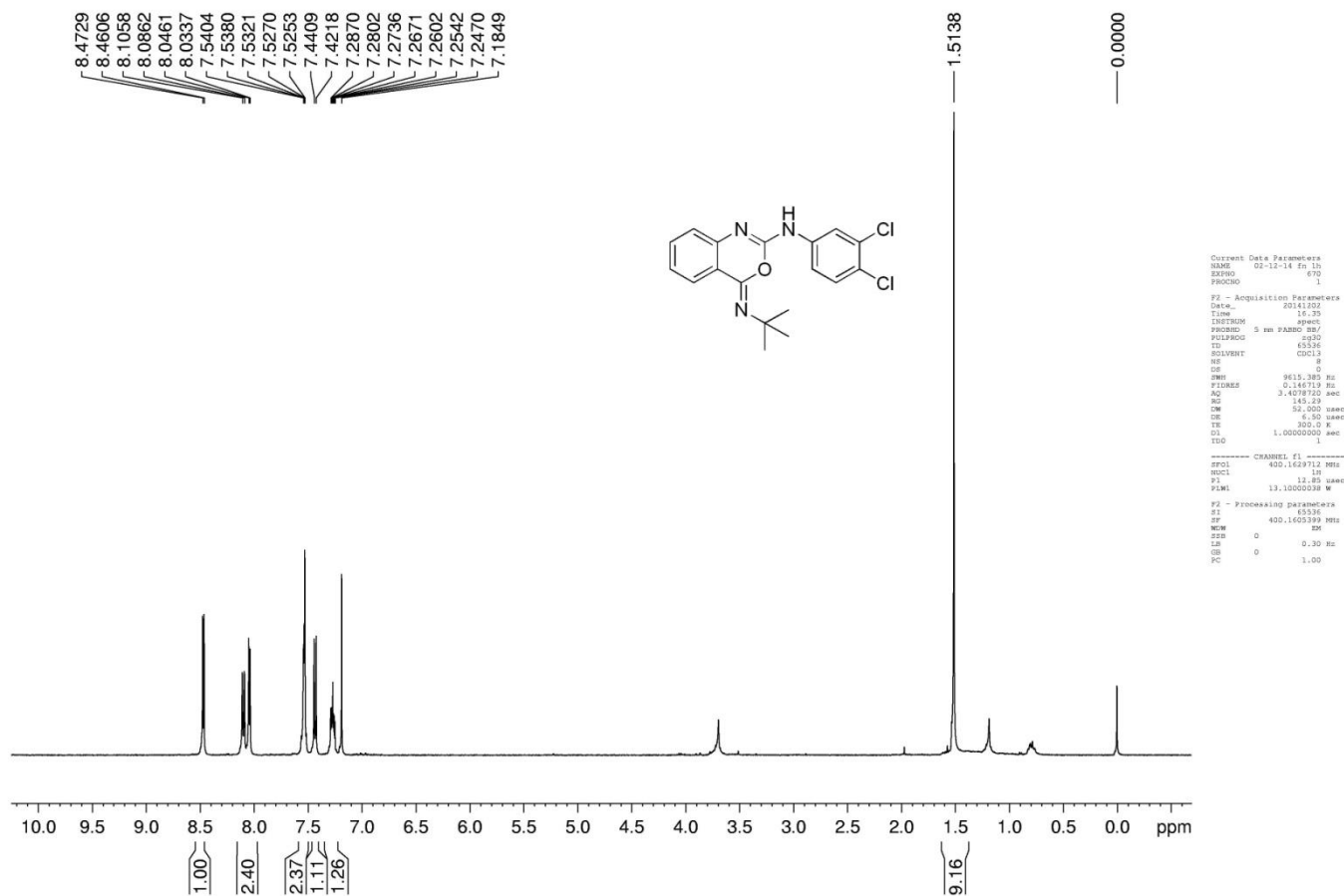


Fig: S-9 ¹H spectrum of 4-(*tert*-Butylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3eA**)

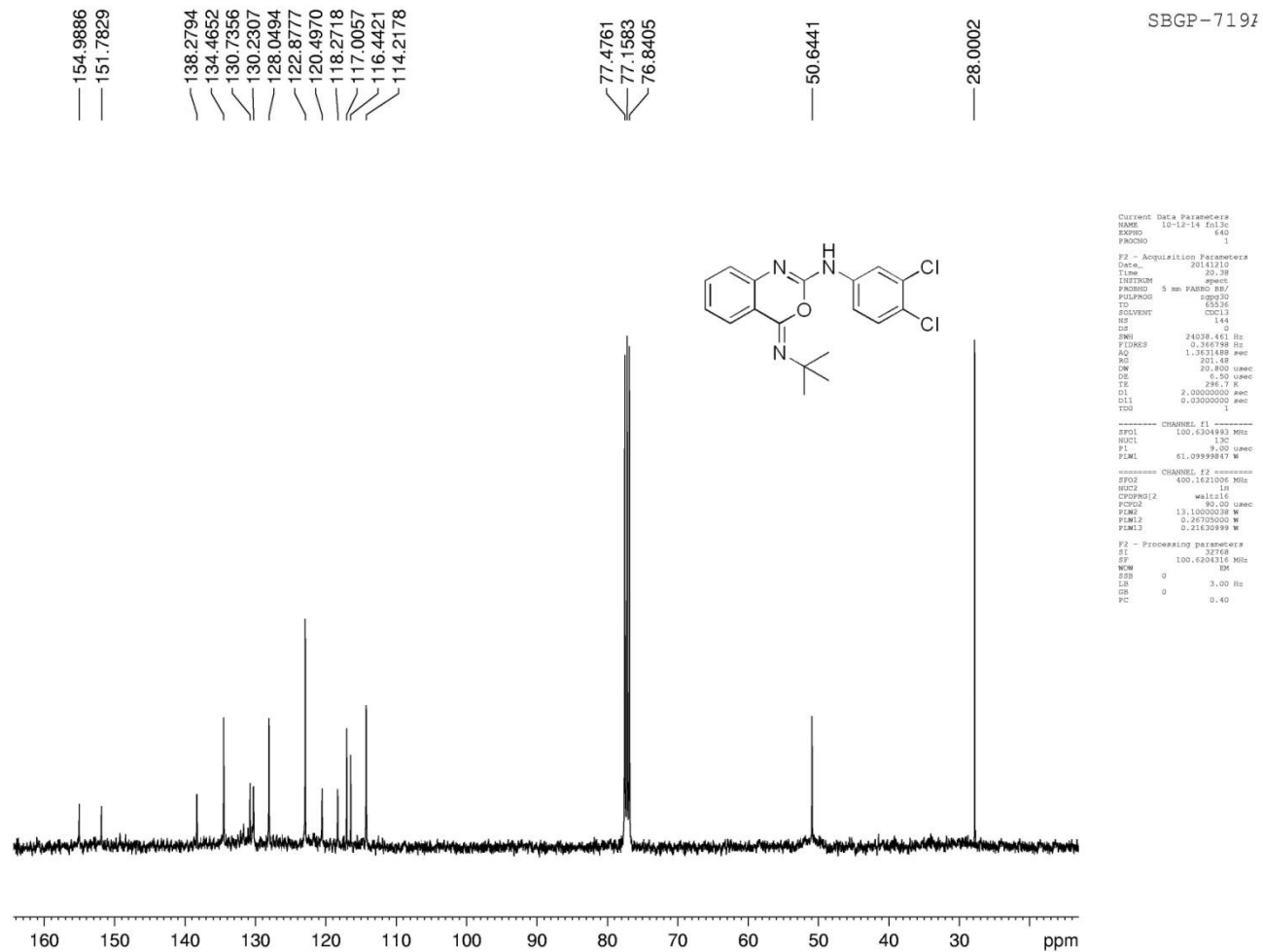


Fig: S-10 ¹³C spectrum of 4-(*tert*-Butylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3eA**)

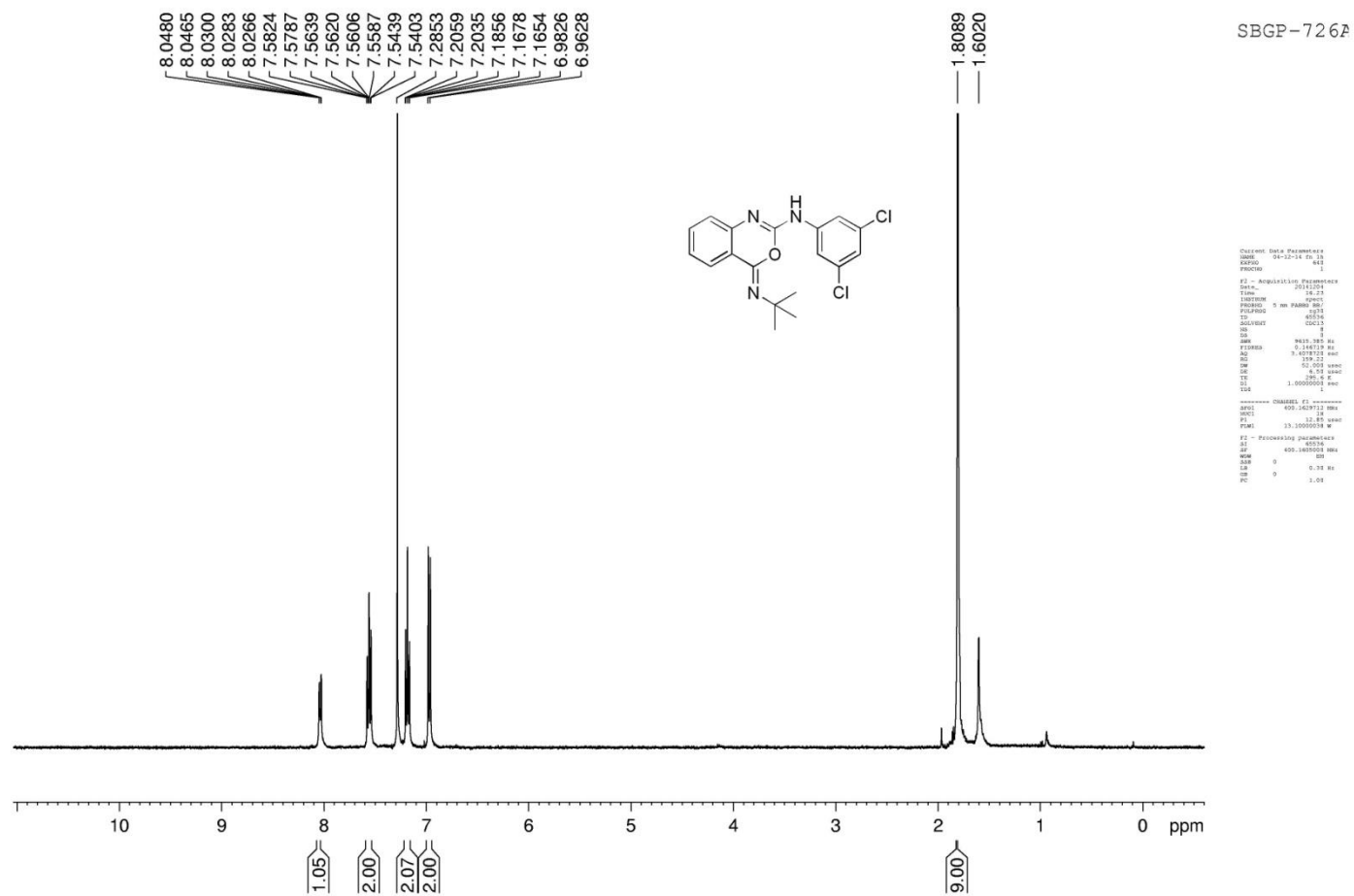


Fig: S-11 ^1H spectrum of 4-(*tert*-Butylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3fA)

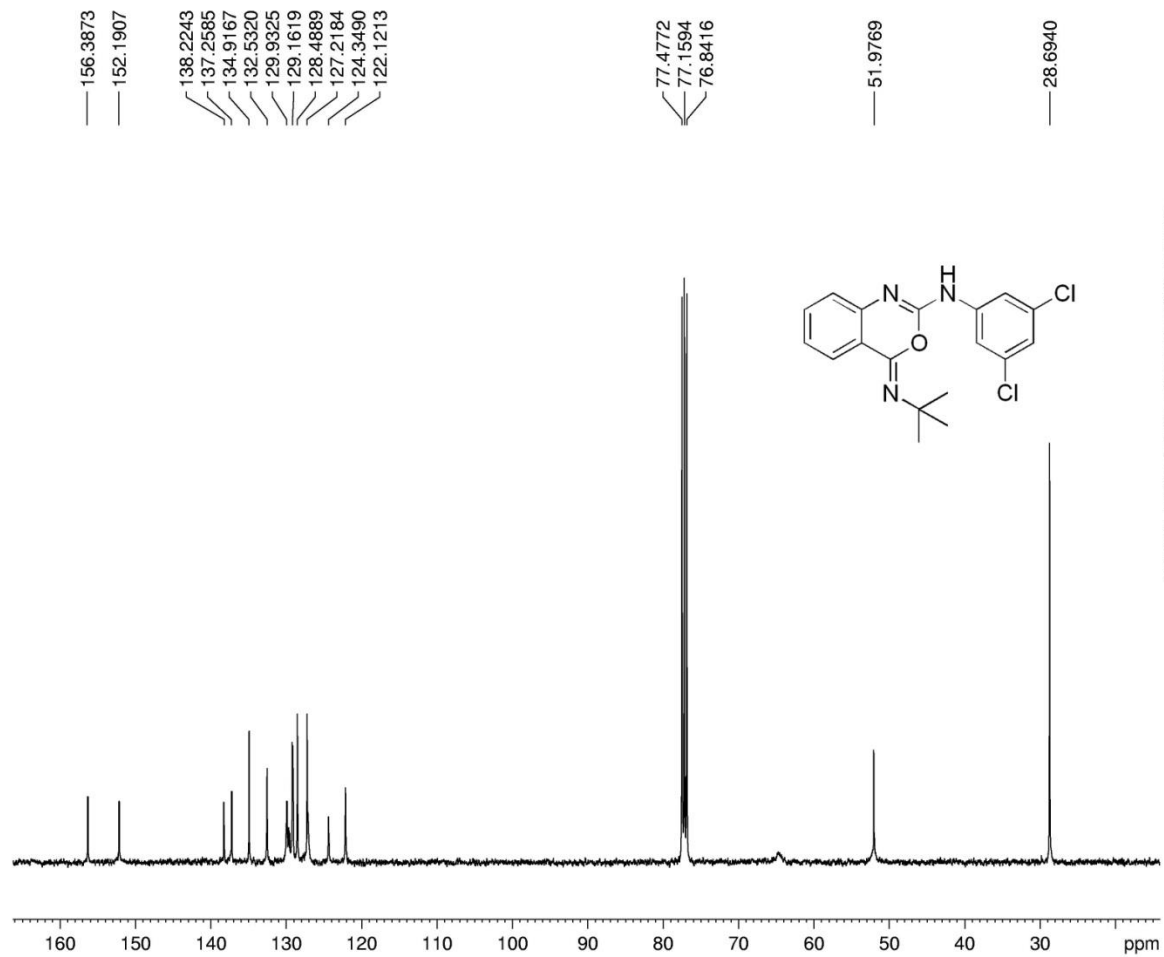


Fig: S-12 ¹³C spectrum of 4-(*tert*-Butylimino)-*N*-(3,5-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3fA**)

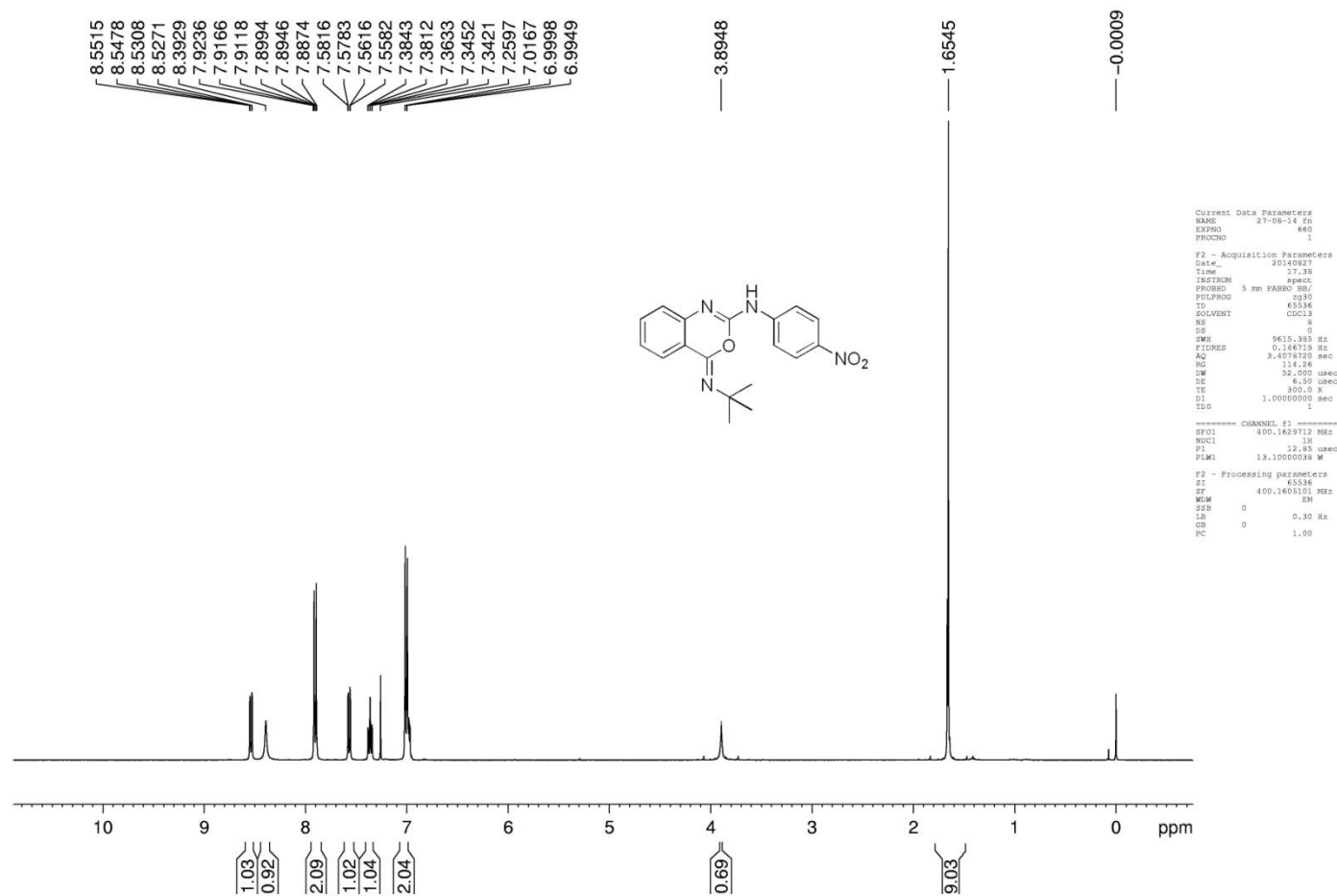


Fig: S-13 ¹H spectrum of 4-(*tert*-Butylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (3gA)

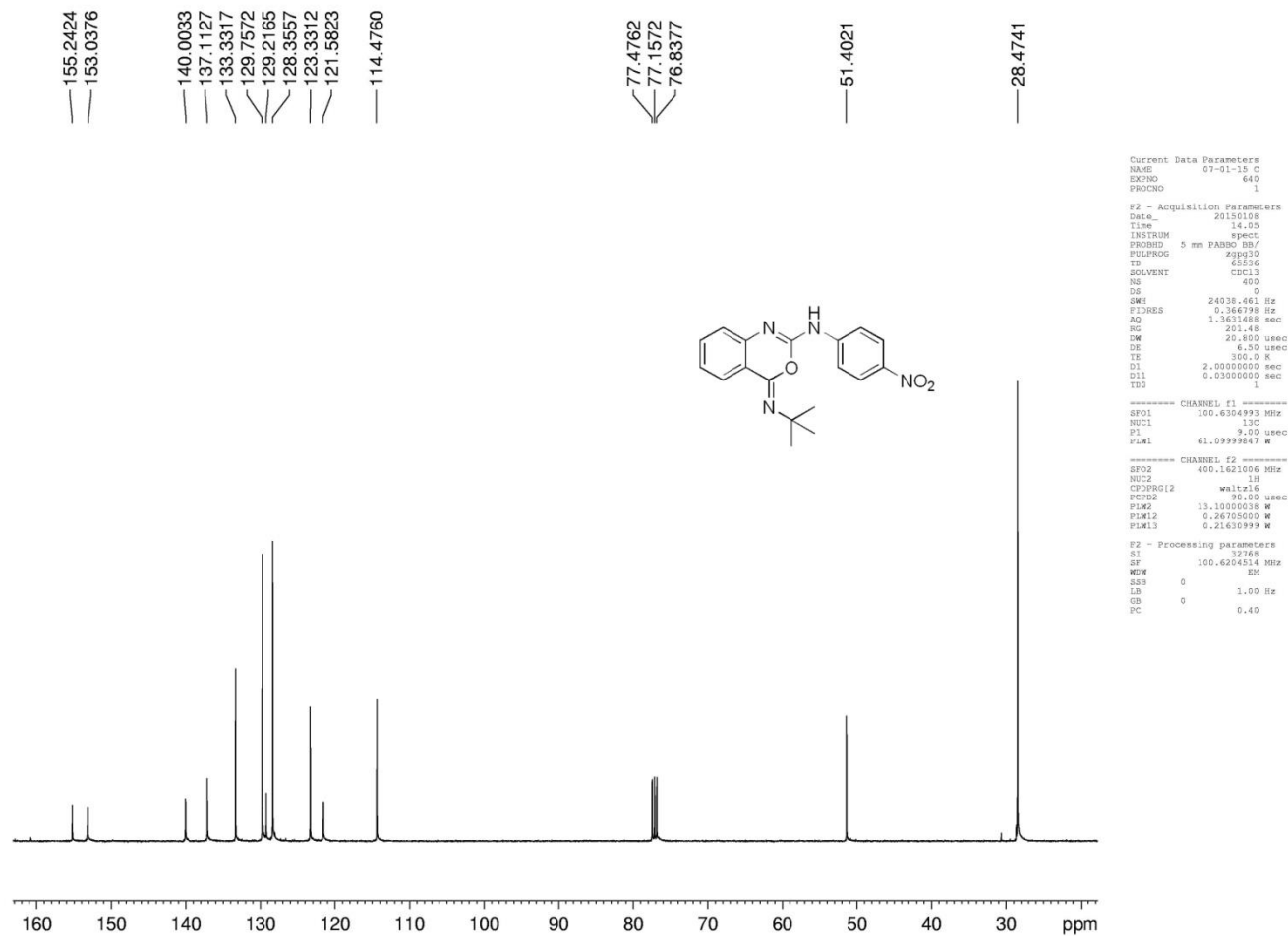


Fig: S-14 ¹³C spectrum of 4-(*tert*-Butylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3gA**)

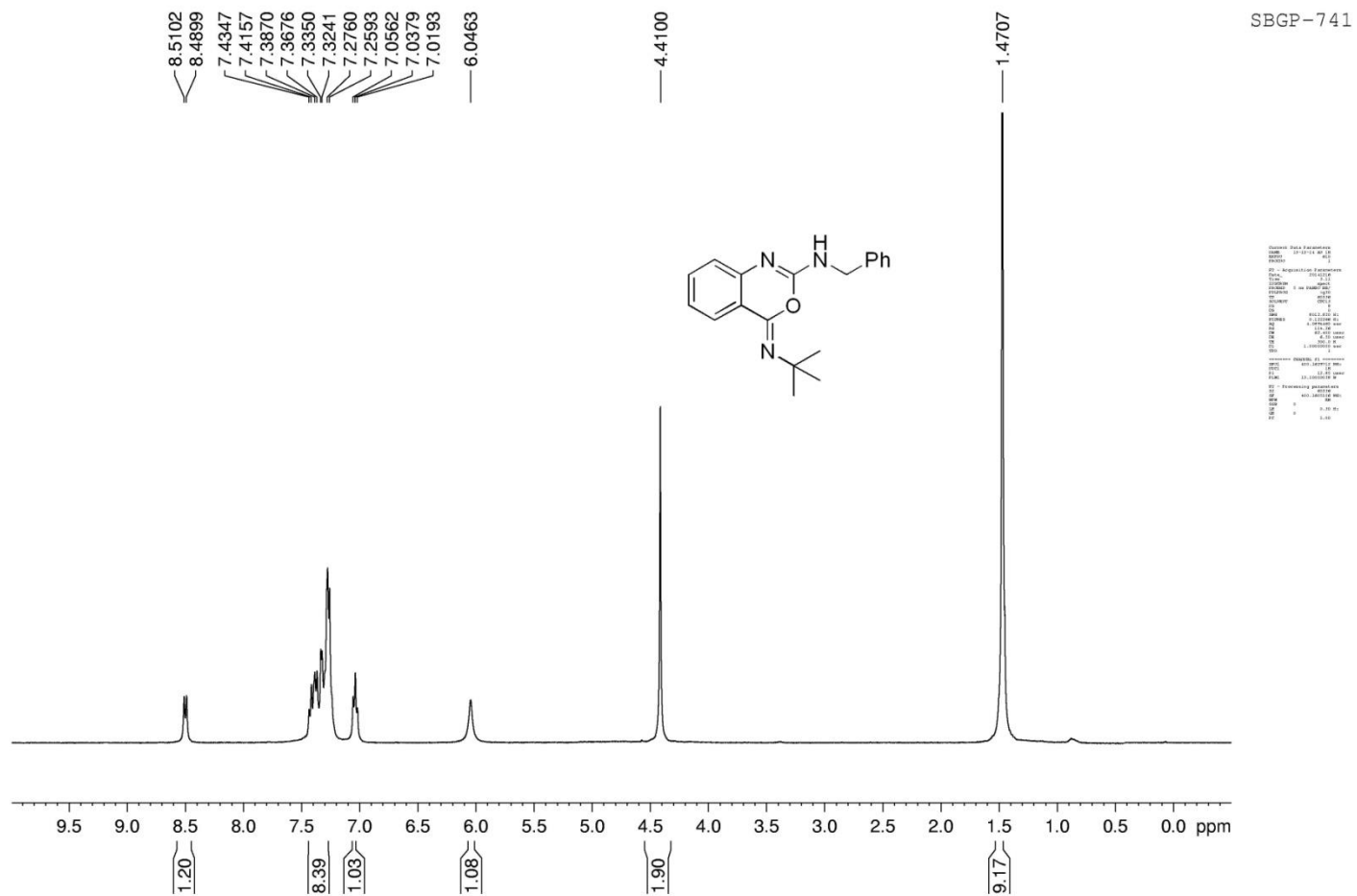


Fig: S-15 ^1H spectrum of *N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3hA**)

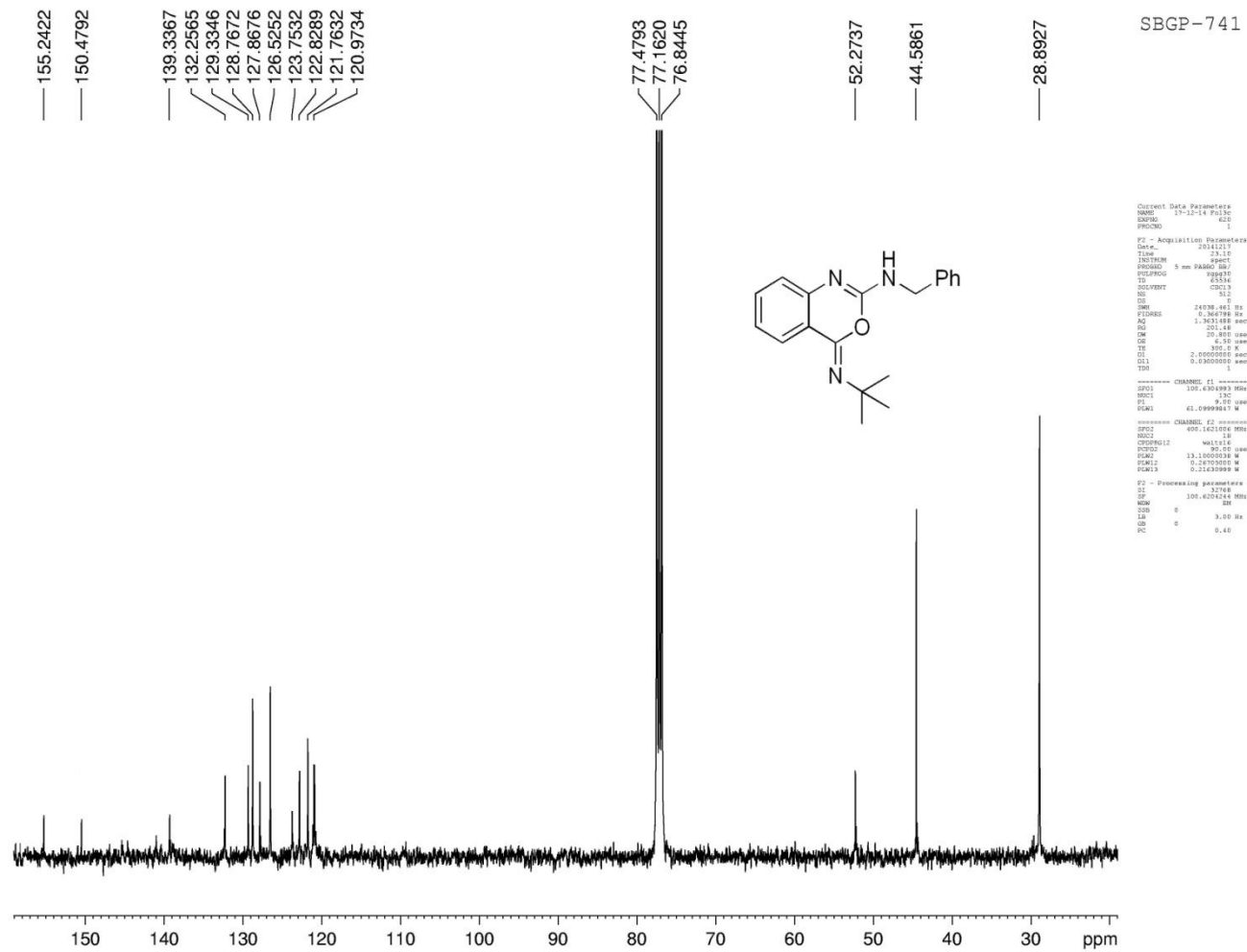


Fig: S-16 ^{13}C spectrum of *N*-benzyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3hA**)

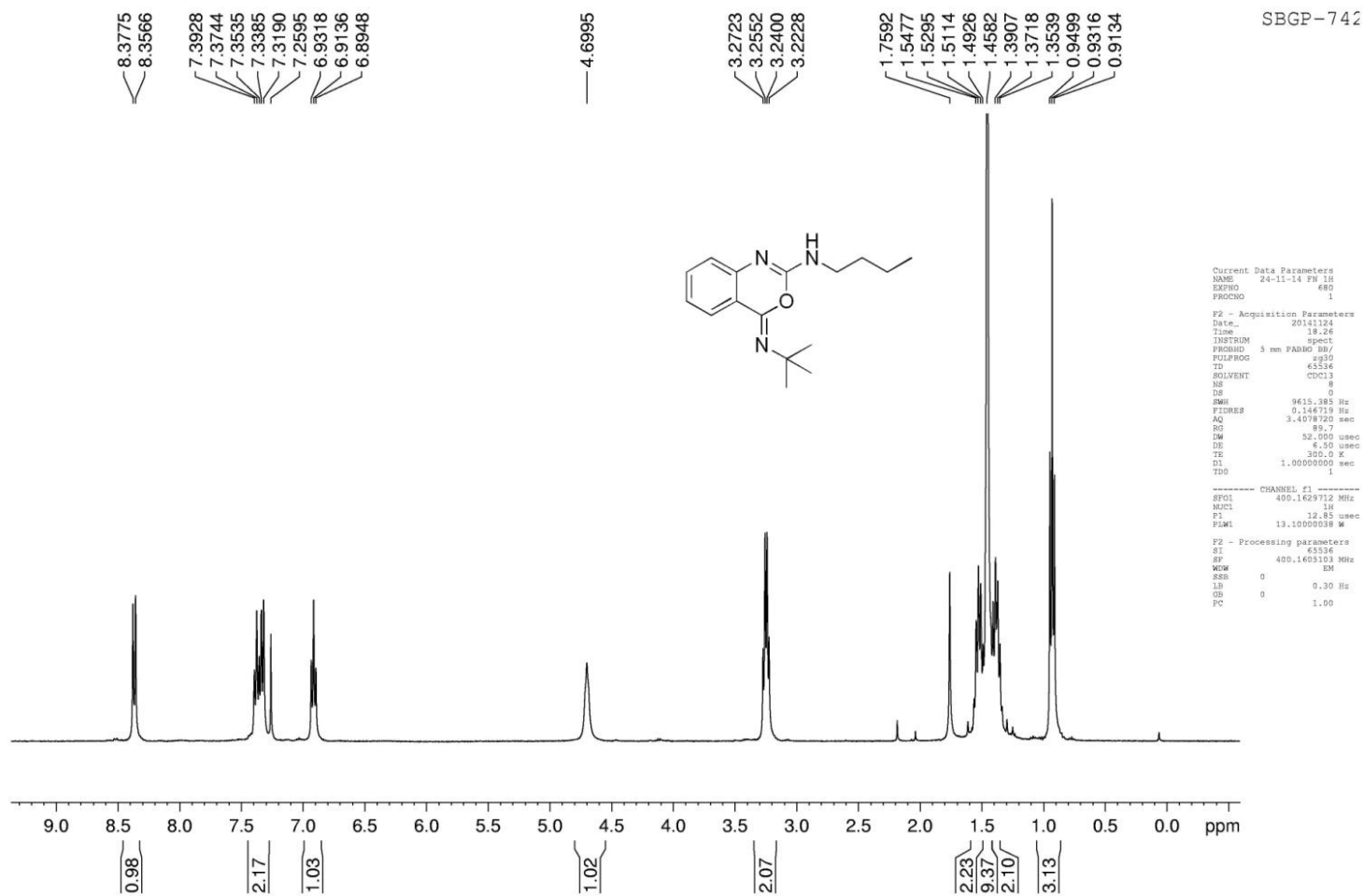


Fig: S-17 ^1H spectrum of *N*-butyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3iA**)

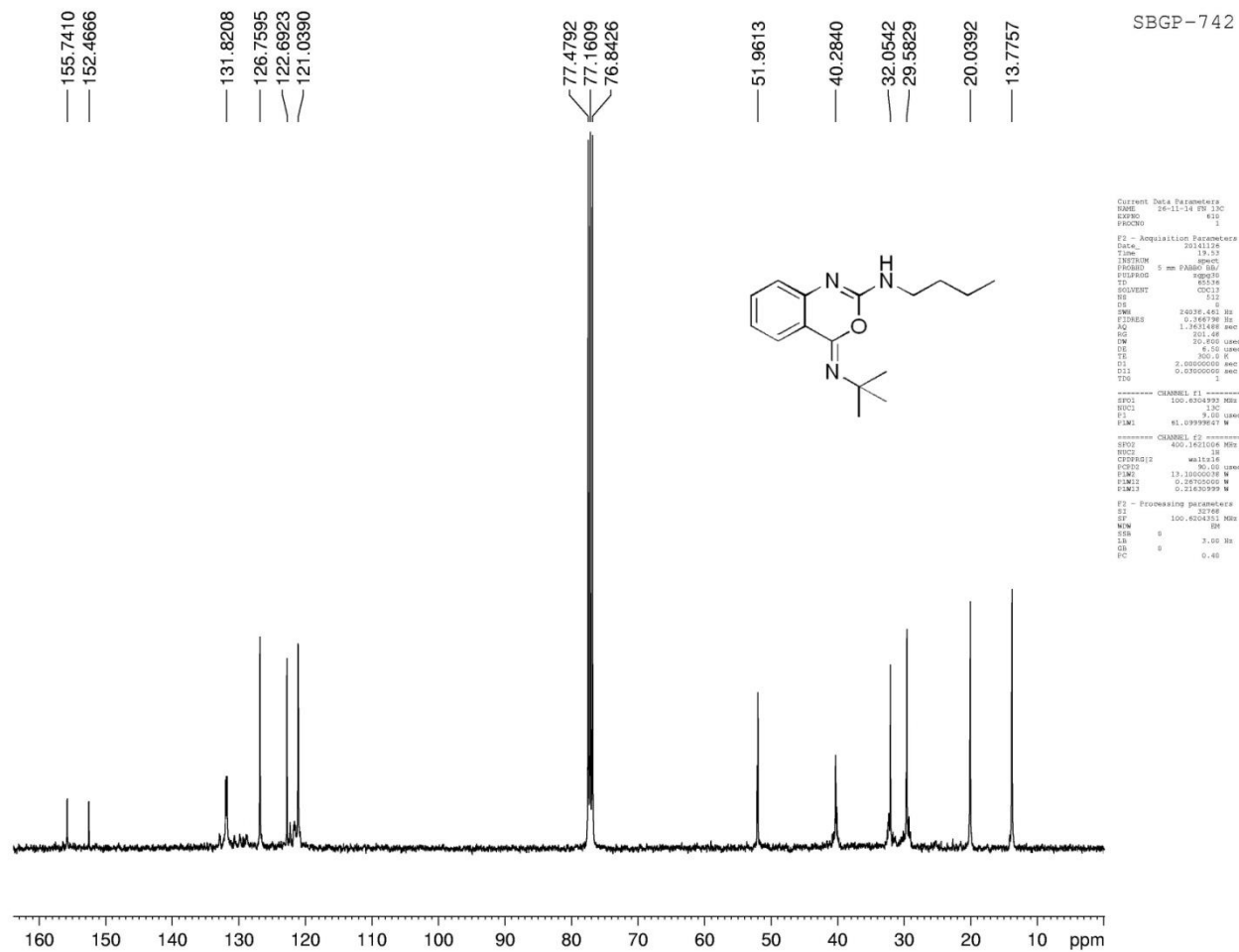


Fig: S-18 ^{13}C spectrum of *N*-butyl-4-(*tert*-Butylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3iA**)

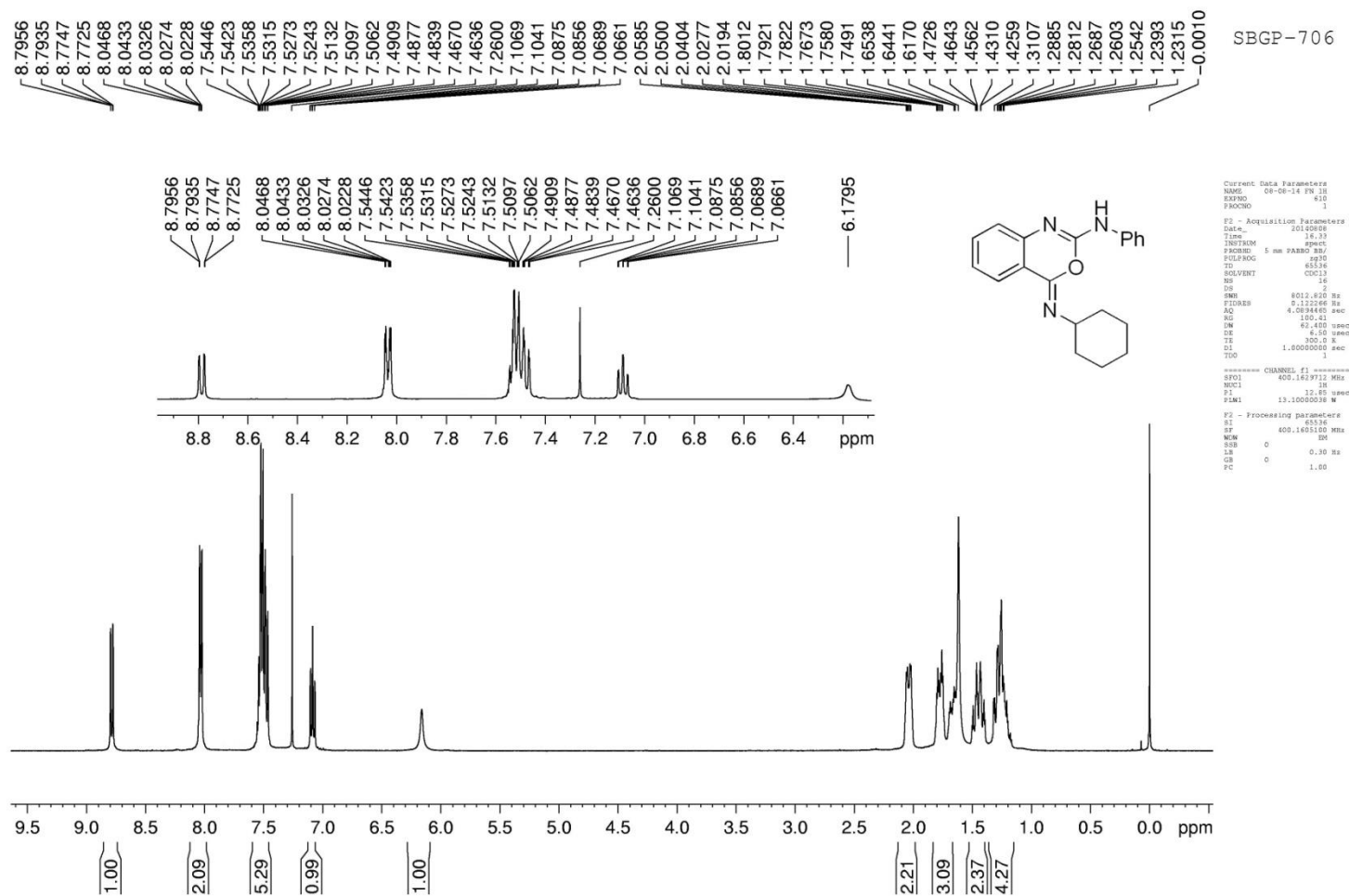


Fig. S-19 ^1H spectrum of 4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3aB**)

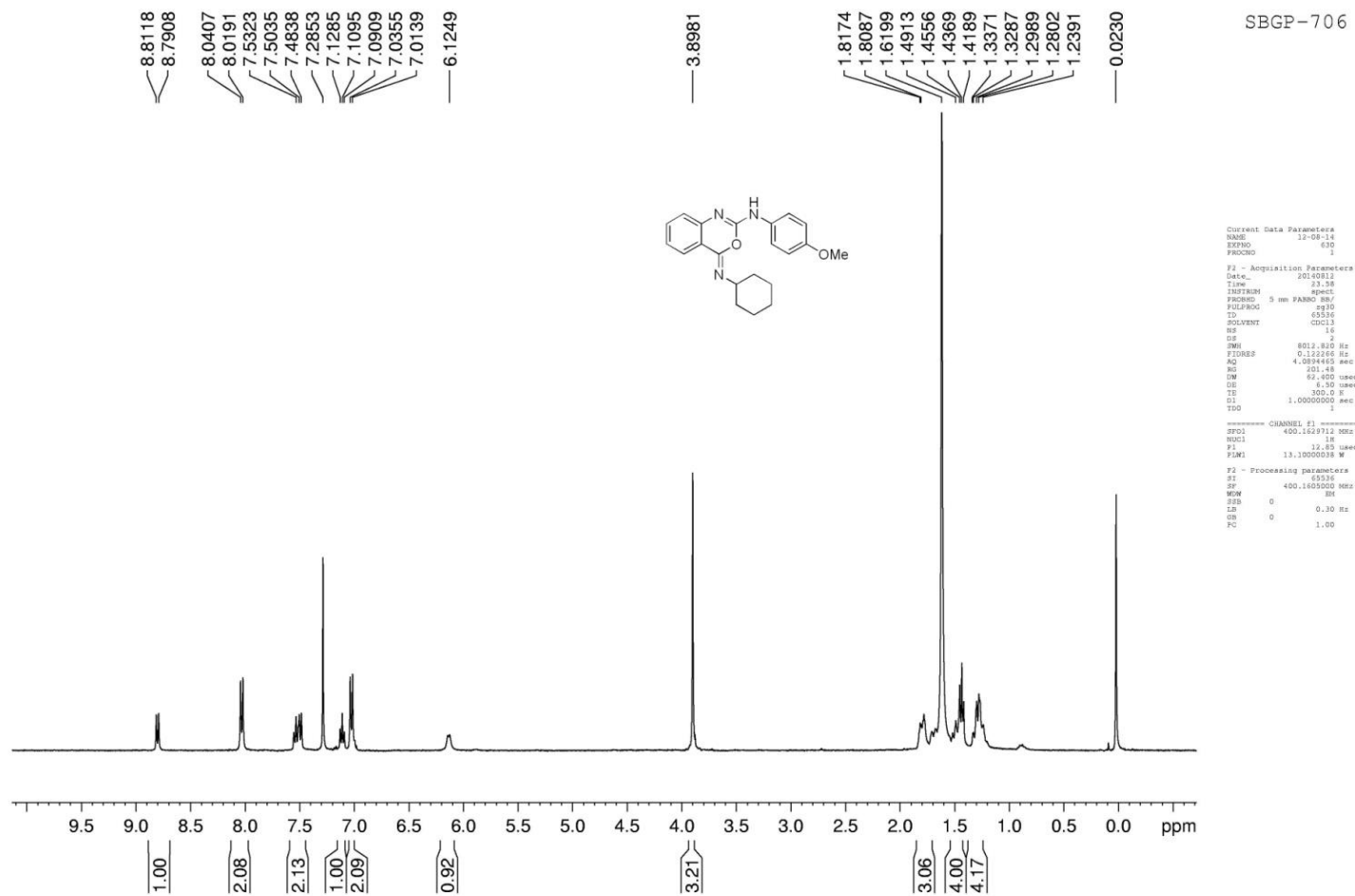


Fig. S-21 ^1H spectrum of 4-(Cyclohexylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3bB**)

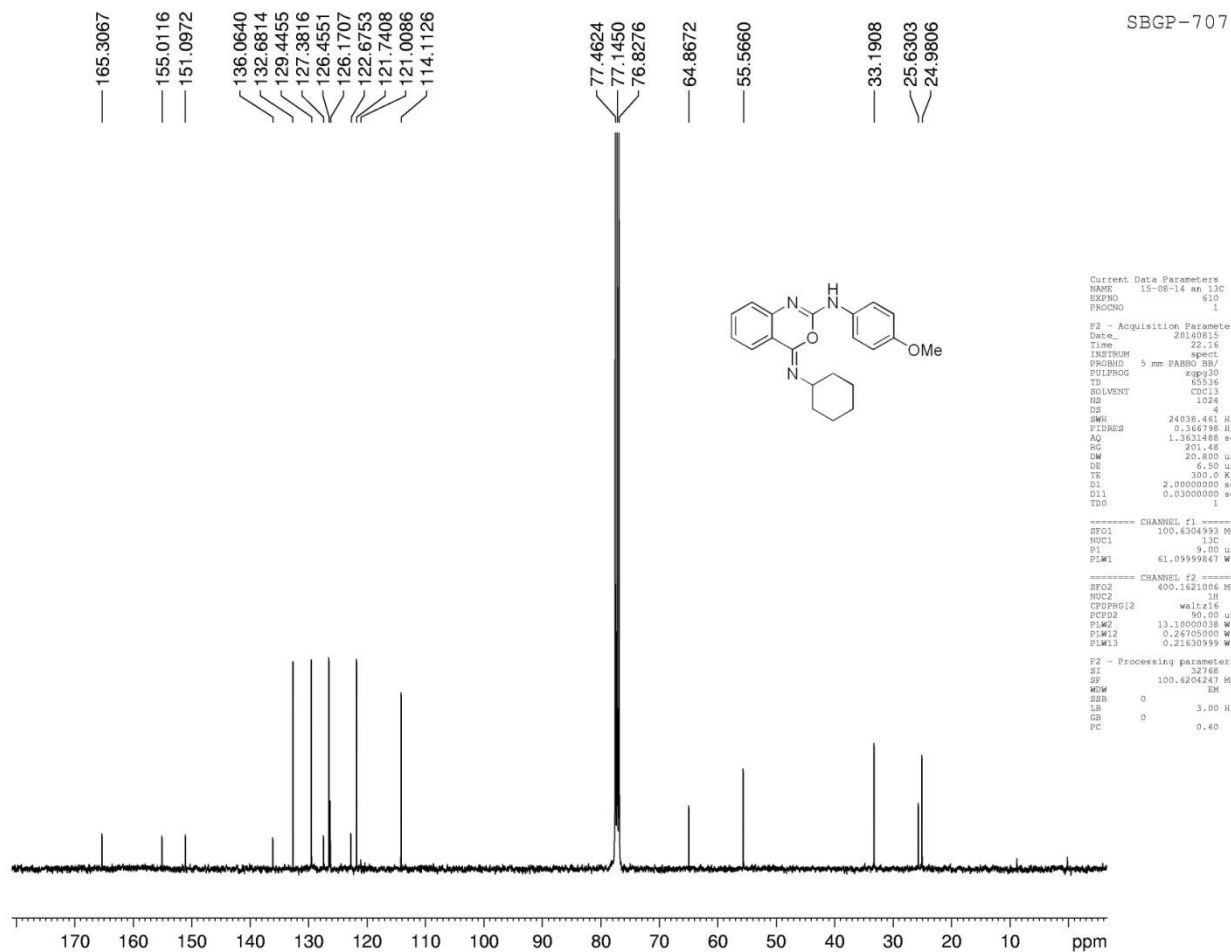


Fig: S-22 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3bB**)

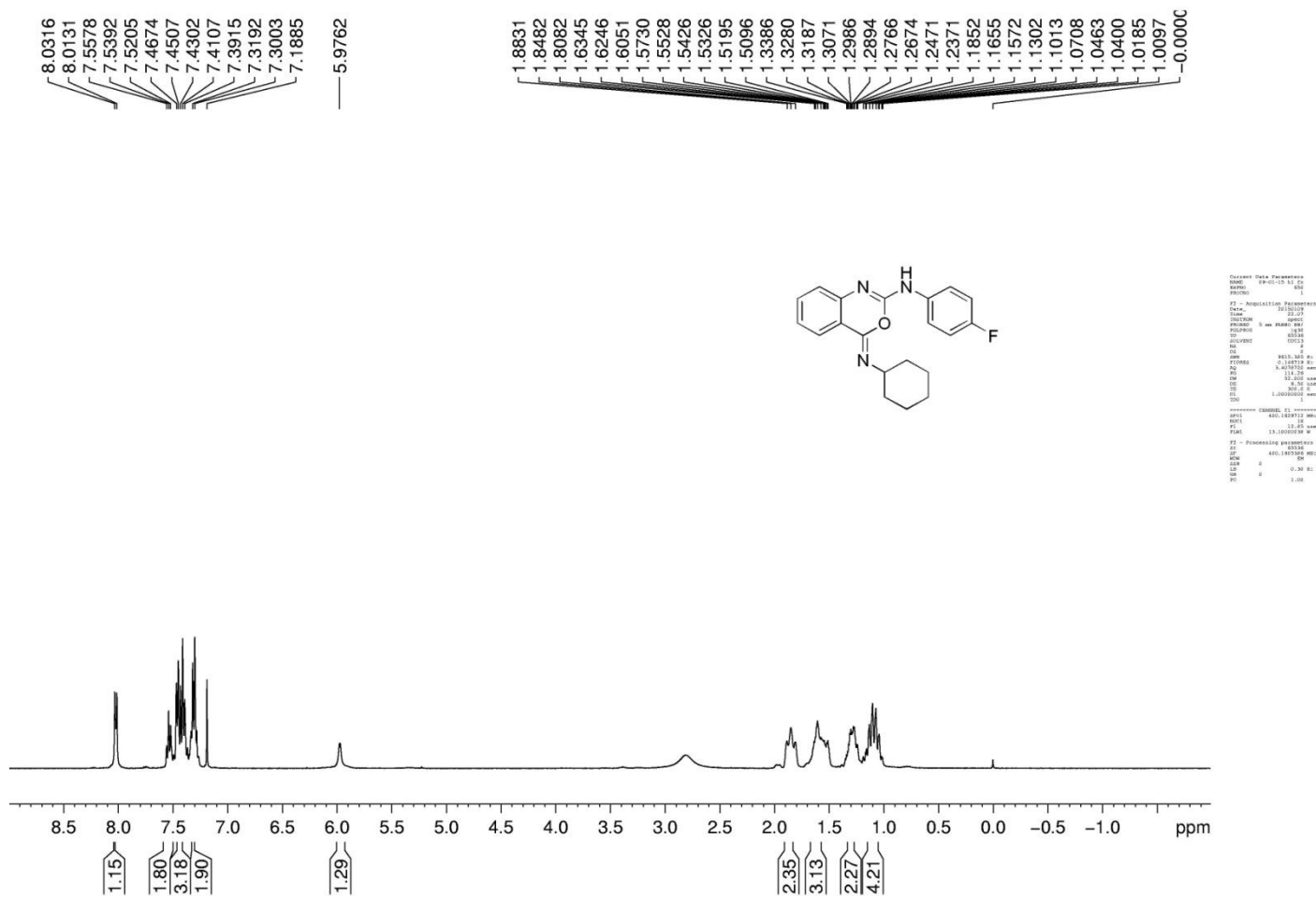


Fig: S-23 ¹H spectrum of 4-(Cyclohexylimino)-N-(4-fluorophenyl)-4H-benzo[d][1,3]oxazin-2-amine (**3cB**)

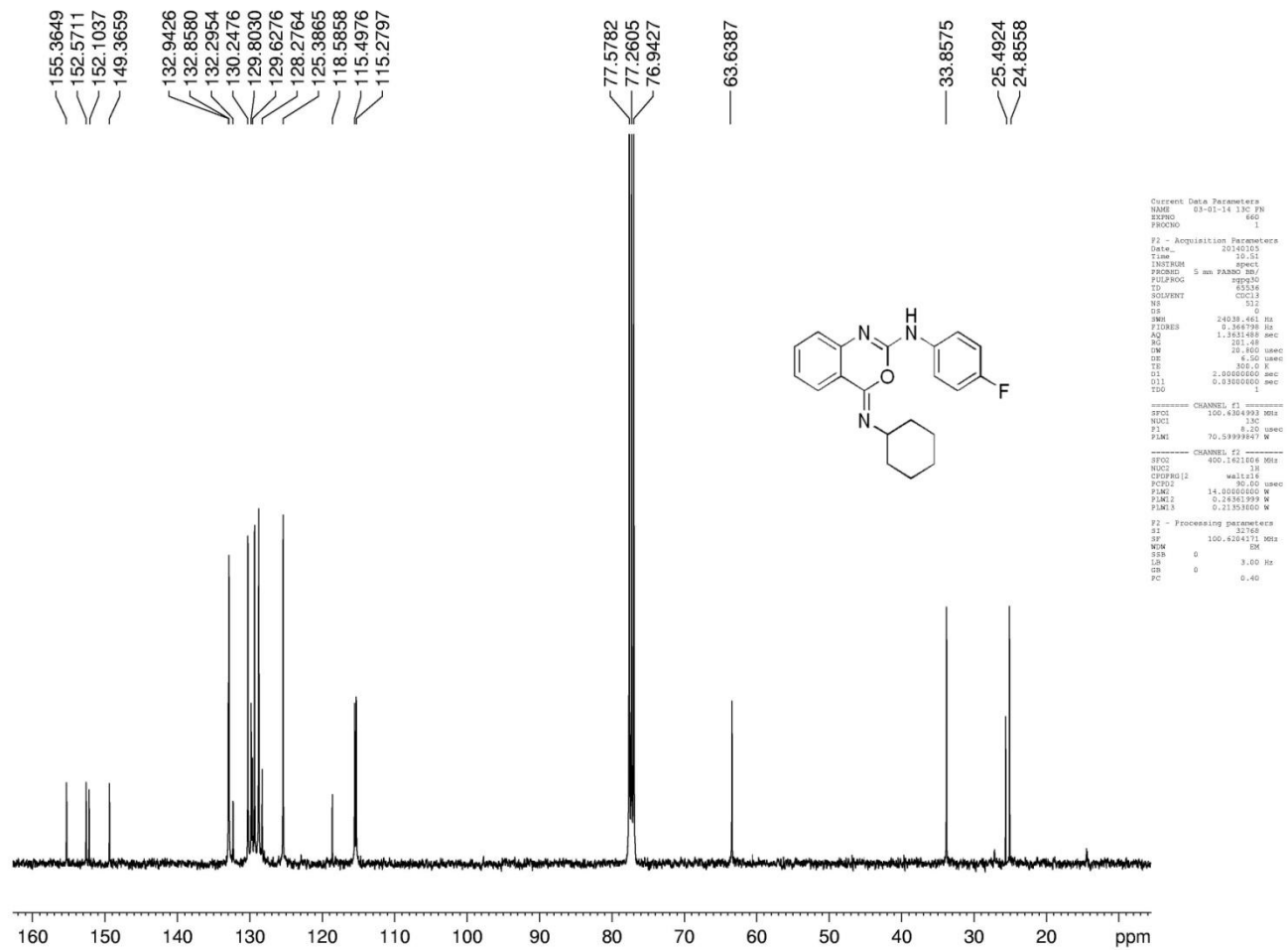


Fig: S-24 ¹³C spectrum of 4-(Cyclohexylimino)-N-(4-fluorophenyl)-4H-benzo[d][1,3]oxazin-2-amine (3cB)

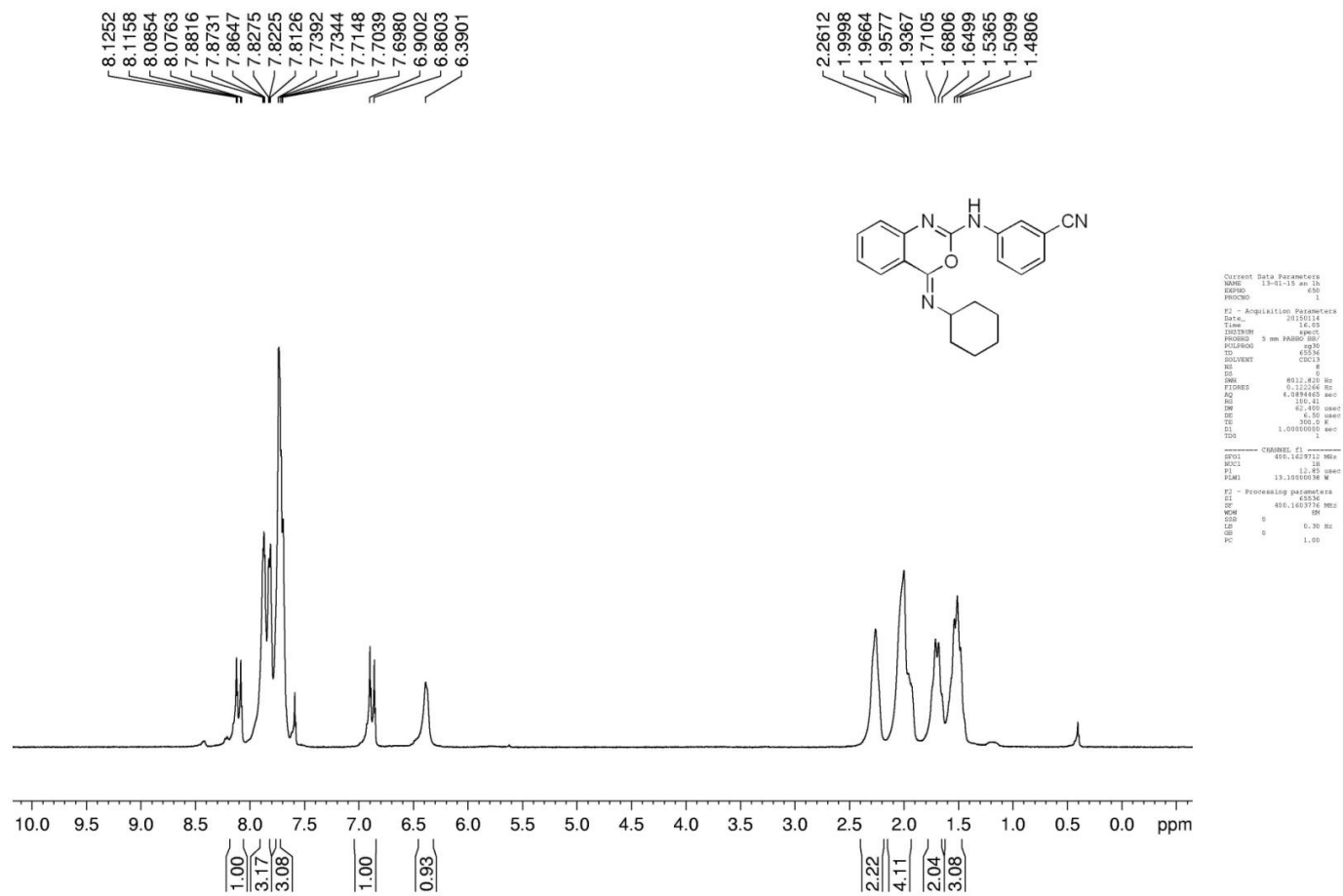
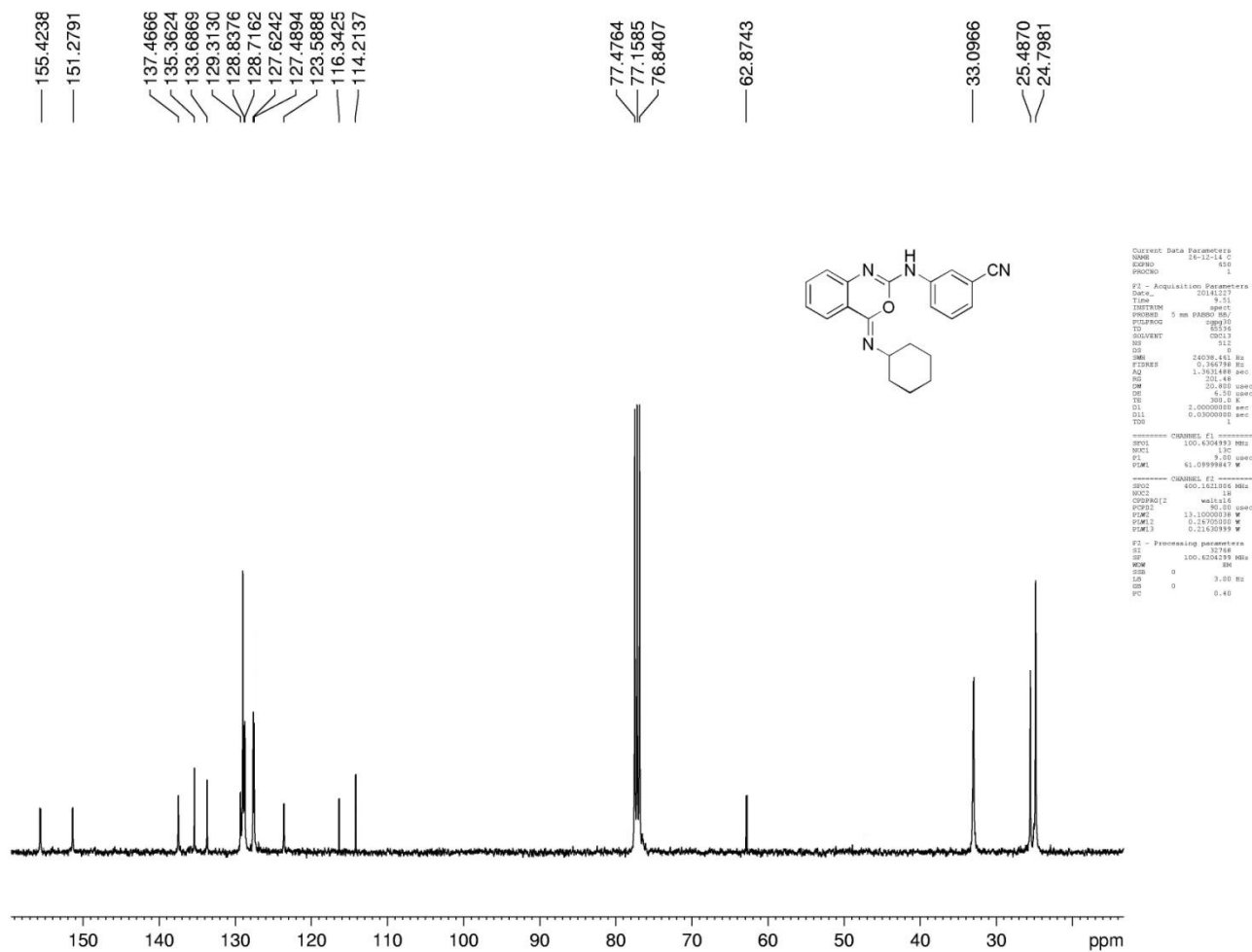


Fig: S-25 ¹H spectrum of 3-(4-(Cyclohexylimino)-4H-benzo[d][1,3]oxazin-2-ylamino)benzonitrile (**3dB**)



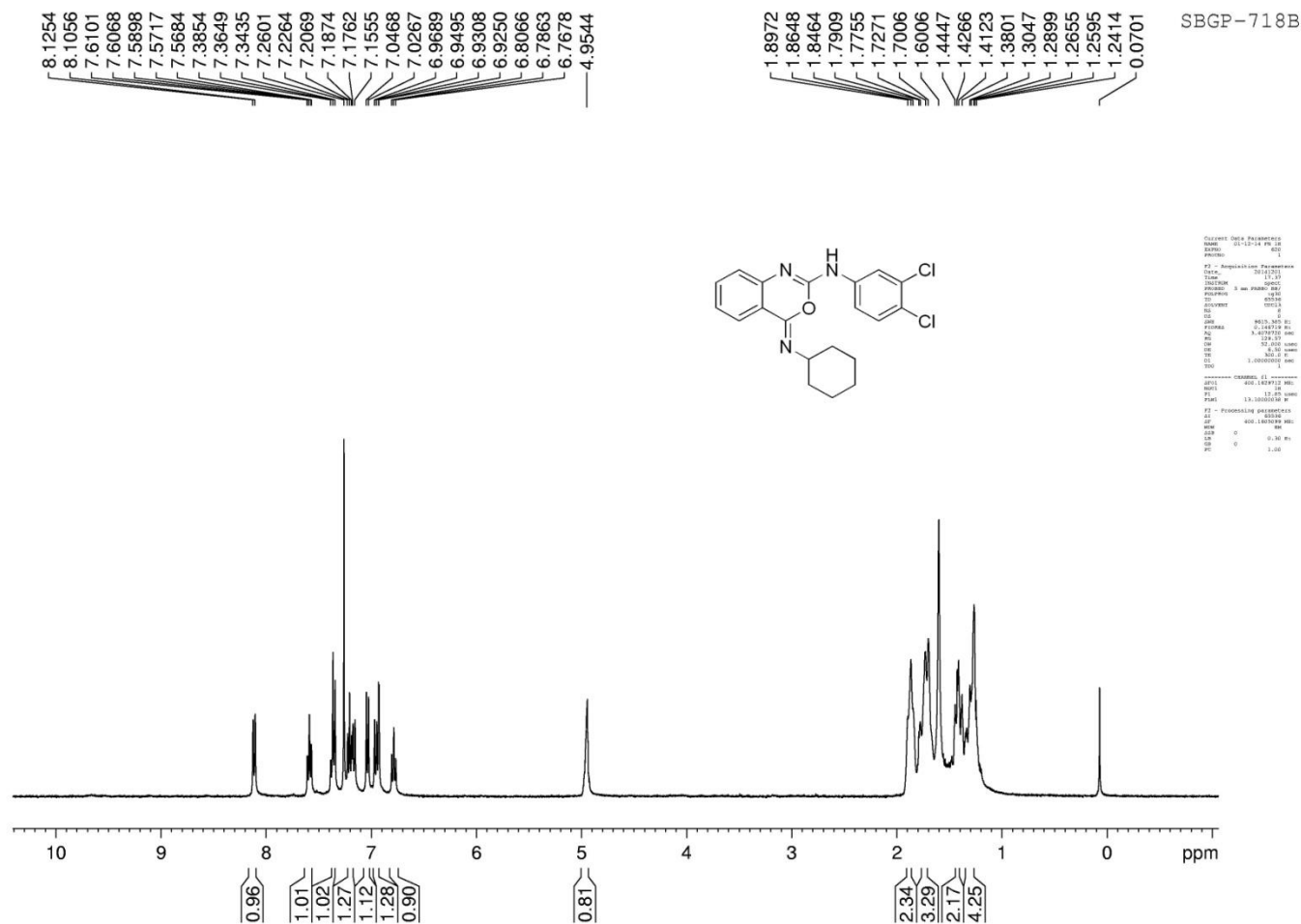


Fig: S-27 ^1H spectrum of 4-(Cyclohexylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3eB**)

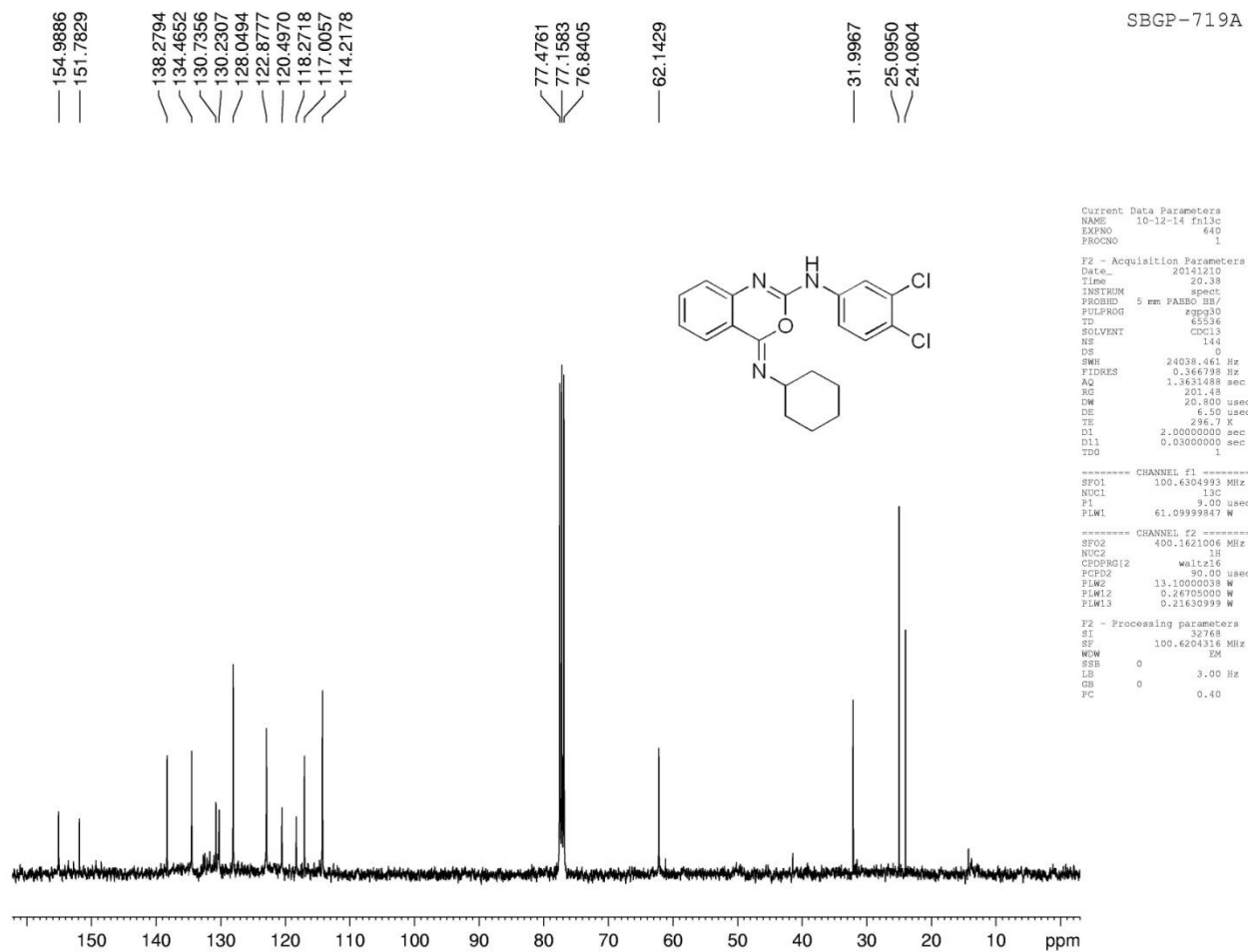


Fig: S-28 ^{13}C spectrum of 4-(Cyclohexylimino)-*N*-(3,4-dichlorophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3eB**)

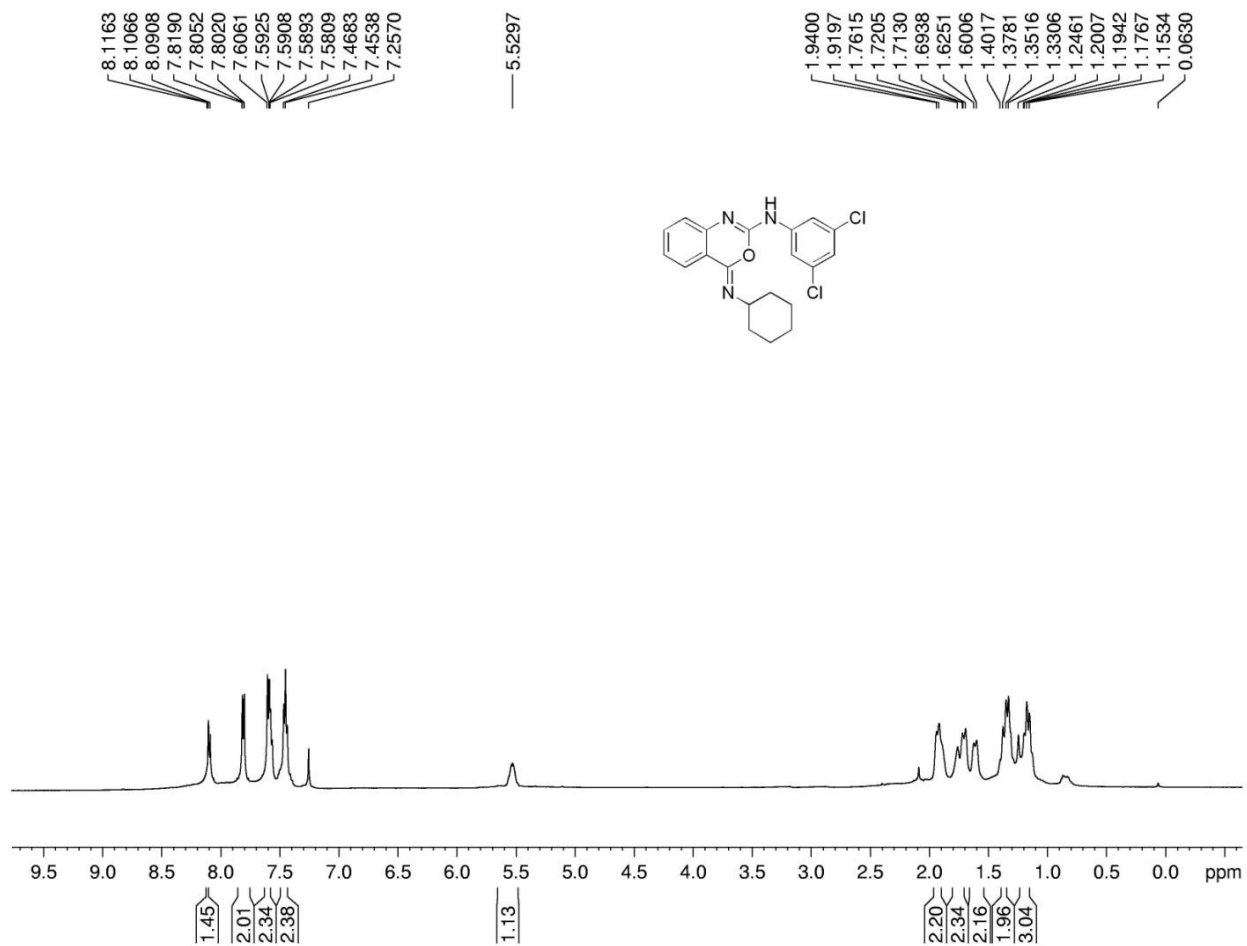
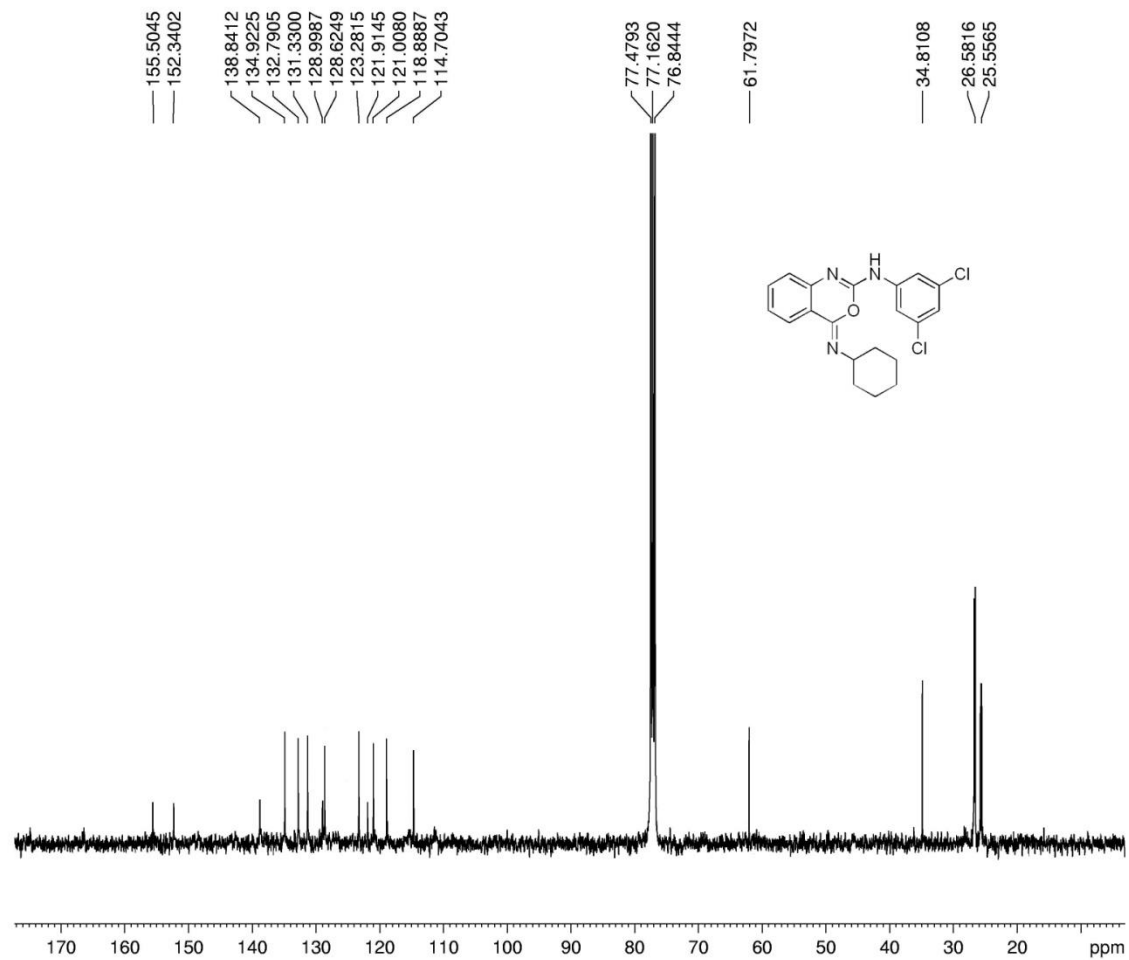


Fig: S-29 ¹H spectrum of 4-(Cyclohexylimino)-N-(3, 5-dichlorophenyl)-4H-benzo[d][1,3]oxazin-2-amine (**3fB**)



```

Current Data Parameters
NAME      03-13-18 Au 13C
EXPNO    800
PROCNO    1

F2 - Acquisition Parameters
Date_    20141204
Time     09:04
INSTRUM  spect
PROBHD   5 mm PABBO 90C
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        312
DS        4
SFO1     34038.462 Hz
SF02     0.161708 Hz
AQ        1.3471489 sec
RG        201.48
DM        20.800 umsec
DE        1.00 umsec
TE        298.4 K
DQ1       0.0000000 sec
DQ2       0.0000000 sec
DQ3       1
DQ4       1

----- CHANNEL f1 -----
NUC1      100.6304993 MHz
P1        2.00 usec
PL1       01.09999617 W

----- CHANNEL f2 -----
NUC2      800.1420000 MHz
P2        10
PL2       10.0000000 W
PL12      13.1000000 W
PL13      0.2870000 W
PL14      0.2130000 W

F2 - Processing parameters
SI        32768
SF        100.6204144 MHz
WDW       EM
SSB       0
GB        3.00 Hz
BB        0
PC        0.40
  
```

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

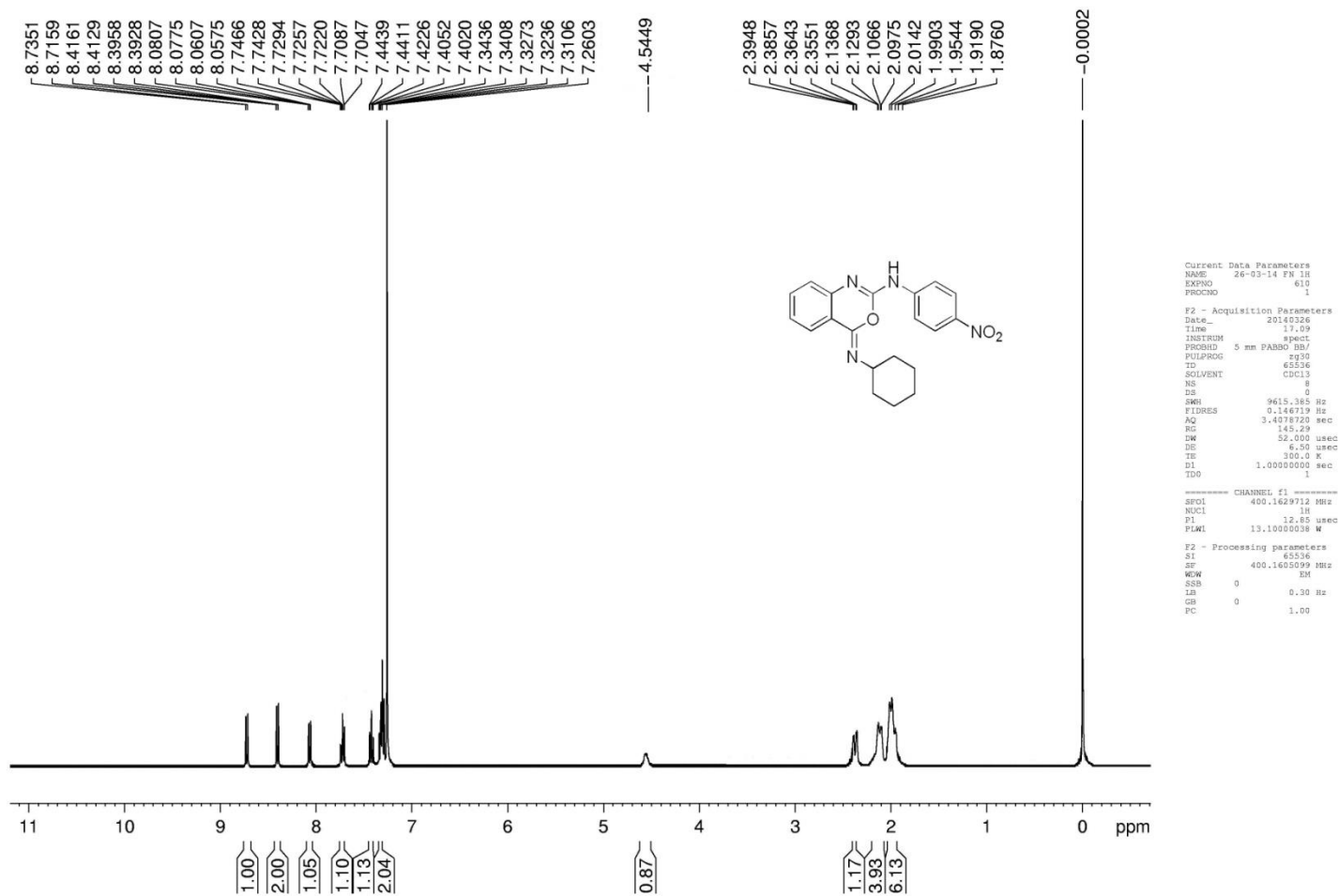


Fig: S-31 ^1H spectrum of 4-(Cyclohexylimino)-*N*-(4-nitrophenyl)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3gB**)

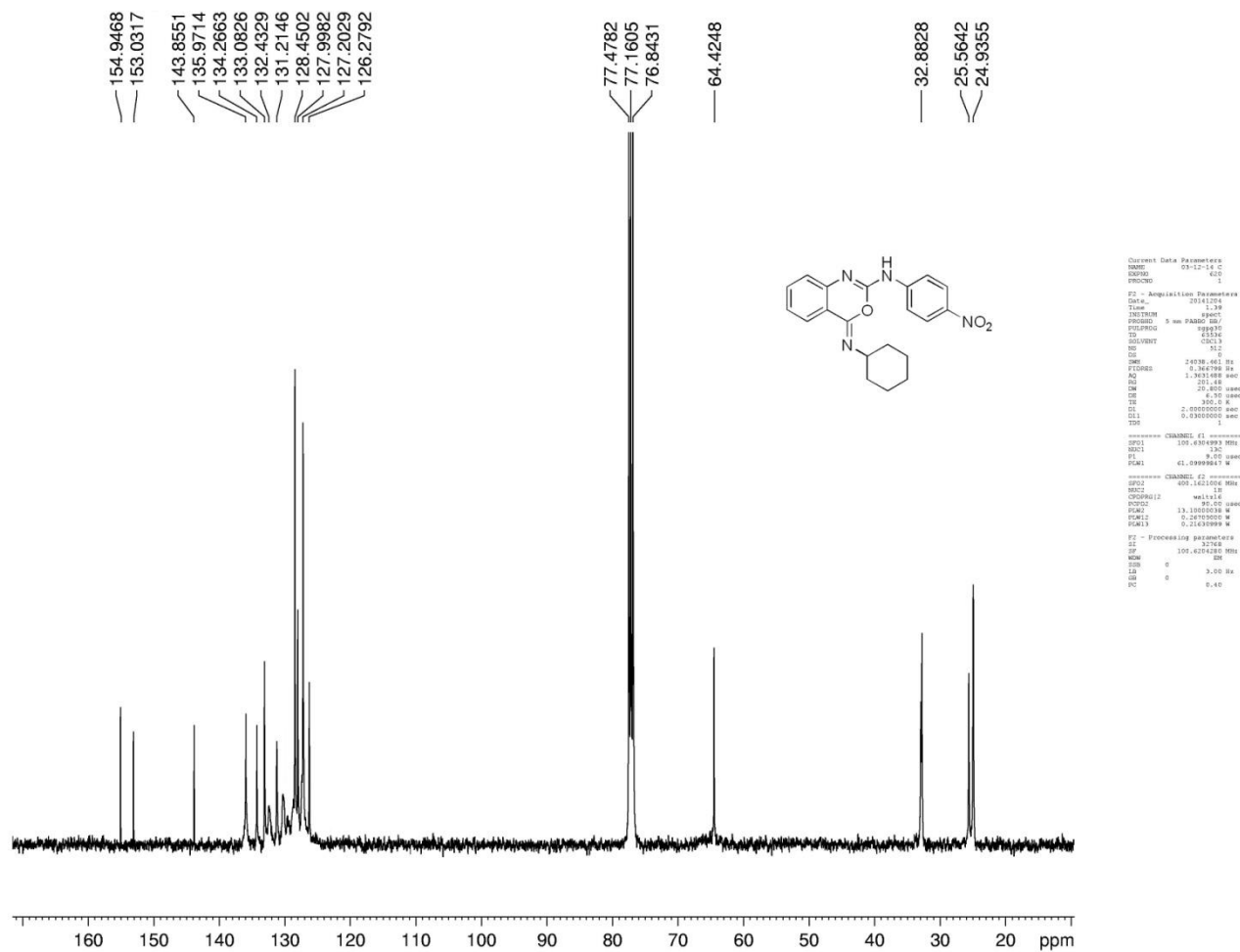


Fig: S-32 ¹³C spectrum of 4-(Cyclohexylimino)-N-(4-nitrophenyl)-4H-benzo[d][1,3]oxazin-2-amine (**3gB**)

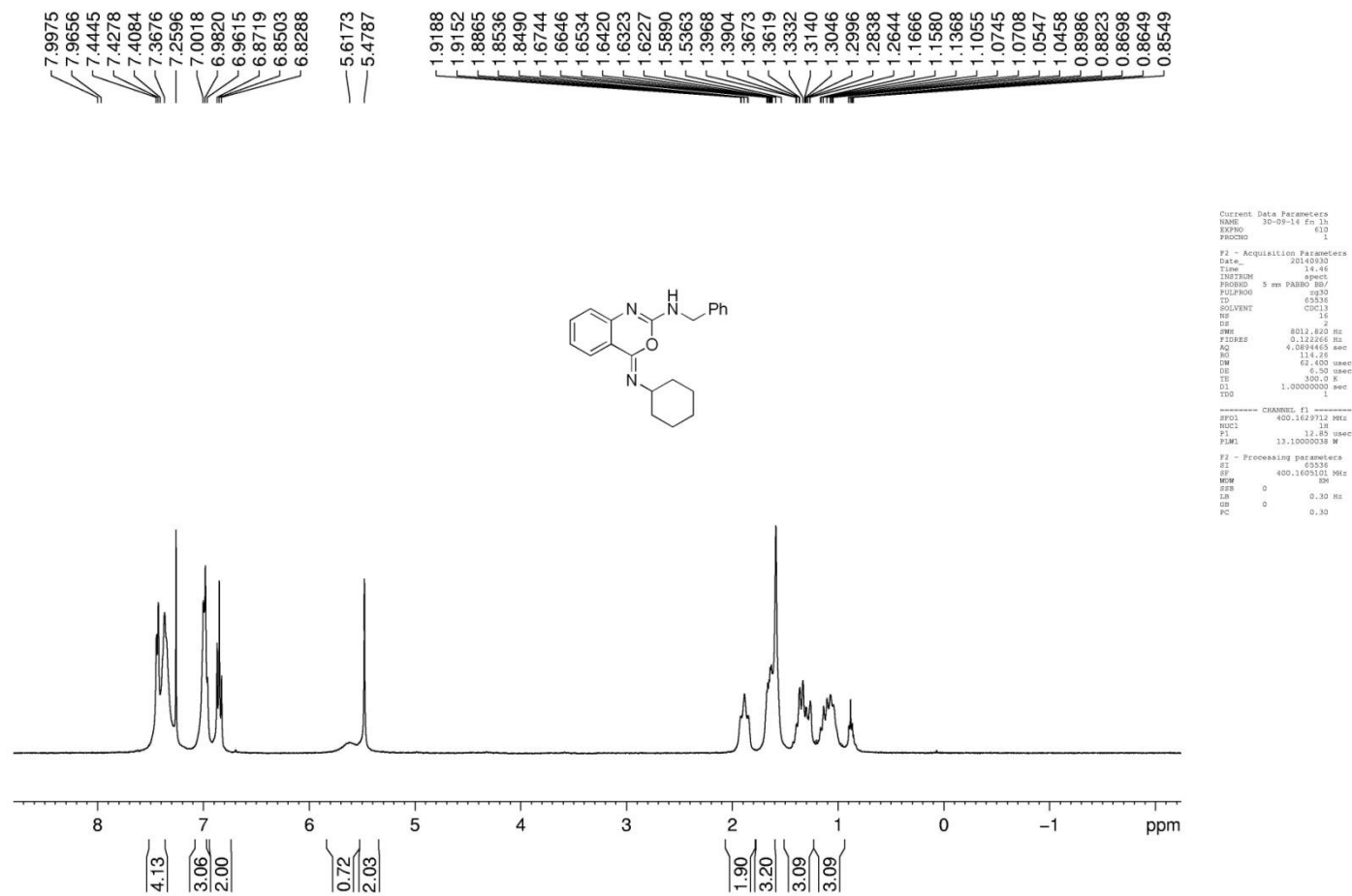


Fig: S-33 ^1H spectrum of *N*-benzyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3hB**)

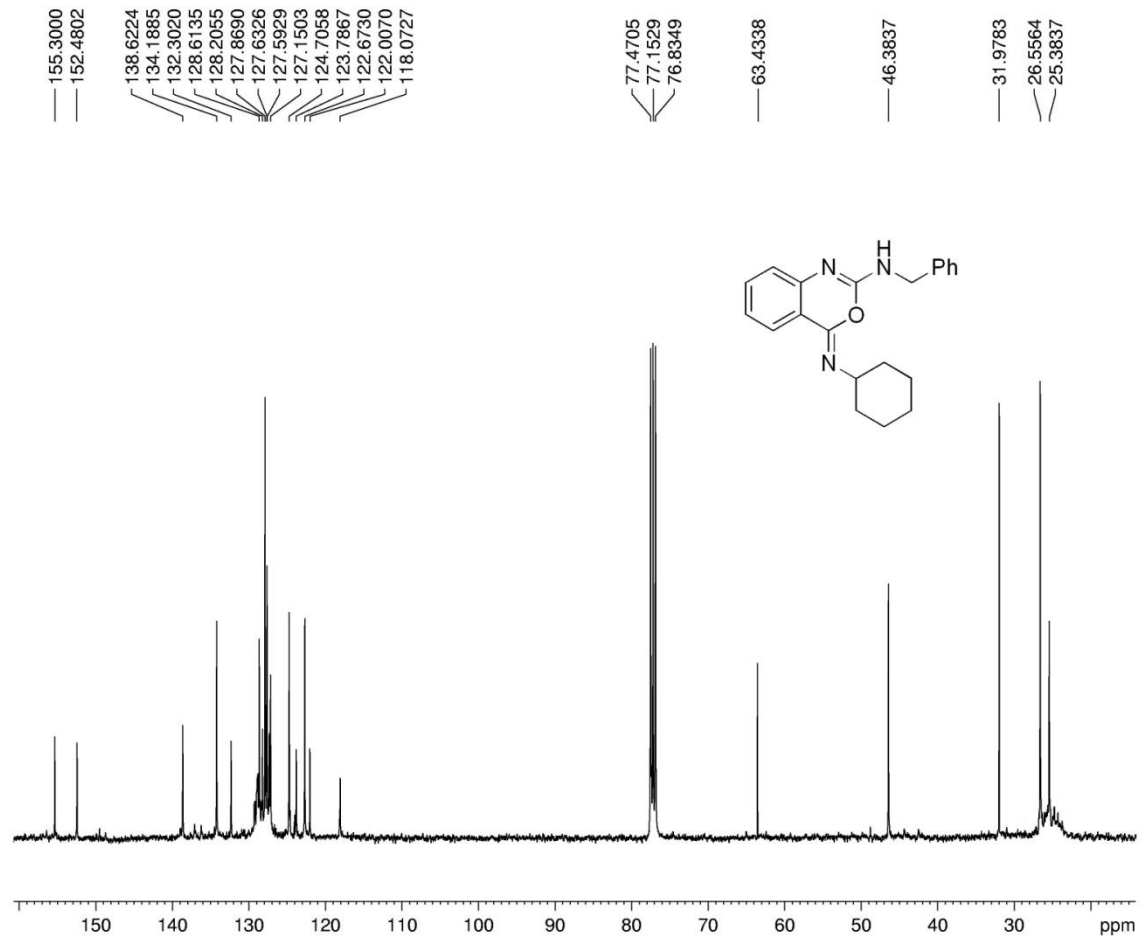


Fig: S-34 ¹³C spectrum of *N*-benzyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3hB**)

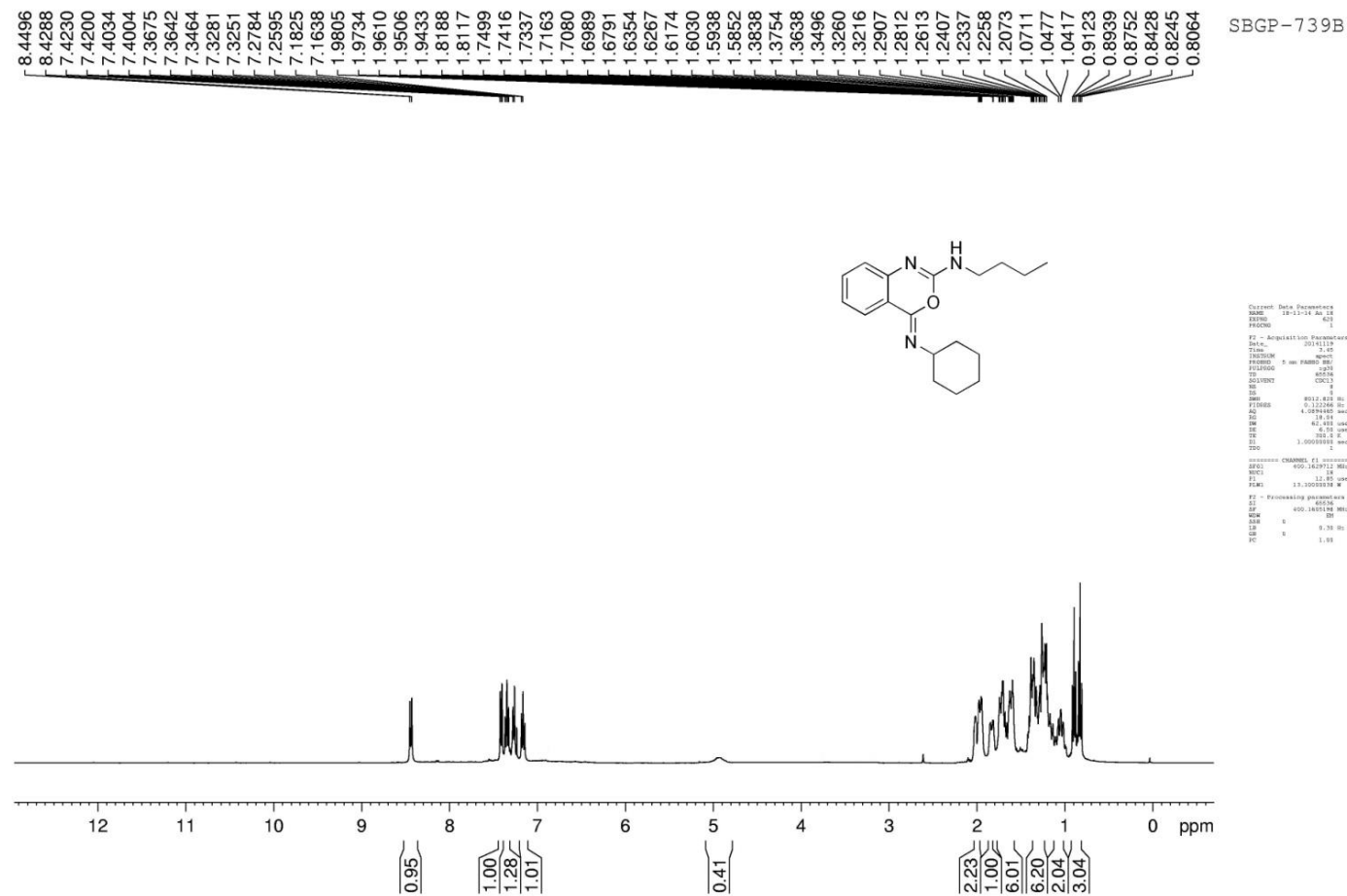
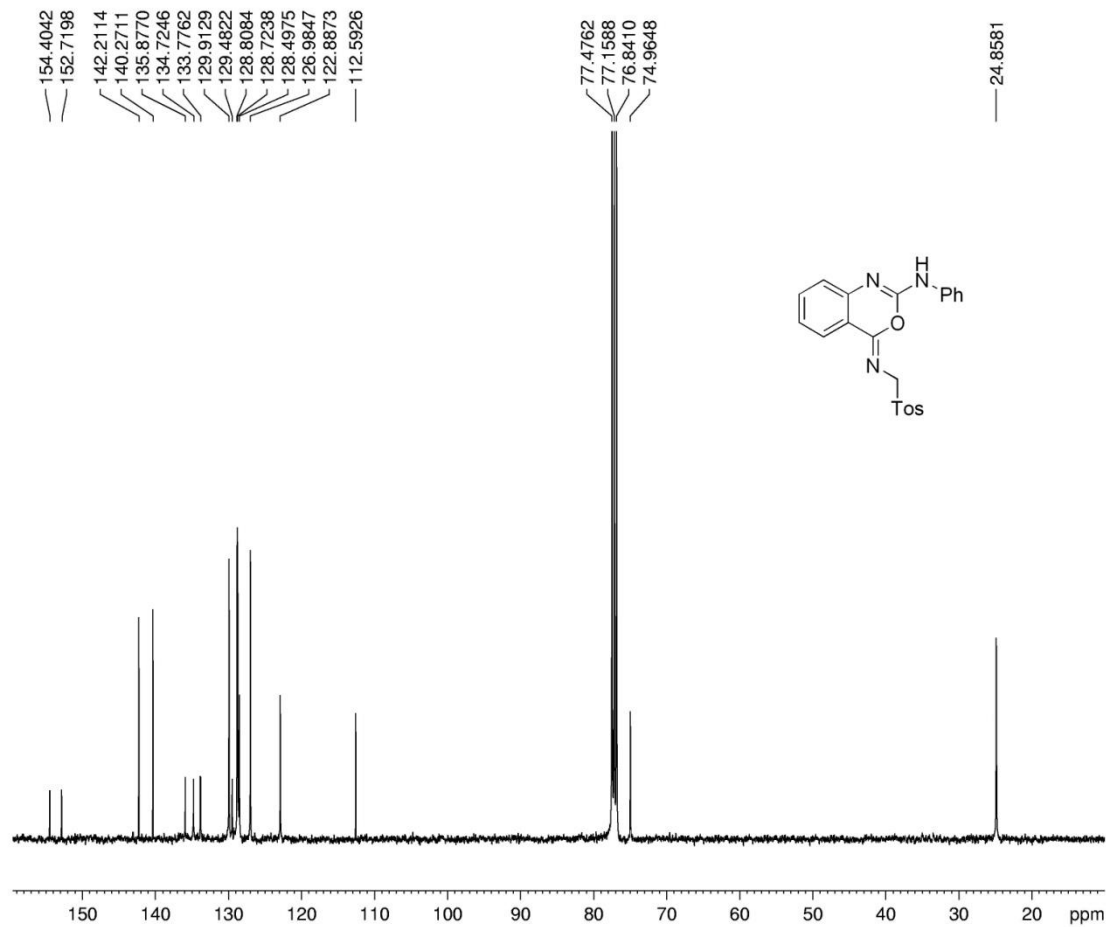


Fig: S-35 ^1H spectrum of *N*-butyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3iB**)



```

Current Data Parameters
NAME      04-12-14 C
EXPNO    642
PROCNO   1

F2 - Acquisition Parameters
Date_    20141221
Time     21:23
INSTRUM  spect
PROBHD   5 mm PABBO BBO
PULPROG  zgpg30
TD       65536
SFO      400.146
AQ       0.9213
RG        512
SR       382.8
FIDRES   0.24276 MHz
AQ       1.181466 sec
RG        201.48
AQ       0.000000 sec
PC        4.00 sec
DE        0.000000 sec
SOL      0.0000000 sec
DIL      0.0000000 sec
DSO      1

===== CHANNEL f1 =====
NUC1     13C
P1       13.00
PC1      0.0000000 sec
RG1      41.0000000 MHz

===== CHANNEL f2 =====
NUC2     13C
P2       13.00
PC2      0.0000000 sec
RG2      41.0000000 MHz

===== CHANNEL f3 =====
NUC3     13C
P3       13.00
PC3      0.0000000 sec
RG3      41.0000000 MHz

===== CHANNEL f4 =====
NUC4     13C
P4       13.00
PC4      0.0000000 sec
RG4      41.0000000 MHz

===== CHANNEL f5 =====
NUC5     13C
P5       13.00
PC5      0.0000000 sec
RG5      41.0000000 MHz

===== CHANNEL f6 =====
NUC6     13C
P6       13.00
PC6      0.0000000 sec
RG6      41.0000000 MHz

===== CHANNEL f7 =====
NUC7     13C
P7       13.00
PC7      0.0000000 sec
RG7      41.0000000 MHz

===== CHANNEL f8 =====
NUC8     13C
P8       13.00
PC8      0.0000000 sec
RG8      41.0000000 MHz

===== CHANNEL f9 =====
NUC9     13C
P9       13.00
PC9      0.0000000 sec
RG9      41.0000000 MHz

===== CHANNEL f10 =====
NUC10    13C
P10      13.00
PC10     0.0000000 sec
RG10     41.0000000 MHz

===== CHANNEL f11 =====
NUC11    13C
P11      13.00
PC11     0.0000000 sec
RG11     41.0000000 MHz

===== CHANNEL f12 =====
NUC12    13C
P12      13.00
PC12     0.0000000 sec
RG12     41.0000000 MHz

===== CHANNEL f13 =====
NUC13    13C
P13      13.00
PC13     0.0000000 sec
RG13     41.0000000 MHz

===== CHANNEL f14 =====
NUC14    13C
P14      13.00
PC14     0.0000000 sec
RG14     41.0000000 MHz

===== CHANNEL f15 =====
NUC15    13C
P15      13.00
PC15     0.0000000 sec
RG15     41.0000000 MHz

===== CHANNEL f16 =====
NUC16    13C
P16      13.00
PC16     0.0000000 sec
RG16     41.0000000 MHz

===== CHANNEL f17 =====
NUC17    13C
P17      13.00
PC17     0.0000000 sec
RG17     41.0000000 MHz

===== CHANNEL f18 =====
NUC18    13C
P18      13.00
PC18     0.0000000 sec
RG18     41.0000000 MHz

===== CHANNEL f19 =====
NUC19    13C
P19      13.00
PC19     0.0000000 sec
RG19     41.0000000 MHz

===== CHANNEL f20 =====
NUC20    13C
P20      13.00
PC20     0.0000000 sec
RG20     41.0000000 MHz

===== CHANNEL f21 =====
NUC21    13C
P21      13.00
PC21     0.0000000 sec
RG21     41.0000000 MHz

===== CHANNEL f22 =====
NUC22    13C
P22      13.00
PC22     0.0000000 sec
RG22     41.0000000 MHz

===== CHANNEL f23 =====
NUC23    13C
P23      13.00
PC23     0.0000000 sec
RG23     41.0000000 MHz

===== CHANNEL f24 =====
NUC24    13C
P24      13.00
PC24     0.0000000 sec
RG24     41.0000000 MHz

===== CHANNEL f25 =====
NUC25    13C
P25      13.00
PC25     0.0000000 sec
RG25     41.0000000 MHz

===== CHANNEL f26 =====
NUC26    13C
P26      13.00
PC26     0.0000000 sec
RG26     41.0000000 MHz

===== CHANNEL f27 =====
NUC27    13C
P27      13.00
PC27     0.0000000 sec
RG27     41.0000000 MHz

===== CHANNEL f28 =====
NUC28    13C
P28      13.00
PC28     0.0000000 sec
RG28     41.0000000 MHz

===== CHANNEL f29 =====
NUC29    13C
P29      13.00
PC29     0.0000000 sec
RG29     41.0000000 MHz

===== CHANNEL f30 =====
NUC30    13C
P30      13.00
PC30     0.0000000 sec
RG30     41.0000000 MHz

===== CHANNEL f31 =====
NUC31    13C
P31      13.00
PC31     0.0000000 sec
RG31     41.0000000 MHz

===== CHANNEL f32 =====
NUC32    13C
P32      13.00
PC32     0.0000000 sec
RG32     41.0000000 MHz

===== CHANNEL f33 =====
NUC33    13C
P33      13.00
PC33     0.0000000 sec
RG33     41.0000000 MHz

===== CHANNEL f34 =====
NUC34    13C
P34      13.00
PC34     0.0000000 sec
RG34     41.0000000 MHz

===== CHANNEL f35 =====
NUC35    13C
P35      13.00
PC35     0.0000000 sec
RG35     41.0000000 MHz

===== CHANNEL f36 =====
NUC36    13C
P36      13.00
PC36     0.0000000 sec
RG36     41.0000000 MHz

===== CHANNEL f37 =====
NUC37    13C
P37      13.00
PC37     0.0000000 sec
RG37     41.0000000 MHz

===== CHANNEL f38 =====
NUC38    13C
P38      13.00
PC38     0.0000000 sec
RG38     41.0000000 MHz

===== CHANNEL f39 =====
NUC39    13C
P39      13.00
PC39     0.0000000 sec
RG39     41.0000000 MHz

===== CHANNEL f40 =====
NUC40    13C
P40      13.00
PC40     0.0000000 sec
RG40     41.0000000 MHz

===== CHANNEL f41 =====
NUC41    13C
P41      13.00
PC41     0.0000000 sec
RG41     41.0000000 MHz

===== CHANNEL f42 =====
NUC42    13C
P42      13.00
PC42     0.0000000 sec
RG42     41.0000000 MHz

===== CHANNEL f43 =====
NUC43    13C
P43      13.00
PC43     0.0000000 sec
RG43     41.0000000 MHz

===== CHANNEL f44 =====
NUC44    13C
P44      13.00
PC44     0.0000000 sec
RG44     41.0000000 MHz

===== CHANNEL f45 =====
NUC45    13C
P45      13.00
PC45     0.0000000 sec
RG45     41.0000000 MHz

===== CHANNEL f46 =====
NUC46    13C
P46      13.00
PC46     0.0000000 sec
RG46     41.0000000 MHz

===== CHANNEL f47 =====
NUC47    13C
P47      13.00
PC47     0.0000000 sec
RG47     41.0000000 MHz

===== CHANNEL f48 =====
NUC48    13C
P48      13.00
PC48     0.0000000 sec
RG48     41.0000000 MHz

===== CHANNEL f49 =====
NUC49    13C
P49      13.00
PC49     0.0000000 sec
RG49     41.0000000 MHz

===== CHANNEL f50 =====
NUC50    13C
P50      13.00
PC50     0.0000000 sec
RG50     41.0000000 MHz

===== CHANNEL f51 =====
NUC51    13C
P51      13.00
PC51     0.0000000 sec
RG51     41.0000000 MHz

===== CHANNEL f52 =====
NUC52    13C
P52      13.00
PC52     0.0000000 sec
RG52     41.0000000 MHz

===== CHANNEL f53 =====
NUC53    13C
P53      13.00
PC53     0.0000000 sec
RG53     41.0000000 MHz

===== CHANNEL f54 =====
NUC54    13C
P54      13.00
PC54     0.0000000 sec
RG54     41.0000000 MHz

===== CHANNEL f55 =====
NUC55    13C
P55      13.00
PC55     0.0000000 sec
RG55     41.0000000 MHz

===== CHANNEL f56 =====
NUC56    13C
P56      13.00
PC56     0.0000000 sec
RG56     41.0000000 MHz

===== CHANNEL f57 =====
NUC57    13C
P57      13.00
PC57     0.0000000 sec
RG57     41.0000000 MHz

===== CHANNEL f58 =====
NUC58    13C
P58      13.00
PC58     0.0000000 sec
RG58     41.0000000 MHz

===== CHANNEL f59 =====
NUC59    13C
P59      13.00
PC59     0.0000000 sec
RG59     41.0000000 MHz

===== CHANNEL f60 =====
NUC60    13C
P60      13.00
PC60     0.0000000 sec
RG60     41.0000000 MHz

===== CHANNEL f61 =====
NUC61    13C
P61      13.00
PC61     0.0000000 sec
RG61     41.0000000 MHz

===== CHANNEL f62 =====
NUC62    13C
P62      13.00
PC62     0.0000000 sec
RG62     41.0000000 MHz

===== CHANNEL f63 =====
NUC63    13C
P63      13.00
PC63     0.0000000 sec
RG63     41.0000000 MHz

===== CHANNEL f64 =====
NUC64    13C
P64      13.00
PC64     0.0000000 sec
RG64     41.0000000 MHz

===== CHANNEL f65 =====
NUC65    13C
P65      13.00
PC65     0.0000000 sec
RG65     41.0000000 MHz

===== CHANNEL f66 =====
NUC66    13C
P66      13.00
PC66     0.0000000 sec
RG66     41.0000000 MHz

===== CHANNEL f67 =====
NUC67    13C
P67      13.00
PC67     0.0000000 sec
RG67     41.0000000 MHz

===== CHANNEL f68 =====
NUC68    13C
P68      13.00
PC68     0.0000000 sec
RG68     41.0000000 MHz

===== CHANNEL f69 =====
NUC69    13C
P69      13.00
PC69     0.0000000 sec
RG69     41.0000000 MHz

===== CHANNEL f70 =====
NUC70    13C
P70      13.00
PC70     0.0000000 sec
RG70     41.0000000 MHz

===== CHANNEL f71 =====
NUC71    13C
P71      13.00
PC71     0.0000000 sec
RG71     41.0000000 MHz

===== CHANNEL f72 =====
NUC72    13C
P72      13.00
PC72     0.0000000 sec
RG72     41.0000000 MHz

===== CHANNEL f73 =====
NUC73    13C
P73      13.00
PC73     0.0000000 sec
RG73     41.0000000 MHz

===== CHANNEL f74 =====
NUC74    13C
P74      13.00
PC74     0.0000000 sec
RG74     41.0000000 MHz

===== CHANNEL f75 =====
NUC75    13C
P75      13.00
PC75     0.0000000 sec
RG75     41.0000000 MHz

===== CHANNEL f76 =====
NUC76    13C
P76      13.00
PC76     0.0000000 sec
RG76     41.0000000 MHz

===== CHANNEL f77 =====
NUC77    13C
P77      13.00
PC77     0.0000000 sec
RG77     41.0000000 MHz

===== CHANNEL f78 =====
NUC78    13C
P78      13.00
PC78     0.0000000 sec
RG78     41.0000000 MHz

===== CHANNEL f79 =====
NUC79    13C
P79      13.00
PC79     0.0000000 sec
RG79     41.0000000 MHz

===== CHANNEL f80 =====
NUC80    13C
P80      13.00
PC80     0.0000000 sec
RG80     41.0000000 MHz

===== CHANNEL f81 =====
NUC81    13C
P81      13.00
PC81     0.0000000 sec
RG81     41.0000000 MHz

===== CHANNEL f82 =====
NUC82    13C
P82      13.00
PC82     0.0000000 sec
RG82     41.0000000 MHz

===== CHANNEL f83 =====
NUC83    13C
P83      13.00
PC83     0.0000000 sec
RG83     41.0000000 MHz

===== CHANNEL f84 =====
NUC84    13C
P84      13.00
PC84     0.0000000 sec
RG84     41.0000000 MHz

===== CHANNEL f85 =====
NUC85    13C
P85      13.00
PC85     0.0000000 sec
RG85     41.0000000 MHz

===== CHANNEL f86 =====
NUC86    13C
P86      13.00
PC86     0.0000000 sec
RG86     41.0000000 MHz

===== CHANNEL f87 =====
NUC87    13C
P87      13.00
PC87     0.0000000 sec
RG87     41.0000000 MHz

===== CHANNEL f88 =====
NUC88    13C
P88      13.00
PC88     0.0000000 sec
RG88     41.0000000 MHz

===== CHANNEL f89 =====
NUC89    13C
P89      13.00
PC89     0.0000000 sec
RG89     41.0000000 MHz

===== CHANNEL f90 =====
NUC90    13C
P90      13.00
PC90     0.0000000 sec
RG90     41.0000000 MHz

===== CHANNEL f91 =====
NUC91    13C
P91      13.00
PC91     0.0000000 sec
RG91     41.0000000 MHz

===== CHANNEL f92 =====
NUC92    13C
P92      13.00
PC92     0.0000000 sec
RG92     41.0000000 MHz

===== CHANNEL f93 =====
NUC93    13C
P93      13.00
PC93     0.0000000 sec
RG93     41.0000000 MHz

===== CHANNEL f94 =====
NUC94    13C
P94      13.00
PC94     0.0000000 sec
RG94     41.0000000 MHz

===== CHANNEL f95 =====
NUC95    13C
P95      13.00
PC95     0.0000000 sec
RG95     41.0000000 MHz

===== CHANNEL f96 =====
NUC96    13C
P96      13.00
PC96     0.0000000 sec
RG96     41.0000000 MHz

===== CHANNEL f97 =====
NUC97    13C
P97      13.00
PC97     0.0000000 sec
RG97     41.0000000 MHz

===== CHANNEL f98 =====
NUC98    13C
P98      13.00
PC98     0.0000000 sec
RG98     41.0000000 MHz

===== CHANNEL f99 =====
NUC99    13C
P99      13.00
PC99     0.0000000 sec
RG99     41.0000000 MHz

===== CHANNEL f100 =====
NUC100   13C
P100     13.00
PC100    0.0000000 sec
RG100    41.0000000 MHz

```

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

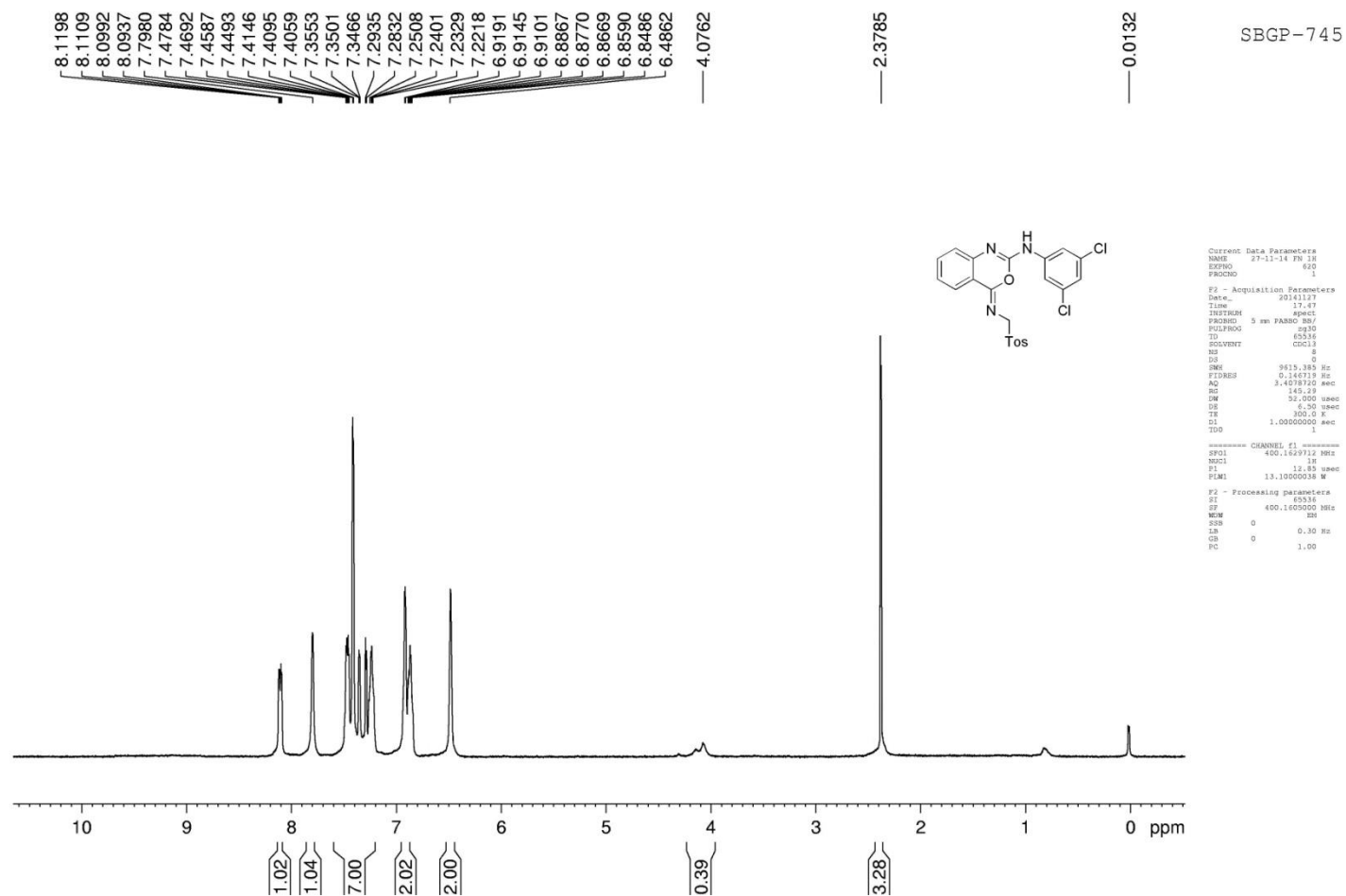
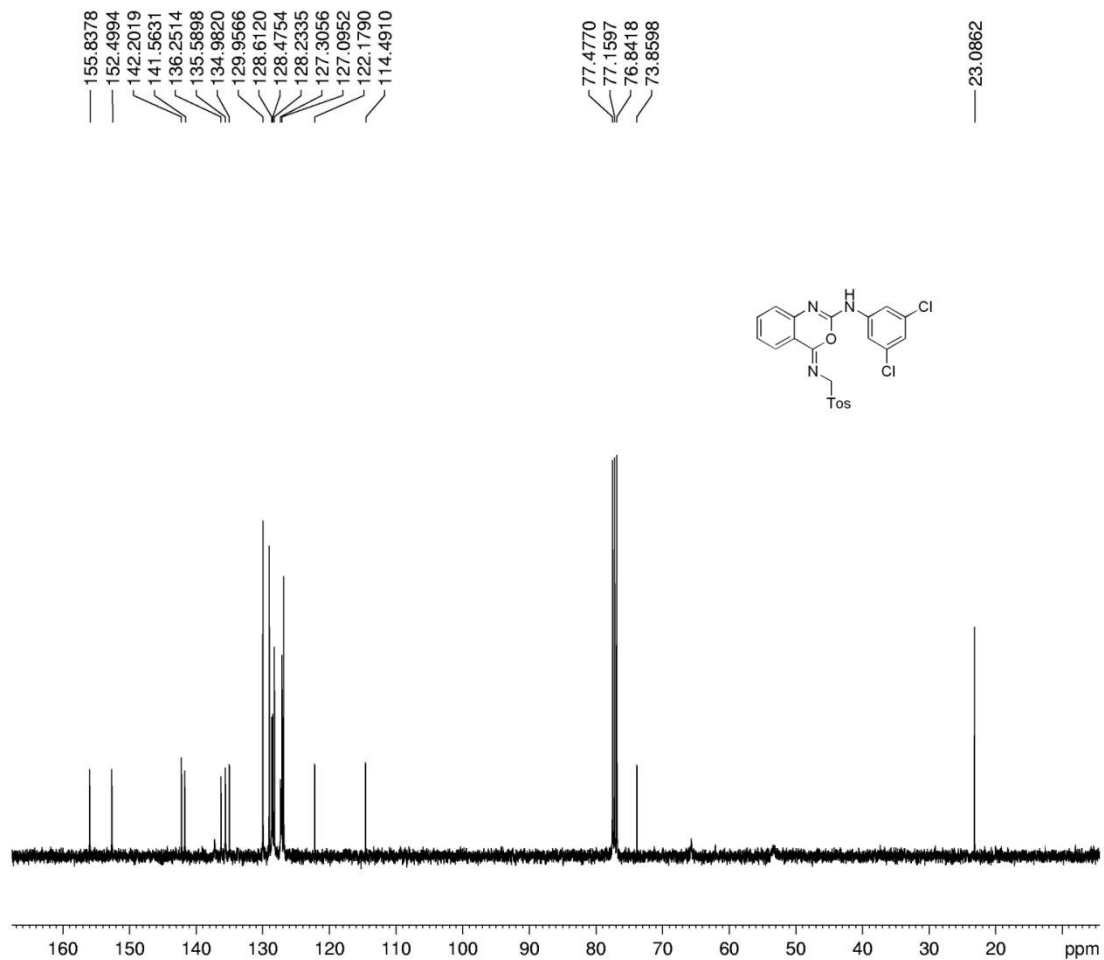


Fig: S-39 ^1H spectrum of *N*-(3,5-Dichlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3fC**)



```

Current Data Parameters
NAME      13-10-14 013
EXPNO    400
PROCNO    1
F2 - Acquisition Parameters
Date_     20141024
Time      13:21
INSTRUM   spect
PROBHD    5 mm PABBO MMJ
PULPROG   zgpg30
SOLVENT   CDCl3
AQ        0.25000000
RG         512
SI         2048
SF         201.26100000
FIDRES    0.26670000
AQ        1.98100000
RG         501.480
SR         39.80000000
SE         4.00000000
SF         385.00000000
SI         2.00000000
SOLVENT   CDCl3
===== CHANNEL f1 =====
NUC1      13C
P1        150
PC1       8.00000000
===== CHANNEL f2 =====
SFOC      400.14210000 MHz
NUC2      13C
P2        150
PC2       8.00000000
===== CHANNEL f3 =====
COPROG13  waltz16
PROBHD    5 mm
PULPROG   zgpg30
SOLVENT   CDCl3
PC1       13.10000000
PC2       13.10000000
PC3       0.28700000
PC4       0.21830000
F2 - Processing parameters
SI         2048
SF         100.62042000 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
MC         0.40
  
```

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

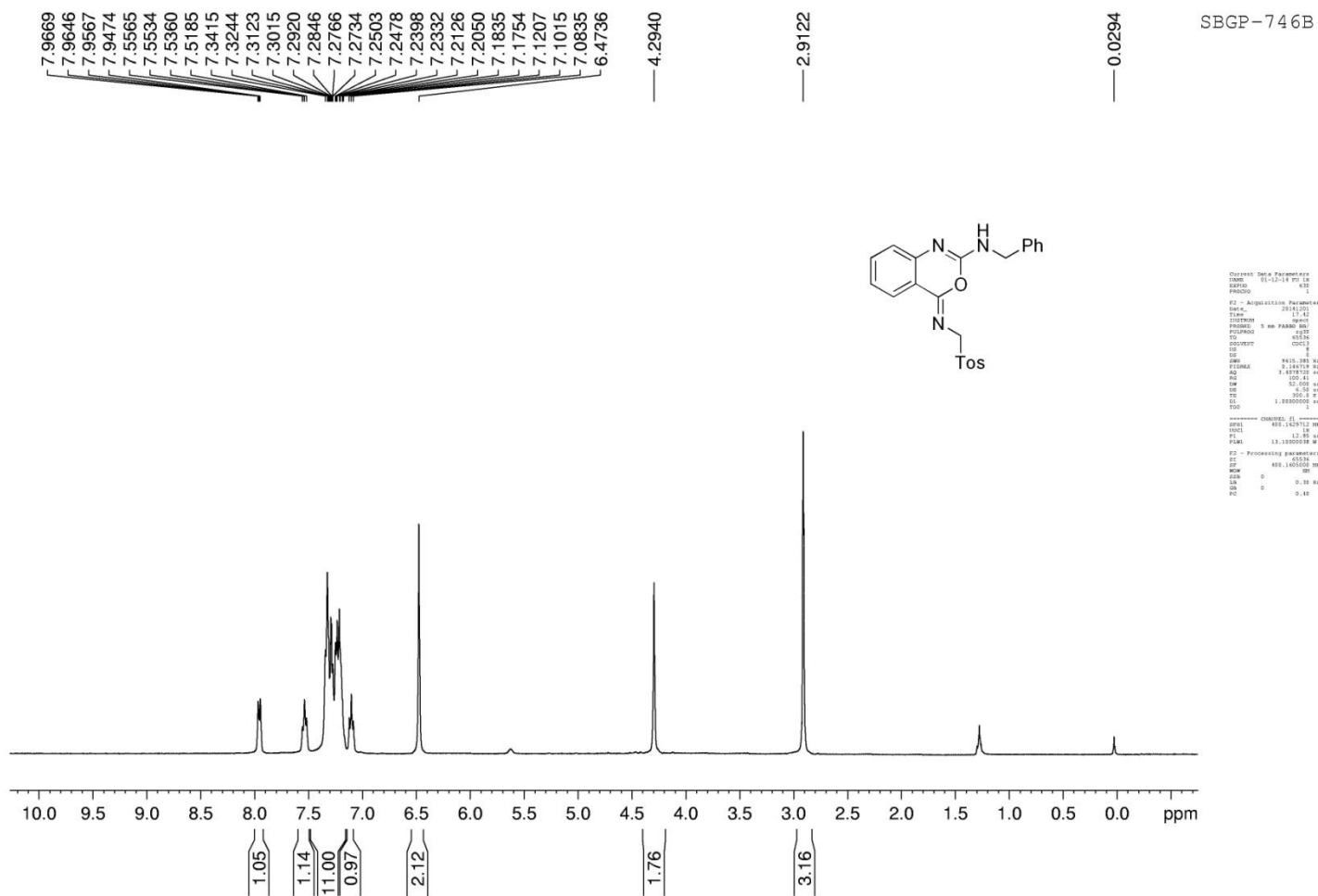
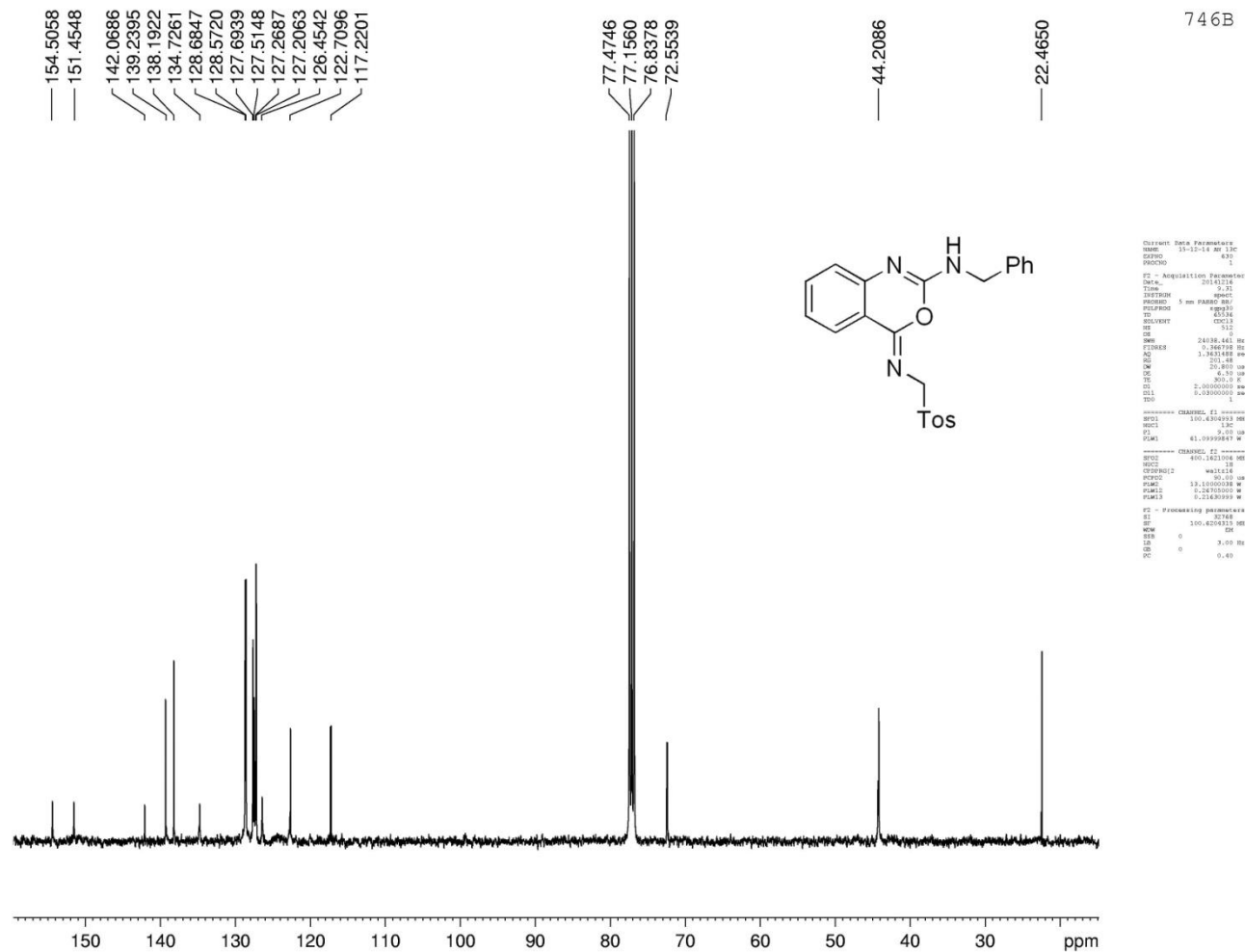


Fig. S-41 ¹H spectrum of *N*-benzyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3hC**)



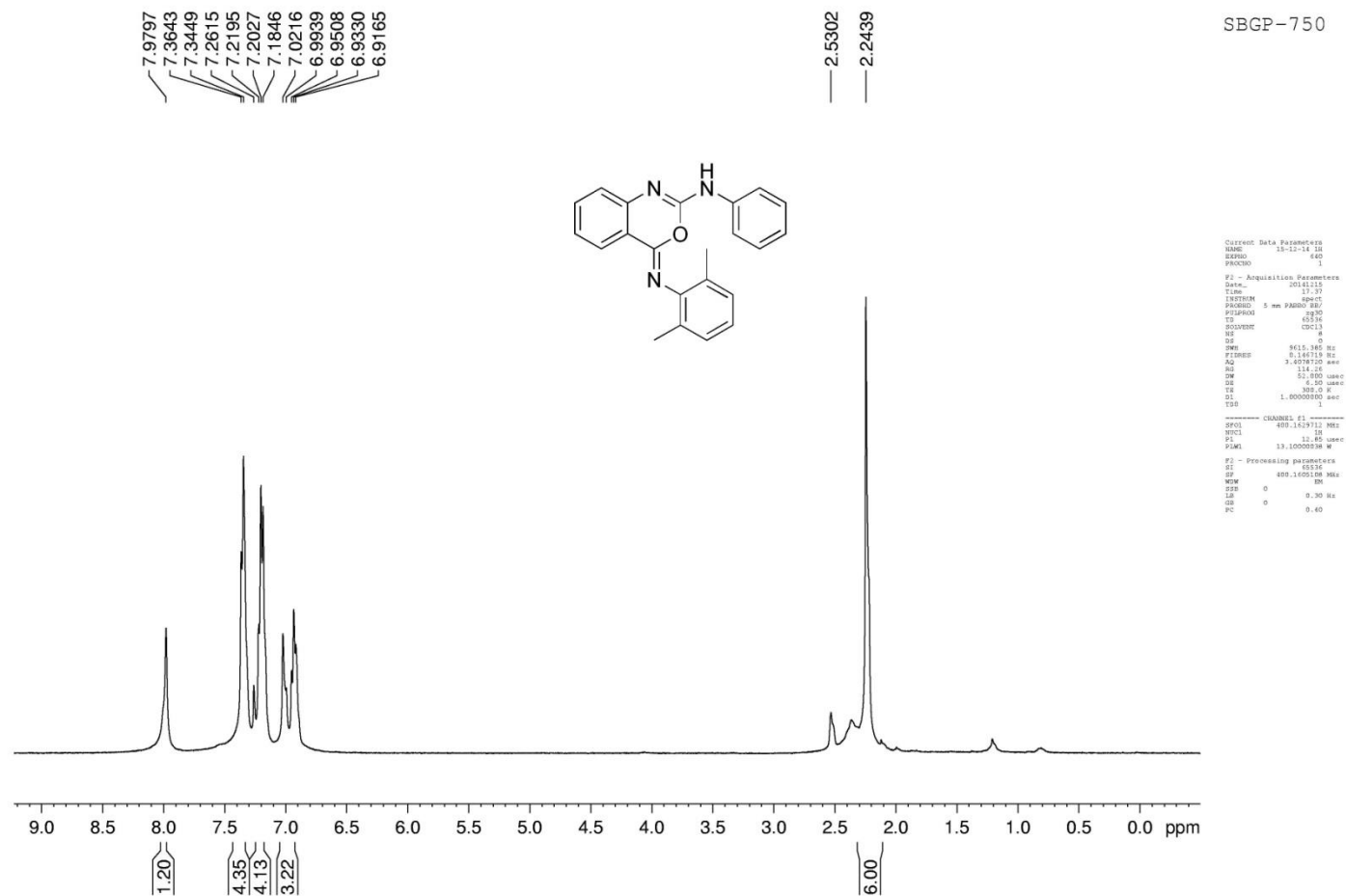


Fig: S-43 ^1H spectrum of (2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3aD**)

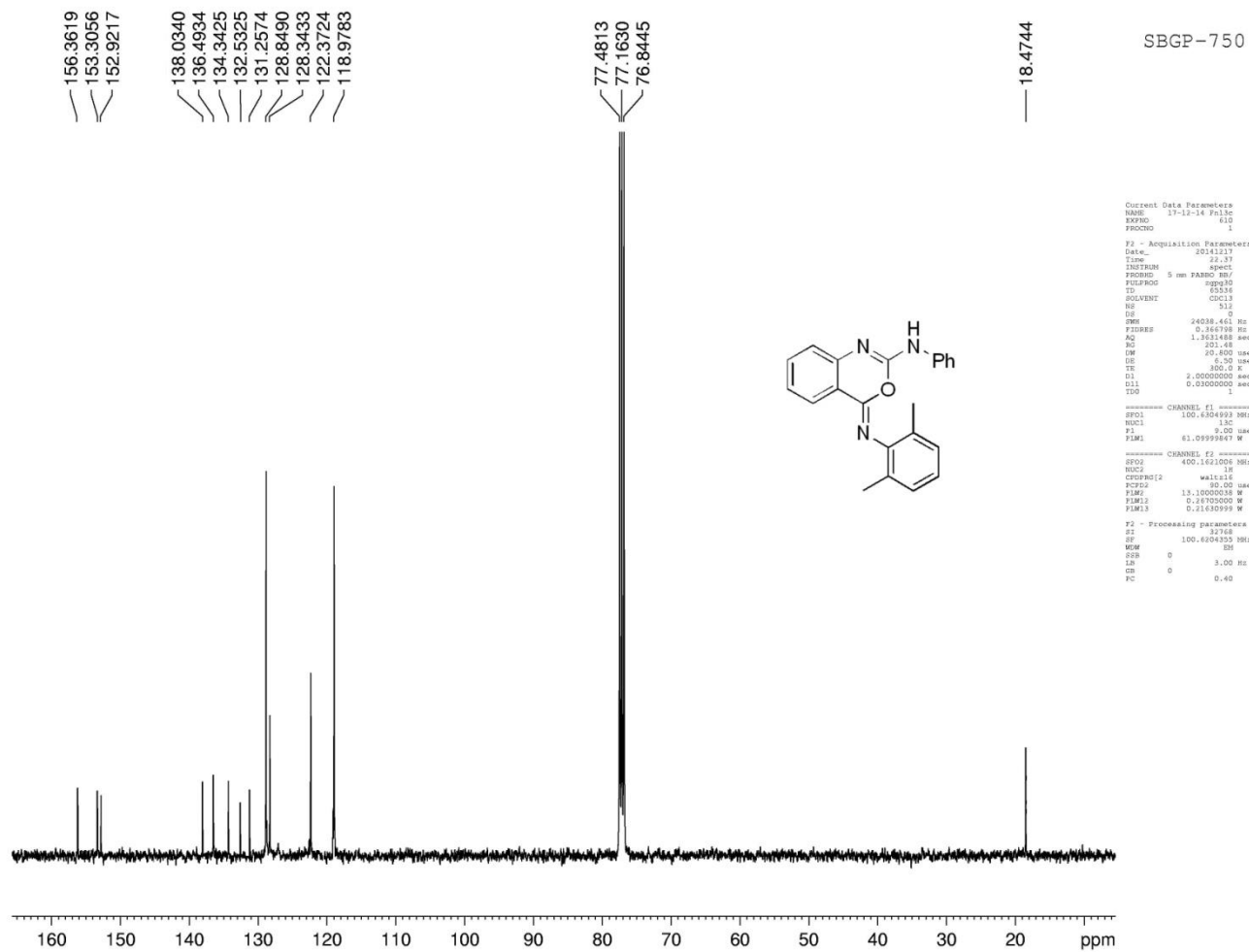


Fig: S-44 ^{13}C spectrum of 4-(2, 6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3aD**)

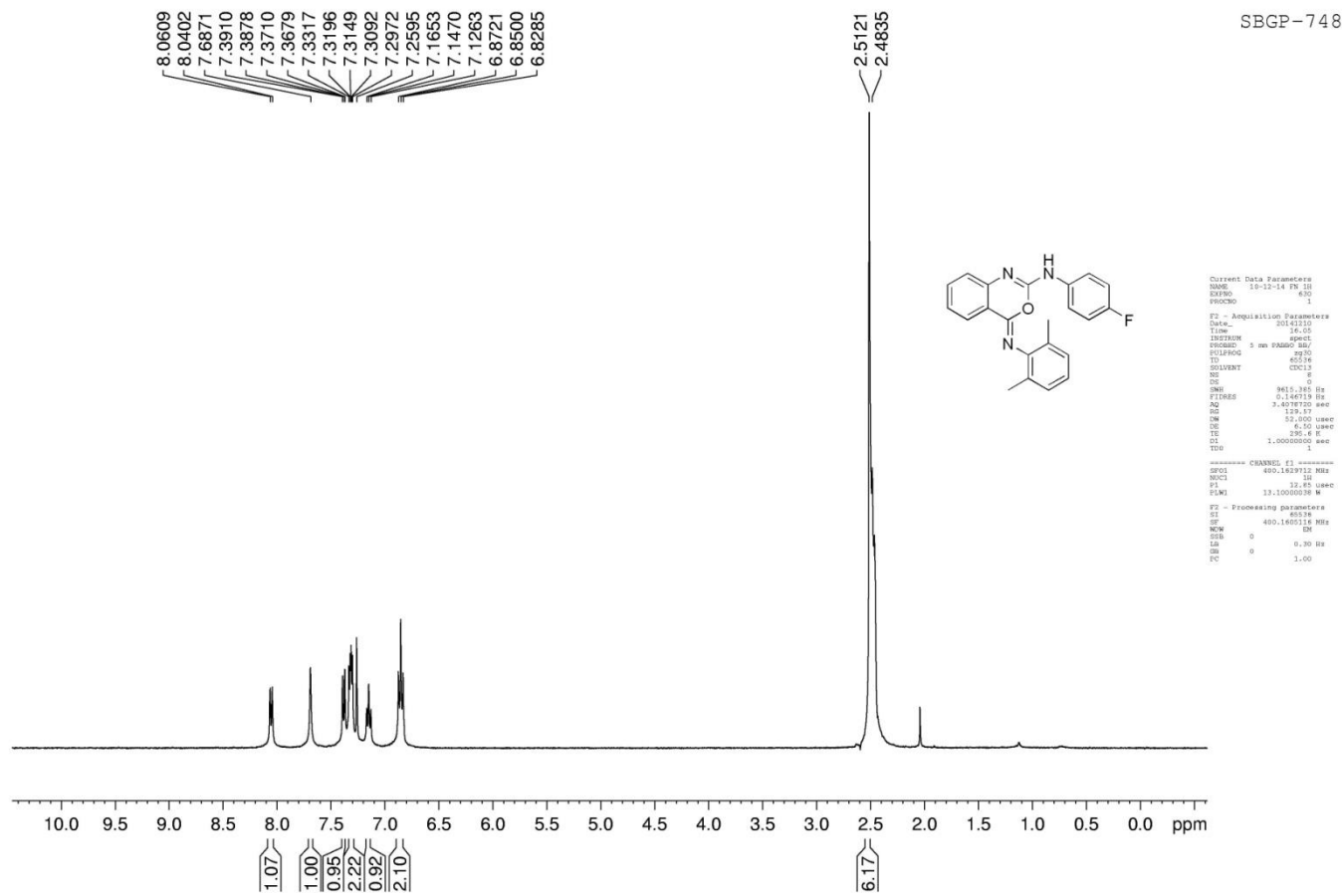


Fig: S-45 ^1H spectrum of 4-(2, 6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**3cD**)

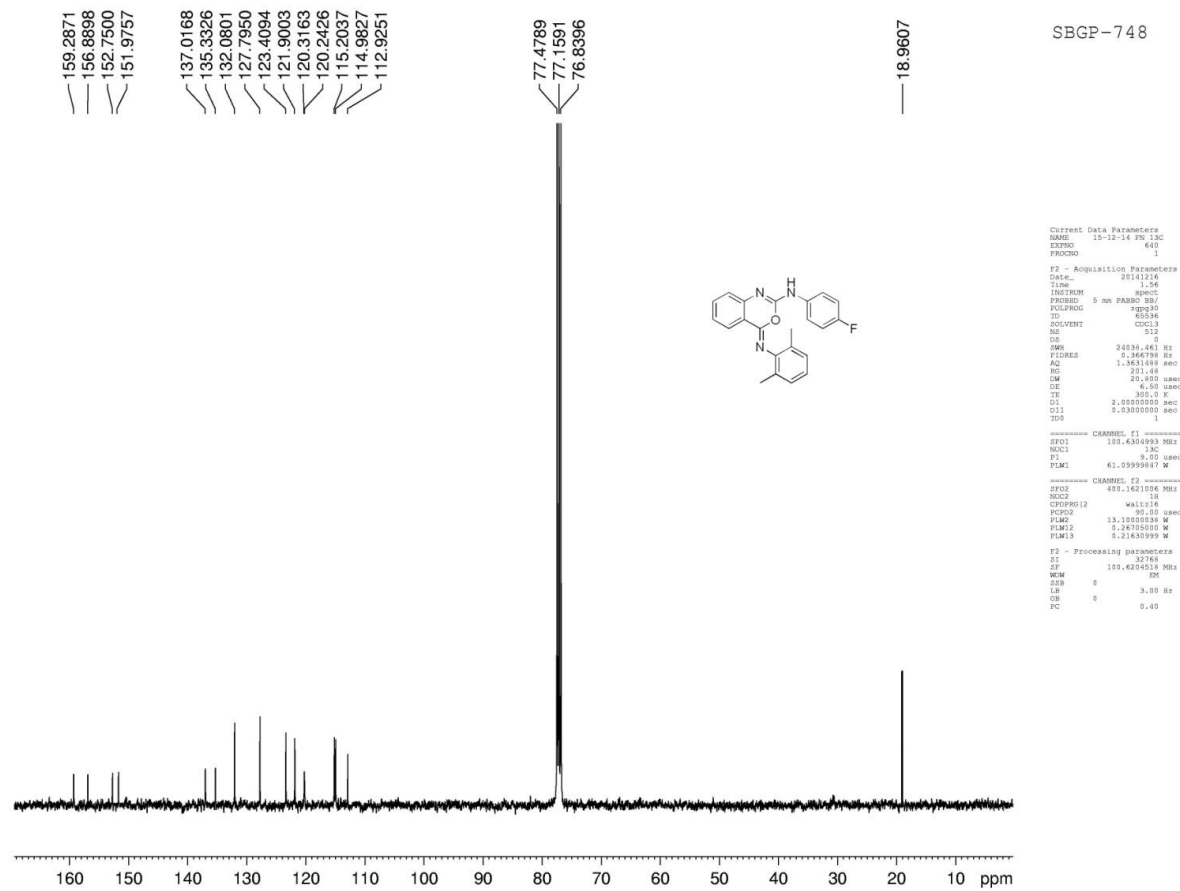


Fig. S-46 ¹³C spectrum of 4-(2,6-Dimethylphenylimino)-N-phenyl-4H-benzo[d][1,3]oxazin-2-amine (3cD)

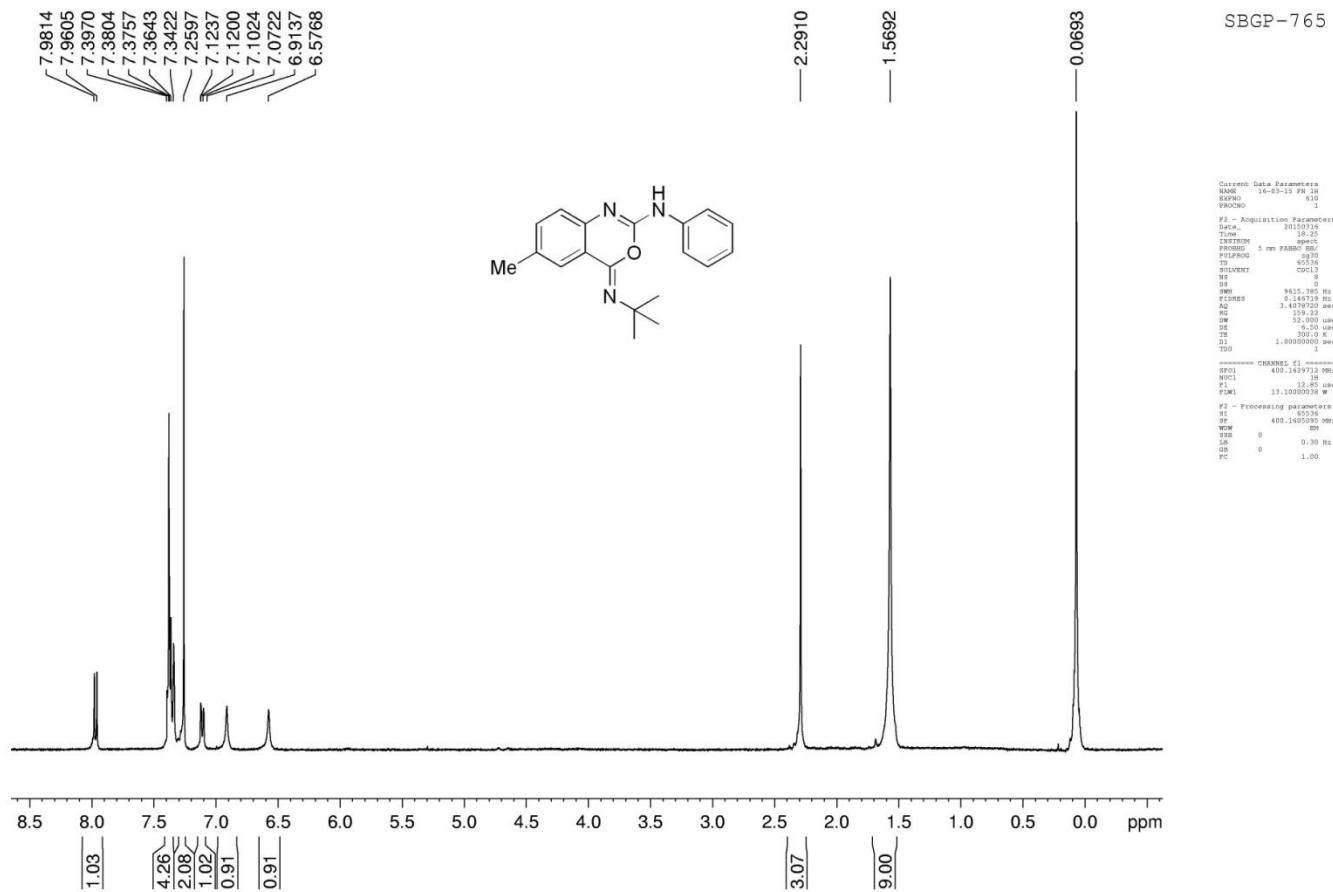


Fig: S-47 ^1H spectrum of 4-(*tert*-butylimino)-6-methyl-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**7**)

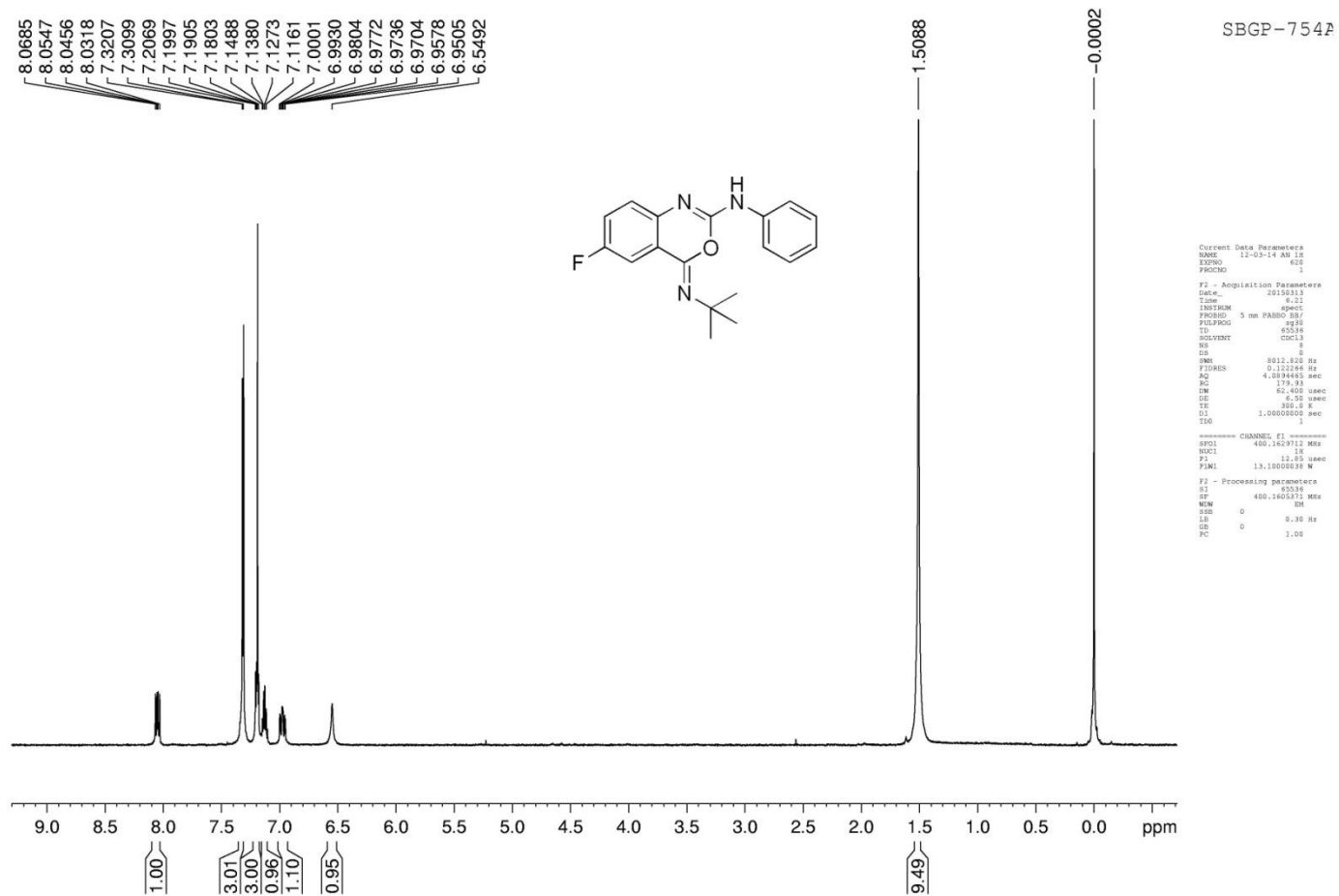


Fig: S-49 ^1H spectrum of 4-(*tert*-butylimino)-6-fluoro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**8**)

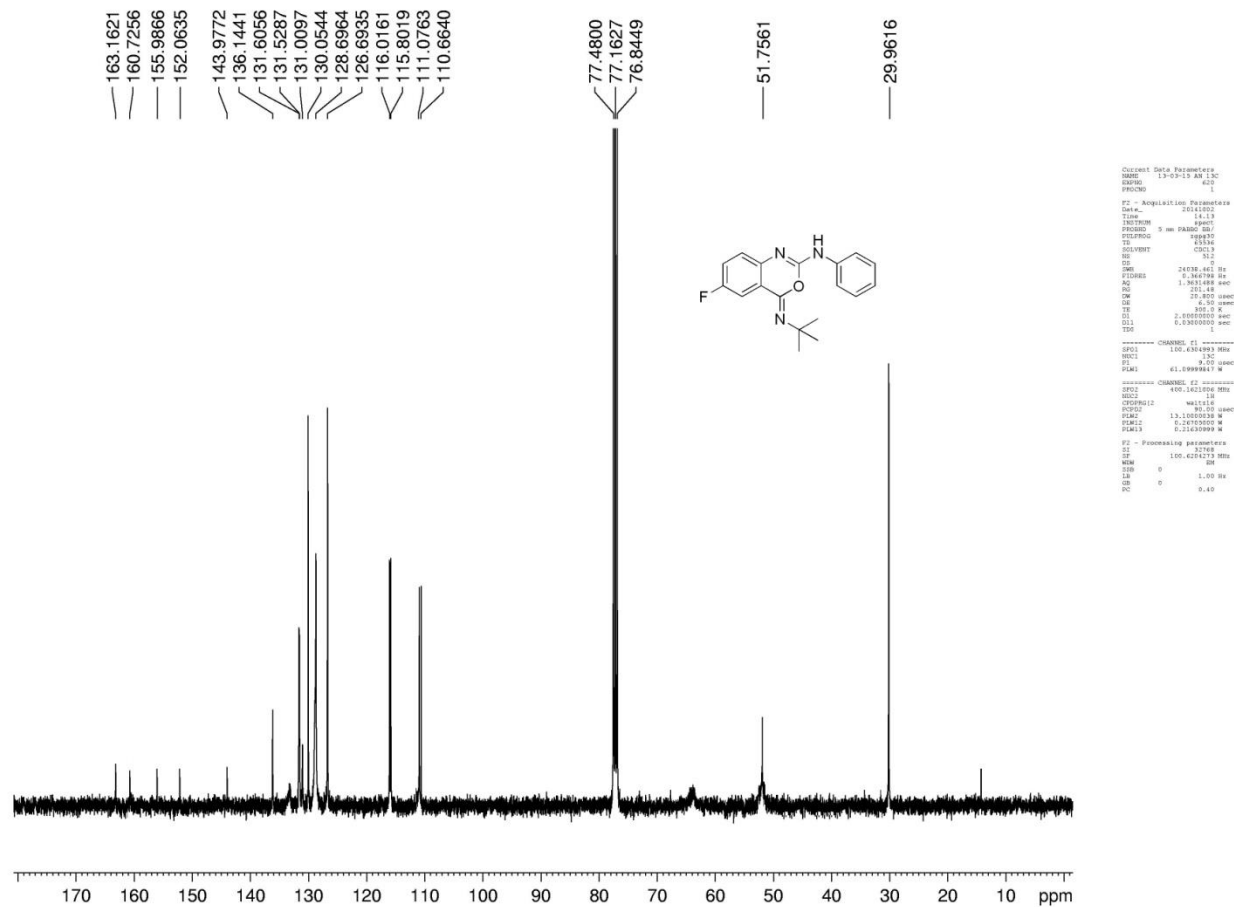


Fig: S-50 ^{13}C spectrum of 4-(*tert*-butylimino)-6-fluoro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (**8**)

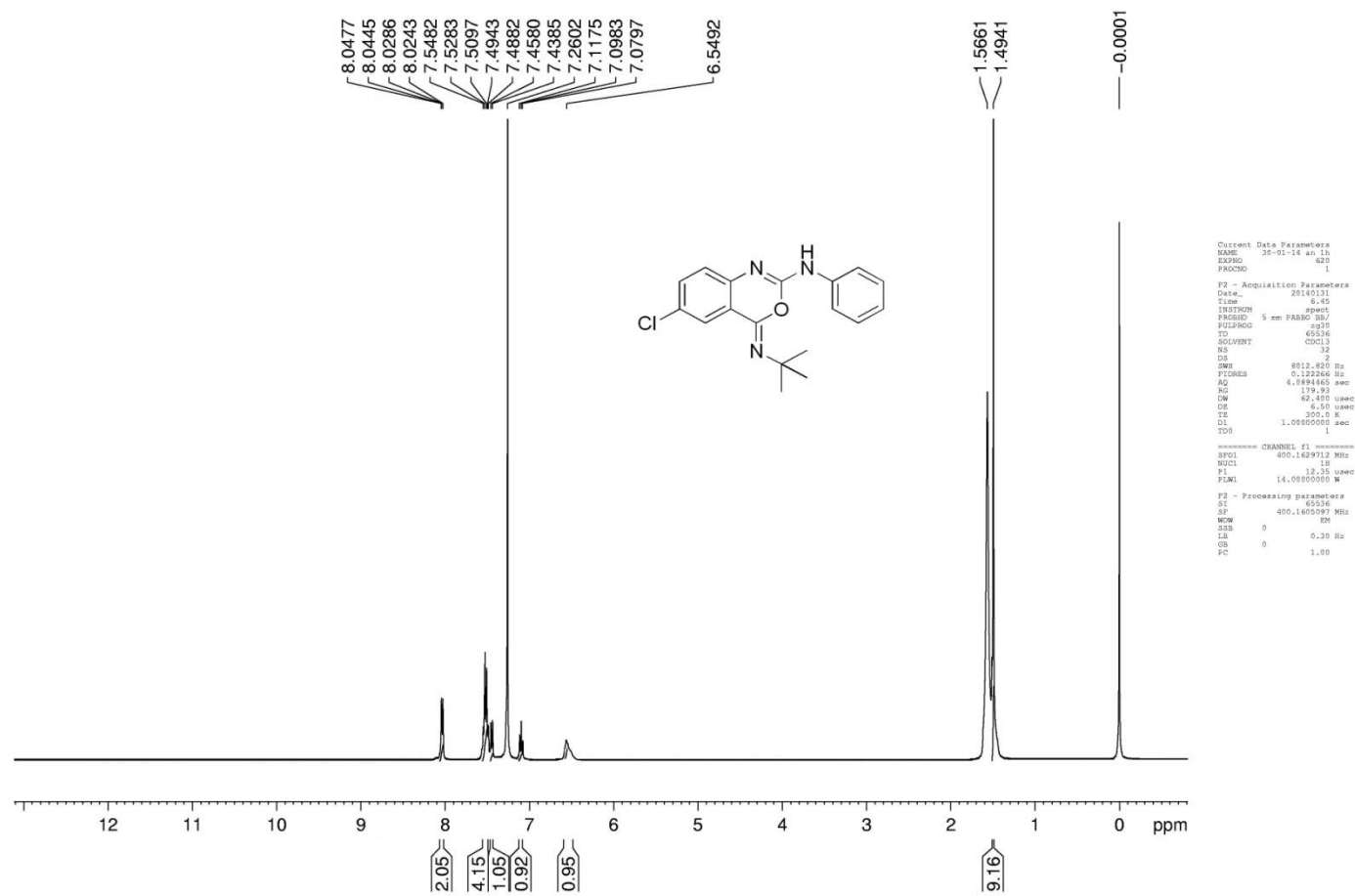
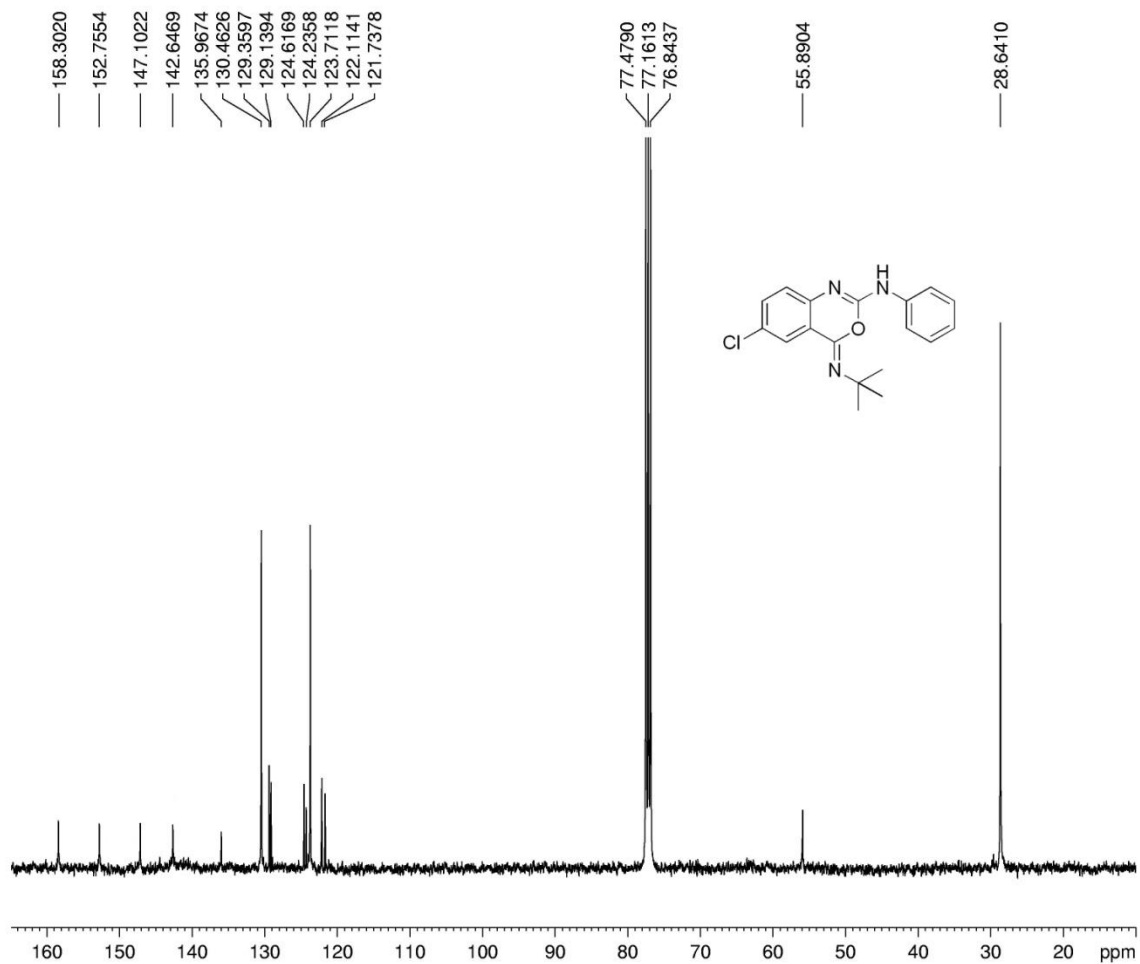


Fig: S-51 ^1H spectrum of 4-(*tert*-butylimino)-6-chloro-*N*-phenyl-4*H*-benzo[*d*][1,3]oxazin-2-amine (9)



```

Current Data Parameters
NAME  13-03-15 AM 130
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_  20121112
TIME  11.11
INSTRUM  spect
PROBHD  5 mm BBOBO HNP
PULPROG  zgpg30
AQ  0.0014
SOLVENT  DMSO
NS  640
DS  4
SWH  24232.441 Hz
F2FREQ  125.761188 MHz
AQ  1.281188 sec
RG  320.148
SQ  25.900
SFO  61.5000000 MHz
SI  0.0000000 sec
SOL  0.0000000 sec
TSD  1
===== CHANNEL f1 =====
NUC1  13C
P1  12.00
PL1  0.00000000 M
===== CHANNEL f2 =====
NUC2  1H
P2  12.00
PL2  0.00000000 M
===== CHANNEL f3 =====
NUC3  13C
P3  12.00
PL3  0.00000000 M
F2 - Processing parameters
SI  0.0000000 sec
SFO  125.761188 MHz
WDW  EM
SSB  0
GB  0
PC  0.40
  
```

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

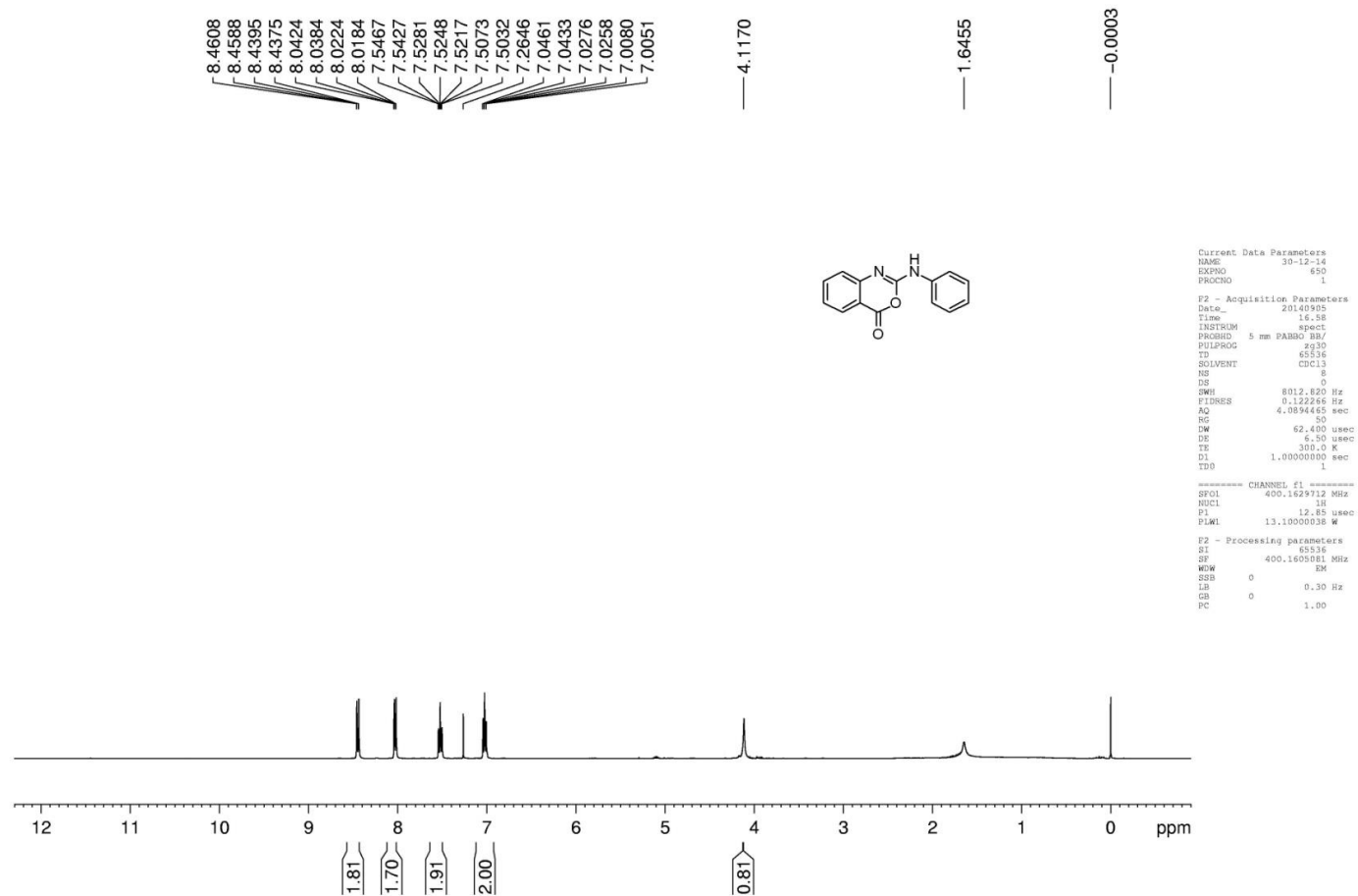
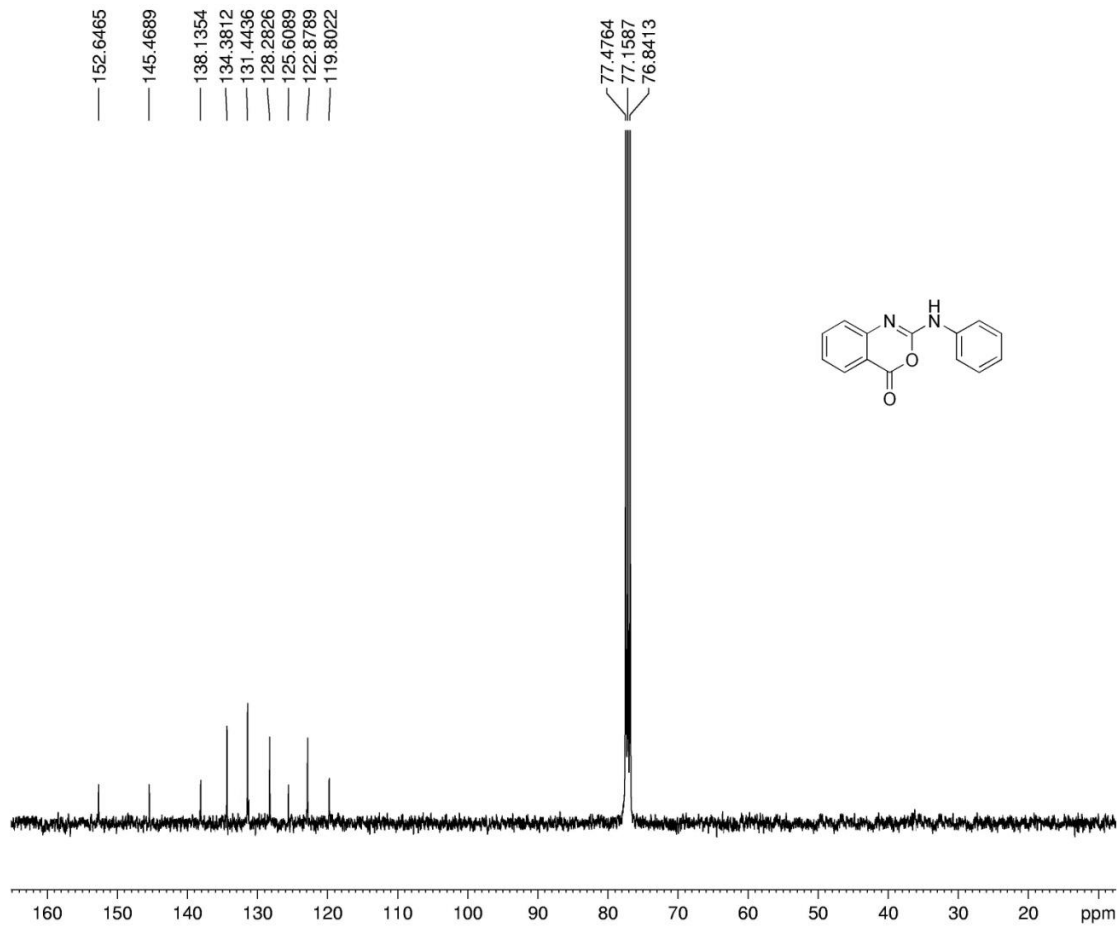


Fig: S-53 ¹H spectrum of 2-(phenylamino)-4*H*-benzo[*d*][1,3]oxazin-4-one (10)



```

Current Data Parameters
NAME 22-08-2014 fo
EXPNO 410
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140201
Time 09:24
INSTRUM spect
PROBHD 5 mm PABBO 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 24032.461 Hz
FIDRES 0.34476 Hz
AQ 1.263189 sec
RG 272.00
AQ 272.00 sec
DE 62.00 um
DQ 62.00 um
D1 3.0000000 sec
D11 0.0000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 13C
P1 0.00 usec
PL1 41.09999847 W
===== CHANNEL f2 =====
NUC2 1H
P2 0.00 usec
PL2 18.1812000 MHz
===== CHANNEL f3 =====
NUC3 1H
P3 0.00 usec
PL3 18.1812000 MHz
===== CHANNEL f4 =====
NUC4 1H
P4 0.00 usec
PL4 18.1812000 MHz
===== CHANNEL f5 =====
NUC5 1H
P5 0.00 usec
PL5 18.1812000 MHz
F2 - Processing parameters
SI 32768
SF 100.626100 MHz
WDW EM
SSB 0
GB 0
PC 1.43

```

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

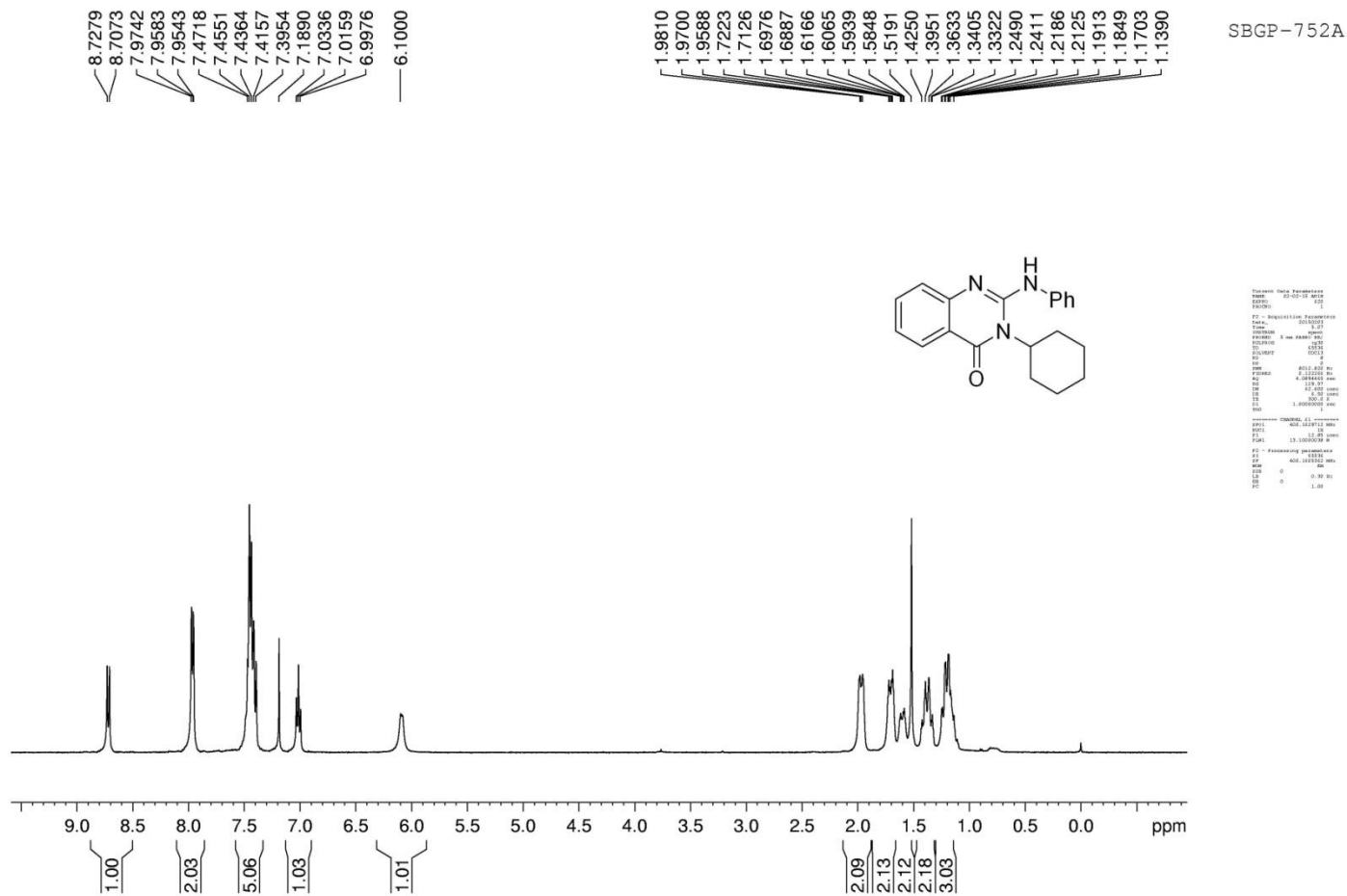


Fig: S-55 ^1H spectrum of 3-cyclohexyl-2-(phenylamino)quinazolin-4(3H)-one (**11**)

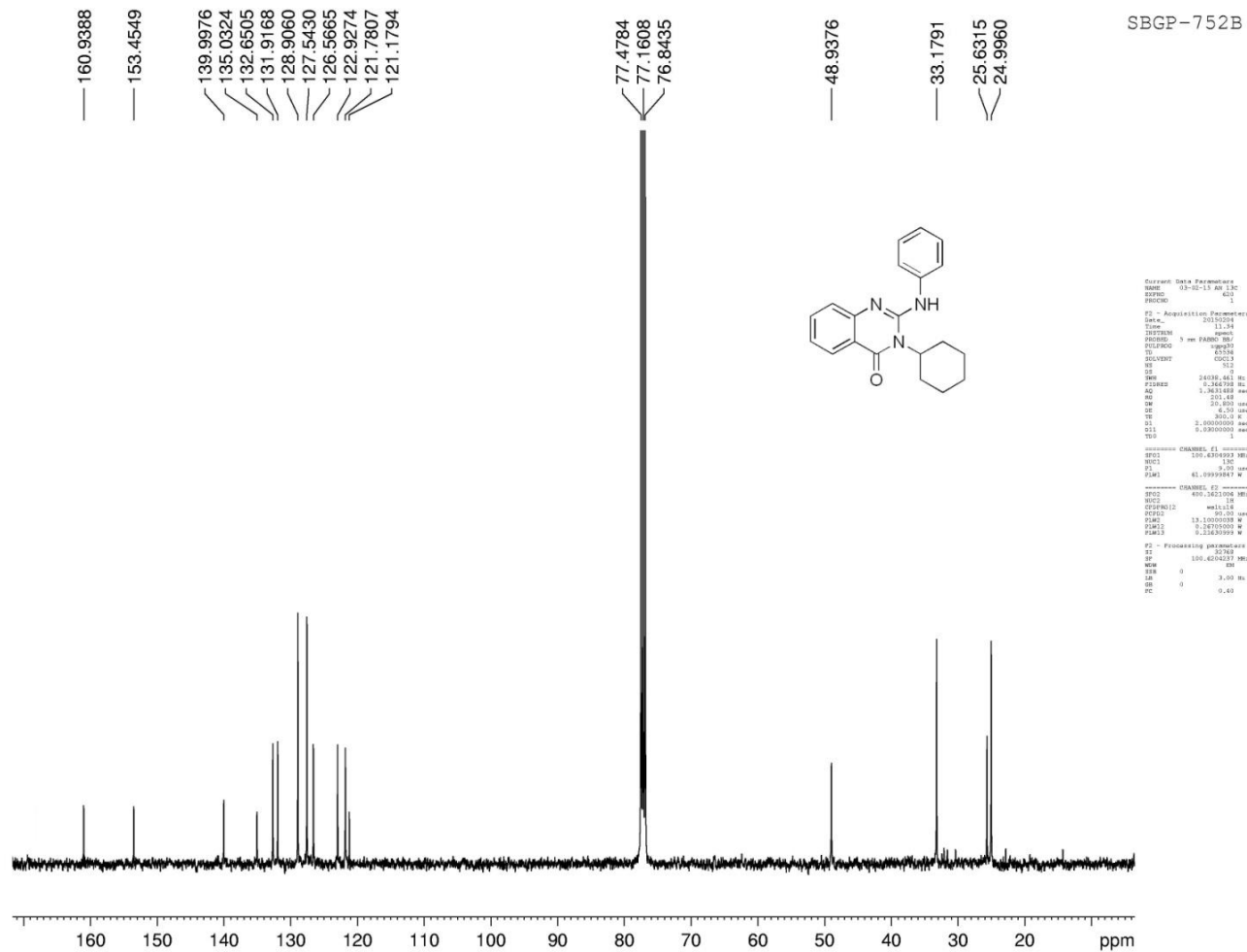


Fig: S-56 ^{13}C spectrum of 3-cyclohexyl-2-(phenylamino)quinazolin-4(3H)-one (**11**)