Electronic Supplementary Material (ESI) for RSC Advances.

Synthesis of 4-substitutedimino-4*H*-benzo[*d*][1,3]thiazin-2-amines via palladium-catalysed isocyanide insertion in 2-bromophenylthioureas

Garima Pandey,[a] Subhendu Bhowmik,[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.*

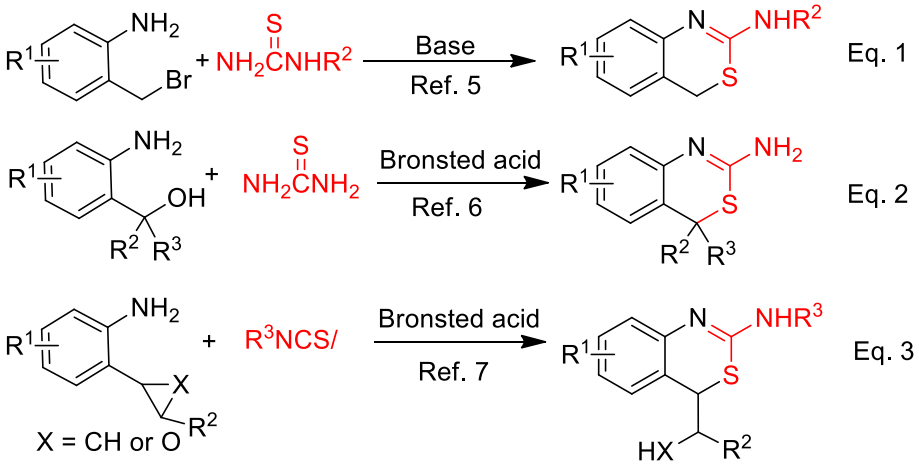
[b]*Academy of Scientific and Innovative Research, New Delhi, India*

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

Contents

Classical approaches to 4*H*-benzo[*d*][1,3]thiazin-2-amines

The classical methods to the synthesis of 4*H*-benzo[*d*][1,3]thiazin-2-amines involve the condensation of aromatic amine or thioureas bearing an *ortho* halomethyl (eq. 1), hydroxymethyl (eq. 2) or cycloalkyl or oxirane (eq. 3) with thioamides or thioureas in the presence of base or bronsted acid.

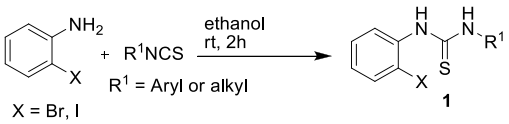


The references cited herein are ref. 5-7 in the manuscript.

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 either 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 ESI-HRMS on Agilent 6520 Q-TOF, LC-MS/MS mass spectrometer. All reagents and solvents were used as obtained commercially or dried by following standard procedure.

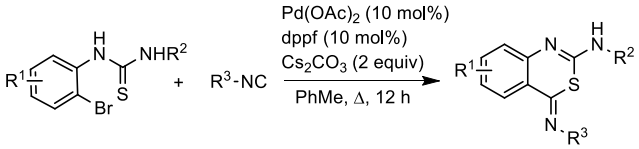
General procedure for the synthesis of 2-halophenylthioureas as exemplified for 1a



To the flask containing aryl / alkyl isothiocyanate (5 mmol) in ethanol (5 mL), 2-halo aniline (5 mmol) was added and kept for stirring at room temperature. Formed thiourea precipitated

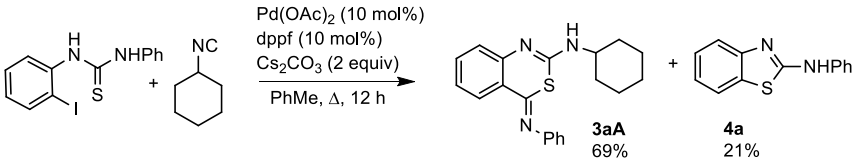
out from the reaction mixture, which was filtered, washed with hexane and dried under vaccum.[1, 2]

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

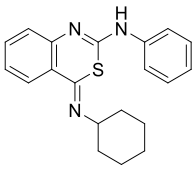


2-Bromophenylthiourea **1a** (0.25 g, 0.82 mmol), cyclohexylisocyanide **2A** (0.25 ml, 1.23 mmol), $Pd(OAc)_2$ (18.4 mg, 10 mol %), dppf (45 mg, 10 mol%) and anhydrous toluene (5.0 mL) were added to a 50 ml of reaction vial equipped with a magnetic stirring bar under nitrogen atmosphere. After 15 min of reaction time Cs_2CO_3 (0.53 g, 2.0 equiv) was added to the reaction and the mixture was heated at 110 ^oC for 12 h. After completion of the reaction as indicated by TLC, the mixture was filtered on a bed of Celite and the solvent removed under vacuo to obtain a residue which was purified via silica gel column chromatography (hexanes/ EtOAc 97/ 3, v/v) to furnish **3aA** (0.29 g, 87%) as a yellow viscous oil.

(During the optimisation studies the reaction was performed with 0.1 g of **1a** to obtain 0.09 g of **3aA** and 0.033g of **4a**)

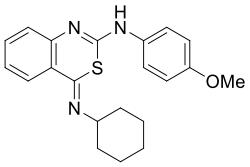


4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aA). Yield: 87% as



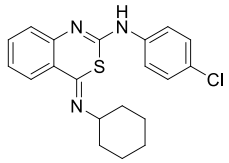
yellow oil (0.24 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1659 (C=N), 3320 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) =1.87-1.98 (m, 2H), 2.01-2.05 (m, 3H), 2.08-2.12 (m, 2H), 6.84 (s, 1H), 7.15-7.25 (m, 1H), 7.25-7.27 (m, 2H), 7.39-7.43 (m, 4H), 7.58-7.60 (m, 1H), 7.60-7.65 (m, 1H), 8.68-8.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.9, 26.6, 36.6, 62.0, 121.0, 124.2, 124.9, 126.0, 129.4, 132.6, 134.6, 141.5, 149.7, 150.6, 156.2; MS (ESI+) *m/z*= 336.0 $(M+H)^+$; ES-HRMS calcd. For $C_{20}H_{22}N_3S$ $[MH]^+$ 336.1534, Found 336.1535.

4-(Cyclohexylimino)-*N*-(3-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3bA). Yield: 86% as yellow oil (0.23 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max}



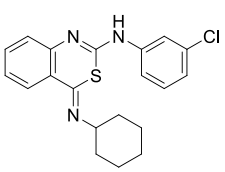
(Neat) 1626 (C=N), 3383 (NH) cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.92-2.01 (m, 6H), 2.10-2.14 (m, 4H), 2.36-2.39 (m, 1H), 3.49 (s, 3H), 4.54 (s, 1H), 7.11 (t, 1H, J = 7.1 Hz), 7.31-7.34 (m, 2H), 7.40-7.44 (m, 1H), 7.70-7.75 (m, 1H), 8.06-8.39 (m, 1H), 8.41 (d, 1H, J = 1.3 Hz), 8.72 (d, 1H, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.8, 26.1, 26.7, 33.2, 54.3, 59.9, 110.2, 116.6, 121.7, 122.9, 125.7, 125.8, 127.1, 134.4, 146.3, 149.2, 151.5, 157.9; MS (ESI+) *m/z* = 366.0 $(M+H)^+$; ES-HRMS calcd. For $C_{21}H_{24}ON_3S$ $[MH]^+$ 366.1640, Found 366.1645.

***N*-(4-chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3cA).** Yield:



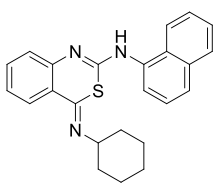
88% as yellow oil (0.24 g from 0.25 g); R_f = 0.56 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1600 (C=N), 3392 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.90-2.06 (m, 11H), 6.81 (s, 1H,), 7.25 (t, 3H, J = 7.0 Hz), 7.33-7.40 (m, 3H), 7.59 (d, 2H, J = 8.2 Hz), 8.67 (d, 2H, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 26.2, 27.1, 27.2, 27.3, 36.9, 37.4, 61.8, 122.1, 125.1, 125.9, 126.9, 129.2, 132.5, 134.6, 136.7, 143.4, 146.5, 150.1, 155.4; MS (ESI+) *m/z* = 369.9 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{21}ClN_3S$ $[MH]^+$ 370.1145, Found 370.1149.

***N*-(3-chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3dA).** Yield:



85% as yellow oil (0.23 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1600 (C=N), 3391 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.85-1.94 (m, 6H), 1.98-2.09 (m, 4H), 2.20 (d, 1H, J = 10.9 Hz), 6.84 (s, 1H), 7.13 (d, 1H, J = 7.7 Hz), 7.32 (t, 2H, J = 8.0 Hz), 7.45 (t, 2H, J = 8.6 Hz), 7.62 (t, 1H, J = 7.0 Hz), 7.80 (s, 1H), 8.68 (d, 1H, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 26.6, 27.1, 27.2, 37.0, 37.4, 61.9, 118.7, 120.8, 124.1, 125.3, 126.1, 128.9, 130.2, 131.0, 132.5, 134.7, 139.4, 143.4, 150.8, 156.1; MS (ESI+) *m/z* = 370.0 $(M+H)^+$; ES-HRMS calcd. for $C_{20}H_{21}ClN_3S$ $[MH]^+$ 370.1145, Found 370.1147.

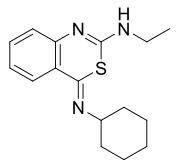
4-(Cyclohexylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3eA). Yield:



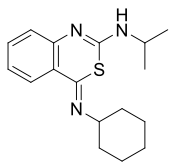
87% as yellow oil (0.23 g from 0.25 g); R_f = 0.46 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1655 (C=N), 3420 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.63-1.75 (m, 4H), 1.86 (brs, 7H), 6.59 (d, 1H, J = 8.2 Hz), 7.06 (t, 1H, J = 2.4 Hz), 7.08-7.20 (m, 1H), 7.29 (d, 1H, J = 2.4 Hz), 7.38-7.54 (m, 5H), 7.60 (d, 1H, J = 7.5 Hz), 7.90 (d, 1H, J = 8.0 Hz), 8.63 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 25.8, 26.8, 31.8, 58.3, 108.1, 116.1, 123.7, 123.9, 124.2, 124.4, 126.0, 126.4, 132.0, 132.6, 133.7, 134.0, 143.1, 149.4, 152.0, 155.7; MS

(ESI+) *m/z* = 386.0 $(M+H)^+$; ES-HRMS calcd. for $C_{24}H_{23}N_3S$ $[MH]^+$ 386.1691, Found 386.1693.

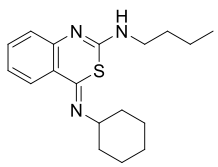
4-(Cyclohexylimino)-*N*-ethyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3fA). Yield: 77% as yellow oil (0.21 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 95:5, v/v); ν_{max} (Neat) 1640 (C=N), 3399 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.34 (t, 3H, *J* = 7.2 Hz), 1.59-1.66 (m, 2H), 1.82-1.93 (m, 2H), 1.96-2.07 (m, 7H), 3.57-3.65 (m, 2H), 4.90 (s, 1H,), 7.13-7.18 (m, 1H), 7.31-7.33 (m, 1H), 7.53-7.57 (m, 1H), 8.64-8.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 14.8, 25.8, 26.5, 30.1, 37.3, 60.9, 123.8, 125.4, 125.8, 132.8, 134.5, 149.3, 153.6, 156.6; MS (ESI+) *m/z* = 288.0 $(M+H)^+$; ES-HRMS calcd. for $C_{16}H_{22}N_3S$ $[MH]^+$ 288.1534, Found 288.1531.



4-(Cyclohexylimino)-*N*-propyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3gA). Yield: 87% as yellow oil (0.24 g from 0.25 g); R_f = 0.51 (hexane: EtOAc, 93:7, v/v); ν_{max} (Neat) 1626, 3397 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.06 (t, 3H, *J* = 14.8 Hz), 1.90 (brs, 2H), 1.93 (brs, 4H), 1.97-2.00 (m, 7H), 3.52-3.57 (m, 2H), 4.95 (brs, 1H), 7.15 (t, 1H, *J* = 7.0 Hz), 7.32 (d, 1H, *J* = 7.6 Hz), 7.52-7.57 (m, 1H), 8.64 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 11.9, 26.2, 26.5, 27.1, 27.2, 37.0, 37.4, 44.1, 60.9, 125.4, 130.0, 132.8, 134.5, 138.9, 145.1, 151.0, 156.1; MS (ESI+) *m/z* = 302.0 $(M+H)^+$; ES-HRMS calcd. for $C_{17}H_{23}N_3S$ $[MH]^+$ 302.1691, found 301.1695.



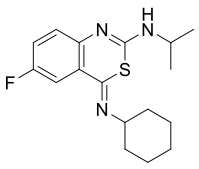
4-(Cyclohexylimino)-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3hA). Yield: 77% as yellow oil (0.21 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 93:7, v/v); ν_{max} (Neat) 1618 (C=N), 3589 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.33 (d, 6H, *J* = 6.5 Hz), 1.73-1.86 (m, 4H), 1.87-2.08 (m, 7H), 4.36-4.41 (m, 1H), 4.80 (d, 1H, *J* = 6.3 Hz,), 7.12-7.16 (m, 1H), 7.30 (t, 1H, *J* = 7.6 Hz), 7.52-7.56 (m, 1H), 8.63-8.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.8, 25.9, 26.4, 36.9, 37.4, 44.0, 60.8, 123.5, 123.6, 125.4, 125.7, 132.7, 134.4, 145.0, 148.5, 150.1, 156.9; MS (ESI+) *m/z* = 302.0 $(M+H)^+$; ES-HRMS calcd. for $C_{17}H_{24}N_3S$ $[MH]^+$ 302.1691, Found 302.1693.



***N*-butyl-4-(Cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3iA).** Yield: 77% as yellow oil (0.21 g from 0.25 g); R_f = 0.54 (hexane: EtOAc, 93:7, v/v); ν_{max} (Neat) 1655 (C=N), 3412 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.01 (t, 3H, *J* = 7.3 Hz), 1.45-1.50 (m, 2H), 1.66-1.74 (m, 2H), 1.82-

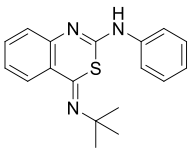
1.97 (m, 4H), 1.99-2.07 (m, 7H), 3.55-3.60 (m, 2H), 4.92 (d, 1H, *J* = 4.0 Hz,), 7.13-7.17 (m, 1H), 7.32 (d, 1H, *J* = 8.2 Hz), 7.52-7.57 (m, 1H), 8.63-8.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 13.8, 20.4, 25.7, 26.4, 31.3, 31.9, 42.0, 60.7, 123.6, 125.3, 125.6, 132.6, 134.4, 144.8, 149.3, 153.4, 155.4; MS (ESI+) *m/z* = 315.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{25}N_3S$ $[MH]^+$ 316.1847, Found 316.1849

4-(Cyclohexylimino)-6-fluoro-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (**3jA).** Yield:



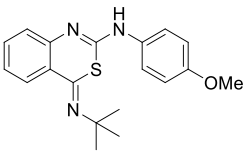
67% as yellow oil (0.18 g from 0.25 g); R_f = 0.56 (hexane: EtOAc, 93:7, v/v); ν_{max} (Neat) 1635 (C=N), 3439 (NH) cm $^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.33 (d, 6H, *J* = 6.4 Hz), 1.93-1.98 (m, 4H), 2.01-2.07 (m, 7H), 4.31-4.39 (m, 1H), 4.77 (d, 1H, *J* = 6.9 Hz,), 7.28- 7.30 (m, 2H), 8.30-8.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.9, 26.2, 26.5, 27.1, 37.0, 37.4, 44.1, 61.2, 116.6 (d, *J* = 24.9 Hz), 123.4 (d, *J* = 24.9 Hz), 127.6 (d, *J* = 7.9 Hz), 141.7, 144.8, 148.3, 155.0 (d, *J* = 272.2 Hz), 158.0; MS (ESI+) *m/z* = 320.0 $(M+H)^+$; ES-HRMS calcd. for $C_{17}H_{23}FN_3S$ $[MH]^+$ 320.1597, Found 320.1592.

4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aB). Yield: 81% as



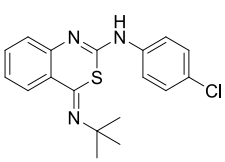
colourless oil (0.21 g from 0.25 g); R_f = 0.51 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1626 (C=N), 3367 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 9H), 6.04 (brs, 1H,), 7.10 (t, 1H, *J* = 7.7 Hz), 7.45 (d, 1H, *J* = 7.8 Hz), 7.49-7.55 (m, 4H), 8.02-8.05 (m, 2H), 8.77 (d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.9, 53.4, 121.9, 123.0, 126.5, 127.6, 128.9, 131.9, 132.4, 135.0, 139.7, 147.1, 154.0, 156.8; MS (ESI+) *m/z* = 310.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{20}N_3S$ $[MH]^+$ 310.1378, Found 310.1379.

4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3bB). Yield:



85% as colourless oil (0.21 g from 0.25 g); R_f = 0.51 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1640 (C=N), 3369 (NH) cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.39 (s, 9H), 3.78 (s, 3H), 5.90 (s, 1H), 6.82 (d, 4H, *J* = 7.6 Hz), 7.02 (d, 4H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 31.7, 55.6, 57.3, 114.7, 114.8, 124.2, 128.3, 128.5, 131.6, 131.7, 133.5, 139.4, 152.2, 156.9, 156.9; MS (ESI+) *m/z* = 340.0 $(M+H)^+$; ES-HRMS calcd. for $C_{19}H_{21}N_3OS$ $[MH]^+$ 340.1484, Found 340.1484.

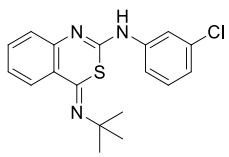
4-(*tert*-Butylimino)-*N*-(4-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3cB). Yield:



84% as colourless oil (0.21 g from 0.25 g); R_f = 0.51 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1626 (C=N), 3380 (NH) cm^{-1}; ^{1}H NMR (400

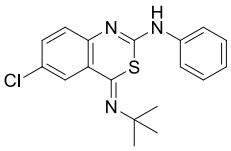
MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 9H), 7.38-7.40 (m, 2H), 7.50-7.52 (m, 2H), 7.61-7.64 (m, 2H), 7.85-7.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 31.8, 59.9, 114.2, 116.1, 119.5, 123.6, 124.2, 128.5, 128.6, 132.7, 135.3, 139.4, 152.0, 153.2; MS (ESI+) *m/z* = 344.0 $(M+H)^+$; ES-HRMS calcd. For $C_{18}H_{19}ClN_3S$ $[MH]^+$ 344.0988, Found 344.0991.

4-(*tert*-Butylimino)-*N*-(3-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3dB). Yield:



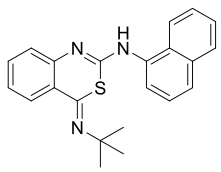
79% as colourless oil (0.2 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1635 (C=N), 3376 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 9H), 4.29 (s, 1H), 7.38 (s, 2H), 7.46 (d, 1H, *J* = 5.0 Hz), 7.59-7.63 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.8, 51.9, 112.2, 116.0, 119.4, 128.3, 128.4, 131.6, 131.7, 136.7, 140.4, 148.2, 152.8, 156.1; MS (ESI+) *m/z* = 344.0 $(M+H)^+$; ES-HRMS calcd. for $C_{18}H_{19}N_3ClS$ $[MH]^+$ 344.0988, Found 344.0992.

4-(*tert*-Butylimino)-6-chloro-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3kB). Yield:



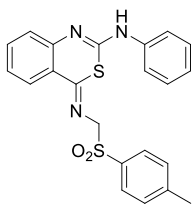
77% as brown oil (0.19 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1640 (C=N), 3326 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 9H), 4.64 (d, 1H, *J* = 1.5 Hz), 7.26 (brs, 3H), 7.37-7.40 (m, 2H), 7.46 (t, 1H, *J* = 1.8 Hz), 7.59-7.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 27.1, 55.6, 125.7, 126.9, 128.0, 129.0, 131.1, 131.3, 131.7, 146.3, 153.4, 157.3; MS (ESI+) *m/z* = 344.0 $(M+H)^+$. ES-HRMS calcd. for $C_{18}H_{19}N_3ClS$ $[MH]^+$ 344.0988, Found 345.0983.

4-(*tert*-Butylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3eB). Yield:



88% as black oil (0.22 g from 0.25 g); R_f = 0.53 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1640 (C=N), 3340 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.26 (s, 9H), 7.07 (d, 1H, *J* = 7.0 Hz), 7.37-7.45 (m, 3H), 7.53-7.58 (m, 3H), 7.68-7.72 (m, 3H), 7.85 (d, 1H, *J* = 7.3 Hz), 8.09 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 28.6, 56.7, 121.7, 122.6, 123.6, 125.8, 125.9, 126.1, 126.4, 126.6, 126.8, 127.4, 127.8, 128.7, 129.5, 130.7, 131.9, 147.9, 148.6, 160.5; MS (ESI+) *m/z* = 359.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{21}N_3S$ $[MH]^+$ 360.1534, Found 360.1538.

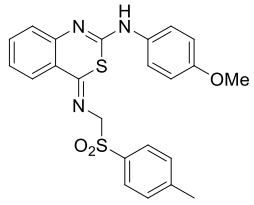
***N*-phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aC).** Yield: 83% as



yellow oil (0.28 g from 0.25 g); R_f = 0.52 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1619, 3359 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.62 (s, 3H), 4.64 (s, 2H), 7.26 (s, 4H), 7.36-7.40 (m, 5H), 7.58-7.64 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 24.9, 60.4, 119.9, 120.9, 123.2, 124.1,

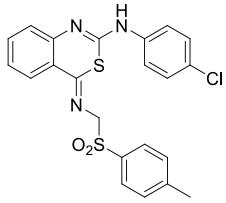
126.2, 128.5, 129.7, 132.3, 132.9, 140.0, 145.1, 151.6, 159.0; MS (ESI+) *m/z*= 422.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{20}N_3O_2S_2$ $[MH]^+$ 422.0997, Found 422.0993.

***N*-(4-methoxyphenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3bC)**



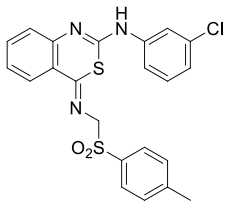
Yield: 86% as yellow oil (0.29 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1635 (C=N), 3376 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.31 (s, 3H), 3.78 (s, 3H), 4.87 (brs, 1H), 5.34 (s, 2H), 6.61 (d, 1H, *J* = 8.2 Hz), 7.10 (d, 4H, *J* = 7.9 Hz), 7.28-7.30 (m, 3H), 7.38 (d, 2H, *J* = 8.2 Hz), 7.72 (d, 1H, *J* = 0.8 Hz), 7.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.8, 51.6, 70.1, 114.2, 116.0, 128.4, 128.6, 131.7, 131.8, 133.0, 133.1, 139.4, 144.3, 149.2, 152.0, 154.4, 156.9; MS (ESI+) *m/z* = 452.0 $(M+H)^+$; ES-HRMS calcd. for $C_{23}H_{22}N_3O_3S_2$ $[MH]^+$ 452.1103, Found 452.1108.

***N*-(4-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[d][1,3]thiazin-2-amine (3cC).** Yield:



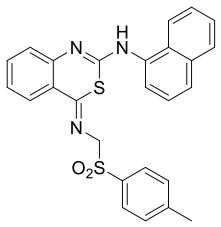
83% as yellow oil (0.28 g from 0.25 g); R_f = 0.51 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1630 (C=N), 3376 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.38 (s, 3H), 4.15 (s, 2H), 5.34 (brs, 1H,), 6.59-6.63 (m, 2H), 6.75-6.77 (m, 1H), 7.06-7.12 (m, 3H), 7.29 (s, 3H), 7.54 (t, 3H, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.8, 70.1, 123.6, 124.2, 127.8, 128.5, 128.6, 131.8, 132.7, 135.3, 139.4, 148.5, 153.2, 156.5; MS (ESI+) *m/z* = 456.0 (M+H); ES-HRMS calcd. for $C_{22}H_{19}ClN_3O_2S_2$ $[MH]^+$ 456.0607, Found 456.0612.

***N*-(3-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[d][1,3]thiazin-2-amine (3dC).**



Yield: 85% as colourless oil (0.28 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1659 (C=N), 3336 (NH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.31 (s, 3H), 4.43 (brs, 1H), 4.78 (s, 2H), 6.60 (d, 2H, *J* = 8.2 Hz), 7.05 (d, 2H, *J* = 2.4 Hz), 7.29 (d, 1H, *J* = 8.2 Hz), 7.37 (s, 3H), 7.39 (s, 3H), 7.51-7.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.8, 70.1, 115.9, 119.5, 123.2, 124.0, 124.1, 128.5, 129.7, 130.1, 131.0, 131.7,131.8, 132.5, 132.7, 133.0, 144.2, 148.7, 150.9, 156.6; MS (ESI+) *m/z* = 456.0 $(M+H)^+$; ES-HRMS: calcd. for $C_{22}H_{19}ClN_3S_2$ $[MH]^+$ 456.0607, Found 456.0609.

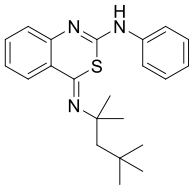
***N*-(Naphthalen-1-yl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3eC).**



Yield: 73% as brown oil (0.24 g from 0.25 g); R_f = 0.55 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1655 (C=N), 3376 (NH) cm-1; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.31 (s, 3H), 5.30 (s, 2H), 6.97 (t, 2H, *J* = 7.8 Hz), 7.10 (d, 2H, *J* = 8.1 Hz), 7.62-7.68 (m, 5H), 7.72-7.77 (m, 5H), 9.00

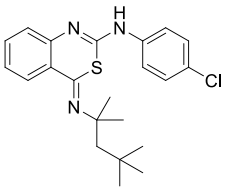
(d, 1H, *J* = 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 22.1, 73.4, 116.0, 117.9, 118.6, 119.2, 120.4, 121.3, 123.6, 124.1, 125.6, 126.1, 129.1, 138.8, 140.2, 147.9, 150.4, 155.1; MS (ESI+) *m/z* = 472.0 $(M+H)^+$; ES-HRMS calcd. for $C_{26}H_{22}N_3O_2S_2$ $[MH]^+$ 472.1153, Found 472.1155.

***N*-Phenyl-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aD).**



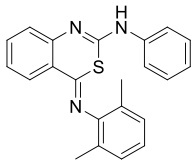
Yield: 75% as yellow oil (0.22 g from 0.25 g); R_f = 0.54 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1633 (C=N), 3356 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.06 (s, 9H), 1.57 (s, 6H), 1.74 (s, 2H), 6.61 (d, 1H, *J* = 7.8 Hz,), 7.07-7.10 (m, 5H), 7.26-7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 29.7, 31.6, 31.9, 51.8, 55.5, 120.8, 122.4, 122.5, 123.2, 123.5, 126.1, 128.9, 129.5, 133.8, 139.8, 149.7, 151.6, 155.3; MS (ESI+) *m/z* = 366.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{28}N_3S$ $[MH]^+$ 366.2004 Found 366.2009.

***N*-(4-Chlorophenyl)-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[*d*][1,3]thiazin-2-**



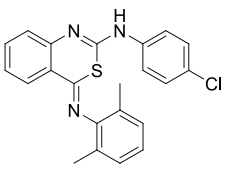
amine (3cD). Yield: 79% as yellow oil (0.23 g from 0.25 g); R_f = 0.54 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1633 (C=N), 3423 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.91 (s, 9H), 1.22 (s, 6H), 1.49 (s, 2H), 7.06-7.10 (m, 1H), 7.15-7.19 (m, 1H), 7.33 (s, 1H), 7.64-7.66 (m, 1H), 7.87 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 31.7, 32.0, 32.1, 58.3, 59.3, 123.3, 124.6, 125.7, 128.5, 130.0, 130.7, 131.2, 132.4, 140.8, 145.5, 150.2, 154.3; MS (ESI+) *m/z* = 400.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{27}ClN_3S$ $[MH]^+$ 400.1614, Found 400.1619.

4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aE). Yield:



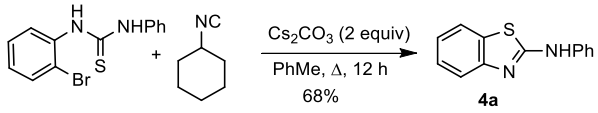
86% as yellow oil (0.25 g from 0.25 g); R_f = 0.43 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1623 (C=N), 3376 (NH) cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.95 (s, 6H), 6.59-6.64 (m, 2H), 6.75-6.77 (m, 2H), 6.96 (d, 2H, *J* = 7.5 Hz), 7.39-7.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 18.3, 121.4, 121.6, 123.5, 123.9, 125.9, 126.1, 128.1, 128.5, 129.9, 130.8, 132.2, 132.7, 136.8, 137.6, 144.2, 147.5, 157.9, 162.1; MS (ESI+) *m/z* = 358.0 $(M+H)^+$; ES-HRMS calcd. for $C_{22}H_{20}N_3S$ $[MH]^+$ 358.1378 Found 358.1381.

***N*-(4-Chlorophenyl)-4-(2,6-dimethylphenylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine**

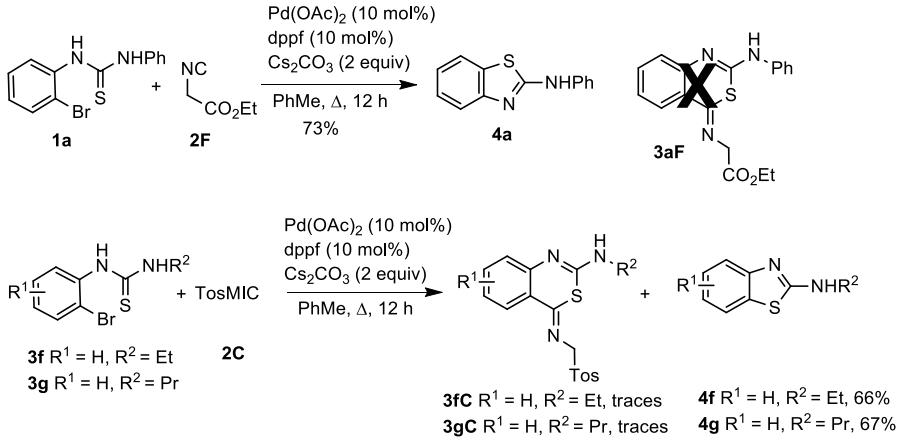


(3cE). Yield: 88% (0.25 g from 0.25 g) as yellow oil; R_f = 0.49 (hexane: EtOAc, 90:10, v/v); ν_{max} (Neat) 1633 (C=N), 3367 (NH) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.16 (s, 6H), 6.12 (s, 1H), 6.93-6.98(m,

2H), 7.27-7.34 (m, 2H), 7.41-7.48 (m, 5H), 7.68-7.71 (m, 1H), 8.70 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 17.6, 122.3, 122.6, 125.1, 125.8, 126.0, 126.4, 128.2, 128.9, 129.1, 130.1, 135.3, 136.0, 136.3, 144.3, 152.0, 156.9, 163.6; MS (ESI+) *m/z* = 392.0 $(M+H)^+$; ES-HRMS; calcd. for $C_{22}H_{19}ClN_3S$ $[MH]^+$ 392.0988, Found 392.0985.



***N*-Phenylbenzo[*d*]thiazol-2-amine (4a).** Yield: 68% (0.05 g from 0.1 g) as a yellow solid, mp = 162-164 ^{o}C, [161-162 ^{o}C][4]; R_f = 0.44 (hexane: EtOAc, 90:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.74 (s, 1H,), 7.26 (s, 1H), 7.39-7.51 (m, 5H), 7.62 (t, 3H, *J* = 6.4 Hz); MS (ESI+) *m/z* = 227.0 $(M+H)^+$; ES-HRMS; calcd. for $C_{13}H_{10}N_2S$ $[MH]^+$ 227.0643, Found 227.0647.



***N*-Ethylbenzo[*d*]thiazol-2-amine(4f).** Yield: 66% (0.11 g from 0.25 g) as a white solid; mp = 114-116 ^{o}C [114-116 ^{o}C] [5]; R_f = 0.43 (hexane: EtOAc, 90:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =1.10 (t, 3H, *J* = 7.5 Hz), 2.38(s, 1H,), 3.20 (d, 2H, *J* = 4.0 Hz), 6.84(t, 1H, *J* = 7.3 Hz), 7.00 (t, 1H, *J* = 7.8 Hz), 7.35 (d, 1H, *J* = 7.9 Hz); MS (ESI+) *m/z* = 179.0 $(M+H)^+$; ES-HRMS; calcd. for $C_9H_{10}N_2S$ $[MH]^+$ 179.0643, Found 179.0648.

***N*-Propylbenzo[*d*]thiazol-2-amine (4g).** Yield: 67% (0.12 g from 0.25 g) as a white solid; mp = 79-80 ^{o}C [79-81 ^{o}C][6]); R_f = 0.44 (hexane: EtOAc, 90:10, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.02 (t, 3H, *J* = 7.4 Hz), 1.78-1.83 (m, 2H), 3.72-3.77 (m, 2H), 4.48-4.52 (m, 1H,), 7.28-7.32 (m, 1H), 7.41-7.45 (m, 1H), 7.70 (d, 1H, *J* = 8.1 Hz); MS (ESI+) *m/z* = 193.0 $(M+H)^+$; ES-HRMS; calcd. for $C_{10}H_{12}N_2S$ $[MH]^+$ 193.0799, Found 199.0797.

References:

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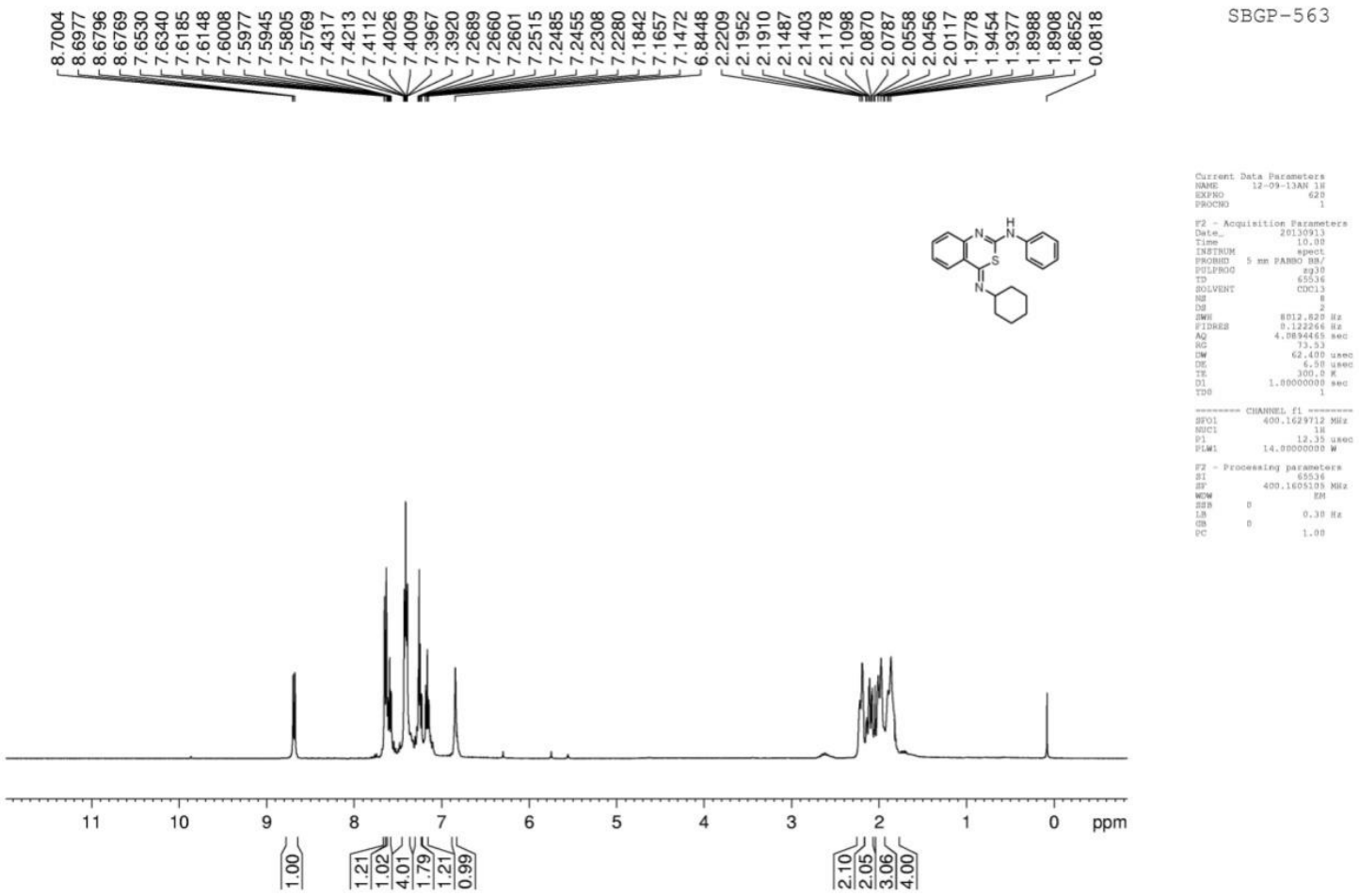


Fig: S-1 ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aA)**

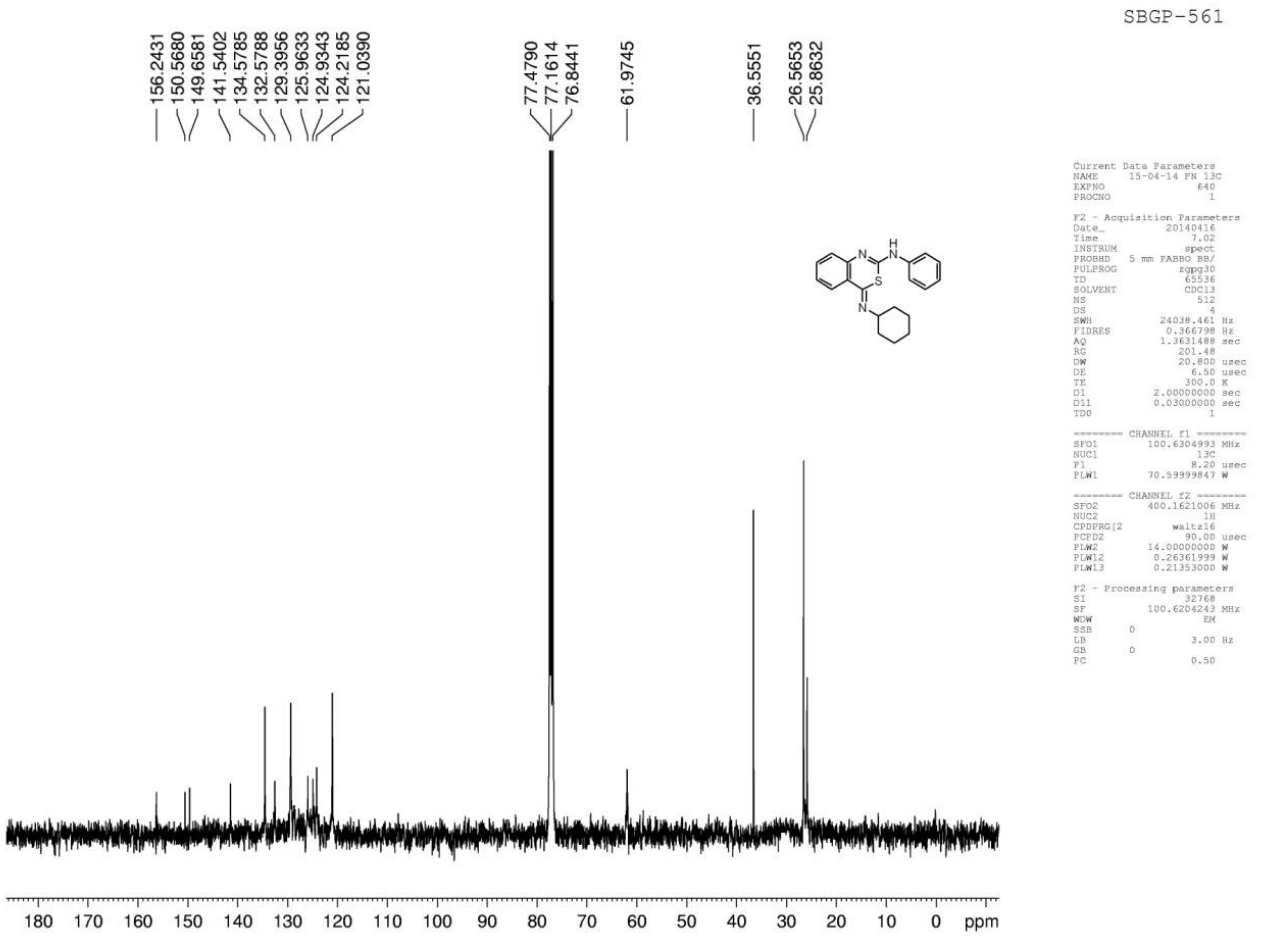


Fig: S-2 ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine (3aA)

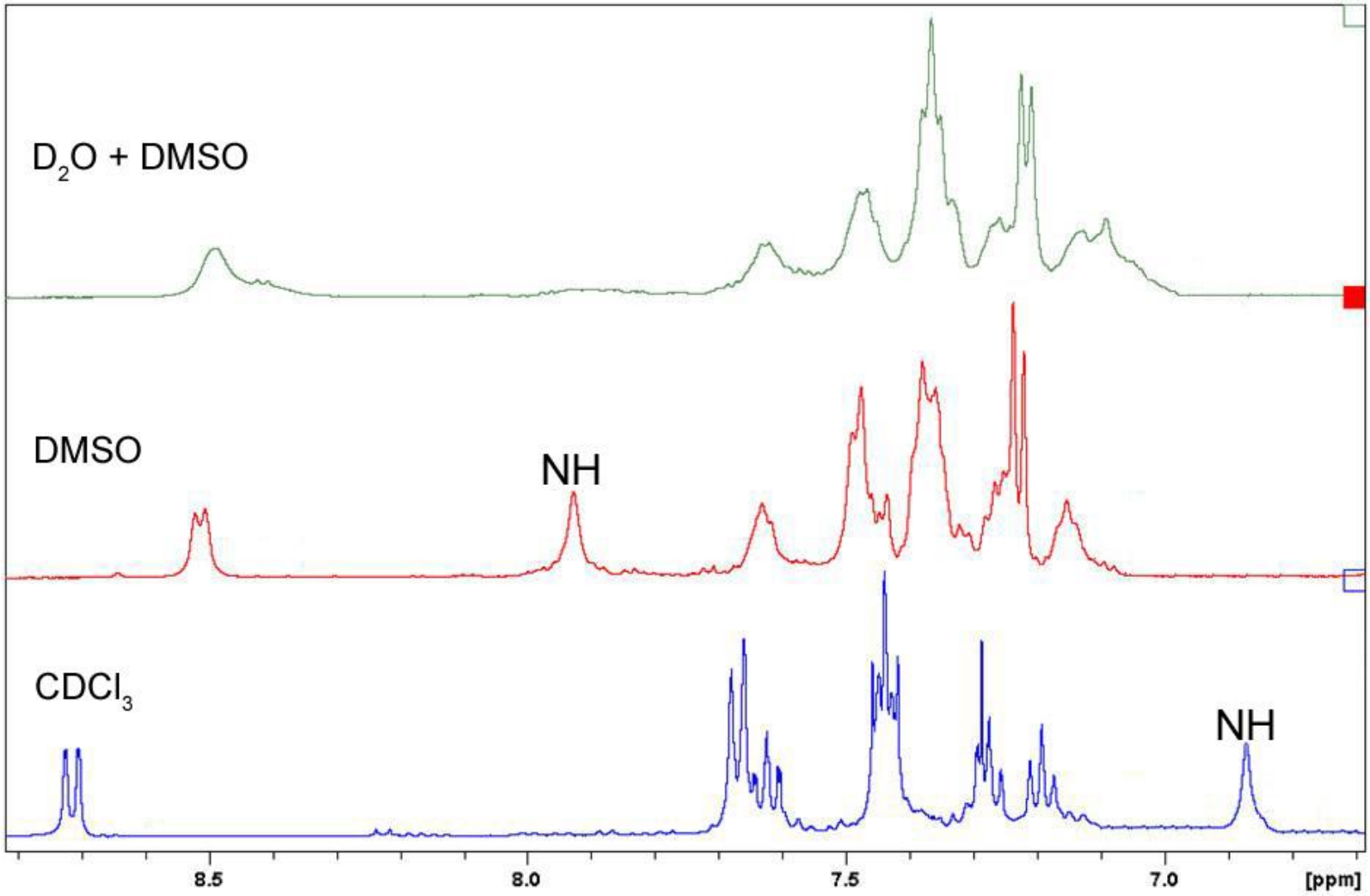


Fig: S-3 Comparison between the ^{1}H spectra of (*Z*)-4-(Cyclohexylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aA)** recorded in $CDCl_3$, DMSO, D_2O + DMSO for confirmation of the exocylic NH group.

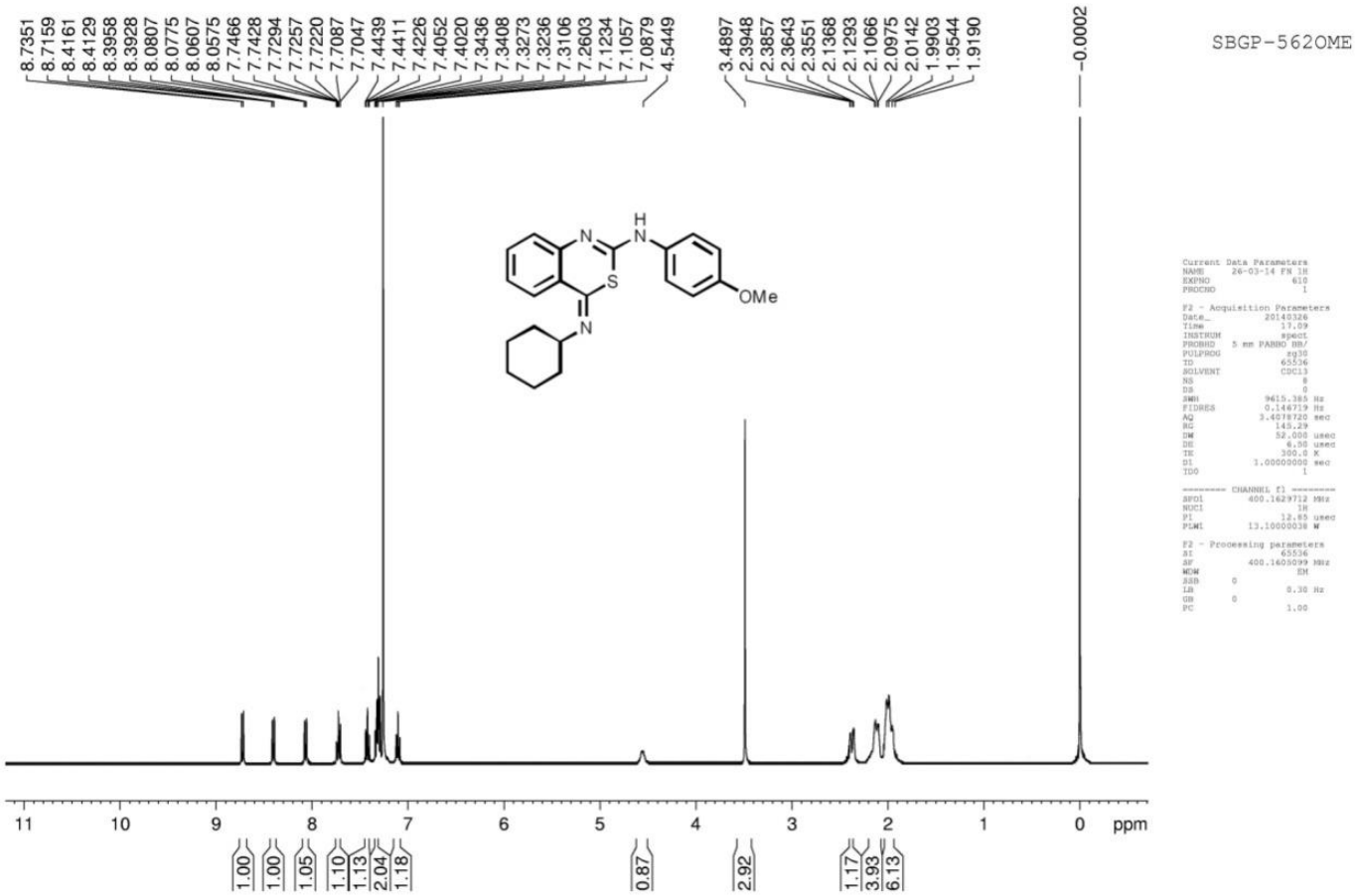


Fig: S-4 ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-(3-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bA)**

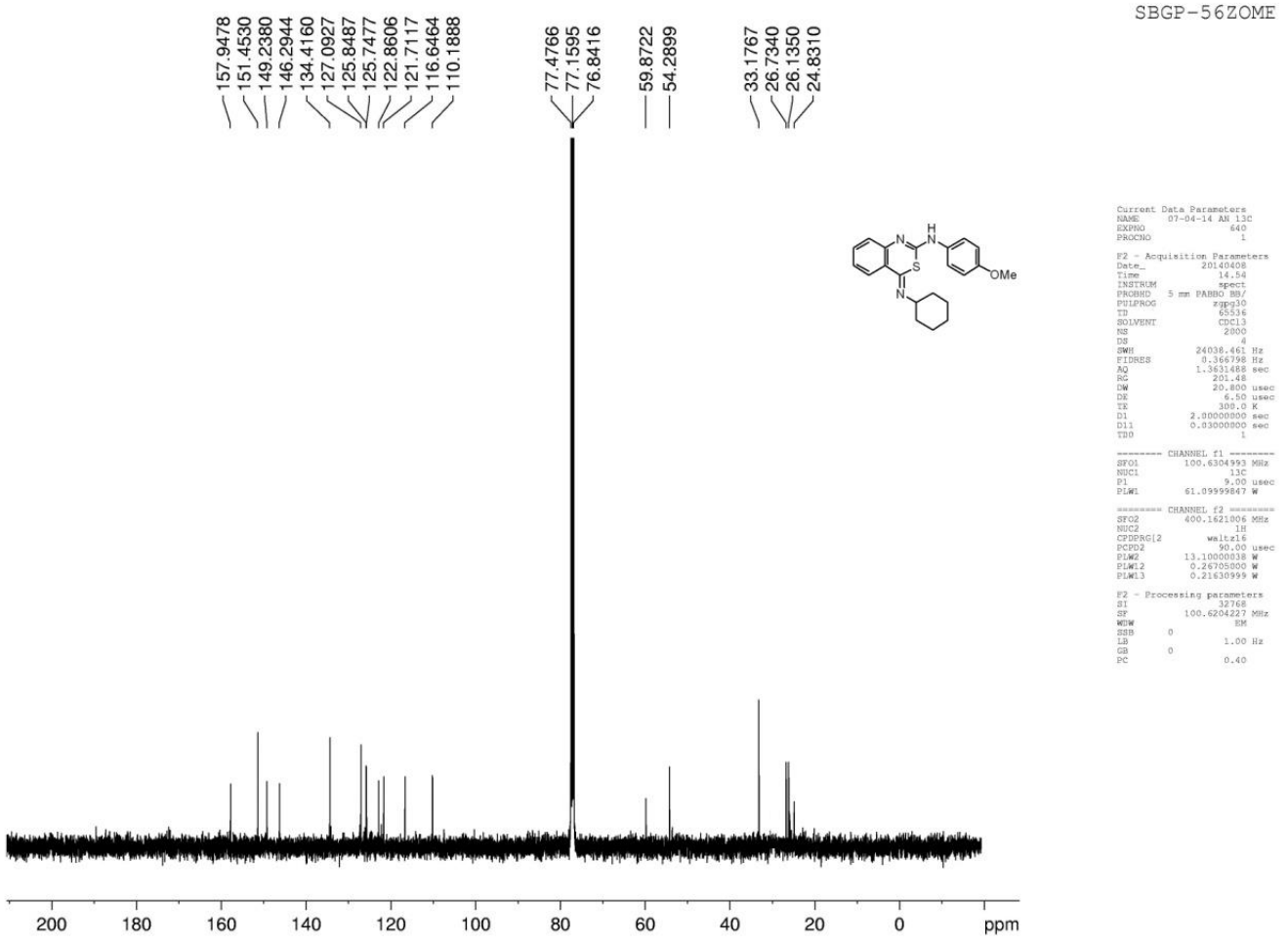


Fig: S-5 ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-(3-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bA)**

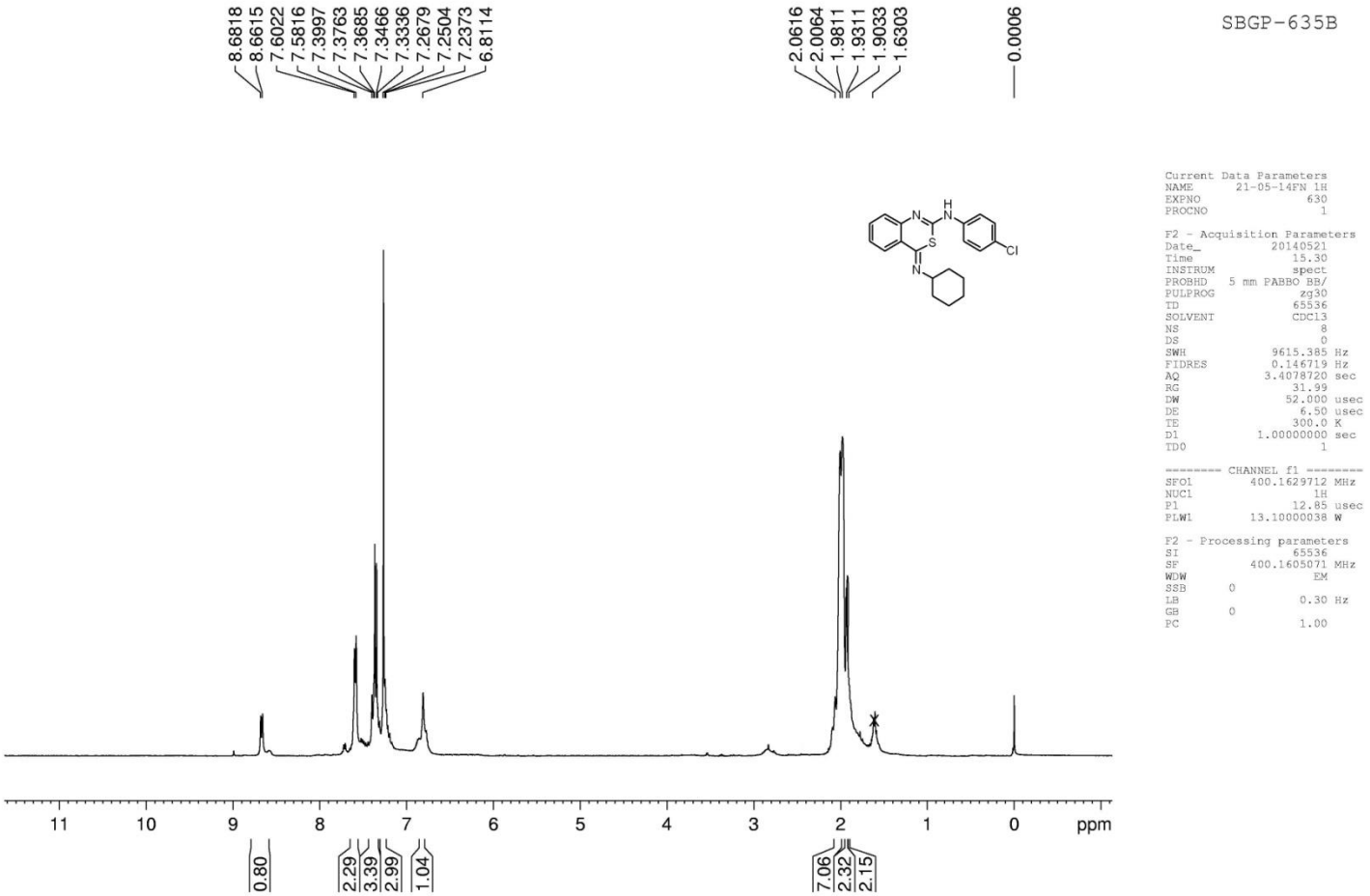


Fig: S-6 ^{1}H spectrum of (*Z*)-*N*-(4-chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cA)**

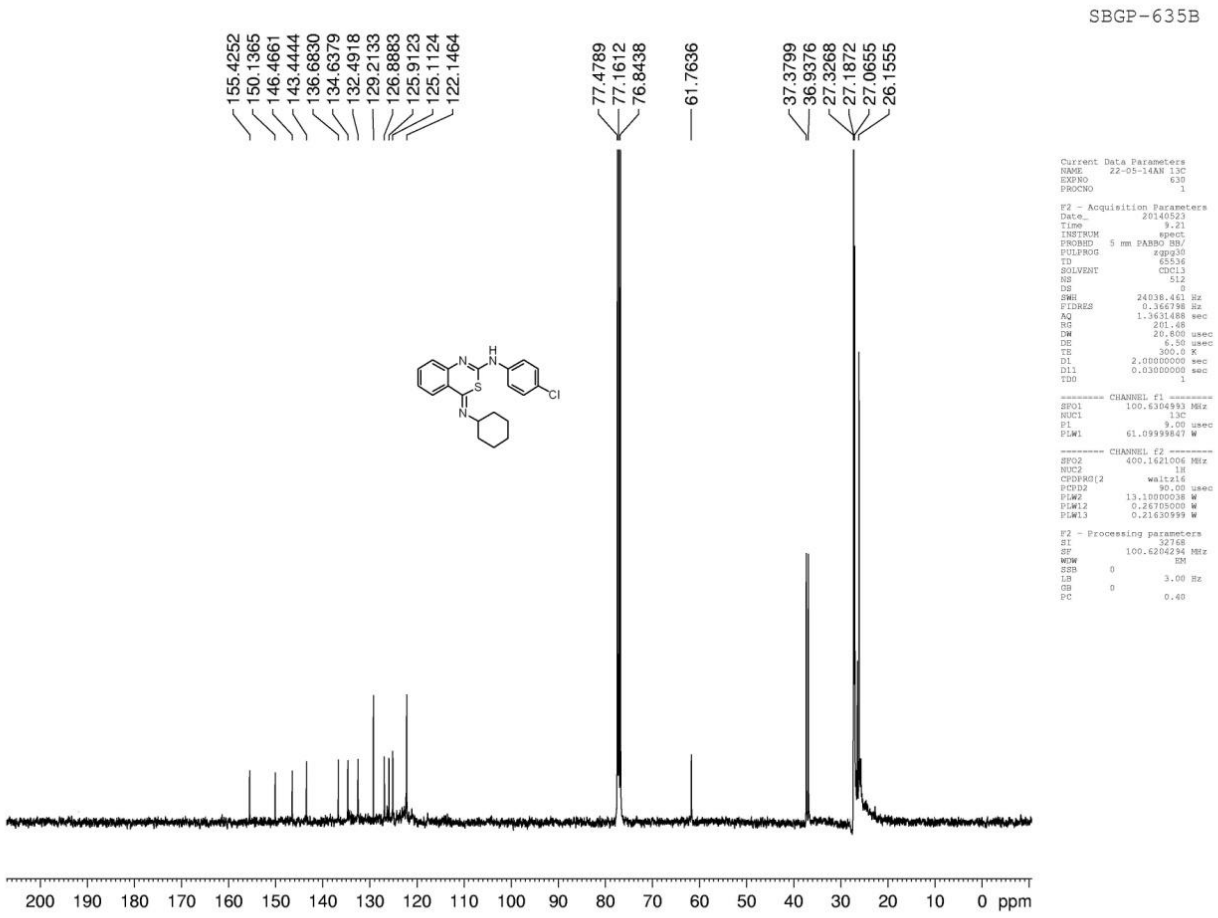


Fig: S-7 ^{13}C spectrum of (*Z*)-*N*-(4-Chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cA)**

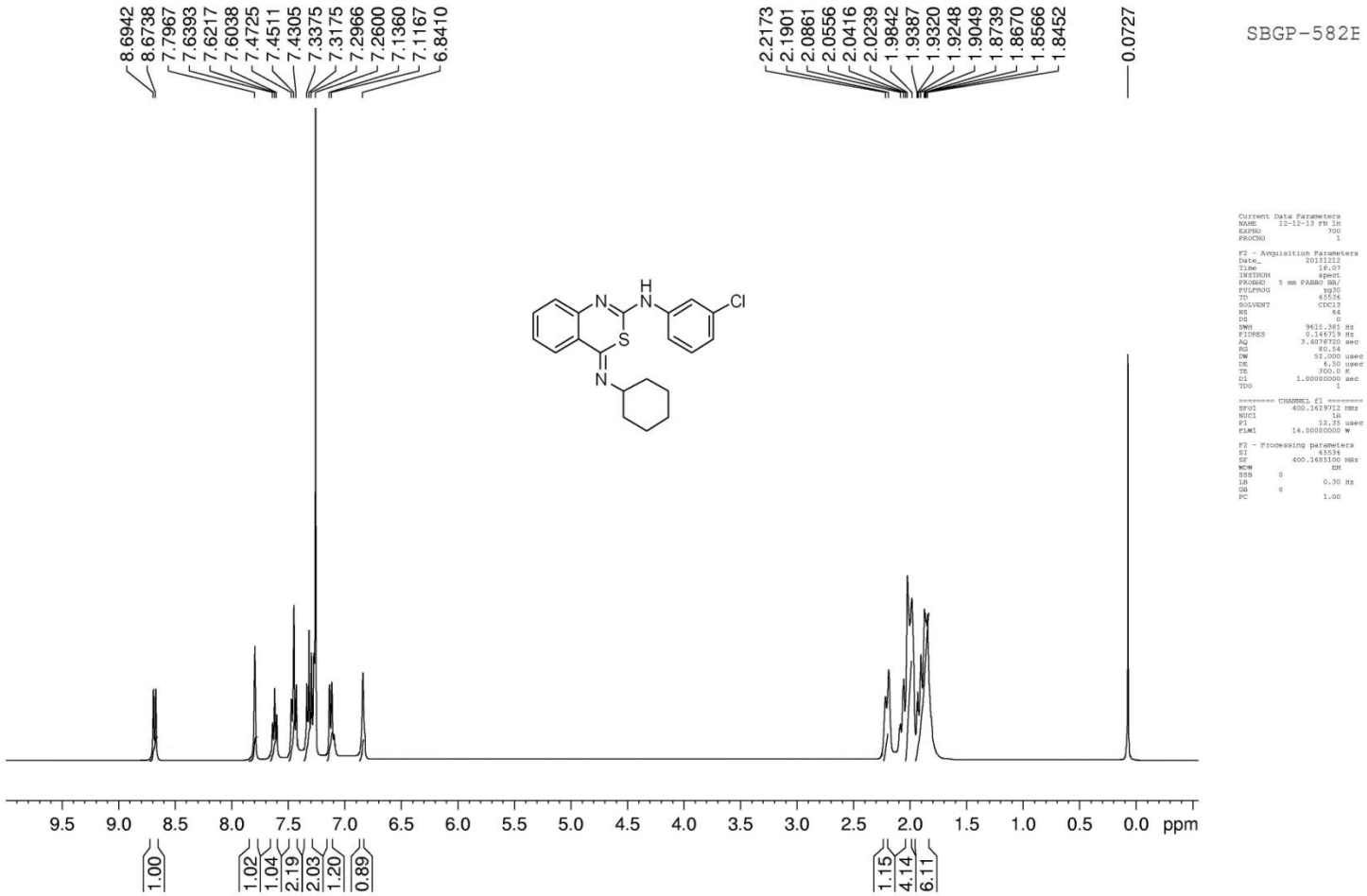


Fig: S-8 ^{1}H spectrum of (*Z*)-*N*-(3-Chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3dA)**

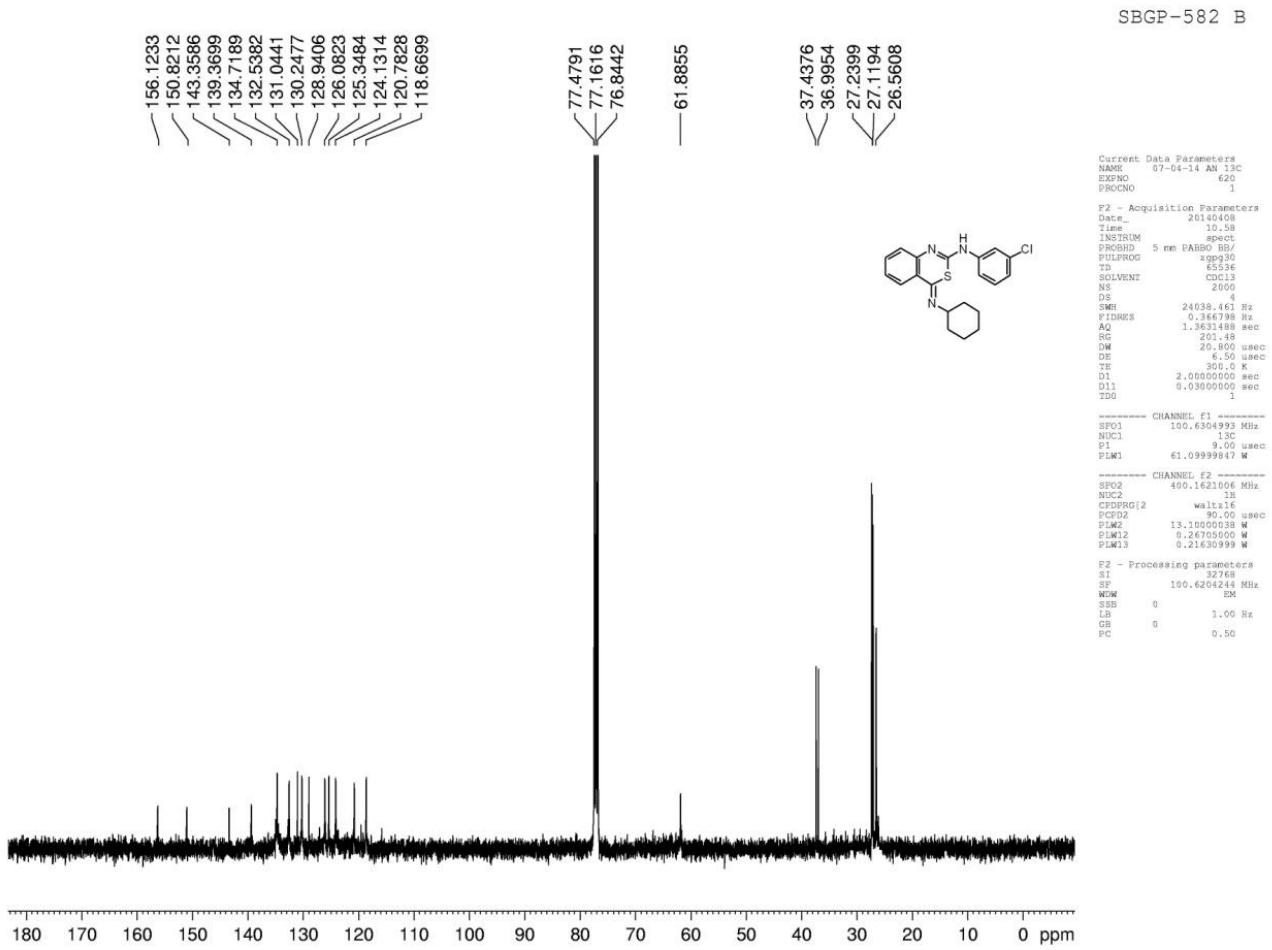


Fig: S-9 ^{13}C spectrum of (*Z*)-*N*-(3-Chlorophenyl)-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3dA)**

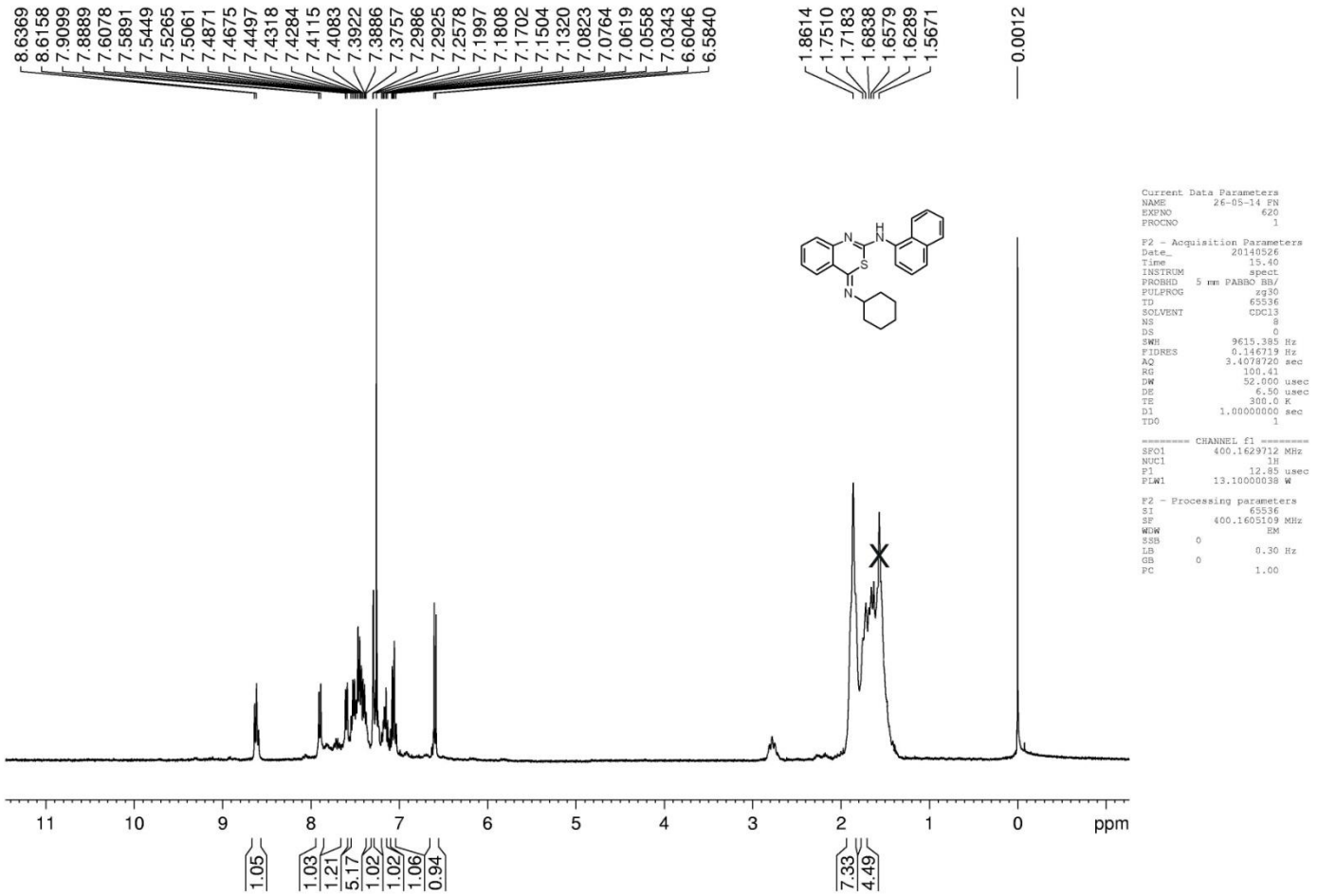


Fig: S-10 ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eA)**

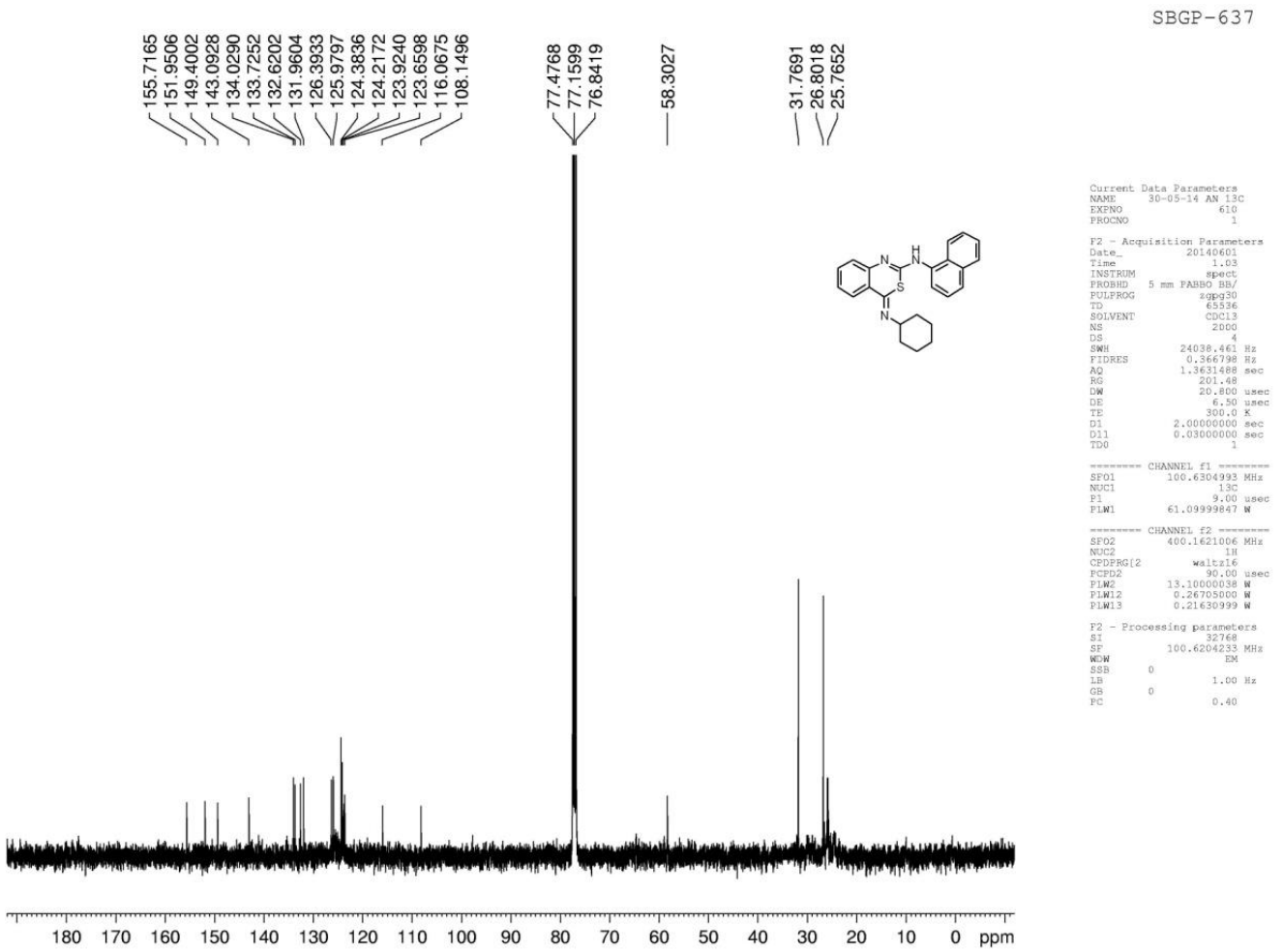


Fig: S-11 ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eA)**

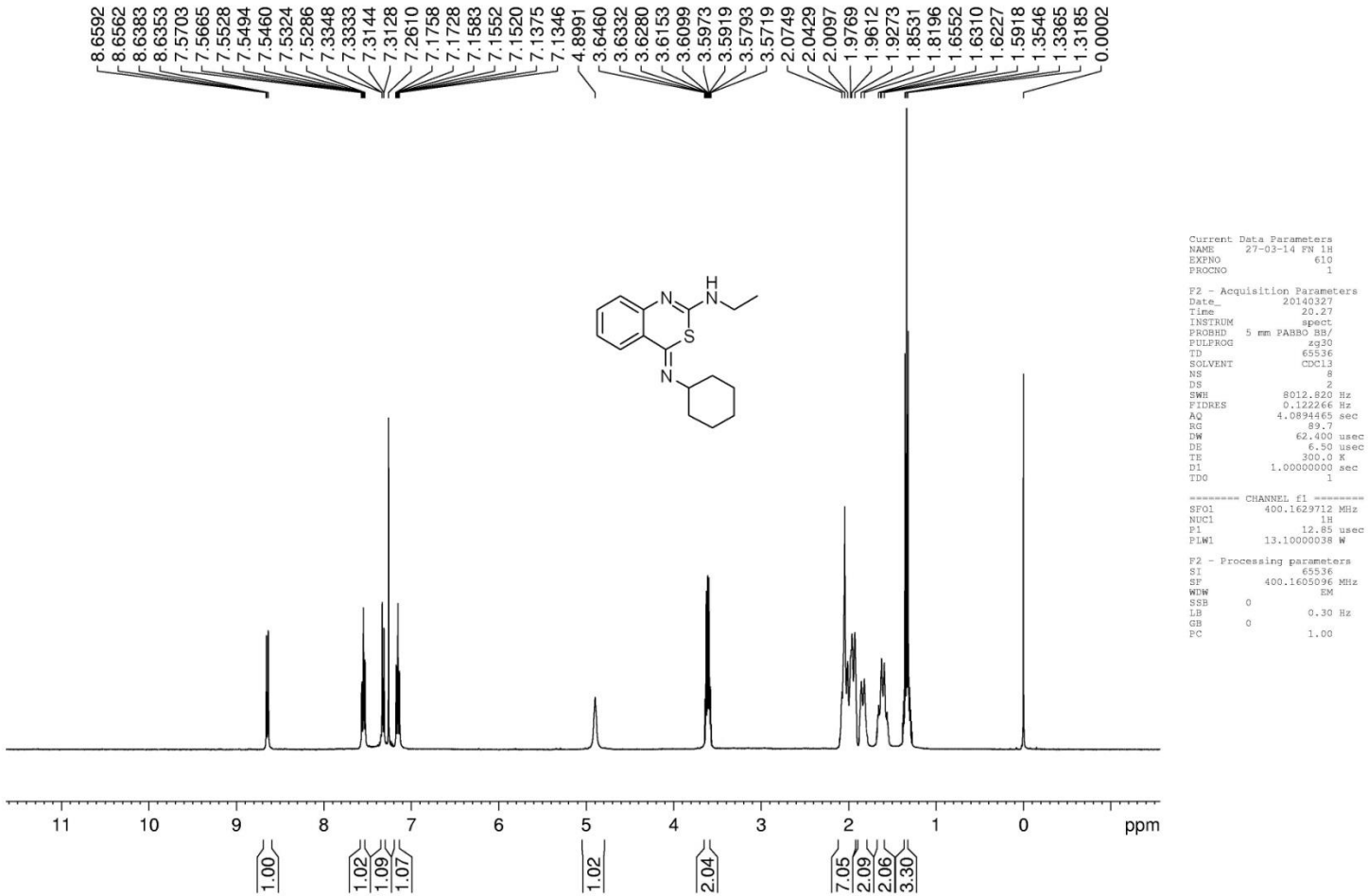


Fig: S.-12 ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-ethyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3fA)**

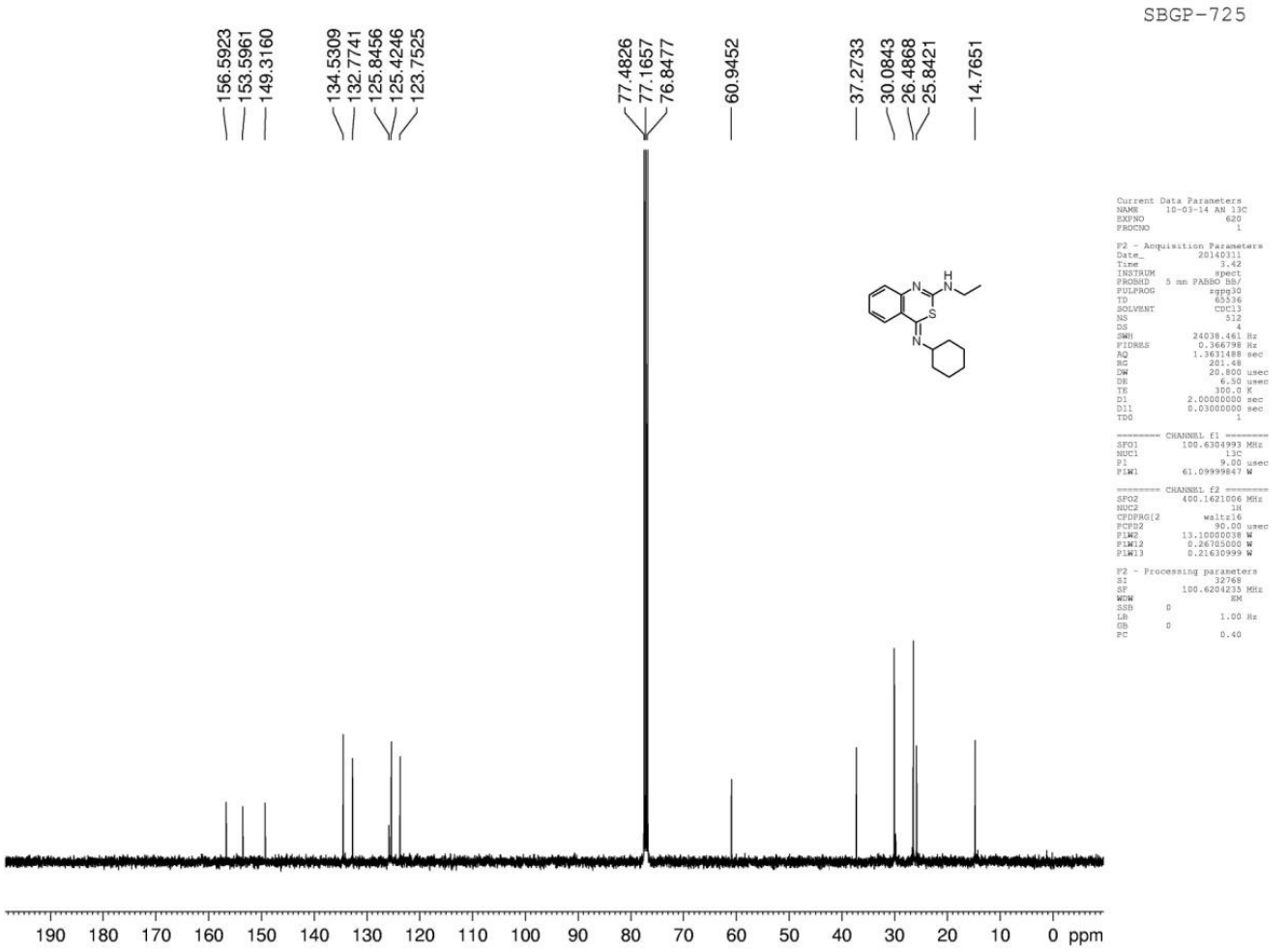


Fig: S-13 ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-ethyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3fA)**

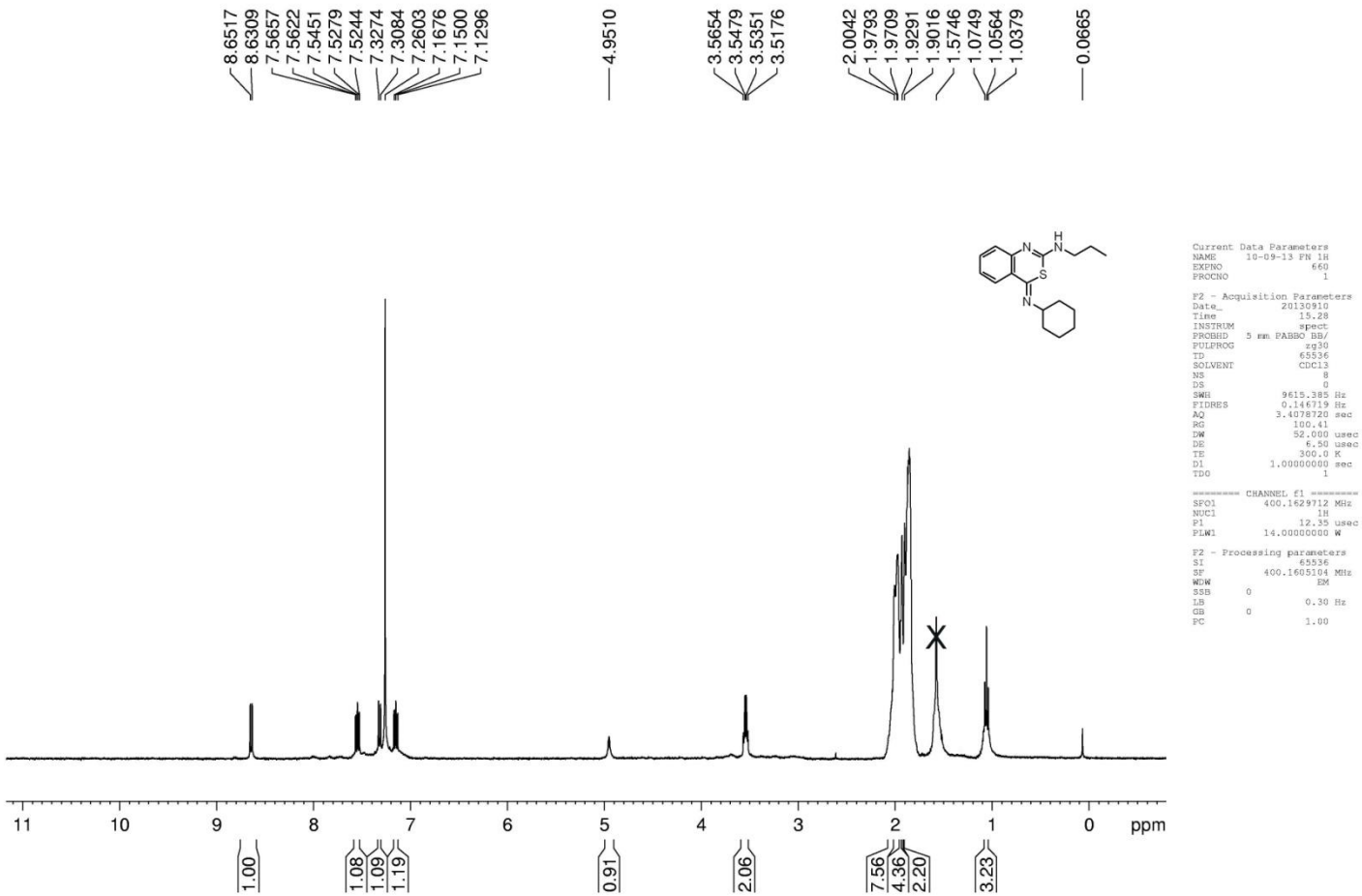


Fig: S-14 ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-propyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3gA)**

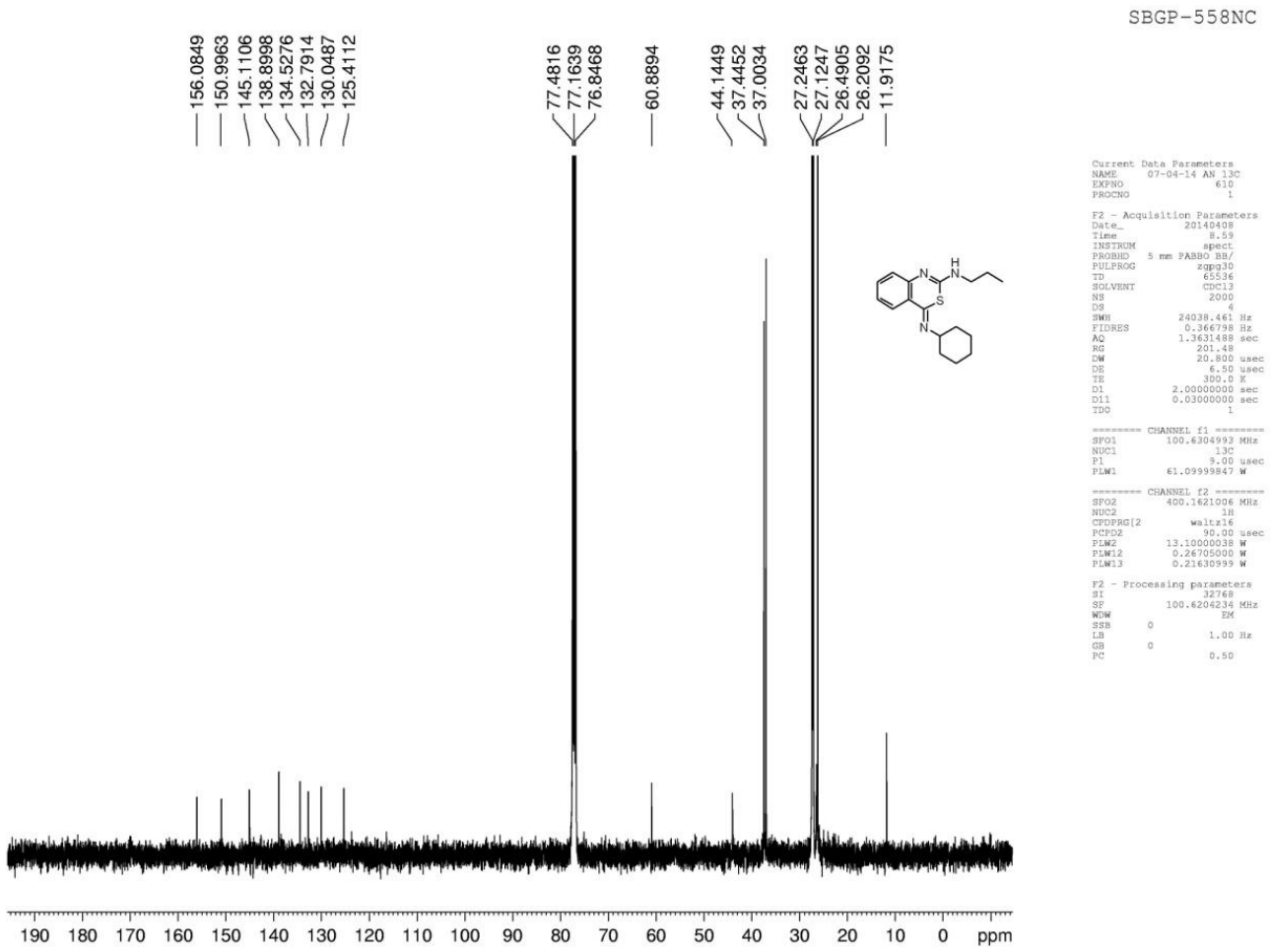


Fig: S-15 ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-*N*-propyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3gA)**

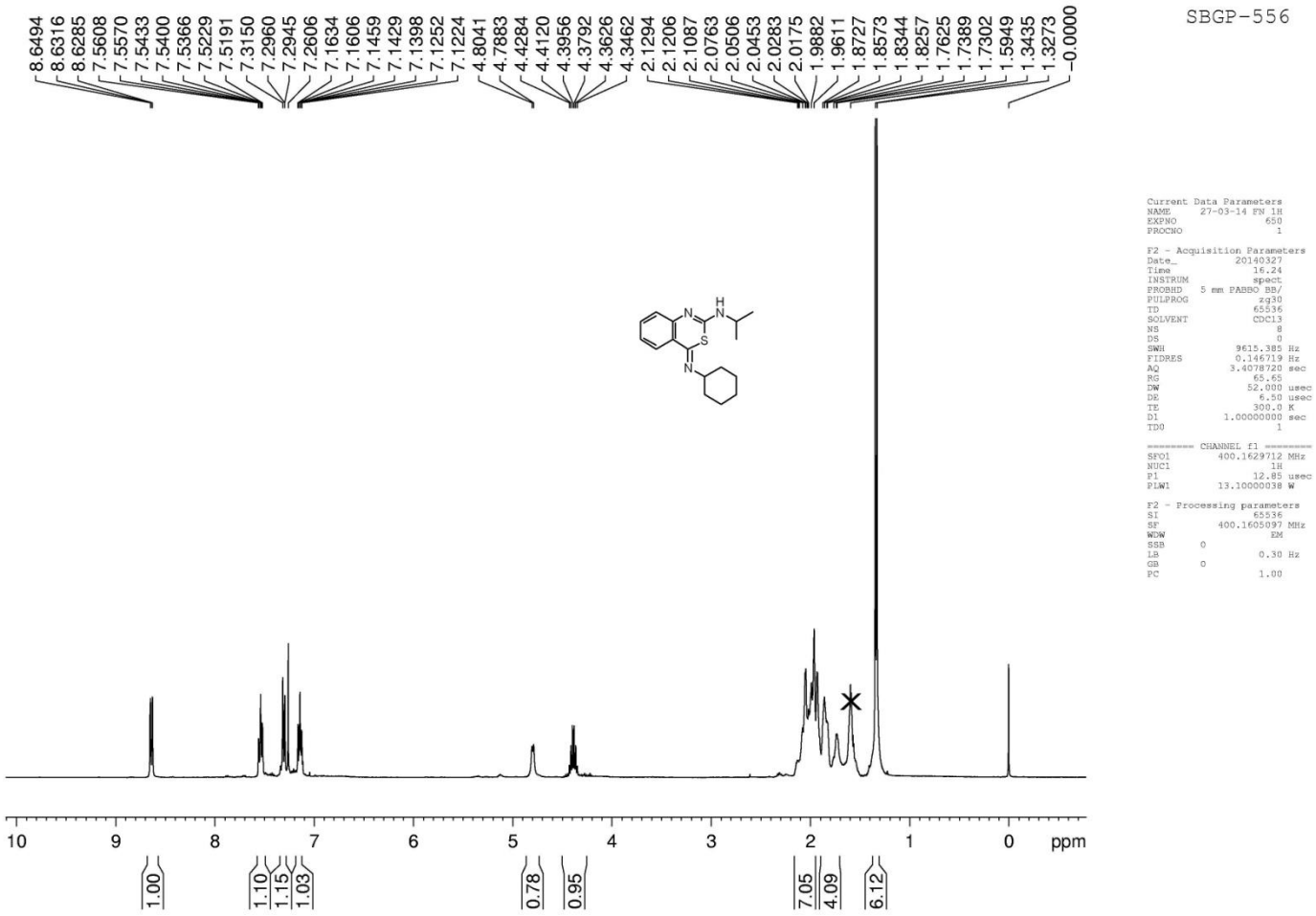


Fig: S-16 ^{1}H spectrum of (*Z*)-4-(cyclohexylimino)-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3hA)**

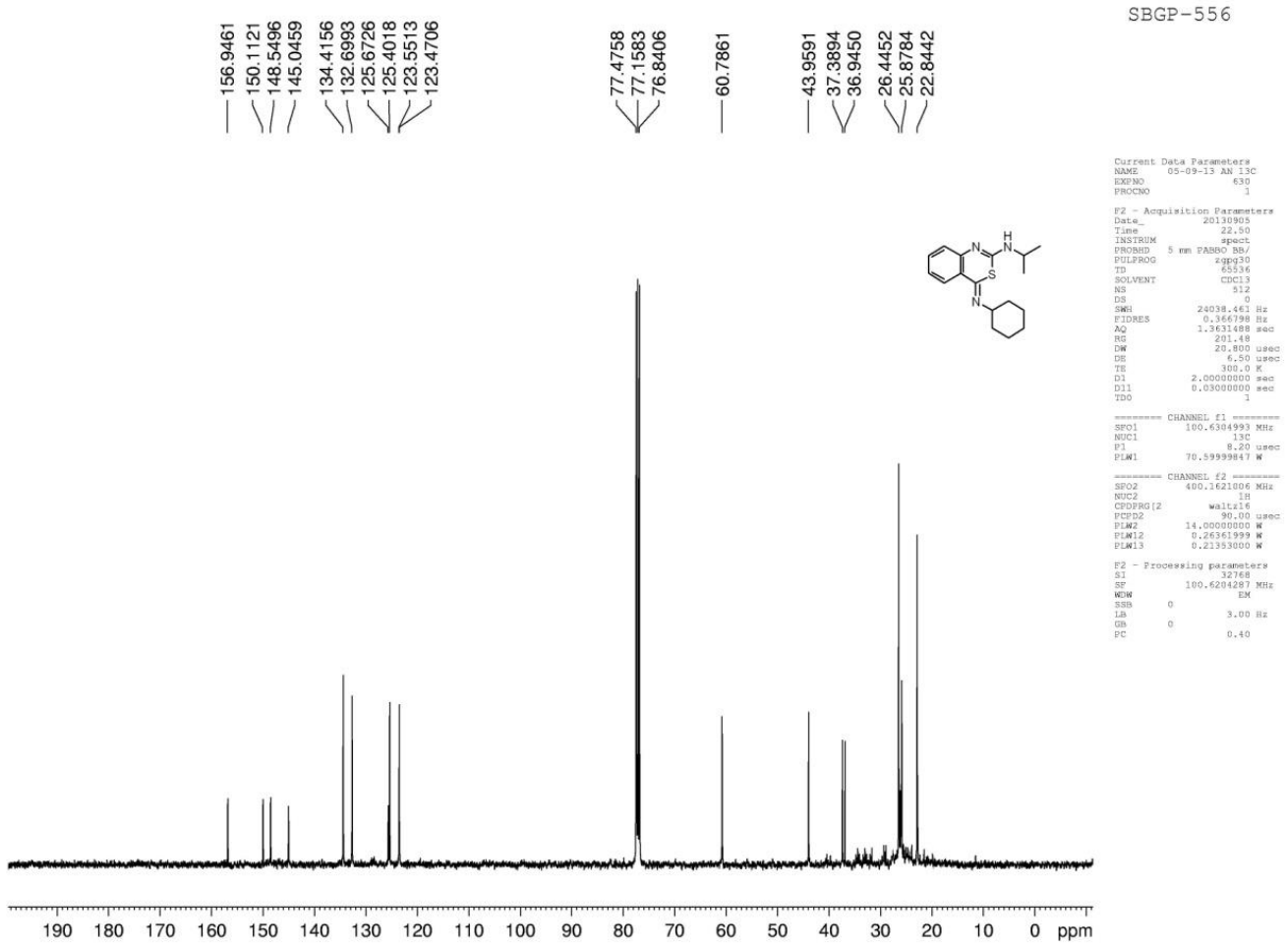


Fig: S-17 ^{13}C spectrum of (*Z*)-4-(cyclohexylimino)-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3hA)**

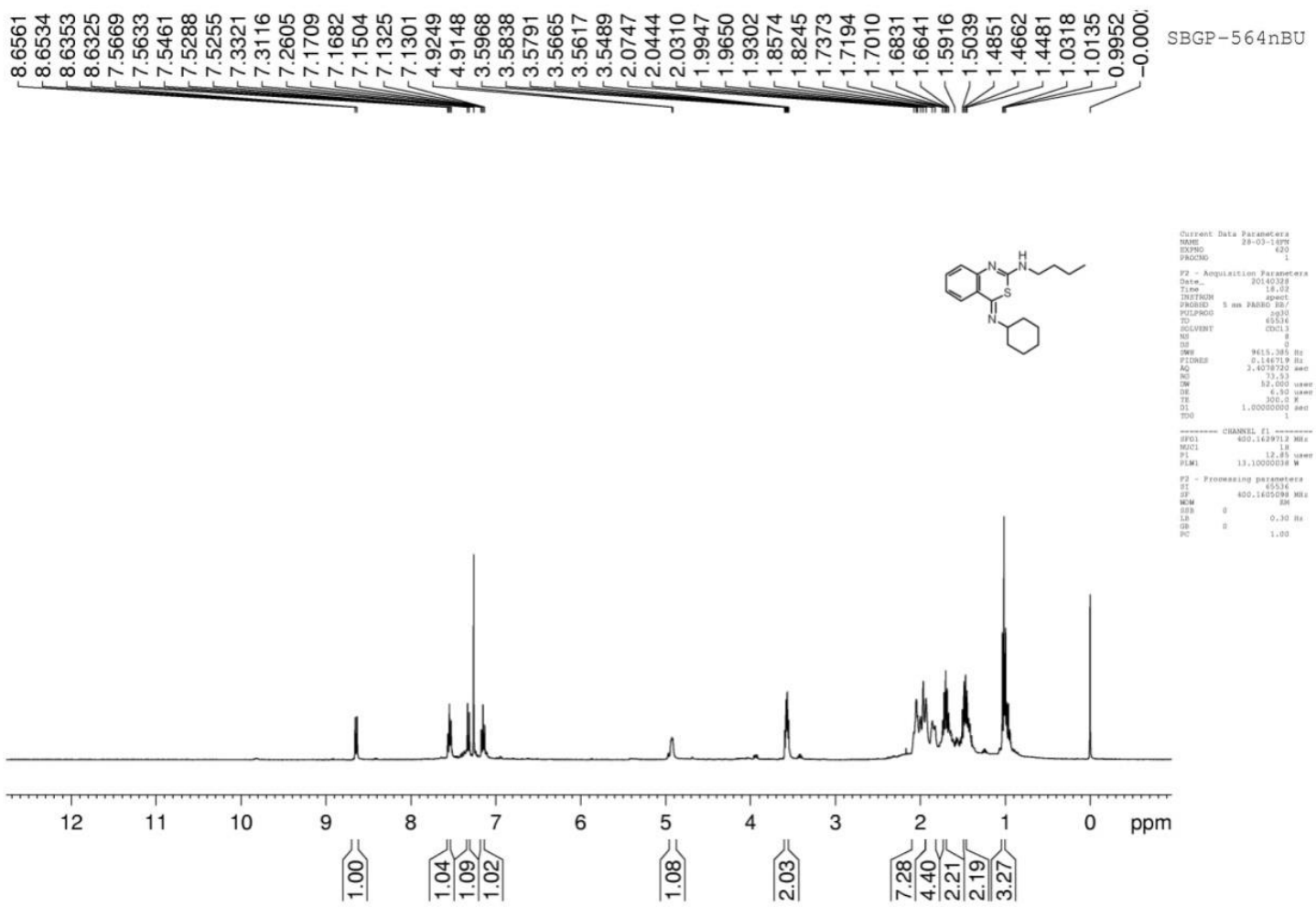


Fig: S-18 ^{1}H spectrum of (*Z*)-*N*-Butyl-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3iA)**

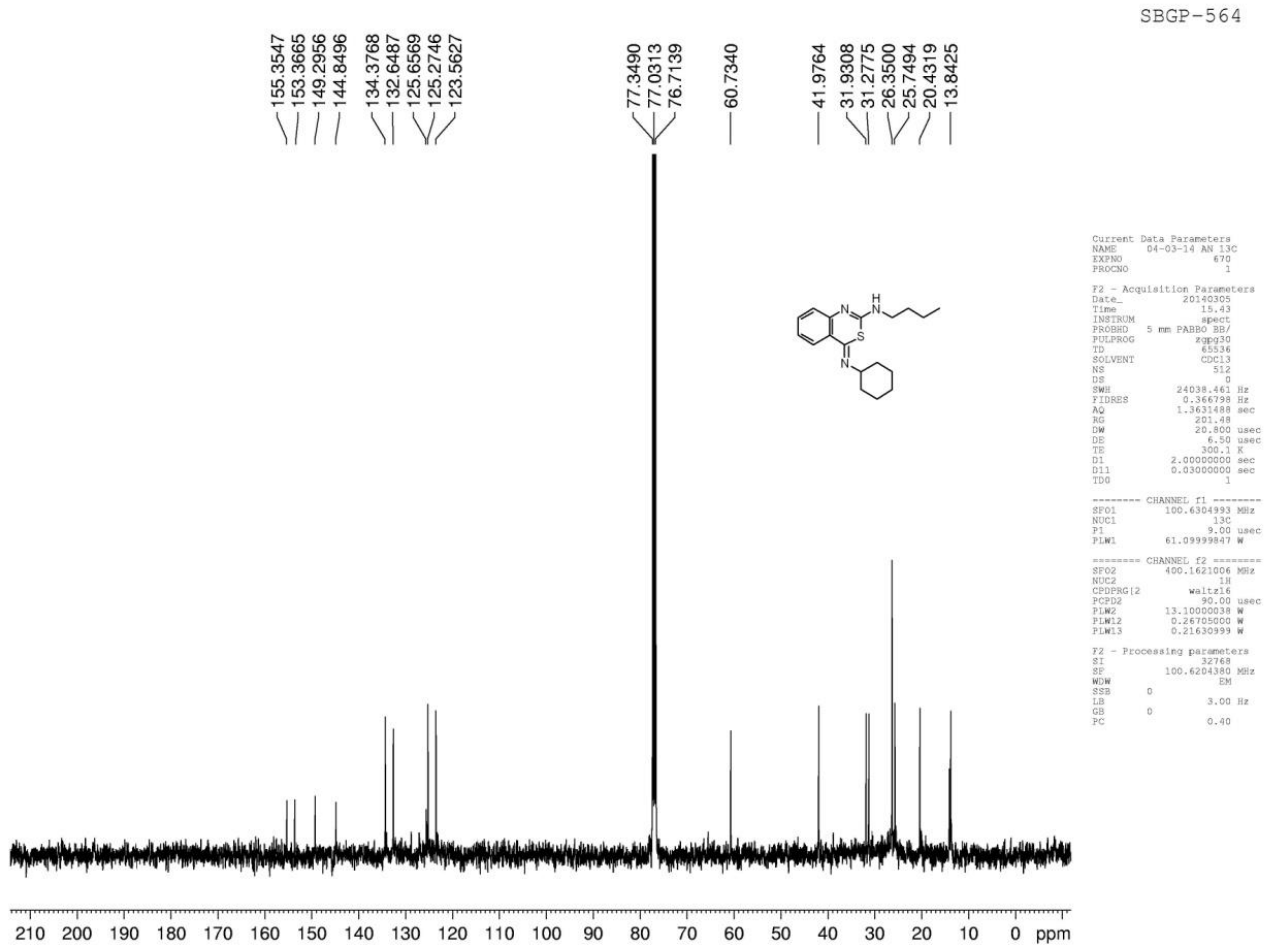


Fig: S-19 ^{13}C spectrum of (*Z*)-*N*-Butyl-4-(cyclohexylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3iA)**

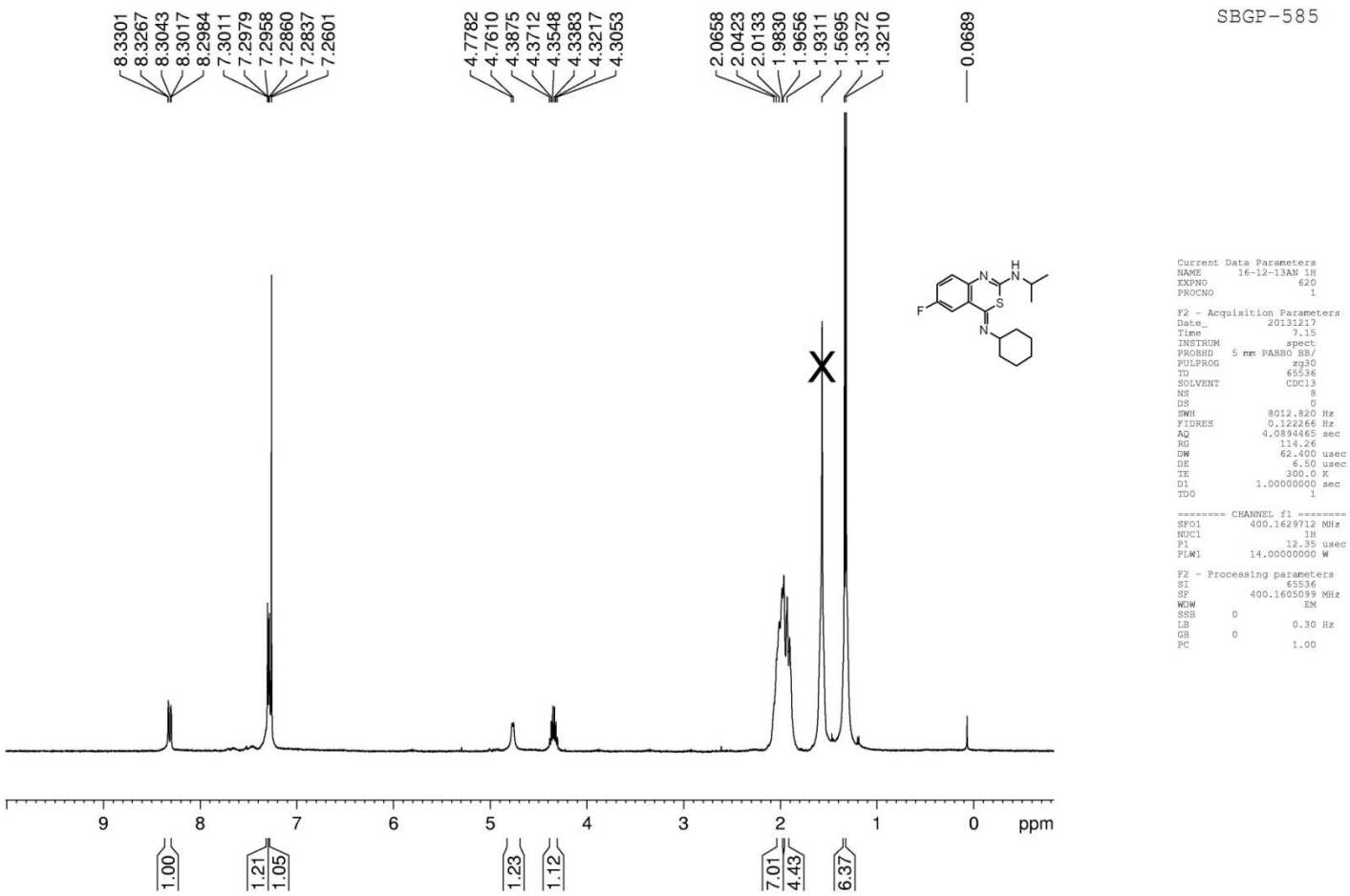


Fig: S-20. ^{1}H spectrum of (*Z*)-4-(Cyclohexylimino)-6-fluoro-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3jA)**

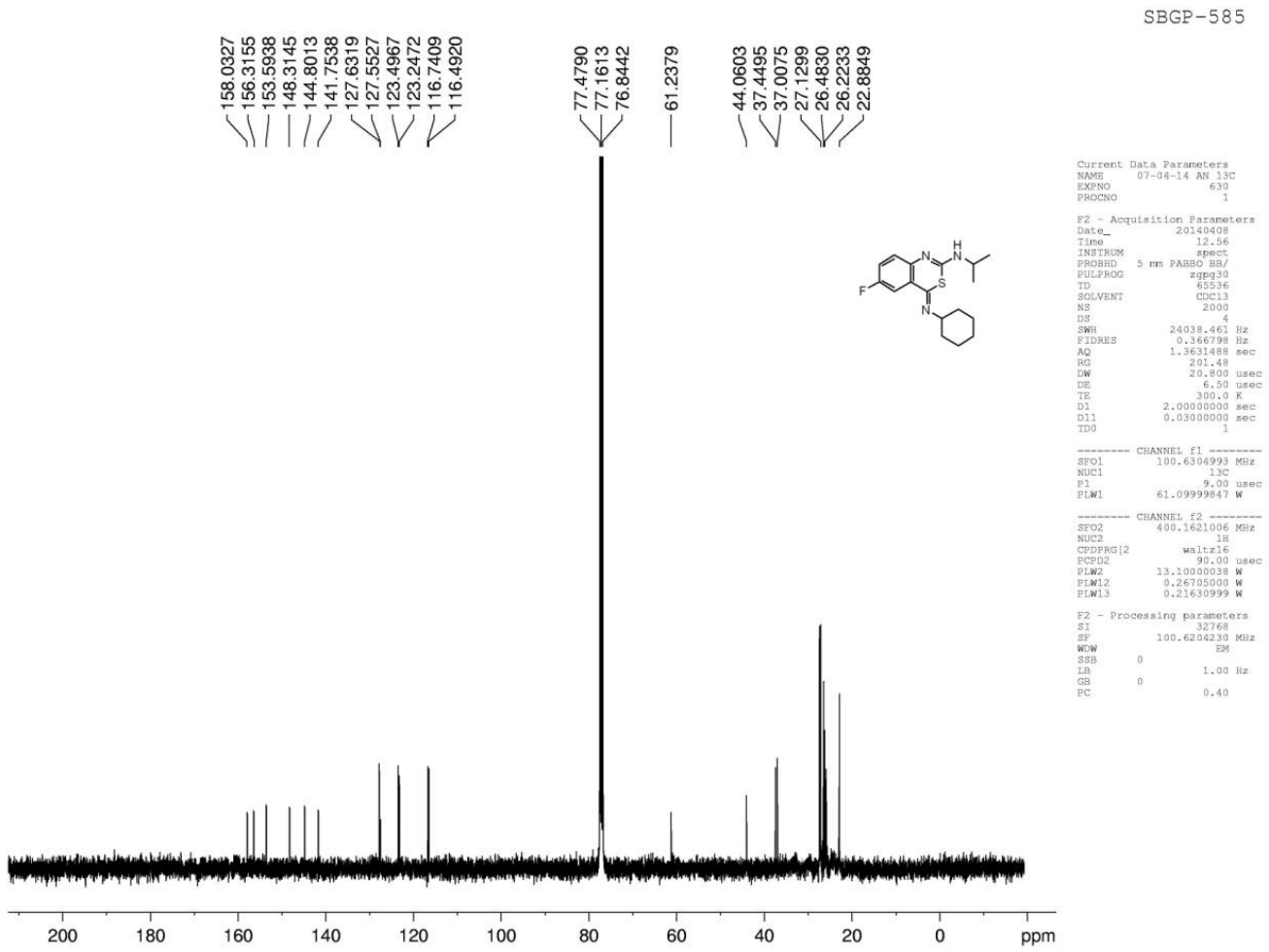


Fig: S-21. ^{13}C spectrum of (*Z*)-4-(Cyclohexylimino)-6-fluoro-*N*-isopropyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3jA)**

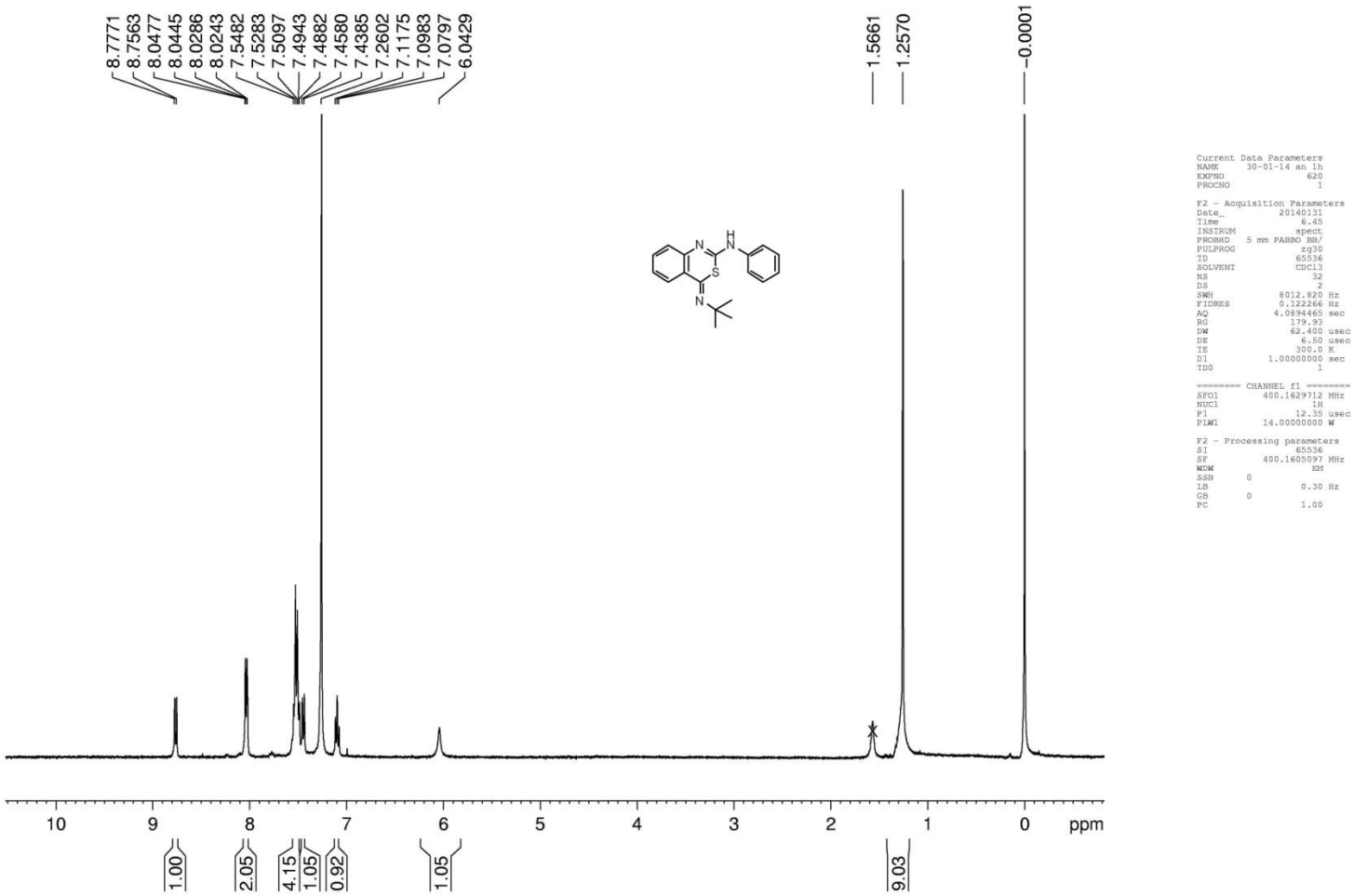


Fig: S-22 ^{1}H spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aB)**

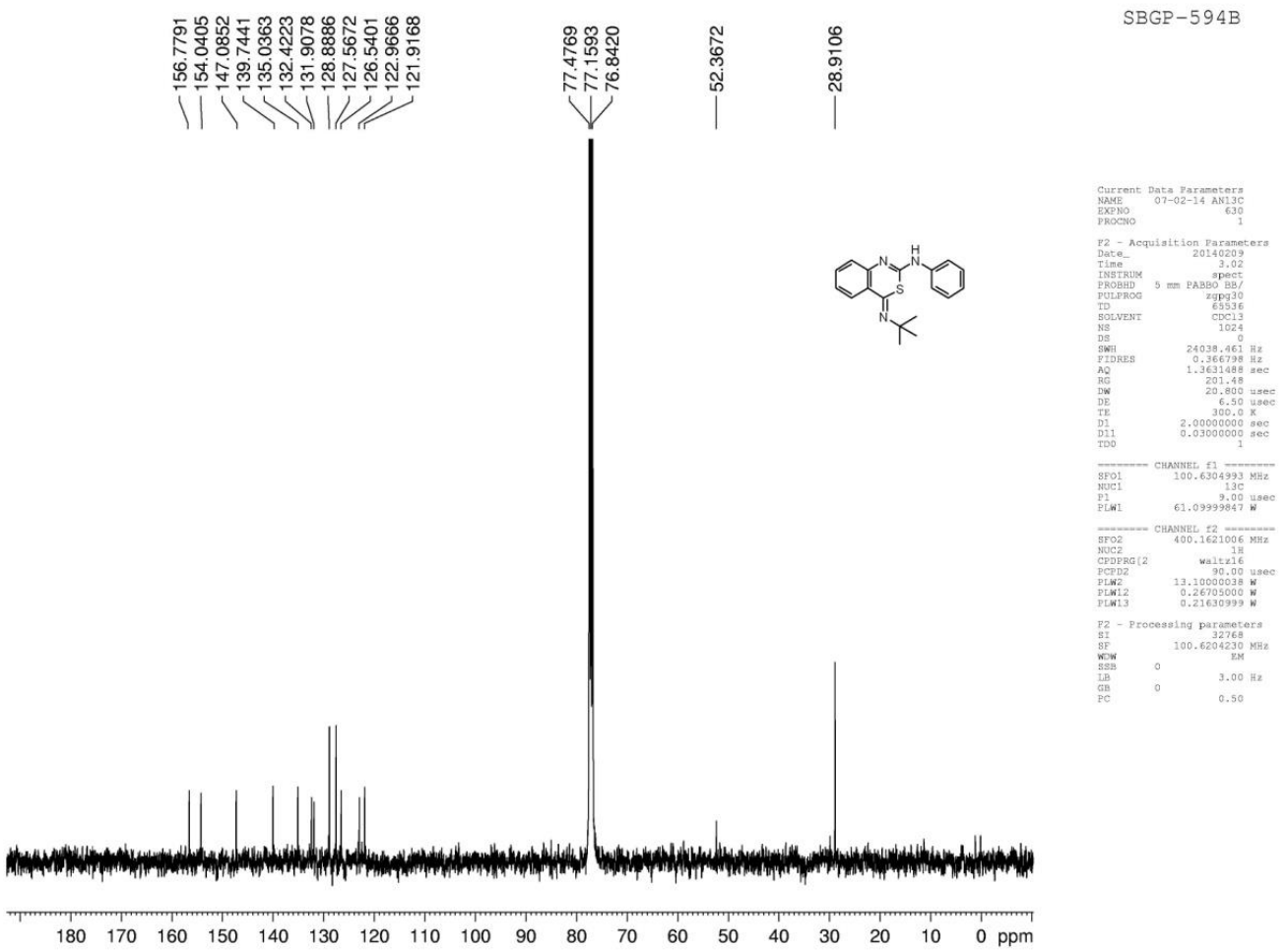


Fig: S-23 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aB)**

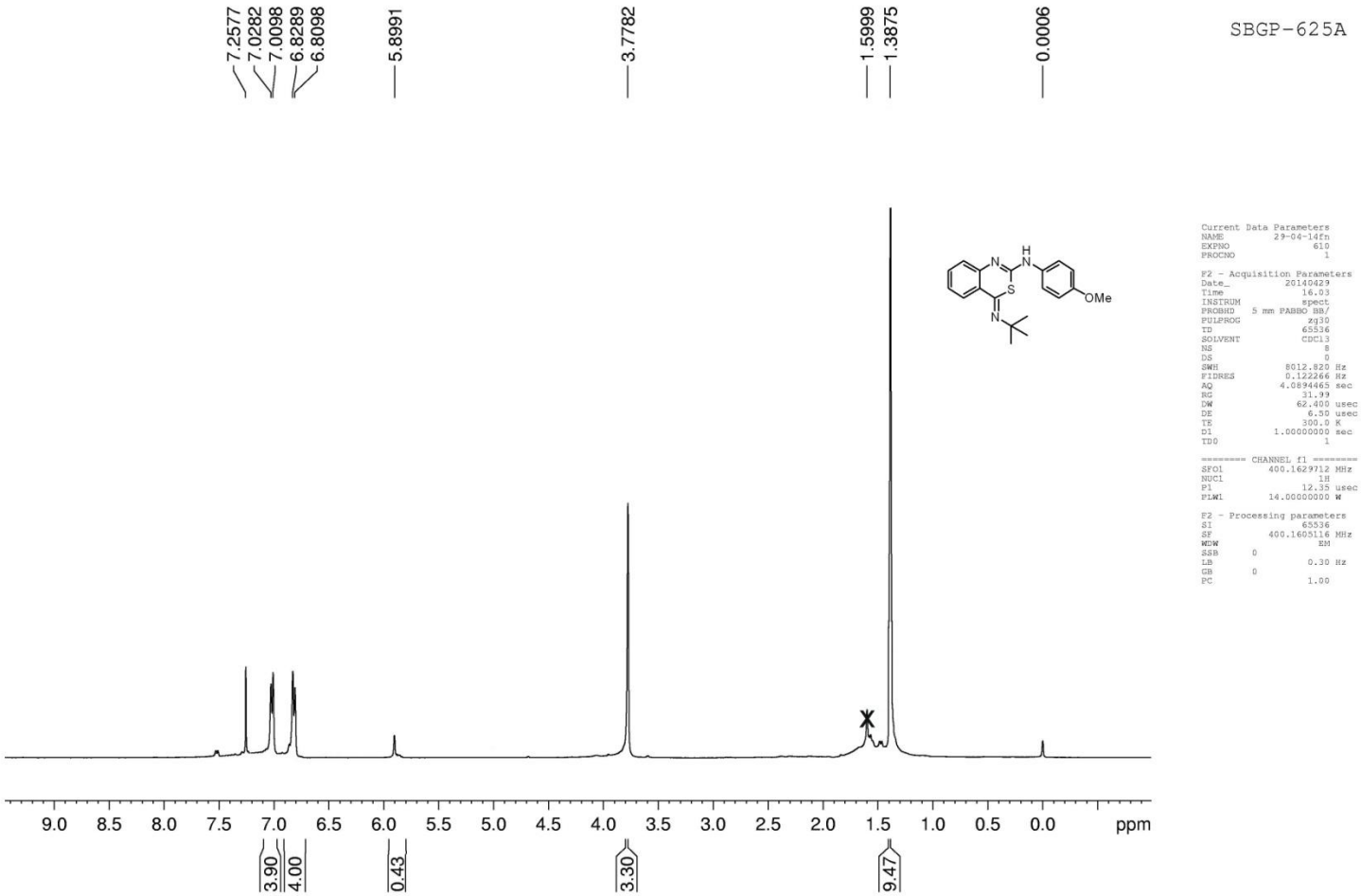


Fig: S-24[1]H spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bB)**

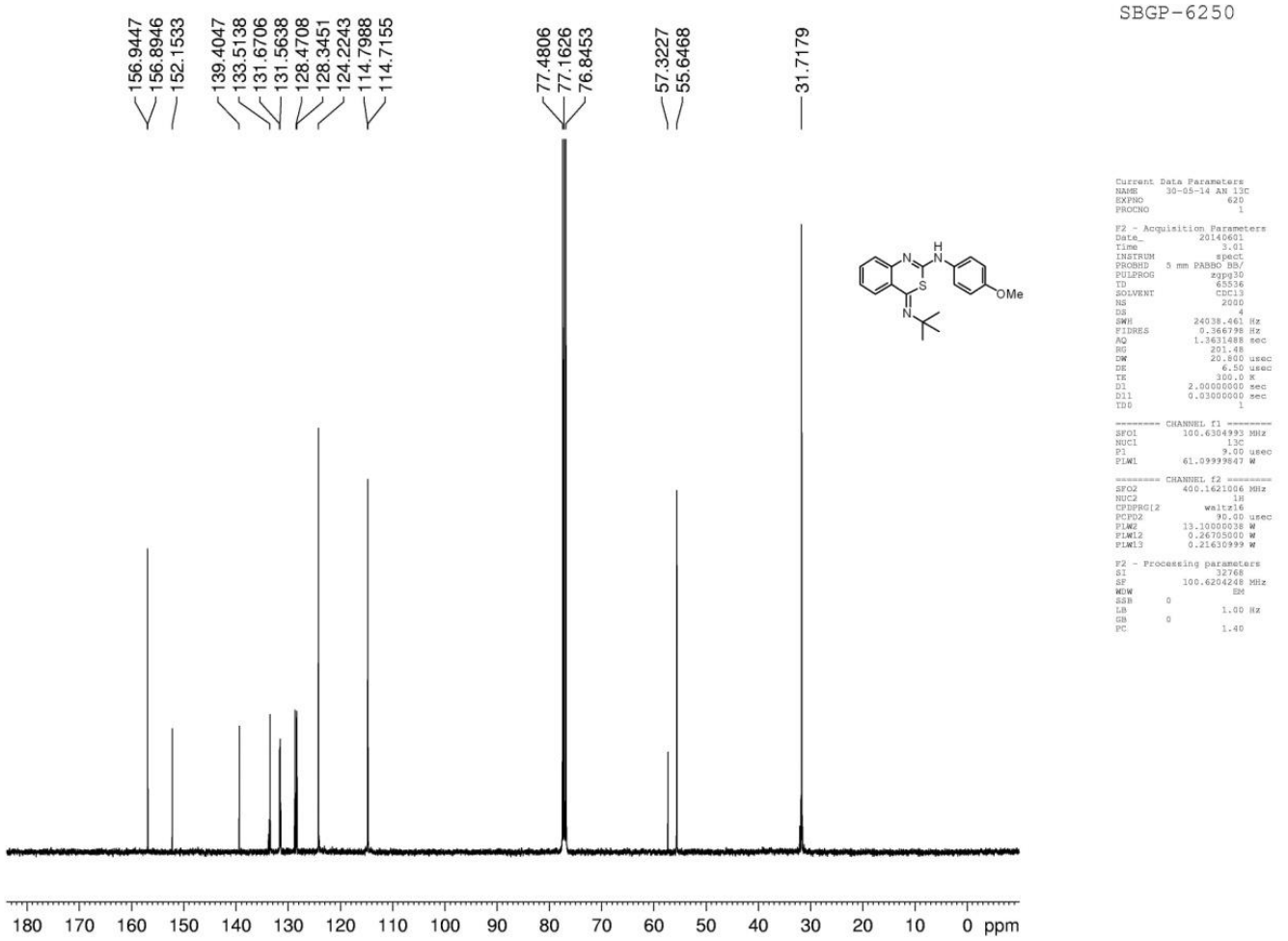


Fig: S-25 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(4-methoxyphenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bB)**

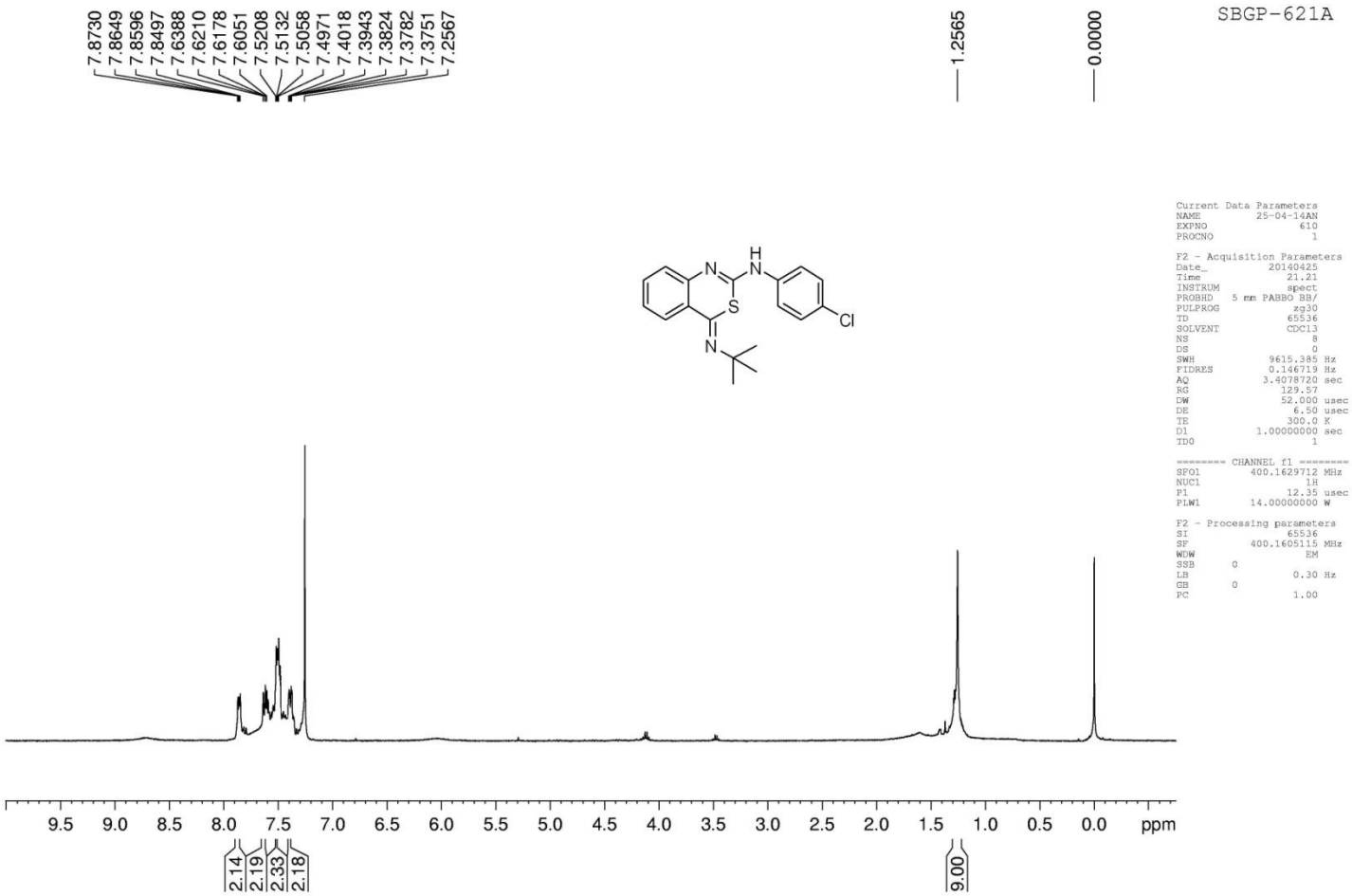


Fig: S-26 ^{1}H spectrum of (*Z*)-4-(*tert*-butylimino)-*N*-(4-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cB)**

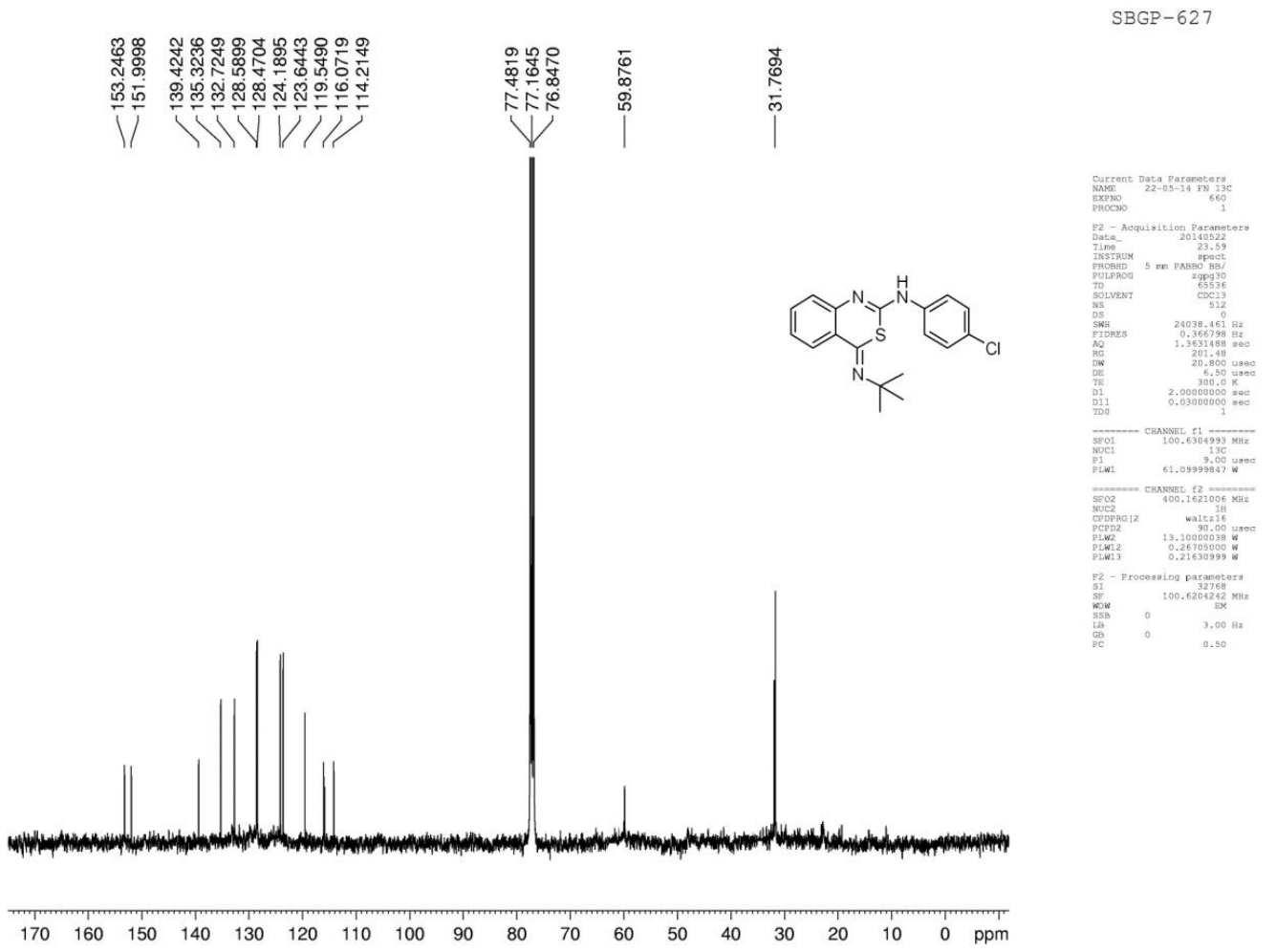


Fig: S-27 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(4-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cB)**

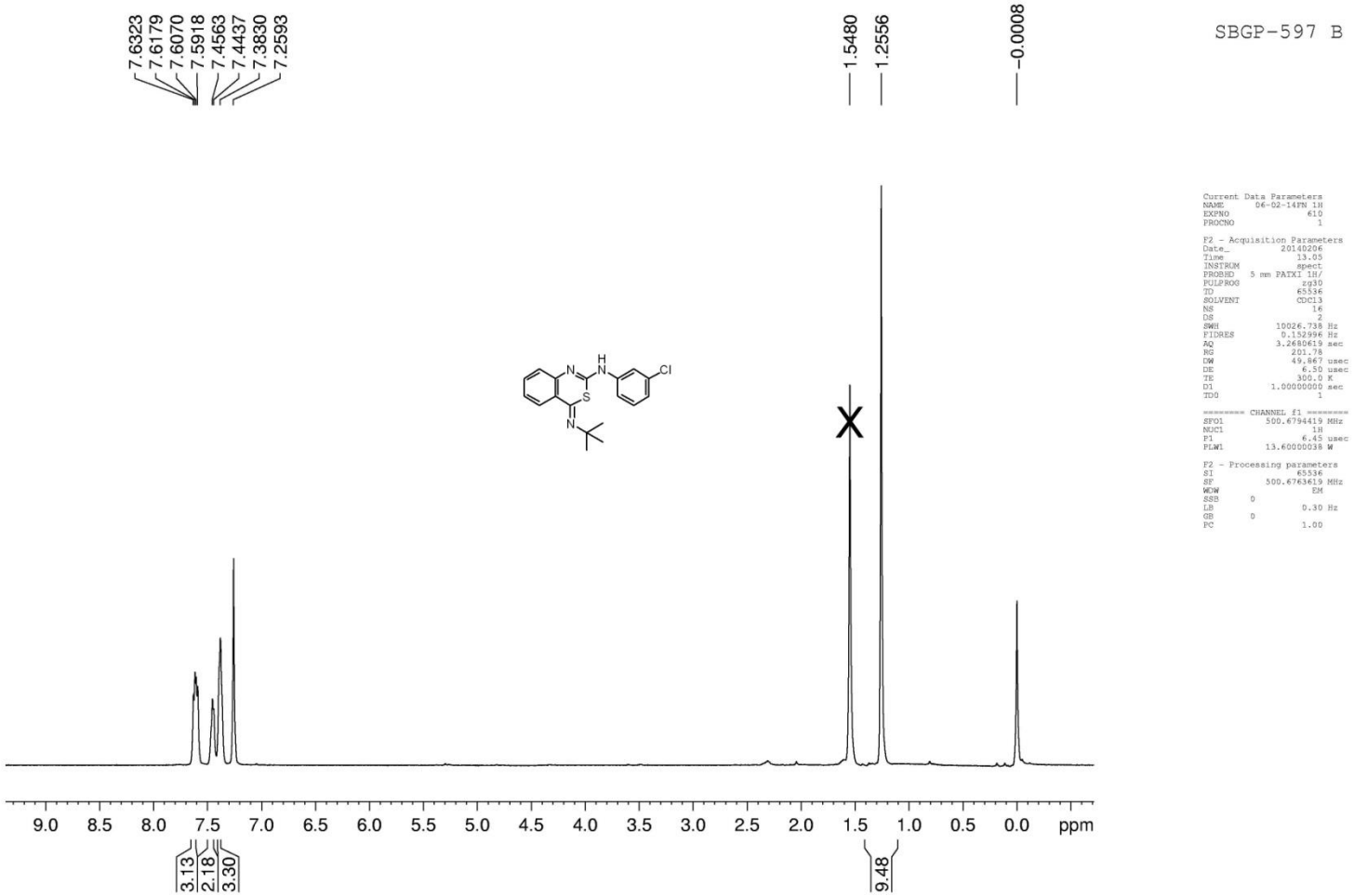


Fig: S-28 ^{1}H spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(3-chlorophenyl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3dB)**

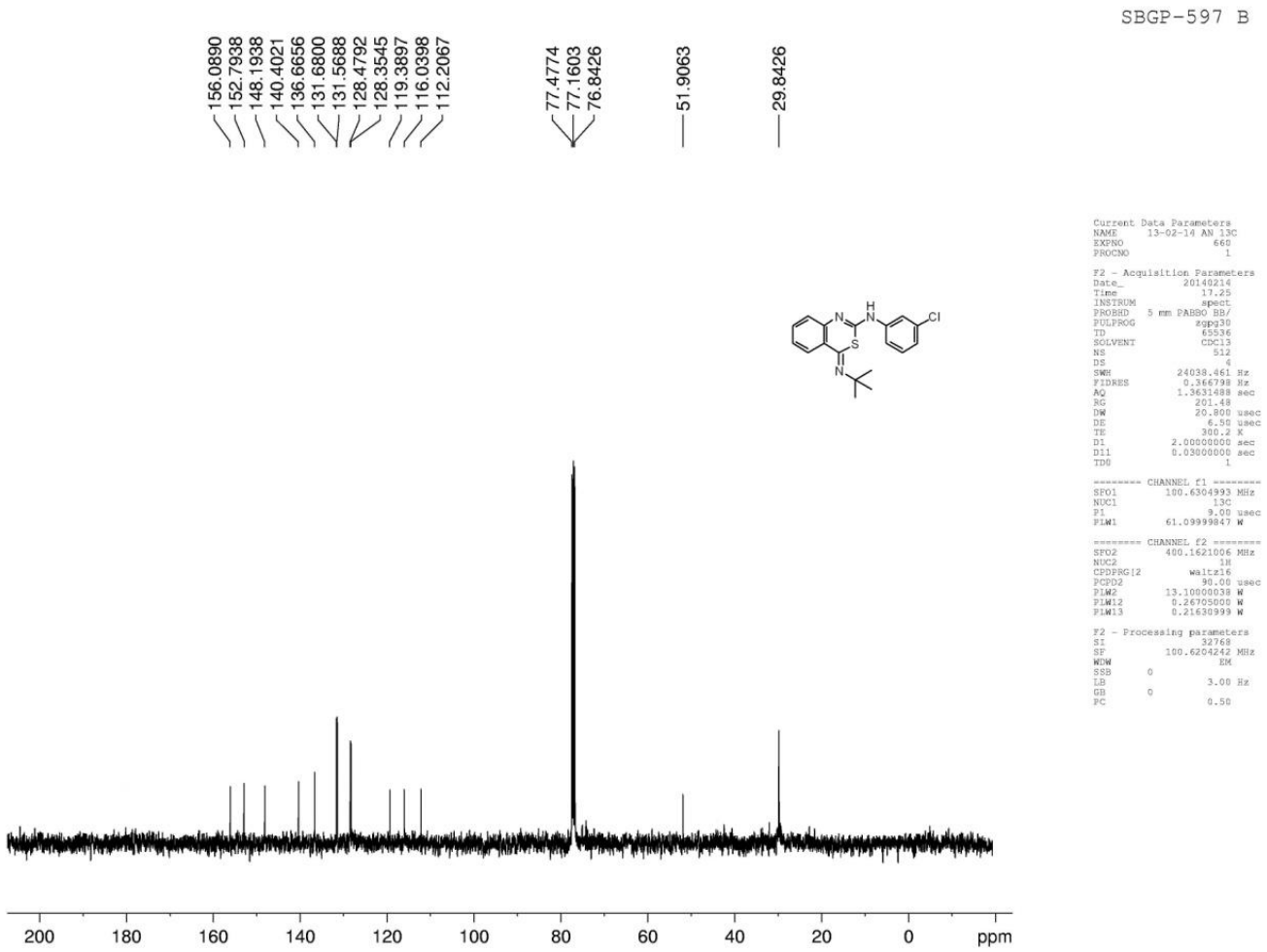


Fig: S-29 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(3-chlorophenyl)-*4H*-benzo[*d*][1,3]thiazin-2-amine **(3dB)**

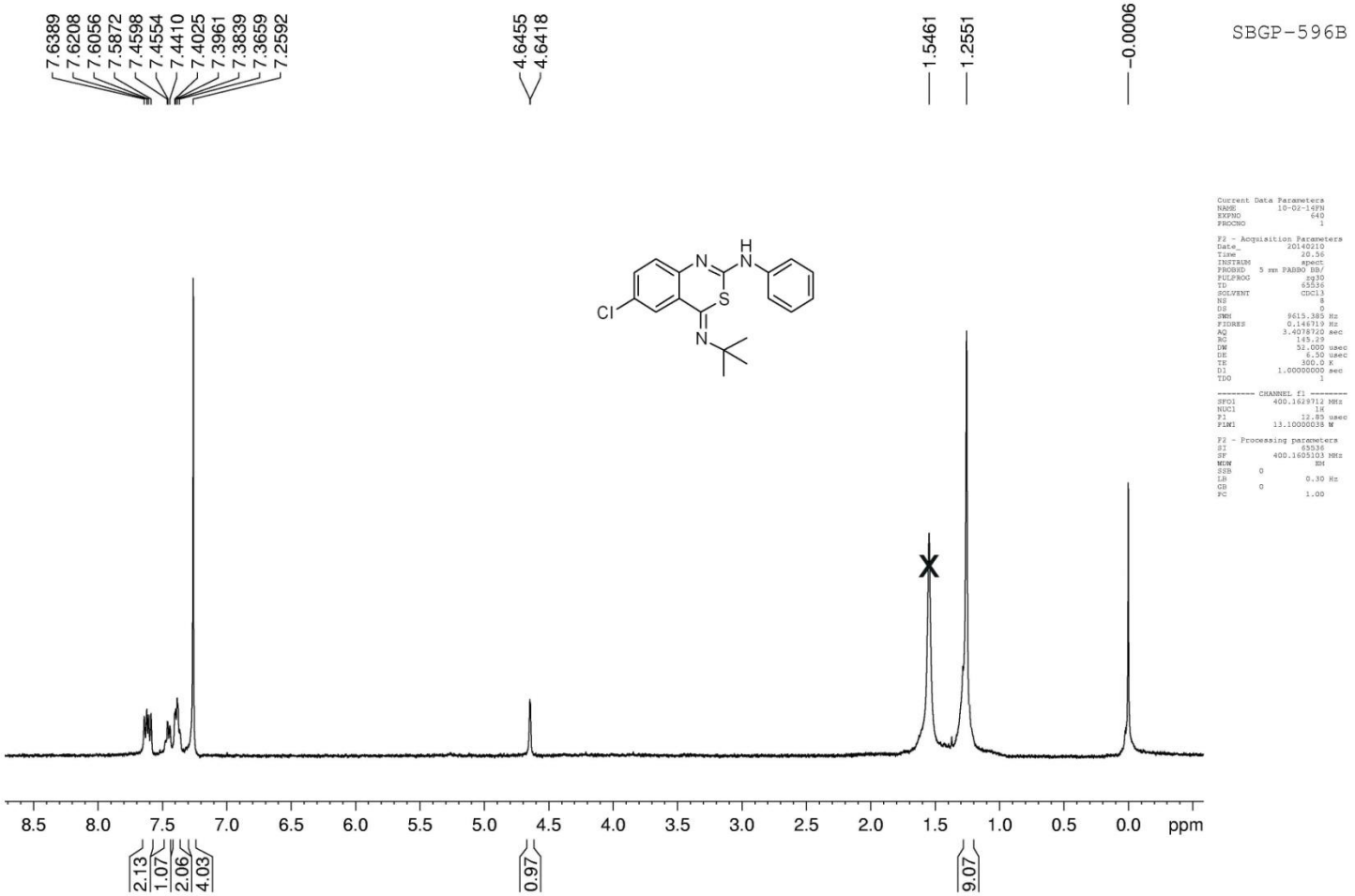


Fig:S-30 ^{1}H spectrum of (*Z*)-4-(*tert*-Butylimino)-6-chloro-*N*-phenyl-*4H*-benzo[*d*][1,3]thiazin-2-amine **(3kB)**

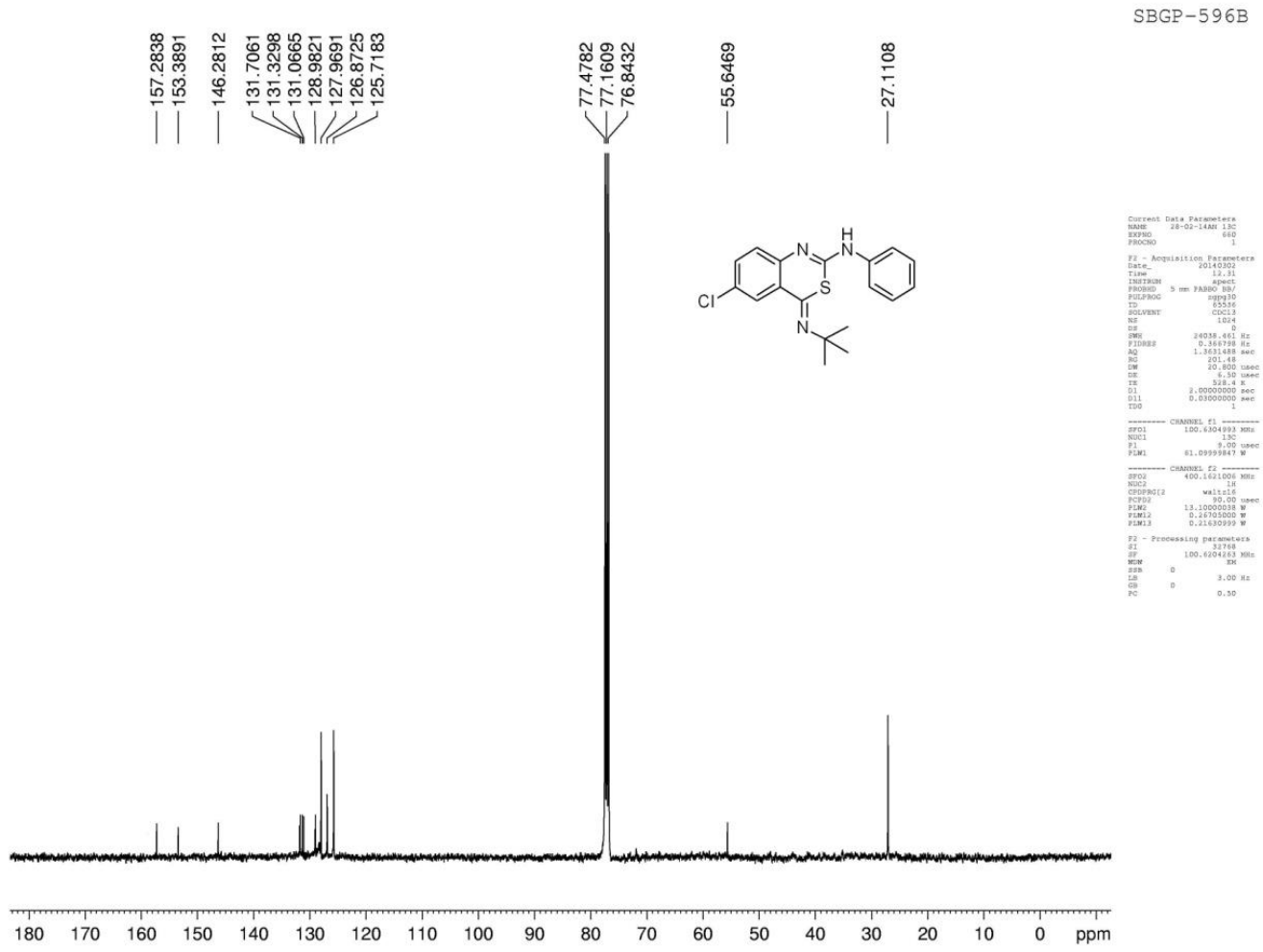


Fig: S-31 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-6-chloro-*N*-phenyl-*4H*-benzo[*d*][1,3]thiazin-2-amine **(3kB)**

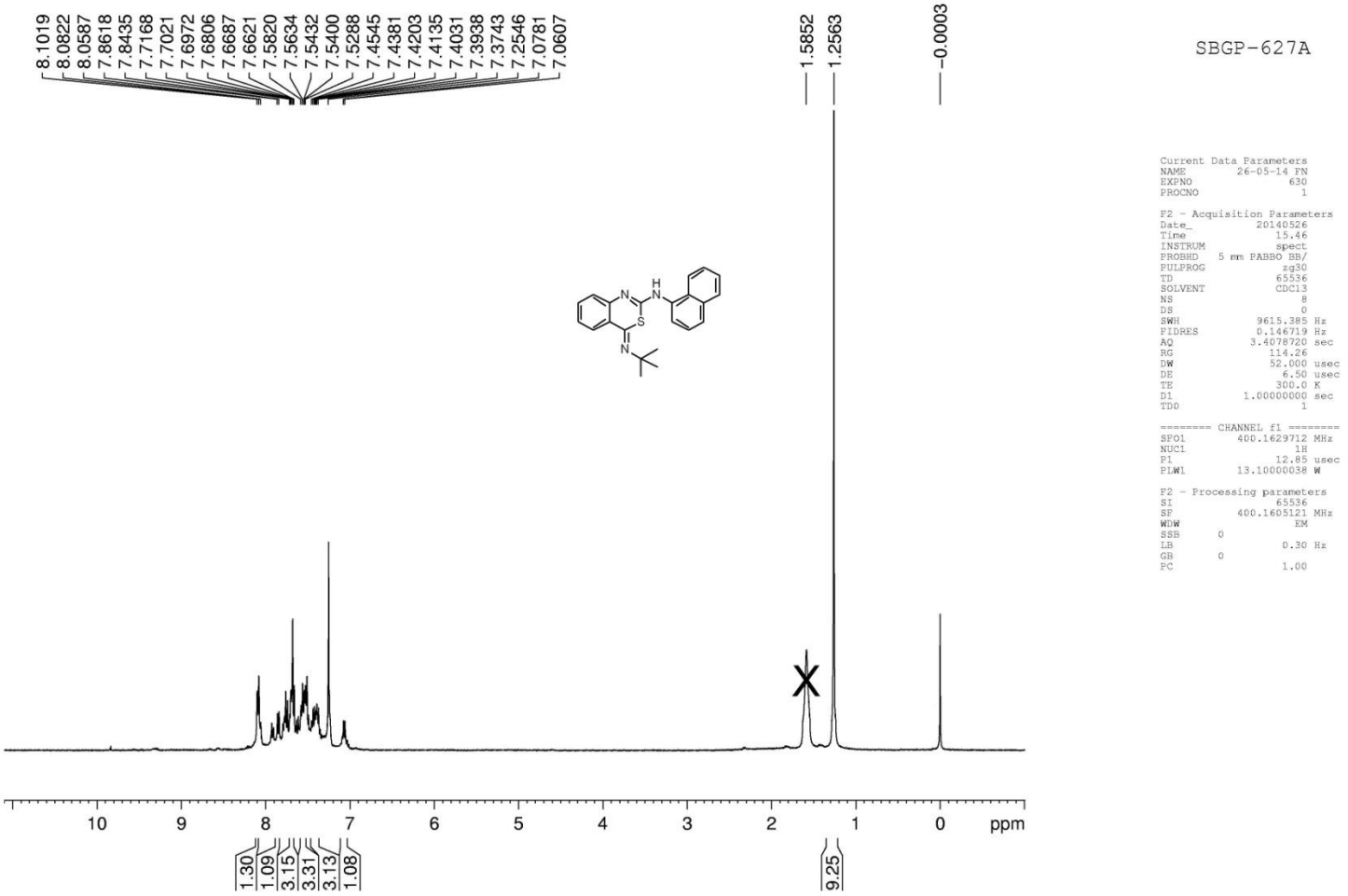


Fig: S-32 ^{1}H spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eB)**

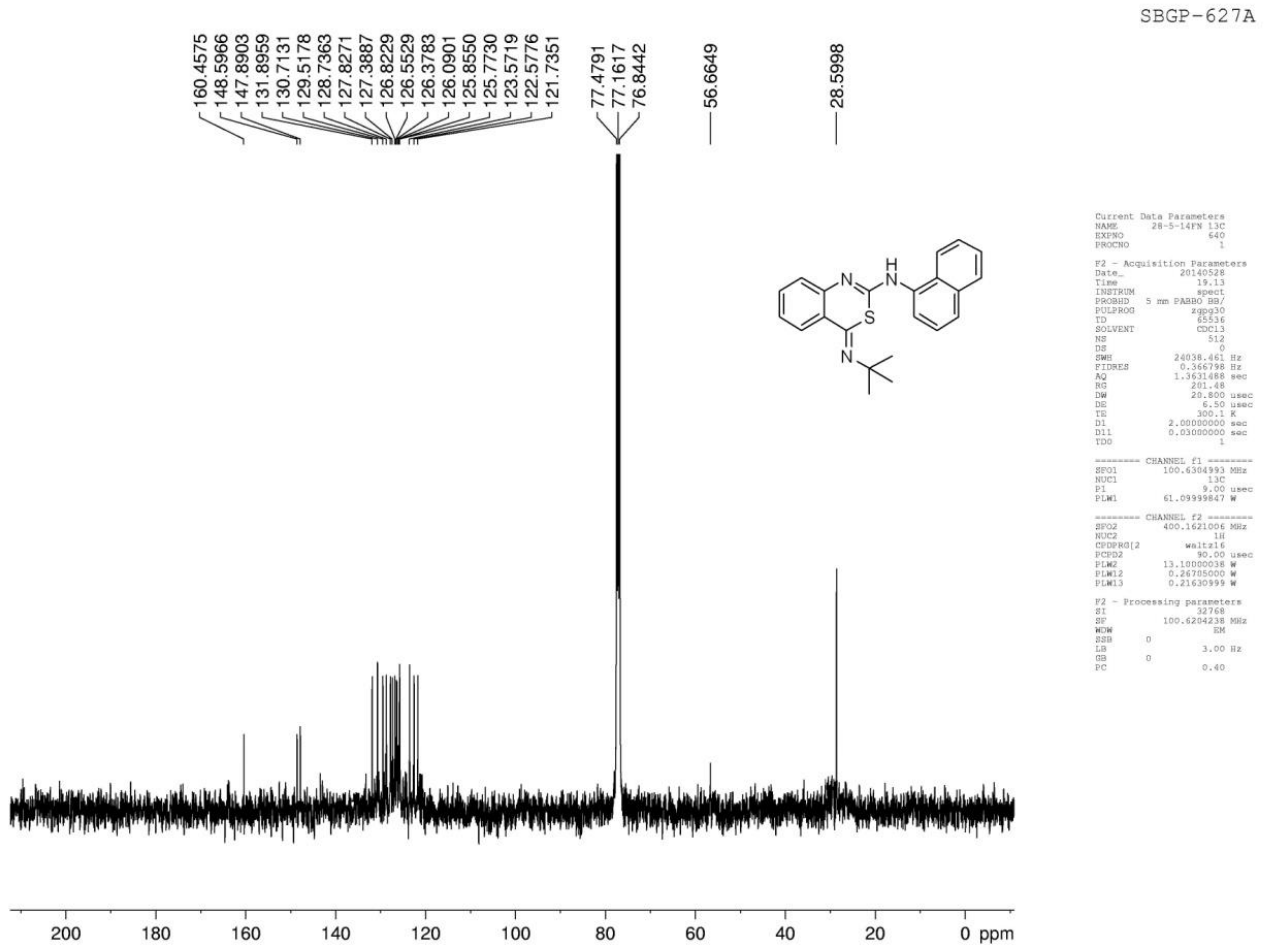


Fig: S-33 ^{13}C spectrum of (*Z*)-4-(*tert*-Butylimino)-*N*-(naphthalen-1-yl)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eB)**

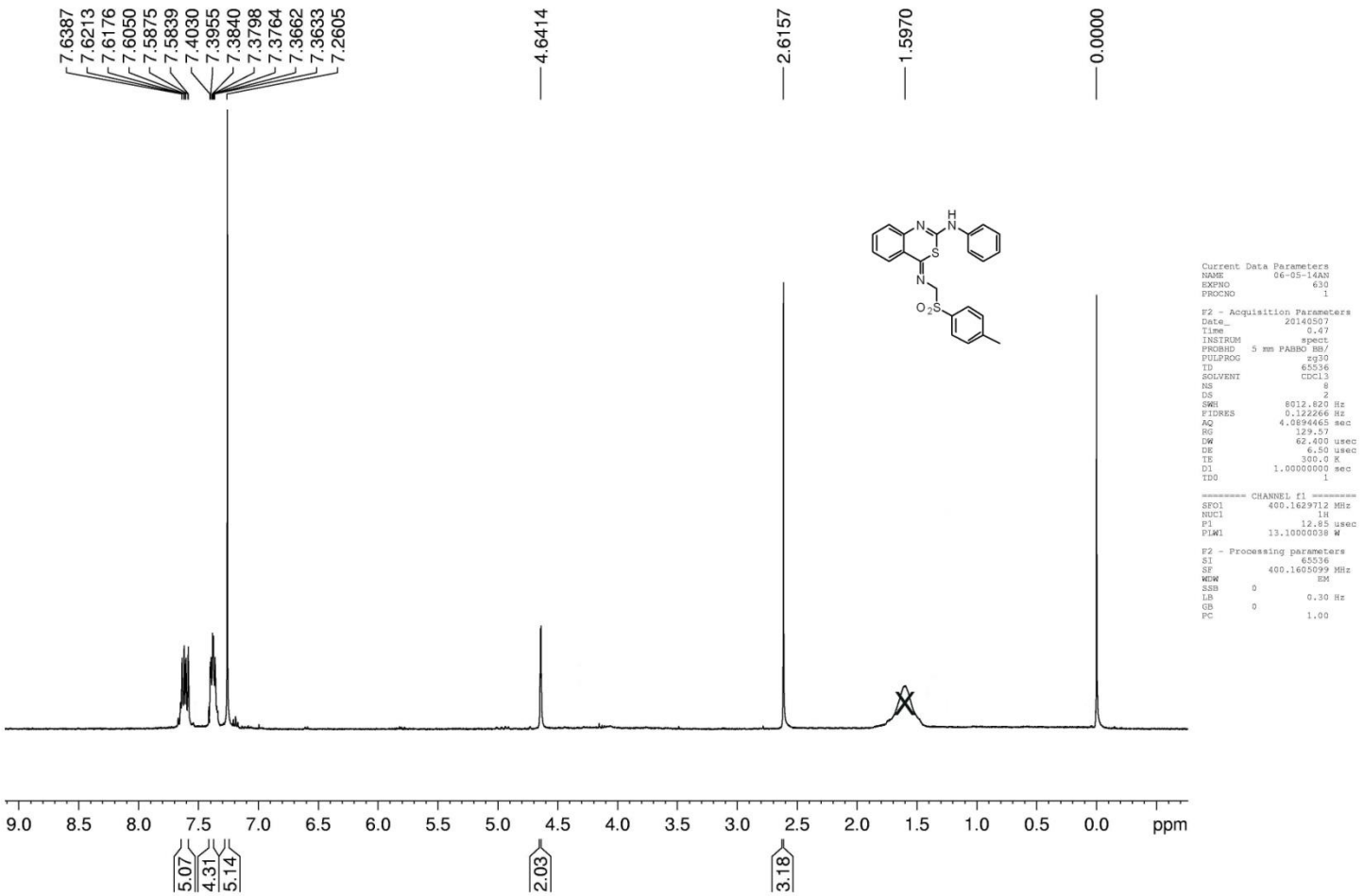


Fig:S-34 ^{1}H spectrum of (*Z*)-*N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aC)**

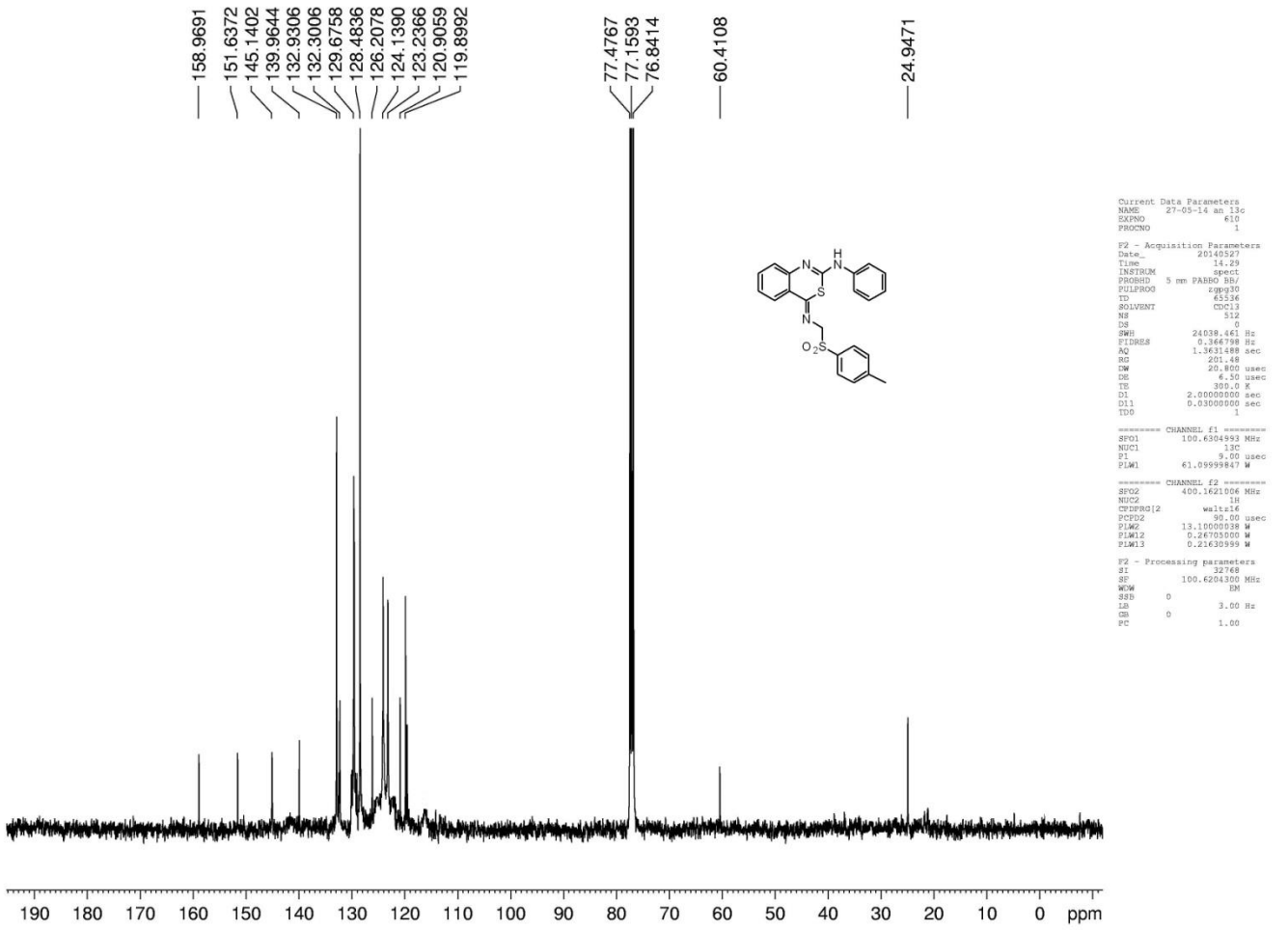


Fig: S-35 ^{13}C spectrum of (*Z*)-*N*-Phenyl-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aC)**

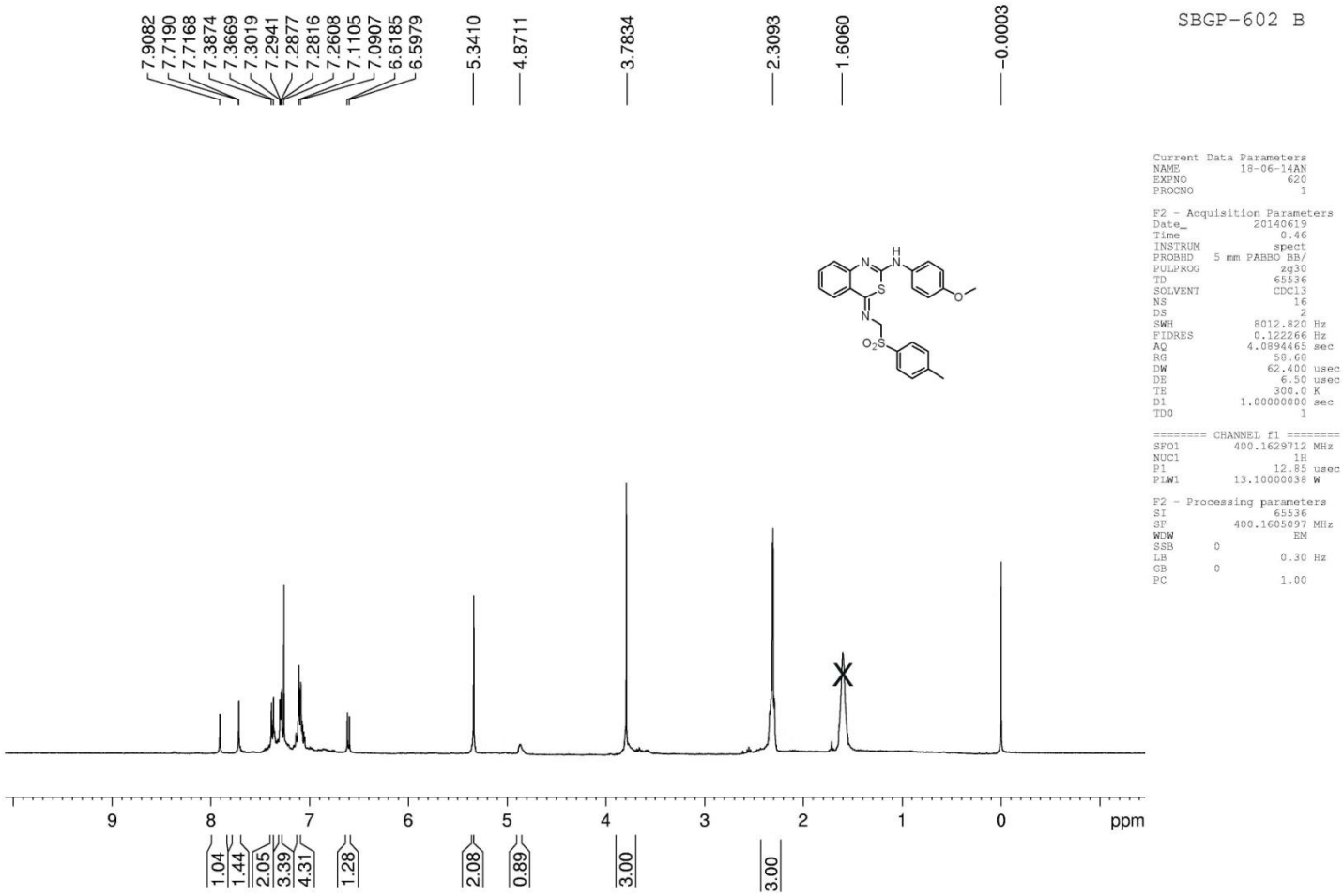


Fig: S-36 ^{1}H spectrum of (*Z*)-*N*-(4-Methoxyphenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bC)**

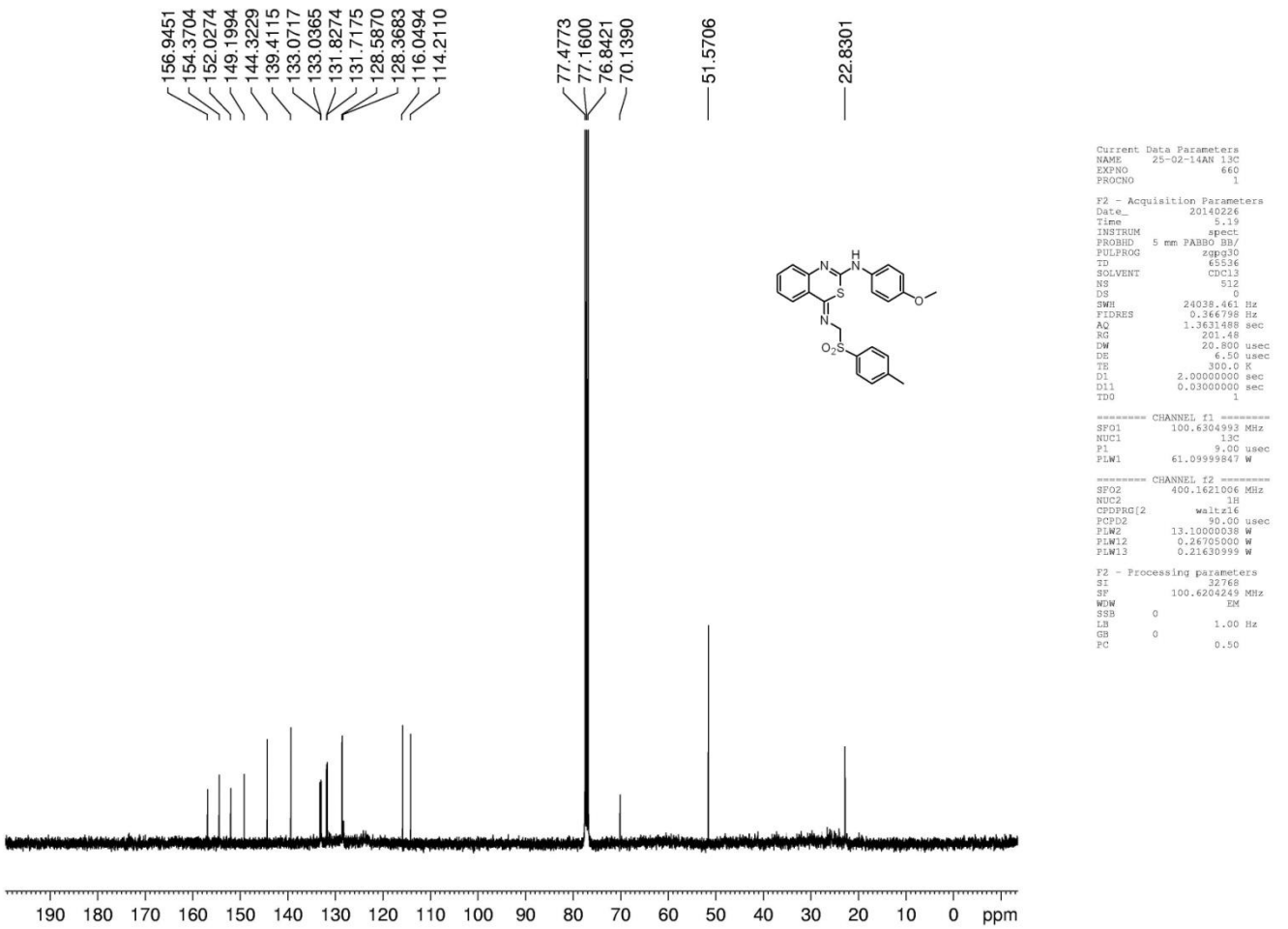


Fig: S-37 ^{13}C spectrum of (*Z*)-*N*-(4-Methoxyphenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3bC)**

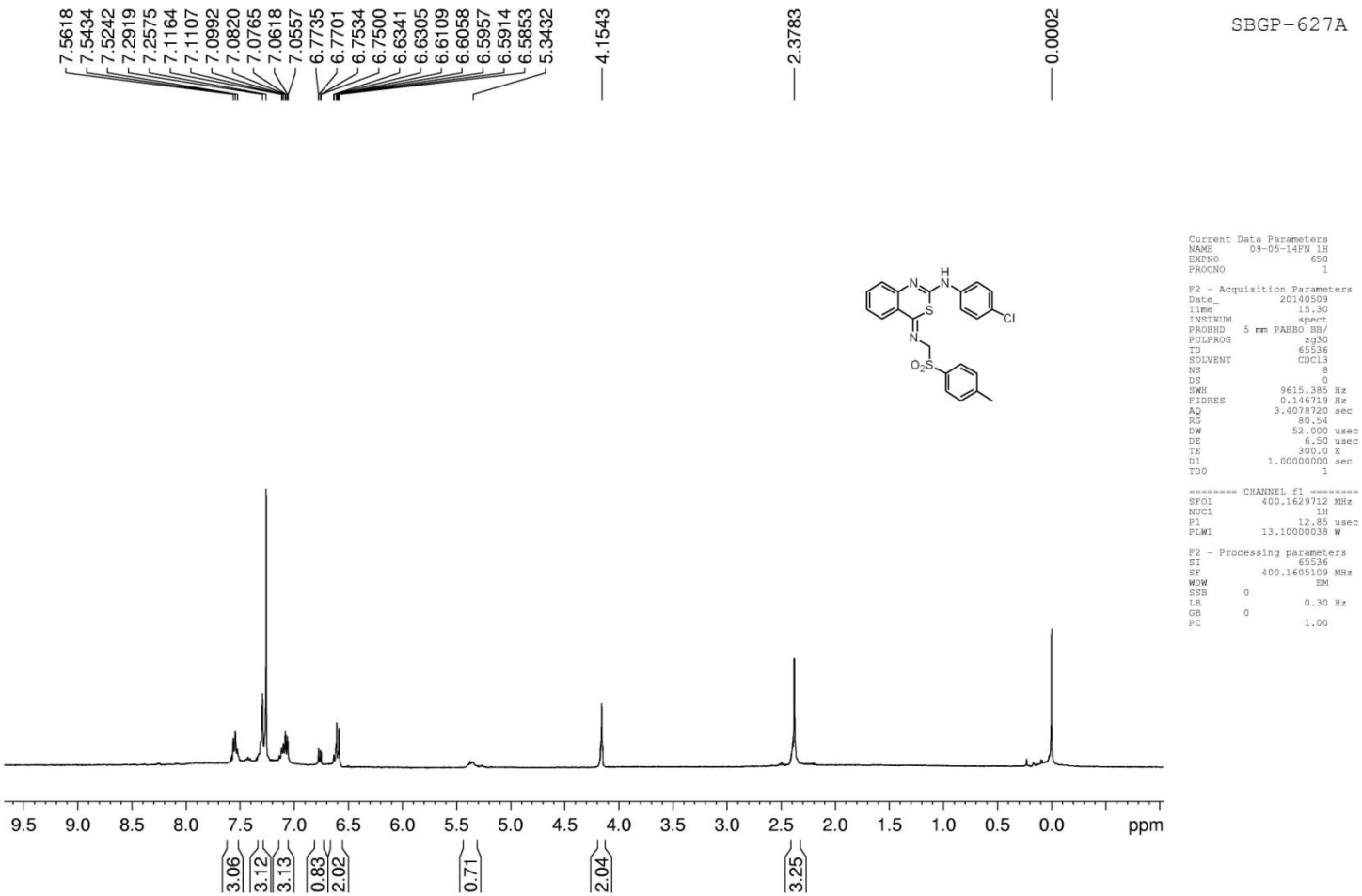


Fig:S-38 ^{1}H spectrum of (*Z*)-*N*-(4-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cC)**

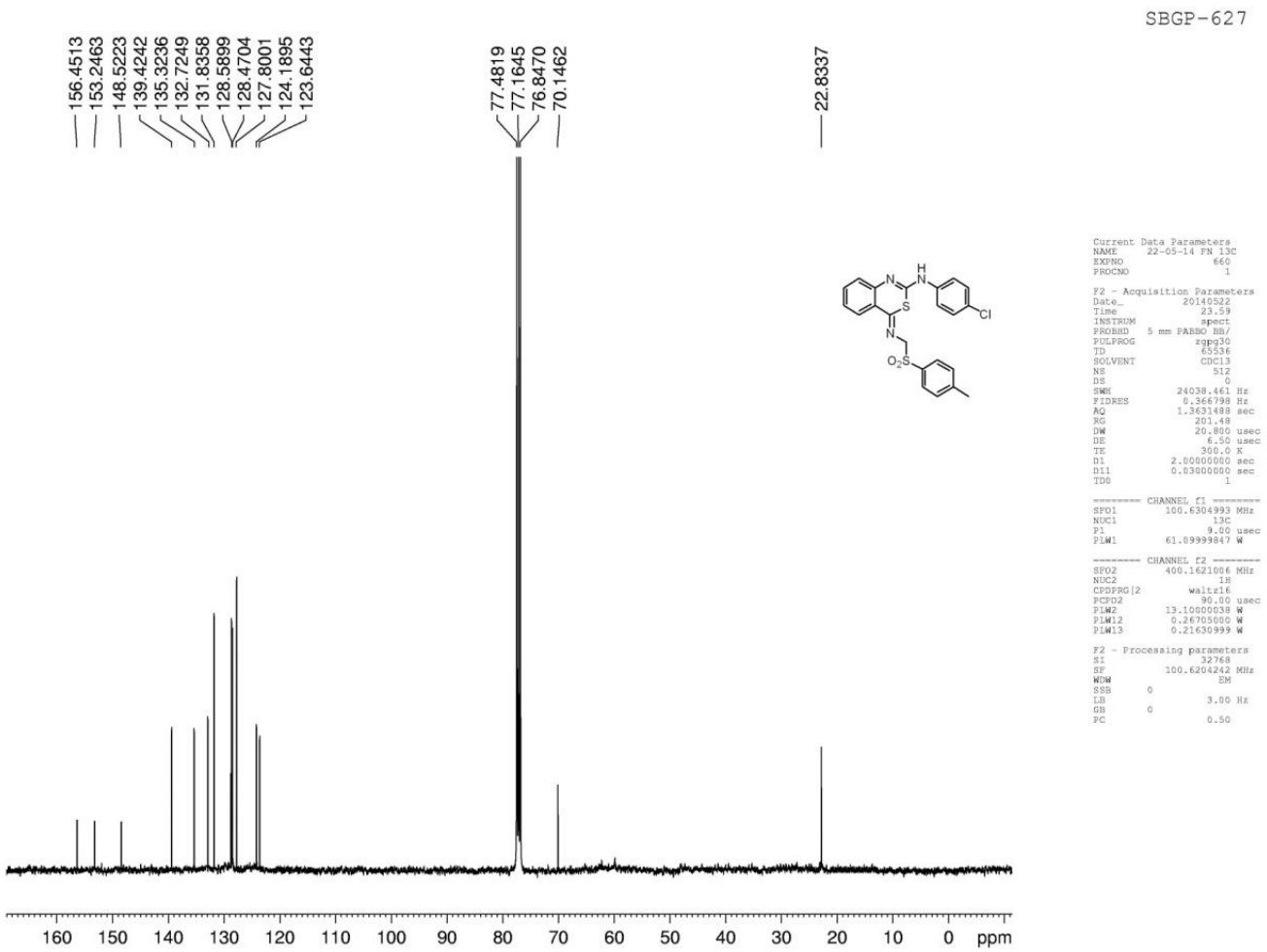


Fig: S-39 ^{13}C spectrum of (*Z*)-*N*-(4-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cC)**

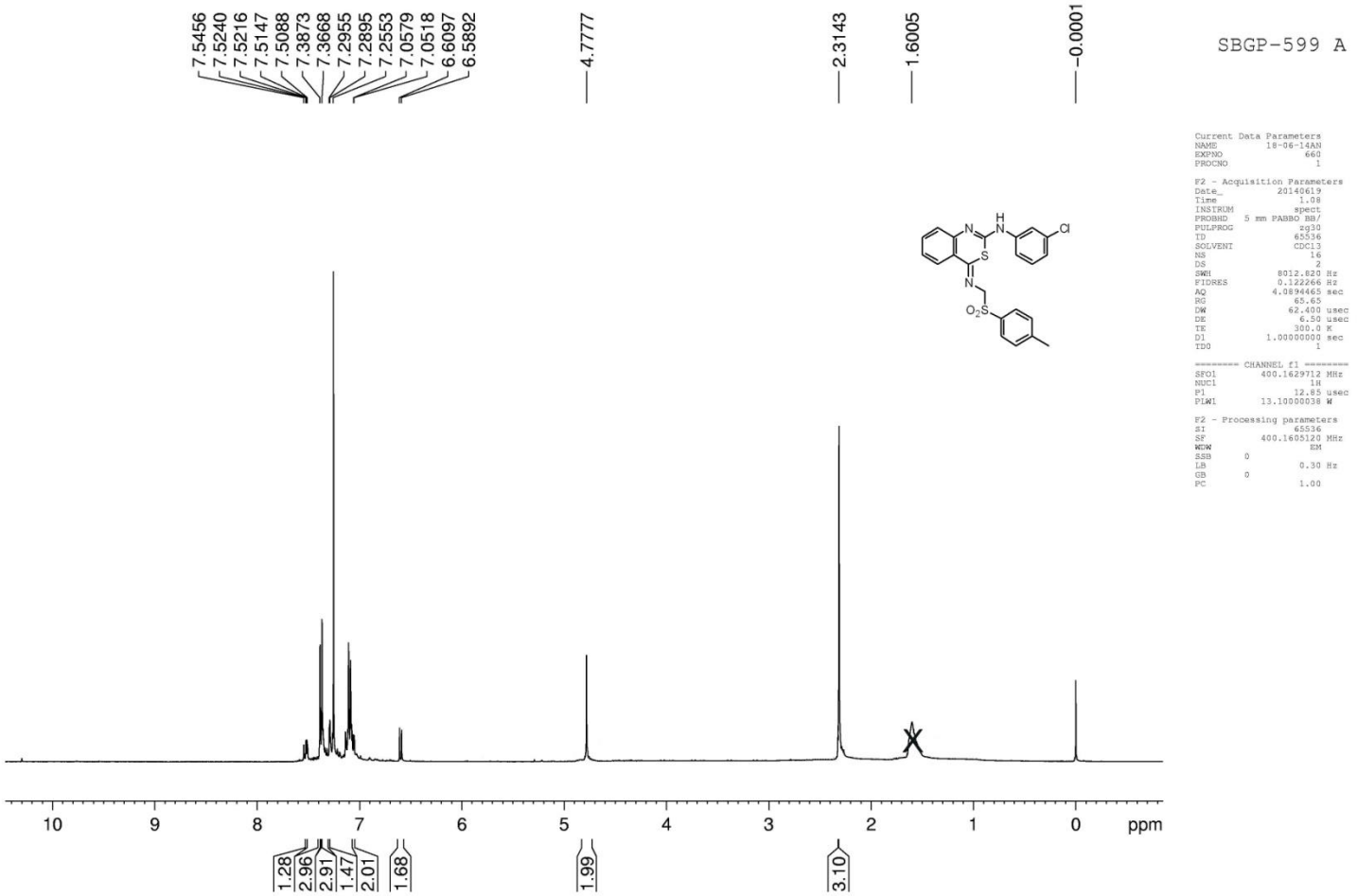
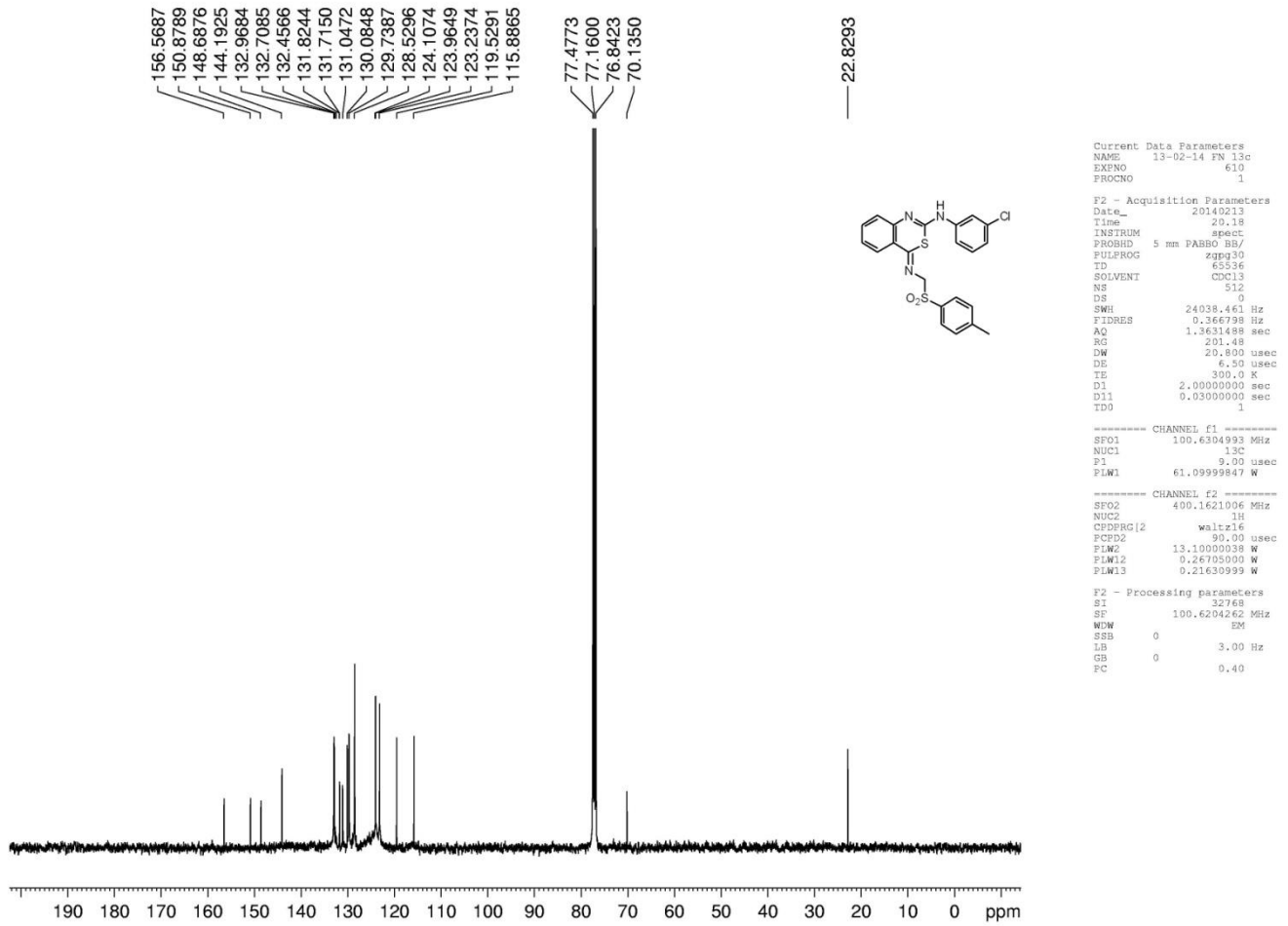


Fig: S-40 ^{1}H spectrum of (*Z*)-*N*-(3-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3dC)**

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PROCNO               1

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PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS                512
DS                  0
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ           1.3631488 sec
RG              201.48
DW              20.800 usec
DE               6.50 usec
TE              300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       100.6304993 MHz
NUC1              13C
P1               9.00 usec
PLW1       61.09999847 W

======== CHANNEL f2 ========
SFO2       400.1621006 MHz
NUC2               1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2       13.10000038 W
PLW12       0.26705000 W
PLW13       0.21630999 W

F2 - Processing parameters
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SF         100.6204262 MHz
WDW                EM
SSB      0
LB               3.00 Hz
GB       0
PC               0.40
```

Fig: S-41 ^{13}C spectrum of (*Z*)-*N*-(3-Chlorophenyl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3dC)**

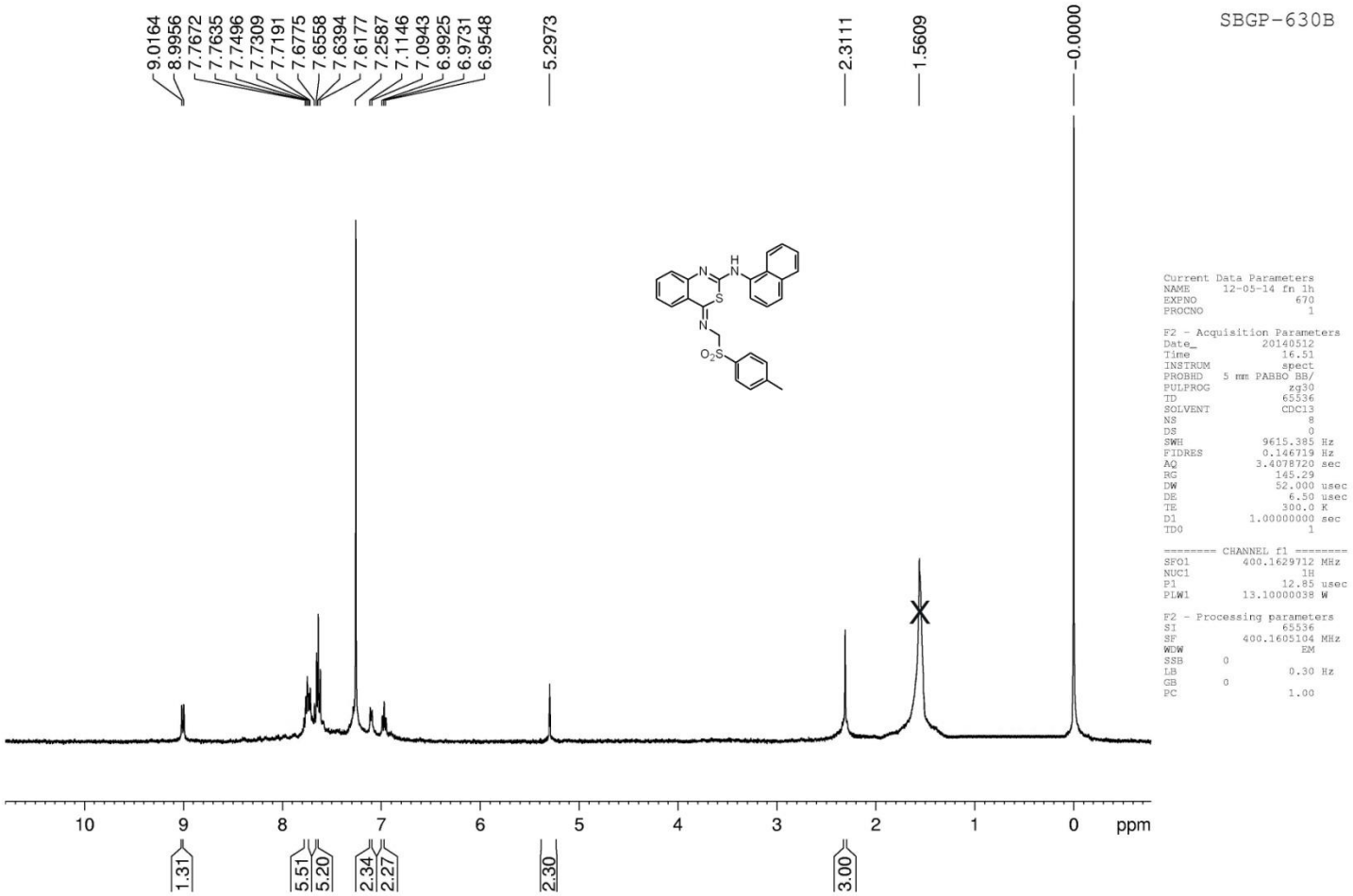


Fig: S-42 ^{1}H spectrum of (*Z*)-*N*-(naphthalen-1-yl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eC)**

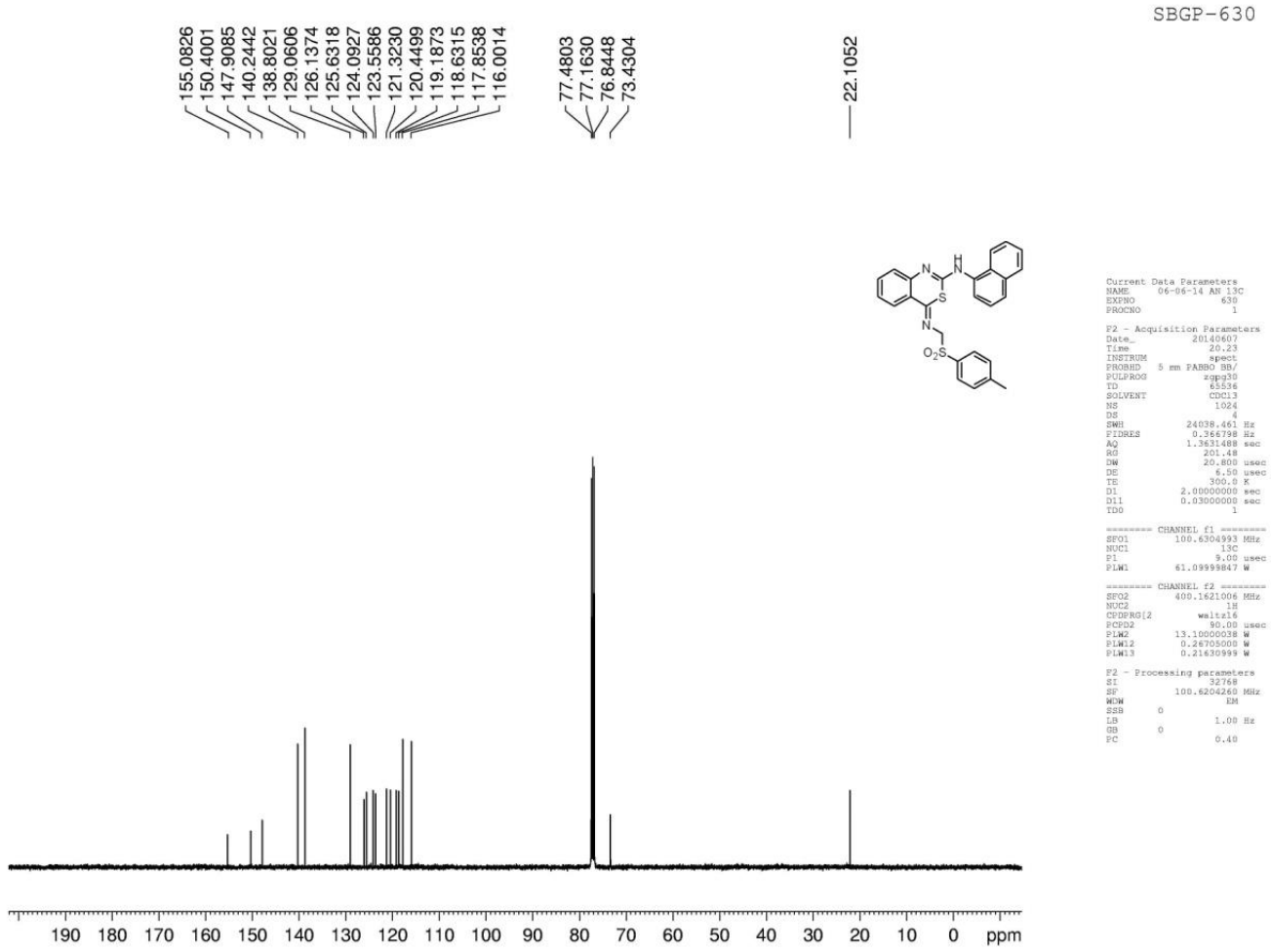


Fig: S-43 ^{13}C spectrum of (*Z*)-*N*-(Naphthalen-1-yl)-4-(tosylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3eC)**

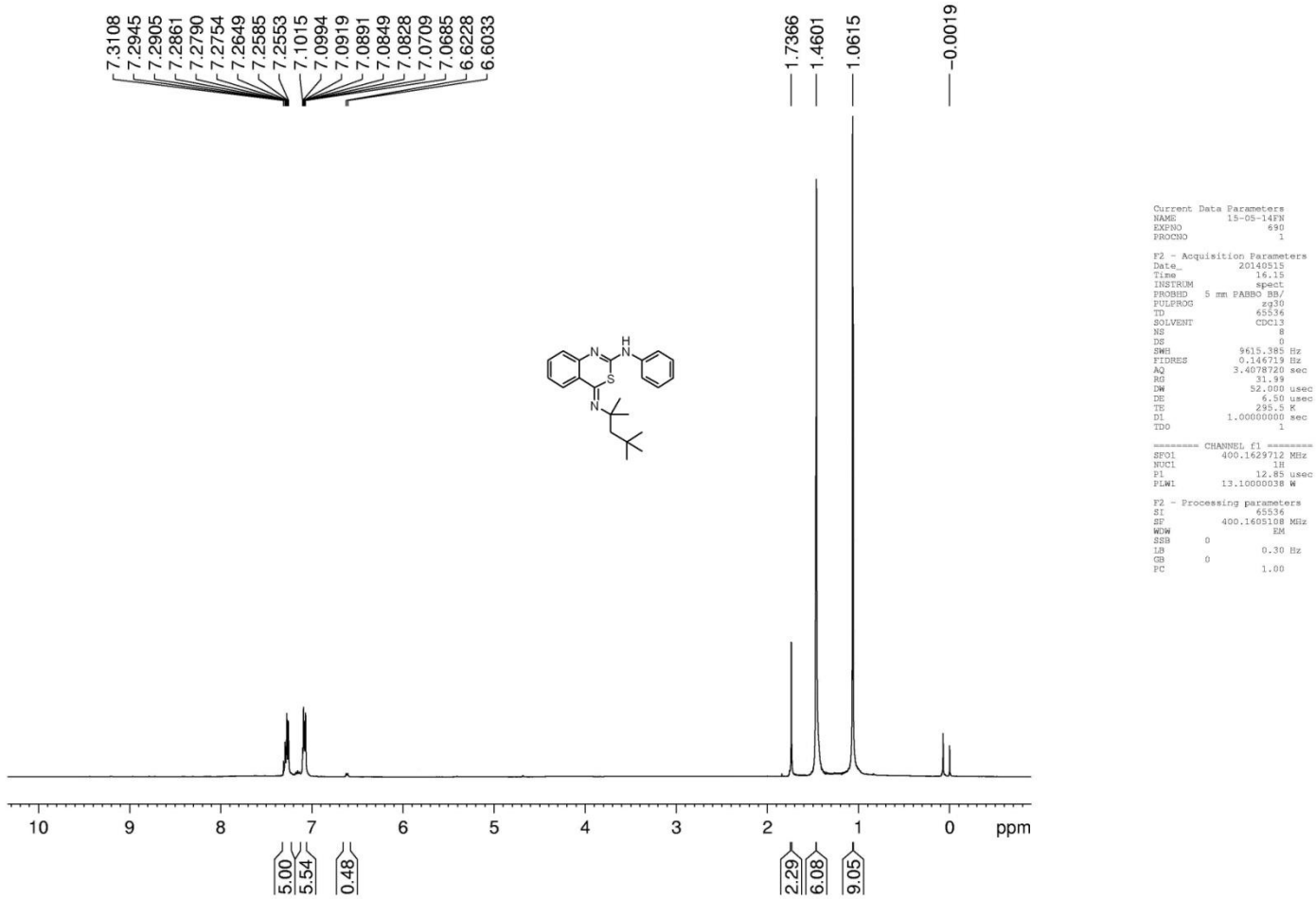


Fig: S-44 ^{1}H spectrum of (*Z*)-*N*-Phenyl-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aD)**

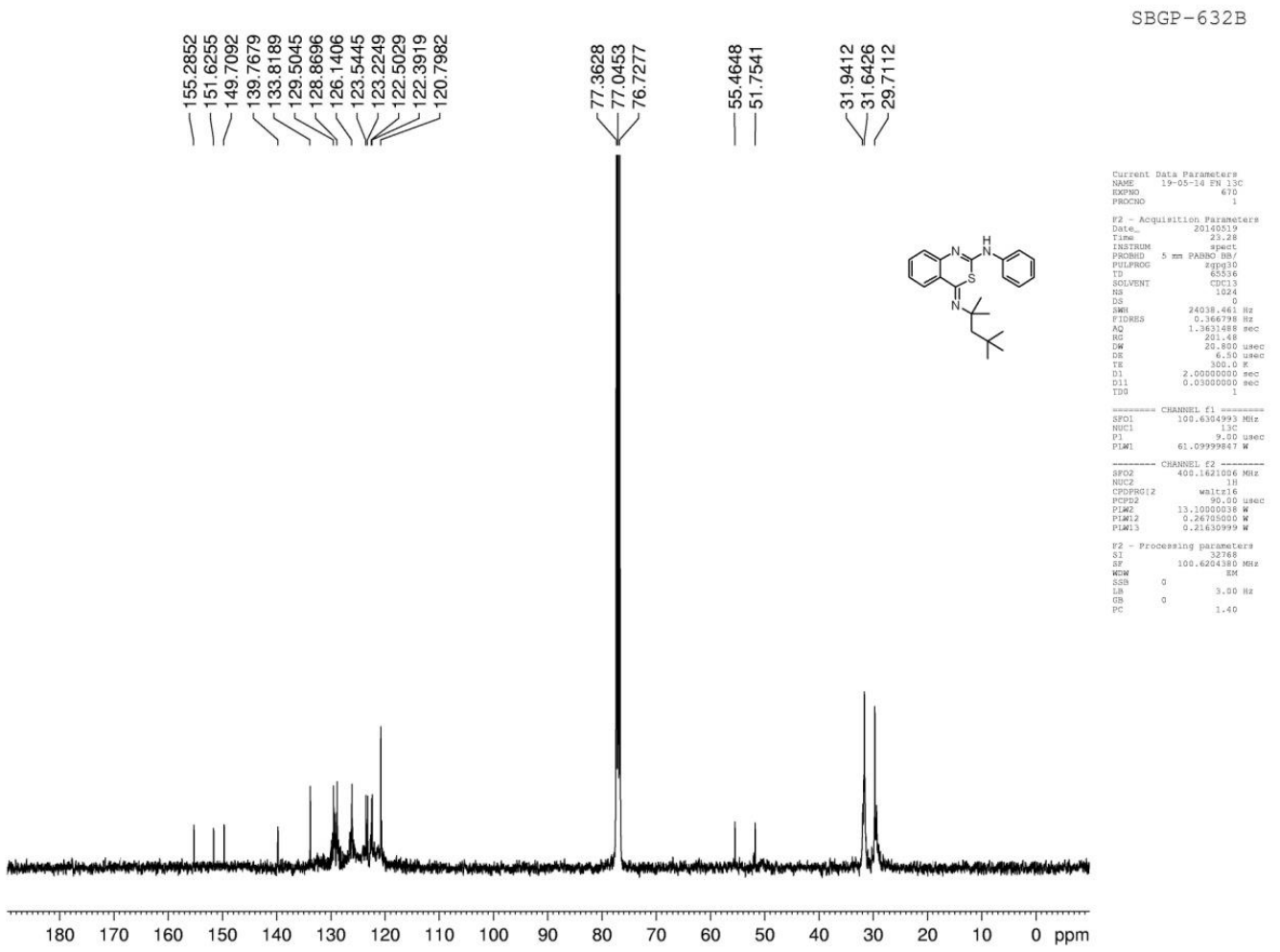


Fig: S-45 ^{13}C spectrum of (Z)-N-phenyl-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[d][1,3]thiazin-2-amine **(3aD)**

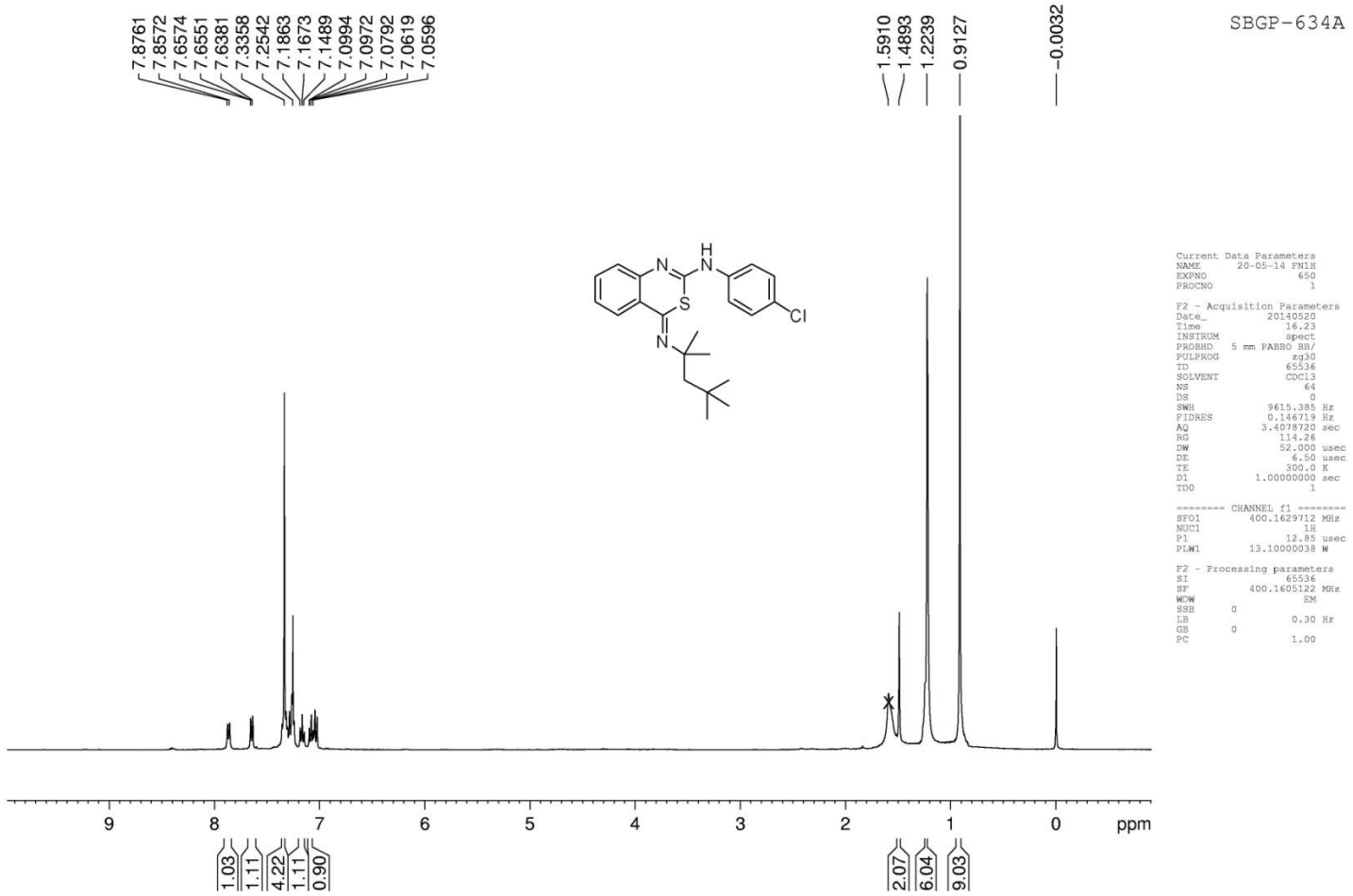


Fig: S-46 ^{1}H spectrum of (*Z*)-*N*-(4-Chlorophenyl)-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cD)**

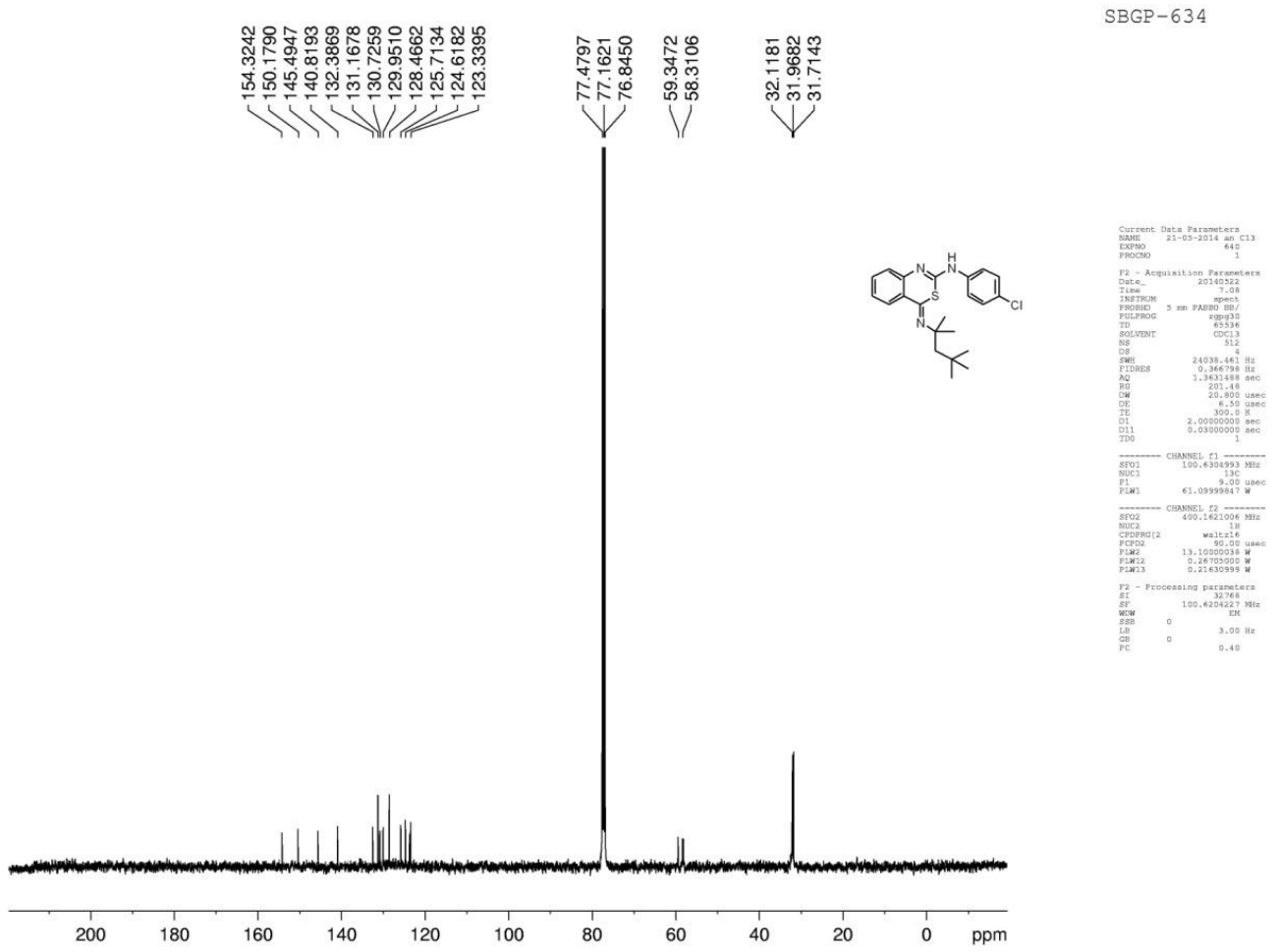


Fig: S-47 ^{13}C spectrum of (*Z*)-*N*-(4-Chlorophenyl)-4-(2,4,4-trimethylpentan-2-ylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cD)**

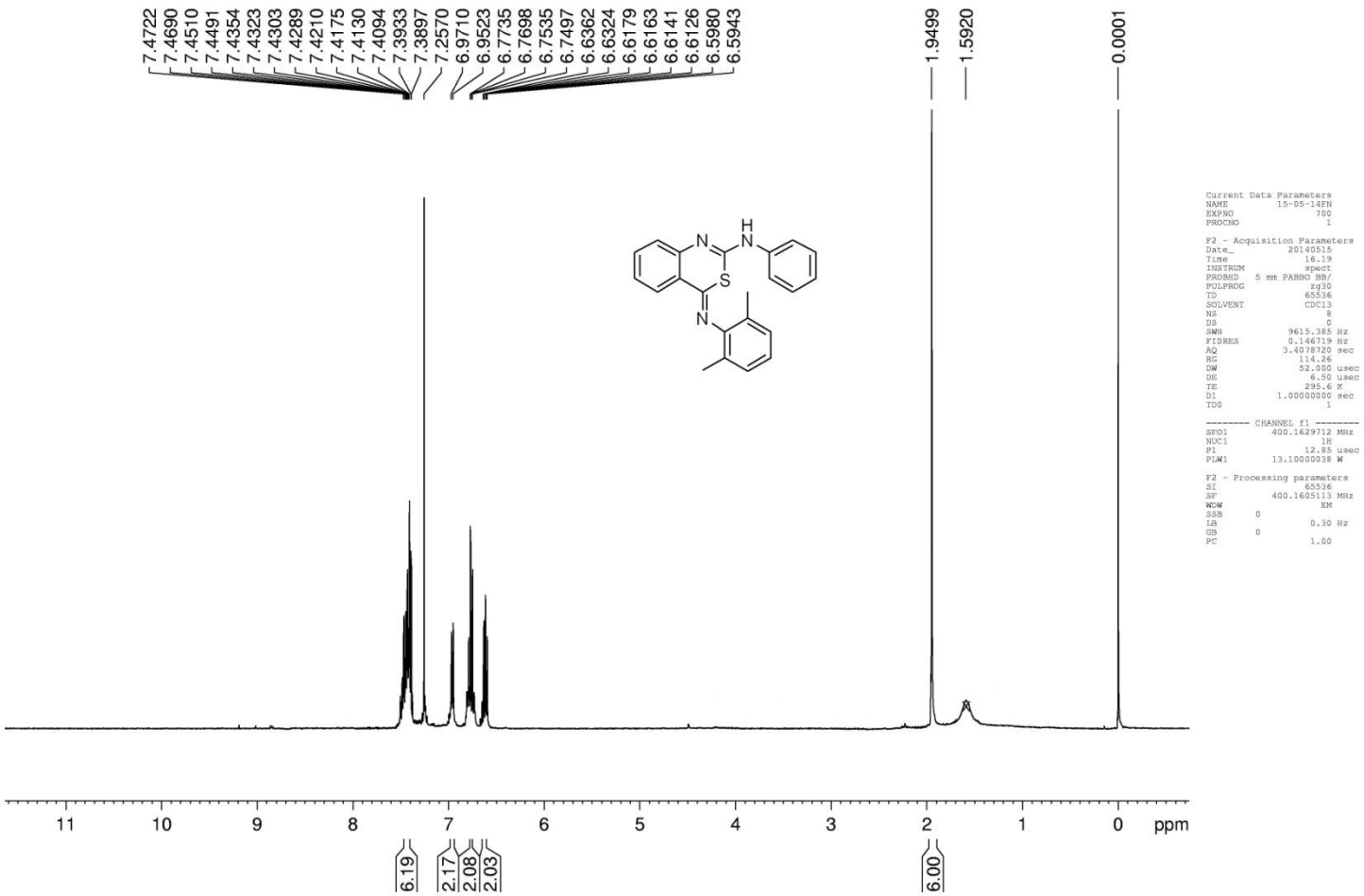


Fig:S-48 ^{1}H spectrum of (*Z*)-4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aE)**

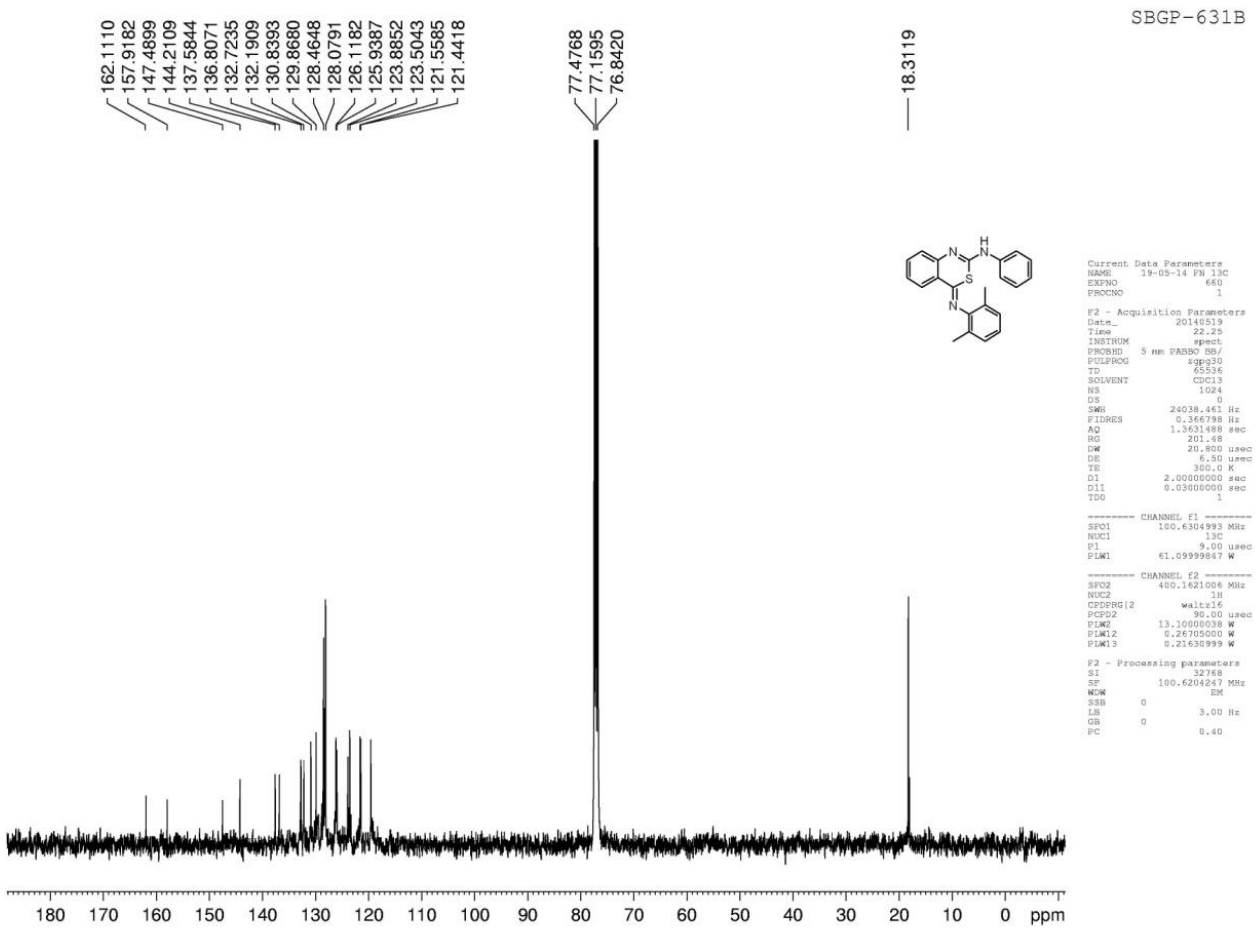


Fig: S-49 ^{13}C spectrum of (*Z*)-4-(2,6-Dimethylphenylimino)-*N*-phenyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3aE)**

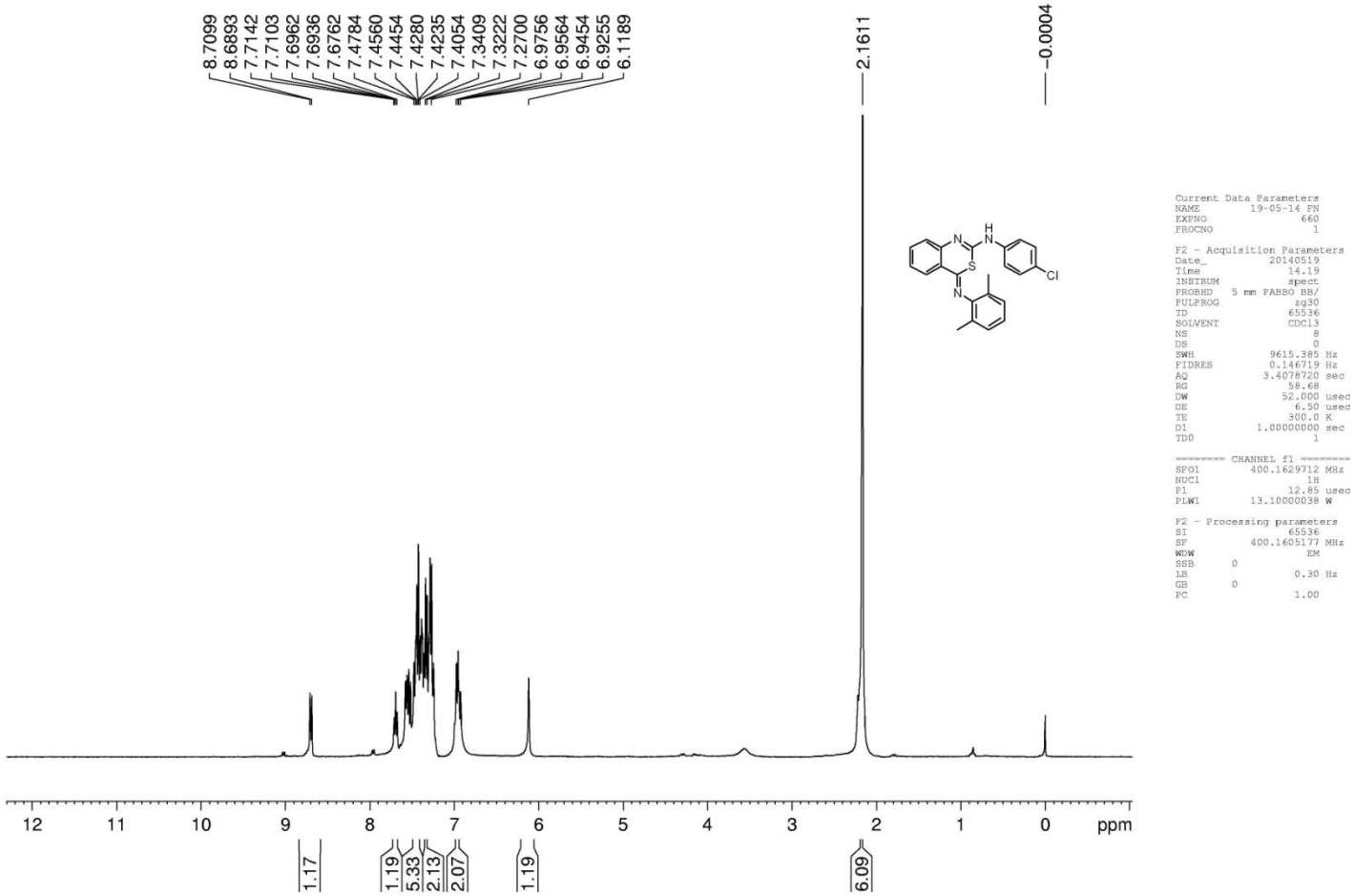


Fig: S-50 ^{1}H spectrum of **(*Z*)-*N*-**(4-Chlorophenyl)-4-(2, 6-dimethylphenylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cE)**

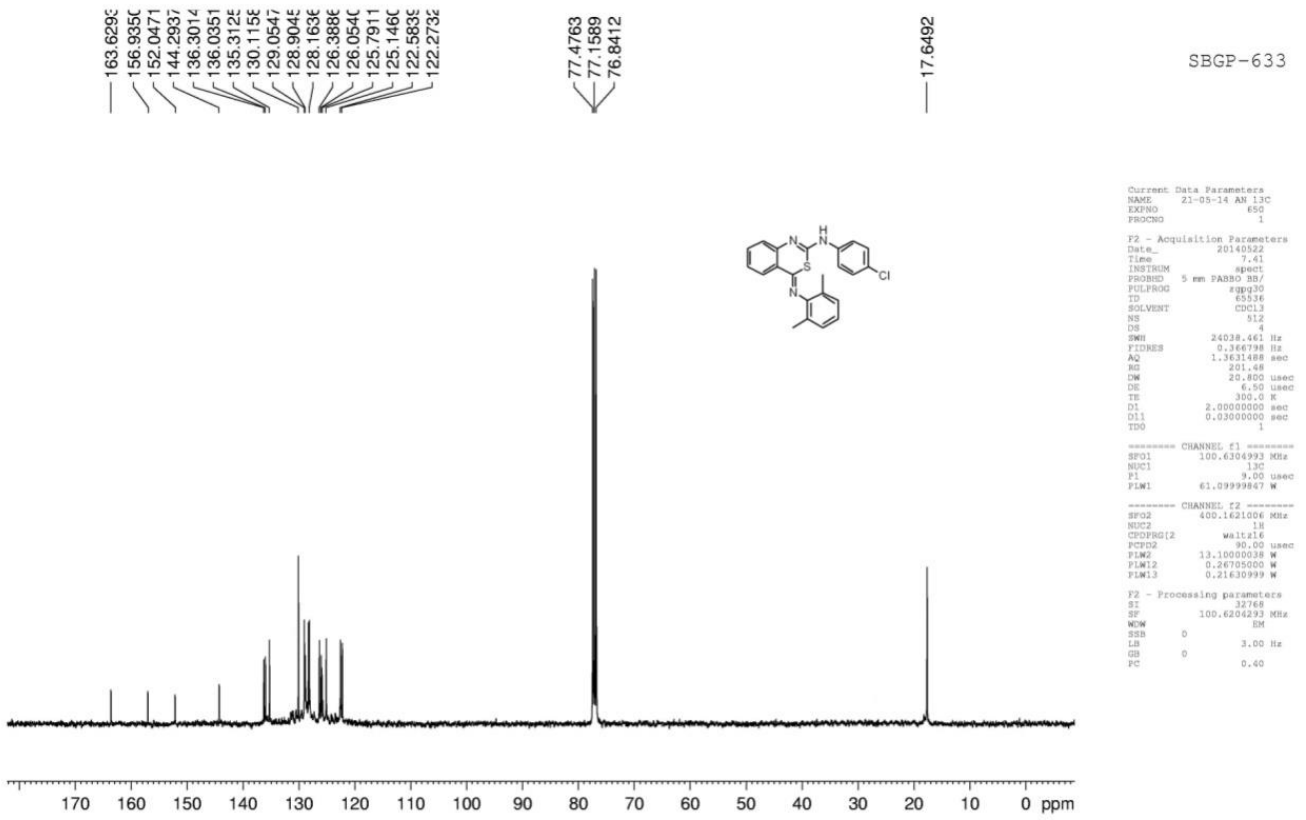


Fig: S-51 ^{13}C spectrum of **(Z)-*N*-**(4-Chlorophenyl)-4-(2,6-dimethylphenylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3cE)**

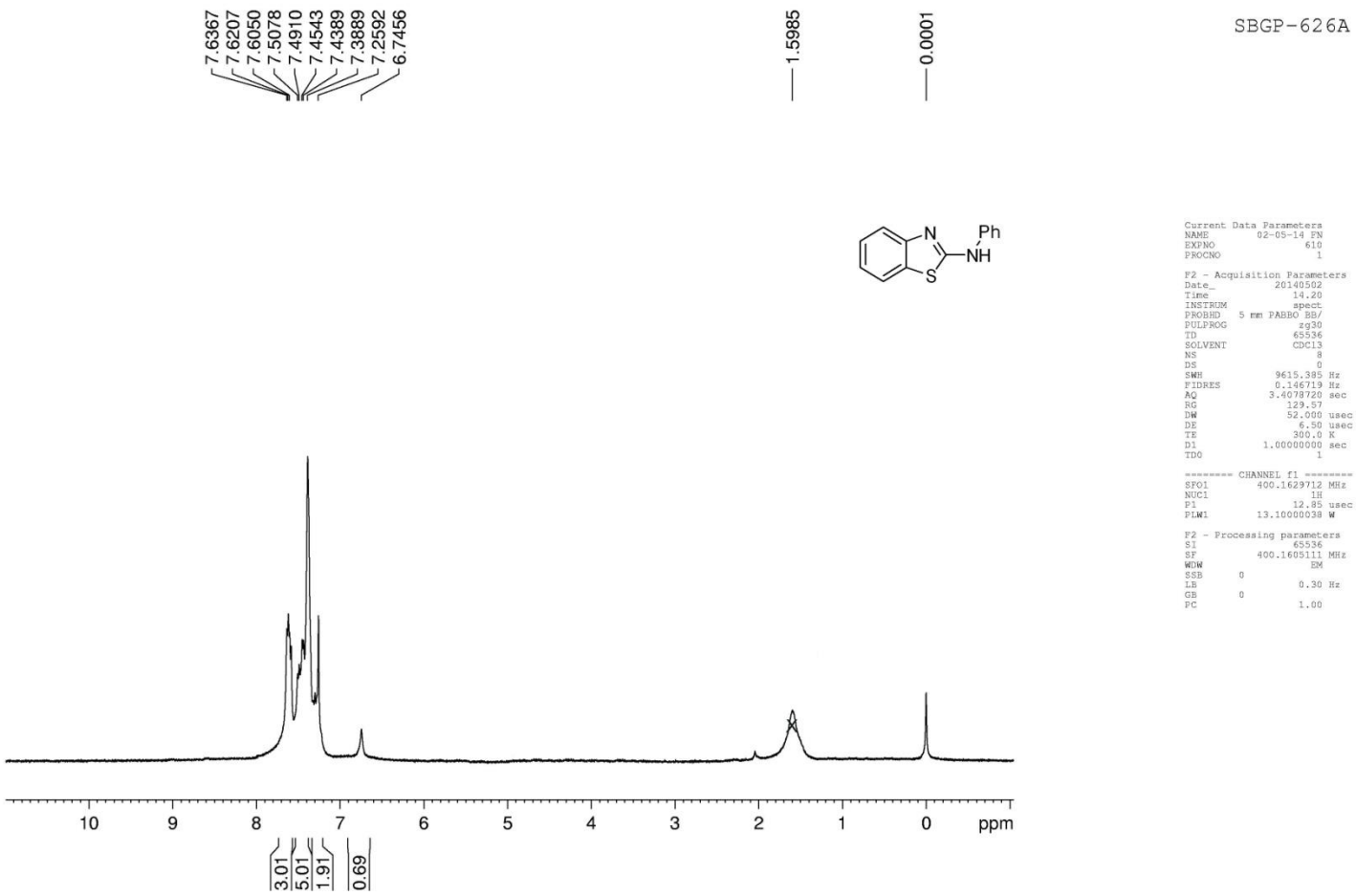
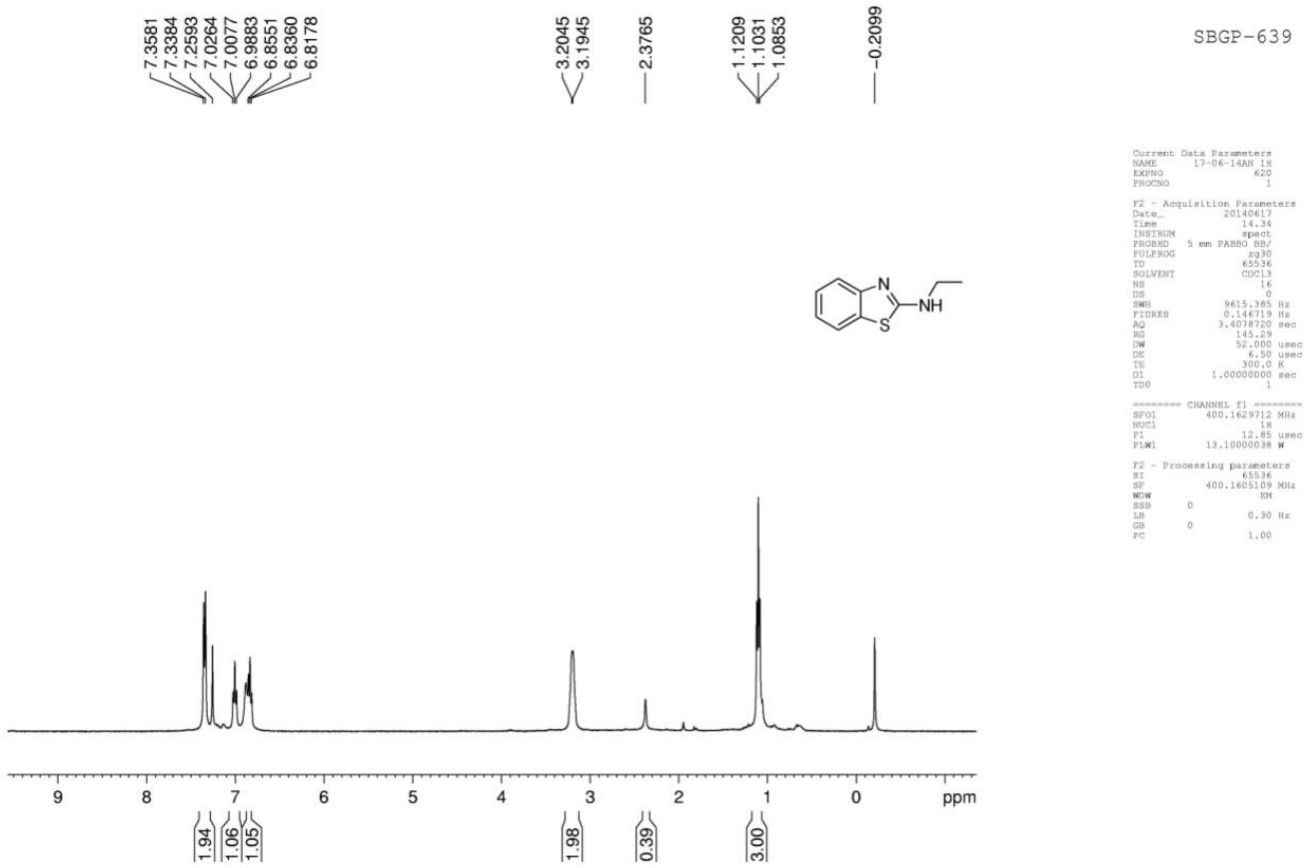


Fig: S-52 ^{1}H spectrum of ***N***-Phenylbenzo[*d*]thiazol-2-amine **(4a)**

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EXPNO             620
PROCNO              1

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Time              14.34
INSTRUM           spect
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PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           9615.385 Hz
FIDRES        0.146719 Hz
AQ            3.4078720 sec
RG             145.29
DW              52.000 usec
DE               6.50 usec
TE              300.0 K
D1          1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       400.1629712 MHz
NUC1              1H
P1               12.85 usec
PLW1       13.10000038 W

F2 - Processing parameters
SI               65536
SF         400.1605109 MHz
WDW                 EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
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Fig: S-53 ^{1}H spectrum of ***N***-Ethylbenzo[*d*]thiazol-2-amine **(4f)**

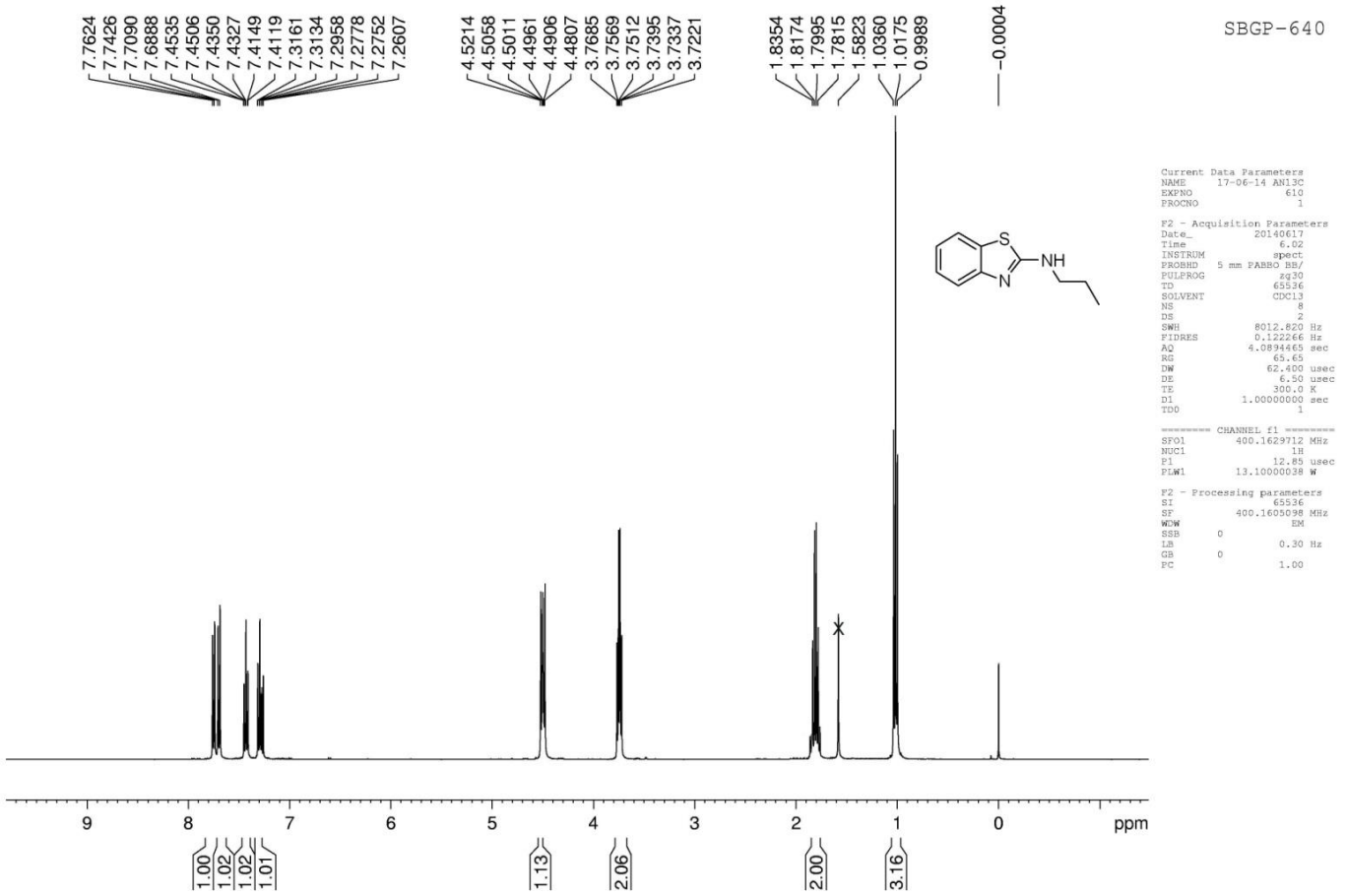

Fig: S-54 ^{1}H spectrum of ***N***-Propylbenzo[*d*]thiazol-2-amine **(4g)**

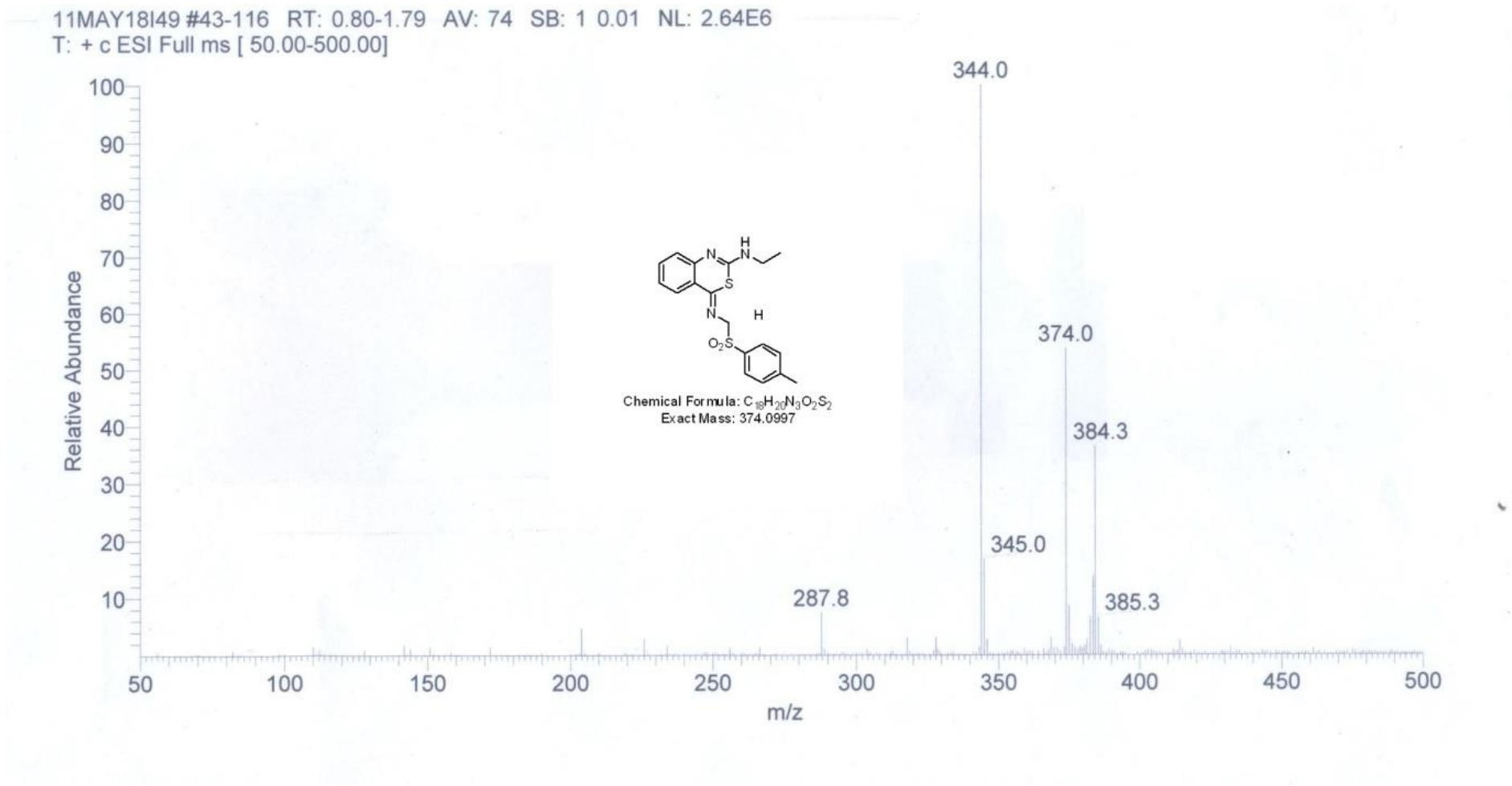

Fig: S-55 ESMS spectra of (*Z*)-*N*-Ethyl-4-(phenylsulfonylmethylimino)-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3fC)** (crude product)

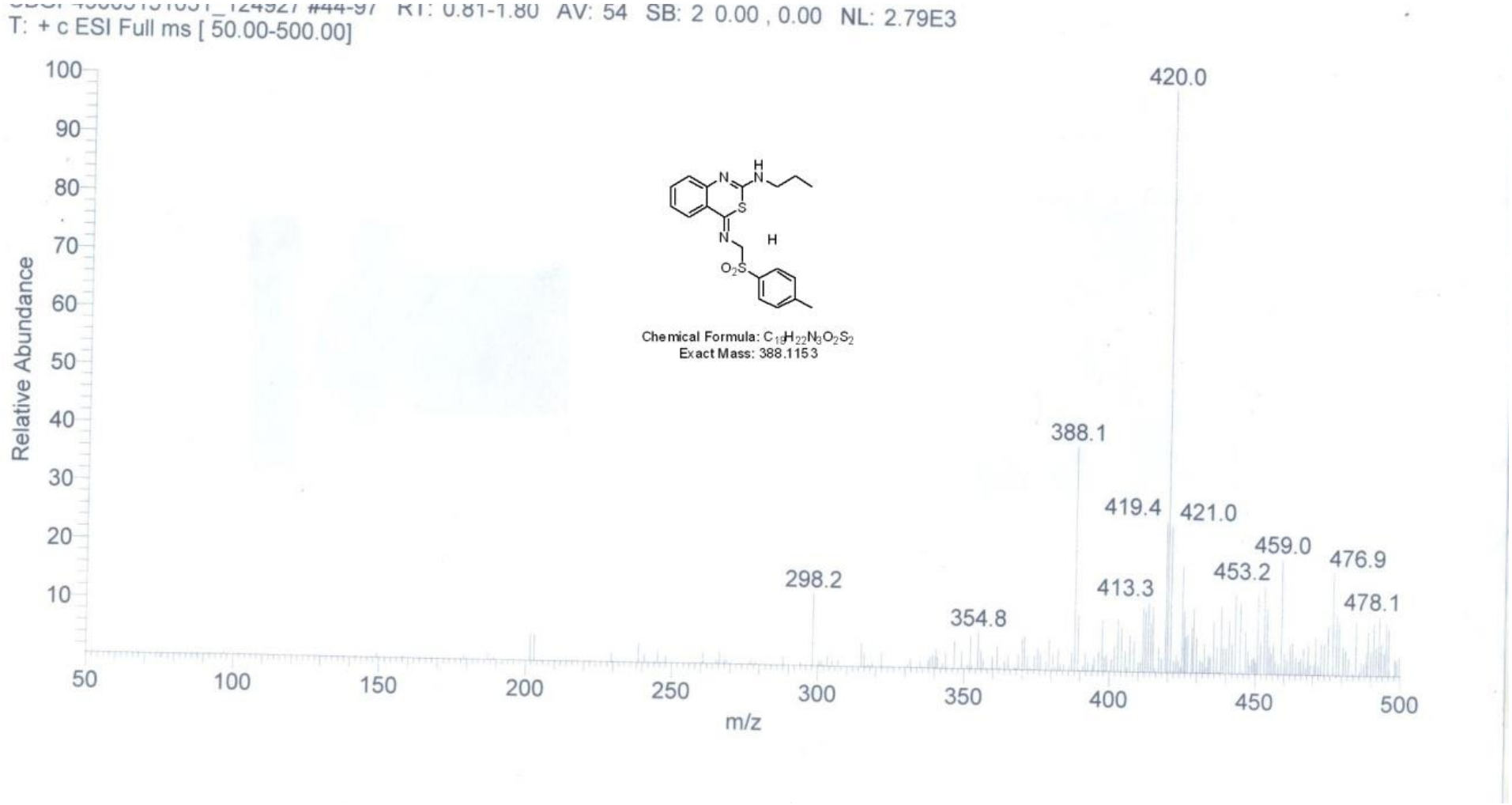

Fig: S-56 ESMS spectra of (*Z*)-4-(phenylsulfonylmethylimino)-*N*-propyl-4*H*-benzo[*d*][1,3]thiazin-2-amine **(3gC)** (crude product)